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

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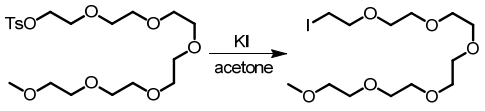
Materials and Instruments.

Hexaethylene glycol monomethyl ether tosylate [1], 2,6-bis(*N*-methylbenzimidazol-2'-yl)-4-hydroxypyridine[2], 2,6-bis(benzimidazol-2'-yl)pyridine[3], and 2,6-bis(benzimidazol-2'-yl)-4-hydroxypyridine[4] were prepared according to the related literatures. All solvents and reagents were of reagent grade quality and purchased commercially. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer, performing in $CDCl_3$ or d_6-DMSO solutions and using TMS as an internal standard. Electrospray ionization mass spectra (ESI-MS) were performed with Bruker microTOF-Q II. Dynamic light scattering (DLS) measurements were performed on a Brookhaven BI-200SM spectrometer. TEM images were obtained with an FEI Tecnai F30 operating at 300 kV. UV-vis absorption spectra were recorded by using a SHIMADZU UV-2550 spectrophotometer. Luminescence measurements were made on a Hitachi F-7000 spectrofluorimeter with a xenon lamp as the excitation source. Quantum yields were measured by absolute method using an Edinburgh FLS920 spectrometer equipped with an integrating sphere. All measurements were carried out at room temperature.

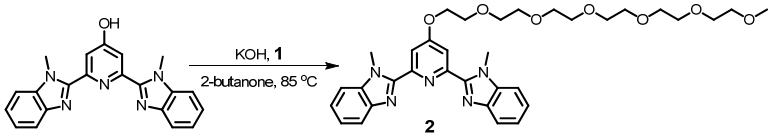


1

Hexaethylene glycol monomethyl ether iodide (1)

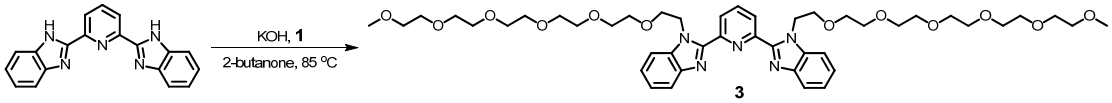
Potassium iodide (7.9 g, 47.4 mmol, 2 eq.) was added to a solution of hexaethylene glycol monomethyl ether tosylate (10.7 g, 23.7 mmol) in 400 mL acetone. The resulting mixture was refluxed for 10 h. When the mixture was cooled to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in water, which was further extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated to yield a crude product. Pure compound **1** was obtained as a highly viscous liquid by column chromatography on silica gel (ethyl acetate/petroleum ether, 2:1, 8.86 g, 92 % yield).

^{1}H NMR (δ, ppm, $CDCl_3$): 3.24 – 3.28 (t, 2H); 3.38 (s, 3H), 3.56 – 3.54 (m, 2H); 3.66 – 3.63 (m, 18H); 3.77 – 3.74 (t, 2H). ^{13}C NMR (δ, ppm, $CDCl_3$): 59.2, 70.4, 70.8, 70.9, 72.1, 72.2.



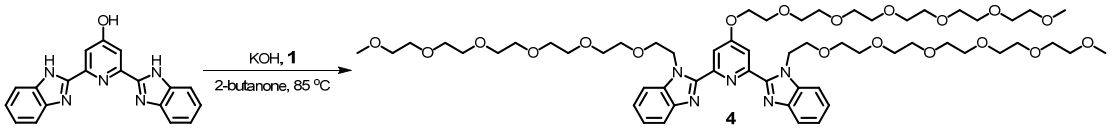
2,6-Bis(*N*-methylbenzimidazol-2'-yl)-4-(hexaethylene glycol monomethyl) pyridine (2)

