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Coupling Tetracyanoquinodimethane to Tetrathiafulvalene: A Fused TCNQ–TTF–TCNQ Triad**

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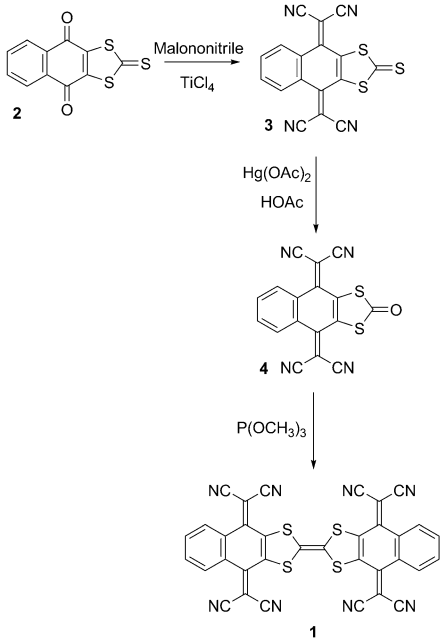
Dedicated to Professor Fred Wudl on the occasion of his 70th birthday

The first marriage of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) took place in 1973, when an intermolecular 1:1 charge-transfer complex was formed, which led to the discovery of the first organic metal.[1] One year later, Aviram and Ratner theoretically predicted a rectifying behavior for a covalently coupled TTF–σ–TCNQ dyad.[2] Since then numerous studies devoted to synthesizing covalent TTF–linker–TCNQ dyads have been undertaken, motivated by potential applications in molecular electronics and optoelectronics.[3–7] However, the task of covalently coupling a strong π-electron donor to a strong π-electron acceptor is extremely difficult.[6,8] Many examples of TTF moieties attached to moderate acceptors have been published.[6,9] Among them, several TTF–quinone dyads and triads have been identified as potential precursors for preparing fused TTF–TCNQ derivatives, but attempts to convert the quinone moiety to the corresponding TCNQ derivative have been in general unsuccessful.[10,11] One of these examples, a *p*-benzoquinone–TTF–*p*-benzoquinone (Q–TTF–Q) fused triad, permitted the study of intramolecular electron transfer (IET) between donor and acceptor and also between acceptor moieties in the mixed-valence compound, thus demonstrating the capability of TTF to behave as a bridge that allows electron transfer.[12] Recently, a small number of well-characterized TTF–linker–TCNQ dyads have been reported,[13–16] and in all cases intramolecular charge transfer was found. Nonetheless, to date, a TCNQ derivative has never been compactly fused to the TTF core; the closest approach was the attempted synthesis reported by Hudhomme and co-workers.[11] Herein we report the synthesis of the first fused TCNQ–TTF–TCNQ triad, compound **1** (Scheme 1), and the study of the IET processes that take place in the neutral compound **1** as well as in the corresponding mixed-valence derivative $\mathbf{1}^{-\cdot}$.



Scheme 1. Synthesis of the TCNQ–TTF–TCNQ triad **1** via key intermediate **3**.

In our synthetic approach, the key intermediate is the TCNQ thione derivative **3** with an extended π-electron system, which was prepared in 42% yield from the reaction of the *p*-benzoquinone counterpart **2**[10] with malononitrile and titanium tetrachloride in dry chloroform. After quantitative conversion of **3** to the 2-oxo-1,3-dithiole compound **4**, the homocoupling of **4** to prepare the target compound **1** was achieved in 69% yield by treatment with freshly distilled trimethylphosphite in toluene. Owing to its poor solubility, especially in nonpolar solvents, the characterization of compound **1** was performed by IR spectroscopy and mass spectrometry as well as elemental analysis. The molecular structure was unambiguously confirmed by single-crystal X-ray analysis. Green single crystals of **1** with rodlike rectangular shape were grown by slow diffusion of ethanol into a

