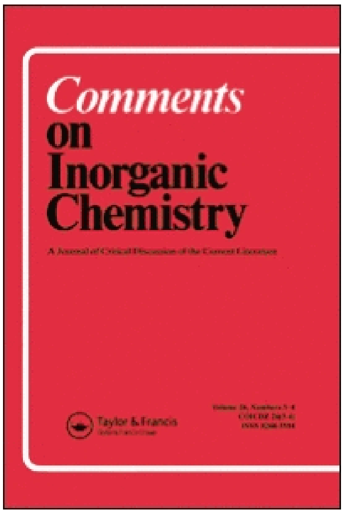

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Self-quenching and Cross-quenching Reactions of Excited Platinum(II) Diimine Complexes

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Self-quenching and Cross-quenching Reactions of Excited Platinum(II) Diimine Complexes

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Neutral platinum(II) diimine complexes undergo self-quenching in fluid solution, characterized by a linear increase in the emission decay rate with concentration. The corresponding quenching rates ($\sim 10^9$–10^{10} $M^{-1}s^{-1}$) are nearly diffusion limited. The accumulated evidence suggests that an excited platinum complex, M, reacts with a ground-state complex, M, to form an excimer, M_2*, which rapidly relaxes to give two ground-state complexes. The reaction mechanism and the nature of the excimer are discussed in context of the electronic structures, spectroscopy, and quenching kinetics of these complexes. Steady-state cross-quenching experiments suggest that an excited platinum complex also can react rapidly ($\sim 10^9$–10^{10} $M^{-1}s^{-1}$) with a different ground-state platinum diimine complex (Q), presumably to form an exciplex, MQ*. In contrast, aromatic molecules and platinum(II) complexes lacking a diimine ligand are relatively ineffective quenchers. These results suggest that both the diimine ligand and platinum center are important for quenching.*

Keywords: self-quenching; cross-quenching; excimer; exciplex; fluid solution emission spectroscopy; luminescence; photoluminescence; phosphorescence; platinum metal complexes; platinum(II) complexes; diimine; arylacetylide; dithiolate; dicyanide; charge transfer excited states; triplet states; photophysics; electronic structures; static quenching; dynamic quenching.

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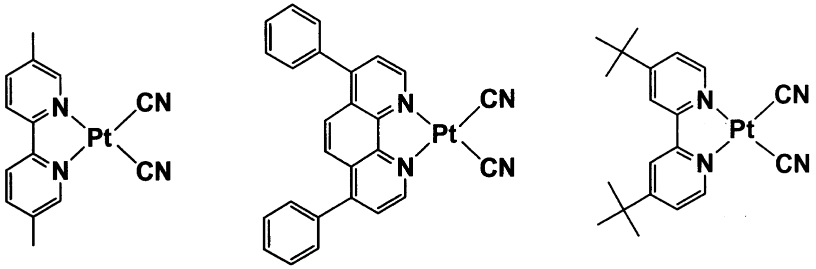
INTRODUCTION

The long-lived solution luminescence exhibited by many neutral square planar platinum(II) diimine complexes has inspired investigations of the spectroscopic, photophysical, and photochemical properties of these compounds and their possible applications in areas as diverse as multi-electron photocatalysis[1,2] and biochemical sensing.[3,4]



Pt(5,5'-dmbpy)(CN)$_2$ Pt(dpphen)(CN)$_2$ Pt(dbbpy)(CN)$_2$

FIGURE 1

During one 1989 study, Che and coworkers[5] noted that the emission lifetime of Pt(5,5′-dmbpy)(CN)$_2$ is concentration dependent. The observed behavior is consistent with an excited-state self-quenching reaction in which an excited platinum complex (M*) reacts with a ground-state complex, M, where M = Pt(diimine)L$_2$ to form an excimer, M$_2$*. The latter species rapidly relaxes to give two ground-state complexes:

$$M^* + M \longrightarrow \underset{\text{excimer}}{M_2^*} \longrightarrow 2\,M$$

FIGURE 2

The rate of excited-state decay (k') was found to decrease linearly with concentration, according to:

$$k' = k_i + k_{sq}(\mathrm{Pt}) \qquad (1)$$

While the predicted excited-state lifetime at infinite dilution ($\tau = 1/k_i =$ 6.3 μs) is long, the observed lifetime in concentrated solutions is severely attenuated by the nearly diffusion-limited self-quenching reaction ($k_{sq} = 4.8 \times 10^9\ \mathrm{M^{-1}s^{-1}}$). The following year, Kunkely and Vogler[6] reported that, with increasing concentration, the green emission from

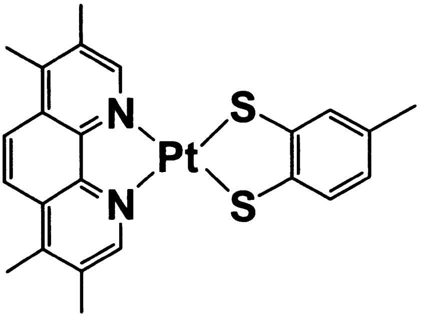
Pt(dpphen)(CN)$_2$ ($\lambda_{\max} = 530$ nm) in polyethylene glycol is gradually replaced by a red emission ($\lambda_{\max} = 630$ nm), attributed to an excimer. Subsequently, Che and coworkers[7] reported self-quenching ($k_{sq} = 0.9 \times 10^9$ M^{-1} s^{-1}) accompanied by excimer emission from solutions of Pt(dbbpy)(CN)$_2$. Transient emission measurements indicate that the excimer luminescence reaches its maximum intensity approximately 100 ns after excitation with a short laser flash, confirming the notion that the excimer is not a ground-state aggregate.

Since these earliest observations, reports by Che,[8,9] Gray,[10] and Nagle and Vogler[11] have noted similar self-quenching behavior. However, it was not until 1999 that Eisenberg and coworkers[12] established that self-quenching, sometimes accompanied by excimer emission, is a general phenomenon, apparently characteristic of all platinum(II) diimine complexes exhibiting long-lived solution emission. These authors also reported several cross-quenching experiments in which M* reacts with a different ground-state complex (Q), presumably to form an exciplex, MQ*:

$$\mathrm{M^* + Q} \longrightarrow \underset{\text{exciplex}}{\mathrm{MQ^*}} \longrightarrow \mathrm{M + Q}$$

FIGURE 3

Quenching of the emission from Pt(tmphen)(tdt) in methylene chloride by Pt(dbbpy)(CN)$_2$ was found to occur at a rate (2×10^9 M^{-1}s^{-1}) intermediate between the self-quenching rates of Pt(tmphen)(tdt) (4.2×10^9 M^{-1}s^{-1}) and Pt(dbbpy)(CN)$_2$.[12]



Pt(tmphen)(tdt)

FIGURE 4

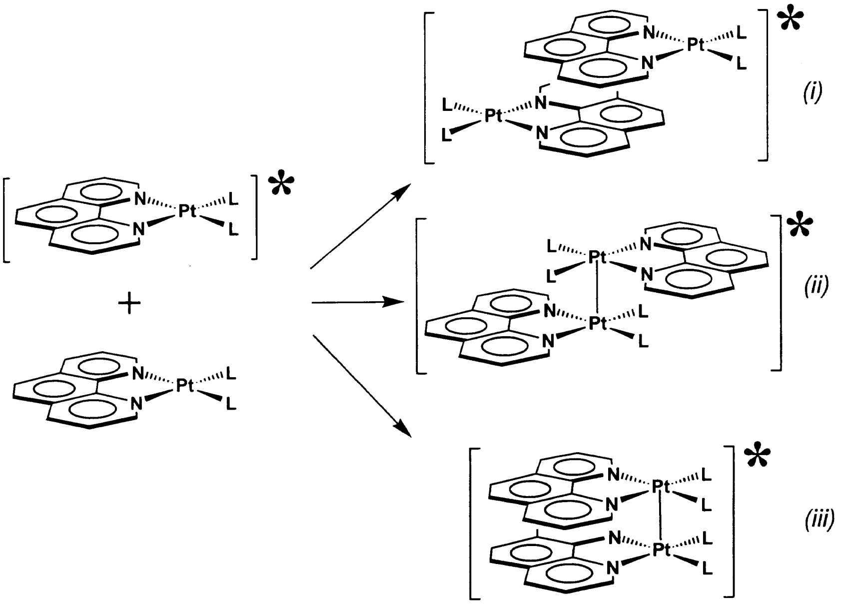


FIGURE 5

Because self-quenching presents a serious problem for applications that require a long-lived excited state, there is strong motivation to learn to control this behavior. However, the exact structure of the M_2* adduct is not known. At least three possible modes of association have been proposed[12] based on (*i*) diimine-diimine interactions, (*ii*) metal-metal interactions, and (*iii*) a combination of these interactions (Figure 5).

