A 2,2'-Bipyridyl-Bridged Tetrathiafulvalene-quinone Dyad: Intramolecular Electron-Transfer Promoted by Metal Ions[†]

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A 2,2'-bipyridyl-bridged tetrathiafulvalene (TTF)-quinone dyad (**1**) was synthesized and characterized. Both absorption and ESR spectroscopic studies clearly indicate that electron transfer occurs from TTF to the quinone unit for dyad **1** in the presence of metal ions. The results manifest that the coordination of dyad **1** with metal ions plays a key role in facilitating the intramolecular electron transfer.

Keywords donor-acceptor system, tetrathiafulvalene, quinone, electron transfer, 2,2'-bipyridine

Introduction

Initially, tetrathiafulvalene (TTF) and its derivatives as electron donors were designed and investigated for organic conducting materials.[1] However, during the past decades, miscellaneous TTF-based functional molecules have been constructed and examined in many fields.[2-4] For example, a number of electron donor (D)-acceptor (A) dyads with TTF units have been reported.[3,4] These TTF based D-A molecules are interesting as models for studies of charge-transfer interactions, photoinduced electron transfer processes and molecular level devices. Recently, we have reported the metal-ions promoted electron transfer within TTF-quinone dyads in which the TTF and quinone units are covalently linked by the oligoethylene glycol chain (Scheme 1).[5a-5d] The results show that the coordination of oligoethylene glycol chain and the radical anion of quinone with metal ions play key role in promoting the intramolecular electron transfer within TTF-oligoethylene glycol-quinone dyads. In other words, coordination of oligoethylene glycol chain with metal ions induces the conformation change for TTF-quinone dyads; thus, TTF and quinone units within the dyad become adjacent upon metal ion coordination, which will facilitate the intramolecular electron transfer.

Besides glycol chain there are many other functional units that can change molecular conformation upon external stimulus. For instance, 2,2'-bipyridyl, an important building block in supramolecular chemistry and material science, prefers '*transoid*' formation in the absence of metal ions;[6] however, if certain metal ions are present, 2,2'-bipyridyl exists in the '*cisoid*' form via coordination with metal ions (Scheme 1). Thus, it is interesting to examine whether the metal-ions promoted intramolecular electron transfer within TTF-quinone dyad can take place by using bipyridyl unit as a bridge instead of oligoethylene glycol chain. In the '*cisoid*' form the TTF and quinone units would be spatially adjacent, and as a result the metal ion promoted electron transfer would become more favorable.

Herein we report a new TTF-quinone dyad (dyad **1**, Scheme 2), in which TTF unit and quinone unit are linked by bipyridyl unit at the 3- and 3'-postions, respectively. The results show that intramolecular electron transfer can take place effectively within dyad **1** in the presence of metal ions.

Experimental

Materials

$CsOH \cdot H_2O$ and *p*-chloranil were purchased from Acros and Alfa, respectively. Other reagents were used as received unless otherwise stated. All solvents were purified and dried following standard procedures unless otherwise stated.

Characterization techniques

Melting points were measured with an XT_4-100X apparatus and uncorrected. ^1H NMR, ^{13}C NMR, MS (including HRMS), absorption and ESR spectra were measured with conventional spectrometers. Cyclic voltammetric measurements were performed in a standard three-electrode cell, with glassy carbon as the working electrode and platinum wire as auxiliary elec-

