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Selected Papers

Synthesis of a Doubly Strapped Light-Harvesting Porphyrin Bearing Energy Donor Molecules Hanging on to the Straps: An Attempt toward Macroscopic Control over Molecular Conformation that Affects the Efficiency of Fluorescence Resonance Energy Transfer

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We report here the synthesis of a light-harvesting molecule **1**, in which 5,5′-diphenyl-2,2′-bithiophene units (energy donors) and a doubly strapped porphyrin (energy acceptor) are three-dimensionally connected through four alkyl chains to form a "universal joint"-like architecture. From the results of the optical properties of **1** in solution, fluorescence resonance energy transfer (FRET) takes place from the donor to the acceptor in **1** with the FRET efficiency of 99.7%. We prepared **1**/polydimethylsiloxane (PDMS) elastomeric films in which **1** is connected to a polysiloxane network through covalent bonds. When we stretched the **1**/PDMS film (elongation: up to 60%), the FRET efficiency decreased by 13.1%. The theoretical analysis suggests that the FRET efficiency of **1** (E) is virtually uninfluenced by any changes in the distance between the donor and acceptor (r). Therefore, the observed change in FRET efficiency should have been derived from the orientation factor (κ^2), which describes the relative orientation of the emission transition dipole of the donor and the absorption transition dipole of the acceptor. The anisotropic absorption spectral measurements support the notion that the transition dipoles of the fluorophores became orthogonally aligned upon stretching, as expected from the molecular design.

Synchronizing *molecular* motion and *human-scale* phenomena, the dimensions of which differ by approximately five to seven orders of magnitude (e.g., from nanometers to millimeters), is attracting much attention. Machinery based on molecular motion—for instance, rotational and/or translational motion in interlocked molecules or structural isomerization induced by photo- or electrical stimuli—has been extended to visible shape changes in macroscopic materials by application of self-assembled supramolecular systems.[1–5] These systems have potential applications as actuators and mechanical devices that take advantage of changes in molecular momentum. In clear contrast to these studies, manipulation of molecular-scale phenomena through macroscopic mechanical stimulation has become an attractive challenge in the past few years.[6–26] The application of a macroscopic mechanical force—one that is independent of thermal, photonic, or electronic input—can lead to novel molecular-level phenomena that cannot be realized using conventional methods. For example, ultrasound-induced mechanical forces can accelerate and alter the course of electrocyclic ring-opening reactions, yielding products that are not obtainable from purely thermal or light-induced reactions.[7] In addition, conformational changes induced by variations in the surface pressure at air–water interfaces have enabled reversible switching of molecular functions.[9,10] This concept should be conducive to the enhancement of inherent molecular properties and even to the creation of unprecedented smart materials that can link molecular-level functions to human-scale dynamics. Moore and co-workers recently provided a comprehensive review of mechanically induced chemical changes in *polymeric* materials: a subject that is related conceptually to the topic of this present paper.[6] Inevitably, rational molecular design is of great importance to transmit the dynamic motion over different hierarchies of size.

Toward this goal, we have designed a light-harvesting molecule **1** featuring 5,5′-diphenyl-2,2′-bithiophene units as energy donors and a porphyrin unit as an acceptor, i.e., an optimal combination for generating fluorescence resonance energy transfer (FRET) (Scheme 1a).[27–29] The three-dimensional architecture of **1** resembles that of a universal joint (or Cardan joint), which enjoys mechanical motion. By manipulating the molecular motion through macroscopic mechanical force, we expect that the light-harvesting ability of **1** can be controlled (see below).

FRET is transfer of the excited-state energy from the initially excited donor to an acceptor. Since FRET efficiency (E) depends on the distances between the donor and acceptor

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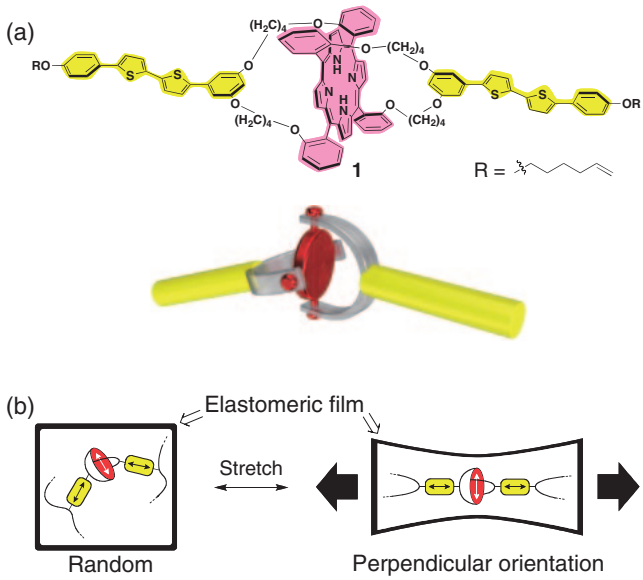


Scheme 1. (a) Chemical structure of **1** and schematic representation of the "universal joint." (b) Cartoon representation of the concept developed in this study.

