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A helicate based three-state molecular switch

Xiaofei Chen,[a] Thomas M. Gerger,[a] Christoph Räuber,[a] Gerhard Raabe,[a] Christian Göb,[b] Iris M. Oppel,[b] Markus Albrecht*[a]

Dedicated to Prof. H. J. Knölker on the occasion of his 60th birthday.

Abstract: The control of structural transformations triggered by external signals is important for the development of novel functional devices. In the present study, it is demonstrated that helicates can be designed to structurally respond to the presence of different counter ions and to adopt either a compressed or an expanded structure. Reversible switching is not only possible between those two states, furthermore, the twist of the aggregate also can be controlled. Thus, three out of four possible states of a helicate (expanded/left-handed, expanded/right-handed, compressed/left-handed) based on an enantiomerically pure ester bridged dicatecholate ligand are specifically addressed by introduction, exchange or removal of counter cations. This is used in order to reversibly switch between the different states or to successively address them.

Supramolecular chemistry offers approaches towards the production of dynamic molecular ensembles like catenanes[1] or rotaxanes[2] acting as molecular switches,[3] rotors[4] or muscles.[5] All those types of supramolecular ensembles represent devices showing some dynamic behavior and may be switched to undergo some structural transformation. Such behavior can be also observed in oligomers/polymers[6] or even in DNA.[7]

In 2010 Yashima described a helicate[8] which sodium dependent could be switched in size and it was described as a "molecular spring".[9] In this case the switching process proceeds with conversion of stereochemistry. Since 2005 we study hierarchically assembled catecholate based helicates.[10,11] (Fig. 1a). In order to obtain a lithium dependent molecular switch, two monomeric complex units of the hierarchically assembled helicates are connected by appropriate spacers (Fig. 1b,c). The stereochemistry of the helicate can be well controlled, if the enantiomerically pure ligand **4**-H_4 is used[12] and it is possible to address three different states (compressed left-handed, expanded right-handed and expanded left-handed). Although some systems are already described which show inversion of stereochemistry upon an external input,[13] the behavior of the present switch is unprecedented.

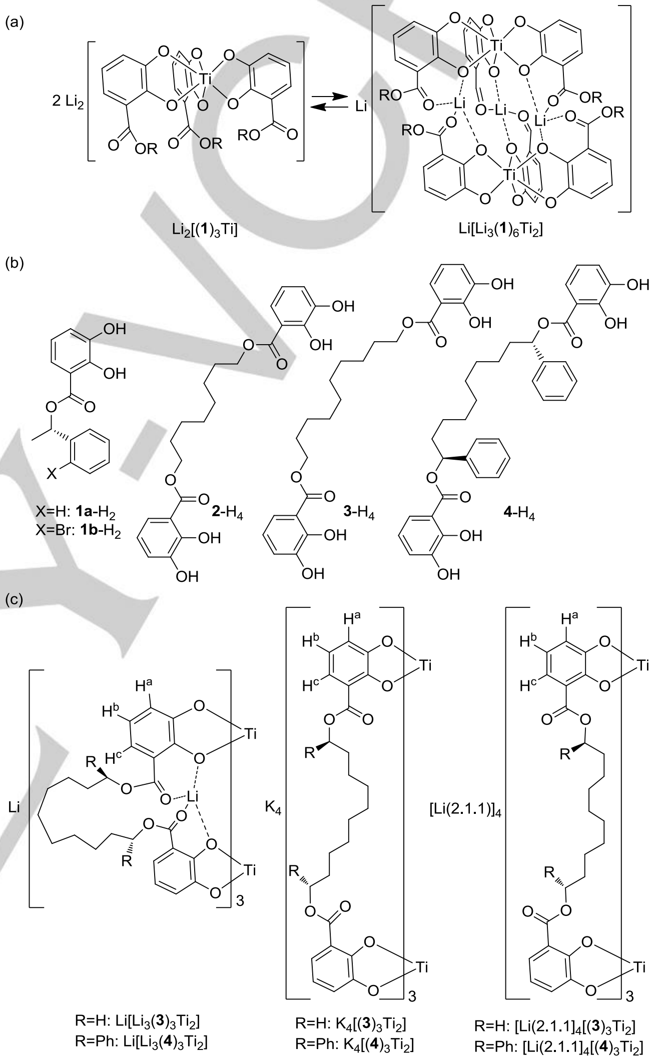

Figure 1. (a) A hierarchically assembled helicate, (b) Ligands **1a/b**-H_2 and **2-4**-H_4 and (c) compressed Li[Li_3Ti_2(**3/4**)$_3$] as well as expanded K_4[Ti_2(**3/4**)$_3$] or [Li(2.1.1)]$_4$[Ti_2(**3/4**)$_3$] ((2.1.1) = [2.1.1] cryptand).

