Chemistry
A European
Journal

Chemistry
Europe
European Chemical
Societies Publishing

Accepted Article

Title: Multinuclear Pt(II) Complexes: Why Three is Better Than Two to Enhance Photophysical Properties

Authors: Luisa De Cola, Sourav Chakraborty, and Alessandro Aliprandi

To be cited as: *Chem. Eur. J.* 10.1002/chem.202001510

Link to VoR: https://doi.org/10.1002/chem.202001510

WILEY-VCH

Multinuclear Pt(II) Complexes: Why Three is Better Than Two to Enhance Photophysical Properties

Sourav Chakraborty,[a] Alessandro Aliprandi,[a] and Luisa De Cola*[a,b]

Dedication ((optional))

Abstract: Self-assembly of platinum complexes is a well documented process that leads to interesting changes of the photophysical and electrochemical behavior as well modify the reactivity of the complexes. However how many metal units must interact in order to achieve the same desired properties of large assembly is still not clear. In this paper we aim to clarify the role of the number of interacting Pt(II) unit lead to an enhancement of the spectroscopic properties and how to address inter- vs intramolecular processes. We have, therefore, synthesized and characterized a series of neutral multinuclear Pt(II) complexes and studied their photophysical properties at different concentration. Going from the monomer to the dimers we observe the growth of a new emission band, and the enhancement of the emission properties. Upon increasing the platinum units up to three, the monomeric blue emission cannot be detected anymore and a concentration independent bright yellow/orange emission due to establishment of intramolecular metallophilic interactions is observed.

Introduction

Square planar Pt(II)-complexes, containing conjugated coordinated ligands, are particularly interesting building blocks for the creation of supramolecular nanostructures since their flat geometry makes them prone to stack through noncovalent interaction such as π–π stacking.[1-10] Furthermore, when Pt(II) complexes are close enough (distance below 3.5 Å)[11-14] metallophilic interactions between Pt centers may be established and stable aggregates[15-17] can be observed possessing spectroscopic properties which can be dramatically different from the monomeric metal complex. [1-4, 18-23] Indeed the establishment of ground state intermolecular interactions between protruding dz^2 orbitals result in the formation of lower-lying molecular orbitals thus new optical transition appears ascribed to Metal-Metal-to-ligand Charge Transfer (MMLCT).[22-28] The changes in the optical properties are directly correlated with the distance between the Pt centers.[6, 11, 29-31] Thus, the shortest is the distance, the strongest is the electronic Pt···Pt electronic interaction, the more bathochromically shifted is the MMLCT band.[32-33] But the formation of assembled species does not only change the absorption and emission energy, but due to a change of the nature of the lowest transition and the increasing rigidity of the packed units often lead to an enhancement of the emission quantum yields (PLQY) and an elongation of the excited state lifetime.[20] Our group has recently reported a phosphorescent mononuclear amphiphilic Pt(II)-complex[20] (PLQY of 1% in aerated dioxane) capable of producing strong orange phosphorescence with a PLQY up to 84% in water/dioxane (95:5) solution. The very high PLQY in aerated solution suggest also a protection of the packed Pt(II) centers from dioxygen. Indeed, due to the triplet nature of the platinum complexes emissions, one would expect strong quenching, by dioxygen, of the long lived (microsecond) excited state. The outstanding photophysical properties of self-assembled structures of Pt(II) complexes have gained high popularity in the last decades due to their good performances into several applications such as organic light-emitting diodes (OLEDs),[18, 34-39] field effect transistors (FETs),[40-41] organic light emitting FETs (OLEFETs[42] and, more recently, as sensors[43-49] and as labels in electrochemiluminescent systems.[20, 50] However the self-assembly of such compounds requires not only a precise chemical design, but also a tight control of several parameters such as solvent composition, temperature and pH.

An interesting open question is however how many units are needed to obtained a full change in the spectroscopic behavior as that observed for large assembled structure. A strategy to anwer such a fundamental problem is to design multinuclear Pt(II) complexes where the establishment of Pt···Pt and/or π-π stacking interactions is obtained by polytopic auxiliary ligands.[51-53] For example Che et al[54] reported a series of trinuclear tridentate cyclometalated platinum(II) complexes, tethered by *tris*-phosphine auxiliary linkers, and compared the photophysical properties with their mono- and binuclear homologues. However the behavior of the reported multinuclear Pt(II)-complexes in solution has not been reported at differet concentration to unravel the intermolecular vs intramolecular interactions.

Despite several reported dinuclear complexes,[25, 55-58] to the best of our knowledge, not a clear answer to the above question has been given. Indeed all the reported cases show a change in the emission color upon a Pt-Pt interaction is established, but how the enhancement of the emission properties is correlated to the number of unit invoved in the assemblies is still under debate.

