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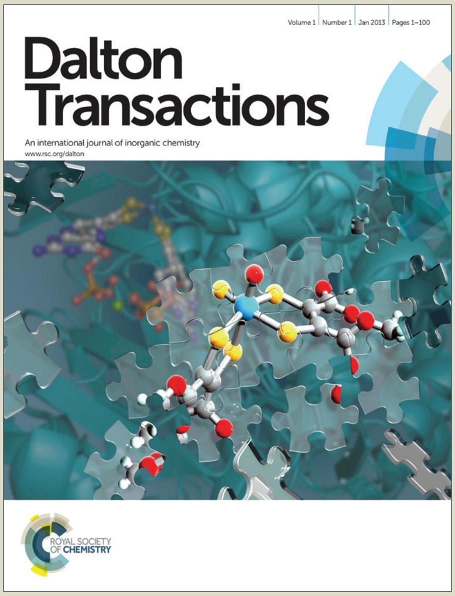

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ARTICLE TYPE

Remarkable luminescence enhancement of chloroplatinum(II) complexes of hexaethylene glycol methyl ether substituted 2,6-bis(benzimidazol-2'-yl)pyridine in water triggered by PF_6^-

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Three chloroplatinum(II) complexes of 2,6-bis(benzimidazol-2'-yl)pyridine bearing hexaethylene glycol methyl ether are almost nonemissive in dilute aqueous solutions. Upon addition of excessive hexafluorophosphate salts to their dilute aqueous solutions, one of them was found to show remarkable luminescence enhancement.

Square-planar platinum(II) complexes are of increasing importance because of their intriguing spectroscopic and luminescence properties and thus potential applications in the fields of chemical sensors and electro-optical devices.[1-4] Among them, the chloroplatinum(II) complexes with N^N^N ligands ([Pt(N^N^N)Cl]$^+$Cl$^-$) shows strong and modifiable triplet emissions in the solid state.[2] However, it is found to be nonemissive or weakly emissive in their dilute aqueous solutions.[2d-f,3] Such quenched excited states are attributed to efficient radiationless decay via a low-lying triplet ligand-field state.[2d-f,3] In this context, the cationic platinum(II) complexes are confined within oppositely charged polyelectrolytes,[1d,4a] block copolymers,[4b] and micelle-like aggregates,[4c-e] leading to strong luminescence enhancement. Still, the luminescence quantum efficiencies are much smaller in the aqueous solutions than in the solid states. This situation limits their applications in the fields of luminescent soft materials and biosensors.

Imidazolium-type ionic liquids are good solvents for polyethylene glycol due to the presence of hydrogen bonding and ion-induced dipole interactions in the solution.[5,6] Here, we report the synthesis and photophysical properties of three chloroplatinum(II) complexes of 2,6-bis(benzimidazol-2'-yl)pyridine (bzimpy) bearing hexaethylene glycol methyl ether (HEME) groups (**Pt-1**, **Pt-2**, and **Pt-3**, Fig. 1). The introduction of HEME groups into the chloroplatinum(II) complexes allows them to dissolve into green solvents, both water and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF$_6$). BMIMPF$_6$ is a typical ionic liquid. Upon addition of excessive hexafluorophosphate salts to the dilute aqueous solutions, **Pt-2** was found to show remarkable luminescence enhancement.

The chloroplatinum(II) complexes were synthesized by the reaction of K_2PtCl_4 with the corresponding bzimpy-based ligands modified by HEME groups and then isolated as highly viscous liquids. The UV-vis spectra of **Pt-2** and **Pt-3** in BMIMPF$_6$ showed intense and structured π–π* absorption bands from 310 to 386 nm, whereas **Pt-1** displayed a broad and structureless absorption band at the same range (Fig. S1 and Table S1). Moderately intense metal-to-ligand charge-transfer (MLCT, 410–500 nm) transitions were observed for all of them. In their aqueous solutions, the UV-vis absorption spectra exhibited broad bands for π–π* (310–390 nm) and MLCT (410–500 nm) transitions (Fig. 2a, 2c, 2e and S2). In the case of **Pt-2**, the shoulder band near 545 nm was typical of a metal–metal-to-ligand charge-transfer (MMLCT) transition originating from an intermolecular association through Pt···Pt and π–π stacking interactions.[2e,f,4b,f]

