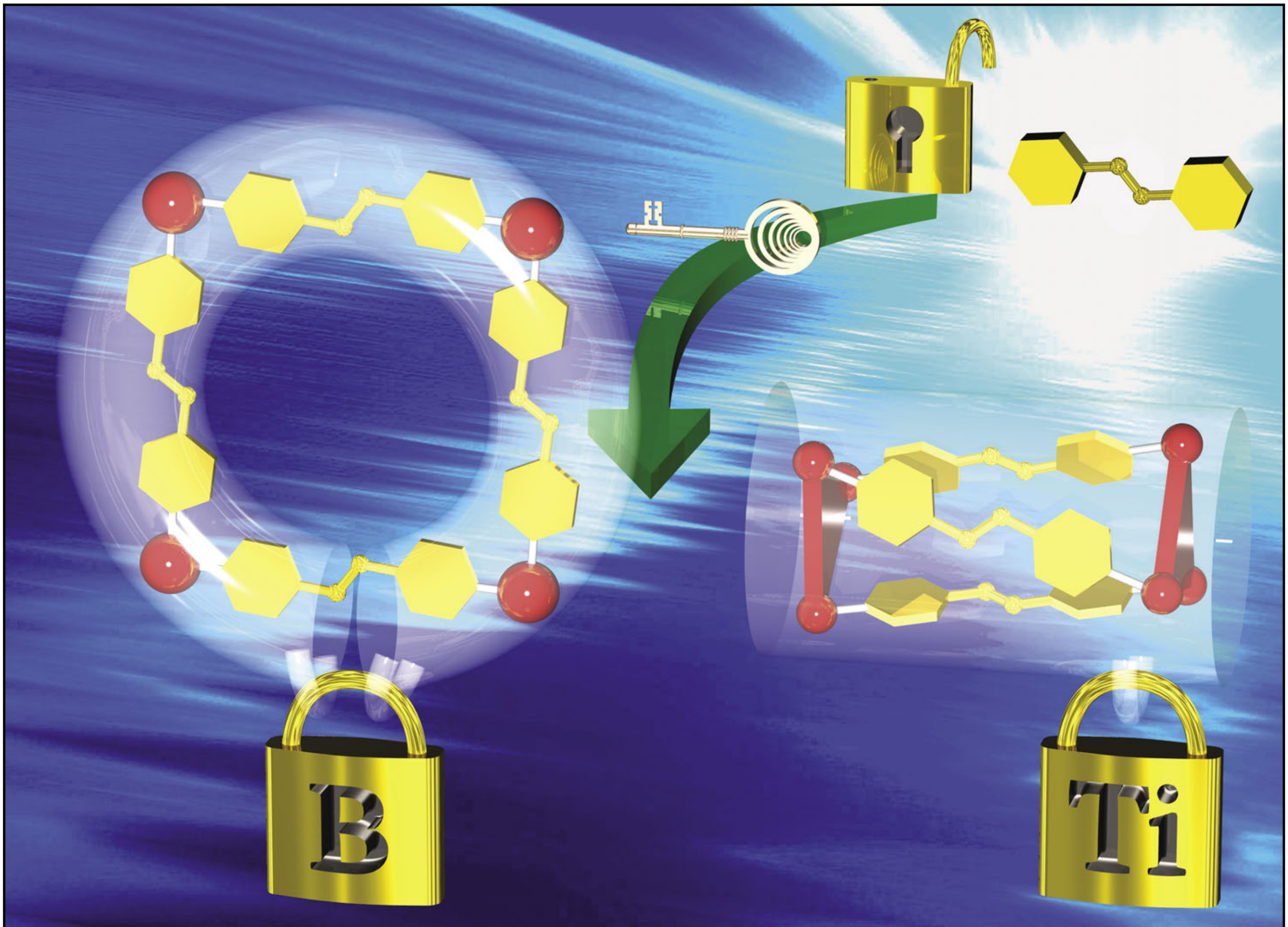

Showcasing research from Tatsuya Nabeshima's Laboratory/Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan.

Photoisomerization locking of azobenzene by formation of self-assembled macrocycle

Self-assembled ring- and cage-shaped complexes of an azobenzene-linked biscatecholate ligand were synthesized, and these complexes were inert to photoisomerization. This fact indicates that the self-assembly approach is an efficient and new method for the photoisomerization locking of azobenzenes.

