Synthesis and Study of the Electrochemical and Optoelectronic Properties of $\pi$-Conjugated Poly-P-Phenylene-Based Molecular Wires

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SYNTHESIS AND STUDY OF THE ELECTROCHEMICAL AND OPTOELECTRONIC PROPERTIES OF \(\pi\)-CONJUGATED POLY-P-PHENYLENE-BASED MOLECULAR WIRES

by

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ABSTRACT
SYNTHESIS AND STUDY OF THE ELECTROCHEMICAL AND OPTOELECTRONIC PROPERTIES OF \(\pi\)-CONJUGATED POLY-P-PHENYLENE-BASED MOLECULAR WIRES

Anitha Boddeda, B.Sc, M.Sc
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Organic photovoltaics will play an important role in supplementing the energy needs of the twenty first century in a most cost-effective way to convert the solar energy into usable forms of energy. One of the bottlenecks in promoting widespread use of photovoltaic devices for solar energy storage is the inefficiency of the devices, which in part arises due to the inefficient charge separation and long-range charge transport. Design and synthesis of efficient charge-transfer materials would require one to first identify and establish the structural features necessary in a given molecular wire, which may promote effective charge transfer to long distances. Accordingly, herein, we describe the syntheses and study of the electrochemical and optoelectronic properties a number of different series of poly-p-phenylene based oligomers in order to probe the mechanism and extent of hole delocalization in molecular wires containing a large number of \(p\)-phenylenes.

In order to develop an understanding of hole delocalization in \(\pi\)-conjugated oligomers/polymers, we have synthesized and systematically studied well-defined series of oligomers of \(\pi\)-conjugated poly-p-phenylene based molecular wires with varying inter-ring dihedral angles (\(\theta\)) between the monomer units (e.g. \(i^{8}\text{PP}_{n}\), \(\theta \sim 33^\circ\); oligofluorenes, \(\theta \sim 37^\circ\) and \(0^\circ\); or \(m\)-Py\(_n\), \(\theta \sim 60-70^\circ\)) together with the effect of end capping groups, such as alkyl (\(i^{8}\text{PP}\)) and alkoxy (\(R\text{PP}\)). The experimental evaluation of redox and optical properties of various molecular wires studied herein showed that the HOMO density distribution extends over the entire chain as expected based on the observed linear cos[\(\pi/(n + 1]\)] trend albeit gravitating toward the center of the molecule, whereas the hole distribution, which determines optoelectronic properties of the oligomer cation radicals, is found to be limited to 7-8 phenylene units.

The study of poly-p-phenylene oligomers with electron-donating end-capping groups (i.e. alkyl- or alkoxy-groups) showed that the hole distribution is strongly impacted by end-capping groups and it gravitates from the central position to the end of the oligomeric chain while the distribution of HOMO density remains in the middle of the \(\pi\)-conjugated wires. Such migration of the hole toward the end of the chain due to the electron-donating alkoxy groups has significant experimental consequences, i.e. the optical and redox properties saturated at five phenylene units in case of alkoxy-capped poly-\(p\)-phenylene wires. These results were further reconciled by DFT calculations and by a recently developed multistate parabolic model.
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Synthesis and Study of the Electrochemical and Optoelectronic Properties of π-Conjugated Poly-p-Phenylene-Based Molecular Wires

GENERAL INTRODUCTION AND SYNOPSIS OF THE THESIS.

Organic photovoltaics will play an important role in supplementing the energy needs of the twenty first century in a most cost-effective way to convert the solar energy into usable forms of energy.\textsuperscript{1-3} One of the bottlenecks in promoting widespread use of photovoltaic devices for solar energy storage is the inefficiency of these devices, which, in part, arises from the inefficient charge separation and long-range charge transport. Design and synthesis of efficient charge-transfer materials would require one to first identify and establish the structural features necessary in a given molecular wire which can promote effective charge transfer to long distances with a desired mechanism of charge transfer (i.e. super-exchange tunneling vs hopping).\textsuperscript{4-8}

\textit{1/n relationship vs extent of hole distribution and role of reorganization energy}

In order to establish an intuitive understanding of 1/n relationship in poly-p-phenylene wires (PP\textsubscript{n}, where \(n\) is number of \(p\)-phenylene units) or effective conjugation length in \(\pi\)-conjugated oligomers/polymers, Rathore group has synthesized and
systematically studied well-defined series of oligomers of variety of π-conjugated molecular wires with varying inter-ring dihedral angles (θ) between the monomer units (e.g. PPn, θ = 33º; gelanders, θ = 47º; oligofluorenes, θ = 37º; or planarized polyfluorenes, θ = 0º) (Figure 4) using a combined computational/experimental approach. These studies revealed that redox and optical properties of all molecular wires in Figure 1.1 show a linear trend against cos[π/(n + 1)], where n is the number of aromatic units.\textsuperscript{9-10} Importantly, it is noted that often-used linear dependence of 1/n coordinate, derived from a particle-in-a-box model,\textsuperscript{11} works reasonably well only for smaller n, while much better agreement with the experimental observables (e.g. redox potentials and excitation energies of neutral and cation radicals) can be obtained with the cos[π/(n + 1)] coordinate derived from the Hückel-like (i.e. tight-binding) model which uses monomer frontier orbitals (Figure 1.1).\textsuperscript{10,11} It is further noted that the 1/n relationship continues to be utilized to determine effective conjugation length because 1/n closely approximates to cos[π/(n + 1)] for small n, i.e. n up to ~6-7 units.

Interestingly, the experimental evaluation of redox and optical properties of various oligo-p-phenylenes in Figure 1.1 was reproduced by the carefully benchmarked DFT calculations [B1LYP-40/6-31G(d)+PCM(CH\textsubscript{2}Cl\textsubscript{2})].\textsuperscript{10,12-17} In addition, DFT calculations showed that the HOMO density distribution extends over the entire chain as expected based on the observed cos[π/(n + 1)] trend albeit gravitating toward the center of the molecule, whereas the hole distribution, which determines optoelectronic properties of the oligomer cation radicals, is found to be limited to 7-8 phenylene units in all cases (Figure 1.1).\textsuperscript{10,12} Also note that hole distribution refers to spin and charge distribution which were found to be identical by the natural population analysis\textsuperscript{18} in all
cases. This observation highlights a fundamental difference between the properties of neutral and cation radical of \( \pi \)-conjugated oligomers and polymers, which arises owing to the structural/solvent reorganization that follows the oxidation event. This confinement of the hole to 7-8 phenylene units in various poly-\( p \)-phenylene chains originates from the interplay between the energetic gain from charge delocalization and concomitant energetic penalty from the structural reorganization (i.e. bond contractions/elongations, angular deformations, and dihedral angles between \( p \)-phenylenes) as well as the solvent reorganization, together referred to simply as reorganization energy. Importantly, we developed an intuitive multistate parabolic model (MPM), which essentially represents a generalization of the Marcus two-state parabolic model (Figure 1.1),\textsuperscript{19} and it reproduces the experimental/computational observables (i.e. redox potentials and excitation energies of the cation radicals) remarkably well (Figure 1.1).\textsuperscript{10,12} The availability of MPM as a versatile and powerful predictive tool, together with the experimental/computational results on various \( \pi \)-conjugated systems allows us to readily predict the redox and optical properties and the extent of hole distribution in various \( \pi \)-conjugated oligomers and polymers.
Figure 1.1. A: Experimental plots of the lowest-energy excitation energies of neutral (left plot) and cation radical (right plot) and redox potentials of various \( p \)-phenylene-based molecular wires (shown in panel B) against \( \cos[\pi/(n + 1)] \), where \( n \) is the number of \( p \)-phenylene units. C: Spatial distribution of HOMOs and spin density [B1LYP-40/6-31G(d)+PCM(CH\(_2\)Cl\(_2\))] in representative examples showing that unlike HOMO, hole distribution is limited to 7-8 phenylene units. D: Per-unit HOMO density and spin/charge distribution (obtained from the natural population analysis*) on the representative example of poly-\( p \)-phenylene wires of various length (\( n = 2-10 \)). E: A cartoon representation of recently published multi-state parabolic model [J. Phys. Chem. C 2014, 118, 21400], which also reproduces the spin/charge distribution in various poly-\( p \)-phenylene cation radicals akin to the one obtain by DFT calculations in panel D (shown by 3D plot for representative series).
It is noteworthy that the mechanisms of charge transfer through \( \pi \)-conjugated oligomers are often studied by linking donors (D) and acceptors (A) as the end-capping groups, i.e. donor-bridge-acceptor (D-bridge-A), where bridge represents a \( \pi \)-conjugated oligomer.\(^{20,21-24} \) A question thus arises as to how our studies of \( \pi \)-conjugated systems as virgin bridges (Figure 1.1) are relevant to the charge transfer mechanisms in D-bridge-A wires. Accordingly, we briefly discuss below the known state-of-the-art understanding of charge transfer mechanisms in molecular wires (i.e. D-bridge-A) in the context of our studies of virgin \( \pi \)-conjugated oligomeric bridges, as follows.

**Mechanisms of charge transfer in D-bridge-A molecular wires vs virgin bridges**

Studies of the charge transfer in \( \pi \)-conjugated oligomers in the D-bridge-A systems have led to the recognition of two different mechanisms of charge transfer, i.e. tunneling and hopping (Figure 1.2).\(^5 \) The tunneling mechanism is the only possibility in case A, where the bridge redox potential or energetics does not allow direct mediation of electron transfer, while in B both tunneling and hopping mechanisms can operate in cases of shorter bridges. As the hopping mechanism has a kinetic barrier, a more facile tunneling mechanism can effectively compete in cases of shorter bridges but in cases of longer bridges (case C) the hopping mechanism operates exclusively.\(^{20} \)
 Importantly, the direct tunneling and super-exchange tunneling are often distinguished by the involvement of the bridge orbitals and its energy levels as a medium for allowing coupling between the donor and acceptor without undergoing structural reorganization during the super-exchange tunneling process. Although in this mechanism bridge does not form an intermediate charged state, its structure and the nodal arrangement of orbitals could play significant role in controlling the rates of super-exchange tunneling. The relevance of the tunneling mechanism is limited to short-distance charge transfer because the probability of tunneling processes exponentially decreases with the length of the bridge. In order to accomplish long-range charge transfer, one must resort to molecular wires that operate via hopping mechanism, i.e. by involving the finite residence of a charge onto the bridge and accompanying structural reorganization. Thus, our recent undertaking of a systematic study of hole distribution in various $\pi$-conjugated oligomers/polymers (Figure 1.1) will undoubtedly play an important role in revealing the importance of the transient intermediates during the course of hole transfer via hopping mechanism in the D-bridge-A assemblies and will guide the

**Figure 2.2.** Schematic representation of the charge-transfer mechanisms in D-bridge-A wires.
design and synthesis of new classes of more effective molecular wires for long-range charge transfer, as follows.

**The effect of the end-capping groups on hole distribution in π-conjugated poly-p-phenylene wires.**

The detailed computational/experimental analysis of various linear poly-p-phenylene cation radicals presented above in Figure 1.1 showed that a positive charge (hole) resides in the center of the molecule and is distributed only over seven monomer units (Figure 1.1C/D). Interestingly, we recently showed that poly-p-phenylene oligomers with electron-donating end-capping groups (i.e. alkyl- or alkoxy-groups, Figure 1.3) which showed that the hole distribution is strongly impacted by end-capping groups and it gravitates from the central position to the end of the oligomeric chain while the distribution of HOMO density remains in the middle of the π-conjugated wires (Figure 1.3). Such migration of the hole toward the end of the chain due to the electron-donating alkoxy groups has significant experimental consequences, i.e. the optical and redox properties saturated at five phenylene units. Moreover, the DFT calculations verified the hole distribution to lie toward the end of the molecule in end-capped poly-p-phenylenes. These results were reconciled by multistate parabolic model with a simple modification that required the lowering of the energies of the parabolas representing phenylene groups containing end-capping substituent while keeping the electronic coupling ($H_{ab}$) and structural reorganization ($\lambda$) parameters constant.
Figure 3.3. **A:** Schematic representation of MPM. **B:** Experimental redox potentials of alkyl- and alkoxy-capped poly-p-phenylenes (left) and $\text{D}_0 \rightarrow \text{D}_1$ excitation energies of their cation radicals (right) plotted against $1/n$, where $n$ is the number of p-phenylene units. **C:** Spatial distribution of HOMOs and spin density [B1LYP-40/6-31G(d)+PCM(CH_2Cl_2)] in representative examples of various end-capped PP. **D:** Free energy profile and per-unit hole distribution of the alkoxy-capped poly-p-phenylene cation radicals obtained by MPM. **E:** Representative free energy surface of $\text{ROP} \text{PP}_{10}^{\bullet \bullet}$ and its valence tautomers predicted by MPM.

Interestingly, MPM representation of longer alkoxy-capped oligomer (e.g. $n = 10$) clearly shows that hole can reside toward the either end of the molecule (distributed over...
~4 phenylene units) or toward the center of the molecule where the hole distribution can extend up to five phenylene units as shown by the three minima on the ground state ($D_0$) free energy surface denoted by the black dots in Figure 1.3E, which can also be referred to as valence tautomers. Thus, the migration of the hole from one end of the molecule to another end must pass through the valence tautomer in which the hole resides toward the center of the molecule. The variable-temperature electronic spectroscopy of alkoxy-capped poly-$p$-phenylene cation radicals provided clear evidence that hole rapidly migrates between the ends of the molecule through a raised minimum. One could readily estimate that the residence time of the hole toward the ends is expected to be high due to the energy difference of roughly 2-3 kcal/mol amongst the minima representing the hole distribution at the ends and in the middle of the wire in longer wires, see Figure 1.3. Note that the energy difference between these minima can be determined using the calculated relative electronic oxidation energies or experimental redox potentials of a long uncapped vs alkoxy-capped poly-$p$-phenylene with $n = 10$ in both cases. Such hopping of a hole across a long chain can be easily facilitated if the multiple minima are of similar energy.

**Turning the interchromophoric electronic coupling on and off by modulating nodal arrangement of HOMOs of PAH-based wires**

The increase of physical distance of charge transfer can be accomplished using large polycyclic aromatic hydrocarbons as monomer units. Such an approach has been explored by constructing poly-porphyrin wires through acetylenic linkers, which allowed effective charge transfer over 50 nm distance. In another example, Müllen and coworkers prepared molecular wires using pyrenes as monomer units, which were...
linked at 2,7-positions (Figure 9), and they studied their reduction and anion radicals by EPR spectroscopy and concluded that the electronic coupling between the pyrene units was non-existent.30,31 This result is not surprising in the light of the fact that the nodal arrangement of the frontier orbitals (i.e. both HOMO and LUMO) are not amicable to interchromophoric electronic coupling (Figure 1.4) as the HOMO or LUMO density on the 2,7-carbons is zero. We synthesized poly-pyrene wires containing up to five pyrene units linked at 1,6-positions (Figure 1.4), and despite the large inter-ring dihedral angles (~60-70°) as compared to isomeric 2,7-poly-pyrene wires (~30-45°), they showed significant electronic coupling. The 1,6-linked poly-pyrene wires showed lowering of their first oxidation potentials by 220 mV when compared to monomeric 1,6-dioctylpyrene and appearance of intense intervalence D0 → D1 transition (λmax ~2400 nm) in their cation radicals. Note that such lowering of redox potentials and the presence of intervalence transition in the cation radical of 2,7-poly-pyrene wires was completely absent. This significant preliminary finding attests to the fact that the interchromophoric electronic coupling in π-conjugated wires requires the overlap between the monomeric HOMOs (see Figure 1.4), which can be further enhanced by a favorable inter-ring dihedral angles. However, the absence of effective overlap between the monomer HOMOs due to the unfavorable nodal arrangement, as in the case of 2,7-poly-pyrene wires, leads to a complete absence of interchromophoric coupling despite the favorable dihedral angle similar to those observed in poly-p-phenylenes, i.e. 30-40°. Indeed, a Hückel theory-based estimation of the inter-ring electronic coupling in isomeric 2,7- and 1,6-linked dipyrenes, as described in a recently published VIP paper in Angewandte
Chemie [DOI: 10.1002/anie.201506402], showed that interchromophoric coupling is completely absent in the case of 2,7-dipyrene.

**Figure 4.4.** A: Examples of various poly-pyrene wires and their frontier orbitals. B: Evolution of the energy of the HOMOs and underlying poly-p-phenylene-like orbitals which may facilitate electronic coupling amongst the pyrenes in 2,7-linked wires.

Based on this general introduction and brief discussion of the research work included within this thesis, it is divided in following chapters.

**Chapter 2: Key Role of End-Capping Groups in Optoelectronic Properties of Poly-\(p\)-phenylene Cation Radicals**

**Chapter 3: Breakdown of the 1/n Trend in \(\pi\)-Conjugated Poly-\(p\)-phenylene Cation Radical is Explained using Huckel Theory and Multi-State Model**

**Chapter 4: Turning ON/OFF the Electronic Coupling by Modulating Nodal Arrangement of HOMOs in Isomeric Pyrene-Based Molecular Wires**

Disclaimer: The results discussed in chapters 1-5 were further supplemented by DFT calculations and by a recently developed multistate parabolic model and a modifies Huckel theory by my coworkers Drs. Marat R Talipov and Maxim V. Ivanov. My contribution to these works is limited to synthesis of various molecules and spectroscopic studies.
References.


(12) Talipov, M.; Rathore, R.; Jasti, R. A Circle Has No End: Role of Cyclic Topology and Accompanying Structural Reorganization on the Hole Distribution in Cyclic and Linear Poly-p-phenylene Molecular Wires. *Submitted as the second revision in JACS.*


CHAPTER 2

Key Role of End-Capping Groups in Optoelectronic Properties of Poly-\(p\)-phenylene Cation Radicals

Introduction

On-going developments in the fields of molecular electronics and photovoltaic devices have led to ever-growing interest in \(\pi\)-conjugated polymers that can be used as molecular wires, donor-acceptor bridges, components of organic light-emitting diodes, etc.\(^1\-^5\) Poly-\(p\)-phenylenes (\(\text{HPP}_n\)) is a paradigm model for investigating the electrical, optical properties of these polymers\(^6\-^{11}\) as well as the charge transport through them.\(^{12,13}\) Unfortunately, systematic studies of the neutral and oxidized/reduced \(\text{HPP}_n\) molecules are seriously hampered by their poor solubility.
Chart 2.1. Structure and naming schemes for various poly-$p$-phenylene wires

Rathore and coworkers have addressed this issue by synthesizing a well-defined series of poly-$p$-phenylene oligomers $^{iA}PP_2^{iA}PP_7$ with end-capping branched $iso$-alkyl groups, $iA = 6$-tetradecyl, Chart 2.1, that dramatically improved their solubility. The systematic study of the $^{iA}PP_n^{iA}PP_n^+\cdot$ series by Rathore and coworkers revealed, for the first time, inverse $1/n$ relationship of their redox and optoelectronic properties. Unfortunately, the solubility issues prevented expanding the $^{iA}PP_n$ series beyond seven $p$-phenylene units. Furthermore, it is not clear what effect the end capping groups may have on the electronic properties of $^{iA}PP_n$ molecules, and to what degree the $^{iA}PP_n$ results can be applicable to other end-capped $RPP_n$ and uncapped $HPP_n$ molecules.

Accordingly, herein, we aim to provide a comprehensive picture of structure-property relationships of $RPP_n^{RPP_n^+\cdot}$ for any length and with various end-capping substituents. Carefully calibrated density functional theory (DFT) calculations also reveal that $RPP_n$ oxidation potentials and the $RPP_n^+\cdot$ optical properties can significantly deviate from, or even not follow, the $1/n$ dependence for longer chains and/or strongly electron-donating
capping groups R; these predictions are further confirmed experimentally for a series of alkoxy-capped $R^0\text{PP}_n$ oligomers, $n = 2–7$. We rationalize these unexpected results using a multi-state parabolic model (MPM)—a generalization of the traditional two-parabola Marcus model—which shows that evolution of the redox and optoelectronic properties of $R^0\text{PP}_n^\bullet$ is determined by the interplay between electronically non-equivalent terminal and internal $p$-phenylene units.

NOTE: Theoretical and computational studies were contributed by Dr. Marat Talipov.
Results and Discussion

DFT Modeling of the Extended $^R$PP$_n$/$^R$PP$_n^+$ Series and Computational Prediction

Delocalized $\pi$-conjugated cation radicals (CRs) such as $^R$PP$_n^+$ are challenging for many DFT methods due to the self-interaction error\textsuperscript{16-19} (SIE) that causes artificial delocalization of the positive charge/hole\textsuperscript{20} and thus leads to increasingly underestimated oxidation potential for the longer chains as well as an incorrect nature of the first excited state of the CRs. The self-interaction error can be reduced by using hybrid DFT methods that add a portion of the exact Hartree-Fock (HF) exchange term into the exchange functional.\textsuperscript{21-25}

However, the contribution of HF exchange in most of the widely used hybrid functionals, $\%\text{HF} < 30$, is not sufficient for correct description of delocalized mixed-valence charged compounds; on the other hand, hybrid DFT functionals with $\%\text{HF} > 50$ (global or long-range) often lead to over-localization of the charge/hole.\textsuperscript{26,27} This necessitates fine-tuning of $\%\text{HF}$ based on the available experimental data.\textsuperscript{17,19,24-26} Therefore, in this work a one-parameter density functional B1LYP\textsuperscript{28} with the Hartree-Fock (HF) exchange term contribution\textsuperscript{17,21,22,26,27} carefully benchmarked and calibrated against the experimental data for the $^{LA}$PP$_n$/$^{LA}$PP$_n^+$ series was used.\textsuperscript{14}
Using this calibrated B1LYP-40 functional, the $iA\text{PP}_n^{iA\text{PP}_n^{+\cdots}}$ series up to ten $p$-phenylene units was calculated and compared it with the experimentally inaccessible uncapped $H\text{PP}_n$ series.\textsuperscript{30,31} Comparison of the $1/n$ plots of the calculated\textsuperscript{32} oxidation energies $\Delta E^{el}$ and CR vertical excitation energies $\lambda_{\text{max}}$ for $H\text{PP}_n$ and $iA\text{PP}_n$ (Figure 2.1) shows two important differences between the two series: (1) $iA\text{PP}_n$ series has a small minimum of $\Delta E^{el}$ at $n = 6$, whereas $H\text{PP}_n$ demonstrate a smooth transition to saturation; (2) $\lambda_{\text{max}}$ abruptly saturates at $n = 7$ for $iA\text{PP}_n^{+\cdots}$, while in $H\text{PP}_n^{+\cdots}$ it approximately follows a linear $1/n$ relationship up to $n = 10$. As this early breakdown of the $1/n$ relationship in the $iA\text{PP}_n^{+\cdots}$ series is likely related to the electron-donating nature of the $iA$ end-capping groups, the $RO\text{PP}_n$ series with strong electron-donating alkoxy ($RO$) end-capping groups was investigated. In this series, the predicted $\lambda_{\text{max}}$ evolution is similar to $iA\text{PP}_n^{+\cdots}$ (Figure 2.1B), although the leveling off is observed much earlier at $n = 4$ for $RO\text{PP}_n^{+\cdots}$ vs $n = 7$ for $iA\text{PP}_n^{+\cdots}$. At the same time, the $\Delta E^{el}$ evolution is dramatically different for $RO\text{PP}_n$ series, as the oxidation energy increases, not decreases, with increasing $n$ and asymptotically saturates for $n > 5$ (Figure 2.1A).
Figure 2.1. Calculated $^{RPP}_n$ energies of oxidation $\Delta E_{\text{el}}$ (A), and vertical excitation energies of the $^{RPP}_n^+$ lowest-energy bright transitions (B) vs $1/n$.\textsuperscript{33} DFT calculations were performed at the B1LYP-40/6-31G(d)+PCM (dichloromethane) level of theory, and the vertical excitation energies were obtained with time-dependent DFT calculations at the same level.

The predicted deviations from the linear $1/n$ evolution of the $^{iAPP}_n/iAPP_{n}^+$ properties become apparent only for $n \geq 8$ and thus could not have been observed in the previous experimental study,\textsuperscript{14} because these longer oligomers were not accessible due to the solubility issues. As these deviations are predicted to appear much earlier in the $^{ROPP}_n$ series, we synthesized a homologous series of alkoxy-capped $^{ROPP}_n$ molecules, $n = 2–7$, and examined their oxidation potentials and recorded the electronic spectra of their cation radicals as follows.

**Synthesis and Properties of $^{ROPP}_n/iROPP_{n}^+$**
Initial attempts to synthesize $RO\text{PP}_n$ oligomers with methoxy end-capping groups produced only 2 and 3-phenylene oligomers that were soluble in dichloromethane while the 4-phenylene oligomer was only sparingly soluble$^{34}$ and could only be characterized by MALDI mass spectrometry (i.e. Figure 2.2).

**Figure 2.2.** The $^1$H NMR spectra of $^{MeO}\text{PP}_2$ and $^{MeO}\text{PP}_3$ in CDCl$_3$ (Left) and the MALDI mass spectrum of sparingly soluble $^{MeO}\text{PP}_4$ (Right).

The $RO\text{PP}_n$ oligomers with 2-ethylhexyloxy end-capping groups produced 2 to 4-phenylene oligomers but the 4-phenylene oligomer was again only partially soluble in dichloromethane. In another attempt, the $RO\text{PP}_n$ oligomers were synthesized using 3,7-dimethyloctyloxy (based on citronellol) end-capping groups and found that 2 to 4-phenylene oligomers were readily soluble but the 5- and 6-phenylene oligomers were only sparingly soluble in dichloromethane (see Experimental Section).
After multiple variations of alkoxy groups, the use of a 17-carbon iso-alkoxy (i.e. 9-heptadecyloxy) group provided more or less soluble $^{RO}PP_n$ oligomers up to 7-$p$-phenylene units. The synthesis of the desired $^{RO}PP_n$ was accomplished via the Suzuki coupling\cite{35,36} between a combinations of 4-alkoxy-1-bromobenzene/4-alkoxy-4'-bromobiphenyl and 1,4-dibromobenzene, 4,4'-dibromobiphenyl, etc. as summarized in Scheme 2.1.

Synthesis of soluble $^{RO}PP_n$ oligomers containing 17-carbon iso-alkoxy (i.e. 9-heptadecyloxy) group required the preparation of 9-bromoheptadecane. It was prepared by a reaction of ~2 equivalent of octyl magnesium bromide with ethyl formate to afford 9-hydroxyheptadecane which was converted to the corresponding 9-bromoheptadecane using concentrated HBr. The conversion of 9-hydroxyheptadecane to 9-bromoheptadecane also produced ~15% of alkene which was separated with the aid of column chromatography (Scheme 2.1). An alkylation of 4-bromophenol with 9-bromoheptadecane in DMF in the presence of anhydrous potassium carbonate provided the first precursor [i.e. 4-bromo-1-(9-heptadecyloxy)benzene] which in combination with readily available bis-boronic esters of phenyl, biphenyl, and terphenyl provided ready syntheses of soluble $^{RO}PP_n$ oligomers (Scheme 2.1).

**Scheme 2.1.** Synthesis of soluble $^{RO}PP_n$ oligomers up to 7-$p$-phenylene units using 9-heptadecyloxy end-capping groups.
The synthesized oligomers showed good solubility in dichloromethane up to \( ROPP_6 \); however, solubility of \( ROPP_7 \) dropped to less than ~1 mg/10 mL. The structures of various \( ROPP_n \) were easily established by \(^1\)H/\(^{13}\)C NMR spectroscopy and further confirmed by MALDI mass spectrometry (Figures 2.3, 2.4, and 2.5).
Figure 2.3. The $^1$H NMR spectra of $^{ROPP}_n$ oligomer in CDCl$_3$ at 22 °C.
Figure 2.4. The $^{13}$C NMR spectra of $^{ROPn}_n$ oligomer in CDCl$_3$ at 22 °C.
Figure 2.5. The MALDI mass-spectra of various $ROPP_n$ oligomers recorded in 9-nitroanthracene matrix. The spectra were truncated to remove peaks due to matrix for clarity.
Electrochemistry of $^{RO}PP_n$

The redox properties of the $^{RO}PP_2-^{RO}PP_7$ were evaluated by electrochemical oxidation at a platinum electrode as a 1 mM solution in dichloromethane containing 0.1 M tetra-$n$-butylammonium hexafluorophosphate ($n$-Bu$_4$NPF$_6$) as the supporting electrolyte. The reversible cyclic voltammograms of various $^{RO}PP_n$ are presented in Figure 2.6. The oxidation potentials of various $^{RO}PP_n$ were referenced to added ferrocene, as an internal standard (Fc/Fc$^+$: $E_{ox} = 0.45$ V vs SCE), vide infra.

The observed evolution of the experimental $E_{ox}$ values of $^{RO}PP_n$ (Figure 2.6B) show an excellent agreement with computational predictions (Figure 2.1A) and reveal drastic differences from the previously reported $E_{ox}$ values for the $^{iA}PP_n$ series. Indeed, addition of each $p$-phenylene unit leads to a linear increase vs $1/n$ of the oxidation potential in $^{RO}PP_n$ (Figure 2.6C). Clearly, this finding suggests that a substitution of the $iso$-alkyl end-capping groups by the $iso$-alkoxy groups causes significant changes in the electronic structure of $^{RO}PP_n^+$. 
Figure 2. 6. A: Cyclic voltammograms of 0.1 mM $^{RO}_{PP_n}$ in CH$_2$Cl$_2$ containing 0.1 M tetra-$n$-butylammonium hexafluorophosphate ($n$-Bu$_4$N$^+$ PF$_6^-$) as the supporting electrolyte at a scan rate 200 mV/sec at 22º C. B: List of oxidation potentials of $^{RO}_{PP_n}$ referenced to both SCE and Fc/Fc$^+$. C: Plot of experimental $^{RO}_{PP_n}$ and $^{iA}_{PP_n}$ first oxidation potentials $E_{ox1}$ vs $1/n$; $^{iA}_{PP_n}$ data from Ref. 14.
Generation of $^{RO}_{PP_n}$ Cation Radical via Redox Titrations

The electrochemical reversibility and relatively low oxidation potentials of $^{RO}_{PP_n}$ allowed generation of the corresponding cation radicals $^{RO}_{PP_n^+}$ in a reaction with hindered naphthalene cation radical (NAP$^{++}$), a robust one-electron oxidant ($E_{ox} = 1.34$ V vs. SCE). The Figure 2.7 shows the spectral changes attendant upon the reduction of a 0.1 mM solution of NAP$^{++}$ ($\lambda_{max} = 672, 616, 503, \text{ and } 396 \text{ nm}; \varepsilon_{672} = 9300 \text{ M}^{-1} \text{ cm}^{-1}$) and oxidation of $^{RO}_{PP_2}$ to its cation radical $^{RO}_{PP_2^+}$ ($\lambda_{max} = 832 \text{ nm}$) by an incremental addition of $^{RO}_{PP_2}$ in dichloromethane at 22 °C. The presence of a clear isosbestic point at $\lambda_{max} = 691 \text{ nm}$ in Figure 2.7A establishes the uncluttered nature of electron transfer from $^{RO}_{PP_2}$ to NAP$^{++}$ (eq 2.1).

$$^{RO}_{PP_2} + \text{NAP}^{++} \rightarrow ^{RO}_{PP_2^+} + \text{NAP}$$

(eq 2.1)

Furthermore, a plot of the depletion of NAP$^{++}$ (i.e. the decrease of the absorbance at 672 nm) and formation of $^{RO}_{PP_2^+}$ (i.e. an increase in the absorbance at 832 nm) against the increments of added $^{RO}_{PP_2}$ (Figure 2.7B), established that NAP$^{++}$ was completely consumed after the addition of 1 equiv. of $^{RO}_{PP_2}$. Moreover, the final absorption spectrum of $^{RO}_{PP_2^+}$, obtained after the addition of 1 equiv. of $^{RO}_{PP_2}$ to NAP$^{++}$ solution, remained unchanged even if a large excess of (i.e. ~5 equiv) of neutral $^{RO}_{PP_2}$ was added.
Also note that decreasing of the concentration of $^{RO}{PP_2}^\bullet$ by ten-fold did not show any changes in its absorption spectrum.

**Figure 2.7.** A: Spectral changes upon the reduction of 0.1 mM naphthalene cation radical by an incremental addition of 0.77 mM solution of $^{RO}{PP_2}$ in dichloromethane at 20 °C (25 µL increment). B: A plot of increase of the absorbance of $^{RO}{PP_2}^\bullet$ (monitored at 832 nm), and depletion of the absorbance of naphthalene cation radical NAP$^\bullet$ (monitored at 672 nm) against the equivalent of added $^{RO}{PP_2}$.

Similarly, other $^{RO}{PP_n}^\bullet$ were generated in dichloromethane (see Experimental Section), and their spectra and optical properties are compiled in Figure 2.8. The $^{RO}{PP_2}^\bullet - ^{RO}{PP_4}^\bullet$ spectra show structured absorption bands that shifted red with increasing number of $p$-phenylene units, while the strikingly similar absorption spectra of $^{RO}{PP_6}^\bullet$ and $^{RO}{PP_7}^\bullet$ show a Gaussian band at ~7150 cm$^{-1}$ (~1400 nm), and the $^{RO}{PP_5}^\bullet$ spectrum shows
intermediate features with two bands at 6452 cm$^{-1}$ (1550 nm) and 5050 cm$^{-1}$ (1980 nm) (vide infra).

Figure 2. 8. A/B: Electronic spectra of various $^{RO}PP_h^+$, generated as in (Figure 2.7). The separation of ~1300 cm$^{-1}$ between vibronic peaks suggests that the vibronic structure arises due to the backbone C–C bond vibrations. C: Tabulation of the optical properties of the $^{RO}PP_h^+$.  

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The experimentally observed evolution of $^{RO}_{PP}$CR excitation energies $\lambda_{\text{max}}$ (Figure 2.8, A and B presented above with previously obtained $^{iA}_{PP}$ data) show an excellent agreement with the computational predictions of the non-$1/n$ behavior induced by electron-donating end-capping groups in $^{R}_{PP}$. Indeed, both predicted unexpected features of $^{RO}_{PP}$ — the saturation of $\lambda_{\text{max}}$ beyond $n = 4$ — are confirmed experimentally (Figure 2.9).

Figure 2.9. Plot of experimental $^{RO}_{PP}$ and $^{iA}_{PP}$ cation radical lowest energy transition ($\lambda_{\text{max}}$ from Figure 2.8) vs $1/n$; $^{iA}_{PP}$ data from Ref. 14.
Description of Hole Position and Distribution in $^{RPP}_n\cdot$

A. Distortion of $^{RPP}_n$ geometries, caused by oxidation. Position of the hole in a given poly-$p$-phenylene molecule can be determined from the geometrical changes induced by 1-$e^-$ oxidation. For example, in $^{RPP}_n$, oxidation causes quinoidal distortion of $p$-phenylene units, which results in shortening of inter-ring C–C bonds and decrease of the inter-ring dihedral angle $\theta$

Maximum geometric distortions predicted with DFT are observed in the case of $^{RPP}_2\cdot$, where the central C–C bond length shortens from $\sim1.48$ to $\sim1.43$ Å, and the dihedral angle reduces from $\sim36^\circ$ to $\sim21^\circ$. In longer $^{RPP}_n\cdot$, the spread of the geometric distortions depends on the chain length and the nature of the end-capping substituents, which suggests significantly different hole distribution patterns in various $^{RPP}_n\cdot$ (Figures 2.10, 2.11, 2.12, and Tables 2.1, 2.2, 2.3).
Figure 2. 10. Shortening of the $R_q$ distance (see structure above the Table) in various $^{n}PP_{n}^{+\star}$ series, caused by oxidation; calculated by means of the B1LYP-40 functional.
Table 2.1. Shortening of the $R_q$ distance (in Å) in various $\text{RPP}^+_n$ series, caused by oxidation; calculated by means of the B1LYP-40 functional.

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Figure 2.11. Shortening of the $R_C$ distance in various $^R\text{PP}_n$ series, caused by oxidation; calculated by means of the B1LYP-40 functional. Note that each bar plot contains $n-1$ bars, as there are $n-1$ bonds between $p$-phenylene units in $^R\text{PP}_n^+$.
Table 2.2. Shortening of the $R_C$ distance (in Å) in various $\text{PP}_n^{++}$ series, caused by oxidation; calculated by means of the B1LYP-40 functional.

\[
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 & 4-5 & 1.480 & 1.44 & 0.03 & 1.48 & 1.46 & 0.01 & 1.48 & 1.46 & 0.01 \\
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Figure 2. Decrease in the central dihedral angle $\theta$ in $\text{RPP}_n$, caused by oxidation; calculated by means of the B1LYP-40 functional. Note that
each barplot contains \( n-1 \) bars, as there are \( n-1 \) bonds between \( p \)-phenylene units in \( \text{PP}^+_n \).

**Table 2.3.** Decrease in the central dihedral angle \( \theta \) in \( \text{PP}_n \), caused by oxidation; calculated by means of the B1LYP-40 functional.

\[
\begin{align*}
\text{Table 2.3. Decrease in the central dihedral angle } \theta \text{ in } \text{PP}_n, \text{ caused by oxidation; calculated by means of the B1LYP-40 functional.} \\

<table>
<thead>
<tr>
<th>( n )</th>
<th>( i-j )</th>
<th>( \text{ROPP}_n )</th>
<th>( \text{iAPP}_n )</th>
<th>( \text{HPP}_n )</th>
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\[
\begin{array}{cccccccc}
2 & 1-2 & 36.7 & -15.1 & 21.6 & 36.8 & 15.0 & 21.8 & 38.0 & 16.3 & 21.7 \\
3 & 1-2 & 35.8 & -18.1 & 17.7 & 36.1 & 19.2 & 16.9 & 36.8 & -20.2 & 16.5 \\
3 & 2-3 & -35.8 & -18.9 & 16.9 & -36.1 & 19.6 & 16.5 & -36.8 & -20.6 & 16.2 \\
4 & 2-3 & 35.5 & -19.4 & 16.1 & 35.6 & -18.3 & 17.3 & 35.8 & -17.7 & 18.1 \\
4 & 3-4 & -35.9 & -23.3 & 12.5 & -36.1 & -24.9 & 11.2 & -36.8 & -26.2 & 10.6 \\
5 & 1-2 & -35.9 & -33.3 & 2.6 & -36.2 & -29.2 & 7.0 & 36.9 & -30.7 & 6.1 \\
5 & 2-3 & -35.6 & -29.4 & 6.2 & 35.7 & -21.2 & 14.5 & -35.7 & -21.2 & 14.5 \\
5 & 3-4 & -35.6 & -22.1 & 13.4 & -35.7 & -19.6 & 16.1 & 35.7 & -20.3 & 15.4 \\
\end{array}
\]
<p>| $n$ | $i-j$ | $^{RO}<em>{PP_n}$ | | $^{H}</em>{PP_n}$ | | $^{iA}_{PP_n}$ |
|-----|------|----------------|----------------|----------------|----------------|
|     |      | N   | CR | $\Delta$ | N   | CR | $\Delta$ | N   | CR | $\Delta$ |
| 5   | 4-5  | 35.9 | -18.3 | 17.5 | 36.2 | -28.5 | 7.7 | -36.9 | -30.5 | 6.4 |
| 6   | 1-2  | -35.8 | -35.2 | 0.6 | -36.2 | -32.3 | 3.8 | -36.8 | -33.7 | 3.1 |
| 6   | 2-3  | 35.6 | -34.5 | 1.0 | 35.7 | -25.1 | 10.7 | 35.7 | -25.1 | 10.6 |
| 6   | 3-4  | -35.7 | -30.8 | 4.9 | -35.7 | -18.3 | 17.4 | -35.7 | -17.7 | 17.9 |
| 6   | 4-5  | 35.5 | -22.3 | 13.2 | 35.7 | -23.8 | 11.9 | 35.7 | -24.3 | 11.4 |
| 6   | 5-6  | -35.8 | -17.8 | 18.1 | -36.2 | -31.4 | 4.8 | -36.8 | -33.5 | 3.3 |
| 7   | 1-2  | -35.8 | -17.7 | 18.1 | -36.2 | -33.7 | 2.5 | -36.8 | -35.0 | 1.8 |
| 7   | 2-3  | -35.5 | -22.1 | 13.4 | 35.7 | -28.1 | 7.6 | 35.7 | -28.5 | 7.2 |
| 7   | 3-4  | -35.6 | -30.6 | 5.1 | -35.7 | -21.6 | 14.1 | -35.6 | -21.4 | 14.2 |
| 7   | 4-5  | 35.6 | -34.8 | 0.8 | 35.7 | -21.6 | 14.1 | 35.6 | -21.4 | 14.2 |
| 7   | 5-6  | -35.6 | -35.9 | -0.3 | -35.7 | -28.1 | 7.6 | -35.7 | -28.5 | 7.2 |
| 7   | 6-7  | 35.7 | -35.9 | -0.2 | 36.2 | -33.6 | 2.5 | 36.8 | -35.0 | 1.8 |
| 8   | 1-2  | -36.0 | -17.7 | 18.3 | -36.2 | -32.0 | 4.2 | -36.8 | -36.4 | 0.5 |
| 8   | 2-3  | 35.5 | -22.4 | 13.1 | 35.7 | -25.2 | 10.5 | 35.7 | -32.5 | 3.2 |
| 8   | 3-4  | -35.7 | -30.5 | 5.3 | -35.6 | -20.3 | 15.4 | -35.7 | -26.0 | 9.6 |
| 8   | 4-5  | 35.6 | -34.3 | 1.3 | 35.7 | -24.6 | 11.1 | 35.7 | -19.8 | 15.9 |
| 8   | 5-6  | -35.7 | -35.3 | 0.4 | -35.7 | -31.5 | 4.2 | -35.7 | -23.0 | 12.7 |</p>
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<th>iAPP$_n$</th>
<th>HPP$_n$</th>
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<td>9-</td>
<td>-35.8</td>
<td>-35.7</td>
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B. Spatial distribution of HOMO density in the neutral and spin density in cation radical forms of $^RPP_n$. Although the geometric distortions shown in Figures 2.10, 2.11, and 2.12 are useful descriptors of the hole distribution in the ground state, they cannot be used for the hole description in the vertically excited $^RPP_n^+$. At the same time, distribution patterns or position of the hole in both ground and vertically excited states of $^RPP_n^+$ can be conveniently visualized by unpaired spin density distribution plots. Moreover, one can easily quantify per-unit unpaired spin $\Delta s$ (Figure S21) and positive charge $\Delta q^+$ values (Figure 4 in the main text) by natural population. Accordingly, Figures 2.13 A-C compiles the spatial distribution of HOMO density in the neutral and spin density in cation radical forms of various $^RPP_n$ using both iso value plots and bar plots.

