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New Heterocyclic Tetrathiafulvalene Compounds with an Azobenzene Moiety: Photomodulation of the Electron-Donating Ability of the Tetrathiafulvalene Moiety

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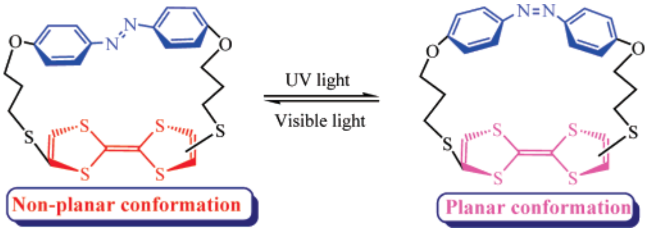

New heterocyclic TTF compounds **1a**−**c** and **2** with an azobenzene moiety were described. The oxidation potential of **1a** could be reversibly modulated by alternating UV and visible light irradiation. As a result, a molecular switch with UV/visible light as the inputs and the electrochemical signal as the output was achieved. Moreover, it was found that the influence of the azobenzene photoisomerization on the electronic property of the TTF unit became stronger with shorter spacers in compounds **1a**−**c**.

Since the synthesis of tetrathiafulvalene (TTF) in the 1970s, TTF and its derivatives have been intensively investigated as building blocks of organic conductors and superconductors.[1] TTF and its derivatives are strong electron donors, and they can be reversibly transformed into the corresponding radical cations and dications. By making use of this unique property of the TTF moiety, a number of electron donor−acceptor molecules and supramolecules have been designed and studied for use as molecular shuttles,[2] molecular switches,[3] logic gates,[4] and chemical sensors.[5]

The electron-donating ability of the TTF moiety is related to its conformation that can be affected by the peripheral substituted groups, in particular, for the heterocyclic tetrathiafulvalene compounds. These peripheral substituted groups may induce the conformational change of the central fulvalene core, and accordingly, it is possible to modulate the electron-donating ability. For example, the deformation of the TTF moieties in tetrathiafulvalenophanes[6] enhanced their electron-donating ability. It should be noted that it is important to find ways to tune the electron-donating ability for designing new functional molecular systems with TTF moieties.

It is well-known that the reversible transformation between the *trans*- and *cis*-forms of azobenzene can occur under UV/visible light irradiation. By taking advantage of this property of azobenzene, a great deal of interesting molecules containing azobenzene moieties have been described for the studies of molecular switches,[7] molecular machines,[8] etc. These molecular systems also show potential applications in optical data storage.

By combining the features of TTF and azobenzene moieties, new heterocyclic TTF compounds (**1a**−**c**, Scheme 1) are

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[1] (a) Kobayashi, H.; Cui, H.; Kobayashi A. *Chem. Rev.* **2004**, *104*, 5265−5288 and further references cited therein. (b) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors* (*Including Fullerenes*); Prentice Hall: Englewood Cliffs, NJ, 1992.

[2] (a) Pease, A. R.; Jeppesen, J. O.; Stoddart, J. F.; Luo, Y.; Collier, C. P.; Heath, J. R. *Acc. Chem. Res.* **2001**, *34*, 433−444 and further references cited therein. (b) Kang, S.; Vignon, S. A.; Tseng, H. R.; Stoddart, J. F. *Chem. Eur. J.* **2004**, *10*, 2555−2564. (c) Liu, Y.; Flood, A. H.; Stoddart, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 9150−9151.

