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Two's Company, Three's a Crowd: Exciton Localization in Cofacially Arrayed Polyfluorenes

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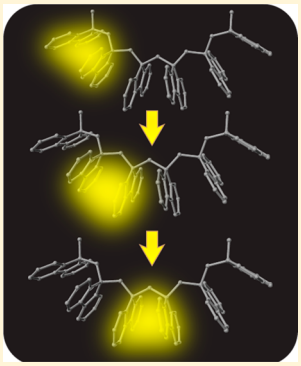
Supporting Information

ABSTRACT: Understanding the mechanisms of long-range energy transfer through polychromophoric assemblies is critically important in photovoltaics and biochemical systems. Using a set of cofacially arrayed polyfluorenes (F*n*), we investigate the mechanism of (singlet) exciton delocalization in π-stacked polychromophoric assemblies. Calculations reveal that effective stabilization of an excimeric state requires an ideal sandwich-like arrangement; yet surprisingly, emission spectroscopy indicates that exciton delocalization is limited to only two fluorene units for all *n*. Herein, we show that delocalization is determined by the interplay between the energetic gain from delocalization, which quickly saturates beyond two units in larger F*n*, and an energetic penalty associated with structural reorganization, which increases linearly with *n*. With these insights, we propose a hopping mechanism for exciton transfer, based upon the presence of multiple excimeric tautomers of similar energy in larger polyfluorenes ($n \geq 4$) together with the anticipated low thermal barrier of their interconversion.



The underlying mechanisms of energy and electron transport through polychromophoric assemblies continue to attract much attention in the field of organic electronics and photovoltaics. We have recently introduced covalently linked cofacially arrayed polyfluorenes containing multiple fluorenes (F2−F6, Figure 1A) that serve as models for the study of charge/energy transfer in π-stacked arrays.[1−4] The cofacially juxtaposed fluorene moieties in F2−F6 are rigidly held in close van der Waals contact with only limited libration of fluorenes along their long axes, as demonstrated by NMR spectroscopy and X-ray crystallography (Figure 1A).[1,5]

The effective electronic coupling among the fluorenes in F2−F6 was demonstrated by the observation that their (vertical) ionization potentials in the gas phase and (adiabatic) oxidation potentials in solution decrease with increasing number of fluorenes (*n*) and follow a $1/n$ trend (Figure 1B).[1,4] Moreover, the delocalization of a hole over multiple fluorene units in F2−F6 was further evidenced in the electronic spectra of their cation−radicals, where the intervalence charge-resonance transition shifted red (to longer wavelength) and intensified with the increasing number of fluorene units (Figure S1 in the SI).

Despite the effective delocalization of the hole in F2−F6, their emission spectra were found to be identical with a broad Gaussian-shaped band at 395 ± 3 nm.[1,4,6] By comparison with the emission spectrum of monomeric F1, which shows a single structured band at 315 nm (Figure 1C), the Gaussian band at 395 nm for F2−F6 can be readily assigned to emission from an excited dimer (or excimer).[7] The observation of nearly identical emission spectra of F2−F6 (Figure 1C) suggests that the exciton most likely resides only over two fluorene moieties, in contrast with the hole in the corresponding cation−radicals (Figure 1B and Figure S1 in the SI).

The central question we address here is why, unlike the hole, is the exciton localized only onto two units? We will also examine whether the exciton occupies the central or outer fluorene units in higher F*n* and probe whether the exciton is dynamic and can migrate along the cofacially juxtaposed π-array and, if so, by what means. In order to address these questions, we undertake a detailed computational study of various polyfluorenes (Figure 1A) in the ground (S_0) and first excited (S_1) states using density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. We will show that formation of an excimeric state has a stringent requirement of structural/conformational reorganization, which limits the delocalization of the exciton beyond two units in F*n*, as the concomitant reorganization penalty outweighs the energetic benefits of additional delocalization.

We performed electronic structure calculations of the ground and excited states of F1−F6 using (TD-)DFT calculations with a modified B1LYP-40 density functional, extensively utilized for the accurate description of electronic structures of ion−radicals of different classes of π-conjugated molecular wires in their ground and excited states.[8−11] Additionally, we performed calculations with benchmarked standard density functionals (PBE0, ωB97X-D) and obtained comparable results (details in sections S3 and S4 in the SI).

