

An Hg²⁺-Gated Chiral Molecular Switch Created by Using Binaphthalene Molecules with Two Anthracene Units and Two 1,3-Dithiole-2-thione (1,3-Dithiole-2-one) Units

Cheng Wang,^[a, b] Deqing Zhang,^{*[a]} Guanxin Zhang,^[a] Junfeng Xiang,^[a] and Daoben Zhu^{*[a]}

Abstract: By integrating the features of anthracene, 1,3-dithiole-2-thione, and binaphthalene units, (*S*)-**1** and its analogue (*S*)-**2**, which contains two 1,3-dithiole-2-one units instead of 1,3-dithiole-2-thione, were studied for creating a new molecular regulation system and building a gated chiral molecular switch. The results show that the photo-

dimerization is controlled by the remote functional-group transformation of C=S into C=O, thus providing an elegant example of molecular regu-

lation. The photodimerization of two anthracene units induces circular dichroism (CD) spectral variation. Overall, the CD spectrum can be remotely modulated by Hg²⁺ in (*S*)-**1**, which leads to an Hg²⁺-gated chiral molecular switch.

Keywords: anthracene • binaphthalene • circular dichroism • dimerization • molecular switches

Introduction

In biological systems the “activity” of one reaction site can be regulated by the response of a remote reaction site to external chemical or physical signals. A number of artificial systems mimicking these regulation phenomena in biological systems have been designed and investigated.^[1] For instance, Mirkin et al. have very recently described allosterically regulated supramolecular catalysis of acyl transfer reactions.^[2] These molecular regulation systems are not only interesting for mimicking biological functions, but they are also appealing for the establishment of new molecular switches, in particular, gated molecular switches^[3] and logic gates.^[4] Herein, we describe a new synthetic system exhibiting a remote regu-

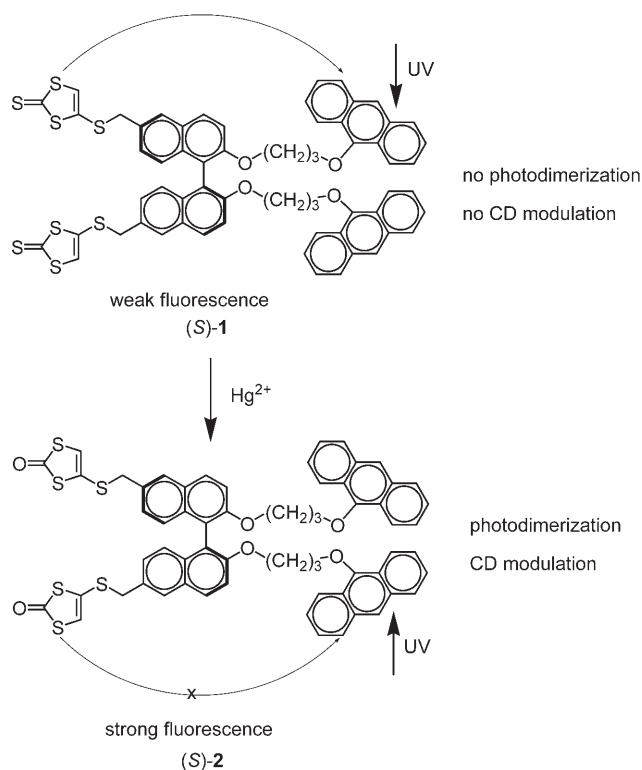
lation phenomenon in which the intramolecular photodimerization of two anthracene units is controlled by the transformation of 1,3-dithiole-2-thione into 1,3-dithiole-2-one in the presence of Hg²⁺.

We have designed a new binaphthalene molecule (*S*)-**1** (Scheme 1) featuring two anthracene units and two 1,3-dithiole-2-thione units to create a new molecular regulation system and build a gated chiral molecular switch. Photodimerization of the two anthracene units can occur upon UV light irradiation if their excited states are not quenched by photoinduced energy-/electron-transfer processes, and the photodimer can be dissociated upon further visible-light irradiation or heating.^[5,6] According to our previous study,^[7] the excited state of anthracene can be quenched by 1,3-dithiole-2-thione, but not by 1,3-dithiole-2-one. When two anthracene units are connected to binaphthalene with a short linker, a new circular dichroism (CD) signal due to the interchromophoric exciton coupling was observed. Furthermore, the corresponding CD spectrum can be reversibly modulated by alternating UV light irradiation and heating, as described by us very recently.^[8a] As the design rationale in Scheme 1 illustrates, the photodimerization of the two anthracene units within (*S*)-**1** cannot occur efficiently, due to the quenching effect of 1,3-dithiole-2-thione. However, the excited states of the anthracene units of (*S*)-**2** are not quenched by the 1,3-dithiole-2-one units; accordingly, the photodimerization of the two anthracene units can take

