

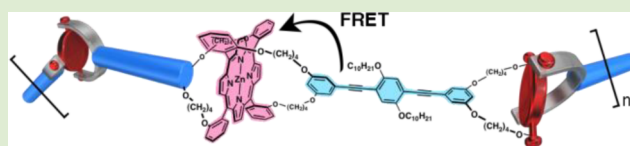
Synthesis and Fluorescence Resonance Energy Transfer Properties of an Alternating Donor–Acceptor Copolymer Featuring Orthogonally Arrayed Transition Dipoles along the Polymer Backbone

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Supporting Information

ABSTRACT: We have synthesized a new entity of polymer structures composed of π -conjugated molecules: alternating donor–acceptor (D–A) copolymers featuring orthogonally arrayed transition dipoles along the polymer backbone. Such a unique structure could lead to novel functional fluorescent materials; therefore, we examined fluorescence resonance energy transfer (FRET) properties of the D–A copolymers using absorption, fluorescence, and fluorescence lifetime measurements based on the principle of FRET. The results suggested that the orthogonal and alternating D–A copolymer could potentially lead to a new FRET system in which the efficiency is sensitive to the polymer conformation.



Defining the distance and angle between π -conjugated molecules is essential for the development of functional photonic and electronic organic materials. In fact, initial photosynthetic systems in nature set examples of how energy and electrons can be transferred directionally and efficiently within well-defined chromophore arrays.^{1,2} In view of the variety of unique structures synthesized in polymer chemistry so far, one can program the spatial arrangements of π -conjugated molecules using these polymer frameworks as scaffolds.^{3–25} For instance, dendrimers,^{3–8} ladder polymers,⁹ cyclic polymers,^{10–12} helical polymers,^{13–17} and so forth have been applied to arrange π -conjugated molecules with a controlled density, distance, angle, and handedness (Scheme 1a). Each unique structure has led to an intriguing function such as light-harvesting ability, efficient energy migration and charge separation, and circular polarized luminescence. Structures and functions are so closely correlated in polymer science that the design and synthesis of unprecedented polymer structures are of great significance. We have thus designed a new unique polymer structure composed of π -conjugated molecules: alternating donor–acceptor (D–A) copolymers featuring orthogonally arrayed transition dipoles along the polymer backbone (Scheme 1b).

One intriguing aspect of our molecular design is that the angle between the transition dipoles of the π -conjugated molecules has a significant influence on the efficiency of fluorescence resonance energy transfer (FRET). The relative orientation of the emission transition dipole of the donor and the absorption transition dipole of the acceptor are described by the orientation factor (κ^2).²⁶ The value of κ^2 can vary between 0 and 4 depending on the angle between the transition dipoles (for example, κ^2 is 0 for a perpendicular orientation). In principle, κ^2 is proportional to the energy transfer rate (k_T) and therefore controls the FRET efficiency (E). Our D–A

copolymer is designed in such a way that the polymer conformation affects κ^2 ; namely, the donor molecule (1,4-bis(phenylethynyl)benzene) is harnessed to the acceptor molecule (zinc(II) tetraphenylporphyrin) at the skew positions of the $\alpha,\beta,\alpha,\beta$ -linked doubly strapped porphyrin, which forms a repeating unit resembling the so-called universal joint (Scheme 1b). Accordingly, if the polymer main chain is extended from a random conformation, the donor dipoles should be oriented orthogonal to the acceptor dipole ($\kappa^2 = 0$); as a consequence, E potentially decreases to 0 ($k_T = 0$). This type of conformation–property relationship could be applicable to, for example, single polymer visualization and mechanically controllable FRET systems.^{27–30} We recently synthesized a D–A–D-typed light-harvesting molecule based on such a molecular design concept and constructed a “mechano-based FRET” system by incorporating the molecule into an elastomeric film.³⁰ The conformation of the D–A–D conjunction was strained upon stretching the elastomeric film, which enhanced the blue emission from the donor relative to the red emission from the acceptor; i.e., E was altered. Herein, we extended our previous D–A–D molecule to a D–A copolymer because the mechano-responsiveness is known to be amplified in polymer systems.^{31–33} In this communication, we report on the synthesis and photophysical properties of alternating and orthogonal D–A copolymers.