A close examination of the electronic structures of F1 in its ground (S_0) and first excited (S_1) states shows that dramatic bond length changes accompany electronic excitation (Figure 2). For example, the central C−C bond (*a*) contracts from 1.467 to 1.387 Å (i.e., by 8.0 pm), while the aromatic bonds of

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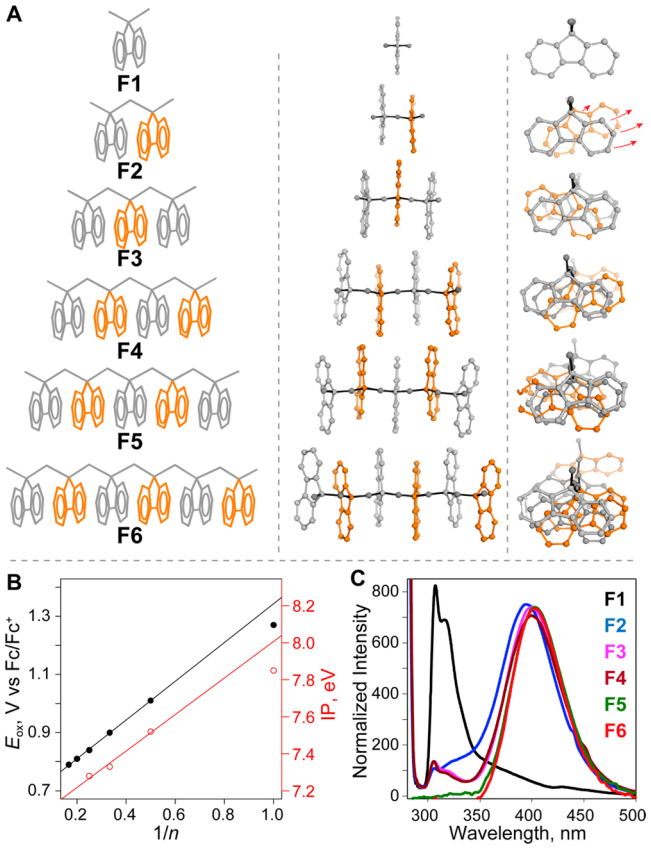

Figure 1. (A) Structures and naming scheme of F1−F6, two views of minimized structures [B1LYP-40/6-3-G(d)+PCM(CH_2Cl_2)] of F1−F6, and representation of the libration of fluorene moieties with red arrows on the example of F2. (B,C) P lot of E_{ox1} values (black axis) and IPs (red axis) vs $1/n$ (B)[1,4] and normalized emission spectra (λ_{exc} = 280 nm) of F1−F6 in CH_2Cl_2 at 22 °C (C). Note that the relative emission intensity of F1 was ∼10 times higher than that of F2−F6.

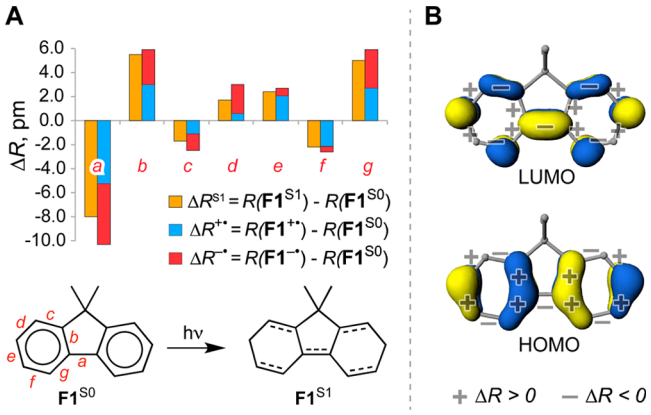

Figure 2. (A) Bar plots showing bond length changes due to the $S_0 \rightarrow S_1$ excitation of F1 as compared with the combined effect of the similar bond length changes due to the oxidation and reduction of F1 [B1LYP-40/6-31G(d)+PCM(CH_2Cl_2)] and cartoon representation of the structural changes accompanying the excitation of fluorene from the ground to the first excited state. (B) Depiction of the HOMO and LUMO of F1, shown together with the sign of the excitation-induced bond length changes.

similar length (i.e., ∼1.39 Å) in the S_0 state undergo elongation (by 5.5, 5.0, 1.7, and 2.4 pm for *b*, *g*, *d*, and *e*, respectively) and contraction (by 1.7 and 2.4 pm for *c* and *f*, respectively), leading to a quinoidal distortion of F1 in the S_1 state. For details, see Figure 2A and Tables S2 and S3 in the SI.

