1978, *17*, 106; G. R. Stevenson in *Molecular Structure and Energetics* (Eds.: J. F. Liebman, A. Greenberg), VCH, New York **1986**, p. 57; *Aromaticity and Antiaromaticity* (Ed.:V. I. Minkin, M. N. Glukhovtsev, B. Y. Simkin), Wiley, New York, **1994**, p. 243. "Aromaticity" in inorganic rings: P. von R. Schleyer, H. Jiao, N. J. R. van Eikema-Hommes, V. G. Malkin, O. L. Malkina, *J. Am. Chem. Soc.* **1997**, *119*, 12669, and references therein.

[16] In an ene/diazene[17] with a structure very similar to that of the bisdiazene **5** (one N–N double bond is replaced by a C–C double bond), after one-electron reduction the spin density remains more strongly localized in the diazene unit (according to calculations:[12] $\rho(\mathrm{N{=}N}) = 0.765$; $\rho(\mathrm{C{=}C}) = 0.168$; ^{14}N hyperfine coupling constant: 0.71/0.77 mT).[2]

[17] W. Berning, S. Hünig, F. Prokschy, *Chem. Ber.* **1984**, *117*, 1455.

Self-Assembling Supramolecular Daisy Chains**

Peter R. Ashton, Ian W. Parsons, Françisco M. Raymo, J. Fraser Stoddart,* Andrew J. P. White, David J. Williams,* and Reinhard Wolf

The design and synthesis of supramolecular polymers[1] is one of the major goals of contemporary supramolecular chemistry.[2] Hydrophobic bonding, hydrogen bonding, and metal coordination have all been used[1] successfully to self-assemble[3] supramolecular polymers in solution and in the solid state. We have devised a self-assembling approach to supramolecular polymer formation (Figure 1) which relies upon the self-complementarity of monomers incorporating a π electron rich macrocyclic "head" and a π electron deficient acyclic "tail" that are unable to interact intramolecularly.[4] Cyclic and/or linear oligomers, self-assemble spontaneously in solution by the insertion of the tail of one monomer through the cavity within the head of another. The driving forces responsible for this recognition event are [C-H⋯O] hydrogen bonds augmented by π–π stacking interactions between the complementary π electron deficient and π electron rich recognition sites. Here, we report a) the syntheses of four different self-complementary monomers, b) the spectroscopic evidence for their self-assembly to afford supramolecular oligomers in solution, and c) the X-ray crystal structure of a homodimeric cyclic supermolecule formed when one of the monomers crystallizes from solution.

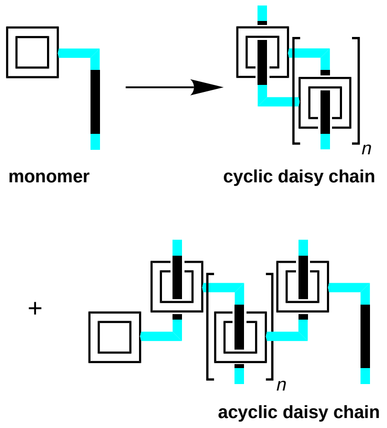

Figure 1. Cyclic and acyclic daisy chains which can be formed by a self-complementary monomer unit.

The four monomers $\mathbf{6}\cdot 2\mathrm{PF_6}$–$\mathbf{9}\cdot 2\mathrm{PF_6}$ (Figure 2) were synthesized[5] as illustrated in Scheme 1. Reaction of *N*-methyl-4,4′-pyridylpyridinium hexafluorophosphate with the macrocyclic polyether **1** gave $\mathbf{6}\cdot 2\mathrm{PF_6}$ in a yield of 14% after counterion exchange. Reaction of 4,4′-bipyridine with the macrocyclic polyethers **2** and **3**, followed by the alkylation of the resulting hexafluorophosphate salts $\mathbf{4}\cdot\mathrm{PF_6}$ and $\mathbf{5}\cdot\mathrm{PF_6}$ with methyl iodide or benzyl chloride, gave the self-complemen-

