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The spontaneous assembly of aromatic cation radicals ($D^{•+}$) with their neutral counterpart ($D$) affords dimer cation radicals ($D_{2}^{•+}$). The intermolecular dimeric cation radicals are readily characterized by the appearance of an intervalence charge-resonance transition in the NIR region of their electronic spectra and by ESR spectroscopy. The X-ray crystal structure analysis and DFT calculations of a representative dimer cation radical (i.e., the octamethylbiphenylene dimer cation radical) have established that a hole (or single positive charge) is completely delocalized over both aromatic moieties. The energetics and the geometrical considerations for the formation of dimer cation radicals is deliberated with the aid of a series of cyclophane-like bichromophoric donors with drastically varied interplanar angles between the cofacially arranged aryl moieties. X-ray crystallography of a number of mixed-valence cation radicals derived from monochromophoric benzenoid donors established that they generally assemble in 1D stacks in the solid state. However, the use of polychromophoric intervalence cation radicals, where a single charge is effectively delocalized among all of the chromophores, can lead to higher-order assemblies with potential applications in long-range charge transport. As a proof of concept, we show that a single charge in the cation radical of a triptycene derivative is evenly distributed on all three benzenoid rings and this triptycene cation radical forms a 2D electronically coupled assembly, as established by X-ray crystallography.

Introduction

Since the discovery of conducting polyacetylenes, the preparation and study of π-conjugated organic materials for use as charge-transport materials in modern photovoltaic devices have been continuing at an unabated pace.(1-6) Tremendous attention has been devoted to the synthesis of a variety of materials derived from traditional π-conjugated organic polymers, such as poly-p-phenylenes,(7, 8) polythiophenes,(9-13) polyphenylvinylenes,(14, 15) and polyfluorenes.(16-19) A few quantitative studies, directed toward understanding the mechanism of charge transport through multiple arene moieties that constitute these polymers, have shown that all electronic and optoelectronic properties of the π-conjugated polymers follow a $1/n$ relationship (where $n$ is the number of repeat units in the polymer).(20, 21) For example, we have recently shown, using a well-defined homologous series of poly-p-phenylenes (Figure 1), that the effective conjugation length in poly-p-phenylenes extends to $\sim 10$ repeat units.(20) Similar studies on polythiophenes estimate that
that the effective conjugation length extends over 20 repeat units.\textsuperscript{(9, 12)} As exemplified in Figure 1, electronic and optoelectronic properties such as redox potentials and optical absorptions and emissions do not change significantly upon increasing the number of repeat units beyond the effective conjugation lengths.\textsuperscript{(20)}

Figure 1

![Diagram](image)

Figure 1. (A) Electronic absorption spectra of 0.1 mM PP\textsubscript{2-7} in dichloromethane at 22 °C and a plot of the $\lambda_{\text{max}}$ in energy units (cm\textsuperscript{-1}) vs $1/n$, where $n$ is the number of phenylene rings in a given poly-p-phenylene oligomer. (B) Emission spectra of 2.5 × 10\textsuperscript{-7} M PP\textsubscript{2-7} in dichloromethane at 22 °C and a plot of $\lambda_{\text{max,emm}}$ in energy units (cm\textsuperscript{-1}) vs $1/n$. (C) Cyclic voltammograms of 2 mM PP\textsubscript{2-7} in CH\textsubscript{2}Cl\textsubscript{2} containing 0.2 M n-Bu\textsubscript{4}NPF\textsubscript{6} at a scan rate of 200 mV s\textsuperscript{-1} at 22 °C and a plot of the oxidation potentials ($E_{\text{ox1}}$) vs $1/n$.

When such π-conjugated materials are employed in photovoltaic devices, the efficiency of charge transport in the conducting layers of these devices is governed by not only the intramolecular electron transport through the backbone of the polymer but also by the intermolecular electron transport through the bulk material, where the amorphous assembly of π-conjugated molecules is generally randomized (Figure 2A, B).\textsuperscript{(22-25)}
Figure 2. (A) Cartoon diagram showing the intrachain versus interchain charge transport (CT) in poly-$p$-phenylene wires and (B) their randomized assembly in amorphous bulk material.

Thus, designing the next generation of conductive organic materials for photovoltaic applications requires careful studies to develop a fundamental understanding of structure–function relationships for both electron and hole transport along the conjugated chains\(^\text{(20, 21)}\) and through cofacially stacked aromatic $\pi$ systems.\(^\text{(22-29)}\) In this regard, we\(^\text{(26-29)}\) and others\(^\text{(22-25)}\) have been probing the structural parameters governing the interchain charge transport using a variety of cofacially arrayed molecules with varying degrees of interchain overlap (e.g., Figure 3).
Figure 3. Representative examples of cofacially arrayed structures for studies of interchain charge transport.

Although the studies of such molecules (Figure 3) have provided valuable insight into the mechanism of charge transport in cofacially arrayed structures, the usefulness of such materials in functional devices remains limited; therefore, the design and synthesis of new functional materials for long-range charge transport remains an active area of research.