Each of these types of interactions commonly occur in crystals and solution aggregates of these complexes;[13–19] however, it is not obvious which will dominate excimer formation.

Herein we summarize present understanding of this behavior and our recent efforts to determine which intermolecular interactions are important in self-quenching and cross-quenching reactions.

ELECTRONIC STRUCTURES

Platinum(II) diimine complexes often exhibit intense, long-lived emissions in the solid-state and fluid solution. In solid samples or at very high concentrations, intermolecular interactions (e.g., Pt· · ·Pt, ligand· · ·ligand) can directly influence the nature of the lowest excited states. The spectroscopic and photophysical properties of those systems have been discussed by

Miskowski[13,14,20–22] and others,[15,17–19,23–29] and we restrict the following comments to the lowest, predominantly triplet excited states of discrete monomers.

From molecular orbital considerations (Figure 6),[13,30] the highest occupied levels are expected to be predominantly metal-centered with *d* orbital character or diimine ligand-centered with π orbital character. Similarly, the lowest unoccupied levels are expected to have $d_{x^2-y^2}$ or π^*(diimine) character. The order of the resulting lowest diimine-localized $^3(\pi-\pi^*)$, ligand field (^{3}LF), and metal-to-ligand charge-transfer (^{3}MLCT) states depends on the nature of the anionic ancillary ligands (Figure 7). Strong σ donor ligands destabilize LF states, resulting in a high-energy, structured emission originating from a $^3(\pi-\pi^*)$ excited state, as observed for Pt(dbbpy)(CN)$_2$ (CH$_2$Cl$_2$ solution: 456, 489, 519, 560 sh nm at 298K; Figure 1a).[7,12] In contrast, complexes with weak σ donor ligands, illustrated by Pt(bpy)Cl$_2$ (solid

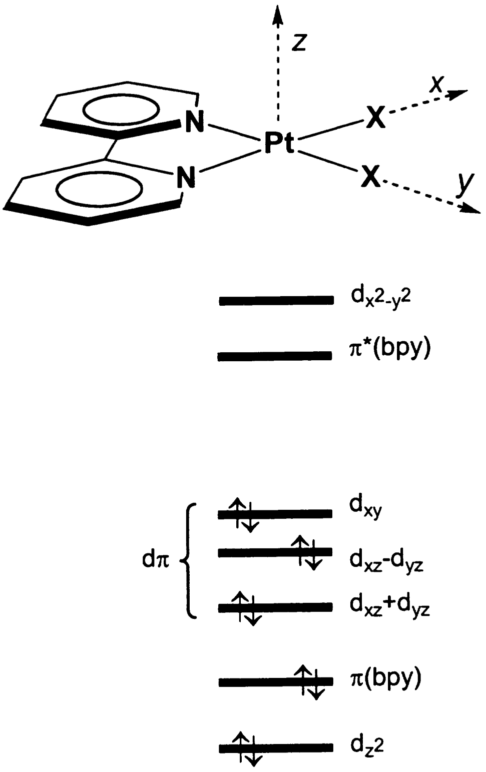


FIGURE 6

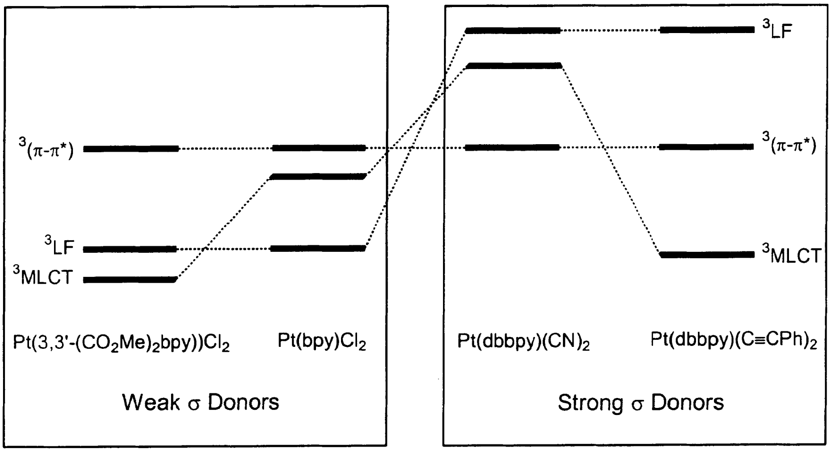
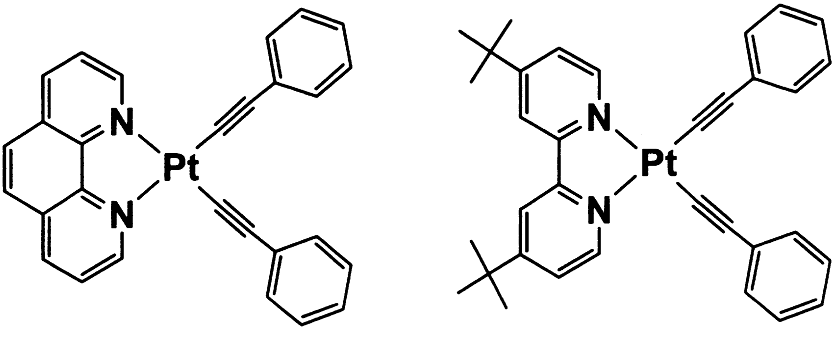


FIGURE 7

state: 641 nm; FWHM = 4000 cm^{-1}; $\tau = 500$ ns at 250K), often exhibit a Stokes-shifted, weak, broad emission originating from a ^{3}LF state.[13]

The presence of low-lying $^3(\pi-\pi^*)$ and ^{3}LF states suggests the proximity (^{3}MLCT) (d[Pt]$\rightarrow\pi^*$[diimine]) state. Indeed, moderately intense ^{1}MLCT transitions ($\varepsilon \sim 3000$–4000 M^{-1}cm^{-1}) are often observed to the red of the $^1(\pi-\pi^*)$ bands. These considerations led Miskowski and coworkers[22,30] to propose two strategies for tuning the electronic structures of these complexes depending on the nature of the ancillary ligands (Figure 7). In the case of weak σ donors, illustrated by Pt(3,3′-[CO_2Me]$_2$bpy)Cl_2 (solid state emission: $\lambda_{max} = 556$ sh, 587, 667 sh nm; $\tau = 350$ ns at 300K), substitution of electron withdrawing groups on the diimine stabilizes the ligand π^* levels relative to the antibonding $d_{x^2-y^2}$ level, resulting in a lowest ^{3}MLCT state.[22] In the case of strong σ donor ligands, as observed for Pt(diimine)R_2 (R = alkyl; aryl; arylacetylide; 3,5-dimethyl-pyrazolate),[30–35] strongly electron-donating ligands effectively destabilize the filled d levels relative to the diimine π levels, resulting in a lowest ^{3}MLCT state (e.g., Pt(dbbpy)(C≡CPh)$_2$, Figures 7,8).

