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Metal-Promoted Intermolecular Electron Transfer in Tetrathiafulvalene–Thiacalix[4]arene Conjugates and Tetrachlorobenzoquinone

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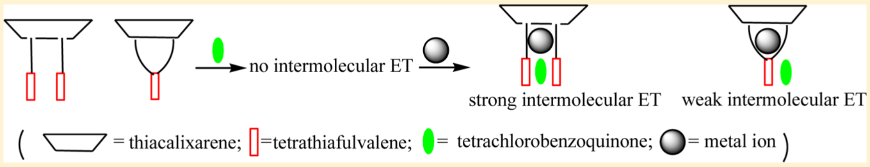
S Supporting Information



ABSTRACT: In this work, two series of tetrathiafulvalene (TTF) and thiacalix[4]arene (TCA) conjugates (TTF–TCA) were designed by CuAAC click reactions. The results obtained from NMR and ^1H NMR NOE indicated that their conformations of thiacalix[4]arene framework may prefer to 1,3-alternate. The cyclic voltammograms of four TTF–TCA compounds containing electroactive TTF units were provided. Meanwhile, their intermolecular electron-transfer (ET) behaviors with tetrachlorobenzoquinone (Q) mediated by different metal ions, Sc^{3+}, Pb^{2+}, Ag^+, Cd^{2+}, and Zn^{2+}, in CH_3CN–CH_2Cl_2 (V/V = 1:1) solution were studied and analyzed via UV–vis spectroscopy. It was determined that intermolecular ET between each TTF–TCA and Q ensemble was not observed without introduction of the metal ions mentioned above. The added specified metal ions most likely induced the intermolecular ET between TTF–TCA and Q ensemble, and the effects of Sc^{3+} functions were the most imperative. The intermolecular ET also proved to be reliant on the structure of TTF–TCA, where TTF–TCA **7a** and **7b** were more effective than TTF–TCA **6a** and **6b**. The difference may be credited to TTF–TCA **7a** or **7b** possessing two independent TTF pendants and providing a more synergic coordination among the TTF radical cation and Q radical anion with a metal ion.

■ INTRODUCTION

Tetrathiafulvalene (TTF) plays an important role in the development of organic conducting materials and the construction of molecular devices.[1−3] TTF and its derivatives are strong electron donors, which allows them to be incorporated into electron donor (D)–acceptor (A) dyads in order to study charge-transfer interactions and photoinduced electron-transfer processes.[4] Zhu and Zhang et al. had reported on metal-ion-promoted intramolecular electron transfer within TTF–quinone systems where TTF and quinone groups are covalently linked by an oligoethylene glycol chain.[5] The results indicate that intramolecular electron transfer is facilitated by the coordination of the metal ion and oxygen atoms in the glycol chain, the quinone anion, and sulfur atoms of the TTF cation. It is assumed that such metal ion coordination induces the transformation from extended to folded conformation in which TTF and quinone units are adjacent in space. Intermolecular electron transfer is essential in the biological processes of photosynthesis and respiration.[6] However, catalytic controlled intermolecular electron-transfer processes have yet to emerge as an identifiable field of TTF-based systems.[7]

On the other hand, calixarenes known as a family of macrocyclic compounds have extensively been studied for molecular recognition and assembly as well as other functions.[8,9] Over the past decade, a series of TTF-calixarene conjugates have been prepared and developed for binding of cations, anions and neutral guests,[10] or for the study of metal-ion-promoted electron transfer.[11]

Thiacalixarenes (TCA), an alternative to "classic" calixarenes, have attracted considerable interest in the broad field of supramolecular chemistry.[12] Thiacalix[4]arenes exhibit unusual chemical behavior, interesting functions, and uncommon conformational preferences due to the replacement of the classical skeleton with sulfur atoms. The irregular features of TCA are accountable for the ability of different functional groups possessing fluorescent and electrochemically active units to attach to the TCA framework and produce valuable supramolecular systems.[13] Nevertheless, until now, only three recent works have reported the preparation of TTF–TCA conguates.[14] Thus, on the basis of copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC) click reaction,[15] four covalent TTF–TCA electron donors were designed in consideration of the above-mentioned and also the fundamental principles for electron transfer. Their intermolecular electron transfer with tetrachlorobenzoquinone (Q) mediated by different metal ions,

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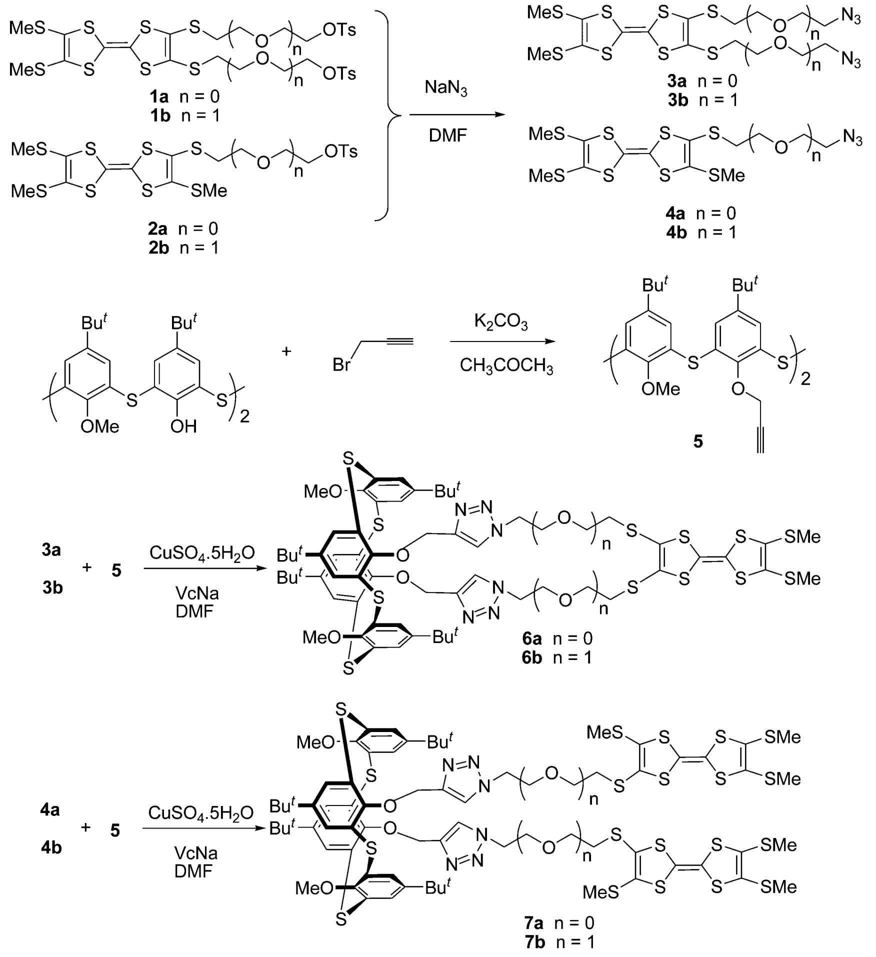
Scheme 1. Synthetic Access to TTF−TCA 6 and 7



