DOI: 10.1002/chem.200902328

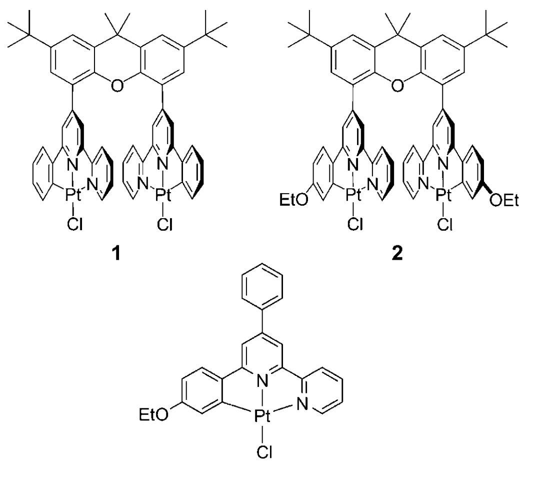
Shape-Persistent Binuclear Cyclometalated Platinum(II) Luminophores: Pushing π-Mediated Excimeric Fluid Emissions into the NIR Region and Ion-Induced Perturbations

Zhengqing Guo and Michael C. W. Chan*[a]

In recent years, researchers have judiciously investigated molecular phenomena, such as restricted rotation, crowded conformation, rigidization, and supramolecular attraction (e.g. π-stacking) in crowded aromatic frameworks in search of desirable electronic,[1] recognition/signaling,[2] mechanical[3] and catalytic properties.[4] Although fluorescent versions have appeared,[5] the incorporation of luminescent metal–organic and phosphorescent components have generally been neglected. We are currently engaged in the creation of congested molecular scaffolds[6] derived from environmentally sensitive platinum(II) luminophores, which may offer possibilities in controllable conformational changes, in the reporting of molecular-level events, and give unusual photophysical and sensing characteristics. In this respect, luminescent square-planar oligopyridyl Pt^{II} complexes and multinuclear assemblies have been extensively studied over the past two decades, owing to their propensity to engage in interplanar stacking and metal–metal interactions and for their diverse excited-state properties. Namely, their "open" geometry facilitates the observation of low-energy fluid emissions in the $\lambda_{max} = 600$–700 nm region that are ascribed to metal–metal-to-ligand charge transfer (MMLCT; $d\sigma^* \rightarrow \pi^*$) transitions,[7–9] but this assignment is complicated[8,10] because $\pi\pi^*$ excimeric emissions occur in a similar spectral region ($\lambda_{max} = 600$–650 nm; often from 77 K glassy solution),[11] hence it is difficult to distinguish between these two states.

Herein, we describe the synthesis and spectroscopic properties of new binuclear cyclometalated 6-aryl-2,2′-bipyridine (C,N,N) platinum(II) complexes tethered by a xanthene backbone. The xanthene bridging unit has been utilized by Tanaka to study electronic interactions in mixed Ru-/Pt-terpyridine derivatives,[12] and very recently by Williams to link together two [2,6-di(2-pyridyl)(σ-aryl)]PtCl moieties to afford intense deep-red excimeric emission.[13] In this work, the rigid bridging unit is chosen to preclude intramolecular metal–metal interactions and hence MMLCT states, while allowing π-stacking interactions within the $[Pt\text{-}C,N,N]_2$ moiety, and this has pushed the associated excimeric-type emission into the near-infrared region. In addition, interesting perturbations of the excimeric emission (and by correlation the weak π-stacking interactions) in different solvents and in response to metal ions have been observed.

The conformationally rigid binuclear complexes **1** and **2** (Figure 1) are prepared by modified Kröhnke-type reactions by using the appropriate xanthene-4,5-bis(aldehyde) precursor to give the corresponding ligands, followed by treatment with K_2PtCl_4 in refluxing glacial acetic acid (see the Sup-



1 **2** **3**

Figure 1. The binuclear structures of **1** and **2** alongside the mononuclear congener **3**.

