Electronic Supplementary Material (ESI) for Dalton Transactions.

Contents

1 Materials and methods

1.1 General notes

Unless stated otherwise, all commercial reagents were used without further purification. Substances and chemicals used in this research were purchased from ABCR, Acros Organics, Alfa Aesar or Sigma Aldrich. 2,3-Bis(benzyloxy)benzoic acid was prepared according to a literature procedure.[1] Moisture or oxygen sensitive compounds were prepared under nitrogen atmosphere using standard Schlenk techniques.

1.2 Analytical methods

Thin layer and column chromatography

TLC was carried out using Merck silica gel 60, F254 precoated aluminium foil plates (d = 0,25 nm). Visualization was performed with UV light irradiation or basic aqueous potassium permanganate staining solution. Silica gel (Fluka silica gel (SiO_2), 40–60 ţm) was purchased by Silicycle and used for medium pressure chromatography ("flash"-chromatography), applying the respective solvent system.

NMR spectroscopy

All samples were dissolved and measured in deuterated solvents ($CDCl_3$, DMSO-d_6). Measurements were performed at 25°C. ^{1}H NMR spectra were recorded applying a Varian Inova 400 MHz or Varian Inova 600 MHz spectrometer operating at 400 Mhz or 600 Mhz. Residual proton signals from deuterated solvents were used as standards. ^{13}C NMR spectra were recorded on a Varian Inova 400 MHz or Varian Inova 600 MHz spectrometer operating at 150 MHz using ^{13}C signals from deuterated solvents as standards. The chemical shift δ is given in ppm. Abbreviations used to denote multiplicity are: s for singlet, d for dublet, t for triplet, q for quartet, p for pentet and m for multiplet. Coupling constants J are reported in Hertz (Hz). The proton numbers were obtained by integration of the corresponding signals.

Mass spectrometry

Mass spectrometry was measured on a Thermo Finnigan LCQ Deca XP Plus applying electrospray ionisation (ESI). All characteristic masses are given with sum formula and electric charge in the mass/charge ratio (m/z).

Elemental analysis

Elemental analysis was performed using a Heraeus CHN-O-Rapid elemental analyzer. Ratios of carbon, hydrogen and if relevant nitrogen are given in mass percentages.

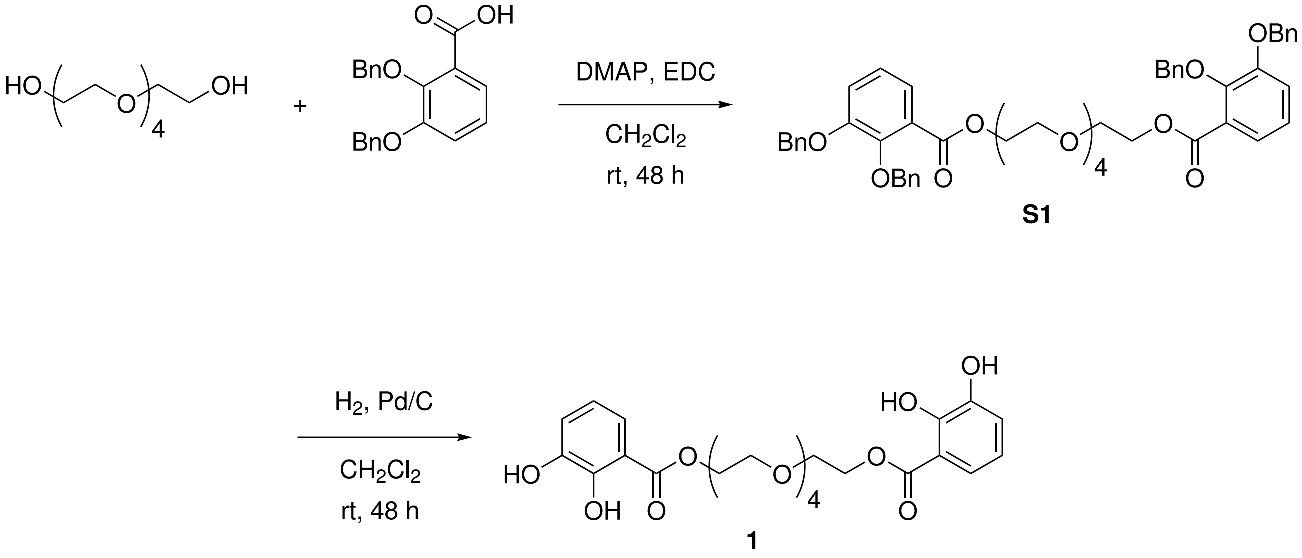
IR spectroscopy

IR measurements were recorded by diffusion in KBr on a Perkin-Elmer 1760 FT machine in the range 4000-400 cm^{-1}. All absorption bands are listed with the location of the bands given in cm^{-1}.

2 Synthetic procedures

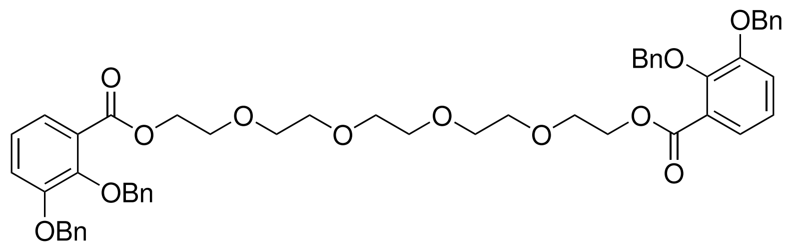
2.1 Ligand synthesis

Ligand **1**-H_4 were synthesized in a two-step procedure from pentaethylene glycol (Scheme 1). The oligoethylene glycol was connected in a Steglich esterification[2] to 2,3-bis(benzyloxy)benzoic acid yielding the protected species (**S1**). Subsequent benzyl deprotection by catalytic hydrogenolysis[3] afforded the desired ligand **1**-H_4.



Scheme 1: *Synthesis of ligands **1**.*

Synthesis of S1



Procedure:

S1 was prepared applying a Steglich esterification.[2] Pentaethylene glycol (1184 mg, 4.96 mmol, 1.0 eq.) was dissolved in dichloromethane (50 mL). 2,3-Bis(benzyloxy)benzoic acid (3746 mg, 14.90 mmol, 3.0 eq.), 4-dimethylaminopyridine (771 mg, 4,96 mmol, 1.0 eq.) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (1821 mg, 14,90 mmol, 3.0 eq.) were added subsequently and the reaction mixture was stirred at 25°C for 48 h. Upon completion, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2, 2:1 pentane: ethyl acetate) to afford the title compound (2105 mg, 2.42 mmol, 49 %) as a white solid.

^{1}H-NMR (600 MHz, DMSO-d$_6$): δ = 7.50 7.45 (m, 4H, 4H$_{arom.}$), 7.43 7.32 (m, 12H, 12H$_{arom.}$), 7.29 (dd, J = 5.0, 2.0 Hz, 6H, 6H$_{arom.}$), 7.22 (dd, J = 7.9, 1.6 Hz, 2H, 2H$_{arom.}$), 7.17 (t, J = 7.9 Hz, 2H, 2H$_{arom.}$), 5.18 (s, 4H, 2CH_2), 5.00 (s, 4H, 2CH_2), 4.38 4.21 (m, 4H, 2CH_2), 3.66 3.59 (m, 4H, 2CH_2), 3.47 (dd, J = 5.8, 3.5 Hz, 4H, 2CH_2), 3.42 (dd, J = 5.8, 3.5 Hz, 4H, 2CH_2), 3.40 (s, 4H, 2CH_2) ppm.

^{13}C-NMR (151 MHz, DMSO-d$_6$: 165.7 (CO_2CH_2), 152.3 (C$_{arom.}$), 146.74, 137.3 (C$_{arom.}$), 136.6 (C$_{arom.}$), 128.4 (C$_{arom.}$), 128.2 (C$_{arom.}$), 128.1 (C$_{arom.}$), 128.0 (C$_{arom.}$), 127.8 (C$_{arom.}$), 127.8 (C$_{arom.}$), 126.6 (C$_{arom.}$), 124.3 (C$_{arom.}$), 121.6 (C$_{arom.}$), 117.6 (C$_{arom.}$), 74.8 (CH_2), 70.2 (CH_2), 69.7 (CH_2), 69.7 (CH_2), 69.7 (CH_2), 68.2 (CH_2), 64.0 (CH_2) ppm.

ESI-MS: m/z: Calculated for $C_{52}H_{54}NaO_{12}^+$ [M+Na]$^+$: 893.3513; found: 893.3519.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3857, 3446, 3063, 3031, 2873, 2328, 2168, 2087, 1994, 1912, 1722, 1579, 1460, 1373, 1260, 1088, 1046, 918, 854, 807, 750, 697.

Elemental analysis: Calculated for $C_{52}H_{54}O_{12}$: C: 71.71%, H: 6.25%; found: C: 71.67%, H: 6.30%.

