Amphiphilic Tetrathiafulvalene Derivative: Charge-Transfer Complexation Behavior in Solutions

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An amphiphilic tetrathiafulvalene (**1**) was prepared by condensation of tetrathiafulvalene-4-carboxylic acid with reduced Triton X-100 to avoid crystallization. Its charge-transfer (CT) complexation behaviors were examined with a strong electron acceptor, i.e., 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), in solutions. Although tetrathiafulvalene, (4-tetrathiafulvalenyl)methyl acetate (**2**), and methyl tetrathiafulvalene-4-carboxylate (**4**) reacted with DDQ to produce a dark red precipitates in $CHCl_3$ and (4-tetrathiafulvalenyl)methyl stearate (**3**) with DDQ formed black red colloidal dispersions in $CHCl_3$, an equimolar amount of DDQ with **1** in $CHCl_3$ formed a dark red solution without any precipitates. The UV spectrum of the solution of **1** and DDQ in $CHCl_3$ shows a broad peak in near-IR regions. The absorption maximum at 1300 nm ($\varepsilon = 3.8 \times 10^2$ $M^{-1}\,cm^{-1}$) that is tailing to beyond 2000 nm is derived from π-stacked arrangement of the TTF moiety and DDQ. UV–vis absorption spectra of **1** with DDQ in several organic solvents, i.e., acetonitrile, acetone, CH_2Cl_2, toluene, and CCl_4, show that the CT complexation behavior of **1** was highly dependent on the solvent polarity.

Derivatives of dithiafulvene, including tetrathiafulvalene (TTF), act as electron donors and form charge-transfer (CT) complexes with organic and inorganic acceptor species.[1–3] These CT complexes and radical ion salts are extensively studied in the solid state due to their conductive properties. Electrically conducting organic crystals have high charge mobilities but are usually impractical. Several approaches to solve this problem have been reported, including polymers,[4–9] Langmuir–Blodgett films,[10] and liquid crystals.[11] Polymers have good processability but usually low electrical mobilities. One of the interesting fields is the preparation of "molecular" scale components based on TTF by utilizing self-assembly principles.[12,13] A gel-forming bis-arborol-TTF derivative was prepared and its absorption spectra were recorded in its gel state after oxidized with iodine.[14] After the TTF moiety self-assembled, the components are easily oxidized to the cation radical. These concepts are based on the idea that TTF moiety assembly is assisted by assembled groups in addition to the CT interaction. However, few studies of CT complexes of TTF derivatives in the solution state have been reported, since the TTF moieties tend to crystallize by charge transfer with strong acceptors such as TCNQ or DDQ in the solution.

TTF-based crystals grow in the direction of their *c*-axis with specific CT interaction of the resulting TTF cation radical with the remaining neutral TTF. If substituent groups are introduced to a TTF moiety, crystal growth of the TTF cation radical with remaining neutral TTF would be disturbed. Here, we report preparation of a tetrathiafulvalene substituted with an amphiphilic oligomeric unit to avoid crystallization and its CT complexation behaviors with a strong electron acceptor, i.e., 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), in solutions. The resulting amphiphilic TTF derivative was soluble in non-polar organic solvents as well as in water. A wide range of solubility should be of advantage for studies of CT interaction which depends on a solvent polarity. Specific aggregation behaviors would be expected from its amphiphilic character. We found that the amphiphilic TTF derivatives formed a 1:1 CT complex in $CHCl_3$, in which the characteristic CT absorption band observed at near-IR region derived from a π-stacked arrangement of the TTF moiety and DDQ in the solution. To our knowledge, this is the first report for a soluble CT complex of an intermolecular π-stacked arrangement of a π-donor and a π-acceptor in a homogeneous solution.

Experimental

Materials and Methods. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under nitrogen atmosphere. Reduced Triton X-100 was obtained from Aldrich Chem. Co. Tetrathiafulvalene-4-carboxylic acid, (4-tetrathiafulvalenyl)methyl acetate (**2**), and (4-tetrathiafulvalenyl)methyl stearate (**3**) were prepared according to the literature.[15] Methyl tetrathiafulvalene-4-carboxylate (**4**)[16] was prepared analogously to **1**.