Compound **1** (0.50 g, 1.41 mmol) was stirred with potassium hydroxide (0.32 g, 5.64 mmol) in 2-butanone (30 mL) at 85 °C for 30 min. 2,6-bis(*N*-methylbenzimidazol-2'-yl)-4-hydroxypyridine (0.63 g, 1.54 mmol) was added. The resultant mixture was kept at 85 °C for 24 h. After removal of the solvents in vacuo, the residue was redissolved in CH_2Cl_2 and the resulting solution was washed with water. The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated. The residue was purified by column chromatography on silica gel (ethyl acetate/methanol, 6:1) to gain pure product **2** with a yield of 0.72 g, 81 %. ^{1}H NMR (δ, ppm, d_6 – DMSO): 3.38 (s, 3H), 3.7 – 3.5 (m, 22H); 4.15 (t, 2H), 4.25 (s, 6H), 7.38 – 7.31 (m, 4H), 7.45 – 7.43 (dd, 2H), 7.86 – 7.84 (dd, 2H). 7.97 (s, 2H). ^{13}C NMR (δ, ppm, d_6 – DMSO): 32.7, 44.9, 59.2, 70.0, 70.5, 70.6, , 70.7, 70.8, 72.1, 76.9, 77.2, 77.4, 77.6, 111.2, 113.0, 129.4, 123.0, 123.8, 136.8, 140.6, 149.5, 150.2, 165.6.



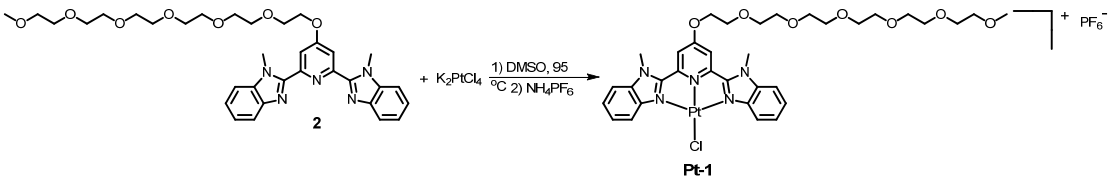
2,6-Bis(*N*-hexaethylene glycol monomethylbenzimidazol-2'-yl)-4-pyridine (3)

The procedure was similar to that for the preparation of compound **2**, except 2,6-bis(benzimidazol-2'-yl)pyridine (0.5 g, 1.61 mmol) was used in place of 2,6-bis(1-methylbenzimidazol-2'-yl)-4-hydroxypyridine. Compound **1** and potassium hydroxide were magnified to 1.44 g (3.54 mmol) and 0.54 g (9.66 mmol), respectively. Compound **3** was obtained as a highly viscous liquid (1.22 g, 87% yield). ^{1}H NMR (δ, ppm, $CDCl_3$): 3.30 (s, 6H), 3.39 – 3.36 (m, 8H); 3.48 – 3.46 (m, 4H), 3.66 – 3.52 (m, 28H), 3.74 – 3.71 (t, 4H), 4.95 – 4.92 (t, 4H), 7.37 – 7.31 (m, 4H), 7.56 – 7.54 (dd, 2H), 7.86 – 7.84 (dd, 2H). 8.07 – 8.03 (t, 2H), 8.34 – 8.32 (d, 2H). ^{13}C NMR (δ, ppm, $CDCl_3$): 44.9, 59.2, 70.0, 70.5, 70.61, 70.65, 70.69, 70.71, 70.74, 70.77, 70.8, 72.1, 76.9, 77.2, 77.4, 77.6, 111.0, 112.4, 120.4, 123.0, 123.8, 135.7, 136.8, 138.2, 142.9, 150.2, 150.6.



2,6-Bis(1-hexaethylene glycol monomethylbenzimidazol-2'-yl)-4-(hexaethylene glycol monomethyl)pyridine (4)

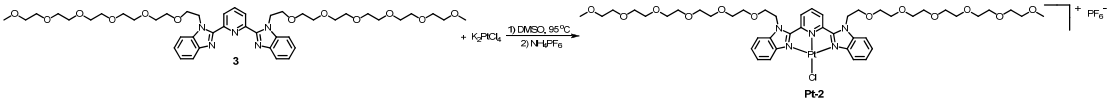
The procedure was similar to that for the preparation of compound **2**, except 2,6-bis(benzimidazol-2'-yl)-4-hydroxypyridine (0.5 g, 1.53 mmol) was used in place of 2,6-bis(*N*-methylbenzimidazol-2'-yl)-4-hydroxypyridine. Compound **1** and potassium hydroxide were magnified to 2.05 g (5.05 mmol) and 0.77 g (13.77 mmol), respectively. Compound **4** was obtained as a highly viscous liquid (1.21 g, 68% yield) ^{1}H NMR (δ, ppm, $CDCl_3$): 3.31 (s, 6H), 3.39 – 3.34 (m, 13H); 3.47 – 3.45 (m, 4H), 3.75 – 3.50 (m, 50H), 3.93 – 3.91 (m, 2H), 4.40 – 4.37 (t, 2H), 4.92 – 4.89 (t, 4H), 7.35 – 7.29 (m, 4H), 7.55 – 7.53 (m, 2H), 7.84 – 7.81 (m, 2H). 8.85 (s, 2H). ^{13}C NMR (δ, ppm, $CDCl_3$): 44.9, 59.2, 68.4, 69.4, 70.1, 70.52, 70.59, 70.62, 70.67, 70.74, 70.8, 71.2, 72.1, 76.9, 77.2, 77.6, 111.0, 112.3, 120.3, 123.0, 123.7, 136.8, 142.7, 150.5, 151.7, 166.5.