The bond length changes observed in the electronically excited $F1^{S1}$ were significantly larger than our earlier observations of the experimental bond length changes in the X-ray structures of a number of different polycyclic aromatic cation−radicals or anion−radicals.[12−17] However, when we compared the bond length changes in F1 cation− and anion−radicals [B1LYP-40/6-31G(d)+PCM(CH_2Cl_2)] with $F1^{S1}$, the exciton-induced bond length changes in $F1^{S1}$ were found to be an approximate sum of the changes in $F1^{+\bullet}$ and $F1^{-\bullet}$, that is, $\Delta R^{S1} \approx \Delta R^{+\bullet} + \Delta R^{-\bullet}$ (Figure 2A).

Analysis of the X-ray structures of several neutral electron donors (or acceptors) and their cation (or anion) radicals[12−17] together with DFT calculations[10,18,19] showed that the 1*e*-oxidation (or reduction)-induced bond length changes in cation (or anion) radicals can be predicted by the disposition of the nodal arrangement of the HOMO (or LUMO).[10,12−19] For example, upon 1*e* oxidation of an electron donor, bonds aligned with bonding lobes of the HOMO undergo elongation, while the bonds aligned with antibonding lobes undergo contraction. In contrast, upon 1*e* reduction of an electron acceptor, bonds aligned along bonding lobes of the LUMO undergo contraction, while bonds aligned with antibonding lobes undergo elongation. Interestingly, the nodal arrangement and disposition of the HOMO and LUMO in F1 (Figure 2B) is such that both oxidation- and reduction-induced bond length changes would lead to elongation and contraction of the same bonds. As the observed bond length changes in $F1^{S1}$ are found to be the sum of the bond length changes in the F1 cation−radical and anion−radical, the excited state of F1 (i.e., promotion of an electron from the HOMO to LUMO) accommodates bond length changes arising from the simultaneous formation of cation−radical and anion−radical states (or an electron−hole pair). Moreover, the observed geometrical reorganization in $F1^{S1}$ is consistent with the analysis of electron densities of F1 in its ground, excited, oxidized, and reduced states using a frozen orbital approximation; see section S5 in the SI.

An excited molecule associates with its ground-state counterpart to form an excimer due to the resonance stabilization of the exciton.[20] In the case of F2, the covalently linked cofacially π-stacked fluorene moieties allow spontaneous formation of the excimeric state. Indeed, the calculated geometry of the optimized excited state $F2^{S1}$ (Figure 3A) shows that the bond length changes within the fluorene units were equally distributed and were half of that in $F1^{S1}$, suggesting that the exciton is evenly delocalized onto both fluorene moieties (compare Figures 2A and 3A; also compare Tables S2−S5 in the SI). In addition to the bond length changes, the effective delocalization of the exciton in $F2^{S1}$ results in an eclipsed sandwich-like arrangement of the fluorene moieties with an interplanar angle of ∼18°, resulting in contacts among the fluorene carbons as close as 3.0−3.2 Å (Figure 3A).

The observation of a close sandwich-like arrangement of the fluorenes in $F2^{S1}$ and complete delocalization of the exciton suggest an effective electronic coupling (V_{ab}) among the fluorenes, which, in turn, demands effective electronic coupling between HOMOs (β_{HOMOs}) and LUMOs (β_{LUMOs}) of the monomeric units, that is, $V_{ab} \approx \beta_{HOMOs}\beta_{LUMOs}$.[21,22] According to the well-known Mulliken approximation,[21,23] coupling between any two orbitals is proportional to the overlap integral. Excimeric coupling V_{ab} will depend on both the

