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Self-Assembly of Photochromic Diarylethenes with Amphiphilic Side Chains: Core-Chain Ratio Dependence on Supramolecular Structures

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Abstract: Photochromic diarylethene derivatives having different lengths and numbers of poly(ethylene glycol) side chains were synthesized and their photochromic property and self-assembling behavior were investigated. The self-assembling behavior of the derivatives strongly depends upon the ratio between the hydrophobic core and the amphiphilic side chain. According to UV/Vis absorption spectroscopy, CD spectroscopy, and dynamic light scattering experiments, these derivatives showed different size distribution of the assembled structures and different solubility in water. The intensity of the induced CD signal, which was observed in the closed-ring isomer, was the largest for the molecule having two hexaethylene glycol side chains. The relationship between the core-chain ratio and regularity of the self-assembled structure has been investigated.

Keywords: circular dichroism · hydrophobic effect · molecular modeling · photochromism · self-assembly

Introduction

Self-organization in water is a very important scientific topic because it is strongly related to the three-dimensional structures of biologically important molecules such as proteins or DNA. In water, hydrophobic interaction plays an important role in the formation of mesoscopic organizations, when the molecule is suitably designed with hydrophobic and hydrophilic moieties.[1] Self-assembled structures constructed by hydrophobic interaction, which is not a site-specific interaction, are relatively flexible in comparison with the structures formed by hydrogen or coordination bonds, and so are expected to easily reorganize with an external stimulus.

Meanwhile, photocontrollable supramolecular architecture is gathering increasing attention as a photofunctional material.[2] An ultimate example of the photocontrollable self-assembled structure is the retinal–rhodopsin system which provides mammalian vision.[3] The initial photoinduced isomerization of the retinal molecule is transmitted to the structural changes of the rhodopsin protein. Therefore, a photocontrollable self-assembled structure formed by hydrophobic interaction is a very challenging and promising target for highly-functional materials.

Recently, we reported the photochromic property and the self-assembling behavior of amphiphilic diarylethenes[4] **1** and **2** (Scheme 1), which have poly(ethylene glycol) (PEG) side chains.[5] While these compounds are molecularly dispersed in common organic solvents such as ethyl acetate, they self-assemble into nanostructures in water. It is of interest that the methyl group introduced near the hydrophobic core as a chiral source, induces an asymmetric supramolecular environment only in the self-assembled structure consisting of the closed-ring isomer **2b**. Consequently, compound **2** shows photoswitching of the induced circular dichroism (ICD) signal, which arises from the chiral environmental change between the open- and the closed-ring isomers upon photoirradiation.

The ICD measurement is one of the most convenient ways to probe chiral structural changes taking place at the molecular level. Furthermore, a strong ICD switch is desirable in applications such as chiral memory. The ICD signal intensity depends on the population difference of the left-

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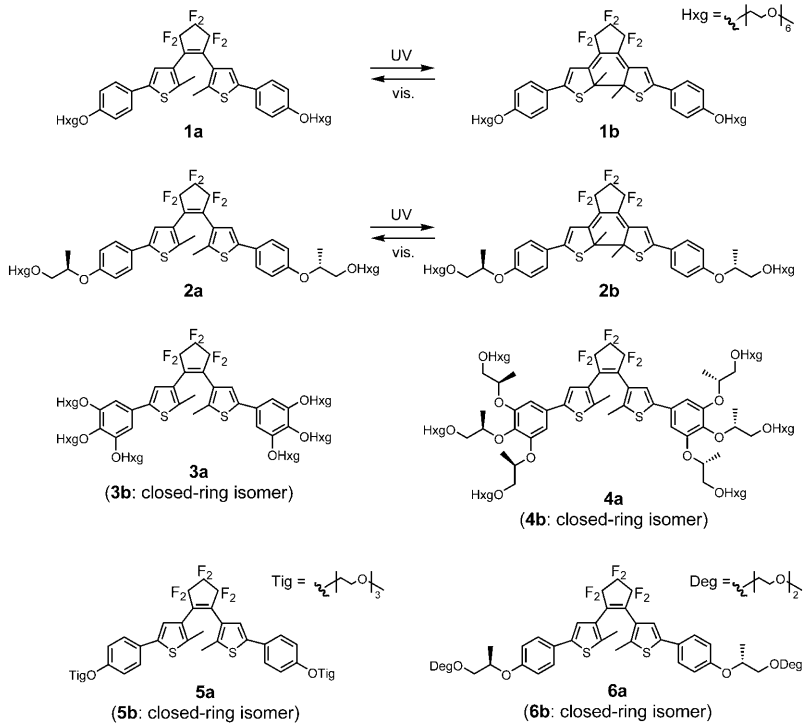


Scheme 1. Photochromism of diarylethenes having PEG side chains.

and right-handed helical structures (i.e., twist sense bias).[6] Therefore, if a more well-defined structure was prepared, the population difference would be enhanced because of the larger energy gap between the two helical structures, which would give rise to a strong ICD signal. The intensity of the ICD signal also depends on the distance, the twist angle, and the strength of the two transition dipole moments.[7] When close molecular packing is achieved, a strong ICD signal would be observed. Thus, a well-defined tightly packed structure is required to exhibit a strong ICD switch.

The volume ratio between the hydrophobic core and the amphiphilic side chain exerts a great influence on the self-assembled nanostructure. Lee et al. reported that different types of structures can be made by changing the rod/coil ratio of the copolymers.[8] In our system, the volume ratio of the amphiphilic side chain can be controlled by changing the length or the number of the PEG side chain.

Here, we report the synthesis, their photochromic property, and self-assembling behavior of diarylethene derivatives that have different lengths and number of PEG side chains.

Abstract in Japanese:

両親媒性側鎖として poly-(ethylene glycol) (PEG) 鎖を有するジアリールエテン誘導体を合成し、水中における自己組織化挙動と光反応性を検討した。疎水性のコア部位に対して両親媒性基の割合が異なる化合物は、その側鎖の長さ・本数に依存して水への溶解性が大きく変化し、化合物によって異なる粒度の組織化構造体を形成することが認められた。興味深いことに、適度な割合の両親媒性側鎖を有する化合物から最も強度の強い励起子分裂型の CD シグナルが観測されたことから、最適な疎水性・親水性の割合が満たされた際に、水溶液中で最も規則性の高いキラル環境を有する超分子構造体が形成されることが示唆された。また、D_2O 中における 2D-NOESY 測定，動的光散乱測定 (DLS) および分子モデルによる考察から、水中では PEG 鎖がジアリールエテン部位を取り囲むように配置した立体構造が提案された。

