Dynamic Behavior of Anionic Binuclear Helicate- and *meso*-Helicate-Type Coordination Compounds

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The racemization/symmetrization of helicate- or *meso*-helicate-type dinuclear titanium(IV) complexes $M_n[(ligand)_3Ti_2]$ ($n = 4$: M = Li, Na, K, Cs; $n = 2$: M = Ca, Sr), which are formed by metal-directed self-assembly of alkyl-bridged bis(catecholate) ligands in the presence of basic alkali-metal or alka-line-earth metal salts, can be monitored by dynamic NMR spectroscopy. The free-energy barrier (ΔG^+) of this process is influenced by the nature of the ligand, the solvent, and the counterion.

Non-covalent interactions between complementary units lead to the formation of defined supramolecular species with defined properties[1]. In metallo-supramolecular chemistry the metals are building blocks which play an active part in the molecular recognition process and thus influence the formation as well as the properties of the obtained aggregates[2].

Dinuclear triple-stranded helicate- or *meso*-helicate-type coordination compounds are formed in spontaneous and cooperative self-assembly processes from three linear ligand strands, each bearing two chelating units, and two metal ions[3–6]. Recently, we introduced alkyl-bridged bis(catecholate) ligands as organic components for such self-assembly processes. We demonstrated that the relative stereochemis-

Figure 1. Enantiomerization of a helicate ($\Delta\Delta \rightarrow \Lambda\Lambda$) and symmetrization of a *meso*-helicate ($\Delta_1\Lambda_2 \rightarrow \Lambda_1\Delta_2$)


helicate (Δ,Δ-form)	helicate (Λ,Λ-form)

meso-helicate (Δ_1,Λ_2-form)	*meso*-helicate (Λ_1,Δ_2-form)

try of the two complex units depends on the nature of the alkyl spacer. Ligands with an even number of methylene units form the chiral helicate[5]; ligands with an odd number lead to the achiral *meso*-helicate[6].

In the solid state as well as in solution, the cryptand-type tetraanionic dinuclear titanium complexes are able to bind one (or more) of the counterions. Therefore, the counterions are not merely "innocent spectators", but are integral parts of the molecular structures and thus should influence the self-assembly process as well as the properties of the formed dinuclear complexes. An important property, which is observed for the catecholate helicates and *meso*-helicates, is the inversion of the configuration at the metal centers. This process can be monitored by dynamic ¹H-NMR spectroscopy by observing the diastereotopic protons of the alkyl spacer[5,7].

In this paper we describe a detailed study of the dynamic behavior of dinuclear titanium(IV) complexes with the linear alkyl-bridged ligands $1\text{-}H_4\text{–}4\text{-}H_4$[8]. The influence of the spacer length, the solvent, and of the alkali-metal or alkaline-earth metal counterions on such systems is investigated.

