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Binaphthalene with substituted tetrathiafulvalene and trichloroquinone: a new example of metal ion-promoted electron transfer

Hui Wu,[a,b] Deqing Zhang[a,*] and Daoben Zhu[a,*]

[a]*Beijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080, China*
[b]*Graduate School of Chinese Academy of Sciences, Beijing 100080, China*

Abstract—A new binaphthalene (R)-**1** with two substituted TTF and trichloroquinone units is reported. Both absorption and ESR spectral studies show that electron transfer occurs between TTF and trichloroquinone units of (R)-**1** in the presence of metal ions (Pb^{2+}, Sc^{3+}, Zn^{2+}, and Ca^{2+}). We also propose a possible mechanism for this electron transfer process. But, the CD spectral change of (R)-**1** in the presence of metal ions is rather small.
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Tetrathiafulvalene (TTF) and its derivatives are strong electron donors, and a number of electron donor (D)–acceptor (A) molecules with TTF as the electron donating units have been described in recent years. These D–A molecules are employed in investigations of charge–transfer interactions, construction of molecular level devices such as molecular rectifiers[1–5] and molecular switches.[6–9] Moreover, they show potential photovoltaic applications by taking advantage of efficient photoinduced electron transfer (PET) processes between TTF and electron accepting units (e.g., C_{60}).[10–14] The electron accepting units which have been covalently linked to TTF units include quinone,[15–18] C_{60}, TCNQ (tetracyano-*p*-quinodimethane),[19–21] perylene diimide,[22,23] naphthalene diimide,[24] and porphyrin/phthalocyanine.[25–28] We have recently described TTF–anthracene dyads with which new redox molecular fluorescence switches and chemical sensors are realized.[29,30]

We have very recently reported substituted TTF–trichloroquinone dyads linked by a glycol chain.[31] There is no detectable interaction between TTF and trichloroqui-

none units within these TTF–trichloroquinone dyads. But, electron transfer between TTF and trichloroquinone is observed in the presence of metal ions (Pb^{2+}, Sc^{3+}, and Zn^{2+}).

We describe here a new binaphthalene [Scheme 1, (R)-**1**] with two TTF and two trichloroquinone units. The motivations of this research include: (1) the two naphthalene rings of binaphthalene are not coplanar and several positions are accessible for substitution. Therefore, it is possible to examine the influence of the spatial distance and orientation of D and A units on the corresponding electron donor–acceptor interactions by linking D and A to the appropriate positions of binaphthalene; (2) the variation of the D–A interaction may induce the change of the dihedral angle between the two naphthalene rings. As a result, it may be possible to construct a new chiral molecular switch with chiral binaphthalene containing TTF and trichloroquinone units, since the CD spectrum of chiral binaphthalene is dependent on the dihedral angle.[32–34]

