The first example of a Pt · · · Pt interaction in platinum(II) complexes bearing bulky tri-*tert*-butyl-2,2':6',2"-terpyridine pendants *via* conformational control of the calix[4]arene moiety†‡

Hiu-Suet Lo, Sung-Kong Yip, Nianyong Zhu and Vivian Wing-Wah Yam*

Received 16th August 2007, Accepted 21st August 2007 First published as an Advance Article on the web 6th September 2007 DOI: 10.1039/b712645j

An unprecedented short $Pt \cdots Pt$ contact between sterically bulky $Pt('Bu_3trpy)$ alkynyl moieties has been observed in the X-ray crystal structure of a dinuclear platinum(II) complex bridged by a diethynylcalix[4]arene derivative; the complex in its crystalline state showed a red shift in the emission maxima at 298 K and 77 K relative to its powder form, which has been attributed to the presence of a metal–metal interaction in the crystal lattice.

Over the past decade, the design and construction of discrete functional supramolecular species has been an area of intense interest.¹ Calix[n]arenes, in addition to their well known ability to serve as ion receptors,² are one of the most important building blocks in supramolecular chemistry and an attractive candidate for molecular design strategies, owing to their unique molecular structures, simple one-pot preparations, easy chemical transformability on the lower and upper rims, as well as their "tunable" molecular shapes and conformations.³ By combining all these intrinsic properties, calix[4]arenes may serve as versatile ligands for the construction of luminescent transition-metal alkynyl supramolecular assemblies.⁴ Since d⁸-d⁸ metal complexes with well defined metal-metal distances are well-known to exhibit unique spectroscopic and luminescence features associated with these metal-metal interactions,5-7 the square-planar coordination geometry of d⁸ platinum(II) polypyridyl complexes has therefore attracted a lot of interest and led to their increasing utilization as versatile building blocks for self-assembly.6,7a-c,e,f

Recently, our group has synthesised a number of platinum(II) terpyridyl alkynyl complexes which show drastic colour changes and luminescence enhancement upon intermolecular aggregation and oligomerisation.^{7a-e} Intramolecular self-association has also been demonstrated in a dinuclear platinum(II) terpyridyl system.^{7f} The reason behind these remarkable spectroscopic changes is suggested to be a result of the formation of inter- or intramolecular Pt ... Pt and $\pi \cdots \pi$ interactions in solution induced by nucleic acids,^{7a} polymers,^{7b} gelation,^{7c} solvents^{7d,e} or intramolecular self-association^{7f} of the metal complexes, leading to a change in its conformation and microenvironment. These changes have

been commonly observed in platinum(II) terpyridyl complexes with no or bulk-free substituents, as it is believed that the presence of bulky groups on the terpyridyl ligands will hinder the molecules from coming into close proximity with each other.7c,e,f,h Recently, we showed that utilization of calix[4]arene-containing ligands in a pre-determined and pre-organised geometry could generate highly novel tetranuclear gold(I) assemblies with short Au...Au contacts.4d We believed that by using appropriately designed calix[4]arene in a pre-organised geometry as the clipping ligand, two platinum metal centres can be brought together at the lower rim to give rise to a short $Pt \cdots Pt$ contact. Herein, we report the synthesis and structural characterisation of dinuclear platinum(II)-alkynylcalix[4]arene assemblies and demonstrate the existence of a short Pt ··· Pt contact for the very first time in platinum(II) terpyridyl complexes bearing sterically-demanding tri-tert-butyl groups; their photophysical properties associated with metal \cdots metal and $\pi \cdots \pi$ interactions will also be discussed.

Complexes 1 and 2 were synthesised according to a modification of a literature procedure for the synthesis of platinum(II) terpyridyl alkynyl complexes,^{7g} in which [Pt('Bu₃trpy)(MeCN)](OTf)₂ and [Pt(trpy)(MeCN)](OTf)₂, respectively, were allowed to react with the calix[4]arene-containing bis-alkynyl ligand, L in MeOH in the presence of KF (Scheme 1). Subsequent diffusion of diethyl ether vapour into a dichloromethane solution of 1 and an acetonitrile solution of 2 gave the corresponding complexes as orange-red crystals and a dark-red solid; the crystals of 1 obtained were suitable for crystallographic analysis.§



Scheme 1

Centre for Carbon-Rich Molecular and Nano-Scale Metal-Based Materials Research, and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China. E-mail: wwyam@hku.hk; Fax: +852 2857-1586; Tel: +852 2859-2153

[†] CCDC reference number 654512. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712645j

