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Long-Lived Emission from Platinum(II) Terpyridyl Acetylide Complexes

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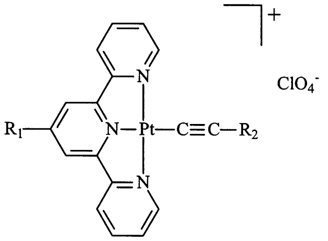
Photoluminescence with high quantum yield and long lifetime from a triplet metal-to-ligand charge transfer (MLCT) excited state in fluid solution at room temperature has been observed for a series of platinum(II) 4′-*p*-tolyl-terpyridyl acetylide complexes.

The platinum(II) terpyridyl complexes have attracted considerable attention in recent years, mainly because of their interesting spectroscopic behavior[1−6] and useful physical and biological properties.[7,8] Indeed, these complexes have been established as important DNA intercalators[7,9] and protein probes.[10] The spectroscopic properties and low-energy absorptions generally arise from metal-to-ligand charge transfer (MLCT) transitions. However, the development of the photochemistry of these complexes is limited by their nonemissive or short-lived MLCT excited states in solution at room temperature.[1] This lack of emission originates from low-lying d−d excited states, which provide facile nonradiative deactivation pathways via molecular distortion. For these complexes, the d−d and MLCT excited states are very close in energy, resulting in fast internal conversion from MLCT to d−d excited states. To obtain emissive platinum(II) terpyridyl complexes with long-lived excited states and high emission quantum yields, many efforts have been performed.[1−6] The main strategy to construct long-lived and emissive platinum(II) terpyridyl complexes involves utilizing substituted terpyridyl ligands with low-lying LUMO and/or ancillary ligands with large electron-donating ability to raise the HOMO of the metal center, hence resulting in the reduction of the MLCT excited state energy. As a result, the energy difference between the MLCT and the d−d states increases, and the nonradiative deactivation via d−d states decreases. However, apart from some 4′-substituted [Pt(trpy)-Cl]$^+$ complexes bearing large aryl groups (the emission of which mainly arises from their intraligand excited states rather than MLCT states[1]), there is no example of a platinum(II) terpyridyl complex which exhibits ^{3}MLCT emission in fluid solution with a lifetime greater than 1 μs and emission quantum yield greater than 1×10^{-2}. Here, we are able to vary the energy of MLCT states of platinum(II) terpyridyl complexes by using a series of substituted acetylide ligands and a 4′-tolyl substituted terpyridyl ligand (Chart 1), and we found that these complexes exhibit long-lived emission from the ^{3}MLCT states with high emission quantum yields. In dichloromethane solution at room temperature, two of these complexes show lifetimes greater than 10 μs and emission quantum yields greater than 0.25.

Chart 1. Structure of Complexes **1**−**6**



1. R_1 = p-tolyl, R_2 = CH_2OH
2. R_1 = p-tolyl, R_2 = n-propyl
3. R_1 = p-tolyl, R_2 = C_6H_4Cl-4
4. R_1 = p-tolyl, R_2 = C_6H_5
5. R_1 = p-tolyl, R_2 = $C_6H_4CH_3$-4
6. R_1 = H, R_2 = C_6H_5

Complexes **1**−**5** (Chart 1) were synthesized by two steps. First, the starting material, [Pt(4′-*p*-tolyl-trpy)Cl]Cl (trpy = 2,2′:6′,2″-terpyridine), was prepared by a literature method[11] using 4′-*p*-tolyl-terpyridine and K_2PtCl_4 as the reagents. This material was then reacted with 2 equivalent amounts of acetylide in DMF in the presence of catalyst CuI and triethylamine at room temperature. After metathesis reaction by $NaClO_4$ and recrystallization of the crude product by vapor diffusion of diethyl ether into an acetonitrile solution, complexes **1**−**5** were obtained as orange crystals with ca.

