Synthesis and Photoisomerization of Dithienylethene-Bridged Diporphyrins

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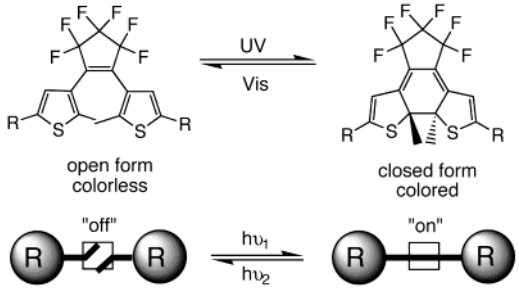
Dithienylethene-bridged diporphyrins **1**−**6** were prepared as photochemical switching molecules. Porphyrin and dithienylethene are directly linked in **1**, and linked, respectively, through a 1,4-phenylene spacer in **2**, through a 4-ethynylphenylene spacer in **3**, and through a di-4-phenylethynylene spacer in **4**, while *meso*-ethynylated porphyrin and dithienylethene are directly connected in **5** and linked through a 1,4-phenylene spacer in **6**. Compounds **1**, **2**, and **5** do not undergo any photochemical isomerization, probably due to efficient quenching of the excited dithienylethene by the attached porphyrin moiety via intramolecular energy transfer. Compounds **4** and **6** undergo open-to-closed and closed-to-open photoisomerizations in quantum yields of 4.3×10^{-2} and 1.8×10^{-3}, and 2.6×10^{-3} and 7.5×10^{-4}, respectively, by irradiation with 313 and 625 nm light, which are considerably smaller than quantum yields of 0.52 and 3.8×10^{-3} for reference dithienylethene molecule **7**. The fluorescence of **4** was regulated in a reversible manner by the photoisomerization of the dithienylethene moiety. In addition, the absorption properties of the porphyrin in **6** changed in response to the photochromic reaction of the dithienylethene bridge.

Introduction

The design of light-driven molecular switches is an active area of research, since they are crucial for devices that operate at molecular and supramolecular scales.[1−4] A promising approach may be to use photochromic molecule as a switching component that offers, as a result of reversible photochemical isomerization, entirely different properties for respective isomeric forms, by which a key process can be modulated.[2−4] Dithienylethene is an ideal photochromic molecule owing to (1) high efficiency of "ring-closure" and "ring-opening" photoisomerizations for excitations at different wavelength, (2) sufficient thermal stability of both the "open" and "closed" forms, (3) very high resistance to photofatigue, and (4) large differences in ability of the transmission of electronic interactions (electronic π-conjugation is interrupted in the open form, while electronic π-conjugation is extended over the closed form).[5] In the course of our program of developing photochemically switchable energy transfer and electron-transfer molecular systems, we prepared dithienylethene-bridged diporphyrins **1**−**6** (Chart 1), and have studied their "closed" and "open" photoisomerization efficiencies. Models **1** and **2** bear two 5,15-diaryl-β-octaalkyl-substituted porphyrins and models **3** and **4** bear two 5,10,15,20-tetraaryl-substituted TPP-type porphyrins, while models **5** and **6** bear two 5-ethynyl-10,20-diaryl-substituted porphyrins that are considered to have a conjugated electronic system well extended to the ethynyl group at the *meso*-position and thus have significantly altered optical properties.[6,7] To examine the effect of the distance between the porphyrin and di-

Chart 1. Photoisomerization of Dithienylethene Molecule and Schematic Representation of Its Use for Photochemical Switching



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(1) (a) Debreceny, M. P.; Svec, W. A.; Wasielewski, M. R. *Science* **1996**, *274*, 585. (b) Debreczeny, M. P.; Svec, W. A.; Marsh, E. M.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 8174. (c) Gosztola, D.; Niemczyk, M. P.; Wasielewski, M. P. *J. Am. Chem. Soc.* **1998**, *120*, 5118. (d) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. *J. Am. Chem. Soc.* **1997**, *119*, 7891. (e) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. *Nature* **1993**, *364*, 42. (f) Otsuki, J.; Tsujino, M.; Iizaki, T.; Araki, K.; Seno, M.; Takatera, K.; Watanabe, T. *J. Am. Chem. Soc.* **1997**, *119*, 7895. (g) Beyeler, A.; Belser, P.; De Cola, L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2779. (h) Koumura, N.; Zijistra, R. W.; van Delden, R. A.; Harada, N.; Feringa, B. L. *Nature* **1999**, *401*, 152.

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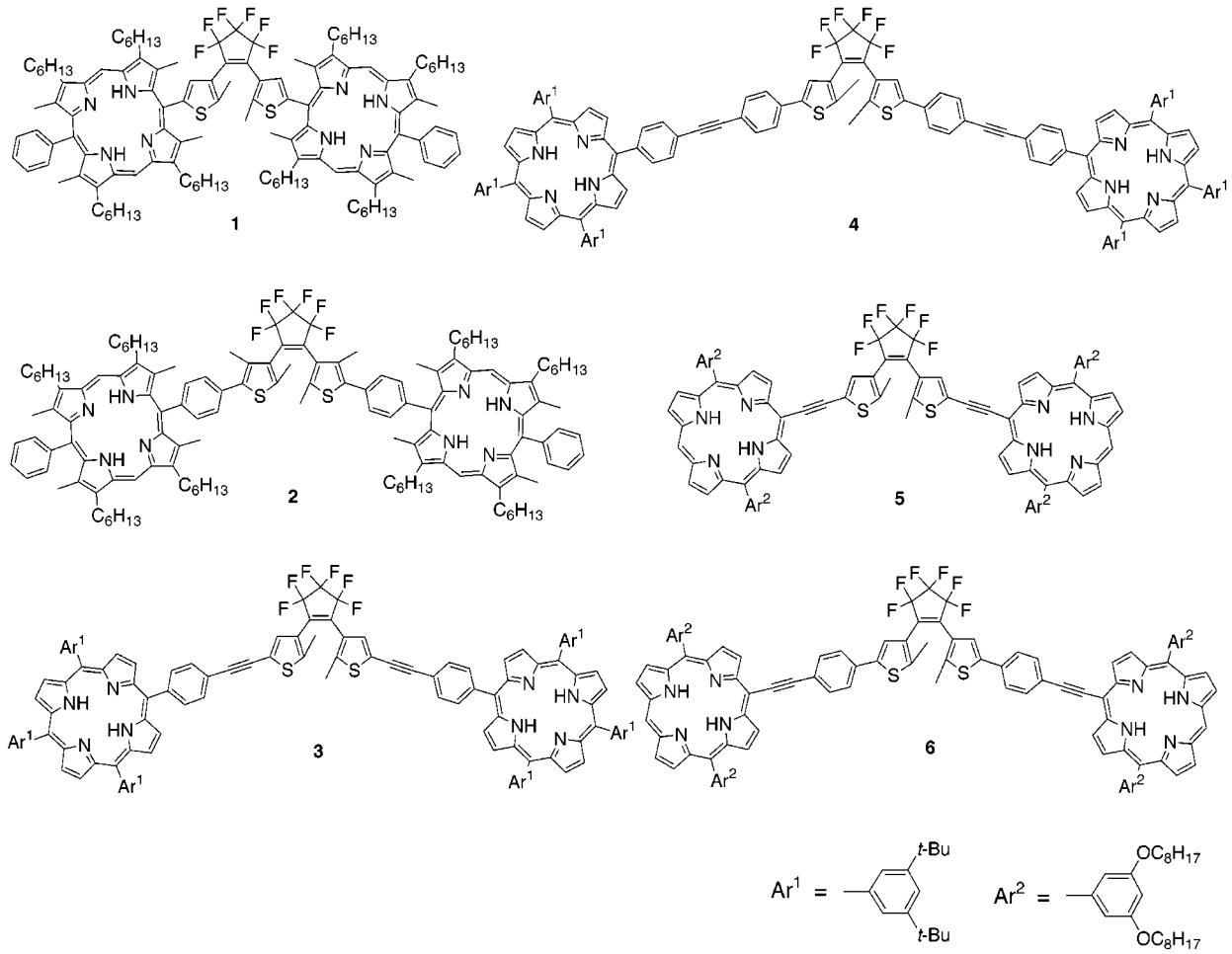
Chart 2. Structures of Dithienylethene-Bridged Diporphyrin Models 1−6



thienylethene, we changed the connecting spaces as follows: (1) directly connected in **1**, (2) bridged by a 1,4-phenylene spacer in **2**, (3) bridged by a 4-ethynylphenylene spacer in **3**, and (4) bridged by a di-4-phenylethynylene spacer in **4**. *meso*-Ethynlated porphyrins are directly connected to dithienylethene in **5** and are bridged by a 1,4-phenylene spacer in **6**. Porphyrin-free dithienylethene **7** was used as the reference molecule. As described below, the photoisomerization reactivity depends heavily on the distance between the porphyrin and dithienylethene moieties, and the fluorescence of the porphyrin is quenched by closed form of the dithienylethene. The latter observation may be interesting from a viewpoint of optical switching of emission signal.

Results and Discussion

Synthesis. Synthetic route to compound **1** is shown in Scheme 1. Formyl group of 3-bromo-5-formyl-2-methylthiophene **8**[2b] was protected with neopentyl glycol to afford acetal **9** which was lithiated with *n*-butyllithium and then reacted with perfluorocyclopentene to give dithienylethene **10**. Depending upon the hydrolysis conditions, **10** was transformed into diformyl-substituted dithienylethene **11**[2b] or monoformyl-substituted dithienylethene **12**. Acid-catalyzed condensation[8] of **11** and benzaldehyde with dipyrrylmethane **13**[9] in a ratio of 1:6:8 followed by oxidation with *p*-chloranil gave a complicated mixture of porphyrin products consisting of higher oligomers as revealed by analytical GPC−HPLC. Separation over size-exclusion chromatography gave diporphyrin **1** in 19% yield, along with trimer **14** (11%), tetramer **15** (5%), and pentamer **16** (3%). Molecular weights of these porphyrin products were determined by MALDI-TOF MS to be 1923 for **1** (Calcd for $C_{123}H_{154}F_6N_8S_2$ = 1921), 2982 for **14** (Calcd for $C_{186}H_{230}F_{12}N_{12}S_4$ = 2988), 4052 for **15** (Calcd for $C_{249}H_{306}F_{18}N_{16}S_6$ = 4054), and 5102 for **16** (Calcd for $C_{312}H_{382}F_{24}N_{20}S_8$ = 5121). The diporphyrin **1** was fully characterized also by 500 MHz ^{1}H NMR but **14**−**16** were mixtures of syn−anti atropisomers and their further characterizations were abandoned. Similar reaction of **12** and benzaldehyde with **13** afforded porphyrin−dithienylethene dyad **17**, and the reaction of diformyl-substituted dithienylethene **18**[10] gave diporphyrin **2** (Scheme 2).

