‘Self-complexing’ tetrathiafulvalene macrocycles; a tetrathiafulvalene switch

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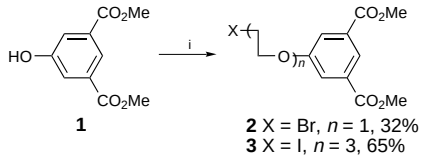
Two ‘self-complexing’ macrocycles based on the electron donor TTF and a cyclic bipyridinium acceptor are prepared.

The construction of molecular devices which can operate as machines upon external energy transfer has been of high interest recently, as such systems may be able to store and process information at the molecular level.[1,2] A recent example is provided by a pseudorotaxane system in which a naphthalene or hydroquinone π-donor and the π-acceptor cyclobis(paraquat-*p*-phenylene) are covalently linked.[3]

We have prepared a number of donor–acceptor catenanes by incorporating the π-donor tetrathiafulvalene (TTF) into macrocyclic systems,[4] as well as systems in which the TTF unit and the bipyridinium unit are linked, either in a rigid conformation, *e.g.* as a donor–acceptor cyclophane, or in a noncyclic system.[5] Here we have extended these concepts by incorporating TTF into macrocycles which may self-complex in order to investigate their switching properties. For synthetic reasons we attached the TTF unit to the unsymmetrical *m*-*p* linked cyclophane of cyclobis(paraquat-*p*-phenylene).[6] The corresponding symmetric *m*-*m* linked cyclophane was discarded due to its poor ability to act as a host, as reported by Stoddart.[7]

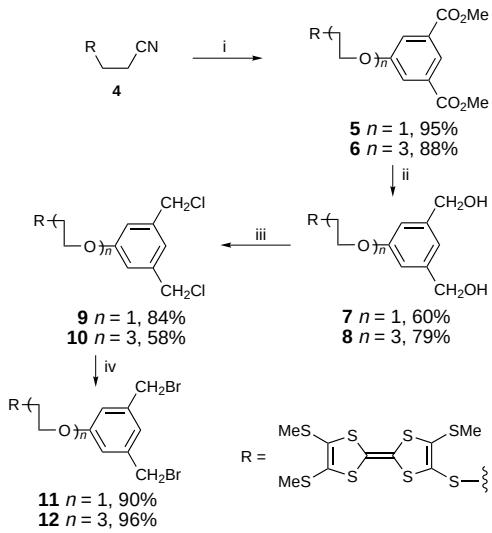
First, **2** and **3** were prepared by *O*-alkylations of dimethyl 5-hydroxyisophthalate **1** (Scheme 1). The TTF derivative **4** was deprotected with CsOH (1 equiv.) (Scheme 2),[8] and the resulting monothiolate was treated *in situ* with **2** or **3** affording **5** and **6**, respectively. The two ester groups were reduced with $LiAlH_4$ followed by mesylation in the presence of DBU. The mesylated compounds were converted directly to the corresponding chloro compounds by reaction with an excess of LiCl, giving fair yields of **9** and **10**. Subsequent Finkelstein reactions with LiBr gave the TTF-linked *m*-xylene dibromides **11** and **12**.†



1

2 X = Br, *n* = 1, 32%
3 X = I, *n* = 3, 65%

Scheme 1 *Reagents and conditions*: i, K_2CO_3, $BrCH_2CH_2Br$ (*n* = 1) or $I(CH_2CH_2O)_2CH_2CH_2I$ (*n* = 3), acetone, reflux, 16 h



5 *n* = 1, 95%
6 *n* = 3, 88%

7 *n* = 1, 60%
8 *n* = 3, 79%

9 *n* = 1, 84%
10 *n* = 3, 58%

11 *n* = 1, 90%
12 *n* = 3, 96%

Scheme 2 *Reagents and conditions*: i, $CsOH·H_2O$ (1 equiv.), **2** or **3**, DMF, room temp., 3 h; ii, $LiAlH_4$, THF, reflux, 2 h; iii, MsCl, DBU, LiCl, CH_2Cl_2, room temp., 24 h; iv, LiBr, acetone, reflux, 24 h

