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. - 1H-NMR (CDCl₃) 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). 13C-NMR (CDCl₃) 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 (CH₃). - EI-MS: m/z = 238 [M]+. IR (cm⁻¹) = 1772, 1692, 1585, 1470, 1423, 1371, 1306, 1205, 1159, 1020, 911, 857, 755, 695. - Calcd. for C₁₁H₁₀O₆: 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.), 2,3-diacetobenzoic acid 3 (1 eq.) and K₂CO₃ (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 (CH₂Cl₂/n-pentane, 3/1). The crude esters 6a-c (1 eq.) and K₂CO₃ (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 (CH₂Cl₂).

1a-H₂: Yield: 74 % colourless solid. Mp 87-89°C. - 1H-NMR (CDCl₃) 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). - 13C-NMR (CDCl₃) 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 (CH₂), 55.4 (CH₃). - EI-MS: m/z = 304 [M]+. - IR (cm⁻¹) = 3476, 1741, 1671, 1601, 1473, 1383, 1459, 1309, 1271, 1236, 1208, 1156, 1066, 1020, 841, 749, 677. – Calcd. for C₁₆H₁₆O₆: C 63.15, H 5.30, found: C 63.24, H 5.14.

1b-H₂: Yield: 66 % colourless solid. Mp 106-109°C. - 1H-NMR (CDCl₃) 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]+. - 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.

$^1$H-2H: 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, 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]-. - 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$_2$CO$_3$, K$_2$CO$_3$, 1 eq.) were dissolved in methanol/CH$_2$Cl$_2$ (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$_2$CO$_3$, K$_2$CO$_3$, 1.5 eq.) to give light yellow solids as products.

Li$_6$(1a)$_6$Ti$_2$: Yield: quanititative, red solid. - $^1$H-NMR (CD$_3$OD) 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$_3$(1a)$_6$Ti$_2$]+, 961 [Li(1a)$_3$Ti]$^+$. - 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$_3$OD) 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$_4$(1a)$_6$Ga$_2$]+, 990 [M$_{Me}$-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.
Li₄(1b)₆Ti₂: Yield: quantitative, red solid. - ¹H-NMR (CD₃OD:CDCl₃, 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 [Li₃(1b)₆Ti₂]⁻. - IR (cm⁻¹) = 1681, 1597, 1447, 1377, 1296, 1255, 1217, 1153, 1061, 1011, 816, 744, 694, 539. – Calcd. for C₈₄H₆₆O₁₈TiLi₂•3MeOH: C 68.69, H 5.17, found: C 68.76, H 5.16.

K₂(1b)₃Ti: Yield: quantitative, red solid. ¹H-NMR (CD₃OD:CDCl₃, 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(1b)₃Ti]⁻. - IR (cm⁻¹) = 1696, 1597, 1448, 1376, 1289, 1257, 1217, 1151, 1060, 1011, 832, 742, 696, 676, 536. – Calcd. for C₈₄H₆₆O₁₈TiK₂•3MeOH: C 65.90, H 4.97, found: C 65.44, H 4.50.

Li₆(1b)₆Ga₂: Yield: quantitative, colourless solid. - ¹H-NMR (CD₃OD/CDCl₃; 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 [Li₆(1b)₆Ga₂(MeOH)₂H]⁻. - IR (cm⁻¹) = 3392, 2927, 1680, 1597, 1457, 1379, 1300, 1266, 1219, 1152, 1065, 1015, 833, 742, 697, 497. – Calcd. for C₈₄H₆₆O₁₈GaLi₃•MeOH: C 68.70, H 4.75, found: C 68.53, H 4.44.

Li₄(1b)₆Ti₂: Yield: quantitative, red solid. - ¹H-NMR (CD₃OD:CDCl₃, 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 C₁₆₈H₁₃₆O₃₀TiLi₂•10H₂O: C 70.09, H 5.53, found: C 70.09, H 5.50.

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$_2$(1c)$_6$] in methanol-d$_4$ / CDCl$_3$, 1/4.

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