Articles

Photobehavior of (α-Diimine)dimesitylplatinum(II) Complexes

Keenan E. Dungey, Brian D. Thompson, Noel A. P. Kane-Maguire,* and Laura L. Wright*

Department of Chemistry, Furman University, Greenville, South Carolina 29613-1120

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The photobehavior of complexes of the type Pt(diimine)(mes)$_2$ is investigated (where diimine = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp), 2,9-dimethyl-1,10-phenanthroline (2,9-dmp), 5,6-dimethyl-1,10-phenanthroline (5,6-dmp), and 4,7-diphenyl-1,10-phenanthroline (dpp) and mes = the mesityl (2,4,6-trimethylphenyl) anion). For all compounds studied, solution RT emission is observed to be weak and excited-state lifetimes are found to be short (≤20 ns) regardless of solvent choice. Evidence is presented for energy-transfer quenching of Pt(dpp)(mes)$_2$ luminescence in toluene by dissolved O$_2$ (primarily producing singlet oxygen) with an observed quenching rate constant of $k_q \geq 1.3 \times 10^9$ M^{-1} s^{-1}. Electron-transfer quenching is also observed in the presence of 3,5-dinitrobenzonitrile, yielding a quenching rate constant of $k_q \geq 1.6 \times 10^9$ M^{-1} s^{-1}. The latter observation suggests that these Pt(II) systems may have future value as excited-state reductants. All of the complexes display a much more intense and longer-lived luminescence in the solid state at room temperature. Several possible explanations for this dependence on phase are proposed, with the most probable mechanism involving radiationless deactivation in solution via rotation of the *o*-methyl groups of the mesityl ligands.

Introduction

The spectroscopy of platinum(II) complexes containing polypyridyl ligands has been the focus of considerable current attention.[1−15] For these square planar d^8 molecules the axial positions are relatively open and vulnerable to both nucleophilic attack and intermolecular Pt−Pt stacking. Thus, the corresponding spectral behavior and electrochemistry of these Pt(II) species often strongly reflect the presence of this coordinatively unsaturated square planar geometry.[3−6,12,13] Interesting exceptions are complexes of the type Pt(α-diimine)(mes)$_2$ recently described by Klein and Kaim, where mes is the mesityl (2,4,6-trimethylphenyl) anion and α-diimine is a bidentate polypyridyl ligand based on the 2,2′-bipyridine or 1,10-phenanthroline framework.[16−18] Their electrochemical studies show that the presence of two mesityl ligands is a necessary condition for reversible oxidation. The unusual stability of the Pt(III) oxidation state was proposed to be due to blocking of the potential axial coordination sites by the *o*-methyl groups on the two mesityl ligands.[17] Klein et al. also reported that the complexes have low-lying MLCT excited states and exhibit room temperature (RT) emission. These observations suggest that these species may be of value as donors in excited-state energy-transfer and electron-transfer studies—an area as yet not extensively explored for Pt(II) diimine complexes.[6,11,14,15]

We have therefore initiated a study of the photobehavior of six Pt(diimine)(mes)$_2$ complexes. The diimines selected for study (see Figure 1) included 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 3,4,7,8-tetramethylphenanthroline (tmp), 2,9-dimethylphenanthroline (2,9-dmp), 5,6-dimethylphenanthroline (5,6-dmp), and 4,7-diphenylphenanthroline (dpp). The complexes include three previously reported by Kaim et al.[16−18] and three new phenanthroline-based complexes whose syntheses are described in the present investigation. Examples of excited-state electron transfer and excited-state energy transfer producing singlet oxygen are reported for Pt(dpp)(mes)$_2$ in RT toluene

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* To whom correspondence should be addressed. Phone: (864) 294-3374 (N.A.P.K.-M.); (864) 294-3375 (L.L.W.). Fax: (864) 294-3559. E-mail: noel.kane-maguire@furman.edu; laura.wright@furman.edu.