Results and Discussion

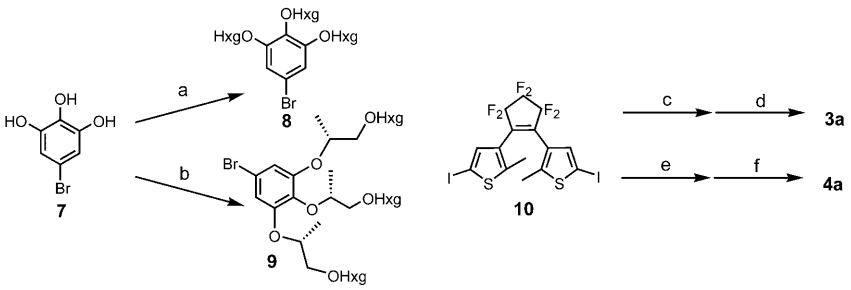
Synthesis

In order to investigate the dependence of the self-assembling behavior upon the proportion of the amphiphilic side chain, we designed compounds **3a**–**6a** (Scheme 1). Compounds **3a** and **4a** have three hexaethylene glycol (Hxg, $n=6$) side chains at both sides of the hydrophobic core. Compounds **5a** and **6a** have two triethylene glycol (Tig, $n=3$) side chains that are about half the length of the Hxg side chain. As described before, the ICD signal intensity depends on the volume ratio between the hydrophobic core and the amphiphilic side chain. The photochemical properties and self-assembling behavior of the compounds were investigated.

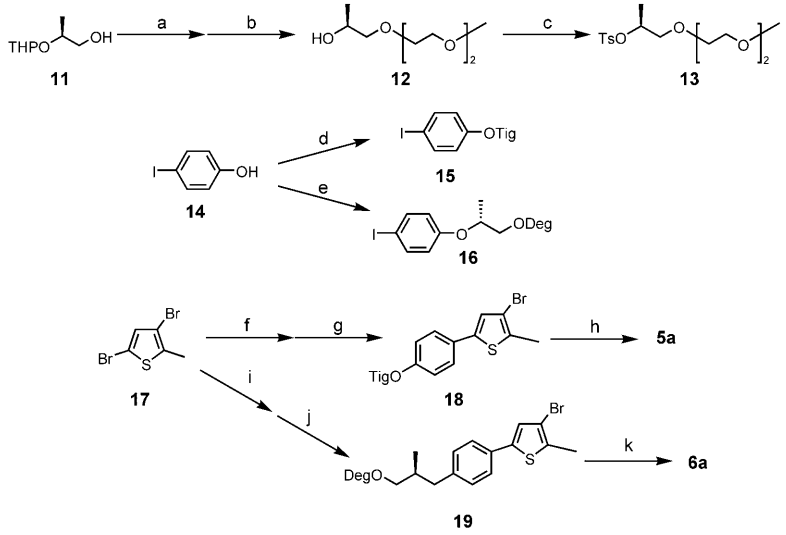
Compounds **3a** and **4a** were synthesized according to Scheme 2 and compounds **5a** and **6a** were synthesized according to Scheme 3. Although compound **5a** was obtained in a similar manner as previously reported for compound **1a**,[5] the synthetic route was modified for compound **3a** because of poor solubility of the bromobenzene derivative **8** in dry THF at low temperature. It was found that the S_N2 reaction of tosylated PEG and phenol derivatives converts the stereocenter from (*S*)- to (*R*)-chirality. When the Mitsunobu reaction, which is known to invert the chirality,[9] was adopted, the compound obtained had exactly the same chirality as the one previously reported (Scheme 4).[5] The expression of the chirality of compound **2** in the previous report was opposite and the chirality has been corrected in Scheme 1. NMR and mass spectroscopy confirmed the structure of the synthesized molecules.

Photochromic Behavior and Induced Circular Dichroism

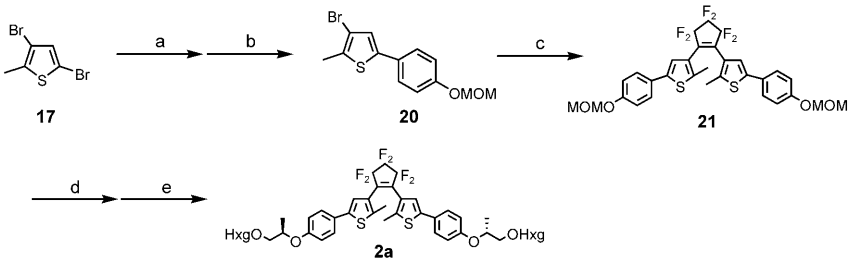
All the synthesized compounds underwent photochromic reaction upon irradiation with UV and visible light. Upon irradiation with UV light (313 nm), the open-ring isomer converted to the closed-ring isomer and the closed-ring isomer returned back to the original open-ring isomer upon irradiation with visible light ($\lambda > 480$ nm). The absorption and CD



Scheme 2. Synthesis of compounds **3a** and **4a**. Reagents and conditions: a) TsOHxg, K_2CO_3, DMF, 86%; b) (*S*)-TsOCHMeCH$_2$OHxg, K_2CO_3, DMF, 42%; c) *n*BuLi, dry THF, and then $(BuO)_3B$; d) **8**, THF, aq. Na_2CO_3, $Pd(PPh_3)_4$, 9% in two steps; e) *n*BuLi, dry THF, and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; f) **9**, THF, aq. Na_2CO_3, $Pd(PPh_3)_4$, 12% in two steps.



Scheme 3. Synthesis of compounds **5a** and **6a**. Reagents and conditions: a) TsODeg, NaH, dry THF; b) PPTS, EtOH, 81% in two steps; c) TsCl, aq. NaOH, THF, 60%; d) TsOTig, K_2CO_3, DMF, 99%; e) **13**, K_2CO_3, DMF, quantitative; f) *n*BuLi, dry THF, and then $(BuO)_3B$; g) **15**, THF, aq. Na_2CO_3, $Pd(PPh_3)_4$, 85% in two steps; h) *n*BuLi, dry THF, and then perfluorocyclopentene, 25%; i) *n*BuLi, dry THF, and then $(BuO)_3B$; j) **16**, THF, aq. Na_2CO_3, $Pd(PPh_3)_4$, 76% in two steps; k) *n*BuLi, dry THF, and then perfluorocyclopentene, 21%.