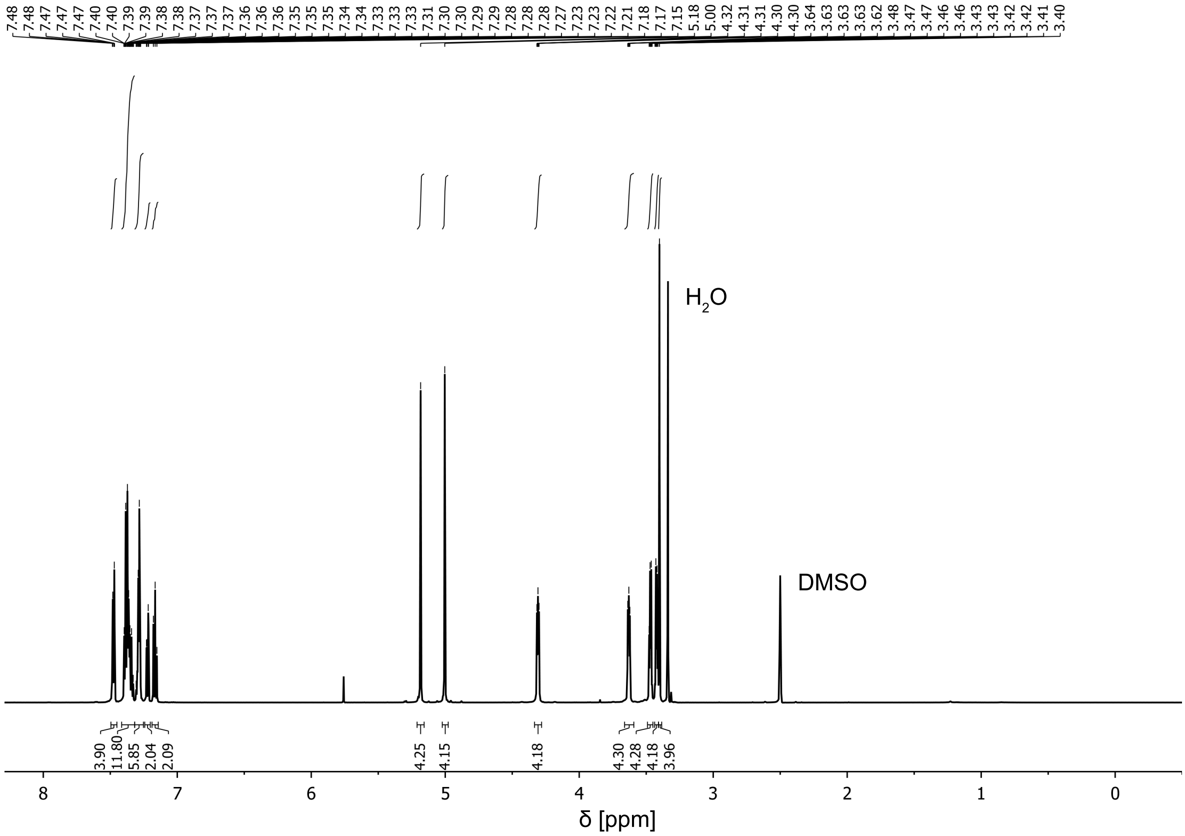


Figure S1: ^{1}*H-NMR spectrum (600 MHz) of **S1** in DMSO at 25° C.*

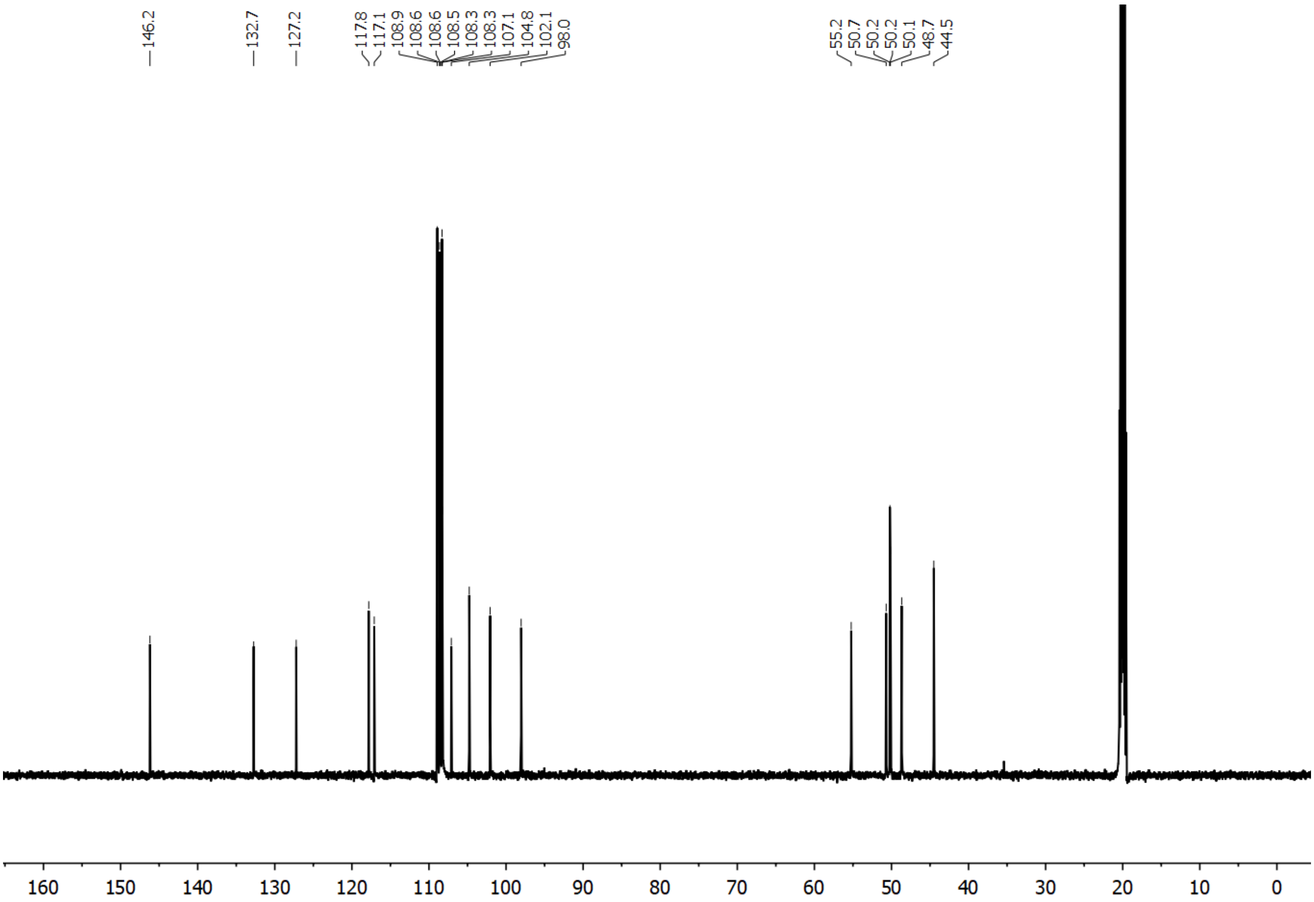
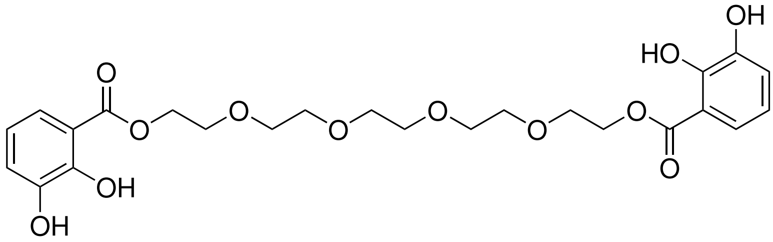


Figure S2: ^{13}*C-NMR spectrum (600 MHz) of **S1** in DMSO at 25° C.*

Synthesis of 1-H$_4$



Procedure:

1-H$_4$ was prepared utilizing a standard[3] benzyl deprotection procedure. **S1** (500 mg, 0.57 mmol) was dissolved in dichloromethane (50 mL). Palladium on carbon (10 wt% Pd on C, 51 mg) was added and the reaction stirred under H$_2$ atmosphere (1 atm) at 25°C for 48 h. Upon completion the reaction mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO$_2$, 2:1 pentane: ethyl acetate) to afford the title compound **1**-H$_4$ (138 mg, 0.27 mmol, 47 %) as a white solid.

^{1}H-NMR (600 MHz, DMSO-d$_6$): δ = 7.22 (dd, J = 7.9, 1.6 Hz, 2H, 2H$_{\text{arom.}}$), 7.01 (dd, J = 7.9, 1.6 Hz, 2H, 2H$_{\text{arom.}}$), 6.73 (t, J = 7.9 Hz, 2H, 2H$_{\text{arom.}}$), 4.42 4.37 (m, 4H, 2CH$_2$), 3.73 3.70 (m, 4H, 2CH$_2$), 3.54 (dd, J = 5.9, 3.6 Hz, 4H, 2CH$_2$), 3.50 3.47 (m, 4H, 2CH$_2$), 3.46 (s, 4H, 2CH$_2$) ppm.

^{13}C-NMR (151 MHz, DMSO-d$_6$: δ = 169.8 (CO$_2$CH$_2$), 150.0 (C$_{\text{arom.}}$), 146.6 (C$_{\text{arom.}}$), 121.2 (C$_{\text{arom.}}$), 120.0 (C$_{\text{arom.}}$), 119.4 (C$_{\text{arom.}}$), 113.5 (C$_{\text{arom.}}$), 70.6 (CH$_2$), 69.9 (CH$_2$), 68.5 (CH$_2$), 64.9 (CH$_2$) ppm.

ESI-MS: m/z: Calculated for $C_{24}H_{30}NaO_{12}^+$ [M+Na]$^+$: 533.1635; found: 533.1616.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3352, 3141, 2905, 2163, 2038, 1674, 1466, 1370, 1298, 1264, 1092, 974, 944, 843, 791, 745, 712.

Elemental analysis: Calculated for $C_{24}H_{30}O_{12}$: C: 56.47%, H: 5.92%; found: C: 55.70%, H: 6.0%.

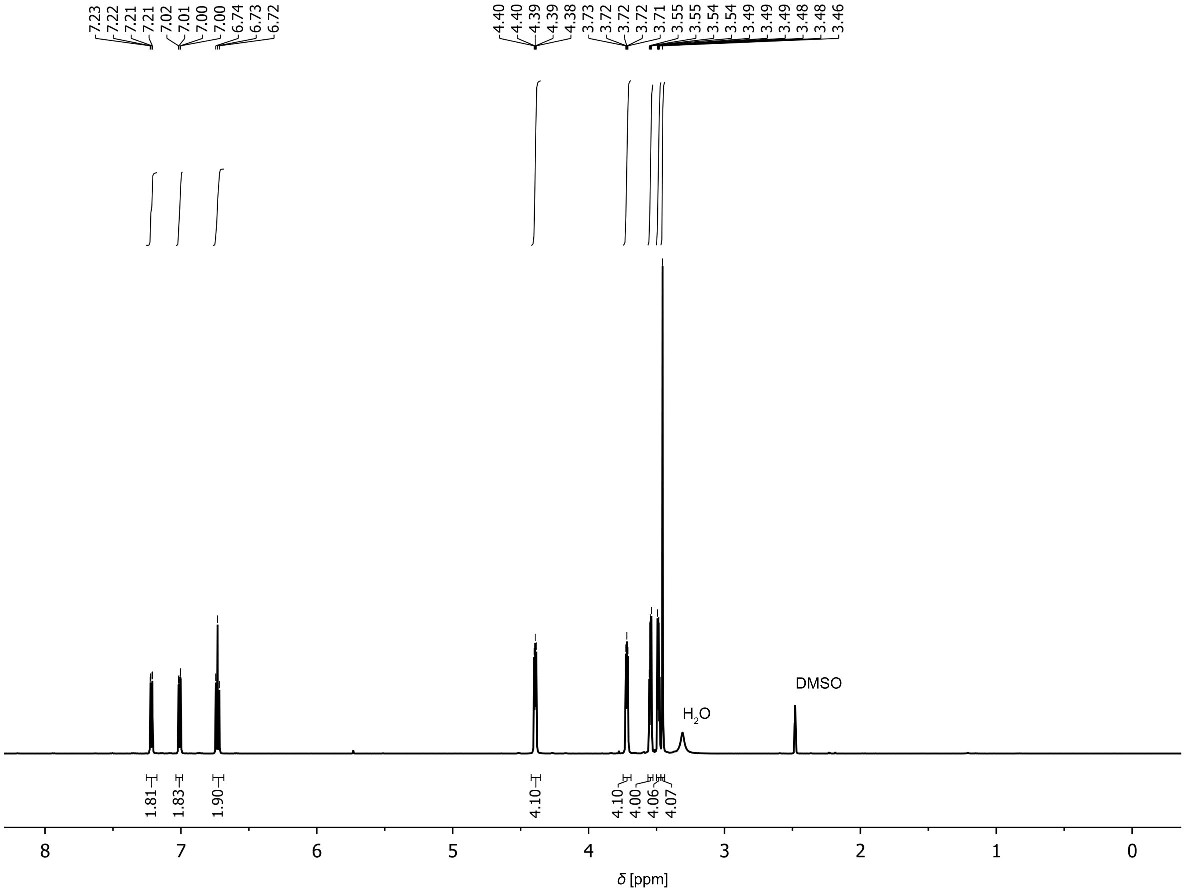


Figure S3: ^{1}*H-NMR spectrum (600 MHz) of* ***1***-H_4 *in DMSO at 25° C.*

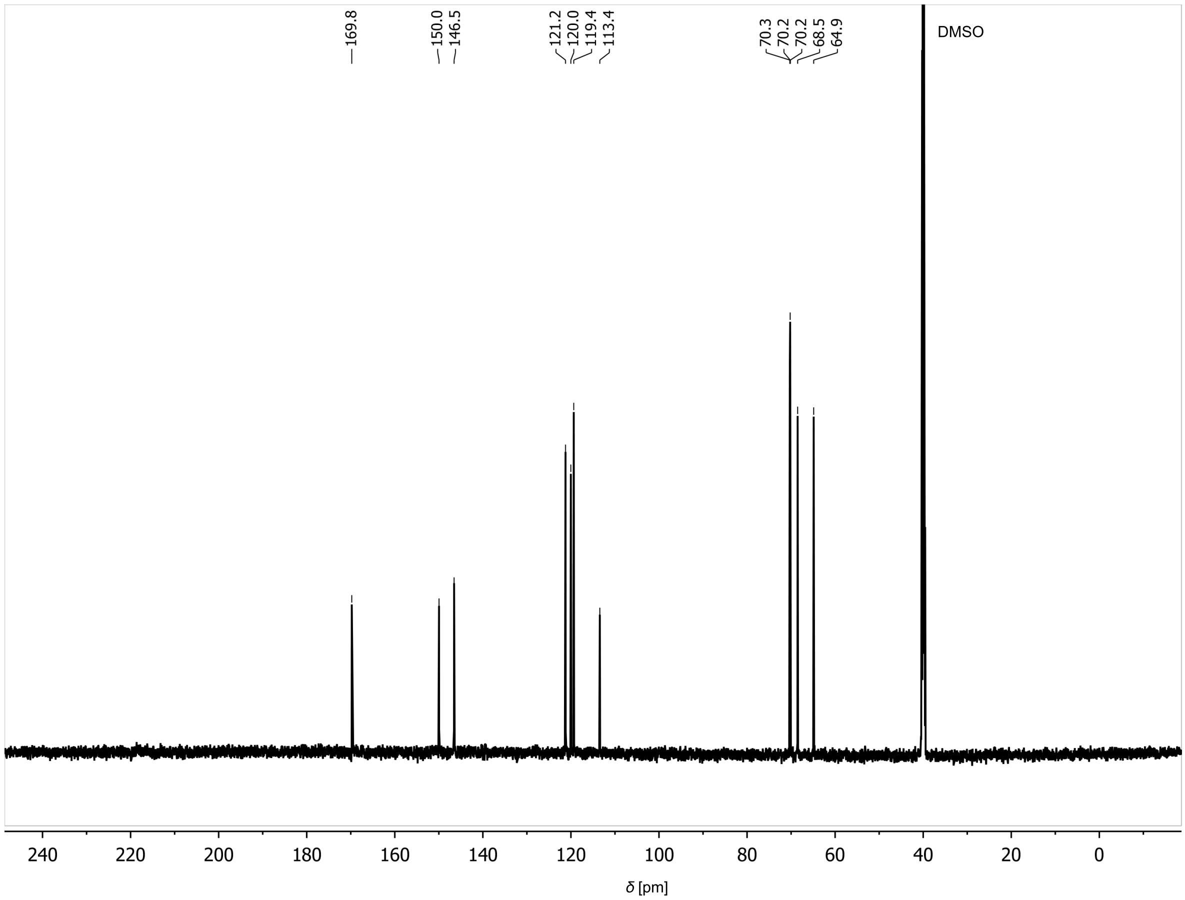


Figure S4: ^{13}*C-NMR spectrum (150 MHz) of* ***1***-H_4 *in DMSO at 25° C.*

2.2 Complex preparation

General procedure for the complex preparation

The ligand **1** (3.0 eq.) was dissolved in a mixture of dichloromethane (1 mL/mg) and MeOH (0.15 mL/mg). After adding titanium(IV) oxybisacetylacetonate (2.0 eq.) the reaction mixture was stirred for 15 min. Subsequently the carbonate of the required alkali metal (2.0 eq.) or metals (1.5 eq. Li_2CO_3, 0.5 eq. M_2CO_3, M=Na, K, Rb, Cs) was added and the reaction mixture stirred for 24 h. Upon completion the solvent was evaporated at 25°C at 1 atm.

