Configurationally selective self-assembly of a *cis*-[3]pseudocatenane incorporating three tetrathiafulvalene units

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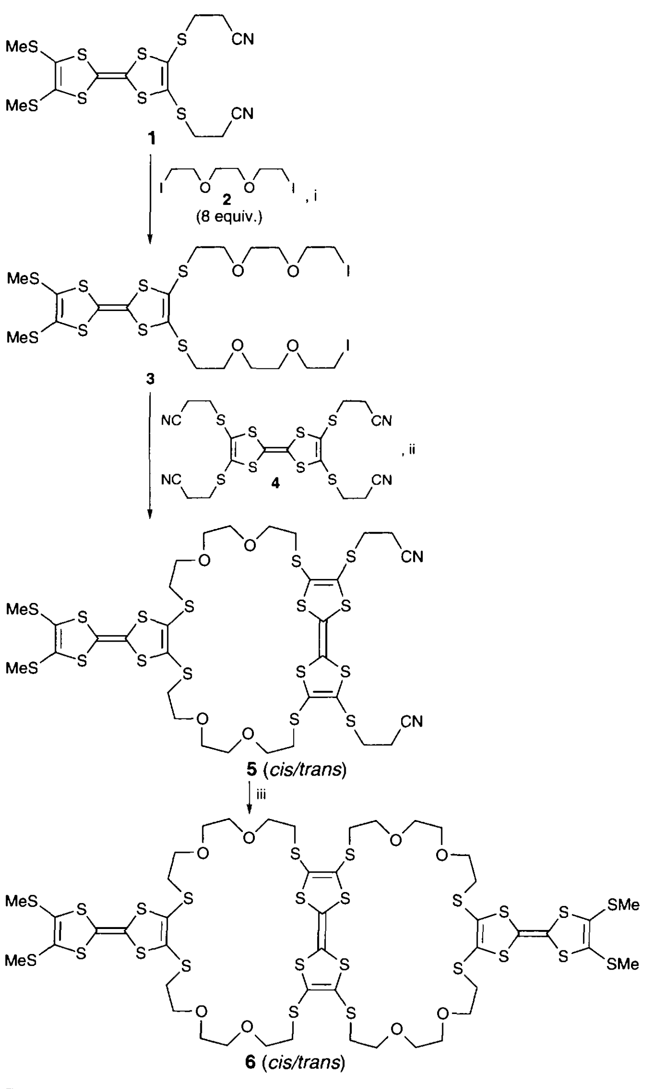
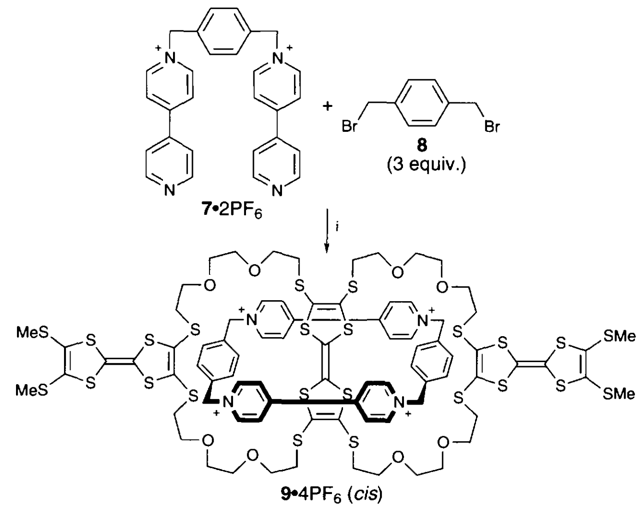
Dimacrocycle 6, incorporating three tetrathiafulvalene units, reacts with dication 7.2PF$_6$ and dibromide 8 under ultra-high pressure (8 × 10^5 kPa), to exclusively give *cis*-[3]pseudocatenane 9.4PF$_6$ in 20% yield.

The formation of catenanes by self-assembly[1] is controlled by the information stored in the 'preprogramed' starting materials.[2] The information, locked within the catenane molecules, also results in catenanes with properties quite different from those of their individual molecular components.[2] Based on donor–acceptor interactions, catenanes of different structures have been prepared from a variety of starting materials.[3] We have recently reported the synthesis of a novel type of [3]pseudocatenanes based on the tetravalency of the tetrathiafulvalene-2,3,6,7-tetrathiolate (TTFTT) unit.[4] By incorporating two dioxyphenylene units into a TTF-based dimacrocyclic system, we succeeded in obtaining both *cis*- and *trans*-[3]pseudocatenanes, whereas replacing the dioxyphenylenes with 9,10-dioxyanthrylenes resulted in the selective formation of the corresponding *trans*-[3]pseudocatenane.[4] Here we report the selective self-assembling synthesis of a *cis*-[3]pseudocatenane, using the dimacrocycle precursor **6**, in which the central TTF unit constitutes the bridge of the dimacrocycle while the peripheral TTF units control the configuration of the resulting catenane.