Scheme 4. Synthesis of compound **2a** by Mitsunobu Reaction. Reagents and conditions: a) *n*BuLi, dry THF, and then $(BuO)_3B$; b) 1-iodo-4-methoxymethoxybenzene, THF, aq. Na_2CO_3, $Pd(PPh_3)_4$, 88% in two steps; c) *n*BuLi, dry THF, and then perfluorocyclopentene, 40%; d) conc. HCl, THF; e) DEAD, PPh_3, then (*S*)-HOCHMeCH$_2$OHxg, THF, 16% in two steps.

spectra of these compounds in water showed different features (Figure 1, center column). Compounds **3** and **4**, which have six Hxg side chains, were well soluble in water and the corresponding absorption spectra were nearly identical with those in ethyl acetate (Figures 1a and 1b). Moreover, the closed-ring isomer **4b** showed almost no exciton-coupled ICD signal in water (Figure 1c). The similarity of the absorption spectra in the two solvents and the very weak ICD signal suggest that compounds **3** and **4** may be molecularly dispersed in both ethyl acetate and water. The six Hxg side chains significantly enhanced the water solubility of the compounds **3** and **4**. On the other hand, compounds **5** and **6**, which have shorter PEG side chains, were hardly soluble in water and their absorption spectra were difficult to record. Therefore, we prepared aqueous solutions by dropping a concentrated acetonitrile solution of compound **5a** or **6a** into an excess of water, and then carried out the measurement (Figure 1h). The spectra of compounds **5** and **6** in water have an apparent absorption edge that extends beyond 400 nm for the open-ring isomers, which was not observed in ethyl acetate (Figure 1g). Although an aqueous solution of **6b** showed a distinctive exciton-coupled CD signal in the visible region, the intensity of the signal was weaker than that of compound **2b** (Figure 1i).

The CD signal of the closed-ring isomer and the absorption edge of the open-ring isomer showed a different dependency on the ratio of the amphiphilic side chains. The absorption spectra of the synthesized compounds are summarized in Figure 1. The absorption spectra of compounds **1**, **3** and **5** in ethyl acetate are similar for both the open- and the closed-ring isomers (Figure 1, left column). On the other hand, the edge increased in the following order: compound **4** (six Hxg chains) < compound **2** (two Hxg chains) < compound **6** (two Tig side chains). The intensity of the absorption edge correlates with the proportion of the PEG side chains. The ab-

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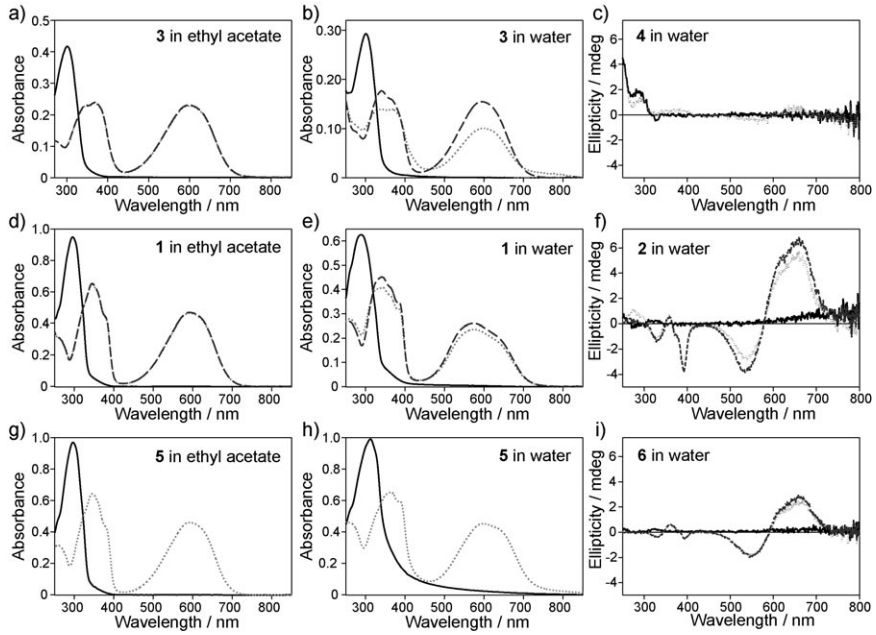

Figure 1. Absorption and CD spectra of diarylethenes along with photochromism: Absorption spectra of compounds **1**, **3**, and **5** in ethyl acetate (left column), in water (center column), and the corresponding CD spectra of compounds **2**, **4**, and **6** in water (right column). (a)–(c): **3** and **4** ; (d)–(f): **1** and **2** ; (g)–(i): **5** and **6**. Black solid line: open-ring isomer; dark gray dashed line: closed-ring isomer; pale gray dotted line: sample in the photostationary state under irradiation with 313 nm light.

sorption edge that extended beyond 400 nm may originate from the light scattering of the turbid aqueous solutions. Thus, this result indicates that strong light scattering was observed as the proportion of the PEG side chains decreased. On the other hand, the CD signal of the closed-ring isomer became larger in the order **4**<**6**<**2**. This result indicates that solubility does not have a direct correlation with the CD signal of the closed-ring isomer.

Figure 2 shows the CD spectra of compound **2** in a mixture of water and methanol. The intensity of the CD spectra was normalized by the absorbance of the visible band of the

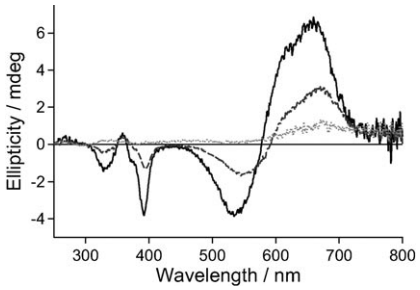

Figure 2. CD spectra of compound **2** in water (black solid line), in MeOH/H_2O=25:75 (dark gray dashed line), and in MeOH/H_2O=50:50 (pale gray dotted line).

closed-ring isomer. The ICD signal became weak as the ratio of methanol increased. This result also confirmed that the ICD signal decreased as the solubility increased.

Compounds **3** and **4** have enough hydrophilic groups to give a molecularly dispersed solution in water. Compounds **5** and **6** had too poor solubility in water to give a good self-assembled structure. Overall, neither compounds **4b** nor **6b** exceeded the ICD intensity of compound **2b**.

Dynamic Light Scattering (DLS) Measurements

Owing to the light scattering intensity dependence on the lengths and numbers of the PEG side chains as determined from absorption spectroscopy, these compounds are considered to form different sizes of self-assembled nanostructures. To examine how the size distribution of the nanostructures depends on the proportion of PEG side chains, DLS measurements were carried out (Figure 3).

In the case of an aqueous solution of compound **3a** that has six Hxg side chains, the light scattering signal was too weak to obtain the size distribution, which suggests that compound **3a** is molecularly dispersed even in water or forms very small aggregates that do not cause light scattering. This result is consistent with the absorption spectrum of **3a** in water which is similar to that obtained in ethyl acetate.