---

[a] Z. Guo, Dr. M. C. W. Chan
Department of Biology and Chemistry
City University of Hong Kong
Tat Chee Avenue, Kowloon, Hong Kong (China)
Fax: (+852) 27887406
E-mail: mcwchan@cityu.edu.hk

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902328 and contains the experimental details and characterization data; photophysical data and spectra; a color version of Figure 4; molecular modeling for **2**.

porting Information for details of synthetic route). Functionalization of the cyclometalated rings in **2** with ethoxy groups is intended to modulate the mechanical (i.e. rotational) and photophysical characteristics of the Pt-C,N,N units, as well as improve solubility.

The photophysical properties of **1–3** have been investigated in detail.[14] The intense absorption bands at $\lambda < 400$ nm for **1** and **2** (slightly red-shifted for the latter) are attributed to intraligand $^1(\pi\pi^*)$ transitions. For **1**, the moderately intense absorptions in the visible region at $\lambda_{max} = 424$ and 443 nm are very similar in shape and energy to known mononuclear congeners,[8,9] while displaying comparable negative solvatochromic behavior,[14] and are therefore ascribed as d(Pt)→π*(bpy) ^{1}MLCT. No absorption tailing is apparent below $\lambda = 500$ nm, in contrast to that observed for binuclear analogues supported by short diphosphine bridges (e.g. dppm),[8] thus signifying the expected absence of ground state Pt···Pt interactions. The visible absorption of **2** at $\lambda_{max} = 444$ nm is less structured than **1**, but comparable in shape to the mononuclear congener **3**, and is assigned to an admixture of π(EtO-aryl)/d(Pt)→π*(bpy) (^{1}ILCT/^{1}MLCT) like that recently proposed for an alkoxy congener of **3**.[15] Using the rationale in a previous report,[8b] the corrected absorption difference spectrum between **2** and **3** contains a discernible band with a maximum at $\lambda = 451$ nm ($\varepsilon \approx 2000$ dm^3 mol^{-1} cm^{-1}; Figure 2), which is tentatively attributed to weak ground-state intramolecular π–π interaction. A similar band at $\lambda_{max} = 458$ nm is apparent in the corrected absorption difference spectrum between **1** and the non-ethoxy congener of **3**.[14]

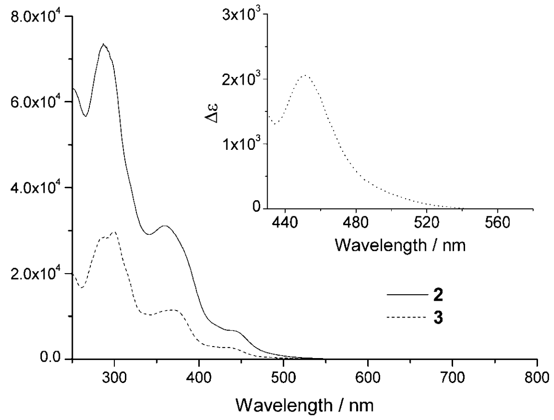


Figure 2. UV/vis absorption spectra of **2** and **3** in CH_2Cl_2 at 298 K. Inset: Plot of $\Delta\varepsilon$ versus wavelength for **2** and **3** (ε values multiplied by 2) in CH_2Cl_2.

