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Lewis Acid and Base Sensing by Platinum(II) Polypyridines

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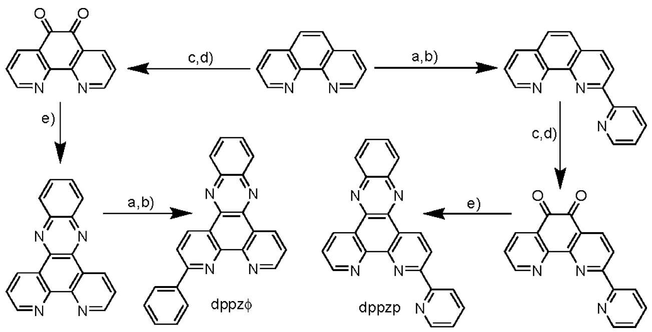
This report describes platinum(II) complexes of 6-(2-pyridyl)-dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppzp) and 6-phenyl-dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppzϕ). The [Pt(dppzp)Cl]$^+$ (**1**) system exhibits an excited-state lifetime of 5.0 μs in deoxygenated dichloromethane. Lewis bases quench the emission with rate constants on the order of 10^7 M^{-1} s^{-1}; however, acetic acid is definitely not a quencher. The carbometalated [Pt(dppzϕ)Cl] (**2**) complex is novel in that it is subject to quenching by acid as well. In deoxygenated 2-chloronaphthalene, the excited-state lifetime of **2** is 270 ns, and acetic acid quenches the emission with a rate constant of 2 × 10^8 M^{-1} s^{-1}. In addition, Lewis bases like dimethyl sulfoxide and dimethylformamide quench the emission of **1** and **2** with similar efficiencies. The coordinatively unsaturated platinum center provides a logical place for attack by Lewis bases, whereas the phenazine extension of dppzϕ introduces potentially acid-sensitive nitrogen centers. The emissive states of **1** and **2** exhibit mainly intraligand character, but enhanced charge-transfer character in **2** accounts for the differences in reactivity.

Scheme 1. Synthesis of the Ligands dppzp and dppzϕ[a]



[a] (a) *n*-BuLi, 2-bromopyridine, or PhLi in THF, 5 h, –78 °C. (b) MnO$_2$, 12 h. (c) 2:1 H$_2$SO$_4$/HNO$_3$, reflux. (d) NaOH(aq) to pH 7. (e) 1,2-Phenylenediamine in EtOH, reflux, 30 min. See the Supporting Information for full synthetic details.

Systems in which the absorption of light triggers responses at spatially separated reactive sites offer possibilities for developing broad-based molecular sensors. In this study, the goal is to develop a system capable of responding to Lewis acids and bases. Platinum(II) is an attractive choice as a metal center because a planar coordination geometry provides the opportunity for attack by Lewis bases/nucleophiles.[1] To facilitate the complementary process, namely, attack by Lewis acids such as the proton, the standard approach has been to employ a ditopic ligand.[2,3]

Scheme 1 shows the 6-(2-pyridyl)-dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppzp)[4,5] and 6-phenyldipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppzϕ) ligands used to make two new platinum complexes. [Pt(dppzp)Cl]$^+$ (**1**) exhibits emission in a dichloromethane solution, and Lewis bases act as quenchers, as expected from studies of pyridylphenanthroline compounds.[1] However, despite analogies with [(phen)$_2$Ru(dppz)]$^{2+}$ (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) and [Ru(dppzp)$_2$]$^{2+}$,[5–7] the presence of acetic acid has no measurable effect on the emission from **1**. In contrast, acetic acid is a potent quencher of the emission from [Pt(dppzϕ)Cl] (**2**) in solution, as are strong Lewis bases. Analysis suggests that the orbital parentage of the reactive excited state conditions the reactivity.