[a] C. Wang, Prof. Dr. D. Zhang, Dr. G. Zhang, Dr. J. Xiang, Prof. D. Zhu
Beijing National Laboratory for Molecular Sciences
Organic Solids Laboratory Institute of Chemistry
Chinese Academy of Sciences, Beijing 100080 (P.R. China)
Fax: (+86)10-6256-2693
E-mail: dqzhang@iccas.ac.cn
zhudb@iccas.ac.cn

[b] C. Wang
Graduate School of Chinese Academy of Sciences
Beijing 100080 (P.R. China)

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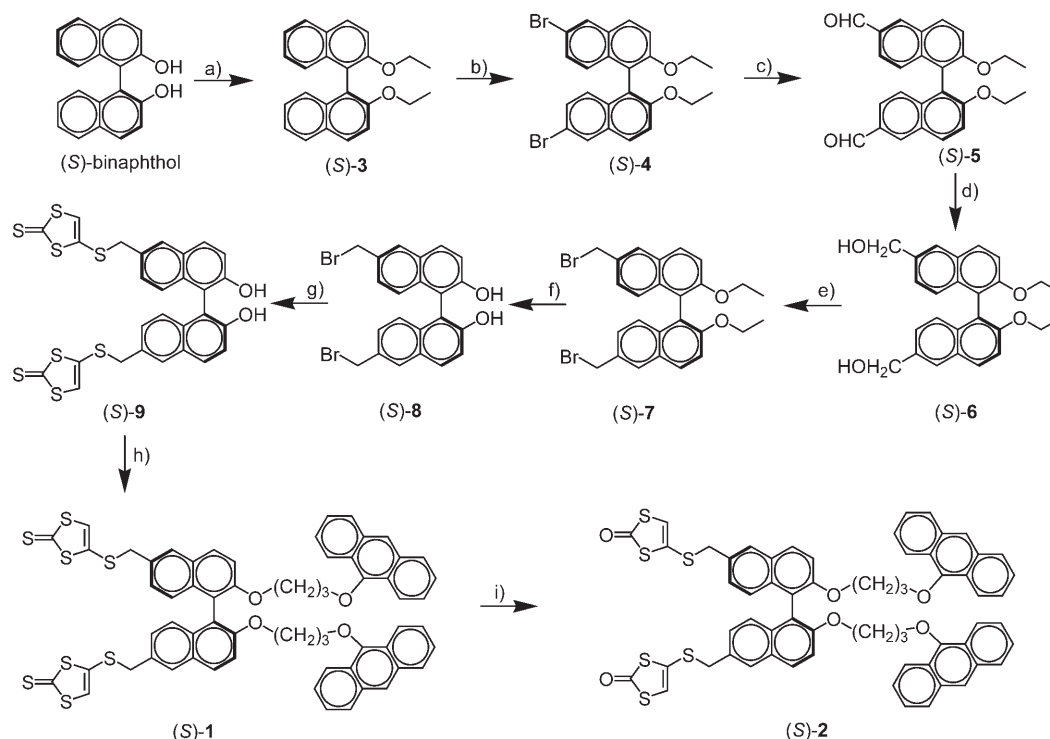


Scheme 1. Chemical structures of (S)-1 and (S)-2 and the schematic representation of the design rationale.

place, which leads to the reversible modulation of the CD spectrum of (S)-2 by UV light irradiation and heating. The 1,3-dithiole-2-thione units of (S)-1 can be transformed into the 1,3-dithiole-2-one units upon reaction with Hg^{2+} ; as a result, the photodimerization takes place easily. Therefore, the photodimerization of two anthracene units within (S)-1 is remotely regulated by the transformation of 1,3-dithiole-2-thione into 1,3-dithiole-2-one in the presence of Hg^{2+} . Accordingly, a new Hg^{2+} -gated chiral molecular switch is constructed with (S)-1. But it should be noted that the transformation of 1,3-dithiole-2-thione units into the 1,3-dithiole-2-one units with Hg^{2+} is irreversible.