[3] (a) Bryce, M. R. *Adv. Mater*. **1999**, *11*, 11−23 and further references cited therein. (b) Nielsen, M. B.; Lomholt, C.; Becher, J. *Chem. Soc. Rev.* **2000**, *29*, 153−164 and further references cited therein. (c) Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372−1409 and further references cited therein. (d) Farren, C.; Christensen, C. A.; FitzGerald, S.; Bryce, M. R.; Beeby, A. *J. Org. Chem.* **2002**, *67*, 9130−9139. (e) Nielsen, M. B.; Nielsen, S. B.; Behcer, J. *Chem. Commun.* **1998**, 475−476. (f) Li, H.; Jeppesen, J. O.; Levillain, E.; Becher, J. *Chem. Commun.* **2003**, 846−847. (f) Zhang, G.; Zhang, D.; Guo, X.; Zhu, D. *Org. Lett.* **2004**, *6*, 1209−1212. (g) Xiao, X.; Xu, W.; Zhang, D.; Xu, H.; Lu, H.; Zhu, D. *J. Mater. Chem.* **2005**, *15*, 2557−2561. (h) Leroy-Lhez, S.; Baffreau, J.; Perrin, L.; Levillain, E.; Allain, M.; Blesa, M. J.; Hudhomme, P. *J. Org. Chem.* **2005**, *70*, 6313−6320. (i) Zhou, Y.; Zhang, D.; Zhu, L.; Shuai, Z.; Zhu, D. *J. Org. Chem.* **2006**, *71*, 2123−2130.

[4] (a) Asakawa, M.; Ashton, P. R.; Balzani, V.; Credi, A.; Mattersteig, G.; Matthews, O. A.; Montalti, M.; Spencer, N.; Stoddart, J. F.; Venturi, M. *Chem. Eur. J.* **1997**, *3*, 1992−1996. (b) Zhou, Y.; Wu, H.; Qu, L.; Zhang, D.; Zhu, D. *J. Phys. Chem. B* **2006**, *110*, 15676−15679.

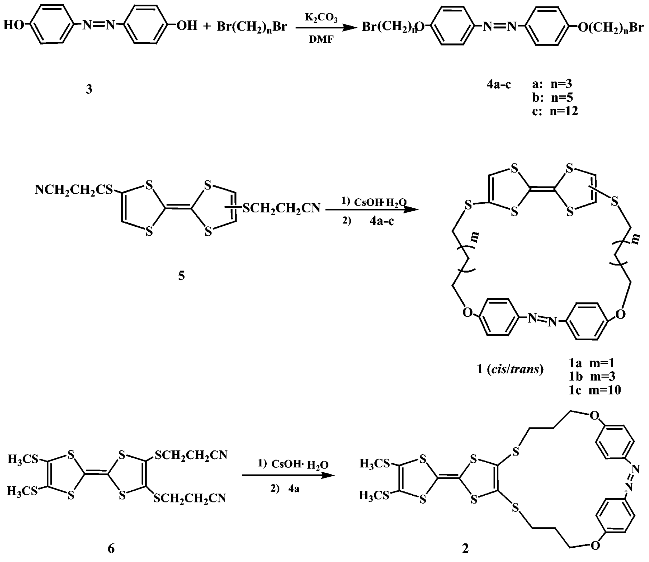
[5] For recent examples, see: (a) Le Derf, F.; Levillain, E.; Trippé, G.; Gorgues, A.; Sallé, M.; Sebastían, R. M.; Caminade, A. M.; Majoral, J. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 224−227. (b) Trippe, G.; Levillain, E.; Le Derf, F.; Gorgues, A.; Sallé, M.; Jeppesen, J. O.; Nielsen, K.; Behcer, J. *Org. Lett.* **2002**, *4*, 2461−2464. (c) Lyskawa, J.; Le Derf, F.; Levillain, E.; Mazari, M.; Sallé, M.; Dubois, L.; Viel, P.; Bureau, C.; Palacin, S. *J. Am. Chem. Soc.* **2004**, *126*, 12194−12195. (d) Nielsen, K. A.; Cho, W. S.; Jeppesen, J. O.; Lynch, V. M.; Becher, J.; Sessler, J. L. *J. Am. Chem. Soc.* **2004**, *126*, 16296−16297. (e) Li, X.; Zhang, G.; Ma, H.; Zhang, D.; Li, J.; Zhu, D. *J. Am. Chem. Soc.* **2004**, *126*, 11543−11548. (f) Zhang, G.; Li, X.; Ma, H.; Zhang, D.; Li, J.; Zhu, D. *Chem. Commun.* **2004**, 2072−2073. (g) Wang, Z.; Zhang, D.; Zhu, D. *J. Org. Chem.* **2005**, *70*, 5729−5732. (h) Lu, H.; Xu, W.; Zhang, D.; Chen, C.; Zhu, D. *Org. Lett.* **2005**, *7*, 4629−4632. (i) Lu, H.; Xu, W.; Zhang, D.; Zhu, D. *Chem. Commun.* **2005**, 4777−4779.