Preparation of complex Li[Li$_3$(1)$_3$Ti$_2$]

Procedure:
The general procedure was performed applying ligand **1**-H_4 (30.0 mg, 0.059 mmol, 3.0 eq.) $TiO(acac)_2$ (10.3 mg, 0.039 mmol, 2.0 eq.) and Li_2CO_3 (2.9 mg, 0.039 mmol, 2.0 eq.) to afford the title compound $[Li[(Li_3)(\mathbf{1})_3(Ti)_2]$ (yield = quant.) as orange-red solid.
^{1}H-NMR (600 MHz, DMSO-d$_6$): 7.05 (dd, J = 8.2, 1.6 Hz, 1H), 6.98 (dd, J = 8.2, 1.6 Hz, 1H), 6.52 (td, J = 7.9, 1.6 Hz, 2H), 6.43 (ddd, J = 8.2, 6.2, 1.6 Hz, 2H), 3.82 (ddd, J = 11.7, 8.1, 3.2 Hz, 1H), 2.98 (ddd, J = 12.2, 6.7, 2.9 Hz, 2H) ppm. Signals not listed are overlapping and cannot be assigned.
IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3405, 2870, 1675, 1593, 1560, 1443, 1378, 1295, 1253, 1214, 1126, 1064, 985, 940, 855, 802, 742, 681.
ESI-MS: m/z: Calculated for $C_{72}H_{78}Li_3O_{36}Ti_2^-$ [M-Li$^+$]: 1635.3717; found: 1635.3604. Calculated for $C_{72}H_{78}Li_5O_{36}Ti_2^+$ ([M+Li]$^+$): 1649.4143; found: 1649.4026.

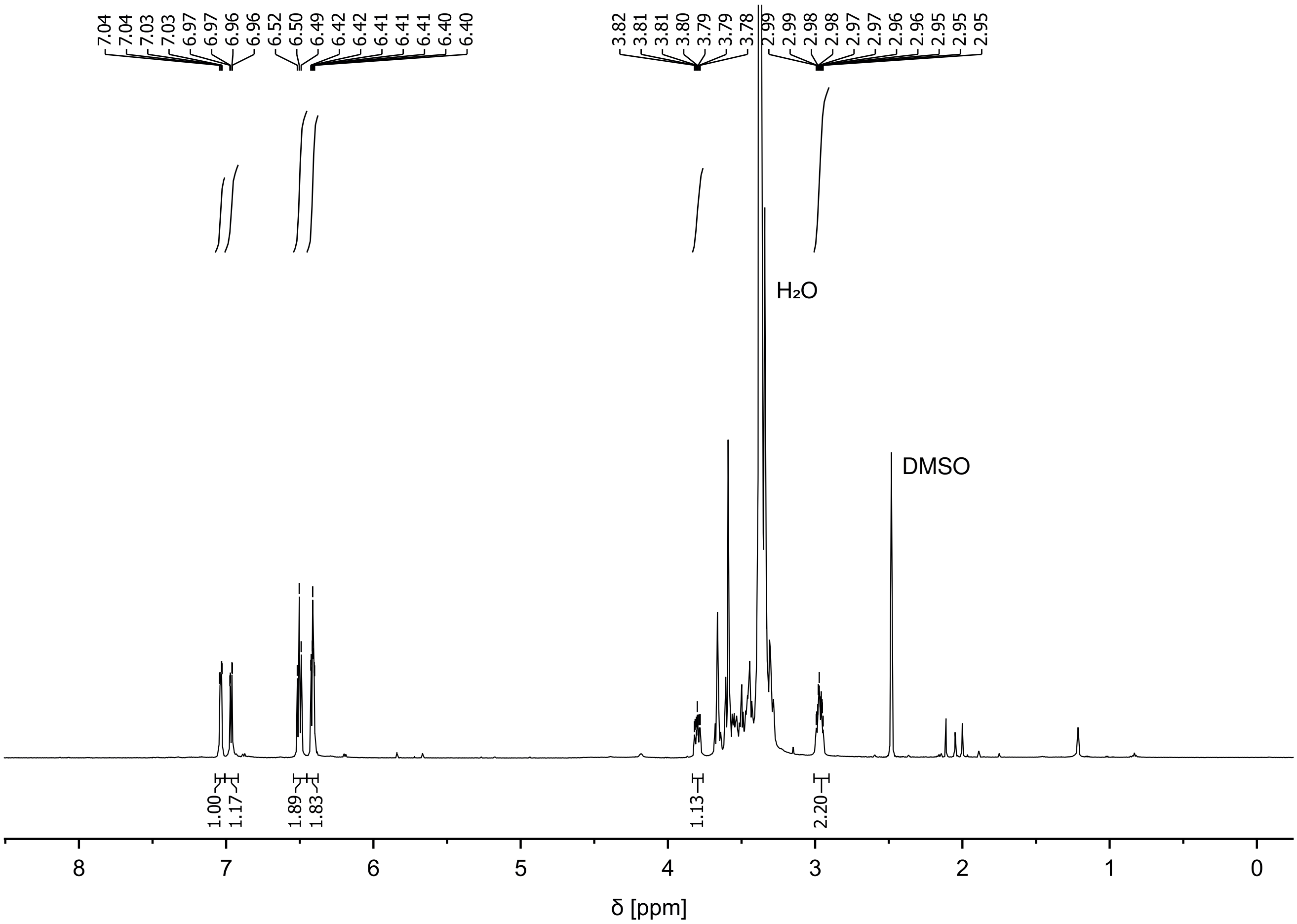


Figure S5: ^{1}*H-NMR spectrum of Li[Li$_3$(**1**)$_3$ Ti$_2$] in DMSO-d$_6$ at 25° C.*

Preparation of complex [Na_4][($\mathbf{1}$)$_3$$Ti_2$]

Procedure:

The general procedure was performed applying ligand **1**-H_4 (30.0 mg, 0.059 mmol, 3.0 eq.) $TiO(acac)_2$ (10.3 mg, 0.039 mmol, 2.0 eq.) and Na_2CO_3 (4.2 mg, 0.039 mmol, 2.0 eq.) to afford the title compound [Na_4][($\mathbf{1}$)$_3$$Ti_2$] (yield = quant.) as orange solid.

^{1}**H-NMR (600 MHz, DMSO-d$_6$):** 6.90 (d, J = 7.8 Hz, 2H), 6.34 (t, J = 7.8 Hz, 2H), 6.24 (d, J = 7.8 Hz, 2H), 4.42 (d, J = 73.5 Hz, 2H), 4.26 (m, 2H), 3.67 (m, 4H) ppm. Signals not listed are overlapping and cannot be assigned.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2874, 21671, 1615, 1463, 13,82, 1301, 1234, 1124, 1032, 946, 851, 749, 669.

ESI-MS: m/z: Calculated for $C_{72}H_{78}Na_3O_{36}Ti_2^-$ [M-Na$^+$]: 1683.2930; found: 1683.2800. Calculated for $C_{72}H_{78}Na_5O_{36}Ti_2^+$ ([M+Na]$^+$): 1729.2715; found: 1729.2715.

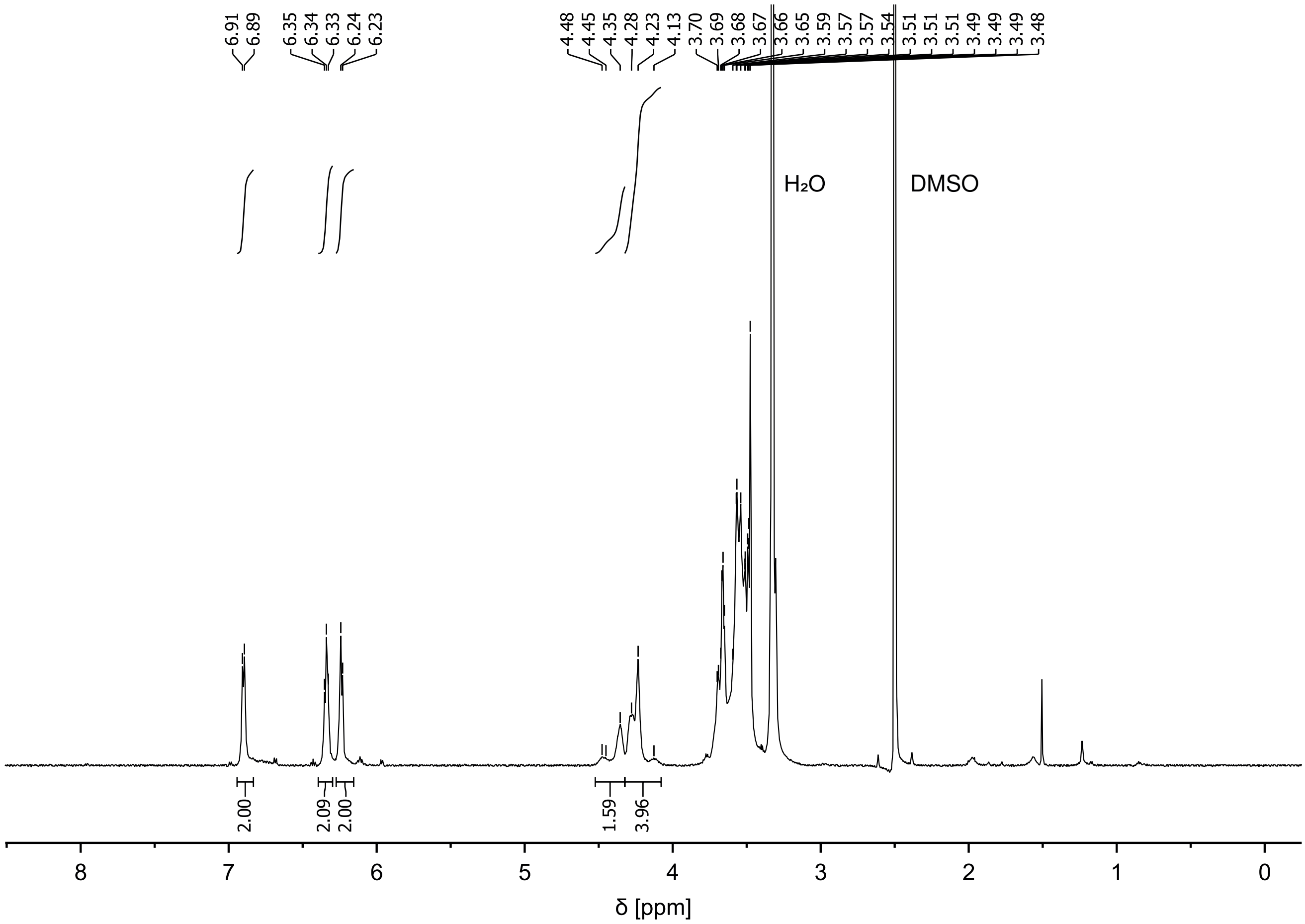


Figure S6: *^{1}H-NMR spectrum of [Na_4][($\mathbf{1}$)$_3$$Ti_2$] in DMSO-d$_6$ at 25° C.*

Preparation of complex [K$_4$][(1)$_3$Ti$_2$]

Procedure:
The general procedure was performed applying ligand **1**-H$_4$ (30.0 mg, 0.059 mmol, 3.0 eq.) TiO(acac)$_2$ (10.3 mg, 0.039 mmol, 2.0 eq.) and K$_2$CO$_3$ (5.4 mg, 0.039 mmol, 2.0 eq.) to afford the title compound [K$_4$][(**1**)$_3$Ti$_2$] (yield = quant.) as orange solid.
^{1}**H-NMR (600 MHz, DMSO-d$_6$):** 6.89 (d, J = 8.1 Hz, 2H), 6.33 (t, J = 7.1 Hz, 2H), 6.23 m, 2H), 4.37 4.18 (m, 4H), 3.66 (dt, J = 15.3, 5.5 Hz, 6H), 3.60 3.41 (m, 15H) ppm. Signals not listed are overlapping and cannot be assigned.
IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2874, 1691, 1589, 1444, 1352, 1286, 1252, 1212, 1180, 1111, 1061, 973, 852, 798, 745, 670.
ESI-MS: m/z: Calculated for $C_{72}H_{78}K_3O_{36}Ti_2^-$ [M-K$^+$]: 1731.2148; found: 1731.2096. Calculated for $C_{72}H_{78}K_5O_{36}Ti_2^+$ ([M+K]$^+$): 1809.1412; found: 1809.1511.