Diethynyl-substituted dithienylethene **21** was prepared from 2,4-dibromo-5-methylthiophene[2a] via **19** and **20** (Scheme 3). Palladium-catalyzed coupling reaction[11] of 4-iodophenyl-substituted TPP-type porphyrin **22**[11,12] and

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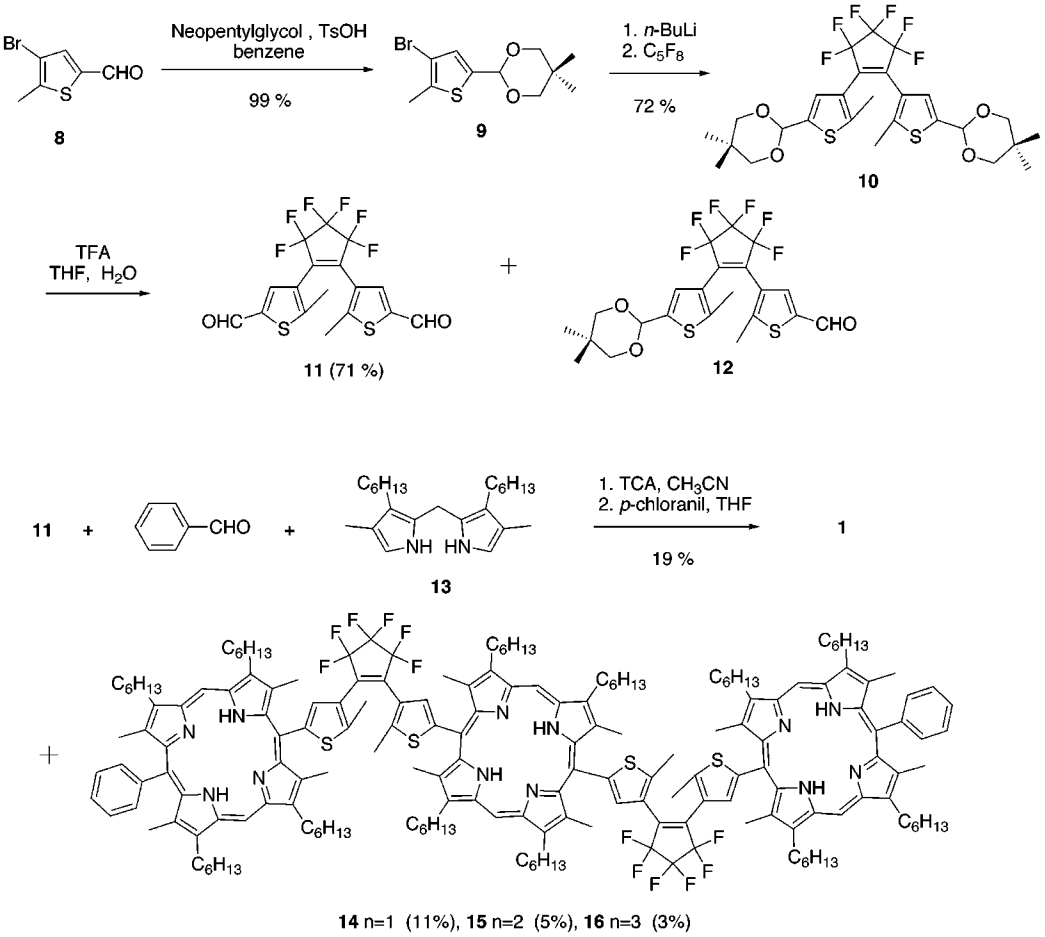
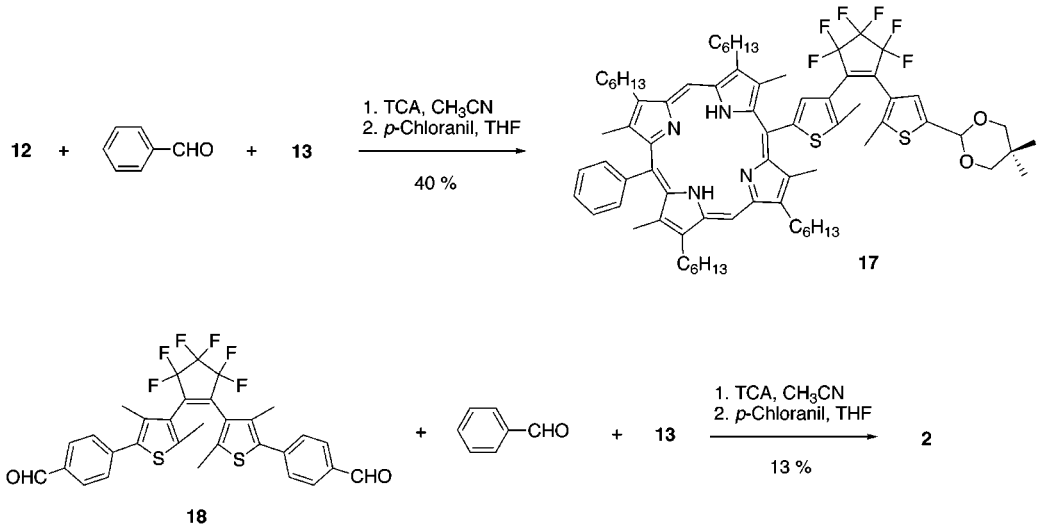
Scheme 1. Synthesis of 1



Scheme 2. Synthesis of 2



21 gave diporphyrin **3**. Suzuki coupling[13] of boronic acid **23**[2b] prepared from 2,5-dibromo-5-methylthiophene with 1-iodo-4-trimethylsilylethynylbenzene **24** gave compound **25**, which was reacted with perfluorocyclopentene to give dithienylethene **7** in 65% yield. The protected dithienylethene was now converted into **26** by treatment with NaOH in methanol. Palladium-catalyzed coupling reaction of **26** and **22** furnished diporphyrin **4** in 51% yield (Scheme 4).

Diporphyrin **5** was prepared by the Sonogashira coupling reaction of *meso*-bromo porphyrin **27**[7d,14] with **21** in 64% yield, and the similar reaction of **26** and **27** gave diporphyrin **6** in 64% yield.

Absorption and Fluorescence Spectra of Diporphyrin Modes in Open Form. The absorption spectra

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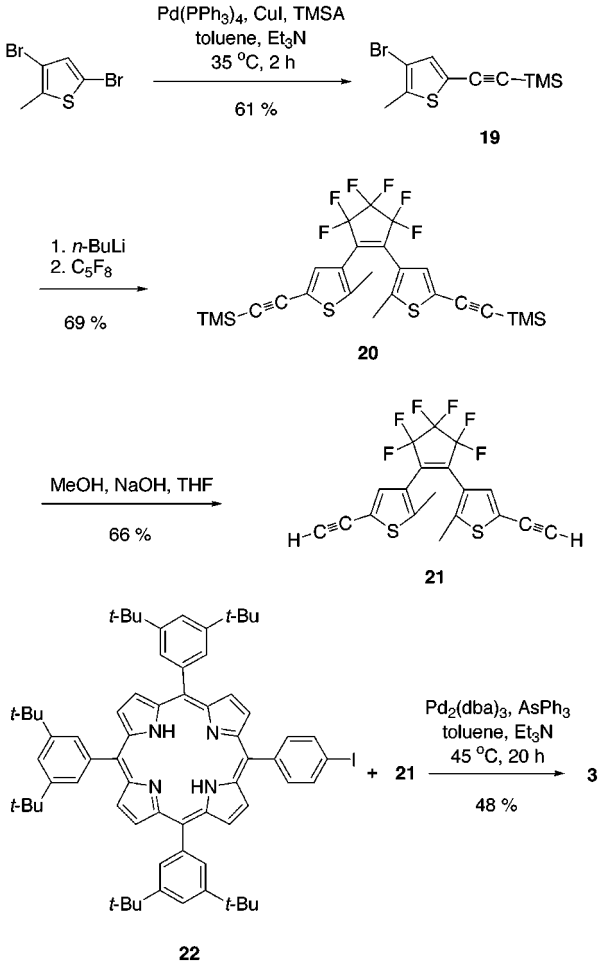
Scheme 3. Synthesis of 3



