Supplementary information for

Hierarchical self-assembly of metallo-dendrimers

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Preparation of the 2,3-Diacetobenzoic acid 3

2,3-Dihydroxybenzoic acid **2** (1eq.), acetic anhydride (3 eq.) and a few drops of sulfuric acid were heated to 100°C for two hours. The mixture was cooled and 5 ml ice water were added. The precipitate was collected, dissolved in chloroform (100 ml) and washed with water (100 ml). The organic phase was dried under reduced pressure to give the crude product.

Yield: 98% colourless solid. Mp 156-159°C. - ^{1}H-NMR ($CDCl_3$) δ = 7.92 (dd, J = 8.0, 1.7 Hz, 1H), 7.37 (dd, J = 8.0, 1.7 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 2.27 (s, 3H), 2.25 (s, 3H).^{13}C-NMR ($CDCl_3$) δ = 186.6 (C), 168.9 (C), 168.2 (C), 143.6 (C), 143.1 (C), 129.6 (CH), 128.8 (CH), 126.2 (C), 123.9 (C), 20.7 (CH_3). - EI-MS: m/z = 238 $[M]^{+\bullet}$. IR (cm^{-1}) = 1772, 1692, 1585, 1470, 1423, 1371, 1306, 1205, 1159, 1020, 911, 857, 755, 695. - Calcd. for $C_{11}H_{10}O_6$: C 55.47, H 4.23, found: C 55.16, H 3.97.

General procedure for the preparation of the dendritic ligands

Bromide **5a-c** (1 eq.),[i] 2,3-diacetobenzoic acid **3** (1 eq.) and K_2CO_3 (6 eq.) were suspended in acetone and the mixture was heated to reflux for three hours. After cooling salts were filtered off and the organic layer was evaporated. The product was purified by chromatography (CH_2Cl_2/*n*-pentane, 3/1). The crude esters **6a-c** (1 eq.) and K_2CO_3 (6 eq.) were suspended in acetone /water (10/1) and heated to reflux for three hours. After cooling, water was added and the obtained precipitate was filtered and purified by chromatography (CH_2Cl_2).

1a-H$_2$: Yield: 74 % colourless solid. Mp 87-89°C. - ^{1}H-NMR ($CDCl_3$) δ = 10.80 (s, 1OH), 7.40 (dd, J = 7.9, 1.7 Hz, 1H), 7.10 (dd, J = 7.9, 1.7 Hz, 1H), 6.76 (t, J = 7.9 Hz, 1H), 6.56 (d, J = 2.5 Hz, 2H), 6.40 (t, J = 2.5 Hz, 1H), 5.83 (br, 1 OH), 5.29 (s, 2H), 3.78 (s, 6H). - ^{13}C-NMR ($CDCl_3$) δ = 170.0 (C), 160.9 (C), 149.0 (C), 145.1 (C), 137.4 (C), 120.7 (CH), 120.1 (CH), 119.3 (CH), 112.4 (C), 106.0 (CH), 100.2 (CH), 67.0 (CH_2), 55.4 (CH_3). - EI-MS: m/z = 304 $[M]^{+\bullet}$. - IR (cm^{-1}) = 3476, 1741, 1671, 1601, 1473, 1383, 1459, 1309, 1271, 1236, 1208, 1156, 1066, 1020, 841, 749, 677. – Calcd. for $C_{16}H_{16}O_6$: C 63.15, H 5.30, found: C 63.24, H 5.14.

1b-H$_2$: Yield: 66 % colourless solid. Mp 106-109°C. - ^{1}H-NMR ($CDCl_3$) δ = 10.76 (s, 1OH), 7.35-7.25 (m, 11H), 7.03 (d, J = 8.1 Hz, 1H), 6.72 (t, J = 8.1 Hz, 1H), 6.57 (d, J = 2.2 Hz, 2H), 6.52 (t, J = 2.2 Hz, 1H), 5.60 (s, 1 OH), 5.21 (s, 2H), 4.95 (s, 4H). - ^{13}C-NMR ($CDCl_3$) δ = 170.0 (C), 160.1 (C), 148.9 (C), 145.0 (C), 137.4 (C), 136.6 (C), 128.6 (CH), 128.1 (CH), 127.5 (CH), 120.7 (CH), 120.0 (CH), 119.3 (CH), 112.4 (C), 107.1 (CH), 102.0 (CH), 70.2 (CH_2), 67.0 (CH_2). - EI-MS: m/z = 456 $[M]^{+\bullet}$. - IR (cm^{-1}) = 3538, 1682, 1598, 1463, 1367, 1301, 1264, 1156, 1061, 829, 755, 735, 696. – Calcd. for $C_{28}H_{24}O_6$: C 73.70, H 5.30, found: C 73.50, H 5.30.

