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Supramolecular Switches

Helicates with Ether-Substituted Catechol Esters as Ligands

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Dedicated to Professor Dr. Elmar Weinhold on the occasion of his 60th birthday.

Abstract: Mono- or biscatechol esters with ether-type substituents or spacers form either triple lithium bridged dimeric helicates or triple stranded helicates with the ability to bind three lithium cations in their interior. Hierarchical helicates with ether or thioether substituents show in solution a monomer-dimer equilibrium which is independent of the heteroatom in the ester substituent. However, dimerization constants are significantly lower than for corresponding alkyl derivatives. Dinuclear helicates with oligoether spacers are well obtained in the presence of lithium cations. Upon removal of the cations the helicates expand and successive addition of LiCl results in compression again.

Introduction

Self-assembly provides a facile way to synthesise complex supramolecular structures starting from easily available building blocks. Dynamic behavior of the obtained supramolecular aggregates, which ideally can be controlled by some external stimuli, leads into the world of molecular devices like machines or switches.[1]

Many chemical devices have been prepared e.g. based on rotaxane and catenane motifs, but other structural moieties have been successfully used as well.[2]

In 2005 we introduced hierarchically[3] formed triple lithium bridged helicates[4] based on dinuclear titanium catecholates,[5] which in solution represent a unique class of lithium dependent molecular switches (Figure 1a). NMR spectroscopy allows to observe the equilibrium between the monomeric and dimeric titanium(IV)triscatecholates.[6] The equilibrium mainly depends on the kind of carbonyl substituent (aldehyde, ketone, thioester,

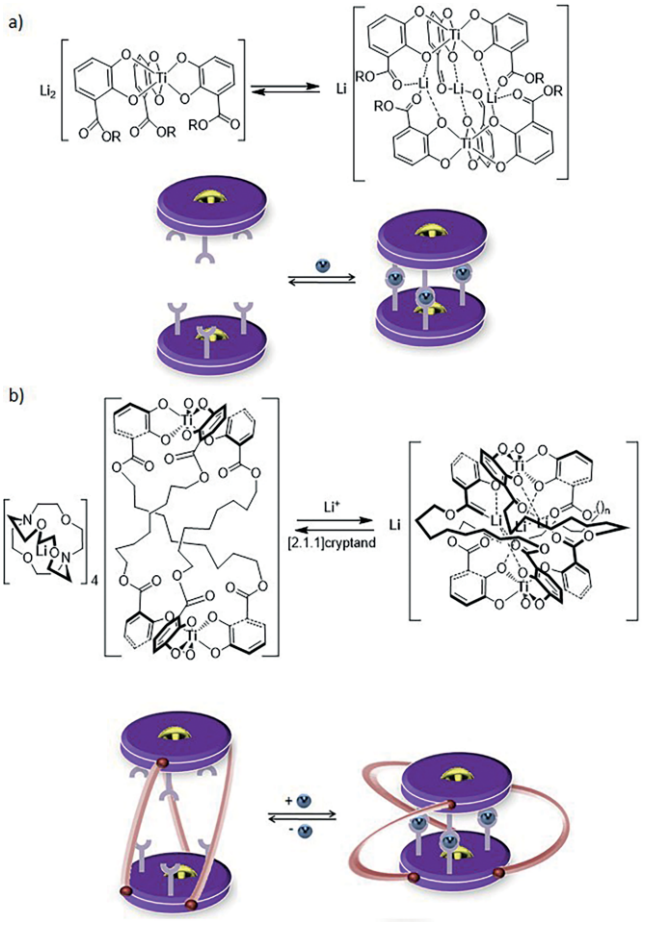

Figure 1. Hierarchically assembled ester substituted helicates and the monomer/dimer equilibrium as observed in solution (a) as well as the corresponding alkyl bridged helicate showing lithium dependent expansion and compression behaviour.

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ester) at the catechol ligand, on the central metal and on the solvent, but the side chains (sterics, solvophobic effects and even dispersion interactions) have an important influence on the equilibrium as well.[7]

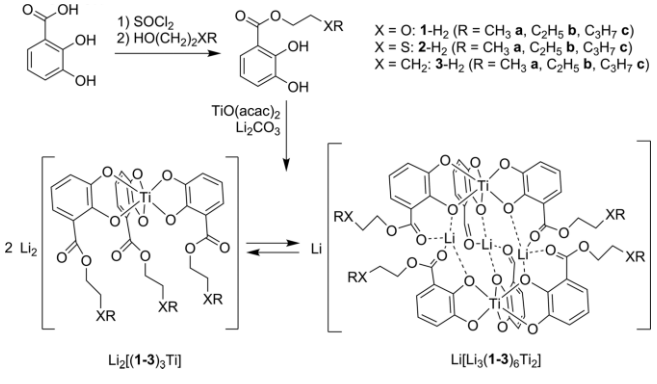
A hierarchically formed helicate of this kind even was used as a platform for stereoselective Diels-Alder reactions. Hereby the selectivity of the reaction can be switched on or off by simply shifting the equilibrium from the dimer to the monomer (or vice versa).[8]

Bridging the two catechol units by alkyl spacers results in a lithium dependent switch[9] showing some spring-type expansion and compression behavior (Figure 1b).[10] Control of the stereochemistry of the complexes by introduction of a phenyl substituent at the ester group leads to a three state supramolecular switch in which it is possible to switch between the compressed and expanded state and in the expanded form between the right- and the left-handed helix.[11]

Herein we present ether substituted catechol esters in order to form non-bridged hierarchical helicates as well as bridged helicates (Figure 1). The monomer/dimer equilibrium is observed for three ethers and their thio-analogues. A series of "spring-type" helicates is made, the switching property is studied and the stereochemistry is influenced by introduction of chiral units in the center of the ligand spacer.

Results and Discussion

Hierarchically assembled helicates with ether side chains. Glycol based esters and their thio-analogues are easily prepared by esterification of 2,3-dihydroxybenzoic acid following a modified Raymond protocol.[12] The ligands **1a–c**-H_2 and **2a–c**-H_2 are obtained in moderate to good yields. The corresponding titanium(IV) complexes Li[Li_3(**1/2**)$_6Ti_2$] are formed in methanol by reaction of the ligands with $TiO(acac)_2$ and Li_2CO_3 (Scheme 1).



Scheme 1. Preparation of the hierarchically formed helicates Li[Li_3(**1/2**)$_6Ti_2$]. Complexes Li[Li_3(**3**)$_6Ti_2$] have been described earlier and are only mentioned for comparison.

Negative ESI MS (methanol) shows the peaks of the dimeric complexes [Li_3(**1/2**)$_6Ti_2$]$^-$ at *m/z* = 1377.26 (**1a**), 1461.35 (**1b**), 1545.44 (**1c**), 1473.12 (**2a**), 1557.23 (**2b**) and 1641.32 (**2c**) while NMR spectroscopy in [D_6]DMSO reveals the characteristic peaks of the monomer as well of the dimer. E. g., by ^{1}H NMR in [D_6]DMSO the signals of the catechol unit of the dimer Li[Li_3(**1a**)$_6Ti_2$] are observed at δ = 6.96, 6.50, and 6.42, and for the dominating monomer Li_2[(**1a**)$_3$Ti] at δ = 6.77, 6.26, and 6.13. In the dimer the methylene group adjacent to the ester splits into two signals of diastereotopic protons at δ = 3.67 and 3.02 ppm (6H each) while in the monomer one signal at δ = 4.18 ppm (12 H) is observed for this group.

From the NMR spectra dimerization constants can be easily extracted (Table 1) at ambient temperature.[6,7] It is observed that the dimerization constants steadily increase with the chain length. However, the observed constants of the glycol and thioglycol derivatives are by one magnitude lower as observed for the corresponding alkyl derivatives. It is assumed that the higher polarity of the heteroatom derivatives results in repulsion between the oxygen or sulfur lone pairs with the hetero atoms and π systems of neighboring catechol units. This effect is strong despite a related high solvophobicity of ethers and alkanes in DMSO which would rather stabilize the dimer. The similarity of the dimerization constants of the oxygen and sulfur derivatives is remarkable, showing the similarity of the two atoms in their solvophobic as well as electronic features in [D_6]DMSO.

Table 1. Kdim [L/mol] for the dimerization monomer dimer equilibrium of Li[Li_3(**1–3**)$_6Ti_2$] in [D_6]DMSO at r.t. determined at a concentration of 10^{-2} mol/L.

Li[Li_3(**1–3**)$_6Ti_2$]	X=O Li[Li_3(**1**)$_6Ti_2$]	X=S Li[Li_3(**2**)$_6Ti_2$]	X=CH_2 Li[Li_3(**3**)$_6Ti_2$]
R = CH_3	170 ± 18	160 ± 17	1195[a]
R = C_2H_6	210 ± 22	275 ± 30	1920[a]
R = C_3H_7	340 ± 38	350 ± 39	1530[a]

[a] Ref.[7]

In addition to the solution studies it was possible to obtain crystal structures of Li[Li_3(**1a**)$_6Ti_2$] and Li[Li_3(**2a**)$_6Ti_2$] (Figure 2). The overall features of the complex structures are similar to the ones observed before for corresponding dimeric helicates.[6,7] The structures seem to indicate, that, due to the repulsion of

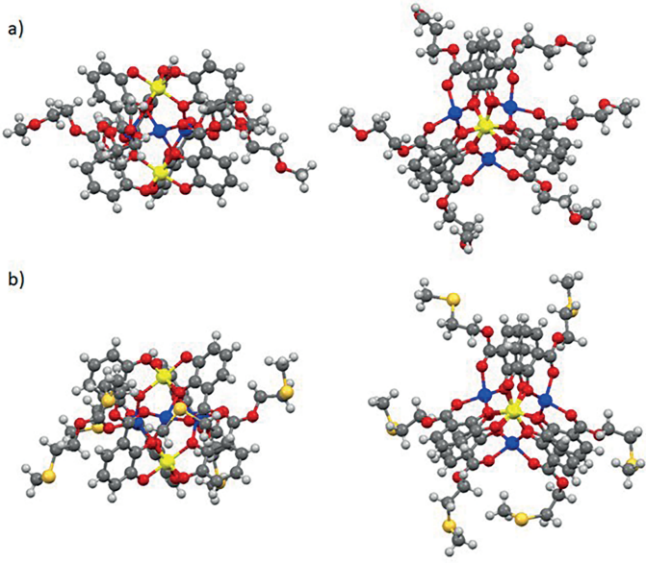


Figure 2. The molecular structures of the anions [Li_3(**1a**)$_6Ti_2$]$^-$ (a) and [Li_3(**2a**)$_6Ti_2$]$^-$ (b) in the crystal.

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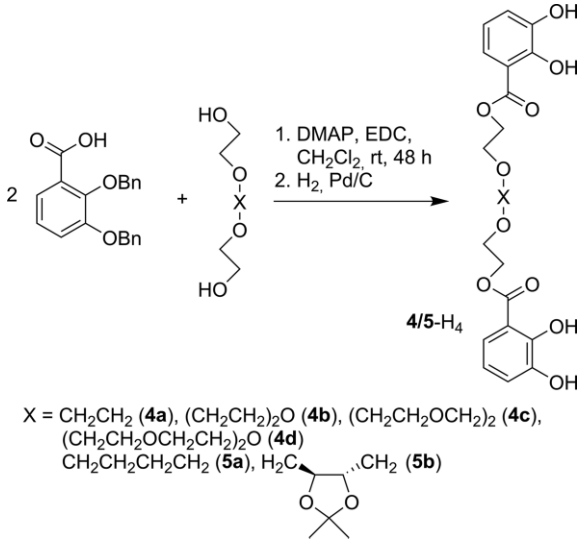
the electron pairs, the heteroatoms in the side chains adopt positions which are located far away from each other. The X-ray structural results can be correlated with NMR, ESI-MS based structural assignments. However, in solution side chains possess some high flexibility at the side chains.

Dinuclear helicates with ether type spacers. Connecting two complex units of the hierarchical helicates leads to compounds which act as lithium dependent expandable/compressable switches. A series of oligoglycol bridged ligands **4,5**-H_4 have been made by Steglich type esterification[13] of appropriate diols with dibenzyl protected dihydroxybenzoic acid followed by removal of the benzyl protecting groups (Scheme 2). The coordination chemistry of the ligands with titanium(IV) in the presence of alkali metal cations has been tested.



Scheme 2. Preparation of oligo ether linked dicatechol esters.

