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Binaphthalene Molecules with Tetrathiafulvalene Units: CD Spectrum Modulation and New Chiral Molecular Switches by Reversible Oxidation and Reduction of Tetrathiafulvalene Units

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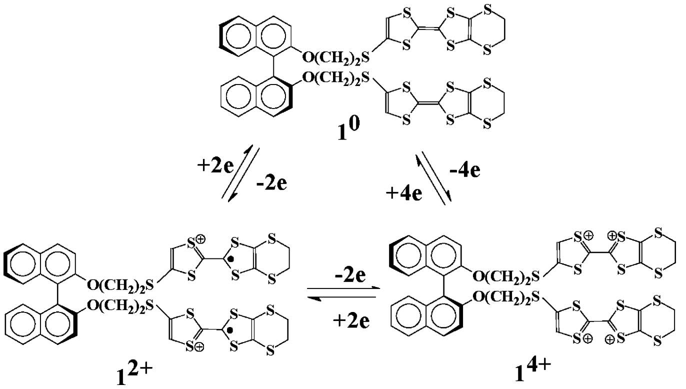

By combining the features of binaphthalene and tetrathiafulvalene (TTF), compounds **1**−**4** were designed for studies of chiral molecular switches. Absorption and CD spectral studies clearly indicate that the CD spectra resulting from axial chiral binaphthalene units can be modulated through the redox reactions of TTF units, which means new chiral molecular switches can be established on the basis of binaphthalene molecules with TTF units. The reference compound **5**, which has one TTF unit rather than two as in the case of compounds **1**, **3**, and **4**, failed to show such property, hinting that the presence of two or more TTF units is required for the realization of CD spectrum modulation. In addition, the manner of the CD spectrum modulation has been found to be dependent on the way TTF units are linked to the binaphthalene skeleton, in terms of the linker length, the positions for substitution, and the number of TTF units.

Introduction

Molecules responsive to external stimuli are the basis for the studies of molecular switches,[1] the key elements in the molecular level devices.[2] If the output signals of molecular switches are chiral properties of molecular systems, they are regarded as chiral molecular switches.[3−16] In fact, to understand, establish, and ultimately control chirality at the molecular and supramolecular level is one of the frontiers of molecular science. Two major categories of chiral molecular switches have been described: one related to the modulation of intrinsic chirality of molecular system represented by sterically overcrowded chiral alkenes[17] and the other based on the magnitude change of chirality.[18]

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Binaphthalene molecules as axially chiral species are widely used as chiral ligands in asymmetric synthesis[19] and as fluorescent sensors for chiral species.[20] In recent years, they have also been employed as building blocks for chiral molecular switches.[18] This is because axially chiral binaphthalene molecules often show strong circular dichroism (CD) signals which serve as the detectable output signals[21] of the chiral switches and which, furthermore, are dependent on the dihedral angles of binaphthalene rings.[22] More interestingly, the dihedral angles of binaphthalene molecules can be modulated when tunable units are introduced into the two naphthalene moieties. Several examples of chiral molecular switches based on the binaphthalene skeleton with redox[18a] or photochromic units[18b−h] have been described. We have recently reported a binaphthalene with two spiropyran units mimicking the behaviors of both a chiral switch and a chiral AND logic gate.[18h]

Tetrathiafulvalene (TTF) and its derivatives[23] have been intensively investigated and were originally prepared for the development of organic conducting materials.[24] The unique property of TTF and its derivatives is that they can be reversibly transformed to the corresponding cation radicals (TTF$^{\bullet+}$) and dications (TTF^{2+}) by either chemical or electrochemical oxidation at easily accessible potentials.[23a,b] By taking use of this unique property, a number of TTF derivatives have been studied for molecular switches,[25] sensors,[26] machines,[27] and even as leaving groups in synthesis.[28] We have recently described TTF−anthracene dyads for redox fluorescent switches,[25f] $^1O_2$ probes,[26f,g] chemical sensors,[26h,i] and modulation of the photoinduced electron transfer process by assembly with gold nanoparticles.[29]

With the features of binaphthalene and TTF in mind, we designed new chiral molecular switches by linking two or more TTF units to binaphthalene skeleton. The design rationale is illustrated in Scheme 1. When the two neutral TTF units of **1**, which is denoted as “0” state, are transformed to two cation radicals (denoted as “2$^+$” state), the conformation of **1**, e.g., the dihedral angle of binaphthalene ring, is varied owing to the Coulombic repulsion of two TTF$^{\bullet+}$ or the formation of cation radical dimer (π-dimer, TTF$_2^{2+}$) depending on the initial orientation of two TTF units.[30] Further oxidation generating two TTF^{2+} in **1** (denoted as “4$^+$” state) would change the dihedral angle of the binaphthalene ring further due to the even stronger Coulombic repulsion. The transformation between TTF, TTF$^{\bullet+}$ and TTF^{2+} can be reversibly performed, and the variation of the dihedral angle of two naphthalene rings can be seen in the

