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**Molecular Actuators in Action: Electron-Transfer-Induced Conformation Transformation in Cofacially Arrayed Polyfluorenes**

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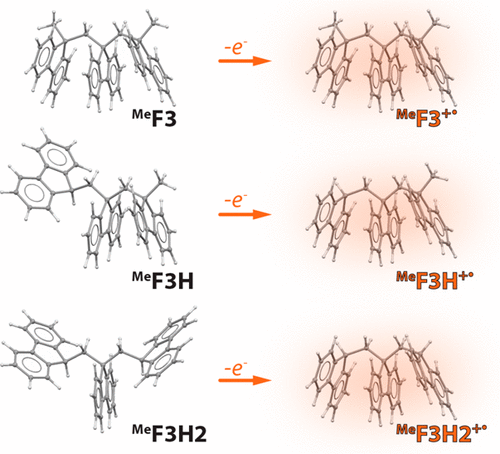
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# Abstract



There is much current interest in the design of molecular actuators, which undergo reversible, controlled motion in response to an external stimulus (light, heat, oxidation, etc.). Here we describe the design and synthesis of a series of cofacially arrayed polyfluorenes (MeF*n*H*m*) with varied end-capping groups, which undergo redox-controlled electromechanical actuation. Such cofacially arrayed polyfluorenes are a model molecular scaffold to investigate fundamental processes of charge and energy transfer across a π-stacked assembly, and we show with the aid of NMR and optical spectroscopies, X-ray crystallography and DFT calculations that in the neutral state the conformation of MeF*n*H1 and MeF*n*H2 is open rather than cofacial, with a conformational dependence that is highly influenced by the local environment. Upon (electro)chemical oxidation, these systems undergo a reversible transformation into a closed fully π-stacked conformation, driven by charge-resonance stabilization of the cationic charge. These findings are expected to aid the design of novel wire-like cofacially arrayed systems capable of undergo redox-controlled actuation.

The design and development of molecular actuators, which exhibit a controlled, reversible motion in response to an external stimulus, continue to attract much interest due to the extensive use of molecular actuators in such applications as biomechanical devices,[(1,2)](javascript:void(0);) molecular electronics,[(3,4)](javascript:void(0);) and supramolecular chemistry.[(5,6)](javascript:void(0);) Among various external stimuli that can induce mechanical actuation, electron transfer is of particular importance.[(7−12)](javascript:void(0);) It is now appreciated that molecular assemblies based on the π-stacked aromatic moieties are capable of substantial charge resonance stabilization,[(13−16)](javascript:void(0);) and thus actuators based upon π-stacked assemblies hold significant promise. In addition, these molecular scaffolds often serve as synthetically designed models of naturally occurring molecular assemblies such as DNA where the paired bases are orderly stacked inside helical strands ([Figure 1](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig1)).

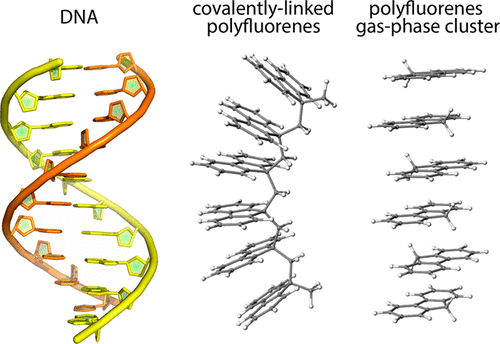
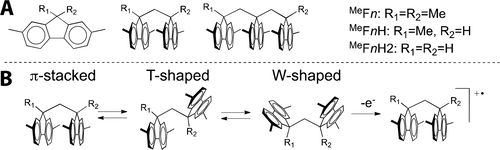


Figure 1. Structures of DNA, covalently linked π-stacked polyfluorene F6 and displaced-stacked fluorene cluster (F)6.

