Electronic Supplementary Information.

Scandium calix[*n*]arenes (n = 4, 6, 8): Structural, cytotoxicity, and ring opening polymerization studies

Abdullah Fahad A Alshamrani,[a,b] Orlando Santoro,[a] Timothy J. Prior,[a] Mohammed A. Alamri,[a] Graeme J. Stasiuk,[c] Mark R. J. Elsegood,[d] and Carl Redshaw[a]*

[a] *Plastics Collaboratory, Department of Chemistry, The University of Hull, Cottingham Road, Hull, HU6 7RX, U.K.*

[b] *Department of Diagnostic Radiology Technology, College of Applied Medical Sciences, Taibah University, Madina, Saudi Arabia.*

[c] *Department of Imaging Chemistry and Biology, School of Biomedical Engineering and Imaging, King's College London, London, SE1 7EH, U.K.*

[d] *Chemistry Department, Loughborough University, Loughborough, Leicestershire, LE11 3TU, U.K.*

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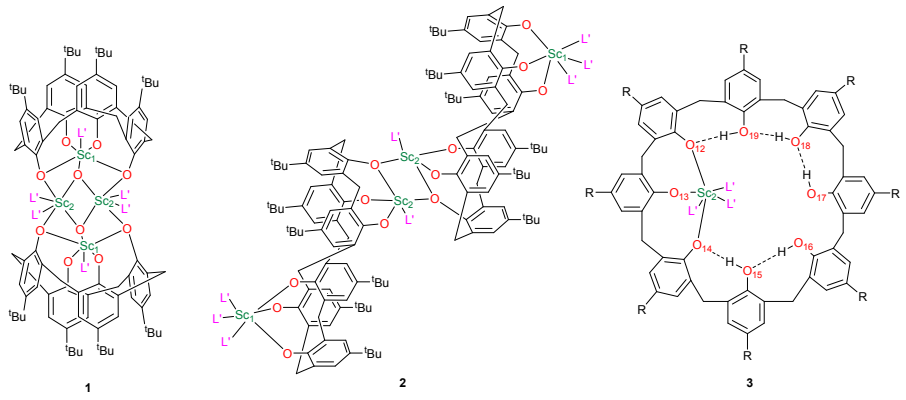
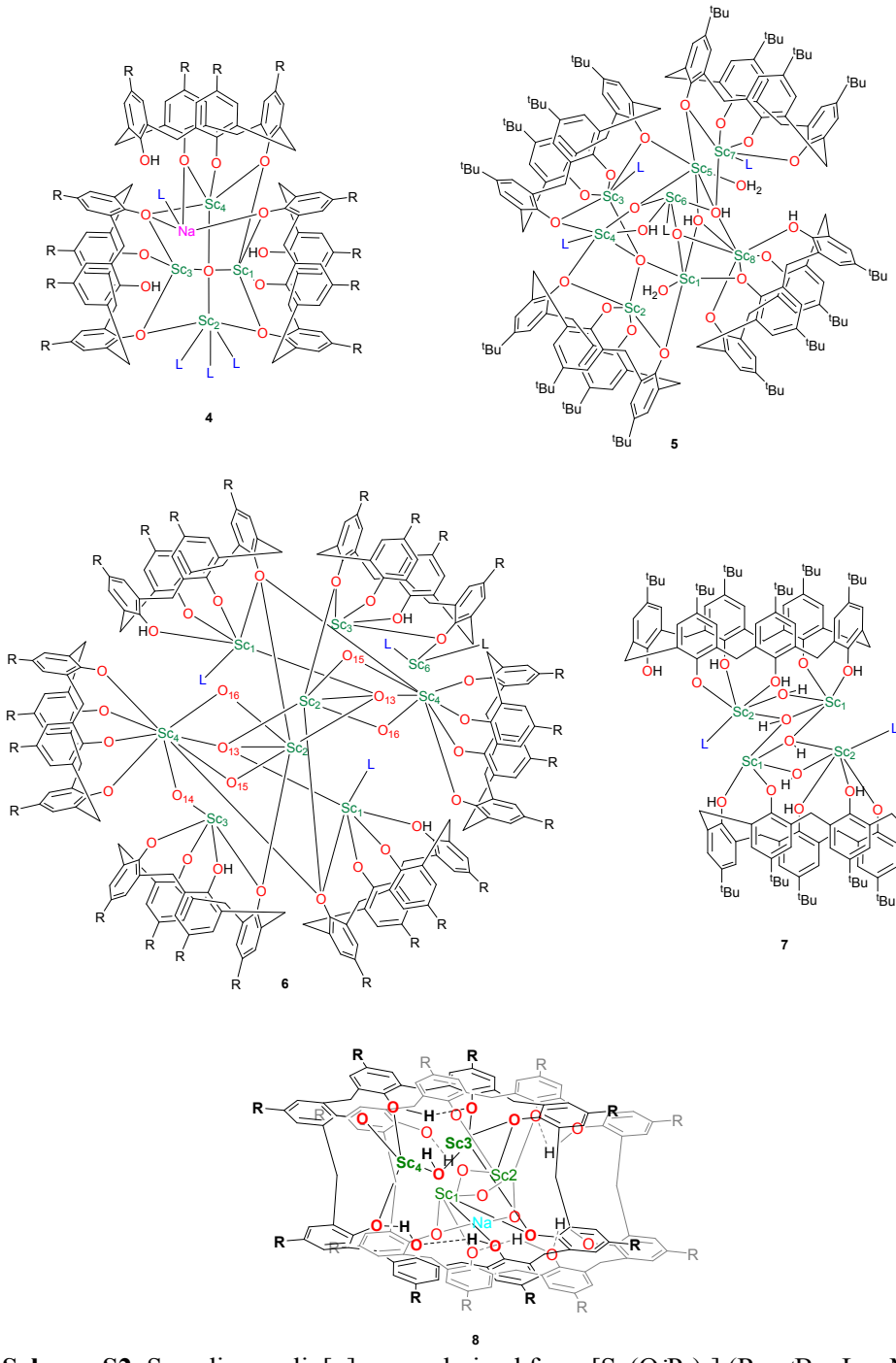


Scheme S1. Scandium calix[*n*]arenes derived from [Sc(OTf)$_3$] (R = *t*Bu, L$^/$ = DMSO).



Scheme S2. Scandium calix[*n*]arenes derived from [Sc(O*i*Pr)$_3$] (R = *t*Bu, L = MeCN).

Experimental

General: All manipulations were carried out under an atmosphere of dry nitrogen using Schlenk and cannula techniques or in a conventional nitrogen-filled glove box. Ethanol was dried over molecular sieves (3 Å). Toluene was dried over sodium, acetonitrile and triethylamine were dried over calcium hydride, and DMSO and acetone were dried over molecular sieves. All solvents were distilled and degassed prior to use. Cyclohexene oxide was dried over CaH_2 and then distilled. Benzyl alcohol was dried over sodium and then distilled. All other chemicals were purchased from Sigma Aldrich or TCI UK and used as received. IR spectra (nujol mulls, KBr windows) were recorded on a Nicolet Avatar 360 FT IR spectrometer. Elemental analyses were performed by the elemental analysis service at the London Metropolitan University, the Department of Chemistry & Biochemistry, University of Hull, and at Nanjing University of Information Science & Technology.

Synthesis of $[(Sc_4O_2)(L^4)_2(DMSO)_6]\cdot 4DMSO$ (**1**·4DMSO)

A solution of (0.37 g, 0.77 mmol) of $[Sc(OTf)_3]$ in DMSO (6.0 ml) was added to a solution of L^4H_4 (0.50 g, 0.77 mmol) and 0.5 ml of dry triethylamine in acetone (20 ml). After stirring for 5 min, the solution was filtered and left standing (1-2 days) at room temperature to afford colourless crystals of **1** (0.25 g, 24%). Calculated values for $C_{100}H_{140}O_{16}S_6Sc_4\cdot 4DMSO$: C 56.62, H 7.57, S 13.19%. Found: C 56.63, H 8.03 S, 11.48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.76-7.12 (m, 8H, aryl*H*), 3.79 (s, 2H, *endo*-CH_2), 3.16-3.17 (m, 2H, *endo*-CH_2), 2.56 (bs, 4H, *exo*-CH_2) 1.01-1.13 (overlapping s, 36H, C(CH_3)). IR (KBr) cm^{-1}: 1595 (w), 1377 (m), 1359 (s), 1320 (w), 1302 (w), 1290 (w), 1198 (s), 1122 (m), 1032 (s), 1010 (s), 969(s), 925 (m), 872 (s), 827 (s), 804 (s), 757 (w), 739 (m), 673 (m), 580 (m), 548 (m). MALDI-ES: *m/z*: 750 [M$^+$].

Synthesis of $[(L^6)_2Sc_4(DMSO)_8]\cdot 2DMSO\cdot 2acetone$ (**2**·2DMSO·2acetone)

A solution of (0.50 g, 1.02 mmol) of $[Sc(OTf)_3]$ in DMSO (6.0 ml) was added to a solution of (0.50 g, 0.51 mmol) L^6H_6 and 0.37 ml of triethylamine in acetone (20 ml). After stirring for 5 minutes, the solution was filtered and left standing (1-2 days) at room temperature to afford colourless crystals of **2** (0.19 g, 38%). Calculated values for $C_{144}H_{192}O_{18}S_6Sc_4\cdot 6(C_3H_6O)$: C 66.36, H 7.84, S 6.55%. Found: C 65.93, H 7.37, S 6.09%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.98-7.14 (m, 12H, aryl*H*), 3.13-3.15 (m, 6H, *endo*-CH_2), 2.62-2.97 (m, 6H, *exo*-CH_2), 1.23-1.40 (overlapping s, 54H, C(CH_3)). IR (KBr) cm^{-1}: 1598 (w), 1377 (m), 1309 (s), 1204 (S), 1031 (s), 851 (m), 823 (m), 754 (m), 639 (m), 544 (w), 539 (w). ES-MS: *m/z*: 1073 [M+H_2O-H]$^-$; ES-MS: *m/z*: 1013 [M –Sc +2H]$^-$.

