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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 monomerdimer 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,

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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**-H₂ and **2a–c**-H₂ are obtained in moderate to good yields. The corresponding titanium(IV) complexes Li[Li₃(**1/2**)₆Ti₂] are formed in methanol by reaction of the ligands with TiO(acac)₂ and Li₂CO₃ (Scheme 1).



Scheme 1. Preparation of the hierarchically formed helicates Li[Li₃(1/2)₆Ti₂]. Complexes Li[Li₃(3)₆Ti₂] 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 ¹H NMR in $[D_6]DMSO$ the signals of the catechol unit of the dimer

Li[Li₃(**1a**)₆Ti₂] are observed at $\delta = 6.96$, 6.50, and 6.42, and for the dominating monomer Li₂[(**1a**)₃Ti] at $\delta = 6.77$, 6.26, and 6.13. In the dimer the methylene group adjacent to the ester splits into two signals of diastereotopic protons at $\delta = 3.67$ and 3.02 ppm (6H each) while in the monomer one signal at $\delta =$ 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 thio-glycol 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 [D₆]DMSO.

Table 1. Kdim [L/mol] for the dimerization monomer dimer equilibrium of Li[Li₃(**1-3**)₆Ti₂] in [D₆]DMSO at r.t. determined at a concentration of 10^{-2} mol/L.

Li[Li ₃ (1–3) ₆ Ti ₂]	X=O	X=S	X=CH ₂
	$Li[Li_3(1)_6Ti_2]$	$Li[Li_3(2)_6Ti_2]$	$Li[Li_3(3)_6Ti_2]$
$R = CH_3$	170 ± 18	160 ± 17	1195 ^[a]
$R = C_2 H_6$	210 ± 22	275 ± 30	1920 ^[a]
$R = C_3 H_7$	340 ± 38	350 ± 39	1530 ^[a]

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.



the electron pairs, the heteroatoms in the side chains adopt positions which are located far away from each other. The Xray 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**-H₄ 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[Li₃(**4b**)₃Ti₂] and Na₂[Na₂(**5a**)₃Ti₂] were communicated recently and their crystal structures were presented (Figure 3). Both compounds show a compressed structure with the expected geometry for Li[Li₃(**4b**)₃Ti₂] while Na₂[Na₂(**5a**)₃Ti₂] 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[Li₃(4b)₃Ti₂] and [Na₂(5a)₃Ti₂]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 $[Li_3(4b)_3Ti_2]^-$. The anionic helicate can be easily observed by ESI MS ($m/z = 1371.2078 \ [Li_3(4a)_3Ti_2]^-$, 1635.3604 $[Li_3(4c)_3Ti_2]^-$, 1767.4446 $[Li_3(4d)_3Ti_2]^-$) supporting this assignment.

However, ¹H NMR spectroscopy reveals some surprises. For Li[Li₃(**4a**)₃Ti₂] and Li[Li₃(**4b**)₃Ti₂] 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[Li₃(**4c**)₃Ti₂] and Li[Li₃(**4d**)₃Ti₂] two sets of signals are observed for the catechol units (Figure 4).



Figure 4. 1H NMR signals of the catechol protons of the compressed helicates Li[Li_3(**4a-d**)_3Ti_2] (in [D_6]DMSO).

The ESI MS results as well as the NMR spectra indicate that in case of Li[Li₃(**4c**,**d**)₃Ti₂] 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[Li₃(**4b**)₃Ti₂] 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 [Li₃(**4d**)₃Ti₂]⁻.

It was possible to obtain crystals of Na[Li₃(**4c**)₃Ti₂] 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.





Figure 5. Cartoon of the type I and type II isomers of [Li₃(**4d**)₃Ti₂]⁻.



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

Ligand **5b**-H₄^[16] represents a chiral version of **5a**-H₄. The coordination compounds $M_4[(5b)_3Ti_2]$ (M = Li, Na, K) can be obtained from this ligand.

The potassium salts $K_4[(\mathbf{5a}, \mathbf{b})_3 Ti_2]$ show two major isomers which cannot be structurally assigned.

In the case of the lithium complex Li[Li₃(**5b**)₃Ti₂] similar shifts as found for Li[Li₃(**5a**)₃Ti₂] 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[Li₃(**5b**)₃Ti₂] by the remote chiral units of the spacer resulting in two different diastereoisomers (SSAA and SS $\Delta\Delta$).

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



Figure 7. ¹H NMR signals ([D₆]DMSO) of the catechol protons of the helicates $M_4[({\bf 5a,b})_3Ti_2]$ (M = Li, Na, K).

CD spectra were measured for the chiral complexes $M_4[(5b)_3Ti_2]$ (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 $[AsPh_4]_2$ - $[Na_2($ **5b** $)_2Ti_2O_2]$ -2MeOH has been obtained. A central bis- μ -oxo bis titanium(IV) moiety is formed. The two titanium centers are



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 $[Na_2(\textbf{5b})_2Ti_2O_2]^{2-}\mbox{-}2MeOH$ 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 Na₄[(**5b**)₃Ti₂] formed from three equivalents of ligand with two equivalents of titanium(IV) ions it is expected that $[Na_2(5b)_2Ti_2O_2]^{2-}$ 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 $M_4[(4/5)_3Ti_2]$, switching in a spring-type fashion is feasible depending on the cations. The corresponding switching of $M_4[(5a)_3Ti_2]$ 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 $Li[Li_3(4a-d)_3Ti_2]$ (Figure 10) or $Li[Li_3(5a,b)_3Ti_2]$



Figure 10. Reversible switching of the compressed complexes Li[Li₃(**4ad**)₃Ti₂]. 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 $Li[Li_3(5a,b)_3Ti_2]$. 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[Li₃(**4c,d**)₃Ti₂] which are assigned to Type I and Type II isomers with different positions of the connecting units.

– In the chiral derivative Li[Li₃(**5b**)₃Ti₂] stereoinduction by the remote chiral unit is not complete. However, with sodium cations the "topological" helicate isomer Na₂[Na₂(**5b**)₃Ti₂] is observed as it also was found for the corresponding achiral Na₂[Na₂(**5a**)₃Ti₂].^[14]