This challenging task of the design and synthesis of new functional materials for long-range charge transport requires the development of a state-of-the-art understanding of fundamental molecular units, such as a dimer cation radical and anion radical, that are responsible for charge transport in large molecular assemblies. Accordingly, this feature article will outline the studies in our laboratory directed toward the characterization of the dimer cation radical (D$_2^{+}$) formed in solution by the self-association of a neutral donor (D) with its cation radical (D$^{+}$) by a variety of spectroscopic methods and a demonstration of long-range charge delocalization in solid-state (1D) assemblies by X-ray crystallography (e.g., Figure 4A).
Figure 4. Cartoon diagrams showing (A) the 1D stacking of the mixed-valence benzenoid cation radicals and (B) the 2D assembly of polychromophoric cation radicals with holes (shown by shaded black spheres) for counteranions in which a single charge is delocalized on all electronically coupled chromophores. Note that the holes in 2D assemblies, shown by shaded black spheres, may allow the incorporation of counteranions and other guest molecules.

The X-ray crystallography of a number of mixed-valence monochromophoric benzenoid cation radicals has shown that owing to the anisotropic nature of the benzenoid donors they generally assemble in 1D stacks (e.g., Figure 4A).(30) To improve the dimensionality of the charge transport in solid-state assemblies, polychromophoric molecules, in which multiple arene moieties are electronically coupled, are required (i.e., Figure 4B). For example, we have recently demonstrated that three cofacially juxtaposed phenylene rings in triptycene are electronically coupled, where a single hole (formed by one-electron oxidation) is completely delocalized onto three benzenoid rings. As a proof of concept, we delineate with the aid of X-ray crystallography that a triptycene derivative allows the preparation of a solid-state assembly for long-range charge transport (i.e., Figure 4B).
Formation and Spectroscopic Characterization of Dimer Cation Radicals in Solution

The one-electron oxidation of a variety of aromatic electron donors (D) generates paramagnetic cation radicals that spontaneously associate with their neutral counterparts to form dimer cation radicals (30) (i.e., eq 1).

\[
D^+\cdot + D \rightleftharpoons [D, D]^+\cdot
\]  

(1)

These dimer cation radicals (D₂⁺) invariably show a diagnostic intervalence (or charge-resonance) transition in the near-IR region in their electronic spectra, together with the absorption bands ascribed to monomer cation radicals. For example, the treatment of a blue solution of the highly robust octamethylbiphenylene cation radical (OMB⁺⁺ SbCl₆⁻), prepared from neutral octamethylbiphenylene (OMB) using nitrosonium hexachloroantimonate (NO⁺ SbCl₆⁻) as an oxidant in dichloromethane (30, 36) with incremental amounts of neutral OMB at 25 °C produces a dimer cation radical, and the accompanying spectral changes are shown in Figure 5A. The spectral changes in Figure 5A showed a merging of the twin absorption bands (λ_max = 600 and 550 nm) due to OMB⁺⁺ into a Gaussian band (λ_max = 570 nm) and the growth of a new broad absorption band in the NIR region (at λ_max = 1850 nm) due to the formation of the (OMB)₂⁺⁺ dimer cation radical (eq 1).

Figure 5

(A) UV–vis spectral changes upon the incremental addition of neutral OMB to a dichloromethane solution of the OMB⁺⁺ SbCl₆⁻ monomer cation radical salt at 22 °C. (B) Benesi–Hildebrand plot for the experiment in A.

The quantitative analysis of the formation of the (OMB)₂⁺⁺ dimer cation radical (Figure 5A) can be carried out using the Benesi–Hildebrand (spectrophotometric) procedure (37) in which the absorbance changes in Figure 5A were treated according to eq 2 (i.e., where A₁₈₅₀ nm is the absorbance and ε₁₈₅₀ nm is the molar extinction coefficient of the charge resonance band due to dimeric OMB₂⁺⁺.

\[
\frac{[OMB^+]_A}{A_{1850}} = \frac{1}{ε_{1850}} + \frac{1}{K_{dimer}ε_{1850}} \frac{1}{[OMB]}
\]  

(2)
Thus, a linear plot of \([\text{OMB}^{**}] / A_{1850}\) versus the reciprocal concentration of added neutral \(\text{OMB}\) (Figure 5B) provided the values of the dimerization constant \(K_{\text{dimer}} = 300 \pm 50 \text{ M}^{-1}\) and the extinction coefficient \(\varepsilon_{1850 \text{ nm}} = 5700 \pm 300 \text{ M}^{-1}\text{cm}^{-1}\) of the charge resonance band from the slope \((K_{\text{dimer}} \varepsilon_{1850 \text{ nm}})^{-1}\) and intercept \(\varepsilon_{1850 \text{ nm}}^{-1}\), respectively. The dimerization equilibrium constant \(K_{\text{dimer}}\) for the octamethylbiphenylene cation radical is of the same order of magnitude as those obtained for transient hexamethylbenzene, naphthalene, and pyrene cation radicals by the pulse-radiolytic and/or laser-spectroscopic methods (Table 1).(38-41)