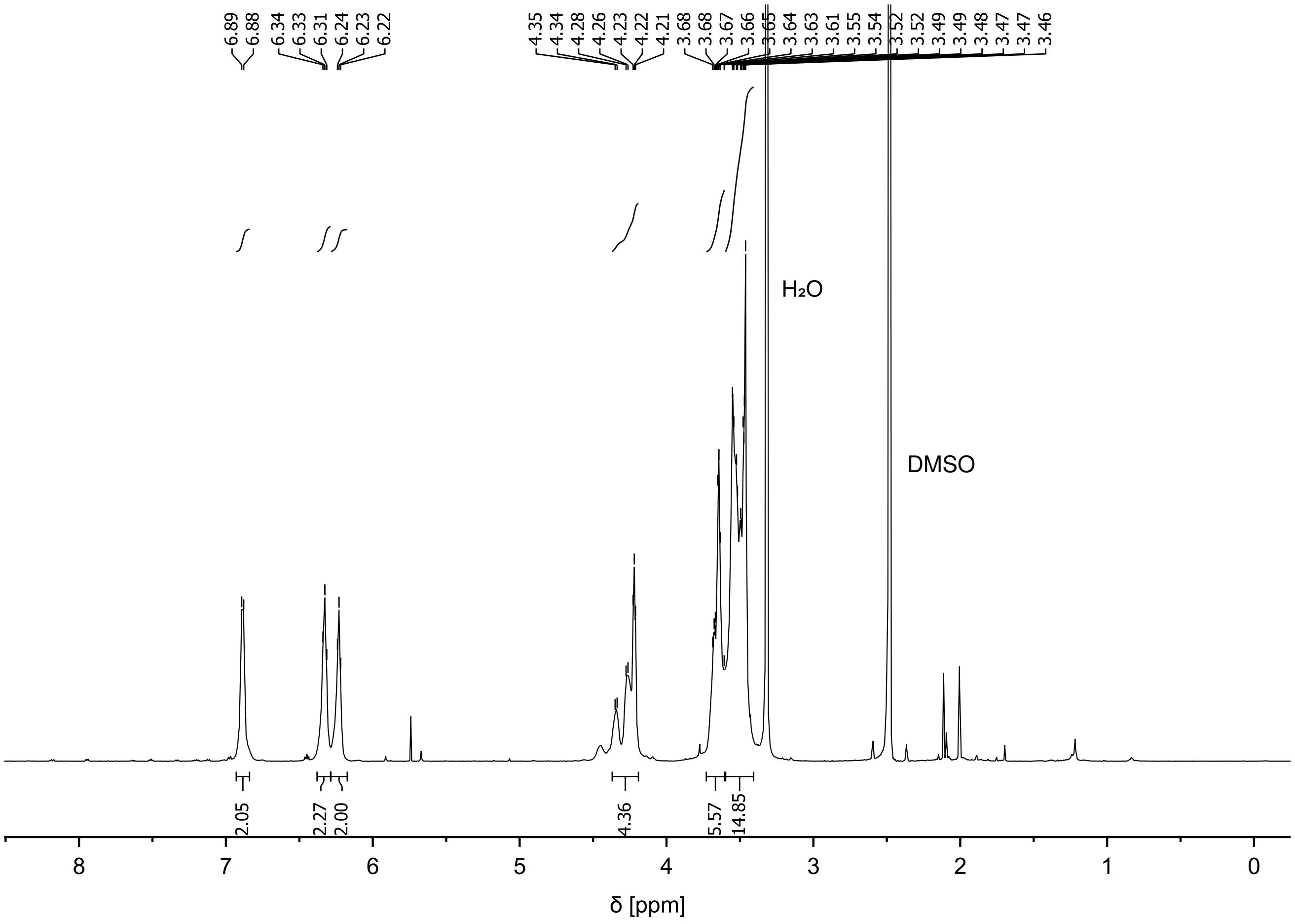


Figure S7: *^{1}H-NMR spectrum of [K$_4$][(**1**)$_3$Ti$_2$] in DMSO-d$_6$ at 25° C.*

Preparation of complex $[Rb_4][(\mathbf{1})_3Ti_2]$

Procedure:
The general procedure was performed applying ligand **1**-H_4 (30.0 mg, 0.059 mmol, 3.0 eq.) $TiO(acac)_2$ (10.3 mg, 0.039 mmol, 2.0 eq.) and Rb_2CO_3 (9.0 mg, 0.039 mmol, 2.0 eq.) to afford the title compound $[Rb_4][(\mathbf{1})_3Ti_2]$ (yield = quant.) as orange solid.
^{1}**H-NMR (600 MHz, DMSO-d$_6$):** 6.89 (d, J = 8.0 Hz, 2H), 6.32 (t, J = 8.0 Hz, 2H), 6.21 (m, 2H) ppm. Signals not listed are overlapping and cannot be assigned.
IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2873, 1690, 1589, 1443, 1352, 1287, 1253, 1212, 1180, 1106, 1061, 972, 852, 797, 745, 670.
ESI-MS: m/z: Calculated for $C_{72}H_{78}Rb_3O_{36}Ti_2^-$ [M-Rb$^+$]: 1871.0564; found: 1871.06390.

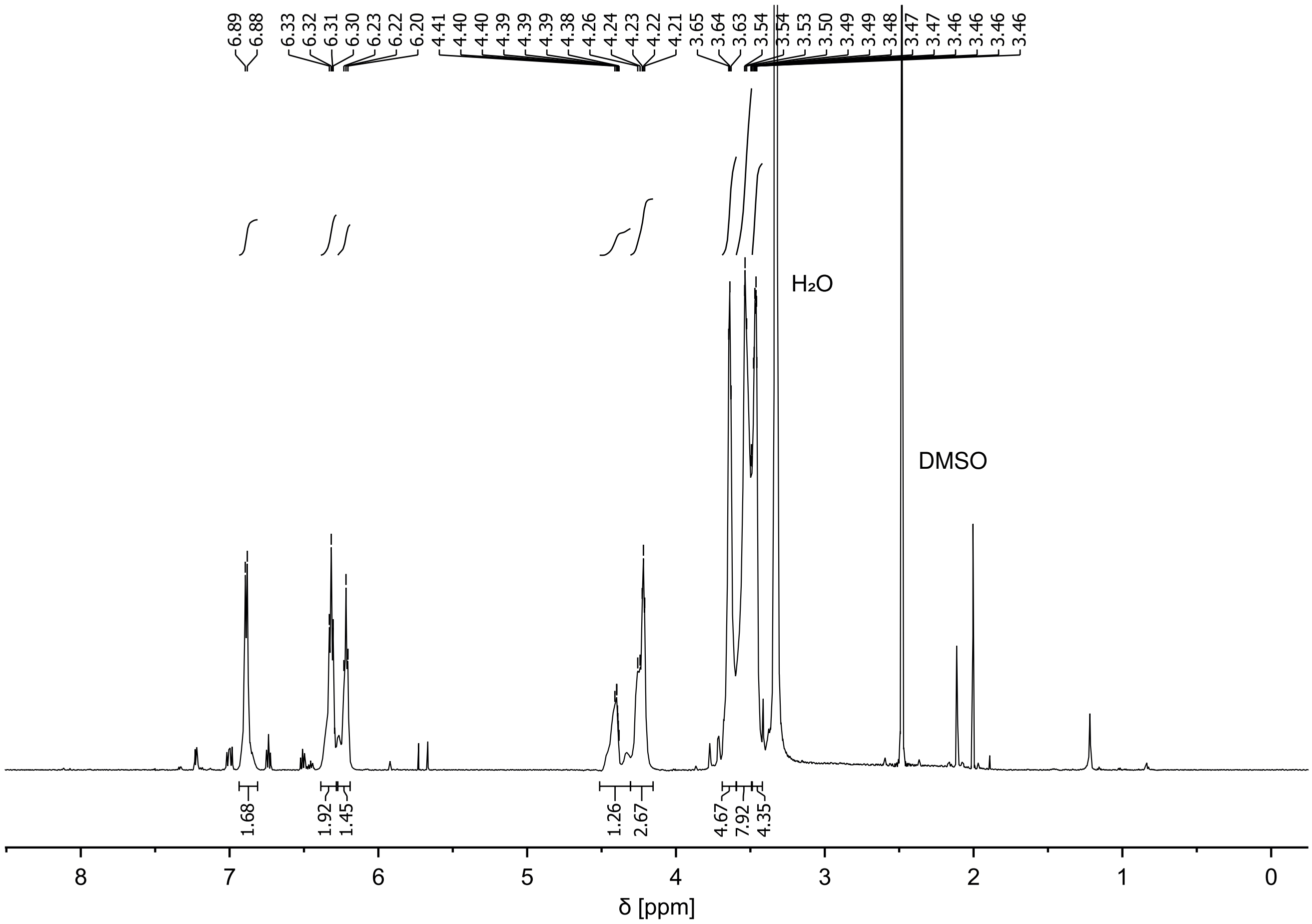


Figure S8: ^{1}*H-NMR spectrum of [Rb$_4$][(**1**)$_3$ Ti$_2$] in DMSO-d$_6$ at 25° C.*

Preparation of complex $[Cs_4][(\mathbf{1})_3Ti_2]$

Procedure:
The general procedure was performed applying ligand **1**-H_4 (30.0 mg, 0.059 mmol, 3.0 eq.) $TiO(acac)_2$ (10.3 mg, 0.039 mmol, 2.0 eq.) and Cs_2CO_3 (12.8 mg, 0.039 mmol, 2.0 eq.) to afford the title compound $[Cs_4][(\mathbf{1})_3Ti_2]$ (yield = quant.) as orange solid.
^{1}**H-NMR (600 MHz, DMSO-d_6):** 6.89 (d, J = 8.0 Hz, 2H), 6.32 (t, J = 8.0 Hz, 2H), 6.21 (m, 2H) ppm. Signals not listed are overlapping and cannot be assigned.
IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2872, 1684, 1588, 1443, 1383, 1351, 1286,1252,1210, 1179, 1106, 1062, 947, 850, 744, 669.
ESI-MS: m/z: Calculated for $C_{72}H_{78}Cs_3O_{36}Ti_2^-$ [M-Cs^+]: 2013.0400; found: 2013.0401. Calculated for $C_{72}H_{78}Cs_5O_{36}Ti_2^+$ ([M+Cs]$^+$): 2278.8499; found: 2278.84395.