1c-H$_2$: Yield: 38 % colourless solid. Mp 119°C. - ^{1}H-NMR ($CDCl_3$) δ = 10.83 (s, 1OH), 7.42-7.30 (m, 21H), 7.08 (d, J = 8.0 Hz, 1H), 6.77 (t, J = 8.0 Hz, 1H), 6.66 (d, J = 2.2 Hz, 4H), 6.63 (d, J = 2.2 Hz, 2H), 6.57 (d, J = 2.2 Hz, 2H), 6.54 (d, J = 2.2 Hz, 1H), 5.65 (s, 1 OH), 5.28 (s, 2H), 5.02 (d, J = 4.1 Hz, 8H), 4.96 (d, J = 4.1 Hz, 4H)). - ^{13}C-NMR ($CDCl_3$) δ = 160.1 (C), 160.0 (C), 159.9 (C), 139.1 (C), 139.0 (C), 138.2 (C), 137.4 (C), 136.8 (C), 136.7(C), 128.6 (CH), 128.0 (CH), 127.6 (CH), 120.7 (CH), 120.0 (CH), 119.3 (CH), 107.2 (CH), 106.4 (CH), 102.0 (CH), 101.6 (CH), 70.2 (CH_2), 70.1 (CH_2), 70.0 (CH_2). - ESI-MS: m/z = 879 $[M-H]^{-\bullet}$. - IR (cm^{-1}) = 3065, 3032, 2932, 2873, 1737, 1673, 1598, 1463, 1377, 1343, 1304, 1150, 1056, 837, 754, 698. – Calcd. for $C_{56}H_{48}O_{10}$: C 76.35, H 5.49, found C 76.16, H 5.83.

General procedure for the preparation of the metal complexes

Ligand **1a-c-H$_2$** (3 eq.), $TiO(acac)_2$ (1 eq.) and base (Li_2CO_3, K_2CO_3, 1 eq.) were dissolved in methanol/CH_2Cl_2 (1:2) and stirred overnight. Solvent was removed under reduced pressure to give the complex as red solid. Gallium complexes were prepared the same way starting from ligand **1a/b-H$_2$** (3 eq.), $Ga(acac)_3$ (1 eq.) and base (Li_2CO_3, K_2CO_3, 1.5 eq.) to give light yellow solids as products.

Li$_4$(1a)$_6$Ti$_2$: Yield: quanititative, red solid. - ^{1}H-NMR (CD_3OD) δ = 7.09 (dd, J = 8.0, 1.6 Hz, 6H), 6.53 (dd, J = 8.0, 1.6 Hz, 6H), 6.49 (t, J= 8.0 Hz, 6H), 6.28 (d, J = 2.2 Hz, 12H), 6.23 (d, J = 2.2 Hz, 6H), 4.37 (d, J = 12.6 Hz, 6H), 3.92 (d, J = 12.6 Hz, 6H), 3.62 (s, 36H). – neg. ESI-MS: m/z = 1929 $[Li_3(\mathbf{1a})_6Ti_2]^-$, 961 $[Li(\mathbf{1a})_3Ti]^-$. - IR (cm^{-1}) = 3433, 1681, 1599, 1447, 1297, 1255, 1217, 1154, 1067, 1213, 816, 749, 690, 538. - Calcd. for $C_{48}H_{42}O_{18}TiLi_2$•6MeOH: C 55.87, H 5.73, found: C 55.56, H 5.33.