such as Sc^{3+}, Pb^{2+}, Ag^{+}, Cd^{2+}, and Zn^{2+}, were studied and analyzed via UV−vis spectroscopy. The results demonstrate that the specific metal ions may facilitate electron transfer between TTF−TCA donors and Q ensembles.

■ RESULTS AND DISCUSSION

Design and Synthesis. The synthetic approaches of compounds **6a**, **6b**, **7a**, and **7b** are shown in Scheme 1. The synthesis of the title compounds started from the bis(mono)-tosylated TTF **1** and **2**, which were transformed into the bis(mono)-azided TTF **3** and **4** after reaction with NaN_3 in satisfactory yields. On the other hand, the reaction of thiacalix[4]arene **4** with propargyl bromide in the presence of potassium carbonate in little excess resulted in dipropargyl thiacalix[4]arene **5**. The final click reaction of azided TTF **3** and **4** with terminal propargyl thiacalix[4]arene **5** was carried out in DMF using $CuSO_4{\cdot}5H_2O$/VcNa to generate target TTF−TCA compounds **6a**, **6b**, **7a**, and **7b** in acceptable yields, respectively. The yields in **7a**,**b** are significantly higher than for **6a**,**b**. This is presumably due to formation of polymers beside the macrocyclic target compounds in the latter case.

The ^1H NMR spectra of compounds **6a**, **6b**, **7a**, and **7b** show two singlets for both the Bu^t and Ar-H protons of TCA framework, which may easily rule out the 1, 2-alternate and partial cone conformation in solution.[16] However, it is not easily assigned a particular one between cone and 1,3-alternate conformation. As seen from Figure 1 and Figures S1−S3 (Supporting Information), the observed NOE contacts between aromatic protons (Ar-H) and protons of triazole rings (C═CH), along with contacts between aromatic protons (Ar-H) and protons of methyl or methylene ($ArOCH_3$ or $ArOCH_2$), which indicate all four TTF−TCA compounds prefer in 1,3-

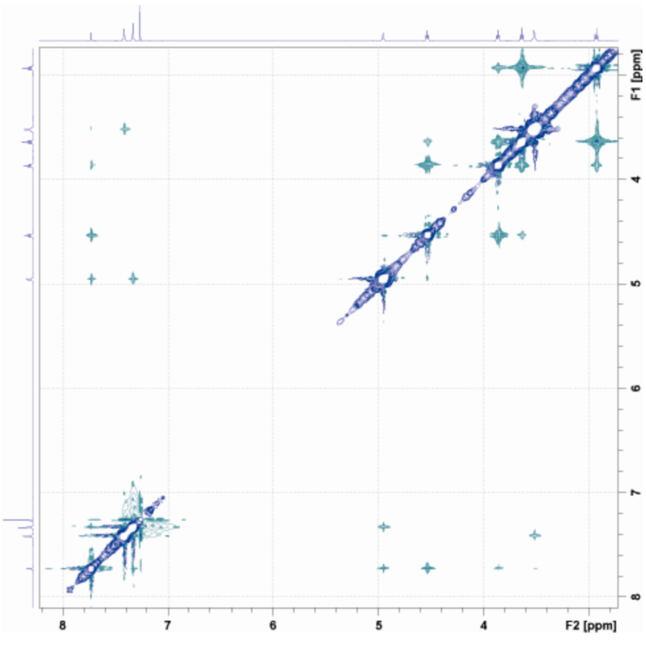


Figure 1. Partial ^1H NMR NOE spectra for **7b**.

alternate conformation. The lack of contacts between protons of methyl ($ArOCH_3$) and that of methylene ($ArOCH_2$) further proves their 1,3-alternate preferences. The chemical structures of compounds **6a**, **6b**, **7a**, and **7b** were also confirmed by ^{13}C NMR, FT-IR, and mass spectroscopic data (see the Experimental Section and Figures S4–S27 of the Supporting Information).

Electrochemical Behavior. The electrochemical properties of TTF **6a**, **6b**, **7a**, and **7b** together with the parent 2,3,6,7-tetrakis(methylthio)tetrathiafulvalene ($TTF(SMe_3)_4$) were carried out in a dichloromethane–acetonitrile (1/1, v/v) mixture on an electrochemistry workstation. The parent $TTF(SMe)_4$ is well-known to undergo two successive reversible, one-electron redox processes resulting in a cation–radical and dicationic species at $E^{1/2}_1$ = 0.53 V and $E^{1/2}_2$ = 0.84 V (vs Ag/AgCl), respectively. As expected from the electrochemical inertness of the thiacalix[4]arene platform, only the TTF redox signatures were observed for TTF–TCA **6a**, **6b**, **7a**, and **7b**. The latter four compounds underwent the expected two reversible redox waves at $E^{1/2}_1$ from 0.56 to 0.60 V and $E^{1/2}_2$ from 0.78 to 0.88 V (vs Ag/AgCl), which corresponds to the successive formation of the stable $TTF/TTF^{\cdot+}$ and $TTF^{\cdot+}/TTF^{2+}$, respectively (Figure 2 and Table 1). The higher $E^{1/2}_1$ (0.60 V) and $E^{1/2}_2$ (0.88 V) potentials for **6a** may be ascribed to the electron-withdrawing ability of the triazolyl groups, which are in closer in proximity to the TTF framework.

