

A metallo-capped polyrotaxane containing calix[4]arenes and cyclodextrins and its highly selective binding for Ca^{2+} †

Yu Liu,* Hao Wang, Heng-Yi Zhang and Peng Liang

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071 P. R., China. E-mail: yuliu@public.tpt.tj.cn

Received (in Cambridge, UK) 21st June 2004, Accepted 3rd August 2004

First published as an Advance Article on the web 6th September 2004

A water-soluble nanometer-scale metalcapped polyrotaxane has been prepared by the inclusion complexation of azocalixarenes with metallo-bridged bis(β -CD)s, displaying highly selective binding for Ca^{2+} .

The assembly of polymeric supramolecules is a powerful alternative to prepare the functional materials that display the unexpected properties.^{1–6} In the last decade, the extensive effort has been devoted to developing the supramolecular assemblies, which reveal the specific molecules/ions selectivity.⁷ Among them, the metal cations, such as Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , are very important and often associated with the regulatory activities of proteins that constitute some of the fundamental chemical life processes. Although the numerous synthetic receptors and proteins as highly selective hosts for Na^+ , K^+ , Mg^{2+} , and Ca^{2+} have been investigated, the specific selectivity for Ca^{2+} based on the supramolecular assemblies are not reported, to the best of our knowledge. Herein, we adopt the molecular recognition strategy⁸ to synthesize a nano-sized polyrotaxane based on the azo-modified calixarenes and β -cyclodextrin dimers (bis-CDs). This water-soluble polymeric supramolecule provides multiple binding sites upon complexation with guest ions. Furthermore, the binding ability and selectivity of polyrotaxane for alkali and alkaline metal ions have been quantitatively evaluated by UV-Vis spectral titrations. The results indicate that the metallo-capped polyrotaxane shows a high affinity ($\log K_S = 4.00$) and ionic selectivity for Ca^{2+} , giving an exciting $\text{Ca}^{2+}/\text{K}^+$ selectivity up to 218.

The polyrotaxane **3** (Chart 1) is prepared by the intermolecular inclusion complexation of bis-CDs–Cu(II) complex⁹ with azocalixarene in 8% yield and comprehensively characterized by the

circular dichroism (CD), UV-Vis spectroscopies, scanning tunneling microscope (STM), and transmission electron microscope (TEM).

It is well known that the achiral compounds located in a chiral environment can produce the induced circular dichroism (ICD) signal(s) in the corresponding transition band(s). The bis-CDs–Cu(II) complex induces an appreciable ICD signal in the π – π^* transition band of the azo groups upon complexation with azocalixarene, while no ICD signal is observed in the absence of bis-CDs–Cu(II) complex. A positive Cotton effect peak at 398 nm ($\Delta\epsilon + 10.14 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) clearly indicates that the azo moieties are incorporated longitudinally into the chiral cavity.¹⁰

The Job's plot of the resulting **3** from bis-CDs–Cu(II) and azocalixarene has been performed, indicating that the complex stoichiometry is 1:1. Generally, CD dimers cooperatively include substrates by the adjacent CD units through the hydrophobic interactions.¹¹ However, in this context, the entity of the metal ligation moiety in a bis-CD molecule prevents the two azobenzole groups in **2** simultaneously inserting two cavities in **1** from the primary hydroxy side by the examination of CPK (Corey–Pauling–Koltun) molecular model and MM2 energy minimization, making the operation of 1:1 stoichiometric intramolecular inclusion complexation difficult. Hence, it is reasonable that the formation of 1:1 intermolecular aggregation occurs.

The IR spectra provide the further coordinated mode of carboxyl groups. The asymmetric (ν_{as}) and symmetric (ν_{s}) CO_2^- absorptions of **3** are 1598 and 1452 cm^{-1} respectively, and their difference, usually reported as A_{ionic} (146 cm^{-1}), is used to evaluate the coordinated environment of carboxyl group. From the previous reports, the $A_{\text{ionic}} = 146 \text{ cm}^{-1}$ suggests that the carboxyl groups are monodentately coordinated with metal ions.¹² Moreover, the molecular weight (M_w) and molecular weight distribution (M_w/M_n) of **3** are estimated by the GPC measurement to be 2.10×10^5 and 2.13, respectively.

