

Synthesis and Luminescent Properties of an Acetylide-Bridged Dinuclear Platinum(II) Terpyridyl Complex

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An acetylide-bridged dinuclear platinum(II) terpyridyl complex, [Pt(4'-p-tolyl-terpy)-≡-phenyl-≡-(4'-p-tolyl-terpy)Pt](ClO₄)₂ (**1**), has been successfully synthesized and its photophysical properties are reported.

Keywords platinum(II) terpyridyl complex, acetylide-bridged, luminescent property

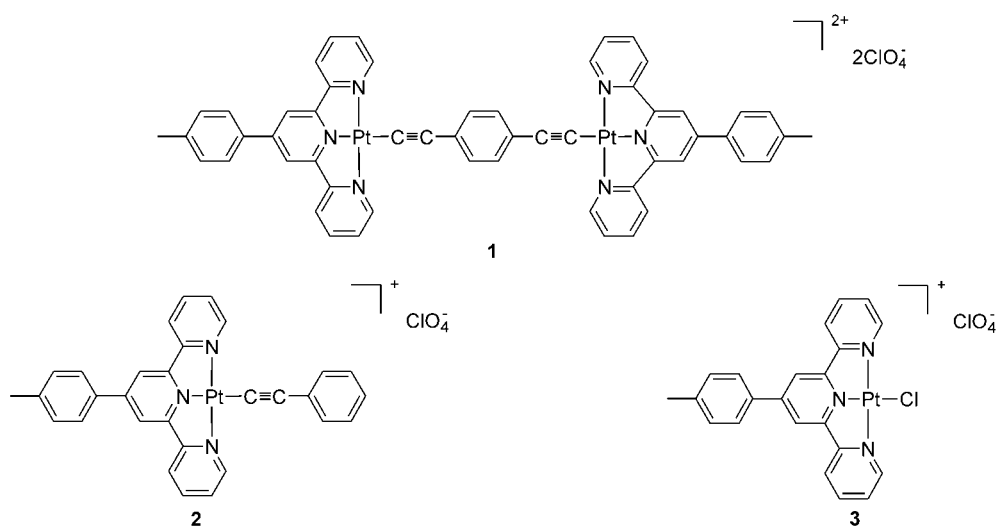
Introduction

Luminescent coordinatively unsaturated platinum(II) complexes are appealing from photochemical and photophysical perspective.^{1,2} In particular, platinum(II) terpyridyl complexes have attracted considerable attention due to their rich spectroscopic^{2a-d} and biological properties.^{2a,e-g} However, the development of the photochemistry of these complexes is limited by their short-lived MLCT excited state in solution at room temperature. The lack of emission originates from low-lying d-d excited state, which provides a facile non-radiative deactivation pathway via molecular distortion.

In the course of finding new luminescent coordinatively unsaturated metal complexes, we have engaged in the investigation of platinum(II) terpyridyl derivatives bearing an ancillary acetylide ligand from a photochemical perspective, since the strongly σ -donating

acetylide ligands are expected to increase the energy gap between the MLCT and the ligand field (d-d) states, and thus slow down the non-radiative deactivation of the lowest MLCT excited state. Indeed, we^{3a,b} and Yam's^{3c} group have demonstrated that long-lived emission from ³MLCT state of platinum(II) terpyridyl complexes in solution at room temperature can be obtained by simply introducing of acetylide ligand to platinum(II) terpyridyl complexes. In order to explore the probability of utilization of platinum(II) terpyridyl complex as a building block to prepare photoactive supramolecular assemblies, herein we report the synthesis, electronic absorption and photophysical properties of acetylene-bridged dinuclear platinum(II) terpyridyl complex, [Pt(4'-p-tolyl-terpy)-≡-phenyl-≡-(4'-p-tolyl-terpy)Pt](ClO₄)₂, abbreviated as **1** and shown in Scheme 1. For comparison, mononuclear [Pt(4'-p-tolyl-terpy)-≡-phe-

Scheme 1



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nyl]ClO₄ (**2**) and [Pt(4'-*p*-tolyl-terpy)Cl]ClO₄ (**3**) (Scheme 1) were also studied. It is anticipated that the rigid rod of acetylide-bridged ligand would display profound influence on the excited state properties of **1**.