Herein we aim to answer such fundamental questions by comparing the spectroscopic properties of a series of neutral *mono*-, *bis*-, and *tris*-Pt(II) complexes at different concentrations in order to assess intra vs intermolecular processes. The luminescent compounds consist of a tridentate dianionic 2,6-*bis*(1H-1,2,4-triazol-5-yl)pyridine[59] chelates and ancillary

---

[a] Dr. S. Chakraborty, Dr. A. Aliprandi, Prof. L. De Cola
Institut de Science et d'Ingénierie Supramoléculaires,
CNRS, UMR 7006, Université de Strasbourg
8 rue Gaspard Monge, 67000 Strasbourg, France.
E-mail: decola@unistra.fr
[b] Prof. L. De Cola
Institute for Nanotechnology (INT), Karlsruhe Institute of Technology
Hermann-von-Helmholtz-Platz 1
76344 Eggenstein-Leopoldshafen (Germany)

Supporting information for this article is given via a link at the end of the document.

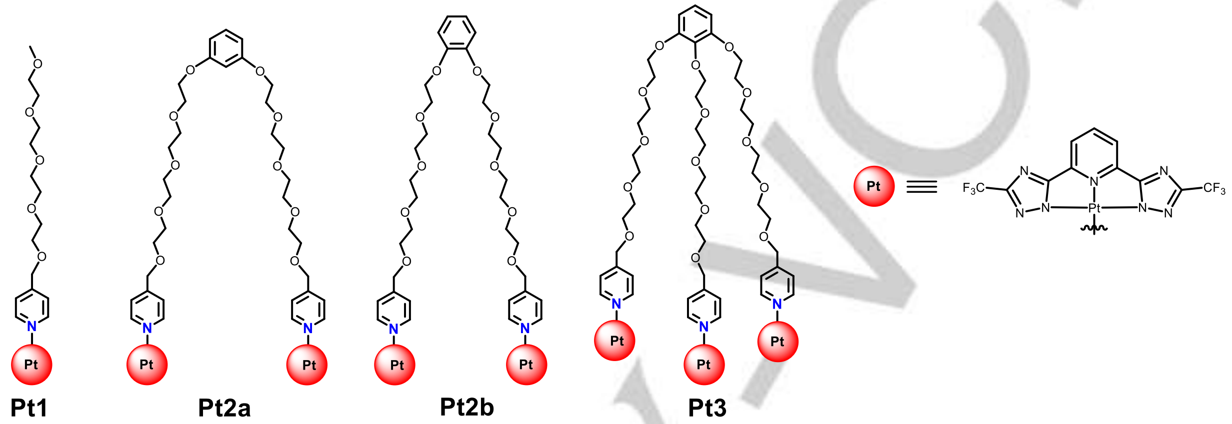
10.1002/chem.202001510

triethylene glycol-substituted pyridine ligands (Scheme 1). We have prepared two dimers where the phenyl ring is substituted in the 1,2 and 1,3 positions to evaluate the effects of inter vs intramolecular interactions on the photophysical properties.

The rationalization of the photophysical behavior observed for the different species at different concentration in solution allow the design of molecularly defined systems possessing high phosphorescence quantum yields and long excited state lifetimes even in aereated solvents.

Results and Discussion

Synthesis and Characterization



Scheme1. Chemical formulas of *mono*Pt(II) **Pt1**, 1,3-*bis*Pt(II), **Pt2a**, 1,2- *bis*Pt(II), **Pt2b**, and 1,2,3-*tris*Pt(II), **Pt3** complexes.

The strategy used to prepare the multinuclear complexes is to attach the pyridines substituted in 4 position with tetraethylene glycol (TEG) chain to di- and tri-hydroxy benzene and then reacting the pyridines with a platinum precursor. In particular, the *mono*-pyridine linker **L1** (see SI, Scheme S1) was functionalized by refluxing a stirred THF solution of tetraethylene glycol monomethyl ether with 4-(chloromethyl)-pyridine hydrochloride in presence of NaH under nitrogen.[60] Whereas, the synthesis of *bis*-pyridine (**L2a**, and **L2b**) and *tris*-pyridine (**L3**) linkers were achieved in two steps. First the condensation of the mono-tosylated tetraethylene glycol with appropriate di- and tri-hydroxy benzene results in the formation of the corresponding di- and tri-TEG precursors (see SI, Scheme S2-S4). These di- and tri-TEG precursors were subsequently treated with 4-(chloromethyl)pyridine hydrochloride in presence of sodium hydride under nitrogen to generate the expected TEG functionalized 1,3-*bis*pyridine (**L2a**), 1,2-*bis*pyridine (**L2b**), and 1,2,3-*tris*pyridine (**L3**) linkers in good to moderate yields (See SI, Scheme S2-S4). The ^{1}H NMR spectra of the linkers (**L1-L3**) shows a distinctive sharp singlet, at $\delta = 4.61$, 4.51, 4.58 and 4.62 ppm respectively, due to the benzylic *–OCH₂* linkage, two doublets for the pyridine protons in aromatic region and the characteristic signals for glycol chains in between 3.5 to 4.3 ppm suggest the formation of the anticipated pyridine linkers which was further supported by the ESI-MS data (see SI for detailed characterization data).

