

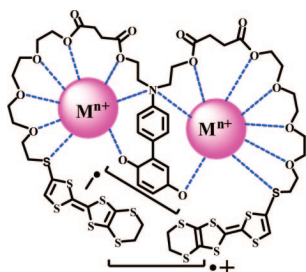
A New
Tetrathiafulvalene–Quinone–Tetrathiafulvalene
Triad: Modulation of the Intramolecular Charge
Transfer by the Electron-Transfer Process
Promoted by Metal Ions

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Electron transfer can occur from the TTF units to the substituted quinone unit in a new TTF–quinone–TTF triad **1** containing the *N,N*-dialkylaniline-substituted quinone unit flanked by two TTF units, in the presence of metal ions (Pb^{2+} , Zn^{2+} , and Sc^{3+}). Simultaneously, the corresponding charge transfer within the substituted quinone unit becomes weak in the presence of metal ions. Moreover, the metal ion-promoted electron transfer and the intramolecular charge transfer can be tuned by alternating UV and visible light irradiation in the presence of spiropyran.

Electron donor (D)–acceptor (A) compounds with TTF (tetrathiafulvalene) as electron donor have been widely investigated for studies of intramolecular charge transfer/photoinduced electron-transfer processes and molecular level devices as well as potential applications in solar cell systems.¹ For instance, fluorescence switches and chemical sensors with TTF based D–A compounds have been reported.²

We have recently described the metal ions-promoted electron transfer within TTF–quinone dyads in which the TTF and quinone units are covalently linked by an oligoethylene glycol chain.³ Moreover, the electron-transfer process can be modulated by alternating UV and visible light irradiations in the presence

of spiropyran.^{3a} The electron transfer promoted by metal ions can occur to TTF–quinone dyads in which the electron accepting abilities of quinone units are rather weak.^{3b} The results also suggest that the synergic coordination of the oligoethylene glycol chain and the radical anion of the quinone unit with metal ion may contribute to stabilizing the corresponding charge-separation state and thus facilitate the electron-transfer process. In fact, electronic properties and even self-assembly morphology were reported to be modulated for chromospheres connected by oligoethylene glycol chain upon binding of metal cations.⁴

In this report, we describe a new TTF–quinone–TTF triad **1** (Scheme 1) in which the quinone unit is substituted with the *N,N*-dialkylaniline unit. According to previous studies,⁵ intramolecular charge transfer (ICT) should exist between the quinone and *N,N*-dialkylaniline units. The absorption and ESR spectral studies show that (1) electron transfer occurs within triad **1** in the presence of metal ions (Pb^{2+} , Zn^{2+} , and Sc^{3+}); (2) simultaneously, the intramolecular charge transfer becomes weak after addition of metal ions, indicating that the electron transfer

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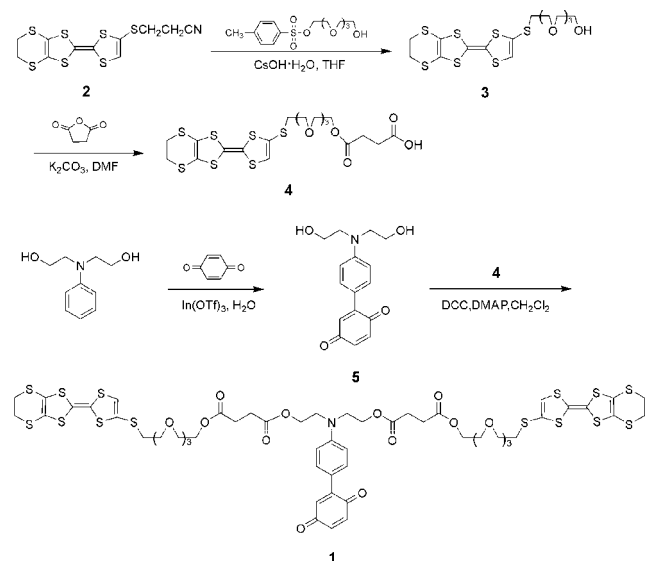
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SCHEME 1. The Chemical Structure and Synthetic Approach for Triad 1


between TTF and quinone units influences the ICT within the substituted quinone unit; and (3) both the electron transfer and ICT processes can be modulated by UV and visible light irradiations in the presence of the photochromic spiropyran.