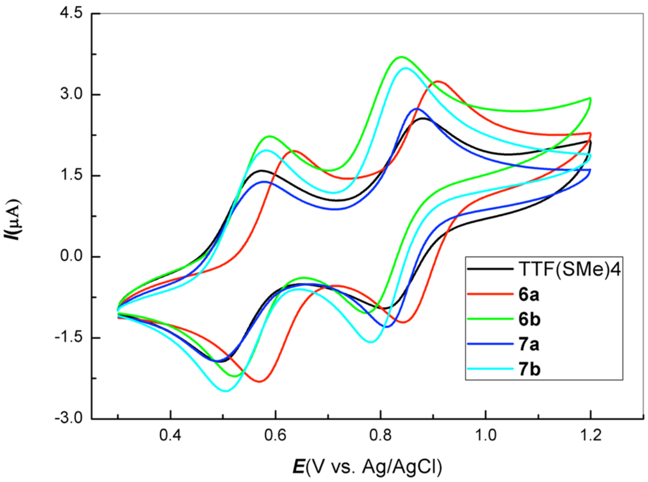


Figure 2. Cyclic voltammetry of TTF–TCA **6a**, **6b**, **7a** and **7b** along with parent $TTF(SMe)_4$ (0.5 mM) in $CH_3CN-CH_2Cl_2$ (V/V = 1:1), Bu_4NPF_6 (0.1 M), ν = 100 mV/s, Pt(ϕ 2 mm), vs Ag/AgCl.

Table 1. Electrochemical Data of TTF–TCA 6a, 6b, 7a, and 7b along with Parent $TTF(SMe)_4$

compd	E_1^{red} (V)	E_1^{ox} (V)	E_2^{red} (V)	E_2^{ox} (V)	$E_1^{1/2}$ (V)	$E_2^{1/2}$ (V)
$TTF(SMe)_4$	0.51	0.57	0.82	0.88	0.54	0.85
6a	0.57	0.64	0.84	0.91	0.60	0.88
6b	0.50	0.57	0.75	0.82	0.53	0.78
7a	0.49	0.58	0.81	0.87	0.53	0.84
7b	0.49	0.56	0.76	0.83	0.53	0.80

UV–vis Titration for Intermolecular ET. The intermolecular ET behaviors between TTF–TCA **6a**, **6b**, **7a**, and **7b** and tetrachlorobenzoquinone (Q) with or without metal ions (such as Sc^{3+}, Pb^{2+}, Ag^+, Cd^{2+}, Zn^{2+}, etc.) were evaluated by UV–vis spectroscopy (CH_2Cl_2). All results are shown in Figures 3–7 together with Figures S28–S32 (Supporting Information).

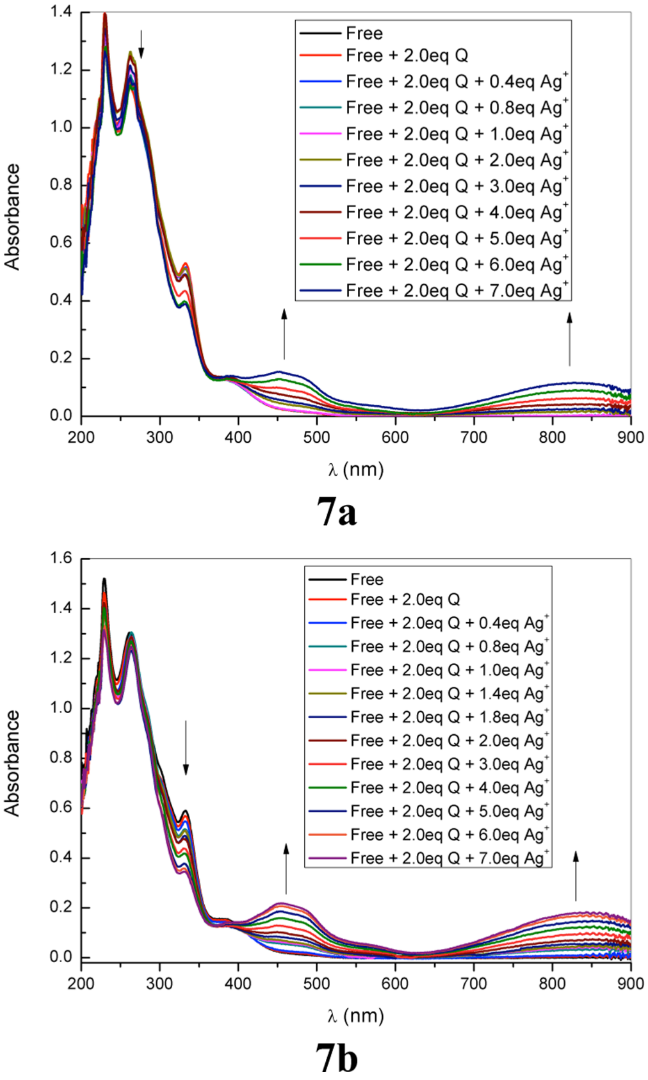


Figure 3. Spectral changes of two TTF–TCA compounds **7a** (up) and **7b** (down) (5.0×10^{-5} M) in the presence of Q (1.0×10^{-4} M) upon addition of different equivalents of Ag^+ ions in $CH_3CN-CH_2Cl_2$ (V/V = 1:1).