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Photoisomerization locking of azobenzene by formation of a self-assembled macrocycle†

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Reaction of an azobenzene-linked biscatecholate ligand with boron and titanium sources gave ring- and cage-shaped complexes in a self-assembly fashion, respectively. These complexes were inert to photoisomerization though the ligand itself was isomerized upon photoirradiation. The self-assembled macrocyclization caused inhibition of the photoisomerization.

Photochromic compounds are fascinating materials because of their application in optical memory devices, molecular machines, and switchable molecular receptors.[1] On the other hand, locking of photoreaction has been investigated because the inhibition plays a critical role in the design of highly stable dyes,[2] photorefractive materials,[3] and luminescent dyes.[4] More recently, a combination of photo and other external stimuli was reported to lead to multi-responsive systems.[5,6] In these multi-responsive systems, photoreaction controlled by an external effector, such as a proton,[7] ion,[8] Lewis acid,[9] or electron,[10] provides molecular switches serving as a dual-input logic system and nondestructive molecular memory based on locked and unlocked photoreactions by the addition of the effector. Here, we focused on a self-assembly approach for the photoisomerization locking by forming a rigid macrocyclic azobenzene (Fig. 1). Azobenzene, one of the most commonly used photochromic units, features a light-induced *trans–cis* isomerization. Locking of the photoswitch on supramolecular macrocycles having photochromic units has potential for tuning the isomerization behaviour due to reversible formation of the macrocyclic structure. Isomerization of macrocyclic azobenzene derivatives inhibited by a guest or in a condensed state was reported;[8] perfect locking of isomerization by self-assembled macrocyclization has not been reported as far as we know.

Herein, an azobenzene-linked biscatechol ligand was designed and synthesized for self-assembled rigid macrocycle formation. The macrocyclic complexes of azobenzene-biscatechol showed locking of the photoisomerization behaviour.

The azobenzene-linked biscatechol ligand *trans*-**LH**$_4$ (Scheme 1) was synthesized as follows: the cross-coupling reaction of 4,4′-dibromoazobenzene with 2,3-dimethoxyphenylboronic acid in the presence of $Pd(PPh_3)_4$ gave a precursor, 4,4′-bis(2,3-dimethoxyphenyl)azobenzene (72% yield), which was demethylated by treatment with BBr_3 to give *trans*-**LH**$_4$ (75% yield).† The structural analysis of *trans*-**LH**$_4$ by X-ray crystallography revealed the usual bond lengths and angles as seen in *trans*-azobenzene.[11] In the UV-vis spectrum, absorption maxima

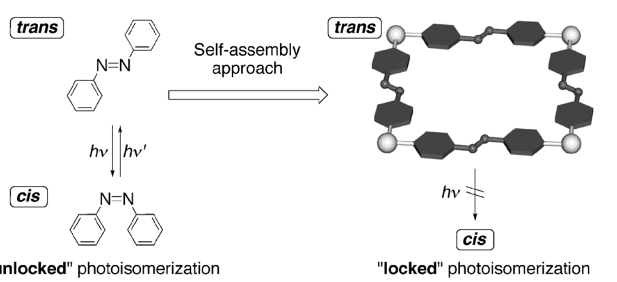
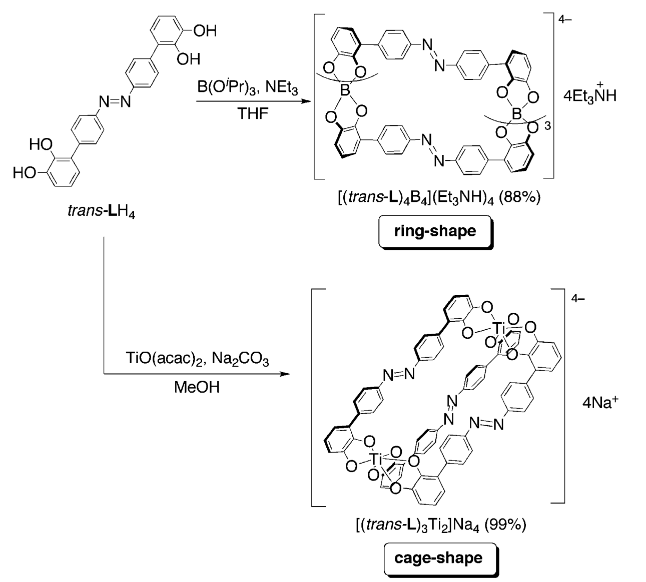


Fig. 1 Control of photoisomerization behaviour of azobenzene by self-assembly approach.



