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Organosulfur Conducting Bridges

Intramolecular Electron Transfer Mediated by a Tetrathiafulvalene Bridge in a Purely Organic Mixed-Valence System**

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Tetrathiafulvalene (TTF) and its derivatives have been successfully used as building blocks of low-dimensional organic conductors and superconductors where intermolecular electron-transfer phenomena play a key role in the electronic transport properties.[1] Important results have been also achieved using TTFs as versatile strong π-donor systems in materials chemistry,[2] particularly in intramolecular charge-transfer materials for donor–acceptor molecules[3] or in photoinduced electron transfer when linked to [60]fullerene.[4] However, TTF has never been used as a bridge to promote electron conduction between two groups. Nowadays, unimolecular electronic devices are at the forefront of research in nanotechnology because of the anticipated limits to the further miniaturization of microelectronics.[5] Moreover, direct electronic conduction through single molecules has recently been demonstrated[6] showing the potential use of integrated molecular-sized devices. As a consequence, there is great interest in studying the role of various parameters that govern the intramolecular electron-transfer (IET) rates. Mixed-valence compounds are the prototypes of molecules able to undergo fast electron transfer through a bridge. Such systems have been widely used to study IET between redox centers of both inorganic[7] and organic nature,[8] with the aim of understanding electron-transfer processes to aid the design of molecular wires.[9]

One way to test the electron conduction through TTF is to use it as a bridge between two redox moieties in a mixed-valence system. Consequently, our target molecule was the TTF-diquinone **1**, Q-TTF-Q, since the *p*-benzoquinone groups are particularly useful organic redox centers to generate mixed-valence systems[10] that form persistent radical anions upon reduction.[11] The behavior of **1** has been studied by electrochemistry and ESR spectroscopy, and we have also performed the synthesis of the TTF-monoquinone **2**, TTF-Q, as a model compound.

Syntheses of **1** and **2** were achieved using the same key intermediate 2-oxo-1,3-dithiole derivative **7** (Scheme 1). The iminium salt **4** was prepared according to a previously described procedure.[12] After quantitative conversion to the 2-thioxo-1,3-dithiole **5**, the hydroquinone functionalities were protected using acetyl or silyl groups by well-established reactions. Further transchalcogenation of **6a** and **6b** furnished the 2-oxo-1,3-dithiole derivatives **7** in excellent yields. The triethylphosphite coupling methodology was applied to **7a** and the resulting TTF derivative **8** was transformed into the bis(1,4-hydroquinone)-TTF derivative by subsequent methanolysis in a methoxide solution and subsequent treatment with *p*-toluenesulfonic acid (PTSA). Without isolating the later intermediate, the fused Q-TTF-Q system **1** was obtained as green-blue crystals by selective oxidation using 2,3-dichloro-5,6-dicyano-1,2-benzoquinone (DDQ).To obtain the TTF-Q assembly **2**, the Horner–Wadsworth–Emmons olefination approach was applied to create the TTF core,[13] which involved the 2-oxo-1,3-dithiole functionality and the anion of phosphonate **9**.[14] After deprotection of the silyl groups of compound **10**, subsequent oxidation with *p*-benzoquinone afforded compound **2** as green crystals.

The cyclic voltammogram of **1** showed two one-electron reversible oxidation waves at $E^0_{ox1} = +0.99$ and $E^0_{ox2} = +1.36$ V (versus a Ag/AgCl electrode), which are characteristic for the TTF moiety, and two distinguishable reversible waves at $E^1_{red} = -0.20$ and -0.28 V, which correspond to the stepwise one-electron reduction of each *p*-quinone moiety. The potential difference of $\Delta E = 0.08$ V between the two waves indicates that the reduction of the second *p*-quinone group is somewhat affected by the presence of the first $Q^{-\bullet}$ center, and suggests that an effective electronic coupling exists between both Q centers, which is mediated by the TTF bridge.

We have studied the intramolecular electron-transfer process in the Q-TTF-$Q^{-\bullet}$ mixed-valence system by temperature-dependent ESR spectroscopy. Electrochemical or chemical reduction[15] of model compound **2** gives the TTF-$Q^{-\bullet}$, which gives an ESR spectrum that is characterized by three lines with 1:2:1 intensities that result from coupling with two equivalent aromatic protons ($a_H = 2.50$ G). This ESR spectrum was singularly invariant over a wide temperature range (270–360 K) and also with concentration, which shows that there is no intermolecular electron transfer in this system. In contrast, the ESR spectrum of the TTF-bridged mixed-valence anion radical Q-TTF-$Q^{-\bullet}$ changes upon cooling from 340 to 260 K (Figure 1). While the spectrum at 260 K was essentially identical to that of model compound TTF-$Q^{-\bullet}$ (three lines in 1:2:1 intensity, $a_H = 2.47$ G), the spectrum at temperatures higher than 340 K is characterized by the coupling of four equivalent aromatic protons (five lines in 1:4:6:4:1 intensity, $a_H = 1.23$ G; Figure 1 a).[16] As the temperature is gradually lowered from 340 to 260 K, the alternate lines broaden and disappear because of extensive dynamic electron exchange between both of the Q electrophores through the TTF bridge (Scheme 2).[17] The lowest temper-