The complexes $Li[Li_3(\mathbf{4b})_3Ti_2]$ and $Na_2[Na_2(\mathbf{5a})_3Ti_2]$ were communicated recently and their crystal structures were presented (Figure 3). Both compounds show a compressed structure with the expected geometry for $Li[Li_3(\mathbf{4b})_3Ti_2]$ while $Na_2[Na_2(\mathbf{5a})_3Ti_2]$ represents a topological isomer to the "classical" helicates with two of the spacers attached to one of the catechols from the inside and to the other from the outside.[14]

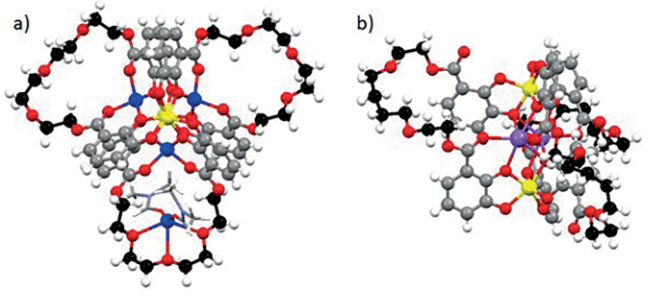


Figure 3. The structures of $Li(DMF)_2[Li_3(\mathbf{4b})_3Ti_2]$ and $[Na_2(\mathbf{5a})_3Ti_2]^{2-}$.

In here the ligands **4a,c,d** are additionally introduced in order to study the influence of different spacer length on the complex formation. Furthermore, the new ligand **5b** represents a chiral version of the earlier investigated **5a**, allowing the study of the stereochemical influence of the remote chiral group.

All ligands **4** form compressed dinuclear titanium(IV) complexes with internally bound lithium cations as had been structurally characterized for $[Li_3(\mathbf{4b})_3Ti_2]^-$. The anionic helicate can be easily observed by ESI MS (m/z = 1371.2078 $[Li_3(\mathbf{4a})_3Ti_2]^-$, 1635.3604 $[Li_3(\mathbf{4c})_3Ti_2]^-$, 1767.4446 $[Li_3(\mathbf{4d})_3Ti_2]^-$) supporting this assignment.

However, ^{1}H NMR spectroscopy reveals some surprises. For $Li[Li_3(\mathbf{4a})_3Ti_2]$ and $Li[Li_3(\mathbf{4b})_3Ti_2]$ the expected spectra are observed which show three resonances for the protons of the catechol units in the aromatic region. In case of the complexes with very long spacers $Li[Li_3(\mathbf{4c})_3Ti_2]$ and $Li[Li_3(\mathbf{4d})_3Ti_2]$ two sets of signals are observed for the catechol units (Figure 4).

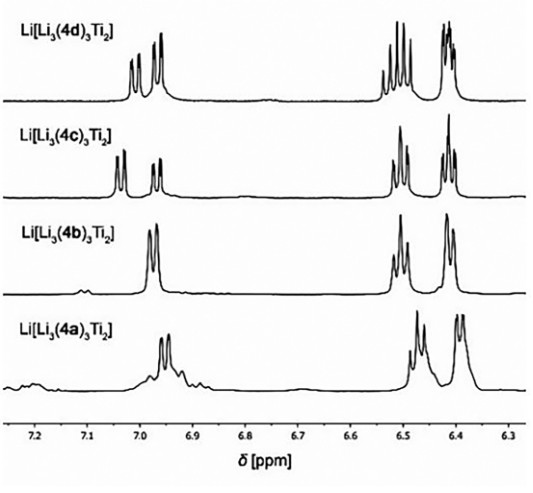


Figure 4. ^{1}H NMR signals of the catechol protons of the compressed helicates $Li[Li_3(\mathbf{4a\text{-}d})_3Ti_2]$ (in $[D_6]$DMSO).

The ESI MS results as well as the NMR spectra indicate that in case of $Li[Li_3(\mathbf{4c,d})_3Ti_2]$ two different isomers with high symmetry are present. We assume that this only can be due to different orientations of the spacers. The structure of $Li[Li_3(\mathbf{4b})_3Ti_2]$ reveals that in this case the spacer bridges the ester units in front of the lithium cations (Type I). This is the only possible arrangement in case of short chain length. With longer spacers the alternative Type II structure with the spacers bridging "over" the aromatics becomes also possible. This is schematically illustrated in Figure 5 for the Type I and Type II structures of $[Li_3(\mathbf{4d})_3Ti_2]^-$.

It was possible to obtain crystals of $Na[Li_3(\mathbf{4c})_3Ti_2]$ which were sufficient for crystal structure analysis. In the crystal the complex adopts a Type I structure with the spacers bridging in front of one lithium cation. Hereby crown ether-type loops are found and in one of those the sodium cation is bound (Figure 6).[15]

The lithium as well as the sodium complexes $M_4[(\mathbf{5a})_3Ti_2]$ (M = Li, Na) have already been described.[14] The potassium salt shows two different sets of signals relating to two complexes which structurally could not be assigned. Based on the ESI MS observations (m/z = 1552.1572 $[K_3(\mathbf{5a})_3Ti_2]^-$, 1629.0768 $K_5[(\mathbf{5a})_3Ti_2]^+$) it is assumed that at least one isomer should adopt the triple stranded helicate structure.

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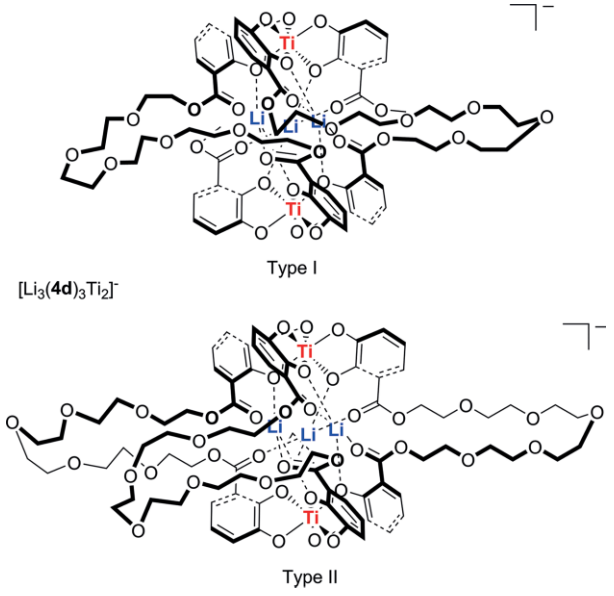

Figure 5. Cartoon of the type I and type II isomers of $[Li_3(\mathbf{4d})_3Ti_2]^-$.

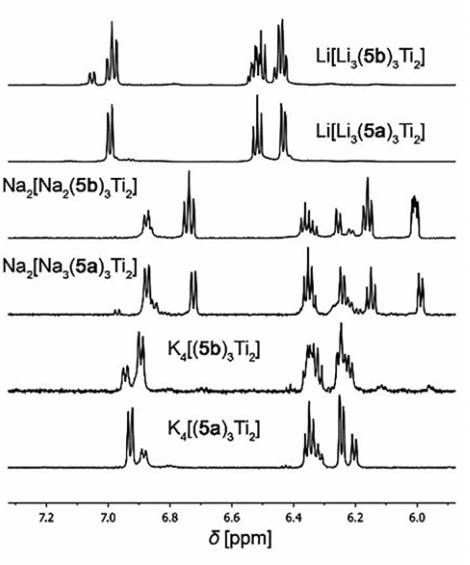

Figure 7. ^{1}H NMR signals ([D$_6$]DMSO) of the catechol protons of the helicates $M_4[(\mathbf{5a,b})_3Ti_2]$ (M = Li, Na, K).

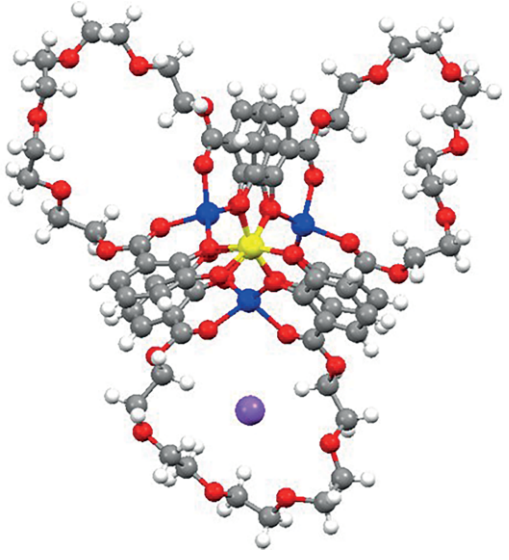

Figure 6. Structure of $Na[Li_3(\mathbf{4c})_3Ti_2]$ as observed in the crystal. View down the Ti-Ti axis.

Ligand **5b**-H_4[16] represents a chiral version of **5a**-H_4. The coordination compounds $M_4[(\mathbf{5b})_3Ti_2]$ (M = Li, Na, K) can be obtained from this ligand.

The potassium salts $K_4[(\mathbf{5a,b})_3Ti_2]$ show two major isomers which cannot be structurally assigned.

In the case of the lithium complex $Li[Li_3(\mathbf{5b})_3Ti_2]$ similar shifts as found for $Li[Li_3(\mathbf{5a})_3Ti_2]$ are observed by proton NMR spectroscopy.[14] However, the dominating signals split into two sets. This is tentatively assigned to the inefficient stereocontrol at $Li[Li_3(\mathbf{5b})_3Ti_2]$ by the remote chiral units of the spacer resulting in two different diastereoisomers (SSΛΛ and SSΔΔ).

The spectrum of the sodium complex $Na_2[Na_2(\mathbf{5b})_3Ti_2]$ correlates with the one of the achiral complex $Na_2[Na_2(\mathbf{5a})_3Ti_2]$ showing that again the "topological" helicate isomer is formed (Figure 7).[14]

CD spectra were measured for the chiral complexes $M_4[(\mathbf{5b})_3Ti_2]$ (M = Li, Na, K). The transitions at the titanium(IV) catecholate moieties provide information on the chirality (Δ vs. Λ).[17] The results show that in the lithium salt, the complexes preferably adopt Δ configuration which is also favored in the sodium complex. However, in the latter case much lower ellipticity is observed. For the potassium salt, the favored stereochemistry at the catecholate complexes is inverted compared to the lithium or sodium salt (Figure 8). A similar stereochemical inversion effect has been already observed earlier with ester catecholate based titanium(IV) complexes and has been discussed in detail at this time.[11,18]

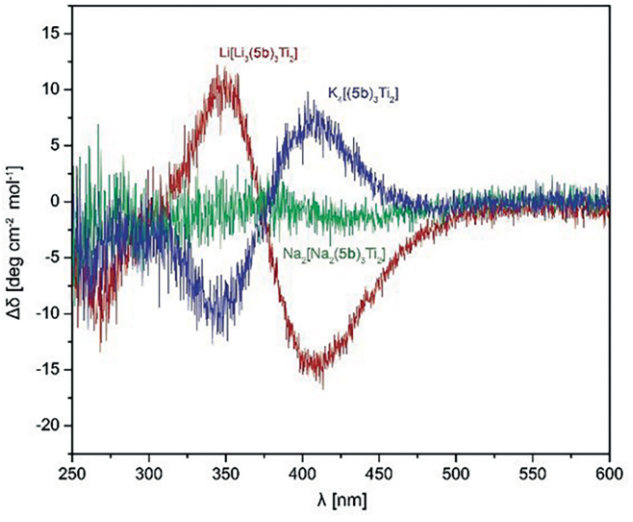

Figure 8. CD spectra of $M_4[(\mathbf{5b})_3Ti_2]$ (M = Li, Na, K) in DMSO.

In order to obtain crystals of the coordination compounds of ligand **5b**, different salts were added to lead to better crystallization properties. Thus, the crystal structure of $[AsPh_4]_2$-$[Na_2(\mathbf{5b})_2Ti_2O_2]$·2MeOH has been obtained. A central bis-μ-oxo bis titanium(IV) moiety is formed. The two titanium centers are

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bridged by two oxygen atoms as well as two ligands **5b**. Two sodium cations are included in the complex, binding to the catecholesters and additionally to one molecule of methanol each (Figure 9). The structure of $[Na_2(\mathbf{5b})_2Ti_2O_2]^{2-}$ is related to the ones observed earlier for dinuclear titanium(IV) complexes with amino acid bridged dicatechol ligands.[19]

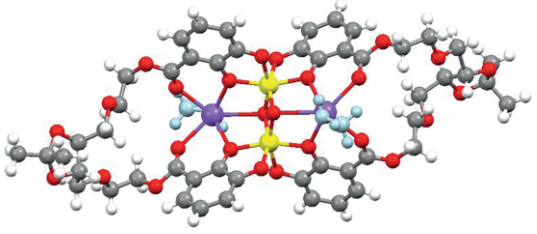

Figure 9. Structure of $[Na_2(\mathbf{5b})_2Ti_2O_2]^{2-}$·2MeOH in the crystal. The methanol molecules are shown in light blue.

However, due to the absence of resonances of the free ligand **5b** in the crude product spectra of $Na_4[(\mathbf{5b})_3Ti_2]$ formed from three equivalents of ligand with two equivalents of titanium(IV) ions it is expected that $[Na_2(\mathbf{5b})_2Ti_2O_2]^{2-}$ is only formed under the crystallization conditions.