Scheme 1 Self-assembly formation of azobenzene-linked ring $[L_4B_4]^{4-}$ and cage $[L_3Ti_2]^{4-}$.

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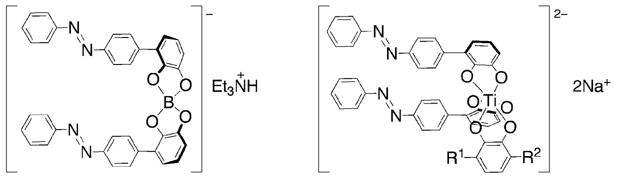
† Electronic supplementary information (ESI) available: The detailed synthetic procedure, X-ray crystallographic analysis, 1D NMR spectra, DOSY, ESI- and MALDI-TOF-MS, and computational study. CCDC 855272. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc18014f

of π–π* and n–π* transitions appeared at 360 and 440 nm, respectively.

Two different types of complexes of *trans*-$\mathbf{LH_4}$ bearing boron and titanium catecholate, which are known as a joint part of ring-[12] and cage-shaped[13] self-assemblies of biscatecholate ligands, respectively, were synthesized to construct the macrocyclic structure. First, the borate complex was synthesized by the reaction of *trans*-$\mathbf{LH_4}$ with triisopropyl borate in the presence of Et_3N to give a red glassy solid in 88% isolated yield (Scheme 1). ^{1}H, ^{13}C and ^{11}B NMR spectra in DMSO-d_6 showed highly symmetric signals assigned to one set of the biscatecholate boron and symmetric azobenzene moieties with Et_3NH^+ as a counter cation (Fig. S2, ESI†). All the protons were characterized by ^{1}H–^{1}H COSY and NOESY. When (^{n}Bu$_4$N)OH was used instead of Et_3N, the product showed the same NMR signals in the aromatic region. No influence of the counter cation on NMR indicates the separation of an ion pair in solution. The elemental analysis corresponds to the cyclic oligomer $[\mathbf{L}_n\mathbf{B}_n](Et_3NH)_n$. In addition, negative mode ESI-TOF-MS measurement also confirmed the formation of the cyclic compound by observation of an ion peak corresponding to $[\mathbf{L}_n\mathbf{B}_n]^{n-}$ at m/z of 405.1 as a main peak and no acyclic oligomer was observed. The isotopic pattern of the ion peak correlated with the theoretical distribution of tetramer $[\mathbf{L_4B_4}]^{4-}$ mixed with trimer $[\mathbf{L_3B_3}]^{3-}$ is shown in Fig. S7, ESI.† A diffusion-ordered NMR spectroscopic (DOSY) experiment strongly supported a single discrete product by the alignment of a single set of diffusion coefficient peaks for the product (Fig. S5, ESI†). The diffusion constant was determined to be 7.06×10^{-11} m^2 s^{-1}, and the corresponding hydrodynamic radius, R_h, was a much larger value, 15.6 Å, than that of *trans*-$\mathbf{LH_4}$, 4.88 Å. A molecular modelling study was performed for the macrocyclic complexes by DFT calculation.[14] There are four diastereomers in the macrocycle $[(trans\text{-}\mathbf{L})_4\mathbf{B}_4]^{4-}$ due to the chirality of the boron catecholate moieties (Fig. S15, ESI†). The modelling study of the four diastereomers suggests that the most stable isomer is the D_4 symmetric one with its four boron centres having the same chirality. The observed R_h was comparable to the molecular size of the calculated model structure of tetramer $[(trans\text{-}\mathbf{L})_4\mathbf{B}_4]^{4-}$ (15.5 Å) rather than trimer $[\mathbf{L_3B_3}]^{3-}$ (12.6 Å, Fig. S14, ESI†). Trimer $[\mathbf{L_3B_3}]^{3-}$ observed in ESI-MS should exist as only a minor species with a very small population to be observed in the NMR spectra. Thus, the ring-shaped self-assembled complex $[(trans\text{-}\mathbf{L})_4\mathbf{B}_4]^{4-}$ was efficiently formed.