An intriguing situation arises when non-innocent ligands, such as dithiolates are coordinated to the Pt center. Complexes such as Pt(tmphen)(tdt) ($\lambda_{max} = 535$ nm, 7160 M^{-1}cm^{-1}, CH_2Cl_2; 526 nm, DMSO; Figure 9c) exhibit a broad, solvent-sensitive, charge-transfer absorption band shifted to the red of the lowest ^{1}MLCT absorption bands. Studies by Eisenberg[36,37] and others[10,38–43] have established that the highest occupied levels in these complexes have considerable dithiolate character, and the lowest unoccupied levels have mostly diimine character. Because of extensive mixing of the Pt and dithiolate orbitals, the low-energy band has



Pt(phen)(C≡CPh)$_2$ Pt(dbbpy)(C≡CPh)$_2$

FIGURE 8

been assigned as a mixed-metal-ligand(dithiolate)-to-ligand(diimine) charge transfer (MMLLCT) transition.[1,44] Intense emission from these complexes is proposed to originate from the corresponding ^{3}MMLLCT state, Pt(tmphen)(tdt): $\lambda_{max} = 720$ nm in CH_2Cl_2; Figure 9c. Thus, these molecules share a converse relationship with asymmetric mixed-valence complexes, e.g., $(CN)_5Ru^{III}(CN)Ru^{II}(NH_3)_5^-$,[45] popularized in studies of intramolecular electron transfer. The ligands assume the roles of donor (dithiolate) and acceptor (diimine), and the metal acts as the bridge mediating electronic coupling. Therefore, it is possible to describe the non-radiative excited-state decay process using the Energy Gap Law[36,46] or semi-classical electron-transfer theory.[47]

The remarkable intensity of the MMLLCT absorption band (6000–19000 $M^{-1}cm^{-1}$),[36,44] as compared to ^{1}MLCT transitions,[10] may be a result of coupling to the intense d→p transitions of platinum. Alternatively, ligand-metal orbital mixing may facilitate partial delocalization across the metal center, giving the complex some of the π-delocalization character attributed to nickel(II) analogues.[48] The lowest triplet component of this charge transfer, presumably buried in the broad absorption band, remains elusive and never has been directly identified in absorption or excitation spectra. Nevertheless, as expected for the MMLLCT states, the apparent singlet-triplet splitting ($\sim$1000 cm^{-1}) is smaller than observed for MLCT states (3000–4000 cm^{-1}), indicating a greater degree of charge separation.[10]

FLUID SOLUTION EMISSION

For reasons that are not fully understood, only some platinum diimine complexes with lowest $^3(\pi-\pi^*)$, ^{3}MLCT, or ^{3}MMLLCT states have been

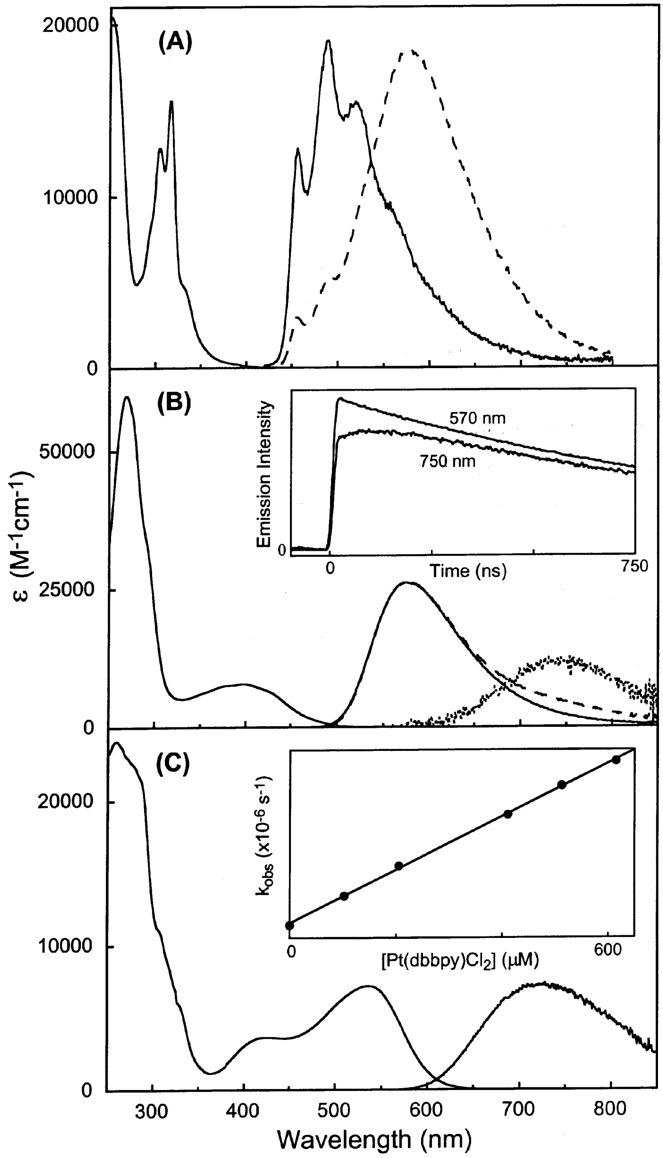


FIGURE 9 Absorption and emission spectra for (A) $Pt(dbbpy)(CN)_2$ (—0.01; - - -, 0.8 mM); (B) $Pt(phen)(C{\equiv}CPh)_2$ (—0.01; - - -, 0.5 mM; ······ difference emission spectrum × 5), and (C) 0.02 mM Pt(tmphen)(tdt) in CH_2Cl_2. (B) Inset shows the emission intensities at 570 and 750 nm after laser excitation ($\lambda_{ex} = 460$ nm). (C) Inset shows k'' for Pt(tmphen)(tdt) as a function of $Pt(dbbpy)Cl_2$ concentration. Emission spectra are arbitrarily scaled. (Reproduced with permission from Reference 12.)

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

Compound[a]	Solvent	Emissive state	λ_{max} (nm)[j]	k_{sq} ($10^9\ M^{-1}s^{-1}$)	τ_0 (ns)
$\mathrm{Pt(dbbpy)(CN)_2}$[c]	$\mathrm{(CH_2Cl)_2}$	$^3(\pi-\pi^*)$	490[l]	0.9	2900
$\mathrm{Pt(dmbpy)(CN)_2}$[d]	$\mathrm{CH_3CN}$	$^3(\pi-\pi^*)$	502[l]	4.8	6300
$\mathrm{Pt(dpphen)(CN)_2}$[e]	PEG[b]	$^3(\pi-\pi^*)$	530	~6[f]	100
	$\mathrm{CH_2Cl_2}$	$^3(\pi-\pi^*)$	520	0.5	13000
$\mathrm{Pt(dbbpy)(C{\equiv}CC_6H_5)_2}$[g]	$\mathrm{CH_3CN}$	^{3}MLCT	570	1.4 ± 0.2	691
$\mathrm{Pt(dbbpy)(C{\equiv}CC_6H_4F)_2}$[g]	$\mathrm{CH_3CN}$	^{3}MLCT	570	1.6 ± 0.1	663
$\mathrm{Pt(dbbpy)(C{\equiv}CC_6H_4CH_3)_2}$[g]	$\mathrm{CH_3CN}$	^{3}MLCT	592	1.0 ± 0.2	440
$\mathrm{Pt(C_6H_5C{\equiv}Cphen)\text{-}(C{\equiv}CC_6H_5)_2}$[g]	$\mathrm{CH_3CN}$	^{3}MLCT	590	4.2 ± 0.3	5600
$\mathrm{Pt(phen)(C{\equiv}CPh)_2}$[h]	$\mathrm{CH_3CN}$	^{3}MLCT	575	6.3	904
	$\mathrm{CH_2Cl_2}$	^{3}MLCT	565	3.3	1888
$\mathrm{Pt(phen)(C{\equiv}CC_6H_4F)_2}$[h]	$\mathrm{CH_3CN}$	^{3}MLCT	584	6.7	814
$\mathrm{Pt(CH_3phen)(C{\equiv}CC_6H_5)_2}$[g]	$\mathrm{CH_3CN}$	^{3}MLCT	575	5.5 ± 0.2	972
$\mathrm{Pt(phen)(C{\equiv}CC_6H_4CH_3)_2}$[h]	$\mathrm{CH_3CN}$	^{3}MLCT	578	6.2	549
$\mathrm{Pt(Brphen)(C{\equiv}CC_6H_5)_2}$[g]	$\mathrm{CH_3CN}$	^{3}MLCT	605	4.6 ± 0.2	366
$\mathrm{Pt(Clphen)(C{\equiv}CC_6H_5)_2}$[g]	$\mathrm{CH_3CN}$	^{3}MLCT	605	5.5 ± 0.7	390
Pt(tmphen)(tdt)[h]	$\mathrm{CH_2Cl_2}$	^{3}MMLLCT	675[k]	4.2	1911
Pt(bpy)(bdt)[i]	$\mathrm{CH_3CN}$	^{3}MMLLCT	700[k]	9.5	460
	$\mathrm{CHCl_3}$	^{3}MMLLCT	705[k]	4.0	560
Pt(dbbpy)(tdt)[h]	$\mathrm{CH_2Cl_2}$	^{3}MMLLCT	720[k]	1.0	489
Pt(dmbpy)(tdt)[h]	$\mathrm{CH_2Cl_2}$	^{3}MMLLCT	720[k]	2	360
Pt(phen)(tdt)[h]	$\mathrm{CH_2Cl_2}$	^{3}MMLLCT	730[k]	4.7	580

