Excited-State Self-Quenching Reactions of Square Planar Platinum(II) Diimine Complexes in Room-Temperature Fluid Solution

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Photoactive coordinatively unsaturated metal complexes are attractive chromophores for solar energy conversion, photocatalysis,[1] and photochemical sensing[2] applications. Square-planar platinum(II) complexes containing a chelating diimine ligand represent a promising class of these molecules as there are now numerous examples of these compounds that exhibit long-lived fluid solution luminescence.[3–9] Three classes of Pt(II) diimine complexes showing fluid solution luminescence are distinguished by the nature of the emissive triplet excited state as either diimine localized $\pi\pi^*$, metal-to-ligand(diimine) charge-transfer (MLCT), or mixed metal/ligand(dithiolate)-to-ligand(diimine) charge-transfer (MMLLCT).[3–8,10] In each case, the LUMO is predominantly centered on the diimine ligand, while the HOMO varies as a function of the ancillary ligands. The Pt(diimine)(CN)$_2$ complexes exhibit a high-energy diimine-centered $^3(\pi\pi^*)$ emission in dilute solutions ($\sim 10^{-5}$ M), but they also show a lower energy excimer emission at higher concentrations ($> 10^{-4}$ M)[4,5,11] reminiscent of planar aromatic systems. The recent observation[9] of self-quenching, albeit without excimer emission, by Pt(bpy)(bdt) (bpy = 2,2′-bipyridine; bdt = 1,2-benzenedithiolate), which has a lowest energy MMLLCT excited state, suggested to us that self-quenching of Pt(II) diimine complexes might be far more general than previously realized. Here we confirm that notion and report that the fluid solution excited-state lifetimes are concentration dependent for all three classes of solution luminescent Pt(II) diimine complexes. The observed self-quenching results from association of excited-state and ground-state molecules and is *not* simply a consequence of the tendency of ground-state Pt(II) complexes to form dimers and oligomers at high concentrations.[12]

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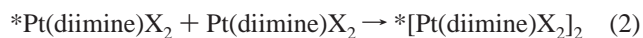(11) Pettijohn, C. N.; Jochnowitz, E. B.; Chuong, B.; Nagle, J. K.; Vogler, A. *Coord. Chem. Rev.* **1998,** 85–92.

Table 1. Self-Quenching Data for Platinum(II) Diimine Complexes

compd[a]	solvent[a]	emissive state	k_q[e]	τ_q (ns)
Pt(dpphen)(CN)$_2$[b]	PEG	$^3(\pi-\pi)^*$	5.6	100
Pt(dbbpy)(CN)$_2$[c]	(CH$_2$Cl)$_2$	$^3(\pi-\pi)^*$	0.9	2900
Pt(phen)(CCPh)$_2$	CH$_3$CN	^{3}MLCT	6.3	904
	CH$_2$Cl$_2$	^{3}MLCT	3.3	1888
Pt(phen)(CCTol)$_2$	CH$_3$CN	^{3}MLCT	6.2	549
Pt(phen)(CCPhF)$_2$	CH$_3$CN	^{3}MLCT	6.7	814
Pt(bpy)(bdt)[d]	CH$_3$CN	^{3}MMLLCT	9.5	460
	CHCl$_3$	^{3}MMLLCT	4	560
Pt(phen)(tdt)	CH$_2$Cl$_2$	^{3}MMLLCT	4.7	580
Pt(dmbpy)(tdt)	CH$_2$Cl$_2$	^{3}MMLLCT	2	360
Pt(tmphen)(tdt)	CH$_2$Cl$_2$	^{3}MMLLCT	4.2	1911
Pt(dbbpy)(tdt)	CH$_2$Cl$_2$	^{3}MMLLCT	1.0	489

[a] dpphen = 4,7-diphenyl-phen; CCTol = *p*-tolylacetylide; CCPhF = *p*-fluoro-phenylacetylide; dmbpy = 4,4′-dimethyl-bpy; PEG = poly(ethylene glycol). [b] Ref 4. [c] Ref 5. [d] Ref 9. [e] 10^9 M^{-1} s^{-1}.

