

Ru(II)-cornered coordination cage that senses guest inclusion by color change†

Ken-ichi Yamashita, Masaki Kawano and Makoto Fujita*

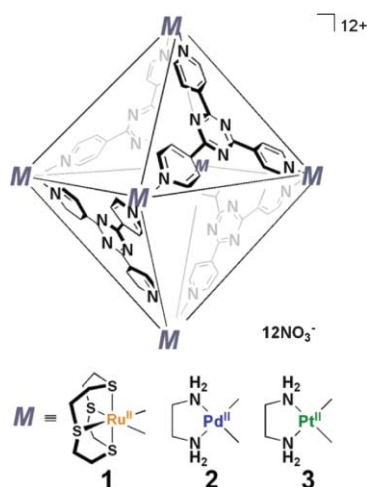
Received (in Austin, TX, USA) 15th August 2007, Accepted 10th September 2007

First published as an Advance Article on the web 24th September 2007

DOI: 10.1039/b712529a

Upon guest recognition, a self-assembled hexa-ruthenium coordination cage shows a chromic shift resulting from the slight conformational change in the panel ligand.

Color change triggered by molecular recognition is a basic phenomenon that leads to applications to sensors. In general, sensor molecules consist of a recognition site (*e.g.*, crown ethers, cyclodextrins, calixarenes, *etc.*) and a chromophore that relays the recognition events.¹ The preparation and combination of both the portions by conventional synthetic methods are usually tedious and the connection of the two functions requires careful molecular design that often makes the molecules sophisticated. Here, we report that, despite its very simple structure, a Ru(II)-cornered coordination cage (**1**) possesses both high molecular recognition ability and sensing function. The analogous Pd(II)- and Pt(II)-cornered cages (**2** and **3**, respectively), which we have previously reported, provide efficient hydrophobic cavities capable of inducing new properties and reactions of the enclathrated molecules.² In addition to the similar unique binding properties, the Ru(II) cage shows a clear chromic shift upon guest inclusion in the cavity. We suggest that the guest inclusion induces a conformational change in the triazine panel which causes a bathochromic shift in the MLCT band.



Department of Applied Chemistry, School of Engineering, The University of Tokyo and CREST, Japan Science and Technology Agency (JST), 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: mfujita@appchem.t.u-tokyo.ac.jp; Fax: (+81) 3 5841 7257; Tel: (+81) 3 5841 7259

† Electronic supplementary information (ESI) available: Experimental details and spectroscopic data. See DOI: 10.1039/b712529a

The Ru(II)-cornered cage complex **1** was readily prepared by treating $[\text{Ru}(\text{[12]aneS}_4)(\text{H}_2\text{O})(\text{dmsO})](\text{NO}_3)_2$ (**4**)³ with 2,4,6-tri(4-pyridyl)-1,3,5-triazine (**5**) in H_2O at 100°C for 2 h (Fig. 1a). Addition of an excess of THF into the resultant red solution precipitated the orange powder of **1** in 98% yield. The structure of **1** was unambiguously confirmed from NMR, CSI-MS, and X-ray analyses. The ^1H NMR spectrum of **1** showed four broad signals in the aromatic region (Fig. 1b) due to two conformations of the coordinated S_4 macrocyclic ligand: a major asymmetric conformation and a minor symmetric conformation.^{3,4} 2D-DOSY analysis clearly showed the appearance of all the signals at the same diffusion coefficient ($\log D = -9.84$), which is the same value as that of the analogous Pd(II)-cage **2**. Cold-spray ionization mass spectrometry (CSI-MS) analysis⁵ clearly confirmed the formation of **1**. The CSI-MS spectrum of **1** showed clear signals for $[\text{1} - (\text{NO}_3^-)_m + (\text{dmsO})_n]^{m+}$ ($m = 4-10$, $n = 0-17$); *e.g.* $m/z = 541.2$ $[\text{1} - (\text{NO}_3^-)_8 + (\text{dmsO})_{10}]^{8+}$, 582.7 $[\text{1} - (\text{NO}_3^-)_7$