Expansion and compression of helicates with ether type spacers. Due to the expanded and compressed structures of the helicates $M_4[(\mathbf{4/5})_3Ti_2]$, switching in a spring-type fashion is feasible depending on the cations. The corresponding switching of $M_4[(\mathbf{5a})_3Ti_2]$ has been already reported.[14]

In here consecutive expansion and compression experiments have been performed in one NMR test tube starting with the compressed forms $Li[Li_3(\mathbf{4a\text{-}d})_3Ti_2]$ (Figure 10) or $Li[Li_3(\mathbf{5a,b})_3Ti_2]$

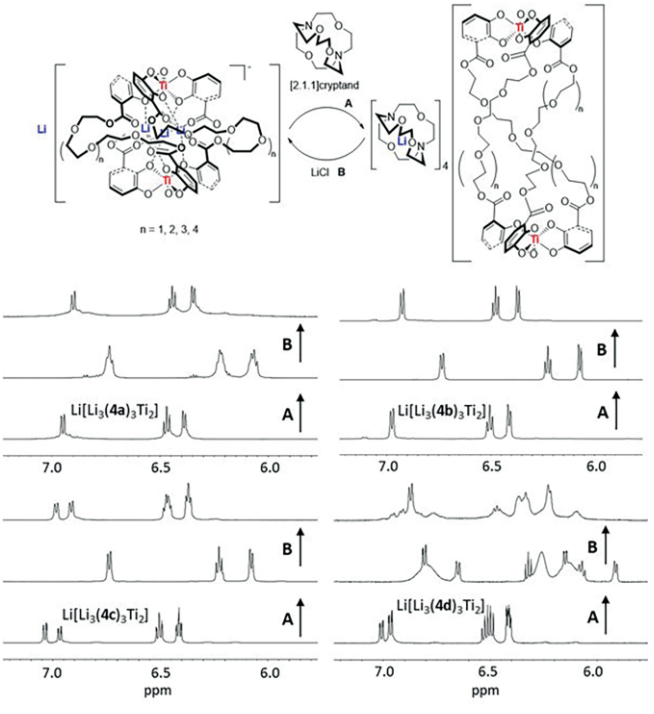

Figure 10. Reversible switching of the compressed complexes $Li[Li_3(\mathbf{4a\text{–}d})_3Ti_2]$. Expansion occurs upon addition of [2.1.1]cryptand (**A**) while compression is induced by addition of LiCl (**B**).

(Figure 11). Upon addition of [2.1.1]cryptand (approx. 10 equiv.) (**A**), lithium cations are removed from the complexes resulting in expansion of the helicates. Successive addition of 10 equiv. of LiCl (**B**) leads to compression. This can be easily followed by observing the resonances of the aromatic protons.

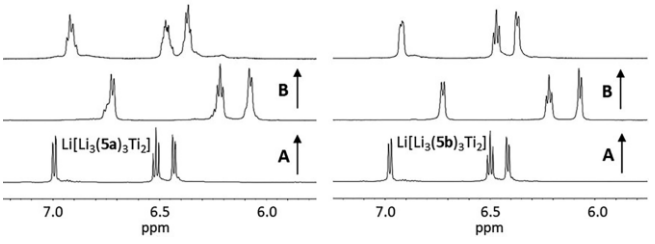

Figure 11. Reversible switching of the compressed complexes $Li[Li_3(\mathbf{5a,b})_3Ti_2]$. Expansion occurs upon addition of [2.1.1]cryptand (**A**) while compression is induced by addition of LiCl (**B**).

Conclusions

In here a series of hierarchical and expandable/compressible helicates with ether-type ester substituents is presented. In many respects those complexes behave as observed for the hydrocarbon analogs. However, some differences are found and some new observations are made:

– Hierarchical helicates with ether or thioether-type substituents dissociate into the monomers more easily compared to the analogous alkyl derivatives. Hereby, the dimer stability is independent on the heteroatom oxygen vs. sulfur in the side chain.

– Helicate based expandable and compressible molecular switches are obtained with ether containing spacers and can easily be switched. However, for the first time two different isomers are observed for the lithium complexes $Li[Li_3(\mathbf{4c,d})_3Ti_2]$ which are assigned to Type I and Type II isomers with different positions of the connecting units.

– In the chiral derivative $Li[Li_3(\mathbf{5b})_3Ti_2]$ stereoinduction by the remote chiral unit is not complete. However, with sodium cations the "topological" helicate isomer $Na_2[Na_2(\mathbf{5b})_3Ti_2]$ is observed as it also was found for the corresponding achiral $Na_2[Na_2(\mathbf{5a})_3Ti_2]$.[14]

– The new structural motif of a double-stranded dinuclear complex $[Na_2(\mathbf{5b})_2Ti_2O_2]^{2-}$·2MeOH could be characterized by X-ray diffraction.

Thus, the coordination chemistry of the ether substituted catechol and dicatechol ester ligands is well explored and in the future will be used for host–guest chemistry with cations which may be bound in the loops[15] of $M_4[(\mathbf{4a\text{-}d})_3Ti_2]$ in the presence of lithium but not of other cations.

Experimental Section

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.

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 (SiO2), 40–60 µm) 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 ($CDCl_3$, $[D_6]$DMSO). 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 doublet, 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 spectra were 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}.

Melting points. Melting points were determined with a BÜCHI B-540 melting point instrument and are reported uncorrected. The given melting points in °C indicate the temperature range between the beginning and the end of the melting process.

X-ray crystallography. The experimental and refinement details for $K[Li_3(\mathbf{1a})_6Ti_2]$, $Li[Li_3(\mathbf{2a})_6Ti_2]$, $Na[Li_3(\mathbf{4c})_3Ti_2]$, $Na_2[(\mathbf{5b})_2Ti_2]$ are given below. Single-crystal X-ray data for $K[Li_3(\mathbf{1a})_6Ti_2]$ was measured using a Rigaku SuperNova dualsource Oxford diffractometer equipped with an Eos detector using mirror-monochromated Mo-K_α (λ = 0.71073 Å) radiation. The data collection and reduction were performed using the program CrysAlisPro7 and Gaussian face index absorption correction method was applied.[20] X-ray data for $Li[Li_3(\mathbf{2a})_6Ti_2]$ was measured using a Bruker-Nonius KappaCCD diffractometer with an APEX-II detector with graphitemonochromatized Mo-K_α (λ = 0.71073 Å) radiation. Data collection and reduction were performed using the program COLLECT[21] and HKL DENZO AND SCALEPACK.[22] respectively, and the intensities were corrected for absorption using SADABS.[23] The structures were solved with intrinsic phasing (SHELXT)[24] and refined by full-matrix least-squares on F^2 using the OLEX2 software,[25] which utilises the SHELXL2015 module.[24] Single crystal X-ray diffraction data for $Na[Li_3(\mathbf{4c})_3Ti_2]$ and $Na_2[(\mathbf{5b})_2Ti_2]$ were collected at 100(2) K by using ω-scans on a Stoe Stadivari Eulerian geometry four-circle diffractometer, equipped with a Cu-K_α micro-focused source (GeniX 3D HF Cu, λ = 1.54178 Å) and a Pilatus 200 K hybrid pixel detector (Dectris). Data collection, reduction and absorption correction were performed with the software package X-Area.[26] The space groups were determined using XPREP9 and the structures were solved with intrinsic phasing (SHELXT). The structures were refined using SHELXL-201813 with a least-squares procedure against F^2. $Na[Li_3(\mathbf{4c})_3Ti_2]$ was refined as a two-component twin (x = –0.017(15)). Due to inadequate data-parameter ratio, the disorder of the crown ether-type moieties could not be refined. The sodium ion was modelled as a disorder over two positions (0.58:0.42). The residual electron density of 1.88 (–0.0699, 0.4020, 0.4446) indicates another likely position for the disordered sodium cation. Disordered solvent in $Na_2[(\mathbf{5b})_2Ti_2]$ was treated by applying a solvent mask in OLEX2. Eight molecules of methanol can be estimated per formula unit. Hydrogen atoms were refined using riding models with Ueq(H) of 1.5 Ueq(C) for terminal methyl groups, and 1.2 Ueq(C) for other groups.

General Procedure for the Preparation of ligands 1,2-H_2. Ligands **1a-c**-H_2 and **2a–c**-H_2 were synthesized by esterification, starting with the conversion of 2,3-Dihydroxybenzoic acid (1 equiv.) into its corresponding acid chloride via refluxing in thionyl chloride (30 equiv.) for 1 hour. The excess thionyl chloride was removed under reduced pressure and the remaining acid chloride used in the next step without further purification. The acid chloride was then reacted with a mixture of the corresponding alcohol (3 equiv.) and triethylamine (6 equiv.) in chloroform to afford the desired product after purification via column chromatography.

1a-H_2. The ligand was prepared from 2-methoxyethan-1-ol (296.01 mg, 3.89 mmol) by modification of the general procedure. The product is isolated by column chromatography (pentane/ethyl acetate, 4:1, R_f = 0.18) as a white solid (53 %, 146 mg, 0.69 mmol). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 10.82 (s, 1H, OH), 7.42 (dd, *J* = 8.0, 1.4 Hz, 1H, $H_{arom.}$), 7.11 (dd, *J* = 8.0, 1.4 Hz, 1$H_{arom.}$), 6.81 (t, *J* = 8.0 Hz, 1H, $H_{arom.}$), 5.65 (s, 1H, OH), 4.50 (t, *J* = 5.3 Hz, 2H, CH_2), 3.73 (t, *J* = 5.3 Hz, 2H, CH_2), 3.42 (s, 3H, CH_3) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$: δ = 170.19 (CO_2CH_2), 148.83 ($C_{arom.}$), 144.98 ($C_{arom.}$), 120.78 ($C_{arom.}$), 119.87 ($C_{arom.}$), 119.20 ($C_{arom.}$), 112.35 ($C_{arom.}$), 70.21 (CH_2), 64.46 (CH_2), 59.14 (CH_3) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{10}H_{12}NaO_5^+$ [M + Na^+]: 235.0582, found 235.0600. IR (KBr): $\tilde{\nu}$ = (cm^{-1}) = 3346, 3056, 2999, 2948, 2832, 2472, 2325, 2161, 2039, 1935, 1876, 1666, 1612, 1539, 1455, 1375, 1301, 1264, 1236, 1156, 1123, 1084, 1032, 967, 912, 862, 836, 784, 743. Elemental analysis: Calculated for $C_{10}H_{12}O_5$·1/20DCM: 55.77 %, H: 5.63 %; found C: 55.53 %, H: 5.54 %.

1b-H_2. The ligand was prepared from 2-ethoxyethan-1-ol (350.57 mg, 3.89 mmol) by modification of the generalprocedure. The product is isolated by column chromatography (pentane/ethyl acetate, 4:1, R_f = 0.21) as colorless oil (46 %, 134 mg, 0.59 mmol). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 10.83 (s, 1H, OH), 7.42 (dd, *J* = 8.0, 1.4 Hz, 1H, $H_{arom.}$), 7.11 (dd, *J* = 8.0,1.5 Hz, 1H, Harom.), 6.80 (t, *J* = 8.0 Hz, 1H, $H_{arom.}$), 5.65 (s, 1H, OH), 4.50 (t, *J* = 6.5 Hz, 2H, CH_2), 3.77 (t, *J* = 6.5 Hz, 2H, CH_2), 3.58 (q, *J* = 7.0 Hz, 2H, CH_2), 1.23 (t, *J* = 7.0 Hz, 3H, CH_3) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$: δ = 170.18 (CO_2CH_2), 148.81 ($C_{arom.}$), 144.98 ($C_{arom.}$), 120.80 ($C_{arom.}$), 119.83 ($C_{arom.}$), 119.19 ($C_{arom.}$), 112.43 ($C_{arom.}$), 68.06 (CH_2), 66.80 (CH_2), 64.69 (CH_2), 15.13 (CH_3) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{11}H_{14}NaO_5^+$ [M + Na^+]: 249.0739, found 249.0761. IR (KBr): $\tilde{\nu}$ = (cm^{-1}) = 3633, 3449, 3203, 2976, 1873, 2466, 2327, 2182, 2072, 1916, 1732, 1671, 1608, 1532, 1467, 1379, 1301, 1267, 1237, 1153, 1120, 1069, 1032, 968, 880, 843, 751, 715. Elemental analysis: Calculated for $C_{11}H_{14}O_5$·1/2H_2O: H: 6.43 %; found C: 56.18 %, H: 6.30 %.