Results and Discussion

The synthesis of compounds (S)-1 and (S)-2 was performed following the procedure shown in Scheme 2. After reduction, bromination, and de-ethyloxylation, compound (S)-5 could be converted into compound (S)-8, which reacted with 4-(2-cyanoethylthio)-1,3-dithiole-2-thione in the presence of CsOH to produce (S)-9. Through a Mitsunobu reaction, compound (S)-1 was synthesized. Accordingly, (S)-2 was prepared through a reaction of (S)-1 with $\text{Hg}(\text{AcO})_2$ at room temperature. The chemical structures of (S)-1, (S)-2, (S)-6, (S)-7, and (S)-9 were established by NMR spectroscopy, MS, and HRMS data, and their optical rotation values were measured. All compounds should retain the *S* configuration.^[9]



Scheme 2. The chemical structures and the synthetic approach: a) K_2CO_3 , $\text{C}_2\text{H}_5\text{I}$, acetone, reflux, 95%; b) Br_2 , CH_3CN , 0°C , 96%; c) *n*BuLi, DMF, -78°C , 53%; d) NaBH_4 , THF/ $\text{C}_2\text{H}_5\text{OH}$, 97%; e) PBr_3 , pyridine, CH_2Cl_2 , 0°C , 82%; f) BBR_3 , CH_2Cl_2 ; g) 4-(2-cyanoethylthio)-1,3-dithiole-2-thione, CsOH , THF, 84%; h) DEAD, PPh_3 , THF, 9-(3-hydroxypropoxy)anthracene, 36%; i) $\text{Hg}(\text{AcO})_2$, CH_2Cl_2 , 85%.

Figure 1 shows the fluorescence spectra of (S)-**1** and (S)-**2**.^[10] Clearly, (S)-**2** with the 1,3-dithiole-2-one units exhibits stronger fluorescence than (S)-**1** with the 1,3-dithiole-2-

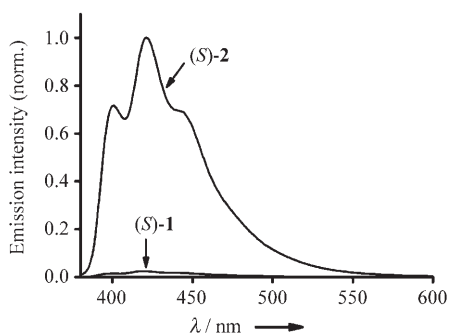
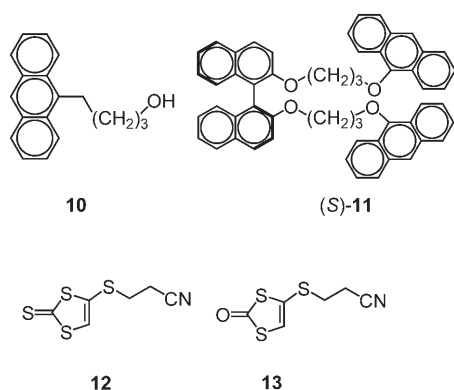


Figure 1. The normalized fluorescence spectra of compounds (S)-**1** (1.0×10^{-5} M) and (S)-**2** (1.0×10^{-5} M) in THF; $\lambda_{\text{ex}} = 370$ nm.

thione units. Moreover, the fluorescence spectral shapes of (S)-**1** and (S)-**2** are almost the same as that of 9-(3-hydroxypropoxy)anthracene (**10**, Scheme 3; see Figure S1 in the



Scheme 3. The chemical structures of reference compound **10** and (S)-**11**, **12**, and **13**.

Supporting Information), which indicates that there is no anthracene excimer emission from (S)-**1** and (S)-**2** under the present conditions. The fluorescence quantum yield of (S)-**1** was lower (0.022) than that of (S)-**2** (0.11).^[10] The fluorescence decays of (S)-**1** and (S)-**2** were recorded (see Figures S2 and S3 in the Supporting Information). The fluorescence decay of (S)-**1** was well fitted to a double-exponential function leading to two lifetimes (0.37 and 3.43 ns),^[11] whereas that of (S)-**2** could be fitted to a single-exponential function and the fluorescence lifetime was estimated to be 3.54 ns (see Table 1). Clearly, the fluorescence lifetime of (S)-**2** is longer than those of (S)-**1**. These results are in agreement with the fact that (S)-**2** shows stronger fluorescence than (S)-**1**.

To understand the fluorescence intensity difference between (S)-**1** and (S)-**2**, the absorption and fluorescence spectra as well as the redox potentials of reference compounds

Table 1. The fluorescence lifetimes of (S)-**1** (1.0×10^{-5} M in dry THF) and (S)-**2** (1.0×10^{-5} M in dry THF) with excitation and observation wavelengths at 370 and 420 nm, respectively.

| | Fluorescence lifetime [ns] |
|------------------------|---|
| compound (S)- 1 | 0.37 ± 0.0129 (83.98%), 3.43 ± 0.0928 (16.02%) ^[a] |
| compound (S)- 2 | 3.54 ± 0.00769 (100%) ^[b] |

[a] $\chi^2 = 1.26$ (χ^2 for (S)-**1** is the difference between the experimental fluorescence decay and the theoretical double-exponential function). [b] $\chi^2 = 1.042$. (χ^2 for (S)-**2** is the difference between the experimental fluorescence decay and the theoretical single-exponential function).