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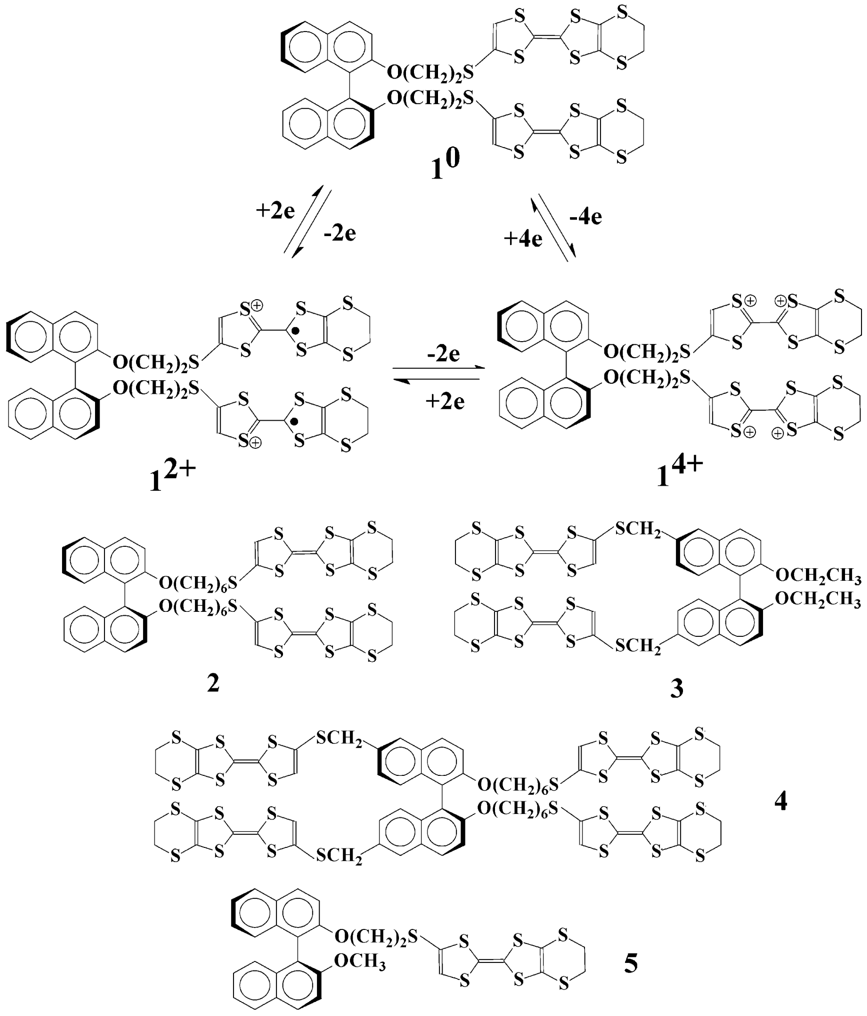
SCHEME 1. Illustration of the Three States of Compound 1 after Oxidation and Reduction and Structures of Compounds 2−5



CD spectrum; therefore, a three-state chiral switch can be realized. In this paper, we first describe the CD spectrum modulation and a new chiral molecular switch based on a binaphthalene skeleton with two TTF units (**1**). To examine the influences of the length of the linker between TTF and binaphthalene units, the substituted position of TTF units, and the number of TTF units on the CD spectrum modulation, we also report the studies of binaphthalene molecules containing TTF units **2**−**4** as well as reference compound **5** (Scheme 1). It should be noted that Martín et al. reported the binaphthalene molecules with two TTF units that are linked to the binaphthalene skeleton at 3,3′ position in a conjugated way.[31] In compounds **1**−**5**, the TTF units are linked to binaphthalene skeleton through alkyl chains in order to make the two moieties well separated and avoid exciton chirality perturbation.[21]

Results and Discussion

Synthesis. As shown in Scheme 2, compounds **1**−**5** were synthesized by the reaction of the corresponding (*R*)-binaphthalene molecules containing bromide-substituted alkyl chains **7**, **8**, **12**, **13**, **15**, respectively, and 4-(2-cyanoethylthio)-4′,5′-(ethylenedithio)tetrathiafulvalene (**9**)[32] in the presence of CsOH·H$_2$O. Compounds **7** and **8** were synthesized similarly through a Mitsunobu reaction[33] as shown in Scheme 2. Compound **12** was synthesized from (*R*)-(+)-2,2′-dihydroxy-1,1′-binaphthyl (**6**) in five steps in a total yield of 49%. Reaction of **8** with HBr/(CH$_2$O)$_n$ led to **13** in 57% yield. Compound **15** was prepared from **6** in two steps in 53% yield. The chemical structures of **1**−**5** were established by NMR and MS data as well as elemental analysis data. Compounds **1**−**5** should retain the *R* configuration,[34] and their optical rotation values were measured.

UV and CD Spectral Studies of 1. It was reported that TTF derivatives can be quantitatively oxidized to the corresponding cation radicals by 1 equiv of Fe^{3+} and even to the dications by more than 1 equiv of Fe^{3+}.[35] For the present studies, Fe(ClO$_4$)$_3$·6H$_2$O was chosen as the oxidant. Figure 1 shows the absorption spectra of **1** in the presence of different amounts of Fe^{3+} in

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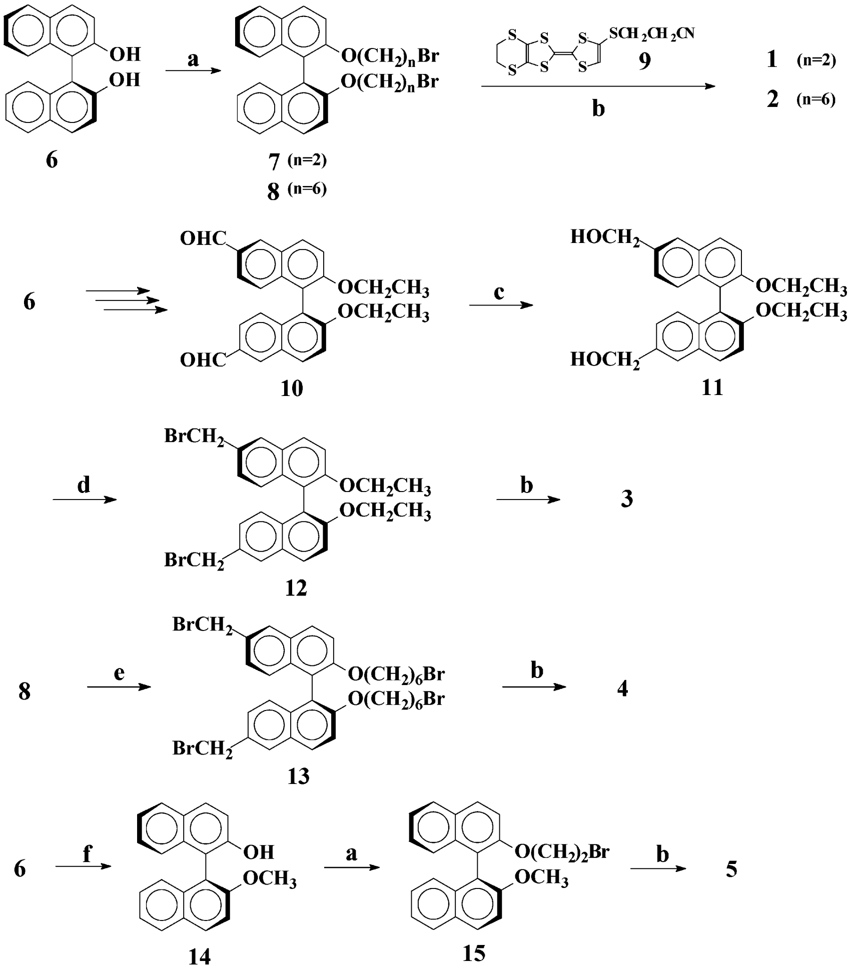
SCHEME 2. Synthetic Scheme of the Preparation of 1−5[a]



