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Hua, Fei; Kinayyigit, Solen; Cable, John R.; and Castellano, Felix, "Green Photoluminescence From Platinum(ii) Complexes Bearing Silylacetylide Ligands" (2005). *Chemistry Faculty Publications*. 146.
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Green Photoluminescence from Platinum(II) Complexes Bearing Silylacetylide Ligands

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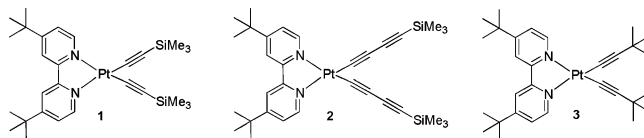
Received October 26, 2004

The synthesis, structural characterization, photoluminescence properties, and density functional theory analysis of three Pt(II) diimine complexes, Pt(dbbpy)(C≡CR)₂ [dbbpy = 4,4'-di(*tert*-butyl-2,2'-bipyridine); R = -SiMe₃, -C≡C-SiMe₃, or -*t*-Bu], are presented. The Pt(dbbpy)(C≡C-*t*-Bu)₂ complex serves as a carbon-based ligand structure for which the photophysical properties of the two silicon-bearing complexes are compared in dichloromethane. Pt(dbbpy)(C≡C-SiMe₃)₂ and Pt(dbbpy)(C≡C-C≡C-SiMe₃)₂ display visible absorptions with strong green emission ($\lambda_{\text{emmax}} = 526$ and 524 nm, respectively) while Pt(dbbpy)(C≡C-*t*-Bu)₂ displays efficient, long-lived yellow emission ($\lambda_{\text{emmax}} = 557$ nm). Direct side by side comparisons of Pt(dbbpy)(C≡C-SiMe₃)₂ and Pt(dbbpy)(C≡C-*t*-Bu)₂ suggest that the difference in excited state energy results from the relative σ -donor strength of the acetylide ligands.

Significant recent research activity has focused on Pt(II) diimine bis(arylacetylide) complexes possessing low energy metal-to-ligand charge transfer (MLCT) excited states.^{1–12} In many cases, these chromophores yield relatively high quantum yield photoluminescence with corresponding long

excited state lifetimes. Several reports have also shown that MLCT excitation in these compounds can internally efficiently sensitize low energy triplet states on appended arylacetylide subunits, some of which are phosphorescent at room temperature.^{9–11} One group has already demonstrated the viability of constructing solid state electroluminescent (EL) materials from this class of compounds.⁸ A recent account described some interesting photophysical observations in [Pt(tpy)(acetylide)]⁺ systems.¹³ This report showed that the introduction of an alkylacetylide ligand increases the oxidation potential of the Pt^{II} center relative to structures bearing a phenylacetylide subunit by 400 mV, thereby increasing the MLCT energy gap. This is undoubtedly a result of decreased σ -donor strength as demonstrated in other organometallic systems.^{14,15} We postulated whether a similar effect would be observed in Pt^{II} bis(acetylide) structures where two σ -donor ligands are fused to the metal center.¹⁶

Interested in the electronic factors that may ultimately lead to efficient and energetic luminophores and EL dye dopants, we decided to prepare three related Pt(dbbpy)(C≡CR)₂ structures, where R = SiMe₃ (**1**), -C≡C-SiMe₃ (**2**), and -*t*-Bu (**3**). Note that while the synthesis and structural characterization of **1** has already been reported,¹² its photophysical properties have not. On the basis of relative differences in σ -donor strength, we believed the introduction of two silylacetylide subunits would serve to increase the MLCT energy gap (relative to using aryl- or alkylacetylides with the same diimine ligand), thereby rendering higher energy emission. Consistent with this design criterion, the relative σ -donor strength of *t*-Bu acetylide is approximately the same as that of phenylacetylide,^{14,15} and the resulting absorption/emission properties are similar in **3** and Pt(dbbpy)-(C≡CPh)₂.^{4,10} Our experiments demonstrate that the weaker σ -donating silylacetylide subunits produce Pt^{II}-dbbpy complexes (**1** and **2**) with green MLCT-based emission.



