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Highly conjugated donor–acceptor dyad based on tetrathiafulvalene covalently attached to porphyrin unit

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ABSTRACT

A novel and highly conjugated donor–acceptor dyad consisting of tetrathiafulvalene unit covalently attached to a porphyrin unit has been synthesized and characterized. As compared to tetraphenylporphyrin, the fluorescence intensity and lifetime of the dyad was decreased owing to photoinduced electron transfer between the tetrathiafulvalene and porphyrin units in the excited state. The fluorescence intensity of the dyad was recovered dramatically upon the addition of $Fe(ClO_4)_3 \cdot 6H_2O$ to a solution of the dyad, and the fluorescence intensity grows with an increasing amount of $Fe(ClO_4)_3 \cdot 6H_2O$. More importantly, the fluorescence intensity of the dyad can be reversibly modulated by the sequential electrochemical oxidation and reduction of the tetrathiafulvalene unit, thus a new redox fluorescence switch based on this dyad has been constructed.

1. Introduction

Porphyrin derivatives have been widely used in biochemistry, medicine, analytical chemistry, sensors, molecular recognition, reaction catalysis, and functional materials because of their unique physical and chemical performance [1]. In recent years, donor–acceptor (D–A) compounds incorporating porphyrin and other molecules, such as fullerenes and quinones [2], have played a conspicuous role in artificial light-harvesting antenna [3], photosynthetic reaction centers [4], photonic wires [5], and molecular switches [6].

Since tetrathiafulvalene (TTF) was synthesized by Wudl et al. [7], it and its derivatives have been intensively investigated [8]. The covalent association of other functional groups (acceptor) with a strong electron donor-TTF unit can form D–A systems which are expected to generate intramolecular charge transfer between donor and acceptor unit [9]. The D–A system can be widely used in organic field-effect transistor (OFET) [10], organic light emitting diode (OLED) [11], photovoltaic devices [12] and non-linear optics (NLO) [13]. Extraordinarily, the most interesting property of TTF is that it can be oxidized successively and reversibly to the radical cation and dication species [7]. Therefore, it may be used as a molecular sensor or switch by modulating its electron-donating ability reversibly by chemical or electrochemical methods [14].

Although there have been some attempts to combine a TTF unit with a porphyrin unit [15], the direct combination of these two important building blocks into the same molecular system in which the TTF units are directly annulated to the porphyrin core has recently been achieved [16], only after the development of a fused mono-pyrrolo-TTF precursor [17], but the reported synthetic approach is complicated and the yield is low.

Here, we designed and synthesized a highly conjugated dyad **1** based on a TTF unit covalently attached to a porphyrin unit by a simple Schiff base reaction (Scheme 1), and the electrochemical, spectral properties and theoretical computations of dyad **1** were also investigated.

2. Experimental details

2.1. Chemicals and instruments

The melting points was taken on an X-4 melting point apparatus. ^1H NMR spectrum was recorded with Bruker AV-300

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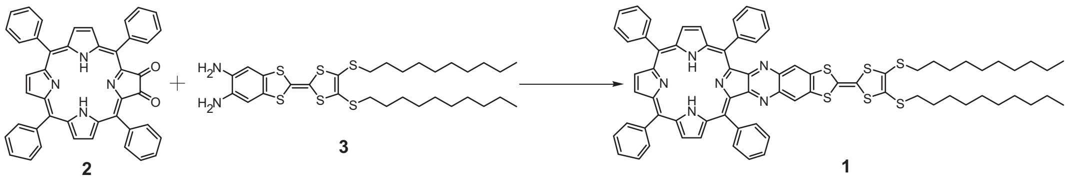


Scheme 1. Synthetic route of dyad **1**.

(300 MHz). All chemical shifts were quoted in ppm relative to TMS. The mass spectrum was determined with a Finnigan LCQDECA. Elemental analysis was performed on Carlo-Erba-1106 instrument. Absorption spectra were measured with SHIMADZU (model UV1700) UV–Vis spectrophotometer. Fluorescence spectra were carried out with a Hitachi spectrophotometer (model RF-5301) in a 1 cm quartz cell. Cyclic voltammetric experiments were performed on a CH Instruments 660C electrochemical workstation with a scan rate of 100 mV in CH_2Cl_2 (5.0×10^{-4} mol/L) using *n*-Bu_4NPF_6 (0.1 mol/L) as electrolyte, platinum as counter and working electrodes and Ag/AgCl as reference electrode.

