HOKKAIDO UNIVERSITY

Title	A dual-emissive ionic liquid based on an anionic platinum(II) complex
Author(s)	Ogawa, Tomohiro; Yoshida, Masaki; Ohara, Hiroki et al.
Citation	Chemical communications, 51(69), 13377-13380 https://doi.org/10.1039/c5cc04407c
Issue Date	2015
Doc URL	https://hdl.handle.net/2115/62321
Type	journal article
File Information	PtIL_revised150711MK.pdf



Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Please do not adjust margins

Journal Name

COMMUNICATION

Dual-emissive ionic liquid based on an anionic platinum(II) complex†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Tomohiro Ogawa,[a] Masaki Yoshida,[a] Hiroki Ohara,[a] Atsushi Kobayashi[a,b] and Masako Kato*[a]

An ionic liquid fabricated by an anioinic cyclometalated platinum(II) complex and an imidazolium cation exhibits dual emission from monomeric and aggregated forms of the platinium complex anions, leading to temperature-dependent color changes of luminescence.

In the last two decades, ionic liquids have received considerable attention due to their wide liquid range, electric conductivity, large electrochemical window, and potential for use as alternative solvents for organic reactions.[1] To add higher functionalities to ionic liquids, metal-containing ionic liquids are attractive because of their diverse magnetic,[2a] electrochemical,[2b,c,d] or spectroscopic[2e] properties generated by metal ions and organic ligands. In particular, metal-containing ionic liquids are very intriguing as novel luminescent soft materials with unique properties such as low vapour pressure, high conductivity, and simple processability. Until now, several metal-containing ionic liquids showing notable luminescent properties have been reported. Well-known examples of luminescent room-temperature ionic liquids containing metal complexes are based on lanthanide complexes, especially Eu(III) complexes.[3] Although some other luminescent ionic liquids containing Mn(II),[4] Ru(II),[5] Cu(I),[6] Ag(I),[7a] Au(I),[7a,b] or Sb(III)[8] have also been developed, their luminescence intensities in the liquid state are too weak to utilize them as photofunctional materials with high flexibility and amorphousness at room temperature, and the exploration of luminescent ionic liquids is still a challenging subject.

To bring out photofunctional properties in ionic liquids, i.e., in flexible condensed matter, we focused on the introduction of luminescent Pt(II) complexes that can be stimuli-responsive emitters. Some Pt(II) complexes are known to exhibit remarkable luminescence colour changes depending on their aggregation forms with different intermolecular Pt···Pt and π···π interactions not only in the solid state but also in the solution state.[9] These properties would be advantageous for organic light-emitting diodes (OLEDs), especially white light-emitting OLEDs, because the colour changes could be achieved by controlling the emitter concentration in the host media.[10] Therefore, ionic liquids consisting of Pt(II) complexes are expected to exhibit sensitive but controllable luminescent properties that could be applicable to light-emitting electrochemical cells (LECs), promising easily fabricated light-emitting devices.[11]

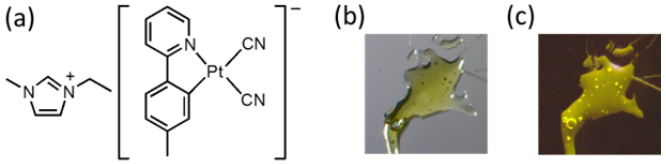


Fig. 1 (a) Structural formula of $[C_2mim][Pt(CN)_2(ptpy)]$ (**1**). Photographs of liquid **1** under (b) bright field and (c) UV light. The ring-shaped and small dotted spots are bubbles in the ionic liquid.

In this communication, we report on the first Pt(II) complex-based ionic liquid, $[C_2mim][Pt(CN)_2(ptpy)]$ (Hptpy = 2-(*p*-tolyl)pyridine, C_2mim = 1-ethyl-3-methylimidazolium ion) (**1**, Fig. 1) and its temperature-dependent luminescence properties. Complex **1** shows dual-emissive properties because of the energy transfer within the disordered structure of the liquid and glass states. The unique properties of ionic liquid **1** were investigated by comparing the properties with those of corresponding crystalline complex salts containing different cations, *n*-$Bu_4N[Pt(CN)_2(ptpy)]$ (**2**) and $K[Pt(CN)_2(ptpy)]$ (**3**).

