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The charge-transfer complexation of tetrathiafulvalene with paraquat and its oligomeric derivatives

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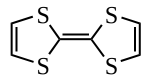
Abstract—The charge-transfer complexation of TTF with paraquat and its oligomeric derivatives are described.

The reversible, redox-controlled complexation of tetrathiafulvalene (TTF, **1**) and its derivatives with the electron deficient cyclophane cyclobis(paraquat-*p*-phenylene) **2** is a burgeoning field of study.[1] Indeed, recent reports have shown complexes of this type have found application as novel molecular electronics devices.[2] Although the intramolecular complexation of tethered TTF–paraquat systems have been described,[3] the complexation of **1** with **3** and its conformationally unrestrained oligomeric derivatives **4**[†] and **5**[‡] have not been reported.[4] This void in the literature is surprising, as compounds **1** and **3**–**5** have well-matched ionisation potentials and electron affinities, respectively, and therefore should readily give rise to charge-transfer (C-T) complexes with interesting electrical conductivity properties. Moreover, the electron deficient oligomeric systems **4** and **5** are potentially capable of encapsulating the electron-rich TTF unit, thereby affording novel redox controllable structures. Here, we report for the first time the formation and characterisation of C-T complexes of **1** with **3** and its oligomeric derivatives **4** and **5**, in both solution and the solid-state, using ^{1}H NMR, UV–vis, EPR, CV and X-ray crystallography.



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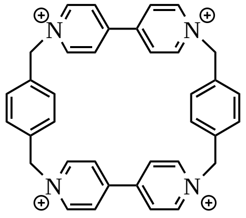

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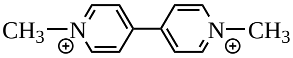

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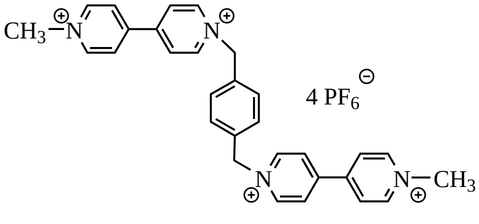

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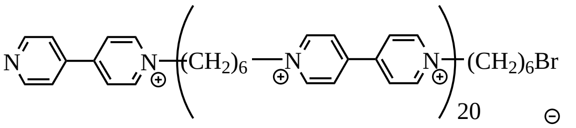

5 41 $PF_6^{\ominus}$

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[†] *Selected data for compound 4*: Compound **4** (bromide salt) was prepared according to the method reported by Neta, P.; Richoux, M.-C.; Harriman, A. R. *J. Chem. Soc., Faraday Trans. 2* **1995**, *81*, 1427–1443. The **4**·Br$^-$ salt was converted to the **4**·PF_6^- salt by ion-exchange using NH_4PF_6 in de-ionised water. Mp >250°C; ^{1}H NMR (CD_3CN): 8.94 (d, 4H), 8.81 (d, 4H), 8.47 (m, 8H), 7.55 (s, 4H), 5.84 (s, 4H), 4.48 (s, 6H).

[‡] *Selected data for compound 5*: Compound **5** (bromide salt) was prepared according to the method reported by Meier, L. P.; Heule, M.; Caseri, W. R.; Shelden, R. A.; Suter, U. W.; Wenz, G.; Keller, B. *Macromolecules* **1996**, *29*, 718–723. The Br$^-$ salt was converted to the PF_6^- by ion-exchange using NH_4PF_6 in de-ionised water. Mp 234–236°C; ^{1}H NMR (CD_3CN): 8.90 (d, 4H), 8.38 (d, 4H), 4.60 (t, 4H), 2.1–1.9 (m, 8H).

