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Novel redox-fluorescence switch based on a triad containing tetrathiafulvalene and pyrene units with tunable monomer and excimer emissions

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The ratio of monomer and excimer emissions of a triad **1** with tetrathiafulvalene (TTF) and pyrene units could be reversibly modulated by the different oxidation states of the TTF unit. The working mechanism of this new fluorescence switch was demonstrated to be the collective result of the tunable photoinduced electron transfer and resonance energy transfer processes.

Introduction

Molecular or supermolecular systems containing redox and photoactive entities have received considerable attention in the past decade, which are subjects for the studies of the process of electron and energy transfer at molecular or supermolecular level as well as for the developing of redox and optoelectronic devices. If a tunable electron or energy transfer process can be achieved in the above system, it will provide a means for a molecular switch. Recently, much effort has been devoted to the development of molecular fluorescence switches because of the high sensitivity of luminescence signals.[1] Besides the main achievement of employing transition metal redox couples as triggers for the adjustment of luminescence of light-emitting-fragments,[2] several fluorescence switches containing tetrathiafulvalene (TTF) moieties as the redox center have been demonstrated very recently.[3]

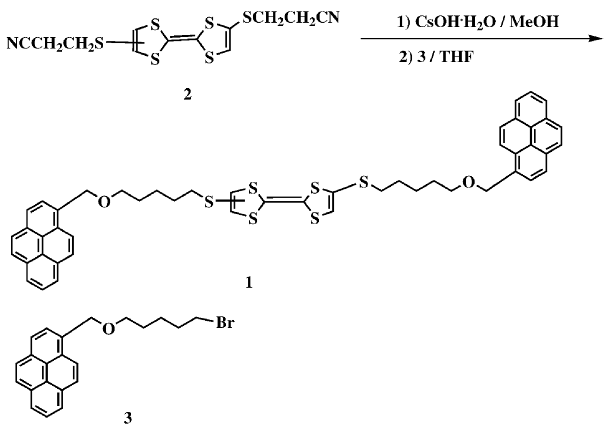
As a fluorogenic unit, pyrene is one of the most useful fluorescence probes because of its relatively efficient excimer formation and emission.[4] It has been widely used as a signal unit for the construction of fluorescent chemosensors.[5] Since the intensity ratio of the excimer to the monomer emission (I_E/I_M) is sensitive to conformational changes of the pyrene-appended molecules, changes in I_E/I_M upon recognition of guest molecules or ions can be an informative parameter in various sensing systems.[6] But, molecules containing pyrene units that can produce changes in I_E/I_M upon electrochemical stimulation have not been reported yet. Here, we present a novel example of redox fluorescence switch based on TTF and pyrene units, compound **1**, for which the fluorescence intensity of the monomer and excimer emissions could be reversibly modulated by electrochemical oxidation and reduction. This is the first example where the pyrene I_E/I_M ratio can be adjusted *via* an electrochemical method. In this paper, the synthesis, electrochemical, and spectral studies of triad **1** are described.

Result and discussion

Syntheses of triad **1** were started from compound **2**[3a,7] (Scheme 1). Removal of the 2-cyanoethyl group with the aid of CsOH and sequential reaction with 5-(methylpyrenyl)oxy-1-bromopentane(**3**) afforded triad **1** in a yield of 23% after purification with column chromatography. There were two isomers (*cis*- and *trans*-) for the triad **1**, and it was difficult to separate them with column chromatography. But this did not affect the spectral studies of triad **1**.

The fluorescence spectrum of neutral triad **1** was recorded in diluted solutions (5×10^{-6} M in acetonitrile) with $\lambda_{ex} = 337$ nm. Both the monomer emissions at 370–430 nm with well resolved vibronic features and broad featureless excimer emission at 480 nm could be observed with $I_E/I_M = 2.44$ (Fig. 1). This was different from it precursor compound **3**, for which only strong monomer bands could be observed under the same concentration. Judging from the concentration of fluorophore and the dilution experiment, in which the intensities of fluorescence of monomer and excimer decreased simultaneously on dilution, the excimer emission of triad **1** should be attributed to intramolecular π–π stacking of two pyrene rings.

