

Synthesis and X-ray crystal structure of the first tetrathiafulvalene-based acceptor–donor–acceptor sandwich

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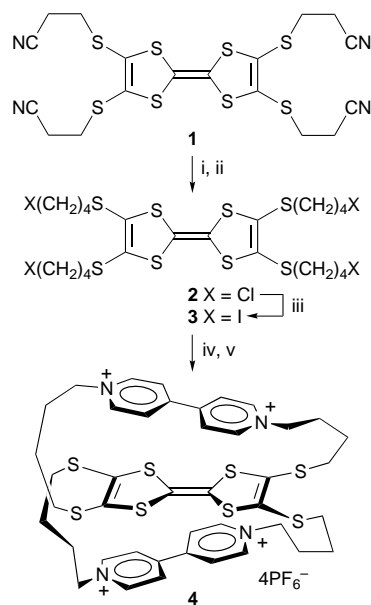
The synthesis and characterization of the bis-macrocylic A–D–A sandwich **4**·4PF₆ produced in a simple one-pot reaction is reported; only one acceptor unit participates in charge-transfer interactions with the TTF unit in the solid state of **4**·4PF₆.

Since Stoddart reported the self-assembly of cyclobis(paraquat-*p*-phenylene) in the presence of electron-donating systems¹ and demonstrated the strong effect of noncovalent interactions, a remarkable number of related catenanes and rotaxanes have been prepared and studied.² These assemblies rely upon molecular recognition based on hydrogen bonding, donor–acceptor and π – π stacking interactions.³ It is known that TTF forms a 1:1 electron-transfer complex with the π -electron deficient, tetracationic cyclobis(paraquat-*p*-phenylene).⁴

We were therefore interested in exploring the possibility of synthesizing a related acceptor–donor–acceptor (A–D–A) system in which the electroactive moieties were covalently fixed within the same molecule. Although, Staab and co-workers have reported a large series of elegant donor–acceptor cyclophanes, and modelled the orientation and distance dependence of charge-transfer (CT) interactions,⁵ the alternative bis-macrocylic A–D–A systems with TTF have not been reported. We have recently demonstrated the facile preparation of macrocylic donor–acceptor systems based on TTF and the bipyridinium acceptor.⁶ The relatively simple synthesis of this macrocycle may rely upon a templating effect due to the formation of a CT complex, which appears to be optimal when butane-1,4-diyl linkers were employed. Here we describe the efficient preparation of the first TTF-containing bis-macrocylic A–D–A complex **4**·4PF₆, in which the π -electron donor TTF is sandwiched between two moderate π -electron acceptors. This unique structure was characterized *via* X-ray structure analysis.

The TTF thiolate protection protocol⁷ developed in our group has made it possible to construct a variety of TTF-containing macrocycles^{7b,8} and TTF-based catenanes.⁹ Compound **4**·4PF₆ was prepared by treatment of **3** [prepared in two steps from tetrakis(2-cyanoethylthio)-TTF^{7a} as outlined in Scheme 1] with 2 equiv. of 4,4'-bipyridine in refluxing MeCN. The macrocycle **4**·4PF₆ was isolated in 32% yield as the *trans* isomer, as a crystalline green solid, after chromatography¹⁰ and anion exchange (NH₄PF₆).[‡] This yield is quite acceptable, considering the formation of two macrocylic rings in a one-pot reaction. The formation of a donor–acceptor complex during the reaction probably assists the ring-forming processes.⁶

The crystal structure of **4**·4PF₆·MeCN was determined by X-ray diffraction,[§] and the structure of the tetracation with atomic numbering is shown in Fig. 1 (anions and solvent molecules have been omitted for clarity). The unit cell contains two formula units, *i.e.*, two complex cations, eight PF₆ anions and six molecules of MeCN. The TTF part of the complex has a boat-like conformation. The dihedral angles between the least-squares planes A [S(1), S(2), C(3), C(42)] and B [S(1), S(2), S(3), S(4), C(1), C(2)] and between B and C [S(3), S(4), C(22), C(23)] are 6.5(1) and 21.3(1)°, respectively. Somewhat similar



