# Dalton Transactions

An international journal of inorganic chemistry

## www.rsc.org/dalton

Number 21 | 7 June 2008 | Pages 2769–2900



ISSN 1477-9226

## RSCPublishing

**HOT ARTICLE** Yip *et al.* Templated assembly of a pseudorotaxane of gold rectangles

**HOT ARTICLE** Alvarez *et al.* Covalent radii revisited



1477-9226(2008)21;1-6

## Templated assembly of a pseudorotaxane of gold rectangles†

Yuanyuan Wang, Ronger Lin and John H. K. Yip\*

Received 20th February 2008, Accepted 28th March 2008 First published as an Advance Article on the web 14th April 2008 DOI: 10.1039/b802957a

A nanoscopic pseudorotaxane  $(1)_2 \supset 2$  composed of the gold rectangle  $[Au_4(\mu-PAnP)_2(\mu-bipy)_2](OTf)_4$  1 and the linear template 4,4'-bis(9"-anthryl)biphenyl 2 was assembled (PAnP = 9,10-bis(diphenylphosphino)anthracene); bipy = 4,4'-bipyridine).

Controlled assembly of molecules is important to bottom-up fabrication of molecular materials.1 Presently many molecular patterns arise from spontaneous aggregation which is governed mainly by forces between individual molecules or between molecules and substrate.<sup>2</sup> Another approach, which should allow better control over topology of the assembly, involves the use of templates. Templated assembly of organic macrocycles into rotaxanes and pseudorotaxanes has been reported.<sup>3</sup> Recently there is a surge of interest in metal-organic polygons and polyhedrons, some of which have been developed into novel receptors and catalysts.<sup>4</sup> It has been demonstrated that arrays of molecular rectangles are formed on surfaces, with or without the aid of templates;<sup>5</sup> however, high-order assembly of the inorganic macrocycles remains to be fully explored. Recently we reported the self-assembly of a nanoscopic gold rectangle [Au<sub>4</sub>(µ- $PAnP_{2}(\mu-bipy)_{2}[OTf)_{4}$  1 from a digold(I) clip  $[Au_{2}(\mu-PAnP)]^{2+}$ (PAnP = 9,10-bis(diphenylphosphino)anthracene); bipy = 4,4'bipyridine).<sup>6</sup>,<sup>‡</sup> The gold rectangle, which has a large cavity  $(\sim 1.7 \times 0.8 \text{ nm})$  can bind to polycyclic aromatics, e.g. anthracene. This propensity suggests a pseudorotaxane composed of two rectangles could be assembled with a shaft-like molecule which contains two terminal aromatic rings (Scheme 1). Described in this communication is the templated formation and structure of the pseudorotaxane in the solid state.



4,4'-Bis(9"-anthryl)biphenyl **2**, which consists of two anthracenyl rings linked by two phenyl rings, was chosen as the shaft and was synthesized according to the reported method.<sup>7</sup>.<sup>‡</sup> The

<sup>1</sup>H NMR spectrum of a solution of **1** and **2** does not show any significant changes in the signals of the two compounds, indicating that the complexation is slow with respect to the NMR timescale. Nevertheless, the compounds **1** and **2** form a 2:1 host– guest complex upon co-crystallization. While **1** is yellow and **2** is white, red crystals of (1)<sub>2</sub> $\supset$ **2**·2CH<sub>3</sub>CN·2CH<sub>2</sub>Cl<sub>2</sub>·4H<sub>2</sub>O were obtained from diffusion of diethyl ether into a CH<sub>3</sub>CN–CH<sub>2</sub>Cl<sub>2</sub> solution of **1** and excess **2** in three days. In the absence of guest molecules, the rectangle slowly decomposes in solution. On the other hand, no decomposition was observed for a mixture of **1** and **2** over weeks, suggesting that the host is stabilized by binding to the guest.

The crystal structure of  $(1)_2 \supset 2 \cdot 2 CH_3 CN \cdot 2 CH_2 Cl_2 \cdot 4H_2 O$ exhibits a dumbbell-like architecture whereby a molecule of 2 is inserted into two rectangles (Fig. 1).§ The two rectangles are parallel and separated by 12.146 Å, which is the shortest intermolecular Au-Au distance. The structure of the rectangle is similar to that of free 1, being composed of two syn-oriented  $[Au_2(\mu$ -PAnP)]<sup>2+</sup> clips connected by two bipy ligands. The Au–P (2.249(3) Å) and Au-N bond distances (2.075(9) Å) and the P-Au-N angles (177.12° and 175.12°) are typical for gold(I) complexes.8 The two anthracenyl rings of 2 are intercalated between the bipy ligands of the rectangles. While the anthracenyl rings in 2 are coplanar, they make a dihedral angle of 53° with the two phenyl rings which are disordered equally over two positions. The overlap of the anthracenyl and bipy rings is staggered with the long axis of the anthracenyl rings and the N-N vector of the bipy forming an angle of 23.3°. The two faces of the rectangle are not equivalent: the opposite bipy ligands are not parallel, with the side  $(\sim 7.5 \text{ Å})$  close to the phenyl rings of 2 being wider than the



