ChemComm

Cite this: *Chem. Commun.*, 2012, **48**, 5980–5982

www.rsc.org/chemcomm

COMMUNICATION

Divergent luminescence behaviour from differential interactions in dinuclear Pt, Au, and mixed Pt–Au complexes built on a xanthene scaffold†

Rebeca Muñoz-Rodríguez,[a] Elena Buñuel,[a] J. A. Gareth Williams*[b] and Diego J. Cárdenas*[a]

Received 27th March 2012, Accepted 24th April 2012
DOI: 10.1039/c2cc32218h

A diethynylxanthene unit is used to tether cyclometallated Pt(II) and Au(III) complexes in a geometry that favours interfacial interactions. This leads to protection from non-radiative decay pathways in the Au_2 dimer and to low-energy 'aggregate-like' emission in a closely related Pt_2 dimer, whilst rapid Au-to-Pt energy transfer occurs in the heterodimer.

The photophysical properties of second and third-row d^6 and d^8 metal ions have attracted much attention due to diverse applications, ranging from molecular photovoltaic cells to light-emitting displays and chemical sensors.[1a–c] Cyclometallating ligands have proved to be particularly successful in generating luminescent complexes, owing to their strong ligand fields.[2] Amongst such systems, tridentate ligands may be superior to their bidentate analogues, due in part to the greater rigidity they confer on the complex.[3]

Square-planar complexes of d^8 metal ions {*e.g.* Pt(II) and Au(III)} offer additional scope for controlling excited states, not normally open to 6-coordinate d^6 metal ions, owing to the possibility of face-to-face interactions between complexes, either in the ground state (*e.g.* aggregation) or in the excited state (*e.g.* excimer formation). Numerous examples of aggregation and excimer formation have been reported for Pt(II) complexes with tridentate cyclometallating ligands. For example, Che and co-workers have pioneered investigations into Pt(II) complexes of N^N^C-coordinating ligands based on 6-phenyl-2,2′-bipyridine.[4] These complexes are typically luminescent in solution at room temperature, emitting from $^3[d \rightarrow \pi^*]$ (MLCT) states. In the solid state, on the other hand, examples were found where the emission was strongly shifted to the red ($\lambda_{max} \sim 700$ nm) compared to the values in solution ($\sim$565 nm). This effect was interpreted in terms of an emissive $^3[d\sigma^* \rightarrow \pi^*]$ MMLCT state (metal–metal-bond-to-ligand charge-transfer), arising from the overlap of d_{z^2} metal orbitals of adjacent molecules in the solid.[4] Similar effects were observed in solution in dinuclear systems comprised of the same class of complex linked by bridging diphosphine ligands of appropriate length to allow interfacial interactions.[5]

More recently, it was shown that, by linking together two cyclometallated Pt(N^C^N)Cl complexes through the 4 and 5 positions of a xanthene core, intense luminescence in the red region of the spectrum could be achieved, apparently due to the formation of an intramolecular excimer {N^C^N represents cyclometallated 1,3-di(2-pyridyl)benzene}.[6]

In contrast to Pt(II), there are far fewer examples of Au(III) complexes that display appreciable luminescence, despite the two metal ions being isoelectronic. The lack of luminescence from many Au(III) complexes may be due to the presence of higher-lying but thermally accessible deactivating states (*e.g.* d–d or LMCT states), and/or to the lower energy of filled metal orbitals in Au(III) complexes compared to similar Pt(II) complexes.[2b,7] This latter feature results in lower metal character in the excited state and hence to less efficient spin-orbit coupling pathways and low radiative rate constants. The use of strong-field cyclometallating ligands and/or σ-donating alkynyl or N-heterocylic carbenes can alleviate both issues;[8] indeed, quite intense luminescence has recently been reported for a group of cyclometallated Au(III) complexes with 2-phenylpyridine ligands and alkynyl co-ligands.[8c] The influence of face-to-face interactions on the luminescence of Au(III) complexes is, however, only rarely addressed,[9] nor have mixed-metal Pt(II)–Au(III) interactions been explored.

