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Multiple Ligand-Based Emissions from a Platinum(II) Terpyridine Complex Attached to Pyrene

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The Pt(trpy)Cl$^+$ (trpy = 2,2′:6′,2″-terpyridine) complex has long been of interest in regard to binding studies with biological macromolecules.[1−3] Despite the existence of a low-lying metal-to-ligand charge-transfer (MLCT) absorption, the complex is virtually nonluminescent in fluid solution,[4] one possible explanation being facile deactivation via a thermally accessible d−d excited state. However, recent studies have shown that complexes of the type Pt(4′-X-T)Cl$^+$, where 4′-X-T denotes a 4′-substituted trpy derivative and X is an electron-donating substituent like the dimethylamino group (NMe$_2$), can have a triplet emission with a lifetime on the order of a microsecond in room-temperature dichloromethane (DCM).[5] In such systems the emitting state takes on intraligand charge-transfer (ILCT) character and the emission lifetime increases even as the excited state shifts to lower energy. The present studies of a series of 4′-Ar-T derivatives, where Ar denotes an aryl substituent, demonstrate how one can prepare systems that have even longer excited-state lifetimes. With pyrene as a substituent, the ILCT character of the absorption becomes dominant, the lifetime extends to 64 μs, and emission from a short-lived singlet (^{1}ILCT) state becomes quite prominent.

The electronic absorption spectra include a series of intraligand $\pi-\pi^*$ transitions below 350 nm and CT absorptions at longer wavelengths. In the compounds of interest Ar ranges from phenyl (Ph) to *p*-methoxyphenyl (pMeOPh) to 1-pyrenyl (Pyre); see Figure 1 and Table 1 for spectra data.[6] Despite the fact that the reduction potentials of the complexes are all very similar (Table 1), the CT absorption energies and intensities vary widely. The aryl substituent can influence the dipole length of the CT transition,[7,8] and the Ar → trpy CT character of the transition becomes increasingly important as the reduction potential of the substituent couple (ArH$^{+/0}$) drops from 2.30 V[9] (benzene) to 1.76 V[10] (anisole) to 1.16 V[9] (pyrene).

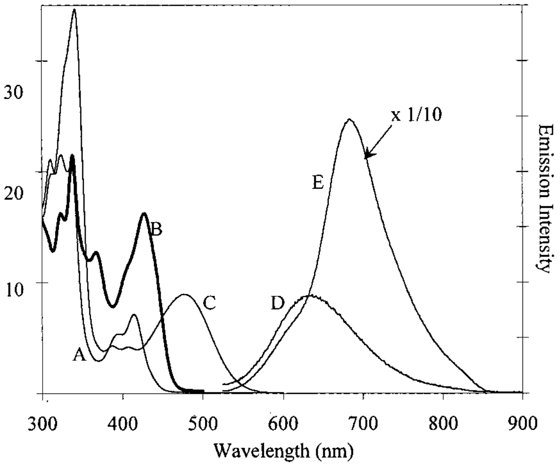

Figure 1. Spectral data in dichloromethane at 293 K showing the absorbance of [Pt(4′-Ph-T)Cl]$^+$ (A), [Pt(4′-pMeOPh-T)Cl]$^+$ (B, thick curve), and [Pt(4′-Pyre-T)Cl]$^+$ (C) and the emission of the 4′-Pyre-T complex in air (D) and under N$_2$ (E). The excitation wavelength was 480 nm in each case.

The aryl substituents have even greater effects on the emission. Thus, even though the nonemissive trpy complex has a higher energy MLCT state, the Pt(4′-Ph-T)Cl$^+$ complex exhibits a structured emission in DCM solution with a lifetime of 85 ns. Due in significant part to the ^{3}ILCT character of their emitting states, the Pt(4′-pMeOPh-T)Cl$^+$ and Pt(4′-Pyre-T)Cl$^+$ complexes exhibit progressively lower energy emissions with even longer lifetimes (Table 1). Thus, the longest wavelength emission comes from the 4′-Pyre-T complex, which exhibits an emission maximum at 685 nm in DCM along with a shoulder at around 640 nm (Figure 1). The introduction of ILCT character also accounts for a systematic moderation of exciplex quenching because the excited state is less susceptible to adduct formation with Lewis bases.[11] The Pt(4′-Ph-T)Cl$^+$ complex is at one extreme where the quenching of the emission is complete in butyronitrile, while in the case of the photoexcited 4′-Pyre-T complex, the basicity of the solvent is of little consequence, and the excited-state lifetime is 18 μs in butyronitrile.