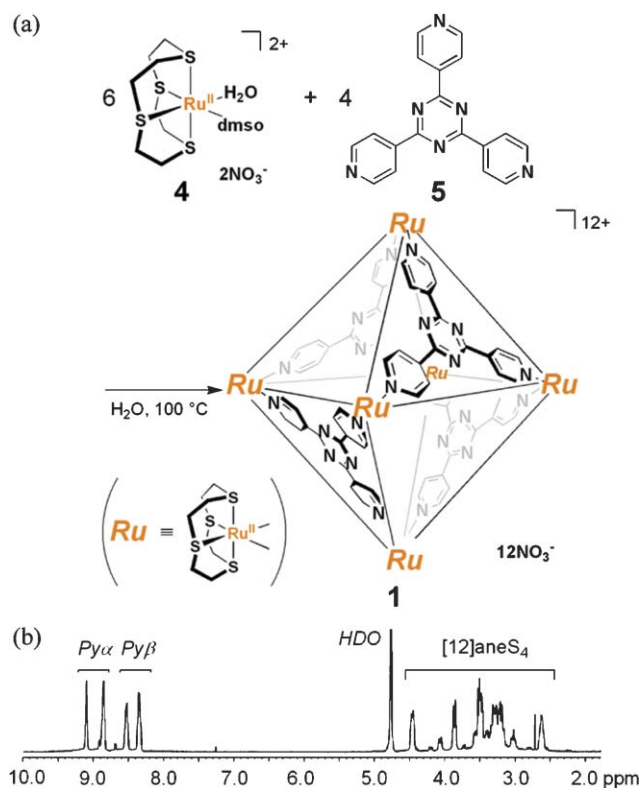


Fig. 1 (a) Schematic representation showing the self-assembly of the Ru(II)-cornered cage complex **1**, and (b) ^1H NMR spectrum of **1** (500 MHz, D_2O , 300 K).

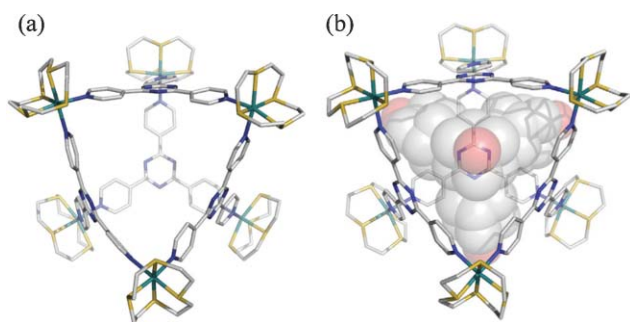


Fig. 2 Crystal structures of (a) **1** and (b) **1**⊃(**6**)₄. Hydrogen atoms, solvent molecules, and counter anions are omitted for clarity.‡

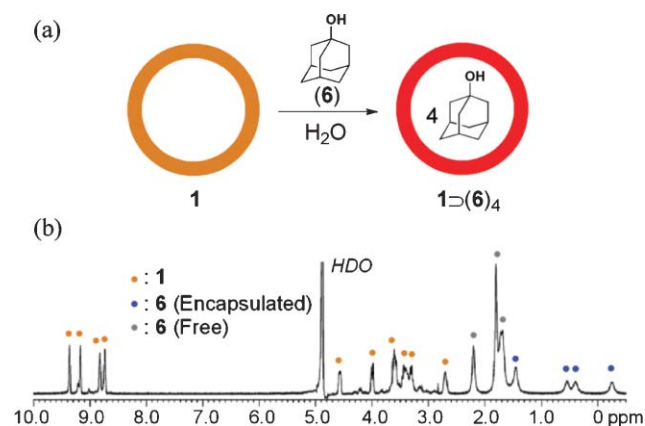


Fig. 3 (a) Schematic representation of the encapsulation of 1-adamantanol (**6**) within **1** (the orange and red circles represent **1**), and (b) ¹H NMR spectrum of **1**⊃(**6**)₄ (500 MHz, D₂O, 300 K).

+ (dmsO)₆]⁷⁺, 638.7 [**1** - (NO₃⁻)₆ + (dmsO)₃]⁶⁺, 762.4 [**1** - (NO₃⁻)₅ + dmsO]⁵⁺.

Single crystals suitable for X-ray analysis were obtained by slow evaporation of water from an aqueous solution of **1** at room temperature. The X-ray crystallographic analysis revealed the expected cage structure (Fig. 2a). The salient structural feature of **1** is that, unlike the Pd(II)-cage **2** or Pt(II)-cage **3**, the pyridine rings attached to the triazine rings are twisted and are no longer coplanar due to the steric effects of the bulky ([12]aneS₄)Ru units.^{4a} The twist angles between the pyridine rings and the triazine rings are 1.4–26.6° (avg. 10.3°).

In water, organic molecules are exchanged within the hydrophobic cavity of cage **1**. Guest encapsulation was performed by suspending an excess of guest molecules (*ca.* 10 eq.) into an aqueous solution of **1** at room temperature for a few minutes. Guest inclusion was monitored by ¹H NMR analyses. For example, on encapsulation of 1-adamantanol (**6**) in **1** in D₂O, the ¹H NMR spectrum showed a down-field shift for the aromatic protons in **1** and an up-field shift for the adamantane protons in **6** (Fig. 3b). The ratios of the integrals for the signals revealed the formation of a 1 : 4 host–guest complex.

