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Cyclometalated platinum(II) complex with C^N^N tridentate ligand as sensitizer for lanthanide luminescence

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ARTICLE INFO

Article history: Received 29 April 2009 Accepted 8 June 2009 Available online 10 June 2009

Keywords: Energy transfer Lanthanide Luminescence Platinum Sensitizer

ABSTRACT

The preparation, characterization and photophysical properties of heterobinuclear complexes $\{Pt(C^N^N)(C \supseteq Cbpy)\}Ln(hfac)_3$ ($C^N^N = 2-(6-(naphthalen-3-yl)-4-phenylpyridin-2-yl)pyridine; HC \supseteq Cbpy = 5-ethynyl-2,2'-bipyridine; Ln = Nd, Eu, Yb; hfac = hexafluoroacetylacetonate) are described. With excitation at <math>390 \leq \lambda_{ex} \leq 500$ nm which is the MLCT/LLCT absorption region of the $Pt(C^N^N)(C \supseteq Cbpy)$ chromophore, lanthanide luminescence is successfully attained by $Pt \rightarrow Ln$ energy transfer from the platinum(II) antenna chromophore to the lanthanide center across the bridging C $\supseteq Cbpy$ ligand.

Lanthanide luminescence is currently attracting considerable interests in many fields due to their extensive applications [1–3]. In order to overcome the weak intensities of the f–f electronic transitions for the lanthanide(III) complexes, energy transfer from transition metal based ³MLCT excited states of the light-harvesting antenna chromophores to f–f levels of the lanthanide ions have been widely applied to achieve long-lived lanthanide emission [4–8]. Current efforts are focused to further optimize the energy transfer process in d–f bimetallic complexes and extend the excitation wavelength throughout the visible and even into the NIR region [9–12].

Utilizing bpyC=CH (5-ethynyl-2,2'-bipyridine) as a conjugated bridging ligand, a family of Pt–Ln multicomponent and heteronuclear complexes have been described, where platinum(II) ion is bound to the acetylide via σ -coordination whereas lanthanide subunit is chelated by the 2,2'-bipyridyl [8]. Because of the excellent π -conjugation and strong σ -donor character, tridentate C^N^N [C^N^N = 2-(6-(naphthalen-3-yl)-4-phenylpyridin-2-yl)pyridine] ligand shows a strong preference for a planar geometry upon complexation with the platinum(II) ion. The neutral Pt(C^N^N)(C=Cbpy) complex (1) exhibits intense luminescence in visible to NIR spectral region, making it as a promising organometallic sensitizer for achieving efficient lanthanide (NIR) luminescence. We report herein the use of 1 as a precursor for construction of neutral Pt–Ln heterobinuclear complexes {Pt(C^N^N)(C=Cbpy)}Ln(hfac)₃ (Ln =

Nd **2**, Eu **3**, Yb **4**; hfac = hexafluoroacetylacetonate), achieving successfully sensitization of long-lived NIR lanthanide luminescence.

Synthetic routes to **1–4** are summarized in Scheme 1. (C^N^N)PtCl was prepared by refluxing K_2PtCl_4 and C^N^N ligand in glacial acetic acid, and the product washed with water, acetone and ether. Compound **1** was synthesized by reaction of an excess of bpyC=CSiMe₃ with (C^N^N)PtCl, catalyzed by cuprous iodide via fluoride-promoted desilylation in the presence of potassium fluoride. Purification by silica gel column chromatography using dichloromethane-methanol (v/v = 100:2) as eluent gave the pure product **1**. The Pt–Ln heterobinuclear complexes were isolated as orange microcrystals by mixing **1** and Ln(hfac)₃(H₂O)₂ in CH₂Cl₂, followed by recrystallization in CH₂Cl₂/n-C₆H₆. These complexes





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were all characterized by elemental analyses, IR spectra, and ESI-MS spectrometry, and by X-ray crystallography for **3**.

A view of **3** is depicted in the Fig. 1. The platinum(II) center exhibits a distorted square-planar environment built by a σ -coordinated C donor from the acetylide and CN₂ donors from the tridentate C^N^N ligand. The Pt atom and C₂N₂ donors are almost coplanar with a torsion angle of ca. 12.8° between the phenyl ring and this plane. The Pt–N and Pt–C distances (2.0–2.1 Å) are comparable to those of analogous platinum(II) complexes in the literature [13]. The Pt–C=C–C array is quasi-linear with C37–C38– Pt = 177.64° and C37–C38–C35 = 178.76°. The Eu^{III} center is eight-coordinated with six oxygen atoms from three hfac and two N atoms from bpy. The Pt…Eu separation through the bridging C=Cbpy is ca. 8.5 Å [8].

UV-vis absorption spectrum of **1** in dichloromethane solution (Fig. 2) displays intense bands at 290–370 nm, assignable to the intraligand transitions since similar absorptions are found in the free RC^N^NH ligand [13]. The low-energy absorption at 390–500 nm arises most likely from Pt-based MLCT transitions, mixed probably with some character from $\pi(C \equiv Cbpy) \rightarrow \pi^*(C^N^N)$ LLCT (ligand-to-ligand charge-transfer) state [13]. Upon formation of the Pt-Ln complexes, apart form the occurrence of a new absorption band at ca 300 nm from hfac [14,15], the low-energy band due to MLCT/LLCT states showed ca. 10 nm blue shift. Titration of **1** with Yb(hfac)₃(H₂O)₂ in dichloromethane solution induced the MLCT/LLCT maximum shift from ca. 453 nm to 445 nm when 1 equiv of Yb(hfac)₃(H₂O)₂ was added (fig. s1, Supplementary material).

