Tuning the Excited-state Properties of Cyclometalated Platinum(II) Complexes of 6-Phenyl-2,2'-bipyridine by Ancillary Acetylide Ligand

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A series of luminescent cyclometalated platinum(II) complexes, (C^N^N)Pt(C≡CR) [HC^N^N = 4-(4-tolyl)-6-phenyl-2,2'-bipyridine; R = 4-chlorophenyl (1), phenyl (2) and 4-tolyl (3)], were synthesized, and their spectroscopic properties have been examined. These complexes are brightly emissive both in fluid solution and in the solid state, attributed to triplet metal-to-ligand charge transfer (³MLCT) state. The excited state energy can be tuned by ancillary acetylide ligands. The emission lifetimes in dichloromethane solution at room temperature were up to 1.64 μs and the emission quantum yields were in the range of 0.03—0.15.

Keywords　cyclometalated platinum(II) complex, acetylide, luminescence, MLCT (metal-to-ligand change transfer)

Luminescent coordinatively unsaturated metal complexes are appealing from photochemical and photophysical perspective.[1,2] Square-planar platinum(II) complexes containing a chelating diimine ligand represent a promising class of these molecules.[2] However, they are usually weak emitters or even nonemissive in fluid solution at room temperature due to a D_{2d} distortion.[3] Therefore, many researchers have diverted their attention to the tridentate ligand, which favors planar geometry and would discourage a D_{2d} distortion. In particular, platinum(II) complexes bearing cyclometalated 6-phenyl-2,2'-bipyridine and related ligands display low-lying metal-to-ligand charge transfer (MLCT) excited states which generally exhibit improved photophysical properties compared to α-diimine platinum(II) complexes.[4a-e] Nevertheless further development of such complexes becomes limited because negligible changes in emission energy have been detected by incorporating different aryl substitutes into the 4-position of 6-phenyl-2,2'-bipyridine.[4b,e-f] Although it is possible to obtain emissive complexes by introducing appropriate ancillary ligand in such complexes, few examples with long lifetime and high quantum yield in solution were observed.[4a,c,g]

In the course of finding new luminescent coordinatively unsaturated metal complexes with long excited state lifetimes and high emission quantum yields, we have engaged in the investigation of platinum(II) derivatives bearing a tridentate ligand and 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 to slow down the radiationless deactivation of the lowest excited state. Herein, the photoluminescent properties of cyclometalated platinum(II) complexes, bearing 6-phenyl-2,2'-bipyridine and an acetylide group, such as (C^N^N)Pt(C≡CR) [HC^N^N = 4-(4-tolyl)-6-phenyl-2,2'-bipyridine; R = 4-chlorophenyl (1), phenyl (2) and 4-tolyl (3)] as shown in Scheme 1, are described. The observation reveals that acetylide ligands show profound influence on the properties of the excited state.

Scheme 1

R = Cl (1), H (2), Me (3)
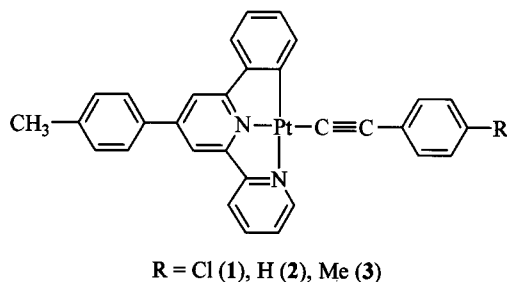
Complexes **1**—**3** were synthesized by the reaction of Pt(C^N^N)Cl,[4b] which was prepared according to the reported method,[4b] with equivalent corresponding acetylene in DMF in the presence of catalyst CuI and triethylamine. After the mixture was sonicated under nitrogen for 8 h at room temperature, the product was obtained as solid and then was filtered, washed with water and diethyl ether and dried. Subsequent recrystallization by diffusion of diethyl ether vapor into a dichloromethane solution of the crude product gave crystals with ca. 70%—74% yields. The identities of all the complexes were confirmed by ¹H NMR spectroscopy, FAB-mass spectrometry and satisfactory elemental analyses.[5] All the

compounds are soluble in organic solvents (CH_2Cl_2 and CH_3CN) and very stable both in solid and solution. They can be stored in air for months without noticeable change.

