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A New Redox-Fluorescence Switch Based on a Triad with Tetrathiafulvalene and Anthracene Units

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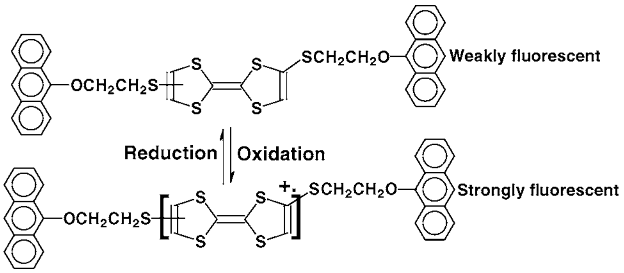
ABSTRACT



The fluorescence of a triad with TTF and anthracence units can be reversibly modulated by sequential oxidation and reduction. Thus, a new redox fluorescence switch can be established on the basis of this new triad.

Since the synthesis of tetrathiafulvalene (TTF),[1] TTF and its derivatives have been intensively investigated as building blocks of organic conductors and even superconductors.[2] In recent years, electron donor−acceptor (D−A) molecules featuring TTF units have received a lot of attention.[3] For instance, D−A molecules containing TTF units have been studied as models for fundamental investigation of charge-transfer interactions and molecular rectifiers.[4] The dyads composed of TTF and C60 have also been subjected to studies as potential materials for solar cell devices.[5] To complete the story, it should be mentioned that TTF units have been widely employed in the construction of catenanes and rotaxanes, which can function as molecular level devices.[6]

One of the distinct properties of TTF-type electron donors is that they can be oxidized to the corresponding cation radical and dication species sequentially and reversibly within a very accessible potential window. Thus, the electron-donating abilities of these TTF-type donors can be reversibly

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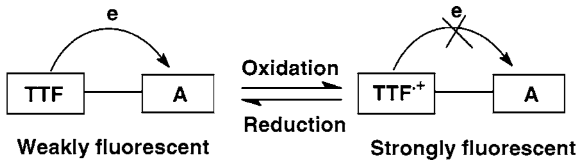
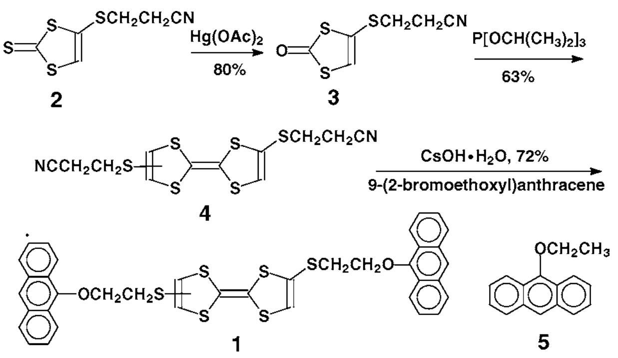
Scheme 1. Illustration of the Redox Fluorescence Switch Based on a TTF-Type Electron Donor



modulated by chemical or electrochemical redox reactions. By taking advantage of this property of TTF-type donors, it is possible to establish a new redox-fluorescence switch based on D−A molecules, in which D is a TTF unit and A is the acceptor unit that fluoresces intrinsically. The working mechanism for such a redox fluorescence switch is proposed as follows (Scheme 1): (1) due to the photoinduced electron transfer (PET) reaction from the TTF unit to the excited state of the A unit, these D−A molecules show weak fluorescence before oxidation; (2) after oxidation, the electron-donating abilities of TTF units are reduced, and as a result the PET reaction would be arrested, leading to fluorescence enhancement; (3) reduction of the cation of TTF to the neutral TTF unit would result in a decrease in the fluorescence. As the transformation between TTF and the cation radical of TTF can be reversibly carried out, such fluorescence switches should be able to operate reversibly.

To prepare such TTF-based redox-fluorescence switches, rational selection of the fluorescent acceptor unit is crucial. At least the following considerations should be taken into account when choosing the acceptor unit: (1) the fluorescence spectrum of this acceptor unit should not be overlapped largely with the absorption spectrum of the corresponding cation radical of TTF unit. Otherwise, intramolecular energy transfer would occur efficiently, and thus the expected fluorescence enhancement would not be observed.[7] (2) The reverse electron transfer from A* to $TTF^{\cdot +}$ cannot take place. If such electron transfer occurs, the fluorescence of the D−A molecules cannot be reversibly modulated by redox reaction.[8] There are only a few reports about TTF-based fluorescence switches, one of which is based on a mono-TTF-annulated porphyrin described recently by Becher et al.[9] Herein we will report the synthesis, electrochemical, and spectral studies of a new triad **1** consisting of one TTF unit and two anthracene units. The results show that a new redox fluorescence switch based on the new triad **1** can be constructed.