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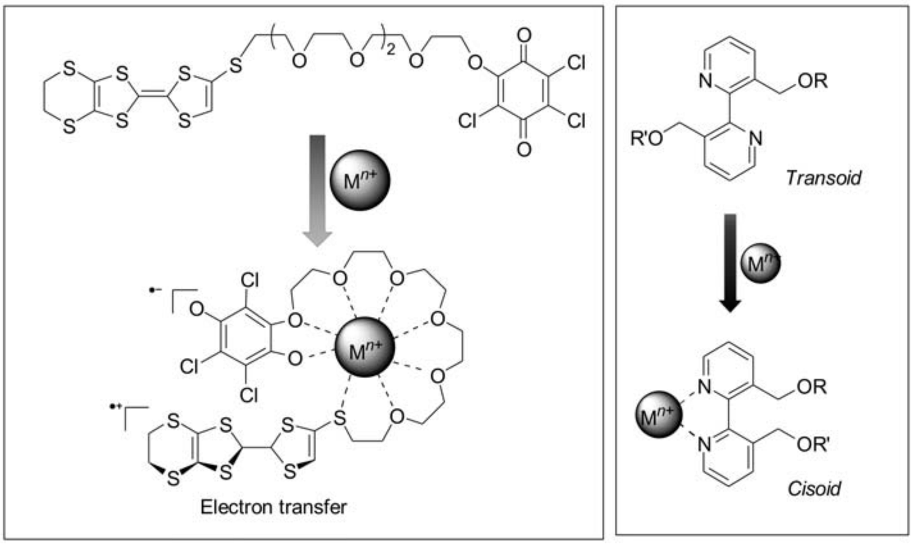
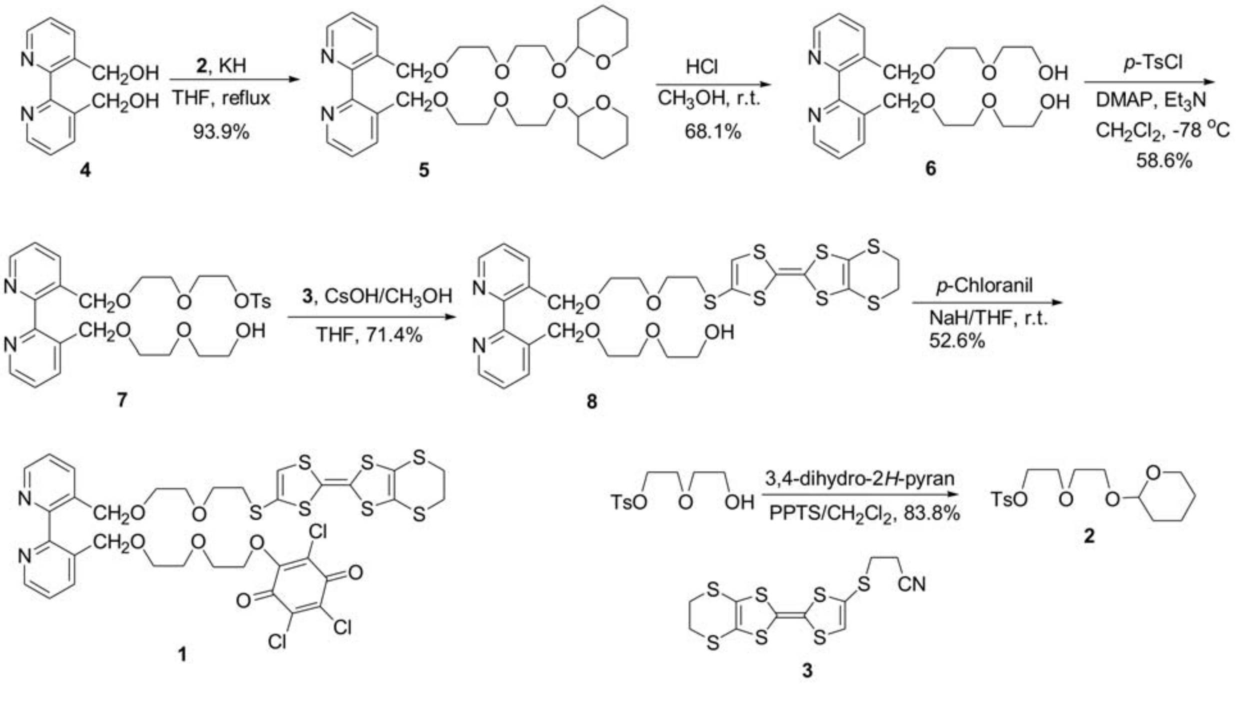
Scheme 1 Illustration of the metal ions-promoted intramolecular electron transfer within TTF-oligoethylene glycol-quinone dyad and the conformation change for 2,2'-bipyridyl unit upon binding metal ions



Scheme 2 Synthetic approach to dyad **1**



trode, and Ag/AgCl electrode (saturated KCl) as the reference electrode; n-Bu_4NPF_6 (0.1 mo/L) was used as supporting electrolyte. Elemental analyses were performed on a Carlo-Erba-1106 instrument.

Synthesis of compound 2 A mixture of 2-(2-hydroxyethoxy)ethyl 4-methyl benzenesulfonate (9.20 g, 35.4 mmol), 3,4-dihydro-2*H*-pyran (4.46 g, 53.1 mmol) and pyridinium *p*-toluenesulfonate (0.44 g, 1.77 mmol) was dissolved in 50 mL dry CH_2Cl_2. The solution was stirred for 12.0 h at room temperature and then quenched with 20 mL of diethyl ether. The resulting solution was washed with saturated brine, dried with Na_2SO_4, and then the solvent was removed. Separation with column chromatography (silica gel, CH_2Cl_2) gave compound **2** as pale yellow oil (10.2 g) in 83.8% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.80 (d, $J=7.8$ Hz, 2H), 7.34 (d, $J=7.7$ Hz, 2H), 4.59 (s, 1H), 4.17—4.16 (m, 2H), 3.86—3.79 (m, 2H), 3.72—3.71 (m, 2H), 3.60—3.59 (m, 2H), 3.55—3.47 (m, 2H), 2.44 (s, 3H), 1.82—1.80 (m, 1H), 1.73—1.68 (m, 1H), 1.58—1.53 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 144.8, 133.1, 129.8, 128.0, 99.0, 70.7, 69.3, 68.7, 66.6, 62.3, 30.6, 25.4, 21.6, 19.5; HRMS calcd for $C_{16}H_{24}O_6S$ 344.1294, found 344.1293.

