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Long-Lived Emissions from 4′-Substituted Pt(trpy)Cl$^+$ Complexes Bearing Aryl Groups. Influence of Orbital Parentage

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Pt(trpy)Cl$^+$, where trpy denotes 2,2′:6′,2″-terpyridine, is a versatile binding agent but has a limited photochemistry due to a short excited-state lifetime. However, this work shows that the introduction of aryl substituents at the 4′ position of the trpy ligand drastically alters the picture. For the substituents phenyl, *p*-methoxyphenyl, 1-naphthyl, 2-naphthyl, 9-phenanthrenyl, and 1-pyrenyl, the ligand abbrevations are 4′-Ph-T, 4′-pMeOPh-T, 4′-Npl-T, 4′-Np2-T, 4′-Phe9-T, and 4′-Pyre1-T, respectively. Techniques utilized include electrochemistry as well as absorption and emission spectroscopies. While the lowest energy excited states of Pt(4′-Ph-T)Cl$^+$ and the parent complex Pt(trpy)Cl$^+$ exhibit mainly metal-to-ligand charge-transfer (MLCT) character, the emitting state takes on aryl-to-trpy intraligand charge-transfer (ILCT) character as the substituents become more electron-donating. Studies of Zn(trpy)Cl$_2$, its aryl-substituted analogues, and the free ligands themselves provide information about the relative energies of participating ILCT and intraligand $^3\pi-\pi^*$ excited states. Even though the emission energy decreases when larger aryl groups are present, the emission lifetime increases all the way from 85 ns for Pt(4′-Ph-T)Cl$^+$ to 64 μs for Pt(4′-Pyre1-T)Cl$^+$. (Data from deoxygenated, room-temperature dichloromethane solution.) Intraligand character appears to dominate in the case of Pt(4′-Pyre1-T)Cl$^+$, which is unique in the series in that it exhibits singlet and triplet emissions in solution. In aerated solution the complex shows prompt as well as delayed fluorescence. Finally, studies in donor media establish that the introduction of intraligand character inhibits solvent-induced exciplex quenching.

Introduction

The distinctive molecular and electronic structures that occur in d^8 platinum(II) systems give rise to some unusual and potentially useful excited-state properties. In particular, axial interactions play a prominent role in this chemistry because the planar coordination geometry permits easy access to important frontier orbitals of the metal center. For example, excimer formation and excimer emission have been observed in some instances when face-to-face complex formation promotes delocalization of the excitation through metal−metal interactions.[1−3] Interactions with Lewis bases at the open coordination sites can induce a type of exciplex quenching,[4,5] and there are also reports describing photoinduced atom-transfer and/or oxidative-addition reactivity.[6] Applications in photomedicine may be feasible in view of the intrinsically high affinity that platinum has for nitrogen and sulfur donors, which are ubiquitous in biological milieu. Indeed, a variety of platinum systems interact with biological macromolecules including DNA, and some systems have proven to be highly effective anticancer agents.[7−11]

A major limitation to the development of the photochemistry is that until recently there have been few examples of platinum(II) complexes that exhibit luminescence or have long-lived ($\tau \approx 1$ μs) excited states in solution. One reason is that the metal-centered, or d−d, excited states are intrinsically short-lived because they involve the population of the strongly metal−ligand antibonding orbital, usually designated as the $d_{x^2-y^2}$ orbital. However, the observation of emission is possible when the complex has relatively low-energy intraligand excited states. Examples include complexes with porphyrins,[12] 8-hydroxyquinolate,[13] and dithiolates attached to heteroaromatic groups.[14,15] A number of cyclometalated complexes containing Pt−C bonds also exhibit emission from low-lying states with substantial $^3\pi-$

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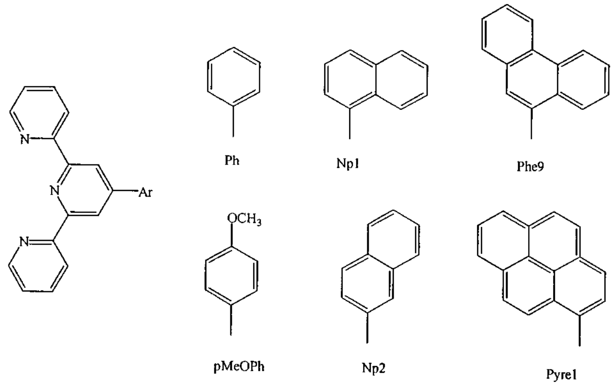
π^* character,[16−20] as do some complexes with polypyridine ligands.[21,22] Complexes that have low-lying charge-transfer (CT) excited states may also exhibit photoluminescence in solution.[23−26]

For a number of reasons our interest has focused on derivatives of Pt(trpy)Cl$^+$ where trpy denotes 2,2′:6′,2″-terpyridine. One is that these systems are bifunctional DNA-binding agents that can intercalate or bind covalently to DNA.[27−29] The fact that trpy acts as a planar, tridentate ligand is another plus. Deactivation via a d−d excited state with a tetrahedral coordination geometry is therefore less likely;[30] unfortunately, relatively low-energy d−d states may still occur because of geometric constraints that weaken the bonds to the outer two pyridines of the ligand.[4] Finally, the complexes are potentially luminescent because the lowest-energy bands in the absorption spectrum of Pt(trpy)Cl$^+$ are metal-to-ligand CT bands.[4,31,32] Although the parent compound Pt(trpy)Cl$^+$ is virtually nonluminescent in solution, it is possible to obtain an emissive complex by introducing appropriate substituents in the 4′ position of the trpy ligand. Both π-accepting substituents like CN and, even more so, π-donating groups like NR_2 dramatically extend the lifetime.[33] Conjugating groups such as phenyl or naphthyl represent another class of potentially useful π-interacting substituents,[34] and there are already indications that complexes of the type Pt(4′-Ar-T)Cl$^+$ can be highly emissive.[32,35] (Herein, the abbreviation 4′-Ar-T denotes a trpy derivative with an aryl substituent in the 4′ position; see Chart 1.) The studies described below reveal that easily ionized, fused-ring aryl substituents with low-lying $\pi-\pi^*$ states can have a profound influence on the photophysics of these complexes.