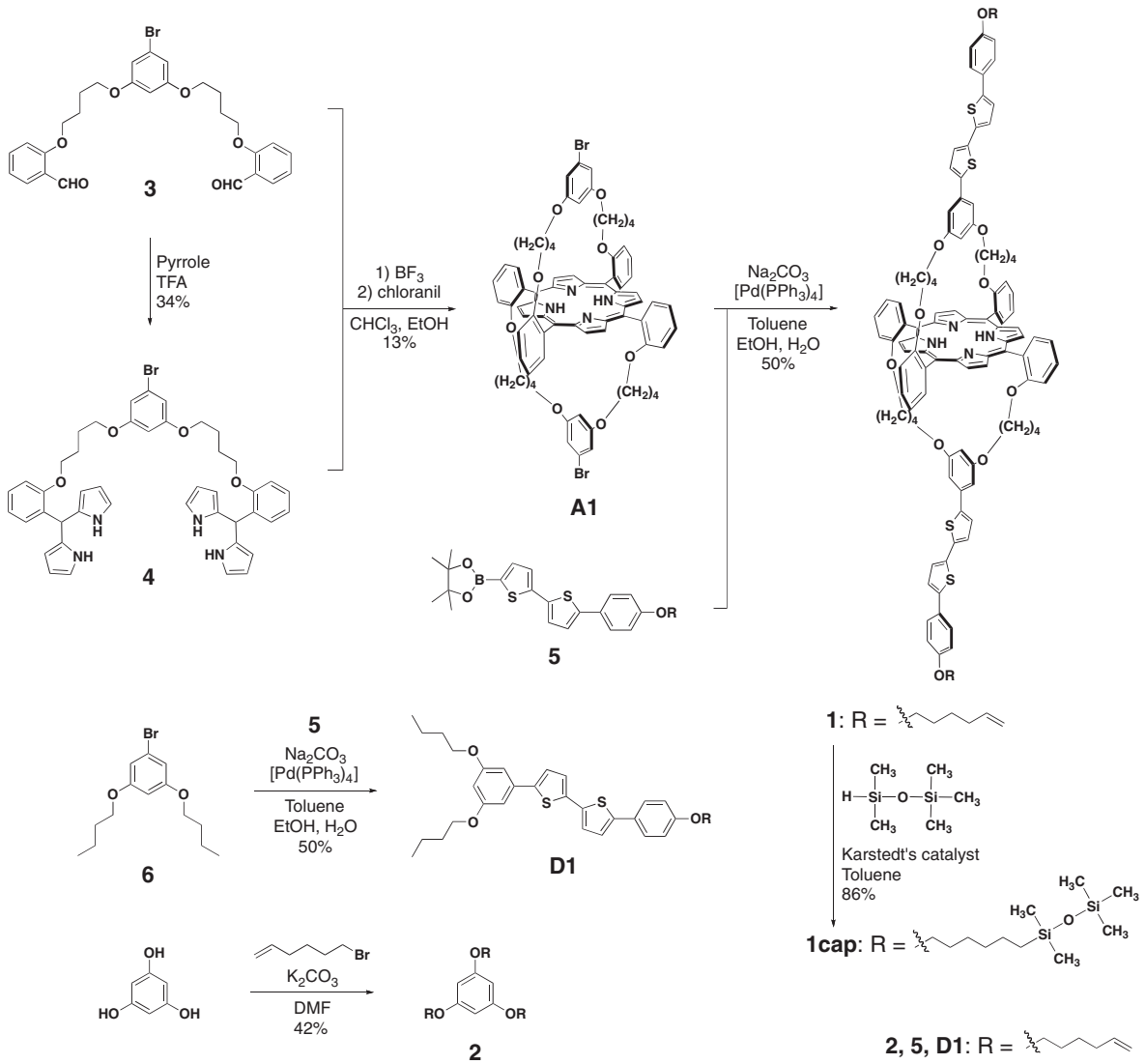
molecules, FRET-based spectral changes can be a reliable "ruler" for measuring the distances between two sites on macromolecules and proteins.[30–35] In addition, Clark et al. and Sijbesma et al. have recently reported a polymeric material in which changes in stress of the polymer matrix is translated into changes in FRET efficiency because the macroscopic deformation affects the donor–acceptor distance.[16,17] Unlike these studies, we have focused our attention on the fact that FRET is the result of long-range dipole–dipole interactions between the donor and acceptor; the FRET efficiency (E) depends on the orientation factor (κ^2), which describes the relative orientation of the emission transition dipole of the donor and the absorption transition dipole of the acceptor.[30,36–39] Thus, the orientation factor is sensitive to molecular conformational changes. In solution, the donor transition dipoles of **1** are directed randomly toward the transition dipole of the porphyrin because they are connected through flexible alkyl chains. In this case, the orientation factor (κ^2) is approximated to be equal to 2/3, which is an average of the values for the donors and acceptor randomized through rotational diffusion prior to energy transfer. The orientation factor (κ^2) can vary from 0 to 4 depending on the angle between the transition dipoles (θ_D): perpendicular (90°) and parallel (0°) orientations correspond to values of κ^2 of 0 and 4, respectively. We harnessed the donor molecules in **1** to the acceptor platform at the skew positions of the $\alpha,\beta,\alpha,\beta$-linked doubly strapped porphyrin. Given the molecular structure of **1**, the donor dipoles should be oriented perpendicular to the acceptor dipole when a tensional force is applied to its termini; thus, the efficiency of FRET would be changed as a result of the controlled molecular conformation of **1**.

Herein, we report the synthesis and the photophysical studies of compound **1** in solution. In addition, we have prepared elastomeric materials in which the molecular conformation of compound **1** can be controlled dynamically in response to a macroscopic stretching operation (Scheme 1b). Upon stretching the elastomeric film, we have observed the changes in the luminescence properties of **1** due to the changes in the efficiency of FRET, which is very much a molecular level phenomenon.

Results and Discussion

Synthesis of the Light-Harvesting Molecule. The synthetic scheme of the light-harvesting molecule **1** and its two structural subunits (i.e., **A1** and **D1**) is shown in Scheme 2. The *meso*-phenyl doubly strapped porphyrin **A1** was synthesized from the bis(formylphenyl) and bis(dipyrrolylmethylphenyl) straps **3** and **4**, respectively under Lindsey conditions. This synthetic approach enables selective formation of $\alpha,\beta,\alpha,\beta$-linked doubly strapped porphyrin.[29] The bromobenzene at the center of each strap is for the Suzuki–Miyaura coupling reaction with **5**, which yields the light-harvesting molecule **1** featuring 5,5′-diphenyl-2,2′-bithiophene units as energy donors and a porphyrin unit as an acceptor. The subunit of donor molecule (**D1**), which lacks porphyrin acceptor, was synthesized from **5** and 1-bromo-3,5-dibutoxybenzene (**6**) through Suzuki–Miyaura coupling reaction. Compound **1** was reacted with pentamethyldisiloxane in Pt-catalyzed hydrosilylation conditions to yield compound **1cap**, which is for a reference experiment (see below and Figure S9 in the Supporting Information). Williamson ether synthesis of phloroglucinol with 6-bromo-1-hexene in the presence of K_2CO_3 led to compound **2**, which is a crosslinker for preparation of PDMS elastomeric films (Scheme 3).

Spectroscopic Measurements of 1 in Solution. Figure 1 displays the optical properties of compound **1** and its two structural subunits, **D1** and **A1**, in solution (see the Supporting Information for the syntheses and characterization of **1**, **D1**, and **A1**). Because the absorption spectrum of **1** is identical to the sum of those of the reference compounds **D1** and **A1**, electronic coupling between the two chromophores in the ground state is negligibly small (Figure 1a). Figure 1b presents the emission spectra of **1**, **D1**, and **A1** excited at 370 nm, which is close to the absorption maximum (λ_{max}) of the donor molecule; the emission of **D1** (at ca. 450 nm) is almost completely quenched in **1**, with the porphyrin emission (at ca. 650 nm) of **A1** exhibiting a 4.4-fold increase in intensity in **1**. This confirms that light harvesting occurred from the 5,5′-diphenyl-2,2′-bithiophene moieties to the porphyrin unit in **1** as a result of suitable spectral overlap between the emission of the donor **D1** and the absorption of the acceptor **A1**. We calculated the efficiency of energy transfer (E) to be 99.7% from a comparison of the spectral integrals of the donor emissions of **D1** and **1**, collected at the same excitation wavelength (370 nm). Perfect overlap between the excitation spectrum and the corresponding absorption spectrum of **1** supports the notion that the fluorescence quenching is entirely a result of the energy transfer in the donor–acceptor system (Figure 1c). In addition, the absorption, fluorescence, and excitation spectra of **1** are virtually independent of solvent polarity (PhMe, $CHCl_3$, THF, and DMF), thus indicating that the contribution of electron transfer from the donors to the porphyrin acceptor is negligible (see Figure S5 in the Supporting Information). This optical property is derived from the average conformation of **1** as it moves randomly in solution.