Spectroelectrochemical experiments were performed in a quartz cell. A thin plate of platinum was used as the working and counter electrodes, while Ag wire was used as the reference electrode. CH_2Cl_2, which was treated with phosphorus pentoxide, followed by careful distillation before use, and *n*-Bu_4NPF_6 are employed as the solvent and the supporting electrolyte, respectively. The fluorescence spectra of oxidation/reduction of the dyad **1** in CH_2Cl_2 (2.0×10^{-5} mol/L) containing *n*-Bu_4NPF_6 (0.1 mol/L) were recorded with a Hitachi spectrophotometer (model RF-5301). The potential was applied with a CH Instruments 660C electrochemical workstation. The fluorescence lifetime study was performed by an Edinburgh FL 900 single-photon counting system. Data were analyzed using a non-linear least-squares fitting program, with deconvolution of the exciting pulse being ~200 ps [18].

Compound **2** was prepared according to Reference [19], and compound **3** was prepared according to Reference [20]. All reagents and solvents (standard grade) were used as received unless otherwise stated. All reactions involving compounds containing TTF unit were carried out under an atmosphere of dry N_2.

2.2. *Synthesis of dyad **1***

A solution of compound **2** (100 mg, 0.16 mmol) and compound **3** (98 mg, 0.16 mmol) in dry ethanol (15 mL) was heated under reflux for 5 h under N_2. After filtration, the precipitate was collected and purified by chromatography (CH_2Cl_2/petroleum ether) to give dyad **1** as a dark purple solid (70%). Mp > 300 °C .^{1}H NMR ($CDCl_3$, 300 MHz) δ: −2.57 (s, 2H, NH), 0.86 (t, *J* = 6.6 Hz, 6H, 2 × CH_3), 1.25 (m, 24H, 12 × CH_2), 1.39 (m, 4H, 2 × CH_2), 1.62 (m, 4H, 2 × CH_2), 2.84 (t, *J* = 7.3 Hz, 4H, 2 × SCH_2), 7.79 (d, *J* = 5.79 Hz, 10H, Ph-H), 7.88 (m, 2H, Ph-H), 8.01 (m, 1H, Ph-H), 8.14 (d, *J* = 7.44 Hz, 4H, Ph-H), 8.23 (m, 4H, Ph-H), 8.49 (app. d, 1H, Ph-H), 8.72 (s, 2H, pyrrole C–H), 8.95 (m, 4H, pyrrole C–H). MS calcd. for $C_{74}H_{72}N_6S_6$: 1236.41; found 1237.44 $[M + H]^+$. Elemental analysis (%) calcd. for $C_{74}H_{72}N_6S_6$: C, 71.80; H, 5.86; N, 6.79; found: C, 71.70; H, 6.09; N, 6.62.

3. Results and discussion

3.1. *Synthesis*

The synthetic approach to dyad **1** was outlined in Scheme 1. The dyad **1** was prepared by direct condensation of compound **2** with **3** in ethanol which leads to a dark purple solid in an overall yield of 70% after purification with column chromatography.

3.2. *Cyclic voltammetry*

The cyclic voltammogram of dyad **1** in dichloromethane shows four redox waves in the anodic direction (Fig. 1). Table 1 lists the redox potentials of dyad **1** together with those of the reference compound **3** and tetraphenylporphyrin (TPP) for comparison. Comparative studies with compound **3** and TPP indicate that the first and second waves of dyad **1** (0.62 V and 1.01 V) correspond to the oxidation of the TTF unit to the radical cation TTF^+ and dication TTF^{2+} respectively, while the third and fourth waves (1.31 V and 1.55 V) are due to the oxidation of porphyrin ring. The first and second oxidation process associated with the TTF unit in dyad **1** takes place at potentials that are more positive (270 mV and 250 mV, respectively) than those observed for compound **3**, the third and fourth waves are both anodic shifted (320 mV and 190 mV, respectively) as compared to TPP. In addition, two irreversible reduction waves (−1.26 V and −0.93 V) were observed for dyad **1**, and this was ascribed to the reduction of the porphyrin unit [15e].

