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An investigation of the complexation behaviour of structurally modified tetrathiafulvalene derivatives with the electron deficient cyclophane cyclobis(paraquat-*p*-phenylene)

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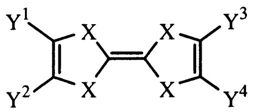
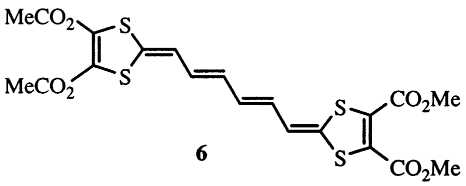
Abstract—This study has shown that easily oxidisable TTF units form charge-transfer (C-T) complexes with **7** which have the largest reported association constants to date. Replacing the sulfur of the TTF unit with selenium or extending the conjugated link between the two dithiole rings reduces the K_a of the complex relative to the parent derivative. © 2001 Published by Elsevier Science Ltd.

The complexation of tetrathiafulvalene (TTF, **1**) and its derivatives with the electron deficient cyclophane cyclobis(paraquat-*p*-phenylene) **7** is a burgeoning field of study.[1] Indeed, a recent report has shown charge-transfer (C-T) complexes of this type have found application as novel molecular electronics devices.[2] In view of the potential applications of these systems to supramolecular[1a] and materials chemistry,[1e] it is surprising that studies to maximise the association constants (K_a) of the complexes of structurally modified TTF units with **7** have received only limited attention.[3] Preliminary studies have shown that TTF units with poor donor properties tend to give rise to weak inclusion complexes, whereas TTF derivatives with lower ionisation potentials tend to give rise to much stronger complexes. However, the donor properties of the TTF units studied to date are essentially the same as that of the parent TTF **1** (ca. 0.33 V versus Ag/AgCl). Here, we report for the first time the complexation behaviour of structurally modified TTF's with **7**, in endeavours to discover the effect that maximising the donor ability, intercomplex interactions and reducing intramolecular Coulombic repulsion between the dicationic states has on the stability of their resulting complexes with **7**. We have investigated the solution complexation behaviour of TTF derivatives **2**–**6** with **7** using ^{1}H NMR, UV–vis, cyclic voltammetry and molecular modelling studies. Compounds **2** and **3** were selected for this study in view of the fact that these derivatives possess some of the lowest ionisation potentials for TTF derivatives reported to date. Moreover, compound **3** was selected as it possesses a proton directly bound to the TTF nucleus which will provide a convenient marker for studying the complexation behaviour by ^{1}H NMR.



X = S, $Y^1 = Y^2 = Y^3 = Y^4$ = H **1**
X = S, $Y^1 = Y^2 = Y^3 = Y^4$ = Me **2**
X = S, $Y^1 = Y^2 = Y^3$ = Me, Y^4 = H **3**
X = Se, $Y^1 = Y^2 = Y^3 = Y^4$ =Me **4**
X = S, $Y^1 = Y^2 = Y^3 = Y^4$ = CO_2Me **5**



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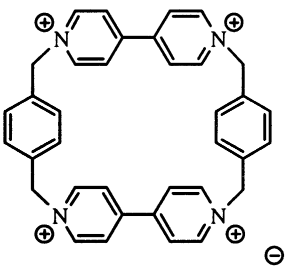

7 $4\,PF_6^{\ominus}$

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Table 1. The ^{1}H NMR chemical shift (δ and $\Delta\delta$) and UV data for compound **7** and its complexes with **2**–**4** in CD_3CN at ambient temperatures

Compound or complex	α-Bipy-CH	β-Bipy-CH	C_6H_4	$^+NCH_2$	TTF (CH_3)	TTF (H)	$\lambda_{CT\ (max)}$
2					1.95		
2·7	9.02	7.89	7.67	5.69	1.87		946
3					2.04, 1.93	6.01	
3·7	8.98	7.87	7.67	5.68	2.08, 1.77	5.84	934
4[a]					1.95		
4·7[a]	9.52	8.56	7.84	5.75	1.73		876
7	8.86	8.16	7.52	5.74			
7[a]	9.46	8.65	7.71	5.81			

α and β are with respect to N in the cyclophane.

