

Stacking Effect of Polyfluorene on the Chemical Shift and Electron Transport

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We investigate the structures, NMR chemical shifts, absorption spectra, frontier molecular orbitals, and transition density matrices of π -stacked polyfluorenes by ab initio calculations. For **F1–F4**, we consider two different conformations, syn and anti. The simulated ¹H NMR chemical shifts are in good agreement with the previous experiment, and the significantly upfielded chemical shifts explain that the fluorene moieties are stacked on each other. It is found that the relative stability for syn and anti conformers is almost equivalent in B3LYP calculations; however, the syn conformer becomes much more stable than the anti conformer in MP2 calculations, which is consistent with the experimental finding that only the syn conformers are relevant. The vertical detachment energy, which is linearly proportional to the ionization potential, shows the same size dependence as the previous experiment. The electron attachment energy decreases exponentially as the size increases, which implies that the electron transport would be possible even for long chains such as **F3** and **F4**. This was evident from the frontier molecular orbitals (HOMO and LUMO). Also, it is found that the syn conformers are very favorable for electron transport through the π -stacked fluorene moieties.

I. Introduction

Intermolecular interactions play a crucial role in all areas of science. The question of how these interactions determine the physical and chemical properties as well as structures of various systems is an area of intense experimental and theoretical activity.^{1–3} Petsko et al. reported the importance of the edge-to-face interactions of aromatic rings in various biological systems.⁴ A similar interaction that is called π -hydrogen bonding^{5–7} was discussed in various experiments ranging from ultraviolet (UV) and infrared spectroscopies⁸ to X-ray crystallography of a variety of proteins⁹ as well as specially designed synthetic materials.¹⁰ Dougherty et al. synthesized a water-soluble anionic macrocyclic host for positively charged ammonium guests and found that the cationic ammonium guests in water moved into the cavity surrounded by aromatic residues through the cation– π interactions.¹¹ In this context, various types of intermolecular interactions involving aromatic systems such as aromatic–aromatic,^{12,13} cation– π ,^{14–16} π -hydrogen,^{17,18} and π -p_z¹⁹ have been investigated in the recent past. Some of the salient results are outlined in a recent review.²⁰

One of the most fascinating research areas is molecular electronics, which involves the use of single or small packets of molecules as the fundamental units for computing.^{21–23} The basic units of an electronic device are the diode and the transistor. These basic units can be realized by introducing a molecular wire and electron confinement.²⁴ Electron confinement is often treated with nonconjugated functional groups such

as methylene, while molecular wires usually contain π -electron conjugated systems.²⁵ Recently, we have studied the charge transfer within a molecule or between molecules²⁶ and found a simple expression to quantify the amount of intramolecular charge transfer in the donor– π -conjugated bridge–acceptor systems.^{26b,c} We also studied the effect of solvent on the intermolecular charge transfer between the donor molecule and the acceptor molecule.^{26a} The possibility that the π -stacked base pairs of DNA might serve as a pathway for charge transfer was advanced over 30 years ago.²⁷ In particular, much interest in the electronic properties of DNA has been stimulated by Barton and Turro's proposal that DNA serves as a molecular wire or " π -way".²⁸ Since then, there has been much interest in the electron transfer phenomena in DNA or its related systems.^{29–31} Also, electron transport in DNA through stacked π -bases³² and the π -stacking phenomenon through the aromatic–aromatic interactions³³ have been studied.

However, because of synthetic difficulties, examples of π -stacked molecules with multiple layers were scarce. Very recently, Rathore et al. synthesized a versatile class of π -stacked polyfluorenes.³⁴ In polyfluorenes, the van der Waals contact between the cofacially oriented fluorene moieties allows effective electronic coupling among them. To provide a fundamental understanding that may prove to be relevant to the electron transport property observed in DNA through π -stacked bases, the family of polyfluorenes are good model compounds to be theoretically investigated. Here, we study the structures, NMR spectra, absorption spectra, and electron–hole interactions in the presence of excitation light based on ab initio calculations and the collective electronic oscillator method. The theoretically obtained NMR spectra are discussed in comparison with previously reported experimental spectra.