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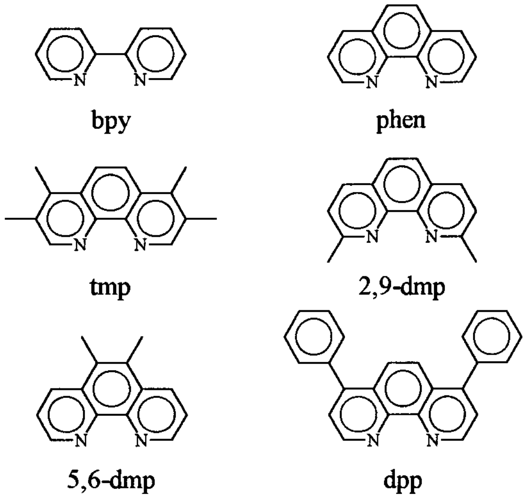

Figure 1. α-Diimine ligands selected for study.

solution. The complexes are weakly emissive in RT solution but exhibit intense luminescence and long excited-state lifetimes in the solid state.

Experimental Section

General Details. Unless noted otherwise, all reactions were performed under inert atmosphere (prepurified N_2) using standard Schlenk techniques. Toluene was predried over Na/benzophenone and distilled under N_2. $Pt(mes)_2(dmso)_2$ (dmso = dimethyl sulfoxide) was prepared according to a literature procedure.[19] Other chemicals were purchased from Aldrich or GFS Chemicals and used as received. CHN analyses were performed by Midwest Microlab.

Instrumentation and Methods. NMR spectra were recorded on Varian VXR-300s and Varian Inova 500 spectrometers. A Perkin-Elmer Paragon 500 spectrometer was employed for IR spectral measurements, and UV−visible absorption spectra were obtained on an HP 8452 diode array spectrophotometer. Solution and solid-state steady-state emission spectra for the $Pt(diimine)(mes)_2$ complexes were collected on an SPEX Fluorolog-2 spectrofluorometer employing a red-sensitive Hamamatsu R928 photomultiplier tube. The emission quantum yield (Q_{Pt}) for an air-saturated toluene solution of $Pt(tmp)(mes)_2$ was estimated from a comparison of the integrated emission signal with that of an absorbance-matched, N_2-saturated, aqueous solution of $Ru(bpy)_3^{2+}$ under identical slit conditions. Q_{Pt} is given by the relationship[20] $Q_{Pt} = Q_{Ru}\,(n_{toluene}/n_{H_2O})^2(D_{Pt}/D_{Ru})$, where Q_{Ru} = absolute quantum yield for $Ru(bpy)_3^{2+}$ = 0.042,[21] n = solvent refractive index, and D = area under the relevant emission spectrum. Corresponding steady-state emission studies of the 1270 nm singlet oxygen, $O_2(^1\Delta_g)$, phosphorescence signal were undertaken using the near-IR accessory of the Fluorolog-2 instrument (which incorporates a germanium photodiode cooled to 77 K). The quantum yield for $^1O_2$ generation by $Pt(dpp)(mes)_2$ was measured by comparing the integrated $^1O_2$ emission signal sensitized by the Pt(II) complex with that of a perinaphthenone standard under identical experimental conditions.[22] Excited-state lifetime studies of $Pt(diimine)(mes)_2$ species utilized a N_2/dye laser system described elsewhere.[23] Cyclic voltammetry studies employed a BAS100b potentiostat and were carried out in toluene solution at approximately 50 °C using 0.2 M tetrahexylammonium perchlorate as the supporting electrolyte.[24] Pt disk working and auxiliary electrodes and a Ag wire quasi-reference electrode were used, and ferrocene was utilized as an added calibrant in the solvent system employed. Observed potentials were converted to voltages vs NHE by assuming $E°\,(Cp_2Fe^{+/0}) = +0.40$ V vs NHE.[25]

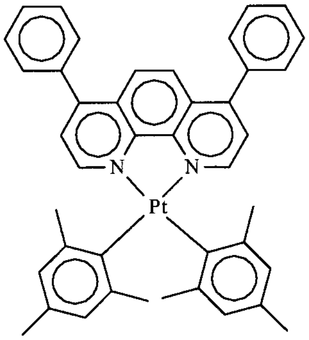

Figure 2. Structure of the $Pt(dpp)(mes)_2$ complex.