[a] Reagents and conditions: (a) 2-bromoethanol for **7** and 6-bromohexanol for **8**, DEAD, PPh_3, THF, reflux; (b) **9**, $CsOH \cdot H_2O$, THF, ambient temperature; (c) $NaBH_4$, ethanol/THF, ambient temperature; (d) PBr_3, pyridine, CH_2Cl_2, 0 °C; (e) HBr, $(CH_2O)_n$, AcOH, ambient temperature, dark; (f) CH_3I, K_2CO_3, acetone, reflux.

THF. Upon addition of Fe^{3+}, two new absorption peaks around 430 and 800 nm, respectively, appeared, and their intensities increased with the amounts of Fe^{3+} added to the solution of **1**. When the solution of **1** was oxidized by more than 2 equiv of Fe^{3+}, the absorption intensities around 430 and 800 nm started to decrease, and a new absorption band emerged around 680 nm. When 4 equiv of Fe^{3+} was employed, the absorption around 680 nm reached the maximum and the absorption spectrum of **1** remained unchanged if more than 4 equiv of Fe^{3+} was added.

According to previous studies,[30] the absorption band around 430 nm is due to the corresponding TTF^+ and that around 800 nm is likely from the dimers of TTF^+ (TTF_2^{2+}), which may be the species generated from the TTF^+ of neighboring molecules of **1** (intermolecular TTF_2^{2+}) or that from the two TTF^+ within **1** (intramolecular TTF_2^{2+}) after reaction with 2 equiv of Fe^{3+}.[36] The absorption band around 680 nm, detected for the solution of **1** after reaction with more than 2 equiv of Fe^{3+}, is attributed to TTF^{2+}.[30d] Therefore, transformation of the "0" state to "2+"

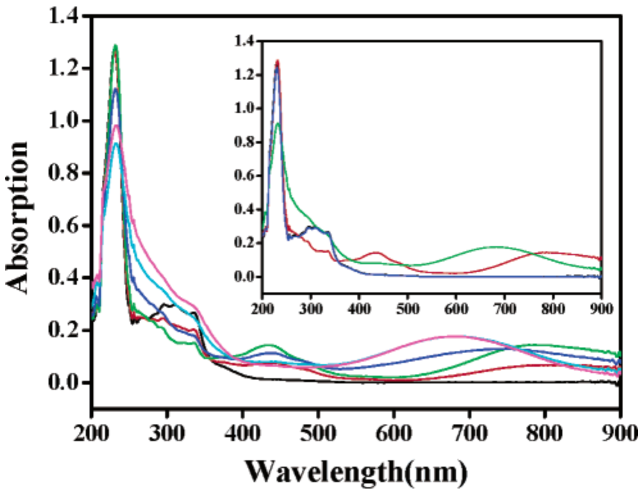


FIGURE 1. UV−vis spectra of **1** (1.0 × 10^{-5} M in THF) before (black) and after addition of 1 equiv (red), 2 equiv (green), 3 equiv (blue), 4 equiv (cyan), and 10 equiv (pink) of $Fe(ClO_4)_3 \cdot 6H_2O$. Inset: UV−vis spectra of **1** (1.0 × 10^{-5} M in THF) before (black) and after addition of 2 equiv (red) and 4 equiv (green) of $Fe(ClO_4)_3 \cdot 6H_2O$ and after addition of 4 equiv of $Fe(ClO_4)_3 \cdot 6H_2O$ followed by addition of excess $Na_2S_2O_3$ powders and stirring for 3 min (blue). The black and blue curves are almost overlapped.

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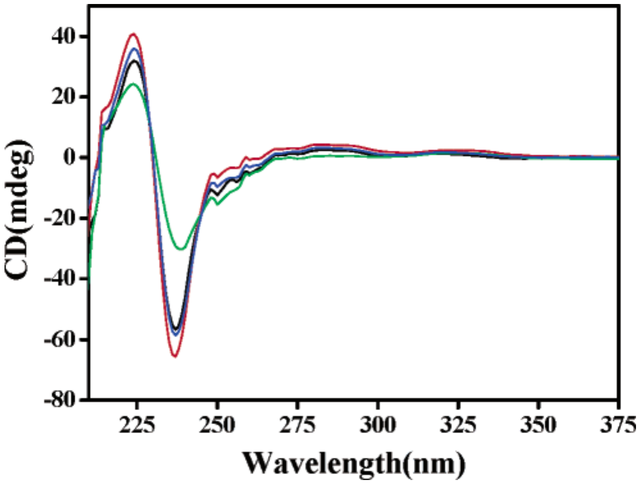