Complex **1** was synthesized by a metathesis method as follows: Stoichiometric amounts of complex **3** and $[C_2mim]Br$ were mixed in dichloromethane, followed by washing with water for removal of the inorganic salts and drying under vacuum at 100°C (see ESI). The resulting yellow substance was found to be a liquid at room temperature in an inert atmosphere, although it exhibited hygroscopicity. Therefore, in order to elucidate its properties in the anhydrous state, complex **1** was dried under reduced pressure at

[a] Department of Chemistry, Faculty of Science, Hokkaido University, North-10 West-8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan.
Fax: +81-11-706-3447; Tel: +81-11-706-3817;
E-mail: mkato@sci.hokudai.ac.jp
[b] A Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), Honcho 4-1-8, Kawaguchi, Saitama 332-0012, Japan.

† Electronic Supplementary Information (ESI) available: Full experimental details, TGA,VT-PXRD of **1**, emission spectra of **1** in solution, emission and excitation spectra of **2** and **3**, and X-ray structures for **2** and **3**. CCDC 1061287 and 1061289, respectively. See DOI: 10.1039/x0xx00000x

Please do not adjust margins

Please do not adjust margins

90°C overnight and then stored under inert atmosphere at room temperature for several hours prior to use. The thermal behaviour of **1** was investigated by differential scanning calorimetry (DSC) measurements (Fig. 2), as well as thermogravimetry-differential thermal analyses (TG-DTA) (Fig. S1). As shown in Fig. 2, the DSC curves exhibited glass transition behaviour in both cooling and heating processes after the first heating from 25 to 60°C, and no other thermal events such as crystalline phase transitions were observed between −30 and 60°C. We estimated the glass transition temperature (T_g) of **1** to be −10°C from the first cooling process. The X-ray diffraction measurements supported that the sample of **1** did not crystallize at all until −192°C, and only one peak at approximately 2θ = 24.2° (d = 3.67 Å) was detected at low temperatures, suggesting that the glass state of **1** included a local periodic structure such as weak π–π stacking without forming any other long-range order (Fig. S2). Although the π systems of $[Pt(CN)_2(ptpy)]^-$ and $[C_2mim]^+$ are considered to stabilize a crystalline state, the dialkyl-imidazolium cation of $[C_2mim]^+$ would significantly destabilize its crystalline state because of the poor symmetry and charge delocalization. As a result, the liquid state of the Pt(II) complex was realized at room temperature, and an amorphous glass phase was formed at low temperature instead of a crystalline state.

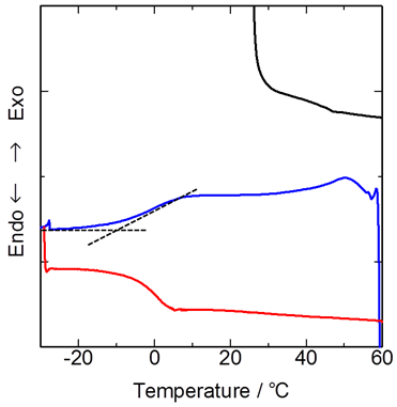


Fig. 2 DSC curves of **1** [first heating (black line), first cooling (blue line), second heating (red line)]. Scan rate: 5 K min^{-1}.