Scheme 1 Reagents and conditions: i, N₂, CsOH·H₂O (6 equiv.), MeOH, DMF, room temp., N₂, 1 h, 79%; ii, 1-bromo-4-chlorobutane (6 equiv.), DMF, room temp., N₂, 2 h, 89%; iii, NaI (40 equiv.), acetone, reflux, N₂, 48 h; iv, 4,4'-bipyridine (2 equiv.), MeCN, reflux, N₂, 4 d; v, NH₄PF₆, 32%

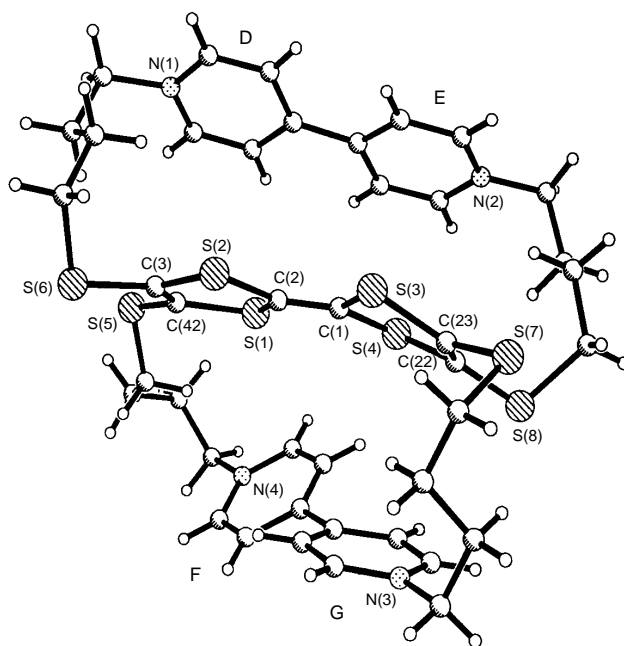


Fig. 1 Structure of **4**·4PF₆·3MeCN

Table 1 Cyclic voltammetry data: oxidation peak potentials

Compound	$E_{1/2}^1/V$	$E_{1/2}^2/V$
2	0.58	0.86
3	0.57	0.85
4	0.64	0.94

distortions have been observed in other TTF systems.¹¹ The bipyridinium units differ in conformation. The dihedral angle between the pyridine rings D(N1) and E(N2) is 7.3(2)°, whereas the angle between F(N4) and G(N3) is 39.3(2)°. The four pyridine rings D, E, F and G make angles of 25.1(1), 17.8(1), 24.1(2) and 55.0(2)° with the central part of TTF (plane B). Thus, the corresponding interplanar distances are not well defined. However, inspection of **4**·4PF₆ in Fig. 1 suggests a stronger interaction between the TTF part and the bipyridine part involving N(1) and N(2) than between TTF and the other bipyridine part, although no short S...N contacts are observed. The displacement parameters for the F atoms of the anions are rather high, indicating orientational disorder. Likewise, the solvent molecules appear to be somewhat disordered. Compound **4**·4PF₆ is prevented from stacking in homologous columnar stacks.¹² The shortest intermolecular S...S distance is 3.744(3) Å [between S(5) and S(7) ($x - 1, y, z$)], likewise indicating a weak interaction. Several C-H...F hydrogen bonds appears to be present, but the disorder of the F positions prevents a detailed description.

The simple ¹H NMR spectrum of **4**·4PF₆ indicates that the system must be flexible in solution as, due to high symmetry, all the butane-1,4-diyl linkers are equivalent in solution. Furthermore the ¹H NMR spectrum of **4**·4PF₆ is independent of temperature in the range 238–303 K.