– The new structural motif of a double-stranded dinuclear complex $[Na_2(\textbf{5b})_2\text{Ti}_2\text{O}_2]^{2-}\textbf{\cdot}2\text{MeOH}$ 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 $M_4[(4a-d)_3Ti_2]$ 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 μ m) 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 (CDCl₃, [D₆]DMSO). Measurements were performed at 25 °C. ¹H 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. ¹³C NMR spectra were recorded on a Varian Inova 400 MHz or Varian Inova 600 MHz spectrometer operating at 150 MHz using ¹³C 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 $K[Li_3(\textbf{1a})_6Ti_2], \ Li[Li_3(\textbf{2a})_6Ti_2], \ Na[Li_3(\textbf{4c})_3Ti_2], \ Na_2[(\textbf{5b})_2Ti_2] \ are \ given$ below. Single-crystal X-ray data for K[Li₃(1a)₆Ti₂] 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[Li₃(2a)₆Ti₂] was measured using a Bruker-Nonius KappaCCD diffractometer with an APEX-II detector with graphitemonochromatized Mo- K_{α} ($\lambda = 0.71073$ 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 leastsquares on F² using the OLEX2 software,^[25] which utilises the SHELXL2015 module.^[24] Single crystal X-ray diffraction data for $Na[Li_3(4c)_3Ti_2]$ and $Na_2[(5b)_2Ti_2]$ were collected at 100(2) K by using ω-scans on a Stoe Stadivari Eulerian geometry four-circle diffractometer, equipped with a Cu- K_{ci} micro-focused source (GeniX 3D HF Cu, $\lambda = 1.54178$ 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 F². Na[Li₃(**4c**)₃Ti₂] 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 Na₂[(**5b**)₂Ti₂] 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-H₂. Ligands **1a-c**-H₂ and **2a-c**-H₂ 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-H2. 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). ¹H-NMR (600 MHz, CDCl₃): 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, $1H_{arom}$), 6.81 (t, J =8.0 Hz, 1H, H_{arom}), 5.65 (s, 1H, OH), 4.50 (t, J = 5.3 Hz, 2H, CH₂), 3.73 (t, J = 5.3 Hz, 2H, CH₂), 3.42 (s, 3H, CH₃) ppm. ¹³C-NMR (151 MHz, $CDCI_3$: δ = 170.19 (CO_2CH_2), 148.83 ($C_{arom.}$), 144.98 ($C_{arom.}$), 120.78 (Carom.), 119.87 (Carom.), 119.20 (Carom.), 112.35 (Carom.), 70.21 (CH₂), 64.46 (CH₂), 59.14 (CH₃) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): m/z: Calculated for C₁₀H₁₂NaO₅⁺ [M + Na⁺]: 235.0582, found 235.0600. IR (KBr): $\tilde{v} = (cm^{-1}) = 3346$, 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 C10H12O5•1/20DCM: 55.77 %, H: 5.63 %; found C: 55.53 %, H: 5.54 %.

1b-H2. 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). ¹H-NMR (600 MHz, CDCl₃): 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, CH₂), 3.77 (t, J = 6.5 Hz, 2H, CH₂), 3.58 (q, J = 7.0 Hz, 2H, CH₂), 1.23 (t, J = 7.0 Hz, 3H, CH₃) ppm. ¹³C-NMR (151 MHz, CDCl₃: 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 (CH₂), 66.80 (CH₂), 64.69 (CH₂), 15.13 (CH₃) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z*: Calculated for C₁₁H₁₄NaO₅⁺ [M + Na⁺]: 249.0739, found 249.0761. IR (KBr): $\tilde{v} = (cm^{-1}) = 3633, 3449, 3203, 2976, 1873, 2466,$ 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 C₁₁H₁₄O₅•1/2H₂O: H: 6.43 %; found C: 56.18 %, H: 6.30 %.

1c-H₂. 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, $R_{\rm f}$ = 0.13) as colorless oil (47 %, 146 mg, 0.61 mmol).



¹H-NMR (600 MHz, CDCl₃): 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, CH₂), 3.77 (t, *J* = 6.8 Hz, 2H, CH₂), 3.51 (t, *J* = 6.9 Hz, 2H, CH₂), 1.63–1.60 (m, 2H, CH₂), 0.92 (t, *J* = 7.0 Hz, 3H, CH₃) ppm. ¹³C-NMR (151 MHz, CDCl₃: δ = 170.18 (CO₂CH₂), 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 (CH₂), 68.22 (CH₂), 64.66 (CH₂), 22.79 (CH₂), 10.47 (CH₃) ppm. ESI-MS (negative ESI-MS, MeOH, acidified): *m/z*: Calculated for C₁₂H₁₅O₅⁻ [M – H⁺]: 239.0928, found 239.0921. IR (KBr): \tilde{v} = (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 C₁₂H₁₆O₅•1/2DCM: 53.10 %, H: 6.06 %; found C: 53.53 %, H: 6.20 %.

2a-H₂. 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). ¹H-NMR (600 MHz, CDCl₃): 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, CH₂), 2.87 (t, J = 6.8 Hz, 2H, CH₂), 2.22 (s, 3H, CH₃) ppm. ¹³C-NMR (151 MHz, $CDCI_3$: 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 (CH₂), 32.44 (CH₂), 15.94 (CH₃) ppm. ESI-MS (negative ESI-MS, MeOH, acidified): m/z: Calculated for C₁₀H₁₁O₄S⁻ [M – H⁺]: 227.0386, found 227.0360. IR (KBr): $\tilde{v} = (cm^{-1}) = 3455$, 3138, 2964, 2920, 2835, 2735, 2325, 2086, 1915, 1669, 1465, 1384, 1302, 1265, 1146, 1067, 987, 843, 750, 704. Elemental analysis: for C₁₀H₁₂O₄S•1/3H₂O: 51.40 %, H: 5.44 %; found C: 51.60 %, H: 5.35 %.

2b-H₂. 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). ¹H-NMR (600 MHz, CDCl₃): 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, CH₂), 2.90 $(t, J = 6.9 \text{ Hz}, 2H, CH_2), 2.65 (q, J = 7.8 \text{ Hz}, 2H, CH_2), 1.29 (t, J =$ 7.8 Hz, 3H, CH₃) ppm. ¹³C-NMR 170.05 (CO₂CH₂), 148.91 (C_{arom.}), 145.03 (C_{arom.}), 120.60 (C_{arom.}), 119.93 (C_{arom.}), 119.28 (C_{arom.}), 112.28 (Carom.), 64.52 (CH2), 29.84 (CH2), 26.30 (CH2), 14.20 (CH3) 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): $\tilde{v} =$ $(cm^{-1}) = 3885, 3458, 3136, 2965, 2928, 2666, 2324, 2099, 1997, 1912,$ 1669, 1465, 1383, 1302, 1146, 1066, 982, 901, 843, 750, 702. Elemental analysis: for C₁₁H₁₄O₄S•1/3H₂O: 54.53 %, H: 5.82 %; found C: 55.19 %, H: 6.03 %.