In order to synthesize the desired Pt(II) complexes, Pyridine linkers **L1-L4** were treated with $PtCl_2(DMSO)_2$ as the platinum precursor, 2,6-*bis*[3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl] pyridine[59] as the tridentate auxiliary ligand (py-CF3-trzH₂) in $CHCl_3$, and in the presence of Hünig base (^{i}Pr$_2$EtN) at 50 °C to obtain the corresponding *mono*Pt(II), **Pt1**, 1,3-*bis*Pt(II) **Pt2a**, 1,2-*bis*Pt(II), **Pt2b**, and 1,2,3-*tris*Pt(II), **Pt3,** complexes (Scheme 1). The ^{1}H-NMR spectra of **Pt1**, **Pt2a** and **Pt2b** complexes (Figures S4, S14, S23) show a large downfield shift of pyridine protons adjacent to the nitrogen donor atom, confirming the metal-ligand coordination. The other pyridine protons, as well as the protons from auxiliary tridentate linkers, also shifts downfield compared to their non-complexed analogs. The appearance of a sharp singlet in ^{19}F-NMR of complex **Pt1**, **Pt2a** and **Pt2b** at $\delta = -64.2$, -64.5 and -64.4 ppm respectively, suggest overall symmetry of these complexes (Figure S6, S15, S24). But in case of complex **Pt3** two peaks (-64.09 and -64.10) were observed in ^{19}F-NMR spectrum (Figure S32), suggesting the presence of two different chemical environments for the three platinum complex units. In ^{1}H-NMR (Figure S33) the appearance of two sets of aromatic peaks, for the **Pt3**, in 1:2 ratio further confirms that we have a trimetallic system in which the central platinum feels a different chemical environment than the external platinum units. The chemical characterization was completed by high resolution mass spectrometry analysis (See SI). All the mass peaks are isotopically resolved and found in well agreement with the theoretically predicted isotopic distribution, further confirming the formation of desired complexes.

Photophysical Characterization

The complexes **Pt1-Pt3** were fully characterized by using electronic absorption, steady-state and time-resolved emission spectroscopy at different concentration from 1 to 100 μM in CH_2Cl_2 (DCM). As shown in Figure 1a, the absorption spectra of

Pt1 display intense bands in the UV region (*λ* = 254 nm, 300 nm, 337 nm). These transitions are mainly attributed to intra-ligand (^{1}IL) and metal-perturbed inter-ligand charge transfer (^{1}ILCT) states. At lower energy, between 360-450 nm, broad and featureless weak bands with molar extinction coefficients, ε, between 0.99 and 4.3×10^3 M^{-1} cm^{-1} (calculated at λ_{abs} = 402 nm) for all the complexes were assigned to transitions involving the spin-allowed singlet-manifold metal-to-ligand charge transfer, ^{1}MLCT, and the forbidden singlet to triplet, ^{3}MLCT, partially allowed because the presence of the heavy atom. These excitation processes have been previously reported for similar cyclometalated platinum(II) complexes.[37] Increasing the concentration from 1 µM to 100 µM does not lead to a change in the features of the absorption spectra suggesting that **Pt1** exist in the monomeric form in such range of concentrations. The absence of concentration dependent aggregation is also evident in the emission spectra that are all characterized by a moderate structured emission (PLQY = 1.5%) in the blue region of the visible spectrum with maximum at 463 nm, and vibrational bands at 491, 525, and a shoulder at 570 nm (figure 1b). Also the excited state lifetimes seems to be unaffected by the concentration, with an average value of 188 ns in aerated DCM solvent (see Table 1 for details). The steady state luminescence as well as the excited-state lifetime of the complex are typical of the monomeric form of such class of compounds.[19-20, 29, 50, 60-61]

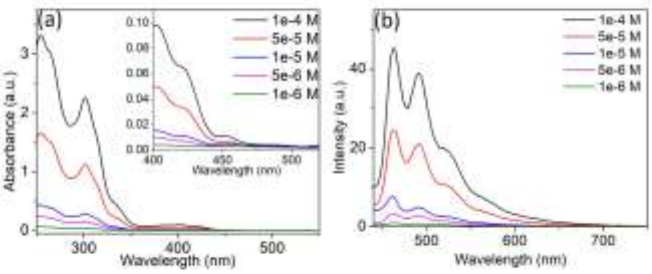


Figure 1. (a) UV-Vis absorption spectra and (b) emission spectra, λ_{exc} = 375 nm, for complex **Pt1** at variable concentration (1 µM to 100 µM) in DCM.

Table 1. Photophysical data of Platinum complexes **Pt1-Pt3** in DCM (5×10^{-5} M) at room temperature.

