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Tetrathiafulvalene–flavin dyads: electron transfer promoted by metal cations

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ABSTRACT

Tetrathiafulvalene–flavin dyads **1** and **2** are reported. Both absorption and ESR spectral studies show that the intramolecular electron transfer occurs from TTF to flavin units in dyads **1** and **2** in the presence of Pb^{2+}/Sc^{3+}. But, the electron transfer is more efficient for dyad **1** in the presence of Pb^{2+}/Sc^{3+}. Electrochemical studies manifest that coordination of dyads **1** and **2** with Pb^{2+}/Sc^{3+} play an important role in facilitating the electron transfer within dyads **1** and **2**.

In the past decades, a number of electron donor (D)–acceptor (A) dyads with tetrathiafulvalene (TTF) unit or its derivatives as the electron donating units have been reported.[1–6] These TTF based D–A molecules are interesting as models for studies of charge-transfer interactions, photoinduced electron transfer processes, and molecular level devices. For instance, fluorescence switches[4] and chemical sensors[5] with D–A dyads or triads with TTF units have been described. 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.[6] The investigations manifest that the electron transfer cannot occur in the absence of metal ions and the coordination of oligoethylene glycol chain and the radical anion of quinone with metal ions is crucial for the electron transfer. Further studies show that such metal ion-promoted electron transfer is dependent on the electron accepting ability of the quinone unit.

Apart from quinone, isoalloxazine compounds, which are also referred to as flavins, are important electron acceptors. As the redox-active parts of flavoenzymes flavins enable flavoenzymes to mediate a variety of electron transfer processes they play an important role in redox reaction in biological organisms.[7] Previous studies indicate that the electron accepting abilities of flavins can be modulated by hydrogen-bonding,[7,8] π–π stacking,[9] donor–acceptor interaction,[10] and in particular coordination to metal ions.[11] The reduction potentials of flavins were positively shifted in the presence of metal ions such as Mg^{2+} and Sc^{3+} and the oxidation reactivity of singlet excited states of flavins could be significantly enhanced by coordination with metal ions.[11,12] Based on the unique electron donating and accepting properties of TTF and flavin, it is interesting to examine whether electron transfer can occur for the TTF–flavin dyads in the presence of metal ions. Herein, we report two TTF–flavin dyads **1** and **2**, in which the TTF and flavin units are linked by the glycol and alkyl chains, respectively.

The synthesis of dyads **1** and **2** started from compound **3**[13] as outlined in Scheme 1. Compound **4** was synthesized by removing the cyanoethyl group in **3** in the presence of CsOH and further reaction with tetraethyleneglycol monotoluenesulfonate. Compound **4** was converted to compound **5** via tosylation. Compound **6** was prepared by the reaction of compound **5** with 4,5-dimethylbenzene-1,2-diamine in the presence of K_2CO_3. Finally, the condensation of compound **6** with alloxan led to dyad **1** in reasonable yield.[14] Dyad **2** was synthesized similarly as shown in Scheme 1. 5-Bromo-1-pentanol was used for the preparation of compound **7**. By following the same procedures dyad **2** yielded compound **7** in three steps. [15]

Figure 1A shows the absorption spectrum of dyad **1** and those in the presence of different amounts of Pb^{2+}. No absorption above 600 nm was detected for dyad **1** before the addition of Pb^{2+}, and the absorptions of **1** around 330, 367 and 450 nm were due to the TTF and flavin units in **1** according to previous studies.[12a,13] This implies that the intramolecular interaction between TTF and flavin units within dyad **1** was negligible. However, new absorption around 780 nm emerged gradually after the addition of Pb^{2+} as depicted in Figure 1A. The absorption in the range of 450–600 nm was also enhanced gradually. In comparison, direct oxidation of compound **3** with $Fe(ClO_4)_3$ also led to two new absorptions around 450 and 780 nm (see Supplementary Fig. S1). Therefore, the appearance of these two absorptions indicates the formation of the TTF$^{\cdot+}$ for dyad **1** in the presence of Pb^{2+}. This is likely due to the electron transfer within dyad **1** in the presence of Pb^{2+} based on the previous investigations of TTF–quinone dyads.[6]

