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Formation of Triple-Stranded Dinuclear Helicates with Dicatecholimine Ligands: The Influence of Steric Hindrance at the Spacer

Ingo Janser,[a] Markus Albrecht,*[a] Katharina Hunger,[a,b] Simon Burk,[a] and Kari Rissanen[b]

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A series of new imine-bridged dicatechol ligands **3a**–**f**-H_4 with sterically demanding groups at the spacers are used for the formation of titanium(IV) complexes $M_4[(\mathbf{3})_3Ti_2]$. All three ligands **3a**–**c**-H_4 form triple-stranded dinuclear helicates. When the bulky ligands **3a**-H_4 or **3c**-H_4 are used with potassium as the countercation, oligomeric or polymeric side products are also observed. The imine-bridged ligand **3e**-H_4 quantitatively forms helicates $M_4[(\mathbf{3e})_3Ti_2]$ and not a M_4L_6 tetrahedron as observed with Raymond's analogous amide-bridged dicatechol ligand **3i**-H_4. NMR spectroscopic investigations at variable temperature show that ligand **3f**-H_4, which possesses a spiro fluorenyl group at the central unit of the spacer, forms the *meso*-helicate $M_4[(\mathbf{3f})_3Ti_2]$.

Introduction

In the last two decades double- and triple-stranded helicates have been investigated very intensely as model compounds in metallosupramolecular chemistry.[1] In order to perform a systematic study on the influences of different geometric factors on the helicate formation we needed an easy way of preparing a variety of different ligands with different geometric constraints and demands. Several groups[2,3] have shown that bis(iminopyridine) ligands can be obtained by simple imine condensation from readily available starting materials. These ligands form double- or triple-stranded helicates with a series of different metal ions. Recently, we[4,5] and others[6] introduced imine condensation to obtain dicatechol ligands for the formation of helicates.[7–11]

Herein we use this concept to obtain several new ligands with different steric demands at the spacer, which can then be used for the self-assembly of triple-stranded dinuclear helicates and *meso*-helicates.

Results and Discussion

Synthesis and Characterisation of the Dicatechol Ligands 3a–f-H_4

The dicatechol ligands **3a**–**f**-H_4 were prepared in two different ways (Scheme 1): (i) The diamines **1a**–**1d** and 2 equiv. 2,3-dihydroxybenzaldehyde (**2**) were dissolved in toluene and heated to reflux in a Dean–Stark apparatus overnight in the presence of catalytic amounts of *p*-TosOH. Water was removed by continuous distillation of the water/toluene azeotrope. After cooling to room temperature, the precipitated product was isolated by filtration, washed with toluene, and the derivatives were obtained in 86% (**3a**-H_4, yellow solid), 81% (**3b**-H_4, red solid), 91% (**3c**-H_4, red solid) and 72% (**3d**-H_4, orange solid) yield. (ii) The diamines **1e** and **1f** and 2 equiv. 2,3-dihydroxybenzaldehyde (**2**) were dissolved in methanol. After 12 h at room temperature, the precipitated diimines were isolated by filtration in 99% (**3e**-H_4, red solid) or 93% (**3f**-H_4, red solid) yield, respectively.

The compounds were characterised by MS, elemental analysis and ^{1}H NMR spectroscopy, and selected examples were also characterised by ^{13}C NMR spectroscopy. The resonance of the imine proton is a characteristic signal in the ^{1}H NMR spectra ([D$_6$]DMSO), which appears for the ligands **3a**–**f**-H_4 in the region of δ = 8.45–9.03 ppm. In two of the cases we were able to observe the signals for the two OH protons of the catechol moieties. For **3e**, two signals at δ = 13.17 and 9.37 ppm are detected. For **3f**, the two resonances of the OH protons can be found at δ = 13.21 and 9.23 ppm. The signal that appears downfield is assigned to the 2-hydroxy group, which forms an unsymmetric intramolecular hydrogen bond to the imine with a transfer of a proton to the nitrogen atom. At low temperatures form **A** is favoured, while form **B** is observed at higher temperatures (Scheme 2). The resonance of the 2-hydroxy group appears downfield because of shielding.[5]

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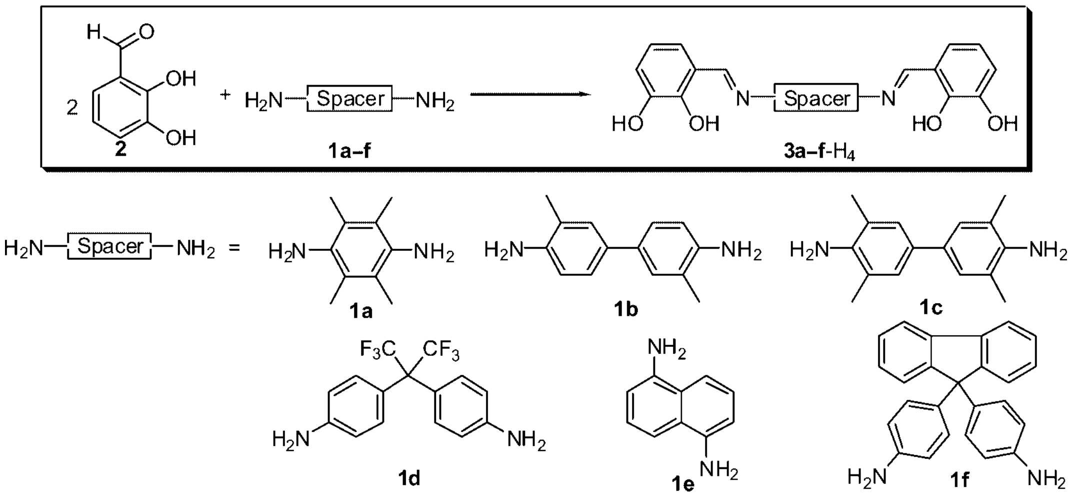
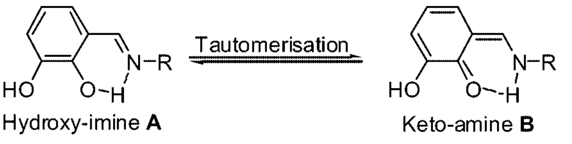
[a] Institut für Organische Chemie der RWTH-Aachen,
Landoltweg 1, 52074 Aachen, Germany
Fax: +49-241-80-92385
E-mail: markus.albrecht@oc.rwth-aachen.de
[b] Nanoscience Center, Department of Chemistry, University of Jyväskylä,
Survontie 9, 40014 Jyväskylä, Finland



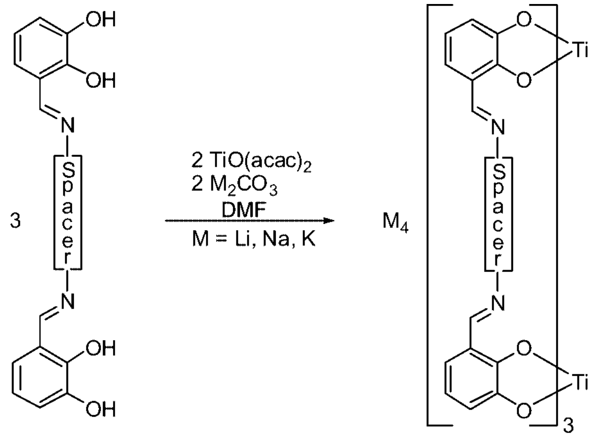
Scheme 1. Preparation of the dicatechol ligands $\mathbf{3a}$–$\mathbf{f}$-H_4 by imine condensation.