Figure 3 and Figure S28 (Supporting Information) show the absorption spectra of compounds **6a**, **6b**, **7a**, and **7b** with added 2 equiv of Q and in the presence of increasing amounts of Ag^+. No absorption above 400 nm was detected for **6a** after addition of Q, which implies that the intermolecular interaction between **6a** and Q molecules is negligible. After addition of Ag^+, no obvious absorption changes occurred for **6a** and **6b**. However, new absorptions around 450 and 840 nm emerged and increased gradually upon addition of Ag^+ for **7a** and **7b**, and maxima were reached when 6 equiv of Ag^+ was added to the solution. According to previous literature reports,[3,5,11] these new absorptions are likely attributed to the generation of the radical cation $TTF^{\cdot+}$. This is potentially due to the Ag^+-triggered intermolecular electron transfer between the TTFs' moieties of **7a** and **7b** and the Q molecules.

As described above, Figure S29 (Supporting Information) shows the absorption spectra behaviors of compounds **6a**, **6b**, **7a**, and **7b** in the presence of 2 equiv of Q and increasing amounts of Cd^{2+}. For compounds **6a** and **6b**, the spectra show no obvious changes upon the addition of Q and Cd^{2+}, implying that Cd $^{2+}$ ions may not promote the intermolecular electron transfer from the TTFs moieties of **6a** and **6b** to the Q molecules. For compounds **7a** and **7b**, new absorptions around 450 and 840 nm emerged and increased gradually upon addition of Cd $^{2+}$, and maxima were reached when 6 and 3 equiv of Cd $^{2+}$ were added to **7a** and **7b**, respectively. This may be explained by the Cd^{2+}-triggered intermolecular electron transfer between the TTFs' moieties of **7a** and **7b** and the Q molecules. After examination of Figures 3 and Figures S28 and 29 (Supporting Information), Ag^{+} and Cd^{2+} ions express same spectral features for compounds **6a**, **6b**, **7a**, and **7b** and Q systems.

In comparison with Ag^{+} and Cd^{2+}, some vital metals such as Zn^{2+}, Sc^{3+}, and Pb^{2+} ions show different spectral behaviors for compounds **6a**, **6b**, **7a**, and **7b** in the presence of 2 equiv of Q. As seen from Figures S30–S32 (Supporting Information), new absorptions around 450 and 840 nm emerged and increased gradually upon addition of Zn^{2+}, Sc^{3+}, and Pb^{2+} ions for all four compounds **6a**, **6b**, **7a**, and **7b**. This is indicative that these ions promote intermolecular electron transfer between the TTFs' moieties of **6a**, **6b**, **7a**, and **7b** and the Q molecules efficiently.

In order to elucidate the effect of different metal ions on intermolecular electron transfer between compounds **6a**, **6b**, **7a**, and **7b** with Q, the UV–vis spectra results are summarized in Figures 4–7. It was determined that the added Sc^{3+} ions promote intermolecular ET between each TTF–TCA compound and Q ensemble in all tested systems. This possible due to the strong binding between Sc^{3+} and the oxygen atoms from Q and nitrogen atoms from triazolyl groups, as well as oxygen or sulfur atoms in linkers between thiacalix[4]arene and TTF units in TTF–TCA **6** or **7**. The different orders of ET efficiency are as follows: $Sc^{3+} > Pb^{2+} > Zn^{2+} > Ag^{+} \approx Cd^{2+}$ for **6a**; $Sc^{3+} > Zn^{2+} > Pb^{2+} \approx Ag^{+} \approx Cd^{2+}$ for **6b**; $Sc^{3+} > Pb^{2+} > Cd^{2+} > Ag^{+} \approx Zn^{2+}$ for **7a**; $Sc^{3+} > Pb^{2+} > Zn^{2+} > Ag^{+} \approx Cd^{2+}$ for **7b**. Additionally, the abilities of intermolecular ET for **7**–Q ensembles are greater than that for **6**–Q ensembles. The mechanism for the metal-ion-promoted intermolecular electron transfer between electron donors TTF–TCA **6** and TTF–TCA **7** and electron acceptor Q can be understood as follows: it is

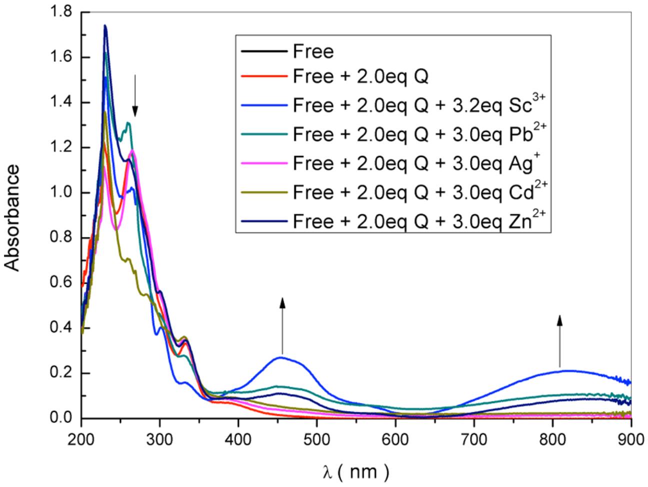


Figure 4. Spectral changes of TTF–TCA **6a** (5.0×10^{-5} M) in the presence of Q (1.0×10^{-4} M) upon addition of 3 equiv of metal ions (Ag^{+}, Cd^{2+}, Zn^{2+}, Sc^{3+}, Pb^{2+}) in CH_3CN–CH_2Cl_2 (V/V = 1:1).