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II. Computational Methods

Four molecular structures of polyfluorenes (**F1**, **F2**, **F3**, and **F4**) were optimized by density functional theory (DFT) calculations using the nonlocal density function of Becke's three parameters employing the Lee–Yang–Parr functional (B3LYP) with 6-31G* basis sets using a suite of Gaussian 98 programs.³⁵ We assumed C_s symmetry for computational convenience in studying the electron transport for syn and anti configurations of polyfluorenes. However, we did not use the symmetry constraint for the study of NMR chemical shifts. To look into the electron correlation effect on the relative energies, Møller–Plesset second-order perturbation (MP2) energies were obtained at the B3LYP/6-31G* optimized geometries. Furthermore, nonadiabatic electron attachment energies (EAE) and vertical detachment energies (VDE) were calculated. The EAE/VDE were defined as $E(\mathbf{F1}^-)/E(\mathbf{F1}^+) - E(\mathbf{F1})$, where $E(\mathbf{F1}^-)/E(\mathbf{F1}^+)$ and $E(\mathbf{F1})$ are the energies of anions/cations at the neutral optimized geometries and neutral energy, respectively.

The NMR shielding tensors were computed with the gauge-independent atomic orbital (GIAO) method.³⁶ Currently available DFT functionals do not include a magnetic field dependence, so DFT methods do not provide systematically better NMR results than Hartree–Fock (HF).³⁷ Therefore, the chemical shifts were calculated using the HF level of theory with 6-31G* basis set at the B3LYP/6-31G* optimized geometries.

The absorption spectra of **F1–F3** were simulated to look into the nature of interactions between the cofacially oriented fluorene moieties. The absorbance is directly connected to the imaginary part of polarizability,³⁸ thus we have only to obtain the frequency-dependent polarizability. To this end, we have used the collective electronic oscillator (CEO) method, which was originally developed by Mukamel³⁹ and has been applied to various molecular systems.^{40–44} Our calculations used the INDO/S semiempirical Hamiltonian which was constructed to reproduce the spectra of simple molecules at the singly excited configuration interaction level. This Hamiltonian introduced by Pople⁴⁵ and parametrized by Zerner and collaborators⁴⁶ is widely used in optical response computations. At the DFT-optimized geometries, we solved time-dependent Hartree–Fock (TDHF) equations⁴⁷ of motion for the density matrix in Liouville space to obtain the frequency-dependent polarizability. The detailed theoretical background and procedures are available elsewhere.⁴⁸

III. Results and Discussion

In the calculated structures, molecules **F2–F4** show cofacial juxtaposition of the fluorene moieties as shown in Figure 1. See Figures S2, S3, and S4 for better pictures in the Supporting Information. For each of the molecules **F2–F4**, we choose two different orientations of fluorene moieties, syn and anti, according to their relative position. In **F2**, the distances between the quaternary carbons of the fluorene rings are 2.7685 and 2.7776 Å for syn and anti configurations, respectively. In **F3**, they are (2.7989 and 2.7989 Å) and (2.8133 and 2.8131 Å) for syn and anti, respectively. In **F4**, they are (2.8060, 2.8343, and 2.8059 Å) and (2.7814, 2.8553, and 2.8155 Å). As the fluorene size increases, the distance becomes longer, which is consistent with the previous X-ray crystal structures where the distances were 2.724 and 2.728 Å in **F3** and 2.71 Å in **F2**. Thus, it appears that the polyfluorenes are almost completely stacked rather than quite displaced, although we used the displaced structures without symmetry to obtain the NMR chemical shifts as seen in Scheme 1.

The stability of the syn and anti configuration is almost equivalent within 0.2 kcal/mol for the B3LYP results, as seen