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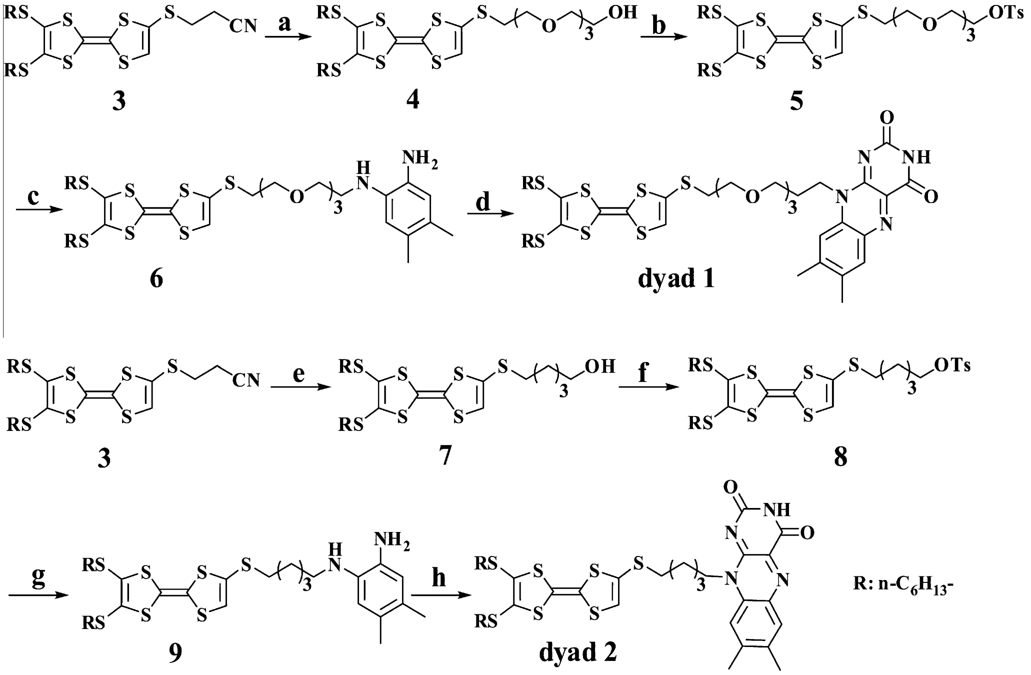


Scheme 1. The chemical structure and synthetic approach for dyad **1** and dyad **2**: (a) CsOH·H_2O, tetraethyleneglycol monotoluenesulfonate, THF, rt, 60%; (b) *p*-tosyl chloride, triethylamine, 0 °C, 84%; (c) 4,5-dimethylbenzene-1,2-diamine, K_2CO_3, DMF, 60 °C; (d) alloxan, H_3BO_3, CH_3OH, rt, 19%; (e) CsOH·H_2O, 5-bromo-1-pentanol, THF, rt, 80%; (f) *p*-tosyl chloride, triethylamine, 0 °C, 84%; (g) 4,5-dimethylbenzene-1,2-diamine, K_2CO_3, DMF, 60 °C; (h) alloxan, H_3BO_3, CH_3OH, rt, 18%.

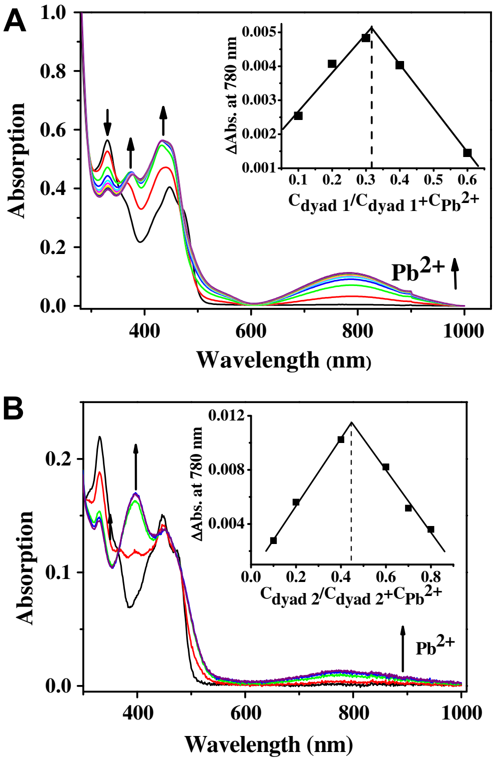


Figure 1. Absorption spectra of dyad **1** (1.0×10^{-5} M in CH_2Cl_2) (A) and dyad **2** (1.0×10^{-5} M in CH_2Cl_2) (B) upon addition of different amounts of Pb^{2+}[$Pb(ClO_4)_2$]; the insets show Job's plot for the binding of **1** (A)/**2** (B) with Pb^{2+}.