The direct evidence for the formation of the polyrotaxane is provided by the scanning tunneling microscope (STM) and transmission electron microscope (TEM) images. STM

† Electronic supplementary information (ESI) available: Experimental details of synthesis and characterization. TEM images of polyrotaxane **3**. Determination of effective binding constants of polyrotaxanes **3** towards alkali and alkaline metal ions and GPC experiments. See <http://www.rsc.org/suppdata/cc/b4/b409356a/>

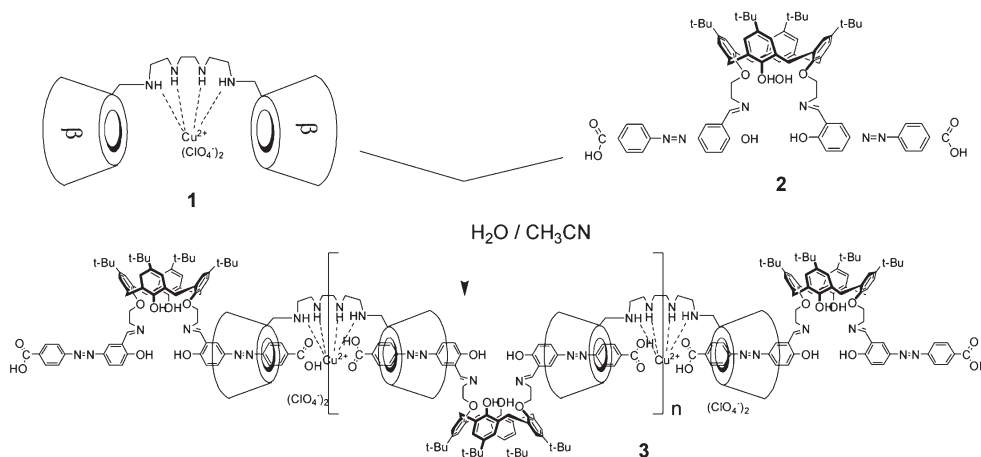


Chart 1 Metallo-capped polyrotaxane **3** constructed by bis-CDs–Cu(II) **1** and azocalixarenes **2**.

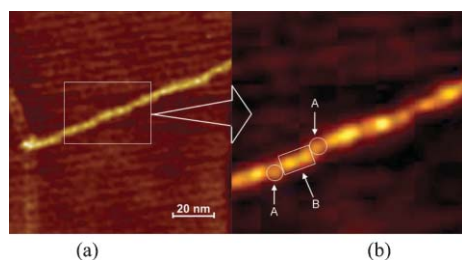


Fig. 1 A typical large-scale STM image (a) of a polyrotaxane on a HOPG surface, and a sectional image (b), recorded using the high-resolution STM. The bias voltage and tunneling current are 210 mV and 1.0 nA, respectively.

experiments have been performed on a highly oriented pyrolytic graphite (HOPG) under an ambient condition using a Pt–Ir tip with a bias voltage of 100–300 mV and a set-point current of 0.6–1.5 nA. As can be seen from Fig. 1, a highly ordered polyrotaxane arrays on the surface of HOPG. To visualize the detailed structure, a high-resolution STM picture is shown in Fig. 1b. One may note easily from Fig. 1b that the linear structure consists of the alternating bright dots (circles A) and brighter columnar protrusions (rectangles B), where each bright dot, with the diameter of roughly 1.0 nm, represents a calixarene unit, and each columnar protrusion containing two adjacent brighter dots is regarded as a dimeric bis-CD unit judging from the size and shape. The average distance between the center of dots and columnar protrusions is 2.7 ± 0.2 nm. The height of linear assembly is 1.8 ± 0.2 nm, which is larger than the theoretical periphery diameter of β -CD (1.54 ± 0.04 nm). It seems reasonable that the CD units in the polyrotaxane cannot be adsorbed on the HOPG surface steadily, and thus the tilted CD or calixarene units make the measured height slightly larger than the theoretical value.