**Table 1.** Comparison of the UV–Vis Spectral Data of Representative Transient Dimeric Aromatic Cation Radicals(38-41)

<table>
<thead>
<tr>
<th>Dimer cation radical ((\text{ArH})_2^{**})</th>
<th>UV-vis bands (\lambda_{\text{max}}) (nm)</th>
<th>Charge resonance band, (\lambda_{\text{max}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Dimer cation radical" /></td>
<td>555</td>
<td>920</td>
</tr>
<tr>
<td><img src="image2" alt="Dimer cation radical" /></td>
<td>476, 508</td>
<td>900</td>
</tr>
<tr>
<td><img src="image3" alt="Dimer cation radical" /></td>
<td>575</td>
<td>1351</td>
</tr>
<tr>
<td><img src="image4" alt="Dimer cation radical" /></td>
<td>680</td>
<td>1050</td>
</tr>
<tr>
<td><img src="image5" alt="Dimer cation radical" /></td>
<td>500</td>
<td>1400</td>
</tr>
</tbody>
</table>

The association of an aromatic cation radical with its neutral counterpart to form a dimer cation radical can also be gauged by EPR spectroscopic analysis.(42) For example, a comparison of the EPR spectra of monomeric \(\text{OMB}^{**}\) and dimeric \((\text{OMB})_2^{**}\) cation radicals in Figure 6 shows the doubling of the EPR lines with half the hyperfine splitting in dimeric \((\text{OMB})_2^{**}\) \((a_H = 2.25 \text{ G (12H)})\) when compared to that of monomeric \(\text{OMB}^{**}\) \((a_H = 4.50 \text{ G (24H)})\). As such, the EPR spectroscopic analysis suggests that a single hole is equally distributed between the two \(\text{OMB}\) moieties.(36) A number of dimeric cation radicals have been characterized by similar EPR analyses.(42)
Energetics of the Formation of Dimer Cation Radicals

To assess the energetics of the formation of intermolecular dimer cation radicals, we first take a closer look at the cyclophane-like bichromophoric electron donors as intramolecular models by cyclic voltammetry and electronic spectroscopy as follows.

The cyclic voltammetry of a representative series of cofacially arrayed (rigid) bichromophoric donors showed that they undergo the loss of a single electron at relatively lower potentials (∼0.2–0.4 V) when compared to the corresponding monochromophoric electron donors (Table 2). In addition, the cation radical of each cofacially arrayed bichromophoric donor showed an intense NIR transition in its electronic spectra that was similar to that observed for the intermolecular dimer cation radicals (cf. Tables 1 and 2).

Table 2. Comparison of Oxidation Potentials and Intervalance Transitions in a Series of Cyclophane-like Bichromophoric Donors and the Corresponding Model Monochromophoric Donors

<table>
<thead>
<tr>
<th>monomer, $E_{ox}$(V)</th>
<th>Dimer, $E_{ox}$(V)</th>
<th>Δ(V)</th>
<th>$\lambda_{max}$(nm) \textsuperscript{b} dimer\textsuperscript{**}</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.74</td>
<td>1.42</td>
<td>0.32</td>
<td>1210</td>
<td>26</td>
</tr>
<tr>
<td>1.11</td>
<td>0.78</td>
<td>0.33</td>
<td>-c-</td>
<td>43</td>
</tr>
<tr>
<td>1.18</td>
<td>0.80</td>
<td>0.38</td>
<td>1200</td>
<td>44</td>
</tr>
</tbody>
</table>

Figure 6. Experimental EPR spectra of monomeric OMB\textsuperscript{**} SbCl\textsubscript{6} (hyperfine splitting $a_H = 4.50$ G, $g$ value = 2.0023) and dimeric (OMB)\textsubscript{2}\textsuperscript{**} SbCl\textsubscript{6} (hyperfine splitting $a_H = 2.25$ G, $g$ value = 2.0023) cation radicals in dichloromethane at room temperature and a comparison with their calculated spectra.
A closer inspection of the X-ray crystal structures of various cyclophane-like bichromophoric donors in Table 2 revealed that the interplanar angles between the cofacially arranged aryl moieties varied from ~0 to 120° (Figure 7). As such, the structural comparison in Figure 7 suggests that a minimal orbital overlap between interacting π systems is sufficient for electronic coupling. Thus, a close but not necessarily complete cofacial approach of π systems in various cation radicals (Figure 7) allows for the stabilization of a single charge by ~0.18–0.38 V. As expected, the reduced overlap between the aryl moieties in ethanoanthracene derivatives (last two entries in Table 2) leads to a somewhat reduced stabilization of the cationic charge in their cation radicals (i.e., ~0.2 V) when compared to that of the corresponding model electron donors. Interestingly, the observation of a similar thermodynamic stabilization of the cationic charge by ~0.35 ± 0.03 V in various cyclophane-like bichromophoric cation radicals suggests that intermolecularly formed dimer cation radicals should also be stabilized by ~0.35 V (i.e., eq 3).

$$D^+ + \frac{K}{[D,D]^+} \quad \Delta G^\circ \approx -0.35 \text{V}$$

The free-energy change (Δ$G^\circ$) for the dimerization process in eq 3 can be readily estimated from the dimerization constant (K) (i.e., Δ$G^\circ = -RT \ln K$). Thus, value for the dimerization of OMB** with neutral OMB (K ≈ 300 M$^{-1}$, Figure 5) yielded a value of Δ$G^\circ = -0.15$ V, which is significantly lower than the value of ~−0.35 V expected on the basis of the stabilization of cyclophane-like bichromophoric cation radicals (Table 2). It is noted that in the case of rigid cyclophane-like bichromophoric donors (Table 2), the entropic component (TΔ$S^\circ$) of the overall Δ$G^\circ$ value (i.e., Δ$G^\circ = \Delta H^\circ - T\Delta S^\circ$) is expected to be negligible (vide infra). In contrast, however, the diffusional entropic penalty (TΔ$S^\circ$) for the formation of the intermolecular dimer cation radical in eq 3 is anticipated to be significant.(47)
Figure 7. Molecular structure of a series of electronically coupled cyclophane-like bichromophoric donors, obtained by X-ray crystallography, with drastically varied interplanar angles between the cofacially arranged aryl moieties ranging from $\sim 0$ to $120^\circ$.