We have examined a series of complexes with aryl-substituted acetylide or toluene-3,4-dithiolate (tdt) ligands since these systems exhibit long-lived solution emission from lowest MLCT[7,13] or MMLLCT[8] excited states, respectively (Table 1). For low concentrations ($\sim 5 \times 10^{-4}$ to 10^{-5} M) in CH$_3$CN or CH$_2$Cl$_2$, these complexes show no evidence for ground-state aggregation as indicated by Beer's Law behavior of the absorption spectra. Similarly, the excitation spectra at λ_{em} are in good agreement with the corresponding absorption spectra. However, for all of the compounds studied, the rates of emission and transient absorption decay decrease with increasing concentration,[14] indicative of self-quenching with no net chemical reaction.[15] The rates of emission decay ($k_{obs} = 1/\tau$) are well modeled by a modified Stern–Volmer expression (eq 1) where k_q is the self-quenching rate constant for eq 2, [Pt] is the concentration of the Pt complex, and k_0 ($= 1/\tau_0$)

$$k_{obs} = k_q[\text{Pt}] + k_0 \qquad (1)$$

$${}^*\text{Pt(diimine)}X_2 + \text{Pt(diimine)}X_2 \rightarrow {}^*[\text{Pt(diimine)}X_2]_2 \quad (2)$$

is the rate of excited-state decay at infinite dilution. The resulting values of k_q (Table 1) approach the diffusion limit indicating efficient association of an excited monomer and a ground-state complex. The fact that emission lifetimes are independent of excitation power (0.5–2 mJ) shows that the quenching does not result from association of two excited-state complexes. Complexes with the dbbpy (4,4′-di-*tert*-butyl-bpy) ligand exhibit the lowest values of k_q, suggesting that self-quenching is modestly sensitive to diimine ligand steric effects.

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(14) Transient decays were measured using previously described instrumentation (Chen, L.; Farahat, M. S.; Gaillard, E. R.; Farid, S.; Whitten, D. G. *J. Photochem. Photobiol.,* A **1996,** *95,* 21–5) with an ∼1 mJ laser pulse.

(15) Photosensitivity of Pt(diimine)(dithiolate) complexes in halogenated solvents has been noted (Vogler, A.; Kunkely, H. *J. Am. Chem. Soc.* **1981,** *103,* 1559), but we see photostability of degassed samples.
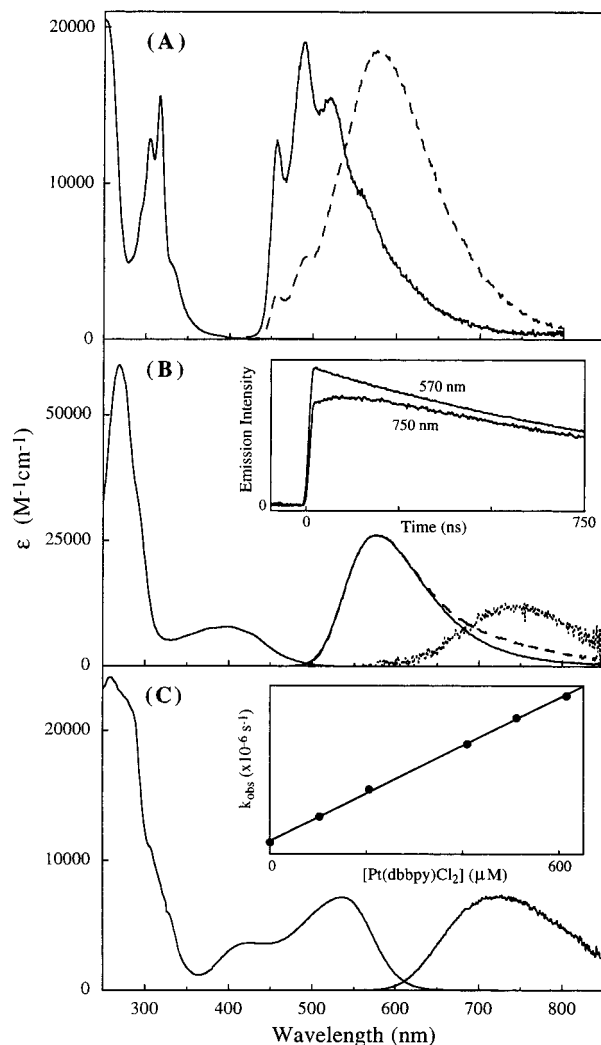
Figure 1. Absorption and emission spectra for (A) Pt(dbbpy)(CN)$_2$ (—, 0.01; ---, 0.8 mM), (B) Pt(phen)(CCPh)$_2$ (—, 0.01; ---, 0.5 mM; ···, difference emission spectrum × 5), and (C) 0.02 mM Pt(tmphen)(tdt) in CH$_2$Cl$_2$. (B) Inset shows emission intensities at 570 and 750 nm after flash (λ_{ex} 460 nm). (C) Inset shows plot of k_{obs} of Pt(tmphen)(tdt) *vs* Pt(dbbpy)Cl$_2$ concentration. Emission spectra arbitrarily scaled.