Scheme 2. Synthesis of Triad **1** and the Chemical Structures of Reference Compounds



Synthesis of triad **1** started from compound **2** (Scheme 2), which was prepared on the basis of the unusual reaction of Zn(dmit)$_2$ anion reported by us recently.[10] Conversion of **2** to **3** with the routine procedure and further coupling in the presence of tri(isopropyl)phosphite led to compound **4**. Deprotection of 2-cyanoethyl groups with the aid of CsOH and sequentially reaction with 9-(2-bromoethoxyl) anthracene afforded triad **1**[11] in a total yield of 36% after purification with column chromatography. There were two isomers (cis- and trans-) for triad **1**, and it was difficult to separate them with column chromatography. But this would not affect the spectral studies of triad **1** discussed below.

Redox Potentials of Triad 1. The redox potentials of triad **1** were measured with cyclic voltammetry. Two reversible oxidation waves with $E^1_{1/2}$ (Ox) = 0.67 V (0.66 V vs SCE) and $E^2_{1/2}$ (Ox) = 0.85 V (0.89 V vs SCE) and one irreversible oxidation wave around 1.43 V (1.42 V vs SCE) were detected as shown in Figure 1. Comparative studies with compounds **4** and **5** indicated that the oxidation peaks at 0.67 and 0.85 V corresponded to the oxidation of TTF unit to the cation radical and dication, respectively, while the irreversible

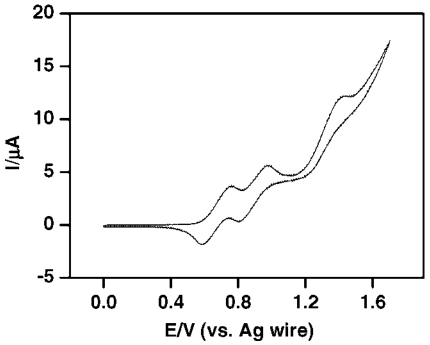


Figure 1. Cyclovoltammogram of triad **1** (scanning rate 50 mV/s) with platinum wires as working and counter electrodes, respectively, Ag wire as a reference electrode, and *n*-Bu4NPF6 as a supporting electrolyte.

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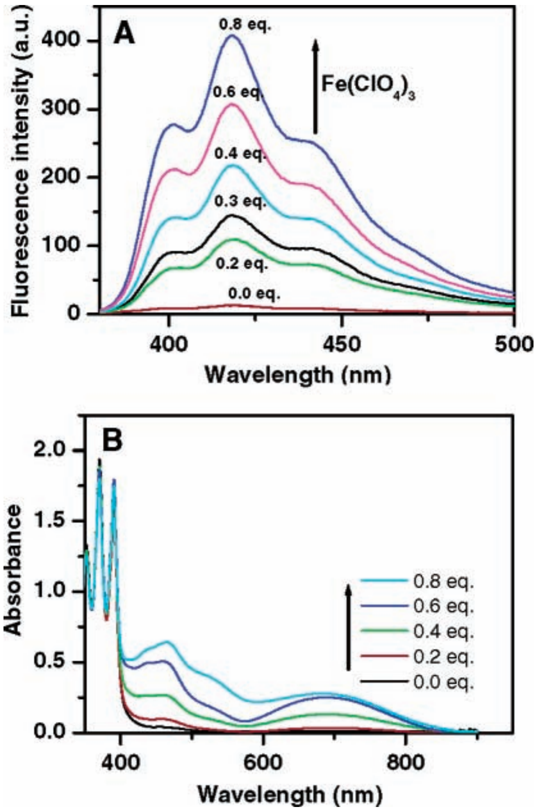

Figure 2. (A) Fluorescence spectra of triad **1** (5. 8 × 10^{-5} M) in THF in the presence of different amounts of Fe(ClO$_4$)$_3$. (B) Absorption spectra of triad **1** (5. 8 × 10^{-5} M) in THF in the presence of different amounts of Fe(ClO$_4$)$_3$.

oxidation peak was due to the oxidation of the anthracene unit. In addition, an irreversible reduction wave (−1.89 V) was observed for triad **1**, and this was ascribed to the reduction of anthracene unit.

As compared to compound **5**, triad **1** showed rather weak fluorescence (the one with the symbol of “0.0 eq.” in Figure 2A). Since the spectral overlap between the fluorescence spectrum of compound **5** and the absorption spectrum of compound **4** is negligible, the possibility that the observed fluorescence quenching is due to resonance energy transfer can be ruled out. The free energy (ΔG_{PET}) for the photoinduced electron transfer from the TTF unit to the anthracene unit is estimated to be −0.70 eV.[12] Such a negative value of ΔG_{PET} indicates that the photoinduced electron transfer from the TTF unit to anthracene units is thermodynamically favorable. Thus, it might be concluded that the quenching of the fluorescence of anthracene units in triad **1** is mainly due to the photoinduced electron-transfer reaction.