Scheme 2. Syntheses and chemical structures of the light-harvesting molecule **1**, its two structural subunits (**A1** and **D1**, which are acceptor and donor units in **1**, respectively), **1cap**, and crosslinker **2** for preparation of PDMS elastomeric films.

The FRET efficiency (E) can be described using eq 1, where r (Å) is the distance between the donor and acceptor molecules and R_0 (Å) is the Förster distance at which the energy-transter efficiency becomes 50%:

$$E = {R_0}^6/[{R_0}^6 + r^6] \quad (1)$$

$${R_0}^6 = 8.79 \times 10^{-5}[\kappa^2 n^{-4} Q_D J(\lambda)] \quad (2)$$

Using eq 2, we calculated the Förster distance (R_0) to be 36.9 Å (Figure 2a): here, we used an orientation factor (κ^2) of 2/3, a refractive index (n) for the solvent of 1.43, a fluorescence quantum yield for the donor (Q_D) of 0.19, and a spectral overlap integral for the donor emission and the acceptor absorption [$J(\lambda)$] of $9.50 \times 10^{14}\,M^{-1}\,cm^{-1}\,nm.^4$ The relationship between the values of E and r for **1** obtained from eq 1 reveals that the value of E is greater than 99.5% even at a value of r_{max} of 14.8 Å, the farthest possible distance between the donor and acceptor units connected through these alkyl chains (Figure 2b). Therefore, we would not expect the FRET efficiency (E) of **1** to be affected by any changes in the distance between the donor and acceptor units (see below).

The orientation factor (κ^2) is given by eq 3:

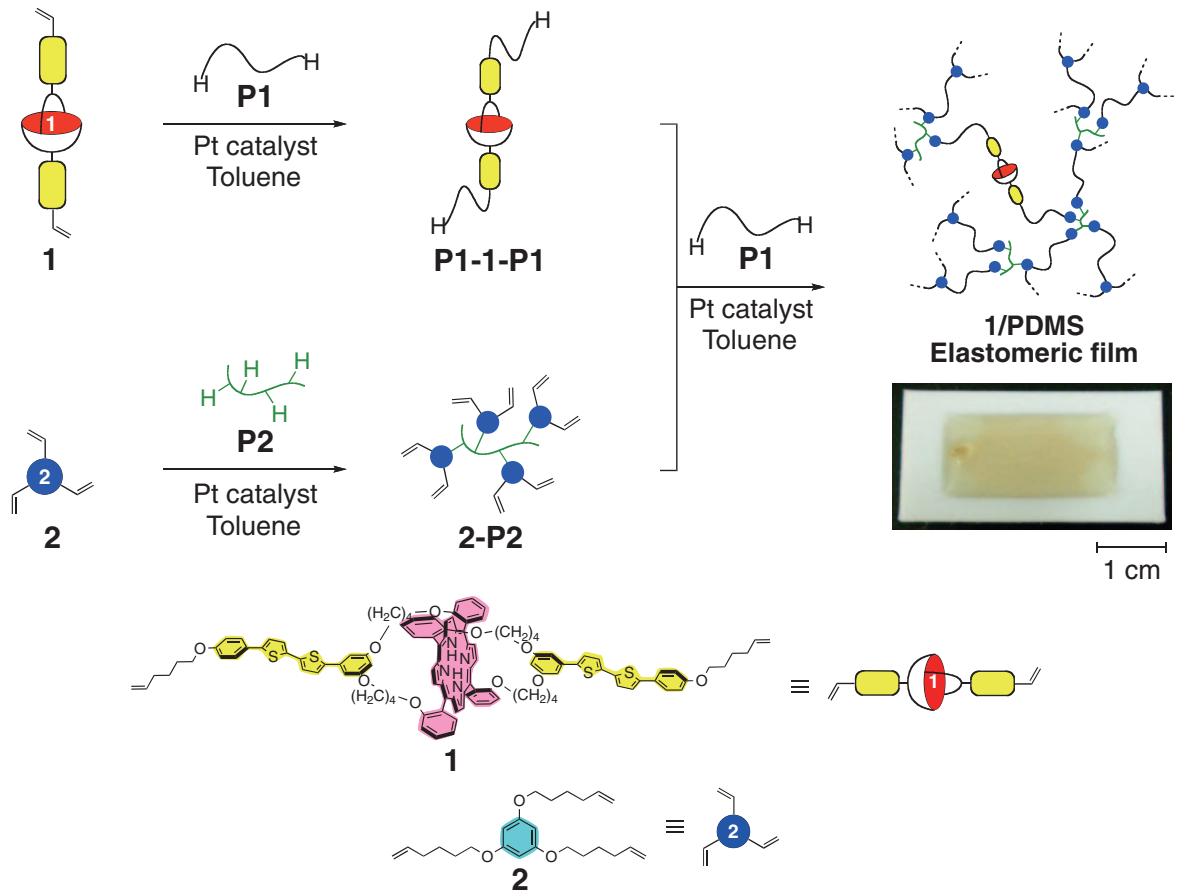
$$\kappa^2 = (\sin\theta_D \sin\theta_A \cos\phi - 2\cos\theta_D \cos\theta_A)^2 \quad (3)$$

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, the orientation factor is simply represented as the angle (θ_D in Figure 2c) between the transition dipoles of donor and acceptor moieties in **1**; in this case, eq 3 transforms into eq 4:

$$\kappa^2 = 4\cos^2\theta_D \quad (4)$$

Thus, the FRET efficiency (E) is a function of θ_D, which can be graphed as shown in Figure 2d; perpendicular ($\theta_D = 90°$) orientation results in E to be zero.

