Supplementary information for: A simple route to novel D spherosilicones; the first crystallographic structures of D6 and D8 cages.

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Experimental

Synthesis of bis(heptyldiethoxysilyl)methane; Bis(dichlorosilyl)methane (0.4929g, 2.303×10^{-3}mol), *n*-heptene (1.04g, 0.0106mol) and 0.20mL of a 0.02mol/L solution of H_2PtCl_6 in isopropyl alcohol were placed in a small vial. The vial was capped and placed in an oil bath at 60°C for 24 hours. After cooling to room temperature, the product was transferred to a solution of ethanol (1.15g, 0.025mol) in 200mL dry THF. Then dry triethylamine (1.20g, 0.0117mol) was added to the solution dropwise, white solid was starting coming out during the dropping. After finishing the dropping, the solution was kept stirring for another 2 hours at room temperature. Then the solution was filtrated and the solution left was put under vacuum to remove THF and other low boiling point impurities. The oil left was purified by column chromatography (SiO_2/ CH_2Cl_2) to give a colourless oil. Yield: 0.8048g, 78%; ^{1}H(300MHz, $CDCl_3$)/ppm: -0.10(2H, s, SiCH_2Si), 0.60(4H, m, SiCH_2CH$_2$), 0.82(6H, m, CH$_2$CH$_2$CH_3), 1.17(32H, m, SiCH$_2$*CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H$_3$ + OCH$_2$*CH$_3$*), 3.71(8H, m, OCH_2); ^{13}C(300MHz, $CDCl_3$) /ppm: -3.11(Si*C*H$_2$Si), 14.00(Si*C*H$_2$CH$_2$), 14.34(CH$_2$CH$_2$*C*H$_3$), 18.28(OCH$_2$*C*H$_3$), 22.63(SiCH$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$), 22.86(SiCH$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$), 28.95(SiCH$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$), 31.76(SiCH$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$), 33.42(SiCH$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$), 57.89(O*C*H$_2$); ^{29}Si(400MHz, $CDCl_3$)/ppm: -7.04;

Synthesis of D6 and D8 cages; (Bis(heptyldiethoxysilyl)methane (0.1275g, 2.846×10^{-4}mol) and TBAF (0.284mL, 1M in THF, 2.84×10^{-4}mol) were mixed together in 50mL CH_2Cl_2 and stirred at room temperature for overnight. Then the solution was put into a separating funnel together with 20mL H_2O and 200mL CH_2Cl_2. After the extraction, the organic layer was dried by $MgSO_4$ before the removal of solvent under vacuum. The product was washed with 20mL acetone to give a wax-like solid. The solid was purified by column chromatography (SiO_2/ Hexane) to give two fractions.

Fraction I: (mixture of two D_8 cages, one confirmed by X-ray crystallography). Yield: 0.0145g, 17%; ^{1}H(300MHz, $CDCl_3$)/ppm: -0.19(8H, m, SiCH_2Si), 0.46(16H, m, SiCH_2CH$_2$), 0.86(24H, m, CH_3), 1.24(80H, m, SiCH$_2$*CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H$_3$); ^{13}C(300MHz, $CDCl_3$) /ppm: 14.36(Si*C*H$_2$CH$_2$), 18.68(*C*H$_3$), 22.99(SiCH$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$CH$_3$), 23.35(SiCH$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$CH$_3$), 29.43(SiCH$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$CH$_3$), 29.95(SiCH$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$CH$_3$), 32.13(SiCH$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$CH$_3$), 33.44(SiCH$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$CH$_3$),

33.54($SiCH_2CH_2CH_2CH_2CH_2CH_2CH_3$); ^{29}Si(400MHz, $CDCl_3$)/ppm: -26.27(Crystal), -26.86; MALDI-TOF: ($C_{60}H_{128}O_8Si_8+H^+$): (found) 1201.63-95%, 1202.60-100%, 1203.58-85%, 1204.67-50%, 1205.53-26%, 1206.50-12%; (cal.) 1201-91%, 1202-100%, 1203-79%, 1204-45%, 1205-21%, 1206-8%.