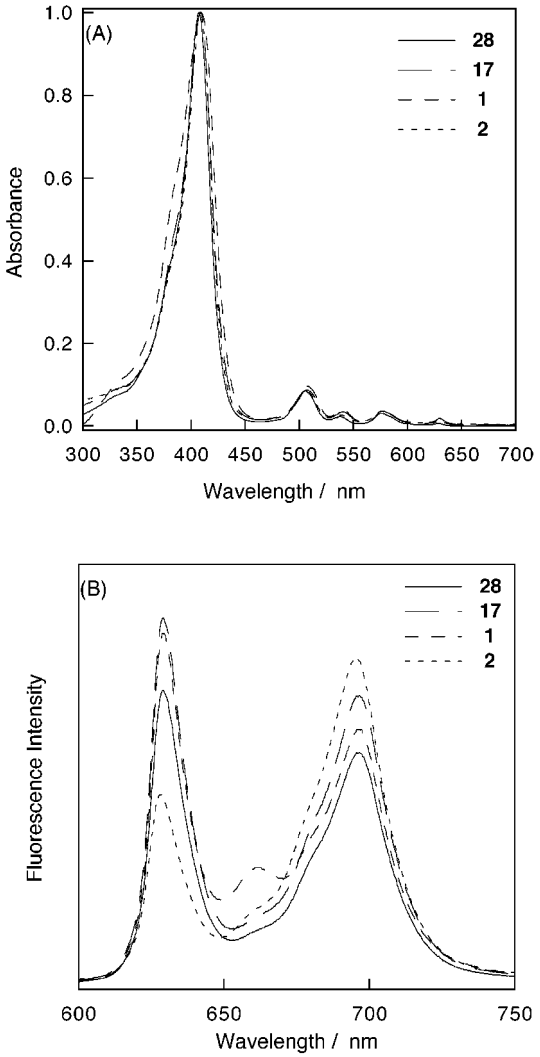
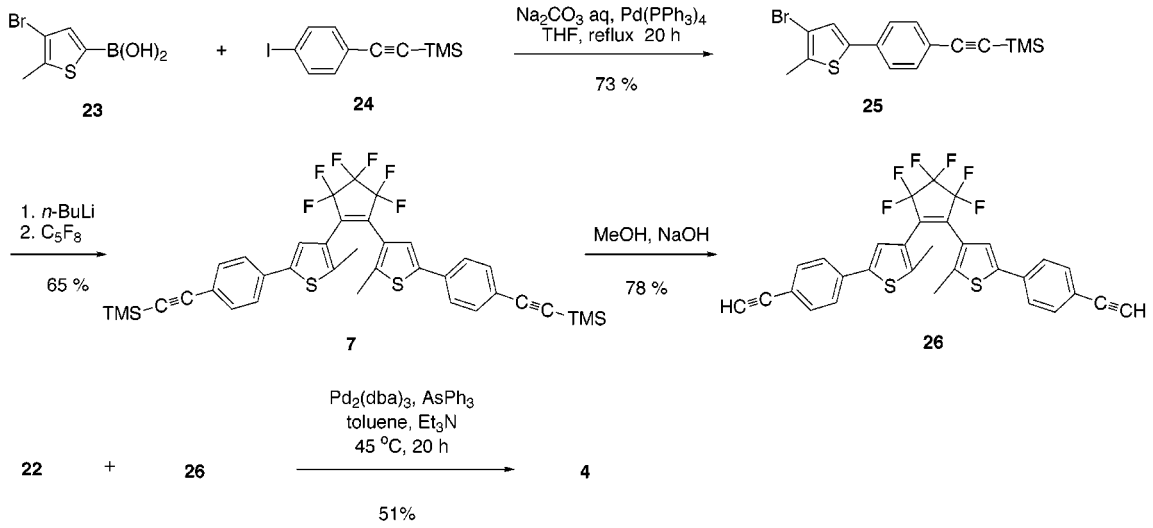


Figure 1. Absorption (A, top) and steady-state fluorescence spectra (B, bottom) of **1**, **2**, **17**, and **28** in THF. Fluorescence spectra were taken at the respective peak position of the Soret bands.

of **1**, **2**, and **17** in THF are shown in Figure 1A, where the absorption spectrum of 5,15-diphenyl-β-octaalkyl-substituted porphyrin **28** was also included for comparison. It was evident that direct attachment of the dithienylethene moiety to the porphyrin had only minor influence on the absorption bands of the porphyrin moiety, since the absorption spectra of **1** and **17** were similar to those of **2** and **28**. This may be partly ascribed to the expected nearly orthogonal conformation of the dithienylethene moiety with respect to the porphyrin mean plane. Further, the similar absorption spectra of **1** and **17** indicated that the exciton coupling between the two porphyrins in **1** was not strong enough to alter the absorption characteristics. This was somewhat in con-

Scheme 4. Synthesis of 4



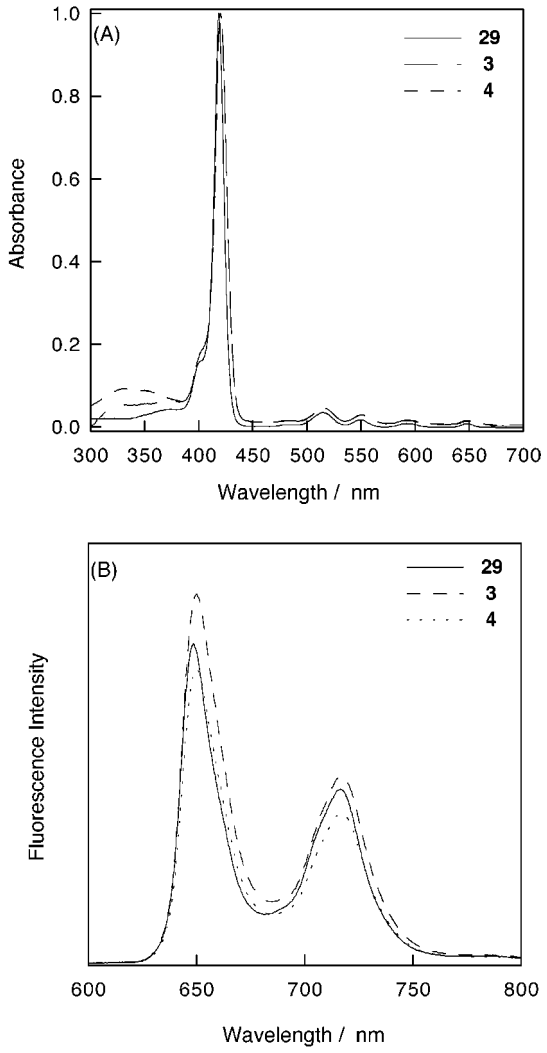


Figure 2. Absorption (A, top) and steady-state fluorescence spectra (B, bottom) of **3**, **4**, and **29** in THF. Fluorescence spectra were taken at the respective peak position of the Soret bands.

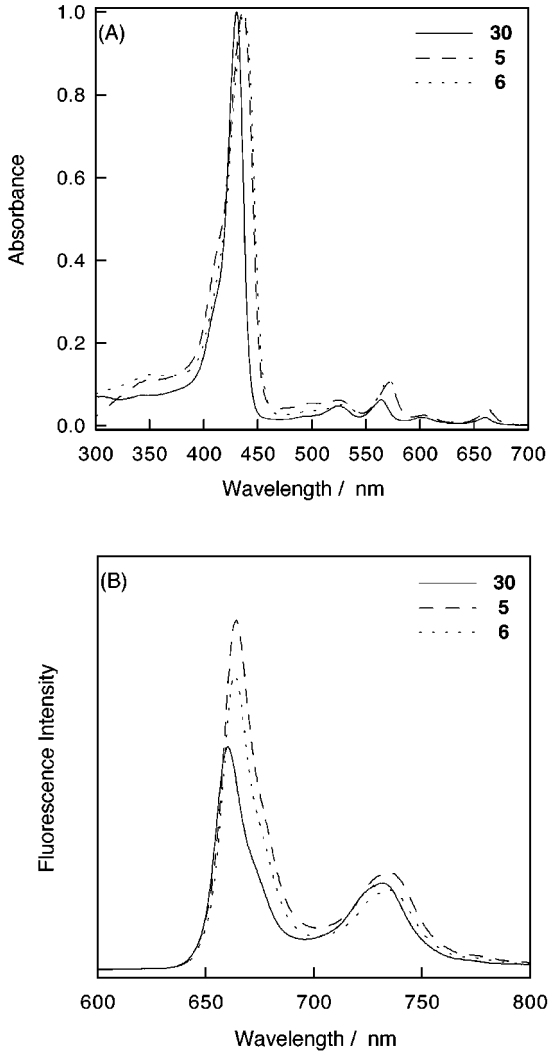


Figure 3. Absorption (A, top) and steady-state fluorescence spectra (B, bottom) of **5**, **6**, and **30** in THF. Fluorescence spectra were taken at the respective peak position of the Soret bands.

trast to the frequently observed strong exciton coupling of covalently linked zinc diporphyrins.[15] The absence of the observable exciton coupling in **1** could be ascribed to smaller oscillator strength of free-base porphyrin that was less than the half of the corresponding zinc porphyrin and to a long distance between the two porphyrin. Figure 1B shows the steady-state fluorescence spectra of **1**, **2**, **17**, and **28**, which did not show the significant fluorescence quenching of the porphyrin moiety by the attached diethinylethene.

Figures 2A,B show the absorption and fluorescence spectra of **3** and **4** along with those of the reference 5,10,15,20-tetrakis(3,5-ditertbutylphenyl)porphyrin **29**. It was also apparent that the optical properties of the porphyrin moiety in **3** and **4** were scarcely affected upon the attachment of the ethynylated dithienylethene moieties. Comparison of the absorption and fluorescence spectra of the *meso*-phenylethnylated porphyrins **5**, **6**, and 5,15-di(3,5-ditertbutylphenyl)-10-phenylethynyl porphyrin **30** revealed that the attachment of the dithienylethene moiety had only minor effects except the observed small red shift in the absorption spectra and the slightly intensified fluorescence spectra of **5** and **6**; the relative fluorescence quantum yields of **5** and **6** to the reference **30** are 1.55 and 1.30 (Figures 3A,B).

Photoisomerization. Reversible photoisomerizations between the open- and closed-ring forms of dithienylethenes have been amply demonstrated.[4] Essentially in the same manner, upon irradiation with 330 nm light in THF open-ring isomer **7** was converted to the closed-ring isomer **7c** (Figure 4A), while irradiation with >550 nm light gave rise to the closed-to-open cycloreversion to reform **7** (Figure 4B). The closed-ring isomer **7c** was isolated as a blue solid from the photolyzed mixture. The photostationary state upon irradiation with 330 nm light that was attained by several minutes irradiation consisted of a mixture of the open- and closed-ring isomers in a ratio of 1:3. The quantum yields of the cyclization and cycloreversion processes were respectively determined for the irradiation with 313 and 625 nm light to be 0.52 and 3.8×10^{-3}.