As a strong electron donor, when a TTF unit was connected with an electron acceptor moiety that fluoresces intrinsically, photoinduced electron transfer (PET) from TTF to acceptor group would result in fluorescence quenching. The fluorescence would then be recovered by chemical or electrochemical oxidation of the TTF unit. This mechanism has already been employed for the construction of molecular fluorescence



Scheme 1 Synthesis of triad **1**.

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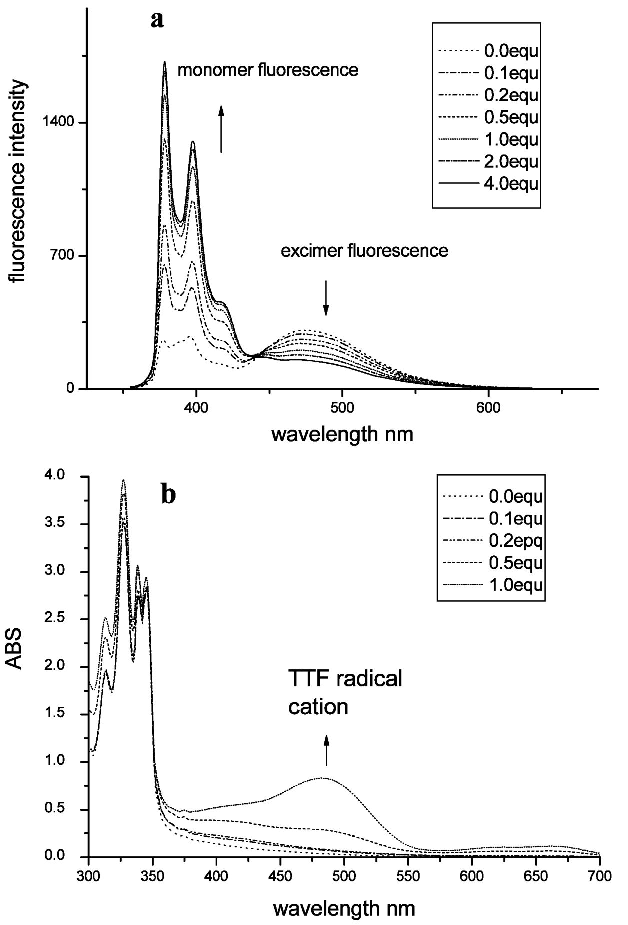


Fig. 1 (a) Fluorescence spectra of triad **1** (5×10^{-6} M) in CH_3CN in the presence of different amounts of $Fe(ClO_4)_3$. Excitation wavelength was 337 nm. (b) Absorption spectra of triad **1** (5×10^{-6} M) in CH_3CN in the presence of different amounts of $Fe(ClO_4)_3$.

switches using porphyrin, phthalocyanine and anthracene as photoactive units, respectively.[3] We supposed that in triad **1**, the photo induced electron transfer from TTF unit to the excited pyrene should also contribute to the quenching of the monomer emission beside the intramolecular excimer formation. In order to confirm this hypothesis, the free energy (ΔG_{PET}) for the photoinduced electron transfer from TTF unit to the pyrene unit was calculated based on the redox potentials of **1** determined by electrochemical method, $\Delta G_{PET} = -0.82$ eV.[8] Such a negative value of ΔG_{PET} indicates that the photoinduced electron transfer from the TTF unit to the pyrene units is thermodynamically favorable. The following computer simulation and chemical and electrochemical oxidation experiments can support this hypothesis further. Meanwhile, the pyrene excimer emission was less sensitive to electron-transfer quenching than the pyrene singlet monomer,[9] which was not affected by the PET process. It can be concluded that the higher I_E/I_M value of neutral triad **1** was a collective result of the formation of excimer and PET process.

In order to test the possibility of **1** to act as a fluorescence switch, chemical oxidation of the TTF unit was performed using $Fe(ClO_4)_3$ as oxidant. As shown in Fig. 1, upon addition of $Fe(ClO_4)_3$, the intensity of monomer emission increased dramatically with the increasing of the amount of $Fe(ClO_4)_3$, meanwhile the intensity of the excimer emission decreased. And the I_E/I_M ratio decreased from the initial value of 2.44 to 0.46 when 1.0 equivalent $Fe(ClO_4)_3$ was added. It was noted that no isoemission point could be observed in these spectra. This should be due to the fact that triad **1** is a mixture of *cis*- and *trans*-isomers. The UV-Vis spectra of triad **1** upon addition of $Fe(ClO_4)_3$ were recorded simultaneously. A new band