The synthetic approach for triad **1** is shown in Scheme 1. Removal of the cyanoethyl⁶ group in compound **2** and further reaction with tetraethyleneglycol monotosylate led to compound **3**, which was further transformed into compound **4** after reaction with succinic anhydride. Compound **5** was separately synthesized from *N,N*-(dihydroxyethyl)aniline and quinone in the presence of $\text{In}(\text{OTf})_3$ according to previous report.⁷ The reaction of compound **5** and compound **4** in the presence of dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) led to triad **1**. The detailed synthetic procedures and characterization data are provided in the Supporting Information.

Figure 1 shows the absorption spectrum of triad **1** in CH_2Cl_2 . A broad absorption around 542 nm was detected for triad **1**. By comparing with the absorption spectrum of **5** (see Figure S1 in the SI), this broad absorption band should be due to the intramolecular charge transfer (ICT) band associated with the *N,N*-dialkylaniline-substituted quinone unit in triad **1**.

After the addition of Pb^{2+} new absorptions around 450 and 850 nm emerged gradually and their intensities increased by increasing the amounts of Pb^{2+} as shown in Figure 1. According to previous studies,⁸ the absorption bands around 450 and 845 nm could be ascribed to the radical cation of TTF ($\text{TTF}^{\cdot+}$) units in triad **1**. Thus, the appearance of these two absorption bands

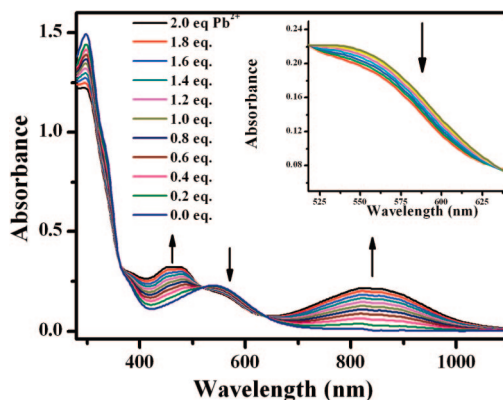


FIGURE 1. Absorption spectra of triad **1** recorded in CH_2Cl_2 (2.5×10^{-5} M) in the presence of increasing amounts of Pb^{2+} [$\text{Pb}(\text{ClO}_4)_2$]; the inset shows the 518–640 nm part of the absorption spectra of triad **1** in the presence of increasing amounts of Pb^{2+} ; the solutions were bubbled with N_2 before measurements.

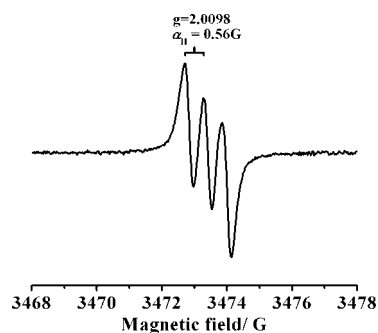


FIGURE 2. The ESR spectra of triad **1** (5.0×10^{-5} M) in CH_2Cl_2 in the presence of 2.0 equiv of Pb^{2+} [$\text{Pb}(\text{ClO}_4)_2$] recorded at room temperature; the solution was bubbled with N_2 before measurement.

indicated the formation of the radical cation of the TTF unit ($\text{TTF}^{\cdot+}$). This conclusion was supported by a direct oxidation of the TTF unit in triad **1** by Fe^{3+} , which also led to two absorptions at 450 and 850 nm (see Figure S2 in the SI). Therefore, it may be concluded that electron transfer occurs between TTF and substituted quinone units of triad **1** in the presence of Pb^{2+} , being similar to the TTF–quinone dyads reported by us recently.³

