

# Dinuclear cyclometallated platinum(II) complex as a sensitive luminescent probe for SDS micelles

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The photoluminescent properties of two dinuclear cyclometallated Pt<sup>II</sup> complexes, [Pt<sub>2</sub>L<sup>1</sup><sub>2</sub>(μ-dppm)]<sup>2+</sup> **1** and [Pt<sub>2</sub>L<sup>2</sup><sub>2</sub>(μ-dppm)]<sup>2+</sup> **2**, in SDS micellar solution are studied and **1** is found to undergo enhancement of luminescence as well as switching of emissive states upon incorporation into SDS micelle.

Metal–metal to ligand charge transfer (MMLCT) emission has been receiving growing interest in the photophysics and photochemistry of dinuclear Pt<sup>II</sup> diimine complexes.<sup>1</sup> Such emission depends on the extent of Pt<sup>II</sup>–Pt<sup>II</sup> and/or ligand–ligand interactions. These interactions are weak under normal circumstances, but are sensitive to the surrounding environment. Thus, with suitable molecular design, such MMLCT emission of dinuclear Pt<sup>II</sup> systems may serve as a means to probe the chemical environment in which the Pt<sup>II</sup> complex is presented. One potentially important application is the probing of transformations in micellar microheterogeneous environments.<sup>2</sup> Here, we highlight a conformational non-rigid dinuclear cyclometallated Pt complex [Pt<sub>2</sub>L<sup>1</sup><sub>2</sub>(μ-dppm)]<sup>2+</sup> **1** (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPH<sub>2</sub>) (Fig. 1) as a new spectroscopic probe for SDS micelles.<sup>3</sup> The flexible conformation of the Pt<sup>II</sup> complex prompts the intramolecular metal–metal and/or ligand–ligand interactions, and hence its MMLCT emission, to be sensitive to the microheterogeneous environments of the SDS micelles (Scheme 1).

The ligand L<sup>1</sup> [4-(*p*-diethylphosphonophenyl)-6-phenyl-2,2'-bipyridine] was obtained from the reaction between 4-(*p*-bromophenyl)-6-phenyl-2,2'-bipyridine and diethyl phosphite in the presence of a Pd<sup>0</sup> catalyst.<sup>4</sup> The dinuclear Pt<sup>II</sup> complex **1** was prepared by stirring [PtL<sup>1</sup>Cl] and 1,2-bis(diphenylphosphino)methane in MeCN–EtOH. It was isolated as a PF<sub>6</sub><sup>−</sup> salt. For comparison, an analogous complex, [Pt<sub>2</sub>L<sup>2</sup><sub>2</sub>(μ-dppm)]<sup>2+</sup> **2** [L<sup>2</sup> = 4-(4-chlorophenyl)-6-phenyl-2,2'-bipyridine] (Fig. 1), without PO(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> groups was also prepared.<sup>‡</sup> The structure of **2**[PF<sub>6</sub>]<sub>2</sub> has been characterized by X-ray crystallography (Fig. 2).§ The two planar [PtL<sup>2</sup>]<sub>2</sub> units are nearly parallel to each other with a dihedral angle of 4.6°, and staggered with a torsion angle of 27.2°. The configurations of

the two [PtL<sup>2</sup>]<sub>2</sub> units are identical and are related by a C<sub>2</sub> axis passing through the –CH<sub>2</sub>– unit of the dppm ligand. The intramolecular Pt–Pt distance is 3.150(1) Å. This is shorter than the intramolecular Pt–Pt distance of [Pt<sub>2</sub>L<sup>3</sup><sub>2</sub>(μ-dppm)]<sup>2+</sup> (L<sup>3</sup> = 6-phenyl-2,2'-bipyridine) (3.301 Å)<sup>5</sup> but is comparable to that in [Pt<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>(μ-C<sub>4</sub>H<sub>5</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> (3.131 Å).<sup>6</sup> The structure of **1** is expected to resemble that of **2** as the spectroscopic properties of **1**[PF<sub>6</sub>]<sub>2</sub> and **2**[PF<sub>6</sub>]<sub>2</sub> are similar,¶ we envisage that there is also weak metal–metal and/or ligand–ligand interactions in the former complex.