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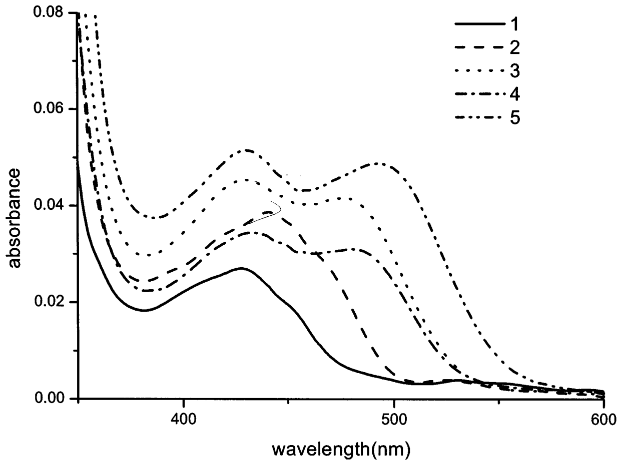

Figure 1. Absorption spectra of complexes **1**−**5** measured in CH_2Cl_2 solution.

Table 1. Photphysical Properties of Complexes **1**−**6** in CH_2Cl_2 at 298 K

complex	λ_{ab}/nm (ϵ/dm^3 mol^{-1} cm^{-1})	λ_{em}	τ (μs)	Φ_{em}
1	274 (35900), 289 (34300), 315 (18500), 328 (18000), 342 (19300), 430 (7260)	552	14.6	0.30
2	276 (37800), 290 (44300), 317 (28100), 345 (28800), 420sh (8250), 441 (10200)	580	10.3	0.25
3	273 (47400), 316 (21500), 342 (21500), 430 (7770), 477 (7280)	611	4.7	0.071
4	266 (45300), 289 (37000), 317 (23900), 342 (23900), 433 (8270), 482 (7340)	619	4.6	0.052
5	268 (43000), 287 (34500), 317 (21700), 343 (20600), 432 (7530), 492 (6660)	639	0.8	0.0076
6	287 (26700), 318 (15600), 329 (13500), 345 (13000), 422 (4570), 477 (4290)	618	1.9	0.036

Table 2. Electrochemical Data for Complexes **1**−**5**[a]

complex	oxidation[b] E_{pa}/V vs SCE	reduction[c] $E_{1/2}$/V vs SCE
1	+1.56	−0.88, −1.30
2	+1.50	−0.84, −1.35
3	+1.17	−0.85, −1.33
4	+1.10	−0.83, −1.31
5	+1.26	−0.83, −1.29

[a] In DMF solution with 0.1 M $^nBu_4NPF_6$ (TBAH) as supporting electrolyte at room temperature; scan rate 200 mV s^{-1}. [b] E_{pa} refers to the anodic peak potential for the irreversible oxidation waves. [c] $E_{1/2} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively.

76% yields. Complex **6** was synthesized by similar procedure. The identities of all of the complexes were confirmed by ^{1}H NMR spectroscopy, HR-MS spectrometry, and satisfactory elemental analyses, which are given in the Supporting Information. All of the complexes are soluble in organic solvents (DMF, CH_3CN, CH_2Cl_2) and very stable both as solids and in solution.