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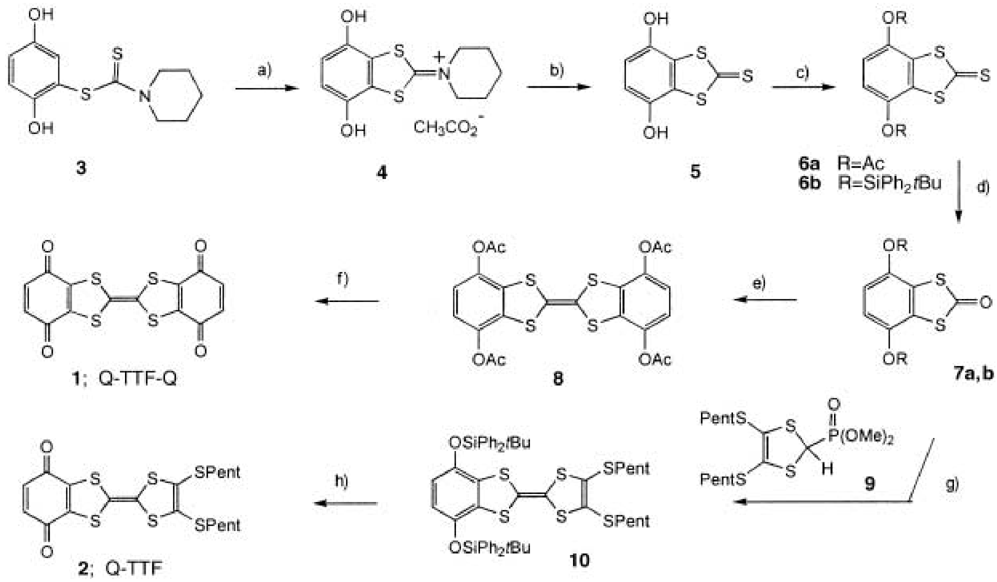


Scheme 1. Syntheses of **1** and **2**. Reagents: a) *p*-benzoquinone then glacial AcOH, 80 °C, 96 %; b) $Na_2S\cdot 9H_2O$, MeOH, 98 %; c) Ac_2O, Et_3N, 80 % for **6a**; $Ph_2tBuSiCl$, DMF, imidazole, 86 % for **6b**; d) $Hg(OAc)_2$, CH_2Cl_2/glacial AcOH, 88 % for **7a**, 85 % for **7b**; e) Δ, $P(OEt)_3$, 45 %; f) MeONa/MeOH, then PTSA and H_2O, then DDQ, 57 %; g) phosphonate **9**, *n*BuLi, THF, −78 °C to 20 °C, 90 %; h) nBu_4NF/THF then *p*-benzoquinone, 75 %.

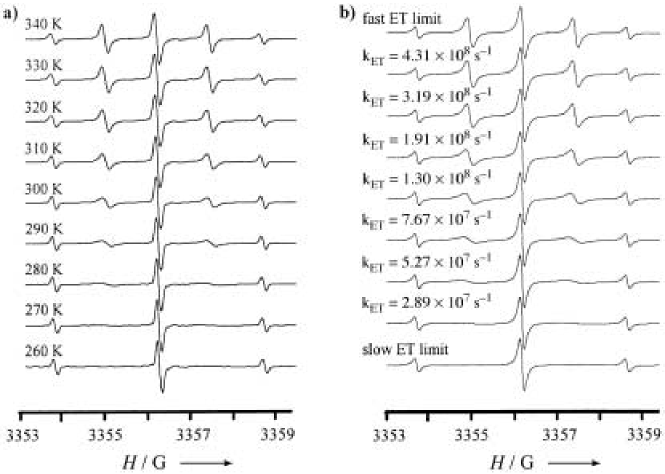
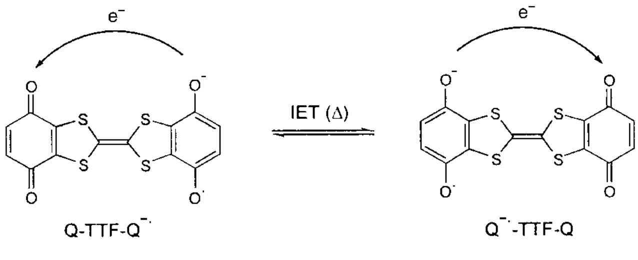


Figure 1. Experimental (a) and simulated (b) ESR spectra of $1^{-\bullet}$ at different temperatures in ethyl acetate/*tert*-butanol (10:1) with PPh_4Br.