Emission spectra of **1**[PF<sub>6</sub>]<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> and **2**[PF<sub>6</sub>]<sub>2</sub> in MeCN show low energy bands at 648 nm and 661 nm, respectively, which are both attributable to the MMLCT {<sup>3</sup>[(dσ\*)σ(π\*)]} transitions.<sup>1</sup> However, in MeOH, no emission from **1** can be observed. This is most probably due to quenching by solvent molecules at the open coordination sites. As shown in Fig. 3(a), addition of SDS micelles to an aqueous solution of **1** leads to an emission with λ<sub>max</sub> at 530 nm (τ = 1.4 μs), which is similar to the MLCT emissions of related mononuclear cyclometallated Pt<sup>II</sup> complexes.<sup>7</sup> Interestingly, no MMLCT emission can be observed. We attribute that the SDS micelle creates a protecting environment for the Pt<sup>II</sup> complex so that enhancement of emission is recorded upon incorporation of the dinuclear Pt<sup>II</sup> complex. The fact that the emission of **1**–SDS micelle is very different from those observed in CH<sub>2</sub>Cl<sub>2</sub> solution and solid state suggests no intramolecular and/or intermolecular Pt<sup>II</sup>–Pt<sup>II</sup> interaction between the two cyclometallated Pt<sup>II</sup> units upon incorporation of the complex in the SDS micelle.

It is well established that with increasing ionic strength, micelles will undergo substantial transformations in size and shape to create cylindrical micelles with large aggregation number and SDS head groups will be brought closer in proximity.<sup>8</sup> We found that the emission properties of **1** in the SDS micelle are dramatically altered by the addition of counter cations. Fig. 3 shows the emission spectra of **1** in the SDS micellar solution recorded at different NaCl concentrations. Initial addition of NaCl slightly enhances the intensity and

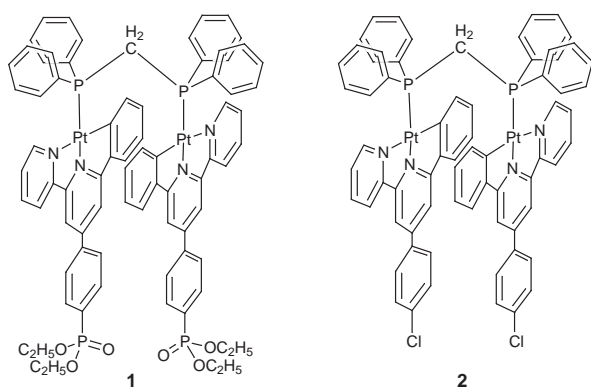
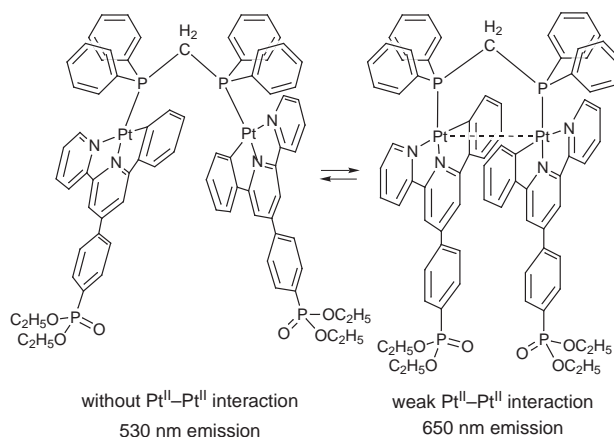
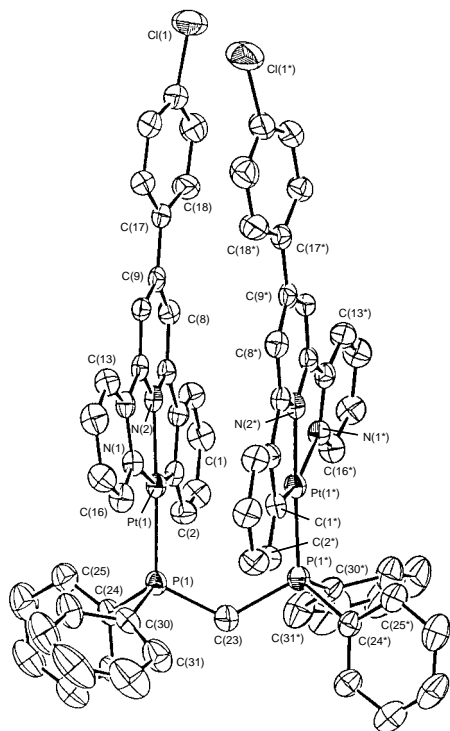