Complex	λ_{abs} nm (ε [10^3 M^{-1} cm^{-1}])	λ_{ex} nm	$\lambda_{em,max}$ nm	Lifetime (τ) ns	Φ_{PL}
Pt1	254 (33.2) 300 (22.2) 337 (3.9) 402 (0.99)	375	460, 485, 525,	τ_1 = 188.2 (88%) τ_2 = 3.8 (12%)	0.015
Pt2a	254 (66.4) 300 (38) 337 (8.3) 402 (2.4)	375	580	τ_1 = 1013.6 (88%) τ_2 = 14.4 (12%)	0.029
			460	τ_1 = 258.1 (88%) τ_2 = 11.7 (12%)	
Pt2b	254 (56) 300 (32) 337 (7.2) 402 (2.1)	375	580	τ_1 = 1029.0 (66%) τ_2 = 21.8 (34%)	0.027
			460	τ_1 = 235.8 (38%) τ_2 = 14.5 (62%)	
Pt3	256 (69.6) 300 (36.6) 337 (9.8) 402(4.3)	400	590	τ = 1093.1	0.38

Both complexes **Pt2a** and **Pt2b** show the aggregate intense emission band at around 580 nm along with the peaks in blue region, which shows slight shifts featuring emission maxima at 466 and 494 mm for **Pt2a** and 468 and 497 mm for complex **Pt2b** (PLQY = 2.9% and 2.7% for **Pt2a** and **Pt2b**, respectively at 5x10^{-6} M). The absorption spectra suggest that the aggregation is already in the ground state as clearly seen (figure 2a and b) compared with the reference compound **Pt1** in which the band in the visible region is much less pronounced than for **Pt2a** and **Pt2b**. This is true even though working at the same molar concentration means that for the dimer we have twice the number of platinum units than for the monomer and therefore a double absorbance, in the absence of other factors. Such data are confirmed by the excitation spectra of both the complexes at λ_{em} = 580 nm, clearly displaying a lower energy excitation band that trace up to 500 nm (see SI, figures S37 and S40) which is ascribed to ^{3}MMLCT transitions due to the establishment of Pt···Pt metallophilic interactions.

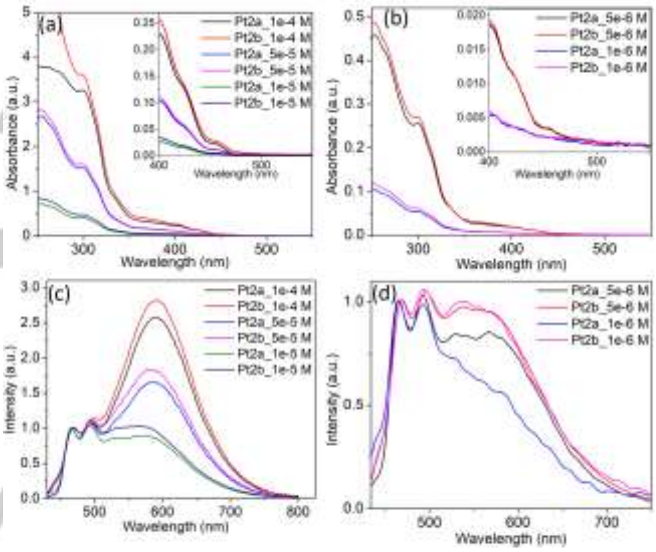
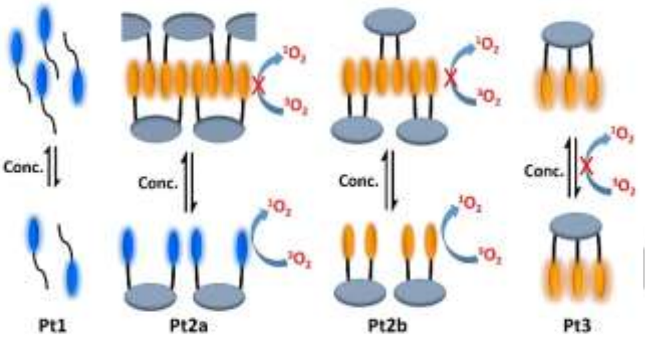


Figure 2. (a, b) UV-Vis absorption spectra and (c, d) Normalized (at 467 nm) Emission spectra (upon λ_{exc} = 375 nm) for complex **Pt2a** (top) and **Pt2b** (bottom) at variable concentration (100 µM to 1 µM) in DCM.