The diaminobenzene unit in compound **3**, which is a strongly electron donating group, is transformed to pyrazine ring as an electron withdrawing unit in dyad **1**. The positive shift for the oxidation wave of the TTF unit is consistent with the electron-withdrawing nature of the pyrazine and porphyrin rings which make the TTF unit more electropositive, hence leading to more difficult oxidation. The third and fourth waves are due to the

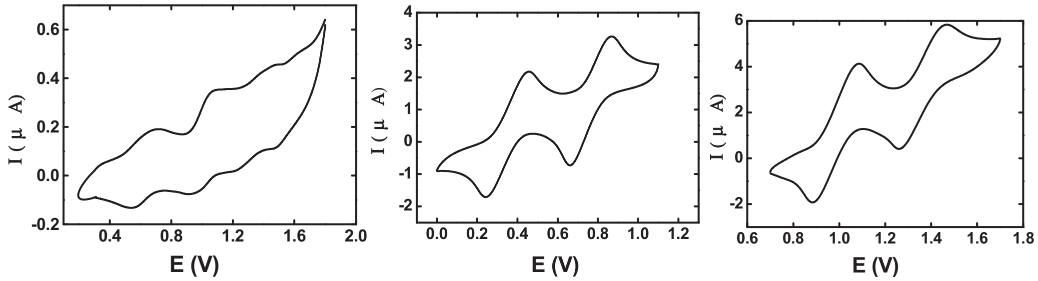


Fig. 1. Cyclovoltammograms of dyad **1** (left), **3** (middle) and TPP (right).

Table 1
Redox potentials of dyad **1**, **3** and TPP (V).

Compound	$TTF^{0/+}$	$TTF^{+/2+}$	$TPP^{0/+}$	$TPP^{+/2+}$
1	0.62	1.01	1.31	1.55
3	0.35	0.76		
TPP			0.99	1.36

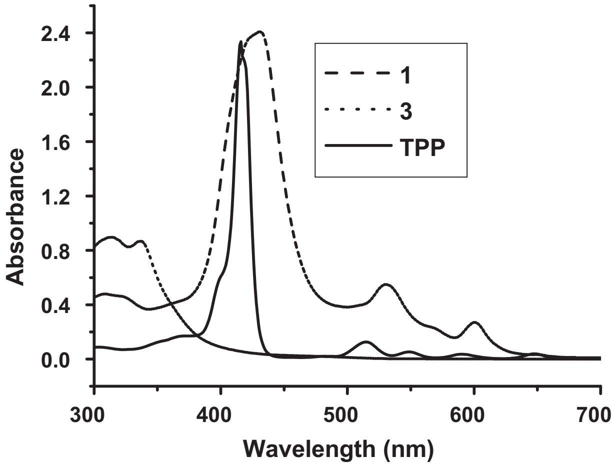


Fig. 2. Absorption spectra of dyad **1**, **3** and TPP in CH_2Cl_2 (2.0×10^{-5} mol/L).

porphyrin ring, and appear at much higher potentials than the redox waves of TPP. This might be attributed to the Coulombic influence of the initially oxidized TTF unit, which retards the subsequent oxidation of the porphyrin ring [21].

3.3. *Absorption spectra*

Fig. 2 shows the absorption spectra of dyad **1** together with those of the reference compound **3** and TPP for comparison (see also Table 2 for the absorption data). The absorption spectrum of dyad **1** shows a wide absorption in the whole range from 300 to 660 nm, with the maximum at 430 nm. No new band or unique spectroscopic shoulder is observed. By comparing with the absorption curve of TPP, there is a 14 nm red shift for the maximum absorption of dyad **1** and the band is broadened which suggests an expansion of the π-conjugation over the porphyrin and TTF units in dyad **1**.

3.4. *Steady-state fluorescence and transient fluorescence spectra*

Diamagnetic porphyrins are well known to display a strong fluorescence-emission feature in the 570–800 nm spectral region [22]. However, comparison of the fluorescence spectra of dyad **1** and TPP (Fig. 3) reveals that the fluorescence of the porphyrin unit in dyad **1** is quenched. Since the spectral overlap between the fluorescence spectrum of porphyrin unit and the absorption spectrum of TTF unit 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 to the porphyrin units is estimated to be −0.90 eV [23]. Such a negative value of ΔG_{PET} indicates that the photoinduced electron transfer from the TTF to porphyrin units is thermodynamically favorable. Thus, it might be concluded that the quenching of the fluorescence of porphyrin unit in dyad **1** is mainly due to the photoinduced electron transfer reaction (PET).