UV−vis spectra were measured on a Shimadzu UV-1601 PC spectrophotometer. All the complexes in dichloromethane solution exhibit intense vibronic-structured absorption bands at $\lambda < 350$ nm with extinction coefficients (ϵ) on the order of 10^4 dm^3 mol^{-1} cm^{-1}, and less intense band at 400−500 nm with ϵ on the order of 10^3 dm^3 mol^{-1} cm^{-1}. The absorption spectral properties were found to follow Beer's Law below saturated concentration (ca. 5×10^{-5} mol dm^{-3}) in this solvent, suggesting no any significant complex aggregation occurred. Table 1 summarizes the band maxima and the extinction coefficients. Figure 1 shows the long-wavelength region of the spectra. With reference to previous spectroscopic work on platinum(II) terpyridyl complexes,[1−6] 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 Pt−C≡CR moieties,[12] while the low energy absorption bands at 400−500 nm are tentatively assigned to the dπ(Pt) → π*(trpy) MLCT transition. However, interpretation of the MLCT bands is complicated by the fact that these bands clearly are composed of two distinct transitions. This observation is precedented for platinum(II) diimine bis(acetylide) complexes.[13] It is noteworthy that as the electron-donating ability of the acetylide ligands increases, the MLCT absorption bands red shift by ca. 2900 cm^{-1} over the series **1**−**5**. 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 dπ(Pt) orbital energy, leading to lower energy absorption. To support this proposal, we performed cyclic voltammetry studies, and the data are listed in Table 2. All the complexes exhibit two quasireversible couples at ca. −0.85 and −1.33 V versus SCE. The insensitivity of the potentials toward the acetylide ligands suggests that these couples originate mainly from the terpyridyl reductions with some mixing of the Pt(II) metal character.[6] Irreversible anodic waves were observed at ca. +1.10 to +1.56 V versus SCE. With reference to the previous studies on other platinum complexes,[6,14] metal-centered oxidation from Pt(II) to Pt(III) is tentatively assigned. The oxidations of complexes **1** and **2** occur at more positive potentials than the other three. This observation could be attributed to the electron delocalization within the aryl and acetylide groups in the aryl-acetylide ligands, resulting in larger electron-donating ability compared to that of the alkyl-acetylide ligands.

Complexes **1**−**5** show well-resolved vibronic structured emission at 510−700 nm in methanol/ethanol (1:1) glass at 77 K. Figure 2 gives the emission spectrum of **4** upon excitation at 430 nm and the excitation spectrum for this emission. The emission mirrors the excitation spectrum. The vibronic internal is ca. 1270 cm^{-1}, which corresponds to the aromatic vibrational mode of the terpyridyl ligands.[6] All these complexes display intense photoluminescence in fluid solution at room temperature. Figure 3 shows the emission spectra of these complexes in degassed dichloromethane at room temperature, obtained on a Perkin Elemer LS50B spectrofluorometer. In addition, the photoluminescence quantum yields (Φ_{em}) were determined by the optical dilute method[15] using a degassed acetonitrile solution of [Ru(bpy)$_3$]-

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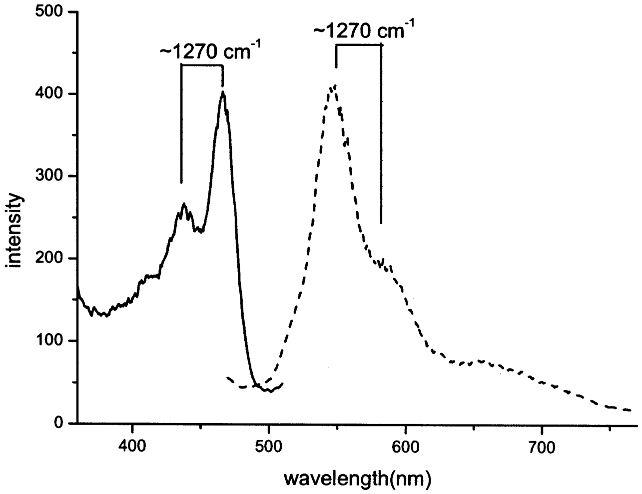

Figure 2. Emission and excitation spectra of complex **4** in methanol/ethanol (1:1) glass at 77 K.

