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Donor–Acceptor Systems

A Rigid Neutral Molecule Involving TTF and TCNQ Moieties with Intrinsic Charge- and Electron-Transfer Properties that Depend on the Polarity of the Solvent**

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Since the discovery[1] of the first organic metal in 1973, much attention has been devoted to the investigation of TTF, its derivatives, and analogues as electron-donor components for many charge-transfer (CT) complexes and ion-radical salts.[2] A proposed model of a unimolecular rectifier[3] involving TTF and TCNQ moieties linked covalently through a rigid saturated spacer has stimulated intensive studies in this direction. A concept involving a number of donor and acceptor units incorporated in a single molecule was later developed[4] that would enable the properties related to molecular organic conductors to be controlled. So far, the realization of this notion has been limited to linking moderate acceptors to TTF derivatives and weak donors to TCNQ fragments,[5] while the incorporation of TTF and TCNQ moieties in a single molecule has proved to be an elusive goal.[6]

In 2003, Bryce and co-workers published[7] a synthesis of a TTF-σ-TCNQ molecule containing a nonconjugated flexible spacer. This compound is expected to exhibit a high degree of intramolecular CT in both solution and the solid state. However, while its IR data are consistent with a degree of charge transfer of about 0.85 in the solid state, only less than 1% biradicals were observed by EPR and UV/Vis/NIR spectroscopy. Also, the redox potentials shifted by only 20 mV with respect to those of the individual donor and acceptor components, thus indicating only a small degree of donor–acceptor interaction. Furthermore the authors' claim of a thermally induced electron transfer in their system, which was based on temperature-dependent EPR measurements, is somewhat misleading. Their calculated HOMO/LUMO gap (0.17–0.75 eV) and measured energy of the CT transition (0.75 eV, red edge 0.45 eV) are much higher than the energy

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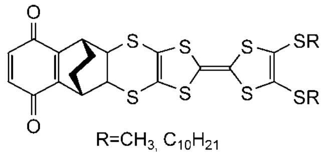
at room temperature (0.025 eV), and therefore, thermal ion-radical generation should be totally excluded. In our view, the discrepancies could stem from the flexible nature of the spacer used allowing several conformations, thus leading to difficulties in the interpretation of the observed results. Consequently, it would be more adequate to study TCNQ–TTF systems involving rigid spacers.

Recently[8] we reported the synthesis of compound **1** containing a TTF moiety covalently linked to *p*-benzoquinone through a rigid saturated spacer with a bent structure that allows an intrinsic through-space charge transfer. Herein, we describe the synthesis, electrochemistry, and spectroscopic results of the rigid TCNQ-σ-TTF-σ-TCNQ derivative **2**. The synthesis was based on the known TCNQ derivative **4** (Scheme 1),[9] which was prepared by a novel procedure, since the reported oxidation was not reproducible in our hands. Intermediate **5** exhibited CT properties as a result of intramolecular through-space interactions between the TCNQ and trithiocarbonate moieties. The combination of zinc dust and bromine in dry acetonitrile[10] was utilized for the self-coupling of 2-ethylthio-1,3-dithiolium salt **6** to obtain a reduced form of **2**. Oxidation of the TCNQ moieties with DDQ in boiling acetonitrile afforded the final product **2**, as a greenish brown powder.



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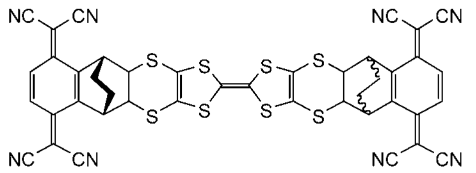

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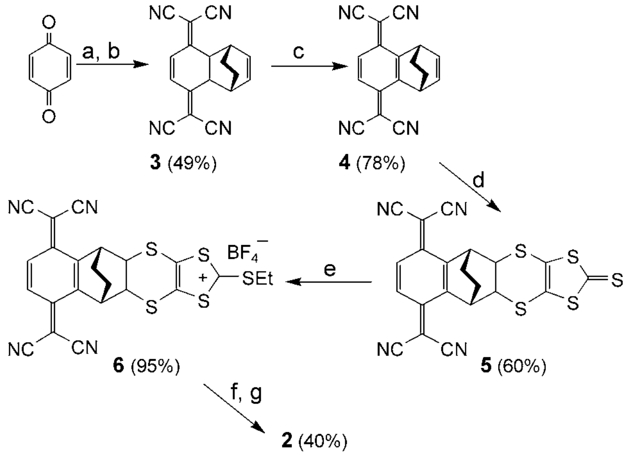