Ionic liquid **1** emitted yellow luminescence under UV light irradiation at room temperature. As shown in Fig. 3(a), it exhibited a broad emission spectrum with several peaks. It was quite different from the methanol solution (1.0×10^{-3} M), in that **1** showed a vibronically structured emission spectrum with maximums at approximately 486 and 517 nm, assignable to the ligand-centred $^3\pi\pi^*$ transition (^{3}LC) with some mixing of ^{3}MLCT character (Fig. S3).[12] The emission spectrum is characteristic of discrete mononuclear complexes without intermolecular interactions. In fact, essentially the same monomeric emission spectrum was observed for the crystal of the *n*-Bu_4N^+ salt **2** [Fig. 3(b)], which includes discrete Pt(II) complex anions surrounded by *n*-Bu_4N cations, as shown in Fig. 4(a). On the other hand, a broad emission spectrum with a maximum of 558 nm was observed for the potassium salt **3** [Fig. 3(b)], in which an interesting dimeric structure of $[Pt(CN)_2(ptpy)]^-$ anions with a short Pt···Pt contact [3.2785(7) Å] was found [Fig. 4 (b)]. Thus, the broad emission spectrum can be assigned to that from the triplet metal-metal-to-ligand charge transfer (^{3}MMLCT) state of the dimerised Pt(II) complexes.[12a] These results suggest that the emission spectrum of ionic liquid **1** could be an overlapped one of an aggregate species of the platinum complexes and the monomeric species. The emission spectrum of **1** changed slightly by excitation at wavelengths longer than 490 nm, which would be due to preferential excitation of the aggregated species (Fig. S4). For the excitation spectra, however, distinct differences depending on the monitoring emission wavelength could not been observed (Fig. S5) as observed for crystalline samples **2** and **3** [Fig. 3(b)]. Also, in the absorption spectrum of ionic liquid **1**, no detectable bands for the assembled species were observed (Fig. S6). These features suggest that the amount of assembled species in the ionic liquid is much less than the amount of monomer species, and thus the dual emission of **1** at room temperature would be attributable to the energy transfer from the excited state of the monomeric species to that of the aggregated species.

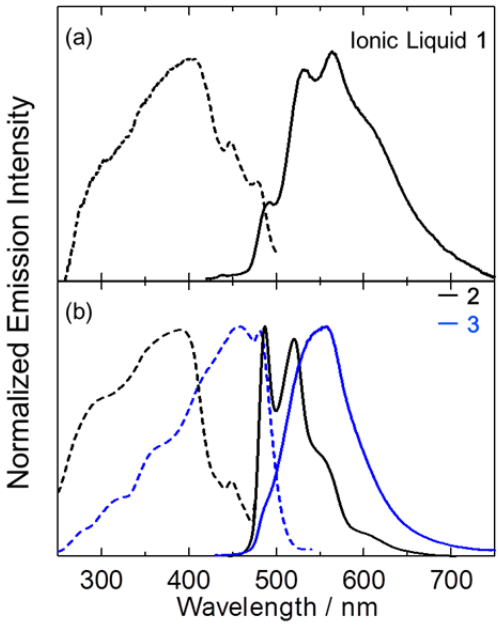


Fig. 3 Emission (solid lines) and excitation (dotted lines) spectra of (a) **1** in liquid state (λ_{ex} = 400 nm, λ_{em} = 560 nm) and (b) **2** (black, λ_{ex} = 400 nm, λ_{em} = 480 nm) and **3** (blue, λ_{ex} = 400 nm, λ_{em} = 560 nm) at room temperature.

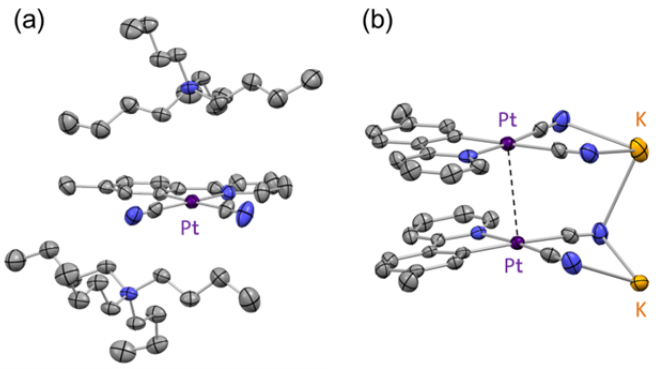


Fig. 4 ORTEP drawings showing the environment of $[Pt(CN)_2(ptpy)]^-$ for (a) the *n*-Bu_4N^+ salt (**2**) and (b) the K^+ salt (**3**). Displacement parameters are

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

Please do not adjust margins

drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Colour code: Pt, purple; C, grey; N, blue; K, orange.

