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Linear and Cyclic Tetrathiafulvalene−Naphthalenediimide Donor−Acceptor Molecules: Metal Ions-Promoted Electron Transfer

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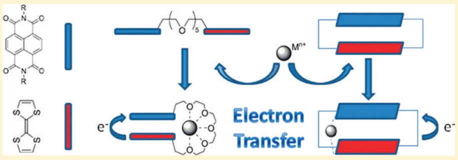
S *Supporting Information*

ABSTRACT: Three linear and one cyclic tetrathiafulvalene−1,4,5,8-naphthalenediimide (TTF−NDI) compounds **1**, **2**, **3**, and **4** were synthesized and studied in the presence of metal ions. Both absorption and electron spin resonance spectroscopic studies clearly indicate that electron transfer occurs from TTF to the NDI unit in the presence of metal ions (Pb^{2+} and Sc^{3+}) for linear compounds **1** and **2**. The mechanism based on the metal ion coordination is proposed for the electron transfer within **1** and **2** after the addition of metal ions. Compound **3** exhibits intramolecular charge-transfer absorption because of the cyclophane framework. Interestingly, intramolecular electron transfer also takes place for **3** after the addition of either Sc^{3+} or Pb^{2+}.



INTRODUCTION

Tetrathiafulvalene (TTF) and its derivatives are strong electron donors. On one hand, they have played an important role in the development of organic conducting materials.[1−4] On the other hand, they are incorporated into a number of electron donor (D)−acceptor (A) systems for studies of charge-transfer (CT) interactions and photoinduced electron-transfer processes as well as molecular devices.[5−19] It is known that electron D and A molecules can interact to form complexes when they are properly arranged or connected.[20] The interactions between D and A molecules are referred to as CT interactions, and the complexes are defined as CT complexes. According to Mulliken theory,[21] the electronic wave function of a CT complex includes a partial CT component in the ground state. Therefore, D and A molecules may bear partial positive and negative charges ($D^{\delta+}\cdot A^{\delta-}$), respectively, within the CT complexes.[22] CT complexes usually exhibit additional electronic absorptions (CT absorptions) that are uncharacteristic of the D and A components.[23]

However, when strong D (e.g., TTF) and A (e.g., TCNQ, tetracyanoquinodimethane) molecules are connected, electron transfer can occur, generating the respective radical cation ($D^{\bullet+}$) and anion ($A^{\bullet-}$) without light irradiations.[24,25] Fukuzumi, Bielawski, and Sessler have just recently reported the electron transfer (without light irradiation) between TTF calix[4]pyrrole and bisimidazolium quinone, leading to the respective $D^{\bullet+}\cdot A^{\bullet-}$ salt under the influence of certain anions.[26] There are some D−A molecules in which the electron transfer cannot take place in the absence of metal ions, but it occurs efficiently in the presence of metal ions.[27] Such metal ion-promoted electron transfer has received significant attention in recent years.[28] In fact, metal ions play a pivotal role in mediating electron transfer in biological systems (e.g., respiration) as either activators, inhibitors, or simple spectators.[29]

We have recently reported a metal ion-promoted intramolecular electron-transfer process within TTF-based D−A systems in which TTF and quinone units were linked covalently by an oligoethylene glycol.[30] The investigations indicate that the coordination of metal ion with the oxygen atoms of the glycol chain, sulfur atoms of TTF cation, and quinone anion plays an important role in facilitating the electron transfer. Furthermore, such metal ion-promoted electron transfer is affected by the electron-accepting abilities of quinone units. It is interesting to know whether such metal ions-promoted electron transfer can occur within TTF-based D−A systems in which A is another kind of electron acceptor, being different from quinone. For instance, we have recently shown that intramolecular electron transfer can take place efficiently for the TTF−flavin dyad in the presence of certain metal ions.[31]

1,4,5,8-Naphthalenediimide (NDI) as a compact, electron-deficient class of aromatic compound is weaker than quinone in terms of electron-accepting ability. NDI and its derivatives have been intensively investigated as electronic materials.[32,33] NDI can be easily functionalized through either the diimide nitrogen atoms or core substitution. In fact, photoinduced electron transfer within TTF−NDI−TTF compounds in which the units are linked by alkyl chains was reported early.[34] In this paper, we want to report the electron transfer within linear TTF−NDI compounds **1** and **2** (Scheme 1) in which the TTF and NDI units are linked by the glycol chain in the presence of certain metal ions. Moreover, we will report a cyclic TTF−NDI compound **3** (Scheme 1) in which the two units are arranged