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Compounds **1–3** were prepared by reaction of Pt(dbbpy)-Cl₂ with the appropriate terminal acetylenic precursor in CH₂-Cl₂/diisopropylamine in the presence of a CuI catalyst. Following alumina chromatography, these compounds were structurally characterized with ¹H and ¹³C NMR, mass spectrometry, and FT-IR. These complexes are air-stable solids and are readily soluble in relatively nonpolar organic solvents such as CH₂Cl₂ and toluene. Due to their two atom (Si vs C) structural difference, direct comparisons will largely be made between complexes **1** and **3** in the running text.

Cyclic voltammetry data were obtained in degassed CH₂-Cl₂/0.15 M TBAPF₆ solutions using a Pt working electrode (200 mV/s). Complexes **1** and **3** display irreversible metal-based oxidations and reversible dbbpy-ligand based reductions. The metal-based oxidations occur at peak potentials of +1.54 and +1.35 V versus Ag/AgCl in **1** and **3**, respectively. As observed in other related Pt^{II} systems,^{4,9} the metal-centered processes are influenced by the electronic properties of the acetylide ligands. In this case, the 190 mV difference is likely attributed to the greater σ -donating ability of the *t*-Bu-acetylide. Reversible one electron dbbpy-centered reductions in **1** and **3** occur at -1.41 and -1.49 V versus Ag/AgCl, respectively. In all 3 molecules, this reduction exhibits nearly identical peak currents ($i_{pa}/i_{pc} \sim 1.0$) and peak-to-peak splittings of ~ 120 mV. These observations are consistent with that measured for the internal ferrocene standard. Since these potentials are clearly distinct, it appears that the relative acetylide σ -donor strength also influences redox chemistry on the remote dbbpy ligand. The differences in the electrochemical energy gaps between compounds **1** and **3** is 0.11 ± 0.02 eV, yielding a rough estimate of that expected for the optical charge transfer transitions.

Figure 1 presents the absorption and photoluminescence spectra of **1–3** measured in freshly distilled CH₂Cl₂. All of the measured and calculated photophysical parameters are contained in Table 1. The lowest energy features in the absorption spectra of **1–3** are consistent with Pt \rightarrow dbbpy metal-to-ligand charge transfer (MLCT) transitions by comparison to other related complexes and the negative solvatochromic behavior of the absorption bands.^{7,9,10} In CH₂Cl₂, the MLCT transitions are significantly blue-shifted in the two silylacetylide bearing complexes (**1** and **2**). The peak separations observed between **1** and **3** (0.12 eV) are consistent with differences observed in the electrochemistry experiments, implying that these transitions are indeed charge transfer based.

Kohn–Sham density functional theory (DFT) calculations were employed to investigate the nature of the low-lying excited electronic states in these complexes. In Pt(bpy)-(C \equiv C–TMS)₂ and Pt(bpy)(C \equiv C–*t*-Bu)₂ (**1** and **3** without the *t*-Bu groups on the bpy ligand), the highest occupied orbitals were found to contain substantial contributions from