(S)-**11**, **12**, and **13** (Scheme 3) were measured (see the Supporting Information). On the one hand, as displayed in Figure S4 of the Supporting Information, there is an overlap between the fluorescence spectrum of (S)-**11** and the absorption spectrum of **12**, which has a 1,3-dithiole-2-thione unit, whereas there is no corresponding spectral overlap for (S)-**11** and **13**, which has a 1,3-dithiole-2-one unit. Therefore, the photoinduced energy-transfer process should contribute to the fluorescence quenching of (S)-**1**. On the other hand, the ΔG values for the photoinduced electron-transfer (PET) reaction from anthracene to 1,3-dithiole-2-thione units within (S)-**1** and from 1,3-dithiole-2-one to anthracene units within (S)-**2** were calculated to be -0.43 and 0.18 eV, respectively, based on the redox potentials of (S)-**11**, **12**, and **13** (see the Supporting Information). Accordingly, the PET reaction within (S)-**1** may also contribute to the fluorescence quenching. In short, both photoinduced electron- and energy-transfer processes may be responsible for the different fluorescence properties of (S)-**1** and (S)-**2**. This conclusion is consistent with our previous study.^[7]

Figure 2 shows the variation of the absorption spectra of (S)-**2** after UV light ($\lambda = 365$ nm) irradiation for different periods. The intensities of the absorption band of (S)-**2** around 257 nm and those in the range 340 to 400 nm decreased gradually after exposure to UV light irradiation. This absorption spectral change indicates the photodimerization of two anthracene units according to previous studies.^[5,8a] It was reported that the possible photoaddition between anthracene and naphthalene units could not occur under the

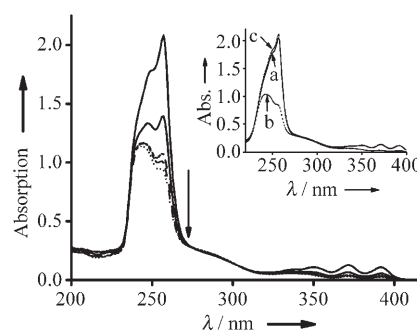


Figure 2. The absorption spectra of (S)-**2** (1.0×10^{-5} M in THF) after UV light (365 nm) irradiation for different periods of time (the arrow indicates increasing UV light irradiation from 0 to 80 s). The inset shows the absorption spectra of (S)-**2** (1.0×10^{-5} M in THF) a) before and b) after UV light irradiation for 90 s, and c) after further heating at 60°C for 40 s.

present conditions.^[8a] By heating, at 60 °C for 40 s, the solution of (*S*)-**2** after exposure to UV light for 90 s, the absorption spectrum of (*S*)-**2** could be recovered as shown in the inset of Figure 2. The absorption spectrum of (*S*)-**1**, however, remained almost unchanged after UV light irradiation, in particular, the absorption bands in the range 340 to 400 nm (see Figure 3), as for (*S*)-**2**. The different behavior of (*S*)-**2**

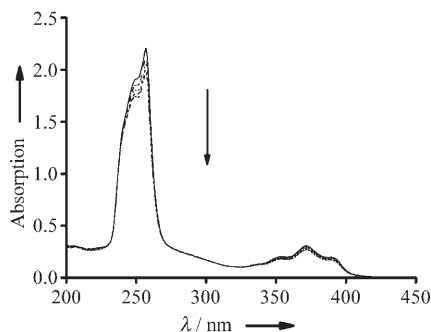


Figure 3. The absorption spectra of (*S*)-**1** (1.0×10^{-5} M in THF) after UV light (365 nm) irradiation for different periods of time (the arrow indicates increasing UV light irradiation from 0 to 80 s).

and (*S*)-**1** in photodimerization of two anthracene units is attributable to the fact that 1,3-dithiole-2-thione units are able to quench the excited states of anthracene units, but the 1,3-dithiole-2-one units are not.^[7]

After UV light irradiation, a new singlet signal in the ¹H NMR spectrum at $\delta = 4.4$ ppm was detected for the solution of (*S*)-**2** in CDCl₃ (1.0×10^{-4} M). This is due to the bridgehead protons of the photodimer according to previous studies (see Figure S5 in the Supporting Information).^[12] Because of the steric strain, it is expected that the head-to-head (h-h) photodimer would be formed for (*S*)-**2**. Preliminary theoretical calculation also indicates that the h-h photodimer is more stable than the head-to-tail (h-t) photodimer. The intensity of the signal at $\delta = 4.4$ ppm was increased by prolonging the irradiation time. However, this new singlet signal disappeared after the solution, which had been exposed to UV light, was left at room temperature for 30 min. (see Figure S5). This result shows that the photodimer can be easily dissociated at room temperature. The absorption and fluorescence spectral studies for (*S*)-**2** are in agreement with ¹H NMR spectroscopy studies (see Figure S7). Therefore, it becomes extremely difficult to isolate the photodimer compound of (*S*)-**2**.