As expected at high concentration both **Pt2a** and **Pt2b** (figure 2c and d) show a great tendency to form intermolecular interactions rather than only intramolecular ones. However, a careful examination of the emission spectra upon excitation at 375 nm, in DCM solutions reveals that the two compounds behave differently at low concentration. Indeed the relative emission intensities of the monomeric band (467 nm) versus the aggregate band (580 nm) is not the same for the two systems, as one would predict from their chemical structure. For **Pt2a** the distance between the two complexes, despite the flexibility of the glycol chains, is definitely larger than for **Pt2b** and indeed at 1x10^{-6} M and at 5x10^{-6} M solutions the ratio between the high and low energy bands (467 vs 580 nm) is much higher for complex **Pt2a** than for **Pt2b** (figure 2d). Such behavior can be rationalized assuming that at such concentration the predominant interactions are intramolecular and therefore the capability to establish

10.1002/chem.202001510

intramolecular metallophilic interactions is higher for **Pt2b** rather than **Pt2a**. Increasing the concentration leads to a large increase of the emission intensity at 580 nm compared to the band at 467 nm suggesting the establishment of intermolecular interactions. Not surprisingly in such range of concentrations both dimers behave similarly (figure 2c). A possible mechanism is depicted in scheme 2 where while **Pt1** is more stable in the solvated monomeric form, the dimers are more prone to intercalation with other molecules. The corresponding excited state lifetimes of the bands at 460 nm and 580 nm of **Pt2a** and **Pt2b** at the different concentrations are shown in table S2 and S3 of the supporting info respectively. The longer lifetime component, attributed to ^{3}MMLCT decay, increases its relative weight at higher concentration (See SI table S2 and S3). Noticeably, for both complexes on decreasing the concentration from 100 to 1 μM the lifetime of the long component attributed to the ^{3}MMLCT transition decreases gradually from 1 to 0.7 μs suggesting an effective dioxygen quenching when the intramolecular interactions are reduced. Indeed the excited state lifetimes recorded in deaerated 1 μM solutions for both complex **Pt2a** and **Pt2b** are close to the one recorded for aerated high concentrated (100 μM) solutions as shown in table 2.



Scheme 2. Mechanistic illustration of the intra and intermolecular aggregation of mono-, *bis*- and *tris*-nuclear Pt(II)-complexes in effect of concentration. The monomeric form of the complexes (at dilution) are shown at bottom and the formation of aggregated species (at higher concentration) on top.

Interestingly, on increasing the number of Pt(II) units from two to three the scenario changes completely as shown in figure 3.

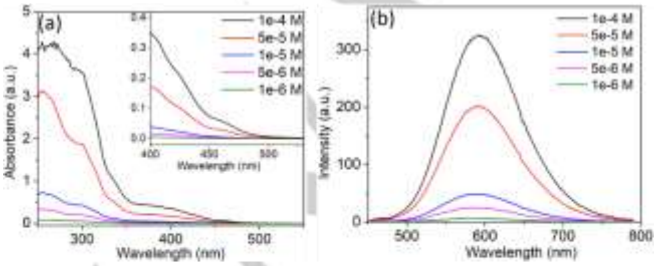


Figure 3. (a) UV-Vis absorption spectra, and (b) Emission spectra (upon λ_{exc} = 400 nm) for complex **Pt3** at variable concentration (0.1 mM to 1.0 μM) in DCM.

Pt3 complex displays a more intense low-energy absorption band centered at ca. 461 nm and stretching towards 500 nm (Figure 3a inset). We ca definitely state that the bands at lowest energy are metal-metal-to-ligand charge transfer (^{1}MMLCT and ^{3}MMLCT) transitions[12, 62] associated to the formation of Pt···Pt and π-π stacking interactions. In the case of **Pt3** the MMLCT bands are independent from the concentration and are present even in very dilute conditions suggesting strong intramolecular electronic interactions. Upon excitation at 400 nm, **Pt3** shows only one very intense emission band centered at 590 nm (Figure 3) with a PLQY value up to 38% in air-equilibrated DCM solutions. The excited state decays with a mono-exponential kinetic of around 1 μs (see table S4), which is ascribed to a ^{3}MMLCT transition resulting from intramolecular metallophilic interactions. The ground state interaction between platinum units is also confirmed by the appearance of the typical MMLCT bands stretching up to 500 nm in the excitation spectra of complex **Pt3**, monitored at the emission maximum. The concentration dependency of the emission spectra in range of 100 to 1 μM shows no effect on the emission profile of complex (figure 3b) as well as the lifetime decay of the excited state component remains unchanged (see table 2). In addition, for such complex the elimination of the dioxygen from the solution does not have any pronounced effect on the exited state life time, which showed only a marginal elongation (scheme 2).

Table 2. Excited state lifetimes (τ) of **Pt2a**, **Pt2b**, and **Pt3** at different conc. with and without oxygen recorded at λ_{em} = 580 nm, upon λ_{exc} = 375 nm.