Experimental Section

Materials. Johnson and Matthey Pharmaceuticals graciously supplied K_2PtCl_4, while the dibenzonitriledichloroplatinum(II) came from Strem Chemicals. Aldrich Chemical Co. was the vendor for $AgSbF_6$, $KSbF_6$, KPF_6, and ferrocene. The $ZnCl_2$ came from Mallinckrodt, and the Na[TFBP]·nH$_2$O was available from a previous study[33] (TFPB = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate). The organics 2-acetylpyridine, naphthalene-1-carboxaldehyde, naphthalene-2-carboxaldehyde, phenanthrene-9-carboxaldehyde, pyrene-1-carboxaldehyde, 1,5-cyclooctadiene, potassium *tert*-butoxide, 2,2′:6′,2″-terpyridine, *p*-anisaldehyde, tetrabutylammonium chloride hydrate, and tetrabutylammonium hexafluorophosphate (TBAH) all came from Aldrich Chemical Co. Exciton supplied the laser dyes. Reagent-grade chemicals proved satisfactory for synthetic purposes, but the purification of the TBAH electrolyte required two recrystallizations from ethanol. For spectral studies the high-purity distilled-in-glass grade solvents acetonitrile (MeCN), *N,N′*-dimethylformamide (DMF), and dichloromethane (DCM) came from Scientific Products, while the ^{1}H NMR solvent $CDCl_3$ was a product of Cambridge Isotope Labs.

Chart 1



Syntheses. Various reports describe the same basic procedure for the synthesis of 4′-Ar-T derivatives that sufficed for the preparation 4′-phenyl-2,2′:6′,2″-terpyridine (4′-Ph-T) as well as 4′-(1-naphthyl)-2,2′:6′,2″-terpyridine (4′-Np1-T).[36,37,39] The method of Albano et al. yielded 4′-(*p*-methoxyphenyl)-2,2′:6′,2″-terpyridine (4′-pMeOPh-T) and other terpyridine derivatives described below.[38] Published methods were also useful for the preparation of Pt(COD)Cl$_2$, where COD denotes 1,5-cyclooctadiene,[40] and the Zn(4′-Ar-T)Cl$_2$ compounds.[41,42] Far-IR spectra confirmed the presence of the zinc chloride stretching frequencies previously identified for Zn(trpy)Cl$_2$.[42] With one exception, the method of Annibale et al.[43] yielded the corresponding platinum complex via reaction with Pt(COD)Cl$_2$. The same method also gave the 4′-Pyre1-T complex; however, the preparations always contained a highly emissive impurity that appeared to have solvent in place of the chloride ligand. As described previously, the method of Büchner et al.[35] gave an analytically pure form of the 4′-Pyre1-T complex.[44] A simple metathesis reaction in DCM allowed for the exchange of counterion as needed. Supporting analytical results appear below.

4′-(1-Naphthyl)-2,2′:6′,2″-terpyridine. Anal. Calcd for $C_{25}H_{17}N_3$: 83.54% C, 4.77% H, 11.69% N. Found: 83.22% C, 4.70% H, 11.49% N. ^{1}H NMR in $CDCl_3$ (in ppm): δ 8.72 (m, 2H), 8.66 (m, 2H), 8.61 (s, 2H), 7.88−7.98 (2H), 7.88 (m, 2H), 7.4−7.6 (5H), 7.33 (m, 2H). Anal. Calcd for [Pt(4′-Np1-T)Cl]PF$_6$·3MeCN ($C_{25}H_{17}ClF_6N_3PPt$·3(CH$_3$CN): 41.10% C, 2.40% H, 6.10% N. Found: 41.48% C, 2.34% H, 5.88% N.

4′-(9-Phenanthrenyl)-2,2′:6′,2″-terpyridine (4′-Phe9-T). Anal. Calcd for $C_{29}H_{19}N_3$: 85.06% C, 4.68% N, 10.26% N. Found: 85.06% C, 4.58% H, 10.20% N. ^{1}H NMR in $CDCl_3$ (in ppm): δ 8.68−8.82 (6H),

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8.67 (s, 2H), 7.82−8.02 (5H), 7.50−7.74 (4H), 7.34 (m, 2H). Anal. Calcd for [Pt(4′-Phe9-T)Cl]PF_6·H_2O ($C_{29}H_{21}ClF_6N_3OPPt$): 43.38% C, 2.64% H, 5.23% N. Found: 43.02% C, 2.55% H, 5.06% N.

4′-(1-Pyrenyl)-2,2′:6′,2″-terpyridine (4′-Pyre1-T). Anal. Calcd for $C_{31}H_{19}N_3$: 85.89% C, 4.42% H, 9.69% N. Found: 85.26% C, 4.19% H, 9.52% N. ^1H NMR in $CDCl_3$ (in ppm): δ 8.72−8.8 (4H), 8.70 (m, 2H), 8.0−8.3 (9H), 7.93 (m, 2H), 7.36 (m, 2H). Anal. Calcd for [Pt-(4′-Pyre1-T)Cl]TFPB ($C_{63}H_{31}BClF_{24}N_3Pt$): 49.55% C, 2.05% H, 2.75% N. Found: 49.45% C, 1.93% H, 2.68% N.

4′-(2-Naphthyl)-2,2′:6′,2″-terpyridine·H_2O (4′-Np2-T·H_2O). Anal. Calcd for $C_{25}H_{19}N_3O$: 79.55% C, 5.07% H, 11.13% N. Found: 79.32% C, 4.99% H, 10.69% N. ^1H NMR in $DCCl_3$ (in ppm): δ 8.87 (s, 2H), 8.76 (d, 2H), 8.70 (d, 2H), 8.41 (s, 1H), 7.95 (m, 6H), 7.53 (m, 2H), 7.36 (m, 2H). Anal. Calcd for [Pt(4′-Np2-T)Cl]TFPB ($C_{57}H_{29}ClF_{24}N_3$-BPt): 47.11% C, 2.01% H, 2.89% N. Found: 47.02% C, 1.93% H, 2.90% N.

[Pt(4′-Ph-T)Cl]TFPB. Anal. Calcd for ($C_{53}H_{27}BClF_{24}N_3Pt$): 45.37% C, 1.94% H, 2.99% N. Found: 45.56% C, 2.03% H, 3.23% N.

