

Synthesis, characterization and molecular recognition of a bis-platinum terpyridine dimer[†]

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A novel bis-platinum(II) terpyridine-based macrocycle has been quantitatively obtained by self-assembly; the Pt(II) host binds neutral planar and electron-rich aromatic guests with good selectivity in DMSO.

Pd(II) and Pt(II)^{1–3} are widely used in molecular self-assembly, which has emerged as one of the most efficient methods to create new materials with controlled physical and chemical properties.^{4–6} The number of examples of Pt(II) self-assembly with conformationally-flexible N-ligands compared to that of Pd(II) analogs remain limited.^{7,8} This can be attributed to the general inertness and the high thermodynamic stability of Pt–N bonds. One way to overcome this limitation is to design self-assembly systems from terpyridyl Pt(II) complexes. These have been shown to facilitate the displacement of the fourth ligand as a consequence of π -back-bonding from the metal to the empty π^* -orbitals of the pyridine sub-units.⁹ Reasoning that a cavity with planar parallel-disposed building units would offer enhanced binding and selectivity for planar aromatic guests, molecular receptors consisting of two terpyridine units present an attractive approach towards application in molecular recognition. Bosnich and co-workers¹⁰ have reported molecular recognition using a rigid spacer-chelator bearing cofacial terpyridyl Pd(II) and Pt(II) complexes. These receptors interact with 9-methylanthracene, not only inside, but also outside the cleft recognition site to give 1 : 1 and 1 : 2 host–guest complexes. For other neutral aromatic guests, gels were formed, indicating extensive self-aggregation.

In this Communication, we describe novel Pt-host **1**, which was quantitatively formed by the simple self-assembly of **5**. Stable metallohost **1** exhibits a unique and selective binding behavior towards electron-rich aromatic compounds with a 1 : 1 stoichiometry.

Synthesis of **5**, the precursor of **1**, is shown in Scheme 1. The bis-platinum complex **1** was quantitatively formed upon addition of 1.85 equiv. of Pt(cod)(BF₄)₂ in acetone to a solution of **5** in acetonitrile/chloroform and isolated as a yellow solid.

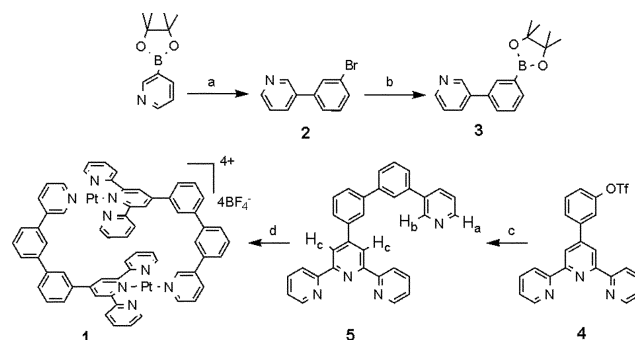
¹H NMR spectra in DMSO-*d*₆ revealed selective dimer formation, in which the two assembled ligands are equivalent. In the platinum complex, for the most part, downfield shifts of

several tenths of a ppm were observed, with particularly significant downfield shifts of the terminal pyridyl protons H_a ($\Delta\delta$ = 0.61 ppm) and H_b ($\Delta\delta$ = 0.86 ppm) (Fig. 1). Additional support for the proposed structure of self-assembly was provided by an ESI-MS analysis of **1** as a tetrafluoroborate salt in MeOH/CHCl₃. The prominent peak at *m/z* = 328.56 was attributed to the 4+ ion.

Host **1** possesses a cavity that permits the recognition of flat aromatic guests. ¹H NMR titration experiments of **1** with benzene and naphthalene derivatives were carried out at 2 mM in DMSO-*d*₆ (Fig. 2). Plots of the chemical shift of H_c vs. the concentration of guests produced isotherms that nicely fitted a 1 : 1 host–guest model to yield binding constants, *K*_a. The NOE cross-correlation peaks in the NOESY spectrum between naphthalene-2,6-diol and **1** cavity protons demonstrate that the guest exclusively locates inside the cavity of **1**. It is noteworthy that the more electron-rich aromatic compounds work better as a guest (Table 1).

The UV/vis spectrum of the host–guest complex of **1** with naphthalene-2,6-diol is dominated by strong absorption bands in the region 230–420 nm. The broad and weak charge-transfer absorption, reaching up to 650 nm, with a maximum extinction coefficient of 860 M^{–1} cm^{–1}, is responsible for the red color of the host–guest complex.