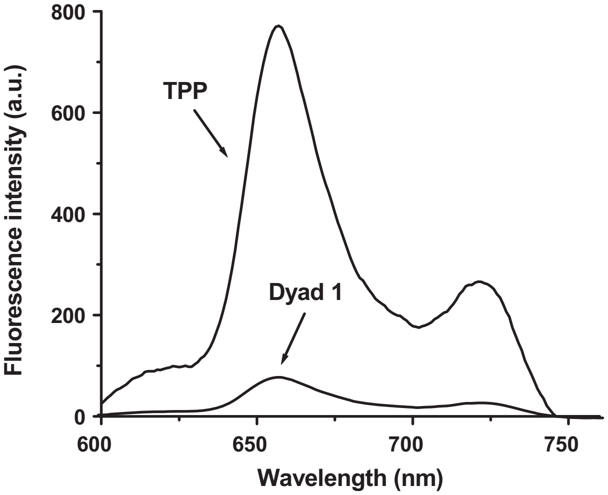


Fig. 3. Fluorescence spectra of dyad **1** and TPP in CH_2Cl_2 (2.0×10^{-5} mol/L).

The PET between the TTF and porphyrin units also could be studied by transient fluorescence spectra. As shown in the Fig. 4 and Table 3, the reference compound TPP exhibits only a single-exponential decay with a fluorescent lifetime of 7.41 ns. In contrast, the dyad **1** which has a TTF unit attached to the porphyrin unit has dual-exponential decay characteristics. For dyad **1**, there are two components with fluorescent lifetimes of 1.00 ns (0.45%) and 6.47 ns (99.55%). The relatively short-lived fluorescent lifetime can be assigned to the residual component after the photochemical communication between TTF and porphyrin units [15e].

3.5. *Chemical and spectroelectrochemistry oxidation*

It is expected that removal of one electron from the TTF unit ($TTF \rightarrow TTF^{\bullet+}$) in dyad **1** would prevent the TTF unit acting as an electron donor, consequently, it would recover the porphyrin fluorescence. To test this hypothesis, chemical oxidation experiment was carried out to dyad **1** firstly. As shown in Fig. 5, dyad **1** shows rather weak fluorescence (identified by the symbol of "0.0 eq."). When the chemical oxidation of the TTF unit is performed using $Fe(ClO_4)_3 \cdot 6H_2O$ as an oxidant, the emission intensity of dyad **1** is recovered dramatically upon the addition of $Fe(ClO_4)_3 \cdot 6H_2O$ to the solution of dyad **1**, and the fluorescence intensity grows with an increasing amount of $Fe(ClO_4)_3 \cdot 6H_2O$.

There are three facts which ensured the fluorescence enhancement when the oxidant was added. (1) The reduced electron-donating ability of the TTF radical cation made the electron transfer less favorable. (2) The ΔG_{PET} for the reverse electron-transfer process from the excited porphyrin unit to the cation radical of TTF unit was estimated to be −2.09 eV [24], such a large negative

Table 2
The absorption spectral data of compound **1**, **3** and TPP.

Compound	λ_{abs}/nm (ε/10^5 mol^{-1} L cm^{-1})						
1	308 (0.24)	323 (0.23)	430 (1.20)	530 (0.27)	568 (0.11)	600 (0.13)	650 (0.02)
3	313 (0.44)	337 (0.43)					
TPP			416 (1.17)	514 (0.07)	549 (0.03)	590 (0.02)	647 (0.02)

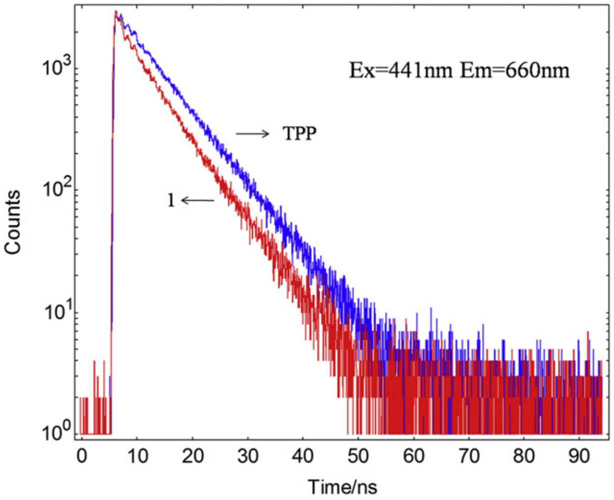


Fig. 4. Fluorescence decay signals of dyad **1** and TPP in CH_2Cl_2 (1.0×10^{-4} mol/L) excited at 441 nm.