2 Pt-1

Chloroplatinum(II) complex Pt-1

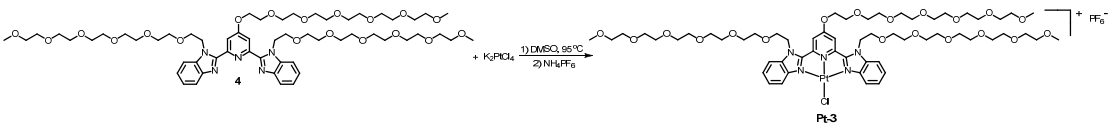
K_2PtCl_4 (0.47 g, 1.14 mmol) was added to a solution of compound **2** (0.72 g, 1.14 mmol) in dimethyl sulfoxide (DMSO, 30 ml). The resultant mixture was kept at 95 °C for 10 h. After removal of the solvents in vacuo, the residue was dissolved in deionized water. And a saturated aqueous solution of NH_4PF_6 was added until precipitation ceased. The precipitate was filtered and rinsed thoroughly with H_2O. **Pt-1** was obtained as a red solid with a yield of 1.05 g, 92%. ^{1}H NMR (δ, ppm, d_6-DMSO): 3.23 (s, 3H), 3.43 – 3.41 (m, 2H), 3.60 – 3.50 (m, 14H), 3.67 – 3.64 (m, 2H), 3.73 – 3.71 (m, 2H), 3.82 (s, 6H), 3.95 (s, 2H), 4.64 (s, 2H), 6.98 – 6.95 (t, 2H), 7.16 – 7.13 (t, 2H), 7.27 – 7.23 (t, 2H). 7.52 – 7.51 (d, 2H), 7.62 (s, 2H). MS (ESI): *m/z* Calcd for $[C_{34}H_{43}N_5O_7ClPt]^+$: 863.2499, found 863.2492.



3 Pt-2

Chloroplatinum(II) complex Pt-2

The procedure was similar to that for the preparation of **Pt-1**, except compound **3** (0.46 g, 0.53 mmol) was used in place of compound **2**. Yield: 0.55 g (83 %). ^{1}H NMR (δ, ppm, $CDCl_3$): 3.36 (s, 6H), 3.48 – 3.45 (m, 8H), 3.55 – 3.55 (m, 10H), 3.63 – 3.57 (m, 18H), 3.95 (s, 4H), 4.52 (s, 4H), 7.04 – 7.00 (t, 2H), 7.26 – 7.09 (dd, 4H), 7.49 – 7.47 (d, 2H). 8.19 – 8.12 (d, 2H), 8.43 – 8.41 (t, 2H). MS (ESI): *m/z* Calcd for $[C_{45}H_{65}N_5O_{12}ClPt]^+$: 1097.3966, found 1097.3970.



4 Pt-3

Chloroplatinum(II) complex Pt-3

The procedure was similar to that for the preparation of **Pt-1**, except compound **4** (0.86 g, 0.74 mmol) were used in place of compound **2**. Yield: 0.76 g (67 %). ^{1}H NMR (δ, ppm, $CDCl_3$): 3.32 (s, 6H), 3.46 – 3.73 (m, 59H), 3.80 (s, 2H), 3.95 – 3.94 (d, 6H), 4.12 (s, 2H), 4.48 (s, 4H), 4.57 (s, 2H), 7.01 (s, 2H), 7.17 (s, 4H), 7.60 (s, 2H), 7.76 (s, 2H).MS (ESI): *m/z* Calcd for $[C_{58}H_{91}N_5O_{19}ClPt]^+$: 1391.5645, found 1391.5662.