First developed by Rathore and co-workers,[(17,18)](javascript:void(0);) π-stacked polyfluorenes (F*n*, [Figure 1](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig1)) have served as a model system to study fundamental process of charge/energy delocalization and transfer across a π-stacked assembly.[(19−22)](javascript:void(0);) For example, efficient (cofacial) orbital overlap between adjacent fluorenes in F*n* promotes extensive hole delocalization, as evidenced from the decreasing (adiabatic) oxidation potentials in solution and (vertical) ionization energies in gas phase with increasing number of fluorenes.[(17,23)](javascript:void(0);) In contrast to the structurally well-defined F*n* series, the van der Waals clusters of fluorenes in the gas phase, i.e., (F)*n*, may exist in numerous conformations stabilized by a combination of CH−π and π–π interactions.[(23)](javascript:void(0);) Yet upon ionization, configurations that consist of displaced fully π-stacked (F)*n* clusters are observed ([Figure 1](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig1)), suggesting the increasing role of the cofacial arrangement in the cation radical state as compared to the neutral state.[(23)](javascript:void(0);) Indeed, it is well-known for the simplest model system, the benzene dimer, that in the neutral state a non-π-stacked conformation is preferred (i.e., T-shaped), while at the cation radical (and also at the excited state) a sandwich-like π-stacked arrangement is the global minimum.[(16,24−26)](javascript:void(0);) In the same vein, many conformationally mobile bichromophoric actuators at neutral state exist in the (noncofacial) open conformation, yet upon ionization reorganize into a (cofacial) closed conformation.[(9−11)](javascript:void(0);)

Motivated by the importance of a polyfluorene scaffold as a model π-stacked assembly and the interest in identification of novel redox-controlled actuators, we designed a set of polyfluorenes (denoted MeF*n*H*m*, *n* = 1–3, *m* = 0–2, [Scheme 1](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#sch1)A) with varied end-capping groups (R1/2 = H or Me). We will show with the aid of electrochemistry, electronic spectroscopy of polyfluorene cation radicals and DFT calculations that depending on the end-capping groups, these MeF*n*H*m* assemblies in the neutral state may exist in the (noncofacial) open conformation, and upon oxidation undergo reorganization into a fully π-stacked assembly, irrespective of the end-capping groups. For example, considering a bifluorene, three neutral state conformations are possible, i.e., π-stacked, T-shaped, and W-shaped. The relative energy ordering of these conformations is controlled by the end-capping group; however, upon oxidation the bifluorene is transformed into a π-stacked conformation *irrespective* of the end-capping group ([Scheme 1](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#sch1)B).



Scheme 1. (A) Structures of MeF*n*H*m* (*n* = 1–3, *m* = 0–2) and (B) Three Possible Conformations of F2H*m* that upon Oxidation Transform into a π-Stacked Structure

Accordingly, in this work, we demonstrate that a series of polyfluorenes MeF*n*H*m* undergoes a redox-controlled mechanical motion that is driven by the charge-resonance stabilization of the cationic charge between adjacent cofacially juxtaposed fluorene rings. The novel MeF*n*H*m* series presents an excellent case to study the conformational transformation induced by electron transfer in extended π-stacked assemblies. These findings will aid to the design and preparation of novel multilayered π-stacked systems, which not only allow the study of charge-transfer phenomenon through stacked aromatic moieties, but will also aid to the development of (next-generation) conducting wire-like assemblies capable of undergoing redox-controlled actuation.

# Exploratory Conformational Analysis of F2, F2H, and F2H2

The bifluorene F2 and its derivatives with varied end-capping groups (i.e., F2H and F2H2) serve as model covalently linked systems that can be used to probe the influence of the end-capping group on the relative stability of various conformations. Initially, we performed a detailed conformation analysis of F2, F2H, and F2H2 at the M06-2X/6-31G(d)+PCM(CH2Cl2) level of theory[(27,28)](javascript:void(0);) with the aid of relaxed potential energy surface (PES) scans of dihedral angles θ and φ, i.e., a pair of geometrical parameters that define the relative arrangement of two fluorenes ([Figure 1](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig1)A). The PES scans of each bifluorene produced contour plots ([Figure 1](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig1)A), where the color represents the relative energy of the bifluorene at fixed values of θ and φ with other geometrical parameters being optimized. These plots show that in all three cases at least three different conformations are possible, i.e., π-stacked, T-shaped, and W-shaped; note that unsymmetrical F2H has two T-shaped conformations.