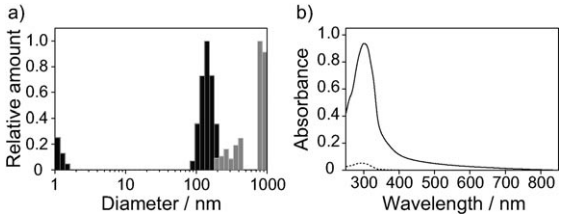

Figure 3. a) Size distribution of the open-ring isomer **5a** in water before filtration (gray bar) and after filtration (black bar). b) The concentration change of an aqueous solution of compound **5a** before (solid line) and after (dashed line) filtration with a 0.2 μm membrane filter.

Corresponding DLS measurements for compound **1a** in water showed a peak corresponding to a size of around 100 nm in water,[5] which is smaller than the wavelength of the visible light, so that an aqueous solution of compound **1a** did not show strong absorption edge that extended beyond 400 nm.

An aqueous solution of compound **5a** looked slightly turbid, but the solution became clear after filtration using a

0.2 μm membrane filter. While the size of the nanostructures was mainly more than 200 nm before filtration, the size distribution of the filtrated sample had a mean diameter of 132 nm (Figure 3a). The absorbance at the absorption maximum was $A=0.936$ ($\lambda_{max}=302$ nm) before filtration, but decreased to $A=0.052$ ($\lambda_{max}=298$ nm) after filtration (Figure 3b). This result implies that 95% of molecules formed nanostructures of more than 200 nm size.

Thus, the compounds that have different lengths of the amphiphilic side chains formed different sizes of self-assembled nanostructures in water, which is consistent with the results from absorption and CD spectroscopies.

Studies on Molecular Conformation

Compound **4**, which has six Hxg side chains, was found to be molecularly dispersed in water. Furthermore, compound **6b**, which has shorter Tig side chains, showed a slightly weak ICD signal when compared with compound **2b**. After all, compound **2b** having an appropriate length of PEG side chains showed the strongest ICD signal. Thus, the self-assembled structure of compounds **1** and **2** showed a higher regularity than the others, and two Hxg side chains were found to be the appropriate length and number for self-assembly. Such behavior can be understood by the following conformational consideration.

In order to understand the conformation of the amphiphilic side chains around the aromatic core, NOESY measurements were carried out (Figure 4). The ^{1}H NMR spectrum of compound **1** in D_2O was too broad to detect NOE signals, owing to aggregation at room temperature,[5] hence NOESY spectra were measured at 50°C to obtain sharp signals.

The signals that appeared at about 3.5–4.5 ppm were assigned to the protons of the Hxg side chains and the signals at about 7.0–8.0 ppm were assigned to the protons of the diarylethene core moiety. NOEs between protons of PEG side chains and protons of diarylethene were detected (Figure 4c). This result supports that the PEG side chains and the diarylethene core are spatially close to each other in water. A similar contact between a PEG chain and nitrobenzene core in PEG substituted nitrobenzene has been reported by Natansohn et al.[10]

By using a molecular modeling kit, the conformations of the amphiphilic diarylethenes were examined. As shown in Figure 5a, the diarylethene core can be sufficiently surrounded by the amphiphilic side chains when the length of the PEG side chain is $n=6$, though in this structure, two Hxg side chains are not adequate to cover the hydrophobic core moiety completely. This partial coverage can be a driving force for directional self-assembly of the molecules by hydrophobic interactions.

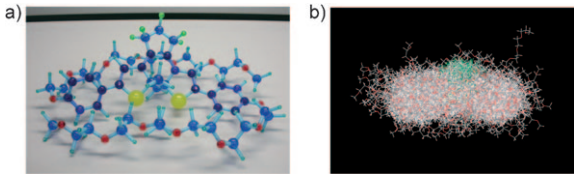

Figure 5. a) Molecular model of compound **1b**. When the length of PEG side chain is $n=6$ (Hxg), the diarylethene core would be surrounded by the amphiphilic side chains moderately. b) The result of the molecular mechanics calculation. The superimposed structures of the most stable 100 conformers are shown. Elements are colored as follows: C grey, H white, O red, F green.

Molecular mechanics structural optimization was carried out to examine the molecular conformation of the compounds. The conformational sampling was performed by Monte Carlo Multiple Minimum method using MacroModel software. Figure 5b shows the superimposed structures of the most stable 100 conformers. This figure shows that the perfluorocyclopentene moiety does not cover the PEG chains. This calculation result also suggests a partial coverage of the hydrophobic core moiety.

On the other hand, simple modeling can confirm that the diarylethene core of compounds **3** and **4** can be covered completely by an additional four Hxg side chains. This complete coverage is the reason for the very good solubility of **3** and **4** in water. In **3** and **4**, complete coverage may prevent self-assembly of the molecules by hydrophobic interactions. This result implies that moderate solubility for water is required for self-assembly by hydrophobic interactions. On the contrary, compounds **5** and **6** having shorter side chains, which cannot cover up the diaryle-

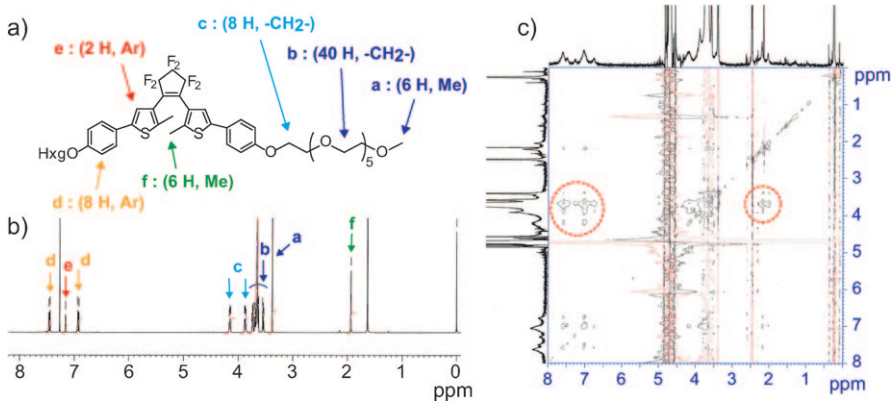

Figure 4. a) The molecular structure of compound **1**. b) ^{1}H NMR spectrum of the open-ring isomer **1a** in $CDCl_3$ at room temperature. c) NOESY spectrum of the sample in the photostationary state under irradiation with 313 nm light (91% closed-ring isomer) in D_2O at 50°C (400 MHz; mixing time, 0.3 sec). NOEs between protons of PEG side chains (a–c) and protons of diarylethene (d–f) were detected (red dashed circles).

thene core sufficiently, showed very poor solubility in water. This poor solubility may prohibit the formation of the ordered self-assembled structure. The self-assembling behavior in water was found to sensitively depend on the proportion of the amphiphilic side chains to the hydrophobic core moiety. It was found that the ordered self-assembled structure was formed in a moderate ratio of amphiphilic and hydrophobic moieties.