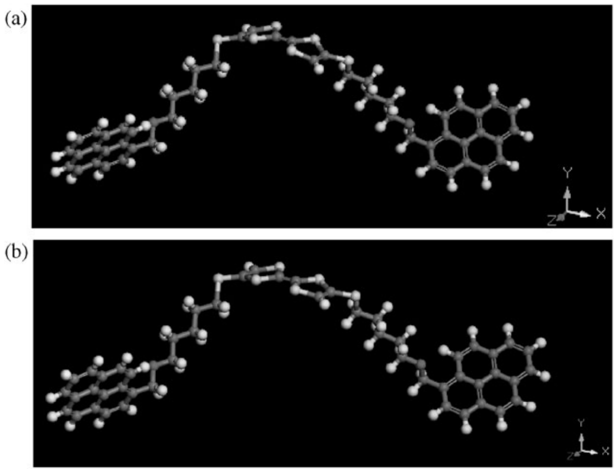
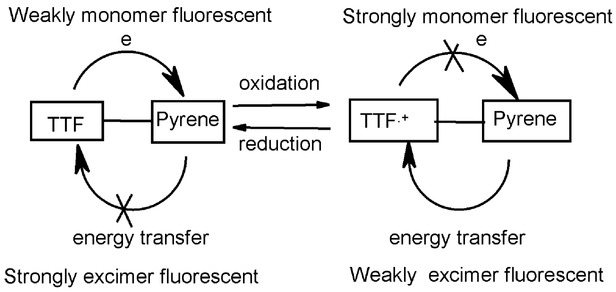


Fig. 2 The computational-optimized geometry of *trans*-isomer of triad **1**(a) and its radical cation $\mathbf{1}^{+}$(b).

corresponding to the formation of TTF radical cation (λ_{max} = 480 nm) appeared,[10] and the absorption bands of the pyrene unit remained almost unchanged (Fig 1b).

Studies on the conformational changes of triad **1** (*trans*-isomer) before and after oxidation were carried out by *ab initio* calculations.[11] The energy-minimized structures of **1** and its radical cation are shown in Fig. 2. In the neutral molecule, the TTF unit adopted a boat conformation with the five-membered ring folded along the S–S vector with a dihedral angle of 161.6°, and the two pyrene sidearms spread from the TTF core in opposite directions. After oxidation, no significant conformation changes could be observed except the dihedral angle of the five-membered ring of the TTF unit increased to 168.6°. As the flexibility of the alkyl ether bridge would not be affected by the oxidation of the TTF unit, the probability of two pyrene rings forming intramolecular π–π stacking will not be affected. So, conformational changes can be ruled out for the I_E/I_M changes. These I_E/I_M changes may be explained as a collective result of the inhibition of the PET process and occurrence of a resonance energy transfer process. As the electron-donating ability of the cation radical of the **TTF** unit is lower than that of the neutral **TTF** unit, after oxidation the corresponding PET would be less favorable, and the monomer emission enhanced. And the absorption spectrum of the **TTF** cation radical being largely overlapped with the excimer emission of pyrenes,[10] resonance energy transfer from excimer pyrene to cation radical **TTF** took place efficiently. As a result, the excimer emission decreased.

The mechanism of the above modulation of the I_E/I_M ratio can be outlined in Scheme 2. (1) Due to the PET reaction from the TTF unit to the excited state of the pyrene unit and the formation of excimer, the molecule shows weak monomer fluorescence and strong excimer emission. Since the spectral overlap between the fluorescence spectrum of pyrene and the absorption of **1** is negligible, the possibility that the observed



Scheme 2 Illustration of the redox fluorescence switch based on the triad **1**.

fluorescent quenching resulted from resonance energy transfer can be ruled out; (2) after oxidation; the electron-donating abilities of TTF units are reduced. The PET reaction would be arrested, leading the monomer fluorescence enhancement. Meanwhile, as the excimer emission spectrum is largely overlapped with the absorption spectrum of the TTF cation radical, the resonance energy transfer can occur efficaciously. As a result, the excimer fluorescence becomes weak. Reduction of the cation of TTF to the neutral TTF unit would result in a decrease in the monomer fluorescence and an enhancement of excimer fluorescence. As the transformation between TTF and the TTF cation radical can be reversibly carried out, such a fluorescence switch should be able to operate reversibly. To test this possibility, spectroelectrochemical studies were performed for triad **1**.