Moreover, ESR signals were detected for triad **1** after introducing Pb^{2+} to the solution as displayed in Figure 2. The solution of triad **1** in the presence of 2.0 equiv of Pb^{2+} exhibited strong triplet signals ($g = 2.0098$, $a_{\text{H}} = 0.56$ G). The triplet signals were likely due to the splitting of the two H atoms of the radical cations of the TTF units in triad **1**. The ESR spectroscopic studies are in agreement with the generation of $\text{TTF}^{\cdot+}$ in the presence of Pb^{2+} . Because of the easy disproportionation of radical anion of the quinone ($\text{Q}^{\cdot-}$) into the corresponding Q^{2-} and neutral Q in the presence of metal ions at room temperature,⁹ the corresponding ESR signals due to $\text{Q}^{\cdot-}$ were not observed. Accordingly, both absorption and ESR spectroscopic investigations show that electron transfer takes place between TTF and substituted quinone units of triad **1** in the presence of Pb^{2+} .

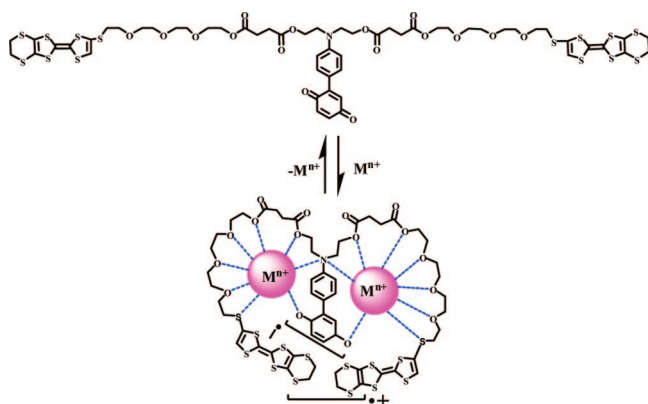
As for the TTF–quinone dyads reported previously,³ the metal ion-promoted electron transfer within triad **1** can be

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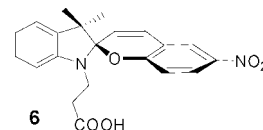
SCHEME 2. The Proposed Mechanism for the Metal Ion-Promoted Electron Transfer in Triad 1


understood as follows: (1) It is known that the reduction potentials of quinone units are positively shifted in the presence of metal ions, and thus the electron transfer between TTF and quinone units becomes thermodynamically more feasible in the presence of these metal ions.¹⁰ As shown in Figure S3 of the SI, the reduction potential of the quinone unit in triad **1** is anodically shifted in the presence of 2.0 equiv of Pb^{2+} . (2) The synergic coordination of oligoethylene glycol chain⁴ and the radical anion of quinone with metal ions as proposed in Scheme 2 would be able to stabilize the electron-transfer state by increasing the interaction between the corresponding cations and anion. This proposition was supported by the following finding: addition of 2,2'-bipyridine to the solution of triad **1** containing Pb^{2+} gradually led to the disappearance of the absorption bands at 450 and 845 nm (seeing Figure S6 in the SI). 2,2'-Bipyridine can bind Pb^{2+} and as a result the complex of **1** with Pb^{2+} would be dissociated; accordingly, back electron transfer from the quinone anion to $\text{TTF}^{\cdot+}$ would occur. Additionally, if polar solvents such as CH_3CN , THF, and DMF were used instead of CH_2Cl_2 , the absorptions around 450 and 850 nm due to $\text{TTF}^{\cdot+}$ could be neglected for the solution of **1** after introducing Pb^{2+} (see Figure S7-1 in the SI). This is probably because the complex of **1** with Pb^{2+} becomes unstable in polar solvents. On the basis of the corresponding Job's plot (see Figure S8-1 in the SI), the stoichiometry of complex formed between **1** and Pb^{2+} was estimated to be 1:2. Furthermore, based on the variation of the absorption intensity at 845 nm of **1** after addition of different amounts of Pb^{2+} , the binding constant of the 1:2 complex was calculated to be $1.38 \times 10^9 \text{ M}^{-2}$ by fitting the data with the Benesi–Hildebrand equation (assuming a single equilibrium process, see Figure S9-1 in the SI).