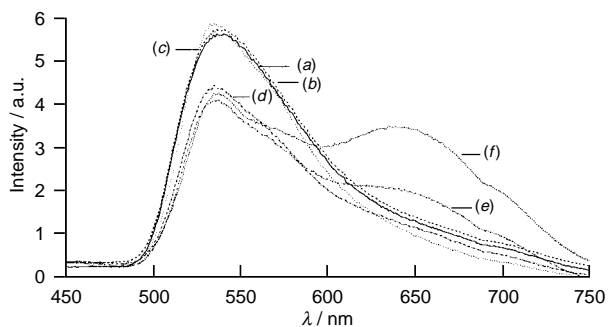
Fig. 1 Complexes **1** and **2**



Scheme 1



**Fig. 2** Perspective view of **2**. Selected bond lengths (Å) and angles (°): Pt–Pt 3.150(1), Pt(1)–N(1) 2.15(1), Pt(1)–C(29) 2.02(1), P(1)–C(2) 1.84(1), N(1)–C(14) 1.34(1), N(2)–C(19) 1.35(1), Pt(1)–P(1) 2.25(1), Pt(1)–N(2) 2.00(1), P(1)–C(1) 1.82(1), P(1)–C(8) 1.82(1), N(1)–C(18) 1.37(1), N(2)–C(23) 1.36(1); P(1)–Pt(1)–N(1) 106.1(2), P(1)–Pt(1)–C(29) 95.5(2), N(1)–Pt(1)–C(29) 104.0(5), Pt(1)–P(1)–C(1) 115.4(3), Pt(1)–P(1)–C(8) 116.2(3), P(1)–Pt(1)–C(29) 95.5(2), N(1)–Pt(1)–N(2) 77.3(2), N(2)–Pt(1)–C(29) 80.9(3), Pt(1)–P(1)–C(2) 113.4(3), C(1)–P(1)–C(2) 105.6(4).



**Fig. 3** Emission spectra of **1** at various [NaCl] in SDS micellar solution. [SDS] =  $1.52 \times 10^{-2}$  mol dm $^{-3}$ , [**1**] =  $3.46 \times 10^{-6}$  mol dm $^{-3}$ , [NaCl] mol dm $^{-3}$ : (a) 0, (b) 0.06, (c) 0.2, (d) 0.3, (e) 0.4, (f) 0.5.

lifetime of the 530 nm emission. An additional emission maximum at 650 nm gradually develops as [NaCl] increases. The 650 nm emission corresponds well to the <sup>3</sup>MMLCT emission of **1** recorded in CH<sub>2</sub>Cl<sub>2</sub> solution and in solid state. Time resolved emission spectra of **1** in SDS micellar solution recorded at [NaCl] = 0.5 M show different decay rates for the 530 and 650 nm emission maxima. This indicated that the two emissions are coming from two different excited states. Presumably they are the MLCT excited states of the two non-interacting cyclometallated Pt<sup>II</sup> units and the MMLCT excited states of two interacting ones (Scheme 1), respectively. The sensitive responses of the luminescent properties of **1** to [NaCl] can be rationalized as follows. The cyclometallated Pt<sup>II</sup> molecules may not reside too deep in the SDS micellar cores and are still subjected to quenching by the solvent molecules. Addition of Na<sup>+</sup> brings the SDS head groups closer in proximity

through a reduction in electrostatic repulsion. This would reduce water penetration at the micellar surface and enhance the hydrophobicity of the medium so that solvent induced non-radiative decay at the open coordination sites is prohibited. Thus, the intensity and lifetime of the 530 nm emission are both enhanced upon initial addition of NaCl. Importantly, the alignment of the SDS head group with Na<sup>+</sup> cations would also force two cyclometallated Pt<sup>II</sup> units close enough for intramolecular metal–metal and/or ligand–ligand interaction (Scheme 1). This ultimately leads to an accessible MMLCT excited state and accounts for the 650 nm emission at high NaCl concentration. The alignment of the SDS head groups in the micellar solution would be expected to depend on the size of the counter cations. We found that addition of K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> gave a similar effect on the photoluminescence of the micellar solution of **1**. However, the bulky NMe<sub>4</sub><sup>+</sup> cation did not give rise to any low energy emission with  $\lambda_{\text{max}} \geq 600$  nm.

The above data show that the emission properties of a cyclometallated dinuclear Pt<sup>II</sup> complex are sensitive to the micelle environment. Switching from MLCT to MMLCT emission is observed upon micellar transformation. This reveals the potential application of weak metal–metal interaction present in a conformational non-rigid molecule as a sensitive probe for micellar microheterogeneous environments.