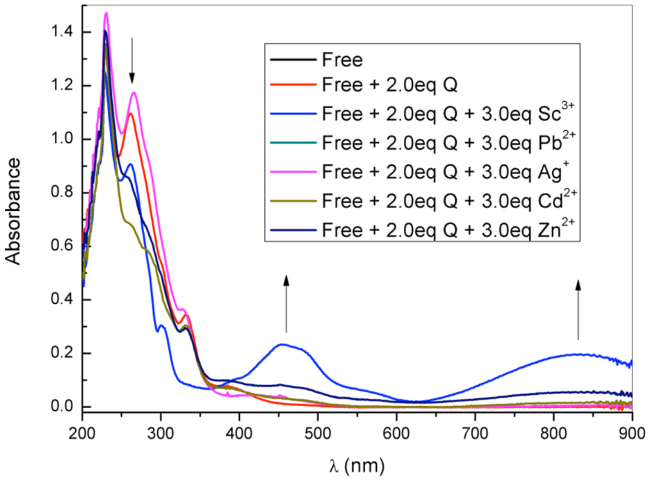


Figure 5. Spectral changes of TTF–TCA **6b** (5.0×10^{-5} M) in the presence of Q (1.0×10^{-4} M) upon addition of 3 equiv of metal ions (Ag^{+}, Cd^{2+}, Zn^{2+}, Sc^{3+}, Pb^{2+}) in CH_3CN–CH_2Cl_2 (V/V = 1:1).

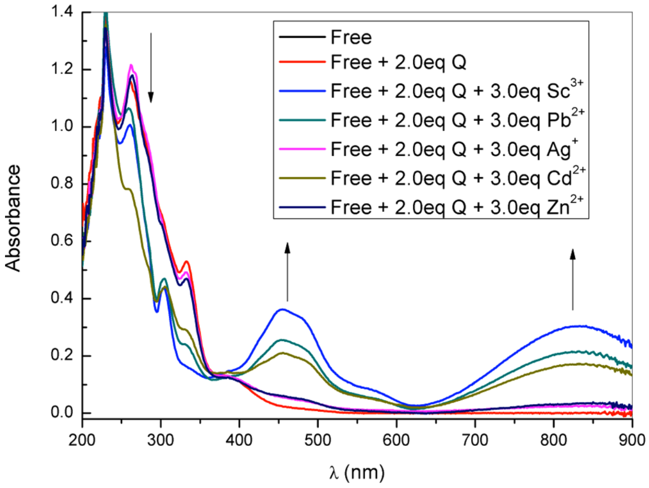


Figure 6. Spectra changes of TTF–TCA **7a** (5.0×10^{-5} M) in the presence of Q (1.0×10^{-4} M) upon addition of 3 equiv of metal ions (Ag^{+}, Cd^{2+}, Zn^{2+}, Sc^{3+}, Pb^{2+}) in CH_3CN–CH_2Cl_2 (V/V = 1:1).

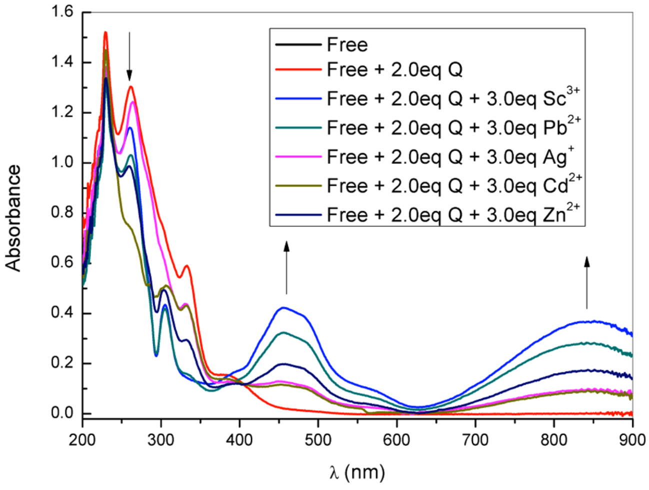
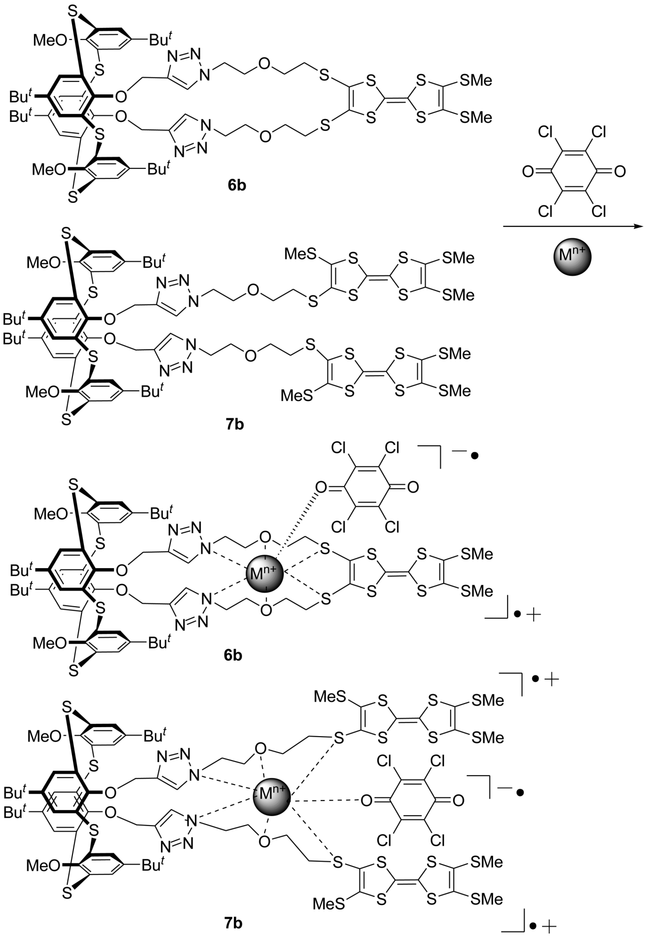


Figure 7. Spectra changes of TTF–TCA **7b** (5.0×10^{-5} M) in the presence of Q (1.0×10^{-4} M) upon addition of 3 equiv of metal ions (Ag^{+}, Cd^{2+}, Zn^{2+}, Sc^{3+}, Pb^{2+}) in CH_3CN–CH_2Cl_2 (V/V = 1:1).