The new anchimeric-complexed‡ macrocycles **14a** and **15a** were obtained by treating **11** and **12**, respectively, with the dipyridinium dication of **13** under ultra-high pressure (10 kbar) for 6 days (Scheme 3). The crude green products were subjected to column chromatography and ion exchange.[4] During work-up of **15a**, partial isomerisation ‘decomplexation’ to the orange coloured form **15b** was observed. Repeated fractional crystallization *via* slow evaporation of Pr^i_2O into MeCN solutions of **14a** and **15a** resulted in removal of small amounts of impurities. In this way it was possible to obtain **14b** and **15b** as orange microcrystalline compounds, *e.g.* in the completely ‘decomplexed’ forms. Redissolution of **15b** in MeCN initially gave an orange solution which slowly turned greener on standing due to partial anchimeric complexation. However, an MeCN solution of ‘decomplexed’ **14** did not change colour, and according to UV–VIS spectroscopy only a very small charge-transfer (CT) absorption could be detected after several days. Thus, when first ‘decomplexed’, the short linker of **14b** more or less prevents the TTF unit from intramolecularly slipping back into the cyclic acceptor. Besides, the persistent orange colour indicates the absence of intermolecular complexation.

The UV–VIS absorption of the initially orange crystals of **15b** dissolved in MeCN was followed over time [Fig. 1(*a*)]. After about 20 h the equilibrium between **15a** and **15b** was established, as seen from the constant CT absorption (λ_{max} ~785 nm). The relatively weak CT absorption indicates that only a small degree of anchimeric complexation occurs, which was confirmed by ^1H NMR spectroscopy (estimated ratio **15a** : **15b**: 1 : 10). The anchimeric complexation results in a complicated set of bipyridinium proton resonances and a downfield shift of the SMe protons in agreement with observations for comparable TTF-based catenanes.[4d] The question is whether the complexation is truly of the auchimeric

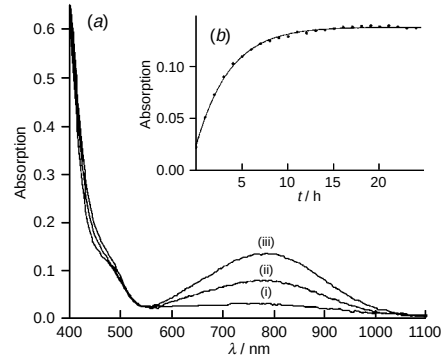
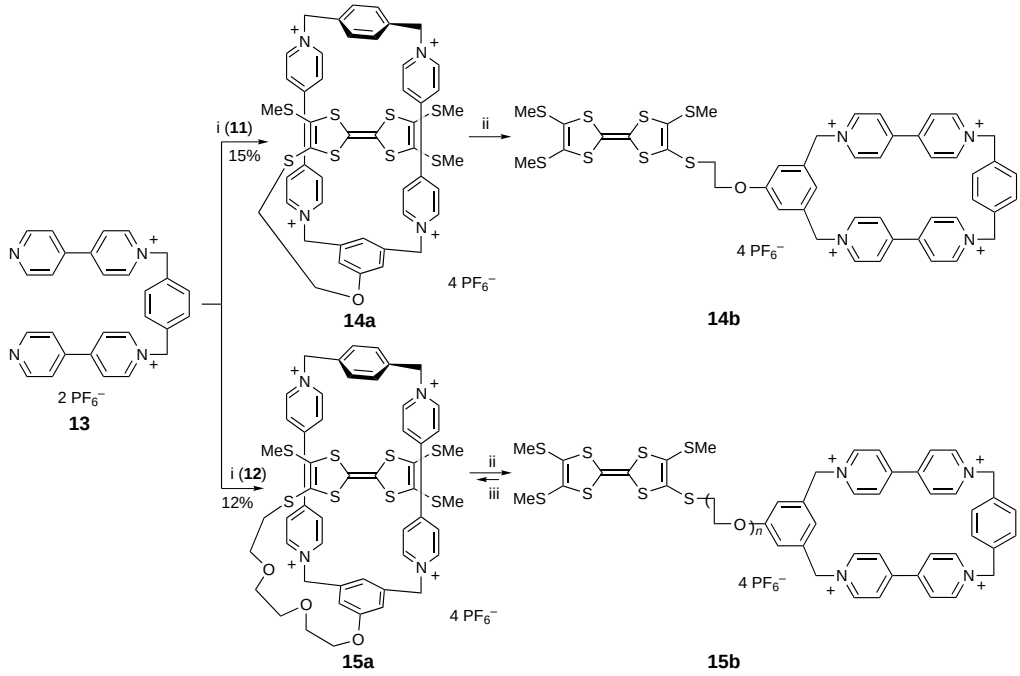