Additionally, the absorption around 330 nm due to the flavin unit in dyad **1** became gradually weak and simultaneously red-shifted. This may indicate the coordination of flavin unit with Pb^{2+} based on the previous report.[12a] Based on the variation of the absorption intensity at 780 nm due to the $TTF^{\cdot+}$ versus the molar fraction of Pb^{2+} in the solution as depicted in the inset of Figure 1A, it may be concluded one molecule of dyad **1** binds two Pb^{2+}.

Of interest is the observation of new absorptions around 450 and 780 nm for dyad **2** after the addition of Pb^{2+} as demonstrated in Figure 1B. Compared to dyad **1**, these new absorptions are rather weak under the same condition. The variation of the absorption at 780 nm versus the molar fraction of Pb^{2+} (see the inset of Fig. 1B) implies that dyad **2** and Pb^{2+} may form a complex with 1:1 stoichiometry. As to be discussed below, ESR signal can be detected for the solution of dyad **2** containing Pb^{2+} (see Supplementary Fig. S7). These results manifest that the Pb^{2+} promoted electron transfer occurs also for dyad **2**, in which the TTF and flavin units are linked by an alkyl chain.

The solution of dyad **1** was ESR silent. However, strong ESR signal was observed for the solution of dyad **1** in the presence of Pb^{2+} as shown in Figure 2. The ESR signal intensity was found to be dependent on the amount of Pb^{2+} in the solution. The ESR signal was not well resolved and it might be due to the magnetic coupling between the radical cation of TTF unit and the radical anion of

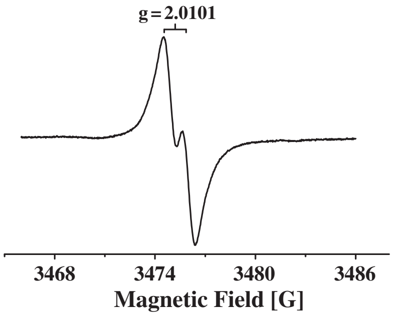


Figure 2. ESR spectrum of dyad **1** (1.0×10^{-3} M) in CH_2Cl_2 in the presence of 4.0 equiv of Pb^{2+} [$Pb(ClO_4)_2$] recorded at room temperature; the solution was degassed before measurement.

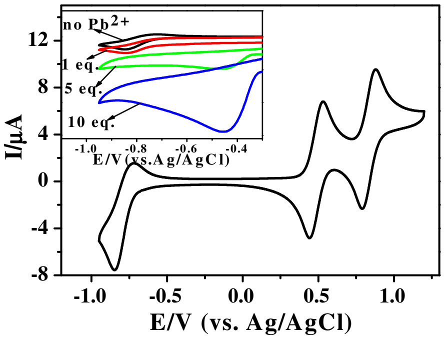


Figure 3. Cyclic voltammograms of dyad **1** (5×10^{-5} M) in CH_2Cl_2; the inset shows partial (flavin unit) cyclic voltammograms of dyad **1** in CH_2Cl_2 in the presence of different amounts of Pb^{2+}; the scanning rate is 50 mV/s.

flavin unit involving Pb^{2+}. Nevertheless, the emergence of ESR signal confirms that electron transfer takes place for dyad **1** in the presence of Pb^{2+}. Similarly, ESR signal was also detected for the solution of dyad **2** containing Pb^{2+} as depicted in Supplementary Figure S7. This result provides further support for the occurrence of electron transfer within dyad **2** in the presence of Pb^{2+}.

The absorption and ESR spectra of dyads **1** and **2** were also measured in the presence of other metal ions including Sc^{3+}, Zn^{2+}, Mg^{2+}, Cd^{2+} and Ba^{2+}. Absorptions around 450 and 780 nm were observed for dyad **1** in the presence of Sc^{3+} (see Supplementary Fig. S2). In addition, strong ESR signal was also detected for the solution of dyad **1** containing Sc^{3+}. In comparison, dyad **1** exhibited rather weak absorptions around 450 and 780 nm after introducing Zn^{2+}, Mg^{2+}, Cd^{2+} and Ba^{2+}. Thus, it can be concluded that Pb^{2+}/Sc^{3+} can promote the electron transfer between TTF and flavin units within dyad **1** more efficiently. Similar results were found for dyad **2**. As displayed in Supplementary Figure S6, the solution of dyad **2** containing Sc^{3+} also showed absorptions around 450 and 780 nm due to the $TTF^{\cdot+}$. Therefore, both Pb^{2+} and Sc^{3+} can trigger the electron transfer within dyad **2**. But, these absorptions were almost not detectable for dyad **2** in the presence of Zn^{2+}, Mg^{2+}, Cd^{2+} and Ba^{2+}.

