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Near-Infrared Luminescence from Platinum(II) Diimine Compounds

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Square-planar Pt(II) complexes of the bis(mesitylimino)acenaphthene (mesBIAN) ligand are emissive from a MMLL′CT excited state in a dichloromethane solution at room temperature. Investigation of the nature of the frontier orbitals in these near-IR emitters by a combination of emission spectroscopy, electron paramagnetic resonance spectroscopy, and density functional theory calculations suggests that emission is enabled by the presence of low-lying ligand π^* orbitals on the mesBIAN.

The past decade has seen growing interest in the photochemistry of Pt(II) compounds of the form Pt(NN)(LL), where NN is a bidentate N-heterocyclic diiimine ligand such as bipyridine or phenanthroline and LL is either one bidentate ligand (for example, a dithiolate) or two monodentate (such as alkynyl) ligands. The reason for this interest is the luminescence in solution at room temperature exhibited by these compounds and the fact that their excited-state properties can be tuned by peripheral modification of the ligands. This property has been thoroughly investigated,[1−3] and Pt(NN)(LL) compounds and derivatives thereof have been incorporated into electroluminescent devices[2a] and dye-sensitized solar cells[4] and utilized for the sensitization of lanthanide excited states.[5]

The nature of the emitting triplet state depends on the electronic structure of the NN and LL ligands. For dithiolate complexes, where LL is a bidentate S donor ligand, it has been described as a "mixed metal−ligand-to-ligand charge transfer" (MMLL′CT), from a highest occupied molecular orbital (HOMO) composed of orbitals from both the metal and the dithiolate ligand to a lowest unoccupied MO (LUMO), which is predominantly localized on the π^* system of the NN ligand.[6] In complexes where L is a terminal alkynyl ligand, it is generally thought to be more MLCT, with a similar LUMO but a HOMO more exclusively based on the Pt atom.[1e]

We report here a series of compounds that absorb strongly across the visible region down to 600 nm and emit at wavelengths longer than 750 nm because they contain the nonheterocyclic bidentate diimine ligand bis(mesitylimino)-acenaphthene (mesBIAN; Scheme 1). The extensively conjugated rigid π system of mesBIAN causes the LUMO of the Pt(mesBIAN)(LL) complexes reported herein to be lower in energy than that in previously reported Pt(NN)(LL) complexes, with a correspondingly smaller HOMO−LUMO gap leading to lower energy absorption and emission.

The reaction of mesBIAN with Zeise's salt affords Pt(mesBIAN)Cl_2 (**1**). The Cl ligands of **1** can then be readily replaced with other ligands, by metathesis with Me_2Sn(dto) (dto = 1,2-dithiooxalate) to form Pt(mesBIAN)(dto) (**2**)[7] and in a copper(I) iodide catalyzed reaction with a terminal alkyne in the presence of triethylamine to form Pt(mesBIAN)$(-CCC_6H_4CF_3)_2$ (**3**).[8]

1−**3** are air-stable crystalline solids and dissolve in solvents such as CH_2Cl_2 and tetrahydrofuran (THF) to form stable solutions. **1**−**3** are darkly colored, with relatively strong absorption bands between 500 and 600 nm. The value of the extinction coefficient (Table 1) and the solvatochromism[1c] (e.g., a shift from 498 nm in CH_3CN to 552 nm in toluene for **1**; see the Supporting Information for details)

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Scheme 1. Synthesis of Compounds **1**−**3**

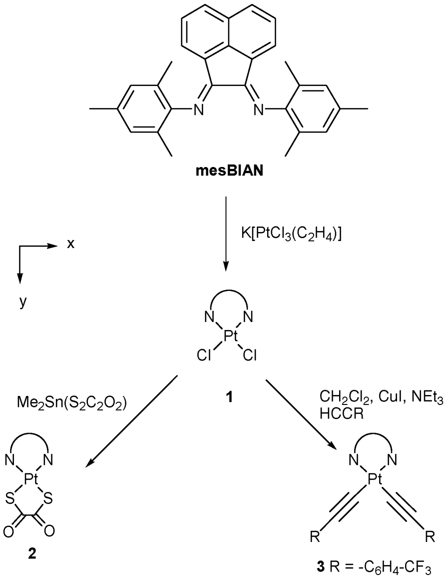

Table 1. Optical Data for **1**−**3** in CH$_2$Cl$_2$ at Ambient Temperature

	absorption[a]	emission		
	λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})	λ_{max}/nm	ϕ/10^{-4}	τ/ns
1	250 (33 910), 358 (17 499), 518 (6910), 670 (170), 740 (120)	777	3	20
2	383 (11 672), 486 (10 615), 530 (10 464), 675 (470), 760 (145)	820	0.4	17
3	299 (43 790), 379 (11 490), 514 (11 809), 720 (280)	800	8	30

[a] In degassed solutions; over 10−300 μmol concentration range, throughout which the absorptions obey Beer's law.