The per-unit distributions of unpaired spin density in $^RPP_n^+$ (Figure 2.13), obtained using the natural population analysis (NPA), provide generally the same picture as the per-unit NPA charge distributions. Subtle differences between these plots are most present on the terminal units (see also Figures 2.14 – 2.16 in the next section). This deviation between spin and charge density distributions originates from the spin polarization inside $p$-phenylene units, in which some atoms might have excess of the $\alpha$-electron (spin-up) density, and the others—excess of the $\beta$-electron (spin-down) density; the per-unit summation of the unpaired spin density leads to (partial) cancellation of these terms. This

<table>
<thead>
<tr>
<th>n</th>
<th>RO$^{PP_n}$</th>
<th>iA$^{PP_n}$</th>
<th>H$^{PP_n}$</th>
</tr>
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<tr>
<td>i-j</td>
<td>N</td>
<td>CR</td>
<td>$\Delta$</td>
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effect can be seen best in the excited $^{RO}PP_{n}^{+}\ast$, $n \geq 5$: while the most occupied terminal unit appears to be not involved in the vertically excited state shows significant occupation and spin-polarization of that unit (Figure 2.13 B).
Figure 2. Isosurface plots of the unpaired spin density in the ground state (A–C) and vertically excited (A’–C’) \( ^{R}PPn^\cdot \), calculated at the B1LYP-40/6-31G(d)+PCM(dichloromethane) level of theory. Regions with excess beta and alpha spin density are colored blue and red colors, respectively. Bar charts of condensed per-unit positive charge \( \Delta q^+ \) in the ground state (dark green) and vertically excited (light green) \( ^{R}PPn^\cdot \) calculated with natural population analysis (A”’-C’’’). Isovalue plots (0.03 a.u) of the highest occupied molecular orbitals of \( ^{i4}PP_n \) (C), \( ^{ii}PP_n \) (A), and \( ^{RO}PP_n \) (B) calculated by means of B1LYP-40 (A”’-C’’’). Note that HOMOs are always centered in the middle of the chain and much more delocalized compared to the corresponding hole distributions.

C. Correlations between different metrics of estimation of hole position/delocalization. The distribution of the hole in various \( ^{R}PPn^\cdot \) series can be established either through the analysis of geometrical distortions (Figures 2.10 - 2.12) with respect to removal of electron, or directly through the analysis of the spin/charge density in the corresponding cation radicals. We used \( \Delta R_q \) parameter as a structural metrics, and employed natural population analysis (NPA) charges \( (q_\alpha + q_\beta) \) and spins \( (q_\alpha - q_\beta) \), summed over each of the monomer units, to analyze the electron density of the \( ^{R}PPn^\cdot \) (Figures 2.13) show that these different approaches predict very similar hole distribution patterns for all three \( ^{R}PPn^\cdot \) series, although internal and external units expectedly demonstrate slightly different trends. Therefore, any of the considered metrics can be used for analysis of hole position/delocalization in \( ^{R}PPn^\cdot \). The spin/charge density distribution in \( ^{R}PPn^\cdot \) are most convenient for visualization purposes as well as availability of evaluation of the hole distribution in the excited state.

D. Hole position/delocalization and reorganization penalty. To understand these dramatic effects of the end-capping groups on the \( ^{R}PPn^\cdot \) properties we turned our
attention to the features of the hole distribution in these systems. Indeed, there are striking differences in the evolution of the hole delocalization patterns in the three \( ^{R}PPn^{+}\) series, \( R = H, iA, \) and \( OR, \) as evident from the unpaired ground-state spin density plots\(^{39}\) (Figure 2.13, A–C) and the condensed per-unit hole distributions evaluated as spin densities \( \Delta s \) and charge \( \Delta q^+ \) (Figure 2.13, A'–C''). In uncapped \( HPPn^{+}\) the hole is symmetrically distributed in the center of the molecule across the entire series, \( n = 2–10, \) which correlates well with a smooth near-\( 1/n \) evolution of the \( \Delta E_{el} \) and \( \lambda_{max} \) for this series (Figures 2.6 and 2.9). In the vertically excited \( HPPn^{+}\) (Figure 2.13, A') the hole also remains symmetrically distributed for the entire series, but spreads towards both ends of the molecule, leaving the central unit (or two central units in the case of even \( n \)) virtually unoccupied.

The hole distribution patterns in the \( ^{iA}PPn^{+}\) series (Figure 2.13, C') share similar features with \( HPPn^{+}\) and \( ROPPn^{+}\) series: for \( n \leq 7 \) the hole is symmetrically distributed in the center—like in \( HPPn^{+}\), while for the longer chains the hole shifts towards one of the capped terminal units—like in \( ROPPn^{+}\). This switch in the hole position in \( ^{iA}PPn^{+}\) with \( n > 7 \) coincides with the deviation of the \( \Delta E_{el} \) and \( \lambda_{max} \) values from the \( 1/n \) linear dependence (Figures 2.6 and 2.9). However, unlike \( ROPPn^{+}\), in longer \( ^{iA}PPn^{+}, n \geq 7, \) the hole is (nearly) symmetrically distributed over \( \sim 6 \) units at the end of the chain, with relatively low occupation of the capped terminal unit. The hole distribution in the vertically excited \( ^{iA}PPn^{+}\) for \( n \leq 7 \) is very similar to the uncapped \( HPPn^{+}\) where the hole symmetrically redistributes from the central units towards the periphery (Figure 2.13, A'-
C'). For \( n \geq 8 \), the hole in the vertically excited state rearranges in similar manner among the ~6 hole-bearing units and also slightly extends into the seventh (internal) unit.

By itself, gravitation of the hole towards one end of the molecule in longer \( {ROPP}_n^+ \) oligomers with strongly electron-donating \( RO \) end-capping groups is not entirely surprising. For shorter \( {ROPP}_n^+ \) the oxygen lone pairs of both \( RO \) groups should be intimately involved in the charge/hole localization, leading to planarization of the internal \( p \)-phenylene units (Figure 2.14), while in longer \( {ROPP}_n^+ \) the involvement of both \( RO \) groups in the hole delocalization would require quinoidal distortion of the entire polyphenylene chain that carries a significant energetic penalty due to the required planarization across the chain.

![Figure 2.14](https://example.com/figure214.png)

*Figure 2.14. Quinoidal distortion in short (A) and longer (B) \( {ROPP}_n^+ \) chains.*

This penalty is minimized by shifting the hole towards a single \( RO \)-capped terminal unit at the price of losing the hole stabilization by another terminal unit (Figure 2.14B).

Breaking the communication between the terminal units should increase \( E_{ox} \) with increasing \( n \), as well as to dramatically affect the \( \lambda_{max} \) evolution. However, it is not immediately obvious how this intuitive picture could apply to the similar gravitation of
the hole towards the end for $^{4}$PP$_{n}$$^{•}$ with $n > 7$. Moreover, the quantitative picture of the evolution of the $^{RO}$PP$_{n}$$^{•}$ properties lacks a satisfactory conceptual explanation. To address these questions, a simple multi-state parabolic model that generalizes well-known two- and three-parabolic models based on Marcus theory of electron transfer was developed, as follows.

**Multi-State Parabolic Model (MPM) Treatment of $^{R}$PP$_{n}$$^{•}$**

The classical two-parabolic Marcus model of electron transfer$^{40-43}$ has been extensively applied for description of the hole delocalization between two aromatic units, as well as—in extended three-parabolic model—to bridged systems.$^{43}$ The two-parabolic model can be straightforwardly applied to the smallest $^{R}$PP$_{2}$$^{•}$ oligomers.

To develop a general multi-state parabolic model of $^{R}$PP$_{n}$$^{•}$, we start with the lowest oligomers $^{R}$PP$_{2}$$^{•}$ with only two redox-active units. In this case, a clear quantitative understanding can be obtained by considering interaction between two diabatic states represented by parabolic functions of the effective geometric/solvent coordinate $x$.$^{24}$ Each diabatic state corresponds to the hole exclusively localized on the respective single unit. Mathematically, the (free) energies of each diabatic states are then represented by two quadratic functions, one with the minimum at $x = 0$, and the other with the minimum at $x = 1$:

$$G_{a} = \lambda x^{2}; G_{b} = \lambda (1 - x)^{2}, \quad \text{(eq. 2.2)}$$
where $\lambda$ is the reorganization energy, which corresponds to the vertical energy gap between the two diabatic states either at $x = 0$ or 1 (Figure 2.15). The two adiabatic states $\Psi_1$ and $\Psi_2$ arise from the two diabatic states $\Psi_a$ and $\Psi_b$ mixed as:

$$
\Psi_1 = c_{11}\psi_a + c_{21}\psi_b, \\
\Psi_2 = c_{12}\psi_a + c_{22}\psi_b.
$$

(qq. 2.3a)

or, in matrix notation:

$$
\begin{bmatrix}
\psi_a \\
\psi_b
\end{bmatrix}
= 
\begin{bmatrix}
1 \\
0
\end{bmatrix}, \\
\Psi =
\begin{bmatrix}
\Psi_1 & \Psi_2
\end{bmatrix}.
$$

(eq. 2.3b)

---

**Figure 2.15.** Free energy curves of the diabatic (thin lines) and adiabatic (thick lines) states in the three coupling regimes of the two-parabolic model: weak $|H_{ab}|/\lambda \approx 0$ (A), strong $|H_{ab}|/\lambda \geq 0.5$ (B), and intermediate $|H_{ab}|/\lambda < 0.5$ (C). Bar plots represent hole distribution in the ground and vertically excited states at the ground-state minimum $x_{\text{min}}$, calculated as squares of corresponding $c_y$ mixing coefficients.
The mixing coefficients $c_{i1}$ for the ground $G_1$ and $c_{i2}$ for the excited $G_2$ adiabatic states along with the corresponding energies $G_1$ and $G_2$ can be obtained by diagonalization of

the $2 \times 2$ effective Hamiltonian matrix:

\[
\mathbf{H} = \begin{bmatrix}
G_a & H_{ab} \\
H_{ab} & G_b
\end{bmatrix} = \begin{bmatrix}
\lambda x^2 & H_{ab} \\
H_{ab} & \lambda (1 - x)^2
\end{bmatrix}, \quad \text{(eq. 2.4a)}
\]

\[
\mathbf{G} = \Psi^{-1} \mathbf{H} \Psi = \begin{bmatrix}
G_1 & 0 \\
0 & G_2
\end{bmatrix}, \quad \text{(eq. 2.4b)}
\]

where the diagonal elements of $\mathbf{H}$ are the diabatic state energies, and the off-diagonal elements $H_{ab} < 0$ are the coupling elements. These coupling elements $H_{ab}$ that describe the strength of the electronic interaction between the two units are considered to be independent of the coordinate $x$. Number of parameters in the parabolic model can be reduced to one by using $\lambda$ as an energy measurement unit. Indeed, dividing both sides of equation 2.4 by $\lambda$ does not change the adiabatic state composition of $\Psi$, while the coupling elements and energies of diabatic and adiabatic states become simply scaled by $\lambda$:

\[
\frac{\mathbf{H}}{\lambda} = \begin{bmatrix}
x^2 & \frac{H_{ab}}{\lambda} \\
\frac{H_{ab}}{\lambda} & (1 - x)^2
\end{bmatrix}, \quad \text{(eq. 2.5a)}
\]

\[
\frac{\mathbf{G}}{\lambda} = \Psi^{-1} \left( \frac{\mathbf{H}}{\lambda} \right) \Psi = \begin{bmatrix}
\frac{G_1}{\lambda} & 0 \\
0 & \frac{G_2}{\lambda}
\end{bmatrix}. \quad \text{(eq. 2.5b)}
\]
The resulting ground-state energy is lowered relative to the original diabatic states,

whereas the excited-state energy is increased:

\[
\begin{align*}
G_1 &= \frac{1}{2} \left\{ (G_b + G_a) - \sqrt{(G_b - G_a)^2 + 4H_{ab}^2} \right\}, \\
G_2 &= \frac{1}{2} \left\{ (G_b + G_a) + \sqrt{(G_b - G_a)^2 + 4H_{ab}^2} \right\},
\end{align*}
\tag{eq. 2.6}
\]

which gives the energy curves for these states in terms of the parabolic diabatic states and the charge-transfer coordinate \( x \):

\[
\begin{align*}
G_1(x)/\lambda &= \frac{1}{2} \left\{ (2x^2 - 2x + 1) - \sqrt{(1 - 2x)^2 + 4(H_{ab}/\lambda)^2} \right\}, \\
G_2(x)/\lambda &= \frac{1}{2} \left\{ (2x^2 - 2x + 1) + \sqrt{(1 - 2x)^2 + 4(H_{ab}/\lambda)^2} \right\}.
\end{align*}
\tag{eq. 2.7}
\]

The distribution of the hole across the two units in the ground, \( Q_1 \), and excited, \( Q_2 \), adiabatic states can then be evaluated as squares of the coefficients \( c_{ij} \) (equation 2.8), each representing weight of the pure diabatic state \( \Psi_i \) in the mixed adiabatic state \( \Psi_j \), and visualized with bar plots (Figure 2.5).

\[
Q_1 = \begin{bmatrix} c_{11}^2 \\ c_{21}^2 \end{bmatrix}, \quad Q_2 = \begin{bmatrix} c_{12}^2 \\ c_{22}^2 \end{bmatrix}.
\tag{eq. 2.8}
\]
Importantly, adiabatic states $\Psi_j$ are orthonormal, i.e. sum of $c_i^j$ for each adiabatic state is equal to one, so the hole is normalized.

Depending on the coupling strength $H_{ab}$ between the diabatic states, three regimes of the hole localization are possible, as shown in Figure 2.5.\textsuperscript{24b} In the case of very weak coupling ($|H_{ab}|/\lambda \approx 0$) the resulting adiabatic states are almost identical to the original diabatic states:

$$
\Psi_1 \approx \psi_a = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \Psi_2 \approx \psi_b = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \quad x < 0.5,
$$

$$
\Psi_1 \approx \psi_b = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \Psi_2 \approx \psi_a = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad x > 0.5.
$$

(eq. 2.9)

The hole position, determined by a minimum on the ground state energy curve, is in this case on a single unit, at $x \approx 0$ or 1. The energy required to transfer the hole to another unit $\Delta G^x$ is then approximately equal to $\lambda/4$, and the vertical excitation energy $\Delta G_{1 \rightarrow 2}$ is equal to $\lambda$ (Figure 2.5).

On the other hand, if the coupling is very strong ($|H_{ab}|/\lambda \geq 0.5$), it gives rise to single-well adiabatic ground and excited states, where the hole is equally shared between the two units, with the energy minimum at $x = 0.5$ (Figure 2.5B). The ground state then becomes an equal mixture of the two diabatic states:
In this case, the vertical excitation energy equals to twice the coupling element, $\Delta G_{1 \rightarrow 2} = 2|H_{ab}|$.

In the intermediate regime ($|H_{ab}|/\lambda < 0.5$), the two diabatic states couple giving rise to a two-minima ground adiabatic state and a single-minimum excited state (Figure 2.5C). In this case, at the ground state minimum $x_{\text{min}}$ the ground and excited states are unequal mixtures of the diabatic states, e.g. $c_{11} > c_{21}$ and $c_{12} < c_{22}$ (equation 2.3). Thus, the hole is only partially localized on one of the units, and its redistribution requires activation energy $[(\lambda - 2|H_{ab}|)^2/4\lambda]$, whereas the vertical excitation energy is simply $\lambda$.

Thus, in two-parabolic model the hole delocalization as well as the ground- and excited state energies depend on the coupling $H_{ab}$ between the two diabatic states $\Psi_a$ and $\Psi_b$ as that correspond to the hole exclusively localized on the respective single unit, and the reorganization energy $\lambda$ that corresponds to the vertical energy gap between the two diabatic states at the minimum of one of them (Figure 2.15). The ground $Q_1$ and excited $Q_2$ adiabatic states of the system arise from the mixing of the diabatic states:

$$
\Psi_1 = \frac{1}{\sqrt{2}} \psi_a + \frac{1}{\sqrt{2}} \psi_b = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix},
$$

$$
\Psi_2 = \frac{1}{\sqrt{2}} \psi_a - \frac{1}{\sqrt{2}} \psi_b = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}.
$$

(eq. 2.10)

$$
\psi_a = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \psi_b = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \Psi = \begin{bmatrix} \Psi_1 \\ \Psi_2 \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{bmatrix}.
$$

(eq 2.11)
where \( c_{ij} \) are mixing coefficients.

The (free) energies of the diabatic states, \( G_a \) and \( G_b \), are represented by quadratic functions of the effective geometric/solvent coordinate \( x \). Composition of the adiabatic states at a given \( x \) and the corresponding energies \( G_1 \) and \( G_2 \) are then obtained by diagonalizing the effective Hamiltonian matrix:

\[
\frac{H}{\lambda} = \begin{bmatrix} x^2 & H_{ab}/\lambda \\ H_{ab}/\lambda & (1-x)^2 \end{bmatrix}.
\]  

(eq. 2.12a)

\[
\frac{G}{\lambda} = \Psi^{-1}(\frac{H}{\lambda})\Psi = \begin{bmatrix} G_1/\lambda & 0 \\ 0 & G_2/\lambda \end{bmatrix}.
\]  

(eq. 2.12b)

The number of parameters used in this model can be reduced to one—\( H_{ab}/\lambda \)—by using \( \lambda \) as the energy unit. Depending on the coupling strength, the hole may be localized on a single unit (weak coupling), perfectly delocalized over two units (strong coupling), or partially delocalized (intermediate coupling), as shown in Figure 2.15A, B, and C, respectively. Strongly delocalized systems have a single-minimum ground and excited states, while partially delocalized systems have two-minima ground and single-minimum excited states.
To describe the hole delocalization in the $^R$PPR$^\cdot$ with arbitrary number of linearly connected units, we generalized this approach to develop a multi-state parabolic model (MPM). In MPM, all units are represented by equivalent parabolic diabatic states with identical $H_{ab}/\lambda$ values, although the terminal parabolas may be shifted down by $\Delta\varepsilon/\lambda$ to account for the better hole stabilization abilities of the terminal units with electron-donating capping group (Figure 2.16).^44

Figure 2.16. MPM representation of $^R$PPR$^\cdot$: each diabatic state corresponds to a single unit; for $R = RO, iA$ the terminal units are shifted by appropriate $\Delta\varepsilon/\lambda$ values.

We obtain the adiabatic state energies $G_i$ and corresponding compositions in terms of mixing coefficients $c_{ij}$ and at a given $x$ by numerically diagonalizing the extended MPM Hamiltonian:

$$H/\lambda = \begin{bmatrix}
  x^2 - \Delta\varepsilon/\lambda & H_{ab}/\lambda & . & 0 & 0 \\
  H_{ab}/\lambda & (1-x)^2 & . & H_{ab}/\lambda & 0 \\
  . & . & . & . & . \\
  0 & H_{ab}/\lambda & . & (n-2-x)^2 & H_{ab}/\lambda \\
  0 & 0 & . & H_{ab}/\lambda & (n-1-x)^2 - \Delta\varepsilon/\lambda
\end{bmatrix}$$

(eq. 2.13)
We considered all units in $\mu PP_n^+$ to have the same energy, $\Delta \varepsilon = 0$, and systematically varied the $H_{ab}/\lambda$ parameter to reproduce the ground-state hole distribution patterns obtained with DFT (Figure 4D) at $H_{ab}/\lambda - 9^{,45}$ as shown in Figure 2.17A. Strikingly, this single-parameter model also faithfully reproduced the vertical excited-state hole distribution (Figure 2.17A), as well as the $E_{ox}$ and $\nu_{max}$ evolution for the entire series (Figure 2.18).
Figure 2.17. Multi-state parabolic modeling of $^{R}PP_{n}^{+*}$: pseudo-3D representation of the ground and first excited adiabatic state curves with respect to effective hole coordinate $x$ for $n = 2-10$. Minima on the curves are shown as black dots, and the bar charts show the hole distributions in the ground (at a minimum) and vertically excited (at the Frank-Condon point) states. Parameters of MPM: $\Delta \varepsilon / \lambda = 0$ ($^{H}PP_{n}^{+}$), $\Delta \varepsilon / \lambda = 8.5$ ($^{RO}PP_{n}^{+*}$), $\Delta \varepsilon / \lambda = 3.7$ ($^{iA}$); in all cases, $H_{ab} / \lambda = 9$. 
Figure 2.18. Stabilization energies of the $^R\text{PP}_n^+$ adiabatic ground states, \( G_1(x_{\text{min}}) \) (A), and the vertical excitation energies \( G_2(x_{\text{min}}) - G_1(x_{\text{min}}) \) (B) of three series of poly-\( p \)-phenylene wires obtained from the MPM (Figure 2.17) vs \( 1/n \).

We further parameterized the \( \Delta \epsilon/\lambda \) values—which describe the difference between the hole stabilization abilities of the capped terminal units relative to the in-chain units—for the $^R\text{PP}_n^+$ and $^i\text{PP}_n^+$ series to reproduce the DFT ground-state hole distributions, while keeping the same \( H_{ab}/\lambda-9 \) value. Again, the parameterized MPM with \( \Delta \epsilon/\lambda = 8.5 \) for $^R\text{PP}_n^+$ and \( \Delta \epsilon/\lambda = 3.7 \) for $^i\text{PP}_n^+$ yielded correct vertical excited-state hole distributions (Figure 2.17B and C), as well as the \( E_{\text{ox}} \) and \( \nu_{\text{max}} \) evolution (Figures 2.18).

The multi-state parabolic model that—despite its apparent simplicity—reproduces all salient features of the hole distribution in the three series $^R\text{PP}_n^+$ as well as their energetic and optoelectronic properties also points to the origin of the approximate \( 1/n \) dependencies in these series as well as their eventual breakdown. Indeed, if the
reorganization energy $\lambda$ is reduced to zero the effective $^HPP_n^{\bullet+}$ Hamiltonian becomes independent of $x$ and thus isomorphic to the Hückel theory Hamiltonian for a linear $\pi$-conjugated polymer. Diagonalization of this Hamiltonian with zero main diagonal yields the ground state energy that evolves proportionally to $\cos[\pi/(n+1)]$,\(^4^6\) that approximates as a $1/n$ trend for small $n$. Thus, for small $\lambda$ or, equivalently, large $|H_{ab}|/\lambda$ values the $^HPP_n^{\bullet+}$ ground state energies should initially evolve in approximate $1/n$-fashion. This evolution is akin to the evolution of HOMO energies in neutral $\pi$-conjugated oligomers, as both are determined by the increasing delocalization of the hole and HOMO, respectively, over the oligomer chain. However, in the case of MPM of cation radicals energy gain due to the hole localization is eventually compensated by the reorganization energy involving the increasing number of units, which eventually halts further delocalization and thus the approximate $1/n$ trends seen in shorter oligomers. Thus, the $^HPP_n^{\bullet+}$ ground adiabatic state energies at their minima, $G_1(x_{\text{min}})$, systematically decrease in approximate $1/n$ fashion until reaching saturation at $n \geq 7$ (Figure 2.18A). The excited state energies decrease in a similar manner, but steeper, thus leading to a linear $\nu_{\text{max}}$ decrease till $n \approx 8$ with subsequent leveling for the longer oligomers (Figure 2.18B).

In the $^{RO}PP_n^{\bullet+}$ series, the two directly coupled low-energy units in the smallest oligomer $n = 2$ are the most efficient in stabilizing the hole. This stabilization becomes less efficient when high-energy bridging parabolas are added in higher oligomers, $n = 3$-$4$ that increases the $^{RO}PP_n^{\bullet+}$ ground state energy, which is equivalent to the observed $E_{\text{ox}}$ increase for $n = 2$-$4$. Further $^{RO}PP_n^{\bullet+}$ lengthening leads to development of a maximum in the middle of the ground-state curve, whose energy keeps increasing until converging at
$n > 8$ to the same limit as in the middle of the $^{3}H\text{PP}_{n}^{+\bullet}$ chains (Figure 2.17). At the same time, the energies of the two equivalent minima on the sides of this maximum change very little for $n > 5$, in accord with the observed $E_{\text{ox}}$ leveling for $n > 5$.

The $^{3}R\text{PP}_{n}^{+\bullet}$ excited-state curves gradually decrease in energy, and develop two minima later than the ground state, at $n = 6$ (Figure 2.17B); as they are constructed from the higher portions of the diabatic parabolas both terminal parabolas can still have significant contributions in center, although their minima are already far enough to have negligible contribution in the middle of ground-state curve. Asynchronous development of the two-minima feature on the ground- and excited-state adiabatic curves explains the complex $\nu_{\text{max}}$ evolution for $^{3}R\text{PP}_{n}^{+\bullet}$. For $n \leq 4$, where both states have minima in the middle, the ground-state minimum increases in energy with $n$, while the excited-state minimum decreases in energy which results in a sharp $\lambda_{\text{max}}$ decrease (Figure 2.18B). For $n = 5–6$, the vertical excitation from one of the ground-state minima leads to the Frank-Condon point on a shoulder of the single-minimum excited-state well, resulting in sharply increasing $\nu_{\text{max}}$ (Figure 2.18B). For $n \geq 7$, both ground- and excited-state curves attain similar double-minimum shapes, and their energies level off, resulting in nearly constant $\nu_{\text{max}}$ (Figure 2.18B).

Ground- and excited-state adiabatic curves of $^{4}i\text{PP}_{n}^{+\bullet}$ appear to be similar to $^{3}H\text{PP}_{n}^{+\bullet}$ (Figures 2.18, C and A), with single-minimum shapes and gradual lowering of their energies with increasing $n$. However, the $^{4}i\text{PP}_{n}^{+\bullet}$ ground state develops a subtle double-minima structure for at $n \geq 8$, followed by the excited state for $n \geq 9$. While the ground state has a single-well character for $n \leq 7$, the energy at the minimum point decreases
only up to \( n \approx 6 \), in accord with the observed \( E_{\text{ox}} \) leveling of at \( n \approx 6 \) (Figures 2.1A and 2.9A). For \( n \geq 8 \), the energies of the two minima on the ground-state curves for are just barely lower than in the center, so their appearance does not affect the \( E_{\text{ox}} \) evolution; however, it leads to slight increase of \( \nu_{\text{max}} \), as the Franck-Condon point ends up on a shoulder of the excited state curve (Figure 2.18C). Thus, although the evolution of the \( ^{IA}{PP}_n^{+\bullet} \) properties is not vastly different from the uncapped \( ^{H}{PP}_n^{+\bullet} \) series, the emergence of the subtle features in the higher \( ^{IA}{PP}_n^{+\bullet} \) homologues, \( n \geq 6 \), is similar to the \( ^{RO}{PP}_n^{+\bullet} \) series.

**Evolution of the Hole Distribution in \( ^{R}{PP}_n^{+\bullet} \) and Breakdown of 1/\( n \) Relationships**

The \( ^{R}{PP}_n^{+\bullet} \) structure-property relationships are related to the position and shape of the hole distributed over monomer units, and, at the same time, the hole distribution depends on the position of the ground state free energy minima with respect to the hole coordinate \( x \) (Figure 2.17). Thus, we next use the MPM to discern the nature of the forces responsible for the formation of these minima and varied distribution of the hole in three \( ^{R}{PP}_n^{+\bullet} \) series.
In \( ^{H}\text{PP}_n^{+}\cdot \), where all units are equivalent, the hole has a symmetric bell-shaped form and resides in the middle of the chain to take advantage from delocalizing over maximum number of monomer units. However, the hole can effectively delocalize over no more than seven \( p\)-phenylene units (Figure 2.19), which leads to saturation of \( E_{\text{ox}} \) and thus emergence of polymeric behavior with respect to the hole delocalization for \( n > 7 \). The ideal bell-shaped hole distribution is distorted by introducing electron-donating \textit{iso}-alkyl (\( ^{i\text{A}}\text{PP}_n^{+} \)) or \textit{iso}-alkoxy (\( ^{\text{RO}}\text{PP}_n^{+} \)) end-capping groups that provide additional mechanism of the hole stabilization (Figure 2.19).
Figure 2. 20. (A, B) Adiabatic ground state curves $RO_1$ for $RO_{PP4^+}$ and $RO_{PP5^+}$ (thick solid lines) and their components $G_{PP}$ (stabilization due to poly-$p$-phenylene chain, thin solid lines), and $G^{RO}$ (stabilization due to end-capping groups, dash-and-dotted lines) and (A’, B’) their first derivatives (thick solid lines) interpreted as forces acting on the hole, $F$. Positive values of $F$ correspond to forces pushing the hole to the left, and negative—to the right. Dominant components of the total force are shown as thin solid lines, and smaller—as dashed lines, and the grey arrows the overall force direction.

Thus, the hole shape and position can be thought to be determined by two forces: $F_{PP}$ that pushes the hole towards the middle of the chain—where it can be more effectively stabilized by poly-$p$-phenylene chain, and $F^R$ that pulls it towards the end—where it can be stabilized by lower-energy terminal units. This picture can be quantified by decomposing the ground state adiabatic energy $G_1$ into two components: the stabilization due to the poly-$p$-phenylene framework $G_{PP}$ (taken simply as the $H_{PP_n^+}$ ground-state energy $H_{G_1}$), and the stabilization due to end-capping groups, $G^R$, which is calculated by
subtraction: $G^R = G_1 - G^{pp} = G_1 - H G_1$. Then, the two effective forces $F^{pp}$ and $F^R$ that determine the hole position can be expressed as first derivatives of $G^{pp}$ and $G^R$, as shown in Figure 2.20 on the example of $ROPP^4\cdot$ and $ROPP^5\cdot$.

In $ROPP^4\cdot$, $F^{pp}$ prevails in the entire range of $x$, so the ground adiabatic state has only one minimum in the middle due to high energetic cost of shifting the hole towards an end of the chain, the same holds true for $ROPP^3\cdot$ and $iAPP^4\cdot$ with $n \leq 7$. On the other hand, in $ROPP^5\cdot$ with $n \geq 5$, $G^{pp}$ curve flattens in the middle due to saturation, so the hole can migrate without much energetic penalty towards a terminal unit, whose strong hole-stabilizing ability attracts a significant fraction of the hole ($\sim 40\%$) and thus causes its significant deformation and pronounces double-minimum ground state curve. As in $iAPP^5\cdot$ the terminal units are much less efficient in terms of hole stabilization, it retains its shape and shifts only marginally towards an end for longer chains, $n \geq 8$. 
In the middle of the chain, the ground-state energy $^RG_1$ of end-capped $^RPPh^+$ is determined by the $^G_{pp}$ component, which monotonously increases in magnitude up to $n \approx 7$ and then levels off; and the $^G_R$ component which sharply decreases in magnitude for $n > 2$ (Figure 2.21). Thus, the energy at the mid-point of the ground-state curve smoothly increases with $n$ for $^ROPPh^+$, where the $^G_R$ component dominates due to large $\Delta \varepsilon/\lambda$ value, or smoothly decreases for $^iAPPh^+$, where the $^G_{pp}$ component dominates. At the polymeric limit, the mid-point ground-state energies for all three $^RPPh^+$ series converge to the same value determined by $^G_{pp}$. Thus, for all $^HPPh^+$ as well as for $^iAPPh^+$ with $n \leq 7$ the $E_{ox}$ and $\nu_{max}$ smoothly evolve towards the polymeric limit, because their ground state curves have a single minimum in the middle. However, in $^ROPPh^+$ with $n > 4$ and in $^iAPPh^+$ with $n > 7$, emergence of the two-minima ground-state shape shifts the hole
towards an end of the chain thereby leading to rapid $E_{ox}$ and $\nu_{max}$ saturation and breakdown their of approximate $1/n$ dependences.

The subtle differences in $1/n$ dependences observed for $^{14}PP\psi^+\bullet$ in comparison with $HPP\psi^+\bullet$ arise because the hole shrinks from seven to six $p$-phenylene units when it shifts towards a terminal unit in longer $^{14}PP\psi^+\bullet$. Due to the shift of the hole towards a terminal unit in $^{14}PP\psi^+\bullet$ (Figure 2.19) further addition of $p$-phenylene units has a little effect, which leads to earlier $E_{ox}$ saturation. Also, vertical excitation in $^{14}PP\psi^+\bullet$ with the hole shifted towards an end of the chain leads to a deformed hole distribution at the Franck-Condon point which results in early $1/n$ breakdown of $\nu_{max}$ in $^{14}PP\psi^+\bullet$ vs $HPP\psi^+\bullet$ series.

Coexistence of the two forms of $^{RO}PP\delta^+\bullet$

The observation of the two absorption bands at 6452 cm$^{-1}$ (1550 nm) and 5050 cm$^{-1}$ (1980 nm) in the $^{RO}PP\delta^+\bullet$ spectrum suggests the presence of two species. In the preceding discussion, we used the slightly more intense absorption band at 6452 cm$^{-1}$ which falls in line with higher $^{RO}PP\psi^+\bullet$ oligomers, $n = 6-7$ (Figure 2.3B). However, when the less intense 5050 cm$^{-1}$ band is included in the $\nu_{max}$ vs $1/n$ plot (Figure 2.13A), it nearly perfectly falls on the linear $1/n$ relation observed for shorter $^{RO}PP\psi^+\bullet$ chains, $n = 2-4$ that suggests that this second form may correspond to the structure with symmetrically distributed hole, similar to shorter $^{RO}PP\psi^+\bullet$, $n = 2-4$. 
Indeed, we were able to locate this structure with symmetrically distributed hole using DFT (Figure S36) and calculate the corresponding vertical excitation energy that again falls on the linear $1/n$ dependence of the $\nu_{\text{max}}$ values observed for $n = 2-4$ (Figure 2.13B).

Furthermore, the energy gap between the ground- and excited-state MPM curves of $^{RO}_{PP}P^*_{5}^+$ (Figure 2.8B) that corresponds to the excitation from the middle of the ground-state curve again aligns with the $1/n$ linear relationship for $n = 2-4$ (Figure 2.13C). This remarkable consistency between the experimental, DFT, and MPM pictures strongly supports the assignment of the second absorption maximum at $5050 \text{ cm}^{-1}$ in the $^{RO}_{PP}P^*_{5}^+$ spectrum to the higher-energy form with symmetrically distributed hole. Thus, $^{RO}_{PP}P^*_{5}^+$ appears to be an intermediate case that falls between the two regimes of hole delocalization in the $^{RO}_{PP}P^*_{n}^+$ series, with symmetrically distributed hole ($n \leq 4$), and with
the hole shifted towards a terminal unit \((n \geq 6)\), as is elegantly illustrated by the evolution of the MPM ground-state curves in Figure 2.8B.\(^{48}\)
Summary and Conclusions

Here, based on the experimental and computational results as well as the multi-state parabolic model, we delineated the factors that determine the redox and optoelectronic properties of $^R{\text{PP}}_n/^R{\text{PP}}_n^+$ with different end-capping substituents ($R = iA, H,$ and $OR$).

DFT calculations with modified B1LYP density functional (B1LYP-40), calibrated against the existing experimental data for the $^iA{\text{PP}}_n/^iA{\text{PP}}_n^+$ series$^{14}$ and validated against the newly synthesized $^RO{\text{PP}}_n^+$ series, showed a dramatic effect of the end-capping groups on the $E_{\text{ox}}$ and $\nu_{\text{max}}$ evolution for $^iA{\text{PP}}_n^+$ and $^RO{\text{PP}}_n^+$ (Figures 2.1 and 2.3). While $E_{\text{ox}}$ decreases in nearly $1/n$ fashion for $^H{\text{PP}}_n$, before leveling off at the polymeric limit, introduction of a strong electron-donating substituent -OR leads to increase in the $E_{\text{ox}}$ values with leveling off for $n > 5$. Evolution of the oxidation energies in the weakly electron-donating groups in the $^iA{\text{PP}}_n$ series is similar to the uncapped series, whereas the $\nu_{\text{max}}$ evolution in $^iA{\text{PP}}_n^+$ is more similar to $^RO{\text{PP}}_n^+$, as it demonstrates abrupt saturation at $n = 8$.

To rationalize these results, we developed a multi-state parabolic model (MPM), an extension of the well-known Marcus two-state parabolic model. The MPM employs an arbitrary number of energetically equivalent parabolas for linearly connected $p$-phenylene units and lower-energy parabolas for the end-capped terminal units. Using only two effective parameters—$H_{ab}/\lambda$, responsible for electronic coupling between $p$-phenylene units, and $\Delta e/\lambda$ the shift of the terminal unit energies—the MPM was able to reproduce the hole distribution patterns and the evolution of the $E_{\text{ox}}$ and $\nu_{\text{max}}$ energies in all three
series. The MPM shows that the $^{R}PP_{n}^{\bullet}$ properties are determined by the hole distribution across the molecule, and that there are two forces that pull the hole in opposite directions: one towards the middle of the chain, where it is stabilized by the $p$-phenylene chain, and another towards the lower-energy terminal units. The subtle interplay between these two forces that determines the position/distribution of the hole entails the key role of the end-capping substituents $R$ in $^{R}PP_{n}^{\bullet}$. Thus, even presumably innocent modulation of $R$ could result in a sizable modulation of the $^{R}PP_{n}^{\bullet}/^{R}PP_{n}^{\bullet}$ optoelectronic properties.

The confluence and remarkable accord between the experimental, computational, and MPM approaches, evident from comparison of Figures 2.1, 2.3, and 2.9, provide a unified picture of the chemical underpinnings behind the structure-property relationships in $\pi$-conjugated aromatic polymers $^{R}PP_{n}/^{R}PP_{n}^{\bullet}$. This simple conceptual model can now guide the rational design of new $\pi$-conjugated systems whose properties can first be predicted using the MPM that can help to pinpoint the required parameters of the interconnected units in the conjugated polymeric $\pi$-system with donor ability $\Delta\varepsilon/\lambda$ and coupling $H_{ab}/\lambda$. The combined investigative approach elaborated in this work can be readily applied to more complex donor-spacer-acceptor systems and doped molecular wires and will allow the design and study of the next generation materials for long-range charge transport and photochromic molecules.
EXPERIMENTAL SECTION

General Experimental Methods and Materials. All reactions were performed under argon atmosphere unless otherwise noted. All commercial reagents were used without further purification unless otherwise noted. Dichloromethane (Aldrich) was repeatedly stirred with fresh aliquots of concentrated sulfuric acid (~10 % by volume) until the acid layer remained colorless. After separation it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P₂O₅ under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexanes and toluene were distilled from P₂O₅ under an argon atmosphere and then refluxed over calcium hydride (~12 h). After distillation from CaH₂, the solvents were stored in Schlenk flasks under an argon atmosphere. Tetrahydrofuran (THF) was dried initially by distilling over lithium aluminum hydride under an argon atmosphere. The THF was further refluxed over metallic sodium in the presence of benzophenone until a persistent blue color was obtained and then it was distilled under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. NMR spectra were recorded on Varian 300 and 400 MHz NMR spectrometers. GC-MS spectra were obtained on a Fissions 8000 trio instrument at an ionization potential of 70 eV.

Cyclic Voltammetry (CV). The CV cell was of an air-tight design with high vacuum Teflon valves and Viton O-ring seals to allow an inert atmosphere to be maintained
without contamination by grease. The working electrode consisted of an adjustable platinum disk embedded in a glass seal to allow periodic polishing (with a fine emery cloth) without changing the surface area (~1 mm²) significantly. The reference SCE electrode (saturated calomel electrode) and its salt bridge were separated from the catholyte by a sintered glass frit. The counter electrode consisted of platinum gauze that was separated from the working electrode by ~3 mm. The CV measurements were carried out in a solution of 0.2 M supporting electrolyte (tetra-n-butyl ammonium hexafluorophosphate, TBAH) and 2-5 x 10⁻³ M substrate in dry dichloromethane under an argon atmosphere. All the cyclic voltammograms were recorded at a sweep rate of 200 mV sec⁻¹, unless otherwise specified and were IR compensated. The oxidation potentials (E₁/₂) were referenced to SCE, which was calibrated with added (equimolar) ferrocene (E₁/₂ = 0.450 V vs. SCE). The E₁/₂ values were calculated by taking the average of anodic and cathodic peak potentials in the reversible cyclic voltammograms.

Synthesis of 1a.
To a Schlenk flask containing activated magnesium turnings (6.5 g, 267.32 mmol) with a crystal of iodine and a few drops of 1,2-dibromoethane, was added 4-bromo anisole (20.0 g, 106.93 mmol) dissolved in 100 mL of dry THF drop wise under argon atmosphere. After this addition, the reaction mixture was refluxed for 5 hr, after 5hr NMR of an aliquot showed complete formation of the Grignard reagent. It was then cooled to room temperature and was then transferred by cannula to a cooled solution (-78°C) of trimethyl borate (18.2 mL, 160.39 mmol) in 80 mL of dry THF. The mixture was then allowed to come to room temperature overnight, and then hydrolyzed with 6N HCl (100 mL) for 4 h. The organic layer was then extracted into diethyl ether (3 x 50 mL), dried over MgSO4, concentrated and chromatographed over silica gel, with hexane-ethyl acetate as eluent to afford the boronic acid as white viscous oil. Yield: 13.0 g, 81% (white solid), 1H NMR (CDCl3, 400 MHz) δ: 3.89-3.90 (3H, s), 6.99-7.04 (2H, d, J = 8.70 Hz) 8.15-8.19 (2H, d, J = 8.66 Hz).
Synthesis of $^{R01}PP_2$.

4-Bromo anisole (1.0 g, 5.35 mmol) and the corresponding boronic ester (1 equiv, 0.98 g, 6.42 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (30 mL) in an oven dried Schlenk flask under an argon atmosphere and the flask was evacuated and filled with argon (3x). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (2.5 g) in water (10 mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3x). To the DME solution, Pd(PPh$_3$)$_4$ (0.05 g) and the salt solution were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3x) after each addition. The flask was covered with aluminum foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The crude product was then purified by column chromatography using a hexane to give the pure product (1.0 g, 87%), m.p: 175-176°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ: 4.21-4.29 (2H, m), 6.92-6.98 (4H, d, $J$ =
8.87 Hz) 7.51-7.56 (4H, d, J = 8.81 Hz) 7.58-7.61 (4H, s); \(^{13}\)C NMR (CDCl\(_3\), 400 MHz) \(\delta\); 29.71, 29.90, 32.03, 34.11, 78.24, 116.20, 127.06, 128.11, 133.03, 139.23, 158.44.

**Synthesis of RO1PP\(_3\).**

1,4-dibromobenzene (0.5 equiv, 2.5 g, 10.59 mmol) and the corresponding boronic ester (1 equiv, 4.8 g, 25.43 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (60 mL) in an oven dried Schlenk flask under an argon atmosphere and the flask was evacuated and filled with argon (3x). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (5.0 g) in water (20 mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3x). To the DME solution, Pd(PPh\(_3\))\(_4\) (50 mg) and the salt solution were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3x) after each addition. The flask was covered with aluminum foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 30 mL). The organic layer was dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The crude product was then purified by column chromatography using a hexane to give the pure product (3.0 g, 98%), m.p: 274-276\(^0\)C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\); 4.21-4.29 (2H, m),
6.92-6.98 (4H, d, J = 8.87 Hz) 7.51-7.56 (4H, d, J = 8.81 Hz) 7.58-7.61 (4H, s); $^{13}$C NMR (CDCl$_3$, 400 MHz) δ 29.71, 29.90, 32.03, 34.11, 78.24, 116.20, 127.06, 128.11, 133.03, 139.23, 158.44.