Synthesis of compound 5 Under nitrogen, a mixture of compound **4** (2.16 g, 10 mmol) and KH (3.20 g, 80 mmol) in 50 mL of anhydrous THF was heated to reflux for 1.0 h. Compound **2** (12.4 g, 36 mmol) in 50 mL of anhydrous THF was then added. After refluxed for 6.0 h, the reaction was quenched with saturated brine. The whole mixture solution was extracted with CH_2Cl_2 and dried with Na_2SO_4. The solvent was removed by evaporation, and the residue was purified by column chromatography (silica gel, EtOAc) to give compound **5** (5.26 g) as a yellow oil in 93.9% yield. ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.54 (d, J=4.0 Hz, 2H), 8.02 (d, J=7.6 Hz, 2H), 7.36—7.33 (m, 2H), 4.62 (s, 2H), 4.53 (s, 4H), 3.88—3.83 (m, 4H), 3.64—3.45 (m, 16H), 1.83—1.52 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.6, 147.5, 136.3, 133.7, 123.3, 99.1, 70.7, 70.6, 70.3, 69.5, 66.8, 62.4, 30.7, 25.6, 19.6; HRMS calcd for $C_{30}H_{45}N_2O_8$ $[M+H]^+$ 561.3176, found 561.3167.

Synthesis of compound 6 To a solution of compound **5** (5.66 g, 10.1 mmol) in methanol (100 mL) was added aqueous HCl (1 mol•L^{-1}, 60 mL). After stirred for 2.0 h at room temperature, NaOH aqueous was added to neutralize excess HCl. The resulting solution was extracted with $CHCl_3$ (150 mL×10), and dried with Na_2SO_4. After removal of solvents the residue was subjected to column chromatography on silica gel to give compound **6** (2.70 g) as a white solid in 68.1% yield. M.p. 95—97 ℃; ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.57 (d, J=4.8 Hz, 2H), 7.95 (d, J=7.8 Hz, 2H), 7.38—7.35 (m, 2H), 4.56 (s, 4H), 3.63 (t, J=4.8 Hz, 4H), 3.56—3.49 (m, 12H), 3.40 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 156.1, 147.8, 136.4, 133.3, 123.4, 72.9, 70.5, 70.2, 69.8, 61.8. Anal. calcd for $C_{20}H_{28}N_2O_6$: C 61.21, H 7.19, N 7.14; found C 61.28, H 7.23, N 7.05.

Synthesis of compound 7 To a solution of compound **6** (685 mg, 1.75 mmol), triethylamine (2.4 mL, 17.3 mmol) and catalytic amount of DMAP in 120 mL of dry CH_2Cl_2 at −78 ℃, *p*-toluenesulfonyl chloride (380 mg, 2.00 mmol) was added. The resulting mixture was stirred for 12 h. Then the organic solution was washed with $NaHCO_3$ aqueous, dried with Na_2SO_4. After removal of solvents, the residue was subjected to column chromatography on silica gel to give compound **7** (560 mg) as a pale yellow oil in 58.6% yield. ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.55 (d, J=3.2 Hz, 2H), 7.98 (d, J=7.5 Hz, 2H), 7.79 (d, J=7.8 Hz, 2H), 7.36—7.31 (m, 4H), 4.54 (s, 2H), 4.51 (s, 2H), 4.14 (s, 2H), 3.66—3.49 (m, 14H), 2.43 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.7, 155.6, 147.6, 147.5, 145.0, 136.4, 136.3, 133.4, 133.1, 130.0, 128.1, 123.4, 72.6, 70.7, 70.5, 70.2, 70.1, 69.6, 69.5, 69.4, 68.8, 61.8, 21.8; HRMS calcd for $C_{27}H_{35}N_2O_8S$ $[M+H]^+$ 547.2114, found 547.2130.

Synthesis of compound 8 Under N_2 atmosphere, a solution of $CsOH•H_2O$ (252 mg, 1.50 mmol) in 2 mL of anhydrous degassed CH_3OH was dropped into a solution of compound **3**[7] (456 mg, 1.2 mmol) in 30 mL of anhydrous degassed THF over a period of 10 min. The mixture was stirred for 30 min, followed by addition of a solution of **7** (546 mg, 1.0 mmol) in 15 mL of anhydrous degassed THF. After being stirred overnight at room temperature, the residue was purified by silica gel column chromatography using the mixture of dichloromethane and methanol (40 : 1, *V/V*) as eluant. Compound **8** (500 mg) was obtained as an orange oil in 71.4% yield. ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.55 (s, 2H), 8.01—7.97 (m, 2H), 7.36 (s, 2H), 6.40 (s, 1H), 4.54 (s, 4H), 3.68 (t, J=4.3 Hz, 2H), 3.65—3.53 (m, 12H), 3.28 (s, 4H), 2.89 (t, J=6.0 Hz, 2H), 2.51 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.6, 155.5, 147.5, 147.4, 136.2, 133.4, 133.3, 126.5, 123.3, 123.0, 117.8, 113.9, 106.8, 72.5, 70.5, 70.4, 70.1, 69.6, 69.5, 61.7, 35.3, 30.2; HRMS calcd for $C_{28}H_{33}N_2O_5S_7$ $[M+H]^+$ 701.0435, found 701.0400.