The synthesis of binaphthalene (R)-**1** started from compound (R)-**2**.[9] Removal of two ethyl groups of (R)-**2** in the presence of BBr_3 led to compound (R)-**3**, which was not further purified and directly reacted with compound **8** in the presence of CsOH yielding compound (R)-**4** in 73% yield. Compound (R)-**4** was transformed
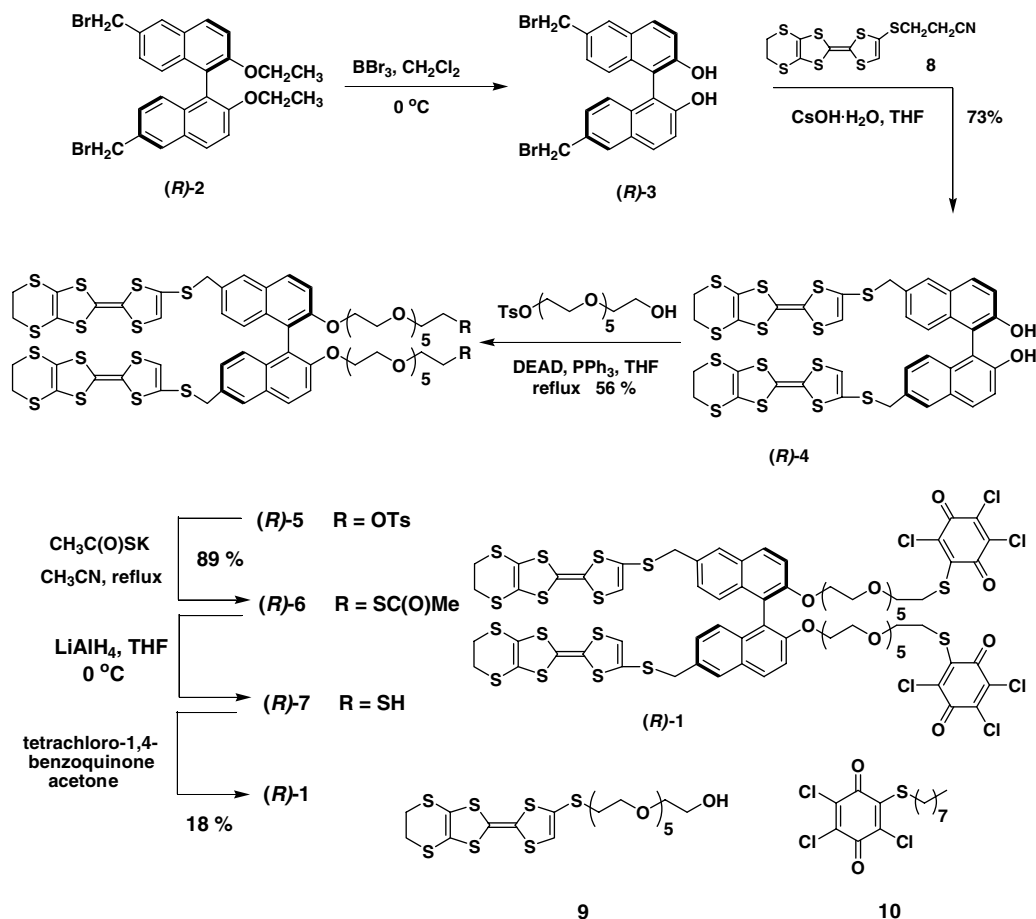
Scheme 1. The synthetic approach to (R)-**1**.

into compound (R)-**5** with Mitsunobu reaction. Compound (R)-**6** was obtained by reaction of compound (R)-**5** with potassium thioacetate. Reduction of compound (R)-**6** led to compound (R)-**7**, which was again not purified and further reacted with tetrachloro-1,4-benzoquinone to yield binaphthalene (R)-**1** in 18% yield.[35]

Figure 1 shows the absorption spectrum of (R)-**1** and those in the presence of different amounts of Pb^{2+}. There is no detectable absorption above 600 nm for the solution of (R)-**1** in the absence of Pb^{2+}, indicating that the interaction between TTF and trichloroquinone units is negligible. In cyclovoltammetric study three quasi-reversible redox waves are detected for (R)-**1**: $E^{1/2}(ox_1) = 0.55$ V, $E^{1/2}(ox_2) = 0.84$ V, and $E^{1/2}(red) = -0.05$ V, which are rather close to the corresponding redox potentials of reference compounds **9**[31] [$E^{1/2}(ox_1) = 0.55$ V, $E^{1/2}(ox_2) = 0.83$ V] and **10** (Scheme 1) [$E^{1/2}(red) = -0.05$ V]. This electrochemical result also suggests that the electron donor and acceptor interaction within binaphthalene (R)-**1** can be neglected.