[Pt(4′-pMeOPh-T)Cl]PF_6. Anal. Calcd for ($C_{22}H_{17}ClF_6N_3OPPt$): 36.96% C, 2.40% H, 5.88% N. Found: 37.03% C, 2.56% H, 5.76% N.

Other Methods. In the electrochemical studies the working electrode was either a gold, platinum, or glassy carbon disk, while the auxiliary electrode was a platinum wire. The experimental setup involved an aqueous Ag/AgCl (3 M NaCl) reference electrode, but it is more useful to quote potentials vs ferrocene in the actual working medium. The potentials reported are the mean of the cathodic ($E_{p,c}$) and anodic ($E_{p,a}$) peaks in the cyclic voltammogram. Except for a few attempted oxidations in dichloromethane and acetonitrile, the electrolyte solution was 0.1 M TBAH in DMF and the scan rate was 50 mV s^{-1}.

Prior to the solution emission studies, a series of freeze−pump−thaw cycles removed dioxygen from the samples. A finger Dewar containing liquid nitrogen facilitated measurements of frozen solutions. Observation of the phosphorescence from 4′-Pyre1-T required the use of a rotating-can phosphoroscope constructed from routine laboratory equipment. The addition of an extra mole equivalent of $ZnCl_2$ helped suppress dissociation of the trpy ligand during emission studies of the Zn(4′-Ar-T)Cl_2 complexes in acetonitrile. The method of Parker and Rees[45] allowed the estimation of emission quantum yields (at 25 °C with $Ru(bpy)_3{}^{2+}$ in water as the standard, $\Phi = 0.042$).[46] As described previously,[47] the corrected spectrum of $Ru(bpy)_3{}^{2+}$ provided a basis for estimating emission correction factors at longer wavelengths (beyond 500 nm). A standard procedure permitted the conversion from a wavelength to an emission-energy scale.[48]

Except for a few measurements with a photon-counting apparatus, the detector for the lifetime measurements was either a photomultiplier tube connected to a sampling oscilloscope or the CCD camera system described below. Appropriate long-pass filters were present to block stray radiation. A fit of the oscilloscope trace to an exponential decay function yielded the lifetime, and in all cases the residual plot justified the single-exponential model. In the case of the CCD measurements, the lifetime estimate came from a semilog plot of the integrated spectral intensity vs time. For the short-lived emission from the 4′-Pyre1-T complex in aerobic solution, it was necessary to convolute the excitation profile with the spectral response in order to extract a lifetime with standard software. It was possible to obtain a crude spectrum of the short-lived transient by plotting the raw intensity (integrated over a fixed time interval and obtained with a fixed number of lamp flashes) vs the wavelength of detection.

Instrumentation. The absorption spectrometer was a Varian Cary 100 Bio instrument, and the spectrofluorometer was a SLM-Aminco SPF-500C. The cryostat was an Oxford Instruments model DN1704 liquid-nitrogen-cooled system complete with an Oxford Instruments model ITC4 temperature controller. A description of the laser excitation system and photomultiplier detector appears in the literature.[49] Other experiments involved the same excitation source, but a LN/CCD-1024EUV CCD camera captured the emission spectrum as a function of time in conjunction with a SpectraPro 275 monochromator/spectrograph from Acton Research Corporation, a ST-135 detector controller, and a PG-200 programmable pulse generator from Princeton Instruments. The controlling microcomputer was a Macintosh Quadra 610 equipped with the program KestrelSpec. The flash-lamp instrument for the short-lived signals was a LS-100 luminescence spectrophotometer from Photon Technology International with a mixture of 30% N_2 and 70% He in the flash lamp. The cyclic voltammetry unit was a model CV-27 from Bioanalytical Systems, Inc., connected to a Hewlett-Packard 7015B *XY* chart recorder. The ^1H NMR spectrometer was a Varian Gemini 200. The FTIR was a Perkin-Elmer 2000.

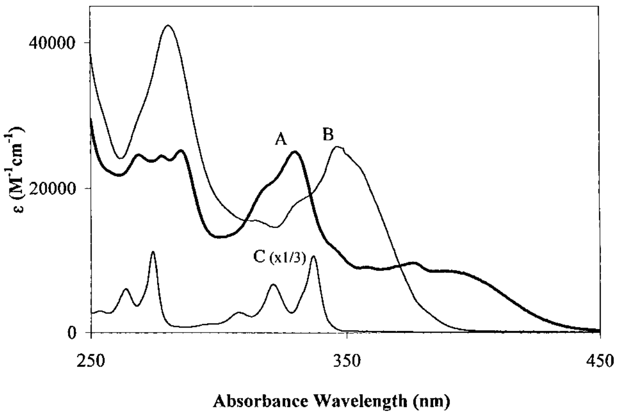

Figure 1. Absorption spectra of 4′-Pyre1-T related systems in DCM at room temperature: (A, thick line): Zn(4′Pyre1-T)Cl_2; (B) 4′-Pyre1-T; (C) pyrene.

Results

Electronic Absorption Data. At wavelengths below about 350 nm, the $\pi-\pi^*$ transitions of the ligand dominate the absorption spectra. Although the $\pi-\pi^*$ absorptions of free trpy fall below 300 nm, coordination to a metal center induces the ligand to convert from the trans−trans to the cis−cis form such that $\pi-\pi^*$ absorption bands occur in the neighborhood of 330 nm.[50,51] When the Ar substituent is a large aromatic group like pyrene, the substituent absorbs in the near-UV as well, and there is apparently some coupling between the chromophores because the spectra are not simply additive. In the case of the free 4′-Pyre1-T ligand, the pyrene moiety is largely responsible for the absorbance at wavelengths greater than 320 nm (Figure 1), but the absorption at around 330 nm in the spectrum of the Zn(4′-Pyre1-T)Cl_2 complex probably reflects $\pi-\pi^*$(trpy) character as well. For a summary of absorption data of the zinc complexes in DCM and acetonitrile, see Table 1. In addition to the quasi-localized transitions discussed so far, Zn(4′-Phe9-T)Cl_2, Zn(4′-Np1-T)Cl_2, and Zn(4′-Pyre1-T)Cl_2 exhibit Ar → trpy intraligand charge-transfer (ILCT) transitions, usually shoulders, beyond about 350 nm. These assignments are consistent with the results of Albano et al., who have investigated a zinc complex of trpy bearing an anthracene substituent in the 4′-position,[38] and the fact that the same absorptions do not appear in the near-UV spectra of the free ligands. In the absence of a metal ion to stabilize the developing charge density,[52] the ILCT transitions