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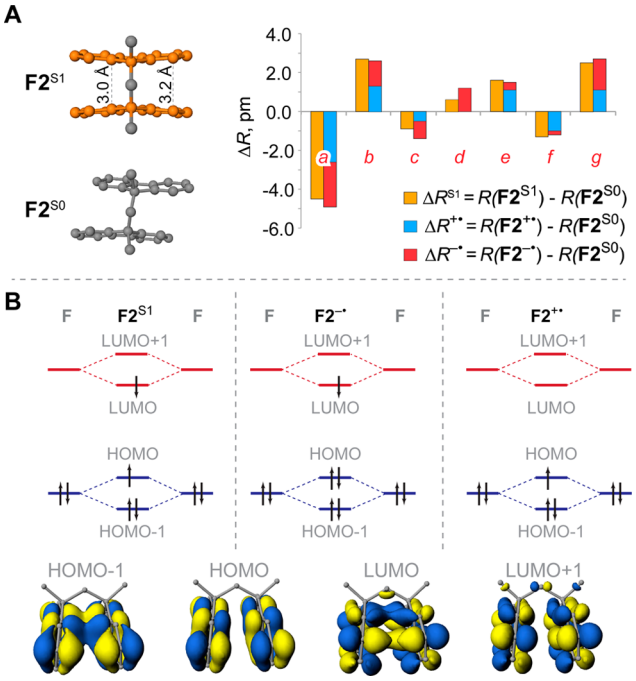

Figure 3. (A) Bar plots showing excitation-induced bond length changes in F2 as compared with the combined effect of the bond length changes due to its oxidation and reduction [B1LYP-40/6-31G(d)+PCM (CH_2Cl_2)]. Note that labeling of bonds in fluorene units corresponds to the structure shown in Figure 2A. (B) Molecular orbital picture of the $S_0 \rightarrow S_1$ excitation, reduction, and oxidation of F2 as well as plots of the relevant molecular orbitals.

LUMO−LUMO and HOMO−HOMO overlaps,[24] whereas the coupling in ion−radicals is proportional to either the HOMO−HOMO or LUMO−LUMO overlap. The product of the HOMO−HOMO/LUMO−LUMO overlap integrals in the excimer will decrease much more rapidly upon displacement of excimeric partners from the ideal sandwich-like arrangement[22,24,25] as compared to the HOMO−HOMO or LUMO−LUMO overlap integrals in cation−radical and anion−radical dimers.[12] Indeed, a simple analysis of the molecular orbital diagram of F2 clearly shows that overlap among the frontier orbitals allows efficient bonding between the monomer units in $F2^{S1}$, which is roughly twice larger than that in $F2^{-\bullet}$ or $F2^{+\bullet}$ alone (Figure 3B).

Consistent with the observation of nearly identical emission spectra of F2−F6 (Figure 1C), optimization of the excited state of higher homologues, that is, $F3^{S1}$ and $F4^{S1}$, showed that the exciton is indeed localized onto only two fluorene moieties in both molecules. For example, the excitation-induced bond length changes in both $F3^{S1}$ and $F6^{S1}$ were localized onto a pair of fluorenes that adopted a close (eclipsed) sandwich-like arrangement akin to that found in $F2^{S1}$ (Figure 4A and section S4 in the SI).

Unlike $F2^{S1}$ and $F3^{S1}$, $F4^{S1}$ can exist in two distinct valence tautomers where the exciton is localized either onto two central fluorenes ($F4^{S1}$) or onto a central and an adjacent terminal fluorene ($F4'^{S1}$),[26] Figure 4A. Comparison of the energies of optimized $F4^{S1}$ and $F4'^{S1}$ showed that they are nearly isoenergetic and differ in energy by only 0.3 kcal/mol (vide infra).[26] The energetic diagrams depicting the absorption−emission cycle of F1−F4 are shown in Figure 4B. A comparison of the electronic energies of the vertically excited state ($S_1//S_0$) and geometrically relaxed excited state ($S_1//S_1$) of $F1^{S1}$−$F4^{S1}$ directly provides the exciton stabilization energy (i.e., $\lambda_1 = E_{S1//S0} - E_{S1//S1}$), whereas the difference in the ground-state electronic energies of $F1^{S0}$−$F4^{S0}$ at the relaxed ($S_0//S_0$) and excited-state ($S_0//S_1$) geometries constitutes the reorganization penalty (i.e., $\lambda_0 = E_{S0//S1} - E_{S0//S0}$) for the accommodation of the exciton (Figure 4B).