1c-H_2. The ligand was prepared from 2-propoxyethan-1-ol (405.14 mg, 3.89 mmol) by modification of the general procedure. The product is isolated by column chromatography (pentane/ethyl acetate, 4:1, R_f = 0.13) as colorless oil (47 %, 146 mg, 0.61 mmol).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 10.83 (s, 1H, OH), 7.42 (dd, *J* = 8.1, 1.0 Hz, 1H, $H_{arom.}$), 7.11 (dd, *J* = 8.1, 1.1 Hz, 1H, $H_{arom.}$), 6.80 (t, *J* = 8.1 Hz, 1H, $H_{arom.}$), 5.66 (s, 1H, OH), 4.49 (t, *J* = 6.8 Hz, 2H, CH_2), 3.77 (t, *J* = 6.8 Hz, 2H, CH_2), 3.51 (t, *J* = 6.9 Hz, 2H, CH_2), 1.63–1.60 (m, 2H, CH_2), 0.92 (t, *J* = 7.0 Hz, 3H, CH_3) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$: δ = 170.18 (CO_2CH_2), 148.80 ($C_{arom.}$), 144.98 ($C_{arom.}$), 120.78 ($C_{arom.}$), 119.81 ($C_{arom.}$), 119.19 ($C_{arom.}$), 112.45 ($C_{arom.}$), 73.14 (CH_2), 68.22 (CH_2), 64.66 (CH_2), 22.79 (CH_2), 10.47 (CH_3) ppm. ESI-MS (negative ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{12}H_{15}O_5^-$ [M – H$^+$]: 239.0928, found 239.0921. IR (KBr): $\tilde{\nu}$ = (cm^{-1}) = 3632, 3560, 3435, 3135, 2963, 2874, 2328, 2185, 2156, 2039, 2003, 1671, 1612, 1467, 1371, 1301, 1266, 1153, 1123, 1068, 1033, 990, 882, 841, 751, 713. Elemental analysis: Calculated for $C_{12}H_{16}O_5$•1/2DCM: 53.10 %, H: 6.06 %; found C: 53.53 %, H: 6.20 %.

2a-H$_2$. The ligand was prepared from 2-methylthioethan-1-ol (358.49 mg, 3.89 mmol) by modification of thegeneral procedure. The product is isolated by column chromatography (pentane/ethyl acetate, 8:1, R_f = 0.12) as colorless oil (46.5 %, 136 mg, 0.60 mmol). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 10.91 (s, 1H, OH), 7.36 (dd, *J* = 8.2, 1.4 Hz, 1H, $H_{arom.}$), 7.10 (dd, *J* = 8.0, 1.6 Hz, 1H, $H_{arom.}$), 6.80 (t, *J* = 8.0 Hz, 1H, $H_{arom.}$), 5.64 (s, 1H, OH), 4.53 (t, *J* = 6.8 Hz, 2H, CH_2), 2.87 (t, *J* = 6.8 Hz, 2H, CH_2), 2.22 (s, 3H, CH_3) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$: δ = 170.05 (CO_2CH_2), 148.91 ($C_{arom.}$), 145.04 ($C_{arom.}$), 120.60 ($C_{arom.}$), 119.94 ($C_{arom.}$), 119.29 ($C_{arom.}$), 112.28 ($C_{arom.}$), 64.06 (CH_2), 32.44 (CH_2), 15.94 (CH_3) ppm. ESI-MS (negative ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{10}H_{11}O_4S^-$ [M – H$^+$]: 227.0386, found 227.0360. IR (KBr): $\tilde{\nu}$ = (cm^{-1}) = 3455, 3138, 2964, 2920, 2835, 2735, 2325, 2086, 1915, 1669, 1465, 1384, 1302, 1265, 1146, 1067, 987, 843, 750, 704. Elemental analysis: for $C_{10}H_{12}O_4S$•1/3H_2O: 51.40 %, H: 5.44 %; found C: 51.60 %, H: 5.35 %.

2b-H$_2$. The ligand was prepared from 2-ethylthioethan-1-ol (413.05 mg, 3.89 mmol) by modification of the general procedure. The product is isolated by column chromatography (pentane/ethyl acetate, 8:1, R_f = 0.15) as colorless oil (38 %, 118 mg, 0.49 mmol). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 10.83 (s, 1H, OH), 7.37 (dd, *J* = 7.8, 1.4 Hz, 1H, $H_{arom.}$), 7.11 (dd, *J* = 7.8, 1.5 Hz, 1H, $H_{arom.}$), 6.81 (t, *J* = 8.0 Hz, 1H, $H_{arom.}$), 5.65 (s, 1H, OH), 4.50 (t, *J* = 6.9 Hz, 2H, CH_2), 2.90 (t, *J* = 6.9 Hz, 2H, CH_2), 2.65 (q, *J* = 7.8 Hz, 2H, CH_2), 1.29 (t, *J* = 7.8 Hz, 3H, CH_3) ppm. ^{13}C-NMR 170.05 (CO_2CH_2), 148.91 ($C_{arom.}$), 145.03 ($C_{arom.}$), 120.60 ($C_{arom.}$), 119.93 ($C_{arom.}$), 119.28 ($C_{arom.}$), 112.28 ($C_{arom.}$), 64.52 (CH_2), 29.84 (CH_2), 26.30 (CH_2), 14.20 (CH_3) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{11}H_{14}O_4SNa^+$ [M + Na$^+$]: 241.0543, found 241.0565. IR (KBr): $\tilde{\nu}$ = (cm^{-1}) = 3885, 3458, 3136, 2965, 2928, 2666, 2324, 2099, 1997, 1912, 1669, 1465, 1383, 1302, 1146, 1066, 982, 901, 843, 750, 702. Elemental analysis: for $C_{11}H_{14}O_4S$•1/3H_2O: 54.53 %, H: 5.82 %; found C: 55.19 %, H: 6.03 %.

2c-H$_2$. The ligand was prepared from 2-propylthioethan-1-ol (467.62 mg, 3.89 mmol) by modification of the general procedure. The product is isolated by column chromatography (pentane/ethyl acetate, 8:1, R_f = 0.18) as colorless oil (45 %, 148 mg, 0.58 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.81 (s, 1H, OH), 7.36 (dd, *J* = 8.0, 1.5 Hz, 1H, $H_{arom.}$), 7.08 (dd, *J* = 8.0, 1.5 Hz, 1H, $H_{arom.}$), 6.78 (t, *J* = 8.0 Hz, 1H, $H_{arom.}$), 5.63 (s, 1H, OH), 4.48 (t, *J* = 7.0 Hz, 2H, CH_2), 2.86 (t, *J* = 7.0 Hz, 2H, CH_2), 2.54 (t, *J* = 6.7 Hz, 2H, CH_2), 1.63–1.60 (m, 2H, CH_2), 0.99 (t, *J* = 7.4 Hz, 3H, CH_3) ppm. ^{13}C-NMR (151 MHz, $CDCl_3$: δ = 170.02 (CO_2CH_2), 148.88 ($C_{arom.}$), 145.03 ($C_{arom.}$), 120.58 ($C_{arom.}$), 119.90 ($C_{arom.}$), 119.24 ($C_{arom.}$), 112.29 ($C_{arom.}$), 64.55 (CH_2), 34.47 (CH_2), 30.23 (CH_2), 22.97 (CH_2), 13.36 (CH_3) ppm. ESI-MS (negative ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{12}H_{17}O_4S^-$ [M – H$^+$]: 255.0699, found 255.0701. IR (KBr): $\tilde{\nu}$ = (cm^{-1}) = 3459, 3137, 2958, 2663, 2462, 2316, 2085, 2000, 1914, 1670, 1465, 1383, 1301, 1147, 1065, 985, 898, 843, 750. Elemental analysis: Calculated for $C_{12}H_{16}O_4S$•1/3H_2O: 55.07 %, H: 6.39 %; found C: 55.26 %, H: 6.73 %.

General procedure for diol esterification *(using **4aII** as an example).* Triethylene glycol **4aI** (200 mg, 1.12 mmol, 1.0 equiv.) was dissolved in dichloromethane (50 mL). 2,3-Bis(benzyloxy)benzoic acid (1126 mg, 3.37 mmol, 3.0 equiv.), 4-dimethylaminopyridine (137 mg, 1.12 mmol, 1.0 equiv.) and 1-ethyl-3-(3-di- methylaminopropyl)carbodiimide (646 mg, 3.37 mmol, 3.0 equiv.) 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, 3:2 pentane/ethyl acetate) to afford the title compound (544 mg, 0.69 mmol, 63 %) as a white solid. ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 7.49–7.46 (m, 4H, $H_{arom.}$), 7.41–7.34 (m, 12H, $12H_{arom.}$), 7.29–7.23 (m, 6H, $6H_{arom.}$), 7.23–7.18 (m, 2H, $2H_{arom.}$), 7.14 (t, *J* = 7.9 Hz, 2H, $2H_{arom.}$), 5.18 (s, 4H, $2CH_2$), 4.98 (s, 4H, $2CH_2$), 4.33–4.21 (m, 4H, $2CH_2$), 3.70–3.57 (m, 4H, $2CH_2$), 3.47 (s, 4H, $2CH_2$) ppm. ^{13}C-NMR (151 MHz, [D_6]DMSO): δ = 165.7 (CO_2CH_2), 152.3 ($C_{arom.}$), 146.73 ($C_{arom.}$), 137.3 ($C_{arom.}$), 136.6 ($C_{arom.}$), 128.5 ($C_{arom.}$), 128.1 ($C_{arom.}$), 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 ($C_{arom.}$), 74.7 (CH_2), 70.2 (CH_2), 69.7 (CH_2), 68.2 (CH_2), 64.0 (CH_2) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{48}H_{46}NaO_{10}^+$ [M + Na$^+$]: 805.2983, found 805.2999. Elemental analysis: Calculated for $C_{48}H_{46}O_{10}$: C: 73.64 %, H: 5.92 %; found C: 73.56 %, H: 5.96 %.

General procedure for removal of benzyl protecting groups *(using **4aIII** as an example).* **4aII** (560 mg, 0.72 mmol) was dissolved in dichloromethane (50 mL). Palladium on carbon (13 wt.-% Pd on C, 73 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, 3:2 pentane/ethyl acetate) to afford the title compound **4a**-H_4 (145 mg, 0.35 mmol, 48 %) as a white solid.

^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 7.22 (dd, *J* = 7.9, 1.6 Hz, 2H, $2H_{arom.}$), 7.02 (dd, *J* = 7.9, 1.6 Hz, 2H, $2H_{arom.}$), 6.73 (t, *J* = 7.9 Hz, 2H, 2 $H_{arom.}$), 4.42–4.36 (m, 4H, $2CH_2$), 3.77–3.73 (m, 4H, $2CH_2$), 3.61 (s, 4H,$2CH_2$) ppm. ^{13}C-NMR (151 MHz, [D_6]DMSO): δ = 169.8 ($C_{arom.}$), 150.0 ($C_{arom.}$), 146.5 ($C_{arom.}$), 121.2 ($C_{arom.}$), 120.0 ($C_{arom.}$), 119.3 ($C_{arom.}$), 113.4 ($C_{arom.}$), 70.3 (CH_2), 68.5 (CH_2), 64.9 (CH_2) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{22}H_{26}NaO_{11}^+$ [M + Na$^+$]: 445.1105, found 445.1095 Elemental analysis: Calculated for $C_{22}H_{26}O_{11}$: C: 56.87 %, H: 5.25 %; found C: 56.97 %, H: 5.54 %.

4bII. The product was prepared applying the general procedure for diol esterification (see ***4aII***) starting form tetraethylene glycol **4bI** (200 mg, 1.03 mmol) to afford the title compound (468 mg, 0.56 mmol, 55 %) as a white solid. ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 7.49–7.45 (m, 4H, $4H_{arom.}$), 7.41–7.32 (m, 12H, $12H_{arom.}$), 7.28 (dd, *J* = 5.1, 2.0 Hz, 6H, $6H_{arom.}$), 7.21 (dd, *J* = 7.9, 1.5 Hz, 2H, $2H_{arom.}$), 7.16 (t, *J* = 7.9 Hz, 2H, $2H_{arom.}$), 5.18 (s, 4H, $2CH_2$), 4.99 (s, 4H, $2CH_2$), 4.33–4.22 (m, 4H, $2CH_2$), 3.64–3.58 (m, 4H, $2CH_2$), 3.45 (dt, *J* = 3.7, 2.3 Hz, 4H, $2CH_2$), 3.41 (dt, *J* = 6.1, 3.7, Hz, 4H, $2CH_2$) ppm. ^{13}C-NMR (151 MHz, [D_6]DMSO): δ = 166.1 (CO_2CH_2), 152.7 ($C_{arom.}$), 147.2 ($C_{arom.}$), 137.8 ($C_{arom.}$), 137.1 ($C_{arom.}$), 128.9 ($C_{arom.}$), 128.6 ($C_{arom.}$), 128.5 ($C_{arom.}$), 128.5 ($C_{arom.}$), 128.3 ($C_{arom.}$), 128.2 ($C_{arom.}$), 127.0 ($C_{arom.}$), 124.7 ($C_{arom.}$), 122.0 ($C_{arom.}$), 118.0 ($C_{arom.}$), 75.17 (CH_2), 70.63 (CH_2), 70.15 (CH_2), 70.10 (CH_2), 68.61 (CH_2), 64.44 (CH_2) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{50}H_{50}NaO_{11}^+$ [M + Na$^+$]: 849.3245, found 849.3253. Elemental analysis: Calculated for $C_{50}H_{50}O_{11}$: C: 72.62 %, H: 6.09 %; found C: 72.08 %, H: 6.09 %.