The structure of **1** is essentially planar and reveals the extended π system of the heteroaromatic ligand (Figure 1). Yet, physical data clearly reveal that the π-electronic system of the dppzp ligand entails two somewhat separate domains. Consider first the electrochemistry (Table 1). Compared with that of [Pt(trpy)Cl]$^+$, the cyclic voltammogram of **1** has an extra wave that occurs at ca. 300 mV more positive potential. A similar effect occurs in ruthenium(II) complexes of the same ligands.[2] In each case, the cathodic process is a

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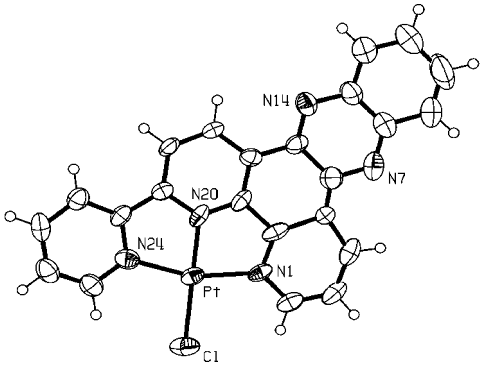

Figure 1. Molecular structure of $[Pt(dppzp)Cl]^+$, with thermal ellipsoids set at 50% probability. Selected bond lengths (Å) and angles (deg) associated with the metal center that illustrate the pseudo-square-planar geometry include the following: N1−Pt 2.038(8), N20−Pt 1.926(8), N24−Pt 2.029(9), Pt−Cl 2.285(3); N1−Pt−N20 79.5(3), N1−Pt−Cl 98.4(2), N24−Pt−Cl 100.8(2), N24−Pt−N20 81.3(3), N1−Pt−N24 160.9(3), N20−Pt−Cl 178.6(2).

Table 1. Reduction Potentials in 0.01 M $[TBA][PF_6]\cdot$DMF versus Ferrocene for the Ligands and Representative Platinum and Ruthenium Compounds

complex	$E°_{1/2}$ (V)		
dppz[a]	−1.60	−2.49	−2.99
dppzp	−1.59	−2.10	
dppzϕ	−1.65		
$[Pt(dppzp)Cl]^+$	−0.96	−1.49	−1.97
[Pt(dppzϕ)Cl]	−1.30		
$[Pt(trpy)Cl]^+$ [b]	−1.24	−1.82	
$[Ru(bpy)_3]^{2+}$ [c]	−1.75	−2.07	−2.31
$[Ru(bpy)_2(dppz)]^{2+}$ [a]	−1.36	−1.79	−1.99
$[Ru(trpy)_2]^{2+}$ [d]	−1.63		
$[Ru(trpy)(dppzp)]^{2+}$ [d]	−1.25	−1.66	
$[Ru(dppzp)_2]^{2+}$ [d]	−1.23	−1.55	

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chemically reversible process that must entail reduction of the polypyridine ligand. As is the case with related dppz systems,[2] the results make sense if the initial reduction occurs in the linear *cata*-condensed phenazine (phz) domain of the ligand. The second indication that the dppzp ligand has a compartmentalized π system is apparent in the absorption spectrum of **1** (Figure 2).

Thus, intense absorption in the vicinity of 290 nm originates in the trpy portion of the ligand, while the absorbance in the range of 350–375 nm is assignable to the phenazine component, analogous to proposed assignments for the UV bands of the dppz ligand.[8] The weak shoulder that appears at around 420 nm corresponds to a metal-to-ligand charge-transfer (MLCT) transition, although the transition may have interligand $\pi-\pi^*$ character as well.

Figure 2 also reveals that **1** exhibits a structured emission signal with a 0–0 transition at 570 nm. Under deoxygenated conditions in the same solvent, the excited-state lifetime is $\tau = 5.0\ \mu$s, and the measured emission quantum yield is $\phi = 0.003$. Previous workers have reported very similar emission spectra from rhenium(I) and copper(I) complexes of dppz-related ligands, and they have assigned the emission to a $^3\pi-\pi^*$(phz) state.[9,10] The existence of a room-temperature emission signal from **1** assures that the excited state has a degree of ^{3}MLCT character. However, there is limited metal involvement because the estimated radiative rate constant is only 600 s^{-1} ($k_r = \phi/\tau$). The spectral band shape and the value of the radiative rate constant are also consistent with dominant $^3\pi-\pi^*$(phz) character.