FIGURE 2. CD spectra of **1** (1.0×10^{-5} M in THF) before (black) and after addition of 2 equiv (red) and 4 equiv (green) of $Fe(ClO_4)_3 \cdot 6H_2O$ and after addition of 4 equiv of $Fe(ClO_4)_3 \cdot 6H_2O$ followed by addition of excess $Na_2S_2O_3$ powders and stirring for 3 min (blue).

state and even to "4^+" state of **1** can be achieved by oxidation with Fe^{3+} as illustrated in Scheme 1. Moreover, the initial absorption spectrum of **1** can be restored after the solution of **1** that had been oxidized by Fe^{3+} was subjected to reaction with excess sodium thiosulfate ($Na_2S_2O_3$) (Figure 1, inset). Accordingly, the transformation among the "0" state, "2^+" state, and "4^+" state of **1** can be reversibly performed.

As shown in Figure 2, the CD spectrum of **1** was modulated upon oxidation by Fe^{3+}, concomitant with the corresponding variation of absorption spectrum of **1** as displayed in Figure 1. The CD spectrum of the THF solution of **1** (1.0×10^{-5} M in THF) shows a strong bisignated band in the region of 215−250 nm, typical for binaphthalene molecules.[21] After oxidation by 2 equiv of Fe^{3+} leading to the oxidation of TTF units of **1** and conversion of the "0" state to the "2^+" state of **1**, the intensities for CD bands at about 220 and 240 nm obviously increased albeit slightly. Also, the CD absorptions in the range of 250−300 nm were varied slightly upon the transformation among the '0' state, "2^+" state, and "4^+" state of **1**.

The energy-minimized structure of **1** is shown in Figure 3 (top). The dihedral angle of binaphthalene ring was calculated to be 72.6°. The dihedral angle was also estimated to be about 74° on the basis of the CD spectrum of **1** according to the method described by Salvadori et al.[22b] On the basis of previous studies,[22a,b] the enhancement of CD band intensities reflects the fact that the dihedral angle is reduced for binaphthalene with the dihedral angle in the range of 70−90°. It is likely that the two TTF^+ units in the "2^+" state of **1** are easily reorientated to form the intramolecular TTF_2^{2+}, and simultaneously the conformation of the binaphthalene skeleton is varied resulting in a smaller dihedral angle compared to that of the "0" state of **1**.

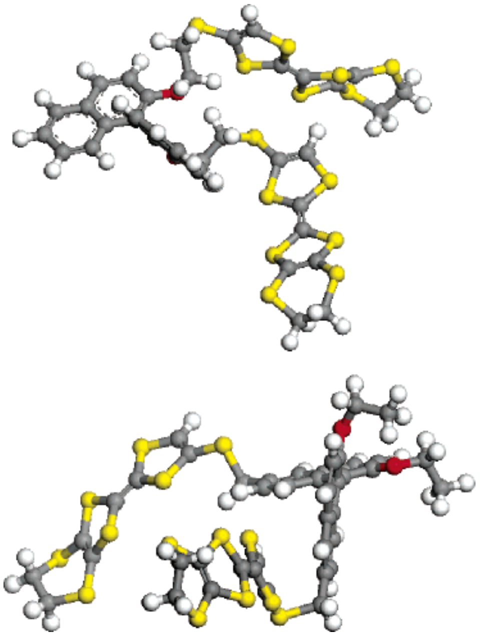

FIGURE 3. Energy-minimized structure of **1** and **3**: carbon (black); hydrogen atom (gray); sulfur atom (yellow); oxygen atom (red).

This assumption provides the explanation for the increase of the CD signal intensities for **1** after reaction with 2 equiv of Fe^{3+}.

Further addition of 2.0 equiv of Fe^{3+} to the solution of **1** in the "2^+" state or direct reaction of **1** with 4 equiv of Fe^{3+} resulted in the formation of the "4^+" state of **1** as discussed above. As shown in Figure 2, compared with the "0" state, the intensities of CD signals at about 220 and 240 nm were obviously reduced for the "4^+" state of **1**. It is understandable that the Coulombic repulsion between two TTF^{2+} would lead to a larger dihedral angle of binaphthalene ring of **1**. For the binaphthalene molecules with the dihedral angle in the range of 70−90°, a larger dihedral angle is associated with lower CD absorption intensity.[22a,b] After addition of $Na_2S_2O_3$ to the solution of **1** either in the "2^+" state or "4^+" state, the initial CD spectrum of **1** was nearly restored (Figure 2). Such CD spectrum modulation can be repeated at least for four cycles. Electrochemical studies (see Figure S1, Supporting Information) indicate that the two TTF units of **1** can be reversibly oxidized by electrochemical method. Thus, it is possible to modulate the CD spectrum of **1** electrochemically. Consequently, it can be concluded that the CD spectrum of **1** can be modulated by reversible redox reaction of TTF units and a three-state chiral switch can be established.