[‡] Electronic supplementary information (ESI) available: Detailed characterisation, UV-vis absorption spectra and emission spectra. See DOI: 10.1039/b712645j

Fig. 1 depicts the structure of the complex cation of 1. The calix[4]arene adopts the "pinch-cone" conformation, which can be clearly revealed in the structure where the aryl rings substituted with ester groups within the calix[4]arene moieties are placed almost parallel to each other (interplanar angle 9.08°), and are tilted so as to increase the separation between the two tert-butyl groups leading to an $O(3) \cdots O(4)$ separation of 4.90 Å. The two phenolic rings in the calix[4] arene are also tilted (interplanar angle 74.55°) so as to place the hydroxyl groups inside the cavity, with an $O(1) \cdots O(2)$ separation of 3.15 Å. This arrangement allows for easy hydrogen bond formation between the proximal hydroxy groups and the ester functionalities. This hydrogen bonding, together with the four bulky tert-butyl groups on the upper rim of calix[4]arene help stabilise and lock the calix[4]arene in the cone conformation.8 The dihedral angles between the plane containing the four methylene carbon atoms linking the aromatic rings and the planes of the aryl rings bearing ester groups are found to be 91.07° and 97.96° , with a difference of close to 7° between the two angles. Compared with other calix[4]arene systems devoid of sterically bulky groups in the lower rims, the difference between these two angles is about 2°. This deviation is probably due to the presence of the sterically demanding tri-tert-butyl groups on each of the terpyridyl ligands.8



Fig. 1 Perspective drawing of the complex cation of **1** with selected atomic numbering scheme. Hydrogen atoms and solvent molecules have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

The two platinum(II) metal centres adopt a distorted squareplanar geometry, with distortion from the idealised 90° and 180° due to the coordination constraints imposed by the terpyridyl ligands (N(1)-Pt(1)-N(3) 161.5-161.9°; N(1)-Pt(1)-N(2) and N(2)-Pt(1)-N(3) 80.2-81.5°). The two platinum(II)-terpyridyl moieties are connected to the calix[4]arene by the alkynyl groups in a linear fashion with Pt-C≡C angles in the range of 178.1-178.9°. The Pt–C (1.964–1.977 Å) and C=C (1.203–1.228 Å) bond lengths are comparable to that found in the related platinum(II)alkynyl systems.7e-i,9 The phenyl rings directly attached to the alkynyl ligands are almost parallel to the planes of the platinumterpyridine with dihedral angles of 4.29° and 7.22°. The two [Pt('Bu3trpy)] coordination planes are essentially parallel, as revealed by the interplanar angle of 11.25°; and the interplanar distance of 3.53 Å, as calculated from the average distances of the atoms on the two least squares planes, suggested the existence of a $\pi \cdots \pi$ stacking interaction. Surprisingly, unlike the other related system,7f,h,9,10a the two terpyridyl groups are found to be in a staggered conformation. With this arrangement, the mutual repulsions between the sterically bulky tri-tert-butyl terpyridyl ligands can be minimised. Astonishingly, the intramolecular Pt \cdots Pt distance is found to be 3.272 Å, which is shorter than the sum of van der Waals' radii of Pt (3.4 Å) and is suggestive of an intramolecular interaction between the two metal centres. Both the Pt \cdots Pt and $\pi \cdots \pi$ stacking interactions are thought to play a role in providing the driving force for locking the Pt('Bu₃trpy) units together. It is interesting to note that mechanical grinding of the orange-red crystals would give rise to a light orange powder. This is probably due to the breakage of Pt \cdots Pt and $\pi \cdots \pi$ stacking interactions caused by the collapse of crystal lattices and the loss of solvents of recrystallisation.51,7d

Dissolution of **1** and **2** in acetonitrile gave a yellow solution, with similar UV-vis absorption patterns. Both spectra are dominated by high-energy intraligand absorption bands at *ca.* 294–314 nm, and an admixture of low-energy metal-to-ligand charge-transfer (MLCT) and alkynyl-to-terpyridine ligand-to-ligand charge-transfer (LLCT) bands at *ca.* 448–456 nm in the visible region (Fig. S2[‡]), typical of monomeric platinum(II) terpyridyl complexes.^{7e,i,10} A slight red shift of the MLCT/LLCT band was observed in **2** relative to **1**. This has been attributed to the electron-richness of the *tert*-butyl substituents on the 'Bu₃trpy units, which raise the energy of the π^* ('Bu₃trpy) orbital. The photophysical data are summarised in Table 1.