Synthesis of $[Sc(L^8H_5)(DMSO)_3]\cdot$½DMSO·4½MeCN (**3**·½DMSO·4½MeCN)

In a Schlenk tube, a solution of $[Sc(OTf)_3]$ (0.17 g, 0.36 mmol) in DMSO (1.0 ml) was added to a solution of L^8H_8 (0.42 g, 0.32 mmol) and triethylamine (0.15 g, 1.45 mmol) in 20 ml of acetone. After stirring for 12 h, the solution was filtered, the solid was dried and was extracted into warm MeCN (20 mL). On standing at 0 °C, colourless crystals formed. Yield 30 %. MALDI-MS: *m*/*z*: 1671

([Sc(L^8H_5)$(DMSO)_3$]+DMSO+½MeCN). ^{1}H NMR (400 MHz, C_6D_6) δ: 9.72 (s, 2H, O*H*), 8,23 (s, 1H, O*H*),* 7.40 (s, 2H, aryl*H*), 7.35 (s, 2H, aryl*H*), 7.34 (d, 2H, J 2.4 Hz, aryl*H*), 7.33-7.30 (m, 4H, aryl*H*), 7.20 (m, 4H, aryl*H*), 7.14 (d, 2H, J 2.8 Hz, aryl*H*), 5.24 (d, 2H, J 11.6 Hz, *endo*-CH_2), 4.89 (d, 2H, J 12.8 Hz, *endo*-CH_2), 4.37 (d, 2H, J 14.0 Hz, *endo*-CH_2), 3.63 (d, 2H, J 14.0 Hz, *endo*-CH_2), 3.30-3.41 (overlapping d, 6H, *exo*-CH_2), 2.81 (s, 6H, *DM*SO), 1.79 (s, 6H, 2x *Me*CN), 1.63 (bs, 3H, *Me*CN), 1.36 (s, 9H, C(CH_3)$_3$), 1.35 (s, 9H, C(CH_3)$_3$), 1.31 (s, 18H, C(CH_3)$_3$), 1.24 (s, 18H, C(CH_3)$_3$), 1.22 (s, 18H, C(CH_3)$_3$), 0.69 (s, 6H, DMSO), 0.52 (s, 3H, ½DMSO); *2x O*H* not observed. IR (KBr) cm^{-1}: 3614 (w), 3280 (m), 2720 (m), 2532 (m), 1747 (w), 1699 (w), 1597 (w), 1568 (w), 1391 (s), 1363 (s), 1290 (s), 1232 (s), 1208 (s), 1121 (m), 1058 (s), 1030 (s), 1010 (s), 959 (s), 909 (m), 878 (m), 814 (m), 800 (m), 773 (m), 754 (m), 743 (m), 734 (m), 705 (w), 698 (w), 669 (w), 665 (w), 638 (m), 599 (w), 572 (w), 518 (m), 496 (w), 467 (m), 456 (m), 437 (m), 415 (m). $C_{94}H_{127}O_{11}S_3Sc\cdot0.5(C_2H_6OS)\cdot3.5(C_2H_3N)$ (sample dried *in-vacuo* for 1h, -MeCN) requires C 69.72, H 8.06, N 2.83%. Found C 69.31, H 7.54, N 2.25%.

Synthesis of {$Sc_3O(L^4H_{1.5})_2[L^4H(Na(NCMe)_{1.5})_{0.5}]Sc(NCMe)_3$}·19MeCN (**4**·19MeCN)

Toluene (30 ml) was added to a Schlenk tube containing L^4H_4 (0.37 g, 0.57 mmol) and [Sc(O*i*Pr)$_3$] (0.25 g, 1.13 mmol). After refluxing for 24 h, the volatiles were removed under reduced pressure, and the residue was refluxed in acetonitrile (30 ml) for 10 min. Filtration and standing (3-4 days) at room temperature afforded colourless crystals of **4**·19MeCN. Yield 59 %. Calculated values for $C_{308}H_{378}N_{23}NaO_{26}Sc_8$: C 71.12, H 7.33, N 6.20%. Found: C, 71.95; H, 7.34; N, 6.18%. MALDI-ToF: *m*/*z* = 2773.7 [$Sc_4O(L^4H_{1.5})_3Na(NCMe)_2$]. IR: (KBr) cm^{-1}: 3186bw, 2319w, 2282w, 2250w, 1601w, 1364s, 1340s, 1299m, 1260s, 1202s, 1156w, 1127m, 1094bs, 1019bm, 946w, 911w, 871m, 818s, 799s, 784m, 738w, 722w, 674w, 660w, 571w, 553w, 533m, 497m, 464w, 451w. ^{1}H NMR (400 MHz, dmso-d_6) δ: 8.28 (s, ~1H, O*H*), 7.91 (s, ~1H, O*H*),* 7.21 (m, 8H, aryl*H*), 7.13 (m, 8H, aryl*H*), 6.88 (bs, 8H, aryl*H*), 4.21 (bd, *J* = ~10.0 Hz, 12H, *endo*-CH_2), 3.12 (bd, 12H, J obscured, *exo*-CH_2), 2.26 (s, 27H, MeCN), 2.03 (s, 2.25H, $^3/_4$MeCN), 0.93-1.24 (overlapping s, 108H, C(CH_3)); *Other O*H* not observed.

Synthesis of [$Sc_8(L^4)_3(L^4H)_1(O^{2-})_3(OH)_3(OH_2)_2(MeCN)_4$]·17MeCN (**5**·17MeCN)

Toluene (30 ml) was added to a Schlenk tube containing L^4H_4 (0.50 g, 0.77 mmol) and [Sc(O*i*Pr)$_3$] (0.22 g, 1.02 mmol) and refluxed for 24h. The solvent was removed under vacuum, and the orange precipitate was extracted into acetonitrile (30 ml). After filtration, the solution prolonged standing (3-4 days) at room temperature afforded colourless crystals of **5**·12MeCN (Yield 0.2 g, 24.1%). Calculated values for $C_{184}H_{220}N_4O_{24}Sc_8$: C 68.39, H 6.86, N 1.73%. Found: C 69.22, H 6.89, N 2.17% (sample dried in vacuum for 12 h, –17MeCN). IR (KBr) cm^{-1}: 2726 (w), 2669 (w), 2319 (m), 2290 (w), 2247(w), 1601 (s), 1377 (m), 1361 (m), 1298 (s), 1203 (s), 1126 (s), 1028 (m), 909 (s), 888 (s), 821 (s), 799 (s), 727 (s), 694 (m), 593 (w), 553 (m), 450 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.31 (s,

3H, O*H*), 7.04 (bs, 32H, aryl*H*) 4.24 (d, *J* = 13.5 Hz, 16H, *endo*-CH_2) 3.47 (d, *J* = 13.5 Hz, 16H, *exo*-CH_2), 1.99 (s, 9H, MeCN), 1.18-1.21 (overlapping s, 144H, C(CH_3)).

Synthesis of $[(L^4)_2(L^4H)_4Sc_9(OH)_7(H_2O)(MeCN)_4]\cdot 11MeCN$ (**6**·11MeCN).

Toluene (30 ml) was added to a Schlenk tube containing L^4H_4 (0.37 g, 0.57 mmol) and [Sc(O*i*Pr)$_3$] (0.25 g, 1.13 mmol). After refluxing for 24 h, the volatiles were removed under reduced pressure, and the residue was extracted into acetonitrile (30 ml). Prolonged standing (3-4 days) at room temperature afforded colourless crystals. Yield <10% %. $Sc_9N_6O_{32}C_{276}H_{358}$ (sample dried *in vacuo* for 3 h, –9MeCN) requires C 71.01, H 7.56, N 1.80%. Found: C 70.48, H 7.12, N 1.46%.

$[(L^6H_4)Sc_2(OH)_2(NCMe)_2]_2\cdot 12MeCN$ (**7**·12MeCN)

Toluene (30 ml) was added to a Schlenk tube containing dry L^6H_6 (0.50 g 0.51 mmol) and [Sc(O*i*Pr)$_3$] (0.22 g, 1.02 mmol) and refluxed at 120°C for 24 h. The solvent was removed under vacuum, then the precipitate was extracted into acetonitrile (30 ml). After filtration, the solution, after prolonged standing at room temperature, afforded colourless crystals (0.10 g, 17%). Calculated values for $C_{136}H_{170}N_2O_{16}Sc_4$ (sample dried *in-vacuo* for 12h, - 12MeCN) C 72.00, H 7.55, N 1.24%. Found: C 71.74, H 8.00, N 0.65%. IR (KBr) cm^{-1}: 2726 (w), 1604 (s), 1297 (m), 1261 (m), 1205 (s), 1122 (s), 1024 (m), 961 (w), 914 (m), 874 (m), 801 (m), 690 (w), 671 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.53 (s, 2H, O*H*)*, 7.06-7.24 (m, 24H, aryl*H*), 4.82 (d, *J* = 16.7 Hz, 2H, *endo*-CH_2), 4.72 (d, *J* = 14.0 Hz, 2H, *endo*-CH_2), 4.50 (d, *J* = 14.9 Hz, 2H, *endo*-CH_2), 4.29 (d, *J* = 13.3 Hz, 2H, *endo*-CH_2), 3.94 (d, *J* = 13.7 Hz, 2H, *exo*-CH_2), 3.71 (d, *J* = 14.4 Hz, 2H, *exo*-CH_2), 3.55 (d, *J* = 13.7 Hz, 2H, *exo*-CH_2), 3.40 (d, *J* = 3.9 Hz, 2H, *exo*-CH_2), 3.36 (d, *J* = 2.3 Hz, 2H, *exo*-CH_2), 3.26 (d, *J* = 16.9 Hz, 2H, *exo*-CH_2), 3.09 (d, *J* = 13.3 Hz, 2H, *exo*-CH_2), 2.89 (d, *J* = 14.6 Hz, 2H, *exo*-CH_2) 2.00 (s, 3H, MeCN), 1.16-1.30 (overlapping s, 108H, C(CH_3)). ES-MS: *m/z*: 1067 [M –Sc –H_2O]$^-$. * H-bonded OH not observed.