For further insight, time-resolved emission behaviours were investigated. As shown in Fig. 5(a), the emission decay curves from the different wavelength regions clearly indicated the existence of several components (Table S2). A fast decay component with a lifetime (τ) of *ca.* 0.2 μs was observed mainly in the short-wavelength region (486–500 nm), where the emission came from the monomeric species, whereas the relatively slow decay components (τ = *ca.* 1 and 4 μs) increased in the ratio in the longer-wavelength regions (501–550 nm and 551–629 nm). Taking into account that the emission decay of the monomeric species is much slower in a diluted MeOH solution (10^{-4} M) as a fluid medium [Fig. 5(b)], the fast decay for the monomeric species in **1** indicates the existence of an additional process in the ionic liquid. It would be reasonable to consider the energy transfer from the monomeric to the aggregated species because the overall quantum yield of **1** (Φ_{em} = 0.06, Table S1) is slightly higher than that in the dilute MeOH solution containing only the monomeric species (Φ_{em} = 0.03, Table S3). Assuming that the emission lifetime in the dilute MeOH solution (τ_{av} = 2.53 μs) corresponds to that for the monomeric species of **1** in fluid media, the energy transfer rate constant from the monomeric to the aggregated species is roughly estimated from the difference in the lifetime value of the monomeric species in the ionic liquid (τ = 0.192 μs, Table S2) to be *ca.* 4.8×10^6 s^{-1}, which is a reasonable value typical for the triplet energy transfer rate constants (10^{6-7} s^{-1}).[13]

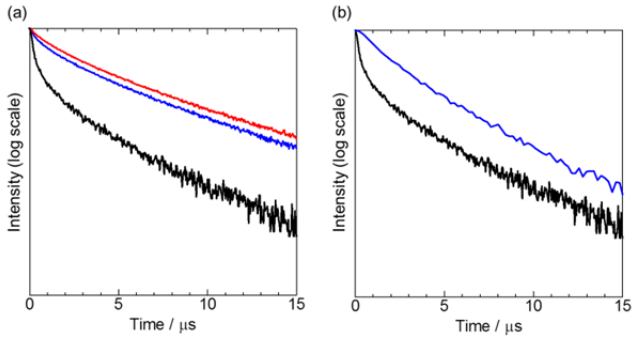


Fig. 5 (a) Emission decay curves of ionic liquid **1** at 298 K detected at 486–500 nm (black line), 501–550 nm (blue line), and 551–629 nm (red line). (b) Comparison of the emission decay curve of **1** (black line, detected at 486–500 nm) with that in MeOH (blue line, 1.0×10^{-4} M). λ_{ex} = 337 nm.

The ionic liquid exhibited distinct emission colour changes depending on temperature (Fig. 6 inset). With decreasing temperature, the emission intensity at shorter wavelength regions increased remarkably, and at 77 K, the luminescent spectrum of **1** reached that of the monomeric species, with the vibronic structure as shown in Fig. 6. The monomeric emission at 77 K exhibited a longer lifetime and thus the decreased decay rate (17.2 μs and 5.8×10^4 s^{-1}, respectively, Fig. S7, Table S1), which supports the claim that the energy transfer was almost suppressed at 77 K due to some energy barrier. However, the spectral change at around the glass-phase transition point (−10°C) was not distinct, indicating that the fluidity or translational motion were not important factors for the dual emission.[14] On the other hand, the excitation spectra monitored at emission wavelengths of 490–650 nm did not exhibit any notable changes in the range from room temperature to 77 K (Fig. S8). This would be reasonable for the energy transfer emission system, as mentioned above.

