Dinuclear Triple-Stranded Helicates from Rigid Oligo-*p*-phenylene Ligands: Self-Assembly and Ligand Self-Recognition

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The rigid rod oligo-*p*-phenylene type dicatechol ligands **1-3**-H_4 form dinuclear triple-stranded helicates $M_4[(\mathbf{1}–\mathbf{3})_3Ti_2]$ in the presence of appropriate counterions (M = Li, Na, K, or NH_4). Studies on the self-recognition ability of the ligands show that self-recognition takes place if mixtures of ligands with significantly different sizes (**1**/**2**) are used in coordination studies, or if ligands are used which do not match for geometric reasons (**1**/**4**). Mixtures of ligands with a similar geometric preference (**2**/**5**) do not lead to self-recognition, but instead give mixtures of hetero- and homoleptic complexes.

Introduction

Supramolecular aggregates are formed from molecular components by non-covalent interactions. The geometrical and electronic information contained in the single building blocks controls the success of the formation of a supermolecule. For a rational design of non-covalently linked structures it is important to understand the factors that control self-assembly processes such as, for example, supramolecular stereochemistry, regiochemistry or templating effects.[1,2]

We are interested in the chemistry of helicates[3−7] and of related complexes[8−12] because those simple supramolecular coordination compounds allow the study of a variety of mechanistic aspects of self-assembly processes. In this context, we have found a way to control the diastereoselectivity[13] and the regioselectivity of complex formation.[14] In addition we have investigated the ligand self-recognition during helicate or meso-helicate formation and found a template control of this process.[15] This is an option for "ligand self-recognition" in addition to the examples described by Lehn,[16] Raymond[17] or Stack,[18,19] where different numbers of metal binding sites, preferred coordination geometry at the metal centers, different ligand length, or chirality is used to control the self-recognition.

The formation of the titanium(IV) complex $K_4[(\mathbf{2})_3Ti_2]$ has already been discussed and its X-ray structural analysis communicated.[20] In this paper, we report the titanium(IV) coordination chemistry of the rigid oligo-*p*-phenylene derivatives **1-3**-H_4, with two catechol binding sites, in the presence of different cations (Li^+, Na^+, K^+) and we introduce them into ligand self-recognition experiments.

Results and Discussion

Coordination Studies

The rigid ligands **1**-H_4, **2**-H_4, and **3**-H_4 (Figure 1) were prepared by use of a Suzuki coupling as a key step in the synthetic procedure. The linear oligo-*p*-phenylene derivatives **1-3**-H_4 have different lengths [9.2 (**1**-H_4), 13.5 (**2**-H_4), and 17.8 Å (**3**-H_4)] and the metal binding sites (catechol units) are fixed at defined distances to each other.[21] However, there is some flexibility at the C(aryl)−C(aryl) single bonds.

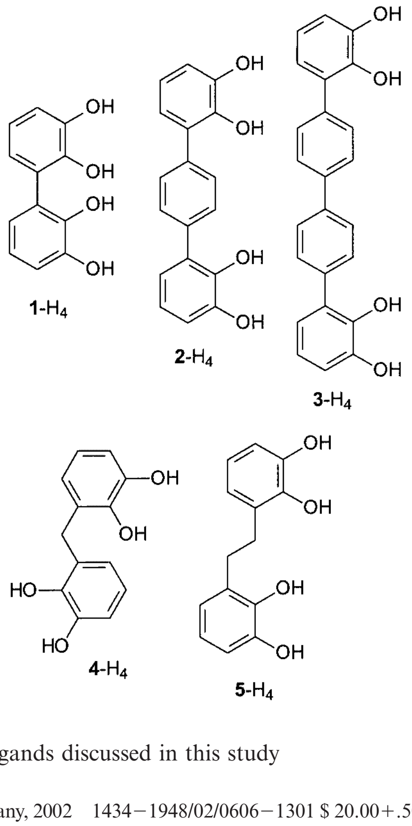

Figure 1. Ligands discussed in this study

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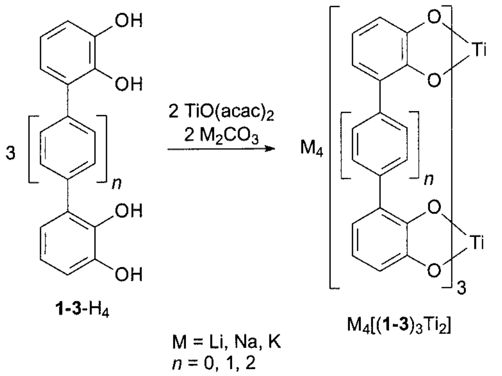
Dinuclear titanium(IV) complexes $M_4[(\mathbf{1-3})_3Ti_2]$ (M = Li, Na, K) of the ligands $\mathbf{1}$-H_4, $\mathbf{2}$-H_4, and $\mathbf{3}$-H_4 were obtained upon stirring a mixture of the ligand (3 equiv.), $TiO(acac)_2$ (2 equiv.) and the corresponding alkali metal carbonate (2 equiv.) in methanol (Scheme 1). After removal of the solvent a red solid material was obtained, which was purified by filtration through Sephadex LH 20.