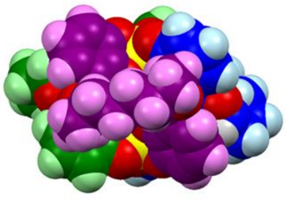

Figure 2. Structure of the compressed anion [Li_3(**2**)$_3Ti_2$]$^-$ as found in the crystal (O: red, Ti: yellow, C and H atoms of the different ligand strands are shown in magenta, green and blue).

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Synthesis and characterization. Compressed helicates Li[Li$_3$(**2-4**)$_3$Ti$_2$] are prepared from titanoyl bisacetylacetonate, **2-4**-H$_4$ and Li$_2$CO$_3$. The crystal structure of Li[Li$_3$(**2**)$_3$Ti$_2$] (Fig. 2) reveals that the alkyl spacer connects two catechol units binding to different titanium(IV) centers but only to one lithium cation. The corresponding expanded complexes K$_4$[(**3,4**)$_3$Ti$_2$] are similarly made using K$_2$CO$_3$ instead of Li$_2$CO$_3$. With ligand **2**, no defined potassium complex is obtained. Due to the close distance of the charged Ti-complex units of K$_4$[(**2**)$_3$Ti$_2$], internal binding of K-cations destabilizes the helicate leading to undefined material.

^{1}H NMR spectra of compressed Li[Li$_3$(**3**)$_3$Ti$_2$] (δ(OCH$_2$) = 3.82 and 2.95 ppm, diastereotopic behaviour) and expanded K$_4$[(**3**)$_3$Ti$_2$] (δ(OCH$_2$) = 4.07 ppm, non-diastereotopic) in DMSO-d$_6$ are remarkably different. The non-diastereotopic behaviour of the O-methylene protons in case of the potassium salt is characteristic for the expanded form in which the titanium complexes can easily racemize.[11]

Addition of [2.1.1] cryptand[14] to Li[Li$_3$(**3**)$_3$Ti$_2$] changes the NMR spectrum significantly (δ(OCH$_2$) = 4.16 ppm, non-diastereotopic) revealing that lithium cations have been extracted from the complex leading to expansion and fast helix inversion.

With the chiral ligand **4**-H$_4$ again ^{1}H NMR spectra were obtained for Li[Li$_3$(**4**)$_3$Ti$_2$], [Li(2.1.1)]$_4$[(**4**)$_3$Ti$_2$] and K$_4$[(**4**)$_3$Ti$_2$] with the spectra of the compressed complex being very different to the two expanded ones (Fig. 3a).

For Li[Li$_3$(**4**)$_3$Ti$_2$] only one peak is observed for [Li$_3$(**4**)$_3$Ti$_2$]$^-$ (m/z = 1900.69) in the negative ESI MS (methanol). The peak vanishes after addition of an excess [2.1.1] cryptand. In the expanded potassium salt, some of the cations are easily exchanged by others (m/z = 1920.62 [H$_2$K(**4**)$_3$Ti$_2$]$^-$, 1942.60 [HNaK(**4**)$_3$Ti$_2$]$^-$, 1958.58 [HK$_2$(**4**)$_3$Ti$_2$]$^-$, 1980.56 [NaK$_2$(**4**)$_3$Ti$_2$]$^-$ or 1996.54 [K$_3$(**4**)$_3$Ti$_2$]$^-$). However, at least one, probably two of the K$^+$ are still bound to the complex.

Helicates [(**3/4**)$_3$Ti$_2$]$^{4-}$ are able to adopt compressed and expanded forms depending on the counter cations. Based on a series of X-ray structure analyses[11,12] and on the structure of [Li$_3$(**2**)$_3$Ti$_2$]$^-$ the length in the compressed form is estimated to be around 10 Å. The expanded form is approximately 24-25 Å long based on model considerations.