[6] (a) Staab, H. A.; Ippen, J.; Tao-pen, C.; Krieger, C.; Starker, B. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 66−67. (b) Ippen, J.; Tao-pen, C.; Starker, B.; Schweitzer, D.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 67−69.

[7] See, for example: (a) Sakai, H.; Orihara, Y.; Kodashima, H.; Matsumura, A.; Ohkubo, T.; Tsuchiya, K.; Abe, M. *J. Am. Chem. Soc.* **2005**, *127*, 13454−13455. (b) Holland, N. B.; Hugel, T.; Neuert, G.; Cattani-Scholz, A.; Renner, C.; Oesterhelt, D.; Moroder, L.; Seitz, M.; Gaub, H. E. *Macromolecules* **2003**, *36*, 2015−2023. (c) Kurihara, S.; Yoneyama, D.; Nonaka, T. *Chem. Mater.* **2001**, *13*, 2807−2812. (d) Pieraccini, S.; Masiero, S.; Spada, G. P.; Gottarelli, G. *Chem. Commun.* **2003**, 598−599. (e) van Delden, R.; Mecca, T.; Rosini, C.; Feringa, B. L. *Chem. Eur. J.* **2004**, *10*, 61−70.

10.1021/jo070651e CCC: $37.00

SCHEME 1. Synthetic Approach to Compounds 1a−c and 2



designed, aimed at developing approaches to modulate the electron-donating ability of the TTF moiety by UV/visible light irradiation. The design rationale is simply described as follows: The transformation of the *trans*-azobenzene to the corresponding *cis*-azobenzene unit would alter the steric strain within the cyclic compounds **1a**−**c**; as a result, the conformation of the TTF moiety and therefore its electron-donating ability would be changed if the spacers linking the azobenzene and TTF moieties are relatively short. The results show that (1) reversible tuning of the electron-donating ability, demonstrated by variation in oxidation potential upon alternating UV and visible light irradiation, is achieved for compounds **1a** and **1b** with $-(CH_2)_3-$ and $-(CH_2)_5-$ as the spacers, respectively; (2) the variation degree of the oxidation potential is dependent on the lengths of spacers. When the spacers are extended to $-(CH_2)_{12}-$, the oxidation potential remains unchanged upon light irradiation; (3) variation of the oxidation potential was found to be negligible for compound **2** in which the azobenzene moiety is linked to TTF moiety in a side manner. These results are also consistent with DFT calculations. From the application perspective, the reversible modulation of the oxidation potentials of by alternating UV and visible light irradiation can be considered as a new molecular switch performing the electronic transduction of optical signals.

Synthesis. Reaction of compound **3** (Scheme 1) with the dibromoalkane in the presence of K_2CO_3 led to compounds **4a**−**c**. Reaction of compound **5**[9] with compounds **4a**−**c** in diluted solution afforded compounds **1a**−**c**, respectively, in acceptable yields. As reported previously, compound **5** has two possible isomers which cannot be separated by column chromatography; azobenzene also has two possible isomers (*cis* and *trans*). Therefore, compounds **1a**−**c** would have four possible isomers. Again, it was not possible to separate the four isomers with column chromatography. For comparison studies later, compound **2** was prepared similarly by reaction of compound **6**[10] with compound **4a** in diluted solution.