The calculations further predict that a (closed) π-stacked conformation of F2 is the global minimum structure, which is consistent with experimental NMR spectra of F2 in CH2Cl2 solution ([Figure 2](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig2)B) as well as with the previous studies. Once the end-capping groups are changed from bulky methyl groups into much smaller hydrogens in F2H and F2H2, calculations predict that (open) non π-stacked conformations become nearly isoenergetic with the π-stacked conformations (Table S2 in the [Supporting Information](https://0-pubs-acs-org.libus.csd.mu.edu/doi/suppl/10.1021/acs.jpclett.8b01918/suppl_file/jz8b01918_si_001.pdf)). Indeed, comparison of the simulated NMR spectra of F2H and F2H2 with the experimental spectra showed that in solution the W-shaped conformation is the global minimum structure for both bifluorenes ([Figure 2](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig2)B).

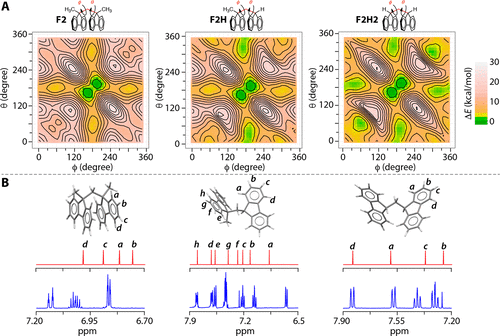
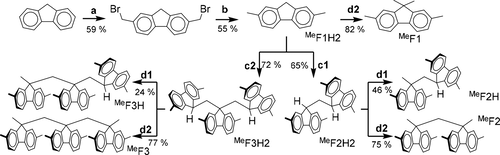


Figure 2. (A) Two-dimensional relaxed potential energy maps of F2, F2H, and F2H2 obtained using M06-2X/6-31G(d)+PCM(CH2Cl2). Dihedral angles θ and φ were varied from 0° to 360° with 15° step size. At each step θ and φ were fixed, while remaining geometrical parameters were optimized. (B) Calculated NMR spectra (red) of π-stacked F2, W-shaped F2H, and F2H2; experimental NMR spectra (blue) of F2, F2H, and F2H2.

Motivated by the accessibility of the open conformation in bifluorenes F2H and F2H2, we have synthesized the polyfluorene series MeF*n*H*m* ([Scheme 1](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#sch1)A) with methyl groups at the 2, 7 positions in each fluorene, which are expected to follow the same trends in conformational stability but better stabilize the cation radical state.

# Synthesis

A series of polyfluorenes MeF*n*H*m* were synthesized from fluorene using the synthetic route illustrated in [Scheme 2](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#sch2).



Scheme 2. Synthetic Route of MeF*n*H*m* (*n* = 1–3, *m* = 0–2)