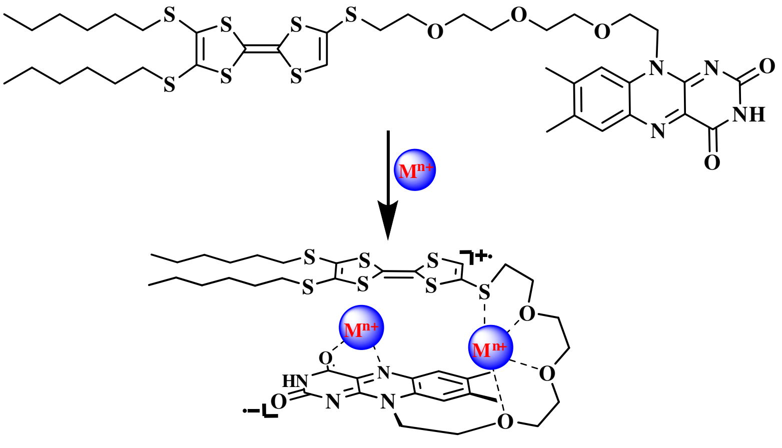
In order to understand the mechanism for Pb^{2+}/Sc^{3+} promoted electron transfer within dyads **1** and **2**, the redox potentials of **1** and **2** in the absence and presence of Pb^{2+}/Sc^{3+} were measured. Figure 3 depicts the cyclic voltammogram of **1** and those in the presence of Pb^{2+}. Three quasi-reversible redox waves were detected for dyad **1**, corresponding to $E_{ox1}^{1/2} = 0.53$ V, $E_{ox2}^{1/2} = 0.88$ V and $E_{red}^{1/2} = -0.85$ V. The two oxidation potentials are close of those of compound **3** (see Scheme 1) ($E_{ox1}^{1/2} = 0.47$ V, $E_{ox2}^{1/2} = 0.85$ V).[13] Thus, the oxidation waves with $E_{ox1}^{1/2} = 0.53$ V and $E_{ox2}^{1/2} = 0.88$ V should be due to the formation of $TTF^{\cdot+}$ and TTF^{2+}, respectively. The reduction wave with $E_{red}^{1/2} = -0.85$ V is owing to the reduction of flavin unit in dyad **1** according to previous study.[8e] In the presence of Pb^{2+}, the reduction wave was positively shifted (see the inset of Fig. 3). For instance, the reduction peak potential was shifted from -0.85 V in the absence of Pb^{2+} to -0.45 V in the presence of 10 equiv of Pb^{2+}. The reduction potential due to the flavin unit in dyad **1** was also positively shifted in the presence of Sc^{3+} (see Supplementary Fig. S5).

Dyad **2** also shows three quasi-reversible redox waves, corresponding to $E_{ox1}^{1/2} = 0.50$ V, $E_{ox2}^{1/2} = 0.87$ V and $E_{red}^{1/2} = -0.86$ V. Similarly, the oxidation and reduction potentials are due to the TTF and flavin units in dyad **2**, respectively. The reduction potential of flavin unit is also positively shifted in the presence of either Pb^{2+} or Sc^{3+} (see Supplementary Fig. S8)

The above electrochemical investigations clearly indicate that the reduction potential of flavin unit in dyads **1** and **2** becomes less negative in the presence of Pb^{2+}/Sc^{3+}; thus, the electron accepting ability of flavin unit was enhanced in the presence of Pb^{2+}/Sc^{3+}.[11,2] Therefore, the electron transfer between TTF and flavins units in dyads **1** and **2** would become more feasible in the presence of these metal ions. By comparing the metal ion-promoted electron transfer within TTF–quinone dyads, we assume that the sulfur atom from $TTF^{\cdot+}$, oxygen atoms of oligoethylene glycol chain and nitrogen/oxygen atoms of the radical anion of flavin unit in dyad **1** may coordinate with Pb^{2+}/Sc^{3+} to stabilize the electron transfer state by increasing the interaction between the corresponding cation and anion (see Scheme 2). The absorption spectral result indicates that one molecule of dyad **1** binds two Pb^{2+}. Therefore, it is probable that binding of dyad **1** with metal ion to form a complex with 1:2 stoichiometry in solution as illustrated in Scheme 2. Formation of such coordination complex would, on one hand, to enhance the electron accepting ability of flavin unit, and on the other hand to stabilize the electron transfer state.