Scheme 1. Formation of triple-stranded helicates $M_4[(\mathbf{1-3})_3Ti_2]$

The smallest ligand $\mathbf{1}$-H_4, with a direct connection of the two catechol moieties, affords dinuclear triple-stranded helicates $M_4[(\mathbf{1})_3Ti_2]$ (M = Li, Na, K) in 61% to quantitative yield. The positive FAB MS spectra show peaks at m/z = 766 $[Li_4\{(\mathbf{1})_3Ti_2\}]^+$ and 760 $[Li_3\{(\mathbf{1})_3Ti_2\}H]^+$, m/z = 809 $[Na_3\{(\mathbf{1})_3Ti_2\}H_2]^+$ and 787 $[Na_2\{(\mathbf{1})_3Ti_2\}H_3]^+$, and m/z = 895 $[K_4(\{(\mathbf{1})_3Ti_2\}H]^+$, 857 $[K_3\{(\mathbf{1})_3Ti_2\}H_2]^+$ and 818 $[K_2\{(\mathbf{1})_3Ti_2\}H_3]^+$ revealing that the helicates are made up from three ligands and two titanium(IV) ions. To our surprise the ^1H NMR spectra of all three compounds were significantly different. The lithium and sodium compounds show a pattern of two doublets of doublets and one (pseudo)triplet at δ = 6.57 (dd), 6.47 (pt), and 6.28 (dd) ($Li_4[(\mathbf{1})_3Ti_2]$) and at δ = 6.62 (dd), 6.56 (pt), and 6.35 (dd) ($Na_4[(\mathbf{1})_3Ti_2]$). For the potassium salt $K_4[(\mathbf{1})_3Ti_2]$ two multiplets are observed at δ = 6.53 (12 H) and 6.34 (6 H).

The different ^1H NMR spectra indicate that the different countercations bind to the triple-stranded dinuclear titanium complex anion $[(\mathbf{1})_3Ti_2]^{4-}$ and thus lead to different anisotropic effects at the ligand protons. However, in contrast to earlier observations, this binding cannot proceed by encapsulation of the cation. The interior of the anion $[(\mathbf{1})_3Ti_2]^{4-}$, which is formed from three ligands $\mathbf{1}$, is too small for the binding of an alkali metal cation. Binding has to occur from the outside of the cavity as was observed for the titanium(IV) complexes of ligand $\mathbf{4}$. However, in the case of the titanium complex of ligand $\mathbf{4}$ a dinuclear species $[(\mathbf{4})_3Ti_2]^{4-}$ can only be stabilized by sodium and lithium cations; potassium destabilizes this complex and leads to a mixture of oligomeric coordination compounds.[22,23] In contrast to the flexible methylene-bridged ligand $\mathbf{4}$ the rigid derivative $\mathbf{1}$ seems to be more preorganized for the formation of dinuclear helicate-type complexes $[(\mathbf{1})_3Ti_2]^{4-}$, and therefore the formation of the dinuclear species does not depend on the countercation which is present. Due to the fixed geometry of the ligand the dinuclear complexes seem to be favored over oligonuclear complexes. $[(\mathbf{1})_3Ti_2]^{4-}$ can even be formed in the presence of ammonium cations, although this cation does not seem to be able to stabilize the dinuclear complex very well and therefore no pure compound which shows a correct elemental analysis could be isolated. Characteristic ^1H NMR signals can be observed at δ = 6.83 (dd), 6.69 (pt), and 6.40 (dd).

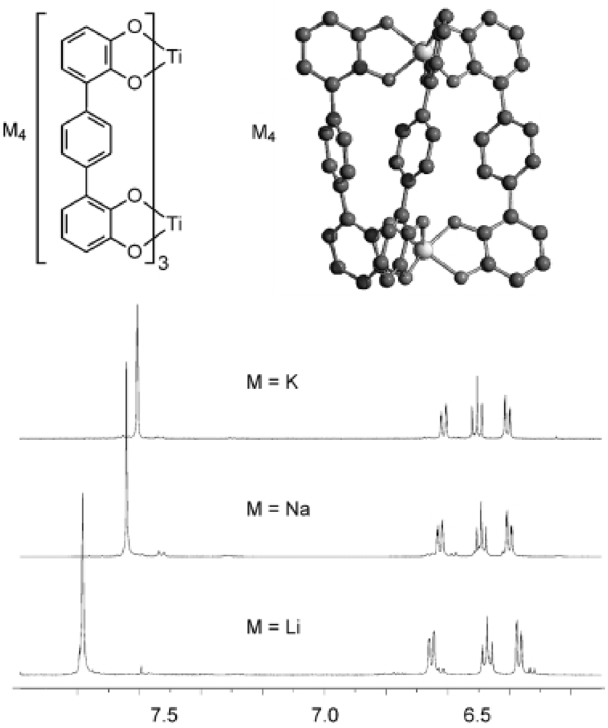


Figure 2. Dinuclear helicates $M_4[(\mathbf{2})_3Ti_2]$, a representation of the X-ray structure of $K_4[(\mathbf{2})_3Ti_2]$[20] and ^1H NMR spectra in [D4]methanol