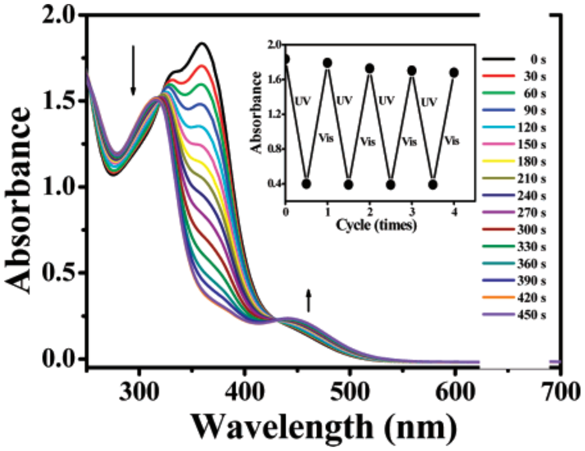


FIGURE 1. Absorption spectra of **1a** (1.0×10^{-4} M in CH_2Cl_2) after UV light irradiation for different periods; inset shows the reversible absorbance variation at 359 nm for **1a** after alternating UV light irradiation (for 8.0 min) and visible light irradiation (for 15 min); a UV lamp (365 nm, 100 W) and a tungsten lamp (>460 nm, 150 W) were used for the UV and visible light irradiation experiments, respectively.

It is widely known that, at thermal equilibrium, azobenzene exists mainly as the *trans* isomers.[11] The ^{1}H NMR data of compounds **1a**−**c** are consistent with this; the signals in the aromatic region (7.0−8.0 ppm) due to the *trans* isomer are predominant (Figures S12, S14, and S16 of the Supporting Information). Based on the analytical HPLC data (Figures S4−S7 of the Supporting Information), 81.8% of **1a** has a *trans* (azo) configuration, and 18.2% adopts the *cis* configuration at thermal equilibrium. Similarly, the molar percentages of *trans* and *cis* configurations were estimated to be 85.6% and 14.4% for compound **1b**, 90.1% and 9.9% for compound **1c**, and 76.2% and 23.8% for compound **2** at thermal equilibrium.

Photoisomerization. As anticipated, photoisomerization can occur to compounds **1a**−**c** and **2** upon UV and visible light irradiation. As an example, Figure 1 shows the absorption spectra of **1a** after UV light irradiation at 365 nm. Obviously, the absorption band around 360 nm gradually decreased, while the absorption bands around 450 nm increased after UV light irradiation. According to previous studies,[11a,b,12] the absorption band around 360 nm is due to the *trans* form of azobenzene moiety while that around 450 nm is ascribed to the *cis* form. Therefore, the absorption spectral variation of **1a** after UV light irradiation indicates the transformation of the *trans*-azobenzene into the *cis*-azobenzene moiety. The photostationary state was reached after UV light irradiation for about 8.0 min. Based on

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(8) See, for example: (a) Muramatsu, S.; Kinbara, K.; Taguchi, H.; Ishii, N.; Aida, T. *J. Am. Chem. Soc.* **2006**, *128*, 3764−3769. (b) Muraoka, T.; Kinbara, K.; Aida, T. *Nature* **2006**, *440*, 512−515. (c) Muraoka, T.; Kinbara, K.; Kobayashi, Y.; Aida, T. *J. Am. Chem. Soc*. **2003**, *125*, 5612−5613. (d) Qu, D.; Wang, Q.; Tian, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 5296−5299. (e) Qu, D.; Wang, Q.; Ren, J.; Tian, H. *Org. Lett.* **2004**, *6*, 2085−2088. (f) Norikane, Y.; Tamaoki, N. *Org. Lett.* **2004**, *6*, 2595−2598. (g) Murakami, H.; Kawabuchi, A.; Kotoo, K.; Kunitake, M.; Nakashima, N. *J. Am. Chem. Soc.* **1997**, *119*, 7605−7606.

(9) (a) Jia, C.; Zhang, D.; Xu, W.; Zhu, D. *Org. Lett.* **2001**, *3*, 1941−1944. (b) Jia, C.; Zhang, D.; Guo, X.; Wan, S.-H.; Xu, W.; Zhu, D. *Synthesis* **2002**, *15*, 2177−2182.

(10) Binet, L.; Fabre, J. M.; Montginoul, C.; Simonsen, K. B.; Becher, J. *J. Chem. Soc., Perkin Trans. 1* **1996**, 783−788.