Synthesis of $[Sc_4Na(L^8H_3)_2(OiPr)(OH)_2(NCMe)_4]\cdot 6.14MeCN$ (**8**)

[Sc(O*i*Pr)$_3$] (0.69 g, 3.11 mmol) and L^8H_8 (1.00 g, 0.77 mmol) were refluxed in toluene (30 ml) led for 12 h. On cooling, volatiles were removed and the residue was extracted into MeCN (30 ml). A colourless crystalline solid formed on standing at 0 °C. Yield: 0.93 g, 73%. $C_{187}H_{235}N_4NaO_{19}Sc_4$ (sample dried *in vacuo* for 2 h, –6.14(C_2H_3N)) requires C 73.74, H 7.78, N, 1.84%. Found C 73.32, H 7.99, N 1.57%. IR (KBr) cm^{-1}: 3663w, 3168w, 1603w, 1304m, 1260s, 1206m, 1094bs, 1020bs, 917w, 875m, 800s, 722s, 664w. ^{1}H NMR (400 MHz, dmso-d_6) δ: 9.52, 9.16, 8.85, 7.97, 7.89 (5x s, 10H, O*H*), 6.61-7.12 (m, 32H, aryl*H*), 5.59 (d, *J* = 12.0 Hz, 4H, *endo*-CH_2), 5.22 (d, *J* = 11.2 Hz, 4H, *endo*-CH_2), 4.55 (d, *J* = 11.2 Hz, 2H, *endo*-CH_2), 4.30 (overlapping d, *J* obscured, 6H, *endo*-CH_2), 3.74 (overlapping sept +d, *J* obscured, 3H, C*H* + *exo*-CH_2), 3.08 (d, *J* = 12.0 Hz, 4H, *exo*-CH_2), 2.98 (d, *J* = 11.2 Hz, 4H, *exo*-CH_2), 2.81 (bd, *J* = 11.6 Hz, 6H, *exo*-CH_2), 2.07 (s, ~30H, MeCN), 1.08-1.18 (overlapping s, 144H, C(CH_3)), 1.00 (d, *J* = Hz, 6H, CH_3).

Crystallography

X-ray diffraction data were collected by the EPSRC National Crystallography Service using a range of modern instrumentation. Crystals were cooled to 100 K during data collection. Data were integrated and corrected for absorption using standard methods. Structures were solved using dual-space methods within SHELXT and refined against F^2 using least squares methods implemented within SHELXL. SQUEEZE was used to model disordered solvent in several of the structures. For **8** it was possible to locate and refine a number of partially-occupied MeCN molecules. This effect and modelling of disorder led to a non-integer number of solvent molecules in the final formula and small discrepancy in the atom counts (2dp).

Each of these crystal structures is complicated because of the nature of the sample. The structures have inherently large unit cells because of the molecules present and there are large regions that are filled by disordered solvent. The scattering from every sample is weak; scattering from some is extremely weak. We have studied these samples using the brightest lab source in the world (UK NCS) using extremely sensitive modern detectors. (Indeed, the NCS report that the advantages of synchrotron radiation are limited compared with their instrumentation). For many of the structure determinations the *R*-factors are relatively poor, or the data have had to be trimmed to less than the *Acta Cryst.* recommended limit. Although there are difficulties with the structures, they provide clear evidence of the atomic connectivity and definitive information about the coordination chemistry of the ligands. These are very difficult structures to finalise and we will gladly share raw data with others.

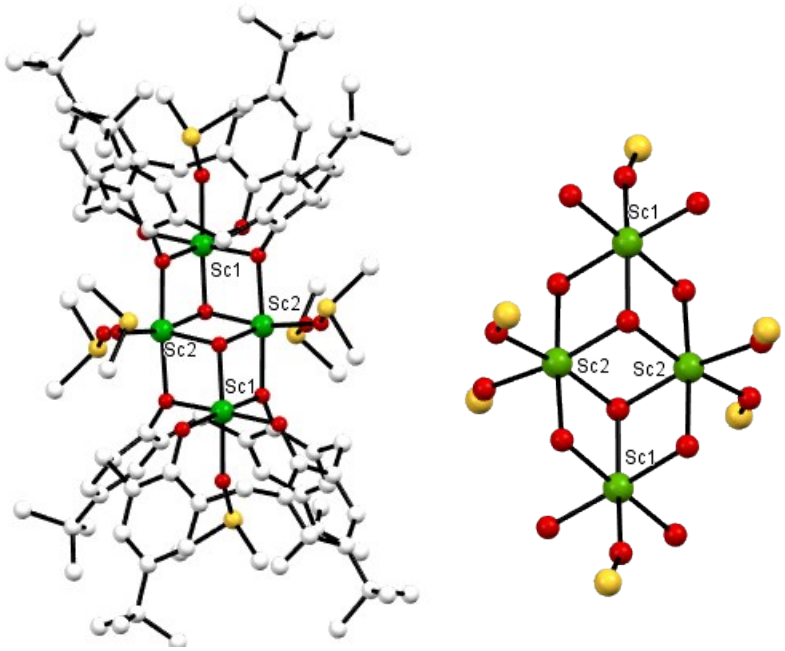


Figure S1. Left: Alternative view of **1**·4DMSO. Right: Core of the Structure.

Selected bond lengths (Å) and angles (°) for $[(Sc_4O_2)L^4{}_2(DMSO)_6]$·4DMSO (**1**·4DMSO): O(1)-Sc(1) 2.1145(12), O(2)-Sc(1) 2.0328(12), O(3)-Sc(1) 2.0101(12), O(4)-Sc(2) 2.1065(12), O(4)-Sc(1) 2.1350(12), O(5)-Sc(1) 2.0109(12), O(5)-Sc(2) 2.0391(12), O(6)-Sc(1) 2.2351(12), O(7)-Sc(2)

2.1494(12), O(8)-Sc(2) 2.1391(13); C(1)-O(1)-Sc(1) 124.30(10), C(12)-O(2)-Sc(1) 115.49(10), C(23)-O(3)-Sc(1) 123.23(11), C(34)-O(4)-Sc(2) 141.95(10), C(34)-O(4)-Sc(1) 119.98(10), Sc(2)-O(4)-Sc(1) 97.83(5), Sc(1)-O(5)-Sc(2) 104.25(5), S(2)-O(7)-Sc(2) 129.57(8), S(3A)-O(8)-Sc(2) 131.12(12), O(5)-Sc(1)-O(3) 103.26(5), O(5)-Sc(1)-O(2) 103.46(5), O(3)-Sc(1)-O(2) 93.99(5), O(5)-Sc(1)-O(1) 79.04(5), O(3)-Sc(1)-O(1) 173.66(5), O(2)-Sc(1)-O(1) 91.17(5), O(5)-Sc(1)-O(4) 78.54(5), O(3)-Sc(1)-O(4) 88.52(5), O(1)-Sc(1)-O(4) 86.15(5), O(5)-Sc(1)-O(6) 158.16(5), O(3)-Sc(1)-O(6) 90.39(5).

Crystal data for compound **1**·4DMSO: $C_{100}H_{140}O_{16}S_6Sc_4$, M = 1970.31, Triclinic, space group $P\ \bar{1}$, a = 12.72128(15), b = 13.4172(2), c = 19.4141(3) Å, α = 103.3612(14) β = 107.4938(12), γ = 101.4307(14) °, V = 2944.18(8) Å^3, Z = 1, Dc = 1.111 g cm^{-3}, F(000) = 1048, T = 100(2) K, μ(Cu-Kα) = 3.321 mm^{-1}, λ(Cu-Kα) = 1.54184 Å, θmax = 70.061°, $R1$ ([$I > 2\sigma(I)$] = 0.0392, $wR2$ *(all data)* = 0.1099.

There are also four DMSO molecules of crystallization, which were modelled using the SQUEEZE routine[1] to give an overall composition of $[(Sc_4O_2)L^4{}_2(DMSO)_6]$·4DMSO (**1**·4DMSO).

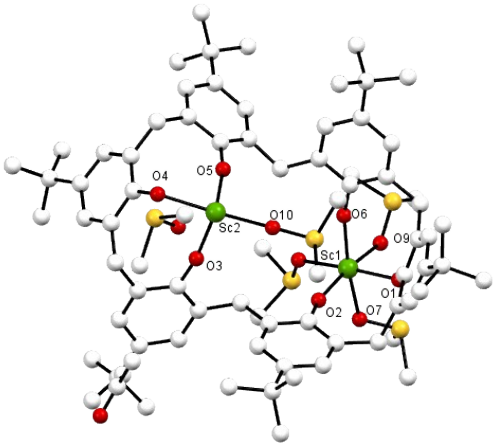


Figure S2. Asymmetric unit of $[(L^6)_2Sc_4(DMSO)_4]$·2DMSO·2acetone (**2**·2DMSO·2acetone). Selected bond lengths (Å) and angles (°): O(1)-Sc(1) 2.0194(16), O(2)-Sc(1) 1.95894(16), O(3)-Sc(2) 1.9082(17), O(4)-Sc(2) 2.0644(16), O(5)-Sc(2) 1.9096(17), O(6)-Sc(1) 1.9796(15), O(7)-Sc(1) 2.1942(16), O(8)-Sc(1) 2.1897(18), O(9)-Sc(1) 2.2324(19), O(10)-Sc(2) 2.0489(18); C(1)-O(1)-Sc(1) 122.89(12), C(12)-O(2)-Sc(1) 163.20(14), C(23)-O(3)-Sc(2) 168.23(15), C(34)-O(4)-Sc(2) 116.69(12), C(45)-O(5)-Sc(2) 166.55(15), C(56)-O(6)-Sc(1) 161.39(14), S(1)-O(7)-Sc(1) 121.80(9), S(4)-O(10)-Sc(2) 176.56(14), O(2)-Sc(1)-O(6) 104.11(7), O(2)-Sc(1)-O(1) 93.16(6), O(6)-Sc(1)-O(1) 94.05(6), O(2)-Sc(1)-O(8) 93.04(7).