Scheme 1 *Reagents and conditions*: i, CsOH·H$_2$O (2 equiv.), DMF, room temp., 1 h, 42%; ii, CsOH·H$_2$O (2 equiv.), DMF, room temp., 16 h, 63%; iii, CsOH·H$_2$O (2 equiv.), H$_2$O, room temp., 16 h, 55%

Preparation of compound **6** was chosen because the investigation of a CPK model suggested that only when the central TTF unit adopts a *cis*-configuration, will the peripheral TTF units be able to form π-π donor–acceptor interactions with the two bipyridinium units, which are essential for the configurational control during the possible self-assembling process. The synthesis of **6** is shown in Scheme 1, compound **3** was prepared in 42% yield *via* deprotection–alkylation of **1**[5] using an excess of **2** (8 equiv.). The two-step macrocyclizations of **3** with **4**[5] under high dilution conditions (perfusor pump) afforded **6** *via* the intermediate **5** in 35% overall yield.†,‡ No catenane products were detected after stirring the solution of **6** in DMF or acetonitrile in the presence of **7**.2PF$_6$[2a] and **8** at room temperature for three weeks at atmospheric pressure. However under ultra-high pressure (8 Kbar), **9**.4PF$_6$ was obtained in 20% yield from the self-assembly of **6**, **7**.2PF$_6$ and **8** at room temperature after 3 d, Scheme 2. After evaporation of the solvent *in vacuo*, the green solid residue was extracted with dichloromethane§ and then purified by column chromatography [silica gel, MeOH–NH$_4$Cl (2 mol dm^{-3})–MeNO$_2$ 7:2:1],



Scheme 2 *Reagents and conditions*: i, **6**, DMF, 8 kbar, room temp., 3 d, 20%

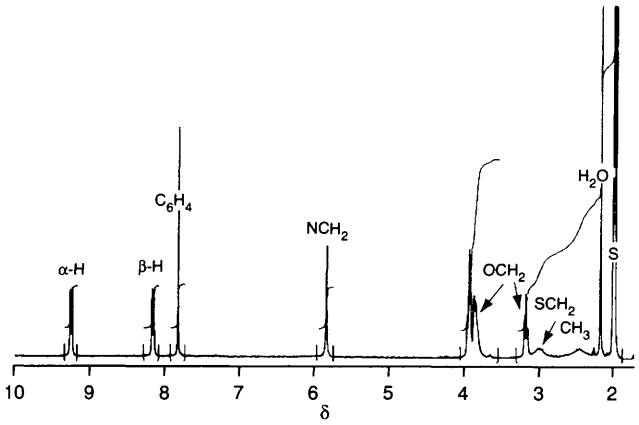


Fig. 1 250 MHz ^{1}H NMR spectrum of **9**.4PF$_6$ in CD$_3$CN at room temp.

giving **9**.4PF$_6$ as a blue solid after anion exchange with saturated NH$_4$PF$_6$ solution.

Catenane **9**.4PF$_6$ was characterized by electrospray mass spectrometry, which exhibited ion peaks at m/z = 1160, 725 and 508, corresponding to $[M - 2PF_6]^{2+}$, $[M - 3PF_6]^{3+}$ and $[M - 4PF_6]^{4+}$, respectively. The configuration of **9**.4PF$_6$ was inferred from its ^{1}H NMR spectrum (Fig. 1). The α- and β-protons of the pyridiniums showed two doublet signals at δ 9.24 and 8.15, respectively, while the methylene and phenylene protons in the tetracyclic cation showed two separate singlets at δ 5.84 and 7.81, respectively, thereby confirming its *cis*-configuration and D_{2h} symmetry. The SCH$_3$ and SCH$_2$ protons exhibited broad signals at δ 2.46 and 2.98, respectively, implying a folded conformation of the glycol chains due to the interactions between the two peripheral TTF units and the π-electron deficient bipyridiniums. As expected,[4] **9**.4PF$_6$ did not isomerize in solution in the presence of trifluoroacetic acid, thus confirming the observation that the two bipyridinium units, clamping the central TTF unit, efficiently prevent the latter's isomerization.