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solution of **1** in dimethylformamide. Compound **1** crystallizes in the monoclinic system (space group $P21/c$) and its structure consists of one crystallographically independent molecule. The TTF core of the molecule is not planar but shows a nonsymmetrically bent boat conformation with angles of 24.5° and 14.7°. Furthermore, as observed in other donor–acceptor systems,[17–21] the tetracyanobenzoquinone (ext-TCNQ) subunits with extended π-electron systems adopt a butterfly-like conformation, with twist angles of 33.1° and 34.3°, to minimize the steric hindrance between the cyano groups and the adjacent atoms in the *peri* positions. Similar butterfly-like bending is observed in the crystal structure of the precursor **4** (see the Supporting Information). Moreover, the conformation of the molecules in vacuum at the minimum energy found with DFT B3LYP/6-31G(d) calculations is very similar to that in the crystal. Such a heavily bent conformation of the molecule prevents the formation of π stacks in the crystal. Instead, the molecules pack by forming dimers; the distorted TTF moieties face each other with an interplanar distance of 3.595 Å but are transposed in both longitudinal and transversal molecular directions. The molecules form chains in the *ac* plane facing alternatively up and down and with the malononitrile groups placed at short distances ($d_{CN\cdots NC} = 3.55$ and 3.56 Å, Figure 1).

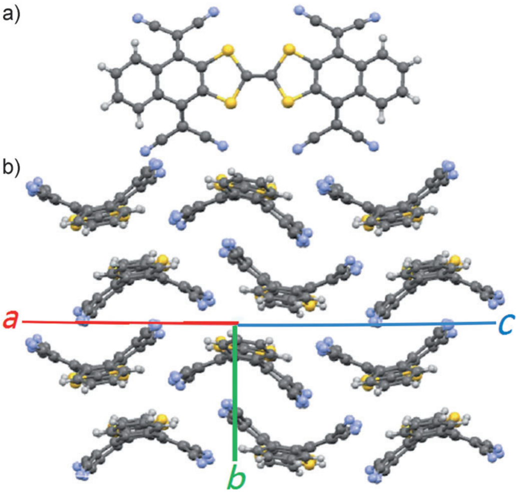


Figure 1. a) Molecular structure of **1**. b) View of the crystal structure of compound **1**.

The IR spectrum of the fused triad **1** in the solid state does not show any sign of a charge transfer between the TTF and ext-TCNQ subunits since the band corresponding to the cyano groups, which is known to be very sensitive to the electronic charge, appears at the same frequency as in the spectra of the precursors **3** and **4**.

The optical and electronic characterization of the neutral derivative **1** and its reduced species was carried out by cyclic voltammetry (CV) as well as UV/Vis/NIR and EPR spectroscopy using the DMSO/benzonitrile (45:55) mixture as solvent. The choice of this solvent was a compromise between solubility and polarity of the media. The latter parameter is very important for performing a detailed EPR spectroscopy study. In the cyclic voltammogram of triad **1**, two very close reduction processes were observed at $E_{1/2}(1) = -0.20$ V and $E_{1/2}(2) = -0.31$ V (vs. $[(C_5H_5)_2Fe]^+/[(C_5H_5)_2Fe]$ (Fc^+/Fc), Figure 2), and on going to lower potentials no additional reduction processes were observed. These electrochemically reversible processes correspond to two consecutive two-electron reductions of each of the two TCNQ moieties, indicating that there is an electronic interaction between the two TCNQ moieties through the TTF bridge. The precursor compounds **3** and **4** also show only one two-electron reduction process, in agreement with the cyclic voltammograms reported for other TCNQ derivatives with extended π-electron systems.[17–21] In the oxidation region of the cyclic voltammogram of **1** only one irreversible peak is observed at $E_p = +0.75$ V (vs. Fc^+/Fc), indicating that the oxidized species is not stable. In accordance with this finding, when compound **1** is oxidized either chemically or electrochemically, no signal is observed in the EPR spectrum. This behavior can be attributed to the bending of the TTF bridge and has also been observed in other bent TTF derivatives.[22,23]