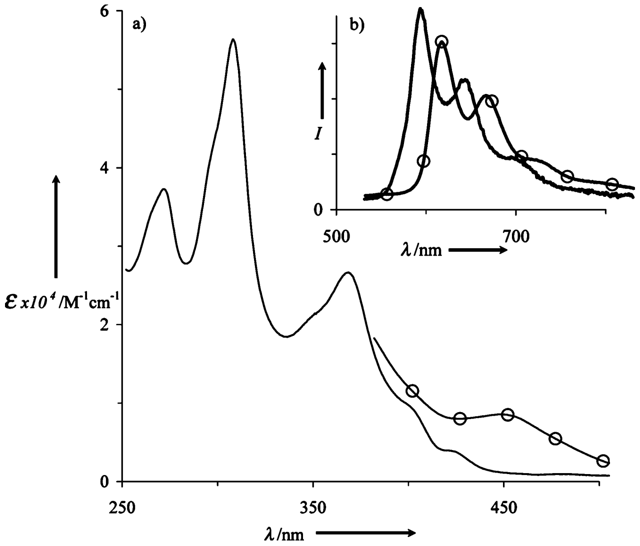

Figure 2. Absorbance of $[Pt(dppzp)Cl]^+$ in CH_2Cl_2 (thin lines) and [Pt(dppzϕ)Cl] in 2-chloronaphthalene (○) Inset: Emission of $[Pt(dppzp)Cl]^+$ in CH_2Cl_2 (thick lines) and [Pt(dppzϕ)Cl] in 2-chloronaphthalene (○).

Table 2. Quenching Constants for $[Pt(dppzp)Cl]^+$ in CH_2Cl_2 and [Pt(dppzϕ)Cl] in 2-Chloronaphthalene

	k_q ($M^{-1}\ s^{-1}$)	
quencher[a]	$[Pt(dppzp)Cl]^+$	[Pt(dppzϕ)Cl]
MeCN (14.1)	3.0×10^6	
acetone (17)	5.0×10^6	
THF (20)	1.0×10^7	9.0×10^5
DMF (26.6)	6.0×10^7	3.0×10^6
DMSO (29.8)		3.0×10^7
pyridine (33)		2.0×10^7
acetic acid		2.0×10^8

[a] Guttman donor numbers are given in parentheses.

In principle, quenching studies involving Lewis acids and bases can provide information about the degree of charge transfer (CT) involved with the excitation. Lewis bases quench the emission with moderate rate constants, on the order of $10^7\ M^{-1}\ s^{-1}$, according to Stern−Volmer analyses (Table 2 and Figure 3). The quenching rate constants increase with the donor number of the base,[11] consistent with the formation of a new coordinate covalent bond to the platinum center of the excited state. At least two factors limit the rates. One is that ligand substitution and/or ligand rearrangement processes are generally slow for third-row transition ions like platinum. The orbital parentage of the excited state may be an even more important consideration because the states most prone to quenching by Lewis bases tend to be MLCT excited

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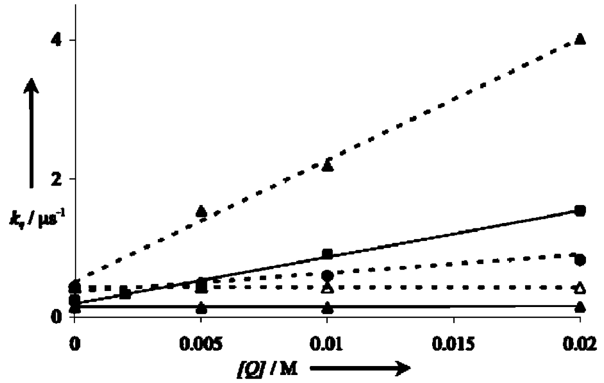

Figure 3. Stern−Volmer plots measured by the lifetime of [Pt(dppzp)Cl]$^+$ in CH_2Cl_2 (solid) with acetic acid (▲) and DMF (■) and [Pt(dppzϕ)Cl] in 2-chloronaphthalene (dotted) with acetic acid (▲), DMSO (●), and ethyl acetate (△).

states that formally involve the formation of platinum(III).[1,12] In the case of **1**, the quenching rates obtained with various Lewis bases are fairly low and are in keeping with an excited state that has a limited degree of platinum(III) character. There also seems to be no charge accumulation at the phz moiety because acetic acid is not a quencher. Interest therefore shifted to **2**.