The formation and the X-ray structure (Figure 2, top) of the potassium salt $K_4[(\mathbf{2})_3Ti_2]$ of the *p*-phenylene bridged ligand $\mathbf{2}$-H_4 was already been communicated by us.[20] A triple-stranded helicate structure $[(\mathbf{2})_3Ti_2]^{4-}$ was found which encapsulates two of the potassium counterions and which forms a dimer by DMF bridges between two potassium cations in the solid state. The two triple-stranded helicates of this dimer possess opposite helicity resulting in a *meso* configuration.[20]

The sodium and lithium salts $M_4[(\mathbf{2})_3Ti_2]$ can also be obtained. Figure 2 (bottom) shows a comparison of the ^1H NMR spectra of the three salts $M_4[(\mathbf{2})_3Ti_2]$ (M = Li, Na, K) in [D4]methanol. At relatively high field two doublets of doublets [δ = 6.37 (Li), 6.40 (Na), 6.41 (K) and δ = 6.65 (Li), 6.63 (Na), 6.61 (K)] and a pseudo triplet [δ = 6.47 (Li), 6.49 (Na), and 6.50 (K)] are observed which show no significant shift differences for the three different alkali metal salts. However, the shift of the protons at the bridging *p*-phenylene moiety depends highly on the countercation which is present. Singlets are observed at δ = 7.78 (Li), 7.64 (Na), and 7.60 (K) for this proton. The observed NMR spectroscopic features indicate that one (or maybe two) of the cations of $M_4[(\mathbf{2})_3Ti_2]$ are bound in the interior of the cavity formed by the three ligand strands **2** and the two titanium(IV) ions. Thus, they are located close to the protons of the spacer and lead to different shifts for the corresponding ^{1}H NMR resonances. The aromatic catechol hydrogen atoms are far away and experience the presence of the cations only in a very moderate way.

Due to the low solubility of the complexes $M_4[(\mathbf{2})_3Ti_2]$ (as well as $M_4[(\mathbf{3})_3Ti_2]$) in the FAB MS matrix (e.g., glycerine, 3-NBA) only poorly resolved positive FAB MS spectra could be obtained. Signals of the dinuclear complexes can be detected but show an extremely low intensity.

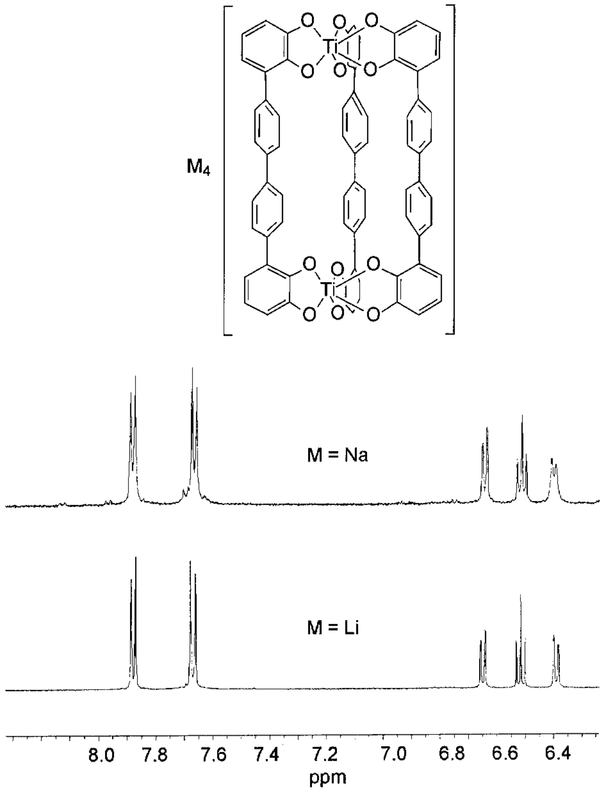


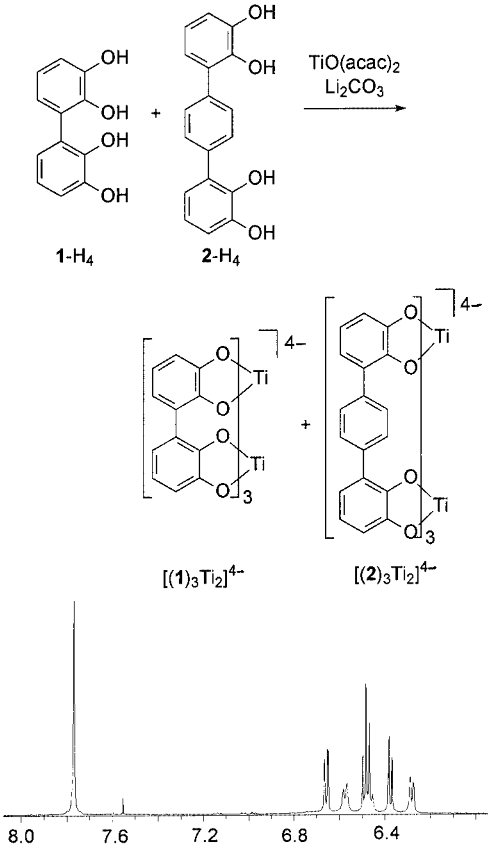
Figure 3. ^{1}H NMR spectra of $M_4[(\mathbf{3})_3Ti_2]$ in [D$_4$]methanol