In this contribution, we report on the synthesis and spectroscopic properties of homo- and heterodinuclear Pt(II) and Au(III) complexes with tridentate, cyclometallated ligands, N^N^C- and C^N^C-coordinating ligands for Pt(II) and Au(III) respectively, tethered by a 4,5-diethynylxanthene derivative. The properties are compared with those of their mononuclear analogues in order to determine the influence of interfacial interactions. The structures of the compounds studied are shown in Fig. 1. The use of the diethynylxanthene unit as an insulating (non-conjugated) scaffold allows the two complex units to be held in close proximity, in a geometry that may facilitate interfacial interactions.[6,10]

The preparation of the compounds was carried out as shown in Scheme 1. Iodination of 2,7-di-*tert*-butyl-4,5-dibromo-9,9-dimethylxanthene, followed by a double Sonogashira coupling with trimethylsilylacetylene and silyl deprotection, gave diyne **4**. In the presence of CuI and Et_3N, treatment of **4** with 1 or 2 equivalents of the Pt(N^N^C)Cl or Au(C^N^C)Cl complexes† gave the desired mononuclear (**Pt** and **Au**) and homodinuclear

---

[a] *Department of Organic Chemistry, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain. E-mail: diego.cardenas@uam.es*
[b] *Department of Chemistry, University of Durham, Durham, DH1 3LE, U.K. E-mail: j.a.g.williams@durham.ac.uk; Fax: 44 191 384 4737*

† Electronic supplementary information (ESI) available: experimental details; characterisation and ^{1}H NMR spectra of all new compounds; additional absorption and emission spectra. See DOI:10.1039/c2cc32218h

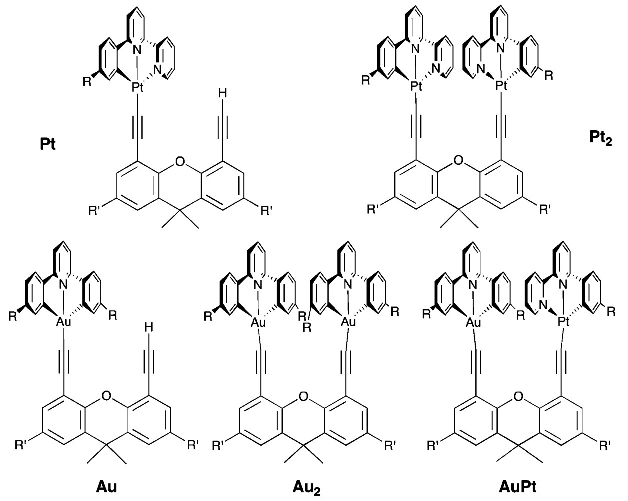
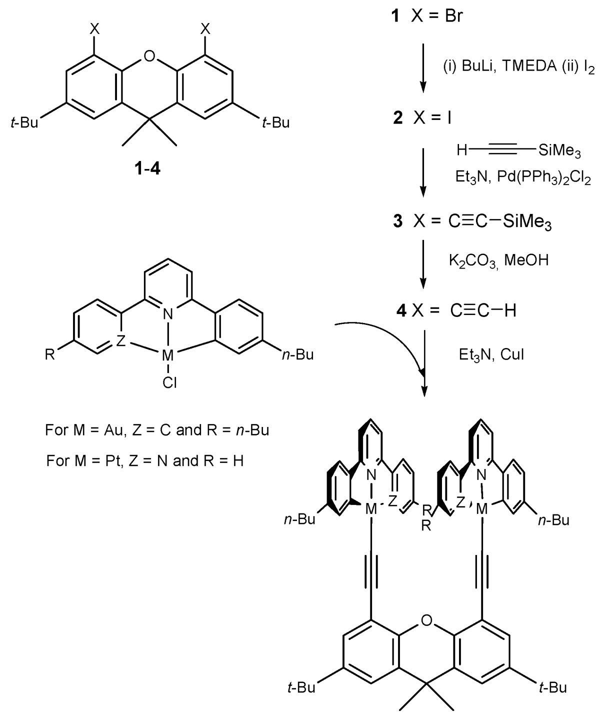


Fig. 1 Molecular structures of the complexes (R = *n*-Bu, R′ = *t*-Bu).



Scheme 1 The synthetic route employed.