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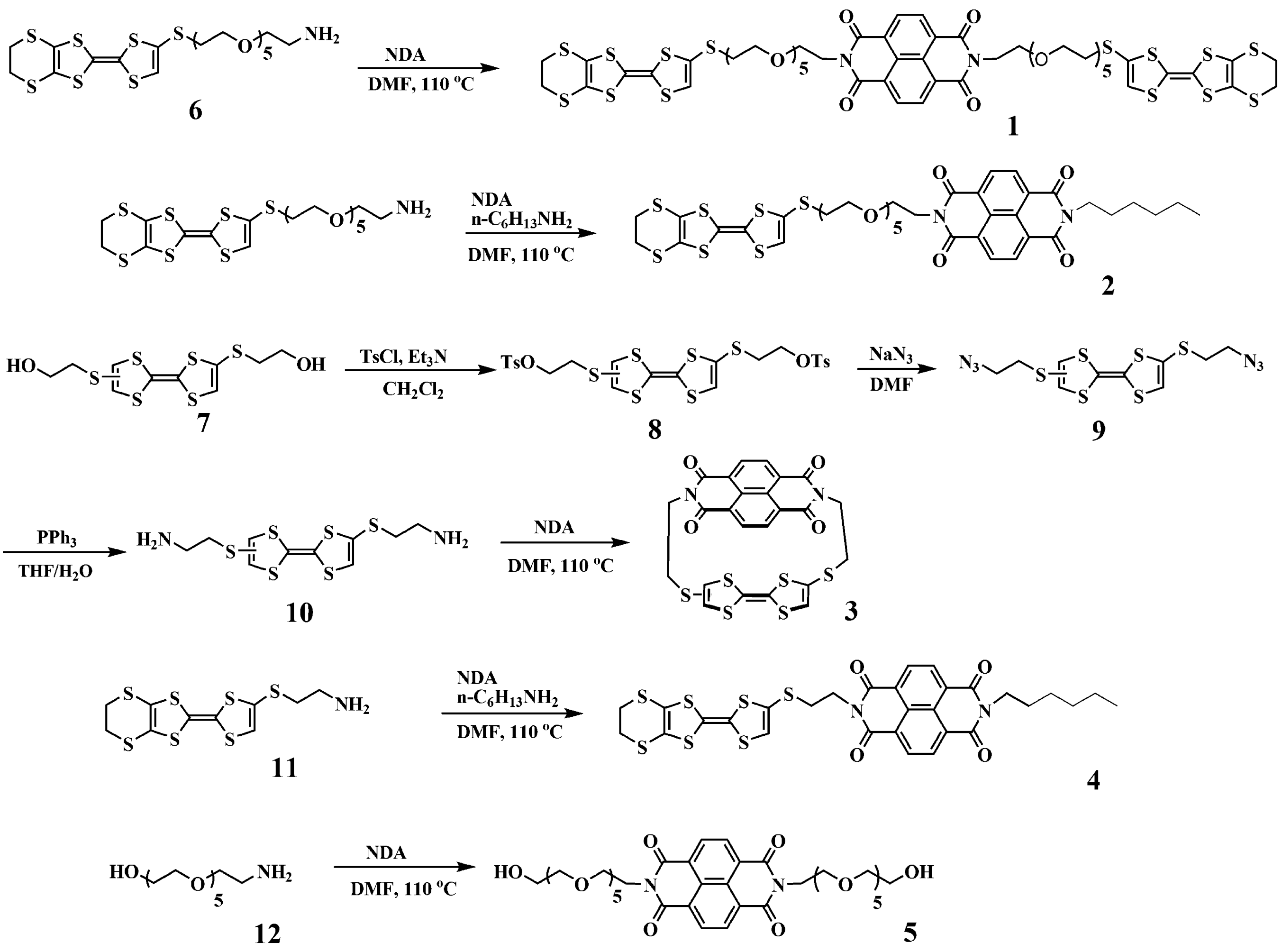
Scheme 1. Chemical Structures and Synthetic Approaches for Compounds 1−5



by two $-CH_2CH_2-$ bridges; both absorption and electron spin resonance (ESR) spectral studies indicate the transformation from the CT state into the electron-transfer state after introducing metal ions.

■ RESULTS AND DISCUSSION

The synthesis of the titled linear and cyclic TTF−NDI compounds **1**, **2**, and **3** is shown in Scheme 1. Compound **1** was obtained in 63% yield by the reaction of **6** and naphthalene anhydride (NDA) at 110 °C in DMF. The condensation of **6** and *n*-$C_6H_{13}NH_2$ with NDA led to compound **2** in 27% yield after separation. The synthesis of compound **3** started from compound **7**. Compound **7** was transformed into compound **8** in 83% yield after reaction with *p*-toluenesulfonyl chloride in the presence of triethylamine. The reaction of compound **8** with NaN_3 led to compound **9** in 80% yield, which was further reduced with PPh_3 to afford compound **10** in 76% yield. Finally, the condensation of **10** with NDA in highly diluted DMF solution yielded compound **3** in an acceptable yield of 18%. For comparison, reference compounds **4** and **5** were also synthesized. The chemical structures of these compounds were confirmed by NMR and mass spectroscopic data (see the Experimental Section).