Initial bromomethylation of fluorene was followed by debromination with lithium aluminum hydride (LAH) to produce 2,7-dimethylfluorene,[(29)](javascript:void(0);) which was converted to MeF*n*H2 (*n* = 2 and 3) by condensation with varying equivalent of paraformaldehyde and potassium *tert*-butyloxide as catalyst. Finally, monomethylation or double-methylation was achieved to generate MeF*n*H (*n* = 2 and 3) and MeF*n* (*n* = 1, 2 and 3) in excellent yield using iodomethane as methylation reagent and *tert*-butyloxide as base. Structures of MeF*n*H*m* were fully characterized by 1H/13C NMR, MALDI-TOF mass spectroscopies and X-ray crystallography of representative compounds (see [Supporting Information](https://0-pubs-acs-org.libus.csd.mu.edu/doi/suppl/10.1021/acs.jpclett.8b01918/suppl_file/jz8b01918_si_001.pdf) for full details). Crystal structures of MeF*n* (*n* = 2, 3) revealed the presence of fully π-stacked structures, while structures of MeF2H and MeF2H2 were found in an open T-shaped conformation stabilized by multiple CH-π interactions ([Figure 3](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig3)). Interestingly, MeF3H2 contains no stacked fragments but rather the open T-shaped configurations of the two bifluorene moieties ([Figure 3](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig3)).

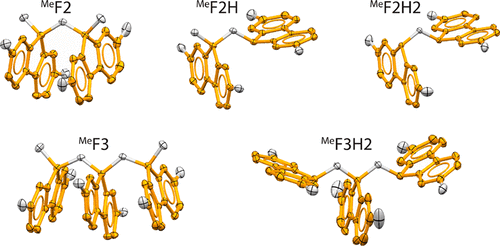


Figure 3. ORTEP diagrams (50% probability) of MeF2, MeF2H, MeF2H2, MeF3, and MeF3H2. Hydrogen atoms have been omitted for the sake of clarity.

# Electrochemistry

The redox properties of MeF*n*H*m* were evaluated by electrochemical oxidation at a platinum electrode as a 2 mM solution in CH2Cl2 containing 0.1 M *n*-Bu4N+PF6– as the supporting electrolyte and referenced to ferrocene (i.e., Fc/Fc+) as internal standard. Although MeF1H2 displays an irreversible CV, the position of its oxidation wave is identical to that of MeF1, which shows the reversible CV with the oxidation potential *E*ox = 1.02 vs Fc/Fc+ ([Figure 4](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig4)A). This suggests that the presence of methyl groups at 9 position does not impact the redox properties of the fluorenes, allowing us to establish whether MeF*n*H*m* (*m* = 1, 2) undergo redox-controlled actuation by comparing their redox properties with those of model MeF*n*, which are known to exist in the closed (π-stacked) conformation in both neutral and cation radical states.[(17)](javascript:void(0);)

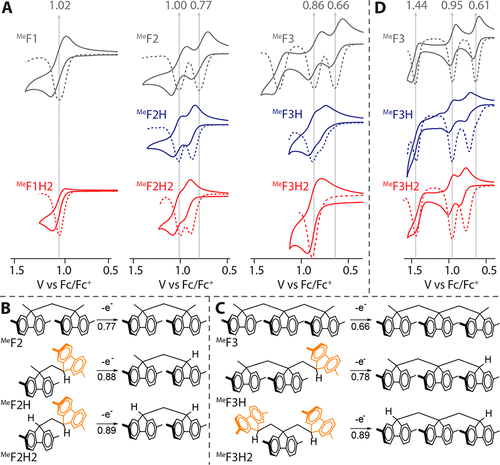


Figure 4. (A) Cyclic voltammograms (solid lines) and square wave voltammograms (dashed lines) of 2.0 mM MeF*n*H*m* in CH2Cl2 (0.1 M *n*-Bu4N+PF6–) with a scan rate of 100 mV/s. Values of the oxidation potentials of model (π-stacked) MeF*n* are indicated in gray color. Schematic description the oxidation-induced conformation transformation in (B) MeF2H*m* and (C) MeF3H*m* (*m* = 0–2). (D) Cyclic voltammograms (solid lines) and square wave voltammograms (dashed lines) of 2.0 mM MeF3H*m* in CH2Cl2 (0.1 M *n*-Bu4N+TFAB–) with a scan rate of 100 mV/s.