Results and Discussion

Preparation of the Complexes

The dinuclear coordination compounds $M_4[(L)_3Ti_2]$ (L = **1–4**, M = Li, Na, K; L = **2**, M = Cs) were obtained from three equivalents of the ligand $1\text{-}H_4\text{–}4\text{-}H_4$ (L-H$_4$) and two equivalents of $[(acac)_2TiO]$ in the presence of two equivalents of alkali-metal carbonate in methanol. Removal of the solvent afforded the dinuclear complexes in good to quantitative yields. When further purification was necessary, this could be achieved by chromatography on Sephadex LH 20 with methanol as solvent. The corresponding salts with alkaline-earth metal cations $M'_2[(2)_3Ti_2]$ (M' = Ca, Sr) were also prepared. The calcium compound was synthesized in a similar manner as the aforementioned alkali-metal salts, while $Sr_2[(2)_3Ti_2]$ could only be obtained when DMF was
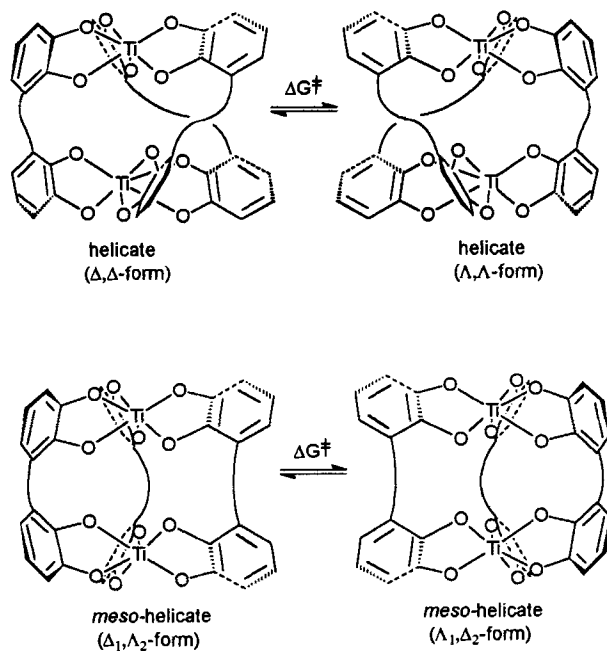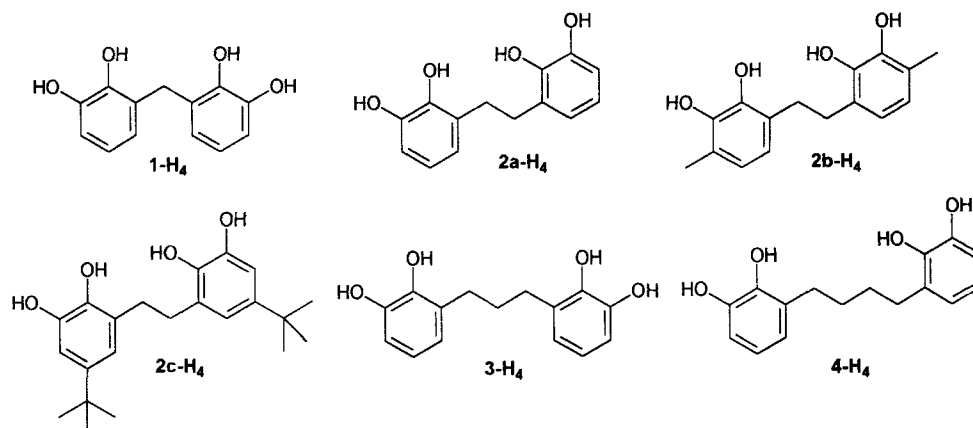
Figure 2. Ligands discussed in this study

used as solvent. No defined complexes could be isolated for M' = Mg or Ba.

The coordination compounds were characterized by NMR and IR spectroscopy and their stoichiometries and molecular masses were established by elemental analyses and FAB mass spectrometry.

NMR-Spectroscopic Studies at Variable Temperature

The ¹H-NMR spectra of the lithium and sodium salts of $[(1)_3Ti_2]^{4-}$ in [D₄]methanol feature two doublets for the diastereotopic protons of the methylene spacer at $\delta = 4.20$ and 2.99 (M = Li, $J = 12.8$ Hz) and $\delta = 3.73$ and 3.19 (M = Na, $J = 13.5$ Hz), respectively. This indicates that the complex possesses the same meso-helicate structure in solution as was observed in the solid state[6]. If $[(1)_3Ti_2]^{4-}$ were to adopt a helical structure or if a fast inversion (on the NMR time scale) of the complex units were to take place, only one resonance would be detected for the methylene protons. The difference in shifts observed for the protons of the lithium and sodium compounds reveals that the cations are in close contact with the anions. Upon heating of the NMR samples, the spectra remain unchanged up to 333 K. Thus, $M_4[(1)_3Ti_2]$ (M = Li, Na) possesses a remarkable configurational stability, which is attributable to the rigidity of this methylene-bridged system.

In contrast to $M_4[(1)_3Ti_2]$, NMR spectroscopy reveals dynamic behavior in the case of the ethylene-bridged compounds $M_4[(2a-c)_3Ti_2]$ (2a: M = Li, Na, K, Cs, Ca, Sr; 2b, c: M = K). As a representative example, the dynamic ¹H-NMR spectra of $K_4[(2a)_3Ti_2]$ in D₂O are shown in Figure 3. At 293 K, signals due to the aromatic moiety can be observed at $\delta = 6.73$ (dd, $J = 7.7$, 1.4 Hz, 6 H), 6.65 (pseudo t, $J = 7.7$ Hz, 6 H) and 6.36 (dd, $J = 7.7$, 1.4 Hz, 6 H). The resonances of the diastereotopic protons of the spacer are observed at $\delta = 2.76$ (6 H) and 2.44 (6 H) as two multiplets. When the sample is heated, broadening of the alkyl resonances can be observed and coalescence is reached at 328 K. From this, a free-energy barrier of $\Delta G^{\ddagger} = 64.4$ kJ/mol can be calculated[9]. At 341 K, a relatively sharp signal is detected at $\delta = 2.59$. The resonances

of the aromatic protons do not change significantly upon heating.