Fig. 1 X-Ray crystal structure of  $(1)_2 \supset 2 \cdot 2 CH_3 CN \cdot 2 CH_2 Cl_2 \cdot 4H_2 O$ . Hydrogen atoms, and solvent molecules are omitted for clarity. Colour scheme: yellow, Au; pink, P; light blue, N; blue, C atoms of PAnP; orange, C atoms of **2**.

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543. E-mail: chmyiphk@nus.edu.sg; Fax: +65 67791691; Tel: +65 65166256

<sup>†</sup> Electronic supplementary information (ESI) available: Solid-state absorption spectra of 1, 2 and (1)<sub>2</sub> $\supset$ 2·2CH<sub>3</sub>CN·2CH<sub>2</sub>Cl<sub>2</sub>·4H<sub>2</sub>O. CCDC reference number 678826. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b802957a



**Fig. 2** Packing diagrams of  $(1)_2 \supset 2 \cdot 2CH_3CN \cdot 2CH_2Cl_2 \cdot 4H_2O$ . Hydrogen atoms and solvent molecules are omitted for clarity. Colour scheme: orange, Au; green, F; red, O; yellow, S; purple, P.

other side (~6.6 Å). The distortion is likely due to steric repulsion between the phenyl rings and the bipy. The hindrance could be the reason for the extremely slow formation of the pseudorotaxane in solution. The average distance between the planes of the bipy and anthracenyl rings is 3.463 Å and falls into the range of  $\pi$ - $\pi$  interactions (~3.5–3.7 Å).

The width of the rectangles in  $(1)_2 \supset 2$  is markedly shortened: the intraannular Au–Au distance is 6.594 Å (*cf.* Au–Au = 7.069 Å in free 1). The contraction brings the guest closer to the bipy, enhancing the  $\pi$ - $\pi$  or charge transfer interactions. In order to bring the Au ions closer, the central rings in the lateral anthracenyl backbones are markedly distorted from planarity with a bow angle of 42.5°. The pseudorotaxanes are packed into columns in the crystals (Fig. 2).

The dimers in a column are separated by a Au–Au distance of 10.7 Å. Each rectangle is surrounded by four rectangles (Fig. 2a). Two triflate ions are located in the pseudorotaxane. Another two anions are outside of the ring but near to the bipy ligands. The remaining four anions are sandwiched between two pseudorotaxanes in a column. Two  $CH_2Cl_2$  molecules are located between the gold rectangles in a dimer while the other solvent molecules are found in interstitial space. The <sup>1</sup>H NMR spectrum of (1)<sub>2</sub> $\supset$ 2 shows signals of free 1 and 2, indicating dissociation of the pseudorotaxane in solution, which is consistent with the low stability of the host–guest complex.

Both 1 ( $\lambda_{max} = 487 \text{ nm}$ ) and 2 ( $\lambda_{max} = 470 \text{ nm}$ ) are strongly emissive in the solid state, displaying  ${}^{1}\pi^{*} \rightarrow \pi$  fluorescence originated from the anthracenyl rings (Fig. 3). However, the solid-state emission of  $(1)_{2} \supset 2$  ( $\lambda_{max} = 483 \text{ nm}$ ), which comprises both emissions of 1 and 2, is very weak.



Fig. 3 Solid-state emission spectra of 1 (red), 2 (black) and  $(1)_2 \supset 2$  (blue).

The emission of  $(1)_2 \supset 2$  is possibly quenched by a rapid energy transfer from the emissive  $\pi\pi^*$  excited state to a nonemissive charge-transfer (CT) excited state which arises from the interactions between the anthracenyl rings of 2 (donors) and the bipy ions of 1 (acceptors) in the host-guest complex. The presence of the CT interactions is suggested by the solid state UV-vis absorption spectrum of the complex which displays a broad, low energy absorption at ~500–600 nm, which is absent in the spectra of 1 and 2 (see ESI†). The absorption, which accounts for the red colour of the complex, is possibly due to a CT transition. Similar CT bands were observed in the inclusion complexes of hosts containing bipy ions (*e.g.* cyclobis(paraquat-*p*-phenylene) and electron-rich guests (*e.g.* hydroquinol).<sup>9</sup> We have demonstrated that a pseudorotaxane can be assembled *via*  $\pi$ - $\pi$  and charge-transfer interactions between an electron-accepting molecular rectangle and a linear template which contains electron-rich anthracenyl rings. This approach could be generalized for other molecular architectures. Syntheses of templates of different geometries are on-going in our laboratory.