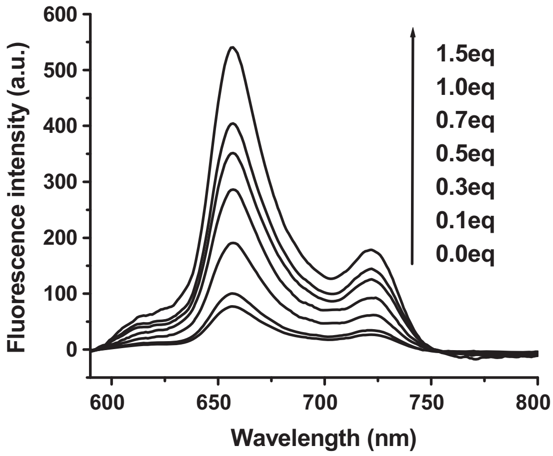


Fig. 5. Fluorescence spectra of dyad **1** in CH_2Cl_2 (2.0×10^{-5} mol/L) upon addition of increasing amounts of the oxidant $Fe(ClO_4)_3 \cdot 6H_2O$ in methanol (1.5×10^{-3} mol/L). Excitation was performed at 430 nm (Soret band).

value of ΔG_{PET} would position this electron-transfer reaction in the inverted region of the Marcus parabola [15b,26]. (3) The spectra overlap between the absorption spectra of the cation radical of TTF (430–580 nm) [25] and the fluorescence spectra of the porphyrin unit was negligible, so the energy transfer from the excited state of tetraphenylporphyrin to the cation radical of the TTF unit could not take place efficiently. These results demonstrated the possibility of constructing a new redox fluorescence switch based on dyad **1** because the transformation between the neutral TTF unit and the radical cation can be operated reversibly. To test this possibility, spectroelectrochemical studies were performed for dyad **1**.

Electrochemical oxidation of dyad **1** was performed by applying an oxidation potential of 0.8 V (vs Ag wire) to its CH_2Cl_2 solution, which led to fluorescence enhancement for dyad **1** as shown in Fig. 6A. 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 radical cation [26], since the oxidation potential (0.8 V vs Ag wire) employed is higher than that of the first oxidation potential of TTF unit in dyad **1**. Considering the oxidation potential of the porphyrin unit of dyad **1** (see Table 1), the porphyrin unit should not be affected under this electrochemical condition.

Interestingly, after application of a potential of 0.1 V (vs Ag wire, to reduce TTF^{+}) to the oxidized solution for 5 min, the gradual decrease of the fluorescence intensity of the solution was noted (Fig. 6B). The initial fluorescence spectra of the solution (before applying an oxidation potential) was almost recovered completely after the 0.1 V potential was applied to the oxidized solution for 6 min. This fluorescence change can be understood as follows: the radical cation of the TTF unit, which was generated during the oxidation process, would be reduced to the neutral unit by applying a potential of 0.1 V (vs Ag wire) to the solution. Consequently, the PET from TTF unit to the porphyrin unit would occur efficiently again, leading to a decrease of the fluorescence of dyad **1**. Therefore, the fluorescence intensity of dyad **1** in solution can be reversibly modulated by sequentially applying oxidation and reduction potentials to the corresponding solution. As a result, a new redox fluorescence switch can be established on the basis of dyad **1** by taking the advantage of the peculiar property of the TTF-type electron donor.

Table 3
The fluorescence lifetime of dyad **1** and TPP detected at 660 nm.