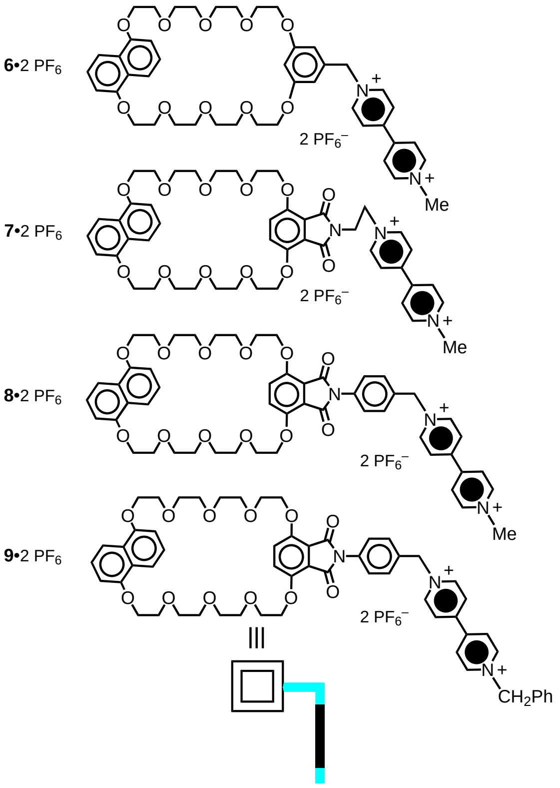

Figure 2. The self-complementary monomers $\mathbf{6}\cdot 2\mathrm{PF_6}$–$\mathbf{9}\cdot 2\mathrm{PF_6}$.

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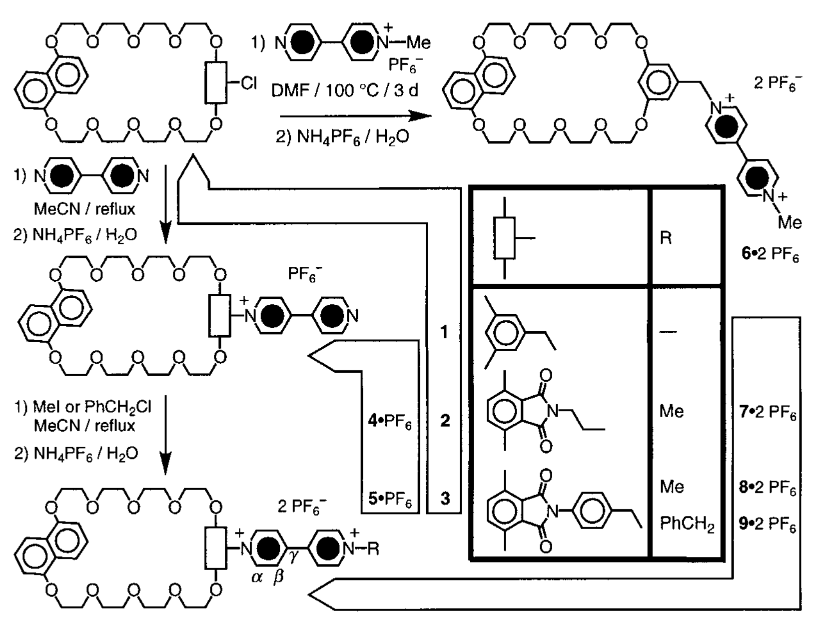

Scheme 1. Synthesis of the bis(hexafluorophosphate) salts $\mathbf{6}\cdot 2PF_6$–$\mathbf{9}\cdot 2PF_6$.

tary monomers $\mathbf{7}\cdot 2PF_6$, $\mathbf{8}\cdot 2PF_6$, and $\mathbf{9}\cdot 2PF_6$ in yields of 82, 91, and 60%, respectively, after counterion exchange.