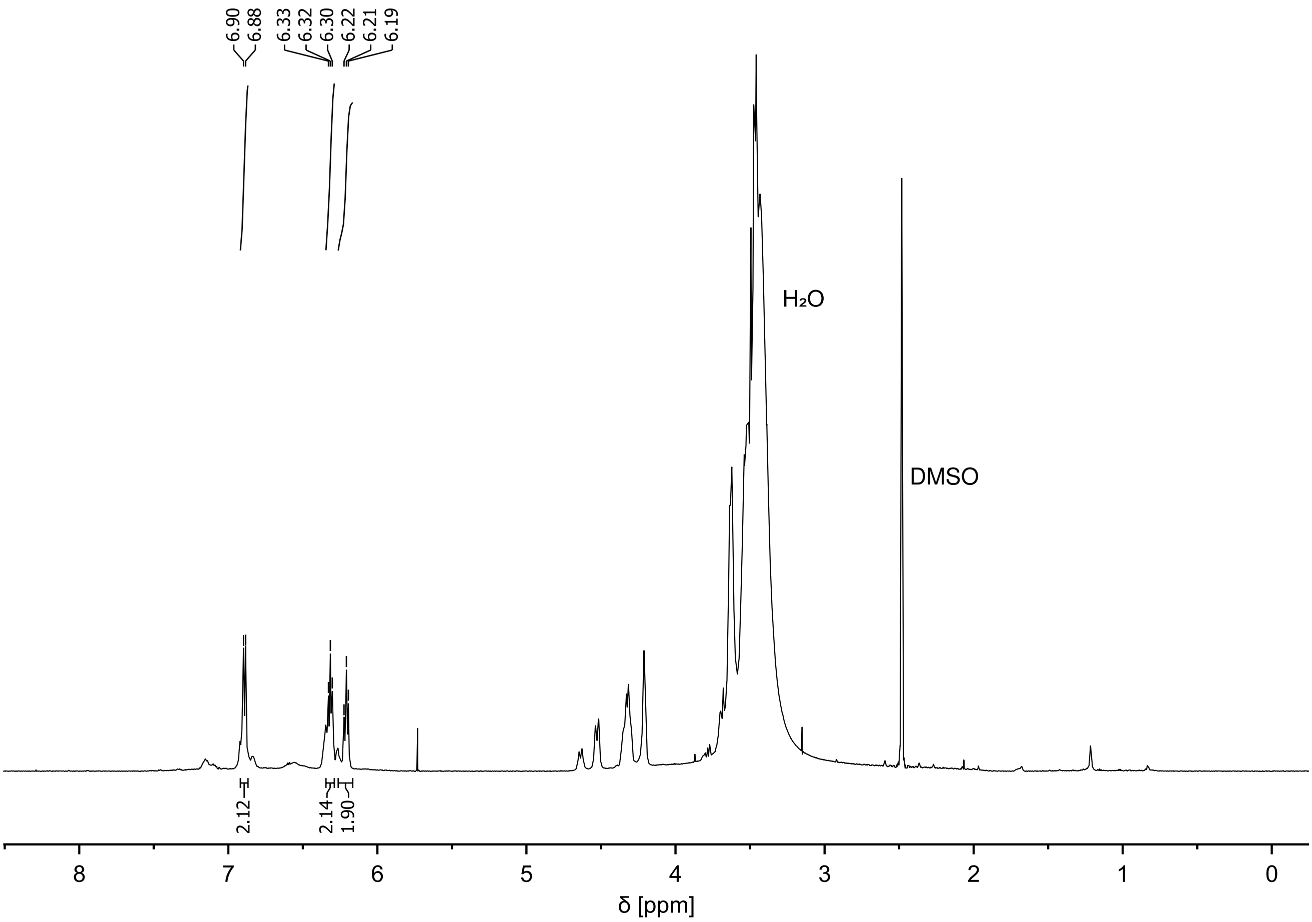


Figure S9: *^{1}H-NMR spectrum of $[Cs_4][(\mathbf{1})_3Ti_2]$ in DMSO-d_6 at 25° C.*

Preparation of complex [Na][Li_3(1)$_3$$Ti_2$]

Procedure:

The general procedure was performed applying ligand **1**-H_4 (60.0 mg, 0.118 mmol, 3.0 eq.) TiO(acac)$_2$ (20.5 mg, 0.078 mmol, 2.0 eq.), Li_2CO_3 (4.3 mg, 0.059 mmol, 1.5 eq.) and Na_2CO_3 (2.1 mg, 0.0,020 mmol, 0.5 eq.). to afford the title compound [Na][Li_3(**1**)$_3$$Ti_2$] (yield = quant.) as red-orange solid.

^{1}H-NMR (600 MHz, DMSO-d$_6$): 7.06 (dd, J = 8.2, 1.6 Hz, 2H), 6.99 (dd, J = 8.2, 1.6 Hz, 2H), 6.92 (dd, J = 7.6, 1.7 Hz, 5H), 6.78 (dd, J = 8.2, 1.6 Hz, 1H), 6.57 6.45 (m, 6H), 6.43 (dd, J = 7.6, 1.7 Hz, 5H), 6.38 (t, J = 7.8 Hz, 6H), 6.31 6.26 (m, 6H), 6.24 6.19 (m, 1H), 6.09 (dd, J = 7.3, 1.6 Hz, 1H) ppm. Signals not listed are overlapping and cannot be assigned.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3427, 2874, 2160, 1676, 1592, 1559, 1443, 1377, 1291, 1252, 1212, 1122, 1062, 983, 853, 802, 743, 674.

ESI-MS: m/z: Calculated for $C_{72}H_{78}Li_3O_{36}Ti_2^-$ [M-Na$^+$]: 1635.3717; found: 1635.3603. Calculated for $C_{72}H_{78}Li_3Na_2O_{36}Ti_2^+$ ([M+Na]$^+$): 1681.3502; found: 1681.3555.

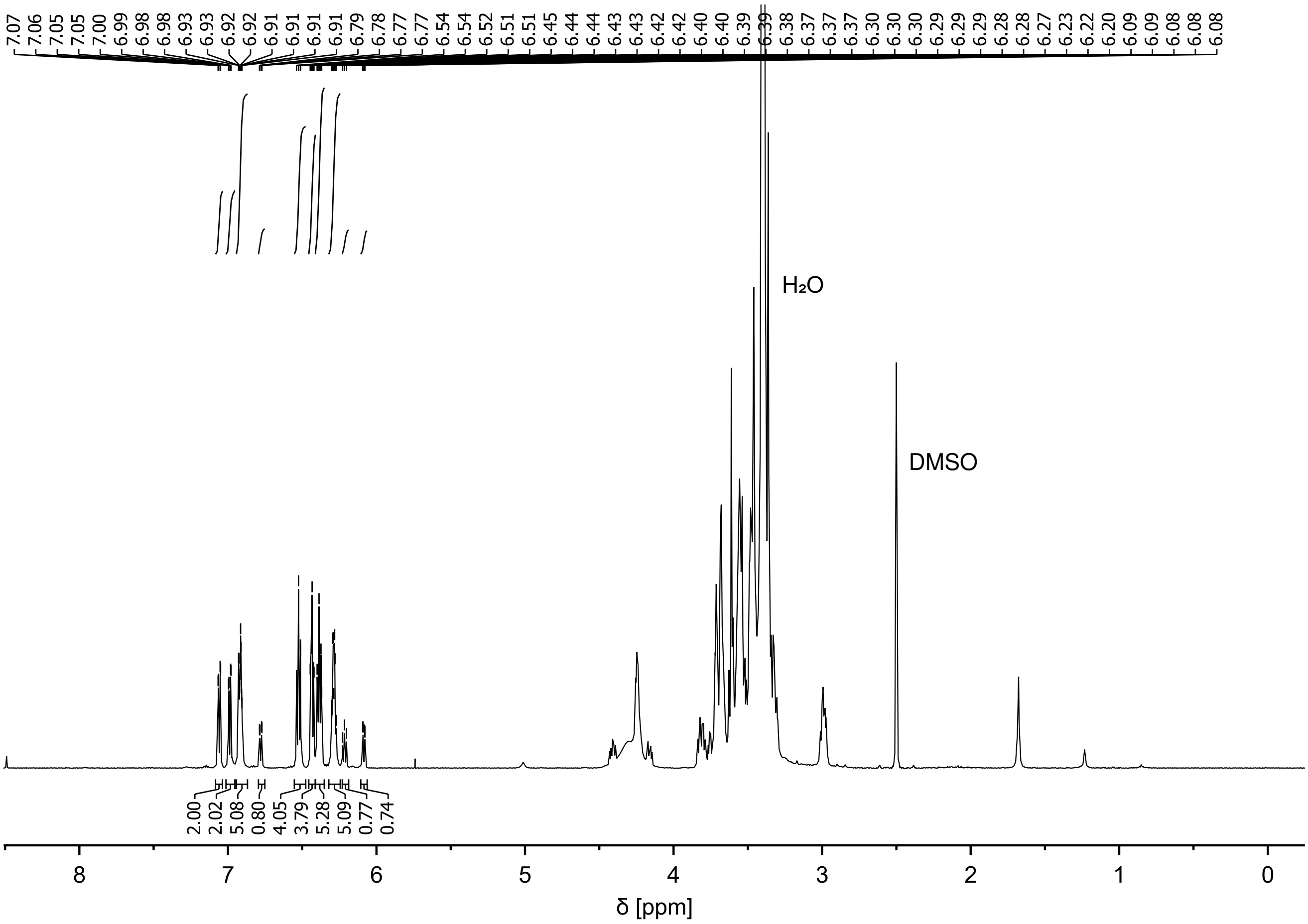


Figure S10: *^{1}H-NMR spectrum of [Na][Li_3(**1**)$_3$$Ti_2$] in DMSO-d$_6$ at 25° C.*

Preparation of complex $[K][Li_3(\mathbf{1})_3Ti_2]$

Procedure:

The general procedure was performed applying ligand **1**-H_4 (60.0 mg, 0.118 mmol, 3.0 eq.) $TiO(acac)_2$ (20.5 mg, 0.078 mmol, 2.0 eq.), Li_2CO_3 (4.3 mg, 0.059 mmol, 1.5 eq.) and K_2CO_3 (2.7 mg, 0.0,020 mmol, 0.5 eq.). to afford the title compound $[K][Li_3(\mathbf{1})_3Ti_2]$ (yield = quant.) as red-orange solid.

^{1}**H-NMR (600 MHz, DMSO-d$_6$):** 6.91 (d, J = 8.1 Hz, 2H), 6.35 (m, J = 7.8 Hz, 2H), 6.25 (m, 2H) ppm. Signals not listed are overlapping and cannot be assigned.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3431, 2873, 1678, 1592, 1559, 1445, 1381, 1352, 1292, 1253, 1213, 1107, 1064, 984, 853, 802, 746, 677.

ESI-MS: m/z: Calculated for $C_{72}H_{78}Li_3O_{36}Ti_2^-$ [M-K$^+$]: 1635.3717; found: 1635.3714. Calculated for $C_{72}H_{78}Li_3K_2O_{36}Ti_2^+$ ([M+K]$^+$): 1713.2981; found: 1713.2983.