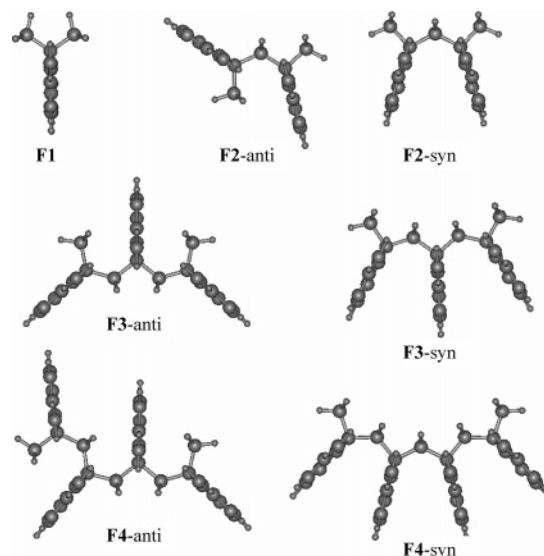
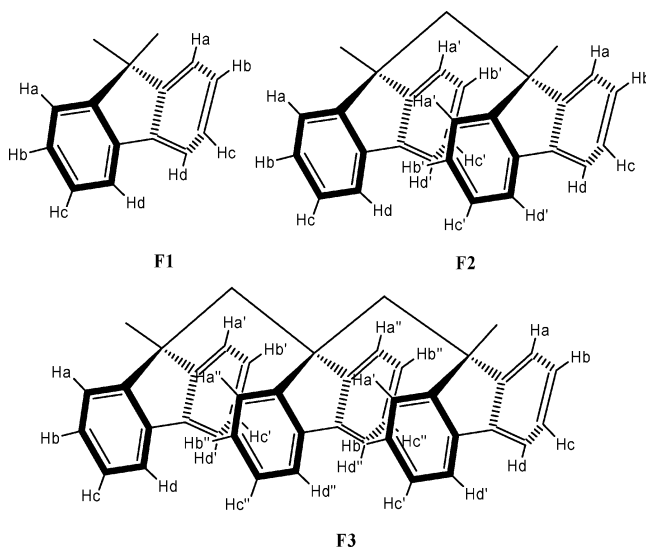


Figure 1. B3LYP/6-31G* predicted structures of **F1–F4**.

SCHEME 1



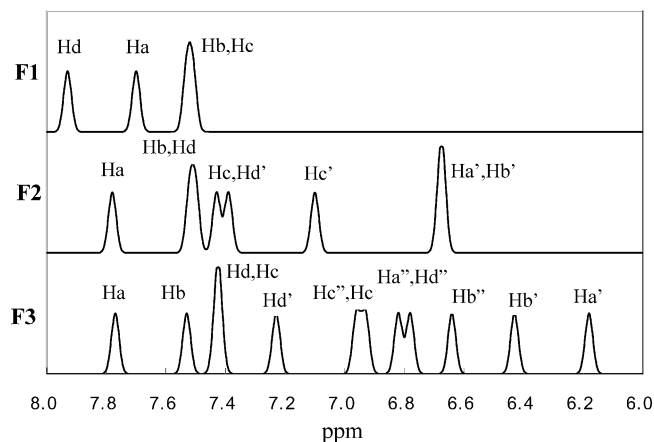
in Table 1. However, the MP2 results show that the syn configuration is much more stable than the anti configuration, and this trend becomes more prominent in the case with more fluorene rings. This is consistent with the experimental finding that only the syn structures were found to be relevant. Thus, as noted previously, the HF and B3LYP methods are not adequate for the correct interaction energy for the aromatic-containing systems mainly due to the importance of electron correlation energy in the π -stacked systems, which are missing in those methods.^{13b,20} For MP2 results, the relative stabilities of syn configurations of **F2**, **F3**, and **F4** with respect to their corresponding anti configurations are 3.76, 7.98, and 9.78 kcal/mol. The larger relative stability is brought by the more π -stacking fluorenes. When we optimize the geometries for **F2** and **F3** without symmetry constraint, that is, C_1 , the structures are helical and the stability with C_1 structures is almost equivalent to that of syn conformers with C_s structures where the fluorene moieties are arranged completely stacked through the π - π interaction stacking.

The simulated NMR spectra of **F1–F3** are represented in Figure 2. The chemical shifts of the aromatic hydrogens (see Scheme 1 for notations) are listed in Table 2. The previous experimental NMR chemical shifts of aromatic hydrogens were

TABLE 1: Relative Stability (E_{rel}), Nonadiabatic Electron Attachment Energy (EAE), and Vertical Detachment Energy (VDE) of Syn and Anti Configurations of F1–F4^a

	F1	F2		F3		F4	
		syn	anti	syn	anti	syn	anti
B3LYP ^b							
E_{rel}		0	0.20	0	0.02	0	-0.10
EAE	0.93	0.49	0.42	0.29	0.17	0.15	0.09
VDE	7.42	6.77	7.02	6.41	6.79	6.19	6.65
MP2 ^b							
E_{rel}		0	3.76	0	7.98	0	9.78
EAE	1.44	1.09	1.15	1.16	0.90	0.93	0.71
VDE	7.40	6.80	7.26	6.75	6.95	6.33	6.84

^a E_{rel} values are in kcal/mol; EAE and VDE are in eV. ^b B3LYP calculations are those optimized with 6-31G* basis sets, and MP2 calculations are those calculated with 6-31G* basis sets at the B3LYP optimized geometries.