Electrochemical oxidation of triad **1** was performed by applying an oxidation potential of 0.60 V (*vs.* Ag wire) to the solution of **1** in acetonitrile (25.0 mM) containing *n*-Bu_4NPF_6 (0.1 M) as supporting electrolyte. The intensity of monomer emission increased gradually with the increasing time of electrochemical oxidation, while the fluorescence intensity of excimer emission decreased gradually. After applying the oxidation potential for 20 seconds no obvious changes were observed in the fluorescence spectra. Interestingly, application of a reduction potential of 0.3 V (*vs.* Ag wire) to the solution which had been electrochemically oxidized for 30 seconds, resulted in the recovery of fluorescence to its neutral state. The fluorescence was almost recovered after the reduction potential was applied for 20 seconds (Fig. 3b).

Obviously, these fluorescence changes were related to the different oxidation states of the TTF unit. Since the oxidation potential employed (0.6 V *vs.* Ag wire) is slightly higher than that of the first oxidation potential of TTF unit in triad **1** (0.5 V *vs.* Ag wire), TTF radical cation generated during the oxidation process, while the pyrene unit remained unchanged due to a much higher oxidation potential (1.25 V *vs.* Ag wire). When a reduction potential was applied the cation radical of the TTF unit would be reduced to the neutral state. So the PET from TTF unit to pyrene unit can be turned off and on sequentially, due to the different donating abilities of the neutral TTF unit and TTF radical cation. Meanwhile, the resonance energy transfer from the excimer emission to TTF radical cation was turned on and off sequentially, due to the appearance or disappearance of the absorption band of the TTF radical cation. Consequently, the I_E/I_M change would occur again and again as the oxidation state of TTF unit changed. As a result, a reversible redox fluorescence switch can be established on the basis of triad **1** by using the peculiar properties of the TTF-type donor.

In conclusion, the synthesis and spectral as well as spectroelectrochemical studies of a new triad **1** have been presented. Chemical oxidation results in modulation of the ratio of monomer/excimer fluorescence intensity. More importantly, the ratio can be reversibly adjusted by sequential electrochemical oxidation and reduction. Therefore a new redox fluorescence switch with tunable I_E/I_M ratio of pyrene emissions can be established on the basis of triad **1**. Such unique behavior of triad **1** was ascribed to the special spectral and redox properties of both TTF and pyrene units. In this molecule, the PET reaction and resonance energy transfer process influenced the pyrene emissions alternately due to the different oxidation states of TTF units. These new triads may find potential application in sensing of oxidants of biological interest.

Experimental

General: melting points were measured with microscope apparatus and uncorrected. ^{1}H-NMR spectra were recorded on a BRUCK300 MHz instrument and ^{13}C-NMR spectra were recorded on a BRUCK300 MHz instrument. TOF-MS spectra were determined with BEFLEX III. Elemental analyses were performed on a Carlo-Erba-1106 instrument.