The titanium complex was quantitatively synthesized by the reaction of *trans*-$\mathbf{LH_4}$ with Ti(O)(acac)$_2$ in the presence of Na_2CO_3 (99% yield, Scheme 1). The ^{1}H NMR spectrum showed only one discrete product (Fig. S3, ESI†). The MALDI-TOF-MS, DOSY experiment, and the model study by DFT calculation suggested the formation of the D_3 symmetric trigonal-pyramidal cage-shaped complex $[(trans\text{-}\mathbf{L})_3\mathbf{Ti}_2]^{4-}$ (Fig. S16, ESI†),[15] similarly to reported cage-shaped triscatecholate Ti complexes.[13] To prove the detailed macrocyclic effect, acyclic boron and titanium complexes $[\mathbf{L'_2B}](Et_3NH)$ and $[\mathbf{L'_3Ti}]Na_2$ were synthesized following a procedure similar to those for $[(trans\text{-}\mathbf{L})_4\mathbf{B}_4]^{4-}$ and $[(trans\text{-}\mathbf{L})_3\mathbf{Ti}_2]^{4-}$,[16] respectively (Chart 1). Finally, synthesis of the self-assembled complexes of *cis*-$\mathbf{LH_4}$ was attempted toward photoisomerization locking of the *cis*-azobenzene. But the reaction of *cis*-$\mathbf{LH_4}$ with boron and titanium sources only gave a mixture of unidentified compounds



[L'2B]Et3NH

fac-isomer: R^1 = 4-C$_6$H$_5$N$_2$C$_6$H$_4$, R^2 = H
mer-isomer: R^1 = H, R^2 = 4-C$_6$H$_5$N$_2$C$_6$H$_4$
[L'3Ti]Na2

Chart 1 Acyclic complexes $[\mathbf{L'_2B}]^-$ and $[\mathbf{L'_3Ti}]^{2-}$.

and the *trans*-isomers, $[(trans\text{-}\mathbf{L})_4\mathbf{B}_4]^{4-}$ and $[(trans\text{-}\mathbf{L})_3\mathbf{Ti}_2]^{4-}$, respectively.

The photoisomerization study of *trans*-$\mathbf{LH_4}$, $[(trans\text{-}\mathbf{L})_4\mathbf{B}_4]^{4-}$ and $[(trans\text{-}\mathbf{L})_3\mathbf{Ti}_2]^{4-}$ was performed using a 400 W high-pressure mercury lamp. Irradiation of UV light (360 nm) onto a DMSO solution of *trans*-$\mathbf{LH_4}$ resulted in a decrease in λ_{max} at 360 nm and an increase at 500 nm in the UV-vis spectra with isosbestic points. This spectral change corresponds to the typical *trans*/*cis* isomerization of azobenzene. The ^{1}H NMR spectrum showed new peaks assigned to the *cis*-isomer after irradiation, and the *trans*/*cis* ratio is 56/44 in the photostationary state at 360 nm. Irradiation of visible light (440 nm) onto the *cis*/*trans* mixture of $\mathbf{LH_4}$ resulted in recovery of the absorption of the *trans*-form, which represents reversible isomerization. In the UV-vis spectra of $[(trans\text{-}\mathbf{L})_4\mathbf{B}_4]^{4-}$ in DMSO, a broad absorption band was observed around 400 nm, which represents a π–π* transition overlapped with an n–π* band. The λ_{max} was red-shifted over 30 nm compared to *trans*-$\mathbf{LH_4}$. This shift is due to the electron-donation of the catecholate complex. The isomerization experiment of $[(trans\text{-}\mathbf{L})_4\mathbf{B}_4]^{4-}$ was carried out by irradiation at different wavelengths (360 nm and 440 nm). However, no spectral change was observed even after prolonged photoirradiation for 60 min (Fig. 2). The inhibition of photoisomerization is based on either the conformational rigidity as shown in azobenzene-linked rigid cyclophanes[17] or the substitution effect of the catecholate complex unit. The photoisomerization of the *trans*-form of acyclic complex $[\mathbf{L'_2B}]^-$ was evaluated under the same conditions, and isomerization was confirmed by UV-vis and NMR spectra; the reaction reached the photostationary state after irradiation at 360 nm for 60 s (Fig. 2). The ratio of isomers in the photostationary state was determined to be 35 : 65 (*trans*/*cis*)