Red needle-like single crystals of **1** with naphthalene-2,6-diol as a guest were obtained by means of the vapor diffusion of benzene into a solution of **1** and naphthalene-2,6-diol in DMSO. The X-ray structure of the complex is depicted in Fig. 3.¹¹ The least-square planes of the two terpyridine rings lie parallel to each other with a 6.67 Å distance, enabling



Scheme 1 Synthesis of **1**. Reagents and conditions: (a) 1,3-dibromobenzene, Pd(PPh₃)₄, K₂CO₃, dioxane, 56%; (b) 4,4,5,5-tetramethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolane, Pd(dppf)Cl₂, dppf, KOAc, dioxane, 94%; (c) **3**, Pd(dppf)Cl₂, dppf, K₂CO₃, dioxane, 33%; (d) Pt(cod)(BF₄)₂, CH₃CN, CHCl₃, CH₃COCH₃, 99%.

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[†] Electronic supplementary information (ESI) available: Experimental details of ¹H NMR and UV-vis titration, ESI-MS analysis of **1**, and NOESY spectrum of the 1:naphthalene-2,6-diol complex. See DOI: 10.1039/b716459a

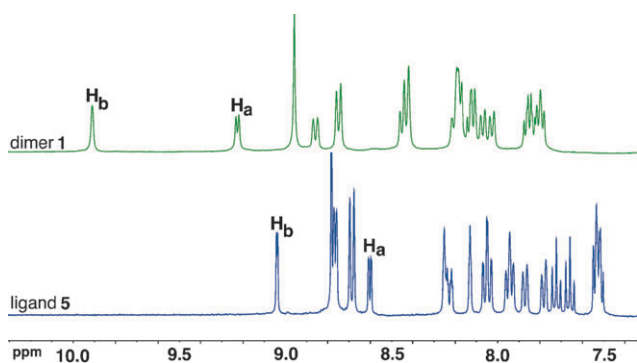


Fig. 1 ^1H NMR spectra of **1** and **5** (400 MHz, $[\mathbf{1}] = [\mathbf{5}] = 4 \text{ mM}$, $\text{DMSO-}d_6$, 25°C).

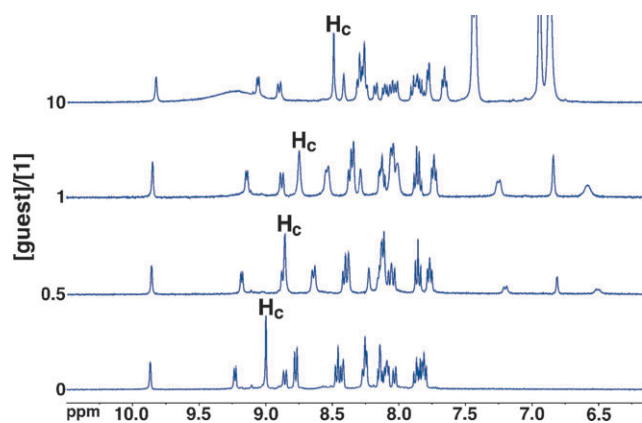


Fig. 2 ^1H NMR spectra upon the addition of naphthalene-2,6-diol to **1** (400 MHz, $[\mathbf{1}] = 2 \text{ mM}$, $\text{DMSO-}d_6$, 25°C).

Table 1 Association constants for various aromatic guests with **1**^a

Guest	K_a/M^{-1}
Naphthalene-2,6-diol	710 ± 30
Naphthalene-2,3-diol	630 ± 30
Benzene-1,4-diol	460 ± 13
Benzene-1,3-diol	300 ± 8
Naphthalene-2-ol	230 ± 3
Benzene-1,2-diol	200 ± 11
Pyrene	83 ± 1
2-Chloronaphthalene	80 ± 3
1,4-Dichlorobenzene	16 ± 1
1,2-Dichlorobenzene	14 ± 1

^a Conditions: ^1H NMR 400 MHz, $[\mathbf{1}] = 2 \text{ mM}$, $\text{DMSO-}d_6$, 25°C .