In the case of bifluorenes, the first oxidation potential (*E*ox1) is the lowest for π-stacked MeF2, while *E*ox1 of MeF2H and MeF2H is by 0.11–0.12 V higher than that in MeF2H2 ([Figure 4](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig4)A, [Table1](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#tbl1)). It has been established that the stabilization of the cationic charge (i.e., hole) is determined by the interplay between the energetic gain from delocalization and energetic penalty from structural, conformational and solvent reorganization.[(30,31)](javascript:void(0);) Therefore, the variation of *E*ox1 in the MeF2H*m* series suggests a different degree of oxidation-induced reorganization between MeF2 and MeF2H/MeF2H2, and somewhat similar reorganization in MeF2H and MeF2H2.

**Table 1. First (*E*ox1) and Second (*E*ox2) Oxidation Potentials of MeF*n*H*m* Referenced to Fc/Fc+ with 0.1 M *n*-Bu4N+PF6– as Supporting Electrolyte, Wavelengths of Maximum Absorption (λ, nm), and Extinction Coefficients (ε, M–1 cm–1) of MeF*n*H*m*+•**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | *E*ox1 | *E*ox2 | λ, nm | ε, M–1cm–1 |
| **MeF1** | **1.02** | **–** | **655** | **–** |
| **MeF1H2** | **1.02** | **–** | **655** | **–** |
| **MeF2** | **0.77** | **1.00** | **1455** | **5134** |
| **MeF2H** | **0.88** | **1.00** | **1454** | **4839** |
| **MeF2H2** | **0.89** | **1.00** | **1494** | **4000** |
| **MeF3** | **0.66** | **0.86** | **1605** | **4040** |
| **MeF3H** | **0.78** | **0.87** | **1528** | **3732** |
| **MeF3H2** | **0.89** | **0.89** | **1530** | **4826** |

While in solution MeF2 exists in π-stacked conformation in both neutral and cation radical states, neutral MeF2H2 and MeF2H exist in open conformations and upon oxidation undergo reorganization into a closed π-stacked conformation ([Figure 4](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig4)B), which requires an additional energetic penalty to overcome the conformational reorganization. As the first oxidation transforms MeF2H2 and MeF2H into a π-stacked conformation, their second oxidation occurs at the same potential as in MeF2 ([Figure 4](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig4)A).

As for the bifluorenes, MeF3 displays the lowest first oxidation potential across the MeF3H*m* series due to the stacked arrangement of fluorenes in both neutral and cation radical states, which affords efficient hole stabilization ([Figure 4](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig4)C). The first oxidation potential of MeF3H is by 0.12 V higher than that of MeF3 due to the additional oxidation-induced reorganization associated with bringing *one* fluorene moiety into the stacked arrangement. In MeF3H2, an additional 0.11 V as compared to MeF3H (or 0.23 as compared to MeF3) is required to bring *two* fluorene moieties into the stack. On the basis of the analysis of the first oxidation potentials of MeF2H*m* and MeF3H*m* series ([Table1](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#tbl1)) we conclude that the energetic cost of bringing one fluorene into the stacked arrangement upon the first oxidation lies in 0.11–0.12 V range. The second oxidation potential is nearly identical across the MeF3H*m* series ([Table1](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#tbl1)) suggesting that after the first electron transfer all three compounds indeed exist in a fully π-stacked conformation.

The increasing reorganization penalty in going from MeF3 to MeF3H to MeF3H2 is clearly seen by inspection of their CVs, which show well-separated first and second oxidation waves in MeF3, two closely spaced waves in MeF3H, and two coalesced waves in MeF3H2 ([Figure 4](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig4)A). However, it is well-known that the separation between first and second oxidation waves is modulated by the ion pairing of the oxidized species with the counteranions.[(32,33)](javascript:void(0);) In order to reduce the effects of ion pairing we performed an additional electrochemical analysis with the bulky tetrakis(pentafluorophenyl)borate (TFAB–) anion. The resulting CVs in [Figure 4](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig4)D show two well separated oxidation waves in all three cases, with the splitting between two waves decreasing when going from MeF3 to MeF3H to MeF3H2, in agreement with the above analysis.