4b-H$_4$. The ligand was prepared applying the general procedure for removal of benzyl protecting groups (see ***4a-H$_4$***) starting form **4bII**

(443 mg, 0.54 mmol) to afford the title compound (219 mg, 0.46 mmol, 87 %) as a white solid. ^{1}H-NMR (600 MHz, [D$_6$]DMSO): δ = 7.49–7.45 (m, 4H, 4H$_{arom.}$), 7.22 (d, *J* = 7.9 Hz, 2H, 2Harom.), 7.01 (d, *J* = 7.9 Hz, 2H, 2Harom.), 6.73 (t, *J* = 7.9 Hz, 2H, 2H$_{arom.}$), 4.41–4.35 (m, 4H, 2CH$_2$), 3.71 (dd, *J* = 5.6, 3.5 Hz, 4H, 2CH$_2$), 3.54 (dd, *J* = 6.2, 3.5 Hz, 4H, 2CH$_2$), 3.51 (dd, *J* = 5.6, 3.5 Hz, 4H, 2CH$_2$) ppm. ^{13}C-NMR (151 MHz, [D$_6$]DMSO): δ = 169.8 (CO$_2$CH$_2$), 145.0 (C$_{arom.}$), 146.5 (C$_{arom.}$), 121.2 (C$_{arom.}$), 120.0 (C$_{arom.}$), 119.4 (C$_{arom.}$), 113.4 (C$_{arom.}$), 70.3 (CH$_2$), 70.2 (CH$_2$), 68.5 (CH$_2$), 64.9 (CH$_2$) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{22}H_{26}NaO_{11}^+$ [M + Na$^+$]: 489.1367, found 489.1355. Elemental analysis: Calculated for $C_{22}H_{26}O_{11}$: C: 56.65 %, H: 5.62 %; found C: 56.67 %, H: 4.91 %.

4cII. The product was prepared applying the general procedure for diol esterification (see ***4aII***) starting form pentaethylene glycol **4cI** (1184 mg, 4.96 mmol) to afford the title compound (2105 mg, 2.42 mmol, 49 %) as a white solid. ^{1}H-NMR (600 MHz, [D$_6$]DMSO): 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, [D$_6$]DMSO): δ = 165.7 (CO$_2$CH$_2$), 152.3 (C$_{arom.}$), 146.74 (C$_{arom.}$), 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 (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{52}H_{54}NaO_{12}^+$ [M + Na$^+$]: 893.3513, found 893.3519. Elemental analysis: Calculated for $C_{52}H_{54}O_{12}$: C: 71.71 %, H: 6.25 %; found C: 71.67 %, H: 6.30 %.

4c-H$_4$. The ligand was prepared applying the general procedure for removal of benzyl protecting groups (see ***4a-H$_4$***) starting form **4cII** (500 mg, 0.57 mmol) to afford the title compound (138 mg, 0.27 mmol, 47 %) as a white solid. ^{1}H-NMR (600 MHz, [D$_6$]DMSO): δ = 7.22 (dd, *J* = 7.9, 1.6 Hz, 2H, 2H$_{arom.}$), 7.01 (dd, *J* = 7.9, 1.6 Hz, 2H, 2H$_{arom.}$), 6.73 (t, *J* = 7.9 Hz, 2H, 2H$_{arom.}$), 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, [D$_6$]DMSO): δ = 169.8 (CO$_2$CH$_2$), 150.0 (C$_{arom.}$), 146.6 (C$_{arom.}$), 121.2 (C$_{arom.}$), 120.0 (C$_{arom.}$), 119.4 (C$_{arom.}$), 113.5 (C$_{arom.}$), 70.6 (CH$_2$), 69.9 (CH$_2$), 68.5 (CH$_2$), 64.9 (CH$_2$) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{24}H_{30}NaO_{12}^+$ [M + Na$^+$]: 533.1635, found 533.1616. Elemental analysis: Calculated for $C_{24}H_{30}O_{12}$: C: 56.47 %, H: 5.92 %; found C: 55.70 %, H: 6.0 %.

4dII. The product was prepared applying the general procedure for diol esterification (see ***4aII***) starting form hexaethylene glycol **4dI** (1200 mg, 4.25 mmol) to afford the title compound (2089 mg, 2.28 mmol, 54 %) as a white solid. ^{1}H-NMR (600 MHz, [D$_6$]DMSO): δ = 7.49–7.43 (m, 4H, 4H$_{arom.}$), 7.42–7.30 (m, 12H, 12H$_{arom.}$), 7.27 (dtd, *J* = 6.2, 4.4, 1.9 Hz, 6H, 6H$_{arom.}$), 7.20 (dd, *J* = 7.8, 1.6 Hz, 2H, 2H$_{arom.}$), 7.15 (t, *J* = 8.0 Hz, 2H, 2H$_{arom.}$), 5.17 (s, 4H, 2CH$_2$), 4.99 (s, 4H, 2CH$_2$), 4.32–4.27 (m, 4H, 2CH$_2$), 3.66–3.60 (m, 4H, 2CH$_2$), 3.47 (dd, *J* = 5.9, 3.5 Hz, 4H, 2CH$_2$), 3.42 (dd, *J* = 5.9, 3.5 Hz, 4H,2CH$_2$), 3.39 (s, 4H, 2CH$_2$) ppm. ^{13}C-NMR (151 MHz, [D$_6$]DMSO): δ = 166.2 (CO$_2$CH$_2$), 152.7, (C$_{arom.}$), 147.2 (C$_{arom.}$), 137.8 (C$_{arom.}$), 137.1 (C$_{arom.}$), 128.9 (C$_{arom.}$), 128.6 (C$_{arom.}$), 128.5 (C$_{arom.}$), 128.4 (C$_{arom.}$), 128.3 (C$_{arom.}$), 127.1 (C$_{arom.}$), 124.7 (C$_{arom.}$), 122.0 (C$_{arom.}$), 118.0 (C$_{arom.}$), 75.2 (CH$_2$), 70.6 (CH$_2$), 70.1 (CH$_2$), 68.6 (CH$_2$), 64.5 (CH$_2$) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{54}H_{58}NaO_{13}^+$ [M + Na$^+$]: 937.3775, found 937.3773. Elemental analysis: Calculated for $C_{54}H_{58}O_{13}$: C: 70.88 %, H: 6.39 %; found C: 70.84 %, H: 6.31 %.

4d-H$_4$. The ligand was prepared applying the general procedure for removal of benzyl protecting groups (see ***4a-H$_4$***) starting form **4dII** (600 mg, 0.66 mmol) to afford the title compound (138 mg, 0.39 mmol, 59 %) as a white solid. ^{1}H-NMR (600 MHz, [D$_6$]DMSO): δ = 7.22 (dd, *J* = 7.9, 1.6 Hz, 2H, 2H$_{arom.}$), 7.01 (dd, *J* = 7.9, 1.6 Hz, 2H, 2H$_{arom.}$), 6.73 (t, *J* = 7.9 Hz, 2H, 2H$_{arom.}$), 4.43–4.37 (m, 4H, 2CH$_2$), 3.75–3.70 (m, 4H, 2CH$_2$), 3.55 (dd, *J* = 5.9, 3.6 Hz, 4H, 2CH$_2$), 3.52–3.42 (m, 8H, 4CH$_2$) ppm. ^{13}C-NMR (151 MHz, [D$_6$]DMSO): δ = 169.8 (CO$_2$CH$_2$), 150.0 (C$_{arom.}$), 146.6 (C$_{arom.}$), 121.2 (C$_{arom.}$), 120.0 (C$_{arom.}$), 119.4 (C$_{arom.}$), 113.5 (C$_{arom.}$), 70.6 (CH$_2$), 69.9 (CH$_2$), 68.5 (CH$_2$), 64.9 (CH$_2$) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{22}H_{26}NaO_{11}^+$ [M + Na$^+$]: 593.1636, found 593.1615. Elemental analysis: Calculated for $C_{22}H_{26}O_{11}$: C: 56.31 %, H: 6.18 %; found C: 55.70 %, H: 6.33 %.

General Procedure for the Preparation of THP protected diols *(using **5aII** as an example).* 1,4-Butanediol **5aI** (200 mg, 0.20 mL, 2.22 mmol, 1.0 equiv.) was dissolved in DMF (15 mL). NaH (60 wt.-% dispersion in mineral oil, 444 mg, 11.10 mmol, 5.0 equiv.) was added portion wise over 15 min. Afterwards 2-(2-Bromoethoxy)tetrahydro-2H-pyran (1.39 g, 1.01 mL, 6.66 mmol, 3 equiv.) was added drop wise and the resulting reaction mixture stirred at 70C for 4 h. After completion the reaction mixture was diluted with water (25 mL), extracted with EtOAc (2 × 40 mL) and washed with saturated NH$_4$Cl solution. The solvent was removed under reduced pressure and the crude product purified by column chromatography (SiO$_2$, 6:1 pentane/ethyl acetate to 1:1 pentane/ethyl acetate) to afford the title compound (740 mg, 2.14 mmol, 96 %) as a colorless oil. ^{1}H-NMR (600 MHz, [D$_6$]DMSO): δ = 4.57 (t, *J* = 3.6 Hz, 2H, 2CH), 3.77–3.71 (m, 2H, 2C*H*H), 3.71–3.66 (m, 2H, m, 2H, 2CH*H*), 3.51–3.44 (m, 6H, 3CH$_2$), 3.44–3.37 (m, 6H, 3CH$_2$), 1.74–1.66 (m, 2H, 2C*H*H), 1.65–1.56 (m, 2H, 2CH*H*), 1.56–1.50 (m, 4H, 2CH$_2$), 1.45 (m, 8H, 4CH$_2$). ^{13}C-NMR (151 MHz, [D$_6$]DMSO): δ = 98.0 (CH), 70.1 (CH$_2$), 69.4 (CH$_2$), 69.4 (CH$_2$), 66.1 (CH$_2$), 61.2 (CH$_2$), 30.2 (CH$_2$), 26.0 (CH$_2$), 25.0 (CH$_2$), 25.0 (CH$_2$), 19.1 (CH$_2$) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{18}H_{34}NaO_6^+$ [M + Na$^+$]: 369,2248, found 369.2261. Elemental analysis: Calculated for $C_{18}H_{34}O_6$: C: 62.40 %, H: 9.89 %; found C: 62.53 %, H: 9.54 %.

General procedure for the removal of THP protecting groups *(using **5aIII** as an example).* **5aII** (700 mg, 2.02 mmol, 1.0 equiv.) was dissolved in MeOH (20 mL). Pyridinium *p*-toluenesulfonate (1523 mg, 6.06 mmol, 3.0 equiv.) was added and the reaction mixture was stirred at 25 °C for 16 h. The solvent was removed under reduced pressure and the crude product purified by column chromatography (SiO$_2$, 20:1 pentane/ethyl acetate to, 10:1 ethyl acetate/methanol) to afford the title compound (193 mg, 1.08 mmol, 54 %) as a colorless oil. ^{1}H-NMR (600 MHz, [D$_6$]DMSO): δ = 4.56 (t, *J* = 5.6 Hz, 2H, CH$_2$), 3.47 (q, *J* = 5.4 Hz, 4H, 2CH$_2$), 3.40–3.35 (m, 8H, 4CH$_2$), 1.52 (h, *J* = 2.9 Hz, 4H, 2CH$_2$). ^{13}C-NMR (151 MHz, [D$_6$]DMSO): δ = 72.0 (2CH$_2$), 70.1 (2CH$_2$), 60.3 (2CH$_2$), 26.0 (2CH$_2$) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_8H_{18}NaO_4^+$ [M + Na$^+$]: 201,1097, found 201,1099. Elemental analysis: Calculated for $C_8H_{18}O_4$·0.5MeOH: C: 52.56 %, H: 10.38 %; found C: 53.12 %, H: 11.09 %.