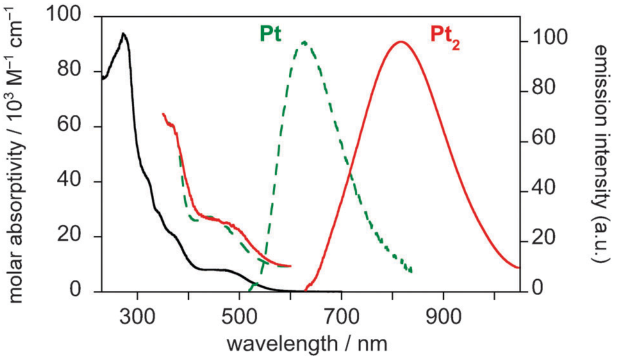


Fig. 2 Absorption spectrum of **Pt$_2$** (black solid line) and the emission and excitation spectra of **Pt** and **Pt$_2$** (solid red and dashed green lines respectively) in CH$_2$Cl$_2$ at 298 K.

(**Pt$_2$** and **Au$_2$**) complexes respectively. The heterodimer **AuPt** was similarly prepared by treatment of **Au** with Pt(N^N^C)Cl.

Due to the lower symmetry of the N^N^C-coordination in the Pt complexes, two possible stereoisomers for **Pt$_2$** (C_s, meso, and C_2, chiral) could be expected, depending on the relative arrangement of both metal complexes. NMR spectra reveal that only one of these isomers is formed. Chiral shift reagents did not lead to signal splitting, though this result does not allow unequivocal assignment of the stereochemistry.

Photophysical data for the complexes are compiled in Table 1 and selected absorption and photoluminescence spectra are shown in Fig. 2 and 3. First we consider the mononuclear and homodinuclear Au(III) complexes. The absorption spectrum of the mononuclear gold complex **Au** displays a moderately intense, vibronically structured band around 400 nm, very similar to that reported previously by Yam and co-workers for Au(C^N^C)(C≡C-Ph), who assigned it to a metal-perturbed intraligand transition on the C^N^C ligand.[8a] Complex **Au** displays a highly structured emission band, λ_{max} = 485 nm, assigned to the corresponding triplet state. The emission is very weak, $\Phi_{lum} = 3.4 \times 10^{-4}$.

Comparing dinuclear complex **Au$_2$** with **Au**, the absorption spectra have essentially identical profiles, with no evidence of low-energy bands arising from intramolecular ground-state interactions between the gold centres in **Au$_2$**. The emission spectra likewise are very similar, **Au$_2$** showing just slightly higher relative intensity of the $v = 1$ and $v = 2$ vibrational bands relative to the fundamental (Fig. 3). Interestingly, however, the luminescence lifetime and quantum yield of **Au$_2$** are around 50 times higher than for **Au**. Inspection of the radiative and non-radiative decay rate constants in Table 1 confirms that the augmentation is due to the decreased rate of non-radiative decay pathways in the dinuclear compound. Given that the spectra scarcely differ from one another, this unprecedented result is intriguing and suggests that the presence of a second Au unit partially protects the other from deactivation pathways, for example, either those involving the solvent, or simply through increased rigidity. Motion of the Au(C^N^C) units should clearly be more limited in **Au$_2$** than in **Au**. We also note that a protective effect of aryl rings positioned parallel to the plane of a terpyridyl ligand was found to enhance emission in Ru(II) complexes, apparently through steric protection against non-radiative deactivation.[11]

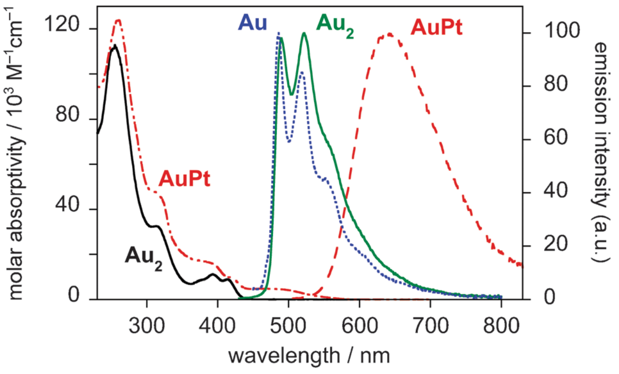


Fig. 3 Absorption spectra of **Au$_2$** (black solid line) and **AuPt** (red dashed-dot line) and the emission spectra of **Au** (blue dotted line), **Au$_2$** (green solid line) and **AuPt** (dashed red line) in CH$_2$Cl$_2$ at 298 K.

