

Synthesis, Structure, and Evaluation of the Effect of Multiple Stacking on the Electron-Donor Properties of π -Stacked Polyfluorenes

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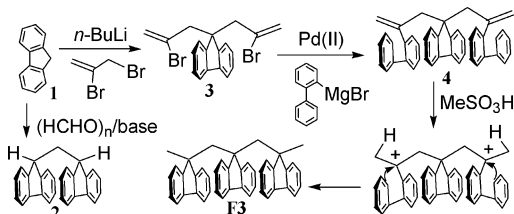
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Interactions between aromatic rings via π -stacking are at the origin of many phenomena of organic material science¹ and biological chemistry including the electron transport in DNA through stacked π -bases.² The π -stacking phenomenon has been studied before, mainly in the form of cyclophanes in which the two π -systems are forced into a sandwichlike geometry that generally imparts extensive deformation of the cofacial aromatic moieties.³ Moreover, because of synthetic difficulties, examples of such π -stacked molecules with multiple layers are scarce.⁴ Clearly, a new synthetic approach is desired for the preparation of multilayered π -stacked systems which will not only allow the study of electron-transport phenomenon through stacked aromatic moieties but will lead to the development of (next-generation) conducting wirelike materials for practical applications in the emerging field of nanotechnology.⁵

We have now designed a versatile class of π -stacked polyfluorenes in which the van der Waals contact between the cofacially oriented fluorene moieties allows effective electronic coupling among them (see structures **F1**–**F4** in Figure 1). Accordingly, we report herein the syntheses, the structures in the solid state by X-ray crystallography and those in solution by NMR spectroscopy, and the quantitative evaluation of electronic coupling among the cofacially oriented fluorene moieties in these multiply stacked polyfluorene systems using photoelectron spectroscopy in the gas phase and using electrochemistry in solution.

The synthetic strategies utilized for the preparation of polyfluorenes **F1**–**F4** are summarized in Scheme 1. The synthesis of **F2** was readily accomplished by methylation of easily prepared difluorenemethane **2** by a reaction of fluorene with paraformaldehyde in DMF in the presence of potassium *tert*-butoxide as a base in excellent yield. The key steps in the synthesis of **F3** involved a facile palladium-catalyzed coupling of the 2-biphenylmagnesium bromide to 9,9-bis(2-bromopropenyl)fluorene **3** followed by an acid-catalyzed (intramolecular) Friedel–Crafts alkylation (see Scheme 1). Similarly, an alkylation of **2** using 2,3-dibromopropene, followed by coupling with biphenylmagnesium bromide and acid-catalyzed cyclization, afforded **F4** in excellent yield.⁶

Scheme 1



The cofacial juxtaposition of the fluorene moieties in **F2**–**F4**, in solution, was strongly supported by ¹H NMR spectroscopy as

follows. For example, Figure 1 shows an upfield shift of the aromatic protons in **F2** when compared to the chemical shifts of the aromatic protons in **F1** due to the anisotropic shielding of the protons in each fluorene ring. Moreover, such a shielding of the protons is considerably more pronounced for the central fluorene moiety in **F3** (indicated by red dots), which is sandwiched between two outer fluorene moieties (signals indicated by blue arrows). The proton resonances due to the two outer fluorene rings and one central fluorene ring in the sandwiched structure of **F3** were readily assigned on the basis of the expected 2:1 integration ratio. The similar cofacial stacking of the fluorene moieties is retained in **F4** as was judged by an even further upfield shift of the proton resonances from the central two fluorene rings as compared to the proton resonances of the central fluorene ring in **F3** (see Figure 1).

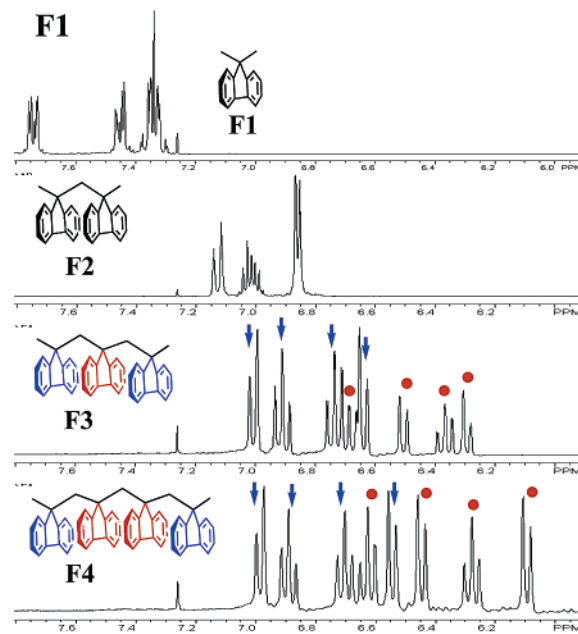


Figure 1. Partial ¹H NMR spectra of **F1**–**F4** in CDCl₃ at 22 °C.

To further confirm the cofacial juxtaposition of the fluorene moieties in **F2**–**F4**, we obtained single crystals of **F2** and **F3** from a dichloromethane/methanol mixture, and their structures were determined by X-ray crystallography.⁷ As expected, on the basis of the NMR studies (see Figure 1), both of these molecules showed cofacial juxtaposition of the fluorene moieties with the distances between the quaternary carbons of the fluorene rings (i.e., C2–C16 and C16–C30) in **F3** being 2.724 and 2.728 Å, respectively. Note that a similar separation of 2.71 Å between the quaternary carbons of the fluorene moieties (i.e., C2–C4) was found in **F2** (see Supporting Information). Although the fluorene moieties in these structures are slightly tilted with respect to each other, the

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close van der Waals contact between the fluorene rings is readily seen in a space-filling representation of **F3** (Figure 2).

