The Complexation of Tetrathiafulvalene by Cyclobis(Paraquat-*p*-phenylene)

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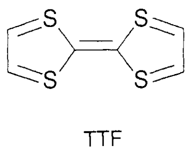
The powerful π-electron donor, tetrathiafulvalene, forms a strong green-coloured 1 : 1 complex with the π-electron accepting tetracationic cyclophane, cyclobis(Paraquat-*p*-phenylene), in both the solid and solution states as demonstrated by X-ray crystallography and spectroscopy (NMR and UV–VIS), respectively.

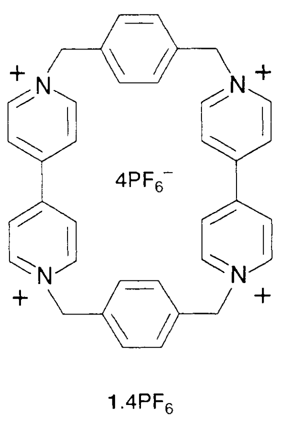
Tetrathiafulvalene (TTF), first reported[1] by Wudl in 1970, is a well-known, powerful π-electron donor. It is easily converted into a stable radical cation which has been widely used to form charge-transfer salts with π-electron deficient systems such as tetracyano-*p*-quinodimethane.[2] Recently, we have shown that the tetracationic cyclophane **1**·4PF$_6$ is a versatile host for π-electron rich systems, such as diphenol methyl ethers,[3] dinaphthol methyl ethers[4] and aromatic amino acids.[5] The solid-state structures of many of these complexes display continuous channel-like arrangements of the macrocyclic tetracations **1**$^{4+}$ with the aryl ether guests threaded, rotaxane-like, through the centres of the macrocycles. This channel-like superstructure has led us to (*i*) design and synthesise[4] a prototype of a molecular abacus which is based on **1**$^{4+}$ and a bisdinaphthol ether and (*ii*) construct a molecular shuttle.[6,7] The electrochemical control of the superstructures of such molecular assemblies poses quite a problem as a result of the high oxidation potential (*ca.* 1.3 V) of the diphenol and dinaphthol ether units. Hence, a system based on TTF, which is easily oxidised (*ca.* 0.4 V) and has a very stable radical cation, is desirable from the point of view of constructing superstructures which might be induced to behave in a machine-like manner. Here, we report the characterisation of the complex [**1**·TTF]$^{4+}$ in both the solution and solid states by ^{1}H and ^{13}C NMR spectroscopy and by X-ray crystallography, respectively.

Mixing **1**·4PF$_6$ and TTF in equimolar proportions in acetonitrile produces an emerald green-coloured solution as a result of the appearance of a charge-transfer absorption band centred on 854 nm. A spectrophotometric titration performed at this wavelength at 27 °C yielded a K_a value of 51 dm^3 mol^{-1} for the 1 : 1 complex formed between **1**·4PF$_6$ and TTF. This corresponds to a free energy of complexation of 2.34 kcal mol^{-1} (1 cal = 4.184 J), a value slightly higher than those obtained[3] for diphenol and dinaphthol methyl ethers, reflecting the greater π-donating ability of the TTF molecule.

The ^{1}H NMR spectrum† of the green-coloured complex [**1**·TTF][PF$_6$]$_4$ shows (Table 1) small, but significant, changes in chemical shifts relative to those for TTF and **1**·4PF$_6$. The largest chemical shift changes (Δδ) are observed for the



TTF



1.4PF$_6$

Table 1 The ^{1}H NMR chemical shift data (δ and Δδ values)[a] for **1**·4PF$_6$, TTF, and [**1**·TTF][PF$_6$]$_4$ in CD$_3$CN at ambient temperature

Compound or complex	Bipy-CH α[b]	Bipy-CH β[b]	C$_6$H$_4$	$^+$NCH$_2$	TTF
1·4PF$_6$	8.86	8.16	7.52	5.74	—
TTF	—	—	—	—	6.44
[**1**·TTF][PF$_6$]$_4$	8.92 (+0.06)	7.88 (−0.28)	7.66 (+0.14)	5.70 (−0.04)	6.15 (−0.29)

[a] The Δδ values (ppm) indicated in parentheses under the respective δ values are those experienced by probe protons in both guest and host on 1 : 1 complex formation. The Δδ values were calculated using the equation, Δδ = δ(complex) − δ(free). [b] α and β with respect to N.