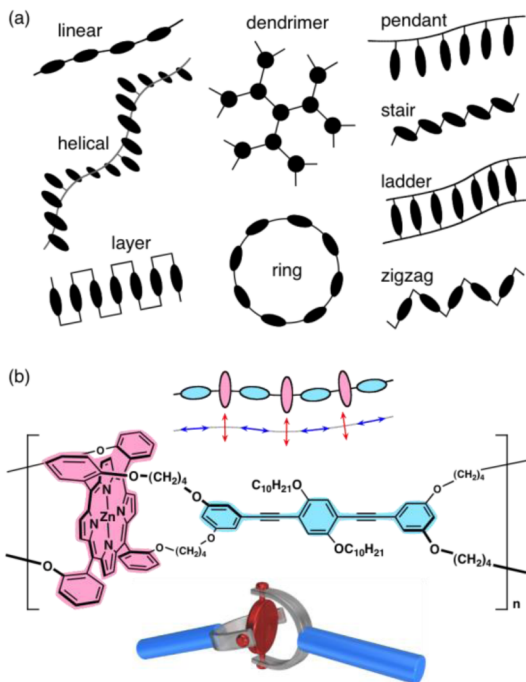
The synthetic approach for the alternating and orthogonal D–A copolymer (P1 and P2) is shown in Scheme 2. The acceptor molecule, a doubly strapped zinc(II) tetraphenylporphyrin (A1), was synthesized according to our previously reported procedure;³⁴ bis(formylphenyl) and bis-

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Scheme 1. (a) Unique Polymer Structures for Programming the Spatial Arrangement of Chromophores and (B) Our Suggested Polymer Framework and Chemical Structure, Which Has a Repeating Unit Resembling the “Universal Joint”



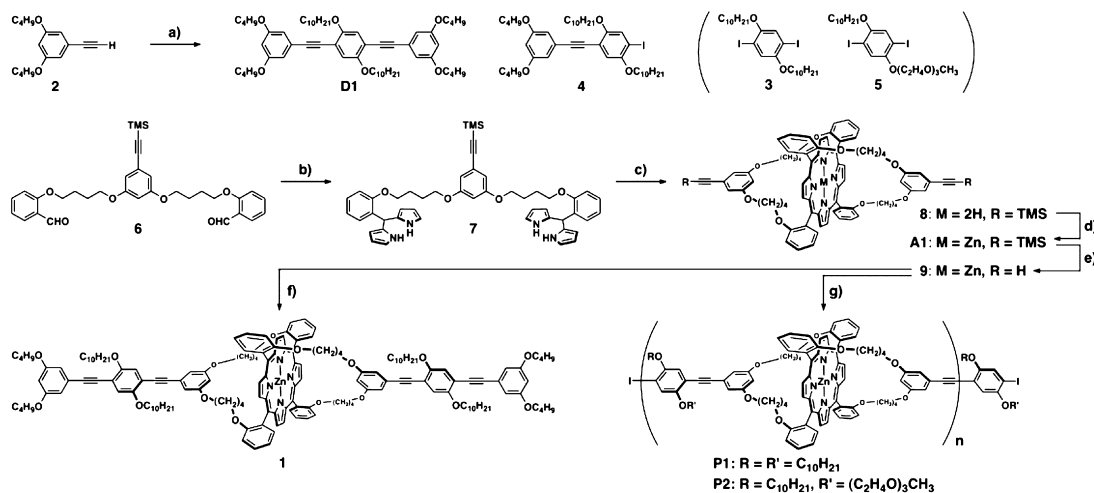
(dipyrrolylmethylphenyl) compounds (**6** and **7**, respectively) underwent condensation followed by oxidation, which selectively yielded $\alpha,\beta,\alpha,\beta$ -linked doubly strapped porphyrin (**8**), and then a zinc insertion reaction was conducted. Deprotection of the trimethylsilyl groups in **A1** was accomplished by treatment with base in tetrahydrofuran to produce a porphyrin monomer (**9**). Aryl diiodide monomers (**3** and **5**) were synthesized according to reported procedures.³⁵

