

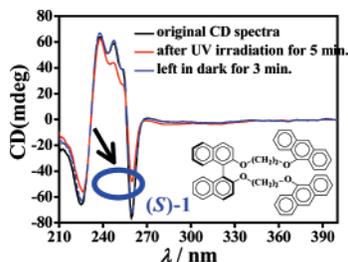
Chiral Molecular Switches Based on Binaphthalene Molecules with Anthracene Moieties: CD Signal Due to Interchromophoric Exciton Coupling and Modulation of the CD Spectrum

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By coupling the features of binaphthalene and anthracene, new binaphthalenes with two anthracene moieties were designed and synthesized, aiming at developing chiral molecular switches. A strong CD signal with negative sign due to the interchromophoric exciton coupling was observed for (*S*)-**1** with $-(\text{CH}_2)_2$ as the linker. This new CD signal became weak and the sign reversed by changing the linker to $-(\text{CH}_2)_3$ in (*S*)-**2** and $-(\text{CH}_2)_6$ in (*S*)-**3**. For (*S*)-**4** with $-(\text{CH}_2)_{11}$ as the linker, no such CD signal was detected. Photodimerization of two anthracene moieties in these binaphthalene molecules can occur. The results show that the CD spectra of (*S*)-**1**, (*S*)-**2**, (*S*)-**3**, and (*R*)-**1** can be reversibly modulated by alternating UV light irradiation and heating. Therefore, chiral molecular switches based on new binaphthalenes with two anthracene moieties are achieved.

Introduction

Manipulation and transcription of molecular chirality have been the subject of increasing attention in recent years. Two

types of chiral molecular switches have been described: one related to the modulation of intrinsic chirality of molecular systems represented by sterically overcrowded chiral alkenes, and the other based on the magnitude change of chirality.¹ Many interesting examples of induced molecular chirality have been reported.² Moreover, chirality control at the supramolecular level also receives significant attention.³ For instance, the photo-

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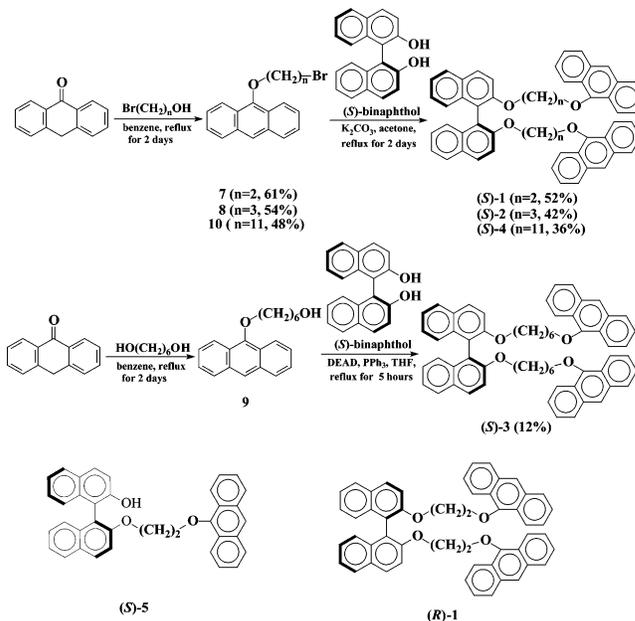
switching of the chirality of the gel phases based on a chiral gelator derived from a dithienylethene derivative has been reported recently.⁴

Binaphthalene molecules are axially chiral species showing strong circular dichroism (CD) signals which are dependent on the dihedral angles of binaphthalene rings and can serve as the detectable output signals of the chiral switches.⁵ Several examples of chiral molecular switches using binaphthalene molecules as building blocks or skeletons with redox or photochromic units have been demonstrated.⁶ We have recently reported chiral molecular switches based on binaphthalene molecules with spiropyran and tetrathiafulvalene units.⁷

The strong CD signals of chiral binaphthalene result from the exciton coupling of two nonplanar naphthalene units.⁸ If a homo-analogue of naphthalene, such as anthracene, is linked to the binaphthalene framework, the exciton interactions between naphthalene and anthracene moieties may occur and new CD signals due to the interchromophoric exciton coupling may be produced. One of the unique features of anthracene is that two properly oriented anthracene units can be transformed into the corresponding dimer under UV light irradiation and the dimer can be dissociated into two anthracene units under visible light irradiation or heating.⁹

With the features of binaphthalene and anthracene in mind, we design new chiral binaphthalene molecules with anthracene moieties (Scheme 1), aiming at developing chiral molecular switches. The design rationale is interpreted as follows: (1) The reversible transformation between the two anthracene units and the photodimer may change the dihedral angle between the two naphthalene rings, thus variation of the CD signals due to the

SCHEME 1. The Chemical Structures of Compounds (S)-1, (S)-2, (S)-3, (S)-4, (S)-5, and (R)-1 and the Synthetic Scheme



binaphthalene framework may be observed. (2) As mentioned above, CD signals due to the interchromophoric exciton coupling may be observed for the binaphthalenes with anthracene units. Transformation of the anthracene units into the photodimers would induce the variation of these CD signals. Therefore, chiral molecular switches based on the binaphthalenes with anthracene units can be constructed. Most of the reported chiral molecular switches are based on the structural changes of functional groups, which are linked to the binaphthalene framework, due to either photoisomerizations^{6a,c,e,7a} or redox reactions.^{6d,7b} This new kind of chiral molecular switch is designed on the basis of the photochemical reactions of two anthracene units in (S)-1, (S)-2, (S)-3, and (R)-1 (Scheme 1).