5aIV. The product was prepared applying the general procedure for diol esterification (see ***4aII***) using **5aIII** (150 mg, 0.84 mmol) as starting material to afford the title compound (471 mg, 0.58 mmol, 69 %) as a white solid. ^{1}H-NMR (600 MHz, [D$_6$]DMSO): δ = 7.50–7.46 (m, 4H, 4Harom.), 7.41–7.32 (m, 12H, 12H$_{arom.}$), 7.28 (dd, *J* = 5.0, 2.0 Hz, 6H, 6H$_{arom.}$), 7.21 (dd, *J* = 7.9, 1.6 Hz, 2H, 2H$_{arom.}$), 7.16 (t, *J* = 7.9 Hz, 2H, 2H$_{arom.}$), 5.18 (s, 4H, 2CH$_2$), 4.99 (s, 4H 2CH$_2$), 4.35–4.18 (m, 4H 2CH$_2$), 3.62–3.50 (m, 4H 2CH$_2$), 3.31 (q, *J* = 5.8, 4.5 Hz, H 2CH$_2$), 1.44–1.39 (m, 4H, 2CH$_2$) ppm. ^{13}C-NMR (151 MHz,

[D_6]DMSO): δ = 165.8 (CO_2CH_2), 152.3 ($C_{arom.}$), 146.8 ($C_{arom.}$), 137.3 ($C_{arom.}$), 136.6 ($C_{arom.}$), 128.5 ($C_{arom.}$), 128.1 ($C_{arom.}$), 128.1 ($C_{arom.}$), 128.0 ($C_{arom.}$), 127.9 ($C_{arom.}$), 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), 70.0 (CH_2), 67.8 (CH_2), 64.1 CH_2), 25.8 (CH_2) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{50}H_{50}NaO_{10}$ [M + Na^+]: 833.3296, found 833.3303. Elemental analysis: Calculated for $C_{50}H_{50}O_{10}$: C: 74.06 %, H: 6.22 %; found C: 74.00 %, H: 6.32 %.

5a-H₄. The ligand was prepared applying the general procedure for removal of benzyl protecting groups (see ***4a-H₄***) starting form **5aIV** (100 mg, 0.12 mmol) to afford the title compound (51 mg, 0.11 mmol, 92 %) as a white solid. ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 7.23 (dd, *J* = 8.1, 1.6 Hz, 2H, $2H_{arom.}$), 7.02 (dd, *J* = 7.8, 1.6 Hz, 2H, $2H_{arom.}$), 6.74 (t, *J* = 7.9 Hz, 2H, $2H_{arom.}$), 4.46–4.33 (m, 4H, 2CH2), 3.71–3.61 (m, 4H, $2CH_2$), 3.44 (s, 4H, $2CH_2$), 1.53 (s, 4H, $2CH_2$) ppm. ^{13}C-NMR (151 MHz, [D_6]DMSO): δ = 169.8 (CO_2CH_2), 150.0 ($C_{arom.}$), 146.5 ($C_{arom.}$), 121.2 ($C_{arom.}$), 112.0 ($C_{arom.}$), 119.4 ($C_{arom.}$), 113.4 ($C_{arom.}$), 70.5 (CH_2), 68.1 (CH_2), 64.9 (CH_2), 26.2 ppm (CH_2) ppm. ESI-MS (negative ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{22}H_{25}O_{10}^-$ [M – H^+]: 449.1453, found 449.1446. Elemental analysis: Calculated for $C_{22}H_{26}O_{10}$•H_2O: C: 56.41 %, H: 6.02 %; found C: 56.56 %, H: 5.70 %.

5bII. The product was prepared applying the general procedure for the preparation of THP protected diols (see ***5aII***) starting form ((4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)dimethanol (200 mg, 1.23 mmol) to afford the title compound (462 mg, 1.10 mmol, 90 %) as a white solid. ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 4.58 (t, *J* = 3.6 Hz, 2H, 2CH), 3.91–3.86 (m, 2H, 2C*H*H), 3.78–3.67 (m, 4H, 2CH), 3.61–3.51 (m, 8H, 4CH), 3.51–3.45 (m, 2H, 2CH*H*), 3.44–3.39 (m, 2H, 2C*H*H), 1.75–1.66 (m, 2H, 2CH*H*), 1.64–1.56 (m, 2H, 2CH*H*), 1.55–1.38 (m, 6H, $3CH_2$), 1.30 (s, 6H, 2CH3) ppm. ^{13}C-NMR (151 MHz, [D_6]DMSO): δ = 108.6 (*C*CH_3), 98.0 (CH), 76.9 (CH_2), 71.0 (CH_2), 70.2 (CH_2), 66.0 (CH_2), 61.2 (CH_2), 30.2 (CH_2), 26.9 (CH_2), 25.1 (CH_3), 19.06 (CH_2) ppm. ESI-MS (negative ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{21}H_{38}NaO_8^+$ [M + Na^+]: 441.2459, found 441.2447. Elemental analysis: Calculated for $C_{21}H_{38}O_8$: C: 60.27 %, H: 9.15 %; found C: 59:30 %, H: 9.18 %.

5bIII. The product was prepared applying the general procedure for the preparation of THP protected diols (see ***5aIII***) starting form **5bII** (540 mg, 2.15 mmol) to afford the title compound (462 mg, 1.10 mmol, 90 %) as a white solid. ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 4.60 (t, *J* = 5.4 Hz, 2H 2CH), 3.87 (dd, *J* = 3.4, 2.2 Hz, 2H, CH*H*), 3.57–3.51 (m, 4H, $2CH_2$), 3.51–3.46 (m, 4H, $2CH_2$), 3.46–3.43 (m, 4H, $2CH_2$), 1.30 (s, 6H, $2CH_3$) ppm. ^{13}C-NMR (151 MHz, [D_6]DMSO): δ = 108.6 (*C*CH3), 76.9 (CH), 72.7 (CH_2), 71.2 (CH_2), 60.2 (CH_2), 26.9 (CH_3) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_8H_{18}NaO_4^+$ [M + Na^+]: 273.13086, found 273,13983. Elemental analysis: Calculated for $C_8H_{18}O_4$: C: 52.79 %, H: 8.86 %; found C: 52.58 %, H: 9.44 %.

5bIV. The product was prepared applying the general procedure for diol esterification (see ***4aII***) using **5bIII** (120 mg, 0.67 mmol) as starting material to afford the title compound (676 mg, 0.46 mmol, 68 %) as a yellowish oil. ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 7.48 (d, *J* = 7.4 Hz, 4H, $4H_{arom.}$), 7.44–7.31 (m, 12H, $12H_{arom.}$), 7.29–7.22 (m, 8H, $8H_{arom.}$), 7.17 (td, *J* = 8.0, 1.5 Hz, 2H, $2H_{arom.}$), 5.20 (s, 4H, $2CH_2$), 4.99 (s, 4H, $2CH_2$), 4.47 (dd, *J* = 12.0, 2.2 Hz, 2H, C*H*H), 4.37–4.23 (m, 2H, CH*H*), 4.21–4.12 (m, 2H, CH), 1.31–1.26 (m, 6H, CH_3) ppm. ^{13}C-NMR (151 MHz, [D_6]DMSO): δ = 165.7 (CO_2CH_2), 152.7 ($C_{arom.}$), 147.4 ($C_{arom.}$), 137.7 ($C_{arom.}$), 137.0 ($C_{arom.}$), 128.9 ($C_{arom.}$), 128.7 ($C_{arom.}$), 128.5 ($C_{arom.}$), 128.3 ($C_{arom.}$), 128.3 ($C_{arom.}$), 126.6 ($C_{arom.}$), 124.8 ($C_{arom.}$), 122.1 ($C_{arom.}$), 118.2 ($C_{arom.}$), 109.9 (*C*CH_3), 75.6 (CH_2), 75.2 (CH_2), 70.7 (CH_2), 64.7 (CH_2), 27.3 (CH_3) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{53}H_{54}NaO_{12}^+$ [M + Na^+]: 905.3508, found 905.3508. Elemental analysis: Calculated for $C_{53}H_{54}O_{12}$: C: 72.09 %, H: 6.16 %; found C: 71.41 %, H: 6.54 %.

5b-H₄. The ligand was prepared applying the general procedure for removal of benzyl protecting groups (see ***4a-H₄***) starting form **5bIV** (100 mg, 0.12 mmol) to afford the title compound (142 mg, 0.27 mmol, 75 % as colorless oil. ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 7.22 (dd, *J* = 7.9, 1.6 Hz, 2H, $2H_{arom.}$), 7.00 (dd, *J* = 7.9, 1.6 Hz, 2H, $2H_{arom.}$), 6.72 (t, *J* = 7.9 Hz, 2H, $2H_{arom.}$), 4.49–4.30 (m, 4H, $2CH_2$), 3.88 (p, *J* = 1.8 Hz, 2H, 2CH), 3.75–3.70 (m, 4H), 3.62–3.52 (m, 4H, $2CH_2$), 1.25 (s, 6H, $2CH_3$) ppm. ^{13}C-NMR (151 MHz, [D_6]DMSO): δ = 169.4 (CO_2CH_2), 149.6 ($C_{arom.}$), 146.1 ($C_{arom.}$), 120.8 ($C_{arom.}$), 119.6 ($C_{arom.}$), 118.9 ($C_{arom.}$), 113.0 ($C_{arom.}$), 108.7 (*C*CH_3), 76.7 (CH), 70.9 (CH_2), 68.5 (CH_2), 64.3 (CH_2), 26.8 (CH_3) ppm. ESI-MS (negative ESI-MS, MeOH, acidified): *m/z:* Calculated for $C_{25}H_{30}NaO_{12}$ [M + Na^+]: 545.1630, found 545.1622. Elemental analysis: Calculated for $C_{25}H_{30}O_{10}$: C: 57.47 %, H: 5.79 %; found C: 56.89 %, H: 5.92 %.

General Procedure for the Preparation of complexes Li[Li₃(1,2)₆Ti₂] The respective catechol ligand (3 equiv.) was mixed with $TiO(acac)_2$ (1 equiv.) and Li_2CO_3 (1 equiv.) and dissolved in methanol. The pure complexes were obtained after stirring this solution for one day followed by removal of the solvent. No further purification is necessary due to quantitative complexation.

Li[Li₃(1a)₆Ti₂]. The complex was prepared according to the general procedure for the preparation of complexes the corresponding ligand **1a**-H_2 (50 mg, 0.24 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (400 MHz, [D_6]DMSO): Dimer (minor component): δ = 6.97 (dd, *J* = 8.0, 1.6 Hz, 1H, $H_{arom.}$), 6.52 (t, *J* = 8.0 Hz, 1H, $H_{arom.}$), 6.43 (dd, *J* = 7.6, 1.6 Hz, 1H, $H_{arom.}$), 4.19 (t, *J* = 4.8 Hz, 1H, OC*H*H), 3.57 (dd, *J* = 5.7, 3.9 Hz, 4H, $2CH_2$), 3.27 (s, 3H, CH_3) 3.02 (ddd, *J* = 12.1, 5.3, 3.1 Hz, 1H, OCH*H*) ppm. Monomer (major component): δ = 6.78 (dd, *J* = 7.8, 1.6 Hz, 2H, Harom.), 6.27 (t, *J* = 7.8 Hz, 2H, $H_{arom.}$), 6.13 (dd, *J* = 7.8, 1.6 Hz, 1H, $H_{arom.}$), 3.74–3.62 (m, 2H, CH_2), 3.23 (ddd, *J* = 11.4, 5.2, 3.1 Hz, 2H, CH_2), 3.16 (s, 3H, CH_3) ppm. ESI-MS (negative/positive ESI-MS, MeOH): *m/z*: Calculated for $C_{60}H_{60}O_{30}Li_3Ti_2^-$ [M_D – Li^+]: 1377.2609, found 1377.2601. Calculated for $C_{60}H_{60}O_{30}Li_5Ti_2^+$ [M_D + Li^+]: 1391.2929, found 1391.2959. IR (KBr): $\tilde{\nu}$ = (cm^{-1}) = 3747, 3626, 3067, 2929, 2662, 2448, 2322, 2162, 2062, 1990, 1924, 1675, 1594, 1560, 1443, 1373, 1296, 1251, 1213, 1156, 1125, 1065, 1034, 970, 895, 858, 801, 744, 681. Elemental analysis: Calculated for $C_{60}H_{60}O_{30}Li_4Ti_2$•$5H_2O$: C: 48.87 %, H: 4.78 %; found C: 48.91 %, H: 4.65 %.