The copolymer (**P1**) was prepared by step-growth polymerization using the Sonogashira–Hagihara cross-coupling reaction. The porphyrin dialkynes (**9**) and the aryl diiodide (**3**) in the presence of catalytic amounts of tetrakis-(triphenylphosphine) palladium(0) and copper iodide were dissolved in toluene with diisopropylamine and stirred at 70 °C for 3 days. The copolymer was yielded as a purple solid after reprecipitation from methanol. Through further purification using gel permeation chromatography (CHCl_3), we fractionated the **P1** into longer and shorter polymers with number-average molecular weights (M_n) of 61.7K (**P1**_{61.7K}, PDI = 1.31, DP = 38) and 25.8K (**P1**_{25.8K}, PDI = 1.18, DP = 16), respectively. Likewise, we also synthesized copolymer **P2** bearing triethylene glycol side chains, **D1** as a structural subunit of the donor molecule, and **1** as a D–A–D-typed model compound (see the Supporting Information (SI) for details).

The three-dimensional structure of the designed **P1** was confirmed using ¹H NMR spectroscopy by comparing the spectrum with those of its subunits **D1**, **9**, and **1** (Figure 1). Through the conjunction with porphyrin, aromatic protons in the donor molecule (**D1**) moved upfield due to the strong ring-current effect.³⁶ Comparison of the chemical shifts of a/a' , b/b' , and c/c' in **P1** and **D1**, respectively, showed that the degree of the upfield shifts is ordered as c/c' ($\Delta\delta = 2.61$ ppm) > b/b' (0.63 ppm) > a/a' (0.21 ppm). In addition, the donor protons in **P1** were symmetric unlike those in **1**, and no terminal protons were observed. These spectral features support the view that the 1,4-bis(phenylethynyl)benzene derivatives in **P1** are symmetrically sandwiched between two aromatic porphyrin planes along the polymer backbone.

To gain insight into the energy transfer phenomena in **P1**, we first measured the absorption and fluorescence spectra of the model compound **1** and its two structural subunits, **D1** and **A1**, in toluene. As shown in Figure 2a, the absorption spectrum of **1** is identical to the sum of those of **D1** and **A1**, thus indicating that electronic coupling between the two chromophores in the ground state is negligibly small. The fluorescence spectra of **1**, **D1**, and **A1** were obtained with an excitation

Scheme 2. Synthetic Routes to the Alternating Donor–acceptor Copolymer (P1 and P2) and the Structural Subunits (A1, D1, and 1)^a



^a(a) **3**, Pd(PPh₃)₂Cl₂, CuI, TEA. (b) Pyrrole, TFA. (c) **6**, BF₃·Et₂O, chloranil, CHCl₃, EtOH. (d) Zn(OAc)₂·2H₂O, CHCl₃, MeOH. (e) TBAF, THF. (f) **4**, Pd(PPh₃)₄, CuI, toluene, diisopropylamine. (g) **3** (for **P1**) or **5** (for **P2**), Pd(PPh₃)₄, CuI, toluene, diisopropylamine.