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Table 1. Absorbance and Emission Data for 4′-Ar-T and Zn(4′-Ar-T)Cl_2 Systems[a]

	λ_{max}, nm (absorbance) Zn(4′-Ar-T)Cl_2		λ_{max}, nm (emission)		
			Zn(4′-Ar-T)Cl_2		4′-Ar-T
4′-Ar-T	DCM	MeCN[b]	DCM	MeCN[b]	butyronitrile, 77 K
trpy	283, 318, 331	282, 318, 331	340,352, 370sh	340, 353, 370sh	434, 453sh, 465, 485, 502sh, 525sh
4′-Ph-T	285, 322, 335	284, 323, 335	349, 364, 380sh	348, 363, 380sh	435, 455sh, 466, 486, 501sh, 525sh
4′-pMeOPh-T	284, 327, 337sh	282, 327, 337sh	410	458	436, 455sh, 467, 487, 503sh, 527sh
4′-Npl-T	286, 322, 333sh, 360sh	283, 322, 334sh, 360sh	427	465	496, 533, 570sh
4′-Phe9-T	283, 296sh, 322, 333sh, 355sh	283, 294sh, 321, 332sh 357sh	432	466	494, 530, 570sh
4′-Pyrel-T	285, 316sh, 331, 345sh, 358, 377, 395sh	284, 315sh, 327, 343sh, 357, 374, 387sh	490	548	494, 531, 570sh

[a] Room-temperature data except as indicated. [b] Solutions contained 1 equiv of excess $ZnCl_2$.

Table 2. Physical Data for Pt(4′-Ar-T)Cl^+ and Related Systems

	λ_{max}, nm (absorbance)		E_0,[a] V vs $Fc^{+/0}$	
Pt(4′-Ar-T)Cl^+	DCM	MeCN[b]	DMF	
trpy[c]	283, 307, 320, 335, 351sh, 388sh, 405	377 (2200), 390sh	−1.24 (70, 1.1)	−1.80 (60, 1.0)
4′-Ph-T[c]	283, 309, 322, 336, 397sh, 412	380sh, 402 (5200)	−1.22 (80, 1.2) [2.30][d]	−1.76 (65, 1.0)
4′-pMeOPh-T[c]	284, 301sh, 321, 336, 366, 405sh, 426	393sh, 413 (14800)	−1.26 (90, 1.0) [1.76][e]	−1.79 (60, 1.1)
4′-Npl-T	285, 306sh, 323sh, 336, 381sh, 423	385sh, 406 (7300)	−1,22 (70, 1.2) [1.60][f]	−1.76 (65, 1.0)
4′-Np2-T	284, 326sh, 338, 405sh, 425	390sh, 411 (10800)	−1.22 (90, 1.1)	−1.75 (60, 1.0)
4′-Phe9-T	285, 296sh, 322sh, 335, 385sh, 429	388sh, 408 (7900)	−1.22 (70, 1.2) [1.58][f]	−1.76 (70, 1.0)
4′-Pyrel-T[c]	284, 310sh, 329sh, 340, 387, 405, 476	380sh, 432 (9100)	−1.22 (70, 1.2) [1.20][f]	−1.74 (70, 1.0)

[a] Peak-to-peak separation and i_c/i_a current ratio in parentheses. E_0 for parent ArH hydrocarbons in square brackets vs SCE. [b] Molar absorptivities (M^{-1} cm^{-1}) in parentheses. [c] Reference 44. [d] Pyse, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124−2130. [e] Vauthey, E.; Högemann, C.; Allonas, X. *J. Phys. Chem. A* **1998**, *102*, 7362−7369. [f] Quoted in the following: Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401−449.

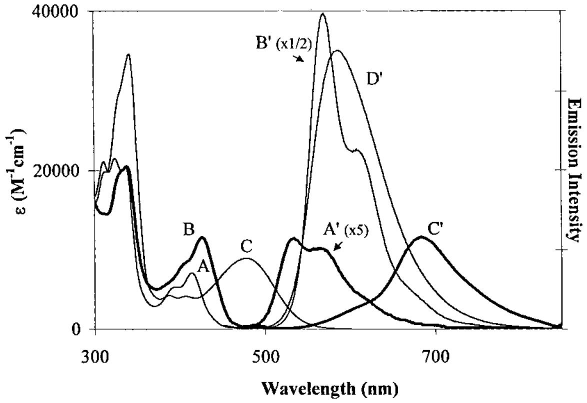

Figure 2. Absorption spectra of Pt(4′-Ar-T)Cl^+ complexes in DCM at room temperature: (A) Pt(4′-Ph-T)Cl^+; (B, thick line) Pt(4′-Np2-T)Cl^+; (C) Pt(4′-Pyre1-T)Cl^+. Spectra A′−C′ are the corresponding (uncorrected) emissions. Spectrum D′ is the emission of the Pt(4′-Np1-T)Cl^+ complex.

shift toward higher energy where identification is difficult. The one exception is the 4′-Pyre1-T ligand, which exhibits ILCT absorptions in the long-wavelength end of its UV spectrum, due to the ease of ionization of pyrene. In contrast, Zn(4′-Ph-T)Cl_2 and Zn(4′-pMeOPh-T)Cl_2 do not exhibit low-lying ILCT states even with the metal present because the 4′-substituents are such weak electron donors (see Table 2 for electrochemical data pertaining to the parent arenes).

Not surprisingly, the results in Table 2 and Figure 2 reveal that Pt(4′-Ar-T)Cl^+ systems also exhibit intraligand $\pi-\pi^*$ absorptions in the UV region. In addition, like the Pt(trpy)Cl^+ system itself,[4,31,32] each of the platinum complexes exhibits moderately intense absorptions in the range 400−500 nm. Consistent with metal-to-ligand charge-transfer (MLCT) character, the CT bands show the same type of solvent dependence as the transitions in other platinum(II) polypyridine complexes (Table 2).[53−55] In particular, a shift toward shorter wavelength in a more polar solvent is consistent with a decrease in molecular dipole moment in the excited state.[4,56] At the same time, the CT bands are remarkably sensitive to the substituent. More specifically, the introduction of a large aryl substituent induces a shift to longer wavelength along with an intensity increase (Figure 2).

