JOC The Journal of Organic Chemistry

NOTE

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Calix[4]arenes with Electroactive Tetrathiafulvalene and Quinone Units: Metal-Ion-Promoted Electron Transfer

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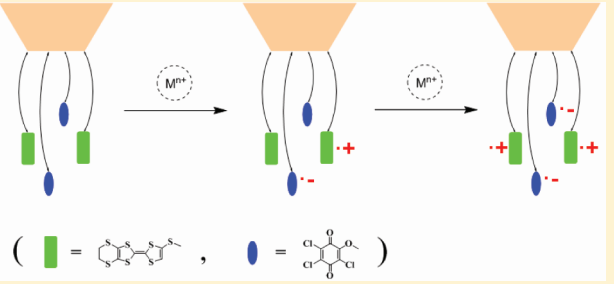
Supporting Information

ABSTRACT: Metal-ion-promoted electron transfer was observed for compounds **1** and **2** based on the absorption and ESR spectral studies. These results imply that spatially adjacent arrangement of TTF and quinone units in **1** and **2** due to the calix[4]arene platform is favorable for the intramolecular electron transfer.



Tetrathiafulvalene (TTF) and its derivatives as components of charge-transfer complexes have been intensively investigated for conducting materials.[1] Meanwhile, TTF derivatives have been widely employed as building blocks for switchable systems.[2−6] All of these versatile applications greatly benefit from the well-defined electrochemical properties of TTF derivatives, which can be easily and reversibly transformed into the corresponding radical cations ($TTF^{\bullet+}$) and dications (TTF^{2+}). TTF derivatives as electron donors are also incorporated into electron donor (D)−acceptor (A) dyads for studies of charge-transfer interactions and photoinduced electron-transfer processes.[7] We have recently reported the metal-ion-promoted electron transfer within TTF−quinone dyads, in which the TTF and quinone groups were covalently linked by an oligoethylene glycol chain.[8] The results manifest that the coordination of a metal ion with the oxygen atoms of the glycol chain and quinone anion as well as sulfur atoms of the TTF cation plays an important role in facilitating the electron transfer. It is assumed that such metal ion coordination induces the conformation transformation from the extended one to the folded one in which the TTF and quinone units are adjacent in space.

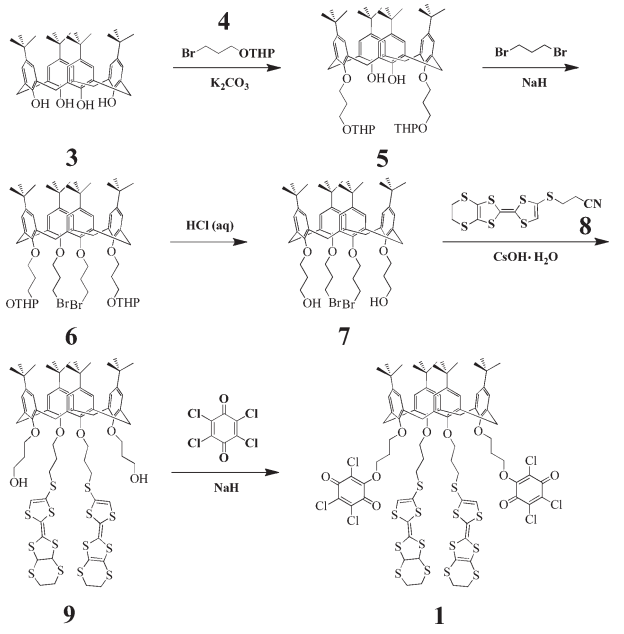
Calixarenes are widely used in supramolecular chemistry as receptors for neutral molecules, cations, anions, and even ion pairs.[9−11] They can be readily modified at the phenolic hydroxy groups (lower rim) as well as at the *para* positions (upper rim).[12] In fact, calixarenes have been employed as versatile molecular scaffolds to control the spatial arrangements of functional groups.[13] In this Note, we describe two *p-tert*-butylcalix[4]arenes **1** and **2** (Schemes 1 and 2) containing TTF and quinone units in the lower rim. It is expected that the calix[4]arene framework enables TTF and quinone groups to be close in space. Both absorption and ESR spectral studies indicate that electron transfer from TTF to quinone units occurs in both compounds **1** and **2** in the presence of certain metal ions.