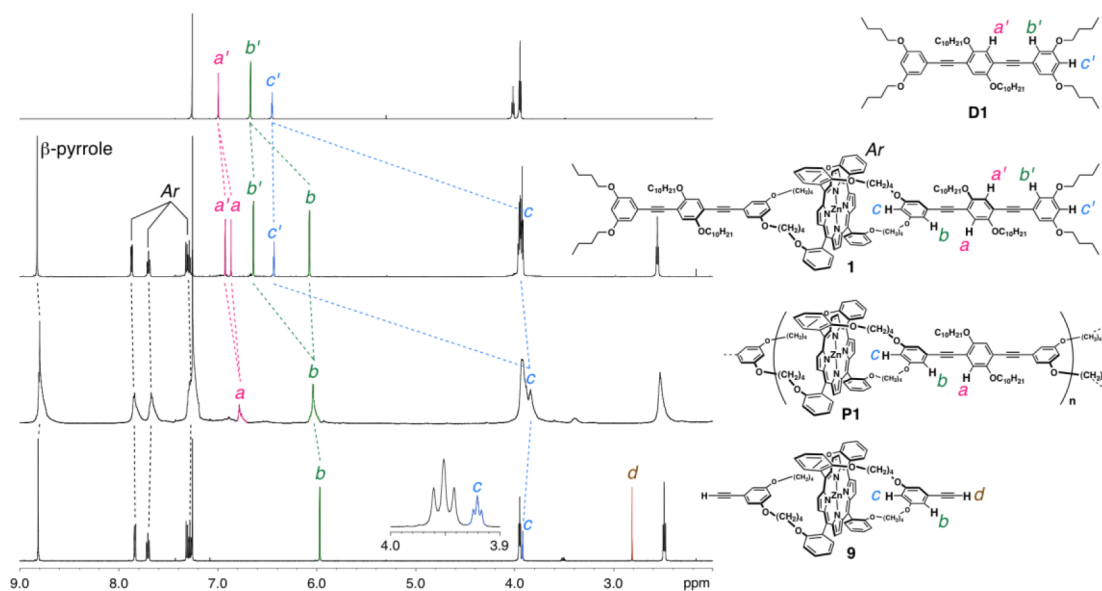


Figure 1. Partial ^1H NMR spectra of **P1** and its model compounds in CDCl_3 .

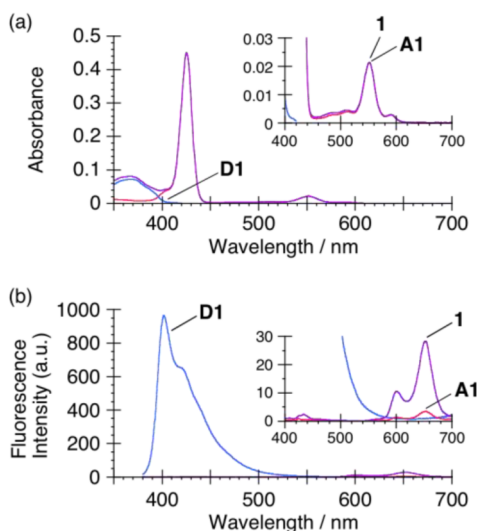


Figure 2. (a) Absorption and (b) fluorescence spectra of **1** (purple line), **D1** (blue line), and **A1** (pink line) in toluene at room temperature: $[\mathbf{1}] = [\mathbf{A1}] = 1 \times 10^{-6}$ M; $[\mathbf{D1}] = 2 \times 10^{-6}$ M; $\lambda_{\text{ex}} = 375$ nm; quartz cell of 1 cm path length. See also Table S1 (SI).

wavelength of 375 nm, the wavelength at which the donor chromophore can be selectively excited (Figure 2b). **D1** showed strong blue fluorescence with a quantum yield (Q_{D}) of 0.86 and a lifetime (τ_{D}) of 1.28 ns. The donor fluorescence spectrum ($\lambda_{\text{D/Flu}} = 402$ nm) overlaps well with the Soret absorption band of the acceptor porphyrin ($\lambda_{\text{A/Abs}} = 426$ nm), which meets the prerequisite for generating FRET. **A1** showed weak red fluorescence with a quantum yield (Q_{A}) of 0.04 and a lifetime (τ_{A}) of 2.47 ns. When the D–A–D conjunction **1** was excited at the same wavelength (375 nm), the blue fluorescence from the donor moieties was completely quenched, while the fluorescence from the acceptor was enhanced by a factor of 7.1 in comparison with **A1** (Figure 2b, inset). A perfect overlap between the excitation ($\lambda_{\text{mon}} = 653$ nm) and absorption spectra of **1** supports the hypothesis that the fluorescence quenching of the donor moieties is entirely a result of the energy transfer (see Figure S6 in the SI). In addition, the fluorescence lifetimes

of the donor molecules in **1** were too short to be determined (τ_{D} in **1** < 50 ps), which is further evidence of efficient energy transfer (Figure S7c, SI). We calculated the FRET efficiency (E) from a comparison of the spectral integrals of the donor fluorescence of **D1** and **1** ($\lambda_{\text{ex}} = 375$ nm), to be 99.8%. On the basis of E and τ_{D} , the energy transfer rate constant (k_{T}) was estimated to be 420 ns^{-1} , which shows good agreement with the values reported for porphyrin-based FRET systems.^{37,38}