The photoisomerizations of the diporphyrins **1**−**6** were also examined in THF. Diporphyrins **1**, **2**, and **5** with short separations did not undergo any photoreaction even

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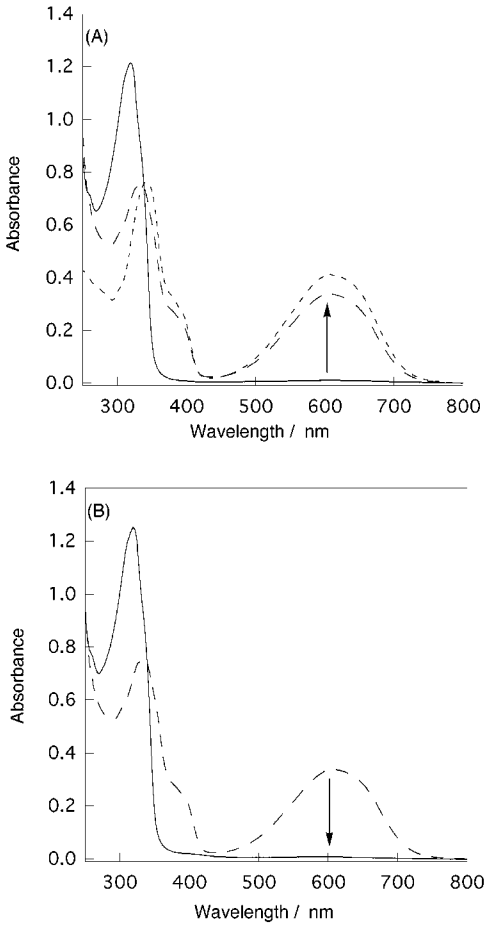


Figure 4. Photoisomerization of **7** in THF. A, top, open-to-close starting from pure open form (—); photostationary state for excitation at 330 nm (— —) and pure closed form (- - -). B, bottom, closed-to-open starting from the photostationary state (— —); photostationary state for excitation at >550 nm (—).

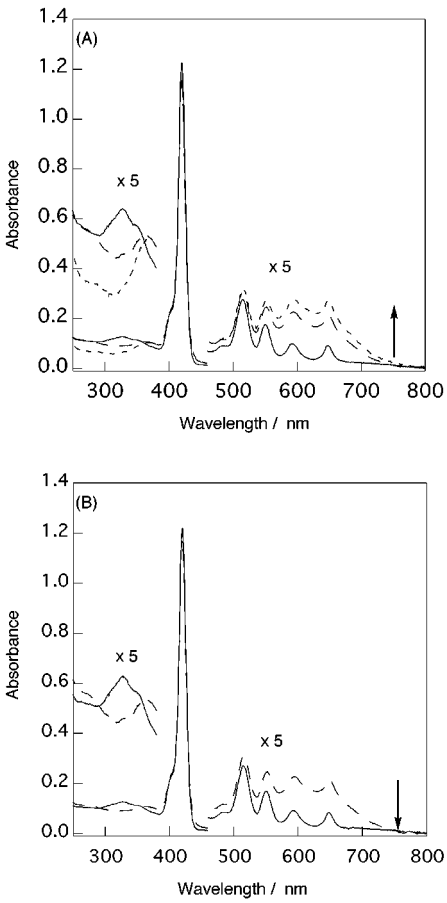


Figure 5. Photoisomerization of **4** in THF. A, top, open-to-closed starting from pure open form (—); photostationary state for excitation at 330 nm (— —) and pure close form (- - -). B, bottom, close-to-open starting from the photostationary state (— —); photostationary state for excitation at >550 nm (—).

for extended irradiation with 330 nm light[16] but diporphyrins **3**, **4**, and **6** underwent the reversible photoisomerization with different efficiencies.[17] Figure 5 shows the absorption spectral changes of **4** upon irradiation with UV light (A, open to closed) and with visible light (B, closed to open). Along with the increase of the irradiation time, the broad absorption band due to the closed-ring isomer of a dithienylethene became intensified around 500−700 nm and reached the photostationary state after several minutes similar to the case of **7**. Based on the spectrum of the closed-ring isomer **4c** isolated from the photoreaction of **4**, the photostationary state was revealed to consist of a 1:3 mixture of **4** and **4c**. Irradiation of this mixture with >550 nm light effected the complete cycloreversion isomerization back to **4**. The quantum yields were determined to be 4.3×10^{-2} and 1.8×10^{-3} for the open-to-closed and closed-to-open photoisomerizations, respectively. Here it is interesting to note that the fluorescence behavior of **4** depended on the degree of the photoisomerization, since the closed form of the dithienylethene bridge quenched the S_1-state fluorescence of

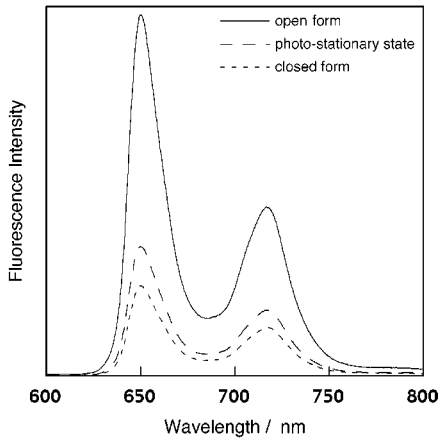


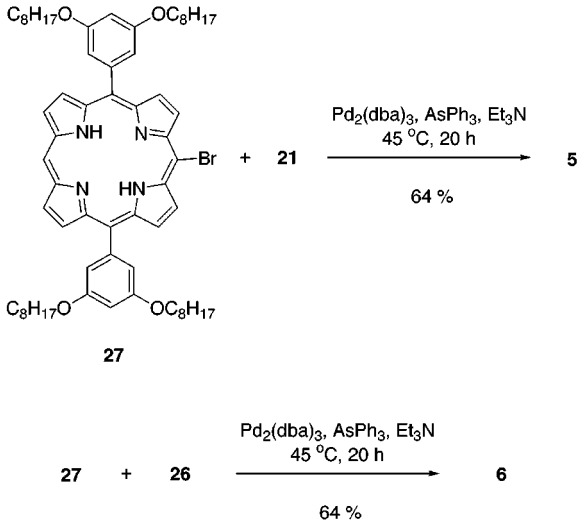
Figure 6. Steady-state fluorescence spectra of **4**, **4c**, and photostationary mixture of **4** and **4c** taken for excitation at 420 nm in THF.

the porphyrin moieties. Comparison of the steady-state fluorescence spectra of **4** and **4c** is shown in Figure 6. The observed fluorescence quenching in **4c** may be ascribed to the intramolecular energy transfer from the porphyrin moiety to the closed dithienylethene bridge, since the energy level of the porphyrin S_1-state was estimated to be 1.91 eV on the basis of the absorption and fluorescence spectra, while the S_1-state of the closed dithienylethene bridge was estimated to be ca. 1.7−1.8

(16) Similar lack of photoreactivity was reported for porphyrin−azobenzene system. Hunter, C. A.; Sarson, L. *Tetrahedron Lett.* **1996**, *37*, 699.

(17) We could not determine the quantum yields of the photoisomerization of **3** due to unsuccessful isolation of the closed form **3c**. But the open-to-closed photoisomerization quantum yield of **3** has been estimated slightly better than that of **6**.

Scheme 5. Synthesis of 5 and 6



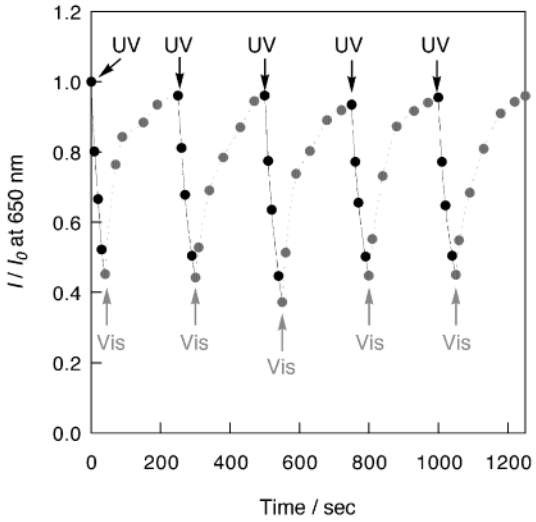
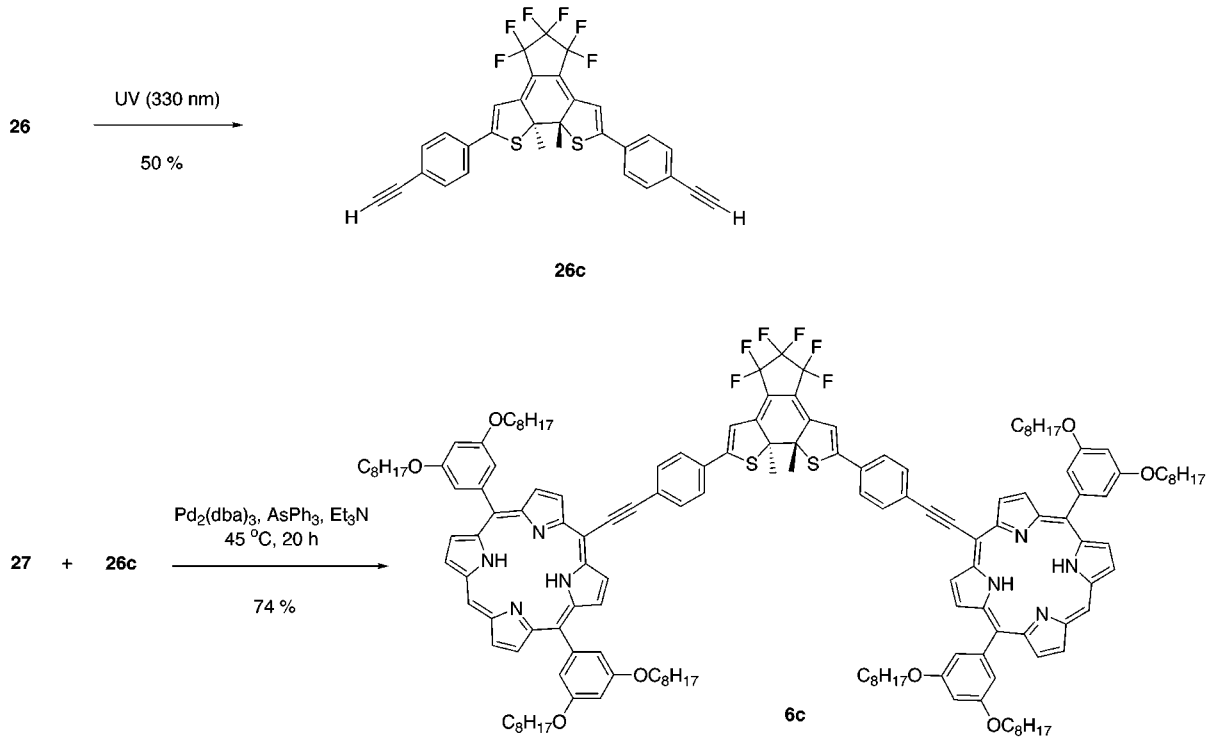


Figure 7. Fluorescence intensity changes of **4** at 650 nm upon photoirradiation at 330 nm (UV) and >550 nm (vis) taken for excitation at 430 nm.

eV on the basis of the absorption spectrum. In the view of the entirely reversible photoisomerization of dithienylethene, these results suggested that the fluorescence of **4** could be controlled by external light. This was indeed demonstrated as shown in Figure 7, in which the fluorescence intensity of **4** was regulated by the photoisomerization of the dithienylethene in a reversible manner.