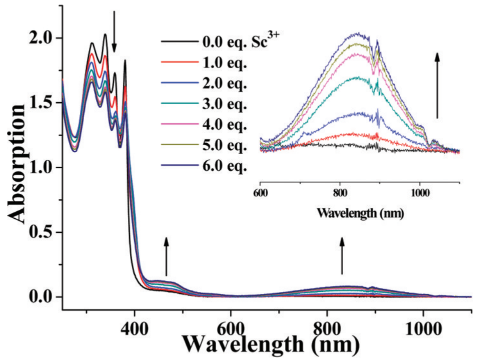


Figure 1. Absorption spectra of compound **1** (5.0×10^{-5} M in CH_2Cl_2) in the presence of different amounts of Sc^{3+} [$Sc(SO_3CF_3)_3$]; the inset shows the 600−1100 nm part of the absorption spectra in the presence of increasing amounts of Sc^{3+}.

Figure 1 shows the absorption spectrum of **1** and those in the presence of different amounts of Sc^{3+}. Compound **1** shows absorptions around 338, 358, and 380 nm, which are due to the TTF and NDI units in **1** according to previous studies,[34] and no new absorptions above 600 nm were detected before the addition of Sc^{3+}. The redox potentials of **1** were measured to be $E^{1/2}(\text{ox}_1) = 0.55$ V, $E^{1/2}(\text{ox}_2) = 0.87$ V, and $E^{1/2}(\text{red}_1) = -0.59$ V, $E^{1/2}(\text{red}_2) = -1.12$ V (vs Ag/AgCl; see Figure S7 in the Supporting Information), which are rather close to those of compounds **6** and **5**. These results manifest that the intramolecular electronic interaction between TTF and NDI units within **1** can be considered negligible. However, new absorption bands around 450 and 845 nm emerged gradually after the addition of Sc^{3+} as depicted in Figure 1; moreover, their absorption intensities increased by increasing the concentration of Sc^{3+} in the solution, reaching the maximum when 6.0 equiv of Sc^{3+} was added as shown in the inset of Figure 1. On the basis of previous results,[30,31] the appearance of these two absorptions indicates the transformation of TTF units of **1** into the corresponding $TTF^{\bullet+}$. According to previous investigations of TTF−quinone systems, this is likely due to the electron transfer within **1** in the presence of Sc^{3+}.[30] Also, new absorptions around 450 and 845 nm were also observed for compound **2** after the addition of Sc^{3+} (see Figure S4 in the Supporting Information). However, their absorption intensities are weaker than those of **1** under the same conditions. Apart from the appearance of these new absorptions, the absorption bands in the range of 300−400 nm were also modified after the addition of Sc^{3+}. This may be because of the binding of Sc^{3+} with TTF and NDI units in **1** and **2**. Moreover, the binding ratios of **1** and **2** with metal ions (e.g., Sc^{3+}) were determined on the basis of the respective Job plots.[35] For instance, the binding ratio of **2** with Sc^{3+} was found to be 1:1 based on the Job plot (see Figure S15 in the Supporting Information), and the corresponding binding constant was estimated to be 611 ± 10 M^{-1} by fitting the titration data (variation of absorption intensity at 396 nm vs the concentration Sc^{3+}) (see the Supporting Information).

The solution of **1** was ESR silent. However, a strong ESR signal was observed for the solution of **1** in the presence of Sc^{3+} as shown in Figure 2. The signals are likely attributed to the radical cation ($TTF^{\bullet+}$) of the TTF moiety within **1**, and the doublet signal stems from the splitting due to one H atom of the TTF unit. Thus, the formation of $TTF^{\bullet+}$ in the presence of Sc^{3+} is also confirmed by ESR spectroscopy. Similarly, the ESR signal due to the $TTF^{\bullet+}$ was detected for **2** after the addition of Sc^{3+} (see Figure S4 in the Supporting Information). However, the corresponding radical anion of NDI unit ($NDI^{\bullet-}$), which should be generated through the intramolecular electron transfer from the TTF moiety to the NDI unit after introduction of Sc^{3+}, was not detected with ESR spectroscopy. This might be due to the easily disproportionation of $NDI^{\bullet-}$ into NDI^{2-}[36,37] and neutral NDI in the presence of metal ions, which has been proved by a control experiment (Figure S6 in the Supporting Information).[38] It is believed that the disproportionation of $NDI^{\bullet-}$ in the presence of metal ions may further facilitate the electron transfer from TTF to NDI units within **1** and **2**: (1) the transformation of $NDI^{\bullet-}$ that is generated from the electron transfer into NDI^{2-} and neutral NDI will drive the electron transfer forward; (2) as compared to $NDI^{\bullet-}$, NDI^{2-}, which may bind more strongly with metal ions, may interact more strongly with $TTF^{\bullet+}$. In short, these absorption and ESR spectral studies indicate that intramolecular electron transfer between TTF and NDI units of **1** and **2** occurs in the presence of Sc^{3+}.