Synthesis of 1-bromo-4-(2-ethyl-1-hexyloxy) benzene.

![Chemical reaction diagram]

To a solution of 4-bromo phenol (15 g, 86.7 mmol) and potassium carbonate (40 g, 289 mmol) dissolved in the 300 ml DMF under an argon atmosphere, 2-ethyl hexyl bromide (20.1 g, 104 mmol) was added drop wise and heated to 70°C for 24 hr in the dark. The reaction mixture was quenched by addition of 1M HCl (50 mL) and extracted with Hexane (3 x 50 mL). Then separated the organic layer and the water was extracted three more times with hexane (50 mL). Then the combined solution of all these extractions were dried over MgSO$_4$. The solvent was removed by rotary evaporation and crude was purified by column chromatography using hexane as an eluent to give product. (24.7 g, 61%).$^1$H NMR (CDCl$_3$, 400 MHz) δ; 0.88-0.96 (6H, t, J = 7.47 Hz), 1.25-1.54 (8H, m), 3.76-3.84 (2H, dd, J = 1.01 Hz), 6.75-6.81 (2H, d, J = 9.05 Hz) 7.34-7.38 (2H, d, J = 9.05 Hz); $^{13}$C NMR (CDCl$_3$, 400 MHz) δ; 11.23, 14.24, 23.18, 23.93, 29.19, 39.42, 70.81, 112.57, 116.41, 132.26, 158.61.
Synthesis of $^{RO2}PP_4$.

A Schlenk flask containing bromo compound (3 g, 10.51 mmol) was added to anhydrous THF (30 mL) under argon, was cooled to -78°C, and n-BuLi (1.5 equiv, 6.32 mL, 15.8 mmol) was added dropwise to this solution. The resulting reaction mixture was stirred for 1 hour, and then added trimethyl borate (3 equiv, 3.5 mL, 31.53 mmol) at -78°C, and allowed the reaction mixture to come to room temperature. To this reaction mixture, 4,4’-dibromobiphenyl (0.76 g, 2.45 mmol), toluene (25 mL), ethanol (25 mL), sodium carbonate solutions (5 g in 20 mL water) and Pd(PPh$_3$)$_4$ (50 mg) were added by sequential degassing. Then the flask was covered with aluminum foil and the reaction mixture was allowed to reflux overnight (~18 h). The resulting mixture was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The crude product was purified by column chromatography on silica gel using hexanes as eluent to afford pure product (1.25 g, 91%), m.p: 154-156°C. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 0.88-0.96 (12H, t), 1.28-1.58 (16H, m), 1.72-1.80 (2H, m), 3.87-3.92 (4H, dd, $J = 1.01$ Hz), 6.97-7.02 (4H, d, $J = 8.75$ Hz) 7.55-7.60 (4H, d, $J = 8.72$ Hz); 7.62-7.67 (4H, d, $J = 8.38$ Hz), 7.67-7.72 (4H, d, $J = 8.50$ Hz).
8.46 Hz; $^{13}$C NMR (CDCl$_3$, 400 MHz) δ; 11.27, 14.26, 23.22, 24.00, 29.23, 30.67, 39.53, 70.67, 114.95, 127.15, 127.15, 127.37, 128.08, 132.99, 139.03, 139.88, 159.19.

Synthesis of 3, 7-dimethyl-1-octylbromide.

To a Schlenk flask containing 48% HBr (100 mL) was added concentrated sulfuric acid (17 mL) with stirring. Then 3, 7-dimethyl-1-octanol (67 mL, 100 g) was added to this mixture, and heated to 120-125°C, and the reaction was running at this temperature for overnight. Then the reaction mixture was allowed to come to room temperature, and quenched by an addition of 10% NaHCO$_3$ (100 mL) and extracted with hexane (3 x 50 mL). The hexane layer was washed with and sodium bicarbonate solution (100 ml) water (3 x 50 mL) and. The organic layer was dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The crude product was then purified by flash column chromatography using a hexane as eluent to give the pure product as a liquid (1.25 g, 91%). $^1$H NMR (CDCl$_3$, 400 MHz) δ 0.84-0.90 (6H, d, $J = 6.88$ Hz), 0.92-0.97 (3H, d, $J = 6.55$HZ), 1.07-1.34 (6H, m), 1.46-1.71 (3H, m), 1.81-1.93 (1H, m), 3.35-3.50 (2H, m), 6.95-7.01 (4H, d, $J = 8.71$ Hz) 7.52-7.58 (4H, d, $J = 8.65$ Hz), 7.62-7.66 (4H,
Synthesis of 1-Bromo-4-(3, 7-dimethyl-1-octylloxy) benzene.

\[
\text{Br} \quad + \quad \begin{array}{c}
\text{K}_2\text{CO}_3 \\
\text{DMF} \\
70^\circ\text{C} \\
24\text{hr}
\end{array} \quad \begin{array}{c}
\text{OH} \\
\text{Br}
\end{array}
\]

To an oven dried Schlenk flask, was added 4-bromo phenol (10 g, 57.8 mmol), potassium carbonate (26 g, 190.74 mmol) and 150 mL DMF under argon. To this reaction mixture 3, 7-dimethyl-1-octylbromide (15.3 g, 69.36 mmol) was added drop wise and the reaction mixture was heated at 70°C for 24 hours in the dark. Then the reaction mixture was quenched by addition of 1M HCl (100 mL) and extracted with Hexane (50 mL). Then separated the organic layer and the water was extracted three more times with hexane (3 x 50 mL). Then the mixture solution of all these extractions were dried over MgSO₄. The solvent was removed by rotary evaporation and crude was purified by column chromatography using hexane as an eluent to give product. \(^1\)H NMR (CDCl₃, 400 MHz) δ: 0.84-0.90 (12H, d, \(J = 6.58\) Hz), 0.92-0.97 (6H, d, \(J = 6.55\) Hz), 1.11-1.39 (12H, m), 1.47-1.75 (6H, m), 1.80-1.90 (2H, m), 3.98-4.07 (4H, m), 6.95-7.01 (4H, d, \(J = 8.71\) Hz) 7.52-7.58 (4H, d, \(J = 8.65\) Hz), 7.62-7.66 (4H, d, \(J = 8.40\) Hz), 7.67-7.71 (4H, d, \(J = 8.40\) Hz), 19.08, 22.73, 22.83, 24.70, 28.09, 31.78, 32.25, 36.86, 39.31, 40.21.
7.67-7.71 (4H, d, J = 8.40 Hz); $^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$; 19.77, 22.75, 22.86, 24.79, 28.10, 29.93, 36.21, 37.40, 39.36, 66.63, 112.26, 116.38, 132.28, 158.34.

Synthesis of 4-Bromo-4’-(3, 7-dimethyl-1-octyloxy) benzene.

A Schlenk flask containing 1-bromo-4-(3, 7-dimethyl-1-octyloxy) benzene (5 g, 15.96 mmol) and anhydrous THF (40 mL), was cooled to -78°C, and n-BuLi (2 equiv, 12.8 mL, 31.92 mmol) was added dropwise under argon atmosphere. The resulting reaction mixture was stirred for 1 hour, and then added trimethyl borate (3 equiv, 5.3 mL, 47.88 mmol) at -78°C, and allowed the reaction mixture to come to room temperature slowly. To this reaction mixture, 1-bromo,4-iodobenzene (4.6 g, 18.5 mmol), toluene (25 mL), ethanol (25 mL), sodium carbonate solutions (5 g in 20 mL water) and Pd(PPh$_3$)$_4$ were added by sequential degassing. Then the flask was covered with aluminum foil and the reaction mixture was allowed to reflux overnight (~18 h). The resulting mixture was cooled to room temperature, quenched with water (50 mL) and extracted with
dichloromethane (3 x 30 mL). The combined organic layers were dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The crude product was purified by column chromatography on silica gel using hexanes as eluent to afford pure product (3.78 g, 60%) 

\[{^1}H\text{ NMR (CDCl}_3, 400 MHz) \delta: 0.84-0.90 (6H, d, J = 6.58 Hz), 0.92-0.97 (3H, d, J = 6.55 Hz), 1.11-1.39 (6H, m), 1.47-1.75 (3H, m), 1.80-190 (1H, m), 3.98-4.07 (2H, m), 6.93-6.99 (2H, d, J = 8.75 Hz) 7.38-7.43 (2H, d, J = 8.55 Hz), 7.44-7.50 (2H, d, J = 8.76 Hz), 7.50-7.55 (2H, d, J = 8.54 Hz); {^{13}}C \text{ NMR (CDCl}_3, 400 MHz) \delta: 19.81, 22.77, 22.88, 24.82, 28.13, 30.00, 36.33, 37.44, 39.39, 66.55, 115.02, 120.84, 128.07, 128.41, 131.91, 132.35, 139.93, 159.11.\]

Synthesis of \(\text{RO}_3\text{PP}_2\).

A Schlenk flask containing 1-bromo,4-(3, 7-dimethyl-1-octyloxy) benzene (2.5 g, 7.98 mmol) and anhydrous THF (30 mL) was cooled to -78°C, and n-BuLi (2 equiv, 6.4 mL, 15.96 mmol) was added dropwise under argon atmosphere. The resulting reaction mixture was stirred for 1 hour, and then added trimethyl borate (3 equiv, 2.7 mL, 23.94 mmol) dropwise at -78°C. The reaction mixture was allowed to warm to room temperature slowly. To this reaction mixture, 4-bromo,1-alkoxy benzene (3.7 g, 11.8 mmol), toluene (25 mL), ethanol (25 mL) and aqueous sodium carbonate solutions (5 g,
in 20 mL water) and Pd(PPh₃)₄ (50 mg) were added by sequential degassing. The flask was covered with aluminum foil and the reaction mixture was allowed to reflux overnight (~18 h). The resulting mixture was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The crude product was purified by column chromatography on silica gel using hexanes as eluent to afford pure product (2.8 g, 76%), m.p: 82-84°C; ¹H NMR (CDCl₃, 400 MHz) δ: 0.84-0.90 (12H, d, J = 6.58 Hz), 0.92-0.97 (6H, d, J = 6.55 Hz), 1.11-1.39 (12H, m), 1.47-1.73 (6H, m), 1.79-1.89 (2H, m), 3.96-4.07 (4H, m), 6.91-6.97 (4H, d, J = 8.79 Hz) 7.42-7.56 (4H, d, J = 8.81 Hz); ¹³C NMR (CDCl₃, 400 MHz) δ; 19.81, 22.76, 22.86, 24.81, 28.12, 30.00, 36.39, 37.44, 39.39, 66.51, 114.86, 127.79, 133.45, 158.34.

Synthesis of RO₃PP₃.

A Schlenk flask containing bromo compound (2.5 g, 7.98 mmol) and anhydrous THF (30 ml) was cooled to -78°C, and n- BuLi (2 equiv, 6.4 mL, 15.96 mmol) was added dropwise under argon atmosphere. The resulting reaction mixture was stirred for 1 hour, and then added trimethyl borate (3 equiv, 2.7 mL, 23.94 mmol) dropwise at -78°C. Then the reaction mixture was allowed to warm to room temperature slowly. To this reaction mixture, 1,4-dibromobenzene (0.62 g, 2.6 mmol), toluene (25 mL), ethanol (25 mL) and
sodium carbonate solutions (5 g, in 20 mL water) and Pd(PPh$_3$)$_4$ (50 mg) were added by sequential degassing. The flask was covered with aluminum foil and the reaction mixture was allowed to reflux overnight (~18 h). The resulting mixture was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The crude product was purified by column chromatography on silica gel using hexanes as eluent to afford pure product (0.9 g, 76%); M.P= 148-150$^\circ$C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 0.84-0.90 (12H, d, $J = 6.58$ Hz), 0.92-0.97 (6H, d, $J = 6.55$ Hz), 1.11-1.39 (12H, m), 1.47-1.75 (6H, m), 1.80-190 (2H, m), 3.98-4.07 (4H, m), 6.95-7.01 (4H, d, $J = 8.74$ Hz), 7.52-7.58 (4H, d, $J = 8.74$ Hz), 7.58-7.62 (4H, s); $^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$: 19.81, 22.76, 22.86, 24.81, 28.12, 30.00, 36.39, 37.44, 39.39, 66.51, 114.94, 127.10, 128.07, 133.21, 139.25, 158.84.

**Synthesis of RO$_3$PP$_4$.**

![Chemical structure](image)

A Schlenk flask containing bromo compound (2.5 g, 7.98 mmol) and anhydrous THF (40 mL) under argon was cooled to -78$^\circ$C, and n- BuLi (2 equiv, 6.4 mL, 15.96 mmol) was added dropwise under argon atmosphere. The resulting reaction mixture was stirred for 1 hour, and then added trimethyl borate (3equiv, 2.7 mL, and 23.94 mmol) was added dropwise at -78$^\circ$C. Then the reaction mixture was allowed to warm to room
temperature slowly. To this reaction mixture, 4,4’-dibromobiphenyl (3.7 g, 11.86 mmol), toluene (25 mL), ethanol (25 mL) and sodium carbonate solutions (5 g, in 10 mL water) and Pd(PPh₃)₄ (50 mg) were added by sequential degassing. The flask was covered with aluminum foil and the reaction mixture was allowed to reflux overnight (~18 h). The resulting mixture was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried over anhydrous magnesium sulfate. It was filtered, evaporated and dried under vacuum. The crude product was purified by column chromatography on silica gel using hexanes as eluent to afford pure product (3.78 g, 60%), m.p = not melted below 210°C; ¹H NMR (CDCl₃, 400 MHz) δ 0.84-0.90 (12H, d, J = 6.58 Hz), 0.92-0.97 (6H, d, J = 6.55 Hz), 1.11-1.39 (12H, m), 1.47-1.75 (6H, m), 1.80-190 (2H, m), 3.98-4.07 (4H, m), 6.95-7.01 (4H, d, J = 8.71 Hz) 7.52-7.58 (4H, d, J = 8.65 Hz), 7.62-7.66 (4H, d, J = 8.40 Hz), 7.67-7.71 (4H, d, J = 8.40 Hz); ¹³C NMR (CDCl₃, 400 MHz) δ; 19.84, 22.76, 22.86, 24.84, 28.15, 30.03, 36.39, 37.46, 39.42, 66.58, 115.00, 127.20, 127.42, 128.15, 133.13, 139.13, 139.93, 158.96.

**Synthesis of R⁵O₃P₅.**
4-Bromo-4’-(alkoxy) benzene (2.2 equiv, 0.8 g, 2.04 mmol) and the corresponding boronicester (1 equiv, 0.28g, 0.93 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (60 mL) in an oven dried Schlenk flask under an argon atmosphere and the flask was evacuated and filled with argon (3x). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (5.0 g) in water (20 mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3x). To the DME solution, Pd(PPh$_3$)$_4$ (50 mg) and the sodium carbonate salt solution (5g in 20 mL water) were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3x) after each addition. The flask was covered with aluminum foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over anhydrous magnesium sulfate. It was filtered, evaporated and dried under vacuum. The crude product was then purified by washing with DCM to give the pure product (0.4 g, 63%), m.p = not melted below 350$^\circ$C; 1H NMR (CDCl$_3$, 400 MHz) $\delta$; 0.84-0.90 (12H, d, $J = 6.58$ Hz), 0.92-0.97 (6H, d, $J = 6.55$ Hz), 1.11-1.39 (12H, m), 1.47-1.75 (6H, m), 1.80-190 (2H, m), 3.98-4.07 (4H, m), 6.97-7.02 (4H, d, $J = 8.74$ Hz) 7.55-7.60 (4H, d, $J = 8.78$ Hz), 7.62-7.67 (4H, d, $J = 8.51$ Hz), 7.69-7.72 (4H, d, $J = 8.48$ Hz), 7.69-7.72 (4H, s).
Synthesis of Heptadecan-9-ol.

\[
\text{n-bromooctane} \quad \rightarrow \quad \text{Mg}\quad \text{dry ether} \quad \text{dry ether} \quad \text{dry ether} \quad \text{CH}_2\text{Cl}_2 \quad \text{MgSO}_4 \quad \text{MeCN} \quad \text{product as a white solid (11.3 g, 82%, mp: 58–62^\circ\text{C})}.1\text{H NMR (CDCl}_3, \text{400 MHz}) \delta; 1.43–1.38 (6H, t, J = 6.85 Hz), 1.16–1.51 (28H, m), 3.52-3.64 (1H, m).13\text{C NMR (400 MHz, CDCl}_3, \text{ppm})}: 14.27, 22.82, 25.81, 29.44, 29.75, 29.90, 32.03, 37.63, 72.17.
Synthesis of Heptadecan-9-bromide.

Concentrated sulfuric acid (2 mL) was added to 48% HBr (39 mL, excess) with stirring, and then secondary octanol (13.0 g) was added to the mixture. The reaction mixture was then heated to 120-125°C, and the reaction was running at this temperature for 24 hr. Then the reaction mixture was cooled to room temperature, and extracted with hexane (3 x 50 mL). The hexane layer was washed with 5% sodium bicarbonate solution (100 mL) and water (3 x 50 mL). The combined organic layers were dried over anhydrous magnesium sulfate. It was filtered, evaporated and dried under vacuum. The crude product was then purified by flash column chromatography using a hexane as eluent to give the pure product as a liquid (13.6 g, 85%).

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$; 3.96–4.06 (m, 1H), 1.72–1.87 (m, 4H), 1.18–1.58 (m, 24H), 0.82–0.92 (t, $J = 6.76$ Hz, 6H).

$^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$; 14.27, 22.84, 27.77, 29.26, 29.44, 29.65, 32.04, 39.36, 59.08.
1-Bromo-4-(heptadecan-9-yloxy) benzene:

A mixture of secondary alkyl bromide (9.6 g, 30.17 mmol), 4-bromophenol (4.35 g, 25.14 mmol), K₂CO₃ (11.4 g, 82.96 mmol), and DMF (80 mL) was stirred overnight at 70°C in a three-necked flask. After cooling to room temperature, the reaction mixture was poured into water (100 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over anhydrous MgSO₄. It was filtered and evaporated to afford crude product was purified through column chromatography (SiO₂, hexane) to obtain product as a colorless oil (4.75 g, 46%). ^1H NMR (400 MHz, CDCl₃, ppm) δ; 7.34 (d, J = 8.7 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H), 4.18–4.11 (m, 1H), 1.64–1.61 (m, 4H), 1.40–1.25 (m, 24H), 0.85 (t, J = 7.2 Hz, 6H). ^13C NMR (400 MHz, CDCl₃, ppm) δ; 14.27, 22.82, 25.47, 29.39, 29.67, 29.83, 32.03, 33.94, 78.59, 112.43, 117.78, 132.37, 158.00.
1-Boronicester-4-(heptadecan-9-yloxy) benzene:

To a Schlenk flask under argon atmosphere, a mixture of 4-bromo-1-(heptadecan-9-yloxy) benzene (14.0 g, 34.02 mmol) and PdCl$_2$(dpff) (100 mg) were added to a solution of dioxane (80 mL) and KOAc (8.3 mL, 9.05 mmol). The mixture was stirred for 10 minutes and then bis(pinacoloto)diboron (8.6 g, 34.02 mmol) was added. The resulting reaction mixture was refluxed for 12 h. After cooling to room temperature, the reaction mixture was poured into water (100 mL) and extracted with DCM (3 x 50 mL). The combined organic layers were washed with water, and dried over anhydrous MgSO$_4$. It was filtered and evaporated to afford crude product was purified through column chromatography (SiO$_2$, hexane) to obtain product as a colorless oil (14.8 g, 95%). $^1$H NMR (CDCl$_3$, 400 MHz) δ; 0.83-0.90 (6H, t, $J = 7.09$ Hz), 1.19-1.50 (24H, m), 1.58-1.74 (4H, m), 4.21-4.29 (1H, m), 6.83-6.90 (2H, d, $J = 8.71$ Hz) 7.71-7.74 (2H, d, $J = 8.71$ Hz); $^{13}$C NMR (CDCl$_3$, 400 MHz) δ; 14.27, 22.82, 24.98, 25.47, 29.39, 29.84, 32.00, 34.03, 77.71, 83.61, 115.14, 136.06, 161.57.
4-Bromo-4\(^\prime\)-(heptadecan-9-yloxy) biphenyl:

1-Bromo-4-iodobenzene (6.17 g, 21.8 mmol) and the corresponding boronic ester (1 equiv, 10 g, 6.25 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (60 mL) in an oven dried Schlenk flask under an argon atmosphere and the flask was evacuated and filled with argon (3×). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (5.0 g) in water (20 mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3×). To the DME solution, Pd(PPh\(_3\))\(_4\) (50 mg) and the salt solution were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3×) after each addition. The flask was covered with aluminum foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3× 50 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, evaporated and dried under vacuum to afford crude product. The crude product was then purified by column chromatography using a hexane to give the pure product as a oil (9.5 g, 90%). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\); 0.83-0.90 (12H, t, \(J = 7.09\) Hz), 1.19-1.50 (48H, m), 1.58-1.74
(8H, m), 4.21-4.29 (2H, m), 6.92-6.98 (4H, d, J = 8.87 Hz) 7.51-7.56 (4H, d, J = 8.81 Hz) 7.58-7.61 (4H, s); $^{13}$C NMR (CDCl$_3$, 400 MHz) δ; 14.27, 22.82, 25.57, 29.44, 29.71, 29.90, 32.03, 34.11, 78.14, 116.21, 120.76, 128.04, 128.29, 131.85, 132.05, 139.90, 158.73.

1, 4-benzenediboronic ester:

A Schlenk flask containing 1,4-benzenediboronic acid (1.24 g, 7.46 mmol) was dissolved in 60 mL of dry benzene dry benzene and neopentylglycol (2.33 g, 22.38 mmol) along with a 0.5 g of p-Toluene sulphonic acid was added as a dehydration catalyst under argon. The mixture was refluxed for 12 h in a Dean-Stark apparatus for the removal of water. The benzene layer was then concentrated and washed with 10% aqueous solution of NaHCO$_3$ (50 mL) and the organic layer extracted into dichloromethane (3 x 20 mL), dried over MgSO$_4$, filtered, evaporated and dried under vacuum to afford crude product 1,4-phenyldiboronic acid bis(neopentylglycol)ester which was sufficiently pure. Yield: (2.2 g, 100%) (White solid), m.p. 221-222°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ; 1.00-1.04 (s, 12H), 3.75-3.78 (s, 8H), 7.76-7.79 (s, 4H); $^{13}$C NMR (CDCl$_3$, 400 MHz) δ; 22.05, 32.01, 72.43, 133.05.
4,4’-diphenyldiboronic ester:

The 4,4’-diphenyldiboronic acid (5.0 g, 20.67 mmol) was dissolved in 60 mL of dry benzene and neopentylglycol (6.46 g, 62.02 mmol) along with a 2 g of p-Toluene sulphonic acid was added as a dehydration catalyst. The mixture was refluxed for 12 h in a Dean-Stark apparatus for the removal of water. The benzene layer was then concentrated and washed with 10% aqueous solution of NaHCO$_3$ (50 mL) and the organic layer extracted into dichloromethane (3 x 50 mL), dried over MgSO$_4$ and concentrated to give the crude 1,4-phenyldiboronic acid bis(neopentylglycol)ester which was sufficiently pure. Yield: 6.24 g, 80% (white solid), m.p: 234-236°C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.02-1.04 (s, 12H), 3.78-3.80 (s, 8H), 7.60-7.64 (4H, d, $J = 8.33$ Hz), 7.83-7.90 (4H, d, $J = 8.29$ Hz); $^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$: 25.03, 83.98, 126.48, 127.74, 135.45, 140.32, 143.42.
6, 6'-terphenyldiboronic ester:

To a Schlenk flask under argon atmosphere, a mixture of 6,6'-dibromoterphenyl (1.0 g, 2.57 mmol) and PdCl$_2$ (dppf) (50 mg) were added to a solution of dioxane (60 mL) and KOAc (1.26 mL, 12.85 mmol). The mixture was stirred for 10 minutes then bis(pinacolato)diboron (1.50 g, 5.92 mmol) was added. The resulting mixture was refluxed for 12 hours. After cooling to room temperature, the reaction mixture was poured into water (50 mL) and extracted with dichloromethane (3 x 25 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, evaporated and dried under vacuum to afford boronic ester (1.24 g, 100%), m.p: not melted below 250°C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 1.31-1.40 (s, 24H), 7.62-7.68 (d, 4H, $J = 7.54$ Hz), 7.68-7.73 (s, 4H), 7.86-7.94 (d, 4H, $J = 7.54$ Hz); $^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$: $\delta$: 25.03, 83.98, 126.48, 127.74, 135.45, 140.32, 143.42.
Synthesis of $^{RO4}\text{PP}_2$:

A Schlenk flask containing 1-Bromo-4-(heptadecan-9-yloxy) benzene (1.0 g, 2.6 mmol) and corresponding boronic ester (1 equiv, 1.2 g, 2.6 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (30 mL) in an oven dried Schlenk flask under an argon atmosphere, and the flask was evacuated and filled with argon (3x). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (2.5 g) in water (10 mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3x). To the DME solution, Pd(PPh$_3$)$_4$ (50 mg) and the salt solution were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3x) after each addition. The flask was covered with aluminum foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 25 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, evaporated and dried under vacuum. The crude product was then purified by column chromatography using a hexane to give the pure product (1.4 g, 80%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 0.83-0.90 (12H, t, $J = 7.09$ Hz), 1.19-1.50 (48H, m), 1.58-1.74 (8H, m), 4.21-4.29 (2H, m), 6.92-6.98 (4H, d, $J = 8.87$ Hz) 7.51-7.56 (4H, d, $J = 8.81$
Hz) 7.58-7.61 (4H, s); $^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$ 14.27, 22.82, 25.57, 29.42, 29.71, 29.90, 32.03, 34.11, 78.25, 116.20, 127.81, 133.35, 157.91.

**Synthesis of RO4PP$_3$:**

A Schlenk flask containing 1-Bromo-4-(heptadecan-9-yloxy) benzene (0.25 g, 1.06 mmol) and the corresponding boronicerter (2.3 equiv, 1.13 g, 2.46 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (30 mL) in an oven dried Schlenk flask under an argon atmosphere, and the flask was evacuated and filled with argon (3x). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (2.5 g) in water (10 mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3x). To the DME solution, Pd(PPh$_3$_)$_4$ (50 mg) and the salt solution were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3x) after each addition. The flask was covered with aluminum foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, evaporated and dried under vacuum. The
crude product was then purified by column chromatography using a hexane to give the pure product (0.62 g, 79%). \(^1\)H NMR (CDCl\(_3\), 400 MHz) δ; 0.83-0.90 (12H, t, \(J = 7.09\) Hz), 1.19-1.50 (48H, m), 1.58-1.74 (8H, m), 4.21-4.29 (2H, m), 6.92-6.98 (4H, d, \(J = 8.87\) Hz), 7.51-7.56 (4H, d, \(J = 8.81\) Hz) 7.58-7.61 (4H, s); \(^1^3\)C NMR (CDCl\(_3\), 400 MHz) δ; 14.27, 22.82, 25.57, 29.42, 29.71, 29.90, 32.03, 34.11, 78.24, 116.20, 127.06, 128.11, 133.03, 139.23, 158.44.

**Synthesis of RO4PP4:**

A Schlenk flask containing 1-Bromo-4-(heptadecan-9-yloxy) benzene (0.9 g, 2.5 mmol) and the corresponding boronicester (1 equiv, 0.95 g, 6.25 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (30 mL) in an oven dried Schlenk flask under an argon atmosphere and the flask was evacuated and filled with argon (3x). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (2.5 g) in water (10 mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3x). To the DME solution, Pd(PPh\(_3\))\(_4\) (50 mg) and the salt solution were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3x) after each addition. The flask was covered with
aluminum foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The crude product was then purified by column chromatography using a hexane to give the pure product (0.8 g, 80%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 0.83-0.92 (12H, t, $J = 7.05$ Hz), 1.19-1.50 (48H, m), 1.58-1.74 (8H, m), 4.21-4.29 (2H, m), 6.93-7.00 (4H, d, $J = 8.79$ Hz) 7.53-7.59 (4H, d, $J = 8.79$ Hz) 7.62--7.66 (4H, d, $J = 8.57$ Hz), 7.67--7.71 (4H, d, $J = 8.52$ Hz); $^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$: 14.27, 22.82, 25.57, 29.42, 29.71, 29.90, 32.03, 34.11, 78.24, 116.24, 127.37, 128.17, 132.92, 139.04, 139.93, 158.44.

**Synthesis of RO4PP$_5$:**

A Schlenk flask containing 1-Bromo-4-(heptadecan-9-yl)oxy) benzene (1.07 g, 2.2 mmol) and the corresponding diboronic ester (1 equiv, 1.0 g, 1.0 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (30 mL) in an oven dried Schlenk flask under an argon atmosphere and the flask was evacuated and filled with argon (3x). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (2.5 g) in water (10
mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3x). To the DME solution, Pd(PPh$_3$)$_4$ (50 mg) and the salt solution were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3x) after each addition. The flask was covered with aluminum foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, evaporated and dried under vacuum. The crude product was then purified by column chromatography using a hexane to give the pure product (0.84 g, 70%), m.p. 138-140°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ; 0.83-0.92 (12H, t, $J$ = 7.09 Hz), 1.19-1.50 (48H, m), 1.58-1.74 (8H, m), 4.21-4.29 (2H, m), 6.93-7.00 (4H, d, $J$ = 8.70 Hz) 7.53-7.59 (4H, d, $J$ = 8.63 Hz) 7.63-7.67 (4H, d, $J$ = 8.11 Hz), 7.68-7.72 (4H, d, $J$ = 8.44 Hz), 7.72-7.74 (4H, s); $^{13}$C NMR (CDCl$_3$, 400 MHz) δ; 14.27, 22.82, 25.57, 29.42, 29.71, 29.90, 32.03, 34.11, 78.24, 116.24, 127.18, 127.43, 128.19, 132.87, 138.93, 139.74, 140.06, 158.58.

**Synthesis of RO4PP$_6$:**

![Synthesis Scheme]

- **Br**
- **O**
- **B**
- **O**
- **Ph**
- **Pd(PPh$_3$)$_4$ 2mol%**
- **DME**
- **Na$_2$CO$_3$**
- **Reflux**
A Schlenk flask containing 4-Bromo-4’-(heptadecan-9-yloxy) biphenyl (0.85 g, 1.74 mmol) and the corresponding di phenyl diboronicester (1 equiv, 0.3 g, 0.8 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (30 mL) in an oven dried Schlenk flask under an argon atmosphere and the flask was evacuated and filled with argon (3x). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (2.5 g) in water (10 mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3x). To the DME solution, Pd(PPh₃)₄ (50 mg) and the salt solution were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3x) after each addition. The flask was covered with aluminum foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The crude product was then purified by column chromatography using a hexane to give the pure product (0.6 g, 80%), m.p: 246-248°C; ¹H NMR (CDCl₃, 400 MHz)  δ; 0.83-0.92 (12H, t, J = 7.09 Hz), 1.19-1.50 (48H, m), 1.58-1.74 (8H, m), 4.21-4.29 (2H, m), 6.93-7.00 (4H, d, J = 8.30 Hz) 7.53-7.59 (4H, d, J = 8.79 Hz) 7.63-7.67 (4H, d, J = 8.45 Hz), 7.68-7.72 (4H, d, J = 7.73 Hz), 7.74-7.76 (8H, s); ¹³C NMR (CDCl₃, 400 MHz) δ; 14.27, 22.82, 25.57, 29.42, 29.71, 29.90, 32.03, 34.11, 78.24, 116.26, 127.20, 127.45, 127.52, 128.20, 132.88, 138.92, 139.68, 139.90, 140.11, 158.60.
Synthesis of $^{RO_4}PP_7$:

A Schlenk flask containing 1-Bromo-4-(heptadecan-9-yloxy)benzene (0.18 g, 0.38 mmol) and the corresponding boronicester (1 equiv, 0.1 g, 0.165 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (30 mL) in an oven dried Schlenk flask under an argon atmosphere and the flask was evacuated and filled with argon (3x). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (2.5 g) in water (10 mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3x). To the DME solution, Pd(PPh$_3$)$_4$ (50 mg) and the salt solution were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3x) after each addition. The flask was covered with aluminum foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, evaporated and dried under vacuum. The crude product was then purified by column chromatography using a hexane to give the pure product (0.17 g, 80%), m.p. not melted below 350°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ; 0.83-0.92 (12H, t, $J = 7.09$ Hz), 1.19-1.50 (48H, m), 1.58-1.74 (8H, m), 4.21-4.29 (2H, m), 6.93-7.00
(4H, d, $J = 8.53$ Hz) 7.53-7.59 (4H, d, $J = 8.48$ Hz), 7.63-7.68 (4H, d, $J = 8.39$ Hz), 7.69-7.74 (4H, d, $J = 8.21$ Hz), 7.74-7.76 (8H, s), 7.76-7.78 (4H, s); $^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$; 14.27, 22.82, 25.57, 29.42, 29.71, 29.90, 32.03, 34.11, 78.24, 116.26, 127.20, 127.45, 127.52, 128.20, 132.88, 138.92, 139.68, 139.90, 140.11, 158.60.

$^1$H NMR spectrum of $^{RO_1}$PP$_2$ ($RO_1$= Methoxy)
$^{13}\text{C NMR spectrum of } ^{ROI}\text{PP}_2 (ROI=\text{Methoxy})$

$^{1}\text{H NMR spectrum of } ^{ROI}\text{PP}_3 (ROI=\text{Methoxy})$
$^{13}$C NMR spectrum of $^{RO}_1$PP$_3$ ($ROI$ = Methoxy)

$^1$H NMR spectrum of 1-bromo-4-(2-ethyl-1-hexyloxy) benzene.
$^{13}$C NMR spectrum of 1-bromo-4-(2-ethyl-1-hexyloxy) benzene.

$^{1}$H NMR spectrum of $^{RO_2}$PP$_4$ ($RO$=2-Ethyl hexyloxy)
$^{13}$C NMR spectrum of $^{RO_2}PP_4$ ($RO_2$=2-Ethyl hexyloxy)

$^1$H NMR spectrum of 3, 7-dimethyl 1-octylbromide
$^{13}$C NMR spectrum of 3, 7-dimethyl 1-octylbromide.

$^1$H NMR spectrum of 1-bromo-4-(3, 7-dimethyl 1-octyloxy) benzene
$^{13}$C NMR spectrum of 1-bromo-4-(3, 7-dimethyl 1-octyloxy) benzene.
$^1$H NMR spectrum of 4-bromo-4’-(3, 7-dimethyl 1-octyloxy) benzene.

$^{13}$C NMR spectrum of 4-bromo-4’-(3, 7-dimethyl 1-octyloxy) benzene.

$^1$H NMR spectrum of $^{RO_3}$PP$_2$ ($RO_3$=3, 7-dimethyl 1-octyloxy).
\(^{13}\)C NMR spectrum of \(RO_3^3\)PP\(_2\) (\(RO_3^3=3, 7\)-dimethyl 1-octyloxy).

\(^1\)H NMR spectrum of \(RO_3^3\)PP\(_3\) (\(RO_3^3=3, 7\)-dimethyl 1-octyloxy).
$^{13}$C NMR spectrum of $^{RO_3}PP_3 (RO_3=3,7$-dimethyl 1-octyloxy)
$^{1}$H NMR spectrum of $^{RO_{3}}P_{4}$ ($RO_{3}$=3, 7-dimethyl 1-octyloxy).

$^{1}$H NMR spectrum of $^{RO_{3}}P_{5}$ ($RO_{3}$=3, 7-dimethyl 1-octyloxy).
$^{13}$C NMR spectrum of $RO_3PP_4$ ($RO_3=3,7$-dimethyl 1-octyloxy).

$^1$H NMR spectrum of 9-heptadecanol.

$^{13}$C NMR spectrum of 9-heptadecanol.
$^1$H NMR spectrum of 9-heptadecylbromide.

$^{13}$C NMR spectrum of 9-heptadecylbromide.
$^1$H NMR spectrum of 1-Bromo-4-(heptadecan-9-yloxy) benzene.

$^{13}$C NMR spectrum of 1-Bromo-4-(heptadecan-9-yloxy) benzene.
$^1$H NMR spectrum of 1-Boronicester-4-(heptadecan-9-yloxy) benzene:

$^{13}$C NMR spectrum of 1-Boronicester-4-(heptadecan-9-yloxy) benzene.

$^1$H NMR spectrum of 4-Bromo-4’-(heptadecan-9-yloxy) biphenyl.
$^{13}$C NMR spectrum of 4-Bromo-4’-(heptadecan-9-yloxy) biphenyl.

$^1$H NMR spectrum of phenyl diboronicester.
$^{13}$C NMR spectrum of phenyl diboronicester

$^1$H NMR spectrum of biphenyl diboronicester
$^1$H NMR spectrum of 6,6’- dibromoterphenylene.

$^{13}$C NMR spectrum of 6,6’- dibromoterphenyl.
$^1$H NMR spectrum of Terphenyl diboronicester

$^{13}$C NMR spectrum of Terphenyl diboronicester
$^1$H NMR spectrum of $^{RO_4}$PP$_2$ ($RO_4$= 9-heptadecyloxy)

$^{13}$C NMR spectrum of $^{RO_4}$PP$_2$ ($RO_4$= 9-heptadecyloxy)

$^1$H NMR spectrum of $^{RO_4}$PP$_3$ ($RO_4$= 9-heptadecyloxy)
$^{13}$C NMR spectrum of $^{RO_4}PP_3$ ($RO_4$ = 9-heptadecyloxy)

$^1$H NMR spectrum of $^{RO_4}PP_4$ ($RO_4$ = 9-heptadecyloxy)
$^{13}$C NMR spectrum of $^{RO_4}$PP$_4$ ($RO_4$= 9-heptadecyloxy)

$^1$H NMR spectrum of $^{RO_4}$PP$_5$ ($RO_4$= 9-heptadecyloxy)
$^{13}$C NMR spectrum of $^{RO}_{4}$PP$_5$ ($RO_4$ = 9-heptadecyloxy)

$^1$H NMR spectrum of $^{RO}_{4}$PP$_6$ ($RO_4$ = 9-heptadecyloxy)
$^{13}$C NMR spectrum of $^{RO4}PP_6 (RO4= 9$-heptadecyloxy$)$

$^1$H NMR spectrum of $^{RO4}PP_7 (RO4= 9$-heptadecyloxy$)$
$^{13}$C NMR spectrum of $^{RO}_{7}$PP ($RO$ = 9-heptadecyloxy)
A comparison of the $^1$H NMR spectra of $^{RO_3}PP_n$ oligomers.
A comparison of the $^{13}$C NMR spectra of $^{\text{RO3PPn}}$ oligomers.
Synthesis of $RO^PnPn$ Oligomers.

Scheme S2.1. (RO1= methoxy oligomers)

\[ \text{Br} \quad \overset{a}{\longrightarrow} \quad \text{Br} \quad \overset{b}{\longrightarrow} \quad \text{Br} \]

a) Mg, THF, reflux, B(OMe)$_3$, -78°C, overnight  
b) Pd(PPh$_3$)$_4$ (2mol%), Na$_2$CO$_3$, H$_2$O, DME, Reflux

Scheme S2.2. Synthetic scheme for the preparation of various $RO^2PPn$ (RO2= 2-Ethyl hexyloxy) oligomers

(a)K$_2$CO$_3$, DMF, 70°C, 24hr, (b) BuLi, THF at -78°C, B(OMe)$_3$, (c)Toulene, Ethanol, H$_2$O, Pd(PPh$_3$)$_4$, Na$_2$CO$_3$, Reflux.
Scheme S2.3. Synthetic scheme for the preparation of various $^{RO3}PPn$ ($RO3 = 3,7$-dimethyloctyloxy) oligomers

a) $\text{HBr, H}_2\text{SO}_4$, 120-125°C, 3hr. b) $\text{K}_2\text{CO}_3$, DMF, 70°C, 24hr. c) BuLi, THF at -78°C, $\text{B(OMe)}_3$ d) Toulene, EtOH$\cdot$H$_2$O, Pd(PPh$_3$)$_4$, Na$_2$CO$_3$, Reflux. d) Pd (PPh$_3$)$_2$ (2mol %), DME, Na$_2$CO$_3$, reflux.
Optical properties.

The absorbance measurements of $RO_{\text{PP}}_n$ Oligomers were carried out by addition of a dichloromethane solution of $RO_{\text{PP}}_n$ oligomers to a 1-cm quartz cuvette containing dichloromethane. The UV-vis spectra of the resulting solution, after the addition of each increment, were recorded at 22$^\circ$C (see Figure in the text).

The extinction coefficients of $RO_{\text{PP}}_n$ oligomers were obtained by applying the Beer-Lambert law ($A = \varepsilon b c$). Furthermore, by plotting the various absorbance’s at their respective concentration and fitting a linear regression to the plot was carried out to determine the extinction coefficients from each $RO_{\text{PP}}_n$ oligomer.
Figure S1. (A) The absorbance spectra obtained by incremental addition of a dichloromethane solution of $RO_3PP_3$ (1.77 mM) to a solution of 3 mL dichloromethane at 22°C. (B) A plot of the various absorbance values of $RO_3PP_3$ vs. their respective concentrations.
Figure S2. (A) The absorbance spectra obtained by incremental addition of a dichloromethane solution of $^{RO_3}PP_4$ (0.4 mM) to a solution of 3 mL dichloromethane at 22°C. (B) A plot of the various absorbance values of $^{RO_3}PP_4$ vs. their respective concentrations.

Figure S3. (A) The absorbance spectra obtained by incremental addition of a dichloromethane solution of $^{RO_3}PP_5$ to a solution of 3 mL dichloromethane at 22°C. (B) A plot of the various absorbance values of $^{RO_3}PP_5$ vs. their respective concentrations.
Figure S4. (A) Cyclic voltammogram of $2.5 \times 10^{-3}$ M $^{RO3}PP_2$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2.5 \times 10^{-3}$ M $^{RO3}PP_2$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.

Figure S5. (A) Cyclic voltammogram of $2.5 \times 10^{-3}$ M $^{RO3}PP_2$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2.5 \times 10^{-3}$ M $^{RO3}PP_2$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.
Figure S6. (A) Cyclic voltammogram of $2.5 \times 10^{-3}$ M $^{RO3}PP_3$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2.5 \times 10^{-3}$ M $^{RO3}PP_2$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.
Figure S7. (A) Cyclic voltammogram of $2.5 \times 10^{-3} \text{ M} \text{RO3PP}_4$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPf$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2.5 \times 10^{-3} \text{ M} \text{RO3PP}_2$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPf$_6$ at a scan rate of 100 mV s$^{-1}$ at 22° C.