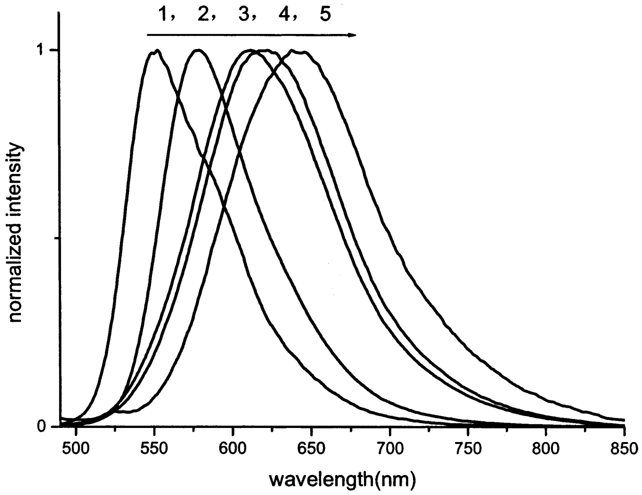

Figure 3. Emission spectra of complexes **1**−**5** measured in deoxygenated CH_2Cl_2 solution.

$(PF_6)_2$ as the reference ($\Phi_{em} = 0.062$).[16] 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 quantum yields and lifetimes for complexes **1**−**5** are listed in Table 1. Yam and co-workers[6] reported the photoluminescence quantum yields and lifetimes in acetonitrile solution of a series of platinum(II) terpyridyl acetylide complexes, $[Pt(trpy)C{\equiv}CR]PF_6$, where R is a substituted phenyl group. These complexes show photoluminescence quantum yields smaller than 0.012 and lifetimes shorter than 0.5 μs in acetonitrile at room temperature. For comparison, we chose one of these complexes, $[Pt(trpy)(C{\equiv}CC_6H_5)]ClO_4$ (**6**), which exhibits the greatest emission quantum yield and the longest lifetime in acetonitrile among these complexes, and we measured its emission quantum yield and lifetime in dichloromethane. The data are also listed in Table 1.

The large Stokes shift and lifetime in the microsecond range for the photoluminescence of **1**−**5** suggest that the emission originates from a triplet parentage, which is tentatively assigned as arising from the ^{3}MLCT state. An excimeric emission assignment is not preferred because the emission maxima are independent of the complex's concentration below saturation. For comparison, the photoluminescence of a chloride derivative [Pt(4′-*p*-tolyl-trpy)Cl]$^{+}$ [11] in dichloromethane at room temperature was measured. The ^{3}MLCT excited state of this complex possesses higher energy (emission occurs at $\lambda_{max} = 540$ nm, $\tau = 0.54$ μs) than those of complexes **1**−**5**. Furthermore, over the series **1**−**5**, the emission maxima shift to longer wavelengths as the electron-donating ability of the acetylide ligands increases (Table 1), which is consistent with the observations by Eisenberg,[17] Yam,[6] and others[13] on the aromatic diimine, terpyridyl, and cyclometalated platinum(II) acetylide complexes. These observations further demonstrate that one can use an electron-rich ancillary ligand to raise the HOMO energy of the metal center, and hence to decrease the energy of the ^{3}MLCT excited states. Significantly, **1**−**5** show high photoluminescence quantum yields and long lifetimes in solution at room temperature. Compounds **1** and **2**, the complexes with alkyl-substituted acetylide ligands, are even more unique in their emission lifetimes and quantum yields. For example, complex **1** shows emission with lifetime of ca. 15 μs and quantum yield of ca. 0.30 in degassed dichloromethane at room temperature. To our knowledge, this is the first example of Pt(II) terpyridyl complexes which exhibit photoluminescence with such a long lifetime and high quantum yield. This observation may be rationalized by the fact that the strong electron-donating acetylide ligands raise the HOMO of the metal center, thus reducing the MLCT excited state energy. On the other hand, the strong ligand field of the C≡CR moiety increases the energy of the d−d excited state. As a result, the energy difference between the MLCT and the d−d states increases, and the radiationless decay of the MLCT state via d−d state is less prevalent. However, inspection of the data in Table 1 reveals that the emission lifetime and quantum yield decrease with the increase in the electron-donating ability of the acetylide ligand across series **1**−**5**. This trend is in accord with the energy gap law.[18]

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Supporting Information Available: The data of ^{1}H NMR spectroscopies, HR-MS spectrometries, elemental analyses, and infrared spectroscopies of complexes **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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