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## Notes and References

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‡ *NMR data*: **1**[PF<sub>6</sub>]<sub>2</sub>: <sup>1</sup>H NMR (CD<sub>3</sub>CN, 270 MHz),  $\delta$  1.40 (t, CH<sub>2</sub>CH<sub>3</sub>, 12 H), 4.29 (q, CH<sub>2</sub>CH<sub>3</sub>, 8 H), 4.88 [t, PCH<sub>2</sub>P, <sup>3</sup>J(PiPCH<sub>2</sub>) 13 Hz]. <sup>31</sup>P{<sup>1</sup>H} NMR (MeCN),  $\delta$  19.46 [PCH<sub>2</sub>P, <sup>1</sup>J(PiP) 2037 Hz], 16.75 [(EtO)OP]. **2**[PF<sub>6</sub>]<sub>2</sub>: <sup>1</sup>H NMR (CD<sub>3</sub>CN, 270 MHz),  $\delta$  5.23 [t, PCH<sub>2</sub>P, <sup>3</sup>J(PiPCH<sub>2</sub>) 13 Hz]. <sup>31</sup>P{<sup>1</sup>H} NMR (MeCN),  $\delta$  19.16, <sup>1</sup>J(PiP) 2060 Hz.

§ *Crystal data* for **2**[PF<sub>6</sub>]<sub>2</sub>: C<sub>69</sub>H<sub>52</sub>Cl<sub>2</sub>F<sub>12</sub>N<sub>4</sub>Pt<sub>2</sub>P<sub>4</sub>·2C<sub>3</sub>H<sub>7</sub>NO, *M* = 1893.33, monoclinic, space group *C2/c* (no. 15), *T* = 301 K, *a* = 13.099(2), *b* = 38.901(4), *c* = 14.259(5) Å,  $\beta$  = 90.98(2)°, *U* = 7264(2) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.732 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 40.75 cm<sup>-1</sup>, *F*(000) = 3720, an orange crystal of dimensions 0.50 × 0.07 × 0.05 mm, data collected by an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å), intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections based on the  $\psi$ -scan of four strong reflections. Convergence for 3551 reflections with *I* > 3 $\sigma$ (*I*) was reached at *R* = 0.029, *wR* = 0.032, goodness-of-fit = 1.48, ( $\Delta/\sigma$ )<sub>max</sub> = 0.03, the final difference Fourier map was featureless with maximum positive and negative peaks of 0.91 and 0.60 e Å<sup>-3</sup> respectively. CCDC 182/806.

¶ *Spectroscopic data*: **1**[PF<sub>6</sub>]<sub>2</sub>: UV–VIS (CH<sub>2</sub>Cl<sub>2</sub>) [ $\lambda$ /nm, ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 290 (6.58 × 10<sup>4</sup>), 320 (4.30 × 10<sup>4</sup>)]. Emission spectrum (CH<sub>2</sub>Cl<sub>2</sub>, 298 K) ( $\lambda_{\text{max}}$ /nm,  $\tau$ / $\mu$ s): 648 (2.30). **2**[PF<sub>6</sub>]<sub>2</sub>: UV–VIS (MeCN) [ $\lambda$ /nm, ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 293 (4.79 × 10<sup>4</sup>), 320 (4.12 × 10<sup>4</sup>), 400–526 (3.90 × 10<sup>3</sup>–1.00 × 10<sup>3</sup>), 532–561 (9.70 × 10<sup>2</sup>–2.00 × 10<sup>2</sup>)]. Emission spectrum (MeCN, 298 K) ( $\lambda_{\text{max}}$ /nm,  $\tau$ / $\mu$ s): 661 (0.19).

- V. H. Holding and V. M. Miskowski, *Coord. Chem. Rev.*, 1991, **111**, 145; J. A. Bailey, V. M. Miskowski and H. B. Gray, *Inorg. Chem.*, 1993, **32**, 369; H. K. Yip, C. M. Che, Z. Y. Zhou and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1992, 1369.
- J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley-Interscience, New York, 1982.
- H. Q. Liu, T. C. Cheung and C. M. Che, *Chem. Commun.*, 1996, 1039.
- T. Hirao, T. Masunaga, Y. Ohshiro and T. Agawa, *Synthesis*, 1981, 56.
- T. C. Cheung, K. K. Cheung, S. M. Peng and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1996, 1645.
- J. P. Laurent, P. Lepage and F. Dahan, *J. Am. Chem. Soc.*, 1982, **104**, 7335.
- C. W. Chan, T. F. Lai, C. M. Che and S. M. Peng, *J. Am. Chem. Soc.*, 1993, **115**, 11245; M. Maestri, V. Sandrini, A. von Zelewsky and P. Jolliet, *Helv. Chim. Acta*, 1988, **71**, 134.
- J. P. Krathovil, *J. Colloid Interface Sci.*, 1980, **75**, 271.

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