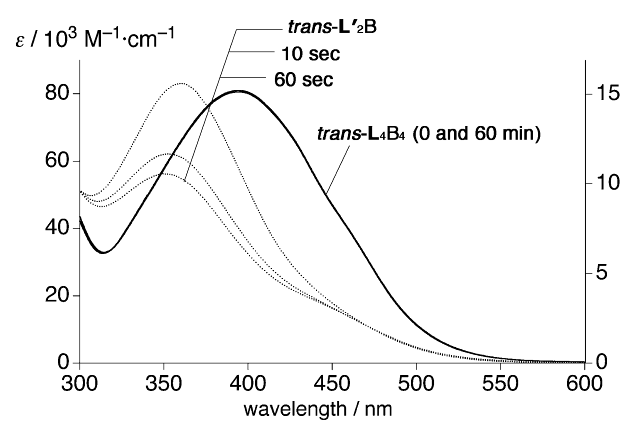


Fig. 2 UV-vis spectral change of $[\mathbf{L'_2B}](Et_3NH)$ (a dotted line, right axis) and $[\mathbf{L_4B_4}](Et_3NH)_4$ (a solid line, left axis) after photoirradiation with a high-pressure mercury lamp (360 nm) in DMSO.

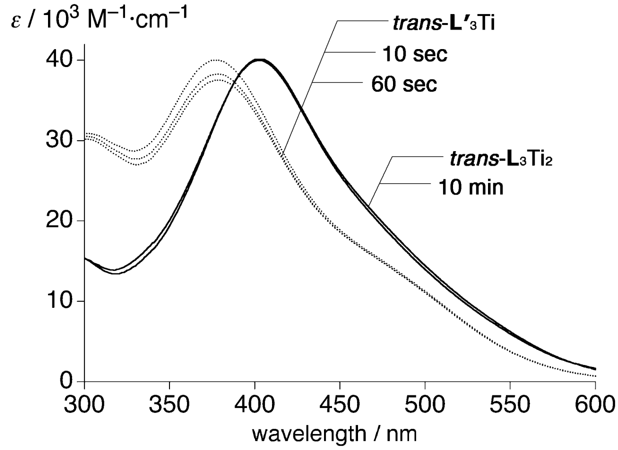


Fig. 3 UV-vis spectral change of $[\mathbf{L}'_3\mathrm{Ti}]\mathrm{Na}_2$ (a dotted line) and $[\mathbf{L}_3\mathrm{Ti}_2]\mathrm{Na}_4$ (a solid line) after photoirradiation with a high-pressure mercury lamp (360 nm) in DMSO.

by the integral ratio in the NMR spectrum. This result is in contrast with the inert nature of macrocycle $[(\textit{trans}\text{-}\mathbf{L})_4\mathrm{B}_4]^{4-}$ to photoirradiation. The locking of photoisomerization of $[(\textit{trans}\text{-}\mathbf{L})_4\mathrm{B}_4]^{4-}$ is ascribed to the molecular rigidity of the macrocyclic structure.