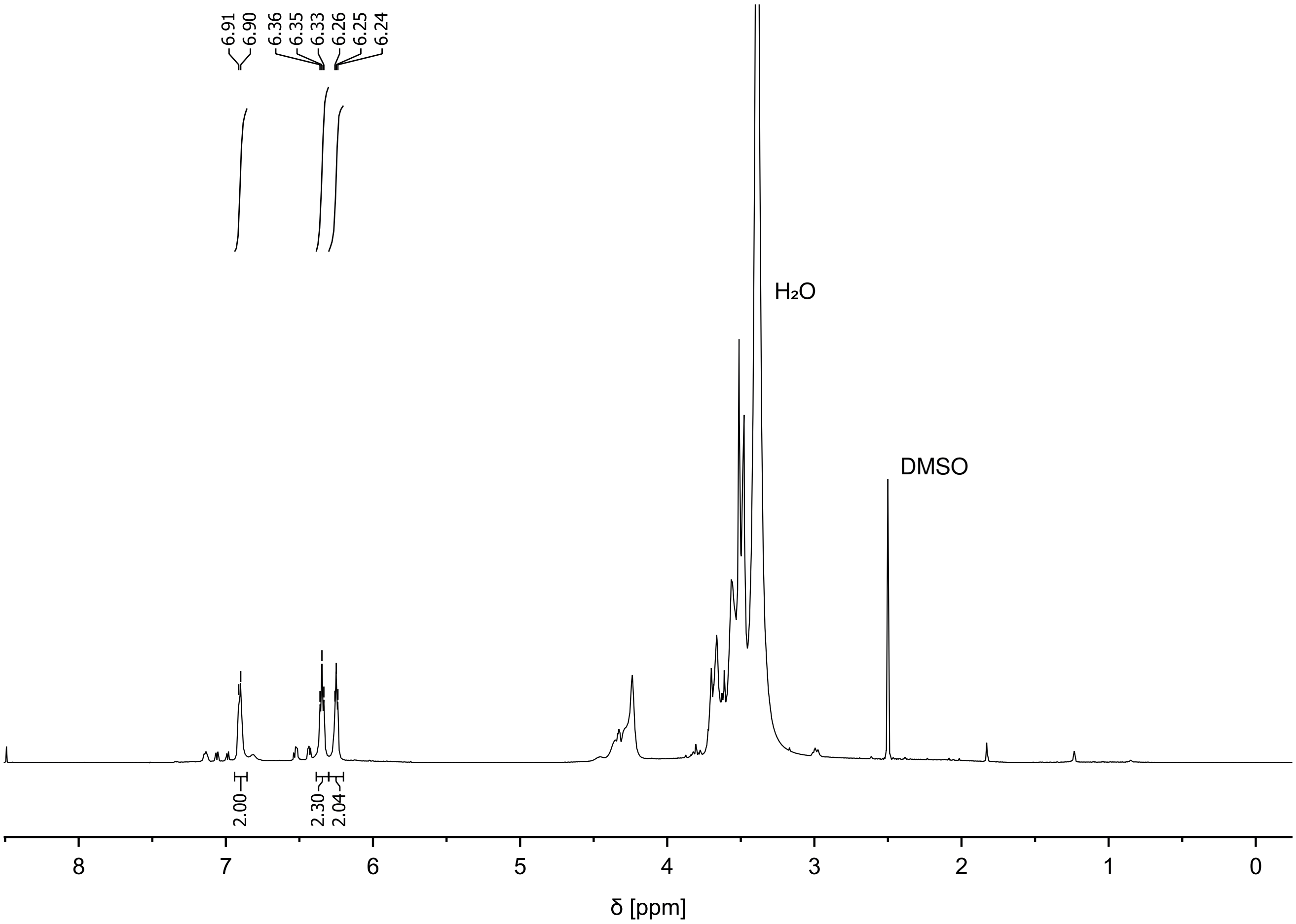


Figure S11: *^{1}H-NMR spectrum of [K][Li$_3$(**1**)$_3$Ti$_2$] in DMSO-d_6 at 25° C.*

Preparation of complex [Rb][Li_3(**1**)$_3$$Ti_2$]

Procedure:
The general procedure was performed applying ligand **1**-H_4 (60.0 mg, 0.118 mmol, 3.0 eq.) TiO(acac)$_2$ (20.5 mg, 0.078 mmol, 2.0 eq.), Li_2CO_3 (4.3 mg, 0.059 mmol, 1.5 eq.) and Rb_2CO_3 (4.5 mg, 0.0,020 mmol, 0.5 eq.). to afford the title compound [Rb][Li_3(**1**)$_3$$Ti_2$] (yield = quant.) as orange solid.
^{1}H-NMR (600 MHz, DMSO-d$_6$): 6.89 (m, 2H), 6.32 (t, J = 7.8 Hz, 1H), 6.22 (t, J = 7.8 Hz, 1H) ppm. Signals not listed are overlapping and cannot be assigned.
IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3464, 2873, 1679, 1591, 1557, 1444, 1353, 1290, 1253, 1212, 1108, 1063, 982, 945, 853, 802, 745, 674.
ESI-MS: m/z: Calculated for $C_{72}H_{78}Li_3O_{36}Ti_2^-$ [M-Rb$^+$]: 1635.3717; found: 1635.3605. Calculated for $C_{72}H_{78}Li_3Rb_2O_{36}Ti_2^+$ ([M+Rb]$^+$): 1713.1807.1961; found: 1713.1962.

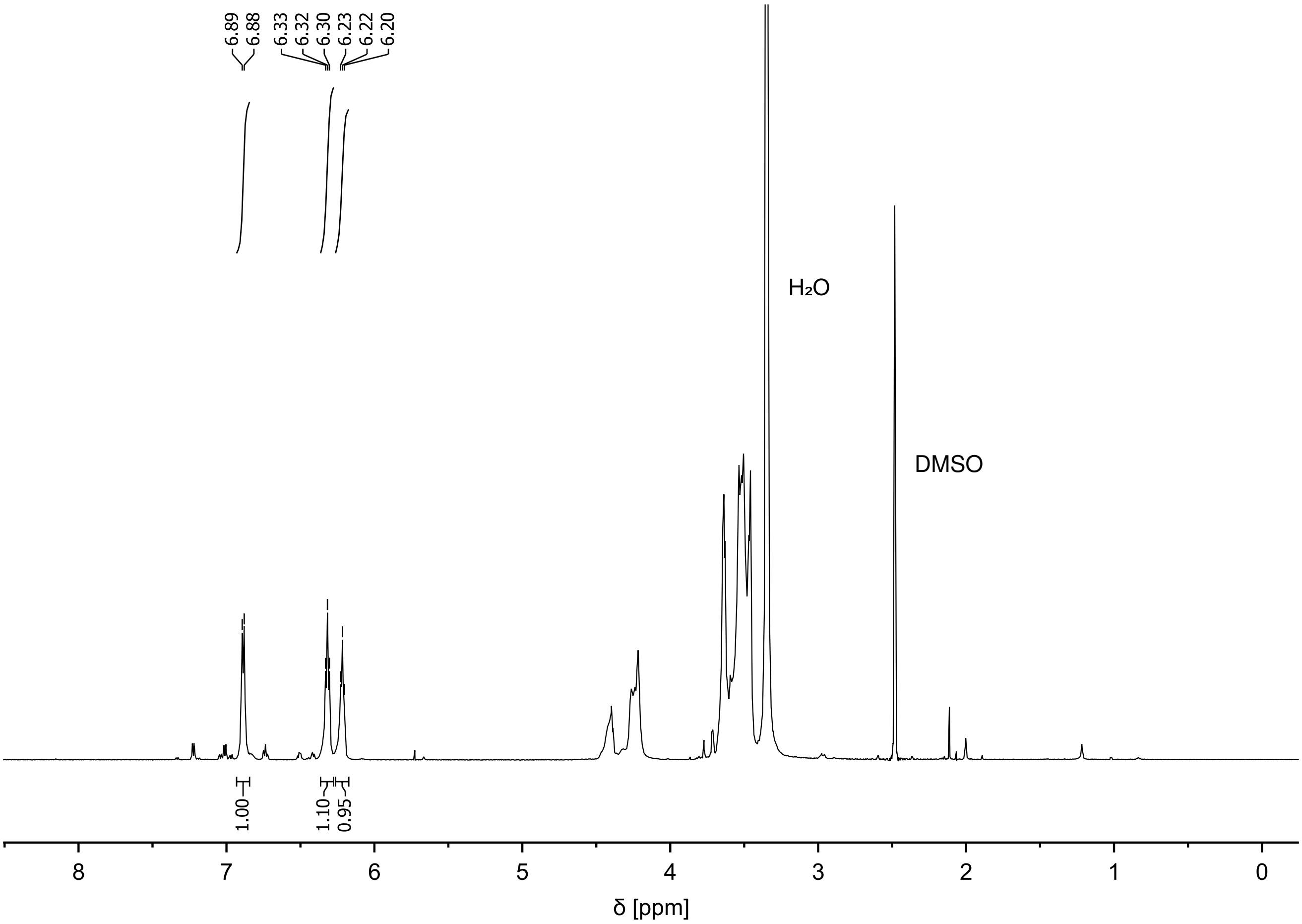


Figure S12: ^{1}*H-NMR spectrum of [Rb][Li$_3$(**1**)$_3$Ti$_2$] in DMSO-d$_6$ at 25° C.*

Preparation of complex [Cs][Li$_3$(1)$_3$Ti$_2$]

Procedure:
The general procedure was performed applying ligand **1**-H$_4$ (60.0 mg, 0.118 mmol, 3.0 eq.) TiO(acac)$_2$ (20.5 mg, 0.078 mmol, 2.0 eq.), Li$_2$CO$_3$ (4.3 mg, 0.059 mmol, 1.5 eq.) and Cs$_2$CO$_3$ (6.4 mg, 0.0,020 mmol, 0.5 eq.). to afford the title compound [Cs][Li$_3$(**1**)$_3$Ti$_2$] (yield = quant.) as orange solid.
^{1}**H-NMR (600 MHz, DMSO-d$_6$):** 6.94 6.89 (m, 2H), 6.39 6.28 (m, 2H), 6.25 6.18 (m, 2H) ppm. Signals not listed are overlapping and cannot be assigned.
IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3466, 2872, 1678, 1590, 1557, 1443, 1354, 1288, 1252, 1210, 1106, 1062, 977, 851, 801, 744, 671.
ESI-MS: m/z: Calculated for $C_{72}H_{78}Li_3O_{36}Ti_2^-$ [M-Cs$^+$]: 1635.3717; found: 1635.3700. Calculated for $C_{72}H_{78}Li_3Cs_2O_{36}Ti_2^+$ ([M+Rb]$^+$): 1901.1815.1961; found: 1901.1814.

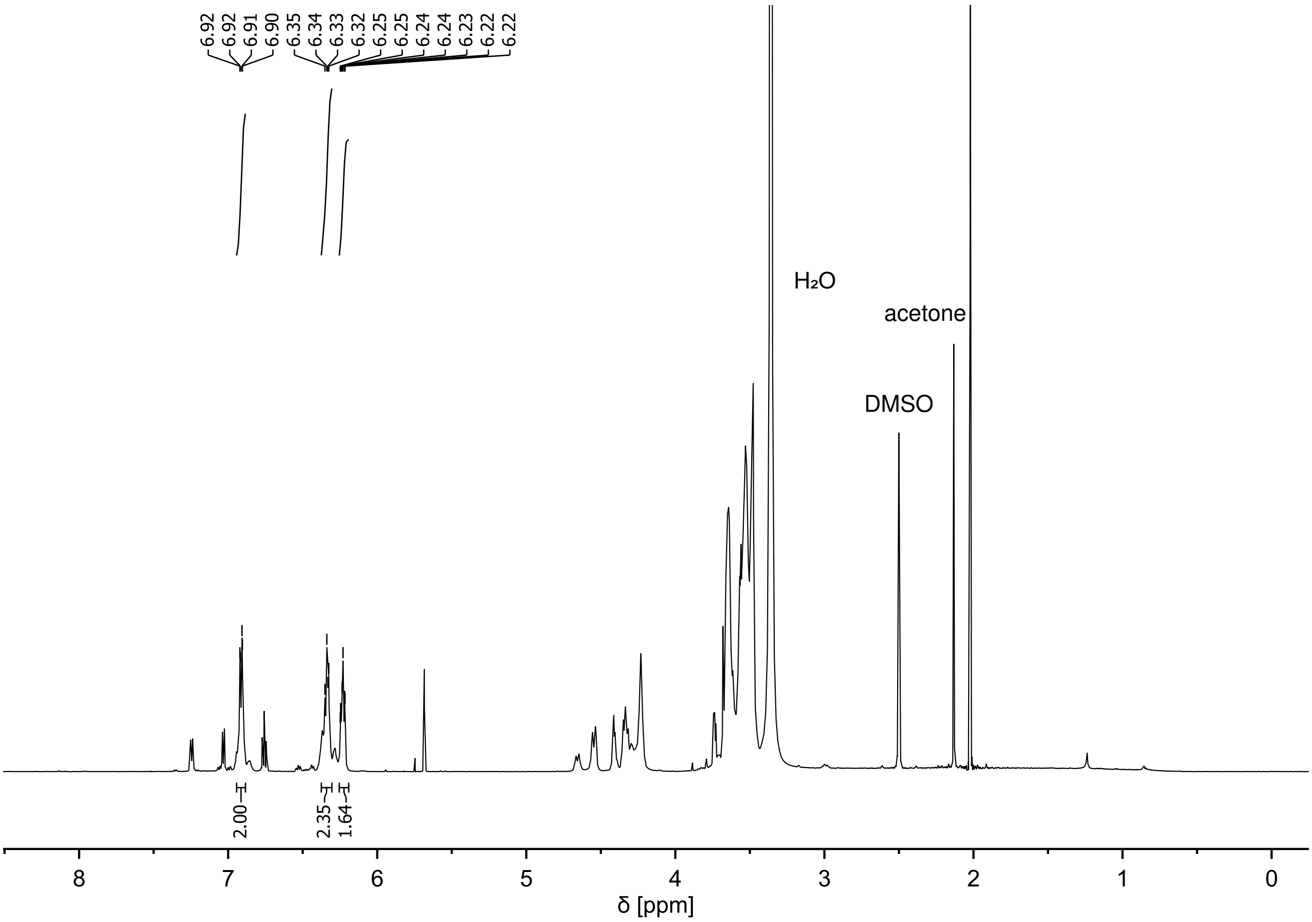


Figure S13: ^{1}*H-NMR spectrum of [Cs][Li$_3$(**1**)$_3$Ti$_2$] in DMSO-d$_6$ at 25° C.*