Photodimerization upon UV light irradiation also altered the CD spectrum of (*S*)-**2** (Figure 4A). Aside from the CD signals due to the binaphthalene framework, a new CD signal at around 258 nm was detected, which can be attributed to the interchromophoric exciton coupling, as described by us recently.^[8a] This new CD signal disappeared after the photodimerization of two anthracene units induced by UV light irradiation. Moreover, the CD signals owing to the binaphthalene framework were slightly blueshifted and the intensities around 240 and 250 nm increased after UV light ir-

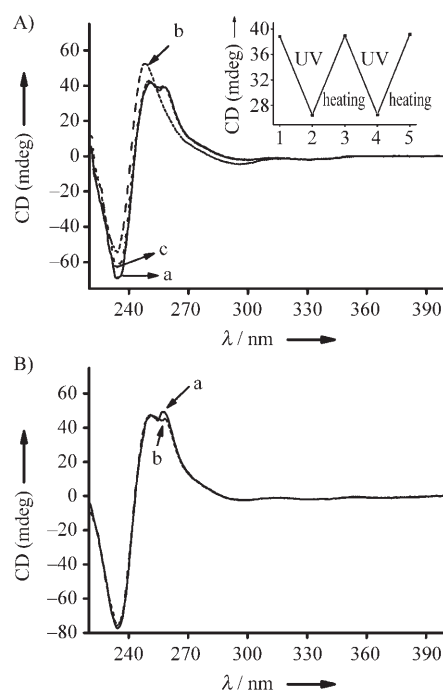


Figure 4. A) The CD spectra of (*S*)-**2** (1.0×10^{-5} M in THF) a) before and b) after UV light irradiation for 90 s, and c) after further heating for 40 s at 60 °C. The inset shows the reversible variation of the new CD signal intensity at 258 nm after alternating UV light irradiation and heating. B) The CD spectra of (*S*)-**1** (1.0×10^{-5} M in THF) a) before and b) after UV light (365 nm) irradiation for 90 s.

radiation. Interestingly, the CD spectrum of (*S*)-**2** can be restored after further heating at 60 °C for 40 s, which is in accordance with the absorption spectral change observed for (*S*)-**2** after UV light irradiation and heating. The inset of Figure 4A shows the reversible variation of the CD signal intensity at 258 nm after alternating UV light irradiation and heating. Therefore, the CD spectrum of (*S*)-**2** can be reversibly modulated by alternating UV light irradiation and heating. In comparison, the variation of the CD spectrum of (*S*)-**1** is negligible (see Figure 4B). This is understandable because the photodimerization of two anthracene units of (*S*)-**1** cannot take place easily due to the quenching effect of the 1,3-dithiole-2-thione units.^[7] Accordingly, (*S*)-**2** can be employed to construct a chiral molecular switch, whereas (*S*)-**1** cannot.

1,3-Dithiole-2-thione can be easily converted to 1,3-dithiole-2-one by reaction with Hg²⁺ at room temperature (but the transformation is irreversible!); thus (*S*)-**1** can be transformed into (*S*)-**2** in the presence of Hg²⁺.^[13] After the addition of Hg²⁺, the fluorescence of the solution of (*S*)-**1** is enhanced significantly (Figure 5).^[13] This is simply due to the transformation of 1,3-dithiole-2-thione units into 1,3-dithiole-2-one units. As a result, the photodimerization of anthracene units within (*S*)-**1** is facilitated in the presence of Hg²⁺, as indicated by its absorption spectral variation after UV light ($\lambda = 365$ nm) irradiation in the presence of six equivalents of Hg²⁺ (Figure 6A). Thus, it may be concluded that the excited states of the anthracene units of (*S*)-**1** are

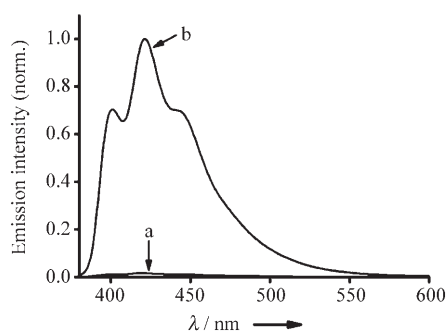


Figure 5. The normalized fluorescence spectra of compound (*S*)-**1** (1.0×10^{-5} M, THF/ CH_2Cl_2) a) before and b) after reaction with 6.0 equiv of $\text{Hg}(\text{AcO})_2$; $\lambda_{\text{ex}} = 370$ nm.