Controlling the twist. *S*-configurated ligand **4** forms only one enantiomerically pure diastereoisomer of the compressed complex Li[Li$_3$(**4**)$_3$Ti$_2$]. The circular dichroism (CD) spectrum (Fig. 3b) shows a negative Cotton effect at 350 nm and a positive one at 420 nm. These bands are indicative for *Λ*-configuration.[15] This is in agreement with observations made for Li[Li$_3$(**1b**)$_6$Ti$_2$] in which the methyl substituents are well preorientated to bridge two catecholates which both coordinate to the same Li$^+$ (see [Li$_3$(**2**)$_3$Ti$_2$]$^-$ in Fig. 2 and SI).[16]

Expanded K$_4$[(**4**)$_3$Ti$_2$] adopts *Δ* configuration (right handed twist, pos. Cotton effect at 340 nm, neg. Cotton effect at 400 nm). The chiral units are orientated as depicted in Figure 3**c**, left.[13] Potassium cations are coordinating within the expanded helicate interacting with three catecholate and three carbonyl oxygens (Fig. 3c**,** center). The inside orientation of the C=O-units by K$^+$ coordination induces a right handed twist (*Δ*) and is demonstrated in the crystal structure of a model compound (Fig. 3**c,** right).

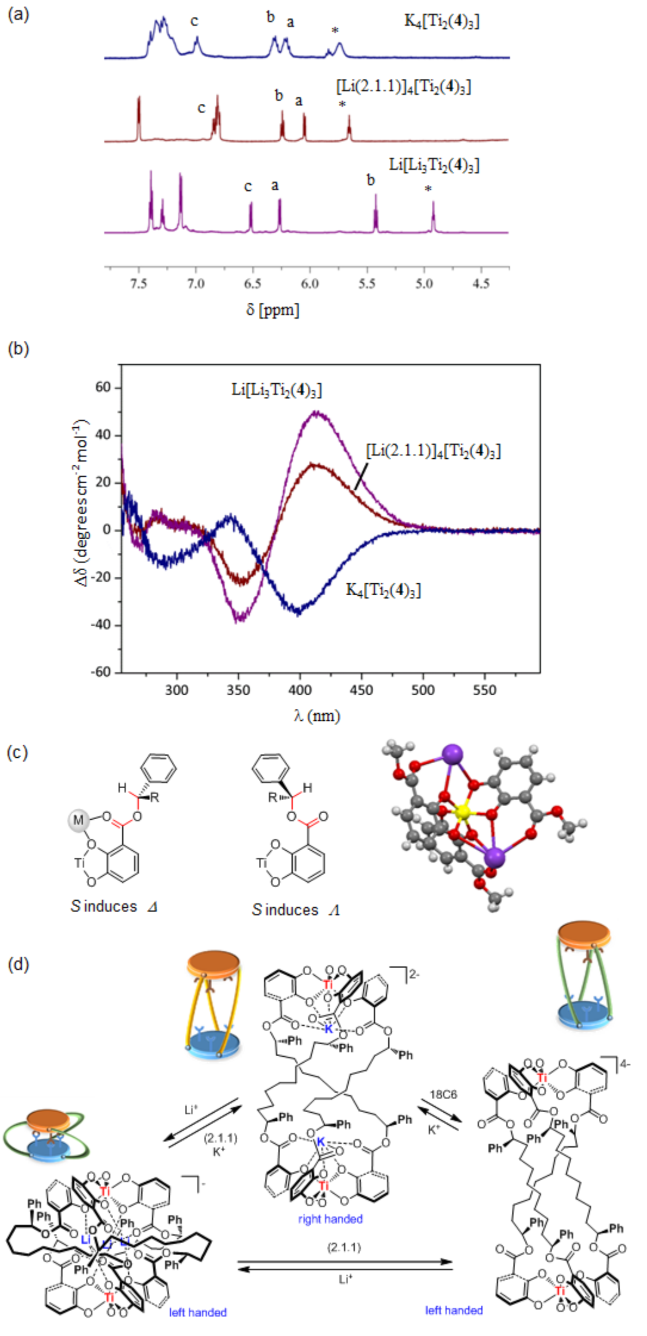