[a] dpphen = 4,7-diphenyl-1,10-phenanthroline; dmbpy = 4,4′-dimethyl-2,2′-bipyridine; dbbpy = 4,4′-di(*t*-butyl)-2,2′-bipyridine. [b] PEG = poly(ethylene glycol). [c] Ref. 7. [d] Ref. 5. [e] Ref. 6, 11. [f] Self-quenching rate obtained from the quenching half-concentration, assuming that $k_{MD} << k_D$. [g] Ref. 34. [h] Ref. 12, estimated errors for k_{sq} are ± 0.1 to ± 0.2. [i] Ref. 10. [j] Corrected emission maximum unless specified. [k] Uncorrected emission maximum. [l] Structured emission.

found to exhibit long-lived emission in room-temperature solution. The absence of solution emission from a ^{3}LF state is consistent with relatively rapid non-radiative decay, and the Laporte and spin-forbidden nature of this transition. Thermally accessible ^{3}LF states have been proposed in order to account for non-emissive platinum diimine complexes with lowest $^3(\pi-\pi^*)$, ^{3}MLCT, or ^{3}MMLLCT states. However, this explanation cannot fully account for the observed wide variations in sigma donor strength of ancillary ligands and energies of the lowest excited states. Strong interactions with solvent and/or non-totally symmetric distortions also are expected to play an important role in non-radiative decay, and these mechanisms are expected to depend on the orbital character of the excited state.[22,30,44,49]

A closer examination of the luminescent complexes in Table 1 reveals some general trends. The $E_{0,0}$ energies decrease along the emitting $^3(\pi-\pi^*)$, ^{3}MLCT, ^{3}MMLLCT series, ranging from ~2.7 to 1.7 eV.[50] The longest emission lifetimes and quantum yields tend to decrease along this series. Complexes with lowest $^3(\pi-\pi^*)$ excited states tend to have the longest emission lifetimes, as expected for highly spin-forbidden transitions. Of these, the di(cyanide) derivatives most often give rise to fluid solution emission. Complexes with a lowest ^{3}MLCT state have slightly longer lifetimes and larger emission quantum yields than those with a lowest ^{3}MMLLCT state. Of the ^{3}MLCT emitters, the di(arylacetylide) complexes frequently exhibit long-lived solution emission, which may be attributed to the orbital character of the excited state, and/or the reduction in ligand rotational motion near the metal center. Complexes with a cyclometalating diimine ligand, such as $Pt(dpp)(CH_3CN)^+$ (dpp = deprotonated 2,9-diphenyl-1,10-phenanthroline), also emit from a lowest ^{3}MLCT excited state with surprisingly long lifetimes (>1 μs).[8,9,51] Of the complexes with a lowest ^{3}MMLLCT state, those containing a toluenedithiolate (tdt^{2-}) ligand exhibit the longest excited-state lifetimes, which is consistent with an emissive state that is strongly stabilized with respect to LF states. For these reasons, fluid solution emission studies have focused on complexes with cyanide, arylacetylide, and toluenedithiolate ligands such as those listed in Table 1.

SELF-QUENCHING REACTIONS

All three classes of fluid-solution emitting platinum(II) diimine complexes, distinguished by their emissive triplet excited states, undergo self-quenching (Table 1). For each complex, the transient emission decay is single-exponential, and the corresponding rate of decay (k') exhibits a linear dependence on concentration according to Eq. (1). For neutral complexes (Table 1), the resulting self-quenching rates (k_{sq}) range from $\sim 10^9$ to $\sim 10^{10}$ $M^{-1}s^{-1}$, indicating a very efficient reaction. Since the unimolecular excited-state decay rates ($k_i = 1/\tau$) are relatively slow ($\sim 10^6$ s^{-1}), the self-quenching reaction plays a significant role in deactivation for concentrations greater than ~10 to 100 μM. Therefore, it is not surprising that self-quenching has not yet been reported for complexes with very short fluid solution lifetimes ($\tau < 100$ ns; $k_i > 10^7$ s^{-1}).[35] Limited solubility, weak emission, and short lifetimes are expected to restrict the range of accessible concentrations and observable emission decay rates.

Inspection of Table 1 provides some insight into the nature of this reaction. There is no firm correlation between the self-quenching rate and the orbital character or energy of the monomer emissive state, suggesting that, within this series, quenching is relatively insensitive to the electronic structure of the

TABLE 2 Excimer Emissions of Platinum(II) Diimine Complexes

		Monomer			Excimer			
Compound	Solvent	Emissive state	τ(ns)	λ_{max}(nm)	τ_D(ns)	λ_{max} (nm)	FWHM[g] (cm^{-1})	ΔE(cm^{-1})[h]
Pt(dpphen)(CN)$_2$[a]	PEG	$^3(\pi-\pi^*)$	100	530[f]	~100	630	~3500	4500
	CH_2Cl_2	$^3(\pi-\pi^*)$	13000	520[f]	~3000	665	~4000	5900
Pt(dppby)(CN)$_2$[b]	$CH_3CH_2Cl_2$	$^3(\pi-\pi^*)$	2900	485[f]	~40	565	~3600	6700
[Pt(dppH)(CH_3CN)](ClO_4)[c]	CH_2Cl_2	^{3}MLCT	14000	550[f]	~900	~700	~4400	3500
Pt(phen)(C≡CPh)$_2$[d]	CH_2Cl_2	^{3}MLCT	904	565	~100	~750	~2800	6700
Pt(C_6H_5C≡Cphen)-(C≡CC_6H_5)$_2$[e]	CH_3CN	^{3}MLCT	5600	590	—	~750	~2600	7000

[a] Ref 6, 11. [b] Ref 7. [c] Ref 9. [d] Ref 12. [e] Ref 34. [f] Structured emission. [g] FWHM = full-width at half maximum intensity. [h] $\Delta E = E_{0,0} - \nu_{max}$ (excimer).

monomer. Nevertheless, it should be noted that all three classes of complexes share a common electronic property, namely a lowest energy unoccupied diimine π^* orbital. On the other hand, it is readily apparent that bulky substituents on the diimine ligand slow the reaction. For example, the *t*-butyl groups of dbbpy appear to reduce the self-quenching rate by a factor of ~5. Unfortunately, there is limited information concerning the steric effects of the ancillary anionic ligands. Similarly, the solvent dependence of these reactions has not yet been examined in detail. However, there is mounting evidence to suggest that halogenated solvents decrease the self-quenching rate slightly more than expected from viscosity considerations for a diffusion-controlled process.[52,53] It also should be noted that charged complexes exhibit self-quenching rates that are ~5–10 times slower than observed for neutral complexes,[8,9,51] as expected from coulombic repulsions. However, the ionic strength dependence of these reactions has not yet been investigated.