Synthesis of compound 1 To a solution of compound **8** (180 mg, 0.26 mmol) in 5 mL dry THF was added NaH (12.5 mg, 0.52 mmol). The mixture was stirred for 30 min. Then tetrachloro-1,4-benzoquinone (128 mg, 0.52 mmol) was added. After being stirred for 5 h, the reaction mixture was filtered. After removal of solvents, the residue was subjected to column chromatography on silica gel to give compound **1** (124 mg) as a black green solid in 52.6% yield. ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.55—8.53 (m, 2H), 7.80 (d, J=7.4 Hz, 1H), 7.92 (d, J=7.4 Hz, 1H), 7.37—7.33 (m, 2H), 6.39 (s, 1H), 4.66 (t, J=4.1 Hz, 2H), 4.53 (s, 2H), 4.46 (s, 2H), 3.73 (t, J=4.1 Hz, 2H), 3.62 (t, J=6.4 Hz, 2H), 3.55—3.51 (m, 6H), 3.43 (t, J=4.3 Hz, 2H), 3.29 (s, 4H), 2.90 (t, J=6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 172.7, 171.9, 155.5, 155.3, 147.5, 140.3, 138.8, 136.3, 136.1, 133.5, 133.3, 126.6, 125.7, 123.4, 123.0, 117.8, 114.0, 106.8, 73.6, 70.9, 70.7, 70.5, 70.1, 70.0, 69.7, 69.5, 69.4, 35.4, 30.3; HRMS calcd for $C_{34}H_{31}Cl_3N_2O_7S_7$ $[M]^+$ 907.9225, found 907.92364.

Results and discussion

Synthesis and characterization

The synthetic approach to dyad **1** is shown in Scheme 2. Reaction of compound **4**[6a] with compound **2** in the presence of KH afforded compound **5**. Removal of the tetrahydropyran group in compound **5** led to compound **6**, which was further transformed into compound **7** after mono-tosylation. Reaction of compounds **7** and **3**[7] in the presence of CsOH yielded compound **8**. Further reaction of compound **8** with tetrachloro-1,4-benzoquinone in the presence of NaH afforded dyad **1** in 52.6% yield.

Absorption and ESR spectral studies

Figure 1 shows the absorption spectrum of dyad **1** and those in the presence of different amount of Sc^{3+}. No absorption above 550 nm was detected for dyad **1** before addition of Sc^{3+}. This implies that the intramolecular interaction between TTF and quinone unit within dyad **1** can be neglected. However, after addition of Sc^{3+} to the solution of dyad **1**, new absorption bands around 450 and 850 nm emerged, and their absorption intensities increased by increasing the amount of Sc^{3+}. The maximum absorption reached after the addition of more than 1.5 equiv. of Sc^{3+} (see inset A of Figure 1). According to previous studies,[5] the absorption bands around 450 and 850 nm can be ascribed to the radical cation of TTF unit of dyad **1**. Therefore, the appearance of these two absorptions indicates the formation of the $TTF^{\bullet +}$ for dyad **1** in the presence of Sc^{3+}. This is likely due to the electron transfer within dyad **1** in the presence of Sc^{3+} based on the previous investigations of TTF-quinone dyads.[5] The corresponding Job plot (see inset B of Figure 1) implies that dyad **1** binds Sc^{3+} to form a complex with 2∶3 stoichiometry.

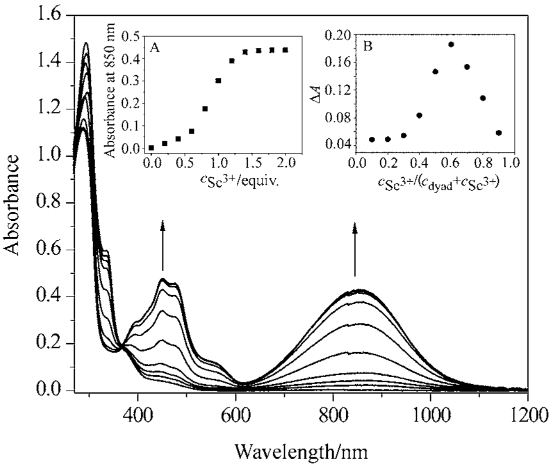


Figure 1 Absorption spectra of dyad **1** recorded in CH_2Cl_2 (5.0×10^{-5} mol/L) in the presence of increasing amount of Sc^{3+} [$Sc(OTf)_3$]; inset A shows the variation of absorbance intensity at 850 nm upon addition of different amounts of Sc^{3+}, inset B shows Job plot for the binding of **1** with Sc^{3+}.