It is interesting to note that new absorption bands around 450 nm and 845 nm were observed after addition of Pb^{2+}. According to the previous studies,[9,36] these new absorption bands are due to the radical cations of TTF units. Their absorption intensities increase by increasing
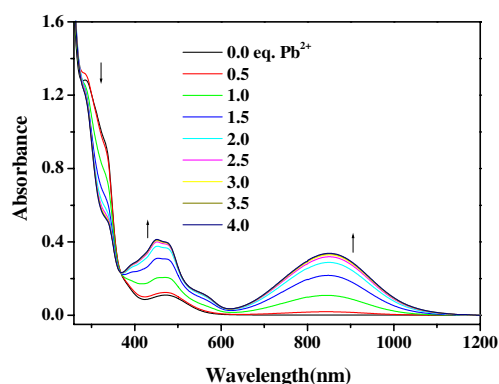

Figure 1. Absorption spectra of (R)-**1** recorded in a mixture of CH_2Cl_2 and CH_3CN (1:1, v/v; 5.0×10^{-5} M) in the presence of increasing amounts of $Pb(ClO_4)_2$.

the amounts of Pb^{2+} added to the solution. But, the increase of the absorption intensities for the bands around 450 nm and 845 nm becomes rather small after the addition of more than 2 equiv of Pb^{2+}. No absorption bands around 450 nm and 845 nm were detected in a control experiment with reference compound **9** in the presence of Pb^{2+}. Thus, the possible direct oxidation of the TTF units of (R)-**1** by Pb^{2+} can be ruled out. These results indicate that the electron transfer between TTF

and trichloroquinone units of (R)-**1** occurs in the presence of Pb^{2+}.

A strong ESR signal was observed for the solution of (R)-**1** in the presence of Pb^{2+} as shown in Figure 2. According to the previous reports,[31] the doublet ESR signals were due to the radical cation of TTF unit of (R)-**1**, and the doublet signals were ascribed to the splitting of one H atom of TTF unit ($g = 2.0085$, $a_H = 1.05$ G). That of the radical anion was not observed here probably because of the facile disproportion of the radical anion of trichloroquinone ($Q^{\cdot-}$) into the corresponding Q^{2-} and neutral Q in the presence of a metal ion at room temperature.[31,37] Therefore, this ESR result also indicates that intramolecular electron transfer occurs between the TTF and trichloroquinone units within binaphthalene (R)-**1** in the presence of Pb^{2+}.

Among the metal ions tested, Sc^{3+}, Zn^{2+}, and Ca^{2+} can also facilitate the intramolecular electron transfer between TTF and trichloroquinone units of binaphthalene (R)-**1**. As shown in Figures S1–S3, absorption bands at 450 nm and 845 nm due to the TTF radical cation were detected in the presence of $Sc^{3+}/Zn^{2+}/Ca^{2+}$. Doublet ESR signals were also observed for the solution of (R)-**1** in the presence of $Sc^{3+}/Zn^{2+}/Ca^{2+}$ (Figures S4–S6). The absorption intensities at 450 nm and 845 nm are rather weak for the solution of (R)-**1** in the presence of Zn^{2+}/Ca^{2+} compared to those containing Pb^{2+}/Sc^{3+}. This result implies that Pb^{2+}/Sc^{3+} can promote the electron transfer between TTF and trichloroquinone units within binaphthalene (R)-**1** more efficiently.