^1H NMR spectra were recorded on a 400 MHz JEOL NMR spectrometer. UV–vis absorption spectra and near-IR spectrum were obtained on a JASCO V-530 and a PerkinElmer Lambda 800, respectively. Vaper pressure osmometry was performed on a Knauer K-7000.

Synthesis of Amphiphilic TTF (1). To a stirred solution of tetrathiafulvalene-4-carboxylic acid (347 mg, 1.40 mmol) and reduced Triton X-100 (911 mg, 1.40 mmol) in 30 mL ethyl acetate under nitrogen atmosphere, dicyclohexylcarbodiimide (500 mg, 2.42 mmol) and 4-dimethylaminopyridine (30 mg, 0.25 mmol) were added. The mixture was refluxed for 12 h. After cooling, the precipitated dicyclohexylurea was removed by filteration and the solution was evaporated in vacuo. Column chromatography

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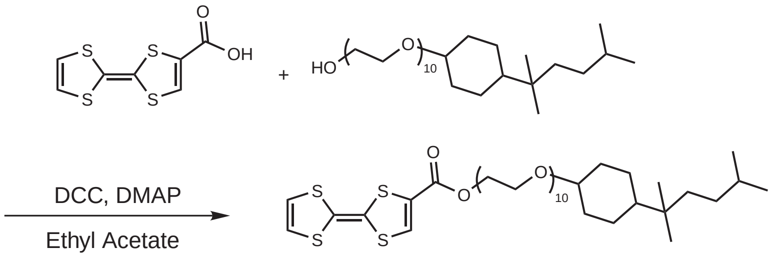

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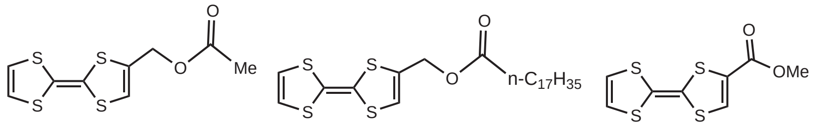
Scheme 1.



2 **3** **4**

Chart 1.

(silica gel) using ethyl acetate as eluent gave **1** as a brown oil; yield: 303 mg (25%).

^{1}H NMR (400 MHz, acetone-d_6/TMS) δ 0.8–2.1 (m, 26H), 3.4–3.8 (m, 39H), 4.37 (t, 2H), 6.35 (s, 2H), 7.40 (s, 1H).

Results and Discussion

We have prepared several TTF derivatives. The amphiphilic TTF (**1**) was prepared by condensation of tetrathiafulvalene-4-carboxylic acid with reduced Triton X-100 (Scheme 1). The ^{1}H NMR confirmed quantitative introduction of the TTF unit. The amphiphilic TTF was soluble in common organic solvents such as toluene, $CHCl_3$, acetonitrile, and THF as well as in water. According to the ^{1}H NMR spectrum and elemental analysis data of **1**, 7 wt % of dicyclohexylurea was contaminated even after purification by silica column chromatography. (4-Tetrathiafulvalenyl)methyl acetate (**2**) and stearate (**3**) were prepared according to the reported method (Chart 1).[15] A methyl ester of TTF (**4**) was also prepared for checking the effect of the electron-withdrawing character of COOR directly attached on the TTF unit.

In $CHCl_3$, TTF reacted with DDQ to produce a dark red precipitate. The combination of TTF and both methyl esters **2** and **4** also formed dark red precipitates in $CHCl_3$. DDQ and **3** formed black red colloidal dispersions in $CHCl_3$. An equimolar amount of DDQ was added to a solution of (0.52 mM) **1** in $CHCl_3$, and the mixture was stirred for 5 min at room temperature. The solution gradually turned to dark red without any precipitates. These results show that the amphiphilic unit avoids precipitation in the solution.

The UV spectrum of the solution of **1** and DDQ in $CHCl_3$ shows broad peak in near-IR regions, with the absorption maximum at 1300 nm ($\varepsilon = 3.8 \times 10^2$ M^{-1} cm^{-1}) tailing to beyond 2000 nm (Fig. 1). No clear peak appeared at around 590 nm assignable to the anion radical of DDQ,[17] while the cation radical of TTF[18] was recognized. Segregated stacked crystalline CT complexes of TTF such as TTF–chloranil CT salts show bands around 1300 nm.[19] These results suggest that a π-stacked arrangement of the TTF moiety and DDQ was formed in the solution.