UV-vis spectra were measured on a Shimadzu UV-1601 PC spectrophotometer. All the complexes in dichloromethane solution exhibit intense vibronic-structrued absorption bands at $\lambda < 370$ nm with extinction coefficients (ε) in the order of 10^4 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$, and less intense band at 400—500 nm with ε on the order of 10^3 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$. The band maxima and the extinction coefficients are listed in Table 1, and the spectra for comparison are shown in Fig. 1. With reference to previous spectroscopic work on cyclometalated platinum(II) complexes,[1b,4a-c,g] the absorption bands at 250—370 nm are assigned to the intraligand (IL) transition of C^N^N ligands, while the low energy absorption bands at 400—500 nm are tentatively assigned to the $d\pi(Pt) \rightarrow \pi^*$ (C^N^N) ^{1}MLCT transition. In addition to IL and ^{1}MLCT transition, [Pt(C^N^N)Cl] exhibits a ^{3}MLCT absorption with $\lambda_{max} = 522$ nm and $\varepsilon = 209$ $dm^3 \cdot mol^{-1} \cdot cm^{-1}$.[4b] It is noteworthy that as the electron-donating ability of the ancillary ligands increases, the ^{1}MLCT absorption bands red-shift from ca. 437 nm for [Pt(C^N^N)Cl] to 465 nm for complex 3. 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 $d\pi(Pt)$ orbital energy, leading to lower energy absorption. The absorption spectral properties of the complexes were found to follow Beer's Law in the concentration range 1×10^{-5}—1×10^{-3} mol/L in CH_2Cl_2, suggesting no any significant complex aggregation occurred in solution.

All these complexes display intense photoluminescencein fluid solution at room temperature. Fig. 2 shows the emission

spectra of these complexes in degassed dichloro-methane at room temperature, obtained on a Perkin Elemer LS50B
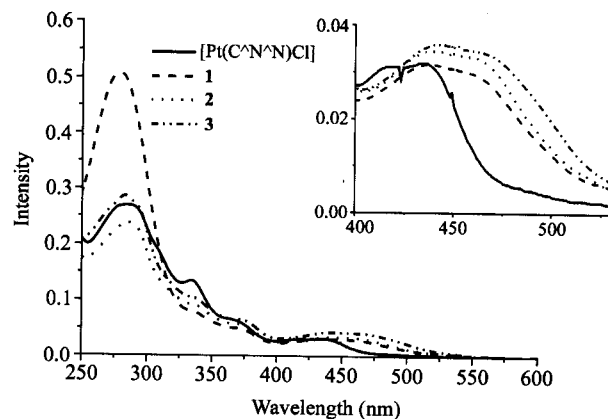

Fig. 1 Absorption spectra of complexes 1—3 and [Pt(C^N^N)Cl] in CH_2Cl_2 at room temperature.
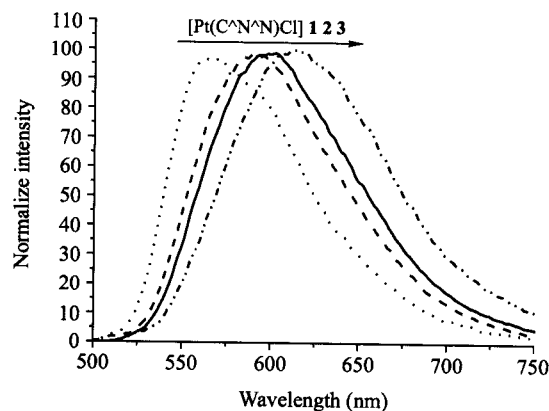
Fig. 2 Emission spectra of complexes 1—3 and [Pt(C^N^N)Cl] in deoxygenated CH_2Cl_2 at room temperature.