Conclusions

In this study, we have reported the synthesis of diarylethene derivatives that have different lengths and numbers of poly(ethylene glycol) side chains and have investigated their photochromic property and self-assembling behavior. The size of the aggregates and the self-assembling behavior are dependent on the proportion of the amphiphilic side chains to the hydrophobic core moiety. As the proportion of PEG side chains increased, the size distribution of aggregates became smaller and the compound showed better solubility in water. The compound that has two hexaethylene glycol side chains showed the most favorable photoswitching of the induced CD signal. The solubility in water and the self-assembling ability of the amphiphilic compounds were understood by the conformational studies.

Experimental Section

Materials

All reactions were monitored by thin-layer chromatography carried out on 0.2 mm Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Kanto Chemical, 63–210 mesh). ^{1}H NMR spectra were recorded on a Varian Gemini 200 or a Bruker AVANCE 400 instrument. Samples were dissolved in $CDCl_3$ and tetramethylsilane was used as an internal standard. Mass spectra were recorded on a JEOL JMS-GCmate II mass spectrometer or a BRUKER Autoflex MALDI TOF mass spectrometer. Compound **7**,[11] **10**,[12] **11**,[13] **17**,[14] and 1-iodo-4-methoxymethoxybenzene[15] were prepared according to the method reported previously. Tosylated derivative of poly(ethylene glycol) monomethyl ether was prepared by the method reported for TsOHxg.[5]

It is worth noting that chiral inversion took place in the S_N2 reaction of tosylated PEG and phenol derivatives (compound **7** to **9** in Scheme 2 and compound **14** to **16** in Scheme 3). The structure of the previously reported compound **2** was revised from (*S*)- to (*R*)-chirality.

5-bromo-1,2,3-tris-{2-[2-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy}-benzene (8): A tosylated derivative of hexaethylene glycol monomethyl ether (TsOHxg) (7.25 g, 16.1 mmol) and 5-bromo-pyrogallol **7** (1.0 g, 4.88 mmol) were added to a solution of K_2CO_3 (6.7 g, 48.8 mmol) in DMF (48 mL). The solution was stirred overnight (24 h) at 70 °C. After cooling, the mixture was poured into aqueous HCl (pH 2, 200 mL) and extracted with CH_2Cl_2 (×3). The organic layer was washed with brine (×2), dried over magnesium sulfate, and the solvent was evaporated in vacuo. The crude product was purified by silica gel column chromatography (CH_2Cl_2/acetone = 3:1) to yield **9** (4.35 g, 4.18 mmol, quantitatively) as a viscous yellow oil. ^{1}H NMR ($CDCl_3$, TMS, 200 MHz): δ = 3.38 (s, 9H), 3.51–4.17 (m, 72H), 6.74 ppm (s, 2H, Ar); MS (MALDI-TOF): *m*/*z* (%) calcd for $C_{45}H_{83}BrNaO_{21}$: 1061.45 $[M+Na]^+$; found: 1060.96, 1062.97.

(*R,R,R*)-5-bromo-1,2,3-tris-{2-[2-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy-2-propoxy}-benzene (9): A tosylated derivative of hexaethylene glycol monomethyl ether ((*S*)-TsOCHMe-CH_2OHxg) (1.23 g, 2.42 mmol) and 5-bromo-pyrogallol **7** (150 mg, 0.732 mmol) were added to a solution of K_2CO_3 (1.00 g, 7.24 mmol) in DMF (7.2 mL). The solution was stirred overnight (12 h) at 70 °C. After cooling, the mixture was poured into aqueous HCl (pH 2, 40 mL) and extracted with CH_2Cl_2 (×3). The organic layer was washed with brine (×2), dried over magnesium sulfate, and the solvent was evaporated in vacuo. The crude product was purified by silica gel column chromatography (CH_2Cl_2/acetone = 3:1–1:1) to yield **9** (360 mg, 0.30 mmol, 41.1%) as a viscous yellow oil. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ = 1.27 (d, *J* = 6 Hz, 3H, Me), 1.31 (d, *J* = 6 Hz, 6H, Me), 3.38 (s, 9H), 3.51–3.88 (m, 78H), 4.24–4.35 (m, 1H), 4.43–4.52 (m, 2H), 6.75 ppm (s, 2H, Ar); MS (MALDI-TOF): *m*/*z* (%) calcd for $C_{54}H_{101}BrNaO_{24}$: 1235.58 $[M+Na]^+$; found: 1235.88, 1237.88.

1,2-Bis[5-(3,4,5-tri{2-[2-(2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}ethoxy)ethoxy]ethoxy} phenyl)2-methylthiophene-3-yl]perfluorocyclopentene (3a): An *n*-butyllithium (*n*BuLi) solution in hexane (1.6 M, 0.123 mL, 0.197 mmol) was slowly added to a solution of 1,2-bis(5-iodo-2-methyl-3-thienyl)perfluorocyclopentene (**10**) (60 mg, 0.096 mmol) in dry THF (1 mL) at −78 °C under an argon atmosphere. The solution was stirred for 1 h at −78 °C. After addition of boric acid tri-*n*-butyl ester (0.077 mL, 0.288 mmol), the reaction mixture was further stirred for 1 h. The reaction was stopped by the addition of water. 5-bromo-1,2,3-tris-{2-[2-(2-{2-[2-(2-methoxy-ethoy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy}-benzene (**8**) (200 mg, 0.192 mmol), $Pd(PPh_3)_4$ (20 mg, 0.0192 mmol) and aqueous $NaCO_3$ (20 w%, 1 mL) were added to the solution. The solution was then refluxed overnight (16 h). The reaction product was extracted with ethyl acetate (×3), and the organic layer was washed with brine (×2), dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by silica gel column chromatography (ethyl acetate, acetone, and methanol) to yield **3a** (20 mg, 0.0087 mmol, 9.1%) as a blue oil. ^{1}H NMR ($CDCl_3$, TMS, 200 MHz): δ = 2.27 (s, 6H, Me), 3.38 (s, 18H, Me), 3.52–4.13 (m, 144H), 6.74 (s, 2H, Ar), 6.98 ppm (s, 2H); MS (MALDI-TOF): *m*/*z* (%) calcd for $C_{105}H_{174}F_6NaO_{42}S_2$: 2308.07 $[M+Na]^+$; found: 2308.23.