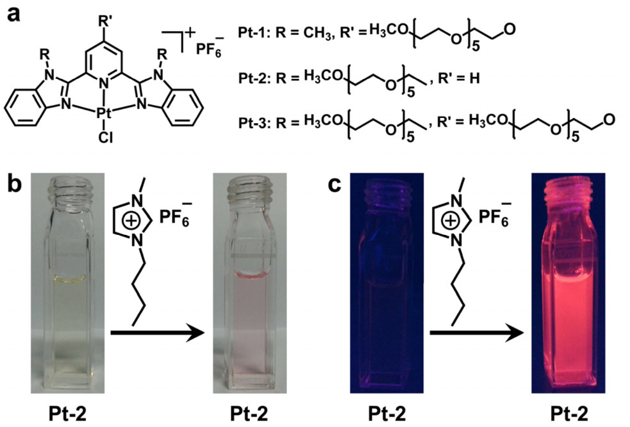

Fig. 1 (a) Molecular structures of **Pt-1**, **Pt-2**, and **Pt-3**. (b) Photographs were taken under sunlight (b) and UV irradiation at 365 nm (c) before and after addition of 0.5 wt% BMIMPF$_6$.

Upon excitation at 420 nm, **Pt-1**, **Pt-2**, and **Pt-3** showed vibronic-structured emission bands at 549, 559, and 546 nm in BMIMPF$_6$ under dilute concentrations, respectively (Fig. S1 and Table S1). The progressional spacings (approximately 1300 cm^{-1}) were characteristic of the vibrational stretching frequencies of the bzimpy ligands. Therefore, these vibronic-structured emissions were tentatively assigned to a metal-perturbed triplet intraligand parentage of the bzimpy ligands (^{3}IL, π→π*). At a concentration of 0.05 mmol/L and lower concentrations, almost no emissions were detected in the aqueous solutions of the chloroplatinum(II) complexes (Fig. S2). When the concentrations were increased ≥ 0.08 mmol/L, moderately intense emission bands were observed at λ_{max} values of 633, 634, and 620 nm for **Pt-1**, **Pt-2**, and **Pt-3**, respectively. The excitation spectra of **Pt-2** showed a shoulder of 545 nm, consistent with the corresponding absorption spectra. These collective features suggested that the structureless emission band of **Pt-2** was accordingly attributed to a ^{3}MMLCT excited state, whereas the emission bands of **Pt-1** and **Pt-3** were tentatively assigned to excimeric emission at high concentrations from an intermolecular association through π–π stacking interactions.

At ambient conditions, the solubility of $BMIMPF_6$ in water is ca. 2.0 wt%.[7] When its concentration is lower than 2.0 wt%, $BMIMPF_6$ molecules are dissolved in water. The addition of 0.5 wt% $BMIMPF_6$ to a dilute aqueous solution of **Pt-2** resulted in an immediate color change from light-yellow to red (Fig. 1). In the resulting UV-vis spectrum, the broad absorption band at 300–390 nm dropped significantly in intensity and new absorption bands appeared at 536 and 571 nm (Fig. 2c). With reference to previous spectroscopic studies on the bzimpy-based platinum(II) complexes,[2e,f,4b,f] the absorption bands originated from MMLCT transitions as a result of an intermolecular association through Pt···Pt and π–π stacking interactions. The absorbance of the band at 571 nm increased linearly with increasing concentrations (0.01–0.1 mmol/L, Fig. S3a). Similarly, 0.5 wt% $BMIMPF_6$ was also added to the dilute aqueous solutions of **Pt-1** and **Pt-3**. In the former case, the absorption intensity of the broad band at 310–390 nm decreased considerably (Fig. 2a), while the absorption band only dropped slightly in the latter case (Fig. 2e). In sharp contrast with **Pt-2**, no MMLCT absorption band was observed in the cases of **Pt-1** and **Pt-3**.