Fraction II: (the D_6 cage).Yield: 0.0359g, 42%; ^1H(300MHz, $CDCl_3$)/ppm: -0.03(6H, m, $SiCH_2Si$), 0.54(12H, m, $SiCH_2CH_2$), 0.86(18H, m, CH_3), 1.25(60H, m, $SiCH_2CH_2CH_2CH_2CH_2CH_2CH_3$); ^{13}C(300MHz, $CDCl_3$) /ppm: 14.34($SiCH_2CH_2$), 22.96(CH_3), 29.30($SiCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 29.34($SiCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 32.13($SiCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 33.19($SiCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$); ^{29}Si(400MHz, $CDCl_3$)/ppm: -12.06, -18.75 (1:2); MALDI-TOF: ($C_{45}H_{96}O_6Si_6+H^+$): (found) 901.36-100%, 902.42-89%, 903.37-65%, 904.32-29%, 905.37-18%; (cal.) 901-100%, 902-82%, 903-54%, 904-24%, 905-9%.

Crystallographic data

Suitable crystals of 2 and 3 was selected and data collected on a Bruker Nonius KappaCCD Area Detector at the window of a Bruker Nonius FR591 rotating anode ($\lambda_{Mo\text{-}K\alpha}$ = 0.71073 Å) driven by COLLECT (Collect: Data collection software, R. Hooft, Nonius B.V., 1998) and DENZO (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. 276: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press) software at 120 K. The structures were determined in SHELXS-97 (G. M. Sheldrick, Acta Cryst. (1990) A46 467–473) and refined using SHELXL-97(G. M. Sheldrick (1997), University of Göttingen, Germany) All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were included in idealized positions with thermal parameters riding on those of the parent atom. Crystallographic data for 2: Colourless needle, size = 0.32 × 0.08 × 0.03 mm^3, $C_{45}H_{96}O_6Si_6$; Mr = 901.76, T = 120(2) K; triclinic, space group *P*–1, a = 11.9106(15) Å, b = 13.264(2) Å, c = 18.823(4) Å, α = 101.383(7)°, β = 93.251(7)°, γ = 111.848(10)°; V = 2678.1(8) $Å^3$, Z = 2; $\rho_{(calcd)}$ = 1.118 Mg/m^3, μ = 0.197 mm^{-1}, reflections collected = 29934, independent reflections = 9172 [R_{int} = 0.2482], final R indices [$I > 2\sigma(I)$], R_1 = 0.1188, wR_2 = 0.2407; R indices (all data), R_1 = 0.2799, wR_2 = 0.3210.
Crystallographic data for 3: Colourless plate, size = 0.46 × 0.22 × 0.03 mm^3, $C_{60}H_{128}O_8Si_8$; Mr = 1202.34, T = 120(2) K; monoclinic, space group *C2/c*, a = 17.1468(8) Å, b = 34.4636(15) Å, c = 13.2620(7) Å, β = 111.651(2)°; V = 7284.1(6) $Å^3$, Z = 4; $\rho_{(calcd)}$ = 1.096 Mg/m^3, μ = 0.193 mm^{-1}, reflections collected = 33358, independent reflections = 8180 [R_{int} = 0.1003], final R indices [$I > 2\sigma(I)$], R_1 = 0.0613, wR_2 = 0.1256; R indices (all data), R_1 = 0.1620, wR_2 = 0.1574.

Crystallographic data (excluding structure factors) for the structure in this paper, has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC670401 and CCDC670402. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Selected bond angles and bond lengths

Octaheptyl D8 cage; selected distances (Å): Si-C (cage) = 1.842(6), Si-O (top face) = 1.642 (2), Si-O (side face) = 1.616 (2). selected bond angles (deg): Si-C-Si = 116.8 (3), O-Si-O = 109.1 (2), C-Si-O (top face) = 108.9 (3), C-Si-O (side face) = 110.0 (3).

Hexaheptyl D6 cage; selected distances (Å): Si-C (cage top face) = 1.860 (10), Si-C (cage bottom edge) = 1.833 (11), Si-O (top face) = 1.632 (7), Si-O (side face upper) = 1.651 (7), Si-O (side face lower) = 1.660 (8). selected bond angles (deg): Si-C-Si (top face) = 112.6 (5), Si-C-Si (bottom edge) = 119.9 (6), Si-O-Si (top face) = 144.7 (5), Si-O-Si (side face) = 135.6 (4), O-Si-O (Si4 ring) = 110.0 (4), O-Si-O (Si3 ring) = 106.8 (4), C-Si-O (top face) = 108.7 (5), C-Si-O (side face) = 110.2 (5) C-Si-O (bottom edge) = 109.6 (4).