In this paper, we will report (1) the synthesis and characterization of binaphthalenes with two anthracene units (S)-1, (S)-2, (S)-3, (S)-4, and (R)-1 (Scheme 1) and (2) the observation of a new CD signal due to the interchromophoric exciton coupling and the CD spectrum modulation under light irradiation and heating for (S)-1, (S)-2, (S)-3, and (R)-1. Besides, the influence of the linkers that connect the anthracene and naphthalene moieties is also addressed by performing comparative studies on compounds (S)-2, (S)-3 and (S)-4.

Results and Discussion

Synthesis and the Crystal Structure of (S)-1. Compound (S)-1 was synthesized by the reaction between (S)-binaphthol and 9-(2-bromoethoxy)anthracene (compound 7) as shown in Scheme 1. Compounds (S)-2, (S)-3, (S)-4 [from (S)-binaphthol], and (R)-1 [from (R)-binaphthol] were prepared similarly. For the sake of comparison, compound (S)-5 containing one anthracene moiety was also synthesized from (S)-binaphthol. The chemical structures of these compounds were confirmed by NMR, MS spectroscopy, and elemental analysis. According

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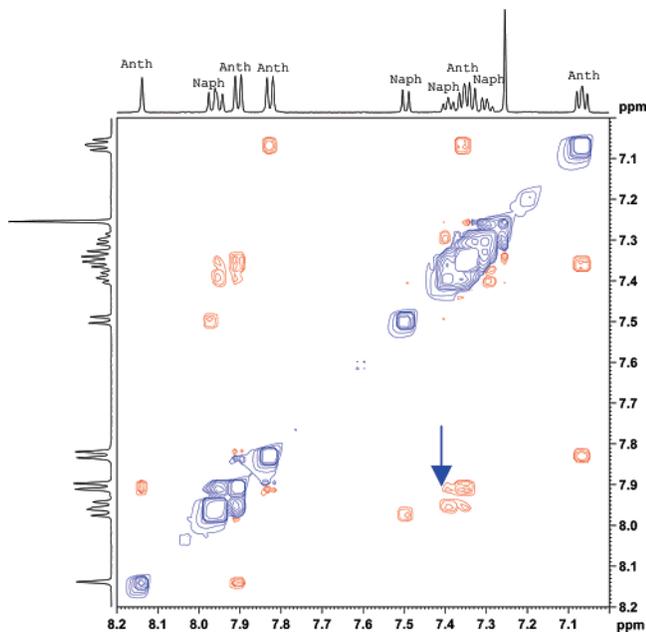


FIGURE 1. The $^1\text{H},^1\text{H}$ NOESY spectrum of (*S*)-**1** recorded in CDCl_3 .

to previous studies,¹⁰ compounds **1**, **2**, **3**, **4**, and **5**, which were synthesized from (*S*)-binaphthol, should retain *S*-configuration while the compound (*R*)-**1** prepared from (*R*)-binaphthol should retain *R*-configuration since all the reactions and purifications were carried out at relatively low temperature. This was also confirmed by the fact that the CD signals attributed to the binaphthalene moieties in compounds (*S*)-**1**, (*S*)-**2**, (*S*)-**3**, (*S*)-**4**, and (*S*)-**5** (see Figure 4, as well as Figure S6 in the Supporting Information) were similar to those of (*S*)-binaphthol while those of the binaphthalene moiety in (*R*)-**1** (see Figure 4) were similar to those of (*R*)-binaphthol.

Figure 1 shows the $^1\text{H},^1\text{H}$ NOESY spectrum of (*S*)-**1**. A cross-signal was detected between the signals at 7.93–7.94 ppm due to the protons of anthracene units and those at 7.39–7.43 ppm due to the protons of naphthalene rings, indicating that the anthracene and naphthalene rings within (*S*)-**1** are closely arranged in space. The chemical shifts of H_1 and H_9 of the anthracene units for (*S*)-**1** are upfield shifted (owing to shielding effects) as indicated in Table S6 (Supporting Information) where the comparison of the chemical shifts of H_1 and H_9 of the anthracene units for (*S*)-**1**, (*S*)-**2**, (*S*)-**3**, (*S*)-**4**, **8**, **9**, and **10** is shown. This result also supports the close arrangement of anthracene and naphthalene units in (*S*)-**1**.

Crystals of (*S*)-**1** suitable for single-crystal structural analysis were successfully formed, and its crystal structure was determined. Figure 2 shows the molecular structure of (*S*)-**1**, and all bond lengths and angles are in the normal range.¹¹ As for the two naphthalene rings with a dihedral angle of 97.0° , the two anthracene rings are not coplanar forming a dihedral angle of 28.4° . Furthermore, each anthracene ring is not coplanar with respect to each of the naphthalene rings; for example, the anthracene ring C39–C40–C41–C42–C43–C44–C45–C46–C47–C48–C49–C50–C51–C52 exhibits a dihedral angle of 86.4° with

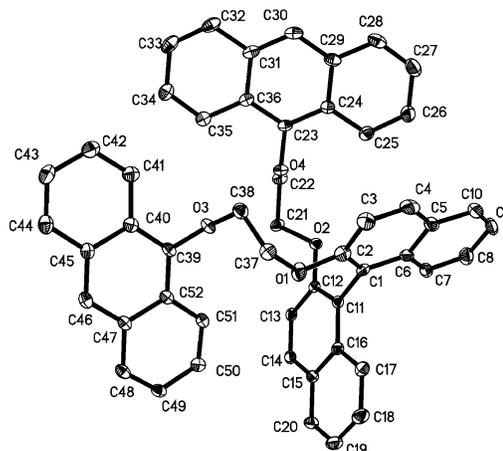


FIGURE 2. The ORTEP diagram for (*S*)-**1**; the lattice CHCl_3 molecules and all hydrogen atoms are omitted for clarity; thermal ellipsoids are 30% probability.