The open-to-closed photoisomerization of **6** proceeded upon irradiation with 330 nm light but was rather slow compared with **7** and **4**. Since the isolation of the closed-ring isomer **6c** from the photoreaction of **6** turned out to be rather tedious, we prepared **6c** by palladium-catalyzed coupling of **27** and **26c** (Scheme 6). It is worthy to note that the closed-ring isomer **26c** prepared by the photoisomerization of **26** was relatively stable and tolerate under the present coupling conditions to provide **6c** in 74% yield. Figure 8 shows the absorption spectra of **6**, its photostationary state (**6** and **6c**), and the pure closed form **6c**. The photostationary state was thus determined to contain only 20% of **6c**. The quantum yields for the open-to-closed and closed-to-open photoisomerizations were 2.6×10^{-3} and 7.5×10^{-4}, respectively, by irradiation with 313 and 625 nm light. Another important finding was that the absorption bands of the porphyrin moieties were considerably perturbed in the closed-ring form, reflecting the substantial electronic interactions between the porphyrin and dithienylethene bridge. As shown in Figure 9, the difference spectrum between **6** and **6c** indicated the strong signal at the Soret band region and the negative absorbances at 571 and 660 nm and the positive absorbances at 620 and 680 nm at the

Scheme 6. Synthesis of 6c



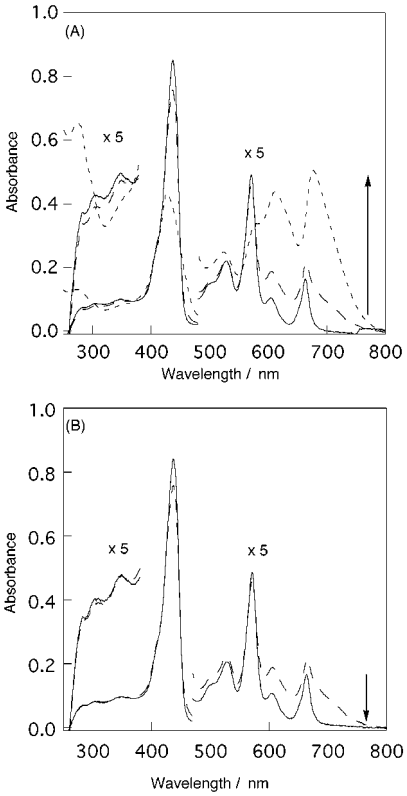


Figure 8. Photoisomerization of **6** in THF. A, top, open-to-closed starting from pure open form (—); photostationary state for excitation at 330 nm (– –) and pure closed form (- - -). B, bottom, closed-to-open starting from the photostationary state (– –); photostationary state for excitation at >550 nm (—).

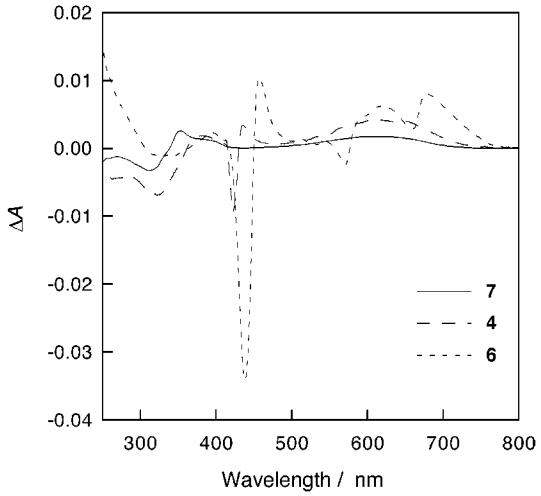


Figure 9. Light−dark differential spectra of **4**, **6**, and **7** in THF.

Q-band region. The negative absorbances roughly corresponded to the Q-bands of **6**. This was in contrast to the difference spectrum of **4**, which merely displayed the broad absorption bands of the closed dithienylethene bridge, being nearly the same as that of **7**. In the case of **4**, therefore, the influences of the structural change of the dithienylethene bridge on the absorption spectral properties of the porphyrins were minor. On the other hand, the structural change of the dithienylethene bridge in **6** affected the electronic properties of the porphyrin moieties through enhanced π-conjugation in the closed form.

In summary, the close attachments of the porphyrin chromophores to the dithienylethene led to loss of its photochromic reactivity probably through the intramolecular energy transfer quenching but the pertinent insertion of a spacer between the dithienylethene and porphyrin ensured the photochromic reactivity that may trigger the change of the electronic properties of the porphyrin as seen in **6**. This encourages the extension of this strategy to the control of intramolecular electron transfer by the reversible dithienylethene photoisomerization that is now actively in progress in our laboratories. In addition, the closed ring form of the dithienylethene quenches the S_1-excited state of the free base porphyrin and the reversible regulation of the fluorescence of the porphyrin is thus possible by the photoisomerization of the dithienylethene moiety.

Experimental Section

Materials and Apparatus. All commercially available materials were used without further purification unless otherwise stated. THF and ether were distilled from sodium−benzophenone ketyl. DMF was dried over molecular sieve 4A for 1 day and distilled under reduced pressure. CH_2Cl_2 was distilled from P_2O_5. Pyridine and triethylamine were dried over KOH for several days and distilled. Toluene was distilled from CaH_2. Solvents used for spectroscopic measurements were all spectrograde. Preparative separations were usually performed by flash column chromatography (Merck, Kieselgel 60H, Art. 7736) and gravity column chromatography (Wako, Wakogel C-200).

^{1}H NMR (500 MHz) spectra were recorded on a JEOL ALPHA-500 FT-NMR spectrometer, and chemical shifts were reported in the δ-scale relative to tetramethylsilane. FAB mass spectra were measured on a JEOL HX-110 spectrometer using positive-FAB ionization method and 3-nitrobenzyl alcohol matrix. MALDI-TOF mass spectra were measured on a Shimadzu/KRATOS MALDI 4 spectrometer. UV−vis absorption spectra were recorded on a Shimadzu UV-2400PC UV−vis spectrophotometer. Steady-state fluorescence spectra were recorded on a Shimadzu PF-5300PC spectrometer. Steady-state UV−vis absorption and fluorescence spectra were taken with 1×10^{-6} M solutions at room temperature. Quantum yields were determined by comparing the reaction yields of the dithienylethenes in THF against the yield of furylfulgide in hexane or toluene.[18] As light source, monochromic light was obtained by passing the light (USHIO 500 W xenon lamp) through a monochromator (Ritsu MV-10N).

3-Bromo-2-methyl-5-thiophenecarboxyaldehyde 2,2-Dimethylpropan-1,3-diyl Acetal (9). 3-Bromo-2-methyl-5-thiophenecarboxyaldehyde (**8**) (10.0 g, 48.8 mmol), neopentylglycol (6.09 g, 58.5 mmol), and *p*-toluenesulfonic acid (1.00 g) were dissolved in benzene (80 mL). The reaction mixture was refluxed for 3 h and then cooled and washed with aqueous sodium bicarbonate (5% w/v, 2 × 150 mL). The combined benzene layers were then dried (Na_2SO_4), filtered and evaporated in vacuo to yield acetal **9** as a yellow solid (14.08 g, 99%). The product was recrystallized from hexane. **9**: mp 54.1−57.8 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.78 (s, 3H, acetal-Me), 1.25 (s, 3H, acetal-CH_3), 2.37 (s, 3H, ArCH_3), 3.60 (d, J = 10.5, 2H, CH_2), 3.72 (d, J = 11.5, 2H, CH_2), 5.51 (s, 1H, CH), and 6.94 (s, 1H, ArH); FTIR (KBr, cm^{-1}) 3080, 2961, 2855, 1091, 1022, 646; MS m/z = 291 (Calcd 290 for $C_{11}H_{15}BrO_2S$). Anal. Calcd for $C_{11}H_{15}BrO_2S \cdot 0.4H_2O$: C, 44.27; H, 5.35. Found: C, 43.94; H, 4.87.

1,2-Bis(5-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)-2-methylthiophen-3-yl)-perfluorocyclopentene (10). A solution of **9** (2.00 g, 6.85 mmol) in dry ether (30 mL) was cooled to −78 °C under nitrogen atmosphere. *n*-Butyllithium (1.6 M in

(18) Yokoyama, Y.; Hayata, H.; Ito, H.; Kurita, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1607.

hexane, 4.5 mL, 7.2 mmol) was then added, after 2 h, followed by perfluorocyclopentene (0.43 mL, 3.44 mmol, added through cooled syringe). The reaction was stirred for 2 h at −78 °C after which time the reaction was allowed to warm to ambient temperature. After an additional 2 h, the reaction was diluted with diethyl ether, washed with dilute hydrochloric acid (1% v/v), saturated aqueous sodium bicarbonate, and water, and extracted with diethyl ether. The combined ether phases were then dried ($MgSO_4$), filtered, and evaporated in vacuo to yield a yellow-brown syrup. Chromatography over silica gel (dichloromethane/hexane = 1:1 to 3:1) afforded diarylethene **10** (1.47 g, 72%) as a yellow solid. **10**: mp 160.0−162.2 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.79 (s, 6H, acetal-CH_3), 1.26 (s, 6H, acetal-CH_3), 1.86 (s, 6H, ArCH_3), 3.60 (d, J = 11.0, 4H, CH_2), 3.72 (d, J = 11.0, 4H, CH_2), 5.54 (s, 2H, CH), and 7.08 (s, 2H, ArH); FTIR (KBr, cm^{-1}) 3087, 2963, 2857, 1277, 1086; MS m/z = 596 (Calcd 596 for $C_{27}H_{30}F_6O_4S_2$). Anal. Calcd for $C_{27}H_{30}F_6O_4S_2$: C, 54.35; H, 5.07. Found: C, 54.33; H, 5.05.

