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Naphthalimide Phosphorescence Finally Exposed in a Platinum(II) Diimine Complex

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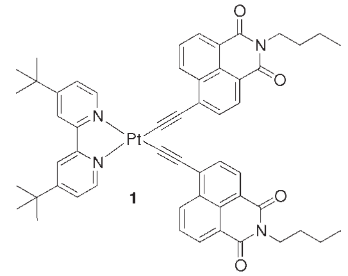
Room temperature (RT) phosphorescence is observed from a naphthalimide species for the first time in the square-planar chromophore Pt(dbbpy)(C≡C—NI)$_2$, where NI = *N*-butyl-4-ethynylnaphthalimide and dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine. The combination of static and time-resolved absorption and photoluminescence data is uniformly consistent with triplet-state photophysics localized on an appended C≡C—NI unit following excitation into the low-energy absorption bands. This molecule features rather impressive long-lifetime, high-quantum-efficiency NI-based RT phosphorescence (τ = 124 μs; Φ = 0.215) centered at 621 nm, exemplifying how the platinum acetylide linkage strongly promotes intersystem crossing in the NI subunit, representative of a class of molecules whose excited states are typically dominated by singlet fluorescence.

The original discovery of room temperature (RT) charge-transfer (CT)-based photoluminescence in Pt(phen)(C≡C—Ph)$_2$ by Che and co-workers in 1994[1] has since inspired an entire genre of related chromophores displaying expansive photophysics.[2,3] These molecules, which employ desirable features of both classical inorganic coordination compounds and organometallics, enable the observation of triplet-state photophysics ranging from CT-based to intraligand (^{3}IL) in nature to a superposition of these extremes.[4] Indeed, the photochemistry and photophysics of platinum(II) polyimine acetylide complexes has already been exploited in a variety of applications including optical limiting,[5] electroluminescence,[6] singlet oxygen sensitization,[7] cation sensing,[8] and solar hydrogen fuel production.[9] A defining feature of these structures is the strong coupling between the metal and acetylide ligand(s), which effectively promotes singlet → triplet intersystem crossing in the pendant chromophore. This bonding motif can provide unrestricted access to long-lived triplet excited states present in organics typically dominated by singlet-state photophysics.[2–4] One such class of molecules is naphthalimides substituted in the 4 position, which are well-established fluorescence probes but have yet to display radiative decay from their triplet manifold at RT.[10] In the present work, we report a new platinum(II) diimine complex, Pt(dbbpy)(C≡C—NI)$_2$ (**1**), where NI = *N*-butyl-4-ethynylnaphthalimide and dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine. Excitation into the low-energy absorption bands of **1** produces extremely long-lived phosphorescence at RT in a fluid solution, emanating from an appended C≡C—NI subunit.



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The three-step synthesis of the acetylide ligand precursor *N*-butyl-4-ethynylnaphthalimide (NI—C≡C—H) originated

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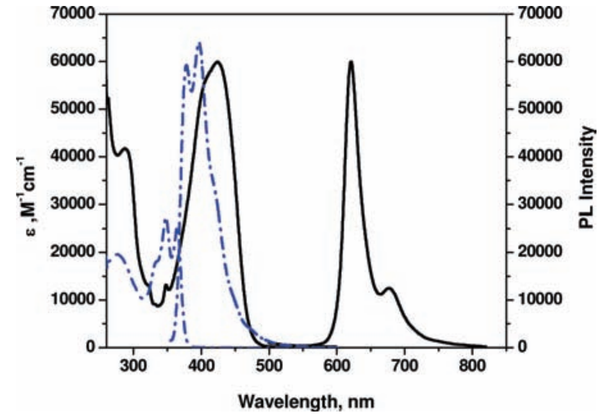

Figure 1. Absorption and photoluminescence spectra of **1** (solid black lines) and $\mathrm{NI{-}C{\equiv}C{-}H}$ (dash-dotted blue lines) in MTHF at RT.

from commercially available 4-bromonaphthalene anhydride, converted to its corresponding imide by the reaction with *N*-butylamine in ethanol at 60 °C. Sonogashira coupling conditions with trimethylsilylacetylene, followed by deprotection with potassium carbonate, produced the desired acetylene. Compound **1** was prepared by the reaction of $\mathrm{Pt(dbbpy)Cl_2}$ and $\mathrm{NI{-}C{\equiv}C{-}H}$ in $\mathrm{CH_2Cl_2}$/diisopropylamine in the presence of a CuI catalyst. Crude **1** was purified by chromatography on silica and structurally characterized by ^{1}H and ^{13}C NMR in addition to HR-MALDI mass spectrometry. The absorption spectrum of **1** measured in 2-methyltetrahydrofuran (MTHF) is displayed in Figure 1. The broad lowest-energy absorption band between 350 and 470 nm is composed of overlapping $\pi \rightarrow \pi^*$ transitions localized on the NI/acetylide chromophores and CT transitions of largely metal-to-ligand $d\pi\,\mathrm{Pt} \rightarrow \pi^*$ dbbpy character. As is typically observed in related platinum(II) arylacetylide complexes, the low-energy absorption features associated with the acetylenic ligand precursor markedly red-shift when covalently linked to the metal center.[2-4] In the case of **1**, this leads to significant absorption cross sections ($\lambda_{\mathrm{max}} = 424$ nm; $\varepsilon = 60\,000$ M^{-1} cm^{-1}) in the blue region of the spectrum.