General Synthetic Procedure for $Pt(diimine)(mes)_2$ Complexes. In analogy to the literature procedure for the synthesis of $Pt(bpy)(mes)_2$,[17] a solution of bis(dimethyl sulfoxide)-dimesitylplatinum(II) (40 mg, 0.068 mmol) and an α-diimine ligand (0.074 mmol) in 11 mL of toluene was prepared and heated to reflux for 3 days. During the course of the reaction, the solution turned from colorless to deep red. Upon cooling, the solvent was removed to yield a yellow-orange solid, which was then dissolved in hot 1,2-dichloroethane. The resulting solution was filtered through a fine frit to remove colloidal platinum; then cold hexanes were added to induce recrystallization.

(a) $Pt(2,9\text{-}dmp)(mes)_2$. Yield: 81%. ^1H NMR ($CDCl_3$): δ 8.29 (d, 1H, 4,7-H), 7.77 (s, 1H, 5,6-H), 7.40 (d, 1H, 3,8-H), 6.44 (s, 2H, mes H), 2.36 (s, 6H, o-CH_3), 2.15 (s, 3H, 2,9-CH_3), 2.12 (s, 3H, p-CH_3). Anal. Calcd for $C_{32}H_{34}N_2Pt$: C, 59.89; H, 5.34; N, 4.37. Found: C, 59.56; H, 5.25; N, 4.38.

(b) $Pt(5,6\text{-}dmp)(mes)_2$. Yield: 45%. ^1H NMR ($CDCl_3$): δ 8.69 (m, 2H, 2,4,-H, 7,9-H), 7.66 (dd, 1H, 3,8-H), 6.70 (s, 2H, mes H), 2.74 (s, 3H, 5,6-CH_3), 2.48 (s, 6H, o-CH_3), 2.24 (s, 3H, p-CH_3). Anal. Calcd for $C_{32}H_{34}N_2Pt$: C, 59.89; H, 5.34; N, 4.37. Found: C, 59.56; H, 5.25; N, 4.36.

(c) $Pt(4,7\text{-}dpp)(mes)_2$. Yield: 43%. ^1H NMR ($CDCl_3$): δ 8.80 (d, 1H, 2,9), 7.98 (s, 1H, 5,6-H), 7.61 (d, 1H, 3,8-H), 7.56 (m, 5H, 4,7-C_6H_5), 6.73 (s, 2H, mes H), 3.73 (s, 1H, CH_2Cl_2), 2.55 (s, 6H, o-CH_3), 2.26 (s, 3H, p-CH_3). Anal. Calcd for $C_{42}H_{38}N_2Pt{\cdot}C_2H_4Cl_2$: C, 61.09; H, 4.90; N, 3.24. Found: C, 60.24; H, 4.80; N, 3.33.

Results and Discussion

Syntheses. Six complexes with the general formula $Pt(diimine)(mes)_2$ were synthesized. The bpy, phen, and tmp complexes had previously been reported by Klein et al., and the new 2,9-dmp, 5,6-dmp, and dpp systems were synthesized using their general method.[17,18] The procedure involved refluxing a toluene solution of bis(dimethyl sulfoxide)dimesitylplatinum(II) and the appropriate α-diimine for 3 days. Upon cooling and concentration of the resulting solution, yellow-orange solids were isolated. A typical structure for the $Pt(diimine)(mes)_2$ complexes is shown in Figure 2. Each complex was recrystallized from dichloroethane/hexane and characterized by ^1H NMR spectroscopy and elemental analysis to confirm purity.

Solution Emission Studies. Preliminary studies revealed that the $Pt(diimine)(mes)_2$ systems were remarkably stable in the solvent toluene. For example, solution absorption spectra of the complexes in this noncoordinating solvent remained unchanged after several weeks of standing at RT. For this reason, most solution steady-state emission data were collected in toluene. Representative UV−vis absorption and emission spectra are presented in Figure 3 for the case of $Pt(dpp)(mes)_2$, and emission

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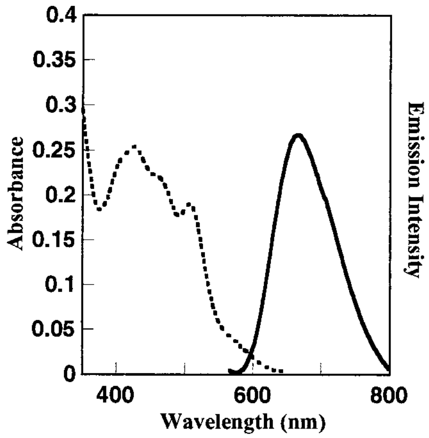

Figure 3. UV−visible absorption spectrum (···) and emission spectrum (—) at RT for a 3.8×10^{-5} M toluene solution of Pt(dpp)(mes)$_2$. Wavelength of excitation for emission = 450 nm (1 cm cell).