The liquid secondary ion (LSI) mass spectra of the bis(hexafluorophosphate) salts $\mathbf{6}\cdot 2PF_6$–$\mathbf{9}\cdot 2PF_6$ revealed the formation of oligomeric supermolecules (Table 1). The LSI mass spectra of $\mathbf{6}\cdot 2PF_6$–$\mathbf{9}\cdot 2PF_6$ show peaks for the tetrameric, trimeric, and dimeric supermolecules corresponding to the loss of one or more hexafluorophosphate counterions. In addition, signals for $[M-PF_6]^+$ and $[M-2PF_6]^+$, corresponding to the loss of one and two hexafluorophosphate counterions, respectively, from the monomers, are also observed. In the case of $\mathbf{6}\cdot 2PF_6$ and $\mathbf{7}\cdot 2PF_6$, the LSI mass spectra show peaks for $[5M-3PF_6]^+$ corresponding to the loss of three hexafluorophosphate counterions from the pentameric supermolecules.

The ^1H NMR spectra of $\mathbf{6}\cdot 2PF_6$–$\mathbf{9}\cdot 2PF_6$ in CD_3CN at 25 °C show time-averaged signals for species with different degrees of aggregation in solution. Significant changes in the chemical shift are observed[6] upon varying the concentrations from 2.5×10^{-2} to 2.5×10^{-4} M. The broad resonances observed at high concentrations shift to lower fields and become sharp and well-resolved upon dilution. The changes in the δ values are particularly evident (up to $\Delta\delta = +0.5$) for the protons in the β-positions on the bipyridinium units. Shifts to lower field and broadening of most of the resonances are also observed in the ^{13}C NMR spectra of $\mathbf{6}\cdot 2PF_6$–$\mathbf{9}\cdot 2PF_6$ in CD_3CN upon increasing the temperature from 0 to 70 °C. The changes in the δ values are particularly evident (up to $\Delta\delta = +10$) for the γ-carbon atoms of the bipyridinium units.

The absorption UV/Vis spectra of $\mathbf{6}\cdot 2PF_6$–$\mathbf{9}\cdot 2PF_6$, recorded in MeCN at 25 °C, show strong charge-transfer bands in the visible region ($\lambda_{max} \approx 470$ nm) arising from the donor–acceptor interactions between the bipyridinium units and the complementary π electron rich aromatic units. In all cases, the presence of several oligomeric supermolecules in solution led to nonlinear correlations between λ_{max} and the concentration over the range 2.5×10^{-2} to 2.5×10^{-4} M.

One of the self-complementary monomers—namely, $\mathbf{6}\cdot 2PF_6$—produced orange single crystals from a benzene/MeCN solution. X-Ray structural analysis[7] on one of these crystals (Figures 3 and 4) reveals that, in the solid state, pairs of $\mathbf{6}^{2+}$ dications interweave with each other to form a C_2-symmetric homodimeric pair.[8] The bipyridinium unit appended to the macrocyclic polyether

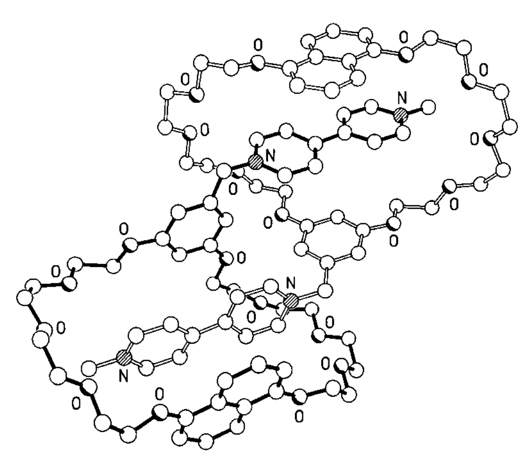

Figure 3. Ball-and-stick representation of the dimeric $\mathbf{6}^{2+}$ complex in the solid state.

Table 1. LSI-MS data for the bis(hexafluorophosphate) salts $\mathbf{6}\cdot 2PF_6$–$\mathbf{9}\cdot 2PF_6$.[a]