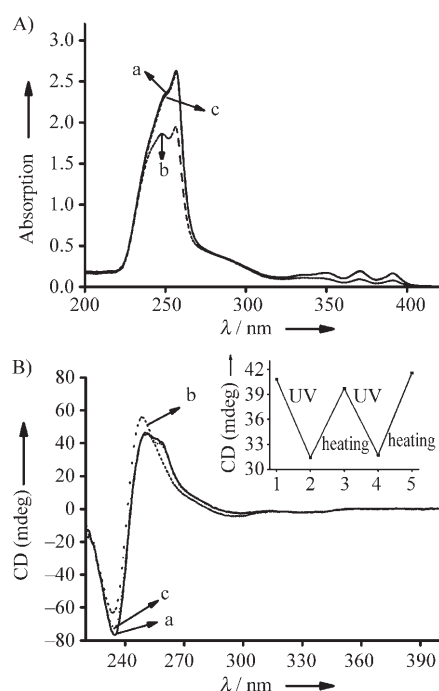


Figure 6. The absorption (A) and CD (B) spectra of (*S*)-**1** (1.0×10^{-5} M in THF) after reaction with 6.0 equiv of $\text{Hg}(\text{AcO})_2$ a) before and b) after UV light irradiation for 90 s, and c) after further heating for 40 s at 60°C ; the inset shows the reversible variation of the new CD signal intensity at 258 nm after alternating UV light irradiation and heating (*S*)-**1** after reaction with Hg^{2+} .

“activated” in the presence of Hg^{2+} , which induces the transformation of the 1,3-dithiole-2-thione units into 1,3-dithiole-2-one units. Reversible CD spectral variation is detected for (*S*)-**1** in the presence of Hg^{2+} , as observed for (*S*)-**2**; the CD spectral changes are detected for both the CD signals due to the binaphthalene unit and the new CD signal due to the interchromophoric exciton coupling (Figure 6B). Similarly, the CD spectral variation for (*S*)-**1** in the presence of Hg^{2+} can be reversibly carried out, as demonstrated in the inset of Figure 6B, in which the reversible variation of the CD signal intensity at 258 nm is displayed after alternating UV light and heating. Therefore, a chiral molecular

switch can be constructed with (*S*)-**1**, but only in the presence of Hg^{2+} . This is an Hg^{2+} -gated chiral molecular switch.

Conclusion

In summary, we report a new binaphthalene molecule (*S*)-**1**, which integrates two anthracene units and two 1,3-dithiole-2-thione units into the binaphthalene framework, and its analogue (*S*)-**2**, which contains two 1,3-dithiole-2-one units instead. Compounds (*S*)-**1** and (*S*)-**2** exhibit big differences in terms of fluorescence, photodimerization, and CD spectral modulation, although they are different only in two atoms. The photodimerization of two anthracene units within (*S*)-**1** can occur efficiently only in the presence of Hg^{2+} ; that is to say, the photodimerization is controlled by the remote functional-group transformation of $\text{C}=\text{S}$ into $\text{C}=\text{O}$, thus providing an elegant example of molecular regulation. On the other hand, reversible CD spectral modulation can be achieved for (*S*)-**1** only in the presence of Hg^{2+} , which leads to an Hg^{2+} -gated chiral molecular switch.

Experimental Section

General: Melting points were measured by using an XT₄-100X apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded by using Bruker 300, 400, and 600 MHz spectrometers. MS spectra were determined by using a BEFLEX III system for TOF-MS and an AEI-MS 50 system for EIMS. HRMS data were determined by using an FTICR-APEX instrument. Optical rotation values were measured at 20°C using the sodium D line ($\lambda = 589$ nm). CD spectra were recorded by using a Jasco J-815 spectrophotometer; the scan rate was 200 nm min^{-1} and all of the spectra were accumulated twice. Absorption spectra were recorded by using a Hitachi (model U-3010) UV/Vis spectrophotometer. Fluorescence spectral measurements were carried out by using a Hitachi (model F-4500) spectrophotometer. Fluorescence decays were recorded by using an Edinburgh Analytical Instruments (FLS920) apparatus; the fluorescence lifetimes were estimated by fitting the fluorescence decays. Differential pulse voltammetry measurements were carried out by using an EGDG PAR 370 system. All the spectral experiments were carried out under ambient conditions in a 1 cm quartz cell with spectroscopic grade THF as the solvent, and for the fluorescence decay measurement spectroscopic grade tetrathiafulvalene (TTF) was carefully dried and distilled before use. For the ultraviolet light irradiation experiment, a 100 W high-pressure mercury lamp ($\lambda = 365$ nm) was used. All solvents were purified and dried following standard procedures unless otherwise stated. Compounds (*S*)-**3**, (*S*)-**4**, and (*S*)-**5** were synthesized according to the literature.^[14] 4-(2-Cyanoethylthio)-1,3-dithiole-2-thione was also synthesized according to the literature.^[15]