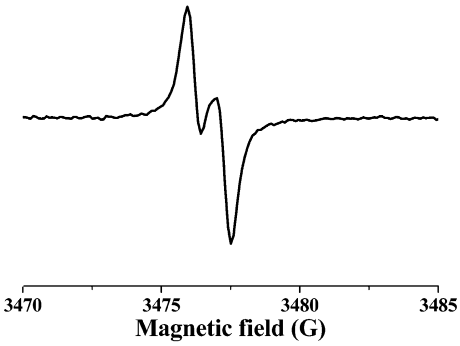


Figure 2. ESR spectrum of **1** (1.0×10^{-4} M) in CH_2Cl_2 in the presence of 5.0 equiv of Sc^{3+} [$Sc(SO_3CF_3)_3$] recorded at room temperature; the solution was degassed before measurement.

The absorption and ESR spectra of **1** and **2** were also measured in the presence of other metal ions including Na^+, K^+, Li^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+}. Among the metal ions tested, Pb^{2+} can induce the appearance of new absorptions around 450 and 845 nm (see Figures S2 and S5 in the Supporting Information). However, their absorption intensities are relatively weak as compared to those of **1** in the presence of Sc^{3+} under the same conditions. The ESR signal was also detected for the solution of **1** after the addition of Pb^{2+} as depicted in Figure S2 in the Supporting Information. Similarly, new absorptions around 450 and 845 nm and ESR signal were observed for **2** in the presence of Pb^{2+} (see Figure S5 in the Supporting Information). Therefore, it can be concluded that both Sc^{3+} and Pb^{2+} can trigger the intramolecular electron transfer between TTF and NDI units within **1** and **2**.

For comparison, the absorption and ESR spectra of **4** in the presence of either Sc^{3+} or Pb^{2+} were measured as for compounds **1** and **2**. Absorptions around 450 and 845 nm as well as ESR signal were not observed for **4** after the addition of either Sc^{3+} or Pb^{2+}. These results implicate that the metal ions-promoted electron transfer between TTF and NDI units in **4** does not occur. In fact, compounds **2** and **4** are structurally similar, but the TTF and NDI units in **4** are linked by $-CH_2CH_2-$ groups, rather than the glycol chains. Thus, this comparison study indicates that the glycol chains in **1** and **2** may play an important role in such metal ions-promoted electron transfer as discussed below. Control experiments were also performed with **2** by measuring the absorption and ESR spectra after the addition of CF_3COOH. Rather weak absorptions around 450 and 845 nm as well as ESR signal were detected (see Figure S16 in the Supporting Information). This is probably due to the direct oxidation of TTF unit according to previous report.[39]

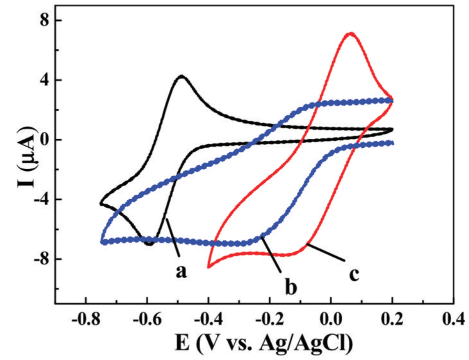
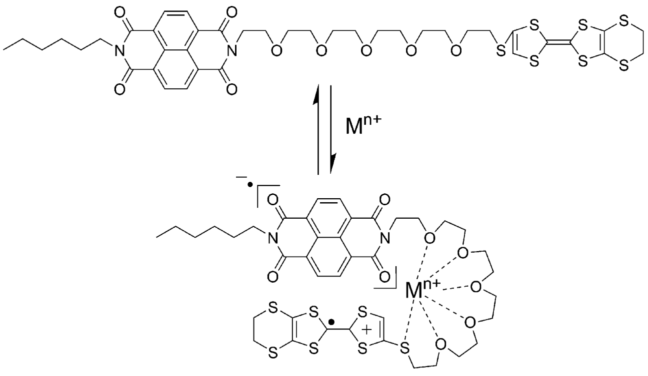


Figure 3. Cyclic voltammograms of **5** (5×10^{-4} M) before (a, black) and after addition of 5.0 equiv of Pb^{2+} [$Pb(ClO_4)_2$] (b, blue) and 5.0 equiv of Sc^{3+} [$Sc(SO_3CF_3)_3$] (c, red) in CH_2Cl_2 at a scan rate of 100 mV/s, respectively.