As expected, stabilization of the excimeric state in F2−F4 (λ_1 = 15.6 ± 0.3 kcal/mol) is ~8.5 kcal/mol larger than stabilization of the exciton in F1 (λ_1 = 7.0 kcal/mol) due to resonance interactions. The increase in reorganization penalty for the accommodation of the exciton onto two fluorenes in F2 (λ_0 = 14.6 kcal/mol) vs one fluorene in F1 (λ_0 = 8.7 kcal/mol) is also understandable, given that the structural reorganization in F1 is limited to only bond length changes in a single fluorene, whereas F2 undergoes additional geometrical

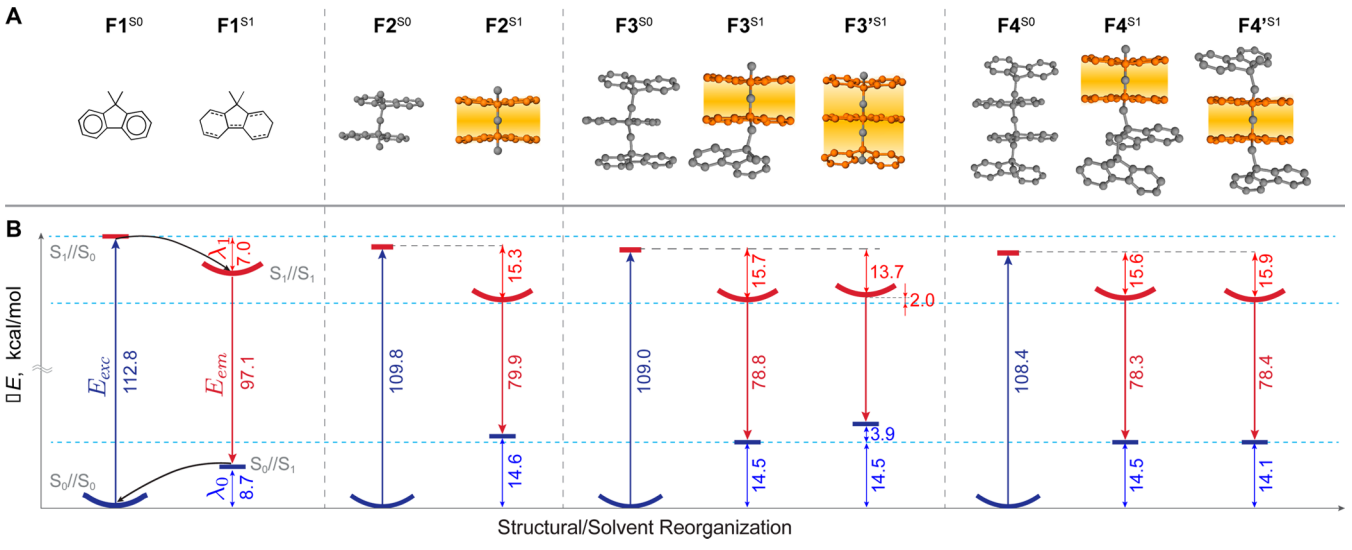

Figure 4. (A) Structures of F1−F4 in their ground (S_0) and first excited (S_1) states [B1LYP-40/6-31G(d)+PCM(CH_2Cl_2)] with hydrogens omitted for clarity. (B) Energetic diagrams of the excitation/emission cycle of F1−F4, where exciton was localized onto two units. Additionally, in F3, full exciton delocalization was enforced by the imposing fully eclipsed conformation of all three fluorenes.

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reorganization leading to an eclipsed sandwich-like arrangement.[27] Homodesmic analysis of the reorganization penalty (see section S6 in the SI) shows that the energy required for the bond length changes distributed over one fluorene in F1 and two fluorenes in F2 is nearly identical (9.0 and 8.7 kcal/mol), and the remaining reorganization energy for F2, that is, ~5.6 kcal/mol, is responsible for the conformational reorganization in an eclipsed sandwich-like arrangement of $F2^{S1}$. The calculated reorganization penalty of ~14.5 kcal/mol for $F3^{S1}$ and $F4^{S1}$, which is similar to that in $F2^{S1}$, further attests that the exciton localizes only onto two fluorenes.