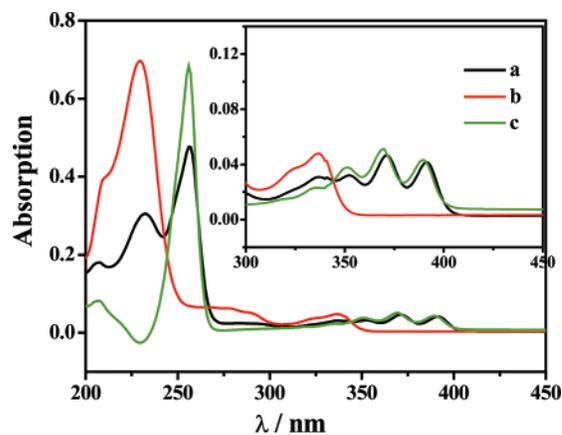


FIGURE 3. The absorption spectra of compound (*S*)-**1** (a, 2.5×10^{-6} M), (*S*)-binaphthol (b, 5.0×10^{-6} M), and compound **7** (c, 5.0×10^{-6} M) in THF.

the naphthalene ring C11–C12–C13–C14–C15–C16–C17–C18–C19–C20. Such intramolecular “moiety arrangement” would facilitate the exciton coupling among the anthracene and naphthalene moieties to generate new CD signals as will be discussed below.

Absorption and CD Spectral Studies of (*S*)-1**.** Figure 3 shows the absorption spectrum of (*S*)-**1** and those of reference compounds (*S*)-binaphthol and 9-(2-bromoethoxy)anthracene (**7**) for comparison. Characteristic absorption bands of the binaphthalene (220–250 and 280–350 nm) and anthracene moieties (250–280 and 350–400 nm) were observed for compound (*S*)-**1**. But, compared with those of (*S*)-binaphthol and 9-(2-bromoethoxy)anthracene, all absorption bands of (*S*)-**1** were slightly red-shifted by about 3.0 nm, indicating the weak interaction between anthracene and naphthalene units in (*S*)-**1**.

(10) It was reported that the optically active 2,2'-substituted binaphthalene enantiomers were very stable and could not be racemized at high temperatures ($>150^\circ\text{C}$); see: (a) Hall, D. M.; Turner, E. E. *J. Chem. Soc.* **1955**, 1242–1251. (b) Pu, L. *Chem. Rev.* **1998**, *98*, 2405–2494. (c) Putala, M. *Enantiomer* **1999**, *4*, 243–262.

(11) Crystal data: $\text{C}_{52}\text{H}_{38}\text{O}_4 \cdot \text{CHCl}_3$, $M = 846.19$, orthorhombic, $P2_12_12_1$, $a = 8.3367(4) \text{ \AA}$, $b = 15.6339(6) \text{ \AA}$, $c = 32.1238(13) \text{ \AA}$, $V = 4186.9(3) \text{ \AA}^3$, $Z = 4$, $D_c = 1.342 \text{ g cm}^{-3}$; $F(000) = 1760$, $\mu = 0.267 \text{ mm}^{-1}$. A total of 31256 reflections of which 9965 are unique ($R_{\text{int}} = 0.0421$) were collected to a θ limit of 1.27 – 27.88° on a Rigaku RAXIS RAPID IP instrument at $113(2) \text{ K}$. The structure was solved by direct methods and refined by a least-squares matrix method. The final cycle of full-matrix least-squares refinement was based on 9965 observed reflections [$I > 2\sigma(I)$] and 544 variable parameters and converged to $R_1 = 0.0498$, $wR_2 = 0.1137$ (R indices for all data: $R_1 = 0.0616$, $wR_2 = 0.1215$), $\text{Goof} = 1.067$. The crystallographic data have been deposited with CCDC (CCDC No. 629120).

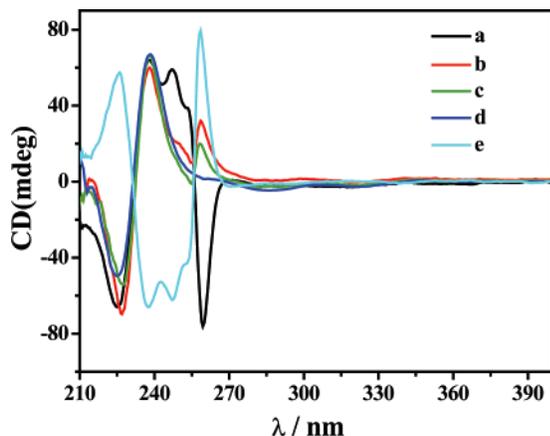


FIGURE 4. The CD spectra of compounds (*S*)-1 (a, 1.0×10^{-5} M), (*S*)-2 (b, 1.0×10^{-5} M), (*S*)-3 (c, 1.0×10^{-5} M), (*S*)-4 (d, 1.0×10^{-5} M), and (*R*)-1 (e, 1.0×10^{-5} M) in THF.

