ChemComm

Cite this: Chem. Commun., 2012, 48, 1120-1122

COMMUNICATION

Hybrid charged heterometallic Pt–Ir complexes: tailoring excited states by taking the best of both worlds[†]

Ahmed M. Soliman, Daniel Fortin, Pierre D. Harvey* and Eli Zysman-Colman*

Received 6th September 2011, Accepted 1st October 2011 DOI: 10.1039/c1cc15507e

The $C \equiv C$ -linkage of $Pt(PR_3)_2(C \equiv CAr)_2$ with $(C^N)_2Ir(N^N)^+$ $(C^N = 2$ -phenylpyridine; $N^N =$ bipyridyl) leads to hetero-biand trimetallic species exhibiting photophysical properties reminiscent of both [Pt]- and [Ir]-containing moieties through the generation of a [Pt] \rightarrow [Ir] charge transfer excited state.

Platinum(II) acetylide and cationic heteroleptic iridium(III) complexes, of the respective forms *trans*-Pt(PR₃)₂(C \equiv C–Ar)₂, [**Pt**], where R and Ar are an alkyl group and an aryl group, respectively, and (C^N)₂Ir(N^N)⁺, [**Ir**], where C^N is a cyclometallating ligand such as 2-phenylpyridine (ppy) and N^N is a diimine ligand such as bipyridine (bpy), have independently attracted considerable interest as luminophores in a myriad of applications. Notably, each class of complexes has been incorporated into organic light emitting diodes (OLEDs),¹ light-emitting electrochemical cells (LEECs),² nonlinear optical materials³ and photovoltaic devices.⁴ Each class exhibits strong spin–orbit coupling, promoting intersystem crossing and emission from the triplet state with enhanced quantum efficiencies. Typical room temperature lifetimes for [**Pt**] and [**Ir**] range from 10–100 µs and from sub-µs to µs, respectively, at 298 K.

Donor–acceptor dyads incorporating either [**Pt**] or [**Ir**] into motifs that are linked by a conjugated rigid spacer ($D-\pi$ –A) have proven to act as molecular wires⁵ or as potentially useful and efficient two-photon absorbers⁶ owing to large changes in polarization upon excitation.⁷ To our knowledge, only a few cationic heterobi-^{5,8} or polymetallic⁹ iridium complexes have been reported thus far but none of which also incorporate a platinum acetylide [**Pt**].

We now wish to report two original polyads, 3 ([Pt]-[Ir]) and 4 ([Ir]-[Pt]-[Ir]), using the building blocks 1 and 2



Chart 1 Structures of complexes 1-4 under study.

(Chart 1). The comparison of the photophysical properties, coupled to DFT computations, demonstrates that the new complexes exhibit unprecedented hybrid charge transfer emissive excited states of the type $[Pt] \rightarrow [Ir]$. Compounds 3 and 4 exhibit red-shifted low energy bands, similar to the [Ir], with higher absorptivities, associated with the presence of the [Pt] residue. Triad 4 also exhibits particularly enhanced quantum efficiency.

Complex 1 was prepared through cleavage of [(ppy₂)IrCl]₂ with 5-ethynylbipyridine (5) (Scheme 1) following the procedure of Nonoyama followed by anion metathesis with NH₄PF₆ (the experimental details are provided in the ESI†).¹⁰ X-Ray analysis confirmed the structure of 1 and matches that recently reported by Castellano and co-workers.¹¹ Complex 2 was formed *via* an initial Hagihara coupling between 5 and 9 equiv. of *trans*-Pt(PBu₃)₂Cl₂ followed by a second coupling with excess 1-ethynyl-4-methylbenzene. With 4 equiv. of *trans*-Pt(PBu₃)₂Cl₂, 2' could be isolated in 28% yield. Heterodimer 3 and -trimer 4 were obtained in 87% and 40% isolated yields, respectively, upon complexation with iridium.

Table 1 lists the spectroscopic and photophysical properties for 1–4, as well as the benchmark complex $[(ppy)_2Ir(bpy)]PF_6$, 6. The 298 K absorption spectra of 1, 3, 4, and 6 are characterized by intense π – π * high-energy ligand-centred (¹LC) bands localized on both the phenylpyridines and the bipyridine (Fig. 1). Intense ¹MLCT (metal-to-ligand charge transfer) bands are also noted in the 300–350 nm region, especially when compared to 6.¹² Hypochromic bands at *ca*. 460 nm, corresponding to spinforbidden ³MLCT transitions, are also noted. Complexes **3** and **4** exhibit much stronger ¹LC and ¹CT bands compared to **1**. The absorptivity of the latter transition is augmented by the

Département de Chimie, Université de Sherbrooke and the Centre Québécois sur les Matériaux Fonctionnels, 2500 Boul. de l'Université, Sherbrooke, QC, Canada J1K 2R1.

