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Room Temperature Phosphorescence from a Platinum(II) Diimine Bis(pyrenylacetylide) Complex

Irina E. Pomestchenko,[†] Charles R. Luman,[†] Muriel Hissler,[‡] Raymond Ziessel,[‡] and Felix N. Castellano*,[†]

Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, and Laboratoire de Chimie Moléculaire, ECPM, 25 rue Becquerel, 67087 Strasbourg Cedex 02, France

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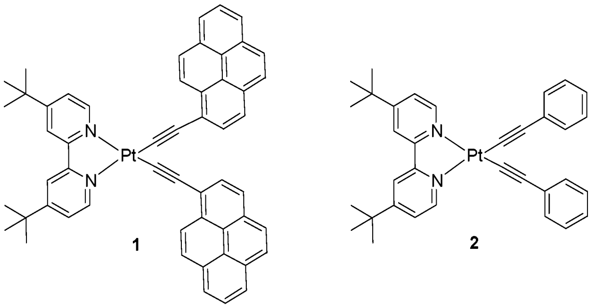
Room temperature phosphorescence has been observed in a synthetically facile Pt(II) complex, Pt(dbbpy)(C≡C-pyrene)$_2$ (dbbpy = 4,4′-di(*tert*-butyl)-2,2′-bipyridine; C≡C-pyrene = 1-ethynylpyrene), in fluid solution. The static and time-resolved absorption and luminescence data are consistent with phosphorescence emerging from the appended C≡C-pyrenyl units following excitation into the low energy dπ Pt → π* dbbpy metal-to-ligand charge transfer absorption bands.

There has been considerable recent interest in transition metal complexes possessing metal-to-ligand charge transfer (MLCT) excited states that display lifetimes well beyond those imposed by the energy gap law.[1−9] Visible-absorbing luminescence probes that possess long decay times are becoming increasingly important in lifetime-based chemical sensing, biophysics, and clinical chemistry.[10] Substantial lifetime lengthening can be accomplished by introducing a select organic chromophore(s) to the diimine ligand structure such that the ligand-localized (intraligand, IL) excited states are strategically positioned below the MLCT manifold. The relative energy differences between these two states dictate whether the MLCT emission is controlled by thermal equilibrium or slow back energy transfer processes.[3−6] Extended lifetimes have also been observed in systems where the excited states have been proposed to consist of mixed $^3\pi-\pi^*$ and intraligand charge transfer (ILCT) character.[7,8] Although rare, direct excitation of the MLCT excited state can lead to IL-centered long-lived $^3\pi-\pi^*$ phosphorescence in room temperature (RT) solutions.[9]



1 **2**

Over the past few years, Pt(II) diimine bis(acetylide) complexes have emerged as chromophores that feature visible MLCT-based absorption with corresponding high quantum yield photoluminescence.[11−13] The detailed study recently completed by Schanze and co-workers demonstrated that the ^{3}IL states of the acetylide ligands can markedly influence excited state decay.[12] We therefore postulated that one could potentially observe significantly extended lifetimes in these synthetically facile Pt(II) systems if the appropriate chro-

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* To whom correspondence should be addressed. E-mail: castell@bgnet.bgsu.edu.

[†] Bowling Green State University.

[‡] Laboratoire de Chimie Moléculaire, ECPM.

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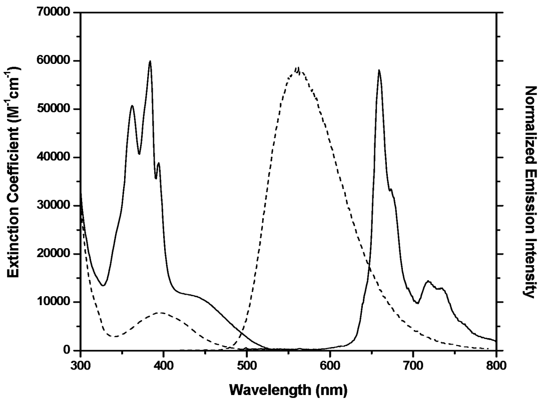

Figure 1. Absorption (left) and emission (right) spectra of compound **1** (—) and **2** (- - -) in deaerated CH_2Cl_2 at room temperature. Emission spectra were recorded using 480 ± 2 nm excitation.

mophores are appended as acetylide ligands. There is an interesting consequence to using a square planar geometry in that the lowest expected ^{3}MLCT (dπ Pt $\rightarrow$ π^* diimine) and ^{3}IL (acetylide $\pi \rightarrow \pi^*$) excited states are located on opposite ends of the molecule.

In the present work, we report a new Pt(II) diimine complex, Pt(dbbpy)(C≡C-pyrene)$_2$ (**1**), where dbbpy is 4,4′-di(*tert*-butyl)-2,2′-bipyridine and C≡C-pyrene is 1-ethynylpyrene. Excitation into the low energy MLCT bands of **1** produces long-lived structured phosphorescence at RT in fluid solution, emanating from the appended C≡C-pyrenyl units.