3 Switching experiments

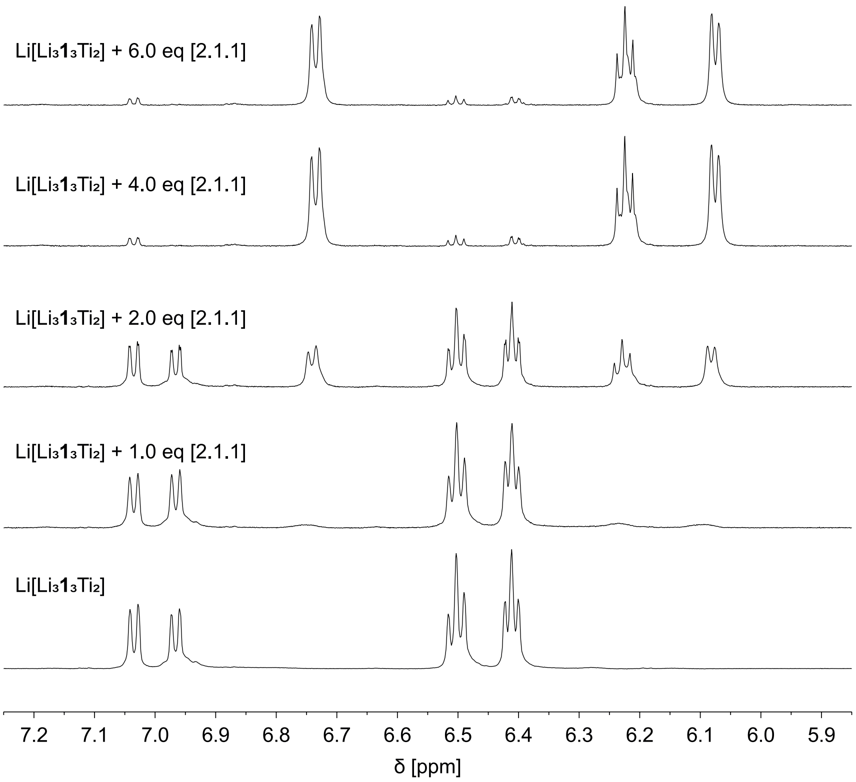


Figure S14: *Aromatic region of the* ^{1}*H-NMR spectra (DMSO-d6) showing the expansion of the triple-stranded helicate* Li[Li$_3$(**1**)$_3$Ti$_2$] *in DMSO-*d_6 *by successive addition of [2.1.1]cryptand and formation of* [(**1**)$_3$Ti$_2$]$^{4-}$*.*

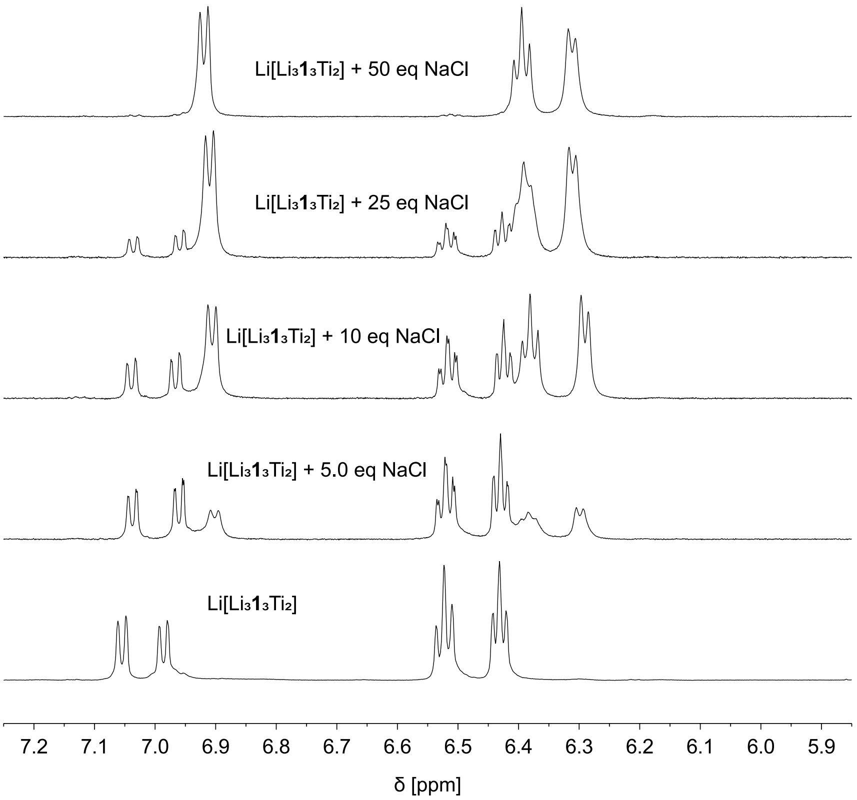


Figure S15: *Aromatic region of the* ^{1}*H-NMR spectra (DMSO-d6) showing the expansion of the triple-stranded helicate* Li[Li$_3$(**1**)$_3$Ti$_2$] *in DMSO-*d_6 *by successive addition of NaCl and formation of* [(**1**)$_3$Ti$_2$]$^{4-}$*.*

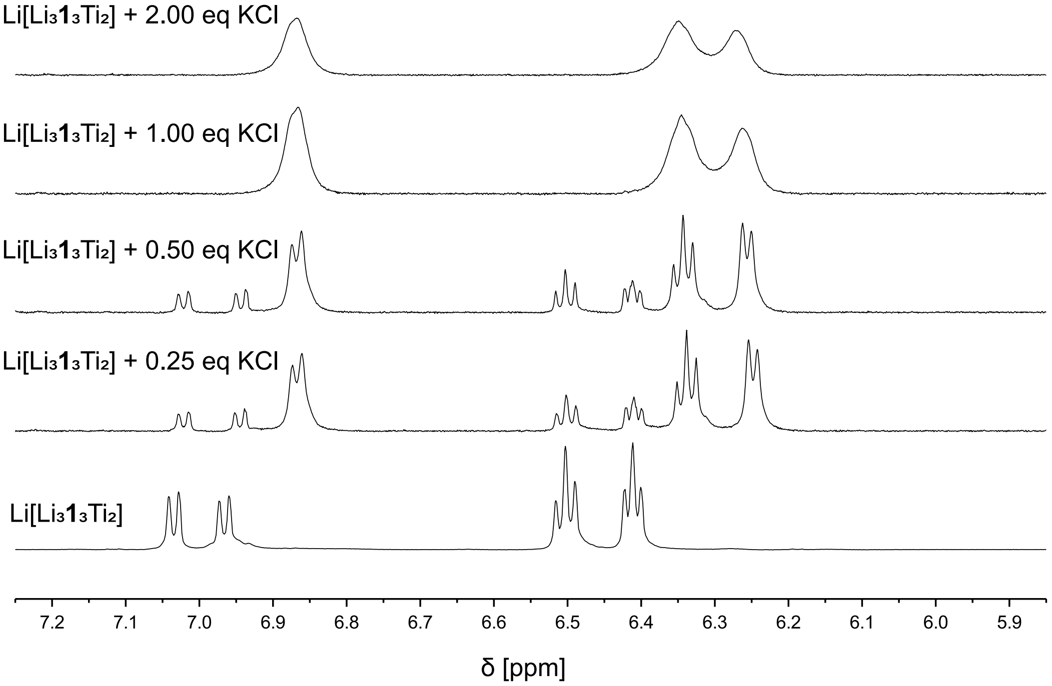


Figure S16: *Aromatic region of the* ^{1}*H-NMR spectra (DMSO-d6) showing the expansion of the triple-stranded helicate* $Li[Li_3(\mathbf{1})_3Ti_2]$ *in DMSO-*d_6 *by successive addition of KCl and formation of* $[(\mathbf{1})_3Ti_2]^{4-}$.

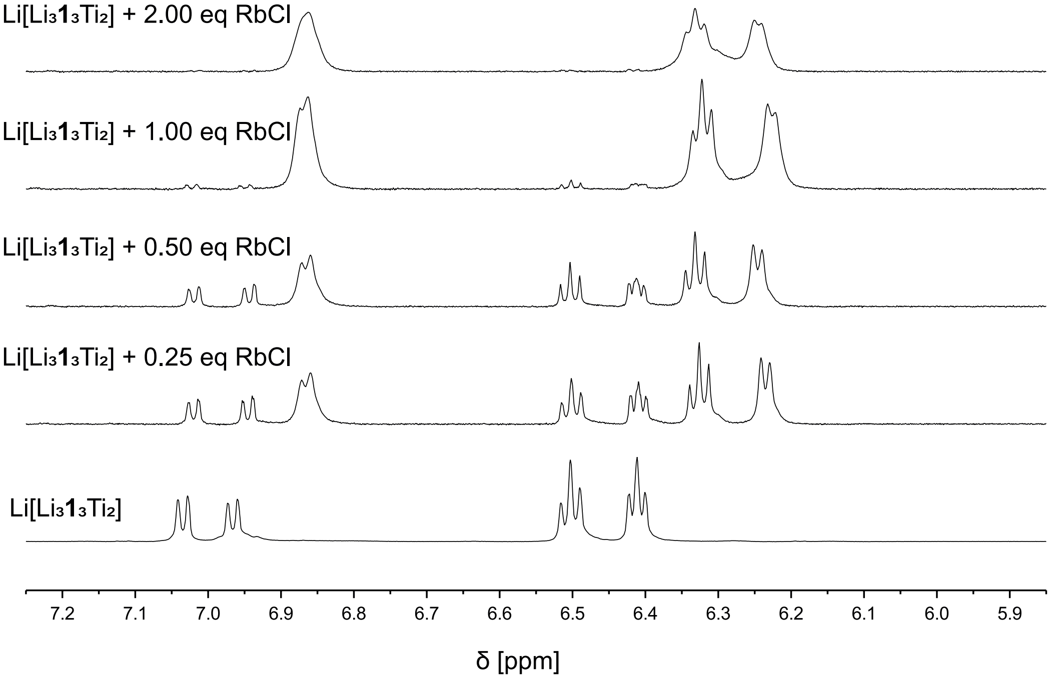


Figure S17: *Aromatic region of the* ^{1}*H-NMR spectra (DMSO-d6) showing the expansion of the triple-stranded helicate* $Li[Li_3(\mathbf{1})_3Ti_2]$ *in DMSO-*d_6 *by successive addition of RbCl and formation of* $[(\mathbf{1})_3Ti_2]^{4-}$.

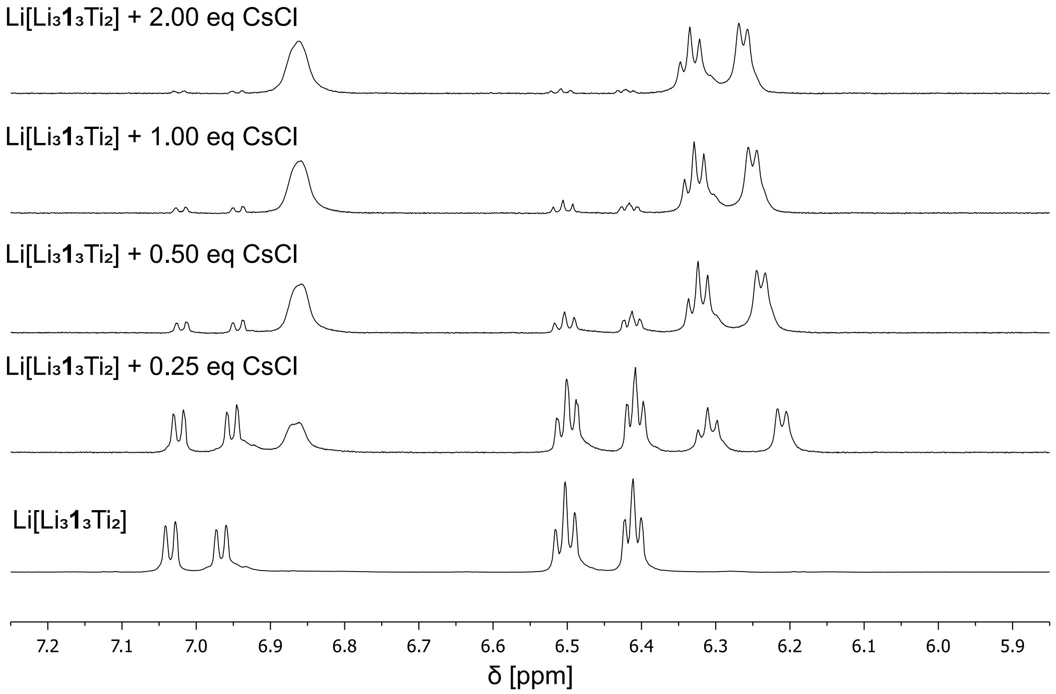


Figure S18: *Aromatic region of the* ^{1}*H-NMR spectra (DMSO-d6) showing the expansion of the triple-stranded helicate* $Li[Li_3(\mathbf{1})_3Ti_2]$ *in DMSO-*d_6 *by successive addition of CsCl and formation of* $[(\mathbf{1})_3Ti_2]^{4-}$.

