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# A tunable degree of intramolecular through-space charge transfer in TTF–σ–PBQ systems

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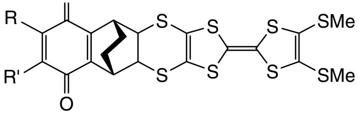
**Abstract**—The synthesis, spectral and electrochemical properties of a series of TTF–σ–PBQ derivatives, along with a demonstration of the fine-tuning of the degree of charge transfer in these systems, are reported.

The discovery of the first organic metal of TTF–TCNQ[1] with a partial degree of charge transfer (CT) promoted much interest towards the investigation of TTF and similar compounds, as electron donor components of many other CT complexes and ion-radical salts.[2] In order to control the stoichiometry of the D (donor) and A (acceptor) components and the degree of charge-transfer in CT complexes, which are crucial parameters in the design of molecular electronic devices, the concept of D–A–D and A–D–A triads in which the D and A fragments are integral parts of a single molecule, has been developed.[3] Additionally, the degree of CT in intramolecular complexes can be tuned by means of changing the redox properties of the D and/or A units, namely, by chemically modifying the electroactive moieties. Moreover, it was realized[4,5] that intramolecular CT properties in D–σ–A systems could be finely tuned by controlling the molecular geometry, that is, by fixing the distances between the D and A moieties and their spatial positions with respect to each other. The importance of the molecular geometry is unequivocally demonstrated in our recent example of a through-space intramolecular charge transfer complex involving a TTF donor and a TCNQ acceptor.[5] Although the principles of controlling the degree of CT are theoretically well understood,[4,5] to date there is no experimental example of a successful tuning of the degree of CT in a given D–σ–A system. Therefore, the design of such an intramolecular CT complex with a capability of controlling the degree of CT through chemical modifications of one or both of the interacting components has been a challenge for synthetic chemists.

Previously, we have prepared and studied the properties of a D–σ–A diad system **1**,[7] which consists of a tetrathiafulvalene (TTF) unit covalently linked, via a rigid saturated spacer, to *p*-benzoquinone (PBQ) as the acceptor unit (TTF–σ–PBQ). This system exhibits a weak intramolecular through-space charge transfer. We then proposed that by the same synthetic approach, new derivatives of **1** with higher and controllable degrees of charge transfer could be prepared. Accordingly, we present here a series of TTF–σ–PBQ derivatives **1**–**3**[8] and demonstrate for the first time, the successful possibility of fine-tuning the degree of charge transfer by slightly changing the electron affinity of the PBQ acceptor moiety. It is noteworthy that previous attempts to modify the substitution pattern on the PBQ moiety in a different PBQ–σ–TTF system (involving two methylenethio spacers) have been made, but no CT band was observed in the electronic spectra.[9]



**1** R = R' = H
**2** R = H, R' = Cl
**3** R = R' = Cl

It is expected that the higher the degree of CT is, the longer the wavelength of the corresponding absorption band in the Vis–NIR will be, due to a smaller

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*Keywords*: Charge transfer; Donor–acceptor systems; Cyclic voltammetry; Tetrathiafulvalene; *p*-Benzoquinones.

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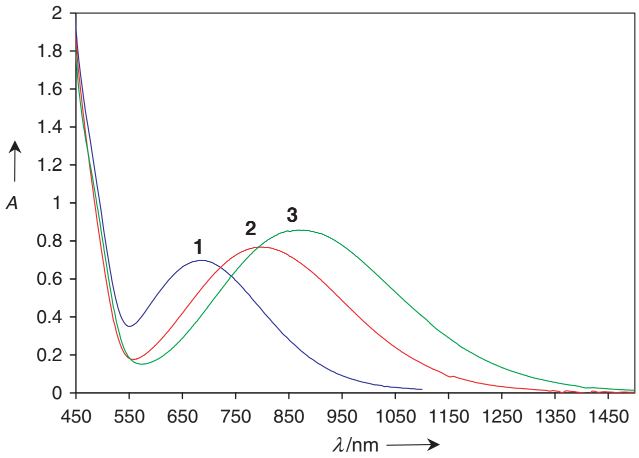

**Figure 1.** Vis–NIR spectra of **1** (blue, $\lambda_{max} \sim 685$ nm), **2** (red, $\lambda_{max} \sim 796$ nm) and **3** (green, $\lambda_{max} \sim 870$ nm) in dichloromethane.

HOMO–LUMO gap.[6] Compound **3** involves a stronger acceptor than **2**, and the latter contains a stronger acceptor than in **1**. Consequently, a higher degree of intramolecular charge transfer is achieved. The CT bands in the Vis–NIR spectra of **2** (796 nm) and **3** (870 nm) are slightly more intense and shifted to longer wavelengths, compared to **1** (685 nm) (Fig. 1). This indicates that the interactions of the TTF moiety with stronger quinone acceptor moieties afford a better overlap with their p-orbitals.