Concentration (M)	**Pt2a** τ, ns	**Pt2b** τ, ns	**Pt3** τ, ns
1×10^{-4}	τ_1 = 1058.1 (94%) τ_2 = 15.4 (6%)	τ_1 = 1072.4 (76%) τ_2 = 22.9 (24%)	1084.7
5×10^{-5}	τ_1 = 1013.6 (88%) τ_2 = 14.6 (12%)	τ_1 = 1029.0 (66%) τ_2 = 21.8 (34%)	1093.1
1×10^{-5}	τ_1 = 851.6 (75%) τ_2 = 13.5 (25%)	τ_1 = 855.4 (52%) τ_2 = 23.9 (48%)	1122.6
5×10^{-6}	τ_1 = 782.7 (71%) τ_2 = 13.2 (28%)	τ_1 = 796.2 (33%) τ_2 = 20.7 (67%)	1126.7
1×10^{-6}	τ_1 = 702.9 (62%) τ_2 = 12.8 ns (38%)	τ_1 = 708.4 (44%) τ_2 = 22.0 (56%)	1222.5
1×10^{-6} Deaerated	τ_1 = 1107.1 (66%) τ_2 = 12.6 (34%)	τ_1 = 902.1 (53%) τ_2 = 24.3 (47%)	1480.4

We can conclude therefore that for Pt3 the ^{3}MMLCT emitting state is tightly packed, as shown by the high emission quantum yield and by the lack of diffusion of the dioxygen that should quench such long lived emitters.

Conclusions

To rationalize the properties emerging from the self-assembly of luminescent platinum complexes, and in particular the role played by the number of units to reach and enhancement of the photophysical properties, we have investigated a series of neutral *mono*-, *bis*- and *tris*-Platinum(II) complexes. The compounds based on platinum metal ions, a tridentate N^N^N chromophoric auxiliary ligand and TEG-functionalized mono-, di- or tri-pyridine linkers. The complex possessing a single Pt center, **Pt1**, is characterized by a blue emission and showed no intermolecular Pt-Pt interactions in a large range of concentration (1-100 μM). Going from monomer to dimers, leads to concentration dependent luminescence where both monomeric and aggregate emissions are observed. Increasing further the number of Pt complexes to three results in the complete disappearance of blue emission and an orange phosphorescence which is unaffected by concentration. We concluded that even though dimeric species can already cause the shift in the emission properties, due to the rising of the MMLCT emission, we need at least 3 units to fully benefit of the assembly emerging properties, with the elongation of the excited state lifetime, protection from the dioxygen quenching and increase in the emission quantum yields.

Acknowledgements

S.C., A.A., and L.D.C. kindly acknowledge the University of Strasbourg, and the CNRS for financial support. L.D.C. is grateful to AXA Research funding and IUF for financial support.

Keywords: Aggregation-Induced Emission • Metallophilic interaction • Multinuclear • Platinum • Luminescence