Calculations of isomeric $F3'^{S1}$, where all three fluorenes are enforced in an eclipsed π-stacked arrangement, show that the exciton is distributed on all three units with a 1:2:1 ratio as judged by the bond length changes within each fluorene (Table S8 in the SI; as well as by the analysis of the molecular orbitals involved in the $S_0 \rightarrow S_1$ transition). Despite the increased delocalization of the exciton in $F3'^{S1}$, its stabilization energy (λ_1 = 13.7 kcal/mol) is 2.0 kcal/mol less than that of $F3^{S1}$ (λ_1 = 15.7 kcal/mol), where the exciton is delocalized onto two fluorenes (Figure 4B). This is not surprising based on the additional reorganization penalty of 3.9 kcal/mol[28] required to geometrically reorganize three fluorenes into an eclipsed multidecker sandwich-like structure.[29]

To gain further insight into the size dependence of the interplay between the energetic gain from the exciton delocalization and the energetic penalty needed for structural reorganization in terms of bond length changes and geometrical reorganization for an optimized sandwich-like arrangement of interacting chromophores in larger F*n*, we carried out additional single-point TD-DFT calculations on a representative polyfluorene F9, as follows.

Single-point (TD-)DFT calculations were performed for a series of F9 molecules in both the ground and excited states, where an increasing number of fluorenes (k) were arranged in eclipsed sandwich-like arrangement akin to that in $F2^{S1}$ while the internal structural parameters for all fluorenes were fixed at the values corresponding to parent $F1^{S0}$ (see section S7 in the SI for details). A compilation of various F9 excited-state structures showing the transition densities of the $S_0 \rightarrow S_1$ excitation in Figure 5A demonstrates that exciton delocalization extends to all fluorenes (k = 2–9), which are arranged in an eclipsed sandwich-like arrangement.

The energies of the structures $E(S_0)$ increased linearly with increasing k, suggesting that the reorganization penalty increases linearly with addition of each fluorene in an eclipsed sandwich-like arrangement, Figure 5B. On the other hand, the excitation energies (E_{exc}), evaluated from the difference of the ground- [$E(S_0)$] and excited- [$E(S_1)$] state energies of various F9 structures, saturate with an increasing number of sandwiched fluorenes (k), and the evolution of $E_{exc}(k)$ follows a familiar $\cos \pi/(k+1)$ trend (Figure 5B).[30−33] Thus, the extent of exciton delocalization should be governed by a cumulative effect of the quickly saturating energetic gain from exciton delocalization and the linearly increasing energetic penalty for conformational reorganization. Due to this interplay, the most effective stabilization of the exciton, that is, the lowest $E(S_1)$, is achieved when the exciton is confined on a limited number of chromophores, for example, three units in the model structure F9 as judged by the presence of a minimum on the $E(S_1)$ curve in Figure 5B. (Note that the bond length changes within fluorenes lead to further localization of the exciton to only two units, vide supra.)

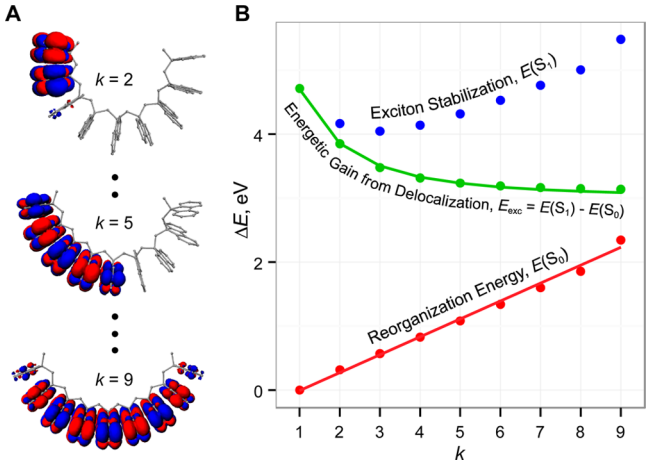
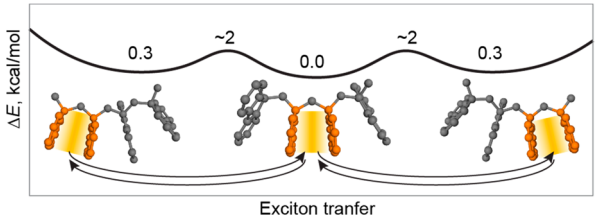


Figure 5. Transition density plots corresponding to the $S_0 \rightarrow S_1$ vertical excitation (A) and energies of the S_0 and S_1 states and the corresponding $E_{exc} = E(S_1) - E(S_0)$ (B) in F9 with a different number (k) of eclipsed fluorene units (see the section S7 in the SI for details). Note that data points for $E(S_0)$ and E_{exc} were fitted by the linear and $\cos \pi/(k+1)$ trends, respectively.