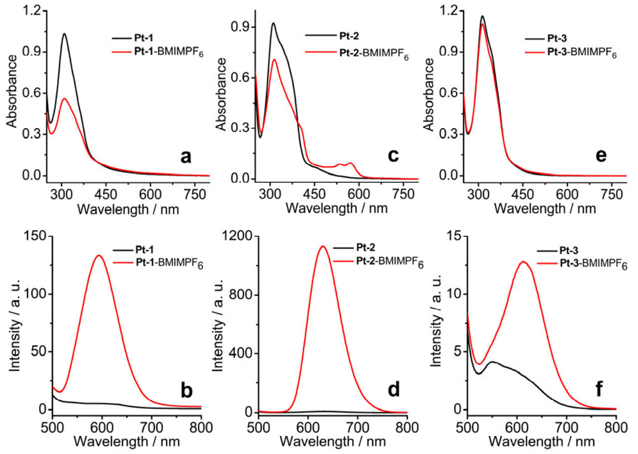

Fig. 2 (a, c, and e) UV-vis and (b, d, and f) emission spectra of **Pt-1**, **Pt-2**, and **Pt-3** in their dilute aqueous solutions (0.05 mmol/L) before and after addition of 0.5 wt% $BMIMPF_6$.

As suggested above, **Pt-1**, **Pt-2**, and **Pt-3** were nonemissive in their aqueous solutions under very dilute conditions (≤ 0.05 mmol/L, Fig. 2b, 2d and 2f). Upon addition of 0.5 wt% $BMIMPF_6$ and excitation at 420 nm, the dilute aqueous solution of **Pt-2** showed a strong emission band at 630 nm (Fig. 2d). The corresponding excitation spectra showed two bands at 536 and 570 nm, consistent with the absorption spectra mentioned above. Therefore, the band at 630 nm was attributed to a ^{3}MMLCT excited state originating again from an intermolecular association through Pt···Pt and π–π stacking interactions. With increasing concentration, a linear increase in the emission intensity was clearly observed (0.01–0.1 mmol/L, Fig. S3b), which was consistent with the absorption spectra listed above. The quantum yield was estimated to be $\Phi = 0.37$ at a concentration of 0.05 mmol/L under ambient conditions by the absolute method using an integrating sphere. This value was rather comparable to the quantum yields of the strong luminescence platinum(II) complexes in the solid state in room temperature.[7] Similarly, **Pt-1** was also found to show strong luminescence enhancement at an emission band of 593 nm upon addition of $BMIMPF_6$ 0.5 wt% to its dilute aqueous solution (Fig. 2b). This emission wavelength was much smaller than that of the aqueous solutions of **Pt-1** at high concentrations (633 nm). Combining the significant decrease in the absorption band at 310–390 nm together with the corresponding excitation spectra, we assigned this emission band to the excimeric emission. Its quantum yield was determined to be $\Phi = 0.20$ under ambient conditions (0.05 mmol/L). However, upon addition of $BMIMPF_6$ 0.5 wt%, the dilute aqueous solution of **Pt-3** exhibited less luminescence enhancement at an emission band of 619 nm with a much smaller quantum yield of $\Phi = 0.085$ (0.05 mmol/L, Fig. 2f). This situation was completely consistent with the slight decrease in the absorption band at 310–390 nm. This less enhanced emission band was again assigned to the excimeric emission.