(*R,R,R,R,R,R*)-1,2-Bis[5-(3,4,5-tris-{2-[2-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy-2-propoxy}-phenyl)2-methylthiophene-3-yl]perfluorocyclopentene (4a): An *n*BuLi solution in hexane (1.6 M, 4.26 mL, 6.82 mmol) was slowly added to a solution of 1,2-bis(5-iodo-2-methyl-3-thienyl)perfluorocyclopentene (**10**) (2.0 g, 3.22 mmol) in dry THF (60 mL) at −78 °C under an argon atmosphere, and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.80 mL, 9.64 mmol) was added. The reaction mixture was stirred for 14 h. The reaction was stopped by the addition of water. The reaction product was extracted with CH_2Cl_2 (×3), and the organic layer was washed with brine (×2), dried over $MgSO_4$, filtrated, and evaporated to yield the boric acid derivative as a brown amorphous solid (1.2 g, 1.93 mmol, 60.0%). The crude product (70 mg, 0.113 mmol) was dissolved in THF (3 mL), and then (*R,R,R*)-5-bromo-1,2,3-tris-{2-[2-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy-2-propoxy}-benzene (**9**) (300 mg, 0.247 mmol), $Pd(PPh_3)_4$ (6 mg, 0.0057 mmol), and aqueous $NaCO_3$ (20 w%, 3 mL) were added to the solution. The solution was refluxed for 8 h. The reaction product was extracted with ethyl acetate (×3), and the organic layer was washed with brine (×2), dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by silica gel column chromatography (ethyl acetate, acetone, and methanol) to yield **4a** (60 mg, 0.0228 mmol, 20.2%) as a blue oil. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ = 1.30 (d, *J* = 6 Hz, 6H, Me), 1.34 (d, *J* = 6 Hz, 12H, Me), 1.91 (s, 6H, Me), 3.37 (s, 18H, Me), 3.44–3.92 (m, 156H), 4.31–4.42 (m, 2H), 4.52–4.65 (m, 4H), 6.78 (s, 4H, Ar), 7.19 ppm (s, 2H); MS (MALDI-TOF): *m*/*z* (%) calcd for $C_{123}H_{210}F_6NaO_{48}S_2$: 2656.32 $[M+Na]^+$; found: 2658.67.

(*S*)-1-[2-(2-Methoxy-ethoxy)-ethoxy]-propan-2-ol (12): Washed NaH (60% in mineral oil, 600 mg, 25 mmol) was added to a solution of (*S*)-2-(tetrahydropyran-2-yloxy)-propan-1-ol (**11**) (2.0 g, 12.5 mmol) and *p*-toluenesulfonic acid diethylene glycol monomethyl ether (TsODeg) (3.4 g, 12.5 mmol) in dry THF (35 mL). The solution was refluxed for 17 h. After cooling, the reaction was quenched by the addition of water, and the solution was evaporated to remove THF. The reaction product was

extracted with CH_2Cl_2, and the organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The crude product was dissolved in EtOH (40 mL), and then pyridinium-*p*-toluene sulfonate (PPTS, 310 mg, 1.25 mmol) was added. The solution was stirred for 6 h at room temperature. The solution was evaporated to remove EtOH, and the product was extracted with CH_2Cl_2, and the organic layer was washed with brine, dried over $MgSO_4$, and evaporated to yield **12** (1.8 g, 10.1 mmol, 80.8%) as a yellow oil. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): $\delta = 1.13$ (d, $J = 6$ Hz, 3H, Me), 2.82 (br s, 1H, OH), 3.23–3.31 (m, 1H), 3.39 (s, 3H, Me), 3.47–3.76 (m, 9H), 3.92–4.03 ppm (m, 1H); MS (FAB HRMS): *m/z* (%) calcd for $C_8H_{19}O_4$: 179.1283 $[M+H]^+$; found: 179.1285.

(*S*)-toluene-4-sulfonic acid 2-[2-(2-methoxy-ethoxy)-ethoxy]-1-methyl-ethyl ester (**13**): A solution of (*S*)-1-[2-(2-methoxy-ethoxy)-ethoxy]-propan-2-ol (**12**) (1.10 g, 6.17 mmol) in THF (1.0 mL) was added to a solution of sodium hydroxide (320 mg, 8.02 mol) in water (0.5 mL) at 0°C. Then a solution of *p*-tosyl chloride (1.24 g, 6.48 mmol) in THF (2.0 mL) was slowly dropped into the solution. After warming to room temperature, the mixture was stirred for 17 h. The reaction mixture was acidified by 6 M H_2SO_4. The reaction product was extracted with CH_2Cl_2, and the organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 1:1) to yield **13** (1.22 g, 3.68 mmol, 59.6%) as a colorless oil. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): $\delta = 1.28$ (d, $J = 7$ Hz, 3H, Me), 3.38 (s, 3H, Me), 3.42–3.65 (m, 10H), 4.65–4.79 (m, 1H), 7.33 (d, $J = 8$ Hz, 2H, Ar), 7.81 ppm (d, $J = 8$ Hz, 2H, Ar); MS (FAB HRMS): *m/z* (%) calcd for $C_{15}H_{25}O_6S$: 333.1383 $[M+H]^+$; found: 333.1383.

1-Iodo-4-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-benzene (15): Toluene-4-sulfonic acid 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl ester (TsOTig) (5.0 g, 0.016 mol) and *p*-iodophenol (**14**) (3.96 g, 0.018 mol) were added to a solution of K_2CO_3 (22.1 g, 0.16 mol) in DMF (225 mL). The solution was stirred overnight (20 h) at 70°C. After cooling, the mixture was poured into aqueous HCl (pH 2, 225 mL) and extracted with CH_2Cl_2 (×3), and the organic layer was washed with brine (×2), dried over $MgSO_4$, and the solvent was evaporated in vacuo to yield **15** (5.8 g, 0.0158 mol, 98.8%) as a brown oil. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): $\delta = 3.38$ (s, 3H, Me), 3.52–4.11 (m, 12H)), 6.69 (d, $J = 9$ Hz, 2H, Ar), 7.54 ppm (d, $J = 9$ Hz, 2H, Ar); MS (FAB HRMS): *m/z* (%) calcd for $C_{13}H_{19}IO_4$: 366.0328 $[M]^+$; found: 366.0320.