Figure S8. The emission spectra obtained by incremental addition of a dichloromethane solution of $\text{RO3PP}_2$ (2.12 mM) to a solution of 3 mL dichloromethane at 22° C.
Figure S9. The emission spectra obtained by incremental addition of a dichloromethane solution of $^{RO}_3 PP_3$ (1.77 mM) to a solution of 3 mL dichloromethane at 22$^0$C.

Figure S10. The emission spectra obtained by incremental addition of a dichloromethane solution of $^{RO}_3 PP_4$ (0.47 mM) to a solution of 3 mL dichloromethane at 22$^0$C.
Figure S11. The emission spectra obtained by incremental addition of a dichloromethane solution of $^{RO_3}PP_3$ (0.36 mM) to a solution of 3 mL dichloromethane at 22°C.

Figure S12. (A) Spectral changes upon the reduction of 0.1 mM naphthyl cation radical by an incremental addition of 0.77 mM solution of $^{RO_3}PP_3$ in 3 mL dichloromethane at 22°C (25 µL increment). (B) A plot of increase of the absorbance of $^{RO_3}PP_3^{\cdot\cdot}$ (monitored at 832 nm), and depletion of the absorbance of NAP$^{\cdot\cdot}$ (monitored at 672 nm) against the equivalent of added $^{RO_3}PP_3$. 
Figure S13. Spectral changes upon the addition of solution of $^{RO_3}PP_5$ in 3 ml dichloromethane at 22$^0$C to NO$^-\text{SbCl}_6^-$. 

Figure S14. (A) The absorbance spectra obtained by incremental addition of a dichloromethane solution of $^{RO_4}PP_2$ (0.65 mM) to a 3 mL dichloromethane solution at 22$^0$C. (B) A plot of the various absorbance value of $^{RO_4}PP_2$ vs. their respective concentrations.
Figure S15. (A) The absorbance spectra obtained by incremental addition of a dichloromethane solution of $RO_4PP_3$ (0.44 mM) to a 3 mL dichloromethane solution at 22$^\circ$C. (B) A plot of the various absorbance value of $RO_4PP_3$ vs. their respective concentrations.

Figure S16. The absorbance spectra obtained by incremental addition of a dichloromethane solution of $RO_4PP_4$ (0.78 mM) to a 3 mL dichloromethane solution at 22$^\circ$C. (B) A plot of the various absorbance value of $RO_4PP_4$ vs. their respective concentrations.
Figure S17. (A) The absorbance spectra obtained by incremental addition of a dichloromethane solution of $^{RO4}PP_5$ (1.09 mM) to a 3 mL dichloromethane solution at 22°C. (B) A plot of the various absorbance value of $^{RO4}PP_5$ vs. their respective concentrations.

Figure S18. (A) The absorbance spectra obtained by incremental addition of a dichloromethane solution of $^{RO4}PP_6$ (0.744 mM) to a 3 mL dichloromethane solution at
22°C. (B) A plot of the various absorbance value of $^{RO_4}PP_6$ vs. their respective concentrations.

Figure S19. (A) The absorbance spectra obtained by incremental addition of a dichloromethane solution of $^{RO_4}PP_7$ (0.095 mM) to a 3 mL dichloromethane solution at 22°C. (B) A plot of the various absorbance value of $^{RO_4}PP_7$ vs. their respective concentrations.
Figure S20. (A) Cyclic voltammogram of $2 \times 10^{-3}$ M $^{\text{ROI}}\text{PP}_2$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2 \times 10^{-3}$ M $^{\text{ROI}}\text{PP}_2$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.

Figure S21. (A) Cyclic voltammogram of $2 \times 10^{-3}$ M $^{\text{ROI}}\text{PP}_2$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2 \times 10^{-3}$ M $^{\text{ROI}}\text{PP}_2$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.
Figure S22. (A) Cyclic voltammogram of $2 \times 10^{-3}$ M $^{RO4}PP_3$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2 \times 10^{-3}$ M $^{RO4}PP_3$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.

Figure S23. (A) Cyclic voltammogram of $2 \times 10^{-3}$ M $^{RO4}PP_3$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2 \times 10^{-3}$ M $^{RO4}PP_3$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.
Figure S24. (A) Cyclic voltammogram of $2 \times 10^{-3}$ M $\text{RO}^{\text{4}}\text{PP}_{4}$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2 \times 10^{-3}$ M $\text{RO}^{\text{4}}\text{PP}_{4}$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.

Figure S25. (A) Cyclic voltammogram of $2 \times 10^{-3}$ M $\text{RO}^{\text{4}}\text{PP}_{4}$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2 \times 10^{-3}$ M $\text{RO}^{\text{4}}\text{PP}_{4}$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.
Figure S26. (A) Cyclic voltammogram of $2 \times 10^{-3}$ M $^{RO4}_{PP_5}$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2 \times 10^{-3}$ M $^{RO4}_{PP_5}$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.

Figure S27. (A) Cyclic voltammogram of $2 \times 10^{-3}$ M $^{RO4}_{PP_4}$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2 \times 10^{-3}$ M $^{RO4}_{PP_4}$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.
Figure S28. (A) Cyclic voltammogram of $2 \times 10^{-3} \text{ M} \, ^{ROI}_4{PP}_5$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2 \times 10^{-3} \text{ M} \, ^{ROI}_4{PP}_5$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.

Figure S29. (A) Cyclic voltammogram of $2 \times 10^{-3} \text{ M} \, ^{ROI}_4{PP}_6$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2 \times 10^{-3} \text{ M} \, ^{ROI}_4{PP}_6$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$ at 22 °C.
Figure S30. (A) Spectral changes upon the reduction of 0.024 mM naphthyl cation radical by an incremental addition of 0.44 mM (20 µL increment) solution of $^{RO}{PP}_3$ in 3 mL dichloromethane at 22°C. (B) A plot of increase of the absorbance of $^{RO}{PP}_3^{+•}$ (monitored at 1210 nm), and depletion of the absorbance of $NAP^{••}$ (monitored at 672 nm) against the equivalent of added $^{RO}{PP}_3$.

Figure S31. Spectral changes upon the reduction of 0.0236 mM naphthyl cation radical by an incremental addition of 0.78 mM (15 µL increment) solution of $^{RO}{PP}_4$ in 3 mL dichloromethane at 22°C. (B) A plot of increase of the absorbance of $^{RO}{PP}_4^{+•}$ (monitored at 1596 nm), and depletion of the absorbance of $NAP^{••}$ (monitored at 672 nm) against the equivalent of added $^{RO}{PP}_4$. 
Figure S32. (A) Spectral changes upon the reduction of 0.1 mM naphthyl cation radical by an incremental addition of 1.09 mM (25 µL increment) solution of $^{RO}_5PP_5$ in 3 mL dichloromethane at 22°C. (B) A plot of increase of the absorbance of $^{RO}_5PP_5^{++}$ (monitored at 1520 nm), and depletion of the absorbance of NAP$^{++}$ (monitored at 672 nm) against the equivalents of added $^{RO}_5PP_5$.

Figure S33. (A) Spectral changes upon the reduction of 0.057 mM naphthyl cation radical by an incremental addition of 0.74 Mm 22°C (25 µL increment) solution of $^{RO}_6PP_5$ in 3
mL dichloromethane at 22°C. (B) A plot of increase of the absorbance of $^{RO4}PP_6^{\text{**}}$ (monitored at 1402 nm), and depletion of the absorbance of $\text{NAP}^{\text{**}}$ (monitored at 672 nm) against the equivalents of added $^{RO4}PP_6$.

Figure S34. (A) Spectral changes upon the dilution (each time 0.5 mL added DCM) of 0.1 mM $^{RO4}PP_5$ in 3 mL dichloromethane at 22°C (25 µL increment).
Figure S35. (A) Spectral changes upon the reducing the temperature by 10°C of 0.1 mM rojPP$_5$ cation radical in 3 ml dichloromethane.
Figure S37. Ground state hole distribution at the minimum on the potential energy surface of $^{RO}_5PP^+$, in which hole is displaced towards the end of the chain (top), and the saddle point, in which hole is symmetrically distributed in the middle of the chain (bottom). Isosurface plots show spatial distribution of the unpaired spin density.

Figure S38. (A) The UV-VIS absorption spectra for dichloromethane solution of oligomers $^{RO}_2PP_2$–$^{RO}_6PP_6$. (B) A plot of the absorption maxima in energy units (i.e. in cm$^{-1}$) versus $1/n$ where $n$=number of phenylene units.
Figure S39. (A) Emission spectra for dichloromethane solution of oligomers $^{RO3}Pp_2 - ^{RO}Pp_5$. (B) A plot of the $\lambda_{\text{max}}$ (cm$^{-1}$) vs n, (B) A plot of the $\lambda_{\text{max}}$ (nm) vs n where n = number of the phenylene rings in various poly-p-phenylene oligomers $^{RO3}Pp_2 - ^{RO3}Pp_6$. 
Figure S40. (A) Stacked Cyclic voltammograms of $^{\text{RO}3}\text{PP}_2$ – $^{\text{RO}3}\text{PP}_5$ obtained as a solution in dichloromethane containing 0.1M tetra-n-butyl ammonium hexafluorophosphate as the supporting electrolyte at scan rate of 100 mv/s at 22$^\circ$C.
Figure S41. Stacked Square waves of $^{RO3}PP_2 - ^{RO3}PP_5$ obtained as a solution in dichloromethane containing 0.1M tetra-n-butyl ammonium hexafluorophosphate as the supporting electrolyte at scan rate of 100 mv/s at 22$^\circ$C. (B) (A) Stacked Cyclic voltammograms of $^{RO3}PP_2 - ^{RO3}PP_5$ obtained as a solution in dichloromethane containing
0.1M tetra-n-butyl ammonium hexafluorophosphate as the supporting electrolyte at scan rate of 100 mv/s at 22^0C.

Figure S42. (A) Spectral changes upon the reduction of 0.0391 mM naphthalene cation radical by an incremental addition of 2.12 mM solution of RO_3PP_2 in dichloromethane at 22^0C (5 µL increment). (B) A plot of increase of the absorbance of RO_3PP_2^{++} (monitored at 83 nm), and depletion of the absorbance of NAP^{++} (monitored at 672 nm) against the equivalent of added RO_3PP_2.

Figure S43. A comparison of the cation radical spectra of various RO_3PP_n^{++} generated using NAP^{++} in dichloromethane at 22^0C.
Disclaimer: The results discussed in this chapter was further supplimented by DFT calculations and by a recently developed multistate parabolic model and a modifies Huckel theory by my coworkers Drs. Marat R Talipov and Maxim V. Ivanov.
REFERENCES


20. A removal of one electron from a neutral donor produces a cation radical which was coined in the term 'hole' by N. Bauld. In this study, the use of term hole also encompasses reorganization of electron density, structural and solvent rearrangements


29. In the DFT calculations, we used iso-propyl as a truncated model of the 6-tetradecyl (iA) end-capping substituent and methoxy group as a truncated model of the 9-heptadecyloxy (RO) end-capping substituent


32. Energetically most stable alternant and helical conformations have been used for neutral molecules and cation radicals, respectively. Alternative conformations are marginally (0.03-0.29 kcal/mol also in the footnote, see Table S9) higher in energy, and have very similar progression of redox and optoelectronic properties.

33. Electronic structure calculations were performed with the Gaussian 09 package, revision C01: Frisch, M. J. et al. Gaussian, Inc., Wallingford CT, 2009.


38. The observed separation of the vibronic peaks, ~1300 cm⁻¹, is similar to the emission spectra of neutral iAPPn (ref. 4a), and likely corresponds to the backbone C–C vibrations: Heimel, G.; Daghofer, M.; Gierschner, J.; List, E. J. W.; Grimsdale, A. C.; Müllen, K.; Beljonne, D.; Brédas, J.-L.; Zojer, E. J. Chem. Phys. 2005, 122, 54501.

39. Unpaired spin density plots in Figure 4 have regions with expected excess beta spin density (blue), as well as the regions with excess alpha spin density (red). This spin polarization is observed for the units that underwent quinoidal distortion of the geometry; thus, if in the vertically excited state the hole is partially transferred to non-distorted units (Figure 4B’), these units only have the regions with excess beta spin density, i.e. no noticeable spin polarization.


45. Whereas a value of $\frac{H_{ab}}{\lambda} = -9$ reproduces the hole distribution accurately in various HPPn cation radicals, an increase of the $|H_{ab}|/\lambda$ beyond 9 leads to more extended delocalization, and decrease below 9 leads to a more compact hole.

47. Interestingly, a transition from the one-minimum regime ($n \leq 7$) to two-minima regime ($n \geq 8$) in the case of $R = iA$ is accompanied by a slight shrinking of the hole from seven to six units. This effect can be understood in the light of the fact that involvement of both terminal units for the hole stabilization would require a deformation of the hole, which has to ‘stretch’ to occupy both ends of the chain. Up to $n = 7$, this deformation is small, and the hole can reside in the middle of the chain without large energetic penalty. However, starting from $n = 8$, energy of the hole deformation exceeds stabilization by both terminal units, and hole migrates towards one end.

48. According to the DFT and MPM, the $RO_{PP5+\cdot}$ structure with symmetrically distributed hole should correspond to a very small maximum on the potential energy surface (0.3 kcal/mol higher in energy than the stable asymmetric structure, from the DFT calculations). Thus, experimentally observed significant population of this structure may arise due to dynamic hole transfer between the two ends of the molecule, enabled by the very low barrier for such transfer; this then may suggest that the symmetric structure corresponds to a shallow minimum on the free energy surface. Experimental verification of this interpretation using X-ray crystallography is underway.
CHAPTER 3

Breakdown of the 1/n Trend in \( \pi \)-Conjugated Poly-\( p \)-phenylene Cation Radicals is Explained using Hückel Theory and Multi-State Model

Introduction

\( \pi \)-Conjugated poly-\( p \)-phenylene molecular wires have been extensively explored as materials for molecular electronics and photovoltaic applications, as they provide an effective medium for long-range charge and exciton transfer.\(^1\)-\(^3\) Our recent studies of the poly-\( p \)-phenylene wires (\( ^R \)PP\( _n \): \( R = H, iA, iAO \) and \( iA_2N \), where \( n \) is the number of phenylene units, Figure 3.1) showed that the experimental redox potentials (\( E_{ox} \)) of \( ^R \)PP\( _n \) and the optical properties (\( \nu_{\text{max}} \)) of the resulting cation radicals (i.e. \( ^R \)PP\( _n ^+ \)) saturate with \( n \leq 8.\(^4\)-\(^7\) The saturation point moves to smaller \( n \) as the electron-donor strength of end-capping group increases, i.e. saturation occurs at \( n = 5 \) for \( ^{iA0} \)PP\( _n \) and \( n = 3 \) for \( ^{iA2N} \)PP\( _n \).

Using DFT calculations and theoretical modeling, we showed that the saturation of the redox and optical properties occurs due to the hole migration towards one end of the molecule in order to continually engage the end-capped \( p \)-phenylene unit in hole stabilization (Figure 3.1).\(^4\)
The observed breakdown from the expected linear trend of the $^{R}\text{PP}_n^{+*}$ properties against $\cos[\pi/(n+1)]$, commonly expressed as $1/n$, was experimentally confirmed for alkoxy- and dialkylamino-capped (i.e. $R = iAO$ and $iA_2N$) wires, however it could not be verified for uncapped or alkyl-capped (i.e. $R = H$ and $iA$) wires due to solubility issues with higher homologues. The deleterious effect of the strong electron-donating end-capping groups and unavailability of the longer virgin $^{H}\text{PP}_n$ and alkyl-capped $^{iA}\text{PP}_n$ hampered our attempts to develop a full understanding of the evolution of the redox and optical properties of the $\pi$-conjugated poly-$p$-phenylene wires and true origin of the breakdown of the $\cos[\pi/(n+1)]$ or $1/n$ trends.

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Amongst the π-conjugated poly-p-phenylene wires, mixtures of oligomers of 9,9’-dialkylfluorene, referred to as OF\(_n\), with \(n \leq 54\) (where \(n\) is the number of fluorenes) have been demonstrated to be highly soluble;\(^9\) and their potential as charge-transfer materials in actual photovoltaic devices has been extensively explored.\(^{10-15}\) Accordingly, in this study we use oligomers of 9,9’-dihexalfluorene as models for longer homologues of poly-p-phenylene wires. These OF\(_n\) oligomers will be referred to hereafter as fluorene-based poly-p-phenylenes, i.e. FPP\(_n\), where \(n\) is the number of phenylene units. For example, the structure of OF\(_8\) shown below contains 16 phenylene units and thus is named FPP\(_{16}\).

![OF\(_8\) = FPP\(_{16}\)](image)

We have successfully synthesized a series of OF\(_n\), \(n = 1-8\) (or FPP\(_n\), \(n = 2-16\)) and recorded their absorption and emission spectra, determined their precise electrochemical redox potentials, and obtained the optical data of their cation radicals generated by careful redox titrations using robust aromatic oxidants.\(^{16,17}\) The availability of the experimental data on FPP\(_n\)/FPP\(_n\)\(^{++}\) with relatively large \(n\) now allows us to show that the evolution of the optical properties of neutral FPP\(_n\) follows a linear trend, while the properties of their cation radicals (i.e. \(E_\text{ox}\) and \(\nu_{\text{max}}\)) show a breakdown of the linear trend against \(\cos[\pi/(n+1)]\).
The study herein will demonstrate, for the first time, with the aid of accurate experimental data, DFT calculations, and theoretical modeling, that the breakdown of the \( \cos[\pi/(n+1)] \) trend reflects the hole localization\textsuperscript{18-22} in poly-\( p \)-phenylene cation radicals onto a limited number of \( p \)-phenylene units (i.e. \( n \approx 8 \)), and occurs due to the interplay between the energetic gain from the hole delocalization and the concomitant energetic penalty from structural/solvent reorganization. Importantly, we will show that the well known Hückel molecular orbital (HMO) theory, which is readily applicable for the description of neutral FPP\textsubscript{n}, can be applied to FPP\textsubscript{n} cation radicals \textit{if the structural reorganization is appropriately accounted for}. Accordingly, we have developed a modified HMO theory that includes structural reorganization, and show that this theory can well reproduce the experimental properties of various poly-\( p \)-phenylene cation radicals. Indeed, the performance of the modified HMO model is remarkably similar to our recently developed Marcus-based multistate model (MSM), which includes the reorganization energy by design. The rationale development of new molecular wires for application in photovoltaic devices and organic electronics requires predictive chemical models, and we suggest that the modified HMO theory and MSM are valuable new tools for elucidation of these properties.

NOTE: Theoretical and computational studies were contributed by Dr. Marat Talipov and Dr. Maxim Ivanov
Results and Discussions

Synthesis/spectroscopy/electrochemistry of FPP$_n$ and generation/spectroscopy of FPP$_n^{**}$

The synthesis of FPP$_2$-FPP$_{16}$ was accomplished using readily available precursors by standard Suzuki coupling reactions, and the detailed synthetic schemes/procedures and characterization data (i.e. $^1$H/$^{13}$C NMR, MALDI, and X-ray crystallography of representative oligomers) are compiled in the Experimental Section. The resulting FPP$_n$ oligomers were rigorously purified by column chromatography and were found to be freely soluble in dichloromethane, chloroform, toluene, THF, and similar solvents.

The electronic absorption spectra of dichloromethane solutions of neutral FPP$_n$ are compiled in Figure 3. 2A. The position of the characteristic absorption band of FPP$_n$ shows a clear red shift (i.e., shift to longer wavelength or lower energy) with increasing $n$ (Figure 3. 2A). The energies of the absorption maxima of FPP$_n$ tracked linearly with $\cos[\pi/(n+1)]$ (Figure 3. 2B). Interestingly, the point for the absorption maximum of FPP$_{108}$ at 388 nm (indicated by a pink symbol in Figure 3. 2B) clearly fell onto the linear trendline, thus confirming that the $\cos[\pi/(n+1)]$ dependence holds up to the polymeric limit (vide infra).
The position of emission maxima shifts red in emission spectra of FPP$_n$ only up to approximately 10 $p$-phenylene units (Figure 3.2C, Table 1). Interestingly, a plot of the energies of emission maxima ($\nu_{em}$, Table 1) against $\cos[\pi/(n+1)]$ showed a linear dependence up to $n = 10$, followed by a breakdown, as the position of the emission band remained
unchanged beyond $n = 10$ (Figure 3. 2D). This contrasting evolution of the emission and absorption characteristics of FPP$_n$ with increasing $n$ suggests that the exciton delocalization does not extend beyond 10 $p$-phenylene units.

The redox properties of the FPP$_n$ were evaluated by electrochemical oxidation at a platinum electrode as a 1 mM solution in dichloromethane containing 0.1 M tetra-$n$-butylammonium hexafluorophosphate as the supporting electrolyte. Except FPP$_2$, which underwent irreversible electrochemical oxidation,$^{25}$ the higher homologues (i.e. FPP$_4$–FPP$_{16}$) showed reversible cyclic voltammograms at ambient temperatures and provided first oxidation potentials ($E_{ox1}$), which were referenced to ferrocene as an internal standard (Figure 3. 3A, Table 1). A plot of $E_{ox1}$ of FPP$_n$ showed a linear dependence against $\cos[\pi/(n+1)]$ up to 8 $p$-phenylene units, followed by the breakdown or saturation (Figure 3. 3B). It is noted that evolution of the second and higher oxidation potentials of FPP$_n$ with increasing $n$ varied drastically when plotted against $\cos[\pi/(n+1)]$ as compared to $E_{ox1}$ (Figure 3. S5 in the Experimental Section). Unlike the exciton delocalization, which does not extend beyond 10 $p$-phenylene units (Figure 3. 2D), the saturation of the $E_{ox1}$ at 8 $p$-phenylene units (Figure 3. 3B) suggests that hole delocalization in FPP$_n^{+\star}$ must not extend beyond 8 $p$-phenylene units.
Reproducible spectra of cation radicals of FPP$_n$-FPP$_{16}$ in dichloromethane displayed in Figure 3. 3C were obtained by quantitative redox titrations using three different aromatic oxidants, i.e. THEO$^{+}\text{SbCl}_6^-$ (THEO = tetrasubstituted $p$-hydroquinone ether, $E_{\text{red1}} = 0.67$ V vs Fc/Fc$^+$, $\lambda_{\text{max}} = 518$ nm, $\lambda_{\text{max}} = 7300$ cm$^{-1}$ M$^{-1}$),$^{28}$ NAP$^{+}\text{SbCl}_6^-$ (NAP = cycloannulated naphthalene derivative, $E_{\text{red1}} = 0.94$ V vs Fc/Fc$^+$, $\lambda_{\text{max}} = 672$ nm, $\lambda_{\text{max}} = 9300$ cm$^{-1}$ M$^{-1}$),$^{29,30}$ and TRUX$^{+}\text{SbCl}_6^-$ (TRUX = cycloannulated truxene derivative, $E_{\text{red1}} = 0.78$ V vs Fc/Fc$^+$, $\lambda_{\text{max}} = 1400$ nm, $\lambda_{\text{max}} = 9216$ cm$^{-1}$ M$^{-1}$), see structures in the in the Experimental Section. As an example, absorption spectra obtained by an incremental substoichiometric addition of a concentrated solution of FPP$_6$ to a solution of NAP$^{+}\text{SbCl}_6^-$ in CH$_2$Cl$_2$ are displayed in Figure 3. 4A. Careful quantification by a simple deconvolution procedure$^{16,31}$ performed at each titration point confirmed a 1:1 stoichiometry of the redox reaction, i.e. FPP$_6$ + NAP$^{+}$ → FPP$_6^{+}\cdot$ + NAP. The cation radical spectra of other FPP$_n$ in Figure 3. 3C were similarly generated using NAP$^{+}$ and THEO$^{+}$ (Figure 3.s S7-S19 in the Experimental Section). Absorption spectra of FPP$_n^{+}\cdot$ in Figure 3. 3C were identical across all oxidants used (i.e. NAP$^{+}$, THEO$^{+}$ and/or TRUX$^{+}$), and did not change either upon a tenfold increase in their concentration or temperature lowering to -40 °C.$^{32}$ Due to the transient nature of FPP$_2^{+}$, this cation radical was generated by laser flash photolysis using photo excited chloranil as an oxidant; it...
absorbs at $\lambda_{\text{max}} = 700$ nm (Table 1).\textsuperscript{26,27} Importantly, a plot of the energies of the absorption maxima of FPP$^{++}_2$–FPP$^{++}_{16}$ (Figure 3. 3C, Table 1) showed a linear $\cos[\pi/(n+1)]$ dependence up to $\sim10$-$12$ $p$-phenylene units (Figure 3. 3D), similarly to that observed for exciton delocalization in Figure 3. 2D.

**Figure 3.4.** A: Spectral changes observed upon the reduction of 0.038 mM NAP$^{++}$ in CH$_2$Cl$_2$ (3 mL) by addition of 30-$\mu$L increments of 0.25 mM solution of FPP$_6$ in CH$_2$Cl$_2$. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. NAP$^{++}$ and FPP$^{++}_6$ (as indicated). C: Plot of the mole fractions of NAP$^{++}$ (blue) and FPP$^{++}_6$ (red) against the added equivalents of FPP$_6$. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = E_{\text{ox}}(\text{FPP}_6) - E_{\text{red}}(\text{NAP}^{++}) = -122$ mV.\textsuperscript{16,31}
Table 3.1. Experimental $E_{\text{ox}1}$ (V vs Fc/Fc$^+$), $\lambda_{\text{abs}}$ (nm)/$\varepsilon_{\text{abs}}$ (M$^{-1}$cm$^{-1}$) and $\lambda_{\text{em}}$ of FPP$_n$, and $\lambda_{\text{abs}}$ (nm)/$\varepsilon_{\text{abs}}$ (M$^{-1}$cm$^{-1}$) of FPP$_n^{\ddagger\ddagger}$.

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DFT modeling of FPP$_n$/FPP$_n^{\ddagger\ddagger}$.

The experimental absorption ($\nu_{\text{abs}}$) and emission ($\nu_{\text{em}}$) energies, oxidation potentials ($E_{\text{ox}1}$) of neutral FPP$_n$ and absorption energies of D$_0$$\rightarrow$$D_1$ transitions of their cation radicals FPP$_n^{\ddagger\ddagger}$ (Table 1) were reproduced by electronic structure calculations (DFT/TD-DFT) of FPP$_n$/FPP$_n^{\ddagger\ddagger}$ using B1LYP-40/6-31G(d)+PCM(CH$_2$Cl)$_2$ level of theory.$^4$ Computed absorption energies (i.e. HOMO-LUMO gap from TD-DFT) of FPP$_n$ followed a linear
cos[π/(n+1)] trend, while the calculated emission energies, oxidation energies, and

\[ \text{D}_0 \rightarrow \text{D}_1 \text{ transitions in FPP}_{n}^{+} \] showed a breakdown from cos[π/(n+1)] trend (see Experimental Section for additional details). Isovalue plots and per-unit barplots of HOMOs of FPP\textsubscript{n} and the spin/charge distributions in the corresponding cation radicals (FPP\textsubscript{n}^{++}) obtained by DFT calculations are displayed in Figure 3.5.

**Figure 3.5.** A: Isosurface (0.02 au) representations of HOMOs

(\( \phi_{\text{HOMO}} = \sum_k c_k X_k \)) where \( c_k \) is a coefficient of basis function \( X_k \) of neutral FPP\textsubscript{n} (\( n = 2-18 \)) with corresponding barplot representations of the per-unit HOMO densities calculated as \( q_m = \sum_n c_{mn}^2 \)), where \( m \) is index of \( p \)-phenylene unit and \( n \) is an index of the basis function in unit \( m \). B: Isosurface representations (0.001 au) of the spin-density distributions of FPP\textsubscript{n}^{++} with corresponding per-unit barplot representations of the Natural Population Analysis (NPA) spin density distributions.
A close look at the HOMOs of neutral FPP\textsubscript{n} showed that they are delocalized over the entire poly-p-phenylene chain (Figure 3. 5A). Notably, the spin/charge distribution in smaller homologues (\textit{n} \leq 8) of FPP\textsubscript{n} is similar to the HOMO distribution; however in higher homologues (\textit{n} > 8) the spin/charge distribution is limited to only \textasciitilde{}8 \textit{p}-phenylene units (Figure 3. 5B). In this context, we note that the X-ray crystal structures of a large number of neutral aromatic hydrocarbons and their cation radicals have established that the spin/charge distribution and accompanying structural reorganization track in accordance with the nodal structure of HOMO, i.e. bonds with bonding HOMO lobes undergo elongations whereas the bonds with antibonding lobes undergo contractions.\textsuperscript{35}

Indeed, an examination of the structural reorganization in FPP\textsubscript{n}\textsuperscript{+•}, i.e. elongation and contraction of C-C bonds and decrease in dihedral angles between the adjacent fluorenes, collectively referred to as a \textit{quinoidal distortion} (Figure 3. 6A), clearly tracks the spin/charge distributions (Figure 3.s 6B and 6C), but not the expected HOMO distribution in neutral FPP\textsubscript{n} (Figure 3. 5A).
Figure 3.6. A: Schematic representation of the quinoidal distortion induced by 1-e oxidation. B: Per-unit barplot representation of the charge-density distribution, which is identical to the spin-density distribution in Figure 3.5B. C: Per-unit barplot representation of the distribution of the quinoidal distortion.

The lack of close correspondence between the HOMO and spin/charge density distributions arises due to the interplay between the energetic gain from the hole delocalization and the countervailing energetic penalty from the structural/solvent reorganization in longer FPP$_n^{++}$ wires. As such, this suggests that the precursor HOMOs for the FPP$_n^{++}$ must be different from the original HOMOs of neutral FPP$_n$. Indeed, analysis of the electronic structures of neutral FPP$_n$ at the cation-radical (structurally reorganized) geometries shows that their HOMO densities closely follow the spin/charge and structural reorganization distributions in FPP$_n^{++}$ (compare Figure 3.s 5, 6 and 7).
As the HOMO distribution in π-conjugated poly-\( p \)-phenylene wires and the \( \cos[\pi/(n+1)] \) dependence of their properties can be accounted for using simple tight-binding approaches such as Hückel molecular orbital (HMO) theory, we examined the HOMOs of original and reorganized \( \text{FPP}_n \) wires in the context of HMO theory, in order to uncover the underlying cause of the breakdown of the \( \cos[\pi/(n+1)] \) dependence of the properties of \( \text{FPP}_n^{+\cdot} \) cation radicals, as follows.

**Figure 3.7.** Isosurface (0.02 au) representations of HOMOs of neutral \( \text{FPP}_n \) (\( n = 2-18 \)) calculated at the equilibrium geometries of \( \text{FPP}_n^{+\cdot} \) and corresponding barplot representations of the per-unit HOMO densities.
Hückel Molecular Orbital (HMO) Theory

Originally, HMO theory was developed to provide energies and a composition of the molecular orbitals (MOs) in $\pi$-conjugated hydrocarbons, where each MO was represented as a linear combination of the atomic orbitals (AOs). The energies of the MOs are determined from the energies of the AOs ($\alpha$) and resonance integral (or electronic coupling) $\beta$ between each pair of the adjacent AOs, while the interactions between non-adjacent AOs are neglected. For example, Figure 3.8A depicts the prediction of HMO theory (eq. 1), where the evolutions of HOMO and LUMO energies follow $\cos[\pi/(n+1)]$ trend with $n$ being the number of atomic orbitals.

$$\varepsilon_{\text{HOMO}} = \alpha - 2\beta \cos\left(\frac{\pi}{n+1}\right) \quad \text{eq. 1}$$

![Figure 3.8](image.png)

Figure 3.8. A: Schematic representation ($\alpha = 0$ and $\beta = 1$) of the evolution of
HOMO and LUMO energies with $n$. B: Schematic representation ($\alpha = 0$ and $\beta = 1$) of the HOMO-LUMO gap, which provides the energy of absorption maximum ($\nu_{abs}$), against $\cos[\pi/(n+1)]$.

Furthermore, the HOMO-LUMO energy gap that provides the energies of the electronic absorption maxima ($\nu_{abs}$) also follows the linear $\cos[\pi/(n+1)]$ trend (eq. 2 and Figure 3.8B), which is often approximated as the $1/n$ trend.$^{8,40-45}$

$$\nu_{abs} \approx \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} \propto \cos\left(\frac{\pi}{n+1}\right) \quad \text{eq. 2}$$

Indeed, the HOMO-LUMO energy gap obtained from TD DFT calculations (Figure 3. S21 in the Experimental Section) and the experimental absorption maxima of neutral FPP$_n$ follow a linear $\cos[\pi/(n+1)]$ trend (Figure 3. 2B, Table 1), suggesting that HOMO/LUMO are delocalized up to the polymeric limit.$^{46-52}$ However, a linear evolution of the experimental oxidation potentials against $\cos[\pi/(n+1)]$ trend was not observed (Figure 3. 3B, Table 1). Moreover, as shown above, oxidation-induced structural/solvent reorganization leads to a mismatch between HOMO of neutral FPP$_n$ and spin/charge density distributions in longer ($n > 8$) FPP$_n^{+\cdot}$ wires (compare Figure 3.s 5, 6 and 7).

Thus, the energies of the precursor HOMOs for neutral FPP$_n$ at cation radical geometry are different than at the neutral geometry. In the context of the Koopmans’ theorem$^{35,53-55}$ one should expect a linear evolution of HOMO energies (eq. 1 and Figure 3. 8A) with vertical ionization energies – not with adiabatic oxidation energies. Thus, a description of
both FPP\textsubscript{n} and FPP\textsubscript{n}^{++} within the HMO theory/Koopmans’ paradigm would require appropriate modifications to account for the structural/solvent reorganization accompanying 1-e\textsuperscript{-} oxidation.

Application of the HMO theory to FPP\textsubscript{n}.

In order to describe properties of the FPP\textsubscript{n} wires within the framework of HMO theory, MOs of FPP\textsubscript{n} are represented as a linear combination of the HOMOs of each monomeric \textit{p}-phenylene unit, an approach referred to hereafter as a coarse-grained HMO theory. Unlike the simple poly-\textit{p}-phenylene wires (\textsuperscript{8}PP\textsubscript{n}, Figure 3.1), in FPP\textsubscript{n} wires the dihedral angle between \textit{p}-phenylenes within one fluorene (~0.08 ± 0.05°) and adjacent fluorenes (~37.15 ± 0.11°) are different and, therefore, the values of the coupling (\(\beta\)) will alternate for each pair of the adjacent \textit{p}-phenylenes as depicted in Figure 3.9.

![Diagram](image)

**Figure 3.9.** A: The structure of FPP\textsubscript{4} with the highlighted alternation in the dihedral angles. B: Isosurface (0.02 au) of ‘bisallylic’ HOMO of benzene and its HOMO energies (\(\alpha\)) used to model the monomeric units in FPP\textsubscript{n}. The alternating couplings between the monomeric units are shown as \(\beta\textsubscript{in}\) and \(\beta\textsubscript{out}\).
The interactions between $p$-phenylenes, following the Hückel's approximations, can be represented using the tight-binding $n \times n$ Hamiltonian matrix:

$$
H = \begin{bmatrix}
\alpha & \beta_{in} & 0 & \cdots & 0 & 0 & 0 \\
\beta_{in} & \alpha & \beta_{out} & \cdots & 0 & 0 & 0 \\
0 & \beta_{out} & \alpha & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \cdots & \alpha & \beta_{out} & 0 \\
0 & 0 & 0 & \cdots & \beta_{out} & \alpha & \beta_{in} \\
0 & 0 & 0 & \cdots & 0 & \beta_{in} & \alpha 
\end{bmatrix}
$$

where $\alpha$ is the HOMO energy of the $p$-phenylene unit, $\beta_{in}$ is the coupling between two $p$-phenylenes within a fluorene and $\beta_{out}$ is the coupling between $p$-phenylenes in two adjacent fluorenes (Figure 3.9A). Numerical diagonalization of the Hamiltonian $H$ will produce the MO energies $\varepsilon_i$ (i.e. eigenvalues) and the corresponding MO density distributions (i.e. eigenvectors), where the eigenvalue with the smallest magnitude corresponds to the HOMO energy $\varepsilon_{HOMO}$, while the coefficients $c_i^2$ in the eigenvector represent HOMO densities at the corresponding units (Figure 3.10A).
**Figure 3.10.** A: Numerical diagonalization of the Hückel Hamiltonian matrix provides HOMO energy and HOMO density distribution as a linear combination of the monomeric HOMOs on the example of FPP$_4$. B, left: Couplings $\beta_{in}$ and $\beta_{out}$ are obtained as a splitting between ‘bisallylic’ MOs from the angular scan of biphenyl. B, right: Linear dependence of HOMO energies of FPP$_n$ against $\cos(\pi/(n+1))$ and their HOMO density distributions shown as per-unit barplot representations.

The HOMO energy for each $p$-phenylene unit in FPP$_n$ for the construction of Hückel Hamiltonian matrix was used as the HOMO energy of benzene,$^{56}$ i.e. $\alpha = -7.4$ eV.

Couplings $\beta_{in} = -1.0$ eV and $\beta_{out} = -0.8$ eV were estimated as a splitting between ‘bisallylic’ MOs from the angular scan of biphenyl (Figure 3.10B). Numerical diagonalization of the resulting Hückel Hamiltonian matrices provided the HOMO energies (eigenvalues) and HOMO densities (eigenvectors) for various FPP$_n$, which were
in excellent agreement with those obtained from the DFT calculations (compare Figure 3.s 10B, right and 5A).

The observation of the linear \( \cos[\pi/(n+1)] \) dependence of the HOMO energies (Figure 3. 10B right) and energies of absorption maxima (\( \nu_{\text{abs}} \) in Table 1, Figure 3. 2B) are consistent with the prediction of the HMO theory. In sharp contrast, however, oxidation potentials of \( \text{FPP}_n \) show a breakdown when plotted against \( \cos[\pi/(n+1)] \) (Figure 3. 3B). The cause of such breakdown lies in the fact that the HMO theory does not account for the structural/solvent reorganization accompanying 1-\( e^- \) oxidation. We hypothesized that an accounting of the reorganizational energy in the Hückel Hamiltonian matrix should allow an accurate description of the redox properties of \( \text{FPP}_n \).

It is expected that the energy of HOMO of a neutral aromatic donor at the (cation-radical) reorganized geometry will be elevated by a certain value \( \Delta \alpha \) as shown on the example of benzene and its cation radical (Figure 3. 11A). Unlike the benzene cation radical, which bears one full charge, in \( \text{FPP}_n^{\pi^+} \) the amount of charge is different for each \( p \)-phenylene unit (Figure 3. 6B). Thus, the HOMO energies \( (\alpha_i) \) for \( p \)-phenylene units in neutral \( \text{FPP}_n \) at the reorganized geometries were elevated by \( q_i \Delta \alpha \), where \( q_i \) is the value of the charge at the \( i \)th unit (Figure 3. 11B). [Note that the DFT calculations have demonstrated that the charge, spin and normalized structural reorganization in each \( p \)-phenylene unit in \( \text{FPP}_n^{\pi^+} \) show identical distributions (Figure 3.s 5 and 6).]
Figure 3.11. A: Comparison of HOMO energies of neutral benzene at neutral geometry with neutral benzene at cation radical geometry. B: Schematic representation of the structural reorganization of FPP₄ upon 1-e⁻ oxidation with the highlighted alternation in the dihedral angles and corresponding elevations in the HOMO energies of the monomeric units.

Thus, the Hückel Hamiltonian matrix was modified (eq. 4) to take into account structural reorganization by elevated HOMO energies ($\alpha_i$) of various p-phenylene units and different couplings ($\beta_{out}$) owing to the reduced dihedral angle in oxidized FPPₙ (Figure 3.11B).

\[
H = \begin{pmatrix}
\alpha_1 & \beta_{in} & 0 & \cdots & 0 & 0 & 0 \\
\beta_{in} & \alpha_2 & \beta_{out}(\theta) & \cdots & 0 & 0 & 0 \\
0 & \beta_{out}(\theta) & \alpha_3 & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \cdots & \alpha_{n-2} & \beta_{out}(\theta) & 0 \\
0 & 0 & 0 & \cdots & \beta_{out}(\theta) & \alpha_{n-1} & \beta_{in} \\
0 & 0 & 0 & \cdots & 0 & \beta_{in} & \alpha_n
\end{pmatrix}, \text{eq. 4}
\]

A numerical diagonalization of the resulting Hamiltonian matrix in eq. 4 provided the HOMO energies and HOMO densities for FPPₙ at reorganized geometries. Figure 3.12A
shows that HOMO energies (eq. 4, eigenvalues) at reorganized geometries show a deviation from the linearity, whereas the HOMO energies (eq. 3, eigenvalues) at non-reorganized (neutral) geometries follow a linear dependence against \( \cos[\pi(n+1)] \). Indeed, the HOMO energies obtained from the modified Hamiltonian matrix (eq. 4, eigenvalues) follow a linear trend with the experimental oxidation potentials of FPP\(_n\) (Figure 3.12B, red line), attesting that the Koopmans’ paradigm does hold true if the structural reorganization accompanying 1-e\(^-\) oxidation is appropriately accounted for in HMO theory.

**Figure 3.12.** A: Evolution of HOMO energies of neutral FPP\(_n\) using Hückel Hamiltonian without reorganization (i.e. @ neutral geometry) in eq. 3 (blue) and neutral FPP\(_n\) using modified Hückel Hamiltonian that includes reorganization (i.e. @ cation-radical geometry) in eq. 4 (red). B: Plot of the HOMO energies from Figure 3.12A against the experimental oxidation potentials (\( E_{ox1} \)) of FPP\(_n\).
Thus, we demonstrated that incorporation of the structural/solvent reorganization, available from the DFT calculations, into the HMO theory allows an accurate prediction of the evolution of the oxidation potentials of $\pi$-conjugated poly-$p$-phenylene wires (e.g. FPP$_n$) as well as the HOMO density distributions, which parallel the spin/charge density distributions obtained from DFT calculations. In this context, it is noteworthy that the Marcus theory, by its construction, takes into account the structural/solvent reorganization and electronic coupling in a parameterized form without the necessity of DFT calculations. Accordingly, next, we examine the applicability of the Marcus-based multistate model (MSM) for the description of FPP$_n^{++}$ and compare with the modified HMO approach.