For Pt(phen)(CCPh)$_2$ (phen = 1,10-phenanthroline) in CH$_2$-Cl$_2$ solution, the self-quenching reaction is accompanied by excimer emission.[16] With increasing concentration, the emission intensity at long wavelengths ($\lambda > 610$ nm) increases relative to the emission maximum at 565 nm, indicating a broad and weak excimer emission band centered near 750 nm (Figure 1B). Indeed, whereas the transient emission signal at 566 nm shows single-exponential decay following a laser flash, the emission signal at 750 nm for a 10^{-4} M solution does not reach its maximum until ∼150 ns *after the laser flash*. On the basis of the emission decay rates at different λ_{em}, the excimer is short-lived (∼100 ns) relative to the excited monomer. For Pt(II) diimine dithiolate complexes in CH$_2$Cl$_2$, the steady-state emission profiles are independent of concentration and excimer emission, anticipated at $\lambda > 800$ nm, is not observed.

Since self-quenching is rapid for Pt(II) diimine complexes with a wide range of ancillary ligands, the excited-state/ground-state quenching interaction most likely involves the metal centers and/or the diimine ligands. To probe this further, a series of quenching

experiments with phen and naphthalene (naph) and cross-quenching experiments using pairs of metal complexes were performed. When either phen or naph ($>10^{-2}$ M) is added to a 2 × 10^{-5} M solution of Pt(tmphen)(tdt) (tmphen = 3,4,7,8-tetramethyl-phen) in CH$_2$Cl$_2$ and irradiated ($\lambda_{ex} = 510$ nm), the emission spectrum and lifetime (1650 ns) of the complex remain unchanged. While capable of forming exciplexes, there exists insufficient driving force for either aromatic to quench the excited complex by electron or energy transfer.[8,17] In cross-quenching reactions, very efficient quenching is observed. Addition of Pt-(tmphen)(tdt) to a 3 × 10^{-5} M solution of Pt(phen)(CCPh)$_2$ in CH$_2$Cl$_2$ results in a decrease in the 565 nm emission from the bis(acetylide) complex, accompanied by the appearance of low-energy emission (720 nm) from the Pt(tmphen)(tdt) complex. The rate of emission decay, k_{obs}, for Pt(phen)(CCPh)$_2$ increases linearly with Pt(tmphen)(tdt) concentration ($k_q = 9.0 \times 10^9$ s^{-1} M^{-1}), indicating energy transfer from the higher energy emitting bis-(acetylide) complex to the lower energy absorbing dithiolate complex. However, k_{obs} at 800 nm, corresponding predominately to Pt(tmphen)(tdt) emission, also increases in the presence of Pt-(phen)(CCPh)$_2$, though this cannot be energy transfer quenching. The value of k_q ((3−5) × 10^9 s^{-1} M^{-1}) is comparable to the self-quenching rate for Pt(phen)(CCPh)$_2$ (3.3 × 10^9 s^{-1} M^{-1}).

When the nonemissive complex Pt(dbbpy)Cl$_2$, which has a lowest ligand field excited state at higher energy (<540 nm) than the MMLLCT excited state of Pt(tmphen)(tdt),[8,10] is added to a 2 × 10^{-5} M solution of Pt(tmphen)(tdt), the rate of emission decay increases with increasing concentration of the dichloride complex (Figure 1C).[18] The value of k_q (2.1 × 10^9 s^{-1} M^{-1}) is only slightly less than the self-quenching rate for Pt(tmphen)(tdt). Addition of Pt(dbbpy)(CN)$_2$ to a 2 × 10^{-5} M solution of Pt(tmphen)(tdt) also increases the rate of emission decay (λ_{ex} 510 nm) with k_q inter-mediate between the self-quenching rates for Pt(tmphen)(tdt) and Pt(dbbpy)(CN)$_2$ (0.9 × 10^9 s^{-1} M^{-1}).[5] In none of these cross-quenching studies are long-lived transient species attributable to outer-sphere electron-transfer products observed. In addition, the emission and transient absorption decays are single exponential with k_q's similar to those obtained for the self-quenching reactions. It seems likely that the rapid cross-quenching reactions involve a mechanism similar to that for self-quenching. On the basis of the efficiency of these quenching reactions and the absence of any corresponding effect with added diimines or other π systems, we propose that self-quenching occurs via excited-state/ground-state Pt···Pt interaction. Indeed, known face-to-face covalent d^8−d^8 dimers exhibit low-lying excited states with enhanced metal−metal interaction relative to the ground state.[19]

In conclusion, our results show that (1) self-quenching by Pt-(II) diimine complexes is a general phenomenon; (2) in dilute solution, emission from the bis(acetylide) and tdt complexes originates from monomeric platinum(II) systems; and (3) self-quenching is sometimes accompanied by excimer emission. The observed self-quenching is clearly distinguished from ground-state aggregation and must be considered in photochemical experiments where long-lived excited complexes are generated.

Supporting Information Available: Stern−Volmer plots for self-quenching and cross-reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

(16) As for Pt(dbbpy)(CN)$_2$,[5] excimer emission is not observed in CH$_3$CN. The coordinating properties of the solvent may increase the nonradiative decay rate of the excimer.

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