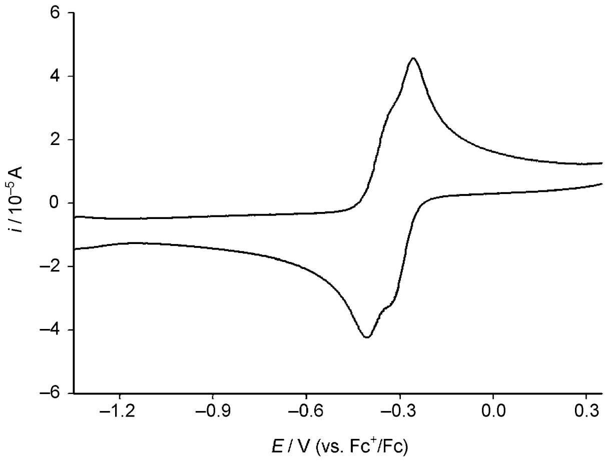


Figure 2. Cyclic voltammogram of compound **1** in DMSO/benzonitrile (45:55) and 0.1 M $[NnBu_4]PF_6$ as supporting electrolyte.

The UV/Vis/NIR electronic spectrum of compound **1** shows the expected bands of the TCNQ and TTF subunits along with a broad absorption around 800 nm ($\varepsilon = 890\,\text{M}^{-1}\,\text{cm}^{-1}$, Figure 3). The latter band has been assigned to an optically induced charge-transfer (CT) process between the TTF core and the TCNQ moieties. Its intramolecular nature was confirmed by dilution experiments, which showed that the intensity of the corresponding absorption follows the Beer–Lambert law. The estimated frontier orbitals, determined from CV and UV/Vis/NIR spectroscopy data,[24] give a HOMO energy of −5.90 eV while the LUMO is at −4.60 eV. These values are in agreement with those obtained by DFT calculations. According to theoretical calculations, the HOMO is located on the TTF core, whereas the LUMO is divided into two different orbitals (LUMO and LUMO + 1) very close in energy and each located on a different TCNQ

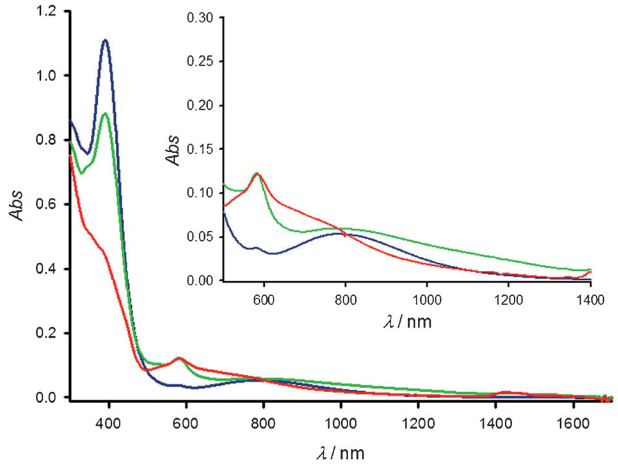
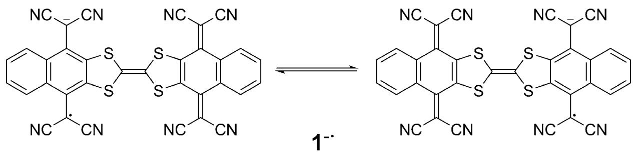


Figure 3. UV/Vis/NIR spectra of compound **1** in its neutral state (blue) and at different reduction stages (green and red). DMSO/benzonitrile (45:55), $c=5\times10^{-4}$ M, in presence of 0.15 M [N*n*Bu$_4$]PF$_6$.