As with dppzp, reduction of dppzϕ involves electron transfer into the phz domain because the potentials exhibited by the free ligands dppz, dppzp, and dppzϕ fall within 50 mV of each other. However, the reduction potential of **2** is 340 mV more negative than that of **1**. Reduction is less facile because the phz moiety resides next to what is formally a negatively charged phenyl group in the carbometalated complex. The carbanionic character of the phenyl group is probably also responsible for the comparatively strong absorption exhibited by **2** in the visible spectrum (Figure 2). In **2**, coordination of the formally carbanionic phenyl ligand should render the platinum(III) oxidation state more accessible; hence, there may be a synergistic enhancement of MLCT character as well.

As shown in Figure 2, the emission spectrum of **2** also exhibits vibronic structure consistent with the participation of ligand-centered vibrations. The dppzϕ complex is not very soluble in common noncoordinating solvents but is sparingly soluble in 2-chloronaphthalene. The presence of dioxygen has little effect on the emission intensity because the lifetime is a comparatively short 270 ns, possibly because of CT quenching involving the solvent. In fact, the deoxygenated lifetime of **1** in the same solvent is only approximately 25 ns. In solution, the complex exhibits an emission quantum yield of 0.0022 and a calculated value of $k_r = 8200\ s^{-1}$. The excited state has CT character because acetic acid acts as a potent quencher of the emission from **2**. According to a Stern−Volmer treatment of lifetime data, the quenching rate constant is $2 \times 10^8\ M^{-1}\ s^{-1}$ (Figure 3 and Table 2). Under the same conditions, ethyl acetate has no effect. Therefore, the acidic proton must be responsible for quenching. Lewis bases can quench the emission; however, the process is only efficient when the donor number is relatively high (Table 2). In the carbometalated complex, triplet intraligand charge-transfer character may account for the activation of the phenazine moiety. Density functional theory calculations support this interpretation. In particular, calculations show that the average charge on the phenazine nitrogens changes from −0.454 to −0.493 units upon vertical excitation into the lowest triplet excited state of the dppzϕ ligand. In contrast, a similar calculation predicts that no significant charging occurs at the same nitrogens in the lowest triplet state of the dppzp ligand.

In conclusion, **2** is a rare example of a transition-metal complex with an emissive excited state susceptible to quenching by *both* Lewis acids and bases. Cummings and Eisenberg have investigated a ternary complex of platinum(II) with 1,10-phenanthroline and quinoxaline-2,3-dithiolate (qdt) ligands that may be similar.[3] In particular, they observed acid- and solvent-induced quenching of the emission; however, the polarity of the solvent appeared to be more important than the basicity. The dppzp complex differs from the qdt complex in that the potentially acid-sensitive nitrogen centers reside on the polypyridine side of **1**. Photoexcited $[(phen)_2Ru(dppz)]^{2+}$ presents the same kind of ligand and *is* subject to acid-induced quenching;[7,8] the difference is probably that the reactive excited state of complex **1** exhibits mainly $^3\pi-\pi^*$(phz) intraligand character, as opposed to metal → π^*(phz) CT character. The excited state of **2** is therefore the more remarkable because the emitting state also has a limited extent of MLCT character. Indeed, any given base quenches **2** less efficiently than **1**. Nevertheless, acetic acid is a potent quencher. It will be interesting to see if the effect translates to other Lewis acids such as alkali-metal ions. However, solubility is an issue with **2**. As a means of addressing the solubility and improving sensitivity, future efforts will focus on modifications of the dppzϕ ligand and replacement of the chloride ligand.

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Supporting Information Available: Synthesis and characterization of compounds and crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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