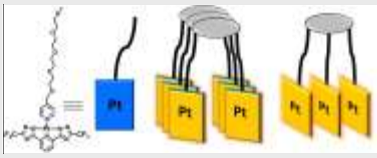
[1] P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597-636.
[2] M. Mauro, A. Aliprandi, D. Septiadi, N. S. Kehr, L. De Cola, *Chem. Soc. Rev.* **2014**, *43*, 4144-4166.
[3] V. W. Yam, V. K. Au, S. Y. Leung, *Chem. Rev.* **2015**, *115*, 7589-7728.
[4] A. Aliprandi, D. Genovese, M. Mauro, L. De Cola, *Chem. Lett.* **2015**, *44*, 1152-1169.
[5] K. Li, G. S. Ming Tong, Q. Wan, G. Cheng, W.-Y. Tong, W.-H. Ang, W.-L. Kwong, C.-M. Che, *Chem. Sci.* **2016**, *7*, 1653-1673.
[6] M. Krikorian, S. Liu, T. M. Swager, *J. Am. Chem. Soc.* **2014**, *136*, 2952-2955.
[7] M. E. Robinson, A. Nazemi, D. J. Lunn, D. W. Hayward, C. E. Boott, M.-S. Hsiao, R. L. Harniman, S. A. Davis, G. R. Whittell, R. M. Richardson, L. De Cola, I. Manners, *ACS Nano* **2017**, *11*, 9162-9175.
[8] V. N. Kozhevnikov, B. Donnio, D. W. Bruce, *Angew. Chem. Int. Ed.* **2008**, *47*, 6286-6289.
[9] K. Y. Kim, J. Kim, C. J. Moon, J. Liu, S. S. Lee, M. Y. Choi, C. Feng, J. H. Jung, *Angew. Chem. Int. Ed.* **2019**.
[10] J. Zhao, Z. Feng, D. Zhong, X. Yang, Y. Wu, G. Zhou, Z. Wu, *Chem. Mater.* **2018**, *30*, 929-946.
[11] B. Ma, J. Li, P. I. Djurovich, M. Yousufuddin, R. Bau, M. E. Thompson, *J. Am. Chem. Soc.* **2005**, *127*, 28-29.
[12] C. A. Strassert, M. Mauro, L. De Cola, in *Adv. Inorg. Chem., Vol. 63* (Eds.: R. v. Eldik, G. Stochel), Academic Press, **2011**, pp. 47-103.
[13] D. Kim, J.-L. Brédas, *J. Am. Chem. Soc.* **2009**, *131*, 11371-11380.
[14] V. M. Miskowski, V. H. Houlding, *Inorg. Chem.* **1991**, *30*, 4446-4452.
[15] A. F. Suleymanova, O. S. Eltsov, D. N. Kozhevnikov, A. O. Lantushenko, M. P. Evstigneev, V. N. Kozhevnikov, *ChemistrySelect* **2017**, *2*, 3353-3355.
[16] M. Yoshida, M. Kato, *Coord. Chem. Rev.* **2018**, *355*, 101-115.
[17] M. Z. Shafikov, R. Daniels, P. Pander, F. B. Dias, J. A. G. Williams, V. N. Kozhevnikov, *ACS Applied Materials & Interfaces* **2019**, *11*, 8182-8193.
[18] C. A. Strassert, C. H. Chien, M. D. Galvez Lopez, D. Kourkoulos, D. Hertel, K. Meerholz, L. De Cola, *Angew. Chem. Int. Ed.* **2011**, *50*, 946-950.
[19] M. Mauro, A. Aliprandi, C. Cebrian, D. Wang, C. Kubel, L. De Cola, *Chem. Commun.* **2014**, *50*, 7269-7272.
[20] A. Aliprandi, M. Mauro, L. De Cola, *Nat. Chem.* **2016**, *8*, 10-15.
[21] H.-L. Au-Yeung, A. Y.-Y. Tam, S. Y.-L. Leung, V. W.-W. Yam, *Chem. Sci.* **2017**, *8*, 2267-2276.
[22] V. C. Wong, C. Po, S. Y. Leung, A. K. Chan, S. Yang, B. Zhu, X. Cui, V. W. Yam, *J. Am. Chem. Soc.* **2018**, *140*, 657-666.
[23] N. Liu, T. Lin, M. Wu, H.-K. Luo, S.-L. Huang, T. S. A. Hor, *J. Am. Chem. Soc.* **2019**, *141*, 9448-9452.
[24] M. E. Robinson, D. J. Lunn, A. Nazemi, G. R. Whittell, L. De Cola, I. Manners, *Chem. Commun.* **2015**, *51*, 15921-15924.
[25] M. H. Chan, S. Y. Leung, V. W. Yam, *J. Am. Chem. Soc.* **2019**, *141*, 12312-12321.
[26] Y. Wang, Y. Cai, L. Cao, M. Cen, Y. Chen, R. Zhang, T. Chen, H. Dai, L. Hu, Y. Yao, *Chem Commun (Camb)* **2019**, *55*, 10132-10134.
[27] C.-Y. Sun, W.-P. To, F.-F. Hung, X.-L. Wang, Z.-M. Su, C.-M. Che, *Chem. Sci.* **2018**, *9*, 2357-2364.
[28] Y. Atoini, E. A. Prasetyanto, P. Chen, S. Silvestrini, J. Harrowfield, L. De Cola, *Chem. Eur. J.* **2018**, *24*, 12054-12060.
[29] S. Sinn, F. Biedermann, M. Vishe, A. Aliprandi, C. Besnard, J. Lacour, L. D. Cola, *ChemPhysChem* **2016**, *17*, 1829-1834.
[30] D. Genovese, A. Aliprandi, E. A. Prasetyanto, M. Mauro, M. Hirtz, H. Fuchs, Y. Fujita, H. Uji-I, S. Lebedkin, M. Kappes, L. De Cola, *Adv. Funct. Mater.* **2016**, *26*, 5271-5278.
[31] A. Aliprandi, C. M. Croisetu, M. Mauro, L. D. Cola, *Chem. Eur. J.* **2017**, *23*, 5957-5961.
[32] M. Yoshida, M. Kato, *Coord. Chem. Rev.* **2020**, *408*, 213194.
[33] Q. Wan, X. S. Xiao, W. P. To, W. Lu, Y. Chen, K. H. Low, C. M. Che, *Angew. Chem. Int. Ed.* **2018**, *57*, 17189-17193.
[34] C. Cebrián, M. Mauro, *Beilstein J. Org. Chem.* **2018**, *14*, 1459-1481.