Synthesis of (*S*)-(-)-6,6'-bis(hydroxymethyl)-2,2'-diethoxy-1,1'-binaphthyl ((*S*)-6**):** Compound (*S*)-**6** was synthesized according to the literature.^[16] M.p. $101\text{--}102^\circ\text{C}$; $[\alpha]_{\text{D}}^{20} = -20.1$ ($c = 1.99$ in CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3 , 25°C , TMS): $\delta = 7.92$ (d, $J = 9.0$ Hz, 2H), 7.82 (s, 2H), 7.42 (d, $J = 9.0$ Hz, 2H), 7.19 (d, $J = 8.7$ Hz, 2H), 7.11 (d, $J = 8.7$ Hz, 2H), 4.77 (s, 4H), 4.04–4.00 (m, 4H), 1.73 (s, 2H), 1.05 ppm (t, $J = 6.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25°C , TMS): $\delta = 154.2$, 135.9, 135.5, 129.1, 129.0, 125.7, 125.64, 125.61, 120.5, 115.9, 65.1, 64.9, 14.9 ppm; HRMS: m/z calcd for $\text{C}_{26}\text{H}_{26}\text{O}_4$: 402.1831 [M]⁺; found 402.1834.

Synthesis of (*S*)-(+)-6,6'-bis(bromomethyl)-2,2'-diethoxy-1,1'-binaphthyl ((*S*)-7**):** Compound (*S*)-**7** was synthesized according to the literature.^[16] M.p. $163\text{--}165^\circ\text{C}$; $[\alpha]_{\text{D}}^{20} = +41.1$ ($c = 2.05$ in CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3 , 25°C , TMS): $\delta = 7.91$ (d, $J = 9.0$ Hz, 2H), 7.85 (s, 2H), 7.42 (d, $J =$

9.0 Hz, 2H), 7.22 (d, $J=8.7$ Hz, 2H), 7.08 (d, $J=8.8$ Hz, 2H), 4.64 (s, 4H), 4.05 (q, $J=7.0$ Hz, 4H), 1.07 ppm (t, $J=7.0$ Hz, 6H); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): $\delta=154.0, 132.9, 131.5, 128.4, 127.8, 127.1, 126.2, 125.3, 119.2, 114.9, 64.0, 33.6, 14.0$ ppm; HRMS: m/z calcd for C₂₆H₂₄O₂Br₂: 526.0143 [M]⁺, 528.0123 [M+2]⁺, 530.0102 [M+4]⁺; found: 526.0144 [M]⁺, 528.0128 [M+2]⁺, 530.0106 [M+4]⁺.

Synthesis of (S)-6,6'-bis(bromomethyl)-1,1'-binaphthol ((S)-8): A solution of BBr₃ (18 mL, 1 mol L⁻¹ in CH₂Cl₂) was added dropwise to a stirred solution of (S)-7 (1.45 g, 2.75 mmol) in anhydrous CH₂Cl₂ (50 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred overnight. After carefully adding saturated NaHCO₃ solution to the mixture, the solution was extracted with dichloromethane (3 × 100 mL). The combined extracts were washed with saturated aqueous NaCl (2 × 30 mL), dried (Na₂SO₄), and concentrated in vacuum to obtain (S)-8 as a white solid (1.10 g). The crude product was used directly for the next reaction step.

Synthesis of (S)-9: A solution of CsOH·H₂O (0.24 g, 1.40 mmol) in anhydrous degassed CH₃OH (3 mL) was added over a period of 10 min to a solution of 4-(2-cyanoethylthio)-1,3-dithiole-2-thione (0.31 g, 1.40 mmol) in anhydrous degassed THF (40 mL) under a nitrogen atmosphere. The mixture was stirred for an additional 1 h and then (S)-8 (0.28 g, 0.60 mmol) was added to the mixture. The solution was stirred overnight. After separation by column chromatography on silica gel using CH₂Cl₂ as eluent, (S)-9 was obtained as a red powder (0.32 g, 84%). M.p. 108–110 °C; [α]_D²⁰ = +124.8 ($c=2.02$ in CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta=7.94$ (d, $J=8.9$ Hz, 2H), 7.71 (s, 2H), 7.41 (d, $J=8.9$ Hz, 2H), 7.24 (2H, m), 7.10 (d, $J=8.6$ Hz, 2H), 6.82 (s, 2H), 5.09 (s, 2H), 4.13 ppm (s, 4H); ¹³C NMR (150 MHz, CDCl₃, 25 °C): $\delta=213.0, 152.2, 134.3, 131.9, 131.8, 130.6, 130.3, 128.2, 127.5, 127.2, 124.1, 117.5, 109.9, 40.7$ ppm; HRMS: m/z calcd for C₂₈H₁₈O₂S₂Na: 664.89647 [M+Na]⁺; found: 664.89646.