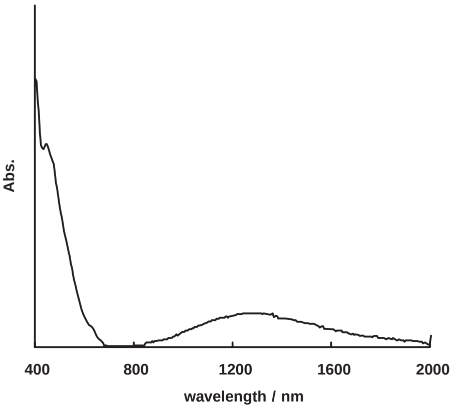


Fig. 1. Near-IR absorption spectrum of **1** in $CHCl_3$ at room temperature.

The reversibility of the complex formation was confirmed by monitoring the CT band by changing the temperature. Heating the solution at 60 °C for 10 min resulted in a decrease of the CT absorption. When the solution was left at room temperature after heating, the absorption of the CT band returned to the same value, indicating the formation of the CT complex. In the ^{1}H NMR spectrum of **1** with DDQ in $CDCl_3$, the proton of the TTF moiety of **1** disappeared (Fig. 2). Broadening of the poly(oxyethylene) moiety was also observed. This indicates a significant spin concentration on the donor and acceptor moieties. Recently, TTF-s-polynitrofluorene diads showed similar broad CT bands at 1300 nm in non-polar organic solvents and paramagnetic broadening in ^{1}H NMR analysis in $CDCl_3$.[20]

A spectrophotometric dilution analysis was performed in $CHCl_3$ at 900 nm at 25 °C yielded an association constant (K_a) of 3 M^{-1}. Vaper pressure osmometry (VPO), a traditional technique to measure the number-average molecular weight of a solute in a solution, has proven useful for the studies of non-covalent aggregation. VPO measurements were made on **1** with DDQ in $CHCl_3$ at 40 °C, using benzil for calibration. The quotients of vapor pressure signal over concentration were plotted against the concentration ([C]). The number-average

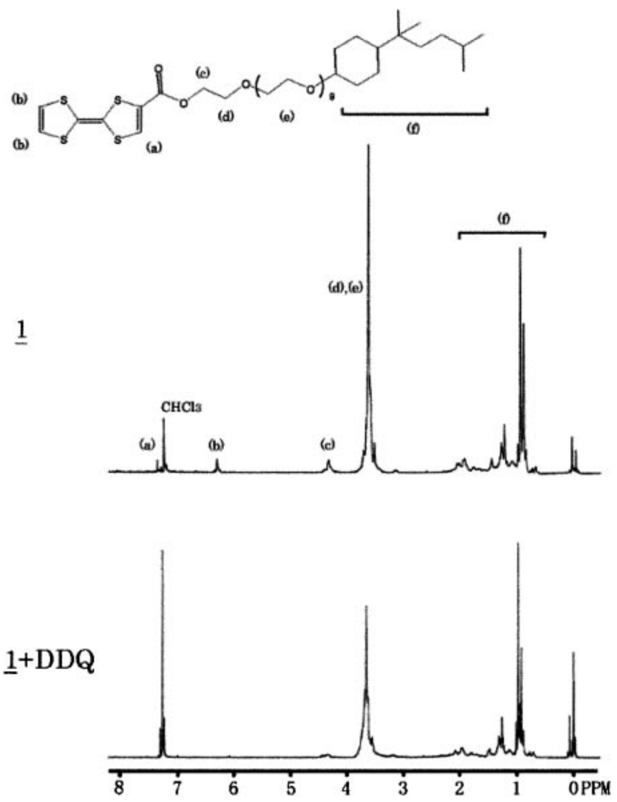


Fig. 2. ^{1}H NMR spectra of **1** and **1** with DDQ in $CDCl_3$.

molecular weight (M_n) value, inversely proportional to the intercept at $[C] = 0$, was determined as 797 $g\,mol^{-1}$. If **1** and DDQ individually existed in the solution after charge transfer, the M_n value should be 555. On the basis of the assumption that **1** and DDQ form a 1:1 complex, K_a is calculated to be 4 M^{-1}. This value was in good agreement with that of the spectrophotometric dilution analysis. The results support the conclusion that the CT complexes are formed in the solution.