2c-H₂. 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). ¹H-NMR (400 MHz, CDCl₃): $\delta = 10.81$ (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}), 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, CH₂), 2.86 (t, J = 7.0 Hz, 2H, CH₂), 2.54 (t, J = 6.7 Hz, 2H, CH₂), 1.63–1.60 (m, 2H, CH₂), 0.99 (t, J = 7.4 Hz, 3H, CH₃) ppm. ¹³C-NMR (151 MHz, CDCl₃: $\delta = 170.02$ (CO₂CH₂), 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 (CH₂), 34.47 (CH₂), 30.23 (CH₂), 22.97 (CH₂), 13.36 (CH₃) ppm. ESI-MS (negative ESI-MS, MeOH, acidified): *m/z*: Calculated for C₁₂H₁₇O₄S⁻ [M – H⁺]: 255.0699, found 255.0701. IR (KBr): $\tilde{v} = (cm^{-1}) = 3459$, 3137, 2958, 2663, 2462, 2316, 2085, 2000, 1914, 1670, 1465, 1383, 1301,

1147, 1065, 985, 898, 843, 750. Elemental analysis: Calculated for $C_{12}H_{16}O_4S\text{-}1/3H_2O\text{:}$ 55.07 %, H: 6.39 %; found C: 55.26 %, H: 6.73 %.

General procedure for diol esterification (using 4all as an example). Triethylene glycol 4al (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 (SiO₂, 3:2 pentane/ethyl acetate) to afford the title compound (544 mg, 0.69 mmol, 63 %) as a white solid. ¹H-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, 2CH₂), 4.98 (s, 4H, 2CH₂), 4.33-4.21 (m, 4H, 2CH₂), 3.70-3.57 (m, 4H, 2CH₂), 3.47 (s, 4H, 2CH₂) ppm. ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 165.7 (CO₂CH₂), 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 (CH₂), 70.2 (CH₂), 69.7 (CH₂), 68.2 (CH₂), 64.0 (CH₂) 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 C₄₈H₄₆O₁₀: C: 73.64 %, H: 5.92 %; found C: 73.56 %, H: 5.96 %.

General procedure for removal of benzyl protecting groups (using **4alli** as an example). **4all** (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 H₂ 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 (SiO₂, 3:2 pentane/ethyl acetate) to afford the title compound **4a**-H₄ (145 mg, 0.35 mmol, 48 %) as a white solid.

¹H-NMR (600 MHz, [D₆]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, 2CH₂), 3.77–3.73 (m, 4H, 2CH₂), 3.61 (s, 4H,2CH₂) ppm. ¹³C-NMR (151 MHz, [D₆]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 (CH₂), 68.5 (CH₂), 64.9 (CH₂) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z*: Calculated for C₂₂H₂₆NaO₁₁⁺ [M + Na⁺]: 445.1105, found 445.1095 Elemental analysis: Calculated for C₂₂H₂₆O₁₁: C: 56.87 %, H: 5.25 %; found C: 56.97 %, H: 5.54 %.

4bil. The product was prepared applying the general procedure for diol esterification (see 4all) starting form tetraethylene glycol 4bl (200 mg, 1.03 mmol) to afford the title compound (468 mg, 0.56 mmol, 55 %) as a white solid. ¹H-NMR (600 MHz, [D₆]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, 2CH₂), 4.99 (s, 4H, 2CH₂), 4.33-4.22 (m, 4H, 2CH₂), 3.64-3.58 (m, 4H, 2CH₂), 3.45 (dt, J = 3.7, 2.3 Hz, 4H, 2CH₂), 3.41 (dt, J = 6.1, 3.7, Hz, 4H, 2CH₂) ppm. ¹³C-NMR (151 MHz, $[D_6]DMSO$): $\delta = 166.1 (CO_2CH_2)$, 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 (CH₂), 70.63 (CH₂), 70.15 (CH₂), 70.10 (CH₂), 68.61 (CH₂), 64.44 (CH₂) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): m/z: Calculated for C₅₀H₅₀NaO₁₁+ [M + Na⁺]: 849.3245, found 849.3253. Elemental analysis: Calculated for C₅₀H₅₀O₁₁: C: 72.62 %, H: 6.09 %; found C: 72.08 %, H: 6.09 %.

4b-H₄. 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. ¹H-NMR (600 MHz, [D₆]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, 2Harom.), 4.41–4.35 (m, 4H, 2CH₂), 3.71 (dd, *J* = 5.6, 3.5 Hz, 4H, 2CH₂), 3.54 (dd, *J* = 6.2, 3.5 Hz, 4H, 2CH₂), 3.51 (dd, *J* = 5.6, 3.5 Hz, 4H, 2CH₂) ppm. ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 169.8 (CO₂CH₂), 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 (CH₂), 70.2 (CH₂), 68.5 (CH₂), 64.9 (CH₂) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z*: Calculated for C₂₂H₂₆NaO₁₁⁺ [M + Na⁺]: 489.1367, found 489.1355. Elemental analysis: Calculated for C₂₂H₂₆O₁₁: C: 56.65 %, H: 5.62 %; found C: 56.67 %, H: 4.91 %.

4cll. The product was prepared applying the general procedure for diol esterification (see 4all) starting form pentaethylene glycol 4cl (1184 mg, 4.96 mmol) to afford the title compound (2105 mg, 2.42 mmol, 49 %) as a white solid. ¹H-NMR (600 MHz, [D₆]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, 2CH₂), 5.00 (s, 4H, 2CH₂), 4.38-4.21 (m, 4H, 2CH₂), 3.66-3.59 (m, 4H, 2CH₂), 3.47 (dd, J = 5.8, 3.5 Hz, 4H, 2CH₂), 3.42 (dd, J = 5.8, 3.5 Hz, 4H, 2CH₂), 3.40 (s, 4H, 2CH₂) ppm. ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 165.7 (CO₂CH₂), 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 (CH₂), 70.2 (CH₂), 69.7 (CH₂), 69.7 (CH₂), 69.7 (CH₂), 68.2 (CH₂), 64.0 (CH₂) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): m/z: Calculated for C₅₂H₅₄NaO₁₂⁺ [M + Na⁺]: 893.3513, found 893.3519. Elemental analysis: Calculated for C₅₂H₅₄O₁₂: C: 71.71 %, H: 6.25 %; found C: 71.67 %, H: 6.30 %.

4c-H₄. The ligand was prepared applying the general procedure for removal of benzyl protecting groups (see **4a-H₄**) starting form **4cll** (500 mg, 0.57 mmol) to afford the title compound (138 mg, 0.27 mmol, 47 %) as a white solid. ¹H-NMR (600 MHz, [D₆]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, 2CH₂), 3.73–3.70 (m, 4H, 2CH₂), 3.54 (dd, *J* = 5.9, 3.6 Hz, 4H, 2CH₂), 3.50–3.47 (m, 4H, 2CH₂), 3.46 (s, 4H, 2CH₂) ppm. ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 169.8 (CO₂CH₂), 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 (CH₂), 69.9 (CH₂), 68.5 (CH₂), 64.9 (CH₂) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z*: Calculated for C₂₄H₃₀NaO₁₂⁺ [M + Na⁺]: 533.1635, found 533.1616. Elemental analysis: Calculated for C₂₄H₃₀O₁₂: C: 56.47 %, H: 5.92 %; found C: 55.70 %, H: 6.0 %.