Dinuclear complexes $M_4[(\mathbf{3})_3Ti_2]$ of ligand **3** (Figure 3) are formed only with sodium or lithium as countercations. With potassium as a cation we rather surprisingly could not obtain a well-defined titanium(IV) complex. The ^{1}H NMR spectra of the two salts $Li_4[(\mathbf{3})_3Ti_2]$ and $Na_4[(\mathbf{3})_3Ti_2]$ in [D$_4$]methanol (Figure 3) are very similar with signals at δ = 7.88 (d), 7.67/7.66 (d, Li/Na), 6.65/6.64 (dd), 6.52/6.51 (pt), and 6.39 (dd). The tetraanion $[(\mathbf{3})_3Ti_2]^{4-}$ possesses a huge internal cavity where it is supposed that lithium or sodium cations can be weakly bound in the interior but can be exchanged very fast.

Self-Recognition Studies

Raymond showed in 1997 that amide-bridged rigid linear dicatechol ligands with significantly different distances between metal binding sites can be introduced into self-recognition experiments and that, upon complex formation with gallium(III) ions, self-sorting of the ligands takes place and only homoleptic complexes (every metal complex contains only one kind of ligand) could be observed.[17] We showed that with alkyl-bridged dicatechol ligands ($\mathbf{4}$-H$_4$, $\mathbf{5}$-H$_4$) the formation of specific dinuclear titanium(IV) complexes is highly dependent on the templating alkali metal countercation.[15]

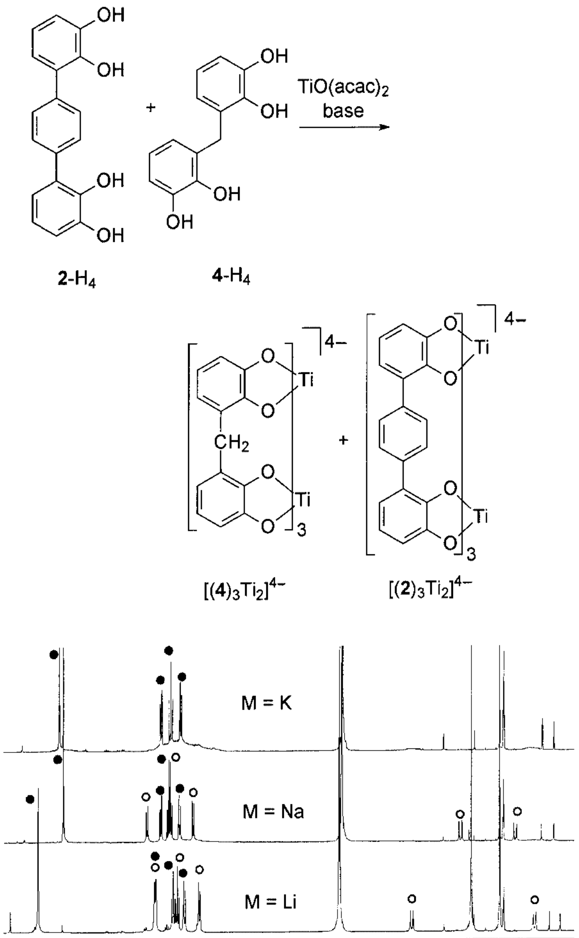
In a first investigation we mixed the two ligands $\mathbf{1}$-H$_4$ and $\mathbf{2}$-H$_4$ (ratio 1:1) and performed coordination studies with titanium(IV) ions in the presence of lithium carbonate (Na_2CO_3 and K_2CO_3 as base lead to essentially the same results).



Scheme 2. Self-recognition experiment with a mixture of ligands $\mathbf{1}$-H$_4$ and $\mathbf{2}$-H$_4$ leading to homoleptic complexes by self-sorting

In Scheme 2 (bottom) the ^{1}H NMR spectrum of the self-recognition experiment with ligands **1** and **2** is presented, showing that only the two homoleptic complexes $Li_4[(\mathbf{1})_3Ti_2]$ and $Li_4[(\mathbf{2})_3Ti_2]$ are present. The signals of $Li_4[(\mathbf{1})_3Ti_2]$ appear at δ = 6.57 (d), 6.47 (pt), and 6.28 (d) while those of $Li_4[(\mathbf{2})_3Ti_2]$ are observed at δ = 7.77 (s), 6.66 (dd), 6.48 (pt), and 6.37 (dd). The ^{13}C NMR spectra also show only the signals of the two homoleptic coordination compounds. In this experiment we observed the same control mechanism as was described earlier by Raymond:[17] rigid linear ligands self-sort in self-recognition experiments due to the match (or mismatch) of the separation of the metal coordination sites.