The CT complex of **1** with DDQ in $CHCl_3$ dissociated into a neutral **1** by addition of ferrocene as a donor. After addition of 4 equivalent molar amounts of ferrocene in $CHCl_3$, black precipitates were formed. The UV–vis absorption spectrum of the solution after removing the black precipitates shows no CT band, but a small peak at 590 nm assignable to the anion radical of DDQ (Fig. 3). The ^{1}H NMR spectrum of the CT complex of **1** with DDQ in $CDCl_3$ with DDQ after addition of ferrocene showed the peaks corresponding to the TTF moiety. These results indicate that the CT complex of **1** with DDQ dissociated into neutral **1** by removal of the CT salts of DDQ and ferrocene as precipitates.

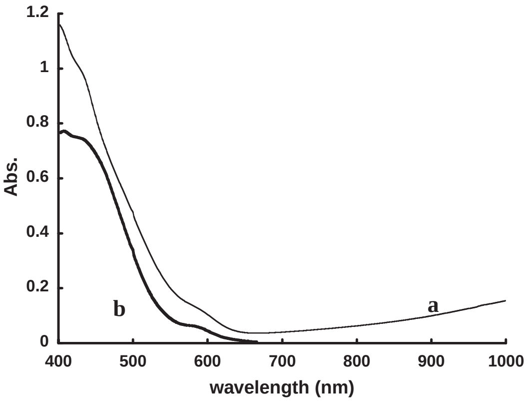


Fig. 3. UV–vis absorption spectra of **1** with DDQ in $CDCl_3$ before (a) and after (b) addition of ferrocene.

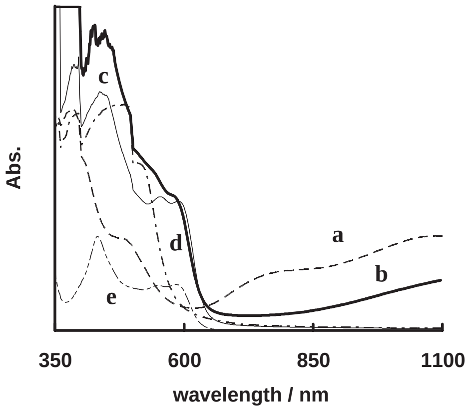


Fig. 4. UV–vis absorption spectra of **1** with DDQ in (a) CCl_4, (b) CH_2Cl_2, (c) acetone, (d) toluene, and (e) CH_3CN.

Figure 4 shows the UV–vis absorption spectra of **1** with DDQ in several organic solvents. No CT bands derived from π-stacked arrangement of the TTF moiety and DDQ were observed in acetonitrile or acetone. Shoulder peaks at ca 540 and 590 nm assignable to the anion radical of DDQ were more clearly observed than those in $CHCl_3$ along with the CT absorption band. Polar solvents promote charge transfer from a donor to an acceptor in their ground states due to stabilization of the resulting CT salt. The UV spectrum of the solution of **1** and DDQ in CH_2Cl_2 also shows broad peaks in near-IR regions. The degree of the formation of the cation radicals and DDQ anion radicals in CH_2Cl_2 was higher than that in $CHCl_3$, which can be explained by the solvent polarity. In toluene, neither CT band nor radical ions were observed, indicating that no CT complex was formed in the less polar solvent. DDQ was added in CCl_4 solution of **1**, resulting in new peaks at $\lambda =$ 750 nm and 1000 nm (Fig. 4). These new peaks are presumably due to TTF dimers or oligomers, and they are observed in π-stacks of TTF salts in the crystalline state.[18]

Conclusion

We have demonstrated that the amphiphilic TTF derivatives formed a 1:1 CT complex in $CHCl_3$, in which characteristic CT absorption band observed at near-IR region was derived from π-stacked arrangement of the TTF moiety and DDQ in the solution. The amphiphilic oligomeric unit attached on the TTF unit avoid crystals growth in the direction of their *c*-axis with specific CT interaction of the resulting TTF cation radical with the remaining neutral TTF in solution. Crystallization of TTF unit was less avoided by long alkyl chains. Since TTF itself is soluble in all the solvents tested, the CT complexation behavior of **1** was dependent on the solvent polarity. Assembly of a TTF moiety of TTF derivatives modified with long alkyl chain would be expected in hydrophobic solvents such as paraffin since the TTF moiety is insoluble in these solvents.

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