Results and discussion

Complex **1** was prepared by a reaction of [Pt(4'-*p*-tolyl-terpy)Cl]Cl with 0.5 equivalent amount of 1,4-diacetylenylbenzene in DMF in the presence of catalyst CuI and triethylamine at room temperature. After metathesis reaction by NaClO₄ and recrystallization of the crude product by vapor diffusion of diethyl ether into an acetonitrile solution, **1** was obtained as dark red crystals in *ca.* 81% yield. The identity of the complex **1** was confirmed by ¹H NMR spectroscopy, MALDI-TOF-MS spectrometry and satisfactory elemental analyses.⁴ Complexes **2** and **3** were also synthesized by the method reported previously.^{3a}

Figure 1 depicts the absorption spectra of complexes **1—3** in acetonitrile solution, which exhibited intense vibronically structured absorption bands at $\lambda < 350$ nm with extinction coefficients (ϵ) in the order of 10^4 dm³ · mol⁻¹ · cm⁻¹, and less intense band at 400—500 nm with ϵ in the order of 10^3 dm³ · mol⁻¹ · cm⁻¹. With reference to previous spectroscopic work on platinum(II) terpyridyl complexes,^{2a} the absorption bands at $\lambda < 350$ nm are assigned to the intraligand (IL) transition of terpyridyl and acetylide ligands as well as the charge transfer transition involved in the PtC≡CR moieties, while the low energy absorption bands at 400—500 nm are tentatively assigned to the $d\pi(\text{Pt}) \rightarrow \pi^*(\text{terpy})$ ¹MLCT transition. It is noteworthy that the low-energy ¹MLCT absorption bands red-shifted from *ca.* 406 nm for **3** to 458 nm, and 487 nm for **2**, and **1** respectively when the σ -donating acetylide ligand was introduced. This phenomenon is consistent with the notion that the HOMO is predominantly metal-based. An electron-rich acetylide ligand would render the metal center more electron-rich and hence raise the $d\pi(\text{Pt})$ orbital energy, leading to lower energy absorption. More interestingly,

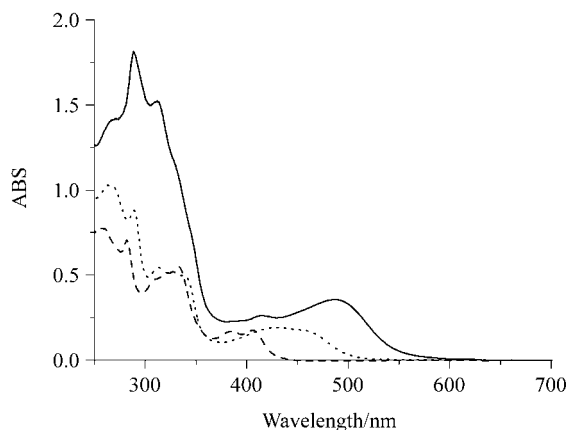


Figure 1 Absorption spectra of complexes **1** (—), **2** (···) and **3** (---) in CH₃CN solution. [1]= 2.65×10^{-5} mol/L, [2]= 2.64×10^{-5} mol/L, [3]= 2.65×10^{-5} mol/L.

the extinction coefficient of the low-energy absorption band ($\lambda=487$ nm, $\epsilon=1.34 \times 10^4$) of **1** is almost double that of the 458 nm band ($\lambda=458$ nm, $\epsilon=0.65 \times 10^4$) of the related mononuclear complex of **2**. The absorption band was found to shift to lower energy with increasing the rigid conjugated length of acetylide ligand, as found in organic polyynes and other metal-alkynyl systems.⁵ The absorption spectral properties of the complexes followed Beer's Law below saturation in CH₃CN, suggesting no occurrence of any significant complex aggregation.

Unlike **3**, complexes **1** and **2** display emission in degassed CH₃CN solution at room temperature, as presented in Figure 2. The spectra are broad and featureless in dilute acetonitrile solution at room temperature. The intensities, band shapes and energies of the emission spectra are characteristic of emission from charge transfer states.⁶ Table 1 summarized the emission maximum (λ_{max}), quantum yield (ϕ_{em}) and lifetimes (τ) of complexes **1—3**. The photoluminescence quantum yields (ϕ_{em}) were determined by the optical dilute method^{7a} using a degassed acetonitrile solution of [Ru(bpy)₃](PF₆)₂ as the reference ($\phi_{\text{em}}=0.062$).^{7b} The photoluminescence decay lifetimes were measured using a conventional laser system. The excitation source was 355 nm output (third harmonic, 10 ns of pulsed Nd:YAG laser 10 Hz). Evidently, the large Stokes shifts and observed lifetimes are suggestive of a triplet parentage, which is tentatively assigned as arising from the ³MLCT state.