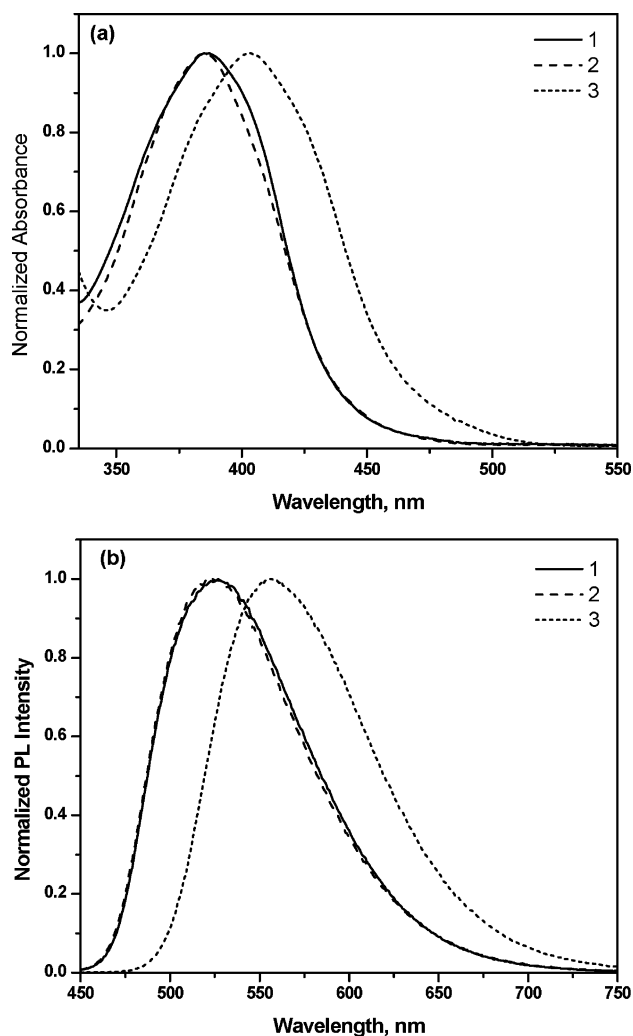


Figure 1. The absorption (a) and photoluminescence (b) spectra of **1–3** in CH₂Cl₂. The emission spectra were obtained using 385 ± 2 nm excitation.

Table 1. Photophysical and Redox Properties of the Platinum(II) Complexes in CH₂Cl₂ at Room Temperature

	$\lambda_{\text{abs}},^a$ nm	$\lambda_{\text{PL}},^a$ nm	$\Phi_{\text{PL}},^b$	$\tau,^b$ ns	$k_r,^c$ 10^5 s^{-1}	$k_{\text{nr}},^d$ 10^6 s^{-1}	$\Delta G_{\text{ES}},^e$ eV	$E_{1/2}^{\text{red},f}$ V	Pt ^{II*/Pt^I,^g}
1	387	526	0.13	236	5.5	3.7	2.68	-1.41	1.27
2	383	524	0.20	370	5.4	2.2	2.68	-1.28	1.40
3	403	557	0.48	1060	4.5	0.49	2.52	-1.49	1.03

^a Absorption and emission maxima, ± 2 nm. ^b PL quantum yields and intensity decays, $\pm 10\%$. ^c $k_r = \Phi/\tau$. ^d $k_{\text{nr}} = (1 - \Phi)/\tau$. ^e Excited state energies (ΔG_{ES}) were estimated ($\pm 5\%$) by drawing a tangent on the high energy side of the emission band. ^f First reduction potential measured in 0.15 M TBAPF₆/CH₂Cl₂ versus Ag/AgCl reference, ± 20 mV. ^g Calculated excited state reduction potentials (vs Ag/AgCl), (Pt^{II*/Pt^I) = (Pt^{II}/Pt^I) + ΔG_{ES} .}

both the metal d and the acetylenic π orbitals. In contrast, the lowest unoccupied molecular orbitals were almost completely localized on the bpy ligand. Time-dependent DFT calculations describe the lowest excited state in both complexes as primarily HOMO \rightarrow LUMO in nature and are therefore consistent with an MLCT assignment. The energies of these lowest lying excited states were calculated at 1.948 and 1.795 eV for the TMS- and *t*-Bu-acetylide complexes, respectively. Although both values lie below the experimental observations, the 0.15 eV difference between the two is in reasonable agreement with that seen in complexes **1** and **3**.

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The photoluminescence (PL) spectra of **1–3** are broad, and each respective excitation spectrum can be superimposed with its corresponding absorption spectrum from 330 to 500 nm, see Supporting Information. The emission energies in CH₂Cl₂ follow the order **2** (524 nm) > **1** (526 nm) > **3** (557 nm). The most notable result is that **1** is blue-shifted from **3** by 31 nm (0.13 eV), illustrative of significant electronic differences imparted by TMS–acetylide and *t*-Bu–acetylide. On the basis of the expected similarities in σ -donor strength,^{17,18} the absorption and PL properties of **1** and **2** are quantitatively similar.