Complexes **1** and **2** are luminescent in solution at room temperature. For **1**, in addition to the solvatochromic ^{3}MLCT emission at $\lambda_{max} = 562$ nm in CH_2Cl_2, a weaker low-energy shoulder is evident at $\lambda_{max} \approx 750$ nm. Upon further investigation in CH_2Cl_2/CH_3OH (1:1), the low-energy feature intriguingly grows (versus the ^{3}MLCT emission) into a distinct peak at $\lambda_{max} \approx 730$ nm. Compared to **1**, the red-shifted emission of **2** at $\lambda_{max} = 594$ nm in CH_2Cl_2 displays minimal solvatochromism and identical emission energy and lifetime to that of **3**, indicating a ^{3}ILCT excited state[15,16] although some ^{3}MLCT character cannot be ruled out. Like **1**, the additional broad, low-energy emission for **2** at $\lambda_{max} \approx 720$ nm alters in intensity against the high-energy band in different solvents: the $\lambda_{max} \approx 720$ nm band is negligible in DMSO (like **3** in CH_2Cl_2), weak in toluene and THF, and intensifies from CH_2Cl_2 to MeOH and becomes the dominant feature in CH_3CN at the expense of the high-energy band (Figure 3).

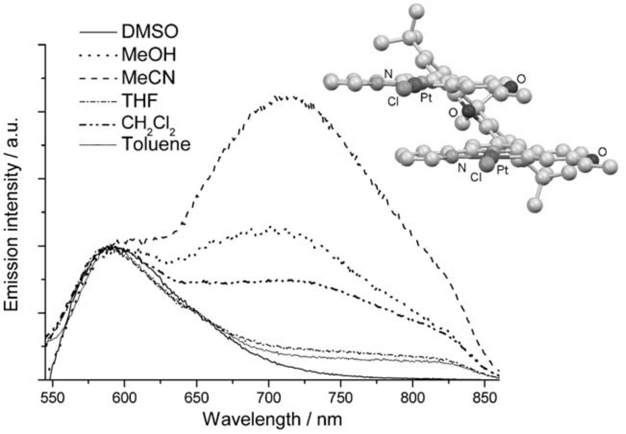


Figure 3. Emission spectra for **2** (10^{-5} mol L^{-1}) in different solvents (normalized with respect to high-energy band; $\lambda_{ex} = 430$ nm) at 298 K (inset: calculated offset π-stacked interactions in **2**).

Interestingly, these emission features and particularly the relative intensities of the high- and low-energy emissions for both **1** and **2** are independent of complex concentration (down to 10^{-6} mol L^{-1}, thus discounting intermolecular aggregation) and excitation wavelength (to reduce possibility of contribution from highly emissive impurities).[14] Furthermore, the same excitation spectra are recorded for the high- and low-energy emissions from **1** and **2** respectively, which closely resemble their UV absorptions, especially for the lowest-energy band at $\lambda_{max} \approx 440$ nm. The broad nature (fwhm ≈ 3400 cm^{-1} in CH_3CN for **2**) and low Φ (10^{-4}) of the low-energy band are consistent with excimer-type emission.[11a,17] In this connection, an energy-minimized (Gaussian) calculated structure of **2** (Figure 3) has predicted weak π-stacked interplanar contacts within the $(Pt\text{-}C,N,N)_2$ moiety (plus a Pt···Pt separation of 5.63 Å).[14] Since Pt···Pt interactions can be disregarded, the low-energy emission is thus assigned to offset π-stacked interactions (i.e. "slipped" intramolecular interplanar contacts such as π–π and d(Pt)–π(aryl and py) within the $(Pt\text{-}C,N,N)_2$ moiety).[18] Owing to the rigid nature of the xanthene backbone, the π-stacking interactions may be very weak in the ground state (as tentatively indicated in Figure 2), but become significantly more favorable in the excited state, especially for **2** in solvents such as CH_3CN (Figure 3), and therefore the term excimer rather than dimer emission is preferred. The relationship between the unusual emission changes in Figure 3 and solvent polarity is tentative, and is presumably related to the capacity of the solvent to favor or compete with π-stacking interactions, leading to intramolecular aggregation and deaggregation respectively.