known that the electron-accepting capacities of quinones are enhanced in the presence of specific metal ions.[17] The mediated metal ions (Sc^{3+}, Pb^{2+}, Ag^{+}, Zn^{2+}, and Cd^{2+}) may synergically coordinate with the oxygen atoms from Q, with the nitrogen atoms from triazolyl groups, and also the oxygen or sulfur atoms in linkers between thiacalix[4]arene and TTF units in TTF−TCA **6** and **7**. Compared to TTF−TCA **6**, TTF−TCA **7** possesses relatively weaker intramolecular hydrogen bonding and two flexible TTF arms attached on the thiacalixarene framework. Therefore, TTF−TCA **7** may allow added metals to interact with the oxygen atom of Q, with nitrogen atoms of triazolyl groups, and with oxygen or sulfur atoms in linkers between thiacalix[4]arene and TTF units in TTF−TCA **7**. Furthermore, the introduced metal ions efficiently facilitate the intermolecular electron transfer from TTF−TCA **7** toward Q. The purposed mode is shown in Scheme 2 and Scheme S1 (Supporting Information).

Scheme 2. Plausible Mode of Intermolecular Electron Transfer between TTF−TCA 6b or 7b and Q Mediated by the Added Metal Ions



CONCLUSIONS

This work describes the synthesis of two series of covalently linked tetrathiafulvalene and thiacalix[4]arene receptors (TTF−TCA) by click reaction and analysis of their electrochemical behaviors by CV. The intermolecular electron-transfer (ET) behaviors between TTF−TCA electron donor and tetrachlorobenzoquinone (Q) electron acceptor were mediated by different metal ions such as Sc^{3+}, Pb^{2+}, Ag^{+}, Cd^{2+}, and Zn^{2+}, and investigated via UV−vis spectroscopy. The following statements are concluded from results: (1) The intermolecular ET between TTF−TCA and Q ensemble was not observed without metal ions, such as Sc^{3+}, Pb^{2+}, Ag^{+}, Cd^{2+}, Zn^{2+}, etc. (2) The added specified metal ions may promote intermolecular ET between TTF−TCA and Q ensemble and effects of Sc^{3+} are most vital in all of the tested systems. (3) Intermolecular ET are dependent on structural TTF−TCA and addition of metal ions. TTF−TCA **7a** and **7b** exhibit more efficient ET than TTF−TCA **6a** and **6b**. This may be attributable to the fact the TTF−TCA 7 possesses two TTF units and also to the synergic coordination of the TTF radical cation and Q radical anion with metal ions.

EXPERIMENTAL SECTION

General Information. Compounds **1a**,[18] **1b**,[19] **2a**,[20] **2b**,[20] **3a**,[21] **3b**,[22] **4a**,[23] and 25,27-dimethoxy-26,28-dihydroxy-*p*-*tert*-butylthiacalix[4]arene[24] were synthesized according to the corresponding literature. All reactions were carried out under dry argon atmosphere. All dry solvents were prepared according to standard procedures. Melting points were determined using a capillary melting point apparatus and were uncorrected. The ^1H (^{13}C) NMR spectra were recorded on a 400 MHz spectrometer. The phase-sensitive NOESY spectra were obtained in the TPPI mode from 512 experimentsin t_1, 32 scans in t_2 and D_1 = 2.0 s. Mixing times τ_m = 800 ms. The FTIR spectra were measured from their KBr pellets. ESI-MS spectra (HRMS) were measured with a mass spectrometer.

Cyclic voltammetry (CV) experiments were performed on an electrochemistry workstation in a three-electrode system served as Pt working electrode (2 mm, diameter), with Ag/AgCl (saturated KCl) and platinum wire acting as reference and counter electrodes, respectively. All electrochemical measurements were carried out in a one-compartment cell under a nitrogen atmosphere at 25 °C. The scan rate was 100 $mV\cdot s^{-1}$, and the supported electrolyte was a 0.10 M $CH_3CN-CH_2Cl_2$ (V/V = 1:1) solution of tetrabutylammonium hexafluorophosphate (TBAPF6).

The UV−vis absorption spectra were measured in a 1 cm path length quartz optical cell. All tested metal ions were used their perchlorates. Stock solutions of metal salts (0.01 M) and four TTF−TCA compounds were prepared in $CH_3CN-CH_2Cl_2$ (V/V = 1:1). Titration experiments were performed with 0.05 mM solutions of each TTF−TCA compound and involved adding various concentrations of metal salts in CH_3CN.

Synthesis. *2,3-Bis(2-azidoethylthio)-6,7-bis(methylthio)tetrathiafulvalene (**3a**).* A solution of TTF ditosylate **1a** (0.90 g, 1.20 mmol) and NaN_3 (0.15 g, 2.46 mmol) in dry DMF (50 mL) was heated at 90 °C under Ar for 10 h. After removal of the solvent, the residue was dissolved in CH_2Cl_2 (50 mL) and then washed with a saturated aqueous solution of NH_4Cl (2 × 30 mL) followed by a saturated aqueous solution of K_2CO_3 (30 mL) followed by drying (Na_2SO_4). The crude product, obtained after the removal of the solvent, was purified by column chromatography (SiO_2: CH_2Cl_2/petroleum ether 1:1) to give the diazide **3a** (0.40 g, 51%) as a orange oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.53 (t, J = 6.40 Hz, 4H, CH_2N_3), 3.00 (t, J = 6.60 Hz, 4H, SCH_2), 2.43 (s, 6H, SCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 128.0, 127.7, 113.1, 109.2, 50.8, 35.3, 19.4.

*2,3-Bis[2-(2-azidoethoxy)ethylthio]-6,7-bis(methylthio)tetrathiafulvalene (**3b**).* A procedure similar to that of **3a** using **1b** (0.68 g, 0.81 mmol) and NaN_3 (0.11 g, 1.79 mmol) in dry DMF (50 mL) produced compound **3b** as an orange oil (0.36 g, 41%). ^1H NMR ($CDCl_3$, 400 MHz): δ 3.71−3.65 (m, 8H, OCH_2), 3.40 (t, J = 5.00 Hz, 4H, CH_2N_3), 3.04 (t, J = 6.60 Hz, 4H, SCH_2), 2.43 (s, 6H, SCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 128.1, 127.7, 111.4, 110.4, 70.2, 70.0, 50.9, 35.6, 19.3.