Li$_6$(1a)$_6$Ga$_2$: Yield: quanititative, light yellow solid. - ^{1}H-NMR (CD_3OD) δ = 6.93 (dd, J = 8.0, 1.4 Hz, 6H), 6.62 (dd, J = 8.0, 1.4 Hz, 6H), 6.40 (s, 12H), 6.27 (s, 6H), 6.15 (t, J = 8.0 Hz, 6H), 4.41 (br, 6H), 4.06 (br, 6H), 3.68 (s, 36H). – neg. ESI-MS: m/z = 1982 $[HLi_4(\mathbf{1a})_6Ga_2]^-$, 990 $[M_M\text{-}Li]^-$. IR (cm^{-1}) = 1681, 1599, 1459, 1301, 1266, 1218, 1153, 1068, 1016, 744. Anal. Calcd. for $C_{48}H_{42}O_{18}GaLi_3$•8MeOH: C 53.65, H 5.94, found: C 53.50, H 5.69.

$Li_4(1b)_6Ti_2$: Yield: quanititative, red solid. - ^{1}H-NMR (CD_3OD:$CDCl_3$, 1:2) δ = 7.18 (m, 60H), 6.97 (dd, J = 8.0, 1.4 Hz, 6H), 6.49 (dd, J= 8.0, 1.4 Hz, 6H), 6.32 (s, 18H), 6.28 (t, J = 8.0 Hz, 6H), 4.78 (s, 24H), 4.35 (d, J = 12.9 Hz, 6H), 3.87 (d, J = 12.9 Hz, 6H). – neg. ESI-MS: m/z = 2843 $[Li_3(\mathbf{1b})_6Ti_2]^-$. - IR (cm^{-1}) = 1681, 1597, 1447, 1377, 1296, 1255, 1217, 1153, 1061, 1011, 816, 744, 694, 539. – Calcd. for $C_{84}H_{66}O_{18}TiLi_2$•3MeOH: C 68.69, H 5.17, found: C 68.76, H 5.16.

$K_2(1b)_3Ti$: Yield: quanititative, red solid. ^{1}H-NMR (CD_3OD:$CDCl_3$, 1:2) δ = 7.25-7.15 (m, 36H), 7.05 (d, J = 6.2 Hz, 3H), 6.42 (br, 9H), 5.05 (s, 6H), 4.90 (s, 12H). - ESI-MS: m/z = 1450 $[K(\mathbf{1b})_3Ti]^-$. - IR (cm^{-1}) = 1696, 1597, 1448, 1376, 1289, 1257, 1217, 1151, 1060, 1011, 832, 742, 696, 676, 536. – Calcd. for $C_{84}H_{66}O_{18}TiK_2$•3MeOH: C 65.90, H 4.97, found: C 65.44, H 4.50.

$Li_6(1b)_6Ga_2$: Yield: quanititative, colourless solid. - ^{1}H-NMR (CD_3OD/$CDCl_3$; 1:4) δ = 7.25-7.15 (m, 60H), 6.95 (dd, J = 8.2, 1.4 Hz, 6H), 6.60 (dd, J = 8.2, 1.4 Hz, 6H), 6.44 (s, 12H), 6.32 (s, 6H), 6.13 (t, J = 8.2 Hz, 6H), 4.79 (s, 24H), 4.43 (d, J = 11.4 Hz, 6H), 3.96 (d, J = 11.4 Hz, 6H). – neg. ESI-MS: m/z = 2960 $[Li_6(\mathbf{1b})_6Ga_2(MeOH)_2H]^-$. - IR (cm^{-1}) = 3392, 2927, 1680, 1597, 1457, 1379, 1300, 1266, 1219, 1152, 1065, 1015, 833, 742, 697, 497. – Calcd. for $C_{84}H_{66}O_{18}GaLi_3$•MeOH: C 68.70, H 4.75, found: C 68.53, H 4.44.