The remarkable luminescence enhancement should be ascribed to the aggregate formation of the chloroplatinum(II) complexes in aqueous solutions containing 0.5wt% $BMIMPF_6$. These aggregates were evidenced by both dynamic light scattering (DLS) and transmission electron microscopy (TEM). In a typical DLS plot for the aqueous solution of **Pt-2** at a concentration of 0.05 mmol/L, two modes were observed at hydrodynamic diameters (D_hs) of 1.4 and 318 nm (Fig. 3a). The first DLS signal was attributed to single **Pt-2** molecules, while the latter signal suggested the formation of supramolecular aggregates that could originate from an intermolecular association through Pt···Pt and π–π stacking interactions. This assignment was in line with the presence of a very low MMLCT absorption shoulder (Fig. 2c). In DLS measurements, a small number of large particles can scatter incident light much more strongly than many more small particles.[8] It was therefore estimated that the occurrence probability of the supramolecular aggregates was smaller than 1%. This is consistent with the nonemissive aqueous solutions under very dilute conditions (≤ 0.05 mmol/L, Fig. 2b, 2d and 2f). Upon addition of 0.5 wt% $BMIMPF_6$ to this dilute aqueous solution, D_h increased to 595 nm, indicative of the presence of larger supramolecular aggregates. Such increase in the aggregate size was confirmed by TEM. In a typical TEM image as cast from the dilute aqueous solution of **Pt-2**, the nanoparticles with 1~2 nm were clearly observed and they were assigned to the single **Pt-2** molecules (Fig. 3b). However, the supramolecular assembly as shown in the DLS plot was not observed in the TEM images. It was therefore speculated that this supramolecular aggregate might be due to a loose packing of **Pt-2** in the aqueous solution. After adding 0.5 wt% $BMIMPF_6$, the TEM image revealed that the nanoparticles increased significantly, ranging from 20~330 nm (Fig. 3c). Similar size increase was also observed in the cases of **Pt-1** and **Pt-3** after adding 0.5 wt% $BMIMPF_6$ to their dilute aqueous solutions (Fig. S4). In the cases of **Pt-2** and **Pt-3**, the small nanoparticles (≤ 50 nm) occupied an occurrence probability of 95 %, while the big ones (≥ 100 nm) possessed an occurrence probability of 5 %. Of difference was that their ratio in the case of **Pt-1** was close to 1:1.

Although the aggregates formed similarly, the quantum yields were in an order of **Pt-2** > **Pt-1** > **Pt-3**. This was different from the number trend of hexaethylene glycol groups (**Pt-3** > **Pt-2** > **Pt-1**). This difference revealed that the steric hindrance for the Pt···Pt and/or π–π stacking interactions of the chloroplatinum(II) complexes dominated at the *para* position of the pyridyl group, leading to a steric hindrance order of **Pt-3** > **Pt-1** > **Pt-2**.

To further clarify the aggregate formation and thus luminescence enhancement mechanism, other hexafluorophosphate salts with identical molar concentrations (18 mmol/L) were also added to the dilute aqueous solution, including TMAPF_6, NH_4PF_6 and KPF_6 (TMA = tetramethylammonium, Fig. S5). The addition of these hexafluorophosphate salts resulted in remarkable MMLCT absorption and ^{3}MMLCT luminescence enhancements. Especially, the quantum yields of **Pt-2** was determined to be **Φ** = 0.45 (Table S2). This value was even larger than those of solid platinum(II) complexes.[7] However, only slight luminescence enhancements were observed when $NaClO_4$ and $NaBF_4$ were added into the aqueous solutions of **Pt-2** (Fig. S6). This situation should be due to much more hydrophobicity of PF_6^- than ClO_4^- and BF_4^-. Therefore, the aggregate formation and luminescence enhancement should be due to common ion effects, where the addition of hexafluorophosphate salts decrease the solubility of the chloroplatinum(II) complexes in the aqueous solutions.