**Figure 2.** Simulated ¹H NMR spectra of syn conformers of **F1–F3**.

reported to be 7.31–7.80 ppm for **F1**, 6.81–7.12 ppm for **F2**, and 6.27–7.12 ppm for **F3**.³⁴ The upfield shift of the aromatic protons in **F2** compared to the chemical shifts of them in **F1** was attributed to the anisotropic shielding of the protons in each fluorene ring. Such a shielding of the protons for the central fluorene moiety in **F3** was considered to be more pronounced. To better understand the NMR spectra and pinpoint the effect of interfluorene interactions, we compare our simulated NMR spectra with the experimental data. We denote the independent protons in **F1** as Ha, Hb, Hc, and Hd as seen in Scheme 1. In **F2**, the two fluorene moieties show the displaced stacking interactions, and we classify the fluorenes into nonoverlapped and overlapped fluorene; hence protons are classified into nonoverlapped fluorene protons and overlapped fluorene protons (Ha', Hb', Hc', and Hd'). In **F3**, the two terminal fluorenes are classified into nonoverlapped and overlapped fluorene, and consistently the protons into (Ha, Hb, Hc, and Hd) and (Ha', Hb', Hc', and Hd'), similar to **F2**, while the central fluorene moiety has four independent protons (Ha'', Hb'', Hc'', and Hd''). All the protons are duplicated by symmetry.

In **F1**, the simulated NMR chemical shifts are 7.70, 7.53, 7.51, and 7.93 ppm for Ha, Hb, Hc, and Hd, respectively, which are in good agreement with the experimental data. It should be noted that the order of downfield shift in **F1** is Hd > Ha > Hb ~ Hc. In **F2**, the overlapped protons are more profoundly upfield shifted than the nonoverlapped protons mainly due to the more anisotropic shielding of the protons in each fluorene ring. The order of downfield shift is Ha (7.78 ppm) > Hb (7.52 ppm) ~ Hd (7.50 ppm) > Hc (7.43 ppm) for nonoverlapped protons, while it is Hd' (7.39 ppm) > Hc' (7.10 ppm) > Ha' (6.68 ppm) ~ Hb' (6.67 ppm) for overlapped protons. Our simulated spectrum of **F2** is qualitatively in agreement with the experimental one considering that the peak for Ha corresponds to the

experimental peak at 7.12 ppm, peaks for Hb, Hd, Hc, Hd', and Hc' correspond to the experimental peaks at 6.95–7.05 ppm, and the peaks for Ha' and Hb' correspond to the experimental peak around 6.83 ppm. Interesting changes in the chemical shifts are as follows: In nonoverlapped fluorene, the peak of Ha is slightly downfield shifted by 0.08 ppm compared with that in **F1** and the peak of Hb is almost equivalent to that in **F1**, while the peaks of Hc and Hd are upfield shifted by 0.08 and 0.43 ppm, respectively.

In **F3**, we partitioned the protons into three classes: overlapped (Ha, Hb, Hc, and Hd), nonoverlapped (Ha', Hb', Hc', and Hd'), and middle (Ha'', Hb'', Hc'', and Hd''). The overlapped and nonoverlapped protons belong to the terminal fluorene rings. The simulated chemical shifts are (6.18, 6.43, 6.93, 7.23), (7.77, 7.53, 7.42, 7.43), and (6.82, 6.64, 6.96, 6.78) for (Ha, Hb, Hc, Hd), (Ha', Hb', Hc', Hd'), and (Ha'', Hb'', Hc'', Hd''), respectively, as depicted in Figure 2. As expected by the shielding effect, the overlapped protons are more upfield shifted than those in **F2**, while the nonoverlapped protons show chemical shifts almost equivalent to those of **F2**. The chemical shifts of middle protons show little variation (6.64–6.96 ppm). Our simulated chemical shifts are in good agreement with the experimental spectra. The simulated NMR spectra were well explained by the cofacial juxtaposition of the fluorene moieties.