The assumption that the CD spectrum modification of **1** is due to the variation of the interaction of two TTF units after redox reactions is fully confirmed by the studies of reference compound **5** featuring only one TTF unit. When compound **5** was subjected to reaction with Fe^{3+} in the same way as for compound **1**, typical absorptions for TTF^+ and TTF^{2+} were observed. However, its CD spectrum remained unchanged (see Figure S2, Supporting Information). These results indicate that the presence of two TTF units is necessary for the modulation of the CD spectrum after oxidation by Fe^{3+}. To summarize, the operation mechanism for the CD spectrum modulation of **1** upon oxidation TTF units is schematically illustrated in Scheme 3. Oxidation of TTF units to the cation radicals TTF^+ leads to

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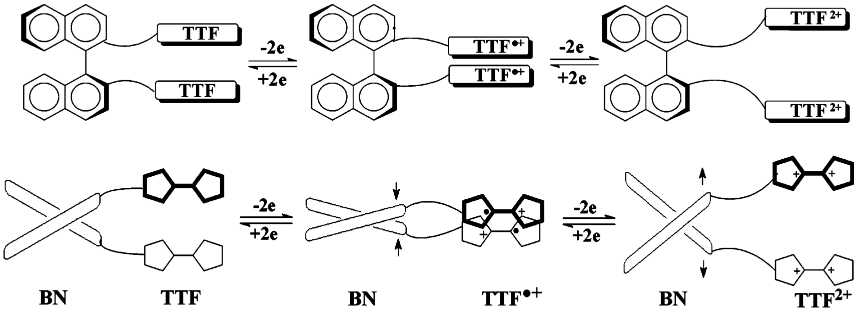
(36) It was reported that intermolecular TTF_2^{2+} can be formed even in diluted solution with concentration lower than 10^{-7} M.[30d] It should be noted that there have been arguments about whether the absorption around 800 nm is a credible proof for the formation of TTF_2^{2+} and even the true existence of TTF_2^{2+} in solution at room temperature; see: Khodorkovsky, V.; Shapiro, L.; Krief, P.; Shames, A.; Mabon, G.; Gorgues, A.; Giffard, M. *Chem. Commun.* **2001**, 2736−2737. However, Kim et al. have recently reported the formation of TTF_2^{2+} encapsulated in a cucurbit[8]uril cavity, and it shows the characteristic absorption band around 800 nm, see: Ziganshina, A. Y.; Ko, Y. H.; Jeon, W. S.; Kim, K. *Chem. Commun.* **2004**, 806−807.

SCHEME 3. Schematic Illustration of the Three States of 1 Showing Different Dihedral Angles after Oxidation of TTF Units (BN, Binaphthalene Unit; TTF, Tetrathiafulvalene Unit)



formation of the intramolecular TTF_2^{2+} which induces the reduction of the dihedral angle between two naphthalene rings and the enhancement of the intensities of CD signals; further oxidation leads to the formation of two TTF^{2+} units, and as a result of the Coulombic repulsion the dihedral angle between two naphthalene rings becomes larger resulting in the reduction of the intensities of CD signals.

Effect of the Linker Length. The linker between the binaphthalene skeleton and TTF units in **1** is $-OCH_2CH_2S-$. For compound **2**, the analogue of **1**, the corresponding linker is $-OCH_2CH_2CH_2CH_2CH_2CH_2S-$. When compound **2** was oxidized by $Fe(ClO_4)_3$ in the same manner as for compound **1**, absorption bands due to TTF^+ and TTF^{2+} were observed. But, its CD spectrum kept unaffected (see Figure S3, Supporting Information). This result hints that the influence of the variation of the interaction between two TTF units upon redox reactions on the conformation of the binaphthalene skeleton weakens largely if the alkyl chain linker becomes longer. This can be well understood by considering the fact that the longer alkyl chain linker will become more flexible and consequently variation of the interaction of two TTF units upon redox reactions will not affect the conformation of binaphthalene unit. But, it can be expected that it would behave differently if the linker is more rigid.

Effects of the Substituted Position and Number of TTF Units. Compound **3** has two TTF units linked to the binaphthalene skeleton at 6,6′ positions. Similar to compound **1**, characteristic absorptions of TTF^+ and TTF^{2+} were observed upon oxidation of the solution of **3** (see Figure S4, Supporting Information). Figure 4 shows the CD spectra of **3** before and after reaction with Fe^{3+}. The intensities of CD signals at about 235 and 250 nm decreased to 76% and 64% of the initial ones, respectively, after oxidation by 2 equiv of Fe^{3+}. Further oxidation led to even weaker CD signals, corresponding to 57% and 48% of the initial ones for the signals at about 235 and 250 nm, respectively. Again, reaction of with $Na_2S_2O_3$ could restore the initial CD spectrum of **3** (Figure 4). Therefore, the CD spectrum of **3** can also be modulated by redox reactions of TTF units.

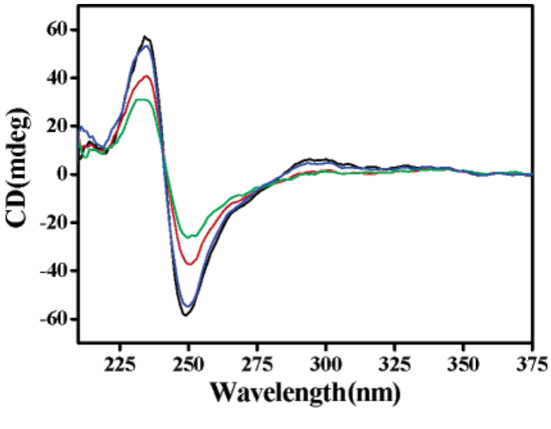


FIGURE 4. CD spectra of **3** (1.0×10^{-5} M in THF) before (black) and after addition of 2 equiv (red) and 4 equiv (green) of $Fe(ClO_4)_3 \cdot 6H_2O$ and after addition of 4 equiv of $Fe(ClO_4)_3 \cdot 6H_2O$ followed by addition of excess $Na_2S_2O_3$ powders and stirring for 3 min (blue).

Different from compound **1**, the transformation of TTF units of **3** to the cation radicals is concomitant with the obvious intensity decrease of the CD signals. This is probably due to the fact that the orientation of two TTF units of **3** is not favorable for the formation of the intramolecular TTF_2^{2+}, and the Coulombic repulsion plays the predominant role. As a result, the dihedral angel of **3** became larger after the transformation of TTF units to the radical cations TTF^+. Figure 3 shows the energy-minimized conformation of compound **3**. The dihedral angle of the binaphthalene ring was calculated to 76.2°, which was close to that estimated from the CD spectrum of **3**.[37] Based on the previous results,[22a,b] large dihedral angle shows relatively weak CD signals for binaphthalene molecules with the dihedral angle in the range of 70−90°. Therefore, the comparative studies with compounds **3** imply that the manner of CD spectrum modulation is dependent on the substituted positions of TTF units.