Scheme 1. Synthesis of TCNQ-σ-TTF-σ-TCNQ system **2**: a) PBQ (19 mmol), cyclohexadiene (60 mmol), EtOH (10 mL), b) $TiCl_4$/pyridine (80 mmol/100 mmol), malononitrile (55 mmol), CH_2Cl_2 (450 mL); c) **3** (1.8 mmol), MnO_2 (10–20 mmol), toluene (40 mL); d) **4** (1,4 mmol), 1,3-dithiole-2,4,5-trithione (1.4 mmol), thiophene (20 mL); e) **5** (0.8 mmol), $(EtO)_3CH/BF_3{\cdot}Et_2O$ (5 mmol/3 mmol), CH_2Cl_2 (40 mL); f) **6** (0.8 mmol), Zn/Br_2 (8 mmol/6 mmol), dry CH_3CN (20 mL); g) DDQ (3.5 mmol), dry CH_3CN (20 mL). PBQ = *para*-benzoquinone, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

The UV/Vis/NIR spectrum of **2** in CH_2Cl_2 (Figure 1) shows a broad absorption band centered at about 1330 nm ($\varepsilon \approx 750 \pm 40$ $cm^{-1}M^{-1}$). The extinction coefficient is concentration and temperature independent and the spectrum remains unchanged upon irradiation. The spectrum in toluene is essentially the same, with a similar minimum at about 750 nm. No radicals have been detected by EPR spectroscopy in either solvent. Therefore, the band at approximately 1330 nm can be attributed to an intramolecular CT transition from the TTF to the TCNQ moieties. In comparison, the cation radical and the dianion diradical of **2**[11] exhibit the expected absorption bands between 650 and 1050 nm, centered at about 850 nm, that are characteristic of these species.[12]

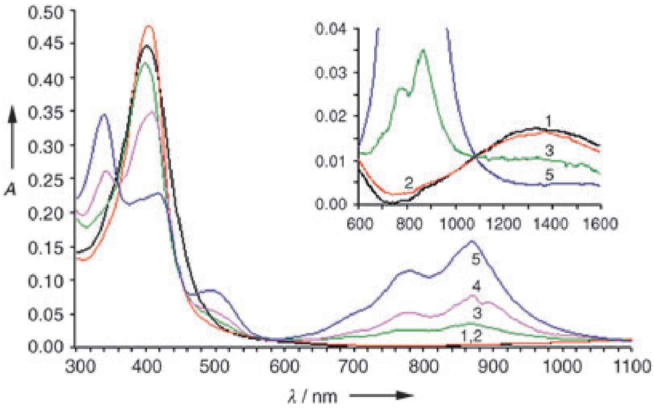

Figure 1. Absorption spectra of **2** in toluene (black, line 1), CH_2Cl_2 (red, line 2), CH_3CN (green, line 3), CH_2Cl_2 + DMF (magenta, line 4), and DMF (blue, line 5).

The cyclic voltammogram of **2** (Figure 2) in dichloromethane exhibits two 2e⁻ reversible reduction waves at $E^{1/2}_{\text{red1}} = 0.14$ V and $E^{1/2}_{\text{red2}} = -0.39$ V, which represent the consecutive reduction steps of the two identical TCNQ moieties

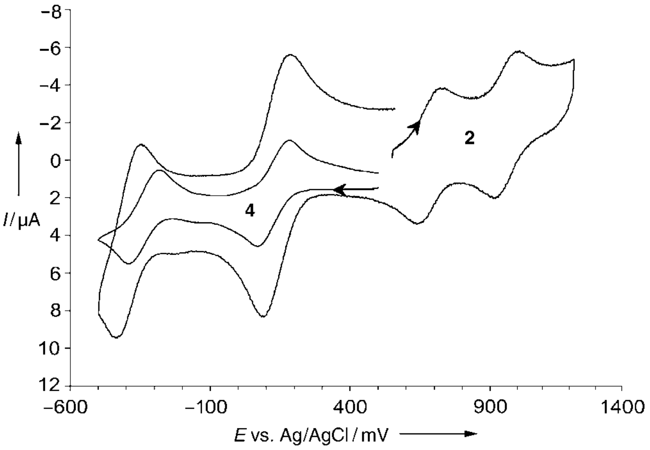

Figure 2. Cyclic voltammograms of **2** and **4** in CH_2Cl_2; 0.1 M $TBA^+PF_6^-$, on glassy carbon electrode versus Ag/AgCl; scan rate 100 mVs^{-1}. TBA = tetrabutylammonium.