Table 1. Absorption and Emission Maxima for Pt(diimine)(mes)$_2$ Complexes in RT Toluene Solutions

diimine	λ_{abs} (nm)	λ_{em} (nm)[a]	rel emission intens[b]
bpy	352 (sh), 406, 432, 459, 504, 570 (sh)	650	0.21
phen	338 (sh), 418, 450, 500, 565 (sh)	640	0.67
tmp	344, 398, 444, 468 (sh), 522 (sh)	600	1.00[c]
5,6-dmp	416, 454, 496, 570 (sh)	640	0.54
2,9-dmp	418, 494	none	
dpp	402 (sh), 426, 460 (sh), 508, 570 (sh)	660	0.75

[a] λ_{ex} = 450 nm. [b] Absorbance-matched solutions at the excitation wavelength. No corrections have been made for wavelength variations in PMT response. Manufacturer data for the R928 detector indicate a 25% decrease in detector quantum efficiency between 600 and 660 nm. [c] The emission quantum yield for Pt(tmp)(mes)$_2$, Q_{Pt}, is approximately 5×10^{-4}, from a comparison of the integrated emission signal with that of an absorbance-matched Ru(bpy)$_3^{2+}$ aqueous solution (see Experimental Section for details).

and absorption maxima in toluene solution for the six complexes studied are collated in Table 1. In all cases, emission decay times were immeasurably short (≤20 ns). The emission spectral band shapes and wavelength maxima are very similar to solution values reported earlier by Klein and Kaim et al.[17] and are thus assigned as π^*(diimine) → d_π(Pt) charge transfer (MLCT) in nature.

Although RT solution emission was invariably weak, a comparison of the luminescence signals of absorbance-matched toluene solutions of Pt(phen)(mes)$_2$ and Pt(bpy)(mes)$_2$ revealed an approximately 3-fold greater emission intensity for the phenanthroline-based systems. Using the complex that had the strongest emission signal, Pt(tmp)(mes)$_2$, steady-state emission spectra were also obtained in acetonitrile, chloroform, deuterated chloroform, dimethylformamide, benzene, benzene-d_6, toluene-d_8, mesitylene, 2-methyltetrahydrofuran (2-MeTHF), and carbon tetrachloride. Only minor variations in emission efficiencies were detected over this range of solvents. A very close agreement between the solution absorption and excitation spectra was observed for these complexes (Figure S1, Supporting Information). This observation is in accord with the emission being associated with the title compounds and not sample impurities.

Solid-State Emission Studies. All six complexes displayed an almost iridescent glow when solid samples were exposed to excitation light of $\lambda \geq 300$ nm at RT. This observation represents a dramatic increase in emission intensity (about 2 orders of magnitude) relative to the corresponding solution data noted earlier. A representative comparison between solution and solid-state emission spectra is provided in Figure 4 for the case of Pt(tmp)(mes)$_2$, while Table 2 summarizes the steady-state emission maxima and emission lifetimes obtained for the solids upon 440 nm excitation. Marked increases in RT emission decay times were also apparent in the solid state, with solids in general exhibiting excited-state lifetimes ≥0.15 μs. The emission spectral band shapes were similar to the corresponding solution values, although emission maxima were consistently at shorter wavelengths (see Tables 1 and 2). This hypsochromic shift may be a reflection of restricted excited-state distortion in the solid-matrix environment. The corresponding solid-state data at 77 K are also provided in Table 2, which reveals 3−6-fold increases in emission lifetimes relative to the RT values.