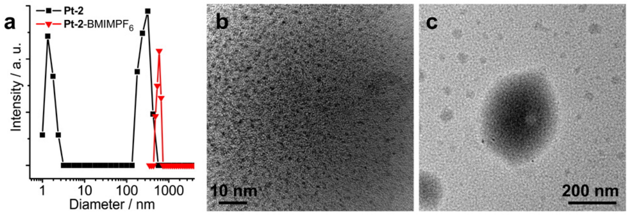

Fig. 3. (a) DLS plots of **Pt-2** in its dilute aqueous solution before and after addition of 0.5 wt% BMIMPF_6, where the concentration was controlled to be 0.05 mmol/L. TEM images of **Pt-2** (b) before and (c) after addition of 0.5 wt% BMIMPF_6.

In conclusion, we have synthesized and characterized a series of chloroplatinum(II) complexes of bzimpy ligands bearing hexaethylene glycol groups. Upon addition of excessive hexafluorophosphate salts to their dilute aqueous solutions, almost nonemissive **Pt-2** was found to show remarkable luminescence enhancement with quantum yields of **Φ** = 0.45. The values are even larger than the quantum yields obtained from highly luminescent platinum(II) complexes in their solid state.[7] The luminescence enhancements are specific for PF_6^- and **Pt-2** can be used as a luminescence sensor of PF_6^- in aqueous solutions. Luminescence enhancement induced by common ion effects in the aqueous solutions of the chloroplatinum(II) complexes represents a new avenue to develop luminescence soft materials.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis and analysis details of the ligands bearing hexaethylene glycol groups and corresponding chloroplatinum(II) complexes and additional characterizations. See DOI: 10.1039/b000000x/

1 (*a*) I. Eryazici, C. N. Moorefield and G. R.Newkome, *Chem. Rev.*, 2008, **108**, 1834; (*b*) S. D. Cummings, *Coord. Chem. Rev.*, 2009, **253**, 449; (*c*) R. McGuire Jr., M. C. McGuire and D. R. McMillin, *Coord. Chem. Rev.*, 2010, **254**, 2574; (*d*) K. M. C. Wong and V. W. W. Yam, *Acc. Chem. Res.*, 2011, **44**, 424; (*e*) J. Kalinowski, V. Fattori, M. Cocchi and J. A. G. Williams, *Coord. Chem. Rev.*, 2011, **255**, 2401; (*f*) X. Zhang, B. Li, Z. H. Chen and Z. N. Chen, *J. Mater. Chem.*, 2012, **22**, 11427; (*g*) W. Lu, Y. Chen, V. A. L. Roy, S. S. Y. Chui and C. M. Che, *Angew. Chem. Int. Ed.*, 2009, **48**, 7621; (*h*) L. B. Xing, S. Yu, X. J. Wang, G. X. Wang, B. Chen, L. P. Zhang, C. H. Tung and L. Z. Wu, *Chem. Commun.*, 2011, **48**, 10886; (*i*) Z. Ji, Y. Li, T. M. Pritchett, N. S. Makarov, J. E. Haley, Z. Li, M. Drobizhev, A. Rebane and W. Sun, *Chem.–Eur. J.*, 2011, **17**, 2479; (*j*) S. Chakraborty, T. J. Wadas, H. Hester, R. Schmehl and R. Eisenberg, *Inorg. Chem.*, 2005, **44**, 6865.

2 (*a*) H. K. Yip, L. K. Cheng, K. K. Cheung, C. M. Che, *J. Chem. Soc. Dalton Trans.*, **1993**, 2933; (*b*) R. Büchner, J. S. Field and R. J. Haines, *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; (d) T. J. Wadas, Q. M. Wang, Y. j. Kim, C. Flaschenreim, T. N. Blanton and R. Eisenberg, *J. Am. Chem. Soc.*, 2004, **126**, 16841; (*e*) Grove, L. J.; Rennekamp, J. M.; Jude, H.; Connick, W. B. *J. Am. Chem. Soc.*, 2004, **126**, 1594; (*f*) E. J. Rivera, C. Figueroa, J. L. Colón, L. Grove and W. B. Connick, *Inorg. Chem.*, 2007, **46**, 8569.