4dll. The product was prepared applying the general procedure for diol esterification (see 4all) starting form hexaethylene glycol 4dl (1200 mg, 4.25 mmol) to afford the title compound (2089 mg, 2.28 mmol, 54 %) as a white solid. ¹H-NMR (600 MHz, [D₆]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, 2CH₂), 4.99 (s, 4H, 2CH₂), 4.32-4.27 (m, 4H, 2CH₂), 3.66-3.60 (m, 4H, 2CH₂), 3.47 (dd, J = 5.9, 3.5 Hz, 4H, 2CH₂), 3.42 (dd, J = 5.9, 3.5 Hz, 4H, 2CH₂), 3.39 (s, 4H, 2CH₂) ppm. ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 166.2 (CO₂CH₂), 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 (CH₂), 70.6 (CH₂), 70.1 (CH₂), 68.6 (CH₂), 64.5 (CH₂) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): m/z: Calculated for C54H58NaO13 [M + Na⁺]: 937.3775, found 937.3773. Elemental analysis: Calculated for C54H58O13: C: 70.88 %, H: 6.39 %; found C: 70.84 %, H: 6.31 %.

4d-H₄. The ligand was prepared applying the general procedure for removal of benzyl protecting groups (see **4a-H**₄) starting form **4dll** (600 mg, 0.66 mmol) to afford the title compound (138 mg, 0.39 mmol, 59 %) as a white solid. ¹H-NMR (600 MHz, [D₆]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, 2CH₂), 3.75–3.70 (m, 4H, 2CH₂), 3.55 (dd, *J* = 5.9, 3.6 Hz, 4H, 2CH₂), 3.52–3.42 (m, 8H, 4CH₂) ppm. ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 169.8 (CO₂CH₂), 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 (CH₂), 69.9 (CH₂), 68.5 (CH₂), 64.9 (CH₂) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z*: Calculated for C₂₂H₂₆NaO₁₁⁺ [M + Na⁺]: 593.1636, found 593.1615. Elemental analysis: Calculated for C₂₂H₂₆O₁₁: C: 56.31 %, H: 6.18 %; found C: 55.70 %, H: 6.33 %.

General Procedure for the Preparation of THP protected diols (using **5all** as an example). 1,4-Butanediol **5al** (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 NH₄Cl solution. The solvent was removed under reduced pressure and the crude product purified by column chromatography (SiO₂, 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. ¹H-NMR (600 MHz, [D₆]DMSO): δ = 4.57 (t, J = 3.6 Hz, 2H, 2CH), 3.77-3.71 (m, 2H, 2CHH), 3.71-3.66 (m, 2H, m, 2H, 2CHH), 3.51-3.44 (m, 6H, 3CH₂), 3.44-3.37 (m, 6H, 3CH₂), 1.74-1.66 (m, 2H, 2CHH), 1.65-1.56 (m, 2H, 2CHH), 1.56-1.50 (m, 4H, 2CH2), 1.45 (m, 8H, 4CH₂). ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 98.0 (CH), 70.1 (CH₂), 69.4 (CH₂), 69.4 (CH₂), 66.1 (CH₂), 61.2 (CH₂), 30.2 (CH₂), 26.0 (CH₂), 25.0 (CH₂), 25.0 (CH₂), 19.1 (CH₂) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): m/z: Calculated for C₁₈H₃₄NaO₆⁺ [M + Na⁺]: 369,2248, found 369.2261. Elemental analysis: Calculated for C18H34O6: C: 62.40 %, H: 9.89 %; found C: 62.53 %, H: 9.54 %.

General procedure for the removal of THP protecting groups (using **5all1** as an example). **5all** (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 (SiO₂, 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. ¹H-NMR (600 MHz, [D₆]DMSO): δ = 4.56 (t, J = 5.6 Hz, 2H, CH₂), 3.47 (q, J = 5.4 Hz, 4H, 2CH₂), 3.40-3.35 (m, 8H, 4CH₂), 1.52 (h, J = 2.9 Hz, 4H, 2CH₂). ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 72.0 (2CH₂), 70.1 (2CH₂), 60.3 (2CH₂), 26.0 (2CH₂) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): m/z: Calculated for C₈H₁₈NaO₄⁺ [M + Na⁺]: 201,1097, found 201,1099. Elemental analysis: Calculated for C₈H₁₈O₄•0.5MeOH: C: 52.56 %, H: 10.38 %; found C: 53.12 %, H: 11.09 %.

SalV. The product was prepared applying the general procedure for diol esterification (see **4all**) using **SalII** (150 mg, 0.84 mmol) as starting material to afford the title compound (471 mg, 0.58 mmol, 69 %) as a white solid. ¹H-NMR (600 MHz, [D₆]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, 2CH₂), 4.99 (s, 4H 2CH₂), 4.35–4.18 (m, 4H 2CH₂), 3.62–3.50 (m, 4H 2CH₂), 3.31 (q, *J* = 5.8, 4.5 Hz, H 2CH₂), 1.44–1.39 (m, 4H, 2CH₂) ppm. ¹³C-NMR (151 MHz,



 $\begin{array}{l} [D_{6}]DMSO): \ \delta = 165.8 \ (CO_{2}CH_{2}), \ 152.3 \ (C_{arom.}), \ 146.8 \ (C_{arom.}), \ 137.3 \\ (C_{arom.}), \ 136.6 \ (C_{arom.}), \ 128.5 \ (C_{arom.}), \ 128.1 \ (C_{ar$

5a-H₄. The ligand was prepared applying the general procedure for removal of benzyl protecting groups (see **4a-H₄**) starting form **5alV** (100 mg, 0.12 mmol) to afford the title compound (51 mg, 0.11 mmol, 92 %) as a white solid. ¹H-NMR (600 MHz, [D₆]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, 2CH₂), 3.44 (s, 4H, 2CH₂), 1.53 (s, 4H, 2CH₂) ppm. ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 169.8 (CO₂CH₂), 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 (CH₂), 68.1 (CH₂), 64.9 (CH₂), 26.2 ppm (CH₂) ppm. ESI-MS (negative ESI-MS, MeOH, acidified): *m/z*: Calculated for C₂₂H₂₅O₁₀⁻ [M – H⁺]: 449.1453, found 449.1446. Elemental analysis: Calculated for C₂₂H₂₆O₁₀•H₂O: C: 56.41 %, H: 6.02 %; found C: 56.56 %, H: 5.70 %.