Crystal data for compound **2**·2DMSO·2acetone: $C_{166}H_{252}O_{28}S_{14}Sc_4$, M = 2855.58, Triclinic, space group $P\ \bar{1}$, a = 16.60531(16), b = 16.72546(15), c = 19.20582(12) Å, α = 84.7397(6), β = 73.4252(7), γ = 63.7025(9) °, V = 4579.58(7) Å^3. Z = 1, Dc = 1.035 g cm^{-3}, F(000) = 1528, T = 100(2) K, μ(Cu-Kα) = 2.499 mm^{-1}, λ(Cu-Kα) = 1.54184 Å, θmax = 68.251°, $R1$ ([$I > 2\sigma(I)$] = 0.0517, $wR2$ *(all data)* = 0.1377.

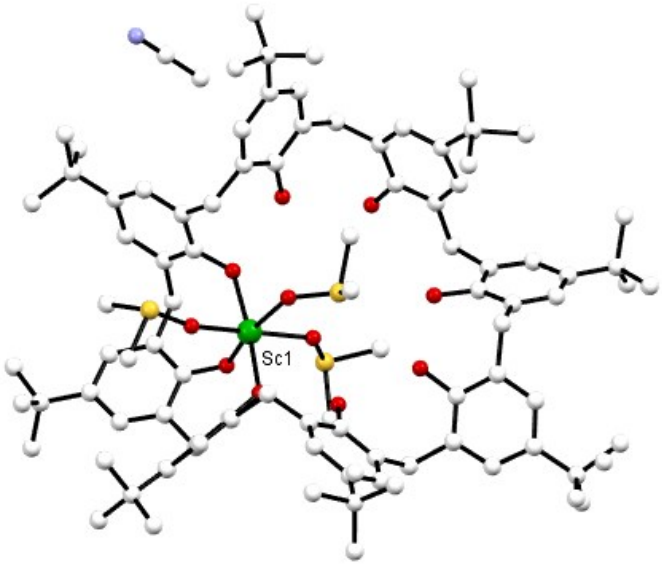


Figure S3. Alternative view of **3**·½DMSO·4½MeCN.

Selected bond lengths (Å) and angles (°) for [Sc(L^{8}H$_5$)(DMSO)$_3$]·½DMSO·4½MeCN (**3**·½DMSO·4½MeCN): Sc(1)-O(1) 2.071(3), Sc(1)-O(2) 1.997(3), Sc(1)-O(3) 2.115(3), Sc(1)-O(9) 2.092(3), Sc(1)-O(10) 2.176(3), Sc(1)-O(11) 2.113(3); O(1) – Sc(1) – O(2) 91.90(11), O(1) – Sc(1) – O(3) 173.26(12), O(2) – Sc(1) – O(9) 101.37(12), O(2) – Sc(1) – O(10) 167.62(12), O(2) – Sc(1) – O(11) 85.76(11).

Crystal data for compound **3**·½DMSO·4½MeCN: $C_{104}H_{143.5}N_{4.5}O_{11.5}S_{3.5}Sc$, M = 1797.89, triclinic, space group $P\ \bar{1}$, a = 16.6936(2), b = 18.2801(3), c = 37.5436(6) Å, α = 101.9761(13), β = 90.9656(13), γ = 110.8224(3) °, V = 10440.3(3) Å^3, Z = 4, Dc = 1.144 g cm^{-3}, F(000) = 3872, T = 100(2) K, μ(Cu-Kα) = 1.71 mm^{-1}, λ(Cu-Kα) = 1.54184 Å, θmax = 58.9°, $R1$ ([$I > 2\sigma(I)$] = 0.076, $wR2$ *(all data)* = 0.235.

There are two Sc complexes, 9½MeCNs and ¼DMSO in the asymmetric unit.

Several *t*Bu groups in **3** were modelled as disordered over two sets of positions; mostly with just the Me groups disordered, but in once case (*) the whole *t*Bu group. Two coordinated DMSOs were also modelled as disordered, either with just the S split over two sites, or with both the S and a Me groups disordered. *t*Bu groups at C(18), C(29)*, C(51), C(62), C(18A), C(40A), C(73A), and DMSOs at S(4), S(6)/C(94A) are the disordered groups. Three unique MeCNs of crystallization were reasonably well defined and were modelled as point atoms. The remaining MeCNs and DMSOs of crystallization were badly disordered, so were modelled with the Platon SQUEEZE procedure.[1] The solvent molecules of crystallisation are located in clefts close to or between complexes. There are no significant interactions between complex molecules.

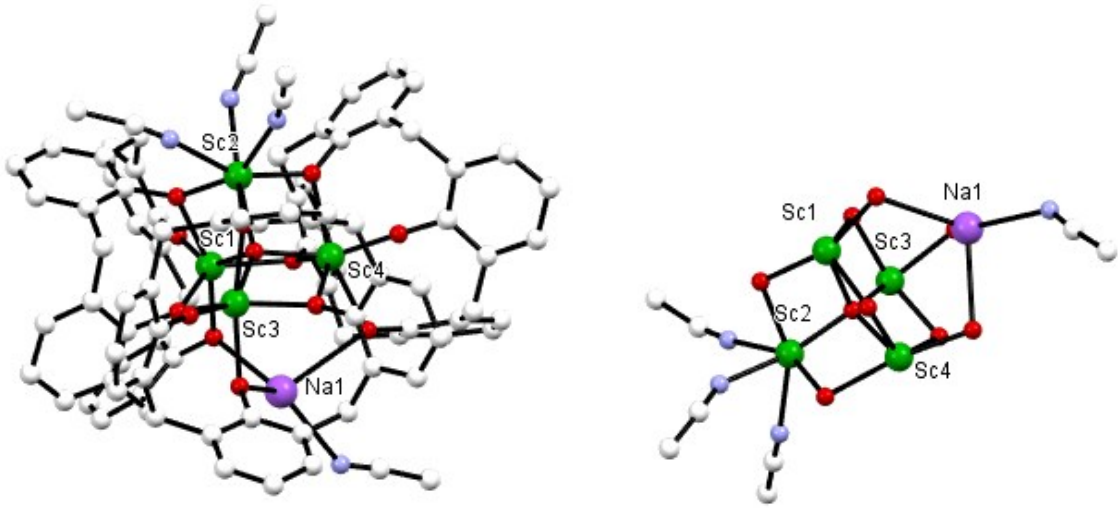


Figure S4. Left: Alternative view of **4**·19MeCN; Right: Core of the structure.

Selected bond lengths (Å) and angles (°): O1-Sc1 1.893(13), O2-Sc1 2.131(12), O3-Sc1 2.096(12), O4-Sc1 2.138(13), O4-Na1 2.690(17); Sc1-O2-Sc2 101.8(5), O2-Sc1-O4 97.4(3), O2-Sc1-O1 82.5(5), O4-Sc1-O1 132.1(4), Sc1-O4-Na1 100.8(5), Sc3-O7-Na1 99.8(5), O2-Sc1-O3 82.6(3), O4-Sc1-O3 103.1(3), O1-Sc1-O3 162.2(5).

Crystal data for compound **4**·19MeCN (10 MeCNs are from Squeeze): $C_{308}H_{378}N_{23}NaO_{26}Sc_8$, M = 5201, Orthorhombic, space group $Pca2_1$, a = 22.5075(10), b = 20.1830(11), c = 32.9663(19) Å, V = 14975.6(14) Å^3, Z = 2, Dc = 1.062 g cm^{-3}, F(000) = 5108, T = 100(2) K, μ(Cu-Kα) = 1.942 mm^{-1}, λ(Cu-Kα) = 1.54178 Å, θmax = 47.837°, $R1$ ([$I > 2\sigma(I)$] = 0.0927, $wR2$ *(all data)* = 0.2804.

Data were very weak beyond 1.05 Å; only noise was recorded beyond this resolution. Therefore, only data to θmax = 47.837° (Cu) were used for refinements.

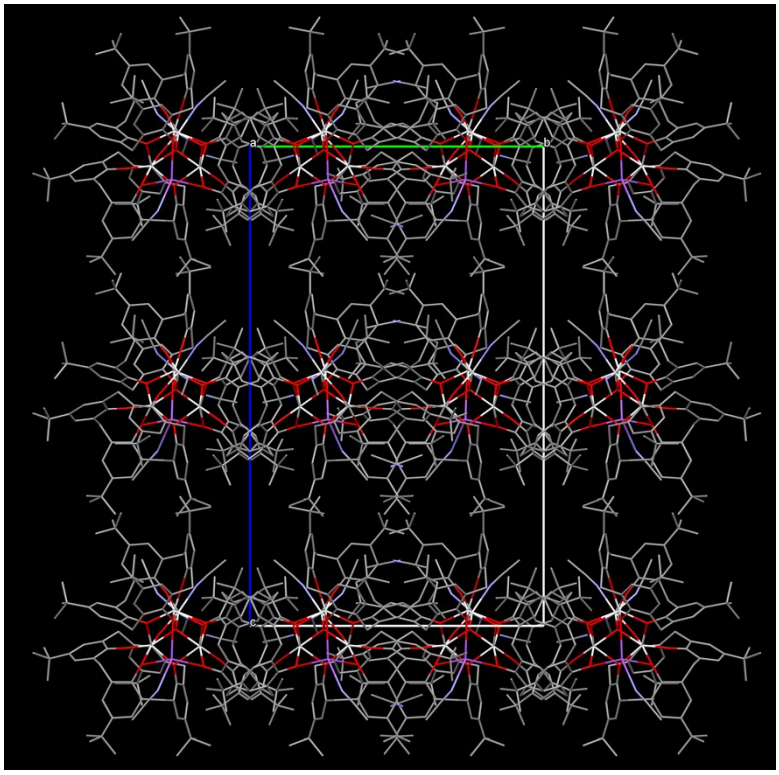


Figure S5. Packing diagram of **4** viewed down *a*.