#### Acknowledgements

The authors would like to thank National University of Singapore for financial support and Ms Tan Geok Kheng and Prof. Koh Lip Lin for determining the crystal structure.

### Notes and references

<sup>‡</sup> [Au<sub>4</sub>(μ-PAnP)<sub>2</sub>(μ-bipy)<sub>2</sub>](OTf)<sub>4</sub> 1<sup>6</sup> and 4,4'-bis(9"-anthryl)biphenyl 2<sup>7</sup> were synthesized according to the reported methods. 1: yield = 90%. Anal. calcd for C<sub>100</sub>H<sub>72</sub>Au<sub>4</sub>F<sub>12</sub>N<sub>4</sub>O<sub>12</sub>P<sub>4</sub>S<sub>4</sub>: C, 43.1; H, 2.6; N, 2.0%. Found: C, 42.3; H, 2.6; N, 1.9%. <sup>†</sup>H NMR (CD<sub>3</sub>CN, 300 MHz): δ 8.65 (d, 8H, H<sup>6</sup> of bipy), 8.41 (dd, 8H, H<sup>23.67</sup> of anthracenyl ring), 8.02 (d, 8H, H<sup>β</sup> of bipy), 7.83–7.61 (m, 40H, Ph), 7.34 (dd, 8H, H<sup>14.58</sup> of anthracenyl ring). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 121 MHz): δ 22.7 (s). **2**: yield = 70%. Anal. calcd for C<sub>40</sub>H<sub>26</sub>: C, 94.8; H, 5.2%. Found: C, 94.4; H, 5.3%. <sup>†</sup>H NMR spectrum (CD<sub>3</sub>CN, 300 MHz): δ 8.53 (s, 2H, H<sup>10</sup>), 8.08 (d, 4H, H<sup>4.5</sup>), 8.00 (d, 4H, H<sup>12.16</sup>), 7.80 (d, 4H, H<sup>1.8</sup>), 7.58 (d, 4H, H<sup>13.15</sup>). 7.48 (td, 4H, H<sup>2.7</sup>), 7.41 (td, 4H, H<sup>3.6</sup>).

 $(1)_2 \supset 2 \cdot 2 CH_3 CN \cdot 2 CH_2 Cl_2 \cdot 4H_2 O$ . A CH<sub>3</sub>CN solution of 1 was mixed with a saturated CH2Cl2 solution of 2. Red crystals of the complex were obtained by slow diffusion of diethyl ether into the mixed solutions at room temperature. Yield = 40%. Anal. calcd for  $(1)_2 \supset 2$ ,  $C_{240}H_{170}Au_8F_{24}N_8O_{24}P_8S_8$ : C, 47.4; H, 2.8; N, 1.8%. Found: C, 46.8; H, 2.7; N, 1.6%. Molecular formula:  $C_{246}H_{188}Au_8Cl_4F_{24}N_{10}O_{28}P_8S_8$ , fw = 6409.84, monoclinic space group C2/m, a = 32.418(2) Å, b = 23.372(1) Å, c = 22.3156(1) Å, a = $90^{\circ}, \beta = 123.530(1)^{\circ}, \gamma = 90^{\circ}, V = 14094.6(14) \text{ Å}^3, \rho_{\text{calcd}} = 1.510 \text{ g cm}^{-3},$ Z = 2, absorption coefficient = 4.364 mm<sup>-1</sup>, for the 40446 reflections collected, 12755 were independent ( $R_{int} = 0.0633$ ). Index range:  $-36 \le h \le$ 38,  $-22 \le k \le 27$ ,  $-26 \le l \le 26$ . Refinement of  $F^2$  converged with  $R_1 =$ 0.0677 for  $I > 2\sigma(I)$  and  $wR_2 = 0.2083$ . The residual electron density is 3.431 and -0.989 e Å<sup>-3</sup>. The large residue is near the gold atoms (0.98 Å). The diffraction experiments were carried out on a Bruker AXS SMART CCD 3-circle diffractometer: (Mo-K<sub>a</sub>) = 0.71073 Å, T = 223(2) K,  $2\theta - \omega$ scan. The software used were: SMART<sup>10</sup> for collecting frames of data, indexing reflection and determination of lattice parameters; SAINT<sup>10</sup> for integration of intensity of reflections and scaling; SADABS11 for empirical absorption correction; and SHELXTL12 for space group determination, structure solution and least-squares refinements on  $|F|^2$ .