Scheme 2. Hydroxy-imine (**A**)/keto-amine (**B**) tautomerisation in Schiff base.

Formation of Dinuclear Triple-Stranded Helicates $M_4[(\mathbf{3a}–\mathbf{f})_3Ti_2]$ (M = Li, Na, K)

For the preparation of the titanium(IV) complexes $M_4[(\mathbf{3a}–\mathbf{f})_3Ti_2]$, the ligands $\mathbf{3a}$–$\mathbf{f}$-H_4 (3 equiv.), $[TiO(acac)_2]$ (2 equiv.) and the corresponding alkali metal carbonate M_2CO_3 (2 equiv., M = Li, Na, K) were mixed in DMF (Scheme 3). Within a few minutes the solution turned orange-red and was stirred overnight at room temperature. Volatile components were removed in vacuo to obtain the complex salts $M_4[(\mathbf{3a}–\mathbf{f})_3Ti_2]$ as red solids.



Scheme 3. Synthesis of the triple-stranded dinuclear helicates $M_4[(\mathbf{3a}–\mathbf{f})_3Ti_2]$.

Formation and Characterisation of $M_4[(3a)_3Ti_2]$ (M = Li, Na, K)

Ligands **3a**–**c** were introduced to study the influence of sterically demanding ligands on the self-assembly of helicates. The dinuclear complex salts $M_4[(\mathbf{3a})_3Ti_2]$ (M = Li, Na, K) of the phenyl-type ligand **3a** were characterised by elemental analysis, FAB MS and ^1H NMR spectroscopy. Positive FAB MS (3-NBA) reveals characteristic peaks at m/z = 1305 $\{H_2Li[(\mathbf{3a})_3Ti_2]^+\}$, 1343 $\{HNa_2[(\mathbf{3a})_3Ti_2]^+\}$, or 1337 $\{H_2K[(\mathbf{3a})_3Ti_2]^+\}$. Upon complex formation, the imine proton, which appears in the ^1H NMR spectrum of $\mathbf{3a}$-H_4 in $[D_6]$DMSO at δ = 8.45 ppm, is shifted upfield to δ = 8.10–8.16 ppm. The signals of the methyl groups of the spacer appear as a singlet at δ = 1.91 (Li), 1.91 (Na), and 1.89 ppm (K), and the catechol resonances [detected at δ = 7.03, 6.36 and 6.17 ppm (M = Li); 7.03, 6.37 and 6.19 ppm (M = Na); 6.93, 6.37 and 6.19 ppm (M =K)] appear as a doublet, triplet and doublet, respectively. No significant differences are observed for the NMR shifts of different salts of $[(\mathbf{3a})_3Ti_2]^{4-}$.

In earlier studies we investigated the complexation of ligand $\mathbf{3g}$-H_4 with titanium(IV) ions (Figure 1). Ligand $\mathbf{3g}$-H_4 possesses a phenyl spacer that is similar to that of ligand $\mathbf{3a}$-H_4 but with protons instead of the four methyl groups. It could be shown that this ligand leads in a quantitative self-assembly process to the triple-stranded dinuclear helicate $M_4[(\mathbf{3g})_3Ti_2]$.[5]

Ligand $\mathbf{3a}$-H_4 with four methyl groups at the phenyl spacer also leads to the triple-stranded dinuclear helicates $M_4[(\mathbf{3a})_3Ti_2]$ (M = Li, Na, K). However, in the case of the potassium salt $K_4[(\mathbf{3a})_3Ti_2]$, additional broad signals appear in the ^1H NMR sprectra ($[D_6]$DMSO) at δ = 8.28, 8.18, 7.20, 7.08, 6.17 ppm, which indicate the presence of polymeric or oligomeric species besides the triple-stranded dinuclear helicate as the main product. As can be seen from the X-ray analysis of $K_4[(\mathbf{3g})_3Ti_2]$ (Figure 1),[5] the complex possesses the structure of a triple-stranded dinuclear helicate. The long imine–aryl–imine spacers lead to a large sepa-

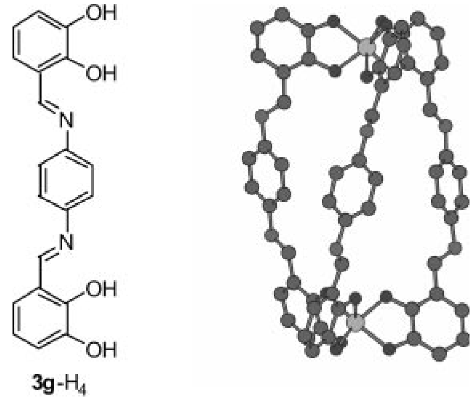


Figure 1. Ligand **3g**-H_4 and part of the X-ray structure of $K_4[(\mathbf{3g})_3Ti_2]$.[5]

ration of the titanium centres, and a big internal cavity is formed. As we know from other catechol-derived helicates, alkaline metal countercations are encapsulated in the interior and bind to the internal oxygen atoms of the catecholate ligands.[12,13] The coordination sphere at the cations is saturated by binding solvent molecules. It seems that the alkali cations act as a template in stabilising the formation of a triple-stranded dinuclear helicate. In the case of ligand **3a**-H_4, the potassium cation is not able to stabilise this formation quantitatively. The reason for this is the steric influence of the methyl groups that are probably directed into the interior of the complex, and this influence therefore suppresses the binding of big potassium cations. The lithium or sodium cations are smaller and because of this they fit into the cavity and stabilise the triple-stranded dinuclear complex more effectively.

Formation and Characterisation of $M_4[(3b–c)_3Ti_2]$ (M = Li, Na, K)

In ligands **3b** and **3c** with elongated aromatic spacers, methyl groups are introduced at the *ortho* position of the imine spacers. In the presence of lithium, sodium or potassium cations, the two ligands **3b**-H_4 and **3c**-H_4 form triple-stranded helicates $M_4[(\mathbf{3b/c})_3Ti_2]$. The dinuclear complexes were characterised by elemental analysis, FAB MS and ^1H NMR spectroscopy. In the ^1H NMR spectrum of **3b**-H_4, the resonance for the imine proton appears at δ = 8.95 ppm and in the complexes at δ = 8.61 (Li), 8.65 (Na), and 8.60 ppm (K). The upfield shift of the resonance indicates that the conformation at the imine unit changes upon metal complexation (vide supra). The signals of the spacer can be detected for $Li_4[(\mathbf{3b})_3Ti_2]$ at δ = 7.43 (s, 6 H), 7.34 (d, *J* = 7.5 Hz, 6 H), 7.00 (d, *J* = 7.5 Hz, 6 H) and 2.30 ppm (s, 18 H) , for $Na_4[(\mathbf{3b})_3Ti_2]$ at δ = 7.44 (s, 6 H), 7.32 (d, *J* = 8.0 Hz, 6 H), 7.05 (d, *J* = 8.0 Hz, 6 H) and 2.30 ppm (s, 18 H) and for $K_4[(\mathbf{3b})_3Ti_2]$ at δ = 7.43 (s, 6 H), 7.33 (d, *J* = 8.0 Hz, 6 H), 7.03 (d, *J* = 8.0 Hz, 6 H) and 2.30 ppm (s, 18 H).

For the Ti^{IV} complexes of ligand **3c**-H_4, similar MS and NMR spectroscopic results can be obtained (see Experimental Section). However, in the case of the potassium salt $K_4[(\mathbf{3c})_3Ti_2]$, additional signals appear in the ^1H NMR spectra ([D$_6$]DMSO) at δ = 8.57, 7.26 (br), 7.10 (br), 6.45 (br), 6.15 ppm (br), which indicate that some polymeric or oligomeric species are formed besides the triple-stranded dinuclear helicate as the main product.

In earlier studies we already investigated the coordination chemistry of the sterically less demanding ligand **3h**-H_4 (Figure 2) with titanium(IV) ions. Ligand **3h**-H_4 possesses a biphenyl spacer that is similar to ligand **3c**-H_4 but without the methyl substituents.[14] As we have shown, ligand **3h**-H_4 leads quantitatively to the formation of a triple-stranded dinuclear helicate $M_4[(\mathbf{3h})_3Ti_2]$. The X-ray structure of the complex $Na_4[(\mathbf{3h})_3Ti_2]$ shows (Figure 2) that the linear rigid ligands form a triple-stranded helicate with two similar-configured titanium(IV) complex units. Three ligands **3h**-H_4 wrap around the metals and adopt a conformation with the imine hydrogen atoms that point into the interior, directed towards the catecholate oxygen atoms, and therefore form a big cavity. In the solid state, two sodium cations are bound in the interior of the helicate, each binding to the internal catecholate oxygen atoms and to three DMF molecules.[14] Following this, it is reasonable to suggest that ligand **3b**-H_4 with its two additional methyl groups is able to form triple-stranded dinuclear complexes with lithium, sodium or potassium cations. The situation changes somewhat by using ligand **3c**-H_4. In the case of potassium as the countercation, the four additional methyl groups of the spacer are too big to fit into the cavity. In this case, potassium is not able to form the triple-stranded dinuclear helicate quantitatively, and therefore some oligomers and polymers are formed as side products, as is the case with ligand **3a**-H_4.

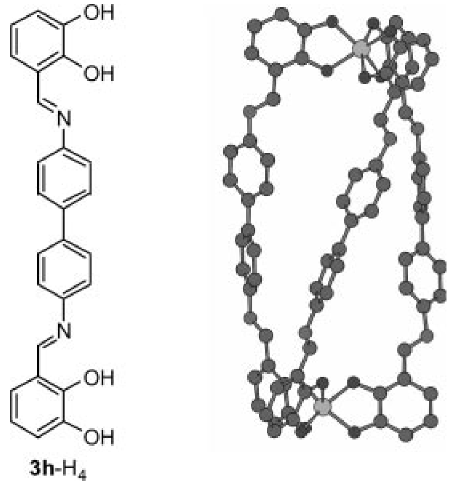


Figure 2. Ligand **3h**-H_4 and part of the X-ray structure $Na_4[(\mathbf{3h})_3Ti_2]$.[14]

These three examples demonstrate the influence of the spacer on the formation of the complexes. Ligand **3a**-H_4, with four methyl groups at the phenyl spacer, exclusively forms triple-stranded dinuclear helicates with lithium and sodium only. When potassium is the countercation both oligomeric and polymeric species can be observed. The size dependence is also observed in the yields of the three complexes $M_4[(\mathbf{3a})_3Ti_2]$. Upon coordination, the oligomeric or polymeric species precipitate and the triple-stranded dinuclear helicates can be isolated by filtration in 66% (M = Li), 60% (M = Na), 37% (M =K) yield. Ligand **3b**-H_4, with an elongated spacer and two methyl groups in the *ortho* position of the imine spacers, forms a triple-stranded helicate in good yields (≥75%) with all three countercations. Ligand **3c**-H_4, with four methyl groups in the *ortho* position of the imine-spacers, leads to the formation of side products upon complexation with titanium(IV)ions and potassium as the countercations, which indicates that the cavity is too small for the four methyl groups and the big potassium cations.

Coordination Studies with Ligand 3d-H_4

Ligand **3d** possesses two CF_3 groups that can act as a stereochemical probe for ^{19}F NMR spectroscopy. Unfortunately, we were not able to obtain triple-stranded dinuclear helicate-type compounds with ligand **3d**-H_4. Upon complex formation, residual water in the solvent hydrolyses the imine bond. ^1H NMR spectra in [D_6]DMSO show only resonances of the products from the cleavage reaction.

Formation of $M_4[(3e)_3Ti_2]$ (M = Li, Na)

The imine-bridged dicatechol ligand **3e**-H_4 with a sterically demanding naphthyl spacer was introduced to study the differences from the amide-bridged dicatechol ligand **3i**-H_4 (Figure 3). With ligand **3i**-H_4, Raymond and coworkers obtained a molecular M_4L_6 tetrahedron, $[Ga_4\mathbf{3i}_6]^{12-}$, and no helicate was observed.[15]

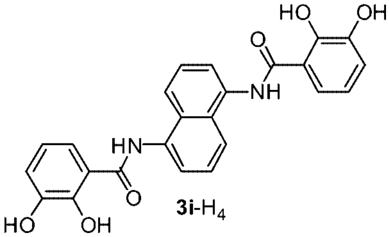


Figure 3. Ligand **3i**-H_4.[15]

In contrast, we obtained the triple-stranded dinuclear complexes $M_4[(\mathbf{3e})_3Ti_2]$ (M = Li, Na) in quantitative yield. Elemental analyses show the correct composition for the compounds, and characteristic peaks are observed in the positive FAB mass spectra for the dinuclear triple-stranded helicate. ^1H NMR spectroscopy in [D_6]DMSO reveals the resonances for the imine proton at δ = 8.26 (M = Li) and 8.34 ppm (M = Na), for the spacer at δ = 7.60, 7.18, and 7.02 (M = Li) and 7.65, 7.25, and 7.11 ppm (M = Na), and for the catecholate units at δ = 6.68, 6.36, and 6.12 (M = Li) and 6.78, 6.44, and 6.21 ppm (M = Na). No significant differences are observed when comparing the spectra of the complex salts $M_4[(\mathbf{3e})_3Ti_2]$ with those of different cations M^+. This shows that the formation of Raymond's tetrahedron in comparison to our helicate depends on the orientation of the amide versus the imine C–N group. In the case of the amide ligand **3i**, overcrowding of the spacers prevents the formation of the helicate. To explain this, we have to consider the different orientations of the imine- or amide-bridged dicatechol ligands **3e**-H_4 and **3i**-H_4 (Figure 4). We have reported earlier that the imine moiety possesses a preferred conformation **B**. In this conformation the C=N double bond is directed towards the outside of the cavity of the complex.[14] This conformation is preferred because there are electrostatic attractions between the internal catecholate oxygen atoms and the imine proton. Additional repulsion takes place between the oxygen and the imine-nitrogen lone pairs. The situation in Raymond's amide-bridged dicatechol ligand **3i**-H_4 is "reversed". Here an inward orientation of the amide nitrogen atom occurs (**D**), which forms an intramolecular hydrogen bond. Therefore, upon complexation of ligand **3e** with titanium(IV), a much bigger cavity is formed. In the case of the ligand **3i**-H_4, hydrogen bonding forces the sterically demanding naphthyl spacers into an orientation facing towards the interior of the complex. This prevents the formation of the helicate because the spacers would be forced "into each other". To prevent this, a molecular M_4L_6 tetrahedron is formed.[16]

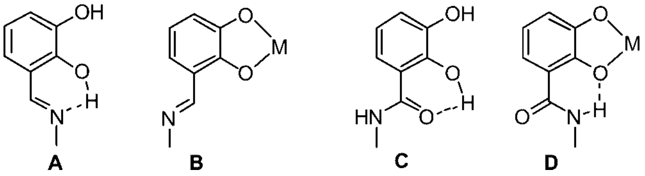
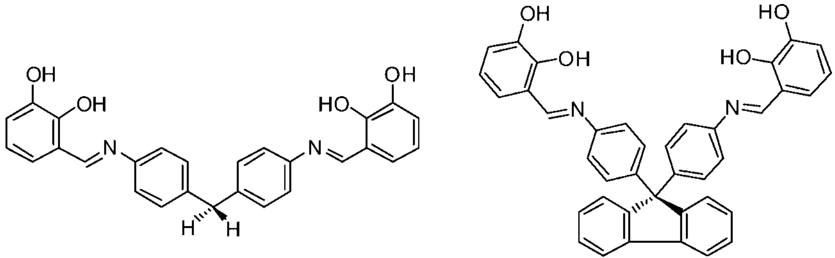


Figure 4. Possible orientations of the imine moiety in the free ligand (**A**) or in the catecholato metal complex (**B**) and of the amino moiety in the free ligand (**C**) or in the catecholato metal complex (**D**).

Formation of $M_4[(3f)_3Ti_2]$ (M = Li, Na, K)

Ligand **3f**-H_4 possesses a big group at the central unit of the spacer and is therefore not as flexible as the related compound **3j**-H_4 (Figure 5). We investigated this ligand **3f**-H_4 in order to determine whether it is able to form *meso*-helicates with titanium(IV) and the corresponding alkali metal counterions as ligand **3j**-H_4 does.[14] Reaction of titanium(IV) ions with ligand **3f**-H_4 in the presence of an alkali metal carbonate in DMF leads to the assembly of dinuclear complex salts $M_4[(\mathbf{3f})_3Ti_2]$ in quantitative yield. The complexes $M_4[(\mathbf{3f})_3Ti_2]$ (M = Li, Na, K) were characterised by elemental analysis, ESI-MS, IR and NMR spectroscopy. In the ESI mass spectra, characteristic peaks can be detected at *m/z* = 1869 $\{Li_3[(\mathbf{3f})_3Ti_2]^-\}$, 1918 $\{Na_3[(\mathbf{3f})_3Ti_2]^-\}$, 1928 $\{HK_2[(\mathbf{3f})_3Ti_2]^-\}$. The lithium salt $Li_4[(\mathbf{3f})_3Ti_2]$ in [D_6]DMSO shows peaks in the ^1H NMR spectrum at δ = 8.53 (s, 6 H, imine), 7.89 (br., 6 H, spacer-fluorenyl), 7.48 (d, *J* = 7.3 Hz, 6 H, spacer-fluorenyl), 7.42–7.32 (m, 12 H, spacer-fluorenyl), 7.14 (d, *J* = 8.0 Hz, 12 H, spacer-phenyl), 7.04 (d, *J* = 8.0 Hz, 12 H, spacer-phenyl), 6.93 (d, *J* = 7.7 Hz, 6 H, cat), 6.30 (t, *J* = 7.7 Hz, 6 H, cat), 6.06 ppm (d, *J* = 7.7 Hz, 6 H, cat). Complex $Na_4[(\mathbf{3f})_3Ti_2]$ as well as $K_4[(\mathbf{3f})_3Ti_2]$ show similar spectra. For all three complexes, the signals for the spacer appear at room temperature as half a set of signals.

Recently, we described the formation of a triple-stranded dinuclear *meso*-helicate $M_4[(\mathbf{3j})_3Ti_2]$ with ligand **3j**-H_4, tita-



3j-H_4 **3f**-H_4

Figure 5. Ligands **3j**-H_4 and **3f**-H_4.

nium(IV) ions and the corresponding countercations (Li^+, Na^+, K^+).[14] The relative stereochemistry of the complex units of $M_4[(\mathbf{3j})_3Ti_2]$ was shown by X-ray diffraction as well as by NMR spectroscopy at variable temperature.

Temperature-Dependent NMR Spectroscopic Investigations of $Na_4[(3f)_3Ti_2]$

For dinuclear helicate-type complexes with an odd number of CH_2 units in the spacer, NMR spectroscopy is a powerful tool for distinguishing between the helicate and the *meso*-helicate form.[17–22]

Figure 6 shows schematic representations of the situation that is found for dinuclear complexes with a C_1 unit incorporated into the spacer of either a helicate or a *meso*-helicate. In the case of the helicate, one set of signals is expected, whereas two diastereotopic groups are present in the *meso*-helicate. Therefore, we can expect two sets of signals for the substituents at the C_1 unit of the *meso*-helicate $[(\mathbf{3f})_3Ti_2]^{4-}$.[17–19,22]

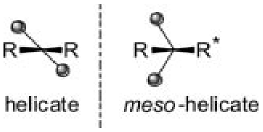


Figure 6. Schematic representation of the orientation of ligands with a C_1 spacer in the helicate and *meso*-helicate. Diasterotopic substituents are indicated.

As shown in Figure 5, spiro compound **3f**-H_4 (like **3j**-H_4) possesses a "C"-shaped conformation, and the *meso*-helicate should therefore be formed upon complexation with titanium(IV) ions. Thus, a full set of signals is expected for the protons of the fluorenyl group. The ^1H NMR spectrum of $Na_4[(\mathbf{3f})_3Ti_2]$ in [D$_4$]methanol at room temperature shows only half a set of signals (two doublets and two triplets) for the protons of the diastereotopic fluorenyl phenyl rings. Upon cooling of the NMR sample, the signals broaden and start to split. At 273 K, a full set of signals is observed, which reveals that the *meso*-helicate $Na_4[(\mathbf{3f})_3Ti_2]$ is present in solution (Figure 7).

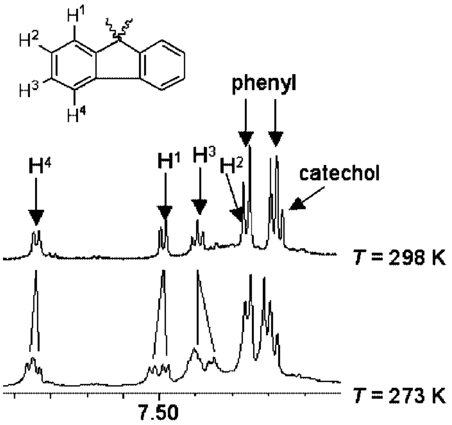


Figure 7. Temperature-dependent NMR spectrum of $Na_4[(\mathbf{3f})_3Ti_2]$ in [D$_4$]methanol at room temperature (298 K) and at 273 K. The signal of the H^2 proton is covered by a signal of the phenyl ring. (Two additional catechol protons are observed at δ = 6.44 and 6.51 ppm.)

Conclusions

In this paper we demonstrated the influence of steric hindrance at the spacer of triple-stranded helicates for the self-assembly process. Therefore, a series of imine-bridged dicatechol ligands **3a**–**f**-H_4 with sterically demanding groups at the spacer were synthesised. The complexation of the ligands with titanium(IV)ions and the corresponding alkaline metal carbonate M_2CO_3 (M = Li, Na, K) has shown that the groups influence the formation of the complexes. In general, triple-stranded dinuclear complexes were formed. However, in some cases oligomeric and polymeric species could be observed as side products. In the case of a ligand with a high steric demand, it is possible that the groups of the spacer do not fit into the cavity and suppress the binding of the countercation. In this case, the cation cannot act as a template to stabilise the formation of a triple-stranded complex, and therefore oligomers or polymers are formed. The ligands **3a**-H_4 and **3c**-H_4 are bulky, and triple-stranded dinuclear helicates $K_4[(\mathbf{3a})_3Ti_2]$ or $K_4[(\mathbf{3c})_3Ti_2]$ are not obtained in quantitative yields.

Ligand **3e**-H_4 quantitatively formed a triple-stranded dinuclear helicate $[(\mathbf{3e})_3Ti_2]^{4-}$. The corresponding amide-bridged dicatechol ligand **3i**-H_4 leads to a molecular M_4L_6

tetrahedron, $K_5[Et_4N]_7[Ga_4\mathbf{3i}_6]\cdot 8H_2O$, and no helicate is observed. Here, hydrogen bonding of the amide group forces the sterically demanding naphthyl spacers to be oriented towards the interior of the complex. This prevents the formation of the helicate because the spacers would be forced "into each other". With ligand **3e**, the spacers are oriented "outwards", and the dinuclear complex can be formed.

Ligand **3f**-H_4 with a sterically demanding group at the central unit of the spacer quantitatively formed a *meso*-helicate. To prove this result, we used temperature-dependent NMR spectroscopy as a tool for distinguishing between the helicate and the *meso*-helicate form. This shows that the big fluorenyl group does not influence the formation of the complexes because the group is not directed into the cavity of the complex but is rather oriented outwards.

Experimental Section

General Remarks: NMR spectra were recorded with a Bruker DRX 500, WM 400 or a Varian Inova 400 spectrometer. FT-IR spectra were recorded by diffuse reflection (KBr) with a Bruker IFS spectrometer. Mass spectra (EI 70 eV, FAB with 3-NBA as matrix) were recorded with a Finnigan MAT 90, 95 or 212 mass spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyser.

General Procedure for the Preparation of the Ligands 3a–f-H_4

Method A: The corresponding diamine **1a**–**d** (1 mmol, 1 equiv.) and 2,3-dihydroxybenzaldehyde (**2**, 2 mmol, 2 equiv.) were heated in toluene in the presence of catalytic amounts of *p*-TosOH. Water was removed by azeotropic distillation. After cooling to room temperature, the precipitated product was isolated by filtration, washed with toluene and dried in vacuo.

Method B: The corresponding diamine **1e**–**f** (1 mmol, 1 equiv.) and 2,3-dihydroxybenzaldehyde (**2**, 2 mmol, 2 equiv.) were dissolved in methanol. After a few minutes, the product started to precipitate, and was then isolated by filtration after standing overnight, washed with ice-cold methanol and dried in vacuo.

Ligand 3a-H_4 (Method A): Yield: 86% of a yellow solid. ^1H NMR ([D_6]DMSO): δ = 8.45 (s, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 6.79 (t, *J* = 8.0 Hz, 2 H), 2.09 (s, 12 H) ppm. MS (EI, 70 eV): *m/z* = 404 (100) $[M]^+$. $C_{24}H_{24}N_2O_4\cdot 1/2H_2O$ (413.47): calcd. C 69.72, H 6.09, N 6.78; found C 69.92, H 5.74, N 6.87.

Ligand 3b-H_4 (Method A): Yield: 91% of a red solid. ^1H NMR ([D_6]DMSO): δ = 8.95 (s, 2 H), 7.70 (s, 2 H), 7.60 (d, *J* = 8.5 Hz, 2 H), 7.48 (d, *J* = 8.5 Hz, 2 H), 7.13 (d, *J* = 7.5 Hz, 2 H), 6.94 (d, *J* = 7.5 Hz, 2 H), 6.77 (t, *J* = 7.5 Hz, 2 H), 2.44 (s, 6 H) ppm. MS (EI, 70 eV): *m/z* = 452 (100) $[M]^+$. $C_{28}H_{24}N_2O_4\cdot 1/3H_2O$ (458.52): calcd. C 73.35, H 5.42, N 6.11; found C 73.31, H 5.17, N 6.11.

Ligand 3c-H_4 (Method A): Yield: 72% of an orange solid. ^1H NMR ([D_6]DMSO): δ = 8.62 (s, 2 H), 7.48 (s, 4 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 6.80 (t, *J* = 8.0 Hz, 2 H), 2.24 (s, 12 H) ppm. MS (EI, 70 eV): *m/z* = 480 (100) $[M]^+$. $C_{30}H_{28}N_2O_4\cdot$ 1/4toluene (503.60): calcd. C 75.72, H 6.00, N 5.56; found C 75.68, H 5.99, N 5.15.

Ligand 3d-H_4 (Method A): Yield: 81% of a red solid. ^1H NMR ([D_6]DMSO): δ = 8.95 (s, 2 H), 7.53–7.44 (m, 8 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 6.96 (d, *J* = 8.0 Hz, 2 H), 6.80 (t, *J* = 8.0 Hz, 2 H) ppm. MS (EI, 70 eV): *m/z* = 574 (100) $[M]^+$. $C_{29}H_{20}F_6N_2O_4\cdot$ $1/4H_2O$ (578.98): calcd. C 60.16, H 3.57, N 4.84; found C 60.19, H 3.63, N 4.54.

Ligand 3e-H_4 (Method B): Yield: quantitative of a red solid. ^1H NMR ([D_6]DMSO): δ = 13.17 (s, 2 H), 9.37 (s, 2 H), 9.03 (s, 2 H), 8.15 (d, *J* = 7.9 Hz, 2 H), 7.71 (t, *J* = 7.9 Hz, 2 H), 7.55 (d, *J* = 7.9 Hz, 2 H), 7.23 (dd, *J* = 7.4, 1.4 Hz, 2 H), 7.03 (dd, *J* = 7.4, 1.4 Hz, 2 H), 6.86 (t, *J* = 7.4 Hz, 2 H) ppm. MS (EI, 70 eV): *m/z* = 398 (100) $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1616, 1460, 1407, 1360, 1273, 1209, 1071, 1026, 981, 928, 781, 734, 522 cm^{-1}. $C_{24}H_{18}N_2O_4$ (398.42): calcd. C 72.35, H 4.55, N 7.03; found C 71.65, H 4.46, N 6.73.

Ligand 3f-H_4 (Method B): Yield: 93% of a red solid. ^1H NMR ([D_6]DMSO): δ = 13.21 (br., 2 H), 9.23 (br., 2 H), 8.88 (s, 2 H), 7.98 (d, *J* = 7.2 Hz, 2 H), 7.52 (d, *J* = 7.4 Hz, 2 H), 7.47–7.39 (m, 4 H), 7.34 (d, *J* = 8.7 Hz, 4 H), 7.24 (d, *J* = 8.7 Hz, 4 H), 7.08 (dd, *J* = 7.8, 1.4 Hz, 2 H), 6.97 (dd, *J* = 7.8, 1.4 Hz, 2 H), 6.79 (t, *J* = 7.8 Hz, 2 H) ppm. ^{13}C NMR ([D_6]DMSO): δ = 164.3 (CH), 150.8 (C), 149.8 (C), 147.0 (C), 146.1 (C), 144.6 (C), 140.0 (C), 129.2 (CH), 128.5 (CH), 128.4 (CH), 126.5 (CH), 123.3 (CH), 121.9 (CH), 121.2 (CH), 119.8 (C), 119.5 (CH), 119.3 (CH), 64.9 (C) ppm. MS (EI, 70 eV): *m/z* = 588 (100) $[M]^+$. IR (KBr): $\tilde{\nu}$ = 3410, 1621, 1583, 1501, 1464, 1366, 1271, 1211, 1016, 873, 827, 735 cm^{-1}. $C_{39}H_{28}N_2O_4$ (588.66): calcd. C 79.57, H 4.79, N 4.76; found C 79.14, H 4.80, N 4.42.

General Procedure for the Preparation of the Complexes $M_4[(\mathbf{3a–f})_3Ti_2]$

Ligand **3a**–**f**-H_4 (3 equiv.), $TiO(acac)_2$ (2 equiv.) and M_2CO_3 (2 equiv., M = Li, Na, K) were dissolved in DMF, and the orange mixture was stirred overnight. Volatiles were removed in vacuo to obtain the dinuclear complexes $M_4[(\mathbf{3a}–\mathbf{f})_3Ti_2]$ as red solids.

Complex $Li_4[(3a)_3Ti_2]$: Yield: 66% of a red solid. ^1H NMR ([D_6]DMSO): δ = 8.16 (s, 6 H), 7.03 (d, *J* = 7.0 Hz, 6 H), 6.36 (t, *J* = 7.0 Hz, 6 H), 6.17 (d, *J* = 7.0 Hz, 6 H), 1.91 (s, 36 H) ppm. MS (pos. FAB, 3-NBA): *m/z* = 1305 $\{H_2Li[(\mathbf{3a})_3Ti_2]^+\}$, 1299 $\{H_3[(\mathbf{3a})_3Ti_2]^+\}$, 649 $\{H_2[(\mathbf{3a})_3Ti_2]^{2+}\}$. $C_{72}H_{60}Li_4N_6O_{12}Ti_2\cdot 6(C_3H_7NO)\cdot 10H_2O$ (1943.59): calcd. C 55.62, H 6.33, N 8.65; found C 55.64, H 5.63, N 8.86.

Complex $Na_4[(3a)_3Ti_2]$: Yield: 60% of a red solid. ^1H NMR ([D_6]DMSO): δ = 8.16 (s, 6 H), 7.03 (d, *J* = 7.0 Hz, 6 H), 6.37 (t, *J* = 7.0 Hz, 6 H), 6.19 (d, *J* = 7.0 Hz, 6 H), 1.91 (s, 36 H) ppm. MS (pos. FAB, 3-NBA): *m/z* = 1343 $\{HNa_2[(\mathbf{3a})_3Ti_2]^+\}$, 1299 $\{H_3[(\mathbf{3a})_3Ti_2]^+\}$, 649 $\{H_2[(\mathbf{3a})_3Ti_2]^{2+}\}$. $C_{72}H_{60}Na_4N_6O_{12}Ti_2\cdot 6(C_3H_7NO)\cdot 7H_2O$ (1953.74): calcd. C 55.33, H 5.98, N 8.60; found C 55.15, H 5.38, N 8.86.

Complex $K_4[(3a)_3Ti_2]$: Yield: 37% of a red solid. ^1H NMR ([D_6]DMSO): δ = 8.10 (s, 6 H), 6.93 (d, *J* = 7.0 Hz, 6 H), 6.37 (t, *J* = 7.0 Hz, 6 H), 6.19 (d, *J* = 7.0 Hz, 6 H), 1.89 (s, 36 H) ppm. MS (pos. FAB, 3-NBA): *m/z* = 1337 $\{H_2K[(\mathbf{3a})_3Ti_2]^+\}$, 1299 $\{H_3[(\mathbf{3a})_3Ti_2]^+\}$, 649 $\{H_2[(\mathbf{3a})_3Ti_2]^{2+}\}$. $C_{72}H_{60}K_4N_6O_{12}Ti_2\cdot 6(C_3H_7NO)\cdot 7H_2O$ (2018.17): C 53.56, H 5.79, N 8.33; found C 53.61, H 5.30, N 8.69.

Complex $Li_4[(3b)_3Ti_2]$: Yield: quantitative of a red solid. ^1H NMR ([D_6]DMSO): δ = 8.61 (s, 6 H), 7.43 (s, 6 H), 7.34 (d, *J* = 7.5 Hz, 6 H), 7.08 (d, *J* = 7.0 Hz, 6 H), 7.00 (d, *J* = 7.5 Hz, 6 H), 6.38 (t, *J* = 7.0 Hz, 6 H), 6.16 (d, *J* = 7.0 Hz, 6 H), 2.30 (s, 18 H) ppm. MS (pos. FAB, 3-NBA): *m/z* = 1443 $\{H_3[(\mathbf{3b})_3Ti_2]^+\}$, 721 $\{H_2[(\mathbf{3b})_3Ti_2]^{2+}\}$. $C_{84}H_{60}Li_4N_6O_{12}Ti_2\cdot 4(C_3H_7NO)\cdot 10H_2O$ (1941.53): calcd. C 59.39, H 5.61, N 7.21; found C 59.09, H 4.90, N 7.32.

Complex $Na_4[(3b)_3Ti_2]$: Yield: 75% of a red solid. ^1H NMR ([D_6]DMSO): δ = 8.65 (s, 6 H), 7.44 (s, 6 H), 7.32 (d, *J* = 8.0 Hz, 6 H), 7.12 (d, J = 7.5 Hz, 6 H), 7.05 (d, J = 8.0 Hz, 6 H), 6.39 (t, J = 7.5 Hz, 6 H), 6.18 (d, J = 7.5 Hz, 6 H), 2.30 (s, 18 H) ppm. MS (pos. FAB, 3-NBA): m/z = 1443 $\{H_3[(\mathbf{3b})_3Ti_2]^+\}$, 721 $\{H_2[(\mathbf{3b})_3Ti_2]^{2+}\}$. $C_{84}H_{60}Na_4N_6O_{12}Ti_2\cdot 5(C_3H_7NO)\cdot 8H_2O$ (2042.79): calcd. C 58.21, H 5.48, N 7.54; found C 58.15, H 4.94, N 7.78.

Complex $K_4[(3b)_3Ti_2]$: Yield: 84% of a red solid. ^{1}H NMR ([D$_6$]DMSO): δ = 8.60 (s, 6 H), 7.43 (s, 6 H), 7.33 (d, J = 8.0 Hz, 6 H), 7.10 (d, J = 7.5 Hz, 6 H), 7.03 (d, J = 8.0 Hz, 6 H), 6.38 (t, J = 7.5 Hz, 6 H), 6.17 (d, J = 7.5 Hz, 6 H), 2.30 (s, 18 H) ppm. MS (pos. FAB, 3-NBA): m/z = 1443 $\{H_3[(\mathbf{3b})_3Ti_2]^+\}$, 721 $\{H_2[(\mathbf{3b})_3Ti_2]^{2+}\}$. $C_{84}H_{60}K_4N_6O_{12}Ti_2\cdot 4(C_3H_7NO)\cdot 6H_2O$ (1998.10): calcd. C 57.71, H 5.04, N 7.01; found C 57.64, H 4.86, N 6.94.

Complex $Li_4[(3c)_3Ti_2]$: Yield: 75% of a red solid. ^{1}H NMR ([D$_6$]DMSO): δ = 8.30 (s, 6 H), 7.29 (s, 12 H), 7.06 (d, J = 8.0 Hz, 6 H), 6.37 (t, J = 8.0 Hz, 6 H), 6.17 (d, J = 8.0 Hz, 6 H), 2.06 (s, 36 H) ppm. MS (pos. FAB, 3-NBA): m/z = 1533 $\{H_2Li[(\mathbf{3c})_3Ti_2]^+\}$, 1527 $\{H_3[(\mathbf{3c})_3Ti_2]^+\}$, 763 $\{H_2[(\mathbf{3c})_3Ti_2]^{2+}\}$. $C_{90}H_{72}Li_4N_6O_{12}Ti_2\cdot 5(C_3H_7NO)\cdot 16H_2O$ (2206.88): calcd. C 57.15, H 6.35, N 6.98; found C 57.25, H 5.52, N 7.27.

Complex $Na_4[(3c)_3Ti_2]$: Yield: 65% of a red solid. ^{1}H NMR ([D$_6$]DMSO): δ = 8.30 (s, 6 H), 7.20 (s, 12 H), 7.06 (d, J = 7.5 Hz, 6 H), 6.38 (t, J = 7.5 Hz, 6 H), 6.20 (d, J = 7.5 Hz, 6 H), 2.06 (s, 36 H) ppm. MS (pos. FAB, 3-NBA): m/z = 1549 $\{H_2Na[(\mathbf{3c})_3Ti_2]^+\}$, 1527 $\{H_3[(\mathbf{3c})_3Ti_2]^+\}$, 763 $\{H_2[(\mathbf{3c})_3Ti_2]^{2+}\}$. $C_{90}H_{72}Na_4N_6O_{12}Ti_2\cdot 5(C_3H_7NO)\cdot 17H_2O$ (2289.09): calcd. C 55.09, H 6.21, N 6.73; found C 54.97, H 5.27, N 7.00.

Complex $K_4[(3c)_3Ti_2]$: Yield: 56% of a red solid. ^{1}H NMR ([D$_6$]DMSO): δ = 8.29 (s, 6 H), 7.20 (s, 12 H), 7.05 (d, J = 7.5 Hz, 6 H), 6.36 (t, J = 7.5 Hz, 6 H), 6.18 (d, J = 7.5 Hz, 6 H), 2.06 (s, 36 H) ppm. MS (pos. FAB, 3-NBA): m/z = 1566 $\{H_2K[(\mathbf{3c})_3Ti_2]^+\}$, 1527 $\{H_3[(\mathbf{3c})_3Ti_2]^+\}$, 763 $\{H_2[(\mathbf{3c})_3Ti_2]^{2+}\}$. $C_{90}H_{72}K_4N_6O_{12}Ti_2\cdot 4(C_3H_7NO)\cdot 18H_2O$ (2298.45): calcd. C 53.30, H 5.96, N 6.09; found C 53.29, H 5.12, N 6.37.