Compound	τ_f, ns	k_f, ns^{-1}
1	6.47	0.15
TPP	7.41	0.13

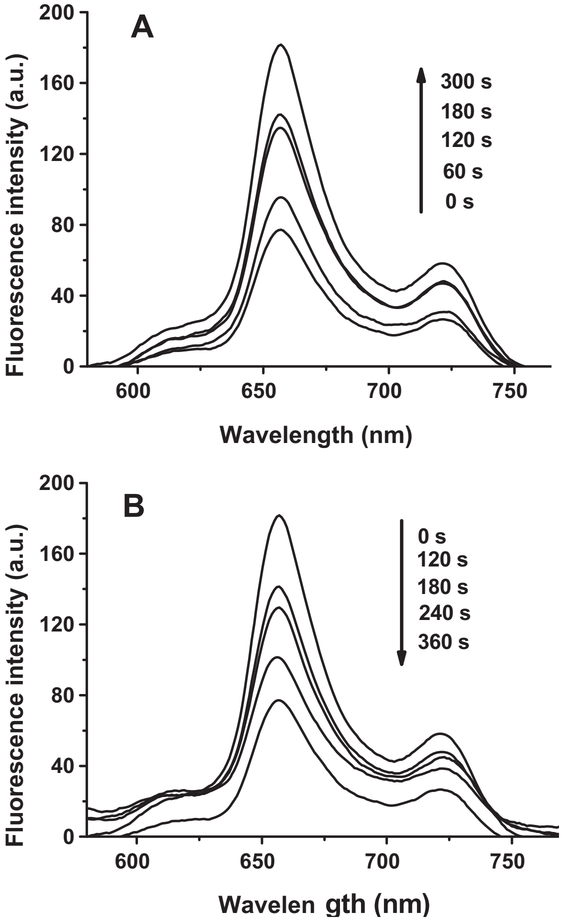
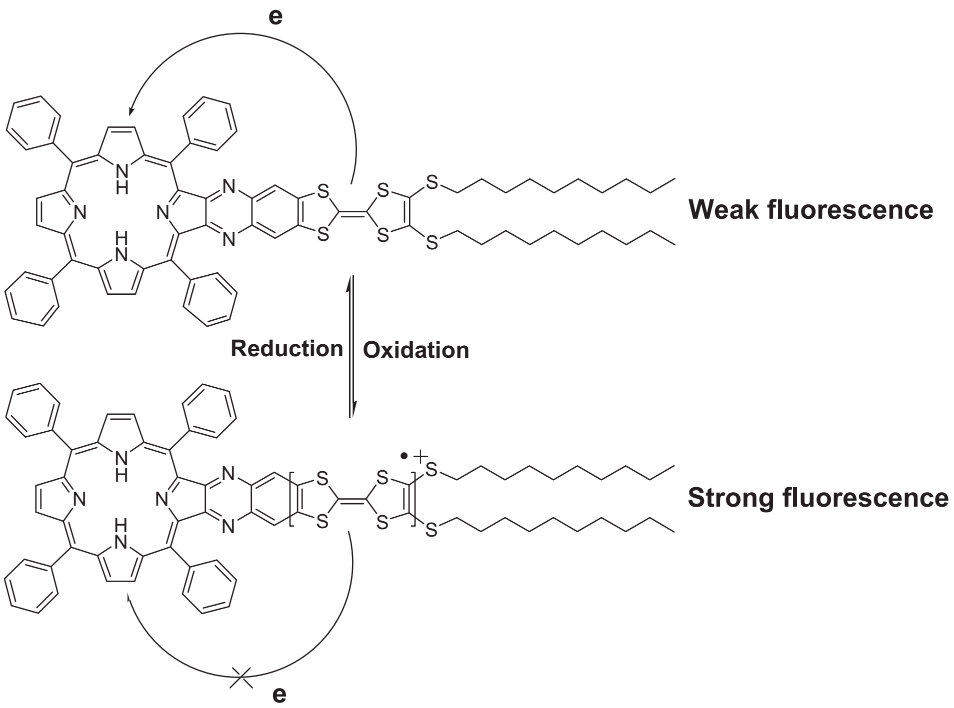


Fig. 6. (A) Fluorescence spectra of dyad **1** in CH_2Cl_2 (2.0×10^{-5} mol/L) after applying an oxidation potential of 0.8 V (vs Ag wire). (B) Fluorescence spectra of dyad **1** in CH_2Cl_2 that had been oxidized electrochemically (0.8 V) for 5 min after applying a potential of 0.1 V (vs Ag wire).



Scheme 2. Mechanism of the fluorescence switch in dyad **1**.