Spectroscopic Measurements of 1/PDMS Elastomeric Films before and after the Macroscopic Stretching Operation. In order to control the orientation factor (κ^2) by macroscopic mechanical force, we have prepared elastomeric



Scheme 3. Schematic representation of the preparation of **1**/PDMS film and a photograph of the final product.

films in which compound **1** is incorporated through covalent bonds (Scheme 3).[40–43] We chose polydimethylsiloxane (PDMS) to be the polymeric matrix because its transparency allowed us to evaluate the optical properties of the incorporated **1**. Compound **1** is readily introduced into PDMS networks through hydrosilylation of its two terminal olefin moieties. **P1** is a hydride-terminated polydimethylsiloxane (M_n, 6000; *d*, 0.97; viscosity, 100 cSt; *n*, 1.403) that we reacted in excess (50 mg, 20 μmol of SiH units) with **1** (8 nmol) in the presence of Karstedt's catalyst (1.5 μL) in toluene (50 μL) under an Ar atmosphere at 30 °C for 1 h, thereby yielding **P1–1–P1**, in which **1** was present in the main chains of PDMS. GPC chromatogram of the product obtained after the hydrosilylation of **1** with **P1** clearly reveals that **1** had reacted with **P1** quantitatively (see Figure S6 in the Supporting Information). **P2** is a copolymer of dimethylsiloxane and methylhydrosiloxane (M_n, 1900–2000; methylhydrosiloxane, 15–18 mol %; *d*, 0.97; viscosity, 25–35 cSt; *n*, 1.400); we synthesized the macro crosslinker **2–P2** from **2** (30 mg, 80 μmol) and **P2** (21 mg, 40 μmol of SiH units) in the presence of Karstedt's catalyst (5 μL) in toluene (500 μL) at room temperature. The resultant solution of **2–P2** and **2** was added to a mixture of **P1–1–P1** (8 nmol) and **P1** (300 mg) in toluene (700 μL) and the mixture was stirred at room temperature. After 15 s, the resultant solution was transferred onto a Teflon substrate (20 mm × 40 mm) and an elastomeric film was obtained by a crosslinking hydrosilylation reaction under gradual evaporation of toluene at 30 °C overnight. FT-IR spectra recorded for the samples before and after the crosslinking reaction revealed that the elastomeric film did not feature SiH bonds (no stretching vibrations at 2127 cm^{-1}),[42] indicating that all of the hydride-terminated polydimethylsiloxane, including **P1–1–P1**, had crosslinked with **2–P2** in the elastomeric film (see Figure S7 in the Supporting Information). The obtained films, which were ca. 20 mm long, 10 mm wide, and 1 mm thick, were about twice stretchable (elongation: up to ca. 100%, see Figure S8 in the Supporting Information).

Figure 3a reveals that the absorption spectrum of the **1**/PDMS elastomeric film was identical to that of **1** in solution (Figure 1a), indicating that **1** had been incorporated into the elastomeric film homogeneously. For reference, when **1cap** was doped (but not connected covalently) within a PDMS film, the Soret band of the porphyrin unit underwent a hypsochromic shift (see Figure S9 in the Supporting Information). Our results indicate that the covalent crosslinking of **1** in the PDMS network prevented the fluorophores from undergoing intra- and intermolecular aggregation, which is a very important requirement for the following photophysical studies of **1**/PDMS films.

The fluorescence spectrum of the **1**/PDMS film excited at 370 nm prior to stretching revealed that efficient FRET also occurred in the film, similar to the situation in solution (cf. purple lines in Figures 1b and 3b), because the donor and acceptor units were harnessed within the Förster distance and the directions of their transition dipoles remained random (i.e.,

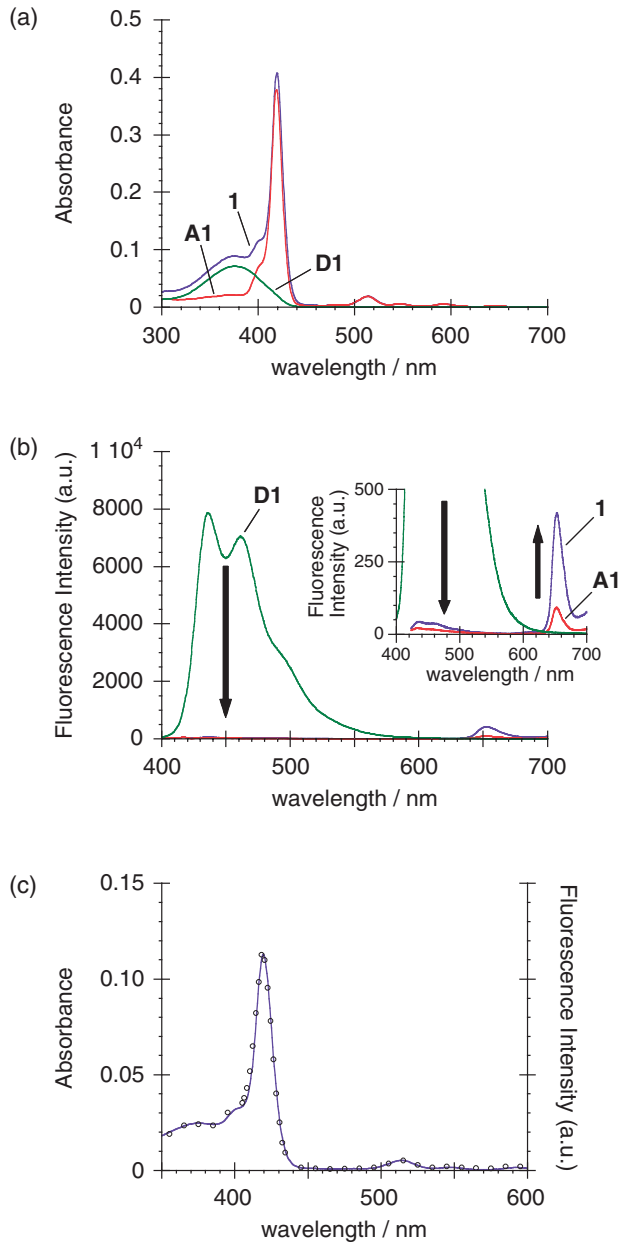


Figure 1. (a) Absorption and (b) fluorescence spectra of **1** (purple line), **D1** (green line), and **A1** (red line) at room temperature in a mixed solvent system of toluene and siloxane oligomer (3:7, v/v): $[\mathbf{1}] = [\mathbf{A1}] = 1 \times 10^{-6}$ M; $[\mathbf{D1}] = 2 \times 10^{-6}$ M; $\lambda_{ex} = 370$ nm (wavelength at which the donor molecules are excited selectively). (c) Absorption (purple solid line) and fluorescence excitation (○) spectra of **1** in a mixed solvent system of toluene and siloxane oligomer (3:7, v/v): $[\mathbf{1}] = 0.3 \times 10^{-6}$ M; $\lambda_{mon} =$ 653 nm; RT.

the orientation factor remained equal to 2/3). Note that the contribution of intermolecular FRET was negligible, as indicated by the observation that elastomeric films prepared using the donor **D2** as a crosslinker preserved the fluorescence intensity of **D2** even in the presence of the acceptor molecule **A1** ($[\mathbf{A1}]/[\mathbf{D1}] = 0$–1.0; see Figure S10 in the Supporting Information).