Synthesis of (S)-1: A mixture of 9-(3-hydroxypropoxy)anthracene (0.20 g, 0.80 mmol) and azodicarboxylic acid diethyl ester (DEAD, 0.14 mL, 0.80 mmol) in anhydrous THF (2 mL) was added dropwise to a stirred solution of (S)-9 (64.2 mg, 0.10 mmol) and triphenylphosphine (0.21 g, 0.80 mmol) in anhydrous THF (8 mL) under a nitrogen atmosphere. 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 CH₂Cl₂/petroleum ether (60–90 °C) (1:1, v/v) as eluent to give (S)-1 as a yellow-green solid (0.04 g, 36%). M.p. 85–87 °C; [α]_D²⁰ = -47.5 ($c=1.01$ in CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS): $\delta=8.24$ (s, 2H), 8.02 (d, $J=8.5$ Hz, 4H), 7.92 (d, $J=8.7$ Hz, 4H), 7.46 (t, $J=7.0$ Hz, 4H), 7.39 (d, $J=9.0$ Hz, 2H), 7.32 (d, $J=7.8$ Hz, 4H), 7.18 (d, $J=9.0$ Hz, 2H), 7.04 (s, 2H), 6.97 (d, $J=8.7$ Hz, 2H), 6.76 (d, $J=8.8$ Hz, 2H), 6.42 (s, 2H), 4.18–4.12 (m, 4H), 3.62 (m, 4H), 3.42 (t, $J=6.9$ Hz, 4H), 2.11 ppm (m, 4H); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): $\delta=213.1, 153.3, 150.0, 134.4, 132.1, 131.4, 131.3, 129.7, 128.2, 127.7, 127.4, 126.6, 125.7, 124.8, 124.5, 124.1, 123.5, 121.3, 121.0, 119.1, 114.8, 71.4, 65.4, 40.3, 29.3$ ppm; HRMS: m/z calcd for C₆₂H₄₆O₄S₂Na: 1133.10539 [M+Na]⁺; found: 1133.10540.

Synthesis of (S)-2: Compound (S)-1 (80.0 mg, 0.07 mmol) was dissolved in CH₂Cl₂ (10 mL). Hg(AcO)₂ (0.14 g, 0.42 mmol) was added to this solution and the mixture was stirred at room temperature for 10 min. The white precipitate was removed by filtration. After removing the solvent from the filtrate, the residue was purified by column chromatography on Al₂O₃ with CH₂Cl₂/petroleum ether (60–90 °C) (3:2, v/v) as eluent to give (S)-2 as a pale yellow solid (66.8 mg, 85.2%). M.p. 76–78 °C; [α]_D²⁰ = -12.3 ($c=0.98$ in CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS): $\delta=8.22$ (s, 2H), 8.00 (d, $J=8.5$ Hz, 4H), 7.92 (d, $J=8.7$ Hz, 4H), 7.44 (t, $J=7.2$ Hz, 4H), 7.38 (d, $J=9.0$ Hz, 2H), 7.31 (d, $J=7.9$ Hz, 4H), 7.15 (d, $J=9.0$ Hz, 2H), 7.04 (s, 2H), 6.95 (d, $J=8.7$ Hz, 2H), 6.75 (d, $J=8.8$ Hz, 2H), 6.23 (s, 2H), 4.16–4.08 (m, 4H), 3.60 (m, 4H), 3.42 (t, $J=7.0$ Hz, 4H), 2.08 ppm (m, 4H); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): $\delta=192.1, 153.3, 150.1, 132.1, 131.4, 130.1, 128.1, 127.8, 127.4, 126.6, 125.8, 124.8, 124.5, 124.1, 124.0, 123.6, 122.1, 121.3, 121.0, 119.2, 114.8, 71.4, 65.4, 39.9, 29.4$ ppm; HRMS: m/z calcd for C₆₂H₄₆O₆S₆Na: 1101.15108 [M+Na]⁺; found: 1101.15109.

Synthesis of 9-(3-hydroxypropoxy)anthracene (10): Compound 10 was prepared from anthrone and 1,3-propanediol according to the literature.^[17] M.p. 115–117 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta=8.30$ (m, 2H), 8.24 (s, 1H), 8.01 (m, 2H), 7.48 (m, 4H), 4.38 (t, $J=6.0$ Hz, 2H), 4.16 (m, 2H), 2.32 ppm (m, 2H); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): $\delta=151.1, 132.6, 128.7, 125.7, 125.5, 124.8, 122.6, 122.4, 74.2, 61.2, 33.4$ ppm; HRMS: m/z calcd for C₁₇H₁₆O₂: 252.1150 [M]⁺; found: 252.1152.

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