The intramolecular π-stacked excimeric emission for **1** and **2**, at $\lambda_{max}\approx 720$–730 nm respectively in CH_3CN at room temperature, is of interest because it approaches the NIR region and is uncharacteristically red-shifted, considering the absence of MMLCT character and in comparison with previously reported $\pi\pi^*$ excimeric emissions at $\lambda_{max}=600$–650 nm[8,11] and fluid MMLCT $d\sigma^*\rightarrow\pi^*$ emissions at $\lambda_{max}=$ 600–700 nm.[7–9,11c,d] To rationalize the red-shifted excimeric emissions for **1** and **2** relative to that reported by Williams[13] for the related [N,C,N] congener ($\lambda_{max}=690$ nm in CH_2Cl_2), we note that the π-stacking interactions in **1** and **2** would involve mixed π(py)–π(aryl) and may be different.

The fragile π-stacked interactions giving rise to the proposed low-energy excimeric emission for **2** is anticipated to be sensitive to mechanical perturbations (e.g. axial twisting) at the molecular level, and the intrinsic luminescent signaling element is attractive. For example, the ethoxy groups may impede rotation of the [Pt-C,N,N] units as well as assist or mediate host–guest interactions. Preliminary studies on the luminescent response for **2** in the presence of various metal ions have been undertaken (Figure 4). While minimal response is evident for the majority of M^{n+} (9.0 equiv), the low-energy excimeric emission is replaced by the ^{3}ILCT band for Cu^{2+} (and to some extent Pb^{2+}), and substantial enhancement of the ^{3}ILCT band is observed for Hg^{2+}. Identical experiments in the presence of Hg^{2+} ions for the mononuclear analogue **3** resulted in emission quenching, whereas complex **1** yielded blue-shifted emission accompanied by partial quenching. We suggest that the transformation from excimeric to high-energy emission upon addition of metal ions for **2** may be attributed to conformational changes and/or π-cation interactions[19] at the [Pt-C,N,N] units, resulting in disruption of the weak π-stacking contacts, whereas the observed enhancement with Hg^{2+} may arise from an increase in the rigidity[20] of the $[Pt\text{-}C,N,N]_2$ moiety, as indicated by ^{1}H NMR studies.[7f,14] Nevertheless, the detailed mechanism for the ion-induced luminescent perturbations and the role of the ethoxy groups are topics under investigation.

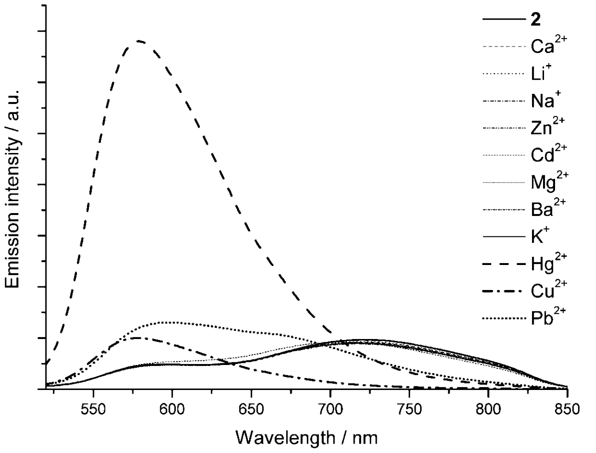


Figure 4. Luminescent spectral change of **2** (5×10^{-5} mol L^{-1}) upon addition of 9.0 equiv of various metal ions (5×10^{-2} mol L^{-1}) in CH_3CN (see the Supporting Information for photograph of **2** in CH_3CN under $\lambda=$ 365 nm excitation before and after addition of Hg^{2+}).

In summary, we have described rigidly tethered binuclear Pt^{II} luminophores that display excimeric-type fluid emissions at $\lambda_{max}\approx 720$–730 nm without ambiguity from MMLCT states. Intriguingly, these emissions are susceptible to perturbations in different solvents and by selected metal ions. The associated intramolecular π-stacking interaction within the $[Pt\text{-}C,N,N]_2$ cavity is observed to push the excimeric emission down into the near-IR region. NIR emissions are desirable reporting tools for biomolecular probes and chemosensing applications, and our future work will aim to exploit the integration of weak interplanar interactions and sensitive luminophores in these systems.