Figure 3. (a) Parts of the ^{1}H NMR spectra of Li[Li$_3$Ti$_2$(**4**)$_3$], K$_4$[Ti$_2$(**4**)$_3$] and [Li(2.1.1)]$_4$[Ti$_2$(**4**)$_3$] in DMSO-d$_6$ (a-c mark the resonances of the catechol protons as depicted in Fig. 1c, * corresponds to the proton at the chiral center); (b) circular dichroism spectra (CD) of ΛΛ-Li[Li$_3$Ti$_2$(**4**)$_3$], ΔΔ-K$_4$[Ti$_2$(**4**)$_3$] and ΛΛ-[Li(2.1.1)]$_4$[Ti$_2$(**4**)$_3$] in DMSO-d$_6$; (c) orientations of the ester carbonyl oxygen atom as influenced by the presence (left) or absence (center) of binding cations and part of the crystal structure of the potassium titanium model complex with methylester ligands (right) showing the orientation of the carbonyl oxygens towards titanium (yellow) enforced by coordination to potassium cations (purple); (d) schematic representation of possible twists at a helicate and options to switch between the different states of [(**4**)$_3$Ti$_2$]$^{4-}$. Full conversion of one state to another takes place within 7-8 hours at 30-40°C.

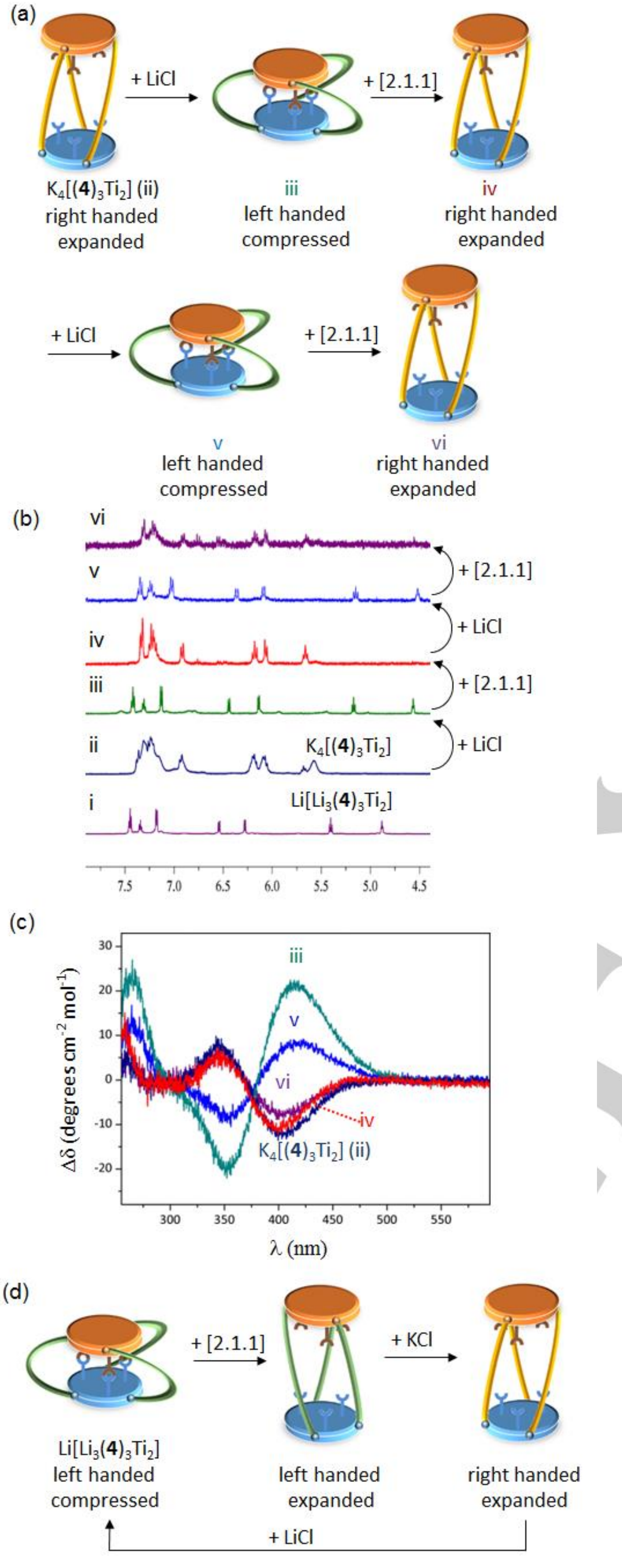

Figure 4. (a) Reversible switching between right handed (ΔΔ) expanded and left handed (ΛΛ) compressed state of $[(\mathbf{4})_3Ti_2]^{4-}$ in DMSO-d_6 by alternating addition of LiCl or [2.1.1] cryptand as followed by ^{1}H NMR (b) as well as CD spectroscopy (c); (d) one cycle of switching between all three possible states of the helicate in DMSO-d_6.