Compound **1** was prepared by reaction of Pt(dbbpy)Cl_2 and pyrene-C≡C—H in CH_2Cl_2/diisopropylamine in the presence of a CuI catalyst.[11,12] Crude **1** was purified by flash chromatography on silica and structurally characterized by ^{1}H NMR, MS, and elemental analysis. Pt(dbbpy)(C≡C—Ph)$_2$ (**2**)[11] and *trans*-Pt(PBu$_3$)$_2$(C≡C-pyrene)$_2$ (**3**)[5b] serve as models for **1**. Compound **3** is vital to this study since it does not possess any MLCT excited states but contains the Pt(II) center (to impart the heavy atom effect) and two pyrenylacetylide units in a *trans*-geometry (to ensure the absence of intramolecular ground-state interactions). The absorption spectra of compounds **1** and **2** in CH_2Cl_2 are displayed in Figure 1. The pyrenylacetylide chromophores in **1** are largely responsible for the structured $\pi-\pi^*$ transitions between 350 and 400 nm. These absorptions are substantially red-shifted relative to those of the free pyrene-C≡C—H species (see Supporting Information), suggesting large σ-donation of the C≡C-pyrenyl electron density to the Pt(II) center. The visible absorption bands near 450 nm are assigned to dπ Pt $\rightarrow$ π^* dbbpy MLCT transitions and, although red-shifted, are qualitatively similar in shape and extinction coefficient (10 300 M^{-1} cm^{-1} at 450 nm) to **2**.[11] The MLCT assignment is consistent with the solvatochromic shifts observed for the low energy absorption bands in **1** (and **2**).[11,14,15] It should be noted that the sharp absorption features between 350 and 400 nm also exhibit solvatochromism, suggesting either that these bands possess some charge transfer character or that they overlap the MLCT bands. The first reduction waves measured for **1** and **2**, obtained with cyclic voltammetry in CH_2Cl_2, occur at the same potential within experimental error (−1.35 V vs Ag/AgCl). Eisenberg and co-workers have already assigned this process to a dbbpy ligand-based reduction in **2**.[11] Reductive electrochemistry performed on pyrene-C≡C—H yielded an irreversible process that initiates at −1.73 V. It is therefore reasonable to assume that the lowest acceptor ligand orbital is located on dbbpy in **1**. Consistent with other related Pt(II) diimine bis(acetylide) complexes, **1** and **2** displayed irreversible metal-based oxidations at +0.95 V and +1.11,[11−13] respectively. The fact that the former is shifted to a more negative potential reflects significant σ-donation of electron density from the C≡C-pyrenyl units to the Pt(II) center, consistent with the red shift observed in the absorption spectrum.

The RT emission spectrum of **2** was easily measured in aerated CH_2Cl_2 whereas the corresponding spectrum for **1** is almost quantitatively quenched by dioxygen, necessitating its removal, Figure 1. Excitation at 480 nm produces a distinct emission spectrum in each case. The luminescence in **2** has already been shown to originate from an MLCT manifold,[11,12] whereas the emission from **1** is red-shifted (over 100 nm), structured, and relatively sharp in comparison. The quantum yield for **1**, measured relative to $[Ru(bpy)_3]^{2+}$, was determined to be 0.011. The corrected excitation spectrum of **1** in CH_2Cl_2 was superimposable with its absorption spectrum at all wavelengths above 300 nm and was completely invariant to the monitoring wavelength. The RT luminescence lifetimes of **1** and **2**, measured with a broadband N_2-pumped dye laser (460 ± 2 nm, 500 ps fwhm) in deaerated CH_2Cl_2, were also strikingly different, 48.5 and 1.25 μs, respectively. Using 360 nm excitation, the lifetime of the phosphorescence of **3** (Figure 2) in deaerated CH_2Cl_2 was 68 μs, similar to that measured for **1** following visible MLCT excitation. The photophysical properties of **1** are clearly not attributed to an excited state composed of MLCT parentage. Since Pt(II) chromophores of this type are known to undergo excited state self-quenching reactions,[11,12,16−18] all luminescence experiments were performed at or below 10 μM, where the measured lifetimes were invariant to concentration.

The emission spectra of **1** and **3** obtained at RT and 77 K in 4:1 EtOH/MeOH are compared in Figure 2. The difference in the RT and 77 K emission energies, or thermally induced Stokes shift (ΔE_s), is extremely small for both compounds, $\sim$ 70 cm^{-1}. Under the same conditions, the luminescence from **2** displayed a substantial ΔE_s value of 2800 cm^{-1} (0.35 eV). Large values of ΔE_s are correlated with significant changes in dipole moment between ground and excited states, such as those attributed to MLCT excited states.[12,15] The small value of ΔE_s in the case of **1** indicates that the emission does not originate from an MLCT excited state. The emission