*2-(2-Azidoethylthio)-6,7-bis(methylthio)-3-methylthiotetrathiafulvalene (**4a**).* A similar procedure similar to that of **3a** using **2a** (0.66 g, 1.16 mmol) and NaN_3 (0.15 g, 2.46 mmol) in dry DMF (50 mL) produced compound **4a** as an orange oil (0.41 g, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.51 (t, J = 6.8 Hz, 2H, CH_2N_3), 2.96 (t, J = 7.00 Hz, 2H, SCH_2), 2.45 (s, 3H, SCH_3), 2.43 (s, 6H, SCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 133.0, 127.8, 127.5, 122.4, 111.9, 110.2, 50.8, 35.1, 19.3.

*2-[2-(2-Azidoethoxy)ethylthio]-6,7-bis(methylthio)-3-(methylthio)tetrathiafulvalene (**4b**).* A procedure similar to that of **3a** using **2b** (1.37 g, 2.30 mmol) and NaN_3 (0.29 g, 4.46 mmol) in dry DMF (50 mL) produced compound **4b** as an orange oil (0.52 g, 46%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.71−3.65 (m, 4H, OCH_2), 3.40 (t, J = 4.80 Hz, 2H, CH_2N_3), 3.00 (t, J = 6.60 Hz, 2H, SCH_2), 2.44 (s, 3H, SCH_3), 2.43 (s, 6H, SCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 131.4, 127.8, 127.5, 124.3, 70.2, 70.0, 50.9, 35.6, 19.3, 19.2. HRMS (ESI$^+$): m/z [M]$^+$ calcd for $C_{13}H_{17}N_3OS_8^+$ 486.9132, found 486.9132.

*25,27-Dimethoxy-26,28-di(2-propynyloxy)-p-tert-butylthiacalix[4]arene (**5**).* A mixture of 25,27-dimethoxy-26,28- dihydroxy-*p*-*tert*-butylthiacalix[4]arene (0.41 g 0.54 mmol), propargyl bromide (0.13 g, 1.10 mmol), and potassium carbonate (0.50 g, 3.60 mmol) in dry acetone (50 mL) was refluxed under Ar for 24 h. After removal of the solvent, the residue was dissolved in $CHCl_3$ (50 mL) and then washed with water followed by drying (Na_2SO_4). The crude product was recrystallized from methanol to give the colorless powder **5** (0.67 g, 80%). Mp: 224.2–227.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (s, 4H, ArH), 7.44 (s, 4H, ArH), 4.62 (s, 4H, $ArOCH_2$), 3.63 (s, 4H, $ArOCH_3$), 2.42 (s, 2H, CCH), 1.32 (s,18H, $C(CH_3)_3$), 1.22 (s, 18H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.9, 146.3, 146.0, 132.5, 128.9, 80.2, 74.5, 59.4, 58.2, 34.3, 34.1, 31. 3. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{48}H_{57}O_4S_4^+$ 825.3134, found 825.3144.

*Compound **6a**.* The TTF−diazide **3a** (0.29 g, 0.09 mmol) and alkyne-functionalized thiacalix[4]arene **5** (0.48 g, 0.58 mmol) were dissolved in dry DMF (15 mL) at rt to afford a deep-red-colored suspension. Then $CuSO_4{\cdot}5H_2O$ (0.058 g, 0.20 mmol) and ascorbic sodium (VcNa) (0.12 mg, 6.14 mmol) were added. The mixture was stirred at 90 °C for 10 h, after which the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 (2 × 50 mL) and then washed with water followed by drying (Na_2SO_4). The crude product was purified by column chromatography (SiO_2, $CHCl_3$/acetate ethyl 20:1) to give **6a** (0.15 g, 20%) as an orange powder. Mp: 260.6 °C dec. ^{1}H NMR($CDCl_3$, 400 MHz): δ 7.52 (s, 4H, ArH), 7.37 (s, 2 H, C=CH), 7.19 (s, 4H, ArH) 5.19 (s, 4H, $ArOCH_2$), 4.44 (t, J = 6.0 Hz, 4H, NCH_2), 3.56 (s, 6H, $ArOCH_3$), 3.43 (t, J = 6.8 Hz, 4H, SCH_2), 2.40 (s, 6H, SCH_3), 1.25 (s, 18H, $C(CH_3)_3$), 1.03 (s, 18H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.2, 157.0, 146.6, 145.7, 145.3, 132.7, 129.9, 129.3, 128.1, 127.6, 122.5, 66.3, 56.8, 50.1, 34.7, 34.1, 33.9 31.2, 31.1. FT-IR (KBr): 2960.4, 2918.1, 2867.1, 2358.1, 1576.2, 1455.2, 1409.1, 1382.2, 1361.2, 1265.9, 1237.7, 1216.8, 1084.6, 1046.3, 1005.5, 971.3, 877.9, 846.2, 794.2, 755.9, 698.9 cm^{-1}. HRMS (ESI$^+$): m/z [M]$^+$ calcd for $C_{60}H_{70}N_6O_4S_{12}^+$ 1322.2102, found 1322.2104.