(*R*)-1-Iodo-4-{2-[2-(2-methoxy-ethoxy)-ethoxy]-1-methyl-ethoxy}-benzene (**16**): (*S*)-toluene-4-sulfonic acid 2-[2-(2-methoxy-ethoxy)-ethoxy]-1-methyl-ethyl ester (**13**) (1.22 g, 3.67 mmol) and *p*-iodophenol **14** (870 mg, 4.04 mmol) were added to a solution of K_2CO_3 (5.07 g, 36.7 mmol) in DMF (60 mL). The solution was stirred overnight (12 h) at 70°C. After cooling, the mixture was poured into aqueous HCl (pH 2, 60 mL) and extracted with CH_2Cl_2 (×3), and the organic layer was washed with brine (×2) and dried over $MgSO_4$. The solvent was evaporated in vacuo to yield **16** (1.43 g, 3.76 mmol, quant.) as a reddish brown oil. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): $\delta = 1.29$ (d, $J = 6$ Hz, 3H, Me), 3.38 (s, 3H, Me), 3.51–3.75 (m, 10H), 4.45–4.58 (m, 1H), 6.71 (d, $J = 9$ Hz, 2H, Ar), 7.51 ppm (d, $J = 8$ Hz, 2H, Ar); MS (FAB HRMS): *m/z* (%) calcd for $C_{14}H_{21}IO_4$: 380.0485 $[M]^+$; found: 380.0487.

3-Bromo-(5-{4-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-phenyl)-2-methyl-thiophene (18): An *n*BuLi solution in hexane (1.6 M, 18.4 mL, 0.029 mmol) was slowly added to a solution of 2,4-dibromo-5-methylthiophene (**17**) (7.17 g, 0.028 mol) in dry THF (200 mL) at −78°C under an argon atmosphere. The solution was stirred for 15 min at −78°C. After addition of boric acid tri-*n*-butyl ester (11.4 mL, 0.043 mmol), the reaction mixture was further stirred for 1 h. The reaction was quenched by the addition of water. 1-Iodo-4-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-benzene (**15**) (5.0 g, 0.0137 mol), $Pd(PPh_3)_4$ (1.0 g, 0.865 mmol), and aqueous $NaCO_3$ (20 w%, 150 mL) were added to the solution. The solution was refluxed overnight (20 h). The reaction product was extracted with ethyl acetate (×3), and the organic layer was washed with brine (×2), dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 1:1) to yield **18** (4.8 g, 0.0116 mol, 84.7%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): $\delta = 2.40$ (s, 3H, Me), 3.38 (s, 3H, Me), 3.53–4.18 (m, 12H), 6.91 (d, $J = 9$ Hz, 2H, Ar), 6.98 (s, 1H), 7.41 ppm (d, $J = 9$ Hz, 2H, Ar); MS (FAB HRMS): *m/z* (%) calcd for $C_{18}H_{23}BrO_4S$: 414.0500 $[M]^+$; found: 414.0509.

1,2-Bis-[5-(4-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-phenyl)-2-methyl-thiophene-3-yl]-perfluorocyclopentene (5a): An *n*BuLi solution in hexane (1.6 M, 3.15 mL, 5.04 mmol) was slowly added to a solution of compound **18** (2.0 g, 4.8 mmol) in dry THF (20 mL) at −78°C under an argon atmosphere. The solution was stirred for 15 min at −78°C. After addition of a solution of perfluorocyclopentene (1.3 mL, 9.6 mmol) in dry THF (25 mL) at −90°C, the reaction mixture was further stirred for 2 h. The reaction was quenched by the addition of water. The reaction product was extracted with ethyl acetate (×3), and the organic layer was washed with brine (×2), dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by silica gel column chromatography (ethyl acetate/acetone = 1:1) to yield **5a** (1.0 g, 1.2 mmol, 24.5%) as a blue oil. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): $\delta = 1.94$ (s, 6H, Me), 3.38 (s, 6H, Me), 3.53–4.18 (m, 24H), 6.93 (d, $J = 9$ Hz, 4H, Ar), 7.16 (s, 2H), 7.45 ppm (d, $J = 9$ Hz, 4H, Ar); MS (FAB HRMS): *m/z* (%) calcd for $C_{41}H_{46}F_6O_8S_2$: 844.2538 $[M]^+$; found: 844.2540.

(*R*)-3-Bromo-5-[4-(2-{2-[2-methoxy-ethoxy]-ethoxy}-1-methyl-ethoxy)-phenyl]-2-methyl-thiophene (**19**): An *n*BuLi solution in hexane (1.6 M, 4.83 mL, 7.73 mmol) was slowly added to a solution of 2,4-dibromo-5-methylthiophene (**17**) (1.88 g, 7.36 mmol) in dry THF (50 mL) at −78°C under an argon atmosphere. The solution was stirred for 10 min at −78°C. After the addition of boric acid tri-*n*-butyl ester (2.94 mL, 11.0 mmol), the reaction mixture was further stirred for 1.5 h. The reaction was quenched by the addition of water. (*R*)-1-Iodo-4-{2-[2-(2-methoxy-ethoxy)-ethoxy]-1-methyl-ethoxy}-benzene (**16**) (1.4 g, 3.7 mmol), $Pd(PPh_3)_4$ (430 mg, 0.37 mmol), and aqueous Na_2CO_3 (20 w%, 40 mL) were added to the solution. The solution was refluxed overnight (20 h). The reaction product was extracted with ether (×3), and the organic layer was washed with brine (×2), dried over MgSO4, filtered, and evaporated. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 1:1) to yield **19** (1.2 g, 2.79 mmol, 75.8%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): $\delta = 1.32$ (d, $J = 6$ Hz, 3H, Me), 2.42 (s, 3H, Me), 3.38 (s, 3H, Me), 3.51–3.76 (m, 10H), 4.52–4.65 (m, 1H), 6.92 (d, $J = 8$ Hz, 2H, Ar), 6.98 (s, 1H), 7.40 ppm (d, $J = 9$ Hz, 2H, Ar); MS (FAB HRMS): *m/z* (%) calcd for $C_{19}H_{25}BrO_4S$: 428.0657 $[M]^+$; found: 428.0660.

(*R,R*)-1,2-Bis-[5-(4-{2-[2-(2-methoxy-ethoxy)-ethoxy]-1-methyl-ethoxy}-phenyl)-2-methyl-thiophene-3-yl]-perfluorocyclopentene (6a): An *n*BuLi solution in hexane (1.6 M, 1.76 mL, 2.81 mmol) was slowly added to a solution of (*R*)-3-bromo-5-[4-(2-{2-[2-methoxy-ethoxy]-ethoxy}-1-methyl-ethoxy)-phenyl]-2-methyl-thiophene (**19**) (1.15 g, 2.68 mmol) in dry THF (10 mL) at −78°C under an argon atmosphere. The solution was stirred for 5 min at −78°C. After the addition of a solution of perfluorocyclopentene (0.56 mL, 4.02 mmol) in dry THF (15 mL), the reaction mixture was further stirred for 2 h at that temperature. The reaction was quenched by the addition of water. The reaction product was extracted with ether (×3), and the organic layer was washed with brine (×3), dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 1:1) to yield **6a** (500 mg, 0.57 mmol, 42.(%) as a green oil. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): $\delta = 1.32$ (d, $J = 6$ Hz, 6H, Me), 1.94 (s, 6H, Me), 3.37 (s, 6H, Me), 3.52–3.79 (m, 20H), 4.53–4.67 (m, 2H), 6.94 (d, $J = 8$ Hz, 4H, Ar), 7.15 (s, 2H), 7.44 ppm (d, $J = 8$ Hz, 4H, Ar); MS (FAB HRMS): *m/z* (%) calcd for $C_{43}H_{50}F_6O_8S_2$: 872.2851 $[M]^+$; found: 872.2853.