Li[Li₃(1b)₆Ti₂]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **1b**-H_2 (50 mg, 0.22 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): Dimer (minor component): δ = 6.96 (dd, *J* = 8.1, 1.5 Hz, 1H, H_{arom}), 6.50 (t, *J* = 8.1 Hz, 1H, $H_{arom.}$), 6.42 (dd, *J* = 8.1, 1.5 Hz, 1H, $H_{arom.}$), 3.01–2.97 (m, 1H, OCH_2) ppm. Monomer (major component): δ = 6.77 (dd, *J* = 8.1, 1.5 Hz, 1H, $H_{arom.}$), 6.26 (t, *J* = 8.1 Hz, 1H, $H_{arom.}$), 6.12 (dd, *J* = 8.1, 1.5 Hz, 1H, $H_{arom.}$), 4.17 (t, *J* = 6.9 Hz, 2H, OCH_2) ppm. Signals not listed are overlapping and cannot be assigned. ESI-MS (negative/positive ESI-MS, MeOH): *m/z*: Calculated for $C_{66}H_{72}O_{30}Li_3Ti_2^-$ [M_D – Li^+]: 1461.3547, found 1461.3525. Calculated for $C_{66}H_{72}O_{30}Li_5Ti_2^+$ [M_D + Li^+]: 1475.3868, found 1475.3873. IR (KBr): $\tilde{\nu}$ = (cm^{-1}) = 3747, 3626, 3067, 2929, 2662, 2448, 2322, 2162, 2062, 1990, 1924, 1675, 1594, 1560, 1443, 1373, 1296, 1251, 1213, 1156, 1125, 1065, 1034, 970, 895, 858, 801, 744, 681. Elemental analysis: Calculated for $C_{60}H_{60}O_{30}Li_4Ti_2$•$5H_2O$: C: 48.87 %, H: 4.78 %; found C: 48.91 %, H: 4.65 %.

Li[Li₃(1c)₆Ti₂]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding

ligand **1c**-H_2 (50 mg, 0.21 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): Dimer (major component): δ = 6.97 (dd, *J* = 8.2, 1.6 Hz, 1H, $H_{arom.}$), 6.26 (t, *J* = 8.2 Hz, 1H, $H_{arom.}$), 6.13 (dd, *J* = 8.2, 1.6 Hz, 1H, $H_{arom.}$), 3.03–2.96 (m, 1H, OCH_2) ppm. Monomer (minor component): δ = 6.77 (dd, *J* = 8.2, 1.6 Hz, 1H, $H_{arom.}$), 6.42 (t, *J* = 8.2 Hz, 1H, $H_{arom.}$), 6.09 (dd, *J* = 8.1, 1.6 Hz, 1H, $H_{arom.}$), 4.17 (t, *J* = 6.5 Hz, 2H, OCH_2) ppm. Signals not listed are overlapped and cannot be assigned. ESI-MS (negative ESI-MS, MeOH): *m/z*: Calculated for $C_{72}H_{84}O_{30}Li_3Ti_2^-$ [M_D – Li^+]: 1545.4486, found 1545.4436. IR (KBr): $\tilde{\nu}$ = (cm^{-1}) = 3438, 3069, 2962, 2930, 2868, 2683, 2448, 2265, 2162, 2104, 2028, 1990, 1910, 1677, 1594, 1558, 1443, 1385, 1352, 1295, 1252, 1215, 1155, 1063, 1014, 963, 891, 856, 806, 742, 683. Elemental analysis: Calculated for $C_{72}H_{84}O_{30}Li_4Ti_2$·$3H_2O$: C: 53.81 %, H: 5.65 %; found C: 53.71 %, H: 5.41 %.

Li[Li$_3$(2a)$_6$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes ***1,2-H$_2$*** with the corresponding ligand **2a**-H_2 (50 mg, 0.22 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (400 MHz, [D_6]DMSO): Dimer (minor component): δ = 6.95 (dd, *J* = 8.2, 1.6 Hz, 1H, $H_{arom.}$), 6.50 (t, *J* = 8.2 Hz, 1H, $H_{arom.}$), 6.42 (dd, *J* = 8.2, 1.6 Hz, 1H, $H_{arom.}$), 3.65–3.60 (m, 1H, OCH_2), 3.12–3.08 (m, 1H, OCH_2), 2.45 (t, *J* = 6.8 Hz, 2H, CH_2), 1.90 (s, 3H, CH_3) ppm. Monomer (major component): δ = 6.75 (dd, *J* = 8.2, 1.6 Hz, 1H, $H_{arom.}$), 6.23 (t, *J* = 8.2 Hz, 1H, $H_{arom.}$), 6.08 (dd, *J* = 8.2, 1.6 Hz, 1H, $H_{arom.}$), 4.19 (t, *J* = 6.8 Hz, 2H, OCH_2), 2.68 (t, *J* = 6.8 Hz, 2H, CH_2), 2.08 (s, 3H, CH_3) ppm. ESI-MS (negative ESI-MS, MeOH): *m/z*: Calculated for $C_{60}H_{60}O_{24}S_6Li_3Ti_2^-$ ([M_D – Li^+]): 1377.2609, found 1473.1200. Calculated for $C_{30}H_{30}O_{12}S_3LiTi^-$ [M_M – Li^+]: 733.0539, found 733.0513. IR (KBr): $\tilde{\nu}$ = (cm^{-1}) = 3363, 3062, 2968, 2915, 2654, 2504, 2290, 2117, 2071, 2025, 1980, 1932, 1745, 1673, 1592, 1552, 1442, 1381, 1297, 1249, 1207, 1147, 1065, 1000, 856, 805, 743, 680. Elemental analysis: Calculated for $C_{60}H_{60}O_{24}S_6Li_4Ti_2$·$2H_2O$: C: 46.40 %, H: 4.41 %; found C: 46.41 %, H: 4.53 %.

Li[Li$_3$(2b)$_6$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **2b**-H_2 (50 mg, 0.21 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): Dimer (major component): δ = 6.94 (dd, *J* = 8.1, 1.5 Hz, 1H, $H_{arom.}$), 6.49 (t, *J* = 8.1 Hz, 1H, $H_{arom.}$), 6.40 (dd, *J* = 8.1, 1.5 Hz, 1H, $H_{arom.}$), 3.58–3.52 (m, 1H, OCH2), 3.07–3.04 (m, 1H, OCH_2), 2.42 (t, *J* = 6.8 Hz, 2H, CH_2), 2.33 (q, *J* = 7.4 Hz, 2H, CH_2), 0.96 (t, *J* = 7.4 Hz, 3H, CH_3) ppm. Monomer (minor component): δ = 6.75 (dd, *J* = 8.1, 1.5 Hz, 1H, $H_{arom.}$), 6.23 (t, *J* = 8.1 Hz, 1H, $H_{arom.}$), 6.10 (dd, *J* = 8.1, 1.5 Hz, 1H, $H_{arom.}$), 4.19 (t, *J* = 6.8 Hz, 2H, OCH_2), 2.73 (t, *J* = 6.8 Hz, 2H, CH_2), 2.55 (q, *J* = 7.4 Hz, 2H, CH_2), 1.13 (t, *J* = 7.4 Hz, 3H, CH_3) ppm. ESI-MS (negative/positive ESI-MS, MeOH): *m/z*: Calculated for $C_{66}H_{72}O_{24}S_6Li_3Ti_2^-$ [M_D – Li^+]: 1557.2176, found 1557.2288, calculated for $C_{33}H_{36}O_{12}S_3LiTi^-$ [M_D – Li^+]: 775.1008, found 775.1058. Calculated for $C_{66}H_{72}O_{24}S_6Li_5Ti_2^+$, [$M_D$ + Li^+]: 1571.2496, found 1571.2510. IR (KBr): $\tilde{\nu}$ = (cm^{-1}) = 3357, 3066, 2964, 2924, 2661, 2503, 2288, 2165, 2047, 2015, 1946, 1908, 1673, 1593, 1560, 1441, 1381, 1344, 1294, 1250, 1210, 1152, 1063, 997, 855, 807, 742, 679. Elemental analysis: Calculated for $C_{66}H_{72}O_{24}S_6Li_4Ti_2$·$H_2O$: C: 49.51 %, H: 4.78 %; found C: 49.51 %, H: 4.77 %.

Li[Li$_3$(2c)$_6$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **2c**-H_2 (50 mg, 0.20 mmol) and obtained as red solid (quantitative). **^{1}H-NMR** (600 MHz, [D_6]DMSO): Dimer (major component): δ = 6.94 (dd, *J* = 8.1, 1.6 Hz, 1H, $H_{arom.}$), 6.49 (t, *J* = 8.1 Hz, 1H, $H_{arom.}$), 6.39 (dd, *J* = 8.1, 1.6 Hz, 1H, $H_{arom.}$), 3.58–3.54 (m, 1H, OCH_2), 3.13–3.09 (m, 1H, OCH_2), 2.51 (t, *J* = 6.9 Hz, 2H, CH_2), 2.29 (t, *J* = 6.8 Hz, 2H, CH_2), 1.32 (m, 2H, CH_2), 0.76 (t, *J* = 7.3 Hz, 3H, CH_3) ppm. Monomer (minor component): δ = 6.75 (dd, *J* = 8.1, 1.6 Hz, 1H, $H_{arom.}$), 6.23 (t, *J* = 8.1 Hz, 1H, $H_{arom.}$), 6.09 (dd, *J* = 8.1, 1.6 Hz, 1H, $H_{arom.}$), 4.16 (t, *J* = 6.9 Hz, 2H, OCH_2), 2.71 (t, *J* = 6.9 Hz, 2H, CH_2), 2.39 (t, *J* = 6.8 Hz, 2H, CH_2), 1.50 (m, 2H, CH_2), 0.88 (t, *J* = 7.3 Hz, 3H, CH_3) ppm. **ESI-MS** (negative/positive ESI-MS, MeOH): *m/z*: Calculated for $C_{72}H_{84}O_{24}S_6Li_3Ti_2^-$ [M_D – Li^+]: 1641.3116, found 1641.3160; calculated for $C_{72}H_{84}O_{24}S_6Li_5Ti_2^-$ [M_D + Li^+]: 1655.3436, found 1655.3464; calculated for $C_{36}H_{42}O_{12}S_3Li_5Ti^+$ [M_M + Li^+]: 831.1798, found 831.1790. **IR** (KBr): $\tilde{\nu}$ = (cm^{-1}) = 3446, 3067, 2960, 2925, 2871, 2686, 2506, 2318, 2189, 2159, 2023, 1977, 1895, 1677, 1594, 1559, 1444, 1382, 1344, 1297, 1253, 1215, 1155, 1063, 999, 945, 893, 859, 811, 744, 683. **Elemental analysis:** Calculated for $C_{72}H_{84}O_{24}S_6Li_4Ti_2$·$9/2H_2O$: C: 47.74 %, H: 5.68 %; found C: 47.99 %, H: 5.51 %.

General Procedure for the Preparation of complexes Li[Li$_3$(4)$_3$Ti$_2$] and M$_4$[(5)$_3$Ti$_2$], (M= Li, Na, K). The respective catechol ligand (3 equiv.) was dissolved in a mixture of dichloromethane (1 mL/mg) and MeOH (0.15 mL/mg). After adding titanium(IV) oxybisacetylacetonate (2.0 equiv.) the reaction mixture was stirred for 15 min. Subsequently the carbonate of the required alkali metal (3.0 equiv.) was added and the reaction mixture stirred for 24 h. Upon completion the solvent was evaporated at 25 °C at 1 atm.

Li[Li$_3$(4a)$_3$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4a**-H_2 (50 mg, 0.12 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 6.95 (dd, *J* = 7.9, 1.6 Hz, 6H, $H_{arom.}$), 6.47 (t, *J* = 7.9 Hz, 6H, $6H_{arom.}$), 6.39 (d, *J* = 7.9, 6H, $H_{arom.}$), 4.28 (t, *J* = 11.7 Hz, 6H, CH_2), 3.49–3.38 (m, 6H, $3CH_2$), 3.20 (ddd, *J* = 14.3, 9.8, 3.6 Hz, H, CH_2), 3.02 (td, *J* = 12.2, 11.0, 7.7 Hz, 12H, CH_2) ppm. ESI-MS (negative/positive ESI-MS, MeOH): *m/z:* Calculated for $C_{60}H_{54}Li_5O_{30}Ti_2^-$ ([M – Li^+]): 1371.2144, found 1371.2078. Calculated for $C_{60}H_{54}Li_5O_{30}Ti_2^+$ ([M + Li^+]): 1385.2454, found 1385.2489.

Li[Li$_3$(4b)$_3$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4b**-H_2 (50 mg, 0.09 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 6.97 (dd, *J* = 8.2, 1.7 Hz, 6H, H_{arom}), 6.50 (t, *J* = 7.9 Hz, 7H, H_{arom}), 6.41 (dd, *J* = 7.6, 1.7 Hz, 6H, H_{arom}), 3.97 (ddd, *J* = 11.9, 8.4, 3.1 Hz, 6H, CH_2), 3.46 (ddd, *J* = 11.6, 8.6, 3.2 Hz, 6H, CH_2), 3.32–3.30 (m, 12H,), 3.27 (dd, *J* = 6.4, 3.4 Hz, 12H, CH_2), 2.97 (dt, *J* = 12.2, 3.7 Hz, 6H, CH_2) ppm. ESI-MS (negative/positive ESI-MS, MeOH): *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.