In a repeat reaction a second polymorph was isolated. This features the same basic cluster as for **4**. These clusters are arranged in layers in the *xy* plane and stacked in ABAB fashion parallel to the crystallographic *c* direction.

Selected bond lengths (Å) and angles (°): O1-Sc1 2.208(8), O2-Sc1 2.087(8), O3-Sc1 2.191(8), O4-Sc1 1.901(8), O1-Na1 2.688(11); Sc1-O2-Sc4 101.5(3), O2-Sc1-O4 124.9(3), O2-Sc1-O1 84.2(3), O4-Sc1-O1 85.2(3), Sc1-O1-Na1 100.3(3), Sc2-O8-Na1 99.6(3), O2-Sc1-O3 89.5(3), O4-Sc1-O3 83.7(3), O1-Sc1-O3 160.9(3).

Crystal data for compound **4′**·10CH_3CN (7 MeCNs are from Squeeze): $C_{160}H_{198}N_{14}NaO_{13}Sc_4$, M = 2728.15, Monoclinic, space group $P2_1/c$, a = 17.3399(12), b = 40.5252(16), c = 22.5953(10) Å, β = 109.804(6) °, V = 14938.7(15) Å^3, Z = 4, Dc = 1.085 g cm^{-3}, F(000) = 5204, T = 100(2) K, μ(Cu-Kα) = 1.969 mm^{-1}, λ(Cu-Kα) = 1.54184 Å, θmax = 42.092°, $R1$ ([$I > 2\sigma(I)$] = 0.1124, $wR2$ *(all data)* = 0.3559.

Data were very weak beyond 1.15 Å; only noise was recorded beyond this resolution. Therefore, only data to θmax = 42.092° (Cu) were used for refinements.

4′ has clusters arranged in sheets in the *yz* plane and these are stacked in AAA fashion parallel to the crystallographic *a* direction.

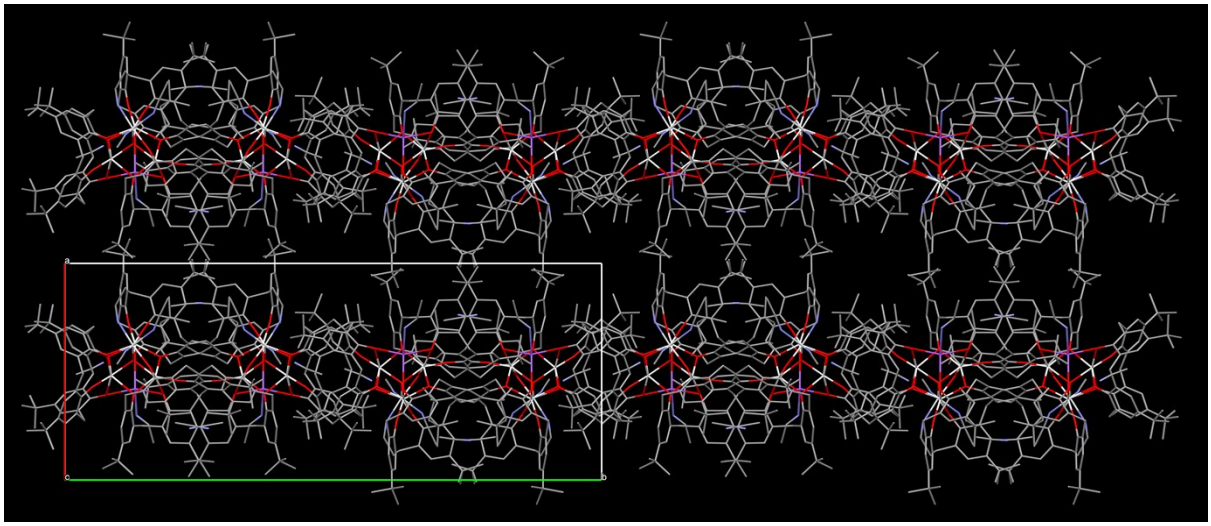


Figure S6. Packing diagram of **4′** viewed down *c*.

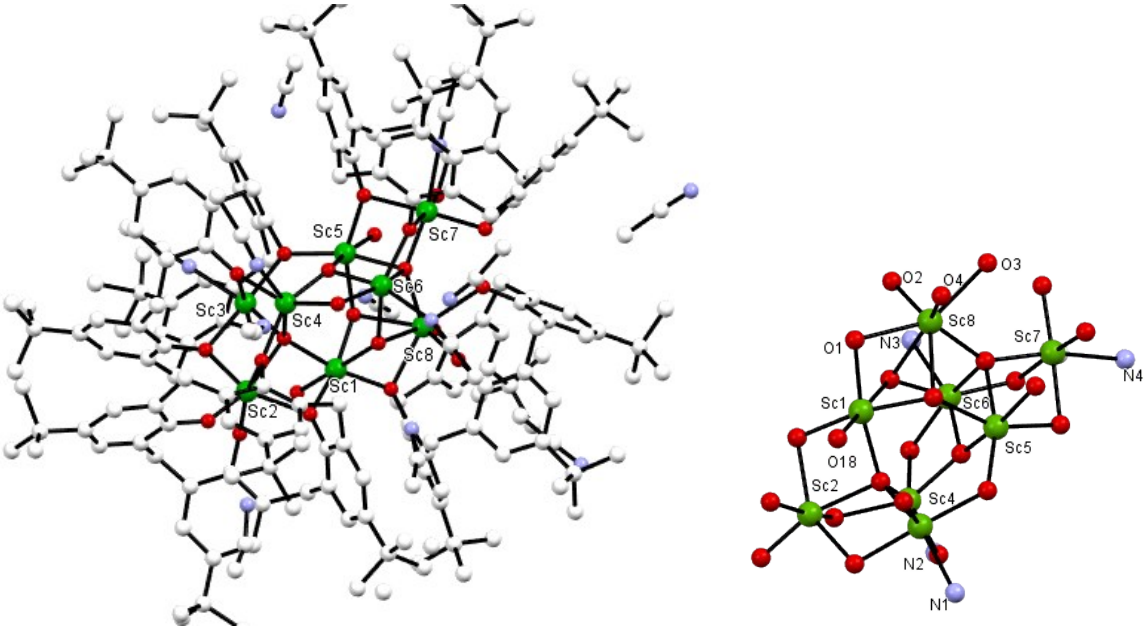


Figure S7. Left: Alternative view of **5**·17MeCN. Right: Core of the structure.

Selected bond lengths (Å) and angles (°) for $[Sc_8(L^4)_3(L^4H)_1(O)_3(OH)_3(OH_2)_2]\cdot 12CH_3CN$ (**5**·17MeCN): Sc(1)-O(1) 2.041(4), Sc(1)-O(5) 2.076(4), Sc(2)-O(5) 2.171(4), Sc(2)-O(6) 2.228(4), Sc(2)-O(7) 1.914(4), Sc(2)-O(8) 2.056(4), Sc(2)-O(12)2.133(4), Sc(3)-O(9) 2.110(4), Sc(3)-O(10) 2.108(4), Sc(3)-O(11) 2.017(4), Sc(3)-O(12) 2.098(4), Sc(4)-O(6) 2.117(4), Sc(4)-O(9) 2.127(4), Sc(5)-O(10) 2.085(3), Sc(5)-O(16) 2.090(4), Sc(6)-O(13) 2.067(4), Sc(7)-O(13) 2.164(4), Sc(7)-O(14) 2.005(4), Sc(7)-O(15) 2.045(4), Sc(7)-O(16) 2.135(4), Sc(8)-O(1) 2.294(4), Sc(8)-O(2) 1.962(4), Sc(8)-O(3) 2.333(4), Sc(8)-O(4) 1.944(4); Sc(1) – O(5) – Sc(2) 99.00(15), Sc(1) – O(8) –

Sc(8) 93.55(15), Sc(2) – O(6) – Sc(4) 102.07(14), Sc(3) – O(9) – Sc(4) 99.25(15), Sc(3) – O(10) – Sc(5) 118.84(17), Sc(4) – O(19) – Sc(6) 103.87(16).

Crystal data for compound **5**·17MeCN (10 MeCNs are from Squeeze): $C_{218}H_{271}N_{21}O_{24}Sc_8$, M = 3929.24, triclinic, space group $P\ \bar{1}$, a = 17.3731(5), b = 18.3311(5), c = 33.3576(7) Å, α = 90.199(2) β = 91.063(2), γ = 90.255(2) °, V = 10621.3(5) Å^3, Z = 2, Dc = 1.100 g cm^{-3}, F(000) = 3732, T = 100(2) K, μ(Cu-Kα) = 2.545 mm^{-1}, λ(Cu-Kα) = 1.54178 Å, θmax = 68.327°, $R1$ ([$I > 2\sigma(I)$]) = 0.0846, $wR2$ *(all data)* = 0.2393.

Whilst the hydrogens in this structure are difficult to locate, the structure can be described as follows by comparisons with known Sc-O and C-O bond lengths in the CCDC.[2] The oxygen atoms bound to scandium are present as either water, hydroxide or bridging oxide. In particular, the O3 centre is a phenol, and the O-H forms a hydrogen bond to O14. The oxygens O(17), O(19) and O(22) are oxide, O(18) and O(24) are water, O(20), O(21) and O(23) are hydroxide, whilst O(3) of one of the calixarenes is protonated.