The increasing degree of charge transfer in the said novel compounds can also be followed by changes in their redox potentials. Thus, cyclic voltammetry (CV) results (Table 1) of the three TTF–σ–PBQ derivatives were found to be consistent with the spectroscopic data. We clearly observed a tendency of a decrease (less negative) in the first reduction potential of the quinone fragment (from **1** to **3**) and an increase in the first oxidation potential (attributed to the TTF fragment). As discussed earlier,[7] compound **1** exhibits rather weak intramolecular CT interactions that do not affect the first oxidation potential of the TTF fragment (relative to individual TTF). However, upon increasing the acceptor strength in **2** and **3**, the first reduction potential becomes less negative, that is, the compound is easier to reduce, whereas the first oxidation potential (which corresponds to the TTF moiety) increases because it becomes more difficult to oxidize due to its linkage to a stronger acceptor). The observation that TTF is more difficult to oxidize attests to stronger CT in **2** and **3** (compared to **1**), that is, a higher degree of CT in the ground state.

Furthermore, the second oxidation potential corresponding to the TTF donor moiety decreases slightly (but systematically) from **1** to **3**, upon increasing the acceptor strength. This phenomenon is not well understood yet.

**Table 1.** Reversible redox potentials of compounds **1**, **2** and **3**[a]

| | $E_{1/2}^{ox1}$ (V) | $E_{1/2}^{ox2}$ (V) | $E_{1/2}^{red1}$ (V) |
|---|---|---|---|
| **1** | 0.550 | 0.825 | −0.525 |
| **2** | 0.572 | 0.812 | −0.352 |
| **3** | 0.589 | 0.808 | −0.256 |

[a] $CH_2Cl_2$–$CH_3CN$ (1:2, v/v) versus Ag/AgCl; $Bu_4NClO_4$ 0.1 M; glassy carbon working electrode; 100 mV/s.

It is noteworthy that the degree ($\rho$) of CT in **2** and **3** can be estimated by comparing their CV data with those of **1**. It was found earlier[7] that the oxidation potential of the TTF moiety in **1** was quite similar to that of the corresponding individual TTF derivative, even though a weak intramolecular CT was observed in **1**. It has been concluded that the CV technique is not sufficiently sensitive to detect small changes in redox potentials resulting from weak CT interactions. Therefore, assuming that $\rho$ in **1** is close to zero, the $E_{ox1}^{1/2}$ and $E_{ox2}^{1/2}$ values of **1** can be adopted as the initial and final points of a degree of CT calibration line. Consequently, the difference of 0.275 V between these two values corresponds to complete CT, namely, $\rho = 1$. As indicated in Table 1, the difference between the first oxidation potentials of **2** and **3** with respect to **1** is 22 and 39 mV, respectively. Eventually, when these values are estimated as percentages of the full scale of 275 mV, the approximate degrees of CT in **2** and **3** are found to be $\rho = 0.08$ and $\rho = 0.14$, respectively. This notion is also supported by using the linear lower portion of the plot of the dependence of the experimental values of $\rho$ on the $E_{ox1}^{1/2} - E_{red1}^{1/2}$ difference measured for over 50 charge transfer complexes and ion-radical salts.[10] Accordingly, a similar trend was observed and the estimated $\rho$ values for **1** and **2** (or **3**) were 0.06 and 0.11, respectively. However, the gradient of the slope in this region was small and therefore, not sufficiently sensitive to small changes in redox potentials to allow a clear distinction between **2** and **3**.

In conclusion, the results of this work demonstrate the usefulness of our recently developed synthetic protocol[7] for preparing D–σ–A systems with a controllable degree of charge transfer. In the present case, fine-tuning of the CT properties occurs through minor modification of the acceptor unit. Apparently, the existence of two sites (A and D) in one molecule, both susceptible to simple chemical modification, makes the present approach suitable for preparing a wide range of diads. Moreover, the possible introduction of hydrophilic and/or hydrophobic substituents on the PBQ and/or TTF units makes the system potentially more useful, due to the capability of film formation. Such systems could become valuable for studies on controlling the degree of charge transfer in layered constructions.

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8. *Spectral data*. Compound **1**.[7] $^1$H NMR (200 MHz, $CDCl_3$): 6.74 (s, 2H), 3.97 (s, 2H), 3.67 (s, 2H), 2.41 (s, 6H), 1.80 (d, 2H, $J = 7.82$ Hz), 1.33 (d, 2H, $J = 8.14$ Hz). IR (KBr): 1649 cm$^{-1}$(C=O). Compound **2**. $^1$H NMR (200 MHz, $CDCl_3$): 6.95 (s, 1H), 3.98 (t, 2H, $J = 1.3$ Hz), 3.77 (d, 1H, $J = 1.41$), 3.69 (d, 1H, $J = 1.45$ Hz), 2.411 (s, 3H), 2.407 (s, 3H), 1.80 (br d, 2H, $J = 8.8$ Hz), 1.32 (br d, 2H, $J = 10$ Hz). HRMS: calculated for $C_{20}H_{15}{}^{35}ClO_2S_8$ 577.853; found, 577.849. Compound **3**. $^1$H NMR (200 MHz, $CDCl_3$): 4.02 (s, 2H), 3.81 (br s, 2H), 2.41 (s, 6H), 1.81 (br d, 2H, $J = 8.2$ Hz), 1.31 (br d, 2H, $J = 8$ Hz). HRMS: calculated for $C_{20}H_{14}{}^{35}Cl_2O_2S_8$ 611.814; found, 611.815.
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