When we stretched the **1**/PDMS film up to 60% of elongation, the fluorescence of the donor was enhanced relative to that of the acceptor (Figure 3b). In contrast, elastomeric films prepared from only **D2** or **A1** resulted in weaker fluorescence upon stretching, because the films became thinner (see Figure S11 in the Supporting Information, for this reason, normalized fluorescence spectra are shown in Figure 3b). Hence, the recovery of the donor fluorescence in the stretched **1**/PDMS film implied that the FRET efficiency decreased as a result of a macroscopic mechanical force. The inset to Figure 3b presents the ratio of the fluorescence intensities of the donor and acceptor (I_D/I_A) plotted with respect to the stretching ratio. Upon stretching, the I_D/I_A ratio increased. Because the I_D/I_A ratio is a function of the FRET efficiency, we calculated the change in the FRET efficiency (ΔE) induced upon elongation of 30 and 60% to be 5.6 and 13.1%, respectively (see Figure S12 in the Supporting Information). As mentioned above, we would expect the FRET efficiency of **1** to be virtually uninfluenced by any changes in the distance between the donor and acceptor. In addition, **1** in the films is so diluted that we can rule out the contribution of intermolecular FRET (see Figure S10 in the Supporting Information). Therefore, the observed change in FRET efficiency (ΔE) should have been derived from the orientation factor (κ^2); according to eqs 1 and 2, as the orientation factor (κ^2) decreases, the FRET efficiency (E) decreases.[44,45] Importantly, the control of the FRET efficiency was reversible in response to the mechanical operation, although the reverse process was slow (several hours), presumably because the conformational relaxation was hampered in such a viscoelastic material.

To provide evidence for the controlled angle of the transition dipoles, we conducted anisotropic absorption spectral measurements with a polarizer placed between the film and the light source. The absorption spectrum of the as-prepared film revealed no anisotropy, indicating a random orientation of the transition dipoles. In contrast, the film elongated by 30% clearly revealed that the transition dipoles of the donor and acceptor units were oriented parallel and perpendicular, respectively, to the stretching direction (Figure 3c).[46] This supports the notion that the transition dipoles of the fluorophores became orthogonally aligned upon stretching, as expected from the molecular design; consequently, the efficiency of the FRET was controllable.

Conclusion

In summary, we have synthesized a light-harvesting molecule **1**, the structure of which is reminiscent of a universal joint. Due to its unique three-dimensional architecture, the light-harvesting ability can be controlled in response to molecular conformational changes. To synchronize the molecular level motion with human-scale dynamics, we have incorporated **1** within PDMS film and examined changes in FRET efficiency of **1** upon stretching the film. Although the observed change was small (ΔE is 13.1% at 60% of elongation), we have demonstrated that elastomeric materials can link the human-scale dynamics to molecular-level function. "Mechano-based FRET" systems have potential application to detect internal damage of polymeric materials: the previously reported concepts are based on the changes in the distance between

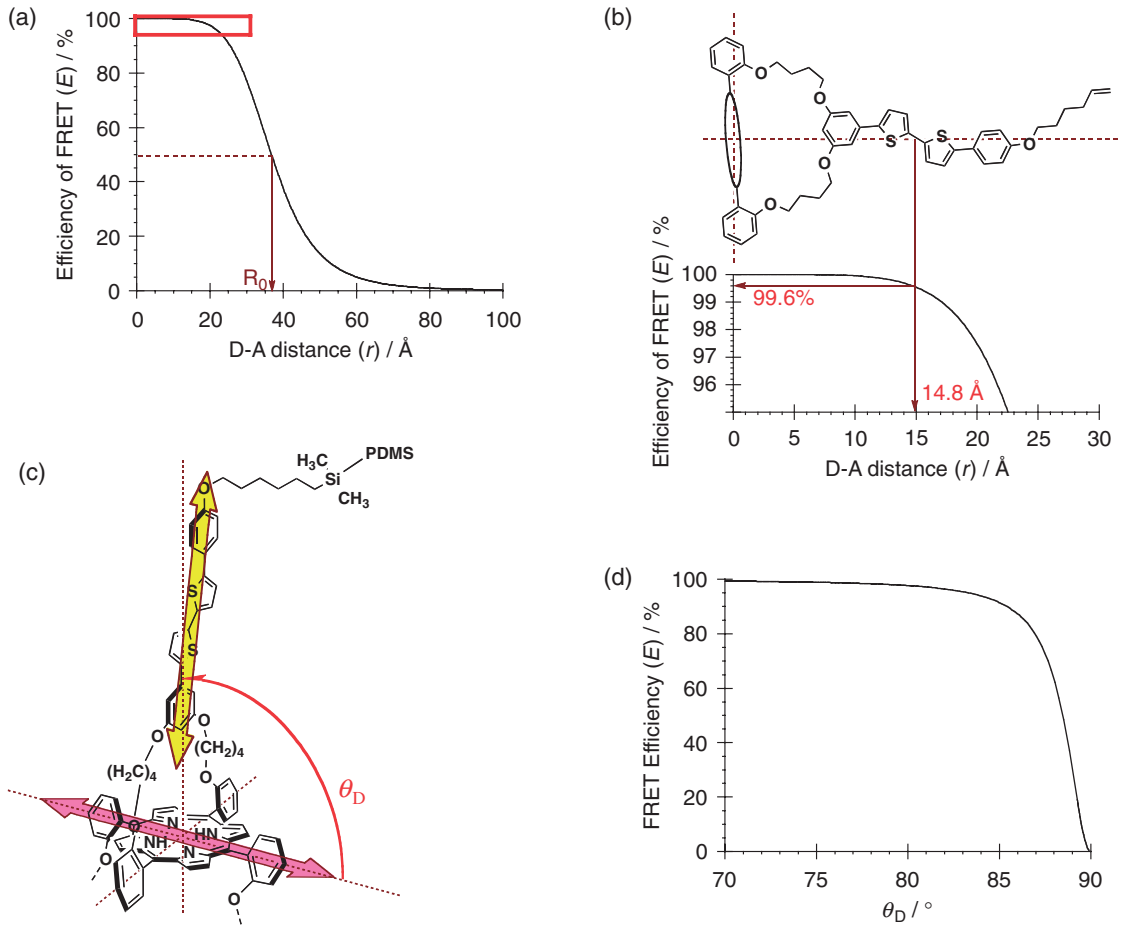


Figure 2. (a) The relationship between the values of the energy-transter efficiency (E) and the distance between the donor and acceptor molecules (r) for **1** obtained from eq 1. The Förster distance (R_0) is calculated to be 36.8 Å at which energy-transter efficiency becomes 50%. (b) The enlarged graph of the red square area in Figure 2a. The graph revealed that the value of E is greater than 99.5% even at a value of r_{max} of 14.8 Å, the farthest possible distance between the donor and acceptor units connected through these alkyl chains. (c) The partial molecular structure of **1** that is connected to a polysiloxane network; θ_D is defined as the angle between the transition dipoles of the donor and acceptor moieties in **1**. (d) The graphic image of the relationship between the values of E and θ_D for **1** obtained from eqs 1, 2, and 4, in which the value of r is 14.8 Å (r_{max}).

the donor and acceptor (i.e., "r" in eq 1).[16,17] To the best of our knowledge, this system is the first example of controlling FRET efficiency through a mechanism based upon the orientation factor (κ^2) being affected by a macroscopic mechanical force. We expect that optimization of the polymer structures and their mechanical properties will improve the mechanical responsiveness of the incorporated molecules. Studies along this line and manipulation by hand of more functional molecular machines are now in progress.