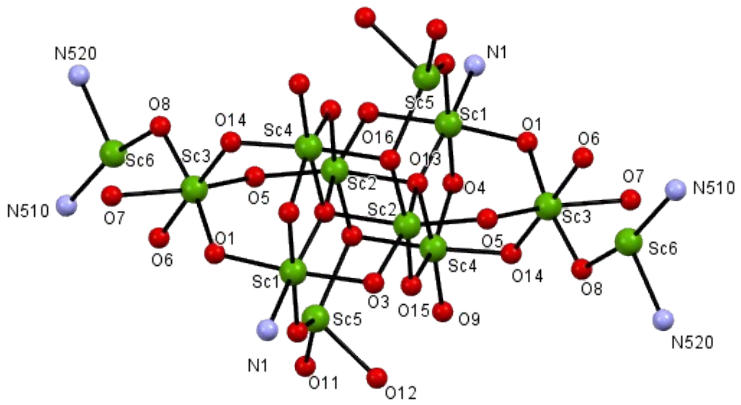


Figure S8. Core of **6**·14MeCN.

Selected bond lengths (Å) and angles (°) for $[(L^4)_2(L^4H)_4Sc_9(OH)_7(H_2O)(MeCN)_4]$·11MeCN (**6**·11MeCN): O1-Sc1 2.110(3), O2-Sc1 1.957(3), O3-Sc1 2.142(3), O4-Sc1 2.110(3), Sc1-Sc2 3.1939(9), Sc1-Sc5 3.654(4); O2-Sc1-O1 94.02(11), O2-Sc1-O4 174.03(10), O1-Sc1-O4 87.98(10), O2-Sc1-O3 90.69(11), O1-Sc1-O3 174.84(10), O4-Sc1-O3 87.54(10), O2-Sc1-Sc2 96.23(8), O1-Sc1-Sc2 136.41(7), O4-Sc1-Sc2 86.14(7), O3-Sc1-Sc2 40.61(6), O2-Sc1-Sc5 32.53(9).

Crystal data for compound **6**·14MeCN (8 MeCNs are from Squeeze): $C_{298}H_{362}N_{18}O_{32}Sc_9$, M = 5112.7, monoclinic, space group $C2/c$, a = 37.2622(14), b = 21.2546(9), c = 37.6585(27) Å, β = 106.414(4) °, V = 28610(2) Å^3, Z = 4, Dc = 1.111 g cm^{-3}, F(000) = 10180, T = 100(2) K, μ(Mo-Kα) = 0.262 mm^{-1}, λ(Mo-Kα) = 0.71075 Å, θmax = 25.03°, $R1$ ([$I > 2\sigma(I)$]) = 0.0825, $wR2$ *(all data)* = 0.2201.

There is further ordered MeCN that is not bound to Sc and other disordered solvent. The structure refinement was completed using the SQUEEZE routine within PLATON to model disordered solvent.[1] This gives the 11MeCN per formula unit. 7 of these are ordered and 4 of these disordered.

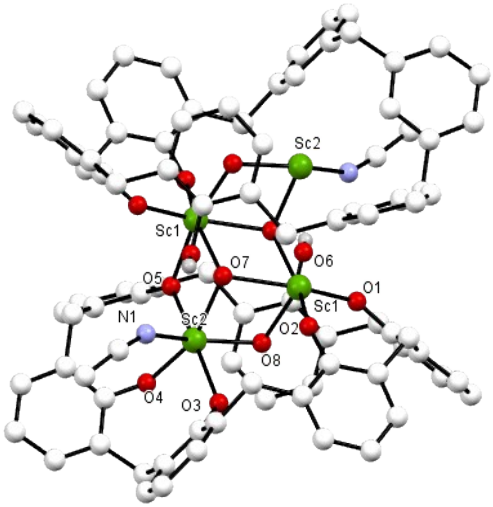


Figure S9. Molecular structure of $[(L^6H_4)Sc_2(OH)_2(NCMe)_2]_2$·12MeCN (**7**·12MeCN)
Selected bond lengths (Å) and angles (°): Sc(1) – O(1) 1.972(2), Sc(1) – O(2) 1.971(2), Sc(1) – O(7) 2.237(2), Sc(1) – O(8) 2.126(2), Sc(2) – O(3) 2.197(2), Sc(2) – O(4) 1.940(2), Sc(2) – O(5) 2.113(2), Sc(2) – O(7) 2.142(2), Sc(2) – O(8) 2.022(2), Sc(1) – Sc(2) 3.3123(7); Sc(1) – O(7) – Sc(2) 98.27(8).

Crystal data for compound **7**·12MeCN: $C_{160}H_{206}N_{14}O_{16}Sc_4$, M = 2761.22, Triclinic, space group $P\ \bar{1}$, a = 14.2475(3), b = 17.6138(2), c = 18.6288(4) Å, α = 113.082, β = 100.137(2), γ = 108.059 °, V = 3844.96(14) Å^3. Z = 1, Dc = 1.192 g cm^{-3}, F(000) = 1476, T = 100(2) K, μ(Cu-Kα) = 1.972 mm^{-1}, λ(MCu-Kα) = 1.54184 Å, θmax = 68.25°, $R1$ ([$I > 2\sigma(I)$] = 0.0816, $wR2$ *(all data)* = 0.2263.
Within the bowl of each *p-tert*-butylcalix[6]areneH is located a disordered acetonitrile molecule.

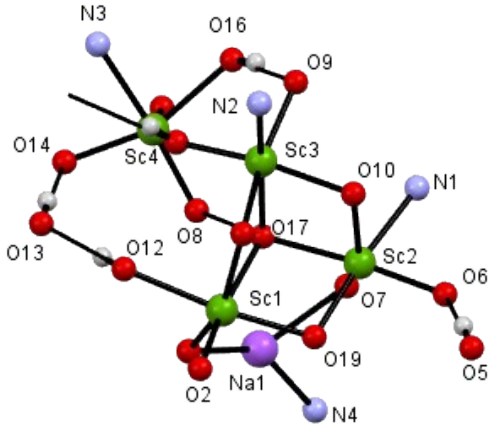


Figure S10. Core of **8**·6.14MeCN.
Selected bond lengths (Å) and angles (°) for $[Sc_4Na(L^8H_3)_2(O\textit{i}Pr)(OH)_2(NCMe)_4]$·6.14MeCN (**8**·6.14MeCN): Sc(1) – O(1) 2.029(1), Sc(1) – O(2) 1.941(2), Sc(1) – O(11) 2.1537(19), Sc(1) – O(12) 2.340(2), Sc(1) – O(17) 2.255(2), Sc(1) – O(19) 2.1364(18), Sc(2) – O(6) 2.020(2), Sc(2) –

O(7) 2.018(2), Sc(2) – O(10) 2.1226(19), Sc(2) – O(17) 2.1902(19), Sc(2) – O(19) 2.1212(19), Sc(2) – N(2) 2.321(3), Sc(3) – O(9) 2.0571(19), Sc(3) – O(10) 2.1391(19), Sc(3) – O(11) 2.1150(19), Sc(3) – O(17) 2.0708(19), Sc(3) – O(18) 2.111(2), Sc(3) – N(2) 2.236(2), Sc(4) – O(8) 2.026(2), Sc(4) – O(14) 2.075(2), Sc(4) – O(15) 1.916(2), Sc(4) – O(16) 2.296(2), Sc(4) – O(18) 2.171(2), Sc(4) – N(3) 2.324(3); Sc(1) – O(19) – Sc(2) 108.71(8), Sc(1) – O(11) – Sc(3) 103.73(8), Sc(2) – O(10) – Sc(3) 104.11(8), Sc(1) – Na(1) – Sc(3) 57.78(2).

Crystal data for compound **8**·6.14MeCN: $C_{199.28}H_{205.42}N_{10.14}O_{15}Sc_4$, M = 3297.60, monoclinic, space group $P2_1/n$, a = 22.06060(16), b = 33.26103(18), c = 28.1751(2) Å, β = 111.4715(9) V = 19238.9(2) Å^3, Z = 4, Dc = 1.138 g cm^{-3}, F(000) = 7068, T = 100(2) K, μ(Cu-Kα) = 1.68 mm^{-1}, λ(Cu-Kα) = 1.54178 Å, θmax = 70.1°, $R1$ ([$I > 2\sigma(I)$] = 0.066, $wR2$ *(all data)* = 0.202.
Sc(1) binds only to oxygens, 4 are from calixarenes of which one is protonated, O(12), then a bond to the μ3-OH$^-$, which connects Sc(1), Sc(2) and Sc(3), and a bond to the O*i*Pr$^-$ ligand which bridges to Sc(2). Sc(2) bonds to 5 oxygens and one N of an MeCN ligand. Apart from the links mentioned previously, there are 3 bonds to calixarene oxygens. Sc(3) bonds to 3 calixarene oxygens, the μ_3-OH$^-$, a μ_2-OH$^-$ which bridges to Sc(4), and the N of an MeCN ligand. Sc(4) lies away from the other three Sc metals and is coordinated by 4 calixarene oxygens, one of which is protonated, the μ_2-OH$^-$, and the N of an MeCN ligand. Na(1) bridges two calixarene oxygens of one calixarene, O(1) and O(7), bonds to one MeCN ligand, and forms π interactions with three C atoms on the phenolate ring attached to O(8). The μ_3-OH$^-$ forms an H-bond to calixarene oxygen O(8), while the μ_2-OH$^-$ form an H-bond to an MeCN of crystallization containing N(5). The former provides an additional bridge between the Sc(1) > Sc(3) triangle and Sc(4), in addition to that provided by the μ2-OH$^-$. Each calixarene has three protonated oxygens, a group of two, then a phenolate, then another OH. However, the pattern is different in each calixarene. In the calixarene containing O(1) > O(8), only non-coordinated OH groups are protonated with links from O(4) to O(3) and then a longer link to coordinated O(2), and a separate link between O(5) and coordinated O(6). The calixarene containing O(9) > O(16), coordinated O(12) is protonated and H-bonds to O(13), which in turn links to phenolate O(14); then non-coordinated O(16) H-bonds to coordinated phenolate O(9). Sc(1), Sc(2), and Sc(4) bind to both calixarenes, but Sc(3) binds only to one of them.