The synthetic approaches of compounds **1** and **2** are shown in Scheme 1 and Scheme 2, respectively. The synthesis of compound **1** started from *p-tert*-butylcalix[4]arene **3**, which was transformed into compound **5** after reaction with compound **4** in 70% yield. Reaction of 1,3-dibromopropane with compound **5** led to compound **6** in 51% yield. After removal of tetrahydropyran (THP) groups with concentrated HCl solution, compound **7** was obtained in 90% yield. Compound **7** was allowed to react with compound **8**, leading to compound **9** in 83% yield, which was further reacted with tetrachloro-1,4-benzoquinone in the presence of NaH to reach compound **1** in 35% yield. Two doublets at 4.33 and 3.18 ppm were detected for the protons of bridging $-CH_2$ groups in the ^1H NMR spectrum of **1** (see Supporting Information, page S2). In the ^{13}C NMR spectrum of **1**, the signals for bridging $-CH_2$ groups appeared around 31 ppm (see Supporting Information, page S2). These NMR data indicate that compound **1** adopts the *cone* conformation according to previous studies,[14] and accordingly, the TTF and quninone units in **1** are spatially adjacent.

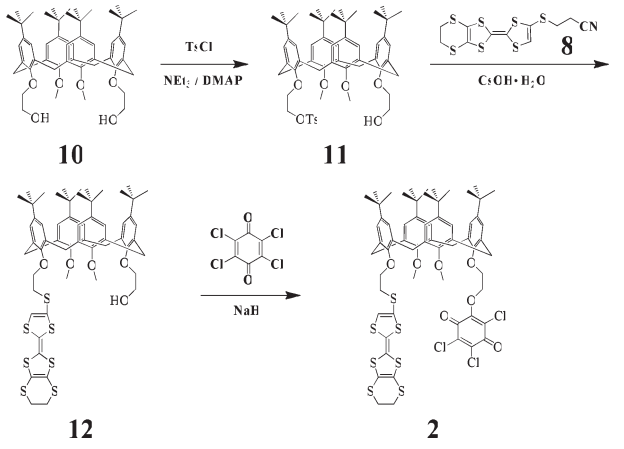
For the synthesis of compound **2**, after reaction with *p*-toluenesulfonyl chloride in the presence of triethylamine, compound **10** (see Experimental Section) was transformed into compound **11** in 34% yield. Reaction of compound **11** and compound **8** led to compound **12** in 70% yield, which was further reacted with tetrachloro-1,4-benzoquinone in the presence of NaH to afford compound **2** in 51% yield. Multiple broad ^1H NMR signals were observed for protons of bridging $-CH_2$

Received: May 20, 2011
Published: July 20, 2011

Scheme 1. Chemical Structure and Synthetic Approach for Compound 1



Scheme 2. Chemical Structure and Synthetic Approach for Compound 2



groups at room temperature (see Supporting Information, page S3). The ^{1}H NMR signals due to protons of bridging $-CH_2$ groups became sharp at low temperatures, but they were still multiple (see Supporting Information, page S4). These ^{1}H NMR data indicate that compound **2** possesses different conformers in solution.

Figure 1 shows the absorption spectrum of compound **1** and those in the presence of increasing amounts of Sc^{3+} $[Sc(SO_3CF_3)_3]$.[15] Compound **1** shows the absorption bands around 230, 296, and 336 nm, which are due to calixarene, neutral quinone, and TTF moieties based on previous studies.[8a,9] Moreover, the redox potentials of compound **1** were determined to be $E^{1/2}(ox_1) = 0.48$ V, $E^{1/2}(ox_2) = 0.89$ V, and $E^{1/2}(red_1) = 0.07$ V, being close to those of compound **8** and similarly substituted quinone.[8a] These results clearly indicate that the interaction between TTF and quinone units in **1** can be considered negligible. However, after introducing Sc^{3+} to the solution of

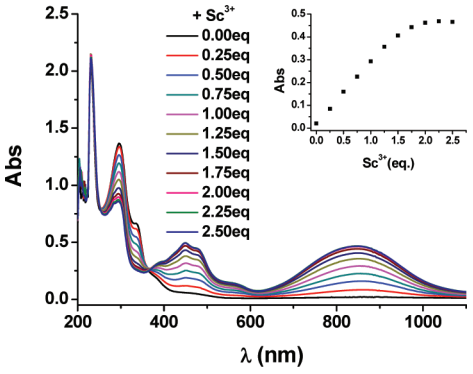


Figure 1. Absorption spectra of compound **1** (3.0×10^{-5} M in CH_2Cl_2) in the presence of different amounts of Sc^{3+} $[Sc(SO_3CF_3)_3]$; inset shows the variation of absorbance at 850 nm upon addition of 0−2.5 equiv of Sc^{3+}.