1,2-Bis(5-formyl-2-methylthiophen-3-yl)perfluorocyclopentene (11). THF (150 mL) and water (40 mL) were added to a flask containing diacetal (**10**) (797 mg, 1.34 mmol). Then, TFA (30 mL) was added to the solution. The resulting reaction mixture was stirred for 50 min at room temperature, quenched with saturated aqueous sodium bicarbonate, and extracted with ether. The combined ether phases were then washed with aqueous sodium bicarbonate (2% w/v), dried (Na_2SO_4), and evaporated in vacuo to yield a yellow syrup. Chromatography over silica gel (dichloromethane/hexane = 3:1) afforded dialdehyde **11** (406 mg, 71%). **11**: mp 179.8−184.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.01 (s, 6H, ArCH_3), 7.71 (s, 2H, ArH), and 9.83 (s, 2H, CHO); FTIR (KBr, cm^{-1}) 3107, 2838, 1666, 1276, 1125; MS m/z = 425 (Calcd 424 for $C_{17}H_{10}F_6O_2S_2$). Anal. Calcd for $C_{17}H_{10}F_6O_2S_2$: C, 48.11; H, 2.38. Found: C, 47.93; H, 2.43.

1-(5-(5,5-Dimethyl-1,3-dioxacyclohex-2-yl)-2-methylthiophen-3-yl)-2-(5-formyl-2-methylthiophen-3-yl)perfluorocyclopentene (12). THF (100 mL) and water (25 mL) were added to a flask containing diacetal **10** (496 mg, 0.825 mmol). Then, TFA (20 mL) was added to the solution. The reaction mixture was stirred for 2.5 h at room temperature, quenched with saturated aqueous sodium bicarbonate (200 mL), extracted with ether (100 mL), and washed with aqueous sodium bicarbonate (2% w/v, 200 mL). The combined ether phases were then dried (Na_2SO_4), filtered, and evaporated in vacuo to yield a yellow syrup. Chromatography over silica gel (dichloromethane/hexane = 3:1) afforded diacetal **10** (56 mg, 11%), monoacetal **12** (290 mg, 69%), and dialdehyde **11** (91 mg, 26%). **12**: mp 115.5−119.8 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.77 (s, 3H, acetal-CH_3), 1.23 (s, 3H, acetal-CH_3), 1.83 (s, 3H, ArCH_3), 1.98 (s, 3H, ArCH_3), 3.60 (d, J = 8, 2H, CH_2), 3.70 (d, J = 12, 2H, CH_2), 5.52 (s, 1H, CH), 7.04 (s, 1H, ArH), 7.71 (s, 1H, ArH), and 9.82 (s, 1H, CHO); FTIR (KBr, cm^{-1}) 3059, 2956, 2834, 1666, 1274, 1100; MS m/z = 510 (Calcd 510 for $C_{22}H_{20}F_6O_3S_2$). Anal. Calcd for $C_{22}H_{20}F_6O_3S_2$: C, 51.76; H, 3.95. Found: C, 52.02; H, 4.03.

Diporphyrin 1. Dialdehyde (**11**) (47 mg, 0.11 mmol), benzaldehyde (74 mg, 0.70 mmol), and bis(4-methyl-3-*n*-hexyl-2-pyrrolyl)methane (**13**) (315 mg, 0.92 mmol) were dissolved in 20 mL of acetonitrile. Trichloroacetic acid (50 mg) was added, and the mixture was stirred for 5 h (dark, under nitrogen, room temperature). *p*-Chloranil (360 mg) in 10 mL of tetrahydrofuran was added, and the mixture was stirred again overnight. The solvent was evaporated, and the resulting solids were suspended in chloroform. Concentrated aqueous hydrochloric acid was added to the solution, and the solution was washed with aqueous sodium bicarbonate solution and with water, dried (Na_2SO_4), and evaporated to yield a black solid. To a solution of the reaction in dichloromethane, a saturated solution of zinc acetate in methanol was added. The mixture was stirred for 30 min at room temperature, washed with water, dried (Na_2SO_4), and evaporated. Chromatography over silica gel (dichloromethane) gave a mixture of zinc porphyrins. A solution of the mixture in dichloromethane was washed with aqueous hydrochloric acid (1 M) twice, washed with saturated aqueous sodium bicarbonate, dried (Na_2SO_4), filtered, and evaporated. A size exclusion chromatography gave diporphyrin **1** (41 mg, 19%). **1**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ −2.31 (s, 4H, NH), 0.61 (t, J = 7.0, 12H, hexyl-6), 0.88 (t, J = 7.0, 12H, hexyl-6), 0.95 (m, 8H, hexyl-5), 1.03 (m, 8H, hexyl-5), 1.18 (m, 8H, hexyl-4), 1.35 (m, 8H, hexyl-4), 1.45 (m, 8H, hexyl-3), 1.71 (m, 8H, hexyl-3), 1.79 (m, 8H, hexyl-2), 2.16 (m, 8H, hexyl-2), 2.49 (s, 12H, ArCH_3), 2.75 (s, 12H, ArCH_3), 2.97 (s, 6H, thiophene-CH_3), 3.53 (m, 4H, hexyl-1), 3.69 (m, 4H, hexyl-1), 3.94 (t, 8H, hexyl-1), 7.76−7.82 (m, 8H, PhH and thiophene-H), 8.07 (m, 4H, PhH), and 10.16 (s, 4H, *meso*-H); MS m/z = 1923 (Calcd 1921 for $C_{123}H_{154}F_6N_8S_2$). UV−vis (THF): λ_{max}(log ϵ) = 410 (5.5), 507 (4.7), 541 (4.2), 578 (4.2), and 630 (4.0). Fluorescence (THF): λ_{max} = 629, 662, and 696 nm.

Porphyrin 17. Aldehyde **12** (147 mg, 0.29 mmol), benzaldehyde (156 mg, 1.47 mmol), and bis(4-methyl-3-*n*-hexyl-2-pyrrolyl)methane (610 mg, 1.78 mmol) were dissolved in 10 mL of acetonitrile. Trichloroacetic acid (20 mg) was added, and the mixture was stirred for 5 h (dark, under nitrogen, room temperature). *p*-Chloranil (720 mg) in 20 mL of tetrahydrofuran was added, and the mixture was stirred again overnight. The solvent was evaporated, and the resulting solids were suspended in chloroform. Concentrated aqueous hydrochloric acid was added to the solution, and the solution was washed with aqueous sodium bicarbonate solution and with water, dried (Na_2SO_4), and evaporated to yield a black solid. The solid was dissolved in dichloromethane, and to the solution of the reaction in dichloromethane was added a saturated solution of zinc acetate in methanol. The mixture was heated to reflux for 30 min and then cooled, washed with water, dried (Na_2SO_4), filtered, and evaporated to yield a red solid. Chromatography over silica gel (dichloromethane/hexane) afforded the zinc complex of porphyrin **17** (161 mg, 42%). A solution of the zinc complex of porphyrin **17** (23 mg, 17 μmol) in dichloromethane was washed with aqueous hydrochloric acid (1 M) twice, washed with saturated aqueous sodium bicarbonate, dried (Na_2SO_4), and evaporated to yield the porphyrin **17** (21 mg, 96%) as a red solid. **17**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ −2.35 (s, 2H, NH), 0.84 (s, 3H, acetal-CH_3), 0.90 (m, 12H, hexyl-6), 1.32 (s, 3H, acetal-CH_3), 1.37 (m, 8H, hexyl-5), 1.51 (m, 8H, hexyl-4), 1.74 (m, 8H, hexyl-3), 2.19 (m, 8H, hexyl-2), 2.32 (s, 3H, thiophene-CH_3), 2.47 (s, 8H, ArCH_3), 2.52 (s, 3H, thiophene-CH_3), 2.82 (s, 6H, ArCH_3), 3.68 (d, J = 12, 2H, CH_2), 3.81 (d, J = 12, 2H, CH_2), 3.99 (m, 8H, hexyl-1), 5.54 (s, 1H, acetal-CH), 7.18 (s, thiophene-H), 7.72−7.79 (m, 4H, PhH and thiophene-H), 8.06 (m, 2H, PhH), and 10.24 (s, 2H, *meso*-H); MS m/z = 1260 (Calcd 1259 for $C_{75}H_{92}F_6N_4O_2S_2$). UV−vis (THF): λ_{max} (log ϵ) = 409 (5.4), 507 (4.3), 540 (3.9), 577 (3.9), and 630 (3.6). Fluorescence (THF): λ_{max} = 629 and 696 nm.

Diporphyrin 2. Dialdehyde **18** (40 mg, 66 μmol), benzaldehyde (47 mg, 443 μmol), and bis(4-methyl-3-*n*-hexyl-2-pyrrolyl)methane (**13**) (176 mg, 514 μmol) were dissolved in 20 mL of acetonitrile. Trichloroacetic acid (27 mg) was added, and the mixture was stirred for 5 h in the dark under nitrogen, at room temperature. *p*-Chloranil (210 mg) in 15 mL of THF was added, and the mixture was stirred again overnight. The solvent was evaporated, and the resulting solids were suspended in chloroform. Concentrated aqueous hydrochloric acid was added to the solution, and the solution was washed with aqueous sodium bicarbonate solution and with water, dried (Na_2SO_4), and evaporated to yield a black solid. To a solution of the reaction in dichloromethane, a saturated solution of zinc acetate in methanol was added. The mixture was stirred for 1 h at room temperature, washed with water, dried (Na_2SO_4), and evaporated. Chromatography over silica gel (dichloromethane/hexane) gave a mixture of zinc porphyrin products. A size exclusion chromatography gave zinc complex of the diporphyrin **2**, which was demetalated with aqueous hydrochloric acid (1 M) to yield the diporphyrin **2** (18 mg, 13% from dialdehyde). **2**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ −2.38 (s, 4H, NH), 0.82−0.91 (m, 24H, hexyl-6), 1.35 (m, 16H, hexyl-5), 1.45 (m, 16H, hexyl-4), 1.71 (m, 16H, hexyl-3), 2.17 (m, 16H, hexyl-2), 2.45 (s, 6H, ArCH_3), 2.49 (s, 6H, ArCH_3), 2.49 (s, 3H, thiophene-CH_3), 2.52 (s, 3H, thiophene-CH_3), 2.57 (s, 6H, ArCH_3), 2.58 (s, 6H, ArCH_3), 2.61 (s, 3H, thiophene-CH_3), 2.65

(s, 3H, thiophene-CH_3), 3.98 (m, 16H, hexyl-1), 7.70−7.80 (m, 6H, PhH), 7.84 (d, J = 8.0, 4H, phenylene), 8.13 (d, J = 7.5, 2H, phenylene), 8.15 (d, J = 8.0, 2H, phenylene), 10.20 (s, 2H, *meso*-H), and 10.24 (s, 2H, *meso*-H); MS m/z = 2102 (Calcd 2101 for $C_{137}H_{166}F_6N_8S_2$). UV−vis (THF): $\lambda_{max}(\log \epsilon)$ = 409 (5.7), 506 (4.7), 538 (4.2), 575 (4.3), and 628 (3.8). Fluorescence (THF): λ_{max}=628 and 695 nm.