The RT emission spectrum of **1** is quantitatively quenched in the presence of dioxygen, mandating its removal by thorough degassing with argon (Figure 1). Excitation at 420 nm produces a structured photoluminescence centered at 621 nm, which cannot be assigned as CT in nature by a direct comparison to $\mathrm{Pt(dbbpy)(C{\equiv}C{-}Ph)_2}$, a benchmark CT model complex ($\lambda_{\mathrm{em\ max}} = 573$ nm; $\Phi = 0.047$).[4a] The quantum yield for **1**, measured relative to a $[\mathrm{Ru(bpy)_3}]^{2+}$ actinometer, was determined to be 0.215 in MTHF. The corrected excitation spectrum of **1** in MTHF could be superimposed with its absorption spectrum at all wavelengths above 300 nm and was completely invariant to the emission monitoring wavelength. The RT luminescence lifetime of **1** was measured with a broad-band dinitrogen-pumped dye laser (420 ± 2 nm; 500 ps fwhm) in freeze−pump−thaw (FPT)-degassed MTHF, $\tau = 124$ μs. The excited-state lifetime of $\mathrm{Pt(dbbpy)(C{\equiv}C{-}Ph)_2}$ in the same solvent is 160 ns.[4a] The photophysical properties of **1** are clearly not attributed to an excited state composed of CT parentage, as evidenced by the corresponding values of k_{r} and k_{nr} listed in Table 1. The emission spectra of **1** obtained at RT and 77 K in MTHF are directly 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 this compound, 131 cm^{-1}. Under the same experimental conditions, the luminescence from $\mathrm{Pt(dbbpy)(C{\equiv}C{-}Ph)_2}$ displayed a substantial ΔE_{s} value of 2470 cm^{-1} (0.31 eV).[4a] Large values of ΔE_{s} can be directly correlated with significant changes in the dipole moment between the ground and excited states, such as those attributed to CT excited states. The small value of ΔE_{s} in the case of **1** strongly supports a ^{3}IL excited-state assignment. The emission spectra obtained for **1** at both temperatures are nearly identical in shape and vibronic spacing, illustrating that the emitting state in **1** is ^{3}IL-based phosphorescence from an appended $\mathrm{C{\equiv}C{-}NI}$ moiety. The excited-state lifetime of **1** measured at 77 K in MTHF is 205 μs. Additional support for sensitization of the $\mathrm{C{\equiv}C{-}NI}$-based ^{3}IL excited states in **1** emerges from nanosecond laser-flash photolysis experiments.

The nanosecond transient absorption experiment with **1** was performed in a flow cell filled with argon-saturated MTHF to avoid potential sample decomposition. The transient absorption difference spectra presented in Figure 3 are emission-corrected to avoid interference of the strong phosphorescence that overlaps some of the absorption transients. Following a 420 nm laser pulse, the difference spectrum displays broad ground-state bleaching at high energy between 400 and 500 nm and two distinctive transient absorptions in the visible and near-IR with clearly resolved peaks at 650 and 990 nm. These characteristic difference spectra bear a similar resemblance to that observed in the ligand-localized triplet-to-triplet absorptions in ruthenium(II) complexes bearing 4-piperidinyl-1,8-naphthalimide subunits, PNI-phen.[11] Unfortunately, the PNI-phen data were confined to the visible portion of the spectrum and are not emission-corrected, thereby obscuring the authentic profile of the major absorption transient in this region. The profile of the difference spectra presented in Figure 3 can also be contrasted with that of the corresponding CT model compound $\mathrm{Pt(dbbpy)(C{\equiv}CPh)_2}$, which was recently measured emission-corrected over the same wavelength range as that presented here.[12] The transient absorption spanning the visible in **1** maximizes in the same region as that of $\mathrm{Pt(dbbpy)(C{\equiv}CPh)_2}$ (660 nm); however, the transient at lower energy produces a well-defined maximum in **1** (990 nm), whereas the long-wavelength feature in the model CT chromophore merely extends past 1400 nm at a relatively constant ΔA value originating at ~750 nm.[12] Another key difference is that ground-state bleaching is completely obscured in the platinum(II) CT model because transient absorptions dominate in that portion of the spectrum, while the opposite is true for **1**. In the latter, the extinction coefficients of the ligand-localized $\pi-\pi^*$ transitions on the two NI/acetylides are sufficiently large that, upon production of the excited state, ground-state bleaching across this higher energy portion of the spectrum is clearly observed in the transient absorption experiments. This implies that the singlet ground-state absorptions are bleached as a result of triplet-state production localized within the NI/acetylide ligand framework.