$Li_4(L^2)_6Ti_2$: Yield: quanititative, red solid. - ^{1}H-NMR (CD_3OD:$CDCl_3$, 1:4) δ = 7.28-7.10 (m, 120H), 7.04 (m, 6H), 6.55 (br, 12H), 6.43 (br, 24H), 6.28 (br, 30H), 4.90 (br, 24H), 4.58 (br, 48H), 4.31 (br, 6H), 3.82 (br, 6H). - IR (cm^{-1}) = 3417, 2934, 2868, 1734, 1682, 1597, 1448, 1379, 1294, 1257, 1216, 1153, 1049, 829, 738, 691. – Calcd. for $C_{168}H_{138}O_{30}TiLi_2$•10$H_2O$: C 70.09, H 5.53, found: C 70.09, H 5.50.

X-ray structure analysis: Data set was collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* **2003**, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122), graphics SCHAKAL (E. Keller, Univ. Freiburg, 1997).

Comparison of the NMR spectra of free ligands and of their complexes

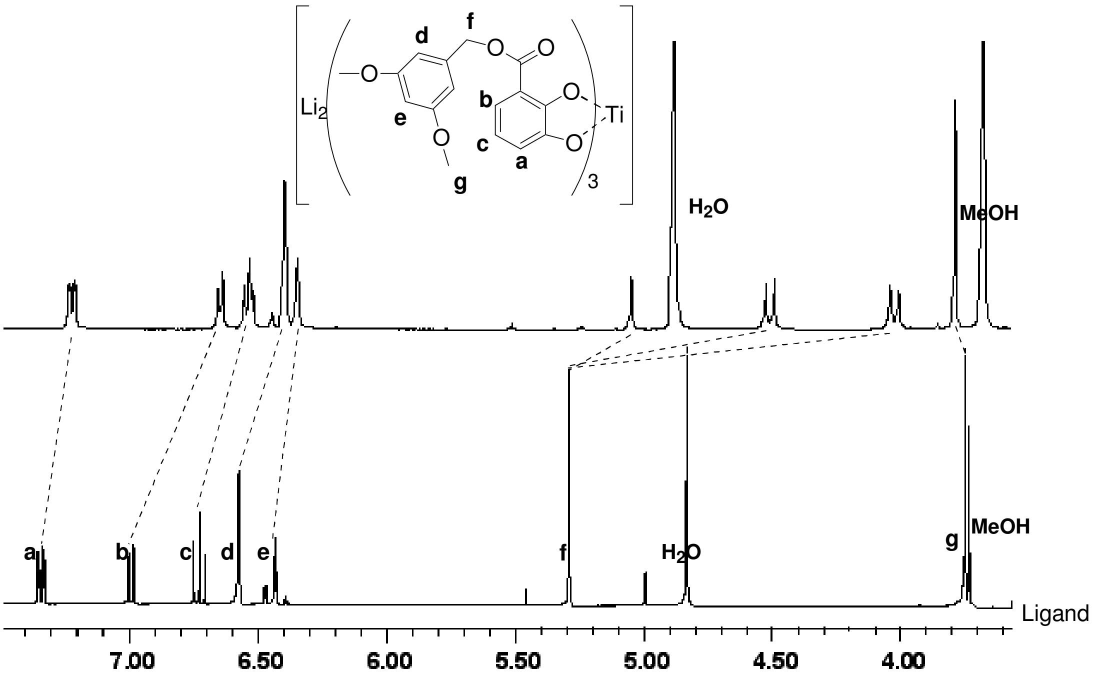

Fig. S1 ^{1}H NMR spectra of **1a-H$_2$** in methanol-d$_4$ (bottom) and of Li$_4$[Ti$_2$(**1a**)$_6$] in methanol-d$_4$ / CDCl$_3$, 2/1 (top). Unfortunately the solubility properties enforce dissolution of the compounds in different solvents. However, remarkable differences (e. g. diastereotopic behavior of CH$_2$ protons) can be observed.