*Compound **6b**.* A procedure similar to that of **6a** using **3b** (0.24 g, 0.41 mmol), **5** (0.34 g, 0.41 mmol), $CuSO_4{\cdot}5H_2O$ (0.04 g, 0.16 mmol), and ascorbic sodium (VcNa) (0.08 mg, 0.41 mmol) in dry DMF (15 mL) gave **6b** as an orange powder (0.15 g, 20%). Mp: 124.1−125.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (s, 2H, C=CH), 7.42 (s, 4H, ArH), 7.37 (s, 4H, ArH) 5.02 (s, 4H, $ArOCH_2$), 4.54 (t, J = 4.0 Hz, 4H, NCH_2), 3.84 (t, J = 4.0 Hz, 4H, OCH_2), 3.59 (t, J = 6.0 Hz, 4H, OCH_2), 3.47 (s, 6H, $ArOCH_3$), 2.83 (t, J = 6.0 Hz, 4H SCH_2), 2.42 (s, 6H, SCH_3), 1.17 (s,18H, $C(CH_3)_3$), 1.09 (s, 18H, $C(CH_3)_3$). ^{13}C NMR($CDCl_3$, 100 MHz): δ 158.8, 157.9, 146.4, 146.2, 145.1, 133.3, 130.9, 130.0, 128.4, 128.2, 127.7, 124.3, 111.7, 109.9, 69.7, 69.5, 58.2, 50.1, 35.7, 34.3, 31.4, 31.2. FT-IR (KBr): 2958.2, 2918.6, 2866.2, 2359.9, 2341.3, 1576.0, 1455.2, 1457.6, 1411.4, 1383.3, 1360.7, 1266.6, 1244.2, 1113.9, 1086.4, 1044.8, 1004.4, 879.6, 842.6, 794.9, 769.4, 697.7 cm^{-1}. HRMS (ESI$^+$): m/z [M]$^+$ calcd for $C_{64}H_{78}N_6O_6S_{12}^+$ 1410.2626, found 1410.2650.

*Compound **7a**.* A procedure similar to that of **6a** using **4a** (0.20 g, 0.45 mmol), **5** (0.18 g, 0.22 mmol), $CuSO_4{\cdot}5H_2O$ (0.02 g, 0.09 mmol), and ascorbic sodium (VcNa) (0.04 mg, 0.20 mmol) in dry DMF (15 mL) gave **7a** as an orange powder (0.18 g, 47%). Mp: 104.5−106.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (s, 2H, C=CH), 7.46 (s, 4H, ArH), 7.29 (s, 4H, ArH), 4.86 (s, 4H, $ArOCH_2$), 4.57 (t, J = 6.0 Hz, 4H, NCH_2), 3.53 (s, 6H, $ArOCH_3$), 3.28 (t, J = 8.0 Hz, 4H, SCH_2), 2.42 (s, 18H, SCH_3), 1.21 (s, 18H, $C(CH_3)_3$), 1.05 (s, 18H, $C(CH_3)_3$). ^{13}C NMR($CDCl_3$, 100 MHz): δ 158.5, 157.7, 146.4, 145.0, 133.9, 133.2, 130.2, 130.0, 128.5, 127.9, 127.6, 123.7, 121.6, 112.3, 109.8, 66.8, 57.9, 49.7, 35.8, 34.2, 31.4, 31.2, 29.8. FT-IR(KBr), 2959.7, 2918.1, 2866.5, 2358.7, 1576.2, 1476.0, 1411.4, 1381.4, 1360.1, 1312.1, 1266.0, 1242.9, 1085.8, 1045.7, 1005.2, 969.3, 879.6, 795.4, 752.5, 697.9 cm^{-1}. HRMS (ESI$^+$): m/z [M]$^+$ calcd for $C_{70}H_{82}N_6O_4S_{20}^+$ 1710.0806, found 1710.0824.

*Compound **7b**.* A procedure similar to that of **6a** using **4b** (0.30 g, 0.61 mmol), **5** (0.25 g, 0.30 mmol), $CuSO_4{\cdot}5H_2O$ (0.03 g, 0.12 mmol), and ascorbic sodium (VcNa) (0.06 mg, 0.30 mmol) in dry DMF (15 mL) gave **7b** as an orange powder (0.17 g, 35%). Mp: 76.3−78.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (s, 2H, C=CH), 7.42 (s, 4H, ArH), 7.39 (s, 4H, ArH) 4.95 (s, 4H, $ArOCH_2$), 4.54 (s, br, 4H, NCH_2), 3.86 ((s, br, 4H, OCH_2), 3.64 (s, br, 4H, OCH_2), 3.52 (s, 6H, $ArOCH_3$), 2.93 (s, br, 4H, SCH_2), 2.40 (s, 18H, SCH_3), 1.19 (s, 18 H, $C(CH_3)_3$), 1.09 (s, 18H, $C(CH_3)_3$). ^{13}C NMR($CDCl_3$, 100 MHz): δ 158.7, 157.9, 146.1, 144.8, 133.2, 131.6, 130.8, 129.8, 128.4, 127.6, 124.3, 111.2, 69.9, 69.4, 66.8, 57.9, 50.1, 35.5, 34.2, 34.1, 31.2. FT-IR(KBr): 2959.0, 2918.6, 2866.3, 2359.3, 2341.8, 1576.0, 1456.9, 1437.0, 1411.9, 1380.4, 1360.8, 1311.9, 1266.8, 1244.0, 1113.7, 1086.3, 1045.6, 1004.7, 880.7, 845.9, 795.7, 770.6, 698.6 cm^{-1}. HRMS (ESI$^+$): m/z [M]$^+$ calcd for $C_{74}H_{90}N_6O_6S_{20}^+$ 1798.1330, found 1798.1366.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectra of compounds **3a**,**b**, **4a**,**b**, **6a**,**b**, and **7a**,**b**, and partial ^{1}H NMR NOE and HR-ESI MS spectra of **6a**,**b** and **7a**,**b**. Spectral changes of four TTF−TCA compounds (**6a**,**b**, **7a**,**b**) (5.0 × 10^{-5} M) in the presence Q (1.0 × 10^{-4} M) with different amounts of metal ions (Ag^+, Cd^{2+}, Zn^{2+}, Sc^{3+}, Pb^{2+}) in $CH_3CN−CH_2Cl_2$ (V/V = 1:1). These materials are available free of charge via the Internet at http://pubs.acs.org.

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Notes

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