Electrochemistry. The Pt(4′-Ar-T)Cl^+ systems each exhibit two reduction waves in DMF (Table 2), and the E_0 values are quite similar to those of Pt(trpy)Cl^+. The differences in the electrochemical potentials are surprisingly small, but there may be compensating forces at work. On one hand, the aryl groups are potentially electron-withdrawing relative to hydrogen because of the σ-bonding interaction with another sp^2 carbon.[57] On the other hand, in the context of the π-bonding framework, easily oxidized aryl groups such as pyrenyl may be electron-donating and shift the reduction potential to more negative values, by analogy with the $-NR_2$ group.[33] It is also possible that the delocalization onto the π system of the substituent counteracts the anticipated electron-donating effect. Previous studies have shown that phenyl substituents have a small effect on the electrochemistry of related $Ru(NN)_2^{2+}$ systems.[57] All attempts to observe any type of oxidation waves from either the platinum complexes or the free ligands, including 4′-Pyre1-T, were unsuccessful in DMF, acetonitrile, and DCM.

Emission Spectra. The band assignments for the phosphorescence signals from the free ligands at 77 K are quite clear-cut. For the systems with simple substituents, like 4′-Ph-T or 4′-pMeOPh-T, the phosphorescence spectrum basically parallels the $^3\pi-\pi^*$ emission spectrum of the trpy ligand itself (Table

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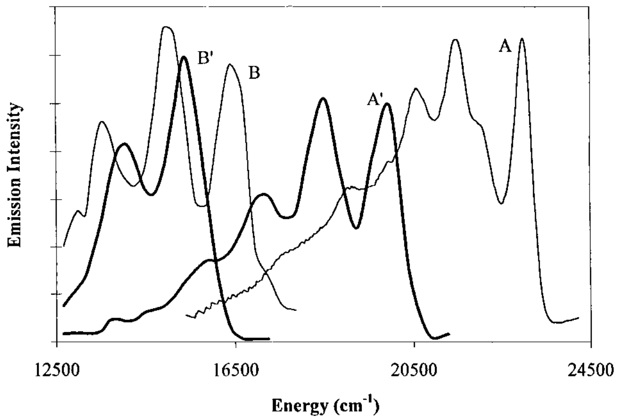

Figure 3. Corrected emission spectra from frozen butyronitrile solutions at 77 K: (A) 4′-Ph-T; (A′, thick line) Pt(4′-Ph-T)Cl^{+}; (B) 4′-Pyre1-T; (B′, thick line) Pt(4′-Pyre1-T)Cl^{+}. Spectra A and B are specifically the phosphorescence signals from the free ligands.

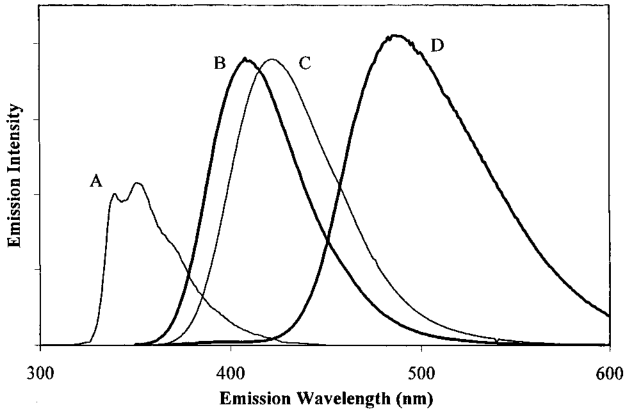

Figure 4. Emission spectra of Zn(4′-Ar-T)Cl$_2$ complexes in DCM at room temperature: (A) Zn(trpy)Cl$_2$; (B, thick line) Zn(4′-pMeOPh-T)Cl$_2$; (C) Zn(4′-Phe9-T)Cl$_2$; (D, thick line) Zn(4′-Pyre1-T)Cl$_2$.

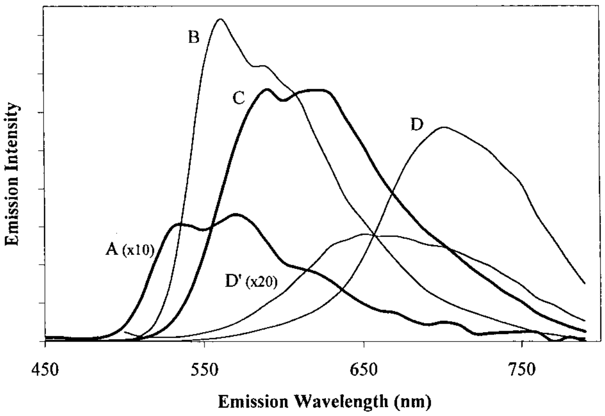

Figure 5. Corrected emission spectra of Pt(4′-Ar-T)Cl^{+} complexes in deoxygenated DCM at room temperature: (A, thick line) Pt(4′-Ph-T)-Cl^{+}; (B) Pt(4′-pMeOPh-T)Cl^{+}; (C, thick line) Pt(4′-Np1-T)Cl^{+}; (D) Pt(4′-Pyre1-T)Cl^{+}; (D′) same as spectrum D but in aerated solution.

1). However, larger substituents have a $^{3}\pi-\pi^{*}$ state at lower energy so that the phosphorescence originates from the substituent instead. The difference in the excitation is obvious in view of the change in the pattern of vibronic band intensities and the shift of the signal to much lower energy (Figure 3).