Vapor diffusion of acetonitrile into an aqueous solution of **1** and an excess of **6** produced orange plate crystals of **1**⊃(**6**)₄. X-Ray analysis of **1**⊃(**6**)₄ clearly revealed that four guest molecules **6** were encapsulated within **1** (Fig. 2b). Unlike guest-free Ru-cage **1**, the host framework of **1**⊃(**6**)₄ is more similar to that of the

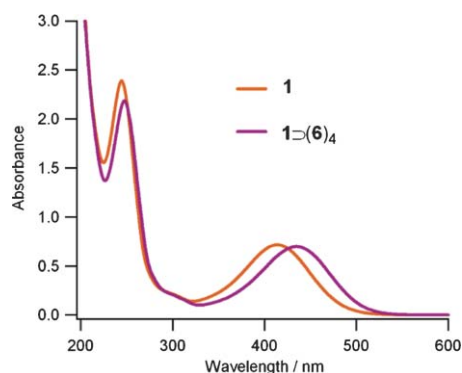


Fig. 4 UV-vis absorption spectra of **1** and **1**⊃(**6**)₄ (0.1 mM in H₂O).

Pd(II)-analogue **2**⊃(**6**)₄.^{2c} As a result of four tightly packed adamantanol molecules, the triazine panels in **1** became more coplanar, and the twist angles between the pyridine rings and triazine rings reduced to 0.2–10.9° (avg. 3.3°).

An orange solution of **1** slightly turns red after the encapsulation of **6**. A UV-vis spectroscopic study clearly showed spectral changes upon guest encapsulation in **1**. Ru(II)-cage **1** has a broad MLCT absorption band in the visible region ($\lambda_{\text{max}} = 414$ nm in H₂O) (Fig. 4). The MLCT band of **1**⊃(**6**)₄ was red-shifted by 20 nm compared to that of guest-free cage **1**.⁶ Similar bathochromic shifts were observed when other adamantane derivatives such as 2-adamantanol and 1-cyanoadamantane were encapsulated in **1** (see ESI†). It is very likely that this spectral change is derived from the change in the extended electronic conjugation between the pyridine rings and the electron deficient triazine ring which is correlated with the planarity of the ligand **5** in **1**.⁷

In summary, we have achieved the self-assembly of hexaruthenium cage complexes that can encapsulate various organic molecules. Unlike the previously reported Pd(II)- or Pt(II)-analogous cage, the Ru(II)-cage shows a clear chromic shift upon guest inclusion in the cavity due to a MLCT transition change.

Notes and references

‡ Crystallographic data: **1**; CCDC 657242. **1**⊃(**6**)₄; CCDC 657243. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b712529a

- (a) J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, John Wiley & Sons, Chichester, UK, 2000, pp. 592–603; (b) R. Martínez-Mañez and F. Sancenón, *Chem. Rev.*, 2003, **103**, 4419.
- (a) M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi and K. Ogura, *Nature*, 1995, **378**, 469; (b) F. Ibukuro, T. Kusukawa and M. Fujita, *J. Am. Chem. Soc.*, 1998, **120**, 8561; (c) T. Kusukawa and M. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 13576; (d) M. Yoshizawa and M. Fujita, *Pure Appl. Chem.*, 2005, **77**, 1107.
- K. Yamashita, M. Kawano and M. Fujita, *J. Am. Chem. Soc.*, 2007, **129**, 1850.
- (a) H. Adams, A. M. Amado, V. Félix, B. E. Mann, J. Antelo-Martinez, M. Newell, P. J. A. Ribeiro-Claro, S. E. Spey and J. A. Thomas, *Chem.–Eur. J.*, 2005, **11**, 2031; (b) T. M. Santos, B. J. Goodfellow, J. Madureira, J. P. de Jesus, V. Félix and M. G. B. Drew, *New J. Chem.*, 1999, **23**, 1015.
- S. Sakamoto, M. Fujita, K. Kim and K. Yamaguchi, *Tetrahedron*, 2000, **56**, 955.
- The π - π^* absorption band of **5** in **1** was also slightly red-shifted through the encapsulation.
- (a) G. Brizius, K. Billingsley, M. D. Smith and U. H. F. Bunz, *Org. Lett.*, 2003, **5**, 3951; (b) P. P. Lainé, I. Ciofini, P. Ochsenbein, E. Amouyal, C. Adamo and F. Bedioui, *Chem.–Eur. J.*, 2005, **11**, 3711.