Recently, it was suggested that the polyfluorenes **F1–F4** do not undergo significant structural changes during (or soon after) electron detachment.³⁴ The experimental ionization potentials (IP_{exp}) were measured to be 7.85, 7.52, 7.33, and 7.28 eV for **F1**, **F2**, **F3**, and **F4**, respectively, from the photoelectron spectra (PES).⁴⁹ Our MP2 (B3LYP) predicted vertical detachment energies (VDE) of 7.40 (7.42), 6.80 (6.77), 6.75 (6.41), and 6.33 eV (6.19 eV) for the syn conformers of **F1**, **F2**, **F3**, and **F4** are comparable to the experimental values. The B3LYP and MP2 values are very close to each other. Figure 3a shows the correlation between experimental ionization potentials (IP_{exp}) and calculated vertical detachment energies (VDE) for syn and anti conformers of **F1–F4**. The values of IP_{exp} and VDE are inversely proportional to the size (n), that is, proportional to $1/n$ where n is the number of fluorene moieties ($n = 1$ for **F1** and $n = 4$ for **F4**), which is implicated from a previous experiment.³⁴ Furthermore, the inversely scaling behavior of IP with polymer size is quite similar to the ionization energies predicted for varying the size of the conjugated polyacenes by Houk et al.⁵⁰ Figure 3b shows an interesting behavior of the nonadiabatic electron attachment energy (EAE) for syn and anti configurations of **F1–F4** as a function of n . The positive value of nonadiabatic EAE implies that the molecule comes to be energetically more unstable when an electron is added nonadiabatically. Then, EAE decreases exponentially for both syn and anti configurations as n increases. This indicates that the

TABLE 2: Simulated Chemical Shifts for the Aromatic Protons of F1–F3^a

	F1	F2		F3		
		overlap	nonoverlap	overlap	middle	nonoverlap
Ha	7.70	6.68	7.78	6.18	6.82	7.77
Hb	7.53	6.67	7.52	6.43	6.64	7.53
Hc	7.51	7.10	7.43	6.93	6.96	7.42
Hd	7.93	7.39	7.50	7.23	6.78	7.43

^a (Ha, Hb, Hc, Hd) represents (Ha', Hb', Hc', Hd') for nonoverlap in F2, and (Ha', Hb', Hc', Hd') and (Ha'', Hb'', Hc'', Hd'') for middle and nonoverlap, respectively, in F3. Units are in ppm.

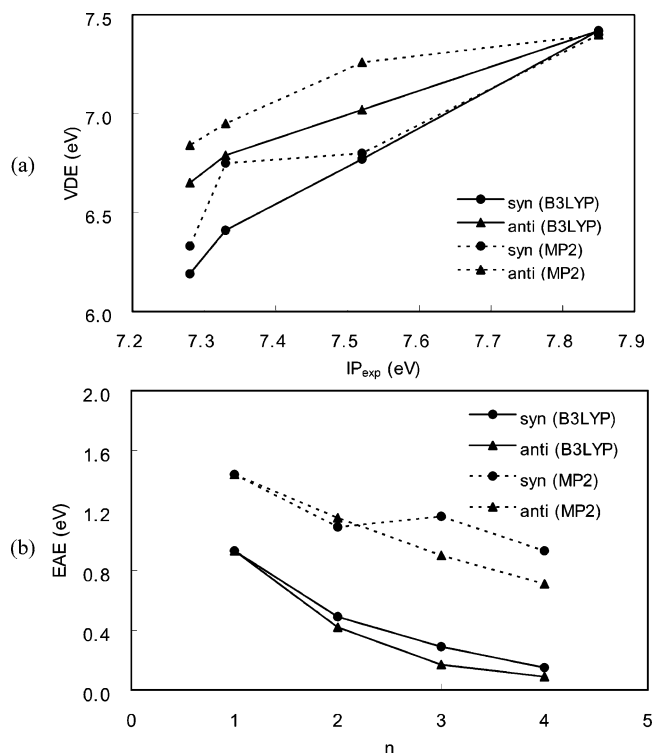


Figure 3. (a) Correlations between vertical detachment energy (VDE) and experimental ionization potential (IP_{exp}) and (b) variation of nonadiabatic electron attachment energy (EAE) with size (n) for syn (filled circles) and anti (filled triangles) conformers of F1–F4 by B3LYP/6-31G* (solid lines) and MP2/6-31G*/B3LYP/6-31G* (dotted lines) calculations.