(11) See, for example: (a) Ruslim, C.; Ichimura, K. *J. Phys. Chem. B* **2000**, *104*, 6529−6535. (b) Aemissegger, A.; Kräutler, V.; van Gunsteren, W. F.; Hilvert, D. *J. Am. Chem. Soc.* **2005**, *127*, 2929−2936. (c) Jousselme, B.; Blanchard, P.; Gallego-Planas, N.; Delaunay, J.; Allain, M.; Richomme, P.; Levillain, E.; Roncali, J. *J. Am. Chem. Soc.* **2003**, *125*, 2888−2889.

(12) Tamai, N.; Miyasaka, H. *Chem. Rev.* **2000**, *100*, 1875−1890 and further references cited therein.

TABLE 1. Molar Percentages (%) of the *Trans* and *Cis* Isomers of Compounds 1a−c and 2 at Thermal Equilibrium and after UV Light (365 nm) Irradiation for 8.0 min, Followed by Visible Irradiation for 15.0 min Based on the Analytical HPLC Results

compd	thermal equilibrium (*trans*/*cis*)	UV light irradiation (*trans*/*cis*)	further vis light irradiation (*trans*/*cis*)
1a	81.8/18.2	39.8/60.2	80.4/19.6
1b	85.6/14.4	26.6/73.4	83.5/16.5
1c	90.1/9.9	9.0/91.0	88.9/11.1
2	76.2/23.8	13.9/86.1	

the reversed-phase HPLC analysis, the photostationary state of **1a** contained 39.8% *trans* isomer and 60.2% *cis* isomer.[13] Further visible light irradiation led to the absorption intensity enhancement for the band around 360 nm and simultaneously induced the decrease of the absorption intensity around 450 nm. The initial absorption spectrum was restored after visible light irradiation for 15 min. The analytical HPLC result showed that the molar ratio between the *trans* isomer and *cis* isomer for the sample of **1a** after sequential UV and visible light irradiation is almost the same as that for the original sample of **1a** before UV light irradiation (see Table 1). The reversible absorption spectral change observed for **1a** can be performed for several cycles as displayed in the inset of Figure 1, where the absorbance variation at 359 nm after alternating UV and visible light irradiations is displayed. But, the photoisomerization process of **1a** exhibits a little fatigue since the absorbance change at 359 nm decreases from 1.43 for the first light irradiation cycle to 1.29 for the fourth light irradiation cycle.

The ^{1}H NMR spectrum of **1a** was measured before and after UV light irradiation. Before UV light irradiation, ^{1}H NMR signals at 7.0−6.7 ppm for the aromatic protons due to the *cis* isomer were rather weak compared to those ascribed to the *trans* isomer. After UV light irradiation, the ^{1}H NMR signal intensities at 7.0−6.7 ppm (due to the *cis* isomer, see Figure S8 of the Supporting Information) increased. This observation is in agreement with the results of absorption spectral studies as discussed above.

Similar absorption spectral variation was also observed for compounds **1b**, **1c**, and **2** (Figures S1−S3 of the Supporting Information). This indicated that the reversible transformation between the corresponding *trans* isomers and *cis* isomers could also occur for compounds **1b**, **1c**, and **2**. The molar percentages of the *trans* and *cis* isomers of compounds **1a**−**c** were listed in Table 1, at thermal equilibrium and after UV light irradiation, followed by visible light irradiation. For compounds **1a**−**c**, by prolonging the length of the spacer the percentage of the *trans* isomer increases at thermal equilibrium. Our explanation is that the disfavored electronic interaction between the nitrogen atom of the *trans*-azobenzene moiety and TTF unit in the case of short spacers favors *cis*-azobenzene instead. At the photostationary state formed by UV light irradiation, the percentage of *cis* isomer increases by prolonging the length of the spacer for compounds **1a**−**c**. The initial composition of *trans* and *cis* isomers of compounds **1a**−**c** can be restored by further visible light irradiation. The molar percentages of the *trans* and *cis* isomers of compound **2** at thermal equilibrium and photostationary state after UV light irradiation were also estimated by analytical HPLC as listed in Table 1.