Besides Pb^{2+} , Zn^{2+} and Sc^{3+} can also induce the intramolecular electron-transfer process within triad **1**. As shown in Figures S10-1 and S10-2 in the SI, absorption bands at 450 and 845 nm due to the TTF radical cation of triad **1** were detected in the presence of Zn^{2+} and Sc^{3+} . Also, triplet ESR signals were observed (see Figures S11-1 and S11-2 in the SI). These results demonstrate that electron transfer occurs for triad **1** in the presence of $\text{Zn}^{2+}/\text{Sc}^{3+}$. According to the corresponding Job's plots, 1:2 complexes were formed between **1** and $\text{Zn}^{2+}/$

Sc^{3+} (see Figures S8-2 and S8-3, SI). The binding constants were calculated to be 3.27×10^9 and $4.19 \times 10^9 \text{ M}^{-2}$ for Zn^{2+} and Sc^{3+} complexes, respectively, by analyzing the absorbance variation at 845 nm vs. the concentrations of $\text{Zn}^{2+}/\text{Sc}^{3+}$ with the Benesi–Hildebrand equation (see Figures S9-2 and S9-3 in the SI). When the absorption and ESR spectra of triad **1** (the same concentration) in the presence of equal amounts of $\text{Sc}^{3+}/\text{Pb}^{2+}/\text{Zn}^{2+}$ are compared, the absorption intensity at 845 nm and the ESR signal intensity varied in the following order: **1** + Sc^{3+} > **1** + Zn^{2+} > **1** + Pb^{2+} . This leads us to conclude that Sc^{3+} can promote the electron transfer within triad **1** more efficiently. This result can be understandable by considering the following fact that Sc^{3+} shows a preference for oxygen coordination. The presence of a nitrogen atom may increase the binding of triad **1** with Zn^{2+} ,¹¹ which may explain why Zn^{2+} facilitates the electron-transfer process more efficiently than Pb^{2+} .

It is interesting to note that the charge transfer absorption band at 542 nm, which is associated with triad **1**, becomes weak simultaneously in the presence of Pb^{2+} , as shown in the inset of Figure 1. Similar phenomena were observed for triad **1** in the presence of Zn^{2+} or Sc^{3+} (see the insets of Figures S10-1 and S10-2 in the SI). This can be understood as follows: the metal ion-promoted electron transfer from TTF to the quinone unit would reduce the electron accepting ability of the quinone unit. Accordingly, the degree of intramolecular charge transfer would decrease within the *N,N*-dialkylaniline-substituted quinone unit and thus the corresponding charge transfer band intensity is reduced in the presence of metal ions (Pb^{2+} , Zn^{2+} , and Sc^{3+}). Thus, the intramolecular charge transfer can be modulated by the metal ion-promoted electron transfer within triad **1**. Additionally, the coordination of the nitrogen atom with metal ions would decrease the electron donating ability and as a result this may also contribute to the weakening of the corresponding charge transfer absorption band at 542 nm.



It was reported that the photochromic spiroopyran can be transformed into the corresponding merocyanine form (MC) upon UV light irradiation and the MC form (in particular, the spiroopyran with the COOH group) can coordinate with metal ions.¹² When the SP compound such as compound **6**¹³ was added to the solution of **1** containing metal ions, the MC form generated by UV light irradiation would bind metal ions and

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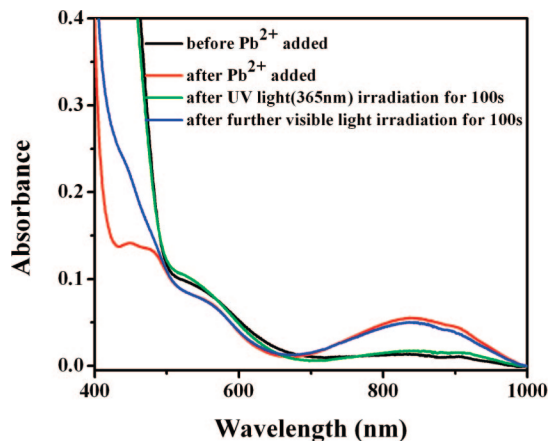