The solution of dyad **1** was ESR silent. However, strong ESR signal was observed for the solution of dyad **1** in the presence of Sc^{3+} as shown in Figure 2. The doublet ESR signals were likely due to the radical cation of TTF unit of dyad **1**, and the doublet signals were ascribed to the splitting of one H atom of TTF unit. However, the radical anion of quinone unit could not be detected for the fast disproportionation of the radical anion of quinone ($Q^{\bullet -}$) into the corresponding Q^{2-} and neutral Q in the presence of metal ion at room temperature.[8] Nevertheless, the emergence of ESR signal confirms that electron transfer takes place for dyad **1** in the presence of Sc^{3+}. Accordingly, both absorption and ESR spectroscopic investigations manifest that electron transfer occurs between TTF and quinone units of dyad **1** in the presence of Sc^{3+}.

The absorption and ESR spectra of dyads **1** were also measured in the presence of other metal ions (including Li^{+}, Na^{+}, K^{+}, Pb^{2+}, Zn^{2+}, Mg^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} and Ba^{2+}). Obvious increasement of absorptions around 450 and 850 nm were observed for dyad **1** in the presence of Pb^{2+} (Figure 3), being simililar to those of dyad **1** with Sc^{3+}. New absorptions around 450 and 850 nm were also observed for dyad **1** in the presence of Zn^{2+}, Cd^{2+} and Co^{2+} (Figure 3). In addition, strong ESR signals were detected for the solution of dyad **1** containing Pb^{2+}/Zn^{2+} (Figure 4). Thus, it can be concluded that $Pb^{2+}/Zn^{2+}/Cd^{2+}/Co^{2+}$ can also promote the electron transfer efficiently between TTF and quinone units within dyad **1**. The Job plots shown in insets of Figure 3 indicate that the solutions exhibit maximum absorbance at 850 nm when the molar ratios of dyad **1** vs. Pb^{2+} and Zn^{2+} were 1∶2 and 2∶3, respectively. Accordingly, it may be concluded that dyad **1** binds Pb^{2+} and Zn^{2+} to form 1∶2 and 2∶3 complexes, respectively.

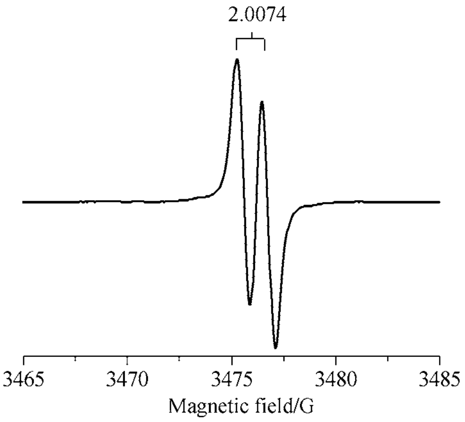


Figure 2 ESR spectrum of dyad **1** (5.0×10^{-5} mol/L) in CH_2Cl_2 in the presence of 5.0 equiv. of Sc^{3+} [$Sc(OTf)_3$] recorded at room temperature; the solution was degassed before measurement.

Cyclic voltammetric studies

In order to understand the mechanism for metal ions promoted electron transfer within dyads **1**, the redox potentials of **1** in the absence and presence of $Sc^{3+}/Pb^{2+}/Zn^{2+}$ were measured. Figure 5 depicts the cyclic voltammogram of **1** and that in the presence of 2.0 equiv. of $Sc^{3+}/Pb^{2+}/Zn^{2+}$. Three quasi-reversible redox waves were detected for dyad **1**, corresponding to $E^{1/2}_{ox1}=0.50$ V, $E^{1/2}_{ox2}=0.89$ V and $E^{1/2}_{red}=-0.14$ V. The two oxidation potentials are close to those of compound **3** (see Scheme 2) ($E^{1/2}_{ox1}=0.49$ V, $E^{1/2}_{ox2}=0.88$ V).[7] Thus, the oxidation waves with $E^{1/2}_{ox1}=0.50$ V and $E^{1/2}_{ox2}=0.89$ V should be due to the formation of $TTF^{\bullet +}$ and TTF^{2+}, respectively. The reduction wave with $E^{1/2}_{red}=-0.14$ V is owing to the reduction of quinone unit in dyad **1** according to previous study.[5] These results can reach the conclusions that the electron donor-acceptor interaction within dyad **1** can be neglected in the ground state, which agrees well with the absorption spectral studies as discussed above. Therefore, the electron