[35] M.-C. Tang, A. K.-W. Chan, M.-Y. Chan, V. W.-W. Yam, *Top. Curr. Chem.* **2016**, *374*, 46.
[36] F. K. Kong, M. C. Tang, Y. C. Wong, M. Ng, M. Y. Chan, V. W. Yam, *J. Am. Chem. Soc.* **2017**, *139*, 6351-6362.
[37] C. Cebrian, M. Mauro, D. Kourkoulos, P. Mercandelli, D. Hertel, K. Meerholz, C. A. Strassert, L. De Cola, *Adv. Mater.* **2013**, *25*, 437-442.
[38] T. Masatsugu, Y. Takuma, A. Chihaya, *Applied Physics Express* **2011**, *4*, 071602.
[39] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151-154.
[40] R. Wawrzinek, K. Muhieddine, M. Ullah, P. B. Koszo, P. E. Shaw, A. Grosjean, F. Maasoumi, D. M. Stoltzfus, J. K. Clegg, P. L. Burn, E. B. Namdas, S.-C. Lo, *Adv. Opt. Mater.* **2016**, *4*, 1867-1874.
[41] C.-M. Che, C.-F. Chow, M.-Y. Yuen, V. A. L. Roy, W. Lu, Y. Chen, S. S.-Y. Chui, N. Zhu, *Chem. Sci.* **2011**, *2*, 216-220.
[42] M.-Y. Yuen, V. A. L. Roy, W. Lu, S. C. F. Kui, G. S. M. Tong, M.-H. So, S. S.-Y. Chui, M. Muccini, J. Q. Ning, S. J. Xu, C.-M. Che, *Angew. Chem. Int. Ed.* **2008**, *47*, 9895-9899.
[43] A. S.-Y. Law, L. C.-C. Lee, M. C.-L. Yeung, K. K.-W. Lo, V. W.-W. Yam, *J. Am. Chem. Soc.* **2019**, *141*, 18570-18577.
[44] J. A. Thomas, *Dalton Trans.* **2011**, *40*, 12005-12016.
[45] E. Spain, S. Carrara, K. Adamson, H. Ma, R. O'Kennedy, L. De Cola, R. J. Forster, *ACS Omega* **2018**, *3*, 17116-17124.
[46] K. Zhang, M. C.-L. Yeung, S. Y.-L. Leung, V. W.-W. Yam, *ACS Applied Materials & Interfaces* **2020**, *12*, 8503-8512.
[47] Y. Shigeta, A. Kobayashi, M. Yoshida, M. Kato, *Crystal Growth & Design* **2018**, *18*, 3419-3427.
[48] K. Masako, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 287-294.
[49] M. J. Bryant, J. M. Skelton, L. E. Hatcher, C. Stubbs, E. Madrid, A. R. Pallipurath, L. H. Thomas, C. H. Woodall, J. Christensen, S. Fuertes, T. P. Robinson, C. M. Beavers, S. J. Teat, M. R. Warren, F. Pradaux-Caggiano, A. Walsh, F. Marken, D. R. Carbery, S. C. Parker, N. B. McKeown, R. Malpass-Evans, M. Carta, P. R. Raithby, *Nat. Commun.* **2017**, *8*, 1800.
[50] S. Carrara, A. Aliprandi, C. F. Hogan, L. De Cola, *J. Am. Chem. Soc.* **2017**, *139*, 14605-14610.
[51] E. V. Puttock, M. T. Walden, J. A. G. Williams, *Coord. Chem. Rev.* **2018**, *367*, 127-162.
[52] W. Sun, H. Zhu, P. M. Barron, *Chem. Mater.* **2006**, *18*, 2602-2610.
[53] H.-X. Zhang, M. Kato, Y. Sasaki, T. Ohba, H. Ito, A. Kobayashi, H.-C. Chang, K. Uosaki, *Dalton Trans.* **2012**, *41*, 11497-11506.
[54] W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, C. Li, Z. Hui, *J. Am. Chem. Soc.* **2004**, *126*, 7639-7651.
[55] P. Xu, H. Wu, H. Jia, S. Ye, P. Du, *Organometallics* **2014**, *33*, 2738-2746.
[56] Z.-L. Gong, Y.-W. Zhong, J. Yao, *Journal of Materials Chemistry C* **2017**, *5*, 7222-7229.
[57] H. L. Au-Yeung, S. Y. Leung, V. W. Yam, *Chem. Commun.* **2018**.
[58] B. Ma, P. I. Djurovich, S. Garon, B. Alleyne, M. E. Thompson, *Adv. Funct. Mater.* **2006**, *16*, 2438-2446.
[59] S. Sinn, F. Biedermann, L. De Cola, *Chem. Eur. J.* **2017**, *23*, 1965-1971.
[60] R. Soldati, A. Aliprandi, M. Mauro, L. De Cola, D. Giacomini, *Eur. J. Org. Chem.* **2014**, *2014*, 7113-7121.
[61] D. Septiadi, A. Aliprandi, M. Mauro, L. De Cola, *RSC Adv.* **2014**, *4*, 25709-25718.
[62] M. Mydlak, M. Mauro, F. Polo, M. Felicetti, J. Leonhardt, G. Diener, L. De Cola, C. A. Strassert, *Chem. Mater.* **2011**, *23*, 3659-3667.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Multinuclear Pt(II) complexes provide valuable insight on the formation of closed shell Pt···Pt metallophilic interactions and on the corresponding MMLCT excited state. Persistent aggregation induced emission, which is independent from the media, is observed for the trinuclear species demonstrating that three is better than two.



*Sourav Chakraborty, Alessandro Aliprandi, Luisa De Cola**

Page No. – Page No.

Multinuclear Pt(II) Complexes: Why Three is Better Than Two to Enhance Photophysical Properties