The quenching results with dioxygen are even more striking for the 4′-Pyre-T complex. The key observation is that dioxygen preferentially quenches the emission intensity at 685 nm while the signal at 640 nm persists. Moreover, under aerobic conditions, it is possible to measure two emission lifetimes in the nanosecond regime. In accordance with the steady-state emission spectrum, time-resolved emission measurements reveal that the major

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(1) Howe-Grant, M.; Lippard, S. J. *Biochemistry* **1979**, *18*, 5762−5769.

(2) Ratilla, E. M. A.; Brothers, H. M., II.; Kostic, N. M. *J. Am. Chem. Soc.* **1987**, *109*, 4592−4599.

(3) Peyratout, C. S.; Aldridge, T. K.; Crites, D. K.; McMillin, D. R. *Inorg. Chem.* **1995**, *34*, 4484−4489.

(4) Aldridge, T. K.; Stacy, E. M.; McMilllin, D. R. *Inorg. Chem.* **1993**, *33*, 722−727.

(5) Crites, D. K.; Cunningham, C. T.; McMillin, D. R. *Inorg. Chim. Acta* **1998**, *273*, 346−353.

(6) Standard synthetic methods yielded the 4′-substituted terpyridines. (Krohnke, F. *Synthesis* **1976**, 1−24. Albano, G.; Balzani, V.; Constable, E. C.; Maestri, M.; Smith, D. R. *Inorg. Chim. Acta* **1998**, *277*, 225−231.) Preparation of the 4′-substituted platinum terpyridine complexes also followed standard synthetic methods. (Büchner, R.; Cunningham, C. T.; Field, J. S.; Haines, R. J.; McMillin, D. R.; Summerton, G. C. *J. Chem. Soc., Dalton Trans.* **1999**, 711−717. Ref. 5.) The complexes all gave good microanalyses as salts of the tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate anion (TFPB). The most difficult synthesis began with the preparation of analytically pure 4′-Pyre-T via (1) aldol condensation of 2-acetylpyridine with pyrene-1-carboxaldehyde, (2) KO^{t}Bu-catalyzed Michael addition of 2-acetylpyridine in THF, (3) ring closure with [NH$_4$]-OAc as well as air oxidation in refluxing ethanol, and (4) recrystallization from MeOH/CHCl$_3$. Formation of [Pt(4′-Pyre-T)Cl]TFPB involved (1) treatment of dibenzonitriledichloroplaninum(II) with 1 equiv of AgSbF$_6$ in acetonitrile, (2) reaction with 4′-Pyre-T and precipitation as the crude SbF$_6^-$ salt, (3) exposure to a small excess of [Bu$_4$N]Cl in warm acetonitrile, and (4) metathesis of the Cl$^-$ salt.

(7) Phifer, C. C.; McMillin, D. R. *Inorg. Chem.* **1986**, *25*, 1329−1333.

(8) Damrauer, N. H.; Boussie, T. R.; Devenney, M.; McCusker, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 8253−8268.

(9) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124−2130.

(10) Vauthey, E.; Högemann, C.; Albros, X. *J. Phys. Chem. A* **1998**, *102*, 7362−7369.

(11) Crites, D. K.; McMillin, D. R. *Coord. Chem. Rev.*, in press.

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Table 1. Physical Data for $[Pt(4'\text{-}X\text{-}T)Cl]^+$ Systems in Solution at 293 K

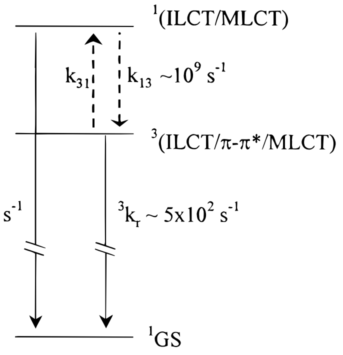
		emission data[a] (two solvents)				
		dichloromethane			butyronitrile	$E°$ [d] DMF
complex	absorbance[b] λ_{max}, nm	λ_{max},[c] nm	τ, μs	$10^3\phi$	λ_{max}, nm	V vs $Fc^{+/0}$
$[Pt(trpy)Cl]^+$	305, 320, 340, 388, 405					−1.24 (70, 1.1)
$[Pt(4'\text{-}Ph\text{-}T)Cl]^+$	310, 323, 336, 390sh, 414 (7100)	535, 570sh, 608sh [538, 572sh, 610sh]	0.085	2.1		−1.23 (80, 1.2)
$[Pt(4'\text{-}pMeOPh\text{-}T)Cl]^+$	303sh, 322, 337, 366, 403sh, 426 (16150)	560, 590sh, 650sh [562, 600sh, 670sh]	5.2	46	555, 585sh	−1.26 (90, 1)
$[Pt(4'\text{-}Pyre\text{-}T)Cl]^+$	310sh, 328sh, 340, 387, 405, 476 (8910)	∼640sh, 685 [700]	64	34	672	−1.22 (70, 1.2)