That the inversion at the metal center proceeds by a non-dissociative mechanism is shown by heating the dinuclear coordination compound in the presence of an excess of ligand. No exchange of bound and "free" ligand can be observed by NMR[10].

Figure 3. Dynamic ¹H-NMR spectra of $K_4[(2a)_3Ti_2]$ in D₂O
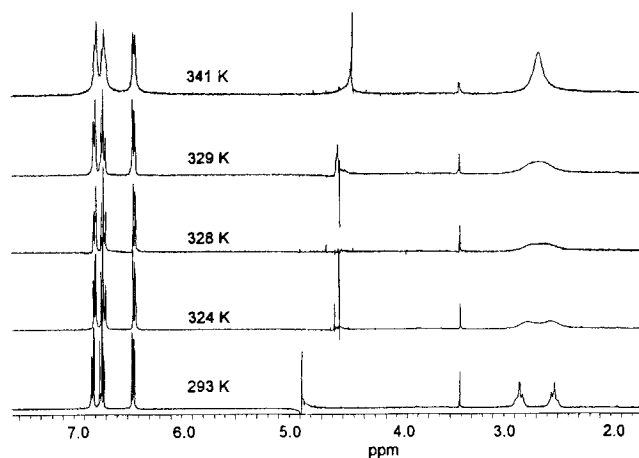
If the dynamic NMR spectroscopy of $K_4[(2a)_3Ti_2]$ is performed in [D₄]methanol, coalescence occurs at 304 K with $\Delta G^{\ddagger} = 58.2$ kJ/mol. The free-energy barrier in methanol is thus about 6.3 kJ/mol lower than in water.

Analogous NMR studies (in D₂O) can be performed with the alkyl-substituted complexes $K_4[(2b)_3Ti_2]$ and $K_4[(2c)_3Ti_2]$. Coalescence is observed at $T_c = 337$ K $(K_4[(2b)_3Ti_2])$ and 330 K $(K_4[(2c)_3Ti_2])$, from which free-energy barriers of $\Delta G^{\ddagger} = 66.5$ and 65.3 kJ/mol, respectively, can be calculated. This shows that the substituents do not have a significant influence on the symmetrization process of the helicate.

The most dramatic influence on the inversion of the triple helix of $[(2a)_3Ti_2]^{4-}$ is shown by the counterions. In Figure 4, the barriers of the symmetrization of $K_4[(2a)_3Ti_2]$ in D₂O is tuned by addition of sodium ions (as NaCl). However,

due to a higher affinity of the tetraanion for potassium[5] a relatively high concentration of Na^+ ions is required before any significant changes in the coalescence temperature can be observed.

Figure 4. Change of the ^{1}H-NMR spectra (D_2O, 296 K) of $K_4[(2a)_3Ti_2]$ upon addition of 100 and 200 equiv. of NaCl
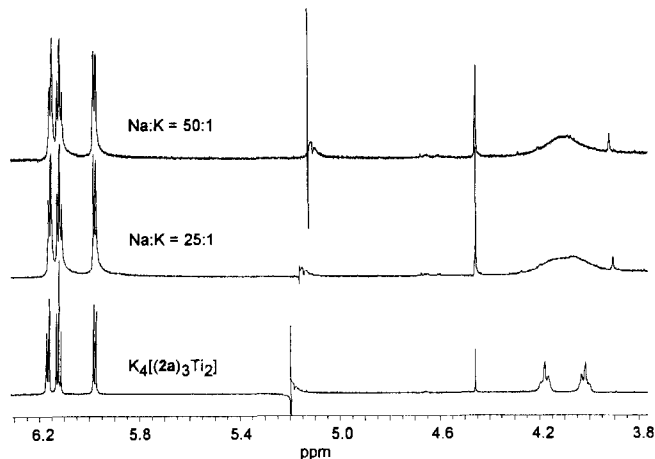
The coalescence temperature of pure $K_4[(2a)_3Ti_2]$ ($T_c = 328$ K) is reduced to 299 K ($\Delta G^+ = 58.6$ kJ/mol) when a K/Na ratio of 1:25 is present. With a K/Na ratio of 1:50 coalescence can be observed at 292 K($\Delta G^+ = 57.3$ kJ/mol).