Compound **4** contains four TTF units; two of them are separately linked to binaphthalene skeleton through $-CH_2S-$ at the 6,6′ positions and the other two through $-OCH_2CH_2CH_2CH_2CH_2CH_2S-$ at the 2,2′ positions. Similar to compound **1**, new absorption bands at about 430, 800, and 680 nm, due to TTF^+, TTF_2^{2+}, and TTF^{2+}, respectively, were observed for compound **4** upon oxidation by Fe^{3+} (see Figure S5, Supporting Information). Figure 5 shows the CD spectra of **4** before and after oxidation by different amounts of Fe^{3+}. Upon reaction with Fe^{3+}, the CD signals started to decrease, and moreover, the maxima of the signals were obviously red-shifted albeit slightly. The variation of the CD spectrum of **4** was maximized when 4 equiv of Fe^{3+} was added to the solution (the intensity was reduced to about 72% and 57% of the initial ones at about 235 and 250 nm, respectively), and further addition of Fe^{3+} led to a rather minor change for the CD spectrum.

The manner of CD spectrum modulation of **4** was different from that of **3** after reaction with Fe^{3+} (see Figures 4 and 5), and the CD spectrum of **2** remained unchanged upon oxidation with Fe^{3+}(see Figure S3, Supporting Information). These facts

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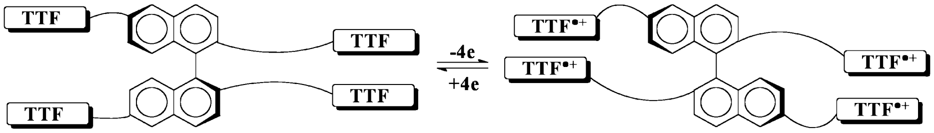
[37] The dihedral angle estimated from the CD spectrum of **3** is about 74° according to the method recorded in ref 22b.

SCHEME 4. Schematic Illustration of the Two States of Compound 4 and Formation of Intramolecular TTF^{2+} Dimers after Transformation of TTF to TTF^{+}



indicate that the two TTF units at the 6,6′positions and those at the 2,2′ positions of **4** were not independent and indeed interacted after oxidation of the TTF units. The mechanism was proposed for the CD spectrum modulation observed for **4** upon oxidation as schematically illustrated in Scheme 4. After the transformation of the TTF units of **4** into the cation radicals TTF^{+}, the TTF^{+} at the 6,6′ positions and those at 2,2′ positions were probably reorientated to form the intramolecular $TTF_2{}^{2+}$ dimers. As a result, the conformation of the binaphthalene skeleton was varied leading to the dihedral angle change and CD spectrum modulation. Further addition of Fe^{3+} would lead to the transformation of TTF^{+} to TTF^{2+}, and Coulombic repulsion would take effect. But, since there was a flexible alkyl chain linker at the 2,2′ positions, such Coulombic repulsion could not cause the CD spectrum variation as observed for compound **2**. The CD spectrum modulation observed for compound **4** upon reaction with Fe^{3+} is consistent with this proposed mechanism.

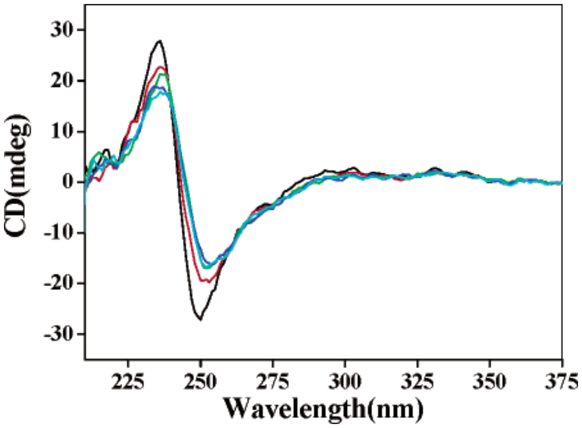


FIGURE 5. CD spectra of **4** (5.0×10^{-6} M in THF) before (black) and after addition of 2.0 equiv (red), 4.0 equiv (green), 6.0 equiv (blue), and 8.0 equiv (cyan) of $Fe(ClO_4)_3{\cdot}6H_2O$.

Conclusions

The transformation of TTF and its derivatives to the corresponding TTF^{+} and TTF^{2+}not only tunes their electron-donating abilities but also endows them with positive charges. By taking these features of TTF derivatives (e.g., the electronic repulsion between TTF^{+}/TTF^{2+} and cyclobis(paraquat-*p*-phenylene)), Stoddart and co-workers have studied a number of elegant external-stimulti-responsive supramolecules exemplified by the molecular shuttles.[27a,b,39] In fact, the interaction of the positively charged TTF species in the solid state also plays a crucial role in determining the conducting behavior of the charge-transfer salts.[24] We take one step further to include two or more TTF units within one chiral molecule to manipulate the interactions among TTF units through redox reactions, and as a result the molecular conformation may be tuned.

In this paper, we report binaphthalene molecules with TTF units since the conformation change of binaphthalene molecules can be seen in the CD spectrum. With these thoughts in mind, compounds **1**−**4** were designed for studies of chiral molecular switches. Absorption and CD spectral studies clearly indicate that it is possible to modulate the CD spectra of **1**, **3**, and **4** through the redox reactions of TTF units. To summarize, the interactions between the TTF units in different states of the redox cycle exert different influences on the dihedral angle between the two naphthalene rings, thus modulating the CD spectrum. Accordingly, new chiral molecular switches can be established based on binaphthalene molecules with TTF units.