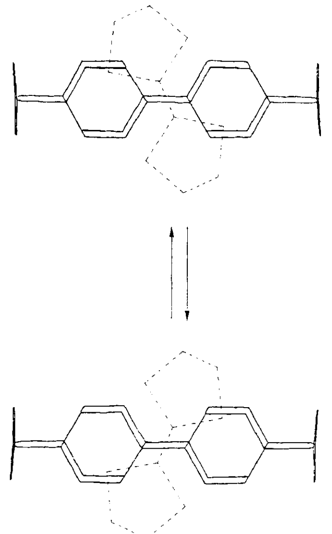


Fig. 1 A schematic representation of the equilibrium established in solution for [**1**·TTF]$^{4+}$. The two degenerate C_{2h} superstructures average to produce a D_{2h} geometry. **1**$^{4+}$ is shown as solid lines, TTF as broken lines.

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† ^{1}H NMR spectra were obtained at 400 MHz in CD$_3$CN at room temperature using a Bruker WH400 spectrometer. ^{13}C NMR spectra were recorded at 100.6 MHz using the same spectrometer and the JMOD pulse sequence with a D1 of 5 s. Since the quaternary alkenic carbon atoms of TTF have an unusually long T_1 they were identified using a coupled DEPT experiment optimised for $^3J_{CH}$ = 10 Hz. Solutions were allowed to stand for three days before recording spectra to permit radical quenching to occur.

Table 2 The ^{13}C NMR chemical shift data (δ and Δδ values)[a] for $1{\cdot}4PF_6$, TTF and $[1{\cdot}TTF][PF_6]_4$ in CD_3CN at ambient temperature

Compound or complex	Bipy carbons α	β	Quat.	$^{+}NCH_2$	Quat.-C_6H_4	CH-C_6H_4	CH-TTF	Quat.-TTF
1.4PF$_6$	146.2	128.3	150.4	65.7	137.0	131.4	—	—
TTF	—	—	—	—	—	—	120.5	110.4
[**1**·TTF][PF$_6$]$_4$	145.4 (−0.8)	126.7 (−1.6)	146.4 (−4.0)	65.6 (−0.1)	136.9 (−0.1)	131.8 (+0.4)	120.9 (+0.4)	109.1 (−1.3)

[a] The Δδ values (ppm) indicated in parentheses under the respective δ values are those experienced by probe carbons in both guest and host on 1:1 complex formation. The Δδ values were calculated using the equation, Δδ = δ(complex) − δ(free).

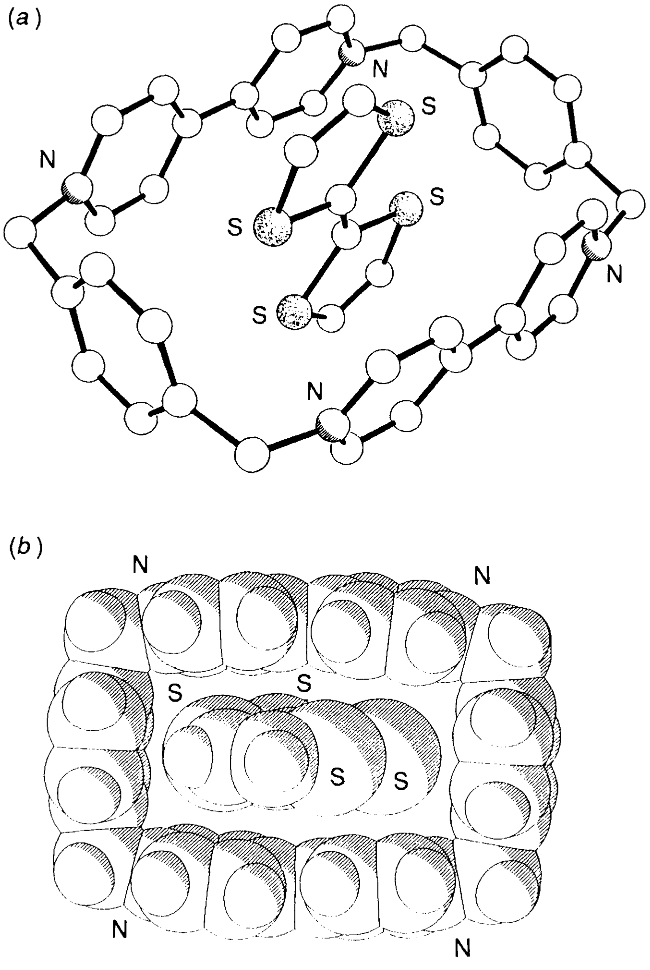

Fig. 2 (*a*) A ball-and-stick representation of $[1{\cdot}TTF]^{4+}$ in the solid state and (*b*) a space-filling representation of the 1:1 complex viewed perpendicular to the mean plane of 1^{4+}