Compound	Pentamer	Tetramer				Trimer				Dimer			Monomer	
	$5M-$	$4M-$				$3M-$				$2M-$			$M-$	
	$3PF_6$	PF_6	$2PF_6$	$3PF_6$	$4PF_6$	PF_6	$2PF_6$	$3PF_6$	$4PF_6$	PF_6	$2PF_6$	$3PF_6$	PF_6	$2PF_6$
$\mathbf{6}\cdot 2PF_6$[b]	4868	4098	3953	3807	–	3037	2892	2747	–	1976	1831	1686	915	770
$\mathbf{7}\cdot 2PF_6$[c]	5285	4430	4284	–	–	3285	3142	–	–	2143	1998	1851	998	853
$\mathbf{8}\cdot 2PF_6$	–	4679	4534	4388	4242	3473	3328	3183	–	2267	2122	1977	1060	915
$\mathbf{9}\cdot 2PF_6$	–	4982	4837	4692	4546	3701	3556	3410	3265	2419	2274	2128	1136	991

[a] LSI mass spectra were obtained from a VG Zabspec mass spectrometer equipped with a 35-keV cesium ion gun. Samples were dissolved in either a 3-nitrobenzyl alcohol or 2-nitrophenyloctyl ether matrix previously coated on to a stainless steel probe tip. The m/z values reported correspond to the centroids of the isotopic distributions of monocationic species in all cases. M is the mass of the monomeric bis(hexafluorophosphate) salt. [b] Signals for $[3M+Na]^+$, $[2M]^+$, $[M+Na]^+$, and $[M]^+$ at m/z values of 3205, 2122, 1084, and 1061, respectively, were also observed. [c] Signals for $[4M+Na]^+$, $[3M+Na]^+$, $[2M+Na]^+$, and $[M+Na]^+$ at m/z values of 4597, 3454, 2311, and 1166, respectively, were also observed.

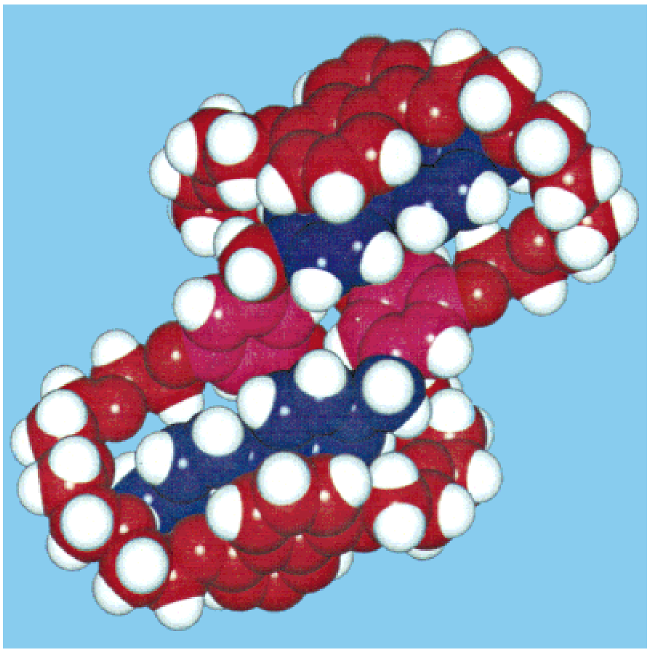

Figure 4. Space-filling representation of the dimeric $\mathbf{6}^{2+}$ complex in the solid state; red: the macrocyclic "head", blue: the acyclic "tail", magenta: the resorcinol unit connecting the two.

of one dication is inserted through the center of the macrocyclic polyether of another, and vice versa, and sandwiched between the resorcinol and 1,5-dioxynaphthalene ring systems. One of the pyridinium rings of the dication is oriented orthogonally to the resorcinol ring of the macrocyclic polyether. This "edge-to-face" geometry results in a marked distortion in the external angles at the C-5 position on the resorcinol ring of about $\pm 6°$; a deformation directly analogous to that observed[9] in diphenyl ethers. Intracomplex stabilization is achieved by $\pi-\pi$ stacking between the bipyridinium ring systems and their sandwiching π electron rich aromatic ring systems.[10] Further complex stabilization is achieved through the cooperative effect of ten [C-H···O] hydrogen bonds. There is an absence of any extended intercomplex interactions, presumably as a result of the inclusion of significant amounts of solvent into the lattice.