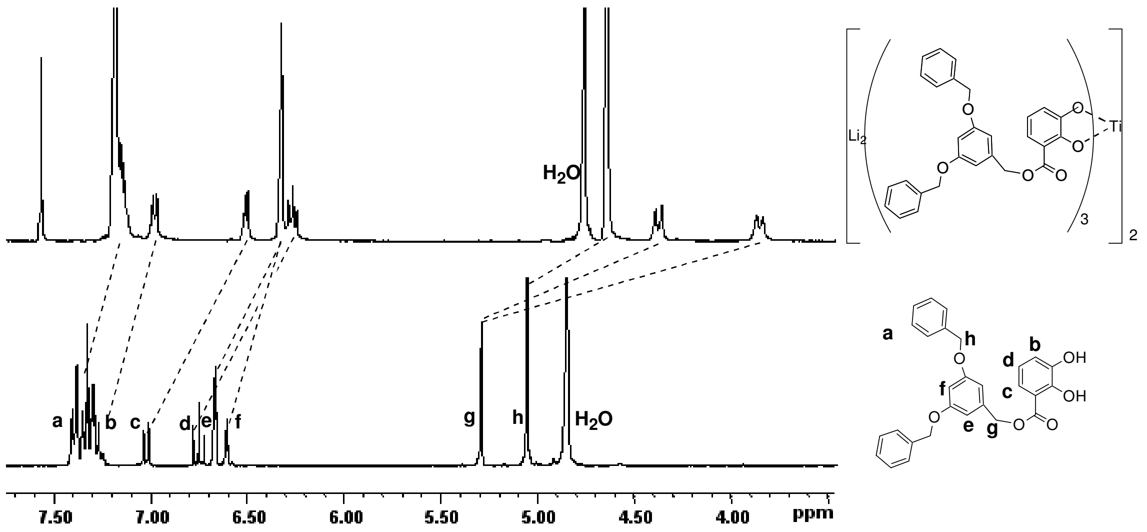

Fig. S2 ^{1}H NMR spectra of **1b-H$_2$** in methanol-d$_4$ (bottom) and of Li$_4$[Ti$_2$(**1b**)$_6$] in methanol-d$_4$ / CDCl$_3$, 1/2 (top).

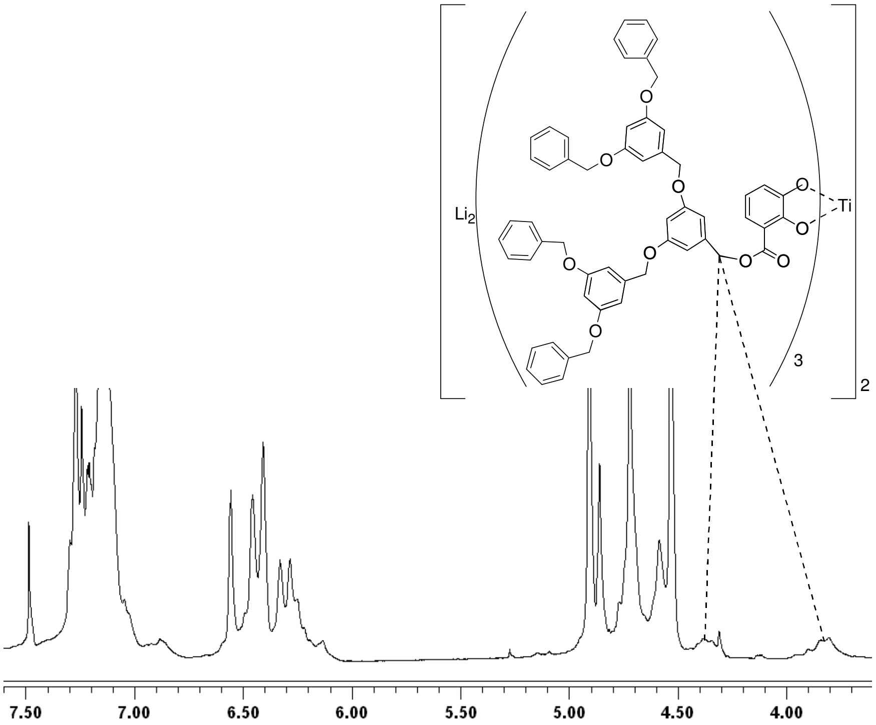

Fig. S3 ^{1}H NMR spectra of $Li_4[Ti_2(\mathbf{1c})_6]$ in methanol-d$_4$ / $CDCl_3$, 1/4.

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[i] C. Hawker and J. M. J. Frechet, Chem. Commun 1990, 1010.