Li[Li$_3$(4c)$_3$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4c**-H_2 (50 mg, 0.09 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 7.05 (dd, *J* = 8.2, 1.6 Hz, 1H, $H_{arom.}$), 6.98 (dd, *J* = 8.2, 1.6 Hz, 1H, $H_{arom.}$), 6.52 (td, *J* = 7.9, 1.6 Hz, 2H, $H_{arom.}$), 6.43 (ddd, *J* = 8.2, 6.2, 1.6 Hz, 2H, $H_{arom.}$), 3.82 (ddd, *J* = 11.7, 8.1, 3.2 Hz, 1H, CH_2), 2.98 (ddd, *J* = 12.2, 6.7, 2.9 Hz, 2H, CH_2) ppm. Signals not listed are overlapping and cannot be assigned. ESI-MS (negative/positive ESI-MS, MeOH): *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.

Li[Li$_3$(4d)$_3$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4d**-H_2 (50 mg, 0.08 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 7.01 (dd, *J* = 8.2, 1.6 Hz, 1H, $H_{arom.}$), 6.97 (dd, *J* = 8.2, 1.6 Hz, 1H, $H_{arom.}$), 6.51 (dt, *J* = 15.6,

7.9 Hz, 2H, $H_{arom.}$), 6.41 (ddd, *J* = 7.6, 4.7, 1.6 Hz, 3H, $H_{arom.}$), 3.69 (ddd, *J* = 11.4, 7.8, 3.2 Hz, 2H, CH_2), 3.01 (ddd, *J* = 11.2, 8.9, 5.2 Hz, 3H, CH_2) ppm. Signals not listed are overlapping and cannot be assigned. ESI-MS (negative/positive ESI-MS, MeOH): *m/z:* Calculated for $C_{78}H_{90}Li_3O_{39}Ti_2^-$ ([M – Li^+]): 1767.4504, found 1767.4446. Calculated for $C_{78}H_{90}Li_5O_{39}Ti_2^+$ [M + Li^+]: 1781.4813, found 1781.4829.

Li[Li$_3$(5a)$_3$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4d**-H_2 (50 mg, 0.11 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 6.99 (dd, *J* = 8.2, 1.6 Hz, 6H, $H_{arom.}$), 6.52 (t, *J* = 7.8 Hz, 6H, $H_{arom.}$), 6.43 (dd, *J* = 7.5, 1.6 Hz, 6H, $H_{arom.}$), 4.06 (ddd, *J* = 12.2, 9.5, 2.4 Hz, 6H, CH_2), 3.42 (ddd, *J* = 12.1, 9.3, 2.2 Hz, 6H, CH_2), 3.25–3.21 (m, 6H, CH_2), 3.20–3.08 (m, 12H, CH_2), 2.90 (dt, *J* = 12.4, 2.9 Hz, 6H, CH_2), 1.20 (q, *J* = 4.4, 3.6 Hz, 12H, CH_2) Signals not listed are overlapping and cannot be assigned. ESI-MS (negative/positive ESI-MS, MeOH): *m/z:* Calculated for $C_{66}H_{66}Li_5O_{30}Ti_2^-$ ([M – Li^+]): 1455.3083, found 1455.3254. Calculated for $C_{66}H_{66}Li_5O_{30}Ti_2^+$ [M + Li^+]: 1469.3393, found 1469.3456.

Na$_4$[(5a)$_3$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4d**-H_2 (50 mg, 0.11 mmol) and obtained as orange solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 6.87 (dd, *J* = 8.2, 1.6 Hz, 1H, $H_{arom.}$), 6.72 (d, *J* = 7.8 Hz, 1H, $H_{arom.}$), 6.35 (t, *J* = 7.4 Hz, 1H, $H_{arom.}$), 6.27–6.21 (m, 1H, $H_{arom.}$), 6.15 (t, *J* = 7.8 Hz, 1H, $H_{arom.}$), 5.99 (d, *J* = 7.3 Hz, 1H, $H_{arom.}$). Signals not listed are overlapping and cannot be assigned. ESI-MS (negative/positive ESI-MS, MeOH): *m/z:* Calculated for $C_{66}H_{66}Li_5O_{30}Ti_2^-$ ([M – Li^+]): 1455.3083, found 1455.3254. Calculated for $C_{66}H_{66}Na_3O_{30}Ti_2^-$ [M – Na^+]: 1503.2296, found 1503.2562. Calculated for $C_{66}H_{66}Na_5O_{30}Ti_2^+$ [M + Na^+]: 1549.2081, found 1549.2105.

K$_4$[(5a)$_3$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4d**-H_2 (50 mg, 0.11 mmol) and obtained as orange solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 7.04–6.81 (m, 1H), 6.34 (dt, *J* = 17.0, 7.7 Hz, 1H, $H_{arom.}$), 6.22 (ddd, *J* = 24.5, 7.5, 1.6 Hz, 1H, $H_{arom.}$). Signals not listed are overlapping and cannot be assigned. ESI-MS (negative/positive ESI-MS, MeOH): *m/z:* Calculated for $C_{66}H_{66}Li_5O_{30}Ti_2^-$ ([M – Li^+]): 1455.3083, found 1455.3254. Calculated for $C_{66}H_{66}K_3O_{30}Ti_2^-$ ([M – K^+]): 1552.1543, found 1552.1572 Calculated for $C_{66}H_{66}K_5O_{30}Ti_2^+$ [M + K^+]: 1629.0778, found 1629.0768.

Li[Li$_3$(5b)$_3$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4d**-H_2 (50 mg, 0.10 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 6.99 (ddd, *J* = 9.9, 8.2, 1.6 Hz, 6H, $H_{arom.}$), 6.51 (dt, *J* = 11.0, 7.9 Hz, 6H, $H_{arom.}$), 6.47–6.39 (m, 6H, $H_{arom.}$), 4.14 (dt, *J* = 50.9, 10.9 Hz, 6H,), 3.97–3.79 (m, 6H, CH_2), 3.63–3.44 (m, 12H, CH_2), 3.28 (dq, *J* = 9.8, 4.2, 3.4 Hz, 9H, CH_2), 3.24–3.19 (m, 6H, CH_2), 2.99–2.87 (m, 6H), 1.34 (s, 6H, CH_2), 1.19–1.16 (s, 18H, CH_2) ppm. ESI-MS (negative/positive ESI-MS, MeOH): *m/z:* Calculated for $C_{75}H_{78}Li_3O_{36}Ti_2-$ ([M – Li^+]): 1671.3717, found 1671.3817. Calculated for $C_{75}H_{78}Li_5O_{36}Ti_2^+$ [M + Li^+]: 1685.4026, found 1685.4087.

Na$_4$[(5b)$_3$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4d**-H_2 (50 mg, 0.10 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 6.91–6.80 (m, 1H, $H_{arom.}$), 6.74 (dd, *J* = 10.1, 8.4 Hz, 2H, $H_{arom.}$), 6.35 (dt, *J* = 14.9, 7.8 Hz, 1H, $H_{arom.}$), 6.26 (dd, *J* = 7.5, 1.6 Hz, 1H, $H_{arom.}$), 6.16 (td, *J* = 7.8, 1.7 Hz, 2H, $H_{arom.}$), 6.01 (ddd, *J* = 7.4, 3.9, 1.5 Hz, 2H, $H_{arom.}$), 4.71–4.62 (m, 1H, CH_2), 4.58 (ddd, *J* = 11.7, 7.4, 4.5 Hz, 1H, CH_2) ppm. The spectrum indicates more than one species. Signals not listed are overlapping and cannot be assigned. ESI-MS (negative/positive ESI-MS, MeOH): *m/z:* Calculated for $C_{75}H_{78}Na_5O_{36}Ti_2^-$ [M – Na^+]: 1719.2930, found 1713.2768. Calculated for $C_{75}H_{78}Na_5O_{36}Ti_2^+$ [M + Na^+]: 1765.2715, found 1765.2795.

K$_4$[(5b)$_3$Ti$_2$]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4d**-H_2 (50 mg, 0.10 mmol) and obtained as red solid (quantitative). ^{1}H-NMR (600 MHz, [D_6]DMSO): δ = 6.92 (dd, *J* = 30.0, 8.1 Hz, 1H, $H_{arom.}$), 6.34 (dq, *J* = 15.5, 7.8 Hz, 1H), 6.29–6.19 (m, 1H,) ppm. Signals not listed are overlapping and cannot be assigned. ESI-MS (negative/positive ESI-MS, MeOH): *m/z:* Calculated for $C_{75}H_{78}K_3O_{36}Ti_2^-$ ([M – K^+]): 1767.2148, found 1769.9190. Calculated for $C_{75}H_{78}K_5O_{36}Ti_2^+$ [M + K^+]: 1845.1412, found 1845.1429.

X-ray Experimental Details.

Crystal data for K[Li_3(**1a**)$_6$$Ti_2$]: CCDC-1997036, $C_{60}H_{60}KLi_3O_{30}Ti_2$, M = 1416.80, orange plate, 0.17 × 0.09 × 0.02 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 12.0584(6) Å, b = 15.4327(10) Å, c = 17.7343(12) Å, α = 77.698(5)°, β = 79.621(5)°, γ = 85.627(5)°, *V* = 3169.2(3) Å3, Z = 2, D_{calc} = 1.485 g cm^3, *F*(000) = 1464, μ = 0.41 mm 1, *T* = 120.0(1) K, θ_{max} = 25.0°, 21166 total reflections, 4091 with Io > 2σ(Io), R_{int} = 0.093, 11218 data, 1033 parameters, 346 restraints, GooF = 1.00, R = 0.093 and wR= 0.177 [Io > 2σ(Io)], R = 0.254 and wR= 0.259 (all reflections), 0.50 < 0.53 e Å^3.

Crystal data for Li[Li_3(**2a**)$_6$$Ti_2$]: CCDC-1997037, $C_{62}H_{68}Li_4O_{26}S_6Ti_2$, M = 1545.08, orange plate, 0.44 × 0.27 × 0.16 mm^3, monoclinic, space group $P2_1/c$, a = 11.8849(2) Å, b = 25.0264(5) Å, c = 23.0211(3) Å, β = 94.953(1)°, *V* = 6821.7(2) Å3, Z = 4, D_{calc} = 1.504 g cm^3, *F*(000) = 3200, μ = 0.50 mm 1, *T* = 170.0(1) K, θ_{max} = 30.5°, 35660 total reflections, 13846 with Io > 2σ(Io), R_{int} = 0.045, 20750 data, 1067 parameters, 300 restraints, GooF = 1.06, R = 0.073 and wR= 0.165 [Io > 2σ(Io)], R = 0.115 and wR= 0.188 (all reflections), 1.22 < 0.73 e/Å^3.

Crystal data for Na[Li_3(**4c**)$_3$$Ti_2$]·2DMF: CCDC-1997473, $C_{78}H_{92}Li_3N_2NaO_{38}Ti_2$, M = 1805.14, orange block, 0.08 × 0.07 × 0.04 mm^3, monoclinic, space group *Cc*, a = 14.711(3) Å, b = 40.989(8) Å, c = 14.494(3) Å, β = 107.72(3)°, *V* = 8326(3) Å^3, Z = 4, D_{calc} = 1.440 g cm^3, *F*(000) = 3768, μ = 2.50 mm 1, *T* = 100(2) K, θ_{max} = 62.5°, 10828 total reflections, 8504 with Io > 2σ(Io), R_{int} = 0.087, 10828 data, 1132 parameters, 0 restraints, GooF = 1.02, R = 0.071 and wR= 0.185 [Io > 2σ(Io)], R = 0.095 and wR= 0.201 (all reflections), 1.88 < 0.36 e/Å^3, Flack-Parameter x = –0.017(15).

Crystal data for Na_2[(**5b**)$_2$$Ti_2$]: CCDC-1994564, $C_{52}H_{60}Na_2O_{28}Ti_2$·2($C_{24}H_{20}As$)·8MeOH, M = 2041.41, yellow block, 0.14 × 0.14 × 0.10 mm^3, monoclinic, space group C2, a = 37.656(8) Å, b = 13.102(3) Å, c = 28.405(6) Å, β = 124.63(3)°, *V* = 11532(5) Å^3, Z = 4, D_{calc} = 1.176 g cm^3, *F*(000) = 4224, μ = 2.436 mm 1, *T* = 100(2) K, θ_{max} = 58.9°, 39070 total reflections, 14670 with Io > 2σ(Io), R_{int} = 0.0191, 12305 data, 1176 parameters, 262 restraints, GooF = 1.01, R = 0.040 and wR= 0.110 [Io > 2σ(Io)], R = 0.047 and wR= 0.110 (all reflections), 0.26 < 0.34 e/Å^3, Flack-Parameter x = 0.057(8).

CCDC-199703 (for K[Li_3(**1a**)$_6$$Ti_2$) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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