Although one of the four plerotopic monomers we have investigated with self-complementary donor–acceptor recognitions sites crystallizes to form [*c*2]daisy chain[11] supermolecules, presumably under kinetic control, there is overwhelming evidence, in the case of two of the monomers, for the existence under thermodynamic control of daisy chain supermolecules containing up to at least five repeating units in solution. This observation is encouraging in the face of the challenge to synthesize acyclic [$a\infty$]daisy chain supermolecules en route to the preparation of mechanically interlocked polymers in the shape of macromolecular daisy chains.

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[1] a) J.-M. Lehn, *Makromol. Chem. Macromol. Symp.* **1993**, *69*, 1–17; b) G. Li, L. McGown, *Science* **1994**, *264*, 249–250; c) G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen, D. M. Gordon, *Acc. Chem. Res.* **1995**, *28*, 37–44; d) P. Blandon, A. C. Griffin, *Macromolecules* **1995**, *28*, 4116–4121; e) J. L. Sessler, A. Andrievsky, P. A. Gale, V. Lynch, *Angew. Chem.* **1996**, *108*, 2954–2957; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2782–2785; f) A. Zanotti-Gerosa, E. Solari, L. Giannini, A. Chiesa-Villa, C. Rizzoli, *Chem. Commun.* **1996**, 119–120; g) M. Dimitrius, A. Terzius, A. W. Coleman, C. de Rango, *Carbohydr. Res.* **1996**, *282*, 125–135; h) R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, *Science* **1997**, *278*, 1601–1604; i) F. M. Raymo, J. F. Stoddart, *Curr. Opin. Coll. Interf. Sci.* **1998**, *3*, 150–159; for an account of "the first polymeric inclusion compound formed from a single species acting both as a guest and a host" in the form of a β-cyclodextrin derivative, see j) K. Hirotsu, T. Higuchi, K. Fujita, T. Ueda, A. Shinoda, T. Imoto, I. Tabushi, *J. Org. Chem.* **1982**, *47*, 1143–1144.

[2] a) F. Vögtle, *Supramolecular Chemistry*, Wiley, New York, **1991**; b) J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**; c) *Comprehensive Supramolecular Chemistry* (Ed.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle), Pergamon, Oxford, **1996**.

[3] a) J.-M. Lehn, *Angew. Chem.* **1990**, *102*, 1347–1362; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304–1319; b) J. S. Lindsey, *New J. Chem.* **1991**, *15*, 153–180; c) G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312–1319; d) D. S. Lawrence, T. Jiang, M. Levett, *Chem. Rev.* **1995**, *95*, 2229–2260; e) D. Philp, J. F. Stoddart, *Angew. Chem*. **1996**, *108*, 1242–1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154–1196; f) S. C. Zimmerman, F. W. Zeng, D. E. C. Reichert, S. V. Kolotuchin, *Science* **1996**, *271*, 1095–1098; g) M. C. T. Fyfe, J. F. Stoddart, *Acc. Chem. Res.* **1997**, *30*, 393–401; h) R. E. Gillard, F. M. Raymo, J. F. Stoddart, *Chem. Eur. J.* **1997**, *3*, 1933–1940; i) M. M. Conn, J. Rebek, Jr., *Chem. Rev.* **1997**, *97*, 1647–1668; j) B. Linton, A. D. Hamilton, *ibid.* **1997**, *97*, 1669–1680; k) S. I. Stupp, V. LeBonheur, K. Walker, L. S. Li, K. E. Huggins, M. Keser, A. Amstutz, *Science* **1997**, *276*, 384–389; l) V. Percec, C. H. Ahn, G. Ungar, *Nature* **1998**, *391*, 161–164.

[4] For examples of intramolecular complexes formed by the insertion of the "tail" of a molecule through the cavity of its own "head", see a) S. Shinkai, M. Ishihara, K. Ueada, *J. Chem. Soc. Perkin Trans. 2* **1995**, 511–518; b) R. Corradini, A. Dossena, R. Marchelli, A. Panagia, G. Sartor, M. Saviano, A. Lombardi, V. Pavone, *Chem. Eur. J.* **1996**, *6*, 373–381; c) 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, D. J. Williams, *ibid.* **1997**, *3*, 152–170.