5bll. The product was prepared applying the general procedure for the preparation of THP protected diols (see **5all**) 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. ¹H-NMR (600 MHz, [D₆]DMSO): δ = 4.58 (t, *J* = 3.6 Hz, 2H, 2CH), 3.91–3.86 (m, 2H, 2CHH), 3.78–3.67 (m, 4H, 2CH), 3.61–3.51 (m, 8H, 4CH), 3.51–3.45 (m, 2H, 2CHH), 3.44–3.39 (m, 2H, 2CHH), 1.75–1.66 (m, 2H, 2CHH), 1.64–1.56 (m, 2H, 2CHH), 1.55–1.38 (m, 6H, 3CH₂), 1.30 (s, 6H, 2CH3) ppm. ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 108.6 (CCH₃), 98.0 (CH), 76.9 (CH₂), 71.0 (CH₂), 70.2 (CH₂), 66.0 (CH₂), 61.2 (CH₂), 30.2 (CH₂), 26.9 (CH₂), 25.1 (CH₃), 19.06 (CH₂) ppm. ESI-MS (negative ESI-MS, MeOH, acidified): *m/z*: Calculated for C₂₁H₃₈NaO₈⁺ [M + Na⁺]: 441.2459, found 441.2447. Elemental analysis: Calculated for C₂₁H₃₈O₈: 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. ¹H-NMR (600 MHz, [D₆]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, 2CH₂), 3.51–3.46 (m, 4H, 2CH₂), 3.46–3.43 (m, 4H, 2CH₂), 1.30 (s, 6H, 2CH₃) ppm. ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 108.6 (CCH3), 76.9 (CH), 72.7 (CH₂), 71.2 (CH₂), 60.2 (CH₂), 26.9 (CH₃) ppm. ESI-MS (positive ESI-MS, MeOH, acidified): *m/z*: Calculated for C₈H₁₈NaO₄⁺ [M + Na⁺]: 273.13086, found 273,13983. Elemental analysis: Calculated for C₈H₁₈O₄: 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 **4all**) 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. ¹H-NMR (600 MHz, [D₆]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, 2CH₂), 4.99 (s, 4H, 2CH₂), 4.47 (dd, J = 12.0, 2.2 Hz, 2H, CHH), 4.37–4.23 (m, 2H, CHH), 4.21–4.12 (m, 2H, CH), 1.31–1.26 (m, 6H, CH₃) ppm. ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 165.7 (CO₂CH₂), 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 (CCH₃), 75.6 (CH₂), 75.2 (CH₂), 70.7 (CH₂), 64.7 (CH₂), 27.3 (CH₃) 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. ¹H-NMR (600 MHz, [D₆]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, 2CH₂), 3.88 (p, *J* = 1.8 Hz, 2H, 2CH), 3.75–3.70 (m, 4H), 3.62–3.52 (m, 4H, 2CH₂), 1.25 (s, 6H, 2CH₃) ppm. ¹³C-NMR (151 MHz, [D₆]DMSO): δ = 169.4 (CO₂CH₂), 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 (CCH₃), 76.7 (CH), 70.9 (CH₂), 68.5 (CH₂), 64.3 (CH₂), 26.8 (CH₃) ppm. ESI-MS (negative ESI-MS, MeOH, acidified): *m/z*: Calculated for C₂₅H₃₀NaO₁₂ [M + Na⁺]: 545.1630, found 545.1622. Elemental analysis: Calculated for C₂₅H₃₀O₁₀: C: 57.47 %, H: 5.79 %; found C: 56.89 %, H: 5.92 %.

General Procedure for the Preparation of complexes $Li[Li_3(1,2)_6Ti_2]$ The respective catechol ligand (3 equiv.) was mixed with TiO(acac)₂ (1 equiv.) and Li₂CO₃ (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-H₂ (50 mg, 0.24 mmol) and obtained as red solid (quantitative). ¹H-NMR (400 MHz, [D₆]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, OCHH), 3.57 (dd, J = 5.7, 3.9 Hz, 4H, 2CH₂), 3.27 (s, 3H, CH₃) 3.02 (ddd, J = 12.1, 5.3, 3.1 Hz, 1H, OCHH) 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, CH₂), 3.23 (ddd, J = 11.4, 5.2, 3.1 Hz, 2H, CH₂), 3.16 (s, 3H, CH₃) ppm. ESI-MS (negative/positive ESI-MS, MeOH): m/z: Calculated for C₆₀H₆₀O₃₀Li₃Ti₂⁻ [M_D – Li⁺]: 1377.2609, found 1377.2601. Calculated for C₆₀H₆₀O₃₀Li₅Ti₂⁺ [M_D + Li⁺]: 1391.2929, found 1391.2959. IR (KBr): $\tilde{v} = (cm^{-1}) = 3747, 3626, 3067, 2929, 2662, 2448, 2322, 2162, 2062,$ 1990, 1924, 1675, 1594, 1560, 1443, 1373, 1296, 1251, 1213, 1156, 1125, 1065, 1034, 970, 895, 858, 801, 744, 681. Elemental analysis: Calculated for C₆₀H₆₀O₃₀Li₄Ti₂•5H₂O: 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-H₂ (50 mg, 0.22 mmol) and obtained as red solid (quantitative). ¹H-NMR (600 MHz, [D₆]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, OCH₂) 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, OCH₂) 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): $\tilde{v} = (cm^{-1}) = 3747$, 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 $C_{60}H_{60}O_{30}Li_{4}Ti_{2}\text{\cdot}5H_{2}O\text{:}$ C: 48.87 %, H: 4.78 %; found C: 48.91 %, H: 4.65 %.

Li[*Li*₃(1*c*)₆*Ti*₂]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding



ligand **1c**-H₂ (50 mg, 0.21 mmol) and obtained as red solid (quantitative). ¹H-NMR (600 MHz, [D₆]DMSO): Dimer (major component): $\delta = 6.97$ (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, OCH₂) ppm. Monomer (minor component): $\delta = 6.77$ (dd, J = 8.2, 1.6 Hz, 1H, H_{arom}), 6.09 (dd, J = 8.2, 1.6 Hz, 1H, H_{arom}), 6.09 (dd, J = 8.1, 1.6 Hz, 1H, H_{arom}), 4.17 (t, J = 6.5 Hz, 2H, OCH₂) ppm. Signals not listed are overlapped and cannot be assigned. ESI-MS (negative ESI-MS, MeOH): m/z: Calculated for C₇₂H₈₄O₃₀Li₃Ti₂⁻ [M_D – Li⁺]: 1545.4486, found 1545.4436. IR (KBr): $\tilde{\nu} = (cm^{-1}) = 3438, 3069, 2962, 2930, 2868, 2683, 2448, 2265, 2162, 2104, 2028, 1990, 1910, 1677, 1594, 1558, 1443, 1385, 1352, 1295, 1252, 1215, 1155, 1063, 1014, 963, 891, 856, 806, 742, 683. Elemental analysis: Calculated for C₇₂H₈₄O₃₀Li₄Ti₂·3H₂O: C: 53.81 %, H: 5.65 %; found C: 53.71 %, H: 5.41 %.$

Li[Li₃(2a)₆Ti₂]. The complex was prepared according to the general procedure for the preparation of complexes 1,2-H₂ with the corresponding ligand 2a-H₂ (50 mg, 0.22 mmol) and obtained as red solid (quantitative). ¹H-NMR (400 MHz, [D₆]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, OCH₂), 3.12–3.08 (m, 1H, OCH₂), 2.45 (t, J = 6.8 Hz, 2H, CH₂), 1.90 (s, 3H, CH₃) 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, OCH₂), 2.68 (t, J = 6.8 Hz, 2H, CH₂), 2.08 (s, 3H, CH₃) 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): $\tilde{v} = (cm^{-1}) = 3363$, 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 C60H60O24S6Li4Ti2•2H2O: C: 46.40 %, H: 4.41 %; found C: 46.41 %, H: 4.53 %.