Table 1 Photophysical data for the mono- and dinuclear complexes in deoxygenated CH_2Cl_2 at 298 K except where indicated otherwise

Complex	Absorption λ_{max}/nm (ε/M^{-1} cm^{-1})	Emission λ_{max}/nm	τ/ns[a]	$\Phi_{lum} \times 10^2$[b]	$k_r/10^3$ s^{-1}[c]	$\sum k_{nr}/10^5$ s^{-1}[c]	Emission at 77 K[d]	
							λ_{max}/nm	τ/μs
Pt	250 (60 500), 284 (49 700), 340sh (17 100), 372 (12 800), 442 (5190), 469sh (4620)	626	53 [45]	0.73	140	190	546, 581	6.7
Pt$_2$	274 (93 500), 320sh (41 100), 342 (28 800), 368sh (20 900), 457 (7900)	817	26 [24]	0.26	100	380	715	1.0
Au	248 (66 200), 262sh (60 600), 308 (19 700), 375 (5120), 392 (6170), 413 (5100)	490, 522, 557sh	96 [89]	0.034	3.5	100	483, 518, 554, 599	220
Au$_2$	255 (113 000), 314 (32 400), 376 (8580), 393 (11 200), 414 (8900)	485, 518, 552, 600	5100 [1100]	1.0	2.0	1.9	478, 516, 550, 596	275
AuPt	260 (123 000), 314 (47 100), 380 (16 800), 420 (9520), 465 (4850)	639	47 [42]	0.76	160	210	549, 589, 640sh	5.4

[a] Values in air-equilibrated solution in parentheses; lifetimes were independent of λ_{em} across the emission bands, in each case. [b] Quantum yield measured using $Ru(bpy)_3Cl_2$ (aq) as the standard. [c] k_r and $\sum k_{nr}$ are the radiative and non-radiative decay rate constants, estimated assuming that the emissive state is formed with unitary effiency, such that $k_r = \Phi_{lum}/\tau$ and $\sum k_{nr} = (1/\tau)–k_r$. [d] Data at 77 K recorded in diethyl ether/isopentane/ethanol (2 : 2 : 1 by volume).

The mononuclear complex **Pt** displays an absorption spectrum typical of cyclometallated platinum(II) complexes of 6-phenyl-bipyridines, with moderately intense bands in the 400–500 nm region associated with ^{1}MLCT transitions.[4,12] Upon photoexcitation, the compound emits in solution at room temperature, displaying a structureless emission band, λ_{max} = 626 nm, $\Phi_{lum} = 7.3 \times 10^{-3}$, τ = 53 ns. Compared to the related N^N^C complex with a simple phenylacetylide co-ligand, namely Pt(phbpy)(C≡C-Ph), for which λ_{max} = 571 nm, $\Phi_{lum} = 8 \times 10^{-2}$ and τ = 1.0 μs,[12] the emission is red-shifted in the xanthene system, and non-radiative decay is surprisingly increased by an order of magnitude.

The emission spectrum of the dinuclear complex **Pt$_2$** is very different from that of **Pt** (Fig. 2). Its emission is substantially red-shifted, falling in the near-infrared region of the spectrum, λ_{max} = 815 nm. This could be due to the formation of an MMLCT state involving interaction of the two metallic units within the compound. In this case, an additional low-energy absorption band would typically be anticipated, as the interaction is already present in the ground state. Although the absorption profiles of **Pt** and **Pt$_2$** are very similar to one another, close inspection of the excitation spectra registered for their respective emission bands does reveal slightly enhanced absorption to long wavelength of the lowest-energy absorption band for **Pt$_2$**, suggestive of some interaction between the two complex centres in the ground state. An alternative explanation may be that the xanthene unit provides some conjugation between the two metallic units; the non-innocence of the xanthene is evident from the difference in properties of **Pt** and Pt(phbpy)(C≡C-Ph)$_2$ discussed above.

