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LETTER

Synthetic Control of Excited States: Electron Transfer from the ^{3}CT State of Biphenyl Coordinated to Platinum(II)

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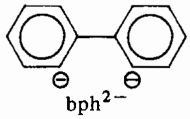
Few complexes of platinum(II) have been reported to be luminescent in solution at room temperature. To our knowledge, those that have are $[Pt_2(P_2O_4H_2)_4]^{4-}$ [1], [Pt(thpy)(phpz)] [2], $[Pt(thpy)_2]$ [2] and $[Pt(5,5'\text{-}Me_2bpy)(CN)_2]$ [3], where $P_2O_4H_2^{2-}$ is $(HO)OP–O–PO(OH)^{2-}$, $(thpy)^-$ is (2-(2-thienyl)pyridine)$^-$, (phpz)$^-$ is (1-phenylpyrazole)$^-$ and (5,5'-Me_2bpy) is 5,5'-dimethyl-2,2'-bipyridine. These complexes have shown excellent photoelectron-transfer properties [1–3]. $[Pt_2(P_2O_4H_2)_4]^{4-}$, for example, was reported to convert isopropanol into acetone and hydrogen photochemically. Such successes have prompted us to begin investigating those features that result in room-temperature luminescence by utilizing our past expertise where we were able to lower the ^{3}MLCT state below the dσ^* state in ruthenium(II) heterocycles by synthetic means and thereby decrease ligand loss [4]. Here we report an effective way to lower the π^* energy level of biphenyl, resulting in a powerful photoreductant.

In this study we have examined the photophysics of a compound containing biphenyl coordinated to platinum(II). The complex $[Pt(bph)(CH_3CN)_2]$, where bph is the biphenyl dianion shown below, was prepared by sonication of $[Pt(bph)((C_2H_5)_2S)]_2$[†] in acetonitrile until a clear solution was obtained.



bph^{2-}

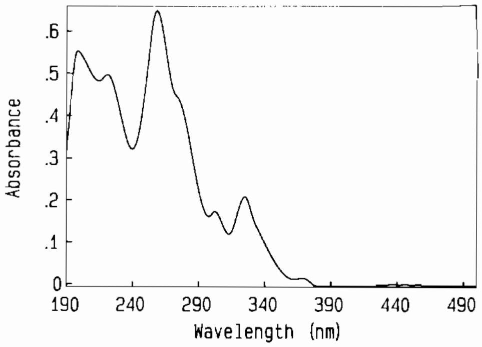


Fig. 1. UV–Vis spectrum of $[Pt(bph)(CH_3CN)_2]$ in acetonitrile at room temperature.

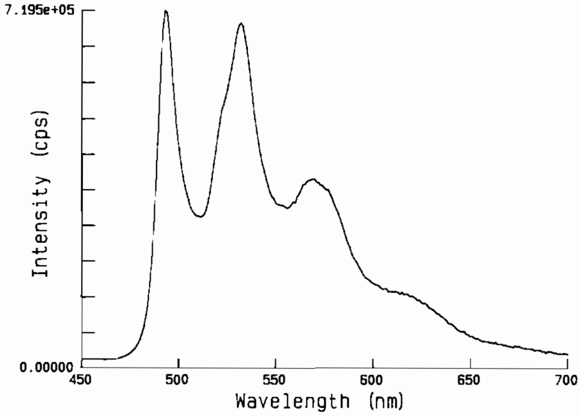


Fig. 2. Emission spectrum of $[Pt(bph)(CH_3CN)_2]$ in acetonitrile at room temperature; λ_{ex} = 355 nm.

The acetonitrile was then removed by rotary evaporation. A yellow solid was obtained and the following elemental analysis for $PtC_{16}H_{14}N_2$ was obtained. *Anal.* Calc.: C, 44.76; H, 3.29; N, 6.52. Found: C, 44.95; H, 3.42; N, 6.17%. Only a trace of sulfur was detected in the analysis[‡].

The electrochemical properties were examined in acetonitrile over the voltage range from +1.9 to −1.9 V. No electrochemical activity was observed in the negative region; however, an irreversible oxidation was found at 0.85 V (Pt versus SSCE, scan rate = 200 mV/s, 0.1 M tetrabutylammonium hexafluorophosphate) in the positive region. The irreversible oxidation most likely is associated with oxidation of Pt(II) to Pt(III), as suggested previously for other platinum(II) complexes [6, 7].

The UV–Vis absorption spectrum of $[Pt(bph)(CH_3CN)_2]$ is shown in Fig. 1. Absorption maxima are located at 325, 301 and 258 nm. In addition, weaker absorptions are observed at lower energies. In related *ortho*-metallated complexes [2–8],

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[†] $[Pt(bph)((C_2H_5)_2S)]_2$ was prepared by the procedures outlined in ref. 5.