The excited-state decay of the absorption transients in **1** displays lifetimes that are attenuated with respect to those acquired with transient luminescence under optically dilute

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Table 1. Photophysical Properties of **1** and NI—C≡C—H in MTHF

compound	λ_{abs}, nm (ε, cm^{-1} M^{-1})[a]	λ_{em}, nm	τ, μs	ϕ	k_r,[f] s^{-1}	k_{nr},[g] s^{-1}
1	424 (6.00×10^4)	621;[a] 616[c]	124;[b] 205[c]	0.215[d]	1.73×10^3	6.33×10^3
NI—C≡C—H	348 (2.74×10^4)	397[a]		0.103[e]		

[a] Measured in MTHF at RT. [b] Measured in MTHF at RT after five cycles of FPT degassing. [c] Measured in MTHF at 77 K. [d] Measured with [Ru(bpy)$_2$(phen)](PF$_6$)$_2$ as the standard (ϕ = 0.060 in MeCN). [e] Measured with quinine sulfate as the standard (ϕ = 0.547 in 0.05 M sulfuric acid). [f] $k_r = \phi/\tau$. [g] $k_{nr} = (1 - \phi)/\tau$.

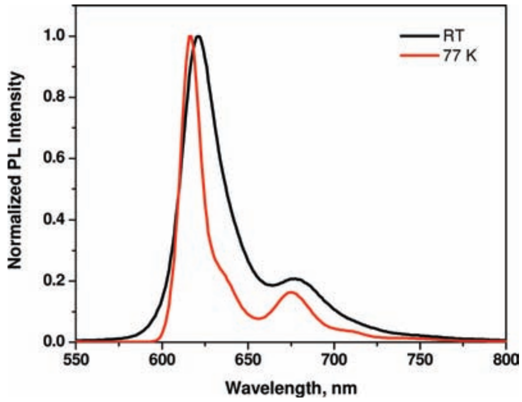

Figure 2. Photoluminescence spectra of **1** in MTHF at RT (black line) and 77 K (red line).

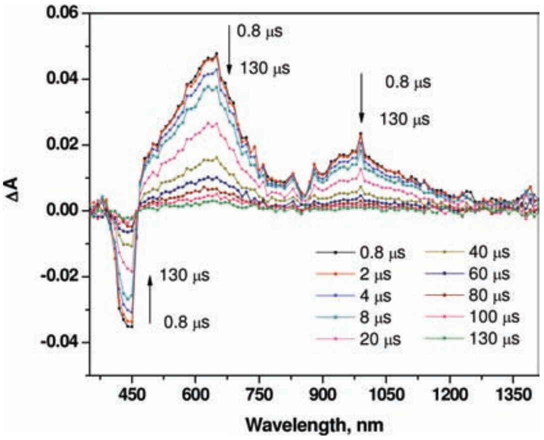

Figure 3. Nanosecond transient absorption difference spectra of **1** in MTHF measured as a function of the delay times indicated following 420 nm pulsed-laser excitation, 2 mJ/pulse.

conditions. However, when the more concentrated transient absorption samples are introduced into our transient photoluminescence apparatus, the measured single-exponential lifetimes are quantitatively the same, τ = 40 μs. Part of the attenuation observed is due to dioxygen quenching because the excited-state lifetime measured with the analogous FPT-degassed samples is 52 μs. Although we did not explore this phenomenon further, it is not surprising that self-quenching appears to be occurring in platinum(II) polychromophores of this type and one plausible lifetime-limiting reaction is bimolecular triplet−triplet annihilation.[13] The combined photophysical data measured for **1** leave little doubt that the phosphorescent ^{3}IL NI/acetylide excited state is produced upon visible light excitation of this complex at RT, and the absorption transients presented in Figure 3 are characteristic of the corresponding triplet-to-triplet absorptions from this species.

Excitation into the lowest-energy absorption bands in **1** sensitizes ^{3}IL phosphorescence in the appended C≡C—NI moieties at RT. The relatively strong ^{3}IL phosphorescence is a consequence of the presence of the internal Pt heavy atom. The current work represents an efficient starting point toward intramolecularly accessing the long-lived NI triplet state, proven to be elusive in the past. The title compound provides a molecular design that imparts long-lifetime red photoluminescence into a synthetically facile metal−organic chromophore. Such molecules have important potential applications in luminescence-based dioxygen sensing, excited-state chemistry schemes, photonics, and photofunctional materials and serve to further enhance the fundamental knowledge regarding the manipulation of molecular excited states.

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

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