The localization of the exciton onto only two units raises the question of the mechanism and efficiency of exciton transfer along the multichromophoric assembly. To examine this issue, we return to F4, which is the smallest assembly that shows two distinct valence tautomers that are nearly isoenergetic with an energy difference of only 0.3 kcal/mol (Scheme 1). The

Scheme 1. Potential Energy Profile of the Singlet Exciton Transfer along the Covalently Linked π-Array of Fluorene Chromophores on the Representative Example of F4



transition state of the exciton transfer or interconversion between these valence tautomers is expected to involve a structure in which the exciton is delocalized on three fluorenes arranged in a sandwich-like configuration. The energetic cost of the formation of F3 in its fully eclipsed conformation is ~2 kcal/mol, and thus, a similar energetic expenditure is expected for the transition state of the F4 tautomer interconversion. Therefore, the coexistence of such tautomers and a low (~2 kcal/mol) barrier of their interconversion indicates a possible mechanism of exciton transfer that involves hopping along the multichromophoric π-stacked assembly (Scheme 1). The nonadiabatic exciton transfer in Scheme 1 via coupling with the associated torsional mode (Figure S4 in the SI) is unlikely as this torsional mode is of extremely low frequency (in the 13–17 cm^{-1} range, Table S19 in the SI), unlike the linearly connected π-conjugated systems where the normal modes associated with the exciton transfer are generally of high frequency.[34]

In summary, we undertook a computational study of cofacially arrayed π-stacked polyfluorenes in their ground (S_0) and first excited (S_1) states by means of the TD-DFT

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calculations based on the carefully calibrated B1LYP-40 density functional. The calculations successfully reproduced the spectroscopic observation of the excimeric state (i.e., exciton delocalization to only two fluorene units) in F2 as well as larger polyfluorenes. In such an excimeric state, excitation-induced bond length changes were evenly distributed over both fluorene units and were half of those observed in monomeric F1. Using a model structure, F9, we demonstrated that the extent of the exciton delocalization (e.g., two units in cofacially arrayed polyfluorenes) is shaped by the interplay between the quickly saturating energetic gain from the delocalization and the linearly increasing reorganization penalty due to the requirement for the perfectly eclipsed sandwich-like arrangement of all involved fluorenes. Localization of the exciton onto two units in F4 and higher polyfluorenes allows for the existence of nearly isoenergetic (within 0.3 kcal/mol) valence tautomers, which differ in the position of the exciton in the polyfluorene chain. The presence of such tautomers and the plausibility of their ready interconversion over a modest (~2 kcal/mol) activation barrier suggests that exciton hopping is a plausible mechanism of singlet energy transfer along the multichromophoric π-stacked assembly in polyfluorenes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b01268.

Materials and methods, figures showing optical spectra, homodesmic analysis, transition density plots, the visual representation of the torsional modes, and tables showing energetics, bond lengths, oscillator strengths, frequencies of the torsional modes, as well as the Python script for the structure of F9 and an archive of the calculation files (PDF)

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Notes

The authors declare no competing financial interest.

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(27) Because two fluorene units are arranged in a completely eclipsed manner, the transition dipole moments for the lowest excited state (S_1) are antiparallel, which would lead to a forbidden $S_1 \rightarrow S_0$ transition, that is, the oscillator strength is expected to be zero. However, a slight misorientation due to torsional vibrations in the excited state gives rise to a discernable oscillator strength and as such also accounts for the long lifetimes of excimers. Also, see Table S18 in the SI for additional details and Diri, K.; Krylov, A. I. Electronic States of the Benzene Dimer: A Simple Case of Complexity. *J. Phys. Chem. A* **2012**, *116*, 653−662.
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(29) It is noted that similar attempts to obtain the exciton delocalized onto four units in F4 by imposing the eclipsed π-stacked arrangement of all fluorenes were unsuccessful and led to a structure in which the exciton was localized onto two units. Such a localization of exciton is likely related to the energetic penalty from the bond length changes within fluorenes and is somewhat similar to the localization of the polaron in mixed-valence systems due to the interplay of electronic coupling and reorganization energy; see e.g.: Brunschwig, B. S.; Creutz, C.; Sutin, N. Optical transitions of symmetrical mixed-valence systems in the Class II−III transition regime. *Chem. Soc. Rev.* **2002**, *31*, 168.
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