Scheme 2. Thermally activated IET process in **1**$^{-\bullet}$.

moiety owing to the broken symmetry of the molecule (see the Supporting Information).

At the first stages of the electrochemical reduction of **1** (at −0.3 V, $c=5\times10^{-4}$ M, DMSO/benzonitrile (45:55), 0.15 M [N*n*Bu$_4$]PF$_6$) its electronic spectrum shows a decreased intensity of the band at 389 nm and the appearance of a new narrow band at 592 nm, which can be ascribed to the formation of TCNQ radical anions. Such radical anions are generated, as is the mixed valence species **1**$^{-\bullet}$, by the comproportionation of the doubly reduced TCNQ subunits and the large amounts of neutral TCNQ subunits present in the solution at the first stages of the reduction as confirmed by EPR spectroscopy (see below). A similar phenomenon has been observed in other related compounds.[18,20] Along with the changes described above, a new band appears at lower energy as a broad shoulder of the CT band of **1** (green spectrum in Figure 3). The deconvolution of the spectrum shows that this new band appears at 9246 cm^{-1} (1080 nm) with a full width at half maximum of 3193 cm^{-1}. When the reduction process continues further, both the new band and the initial CT band disappear (red spectrum in Figure 3), because the triad **1** and its mixed-valence derivative **1**$^{-\bullet}$ disappear at the expense of the formation of more highly reduced species. Therefore, the band at 1080 nm has been assigned to an intervalence charge-transfer (IVCT) band of the mixed-valence species **1**$^{-\bullet}$, in which an IET from the reduced TCNQ moiety to the nonreduced one occurs as observed similarly in the one-electron-reduced Q–TTF–Q triad.[12] When the Hush theory[25] is applied to the IVCT band of **1**$^{-\bullet}$, a value of 581 cm^{-1} for the electronic coupling parameter H_{ab} and a value of 0.063 for the delocalization coefficient α (considering the distance $r_{\text{ox-red}}=3.125$ Å) are found. By analyzing the form of the band,[26] the Γ parameter, which relates the width of the band to a theoretical one, shows a value of 0.309, which is characteristic of a weakly coupled IVCT process. Therefore, all results support the conclusion that the mixed-valence compound **1**$^{-\bullet}$ belongs to class II in the Robin and Day classification with a weak or moderate interaction between the two redox centers (Scheme 2).[27]

Spectroelectrochemical EPR spectroscopy studies revealed an intense EPR signal for the last reduction stages of **1**. The same results were obtained with the model compound **3**. Under such conditions the EPR spectrum of compound **3**$^{-\bullet}$ is characterized by 21 lines, which result from the coupling of the unpaired electron with four equivalent N and H atoms with a_N (4N) = 0.96 G, a_H (4H) = 0.39 G. A very similar spectrum (21 lines with a_N (4N) = 0.93 G, a_H (4H) = 0.53 G) was observed when compound **1** was extensively reduced. At such reduction stages the dominant species in equilibrium should be the EPR-silent tetranionic species along with the EPR-active three-electron-reduced one. Since the EPR spectrum coincides with that of compound **3**$^{-\bullet}$, which has only one radical center, it can be assumed that the electrons on the two extremes of the triad are localized on the time scale of EPR spectroscopy (see the Supporting Information).

A different spectrum is nevertheless observed for the first reduction stages of **1** (Figure 4), where the mixed-valence species **1**$^{-\bullet}$ is the main EPR-active component present in the solution. We have studied the thermally activated IET process of **1**$^{-\bullet}$ (Scheme 2) by variable-temperature EPR spectroscopy (VT-EPR). The EPR spectra of **1**$^{-\bullet}$ were recorded from 280 to 340 K. The spectrum of **1**$^{-\bullet}$ at 280 K (Figure 4) shows 21 lines, which result from the coupling of the odd electron with four