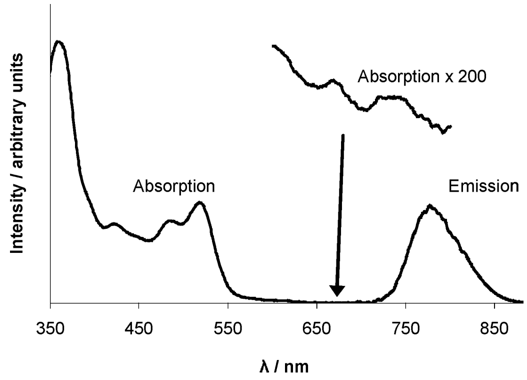

Figure 1. Absorption and emission spectra of **1** in CH$_2$Cl$_2$.

observed for this absorption band indicate that the corresponding electronic transition is at least partly CT in nature. Each compound also has very weak absorption bands at longer wavelength (>650 nm), which, as in the case of previously reported Pt(II) chromophores,[3] are attributed to the direct population of triplet states, a process facilitated by the high spin−orbit coupling associated with the Pt(II) ion.

Compounds **1**−**3** are luminescent in a CH$_2$Cl$_2$ solution at room temperature. Their emission spectra are structureless, and in each case, the emission maximum is close in energy to the weak, lowest-energy absorption band (e.g., 777 and 740 nm, respectively, for **1**; Figure 1 and Table 1). The small Stokes shift supports further the triplet assignment of the weak low-energy absorption band. A good match between the excitation spectrum and the corresponding absorption spectrum is consistent with emission originating from the parent compounds. The emission lifetimes of **1**−**3** are considerable for near-IR emitters based on transition-metal complexes.[9]

To further understand the frontier orbitals of **1**−**3** and thus their absorption and emission spectra, we have investigated their electro- and spectroelectrochemical behavior (Table 2). All of the compounds display at least two well-defined electrochemical processes, consisting of a fully reversible reduction at around −0.7 V, a quasi-reversible reduction at around −1.3 V, and in the case of **3** an irreversible oxidation at +1.5 V (all values are versus SCE). Performing a single-electron reduction populates the LUMO of the neutral species, and the nature of the resulting singly occupied MO (SOMO) has been probed by electron spin resonance (ESR) spectroscopy.

As a representative example, the experimental and simulated ESR spectra at 110 K of a sample of **1** chemically reduced with cobaltocene are shown in Figure 2. The parameters used for the simulation are given in Table 2; assignment of the g values and couplings follows the methodology of McInnes and co-workers for reduced Pt(bipy)Cl$_2$ compounds.[10] Using their approach, we can calculate the contribution of orbitals from the metal to the SOMO, which for **1** gives values for the 5d$_{yz}$ unpaired electron density of 9.6% and for the 6p$_z$ unpaired electron density of 4.6%. Thus, we may conclude that the SOMO of the anion **1**$^-$ (and, by extension, the LUMO of **1**) is approximately 14% metal-based. The spectra of **1**$^-$−**3**$^-$ show a much better resolution of the N hyperfine coupling on the high-field component than their bipyridyl[10] and diazabutadiene[11] equivalents.

Conclusions about the LUMO drawn from the ESR data are supported by density functional theory studies. These studies consisted of in vacuo geometry optimizations, followed by the application of an $\epsilon = 8.93$ continuum to model a CH$_2$Cl$_2$ solvation field for determination of the MOs (see the Supporting Information for details).

The calculations show that for **1** the LUMO (Figure 3) is an orbital of b$_1$ symmetry (in the C_{2v} point group) that is mainly formed from the π* system of the mesBIAN ligand, particularly the N=C−C=N backbone of the chelate ring, with an approximately 11% contribution from the metal orbitals. **1**$^-$ is computed to have 12% of the unpaired electron spin density on the Pt atom, contained in a virtually identical orbital. Similar LUMOs are calculated for **2** and **3** (9 and 8% metal-based, respectively), and their anions give similar

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Table 2. Electrochemical and ESR Data for **1**−**3** and **1**$^-$−**3**$^-$ [a]

	E_o'/V													
	oxidation	reduction		g_{iso}	g_y	g_x	g_z	$\langle g \rangle$	A_{iso}	A_y(Pt)	A_x(Pt)	A_z(Pt)	$\langle A \rangle$	A_z(N)
1		−0.60 −1.85	**1**$^-$	2.011	2.074	2.003	1.952	2.009	75.1	−72.6	−112.2	−48.3	−77.7	13.6
2		−0.57 −1.48	**2**$^-$	2.014	2.043	2.017	1.978	2.012	50.0	−55.2	−72.5	−22.1	−49.9	13.5
3	1.53	−0.69 −1.74	**3**$^-$	2.008	2.034	2.010	1.979	2.007		−46.8	−50.0	−6.0	−34.3	13.0

[a] Potentials vs SCE, in a CH_2Cl_2 solution with a 0.1 M $[Bu_4N][PF_6]$ supporting electrolyte. ESR spectra were recorded at X band at 110 K in 2:1 THF/CH_2Cl_2. Hyperfine coupling constants are 10^{-4} cm^{-1}.