compound **1**, new absorption bands around 450 and 850 nm emerged; their absorption intensities increased with the amounts of Sc^{3+} added to the solution, reaching the maxima after addition of approximately 2.0 equiv of Sc^{3+}, as shown in the inset of Figure 1. According to previous studies,[8] these new absorption bands are due to the generation of the radical cation $TTF^{\bullet+}$. Indeed, direct oxidation of compound **1** with Fe^{3+} $[Fe(ClO_4)_3]$ also led to new absorption bands around 450 and 850 nm, as shown in Figure S1. Therefore, it can be concluded that intramolecular electron transfer occurs between TTF and quinone units of compound **1** in the presence of Sc^{3+}, being in line with previous results reported by us recently.[8] The fact that the absorption intensity at 850 nm for the solution of **1** (3.0×10^{-5} M) after addition of more than 2.0 equiv of Sc^{3+} is almost equal to that by direct oxidation with 2.0 equiv of Fe^{3+} (see Figure S1) implies that both TTF units in **1** can be oxidized into the $TTF^{\bullet+}$ species in the presence of enough Sc^{3+}. Notably, further addition of 2,2′-bipyridine to the solution of **1** and Sc^{3+} led to gradual decrease for the absorptions at 450 and 850 nm (see Figure S4). 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 quinone units in **1**. Interestingly, the absorptions at 450 and 850 nm due to $TTF^{\bullet+}$ re-emerged after more Sc^{3+} was introduced (see Figure S4).

It should be noted that the absorptions around 450 and 850 nm due to respective $TTF^{\bullet+}$ could be neglected for the mixture of compound **8** and tetrachloro-*p*-benzoquinone after addition of Sc^{3+} under similar conditions (see Figure S5). In fact, the absorptions around 450 and 850 nm did not emerge for the TTF−quinone dyad in which the TTF and quinone units were linked by a $-CH_2CH_2-$ group after addition of metal ions.[8a]

It was anticipated that such successive oxidation of TTF units may induce the formation of mixed-valence complex $[(TTF)]_2^{\bullet+}$ and radical cation dimer $(TTF^{\bullet+})_2$.[16] However, typical absorptions of both $[(TTF)]_2^{\bullet+}$ and $(TTF^{\bullet+})_2$ in the near-infrared region were not detected for compound **1** upon gradual addition of Sc^{3+} (see Figure S6). In addition, cyclic voltammograms of compound **1** in the presence of increasing amounts of Sc^{3+} at different scan rates were measured. Only two oxidation waves corresponding to the oxidation of TTF into $TTF^{\bullet+}$ and TTF^{2+} were detected, and no intermediate oxidation peaks were observed (see Figure S7). Such electrochemical studies also indicate

dx.doi.org/10.1021/jo200985y |J. Org. Chem. 2011, 76, 6883–6888

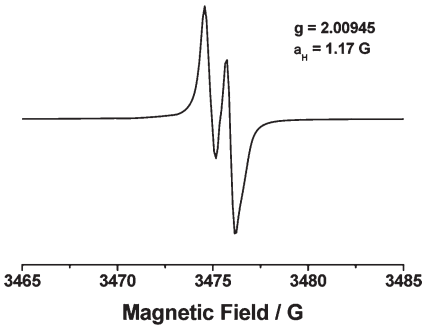


Figure 2. ESR spectrum of compound **1** in CH_2Cl_2 (1.0×10^{-4} M) in the presence of 2.0 equiv of Sc^{3+} [$Sc(SO_3CF_3)_3$] recorded at room temperature; the solution was degassed before measurement.

that neither $[(TTF)]_2^{\bullet+}$ nor $(TTF^{\bullet+})_2$ is formed for compound **1** in the presence of Sc^{3+}. This observation is likely due to the fact that the two TTF units in the lower rim of **1** are well separated, and accordingly, the formation of both $[(TTF)]_2^{\bullet+}$ and $(TTF^{\bullet+})_2$ is not favorable.

Both compound **1** and Sc^{3+} are ESR silent. However, the mixture solution of compound **1** and Sc^{3+} exhibited strong doublet ESR signals, as depicted in Figure 2. The signals are likely attributed to the radical cation ($TTF^{\bullet+}$) of the TTF moiety of compound **1**, and the doublet signal stems from the splitting of one H atom of the TTF unit ($g = 2.00945$, $\alpha_H = 1.17$ G). Thus, the formation of $TTF^{\bullet+}$ in the presence of Sc^{3+} is also confirmed by ESR spectroscopy. Nevertheless, the corresponding radical anion of the quinone unit, which should be generated through the intramolecular electron transfer from the TTF moiety to the quinone unit after introduction of Sc^{3+}, was not detected with ESR spectroscopy. It is probably due to the facile disproportionation of the radical anion of quinone ($Q^{\bullet-}$) into the corresponding neutral (Q) and dianion (Q^{2-}) species in the presence of metal ions according to previous studies.[8a,17]