Studies of the reference compound **5** hint that the presence of two or more TTF units is required for the realization of CD spectrum modulation. Moreover, the manner of the CD spectrum modulation has been found to be dependent on the way how TTF units are linked to the binaphthalene skeleton, in terms of the length of the linker, the substituted position and the number of TTF units. It would be interesting to extend the present idea further by introducing both TTF and electron acceptor units to binaphthalene skeleton to tune the CD spectrum and establish new chiral molecular switches by manipulating the charge-transfer interactions. This will be included in our further investigations of chiral molecular switches based on binaphthalene systems.

Experimental Section

General Methods. ^1H NMR spectra were recorded at 600 MHz, and ^{13}C NMR data were recorded at 150.9 MHz. Mass spectra were determined with BEFLEX III for TOF-MS. Optical rotation values were measured at 20 °C using the sodium D line (589 nm). For recording the CD spectra the scan rate was 500 nm/min, and each CD spectrum was accumulated two times. To obtain reliable CD data, the concentration of the solution was not higher than 1.0×10^{-5} mol/L. UV−vis and CD spectral experiments were carried out under ambient conditions.

(*R*)-2,2′-Diethoxy-1,1′-binaphthyl-6,6′-dicarbaldehyde (**10**) was synthesized according to the literature.[40] HPLC-grade THF was used as solvent and distilled over sodium/benzophenone immediately before use. All other solvents were purified and dried with standard procedures unless otherwise stated.

Theoretical Calcultions. The molecular geometries and minimum energy configurations were optimized using the density functional theory (DFT) method as implemented in the DMol3 package,[41] which is available as part of Materials Studio. The basis set chosen was the double numerical plus d-function (DND). The local functional for the exchange correlation potential was the

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(38) The possibility of formation of the MV dimer $TTF_2{}^{+}$ cannot ruled out since formation of MV dimer would similarly cause the reorientation of TTF units as the mechanism shown in Scheme 4. For a recent example of the TTF MV dimer, see: Yoshizawa, M.; Kumazwa, K.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 13456−13457.

(39) Liu, Y.; et al. *J. Am. Chem. Soc.* **2005**, *127*, 9745−9759.

(40) Deussen, H.-J.; Hendrickx, E.; Boutton, C.; Krog, D.; Clays, K.; Bechgaard, K.; Persoons, A.; Bjørnholm, T. *J. Am. Chem. Soc.* **1996**, *118*, 6841−6852.

(41) (a) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508−517. (b) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756−7764.

Perden−Wang LDA functional (PWC).[42] All of the molecules were placed in a vacuum. Solvent effect and interactions between molecules were not considered.

Synthesis of Compound 1. To a solution of 4-(2-cyanoethylthio)-4′,5′-(ethylenedithio)tetrathiafulvalene (**9**, 0.83 g, 2.19 mmol) in 30 mL of THF with a N_2 bubbling was added dropwise a degassed solution of $CsOH \cdot H_2O$ (0.40 g, 2.40 mmol) in 5 mL of CH_3OH over a period of 10 min at ambient temperature. After being stirred for an additional 30 min, a degassed solution of (*R*)-(+)-2,2′-bis(2-bromoethoxy)-1,1′-binaphthyl (**7**) (see the Supporting Information) (0.41 g, 0.82 mmol) in 10 mL of THF was added. The reaction mixture was stirred overnight at ambient temperature and then concentrated in a vacuum. The crude product was subjected to a column chromatography (silica gel) using CH_2Cl_2/petroleum ether (3:2) as eluant to give **1** (0.48 g, 59%) as an orange solid. Recrystallization from CH_2Cl_2/*n*-hexane afforded an analytical sample: mp 108.1−110.3 °C; $[\alpha]^{20}_{\mathrm{D}}$ +16.1 (*c* 0.99, THF); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.72 (4H, t, J = 6.7 Hz), 3.31 (8H, s), 4.02−4.14 (4H, m), 5.98 (2H, s), 7.13 (2H, d, J = 8.5 Hz), 7.23−7.26 (2H, m), 7.35−7.37 (2H, m), 7.42 (2H, d, J = 9.0 Hz), 7.88 (2H, d, J = 8.1 Hz), 7.97 (2H, d, J = 9.0 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 30.2, 34.9, 68.6, 106.7, 114.0, 114.0, 116.6, 118.2, 121.1, 123.0, 124.1, 125.4, 126.1, 126.5, 128.0, 129.7, 129.8, 134.0, 153.8; MS (MALDI-TOF) *m/z* 989.4 (M^+). Anal. Calcd for $C_{40}H_{30}O_2S_{14}$: C, 48.45; H, 3.05; S, 45.27. Found: C, 48.36; H, 3.10; S, 45.27.

Synthesis of Compound 2. (*R*)-**2** was prepared from **9** and (*R*)-(+)-2,2′-bis(6-bromohexyloxy)-1,1′-binaphthyl (**8**) (see the Supporting Information) by the same procedure as described for the synthesis of **1** as an orange solid: yield 62%; mp 77.8−78.6 °C; $[\alpha]^{20}_{\mathrm{D}}$ +18.9 (*c* 1.75, THF); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.81−0.83 (4H, m), 0.99−1.03 (4H, m), 1.27−1.29 (4H, m), 1.36−1.40 (4H, m), 2.49 (4H, t, J = 7.5 Hz), 3.30 (8H, s), 3.88−4.00 (4H, m), 6.31 (2H, s), 7.15 (2H, d, J = 8.4 Hz), 7.20−7.22 (2H, m), 7.31−7.33 (2H, m), 7.41 (2H, d, J = 9.0 Hz), 7.86 (2H, d, J = 8.1 Hz), 7.94 (2H, d, J = 9.0 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 25.1, 27.8, 29.2, 29.3, 30.2, 35.7, 69.6, 106.3, 114.0, 115.9, 118.3, 120.8, 121.4, 123.5, 125.5, 126.1, 127.6, 127.9, 129.2, 129.3, 134.2, 154.5; MS (MALDI-TOF) *m/z* 1102.2 (M^+). Anal. Calcd for $C_{48}H_{46}O_2S_{14} \cdot 0.2\ C_6H_{14}$: C, 52.71; H, 4.39; S, 40.04. Found: C, 52.47; H, 4.53; S, 39.96.