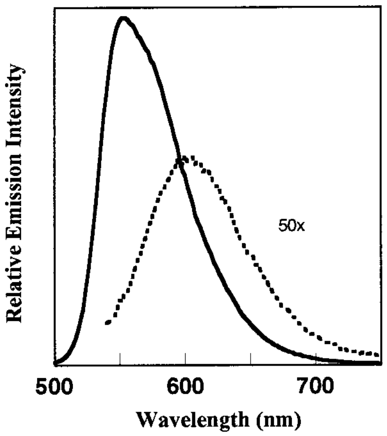

Figure 4. Steady-state RT emission spectra of Pt(tmp)(mes)$_2$ in the solid state (—) and for a 4.0×10^{-5} M toluene solution (···). Wavelength of excitation = 440 nm.

Table 2. Photoluminescence Lifetimes (τ) of Pt(diimine)(mes)$_2$ Complexes in the Solid State[a]

	RT		77 K	
diimine	λ_{em} (nm)	τ (μs)	λ_{em} (nm)	τ (μs)
bpy	610	0.15	590	0.9
phen	600	0.30	600	1.8
tmp	575	0.62	560	2.1
5,6-dmp	580	0.38	570	1.7
2,9-dmp		<20 ns	620	1.2
dpp	620	0.30	610	1.3

[a] λ_{ex} = 440 nm.

Origin of Weak Solution Emission. Although RT solution emission was uniformly weak and emission lifetimes were short (≤20 ns), at 77 K in 2-methyltetrahydrofuran (2-MeTHF) glass the compound Pt(tmp)(mes)$_2$ yielded an excited-state lifetime of 3.7 μs. A thermally activated excited-state decay process is therefore assumed to be responsible for the weak emission signals in RT solutions. The relative likelihood of a variety of possible deactivation pathways is discussed below.

(a) MLCT → dd Thermal Conversion. It has been suggested that the absence of solution emission for the majority of known mononuclear Pt(II) complexes is due to the presence of low-lying, thermally accessible dd states.[2,5] Such a pathway in the present systems does not appear probable in view of the strong σ-donating ability of the mesityl carbanion ligands. This should increase the energy gap between the MLCT and dd states and is in accord with the intense, long-lived solution luminescence recently reported for related Pt(diimine)(CN)$_2$ and Pt(diimine)(acetylide)$_2$ systems.[3,5,15]

(b) Solvent Deactivation. Excited-state deactivation via solvent nucleophilic attack or compound to solvent vibrational

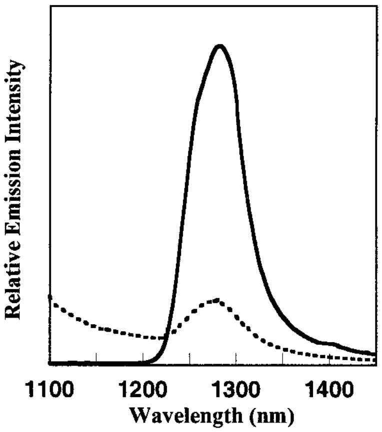

Figure 5. Singlet oxygen, $O_2(^1\Delta_g)$, phosphorescence spectra obtained at RT for absorbance-matched ($A_{400} = 0.57$) oxygen-saturated toluene solutions of Pt(dpp)(mes)$_2$ (···) and perinaphthenone (—). Wavelength of excitation = 400 nm.

energy transfer is considered unlikely for the title complexes, owing the small variations in emission efficiencies for solvents with markedly different ligating abilities and the absence of solvent deuterium isotope effects. This conclusion is also consistent with steric constraints on solvent access to axial coordination sites.

(c) Agostic Interactions. On the basis of X-ray crystallographic data reported by Kaim et al. for Pt(bpy)(mes)$_2$ and Pt(phen)(mes)$_2$,[16,18] an alternative relaxation pathway might involve an agostic interaction between hydrogens on the mesityl methyls and the platinum center. This type of interaction could deactivate the excited state by utilizing the C−H bond stretching motion of the methyl groups. However, this type of interaction may be more prevalent in the solid state than in fluid solution, which would result in a reversal of the relative luminescence intensity from what is actually observed.