The Förster distance (R_{DA}) is defined as the distance between the donor and acceptor at which E becomes 50% and is described by

$$R_{\text{DA}}^6 = 8.79 \times 10^{-5} \frac{\kappa^2 Q_{\text{D}}}{n^4} J(r) \quad (1)$$

For compound **1** in toluene, a refractive index (n) of the solvent, 1.497; Q_{D} of 0.86; a spectral overlap integral of the donor emission and the acceptor absorption [$J(r)$] of $3.41 \times 10^{15} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$; and a κ^2 of 2/3 give R_{DA} as 57.0 Å. The R_{DA} value is much larger than the actual D–A distance in **1** (15.3 Å), which was estimated from a computer-generated model (Figure S8, SI). Thus, the result implies that E is virtually unaffected by any changes in the distance between the donor and acceptor in **1** (refer to the SI, Figure S9).

The factor κ^2 is given by

$$\kappa^2 = (\sin \theta_{\text{D}} \sin \theta_{\text{A}} \cos \phi - 2 \cos \theta_{\text{D}} \cos \theta_{\text{A}})^2 \quad (2)$$

where θ_{D} and θ_{A} are the angles of the emission transition dipole of the donor and the absorption transition dipole of the acceptor (with respect to the vector joining the donor and the acceptor), respectively, and ϕ is the angle between the planes. When the acceptor transition dipole is placed parallel to one axis, κ^2 is simply represented as the angle between the transition dipoles of donor and acceptor moieties in **1** (θ_{D} in Figure 3a); in this case, eq 2 transforms into

$$\kappa^2 = 4 \cos^2 \theta_{\text{D}} \quad (3)$$

As such, FRET theory predicts that E is a function of θ_{D} and can be graphed as in Figure 3b; E of **1** can be changed sensitively within the range $85^\circ < \theta_{\text{D}} < 95^\circ$ (Figure 3b).

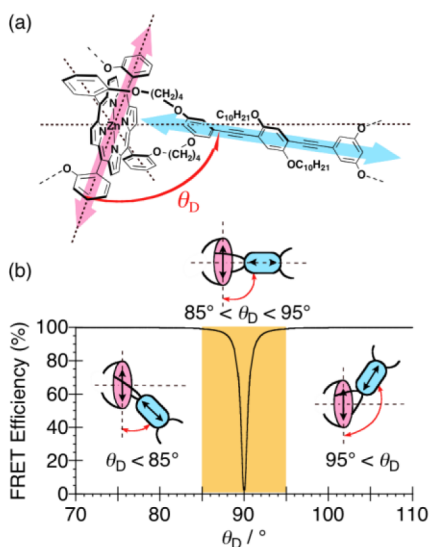


Figure 3. (a) Partial molecular structure of **1** and **P1** where θ_D is defined as the angle between the transition dipoles of the donor and acceptor chromophores. (b) The relationship between the values of the FRET efficiency (E) and θ_D .

With the photophysical characteristics of the model compound (**1**) in mind, we measured the absorption and fluorescence spectra of the copolymer **P1**_{61.7K} (Figure 4a).