The absorption spectrum of the heterodinuclear complex **AuPt** displays features characteristic of both **Au** and **Pt**; indeed, the experimental spectrum is very similar to that simulated by addition of the spectra of the two mononuclear complexes (see ESI†). On the other hand, excitation of **AuPt** at any wavelength > 250 nm at room temperature results in a single emission band of similar energy to that displayed by **Pt** (Fig. 3). The quantum yield and lifetime of this band are likewise similar to the values for **Pt**. There is no evidence of emission from the Au unit. It is not possible to excite the Au unit of **AuPt** selectively. However, the fact that a **Pt**-like emission band is exclusively observed, irrespective of λ_{ex}, together with the good match between excitation and absorption spectra,† strongly suggest that excitation of the Au unit is followed by very rapid energy transfer to the Pt unit. Although there is no evidence of a ground-state interaction between the two metal units, through-space energy transfer will be facilitated by their close proximity. At 77 K, a very weak band assignable to Au emission is detected.† Though this could be indicative of a reduced rate of energy transfer, it more likely reflects simply the reduction in other non-radiative decay pathways of the Au centre (*e.g.* τ = 220 μs for **Au** at 77 K, Table 1).

In summary, the diethynylxanthene unit offers a versatile platform for the design of homo-and heterodinuclear d^8 metal complexes with interesting photophysical properties. The unexpected reduced non-radiative decay observed for the di-gold species points to a potential new strategy to be explored for improving the performance of gold(III) emitters.

We acknowledge MICINN (projects CTQ2007-60494/BQU and CTQ2010-15927, and FPU fellowship to R.M.R.) and CAM (AVANCAT) for financial support.

Notes and references

1 (*a*) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595; (*b*) *Highly Efficient OLEDs with Phosphorescent Materials*, ed. H. Yersin, Wiley-VCH, Berlin, 2007; (*c*) Q. Zhao, F. Li and C. Huang, *Chem. Soc. Rev.*, 2010, **39**, 3007.
2 (*a*) J. A. G. Williams, *Top. Curr. Chem.*, 2007, **281**, 205; (*b*) C. Bronner and O. S. Wenger, *Dalton Trans.*, 2011, **40**, 12409.
3 S. Develay, O. Blackburn, A. L. Thompson and J. A. G. Williams, *Inorg. Chem.*, 2008, **47**, 11129.
4 S.-W. Lai, M. C.-W. Chan, T.-C. Cheung, S. M. Peng and C.-M. Che, *Inorg. Chem.*, 1999, **38**, 4046.
5 W. Lu, M. C.-W. Chan, N. Zhu, C.-M. Che, C. Li and Z. Hui, *J. Am. Chem. Soc.*, 2004, **126**, 7639.
6 S. Develay and J. A. G. Williams, *Dalton Trans.*, 2008, 4562.
7 V. W.-W. Yam and E. C.-C. Cheng, *Chem. Soc. Rev.*, 2008, **37**, 1806.
8 (*a*) V. W.-W. Yam, K. M.-C. Wong, L.-L. Hung and N. Zhu, *Angew. Chem., Int. Ed.*, 2005, **44**, 3107; (*b*) V. K.-M. Au, K. M.-C. Wong, N. Zhu and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2009, **131**, 9076; (*c*) V. K.-M. Au, K. M.-C. Wong, N. Zhu and V. W.-W. Yam, *Chem.–Eur. J.*, 2011, **17**, 130.
9 K. M.-C. Wong, X. Zhu, L.-L. Hung, N. Zhu, V. W.-W. Yam and H.-S. Kwok, *Chem. Commun.*, 2005, 2906.
10 R. Okamura, T. Wada, K. Aikawa, T. Nagata and K. Tanaka, *Inorg. Chem.*, 2004, **43**, 7210.
11 F. Barigelletti, B. Ventura, J. P. Collin, R. Kayhanian, P. Gaviña and J. P. Sauvage, *Eur. J. Inorg. Chem.*, 2000, 113.
12 W. Lu, B.-X. Mi, M. C.-W. Chan, Z. Hui, C.-M. Che, N. Zhu and S.-T. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 4958.