The accumulated evidence suggests that self-quenching is predominantly a dynamic process, resulting from a collisional encounter between an excited complex and a ground-state complex. The absorption spectra of the compounds in Table 1 obey Beer's Law over the investigated concentration ranges. Similarly, the excitation spectra are in good agreement with the absorption spectra. For several complexes, the observed decay rates (k') and quantum yields are known to be insensitive to excitation wavelength, indicating that self-quenching is not a static process. Also, these rates are invariant over modest ranges of excitation power, suggesting that self-quenching is not dominated by triplet-triplet annihilation.[10,12,54]

EXCIMER FORMATION

Fluid solution excimer emission has been reported for five platinum diimine complexes with lowest $^3(\pi-\pi^*)$ or ^{3}MLCT monomer excited states (Table 2).[6,7,9,11,12,34] In each case, concentrated solutions give rise to a new emission band, shifted to the red of the monomer emission. At modest concentrations (10^{-3} M), there is considerable evidence to support the view that this new emission band does not arise from ground-state aggregation. (At high concentrations, ground-state aggregation can significantly contribute to excimer emission, and careful control experiments are necessary to address this possibility.) Notably, Che and coworkers[7] reported that the excitation spectrum for the red excimer emission from concentrated solutions of $Pt(dbbpy)(CN)_2$ agrees with the excitation spectrum for the green monomer emission from dilute solutions. In the case of 10^{-4} M $Pt(phen)(C{\equiv}CPh)_2$, the transient monomer emission signal at 565 nm shows single-exponential decay kinetics following a laser flash, whereas the excimer emission signal at 750 nm is biexponential, reaching its maximum intensity ~150 ns after the laser flash (Figure 9b).[12] Unfortunately, direct characterization of these excimers has been somewhat hampered by their apparent short lifetimes as compared to the lifetimes of the excited monomers. In most instances, the observed excimer emission signal decays at nearly the same rate as the monomer emission, as expected for a relatively short-lived species.

Steady-state emission spectra suggest that ligand-ligand and/or Pt-Pt interactions may stabilize the excited dimer. The emission profiles are moderately broad (FWHM ~2800–4400 cm^{-1}) and unstructured.[55] The maxima span a wide range of energies, indicating that the emission energy is dependent on the ligands surrounding the platinum center. For example, Pt(dbbpy)$(\mathrm{CN})_2$ excimer emission maximizes at 575 nm (Figure 9a), whereas Pt(phen)$(\mathrm{C{\equiv}CPh})_2$ excimer emission maximizes at 750 nm (Figure 9b) in methylene chloride solution.[12] In Table 2, the red shift in the excimer emission relative to the monomer emission is represented by ΔE, corresponding to the difference between the monomer emission $E_{0,0}$ and the excimer peak transition energy. These large shifts (3500–7000 cm^{-1}) are comparable to those found for organic aromatics (e.g., benzene, 5700; naphthalene, 6500; pyrene, ~6000 cm^{-1}),[53] suggesting comparably strong intermolecular interactions (>5 kcal/ mole). In addition, the solution excimer emission profiles are similar to those observed for room-temperature solid samples of platinum diimine complexes.[13–15,19–22,26] For example, $[\mathrm{Pt(phen)_2}]\mathrm{Cl_2}$ exhibits a low-energy ligand-ligand excimer emission that is very sensitive to moisture and sample history ($\lambda_{\mathrm{max}} \sim 530$–640 nm, ΔE ~3300–6600 cm^{-1}, FWHM ~2400–4200 cm^{-1}). Similarly, discrete $\mathrm{Pt(tpy)Cl^+}$ dimers (tpy = 2,2′:6′,2″-terpyridine) and extended chains of platinum diimine complexes with short Pt-Pt interactions exhibit low-energy and slightly asymmetric emission profiles ($\lambda_{\mathrm{max}} \sim 600$–780 nm, $\Delta E \sim 4500$–9400 cm^{-1}, FWHM ~2000–4300 cm^{-1}).[13,14,18,20,21,56] Interestingly, both ligand···ligand and Pt···Pt interactions are present in the ground-state structure of the head-to-tail isomer of $[\mathrm{Pt(dbbpy)}(\mu\text{-pyS})]_2^{2+}$ (Pt-Pt, 2.917[2] Å), resulting in a weak, symmetric emission in methylene chloride solution ($\lambda_{\mathrm{max}} \sim 603$ nm, FWHM ~3500 cm^{-1}, $\tau = 320$ ns).[57]

Excimer emission quantum yields are not available for all of the complexes listed in Table 2. Nevertheless, from the relative intensities of the monomer and excimer emissions,[6,7,9,11,34] it appears that complexes with lowest $^3(\pi-\pi^*)$ monomer states have higher quantum yields than those with lowest ^{3}MLCT monomer states. This trend could account for the fact that excimer emission has not been reported for a diimine dithiolate complex. Additionally, Table 2 suggests that emission from those complexes will lie to the red of 800 nm, where multialkali photocathode photomultiplier tubes are relatively insensitive.

QUENCHING KINETICS

Formation of a metastable $\mathrm{M_2}^*$ excimer suggests the possibility of the reverse reaction, namely dissociation to reform the excited monomer (M*)

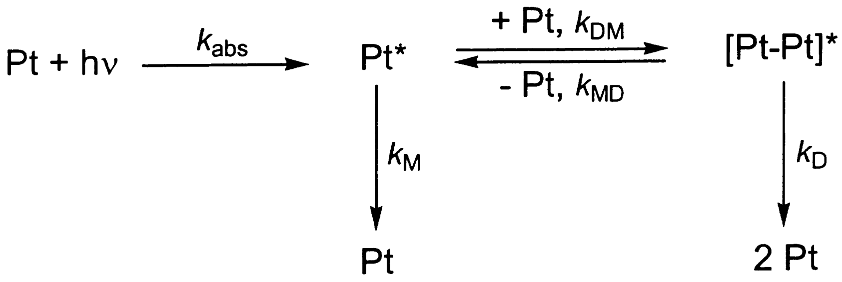


FIGURE 10

and a ground-state complex (M). This situation is illustrated in Figure 10, in which k_{abs}, k_{M}, k_{MD}, and k_{D} represent unimolecular rate constants, and k_{DM} is the bimolecular rate constant for formation of the excimer. A similar model was used by Birks[58] to describe monomer/excimer fluorescence kinetics of aromatic hydrocarbons, with the chief distinction being that, in the present case, the excited platinum complexes have predominantly triplet spin character. Unfortunately, the kinetics parameters have not been fully determined for any of the complexes in Table 1, and present estimates of k_{D} $(=1/\tau_{\text{D}}$, Table 2), k_{DM}, and k_{MD} should be regarded as approximate.

It is intriguing that this model predicts biexponential kinetics for monomer emission decay, whereas each of the compounds listed in Table 1 exhibit single-exponential emission decay kinetics over the investigated concentration ranges ($\sim 10^{-6}$–10^{-3} M). The predicted time-dependences of the emissions provide a possible explanation for this behavior.[59] Following excitation using a short laser flash, the monomer emission intensity, $i_{\text{M}}(t)$, and excimer emission intensity, $i_{\text{D}}(t)$, obey proportionalities (2) and (3), respectively:[58]

$$i_{\text{M}}(t) \propto e^{-\lambda_1 t} + Ae^{-\lambda_2 t} \tag{2}$$

$$i_{\text{D}}(t) \propto e^{-\lambda_1 t} - e^{-\lambda_2 t} \tag{3}$$

where:

$$A = \frac{k_{\text{M}} + k_{\text{DM}}(\text{Pt}) - \lambda_1}{\lambda_2 - k_{\text{M}} + k_{\text{DM}}(\text{Pt})}$$

$$\begin{aligned} \lambda_{1,2} = \frac{1}{2}\Bigg(& k_M + k_{\text{MD}}(\text{Pt}) + k_{\text{D}} + k_{\text{MD}} \\ & \mp \sqrt{\left[k_D + k_{\text{MD}} - k_M - k_{\text{MD}}(\text{Pt})\right]^2 + 4k_{\text{MD}}k_{\text{DM}}(\text{Pt})}\Bigg) \end{aligned} \tag{4}$$

For the only two reported cases, Pt(dbbpy)(CN)$_2$ (4×10^{-3} M)[7] and Pt(phen)(C≡CPh)$_2$ (10^{-4} M),[12] fitting of the biexponential excimer emission decay gives values for λ_1 and λ_2 of $\sim 10^6$ and $\sim 10^7$ s^{-1}, respectively. For these rates, the predicted biexponential behavior of the monomer emission should have been evident in the transient emission decay. Thus, the observed single-exponential emission decay can only be explained if $A \ll 1$, as expected for a linear dependence of λ_1 on concentration according to:

$$\lambda_1 \approx k_M + k_{\mathrm{DM}}(\mathrm{Pt}) \tag{5}$$

This condition holds when:

$$[k_D + k_{\mathrm{MD}} - k_M - k_{\mathrm{MD}}(\mathrm{Pt})] \gg \sqrt{4k_{\mathrm{MD}}k_{\mathrm{DM}}(\mathrm{Pt})}$$

which is satisfied for relatively small values of k_{MD} ($\leq 10^6$ s^{-1}) and low to modest concentrations.