multiply stacked fluorene moieties can hold an electron without much difficulty energetically. Once an electron is coming to the multiply stacked fluorene rings, the electron is considered to move through the lowest unoccupied molecular orbitals (LUMO).^{22a}

We investigated the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of F1–F4, and Figure 4 shows the molecular orbitals of F3 and F4 as representatives. For anti configurations, in both F3 and F4 the HOMO shows the electron is located in the terminal fluorene moieties, whereas the LUMO electrons are located in the central fluorenes. Quite differently, for syn configurations, the HOMO electrons are quite localized in each fluorene ring without interfluorene interactions, which can be noted from the existence of nodes between fluorene rings. Most interestingly, the LUMO electrons for syn configuration reveal the strong interfluorene interactions as noted from the disappearance of nodes and orbital overlap. This suggests that the multiply stacked fluorenes with syn configuration should be very efficient for electron transport, while fluorenes with anti configuration may not.

The absorption spectra of F1–F3 were obtained by the CEO method. Each fluorene shows two unique absorption peaks

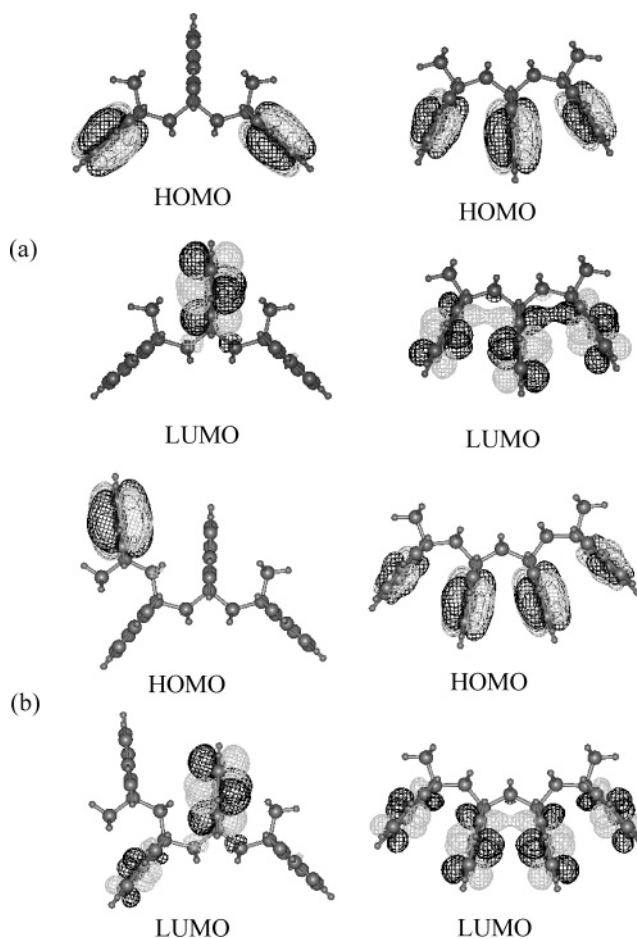


Figure 4. Highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of syn (right column) and anti (left column) conformers of F3 (a) and F4 (b).

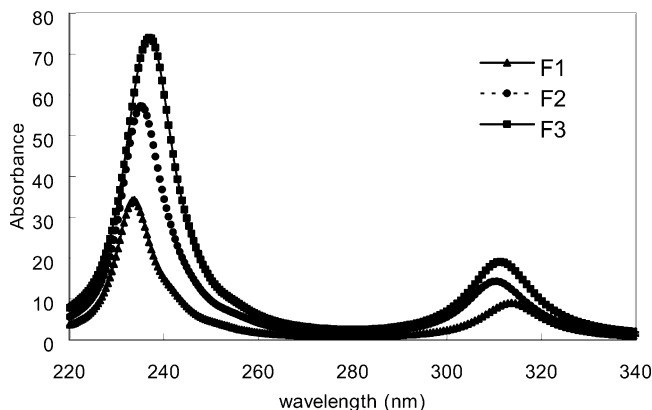


Figure 5. Simulated absorption spectra of F1–F3.

