Synthesis of a novel rigid tetrathiafulvalene-σ-*p*-benzoquinone diad (TTF-σ-Q) with inherent structural configuration suitable for intramolecular charge-transfer

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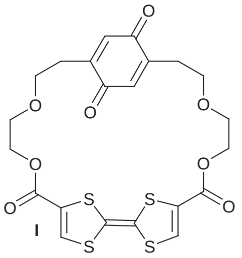
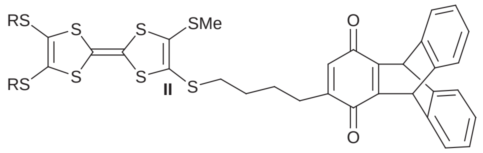
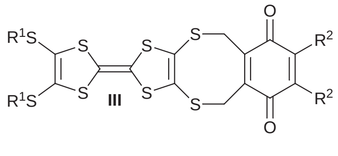
The synthesis of a novel D–A diad, involving a TTF moiety covalently linked to *p*-benzoquinone *via* a rigid spacer, shows a bent structure in the solid state which provides intrinsic through-space intramolecular charge-transfer interaction.

Since the discovery[1] of the first organic metal in 1973, much attention has been devoted to the investigation of TTF, its derivatives and analogs, as electron donor components of many charge transfer (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 'organic metals', the concept of D–A–D and A–D–A triads was developed,[3] in which the D and A fragments are integral parts of a single molecule. Several D–TCNQ–D,[3] D–TCNAQ–D[4] and A–TTF–A[5] systems have been studied. In this context, TTF-σ-TCNQ systems have obvious appeal,[6] but have proved to be an elusive goal.[7,8] However, systems involving TTF-π-TCNQ are known.[9]

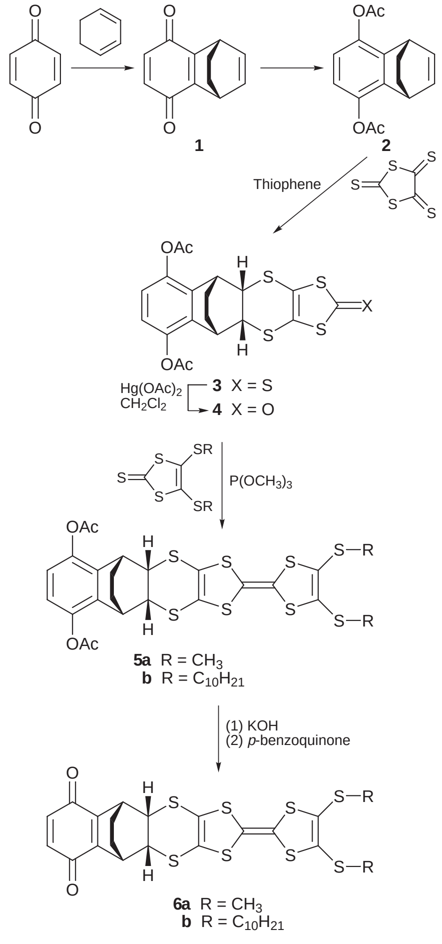






'TTF-σ-quinone' systems are known both in cyclic (**I**)[10] and non-cyclic (**II**) derivatives.[11] Recently, rigid TTF-σ-quinone derivatives (**III**) (containing two linking σ bonds) were synthesized.[12] In none of these systems, was an intramolecular CT band discernible in the UV–VIS spectrum, for different reasons.[8] Evidently, there is a need to design a molecule in which both the distance and orientation between the TTF and the quinone moieties are fixed, in order to achieve a CT interaction.

We now present the synthesis (Scheme 1), electrochemistry, X-ray structure and intramolecular charge-transfer properties of new rigid TTF-σ-Q (**6a**,**b**) molecules, involving TTF moieties chemically linked to *p*-benzoquinone by nonconjugated rigid cyclic rings, *via* two σ linkers. This type of molecule could be a potential precursor for TTF-σ-TCNQ systems. The unique bent structure of **6a** in the solid state (Fig. 1), in which the plane of the D moiety lies above the plane of the A moiety, with essentially eclipsed overlap, affords the first example of a non-cyclic system with built-in through-space σ-type interaction between the π-systems of the D and A components.[13] The synthesis of **6** involves two cycloaddition reactions[14] to afford **3** as the sole *R,S,R,S* stereoisomer in which the 1,3-dithiole-2-thione moiety is located opposite to the aryl ring, probably due to steric hindrance in the *S,R,R,S* isomer. The hydrogens on the carbons adjacent to the sulfur atoms are orientated in the same spatial direction with respect to the bent planes of the molecule. This configuration was confirmed by X-ray structure determination for the 'oxo' derivative **4**, which was generated from **3** (2 mmol). The latter reaction and the following ones