Addition of Fe(ClO$_4$)$_3$ to the solution of triad **1** led to fluorescence enhancement, and the fluorescence intensity increased with the increasing amounts of Fe(ClO$_4$)$_3$ added to the solution (Figure 2A).[13] Concomitantly, new absorptions in the range of 460−850 nm appeared (Figure 2B). Likewise, the absorption intensities of these new absorption bands became large by increasing the amounts of Fe(ClO$_4$)$_3$ added to the solution. According to previous results,[14] the absorption bands with $\lambda_{\max} = 464$ and 694 nm are ascribed to the cation radical of TTF unit and the corresponding π-dimer of the cation radical of TTF unit, respectively. This is in agreement with previous reports.[15] As the electron-donating ability of the cation radical of TTF unit is lowered compared with the neutral TTF unit, the corresponding photoinduced electron transfer would become less favorable. As a result, the fluorescence of triad **1** would be enhanced, which is in accordance with the experimental result as mentioned above (see Figure 2A).[16]

It seems that the two possible fluorescence quenching mechanisms do not occur for triad **1**: the ΔG_{PET} for the reverse electron-transfer process from the excited anthracene unit to the cation radical of TTF unit was estimated to be −2.5 eV.[17] Such a large negative value of ΔG_{PET} would position this electron-transfer reaction in the inverted region of the Marcus parabola. As displayed in Figure 2A and Figure 2B, the spectral overlap between the absorption spectrum of the cation radical of TTF unit and the fluorescence spectrum of anthracene unit is small. Consequently, the resonance energy transfer from the excited state of anthracene to the cation radical of TTF unit cannot take place efficiently. These results demonstrate the possibility of constructing a new redox fluorescence switch based on triad **1**, as the transformation between the neutral TTF unit and the cation radical can be operated reversibly. To test this possibility, spectroelectrochemical studies[18] were performed for triad **1**.

Oxidation of the solution of triad **1** containing n-Bu$_4$NPF$_6$ (27.8 mM), which was performed by applying an oxidation

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(11) Characterization data of dyad **1**: mp 155−157 °C.; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.50 (t, 4H), 4.33 (t, 4H), 7.08 (s, 2H), 7.56 (m, 8H), 8.11 (m, 4H), 8.33 (m, 4H), 8.43 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 35.91, 73.37, 112.37, 122.14, 123.36, 124.53, 125.39, 125.48, 126.32, 126.38, 128.42, 132.30, 150.23; MALDI-TOF 708.2 (M$^+$). Anal. Calcd for $C_{38}H_{28}S_6O_2$: C, 64.37; H, 3.98; S, 27.13. Found: C, 64.15; H, 3.85; S, 27.39.

(12) This was calculated with the Rehm−Weller equation: $\Delta G_{\mathrm{PET}} = -E(\mathrm{ex}) - E(\mathrm{red}) + E(\mathrm{ox}) - e^2/\epsilon r$, with $E(\mathrm{ox}) = 0.67$ eV, $E(\mathrm{red}) = -1.89$ eV, $\lambda(\mathrm{ex}) = 370$ nm, and $e^2/\epsilon r = -0.1$ eV. See: a) Rehm, D.; Weller, A. *Isr. J. Chem.*, **1970**, *8*, 259. (b) Grabowski, Z. R.; Dobkowski, J. *Pure Appl. Chem.* **1983**, *55*, 245.

(13) It should be mentioned that the fluorescence intensity of the solution of triad **1** would decrease if more than 1 equiv of Fe(ClO$_4$)$_3$ was employed. This may be due to the fact that additional ferric ion can quench the fluorescence of anthracene units. A control experiment with compound **5** supported this conclusion.

(14) Spanggaard, H.; Prehn, J.; Nielsen, M. B.; Levillain, E.; Allain, M.; Becher, J. *J. Am. Chem. Soc.* **2000**, *122*, 9486 and references cited therein.

(15) Asakawa M.; Higuchi, M.; Mattersteig, G.; Nakamura, T.; Pease, A. R.; Raymo, F. M.; Shimizu, T.; Stoddart, J. F. *Adv. Mater.* **2000**, *12*, 1099.

(16) However, this result is different from that of the previous report, in which the quenching of the fluorescence of anthracene derivative by the cation radical of TTF unit was implied. See: (a) ref 8. (b) De Cremiers, H. A.; Clavier, G.; Ilhan, F.; Cooke, G.; Rotello, V. M. *Chem. Commun.* **2001**, 2232.

(17) This was again calculated with the Rehm−Weller equation: $\Delta G_{\mathrm{PET}} = -E(\mathrm{ex}) - E(\mathrm{red}) + E(\mathrm{ox}) - e^2/\epsilon r$, with $E(\mathrm{ox}) = 1.43$ eV, $E(\mathrm{red}) = 0.67$ eV, $\lambda(\mathrm{ex}) = 370$ nm, and $e^2/\epsilon r = -0.1$ eV.