π -stacking interactions with the guest.^{12–15} Both **1** and the naphthalene-2,6-diol molecule lie about the same inversion centre at (0.5, 0.5, 0.5) in the crystal. The dihedral angle between the plane of the naphthalene ring and the mean least-square plane of the terpyridyl moiety is $4.67 \pm 0.19^\circ$. The Pt–N distances in the terpyridine are in excellent agreement with those previously reported for terpyridyl Pt(II) complexes.^{16–21}

In summary, novel bis-platinum dimer **1**, as a metallohost, was quantitatively synthesized in a very facile self-assembling way. The size of the cavity enables efficient π -stacking interactions with neutral planar and electron-rich aromatic guests.

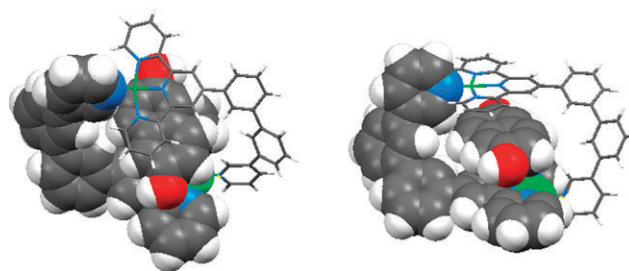


Fig. 3 X-Ray structure of **1** with naphthalene-2,6-diol as a guest; for clarity, one part of **1** is shown in a capped-stick representation, and the second part in a space-filling representation: top view (left), side view (right); platinum is colored green, nitrogen colored blue and oxygen colored red.

Since the simple efficient synthetic route and promising recognition properties of **1** warrant further scrutiny, these results will be reported in due course.

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Notes and references

- M. Yoshizawa and M. Fujita, *Pure Appl. Chem.*, 2005, **77**, 1107.
- A. Kaiser and P. Bäuerle, *Top. Curr. Chem.*, 2005, **249**, 127.
- S. R. Seidel and P. J. Stang, *Acc. Chem. Res.*, 2002, **35**, 972.
- S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853.
- J. S. Siegel, *Science*, 1996, **271**, 949.
- M. W. Cooke and G. S. Hanan, *Chem. Soc. Rev.*, 2007, **36**, 1466.
- M. Fujita and K. Ogura, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1471.
- P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502.
- R. Romeo, M. R. Plutino, L. M. Scolaro, S. Stoccoro and G. Minghetti, *Inorg. Chem.*, 2000, **39**, 4749.
- J. D. Crowley, I. M. Steele and B. Bosnich, *Inorg. Chem.*, 2005, **44**, 2989.
- Crystal data for **1**·naphthalene-2,6-diol·6DMSO·5H₂O: formula C₈₆H₁₀₆B₄F₁₆N₈O₁₃Pt₂S₆, formula weight 2381.50, crystal system triclinic, space group *P1*, $a = 10.382(4)$, $b = 17.061(7)$, $c = 18.049(7)$ Å, $\alpha = 114.721(16)$, $\beta = 91.774(13)$, $\gamma = 101.924(14)^\circ$, $V = 2816.3(19)$ Å³, $Z = 1$, reflections measured 22 301, unique reflections 9888 ($R_{\text{int}} = 0.1062$), temperature = 120 K, $R1$ ($I > 2\sigma(I)$) = 0.0796, $wR2$ (all data) = 0.2052.²² CCDC 665387. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716459a.
- C. A. Hunter, M. N. Meah and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5773.
- C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
- C. A. Hunter, K. R. Lawson, J. Perkins and C. J. Urch, *J. Chem. Soc., Perkin Trans. 2*, 2001, 651.
- C. G. Claessens and J. F. Stoddart, *J. Phys. Org. Chem.*, 1997, **10**, 254.
- R. Büchner, J. S. Field, R. J. Haines, C. T. Cunningham and D. R. McMillin, *Inorg. Chem.*, 1997, **36**, 3952.
- M. Akiba, K. Umakoshi and Y. Sasaki, *Chem. Lett.*, 1995, 607.
- K. W. Jennette, J. T. Gill, J. A. Sadownik and S. J. Lippard, *J. Am. Chem. Soc.*, 1976, **98**, 6159.
- J. A. Bailey, M. G. Hill, R. E. Marsh, V. M. Miskowski, W. P. Schaefer and H. B. Gray, *Inorg. Chem.*, 1995, **34**, 4591.
- J. A. Bailey and H. B. Gray, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1992, **48**, 1420.
- A. Chernega, A. S. Droz, K. Prout, T. Vilaivan, G. W. Weaver and G. Lowe, *J. Chem. Res. (S)*, 1996, 402.
- G. M. Sheldrick, *SHELXL-97, Program for the refinement of crystal structures*, University of Göttingen, Germany, 1997.