Table 1 Photophysical properties of complexes 1—3 in CH_2Cl_2

Complex	λ_{abs}(nm) in CH_2Cl_2 [ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)]	λ_{em}(nm)		λ_{em}(nm) solid		ϕ_{em} (CH_2Cl_2, 298 K)	$\tau_0(\mu s)$ (CH_2Cl_2 298 K)
		CH_2Cl_2, 298 K	MeOH/EtOH (1/1, V/V), 77 K	298 K	77 K		
1	289 (52718) 335 (20763) 371 (12843) 438 (7829) 459 (7394)	589	546, 578	606	601, 642 (sh)	0.152	1.64
2	288 (48336) 337 (19269) 372 (12270) 440 (7773) 462 (7426)	598	545, 580	585	584, 630 (sh)	0.111	1.50
3	288 (49342) 336 (19465) 371 (12192) 441 (7603) 465 (7245)	613	554	620	633	0.033	0.67

spectrafluo rometer. In addition, the photoluminescence quantum yields (ϕ_{em}) were determined by the optical dilute method[9] using a degassed acetonitrile solution of [Ru(bpy)$_3$]-(PF$_6$)$_2$ as the reference ($\phi_{em} = 0.062$).[10] 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). The photoluminescence λ_{max} quantum yields and lifetimes for complexes **1—3** are listed in Table 1. The large Stokes shift and lifetime in the microsecond range for the photoluminescence suggest that the emission originates from a triplet parentage, which is tentatively assigned as arising from the ^{3}MLCT state. As other established cyclometalated platinum(II) complexes,[4b,f,g] self-quenching of ^{3}MLCT emission for complex concentrations in the range of 10^{-5}—10^{-3} mol·dm^{-3} is evident for **1—3** in dichloromethane. The ^{3}MLCT excited state of [Pt(C^N^N)Cl] possesses higher energy (emission occurs at $\lambda_{max} = 565$ nm) than those of complexes **1—3**. Furthermore, over the series of **1—3**, the emission maxima shift to longer wavelength as the electron-donating ability of the acetylide ligands increases (Table 1). These observations further demonstrate that an electron-rich ancillary ligand can raise the HOMO energy of the metal center, and hence decrease the energy of the ^{3}MLCT excited states. Complexes **1** and **2** exhibit much longer emission lifetimes and greater emission quantum yields compared with [Pt(C^N^N)Cl]. Obviously, these results are attributed to the electron-donation of the acetylide ligand, which reduces the energy of the ^{3}MLCT excited states and hence increases the energy gap between the ^{3}MLCT state and ^{3}d-d states. As a result, the nonradiative decay of the ^{3}MLCT state via the ^{3}d-d state is blocked. However, inspection of the data in Table 1 reveals that the emission lifetime and quantum yield decrease with increase in electron-donating ability of the acetylide ligand for series **1—3**. This trend is in accord with the energy gap law.[11] Thus, a platinum(II) complex which possesses a ^{3}MLCT excited state just below the ^{3}d-d state may exhibit photoluminescence with long lifetime and high quantum yield in fluid solution.

The photoluminescence of **1—3** in methanol/ethanol (1:1, V/V) glass solution at 77 K was also examined. Since the solubility of these complexes in the glass solution is limited, only the emissive behavior in dilute glass solution was investigated. Fig. 3 gives the emission and excitation spectra of **2**, and the λ_{em} of **1—3** are listed in Table 1. The emission spectrum is poorly vibronically structured and mirrors the excitation spectrum. The vibrational progressions of *ca*. 1270 cm^{-1} correspond to the skeletal stretching of the free H^C^N^N ligand.[4g]

The emission behavior of **1—3** in solid state both at room temperature and 77 K was investigated, and the data are listed in Table 1. Complexes **1** and **2** display structureless luminescences at room temperature. The emissions slightly blueshift and become poorly vibronically resolved. These emissions are attributed to ^{3}MLCT excited with excimeric character due to weak C^N^N π-π interactions. On the other
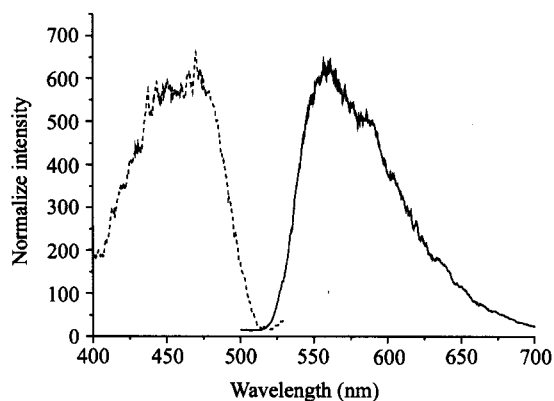