To further assess the entropic contribution ($T\Delta S$) to the overall thermodynamic stabilization ($\Delta G$) of the hole in a dimer cation radical, we carefully scrutinize the energetics of the electron transfer of conformationally mobile bichromophoric electron donor tetramethoxydibenzo-bicyclo[4.4.1]undecane (1), its rigid cyclophane-like analog 2, and monochromophoric model compound 3 as follows.
Conformationally mobile bichromophoric electron donor 1 exists in rapidly interchanging mirror image (extended) conformations in the neutral state (eq 4). Upon one-electron oxidation, the extended conformation of 1 readily transforms into a cyclophane-like π-stacked structure (eq 4) as discussed below.

The electron-transfer-induced transformation of the extended conformer of 1 to its cofacially folded conformer in eq 4 was unequivocally established by isolation and X-ray crystallographic characterization of its cation radical 1** (Figure 8A). Furthermore, the observation of a highly characteristic charge-resonance transition at ~1200 nm in both 1** and 2** and its singular absence in monochromorphic 3** (Figure 8B) further corroborates that 1** adopts a cofacial conformation similar to that of cofacially locked 2**. Finally, the cyclic voltammograms of 1 and 2 showed their first reversible oxidation waves at potentials of 0.96 and 0.87 V vs SCE, respectively, whereas monochromophoric model donor 3 showed its reversible oxidation wave at a potential of 1.22 V (Figure 8C). A comparison of the thermodynamic oxidation potential in Figure 9 reveals that the $E_{\text{ox1}}$ values of 1 and 2 are lowered by 0.26 and 0.35 V, respectively, when compared to that of monochromophoric 3 (Figure 8C).

Because the charges in both 1** and 2** are stabilized by a similar cofacial conformation, a difference of ~90 mV between the $E_{\text{ox1}}$ values of 1 and 2 thus must arise from the entropic penalty for the conformational transformation of 1 upon one-electron oxidation in eq 4 (Figure 9).
**Figure 9.** Comparison of the relative oxidation potentials of the extended and folded conformers of 1 and monochromophoric model donor 3. Note that the oxidation potential of extended 1 was presumed to be same as for model monochromophoric 3.

Direct evidence for the conformation transformation of the extended cation radical of 1 into the cofacially stacked structure (eq 4 and Figure 9) was obtained by laser flash photolysis experiments. Thus, the transient absorption spectra in the NIR region obtained 100 ns after the laser excitation (10 ns) of chloranil in the presence of conformationally mobile 1 showed a weak absorption band centered at $\lambda_{\text{max}} \approx 1200 \text{ nm}$ (Figure 10C) that intensified as a function of time and acquired the maximum intensity in $\sim 2$ to 3 $\mu$s. In contrast, the transient spectrum of the cation radical of conformationally locked 2 in Figure 10A, generated under identical conditions, was formed within the laser pulse and attained the maximum intensity in only $\sim 100$ ns. It is further emphasized that the cation radical of monochromophoric model donor 3, generated similarly, lacked any absorption in the near-IR region. The fully evolved NIR transients at $\sim 1200 \text{ nm}$ in Figure 10C,A for $1^+$ and $2^+$, respectively, were characteristically similar to near-IR transitions observed in the steady-state spectra of $1^+$ and $2^+$ (cf. Figures 8 and 10).

**Figure 10.** Transient NIR absorption spectra of cation radicals of (C) 1 and (A) 2 from the laser flash photolysis of a 0.005 M solution of chloranil and 0.01 M 1 or 2 in a 1:1 acetonitrile–dichloromethane mixture following the 10 ns laser excitation at 355 nm. (B) Kinetic traces of the formation and decay of cation radicals of 1 (blue trace) and 2 (gray trace) at 22 °C.
A comparison of the kinetic traces for the formation and decay of cation radicals 1** and 2** at 1200 nm as a function of time confirms that the transient at 1200 nm for the cation radical of conformationally locked 2 was formed faster than the response function of our germanium detector (i.e., ~150 ns), whereas the transient at 1200 nm for the cation radical of conformationally mobile 1 grew in with a time constant of $t_{\text{rise}} \approx 1 \, \mu s.$\textsuperscript{48}

The discussion above establishes that an intermolecular association of a donor cation radical with its neutral counterpart stabilizes a cationic charge by $\sim 0.35 \, \text{V versus SCE}$ and the dimerization event is easily visualized by the appearance of an intense charge-resonance transition in the near-IR region of its electronic spectrum. It is also noted that a cationic charge in various cyclophane-like bichromophoric cation radicals is also stabilized by $\sim 0.35 \pm 0.03 \, \text{V}$ and thus suggests that intermolecularly formed dimer cation radicals must adopt a cofacially $\pi$-stacked structure similar to that of cyclophanes (Figure 7). Indeed, the X-ray crystallographic studies of representative dimer cation radicals, presented below, demonstrate that a single charge in a dimer cation radical is stabilized by a pair of cofacially arrayed sandwich-like donor moieties.