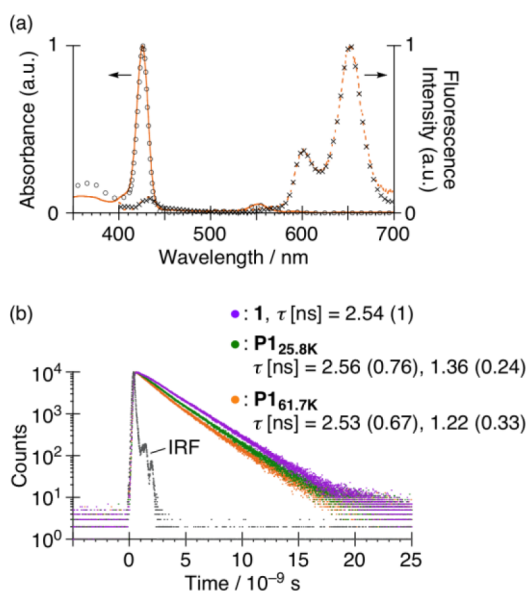


Figure 4. (a) Absorption and fluorescence spectra of **P1**_{61.7K} (orange solid and dashed lines, respectively) and **1** (O and X, respectively) at room temperature in toluene: [**P1**_{61.7K}] = 1.1×10^{-3} g L⁻¹; [**1**] = 1×10^{-6} M; λ_{ex} = 375 nm. For comparison, the absorbance and fluorescence intensity are normalized to unity at 426 and 652 nm, respectively. (b) Time-resolved fluorescence decays (τ) of **1**, **P1**_{25.8K}, and **P1**_{61.7K} in toluene obtained with excitation at 375 nm and detection at 650 nm.

P1_{61.7K} showed an absorption maximum at 426 nm; as in the case of **1**, we did not confirm any ground state interaction among the chromophores in **P1**_{61.7K}, although the chromophores should be locally concentrated along the polymer chain. The fluorescence and excitation spectra of **P1**_{61.7K} indicated quantitative energy transfer from the donor to the acceptor. In

addition, very fast decay of the donor fluorescence was confirmed ($\tau_D < 50$ ps), which also supports very efficient FRET (Figure S10a and S10c, SI). Interestingly, the fluorescence decay of the acceptor porphyrin in **P1**_{61.7K} could be fitted with biexponential decays, namely, 2.53 and 1.22 ns, as summarized in Figure 4b. The longer lifetime was close to the lifetime of **A1** (τ_A) and thus assignable to the intrinsic fluorescence lifetime of the porphyrin chromophore. In contrast, the shorter lifetime most likely arises from the homo energy transfer between the porphyrin chromophores within a polymer chain.^{22,26,39} On the basis of a similar consideration using eq 1, the Förster distance for the homotransfer (R_{AA}) was calculated to be 18.1 Å.⁴⁰ Since the porphyrin acceptors are repeated along the polymer chain at intervals of about 30 Å, which is much larger than R_{AA} , homotransfer between two adjacent porphyrins is unlikely. Given the flexible structure of **P1**, the main chain should coil and entwine randomly in solution, which then allows remote porphyrin molecules to approach each other and gives rise to the homotransfer. In fact, the contribution of the homotransfer is larger in the longer polymer in which there should be a larger number of intersections of the polymer chain (Figure 4b). Therefore, the energy transfer efficiency in the polymer system is influenced not only by the local conformation that defines θ_D but also by the coiled structure of the polymer main chain. Hence, we expect that our polymer would lead to a unique FRET system that is sensitive to the structural changes of the polymer backbone (Figure S11, SI).

To mechanically control the conformation of our D–A copolymer, manipulation of the amphiphilic **P2** at the air/water interface is worth attempting.³⁵ Another approach, which we are currently pursuing, is incorporation of **P1** into a polymeric matrix to take advantage of the elasticity or crystallinity of the matrix.^{30,41,42} In preliminary experiments, we have confirmed that the photophysical characteristics of **P1** were preserved intact in the polymer matrix, and as such, the composite material could be processed through spin coating and electrospinning methods (Figures S12–S14, SI). Studies on controlling the FRET efficiency of **P1** by applying mechanical perturbations to the composite materials are now in progress.

In summary, we have synthesized a new structural entity: a D–A copolymer featuring orthogonally and alternately arrayed transition dipoles along the polymer backbone. As far as we are aware, such a polymer design concept has not been reported so far. The energy transfer phenomena of the new polymer were investigated by using spectroscopic methods and discussed based on the principle of FRET. The results suggested that the orthogonal and alternating D–A copolymer could potentially lead to a new FRET system in which the efficiency is sensitive to the polymer conformation (Figure S11, SI). We believe that our copolymers will join the family of the unique polymer structures composed of π -conjugated molecules (Scheme 1a) that have provided a variety of intriguing concepts and functional materials.⁴³

■ ASSOCIATED CONTENT

Supporting Information

Instrumentation, detailed synthetic procedures and identification, photophysical characteristics in solution, and composite materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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