# Generation of Cation Radicals of MeF*n*H*m*

In order to further probe whether upon oxidation of MeF*n*H*m* the corresponding cation radical exists in a fully π-stacked conformation, we resorted to electronic spectroscopy. Cation radicals of MeF*n*H*m* were generated in solution via quantitative[(34,35)](javascript:void(0);) redox titrations using a stable one-electron aromatic oxidant, such as [THEO+•SbCl6–] (1,4,5,8-dimethano-1,2,3,4,5,6,7,8-octahydro-9,10-dimethoxyanthracene hexachloroantimonate; *E*red = 0.67 V vs Fc/Fc+, λmax = 518, ε = 7300 M–1 cm–1) and [NAP+•SbCl6–] (NAP = 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrotetracene, *E*red = 0.94 V vs Fc/Fc+, λmax = 673 nm, εmax = 9300 cm–1 M–1). Each redox titration experiment was carried out by an incremental addition of substoichiometric amounts of MeF*n*H*m* to the solution of oxidant (i.e., THEO+• or NAP+•). At each titration point a numerical deconvolution procedure was employed to produce mole fraction plots of each species involved in the redox reaction.

[Figure 5](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig5)A shows the electronic absorption spectra obtained upon an incremental (substoichiometric) addition of a CH2Cl2 solution of MeF3H to a solution of [NAP+•SbCl6–] at 22 °C. A plot of the mole fractions of NAP+• and MeF3H+• against the added equivalents of MeF3H+• established a 1:1 stoichiometry of the redox reaction ([Figure 5](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig5)B), i.e. the one-electron oxidation of MeF3H to MeF3H+• and reduction of NAP+• to NAP can be described by an equilibrium: NAP+• + MeF3H ⇄ NAP + MeF3H+•. Following this approach cation radical spectra of the MeF*n*H*m*+• have been generated and the complete details are shown in the [Supporting Information](https://0-pubs-acs-org.libus.csd.mu.edu/doi/suppl/10.1021/acs.jpclett.8b01918/suppl_file/jz8b01918_si_001.pdf).

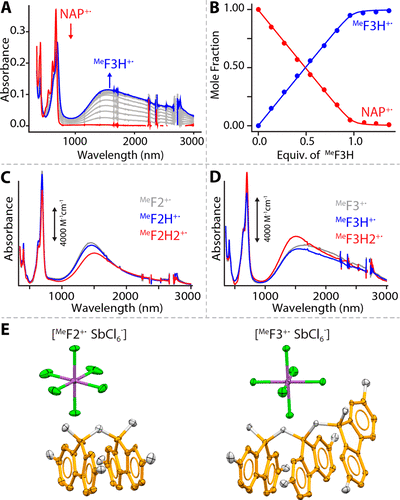


Figure 5. (A) Spectral changes observed upon the reduction of 0.024 mM **NAP**+• in CH2Cl2 by incremental addition of 1.04 mM solution of MeF3H2 in CH2Cl2 at 22 °C. (B) Plot of the mole fractions of **NAP**+• (red) and MeF3H2+• (black) against added equivalents of neutral MeF3H2. Symbols represent experimental points, while the solid lines show best-fit to experimental points using Δ*G* = *E*ox(MeF3H2) - *E*red(**NAP**+•) = 3 mV. (C and D) Electronic absorption spectra of (C) MeF2H*m*+• and (D) MeF3H*m*+• (*m* = 0–2). (E) The ORTEP diagrams (50% probability) of [MeF2+•SbCl6–] and [MeF3SbCl6–]. Hydrogen atoms have been omitted for the sake of clarity.