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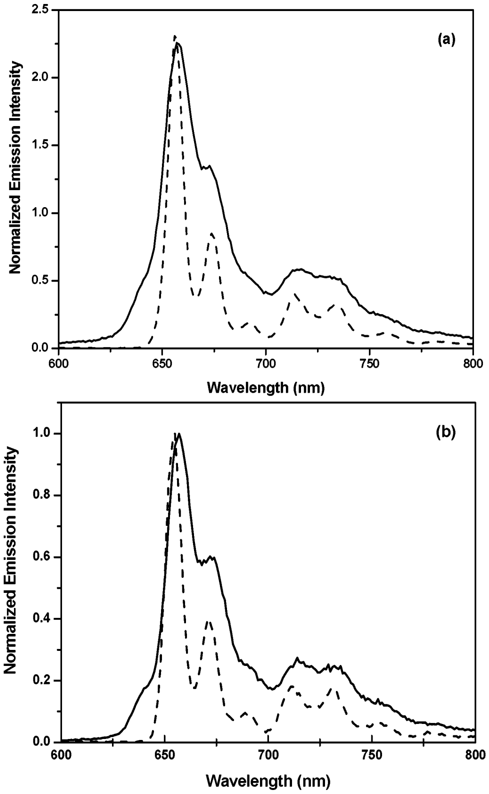

Figure 2. (a) Emission spectrum ($\lambda_{ex} = 480 \pm 2$ nm) measured for **1** in deaerated 4:1 EtOH/MeOH at room temperature (—) and at 77 K (- - -). (b) Emission spectrum ($\lambda_{ex} = 400 \pm 2$ nm) measured for **3** in deaerated 4:1 EtOH/MeOH at room temperature (—) and at 77 K (- - -).

spectra obtained for **1** and **3** at both temperatures are nearly identical in shape and vibronic spacing, illustrating that the emitting state in **1** is ^{3}IL phosphorescence from the appended $C{\equiv}C$-pyrenyl units. Surprisingly, the spectra are identical even though the pyrenyl fragments are in different molecular geometries around the Pt(II) center (*cis* in **1** and *trans* in **3**). The emission results strongly suggest that the two pyrenyl units do not interact (intramolecularly) at all in **1**.

Additional support for the sensitization of the $C{\equiv}C$-pyrenyl-based ^{3}IL excited states in **1** comes from transient absorption measurements. Figure 3 displays the absorption transients obtained for **1** in CH_2Cl_2 following a 355 nm nanosecond laser flash. Since the concentrations required for flash photolysis resulted in self-quenching, no detailed quantitative kinetic analyses of these data were performed. The absorption features observed for **2** are consistent with an MLCT excited state (see Supporting Information),[12] whereas the transients in **1** are completely different. The spectrum observed for **1** appeared promptly within the 15 ns instrument response so no information could be obtained on the evolution of the transients. Flash photolysis performed on **3** generated a similar transient spectrum throughout the visible; however, the ground state bleaching of the pyrenyl units occurs at lower energy in **3**, consistent with differences in their relative $C{\equiv}C$-pyrenyl absorption band positions (see Supporting Information). On the basis of these data, the absorptions are assigned to ground-state bleaching ($\lambda < 410$ nm) and to the triplet-to-triplet absorption (410−700 nm) of the $-C{\equiv}C$-pyrenyl moieties. The bleach recovery and the absorption decays followed similar single exponential kinetics that exhibit concentration-dependent lifetimes on the order of tens of microseconds. The absorption kinetics paralleled the time-resolved emission decays in all cases, illustrating that the absorption transients are likely of the same origin as the phosphorescence. Future planned ultrafast transient absorption measurements will undoubtedly shed light on energy migration processes within this chromophore. The acetylide linkages in **1** may also permit time-resolved IR spectroscopic investigations.[12]

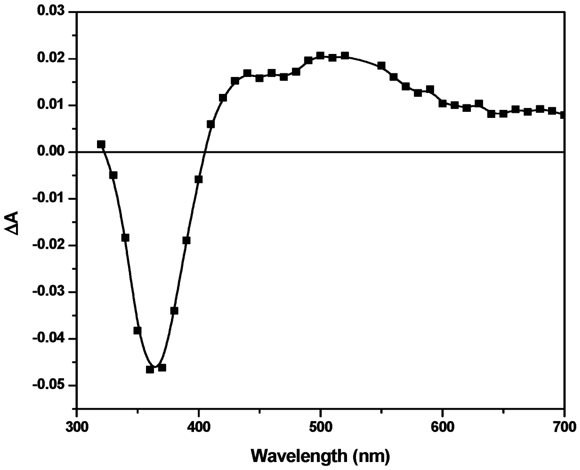

Figure 3. Transient absorption difference spectrum of **1** in deaerated CH_2Cl_2 measured 500 ns after a 355 nm laser pulse.

Excitation into the low energy MLCT absorption bands in **1** produces sensitized ^{3}IL phosphorescence in the appended $C{\equiv}C$-pyrenyl moieties at RT. The relatively strong ^{3}IL phosphorescence is a consequence to the presence of the internal Pt heavy atom. Compound **1** represents an alternative molecular design that imparts long lifetime red photoluminescence into a synthetically facile metal−organic system. Such molecules have important potential applications in emerging luminescence-based technologies and excited state chemistry schemes and serve to further enhance our knowledge regarding manipulation of molecular excited states.

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Supporting Information Available: Synthesis, characterization details, and additional spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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