In fact, using rate parameters obtained from modeling the emission decays for Pt(dbbpy)(CN)$_2$ and Pt(phen)(C≡CPh)$_2$, we have found that λ_1 scales linearly with concentration up to $\sim 7 \times 10^{-3}$ and $\sim 3 \times 10^{-3}$ M, respectively.[60] The observed linear dependence of the emission decay (k') on concentration for all of the complexes listed in Table 1, as described by Eq. (1), supports this interpretation and suggests $k_{\mathrm{sq}} \sim k_{\mathrm{DM}}$. Thus, it appears that these excimers are moderately stable (> 4 kcal/mol), exhibiting relatively large $k_{\mathrm{DM}}/k_{\mathrm{MD}}$ ratios, as recently suggested for Pt(dpphen) (CN)$_2$ ($\sim 3 \times 10^4$ M^{-1}).[11,61] Evidently, the low solubility of these metal complexes has prevented measurements of λ_1 (and λ_2) at higher concentrations where a non-linear dependence on concentration is expected. Clearly, reliable measurements at high concentrations are needed to evaluate these rate constants and assess the validity of Figure 10. Moreover, variable temperature measurements are necessary to determine the excimer binding energies.

Integration of Eq. (2) leads to the familiar result that the reciprocal of the emission quantum yield (Φ_{M}) is linearly dependent on concentration for diffusional quenching:[58]

$$\frac{1}{\Phi_M} = \frac{1}{\Phi_M^0} + \frac{k_{\mathrm{sq}}}{\Phi_M^0 k_i}(\mathrm{Pt}) \tag{6}$$

where Φ_{M}^0 is the emission quantum yield at infinite dilution, and:

$$k_{\mathrm{sq}} = \frac{k_{\mathrm{DM}}k_D}{(k_D + k_{\mathrm{MD}})}$$

If $k_{\mathrm{D}} \gg k_{\mathrm{MD}}$, it can be concluded that: $k_{\mathrm{sq}} \sim k_{\mathrm{DM}}$. In fact, Φ_{M} has been reported to decrease with concentration, and Eq. (6) has been used to estimate

Φ_M^0, using the self-quenching rate (k_{sq}) obtained from time-resolved emission measurements.[9,34] However, the validity of Eq. (6) has not been confirmed by independent quantum yield studies. Such investigations are warranted because they would help to evaluate the role (if any) of ground-state association. The reciprocal of Φ_M is expected to show a quadratic dependence on concentration if both static and dynamic quenching mechanisms are active.[53]

CROSS-QUENCHING REACTIONS

Because of the limited solubility of these complexes and difficulties in characterizing their excimers, indirect approaches, such as studies of cross-quenching, can provide valuable insight into the mechanism of quenching. In these reactions, it is believed that the excited platinum complex (M*) reacts with a ground-state complex (Q) to form an exciplex, MQ*. Thus, this reactivity is consistent with Figure 10, except an exciplex is formed instead of an excimer. Suitable quenchers are selected based on energetics in order to ensure that quenching cannot occur by an electron-transfer or energy-transfer mechanism.

Eisenberg and coworkers[12] have measured the rate of Pt(tmphen)(tdt) emission decay ($\lambda_{max} = 720$ nm) in the presence of several potential quenchers. Interestingly, the emission lifetime was observed to be independent of added phenanthroline or naphthalene up to very high concentrations ($> 10^{-2}$ M), suggesting that aromatic molecules do not act as quenchers. However, in the presence of other platinum diimine complexes, the rate of Pt(tmphen)(tdt) emission decay ($k'' = 1/\tau$) was found to depend linearly on the concentration of the added platinum diimine quencher (Q) according to:

$$k'' = k_{cq}(Q) + k' \tag{7}$$

For example, when Pt(phen)($C{\equiv}CPh)_2$ is added to a methylene chloride solution of Pt(tmphen)(tdt), the observed cross-quenching rate ($k_{cq} = 3 - 5 \times 10^9\ M^{-1}s^{-1}$) is similar to the self-quenching rates for Pt(phen)($C{\equiv}CPh)_2$ ($3.3 \times 10^9\ M^{-1}s^{-1}$) and Pt(tmphen)(tdt) ($4.2 \times 10^9\ M^{-1}s^{-1}$). Addition of Pt(dbbpy)$Cl_2$ or Pt(dbbpy)$(CN)_2$ to a methylene chloride solution of Pt(tmphen)(tdt) also increases the rate of emission decay with cross-quenching rates of $2.1 \times 10^9\ M^{-1}s^{-1}$ and $0.9 \times 10^9\ M^{-1}s^{-1}$, respectively. When Pt(tmphen)(tdt) is added to a solution of Pt(phen)($C{\equiv}CPh)_2$, the rate of Pt(phen)($C{\equiv}CPh)_2$ emission decay increases linearly with Pt(tmphen)(tdt) concentration. The remarkably fast quenching rate ($9.0 \times 10^9\ M^{-1}s^{-1}$) is entirely consistent with energy transfer from the higher energy emitting di(arylacetylide) complex ($E_{0,0} = 2.5$ eV) to the dithiolate complex ($E_{0,0} = 2.1$ eV). Though limited in scope, these preliminary studies establish that cross-quenching reactions between platinum diimine complexes occur at rates ($\sim 10^9$–10^{10} $M^{-1}s^{-1}$) comparable to self-quenching rates, suggesting a similar mechanism. However, it must be emphasized that exciplex emission has not been reported for these systems.

STEADY-STATE CROSS-QUENCHING STUDIES

We have recently performed a series of cross-quenching experiments using steady-state emission spectroscopy. Quenching was assessed by monitoring the decrease in emission intensity with increasing quencher concentration. For a dynamic quenching process, the reciprocal of the integrated emission intensity (I) of the chromophore is expected to depend linearly on quencher concentration, (Q):

$$\frac{1}{I} = \frac{1}{I_0} + \frac{k_{cq}}{I_0 k'}(Q) \tag{8}$$

where I_0 is emission intensity in absence of quencher.

Pt(tmphen)(tdt) was selected as the chromophore for these studies, because it possesses: *(1)* a modest emission quantum yield ($\sim 6 \times 10^{-3}$ at 298K in CH_2Cl_2);[36] *(2)* a low-energy intense absorption band allowing selective excitation; and *(3)* a long excited-state lifetime ($\tau = 1900$ ns).[12] Suitable quenchers meet several requirements, including high solubility in methylene chloride, thermal inertness to Pt(tmphen)(tdt),[62] and a lowest excited-state > 2.1 eV to avoid energy-transfer quenching. In addition, we have chosen to focus on neutral quenchers to avoid complications of ionic strength.

To establish the validity of this approach, steady-state emission spectra of methylene chloride solutions of Pt(tmphen)(tdt) were measured in the presence of varying concentrations of Pt(dbbpy)Cl_2. The reciprocal of the integrated emission intensity exhibits a linear dependence on concentration according to Eq. (8) (Figure 11). The observed cross-quenching rate (2.3×10^9 $M^{-1}s^{-1}$) is in excellent agreement with the value (2.1×10^9 $M^{-1}s^{-1}$)[12] obtained from emission decay measurements. These results firmly establish that this cross-quenching behavior is dominated by diffusional quenching rather than ground-state association.