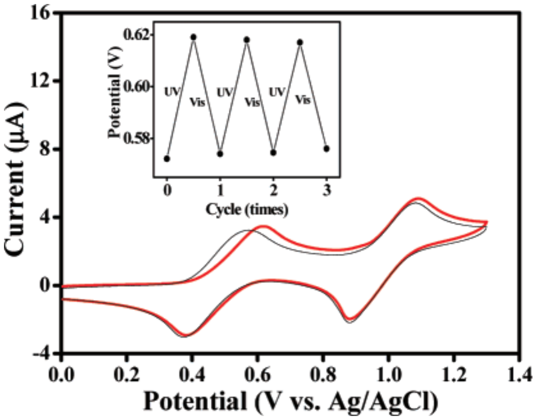

FIGURE 2. Cyclic voltammograms of compound **1a** before (black line) and after UV light (365 nm) irradiation for 8.0 min (red line); inset shows the reversible variation of the peak potential (E_p^1) under alternating UV light (8.0 min) and visible light irradiations (15.0 min); a UV lamp (365 nm, 100 W) and a tungsten lamp (>460 nm, 150 W) were used for the UV and visible light irradiation experiments, respectively.

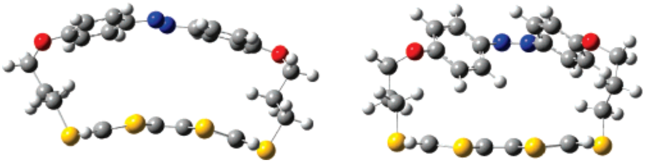

FIGURE 3. Optimized geometries for compound **1a**: *trans* isomer (left) and *cis* isomer (right); the theoretical calculations were performed at the density functional theory (DFT) level with the hybrid B3LYP functional and the 6-31G* basis set, as implemented in the Gaussian-03 package.

Electrochemical and Theoretical Studies. The electron-donating abilities of compounds **1a**−**c** and **2** can be represented by their oxidation potentials, which are related to the corresponding HOMO energies. Thus, oxidation potentials for compounds **1a**−**c** and **2** after UV and visible light irradiation will provide information about their electron-donating abilities. As an example, the cyclic voltammogramms of compound **1a** before and after UV irradiation is shown in Figure 2. Two quasi-reversible redox waves at $E_{ox}^1 = 0.572$ and $E_{ox}^2 = 1.081$ (vs Ag/AgCl) were observed at thermal equilibrium, corresponding to the redox reactions TTF/TTF$^{\cdot+}$ and TTF$^{\cdot+}$/TTF^{2+}, respectively. After the solution of **1a** was exposed to UV light (365 nm) for 8.0 min, the peak potential (E_p^1) of the first anodic wave was shifted to the positive region by ca. 46 mV; the peak potential (E_p^2) of the second anodic wave was also slightly shifted. Interestingly, the initial cyclic voltammogram was almost restored after visible light irradiation for another 15 min. The inset of Figure 2 demonstrates the reversible variation of the E_p^1 upon alternating UV and visible light irradiations. This can be employed to construct a molecular switch with UV/visible light as the inputs and the electrochemical signal as the output. But, the variation of E_p^1 decreases from 46 mV for the first light irradiation cycle to 41 mV for the 3th light irradiation cycle. This is likely due to the little fatigue exhibited by the photoisomerization process of **1a**.

The mechanism underlining the variation of the oxidation potential of **1a** was the conformational change of TTF unit resulting from the *trans* and *cis* transformation of the azobenzene

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[13] Both the *trans* and *cis* isomers are related to the azobenzene moiety.

moiety, according to our DFT study. As shown in Figure 3, the TTF unit in the *trans* isomer of **1a** adopts a nonplanar conformation, whereas that in the *cis* isomer is planar.[14] It was reported early[6] that the conformational change of TTF unit would affect the HOMO energy and therefore the electron-donating ability. Our calculation results indicated that HOMOs of both the *trans* and *cis* isomers of **1a** were mainly located on the TTF unit, and the HOMO energy of the *trans* isomer was found to be higher than that of the *cis* isomer ($E_{\mathrm{HOMO}} = -4.75$ eV for the *trans* isomer, and $E_{\mathrm{HOMO}} = -4.77$ eV for the *cis* isomer). This is consistent with our experimental results as discussed above.