The TEM experiment has been performed on a carbon-coated copper grid and the samples are shaded with a palladium-iridium alloy to thicken and make the images more clear. It can be seen that there also exist some regular linear aggregates, and the lengths of the aggregate are more than 200 nm, indicating the formation of the nanometer-scale linear aggregates by the host–guest inclusion complexation.

Assembly behavior of the polyrotaxane is quantitatively evaluated by the differential spectral titrations in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ at 25 °C. Upon the addition of bis-CDs–Cu(II), the absorption intensity of azo-calixarene at 386 nm gradually decreases with a red shift and two clear isosbestic points appeared at 522 and 358 nm, respectively. The effective binding constant (K_{ES}) and free energy change ($-\Delta G^\circ$), assuming 1:1 stoichiometry, can be obtained from the analysis of the sequential changes of absorption (ΔA) at the various CD dimer concentration, with a nonlinear least-squares method according to the curve fitting equation reported before.¹³ The $\log K_{\text{ES}}$ and corresponding $-\Delta G^\circ$ values for the formation of the polyrotaxane are 4.30 and 24.5 kJ mol⁻¹, respectively. In the control experiments, the $\log K_{\text{ES}}$ and corresponding $-\Delta G^\circ$ values for the complexation of non-metal coordinated dimeric CDs (bis-CDs) with azo-calixarene are 2.72 and 15.5 kJ mol⁻¹, respectively. The remarkable enhancement of the binding ability of metallo-bridged-CDs with azo-calixarene is attributed to the conformational fixation of CD dimer and the strong electrostatic interactions. Moreover, the kinetic studies show that the recombination rate constant k_{R} is $1.5 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ and the dissociation rate constant k_{D} is $8.4 \times 10^2 \text{ sec}^{-1}$.

It is noted that the metallo-capped polyrotaxane possesses the chelating units like the salen derivatives, and hence it could further selectively bind guest ions. The complexation between the polyrotaxanes and the alkali (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+), alkaline ions (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) is investigated by the method of spectral titrations. The obtained effective binding constants ($\log K_{\text{ES}}$) of polyrotaxane for cations decrease in the order: Ca^{2+} (4.00) > Mg^{2+} (3.10) > Sr^{2+} (2.71) \approx Ba^{2+} (2.63) > Na^+ (1.93) > K^+ (1.65) > Li^+ (1.48) \approx Rb^+ (1.34) > Cs^+ (<1.00).

The obtained results indicate that the polyrotaxane exhibits high binding ability for Ca^{2+} over other ions, and the ionic selectivities for $\text{Ca}^{2+}/\text{Mg}^{2+}$, $\text{Ca}^{2+}/\text{Na}^+$, and $\text{Ca}^{2+}/\text{K}^+$ are 8, 115, and 218, respectively. To examine the relationship between the structure and the function of polyrotaxane, a control experiment has been performed under the same condition. The spectral changes of azo-calixarene with the addition of metal ions are too small to calculate the binding constants according to a 1:1 or 1:2 stoichiometry. These results suggest that the multiple metal-capped polyrotaxane not only enhances the binding ability to metal ions but also gives the highest selectivity for Ca^{2+} . Evidently, the high affinity of polyrotaxane to Ca^{2+} can not be explained by the “ionic charge density selectivity”.¹⁴ This charge density sequence is not consistent with the results obtained by us. It can be seen that the assembly system involves the rigid CD units and the strong electrostatic interaction between Cu^{2+} and the carboxylate groups of calixarenes,¹⁵ and thus this system shows a higher structural rigidity and a relatively fixed size of salen moieties. Calixarenes and salen units create the hosting cages, where the cations are shielded more efficiently from the competitive solvent coordination. In the complexation with the cations, CDs in the polyrotaxane fix the geometrical disposition of azo-calixarene, making the operation of restrict size-fit easily. Herein, the dimensions of the metal ions, rather than their charge density, become the main factor in determining the binding ability of the polyrotaxane to a series of metal ions.

This work was supported by NNSFC (Nos. 90306009 and 20272028).