This is in agreement with the $^1\text{H}, ^1\text{H}$ NOESY spectrum of (*S*)-1 (Figure 1), which indicates that the anthracene and naphthalene rings in (*S*)-1 are closely arranged as discussed above.

Figure 4 shows the CD spectrum of compound (*S*)-1 (curve a). According to the previous studies,⁵ the intense exciton couplet ($\lambda_{\text{max}} = 239$ nm, $\lambda_{\text{min}} = 225$ nm split from $\lambda_{\theta=0} = 232$ nm) should be due to the coupling of $^1\text{B}_b$ transitions of the two naphthalene moieties. Interestingly, an additional intense exciton couplet between 242 to 270 nm ($\lambda_{\theta=0} = 256$ nm) was detected. On the basis of the absorption spectrum of (*S*)-1, this new CD signal with negative sign could be ascribed to the absorption band at 256 nm at which the anthracene moieties of (*S*)-1 strongly absorb. To understand the origin of this new CD signal of (*S*)-1, a quantum chemical calculation of its CD spectrum was carried out. The theoretical analysis indicates that this new CD signal is mainly owing to the exciton coupling between anthracene and naphthalene moieties.¹² Note that new CD signals have been described for chiral binaphthalenes to which chromophores are connected in a conjugated manner.^{6,7} However, to the best of our knowledge, CD signals due to the interchromophoric exciton coupling were seldom found to occur for chiral binaphthalenes to which chromophores are linked through saturated σ bonds.

The CD spectrum of compound (*R*)-1, which is the enantiomer of (*S*)-1, was also studied (curve e of Figure 4, and also Figure S13 in the Supporting Information). A strong new CD signal with positive sign was observed. That is to say, the sign of this new CD signal is determined by the configuration of the binaphthalene unit. This result supports the assumption that this new CD signal results from the exciton coupling between anthracene and naphthalene moieties.

Photomodulation of the CD Spectrum of (*S*)-1. It is established that the two anthracene units can be transformed to the corresponding dimer by UV light irradiation and the dimer can be disassociated by either visible light irradiation or heating.⁹ Thus, the two anthracene moieties of (*S*)-1 should be able to be reversibly converted to the dimer by UV/visible light irradiation or heating. As a result, the CD signal of (*S*)-1 due to the interchromophoric exciton coupling would be modulated

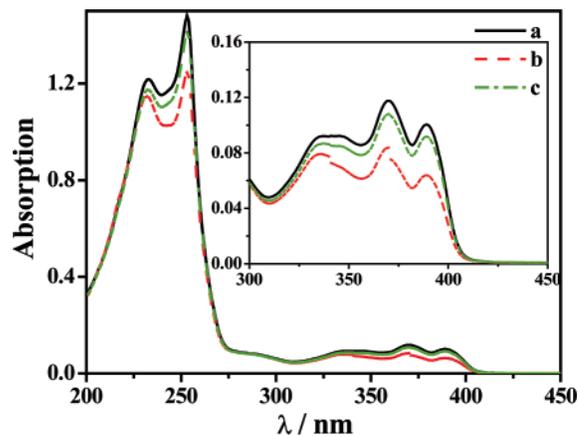


FIGURE 5. The absorption spectra of (*S*)-1 (1.0×10^{-5} M in THF): (a) before irradiation; (b) after irradiation with UV light (365 nm) after 5 min; and (c) left in the dark for 3 min.

in association with the reversible transformation between the two anthracene units and the dimer; moreover, the CD signals of the binaphthalene moiety of (*S*)-1 also may be tuned by altering the dihedral angle between two naphthalene rings. As shown in Figure 5 where the variation of the absorption spectrum of (*S*)-1 under UV light irradiation was displayed, the intensity for the absorption bands in the range of 220–260 and 310–400 nm decreased gradually after exposure to UV light irradiation. According to previous results,⁹ this absorption spectral change indicated the photodimerization of the two anthracene units in (*S*)-1. In comparison, no absorption spectral variation was detected for compound (*S*)-5 with only one anthracene unit (see Figure S6 in the Supporting Information), confirming that two anthracene units are needed for such photodimerization and photodimerization occurs only between two anthracene units. Alternatively, the fluorescence spectra of (*S*)-1 were measured before and after UV light irradiation. The fluorescence intensity of the solution of (*S*)-1 was reduced by 30% after UV light (365 nm) for 5.0 min (see Figure S7 in the Supporting Information). This fluorescence variation also indicates the photodimerization of the two anthracene units in (*S*)-1. Interestingly, the initial absorption spectrum of (*S*)-1 was almost recovered after the solution of (*S*)-1 that had been illuminated by UV light was left in the dark for 3 min. This indicates that the generated anthracene-dimer of (*S*)-1 was not stable because of the steric strain.

Correspondingly, variation of the CD spectrum of (*S*)-1 was observed after UV light irradiation as shown in Figure 6. After the solution of (*S*)-1 was exposed to UV light (365 nm) for 5 min, the intensity of the CD signal due to the interchromophoric exciton coupling was reduced by 37%. Besides, the CD signals ascribed to the binaphthalene moiety changed slightly. Similarly, the CD spectrum of (*S*)-1 can be restored after the solution was left in the dark for 3 min. The inset of Figure 6 shows the reversible variation of the new CD signal intensity. Therefore, the CD spectrum of (*S*)-1 can be reversibly modulated and this can be employed to build a chiral molecular switch.