For the TTF−quinone compounds, the positive shift of the reduction potentials of quinone units facilitates the intramolecular electron transfer as reported early.[30] Thus, it is interesting to examine the variation of the reduction potential of NDI after the addition of metal ions. Compound **5** is considered to be a good reference for NDI units in **1** and **2**. The reduction potential of **5** was measured to be −0.59 V (vs Ag/AgCl). However, it is shifted positively after addition of either Sc^{3+} or Pb^{2+}; for example, the reduction peak moved from −0.59 to −0.12 V in the presence of 5.0 equiv of Sc^{3+} and to −0.27 V in the presence of 5.0 equiv of Pb^{2+} (see Figure 3). By following Fukuzumi's method,[40] the reduction potential of **5** was estimated to be −0.083 V in the presence of 5.0 equiv of Sc^{3+} (see the Supporting Information for details, Figures S8 and S9), and the reduction potential of **5** was about −0.14 V in the presence of 5.0 equiv of Pb^{2+}. Obviously, the electron-accepting ability of NDI is enhanced in the presence of Sc^{3+}/Pb^{2+}. Thus, the electron transfer between TTF and NDI units in **1** and **2** would become more feasible in the presence of these metal ions. However, the electron transfer between TTF and NDI units in **1** and **2** is still not thermodynamically favorable by considering the oxidation potential of TTF units [$E^{1/2}(_{\text{ox1}})$ = 0.55 V vs Ag/AgCl] in **1** and **2**. Therefore, it is assumed that oxygen atoms of the glycol chains and the imide groups of NDI unit as well as the sulfur atoms of TTF units may coordinate with Sc^{3+}/Pb^{2+} to stabilize the electron-transfer state by increasing the electrostatic interaction between the corresponding cation and anion as illustrated in Scheme 2, thus facilitating the intramolecular electron transfer as reported for TTF−quinone compounds.

Scheme 2. Proposed Mechanism for the Metal Ion-Promoted Electron Transfer within TTF−NDI Molecules (Compound 2 as an Example)



In fact, further addition of 2,2′-bipyridine to the solution of **1** and Sc^{3+} led to the disappearance of the absorptions at 450 and 850 nm as depicted in Figure 4. This is probably due to the release of Sc^{3+} from **1** because of the strong binding of Sc^{3+} with 2,2′-bipyridine and as a result back electron transfer takes place, regenerating the neutral TTF and NDI units in **1**. This result provides further support for the assumption that metal ion coordination plays an important role in promoting intramolecular electron transfer within such TTF−NDI compounds.

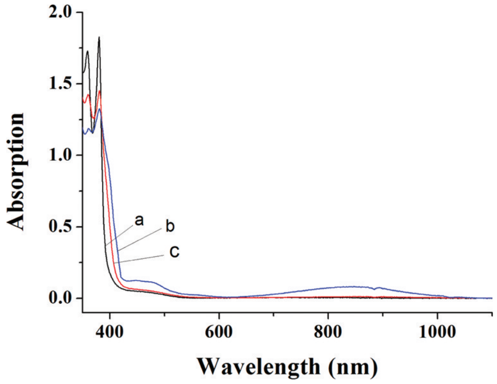


Figure 4. Absorption spectra of compound **1** (5×10^{-5} M, a, black) in presence of 6.0 equiv of Sc^{3+} [$Sc(SO_3CF_3)_3$] (b, blue) and that after further addition of 12.0 equiv; 2,2′-bipyridine (c, red).