Notes and references

- D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, 1995, **95**, 2725–2828, and references therein.
- J. Li, X. Ni and K. Leong, *Angew. Chem., Int. Ed. Engl.*, 2003, **42**, 69–72.
- (a) K. Kim, *Chem. Soc. Rev.*, 2002, **31**, 96–107; (b) D. Whang, J. Heo, C. A. Kim and K. Kim, *Chem. Commun.*, 1997, 2361–2362.
- D.-Q. Yuan, N. Kishikawa, C. Yang, K. Koga, N. Kuroda and K. Fujita, *Chem. Commun.*, 2003, 416–417.
- T. Hayashita, D. Qing, M. Minagawa, J. C. Lee, C. H. Ku and N. Teramae, *Chem. Commun.*, 2003, 2160–2161.
- H. A. Klok, K. A. Jolliffe, C. L. Schauer, L. J. Prins, J. P. Spatz, M. Möller, P. Timmerman and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1999, **121**, 7154–7155.
- U. Lücking, F. C. Tucci, D. M. Rudkevich and J. Rebek, Jr., *J. Am. Chem. Soc.*, 2000, **122**, 8880–8889.
- (a) Y. Liu, L. Li, Z. Fan, H. Y. Zhang, X. Wu, X. D. Guan and S. X. Liu, *Nano. Lett.*, 2002, **2**, 257–261; (b) Y. Liu, H. Wang, H. Y. Zhang, L. H. Wang and Y. Song, *Chem. Lett.*, 2003, **32**, 884–885; (c) Y. Liu, H. Wang, P. Liang and H. Y. Zhang, *Angew. Chem., Int. Ed. Engl.*, 2004, **43**, 2690–2694.
- Y. Liu, C. C. You, T. Wada and Y. Inoue, *Tetrahedron Lett.*, 2000, **41**, 6869–6873.
- Y. Liu, C. C. You and B. Li, *Chem. Eur. J.*, 2001, **7**, 1281–1288.
- R. Breslow and S. D. Dong, *Chem. Rev.*, 1998, **98**, 1997–2011.
- (a) G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227–250; (b) J.-P. Costes, F. Dahan and J.-P. Laurent, *Inorg. Chem.*, 1985, **24**, 1018–1022; (c) G. Lemerrier, E. Mulliez, C. Brouca-Cabarrecq, F. Dahan and J.-P. Tuchagues, *Inorg. Chem.*, 2004, **43**, 2105–2113.
- Y. Liu, Y. Song, H. Wang, H. Y. Zhang, T. Wada and Y. Inoue, *J. Org. Chem.*, 2003, **68**, 3687–3690.
- The charge density (ρ) is defined as the amount of electric charge per unit volume. It is here given by $\rho = q/(4\pi r^3/3)$, where q is the formal charge (+1 or +2) and r is effective ionic radius (corresponding to a seven-coordinate metal from Shannon, 1976). The following values of r (Å) were used: Li^+ (0.84), Na^+ (1.12), K^+ (1.46), Rb^+ (1.56), Cs^+ (1.72), Mg^{2+} (0.81), Ca^{2+} (1.06), Sr^{2+} (1.21), Ba^{2+} (1.38). The charge densities of the metal ions increase in following order: Cs^+ (0.047) < Rb^+ (0.063) < K^+ (0.077) < Ba^{2+} (0.091) < Sr^{2+} (0.135) < Na^+ (0.170) < Ca^{2+} (0.201) < Li^+ (0.403) < Mg^{2+} (0.449). (a) R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **A32**, 751; (b) T. Dudev and C. Lim, *Chem. Rev.*, 2003, **103**, 773–787; (c) S. Watanabe, S. Ikshima, T. Matsuo and K. Yoshida, *J. Am. Chem. Soc.*, 2001, **123**, 8402–8403.
- In the control experiments, the original C=O stretching vibration bands at 1720 cm⁻¹ for *p*-carboxylazosalicyl-aldehyde shifted to 1654 cm⁻¹ upon complexation with copper ions. The IR spectra refer to the ESIF.