Complexes **1** and **2** are high quantum yield green emitters in CH₂Cl₂, $\Phi = 0.13$ and 0.20 , respectively, while **3** is an exceptionally strong yellow emitter with $\Phi = 0.48$. The quantum yields were determined by comparison of **1** and **2** to fluorescein in 0.1 M NaOH ($\Phi = 0.95$)¹⁹ and by reference of **3** to [Ru(bpy)₃]²⁺ in CH₃CN ($\Phi = 0.062$).²⁰ Compounds **1** and **2** represent two of the highest energy emitters that have been reported to date in this particular class of chromophores.²¹ Interesting to note is that the emission profiles of **1** and **2** almost completely envelop the spectrum of Ir(ppy)₃ [ppy = 2-phenylpyridine] in CH₂Cl₂,^{22,23} see Supporting Information. In essence, these compounds provide viable alternatives for green color-matched triplet state emitters for potential applications in EL and light-emitting electrochemical cell (LEC) device configurations.^{8,23,24} The excited state lifetimes of **1–3** measured in degassed CH₂-Cl₂ are 236, 370, and 1060 ns, respectively. These lifetimes were measured with a broadband N₂-pumped dye laser ($\lambda_{\text{ex}} = 390$ nm, 500 ps fwhm) and are completely independent of monitoring wavelength over each emission envelope. The PL intensity decay transients were all adequately fit to single-exponential functions, and the lifetimes are consistent with an MLCT excited state assignment. Interesting to note is that the complex with the smallest energy gap possesses the longest lifetime and highest quantum yield in CH₂Cl₂. Taking into account the luminescence quantum yields and lifetimes, k_r and k_{nr} were calculated for each complex, Table 1. The relative values of both rate constants show that radiative decay effectively competes with nonradiative decay in all 3 molecules, most impressively in **3**. This is similar to what

has been observed in related Pt(diimine)(C≡CAr)₂ systems, where Ar = Ph or substituted phenyl.^{4,5,8} The calculated values of k_r and k_{nr} in all three instances are also consistent with emission from a lowest MLCT excited state. The excited state reduction potentials (Pt^{III}/Pt^I) compiled in Table 1 reveal that the compounds in the present study are good photo-oxidants, potentially useful for driving excited state electron transfer processes.^{4,6,7} As the metal-based oxidations were irreversible, we did not calculate excited state oxidation potentials.

The present study explored the viability of generating higher energy MLCT-based emission in Pt^{II} diimine chromophores through the use of “weaker” σ -donor acetylide ligands. The use of acetylides bearing terminal TMS groups successfully yielded compounds (**1** and **2**) with strong green MLCT based PL whose emission profiles are nearly identical to that of Ir(ppy)₃. A thorough photophysical and electrochemical examination revealed that the relative σ -donor strength revealed itself in both the metal-based oxidation in addition to the remote diimine ligand-based reduction. The excited state reduction potentials of **1–3** are in a range where they could be quite useful in photoinduced electron transfer chemistry. DFT calculations were able to predict the relative energy positions and separations in **1** and **3**. This suggests that future application of such calculations may prove useful toward the design of structures with predetermined photophysical properties. Proper variation of diimine ligand along with selected acetylide subunits may prove useful in the struggle to obtain red, green, and blue structurally compatible triplet emitters that are stable for solution and solid state electrooptical applications. Although there have not been any specific reports on TGA or DSC analysis of Pt(diimine)-(C≡CR)₂ complexes, studies on related systems have demonstrated that vacuum deposition of related complexes into various EL device configurations have realized success.^{25,26} Further studies are clearly necessary to test the sublimability of Pt(diimine)(C≡CR)₂ complexes for solid state multilayer EL device configurations.

Acknowledgment. This work was supported by the NSF (CAREER Award CHE-0134782 to F.N.C.).

Supporting Information Available: Synthesis and characterization details along with additional spectra and DFT surfaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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