Upon excitation at $\lambda > 400$ nm, both 1 and 2 exhibited luminescence at about 641–742 nm in acetonitrile solution at room temperature and butyronitrile glass at 77 K. With reference to the spectroscopic studies on other related platinium(II)– terpyridyl systems,^{7e-i,10} the origin of the luminescence is assigned

Complex	Medium (T/K)	Absorption $\lambda_{max}/nm (\epsilon_{max}/dm^3 \text{ mol}^{-1} \text{ cm}^{-1})$	Emission $\lambda_{max}/nm(\tau_0/\mu s)$
2	MeCN (298) Powder solid (298) Crystalline solid (298) Powder solid (77) Crystalline solid (77) Glass (77) MeCN (298) Solid (298) Solid (77)	294 (88 380), 314 sh (82 590), 448 (16 180) 294 (65 490), 312 sh (51 160), 456 (10 445)	$\begin{array}{c} 693 \ (0.6) \\ 640 \ (0.2) \\ 663 \ (0.3) \\ 626 \ (1.5) \\ 652 \ (2.0) \\ 641 \ (2.3) \\ 742 \ (<0.1) \\ 834 \ (0.1) \\ 825 \ (0.3) \end{array}$
	Glass (77)		654 (2.3)

Table 1Photophysical spectral data for 1 and 2

as being derived from states of predominantly ³MLCT [$d\pi(Pt) \rightarrow \pi^*({}^{\prime}Bu_3trpy)$] character, mixed with some intraligand ³LLCT [$\pi(C \equiv CR) \rightarrow \pi^*({}^{\prime}Bu_3trpy)$] character. Again, the red shift in the emission bands of **2** relative to that of **1** is consistent with the electron-donating ability of the tri-*tert*-butyl groups on the terpyridyl ligands.

Both the crystalline and powder solids of 1 exhibited rich luminescent properties at 298 K and 77 K, with the ³MLCT emissive state energy of the crystalline solid slightly lower than that of the powder form (Fig. S3[‡]). This may be attributed to the existence of a weak Pt ··· Pt interaction and little partial $\pi \cdots \pi$ stacking as observed in its crystal lattice. However, the emission maxima of the two forms do not vary to a large extent as is observed in the related platinum(II)-terpyridyl complexes.^{7e} This may probably be attributed to the staggered arrangement of the tri-tert-butylterpyridine units, leading to poor spatial overlap. The solid-state emission of 2 showed emission maxima at $\lambda > 820$ nm at 298 K and 77 K. With reference to previous spectroscopic studies on platinum(II)-terpyridyl complexes,7a-g these low-energy emissions are assigned as originating from triplet states of MMLCT character, associated with the presence of Pt \cdots Pt and $\pi \cdots \pi$ stacking interactions. It is likely that in the absence of the bulky *tert*-butyl groups on the terpyridine unit in 2, stronger Pt · · · Pt and $\pi \cdot \cdot \cdot \pi$ stacking interactions can exist. This, together with the lower π^* orbital energy of trpy than 'Bu₃trpy, would give rise to a low-energy MMLCT emission at $\lambda > 800$ nm in the solid state.

In conclusion, a new class of luminescent dinuclear platinum-(II)-terpyridyl calix[4]arene-containing bis-alkynyl complexes has been demonstrated to possess Pt...Pt and $\pi \cdots \pi$ interactions in the solid state. An unprecedented Pt...Pt close contact of 3.272 Å was observed in the dinuclear platinum(II) calix[4]arenebis-alkynyl complex, representing the very first example of a Pt...Pt interaction in platinum(II) complexes containing the bulky tri-*tert*-butyl terpyridine ligand. This probably arises from the unique conformational arrangement of the calix[4]arene moiety as well as the propensity of Pt metal centres and π -aromatic ligands for non-covalent interactions that lock the two Pt– 'Bu₃trpy units together. The formation of Pt...Pt and $\pi \cdots \pi$ stacking interactions also provides the driving force for such a phenomenon.

Acknowledgements

V. W.-W. Y. acknowledges support from the URC Seed Funding for Strategic Research Theme on Organic Optoelectronics and the Faculty Development Fund of The University of Hong Kong. The work described in this paper has been supported by a Central Allocation Vote (CAV) Grant from the Research Grants Council of Hong Kong Special Administrative Region, China (Project No. HKU 2/05C). H.-S. L. acknowledges the receipt of a postgraduate studentship, administered by The University of Hong Kong.

