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

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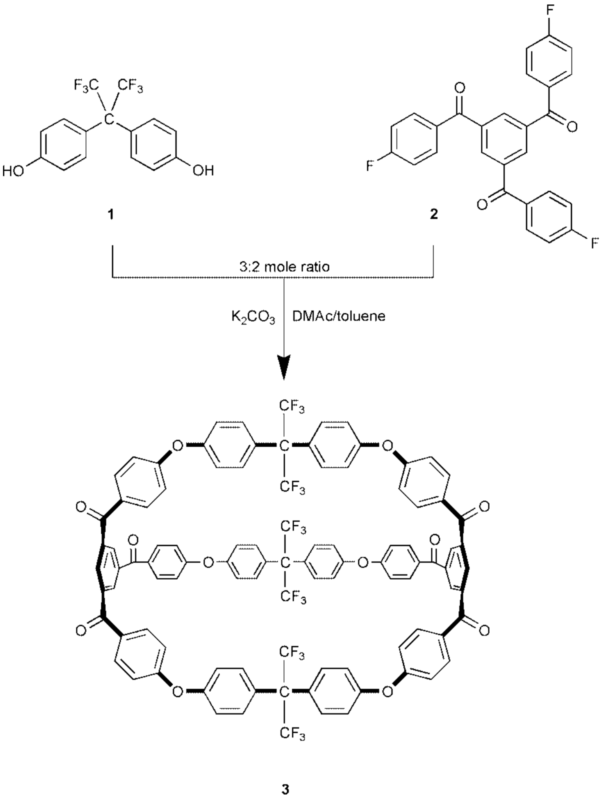
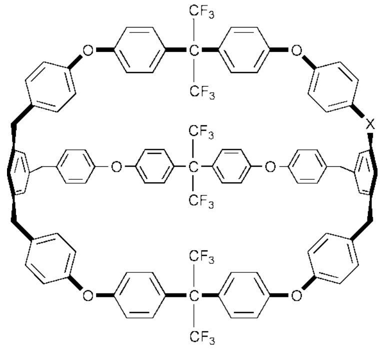
Polycondensation of a trifunctional, ketone-activated fluoroarene with bis- or tris-phenoxides under *pseudo*-high dilution conditions affords a series of very large macropolycyclic aromatic ether ketones; isolation and characterisation of these materials by NMR, MALDI-TOF MS and, for one example (after 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 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]



Scheme 1



4 (X = CH_2), **5** (X = CO)

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 ^{1}H and ^{13}C 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

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

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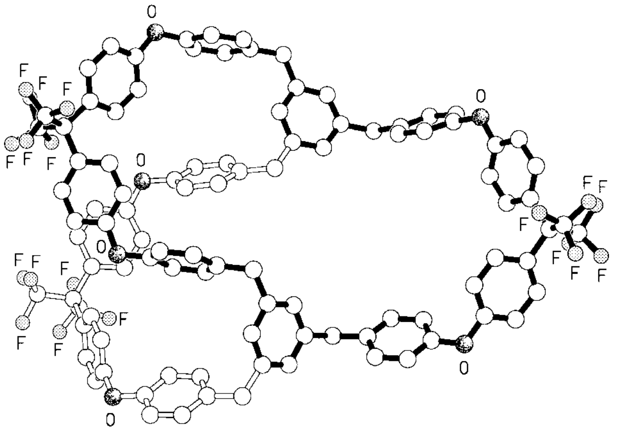
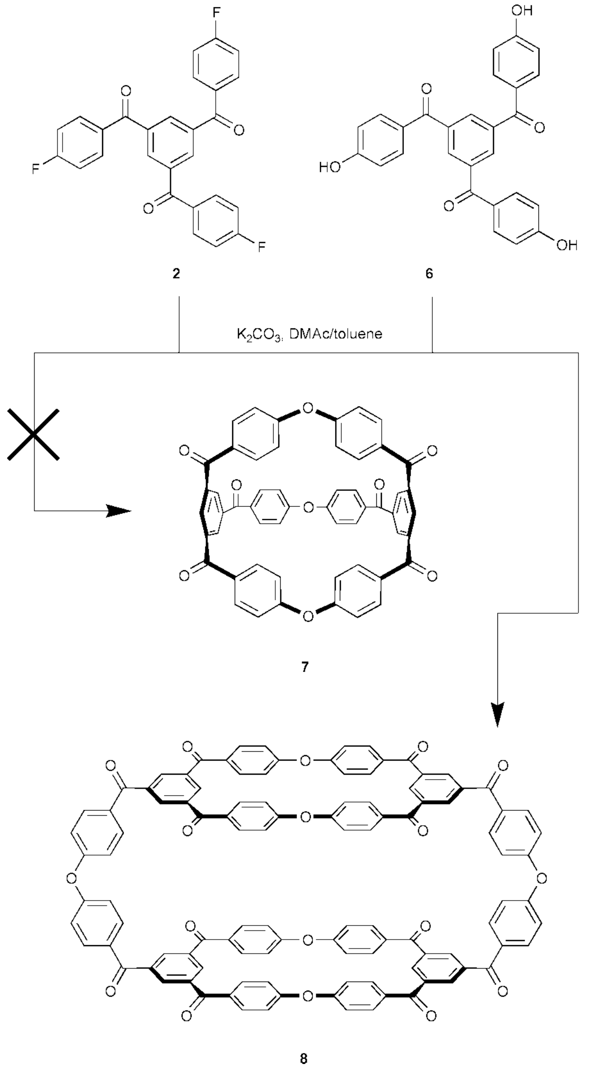


Fig. 1 Molecular structure of the reduced cage-compound **4** (hydrogen atoms are omitted for clarity).

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 macropolycyclic trimer and tetramer. Evidence to date, mainly from the ^{1}H 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 umit) 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.

We thank Professor F. H. Kohnke of the University of Messina for stimulating discussions.

Notes and references

‡ *Crystal data* for **4**: $C_{99}H_{66}F_{18}O_6$.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, α = 97.04(2), β = 109.61(1), γ = 112.31(2)°.V = 4255(1) Å^3, T = 293 K, Z = 2, D_c 1.371 g cm^{-3}, μ(Cu-Kα) = 1.371 mm^{-1}, F(000) = 1803. Independent measured reflections 11444. R_1 = 0.077, wR_2 = 0.166 for 5472 independent observed reflections [$2\theta \leq 115°$, $I > 2\sigma(I)$]. CCDC 171849. See http://www.rsc.org/suppdata/cc/b1/b108124c/ for crystallographic files in .cif format.

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