3-Bromo-2-methyl-5-trimethylsilylethynylthiophene (19). A degassed solution of 3,5-dibromo-2-methylthiophene (5.23 g, 20.4 mmol) in 200 mL of Et_3N was added $Pd(PPh_3)_4$ (961 mg, 0.83 mmol), CuI (314 mg, 1.65 mmol), and trimethylsilylacetylene (TMSA) (1.0 mL, 7.1 mmol). The resulting mixture was stirred at 45 °C for 7 h. The solvent was removed under reduced pressure and the residue was filtered through a short plug of silica gel eluting with hexane. The solvent was evaporated, and the residue was purified by column chromatography (hexane) to yield **1** as a yellow solid (1.17 g, 4.30 mmol, 61% from TMSA). **19**: mp 58.5−60.2 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.24 (s, 9H, $Si(CH_3)_3$), 2.36 (s, 3H, $ArCH_3$), and 7.02 (s, 1H, ArH); FTIR (KBr, cm^{-1}) 3103, 2961, 2896, 2150, 849, 646; MS m/z = 274 (Calcd 274 for $C_{10}H_{13}BrSSi$). Anal. Calcd for $C_{10}H_{13}BrSSi$: C, 43.95; H, 4.80. Found: C, 43.92; H, 4.60.

1,2-Bis(5-(4-trimethylsilylethynyl)-2-methylthiophen-3-yl)perfluorocyclopentene (20). A solution of bromide **19** (1.81 g, 6.64 mmol) in dry ether (45 mL) was cooled to −78 °C under a nitrogen atmosphere. *n*-Butyllithium (1.5 M in hexane, 4.4 mL, 3.5 mmol) was added, and after 2 h perfluorocyclopentene was added (0.44 mL, 3.2 mmol, added through cooled syringe). The reaction mixture was stirred for 2 h at −78 °C, after which time the reaction was allowed to warm to ambient temperature. After an additional 2 h, the reaction was diluted with diethyl ether, washed with dilute hydrochloric acid (1% v/v) and water, and extracted with diethyl ether. The combined ether phases were then dried (Na_2SO_4) and evaporated in vacuo to yield a yellow-brown syrup. Chromatography over silica gel (dichloromethane/hexane) afforded diarylethene **20** (1.28 g, 69%) as a bluish white solid. **20**: mp 99.5−101.8 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.25 (s, 18H, $Si(CH_3)_3$), 1.88 (s, 6H, $ArCH_3$), and 7.19 (s, 2H, ArH); FTIR (KBr, cm^{-1}) 2962, 2150, 1275, 1136, 846; MS m/z = 560 (Calcd 560 for $C_{25}H_{26}F_6S_2Si_2$). Anal. Calcd for $C_{25}H_{26}F_6S_2Si_2$: C, 53.55; H, 4.67. Found: C, 53.59; H, 4.65.

1,2-Bis(5-(4-ethynyl)-2-methylthiophen-3-yl)perfluorocyclopentene (21). To a flask containing **20** (600 mg, 1.07 mmol) was added a solution of NaOH (428 mg, 10.7 mmol) in methanol/THF (60 mL/15 mL), and the resulting mixture was stirred at room temperature for 30 min. The reaction was diluted with dichloromethane, washed with water, and extracted with dichloromethane. The combined dichloromethane phases were then dried (Na_2SO_4) and evaporated. Chromatography over silica gel (dichloromethane/hexane) afforded **21** (296 mg, 0.71 mmol, 66%) as a bluish white solid. **21**: mp 95.1−96.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.91 (s, 6H, $ArCH_3$), 3.35 (s, 2H, CH), and 7.23 (s, 2H, ArH); FTIR (KBr, cm^{-1}) 3305, 2909, 2108, 1274, 1134, 669, 625; MS m/z = 416 (Calcd 416 for $C_{19}H_{10}F_6S_2$). Anal. Calcd for $C_{19}H_{10}F_6S_2Si_2$: C, 54.80; H, 2.42. Found: C, 54.93; H, 2.53.

Diporphyrin 3. A degassed solution of **21** (36 mg, 86 μmol) and 5-(4-iodophenyl)-10,15,20-tris(3,5-ditertbutylphenyl)porphine (**22**) (193 mg, 179 μmol) in 25 mL of toluene/Et_3N (1:4) were added $Pd_2(dba)_3$ (14 mg, 15 μmol) and $AsPh_3$ (46 mg, 150 μmol). The resulting solution was stirred at 45 °C for 20 h. The solvent was removed under reduced pressure, and the residue was filtered through a short plug of silica gel eluting with dichloromethane. The solvent was evaporated, and the residue was purified by column chromatography (dichloromethane/hexane) to yield diporphyrin **3** (95 mg, 41 μmol, 48%). **3**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ −2.69 (s, 4H, NH), 1.52 (s, 54H, t-Bu), 2.09 (s, 6H, thiophene-CH_3), 7.45 (s, 2H, thiophene-H), 7.79 (s, 3H, Ph-H), 7.92 (d, J = 8.0, 4H, phenylene-H), 8.07 (d, J = 2.0, 4H, Ph-H), 8.08 (d, J = 2.0, 8H, Ph-H), 8.25 (d, J = 8.0, 4H, phenylene-H), 8.84 (d, J = 1.5, 4H, β-H), and 8.90 (s+d, J = 6.5, 8H+4H, β-H); MS m/z = 2314 (Calcd 2313 for $C_{155}H_{162}F_6N_8S_2$). UV−vis (THF): $\lambda_{max}(\log \epsilon)$ = 421 (6.0), 516 (4.6), 551 (4.4), 592 (4.1), and 648 (3.8). Fluorescence (THF): λ_{max} = 650 and 717 nm.

3-Bromo-2-methyl-5-(4-trimethylsilylethynylphenyl)-thiophene (25). A degassed solution of boronic acid **23** (1.77 g, 8.02 mmol) and iodide **24** (2.43 g, 8.09 mmol) in tetrahydrofuran (40 mL) and aqueous sodium carbonate (20% w/v, 25 mL) was added tetrakis(triphenylphosphine)palladium(0) (347 mg, 0.30 mmol). The reaction was refluxed under a argon atmosphere for 20 h and then cooled, extracted with chloroform, and washed with water. The combined organic phases were dried (Na_2SO_4) and evaporated. Chromatography over silica gel (hexane) and recrystallization from methanol gave **25** as a white solid (2.06 g, 5.90 mmol, 73%). **25**: mp 78.8−82.2 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.26 (s, 9H, $Si(CH_3)_3$), 2.42 (s, 3H, thiophene-CH_3), 7.12 (s, 1H, thiophene-H), and 7.44 (s, 4H, phenylene-H); FTIR (KBr, cm^{-1}) 3027, 2959, 2158, 1505, 838, 633; MS m/z = 348 (Calcd 348 for $C_{16}H_{17}BrSSi$). Anal. Calcd for $C_{16}H_{17}BrSSi$: C, 55.01; H, 4.90. Found: C, 54.95; H, 4.70.

1,2-Bis(5-(4-trimethylsilylethynylphenyl)-2-methylthiophen-3-yl)perfluorocyclopentene (7). A solution of bromide **25** (1.12 g, 3.21 mmol) in dry ether (30 mL) was cooled to −78 °C under a nitrogen atmosphere. *n*-Butyllithium (1.6 M in hexane, 2.1 mL, 3.4 mmol) was then added, after 2 h, followed by perfluorocyclopentene (0.20 mL, 1.6 mmol, added through cooled syringe). The reaction mixture was stirred for 1 h at −78 °C, after which time the reaction was allowed to warm to ambient temperature. After an additional 2 h, the reaction was diluted with diethyl ether, washed with dilute hydrochloric acid (1% v/v) and water, and reextracted with diethyl ether. The combined ether phases were then dried (Na_2SO_4), filtered, and evaporated in vacuo to yield a yellow-brown syrup. Chromatography over silica gel (dichloromethane/hexane) afforded dithienylethene **7** (745 mg, 65%) as a bluish white solid. **7**: mp 92.5−94.8 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.26 (s, 18H, $Si(CH_3)_3$), 1.97 (s, 6H, thiophene-CH_3), 7.28 (s, 2H, thiophene-H), and 7.46 (s, 8H, phenylene-H); FTIR (KBr, cm^{-1}) 3032, 2960, 2157, 1508, 1275, 1139, 865; MS m/z = 712 (Calcd 712 for $C_{37}H_{34}F_6S_2Si_2$). Anal. Calcd for $C_{37}H_{34}F_6S_2Si_2$: C, 62.33; H, 4.81. Found: C, 62.57; H, 4.57.

1,2-Bis(5-(4-ethynylphenyl)-2-methylthiophen-3-yl)-perfluorocyclopentene (26). To a flask containing **7** (307 mg, 0.43 mmol) was added a solution of NaOH (252 mg, 6.3 mmol) in methanol (20 mL), and the mixture was stirred at room temperature for 3 h. The reaction was diluted with diethyl ether, washed with water, and reextracted with diethyl ether. The combined ether phases were then dried (Na_2SO_4) and evaporated. Chromatography over silica gel (dichloromethane/hexane) afforded **26** (192 mg, 0.34 mmol, 78%) as a bluish white solid. **26**: mp 164.2−166.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.98 (s, 6H, thiophene-CH_3), 3.15 (s, 2H, ethynyl-H), 7.29 (s, 2H, thiophene-H), and 7.49 (s, 8H, phenylene-H); FTIR (KBr, cm^{-1}) 3305, 3030, 2917, 2107, 1471, 1273, 1104, 648, 612; MS m/z = 568 (Calcd 568 for $C_{31}H_{18}F_6S_2$). Anal. Calcd for $C_{31}H_{18}F_6S_2$: C, 65.48; H, 3.19. Found: C, 65.32; H, 3.40.