(d) Complex Self-Quenching. Recent studies have demonstrated that excited-state self-quenching is a common phenomenon in RT solutions for strongly emissive Pt(II) diimine complexes.[13,14] In some cases, such as that of the phenylacetylide complex Pt(phen)(CCPh)$_2$,[13] quenching of monometallic luminescence is accompanied by excimer emission. A bimolecular process of this type is unlikely for our systems due to steric constrictions along the Pt···Pt axis and the very short solution emission lifetimes (even under very dilute conditions). In addition, we observed no evidence for excimer formation as solution concentrations were increased. An alternative self-quenching pathway involving overlap of the diimine π clouds on separate complex molecules is also improbable on the basis of our observation of no emission quenching upon the addition of excess free phenanthroline to toluene solutions of Pt(dpp)(mes)$_2$ complexes.[13]

(e) Mesityl *o*-Methyl Group Rotation. We suggest that the most likely solution-phase excited-state-deactivation pathway may be rotation of the *o*-methyl groups on the mesityl ligands. This rotation would be hindered in the solid state at room temperature and would be largely eliminated at 77 K. Modest support for this hypothesis comes from the 35% increase observed in the emission intensity of Pt(dpp)(mes)$_2$ in mol wt 400 poly(ethylene glycol) solvent compared with that for an absorbance matched solution in toluene (Figure S2, Supporting Information). A more viscous, higher molecular weight solvent should slow the rotation of the methyl groups on the complex and thus enhance the probability of excited-state decay via luminescence.[26]

Energy-Transfer Studies. Quenching by O$_2$. Despite the weak emission signatures of Pt(diimine)(mes)$_2$ complexes in RT solutions, their luminescent excited states are sufficiently long-lived to be intercepted by dissolved oxygen. A reproducible 20% decrease in the steady-state emission intensity is observed on progressing from an N$_2$-saturated to an O$_2$-saturated solution (Figure S3, Supporting Information). The linear Stern−Volmer plot of I_o/I vs $[O_2]$ yields a Stern−Volmer slope, K_{SV}, of 26.7 M^{-1} (where I_o and I are the steady-state emission intensities in the absence and presence of oxygen, respectively).[27] Since $K_{SV} = \tau_o k_q$ and $\tau_o \leq 20$ ns (where τ_o is the emission lifetime in the absence of O$_2$), the bimolecular quenching rate constant, k_q, is $\geq 1.3 \times 10^9$ M^{-1} s^{-1} (i.e., $k_q \geq (1/20)k_d$, where k_d is the diffusion-controlled rate constant obtained in toluene solution).[28,29]

Oxygen quenching of the ^{3}MLCT state of Pt(dpp)(mes)$_2$ may proceed by an energy transfer mechanism producing singlet oxygen, $^1O_2$, and/or an electron-transfer mechanism, as depicted in eqs 1 and 2, respectively. For the present systems, both

$$^3\mathrm{MLCT\ Pt}^{2+} + {}^3\mathrm{O}_2 \rightarrow \mathrm{Pt}^{2+} + \mathrm{O}_2\ (^1\Delta_g) \tag{1}$$

$$^3\mathrm{MLCT\ Pt}^{2+} + \mathrm{O}_2 \rightarrow \mathrm{Pt}^{3+} + \mathrm{O}_2^{\,-} \tag{2}$$

processes are thermodynamically feasible, but in this report, we provide *direct* experimental confirmation that oxygen quenching proceeds primarily via the $^1O_2$ pathway.[30,31] When an oxygen-saturated toluene solution of Pt(dpp)(mes)$_2$ was excited at 440 nm, the diagnostic $O_2(^1\Delta_g) \rightarrow {}^3O_2$ phosphorescence signal was detected at 1270 nm.[22] An 8-fold increase in the intensity of the 1270 nm emission was observed in an analogous study of an absorbance-matched solution of Pt(dpp)(mes)$_2$ in toluene-d_8 (Figure S4, Supporting Information). This observation is consistent with the much longer singlet-oxygen lifetime in the deuterated solvent.[32] The quantum yield for $^1O_2$ production, Φ_Δ(Pt), was determined by comparing the steady-state 1270 nm signal upon 400 nm excitation of Pt(dpp)(mes)$_2$, I_o(Pt), with that of an absorbance-matched solution of the reference standard perinaphthenone, I_o(PN). Inspection of Figure 5 reveals an $I_o(\mathrm{Pt})/I_o(\mathrm{PN})$ ratio of 1/8, which is then inserted into eq 3 for the

$$\Phi_\Delta(\mathrm{Pt}) = [I_o(\mathrm{Pt})/I_o(\mathrm{PN})][\Phi_\Delta(\mathrm{PN})/\Phi_{\mathrm{ISC}}(\mathrm{Pt})][f(\mathrm{PN})/f(\mathrm{Pt})] \tag{3}$$