Based on the oxidation and reduction potentials of the TTF and trichloroquinone units of (R)-**1** (see above), the corresponding electron transfer between the TTF and trichloroquinone units within (R)-**1** is not thermodynamically feasible. It is known that the reduction potential of quinone is positively shifted in the presence of metal ions.[31,38,39] For instance, the reduction potentials of reference compound **10** were estimated to be 0.28 V and 0.16 V, respectively, in the presence of
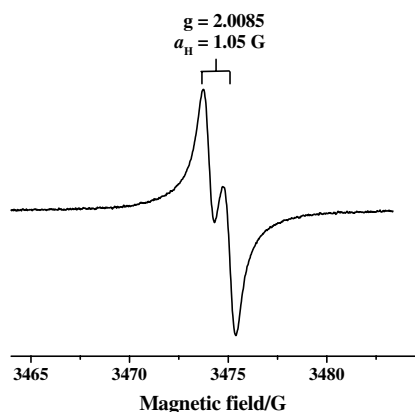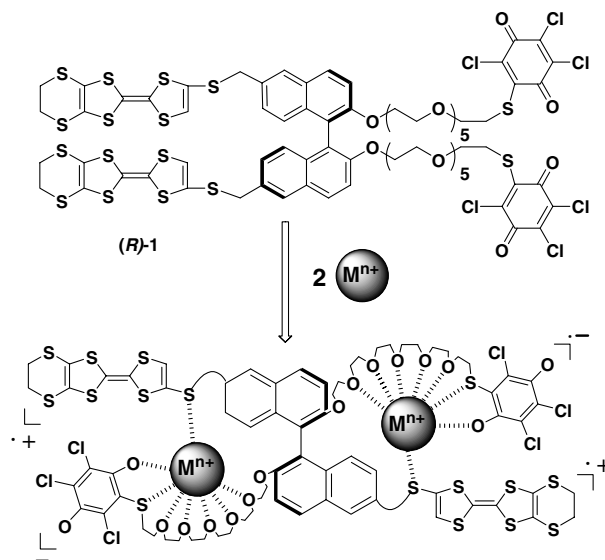
4.0 equiv of Pb^{2+} and Sc^{3+} (see Supporting data) by using Fukuzumi's method.[37,40] In comparison, the reduction potentials of **10** in the presence of Zn^{2+}/Ca^{2+} were slightly shifted anodically (see Supporting data). The positive shift of the reduction potential of **10** is attributed to the coordination of metal ions with the radical anion of trichloroquinone. Therefore, it can be concluded that the electron transfer between TTF and trichloroquinone units of (R)-**1** would become thermodynamically more feasible in the presence of these metal ions. But the electron transfer process within (R)-**1** is still endothermic by just considering the redox potentials of the TTF ($E^{1/2}(ox_1) = 0.55$ V, $E^{1/2}(ox_2) = 0.84$ V as discussed above) and trichloroquinone units in the presence of metal ions (Pb^{2+}, Sc^{3+}, Zn^{2+}, and Ca^{2+}). It is probable that the oligoethylene glycol chains of (R)-**1** are also coordinated with metal ions besides the radical anions of trichloroquinone units (Scheme 2). Such synergic coordination with metal ions may stabilize the corresponding charge-separation state by enhancing the intramolecular electronic attraction between the radical cations of TTF units and the radical anions of trichloroquinone units, thus further facilitating the electron transfer processes within (R)-**1**. It is known that Sc^{3+} shows a preference for oxygen coordination. Apart from the oxygen atoms of the oligoethylene glycol chains, the sulfur atoms of the TTF unit may also be involved in the coordination with metal ions, in particular for Pb^{2+}, which is a very poor oxyphile, preferring the much softer sulfur ligands. This may also explain the fact that Pb^{2+} can facilitate the electron transfer processes within (R)-**1**.

As discussed above, the electron transfer between TTF and trichloroquinone units of (R)-**1** promoted by metal ions would induce the formation of the radical cations of TTF units and radical anions of trichloroquinone units.[41] In addition, the glycol chains of (R)-**1** may participate in the coordination with metal ions together

Figure 2. ESR spectrum of (R)-**1** (1.0×10^{-4} M) in CH_2Cl_2/CH_3CN (1:1, v/v) in the presence of 2.0 equiv of Pb^{2+} [$Pb(ClO_4)_2$] recorded at room temperature; the solution was degassed before measurement.