The same effect occurs in the intraligand fluorescence except that an ^{1}ILCT state can come into play when zinc is present. This is, however, not the case for either Zn(trpy)Cl$_2$ or Zn(4′-Ph-T)Cl$_2$, which show a structured, trpy-based $^{1}\pi-\pi^{*}$ fluorescence signal with practically the same band maxima in DCM and acetonitrile (Table 1). In contrast, the fluorescence spectra of the other zinc complexes exhibit little or no vibronic structure and the emissions shift to lower energies in a more polar solvent (Figure 4 and Table 1). Such a solvent dependence is incompatible with localized $^{1}\pi-\pi^{*}$ emission from either the trpy or the arene moiety, but it is in keeping with emission from a ^{1}ILCT excited state, which is a low-energy state whenever ionization of the substituent is facile. Maximum charge separation develops in excited states that evolve into TICT (twisted intramolecular charge-transfer) states, but this is not a universal phenomenon.[58,59] In line with the proposed assignments, except for Zn-(4′-pMeOPh-T)Cl$_2$, all zinc complexes that exhibit ILCT fluorescence clearly exhibit low-energy charge-transfer bands in the corresponding absorption spectra.

Emission data for the Pt(4′-Ar-T)Cl^{+} series appear in Figure 5 and Table 3. In contrast to to what one finds for the zinc complexes, the emissions from the platinum analogues generally exhibit a small blue shift when a more polar solvent is used. In general, the lifetimes are shorter in the nitrile solvent than in DCM, but they increase with the size of the arene substituent even though the emission maxima shift to longer wavelength. Except for the Pt(4′-Pyre1-T)Cl^{+} system, the corrected emission spectra exhibit weakly resolved vibronic structure in DCM solution at room temperature. The 4′-Np2-T complex is interesting because it has an emission spectrum with a more pronounced structure than the 4′-Np1-T analogue (Figure 2). The explanation is probably that the sterically less demanding C2 linkage allows the substituent to adopt a similar orientation in both the ground and the excited states. Note that the higher molar absorptivity in the CT absorption spectrum of the 4′-Np2-T complex is consistent with a more nearly planar ligand in the ground state. In a rigid glass at 77 K, all of the emissions exhibit enhanced vibronic structure and shift to somewhat higher energies (Figure 6). For a comparison of the 77 K emission spectra of representative 4′-Ar-T ligands along with the corresponding Pt-(4′-Ar-T)Cl^{+} complexes, see Figure 3.

The Pt(4′-Pyre1-T)Cl^{+} complex shows the most unique emission properties in fluid solution. In deoxygenated DCM at room temperature, the uncorrected emission maximum occurs at 685 nm, but there is a small shoulder at ca. 640 nm (Figure 2). Except for changes in intensity, the emission spectrum is independent of concentration in the range investigated (3−40 μM), but the spectral band shape is temperature-dependent. In particular, Figure 7 shows that the relative intensity of the 640 nm shoulder decreases at lower temperatures. Under anaerobic conditions, time-resolved emission data reveal that the entire room-temperature emission spectrum decays with a lifetime of 64 μs. Nevertheless, the emission involves two separate states because the introduction of dioxygen leads to practically complete quenching of the 685 nm component while the emission maximum at 640 nm persists. Both signals originate from the same 4′-Pyre1-T complex because the excitation spectrum matches the absorption spectrum with or without the presence of dioxgen. In aerated DCM at room temperature, the lifetime of the 640 nm component is about 1 ns; however, it is still possible to observe the 685 nm emission if one triggers the CCD detector several nanoseconds after the laser flash. The weak signal obtained under these conditions is complete with the 640 nm shoulder and has a lifetime of 910 ns.

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Table 3. Emission Data for Pt(4′-Ar-T)Cl^+ Complexes in Butyronitrile and Dichloromethane

	butyronitrile		DCM			
Pt(4′-Ar-T)Cl^+	λ_{max}, nm 77 K	λ_{max}, nm 298 K	λ_{max},^{a} nm 298 K	τ, μs 298 K	Φ 298 K	k_r, s^{-1} (Φ/τ)
Pt(trpy)Cl^{+b}	470, 506, 546, 580					
Pt(4′-Ph-T)Cl^{+b}	503, 540, 582		535, 570sh, 608sh [538, 572(s), 610(s)]	0.085	0.0021	2.5×10^4
Pt(4′-pMeOPh-T)Cl^{+b}	526, 564, 613	555, 585sh	560, 590sh, 650sh [562, 600sh, 670sh]	5.2	0.046	8.8×10^3
Pt(4′-Npl-T)Cl^+	540, 587	581	588 [600]	16.6	0.047	2.8×10^3
Pt(4′-Np2-T)Cl^+	542, 583, 625sh	564, 595sh	570, 610sh, 665sh [570, 620, 670sh]	12.1	0.068	5.6×10^3
Pt(4′-Phe9-T)Cl^+	538, 572	581	595 [610]	21.0	0.070	3.3×10^3
Pt(4′-Pyrel-T)Cl^{+b}	648, 702	650 (broad)	640 [650]	1 ns	0.001	1.0×10^6
		673	640sh, 685 [700]	64	0.034	5.3×10^2

[a] Corrected emission data in square brackets. [b] Reference 44.

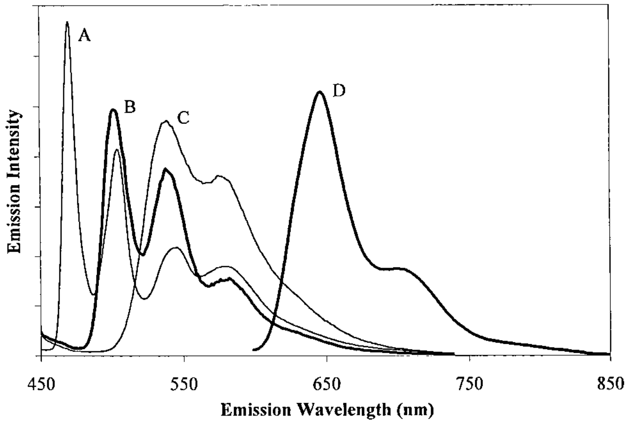


Figure 6. Emission spectra of platinum complexes in butyronitrile at 77 K: (A) Pt(trpy)Cl^+; (B, thick) Pt(4′-Ph-T)Cl^+; (C) Pt(4′-Np1-T)-Cl^+; (D, thick) Pt(4′-Pyre1-T)Cl^+.