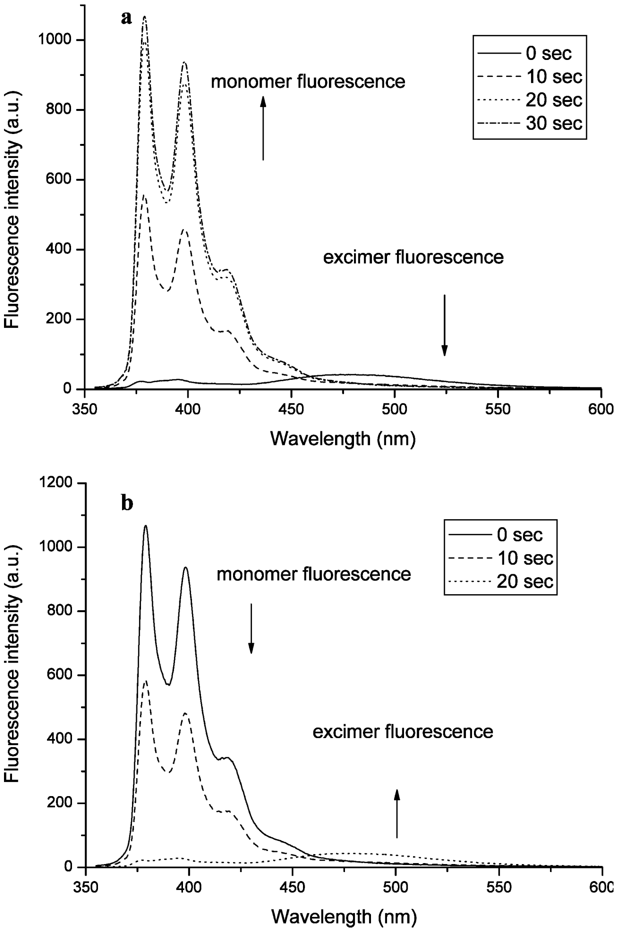


Fig. 3 (a) Fluorescence spectra of triad **1** (5×10^{-6} M) in CH_3CN containing *n*-Bu_4NPF_6 (25 mM) after applying an oxidation potential of 0.7 V (*vs.* Ag wire). (b) Fluorescence spectra of the solution of triad **1** that had been oxidized electrochemically for 30 seconds after applying a reduction potential of 0.3 V (*vs.* Ag wire). Excitation wavelength was 337 nm.

Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer. Fluorescence measurements were carried out with a Hitachi (model F-4500) spectrophotometer in a 1 cm quartz cell. Cyclic voltammetric measurements were carried out on an EGDG PAR 370 system with platinum as the working and counter electrodes, and Ag wire as the reference electrode, and *n*-Bu_4NPF_6 (25 mM) as supporting electrolyte.

Synthesis of triad **1**: To a solution of 4,4′(5′)-bis(2-cyanoethylthio)tetrathiafulvalene (0.19 g, 0.51 mmol) in anhydrous degassed THF (50 ml) was added a solution of $CsOH \cdot H_2O$ (0.20 g, 1.15 mmol) in anhydrous degassed MeOH (5 ml) over a period of 30 min. The mixture was stirred for another 30 min, to which a solution of compound **3** (5-(methylpyrenyl)-oxy-1-bromopentane) (0.39 g 1.02 mmol) in anhydrous degassed THF (10 ml) was added. The solution was stirred overnight. After removing solvents under reduced pressure and separation by column chromatography, compound triad **1** was obtained as a light yellow solid (0.10 g). Mp: 142–144 °C; ^{1}H NMR ($CDCl_3$): δ: 8.01 (m 18H), 6.24 (s 2H), 5.20 (s 4H), 3.57 (p 4H), 2.70 (t 4H), 1.63 (p 4H), 1.47 (p 4H), 1.29 (p 4H); ^{13}C NMR ($CDCl_3$): 24.1, 28.1, 31.6, 32.8, 70.1, 71.8, 113.7, 123.0, 124.0, 124.3, 124.5, 124.8, 124.9, 125.5, 126.5, 126.8, 126.9, 127.0, 127.2, 128.9, 130.4, 130.8, 131.2, 150.5; MALDI-TOF MS: 868.2; Calcd. for $C_{50}H_{44}S_6O_2$: C, 69.11; H, 5.07; S, 11.06; Found: C, 69.38; H, 5.28; S, 10.70%.

Redox potentials of triad **1**: Electrochemical studies used cyclic voltammetry. Two reversible oxidation waves with

$E_1^{1/2} = 0.50$ V (*vs.* Ag wire), $E_2^{1/2} = 0.95$ V (*vs.* Ag wire), one irreversible oxidation wave around 1.29 V (*vs.* Ag wire) were detected. Comparative studies with compounds **2** and **3** indicated that the oxidation peaks at 0.50 and 0.95 V corresponded to the oxidation of the TTF unit to the cation radical and dication, respectively, and the irreversible oxidation and reduction wave were ascribed to the pyrene unit. In addition an irreversible reduction wave -2.11 V was observed for triad **1**, and this was ascribed to the reduction of the pyrene unit.

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 as the solvent, n-Bu_4NPF_6 (25 mM) were employed as 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.

The quantum chemical calculations were carried out with LDA-DFT as implemented in the DMol3 package. The basis set chosen is the double numerical plus d-function (DND). The local functional for the exchange correlation potential is the Perden-Wang LDA functional (PWC).[11]

Acknowledgements

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