The left handed expanded helicate is obtained by simply removing potassium or lithium cations which force the carbonyl oxygen atoms to the interior. Reaction of right handed expanded $K_4[(\mathbf{4})_3Ti_2]$ with 18crown6 (18C6) or of left handed compressed $Li[Li_3(\mathbf{4})_3Ti_2]$ with [2.1.1]cryptand (2.1.1) results in $M_4[(\mathbf{4})_3Ti_2]$ (M = K(18C6) or Li(2.1.1)). No alkali metal cation binds to the helicate and repulsion occurs between carbonyl and catecholate oxygen atoms. The carbonyl unit rotates “outwards” (Fig. 3**c**, center) and the complexes adopt a left handed twist (Fig. 3b).

Three different states (Fig. 3d) of the helicate with ligand **4** are available: (i) compressed left-handed (with Li^+), (ii) expanded right-handed (with K^+) and expanded left-handed. The potential of such helicates to be used as mechanical devices highly depends on the possibility to switch between the three different states as shown in Figure 3d.

Expansion and compression with retention or inversion. $[(\mathbf{4})_3Ti_2]^{4-}$ shows ^{1}H NMR spectra of the compressed left-handed lithium or of the expanded right-handed potassium salt. Due to the strong binding of lithium in compressed $[Li_3(\mathbf{4})_3Ti_2]^-$ it is easy to substitute potassium of $K_4[(\mathbf{4})_3Ti_2]$ by adding LiCl. Lithium cations are removed by addition of [2.1.1]cryptand enabling interaction of $[(\mathbf{4})_3Ti_2]^{4-}$ with the potassium cations which are still present in solution (Fig. 4a). The switching of the structures is easily followed by ^{1}H NMR (Fig. 4b) as well as by CD spectroscopy (Fig. 4c) showing that expansion and compression are accompanied by inversion of the twist.

Switching between all three states of $[(\mathbf{4})_3Ti_2]^{4-}$ is also possible in one test tube (Fig. 4d). Addition of [2.1.1] cryptand to left-handed compressed $[Li_3(\mathbf{4})_3Ti_2]^-$ removes lithium ions and left-handed expanded $[(\mathbf{4})_3Ti_2]^{4-}$ is obtained. The twist of this complex is inverted by addition of potassium chloride to obtain right-handed expanded $K_4[(\mathbf{4})_3Ti_2]$. Subsequent addition of lithium chloride leads to the left-handed compressed $[Li_3(\mathbf{4})_3Ti_2]^-$ which has been the starting point of the switching sequence. The switching process can be easily followed by proton NMR as well as CD spectroscopy revealing spectra as depicted in Figure 4b,c for the different species.

In here a helicate is introduced which allows reversible switching between an expanded or a compressed state. Upon this process the complex increases its extension from 10 to about 25 Å. This behavior can be described to be spring type. Compression is enforced by internal binding of Li-ions but not to an outer pressure. Removal of the lithium based charge compensation between the negative complexes results in repulsion and enforces expansion. This is of course different to the function of macroscopic springs which are driven by internal tension.

In addition it is possible to invert the helicity of the helicate during expansion and compression as well as between the different expanded states. Therefore the present system should be described as a three state stereochemical switch. The importance of chirality in chemistry makes switches like this interesting for the development of e.g. novel catalysts or reaction platforms.[17]

Acknowledgements

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Keywords: self-assembly • molecular switch • helicate • catechol ester • stereochemistry

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Layout 1:

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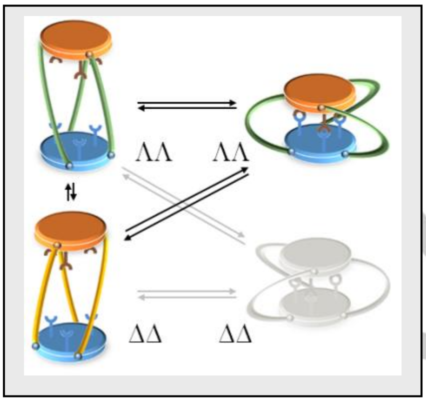
Up and down and left and right. A triple stranded helicate can be switched between three different extended and twisted states. This behaviour is reversible and several switching cycles can be performed.



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Page No. – Page No.

A helicate based three-state molecular switch

Layout 2:

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Page No. – Page No.

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Text for Table of Contents