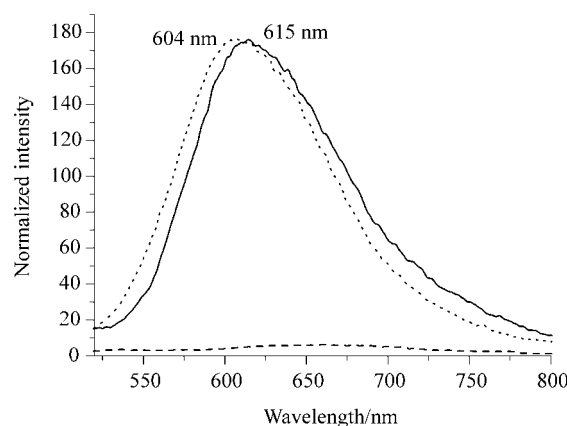


Figure 2 Emission spectra of complexes **1** (—), **2** (···) and **3** (---) in degassed CH₃CN solution at room temperature.

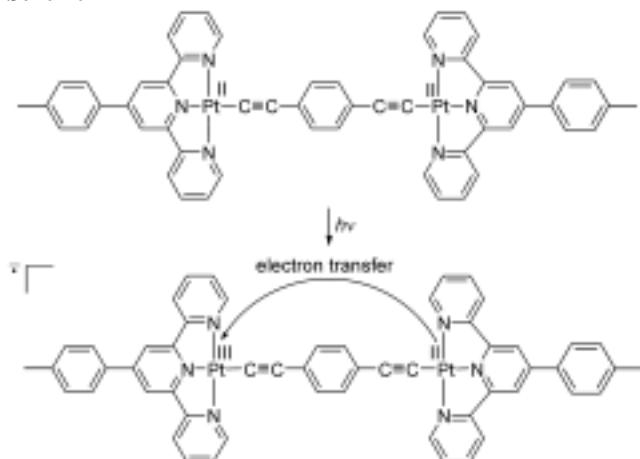
Table 1 Photophysical properties of complexes **1—3** in CH₃CN at room temperature

	$\lambda_{\text{max}}^{\text{ab}}$ / nm ($\epsilon / \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	$\lambda_{\text{max}}^{\text{em}}$ / nm	ϕ_{em}	$\tau / \mu\text{s}$
1	487 (1.34×10^4)	615	0.0012	0.018
2	458 (6.50×10^3)	604	0.020	1.03
3	406 (6.60×10^3)	— ^a	— ^a	— ^a

^a The emission was too weak to be detected.

Importantly, the acetylide ligands have interesting consequences on the excited state behavior of the complexes. As shown in Table 1, the emission maximum shifted to longer wavelength as the electron-donating acetylide ligand was introduced. Complexes **1** and **2** exhibit much longer emission lifetimes and greater emission quantum yields compared with **3**. This may be attributed to the electron-donation of the acetylide ligand, which reduces the energy of the ³MLCT excited state and increases the energy of d-d excited state. As a result, the energy gap between the ³MLCT and ³d-d states increases and the nonradiative decay of the ³MLCT state via the ³d-d state is blocked. Inspection of the data in Table 1 also reveals that the emission lifetimes and quantum yields decrease from **2** ($\phi_{em}=0.02$, $\tau=1.02$ μ s) to **1** ($\phi_{em}=0.0012$, $\tau=0.02$ μ s) with increasing the conjugated length of the acetylide ligand. This observation may be rationalized as follows. When the acetylide-bridged dinuclear platinum(II) complex **1** was excited, MLCT [Pt(III)(terpy)⁺] was then produced. As shown in Scheme 2, complex **1** becomes [(terpy)⁺Pt(III)(bridge)Pt(II)(terpy)]. Since the bridge is so rigid and short, electron transfer from Pt(II) to Pt(III) in complex **1** is prevalent, resulting in short-lived excited state with low emission quantum yield.

Scheme 2



This study demonstrates that one can prepare luminescent terpyridyl platinum(II) complex with tunable excited state by variations in molecular design. The change in the nature of the lowest excited state by altering the energy of HOMO through ancillary acetylide ligand is an extreme example. The improved photophysical properties of complexes **1** and **2**, compared to that of unsubstituted complex of **3**, provide new opportunities to construct elaborate molecular assemblies around the photoactive platinum(II) terpyridyl unit.