Apart from Sc^{3+}, both absorption and ESR spectral studies indicate that other metal ions including Pb^{2+} [$Pb(ClO_4)_2$] and Zn^{2+} [$Zn(ClO_4)_2$] can also trigger the intramolecular electron transfer between TTF and quinone units within compound **1** (see Figures S2 and S3 in Supporting Information). Only absorptions around 450 and 850 nm were observed, and characteristic absorptions for $[(TTF)]_2^{\bullet+}$ and $(TTF^{\bullet+})_2$ were not detected in all cases for compound **1** after addition of metal ions.

The mechanism for the metal-ion-promoted intramolecular electron transfer within **1** can be understood as follows: it is known that the electron-accepting capacities of quinones are enhanced in the presence of certain metal ions.[8,17] The TTF and quinone units in compound **1** are spatially adjacent because of the cone conformation of calix[4]arene, and such conformation is beneficial for intramolecular electron transfer from TTF to the quinone unit. Moreover, the coordination of metal ions, which may involve oxygen atoms from quinone units and those of alkoxyl groups in the lower rim of calix[4]arene as well as sulfur atoms from TTF units, may further contribute to the intramolecular electron transfer in compound **1**.[18]

Metal-ion-promoted electron transfer was also observed for compound **2** after addition of certain metal ions. Figure 3 shows the absorption spectra of compound **2** after addition of increasing amounts of Sc^{3+}. New absorption bands around 450 and 850 nm appeared for compound **2** upon addition of Sc^{3+}. The absorption intensity at 850 nm increased by increasing the

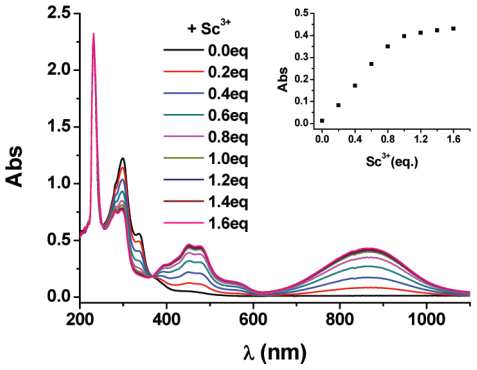


Figure 3. Absorption spectra of compound **2** (5.0×10^{-5} M in CH_2Cl_2) in the presence of different amounts of Sc^{3+} [$Sc(SO_3CF_3)_3$]; inset shows the variation of absorbance at 850 nm upon addition of 0−1.6 equiv of Sc^{3+}.

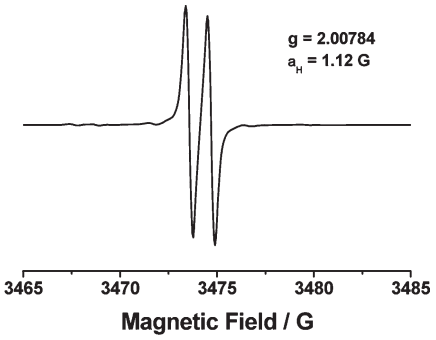


Figure 4. ESR spectrum of compound **2** (1.0×10^{-4} M in CH_2Cl_2) in the presence of 1.0 equiv of Sc^{3+} [$Sc(SO_3CF_3)_3$] recorded at room temperature; the solution was degassed before measurement.

concentration of Sc^{3+} in the solution, as depicted in the inset of Figure 3. Furthermore, the absorption intensity at 850 nm of **2** (5.0×10^{-5} M) in the presence of 1.6 equiv of Sc^{3+} is comparable to that of **1** (3.0×10^{-5} M) in the presence of 2.5 equiv of Sc^{3+}.[19] As detailed above, those two absorption bands are ascribed to the formation of $TTF^{\bullet+}$ in the solution. Strong doublet ESR signal due to $TTF^{\bullet+}$ was also detected for the mixture solution of compound **2** and Sc^{3+}, as depicted in Figure 4 ($g = 2.00784$, $\alpha_H = 1.12$ G). These spectral results indicate that intramolecular electron transfer occurs between TTF and quinone units within compound **2** in the presence of Sc^{3+} as discussed for compound **1**.