The oxidation potentials of compounds **1b**−**c** and **2** were also measured after UV and visible light irradiation. The E_p^1 of **1b** was anodically shifted by ca. 30 mV after UV light irradiation for 8.0 min, and the E_p^2 remained almost unchanged (Figure S9 of the Supporting Information). For compound **1c** in which the spacer was further extended, the variation of both E_p^1 and E_p^2 was found to be rather negligible after UV light irradiation (Figure S10 of the Supporting Information). These results may be due to the fact that a longer spacer will reduce the influence of the *trans* and *cis* transformation of the azobenzene unit on the electronic property of the TTF unit. It is interesting to note that almost no oxidation potential change was detected after UV light irradiation for compound **2**, in which the azobenzene moiety was linked to the TTF unit in a side manner (Figure S11 of the Supporting Information). This result implies that it may not be probable to modulate the electronic property of TTF unit by modifying the TTF unit in the side manner.

New heterocyclic TTF compounds **1a**−**c** and **2** with azobenzene moiety were synthesized and characterized, with a view to modulating the electronic property of TTF unit by light irradiation and developing new molecular switches that can carry out the electronic transduction of optical signals. Absorption and ^{1}H NMR spectral studies show that photoisomerization of azobenzene units in compounds **1a**−**c** and **2** can occur easily. The oxidation potential of **1a** can be shifted anodically after UV light irradiation, and the variation of the oxidation potential can be reversibly realized by alternating UV and visible light irradiation. As a result, a molecular switch is achieved with UV/visible light as the inputs and the electrochemical signal as the output. Moreover, it was found that the influence of the azobenzene photoisomerization on the electronic property of the TTF unit became attenuated by prolonging the spacer for compounds **1a**−**c**. It is also interesting to note that it may not be probable to modulate the electronic property of TTF unit by modifying the TTF unit in the side manner.

Experimental Section

Synthesis of Compound 1a. To a solution of **5** (0.10 g, 0.27 mmol) in anhydrous degassed DMF (50 mL) was added a solution of $CsOH \cdot H_2O$ (0.10 g, 0.53 mmol) in anhydrous degassed MeOH (5 mL) over a period 30 min. The mixture was stirred for an additional 30 min. The above solution and a solution of compound **4a** (0.12 g, 0.27 mmol) (see the Supporting Information) in anhydrous degassed THF (50 mL) were added simultaneously over 8 h at room temperature to 200 mL of anhydrous degassed DMF under stirring. The solution was then stirred overnight, and the reaction mixture was concentrated in vacuum. The residue was the dissolved in CH_2Cl_2 (150 mL) and washed with water (3 × 100 mL). The orange phase was dried (Na_2SO_4) and concentrated to afford orange solid. Then, the residue was purified by column chromatography using ethyl acetate/CH_2Cl_2/petroleumether (1:1:10) as eluant, affording compound **1a** as a yellow powder (0.04 g, 26.5%): mp 160−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$, *trans* isomer) δ 7.92 (d, $J = 8.68$ Hz, 4H), 7.08 (d, $J = 8.76$ Hz, 4H), 5.56 (s, 2H), 4.41 (t, $J = 5.6$ Hz, 4H), 2.69 (t, $J = 6.0$ Hz, 4H), 2.04 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 147.7, 125.8, 124.8, 124.6, 118.8, 118.0, 117.6, 66.3, 30.9, 29.7; IR (KBr pellet) 2923, 2854, 1597, 1494, 1234, 1144, 1023, 847 cm^{-1}; HRMS calcd for $C_{24}H_{22}N_2O_2S_6$ [M$^+$] 562.0006, found 562.0004.

The synthesis and characterization of compounds**1b**,**c** and **2** were provided in the Supporting Information.

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Supporting Information Available: Experimental procedures and characterization data (absorption spectra, HPLC, CV, ^{1}H NMR, ^{13}C NMR, and computational data). This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] The calculation details are provided in the Supporting Information.