References

[1] Roy, R. K.; Gowd, E. B.; Ramakrishnan, S. *Macromolecules* **2012**, *45*, 3063.

[2] Largy, E.; Hamon, F.; Rosu, F.; Gabelica, V.; De Pauw, E.; Guédin, A.; Mergny, J.-L.; Teulade-Fichou, M.-P. *Chem. Eur. J.* **2011**, *17*, 13274.

[3] Tam, A. Y.-Y.; Lam, W. H.; Wong, K. M.-C.; Zhu, N.; Yam, V. W.-W. *Chem. Eur. J.* **2008**, *14*, 4562.

[4] Froidevaux, P.; Harrowfield, J. M.; Sobolev, A. N. *Inorg. Chem.* **2000**, *39,* 4678.

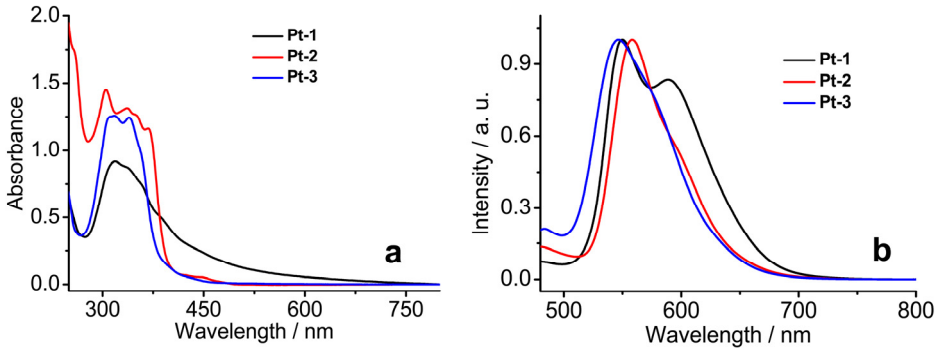


Fig. S1 UV-vis (a) and emission spectra (b) of **Pt-1**, **Pt-2**, and **Pt-3** in $BMIMPF_6$ solutions (0.05 mmol/L).

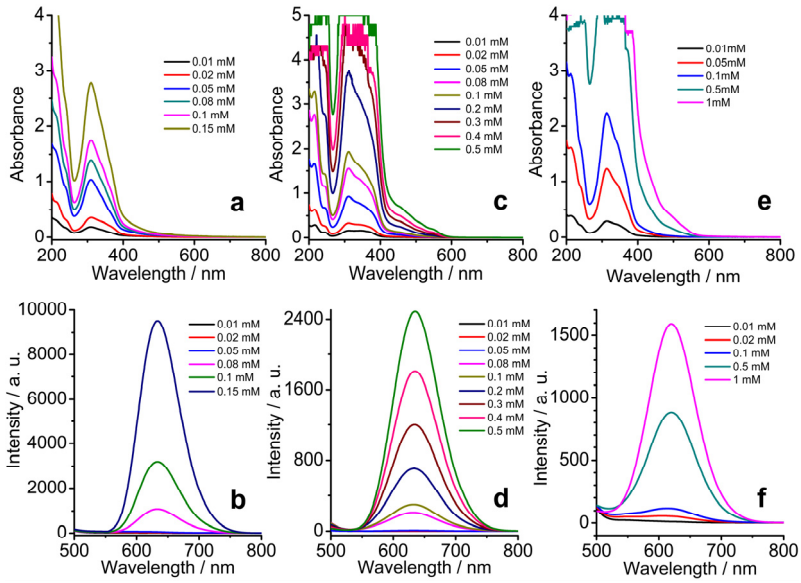


Fig. S2 Concentration-dependence UV-vis (a, c, e) and emission spectra (b, d, f) of **Pt-1**, **Pt-2**, and **Pt-3** in aqueous solutions.