Scheme 2. Electron exchange through the TTF bridge.

ature spectrum unequivocally demonstrates that the odd electron of Q-TTF-$Q^{-\bullet}$ is localized on one particular Q unit on the ESR time scale, and as the temperature is raised the activation energy barrier is overcome, which promotes a faster IET process between the two Q moieties.

The dynamics of the intramolecular exchange process was theoretically simulated[18] (Figure 1 b) and first-order rate constants for the thermally activated IET process were extracted by fitting the experimental ESR spectra. The simulation leads to a linear Arrhenius plot over the 330–270 K temperature range, which gives the activation parameters: $E_{act} = 7.96\ \text{kcal mol}^{-1}$; $\log A = 13.9$ ($\Delta G^{\ddagger}_{298K} = 6.4\ \text{kcal mol}^{-1}$; $\Delta H^{\ddagger} = 7.4\ \text{kcal mol}^{-1}$; $\Delta S^{\ddagger} = 3.1$ e.u.). The activation parameters for compound **1** are close to those previously reported for the anthracene-diquinone anion radical.[10e] This is one of the very few cases of an intervalence system for which the IET process can be followed by ESR spectroscopy,[8a,b,d,l,10e] which allows an accurately determination of the rate constant for thermally activated electron transfer. Figure 1 shows the results obtained in a 10:1 mixture of ethyl acetate/*tert*-butanol. However, the rate constants of the electron-transfer (ET) process have been determined in different solvents, which gives rise to different rate constants because of energy variations resulting from solvent reorganization. For example, the rate constants at 300 K are very similar in dichloromethane and ethyl acetate ($k_{ET} = 2.58 \times 10^8\ s^{-1}$ and $2.10 \times 10^8\ s^{-1}$, respectively) and of the same order in the 10:1 mixture of ethyl acetate/*tert*-butanol ($k_{ET} = 1.30 \times 10^8\ s^{-1}$), whereas in *tert*-butanol the ET process is slower ($k_{ET} = 2.89 \times 10^7\ s^{-1}$). It is important to indicate that the thermally activated IET process can only be fully studied using the 10:1 ethyl acetate/*tert*-butanol mixture, since other solvent systems exhibit interfering precipitation processes. As a result of the high insolubility of the monoanion radical species in any solvent, we have not been able to generate the corresponding dianion by chemical reduction or electrochemical reduction at −0.5 V.

The high insolubility of the Q-TTF-$Q^{-\bullet}$ mixed-valence species also prevents the quantitative study of the IET process by Vis/NIR spectroelectrochemical methods, since the compound starts to precipitate after passing a very small quantity of charge. Nevertheless, by deconvoluting the Vis/NIR spectra at different reduction steps, a broad charge-transfer band centered around 1300 nm is clearly observed for the generated Q-TTF-Q$^{-\bullet}$ mixed-valence species. Moreover, this band is completely absent for both the neutral species and in the TTF-Q$^{-\bullet}$ model compound.

The Q-TTF-Q$^{-\bullet}$ species is, therefore, a prototypical class II mixed-valence system involving moderately coupled redox centers.[19]

In summary, we have obtained a new, purely organic mixed-valence compound in which the existence of a temperature-dependent intramolecular electron transfer has not only been undoubtedly established but for which the rate constant for the thermally activated IET process has been accurately determined. In addition, this is the first time that a bridge exhibiting a strong electron-donating character, such as TTF, has been used in a mixed-valence system. The results here demonstrate that TTF is a suitable molecular bridge for the promotion of intramolecular electron transfer between two redox centers and constitutes a natural route towards the measurement of an electrical current through metal-TTF-metal nanojunctions. In that sense, TTF can be considered as the prototype of a huge family of electron donors in which the ionization potential (I_{D}) is small and can be tuned by changing the substituents and the conjugated extension. These characteristics are very important since one of the criteria for a good donor molecular wire is that the I_{D} value must be small, and must closely match the work function of the metal layer that acts as an electrode.[6c] We are currently working on the introduction of conjugated spacers between the 1,3-dithiole moieties of compound **1** to elongate the TTF bridge, and also on the utilization of other redox centers to replace *p*-benzoquinone groups.

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[16] As the coupling constant a_{H} is dependent on the spin density, the delocalization of the electron over both quinone groups means that this constant is half as large for compound **1** as for **2**.

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