**Multistate Model**

The multistate model (MSM) utilizes a bell-shaped composite quadratic/reciprocal function (rather than a simple parabolic function as in the Marcus two-state model) for the realistic description of the charge distribution along the reaction coordinate $\chi$ (Figure 3.13A). The application of MSM to FPP$_n^{++}$ required a simple modification where alternating couplings $H_{in}^{ab}$ and $H_{cut}^{ab}$ were used to account for the different dihedral angles between $p$-phenylenes within a fluorene and between adjacent fluorenes (Figure 3.13B).
Figure 3.13. A: Schematic representation of the bell-shaped diabatic state, where structural/solvent reorganization is fixed at the single \( p \)-phenylene and the position of the hole is varied along the reaction coordinate \( x \). In the vicinity of the reorganized unit \( H(x) \) is quadratic and at larger separation distances it follows Coulomb law of electrostatic interaction. B: Representation of several diabatic states in FPP_\( n \) with alternating couplings \( H_{in}^{ab} \) and \( H_{out}^{ab} \).
Thus, the MSM Hamiltonian matrix applicable to FPP$_n^{+\cdot}$ can be expressed as a tight-binding $n \times n$ matrix that depends on the reaction coordinate $x$ (eq. 5). Numerical diagonalization of the Hamiltonian matrix $H(x)$ for each $x$ results in the adiabatic potential energy surface with the lowest-energy surface $E_0(x)$ corresponding to the ground state of FPP$_n^{+\cdot}$. The minimum on the ground state surface $E_0(x)$ defines the position $x_{min}$ of the center of the hole distribution and the energy at this point $E_0(x_{min})$ directly corresponds to the oxidation energy of FPP$_n$.

$$H(x) = \begin{bmatrix} H_1(x) & H_{1b} & 0 & \cdots & 0 & 0 & 0 \\ H_{1b} & H_2(x) & H_{2b} & \cdots & 0 & 0 & 0 \\ 0 & H_{2b} & H_3(x) & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & H_{n-2}(x) & H_{n-2b} & 0 \\ 0 & 0 & 0 & \cdots & H_{n-1b} & H_{n-1}(x) & H_{n-1b} \\ 0 & 0 & 0 & \cdots & 0 & H_{nb} & H_n(x) \end{bmatrix}, \text{ eq 5}$$
Numerical solution of the MSM Hamiltonian matrix (eq. 5) for FPP\(_n^{+}\) with parameters \(\lambda = 2, \lambda^\infty = 12, H_{\text{in}}^{ab} = 19, H_{\text{out}}^{ab} = 15\) provided the oxidation energies (eigenvalues), vertical D\(_0\)→D\(_1\) excitation energies and hole distributions (eigenvectors) in the ground and excited state (see Section 6 in the Experimental Section for additional details). The plots of the oxidation energies obtained by MSM against the \(\cos[\pi/(n+1)]\) trend reproduce the breakdown from the linearity for \(n > 8\) as observed with experimental oxidation potentials of FPP\(_n\) (compare Figure 3.14A and 3B). Moreover, the hole distributions in FPP\(_n^{+}\) obtained from MSM closely resemble those obtained from DFT calculations (compare Figure 3.14B and 6).

![Figure 3.14](image)

**Figure 3.14.** A: Plot of oxidation energies of various FPP\(_n^{+}\) obtained by MSM against \(\cos[\pi/(n+1)]\) trend. Oxidation energies were scaled to reproduce experimental oxidation potentials \(E_{\text{ox1}}\). B: Per-unit barplot representation of the hole distributions in various FPP\(_n^{+}\) obtained by MSM.
A close examination of the potential energy surfaces of various FPP$_n^{\bullet\bullet}$ obtained from the MSM (Figure 3.15A) reveals the presence of several minima within ~10 meV of each other, with different hole distributions extending to ~8 $p$-phenylene units (see insets in Figure 3.15B). As such, this analysis suggests that in higher homologues of FPP$_n^{\bullet\bullet}$ ($n > 8$) multiple isomeric electronic structures are feasible. Indeed, the DFT calculations identified two almost isoenergetic electronic isomers of FPP$_{18}^{\bullet\bullet}$ and FPP$_{16}^{\bullet\bullet}$ with different positions of the spin/charge distribution center in the poly-$p$-phenylene chain in excellent agreement with MSM predictions (Figure 3.15C).$^{62}$

\[\text{Figure 3.15. A: Ground state surfaces of FPP}_n^{\bullet\bullet}$ ($n = 2-18$) with respect to the reaction coordinate $x$ from MSM. B: Zoomed-in ground state surface of FPP$_{18}^{\bullet\bullet}$ and hole distributions shown for three distinct minima (as indicated). C: Electronic isomers of FPP$_{18}^{\bullet\bullet}$ and FPP$_{16}^{\bullet\bullet}$ showing their spin-density distributions as isosurface plots and per-unit barplot representations. Energies of these electronic isomers for a given FPP$_n^{\bullet\bullet}$ differ only by ~0.01 kcal/mol.\]
Modified Hückel Molecular Orbital Theory vs Marcus-based Multistate Model

Hückel molecular orbital (HMO) theory has been extensively used as an effective model to predict energies and a composition of the molecular orbitals of $\pi$-conjugated hydrocarbons.$^{36-39}$ The HOMO energy obtained by HMO theory can be used to approximate vertical ionization energy based on the Koopmans’ paradigm.$^{53,54}$ However, HMO theory as originally formulated fails to predict adiabatic oxidation potentials, because the oxidation-induced structural/solvent reorganization is not accounted for.

Here, on the example of the fluorene-based poly-$p$-phenylene cation radicals, we have introduced a modified HMO theory, where structural/solvent reorganization was incorporated by adjusting the HOMO energies ($\alpha$) of interacting (via electronic coupling $\beta$) monomeric $p$-phenylenes with the aid of DFT calculations (Figure 3. 16A). The degree of the HOMO energy elevation ($\Delta\alpha$) of each unit was set in proportion to the amount of charge at the corresponding $p$-phenylene unit using benzene as a model monomeric unit. This modified HMO model provided the HOMO energies and density distributions and, in turn, predicts the evolution of the oxidation potentials of FPP$_n$. 
In this context, it is significant to note that the modified HMO model provides similar evolution of the oxidation potentials of FPP$_n$, as the Marcus-based multistate model (MSM), which by its design, takes into account structural/solvent reorganization as a function of the charge transfer coordinate $x$ with empirically adjusted parameters, i.e. reorganization energy ($\lambda$) and electronic coupling ($H_{ab}$). An extension of the two-state model into a multistate model using the interaction amongst several diabatic states provides position and distribution of the hole and stabilization energy in FPP$_n^{+\ast}$ (Figure 3.16B). We have, thus, demonstrated that the modified HMO model (where reorganization energy is introduced with the aid of DFT calculations) and MSM (where reorganization energies and electronic couplings parameters are adjusted until the experimental properties and/or spin/charge distributions in FPP$_n^{+\ast}$ are reproduced) both provide an accurate description of the evolution of the redox properties and the charge distribution of
the poly-$p$-phenylene cation radicals. This comparative analysis presented above highlights the importance of the structural/solvent reorganization in limiting the hole distribution to $\sim 8$ $p$-phenylene units in long poly-$p$-phenylene wires and, thereby, accounts for the breakdown of their redox and optical properties against $\cos[\pi/(n+1)]$ trend.
Conclusions

In this contribution, we have examined the evolution of the redox and optical properties of the $\pi$-conjugated poly-$p$-phenylene wires, using fluorene-based poly-$p$-phenylene (FPP$_n$) wires, where $n = 2$-$16$. Both experimental data and DFT clearly demonstrate that the absorption energies $\nu_{\text{abs}}$ of neutral FPP$_n$ follow a linear trend against $\cos[\pi/(n+1)]$ up to the polymeric limit, while oxidation potentials $E_{\text{ox}}$, demonstrate a breakdown from the linearity for large $n$. In parallel, DFT calculations demonstrate that the HOMO densities of neutral FPP$_n$ are delocalized over the entire chain, while the spin/charge and structural reorganization in FPP$_n^{+\cdot}$ extend only to $\approx 8$ $p$-phenylene units.

Application of the coarse-grained Hückel Molecular Orbital (HMO) theory on the example of neutral FPP$_n$ provides HOMO-LUMO energy gaps (or the energies of absorption maximum), which follow a linear $\cos[\pi/(n+1)]$ trend up to the polymeric limit. However, HOMO energies (i.e. vertical ionization energies) from HMO theory fail to reproduce evolution of the adiabatic oxidation potentials, because HMO theory, in its original formulation, does not account for the structural/solvent reorganization that accompanies 1-e$^-$ oxidation. To account for the structural/solvent reorganization in FPP$_n$, we introduce reorganization energy into a HMO theory by elevating HOMO energies of each $p$-phenylene unit proportionally to the amount of charge at the unit in the corresponding cation radical (FPP$_n^{+\cdot}$) with the aid of DFT calculations. Once the structural/solvent reorganization is included, the HOMO energies and HOMO density obtained from the modified HMO theory become consistent with the evolution of the experimental adiabatic oxidation potentials of FPP$_n$. 
Thus, by contrasting the results from original and modified HMO theories against experimentally observed oxidation potentials, we have shown that the origin of the \( \cos[\pi/(n+1)] \) trend breakdown, which limits the hole distribution to \( \sim 8 \) \( p \)-phenylene units, is due to the structural/solvent reorganization that accompanies \( 1-e^- \) oxidation.

Furthermore, the modified HMO model predictions are fully consistent with our recently developed Marcus-based multistate (MSM) to \( \text{FPP}_n^{+*} \), which by its construction, accounts for the structural/solvent reorganization. Therefore, \textit{Huckel theory which incorporates reorganization energy equals Marcus Theory}. We believe that the modified HMO model can serve as an effective tool for understanding the fundamental properties of poly-\( p \)-phenylene wires and will aid toward the rational design of the next-generation long-range charge and energy transfer materials for photovoltaics applications.
EXPERIMENTAL

General Experimental Methods and Materials.

All reactions were performed under argon atmosphere unless otherwise noted. All commercial reagents were used without further purification unless otherwise noted. Dichloromethane (Aldrich) was repeatedly stirred with fresh aliquots of concentrated sulfuric acid (~10 % by volume) until the acid layer remained colorless. After separation it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P₂O₅ under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexanes and toluene were distilled from P₂O₅ under an argon atmosphere and then refluxed over calcium hydride (~12 h). After distillation from CaH₂, the solvents were stored in Schlenk flasks under an argon atmosphere. Tetrahydrofuran (THF) was dried initially by distilling over lithium aluminum hydride under an argon atmosphere. The THF was further refluxed over metallic sodium in the presence of benzophenone until a persistent blue color was obtained and then it was distilled under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. NMR spectra were recorded on Varian 300 and 400 MHz NMR spectrometers. GC-MS spectra were obtained on a Fissions 8000 trio instrument at an ionization potential of 70 eV.
**Cyclic Voltammetry (CV).** The CV cell was of an air-tight design with high vacuum Teflon valves and Viton O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The working electrode consisted of an adjustable platinum disk embedded in a glass seal to allow periodic polishing (with a fine emery cloth) without changing the surface area (~1 mm²) significantly. The reference SCE electrode (saturated calomel electrode) and its salt bridge were separated from the catholyte by a sintered glass frit. The counter electrode consisted of platinum gauze that was separated from the working electrode by ~3 mm. The CV measurements were carried out in a solution of 0.2 M supporting electrolyte (tetra-**n**-butyl ammonium hexafluorophosphate, TBAH) and 2-5 x 10⁻³ M substrate in dry dichloromethane under an argon atmosphere. All the cyclic voltammograms were recorded at a sweep rate of 200 mV sec⁻¹, unless otherwise specified and were IR compensated. The oxidation potentials \(E_{1/2}\) were referenced to SCE, which was calibrated with added (equimolar) ferrocene \(E_{1/2} = 0.450 \text{ V vs. SCE}\). The \(E_{1/2}\) values were calculated by taking the average of anodic and cathodic peak potentials in the reversible cyclic voltammograms.
Synthesis of FPPₙ

Scheme 3 S1. Synthesis of FPP₄ (OF₂)

**Synthesis of S1-1.** A Schlenk flask containing 2-bromofluorene (2.0 g, 8.2 mmol) and THF (20 mL) was cooled to 0 °C; and tBuOK (2.7 g, 20.4 mmol) was added under an argon atmosphere. The resulting dark red reaction mixture was stirred for 30 minutes and then 1-bromohexane (3.4 g, 20.4 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for additional 12 hours. The reaction was quenched by an addition of 5% HCl (50 mL) and it was extracted with CH₂Cl₂ (3 x 25 mL). The combined organic layers were washed with water, saturated brine, and dried over anhydrous MgSO₄. It was filtered and evaporated to afford crude product as an oil, which was purified by column chromatography using silica gel and hexanes as eluent (colorless oil, 3.2 g, 94%). ¹H NMR (CDCl₃) δ: 0.50-0.65 (4H, m), 0.71-0.80 (6H, t, J = 7.24 Hz), 0.96-1.17 (12H, m), 1.85-2.00 (4H, m), 7.29-7.34 (3H, m), 7.42-7.46 (2H, m), 7.52-7.57 (1H, dd, J = 8.75 Hz), 7.63-7.68 (1H, m). ¹³C NMR (CDCl₃)
Synthesis of S1-2. To a Schlenk flask containing a degassed solution of KOAc (1.8 g, 18.12 mmol) in dioxane (50 mL) were added S1-1 (2.3 g, 5.6 mmol) and Pd(dppf)Cl₂ (60 mg) under an argon atmosphere. The mixture was stirred for 10 min and then bis(pinacolato)diboron (1.7 g, 6.7 mmol) was added. The resulting mixture was refluxed for 12 h. After cooling to room temperature, the reaction mixture was poured into water (100 mL); and extracted with CH₂Cl₂ (3 x 50 mL). The combined organic layers were washed with water and evaporated. The crude product was purified by column chromatography (SiO₂, hexanes) to afford S1-2 as a colorless liquid (1.97 g, 77%).

\[ \delta: 14.17, 22.74, 23.81, 29.81, 31.63, 40.46, 55.50, 119.88, 121.13, 121.15, 122.98, 126.25, 127.06, 127.60, 130.02, 140.16, 140.27, 150.42, 153.09. \]

Synthesis of OF₂. The S1-1 (0.75 g, 1.82 mmol) and S1-2 (0.84 g, 1.82 mmol) were added to degassed anhydrous 1,2-dimethoxyethane (60 mL) in an oven dried Schlenk flask under an argon atmosphere and the flask was further evacuated and filled with argon (3x). In another oven dried Schlenk flask, a solution of anhydrous sodium carbonate (5.0 g) in degassed water (20 mL) was prepared under an argon atmosphere
and the flask was repeatedly evacuated and filled with argon (3x). To the first Schlenk flask, Pd(PPh$_3$)$_4$ (90 mg) was added followed by the aqueous sodium carbonate solution under a strict argon atmosphere. Note that the reaction flask was subjected to repeated evacuation and filling the flask with argon cycles (3x) after addition of each reagent. The flask was covered with aluminum foil and the reaction mixture was allowed to reflux overnight (~12 h). The resulting mixture was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 25 mL). The combined organic layers were dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The crude product was purified by column chromatography on silica gel using hexanes as eluent to afford pure OF$_2$ (0.67 g, 62%). m.p: 72-73 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.65-0.75 (8H, m), 0.75-0.82 (12H, t), 1.01-1.20 (24H, m), 1.97-2.16 (8H, m), 7.29-7.42 (6H, m), 7.60-7.64 (2H, S), 7.64-7.68 (2H, dd, $J = 7.88$ Hz), 7.72-7.77 (2H, d, $J = 6.85$ Hz), 7.77-7.81 (2H, d, $J = 7.85$ Hz); $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 14.18, 22.72, 23.91, 29.85, 31.62, 40.53, 55.30, 119.86, 120.02, 121.55, 123.05, 126.17, 126.92, 127.12, 140.43, 140.65, 140.94, 151.13, 151.59.

Scheme 3.S2. Synthesis of FPP$_6$ (O$F_3$)
**Synthesis of S2-1.** 2,7-Dibromofluorene (5 g, 15.5 mmol) was converted to 9,9-dihexyl-2,7-dibromofluorene (S2-1) in THF (50 mL) using tBuOK (5.2 g, 46.6 mmol) and 1-bromohexane (6.4 g, 38.8 mmol) at 0 °C using the procedure described for the preparation of S1-1 above. The crude product was further purified by column chromatography on silica gel using hexanes as eluent to afford S2-1 as a thick colorless liquid (6.5 g, 86%). $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.50-0.64 (4H, m), 0.73-0.82 (6H, t, $J = 6.99$ Hz), 0.95-1.17 (12H, m), 1.84-1.95 (4H, M), 7.42-7.47 (4H, m), 7.49-7.53 (2H, dd, $J = 7.72$, 0.84 Hz). $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 14.16, 22.73, 23.78, 29.73, 31.61, 40.35, 55.82, 121.28, 121.61, 126.30, 130.29, 139.20, 152.68.

**Synthesis of S2-2.** The S2-1 (4.4 g, 8.90 mmol) was bornylated using PdCl$_2$(dpdf) (60 mg), dioxane (50 mL), and KOAc (5.3 g, 54.0 mmol), bis(pinacolato)diboron (5.0 g, 19.7 mmol) using the procedure described above for S1-2. The crude product was purified by column chromatography (SiO$_2$, hexanes) to afford S2-2 as a white powder (4.3 g, 82%). m.p: 82-84 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.45-0.62 (4H, m), 0.68-0.78
(6H, t, $J = 6.86$ Hz), 0.92-1.13 (12H, m), 1.34-1.43 (24H, s), 1.93-2.05 (4H, m), 7.69-7.74 (2H, d, $J = 7.61$ Hz), 7.74-7.76 (2H, s), 7.78-7.83 (2H, dd, $J = 7.55$ Hz); $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 14.16, 22.70, 23.68, 25.06, 25.16, 29.75, 31.56, 40.22, 55.29, 83.83, 119.51, 129.03, 133.79, 144.04, 150.57.

**Synthesis of OF$_3$.** The monobromide S1-1 (1.73 g, 5.17 mmol) and *bis*(boronic) ester S2-2 (1.02 g, 2.07 mmol) were subjected to Suzuki coupling in degassed 1,2-dimethoxyethane (60 mL) containing a solution of sodium carbonate (5.0 g) in water (20 mL) and Pd(PPh$_3$)$_4$ (90 mg) as a catalyst using the procedure described above for OF$_2$. Crude product was then purified by column chromatography (silica, hexanes) to afford pure OF$_3$ (0.88 g, 51%). m.p: 92-94°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.60-0.87 (30H, m), 0.99-1.20 (38H, m), 1.97-2.16 (12H, m), 7.29-7.42 (6H, m), 7.60-7.70 (8H, m), 7.72-7.77 (2H, d, $J = 6.94$ Hz), 7.77-7.79 (1H, s), 7.79-7.81 (2H, d, $J = 2.95$ Hz); $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 14.18, 22.72, 23.93, 29.81, 29.85, 31.60, 31.60, 40.53, 55.30, 55.45, 119.87, 120.04, 120.09, 121.55, 121.64, 123.06, 126.17, 126.29, 126.93, 127.14, 140.12, 140.46, 140.63, 140.66, 140.94, 151.13, 151.61, 151.92.

**Scheme 3.** Synthesis of FPP$_8$ (OF$_4$)
Synthesis of S3-1. A solution of OF$_2$ (2.8 g, 4.2 mmol) in CH$_2$Cl$_2$ (30 mL) under an argon atmosphere was treated dropwise with a solution of Br$_2$ (1.54 g) in CH$_2$Cl$_2$ (10 mL) with the aid of a dropping funnel. After addition was completed (~10 min), the resulting mixture was stirred for additional 2 h at room temperature. The reaction mixture was poured into 5% aqueous NaOH solution (100 mL), CH$_2$Cl$_2$ layer was separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 25 mL). The combined organic layers were then washed with water (3 x 25 mL), dried over anhydrous MgSO$_4$ and evaporated in vacuo. The crude product was purified by column chromatography (SiO$_2$, hexanes) to afford pure S3-1 (1.8 g, 53%). m.p: 108-110 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.65-0.75 (8H, m), 0.75-0.82 (12H, t, $J = 6.8$ Hz), 1.01-1.20 (24H, m), 1.91-2.10 (8H, m), 7.46-7.50 (4H, m), 7.56-7.65 (6H, m), 7.72-7.76 (2H, d, $J = 7.89$ Hz); $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 14.16, 22.71, 23.86, 29.75, 31.59, 40.41, 55.66, 120.17, 120.99, 121.24, 121.54, 126.35, 126.42, 130.15, 139.48, 139.90, 140.92, 151.27, 153.37.
Synthesis of OF₄. The dibromide S3-1 (0.1 g, 0.12 mmol) and the boronic ester S1-2 (0.13 g, 0.28 mmol) were subjected to Suzuki coupling in degassed 1,2-dimethoxyethane (20 mL) containing a solution of sodium carbonate (2.5 g) in water (10 mL) and Pd(PPh₃)₄ (25 mg) as a catalyst using the procedure described above for OF₂. Crude product was then purified by column chromatography (silica, hexanes) to afford pure OF₄ (0.09 g, 55%). m.p: 80-82 °C; ¹H NMR (CDCl₃, 400 MHz) δ: 0.60-0.87 (40H, m), 0.99-1.20 (48H, m), 1.97-2.16 (16H, m), 7.29-7.42 (6H, m), 7.60-7.73 (12H, m), 7.72-7.77 (2H, dd, J = 7.11 Hz), 7.77-7.82 (2H, d, J = 7.86 Hz), 7.82-7.87 (4H, dd, J = 7.83 Hz); ¹³C NMR (CDCl₃, 400 MHz) δ: 14.19, 22.72, 23.93, 23.99, 29.83, 29.86, 31.60, 31.61, 31.64, 40.53, 55.32, 55.47, 119.88, 120.05, 120.12, 121.57, 121.65, 123.07, 126.19, 126.30, 126.95, 127.15, 140.13, 140.17, 140.48, 140.63, 140.69, 140.94, 151.15, 151.61, 151.94, 151.95.

Scheme 3.S4. Synthesis of FPP₁₀ (OF₃)

Synthesis of S4-1. A cooled (~0°C) solution of OF₂ (2.8 g, 4.2 mmol) and catalytic amount of I₂ (~50 mg) in CH₂Cl₂ (30 mL) was stirred for 5 min under an argon
atmosphere and was then treated dropwise with a solution of Br₂ (0.67 g, 4.2 mmol) in CH₂Cl₂ (10 mL) with the aid of a dropping funnel. After addition was completed (~10 min), the resulting mixture was stirred for additional 2 h at ~0°C. The reaction mixture was poured into 5% aqueous NaOH solution (100 mL), CH₂Cl₂ layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 25 mL). The combined organic layers were then washed with water (3 x 25 mL), dried over anhydrous MgSO₄ and evaporated in vacuo. The crude product was purified by column chromatography (SiO₂, hexanes) to afford pure S₄-I (1.2 g, 35%). m.p: 90-92°C; ¹H NMR (CDCl₃, 400 MHz) δ: 0.60-0.81 (20H, m), 0.98-1.19 (24H, m), 1.90-2.09 (8H, m), 7.28-7.39 (3H, m), 7.44-7.50 (2H, m), 7.55-7.67 (5H, m), 7.70-7.76 (2H, d J = 7.65 Hz), 7.76-7.79 (1H, d, J = 7.81 Hz); ¹³C NMR (CDCl₃, 400 MHz) δ: 14.19, 22.73, 23.87, 23.90, 23.78, 29.84, 31.61, 31.62, 40.45, 40.52, 55.30, 55.65, 119.90, 120.07, 120.15, 121.13, 121.22, 121.52, 121.53, 123.05, 126.19, 126.32, 126.42, 126.95, 127.20, 130.13, 139.31, 139.97, 140.38, 140.60, 140.84, 141.16, 151.10, 151.21, 151.62, 153.37.

**Synthesis of OF₅.** The monobromide S₄-I (1.89 g, 2.53 mmol) and bis(boronic) ester S₂-2 (0.5 g, 1.01 mmol) were subjected to Suzuki coupling in degassed 1,2-dimethoxyethane (30 mL) containing a solution of sodium carbonate (2.5 g) in water (10 mL) and Pd(PPh₃)₄ (50 mg) as a catalyst using the procedure described above for OF₂. Crude product was then purified by column chromatography (silica, hexanes) to afford pure OF₅ (0.90 g, 54%). m.p: 88-90°C; ¹H NMR (CDCl₃, 400 MHz) δ: 0.60-0.90 (50H, m), 0.99-1.20 (60H, m), 1.97-2.19 (20H, m), 7.29-7.42 (6H, m), 7.60-7.90 (26H, m); ¹³C NMR (CDCl₃, 400 MHz) δ: 14.19, 22.72, 23.93, 23.94, 23.96, 23.97, 24.00, 29.83, 29.86,
Scheme 3.5. Synthesis of FPP$_{12}$ (OF$_6$)

$\text{S4-1}$

$\text{S5-1}$

1H NMR (CDCl$_3$, 400 MHz) $\delta$: 0.65-0.82 (20H, m), 1.01-1.20 (24H, m), 1.36-1.44 (12H, s), 1.91-2.10 (8H, m), 7.28-7.40 (3H, m), 7.57-7.67 (4H, m), 7.71-7.86 (6H, m);

$\text{S3-1}$

$\text{OF}_6$ (or FPP$_{12}$)

13C NMR (CDCl$_3$, 400 MHz) $\delta$: 14.16, 22.71, 23.83, 25.09, 29.78, 29.83, 31.58, 31.60, 40.37, 40.51, 55.28, 55.37, 83.84, 119.18, 119.86, 120.01, 120.48, 121.58, 121.63, 123.03, 126.19, 126.92, 127.13, 129.02, 133.96, 140.24, 140.49, 140.90, 141.16, 143.96, 150.32, 151.12, 151.57, 152.19.

Synthesis of S5-1. The S4-1 (2.3 g, 3.08 mmol) was bornylated using PdCl$_2$(dpdf) (60 mg), dioxane (50 mL), and KOAc (0.96 g, 9.24 mmol), $\text{bis(pinacolato)diboron}$ (0.94 g, 3.70 mmol) using the procedure described above for S1-2. The crude product was purified by column chromatography (SiO$_2$, hexanes) to afford S5-1 as an oil (1.95 g, 80%).

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 0.65-0.82 (20H, m), 1.01-1.20 (24H, m), 1.36-1.44 (12H, s), 1.91-2.10 (8H, m), 7.28-7.40 (3H, m), 7.57-7.67 (4H, m), 7.71-7.86 (6H, m);

$^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$: 14.16, 22.71, 23.83, 25.09, 29.78, 29.83, 31.58, 31.60, 40.37, 40.51, 55.28, 55.37, 83.84, 119.18, 119.86, 120.01, 120.48, 121.58, 121.63, 123.03, 126.19, 126.92, 127.13, 129.02, 133.96, 140.24, 140.49, 140.90, 141.16, 143.96, 150.32, 151.12, 151.57, 152.19.
**Synthesis of OF**

The dibromide **S3-1** (0.1 g, 0.12 mmol) and the boronic ester **S5-1** (0.22 g, 0.28 mmol) were subjected to Suzuki coupling in degassed 1,2-dimethoxyethane (30 mL) containing a solution of sodium carbonate (2.5 g) in water (10 mL) and Pd(PPh$_3$)$_4$ (50 mg) as a catalyst, using the procedure described above for **OF$_2$**. Crude product was then purified by column chromatography (silica, hexanes) to afford pure **OF$_6$** (0.14 g, 61%). m.p: 82-84 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ; 0.60-0.90 (60H, m), 0.99-1.20 (72H, m), 1.97-2.19 (24H, m), 7.29-7.42 (6H, m), 7.60-7.90 (32H, m); $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 14.19, 22.72, 23.94, 23.96, 24.00, 29.83, 31.62, 40.53, 55.32, 55.48, 119.88, 120.05, 120.13, 121.58, 121.66, 123.07, 126.95, 127.15, 140.13, 140.17, 140.49, 140.66, 140.68, 140.70, 140.69, 140.94, 151.15, 151.62, 151.96.


**Synthesis of S6-1.** A cooled (~0 °C) solution of **OF$_3$** (0.3 g, 0.3 mmol) and catalytic amount of I$_2$ (50 mg) in CH$_2$Cl$_2$ (20 mL) under an argon atmosphere was treated dropwise with a solution of Br$_2$ (0.12 g, 0.75 mmol) in CH$_2$Cl$_2$ (10 mL) with the aid of a dropping funnel. After addition was completed (~10 min), the resulting mixture was stirred for additional 2 h at ~0°C. The reaction mixture was poured into 5% aqueous NaOH solution.
(100 mL), CH$_2$Cl$_2$ layer was separated and the aqueous layer was extracted with CH$_2$Cl$_2$
(3 x 25 mL). The combined organic layers were then washed with water (3 x 25 mL),
dried over anhydrous MgSO$_4$ and evaporated in vacuo. The crude product was purified
by column chromatography (SiO$_2$, hexanes) to afford pure S6-1 (0.25 g, 72%). m.p: 76-
78 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.65-0.75 (12H, m), 0.75-0.86 (18H, t $J$ = 6.8 Hz),
1.01-1.20 (36H, m), 1.91-2.10 (12H, m), 7.46-7.52 (4H, m), 7.57-7.69 (10H, m), 7.74-
7.78 (2H, d, $J$ = 7.85 Hz), 7.80-7.85 (2H, d, $J$ = 7.85 Hz); $^{13}$C NMR (CDCl$_3$, 400 MHz) δ:
14.18, 22.69, 22.72, 23.88, 23.96, 29.77, 31.58, 31.60, 40.44, 55.47, 55.66, 120.17,
121.16, 121.22, 121.55, 121.62, 126.33, 126.42, 130.15, 139.37, 139.96, 140.21, 140.48,
141.12, 151.24, 151.95, 153.37.

**Synthesis of OF$_7$.** The dibromide S6-1 (0.2 g, 0.17 mmol) and the boronic ester S5-1
(0.31 g, 0.40 mmol) were subjected to Suzuki coupling in degassed 1,2-dimethoxyethane
(30 mL) containing a solution of sodium carbonate (2.5 g) in water (10 mL) and
Pd(PPh$_3$)$_4$ (50 mg) as a catalyst using the procedure described above for OF$_2$. Crude
product was then purified by column chromatography (silica, hexanes) to afford pure
OF$_7$ (0.20 g, 38 %). m.p: 116-118 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.60-0.90 (70H,
m), 0.99-1.22 (84H, m), 1.97-2.19 (28H, m), 7.29-7.42 (6H, m), 7.60-7.90 (38H, m); $^{13}$C
NMR (CDCl$_3$, 400 MHz) δ: 14.19, 22.72, 23.94, 24.00, 29.83, 29.86, 31.62, 40.53, 55.32,
55.48, 119.88, 120.05, 120.13, 121.58, 121.66, 123.07, 126.18, 126.31, 126.95, 127.15,
127.37, 140.13, 140.17, 140.49, 140.68, 140.95, 151.15, 151.62, 151.96.
Scheme 3.S7, Synthesis of FPP<sub>16</sub> (OF<sub>4</sub>)

**Synthesis of S7-1.** A cooled (~0 °C) solution of OF<sub>4</sub> (0.25 g, 0.19 mmol) and catalytic amount of I<sub>2</sub> (50 mg) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) under an argon atmosphere was treated dropwise with a solution of Br<sub>2</sub> (0.08 g, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) with the aid of a dropping funnel. After addition was completed (~10 min), the resulting mixture was stirred for additional 2 h at ~0°C. The reaction mixture was poured into 5% aqueous NaOH solution (100 mL), CH<sub>2</sub>Cl<sub>2</sub> layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 25 mL). The combined organic layers were then washed with water (3 x 25 mL), dried over anhydrous MgSO<sub>4</sub> and evaporated in vacuo. The crude product was purified by column chromatography (SiO<sub>2</sub>, hexanes) to afford pure S7-1 (0.2 g, 71%). m.p: 84-86 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 0.65-0.88 (40H, m), 1.01-1.20 (48H, m), 1.91-2.16 (16H, m), 7.46-7.52 (4H, m), 7.57-7.71 (14H, m), 7.74-7.78 (2H, d, J = 7.85 Hz), 7.80-7.85 (4H, d, J = 7.85 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz) δ: 14.18, 22.69, 22.72, 23.88, 23.96, 29.77, 29.80, 31.60, 40.44, 40.47, 40.48, 40.49, 55.47, 55.66, 120.17, 121.13, 121.22, 121.55, 121.62, 121.65, 126.33, 126.42, 130.15, 139.37, 139.96, 140.09, 140.27, 140.42, 140.68, 141.14, 151.24, 151.25, 151.93, 151.96, 153.38.
**Synthesis of OF₈.** The dibromide S7-1 (0.14 g, 0.1 mmol) and the boronic ester S5-1 (0.20 g, 0.25 mmol) were subjected to Suzuki coupling in degassed 1,2-dimethoxyethane (30 mL) containing a solution of sodium carbonate (2.5 g) in water (10 mL) and Pd(PPh₃)₄ (50 mg) as a catalyst using the procedure described above for OF₂. Crude product was then purified by column chromatography (silica, hexanes) to afford pure OF₈ (0.06 g, 26%). m.p: 115-116 °C; ¹H NMR (CDCl₃, 400 MHz) δ: 0.60-0.90 (80H, m), 0.99-1.22 (96H, m), 1.97-2.19 (32H, m), 7.29-7.42 (6H, m), 7.60-7.90 (44H, m); ¹³C NMR (CDCl₃, 400 MHz) δ: 14.19, 22.72, 23.94, 23.99, 24.01, 29.83, 31.62, 40.53, 55.32, 55.48, 119.88, 120.05, 120.15, 121.66, 123.07, 126.18, 126.31, 126.95, 127.19, 140.13, 140.17, 140.49, 140.68, 140.95, 151.15, 151.62, 151.96.
$^1$H NMR spectrum of S1-1 in CDCl$_3$

$^{13}$C NMR spectrum of S1-1 in CDCl$_3$

$^1$H NMR spectrum of S1-2 in CDCl$_3$
$^{13}$C NMR spectrum of S1-2 in CDCl$_3$

$^1$H NMR spectrum of OF$_2$ (or FPP$_4$) in CDCl$_3$
$^{13}$C NMR spectrum of OF$_2$ (or FPP$_4$) in CDCl$_3$

$^1$H NMR spectrum of S2-1 in CDCl$_3$
C NMR spectrum of S2-1 in CDCl₃

1H NMR spectrum of OF₃ (or FPP₆) in CDCl₃
$^1$H NMR spectrum of S3-1 in CDCl$_3$

$^{13}$C NMR spectrum of OF$_3$ (or FPP$_6$) in CDCl$_3$
$^{13}$C NMR spectrum of S3-1 in CDCl$_3$

$^1$H NMR spectrum of OF$_4$ (or FPP$_8$) in CDCl$_3$
$^{13}$C NMR spectrum of OF$_4$ (or FPP$_8$) in CDCl$_3$

$^1$H NMR spectrum of S4-1 in CDCl$_3$
$^{13}$C NMR spectrum of S4-1 in CDCl$_3$

$^1$H NMR spectrum of OF$_5$ (or FPP$_{10}$) in CDCl$_3$
$^{13}$C NMR spectrum of OF$_5$ (or FPP$_{10}$) in CDCl$_3$

$^1$H NMR spectrum of S5-1 in CDCl$_3$
$^{13}$C NMR spectrum of S5-1 in CDCl₃

$^1$H NMR spectrum of OF₆ (or FPP₁₂) in CDCl₃
$^{13}$C NMR spectrum of OF$_6$ (or FPP$_{12}$) in CDCl$_3$

$^1$H NMR spectrum of S6-1 in CDCl$_3$
$^{13}$C NMR spectrum of S6-1 in CDCl$_3$

$^1$H NMR spectrum of OF$_7$ (or FPP$_{14}$) in CDCl$_3$
$^{13}$C NMR spectrum of OF$_7$ (or FPP$_{14}$) in CDCl$_3$

$^1$H NMR spectrum of S7-1 in CDCl$_3$
$^{13}$C NMR spectrum of S7-1 in CDCl$_3$

$^1$H NMR spectrum of OF$_8$ (or FPP$_{16}$) in CDCl$_3$
$^{13}$C NMR spectrum of OF$_8$ (or FPP$_{16}$) in CDCl$_3$
X-ray crystallography

Figure 3.S1. Thermal ellipsoid plots (50% probability) derived from the X-ray crystal structures of FPP₄.

Figure 3.S2. Thermal ellipsoid plots (50% probability) derived from the X-ray crystal structures of S6-1.
Table 3.S1. Summary of X-ray crystallographic data collection and structure refinement for FPP4 and S6-1.

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<td>14433.0(3)</td>
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<tr>
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<td>8</td>
</tr>
<tr>
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<td>1.226</td>
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<td>µ/mm⁻¹</td>
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<td>3.136</td>
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<tr>
<td>F(000)</td>
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<td>5619.0</td>
</tr>
<tr>
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<td>0.3989 × 0.3238 × 0.0373</td>
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<tr>
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<td></td>
<td>2Θ range for data collection/°</td>
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<td></td>
<td>7.08 to 147.48</td>
<td>-16 \leq h \leq 19, -18 \leq k \leq 19, -20 \leq l \leq 20</td>
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<tr>
<td></td>
<td>6.2 to 147.34°</td>
<td>-25 \leq h \leq 21, -29 \leq k \leq 27, -38 \leq l \leq 38</td>
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Figure 3.S3. MALDI mass spectroscopy of FPPₙ.

Figure 3.S4A. Cyclic voltammogram of OF₁ in CH₂Cl₂ at 22 °C. Note that OF₁ undergoes irreversible electrochemical oxidation due to a facile coupling of OF₁ cation radical with neutral OF₁ to form OF₂, whose redox peaks can be seen on the return scan.¹
**Figure 3. S4B.** (A) Cyclic voltammogram of $2.0 \times 10^{-3}$ M OF$_2$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2.0 \times 10^{-3}$ M OF$_2$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 200 mV s$^{-1}$ at 22°C.

**Figure 3. S4C.** (A) Cyclic voltammogram of $2.0 \times 10^{-3}$ M OF$_3$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2.0 \times 10^{-3}$ M OF$_3$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 200 mV s$^{-1}$ at 22°C.
**Figure 3. S4D.** (A) Cyclic voltammogram of $2.0 \times 10^{-3} \text{ M } \text{OF}_4$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2.0 \times 10^{-3} \text{ M } \text{OF}_4$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 200 mV s$^{-1}$ at 22 °C.

**Figure 3. S4E.** (A) Cyclic voltammogram of $2.0 \times 10^{-3} \text{ M } \text{OF}_5$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C.
Figure 3. S4F. (A) Cyclic voltammogram of $2.0 \times 10^{-3}$ M OF$_6$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 100-500 mV s$^{-1}$ at 22 °C. (B) A comparison spectra of a Cyclic voltammogram and square wave of $2.0 \times 10^{-3}$ M OF$_6$ in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NPF$_6$ at a scan rate of 200 mV s$^{-1}$ at 22 °C.

A discussion of Higher Oxidation Potentials of FPP$_n$

A plot of the first oxidation potentials $E_{ox1}$ of FPP$_n$ against $\cos(\pi/(n + 1))$ showed a linear decrease up to 8 $p$-phenylene units followed by an abrupt breakdown from linearity, i.e. $E_{ox1}$ remained almost unchanged going from FPP$_{10}$ to FPP$_{16}$ (Table S2). It is noted that evolution of the second and higher oxidation potentials of FPP$_n$ with
increasing \( n \) show drastically varied slopes in \( E_{\text{ox}} \) vs \( \cos(\pi/(n+1)) \) plots as compared to \( E_{\text{ox}1} \) (Figure 3. S5), suggesting that stabilization of polycations (i.e. dications and trications) is much more effective as compared to cation radicals with increasing \( n \). It is interesting to note that the first, second and third oxidation potentials are converging to a single potential. A detailed experimental and computational investigation is planned to explore the role of multiplicity, i.e. singlet vs triplet dications and doublet vs quintet trications, and their respective stabilities in comparison to doublet cation radicals.

**Figure 3.55.** Experimental first, second and third oxidation potentials \( E_{\text{ox}} \) of \( \text{FPP}_n \) against \( \cos(\pi/(n+1)) \).
Table S2. First, second and third oxidation potentials of FPPₙ in V vs Fc/Fc⁺.

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<td>$E_{\text{ox}1}$</td>
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<td>0.84</td>
<td>0.73</td>
<td></td>
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</tr>
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</table>

S2. Generation of FPPₙ⁺⁺ by redox titrations

The reproducible spectra of cation radicals of FPPₙ in dichloromethane at 22 °C were obtained by quantitative redox titrations using three different aromatic oxidants, i.e. THEO⁺⁺SbCl₆⁻ ($E_{\text{red}1} = 0.67$ V vs Fc/Fc⁺, $\lambda_{\text{max}} = 518$ nm, $\varepsilon_{\text{max}} = 7300$ cm⁻¹ M⁻¹),¹² NAP⁺⁺SbCl₆⁻ ($E_{\text{red}1} = 0.94$ V vs Fc/Fc⁺, $\lambda_{\text{max}} = 672$ nm, $\varepsilon_{\text{max}} = 9300$ cm⁻¹ M⁻¹)³⁻⁵ and TRUX⁺⁺SbCl₆⁻ ($E_{\text{red}1} = 0.78$ V vs Fc/Fc⁺, $\lambda_{\text{max}} = 1400$ nm, $\varepsilon_{\text{max}} = 9216$ cm⁻¹ M⁻¹).

Figure 3.S6. Chemical structures and names of three aromatic oxidants used in redox titrations.
Each redox titration experiment was carried out by an incremental addition of sub-stoichiometric amounts of electron donor (FPP$_n$) to the solution of an oxidant cation radical (Ox$^{••}$). The 1-$e^-$ oxidation of FPP$_n$ to FPP$_n$•• and reduction of Ox$^{••}$ to Ox can be described by an equilibrium shown in eq. 1.

$$\text{Ox}^{••} + \text{FPP}_n \rightleftharpoons \text{Ox} + \text{FPP}_n^{••} \quad (\text{eq. 1})$$

The redox titrations with two successive 1-$e^-$ oxidations involve multiple equilibria: one- and two-electron redox reactions between the donor and oxidant (eqs. 2 and 3) and comproportionation/disproportionation of D$^{2+}$/D$^{••}$ (eq. 4).

$$\text{Ox}^{••} + \text{D} \rightleftharpoons \text{Ox} + \text{D}^{••} \quad (\text{eq. 2})$$

$$\text{Ox}^{••} + \text{D}^{••} \rightleftharpoons \text{Ox} + \text{D}^{2+} \quad (\text{eq. 3})$$

$$\text{D}^{2+} + \text{D} \rightleftharpoons 2\text{D}^{••} \quad (\text{eq. 4})$$

Numerical deconvolution$^6$ of the UV-VIS absorption spectrum at each increment (Figure 3.s S7-S19, A) produced the individual spectra of FPP$_n^{••}$ and/or FPP$_n^{2+}$ and Ox$^{••}$ (Figure 3.s S7-S19, B). Moreover, the resulting individual spectra of Ox$^{••}$, FPP$_n^{••}$, and FPP$_n^{2+}$ provided the mole fractions of each species which were plotted against the added equivalents of FPP$_n$ (Figure 3.s S7-S19, C). The mole fraction/equivalent of added donor
FPPₙ (MF/D) plots were fitted by varying $\Delta G_1 (= E_{ox1}^{\text{FPP}_n} - E_{red}^{\text{Ox}_n})$ and $\Delta G_{12} (= E_{ox2}^{\text{FPP}_n} - E_{ox1}^{\text{FPP}_n})$.