Acknowledgements

The work described in this paper was fully supported by grants from the Research Grants Council of the Hong Kong Special Administrative Region, China (CityU 100408) and City University of Hong Kong (7002278). We are grateful to Wai-Kit Cheng and Wah-Leung Tong for technical assistance.

Keywords: excimeric emission • platinum • restricted conformation • rigidization • pi interactions

[1] a) T. Nakano, T. Yade, *J. Am. Chem. Soc.* **2003**, *125*, 15474–15484; b) T.-Q. Nguyen, R. Martel, P. Avouris, M. L. Bushey, L. Brus, C. Nuckolls, *J. Am. Chem. Soc.* **2004**, *126*, 5234–5242; c) M. M. Elmahdy, X. Dou, M. Mondeshki, G. Floudas, H.-J. Butt, H. W. Spiess, K. Müllen, *J. Am. Chem. Soc.* **2008**, *130*, 5311–5319.

[2] a) A. J. Goshe, I. M. Steele, B. Bosnich, *J. Am. Chem. Soc.* **2003**, *125*, 444–451; b) V. J. Chebny, R. Rathore, *J. Am. Chem. Soc.* **2007**, *129*, 8458–8465.

[3] S. Ulrich, J.-M. Lehn, *Chem. Eur. J.* **2009**, *15*, 5640–5645.

[4] a) S-Y. Liu, D. G. Nocera, *J. Am. Chem. Soc.* **2005**, *127*, 5278–5279; b) J. Y. Yang, D. G. Nocera, *J. Am. Chem. Soc.* **2007**, *129*, 8192–8198.

[5] a) S. A. McFarland, N. S. Finney, *J. Am. Chem. Soc.* **2001**, *123*, 1260–1261; b) M. Barboiu, L. Prodi, M. Montalti, N. Zaccheroni, N. Kyritsakas, J.-M. Lehn, *Chem. Eur. J.* **2004**, *10*, 2953–2959; c) X. Mei, C. Wolf, *J. Am. Chem. Soc.* **2004**, *126*, 14736–14737.

[6] a) W. L. Tong, M. C. W Chan, N. Zhu, S. K. Leung, *Dalton Trans.* **2009**, 4741–4746; b) Z. Guo, W. L. Tong, M. C. W Chan, *Chem. Commun.* **2009**, 6189–6191.

[7] a) V. M. Miskowski, V. H. Houlding, *Inorg. Chem.* **1981**, *20*, 4446–4452; b) G. Arena, G. Calogero, S. Campagna, L. Monsu Scolaro, V. Ricevuto, R. Romeo, *Inorg. Chem.* **1998**, *37*, 2763–2769; c) R. Büchner, C. T. Cunningham, J. S. Field, R. J. Haines, D. R. McMillin, G. C. Summerton, *J. Chem. Soc. Dalton Trans.* **1999**, 711–717; d) H. Yersin, D. Donges, W. Humbs, J. Strasser, R. Sitters, M. Glasbeek, *Inorg. Chem.* **2002**, *41*, 4915–4922; e) T. J. Wadas, Q.-M. Wang, Y.-J. Kim, C. Flaschenreim, T. N. Blanton, R. Eisenberg, *J. Am. Chem. Soc.* **2004**, *126*, 16841–16849. Reports of MMLCT emissions above 700 nm: f) V. W.-W. Yam, K. H.-Y. Chan, K. M.-C. Wong, B. W.-K.

Chu, *Angew. Chem.* **2006**, *118*, 6315–6319; *Angew. Chem. Int. Ed.* **2006**, *45*, 6169–6173 (from aggregation); g) V. W.-W. Yam, K. M.-C. Wong, N. Zhu, *J. Am. Chem. Soc.* **2002**, *124*, 6506–6507; h) M. Kato, A. Omura, A. Toshikawa, S. Kishi, Y. Sugimoto, *Angew. Chem.* **2002**, *114*, 3315–3317; *Angew. Chem. Int. Ed.* **2002**, *41*, 3183–3185 (solid emission).