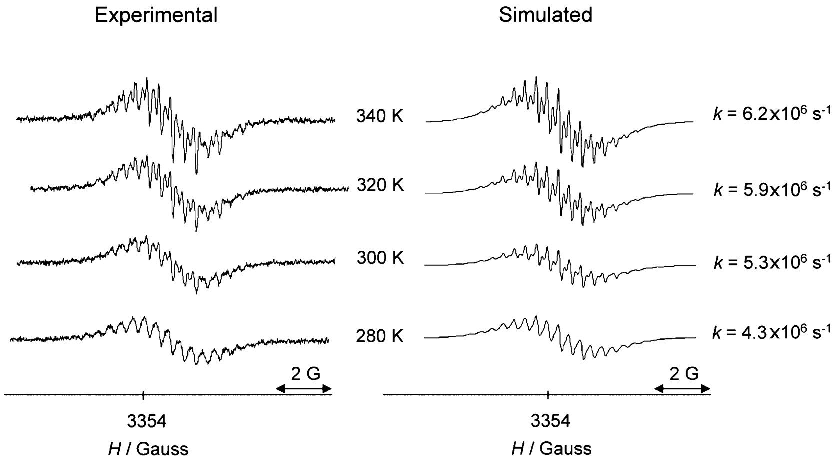


Figure 4. Experimental (left) and simulated (right) EPR spectra of the mixed valence species **1**$^{-\bullet}$ at different temperatures in DMSO/benzonitrile (45:55) and 0.15 M [N*n*Bu$_4$]PF$_6$.

equivalent N and H atoms of one benzo-TCNQ moiety with a_N (4 N) = 0.93 G, a_H (4 H) = 0.53 G. This spectrum is essentially the same as that observed at the latter reduction stages (see the Supporting Information), but it is superimposed on a broad line. This specific feature can be considered as the signature of a dynamic process on the time scale of EPR spectroscopy. At this temperature the IET process between the two benzo-TCNQ moieties starts to be promoted at a very slow rate, so that the odd electron is not completely localized on one particular TCNQ subunit on the time scale of EPR spectroscopy, although it is close to that limit. As the temperature is raised, the lines are split and the new lines start to increase in intensity as a consequence of a faster IET process, which implies the coupling of the unpaired electron with the 8 N and 8 H atoms from both benzo-TCNQ moieties, with half the value of the coupling constants. Then, a 41-line spectrum starts to be defined. Unfortunately, it is not possible to follow the IET process at temperatures higher than 340 K, because above this temperature a quick over-reduction takes place, promoted by the DMSO (see the Supporting Information).

The dynamics of the intramolecular exchange process in $\mathbf{1}^{-\bullet}$ was theoretically simulated,[28] and first-order rate constants were extracted by fitting the experimental spectra. Kinetic data leads to a linear Arrhenius plot over the 280–340 K temperature range, which gives the activation parameters $E_{act} = 1.13$ kcal mol^{-1} and $\log A = 7.53$ ($\Delta G^{\neq}_{300\,K} =$ 8.3 kcal mol^{-1}, $\Delta H^{\neq} = 0.52$ kcal mol^{-1}, and $\Delta S^{\neq} = -25.8$ e.u.). The obtained rate constants show that the IET process is very slow (4.3×10^6–6.2×10^6 s^{-1}) and is in fact at the very low electron transfer limit of the time scale of EPR spectroscopy. By contrast, the reported Q–TTF–Q parent molecule, with the same TTF bridge but with two *p*-benzoquinone groups as redox centers,[12] exhibited IET rate constants in the range of 2.9×10^7–4.3×10^8 s^{-1}. In accordance, the $\Delta G^{\neq}_{300\,K}$ value obtained for the compound Q–TTF–Q$^{\bullet-}$ (6.4 kcal mol^{-1}) is lower than that for **1**. As benzo-TCNQ moieties are much stronger electron acceptors than quinone units, the odd electron is stabilized and therefore tends to spend more time on the TCNQ unit, making the intramolecular electron-transfer process more difficult. This trend has been observed in other kinds of organic compounds with the same bridge (polyacene) but with different organic redox centers, such as quinones and imides.[29] Another added reason for the different rate constants can be the fact that in triad **1** the TTF bridge is bent whereas the Q–TTF–Q triad is planar. Indeed, the nature of the bridge has a great influence on the electron-transfer rate, as it can be clearly elucidated when the triad **1** is compared to a fused twin TCNQ molecule with a benzene ring as a bridge.[30] In that case, it was demonstrated by EPR spectroscopy of the corresponding radical anion that the odd electron is completely delocalized over the whole molecule.