β-bipy-CH protons (−0.28 ppm) of the host with a comparable movement of −0.29 ppm in the signal for the TTF protons. ^{13}C NMR spectroscopy† provided further evidence for the inclusion of a TTF molecule within the cavity of 1^{4+}. In addition to the upfield chemical shift change (Δδ) displayed (Table 2) by the signals for the α- and β-bipy carbon atoms of 1^{4+}, the signal for the quaternary carbon atom of the bipyridinium unit of 1^{4+} is shifted dramatically upfield by 4 ppm. Furthermore, the signal for the quaternary alkenic carbon atoms of the TTF molecule is moved upfield by 1.3 ppm. This pattern of chemical shift changes suggests that the TTF molecule is inserted into the cavity of 1^{4+} creating a 1:1 complex with pseudo D_{2h} geometry, *i.e.* an average superstructure with the long axis of the centrally-located TTF molecule perpendicular to the $N^{+}\cdots N^{+}$ vector of 1^{4+}. However, the stable superstructure is more likely to involve the TTF molecule occupying two degenerate pseudo C_{2h} geometries (Fig. 1), exchange between the two sites being rapid on the NMR time-scale. We have previously observed[6] such a rocking motion in superstructures involving the tetracationic cyclophane 1^{4+}.

Single crystals of $1{\cdot}TTF{\cdot}4PF_6{\cdot}4MeCN$, dark green in colour, and suitable for X-ray crystallography, were grown by vapour diffusion of diisopropyl ether into an acetonitrile solution containing equimolar amounts of $1{\cdot}4PF_6$ and TTF. The crystals were highly unstable, instantly desolvating on removal from their mother liquor. Despite encapsulation in epoxy resin, they slowly decomposed and so consequently three different crystals had to be used for the data collection. The solid state structure‡ shows (Fig. 2) that a TTF molecule is inserted in a centrosymmetric fashion through the centre of the tetracationic cyclophane 1^{4+} which displays a characteristic barrel-like shape[3] with slight twisting within its bipyridinium units. The transannular C · · · C distance between the directly opposite quaternary carbon atoms of the bipyridium units in the 1^{4+} component is 6.87 Å. The TTF molecule is oriented with its long axis inclined at 66° to the $N^{+}\cdots N^{+}$ vector of each bipyridium residue. This geometry [Fig. 2(*b*)], in which the TTF molecule is inserted into 1^{4+} at an angle, maximises the π interactions[8] between the two systems subject to the spatial constraints of the receptor. The 1:1 complexes $[1{\cdot}TTF]^{4+}$ form continuous stacks (Fig. 3) in the crystallographic *a* direction (by unit lattice translation, 11.01 Å) with no hindrance of the central channel by either the MeCN molecules or PF_6^- counterions.§ The TTF molecules have their long axes almost perfectly aligned along this direction [Fig. 3(*b*)] with a separation of 4.87 Å between the tertiary alkenic carbon atoms in adjacently located TTF molecules. One sulphur atom of each dithiolene ring is positioned approximately midway between the directly opposite β carbon atoms of the bipyridium units at a mean distance of 3.54 Å.

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‡ *Crystal data* for $1{\cdot}TTF{\cdot}4PF_6{\cdot}4MeCN$: $C_{50}H_{48}F_{24}N_8P_4S_4$, M = 1469.1, triclinic, a = 11.010(3), b = 11.243(3), c = 14.012(3) Å, α = 77.89(2), β = 70.94(2), γ = 69.91(2)°, V = 1530 Å^3, space group $P\bar{1}$, Z = 1 (the molecule is disposed about a centre of symmetry), D_c = 1.59 g cm^{-3}, μ = 35 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans. The structure was solved by direct methods and refined anisotropically to give R = 0.094, R_w = 0.092 for 3069 independent observed reflections [$|F_o| \geq 3\sigma(|F_o|)$, $2\theta \leq 116°$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ It is noteworthy that, although the tetracationic complex $[1{\cdot}TTF]^{4+}$ is positioned about one crystallographic centre of symmetry and is related to the adjacent 1:1 complex within the infinite stacks by another, a feature common to that observed in the solid-state structures of both the free 1^{4+} tetracation and in complexes with simple diphenol and dinaphthol methyl ethers (ref. 3), the gross structure and, in particular, the positions of the counterions are markedly different: the former crystallise in the monoclinic crystal system whereas the crystals of the structure reported here are triclinic.