The influence of the counterions also is evident from the ^{1}H-NMR spectra of the pure salts $K_4[(2a)_3Ti_2]$, $Na_4[(2a)_3Ti_2]$ and $Li_4[(2a)_3Ti_2]$ in [D$_4$]methanol. While the potassium salt $K_4[(2a)_3Ti_2]$ shows two resonances of diastereotopic protons of the spacer at room temperature ($T_c = 304$ K), only a broad signal can be observed at $\delta = 2.77$ for the lithium salt $Li_4[(2a)_3Ti_2]$. Coalescence for the latter can be detected at $T_c = 233$ K ($\Delta G^+ = 43.1$ kJ/mol) by low-temperature NMR spectroscopy. The sodium salt $Na_4[(2a)_3Ti_2]$ shows a singlet at $\delta = 2.68$ at room temperature. Low-temperature studies show that coalescence occurs at $T_c = 244$ K ($\Delta G^+ = 45.2$ kJ/mol).

The caesium $\{Cs_4[(2a)_3Ti_2]\}$, calcium $\{Ca_2[(2a)_3Ti_2]\}$ and strontium salts $\{Sr_2[(2a)_3Ti_2]\}$ each exhibit similar behavior. Coalescence temperatures are detected for the alkyl protons at $T_c = 316$ K (Cs, $\Delta G^+ = 59.4$ kJ/mol), 318 K (Ca, $\Delta G^+ = 59.8$ kJ/mol) and 314 K (Sr, $\Delta G^+ = 59.0$ kJ/mol), respectively, in D_2O.

Similar results as for the ethylene-bridged binuclear complexes are obtained for the compounds with [CH$_2$]$_3$ or [CH$_2$]$_4$ spacers.

As we reported previously[6], the ^{1}H-NMR spectrum (D_2O) of $K_4[(3)_3Ti_2]$ features signals for the two sets of diastereotopic protons of the spacer (benzylic and central positions) and coalescence is observed at $T_c = 356$ and 357 K ($\Delta G^+ = 69.5$ kJ/mol). This dynamic behavior is again strongly dependent on the solvent and on the counterions. The free-energy barrier for the inversion of $K_4[(3)_3Ti_2]$ in [D$_4$]methanol is again about 6.3 kJ/mol lower than that observed in D_2O ($T_c = 331$ K, $\Delta G^+ = 63.2$ kJ/mol). Coalescence of the benzylic protons is detected at 285 K ($\Delta G^+ =$

54.0 kJ/mol) for $Na_4[(3)_3Ti_2]$ and at 327 K ($\Delta G^+ = 62.3$ kJ/mol) for $Li_4[(3)_3Ti_2]$ ([D$_4$]methanol).

In case of the [CH$_2$]$_4$-bridged complex $K_4[(4)_3Ti_2]$, only two signals at $\delta = 2.59$ (benzylic protons) and 1.75 (central protons) are observed for the spacer at room temperature. Thus, low-temperature ^{1}H-NMR investigations were performed in [D$_4$]methanol.

Figure 5. ^{1}H-NMR spectra of $K_4[(4)_3Ti_2]$ at low temperature ([D$_4$]methanol)
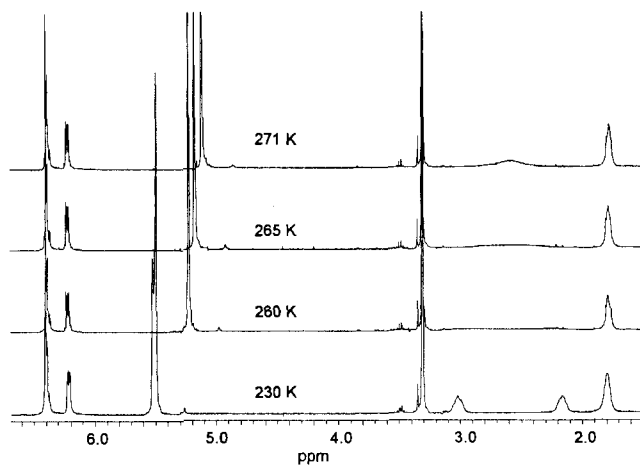
Upon cooling, the resonance of the benzylic protons starts to broaden and coalescence occurs at 261 K. At 230 K, two multiplets are observed ($\Delta G^+ = 49.0$ kJ/mol). In contrast, no splitting is observed for the proton signals of the central methylene groups. They seem to be too remote from the stereocenter to be significantly influenced.