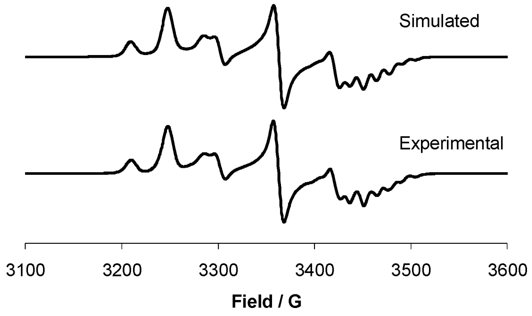

Figure 2. Simulated and experimental X-band ESR spectra of **1**$^-$.

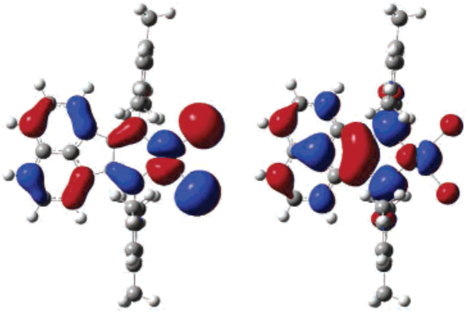

Figure 3. Computed HOMO (left) and LUMO (right) of **1**.

ESR spectra (Table 2) but with reduced Pt hyperfine coupling consistent with a smaller metal-derived component.

The calculations also show that the HOMOs of **1**−**3** are the antibonding combination of the metal d_{xz} orbital with the p_z or π orbitals of the ligands LL. The precise distribution of the orbital over the metal and ligands varies between compounds, being 44, 32, and 26% metal-based for **1**−**3,** respectively, with contributions of 20, 27, and 8% from the bonded atoms of the ligands L. The *total* contribution from each alkynyl ligand in **3** is 35%, and that from the dithiooxalate ligand in **2** is 62%. The calculated orbitals suggest that the complexes' HOMOs are mixed metal−ligand in nature and the LUMOs are mainly ligand-based, and thus the excited-state responsible for the observed lowest-energy absorptions and the emission of **1**−**3** is best regarded as MMLL′CT.

It is worth comparing our results to those of Klein and co-workers, who have studied Pt(^{i}PrDAB)(R)$_2$ compounds, where R was a variety of saturated and unsaturated organic ligands and ^{i}PrDAB is *N*,*N*′-diisopropyl-1,4-diazabutadiene, an analogue of mesBIAN without the rigid aromatic backbone.[12] When R was a π donor such as acetylide, they found frontier orbitals of character and symmetry similar to those of **1** and also concluded that the lowest-energy transition in the absorption spectrum is of MMLL′CT character. However, in contrast to **1**−**3**, they reported that the Pt(^{i}PrDAB)(R)$_2$ complexes were not luminescent from a MLCT excited state in a fluid solution.[12c]

In Pt(II) complexes, emission from a CT state is often quenched by the presence of a deactivating d−d state close in energy. The strategy commonly adopted for the synthesis of luminescent Pt(II) compounds typically employs high-field ligands such as alkynyl, dithiolate, or cyclometalated phenylpyridine type ligands in order to raise the energy of the deactivating d−d excited state. While **2** and **3** contain strong-field ligands, the luminescence from a CT state of the low-field ligand complex **1** and the results of the calculations suggest that the mesBIAN π* system lies well below the d orbitals in all three cases reported herein, largely forming the LUMO and thereby allowing the generation of a MMLL′CT excited state that is sufficiently below any d−d states to avoid becoming deactivated. The shift of the lowest singlet absorption maximum from 390 to 470 to 518 nm in Pt(NN)Cl_2 complexes along the sequence of NN ligands bipy to ^{i}Pr-DAB to mesBIAN also supports this interpretation.

To summarize, employing a highly conjugated rigid diimine ligand with a low-lying LUMO allows Pt(II) compounds even with weak-field ligands to possess lowest CT excited states, which exhibit relatively long-lived red luminescence in a fluid solution at room temperature. To the best of our knowledge, **1** is the first example of a platinum diimine dichloride complex that emits in a fluid solution at room temperature. Further studies on the subclasses of dithiolate, alkynyl, halide, and pseudohalide complexes originating from the parent mesBIAN complex, to explore near-IR emission tuneability, are ongoing.

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Supporting Information Available: Details of synthetic procedures for **1**−**3**, of computational studies, and of optical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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