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Review

Excimer and electron transfer quenching studies of a cyclometalated platinum complex

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Abstract

Luminescence quenching studies of a cyclometalated complex, platinum(II) (2-(4′,6′-difluorophenyl)pyridinato-*N*,$C^{2'}$)(2,4-pentanedionato-*O*,*O*) (**FPt**), in solution at room temperature are reported. The **FPt** complex undergoes efficient self-quenching in solution at room temperature that can be successfully modeled by a monomer/excimer phosphorescence mechanism with a diffusion limited rate constant ($4.2 \pm 0.3 \times 10^9\ M^{-1}\ s^{-1}$). The emission lifetimes for **FPt** monomer and excimer in 2-methyltetrahydrofuran at room temperature are 330 ns (±15 ns) and 135 ns (±10 ns), respectively. The excited state properties of **FPt** were also investigated. A triplet energy E_T of 2.8 eV and excited-state reduction potential $E(\mathrm{FPt}^{*/-})$ of 0.81 V versus SCE were determined from quenching studies in agreement with values estimated from emission spectra and a thermochemical cycle. The excited-state oxidation potential $E(\mathrm{FPt}^{*/+})$ cannot be determined from electrochemical data since **FPt** undergoes irreversible oxidation. However, a value of $E(\mathrm{FPt}^{*/+}) = -1.41$ V versus SCE was established from an electron transfer quenching study and thus, a ground state oxidation potential for **FPt** can be estimated to be 1.30 V versus SCE.

Keywords: Quenching; Platinum complex; Excimer; Energy transfer; Electron transfer; OLEDs

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1. Introduction

Square planar platinum complexes have attracted considerable interest for their potential use in a wide range of applications such as optical chemosensors [1], photocatalysis [2], and molecular photochemical devices for solar energy conversion [3]. Platinum complexes have also been applied successfully as phosphorescent emitters in organic light-emitting diodes (OLEDs) [4]. OLEDs fabricated with platinum complexes can exhibit high emission efficiency, as the strong spin-orbital coupling of platinum allows for efficient phosphorescence at room temperature [5]. Efficient phosphorescent dopants are important components in OLEDs since the hole–electron recombination process leads to a mixture of singlet and triplet excited states in the device [6]. Recently, white OLEDs have been prepared with an organometallic Pt complex, platinum(II) (2-(4′,6′-difluorophenyl)pyridinato-$N,C^{2'}$)(2,4-pentanedionato-*O*,*O*) (**FPt**), with emission that originates from both isolated Pt complexes and excimers or aggregates of the same complex [7]. The devices utilized a very simple device structure since only a single dopant is used in the emissive layer and were highly efficient. In order to better understand the excited state properties of **FPt**, we have carried out an extensive photophysical quenching study of this complex and report it herein.

Self-quenching of platinum complexes has been well known since Che and co-workers reported concentration dependence of the emission intensity for the complex Pt(5,5′-dimethyl-2,2′-bipyridine)$(CN)_2$ [8a]. Other researchers have reported similar self-quenching for related square planar platinum complexes, as well as the observation of weak excimer emission at high platinum complex concentrations [8,9]. The self-quenching mechanism used to explain this concentration dependent quenching process involves initial formation of the excited complex, M^*, followed by association with a ground state complex to give a weakly emissive excimer, $[M, M]^*$. The latter process is clearly dependent on the concentration of the metal complex. The model is identical to one used to describe the monomer/excimer fluorescence kinetics of aromatic hydrocarbons [10]. Using this model, the diffusion controlled self-quenching rate constants have been determined for a number of platinum complexes by monitoring the self-quenching reactions of the Pt complex as a function of concentration. Direct characterization of these platinum excimers, however, has been less documented due to limited solubility of the complexes, as well as weak emission and short lifetimes for the excimers [9].

Metal complexes in their excited states may be potent oxidizing and reducing agents [11], making them potentially useful as sensitizers for photochemical energy conversion (i.e. solar energy conversion). In this context, it is important to know the redox properties of excited metal complex, in order to design the optimal combination of donor and acceptor materials to interact with the sensitizer in a solar cell configuration. Likewise, in organic light-emitting diodes, a good understanding of the excited state redox properties is also important, since such knowledge will enable the best materials to be chosen in order to eliminate luminescent quenching by electron transfer between the excited dopant and the other materials in the device, processes that lead to a decreased OLED efficiency.

In this paper, we present a number of photophysical studies of **FPt** in solution at room temperature. The concentration dependent luminescent behavior of **FPt** was studied by static and transient spectroscopy. The **FPt** complex was found to undergo luminescent self-quenching at near diffusion controlled rates from monomer/excimer phosphorescence kinetic analysis. Energy transfer and electron transfer quenching studies of the complex **FPt** were also carried out to estimate the redox properties of the **FPt** ground and excited state [12].

2. Experimental

2.1. Materials

All of the neutral organic quenchers used here were commercially available and used as received. The pyridinium salts were prepared by refluxing the corresponding substituted pyridine with appropriate alkylating reagent in an acetone–methanol mixture overnight, followed by metathesis in water with NH_4PF_6. The solvent 2-methyltetrahydrofuran (2-MeTHF) was distilled under N_2 after being refluxed over sodium prior to use. The acetonitrile used was EM Science DriSolv solvent and used as received. **FPt** was prepared by a literature procedure [5].

2.2. Physical measurements

The UV–vis spectra were recorded on an Aviv model 14DS spectrophotometer (a re-engineered Cary 14 spectrophotometer). Photoluminescent spectra were measured using a Photon Technology International fluorimeter. Emission lifetime measurements were performed using time-correlated single photon counting on an IBH Fluorocube instrument. Samples were excited with 405 nm pulsed diode laser having a pulse duration of ca. 1.2 ns and an energy of 500 nJ/pulse. The energy per laser pulse was adequate to provide a transient signal yet low enough to prevent formation of high concentrations of excited state species, which would lead to quenching by triplet–triplet annihilation. The measured lifetimes have an error of 5%.

Quantum efficiency measurements were carried out at room temperature in a 2-methyltetrahydrofuran solution. Before spectra were measured, the solution was degassed by several freeze–pump–thaw cycles using a diffusion pump. Solutions of coumarin-47 in ethanol ($\Phi = 0.60$) were used as a reference. The equation $\Phi_s = \Phi_r(\eta_s^2 A_r I_s / \eta_r^2 A_s I_r)$ was used to calculate quantum yields, where Φ_s is the quantum yield of the sample, Φ_r is the quantum yield of the reference, η is the refractive index of the solvent, A_s and A_r are the ab-