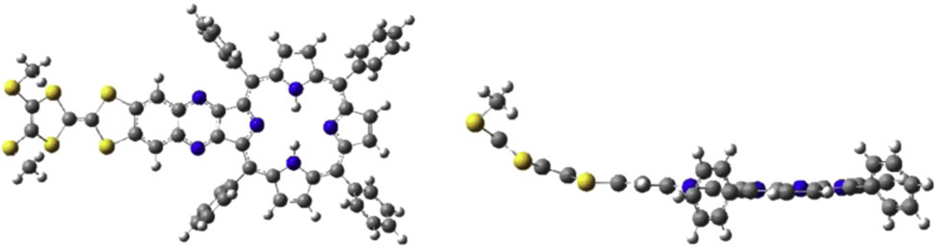


Fig. 7. The optimized structure of model **1**.

The working mechanism for such a redox fluorescence switch based on dyad **1** is proposed as follows in Scheme 2 [26]. When dyad **1** is in its neutral state, the PET from the TTF unit to the porphyrin unit would result in the quenching of the fluorescence of the porphyrin unit. Once the TTF unit is oxidized, the electron-donating ability of the TTF unit is depressed, and the PET from the TTF unit to the porphyrin unit would be arrested, leading to the recovery of the fluorescence of the porphyrin unit. If the oxidized

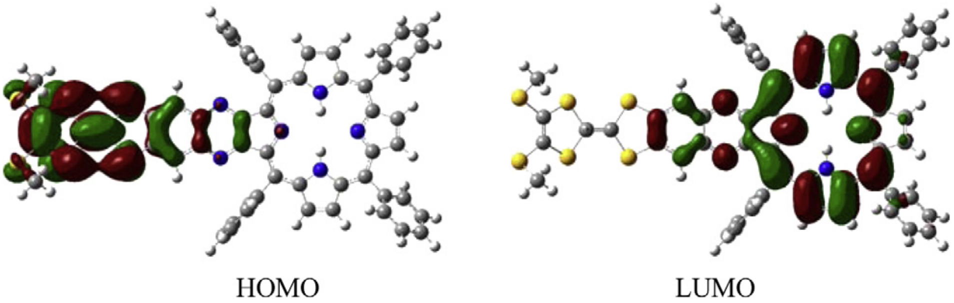


Fig. 8. The frontier molecular orbitals of model **1**.

TTF unit is reduced to its corresponding neutral state, which would led to the fluorescence of porphyrin unit decreased again due to the PET reaction. As the transformation between TTF and the radical cation of TTF can be reversibly carried out, such fluorescence switch could be operated reversibly.

3.6. Theoretical computations

To gain insight into the molecular structure and electronic configurations, dyad **1** is further examined by theoretical calculations. The peripherally longer alkyl groups are removed for simplification as they are not expected to significantly affect the conformation and energy levels. The simplified molecule is labeled as model **1**. The molecular geometry is optimized by using B3LYP/6-31G** basis set. All calculations have been performed with the Gaussian 09 package [27]. The optimized structure of model **1** displays in Fig. 7. As has been shown, the porphyrin ring and pyrazine ring are nearly in an identical plane.

The electronic density distributions of the HOMO and LUMO are illustrated in Fig. 8. A particularly interesting feature is the localization and spatial separation of the HOMO and the LUMO. In the HOMO, electron density is mainly localized on the TTF unit and pyrazine ring of model **1**, while the LUMO is localized on the porphyrin and pyrazine ring. This suggests that the process of PET, from the TTF unit to the porphyrin unit, can occur under the photoexcitation of dyad **1**.

4. Conclusions

In summary, a novel and highly conjugated donor–acceptor dyad **1** consisting of a TTF unit covalently attached to a porphyrin unit has been synthesized and characterized. The fluorescence intensity and lifetime of dyad **1** was decreased, compared to TPP, which evidently indicates that PET occurs from the TTF unit to the porphyrin unit in the excited state. The fluorescence intensity of dyad **1** can be recovered dramatically upon addition of $Fe(ClO_4)_3 \cdot 6H_2O$ to the solution of dyad **1**, and the fluorescence intensity grows with an increasing amount of $Fe(ClO_4)_3 \cdot 6H_2O$. More importantly, the fluorescence intensity of the solution of dyad **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 dyad **1**.

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