To exclude the possibility that the electron-transfer process in $\mathbf{1}^{-\bullet}$ has an intermolecular nature, we have added aliquots of the neutral **1** to the solution containing the mixed-valence species $\mathbf{1}^{-\bullet}$, and no changes in the lines in the EPR spectrum were observed. Only a decrease in the signal intensity owing to the dilution was observed (see the Supporting Information). By contrast, when the neutral compound **1** was added to the highly reduced species of **1**, a progressive evolution of the EPR spectrum towards that exhibited by the mixed-valence species $\mathbf{1}^{-\bullet}$ was observed, caused by comproportionation of the two species (Figure 5). On the other hand, the VT-EPR spectroscopy study of the electrochemically reduced model compound **3**, which has only one TCNQ moiety, did not show any change in the EPR spectra (see the Supporting Information). These experiments clearly demonstrate the existence of the IET process in $\mathbf{1}^{-\bullet}$ and verify the reversibility of the reduction process. It has thus been conclusively shown that mixed-valence compound $\mathbf{1}^{-\bullet}$ experiences an IET process in which the TTF acts as a bridge; this phenomenon is also evidenced by the presence of an IVCT band in the UV/Vis/NIR spectrum.

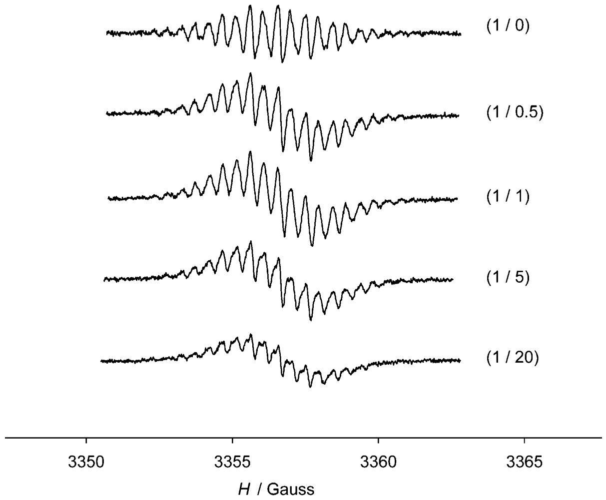


Figure 5. EPR spectra of mixtures of highly reduced species of **1** with *n* equivalents of the corresponding neutral compound **1** (from top to bottom *n* = 0, 0.5, 1, 5, and 20) in DMSO/benzonitrile (45:55) at 300 K.

In conclusion, we have synthesized the first fused TCNQ–TTF–TCNQ triad, a molecule that has been pursued for many years. The crystal structure of this compound reveals strong bending in both the TTF bridge and the benzo-TCNQ moieties, which prevents a good packing for an intermolecular charge transfer in the solid state. The study of the electronic properties in the neutral compound as well as in the reduced species shows that there is a charge-transfer absorption in solution. Interestingly, the UV/Vis/NIR and VT-EPR spectroscopy studies of the mixed-valence compound $\mathbf{1}^{-\bullet}$, in which only one of the acceptor moieties is charged, indicate that this is a class II mixed-valence species in which electrons are moving from one acceptor moiety to the other through the donor TTF bridge.

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