Experimental

Acetonitrile was purified and distilled using standard procedures before use. 1,4-Diacetylenylbenzene was synthesized according to the reported method.⁸ All solutions for photophysical studies were degassed on a

high-vacuum line in a two-compartment cell consisting of a 10 mL Pyrex bulk and a 1 cm-path length quartz cuvette sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were subjected to more than four freeze-pump-thaw cycles. ¹H NMR spectra were measured on 400 MHz with a Gemini spectrometer. MALDI-TOF-MS spectra were obtained on a BIFLEXIII spectrometer. Elemental analyses were performed on a Carlo Erba1106 autoanalyser. Fluorescence spectra were run on a Perkin Elmer LS50B Luminescence spectrometer. UV-vis spectra were recorded with a Shimadzu UV-1601PC spectrometer.

References and note

- (a) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*, Horwood, Chichester, U. K., **1991**.
(b) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 795.
(c) Roundhill, D. M.; Gray, H. B.; Che, C. M. *Acc. Chem. Res.* **1989**, *22*, 55.
- (a) McMillin, D. R.; Moore, J. J. *Coord. Chem. Rev.* **2002**, *229*, 113 and references therein.
(b) Sun, W. F.; Wu, Z. X.; Yang, Q. Z.; Wu, L. Z.; Tung, C. H. *Appl. Phys. Lett.* **2003**, *82*, 850.
(c) Yam, V. W. W.; Wong, K. M. C.; Zhu, N. Y. *J. Am. Chem. Soc.* **2002**, *124*, 6506.
(d) Pomestchenko, I. E.; Luman, C. R.; Hissler, M.; Ziessel, R.; Castellano, F. N. *Inorg. Chem.* **2003**, *42*, 1394.
(e) Lippard, S. J. *Acc. Chem. Res.* **1978**, *11*, 211.
(f) Arena, G.; Monsu Scolaro, L.; Pasternack, R. F.; Rometo, R. *Inorg. Chem.* **1995**, *34*, 2994.
(g) Ralilla, E. M. A.; Brothevs, H. M.; Kostic, N. M. *J. Am. Chem. Soc.* **1987**, *109*, 4592.
- (a) Yang, Q. Z.; Wu, L. Z.; Wu, Z. X.; Zhang, L. P.; Tung, C. H. *Inorg. Chem.* **2002**, *41*, 5653.
(b) Wu, Z. X.; Wu, L. Z.; Yang, Q. Z.; Zhang, L. P.; Tung, C. H. *Chin. J. Chem.* **2003**, *21*, 196.
(c) Yam, V. W. W.; Tang, R. P. L.; Wong, K. M. C.; Cheung, K. K. *Organometallics* **2001**, *20*, 4476.
- Complex **1**: ¹H NMR (DMSO-*d*₆, 400 MHz) δ : 2.32 (s, 6H, Me), 7.19 (d, $J=7.83$ Hz, 4H), 7.35 (s, 4H), 7.62—7.66 (m, 4H), 7.75—7.78 (m, 4H), 8.23—8.27 (m, 4H), 8.43—8.47 (m, 4H), 8.50 (s, 4H), 8.92—8.97 (m, 4H); IR (KBr) $\nu_{C=C}$: 2118 cm⁻¹; MALDI-TOF-MS m/z : 1260 [M—ClO₄]⁺, 1160 [M—2ClO₄]²⁺. Anal. calcd for C₅₄H₃₈N₆Pt₂·2ClO₄·H₂O: C 47.07, N 6.10, H 2.93; found C 46.71, N 6.16, H 3.12.
- (a) Schermann, G.; Grosser, T.; Hampel, F.; Hirsch, A. *Chem.-Eur. J.* **1997**, *3*, 1105.
(b) Che, C. M.; Chao, H. Y.; Miskowski, V. M.; Li, Y.; Cheung, K. K. *J. Am. Chem. Soc.* **2001**, *123*, 4985.
- Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, **1991**.
- (a) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1997**, *75*, 991.
(b) Calvert, J. M.; Caspar, J. V.; Binstead, R. A.; Westmoreland, T. D.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 6620.
- Khatyr, A.; Ziessel, R. *J. Org. Chem.* **2000**, *65*, 3126.