**Figure 3.S7.** A: Spectral changes observed upon the reduction of 0.061 mM NAP$^{+\cdot}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 0.96 mM solution of FPP$_4$ in CH$_2$Cl$_2$. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. NAP$^{+\cdot}$ and FPP$_4^{+\cdot}$ (as indicated). C: Plot of the mole fractions of NAP$^{+\cdot}$ (red) and FPP$_4^{+\cdot}$ (blue) against the added equivalents of FPP$_4$. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using $\Delta G_1 = -29$ mV.
Figure 3. S8. A: Spectral changes observed upon the reduction of 0.038 mM NAP$^{+•}$ in CH$_2$Cl$_2$ (3 mL) by addition of 30-µL increments of 0.25 mM solution of FPP$_6$ in CH$_2$Cl$_2$. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. NAP$^{+•}$ and FPP$_6^{+•}$ (as indicated). C: Plot of the mole fractions of NAP$^{+•}$ (red) and FPP$_6^{+•}$ (blue) against the added equivalents of FPP$_4$. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = -122$ mV.

Figure 3. S9. A: Spectral changes observed upon the reduction of 0.06 mM NAP$^{+•}$ in CH$_2$Cl$_2$ (3 mL) by addition of 14-µL increments of 0.45 mM solution of FPP$_8$ in CH$_2$Cl$_2$. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. NAP$^{+•}$, FPP$_8^{+•}$ and FPP$_8^{2+}$. C: Plot of the mole fractions of NAP$^{+•}$ (red), FPP$_8^{+•}$ (blue) and FPP$_8^{2+}$ (green) against the added equivalents of FPP$_8$. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = -123$ mV and $\Delta G_{12} = 149$ mV.
Figure 3. S10. A: Spectral changes observed upon the reduction of 0.044 mM NAP$^{••}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 0.29 mM solution of FPP$_{10}$ in CH$_2$Cl$_2$. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. NAP$^{••}$, FPP$_{10}^{••}$ and FPP$_{10}^{2+}$. C: Plot of the mole fractions of NAP$^{••}$ (red), FPP$_{10}^{••}$ (blue) and FPP$_{10}^{2+}$ (green) against the added equivalents of FPP$_{10}$. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = -152$ mV and $\Delta G_{12} = 144$ mV.

Figure 3. S11. A: Spectral changes observed upon the reduction of 0.07 mM THEO$^{••}$ in CH$_2$Cl$_2$ (3 mL) by an addition of 15-µL increments of 0.7 mM solution of FPP$_{10}$ in CH$_2$Cl$_2$. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. THEO$^{••}$ and FPP$_{10}^{••}$. C: Plot of the mole fractions of THEO$^{••}$ (red) and FPP$_{10}^{••}$ (blue) against the added equivalents of FPP$_{10}$. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = 10$ mV.
Figure 3. S12. A: Spectral changes observed upon the reduction of 0.019 mM TRUX$^{+}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 0.4 mM solution of FPP$_{10}$ in CH$_2$Cl$_2$. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. TRUX$^{+}$ and FPP$_{10}^{+}$. C: Plot of the mole fractions of TRUX$^{+}$ (red) and FPP$_{10}^{+}$ (blue) against the added equivalents of FPP$_{10}$. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = -56$ mV.

Figure 3. S13. A: Spectral changes observed upon the reduction of 0.123 mM NAP$^{+}$ in CH$_2$Cl$_2$ (3 mL) by addition of 10-µL increments of 0.41 mM solution of FPP$_{12}$ in CH$_2$Cl$_2$. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. NAP$^{+}$, FPP$_{12}^{+}$ and FPP$_{12}^{2+}$. C: Plot of the mole fractions of NAP$^{+}$ (red), FPP$_{12}^{+}$ (blue) and FPP$_{12}^{2+}$ (green) against the added equivalents of FPP$_{12}$. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = -155$ mV and $\Delta G_{12} = 144$ mV.
Figure 3. S14. A: Spectral changes observed upon the reduction of 0.058 mM THEO\\textsuperscript{**} in CH\textsubscript{2}Cl\textsubscript{2} (3 mL) by addition of 15-\textmu L increments of 0.68 mM solution of FPP\textsubscript{12} in CH\textsubscript{2}Cl\textsubscript{2}. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. THEO\\textsuperscript{**} and FPP\textsubscript{12}\\textsuperscript{**}. C: Plot of the mole fractions of THEO\\textsuperscript{**} (red) and FPP\textsubscript{12}\\textsuperscript{**} (blue) against the added equivalents of FPP\textsubscript{12}. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = -14$ mV.

Figure 3. S15. A: Spectral changes observed upon the reduction of 0.031 mM TRUX\\textsuperscript{**} in CH\textsubscript{2}Cl\textsubscript{2} (3 mL) by addition of 15-\textmu L increments of 0.4 mM solution of FPP\textsubscript{10} in CH\textsubscript{2}Cl\textsubscript{2}. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. TRUX\\textsuperscript{**} and FPP\textsubscript{10}\\textsuperscript{**}. C: Plot of the mole fractions of TRUX\\textsuperscript{**} (red) and FPP\textsubscript{10}\\textsuperscript{**} (blue) against the added equivalents of FPP\textsubscript{10}. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = -53$ mV.
Figure 3. S16. A: Spectral changes observed upon the reduction of 0.113 mM NAP$^{•-}$ in CH$_2$Cl$_2$ (3 mL) by addition of 18-$\mu$L increments of 0.34 mM solution of FPP$_{14}$ in CH$_2$Cl$_2$. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. NAP$^{•-}$, FPP$_{14}^{•-}$ and FPP$_{14}^{2+}$. C: Plot of the mole fractions of NAP$^{•-}$ (red), FPP$_{14}^{•-}$ (blue) and FPP$_{14}^{2+}$ (green) against the added equivalents of FPP$_{14}$. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = -145$ mV and $\Delta G_{12} = 149$ mV.

Figure 3. S17. A: Spectral changes observed upon the reduction of 0.058 mM THEO$^{•-}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-$\mu$L increments of 0.68 mM solution of FPP$_{12}$ in CH$_2$Cl$_2$. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. THEO$^{•-}$ and FPP$_{12}^{•-}$. C: Plot of the mole fractions of THEO$^{•-}$ (red) and FPP$_{12}^{•-}$ (blue) against the added equivalents of FPP$_{12}$. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = -27$ mV.
**Figure 3. S18.** A: Spectral changes observed upon the reduction of 0.026 mM TRUX$^{+•}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 0.3 mM solution of FPP$_{14}$ in CH$_2$Cl$_2$. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. TRUX$^{••}$, FPP$_{14}^{••}$ and FPP$_{14}^{2+}$. C: Plot of the mole fractions of TRUX$^{••}$ (red), FPP$_{14}^{••}$ (blue) and FPP$_{14}^{2+}$ (green) against the added equivalents of FPP$_{14}$. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = -51$ mV and $\Delta G_{12} = 109$ mV.

**Figure 3. S19.** A: Spectral changes observed upon the reduction of 0.11 mM NAP$^{+•}$ in CH$_2$Cl$_2$ (3 mL) by addition of 18-µL increments of 0.16 mM solution of FPP$_{16}$ in CH$_2$Cl$_2$. B: Deconvolution of each UV-VIS absorption spectrum from Figure 3. A into its component spectra, i.e. NAP$^{••}$, FPP$_{16}^{••}$ and FPP$_{16}^{2+}$. C: Plot of the mole fractions of NAP$^{••}$ (red), FPP$_{16}^{••}$ (blue) and FPP$_{16}^{2+}$ (green) against the added equivalents of FPP$_{16}$. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = -122$ mV and $\Delta G_{12} = 83$ mV.
**Disclaimer**: The results discussed in this chapter was further supplemented by DFT calculations and by a recently developed multistate parabolic model and a modifies Huckel theory by my coworkers Drs. Marat R Talipov and Maxim V. Ivanov.


(8) While in the range of small \(n\) both \(1/n\) and \(\cos[\pi/(n+1)]\) dependences provide a similar description of the evolution of redox and optical properties of poly-p-phenylene wires, for larger \(n\), \(1/n\) trend deviates from the \(\cos[\pi/(n+1)]\) and leads to incorrect extrapolation to the polymeric limit, see Figure 3. S32 in the Experimental Section for additional details.


(25) Note that FPP$_2$ (i.e. OF$_1$) undergoes irreversible electrochemical oxidation due to a facile coupling of OF$_1$ cation radical with neutral OF$_1$ to form OF$_2$, whose redox peaks can be seen on the return scan (Figure 3. S4 in the Experimental Section), see Zhai, L.; Shukla, R.; Wadumethrigie, S. H.; and Rathore, R. *J. Org. Chem.* **2010**, *75*, 4748.


(28) Rathore, R.; Burns, C. L.; Deselnicu, M. I. Preparation of 1, 4: 5, 8-Dimethano-1, 2, 3, 4, 5, 6, 7, 8-Octahydro-9, 10-Dimethoxyanthracenium Hexachloroantimonate (4+ SbCl$_6$−): A Highly Robust Radical-Cation Salt. *Org. Synth.* **2005**, *1*.


(27) Rathore, R.; Burns, C. L.; Deselnicu, M. I. Preparation of 1, 4: 5, 8-Dimethano-1, 2, 3, 4, 5, 6, 7, 8-Octahydro-9, 10-Dimethoxyanthracenium Hexachloroantimonate (4+ SbCl$_6$−): A Highly Robust Radical-Cation Salt. *Org. Synth.* **2005**, *1*.

(32) Further temperature lowering was not possible due to the precipitation of cation radical salts.

(33) It is noted that both exciton and hole delocalization in excited FPP$_n$ and FPP$_n^+$, respectively, undergo similar structural reorganization, however a complete description/comparison of both exciton and hole delocalization will sacrifice clarity due to undue repetition. Accordingly, a detailed comparison of exciton and hole delocalization in FPP$_n$ wires will be deferred for a later publication.


(46) The observation that (experimental) absorption $\nu_{\text{max}}$ of FPP$_{108}$ falls onto the $\cos[\pi/(n+1)]$ trend suggests that HOMO/LUMO in large FPP$_n$ are delocalized up to a polymeric limit possibly due to a narrow distribution of the dihedral angles $0-37^\circ$ which allow sufficient electronic coupling and should be contrasted with poly-phenylenevinylene where multiple dihedral angles between vinylenic and aromatic chromophores are responsible for localization of the HOMO/LUMO, see Refs. 47-52.


(56) Alternatively, HOMO energy ($\alpha$) of a monomeric unit could be approximated as the average between HOMO and HOMO-3 of FPP<sub>2</sub>.


(62) The dynamic interconversion between $\text{FPP}_n^{\text{**}}$ isomers could contribute to the additional stabilization as indicated by the non-zero slope in the plot of almost invariant oxidation potentials of $\text{FPP}_n$ ($n > 8$) (Figure 3.3B) and may play an important role in the incoherent charge-transfer mechanism along the long poly-$p$-phenylene wires.
CHAPTER 4

Turning ON/OFF the Electronic Coupling by Modulating Nodal Arrangement of HOMOs in Isomeric Pyrene-Based Molecular Wires

Introduction

Development of new $\pi$-conjugated wires with enhanced redox and optical properties is critical for molecular electronics and photovoltaic applications.$^{1-4}$ During the rational design of new materials, one should take into account the interchromophoric electronic coupling that is governed by a number of geometrical parameters, e.g. interchromophoric dihedral angle, as well as the electronic structure of the chromophore.$^{5-8}$ For example, linking a pair of fluorenes at 2,2’ position (i.e. $F_2$) allows effective electronic coupling and thereby leads to a significant stabilization of the cationic charge (hole) as judged by the lowering of the oxidation potential by 370 mV decrease as compared with monomer (Scheme 4.1).
Scheme 4.1. Structures of bifluorene, 2,2’-linked and 3,3’-linked bipyrenes. Note that \( \Delta E_{\text{ox}} \) refers to difference between \( E_{\text{ox}} \) (dimer) and \( E_{\text{ox}} \) (monomer).

On the other hand, Mullen and coworkers have synthesized a series of poly-pyrene wires and concluded that linking a pair of pyrenes at 2,2’ (para) positions, leads to a little or no stabilization of their anion radicals, i.e. the reduction potentials of pyrene and bipyrene remained unchanged.\(^9,10\) Furthermore, we have observed that the oxidation potential of 2,2’-linked bipyrenes also did not change when compared to pyrene (Scheme 4.1) despite the interchromophoric dihedral angles being the same as in \( \text{F}_2 \). Even more surprising is the fact that a bipyrene, linked at 3,3’ (meta) positions, with a large interplanar dihedral angle of \( \sim70^\circ \), leads to sizable hole stabilization as indicated by the lowering of its first oxidation potential by 100 mV (Scheme 4.1).

In this work we explore experimentally and computationally the extent of hole delocalization in poly-pyrene wires connected at 3,3’ (meta) positions (\( m\text{-Py}_n \)). We have synthesized a series of poly-pyrenes (\( m\text{-Py}_n, n = 1\text{--}5 \)) with long alkyl chain for better solubility and recorded their absorption, emission spectra, determined their electrochemical oxidation potentials, and obtained the optical data of their cation radicals \( m\text{-Py}_n'^+ \) generated by careful redox titrations using robust aromatic oxidants.
We will show that despite a relatively weak coupling between pyrenes in $m$-$\text{Py}_n$, there is a sizable delocalization of the charge in $m$-$\text{Py}_n^{\ddagger\ddagger}$ that extends to 3 pyrene units, i.e. 6 phenylene units, which is only $\sim$2 phenylene units less than in poly-$p$-phenylene ($\text{PP}_n^{\ddagger\ddagger}$) or poly-fluorene ($\text{F}_n^{\ddagger\ddagger}$) wires.

We will also demonstrate that the nodal arrangement of HOMO dictates which linkage allows effective interchromophoric coupling irrespective of the geometrical considerations.

The availability of the experimental data on $m$-$\text{Py}_n$ together with DFT calculations and theoretical modeling allows us to show how the small interchromophoric coupling affects the redox and optical properties of $\pi$-conjugated wires and discuss its consequences toward the charge stabilization and transfer along the oligomer chain.

NOTE: Theoretical and computational studies were contributed by Dr. Maxim Ivanov.
Results and discussion

**Synthesis.** The synthesis of soluble oligomers of polypyrenes linked at 3,3’ positions (\(m\text{-Py}_n, n = 1-5\)) was accomplished from 2,7-dioctylpyrene (\(\text{Py}_1\), see Scheme 4.2), which was prepared from parent pyrene by adapting standard literature procedures. An oxidative coupling of \(\text{Py}_1\) using DDQ/\(\text{CH}_3\text{SO}_3\text{H}\) as an oxidant afforded \(\text{Py}_2\) in excellent yield. Synthesis of \(\text{Py}_3\) was accomplished by Suzuki coupling\(^{11,12}\) between mono and bis-boronic esters of dioctylpyrene obtained from the corresponding mono and dibromo-dioctylpyrene (Scheme 4.2). The synthesis of higher homologues (\(n = 4–5\)) was similarly accomplished by Suzuki coupling of dibromo derivatives of \(\text{Py}_2\) and \(\text{Py}_3\) with monoboronic ester of \(\text{Py}_1\) (see Scheme 4.2).
Scheme 4.2. Synthetic scheme of Py\textsubscript{n} (n = 1-5). a. Aqueous HBr (48%), H\textsubscript{2}O\textsubscript{2} (30%), ether/methanol (1:1). b. 1-octyne, (PPh\textsubscript{3})\textsubscript{2}PdCl\textsubscript{2}, (iPr\textsubscript{2})NH/THF, 50 °C. c. Repeated crystallization from n-hexanes. d. Pd-C/H\textsubscript{2}, EtOAc/EtOH (2:1). e. DDQ, CH\textsubscript{3}Cl\textsubscript{2}/MeSO\textsubscript{3}H (9:1). f. NBS (2 equiv), NH\textsubscript{4}NO\textsubscript{3}/MeCN. g. 2,7-Dioctylypyrene-3-boranate ester, Pd(PPh\textsubscript{3})\textsubscript{4}, aq. Na\textsubscript{2}CO\textsubscript{3}, DME, reflux. h. NBS (1 equiv), NH\textsubscript{4}NO\textsubscript{3}, MeCN. i.
Pinacolotodiborane, Pd(dppf)Cl₂, KOAc, dioxane, reflux. j. Pd(PPh₃)₄, aq Na₂CO₃, DME, reflux.

The structures of various \textit{m-Py}_n were established by $^1$H/$^{13}$C NMR spectroscopy, MALDI mass spectrometry, and were further confirmed by X-ray crystallography of \textit{m-Py}_2 as a representative molecule (see Section 1 in the Experimental Section for details). Based on the X-ray structure of \textit{Py}_2, the interplanar dihedral angle was found to be $\sim$70°, and was further corroborated by DFT calculations, \textit{vide infra}.

\textit{Electronic absorption and emission spectroscopy of m-Py}_n

Structured absorption band of \textit{Py}_1 shifts red with increasing \textit{n} as measured by the onset (Figure 4.1A) and follows a linear trend with $\cos[\pi/(n+1)]$ (Figure 4.1B). The slope of the trendline for \textit{m-Py}_n in Figure 4.1B is roughly half of the slope for poly-fluorene (\textit{F}_n) wires, and thus suggesting a smaller interchromophoric coupling in \textit{m-Py}_n as compared to \textit{F}_n.
Figure 4.5. A: UV-vis absorption spectra of $m$-Py$_n$ ($n = 1$-$5$) in the units of molar absorptivity in CH$_2$Cl$_2$. B: Plot of the onset energies (see inset in Figure 1A) against $\cos(\pi/\frac{1}{n+1})$ trend. C: Emission spectra of 1.1-$7.4$ mM $m$-Py$_n$ ($n = 1$-$5$) in CH$_2$Cl$_2$. D: Plot of emission energy maxima of $m$-Py$_n$ against $\cos[\pi/(n+1)]$ trend compared with the emission energy maxima of F$_n$.

Compilation of the emission spectra of $m$-Py$_n$ in Figure 4.1C shows that structured emission of $m$-Py$_1$ turns into structureless band that shifts red with increasing $n$. The plot of $\nu_{em}$ vs $\cos[\pi/(n+1)]$ (Figure 4.1D) shows the slope in $m$-Py$_n$ is roughly one
fifths of the slope in $F_n$, suggesting that the smaller interchromophoric coupling in $m$-$\text{Py}_n$ has much more pronounced impact in the evolution of the emission energies, which saturate at $n = 3-4$ as compared to $n = 5-6$ in $F_n$. Thus, the reduced coupling in $m$-$\text{Py}_n$ seem to limit the exciton delocalization to 3-4 units.

*Electrochemistry and electronic spectroscopy of $m$-$\text{Py}_n^{+\ast}$.*

The cyclic voltammograms of $m$-$\text{Py}_n$ showed that the number of reversible waves corresponds to the number of pyrenes in a given $m$-$\text{Py}_n$ (Figure 4.2A). A list of oxidation potentials referenced to ferrocene is compiled in Table 1. A plot of first oxidation potentials ($E_{\text{ox1}}$) against $\cos[\pi/(n+1)]$ showed a rapid saturation beyond $m$-$\text{Py}_3$, suggesting that the hole delocalization does not extend beyond 3 pyrene units (Figure 4.2B). Moreover, the slope of the trend line in $E_{\text{ox1}}/\cos[\pi/(n+1)]$ plot of $m$-$\text{Py}_n$ is roughly half of the slope for $F_n$, suggesting a much smaller interchromophoric coupling in $m$-$\text{Py}_n^{+\ast}$ as compared to $F_n^{+\ast}$ (Figure 4.2B).\(^{13}\)
Figure 4.6. A: Cyclic and square-wave voltammograms of 1 mM m-Py$_n$ in CH$_2$Cl$_2$ (0.1 M $n$-Bu$_4$NPF$_6$) at a scan rate of 200 mV s$^{-1}$ and 22 °C. B:
Plot of the first oxidation potentials ($E_{ox1}$) of $m$-Py$_n$ (red) and F$_n$ (blue) against $\cos[\pi/(n+1)]$ trend. C: Absorption spectra of $m$-Py$_n^{++}$ in the units of molar absorptivity in CH$_2$Cl$_2$ at 22 °C. D: Plot of energies of the absorption maxima of Py$_n^{++}$ (red) and F$_n^{++}$ (blue) against $\cos[\pi/(n+1)]$ trend. E: Spectral changes observed upon the reduction of 0.031 mM THEO$^{++}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 0.86 mM solution of $m$-Py$_2$ in CH$_2$Cl$_2$. F: Deconvolution of each UV-VIS absorption spectrum from Figure E into its component spectra, i.e. THEO$^{++}$ and $m$-Py$_2^{++}$ (as indicated). C: Plot of the mole fractions of THEO$^{++}$ (red) and $m$-Py$_2^{++}$ (blue) against the added equivalents of $m$-Py$_2$. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G_1 = E_{ox}(m$-Py$_2) - E_{red}$(THEO$^{++}$) = -116 mV.

Electronic absorption spectra of cation radicals of $m$-Py$_n$ (Figure 4.2C) were obtained by quantitative redox titrations using three different aromatic oxidants, i.e. THEO$^{++}$, NAP$^{++}$ and ANT$^{++}$ as SbCl$_6^-$ salts, see Section 4 in the Experimental Section. As an example, absorption spectra of $m$-Py$_2^{++}$ were obtained by an incremental addition of a concentrated solution of $m$-Py$_2$ to a solution of THEO$^{++}$SbCl$_6^-$ (Figure 4.2E), followed by the numerical deconvolution procedure performed at each titration point (Figures 4.2F and G), which confirmed a 1:1 stoichiometry of the redox reaction, i.e. THEO$^{++}$ + $m$-Py$_2$ → THEO + $m$-Py$_2^{++}$:
Reliable energies of the absorption maxima, obtained from reproducible electronic absorption spectra, of $m$-$\text{Py}_n^{\text{+}}$ showed a linear $\cos[\pi/(n+1)]$ dependence only up to 3-4 pyrene units followed by a saturation, suggesting that the hole in the vertically excited state does not extend beyond 3-4 pyrene units (Figure 4.2D, Table 4.1).\textsuperscript{18}

**Table 4.1.** Experimental onset $\lambda_{\text{onset}}$ (nm) of the absorption spectra, $\lambda_{\text{max}}$ (nm) of the emission maxima, oxidation potentials $E_{\text{ox1}}$ (V vs Fc/Fc$^+$) of $m$-$\text{Py}_n$, and $\lambda_{\text{abs}}$ (nm)/$\varepsilon_{\text{abs}}$ (M$^{-1}$cm$^{-1}$) of the absorption maxima of $m$-$\text{Py}_n^{\text{+}}$.

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DFT calculations.

The $\nu_{abs}$, $E_{ox1}$ of $m$-Py$_n$ and $\nu_{abs}$ of their cation radicals calculated using (TD-) B1LYP-40/6-31G(d)+PCM(CH$_2$Cl$_2$)$_{19,20}$ are in excellent agreement with the experiment (Table 4.1, Figures SX in the Experimental Section). Computed $\nu_{abs}$ of $m$-Py$_n$ ($n = 1$-$7$) followed a linear cos[$\pi/(n+1)$] trend, while $E_{ox1}$ and the energies of $D_0\rightarrow D_1$ transitions in $m$-Py$_n$+• showed a breakdown from cos[$\pi/(n+1)$] trend (see in the Experimental Section) as observed experimentally (Figures 4.1 and 4.2).

In neutral $m$-Py$_n$, HOMOs are delocalized over the entire chain with the bell-shaped distribution (Figure 4.3). In $m$-Py$_2$+•, spin/charge (hole) in ground ($D_0$) state is evenly distributed amongst a pair of pyrenes, while in $m$-Py$_3$+• and higher homologues, the hole distribution does not extend beyond 3 pyrene units and it is largely concentrated (~70%) at the middle unit (Figure 4.3). In the vertically excited ($D_1$) state the hole distribution extends away from the middle unit and shows a slight spillover beyond 3 units (e.g. 0.07 $e$ in the outer units in $m$-Py$_5$+•, Figure 4.3).
Figure 4.7. Isovalue (0.001 au) and (superimposed) per-unit barplot representations of HOMOs of $m$-Py$_n$, spin densities of $m$-Py$_n^{••}$ in $D_0$ and $D_1$ states. Quantification (bar-plots) of HOMO-densities in $m$-Py$_n$ and identical spin/charge densities in $m$-Py$_n^{••}$ were obtained from the coefficients of the basis functions and natural population analysis (NPA),$^{21,22}$ respectively (also see in the Experimental Section).

Notably, availability of X-ray structures of neutral and cation radical of tetraisopropylpyrene (TIP) allowed us to examine the oxidation-induced bond length changes in TIP$^{••}$ obtained by X-ray crystallography,$^{23}$ which showed excellent linear correlation with DFT calculations (Figure 4.4A). The spin/charge distribution and the bond length changes in TIP$^{••}$ track in accordance with the nodal structure of HOMO.
Moreover, the bonds with bonding HOMO lobes undergo elongations, while the bonds with antibonding lobes undergo contractions (Figure 4.4A).

**Figure 4.8.** A: Comparison of the oxidation-induced bond length changes in TIP**+** obtained by X-ray crystallography and DFT calculations. B: Distribution of the oxidation-induced changes of the selected C-C bonds and dihedral angles between adjacent pyrenes in m-Py**n**+• obtained from DFT calculations.

The oxidation-induced bond-length changes in TIP**+** are remarkably similar to the bond-length changes in Py**i**+• (Figure 4.5B). The analysis of the geometrical changes in higher homologues of m-Py**n**+• showed that the distribution of the bond-length changes (shown by representative bonds ‘c’ and ‘d’, Figure 4.5B) tracks in accordance with the spin/charge distributions in various pyrene units (compare Figures 4.5B and 4.3). Importantly, an even hole distribution over both pyrene units in m-Py**2**+• is accompanied by a reduction in the single interchromophoric dihedral angle from 70° to 49°. In m-Py**3**+•
and higher homologues, the hole distribution is largely limited to 3 pyrene units and thus the reduction occurs only in two dihedral angles that are associated with the spin/charge-bearing pyrenes (see Figure 4.5B, rightmost column).

Interestingly, despite that the interchromophoric dihedral angles in \( m-\text{Py}_n^{+*} \) are twice the corresponding angles in \( F_n^{+*} \) (e.g. 49° vs 20° for \( n = 2 \)) the hole distribution in \( m-\text{Py}_n^{+*} \), is extended over 3 pyrenes units (i.e. 6 phenylenes) as compared with 4 fluorene units in \( F_n^{+*} \) (i.e. 8 phenylenes), which is a difference in only 2 phenylenes. At the same time, in poly-pyrene cation radicals connected at 2,2’ \( (\text{para}) \) positions \( (p-\text{Py}_n^{+*}) \), the hole distributions is limited to one pyrene unit irrespective of number of pyrene units in the chain, i.e. \( n = 1-7 \) (Experimental Section).

**Molecular orbital theory interpretation.**

As the hole (i.e. charge, spin and structural reorganization) distribution in mono- and bi-chromophoric cation radicals definitely follows the distribution of HOMO, let us examine the HOMOs of three model biaryls (Scheme 4.1), i.e. bifluorene \( (F_2) \), and bipyrenes linked at \( \text{meta} \) and \( \text{para} \) positions \( (m-\text{Py}_2 \text{ and } p-\text{Py}_2, \text{respectively}) \).
The HOMO/HOMO-1 of the biaryls arises as the antibonding/bonding combinations due to the interaction between HOMOs of the corresponding monomers (Figure 4.6). The gap between HOMO and HOMO-1 is twice of the electronic coupling (i.e. $2\beta$) between interacting units, which, in turn, is proportional to the orbital overlap.\textsuperscript{24} A simple visual inspection of HOMOs in Figure 4.6 shows that the electronic coupling in $\text{F}_2$ is significantly larger than in $m$-Py$_2$ due to the difference in dihedral angle ($37^\circ$ vs $69^\circ$). Interestingly, despite a similar dihedral angle in $p$-Py$_2$ as in $\text{F}_2$ ($39^\circ$ vs $37^\circ$), the unfavorable nodal arrangement completely prevents the orbital overlap and thus results in negligible electronic coupling.\textsuperscript{25} Indeed, as suggested by DFT calculations on larger homologues of $p$-Py$_n^{\ddagger}$, the absence of the interchromophoric coupling leads to a hole distribution that is limited to a single unit and does not lead to any reduction in $E_{\text{ox}}$ (see Experimental Section).
Marcus theory interpretation.

In order to probe the hole delocalization/stabilization in the model biaryl cation radicals (Scheme 4.1), we performed a scan of D$_0$→D$_1$ excitation energies ($\nu_{abs}$) against the interchromophoric dihedral angle $\phi$ (Figure 4.7A).$^{26}$ Starting from completely planar geometry, an increase in $\phi$ leads to a switchover of the mechanism of hole stabilization from the delocalization over two units, as indicated by the linear dependence of the $\nu_{abs}$ ($= 2H_{ab}$) on the $\cos(\phi)$, to the localization onto a single unit, where the switchover angle corresponds to a case when $2H_{ab} = \lambda$ (Figure 4.6A)$^{28}$.

In F$_2^+$, due to its equilibrium angle much smaller than the switchover angle (20° vs 35°), the hole is evenly distributed over both units (i.e. $2H_{ab} > \lambda$, Figure 4.6B). However, in m-Py$_2^+$, where the equilibrium angle is similar to the switchover angle (49° vs 70°), the mechanism of the hole stabilization lies at the borderline between two mechanisms (i.e. $2H_{ab} \approx \lambda$, Figure 4.6B). Finally, as judged by the $\lambda_{abs}/\cos(\phi)$ plot, the mechanism of the hole stabilization in $p$-Py$_2^+$ is insensitive to the dihedral angle and always corresponds to the localization onto a single unit (i.e. $2H_{ab} < \lambda$, Figure 4.6B).
Figure 4.10. A: Computation scans of the model biaryls (Scheme 4.1) obtained as series of constrained optimizations with fixed interchromophoric dihedral angle ($\varphi = 0^\circ$-$90^\circ$) and subsequent calculation of $D_0 \rightarrow D_1$ excitation energies (using single-point TD-DFT). The linear/quadratic trend lines were plotted for different regimes of the hole stabilization, i.e. Robin-Day class II/class III$^{27,28}$ respectively. B: Two-state models of the biaryls (Scheme 4.1) with parameters $H_{ab}$ and $\lambda$ obtained from the scan in Figure 4.6A, see Experimental Section for details.

Next, we apply the multistate model (MSM)$^{19,29}$ that utilizes a composite quadratic/reciprocal function, rather than a parabola, in order to accurately account for the hole distribution in longer homologues of $m$-$\text{Py}_n$$^+$/F$^+$. The MSM Hamiltonian matrices $H(x)$ can be constructed as a tight-binding $n \times n$ matrices for a range of values $x$ along the reaction coordinate.

Numerical diagonalization of the Hamiltonian matrices at each $x$ provides the adiabatic ground state potential energy surface $G_0(x)$. The minimum of $G_0(x)$ defines position of the hole (i.e. $x_{\text{min}}$), the lowest-energy eigenvalue at this point defines the
oxidation energy (i.e. $G_0(x_{\text{min}})$) and the corresponding eigenvector defined the hole distribution. The difference between two lowest energies at point $x_{\text{min}}$ provides the vertical excitation energy, i.e. $\Delta G(x_{\text{min}}) = G_1(x_{\text{min}}) - G_0(x_{\text{min}})$.

The plots of the oxidation energies $G_0(x_{\text{min}})$ and vertical excitation energies $\Delta G(x_{\text{min}})$ obtained by MSM against the $\cos[\pi/(n+1)]$ trend reproduce the experimentally observed evolution of the oxidation potentials of $m$-Py$_n$ and absorption energies of $m$-Py$_n^{\ast\ast}$ (compare Figures 4.8B and 4.2). In particular, the MSM captures a much more modest reduction of the oxidation energies in $m$-Py$_n$ as compared with F$_n$ (-60 mV vs -170 mV, Figure 4.8A), further confirming the role of the electronic coupling in the hole stabilization. Furthermore, the lower interchromophoric coupling in $m$-Py$_n^{\ast\ast}$ leads to an earlier ($n = 3\text{-}4$) saturation of the oxidation energies of $m$-Py$_n$ as compared with the $n = 4\text{-}5$ for F$_n$ (Figure 4.8A). In parallel, the hole distributions in $m$-Py$_n^{\ast\ast}$, obtained from MSM, do not extend beyond 3 pyrene units, which is in close agreement with the results obtained from DFT calculations (compare Figures 4.3 and 4.7B).
Figure 4.11. A: Plot of oxidation energies $G_0(x_{\text{min}})$ of $m$-Py$_n$ and F$_n$ against $\cos(\pi i/(n+1))$ obtained from MSM using the parameters of $H_{ab}$ and $\Theta$ obtained from the angular scans in Figure 4.6A. B: Potential energy surfaces and barplot representations of the hole distributions in $m$-Py$_n^{**}$ obtained from MSM.

A closer look at the potential energy surfaces of various $m$-Py$_n^{**}$, obtained from the MSM, suggests that starting from $n = 4$, multiple isoenergetic structures with small interconversion barriers ($\sim$10 mV or 0.23 kcal/mol) are possible (Figure 4.7B). Indeed, DFT calculations of $m$-Py$_4^{**}$ identified a transition state structure, where hole is distributed over two units in the middle of the chain and its electronic energy is $\sim$8 mV (or 0.19 kcal/mol) higher than two equilibrium structures, where hole resides over one side of the chain. Notably, the single imaginary frequency of the transition state structure corresponds to a mode that involves high-frequency oscillations ($\sim$550 cm$^{-1}$) of the C-C bonds within two middle pyrene units (see in the Experimental Section).
Conclusion

In this contribution, we have explored the evolution of the redox and optical properties of the poly-pyrenes, linked at 3,3’ (meta) positions, i.e. $m$-$\text{Py}_n$, which have shown a much smaller interchromophoric coupling as compared to the strong coupling in linearly connected poly-fluorenes, i.e. $F_n$.

Due to a much smaller coupling, the evolutions of the experimental absorption energies, emission energies and oxidation potentials of $m$-$\text{Py}_n$, as well as the absorption energies of $m$-$\text{Py}_n^{++}$, showed moderate slopes as compared with corresponding trends for $F_n$, when plotted against $\cos[\pi/(n+1)]$ trend.

Notably, despite roughly threefold decrease in the electronic coupling in $m$-$\text{Py}_2$ as compared with $F_2$, the hole distribution in longer homologues of $\text{Py}_n^{++}$ is limited to 3 pyrene units, i.e. only two phenylene units less than in $F_n^{++}$, as judged by the saturation of the oxidation potentials and spin/charge/structural reorganization distributions obtained by DFT and hole distributions obtained by the multistate model (MSM). As consequence of a more confined hole distribution, starting from $m$-$\text{Py}_4^{++}$, the hole can exist in several isoenergetic equilibrium structures with small interconversion barriers.

Finally, by contrasting $m$-$\text{Py}_n^{++}$, linked at 2,2’ (meta) positions, where hole is distributed over 3 pyrenes, against $p$-$\text{Py}_n^{++}$, linked at 3,3’ (para) positions, where hole is limited to a single unit, we have demonstrated that a simple repositioning of the interchromophoric linkage can have a dramatic effect on the hole stabilization, which can be easily explained by unfavorable nodal arrangement of HOMO. In this context, it is important to note that a simple visual inspection of the HOMOs can serve as a valuable
tool for a qualitative estimation of the strength of electronic communication in \( \pi \)-conjugated wires.
EXPERIMENTAL SECTION

**General Experimental Methods and Materials.** All reactions were performed under argon atmosphere unless otherwise noted. All commercial reagents were used without further purification unless otherwise noted. Dichloromethane (Aldrich) was repeatedly stirred with fresh aliquots of concentrated sulfuric acid (~10 % by volume) until the acid layer remained colorless. After separation it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P₂O₅ under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexanes and toluene were distilled from P₂O₅ under an argon atmosphere and then refluxed over calcium hydride (~12 h). After distillation from CaH₂, the solvents were stored in Schlenk flasks under an argon atmosphere. Tetrahydrofuran (THF) was dried initially by distilling over lithium aluminum hydride under an argon atmosphere. The THF was further refluxed over metallic sodium in the presence of benzophenone until a persistent blue color was obtained and then it was distilled under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. NMR spectra were recorded on Varian 300 and 400 MHz NMR spectrometers. GC-MS spectra were obtained on a Fissions 8000 trio instrument at an ionization potential of 70 eV.
Cyclic Voltammetry (CV). The CV cell was of an air-tight design with high vacuum Teflon valves and Viton O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The working electrode consisted of an adjustable platinum disk embedded in a glass seal to allow periodic polishing (with a fine emery cloth) without changing the surface area (~1 mm2) significantly. The reference SCE electrode (saturated calomel electrode) and its salt bridge were separated from the catholyte by a sintered glass frit. The counter electrode consisted of platinum gauze that was separated from the working electrode by ~3 mm. The CV measurements were carried out in a solution of 0.2 M supporting electrolyte (tetra-n-butyl ammonium hexafluorophosphate, TBAH) and 2-5 x 10^{-3} M substrate in dry dichloromethane under an argon atmosphere. All the cyclic voltammograms were recorded at a sweep rate of 200 mV sec^{-1}, unless otherwise specified and were IR compensated. The oxidation potentials ($E_{1/2}$) were referenced to SCE, which was calibrated with added (equimolar) ferrocene ($E_{1/2} = 0.450$ V vs. SCE). The $E_{1/2}$ values were calculated by taking the average of anodic and cathodic peak potentials in the reversible cyclic voltammograms.
Synthesis

Scheme S1: Synthesis of Py

Synthesis of S1-1. The isomeric mixture of dibromopyrenes was prepared by following a slightly modified literature procedure as detailed below. Thus, aqueous HBr (48%, 14.8 mL) was added to a solution of pyrene (12.0 g, 59.3 mmol) in a mixture of ether (150 mL) and methanol (150 mL) under an argon atmosphere. To the resulting mixture, an aqueous solution of H₂O₂ (30%, 12.2 mL) was added dropwise over 20 min period and it was allowed to stir for 24 hr at 22 °C. After 24 hrs of stirring, a voluminous
precipitate was formed, which was filtered and washed with hot ethanol (2 × 30 mL) and the resulting solid was dried under vacuum. Yield: 8.0 g, 74%, m.p: 120-122 °C, $^1$H NMR (CDCl$_3$, 400 MHz) δ: 8.03-8.08 (3H, m), 8.09-8.15 (1H, d, $J = 9.26$ Hz), 8.24-8.30 (2H, dd, $J = 8.20$ Hz), 8.43, 8.49 (1H, d, $J = 9.24$ Hz), 8.52-8.56 (1H, s). $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 120.6, 120.89, 125.25, 125.28, 126.06, 126.28, 126.37, 127.50, 127.58, 128.74, 129.56, 129.74, 130.48, 130.67, 130.76, 130.81.

Note that bromination of pyrene produced an isomeric mixture of dibrominated derivatives (i.e. syn and anti, see Scheme S1), which could be separated by recrystallization with difficulty and therefore the mixture was used as such for the next step.

**Synthesis of S1-2.** To the mixture of syn/anti dibromopyrene (S1-1) (6.0 g, 16.7 mmol) in dry THF (40 mL), PdCl$_2$(PPh$_3$)$_2$ (80 mg) and 1-octyne (5.50 g, 49.98 mmol) in NH(iPr)$_2$ (40 mL) and CuI (120 mg) were added in an oven dried Schlenk flask under argon atmosphere. The resulting mixture was stirred at 50°C for 12 hours. The resulting mixture was cooled to room temperature, and insoluble materials were removed by filtration and filtrate was washed with water and extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The resulting crude product was purified by flash column to afford mixture of cis and trans isomers (S1-2). Further separation of cis and trans isomers was accomplished by repeated recrystallizations from n-hxane to afford pure cis/trans isomers of S1-3. **Trans:** $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.95 (6H, m), 1.40 (8H, m), 1.60 (4H, m), 1.77 (4H, m), 2.65 (4H, t, $J = 7.05$ Hz), 8.04-8.11 (6H, s), 8.55 (2H, d, $J = 9.29$ Hz). $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 14.27, 20.10, 22.79, 28.93, 29.10,
**Synthesis of Pyrene**. The trans S1-3 (2.0 g) from above was placed into a Parr apparatus along with a stir bar and dissolved in 4:1 mixture of ethyl acetate/ethanol (25 mL). To this solution, 10% palladium on activated carbon catalyst (100 mg) was added. The vessel was then put under hydrogen pressure (3 bar) for 2 hours after which time the solution was filtered over a short pad of silica gel. The silica gel was washed with ethyl acetate (2 x 30 mL), the solvent was evaporated and the resulting 1,8-dioctanepyrene was purified by column chromatography using n-hexanes as a solvent. Yield: 2.0 g, 98%, m.p: 92-93 °C. \( ^1 \)H NMR (CDCl\(_3\), 400 MHz) \( \delta \): 0.88 (6H, m), 1.22-1.42 (16H, m), 1.47 (4H, m), 1.84 (4H, m), 3.32 (4H, m), 7.84 (2H, d, \( J = 7.82 \) Hz), 8.05 (2H, d, \( J = 9.32 \) Hz), 8.08 (2H, d, \( J = 7.82 \) Hz), 8.21 (2H, d, \( J = 9.32 \) Hz). \( ^{13} \)C NMR (CDCl\(_3\), 400 MHz) \( \delta \): 14.29, 22.84, 29.49, 29.74, 30.02, 32.07, 33.90, 122.69, 124.53, 127.31, 127.35, 128.99, 129.61, 137.18.
Scheme S2: Synthesis of Py$_2$

To a solution of Py$_1$ (0.1 g, 0.23 mmol) in anhydrous DCM (9 mL) was added methanesulfonic acid (1 mL) in an oven dried Schlenk flask under an argon atmosphere. Upon stirring color of the solution changed from red to purple to green. To the stirring solution was added DDQ (0.03 g, 0.12 mmol) and reaction mixture was stirred for another 30 minutes. The resulting reaction mixture was quenched by pouring onto the saturated aqueous NaHCO$_3$ solution (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with water and brine, dried over anhydrous MgSO$_4$, filtered and evaporated under vacuum to afford crude Py$_2$ which was purified by column chromatography using $n$-hexanes as an eluent (0.05 g, 98%), m.p: 110-111 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.79- 0.92 (12H, m), 1.17- 1.55 (40H, m), 1.72- 1.83 (4H, m), 1.89-1.99 (4H, m), 3.20- 3.28 (4H, m), 3.38- 3.45 (4H, m), 7.68 (2H, d, $J = 9.58$ Hz), 7.86 (2H, d, $J = 7.81$ Hz ), 7.99- 8.03 (4H, m), 8.14 (4H, d, $J = 8.91$ Hz), 8.35 (2H, d, $J = 9.29$ Hz). $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 14.24, 14.29, 22.79, 22.85, 29.44, 29.54, 29.73, 29.96, 30.08, 32.01, 32.05, 33.85, 122.77, 122.83, 124.82, 125.81, 125.87, 127.49, 128.60, 128.78, 128.86, 129.97, 130.30, 136.00, 136.53, 137.27.
**Synthesis of S3-1.** To the solution of 1,8-dioctylypyrene (Pyrene1) (0.6 g, 1.4 mmol) in CHCl₃ (40 mL) was added NBS (0.25 g, 1.4 mmol) and NH₄NO₃ (0.011 g, 0.14 mmol) in oven dried Schlenk flask under argon atmosphere and the resulting reaction mixture was allowed to stir at room temperature for overnight. Then the reaction mixture quenched with water (30 mL) and extracted with DCM (3 x 25 mL). The combined organic layers were dried over MgSO₄, filtered and evaporated under reduced pressure to give (S3-1) (0.6 g, 84.5%). ¹H NMR (CDCl₃, 400 MHz) δ: 0.87 (6H, m), 1.16-1.56 (20H, m), 1.83-
(4H, m), 3.29 (4H, m), 7.83 (1H, d, J = 7.76 Hz), 8.01-8.14 (3H, m), 8.17-8.27 (2H, m), 8.44 (1H, d, J = 9.44 Hz). $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 13.9, 22.5, 29.1, 29.3, 29.4, 29.6, 31.4, 31.7, 31.8, 33.2, 33.5, 119.2, 122.0, 123.8, 124.6, 124.9, 125.4, 126.5, 127.2, 127.4, 128.4, 129.3, 130.7, 137.4, 137.6.