(18) Spectroelectrochemical experiments were performed in a quartz cell. Thin-plates of platinum were used as working and counter electrodes, while Ag wire acted as the reference electrode. THF, which was treated with sodium, followed by careful distillation before use, and n-Bu$_4$NPF$_6$ (27.8 mM) were employed as the solvent and the supporting electrolyte, respectively. The fluorescence spectra were recorded with a Hitachi spectrophotometer (model F-4500). The potential was applied with a potentiostat EGDG PAR 370 system.

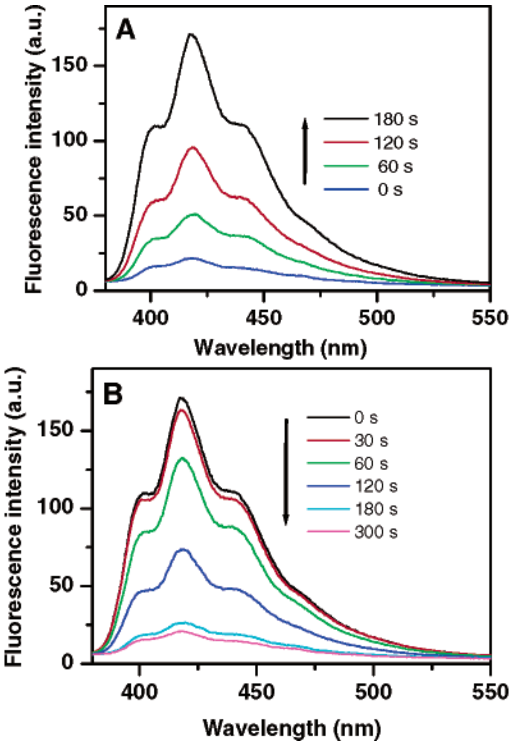

Figure 3. (A) Fluorescence spectra of the solution of triad **1** in THF (4.94×10^{-5} M) containing *n*-Bu_4NPF_6 (27.8 mM) after applying an oxidation potential of 0.7 V (vs Ag wire). (B) Fluorescence spectra of the solution of triad **1** that had been oxidized electrochemically for 3.0 min after applying a reduction potential of 0.2 V (vs Ag wire).

potential of 0.70 V (vs Ag wire) to the solution, led to fluorescence enhancement for triad **1** as shown in Figure 3A. The fluorescence intensity of the solution gradually increased with the time of the electrochemical oxidation.

Obviously, such fluorescence enhancement is due to the transformation of the neutral TTF unit into the corresponding cation radical, since the oxidation potential (0.70 V vs Ag wire) employed for the above experiment is higher than that of the first oxidation potential of TTF unit of triad **1** determined by cyclic voltammetry (see Figure 1). Considering the oxidation potential of the anthracene units of triad **1** (see Figure 1), the anthracene units should not be affected under this electrochemical condition. Interestingly, application of a reduction potential of 0.2 V (vs Ag wire) to the solution to which an oxidation potential was applied for 3.0 min resulted in the gradual decrease of the fluorescence intensity of the solution (Figure 3B). After the electrochemical reduction was carried out for 5.0 min, the initial fluorescence spectrum of the solution (before applying an oxidation potential) was almost recovered completely. This fluorescence change can be understood as follows: by reference to the cyclic voltammogram of triad **1** (Figure 1), the cation radical of the TTF unit generated during the oxidation process would be reduced to the neutral unit by applying a potential of 0.2 V (vs Ag wire) to the solution. Consequently, the photoinduced electron transfer from TTF unit to the anthracene unit would occur efficiently again, leading to the fluorescence decrease for the solution of triad **1**. Therefore, the fluorescence intensity of the solution of triad **1** can be reversibly modulated by sequentially applying oxidation and reduction potentials to the solution. As a result, a new redox fluorescence switch can be established on the basis of triad **1** by taking the advantage of the peculiar properties of the TTF-type electron donor.

In summary, the synthesis and spectral as well as spectroelectrochemical studies of a new triad **1** are presented. Chemical oxidation can lead to the fluorescence enhancement for the solution of triad **1**. More importantly, the fluorescence intensity of the solution of triad **1** can be reversibly modulated by the sequential electrochemical oxidation and reduction. Therefore, a new redox fluorescence switch can be established on the basis of triad **1**. Such unique behavior of triad **1** should be ascribed to the special spectral and redox properties of both TTF and anthracene units. Synthesis and investigations of new TTF-based dyads and triads with other fluorescent cores such as pyrene are underway. These new dyads may find potential application in sensing of oxidants of biological interests.

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Supporting Information Available: Experimental conditions, measuring techniques, and the synthetic approach to triad **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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