Crystallographic and Theoretical Evidence of Charge Delocalization in an OMB Dimer Cation Radical

To demonstrate that a single positive charge in a dimer cation radical is equally distributed between the two cofacially arrayed donor moieties, we carefully scrutinize the subtle structural changes in the octamethylbiphenylene (OMB) monomer and dimer cation radicals (i.e., OMB** and (OMB)$_2$**) in comparison to those in neutral OMB with the aid of X-ray crystallography and by DFT calculations as follows.

Thus, a deep blue solution of OMB** in dichloromethane was prepared by $1 - e^-$ oxidation using either triethyloloxonium hexachloroantimonate (Et$_3$O$^+\text{SbCl}_6^-$)\textsuperscript{30} or nitrosonium hexachloroantimonate (NO$^+\text{SbCl}_6^-$)\textsuperscript{49} at $\sim 0 \, ^\circ \text{C}$. The deep blue solution was cooled to $-50 \, ^\circ \text{C}$, and prechilled toluene was added. The resulting dark-blue precipitate of OMB** SbCl$_6^-$ was filtered and dried in vacuo. The subsequent recrystallization of the blue powder from a mixture of dichloromethane and hexane at $-30 \, ^\circ \text{C}$ afforded a good crop of single crystals of OMB** SbCl$_6^-$. The single crystals of dimer (OMB)$_2$** SbCl$_6^-$ were obtained from a mixture of dichloromethane and toluene at $-30 \, ^\circ \text{C}$ using a 1:1 mixture of OMB** SbCl$_6^-$ and neutral OMB. The molecular structures of OMB** SbCl$_6^-$ and (OMB)$_2$** SbCl$_6^-$ were unambiguously established by crystal structure analysis\textsuperscript{30,36} (Figure 11).

Figure 11

Figure 11. (A) Packing of pairs of OMB** cations with pairs of SbCl$_6^-$ anions in the crystal structure of OMB** SbCl$_6^-$. (B) Infinite stacks of octamethylbiphenylenes separated by columns of hexachloroantimonate anions in the crystal structure of (OMB)$_2$** SbCl$_6^-$. The packing arrangement of the crystals of monomeric OMB** SbCl$_6^-$ shows that they are packed as pairs of OMB** species separated by pairs of SbCl$_6^-$ anions in infinite alternating stacks (Figure 11A). The close cofacial proximity (with an interplanar separation of 3.2 Å) of two cationic OMB** moieties induces a slight bending of the OMB ring system. In contrast, the OMB molecules in crystals of (OMB)$_2$** SbCl$_6^-$ were absolutely planar and
were arranged in infinite stacks (with an interplanar separation of 3.4 Å) that were separated by intertwined columns of hexachloroantimonate anions as illustrated in Figure 11B.

For convenience, the equivalent bonds in OMB are denoted by lower-case bold letters a–e (Table 3). The molecular structure of neutral OMB shows considerable bond alternation due to the antiaromatic nature of the cyclobutane ring.\(^{[50, 51]}\) For example, C–C bond a in the cyclobutane ring of neutral OMB is considerably longer (1.522 Å) than the C\(_{ar}–C_{ar}\) bond (1.490 Å) found in various biphenyls.\(^{[52]}\) Moreover, bonds b and d are significantly elongated as compared to bonds c and e in the two benzene rings (Table 3). In monomeric cation radical OMB\(^{•+}\), the removal of an electron resulted in a considerable shortening (5 pm) of bonds a in the cyclobutane ring and a lengthening of bonds b (3 pm) and e (4 pm) in the aromatic rings. Interestingly, adjacent bonds c and d were elongated and contracted, respectively, by about 2 pm (Table 3). Furthermore, a comparison of the contraction and elongation of bonds a–e in dimeric cation radical (OMB)\(^{•+}_{2}\) with neutral OMB showed that the changes in various bond lengths were approximately one-half of those in monomeric cation radical OMB\(^{•+}\) (Table 3). As such, the structural comparisons above confirm the complete delocalization of a single positive charge over two OMB molecules within a dimeric cation radical.

Table 3. Experimental and Calculated Bond Lengths of the Neutral, Monomer, and Dimer Cation Radicals of Octamethylbiphenylene (OMB) in Picometers, with the Labeling Scheme for the Bonds in OMB and its HOMO Obtained by DFT Calculations at the B3LYP/6-31G* Level Shown Below\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>X-ray crystallography</th>
<th>B3LYP/6-31G*</th>
</tr>
</thead>
<tbody>
<tr>
<td>bond (b)</td>
<td>OMB</td>
<td>OMB</td>
</tr>
<tr>
<td>a</td>
<td>152.2</td>
<td>147.5 (−4.7)</td>
</tr>
<tr>
<td>b</td>
<td>141.8</td>
<td>145.0 (+3.2)</td>
</tr>
<tr>
<td>c</td>
<td>136.5</td>
<td>138.6 (+2.1)</td>
</tr>
<tr>
<td>d</td>
<td>143.5</td>
<td>141.6 (−1.9)</td>
</tr>
<tr>
<td>e</td>
<td>139.1</td>
<td>143.3 (+4.2)</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>0.5</td>
<td>0.4</td>
</tr>
</tbody>
</table>

\(^a\) Numbers in parentheses indicate the bond length changes relative to neutral OMB. Calculations were performed using the Spartan 08 software package.