Scheme 2. The proposed mechanism for the metal ion-promoted electron transfer within (R)-**1**.
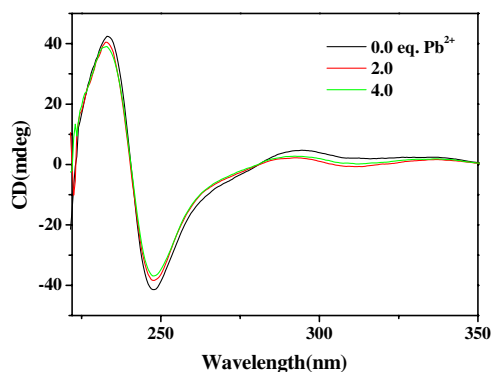
Figure 3. CD spectra of (*R*)-**1** recorded in a mixture of CH$_2$Cl$_2$ and CH$_3$CN (1:1, v/v; 1.0×10^{-5} M) in the presence of increasing amounts of Pb(ClO$_4$)$_2$.

with the radical anions of trichloroquinone units. It is anticipated that such structural variation of (*R*)-**1** in the presence of metal ions would result in the change of the dihedral angle between two naphthalene rings; accordingly, the CD spectrum of (*R*)-**1** would be varied in the presence of metal ions.

Figure 3 shows the CD spectrum of (*R*)-**1** in the presence of Pb^{2+}. After addition of Pb^{2+}, the CD signal intensities at 233 nm and 248 nm decrease slightly, and minor CD spectral variation in the range of 285–330 nm is observed. Similar CD spectral change also occurs for (*R*)-**1** in the presence of Sc^{3+} (see Figure S7). But, the CD spectral change of (*R*)-**1** after addition of Zn^{2+}/Ca^{2+} can be negligible. Thus, in contrast to our expectation the CD spectral change of (*R*)-**1** in the presence of metal ions is rather small. It is probable that the influence of the electron transfer within one pair of TTF–glycol chain–trichloroquinone of (*R*)-**1** on the dihedral angle change is cancelled by that within another pair of TTF–glycol chain–trichloroquinone of (*R*)-**1**. Investigation of the binaphthalene with one pair of TTF–glycol chain–trichloroquinone is in progress.

In summary, a new binapthalene (*R*)-**1** with two substituted TTF and trichloroquinone units is described. Both absorption and ESR spectral studies show that electron transfer occurs between TTF and trichloroquinone units of (*R*)-**1** in the presence of metal ions (Pb^{2+}, Sc^{3+}, Zn^{2+}, and Ca^{2+}). Moreover, possible mechanism for this electron transfer process is proposed based on previous studies.[31,42–45] But, in contrast to our expectation the CD spectral change of (*R*)-**1** in the presence of metal ions is rather small.

Acknowledgments

Supplementary data

Supplementary data contains experimental details of the synthesis, absorption, ESR, CD and cyclic voltammo-grams of (*R*)-**1** and those in the presence of metal ions. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet. 2007.10.134.

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35. *Characterization data for* (*R*)-**1**: FT-IR (KBr, cm^{-1}) 1676 (C=O); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.88 (2H, d, $J = 8.8$ Hz), 7.68 (2H, s), 7.42 (2H, d, $J = 8.8$ Hz), 7.16 (2H, d, $J = 8.9$ Hz), 7.10 (2H, d, $J = 8.9$ Hz), 6.15 (2H, s), 4.09–4.05 (8H, m), 3.73 (4H, t, $J = 5.2$ Hz) 3.54–3.50 (20H, m), 3.50–3.45 (12H, m), 3.30 (8H, s), 3.25 (4H, t, $J = 4.2$ Hz), 3.17–3.12 (4H, m); ^{13}C NMR (100 MHz, CDCl$_3$): δ 171.6, 167.9, 153.6, 146.8, 140.2, 139.1, 135.1, 132.3, 130.9, 128.3, 128.1, 126.9, 126.3, 125.1, 123.1, 119.3, 117.9, 115.1, 113.5, 106.4, 70.3, 69.6, 69.54, 69.50, 69.47, 69.46, 69.42, 69.37, 68.8, 68.6, 40.2, 32.8, 29.2, 28.7; MS (MALDI-TOF) m/z 1943.9 (M$^+$); HR-MS (MALDI-TOF) calcd for C$_{74}$H$_{72}$Cl$_6$O$_{16}$S$_{16}$: 1937.8483; found: 1938.8515 [M+H]$^+$.
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