Experimental

Measurements. ^{1}H NMR spectra were recorded on a Bruker Biospin DRX-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane (0 ppm for ^{1}H) or residual $CHCl_3$ (77 ppm for ^{13}C) as an internal standard. Mass spectral data were obtained using a SHIMADZU AXIMA-CFR Plus MALDI TOF mass spectrometer. Melting points were determined with a Yanako NP-500P micro melting point apparatus. UV–vis absorption spectra and fluorescence spectra were obtained on a Hitachi U-2900 spectrophotometer and a Hitachi F-7000 spectrophotometer, respectively. Relative fluorescence quantum yield of **D1** was determined using quaterthiophene ($\Phi = 0.18$, benzene) as standard.[47]

Materials. A hydride-terminated polydimethylsiloxane **P1** and a copolymer of dimethylsiloxane and methylhydrosiloxane **P2** were purchased from GELEST, Inc. Platinum(0)–(1,1,3,3-tetramethyl-1,3-divinyldisiloxane) complex in xylene (Karstedt's catalyst) was purchased from Aldrich. All other reagents and solvents were purchased from Aldrich, Kanto Chemical Co., or Wako Chemicals and used as received.

Synthesis of A1. A mixture of 1-bromo-3,5-bis[4-(2-formylphenoxy)butoxy]benzene (**3**) (604 mg, 1.12 mmol) and compound **4** (863 mg, 1.12 mmol) in $CHCl_3$ (1000 mL), EtOH (8 mL) was bubbled with argon for 2 h. Boron trifluoride diethyl etherate (196 µL, 1.56 mmol) was added to the solution under argon atmosphere and the mixture was stirred at room temperature. After 3 h, chloranil (760 mg, 3.35 mmol) was added and the resulting solution was stirred for 3 h. After purification through flash column chromatography (SiO_2;

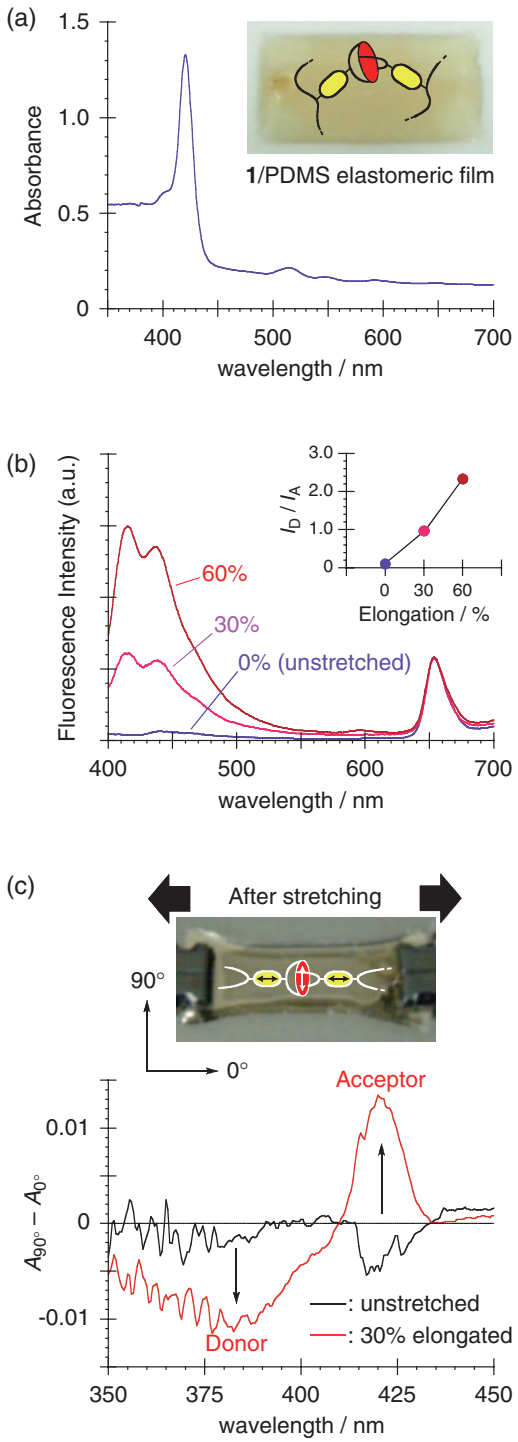


Figure 3. (a) Absorption spectrum of the **1**/PDMS film. (b) Fluorescence spectral changes of the **1**/PDMS elastomeric film upon stretching: Intensities are normalized at 653 nm, $\lambda_{ex} = 370$ nm. Inset to (b): I_D/I_A ratio plotted with respect to the stretching ratio. (c) Differential anisotropic absorption spectra of the **1**/PDMS film before (black line) and after (red line) stretching.

$CHCl_3$) and column chromatography (SiO_2; *n*-hexane/$CHCl_3$, from 1:3 to 1:4), a purple powder was obtained (180 mg, 13%). Mp 156.0–158.0 °C. ^{1}H NMR ($CDCl_3$, 298 K): δ −2.61 (2H, s, inner-N*H*), 0.80–0.88 (8H, m, –O–CH_2–(CH_2)$_2$–CH_2–O–), 1.05–1.10 (8H, m, –O–CH_2–(CH_2)$_2$–CH_2–O–), 2.55 (8H, t, $J = 6.3$ Hz, –O–CH_2–), 3.92 (8H, t, $J = 5.4$ Hz, –O–CH_2–), 4.06 (2H, t, $J = 2.1$ Hz, C_6H_3–Br), 6.14 (4H, d, $J = 1.8$ Hz, C_6H_3–Br), 7.28–7.32 (8H, m, –O–C_6H_4–), 7.71 (4H, t, $J = 8.1$ Hz, –O–C_6H_4–), 7.86 (4H, dd, $J = 7.8$, 1.8 Hz, –O–C_6H_4–), 8.74 (8H, s, β-pyrrole). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ 24.99, 25.18, 67.15, 68.10, 99.09, 110.28, 112.34, 115.69, 119.67, 122.01, 129.61, 131.76, 135.46, 158.87, 159.74. MALDI-TOF-MS (dithranol): Found $m/z = 1272.48$, Calculated for $[M]^+$ ($C_{72}H_{64}Br_2N_4O_8$) = 1272.31.