Table 1. Comparison of the results from the variable-temperature ^{1}H-NMR-spectroscopic investigations

Complex	D$_2$O		[D$_4$]Methanol	
	T_c	ΔG^+	T_c	ΔG^+
Li$_4$[(1)$_3$Ti$_2$] or				
Na$_4$[(1)$_3$Ti$_2$][a]				not observed
K$_4$[(2a)$_3$Ti$_2$][a]	328 K	64.4 kJ/mol	304 K	58.2 kJ/mol
Na$_4$[(2a)$_3$Ti$_2$][a]			244 K	45.2 kJ/mol
K$_4$[(2a)$_3$Ti$_2$]				
+ 100 NaCl[a]	299 K	58.6 kJ/mol		
K$_4$[(2a)$_3$Ti$_2$]				
+ 200 NaCl[a]	292 K	57.3 kJ/mol		
Li$_4$[(2a)$_3$Ti$_2$][a]			233 K	43.1 kJ/mol
Cs$_4$[(2a)$_3$Ti$_2$][b]	316 K	59.4 kJ/mol		
Ca$_2$[(2a)$_3$Ti$_2$][b]	318 K	59.8 kJ/mol		
Sr$_2$[(2a)$_3$Ti$_2$][b]	314 K	59.0 kJ/mol		
K$_4$[(2b)$_3$Ti$_2$][a]	337 K	66.5 kJ/mol		
K$_4$[(2c)$_3$Ti$_2$][a]	330 K	65.3 kJ/mol		
K$_4$[(3)$_3$Ti$_2$][a]	356 K[c]		331 K[c]	63.2 kJ/mol
	357 K[d]	69.5 kJ/mol		
Na$_4$[(3)$_3$Ti$_2$][a]			285 K[c]	54.0 kJ/mol
Li$_4$[(3)$_3$Ti$_2$][a]			327 K[c]	62.3 kJ/mol
K$_4$[(4)$_3$Ti$_2$][a]			261 K[c]	49.0 kJ/mol

[a] 400 MHz. – [b] 500 MHz. – [c] Benzylic protons. – [d] Central alkyl protons.

In Table 1, the results of the varible-temperature NMR investigations are collected. Although no dynamic behavior was observed for [(1)$_3$Ti$_2$]$^{4-}$, it is clear that the symmetrization of the helicates [(2)$_3$Ti$_2$]$^{4-}$ and [(4)$_3$Ti$_2$]$^{4-}$, and of the *meso*-helicate [(3)$_3$Ti$_2$]$^{4-}$, is influenced by several different factors:

(1) The inversion barriers of the *meso*-helicates are higher than those observed for the helicates.

(2) Within the helicate or *meso*-helicate series, the free-energy barriers are lower for compounds with longer chain length.

(3) The counterions have an enormous influence on the dynamic behavior of the complexes. However, this behavior does not appear to vary in a systematic manner in relation to the size of the cation. Thus, it would seem that the inversion of configuration of the complexes depends not on the size of the cations, but on the nature of their coordination to the tetraanions.

(4) The differences observed between the studies in D$_2$O and those in [D$_4$]methanol can probably be attributed to differential solvation of the cations.

(5) Substituents at the catecholate units seem to have no influence on the dynamic behavior of the complexes.

Conclusions

Diastereotopic protons are important NMR-spectroscopic probes for the observation of the symmetrization of dinuclear helicate- and *meso*-helicate-type coordination compounds. In analogy to recent studies by Raymond, the observed symmetrization should proceed by a stepwise inversion mechanism without dissociation of the tetraanionic dinuclear complexes[7]. However, the dynamic processes described in this study are strongly influenced by the nature of the tetraanions (helicate versus *meso*-helicate; spacer length) as well as by the counterions. This shows that the alkali-metal or alkaline-earth metal cations in solution bind to the dinuclear titanium compounds and are an integral part of their molecular structures[5]. Consequently, the metal ions play a key role in determining the properties (e.g. symmetrization) of the complexes.