CD Spectral Photomodulation of (*S*)-2, (*S*)-3, and (*S*)-4. By increasing the length of the linker, the CD signal due to the interchromophoric exciton coupling would become weak since the exciton couplet amplitude is inversely proportional to the square of the interchromophoric distance. Therefore, it is interesting to investigate how long the linker between anthracene and naphthalene units provides distinct new CD signals, making

(12) To understand the origin of the new CD signal of (*S*)-1, a quantum chemical approach based on time-dependent density functional theory (TDDFT) at the B3LYP/6-31g* level was carried out to calculate the CD spectrum. The calculation details are provided in the Supporting Information.

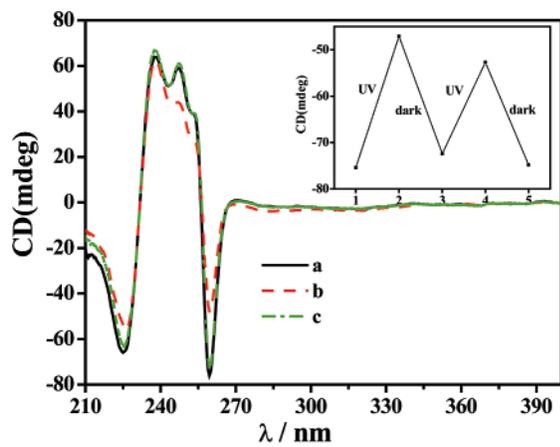


FIGURE 6. The CD spectra of (*S*)-1 (1.0×10^{-5} M in THF): (a) before irradiation; (b) after irradiation with UV light (365 nm) after 5 min; and (c) left in the dark for 3 min. The inset shows the reversible variation of the new CD signal intensity at 259 nm.

the existence of the chiral molecular switch possible. For this purpose, (*S*)-2, (*S*)-3, and (*S*)-4 (Scheme 1), the analogues of (*S*)-1, were synthesized. The linkers of (*S*)-2, (*S*)-3, and (*S*)-4 are $-(\text{CH}_2)_3$, $-(\text{CH}_2)_6$, and $-(\text{CH}_2)_{11}$, respectively, and their CD spectra are shown in Figure 4. For (*S*)-2 and (*S*)-3, besides the CD signals of the chiral binaphthalene moieties, new CD signals around 259 nm with positive sign were also detected. The intensities of these new CD signals for (*S*)-2 and (*S*)-3 are weaker than that of compound (*S*)-1. Moreover, the intensity of the new CD signal of (*S*)-3 is much weaker. For (*S*)-4, however, no such new CD signal was observed. These results clearly showed that the linker length exerted a significant influence on the CD signal due to the interchromophoric exciton coupling for the chiral binaphthalene with anthracene moieties. By prolonging the linker length, the sign reversed and the intensity of this new CD signal became gradually weaker. This means that a long linker would weaken the exciton coupling between anthracene and naphthalene moieties.

Similar theoretical calculation of the CD spectrum of (*S*)-2 was performed based on the optimized molecular geometry,¹³ in which the torsion angle between two naphthalene rings and that between two anthracene units was estimated to be 85.6° and 23.3° , respectively (see Figure S1 in the Supporting Information). The calculation results indicate that the new weak CD signal of (*S*)-2 is mainly due to the exciton coupling of two anthracene moieties, rather than between anthracene and naphthalene moieties. The new weak CD signal with positive sign for (*S*)-3 may be also attributed to the exciton coupling of two anthracene moieties. This calculation result may explain the fact that the sign of the new CD signals for (*S*)-2 and (*S*)-3 is just opposite that for (*S*)-1, for which the CD signal is attributed to the exciton coupling between anthracene and naphthalene moieties.¹²

Like (*S*)-1, the photodimerization of two anthracene moieties can also occur for (*S*)-2, (*S*)-3, and (*S*)-4 as shown in Figures S9–S11 (Supporting Information).¹⁴ The absorption spectra of (*S*)-2, (*S*)-3, and (*S*)-4 which had been treated by UV light irradiation remained almost unchanged after the solutions were

(13) Similar theoretical calculation was performed with (*S*)-2 based on the optimized molecular geometry, and the calculated CD spectrum is displayed in Figure S2 in the Supporting Information. The calculation details are provided in the Supporting Information as well.