Synthesis of D1. A mixture of 2,3-dimethyl-2,3-butylidene 5′-[4-(5-hexenyloxy)phenyl]-2,2′-bithiophene-5-boronate (**5**) (133 mg, 285 µmol), 1-bromo-3,5-dibutoxybenzene (**6**) (72.3 mg, 240 µmol), sodium carbonate (170 mg, 1.37 mmol) in toluene (9.0 mL), EtOH (2.2 mL), water (2.2 mL) was bubbled with argon for 2.5 h. Tetrakis(triphenylphosphine)palladium(0) (19.8 mg, 17.1 µmol) was added to the solution and the mixture was refluxed for 6.5 h. After cooling to room temperature, the reaction mixture was washed with water and the organic layer was dried over anhydrous Na_2SO_4. The filtrate was evaporated and the crude product was purified by column chromatography (SiO_2; *n*-hexane/$CHCl_3$) to produce a yellow powder (66.8 mg, 50%). Mp 102.4–103.0 °C. ^{1}H NMR ($CDCl_3$, 298 K): δ 0.99 (6H, t, $J = 7.5$ Hz, –O–CH_2–(CH_2)$_2$–CH_3), 1.48–1.55 (4H, m, –O–CH_2–(CH_2)$_2$–CH_3), 1.56–1.62 (2H, m, –O–CH_2–(CH_2)$_3$–CH=CH_2), 1.76–1.87 (6H, m, –O–CH_2–(CH_2)$_3$–CH=CH_2 and –O–CH_2–(CH_2)$_2$–CH_3), 2.13–2.16 (2H, m, –O–CH_2–(CH_2)$_3$–CH=CH_2), 3.97–4.01 (6H, m, –O–CH_2–(CH_2)$_4$–CH=CH_2 and –O–CH_2–(CH_2)$_2$–CH_3), 4.98–5.07 (2H, m, –O–CH_2–(CH_2)$_3$–CH=CH_2), 5.81–5.87 (1H, m, –O–CH_2–(CH_2)$_3$–CH=CH_2), 6.40 (1H, t, $J = 2.1$ Hz, *p*-H in C_6H_3), 6.74 (2H, d, $J = 1.8$ Hz, *o*-H in C_6H_3), 6.91 (2H, d, $J = 8.4$ Hz, *m*-H in C_6H_4), 7.11–7.14 (3H, m, C_4H_2S), 7.21 (1H, d, $J = 3.6$ Hz, C_4H_2S), 7.52 (2H, d, $J = 8.4$ Hz, *o*-H in C_6H_4). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ 13.85, 19.25, 25.29, 28.66, 31.31, 33.41, 67.82, 67.87, 100.56, 104.37, 114.77, 114.88, 122.63, 123.98, 123.99, 124.42, 126.69, 126.86, 135.59, 135.70, 136.83, 138.48, 142.85, 143.25, 158.83, 160.62. MALDI-TOF-MS (dithranol): Found $m/z = 560.20$, Calculated for $[M]^+$ ($C_{34}H_{40}O_3S_2$) = 560.24.

Synthesis of 1. A mixture of compound **A1** (171 mg, 134 µmol), 2,3-dimethyl-2,3-butylidene 5′-[4-(5-hexenyloxy)-phenyl]-2,2′-bithiophene-5-boronate (**5**) (150 mg, 322 mmol), sodium carbonate (191 mg, 1.54 mmol) in toluene (10.2 mL), EtOH (2.4 mL), water (2.4 mL) was bubbled with argon for 3 h. Tetrakis(triphenylphosphine)palladium(0) (22.3 mg, 19.3 µmol) was added to the solution and the mixture was refluxed for 6 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 and washed with water and the organic layer was dried over anhydrous Na_2SO_4. The filtrate was evaporated and the crude product was purified by column chromatography (SiO_2; *n*-hexane/$CHCl_3$, 1:1) to produce a purple powder (121 mg, 50%). Mp 161.1–162.1 °C. ^{1}H NMR ($CDCl_3$, 298 K): δ −2.55 (2H, s, inner-N*H*), 0.83–0.88 (8H, m, –O–CH_2–(CH_2)$_2$–CH_2–O–), 1.09–1.13 (8H, m, –O–CH_2–(CH_2)$_2$–CH_2–O–), 1.55–1.60 (4H, m, –O–CH_2–(CH_2)$_3$–CH=CH_2), 1.79–1.83 (4H, m, –O–CH_2–(CH_2)$_3$–CH=CH_2), 2.13 (4H, q, $J = 7.2$ Hz, –O–CH_2–(CH_2)$_3$–CH=CH_2), 2.59 (8H, t, $J = 6.3$ Hz, –O–CH_2–(CH_2)$_2$–CH_2–O–C_6H_3), 3.94 (8H,

t, $J = 5.7$ Hz, C_6H_4–O–CH_2–$(CH_2)_2$–CH_2–O–), 3.98 (4H, t, $J =$ 6.6 Hz, –O–CH_2–$(CH_2)_4$–CH=CH_2), 4.15 (2H, t, $J = 2.1$ Hz, C_6H_3), 4.97–5.06 (4H, m, –O–CH_2–$(CH_2)_3$–CH=CH_2), 5.80–5.86 (2H, m, –O–CH_2–$(CH_2)_3$–CH=CH_2), 6.26 (4H, d, $J = 2.4$ Hz, C_6H_3), 6.89 (4H, d, $J = 9.0$ Hz, C_6H_4), 6.98 (2H, d, $J = 3.6$ Hz, C_4H_2S), 7.02 (2H, d, $J = 3.6$ Hz, C_4H_2S), 7.05 (2H, d, $J = 3.6$ Hz, C_4H_2S), 7.07 (2H, d, $J = 3.6$ Hz, C_4H_2S), 7.26 (4H, t, J =7.5 Hz, C_6H_4), 7.30 (4H, d, $J = 7.8$ Hz, C_6H_4), 7.48 (4H, d, $J = 8.4$ Hz, C_6H_4), 7.70 (4H, t, $J = 8.0$ Hz, C_6H_4), 7.93 (4H, dd, $J = 7.2$, 1.8 Hz, C_6H_4), 8.76 (8H, s, β-pyrrole). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ 25.07, 25.27, 28.65, 33.40, 67.02, 67.85, 68.15, 99.10, 104.52, 112.33, 114.76, 114.86, 115.71, 119.64, 122.58, 123.66, 123.88, 124.30, 126.68, 126.83, 129.59, 131.78, 134.93, 135.43, 135.60, 136.53, 138.47, 142.69, 143.12, 158.80, 158.94, 159.63. MALDI-TOF-MS (dithranol): Found $m/z = 1792.73$, Calculated for $[M + H]^+$ ($C_{112}H_{103}N_4O_{10}S_4$) = 1792.66.