[a] Data obtained in CD_3SOCD_3. UV–vis spectra were measured in CH_3CN.

Solution phase complexation of **2**–**6** with **7** was confirmed using ^{1}H NMR and UV–vis spectroscopy (Table 1). Mixing **2**–**4** with **7** 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. The ^{1}H NMR spectra of the green-coloured complexes showed small but significant changes in the chemical shifts relative to those of non-complexed **2**–**4**, and are in accordance with previously reported data for **1·7**.[1d] An interesting feature of the spectra for complexes **2·7** and **3·7** is the relatively large changes in the chemical shifts of the methyl protons of these derivatives, thereby indicating these moieties may play an important structural role in the stability of these complexes. The ^{1}H NMR spectra of complexes **5·7** and **6·7** indicated that incomplete complexation had occurred by revealing the presence of both complexed and uncomplexed cyclophane proton resonances.[1a]

The solution electrochemistry of the parent derivatives and their resulting complexes have been investigated using cyclic voltammetry (CV) (Table 2).[4] Upon the addition of excess **7** to the CV cell containing **2**–**4**, the first oxidation of the TTF derivatives was immediately shifted to a more positive potential (~60 mV), whilst the second oxidation due to the formation of the dication species was unaffected. The current intensities of the first oxidation process of the complexes are about 30–40% less than that obtained for the free TTF derivative, due to the smaller diffusion coefficients of the former. This complexation behaviour is consistent with previously reported CV data for **1·7** and suggests that these new C-T materials also decomplex when the TTF guest unit experiences its first electrochemical oxidation.[1b] Upon the addition of **7** to a CV cell containing **5** or **6**, negligible changes in the first oxidation potentials of the TTF unit were observed.

We have determined the association constants (K_a) and the ΔG for these complexes and the results are presented in Table 3. It is evident from these data that replacing the hydrogens of derivative **1** with methyl groups (as in **3** and **4**) results in a considerable increase in the K_a of their complexes with **7**. This is probably due to the combination of the considerably lower ionisation potential of these derivatives with respect to **1**, together with the favourable steric interactions promoted by the methyl groups. K_a values calculated for complexes **5·7** and **6·7** were much lower than those observed for derivatives **1**–**3**, and are consistent with values determined for other TTF units bearing electron withdrawing functionalities.[3]

We have modelled the C-T systems **1·7** and **2·7** using a modification of previously reported procedures and the resulting structures are provided in Fig. 1.[6] Energy minimised structures were obtained for the non-complexed components **1**, **2** and **7** using the AM1 semi-empirical procedures, the components of the complexes were then merged and the MM+ molecular mechanics force-field was applied to generate the complexes shown below. Using this method, a remarkably similar centrosymmetric architecture for **1·7** was obtained to that reported using X-ray crystallography.[1d] The modelled structure accurately depicts the barrel-like shape and the slight twisting within the bipyridinium units of **7**. The angle of incline of **1** with respect to the $N^+\cdots N^+$ vector of each pyridinium moiety of **7** in the modelled structure is 62°, as compared to the value of 66° for the X-ray determined structure. The transannular C···C distance between directly opposite quaternary carbons of the bipyridinium units of **7** is 7.30 Å, compared to the X-ray determined distance of 6.87 Å, which is reflected by the bow-shaped conformation of the bipyridyl unit of the modelled structure. For complex **2·7**, a more obtuse angle of incline of 72° with respect

Table 2. Cyclic voltammetry data recorded in MeCN containing 0.1 M Bu_4NPF_6 at 298 K versus Ag/AgCl

Compound/complex	$E^1_{1/2}$ (V)	$E^2_{1/2}$ (V)
2	0.27	0.67
2·7	0.33	0.67
3	0.31	0.71
3·7	0.36	0.71
4	0.45	0.76
4·7	0.51	0.76
5	0.82	1.13
5·7	0.83	1.13
6	0.56	
6·7	0.57	

Scan rate 100 mV s^{-1}. Complexes were formed by adding a 20-fold excess of **7** to the CV cell.

Table 3.