Electronic absorption spectra of MeF2H*m*+• showed nearly identical intervalence transitions centered at ∼1500 nm ([Figure 5](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig5)C), suggesting that the structures of MeF2H+• and MeF2H2+• are identical to that of MeF2+•, i.e., the π-stacked conformation. Similarly, absorption spectra of MeF3H*m*+• display an intervalence band that is red-shifted by 30–100 nm as compared to the corresponding band in MeF2H*m*+• series ([Figure 5](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig5)D), signifying extended hole delocalization across the π-stacked arrangement. Interestingly, all three MeF3H*m*+• exhibit a characteristic tail of in their absorption band extending beyond 3000 nm.

Preparative isolation of the polyfluorene cation radicals was carried out by chemical oxidation using nitrosonium hexachloroantimonate, i.e., [NO+SbCl6–]. Solution of polyfluorene and [NO+SbCl6–] in anhydrous CH2Cl2 with 1:1 ratio was stirred under an argon atmosphere at ∼0 °C, while bubbling argon through the solution to entrain gaseous nitric oxide. The resulting solution was carefully layered with toluene and stored in a refrigerator (−10 °C) for 2 days, which in case of [MeF2+•SbCl6–] and [MeF3+•SbCl6–] yielded single crystals that were suitable for X-ray crystallography. Both structures reveal the π-stacked arrangement of the fluorenes ([Figure 5](https://0-pubs-acs-org.libus.csd.mu.edu/doi/10.1021/acs.jpclett.8b01918#fig5)E). Unfortunately, recrystallization of mono and nonmethylated species, i.e., [MeF2H*m*+•SbCl6–] and [MeF3H*m*+•SbCl6–] (*m* = 1, 2), was thus far unsuccessful due to instability of the resulting cation radicals.

To conclude, in this manuscript, we have designed and synthesized a series of cofacially arrayed polyfluorenes with varied end-capping groups (MeF*n*H*m*, *n* = 1–3, *m* = 0–2) from readily available fluorene in excellent yield. We have shown with the aid of NMR, X-ray crystallography and DFT calculations that in the neutral state the conformation of MeF*n*H*m* is highly dependent on the end-capping groups and the environment. For example, when both end-capping groups are methyl, fully π-stacked structure is adopted in the gas, liquid, and solid states. In contrast, when one or both of the end-capping groups are hydrogens, W-shaped conformation is favored in solution, while the T-shaped conformer was found in the solid state as has been demonstrated for the case of MeF2H and MeF2H2. However, upon (electro)chemical oxidation MeF*n*H*m* is transformed into the fully π-stacked conformation irrespective of the end-capping groups, as evidenced from the electronic spectroscopy and X-ray crystallography of the cation radicals. Accordingly, we have shown that MeF*n*H and MeF*n*H2 undergo a redox-controlled mechanical actuation that is driven by the charge-resonance stabilization of the cationic charge. These findings will aid in the design of novel wire-like cofacially arrayed systems capable to undergo the redox-controlled actuation.

# [Supporting Information](https://0-pubs-acs-org.libus.csd.mu.edu/doi/suppl/10.1021/acs.jpclett.8b01918)

The Supporting Information is available free of charge on the [ACS Publications website](https://0-pubs-acs-org.libus.csd.mu.edu/) at DOI: [10.1021/acs.jpclett.8b01918](https://0-pubs-acs-org.libus.csd.mu.edu/doi/abs/10.1021/acs.jpclett.8b01918).

* Synthetic details, characterization data, details on generation of the cation radicals, crystal structure data and computational details ([PDF](https://0-pubs-acs-org.libus.csd.mu.edu/doi/suppl/10.1021/acs.jpclett.8b01918/suppl_file/jz8b01918_si_001.pdf))

### pdf

* + [jz8b01918\_si\_001.pdf (6.03 MB)](https://0-pubs-acs-org.libus.csd.mu.edu/doi/suppl/10.1021/acs.jpclett.8b01918/suppl_file/jz8b01918_si_001.pdf)

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