It can be inferred from the above results that the spatially adjacent arrangement of TTF and NDI units induced by coordination of metal ions is crucial for promoting the intramolecular electron transfer within **1** and **2**. Along this vein, it is appealing to examine whether the metal ions-promoted electron transfer between TTF and NDI units can occur within the cyclic TTF−NDI compound **3** (Scheme 1), in which TTF and NDI units are linked with two $-CH_2CH_2-$ groups, and as a result, the two units are arranged in a face-to-face conformation. Figure 5 shows the absorption spectrum of **3** and those after the addition of different amounts of Sc^{3+}. Compound **3** shows a broad absorption from 600 to 1000 nm apart from those around 350 nm. This new broad absorption of **3** should be due to the intramolecular CT between TTF and NDI units as anticipated for the cyclophane framework of the D−A compound.[41] After the addition of Sc^{3+}, the broad absorption around 850 nm is gradually blue-shifted and becomes slightly weak, but the absorption around 450 nm is slightly enhanced. Furthermore, the absorptions around 350 nm are also modified. Such absorption spectral changes are likely due to the fact that the TTF unit in **3** is transformed into $TTF^{\bullet+}$ and Sc^{3+} is bound with **3**,[42] based on the studies for compounds **1** and **2** in the presence of Sc^{3+}. This assumption is confirmed by the ESR studies for **3** in the absence and presence of Sc^{3+}. The solution of **3** is ESR inactive in the absence of Sc^{3+}. However, compound **3** exhibits a strong triplet ESR signal in the presence of Sc^{3+} as depicted in Figure 6. The appearance of triplet ESR signal is because of the splitting from two hydrogen atoms in TTF unit of **3**. Similar absorption and ESR spectra were also observed for **3** in the presence of Pb^{2+} (see Figure S11 in the Supporting Information). These absorption and ESR studies obviously show that metal ion-promoted electron transfer can also take place between TTF and NDI units within cyclophane **3**. These studies provide support for the assumption that the spatially adjacent arrangement of TTF and

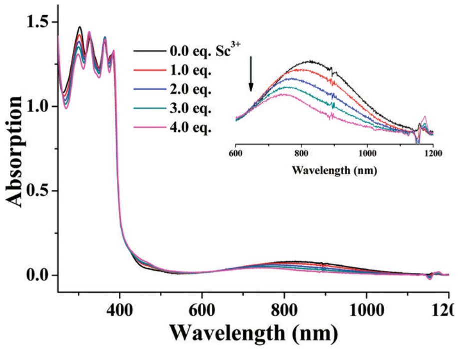


Figure 5. Absorption spectra of compound **3** (5.0×10^{-5} M in CH_2Cl_2) in the presence of different amounts of Sc^{3+} [$Sc(SO_3CF_3)_3$]; the inset shows the 600−1100 nm part of the absorption spectra of **3** in the presence of increasing amounts of Sc^{3+}.

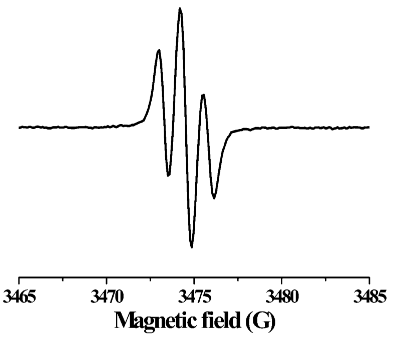


Figure 6. ESR spectrum of **3** (1.0×10^{-4} M) in CH_2Cl_2 in the presence of 5.0 equiv of Sc^{3+} [$Sc(SO_3CF_3)_3$] recorded at room temperature; the solution was degassed before measurement.

acceptor units is one of the important structural parameter for the metal ion-promoted electron transfer.

■ CONCLUSION

In summary, three linear and one cyclic TTF−NDI compounds **1**, **2**, **3**, and **4** were synthesized and studied in the presence of metal ions. Both absorption and ESR spectroscopic studies clearly indicate that electron transfer occurs from TTF to the NDI unit in the presence of metal ions (Pb^{2+} and Sc^{3+}) for linear compounds **1** and **2** in which the TTF and NDI units are linked by glycol chains, but not for **4** in which the TTF and NDI units are connected by $-CH_2CH_2-$ groups. The coordination of metal ions, which induces (1) the positive shift of the reduction potentials of NDI units and (2) the spatially adjacent arrangement of TTF and NDI units, promotes the intramolecular electron transfer within **1** and **2**. Compound **3** exhibits intramolecular CT absorption because of the cyclophane framework. Interestingly, intramolecular electron transfer also takes place for **3** after the addition of either Sc^{3+} or Pb^{2+}. Current studies demonstrate an elegant example for tuning the electronic interaction between electron donor and acceptor units: (1) the interactions between TTF and NDI unit in linear D−A compounds **1** and **2** can be negligible; (2) a CT interaction occurs between TTF and NDI units in cyclophane **3**; and (3) electron transfer takes place for both linear and cyclic D−A compounds **1**, **2**, and **3** in the presence of metal ions. These studies and our previous works indicate that metal ions-promoted electron transfer may be universal for TTF-based D−A compounds in which the D and A units can be close in space.

■ EXPERIMENTAL SECTION

General Information. Compound **6**, **7**, **11**, and **12** were synthesized according to the literature.[30,43,44] The general chemical reagents were purchased without further purification. All solvents were purified and dried by following standard procedures unless otherwise stated.