The absorption and ESR spectra of compound **2** were also measured upon addition of other metal ions. Metal ions including Pb^{2+} and Zn^{2+} can also facilitate the intramolecular electron transfer within compound **2**. New absorption bands around 450 and 850 nm were also observed for compound **2** in the presence of these metal ions (see Figures S11−S13). Moreover, absorption intensities at 850 nm were found to be higher with Sc^{3+} or Pb^{2+} than with Zn^{2+} and Cd^{2+} under the same conditions. Thus, Sc^{3+} and Pb^{2+} can promote the intramolecular electron transfer within **2** more efficiently. ESR signals due to the radical cation of the TTF moiety in compound **2** were detected after addition of metal ions including Pb^{2+}, Zn^{2+}, and Cd^{2+}, as depicted in Figures S11−S13, respectively.

As mentioned above, different conformers of **2** exist in solution based on the ^1H NMR data, but this is probably due to the

dx.doi.org/10.1021/jo200985y |*J. Org. Chem.* 2011, 76, 6883–6888

inversion of two methoxyl groups.[20] The TTF and quinone units of **2** may still be spatially adjacent, and accordingly, intramolecular electron transfer can take place within **2** in the presence of certain metal ions.

In summary, two calix[4]arenes **1** and **2** with TTF and quinone units were synthesized and characterized. Both absorption and ESR spectral studies indicate that TTF units in **1** and **2** can be successively oxidized upon addition of metal ions (e.g., Sc^{3+}, Pb^{2+}). Thus, intramolecular electron transfer occurs among the TTF and quinone units in **1** and **2** in the presence of metal ions as reported for TTF−quinone dyads linked with glycol chains.[8] These results have the following implications: (1) the adjacent arrangement of TTF and quinone units in space is favorable for the metal-ion-promoted intramolecular electron transfer. This is consistent with the mechanism proposed for the metal-ion-promoted electron transfer within TTF−quinone dyads.[8] (2) The metal-ion-promoted electron transfer may be universal for compounds with TTF and quinone units which can be spatially close.

EXPERIMENTAL SECTION

General Information. ^{1}H NMR, ^{13}C NMR, MS (including HRMS), elemental analysis, UV−vis absorption, and ESR spectra were measured with conventional spectrometers. All solvents were purified and dried by following standard procedures unless otherwise stated. Compounds **3**, **4**, **8**, and **10** were prepared according to reported procedures.[21]

Synthesis of Compound 5. A suspension of **3** (5.85 g, 9.0 mmol), **4** (4.0 g, 18 mmol), and anhydrous K_2CO_3 (15.8 g, 115 mmol) in CH_3CN (50 mL) was heated to reflux for 24 h under nitrogen atmosphere. After being cooled to room temperature, the mixture was poured into water (100 mL) and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was subjected to column chromatography with CH_2Cl_2/ethyl acetate (v/v, 20/1) as eluent. Compound **5** was obtained as a white powder (5.88 g) in 70% yield: mp 59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (1H, s), 7.75 (1H, d, J = 4.0 Hz), 7.05 (4H, m), 6.86 (4H, m), 4.73 (2H, m), 4.38−3.85 (14H, m), 3.53 (2H, m), 3.32 (4H, dd, J = 22.0 Hz, 12.7 Hz), 2.30 (4H, m), 1.83 (2H, m), 1.72 (2H, m), 1.61−1.45 (8H, m), 1.29 (18H, s), 1.02 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 150.0, 149.9, 146.9, 141.4, 133.2, 132.9, 132.8, 128.1, 127.9, 127.8, 127.6, 125.8, 125.6, 125.5, 125.3, 125.2, 99.2, 73.4, 73.3, 64.1, 64.0, 62.5, 34.1, 33.9, 32.2, 32.0, 31.8, 31.6, 31.2, 30.9, 30.5 25.7, 19.8; MS (MALDI-TOF) m/z 955.5 [M + Na^+]. Anal. Calcd for $C_{60}H_{84}O_8$: C, 77.21; H, 9.07. Found: C, 77.23; H, 9.15.

Synthesis of Compound 6. A suspension of **5** (0.93 g, 1.0 mmol) and NaH (0.12 g, 5.0 mmol) in DMF (70 mL) was stirred for 1.0 h under nitrogen atmosphere. Then 1,3-dibromopropane (2.0 mL, 20 mmol) was added. The mixture was heated to 75 °C and stirred for 12 h. After being cooled to room temperature, the solvents were removed under reduced pressure. The residue was taken up in CH_2Cl_2, and the organic phase was washed with 3 M HCl, brine, and water. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was subjected to column chromatography with CH_2Cl_2/petroleum ether (60−90 °C) (v/v, 2/3) as eluent. Compound **6** was obtained as a white powder (0.6 g) in 51% yield: mp 47 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (4H, s), 6.64 (4H, s), 4.60 (2H, s), 4.35 (4H, d, J = 12.5 Hz), 4.06 (4H, t, J = 6.9 Hz), 3.93 (6H, m), 3.85 (2H, m), 3.67 (4H, t, J = 6.4 Hz), 3.59 (2H, m), 3.50 (2H, m), 3.16 (4H, d, J = 12.6 Hz), 2.59 (4H, m), 2.26 (4H, m), 1.83 (2H, m), 1.71 (2H, m), 1.56 (8H, m), 1.19 (18H, s), 0.97 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 153.0, 145.1, 144.5, 134.6, 133.0, 125.5, 125.0, 99.1, 73.2, 73.1, 65.0, 62.4, 34.1, 33.9, 33.3, 31.7, 31.4, 31.2, 31.0, 30.9, 30.8, 29.8, 25.6, 19.8; MS (MALDI-TOF) m/z 1195.5 [M + Na^+].