Synthesis of Compound 3. (*R*)-**3** was prepared from **9** and (*R*)-(−)-6,6′-bis(bromomethyl)-2,2′-diethoxy-1,1′-binaphthyl (**12**) (see the Supporting Information) by a procedure similar to that described for the synthesis of **1** as an orange solid: yield 85%; mp 127.3−128.5 °C; $[\alpha]^{20}_{\mathrm{D}}$ +8.2 (*c* 1.48, THF); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.07 (6H, t, J = 6.9 Hz), 3.31 (8H, s), 4.05−4.07 (8H, m), 6.11 (2H, s), 7.09 (2H, d, J = 8.4 Hz), 7.14 (2H, dd, J_1 = 8.7 Hz, J_2 = 1.3 Hz), 7.42 (2H, d, J = 9.0 Hz), 7.69 (2H, d, J = 1.2 Hz), 7.89 (2H, d, J = 9.0 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 15.1, 30.3, 41.0, 65.2, 106.4, 113.9, 114.0, 116.1, 118.2, 120.4, 123.9, 126.1, 126.4, 127.1, 127.9, 128.9, 129.1, 131.5, 133.4, 154.6; MS (MALDI-TOF) *m/z* 1018.1 (M^+). Anal. Calcd for $C_{42}H_{34}O_2S_{14}$: C, 49.47; H, 3.36; S, 44.03. Found: C, 49.13; H, 3.52; S, 44.16.

Synthesis of Compound 4. (*R*)-**4** was prepared from **9** and (*R*)-(+)-2,2′-bis(6-bromohexyloxy)-6,6′-dibromomethyl-1,1′-binaphthyl (**13**) by a procedure similar to that described for the synthesis of **1** as an orange solid: yield 41%; mp 96.1−98.2 °C; $[\alpha]^{20}_{\mathrm{D}}$ +16.0 (*c* 1.13, THF); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.82−0.86 (4H, m), 1.00−1.03 (4H, m), 1.27−1.31 (4H, m), 1.36−1.41 (4H, m), 2.50 (4H, t, J = 7.5 Hz), 3.31 (16H, s), 3.89−4.00 (4H, m), 4.08 (4H, s), 6.13 (2H, s), 6.32 (2H, s), 7.11 (2H, d, J = 9.0 Hz), 7.15 (2H, d, J = 8.8 Hz), 7.40 (2H, d, J = 9.0 Hz), 7.70 (2H, s), 7.88 (2H, d, J = 9.0 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 25.2, 27.8, 29.2, 29.4, 30.3, 35.8, 41.1, 69.6, 106.4, 106.4, 113.9, 114.0, 114.0, 116.2, 118.2, 118.2, 120.5, 121.5, 123.7, 126.1, 126.5, 127.12, 127.6, 128.0, 129.0, 129.2, 131.6, 133.4, 154.7; MS (MALDI-TOF) *m/z* 1778.6 (M^+). Anal. Calcd for $C_{66}H_{58}O_2S_{28} \cdot 0.7C_6H_{14}$: C, 45.79; H, 3.71; S, 48.76. Found: C, 45.40; H, 3.82; S, 48.15.

Synthesis of Compound 5. (*R*)-**5** was prepared from **9** and (*R*)-(+)-2-(2-bromoethoxy)-2′-methoxy-1,1′-binaphthyl (**15**) (see the Supporting Information) by a procedure similar to that described for the synthesis of **1** as an orange solid: yield 75%; mp 97.8−99.4 °C; $[\alpha]^{20}_{\mathrm{D}}$ +52.0 (*c* 0.99, THF); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.70 (2H, t, J = 6.6 Hz), 3.30 (4H, s), 3.78 (3H, s), 4.00−4.11 (2H, m), 5.97 (1H, s), 7.08 (1H, d, J = 8.4 Hz), 7.13 (1H, d, J = 8.4 Hz), 7.20−7.24 (2H, m), 7.30−7.36 (2H, m), 7.41−7.46 (2H, m), 7.87 (2H, d, J = 7.8 Hz), 7.95 (1H, d, J = 9.0 Hz), 7.99 (1H, d, J = 9.0 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 30.2, 34.8, 56.7, 68.6, 106.7, 113.9, 114.0, 116.9, 118.1, 121.5, 123.0, 123.5, 124.0, 125.2, 125.5, 126.1, 126.3, 126.4, 127.9, 129.1, 129.5, 129.6, 129.9, 134.0, 134.1, 153.8, 154.9; MS (MALDI-TOF) *m/z* 652.0 (M^+). Anal. Calcd for $C_{31}H_{24}O_2S_7$: C, 57.02; H, 3.71; S, 34.37. Found: C, 56.71; H, 4.10; S, 34.23.

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Supporting Information Available: The complete list of authors for refs 25b, 26b, 35a,d, and 39, detailed synthetic procedures for compounds **7**, **8**, and **11**−**15**, UV−vis and/or CD spectra of compounds **2**−**4** and **5** oxidized by $Fe(ClO_4)_3 \cdot 6H_2O$ in THF, cyclic voltammograms of compounds **1**−**5**, computational details for **1**, **3**, and **4** including relevant input parameters, and Cartesian coordinates and computed total energies as well as the energy-minimized structure of compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO052579V

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