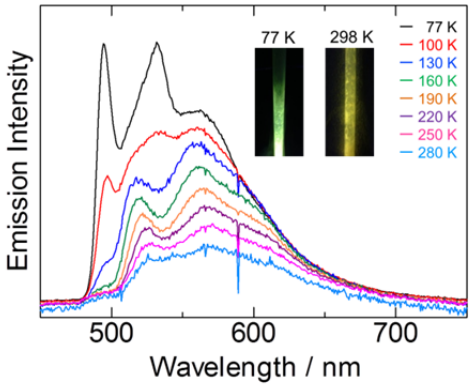
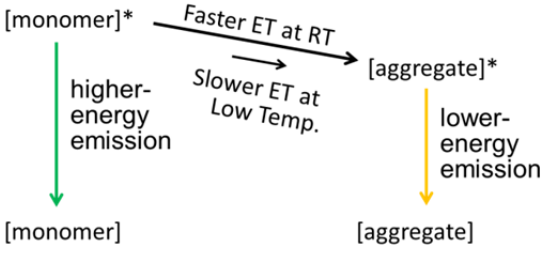


Fig. 6 Emission spectra of **1** at different temperatures. λ_{ex} = 337 nm. The relative emission intensities were adjusted for clarity.

Two different mechanisms have been suggested for dual emission from electronically coupled systems.[15] One is a thermal equilibrium model, which is based on the Boltzmann population between two emission states in thermal equilibrium. In this model, the emission intensity of the lower energy band increases at low temperatures. The other mechanism is a competing system of emission and energy transfer processes with an energy barrier. The dual emission behaviour for **1** could be assigned to the latter case because the emission intensity ratio of the lower energy band increased with increasing temperature. The shape of the spectrum of **1** changed when the excitation wavelength was longer than 490 nm, as mentioned above (Fig. S4). The fact that the emission intensity from the monomeric species at 530 nm decreased at excitations with longer wavelengths also indicates that the back energy transfer from the aggregated species to the monomer did not occur. The plausible mechanism of this energy transfer is depicted in Scheme 1. The energy transfer should play a key role in temperature-dependent dual emission. Overall, the phosphorescent cyclometalated Pt(II) complex would be advantageous to dual emission of the ionic liquid because of the competitive quenching by energy transfer and other nonradiative decay and relatively slow radiative rate constants (k_r, Table S1).



Scheme 1 Plausible mechanism of the dual emissive property of **1**.

Please do not adjust margins

Please do not adjust margins

In conclusion, we succeeded in the synthesis of the first ionic liquid based on a Pt(II) complex. This ionic liquid exhibited dual emission from both the monomeric and aggregated excited states, and these dual-emissive properties gave rise to distinct thermochromic luminescence. Because of the co-existence of monomeric and aggregated forms in disordered liquid and glass phases, the energy transfer from the monomeric excited states to the aggregated states led to dual emission. To our knowledge, this is also the first report of a well-defined dual-emissive ionic liquid. Such dual-emissive phosphorescent ionic liquids could potentially be used as luminescent materials for simple light-emitting and/or -sensing devices. Further studies concerning Pt(II)-based ionic liquids are now in progress.

This research was partially supported by Grants-in-Aid for Scientific Research on Innovative Areas "Artificial Photosynthesis" (25107502 and 15H00858), Scientific research (C) (50437753), from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. We also gratefully acknowledge Prof. Sadamu Takeda and Mr. Jun-ya Okamoto (Hokkaido University) for the DSC measurements.

Notes and references

1 (*a*) J. P. Hallett and T. Welton, *Chem. Rev*. 2011, **111**, 3508; (*b*) P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.*, 2000, **39**, 3772; (*c*) M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mat.* 2009, **8**, 621; (*d*) S.-G. Lee, *Chem. Commun*., 2006, 1049.

2 (*a*) M. Okuhata, Y. Funasako, K. Takahashi and T. Mochida, *Chem. Commun*., 2013, **49**, 7662; (*b*) A. Branso, L. C. Branco and F. Pina, *Chem. Commun*., 2011, **47**, 2300; (*c*) M. Steichen, N. R. Brooks, L. V. Meervelt, J. Fransaerc and K. Binnemans, *Dalton Trans*., 2014, **43**, 12329; (*d*) N. R. Brooks, S. Schaltin, K. V. Hecke, L. V. Meervelt, K. Binnemans and J. Fransear, *Chem. Eur. J.* 2011, **17**, 5054; (*e*) Y. Funasako, T. Mochida, K. Takahashi, T. Sakurai and H. Ohta, *Chem. Eur. J.*, 2012, **18**, 11929.