E-mail: pierre.harvey@uhsebrooke.ca, eli.zysman-colman@usherbrooke.ca; Fax: +1 819-821-8017

[†] Electronic supplementary information (ESI) available: Complete experimental section and compound characterization. Absorption and emission spectra for each complex. Experimental protocol for photophysical characterization. Details of computational methodology. Full computational output, including figures of calculated absorption spectra, tables of 100 lowest energy transitions calculated by TDDFT and tables of calculated emission energies and isodensity surface plots for selected orbitals. CCDC 846806. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc15507e



Scheme 1 Synthesis of 1–4. *i.* 9 equiv. *trans*-Pt(PBu₃)₂Cl₂, DCM, NH*i*Pr₂, CuI; *ii.* 4.6 equiv. 4-MeC₆H₄CCH, DCM, NH*i*Pr₂, CuI; *iii.* 4 equiv. *trans*-Pt(PBu₃)₂Cl₂, DCM, NH*i*Pr₂, CuI; *iv.* (a) 0.5 equiv. [(ppy₂)IrCl]₂/DCM:MeOH, 60 °C; b) NH₄PF₆ (aq); *v.* (a) 1 equiv. [(ppy₂)IrCl]₂/DCM:MeOH, 60 °C; (b) NH₄PF₆ (aq).

presence of the CT-band of the Pt-acetylide unit, which absorbs intensely at *ca*. 350 nm as is the case for **2**.¹³ The 390 nm band for **3** ($\varepsilon = 1.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) is red-shifted by 1390 cm⁻¹ compared to the 370 nm band in **4** ($\varepsilon = 4.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

The emission band of **1** at 298 K is broad and featureless with a λ_{max} of 623 nm that is red-shifted by 420 cm⁻¹ compared to **6** owing to the extended conjugation imparted by the ethynyl unit. The emission quantum yield (Φ_{PL}) (standard: [Ru(bpy)₃](PF₆)₂; $\Phi_{PL} = 9.5\%$),¹⁴ and lifetime, τ_e , at 298 K are 8.5% and 160 ns, respectively. The behaviour of **1** in 2-MeTHF is similar to that reported in DCM.¹¹

Unlike *trans*-Pt(PBu₃)₂(PCC)₂,^{13b} which exhibits no emission at 298 K, **2** emits at $\lambda_{max} = 519$ nm with a shoulder at 550 nm. Φ_{PL} and τ_e are, respectively, 12.5% and 33 µs at 298 K. The large Stokes shift and the long τ_e indicate that the emission originates from the triplet state. The 298 K emission is due to the increased conjugation imparted by the bipyridyl.^{13b} Schanze and co-workers also reported emission for the related Pt₂BpyPh₂.¹⁵ Both the radiative, k_r , and non-radiative, k_{nr} , rate constants of **2** are significantly lower by 3 orders of magnitude than those found for **1**.

The emission band of **3** exhibits several features, the two most intense of which are found at 571 and 611 nm. The latter coincides with the λ_{max} found in **1**. The 298 K Φ_{PL} is quasi identical to that of **1** at 8.3% while τ_e is 0.7 µs. The band shape



Fig. 1 Normalized (a) absorption and (b) emission spectra of **1–4**, **6** in 2-MeTHF at 298 K.

and photophysical data found in 3 suggest that it is a new chromophore with an $E_{0,0}$ that is midway between those of 1 and 2.

Upon addition of a second [Ir] unit in 4, the two emission bands, located at 566 and 595 nm, blue-shift, respectively, by 155 and 440 cm⁻¹. The Φ_{PL} (31.9%) and τ_e (2.9 µs) significantly increase compared to 3. The main source of the increased Φ_{PL} and long-lived excited state stems from a 4.9 fold decrease in k_{nr} . Noteworthy, k_r for both 3 and 4 is of an intermediate magnitude to that found in 1 and 2. The nature of the excited state is now addressed with the use of DFT and time-dependent DFT (TDDFT) computations.

DFT calculations reveal that 1 expectedly exhibits a HOMO that is mainly localized on the metal and on the phenylpyridines (see ESI[†])¹² similar to complexes of the form $[(C^N)_2 Ir(N^N)]^+$.^{1b,17} The LUMO density is located mainly on the bipyridine moiety, extending onto the ethynyl unit. TDDFT analysis indicates that the intense low energy $S_0 \rightarrow S_n$ absorptions stem from the HOMO $-1 \rightarrow$ LUMO and HOMO \rightarrow LUMO + 1 transitions, which are consistent with the mixed ¹MLCT/¹LLCT assignment for the emissive excited state. Emission is predicted to be at 574 nm, red-shifted to that observed at 77 K ($\lambda_{max} = 536$ nm). TDDFT calculations also indicate that the intense low energy absorption band in 2 results from a HOMO-LUMO transition, characterized as a mixed ${}^{1}MLCT/{}^{1}LLCT$ transition (ESI^{\dagger}). Moreover, the predicted emission at 510 nm fits well with the observed value of 517 nm.