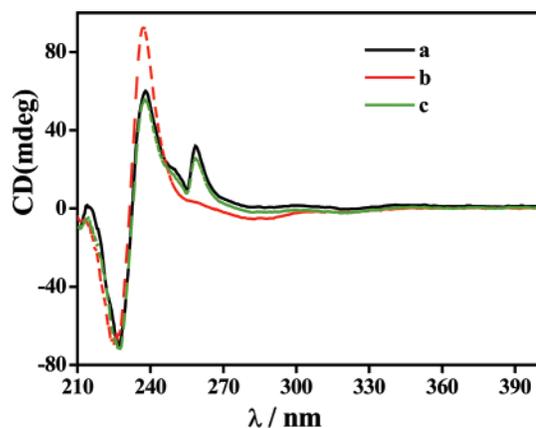


FIGURE 7. The CD spectra of (*S*)-2 (1.0×10^{-5} M in THF): (a) before irradiation; (b) after UV irradiation (365 nm) for 2 min; and (c) after heating for 0.5 min at 50°C .

left in the dark for 5 min. This result implied that the photodimers of (*S*)-2, (*S*)-3, and (*S*)-4 were more stable than that of (*S*)-1. But, the absorption spectra could be recovered by heating the solution at 50°C for 0.5 min as indicated in Figures S9–S11 (Supporting Information). The fluorescence intensities of the solutions of (*S*)-2, (*S*)-3, and (*S*)-4 were reduced by ca. 80% after UV light irradiation for 5.0 min (see Figures S7–S8 in the Supporting Information). The fluorescence reduction should be due to the photodimerization of two anthracene units in (*S*)-2, (*S*)-3, and (*S*)-4. In addition, the ^1H NMR spectra of the samples of (*S*)-2, (*S*)-3, and (*S*)-4 after UV light irradiation for 5.0 min were measured, and the singlet signals around 4.40 ppm due to the bridgehead protons of the photodimers were detected.¹⁴ The ^1H NMR spectral results clearly confirmed the photodimerization of anthracene units in (*S*)-2, (*S*)-3, and (*S*)-4. Their transformation yields are similar (ca. 80%) based on the ^1H NMR spectral data, which is consistent with their absorption and fluorescence spectral variations.

As anticipated, the CD spectra of (*S*)-2 and (*S*)-3 varied after UV light irradiation (see Figures 7 and 8). The CD signals due to the interchromophoric exciton coupling disappeared and the CD signals of chiral binaphthalene moieties of (*S*)-2 and (*S*)-3 changed slightly due to the variation of the dihedral angle between two naphthalene rings after photodimerization of two anthracene moieties. Similarly, the CD spectra of (*S*)-2 and (*S*)-3 can be restored by heating the solutions at 50°C for 0.5 min. But, rather slight CD spectral changes were detected for (*S*)-4 after photodimerization (see Figure S12 in the Supporting Information), which may be understandable by considering the long spacer $[-(\text{CH}_2)_{11}-]$ in (*S*)-4.

Conclusions

In summary, new chiral binaphthalene (*S*)-1 with two anthracene moieties was synthesized and characterized. A new strong CD signal with negative sign was observed for (*S*)-1 while a new strong positive CD signal was detected for compound (*R*)-1, the enantiomer of compound (*S*)-1. Quantum

(14) Only one ^1H NMR singlet signal was observed for the bridgehead protons for (*S*)-2 (4.40 ppm) and (*S*)-3 (4.41 ppm), while two ^1H NMR singlet signals (4.42 and 4.49 ppm) were observed for those of (*S*)-4. These results imply that only *h-h* dimer was formed for (*S*)-2 and (*S*)-3 because of the steric strain. For (*S*)-4, however, both *h-h* and *h-t* dimers were produced. This may be understandable by considering the long spacer in (*S*)-4.

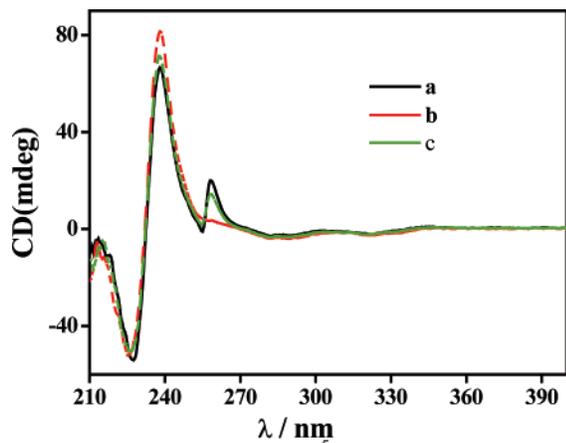


FIGURE 8. The CD spectra of (*S*)-**3** (1.0×10^{-5} M in THF): (a) before irradiation; (b) after UV irradiation (365 nm) for 2 min; and (c) after heating for 0.5 min at 50 °C.

mechanical calculations indicated that this new CD signal could be attributed to the exciton coupling between the naphthalene and the anthracene moieties. The analogues of (*S*)-**1**, (*S*)-**2**, (*S*)-**3**, and (*S*)-**4** were prepared. It was found that the CD signal due to the interchromophoric exciton coupling became weak and the sign reversed by changing the linker to $-(\text{CH}_2)_3-$ in (*S*)-**2** and $-(\text{CH}_2)_6$ in (*S*)-**3**. For (*S*)-**4** with $-(\text{CH}_2)_{11}-$ as the linker, no such new CD signal was detected. It should be noted that the CD signal due to the interchromophoric exciton coupling was seldom reported for binaphthalene derivatives to which chromophores are linked through σ -bonds. Photodimerization of two anthracene moieties can occur to (*S*)-**1**, (*S*)-**2**, (*S*)-**3**, (*S*)-**4**, and (*R*)-**1**, and the CD spectra of (*S*)-**1**, (*S*)-**2**, (*S*)-**3**, and (*R*)-**1** can be reversibly modulated by alternating UV light irradiation and heating. Therefore, chiral molecular switches based on these new binaphthalenes are achieved.