FIGURE 3. Absorption spectra of the solution of triad **1** (1.0×10^{-5} M) and SP (1.0×10^{-4} M) before and after addition of $\text{Pb}(\text{ClO}_4)_2$ (2.0×10^{-5} M), followed by UV light (365 nm) irradiation for 100 s, and further visible light irradiation for 100 s.

as a result the complex of **1** with metal ions would be partially dissociated; the MC complex would be transformed into SP under further visible light irradiation and triad **1** can bind metal ions again. Therefore, it would be possible to tune the metal ion-promoted electron transfer and the intramolecular charge transfer within triad **1** in the presence of spiropyran by alternating UV and visible light irradiation. As shown in Figure 3, the absorption intensity at 845 nm for the solution of triad **1** containing Pb^{2+} was reduced to 24% of that of the initial value after UV light (365 nm) irradiation for 100 s. Simultaneously, the corresponding charge transfer absorption band intensity was enhanced. This is simply because the MC form of spiropyran (SP) can coordinate with the metal ions such as Pb^{2+} ; as a result the competing binding of metal ions between triad **1** and the MC form occurs. Further visible light irradiation of the solution, which had been treated by UV light irradiation, led to the restoration of the absorption intensities at 450, 845, and 542 nm (due to ICT). Such reversible modulation of the absorption spectrum of triad **1** containing Pb^{2+} in the presence of spiropyran by light irradiation can be repeated for several cycles.

In summary, a new TTF–quinone–TTF triad **1**, in which the *N,N*-dialkylaniline-substituted quinone unit is flanked by two TTF units, was synthesized and investigated. Both absorption and ESR spectroscopic studies clearly indicate that electron transfer occurs from the TTF to the substituted quinone units

in the presence of metal ions (Pb^{2+} , Zn^{2+} , and Sc^{3+}). Simultaneously, the corresponding charge transfer within the substituted quinone unit becomes weak in the presence of metal ions. Moreover, the metal ion-promoted electron transfer and the intramolecular charge transfer can be tuned by alternating UV and visible light irradiation in the presence of spiropyran, by taking advantage of the unique features of photochromic spiropyran. These results further confirm that the metal ion-promoted electron transfer is general for TTF–quinone compounds with glycol chain as the spacer.

Experimental Section

The synthesis and characterization of compounds **3–5** were provided in the Supporting Information.

Synthesis of Triad 1. To a solution of **4** (0.47 g, 0.77 mmol), **5** (0.11 g, 0.38 mmol), and DMAP (25 mg, 0.2 mmol) in 30 mL of dry CH_2Cl_2 at 0 °C was dropwise added a solution of DCC (0.22 g, 1.0 mmol) in 10 mL of dry CH_2Cl_2 . Then, the mixture was allowed to reach room temperature and stirred overnight. After the white precipitate was removed by filtration, the residue was purified by column chromatography with acetone/petroleum ether (1:1, v/v) as eluent to give triad **1** as a purple oil (0.20 g, 17.6%). ^1H NMR (400 MHz, CDCl_3) δ 7.47 (2H, d, $J = 9.0$ Hz), 6.80–6.78 (5H, m), 6.43 (2H, s), 4.28 (4H, t, $J = 6.2$ Hz), 4.24 (4H, t, $J = 4.9$ Hz), 3.70–3.63 (28H, m), 3.28, (8H, s), 2.92 (4H, t, $J = 6.4$ Hz), 2.64–2.57 (8H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 187.9, 187.7, 172.34, 172.33, 149.1, 145.1, 137.1, 136.4, 131.2, 129.1, 126.7, 123.1, 121.0, 118.0, 114.1, 114.06, 111.9, 106.8, 70.78, 70.75, 70.71, 70.6, 69.8, 69.2, 64.1, 61.6, 49.6, 35.4, 30.3, 29.8, 29.1, 29.0; HR-MS (FAB) calcd for $\text{C}_{56}\text{H}_{67}\text{NO}_{16}\text{S}_{14}$ [$\text{M} + 2\text{H}^+$] 1457.0544, found 1457.0549.

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Supporting Information Available: The synthesis details and characterization of compounds **3–5**, cyclic voltammograms in the presence of metal ion, and absorption spectral studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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