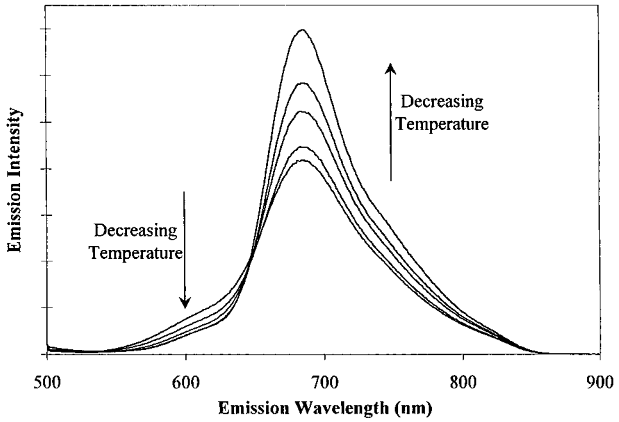
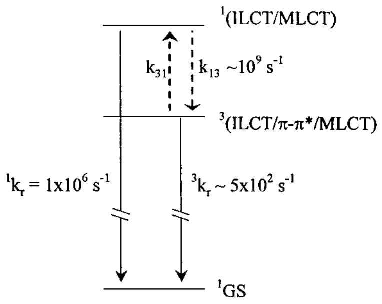


Figure 7. Emission spectra of Pt(4′-Pyre1-T)Cl^+ in deoxygenated DCM solution. The emission intensity at 680 nm increases as the temperature drops through the settings: 293, 275, 250, 225, and 200 K.

Scheme 1



Discussion

Influence of Orbital Parentage. Charge-transfer absorption occurs at comparatively low energies in the spectra of the Pt-(4′-Ar-T)Cl^+ complexes. As already noted, literature precedents argue for MLCT, or d−π*, band assignments;[4,31] however, that would not account for the huge shift that occurs in the absorption maximum upon introduction of a large fused-ring substituent. Added delocalization of the π* orbital helps stabilize the acceptor level but ordinarily gives rise to a relatively modest spectral shift.[57] Moreover, none of the substituents has much of an effect on the reduction potential, which is the main influence the ligand has on the energy of a MLCT state.[60] In their studies of Pt(trpy)Cl^+ systems with electron-donating substituents, Crites et al. rationalized similar energy shifts in terms of configurational mixing within the excited-state manifold,[33] and the same effect is undoubtedly at work here. The existence of the ILCT state is evident in the spectra of the Zn-(4′-Ar-T)Cl_2 systems with readily ionized aryl substituents, and as Crosby and co-workers have emphasized, configurational mixing is almost inevitable between close-lying excited states.[61,62] An added complication is that the mixing of metal dπ and ligand π* orbitals also occurs in occupied molecular orbitals of the ground-state configuration.[63] In the case of the excited states, electron−electron repulsion interactions are responsible for the resonant coupling between different excitations, whereas one-electron terms of the Hamiltonian operator may induce orbital mixing in the ground state. Since the substituents have so little effect on the ground-state electrochemistry of the Pt(4′-Ar-T)-Cl^+ systems, inter-excited-state configurational mixing is likely to be a more important influence on the photophysical properties.

The same principles apply to the triplet state manifold, but the picture is even more complicated. Because of the relative magnitudes of the exchange energies, the singlet−triplet splitting is larger for a π−π* state than for a CT state,[64] so the $^3\pi$−π* emission of the ligand also occurs in the neighborhood of the emission from the Pt(4′-Ar-T)Cl^+ complex (Figure 3). Therefore, as suggested by Scheme 1 for the particular case of Pt(4′-Pyre1-T)Cl^+, the emission could originate from a state involving as many as three configurationally distinct types of excitation: MLCT, ILCT, and π−π*. Each excitation involves the population of a π* orbital, and the resolved vibrational spacings of ca. 1300 cm^{-1} in the low-temperature spectra are consistent with the deposition of energy in a stretching mode of an aromatic ring system. Consistent with having CT character, the 77 K

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emission spectrum of the complex exhibits a zero–zero transition with a higher relative intensity than does that of the free ligand. The reason is that a greater distortion of the ligand framework occurs in the $\pi-\pi^*$ state, which entails the depopulation of a π-bonding orbital as well as the population of a π-antibonding level.[63]

The most dramatic consequence of the configurational mixing is that the excited-state lifetimes increase with the wavelength of the emission. The energy gap law would predict exactly the opposite trend;[65,66] however, this rule of thumb is only applicable if there is a common type of excited state throughout the series and the decay occurs by direct relaxation to a nested, ground-state potential energy surface. Here, the orbital parentage tends to change with the substituent, and intraligand states can have much longer lifetimes. However, the admixture of ILCT character should be minimal in the case of the Pt(4′-Ph-T)Cl$^+$ and Pt(trpy)Cl$^+$ systems. Differential participation of $^3\pi-\pi^*$ character may account for the longer lifetime of the 4′-Ph-T complex, but thermally activated decay is another possible factor. Deactivation via a higher energy ^{3}d–d excited state is feasible in platinum(II) complexes,[67] and delocalization of the π^*(trpy) orbital onto the phenyl substituent could affect the energy separation between the ^{3}MLCT and the ^{3}d–d excited states. Alternatively, the increase in delocalization may simply result in an intrinsically smaller distortion of the ^{3}MLCT state and slower intersystem crossing to the ground state.[57,68]

Solvent Effects. The solvent influences both the ground- and the excited-state chemistry. For example, in a coordinating solvent like MeCN or DMF, the absorption and emission spectra of solutions of Zn(4′-Pyre1-T)Cl$_2$ show evidence of the free-ligand 4′-Pyre1-T. The dissociation of a multidentate ligand may seem unusual, but Zn(dap)$_2{}^{2+}$ shows the same tendency[69] (dap = 2,9-dianisyl-1,10-phenanthroline). The addition of excess ZnCl$_2$ ensures that there is no free trpy ligand in solution, but one cannot rule out the possibility that other equilibria, such as ligand disproportionation or halide dissociation, are operative. Platinum(II) complexes may spontaneously release ligand as well, but the phenomenon could be difficult to observe in practice because the ligand-exchange kinetics are much slower for the third-row d^8 transition ion.