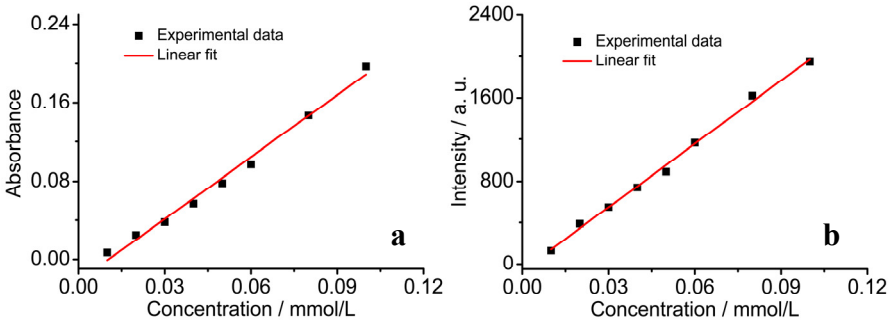


Fig. S3 The absorption (571 nm, a) and emission (630 nm, b) intensities increased linearly with increasing concentrations of **Pt-2**, where the concentration of $BMIMPF_6$ was 0.5 wt%.

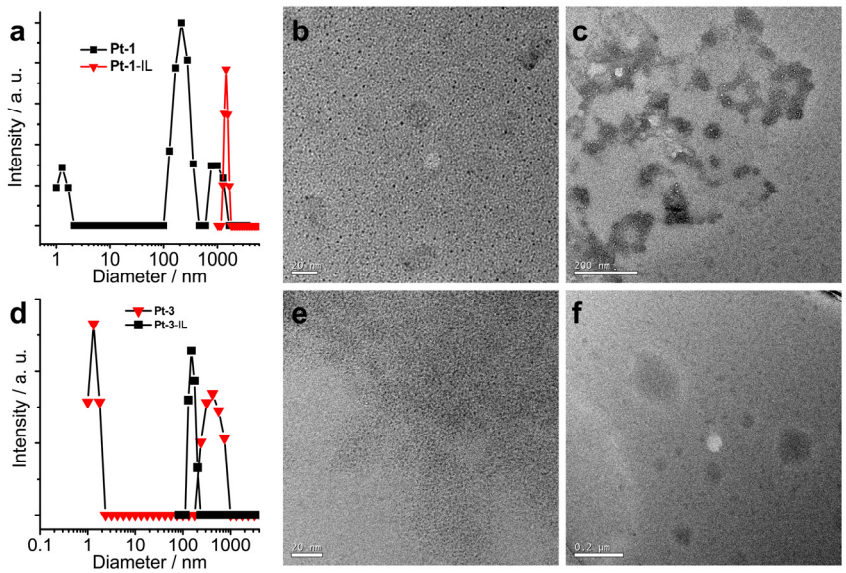


Fig. S4 (a) DLS plots of **Pt-1** in its dilute aqueous solution before and after addition of 0.5 wt% BMIMPF6, where the concentration was controlled to be 0.05 mmol/L. TEM images of **Pt-3** (b) before and (c) after addition of 0.5 wt% $BMIMPF_6$. (d) DLS plots of **Pt-1** in its dilute aqueous solution before and after addition of 0.5 wt% BMIMPF6, where the concentration was controlled to be 0.05 mmol/L. TEM images of **Pt-3** (e) before and (f) after addition of 0.5 wt% $BMIMPF_6$.

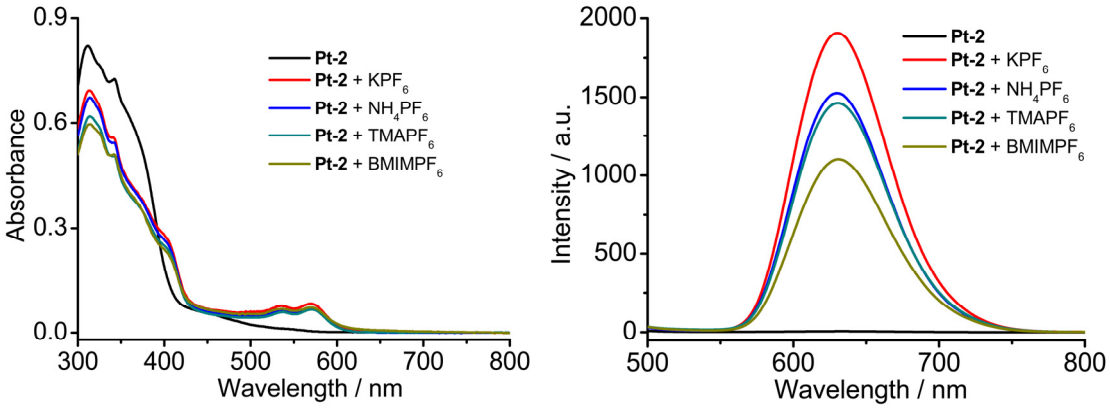


Fig. S5 (Left) UV-vis and (Right) emission spectra of **Pt-2** in the dilute aqueous solutions (0.05 mmol/L) before and after addition of hexafluorophosphate salts. The concentrations of PF_6^- were controlled at 18 mmol/L.