3 (*a*) S. Tang, A. Babai and A.-V. Mudring, *Angew. Chem. Int. Ed*., 2008, **47**, 7631; (*b*) A. Getsis, S. Tang and A.-V. Mudring, *Eur. J. Inorg. Chem*., 2010, 2172.

4 S. Pitula and A.-V. Mudring, *Chem. Eur. J*. 2010, **16**, 3355.

5 S. Gago, L. Cabrita, J. C. Lima, L. C. Branco and F. Pina, *Dalton Trans.*, 2013, **42**, 6213.

6 E. T. Spielberg, E. Edengeiser, B. Mallick, M. Havenith and A.-V. Mudring, *Chem. Eur. J.* 2014, **20**, 5338.

7 (*a*) A. Tokarev, J. Larionova, Y. Guari, J. M. López-de-Luzuriaga, M. Monge, P. Dieudonné and C. Blanc, *Dalton Trans*., 2010, **39**, 10574; (*b*) Y. Yoshida, J. Fujii, G. Saito, T. Hiramatsu and N. Sato, *J. Mater. Chem*., 2006, **16**, 724.

8 Z.-P. Wang, J.-Y. Wang, J.-R. Li, M.-L. Feng, G.-D. Zou and X.-Y. Huang, *Chem. Commun.*, 2015, **51**, 3094.

9 (*a*) M. Kato, *Bull. Chem. Soc. Jpn*., 2007, **8**, 287; (*b*) B. Ma, P. I. Djurovich and M. E. Thompson, *Coord. Chem. Rev*., 2005, **249**, 1501; (*c*) K. M.-C. G Wong and V. W.-W. Yam, *Acc. Chem. Res.*, 2011, **44**, 424; (*d*) A. Kobayashi and M. Kato, *Eur. J. Inorg. Chem.,* 2014, **27**, 4469.

10 (*a*) B. W. D'Andrade, J. Brooks, V. Adamovich, M. E. Thompson and S. R. Forrest, *Adv. Mater.*, 2002, **14**, 1032; (*b*) J. Kalonowski, M. Cocchi, D. Virgili, V. Fattori and J. A. G. Williams, *Adv. Mater*., 2007, **19**, 4000; (*c*) J. Kalinowski, M. Cocchi, L. Murphy, J. A. G. Williams and V. Fattori, *Chem. Phys.*, 2010, **378**, 47; (*d*) L. Murphy, P. Brulatti, V. Fattori, M. Cocchi and J. A. G. Williams, *Chem. Commun*., 2012, **48**, 5817; (*e*) G. Zhou, Q. Wang, X. Wang, C.-L. Ho, W.-Y. Wong, D. Ma, L. Wang and Z. Lin, *J. Mater. Chem.*, 2010, **20**, 7472.

11 R. Costa, E. Ortí, H. J. Bolink, F. Monti, G. Accorsi and N. Armaroli, *Angew. Chem. Int. Ed*., 2012, **51**, 8178.

12 (*a*) J. Forniés, S. Fuertes, J. A. López, A. Martín and V. Sicilia, *Inorg. Chem*., 2008, **47**, 7166; (*b*) A. F. Rausch, U. V. Monkowius, M. Zabel and H. Yersin, *Inorg. Chem*., 2010, **49**, 7818; (*c*) J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau and M. E. Thompson, *Inorg. Chem*., 2002, **41**, 3055.

13 (*a*) G. L. Closs, P. Piotrowiak, J. M. MacInnis and G. R. Fleming, *J. Am. Chem. Soc.*, 1988, **110**, 2652; (*b*) G. L. Closs, M. D. Johnson, J. R. Miller and P. Piotrowiak, *J. Am. Chem. Soc.*, 1989, **111**, 3751.

14 M. Han, Y. Tian, Z. Yuan, L. Zhu and B. Ma, *Angew. Chem. Int. Ed*., 2014, **53**, 10908.

15 E. J. McLaurin, L. R. Bradshaw and D. R. Gamelin, *Chem. Mater*., 2013, **25**, 1283.

 This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins