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The photochromic and self-assembling properties of diarylethenes having chiral amphiphilic chains at the reactive carbon atoms†

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A photochromic diarylethene derivative having chiral polyethylene glycol side chains at the reactive carbon atoms was synthesized. The diarylethene showed a photochromic reaction upon irradiation with UV and visible light in both ethyl acetate and water. The open- and the closed-ring isomers showed a non-exciton-coupled-type of CD spectrum, and the compound underwent a diastereoselective cyclization reaction.

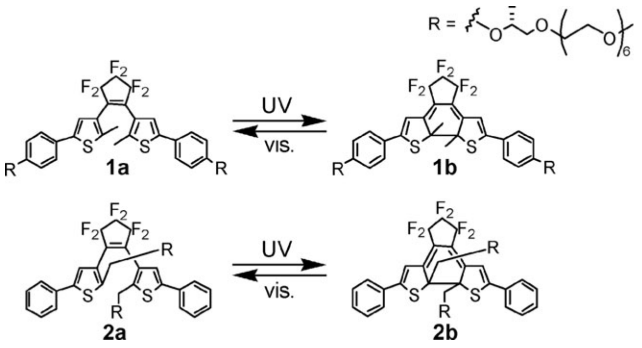
Photochromic diarylethene derivatives are promising candidates for future optoelectronic devices.[1] Among them, compounds that switch optical rotation are nominees for non-destructive readout.[2] Photochemical conrotatory cyclization produces two enantiomeric closed-ring isomers (*R*,*R* and *S*,*S*), in which the chirality originates from the asymmetric carbon atoms. By controlling the molecular conformation of the open-ring isomer, a stereoselective cyclization is possible. The *P*-helix conformer of the open-ring isomer produces an (*R*,*R*) isomer and the *M*-helix conformer produces an (*S*,*S*) isomer. Such stereoselective cyclizations in various chiral environments have been accomplished in solution and in the single-crystalline phase.[3]

It is known that compounds that have both a hydrophobic core and hydrophilic side chains self-assemble into nanostructures in polar solvents.[4] We have reported that amphiphilic diarylethene derivative **1** self-assembles by hydrophobic interactions (Scheme 1).[5] It is of interest that the methyl group introduced near to the hydrophobic core as a chiral source induces a chiral supramolecular environment to exhibit an exciton-coupled-type of CD spectrum only for closed-ring isomer **1b**.

Herein, we report the synthesis and photochromic properties of a diarylethene derivative having chiral polyethylene glycol (PEG) chains at the reactive carbon atoms.

Because previously synthesized compound **1a** has chiral PEG chains at the periphery of the diarylethene molecule, conformational control was not effective and no diastereoselective cyclization was observed.[5] On the contrary, PEG chains at the periphery seem to be advantageous for intermolecular chiral recognition between the stacked molecules. In order to see the effect of the substitution position of the amphiphilic chain, diarylethene derivative **2a**, which has chiral PEG chains at the reactive carbon atoms, was designed (Scheme 1). The chiral PEG chains at the reactive carbon atoms seem to be advantageous for stereoselective cyclization due to the controlled conformation of the open-ring isomer but disadvantageous for intermolecular chiral recognition.

The synthesis of diarylethene **2a** was performed according to the general synthetic method for diarylethenes (see ESI†). The expression of chirality in compound **1** in our previous report was found to be opposite to that described, and the chirality has been corrected in Scheme 1.[6] It was found that the S_N2 reaction of tosylated PEG and phenol derivatives converts the stereocenter from (*S*)- to (*R*)-chirality. The structure of diarylethene **2a** was confirmed by NMR and mass spectroscopy. The absorption and CD spectral changes of diarylethenes **2** are summarized in Fig. 1. Diarylethenes **2** showed excellent photochromic performance in both ethyl acetate and water, in the same manner as previously reported for compound **1**. In contrast with **1**, both the open-ring **2a** and closed-ring **2b** isomers showed a CD signal, both in ethyl acetate and water. The strong exciton-coupled-type signal was not observed in all cases. The exciton-coupled-type CD signal, which was observed for the closed-ring isomer **1b** in water, significantly decreased. This result indicates that in the cases of both the open- and closed-ring isomers of **2**, the origin of the CD signal is not mainly the transition dipole moments in a spatially-twisted position, but the chiral structure of the molecule itself.



Scheme 1 Photochromism of diarylethene derivatives having hexaethylene glycol side chains with a chiral methyl group.

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† Electronic supplementary information (ESI) available: Full experimental procedure, the results of HPLC analyses and the calculated CD spectrum. See DOI: 10.1039/b822880a

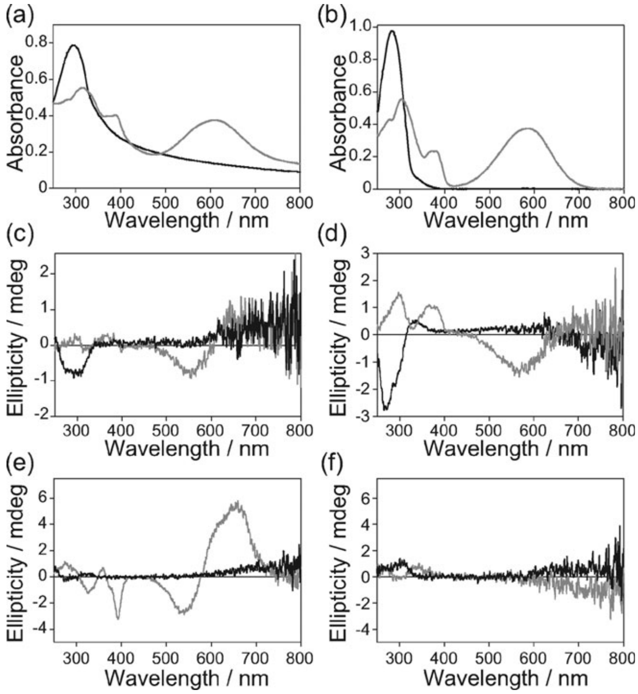

Fig. 1 Absorption spectral changes of compound **2** (a) in water and (b) in ethyl acetate. Corresponding CD spectral changes (c) in water and (d) in ethyl acetate. CD spectra of compound **1** (e) in water and (f) in ethyl acetate. The black line denotes the open-ring isomer and the gray line denotes the sample in the photostationary state (PSS) under irradiation with 313 nm light.

Closed form **1b** has PEG chains at both ends of the molecule. Therefore, its shape is rather rod-like, and it may form a stable aggregate. On the contrary, **2b** has two long PEG chains perpendicular to the molecular plane. Therefore, it is expected that molecular aggregates of **2b** will not be stable because of its central fat core in the PEG thread. This may be the origin of the weak aggregation and weak exciton-coupled CD signal seen for **2b**.

Since open-ring isomer **2a** took the conformation biased to *P*- or *M*-helical conformation, diastereoselective cyclization was expected. The diastereomer excess (de) of the cyclization reaction in ethyl acetate was measured by HPLC analysis using a chiral column (DAICEL, CHIRALPAC AD-H). The observed de was 3.6%. Although the de is not significant, it is large enough to give a CD signal. The CD spectra of the separated diastereomers of closed-ring isomer **2b** were measured (Fig. 2), the diastereomers showing mirror-image spectra. Upon irradiation with visible light, both the (*R*,*R*) and (*S*,*S*) isomers exhibited a decrease in their CD signal to give a CD spectrum identical to that of the open-ring isomer shown in Fig. 1(d). Progressive irradiation with UV light gave a CD spectrum identical to that of **2b**, as shown in Fig. 1(d). By calculating the CD intensity with 3.6% de, the observed spectrum was clearly reproduced (see ESI†).

Although the CD spectrum of open-ring isomer **2a** was not of the exciton-coupled-type, the CD signal of the visible band of closed-ring isomer **2b** was slightly influenced by the exciton-coupled signal. However, the strength of the exciton-coupled signal was very small compared to previously reported **1b**.

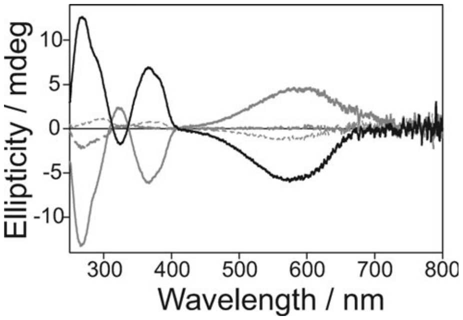

Fig. 2 CD spectra of the two separated diastereomers in ethyl acetate. Black and gray solid lines denote the two diastereomers of closed-ring isomer **2b**. The gray dashed line is corresponding open-ring isomer **2a**, measured after irradiating the diastereomer of the gray solid line with visible light. The gray dotted line is the sample in the photostationary state measured after progressive irradiation with 313 nm light.

An aqueous solution of open-ring isomer **2a** was turbid at room temperature (25 °C), but the clouding cleared at 15 °C. This phenomenon is typical lower critical solution temperature (LCST) behavior, which is often observed in PEG derivatives.[7]

The measurement of de in aqueous solution gave 3.0% and 2.6% for the sample irradiated at 25 °C and 15 °C, respectively. The de did not vary by changing the temperature below or above the LCST. The observed de value was similar to the value observed in ethyl acetate solution, suggesting that the conformation of the open-ring isomer is similar in both solvents. This result also indicates that the LSCT transition does not influence the diastereoselection significantly.

It is known that the (*R*,*R*) isomer of the closed-ring isomer of 1,2-bis(2-methyl-5-phenyl-3-thienyl)hexafluorocyclopentene shows a negative CD signal.[8] The origin of the observed CD signal should be excess (*R*,*R*) isomer, meaning that the *P*-helix conformer should be energetically favorable. The detailed mechanism is under consideration.

In conclusion, in contrast to the **1a**/**1b** system, in the **2a**/**2b** system, the exciton-coupled-type CD signal was not strong, indicating that self-assembly into a chiral nanostructure was not significant. On the contrary, both the open-ring **2a** and closed-ring **2b** isomers show a non-exciton-coupled-type CD signal, and a slight diastereoselective cyclization was observed. The effect of the chiral amphiphilic chain varies, depending on the substitution position in the photochromic diarylethene molecule.

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Experimental

Synthesis of 2a

To a solution of (*S*)-3-bromo-2-(2-{2-[2-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy}-1-methylethoxymethyl)-5-phenyl-thiophene[9] (90 mg, 0.149 mmol) in dry THF (0.5 mL) was slowly added an *n*-butyllithium–hexane solution (1.6 M, 0.098 mL, 0.156 mmol) at −78 °C. After the addition of a solution of perfluorocyclopentene (10 μL, 0.074 mmol) in dry THF (1 mL), the reaction mixture was further stirred for 1 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 (×2), dried over $MgSO_4$, filtered and evaporated. The crude product was purified by silica gel column chromatography (ethyl acetate : acetone = 1 : 0 > 1 : 1) to yield **2a** (22 mg, 0.018 mmol, 24%) as a blue oil.

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ 1.04 (d, J = 6 Hz, 6 H), 3.39 (s, 6 H), 3.35–3.69 (m, 54 H), 4.02–4.15 (m, 4 H), 7.31–7.37 (m, 4 H), 7.38–7.45 (m, 4 H) and 7.57–7.63 (m, 4 H). MALDI-TOF MS (*m*/*z*): calc. for $C_{59}H_{82}F_6O_{16}S_2Na$ 1247.48 $[M + Na]^+$, found 1247.29 $[M + Na]^+$.

Corresponding closed-ring isomer UV-vis: λ_{max} = 585 nm.

Photochemical measurements

Absorption spectra were measured on a Hitachi U-3500 spectrophotometer. CD 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 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-20L). Each diastereomer was separated by chiral HPLC (DAICEL, CHIRALPAC AD-H [4.6 × 250 mm, 5 μm], hexane : 2-propanol : ethanol = 10 : 65 : 25, flow rate = 0.25 mL min^{-1}) for compounds **2**.

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9 For the full synthetic procedure, see the ESI†.