around 311 and 235 nm, as shown in Figure 5. Each absorption peak appears at an almost equivalent wavelength within 2 nm for F1, F2, and F3. To pinpoint the characteristic property of each peak, we looked into the transition densities corresponding

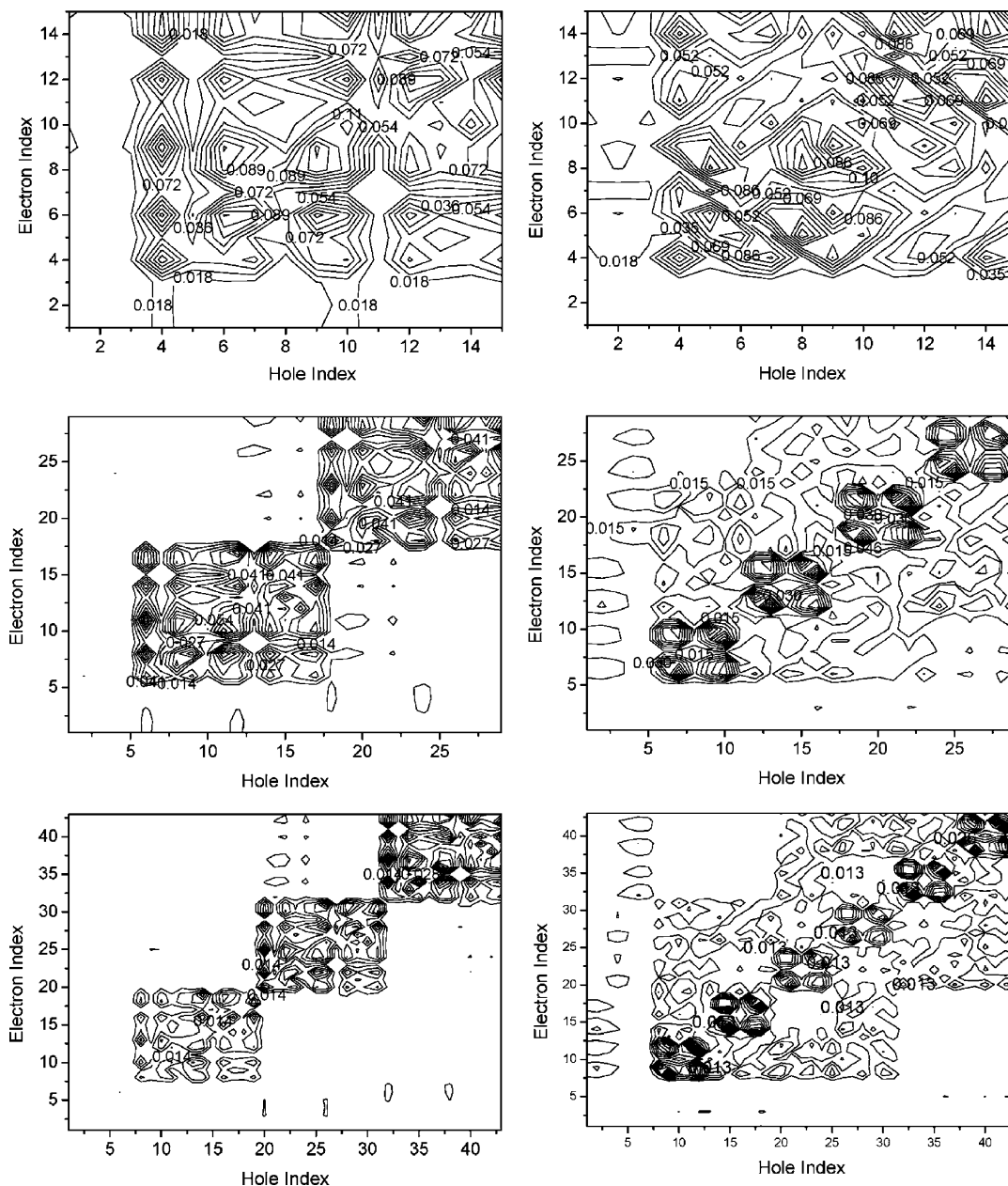


Figure 6. Contour plots of transition density matrices corresponding to the lowest energy absorption peaks near 311 nm (left column) and the second lowest energy absorption peaks near 235 nm (right column) for syn conformers of **F1** (top), **F2** (middle), and **F3** (bottom).