Synthesis of Compound 7. In a 50 mL round-bottom flask, **6** (0.4 g, 0.34 mmol) was dissolved in 20 mL of the mixture of CH_2Cl_2 and CH_3OH (v/v, 1/1). Then, 0.1 mL of the concentrated HCl was added to the above solution. The mixture was stirred at room temperature for 2.0 h. After that, 15 mL of 2.0 M NaOH was added and extracted with CH_2Cl_2. The organic layer was washed with brine and water, and it was further dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was subjected to column chromatography with CH_2Cl_2/ethyl acetate (v/v, 10/1) as eluent. Compound **7** was obtained as a white powder (0.31 g) in 90% yield: mp 107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (4H, s), 6.70 (4H, s), 4.36 (4H, d, J = 12.5 Hz), 4.05 (4H, t, J = 7.2 Hz), 3.97 (4H, t, J = 6.7 Hz), 3.92 (4H, t, J = 6.3 Hz), 3.69 (4H, t, J = 6.6 Hz), 3.18 (4H, d, J = 12.6 Hz), 2.50 (4H, m), 2.25 (4H, m), 1.16 (18H, s), 1.01 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 152.7, 144.9, 134.2, 133.2, 125.4, 125.2, 73.5, 72.4, 60.4, 34.1, 33.9, 33.2, 31.7, 31.5, 31.1, 31.0; MS (MALDI-TOF) m/z 1029.4 [M + Na^+]. Anal. Calcd for $C_{56}H_{78}Br_2O_6$: C, 66.79; H, 7.81; Br, 15.87. Found: C, 67.06; H, 7.98; Br, 15.60.

Synthesis of Compound 9. To a degassed solution (10 mL) of **8** (0.23 g, 0.6 mmol) in THF was added a degassed solution (5.0 mL) of $CsOH·H_2O$ (0.15 g, 0.9 mmol) in CH_3OH over a period of 5.0 min under nitrogen atmosphere. The mixture was stirred for an additional 30 min, followed by the addition of a degassed solution (8.0 mL) of **7** (0.22 g, 0.22 mmol) in THF. The reaction mixture was stirred overnight at room temperature. Then, the solvents were evaporated under reduced pressure, and the residue was subjected to column chromatography with CH_2Cl_2 as eluent. Compound **9** was obtained as an orange powder (0.28 g) in 83% yield: Mmp 131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (4H, s), 6.63 (4H, s), 4.33 (4H, d, J = 12.4 Hz), 4.05 (4H, t, J = 7.1 Hz), 3.90 (8H, m), 3.28 (8H, s), 3.16 (4H, d, J = 12.5 Hz), 2.95 (4H, t, J = 7.0 Hz), 2.23 (8H, m), 1.21 (18H, s), 0.95 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 152.4, 144.9, 144.7, 134.6, 132.9, 125.5, 125.1, 73.6, 72.5, 60.5, 34.1, 33.9, 33.2, 31.7, 31.4, 31.1, 30.4, 29.7; MS (MALDI-TOF) m/z 1496.0 [M]. Anal. Calcd for $C_{72}H_{88}O_6S_{14}$: C, 57.71; H, 5.92; S, 29.96. Found: C, 57.86; H, 6.05; S, 29.68.