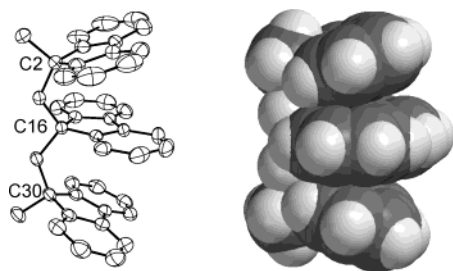


Figure 2. An X-ray structure of **F3** (left, ORTEP, and right, space-filling representation) showing cofacial juxtaposition of the three fluorene moieties.

The consequence of electronic coupling among the stacked fluorene moieties of **F2–F4** in comparison to the model electron-donor **F1** was evaluated by cyclic voltammetry in solution and photoelectron spectroscopy in the gas phase as follows. Polyfluorene donors **F2–F4** in dichloromethane solution (in the presence of tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte) at a scan rate of 200 mV s⁻¹ showed reversible cyclic voltammograms with oxidation potentials (E_{ox}) that progressively decreased with an increasing number of fluorene moieties.⁸ Moreover, the E_{ox} values for **F2** (1.42 V), **F3** (1.25 V), and **F4** (1.14 V) are significantly lower than that of the parent 9,9-dimethylfluorene⁹ **F1** (1.74 V vs SCE), which only showed an irreversible oxidation wave.

The measurement of (gas-phase) helium(I) photoelectron spectra (PES) of **F1–F4** (see Figure S1, Supporting Information)¹⁰ provided the vertical ionization energies for various polyfluorene electron donors, and the values of experimental ionization potentials (IP) for **F1** (7.85 eV), **F2** (7.52 eV), **F3** (7.33 eV), and **F4** (7.28 eV) decreased in a manner similar to that of the electrochemical potentials with an increasing number of fluorene moieties. Moreover, the linear relationship between the vertical ionization potentials (IP, in gas phase) and the oxidation potentials (E_{ox} , in solution) for **F1–F4**, illustrated in Figure 3A, suggests that the polyfluorene donors **F1–F4** do not undergo significant structural changes during (or soon after) electron detachment.¹¹

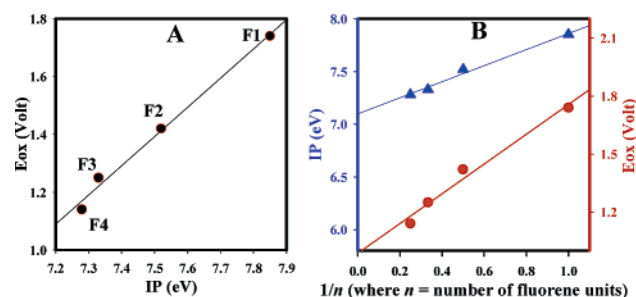


Figure 3. (A) Correlation of the IP values of **F1–F4** in the gas phase and E_{ox} values in solution. (B) A plot of the IP (blue axis) values and E_{ox} (red axis) values versus $1/nF$.

Interestingly, a closer inspection of the values of electron-detachment energies from **F1–F4**, both in solution and in the gas phase, indicated that the changes in IP and E_{ox} values are not linear with an increasing number of fluorene moieties in various stacked polyfluorene donors. However, both IP and E_{ox} values of **F1–F4**

showed linear correlations with quantity $1/n$, where n is the number of fluorene moieties, as shown in Figure 3B. Extrapolation of the plots in Figure 3B to $1/n = 0$ gave the vertical ionization potential of 7.10 eV and the oxidation potential of 0.97 V versus SCE for the multiply stacked polyfluorene donor with an infinite number of fluorene moieties. Interestingly, the observed linear relationship of electron-detachment energies and $1/n$ in **F1–F4** is highly reminiscent of the ionization energies predicted for varying lengths of fully conjugated polyacenes by recent theoretical studies by Houk et al.¹²

In summary, we have successfully synthesized multiply π -stacked polyfluorenes which retain their cofacial conformations both in solution and in the solid state as was judged by NMR spectroscopy and X-ray crystallography. The availability of the experimental electron-detachment energies of **F1–F4** should spur theoretical interest which will provide a fundamental understanding that may prove to be highly relevant to the electron-transport phenomenon observed in DNA through π -stacked bases.²

We are presently exploring these π -stacked polyfluorene spacers for the construction of a variety of wirelike materials to examine the electron-transport phenomenon through these systems using a variety of spectral methods¹³ including time-resolved spectroscopy and X-ray crystallography.

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Supporting Information Available: Various spectral data for **F1–F4** and the X-ray crystallographic data for **F2** and **F3** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) X-ray crystallography data for **F2** and **F3** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC207410 and CCDC207411, respectively. Also see Supporting Information.
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- (13) Preliminary spectral studies show strong through-space interactions in **F2–F4** cation radicals as evidenced by the appearance of new broad bands in the near-IR region. Full details will be disclosed in a separate manuscript.

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