[8] a) S.-W. Lai, M. C. W. Chan, T.-C. Cheung, S.-M. Peng, C.-M. Che, *Inorg. Chem.* **1999**, *38*, 4046–4055; b) W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, C. Li, Z. Hui, *J. Am. Chem. Soc.* **2004**, *126*, 7639–7651.

[9] a) S.-W. Lai, H.-W. Lam, W. Lu, K.-K. Cheung, C.-M. Che, *Organometallics* **2002**, *21*, 226–234; b) S. C. F. Kui, I. H. T. Sham, C. C. C. Cheung, C.-W. Ma, B. Yan, N. Zhu, C.-M. Che, W.-F. Fu, *Chem. Eur. J.* **2007**, *13*, 417–435.

[10] D. Kim, J.-L. Brédas, *J. Am. Chem. Soc.* **2009**, *131*, 11371–11380.

[11] a) V. M. Miskowski, V. H. Houlding, *Inorg. Chem.* **1989**, *28*, 1529–1533; b) K.-T. Wan, C.-M. Che, K.-C. Cho, *J. Chem. Soc. Dalton Trans.* **1991**, 1077–1080; c) J. A. Bailey, V. M. Miskowski, H. B. Gray, *Inorg. Chem.* **1993**, *32*, 369–370; d) J. A. Bailey, M. G. Hill, R. E. Marsh, V. M. Miskowski, W. P. Schaefer, H. B. Gray, *Inorg. Chem.* **1995**, *34*, 4591–4599; e) S.-W. Lai, T.-C. Cheung, M. C. W. Chan, K.-K. Cheung, S.-M. Peng, C.-M. Che, *Inorg. Chem.* **2000**, *39*, 255–262; f) W. Lu, M. C. W. Chan, K.-K. Cheung, C.-M. Che, *Organometallics* **2001**, *20*, 2477–2486; g) S. C. F. Kui, S. S.-Y. Chui, C.-M. Che, N. Zhu, *J. Am. Chem. Soc.* **2006**, *128*, 8297–8309.

[12] R. Okamura, T. Wada, K. Aikawa, T. Nagata, K. Tanaka, *Inorg. Chem.* **2004**, *43*, 7210–7217.

[13] S. Develay, J. A. G. Williams, *Dalton Trans.* **2008**, 4562–4564.

[14] See the Supporting Information for additional details and figures.

[15] P. Shao, Y. Li, A. Azenkeng, M. R. Hoffmann, W. Sun, *Inorg. Chem.* **2009**, *48*, 2407—2419.

[16] a) J. F. Michalec, S. A. Bejune, D. G. Cuttell, G. C. Summerton, J. A. Gertenbach, J. S. Field, R. J. Haines, D. R. McMillin, *Inorg. Chem.* **2001**, *40*, 2193–2200; b) W. Lu, B. X. Mi, M. C. W. Chan, Z. Hui, C. M. Che, N. Zhu, S. T. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 4958–4971.

[17] B. D′Andrade, S. R. Forrest, *Chem. Phys.* **2003**, *286*, 321–335.

[18] Owing to the separation of the [Pt-C,N,N] units by the xanthene backbone (point-to-point distance from 4- to 5-positions is >4.5 Å), an eclipsed conformation would be non-interacting.

[19] M. Cametti, M. Nissinen, A. Dalla Cort, L. Mandolini, K. Rissanen, *J. Am. Chem. Soc.* **2005**, *127*, 3831–3837.

[20] a) J. J. Moore, J. J. Nash, P. E. Fanwick, D. R. McMillin, *Inorg. Chem.* **2002**, *41*, 6387–6396; b) K. Rurack, U. Resch-Genger, *Chem. Soc. Rev.* **2002**, *31*, 116–127.

Received: August 24, 2009