Complex $Li_4[(3e)_3Ti_2]$: Yield: quantitative of a red solid. ^{1}H NMR ([D$_6$]DMSO): δ = 8.26 (s, 6 H), 7.60 (d, J = 8.0 Hz, 6 H), 7.18 (t, J = 8.0 Hz, 6 H), 7.02 (d, J = 8.0 Hz, 6 H), 6.68 (d, J = 7.4 Hz, 6 H), 6.36 (t, J = 7.4 Hz, 6 H), 6.12 (d, J = 7.4 Hz, 6 H) ppm. MS (pos. ESI-MS, methanol): m/z = 1299 $\{Li_3[(\mathbf{3e})_3Ti_2]^+\}$, 646 $\{Li_2[(\mathbf{3e})_3Ti_2]^{2+}\}$, 643 $\{HLi[(\mathbf{3e})_3Ti_2]^{2+}\}$. IR (KBr): $\tilde{\nu}$ = 3412, 1664, 1608, 1551, 1501, 1445, 1286, 1250, 1099, 1053, 924, 855, 789, 742, 712, 671, 617, 519 cm^{-1}. $C_{72}H_{42}Li_4N_6O_{12}Ti_2\cdot 7(C_3H_7NO)\cdot 7H_2O$ (1944.50): calcd. C 57.45, H 5.44, N 9.36; found C 57.71, H 5.11, N 9.27.

Complex $Na_4[(3e)_3Ti_2]$: Yield: quantitative of a red solid. ^{1}H NMR ([D$_6$]DMSO): δ = 8.34 (s, 6 H), 7.65 (d, J = 7.8 Hz, 6 H), 7.25 (t, J = 7.8 Hz, 6 H), 7.11 (d, J = 7.8 Hz, 6 H), 6.78 (d, J = 7.4 Hz, 6 H), 6.44 (t, J = 7.4 Hz, 6 H), 6.21 (d, J = 7.4 Hz, 6 H) ppm. MS (pos. ESI-MS, methanol): m/z = 1347 $\{Na_3[(\mathbf{3e})_3Ti_2]^+\}$, 686 $\{H_2Na_4[(\mathbf{3e})_3Ti_2]^{2+}\}$, 662 $\{Na_2[(\mathbf{3e})_3Ti_2]^{2+}\}$, 640 $\{H_2[(\mathbf{3e})_3Ti_2]^{2+}\}$. IR (KBr): $\tilde{\nu}$ = 2927, 1665, 1610, 1551, 1501, 1446, 1388, 1250, 1213, 1095, 1053, 1006, 923, 854, 789, 741, 711, 666, 617, 519 cm^{-1}. $C_{72}H_{42}Na_4N_6O_{12}Ti_2\cdot 7(C_3H_7NO)\cdot 5H_2O$ (1972.66): calcd. C 56.63, H 5.16, N 9.23; found C 56.99, H 4.55, N 9.14.

Complex $Li_4[(3f)_3Ti_2]$: Yield: quantitative of a red solid. ^{1}H NMR ([D$_6$]DMSO): δ = 8.53 (s, 6 H), 7.89 (br., 6 H), 7.48 (d, J = 7.3 Hz, 6 H), 7.42–7.32 (m, 12 H), 7.14 (d, J = 8.0 Hz, 12 H), 7.04 (d, J = 8.0 Hz, 12 H), 6.93 (d, J = 7.7 Hz, 6 H), 6.30 (t, J = 7.7 Hz, 6 H), 6.06 (d, J = 7.7 Hz, 6 H) ppm. MS (neg. ESI-MS, methanol): m/z = 1869 $\{Li_3[(\mathbf{3f})_3Ti_2]^-\}$, 1864 $\{HLi_2[(\mathbf{3f})_3Ti_2]^-\}$, 1852 $\{H_3[(\mathbf{3f})_3Ti_2]^-\}$, 932 $\{Li_2[(\mathbf{3f})_3Ti_2]^{2-}\}$. IR (KBr): $\tilde{\nu}$ = 3444, 1666, 1618, 1590, 1501, 1446, 1386, 1252, 1209, 744, 666, 599, 514 cm^{-1}. $C_{117}H_{72}Li_4N_6O_{12}Ti_2\cdot 6(C_3H_7NO)\cdot 9H_2O$ (2478.17): calcd. C 65.43, H 5.37, N 6.78; found C 65.38, H 5.31, N 7.36.

Complex $Na_4[(3f)_3Ti_2]$: Yield: quantitative of a red solid. ^{1}H NMR ([D$_6$]DMSO): δ = 8.57 (s, 6 H), 7.91 (br., 6 H), 7.44–7.31 (m, 18 H), 7.17 (d, J = 8.7 Hz, 12 H), 7.06 (d, J = 8.7 Hz, 12 H), 6.99 (dd, J = 7.9, 1.5 Hz, 6 H), 6.34 (t, J = 7.9 Hz, 6 H), 6.12 (dd, J = 7.9, 1.5 Hz, 6 H) ppm. MS (neg. ESI-MS, methanol): m/z = 1918 $\{Na_3[(\mathbf{3f})_3Ti_2]^-\}$, 1896 $\{HNa_2[(\mathbf{3f})_3Ti_2]^-\}$, 1874 $\{H_2Na[(\mathbf{3f})_3Ti_2]^-\}$, 1852 $\{H_3[(\mathbf{3f})_3Ti_2]^-\}$. IR (KBr): $\tilde{\nu}$ = 3442, 1666, 1615, 1588, 1499, 1445, 1386, 1252, 1211, 1093, 743, 664, 595, 513 cm^{-1}. $C_{117}H_{72}Na_4N_6O_{12}Ti_2\cdot 7(C_3H_7NO)\cdot 8H_2O$ (2597.44): calcd. C 63.81, H 5.32, N 7.01; found C 63.60, H 5.35, N 7.10.

Complex $K_4[(3f)_3Ti_2]$: Yield: quantitative of a red solid. ^{1}H NMR ([D$_6$]DMSO): δ = 8.59 (s, 6 H), 7.92 (d, J = 6.9 Hz, 6 H), 7.46–7.30 (m, 18 H), 7.16 (d, J = 8.7 Hz, 12 H), 7.10 (d, J = 8.7 Hz, 12 H), 7.04 (d, J = 7.7 Hz, 6 H), 6.34 (t, J = 7.7 Hz, 6 H), 6.12 (d, J = 7.7 Hz, 6 H) ppm. MS (neg. ESI-MS, methanol): m/z = 1928 $\{HK_2[(\mathbf{3f})_3Ti_2]^-\}$, 923 $\{H_2[(\mathbf{3f})_3Ti_2]^{2-}\}$, 617 $\{H[(\mathbf{3f})_3Ti_2]^{3-}\}$. IR (KBr): $\tilde{\nu}$ = 3430, 1666, 1616, 1587, 1499, 1444, 1386, 1252, 1212, 1094, 781, 742, 663, 511 cm^{-1}. $C_{117}H_{72}K_4N_6O_{12}Ti_2\cdot 6(C_3H_7NO)\cdot 6H_2O$ (2552.75): calcd. C 63.52, H 4.98, N 6.58; found C 63.50, H 5.04, N 6.62.

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