^1H NMR, ^{13}C NMR, mass, ESR, and UV−vis absorption spectra were measured with conventional equipments. Cyclic voltammetric measurements were performed in a standard three-electrode cell, with Pt as the working and counter electrodes and a Ag/AgCl electrode (saturated KCl) as the reference electrode, which was connected to the electrochemical cell through a Luggin capillary. The scan rate was 100 mV s^{-1}, and nBu_4-NPF_6 (0.1 M) was used as the supporting electrolyte.

Compound 1. Compound **6** (300 mg, 0.52 mmol) was dissolved in 50 mL of DMF, and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA) (64 mg, 0.24 mmol) was added. The mixture was then heated to 110 °C in N_2 atmosphere for 8 h. Then, the solvent were removed by vacuum distillation, and the residue was dissolved in CH_2Cl_2 and washed by water several times. The organic layer was the dried by $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by flash chromatography on a silica gel column (CH_2Cl_2/EtOAc, 3:1) to give **1** (212 m g) as a greenish oil in 63% yield. ^1H NMR (600 MHz, CD_2Cl_2): δ 8.75 (4H, s), 6.47 (2H, s), 4.45 (4H, t, J = 5.8 Hz), 3.83 (4H, t, J = 5.8 Hz), 3.67 (8H, m), 3.63−3.55 (28H, m), 3.31 (8H, s), 2.96 (4H, t, J = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 131.2, 126.9, 126.8, 126.7, 123.1, 117.5, 113.97, 113.92, 106.5, 70.9, 70.87, 70.81, 70.3, 69.8, 68.0, 64.6, 39.8, 35.5, 30.3, 25.6. HR-MS (MALDI): calcd for $C_{54}H_{62}N_2O_{14}S_{14}$ (m/z), 1410.0285; found, 1410.0259.

Compound 2. It was synthesized in the same way as for compound **1** with compound **6** (300 mg, 0.52 mmol), n-hexylamine (52 mg, 0.52 mmol), and NDA (128 mg, 0.52 mmol) to give **2** (127 mg) also as a greenish oil in 27% yield. ^1H NMR (600 MHz, CD_2Cl_2): δ 8.74 (4H, s), 6.47 (1H, s), 4.37 (2H, t, J = 5.8 Hz), 4.17 (2H, t, J = 7.4 Hz), 3.83 (2H, t, J = 5.8 Hz), 3.67 (4H, m), 3.63−3.55 (14H, m), 3.31 (4H, s), 2.96 (2H, t, 5.8 Hz), 1.75 (2H, t, J = 7.4 Hz), 1.45−1.28 (6H, m), 0.93 (3H, t, J = 6.4 Hz). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 163.0, 130.9, 130.8, 126.8, 126.7, 123.0, 117.4, 113.9, 113.8, 106.1, 70.7, 70.6, 70.4, 69.6, 67.9, 41.0, 39.8, 35.6, 31.7, 30.4, 28.1, 26.9, 22.7, 13.9. HR-MS (MALDI): calcd for $C_{40}H_{46}N_2O_9S_7$ (m/z), 922.1230; found, 922.1243.

Compound 8. Compound 7 (800 mg, 2.2 mmol) was dissolved in dry CH_2Cl_2 under N_2 atmosphere. Et_3N (5.6 mL, 22 mmol) and p-toluenesulfonyl chloride (950 mg, 5 mmol) were added, and the mixture was stirred overnight. After that, the mixture was washed with water several times, and the organic layer was dried by $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by flash chromatography on a silica gel column (petroleum/CH_2Cl_2, 5:1) to give **8** (1.2 g) as orange oil in 83% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (4H, d, J = 7.7 Hz), 7.33 (4H, d, J = 7.6 Hz), 6.24 (2H, s), 4.12 (4H, t, J = 6.1 Hz), 2.91 (4H, br), 2.40 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 132.7, 130.2, 128.1, 125.38, 125.32, 124.81, 124.78, 112.2, 67.6, 34.0, 21.9. HR-MS (EI): calcd for $C_{24}H_{24}O_6S_8$, 663.9339; found, 663.9346.

Compound 9. Compound **8** (1.2 g, 1.8 mmol) was dissolved in 80 mL of DMF under N_2 atmosphere, and NaN_3 (585 mg, 9 mmol) was added. The mixture was heated to 90 °C for 5 h. Then, the solvent was moved by vacuum distillation, and the residue was dissolved in CH_2Cl_2 and washed with water several times. The organic layer was dried with $MgSO_4$ and concentrated by rotary evaporation. The residue was then purified by flash chromatography on a silica gel column (petroleum/CH_2Cl_2, 10:1) to give **9** (584 mg, 80%) as an orange oil. ^1H NMR (400 MHz, $CDCl_3$): δ 6.46 (2H, s), 3.48 (4H, t, J = 6.0 Hz), 2.90 (4H, t, J = 6.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 125.43, 125.38, 124.7, 124.6, 112.5, 50.3, 35.1. HR-MS (EI): calcd for $C_{10}H_{10}N_6S_6$, 405.9291; found, 405.9296.