The frontier MOs of **3** and **4** are shown in Fig. 2. TDDFT for **3** reveals the emergence of two important low-energy absorptions characterized as a mixture of HOMO–LUMO and HOMO – 1 \rightarrow LUMO (53 and 45% contribution, respectively, ESI†) that is reminiscent of the respective transitions computed for **2** and **1**. DFT calculations on the triplet manifold indicate that emission stems from a mixed $\pi^*_{bpy}d_{Pt}$ and $\pi^*_{bpy}\pi_{tol}$ state, predicted to occur at 602 nm. To the best of our knowledge, the nature of this transition has only been

Table 1Photophysical and spectroscopic properties of 1–4 and 6^a

	Absorbance at 298 K/nm [Molar absorptivities (×10 ⁴ M ⁻¹ cm ⁻¹)]	$\lambda_{max}\!/nm$		Stokes shifts/cm ⁻¹		$ au_{e}/\mu s$				
Complex		77 K	298 K	77 K	298 K	$\Phi_{\mathrm{PL}}{}^{b}(\%)$	77 K	298 K	$k_{\rm r} (10^5 {\rm s}^{-1})$) $k_{\rm nr} (10^5 {\rm s}^{-1})$
1	265 [2.3]; 310 [1.0]; 325 [0.9); 380 [0.2]; 450 [0.1]	536	623	2620	5230	8.5	4.12	0.16	5.3	57.2
2	240 [1.7]; 260 [2.4]; 280 [2.0]; 345 [4.7]	517	519	9640	9720	12.5	155	33.6	0.04	0.3
3	260 [3.6]; 295 [2.0]; 390 [1.9]; 450] [0.2]	549	611	4010	5856	8.3	3.44	0.72	1.2	12.7
4	260 [6.8]; 300 [4.1]; 350 [4.0]; 370 [4.0]; 460 [0.2]	546	595	3460	4930	31.9	11.0	2.90	0.9	2.6
6	255 [2.9]; 300 [1.7]; 335 [0.6]; 370 [0.4]; 465 [0.1]	532	607	2710	5030	8.9	5.82	0.55	1.6	16.6
						,				

^{*a*} Spectra were obtained in 2-MeTHF. Emission spectra were obtained in deaerated solutions. ^{*b*} Measured at 298 K using $[Ru(bpy)_3](PF_6)_2$ ($\Phi_{PL} = 9.5\%$ in ACN) as the reference (see ref. 14).



Fig. 2 Isodensity surface plots obtained by DFT for selected orbitals of 3 and 4. A quantum mechanical THF solvation model was employed.¹⁶

described once previously in a neutral heterobimetallic Ir^{III} and Pt^{II} complex.¹⁸ Interestingly, the weakly allowed and quasiisoenergetic HOMO-LUMO and HOMO - 1 \rightarrow LUMO transitions do not involve the Pt centre in 4. The intense absorption band observed at 460 nm, attributed to a HOMO $-2 \rightarrow$ LUMO transition ($\lambda = 453$ nm), is predicted to originate primarily from a $d_{Pt}\pi^*_{bpy}$ state. By contrast, the emission, computed at 554 nm, is localized exclusively on the [Ir] moiety and is ³MLCT/LLCT in nature, which may account for the larger observed quantum efficiency. The long-lived τ_e results from the contribution of the Pt-centred excited state.

Hence, the synthesis of the first cationic heterobimetallic hybrid complexes bearing Ir^{III} and Pt^{II} units is herein reported. Compound 3 emits from a mixed $\pi^*_{bpy}d_{Pt}$ and $\pi^*_{bpy}\pi_{tol}$ state while 4 emits from a mixed ³MLCT/LLCT state localized on Ir. The incorporation of a [Pt] moiety creates hybrid excited states and a blue-shift of the emission band compared to 1 is observed. Emission τ_e 's were significantly longer for the hybrids while Φ_{PL} and molar absorptivities for 4 were noticeably enhanced.

EZ-C acknowledges CFI (Canadian Foundation for Innovation), NSERC (the National Sciences and Engineering Research Council of Canada), FQRNT (Le Fonds quebecois de la recherche sur la nature et les technologies) and the Universite de Sherbrooke for financial support. PDH acknowledges NSERC for financial support. The project was underwritten by the CQMF (Centre Québécois sur les Matériaux Fonctionnels).

