Supplementary Material

Catechol-based macrocyclic aromatic ether-sulfones: Synthesis, characterization and ring-opening polymerization

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Chart S1: Labelled structures for $^1$H NMR assignments (refer to Experimental Section).
**Figure S1:** $^1$H NMR spectrum of macrocycle 2 (250 MHz, CD$_2$Cl$_2$/CH$_3$SO$_3$H 4/1 v/v).

**Figure S2:** $^{13}$C NMR spectrum of macrocycle 2 (62.5 MHz, CDCl$_3$/CF$_3$CO$_2$H 5/1 v/v). *Note:* the strong quartet resonances centred at 114 and 162 ppm are due to trifluoroacetic acid co-solvent.
Figure S3: MALDI-TOF mass spectrum of macrocycle 2. (Calc. m/z for [C_{60}H_{40}S_{4}O_{12}Na]^+ = 1104.2).
Figure S4: $^1$H NMR spectrum of macrocycle 3 (250 MHz, CD$_2$Cl$_2$/CH$_3$SO$_3$H 4/1 v/v).

Figure S5: $^{13}$C NMR spectrum of macrocycle 3 (62.5 MHz, CD$_2$Cl$_2$/CH$_3$SO$_3$H 4/1 v/v).
Figure S6: MALDI-TOF mass spectrum of macrocycle 3. (Calc. $m/z$ for $[C_{90}H_{60}S_{6}O_{18}Na]^{+} = 1644.8$).
**Figure S7:** $^1$H NMR spectrum of macrocycle 4 (250 MHz, CD$_2$Cl$_2$/CH$_3$SO$_3$H 4/1 v/v).

**Figure S8:** $^{13}$C NMR spectrum of macrocycle 4 (62.5 MHz, CD$_2$Cl$_2$/CH$_3$SO$_3$H 4/1 v/v).
Figure S9: MALDI-TOF mass spectrum of macrocycle 4. (Calc. m/z for \([\text{C}_{120}\text{H}_{80}\text{S}_8\text{O}_{24}\text{Na}]^+ = 2185.4\).)
Figure S10: $^1$H NMR spectrum of macrocycle 5 (250 MHz, CD$_2$Cl$_2$/CH$_3$SO$_3$H 4/1 v/v).

Figure S11: $^{13}$C NMR spectrum of macrocycle 5 (62.5 MHz, CD$_2$Cl$_2$/CH$_3$SO$_3$H 4/1 v/v).
Figure S12: MALDI-TOF mass spectrum of macrocycle 5. (Calc. m/z for [C$_{150}$H$_{100}$S$_{10}$O$_{30}$Na]$^+$ = 2726.0).
Figure S13: $^1$H NMR spectrum of linear oligomer 7 (250 MHz, CDCl₃/CF₃COOH 5/1 v/v).

Figure S14: $^{13}$C NMR spectrum of linear oligomer 7 (62.5 MHz, CDCl₃/CF₃COOH 5/1 v/v). Note: the strong quartet resonances centred at 114 and 162 ppm are due to trifluoroacetic acid co-solvent.
**Figure S15:** MALDI-TOF mass spectrum of linear oligomer 7. (Calc. $m/z$ for [\(C_{44}H_{28}S_2O_6Cl_2Na\)]$^+$ = 810.7).
Figure S16: $^1$H NMR spectrum of macrocycle 8 (400 MHz, CDCl$_3$/CF$_3$COOH 5/1 v/v).

Figure S17: $^{13}$C NMR spectrum of macrocycle 8 (100 MHz, CDCl$_3$/CF$_3$COOH 5/1 v/v). Note: the strong quartet resonances centred at 114 and 162 ppm are due to trifluoroacetic acid co-solvent.
Figure S18: $^1$H-$^1$H COSY NMR spectrum of macrocycle 8 (400 MHz, CDCl$_3$/CF$_3$COOH 5/1 v/v).
**Figure S19**: MALDI-TOF mass spectrum of macrocycle 8 (Calc. m/z for [C$_{50}$H$_{32}$S$_2$O$_8$Na]$^+$ = 847.9).
Figure S20: $^1$H NMR spectrum of macrocycle 9 (400 MHz, CDCl$_3$/CF$_3$COOH 5/1 v/v).

Figure S21: $^{13}$C NMR spectrum of macrocycle 9 (100 MHz, CDCl$_3$/CF$_3$COOH 5/1 v/v). Note: the strong quartet resonances centred at 114 and 162 ppm are due to trifluoroacetic acid co-solvent.
Figure S19: MALDI-TOF mass spectrum of macrocycle 9 (Calc. $m/z$ for $[C_{100}H_{64}S_4O_{16}Na]^+ = 1672.8$).

Computational modelling of macrocycles 8 and 9

Models of macrocycles 8 and 9 were constructed on a SGI-O2 workstation using the Cerius2 suite of programs, v. 3.5, Accelrys, San Diego. Models were minimised initially using the Dreiding-II force field (molecular mechanics with charge-equilibration), and the resulting models were then re-minimised with a modified version of this force field in which aromatic ether, ketone, and sulfone linkages were constrained to experimentally-established bond lengths and bond angles.

Atomic coordinates of the final models for 8 and 9 are available from the authors as electronic data files in pdb format. Email: fabio.arico@unive.it; or h.m.colquhoun@rdg.ac.uk

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