Li[Li₃(2b)₆Ti₂]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand 2b-H₂ (50 mg, 0.21 mmol) and obtained as red solid (guantitative). ¹H-NMR (600 MHz, [D₆]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, OCH₂), 2.42 (t, J = 6.8 Hz, 2H, CH₂), 2.33 (q, J = 7.4 Hz, 2H, CH₂), 0.96 (t, J = 7.4 Hz, 3H, CH₃) 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, OCH₂), 2.73 (t, J = 6.8 Hz, 2H, CH₂), 2.55 (q, J = 7.4 Hz, 2H, CH₂), 1.13 (t, J = 7.4 Hz, 3H, CH₃) 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): $\tilde{v} = (cm^{-1}) = 3357$, 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 C₆₆H₇₂O₂₄S₆Li₄Ti₂•H₂O: 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**-H₂ (50 mg, 0.20 mmol) and obtained as red solid (quantitative). ¹H-NMR (600 MHz, [D₆]DMSO): Dimer (major component): $\delta = 6.94$ (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, OCH₂), 3.13–3.09 (m, 1H, OCH₂), 2.51 (t, J = 6.9 Hz, 2H, CH₂), 2.29 (t, J = 8.1

6.8 Hz, 2H, CH₂), 1.32 (m, 2H, CH₂), 0.76 (t, J = 7.3 Hz, 3H, CH₃) ppm. Monomer (minor component): $\delta = 6.75$ (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, OCH₂), 2.71 (t, J = 6.9 Hz, 2H, CH₂), 2.39 (t, J = 6.8 Hz, 2H, CH₂), 1.50 (m, 2H, CH₂), 0.88 (t, J = 7.3 Hz, 3H, CH₃) ppm. **ESI-MS** (negative/positive ESI-MS, MeOH): *m/z*: Calculated for C₇₂H₈₄O₂₄S₆Li₃Ti₂⁻ [M_D - Li⁺]: 1641.3116, found 1641.3160; calculated for C₇₂H₈₄O₂₄S₆Li₅Ti₂⁻ [M_D + Li⁺]: 1655.3436, found 1655.3464; calculated for C₃₆H₄₂O₁₂S₃Li₅Ti⁺ [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 C₇₂H₈₄O₂₄S₆Li₄Ti₂·9/2H₂O: C: 47.74 %, H: 5.68 %; found C: 47.99 %, H: 5.51 %.

General Procedure for the Preparation of complexes $Li[Li_3(4)_3Ti_2]$ and $M_4[(5)_3Ti_2]$, (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[Li₃(4a)₃Ti₂]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4a**-H₂ (50 mg, 0.12 mmol) and obtained as red solid (quantitative). ¹H-NMR (600 MHz, [D₆]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, CH₂), 3.49–3.38 (m, 6H, 3CH₂), 3.20 (ddd, *J* = 14.3, 9.8, 3.6 Hz, H, CH₂), 3.02 (td, *J* = 12.2, 11.0, 7.7 Hz, 12H, CH₂) ppm. ESI-MS (negative/positive ESI-MS, MeOH): *m/z*: Calculated for C₆₀H₅₄Li₅O₃₀Ti₂⁻¹ ([M - Li⁺]): 1371.2144, found 1371.2078. Calculated for C₆₀H₅₄Li₅O₃₀Ti₂⁺¹ ([M + Li⁺]): 1385.2454, found 1385.2489.

Li[Li₃(4b)₃Ti₂]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4b**-H₂ (50 mg, 0.09 mmol) and obtained as red solid (quantitative). ¹H-NMR (600 MHz, [D₆]DMSO): $\delta = 6.97$ (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, CH₂), 3.46 (ddd, J = 11.6, 8.6, 3.2 Hz, 6H, CH₂), 3.32–3.30 (m, 12H,), 3.27 (dd, J = 6.4, 3.4 Hz, 12H, CH₂), 2.97 (dt, J = 12.2, 3.7 Hz, 6H, CH₂) ppm. ESI-MS (negative/positive ESI-MS, MeOH): m/z: Calculated for C₇₂H₇₈Li₃O₃₆Ti₂⁻ [M – Li⁺]: 1635.3717, found 1635.3604. Calculated for C₇₂H₇₈Li₅O₃₆Ti₂⁺ ([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*-H₂ (50 mg, 0.09 mmol) and obtained as red solid (quantitative). ¹H-NMR (600 MHz, [D₆]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, CH₂), 2.98 (ddd, *J* = 12.2, 6.7, 2.9 Hz, 2H, CH₂) ppm. Signals not listed are overlapping and cannot be assigned. ESI-MS (negative/positive ESI-MS, MeOH): *m/z*: Calculated for C₇₂H₇₈Li₃O₃₆Ti₂⁻ [M - Li⁺]: 1635.3717, found 1635.3604. Calculated for C₇₂H₇₈Li₅O₃₆Ti₂⁺ ([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*-H₂ (50 mg, 0.08 mmol) and obtained as red solid (quantitative). ¹H-NMR (600 MHz, [D₆]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, CH₂), 3.01 (ddd, J = 11.2, 8.9, 5.2 Hz, 3H, CH₂) ppm. Signals not listed are overlapping and cannot be assigned. ESI-MS (negative/positive ESI-MS, MeOH): *m/z*: Calculated for C₇₈H₉₀Li₃O₃₉Ti₂⁻ ([M - Li⁺]): 1767.4504, found 1767.4446. Calculated for C₇₈H₉₀Li₅O₃₉Ti₂⁺ [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**-H₂ (50 mg, 0.11 mmol) and obtained as red solid (quantitative). ¹H-NMR (600 MHz, [D₆]DMSO): $\delta = 6.99$ (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, CH₂), 3.42 (ddd, J = 12.1, 9.3, 2.2 Hz, 6H, CH₂), 3.25–3.21 (m, 6H, CH₂), 3.20–3.08 (m, 12H, CH₂), 2.90 (dt, J = 12.4, 2.9 Hz, 6H, CH₂), 1.20 (q, J = 4.4, 3.6 Hz, 12H, CH₂) Signals not listed are overlapping and cannot be assigned. ESI-MS (negative/positive ESI-MS, MeOH): *m/z*: Calculated for C₆₆H₆₆Li₅O₃₀Ti₂⁻⁺ [(M + Li⁺]): 1455.3083, 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**-H₂ (50 mg, 0.11 mmol) and obtained as orange solid (quantitative). ¹H-NMR (600 MHz, [D₆]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 C₆₆H₆₆Li₅O₃₀Ti₂⁻⁻ [(M - Li⁺]): 1455.3083, found 1455.3254. Calculated for C₆₆H₆₆Na₃O₃₀Ti₂⁻⁻ [M - Na⁺]: 1503.2296, found 1503.2562. Calculated for C₆₆H₆₆Na₅O₃₀Ti₂⁺⁻ [M + Na⁺]: 1549.2081, found 1549.2105.

K₄[(*Sa*)₃*T*i₂]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4d**-H₂ (50 mg, 0.11 mmol) and obtained as orange solid (quantitative). ¹H-NMR (600 MHz, [D₆]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 C₆₆H₆₆Li₅O₃₀Ti₂⁻ ([M – Li⁺]): 1455.3083, found 1455.3254. Calculated for C₆₆H₆₆K₃O₃₀Ti₂⁻ ([M – K⁺]): 1552.1543, found 1552.1572 Calculated for C₆₆H₆₆K₅O₃₀Ti₂⁺ [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**-H₂ (50 mg, 0.10 mmol) and obtained as red solid (quantitative). ¹H-NMR (600 MHz, [D₆]DMSO): $\delta = 6.99$ (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, CH₂), 3.63–3.44 (m, 12H, CH₂), 3.28 (dq, J = 9.8, 4.2, 3.4 Hz, 9H, CH₂), 3.24–3.19 (m, 6H, CH₂), 2.99–2.87 (m, 6H), 1.34 (s, 6H, CH₂), 1.19–1.16 (s, 18H, CH₂) ppm. ESI-MS (negative/positive ESI-MS, MeOH): *m/z:* Calculated for C₇₅H₇₈Li₃O₃₆Ti₂+ [M + Li⁺]: 1685.4026, found 1685.4087.

Na₄[(5b)₃Ti₂]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4d**-H₂ (50 mg, 0.10 mmol) and obtained as red solid (quantitative). ¹H-NMR (600 MHz, [D₆]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, CH₂), 4.58 (ddd, *J* = 11.7, 7.4, 4.5 Hz, 1H, CH₂) ppm. The spec-

trum 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 $C_{75}H_{78}Na_5O_{36}Ti_2^{-1}$ [M - Na⁺]: 1719.2930, found 1713.2768. Calculated for $C_{75}H_{78}Na_5O_{36}Ti_2^{+1}$ [M + Na⁺]: 1765.2715, found 1765.2795.

K₄[(5b)₃Ti₂]. The complex was prepared according to the general procedure for the preparation of complexes with the corresponding ligand **4d**-H₂ (50 mg, 0.10 mmol) and obtained as red solid (quantitative). ¹H-NMR (600 MHz, [D₆]DMSO): $\delta = 6.92$ (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 C₇₅H₇₈K₅O₃₆Ti₂⁻¹ [(M – K⁺]): 1767.2148, found 1769.9190. Calculated for C₇₅H₇₈K₅O₃₆Ti₂⁺¹ [M + K⁺]: 1845.1412, found 1845.1429.

X-ray Experimental Details.

Crystal data for K[Li₃(**1a**)₆Ti₂]: CCDC-1997036, C₆₀H₆₀KLi₃O₃₀Ti₂, M = 1416.80, orange plate, 0.17 × 0.09 × 0.02 mm³, triclinic, space group *P*[†] (No. 2), a = 12.0584(6) Å, b = 15.4327(10) Å, c = 17.7343(12) Å, $\alpha = 77.698(5)^{\circ}$, $\beta = 79.621(5)^{\circ}$, $\gamma = 85.627(5)^{\circ}$, V = 3169.2(3) Å3, Z = 2, $D_{calc} = 1.485$ g cm³, *F*(000) = 1464, $\mu = 0.41$ mm 1, *T* = 120.0(1) K, $\theta_{max} = 25.0^{\circ}$, 21166 total reflections, 4091 with Io > 2 σ (Io), R_{int} = 0.093, 11218 data, 1033 parameters, 346 restraints, GooF = 1.00, R = 0.093 and wR= 0.177 [Io > 2 σ (Io)], R = 0.254 and wR= 0.259 (all reflections), 0.50 < 0.53 e Å³.

Crystal data for Li[Li₃(**2a**)₆Ti₂]: CCDC-1997037, C₆₂H₆₈Li₄O₂₆S₆Ti₂, M = 1545.08, orange plate, 0.44 × 0.27 × 0.16 mm³, monoclinic, space group *P*2₁/*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 cm³, *F*(000) = 3200, μ = 0.50 mm 1, *T* = 170.0(1) K, θ_{max} = 30.5°, 35660 total reflections, 13846 with lo > 2 σ (lo), R_{int} = 0.045, 20750 data, 1067 parameters, 300 restraints, GooF = 1.06, R = 0.073 and wR= 0.165 [lo > 2 σ (lo)], R = 0.115 and wR= 0.188 (all reflections), 1.22 < 0.73 e/Å³.

Crystal data for Na[Li₃(**4**c)₃Ti₂]-2DMF: CCDC-1997473, C₇₈H₉₂Li₃N₂NaO₃₈Ti₂, M = 1805.14, orange block, 0.08 × 0.07 × 0.04 mm³, 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) Å³, *Z* = 4, *D*_{calc} = 1.440 g cm³, *F*(000) = 3768, μ = 2.50 mm 1, *T* = 100(2) K, θ_{max} = 62.5°, 10828 total reflections, 8504 with lo > 2 σ (lo), R_{int} = 0.087, 10828 data, 1132 parameters, 0 restraints, GooF = 1.02, R = 0.071 and wR= 0.185 [lo > 2 σ (lo)], R = 0.095 and wR= 0.201 (all reflections), 1.88 < 0.36 e/Å³, Flack-Parameter x = -0.017(15).

Crystal data for Na₂[(**5b**)₂Ti₂]: CCDC-1994564, C₅₂H₆₀Na₂O₂₈Ti₂· 2(C₂₄H₂₀As)·8MeOH, M = 2041.41, yellow block, 0.14 × 0.14 × 0.10 mm³, 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) Å³, Z = 4, D_{calc} = 1.176 g cm³, F(000) = 4224, μ = 2.436 mm 1, T = 100(2) K, θ_{max} = 58.9°, 39070 total reflections, 14670 with lo > 2 σ (lo), R_{int} = 0.0191, 12305 data, 1176 parameters, 262 restraints, GooF = 1.01, R = 0.040 and wR= 0.110 [lo > 2 σ (lo)], R = 0.047 and wR= 0.110 (all reflections), 0.26 < 0.34 e/Å³, Flack-Parameter x = 0.057(8).