Photophysical data of **1–4** are summarized in Table 1. The emissive quantum yield in degassed dichloromethane at 298 K is 0.17 for **1**. Upon excitation at 390–500 nm, which is the absorption region of Pt-based antenna chromophore, the Pt–Ln (**2–4**) complexes exhibit characteristic line-like emission from the corresponding Ln^{III} ions in both solid states and dichloromethane solutions (Fig. 3), demonstrating unambiguously that sensitized lanthanide luminescence is indeed achieved by Pt \rightarrow Ln energy transfer from the Pt-based ³MLCT excited triplet state. As the precursor Ln(haf-c)₃(H₂O)₂ is non-emissive at excitation $\lambda_{ex} > 350$ nm [15], the lanthanide emission in Pt–Ln complexes should be sensitized by energy transfer from Pt^{II}-based light-harvesting chromophores with near-UV irradiation at 390 nm < $\lambda_{ex} < 500$ nm. On the other hand, the Pt-based emission from ³[MLCT] triplet state is mostly



Fig. 2. UV-vis is absorption spectra of 1 (solid), and 4 (dot) in dichloromethane solutions.

quenched, but does not vanish completely. This was further verified by titration of **1** with $Yb(hfac)_3(H_2O)_2$ in dichloromethane, where rapid attenuation of the Pt-based emission was detected when 1 equiv. of $Yb(hfac)_3(H_2O)_2$ was added (fig. s3, Supplementary material).

For Pt–Nd species **2**, the residual Pt^{II} chromophore-based emission is too weak so that the lifetime could not be detected (<10 ns), suggesting that $Pt \rightarrow Nd$ energy transfer rates is very fast $(>10^8 \text{ s}^{-1})$. For Pt–Eu species **3**, severely spectral overlapping (Fig. 3) between unquenched Pt-based ³MLCT emission and Eucentered emission excluded the possibility to estimate the radiative lifetime $\tau_{\rm r}$, the Eu-centered luminescence quantum yield $\Phi_{\rm Eu}$, and the efficiency and rate of the $Pt \rightarrow Eu$ energy transfer. For Pt–Yb complex **4**, the Pt \rightarrow Yb energy transfer rates k_{ET} from the Pt(C^N^N)(acetylide) chromophore to the Yb^{III} centers can be estimated by the equation $k_{\text{ET}} = 1/\tau - 1/\tau_0$, where τ (47 ns) is the lifetime of residual Pt-based emission, and τ_0 (251 ns) is the lifetime in the reference Pt-Gd complex which lacks energy transfer from the Pt^{II}-based antenna triplet states. The energy transfer rates $(k_{\rm ET})$ can thus be calculated as $k_{\rm ET} = 1/\tau_{\rm PtYb} - 1/\tau_{\rm PtGd} = 1.7 \times 10^7 \, {\rm s}^{-1}$ for PtYb (4) species.

As the Nd^{$l\bar{l}$} complex displays transitions at 880 and 1055 nm, it has three ff levels lying within 15,400–20,000 cm⁻¹ (650–500 nm)



Fig. 1. ORTEP drawing of 3 with atom labeling scheme showing 30% thermal ellipsoids. The F atoms on the trifluoromethyl are omitted for clarity.

Table 1				
Luminescence	data fo	or compounds	1–4 at	298 K.

Compound	Medium	$\lambda_{abs}/nm \ (\epsilon/M^{-1} \ cm^{-1})$	$\lambda_{\rm em}/{\rm nm}~(\tau_{\rm em}/{\rm \mu s})^{\rm a}$ at 298 K
1	Solid		746 (0.34)
	CH ₂ Cl ₂	282 (8200), 305 (8700), 388 (2400), 453 (1600)	584 (0.28)
2	Solid		1061 (weak)
	CH ₂ Cl ₂	298 (23,600), 370 (9000), 382 (8300), 445 (5200)	1061 (weak)
3	Solid		613 (449.9)
	CH ₂ Cl ₂	298 (23,600), 370 (8700), 382 (8300), 445 (5000)	613 (172.7)
4	Solid		980 (12.4)
	CH ₂ Cl ₂	295 (26,500), 370 (10,000), 382 (9600), 445 (5800)	980 (13)

^a In degassed dichloromethane at 298 K.



Fig. 3. Emission spectra of 1 (short dot), 2 (dash dot), 3 (short dash) and 4 (solid) with λ_{ex} = 400 nm in dichloromethane solutions at 298 K.

which tend to be convoluted with the MLCT emissions to a significant degree, causing better spectroscopic overlapping with the Ptbased ³MLCT emission band (584 nm). For Yb^{III} ion, a single f-f absorption at ca. 980 nm $(10,240 \text{ cm}^{-1})$ can only overlap with the very weak low-energy tail of the Pt^{II}-based emission. Undoubtedly, energy matching degree for $Pt \rightarrow Ln$ energy transfer is Pt-Nd(2) > Pt-Yb (4) [15d,16], resulting in a faster transfer rate for the former than the latter.

In summary, designed preparation of three Pt-Ln heterobinuclear complexes have been carried out using C^N^N tridentate cyclometalated ligand. Sensitization of NIR lanthanide luminescence by the $d(Pt) \rightarrow \pi(C^N^N)[MLCT]$ excited triplet state is successfully achieved through efficient $Pt \rightarrow Ln$ energy transfer from the Pt-based chromophore to the lanthanide center. It is demonstrated that $Pt \rightarrow Ln$ energy transfer in Pt–Nd complex 2 is more rapid than that in Pt-Yb species 4 because of the more favorable energy match for the former.

Acknowledgments

This work was financially supported by the NSFC (20625101, 20773128 and 20821061), the 973 Project (2007CB815304) from MSTC, and NSF of Fujian Province (200810027 and 2008F3117).

Appendix A. Supplementary material

CCDC 729706 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.inoche.2009.06.004.

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