Fig. 3   Excitation ($\lambda_{em} = 560$ nm) and emission ($\lambda_{ex} = 450$ nm) spectra of complex **2** in methanol/ethanol (1:1, $V:V$) glass at 77 K.

hand, **3** exhibits a broad structureless emission at λ_{max} 620 nm at room temperature, but red-shift to 633 nm with reduced bandwidth. This is reminiscent of an excimeric ^{3}IL transition or metal-metal interaction resulting from π-stacking of C^N^N ligands in the [Pt(C^N^N)PPh$_3$]ClO$_4$[4a] and [(C^N^N)Pt-(C≡N-cyclohexyl)ClO$_4$[4g] solid.

This work demonstrates that one can prepare luminescent cyclometalated platinum(II) complex [Pt(C^N^N)X] with long excited state lifetimes and high emission quantum yields and systematically tune their photoluminescent properties through modification of the ancillary ligands.

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5   Complexes **1—3**:

    1 ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.41 (s, 3H, Me), 7.06—7.15 (m, 2H), 7.33 (d, J = 8.5 Hz, 2H), 7.37—7.43 (m, 4H), 7.75 (d, J = 7.31 Hz, 1H), 7.86—7.89 (m, 2H), 8.05 (d, J = 8.13 Hz, 2H), 8.33 (s, 1H), 8.40 (t, J = 7.23 Hz, 1H), 8.57 (s, 1H), 8.77 (d, J = 8.08 Hz, 1H), 9.06 (d, J = 5.07 Hz, 1H); IR (KBr) $\nu_{C\equiv C}$: 2103 cm^{-1}; FAB-MS m/z: 651 (M$^+$). Anal. calcd for **1**·H$_2$O: C 55.56; N 4.18; H 3.43; found C 55.06; N 4.02; H 3.28.

    2 ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.41 (s, 3H, Me), 7.06—7.18 (m, 3H), 7.28 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 7.08 Hz, 2H), 7.42 (d, J = 8.05 Hz, 2H), 7.76 (d, J = 7.24 Hz, 1H), 7.86—7.90 (m, 2H), 8.04 (d, J = 8.16 Hz, 2H), 8.32 (s, 1H), 8.38 (t, J = 7.80 Hz, 1H), 8.57 (s, 1H), 8.77 (d, J = 8.40 Hz, 1H), 9.08 (d, J = 4.5 Hz, 1H); IR (KBr) $\nu_{C\equiv C}$: 2100 cm^{-1}; FAB-MS m/z: 617 (M$^+$). Anal. calcd for **2**: C 60.29; N 4.54; H 3.57; found C 60.43; N

4.37; H 3.53.

    3 ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.28 (s, 3H, Me), 2.41(s, 3H, Me), 7.01—7.10 (m, 4H), 7.28 (d, J = 8.50 Hz, 2H), 7.40 (d, J = 7.59 Hz, 2H), 7.73 (d, J = 7.24 Hz, 1H), 7.86—7.90 (m, 2H), 8.02 (d, J = 7.07 Hz, 2H), 8.28 (s, 1H), 8.36 (t, J = 7.40 Hz, 1H), 8.53 (s, 1H), 8.73 (d, J = 8.41 Hz, 1H), 9.08 (s, 1H); IR (KBr) $\nu_{C\equiv C}$: 2098 cm^{-1}; FAB-MS m/z: 631 (M$^+$). Anal. calcd for **3**·H$_2$O: C 59.17, N 4.31, H 4.00; found C 59.70, N 3.94, H 3.78.

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