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Footnotes

† Both macrocycles **5** and **6** are mixtures of *cis/trans* isomers which could not be separated from each other because of their slow isomerization in solution.

‡ All new compounds gave satisfactory analytical and spectral data. *Selected spectral data* for **3**: ^{1}H NMR (CDCl$_3$): δ_H 2.42 (6 H, s), 3.04 (4 H, t), 3.25 (4 H, t), 3.64 (12 H, m) and 3.68 (4 H, t). EIMS: (m/z, %) 844 (M$^+$, 55), 474 (70), 386 (33), 155 (100) and 142 (75). For **5**: ^{1}H NMR (CDCl$_3$): δ_H 2.43 (6 H, s), 2.74 (4 H, m), 3.07 (12 H, m), 3.64 (12 H, m) and 3.71 (4 H, m). PDMS: (m/z) 1027.5 (M$^+$). For **6**: ^{1}H NMR (CDCl$_3$): δ_H 2.43 (12 H, s), 3.02 (16 H, m) and 3.63–3.73 (32 H, m). PDMS: (m/z) 1509.2 (M$^+$) and 756.1 (M$^+$/2). For **9**.4PF$_6$: ^{1}H NMR (CD$_3$CN): δ_H 2.46 (12 H, w, SCH$_3$), 2.98 (8 H, w, SCH$_2$), 3.17 (4 H, t, OCH$_2$), 3.86 (16 H, m, OCH$_2$), 3.93 (16 H, m, OCH$_2$), 5.84 (8 H, s, NCH$_2$), 7.81 (8 H, s, C$_6$H$_4$), 8.15 [8 H, d, β-H (py)] and 9.24 [8 H, d, α-H (py)].

§ Compound **6** was recovered in 75% yield after workup.

References

1 J. S. Lindsey, *New J. Chem.*, 1991, **15**, 153; G. M. Whitesides, J. P. Mathias and C. T. Seto, *Science*, 1991, **254**, 1312; D. Philp and J. F. Stoddart, *Synlett*, 1991, 445.

2 (*a*) P. L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietrazkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent and D. J. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 193; (*b*) D. B. Amabillino, P. R. Ashton, C. L. Brown, E. Cordova, L. A. Godinez, T. T. Goodnow, A. E. Kaifer, S. P. Newton, M. Pietraszkiewicz, D. Philp, F. M. Rayma, A. S. Reder, J. F. Stoddart and D. J. Williams, *J. Am. Chem. Soc.*, 1995, **117**, 1271; (*c*) C. Dietrich-Buchecker and J.-P. Sauvage, *Bull. Soc. Chim. Fr.*, 1992, **129**, 113; (*d*) J.-C. Chambron, V. Heitz and J.-P. Sauvage, *Bull. Soc. Chim. Fr.*, 1995, **132**, 340; (*e*) C. A. Hunter, *J. Am. Chem. Soc.*, 1992, **114**, 5303; (*f*) M. J. Gunter, D. C. R. Hockless, M. R. Johnston, B. W. Skelton and A. H. White, *J. Am. Chem. Soc.*, 1994, **116**, 4810.

3 P. R. Ashton, R. Ballardini, V. Balzani, M. Blower, M. Ciano, M. T. Gandoni, L. Prodi, C. H. McLean, D. Philp, N. Spencer, J. F. Stoddart and M. S. Tolley, *New J. Chem.*, 1993, **17**, 689; P. R. Ashton, R. Ballardini, V. Balzani, M. T. Gandolfi, D. J.-F. Marquis, L. Péres-Gárcia, L. Prodi, J. F. Stoddart and M. Venturi, *J. Chem. Soc., Chem. Commun.*, 1994, 177; F. Vögtle, W. M. Müller, M. Bauer, K. Rissanen, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1295; M. Bauer, W. M. Müller, U. Müller, K. Rissanen and F. Vögtle, *Liebigs Ann. Chem.*, 1995, 649; D. B. Amabilino, P. R. Ashton, M. S. Tolley, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1297; P. R. Ashton, L. Péres-Gárcia, J. F. Stoddart, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 571.

4 Z.-T. Li, P. C. Stein, N. Svenstrup, K. H. Lund and J. Becher, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2524.

5 N. Svenstrup, K. M. Rasmussen, T. K. Hansen and J. Becher, *Synthesis*, 1994, 809.

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