What is certain is that the solvent can influence the emission from a Pt(4′-Ar-T)Cl$^+$ system in at least two ways. First, the signal shifts to somewhat shorter wavelength in butyronitrile compared with DCM. The trend is consistent with emission from a relatively nonpolar excited state or a state with a polarity similar to that of the ground state, such as a $\pi-\pi^*$ state. Here, the MLCT state has a relatively small dipole moment because it has formally negative chloride and 4′-Ar-T ligands on either side of the central metal ion. Solvent-induced exciplex quenching also occurs in coordinating media when the excited state has significant MLCT character. The availability of open coordination sites at platinum, the increase in the formal oxidation state at the metal center, and the switch from a d^8 to a d^7 configuration all favor attack by Lewis bases.[5] However, previous studies of the Pt(4′-NMe$_2$-T)Cl$^+$ system have also shown that incorporation of ILCT character suppresses exciplex quenching,[5] and the same effect is evident here. Compare, for example, the Pt(4′-Ph-T)Cl$^+$ and Pt(4′-pMeOPh-T)Cl$^+$ systems. The 4′-Ph-T complex arguably has the highest percentage participation of ^{3}MLCT character in its emitting state, and not surprisingly, the quenching of the emission is essentially complete in butyronitrile. In contrast, the 4′-pMeOPh-T complex remains weakly emissive in the donor solvent because of the increased importance of the ^{3}ILCT configuration in the makeup of the excited state. Solvent-induced exciplex quenching is almost nonexistent in the case of the Pt(4′-Pyre1-T)Cl$^+$ complex, which has a lifetime of 18 μs in butyronitrile.

Pt(4′-Pyre1-T)Cl$^+$ Emissions. The 4′-Pyre1-T complex of platinum is distinctive because it exhibits emission from two different excited states in fluid solution at room temperature. Despite the presence of the heavy metal center, the 640 nm component, which becomes dominant in an aerated solution, originates from a state with a singlet multiplicity. One indication of the multiplicity is that the 640 nm emission tails into the CT absorption band in accordance with simple, Stokes shifted emission (Figure 2). However, the most telling observations are the lifetime and the emission yield. Together, these data imply a radiative rate constant (^1k_r) of ca. 10^6 s^{-1}, almost 2 orders of magnitude greater than what one measures for the ^{3}MLCT emission from Pt(4′-Ph-T)Cl$^+$. Pilato and co-workers observed similar rate constants from some platinum(II) dithiolate complexes that exhibit ^{1}ILCT emission.[14,15] Consistent with that same orbital parentage, the 640 nm component shows the same solvent dependence as fluorescence of the Zn(4′-Pyre1-T)Cl$_2$ system. Note that the intraligand character is the only reason the Pt(4′-Pyre1-T)Cl$^+$ complex exhibits fluorescence. If the excited state had mainly ^{1}MLCT character, the heavy atom effect would dramatically enhance the rate of intersystem crossing to the nearby ^{3}MLCT state, and the yield of prompt emission would be next to nil. The longer-lived emission that maximizes at 685 nm in deoxygenated DCM must, however, have a somewhat different character because it shows the opposite solvent dependence. The radiative rate constant ($^3k_r \approx 5 \times 10^2$ s^{-1}) is too low for a pure ^{3}MLCT state but is in keeping with a state that reflects significant intraligand character.[70] In this case an admixture of $^3\pi-\pi^*$(pyrene) character becomes feasible because the phosphorescence from the free 4′-Pyre1-T ligand occurs at a similar energy (Figure 3).

All considered, the data argue that the emission from the Pt(4′-Pyre1-T)Cl$^+$ system involves at least two different excited states and the combined influence of at least five different kinds of excitation: ^{1,3}MLCT, ^{1,3}ILCT, and $^3\pi-\pi^*$(pyrene). In the presence of dioxygen, the principal emission stems from a singlet state with mainly ^{1}ILCT character, though there must be ^{1}MLCT character as well in view of the close analogy with the other complexes in the series. Indeed, it would be surprising if the two types of excitation did not couple because the transition dipoles lie end to end and share the trpy moiety as one terminus. The long-lived emission, which maximizes at ca. 680 nm in the uncorrected spectrum of an oxygen-free solution, logically stems from the corresponding ^{3}ILCT state, but admixtures of ^{3}MLCT and $^3\pi-\pi^*$(Pyre) character are energetically feasible as well. Indeed, without the MLCT character the radiative rate constant would probably be much smaller.[71] Because of the relatively long triplet lifetime and the small

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singlet−triplet splitting, thermal repopulation of the singlet state can occur and is responsible for the shoulder on the high-energy side of the emission. Scheme 1 presents the simplest energy level picture that can accommodate all of the results. The model assumes that there is one triplet state with a mixed orbital parentage; however, it is possible that there is an equilibrium involving the $^3\pi-\pi^*$ state associated with the pyrene moiety. The observation of multiple emissions including a signal with a singlet multiplicity is unusual for platinum complexes, but the phenomenon has been observed from other systems with ligand-based emission[15,72] as well as from the d^8-d^8 lantern-shaped dimer $Pt(pop)_4^{4-}$.[73]

Summary

The $Pt(trpy)Cl^+$ system has a low-lying ^{3}MLCT excited state that exhibits a very short lifetime in fluid solution. However, the research shows that derivatives with aryl substituents in the 4′ position of the trpy ligand can exhibit extremely long-lived emissions. While $Pt(4'\text{-Ph-T})Cl^+$ has an excited-state lifetime of only 85 ns in room-temperature, deoxygenated DCM solution, the lifetimes of the 4′-Np1-T and the 4′-Phe9-T derivatives are 16.6 and 21.0 μs, respectively. And under the same conditions, photoexcited $Pt(4'\text{-Pyre1-T})Cl^+$ exhibits a lifetime of 64 μs. The lifetime increases, even though the emission energy decreases, with the addition of a larger, more easily ionized fused-ring substituent because the emissive excited state takes on an admixture of ILCT character, and possibly $\pi-\pi^*$(Ar) character as well. Parallel studies of $Zn(4'\text{-Ar-T})Cl_2$ systems confirm the existence of the contributing ILCT excited states. When pyrene is the substituent, the intraligand character is clearly dominant and the $Pt(4'\text{-Pyre1-T})Cl^+$ complex exhibits fluorescence as well as long-lived triplet emission. Furthermore, for the latter complex, solvent-induced exciplex quenching is of little consequence in acetonitrile.

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