\(^b\) Average of equivalent bonds.

The experimental observation of the bond-length changes in OMB\(^{•+}\) and (OMB)\(^{•+}_{2}\) can be reproduced by DFT calculations on the B3LYP/6-31G* level\(^{[53]}\) (Table 1). Furthermore, the experimentally observed elongation and contraction of the bonds in OMB\(^{•+}\) track remarkably well with the nodal structure of the HOMO (Table 3). Thus, the bonds in OMB that undergo elongation (i.e., bonds b, c, and e) upon oxidation position the largest bonding character of HOMO, and the bonds that undergo contraction (i.e., bonds a and d) position the largest antibonding character of HOMO (Table 3).

The crystallographic and theoretical analyses of the structural changes in (OMB)\(^{•+}_{2}\) in comparison to those of neutral OMB, presented above, clearly demonstrate that a single positive charge in a dimer cation radical is equally distributed between a pair of cofacially arrayed OMB moieties, resulting in intervalence OMB molecules (i.e., with each OMB bearing half of the positive charge). The packing arrangement of (OMB)\(^{•+}_{2}\) SbCl\(_6\)\(^−\) in Figure
Polychromophoric Mixed-Valence Cation Radicals for Two-Dimensional Charge-Transport Assemblies

The X-ray crystallography of a number of mixed-valence monochromophoric benzenoid cation radicals, including the mixed valence OMB cation radicals discussed above, has shown that owing to the anisotropic nature of the benzenoid donors they generally assemble in 1D stacks that are separated by counteranions. Figure 12 shows additional representative examples of the 1D stacking of mixed-valence cation radicals derived from naphthalene, octamethylandrocene, and perylene.

Figure 12. Representative examples of 1D π stacking in mixed-valence (naphthalene)$_2$PF$_6$– (A), (octamethylandrocene)$_2$SbCl$_6$– (B), and (perylene)$_2$PF$_6$– (C) cation radicals, as established by X-ray crystallography.

To design materials in which the charge transport in solid-state assemblies can occur in two or three dimensions, one requires well-defined rigid polychromophoric molecules in which the chromophores are electronically coupled. The assembly of such mixed-valence polychromophoric cation radicals, where the charge is delocalized onto all of the chromophores, may lead to 2D or 3D charge-transport arrays (e.g., Figure 4B).

As discussed above with the aid of a series of bichromophoric molecules (Figure 7), the electronic coupling among the cofacially oriented aryl moieties does not necessarily require a perfect sandwich-like geometry. A single hole (or cationic charge) can be effectively delocalized over a pair of arene moieties even if the interplanar angles between the cofacially arranged aryl moieties varied to as large as 120°. For example, we and others have shown that a hole (formed by the removal of a single electron) can hop among multiple cofacially oriented aryl moieties in various hexaarylbenzene derivatives as judged by the appearance of a characteristic near-infrared (NIR) intervalence transition in the absorption spectra of their cation radicals (e.g., Figure 13).
From the standpoint of the preparation of higher-order charge-transport materials, triptycene and its derivatives are fundamentally important molecules in which three equivalent benzenoid rings are cofacially oriented at an angle of \( \sim 120^\circ \). For example, we will show with the aid of electrochemistry, electronic spectroscopy, and X-ray crystallography that there is effective electronic coupling among the three benzenoid rings in triptycene derivatives.\(^{(64)}\)

To demonstrate that a single charge is effectively delocalized among all three benzenoid rings in hexamethoxytriptycene (T3), we also employed two model compounds containing one and two dimethoxybenzene rings (i.e., T1 and T2 (Figure 14A)).

First, the electrochemical oxidation of T1–T3 in CH\(_2\)Cl\(_2\) revealed that the first wave in the reversible cyclic voltammograms of T1–T3 corresponds to the production of the monocation radical (by transfer of one electron) at \( E_{\text{ox1}} = 1.22, 1.11, \) and 1.00 (V vs SCE), respectively (Figure 14B). The second oxidation in T2 (\( E_{\text{ox2}} = 1.39 \) V) and the second and third oxidations in T3 (\( E_{\text{ox2}} = 1.29 \) and \( E_{\text{ox3}} = 1.78 \) V) occur at relatively higher potentials and thus are indicative of the fact that the cationic charge introduced by the removal of first electron is effectively delocalized among the cofacially oriented dimethoxybenzenoid moieties. As such, the lowered first oxidation potentials of T2 and T3 by \( \sim 110 \) and \( \sim 220 \) mV, respectively, as compared to those of model monochromophoric donor T1 corroborate the significant stabilization of the cationic charge by the cofacially arrayed dimethoxybenzenoid rings in T2 and T3.

The cation radicals of T1–T3 in solution were easily generated by one-electron oxidation using a hydroquinone ether cation radical\(^{(65)}\) (CRET\({}^{\ddagger}\)), \( E_{\text{red}} = 1.11 \) V vs SCE, \( \lambda_{\text{max}} = 518 \) nm, \( \varepsilon_{518} = 7300 \) M\(^{-1}\) cm\(^{-1}\)) or a hindered
naphthalene cation radical\(^{(66)}\) \((\text{NAP}^+\cdot, E_{\text{red}} = 1.34 \text{ V vs SCE}, \lambda_{\text{max}} = 672, 616, 503, \text{ and } 396 \text{ nm}, \varepsilon_{672} = 9300 \text{ M}^{-1} \text{ cm}^{-1})\)(34) as stable (aromatic) one-electron oxidants.