Synthesis of Compound 1. An anhydrous solution (25 mL) of **9** (0.18 g, 0.12 mmol) in THF was cooled to 0 °C with an ice bath. After 5.0 min, NaH (58 mg, 2.4 mmol) was added to the solution in one portion under nitrogen atmosphere. The mixture was stirred for 30 min, followed by the addition of *p*-chloranil (0.30 g, 1.2 mmol). The reaction mixture was stirred overnight. Then, the solvents were evaporated under reduced pressure, and the residue was subjected to column chromatography with CH_2Cl_2/petroleum ether (60−90 °C) (v/v, 2/1) as eluent. Compound **1** was obtained as a brown powder (80 mg) in 35% yield: mp 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (4H, s), 6.68 (4H, s), 4.63 (4H, t, J = 6.0 Hz), 4.33 (4H, d, J = 12.5 Hz), 4.14 (4H, t, J = 7.3 Hz), 3.93 (4H, t, J = 7.1 Hz), 3.26 (8H, s), 3.18 (4H, d, J = 12.6 Hz), 2.98 (4H, t, J = 7.0 Hz), 2.54 (4H, m), 2.30 (4H, m), 1.17 (18H, s), 0.99 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 171.8, 154.6, 153.5, 152.7, 145.2, 144.9, 140.6, 138.9, 134.3, 133.0, 126.2, 125.5, 125.2, 122.9, 73.6, 73.4, 71.5, 34.1, 33.9, 31.7, 31.4, 31.2, 30.2, 30.0, 29.8; HR-MS (ESI) calcd for $C_{84}H_{86}Cl_6O_{10}S_{14}$ (m/z) 1912.04366, found 1912.04066.

Synthesis of Compound 11. A solution (50 mL) of **10** (3.06 g, 4.0 mmol), triethylamine (2.1 mL, 15 mmol), and catalytic amount of DMAP in CH_2Cl_2 was cooled to 0 °C with an ice bath. Then, a solution (30 mL) of *p*-toluenesulfonyl chloride (1.14 g, 6 mmol) in CH_2Cl_2 was added dropwise to the mixture over a period of 2.0 h under nitrogen atmosphere. The reaction mixture was stirred overnight at room temperature. After the reaction was complete, 3 M HCl (50 mL) was added and the mixture was stirred for additional 30 min. The organic layer was washed with brine and water and dried over anhydrous $MgSO_4$. After filtration, the solvents were evaporated under reduced pressure. The residue was subjected to column chromatography with CH_2Cl_2 as eluent. Compound **11** was obtained as a white powder

(1.22 g) in 34% yield: mp 97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (2H, d, J = 8.0 Hz), 7.33 (2H, d, J = 7.9 Hz), 7.11−6.58 (8H, m), 4.57 (1H, s), 4.35−2.94 (22H, m), 2.45 (3H, s), 1.29−0.83 (36H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 154.0, 153.6, 153.2, 152.8, 146.3, 145.6, 145.1, 144.8, 135.2, 134.8, 133.5, 133.3, 132.5, 129.9, 128.2, 125.6, 125.0, 76.2, 70.1, 68.5, 62.4, 58.9, 38.9, 37.6, 34.2, 34.1, 33.8, 31.7, 31.3, 31.0, 30.8, 21.8; MS (MALDI-TOF) m/z 941.7 [M + Na^+]. Anal. Calcd for $C_{57}H_{74}O_8S$: C, 74.47; H, 8.11; S, 3.49. Found: C, 74.32; H, 8.39; S, 3.32.

Synthesis of Compound 12. To a degassed solution (20 mL) of **8** (0.4 g, 1.06 mmol) in THF was added a degassed solution (8.0 mL) of $CsOH\cdot H_2O$ (0.2 g, 1.2 mmol) in CH_3OH over a period of 5.0 min under nitrogen atmosphere. The mixture was stirred for an additional 30 min, and then a degassed solution (10 mL) of **11** (0.75 g, 0.8 mmol) in THF was added in one time. The reaction mixture was stirred overnight at room temperature. Then, the solvents were evaporated under reduced pressure, and the residue was subjected to column chromatography with CH_2Cl_2 as eluent. Compound **12** was obtained as an orange powder (0.60 g) in 70% yield: mp 139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−6.57 (8H, m), 6.30−6.25 (1H, m), 4.44−2.95 (26H, m), 1.34−0.87 (36H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 154.0, 153.7, 153.3, 152.8, 146.2, 145.7, 145.1, 135.3, 135.0, 133.2, 132.4, 126.9, 126.5, 126.1, 125.6, 125.0, 114.1, 71.9, 62.9, 62.6, 61.8, 59.0, 39.2, 37.8, 34.2, 33.8, 31.7, 31.3, 30.8, 30.3; MS (MALDI-TOF) m/z 1072.4. Anal. Calcd for $C_{58}H_{72}O_5S_7$: C, 64.88; H, 6.76; S, 20.91. Found: C, 64.94; H, 6.90; S, 20.65.