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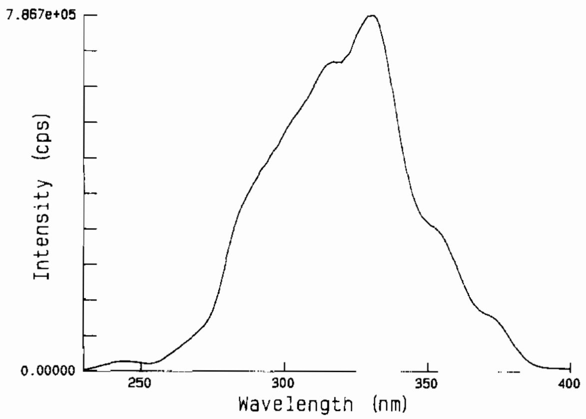

Fig. 3. Excitation spectrum of $[Pt(bph)(CH_3CN)_2]$ in acetonitrile at room temperature; $\lambda_{em} = 493$ nm.

transitions in the 250 nm region were attributed to intraligand processes, ones near 300 nm to $\pi \rightarrow \pi^*$ transitions associated with the ligands, and the weaker absorptions at lower energies to metal-centered transitions. Excitation of the complex at 355 nm in acetonitrile resulted in highly structured emission, as shown in Fig. 2, with maxima located at 493, 532, 569 and 612 nm. The vibronic progressions were approximately 1260 cm^{-1} and correspond to ring stretching modes [9]. The emission energy was independent of the excitation wavelength and the intensity was only weakly dependent on the absolute temperature. The excitation spectrum shown in Fig. 3 displays a maximum at 331 nm, slightly red-shifted from the absorption maximum at 325 nm. The excited-state lifetime of the emission ($\lambda_{ex} = 355$ nm) at room temperature in acetonitrile was 14 μs; the radiative quantum yield, ϕ_r, was 0.031 relative to rhodamine B. We conclude that emission occurs from a ^3CT state localized on the biphenyl ligand. The $[Pt(bph)((C_2H_5)_2S)]_2$ complex in CH_2Cl_2 displays similar emission characteristics to $[Pt(bph)(CH_3CN)_2]$, including the highly structured manifold when excited at 355 nm. The energy spacings are on the order of 1260 cm^{-1} as found for $[Pt(bph)(CH_3CN)_2]$.

The redox potential of the $[Pt(bph)(CH_3CN)_2]^{*/+}$ couple (estimated to be 1.65 V by the difference in the emission energy in eV and the peak potential for the irreversible oxidation) suggested that the excited state species would be a powerful reductant. Experimentally, oxidative quenching was verified in acetonitrile (eqns. (1) and (2)) with the electron acceptor, methyl viologen (MV^{2+}). Stern–Volmer

$$[Pt(bph)(CH_3CN)_2] \xrightarrow[\lambda = 355\text{ nm}]{h\nu} [Pt(bph)(CH_3CN)_2]^* \qquad (1)$$

$$[Pt(bph)(CH_3CN)_2]^* + MV^{2+} \xrightarrow{k_q} [Pt(bph)(CH_3CN)_2]^+ + MV^+ \qquad (2)$$

behavior was followed with $K_{SV} = 1.34 \times 10^5$ M^{-1} s^{-1} and $k_q = 9.6 \times 10^9$ M^{-1} s^{-1}. Laser flash photolysis provided spectroscopic evidence for MV^+ ($\lambda_{max} = 605$ nm, $\epsilon = 13700$ M^{-1} cm^{-1}) [9]. A back electron-transfer for the process illustrated in eqn. (3) was observed at 600 nm and had a calculated rate constant of 1.54×10^{10} M^{-1} s^{-1}.

$$[Pt(bph)(CH_3CN)_2]^+ + MV^+ \xrightarrow{k_b} [Pt(bph)(CH_3CN)_2] + MV^{2+} \qquad (3)$$

The results indicate that the ^3CT state of the biphenyl ligand is brought below the ^3MLCT and $d\sigma^*$ states of the complex and electron transfer occurs from the ^3CT state of biphenyl. In other studies, aromatic hydrocarbons containing electron-donating substituents have also been shown to exhibit electron transfer from photoexcited states [10]. In this study, we have exploited this behavior and enhanced the process by coordinating the biphenyl dianion to a metal center. The metal center, platinum(II), acts as a template to hold the biphenyl rings 'flat' for maximum π delocalization and also acts as an electrostatic center which has the effect of lowering the π^* energy levels [11], making them more accessible for enhanced energy photoactivity.

Acknowledgements

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