In an additional experiment we mixed the rigid derivative $\mathbf{2}$-H$_4$ with the more flexible ligands $\mathbf{4}$-H$_4$ or $\mathbf{5}$-H$_4$. The result of the coordination studies with a $\mathbf{2}$-H$_4$/$\mathbf{4}$-H$_4$ mixture (1:1) depends strongly on the templating cation which is present. It was shown earlier that the dinuclear complex $[(\mathbf{4})_3Ti_2]^{4-}$ only assembles in the presence of lithium or sodium cations, while the larger potassium cation leads to the formation of a mixture of oligomeric complexes. This has to be taken into account when the self-recognition studies are performed.



Scheme 3. Alkali metal cation dependant self-recognition of the ligands **2**-H_4 and **4**-H_4. ($[(\mathbf{2})_3Ti_2]^{4-}$: •; $[(\mathbf{4})_3Ti_2]^{4-}$: ○)

Scheme 3 shows the NMR spectra of the crude product of the reaction of a mixture of **2**- and **4**-H_4 (1:1) with titanium(IV) ions in the presence of alkali metal carbonates. If the experiment is performed with potassium carbonate the dinuclear helicate complex $K_4[(\mathbf{2})_3Ti_2]$ can be observed in the ^1H NMR spectrum ([D$_4$]methanol) at $\delta = 7.58$, 6.61, 6.52, and 6.42. (The shifts differ slightly from those observed for the pure complex due to the presence of several different species in solution.) No resolved resonances can be assigned to a titanium complex of ligand **4**. However, according to our earlier results,[22] broad signals of oligomeric material $\{K_4[(\mathbf{4})_3Ti_2]\}_n$ are detected at $\delta = 4.20$, 3.03 and in the region of aromatic signals. With lithium or sodium carbonate, however, nicely resolved NMR spectra are obtained showing the formation of only homoleptic complexes $M_4[(\mathbf{2})_3Ti_2]$ and $M_4[(\mathbf{4})_3Ti_2]$ by self-recognition of the dicatecholates. In Scheme 3 the signals of the dinuclear complex $[(\mathbf{2})_3Ti_2]^{4-}$ are marked with a• and those of $[(\mathbf{4})_3Ti_2]^{4-}$ with a ○. No significant amounts of additional metal complexes were observed.

If a similar self-recognition experiment is performed with a mixture of ligands **2**-H_4 and **5**-H_4, no specific titanium(IV) complexes could be observed by NMR spectroscopy. An unspecific complex formation takes place.

The discrepancy in the results obtained in the self-recognition experiments of ligand **2** and **4** or **2** and **5** shows that subtle changes in the system can be important for observing selectivity in self-assembly processes. The ligand **5**-H_4 possesses only one methylene unit more in the spacer than **4**-H_4. This results in a somewhat larger separation of the binding sites and, maybe even more importantly, also results in a dramatic difference in the geometry of the compound.

Due to the rigidity of ligand **2**-H_4 only helical structures can be obtained in the dinuclear coordination compounds $[(\mathbf{2})_3Ti_2]^{4-}$ (for a non-helical complex the ligand has to adopt a very strained "C" type conformation). The ligand **4**-H_4, on the other hand, is predisposed to form the *meso*-helicate $[(\mathbf{4})_3Ti_2]^{4-}$ with two oppositely configured complex units. Therefore the geometries of the two ligands **2** and **4** do not match and only homoleptic complexes can be formed. Ligand **5**, like **2**, is predisposed for the formation of dinuclear helicates, so that for geometric reasons a matched situation results between those two ligands. No specificity is found in the coordination study.

Here the self-recognition in the formation of $[(\mathbf{2})_3Ti_2]^{4-}$ and $[(\mathbf{4})_3Ti_2]^{4-}$ from a mixture of the two ligands seems to be due to a geometric mismatch of the ligand strands. Thus, molecular recognition of the matching strands during complex formation leads to self-sorting and formation of the homoleptic complexes.

Conclusion

In this paper we have described the formation of dinuclear triple-stranded titanium(IV) helicates from rigid rod-type dicatechol ligands **1-3**-H_4 with two binding sites for metals. The formation of these coordination compounds seems not to be templated by the countercation, although interaction of the cations with the tetraanionic complexes $[(\mathbf{1/2})_3Ti_2]^{4-}$ can be deduced from the ^1H NMR spectra. Obviously the linear rigid ligand systems are suitably preorganized for the formation of dinuclear helicates.

In self-recognition studies with titanium(IV) ions a mixture of the derivatives **1**-H_4 and **2**-H_4 leads to the formation of only homoleptic complexes $[(\mathbf{1})_3Ti_2]^{4-}$ and $[(\mathbf{2})_3Ti_2]^{4-}$. This complex formation is controlled by the different length of the ligands.

Self recognition also takes place if a mixture of derivatives **2**-H_4 and **4**-H_4 is used, although not with a mixture of **2**-H_4 and **5**-H_4. Here a mismatch of the ligand geometries of **2** and **4** is supposed which leads to the formation of dinuclear complexes with only one kind of ligand. In the case of **2** and **5**, however, both ligands possess a geometry that is ideal for the formation of helical complexes and therefore the geometric match of the derivatives prevents self-recognition.