calculation of Φ_Δ(Pt). Here $\Phi_\Delta(\mathrm{PN}) = 1.0$,[22] $f(\mathrm{PN}) = 1.0$ is the fraction of triplet excited state of perinaphthenone quenched by O$_2$,[22] $f(\mathrm{Pt}) = 0.20$ is the fraction of the ^{3}MLCT excited state of Pt(dpp)(mes)$_2$ quenched by O$_2$, and Φ_{ISC}(Pt) is the ^{1}MLCT → ^{3}MLCT intersystem crossing yield for Pt(dpp)(mes)$_2$. Since the value for Φ_{ISC}(Pt) is 1.0 or less, the quantum yield for singlet-oxygen production, Φ_Δ(Pt), is ≥ 0.63. We conclude therefore that the majority of oxygen quenching occurs via the

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formation of $^1O_2$, although a significant electron-transfer component (eq 2) may also be operative.

Electron-Transfer Studies. Nitroaromatics have been widely employed as test-case substrates for evaluating transition metal complexes as excited-state reducing agents.[33] We utilized quenching of the Pt(dpp)(mes)$_2$ emission signal by added nitroaromatics as a probe of photoinitiated electron transfer. The reductive power of the ^{3}MLCT excited state of Pt(dpp)(mes)$_2$ in toluene solution was estimated from a combination of cyclic voltammetry (CV) and luminescence data obtained in toluene solution. A semireversible Pt$^{2+/3+}$ redox couple was observed by CV at 0.89 V vs NHE, while the 0−0 transition energy for the ^{3}MLCT excited state was assessed as 2.07 V from the position of overlap of the emission and excitation spectra.[14] The complex Pt(dpp)(mes)$_2$ is thus a potentially strong photoreductant ($E°(*Pt^{2+}/Pt^{3+}) \approx 1.18$ V vs NHE), which should be thermodynamically capable of reducing 3,5-dinitrobenzonitrile ($E°(Q/Q^-) = -0.86$ V vs NHE), whereas the corresponding reduction of nitrobenzene ($E°(Q/Q^-) = -1.24$ V vs NHE) is marginally disfavored.

These expectations have been borne out experimentally, as evident from inspection of the Stern−Volmer quenching plots for the two aromatics (Figure S5, Supporting Information). Only in the case of 3,5-dinitrobenzonitrile is strong emission quenching apparent, with a slope, K_{SV}, of 32.5 M^{-1}. Since $K_{SV} = \tau_0 k_q$ and $\tau_0 \leq 20$ ns, the bimolecular quenching rate constant, k_q, is $\geq 1.6 \times 10^9$ M^{-1} s^{-1}.[34]

Conclusions

For all Pt(diimine)(mes)$_2$ compounds studied, we found solution RT emission to be weak and excited-state lifetimes short (≤20 ns). Despite these short solution lifetimes, evidence has been presented for energy-transfer quenching by dissolved O$_2$ (primarily producing singlet oxygen) and electron-transfer quenching by nitroaromatics. The latter observation suggests that these Pt(II) systems may have future value as excited-state reductants. Interestingly, all of the complexes displayed a much more intense and longer-lived luminescence in the solid state at RT. Several possible explanations for this marked phase difference were proposed, with the most probable mechanism involving radiationless deactivation in solution via mesityl *o*-methyl group rotation.

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Supporting Information Available: For Pt(dpp)(mes)$_2$, UV−vis absorption and excitation spectra (Figure S1), Emission spectra in toluene vs poly(ethylene glycol) (Figure S2), emission spectra in the presence and absence of dissolved O$_2$ (Figure S3), singlet-oxygen phosphorescence spectra in toluene and toluene-d_8 (Figure S4), and Stern−Volmer plots of quenching by nitroaromatics (Figure S5). This information is available free of charge via the Internet at http://pubs.acs.org.

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(34) Extended irradiation of Pt(dpp)(mes)$_2$/dinitrobenzonitrile solutions using the 488 nm line of an Ar ion laser (125 mW, 20 min) revealed only minimal photodecomposition, suggestive of a rapid thermal back-reaction.