[5] For the experimental procedures for the synthesis of **1**–**9**·2PF$_6$ and of their precursors, see the supporting information. The yields, melting points, and some selected spectroscopic data (UV/Vis: MeCN, 25 °C; ^{1}H and ^{13}C NMR: 300 and 75.5 MHz, respectively, CD$_3$CN, 25 °C; high-resolution (HR) mass spectrometry: LSIMS): **6**·2PF$_6$: yield 14%; m.p. 270 °C (decomp); UV/Vis (2.01×10^{-3} M): λ_{max} (ε) = 482 nm (180); HR-MS: calcd for ($C_{44}H_{54}F_6N_2O_{10}P$) [$M-PF_6$]$^+$: 915.3420, found: 915.3486; ^{1}H NMR (1.88×10^{-2} M): δ = 8.78 (m, 4H), 7.98 (d, ^{3}J = 7 Hz, 2H), 7.94 (d, ^{3}J = 7 Hz, 2H), 7.52 (d, ^{3}J = 8 Hz, 2H), 7.18 (t, ^{3}J = 8 Hz, 2H), 6.68 (d, ^{3}J = 8 Hz, 2H), 6.34 (s, 2H), 5.93 (s, 1H), 5.62 (s, 2H), 4.42 (s, 3H), 4.08–4.13 (m, 4H), 3.88–3.92 (m, 4H), 3.70–3.76 (m, 8H), 3.60–3–68 (m, 8H), 3.50–3.60 (m, 8H); ^{13}C NMR ($1.88 - 10^{-2}$ M): δ = 161.6, 155.0, 149.7, 148.9, 147.5, 146.6, 135.7, 127.3, 127.1, 126.9, 126.6, 115.0, 108.6, 106.9, 102.1, 71.5, 71.4, 71.4, 70.5, 70.3, 69.2, 68.9, 65.2, 49.5. **7**·2PF$_6$: yield 82%; m.p. 270 °C (decomp); UV/Vis (1.25×10^{-3} M): λ_{max} (ε) = 473 nm (87); HR-MS: calcd for ($C_{47}H_{55}F_6N_3O_{12}P$) [$M-PF_6$]$^+$: 998.3428, found: 998.3384; ^{1}H NMR (1.60×10^{-2} M): δ = 8.80 (d, ^{3}J = 6 Hz, 2H), 8.65 (d, ^{3}J = 6 Hz, 2H), 7.96 (d, ^{3}J = 6 Hz, 2H), 7.90 (d, ^{3}J = 6 Hz, 2H), 7.59 (d, ^{3}J = 8 Hz, 2H), 7.19 (t, ^{3}J = 8 Hz, 2H), 6.92 (s, 2H), 6.71 (d, ^{3}J = 8 Hz, 2H), 4.64 (t, ^{3}J = 5 Hz, 2H), 4.40 (s, 3H), 4.13 (m, 4H), 3.88–4.03 (m, 10H), 3.58–3.77 (m, 20H); ^{13}C NMR (1.60×10^{-2} M): δ = 166.5, 155.2, 151.0, 147.3, 147.0, 127.7, 127.4, 127.3, 126.4, 123.4, 115.1, 106.9, 71.4, 71.4, 71.3, 70.5, 70.4, 70.0, 69.2, 49.6, 49.1, 38.7. **8**·2PF$_6$: yield 91%; m.p. 270 °C (decomp); UV/Vis (1.30×10^{-2} M): λ_{max} (ε) = 466 nm (245); HR-MS: calcd for ($C_{52}H_{57}N_3O_{12}$) [$M-2PF_6$]$^+$: 915.3942, found: 915.3949; ^{1}H

