

One-step syntheses of very large cage-type molecules from aromatic sub-units†

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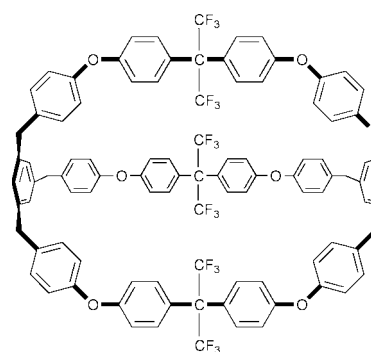
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Polycondensation of a trifunctional, ketone-activated fluoroarene with bis- or tris-phenoxides under *pseudo*-high dilution conditions affords a series of very large macro-polycyclic aromatic ether ketones; isolation and characterisation of these materials by NMR, MALDI-TOF MS and, for one example (after reduction of the carbonyl groups to methylene linkages) by X-ray crystallography, confirms that polycondensations which would normally lead to highly branched or cross-linked polymers can also give rise to large, closed-network molecules.

The synthetic and structural relationships between linear aromatic polymers and their macrocyclic homologues have been intensively investigated over the past decade,¹ work focusing mainly on the potential of macrocyclic ring-opening polymerisation for reactive fabrication of linear polymers. The reverse reaction—ring closing depolymerisation—has however also been explored for application in the recovery and recycling

of high-value condensation polymers.² Macrocyclic aromatic oligo-amides are, in addition, of considerable value for the generation of novel supramolecular architectures including



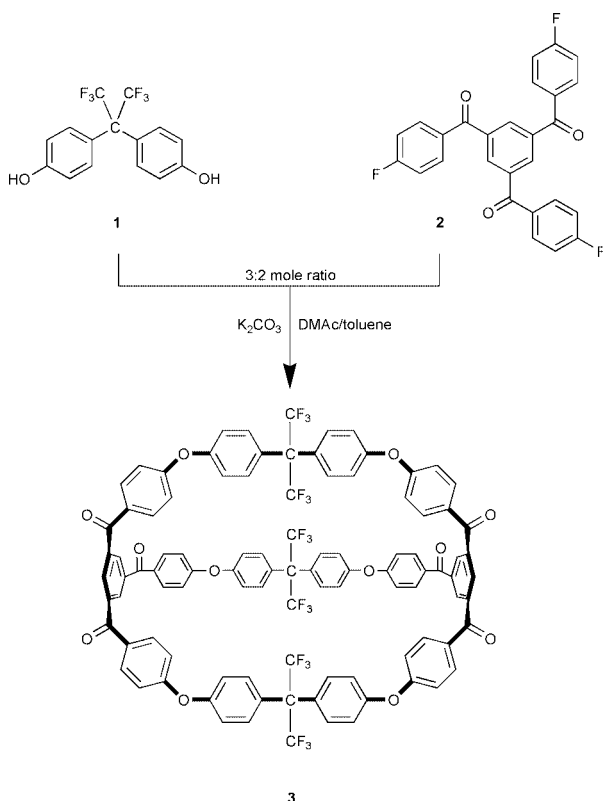
4 (X = CH₂), 5 (X = CO)

catenanes,³ rotaxanes,⁴ and knots.⁵ We now describe some preliminary experiments which demonstrate that the ring-chain relationship can be extended to a third dimension. Thus, polycondensations involving trifunctional monomers, which would normally afford highly branched or even fully cross-linked polymers, are here shown also to give, under *pseudo*-high dilution conditions, a series of very large aromatic cage-type molecules.⁶

Reaction of 4,4'-hexafluoroisopropylidenediphenol (**1**) with 1,3,5-tris(4-fluorobenzoyl)benzene (**2**) was carried out by slow addition of a solution of the two monomers (3:2 mole ratio) in dimethylacetamide (DMAc) to potassium carbonate in refluxing DMAc-toluene, with continuous azeotropic removal of water (Scheme 1). A complex mixture of oligomeric and polymeric materials was obtained but the macrobicyclic cage-compound **3** (mp 450 °C) could be isolated straightforwardly from this mixture, albeit in low yield (~5%), by column chromatography.

Spectroscopic analyses of **3** by MALDI-TOF MS and by ¹H and ¹³C NMR were entirely consistent with the structure shown in Scheme 1, but efforts to obtain single crystals suitable for X-ray analysis were unsuccessful. However, reduction of the carbonyl groups in **3** to methylene linkages using triethylsilane and trifluoroacetic acid (Scheme 1)⁷ afforded the fully-reduced cage-compound **4** (42% yield), together with a compound (**5**) in 21% yield in which one ketone group remains unreduced.† Compounds **4** and **5** were readily separated by column chromatography, and **4** eventually yielded crystals suitable for X-ray analysis.‡ Its structure is shown in Fig. 1, from which it is evident that the composition and topology proposed for this compound (and thus by inference for **3**) are correct.