Fig. 1 (*a*) The UV–VIS absorption spectrum of the initially decomplexed **15b** in MeCN at (i) 0, (ii) 3 and (iii) 19 h. (*b*) The time variation of the maximum absorbance (λ_{max} ~785 nm) of initially decomplexed **15b**. A first-order fit matches the points very well. Concentration of compound = 0.26 mmol dm^{-3}.



Scheme 3 *Reagents and conditions*: i, DMF, 10 kbar, room temp., 6 d; ii, fractional crystallization; iii, equilibrium in MeCN

type. The formation of an intramolecular 'complex' by anchimeric complexation would be expected to follow a first-order rate equation. In Fig. 1(*b*) the observed absorption maxima are plotted against time, and a curve fitted using eqn. (1)§ confirms that the data are in good agreement with first-order conditions. Of course this is not a final proof for exclusive anchimeric complexation. Nevertheless, since **14b** did not readily undergo intermolecular slipping in dilute solution, we would not expect this to be likely for **15b** either.

Refluxing the equilibrium solution of **15a,b** in MeCN for 45 min caused almost complete conversion to **15b**. However, the next day a CT absorption close to the starting equilibrium absorption at room temperature was reestablished. This anchimeric decomplexation/recomplexation could be repeated.¶ Thus, **15** behaves as a thermal molecular switch, the state of which is determined by both thermodynamics and kinetics. The solution of **15a,b** was subjected to 10 kbars of pressure (room temp., 4 days); however, this caused no significant change in absorption, *i.e.* in no displacement of the equilibrium.

Compounds **14** and **15** were characterized by electrospray mass spectrometry (ESMS) showing peaks assignable to $[M - nPF_6]^{n+}$ (n = 1–4), $[M - nPF_6]^{(n+1)+}$ (n = 1–3) and $[M - nPF_6]^{(n-1)+}$ (**14**, n = 3,4). Furthermore, a $[2M - 3PF_6]^{3+}$ ion was observed in the gas phase, but whether this is a real dimer or a dimeric cluster ion cannot be concluded. Collisional activation (MS/MS) of the mass selected $[M - 4PF_6]^{4+}$ ions caused similar fragmentations of the cyclic acceptor, as already observed for related TTF based catenanes.[4d]

Notes and References

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† According to plasma desorption mass spectrometry (PDMS), **11** and **12** could not be separated by chromatography from a small amount of the monobrominated compounds (Cl, Br). All other compounds were obtained pure and gave satisfactory elemental analyses. *Selected data* for **5**: $\delta_H(CDCl_3)$ 2.41–2.43 (3 s, 9 H, SCH_3), 3.21 (t, *J* 6.4, 2 H, SCH_2), 3.95 (s, 6 H, CO_2CH_3), 4.26 (t, *J* 6.4, 2 H, OCH_2), 7.77 (d, *J* 1.4, 2 H, Ar.), 8.30 (t, *J* 1.4, 1 H, Ar.); PDMS: *m/z* 610.1 (M^+). For **7**: $\delta_H(CDCl_3)$ 2.40–2.44 (3 s, 9 H, SCH_3), 3.18 (t, *J* 6.5, 2 H, SCH_2), 4.21 (t, *J* 6.7, 2 H, OCH_2), 4.68 (d, *J* 5.2, 4 H, CH_2OH), 6.85 (s, 2H, Ar), 6.97 (s, 1 H, Ar); PDMS: *m/z* 554.2 (M^+). For **9**: $\delta_H(CDCl_3)$ 2.39–2.45 (3 s, 9 H, SCH_3), 3.17 (t, *J* 4.9, 2 H, SCH_2), 4.21 (m, 2 H, OCH_2), 4.55 (s, 4 H, $ClCH_2$), 6.89 (d, *J* 1.2, 2 H, Ar), 7.02 (s, 1 H, Ar); PDMS: *m/z* 590.4 (M^+). For **11**: $\delta_H(CDCl_3)$ 2.39–2.44 (3 s, 9 H, SCH_3), 3.17 (t, *J* 6.5, 2 H, SCH_2), 4.20 (t, *J* 6.5, 2 H, OCH_2), 4.43 (s, 4 H, $BrCH_2$), 6.86 (d, *J* 1.1, 2 H, Ar), 7.02 (s, 1 H, Ar); PDMS: *m/z* 680.2 (M^+). For **14b**: $\delta_H(CD_3CN)$ 2.40–2.41 (2 s, 9 H, SCH_3), 3.28 (t, *J* 5.9, 2 H, SCH_2), 4.34 (t, *J* 6.0, 2 H, OCH_2), 5.69 (s, 4 H, NCH_2), 5.76 (s, 4 H, NCH_2), 6.89 (s, 1 H, Ar), 7.30 (d, *J* 1.3, 2 H, Ar), 7.60 (s, 4 H, Ar), 8.05 (d, *J* 6.8, 4 H, β-H), 8.07 (d, *J* 6.9, 4 H, β-H), 8.74 (d, *J* 6.9, 4 H, α-H), 8.85 (d, *J* 7.1, 4 H, α-H).