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NMR (2.50×10^{-2} M): 8.85 (brs, 2H), 8.69 (brs, 2H), 7.90 (brs, 2H), 7.83 (brs, 2H), 7.69 (brd, $^3J = 7$ Hz, 2H), 7.32–7.50 (m, 4H), 7.11 (brt, $^3J = 7$ Hz, 2H), 6.83 (s, 2H), 6.64 (brd, $^3J = 7$ Hz, 2H), 5.93 (brs, 2H), 4.41(brs, 3H), 4.05 (brs, 4H), 3.89 (brs, 8H), 3.60–3.80 (m, 20H); ^{13}C NMR (2.50×10^{-2} M): $\delta = 154.9$, 150.8, 148.1, 147.2, 146.4, 142.3, 141.6, 134.6, 132.4, 131.5, 129.2, 127.0, 126.6, 126.5, 122.9, 114.9, 106.8, 71.5, 71.2, 70.5, 70.4, 70.2, 69.2, 64.9, 49.6. **9**$\cdot 2PF_6$: yield 60%; m.p. 270 °C (decomp); UV/Vis (1.60×10^{-2} M): λ_{max} (ε) = 472 nm (255); HR-MS: calcd for ($C_{98}H_{61}F_6N_3O_{12}P$) $[M - PF_6]^+$: 1136.3897, found: 1136.3885; ^{1}H NMR: (1.58×10^{-2} M): $\delta = 8.88$ (d, $^3J = 7$ Hz, 2H), 8.60 (d, $^3J = 7$ Hz, 2H), 8.27 (d, $^3J = 7$ Hz, 2H), 7.74 (brd, $^3J = 5$ Hz, 2H), 7.63 (d, $^3J = 8$ Hz, 2H), 7.54 (d, $^3J_{AB} = 8$ Hz, 2H), 7.50–7.40 (m, 5H), 7.36 (d, $^3J_{AB} = 8$ Hz, 2H), 7.20 (t, $^3J = 8$ Hz, 2H), 6.95 (s, 2H), 6.75 (d, $^3J = 8$ Hz, 2H), 5.78 (s, 2H), 5.10 (s, 2H), 4.15 (t, $^3J = 4$ Hz, 4H), 4.03 (t, $^3J = 4$ Hz, 4H), 3.90 (t, $^3J = 4$ Hz, 4H), 3.77 (t, $^3J = 4$ Hz, 4H), 3.59–3.72 (m, 16H); ^{13}C NMR (1.58×10^{-2} M): $\delta = 165.5$, 155.0, 151.0, 150.0, 146.5, 146.4, 134.7, 133.5, 132.7, 131.2, 131.1, 130.6, 130.4, 129.2, 127.8, 127.8, 127.2, 126.5, 123.0, 71.4, 70.4, 70.4, 70.1, 69.1, 65.8, 65.1.

[6] For tables listing the chemical shifts of selected resonances observed in the ^{1}H NMR spectra of **6**$\cdot 2PF_6$–**9**$\cdot 2PF_6$ at various concentrations, see the supporting information.

[7] Crystal data for **6**$\cdot 2PF_6$: $C_{44}H_{54}N_2O_{10} \cdot 2PF_6 \cdot 4PhH \cdot 0.5MeCN$, $M_r = 1393.8$, monoclinic, space group $C2/c$ (no. 15), $a = 22.497(5)$, $b = 17.912(4)$, $c = 34.814(10)$ Å, $\beta = 103.67(2)°$, $V = 13632(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.358$ g cm^{-3}, $\mu(Cu_{K\alpha}) = 13.8$ cm^{-1}, $F(000) = 5832$, $T = 213$ K. An orange block of dimensions $0.40 \times 0.40 \times 0.27$ mm was used for the data collected, and 3477 independent reflections were measured on a Siemens P4/RA diffractometer with $Cu_{K\alpha}$ radiation (graphite monochromator) and ω-scans. The structure was solved by direct methods. On account of a shortage of observed data, only the oxygen and nitrogen atoms of the ordered portions of the cyclophane were refined anisotropically—the carbon atoms, and all of the non-hydrogen atoms of the disordered section of one of the polyether arms (for which two partial occupancy orientations were identified), were refined isotropically. The aromatic rings were refined as idealized rigid bodies. The hexafluorophosphate counterions were disordered, and in each case two partial-occupancy orientations were identified with only the atoms of the major-occupancy orientations being refined anisotropically. The included benzene solvent molecules were distributed over a mixture of full- and partial-occupancy sites, and they were refined isotropically as idealized rigid bodies. The 50% occupancy MeCN molecule was refined isotropically. Refinement was by full matrix least-squares based on F^2 to give $R_1 = 0.114$ and $wR_2 = 0.305$ for 2202 independent observed reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 106°$) and 496 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101199. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] For a recent example of a cyclic homodimeric complex held together primarily by [N$^+$-H ⋯ O] and [C-H ⋯ O] hydrogen bonding, see P. R. Ashton, I. Baxter, S. J. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 1344–1347; *Angew. Chem. Int. Ed.* **1998**, *37*, 1294–1297.