CCDC 2050782-2050789 and 2051060 contain the supplementary crystallographic data for **1**-**8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

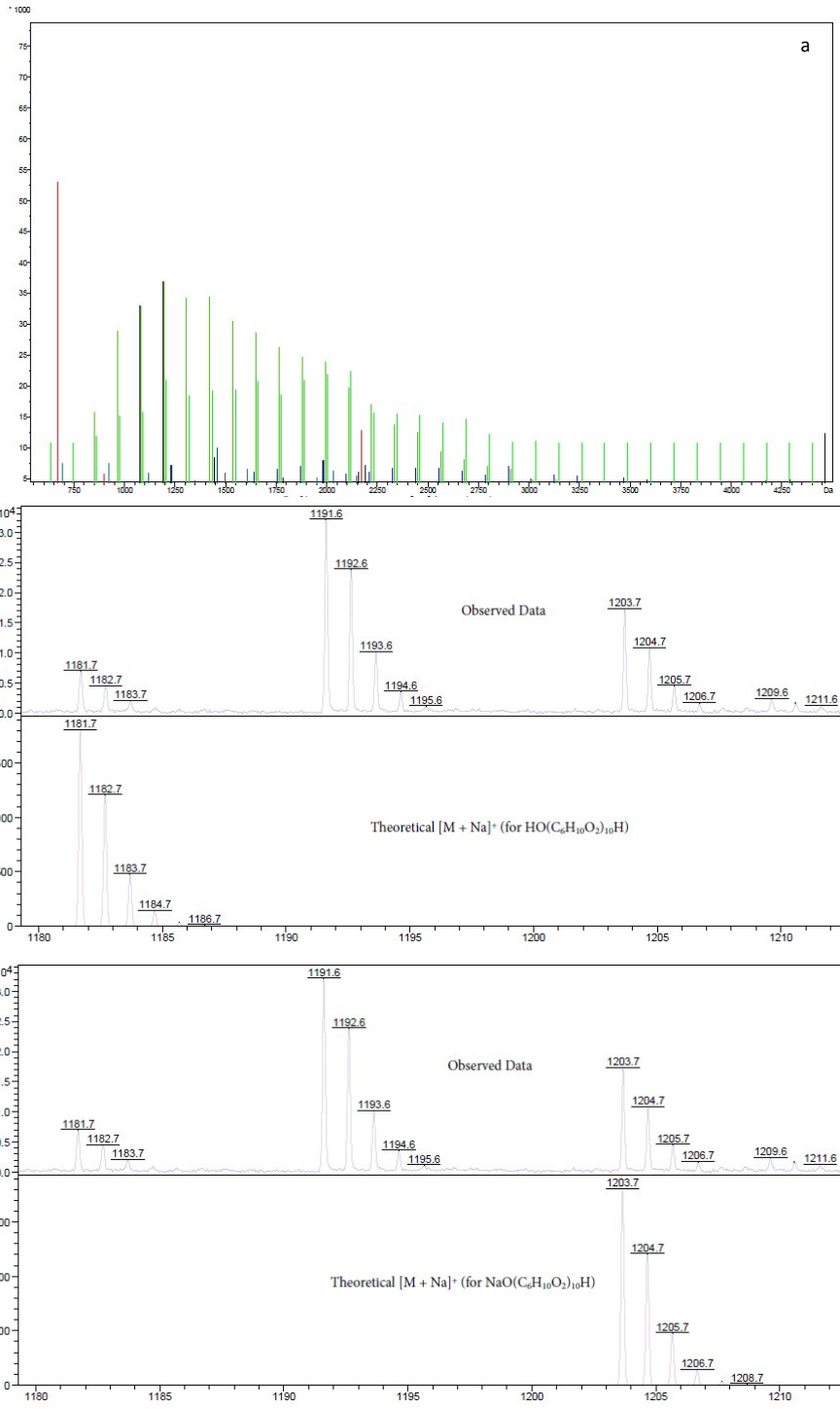
Catalysis

ROP Studies

Under a nitrogen atmosphere, a Schlenk flask was charged with 1 mL of a solution of the scandium complex in dry toluene (0.10 g/10 mL) and the required amount of a toluene solution of BnOH (1 equiv. per Sc center). The monomer (200 equiv. per Sc center) was then added and the mixture stirred at the required temperature (75 or 130 °C) for 24 h. The reaction was quenched with glacial acetic acid (0.2 mL) and the solution was then poured into cold MeOH (200 mL) allowing the precipitation of the polymer, which was recovered by filtration and dried overnight at 60 °C.
In the case the reactions performed in *solvent-free* conditions, the toluene from the catalyst- and, if added, the BnOH solutions was removed under reduced pressure at room temperature prior to adding the monomer. The reaction was quenched by addition of wet chloroform (5 mL) and the polymer was precipitated by pouring the resulting solution into cold acidified MeOH (200 mL).

Mass spectrometry

The PCL obtained with **4** (Table 1 entry 5) was characterized by MALDI-ToF spectrometry (Fig S11). The sample displayed series having the expected repeating unit mass of 114 for PLC. A population accountable to $HO(C_6H_{10}O_2)_nH$ species was observed (Figure S11b), along with a series corresponding to the –COONa-terminated derivatives (Figure S11c). The population with effectively no end-groups (cyclic *n*-mers) was also identified and appears to be the main series in the higher mass mode (Figure S11d-e).


a
b
Observed Data
Theoretical [M + Na]+ (for HO(C6H10O2)10H)
c
Observed Data
Theoretical [M + Na]+ (for NaO(C6H10O2)10H)
Intens. [a.u.]
Da

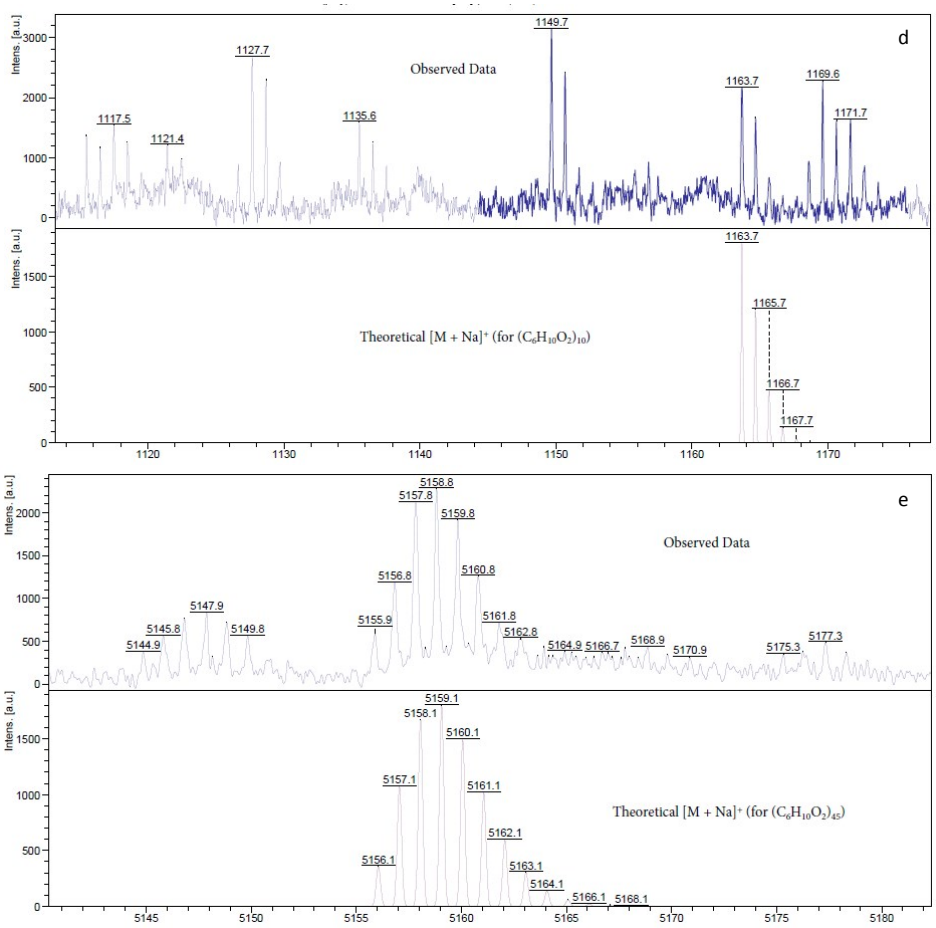


Figure S11. MALDI-ToF spectrum of the PCL synthesised with **4** (Table 1, entry 5). (a) complete overview; (b) Series corresponding to $HO(C_6H_{10}O_2)_nH$ species; (c) series corresponding to $NaO(C_6H_{10}O_2)_nH$ species; (d) series corresponding to cyclic species – low M_n fraction; (e) series corresponding to cyclic species – high M_n fraction.