**Synthesis of S3-2.** To the solution of pyrene1 (0.3 g, 0.703 mmol) in CHCl$_3$ (40 mL) was added NBS (0.25 g, 1.4 mmol) and NH$_4$NO$_3$ (0.011 g, 0.14 mmol) in oven dried Schlenk flask under argon atmosphere and the reaction mixture was allowed to stir at room temperature for overnight. Then the reaction was quenched by addition of water (30 ml) and it was extracted with DCM (3 x 20 mL). The combined organic layers were dried over MgSO$_4$, filtered and evaporated under reduced pressure to give S3-2 (0.3g, 73%), m.p: 98-100$^0$C. $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.88 (6H, m), 1.19-1.53 (20H, m), 1.82 (4H, m), 3.27 (4H, m), 8.12 (2H, s), 8.23 (2H, d, J = 9.54 Hz), 8.42 (2H, d, J = 9.54 Hz). $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 14.29, 22.84, 29.49, 29.74, 30.02, 32.07, 33.91, 122.70, 124.54, 127.32, 127.35, 128.99, 129.61, 137.19.

**Synthesis of S3-3.** To oven dried Schlenk flask under argon atmosphere, mixture of S1-1 (0.70 g, 1.38 mmol), Pd(dppf)Cl$_2$ (50 mg) in 1,4-Dioxane (30 mL), potassium acetate (0.34 g, 3.46 mmol) and bis(pinacolato) diboron (0.70 g, 2.77 mmol) were added and the resulting reaction mixture was allowed to reflux overnight. Then the reaction was quenched by addition of water (30 mL). It was then extracted with DCM (3 x 25 mL), dried over MgSO$_4$, filtered and evaporated under vacuum to yield crude
product. It was then subjected to column chromatography with hexane as solvent to give pure product \textbf{S3-3} (0.6 g, 78\%), m.p: 78-80^\circ C. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 0.89 (6H, m), 1.20-1.43 (20H, m), 1.49 (12H, m), 1.84 (4H, m), 3.32 (4H, m), 7.84 (1H, d, $J = 7.74$ Hz), 8.06 (2H, t, $J = 10.09$ Hz), 8.21 (1H, d, $J = 9.26$ Hz), 8.30 (1H, d, $J = 9.26$ Hz), 8.35 (1H, s), 9.11 (1H, d, $J = 7.51$ Hz). $^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$: 14.35, 22.91, 25.26, 29.56, 29.58, 29.80, 29.81, 30.13, 30.29, 32.14, 32.31, 32.37, 34.09, 34.11, 83.45, 122.77, 123.19, 124.87, 125.48, 125.64, 127.22, 127.92, 128.64, 128.68, 129.61, 131.50, 135.04, 135.35, 136.05, 137.74.

\textit{Synthesis of S3-4.} To an oven dried Schlenk flask under argon atmosphere, mixture of S1-2 (0.50 g, 0.86 mmol), Pd(dppf)Cl$_2$ (50 mg) in 1,4-Dioxane (30 mL), potassium acetate (0.25 g, 2.58 mmol) and \textit{bis(pinacolato)diboron} (0.48 g, 1.90 mmol) were added and the resulting reaction mixture was allowed to reflux overnight. And the reaction was quenched by addition of water (30 mL). It was then extracted with DCM (3 x 20 mL), dried over MgSO$_4$, filtered and evaporated under vacuum to yield crude product. It was then purified by column chromatography with hexane/ethyl acetate mixture as a solvent to give pure product \textbf{S1-4} (0.36 g, 63\%), m.p: 126-128^\circ C. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 0.88 (6H, m), 1.18-1.42 (20H, m), 1.48 (24H, m), 1.84 (4H, m), 3.32 (4H, m), 8.30 (2H, d, $J = 9.5$ Hz), 8.35 (2H, s), 9.11 (2H, d, $J = 9.5$ Hz). $^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$: 14.30, 22.85, 25.18, 29.53, 29.75, 30.29, 32.08, 32.49, 34.17, 83.91, 123.18, 125.39, 129.01, 130.99, 134.87, 135.11, 136.49.

\textit{Synthesis of Pyrene3.} The \textbf{S3-4} (0.6 g, 0.884 mmol) and \textbf{S3-1} (1.0 g, 1.94 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (60 mL) in an oven dried
Schlenk flask under an argon atmosphere and the flask was evacuated and filled with argon (3x). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (5.0 g) in water (20 mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3x). To the DME solution, Pd(PPh$_3$)$_4$ (50 mg) and the salt solution were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3x) after each addition. The flask was covered with foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 25 mL). The organic layer was dried over anhydrous magnesium sulfate, evaporated and dried under vacuum to afford crude product. The crude product was purified by column chromatography using a hexanes/ethyl acetate mixture to give the pure **Pyrene3** (0.45g, 40%), m.p: 146-148°C. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 0.77-0.92 (18H, m), 1.14-1.60 (60H, m), 1.75-2.03 (12H, m), 3.21-3.50 (12H, m), 7.70-7.80 (4H, m), 7.88 (2H, d), 8.02 (2H, s), 8.04-8.87 (4H, m), 8.13-8.19 (6H, m), 8.37 (2H, d). $^{13}$C NMR (CDCl$_3$, 400 MHz) $\delta$: 14.23, 14.25, 14.30, 22.79, 22.80, 22.87, 29.47, 29.48, 29.56, 29.65, 29.69, 29.76, 29.98, 30.02, 30.11, 31.98, 32.03, 32.07, 33.87, 33.90, 34.01, 122.80, 122.87, 124.86, 125.84, 125.91, 125.93, 126.04, 127.53, 128.63, 128.65, 128.82, 128.88, 128.95, 129.99, 130.33, 130.49, 136.10, 136.24, 136.27, 136.56, 136.60, 136.62, 137.31.

*Schemer S4: Synthesis of Pyrene4*
**Synthesis of S4-1.** To the solution of **pyrene2** (0.2 g, 0.24 mmol) in CHCl₃ (20 mL) was added NBS (0.08 g, 0.48 mmol) and NH₄NO₃ (0.02 g, 0.02 mmol) under argon and the resulting reaction mixture was allowed to stir at room temperature for overnight. Then the reaction was quenched by addition of water (30 mL) and it was extracted with DCM (3 x 20 mL). The combined organic layers were dried over MgSO₄, filtered and evaporated under reduced pressure to give crude product which was further purified by column chromatography using hexane and ethyl acetate mixture as eluent to afford pure S5-1 (0.15 g, 63%), m.p: 134-135°C. **¹H NMR (CDCl₃, 400 MHz)** δ: 0.76-0.90 (12H, m), 1.14-1.55 (40H, m), 1.70-1.81 (4H, m), 1.87-1.98 (4H, m), 3.15-3.22 (4H, m), 3.37-3.45 (4H, m), 7.65 (2H, d, J = 9.53 Hz), 7.96 (2H, d, J = 9.53 Hz), 8.00 (2H, s), 8.12 (2H, s), 8.44 (2H, d, J = 9.53 Hz), 8.52 (2H, d, J = 9.53 Hz). **¹³C NMR (CDCl₃, 400 MHz)** δ: 14.25, 14.29, 22.79, 22.85, 29.40, 29.53, 29.61, 29.71, 29.89, 30.06, 31.74, 31.99, 32.04,
Synthesis of Pyrene4. The S4-1 (0.35 g, 0.24 mmol) and S3-3 (0.34 g, 0.61 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (60 mL) in an oven dried Schlenk flask under an argon atmosphere and the flask was evacuated and filled with argon (3x). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (5.0 g) in water (20 mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3x). To the DME solution, Pd(PPh₃)₄ (50 mg) and the salt solution were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3x) after each addition. The flask was covered with foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 25 mL). The organic layer was dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The crude product was purified by column chromatography using a hexanes/ethyl acetate mixture to give the pure Pyrene4 (0.2 g, 40%), m.p: 162-164°C. ^1H NMR (CDCl₃, 400 MHz) δ: 0.77-0.94 (24H, m), 1.16-1.61 (80H, m), 1.74-2.06 (16H, m), 3.23-3.51 (16H, m), 7.70-7.92 (8H, m), 8.01-8.10 (8H, m), 8.14-8.21 (8H, m), 8.37 (2H, d). ^13C NMR (CDCl₃, 400 MHz) δ: 14.25, 14.30, 22.80, 22.87, 29.49, 29.56, 29.67, 29.76, 29.99, 30.04, 30.11, 32.00, 32.03, 32.07, 33.93, 34.01, 122.82, 124.87, 125.84, 125.91, 125.95, 126.05, 127.54, 128.65, 128.82, 128.89, 128.97, 128.98, 130.00, 130.34, 130.51, 136.10, 136.27, 136.30, 136.33, 136.35, 136.40, 136.58, 136.61, 136.65, 137.33.
**Scheme S5: Synthesis of Pyrene5**

*Synthesis of S5-1.* To the solution of pyrene\textsuperscript{3} (0.25 g, 0.2 mmol) in CHCl\textsubscript{3} (30 mL) was added NBS (0.07 g, 0.4 mmol) and NH\textsubscript{4}NO\textsubscript{3} (0.02 g, 0.02 mmol) under argon and the resulting reaction mixture was allowed to stir at room temperature for overnight. Then the reaction was quenched by addition of water (30 mL) and it was extracted with DCM (3 x 20 mL). The combined organic layers were dried over MgSO\textsubscript{4}, filtered and evaporated under reduced pressure to give crude product which was further purified by column chromatography using hexane and ethyl acetate mixture as eluent to afford pure S5-1 (0.35 g, 77%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) δ: 0.72-0.94 (18H, m), 1.10-1.60 (60H, m), 1.70-2.03 (12H, m), 3.14-3.51 (12H, m), 7.73 (4H, d), 7.95-8.17 (10H, m), 8.43-8.57
(4H, m). $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 14.25, 14.31, 22.80, 22.87, 29.43, 29.48, 29.55, 29.65, 29.75, 29.93, 30.03, 30.09, 31.78, 31.99, 32.02, 32.07, 32.15, 33.56, 33.90, 33.98, 119.90, 122.62, 122.65, 123.00, 124.37, 125.38, 125.89, 126.00, 126.03, 126.13, 126.14, 126.16, 127.18, 128.40, 128.55, 128.67, 128.70, 128.81, 128.93, 130.47, 130.95, 131.39, 136.01, 136.73, 136.92, 137.25, 137.30, 138.13, 138.14.

**Synthesis of Pyrene5.** The S5-1 (0.3 g, 0.3 mmol) and S3-3 (0.41 g, 0.74 mmol) were dissolved in anhydrous 1,2-dimethoxyethane (DME) (60 mL) in an oven dried Schlenk flask under an argon atmosphere and the flask was evacuated and filled with argon (3x). In another oven dried Schlenk flask a solution of anhydrous sodium carbonate (5.0 g) in water (20 mL) was prepared under an argon atmosphere and the flask was also evacuated and filled with argon (3x). To the DME solution, Pd(PPh$_3$)$_4$ (50 mg) and the salt solution were added sequentially under a strict argon atmosphere followed by evacuation and filling the flask with argon (3x) after each addition. The flask was covered with foil and the solution was allowed to reflux overnight. The resulting solution was cooled to room temperature, quenched with water (50 mL) and extracted with dichloromethane (3 x 25 mL). The organic layer was dried over anhydrous magnesium sulfate, evaporated and dried under vacuum. The crude product was purified by column chromatography using a hexanes/ethyl acetate mixture to give the pure Pyrene5 (0.09 g, 30%), m.p: 198-200°C. $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.73-0.94 (30H, m), 1.09-1.61 (100H, m), 1.70-2.07 (20H, m), 3.19-3.53 (20H, m), 7.68-7.78 (4H, m), 7.84-7.91 (4H, m), 7.99-8.20 (20H, m), 8.33-8.41 (4H, m). $^{13}$C NMR (CDCl$_3$, 400 MHz) δ: 14.25, 14.30, 22.81, 22.87, 29.51, 29.56, 29.69, 29.76, 30.00, 30.06, 30.12, 32.01, 32.07, 33.96, 122.83, 122.85, 122.89, 122.90, 122.92, 122.94, 124.88,125.85,125.91, 125.97,125.98, 126.02,
126.07, 127.55, 128.66, 128.83, 128.90, 128.97, 129.01, 130.01, 130.36, 130.52, 136.11,
136.36 (broad), 136.60, 136.63, 136.63, 136.67, 136.69, 136.70, 137.35.
NMR Spectroscopy

$^1$H NMR spectrum of S1-1(anti) and S1-1(syn) in CDCl$_3$

$^{13}$C NMR spectrum of S1-1(anti) and S1-1(syn) in CDCl$_3$
$^1$H NMR spectrum of S1-1(syn) in CDCl$_3$

$^1$H NMR spectrum of S1-1(anti) in CDCl$_3$
$^1$H NMR spectrum of S1-2 (syn) in CDCl$_3$
$^1$H NMR spectrum of S1-2 (anti) in CDCl$_3$

$^1$H NMR spectrum of Py1 in CDCl$_3$
$^{13}$C NMR spectrum of Py1 in CDCl$_3$
$^1$H NMR spectrum of Py2 in CDCl$_3$

$^{13}$C NMR spectrum of Py2 in CDCl$_3$
$^1$H NMR spectrum of S3-1 in CDCl$_3$

$^{13}$C NMR spectrum of S3-1 in CDCl$_3$
\(^1\text{H NMR spectrum of S3-2 in CDCl}_3\)
$^{13}$C NMR spectrum of S3-2 in CDCl₃

$^1$H NMR spectrum of S3-3 in CDCl₃
$^{13}$C NMR spectrum of S3-3 in CDCl$_3$

$^1$H NMR spectrum of S3-4 in CDCl$_3$
$^{13}$C NMR spectrum of S3-4 in CDCl$_3$
$^1$H NMR spectrum of Py3 in CDCl$_3$

$^{13}$C NMR spectrum of Py3 in CDCl$_3$
$^1$H NMR spectrum of S4-1 in CDCl$_3$

$^{13}$C NMR spectrum of S4-1 in CDCl$_3$
$^1$H NMR spectrum of Py4 in CDCl$_3$

$^{13}$C NMR spectrum of Py4 in CDCl$_3$
$^1$H NMR spectrum of S5-1 in CDCl$_3$
$^{13}$C NMR spectrum of S5-1 in CDCl$_3$

[H NMR spectrum of Py5 in CDCl$_3$]
$^{13}$C NMR spectrum of Py5 in CDCl$_3$
Figure S12. MALDI spectra of Py$_n$
**X-ray crystallography**

Figure S13. Crystal structure of Py₁

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\item γ/° \hspace{1cm} 90.00
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\item F(000) \hspace{1cm} 936.0
\item Crystal size/mm\textsuperscript{3} \hspace{1cm} 0.7503 \times 0.1022 \times 0.0544
\item Radiation \hspace{1cm} CuKα (λ = 1.54184)
\item 2θ range for data collection/° \hspace{1cm} 9.92 to 148.32
\item Index ranges \hspace{1cm} -9 \leq h \leq 9, -42 \leq k \leq 42, -11 \leq l \leq 10
\item Reflections collected \hspace{1cm} 23509
\item Independent reflections \hspace{1cm} 4912 [R\textsubscript{int} = 0.0337, R\textsubscript{sigma} = 0.0216]
\item Data/restraints/parameters \hspace{1cm} 4912/0/292
\item Goodness-of-fit on F\textsuperscript{2} \hspace{1cm} 1.071
\item Final R indexes [I>=2σ(I)] \hspace{1cm} R\textsubscript{1} = 0.0403, wR\textsubscript{2} = 0.1106
\item Final R indexes [all data] \hspace{1cm} R\textsubscript{1} = 0.0504, wR\textsubscript{2} = 0.1201
\item Largest diff. peak/hole / e Å\textsuperscript{-3} \hspace{1cm} 0.28/-0.20
\end{itemize}
Figure S14. Crystal structure of \( m \)-Py\(_2\).

Table S3. Crystal data and structure refinement for raj27p.

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Z & \quad 4 \\
\rho_{\text{calc}} \text{g/cm}^3 & \quad 1.109 \\
\mu/\text{mm}^{-1} & \quad 0.456 \\
F(000) & \quad 1864.0 \\
\text{Crystal size/mm}^3 & \quad 0.1 \times 0.05 \times 0.03 \\
\text{Radiation} & \quad \text{CuKα (λ = 1.54184)} \\
2θ \text{ range for data collection/°} & \quad 10.08 \text{ to } 148.38 \\
\text{Index ranges} & \quad -20 \leq h \leq 20, \ -11 \leq k \leq 11, \ -38 \leq l \leq 43 \\
\text{Reflections collected} & \quad 23202 \\
\text{Independent reflections} & \quad 5118 \ [R_{\text{int}} = 0.0379, R_{\text{sigma}} = 0.0267] \\
\text{Data/restraints/parameters} & \quad 5118/0/291 \\
\text{Goodness-of-fit on } F^2 & \quad 1.023 \\
\text{Final R indexes [I≥2σ (I)]} & \quad R_1 = 0.0542, \ wR_2 = 0.1530 \\
\text{Final R indexes [all data]} & \quad R_1 = 0.0832, \ wR_2 = 0.1822 \\
\text{Largest diff. peak/hole / e Å}^{-3} & \quad 0.26/-0.19
\end{align*}
\]
Electrochemistry

Figure S15. Plot of the Experimental first (red), second (green), third (blue), forth (orange) and fifth (cyan) oxidation potentials (V vs Fc/Fc') of Py\textsubscript{n} \textit{(n = 1-5)} against \(\cos(\pi/(n+1))\) trend.

Table S4. Experimental first, second, third, forth and fifth oxidation potentials (V vs Fc/Fc') of Py\textsubscript{n} \textit{(n = 1-5)}.

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<th>(n)</th>
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Table S5. Comparison of the oxidation potentials.

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<td>0.91</td>
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<td>-100</td>
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</table>
S4. Generation of Py$_n$$^{++}$ by redox titrations

The reproducible spectra of cation radicals of Py$_n$ in CH$_2$Cl$_2$ at 22 °C were obtained by quantitative redox titrations using three different aromatic oxidants, i.e. THEO$^{++}$SbCl$_6^-$ ($E_{\text{red1}} = 0.67$ V vs Fc/Fc$^+$, $\lambda_{\text{max}} = 518$ nm, $\varepsilon_{\text{max}} = 7300$ cm$^{-1}$ M$^{-1}$), NAP$^{++}$SbCl$_6^-$ ($E_{\text{red1}} = 0.94$ V vs Fc/Fc$^+$, $\lambda_{\text{max}} = 672$ nm, $\varepsilon_{\text{max}} = 9300$ cm$^{-1}$ M$^{-1}$)$^2$ and ANT$^{++}$ ($E_{\text{red1}} = 0.53$ V vs Fc/Fc$^+$, $\lambda_{\text{max}} = 744$ nm, $\varepsilon_{\text{max}} = 23400$ cm$^{-1}$ M$^{-1}$) obtained via redox titration with NAP$^{++}$.

Figure S16. Chemical structures and names of three aromatic oxidants used in redox titrations.

Each redox titration experiment was carried out by an incremental addition of sub-stoichiometric amounts of electron donor (Py$_n$) to the solution of an oxidant cation radical (Ox$^{++}$). The 1-e$^-$ oxidation of Py$_n$ to Py$_n$$^{++}$ and reduction of Ox$^{++}$ to Ox can be described by an equilibrium shown in eq. 1.

$$\text{Ox}^{++} + \text{Py}_n \rightleftharpoons \text{Ox} + \text{Py}_n^{++} \quad \text{(eq. 1)}$$

The redox titrations with two successive 1-e$^-$ oxidations involve multiple equilibria: one- and two-electron redox reactions between the donor and oxidant (eqs. 2 and 3) and comproportionation/disproportionation of D$^{2+}$/D$^{++}$ (eq. 4).

$$\text{Ox}^{++} + \text{D} \rightleftharpoons K_1 \text{Ox} + \text{D}^{++} \quad \text{(eq. 2)}$$

$$\text{Ox}^{++} + \text{D}^{++} \rightleftharpoons K_2 \text{Ox} + \text{D}^{2+} \quad \text{(eq. 3)}$$

$$\text{D}^{2+} + \text{D} \rightleftharpoons K_3 2\text{D}^{++} \quad \text{(eq. 4)}$$
Numerical deconvolution of the absorption spectrum at each increment (Figures SX-SX, left) produced mole fractions of each species ($\text{Ox}^{\cdot\cdot}$ and $\text{Py}_n^{\cdot\cdot}$ and/or $\text{Py}_n^{2\cdot}$) against the added equivalents of $\text{Py}_n$ (Figures SY-SY, right), confirming a 1:1 stoichiometry of each redox reaction. The experimental points of mole fraction vs equivalent of added donor $\text{Py}_n$ were fitted by varying $\Delta G_1 (= E_{\text{Py}_n}^{\text{ox1}} - E_{\text{red}}^{\text{ox}^{\cdot\cdot}})$ and $\Delta G_{12} (= E_{\text{Py}_n}^{\text{ox2}} - E_{\text{ox1}}^{\text{Py}_n})$.5,6
Table 6. Values of $\Delta G_1$ and $\Delta G_{12}$ obtained by fitting to the experimental mole fraction plots (Figures SX-SY).^5,6

<table>
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<tr>
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<th>THEO$^{\ast\ast}$+Py$_n$</th>
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</tr>
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<td>-9</td>
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<td>--</td>
</tr>
<tr>
<td>5</td>
<td>-22</td>
<td>-131</td>
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</tr>
</tbody>
</table>

Figure S17. Left: Spectral changes observed upon the reduction of 0.038 mM NAP$^{\ast\ast}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 2.38 mM solution of ANT in CH$_2$Cl$_2$. Right: Plot of the mole fractions of NAP$^{\ast\ast}$ (red) and ANT$^{\ast\ast}$ (black) against the added equivalents of ANT. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using $\Delta G_1 = -1.3$ eV.

Figure S18. Left: Spectral changes observed upon the reduction of 0.012 mM THEO$^{\ast\ast}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 1.45 mM solution of Py$_1$ in CH$_2$Cl$_2$. Right: Plot of the mole fractions of THEO$^{\ast\ast}$ (red) and Py$_1^{\ast\ast}$ (black) against the added equivalents.
equivalents of Py. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using $\Delta G_1 = 30$ meV.

Figure S19. Left: Spectral changes observed upon the reduction of 0.031 mM THEO$^{++}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 0.86 mM solution of Py$_2$ in CH$_2$Cl$_2$. Right: Plot of the mole fractions of THEO$^{++}$ (red) and Py$_2^{++}$ (black) against the added equivalents of Py$_2$. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using $\Delta G_1 = -116$ meV.

Figure S20. Left: Spectral changes observed upon the reduction of 0.029 mM THEO$^{++}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 0.76 mM solution of Py$_3$ in CH$_2$Cl$_2$. Right: Plot of the mole fractions of THEO$^{++}$ (red) and Py$_3^{++}$ (black) against the added equivalents of Py$_3$. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using $\Delta G_1 = -146$ meV.

Figure S21. Left: Spectral changes observed upon the reduction of 0.035 mM THEO$^{++}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 0.48 mM solution of Py$_4$ in CH$_2$Cl$_2$. 

THEO$^{++}$

THEO$^{++}$

THEO$^{++}$

THEO$^{++}$
Right: Plot of the mole fractions of THEO°° (red) and Py₄°° (black) against the added equivalents of Py₄. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using $\Delta G_1 = -144$ meV.

Figure S22. Left: Spectral changes observed upon the reduction of 0.022 mM THEO°° in CH₂Cl₂ (3 mL) by addition of 15-µL increments of 0.41 mM solution of Py₅ in CH₂Cl₂. Right: Plot of the mole fractions of THEO°° (red) and Py₅°° (black) against the added equivalents of Py₅. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using $\Delta G_1 = -131$ meV.

Figure S23. Left: Spectral changes observed upon the reduction of 0.0097 mM NAP°° in CH₂Cl₂ (3 mL) by addition of 15-µL increments of 2.23 mM solution of Py₁ in CH₂Cl₂. Right: Plot of the mole fractions of NAP°° (red) and Py₁°° (black) against the added equivalents of Py₁. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using $\Delta G_1 = -176$ meV.
Figure S24. Left: Spectral changes observed upon the reduction of 0.041 mM NAP\(^{2+}\) in CH\(_2\)Cl\(_2\) (3 mL) by addition of 15-µL increments of 1.39 mM solution of Py\(_2\) in CH\(_2\)Cl\(_2\). Right: Plot of the mole fractions of NAP\(^{2+}\) (red), Py\(_2\)\(^{2+}\) (black) and Py\(_2\)\(^{2+}\) (blue) against the added equivalents of Py\(_2\). Symbols represent experimental points, while the solid lines show best-fit to the experimental points using \(\Delta G_1 = -253\) meV and \(\Delta G_{12} = 229\) meV.

Figure S25. Left: Spectral changes observed upon the reduction of 0.033 mM NAP\(^{2+}\) in CH\(_2\)Cl\(_2\) (3 mL) by addition of 15-µL increments of 1.18 mM solution of Py\(_3\) in CH\(_2\)Cl\(_2\). Right: Plot of the mole fractions of NAP\(^{2+}\) (red), Py\(_3\)\(^{2+}\) (black) and Py\(_3\)\(^{2+}\) (blue) against the added equivalents of Py\(_3\). Symbols represent experimental points, while the solid lines show best-fit to the experimental points using \(\Delta G_1 = -266\) meV and \(\Delta G_{12} = 169\) meV.

Figure S26. Left: Spectral changes observed upon the reduction of 0.028 mM NAP\(^{2+}\) in CH\(_2\)Cl\(_2\) (3 mL) by addition of 15-µL increments of 0.60 mM solution of Py\(_4\) in CH\(_2\)Cl\(_2\). Right: Spectral changes observed upon the reduction of 0.032 mM NAP\(^{2+}\) in CH\(_2\)Cl\(_2\) (3 mL) by addition of 15-µL increments of 0.53 mM solution of Py\(_5\) in CH\(_2\)Cl\(_2\).
Figure S27. Left: Spectral changes observed upon the reduction of 0.036 mM ANT$^{+•}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 1.78 mM solution of Py$_1$ in CH$_2$Cl$_2$. Right: Plot of the mole fractions of ANT$^{+•}$ (red) and Py$_1$$^{+•}$ (black) against the added equivalents of Py$_1$. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using $\Delta G_1 = 65$ mV.

Figure S28. Left: Spectral changes observed upon the reduction of 0.028 mM ANT$^{+•}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 1.14 mM solution of Py$_2$ in CH$_2$Cl$_2$. Right: Plot of the mole fractions of ANT$^{+•}$ (red) and Py$_2$$^{+•}$ (black) against the added equivalents of Py$_1$. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using $\Delta G_1 = 26$ mV.

Figure S29. Left: Spectral changes observed upon the reduction of 0.029 mM ANT$^{+•}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 0.74 mM solution of Py$_3$ in CH$_2$Cl$_2$. Right: Plot of the mole fractions of ANT$^{+•}$ (red) and Py$_3$$^{+•}$ (black) against the added
equivalents of Py₃. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using ΔG₁ = -4 mV.

Figure S30. Left: Spectral changes observed upon the reduction of 0.046 mM ANT⁺⁺ in CH₂Cl₂ (3 mL) by addition of 15-µL increments of 0.44 mM solution of Py₄ in CH₂Cl₂. Right: Plot of the mole fractions of ANT⁺⁺ (red) and Py₄⁺⁺ (black) against the added equivalents of Py₄. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using ΔG₁ = -9 mV.

Figure S31. Left: Spectral changes observed upon the reduction of 0.035 mM ANT⁺⁺ in CH₂Cl₂ (3 mL) by addition of 15-µL increments of 0.26 mM solution of Py₅ in CH₂Cl₂. Right: Plot of the mole fractions of ANT⁺⁺ (red) and Py₅⁺⁺ (black) against the added equivalents of Py₅. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using ΔG₁ = -22 mV.
Figure S32. Left: Spectral changes observed upon the reduction of 0.024 mM THEO⁺⁺ in CH₂Cl₂ (3 mL) by addition of 15-µL increments of 0.30 mM solution of bipyrene in CH₂Cl₂. Right: Plot of the mole fractions of THEO⁺⁺ (red) and bipyrene cation radical (black) against the added equivalents of bipyrene. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using ΔG₁ = 89 mV.

Figure S33. Left: Spectral changes observed upon the reduction of 0.023 mM THEO⁺⁺ in CH₂Cl₂ (3 mL) by addition of 15-µL increments of 0.18 mM solution of trimethyl-Py₂ in CH₂Cl₂. Right: Plot of the mole fractions of THEO⁺⁺ (red) and trimethyl-Py₂⁺ (black) against the added equivalents of trimethyl-Py₂. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using ΔG₁ = -160 mV.
Figure S34. A (left): Spectral changes observed upon the reduction of 0.048 mM THEO$^{+•}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 0.96 mM solution of triisopropyl-Py$_2$ in CH$_2$Cl$_2$. A (right): Plot of the mole fractions of THEO$^{+•}$ (red) and triisopropyl-Py$_2^{+•}$ (black) against the added equivalents of triisopropyl-Py$_2$. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using $\Delta G_1 = -176$ mV. B (left): Spectral changes observed upon the reduction of 0.025 mM NAP$^{+•}$ in CH$_2$Cl$_2$ (3 mL) by addition of 15-µL increments of 0.69 mM solution of triisopropyl-Py$_2$ in CH$_2$Cl$_2$. B (right): Plot of the mole fractions of NAP$^{+•}$ (red) and triisopropyl-Py$_2^{+•}$ (black) and triisopropyl-Py$_2^{2+}$ (blue) against the added equivalents of triisopropyl-Py$_2$. Symbols represent experimental points, while the solid lines show best-fit to the experimental points using $\Delta G_1 = -368$ mV and $\Delta G_{12} = 285$ mV.

Density functional theory calculations
Computational details
The electronic structure calculations were performed using density functional theory (DFT) as implemented in Gaussian 09 package, revision D.01. We used B1LYP-40/6-31G(d) level of theory with 40% contribution of the Hartree-Fock exchange term that was previously benchmarked against experimental data. Solvent effects were included using the implicit integral equation formalism polarizable continuum model (IEF-PCM) with dichloromethane solvent parameters ($\varepsilon = 8.93$). In all DFT
calculations, ultrafine Lebedev’s grid was used with 99 radial shells per atom and 590 angular points in each shell. Tight cutoffs on forces and atomic displacement were used to determine convergence in geometry optimization procedure. Harmonic vibrational frequency calculations were performed for the optimized Py\textsubscript{n}/Py\textsubscript{n}\textsuperscript{+•} (n = 1-4) structures to confirm absence of imaginary frequencies. The transition state of Py\textsubscript{n}\textsuperscript{+•} was confirmed by the presence of single imaginary frequency (i549.6) and IRC calculations\textsuperscript{20} that led to expected structures.

For cation radicals, wavefunction stability tests\textsuperscript{21} were performed to ensure absence of solutions with lower energy. The values of \( <S^2> \) operator after spin annihilation were confirmed to be close to the expectation value of 0.75. Unpaired spin density surface were obtained using isovalue of 0.001 a.u. Atomic charges were calculated using Natural Population Analysis approach.\textsuperscript{22,23} Calculations of the first excited state of Py\textsubscript{n} and Py\textsubscript{n}\textsuperscript{+•} were performed using the time-dependent density functional theory (TD-DFT) method.\textsuperscript{24-28}
Table S7. Energies (E_{ox1}) and oscillator strength (f_{osc}) of S_0->S_1 transitions, oxidation energies (E_{ox1}) of Py_n, energies (\cdot) and oscillator strengths (f_{osc}) of D_0->D_1 transitions in Py_n^+ calculated using (TD) B1LYP-40/6-31G(d)+PCM(CH_2Cl_2).

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<th>Py_n^+ absorption D_0&gt;D_1</th>
<th>E_{ox1}, eV</th>
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<td>\lambda, nm</td>
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Figure S35. Plots of S_0->S_1 excitation energies of Py_n (A), D_0->D_1 excitation energies of Py_n^+ (B; blue: DFT, black: experiment) and first oxidation energies E_{ox1} of Py_n against cos[(n+1)] trend calculated using (TD) B1LYP-40/6-31G(d)+PCM(CH_2Cl_2) level of theory.
Figure S36. Oscillators strengths ($f_{osc}$) of $S_0 \rightarrow S_1$ transitions in Py$_n$, $n = 1$-6 (A) and D$_0$-$D_1$ transitions in Py$_n^{+\ast}$, $n = 1$-7 (B).

Figure S37. Correlation plot between experimental first oxidation potential $E_{ox1}$ (V vs Fc/Fc$^+$) and first oxidation energies $E_{ox1}$ (eV) calculated at B1LYP-40/6-31G(d)+PCM(CH$_2$Cl$_2$) level of theory.
Figure 38. Per-unit barplot representations of HOMOs of neutral Pyₙ, NPA spin densities and charges of Pyₙ⁺ in ground state.

Table 8. Comparison of the oxidation-induced bond length changes in the tetraisopropylpyrene obtained from X-ray crystallography and from calculations using B1LYP-40/6-31G(d)+PCM(CH₂Cl₂).[^1]

<table>
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<th>Δ X-Ray, pm</th>
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<td>b</td>
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</tr>
<tr>
<td>c</td>
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</tr>
<tr>
<td>d</td>
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<tr>
<td>e</td>
<td>142.6</td>
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<tr>
<td>f</td>
<td>143.8</td>
<td>142.5</td>
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</tr>
</tbody>
</table>
Figure 39. Distribution of the oxidation-induced bond lengths and dihedral angle changes in Py<sub>n</sub>/Py<sub>n</sub>+• calculated using B1LYP-40/6-31G(d)+PCM(CH<sub>2</sub>Cl<sub>2</sub>).

*p*-Py<sub>n</sub> in neutral and cation radical states

**Table S9.** Energies (●) and oscillator strength (f<sub>osc</sub>) of S<sub>0</sub>→S<sub>1</sub> transitions, oxidation energies (E<sub>ox1</sub>) of para-Py<sub>n</sub>, energies (●) and oscillator strengths (f<sub>osc</sub>) of D<sub>0</sub>→D<sub>1</sub> transitions in para-Py<sub>n</sub>+• calculated using (TD) B1LYP-40/6-31G(d)+PCM(CH<sub>2</sub>Cl<sub>2</sub>). Note that para-Py<sub>1</sub> is identical to Py<sub>1</sub>.
### Table

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<th>$\text{para-Py}_n^{\ast}$ absorption $D_0 \rightarrow D_1$</th>
<th>$E_{\text{ox1}}, \text{ eV}$</th>
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<tr>
<td>5</td>
<td>3.60 eV, 344 nm, 4.381 f_{osc}</td>
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### Figure S40

Figure S40. Comparisons of the evolutions of the $S_0 \rightarrow S_1$ transition energies in $p$-Py$_n$ and $m$-Py$_n$ against $\cos[\pi/(n+1)]$ (A) and $1/n$ (B) trends calculated using TD-B1LYP-40/6-31G(d)+PCM(CH$_2$Cl$_2$).
Figure S41. Isovalue plots of HOMOs (0.03 au) of neutral para-Py\textsubscript{n} and spin-densities (0.001 au) of para-Py\textsubscript{n}^+ calculated using B1LYP-40/6-31G(d)+PCM(CH\textsubscript{2}Cl\textsubscript{2}).

**Application of the multistate model**

From the scan in two-state model:

F2, Hab = 0.60 eV, l = 0.33

\[ y = 1.00 \cos(\theta) + 0.25 \]

m-Py2, Hab = 0.30 eV, l = 0.56 eV

\[ y = 1.01 \cos(\theta) + 0.06 \]

Complete oxidation of the pyrene unit with coordinate \( x_i \) leads to the structural distortions of this unit and accumulation of the negative charge from the solvent around the unit. Then, with the geometry of the wire and solvent arrangement being fixed, a variation of the reaction coordinate \( x \) in the vicinity of the reorganized unit leads to the quadratic increase in energy, while at a larger separation distance (i.e. \( x - x_i \)) the energy reaches a finite value following the Coulomb law of the electrostatic interaction.\textsuperscript{30} Accordingly, the diabatic state \( H_i(x) \) can be represented as a bell-shaped continuous
function of the charge coordinate $x$ using the composite quadratic/reciprocal dependence:\textsuperscript{30}

$$H_i(x) = \begin{cases} 
\lambda (x - x_i)^2, & \text{if } |x - x_i| \leq t \\
\lambda^\infty - a/|x - x_i|, & \text{if } |x - x_i| \geq t
\end{cases}$$

where $\lambda$ is the structural reorganization, $\lambda^\infty$ is the energy of the completely separated hole and reorganization, parameters $t = \sqrt{\lambda^\infty/3\lambda}$ and $a = 2\lambda t^3$ are defined by the continuity of $H_i(x)$ and its first derivative. Parameter $t$ defines a separation distance after which the interaction mechanism switches from the short-range to the long-range interaction.

The Hamiltonian matrix can be represented as:

$$
\mathbf{H}(x) = \begin{bmatrix}
H_1(x) & H_{ab} & \cdots & 0 & 0 \\
H_{ab} & H_2(x) & \cdots & 0 & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & \cdots & H_{n-1}(x) & H_{ab} \\
0 & 0 & \cdots & H_{ab} & H_n(x)
\end{bmatrix}
$$

Numerical diagonalization of the Hamiltonian matrix $\mathbf{H}(x)$ for each $x$ results in the adiabatic potential energy surface with the lowest-energy surface $G_0(x)$ corresponding to the ground state of $\text{Py}_n^{++}$. The minimum on the ground state surface $G_0(x)$ defines the position $x_{\text{min}}$ of the center of the hole distribution and the energy at this point $G_0(x_{\text{min}})$ directly corresponds to the oxidation potential $E_{\text{ox}1}$ of $\text{Py}_n$. The difference between two lowest energies at point $x_{\text{min}}$ provides the vertical excitation energy, i.e. $\Delta G(x_{\text{min}}) = G_1(x_{\text{min}}) - G_0(x_{\text{min}})$. 
Figure 42. A: Plot of excitation energies of $m$-Py$_n^{++}$ and F$_n^{++}$ from MSM. B: Barplot representation of the hole of $m$-Py$_n^{++}$ and F$_n^{++}$ in the ground and vertically excited state from MSM.

Disclaimer: The results discussed in this chapter was further supplemented by DFT calculations and by a recently developed multistate parabolic model and a modifies Huckel theory by my coworkers Drs. Marat R Talipov and Maxim V. Ivanov.
References


(7)


CHAPTER 5

Quantitative Generation of Cation Radicals and Dications Using Aromatic Oxidants: Effect of Added Electrolyte on the Redox Potentials of Aromatic Electron Donors

Introduction

Redox titrations using robust aromatic oxidants allow for a quantitative analysis of redox and optical properties of organic electron donors in their oxidized states. Unlike spectro electrochemistry, redox titrations can be performed without added electrolyte in relatively nonpolar solvents, affording quick access to the redox and optical properties of a given electron donor without the need of a complex electrochemical setup. However, the redox potentials obtained by the two methods are not the same. To establish the direction and magnitude of this discrepancy, we have performed a systematic case study using a set of cycloannulated compounds, tetraarylethylene donors and a tetra substituted hydroquinone ether cation radical (THEO$^{+}$) as a stable aromatic oxidant. We show that redox potentials (especially second and higher oxidation potentials) measured by electrochemical methods are systematically lower compared to the redox potentials obtained by redox titrations in the absence of electrolyte, because of the enhanced stabilization of dications and polycations by electrolyte. We have also uncovered that the smaller cation radicals (e.g. a para- or ortho-hydroquinone ether cation radicals) are much more effectively stabilized when compared with the cation radicals in which charge is
delocalized over larger area (e.g. tetraarylethylene cation radicals) in the presence of electrolyte due to increased ionic strength of the solution.