- 1 J. M. Lehn, *Science*, 2002, **295**, 2400; V. Balzaini, A. Credi and M. Venturi, *Chem.-Eur. J.*, 2002, **8**, 5525.
- S. K. Dey, T. S. M. Abedin, L. N. Dawe, S. S. Tandon, J. L. Collins, L. K. Thompson, A. V. Postnikov, M. S. Alam and P. Muller, *Inorg. Chem.*, 2007, 46, 7767; I. Goldberg, *Chem. Commun.*, 2005, 1243; J. P. Hill, Y. Wakayama, M. Akada and K. Ariga, *J. Phys. Chem. C*, 2007, 111, 16174; M. A. Lingenfelder, H. Spillmann, A. Dimitriev, S. Stepanow, N. Lin, J. V. Barth and K. Kern, *Chem.-Eur. J.*, 2004, 10, 1913; X. Lin, D. M. J. Doble, A. J. Blake, A. Harrison, C. Wilson and M Schröder, *J. Am. Chem. Soc.*, 2003, 125, 9476.
- B. Champin, P. Mobian and J. P. Sauvage, *Chem. Soc. Rev.*, 2007, 36, 358;
  S. J. Loeb, *Chem. Soc. Rev.*, 2007, 36, 226;
  M. S. Vickers and P. D. Beer, *Chem. Soc. Rev.*, 2007, 36, 211;
  V. Aucagne, J. Berna, J. D. Crowley, S. M. Goldup, K. D. Hanni, D. A. Leigh, P. J. Lusby, V. E. Ronaldson, A. M. Z. Slawin, A. Viterisi and D. B. Walker, *J. Am. Chem. Soc.*, 2007, 129, 11950;
  F. Huang, C. Slebodnick, E. J. Mahan and H. W. Gibson, *Tetrahedron*, 2007, 63, 2875.
- 4 M. D. Pluth, R. G. Bergman and K. N. Raymond, Angew. Chem., Int. Ed., 2007, 46, 8587; Y.-F. Han, Y.-J. Lin, W.-G. Jia, L.-H. Weng and G.-X. Jin, Organometallics, 2007, 26, 5848; M. Yoshizawa, M. Tamura and M. Fujita, Science, 2006, 312, 251; R. P. John, J. Park, D. Moon, K. Lee and M. S. Lah, Chem. Commun., 2006, 3699; D. M. Vriezema, M. C. Aragones, J. A. A. W. Elemans, J. J. L. M. Cornelissen, A. E. Rowan and R. J. M. Nolte, Chem. Rev., 2005, 105, 1445; S. S. Sun, C. L. Stern, S. T. Nguyen and J. T. Hupp, J. Am. Chem. Soc., 2004, 126, 6314; H. Jiang and W. Lin, J. Am. Chem. Soc., 2003, 125, 8084; M. Fujita, M. Tominaga, A. Hori and B. Therrien, Acc. Chem. Res., 2005, 38, 369.
- 5 J.-R. Gong, L.-J. Wan, Q.-H. Yuan, C.-L. Bai, H. Jude and P. J. Stang, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 971; S. S. Li, H. J. Yan, L. J. Wan, H. B. Yang, B. H. Northrop and P. J. Stang, *J. Am. Chem. Soc.*, 2007, **129**, 9268; L. J. Wan, *Acc. Chem. Res.*, 2006, **39**, 334; G. M. Whitesides and M. Boncheva, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4769; K. W. Hipps, L. Scudiero, D. E. Barlow and M. P. Cooke, Jr., *J. Am. Chem. Soc.*, 2002, **124**, 2126; A. Ulman, *Chem. Rev.*, 1996, **96**, 1533.
- 6 R. Lin, J. H. K. Yip, K. Zhang, L. L. Koh, K. Y. Wong and K. P. Ho, J. Am. Chem. Soc., 2004, 126, 15852.
- 7 B. Becher, R. Cosmo and K. Mullen, Tetrahedron Lett., 1989, 30, 1629.
- 8 S. E. Thwaite, A. Schier and H. Schmidbaur, *Inorg. Chim. Acta*, 2004, **357**, 1549.
- 9 B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem.*, *Int. Ed. Engl.*, 1988, 27, 1547.
- 10 SMART & SAINT Software Reference Manuals, Version 4.0, Siemens Energy & Automation, Inc., Analytical Instrumentation, Madison, WI, USA, 1996.
- 11 G. M. Sheldrick, SADABS, Program for area detector adsorption correction, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.
- 12 G. M. Sheldrick, SHELXTL Reference Manual, Version 5.03, Siemens Energy & Automation, Inc., Analytical Instrumentation, Madison, WI, USA, 1996.