Scheme 1

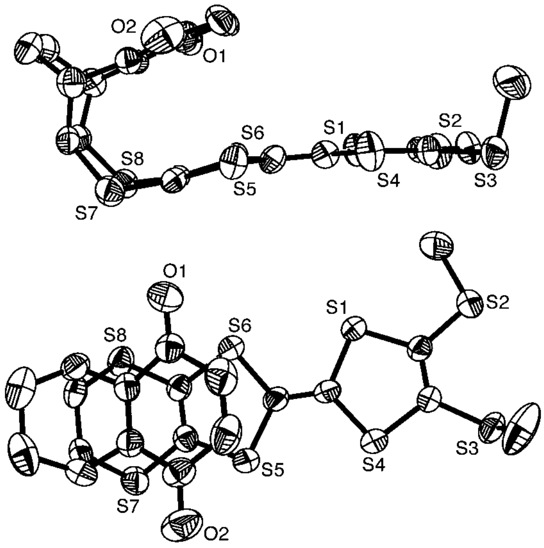


Fig. 1 ORTEP drawing of **6a** at the 50% probability level. Hydrogen atoms and the numbering of the carbon atoms have been omitted for clarity. Side-view of the molecule (above) and view in the plane of the TTF moiety (below).

which are described in Scheme 1 were performed according to known procedures.[15] Products **6a** and **6b** were separated from their reaction mixtures by silica gel column chromatography (CH_2Cl_2); both had a deep green color.

The UV–VIS spectrum of **6a** shows a broad absorption band in the 550–950 nm region, centered at *ca.* 685 nm ($\varepsilon \sim 310$), which points to a weak charge transfer interaction. The spectra were recorded at various concentrations of **6a**, and the extinction coefficient of this low energy band varied in accordance with Beer–Lambert law. Therefore, this band is assigned to an intramolecular charge-transfer interaction.

The cyclic voltammogram[16] of **6a** shows two one-electron reversible oxidation waves at $E^1{}_{1/2} = 0.55$ and $E^2{}_{1/2} = 0.825$ V, characteristic for tetraalkylthio-TTF derivatives,[2a] and two reversible reduction waves, one at -0.525 V (one-electron) and a smaller one at -1.20 V, for the reduction of the disubstituted *p*-benzoquinone moiety. (At slower scan rates a trace of an ill-defined 'third' reversible couple is observed in between the above two reduction waves, which is related to a product derived from the decomposition of the dianion.) Product **6b** affords a similar cyclic voltammogram pattern, with similar redox potentials. It is generally expected that a weak CT interaction will not affect the redox potentials pattern given by the relatively insensitive cyclic voltammetry technique.

Deep green needles of **6a**[17] were crystallized from CH_2Cl_2 by slow evaporation of the solvent. The X-ray structure (Fig. 1) verifies the bent configuration of the molecule and shows that the acceptor *p*-benzoquinone moiety is spatially located above the donor dimethylthio-TTF unit. Indeed, the intramolecular distance between the face-to-face planes of the donor and acceptor moieties is 3.29 Å, which may be compared to the plane-to-plane distances between donor and acceptor molecules in crystal packings of mixed-stacks intermolecular charge transfer of HMTSF–TCNQ[18] and ET–TCNQ[19] complexes. The apparently low degree of CT in the ground state of **6** was also confirmed by EPR measurements, which after sunlight irradiation gave rise to a photoinduced intramolecular electron transfer process, resulting in the appearance of broad signals (yet to be analyzed), with two '*g*' factors ($g_1 = 2.0050$; $g_2 = 2.0064$).

Compounds **6a** and **6b** are among the first examples of systems with inherent intramolecular through space charge transfer properties. Their synthesis opens up a way to obtain new compounds with controllable overlap between the donor and acceptor units, as well as controllable degree of charge transfer, *e.g.* by changing the strength of the acceptor moiety. Also, it is noteworthy that **6b** and its derivatives could be potential candidates for constructing Langmuir–Blodgett films and investigating their physical properties.

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17 *Crystal data* for **6a**: A shiny deep green needle (0.4 × 0.15 × 0.15 mm) of $C_{20}H_{16}O_2S_8$ was used for X-ray intensity data measurements on a standard Bruker SMART CCD 1000™ diffractometer [λ(Mo-Kα) = 0.711069 Å, graphite monochromator, a scan width of 0.3° in ω and exposure time of 10 s frame^{-1}, detector–crystal distance = 4.95 cm]. A total of 1080 frames were collected and integrated with the Bruker Saint software package using a wide-frame integration algorithm. The crystal is monoclinic, space group $P2_1$, at 298 K, a = 8.486(1), b = 8.770(1), c = 15.430(3) Å, β = 98.740(3)°, Z = 2, V = 1135.0(3) Å^3, F(000) = 560, 7221 reflections were collected (2θ < 56.82°), of which 4931 reflections were independent ($R_{\rm int}$ = 3.18%) and 2823 with $F_o > 4\sigma(F_o)$. Data were corrected for absorption using SADABS program. The structure was solved by direct methods and refined by least-squares in full-matrix approximation: 273 parameters, $R1$ = 4.04%, $wR2$ = 6.20%, GOF = 0.796. Bruker SHELX Software package was used for all calculations and drawings. CCDC 182/1252. See http://www.rsc.org./suppdata/cc/1999/1125 for crystallographic data in .cif format.

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