Synthesis of Compound 2. An anhydrous solution (30 mL) of **12** (0.28 g, 0.26 mmol) in THF was cooled to 0 °C with an ice bath. Then, NaH (0.1 g, 4.2 mmol) was added to the solution in one portion under nitrogen atmosphere. The mixture was stirred for 30 min, followed by the addition of *p*-chloranil (0.13 g, 0.52 mmol). The reaction mixture was stirred overnight. Then, the solvents were evaporated under reduced pressure, and the residue was subjected to column chromatography with CH_2Cl_2/petroleum ether (60−90 °C) (v/v, 1/3) as eluent. Compound **2** was obtained as a brown powder (0.17 g) in 51% yield: mp 123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.17 (1H, m), 7.15−6.83 (4H, m), 6.82−6.40 (3H, m), 5.00−4.52 (2H, m), 4.50−4.10 (4H, m), 4.08−3.90 (4H, m), 3.88−3.50 (4H, m), 3.45−3.25 (6H, m), 3.25−3.08 (4H, m), 3.05−2.90 (2H, m), 1.50−1.36 (5H, m), 1.35−1.20 (14H, s), 1.20−1.03 (10H, s), 0.98−0.82 (7H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 171.7, 167.8, 155.9, 155.4, 154.3, 153.4, 152.8, 145.3, 144.9, 144.8, 143.7, 140.5, 138.7, 135.2, 133.4, 133.1, 132.6, 131.9, 131.9, 131.0, 128.9, 127.4, 126.2, 125.3, 124.7, 122.8, 74.2, 65.7, 61.0, 60.4, 58.1, 38.0, 34.2, 33.8, 31.7, 31.4, 30.7, 30.2, 29.8; MS (MALDI-TOF) m/z 1282.6; HR-MS (ESI) calcd for $C_{64}H_{71}Cl_3O_7S_7$ (m/z) 1280.23048, found 1280.22929.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H NMR and ^{13}C NMR spectra of compounds **1**, **2**, **5**, **6**, **7**, **9**, **11**, and **12**; absorption, ESR spectra, cyclic voltammograms, and ^{1}H NMR spectra of **1**, **2**, **9**, and **12** 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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■ ACKNOWLEDGMENT

The present research was financially supported by NSFC, TRR61, Chinese Academy of Sciences, and State Key Basic Research Program. The authors also thank the anonymous reviewers for their critical comments and suggestions.

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(15) Previous studies (see ref 8) indicate that Sc^{3+} can induce the positive shift of the reduction potentials of quinones and trigger the intramolecular electron transfer within TTF−quinone dyads. For this

reason, Sc^{3+} was selected for the current investigations of compounds **1** and **2**.

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(18) In order to understand the coordination mode of Sc^{3+} with **1**, ^{1}H NMR spectra of **9** and **1** were recorded in the presence of different amounts of Sc^{3+} as shown in Figures S8 and S9 (Supporting Information), respectively. The ^{1}H NMR signals, especially those due to $-CH_2CH_2CH_2-$ and TTF moieties in the region of 4.10−2.10 ppm for compound **9**, kept almost unaltered after addition of Sc^{3+}. This result suggests that the binding of Sc^{3+} with oxygen atoms of alkoxyl groups in the lower rim of calix[4]arene and sulfur atoms of TTF moieties in **9** should be rather weak. The coordination of Sc^{3+} with the radical anion of quinone was reported previously (see refs 8 and 17). However, the ^{1}H NMR signals due to the $-CH_2CH_2CH_2-$ and TTF moieties in the region of 4.80−2.20 ppm became broad because the solution of **1** was paramagnetic after the addition of Sc^{3+} (see Figure S9). Accordingly, it is rather difficult to determine the exact coordination mode of Sc^{3+} with **1** based on ^{1}H NMR spectra of **1** in the presence of Sc^{3+}. It is assumed that oxygen atoms of quinone units in **1** are coordinated to Sc^{3+} (or Pb^{2+}), and oxygen atoms of alkoxyl groups and sulfur atoms from TTF units in the lower rim of calix[4]arene may also involve in the coordination to stabilize the coordination complex.

(19) The binding stoichiometry between compound **2** and Sc^{3+} or Pb^{2+} was estimated to be 1:1 based on the corresponding Job plots (see Figures S15 and S16).

(20) Shinkai and other groups have already indicated that methoxyl group is not bulky enough to suppress the oxygen through the annulus rotation, and accordingly, the methoxy group can penetrate through the cavity of calix[4]arenas (see ref 14). ^{1}H and ^{13}C NMR spectra of compound **2** were recorded after addition of different amounts of Sc^{3+}. Because the solution of **2** became paramagnetic after addition of Sc^{3+}, ^{1}H NMR signals of **2** were broad (see Figure S18). Thus, it is rather difficult to obtain structural information from these data.

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