4 Crystallographic data

The experimental and refinement details for Na[Li$_3$**1**$_3$Ti$_2$], and Rb[Li$_3$**1**$_3$Ti$_2$] are given below. Single-crystal X-ray data using a dual-source Rigaku SuperNova diffractometer equipped with an Atlas detector and an Oxford Cryostream cooling system using mirror-monochromated Cu-K$_\alpha$ radiation (= 1.54184 Å). Data collection and reduction for all complexes were performed using the program *CrysAlisPro*[4] and Gaussian face-index absorption correction method was applied.[4] The structures were solved with Direct Methods (*SHELXS*)[5–7] and refined by full-matrix least-squares based on F^2 using *SHELXL*-2017.[5–7] Non-hydrogen atoms were assigned anisotropic displacement parameters unless stated otherwise. The hydrogen atom bonded to nitrogen was located from Fourier difference maps and refined with an OH distance restraint of approximately 0.92 Å. Other hydrogen atoms were placed in idealized positions and included as riding. Isotropic displacement parameters for all H atoms were constrained to multiples of the equivalent displacement parameters of their parent atoms with U$_{iso}$(H) = 1.2 U$_{eq}$(parent atom). A few reflections with large discrepancies between the calculated and observed structure factors have been omitted from the least-squares refinement as outliers. Enhanced rigid bond restraints[8,9] with standard uncertainties of 0.001 Å^2 were applied for several atom pairs as well as distance restraints (DFIX). The X-ray single crystal data and experimental details as well as CCDC numbers are given below.

Crystal data for Na[Li$_3$**1**$_3$Ti$_2$] (obtained *via* vapor diffusion from DMF and MTBE): CCDC-2069786, $C_{78}H_{96}Li_3N_2NaO_{40}Ti_2$, M = 1841.17 gmol^{-1}, orange plate, 0.23 Œ 0.21 Œ 0.04 mm^3, monoclinic, space group *Cc* (No. 9), a = 14.6785(2) Å, b = 40.9426(5) Å, c = 14.4762(2) Å, = 90ř, = 107.797(2) ř, = 90ř, V = 8283.5(2) Å^3, Z = 4, Dcalc = 1.476 gcm$^-$3, F(000) = 3848, ţ = 2.537 mm^{-1}, T = 120(2) K, max = 75.90ř, 77475 total reflections, 12018 with I$_o$ > 2(I$_o$), Rint = 0.0459, 15371 data, 1058 parameters, 124 restraints, GooF = 1.090, R$_1$ = 0.0726 and wR$_2$ = 0.1799 [I$_o$ > 2(I$_o$)], R$_1$ = 0.0850 and wR$_2$ = 0.1880 (all reflections), 1.101 < d < -0.746 eÅ^{-3}, Flack parameter x = 0.094(3).

Crystal data for Rb[Li$_3$**1**$_3$Ti$_2$] (obtained *via* vapor diffusion from DMF and MTBE): CCDC-2069787, $C_{312}H_{376}Li_{12}N_8O_{157}Rb_4Ti_8$, M = 7558.55 gmol^{-1}, yellow plate, 0.19 Œ 0.16 Œ 0.05 mm^3, monoclinic, space group *P*2$_1$/*n* (No. 14), a = 14.5024(7) Å, b = 41.3843(18) Å, c = 14.6141(7) Å, = 90ř, = 107.933(2) ř, = 90ř, V = 8344.8(7) Å3, Z = 1, Dcalc = 1.504 gcm^{-3}, F(000) = 3920, ţ = 3.162 mm^{-1}, T = 120(2) K, max = 73.87ř, 31191 total reflections, 8262 with I$_o$ > 2(I$_o$), Rint = 0.0757, 15693 data, 1107 parameters, 113 restraints, GooF = 1.078, R1 = 0.0920 and wR2 = 0.2167 [I$_o$ > 2(I$_o$)], R$_1$ = 0.1617 and wR$_2$ = 0.2566 (all reflections), 1.456 < d < -0.981 eÅ^{-3}.

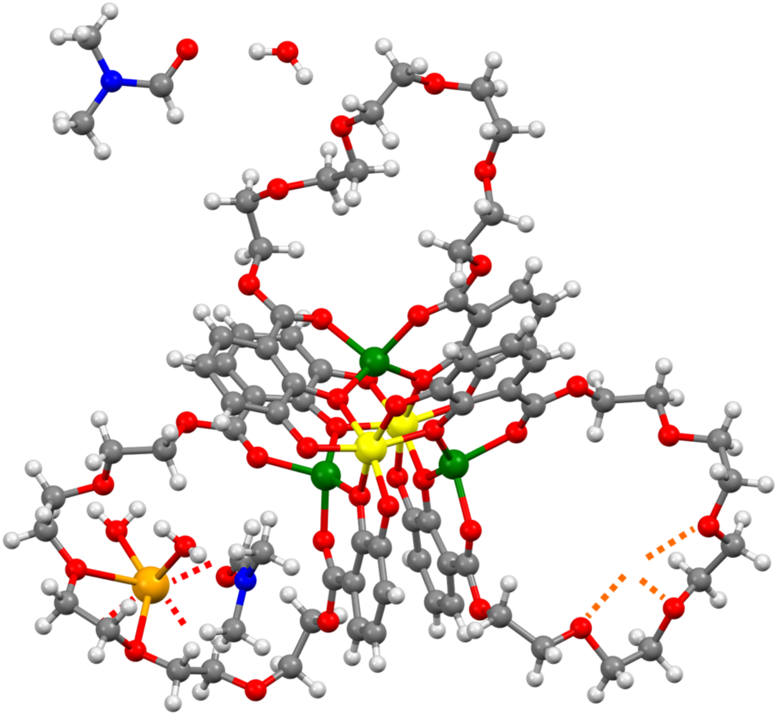


Figure S19: *Ball-and-stick-model of Na[Li$_3$**1**$_3$Ti$_2$] showing the asymmetric unit (C: grey, H: white, N: blue, O: red, Li: green, Na: orange, Ti: yellow; dotted lines represent connectivity to neighbouring helicates).*

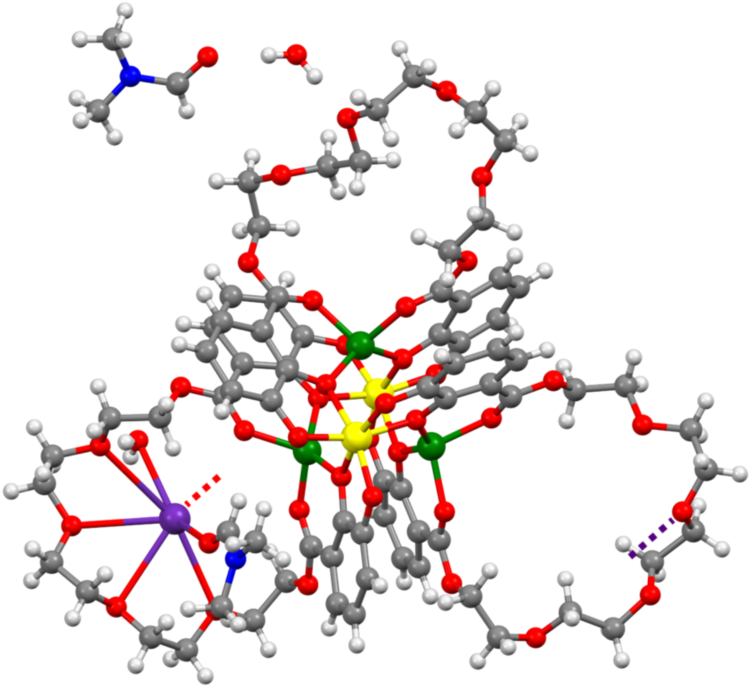


Figure S20: *Ball-and-stick-model of Rb[Li$_3$**1**$_3$Ti$_2$] showing the asymmetric unit (C: grey, H: white, N: blue, O: red, Li: green, Rb: purple, Ti: yellow; dotted lines represent connectivity to neighbouring helicates).*

Table 1: *Selected interatomic distances (Å) in* $Na[Li_3\mathbf{1}_3Ti_2]$*. Symmetry operator: a = 1+x, y, z.*

M···O	**d(M···O) [Å]**	**M···O**	**d(M···O) [Å]**	**M···O**	**d(M···O) [Å]**
Ti1···O1	1.897(6)	Li1···O2	1.925(13)	Na1···O6	2.516(16)
Ti1···O2	2.022(5)	Li1···O3	1.965(13)	Na1···O7	2.566(13)
Ti1···O13	1.914(5)	Li1···O10	1.934(13)	Na1···O37	2.38(2)
Ti1···O14	2.021(5)	Li1···O11	1.950(13)	Na1···O38	2.375(16)
Ti1···O25	1.908(6)	Li2···O26	1.947(15)	Na1···O29^a	2.80(2)
Ti1···O26	2.034(5)	Li2···O27	1.912(14)	Na1···O30^a	2.614(18)
Ti2···O11	2.023(6)	Li2···O34	1.948(15)	Na1···O31^a	2.625(16)
Ti2···O12	1.901(6)	Li2···O35	1.944(14)		
Ti2···O23	2.032(5)	Li3···O14	1.973(14)		
Ti2···O24	1.907(5)	Li3···O15	1.928(15)		
Ti2···O35	2.012(5)	Li3···O22	1.929(15)		
Ti2···O36	1.893(6)	Li3···O23	1.940(14)		
M···M	**d(M···M) [Å]**	M···M	**d(M···M) [Å]**		
Ti1···Li1	3.409(12)	Li1···Li2	3.618(17)		
Ti1···Li2	3.436(14)	Li1···Li3	3.485(17)		
Ti1···Li3	3.452(13)	Li2···Li3	3.595(17)		
Ti2···Li1	3.430(13)				
Ti2···Li2	3.412(13)				
Ti2···Li3	3.459(13)				

Table 2: *Selected interatomic distances (Å) in* $Rb[Li_3\mathbf{1}_3Ti_2]$*. Symmetry operator: a = 1+x, y, z.*

M···O	**d(M···O) [Å]**	**M···O**	**d(M···O) [Å]**	**M···O**	**d(M···O) [Å]**
Ti1···O1	1.904(5)	Li1···O2	1.960(11)	Rb1···O29	3.317(6)
Ti1···O2	2.026(4)	Li1···O3	1.942(12)	Rb1···O30	3.004(9)
Ti1···O13	1.901(5)	Li1···O10	1.934(13)	Rb1···O31	3.097(7)
Ti1···O14	2.023(5)	Li1···O11	1.932(11)	Rb1···O32	2.942(7)
Ti1···O25	1.889(4)	Li2···O26	1.952(12)	Rb1···O37	2.834(8)
Ti1···O26	2.022(4)	Li2···O27	1.947(12)	Rb1···O38	2.726(14)
Ti2···O11	2.019(4)	Li2···O34	1.941(12)	Rb1···O39	3.60(3)
Ti2···O12	1.898(5)	Li2···O35	1.929(11)	Rb1···O7^a	2.976(6)
Ti2···O23	2.030(4)	Li3···O14	1.974(12)		
Ti2···O24	1.903(5)	Li3···O15	1.920(13)		
Ti2···O35	2.039(5)	Li3···O22	1.914(13)		
Ti2···O36	1.900(5)	Li3···O23	1.938(11)		
M···M	**d(M···M) [Å]**	M···M	**d(M···M) [Å]**		
Ti1···Li1	3.435(11)	Li1···Li2			
Ti1···Li2	3.433(12)	Li1···Li3			
Ti1···Li3	3.448(12)	Li2···Li3			
Ti2···Li1	3.416(11)				
Ti2···Li2	3.440(11)				
Ti2···Li3	3.457(11)				

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