The absorption spectra of \(\text{T1}^{+\cdot} (\lambda_{\text{max}} = 461 \text{ nm}, \varepsilon_{461} = 5200 \text{ M}^{-1} \text{ cm}^{-1}), \text{T2}^{+\cdot} (\lambda_{\text{max}} = 420, 1560 \text{ nm}, \varepsilon_{1560} = 8400 \text{ M}^{-1} \text{ cm}^{-1}),\) and \(\text{T3}^{+\cdot} (\lambda_{\text{max}} = 408, 1510 \text{ nm}, \varepsilon_{1510} = 18\,300 \text{ M}^{-1} \text{ cm}^{-1})\) in dichloromethane solutions are compiled in Figure 14C. The observation of intense NIR transitions in the absorption spectra of bichromophoric \(\text{T2}^{+\cdot}\) and trichromophoric \(\text{T3}^{+\cdot}\) should be contrasted with a singular lack of any absorption beyond 500 nm in the absorption spectrum of monochromophoric cation radical \(\text{T1}^{+\cdot}\) (Figure 14C). Moreover, the fact that the NIR transition in \(\text{T3}^{+\cdot} (\lambda_{\text{max}} = 1510 \text{ nm})\) is roughly twice as intense as in \(\text{T2}^{+\cdot} (\lambda_{\text{max}} = 1560 \text{ nm})\) further indicated the increased probability of hole migration over three dimethoxybenzenoid rings in \(\text{T3}^{+\cdot}\) as opposed to only two rings in \(\text{T2}^{+\cdot}\).

Finally, the molecular structure of \(\text{T3}^{+\cdot} \text{SbCl}_6^{-}\), generated using equimolar \text{NO}^+ \text{SbCl}_6^{-} \text{ at } -10 \text{ °C in a mixture of dichloromethane and toluene, was established by X-ray crystallography (Figure 14D). A closer look at the structural parameters of the dimethoxybenzenoid groups in } \text{T3}^{+\cdot} \text{ suggests that they are identical (within the experimental precision of } \sim 0.006 \text{ Å for various C}–\text{C/C}–\text{O bond lengths) and thus that the cationic charge is evenly distributed over all three aryl rings in } \text{T3} \text{ (Table 4).(11, 12) Furthermore, the bond-length changes in } \text{T3}^{+\cdot} \text{ in comparison with those of neutral } \text{T3} \text{, the structure of which was established by X-ray crystallography, correspond to the significant shortening of bonds labeled a and the elongation of bonds labeled e and f, along with a marginal shortening of bonds labeled b and c (Table 4). More importantly, the experimentally observed contraction and elongation of various bonds in } \text{T3}^{+\cdot} \text{ are roughly one-third when compared to the corresponding bond-length changes in } \text{T1}^{+\cdot}, \text{ the structure of which was similarly established by X-ray crystallography. Such an observation is consistent with the fact that a single hole (or cationic charge) is delocalized over three benzenoid rings in } \text{T3}^{+\cdot}, \text{ whereas in } \text{T1}^{+\cdot} \text{ a single charge is localized onto only one aromatic ring.}

**Table 4.** Experimental and Theoretical Bond Lengths of the Neutral and Cation Radicals of \(\text{T1}\) and \(\text{T3}\) in Picometers

<table>
<thead>
<tr>
<th>bond</th>
<th>(\text{T3})</th>
<th>(\text{T3}^{+\cdot})</th>
<th>(\text{T1})</th>
<th>(\text{T1}^{+\cdot})</th>
<th>(\text{T3})</th>
<th>(\text{T3}^{+\cdot})</th>
<th>(\text{T1})</th>
<th>(\text{T1}^{+\cdot})</th>
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<tbody>
<tr>
<td>a</td>
<td>134.3 ((-2.3))</td>
<td>137.5</td>
<td>132.2 ((-5.3))</td>
<td>137.2</td>
<td>135.0 ((-2.2))</td>
<td>136.5</td>
<td>131.9 ((-4.6))</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>139.8</td>
<td>139.6 ((-0.2))</td>
<td>137.7</td>
<td>139.1 (+1.4))</td>
<td>139.2</td>
<td>138.4 ((-0.8))</td>
<td>138.7</td>
<td>139.7 (+1.0))</td>
</tr>
<tr>
<td>c</td>
<td>139.6</td>
<td>139.5 ((-0.1))</td>
<td>141.1</td>
<td>138.1 ((-3.0))</td>
<td>139.0</td>
<td>138.9 ((-0.1))</td>
<td>141.2</td>
<td>138.3 ((-2.9))</td>
</tr>
<tr>
<td>d</td>
<td>154.2</td>
<td>153.4 ((-0.8))</td>
<td>153.6</td>
<td>152.5 ((-1.1))</td>
<td>154.0</td>
<td>153.0 ((-1.0))</td>
<td>153.8</td>
<td>152.9 ((-0.9))</td>
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<tr>
<td>e</td>
<td>141.3</td>
<td>143.4 (+2.1)</td>
<td>140.7</td>
<td>144.2 (+3.5)</td>
<td>141.1</td>
<td>142.3 (+1.2)</td>
<td>141.5</td>
<td>145.6 (+4.1)</td>
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<tr>
<td>f</td>
<td>139.6</td>
<td>141.2 (+1.6)</td>
<td>139.3</td>
<td>144.6 (+5.3)</td>
<td>138.8</td>
<td>140.5 (+1.7)</td>
<td>140.3</td>
<td>145.8 (+5.5)</td>
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<td>g</td>
<td>141.5</td>
<td>142.7 (+1.2)</td>
<td>142.2</td>
<td>145.7 (+3.5)</td>
<td>142.7</td>
<td>143.8 (+1.1)</td>
<td>141.6</td>
<td>144.3 (+2.7)</td>
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<tr>
<td>σ</td>
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<td>0.3</td>
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*a Average of equivalent bonds.