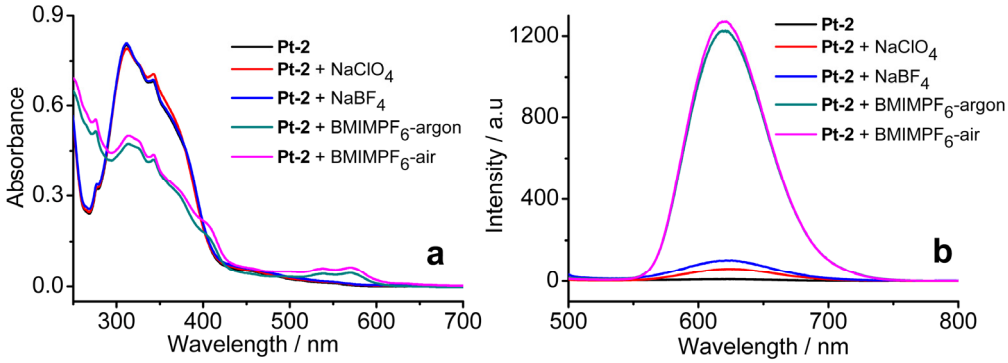


Fig. S6 (a) UV-vis and (b) emission spectra of **Pt-2** in the dilute aqueous solutions (0.05 mmol/L) before and after addition of $BMIMPF_6$, $NaClO_4$, and $NaBF_4$ salts. The concentrations of all anions were controlled at 18 mmol/L. In the present case, the aggregation induced emission of **Pt-2** in argon did not showed significant changes in comparison with those in air. Upon addition of the ionic liquid, 0.5 wt% $BMIMPF_6$, aggregates formed and the luminescence takes on the characteristic of the solid more than the solution. Therefore, it is reasonable that the phosphorescence was not sensitive to O_2.

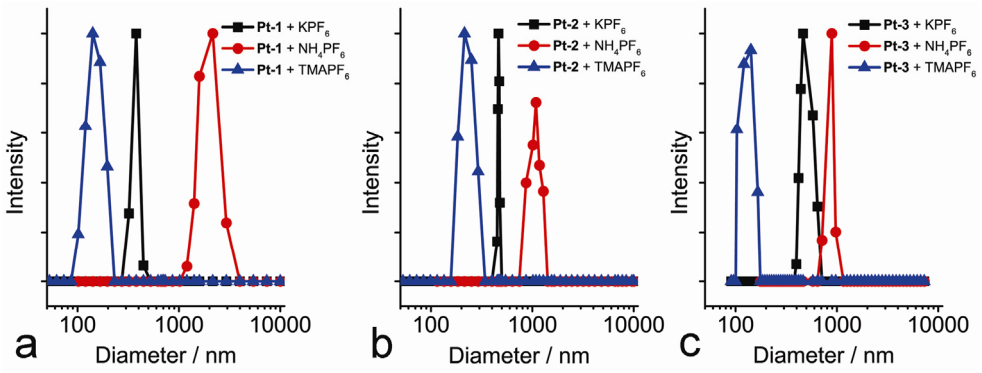


Fig. S7 DLS plots of (a) **Pt-1**, (b) **Pt-2**, and (c) **Pt-3** in their dilute aqueous solutions (0.05 mmol/L) after addition of KPF_6, NH_4PF_6, and $TMAPF_6$, respectively. The concentrations of PF_6^- were controlled at 18 mmol/L.

Upon addition of excessive hexafluorophosphate salts (KPF_6, NH_4PF_6, and $TMAPF_6$) to this dilute aqueous solution, D_hs increased significantly (Fig. S7), indicative of the presence of larger supramolecular aggregates. These pictures were consistent with those obtained with $BMIMPF_6$.

Table S1. UV-vis and emission spectral data for **Pt-1**, **Pt-2**, and **Pt-3**.