Experimental Section

Synthesis of (*S*)-1**.** Anhydrous K_2CO_3 (0.19 g, 1.40 mmol) was added to a solution of (*S*)-binaphthol (0.11 g, 0.40 mmol) and 9-(2-bromoethoxy)anthracene (compound **7**) (0.36 g, 1.20 mmol) in anhydrous acetone (30 mL) under nitrogen. The reaction mixture was heated to reflux for 48 h. After the solution was cooled to room temperature, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel with CH_2Cl_2 /petroleum ether (60–90 °C) (1:3, v/v) as eluant, and then recrystallized from cyclohexane. The colorless needles were filtered off and washed twice with cyclohexane and dried in vacuum to give 0.15 g of (*S*)-**1** in 52% yield. Mp 138–139 °C; $[\alpha]_D^{20} +137.2$ (*c* 3.00, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 8.14 (2H, s), 7.94 (4H, t, $J = 8.8$ Hz), 7.91 (4H, d, $J = 8.6$ Hz), 7.84 (4H, d, $J = 8.7$ Hz), 7.50 (2H, d, $J = 9.0$ Hz), 7.42–7.30 (10H, m), 7.07 (4H, t, $J = 7.5$ Hz), 4.62 (2H, m), 4.49 (2H, m), 4.23–4.15 (4H, m); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm) δ 155.0, 150.8, 134.8, 132.7, 130.1, 130.0, 128.6, 128.5, 126.9, 126.2, 125.8, 125.6, 125.0, 124.2, 122.8, 122.6, 121.0, 116.0, 74.4, 69.3; HRMS calcd for $\text{C}_{52}\text{H}_{38}\text{O}_4$ 726.2774, found 726.2764.

Synthesis of (*S*)-2**.** Compound (*S*)-**2** was prepared from (*S*)-binaphthol and compound **8** as described for the synthesis of compound (*S*)-**1**. After column chromatography on silica gel with CH_2Cl_2 /petroleum ether (60–90 °C) (2:5, v/v) as eluant, the product was recrystallized from cyclohexane and ethyl acetate. The pale-yellow microcrystals were filtered off and washed twice with cyclohexane and dried in vacuum to give (*S*)-**2** in 42% yield. Mp 188–189 °C; $[\alpha]_D^{20} +3.2$ (*c* 2.50, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz,

CDCl_3 , ppm) δ 8.21 (2H, s), 7.99 (4H, d, $J = 8.5$ Hz), 7.93 (4H, d, $J = 8.7$ Hz), 7.47–7.42 (6H, m), 7.37 (2H, m), 7.31 (4H, t, $J = 7.0$ Hz), 7.12 (2H, d, $J = 9.0$ Hz), 7.03 (2H, m), 6.95 (4H, m), 4.13–4.05 (4H, m), 3.47 (4H, t, $J = 6.9$ Hz), 2.04 (4H, m); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 153.9, 151.1, 133.8, 132.3, 129.2, 129.0, 128.2, 127.5, 125.9, 125.3, 125.0, 124.8, 124.5, 123.3, 122.3, 121.7, 120.7, 115.6, 72.5, 66.7, 30.4; HRMS calcd for $\text{C}_{54}\text{H}_{42}\text{O}_4$ 754.3083, found 754.3097. Anal. Calcd for $\text{C}_{54}\text{H}_{42}\text{O}_4$: C, 85.91; H, 5.61. Found: C, 85.51; H, 5.59.

Synthesis of (*S*)-3**.** To a stirred solution of (*S*)-binaphthol (0.14 g, 0.50 mmol) and triphenylphosphine (0.52 g, 2.0 mmol) in 30 mL of anhydrous THF at ambient temperature under nitrogen atmosphere was added dropwise a mixture of compound **9** (0.59 g, 2.0 mmol) and azodicarboxylic acid diethyl ester (DEAD, 40% in toluene, 0.92 mL, 2.0 mmol) in 20 mL of anhydrous THF. The reaction mixture was then slowly heated to reflux. After being kept under reflux for 5 h, the mixture was cooled to room temperature. Then the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel with CH_2Cl_2 /petroleum ether (60–90 °C) (2:5, v/v) as eluant; (*S*)-**3** was obtained as a yellow solid (0.05 g) in 12% yield. Mp 131–132 °C; $[\alpha]_D^{20} -40.0$ (*c* 2.00, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 8.23–8.21 (6H, m), 8.01–7.99 (4H, m), 7.72 (2H, d, $J = 9.3$ Hz), 7.68 (2H, d, $J = 7.2$ Hz), 7.47–7.45 (8H, m), 7.23–7.17 (8H, m), 3.97 (4H, t, $J = 6.7$ Hz), 3.93–3.81 (4H, m), 1.69 (4H, m), 1.43 (4H, m), 1.29–0.85 (8H, m); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm): δ 154.4, 151.6, 134.1, 132.5, 129.2, 129.0, 128.4, 127.7, 127.2, 126.0, 125.5, 125.0, 124.8, 123.4, 122.5, 121.9, 120.8, 115.8, 76.1, 69.6, 30.4, 29.4, 25.61, 25.57; MS (MALDI-TOF) 838.8 (M^+); HRMS calcd for $\text{C}_{60}\text{H}_{54}\text{O}_4$ 838.4022, found 838.4002.