Notes and references

§ Crystallographic data. 1: C_{127.5}H₁₅₅Cl₃F₆N₆O₁₅Pt₂S₂, M_r = 2686.23, monoclinic, space group *P*2₁/*c*, *a* = 26.746(5) Å, *b* = 22.659(5) Å, *c* = 22.886(5) Å, β = 92.19(3)°, *V* = 13860(5) Å³, *Z* = 4, ρ_{calcd} = 1.287 g cm⁻³, μ (Mo-Kα) = 2.170 mm⁻¹. 57034 reflections measured. With the use of

16661 unique reflections collected at 253 K with Mo-K_a radiation ($\lambda = 0.71073$ Å) equal to $2\theta_{max} = 48.84^{\circ}$ on a single crystal X-ray MAR imageplate diffractometer, the structure was solved on a PC using the SIR-97 programme and refined by full-matrix least squares methods. The refinement converged to final $R_1 = 0.0553$ and $wR_2 = 0.1491$ with a goodness-of-fit of 0.91; the largest difference peak and hole 1.812 and -0.809 e Å⁻³ respectively.

- (a) D. B. Amabilino and J. F. Stoddart, Chem. Rev., 1995, 95, 2725;
 (b) P. Baxter, J. M. Lehn, A. Decian and J. Fischer, Angew. Chem., Int. Ed. Engl., 1993, 32, 69;
 (c) D. L. Caulder and K. N. Raymond, Acc. Chem. Res., 1999, 32, 975;
 (d) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa and K. Biradha, Chem. Commun., 2001, 509;
 (e) J. M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, Wiley-VCH, Weinheim, Germany, 1995;
 (f) S. Leininger, B. Olenyuk and P. J. Stang, Chem. Rev., 2000, 100, 853;
 (g) T. Evan-Salem, I. Baruch, L. Avram, Y. Cohen, L. C. Palmer and J. Rebek, Proc. Natl. Acad. Sci. USA, 2006, 103, 12296;
 (h) S. M. Biros and J. Rebek, Chem. Soc. Rev., 2007, 36, 93.
- 2 (a) A. F. D. de Namor, R. M. Cleverley and M. L. Zapata-Ormachea, *Chem. Rev.*, 1998, 98, 2495; (b) R. Ungaro, A. Arduini, A. Casnati, A. Pochini and F. Ugozzoli, *Pure Appl. Chem.*, 1996, 68, 1213; (c) W. Xu, J. P. Rourke, J. J. Vittal and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1993, 145.
- 3 (a) C. D. Gutsche, *Calixarenes*, Royal Society of Chemistry, Cambridge, UK, 1989; (b) S. Shinkai, *Tetrahedron*, 1993, 49, 8933; (c) C. D. Gutsche, *Calixarenes Revisited*, Royal Society of Chemistry, Cambridge, UK, 1998; (d) Z. Asfari, V. Bohmer, J. Harrowfield and J. Vicens, *Calixarenes 2001*, Kluwer, Dordrecht, Netherlands, 2001; (e) P. D. Harvey, *Coord. Chem. Rev.*, 2002, 233–234, 289.
- 4 (a) H. S. Lo, S. K. Yip, K. M. C. Wong, N. Y. Zhu and V. W. W. Yam, *Organometallics*, 2006, **25**, 3537; (b) V. W. W. Yam, K. L. Cheung, L. H. Yuan, K. M. C. Wong and K. K. Cheung, *Chem. Commun.*, 2000, 1513; (c) V. W. W. Yam, S. K. Yip, L. H. Yuan, K. L. Cheung, N. Y. Zhu and K. K. Cheung, *Organometallics*, 2003, **22**, 2630; (d) S. K. Yip, E. C. C. Cheng, L. H. Yuan, N. Y. Zhu and V. W. W. Yam, *Angew. Chem., Int. Ed.*, 2004, **43**, 4954.
- 5 (a) A. L. Balch, J. Am. Chem. Soc., 1976, 98, 8049; (b) N. S. Lewis, K. R. Mann, J. G. Gordon and H. B. Gray, J. Am. Chem. Soc., 1976, 98, 7461; (c) C. M. Che, V. W. W. Yam, W. T. Wong and T. F. Lai, Inorg. Chem., 1989, 28, 2908; (d) D. M. Roundhill, H. B. Gray and C. M. Che, Acc. Chem. Res., 1989, 22, 55; (e) D. C. Smith and H. B. Gray, Coord. Chem. Rev., 1990, 100, 169; (f) H. K. Yip, C. M. Che, Z. Y. Zhou and T. C. W. Mak, J. Chem. Soc., Chem. Commun., 1992, 1369; (g) H. K. Yip, L. K. Cheng, K. K. Cheung and C. M. Che, J. Chem. Soc., Dalton Trans., 1993, 2933; (h) D. R. Striplin and G. A. Crosby, J. Phys. Chem., 1995, 99, 7977; (i) T. V. O'Halloran, M. M. Roberts and S. J. Lippard, J. Am. Chem. Soc., 1983, 105, 3494; (k) H. Kunkely and A. Vogler, J. Am. Chem. Soc., 1990, 112, 5625; (l) S. C. F. Kui, S. S. Y. Chui, C. M. Che and N Zhu, J. Am. Chem. Soc., 2006, 128, 8297.
- 6 (a) C. K. Hui, B. W. K. Chu, N. Y. Zhu and V. W. W. Yam, *Inorg. Chem.*, 2002, **41**, 6178; (b) K. W. Jennette, J. T. Gill, J. A Sadownick and S. J. Lippard, *J. Am. Chem. Soc.*, 1976, **98**, 6159.
- 7 (a) C. Yu, K. H. Y. Chan, K. M. C. Wong and V. W. W. Yam, Proc. Natl. Acad. Sci. USA, 2006, 103, 19652; (b) C. Yu, K. M. C. Wong, K. H. Y. Chan and V. W. Yam, Angew. Chem., Int. Ed., 2005, 44, 791; (c) A. Y. Y. Tam, K. M. C. Wong, G. Wang and V. W. W. Yam, Chem. Commun., 2007, 2028; (d) V. W. W. Yam, K. H. Y. Chan, K. M. C. Wong and N. Y. Zhu, Chem.-Eur. J., 2005, 11, 4535; (e) V. W. W. Yam, K. M. C. Wong and N. Y. Zhu, J. Am. Chem. Soc., 2002, 124, 6506; (f) V. W. W. Yam, K. H. Y. Chan, K. M. C. Wong and N. Y. Zhu, J. Am. Chem. Soc., 2002, 124, 6566; (f) V. W. W. Yam, K. H. Y. Chan, K. M. C. Wong and B. W. K. Chu, Angew. Chem., Int. Ed., 2006, 45, 6169; (g) V. W. W. Yam, R. P. L. Tang, K. M. C. Wong and K. K. Cheung, Organometallics, 2001, 20, 4476; (h) V. W. W. Yam, K. M. C. Wong, W. S. Tang, B. W. K. Chu, N. Zhu and V. W. Yam, Organometallics, 2004, 23, 3459.
- 8 (a) M. A. McKervey, E. M. Seward, G. Ferguson, B. Ruhl and S. J. Harris, J. Chem. Soc., Chem. Commun., 1985, 388; (b) F. Arnaudneu, E. M. Collins, M. Deasy, G. Ferguson, S. J. Harris, B. Kaitner, A. J. Lough, M. A. McKervey, E. Marques, B. L. Ruhl, M. J. Schwing-Weill and E. M. Seward, J. Am. Chem. Soc., 1989, 111, 8681.