Synthesis of 1cap. A mixture of compound **1** (20.5 mg, 11.4 μmol) and Platinum(0)–(1,1,3,3-tetramethyl-1,3-divinyldisiloxane) complex (1.5 μL, 2%Pt in xylene, Aldrich) in toluene (1.0 mL) was added to pentamethyldisiloxane (433 mL, 2.29 mmol) and the mixture was stirred under argon atmosphere at room temperature overnight. The reaction mixture was purified by column chromatography (SiO_2, *n*-hexane/$CHCl_3$, 1:4) to produce a purple powder (20.1 mg, 86%). Mp 131.6–132.6 °C. ^{1}H NMR ($CDCl_3$, 298 K): δ −2.54 (2H, s, inner-NH), 0.04 (12H, s, –Si(CH_3)$_2$–O–), 0.06 (18H, s, –O–Si(CH_3)$_3$), 0.51–0.53 (4H, m, –O–CH_2–$(CH_2)_4$–CH_2–Si–), 0.83–0.88 (8H, m, –C_6H_4–O–CH_2–(CH_2)$_2$–CH_2–O–), 1.09–1.13 (8H, m, –C_6H_4–O–CH_2–(CH_2)$_2$–CH_2–O–), 1.33–1.41 (8H, m, –O–CH_2–(CH_2)$_4$–CH_2–Si–), 1.44–1.49 (4H, m, –O–CH_2–(CH_2)$_4$–CH_2–Si–), 1.76–1.81 (4H, m, –O–CH_2–(CH_2)$_4$–CH_2–Si–), 2.58 (8H, t, $J = 6.6$ Hz, –C_6H_4–O–CH_2–$(CH_2)_2$–CH_2–O–), 3.94 (8H, t, $J = 5.4$ Hz, –C_6H_4–O–CH_2–$(CH_2)_2$–CH_2–O–), 3.97 (4H, t, $J = 6.6$ Hz, –O–CH_2–$(CH_2)_4$–CH=CH_2), 4.14–4.15 (2H, m, C_6H_3), 6.26 (4H, d, $J = 2.4$ Hz, C_6H_3), 6.91 (4H, d, $J = 9.0$ Hz, C_6H_4), 6.98 (2H, d, $J = 3.6$ Hz, C_4H_2S), 7.01 (2H, d, $J = 3.6$ Hz, C_4H_2S), 7.05 (2H, d, $J = 3.6$ Hz, C_4H_2S), 7.07 (2H, d, $J = 3.6$ Hz, C_4H_2S), 7.26 (4H, t, J =7.5 Hz, C_6H_4), 7.30 (4H, d, $J = 8.4$ Hz, C_6H_4), 7.48 (4H, d, $J = 9.0$ Hz, C_6H_4), 7.70 (4H, t, $J = 8.0$ Hz, C_6H_4), 7.93 (4H, dd, $J = 7.2$, 1.8 Hz, C_6H_4), 8.75 (8H, s, β-pyrrole). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ 0.34, 1.98, 18.30, 23.21, 25.09, 25.29, 25.75, 29.17, 33.10, 67.04, 68.15, 99.11, 104.54, 112.35, 114.89, 115.72, 119.66, 122.57, 123.67, 123.88, 124.31, 126.64, 126.84, 129.60, 131.81, 134.96, 135.45, 135.60, 136.56, 142.70, 143.18, 158.89, 158.96, 159.65. MALDI-TOF-MS (dithranol): Found $m/z = 2088.80$, Calculated for $[M + H]^+$ ($C_{122}H_{135}N_4O_{12}S_4Si_4$) = 2088.81.

Synthesis of 2. A mixture of phloroglucinol (472 mg, 3.74 mmol) and potassium carbonate (6.20 g, 44.9 mmol) in *N*,*N*-dimethylformamide (15 mL) was stirred at 70 °C for 2 h, then, 6-bromo-1-hexene (2.00 mL, 15.0 mmol) was added. The reaction mixture was further stirred at 70 °C for 6 h. After cooling to room temperature, the reaction mixture was diluted in ether, washed with water, and the organic layer was dried over anhydrous Na_2SO_4. The filtrate was evaporated and obtained liquid material was purified by column chromatography (SiO_2; *n*-hexane/$CHCl_3$, 7:3) to produce colorless oily matter (583 g, 42%). ^{1}H NMR ($CDCl_3$, 298 K): δ 1.53–1.58 (6H, m, –O–CH_2–(CH_2)$_3$–CH=CH_2), 1.75–1.80 (6H, m, –O–CH_2–(CH_2)$_3$–CH=CH_2), 2.10–2.14 (6H, m, –O–CH_2–(CH_2)$_3$–CH=CH_2), 3.91 (6H, t, $J = 6.6$ Hz, –O–CH_2–$(CH_2)_4$–CH=CH_2), 4.96–5.05 (6H, m, –O–CH_2–$(CH_2)_3$–CH=CH_2), 5.79–5.86 (3H, m, –O–CH_2–$(CH_2)_3$–CH=CH_2), 6.06 (3H, s, C_6H_3). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ 25.30, 28.65, 33.40, 67.72, 93.73, 114.70, 138.51, 160.88. MALDI-TOF-MS (dithranol): Found $m/z = 373.31$, Calculated for $[M + H]^+$ ($C_{24}H_{37}O_3$) = 373.27.

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Supporting Information

Synthesis and characterization of light-harvesting molecule **1** and its reference compounds; preparation procedure, characterization, and optical properties of the elastomeric films; the relationship between the FRET efficiency (E) and the ratio of the fluorescence intensities of the donor and acceptor (I_D/I_A). This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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44 The fluorescence spectrum of the donor units in the stretched **1**/PDMS film (Figure 3b) was blue-shifted compared to that of **D1** in solution (Figure 1b) or that of **D2** in the elastomeric films (see Figure S11 in the Supporting Information). It is unclear at present why the spectral shift was induced upon stretching. It should be noted that the blue-shifted donor fluorescence changes the spectral overlap integral [$J(\lambda)$] that is the factor affecting the FRET efficiency (E) as represented in eq 2. In fact, the blue-shifted donor fluorescence results in a larger spectral overlap integral [$J(\lambda)$]. Importantly, eqs 1 and 2 suggest that the FRET efficiency (E) will increase upon stretching in case a spectral overlap integral [$J(\lambda)$] increases. This predicted phenomenon is opposite to our results in which we observed the decrease of E upon stretching. Thus, we could at least rule out the effect of the blue-shifted donor fluorescence on our proposed mechanism.
45 The orientation factors (and average angles, θ_D) of **1** when elongated by 30 and 60% were calculated to be 0.045 (83.9°) and 0.019 (86.1°), respectively.
46 60% elongating induces deformation of the film and decrease of the absorbance (thickness of the film), which makes the absorption measurement difficult. Therefore, the data of only 30% elongated film is shown. Inportantly, this deformation is not a issue in fluorescence measurements, because we evaluate the FRET efficiency using the ratio of I_D/I_A.
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