3-Bromo-5-(4-methoxymethoxy-phenyl)-2-methyl-thiophene (20): An *n*BuLi solution in hexane (1.6 M, 23.6 mL, 37.7 mmol) was slowly added to a solution of 2,4-dibromo-5-methylthiophene (**17**) (9.2 g, 35.9 mmol) in dry THF (150 mL) at −78°C under an argon atmosphere. The solution was stirred for 5 min at −78°C. After addition of boric acid tri-*n*-butyl ester (14.4 mL, 53.9 mmol), the reaction mixture was further stirred for 1.5 h. The reaction was quenched by the addition of water. 1-Iodo-4-methoxymethoxybenzene (9.5 g, 35.9 mmol), $Pd(PPh_3)_4$ (1.3 g, 1.12 mmol) and aqueous $NaCO_3$ (20 w%, 150 mL) were added to the solution. The solution was refluxed overnight (20 h). The reaction product was extracted with ethyl acetate (×3), and the organic layer was washed with brine (×2), dried over $MgSO_4$, filtrated, and evaporated. The crude product

was purified by recrystallization from hexane to yield **20** (9.9 g, 31.6 mmol, 88.0%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): $\delta = 2.40$ (s, 3H, Me), 3.49 (s, 3H), 5.19 (s, 2H), 6.99 (s, 1H), 7.04 (d, $J = 9$ Hz, 2H, Ar), 7.43 ppm (d, $J = 9$ Hz, 2H, Ar); MS (FAB HRMS): m/z (%) calcd for $C_{13}H_{13}BrO_2S$: 311.9820 $[M]^+$; found: 311.9826.

1,2-Bis[2-methyl-5-(4-methoxymethoxyphenyl)thiophen-3-yl]perfluorocyclopentene (21): An *n*BuLi solution in hexane (1.6 M, 8.8 mL, 14.1 mmol) was slowly added to a solution of 3-bromo-5-(4-methoxymethoxyphenyl)-2-methyl-thiophene (**20**) (4.2 g, 13.4 mmol) in dry THF (40 mL) at −78 °C under an argon atmosphere. The solution was stirred for 5 min at −78 °C. After addition of a solution of perfluorocyclopentene (0.84 mL, 6.03 mmol) in dry THF (2 mL) at −78 °C, the reaction mixture was further stirred for 1 h. The reaction was quenched by the addition of water. The reaction product was extracted with ether (×3), and the organic layer was washed with brine (×2), dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by silica gel column chromatography (hexane/dichloromethane = 1:1) to yield **21** (1.7 g, 2.65 mmol, 39.6%) as a pale blue solid. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): $\delta = 1.94$ (s, 6H, Me), 3.47 (s, 6H), 5.18 (s, 4H), 7.04 (d, $J = 9$ Hz, 4H, Ar), 7.17 (s, 2H), 7.45 ppm (d, $J = 9$ Hz, 4H, Ar); MS (FAB HRMS): m/z (%) calcd for $C_{31}H_{26}F_6O_4S_2$: 640.1177 $[M]^+$; found: 640.1178.

(*R*,*R*)-1,2-Bis-[5-(4-{2-[2-(2-{2-[2-(2-{2-methoxy-ethoxy}-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-1-methyl-ethoxy}-phenyl)-2-methyl-thiophene-3-yl]-perfluorocyclopentene (2a): Concentrated aqueous HCl (35%, 0.4 mL) was added to a solution of 1,2-bis-[5-(4-methoxymethoxy phenyl)-2-methyl thiophen-3-yl]perfluorocyclopentene (21) (100 mg, 0.156 mmol) in THF (2 mL) . The solution was stirred for 5 h at room temperature under an argon atmosphere. The reaction mixture was extracted with CH_2Cl_2, and the combined organic layer was washed with aq. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtrated, and evaporated. The resulting mixture was used for the next step without further purification. The obtained blue amorphous solid was dissolved in dry THF (3 mL). Triphenylphosphine (PPh_3) (360 mg, 1.37 mmol) and diethyl azodicarboxylate (DEAD) (240 mg, 1.37 mmol) were added and the solution was stirred for 4 days at room temperature under an argon atmosphere. The reaction mixture was extracted with CH_2Cl_2, and the combined organic layer was washed with brine. The organic layer was dried over $MgSO_4$, filtrated, and evaporated. The crude mixture was purified by silica gel column chromatography (ethyl acetate) and GPC to yield **2a** (30 mg, 0.025 mmol, 16%) as a blue oil. The spectroscopic data was identical with the reported data.[5]

Photochemical Measurement

Absorption spectra were measured on a Hitachi U-3500 spectrophotometer. CD and ORD spectra were recorded on a JASCO J-720S spectrophotometer. Photoirradiation was carried out using a USHIO 500 W super high-pressure mercury lamp or a USHIO 500 W xenon lamp. Mercury lines of 313 nm and 578 nm were isolated by passing the light through a combination of band-pass filter (UV-D33S) or sharp-cut filter (Y-48) and monochromator (Ritsu MC-20 L). Closed-ring isomers were separated by reversed phase HPLC (Kanto Chemical co., Mightysil RP-18(H), $CH_3CN/MeOH/H_2O = 9:1:10$, flow = 1.5 mL min^{-1} for compounds **3**, **4**; $CH_3CN/MeOH/H_2O = 9:1:2$, flow = 2.0 mL min^{-1} for compounds **5**, **6**.

DLS Measurement

Particle size distribution was measured on a Nicomp 380ZLS particle sizer equipped with a 785 nm red laser as light source, using a fixed angle (90°). The samples were filtrated by MILLIPORE Millex membrane filter (0.20 μm) before measurement. The samples were kept at 30 °C during measurement.

Molecular Modeling

Molecular modeling was performed using Macromodel 9.1 (OPLS forcefield). Conformational sampling was carried out by the Monte Carlo Multiple Minimum method. Initially sampled 10000 conformations were grouped into 3981 independent conformers. The most stable 200 conformers were minimized to convergence. The most stable 100 conformers were displayed.

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