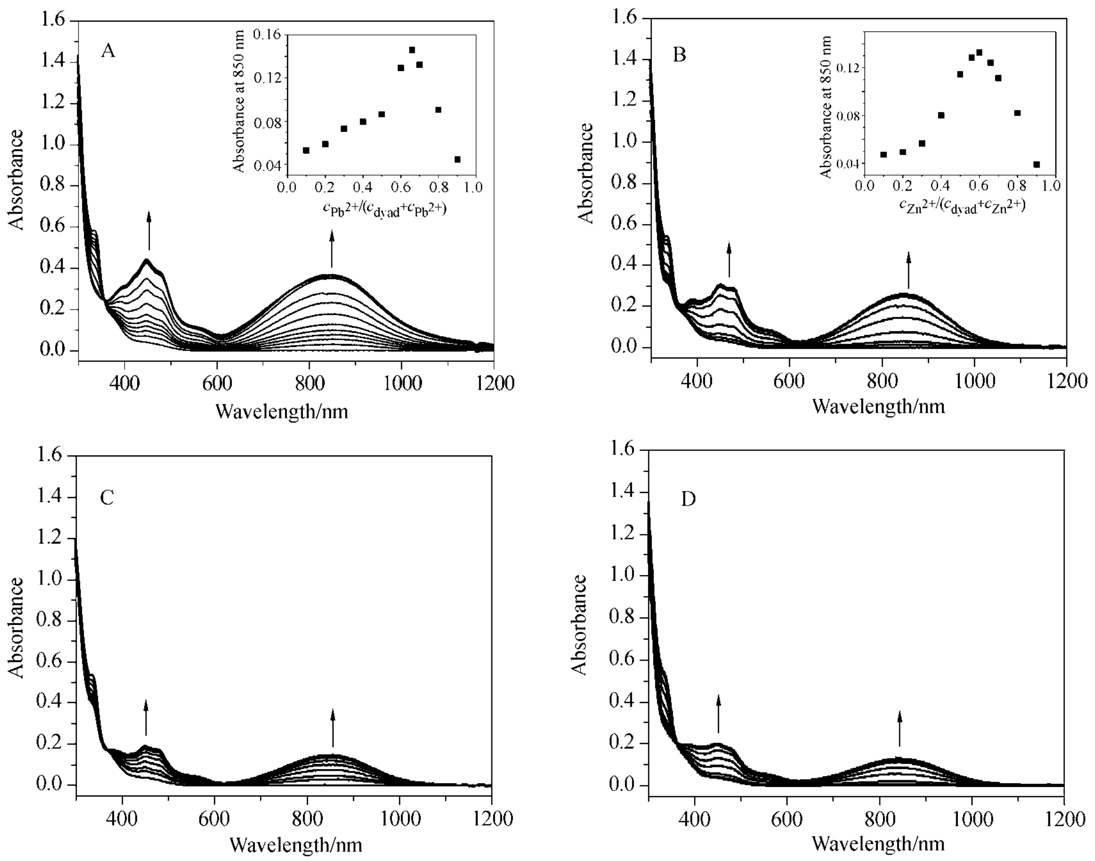


Figure 3 Absorption spectra of dyad **1** recorded in CH_2Cl_2 (5.0×10^{-5} mol/L) in the presence of increasing amount of Pb^{2+} (A), Zn^{2+} (B), Cd^{2+} (C) and Co^{2+} (D); insets show the corresponding Job plots for the binding of **1** with Pb^{2+} and Zn^{2+}.

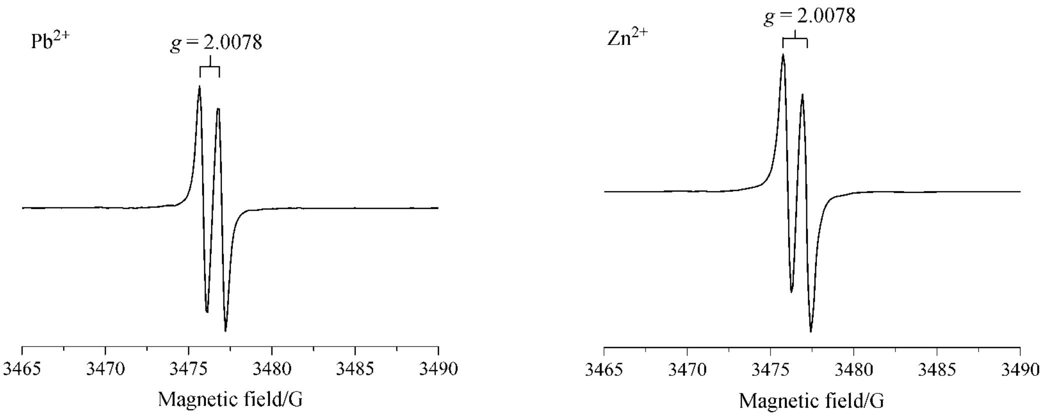


Figure 4 ESR spectra of dyad **1** (5.0×10^{-5} mol/L) in CH_2Cl_2 in the presence of 5.0 equiv. of Pb^{2+} and Zn^{2+} recorded at room temperature; the solution was degassed before measurement.