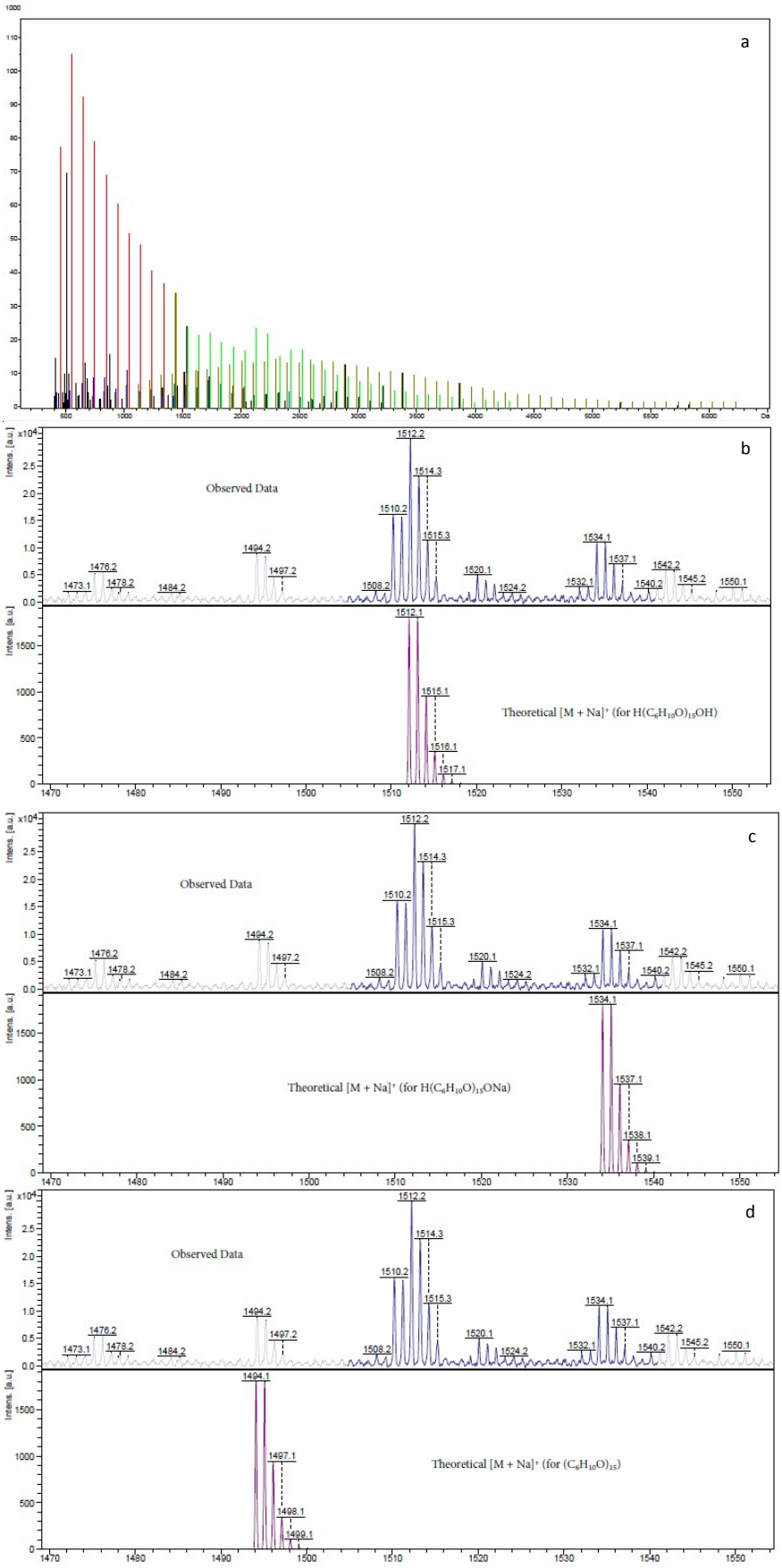


Figure S12. MALDI-ToF spectrum of the PCHO synthesised with Sc-oxacalix[3]arene. (a) complete overview; (b) Series corresponding to $HO(C_6H_{10}O_2)_{15}H$ species; (c) series corresponding to $NaO(C_6H_{10}O_2)_{15}H$ species; (d) series corresponding to cyclic $(C_6H_{10}O_2)_{15}$ species.

Cytotoxicity

MTS assay was used to calculate the percentage of viable cells in the culture media. This assay depends on the transformation of a tetrazolium salt into formazan in viable cells by mitochondrial dehydrogenase enzyme activity. There is a positive correlation between the amount of formazan and the number of viable cells in the culture media. HCT116 and HT-29 cells were seeded in 96 flat-bottomed microliter tissue culture plates with 20,000 cells per well in 200 μL media of McCoy's and Dulbecco's Modified Eagle's Medium (DMEM). In order to attach the cells to the well base in the microliter plates, the plates were incubated overnight in a 5% CO_2 incubator at 37 °C. After 24 h, the media was removed from the wells and 100 μL of the compound in the media was added. Various concentrations of compounds in the range of 0.78 mM to 1.56 nM were tested. After 24 h of incubation, the contents of the wells were removed using a multipipette, and then 180 μL of sterilized PBS was added followed by the addition of 20 μL of MTS reagent (Promega, U.K.). Plates were then returned to the incubator for 4 h. Colour intensity (absorbance) of the treated wells was measured at 490 nm using a Synergy HT microplate reader. The percentages of the cell viability of the treated cells were calculated based on positive and negative control where they represent 100% and 0% viable cells, respectively. IC_{50} values were calculated using GraphPad Prism software.

Cell Viability Studies

The compounds **1**, **2** and **7** were tested for cytotoxicity against cancerous cell lines (HCT116 and HT-29) to show that they are nontoxic at concentrations used for imaging. The IC_{50} values were determined using the cell viability assay, MTS. All compounds in this study are nontoxic in the concentration range nM−pM with IC_{50} values in the range of 2.23−14.96 μM. MTS graphs for treatment of HCT116 and HT-29 cells with compounds **1**, **2** and **7** are shown Figure S13.

To obtain more information on the mechanism of cell death induced by **1**, **2** and **7** compounds, a colorimetric MTS test was performed. It is worth noting that all probes at higher concentrations ranged 780 to 1.59 μM are significantly toxic. However, at lower concentrations ranged from 0.78 to 0.00156 μM, all probes exhibit non-toxicity to all cells tested. The relatively higher number of the counted viable cells found at these concentrations after 24 h of treatment indicates that the complexes are safe and can be used for catalytic purpose.

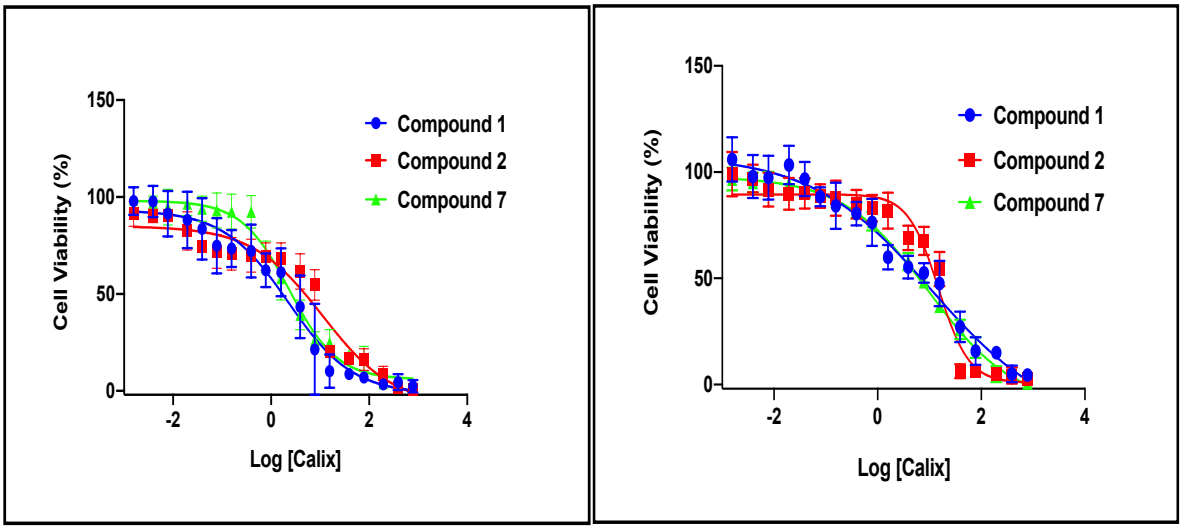


Figure S13. Left: MTS graph for complex **1, 2** and **7** against HCT116 cells. Right: MTS graph for complex **1, 2** and **7** against HT-29 cells.

As reports of scandium calix[*n*]arenes are scant, comparison with previous titanium-calixarene compounds are made. When compared with some previous titanium-calixarene based anti-cancer agents, there are more effective monomeric compounds in the literature, particularly among the phenolato derivatives. As a comparator, cisplatin, gives IC_{50} values about 20 μM against HT-29 cell line. At the same cell line (HT-29) a bis(β-diketonato)titanium complex $[(bzac)_2Ti(O\textit{i}Pr)_2]$ shows an IC_{50} value 11.6 μM. Furthermore, a number of Ti-SALAN complexes gives IC_{50} values from 1–10 μM. Table S1 summarises the IC_{50} values of selected known Ti based anti-cancer agents.[3] Synthesised compounds **1** and **7** are less toxic compared to known Ti compounds at the same cell line HT-29.

Table S1. Shows the IC_{50} (uM) values for known calixarene compounds and cisplatin.[4]

Compound	**HT-29**
Cisplatin	20
$[(bzac)_2Ti(O\textit{i}Pr)_2]$	11.6
$[Lig^1Ti(OArMe_2)_2]$	10
$[Lig^2Ti(OArMe_2)_2]$	3.5
$[Lig^3Ti(OArMe_2)_2]$	1.2

References

[1] A. L. Spek, *Acta Crysallogr. Sect. A: Fundam. Crystalogr.* 1990, **46**, C34.

[2] A search of the CSD database on 23.2.21 revealed 73 hits for Sc-OH_2 with a total of 201 Sc-OH_2 bonds with a mean of 2.17(7) Å; 1 hit for a terminal Sc-OH at a distance of 2.188(3) Å; 26 hits for

bridging Sc-OH giving 45 distances with a mean of 2.09(5) Å; 9 hits for strictly two-coordinate Sc-O-Sc oxide with a mean of 1.92(8) Å; 11 hits for strictly three-coordinate Sc-O-Sc oxide with a mean of 2.026(815) Å (for 13 bonds). F. H. Allen, *Acta Crysallogr. Sect. B: Struct. Sci.* 2002, **58**, 380-388.

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