In order to probe the role of intermolecular ligand-ligand interactions in quenching, the emission intensity of Pt(tmphen)(tdt) was measured in the presence of varying concentrations ($< 10^{-2}$ M) of 2-2′-bipyridine, 4,4′-bipyridine, and anthracene. In agreement with Eisenberg's observations,[12] 2-2′-bipyridine ($k_{cq} < 10^6$ $M^{-1}s^{-1}$) and 4,4′-bipyridine ($k_{cq} < 10^7$ $M^{-1}s^{-1}$) have little effect on the Pt(tmphen)(tdt) emission, within the detection limits of our instrumentation ($< 10^6$ $M^{-1}s^{-1}$). These results suggest organic aromatics and nitrogen-based nucleophiles are relatively ineffective quenchers. In contrast, addition of anthracene to a solution of Pt(tmphen)(tdt) results

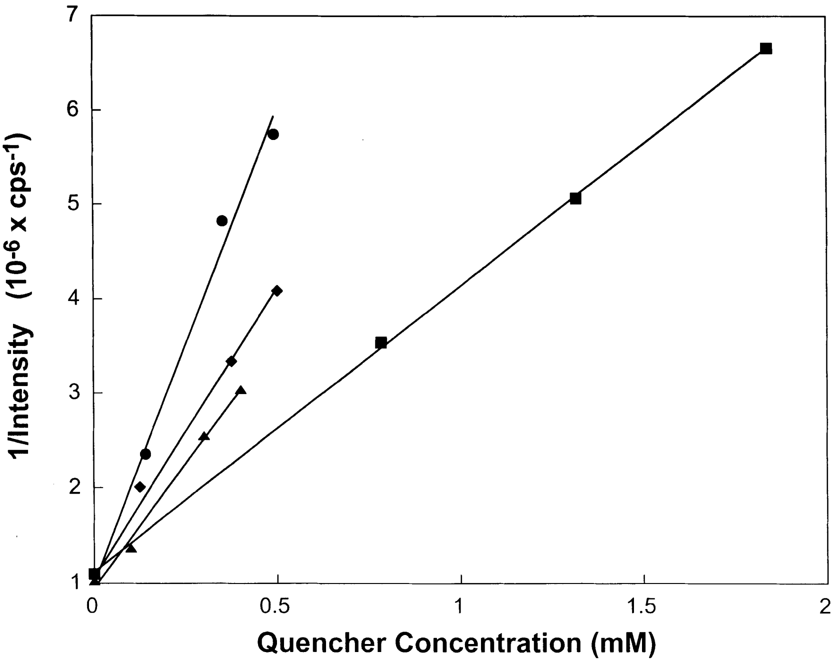
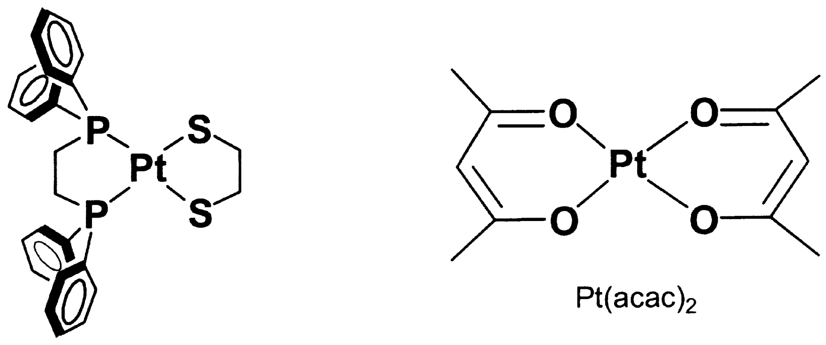


FIGURE 11 Stern-Volmer plots showing the reciprocal of Pt(tmphen)(tdt) emission intensity as a function of quencher concentration in CH_2Cl_2: Pt(bpy)Cl_2 (●), Pt(dmbpy)Cl_2 (◆), Pt(dbbpy)Cl_2 (■), Pt(phen)$(Ph)_2$ (▲).

in a decrease in emission intensity, corresponding to a cross-quenching rate (5.0×10^8 $M^{-1}s^{-1}$) that is somewhat slower than the self-quenching rate of Pt(tmphen)(tdt) (4.2×10^9 $M^{-1}s^{-1}$). The low triplet excited-state energy of anthracene ($E_{0,0} = 1.85$ eV) is consistent with quenching by energy transfer.

Similarly, complexes lacking a diimine ligand were chosen to investigate the role of intermolecular Pt-Pt interactions in quenching. No quenching ($<10^6$ $M^{-1}s^{-1}$) of the Pt(tmphen)(tdt) emission was observed upon addition of Pt(dppe)($C_2H_4S_2$) up to concentrations of 10^{-2} M. However, addition of a large excess of Pt$(acac)_2$ (1.5×10^{-2} M) to a solution of Pt(tmphen)(tdt) results in a slight but discernible decrease in emission intensity, apparently not attributable to thermal or irreversible photochemistry. Although the platinum center is relatively exposed, the corresponding cross-quenching rate ($< 10^7$ $M^{-1}s^{-1}$) is slow compared to self-quenching rates.

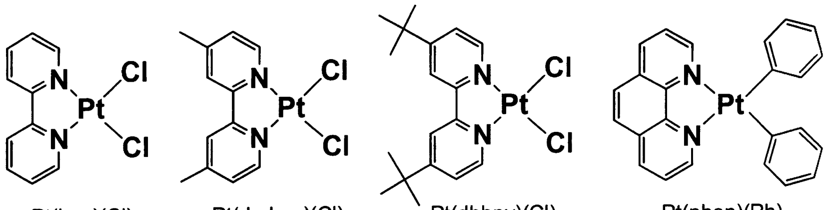
In fact, rapid quenching ($\sim 10^9$–10^{10} $M^{-1}s^{-1}$) was only observed with quenchers that contain both a diimine and the platinum center. The Pt(tmphen)(tdt) emission intensity was found to depend linearly on quencher



Pt(dppe)($C_2H_4S_2$)

Pt(acac)$_2$

FIGURE 12



Pt(bpy)(Cl)$_2$ Pt(dmbpy)(Cl)$_2$ Pt(dbbpy)(Cl)$_2$ Pt(phen)(Ph)$_2$

FIGURE 13

concentration (0–1.8 × 10^{-3} M) according to Eq. (8). The resulting Stern-Volmer plots are shown in Figure 11 and the cross-quenching rates, ranging from 2.3–8.3 × 10^9 $M^{-1}s^{-1}$, are given in Table 3. The observed rates are readily explained in terms of the steric properties of the quencher complexes. The least sterically hindered complex, Pt(bpy)Cl_2, was found to be the most efficient quencher ($k_{cq} = 8.3 \times 10^9$ M^{-1} s^{-1}) of this series. If methyl groups are substituted on the diimine as in Pt(dmbpy)Cl_2, the rate decreases by a factor of ~1.4. Substitution of *t*-butyl groups decreases the rate by a factor of ~4. A similar dependence on steric properties is evident for self-quenching reactions (Table 1), although slightly more pronounced since the steric properties of both the chromophore and quencher are affected by substitution. Steric effects around the metal center also influence the cross-quenching rate. For example, Pt(phen)(Ph)$_2$ gives a moderate cross-quenching rate (4.6 × 10^9 M^{-1} s^{-1}), suggesting that increased steric bulk near the platinum center also interferes with quenching.

QUENCHING MECHANISM

Self-quenching is a general property of platinum(II) diimine complexes exhibiting long-lived fluid solution emission. The accumulated evidence suggests a dynamic process, involving a diffusion-controlled collisional encounter between an excited complex and a ground-state complex to give a moderately stable excimer. The steady-state emission spectroscopy and the observed kinetics are consistent with the mechanism in Figure 10. The reaction is apparently insensitive to the nature of the lowest monomer excited state, and variations in rates can be understood in terms of the steric demands of substituents on the diimine ligands. Bulky substituents interfere with quenching, although the effects are modest in comparison to other excimers and exciplexes.[53,63]

There is little evidence to support the notion that self-quenching occurs by electron transfer. From the excited-state redox potentials we have estimated the photoinduced electron-transfer reaction driving forces (ΔG) for nine of the compounds in Table 1:

$$\mathrm{Pt}^{*} + \mathrm{Pt} \longrightarrow \mathrm{Pt}^{+} + \mathrm{Pt}^{-}$$

FIGURE 14

For the dithiolate complexes, with lowest MMLLCT states, the reaction is slightly unfavorable ($\Delta G = 0.011$ to 0.15 eV), whereas for the other two

TABLE 3 Cross-quenching Data of Pt(tmphen)(tdt) Emission in CH_2Cl_2

Quencher	k_{cq} 10^9 $M^{-1}s^{-1}$
$Pt(bpy)Cl_2$	8.3 ± 0.8^{a}
$Pt(dmbpy)Cl_2$	6.0 ± 0.6^{a}
$Pt(phen)Ph_2$	4.6 ± 0.4^{a}
$Pt(phen)(C{\equiv}CPh_2)^{c}$	$3\text{–}5^{b}$
$Pt(dbbpy)Cl_2$	2.3 ± 0.1^{a}, $2.1^{b,c}$
$Pt(dbbpy)(CN)_2^{c}$	0.9 ± 0.1^{b}
$Pt(acac)_2$	$< 0.01^{a}$
$Pt(dppe)(C_2H_4S_2)$	$< 0.001^{a,d}$
2,2′-bipyridine	$< 0.001^{a,d}$
4,4′-bipyridine	$< 0.001^{a,d}$

[a] From steady-state emission measurements. [b] From emission decay rate measurements. [c] Ref 12. [d] No quenching was observed, and this value represents the experimental detection limit.