Notes and references

- 1 (a) J. S. Wilson, A. S. Dhoot, A. J. A. B. Seeley, M. S. Khan, A. Kohler and R. H. Friend, Nature, 2001, 413, 828-831; (b) L. Flamigni, A. Barbieri, C. Sabatini, B. Ventura and F. Barigelletti, Top. Curr. Chem., 2007, 281, 143-203.
- 2 (a) J. D. Slinker, J. Rivnay, J. S. Moskowitz, J. B. Parker, S. Bernhard, H. D. Abruña and G. G. Malliaras, J. Mater. Chem., 2007, 17, 2976-2988; (b) C. Ulbricht, B. Beyer, C. Friebe, A. Winter and U. S. Schubert, Adv. Mater., 2009, 21, 4418-4441.
- 3 W.-Y. Wong and P. D. Harvey, Macromol. Rapid Commun., 2010, 31. 671-713.
- (a) E. I. Mayo, K. Kilsa, T. Tirrell, P. I. Djurovich, A. Tamayo, 4 M. E. Thompson, N. S. Lewis and H. B. Gray, Photochem. Photobiol. Sci., 2006, 5, 871-873; (b) W. Wu, X. Xu, H. Yang, J. Hua, X. Zhang, L. Zhang, Y. Long and H. Tian, J. Mater. Chem., 2011, 21, 10666-10671.
- 5 S. Welter, F. Lafolet, E. Cecchetto, F. Vergeer and L. De Cola, ChemPhysChem, 2005, 6, 2417-2427.
- (a) J. E. Rogers, J. E. Slagle, D. M. Krein, A. R. Burke, B. C. Hall, A. Fratini, D. G. McLean, P. A. Fleitz, T. M. Cooper, M. Drobizhev, N. S. Makarov, A. Rebane, K.-Y. Kim, R. Farley and K. S. Schanze, Inorg. Chem., 2007, 46, 6483-6494; (b) J. E. Haley, D. M. Krein, J. L. Monahan, A. R. Burke, D. G. McLean, J. E. Slagle, A. Fratini and T. M. Cooper, J. Phys. Chem. A, 2011, 115, 265-273.
- 7 S. R. Marder, C. B. Gorman, F. Meyers, J. W. Perry, G. Bourhill, J.-L. Brédas and B. M. Pierce, Science, 1994, 265, 632-635.
- 8 (a) J. H. Van Diemen, R. Hage, J. G. Haasnoot, H. E. B. Lempers, J. Reedijk, J. G. Vos, L. De Cola, F. Barigelletti and V. Balzani, Inorg. Chem., 1992, 31, 3518-3522; (b) F. Neve, A. Crispini, S. Serroni, F. Loiseau and S. Campagna, Inorg. Chem., 2001, 40, 1093-1101; (c) V. L. Whittle and J. A. G. Williams, Dalton Trans., 2009, 3929-3940.
- 9 K. J. Arm and J. A. G. Williams, Chem. Commun., 2005, 230-232.
- 10 M. Nonoyama, Bull. Chem. Soc. Jpn., 1974, 47, 767. 11 A. A. Rachford, R. Ziessel, T. Bura, P. Retailleau and F. N. Castellano, Inorg. Chem., 2010, 49, 3730-3736.
- 12 S. Ladouceur, D. Fortin and E. Zysman-Colman, Inorg. Chem., 2010, 49, 5625-5641
- 13 (a) K. Gagnon, S. Mohammed Aly, A. Brisach-Wittmeyer, D. Bellows, J.-F. Bérubé, L. Caron, A. S. Abd-El-Aziz, D. Fortin and P. D. Harvey, Organometallics, 2008, 27, 2201-2214; (b) J. E. Rogers, T. M. Cooper, P. A. Fleitz, D. J. Glass and D. G. McLean, J. Phys. Chem. A, 2002, 106, 10108-10115.
- 14 H. Ishida, S. Tobita, Y. Hasegawa, R. Katoh and K. Nozaki, Coord. Chem. Rev., 2010, 254, 2449-2458.
- K. Ogawa, F. Guo and K. S. Schanze, J. Photochem. Photobiol., A, 15 2009. 207. 79-85.
- 16 J. Tomasi, B. Mennucci and R. Cammi, Chem. Rev., 2005, 105, 2999-3094.
- 17 M. S. Lowry and S. Bernhard, Chem.-Eur. J., 2006, 12, 7970-7977.
- 18 G. Zhou, Y. He, B. Yao, J. Dang, W.-Y. Wong, Z. Xie, X. Zhao and L. Wang, Chem.-Asian J., 2010, 5, 2405-2414.