The molecule adopts a semi-collapsed and flattened conformation with no obvious intramolecular interactions other than a weak π-stacking arrangement between a pair of aromatic ether-containing ring systems in the two adjacent arms of the



Scheme 1

† Electronic supplementary data (ESI) available: analytical and spectroscopic data for compounds **3–5** and **8**. See <http://www.rsc.org/suppdata/cc/b1/b108124c/>

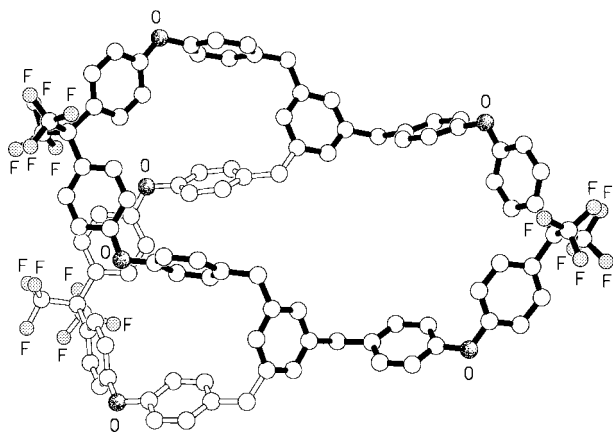
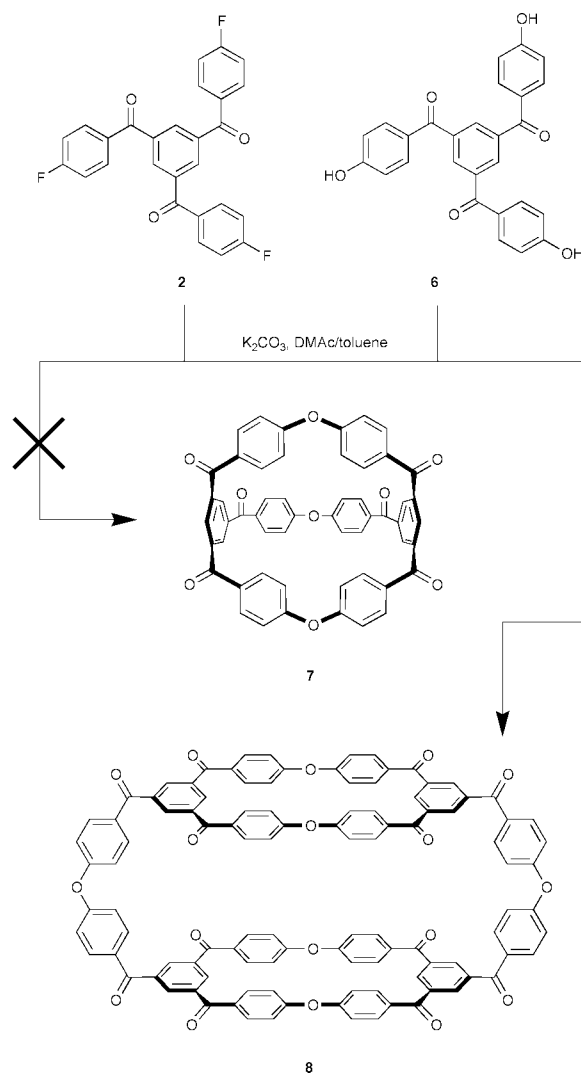


Fig. 1 Molecular structure of the reduced cage-compound **4** (hydrogen atoms are omitted for clarity).

macrocycle. The hexafluoroisopropylidene-linked aromatic residues here display a consistently skewed conformation, but the diarylene-ether units have geometries that range from symmetrically-skewed to near-orthogonal.



Scheme 2

An analogous polycondensation between the trifluoro-compound **2** and tris-phenol **6** (derived from **2** by hydrolysis with potassium hydroxide in DMSO) afforded not the expected cage-compound **7**—a direct analogue of **3**—but its macrotricyclic dimer **8** (Scheme 2). This compound was isolated in pure form by column chromatography (4% yield) and characterised in detail.[†] It shows a sharp, clearly-defined melting point by DSC at the astonishingly high temperature of 556 °C, reflecting both extreme rigidity of the molecular structure and a quite remarkable thermal stability. The MALDI-TOF spectrum of the original product mixture showed a strong $[M + Na]^+$ peak for compound **8**, but gave no evidence for the monomeric cage **7**. The MALDI-TOF analysis did however indicate the presence of higher polycyclic oligomers of **7**, including the macro-polycyclic trimer and tetramer. Evidence to date, mainly from the 1H NMR spectra of partially-resolved chromatographic fractions, suggests that the higher-order polycyclic oligomers of **7** comprise increasing numbers of the structural repeat (a six-ring macrocycle with a two-ring linking unit) found in oligomer **8**.

This approach to large, closed-network molecules is clearly not restricted to the aromatic polyetherketone systems described here, but should be generally applicable to *any* type of branching polycondensation, including esterification, amidation and imidation. Such possibilities are currently under investigation, as are the potential applications of these molecules in supramolecular assembly and in cage-opening polymerisation.

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Notes and references

† Crystal data for **4**: $C_{99}H_{66}F_{18}O_6 \cdot 0.75 CH_2Cl_2$, $M_r = 1757.21$, triclinic, $P\bar{1}$, $a = 14.291(3)$, $b = 17.673(4)$, $c = 20.181(3)$ Å, $\alpha = 97.04(2)$, $\beta = 109.61(1)$, $\gamma = 112.31(2)^\circ$, $V = 4255(1)$ Å³, $T = 293$ K, $Z = 2$, D_c 1.371 g cm⁻³, μ (Cu-K α) = 1.371 mm⁻¹, $F(000) = 1803$. Independent measured reflections 11444. $R_1 = 0.077$, $wR_2 = 0.166$ for 5472 independent observed reflections [$2\theta \leq 115^\circ$, $I > 2\sigma(I)$]. CCDC 171849. See <http://www.rsc.org/suppdata/cc/b1/b108124c/> for crystallographic files in .cif format.

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