‡ Anchimeric assistance is normally used to describe neighbouring group participation in a reaction. The expression 'complexation' is incorrect when used to describe an intramolecular reaction. We suggest using the expression 'anchimeric complexation' to describe the present type of isomerisation ('self-complexation') taking place between two covalently linked groups.

§ The time-dependence of the absorbance (A) for first-order recomplexations with rate constant k_+ is shown by eqn. (1),

$$A = A_0 \exp[-(k_+ + k_-)t] + \text{constant}\cdot\{1 - \exp[-(k_+ + k_-)t] \qquad (1)$$

where k_- is the rate constant for the decomplexation reaction.

¶ A small decrease of the equilibrium CT absorption (*ca*. 5%) was observed after each experiment, which may be due to a chemical decomposition upon refluxing.

1 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89; 1990, **29**, 1304.
2 R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, S. J. Langford, S. Menzer, L. Prodi, J. F. Stoddart, M. Venturi and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 978 and references therein.
3 P. R. Ashton, R. Ballardini, V. Balzani, S. E. Boyd, A. Credi, M. T. Gandolfi, M. Gómez-López, S. Iqbal, D. Philp, J. A. Preece, L. Prodi, H. G. Ricketts, J. F. Stoddart, M. S. Tolley, M. Venturi, A. J. P. White and D. J. Williams, *Chem. Eur. J.*, 1997, **3**, 152.
4 (*a*) Z.-T. Li, P. C. Stein, N. Svenstrup, K. H. Lund and J. Becher, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2524; (*b*) Z.-T. Li, P. C. Stein, J. Becher, D. Jensen, P. Mørk and N. Svenstrup, *Chem. Eur. J.*, 1996, **2**, 624; (*c*) Z.-T. Li and J. Becher, *Chem. Commun.*, 1996, 639; (*d*) M. B. Nielsen, Z.-T. Li and J. Becher, *J. Mater. Chem.*, 1997, **7**, 1175.
5 K. B. Simonsen, K. Zong, R. D. Rogers, M. P. Cava and J. Becher, *J. Org. Chem.*, 1997, **62**, 679.
6 D. Philp, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 1584; P. R. Ashton, R. A. Bissel, R. A. Spencer, J. F. Stoddart and M. S. Tolley, *Synlett*, 1992, 923; W. Devonport, M. A. Blower, M. R. Bryce and L. M. Goldenberg, *J. Org. Chem.*, 1997, **62**, 885; P.-L. Anelli, M. Asakawa, P. R. Ashton, R. A. Bissel, G. Clavier, R. Górski, A. E. Kaifer, S. J. Langford, G. Mattersteig, S. Menzer, D. Philp, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, M. S. Tolley and D. J. Williams, *Chem. Eur. J.*, 1997, **3**, 1113.
7 D. B. Amabilino, P. R. Ashton, M. S. Tolley, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1297.
8 J. Becher, Z.-T. Li, P. Blanchard, N. Svenstrup, J. Lau, M. B. Nielsen and P. Leriche, *Pure Appl. Chem.*, 1997, **69**, 465 and references therein.

Received in Liverpool, UK, 29th September 1997; 7/07026H