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Solution phase complexation of **1** with **3**–**5** was confirmed using UV–vis spectroscopy. Mixing **1** with **3**–**5** in equimolar proportions in CH_3CN resulted in the immediate formation of an emerald green-coloured solution as a result of the appearance of a C-T band in the visible region of their spectra centred at around 688 nm (for **1**·**3**), 741 nm (for **1**·**4**) and 775 (weak) nm (for **1**·**5**). The aforementioned C-T absorption values are considerably lower than the observed value for **1**·**2** (854 nm in CH_3CN), and are in accordance with UV–vis data for intramolecular C-T absorptions associated with tethered viologen–TTF systems.[3] The ^{1}H NMR spectra of complexes **1**·**3**, **1**·**4** and **1**·**5** revealed an absence of signals arising from the TTF protons, indicating that the paramagnetic $\mathbf{1}^{+\bullet}$ species may be implicated in the C-T complexation. However, when ^{1}H NMR spectra were recorded on a freshly prepared mixture of **1** and **3** (2:1 stoichiometry), the TTF protons are initially clearly visible, but over the course of several days gradually broaden and disappear. The signals for the protons of the bipyridinium units and their associated alkyl- or aryl- chains, are essentially identical to the non-complexed spectra of derivatives **3**, **4** and **5**, indicating that the paramagnetic radical cation states of the viologen systems are not implicated in the complexation process.[5] This is markedly different to the NMR studies performed on the complex of **1**·**2**, where the protons of **1** and **2** although shifted, are clearly visible.[1e] The presence of the $\mathbf{1}^{+\bullet}$ species in **1**·**3** has been confirmed by solution EPR measurements, which gave rise to a singlet in its spectrum indicating the components of the complex are rotationally and vibrationally mobile in the EPR timescale (Fig. 1). No other signals were observed in the EPR, which corroborates the indication from the NMR data that $\mathbf{3}^{+\bullet}$ is not implicated in the C-T process.

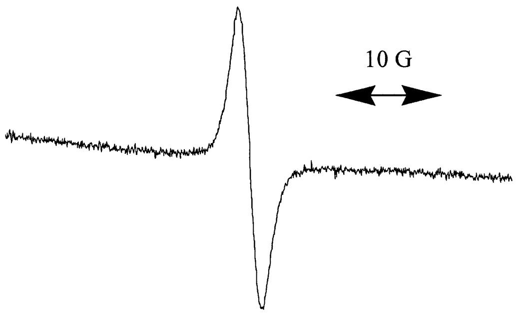

Figure 1. EPR of (**1**)·(**3**) in CH_2Cl_2.

The solution electrochemistry of complexes **1**·**3**, **1**·**4** and **1**·**5** have been studied using cyclic voltammetry (CV) in CH_3CN, and in all cases led to a negative change (−15 to −30 mV) in the half wave potentials for the formation of the $\mathbf{1}^{+\bullet}$ and the $\mathbf{1}^{2+}$ states as compared to that of free TTF in the same media. These data suggest that the generation of the $\mathbf{1}^{+\bullet}$ and $\mathbf{1}^{2+}$ is made easier when complexed with **3**–**5**.[6] This is markedly different to the +70 and +20 mV positive shifts of the half wave potentials of **1** observed in the **1**·**2**[1c] and the tethered TTF–paraquat systems,[3] respectively, indicating that generation of the TTF radical cation and dicationic states in these systems are more difficult, presumably due to Coulombic repulsion between $\mathbf{1}^{+\bullet}$ or $\mathbf{1}^{2+}$ and the tetracationic cyclophane **2**. The CV data for systems **1**·**4** and **1**·**5** suggest there is little Coulombic repulsion between the oxidised states of the TTF and the paraquat derivatives, thereby arguing against encapsulation of the TTF unit and suggesting the non complexed paraquat units of **4** or **5** are not in sufficiently close proximity to evoke Coulombic repulsion. When a 10-fold excess of **4** or **5** was added to a 10^{-5} M solution of **1** in CH_3CN, apart from the negative shifts in the half wave potentials of the TTF described earlier, there were no observable changes in the peak-to-peak current for both the TTF oxidation waves, thereby casting further doubt over encapsulation of **1** by the oligomeric derivatives **4** and **5**.[7] This is again in stark contrast to the CV data for inclusion complex **1**·**2**, which revealed a one-third decrease in the peak-to-peak current associated with the formation of $\mathbf{1}^{+\bullet}$.[1c]