[a] Estimated errors in lifetime (τ) and quantum yield (ϕ) are ±10%. Deoxygenated solution. [b] Molar absorptivity ($M^{-1}\ cm^{-1}$) in parentheses. Solvent DCM. [c] Maxima from corrected spectra in brackets. [d] Ferrocene reference. $E_{p,c}-E_{p,a}$ peak-to-peak separation in mV and i_c/i_a current ratio in parentheses.

component has a 1 ns lifetime and an emission maximum at around 640 nm. On the other hand, with a CCD detector, one can still observe the signal with a maximum at 685 nm, though the lifetime has dropped to 910 ns. Both signals originate from the complex because the excitation spectrum matches the absorption spectrum of $Pt(4'\text{-}Pyre\text{-}T)Cl^+$ with or without the presence of dioxygen. Except for changes in intensity, the emission spectrum does not depend on concentration (3−40 μM in DCM). The radiative rate constant associated with the long-lived (685 nm) emission is about 530 s^{-1} and is more than an order of magnitude smaller than that expected for typical ^{3}MLCT emission (for $Pt(4'\text{-}Ph\text{-}T)Cl^+$ $k_r = 2.6 \times 10^4\ s^{-1}$). In contrast, with an emission yield on the order of 10^{-3} in an aerated solution, the 640 nm component exhibits a radiative rate constant of ca. $10^6\ s^{-1}$. This value agrees with those of the ^{1}ILCT emissions reported by Pilato and co-workers,[12] and a similar assignment applies here.

The temperature dependence of the luminescence confirms that two distinct excited states contribute to the emission. Thus, in the absense of dioxygen the intensity at the 685 nm maximum *increases* but the intensity of the high-energy shoulder *decreases* at progressively lower temperatures. These results indicate that there is an equilibrium involving two excited states and that the shoulder arises from the thermal population of the higher lying of the two emitting states. Examination of the spectra in Figure 1 strongly suggests that the latter component stems from the ^{1}ILCT state.[13] Since the singlet−triplet splitting is relatively small for CT states, the 685 nm component logically corresponds to the associated ^{3}ILCT state; however, pyrene itself has a low-lying $^3\pi-\pi$ state at about this energy.[14] The simplest three-state model that can explain the results appears in Scheme 1 along with estimated rate constants and plausible, mixed-parentage state assignments. This model assumes the participation of only one triplet state, but a more complicated equilibrium that includes close-lying ^{3}ILCT and $^3\pi-\pi$(Pyre) states is also feasible, analogous to results with ruthenium polypyridine complexes bearing a covalently attached pyrene group.[15,16] Although the emission from the 4′-Pyre-T complex primarily represents intraligand excitation, the emitting states undoubtedly have an admixture of MLCT character as indicated in Scheme 1. Indeed, d-orbital participation is necessary to explain the emission yield of the 685 nm component because the radiative process would be strongly spin-forbidden in a pure intraligand triplet state.[17]

Scheme 1



In summary, these results demonstrate the ease with which one can alter the orbital parentage of the lowest energy excited state of the platinum(II) terpyridine system. By a simple change of a substituent, it is possible to adjust the energy and the intensity of the absorbance and at the same time tune the energy, lifetime, emission yield, and reactivity of the luminescent excited state over a wide range.

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Supporting Information Available: Figures showing the time-resolved emission spectrum of $Pt(4'\text{-}Pyre\text{-}T)Cl^+$ at 293 K in deoxygenated DCM and the temperature-dependent emission spectrum of $Pt(4'\text{-}Pyre\text{-}T)Cl^+$ in deoxygenated DCM. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Kaiwar, S. P.; Vodacek, A.; Blough, N. V.; Pilato, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 3311−3316.

(13) Note that the 640 nm emission component (Figure 1D, which also tracks the shoulder on the signal from the deoxygenated sample) tails into the ^{1}ILCT absorption band in accordance with Stokes shifted emission from the same absorbing state.

(14) The highest energy vibronic component of the 77 K emission from the free 4′-Pyre-T ligand appears at 608 nm.

(15) Simon, J. A.; Curry, S. L.; Schmehl, R. H.; Schatz, T. R.; Piotrowiak, P.; Jin, X. Q.; Thummel, R. P. *J. Am. Chem. Soc.* **1997**, *119*, 11012−11022.

(16) Harriman, A.; Hissler, M.; Khatyr, A.; Ziessel, R. *Chem. Commun.* **1999**, 735−736.

(17) Colombo, M. G.; Hauser, A.; Güdel, H. U. *Inorg. Chem.* **1993**, *32*, 3088−3092.