Complex	Medium	Absorption / nm	Emission / nm
Pt-1	Water	309, 370, 438	633 [a]
	$BMIMPF_6$	318, 337, 359, 410–500 (broad band)	549, 588
	0.5 wt% $BMIMPF_6$ in water	309, 370, 438	593 [b]
Pt-2	Water	311, 326, 343, 370, 452, 545	634 [a]
	$BMIMPF_6$	304, 337, 351, 368, 422, 449	559
	0.5 wt% $BMIMPF_6$ in water	313, 325, 344, 373, 403, 467, 536, 570	630 [b]
Pt-3	Water	313, 351, 430, 501	620 [a]
	$BMIMPF_6$	311, 319, 340, 358, 430	546
	0.5 wt% $BMIMPF_6$ in water	313, 351, 430, 501	619 [b]

[a] At the concentrations of ≥ 0.08 mmol/L; [b] At a concentration of 0.05 mmol/L.

Table S2. Quantum yield (**Φ**) [a] for **Pt-1**, **Pt-2** and **Pt-3** in their respective aqueous solutions before and after addition of $BMIMPF_6$, KPF_6, NH4PF_6, and $TMAPF_6$.

		$BMIMPF_6$	KPF_6	NH_4PF_6	$TMAPF_6$
Pt-1	0.10	0.20	0.15	0.16	0.15
Pt-2	0.08	0.37	0.44	0.46	0.45
Pt-3	0.08	0.085	0.078	0.062	0.076

[a] The concentrations of the platinum(II) complexes were controlled at 0.05 mmol/L, and hexafluorophosphate salts were 18 mmol/L. Aqueous solutions of **Pt-1**, **Pt-2**, and **Pt-3** were monitored at 593 nm, 630 nm, and 619 nm respectively, and the excitation wavelength was set at 420 nm.

Upon addition of hexafluorophosphate salts, the quantum yields of three chloroplatinum(II) complexes were in an order of **Pt-2** > **Pt-1** > **Pt-3**, which consisted with the result after addition of $BMIMPF_6$.

Table S3. Luminescence lifetimes [a] (τ_1, τ_2 and τ_3) for **Pt-1**, **Pt-2** and **Pt-3** in their respective aqueous solutions before and after addition of $BMIMPF_6$, KPF_6, NH4PF_6, and $TMAPF_6$.

		τ_1 (μs)	RW_1 [b]	τ_2 (μs)	RW_2 [b]	τ_3 (μs)	RW_3 [b]
		0.77	29.54	8.74	70.46		
	$BMIMPF_6$	0.95	20.35	9.05	79.65		
Pt-1	KPF_6	2.32	17.57	10.40	82.43		
	NH_4PF_6	2.37	16.30	10.07	83.70		
	$TMAPF_6$	2.57	20.79	10.62	79.21		
		0.85	27.13	9.12	72.87		
	$BMIMPF_6$	0.90	19.93	9.11	80.07		
Pt-2	KPF_6	2.23	16.96	10.19	83.04		
	NH_4PF_6	2.83	22.71	11.65	77.29		
	$TMAPF_6$	2.56	19.79	11.01	80.21		
		0.54	34.93	2.94	19.38	10.73	45.69
	$BMIMPF_6$	0.57	37.32	2.55	17.17	9.95	45.51
Pt-3	KPF_6	2.82	17.06	10.26	82.94		
	NH_4PF_6	2.57	18.43	10.39	81.57		
	$TMAPF_6$	2.46	20.57	10.56	79.43		

[a] The concentrations of the platinum(II) complexes were controlled at 0.05 mmol/L, and hexafluorophosphate salts were 18 mmol/L. Aqueous solutions of **Pt-1**, **Pt-2**, and **Pt-3** were monitored at 593 nm, 630 nm, and 619 nm respectively, and the excitation wavelength was set at 420 nm. [b] Relative weighting (RW) of components in double or triple exponential fits.

The luminescence decay profiles were almost well-fitted by double exponential curves. Of difference is that the luminescence decay profile of **Pt-3** was well-fitted by triple exponential curves before and after addition of $BMIMPF_6$. Luminescence lifetimes moderately increase upon addition of hexafluorophosphate salts, which may be due to the formation of the supramolecular aggregates in the aqueous solutions.