For dyad **2** the TTF and flavin units are linked with an alkyl chain. Only the sulfur atom from $TTF^{\cdot+}$ and nitrogen/oxygen atoms of the radical anion of flavin unit in dyad **2** may be involved in the coordination with Pb^{2+}/Sc^{3+}. Therefore, the complex of dayd **2** with Pb^{2+}/Sc^{3+}may be less stable compared to the corresponding complex of dyad **1** with Pb^{2+}/Sc^{3+}. This is in agreement with the fact that the absorption around 450 and 780 nm for dyad **2** in the presence of Pb^{2+}/Sc^{3+} is weaker than that observed for dyad **1** under the same condition.

In summary, TTF–flavin dyads **1** and **2** were synthesized and characterized. Both absorption and ESR spectroscopic studies clearly indicate that electron transfer occurs from TTF to the flavin unit in the presence of metal ions (Pb^{2+} and Sc^{3+}) for both dyad **1**



Scheme 2. The proposed mechanism for the metal ion-promoted electron transfer in dyad **1**.

and dyad **2**. However, the electron transfer within dyad **1** in the presence of Pb^{2+}/Sc^{3+} is more efficient than that in dyad **2** under the same condition. The coordination with metal ions plays an important role in facilitating the electron transfer within dyads **1** and **2**. The present studies will not only enrich the TTF chemistry, but also provide new aspect of flavin chemistry.

Acknowledgments

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Supplementary data

Supplementary data associated (Synthesis and characterization; absorption and ESR spectra; cyclic voltammogram) with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.06.095.

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14. *Characterization data for dyad* **1**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.49 (1H, s), 8.03 (1H, s), 7.74 (1H, s), 6.40 (1H, br), 4.93 (2H, t, J = 5.26 Hz), 4.02 (2H, t, J = 5.30 Hz), 3.65–3.60 (4H, m), 3.54 (6H, d, J = 2.73 Hz), 2.92 (2H, t, J = 6.44 Hz), 2.80 (4H, t, J = 6.96 Hz), 2.55 (3H, s), 2.45 (3H, s), 1.64–1.60 (4H, m), 1.44–1.36 (4H, m,), 1.33–1.26 (8H, m), 0.89 (6H, t, J = 6.52). ^{13}C NMR (100 MHz, CDCl$_3$): δ 159.52, 154.98, 150.31, 148.00, 137.05, 135.94, 135.00, 132.30, 132.20, 127.86, 127.68, 126.47, 122.97, 116.91, 113.30, 70.91, 70.59, 70.55, 70.48, 69.73, 67.98, 45.81, 36.28, 35.24, 31.31, 29.71, 28.20, 22.53, 21.55, 19.53, 14.02. HR-MS(EI): calcd for $C_{38}H_{52}N_4O_5S_7$ 868.1983; found, 868.1989.
15. *Characterization data for dyad* **2**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.42 (1H, s), 8.07 (1H, s), 7.38 (1H, s), 4.70 (2H, br), 2.81–2.77 (6H, m), 2.57 (3H, s), 2.46 (3H, s), 1.93–1.85 (2H, m), 1.88–1.86 (2H, m), 1.64–1.62 (2H, m), 1.41–1.32 (4H, m), 1.29–1.25 (12H, m), 0.88 (6H, t, J = 6.56).^{13}C NMR (100 MHz, CDCl$_3$): 159.73, 155.54, 150.28, 148.60, 137.35, 136.34, 135.18, 133.11, 131.20, 115.46, 45.27, 36.54, 31.52, 29.91, 29.57, 29.29, 28.42, 28.23, 26.87, 25.71, 22.90, 22.75, 22.02, 19.76, 14.24, 14.06. HR-MS(EI): calcd for $C_{35}H_{46}N_4O_2S_7$, 778.1666; found, 778.1672.