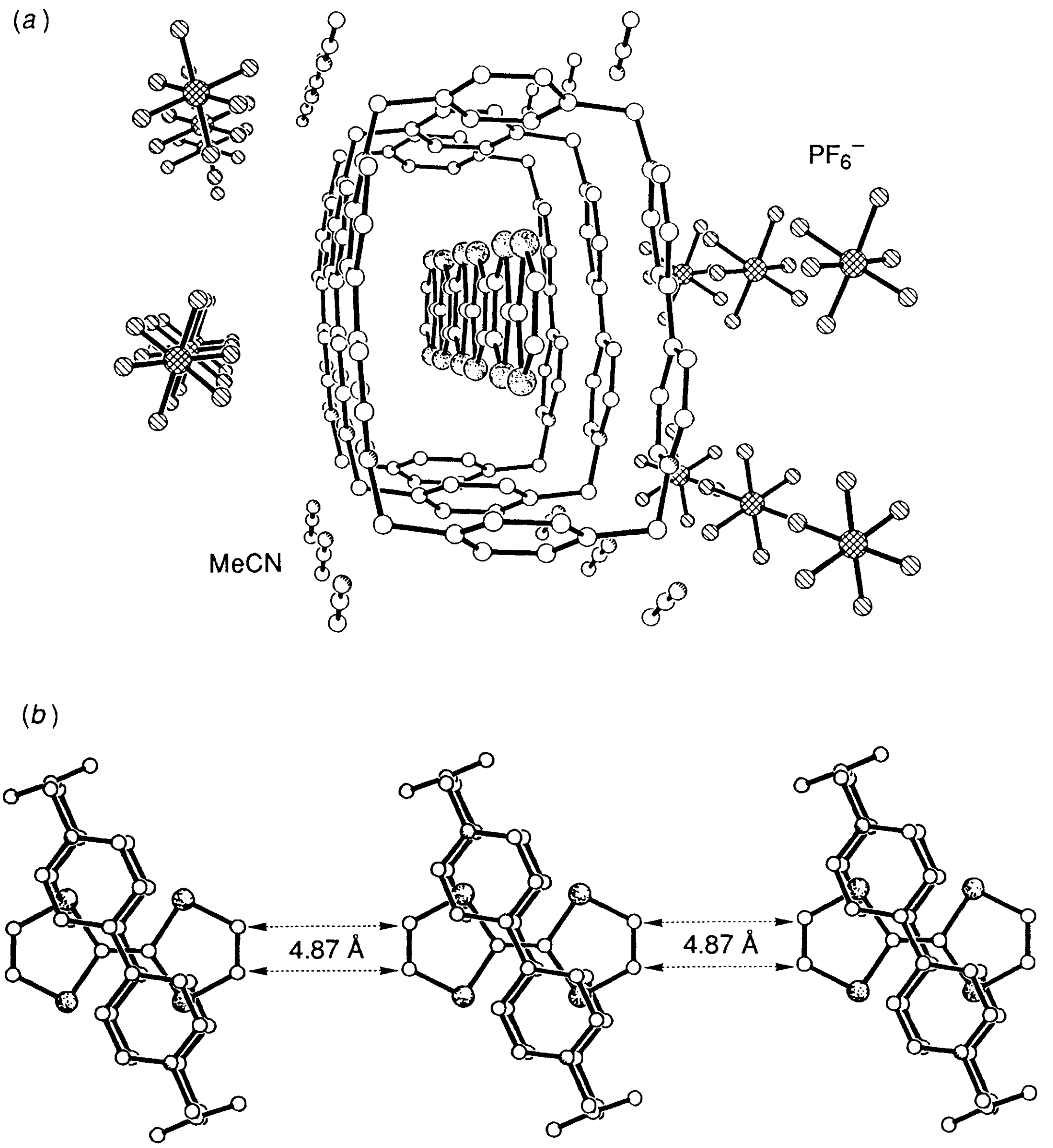

Fig. 3 (*a*) Part of one of the continuous stacks of **1**·TTF·4PF$_6$·4MeCN in the solid state. (*b*) The alignment of the adjacent TTF molecules within the tetracationic channel. MeCN molecules and PF$_6^-$ counterions have been removed for clarity.

This supramolecular structural arrangement once again demonstrates the potential of **1**$^{4+}$ to form polyrotaxane-like assemblies with suitable oligomeric π-donor compounds.

The building of relatively simple molecules into complex multimolecular assemblies with precise control of the ordering of the components is an increasingly important scientific goal out of which new technologies are going to emerge.[9]

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