transfer between the TTF and quinone units of dyads **1** is not thermodynamically feasible. However, in the presence of $Sc^{3+}/Pb^{2+}/Zn^{2+}$, the reduction wave was positively shifted (see Figure 5). For instances, the reduction peak potential of the quinone unit in dyad **1** was shifted from −0.18 to 0.05 and 0.02 V in the presence of 2.0 equiv. of Sc^{3+} and Pb^{2+}, respectively (see Figure 5). On the basis of previous studies,[5] positive shifts of reduction potential of quinone unit in dyad **1** in the presence of metal ions make the intramolecular electron transfer from TTF unit to quinone unit more feasible.

By comparing the metal ion-promoted electron transfer within TTF-oligoethylene glycol chain-quinone dyads, we assume that sulfur atoms from $TTF^{\bullet+}$, oxygen atoms of biglycol chain and oxygen atoms of the radical anion of quinone unit in dyad **1** may coordinate with $Sc^{3+}/Pb^{2+}/Zn^{2+}$ to stabilize the electron-transfer state by increasing the interaction between the corresponding cation and anion (see Scheme 3). However, there is still some difference in their coordination geometry for dyad **1** complex with different metal ions. For example, the stoichiometry of complex formed between **1** and Sc^{3+}/

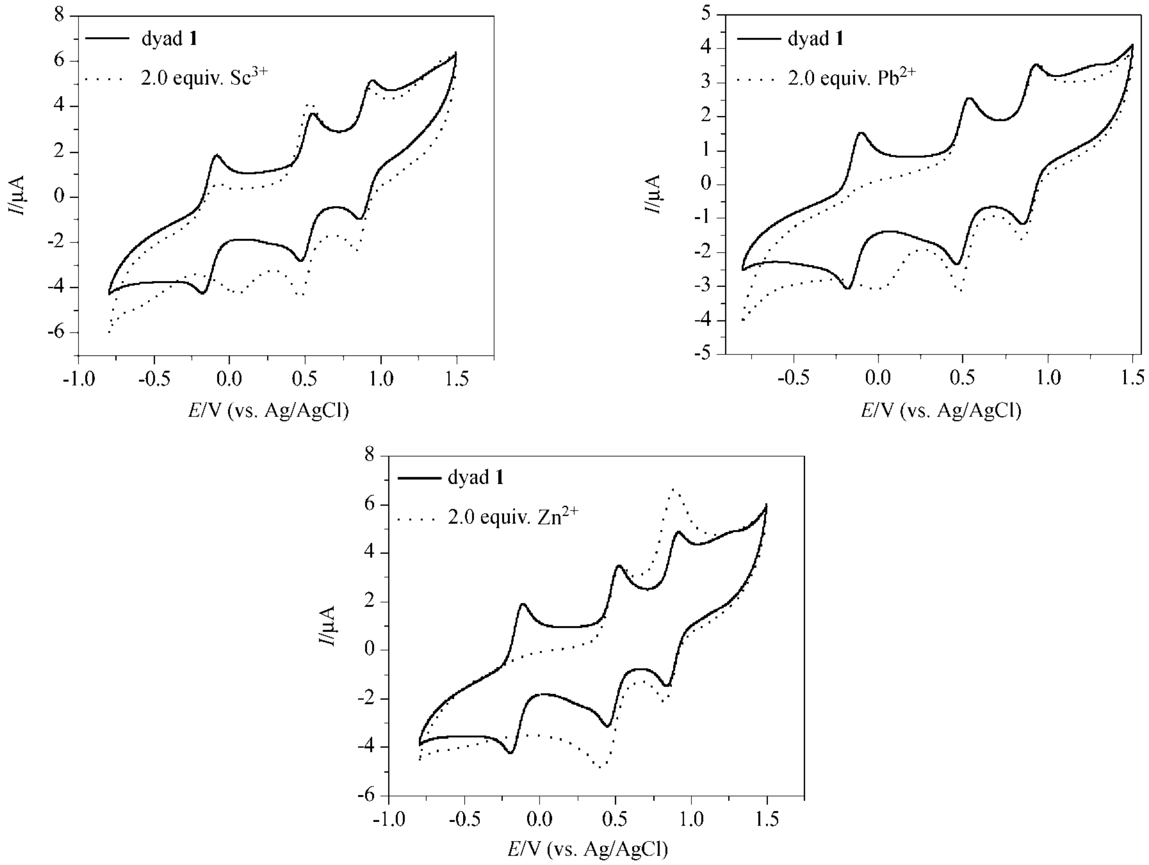
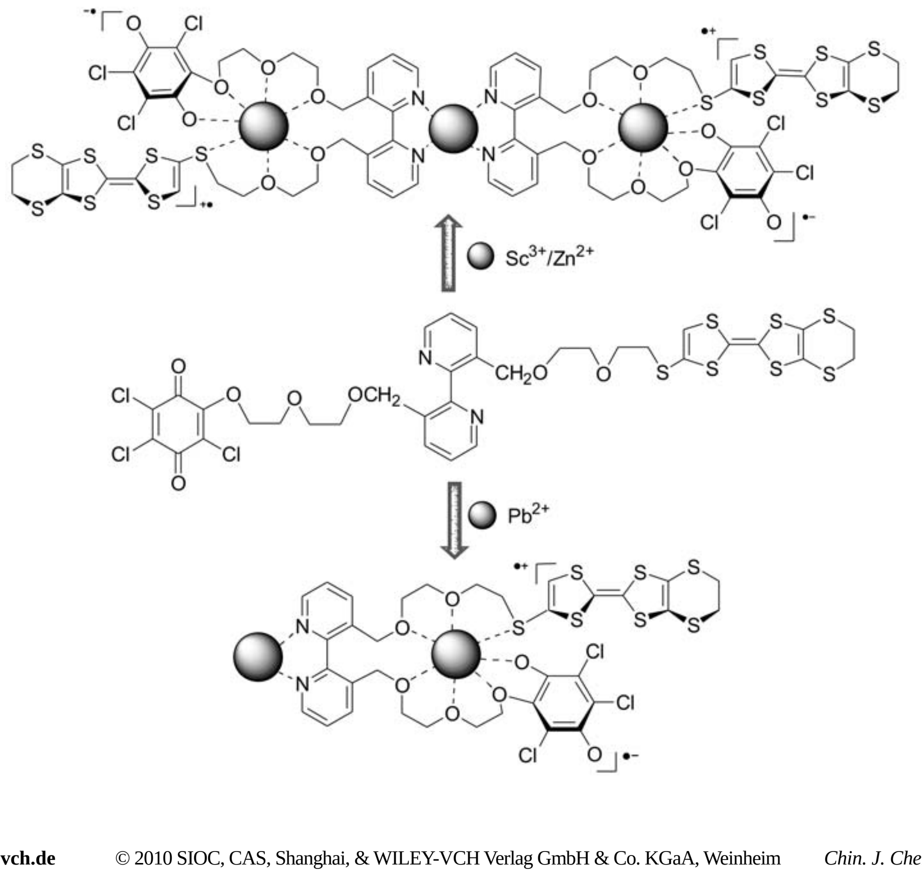