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer using DEPT techniques for the assignment of the multiplicity of carbon atoms. FT-IR spectra were recorded by diffuse reflection (KBr) on a Bruker IFS spectrometer. UV/Vis spectra were recorded on a Perkin−Elmer Lambda 2 spectrometer. Mass spectra (EI, 70 eV) were recorded on a Finnigan MAT 90 mass spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyzer. All commercial reagents were purchased from Aldrich or Fluka. The ligands **1-3**-H$_4$ and **4/5**-H$_4$ were prepared as described previously.[21,24,25]

General Procedure for the Preparation of Dinuclear Titanium(IV) Complexes: A mixture of ligand (3 equiv.), TiO(acac)$_2$ (2 equiv.) and alkali metal carbonate (2 equiv.) in methanol was stirred overnight until a clear red solution had formed. The solvent was then removed under vacuum and the residue purified by filtration through Sephadex LH 20.

Li$_4$[(1)$_3$Ti$_2$]: Yield: 56 mg (100%), orange solid. ^{1}H NMR ([D$_4$]methanol): δ = 6.28 (dd, J = 7.7, 1.4 Hz, 6 H), 6.47 (pt, J = 7.7 Hz, 6 H), 6.57 (dd, J = 7.7, 1.4 Hz, 6 H). ^{13}C NMR ([D$_4$]methanol): δ = 111.0 (CH), 118.8 (CH), 122.1 (CH), 126.1 (C), 157.3 (C), 157.5 (C). IR (KBr): $\tilde{\nu}$ = 3371, 3057, 1602, 1519, 1420, 1250, 1181, 1135, 1059, 996, 871, 777, 742, 711 cm^{-1}. Positive FAB MS (3-NBA): *m/z* = 766 [Li$_4${(**1**)$_3$Ti$_2$}]$^+$, 760 [Li$_3${(**1**)$_3$Ti$_2$H}]$^+$. UV/Vis (methanol): λ = 214, 352 nm. $C_{36}H_{18}Li_4O_{12}Ti_2\cdot12H_2O$ (982.28): calcd. C 44.02, H 4.31; found C 43.74, H 4.13.

Na$_4$[(1)$_3$Ti$_2$]: Yield: 31 mg (61%), red solid. ^{1}H NMR ([D$_4$]methanol): δ = 6.35 (dd, J = 7.7, 1.4 Hz, 6 H), 6.56 (pt, J = 7.7 Hz, 6 H), 6.62 (dd, J = 7.7, 1.4 Hz, 6 H). ^{13}C NMR ([D$_4$]methanol): δ = 111.9 (CH), 120.4 (CH), 121.0 (CH), 123.8 (C), 155.4 (C), 157.7 (C). IR (KBr): $\tilde{\nu}$ = 3421, 3053, 1700, 1420, 1251, 1056, 998, 871, 778, 698, 647, 617 cm^{-1}. Positive FAB MS (3-NBA): *m/z* = 809 [Na$_3${(**1**)$_3$Ti$_2$}H$_2$]$^+$, 787 [Na$_2${(**1**)$_3$Ti$_2$}H$_3$]$^+$. UV/Vis (methanol): λ = 215, 354 nm. $C_{36}H_{18}Na_4O_{12}Ti_2\cdot8H_2O$ (974.41): calcd. C 44.37, H 3.52; found C 44.54, H 3.97.

K$_4$[(1)$_3$Ti$_2$]: Yield: 42 mg (84%), red solid. ^{1}H NMR ([D$_4$]methanol): δ = 6.34 (m, 6 H), 6.53 (m, 12 H). ^{13}C NMR ([D$_4$]methanol): δ = 111.9 (CH), 119.6 (CH), 119.9 (CH), 123.7 (C), 156.8 (C), 157.5 (C). IR (KBr): $\tilde{\nu}$ = 3403, 3051, 1421, 1251, 1055, 999, 871, 774, 646, 615 cm^{-1}. Positive FAB MS (3-NBA): *m/z* = 895 [K$_4${(**1**)$_3$Ti$_2$}H]$^+$, 857 [K$_3${(**1**)$_3$Ti$_2$}H$_2$]$^+$, 818 [K$_2${(**1**)$_3$Ti$_2$}H$_3$]$^+$. UV/Vis (methanol): λ = 214, 360 nm. $C_{36}H_{18}K_4O_{12}Ti_2\cdot9H_2O$ (1056.86): calcd. C 40.91, H 3.43; found C 41.25, H 3.50.

(NH$_4$)$_4$[(1)$_3$Ti$_2$]: A red solid is obtained by use of ammonium acetate as base. ^{1}H NMR ([D$_4$]methanol): δ = 6.40 (dd, J = 7.8, 1.1 Hz, 6 H), 6.69 (pt, J = 7.8 Hz, 6 H), 6.83 (dd, J = 7.8, 1.1 Hz, 6 H). IR (KBr): $\tilde{\nu}$ = 3237, 3061, 1558, 1420, 1251, 1114, 1057, 993, 871, 773, 713 cm^{-1}. UV/Vis (methanol): λ = 214, 355 nm.