(**4** shows (Figure 2) $E^{1/2}_{\text{red1}} = 0.10$ V, $E^{1/2}_{\text{red2}} = -0.34$ V), and two reversible 1 e^- oxidation waves at $E^{1/2}_{\text{ox1}} = 0.69$ V and $E^{1/2}_{\text{ox2}} = 0.96$ V, for the oxidation of the TTF fragment. As can be seen by comparing the oxidation of **2** with that of BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene; $E^{1/2}_{\text{ox1}} = 0.48$ V, $E^{1/2}_{\text{ox2}} = 0.90$ V), the two waves are shifted by about 200 and 60 mV, respectively. These shifts indicate a relatively high degree of CT between the TTF and one (or both) of the TCNQ fragments, thus causing the TTF moiety to be partially charged, and therefore, more difficult to oxidize. The positive shift of the first reduction potential of **2** with respect to that of **4**, which was observed under various experimental conditions, is not fully understood yet.

A significant degree of CT in solid **2** was also observed by IR spectroscopic analysis, with the band corresponding to the cyano groups shifted to a smaller wave number with respect to the similar band in **4** and **5**. On the basis of the well-studied and widely used correlation between the degree of CT and the stretching frequency of the CN groups in TCNQ,[13] we estimated the degree of CT in solid **2** to be of about 0.2. This estimation is based on the absorption bands of the CN groups in the IR spectra of **2** (2206 cm^{-1}), **5** (2213 cm^{-1}), and their corresponding lithium salts (2175 cm^{-1} for both). It is noteworthy that our result is consistent with the absence of signals in the EPR spectrum of solid **2**.

Thus, both in the solid state and relatively nonpolar solvents, derivative **2** exists as an intramolecular CT complex with a degree of CT about 0.2. However, **2** undergo gradual changes in its properties when the polarity of the is solvent increased. For example, the shape of the UV/Vis/NIR spectrum changes completely in DMF solution (Figure 1): the broad NIR absorption band disappears and a strong band centered at 850 nm appears. The spectrum becomes similar to the superimposed spectra of the cation radical and dianion biradical of **2**. The solution also shows a strong EPR signal with $g = 2.0055$, which is an average of the g-factors of the corresponding cation and anion radicals. According to a simulation we performed, the signal is split by four equivalent hydrogen atoms (Figure 3). Both ion radicals and CT complexes can be observed in less-polar solvents or mixtures of solvents (Figure 1).

In summary, a strategy has been developed for preparing a novel system involving TTF and TCNQ moieties covalently linked through rigid saturated spacers. We have shown the first example of a rigid unimolecular system of type TCNQ-σ-TTF-σ-TCNQ that is capable of both through-space intramolecular charge and electron transfer, depending on the polarity of the surroundings. The strong dependence of the ground-state electronic structure on the polarity of solvents, which is a unique and unprecedented case of solvatochromism, can be useful for imaging since the more polar zones will contain larger amounts of ion radicals. The observed polarizing effect in the solid state was not sufficiently strong to give rise to ion radicals, but subtle changes in molecular structure could bring about drastic changes in molecular packing that may lead to different degrees of charge transfer.

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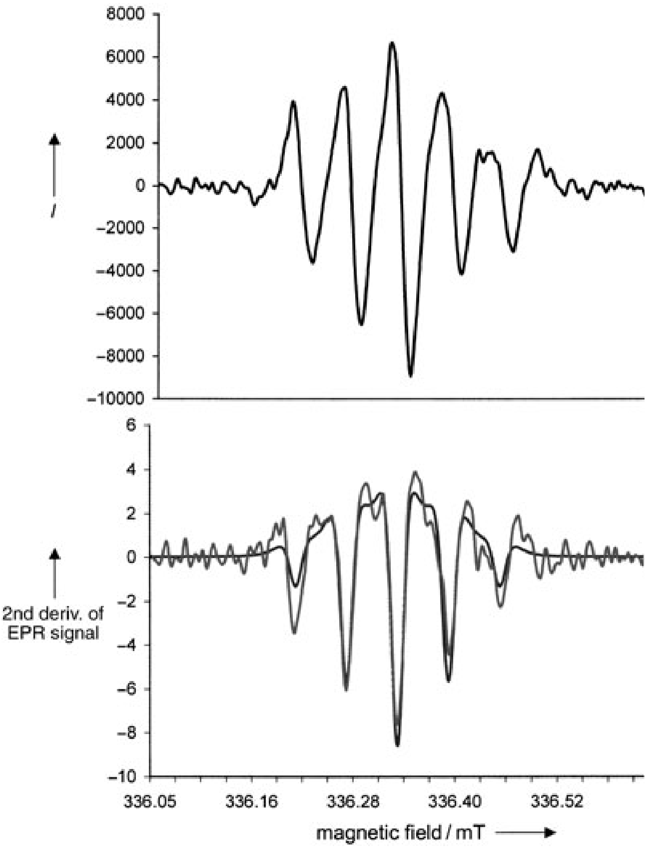

Figure 3. EPR signal of **2** in DMF (black: experimental; gray: simulated).

Keywords: charge transfer · donor–acceptor systems · electron transfer · solvent effects · tetrathiafulvalenes

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