In the UV-vis spectra, the broad shoulder peaks of $[(\textit{trans}\text{-}\mathbf{L})_3\mathrm{Ti}_2]^{4-}$ and $[(\textit{trans}\text{-}\mathbf{L}')_3\mathrm{Ti}]^{4-}$, overlapped with the absorptions of azobenzene, reached the region of over 600 nm assigned to the MLCT bands (Fig. 3). Cage-shaped titanium complex $[(\textit{trans}\text{-}\mathbf{L})_3\mathrm{Ti}_2]^{4-}$ did not isomerize upon photoirradiation. In contrast, photoirradiation of acyclic $[(\textit{trans}\text{-}\mathbf{L}')_3\mathrm{Ti}]^{4-}$ resulted in a small but detectable spectral change. The spectrum was recovered by allowing the sample to stand in the dark, indicating the thermal back-isomerization of the *cis*-isomer of $[\mathbf{L}'_3\mathrm{Ti}]^{2-}$. A prolonged photoirradiation time or heating of $[(\textit{trans}\text{-}\mathbf{L}')_3\mathrm{Ti}]^{2-}$ produced decomposed products. Conversely, cage-shaped $[(\textit{trans}\text{-}\mathbf{L})_3\mathrm{Ti}_2]^{4-}$ did not change under the same conditions, revealing the photoisomerization locking and high stability of $[(\textit{trans}\text{-}\mathbf{L})_3\mathrm{Ti}_2]^{4-}$. In addition, the NMR study also showed no isomerization of $[(\textit{trans}\text{-}\mathbf{L})_3\mathrm{Ti}_2]^{4-}$ and isomerization of $[(\textit{trans}\text{-}\mathbf{L}')_3\mathrm{Ti}]^{4-}$. Inhibition of the isomerization of $[(\textit{trans}\text{-}\mathbf{L})_3\mathrm{Ti}_2]^{4-}$ should be ascribed to the macrocyclic structure.

In summary, the azobenzene-linked ring $[(\textit{trans}\text{-}\mathbf{L})_4\mathrm{B}_4]^{4-}$ and cage $[(\textit{trans}\text{-}\mathbf{L})_3\mathrm{Ti}_2]^{4-}$ were efficiently synthesized by a coordination-driven self-assembly of the azobenzene-linked biscatechol ligand *trans*-$\mathbf{LH}_4$. The acyclic azobenzenes bearing catecholate moieties *trans*-$\mathbf{LH}_4$, $[(\textit{trans}\text{-}\mathbf{L}')_2\mathrm{B}]^{-}$, and $[(\textit{trans}\text{-}\mathbf{L}')_3\mathrm{Ti}]^{2-}$ were isomerized by photoirradiation though the photoisomerization of the self-assembled macrocyclic azobenzenes $[(\textit{trans}\text{-}\mathbf{L})_4\mathrm{B}_4]^{4-}$ and $[(\textit{trans}\text{-}\mathbf{L})_3\mathrm{Ti}_2]^{4-}$ did not proceed at all. This fact indicates that the self-assembly approach is an efficient and new method for the photoisomerization locking of azobenzenes. Now we are investigating the application of this strategy for construction of more sophisticated molecular switches.