- 9 (a) W. Mohr, J. Stahl, F. Hampel and J. A. Gladysz, *Inorg. Chem.*, 2001, 40, 3263; (b) T. B. Peters, J. C. Bohling, A. M. Arif and J. A. Gladysz, *Organometallics*, 1999, 18, 3261; (c) J. Stahl, J. C. Bohling, E. B. Bauer, T. B. Peters, W. Mohr, J. M. Martin-Alvarez, F. Hampel and J. A. Gladysz, *Angew. Chem., Int. Ed.*, 2002, 41, 1872; (d) W. Lu, M. C. W. Chan, N. Y. Zhu, C. M. Che, Z. He and K. Y. Wong, *Chem.–Eur. J.*, 2003, 9, 6155.
- 10 (a) E. Shikhova, E. O. Danilov, S. Kinayyigit, I. E. Pomestchenko, A. D. Tregubov, F. Camerel, P. Retailleau, R. Ziessel and F. N. Castellano, *Inorg. Chem.*, 2007, 46, 3038; (b) R. Buechner, J. S. Field, R. J. Haines, C. T. Cunningham and D. R. McMillin, *Inorg. Chem.*, 1997, 36, 3952; (c) J. A. Bailey, M. G. Hill, R. E. Marsh, V. M. Miskowski, W. P. Schaefer and H. B. Gray, *Inorg. Chem.*, 1995, 34, 4591.