Experimental Section

IR: Bruker IFS 88. — Finnigan MAT 90. — UV/Vis: Perkin-Elmer UV-Vis Lambda 2. — ^{1}H NMR and ^{13}C NMR (BB/(DEPT): Bruker DRX 500, AM 400 or AC 250; internal standard: HD$_2$COD or DOH; dynamic NMR spectroscopy was performed at a concentration of 2 mM; temperatures were calibrated at the coalescence temperature by use of glycol or methanol. — The ligands 1-H$_4$–4-H$_4$[8] and the complexes M$_4$[(1)$_3$Ti$_2$] (M = Li, Na), M$_4$[(2a)$_3$Ti$_2$] (M = Na, K), and M$_4$[(3)$_3$Ti$_2$] (M = Na, K)[5,6] were prepared as described previously.

Ca$_2$[(2a)$_3$Ti$_2$]: Ligand **2a-H$_4$** (64 mg, 0.260 mmol), [TiO(acac)$_2$] (45 mg, 0.173 mmol) and Ca(OAc)$_2$ · H$_2$O (30 mg, 0.173 mmol) were stirred overnight in methanol (20 ml). Insoluble material was filtered off and the solvent was removed in vacuo. Yield: 64 mg (71%) of a red, hygroscopic solid. — ^{1}H NMR (D$_2$O, 296 K): δ =

6.49 (m, 12 H), 6.20 (m, 6 H), 2.93 (m, 6 H), 2.22 (m, 6 H). — ^{13}C NMR (D$_2$O): δ = 159.1 (C), 157.0 (C), 128.0 (C), 120.3 (CH), 119.8 (CH), 111.3 (CH), 31.4 (CH$_2$). — IR (KBr): ν̃ = 3390, 3056, 2943, 1568, 1457, 1346, 1264, 1029, 736 cm^{-1}. — UV/Vis (methanol): λ = 207, 273, 362 nm. — C$_{42}$H$_{30}$Ca$_2$O$_{12}$Ti$_2$ · 8 H$_2$O (1046.78): calcd. C 48.19, H 4.43; found C 48.06, H 4.92.

Sr$_2$[(2a)$_3$Ti$_2$]: Ligand **2a-H$_4$** (63 mg, 0.256 mmol), [TiO(acac)$_2$] (45 mg, 0.173 mmol) and Sr(OAc)$_2$ (35 mg, 0.171 mmol) were stirred overnight in DMF (20 ml). The mixture was filtered and then the solvent was removed in vacuo. Yield: 92 mg (85% of a brown, hygroscopic solid. — ^{1}H NMR (D$_2$O, 296 K): δ = 6.50 (m, 12 H), 6.23 (m, 6 H), 2.96 (m, 6 H), 2.23 (m, 6 H). — ^{13}C NMR (D$_2$O): δ = 159.2, 157.1, 128.0, 120.1, 119.7, 111.3, 31.2. — IR (KBr): ν̃ = 3570, 1597, 1572, 1322, 1266 cm^{-1}. — UV/Vis (methanol): λ = 207, 273, 361 nm. — C$_{42}$H$_{30}$Sr$_2$O$_{12}$Ti$_2$ · 3 H$_2$O · 3 DMF (1271.07): calcd. C 48.19, H 4.52; found C 47.89, H 4.79.

General Procedure for the Preparation of Titanium(IV) Complexes with Alkali-Metal Cations: Ligand (3 equiv.), M$_2$CO$_3$ (M = Li, Na, K, Cs; 2 equiv.) and (acac)$_2$TiO (2 equiv.) were dissolved in methanol and stirred overnight. The mixture was then concentrated to dryness and a yellow to red-orange solid was obtained. Where necessary, the coordination compounds could be purified by chromatography (sephadex LH 20, methanol), but the crude reaction products were often sufficiently pure.