Li$_4$[(2)$_3$Ti$_2$]: Yield: 28 mg (100%), red solid. ^{1}H NMR ([D$_4$]methanol): δ = 6.37 (dd, J = 7.7, 1.2 Hz, 6 H), 6.47 (pt, J = 7.7 Hz, 6 H), 6.65 (dd, J = 7.7, 1.2 Hz, 6 H),7.78 (s, 12 H). ^{13}C NMR ([D$_4$]methanol): δ = 111.2 (CH), 117.3 (CH), 118.3 (CH), 125.8 (C), 129.4 (CH, double intensity), 138.6 (C), 158.4 (C), 160.6 (C). IR (KBr): $\tilde{\nu}$ = 3528, 3056, 1617, 1520, 1448, 1392, 1329, 1255, 1218, 1170, 1093, 1058, 918, 893, 782, 737, 688, 640 cm^{-1}. UV/Vis: λ = 206, 278 nm. $C_{54}H_{30}Li_4O_{12}Ti_2\cdot8H_2O$ (1138.51): calcd. C 56.97, H 4.07; found C 57.27, H 4.53.

Na$_4$[(2)$_3$Ti$_2$]: Yield: 84 mg (100%), orange solid. ^{1}H NMR ([D$_4$]methanol): δ = 6.40 (dd, J = 7.7, 1.4 Hz, 6 H), 6.49 (pt, J = 7.7 Hz, 6 H), 6.63 (dd, J = 7.7, 1.4 Hz, 6 H), 7.64 (s, 12 H). ^{13}C NMR ([D$_4$]methanol): δ = 111.5 (CH), 118.1 (CH), 118.3 (CH), 125.8 (C), 129.5 (CH, double intensity), 138.9 (C), 158.4 (C), 160.6 (C). IR (KBr): $\tilde{\nu}$ = 3567, 3422, 3054, 1635, 1559, 1517, 1447, 1390, 1330, 1252, 1220, 1092, 1058, 917, 839, 783, 735, 683, 636 cm^{-1}. UV/Vis (methanol): λ = 205, 273 nm. $C_{54}H_{30}Na_4O_{12}Ti_2\cdot10H_2O$ (1238.74): calcd. C 52.36, H 4.07; found C 52.39, H 4.03.

K$_4$[(2)$_3$Ti$_2$]: Yield: 50 mg (100%), red solid. ^{1}H NMR ([D$_4$]methanol): δ = 6.41 (dd, J = 7.7, 1.4 Hz, 6 H), 6.50 (pt, J = 7.7 Hz, 6 H), 6.61 (dd, J = 7.7, 1.4 Hz, 6 H), 7.60 (s, 12 H). ^{13}C NMR ([D$_4$]methanol): δ = 111.6 (CH), 118.1 (CH), 118.5 (CH), 125.5 (C), 129.7 (CH, double intensity), 139.3 (C), 158.3 (C), 160.7 (C). IR (KBr): $\tilde{\nu}$ = 3404, 3052, 1630, 1517, 1446, 1390, 1333, 1252, 1093, 1057, 917, 838, 783, 735, 635 cm^{-1}. UV/Vis (methanol): λ = 205, 270 nm. $C_{54}H_{30}K_4O_{12}Ti_2\cdot8H_2O$ (1267.14): calcd. C 51.19, H 3.66; found C 51.10, H 3.58.

Li$_4$[(3)$_3$Ti$_2$]: Yield: 26 mg (48%), orange solid. ^{1}H NMR ([D$_4$]methanol): δ = 6.39 (dd, J = 7.7, 1.2 Hz, 6 H), 6.52 (pt, J = 7.7 Hz, 6 H), 6.65 (dd, J = 7.7, 1.2 Hz, 6 H), 7.67 (d, J = 8.3 Hz, 12 H), 7.88 (d, J = 8.3 Hz, 12 H). ^{13}C NMR ([D$_4$]methanol): δ = 111.5 (CH), 118.5 (CH), 118.7 (CH), 125.4 (C), 127.0 (CH, double intensity), 130.7 (CH, double intensity), 139.5 (C), 140.1 (C), 158.1 (C), 160.8 (C). IR (KBr): $\tilde{\nu}$ = 3617, 3055, 3026, 1609, 1444, 1391, 1333, 1252, 1219, 1102, 1059, 1005, 916, 849, 828, 782, 765, 738, 678, 628 cm^{-1}. UV/Vis (methanol): λ = 210, 304 nm. $C_{72}H_{42}Li_4O_{12}Ti_2\cdot7H_2O$ (1348.79): calcd. C 64.12, H 4.18; found C 64.06, H 4.51.