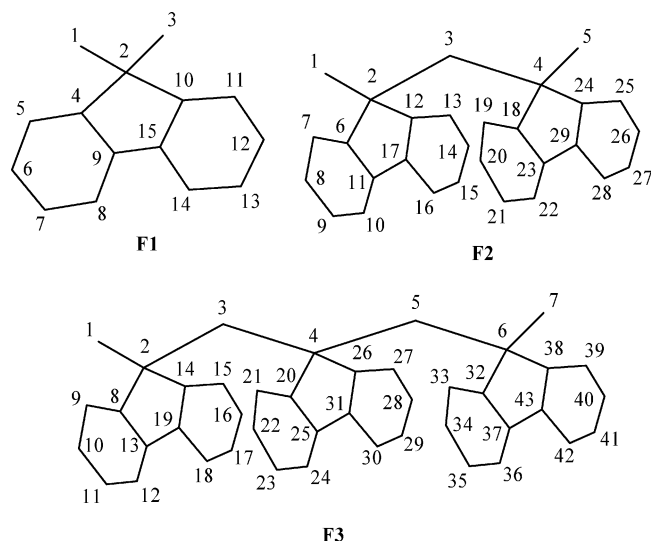
to the absorption peaks using the CEO method, which are represented in Figure 6. The transition density represents the electron–hole interactions. For example, the density at $(X,Y) = (10,5)$ represents the interactions between the electron at atom 5 and the hole at atom 10, as previously described in detail.⁴⁸ For the indexes of electrons and holes, the atomic numbers are shown in Scheme 2. From the transition densities, it should be noted that the absorption peak around 311 nm is due to the electron–hole interactions between electrons in one benzene group and holes in the other benzene group in the same fluorene moieties, and the electron–hole interactions between neighboring fluorene moieties are negligible. This may be the reason for the almost equivalent absorption peak for different fluorene systems. The absorption wavelengths around 311 nm for **F1**–**F3** should be significantly shifted if the electron–hole interactions between neighboring fluorene moieties are eminent. Similarly, the transition densities reveal that the absorption peaks at 234, 235, and 237 nm for **F1**, **F2**, and **F3**, respectively, are due to the electron–hole interactions within benzene groups,

where the interactions between a benzene and the other benzene are negligible even in the same fluorene moieties.

IV. Conclusion

We investigated the structures, NMR chemical shifts, absorption spectra, frontier molecular orbitals, and transition density matrices of π -stacked polyfluorenes by ab initio calculations. The stabilities of the syn and anti configurations are calculated to be almost equivalent within 0.2 kcal/mol in B3LYP calculations; however, the syn conformer becomes much more stable than the anti conformer in MP2 calculations, indicating that electron correlation is critical and favors π -stacking. The upfield shift of the aromatic protons in **F2** in comparison with the chemical shifts in **F1** revealed that there exists a significant anisotropic shielding of the aromatic protons in each fluorene ring, which in turn proves the existence of π -stacked fluorene moieties. Such a shielding of the protons for the central fluorene moiety in **F3** was considered to be more pronounced. Our

SCHEME 2



simulated NMR spectra were in good agreement with the previous experimental data. We compared the values of the vertical detachment energy (VDE), which is directly connected to the ionization potential and nonadiabatic electron attachment energy (EAE), for **F1–F4**. The vertical detachment energy is linearly proportional to the ionization potential, which was reported to be inversely proportional to size in the previous experiment, while the electron attachment energy decreases exponentially as size increases, which implies that electron transport would be possible even for long chains such as **F3** and **F4**. This was evident from the frontier molecular orbitals (HOMO and LUMO). The syn conformers are much more favorable for electron transport through the π -stacked fluorene moieties, and electron transport in DNA may be facilitated through the π -stacked domains.

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Supporting Information Available: Optimized structures of **F1–F3** for NMR chemical shifts, and optimized structures for the syn and anti configurations with C_s symmetry of **F2–F4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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