3 (*a*) T. Aldridge, E. Stacy and D. R. McMillin, *Inorg. Chem.*, 1994, **33**, 722; (*b*) J. F. Michalec, S. A. Bejune, D. G. Cuttell, G. C. Summerton, J. A. Gertenbach, J. S. Field, R. J. Haines and D. R. McMillin, *Inorg. Chem.*, 2001, **40**, 2193; (*c*) D. R. McMillin and J. J. Moore, *Coord. Chem. Rev.*, 2002, **229**, 113; (*d*) S. E. Hobert, J. T. Carney and S. D. Cummings, *Inorg. Chim. Acta*, 2001, **318**, 89.

4 (*a*) C. Y. S. Chung and V. W. W. Yam, *J. Am. Chem. Soc.*, 2011, **133**, 18775; (*b*) N. Liu, B. Wang, W. Liu and W. Bu, *Chem. Commun.*, 2011, **47**, 9336; (*c*) C. Po, A. Y.-Y. Tam, K. M. C. Wong and V. W. W. Yam, *J. Am. Chem. Soc.*, 2011, **133**, 12136; (*d*) K. Y. Wong and W. W.-S. Lee, *J. Photochem. Photobiol. A: Chem.*, 1997, **102**, 231; (*e*) N. A. Larew, A. R. V. Wassen, K. E. Wetzel, M. M. Machala and S. D. Cummings, *Inorg. Chim. Acta*, 2010, **363**, 57; (*f*) N. Liu, B. Wang, W. Liu and W. Bu, *J. Mater. Chem. C*, 2013, **1**, 1130.

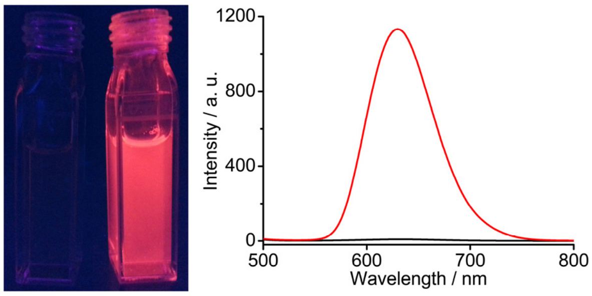
5 (*a*) J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508; (*b*) J. Dupont, *Acc. Chem. Res.*, 2011, **44**, 1223; (*c*) N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123; (*d*) R. D. Rogers and G. A. Voth, *Acc. Chem. Res.*, 2007, **40**, 1077.

6 (*a*) A. Triolo, O. Russina, U. Keiderling and J. Kohlbrecher, *J. Phys. Chem. B*, 2006, **110**, 1513; (*b*) Y. Lian and K. Zhao, *Soft Matter*, 2011, **7**, 8828; (*c*) K. Behera, P. Dahiya and S. Pandey, *J. Colloid Interface Sci.*, 2007, **307**, 235; (*d*) J. L. Anthony, E. J. Maginn and J. F. Brennecke, *J. Phys. Chem. B*, 2001, **105**, 10942.

7 (*a*) Y. Sun, K. Ye, H. Zhang, J. Zhang, L. Zhao, B. Li, G. Yang, B. Yang, Y. Wang, S. W. Lai, C. M. Che, *Angew. Chem. Int. Ed.*, 2006, **45**, 5610; (*b*) N. Komiya, M. Okada, K. Fukumoto, D. Jomori and T. Naota, *J. Am. Chem. Soc.*, 2011, **133**, 6493.

8 G. Liu, T. Liu, S. S. Mal and U. Kortz, *J. Am. Chem. Soc.*, 2006, **128**, 10103.

Graphical Abstract



Remarkable luminescence enhancement of chloroplatinum(II) complexes of hexaethylene glycol methyl ether substituted 2,6-Bis(benzimidazol-2'-yl)pyridine in water triggered by PF_6^-

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