Na$_4$[(3)$_3$Ti$_2$]: Yield: 18 mg (34%), orange solid. ^{1}H NMR ([D$_4$]methanol): δ = 6.39 (d, J = 7.4 Hz, 6 H), 6.51 (pt, J = 7.4 Hz, 6 H), 6.64 (d, J = 7.4 Hz, 6 H), 7.66 (d, J = 8.1 Hz, 12 H), 7.88 (d, J = 8.1 Hz, 12 H). ^{13}C NMR ([D$_4$]methanol): δ = 111.6 (CH), 118.1 (CH), 118.7 (CH), 125.1 (C), 127.2 (CH, double intensity), 130.7 (CH, double intensity), 139.5 (C), 140.4 (C), 158.2 (C), 161.2 (C). IR (KBr): $\tilde{\nu}$ = 3454, 3052, 1606, 1502, 1443, 1251, 1222, 1102, 1058, 916, 846, 828, 783, 765, 738, 673, 627 cm^{-1}. UV/Vis (methanol): λ = 209, 303 nm. $C_{72}H_{42}Na_4O_{12}Ti_2\cdot7H_2O$ (1412.99): calcd. C 60.43, H 4.09; found C 60.26, H: 4.44.

General Procedure for the Self-Recognition Studies: Ligand **A** (1.5 equiv.), ligand **B** (1.5 equiv.) TiO(acac)$_2$ (2 equiv.) and alkali metal carbonate (2 equiv.) were stirred overnight in methano until a clear red solution had formed. The solvent was removed under vacuum and the residue analyzed by ^{1}H and ^{13}C NMR spectroscopy.

Self-Recognition Studies with a 1:1 Mixture of Ligands 1-H$_4$ and 2-H$_4$ in the Presence of Lithium Carbonate: ^{1}H NMR ([D$_4$]methanol): δ = 6.28 (br. d, J = 7.1 Hz, 6 H), 6.37 (dd, J = 7.8, 1.4 Hz, 6 H), 6.47 (pt, J = 7.1 Hz, 6 H), 6.48 (t, J = 7.8 Hz, 6 H), 6.57 (br. d, J = 7.1 Hz, 6 H), 6.66 (dd, J = 7.8, 1.4 Hz, 6 H), 7.77 (s, 12 H). ^{13}C NMR ([D$_4$]methanol): δ = 111.0 (CH), 111.2 (CH), 117.3 (CH), 118.3 (CH), 118.8 (CH), 122.1 (CH), 125.8 (C), 126.1 (C), 129.4 (CH), 138.6 (C), 157.3 (C), 157.5 (C), 158.4 (C), 160.6 (C).

Self-Recognition Studies with a 1:1 Mixture of Ligands 2-H$_4$ and 4-H$_4$

Lithium Carbonate as Base: ^{1}H NMR ([D$_4$]methanol): δ = 3.01 (d, J = 12.9 Hz, 3 H), 4.19 (d, J = 12.9 Hz, 3 H), 6.28 (dd, J = 7.2, 1.1 Hz, 6 H), 6.39 (dd, J = 7.8, 1.4 Hz, 6 H), 6.47 (pt, J = 7.2 Hz, 6 H), 6.49 (pt, J = 7.8 Hz, 6 H), 6.66 (dd, J = 7.8, 1.4 Hz, 6 H), 6.67 (dd, J = 7.2, 1.1 Hz, 6 H), 7.78 (s, 12 H). ^{13}C NMR ([D$_4$]methanol): δ = 31.9 (CH$_2$), 111.0 (CH), 111.2 (CH), 117.9 (CH), 118.3 (CH), 119.0 (CH), 122.0 (CH), 125.9 (C), 127.6 (C), 129.4 (CH), 138.6 (C), 156.9 (C), 158.1 (C), 158.3 (C), 160.6 (C).

Sodium Carbonate as Base: ^{1}H NMR ([D$_4$]methanol): δ = 3.20 (d, J = 13.4 Hz, 3 H), 3.72 (d, J = 13.4 Hz, 3 H), 6.30 (dd, J = 7.8, 1.1 Hz, 6 H), 6.43 (dd, J = 7.8, 1.4 Hz, 6 H), 6.52 (pt, J = 7.8 Hz, 6 H), 6.54 (pt, J = 7.8 Hz, 6 H), 6.61 (dd, J = 7.8, 1.4 Hz, 6 H), 6.74 (dd, J = 7.8, 1.1 Hz, 6 H), 7.54 (s, 12 H). ^{13}C NMR ([D$_4$]methanol): δ = 31.5 (CH$_2$), 111.7 (CH), 111.7 (CH), 118.4 (CH), 118.4 (CH), 120.2 (CH), 122.8 (CH), 126.1 (CH), 126.8 (C), 129.6 (CH), 139.0 (C), 155.7 (C), 157.9 (C), 158.4 (C), 160.3 (C).

Potassium Carbonate as Base: ^{1}H NMR ([D$_4$]methanol): δ = 6.42 (dd, J = 7.7, 1.4 Hz, 6 H), 6.52 (pt, J = 7.7 Hz, 6 H), 6.61 (dd, J = 7.7, 1.4 Hz, 6 H), 7.58 (s, 12 H); additional broad signals were detected at δ = 4.20 and 3.03 as well as in the aromatic region. ^{13}C NMR ([D$_4$]methanol): δ = 111.7 (CH), 118.3 (CH), 118.5 (CH), 125.6 (C), 129.8 (CH), 139.4 (C), 158.3 (C), 160.6 (C).

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