CCDC-199703 (for K[Li₃(1a)₆Ti₂) 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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- [1] A. Goswami, S. Saha, P. K. Biswas, M. Schmittel, Chem. Rev. 2020, 120, 125–199.
- [2] V. Balzani, M. Venturi, A. Credi, *Molecular devices and machines*, Wiley-VCH, Weinheim **2003**.
- [3] For catechol based hierarchical helicates by other see: a) X. Sun, D. W. Johnson, D. L. Caulder, R. E. Powers, K. N. Raymond, E. H. Wong, Angew. Chem. Int. Ed. 1999, 38, 1303–1307; Angew. Chem. 1999, 111, 1386; b) X. Sun, D. W. Johnson, K. N. Raymond, E. H. Wong, Inorg. Chem. 2001, 40, 4504–4506; c) X. Sun, D. W. Johnson, D. L. Caulder, K. N. Raymond, E. H. Wong, J. Am. Chem. Soc. 2001, 123, 2752–2763; d) Y. Sakata, S. Hiraoka, M. Shionoya, Chem. Eur. J. 2010, 16, 3318–3325; e) S. Hiraoka, Y. Sakata, M. Shionoya, J. Am. Chem. Soc. 2008, 130, 10058–10059; f) T. Nakagawa, H. Danjo, M. Kawahata, K. Yamaguchi, Tetrahedron 2019, 75, 315–323.
- [4] a) J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 2565–2569; b) C. Piguet, G. Bernardin- elli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062; c) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457–3497.
- [5] For catecholate based helicates see e.g a) M. Albrecht, Chem. Soc. Rev.
 1998, 27, 281–288; b) E. J. Enemark, T. D. P. Stack, Angew. Chem. Int. Ed. Engl. 1995, 34, 996–998; Angew. Chem. 1995, 107, 1082; c) B. Kersting, M. Meyer, R. E. Powers, K. N. Raymond, J. Am. Chem. Soc. 1996, 118, 7221–7222; d) U. Kiehne, A. Lützen, Eur. J. Org. Chem. 2007, 2007, 5703– 5711; e) T. Haino, H. Shio, R. Takano, Y. Fukazawa, Chem. Commun. 2009, 2481–2483; f) Y. Yamasaki, H. Shio, R. Sekiya, T. Haino, Chem. Eur. J. 2018, 24, 8558–8568.
- [6] M. Albrecht, S. Mirtschin, M. de Groot, I. Janser, J. Runsink, G. Raabe, M. Kogej, C. A. Schalley, R. Fröhlich, J. Am. Chem. Soc. 2005, 127, 10371–10387.
- [7] a) D. Van Craen, W. H. Rath, M. Huth, L. Kemp, C. Räuber, J. Wollschläger, C. Schalley, A. Valkonen, K. Rissanen, M. Albrecht, J. Am. Chem. Soc. 2017, 139, 16959–16966; b) A. C. N. Kwamen, M. Schlottmann, D. Van Craen, E. Isaak, J. Baums, L. Shen, A. Massomi, C. Räuber, B. P. Joseph, G. Raabe, C. Göb, I. M. Oppel, R. Puttreddy, J. S. Ward, K. Rissanen, R. Fröhlich, M. Albrecht, Chem. Eur. J. 2020, 26, 1396–1405; c) A. C. N. Kwamen, G. S. de Macedo, C. Wiederhold, I. M. Oppel, M. Albrecht, Chem. Eur. J. 2020, DOI: 10.1002/chem.201905212.
- [8] D. VanCraen, M. Albrecht, G. Raabe, F. Pan, K. Rissanen, Chem. Eur. J. 2016, 22, 3255–3258.
- [9] X. Chen, M. Baumert, R. Fröhlich, M. Albrecht, J. Inclusion Phenom. Macrocyclic Chem. 2019, 94, 133–140.

- [10] a) For helicate based switches see e.g. K. Miwa, Y. Furusho, E. Yashima, *Nat. Chem.* **2010**, *2*, 444–449; b) see also for comparison: K. Harada, R. Sekiya, T. Haino, *Chem. Eur. J.* **2020**, *26*, 5810–5817.
- [11] X. Chen, T. M. Gerger, C. Räuber, G. Raabe, C. Göb, I. M. Oppel, M. Albrecht, *Angew. Chem. Int. Ed.* **2018**, *57*, 11817–11820; *Angew. Chem.* **2018**, *130*, 11991.
- [12] C. J. Gramer, K. N. Raymond, Org. Lett. 2001, 3, 2827–2830.
- [13] B. Neises, W. Steglich, Angew. Chem. Int. Ed. Engl. 1978, 17, 522–524; Angew. Chem. 1978, 90, 556.
- [14] X. Chen, C. Mevissen, S. Huda, C. Göb, I. M. Oppel, M. Albrecht, Angew. Chem. Int. Ed. 2019, 58, 12879–12882; Angew. Chem. 2019, 131, 4753.
- [15] See for comparison: a) C. J. Baylies, J. C. Jeffery, T. A. Miller, R. Moon, C. R. Rice, T. Riis-Johannessen, *Chem. Commun.* **2005**, 4158–4160; b) T. Riis-Johannessen, L. P. Harding, J. C. Jeffery, R. Moon, C. R. Rice, *Dalton Trans.* **2007**, 1577–1587.
- [16] For enantiomerically pure helicates with dimethyldioxolane spacers see: M. Albrecht, S. Schmid, M. deGroot, P. Weis, R. Fröhlich, *Chem. Commun.* 2003, 2526–2527.
- [17] M. Albrecht, I. Janser, J. Fleischhauer, Y. Wang, G. Raabe, R. Fröhlich, Mendeleev Commun. 2004, 14, 250–253.
- [18] a) M. Albrecht, E. Isaak, M. Baumert, V. Gossen, G. Raabe, R. Fröhlich, Angew. Chem. Int. Ed. 2011, 50, 2850–2853; Angew. Chem. 2011, 123, 2903; b) M. Albrecht, E. Isaak, H. Shigemitsu, V. Moha, G. Raabe, R. Fröhlich, Dalton Trans. 2014, 43, 14636–14643.
- [19] a) M. Albrecht, M. Napp, M. Schneider, P. Weis, R. Fröhlich, *Chem. Commun.* **2001**, 409–410; b) M. Albrecht, M. Napp, M. Schneider, P. Weis, R. Fröhlich, *Chem. Eur. J.* **2001**, *7*, 3966–3975.
- [20] RigakuOxfordDiffraction, CrysAlisPro Software system, version 38.46, Rigaku Corporation, Oxford, UK, 2018.
- [21] R. Hooft, COLLECT, Nonius BV, Delft, The Netherlands, 1998.
- [22] W. Otwinowski, Z. Minor in *Methods in Enzymology* (Ed.: C. W. Carter, R. M. Sweet), New York: Academic Press, **1997**, pp. 307–326.
- [23] G. M. Sheldrick, SADABS Version 2008/2, University of Göttingen, Germany, 1996.
- [24] G. M. Sheldrick, Acta Crystallogr., Sect. C 2015, 71, 3-8.
- [25] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341.
- [26] Stoe, Stoe X-Area, version 1.82, Stoe & Cie GmbH, Darmstadt, Germany, 2018.

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