Diporphyrin 4. A degassed solution of **26** (86 mg, 151 μmol) and 5-(4-iodophenyl)-10,15,20-tris(3,5-ditertbutylphenyl)porphine (**22**) (402 mg, 373 μmol) in 50 mL of toluene/Et_3N (1:4) were added $Pd_2(dba)_3$ (84 mg, 91 μmol) and $AsPh_3$ (233 mg, 761 μmol). The resulting mixture was stirred at 35 °C for 4 h. The solvent was removed under reduced pressure, and the residue was filtered through a short plug of silica gel eluting with dichloromethane. The solvent was evaporated, and the residue was purified by a size exclusion chromatography and column chromatography (dichloromethane/hexane) to yield porphyrin dimer **4** (190 mg, 77 μmol, 51%). **4**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ −2.68 (s, 4H, NH), 1.53 (s, 54H, *t*-Bu), 2.06 (s, 6H, thiophene-CH_3), 7.40 (s, 2H, thiophene-H), 7.64 (d, J = 8.0, 4H, phenylene-H), 7.71 (d, J = 8.0, 4H, phenylene-H), 7.79 (s, 2H, Ph-H), 7.80 (s, 4H, Ph-H), 7.95 (d, J = 8.0, 4H, phenylene-H), 8.07 (d, J = 1.5, 4H, Ph-H), 8.09 (d, J = 1.5, 8H, Ph-H), 8.25 (d, J = 7.5, 4H, phenylene-H), 8.86 (d, J = 4.5, 4H, β-H), and 8.90 (s+d, 4H+2H, β-H); MS m/z = 2466 (Calcd 2466 for $C_{167}H_{170}F_6N_8S_2$). UV−vis (THF): λ_{max} ($\log \epsilon$)

= 420 (6.1), 515 (4.7), 551 (4.5), 592 (4.1), and 648 (4.1). Fluorescence (THF): λ_{max}= 650 and 717 nm.

Closed Form of Diporphyrin 4c. A solution of **4** in THF was irradiated with UV light (330 nm) for 5 min. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (dichloromethane/hexane) to isolate porphyrindimer **4c**. **4c**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ −2.68 (s, 4H, NH), 1.53 (s, 54H, *t*-Bu), 2.27 (s, 6H, thiophene-CH_3), 6.79 (s, 2H, thiophene-H), 7.66 (d, J = 7.5, 4H, phenylene-H), 7.73 (d, J = 8.0, 4H, phenylene-H), 7.80 (s, 6H, Ph-H), 7.95 (d, J = 8.0, 4H, phenylene-H), 8.07 (d, J = 2.0, 4H, Ph-H), 8.09 (d, J = 1.5, 8H, Ph-H), 8.26 (d, J = 8.0, 4H, phenylene-H), 8.86 (d, J = 5.0, 4H, β-H), and 8.90 (s+d, 4H+2H, β-H); MS m/z = 2466 (Calcd 2466 for $C_{167}H_{170}F_6N_8S_2$). UV−vis (THF): λ_{max}(log ϵ) = 420 (6.1), 516 (4.8), 552 (4.7), 597 (4.7), and 649 (4.7). Fluorescence (THF): λ_{max} = 650 and 718 nm.

Diporphyrin 5. A degassed solution of **21** (27 mg, 65 μmol) and 10-bromo-5,15-bis(3,5-dioctyloxyphenyl)porphine (**27**) (137 mg, 130 μmol) in 20 mL of Et_3N were added $Pd_2(dba)_3$ (12 mg, 13 μmol) and $AsPh_3$ (40 mg, 130 μmol). The resulting mixture was stirred at 50 °C for 20 h. The solvent was removed under reduced pressure, and the residue was filtered through a short plug of silica gel eluting with dichloromethane. The solvent was evaporated, and the residue was purified by column chromatography (dichloromethane/hexane) to yield diporphyrin **5** (98 mg, 41 μmol, 64%). **5**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ −2.55 (s, 4H, NH), 0.87 (t, J = 7.0, 12H, octyl-8), 1.28 (m, 64H, octyl-4,5,6,7), 1.53 (m, 16H, octyl-3), 1.88 (m, 16H, octyl-2), 2.25 (s, 6H, thiophene-CH_3), 4.15 (t, J = 6.5, 16H, octyl-1), 6.91 (s, 4H, Ph-H), 7.39 (d, J = 2.0, 8H, Ph-H), 7.82 (s, 2H, thiophene-H), 9.06 (d, J = 4.5, 4H, β-H), 9.11 (d, J = 4.5, 4H, β-H), 9.26 (d, J = 4.5, 4H, β-H), 9.73 (d, J = 4.5, 4H, β-H), and 10.16 (s, 2H, *meso*-H); MS m/z = 2364 (Calcd 2361 for $C_{147}H_{178}F_6N_8O_8S_2$). UV−vis (THF): λ_{max}(log ϵ) = 437 (5.7), 526 (4.5), 572 (4.7), 604 (4.1), and 663 (4.3). Fluorescence (THF): λ_{max} = 664 and 735 nm.

Diporphyrin 6. A degassed solution of **26** (28 mg, 49 μmol) and 10-bromo-5,15-bis(3,5-dioctyloxyphenyl)porphyrin (**27**) (100 mg, 95 μmol) in 20 mL of Et_3N were added $Pd_2(dba)_3$ (9 mg, 10 μmol) and $AsPh_3$ (31 mg, 101 μmol). The resulting mixture was stirred at 45 °C for 20 h. The solvent was removed under reduced pressure, and the residue was filtered through a short plug of silica gel eluting with dichloromethane. The solvent was evaporated, and the residue was purified by column chromatography (dichloromethane/hexane) to yield diporphyrin **6** (80 mg, 32 μmol, 64%). **6**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ −2.55 (s, 4H, NH), 0.86 (t, J = 7.0, 12H, octyl-8), 1.28 (m, 64H, octyl-4,5,6,7), 1.54 (m, 16H, octyl-3), 1.88 (m, 16H, octyl-2), 2.09 (s, 6H, thiophene-CH_3), 4.15 (t, J = 7.0, 16H, octyl-1), 6.91 (s, 4H, Ph-H), 7.39 (d, J = 2.0, 8H, Ph-H), 7.50 (s, 2H, thiophene-H), 7.79 (d, J = 8.0, 4H, phenylene-H), 8.07 (d, J = 8.5, 4H, phenylene-H), 9.05 (d, J = 4.5, 4H, β-H), 9.10 (d, J = 4.5, 4H, β-H), 9.26 (d, J = 4.5, 4H, β-H), 9.80 (d, J = 4.5, 4H, β-H), and 10.14 (s, 2H, *meso*-H); MS m/z = 2515 (Calcd 2513 for $C_{159}H_{186}F_6N_8O_8S_2$). UV−vis (THF): λ_{max} (log ϵ) = 437 (5.8), 527.5 (4.5), 571 (4.9), 604 (4.2), and 663 (4.4). Fluorescence (THF): λ_{max} = 663 and 735 nm.

Closed Form of Dithienylethene 26c. A solution of **26** in THF was irradiated with UV light (330 nm) for 5 min. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (dichloromethane/hexane) to isolate **26c** as a blue solid. **26c**: mp 92.5−95.8 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.18 (s, 6H, thiophene-CH_3), 3.23 (s, 2H, ethynyl-H), 6.69 (s, 2H, thiophene-H), and 7.53 (s, 8H, phenylene-H); FTIR (KBr, cm^{-1}) 3302, 3033, 2926, 2107, 1491, 1341, 1125, 657, 628; MS m/z = 568 (Calcd 568 for $C_{31}H_{18}F_6S_2$). Anal. Calcd for $C_{31}H_{18}F_6S_2$: C, 65.48; H, 3.19. Found: C, 65.21; H, 3.46.

Closed Form of Diporphyrin 6c. Air was removed from a solution of **26c** (11 mg, 19 μmol) and 10-bromo-5,15-bis(3,5-dioctyloxyphenyl)porphine (45 mg, 43 μmol) in 10 mL of Et_3N by blowing argon for 10 min. Then, $Pd_2(dba)_3$ (4 mg, 4 μmol) and $AsPh_3$ (13 mg, 42 μmol) were added, and the mixture was stirred at 45 °C for 20 h. The solvent was removed under reduced pressure, and the residue was filtered through a short plug of silica gel eluting with dichloromethane. The solvent was evaporated, and the residue was purified by column chromatography (dichloromethane/hexane) to yield porphyrin dimer **6c** (36 mg, 14 μmol, 74%). **6c**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ −2.53 (s, 4H, NH), 0.88 (t, J = 7.0, 12H, octyl-8), 1.29 (m, 64H, octyl-4,5,6,7), 1.54 (m, 16H, octyl-3), 1.90 (m, 16H, octyl-2), 2.33 (s, 6H, thiophene-CH_3), 4.16 (t, J = 7.0, 16H, octyl-1), 6.88 (s, 2H, thiophene-H), 6.93 (s, 4H, Ph-H), 7.40 (d, J = 2.5, 8H, Ph-H), 7.81 (d, J = 8.0, 4H, phenylene-H), 8.09 (d, J = 8.5, 4H, phenylene-H), 9.06 (d, J = 4.5, 4H, β-H), 9.12 (d, J = 5.0, 4H, β-H), 9.27 (d, J = 4.5, 4H, β-H), 9.80 (d, J = 4.5, 4H, β-H), and 10.16 (s, 2H, *meso*-H); MS m/z = 2515 (Calcd 2513 for $C_{159}H_{186}F_6N_8O_8S_2$). UV−vis (THF): λ_{max}(log ϵ) = 428 (5.5), 525 (4.6), 582 (4.7), 611 (4.8), and 677 (4.9). Fluorescence (THF): λ_{max} = 663 and 736 nm.

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Supporting Information Available: ^{1}H NMR spectra of **1**, **2**, **3**, **4**, **4c**, **5**, **6**, and **6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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