Slow crystallisation from a concentrated CH_3CN solution of a 1:1 mixture of **1** and **3** led to the formation of X-ray quality crystals, for which X-ray diffraction studies afforded the crystal structure shown in Fig. 2.[§] The molecular structure of this complex clearly shows a 2(**1**):(**3**) stoichiometry, in which the cations and anions form a mixed stack arranged in alternating DAD-DAD fashion (Fig. 2a). The stacks of the anions and cations are tilted in opposite directions, and the normals to the paraquat planes in neighbouring stacks are inclined at 39° relative to each other, thereby adopting a herringbone motif similar to that observed in the TTF/TCNQ complex (Fig. 2b).[8] The approximate interplanar distance for the TTF moieties is 3.54 Å (D-D), which is mid-way between the value observed for neutral TTF (3.62 Å) and for the stacked TTF units in its complex with TCNQ (3.47 Å). However, this interplanar spacing is much smaller than the 4.30 Å observed for TTFs in their complex with bis(maleonitrile-1,2-dithiolato)nickelate(II), which adopts a similar architecture to 2(**1**)·(**3**) in its solid state.[9] The room temperature conductivity of a single crystal of the complex (measured using the 4 probe DC technique) was found to be 2.1×10^{-8} S cm^{-1}. This value is in accordance with other mixed stack C-T complexes.[10]

[§] *Selected data for 2(**1**)·(**3**)*: mp 192°C dec. calcd for $C_{22}H_{22}F_{12}N_2P_2S_8$: C, 32.58; H, 2.51; N, 3.17. Found: C, 32.62; H, 2.52; N, 3.00%. *Crystal data for 2(**1**)·(**3**)*: $C_{22}H_{22}F_{12}N_2P_2S_8$, $M=442.43$; monoclinic, $a=8.1817(15)$, $b=23.560(3)$, $c=8.5242(11)$ Å, $\beta=96.801(19)°$, $V=1631.5(4)$ Å^3, space group $=P2(1)/n$, $D=1.801$ Mg/m^3, $F(000)=892$, graphite-monochromated Mo-Kα radiation, $\lambda=0.71073$ Å, $\mu=0.738$ mm^{-1}, $T=160(2)$ K. Crystal size: 0.14×0.54×0.25 mm.[3] The intensities of 3691 reflections were measured on a Bruker AXS P4 four-circle diffractometer[11] covering 99.8% of a complete quadrant with $\theta_{max}=25.00°$, $R_{int}=0.0307$. Structure solution, and refinement were carried out using the SHELXTL suite of programs.[12] The refinement of 218 parameters on F^2 using all 2865 unique reflections converged at $R_1=0.0315$ [$F_o>2\sigma(F_o)$]and $wR_2=0.0762$ for all reflections. Data have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, deposition number CCDC 158713.

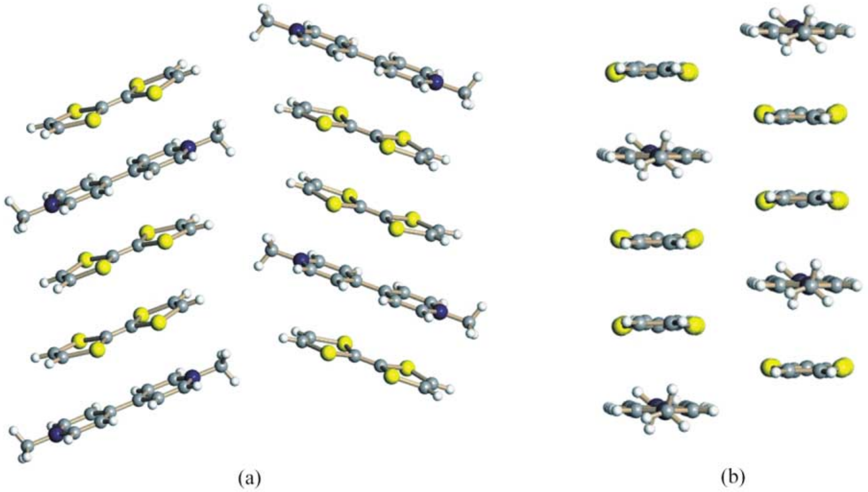
(a) (b)

Figure 2. Crystal structure of complex 2(**1**)·(**3**). PF_6^- counter anions have been removed for clarity.

In conclusion, we have shown that $\mathbf{1}^{+\bullet}$ forms a C-T complex with **3**, **4** and **5**. The electrochemically controllable inclusion/encapsulation of **1** by **2** is not mirrored when **2** is replaced by conformationally unrestrained derivatives **4** or **5**. In these C-T systems, intramolecular Coulombic repulsion of the bipyridinium units of **4** and **5** prevent inclusion/encapsulation of **1**. We are in the process of preparing analogous oligomeric derivatives to **4** and **5**, which should have the ability to reversibly encapsulate **1**, and these studies will be reported in due course.

Acknowledgements

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