Cs$_4$[(2a)$_3$Ti$_2$]: Yield: 100% of a hygroscopic, yellow solid.— ^{1}H NMR (D$_2$O, 296 K): δ = 6.48 (m, 12 H), 6.21 (m, 6 H), 2.95 (m, 6 H), 2.22 (m, 6 H). — ^{13}C NMR (D$_2$O): δ = 158.3, 157.2, 128.0, 120.2, 119.7, 111.3, 31.2. — IR (KBr): ν̃ = 3400, 1564, 1452, 1260 cm^{-1}. — UV/Vis (methanol): λ = 209, 273, 368 nm. — C$_{42}$H$_{30}$Cs$_4$O$_{12}$Ti$_2$ · 4 H$_2$O (1426.18): calcd. C 35.37, H 2.69; found C 35.42, H 3.18.

K$_4$[(2b)$_3$Ti$_2$]: Yield: 84% of a hygroscopic, orange solid. — ^{1}H NMR (D$_2$O, 296 K): δ = 6.66 (d, J = 7.7 Hz, 6 H), 6.54 (d, J = 7.7 Hz, 6 H), 2.72 (m, 6 H), 2.40 (m, 6 H), 2.09 (s, 18 H). — ^{13}C NMR (D$_2$O): δ = 156.5 (C), 156.4 (C), 125.1 (C), 121.2 (CH), 120.8 (C), 120.6 (CH), 32.7 (CH$_2$), 15.9 (CH$_3$). — IR (KBr): ν̃ = 2924, 2855, 1456, 1416, 1266, 1067, 953 cm^{-1}. — Positive FAB MS (glycerine as matrix); m/z: 1063 [M + H]$^+$, 1025 [M + K]$^+$. — C$_{48}$H$_{42}$K$_4$O$_{12}$Ti$_2$ · 3 H$_2$O · 3 MeOH (1213.22): calcd. C 50.49, H 4.98; found C 50.45, H 5.07.

K$_4$[(2c)$_3$Ti$_2$]: Yield: 85% of a hygroscopic, orange solid. — ^{1}H NMR (D$_2$O, 296 K): δ = 6.78 (d, J = 2.1 Hz, 6 H), 6.47 (d, J = 2.1 Hz, 6 H), 2.75 (m, 6 H), 2.44 (m, 6 H), 1.23 (s, 54 H). — ^{13}C NMR (D$_2$O): δ = 157.9, 154.2, 143.6, 126.3, 117.2, 108.8, 34.7, 32.5, 32.1. — IR (KBr): ν̃ = 2954, 1471, 1420, 1280, 833, 802 cm^{-1}. — Positive FAB MS (glycerine as matrix); m/z: 1315 [M + H]$^+$, 1353 [M + K]$^+$. — C$_{66}$H$_{72}$Ti$_2$K$_4$O$_{12}$ · 11 H$_2$O (1507.66): calcd. C 52.58, H 6.28; found C 52.38, H 6.16.

Li$_4$[(3)$_3$Ti$_2$]: Yield: 93% of a hygroscopic, orange solid. — ^{1}H NMR (250 MHz, [D$_4$]methanol, 296 K): δ = 6.41 (m, 12 H), 6.23 (m, 6 H), 2.89 (m, 6 H), 2.19 (m, 6 H), 2.09 (m, 3 H), 1.58 (m, 3 H). — IR (KBr): ν̃ = 3413, 2934, 1588, 1454, 1252, 761, 739 cm^{-1}. — C$_{45}$H$_{36}$Li$_4$O$_{12}$Ti$_2$ · 13 H$_2$O (1126.54): calcd. C 47.98, H 5.55; found C 47.50, H 5.09.

K$_4$[(4)$_3$Ti$_2$]: Yield: 95% of a hygroscopic, orange solid. — ^{1}H NMR (296 K, [D$_4$]methanol): δ = 6.40 (m, 12 H), 6.24 (m, 6 H), 2.59 (br., 12 H), 1.75 (br., 12 H). — ^{13}C NMR ([D$_4$]methanol): δ = 159.4, 157.5, 127.2, 118.8, 118.5, 110.4, 31.3, 29.8. — IR (KBr): ν̃ = 3588, 3393, 2930, 2856, 1454, 1258, 739 cm^{-1}. — Positive FAB MS (glycerine as matrix); m/z: 1025 [M − K + 2H]$^+$, 1063 [M +

$H]^+$, 1101 $[M + K]^+$. − $C_{48}H_{42}K_4O_{12}Ti_2$ · 5 H_2O · 2 MeOH (1217.21): calcd. C 49.34, H 4.97; found C 49.33, H 5.03.

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