Compound 10. Compound **9** (584 mg 1.4 mmol) was dissolved in 60 mL of THF under N_2 atmosphere. PPh_3 (1.8 g 7 mmol) and water (1.2 mL) were added. The mixture was heated to 45 °C overnight. After that, 40 mL of water was added, the mixture was extracted by CH_2Cl_2, and the organic layer was dried with $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by flash chromatography on a silica gel column (CH_2Cl_2/MeOH/Et_3N, 300:10:1) to give **10** (376 mg, 76%). The crude product was examined by HNMR and MS and used directly for the next step without further purification. ^1H NMR (400 MHz, $CDCl_3$): δ 6.35 (2H, s), 2.89 (4H, t, J = 6.0 Hz), 2.79 (4H, t, J = 6.0 Hz), 1.42 (4H, br). MS (GCT-MS): 354.

Compound 3. Two separate solutions of NDA (200 mg, 0.75 mmol) in 100 mL of DMF and compound **10** (265 mg, 0.75 mmol) also in 100 mL of DMF were added slowly to 200 mL of DMF that was heated to 110 °C under N_2 atomsphere over 10 h. After the complete addition, the solvents were removed under reduced pressure, and the residue was purified by flash chromatography on a silica gel column (CH_2Cl_2/$CHCl_3$, 1/1). The crude product was recrystallized by $CHCl_3$/EtOH to give **3** (80 mg, 18%) as a green powder. ^1H NMR (400 MHz, $CDCl_3$): δ 8.80 (4H, s), 6.07 (2H, s), 4.64 (4H, t, J = 5.5

Hz), 3.52 (4H, t, J = 5.4 Hz). ^{13}C NMR (150 MHz, $CHCl_3$): δ 163.6, 130.7, 127.4, 126.9, 125.9, 121.9, 107.5, 40.0, 36.1. Because of its poor solubility, the solution ^{13}C NMR spectrum was poor, and the solid ^{13}C NMR data were also obtained (see the Supporting Information). HR-MS (EI): calcd for $C_{24}H_{14}N_2O_4S_6$, 585.9278; found, 585.9274.

*Compound **4**.* Compound **4** was synthesized in the same way as for **1** with compound **11** (200 mg, 0.54 mmol), *n*-hexylamine (54 mg, 0.54 mmol), and NDA (144 mg, 0.54 mmol) to give **4** (117 mg, 31%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (4H, s), 6.17 (1H, s), 4.66 (2H, br), 4.19 (2H, t, J = 7.4 Hz), 3.37−3.31 (4H, m), 3.25 (2H, br), 1.75 (2H, br), 1.50−1.34 (6H, m), 0.91 (3H, br). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 162.9, 131.1, 130.6, 126.9, 126.8, 126.7, 126.6, 126.1, 121.1, 112.8, 112.6, 106.9, 41.5, 41.2, 31.6, 31.5, 29.7, 29.5, 28.0, 26.8, 22.6, 14.1. HR-MS (MALDI): calcd for $C_{30}H_{26}N_2O_4S_7$ (m/z), 701.9938; found, 701.9945.

*Compound **5**.* The condensation of compound **12** (200 mg, 0.71 mmol) and NDA (86 mg, 0.33 mmol) gave compound **5** (191 mg, 71%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (4H, s), 4.36 (4H, t, J = 5.7 Hz), 3.76 (4H, t, J = 5.7 Hz), 3.61−3.50 (40H, m), 2.91 (2H, br). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 131.0, 126.7, 126.6, 72.6, 70.6, 70.5, 70.3, 70.1, 67.8, 61.7, 39.6. HR-MS (MALDI-TOF): calcd for $C_{38}H_{54}N_2O_{16}Na$ (M + Na^+), 817.3364; found, 817.3366.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectra of compounds **1−5** and **8−10**; cyclic voltammograms of **1**, **2**, and **5**; and absorption and ESR spectra of **1−3** in the presence of metal ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) Cyclic voltammograms of **1**, **2**, and **5** (see Figure S7 in the Supporting Information) indicate that NDI^{2-} is stable in solutions under ambient conditions.

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(38) To understand why the ESR signal of NDI radical ions could not be detected in our system, a control experiment was carried out. Strong ESR signals appeared for NDI radical anion generated by the addition of F^- to solution of **5**, but the ESR signals disappeared after further addition of Sc^{3+} (see Figure S6 in the Supporting Information).

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