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Notes and references

1 *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001; D. Bléger, Z. Yu and S. Hecht, *Chem. Commun.*, 2011, **47**, 12260–12266.
2 J. Griffiths, *Chem. Soc. Rev.*, 1972, **1**, 481–493.
3 O. Ostroverkhova and W. E. Moerner, *Chem. Rev.*, 2004, **104**, 3267–3314.
4 M. Shimomura and T. Kunitake, *J. Am. Chem. Soc.*, 1987, **109**, 5175–5183; M. Han and M. Hara, *J. Am. Chem. Soc.*, 2005, **127**, 10951–10955; J. Yoshino, N. Kano and T. Kawashima, *Chem. Commun.*, 2007, 559–561.
5 H. Nishihara, *Coord. Chem. Rev.*, 2005, **249**, 1468–1475; M. Akita, *Organometallics*, 2011, **30**, 43–51.
6 S.-S. Sun and A. J. Lees, *J. Am. Chem. Soc.*, 2000, **122**, 8956–8967; S.-S. Sun, J. A. Anspach and A. J. Lees, *Inorg. Chem.*, 2002, **41**, 1862–1869; C. S. Pecinovsky, E. S. Hatakeyama and D. L. Gin, *Adv. Mater.*, 2008, **20**, 174–178.
7 M. Irie, O. Miyatake and K. Uchida, *J. Am. Chem. Soc.*, 1992, **114**, 8715–8716; H. M. D. Bandara, T. R. Friss, M. M. Enriquez, W. Isley, C. Incarvito, H. A. Frank, J. Gascon and S. C. Burdette, *J. Org. Chem.*, 2010, **75**, 4817–4827.
8 M. Takeshita, C. F. Soong and M. Irie, *Tetrahedron Lett.*, 1998, **39**, 7717–7720; H.-S. Tang, N. Zhu and V. W.-W. Yam, *Organometallics*, 2007, **26**, 22–25; X. Li, Y. Ma, B. Wang and G. Li, *Org. Lett.*, 2008, **10**, 3639–3642; S. Venkataramani, U. Jana, M. Dommaschk, F. D. Sönnichsen, F. Tuczek and R. Herges, *Science*, 2011, **331**, 445–448.
9 Y. Wu, S. Chen, Y. Yang, Q. Zhang, Y. Xie, H. Tian and W. Zhu, *Chem. Commun.*, 2012, **48**, 528–530.
10 Y. F. Liu, C. Lagrost, K. Costuas, N. Touchar, H. Le Bozec and S. Rigaut, *Chem. Commun.*, 2008, 6117–6119; K. Motoyama, T. Koike and M. Akita, *Chem. Commun.*, 2008, 5812–5814; Y. Tanaka, T. Ishisaka, A. Inagaki, T. Koike, C. Lapinte and M. Akita, *Chem.–Eur. J.*, 2010, **16**, 4762–4776.
11 Crystallographic data for $\mathbf{LH}_4\cdot\mathrm{thf}_2$: $C_{32}H_{34}N_2O_6$, M_w = 542.61, triclinic, $P\bar{1}$, a = 8.9085(12), b = 11.6096(15), c = 14.9458(19) Å, α = 69.838(2), β = 74.1440(10), γ = 85.913(2)°, V = 1395.4(3) Å³, Z = 2, D_{calcd} = 1.291 g cm⁻³, λ = 0.71073 Å, μ = 0.089 mm⁻¹, T = 120(2) K, 6662 reflections, 4796 unique (R_{int} = 0.0109), GOF = 1.015, R_1 = 0.0360 ($I > 2\sigma(I)$), wR_2 = 0.1064 (all data), CCDC 855272.
12 B. F. Abrahams, D. J. Price and R. Robson, *Angew. Chem., Int. Ed. Engl.*, 2006, **45**, 806–810; B. F. Abrahams, B. A. Boughton, H. Choy, O. Clarke, M. J. Grannas, D. J. Price and R. Robson, *Inorg. Chem.*, 2008, **47**, 9797–9803; H. Danjo, K. Hirata, S. Yoshigai, I. Azumaya and K. Yamaguchi, *J. Am. Chem. Soc.*, 2009, **131**, 1638–1639.
13 M. Albrecht and S. Kotila, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2134–2137; M. Albrecht, H. Rottele and P. Burger, *Chem.–Eur. J.*, 1996, **2**, 1264–1268; D. L. Caulder, C. Brückner, R. E. Powers, S. König, T. N. Parac, J. A. Leary and K. N. Raymond, *J. Am. Chem. Soc.*, 2001, **123**, 8923–8938; M. Albrecht, I. Jansera and R. Fröhlich, *Chem. Commun.*, 2005, 157–165.
14 Firstly, equilibrium conformations were determined by Monte-Carlo method at the PM3 level. Then, each equilibrium conformer was optimized at the BLYP/6-31G* level.
15 In the negative mode MALDI-TOF-MS of the product, a main ion peak is observed as an isotopic cluster centred at m/z 1303.1 that matches with the theoretical isotope distribution for $[\mathbf{L}_3\mathrm{Ti}_2 + \mathrm{Na} + 2\mathrm{H}]^{-}$. R_h of $\mathbf{L}_3\mathrm{Ti}_2$ in DMSO-d_6 was estimated to be 8.8 Å by DOSY experiment. The R_h value of $[\mathbf{L}_3\mathrm{Ti}_2]^{4-}$ is smaller than that of $[\mathbf{L}_4\mathrm{B}_4]^{4-}$ and well comparable with the calculated model structure.
16 $[\mathbf{L}'_3\mathrm{Ti}]^{2-}$ was obtained as a mixture of the *fac* and *mer* isomers because of their fast interconversion. See references for the interconversion of titanium triscatecholate complexes: A. Rosenheim, B. Raibmann and G. Z. Schendel, *Z. Anorg. Allg. Chem.*, 1931, **196**, 160–176; A. V. Davis, T. K. Firman, B. P. Hay and K. N. Raymond, *J. Am. Chem. Soc.*, 2006, **128**, 9484–9496.
17 R. Reuter and H. A. Wegner, *Chem. Commun.*, 2011, **47**, 12267–12276.