A quantitative oxidation of organic electron donors (D) to the corresponding cation radicals $D^{+•}$ and dications $D^{2+}$ can be accomplished by electrochemical methods, i.e. coulometry. The electronic absorption spectra of $D^{+•}$ and $D^{2+}$ can be obtained by spectroelectrochemistry, where the redox and optical properties are measured simultaneously. However, electrochemical generation of $D^{+•}$ and $D^{2+}$ can be tedious not only because of the availability of necessary instrumentation, but also due to the necessary presence of large quantity of electrolyte in the solution. In our laboratory, we generally make use of the redox titrations using aromatic oxidants and mildly polar organic solvents (e.g. CH$_2$Cl$_2$), without added electrolyte, for the spectroscopic characterizations of $D^{+•}$ and $D^{2+}$. Importantly, such redox titrations allow one to quickly ascertain not only the optical properties of $D^{+•}$ and $D^{2+}$ but may also provide the estimates of redox potentials without the need of a complex electrochemical setup. It is noteworthy that characterizations of redox centers in proteins involved in biochemical transformations invariably make use of redox titrations in water containing ample electrolyte. In the absence of electrolyte, oxidized states of D are expected to be less stabilized as compared to electrochemical conditions and/or in the biochemical transformations in water due to the reduced ionic strength and possibly lack of specific ion-pairing interactions. To examine the effect of electrolyte on the redox potentials derived from titration vs. electrochemical methods, we undertook a systematic case study using a set of cyclo annulated compounds and tetraarylethylene donors and a tetra substituted hydroquinone ether cation radical, THE-Orange$^{+•}$ or THEO$^{+•}$, as a
stable aromatic oxidant (Figure 5.1). We demonstrate that redox titrations in the absence of electrolyte show significantly increased redox potentials of a donor (D) when compared to the corresponding electrochemical potentials in the presence of an electrolyte. A detailed description of the method and models utilized for the analyses of the redox titrations in dichloromethane using electronic spectroscopy is presented in order to systematically evaluate the effect of added electrolyte in various redox equilibria involving cation radicals and dications.\[18\]

**Results and discussion**

The choice of tetraarylethylene donors in Figure 5.1A stems from the fact that they form stable cation radicals and dications which can be isolated and characterized by X-ray crystallography.\[14\] Furthermore, these donors undergo reversible electrochemical oxidations (TTE: $E_{ox1} = 0.67$, $E_{ox2} = 0.93$; DAE: $E_{ox1} = 0.51$, $E_{ox2} = 0.65$; TAE: $E_{ox1} = 0.40$, $E_{ox2} = 0.51$ V vs Fc/Fc$^+$) and the difference between the second and first oxidation potentials (i.e. $E_{ox2} - E_{ox1}$) varied from 0.26 (TTE) to 0.14 (DAE) to 0.11 (TAE) V. Selection of THEO$^{\text{ox}^+}$ as an oxidant (Figure 13C, $E_{red}^{\text{ox}^+} = 0.67$ V vs Fc/Fc$^+$) arose from the fact that it can oxidize TTE only to its cation radical ( $\Delta G_1 = 0$ and $\Delta G_2 = +0.26$V) while it can oxidize DAE ( $\Delta G_1 = -0.16$ and $\Delta G_2 = -0.02$V) or TAE ( $\Delta G_1 = -0.27$ and $\Delta G_2 = -0.16$) to both its cation radical and dication based on the $\Delta G$ values assessed from the electrochemical redox potentials (Figure 5.1B).
Figure 5.1. Structures (A) and cyclic voltammograms (B) of 5 mM tetraarylethylenes TAE, DAE, and TTE (as indicated) in dichloromethane containing 0.2 M tetrabutylammonium hexafluorophosphate at a scan rate of $v = 200$ mV s$^{-1}$ (22°C).

Theoretical Analysis of One-electron Oxidation Chemical Equilibria.

A typical redox titration experiment can be carried out by an incremental addition of sub-stoichiometric amounts of electron donor (D) to the solution of an oxidant cation radical (Ox$^{••}$), which leads to a partial oxidation of D to D$^{••}$ and reduction of Ox$^{••}$ to Ox and establishes an equilibrium shown in eq. 1:

$$\text{Ox}^{••} + \text{D} \rightleftharpoons \text{Ox} + \text{D}^{••} \quad (\text{eq. 1})$$
\[ K = \frac{[D^{++}][Ox]}{[D][Ox^{++}]} \]

\[ \Delta G = -RT \ln K \]

\[ \Delta G = E_{ox}^{D} - E_{ox}^{0} \]

\[ [Ox^{++}] + [Ox] = c_{0}^{ox^{++}} \quad \text{eq. 3} \]

\[ [D^{++}] + [D] = c_{0}^{D} \quad \text{eq. 4} \]

\[ [Ox^{++}] + [D^{++}] = c_{0}^{ox^{++}} \quad \text{eq. 5} \]

\[ [D^{+}] = c_{0}^{Ox^{+}} - [Ox^{+}] \]

\[ [Ox] = c_{0}^{Ox^{+}} - [Ox^{+}] \quad \text{(note that } [Ox] = [D^{+}] \text{)} \]

\[ [D] = c_{0}^{(D)} - [D^{+}] = c_{0}^{(D)} - c_{0}^{(Ox^{+})} + [Ox^{+}] \]

Where \( C_{0}^{Ox^{++}} \) and \( C_{0}^{D} \) are the initial concentrations of oxidant \( Ox^{++} \) and added donor \( D \), and \( K \) is the equilibrium constant that corresponds to the reaction in eq 1.

Moreover, based on the free energy change (\( \Delta G \)) in the redox reaction in eq. 1, which can be obtained as a difference between the redox potentials of donor \( D \) and oxidant \( Ox^{++} \), one can directly assess the value of the equilibrium constant \( K \) according to eq. 6:

\[ K_{eq} = \exp(\Delta G / RT), \quad \text{where } \Delta G = E_{ox1}^{D} - E_{ox1}^{Ox} \]

By substituting the concentrations of the various species in eq. 2 in terms of oxidant concentration \( [Ox^{++}] \), and making use of mass and charge balance (eqs 3-5) and the value of \( K \) (eq. 6), one can obtain a quadratic equation (eq 7) that can be solved for \( [Ox^{++}] \) at a given initial concentrations of oxidant \( C_{0}^{Ox^{++}} \) and donor \( C_{0}^{D} \) and a given value of equilibrium constant \( K \).
Figure 5.2. Plots of the mole fractions of Ox$^{\ast\ast}$ and D$^{\ast\ast}$ vs number of equivalents of added D at the equilibrium for the redox reaction Ox$^{\ast\ast}$ + D ⇌ Ox + D$^{\ast\ast}$, simulated using eq. 7 at different values of ΔG and at 22°C.

With eq 7, one can simulate the model titration plots representing a relationship of the mole fractions of D$^{\ast\ast}$ and Ox$^{\ast\ast}$ with respect to the added increment of D at a given ΔG value for the redox reaction in eq. 1 (Figure 7.2). Visual inspection of the “mole fraction vs equivalents of added D” plots, hereafter referred to as MF/D plots, quickly
provides the information concerning free energy changes in a given redox reaction based on the shape of the curve. For example, sharp intersecting MF/D curves (Figure 7.2) are obtained only when the exothermicity of a redox reaction (-ΔG) exceeds by 200 mV, whereas the MF/D curves that correspond to lower exothermicity have a much smoother character that is highly dependent on the value of ΔG (Figure 5.2). Therefore, a fitting of a MF/D curve obtained from experiment allows for the accurate evaluation of the ΔG value of a redox reaction and, in turn, of the oxidation potential of the added donor D.

Theoretical Analysis of Two-electron Oxidation Chemical Equilibria.

The redox titrations of the donors that involve two successive 1-electron oxidations are much more complex due to the multiple equilibria involving one- and two-electron redox reactions between the donor and oxidant as well as comproportionation/disproportionation of D^{2+}/D^{+•} (i.e. eqs 8-10).

\[
\begin{align*}
&Ox^{+•} + D \rightleftharpoons Ox + D^{+•} \quad \text{eq. 8} \\
&Ox^{+•} + D^{+•} \rightleftharpoons Ox + D^{2+} \quad \text{eq. 9} \\
&D^{2+} + D \rightleftharpoons 2D^{+•} \quad \text{eq. 10}
\end{align*}
\]

Three equilibrium constants from eqs 8-10 can be reduced to two equilibria because the third one (K3) can be obtained as a simple ratio between K1/K2. The equilibrium concentrations of the species in eqs 8 and 9 can be determined from the equations of chemical equilibria and equations of mass and charge balance (eqs 11-15).
combined into a cubic equation of one variable (eq 16) in terms of oxidant concentration \([\text{Ox}^{+*}]\), which can be solved either analytically or numerically.

\[
K_1 = \frac{[\text{D}^{+*}][\text{Ox}]}{[\text{D}][\text{Ox}^{+*}]} \tag{eq. 11}
\]

\[
K_2 = \frac{[\text{D}^{2+}][\text{Ox}]}{[\text{Ox}^{+*}][\text{D}^{+*}]} \tag{eq. 12}
\]

\[
[\text{Ox}^{+*}] + [\text{Ox}] = c_0^{\text{Ox}^{+*}} \tag{eq. 13}
\]

\[
[D^{2+}] + [\text{D}^{+*}] + [\text{D}] = c_0^{\text{D}} \tag{eq. 14}
\]

\[
[\text{Ox}^{+*}] + [\text{D}^{+*}] + [\text{D}^{2+}]/2 = c_0^{\text{Ox}^{+*}} \tag{eq. 15}
\]

\[
(K_1K_2 - K_1 + 1)[\text{Ox}^{+*}]^3 + \left(\frac{3}{2}c_0^{\text{Ox}}(K_1 - 2) + K_1(c_0^{\text{D}} - \frac{1}{2}c_0^{\text{Ox}}(2K_2 - 1))[\text{Ox}^{+*}]^2 + \right.
\]

\[
\left.\{K_1(c_0^{\text{D}} - c_0^{\text{Ox}}) + 3c_0^{\text{Ox}}\}c_0^{\text{Ox}}[\text{Ox}^{+*}] - (c_0^{\text{Ox}})^3 \right) = 0 \tag{eq. 16}
\]

Based on eq. 16, the model titration plots (MF/D plots) can be simulated to represent relationships of the mole fractions of \(\text{D}^{+*}\), \(\text{Ox}^{+*}\), and \(\text{D}^{2+}\) with respect to the added increment of \(\text{D}\) at given \(\Delta G_1 (= E_{\text{ox1}}(\text{D}) - E_{\text{red}}(\text{Ox}^{+*}))\) and \(\Delta G_2 (= E_{\text{ox2}}(\text{D}) - E_{\text{red}}(\text{Ox}^{+*}))\) values for the redox reactions in eqs. 8 and 9. Accordingly, Figure 14 shows the predicted MF/D plots for TTE, DAE, and TAE using THEO\(^{+*}\) as the oxidant, based on eq. 16 where the redox potentials, used for \(\Delta G\) calculations, were obtained by electrochemical method. Predicted MF/D plots for the case of TTE (Figure 7.3A) show that addition of neutral TTE to the solution of THEO\(^{+*}\) will lead to the exclusive formation of TTE\(^{+}\) and complete absence of TTE\(^{2+}\) because \(E_{\text{ox2}}(\text{TTE})\) is significantly higher than \(E_{\text{red}}(\text{Ox}^{+*})\) (\(\Delta G_2 = E_{\text{ox2}}(\text{TTE}) - E_{\text{red}}(\text{Ox}^{+*}) = 260\, \text{mV}\)). The electron transfer equilibrium between THEO\(^{+*}\) and TTE can be substantially shifted toward the formation of TTE\(^{+}\) and THEO\(^0\) only by addition of \(~15-20\) equivalents of neutral TTE because their redox potentials are identical (i.e. \(\Delta G_1 = 0\)). Unlike the case of TTE, titration of
THEO$^{+\cdot}$ with up to 0.5 equivalents of DAE (Figure 5.3B) leads to formation of a significant mole fraction of DAE$^{2+}$ since $E_{\text{ox}2}$ (DAE) is only marginally lower than $E_{\text{red}}$ (Ox$^{+\cdot}$) ($\Delta G_2 = -20$ mV). At the same time, mole fraction of DAE$^{+\cdot}$ has an S-shaped profile which saturates at addition of two equivalents of DAE owing to the large driving force of the formation of DAE$^{+\cdot}$, ($\Delta G_1 = -160$ mV). Interestingly, in the case of TAE (Figure 7.3C), titration up to half equivalent results in the exclusive formation of TAE$^{2+}$ ($\Delta G_2 = -160$ mV) while TAE$^{+\cdot}$ is formed only after the point of half equivalent (of added donor) by comproportionation of TAE$^{2+}$ with TAE ($E_{\text{ox}2}$ (TAE) – $E_{\text{ox}1}$ (TAE) = 110 mV)).

![Figure 5.3](image.png)

**Figure 5.3.** Predicted MF/D plots for the redox titrations of various tetraarylethylenes using THEO$^{+\cdot}$ as the oxidant ($E_{\text{red}} = 0.67$ V vs FC/FC$^{+}$).

Importantly, the analysis presented above is based on the electrochemical oxidation potentials obtained in the presence of electrolyte, while the actual redox
titrations are typically performed without added electrolyte. In order to establish the role of electrolyte on the redox potentials of various participants, we performed the redox titrations of various tetraarylethylenes with THEO\(^{\ddagger}\), and obtained corresponding experimental MF/D plots, which can be fitted using eq. 16 to extract various redox potentials in the absence of electrolyte, as follows.

Redox titration of TTE, a case of one-electron oxidation. Figure 7.4A shows the spectral changes observed upon the incremental addition of sub-stoichiometric amounts of TTE to a 6.6×10\(^{-5}\) M THEO\(^{\ddagger}\) in dichloromethane at 22°C (see the Supporting Information for experimental details). Unfortunately, due to the extensive spectral overlap and significant difference in the molar absorptivity of THEO\(^{\ddagger}\) and TTE\(^{\ddagger}\) one cannot monitor the disappearance of THEO\(^{\ddagger}\) and concomitant appearance of TTE\(^{\ddagger}\) directly (Figure 7.4). For this reason, we developed a simple procedure to deconvolute individual spectra of THEO\(^{\ddagger}\) and TTE\(^{\ddagger}\) by means of the least square minimization procedure (see Figure 7.5 for the representative examples and the Supporting Information for details of the deconvolution procedure). The spectral deconvolution procedure was applied at every titration point, which allowed for accurate determination of the concentrations of THEO\(^{\ddagger}\) and TTE\(^{\ddagger}\) along the entire course of titration in Figure 7.4. The resulting concentrations were utilized to construct the MF/D plot shown in Figure 7.6.
Figure 5.4. (A) Spectral changes attendant upon the reduction of $6.6 \times 10^{-5}$ M THEO$^{++}$ upon an incremental addition of 6.3 mM TTE$^{0}$ in CH$_2$Cl$_2$ at 22°C. (B) A plot of the evolution of absorbance at 518 nm and 885 nm against the equivalent of added neutral TTE$^{0}$ (data point
Figure 5.5. Deconvolution of the redox titration spectra in Figure 5.4A into its component spectra, THEO$^{••}$ and TTE$^{••}$, at 0.25 (A), 0.5 (B), and 1.0 (C) equivalents of added TTE.

Figure 7.6 clearly shows that both predicted and experimental MF/D plots are consistent with the fact that titration of TTE with THEO$^{••}$ is simply a one-electron oxidation process that does not produce TTE$^{2+}$. Moreover, the experimental points in Figure 7.6 were accurately fitted using eq. 7, in which the equilibrium constant was varied to minimize the squared residuals between the predicted and experimental mole...
fractions, which yielded the $E_{\text{ox}1}(\text{TTE}) = 0.61$ V that is 60 mV lower than the electrochemical oxidation potential of $E_{\text{ox}1}(\text{THE-O}) = 0.67$ V. This discrepancy is somewhat surprising based on the fact that the first oxidation potentials of both THEO and TTE should have been impacted equally by the presence/absence of electrolyte as the TTE/THEO$^{\text{+•}}$ redox titration involves only one electron oxidation. However, due to the smaller size of THEO as compared to TTE, the positive charge in TTE$^{\text{+•}}$ is delocalized over a larger area than in THEO$^{\text{+•}}$ (Figure 7.7). Thus, the increased ionic strength of the solution should be relatively effective in stabilization of THEO$^{\text{+•}}$ in which the charge is concentrated on a single aromatic ring, as compared to TTE$^{\text{+•}}$.

![Figure 5.6](image)

**Figure 5.6.** Plot of the mole fractions of THEO$^{\text{+•}}$ (red circles) and TTE$^{\text{+•}}$ (black circles), obtained from the deconvolution of the spectra in Figure 4A, against the added equivalents of TTE. Solid lines were fitted using the redox potential $E_{\text{ox}1}^{\text{TTE}} = 0.61$ V, $E_{\text{red}}^{\text{OX+•}} = 0.67$ V. The predicted MF/D plots in Figure 3, obtained using electrochemical value of $E_{\text{ox}1}^{\text{TTE}} = E_{\text{red}}^{\text{OX+•}} = 0.67$ V are superimposed as dashed lines.
Figure 5.7. Calculated spin/charge (i.e. hole) distribution in THEO$^{++}$ and TTE$^{++}$ [B1LYP-40/6-31G(d)+PCM(CH2Cl2)].\textsuperscript{[16]}

Indeed, this suggestion of differential stabilization of THEO$^{++}$ and TTE$^{++}$ owing to their drastically varied sizes can be verified by titration of THEO$^{++}$ with an electron donor of similar size, i.e. cycloannulated veratrole (DMB). Thus, Figure 7.8 compiles spectral changes attendant upon incremental addition of DMB to a solution of THEO$^{++}$, and the corresponding MF/D points obtained by the deconvolution procedure discussed above (Figure 7.5). Indeed, the experimental MF/D points fall exactly on the predicted lines, obtained using the electrochemical redox potential $E_{ox1}$ (DMB) = 0.82 V,\textsuperscript{[19]} confirming that the relative first oxidation potentials of THEO and DMB are not impacted by the presence/absence of electrolyte.
Figure 5.8. (A) Spectral changes observed upon the reduction of THEO$^{+}$ by an incremental addition of 11.2 mM DMB in CH$_2$Cl$_2$ at 22 °C. (B) The MF/D points obtained from the deconvolution of the corresponding spectra in panel (A). Dashed lines show predicted MF/D plots based on the electrochemical $E_{\text{ox}1}$ (DMB) = 0.82 V.

Redox titrations of DAE and TAE, the cases of two-electron oxidation. Unlike TTE, the predicted MF/D plots (Figure 7.3) suggest that DAE and TAE can be oxidized to both cation radicals and dications by THEO$^{+}$. For example, Figure 7.9A shows the spectral changes observed upon the incremental addition of sub-stoichiometric amounts of DAE to a 7.2×10$^{-5}$ M THEO$^{+}$. The MF/D points obtained by spectral deconvolution (Figure 7.9B) are in qualitative agreement with the corresponding predicted MF/D plots (dashed lines). However, fitting of the experimental MF/D points (shown as solid lines) resulted in $E_{\text{ox}2}^{\text{DAE}} = 0.706$ V, which is significantly higher than the electrochemical $E_{\text{ox}2}^{\text{DAE}} = 0.650$ V (see Table 1).$^{[20]}$ As such, the increased second oxidation potential of DAE in the absence of electrolyte can be clearly seen at half-equivalency point, where
the observed mole fraction of DAE\(^{2+}\) is only 0.1 as compared to the predicted value of 0.23 (Figure 7.9B). This observation is expected in the light of the fact that presence of electrolyte should dramatically impact the stabilization of tetraarylethylene dications as opposed to cation radicals, and hence should lead to increase of the second oxidation potentials in the absence of electrolyte.

Figure 5.9. (A) Spectral changes observed upon the reduction of THEO\(^{+}\) by an incremental addition of 2.3 mM DAE\(^{0}\) in CH\(_2\)Cl\(_2\) at 22 °C. (B) The MF/D plots obtained from the deconvolution of the corresponding spectra in panel (A). Solid lines show best-fitting MF/D plots using the values of \(E_{ox1}^{DAE} = 0.490\) V and \(E_{ox2}^{DAE} = 0.706\) V, while dashed lines show predicted MF/D plots based on the electrochemical oxidation potentials (0.51 and 0.65 V).

To verify that the observed deviation between the experimental and predicted MF/D plots for DAE arises due to the effect of electrolyte, we performed the redox titrations in the presence of added electrolyte to mimic the electrochemical conditions
(Figure 7.10). The MF/D points, obtained from the redox titrations in the presence of increasing amount of electrolyte are compiled in Figure 7.10A-D. The best-fitting lines of the experimental MF/D points, and the predicted MF/D plots became increasingly similar with increasing concentration of the electrolyte and were essentially identical at 0.2 M electrolyte concentration (also see Table 1). Note that electrochemical oxidation potentials of various tetraarylethylenes were measured in dichloromethane containing 0.2 M electrolyte.

Figure 5.10. The MF/D plots obtained from the titration of THEO$^+$ with DAE in the presence of $5 \times 10^{-5}$ (A), $5 \times 10^{-4}$ (B), 0.05 (C), and 0.2 M (D) of nBu$_4$NPF$_6$. Solid lines show best-fitting MF/D plots (see Table 1 for the values of $E_{\text{ox1}}$ and $E_{\text{ox2}}$), while dashed lines show predicted MF/D plots based on the electrochemical oxidation potentials (0.51 and 0.65 V).

It is interesting to note that redox titrations of TAE with THEO$^+$ and the resulting MF/D points fell much more closely to the predicted MF/D plots (dashed lines) based on the electrochemical redox potentials (Figure 7.11A/B). It is noted that the subtle discrepancy in the predicted/experimental MF/D plots in Figure 7.11B arises owing to the
increase in the value of $\Delta G_2 = E_{ox^2}^{D} - E_{red}^{ox^{+\cdot}}$ by $\sim 80$ mV in the absence of electrolyte (Table 1). Not surprising that the same redox titration of TAE with THEO$^{+\cdot}$ in the presence of only 0.2 M of electrolyte closely matched the predicted (dashed lines) and experimental (solid lines) MF/D plots (Figure 22C/D).

![Figure 5.11](image)

**Figure 5.11.** Spectral changes observed upon the reduction of THEO$^{+\cdot}$ by an incremental addition of TAE in CH$_2$Cl$_2$ at 22°C in absence (A) and presence of the 0.2 M solution of nBu$_4$NPF$_6$ (C), and the corresponding
MF/D plots (panels B and D). Solid lines show best-fitting MF/D plots (see Table 1 for the values of $E_{\text{ox}1}$ and $E_{\text{ox}2}$), while dashed lines show predicted MF/D plots based on the electrochemical oxidation potentials (0.40 and 0.51 V).

The observed increase of the second oxidation potentials of tetraarylethylenes in the absence of electrolyte is expected to be a general phenomenon. For example, the dramatic impact of absence of electrolyte on the mole fractions of the cation radicals and dications of a given donor (D) with respect to the amount of added D can also be seen in the redox titration of a structurally different tetraarylbenzidine\textsuperscript{[21]} TAB ($E_{\text{ox1}}^\text{TAB}$ and $E_{\text{ox2}}^\text{TAB} = 0.44$ and 0.64 V, respectively) with THEO$^{++}$ as oxidant.
Table 5.1. The values of $E_{\text{ox}1}^D$, $E_{\text{ox}2}^D$, $\Delta G_{12} = E_{\text{ox}2}^D - E_{\text{ox}1}^D$ and $\Delta G_2 = E_{\text{ox}2}^D - E_{\text{red}^{ox+}}$, obtained by the analysis of redox titrations and from the electrochemical redox potentials (vs Fc/Fc$^+$).

<table>
<thead>
<tr>
<th>Electron Donor D</th>
<th>Salt $^a$</th>
<th>$E_{\text{ar}1}^D$, V</th>
<th>$E_{\text{ox}2}^D$, V</th>
<th>$\Delta G_{12}$, mV</th>
<th>$\Delta G_2$, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTE</td>
<td>-</td>
<td>0.613</td>
<td>&gt;0.8</td>
<td>&gt;190</td>
<td>&gt;130</td>
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<tr>
<td>TTE (CV)</td>
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<td>0.928</td>
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<td>258</td>
</tr>
<tr>
<td>DAE</td>
<td>-</td>
<td>&lt;0.47</td>
<td>0.706</td>
<td>&gt;240</td>
<td>30</td>
</tr>
<tr>
<td>DAE</td>
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<td>0.689</td>
<td>&gt;200</td>
<td>19</td>
</tr>
<tr>
<td>DAE</td>
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<td>0.651</td>
<td>~170</td>
<td>~19</td>
</tr>
<tr>
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<td>0.640</td>
<td>166</td>
<td>~30</td>
</tr>
<tr>
<td>DAE</td>
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<td>0.495</td>
<td>0.640</td>
<td>145</td>
<td>~30</td>
</tr>
<tr>
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<td>138</td>
<td>~20</td>
</tr>
<tr>
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<td>0.532</td>
<td>131</td>
<td>~138</td>
</tr>
<tr>
<td>TAE (CV)</td>
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<td>0.401</td>
<td>0.513</td>
<td>112</td>
<td>~157</td>
</tr>
<tr>
<td>TAB</td>
<td>-</td>
<td>&lt;0.48</td>
<td>0.723</td>
<td>&gt;240</td>
<td>53</td>
</tr>
<tr>
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<td>0.644</td>
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<td>~26</td>
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<td>0.436</td>
<td>0.636</td>
<td>200</td>
<td>~34</td>
</tr>
</tbody>
</table>

$^a$Concentration of nBu 4NPF6 (M)

Inspection of the experimental and predicted MF/D plots for the redox titration of TAB with THEO$^{++}$ clearly show the presence of little TAB$^{2+}$ (Figure 7.12) despite the fact that its second oxidation potential is rather close to the oxidant (i.e. 0.64 vs 0.67 V), which is not surprising based on the fact that the second oxidation potential of TAB is
expected to significantly increase in the absence of electrolyte (Table 4). Indeed, in the presence of 0.2 M of electrolyte, the redox titration demonstrates the formation of significant quantities of TAB$^{2+}$ at half-equivalency point, and furthermore, the experimental and predicted MF/D plots match closely with each other.

**Figure 5.12.** Spectral changes observed upon the reduction of THEO$^{+•}$ by an incremental addition of TAB in CH$_2$Cl$_2$ at 22°C in absence (A) and presence of the 0.2 M solution of the nBu$_4$NPF$_6$ (C), and the corresponding MF/D plots (B, D). Solid lines show best-fitting MF/D plots (see Table 1 for the values of $E_{ox1}$ and $E_{ox2}$), while dashed lines show
predicted MF/D plots based on the electrochemical oxidation potentials (0.44 and 0.64 V).

In summary, we have demonstrated ready usage of highly robust THEO$^{+\bullet}$ for quantitative oxidation of various electron donors (D) to their cation radical and dication states via redox titrations in dichloromethane using UV-vis spectroscopy. Moreover, redox titrations are not only useful for optical characterization of D$^{+\bullet}$ and/or D$^{2+}$ but they can also allow one to quantitatively estimate the redox potentials of D (in the absence of electrolyte) and to ascertain how different they are from the redox potentials obtained by electrochemical method (in the presence of electrolyte). It is noted that the equilibrium concentrations or mole fractions (MF) of various species at initial concentrations of oxidant Ox$^{+\bullet}$ and added donor D can be determined using equilibrium equations (i.e. eqs 2-7 for one-electron oxidation, eqs 11-16 for two-electron oxidation) at a given equilibrium constant, which in turn can be calculated from the electrochemical redox potentials. Thus, using the mole fractions of various species, one can simulate titration curves, which can be represented in the form of the “mole fraction vs equivalents of added D” (MF/D) plots (e.g. see Figures 5.2 and 5.3).

Similar experimental MF/D plots can also be constructed from the redox titrations; however, overlapping absorption spectra of the oxidant, D$^{+\bullet}$ and/or D$^{2+}$ often complicate an accurate determination of their concentrations and mole fractions. We overcame this problem by developing a simple numerical deconvolution procedure (Figure 7.5) using clean absorption spectra of the Ox$^{+\bullet}$, D$^{+\bullet}$ and/or D$^{2+}$, which allowed the determination of mole fractions of each of the species, involved in equilibrium, at
each titration point. Using this procedure, the experimental MF/D points can be fitted by eqs 7 or 16, and the best-fitting values of \( K \) then easily provide the oxidation potentials of \( D \) relative to \( \text{E}_{\text{red}}^{\text{ox}+} \).

It was demonstrated using Cycloannulated compounds and tetraarylethylenes as electron donors that the oxidation potentials of tetraarylethylenes obtained from redox titrations (i.e. in absence of electrolyte) were different from the oxidation potentials obtained by the electrochemical method (i.e. in presence of electrolyte). In cases of one-electron oxidation (Cycloannulated compounds) one expects that the first oxidation potentials to be equally impacted by the presence/absence of electrolyte. However, due to the dissimilar sizes of tetraarylethylene cation radicals and THEO\(^{+}\), charge is much more concentrated in THEO\(^{+}\) as compared to tetraarylethylene cation radicals (Figure 5.7), hence their differential stabilization in the presence of electrolyte (Table 1). This premise was confirmed by the redox titration of THEO\(^{+}\) with an electron donor of similar size (DMB), where it was found that their relative first oxidation potentials, obtained either by redox titrations or electrochemical method (i.e. in the presence/absence of electrolyte), were identical (Figure 5.8).

The analysis of the redox titrations involving two-electron oxidation of three different donors (DAE, TAE, and TAB) with THEO\(^{+}\) unequivocally showed that the second oxidation potentials of \( D \) (\( E_{\text{ox2}}^{D} \)) were systematically higher (by 50-100 mV) than the electrochemical (\( E_{\text{ox2}}^{D} \)). This difference was sufficient to involve/exclude formation of dication during the titration course, as predicted by the calculated MF/D plots based on the electrochemical potentials (Figures 9-12). In other words, the difference between first and second oxidation potentials from the electrochemical method is invariably
smaller as compared to the redox titration method because of the enhanced stabilization of dications by electrolyte. This notion was further confirmed by performing the redox titrations in the presence of electrolyte, which resulted in the oxidation potentials that closely matched the electrochemical potentials (e.g. Figure 5.12 and Table 5.1).

In conclusion, we demonstrated that redox titrations with readily available and highly robust THEO$^+$ allow one to quickly ascertain the redox and optical properties of a given electron donor without the need of complex electrochemical setup. This study also demonstrated that redox potentials (especially second and higher oxidation potentials) measured by electrochemical method are expected to be lower compared to the redox potentials obtained by redox titration in the absence of electrolyte.
General Experimental Methods and Materials.

All reactions were performed under argon atmosphere unless otherwise noted. All commercial reagents were used without further purification unless otherwise noted. Dichloromethane (Aldrich) was repeatedly stirred with fresh aliquots of concentrated sulfuric acid (~10 % by volume) until the acid layer remained colorless. After separation it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P$_2$O$_5$ under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. Acetonitrile was stirred with molecular sieves for overnight. Then it was filtered and again stirred with CaCl$_2$ for overnight. After that it was filtered and distilled twice from P$_2$O$_5$ under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexanes and toluene were distilled from P$_2$O$_5$ under an argon atmosphere and then refluxed over calcium hydride (~12 h). After distillation from CaH2, the solvents were stored in Schlenk flasks under an argon atmosphere. Tetrahydrofuran (THF) was dried initially by distilling over lithium aluminum hydride under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. NMR spectra were recorded on Varian 400 MHz NMR spectrometers. S2.

Experimental Details of Redox Titrations. A stock solution of T HE -Orange$^+$ (λ$_{max}$ = 518 nm, ε51 8 = 7300 M$^{-1}$ cm$^{-1}$) was prepared by dissolving [THE -Orange$^+$ SbCl$_6$ - ] (2.7 mg, 4.4 x 10$^{-3}$ mmol) in anhydrous dichloromethane (20 mL) at 22 °C under an argon atmosphere. A 3 - mL aliquot of the red-orange solution was transferred to a 1 -
cm quartz cuvette equipped with a Schlenk adapter (under an argon atmosphere). The redox titrations were carried out by adding the increments of an electron donor (Cyclic annulated compounds, tetraarylethylenes and tetraarylbenzidine) dissolved in dichloromethane to the above solution of T HE Orange••; and the accompanied color changes were monitored by UV-vis-NIR spectroscopy.

**Details of Numerical Analysis**

5.1. Spectral Deconvolution

The spectral deconvolution can be performed by using the least squares fitting procedure:

$$\chi^2(C = |A - EC|^2)$$

where $\chi^2$ is the least residual squares sum, which needs to be minimized, $A$ is the $N \times T$ matrix of experimentally observed absorptions (rows correspond to $N$ wavelengths, columns correspond to $T$ titration points), $C$ is the $K \times T$ matrix of concentrations (rows correspond to $K$ various compounds, columns correspond to $T$ titration points), and $E$ is the $N \times K$ matrix of the absorption spectra of individual compounds (rows correspond to $N$ extinction coefficients at various wavelengths, columns correspond to $K$ various compounds). The solution of the least-squares problem can be found in the form:

$$E^T EC = E^T A$$

From which, concentrations of all involved compounds at every titration points ($C$) can be computed for given $A$ and $E$ as

$$C = (E^T EC)^{-1} E^T A$$
Fitting of the experimental MF/D points to eqs 2-6 (one-electron oxidation) and 10-17 (two electron oxidation) was achieved by variation of the equilibrium constants $K$ (one-electron oxidation) or $K_1$ and $K_2$ (two-electron oxidation) in order to minimize the least squares of the residuals $\chi^2$ for the cases of one- and two-electron oxidation, respectively:

**Description of the Program**

To implement the algorithms described above, we developed the in-house program package for quantitative analysis of redox titrations. The functionality of the program includes:

1. Import of the spectroscopic data in the format that can be used for the further statistical/numerical analysis, and accurate calculation of the number of added equivalents of electron donor ($D_i$), which takes into account the factor of the eventual dilution during the titration course due to the added volume.

2. Semi-automatic extraction of the spectra of pure species based on the analysis of the characteristic peaks in the spectra of these species.

3. Deconvolution of the spectra at each titration points, which produces concentrations and mole fractions of every compound, involved in the equilibrium, at each titration point.

4. Prediction of the MF/D plots for any given equilibrium constants, and fitting of the experimental MF/D points to the calculated curves (Section S5.2) in order to produce the oxidation potentials of a given electron donor.
These features are conveniently available via the user-friendly web-based interface.[5]

**Figure 5.S1.** (A) Spectral changes upon the reduction of 0.07 mM cret cation radical by an incremental addition of 2.28 mM solution of DADTE in dichloromethane at 22°C. (B) A plot of increase of the absorbance of DADTE^{2+} (monitored at 744 nm), and depletion of the absorbance of cret^{2+} (monitored at 518 nm) against the equivalent of added DADTE^{2+}. (C) A plot of increase of the concentration or mole fraction of DADTE^{2+} (black circles monitored at 744 nm), increase of the concentration or mole fraction of DADTE^{2+} (blue circles), and depletion of the concentration of cret^{2+} (red circles monitored at 518 nm) against the equivalent of added DADTE^{2+}. Solid lines show best-fitting MF/D plots while the dotted lines are experimental redox titration points.

**Figure 5.S2.** (A) Spectral changes upon the reduction of 0.048 mM cret cation radical by an incremental addition of 4.88 mM solution of TAE in dichloromethane at 22°C. (B) A
plot of increase of the absorbance of TAE$^{**}$ (monitored at 744nm), and depletion of the absorbance of cret$^{**}$ (monitored at 518 nm) against the equivalent of added TAE$^{**}$.

A plot of increase of the concentration or mole fraction of TAE$^{**}$ (black circles monitored at 744 nm), increase of the concentration or mole fraction of TAE$^{2+•}$ (blue circles), and depletion of the concentration of cret$^{**}$ (red circles monitored at 518 nm) against the equivalent of added TAE$^{**}$. Solid lines show best-fitting MF/D plots while the dotted lines are experimental redox titration points.

**Figure 5.S3.** (A) Spectral changes upon the reduction of 0.066 mM cret cation radical by an incremental addition of 6.33 mM solution of TTE in dichloromethane at 22°C. (B) A plot of increase of the absorbance of TTE$^{**}$ (monitored at 744nm), and depletion of the absorbance of cret$^{**}$ (monitored at 518 nm) against the equivalent of added TTE$^{**}$. (C) A plot of increase of the concentration or mole fraction of TTE$^{**}$ (black circles monitored at 744 nm), increase of the concentration or mole fraction of TTE$^{2+•}$ (blue circles), and depletion of the concentration of cret$^{**}$ (red circles monitored at 518 nm) against the equivalent of added TTE$^{**}$. Solid lines show best-fitting MF/D plots while the dotted lines are experimental redox titration points.
Figure 5.S4. (A) Spectral changes upon the reduction of 0.055 mM cret cation radical by an incremental addition of 4.59 mM solution of DADTE in the presence of 0.00005M nBu4NPF6 in dichloromethane at 22°C. (B) A plot of increase of the absorbance of DADTE\textsuperscript{2+} (monitored at 744 nm), and depletion of the absorbance of cret\textsuperscript{2+} (monitored at 518 nm) against the equivalent of added DADTE\textsuperscript{2+}. (C) A plot of increase of the concentration or mole fraction of DADTE\textsuperscript{2+} (black circles monitored at 744 nm), and depletion of the concentration of cret\textsuperscript{2+} (red circles monitored at 518 nm) against the equivalent of added DADTE\textsuperscript{2+}. Solid lines show best-fitting MF/D plots while the dotted lines are experimental redox titration points.

Figure 5.S5. (A) Spectral changes upon the reduction of 0.07 mM cret cation radical by an incremental addition of 3.9 mM solution of DADTE in the presence of 0.0005M nBu4NPF6 in dichloromethane at 22°C. (B) A plot of increase of the absorbance of DADTE\textsuperscript{2+} (monitored at 744 nm), and depletion of the absorbance of cret\textsuperscript{2+} (monitored at 518 nm) against the equivalent of added DADTE\textsuperscript{2+}. (C) A plot of increase of the concentration or mole fraction of DADTE\textsuperscript{2+} (black circles monitored at 744 nm), and depletion of the concentration of cret\textsuperscript{2+} (red circles monitored at 518 nm) against the equivalent of added DADTE\textsuperscript{2+}. Solid lines show best-fitting MF/D plots while the dotted lines are experimental redox titration points.
Figure 5S6. (A) Spectral changes upon the reduction of 0.05 mM cret cation radical by an incremental addition of 6.72 mM solution of DADTE in the presence of 0.005M nBu₄NPF₆ in dichloromethane at 22°C. (B) A plot of increase of the absorbance of DADTE⁺⁺ (monitored at 744 nm), and depletion of the absorbance of cret⁺⁺ (monitored at 518 nm) against the equivalent of added DADTE⁺⁺. (C) A plot of increase of the concentration or mole fraction of DADTE⁺⁺ (black circles monitored at 744 nm), and depletion of the concentration of cret⁺⁺ (red circles monitored at 518 nm) against the equivalent of added DADTE⁺⁺. Solid lines show best-fitting MF/D plots while the dotted lines are experimental redox titration points.

Figure 5.S7. (A) Spectral changes upon the reduction of 0.064 mM cret cation radical by an incremental addition of 5.82 mM solution of DADTE in the presence of 0.05M nBu₄NPF₆ in dichloromethane at 22°C. (B) A plot of increase of the absorbance of DADTE⁺⁺ (monitored at 744 nm), and depletion of the absorbance of cret⁺⁺ (monitored at 518 nm) against the equivalent of added DADTE⁺⁺. (C) A plot of increase of the
concentration or mole fraction of DADTE$^{**}$ (black circles monitored at 744 nm), and depletion of the concentration of cret$^{**}$ (red circles monitored at 518 nm) against the equivalent of added DADTE$^{**}$. Solid lines show best-fitting MF/D plots while the dotted lines are experimental redox titration points.
References


[18] In the context of this study we note that Parker and co-workers have studied the effect of the supporting electrolyte concentration on the well-separated first and second reduction potentials of PAHs, and showed that increasing salt concentration leads to an increased gap between the first and second reduction potentials, see B. S. Jensen, V. D. Parker, *J. Am. Chem. Soc.*, **1975**, *97*, 5211-5217 and A. J. Fry, *Tetrahedron*, **2006**, *62*, 6558-6565.


[20] The first oxidation potential was estimated to be lower than 0.49 V; more accurate evaluation was prohibited by a large, i.e. >200 mV, exothermicity of the DAE•• formation from either THEO•• or DAE2+. 
Summery and conclusion of thesis

In order to develop an intuitive understanding of the hole delocalization in poly-p-phenylene-based wires ($^{ \mathit{R} } \text{PP}_n$, where $n$ is number of $p$-phenylene units) and, in turn, the effective conjugation length of $^{ \mathit{R} } \text{PP}_n$ wires, we have synthesized and systematically studied well-defined series of oligomers of a number of $\pi$-conjugated poly-$p$-phenylene molecular wires with varying inter-ring dihedral angles ($\theta$) between the monomer units (e.g. $^{ \mathit{R} } \text{PP}_n$, $\theta \sim 33^\circ$; oligofluorenes, $\theta \sim 37^\circ$ and $0^\circ$; or $m$-$\text{Py}_n$, $\theta \sim 60-70^\circ$) using a combined computational/experimental approach. These studies revealed that redox and optical properties of all molecular wires the HOMO density distribution extends over the entire chain as expected based on the observed linear $\cos[\pi/(n + 1)]$ trend albeit gravitating toward the center of the molecule, whereas the hole distribution, which determines optoelectronic properties of the oligomer cation radicals, is found to be limited to 7-8 phenylene units.

The study of poly-$p$-phenylene oligomers with electron-donating end-capping groups (i.e. alkyl- or alkoxy-groups) showed that the hole distribution is strongly impacted by end-capping groups and it gravitates from the central position to the end of the oligomeric chain while the distribution of HOMO density remains in the middle of the $\pi$-conjugated wires. Such migration of the hole toward the end of the chain due to the electron-donating alkoxy groups has significant experimental consequences, i.e. the optical and redox properties saturated at five phenylene units in case of alkoxy-capped poly-$p$-phenylene wires.
Additionally, the evolution of the redox and optical properties of the poly-pyrenes, linked at 3,3’ (meta) positions, i.e. \( m\text{-Py}_n \), which have shown a much smaller interchromophoric coupling as compared to the strong coupling in linearly connected polyfluorenes, i.e. \( OF_n \). Due to a much smaller coupling, the evolutions of the experimental redox and optical properties of \( m\text{-Py}_n \), showed moderate slopes as compared with corresponding trends for \( OF_n \), when plotted against \( \cos[\pi/(n+1)] \) trend, and the hole distribution in longer homologues of \( Py_{n^+} \) is limited to 3 pyrene units, i.e. only two phenylene units less than in \( OF_{n^+} \). We also demonstrated that a simple repositioning of the interchromophoric linkage can have a dramatic effect on the hole stabilization, which can be easily explained by an unfavorable nodal arrangement of HOMO, which prevents the electronic coupling between the molecular orbitals of monomeric HOMOs.

These results were further reconciled by DFT calculations and by a recently developed multistate parabolic model by my coworkers Dr. Marat R Talipov and Maxim V. Ivanov.