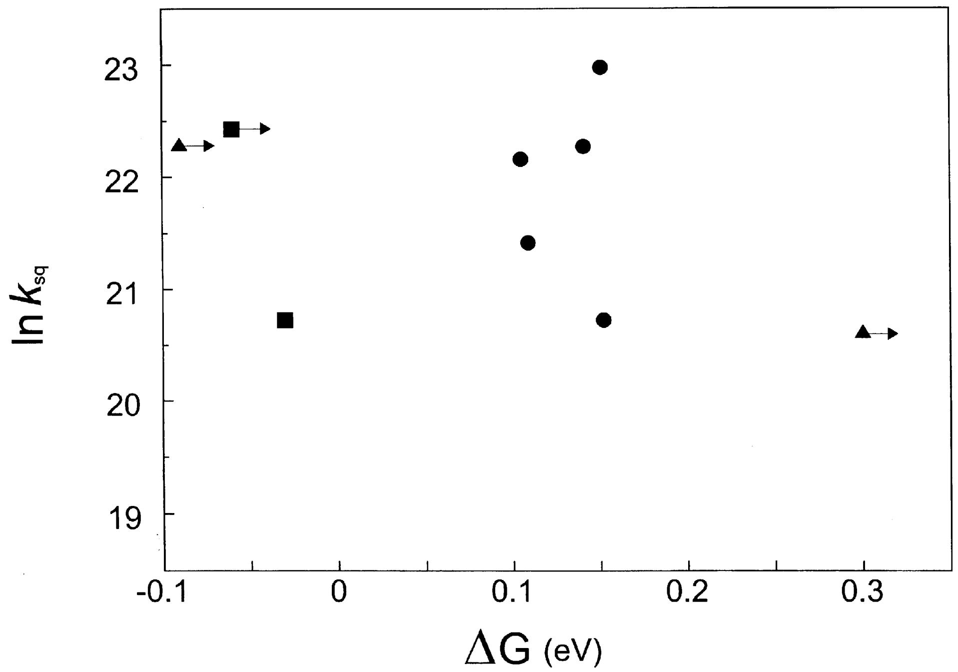


FIGURE 15 Electron-transfer driving force (ΔG) dependence of the self-quenching rates: (▲) Pt(dbbpy)(CN)$_2$ (0.300 eV), Pt(dmbpy)(CN)$_2$ (> −0.090 eV); (■) Pt(dbbpy)(C≡C$_6$H$_4$CH$_3$)$_2$ (> − 0.030 eV), Pt(CH$_3$phen)(C≡CC$_6$H$_5$)$_2$ (> −0.060 eV); (●) Pt(dbbpy)(tdt) (0.152 eV), Pt(bpy)(tdt) (0.151 eV), Pt(phen)(tdt) (0.141 eV), Pt(dmbpy)(tdt) (0.109 eV), Pt(tmphen)(tdt) (0.105 eV).

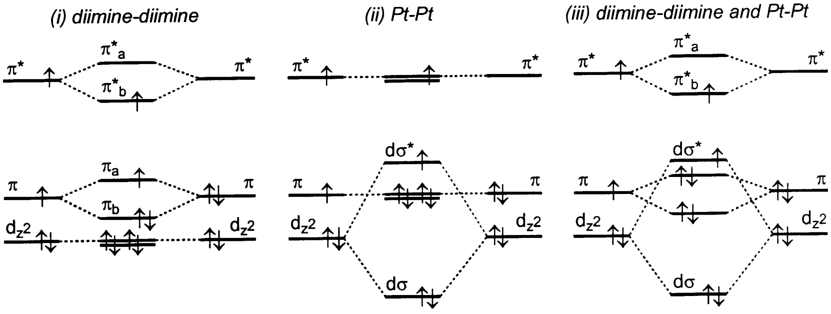


FIGURE 16

classes, the reaction is moderately favorable ($\Delta G = -0.03$ to $+0.30$ eV). If charge transfer plays a significant role, the self-quenching rate is expected to increase with driving force. However, Figure 15 gives no indication of a relationship between the two parameters, suggesting that any correlation is masked by steric effects. On the other hand, the role of charge-transfer in cross-quenching reactions is not known, and a similar analysis is warranted because of the intrinsically asymmetric nature of the proposed exciplexes.

It is likely that the excimer is stabilized by diimine-diimine and/or metal-metal interactions (Figure 5). Molecular orbital diagrams in Figure 16 illustrate the energetic benefits of each mode of association.[7,13] However, from emission spectra, it is not possible to distinguish conclusively which interactions are most important. In contrast, the results of cross-quenching experiments indicate that *both* the diimine ligand and platinum center are necessary for rapid quenching, suggesting that *both* diimine-diimine and metal-metal interactions stabilize the excited dimer. Alternatively, metal-diimine orbital mixing may play a critical role in optimizing the interactions associated with the other two modes of association.

EXPERIMENTAL

All reagents were obtained from Aldrich, Pressure Chemical, or Acros and used as received. Pt(tmphen)(tdt) was prepared using the method reported by Gray[10] for the synthesis of Pt(bpy)(bdt). Quenchers of the general formula Pt(diimine)X_2 were prepared by known procedures.[36,64–67] Freshly distilled CH_2Cl_2 was used to prepare the Pt(tmphen)(tdt) (60–70 μM) and quencher ($0–1.8 \times 10^{-3}$ M) solutions. Emission samples were freeze-pump-thaw degassed (three cycles) using a high vacuum line ($<10^{-5}$ torr). Steady-state emission spectra were recorded using a Spex Fluorolog-3 fluorimeter with a single excitation monochromator and a double emission monochromator. Samples were excited at 535 nm (absorbance 0.4–0.5), and a 570 nm cutoff filter was used to minimize scattered light. Each sample was monitored by absorption spectroscopy during the course of the experiment using an HP-8453 diode array spectrometer.

In a typical experiment, emission spectra were recorded for four samples with the same concentration of chromophore and varying amounts of quencher. One sample contained only the chromophore. The Pt(tmphen)(tdt) uncorrected emission band was integrated between 650–700 nm to give the total emission intensity (*I*). Using a Stern-Volmer analysis, the reciprocal of *I* was plotted against quencher concentration according to Eq. (8). For Pt(tmphen)(tdt), k_i (5.23×10^5 s^{-1}) and k_{sq} (4.2×10^9 $M^{-1}s^{-1}$) have previously been determined.[12] Cross-quenching rate estimated standard deviations (σ) represented as $\pm 2\sigma$ were determined by propagating estimated uncertainties in concentrations and emission intensity measurements. Because of the photo-instability of Pt(tmphen)(tdt) in halogenated solvents,[68] care was taken to minimize unnecessary exposure to light. Decomposition during any set of quenching rate measurements was less than 2.0%.

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63. A similar situation, namely A<<1 and linear dependence of λ_1 on concentration (298K, $k_{DM} = 6.7 \times 10^9$ M^{-1} s^{-1}, $k_{MD} = 6.5 \times 10^6$ s^{-1}), is encountered for pyrene self-quenching at low to moderate concentrations ($< 2 \times 10^{-3}$ M, Ref. 58).

64. Some prospective quenchers have been found to react thermally with Pt(tmphen)(tdt) in solution, and several complexes have been excluded as possible quenchers, including Pt(phen)$(CH_3)_2$, Pt(dpphen)Cl_2, and Pt(bpy)$(\text{pyrazolate})_2$.
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