The redox behavior of the precursors **2** and **3** and the donor acceptor complex **4**·4PF₆ were investigated by cyclic voltammetry (CV) (Table 1). The positive changes in the redox pattern are significant when going from the isolated TTF systems (**2** and **3**) to **4**·4PF₆. The change for the first potential ($\Delta E^1 = 70$ mV) are a consequence of two factors. First, the charge transfer interactions are comparable with systems containing only one acceptor unit,⁶ as evidenced by the UV–VIS (MeCN) spectrum, where **4**·4PF₆ showed a broad charge-transfer absorption band centered at 645 nm (470 M⁻¹ cm⁻¹), similar to the one reported for the simpler systems.⁶ Because of conformational restrictions the TTF unit is unable to interact with both of the acceptor units at the same time and therefore only a part of the change (*ca.* 30–40 mV) can be attributed to the charge transfer interactions. The rest is due to electrostatic repulsion, because the proximity of four positive charges on nitrogen makes it less favorable for the TTF moiety to generate the radical cation. The significant positive change for the second potential ($\Delta E^2 = 90$ mV) can only be explained by electrostatic repulsion from the four pyridinium cations and the TTF radical cation, making the second oxidation less favorable, as no effect was observed in the parent system.⁶

The template-directed synthesis of the bismacrocylic A–D–A sandwich **4**·4PF₆ shows the effect of charge-transfer interaction upon macrocyclization. The crystal structure of **4**·4PF₆ revealed two different bipyridinium units in the solid state, while NMR, UV–VIS and CV analyses illustrate that the system is very flexible in solution.

Notes and References

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‡ All new compounds were characterized using NMR spectroscopy (¹H and ¹³C), plasma desorption mass spectrometry, CV and elemental analysis. CV: counter and working electrode, platinum; reference electrode, Ag/AgCl; supporting electrolyte, Bu₄NPF₆. Measurement carried out in MeCN at room temperature with scan speed = 100 mV s⁻¹. Selected data for

4·4PF₆: mp 175 °C (decomp.); δ_{H} ([²H₆]DMSO) 9.37 (d, *J* 6.6, 8 H), 8.79 (d, *J* 6.6, 8 H), 4.80 (br s, 8 H), 2.85 (m, 8 H), 2.2–1.9 (br m, 8 H), 1.3–1.0 (br m, 8 H); δ_{C} ([²H₆]DMSO) 147.55, 145.92, 125.99, 125.76, 105.79, 60.26, 33.27, 27.80, 23.91; *m/z* (PDMS) 1445 (M⁺), 1300 (M – PF₆⁻), 1155 (M – 2PF₆⁻), 1010 (M – 3PF₆⁻) (Calc. for C₄₂H₄₈F₂₄N₄P₄S₈: C, 34.91; H, 3.35; N, 3.88. Found: C, 34.91; H, 3.55; N, 3.98%.

§ *Crystal data* for **4**·4PF₆: the growth of single crystals of **4**·4PF₆·3MeCN was achieved by solvent diffusion of Et₂O into a solution of **4**·4PF₆ in MeCN: C₄₈H₅₇F₂₄N₇P₄S₈, *M* = 1568.37, triclinic, *a* = 13.1042(5), *b* = 16.2627(6), *c* = 17.1183(7) Å, α = 72.114(1), β = 81.395(1), γ = 73.180(1)°, *V* = 3315.8(2) Å³, space group *P* $\bar{1}$, *Z* = 2, *D*_c = 1.571 g cm⁻³, *F*(000) = 1596, graphite monochromated Mo-K α radiation, λ = 0.71073 Å, μ = 0.47 mm⁻¹, *T* = 294(1) K. Crystal size: 0.50 × 0.50 × 0.20 mm. The intensities of 28724 reflections were measured on a Siemens SMART CCD diffractometer covering 99.3% of a complete hemisphere with θ_{max} = 26.37°, *R*_{int} = 0.0247. Structure solution, refinement of the structure and production of crystallographic illustrations were carried out using the Siemens SHELXTL package (ref. 13) and SHELX-97 (ref. 14). The refinement of 821 parameters on *F*² using all 12477 unique reflections converged at *R*₁ = 0.0757 [for *F*_o > 4 σ (*F*_o)] and *wR*₂ = 0.21 for all reflections. CCDC 182/797.

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