Complex	K_a (M^{-1})	ΔG (kcal mol^{-1})
1·7	10 000^{1b} (±500)	5.4
2·7	183 000^{a} (±9150)	7.0
3·7	55 000^{a} (±2750)	6.4
4·7	47 000^{a} (±2350)	6.3
5·7	170^{b} (±8.5)	3.0
6·7	70^{b} (±3.5)	2.5

[a] Obtained from λ_{max} values using spectrophotometric dilution methods measured in CH_3CN at 21°C.[5]

[b] Calculated from the ratio of the complexed/uncomplexed integrals of their cyclophane proton resonances in their ^1H NMR spectra in CD_3CN.[1a]

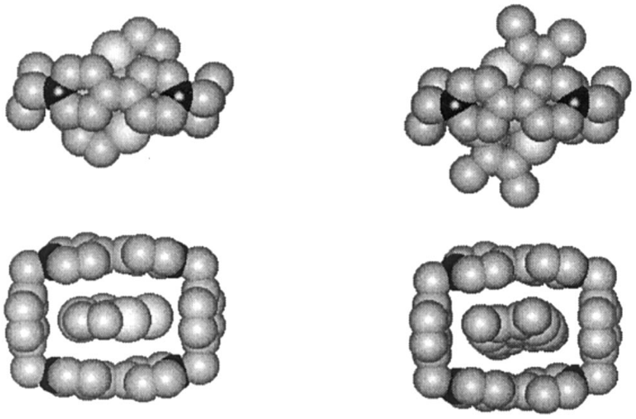

Figure 1. Energy minimised structures of **1·7** and **2·7**.

to the $N^+ \cdots N^+$ vector of each pyridinium moiety is observed, presumably due to steric interactions between the methyl groups of unit **2** and the phenyl units of cyclophane **7**. The transannular separation of the pyridinium moieties is almost identical to that of **1·7** (7.38 Å). Furthermore, moiety **2** is at an angle of 12° with respect to the plane of the pyridinium moieties of **7**.

In conclusion, we have established that structurally modified TTF units which have low ionisation potentials possess the ability to form C-T complexes with **7** displaying very large K_a's. Moreover, increasing the size of the chalcogen or the extent of the conjugation between the dithiole rings of the TTF unit decreases the K_a of its complex with **7** relative to the parent TTF derivative. We are in the process of exploiting the very large K_a values of analogues of complexes **2·7** and **3·7** to fabricate novel redox controlled devices, and the results will be reported in due course.

Acknowledgements

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References

1. (a) Nielsen, M. B.; Lombolt, C.; Becher, J. *Chem. Soc. Rev.* **2000**, *29*, 153–164; (b) Ashton, P. R.; Balzani, V.; Becher, J.; Credi, A.; Fyfe, M. C. T.; Mattersteig, G.; Menzer, S.; Nielsen, M. B.; Raymo, F. M.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 3951–3957; (c) Devonport, W.; Blower, M. A.; Bryce, M. R.; Goldenberg, L. M. *J. Org. Chem.* **1997**, *62*, 885–887; (d) Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1584–1586.
2. Collier, C. P.; Mattersteig, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289*, 1172–1175.
3. Lau, J.; Nielsen, M. B.; Thorup, N.; Cava, M. P.; Becher, J. *Eur. J. Org. Chem.* **1999**, 2807.
4. All electrochemical experiments were performed using a BAS-100W system. Electrolyte solutions were prepared from recrystallised Bu_4NPF_6 using spectroscopic grade MeCN and purged with nitrogen prior to use. A three electrode configuration was used with a Pt working electrode, Ag/AgCl reference electrode and a platinum wire as the counter electrode.
5. Colquhoun, H. M.; Gooding, E. P.; Maud, J. M.; Stoddart, J. F.; Wolstenholme, J. B.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 607.
6. As implemented in HyperChem 5.1, Hypercube Inc., Gainesville, Florida. Initial geometries were obtained using an AM1 geometry optimisation [RHF for **1** and **2**, UHF for **7**]. The components of the complexes were merged and the geometries of these systems were then re-optimised using the MM+ force-field to yield the structures provided in this manuscript.