*b Numbers in parentheses indicate the bond length changes relative to a neutral donor. Calculations were performed using the Spartan 08 software package.

It is also noted that the experimental observations of the bond-length changes in monochromoporic \(\text{T}1^{+\bullet}\), where a single charge is localized onto one dimethoxybenzene ring, and terchromophoric \(\text{T}3^{+\bullet}\), where a single charge is delocalized onto three dimethoxybenzene rings, were found to be in good agreement with the values obtained by DFT calculations at the B3LYP/6-31G* level (Table 4).

The molecules of intervalence triptycene cation radicals (\(\text{T}3^{+\bullet}\)) can pack closely to each other in solid-state assemblies via the energetically favorable cofacial stacking of their dimethoxybenzenoid moieties. As depicted in Figure 15, the molecules of \(\text{T}3^{+\bullet}\) produce a 2D quasi-hexagonal assembly in which all of the aryl rings are electronically coupled either because they are part of the triptycene framework or they are stacked in a sandwich-like geometry with the aryl group of the neighboring triptycene molecule and therefore produce a 2D electronically coupled assembly of intervalence \(\text{T}3^{+\bullet}\) in its crystal structure.

**Figure 15**

![Ultimate 2D electronically coupled solid-state assembly of the hexamethoxytriptycene cation radical (T3** SbCl6−) as determined by X-ray crystallography.](image)

The complete packing diagram of the highly colored crystals of \(\text{T}3^{+\bullet}\) SbCl6− contains 2D layers of cationic \(\text{T}3^{+\bullet}\) (shown in Figure 15) in crystallographic plane \(ac\) and disordered dichloromethane molecules that fill the holes in these layers (Figure 16). The \(\text{T}3^{+\bullet}\) layers are separated from each other along the \(y\) axis with layers of hexachloroantimonate anions and solvent molecules (Figure 16).
Figure 16. Packing diagram of T3** SbCl6– showing that the SbCl6– counteranions are embedded between layers of cationic T3** and an additional disordered chain of solvent molecules fills the holes in the T3** layers.

It is further emphasized that in the T3** layers each benzenoid ring is involved in cofacial interactions with the aryl ring of neighboring molecules, with a center-to-center interplanar distance that is close to the van der Waals separation (i.e., ~3.4 Å). As such, all of the aryl rings in 2D triptycene layers in Figure 15 or 16 are electronically coupled[36, 64] and thus are capable of long-range charge transport.

Conclusions

In summary, we demonstrate that the close cofacial approach ($d \approx 3.4$ Å) of the octamethylbiphenylene (OMB) cation radical to its neutral counterpart leads to strong electronic interactions between the two OMB moieties, which results in a charge-resonance transition[67] in the NIR region in the electronic absorption spectrum. The comparison of the X-ray structures of monomeric and dimeric cation radicals of OMB further confirmed that this charge resonance results in an even delocalization of the positive charge over two donor molecules as established by the analysis of the changes in bond lengths and DFT calculations.

Using a series of cyclophane-like bichromophoric donors with varied interplanar angles ranging from 0 to 120° between the two benzenoid rings, we demonstrate that a close, but not necessarily complete, cofacial approach of π systems in various bichromophoric cation radicals allows effective electronic coupling between the interacting aryl moieties and results in charge-resonance transitions in the UV–vis–NIR absorption spectra similar to those observed for the intermolecular dimeric cation radicals.
The isolation and X-ray crystal structure determination of the neutral and cation radical of a terchromophoric triptycene donor (T3) and the DFT calculations provided unequivocal evidence that a single charge is evenly distributed over all three benzenoid moieties oriented at 120°. As a proof of concept, we also demonstrated with the aid of X-ray crystallography that the hexamethoxytriptycene cation radical assembles into a 2D solid-state assembly for efficient long-range charge transport and that such polychromophoric molecules may hold potential for photovoltaic applications. Continuing efforts are needed to identify novel electronically coupled polychromophoric donors that can produce 3D charge-transport assemblies for long-range charge transport for modern material applications.

Acknowledgment

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The preliminary determination of the entropy of the dimerization of OMB** and neutral OMB showed a value of \( \sim 0.18 \text{ eV} \) at 22 \(^\circ\text{C}\).
transfer complexes in which the positive charge is completely delocalized over both the donor (D) and acceptor (D••).