Figure 5 Cyclic voltammograms of dyad **1** (5.0×10^{-4} mol/L) in CH_2Cl_2 before (solid) and after (dot) addition of 2.0 equiv. of Sc^{3+}/Pb^{2+}/Zn^{2+}.

Scheme 3 The proposed mechanism for the metal ion-promoted electron transfer within dyad **1**



Zn^{2+} was estimated to be 2∶3 via the job plots (insets of Figure 1 and Figure 3). As illustrated in Scheme 3, one Sc^{3+}/Zn^{2+} may firstly coordinate with two 2,2'-bipyridyl units leading to conformation change of 2,2'-bipyridyl unit from '*transoid*' to '*cisoid*'. The favorable '*cisoid*' conformation would cause the TTF and quinone units in dyad **1** to be spatially adjacent; further synergic coordination of the radical anion of quinone and the diglycol chain with two Sc^{3+}/Zn^{2+} results in electron transfer efficiently in dyad **1**. For Pb^{2+}, however, the complex of dyad **1** with Pb^{2+} adopts 1∶2 stoichiometry and the coordination mode is proposed as shown in Scheme 3. Similarly, because of the '*cisoid*' conformation of 2,2'-bipyridyl unit after coordination with Pb^{2+}, the TTF and quinone units in dyad **1** would be spatially adjacent, which is favorable for the intramolecular electron transfer in the presence of Pb^{2+}.

Conclusion

In summary, the 2,2'-bipyridyl linked TTF-quinone dyad **1** was synthesized and characterized. Both absorption and ESR spectroscopic studies clearly indicate that electron transfer occurs from TTF to the quinone unit within dyad **1** in the presence of metal ions (Sc^{3+}, Pb^{2+}, Zn^{2+}, $Cd^{2+}$and Co^{2+}). The coordination of dyad **1** with metal ions plays a key role in facilitating the intramolecular electron transfer: (1) the metal ion coordination induces the positive shift of the reduction potential of the quinone unit which makes the intramolecular electron transfer from TTF unit to quinone unit more feasible; (2) the coordination with metal ions induces the conformation change of bipyridyl unit from '*transoid*' to '*cisoid*' which would be favorable for the synergic coordination of the radical anion of quinone and the diglycol chain with metal ions. These results provide a new example of metal ions-promoted electron transfer within TTF-quinone dyads. Further studies regarding the application of such metal ions-promoted electron transfer are underway.

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