[9] H. M. Colquhoun, C. A. O'Mahoney, D. J. Williams, *Polymer* **1993**, *34*, 218–221.

[10] The mean interplanar separation between the bipyridinium unit and the 1,5-dioxynaphthalene and resorcinol ring systems are 3.42 and 3.56 Å, respectively, and the N ⋯ N vector of the bipyridinium unit is inclined by 25° to the $OC_{10}H_6O$ axis of the 1,5-dioxynaphthalene ring system.

[11] We describe daisy chain arrays and assemblies as being acyclic [*a*] or cyclic [*c*] and use these two letters, along with numbers in the conventional manner, to define the nature and repeating unit, respectively, present in a particular supramolecular array or molecular assembly.[8] Note that only [*c*]daisy chains experience maximal (recognition) site occupancy (ref. [2b], p. 182–183) and that small [*c*]daisy chains (supermolecules) are also favored entropically with respect to large [*a*]daisy chains (supramolecular arrays).

Pt^{II}-Directed Self-Assembly of a Dinuclear Cyclophane Containing Two Fullerenes[**]

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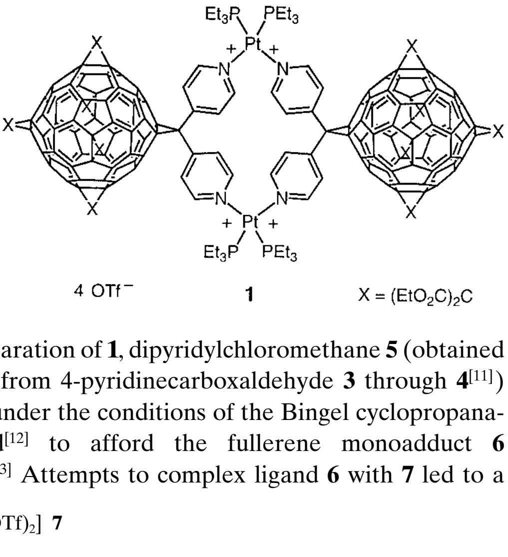
In order to develop fullerene-containing supramolecular assemblies and advanced materials,[1] C_{60} has been incorporated into multicomponent molecular systems such as rotaxanes,[2] catenanes,[3] and oligopyridine Ru^{II} complexes.[4] The properties of these C_{60} hybrids are encouraging and have generated our interest in the construction of even more complex two- and three-dimensional systems. To achieve this objective, we wished to take advantage of the self-assembly of multidentate ligand precursors with transition metal centers[5] which, in the hands of Fujita,[6] Stang,[7, 8] and others,[9] has led to the formation of some spectacular molecular architectures consisting of multinanometer-sized polynuclear molecular squares and three-dimensional molecular objects.[10] Here, we report the synthesis and X-ray crystal structure of the fullerene-containing rigid dinuclear cyclophane **1** which is obtained by self-assembly of the novel fullerene ligand **2** with Pt^{II} centers.



4 OTf$^-$ **1** X = $(EtO_2C)_2C$

In the preparation of **1**, dipyridylchloromethane **5** (obtained in two steps from 4-pyridinecarboxaldehyde **3** through **4**[11]) was treated under the conditions of the Bingel cyclopropanation method[12] to afford the fullerene monoadduct **6** (Scheme 1).[13] Attempts to complex ligand **6** with **7** led to a

[*cis*-$Pt(PEt_3)_2(OTf)_2$] **7**

black, completely insoluble precipitate. In order to solubilize the expected complex, we prepared the yellow C_{2v}-symmetrical fullerene hexakis-adduct **2**[14] (m.p. > 270 °C) using the

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