Synthesis of (*S*)-4**.** Compound (*S*)-**4** was prepared from (*S*)-binaphthol and compound **10** as described for the synthesis of compound (*S*)-**1**. After column chromatography on silica gel with CH_2Cl_2 /petroleum ether (60–90 °C) (2:5, v/v) as eluant, (*S*)-**4** was obtained as yellow oil in 36%. $[\alpha]_D^{20} -25.5$ (*c* 3.10, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 8.31 (4H, d, $J = 8.9$ Hz), 8.22 (2H, s), 8.00 (4H, d, $J = 8.9$ Hz), 7.93 (2H, d, $J = 9.0$ Hz), 7.85 (2H, d, $J = 8.1$ Hz), 7.47 (8H, m), 7.41 (2H, d, $J = 9.0$ Hz), 7.31 (2H, t, $J = 7.4$ Hz), 7.21 (2H, t, $J = 8.4$ Hz), 7.16 (2H, t, $J = 8.4$ Hz), 4.21 (4H, t, $J = 6.6$ Hz), 4.00–3.88 (4H, m), 2.06 (4H, m), 1.66 (4H, m), 1.41 (8H, m), 1.31 (4H, m), 1.17 (4H, m), 1.03 (8H, m), 0.92 (4H, m); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm) δ 154.9, 151.9, 134.6, 132.9, 129.7, 129.4, 128.8, 128.2, 126.4, 125.9, 125.8, 125.4, 125.2, 123.8, 122.9, 122.3, 121.2, 116.3, 76.6, 70.2, 31.1, 30.0, 29.9, 29.5, 26.7, 26.0; HRMS calcd for $\text{C}_{70}\text{H}_{74}\text{O}_4$ 978.5587, found 978.5590.

Synthesis of (*R*)-1**.** Compound (*R*)-**1** was prepared from (*R*)-binaphthol and compound **7** as described for the synthesis of compound (*S*)-**1**. $[\alpha]_D^{20} -132.4$ (*c* 2.10, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 8.15 (2H, s), 7.96 (4H, t, $J = 9.5$ Hz), 7.91 (4H, d, $J = 8.7$ Hz), 7.82 (4H, d, $J = 8.9$ Hz), 7.50 (2H, d, $J = 9.1$ Hz), 7.38–7.32 (10H, m), 7.06 (4H, t, $J = 7.6$ Hz), 4.62 (2H, m), 4.47 (2H, m), 4.23–4.16 (4H, m); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm) δ 155.0, 150.9, 134.8, 132.7, 130.1, 130.0, 128.6, 128.5, 126.9, 126.2, 125.8, 125.6, 125.0, 124.2, 122.8, 122.6, 121.1, 116.1, 74.4, 69.4; HRMS calcd for $\text{C}_{52}\text{H}_{38}\text{O}_4$ 726.2774, found 726.2767.

Synthesis of (*S*)-5**.** Anhydrous K_2CO_3 (0.10 g, 0.70 mmol) was added to a solution of (*S*)-binaphthol (0.12 g, 0.40 mmol) and compound **7** (0.12 g, 0.40 mmol) in anhydrous acetone (30 mL) under nitrogen. The reaction mixture was kept under reflux for 8 h. After the mixture was cooled to the room temperature, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel with CH_2Cl_2 /petroleum ether (60–90 °C) (2:3, v/v) as eluant, and then recrystallized from cyclohexane and ethyl acetate. The pale-yellow microcrystals were filtered off and washed twice with cyclohexane and dried in vacuum to give (*S*)-**5** in 59% yield. Mp 184–186 °C; $[\alpha]_D^{20} +45.6$ (*c* 2.10, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 8.17 (1H, s), 8.10 (1H, d, $J = 9.0$ Hz), 7.94 (6H, m), 7.88 (1H, d, $J = 8.1$ Hz), 7.67 (1H,

d, $J = 12.2$ Hz), 7.39 (4H, m), 7.33–7.28 (4H, m), 7.25–7.23 (2H, m), 7.18 (1H, d, $J = 8.3$ Hz), 5.10 (1H, s), 4.60–4.46 (2H, m), 4.23 (2H, t, $J = 4$ Hz); ^{13}C NMR (75 MHz, CDCl_3 , ppm) δ 155.9, 151.9, 150.6, 134.6, 134.4, 132.7, 131.5, 130.3, 129.7, 128.70, 128.66, 128.6, 127.8, 126.9, 125.8, 125.7, 125.6, 125.4, 124.9, 127.7, 122.9, 122.6, 118.3, 117.2, 116.0, 115.7, 74.0, 69.6; HRMS calcd for $\text{C}_{36}\text{H}_{26}\text{O}_3$ 506.1877, found 506.1876. Anal. calcd for $\text{C}_{36}\text{H}_{26}\text{O}_3$: C, 85.40; H, 5.20. Found: C, 85.13, 5.04.

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Supporting Information Available: Synthesis of compounds **8**, **9**, and **10**, theoretical calculations with compounds (*S*)-**1** and (*S*)-**2**, calculated CD spectrum and absorption spectra after UV light irradiation of (*S*)-**5**, variation of fluorescence, absorption, and CD spectra of compounds (*S*)-**2**, (*S*)-**3**, (*S*)-**4**, and (*R*)-**1** after UV light irradiation and heating, ^1H NMR spectra and ^{13}C NMR of compounds (*S*)-**1**, (*S*)-**2**, (*S*)-**3**, (*S*)-**4**, (*S*)-**5**, and (*R*)-**1** and compounds **8**, **9**, and **10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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