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Metal Coordination Induced π-Extension and Triplet State Production in Diketopyrrolopyrrole Chromophores

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Supporting Information

ABSTRACT: Triplet state photophysics has been generated in two distinct diketopyrrolopyrrole (DPP) chromophores terminated with either phenyl (**1**) or thienyl (**2**) spacers, when sandwiched between two Ir(III) complexes using bipyridyl linkers. Upon coordination of the bpy-DPP-bpy subunit resulting in its planarization, the π-conjugation in the DPP chromophore formally extends and was manifested as a substantial red shift in the absorption and fluorescence profiles of **1** and **2**. Low energy excitation of these dinuclear metal complexes produced strongly quenched singlet fluorescence, generated quite intense long-lived ($\tau \sim 3$ μs) absorption transients in the red, sensitized $^1O_2$ photoluminescence centered at 1270 nm in aerated solutions, and yielded low temperature near-IR phosphorescence in **1** centered at 950 nm.

Diketopyrrolopyrrole (DPP) dyes represent a synthetically versatile class of visible light-harvesting chromophores largely exploited in both small molecule and polymeric formats for their high singlet fluorescence quantum efficiencies in areas as diverse as photorefractive materials,[1] fluorescence sensors,[2] thin film transistors,[3] and light-emitting diodes.[4,5] DPP-based sensitizers have also emerged as promising candidates for adaptation in low cost photovolatics (PVs) based on organic bulk heterojunctions[6−12] in addition to dye-sensitized solar cells.[13] The ability to systematically color tune these chromophores for sunlight capture and conversion is therefore of quintessential importance.[14] Similarly, given the significance of how triplet excitons can be utilized to enhance PV performance in a variety of devices[15] prompts the question of how one might access the triplet excited states of DPP dyes in a facile manner. This manuscript simultaneously demonstrates both of these desirable outcomes by incorporating two Ir(III) coordination compounds that formally extend the π-conjugation in distinct DPP metal−organic chromophores (**1** and **2**) while imparting internal heavy atoms that facilitate triplet state production and DPP-centered phosphorescence. This effort strongly differs from a previous investigation where DPP dianions were used to coordinate a variety of transition metals resulting in molecules exhibiting ligand localized singlet state photophysics.[16]

Molecules **1** and **2** were prepared by postfunctionalization of the preformed brominated DPP frameworks **3**[17] and **4** (see Chart 1).[11] Cross-coupling with the functionalized iridium complex **5**[18] was promoted by low valent $[Pd(PPh_3)_4]$ under mild conditions, where the formed HBr was quenched by triethylamine. The course of the reaction was followed by thin-layer-chromatography, and the purification was extremely facile. On the basis of ^1H NMR spectroscopy, a single isomer (*trans,trans-N,N* on each iridium center) was obtained, a result consistent with previous observations.[14] The isolated compounds were structurally characterized by NMR, MS, and elemental analysis.

Chart 1. Numbering Scheme of the Molecules Investigated

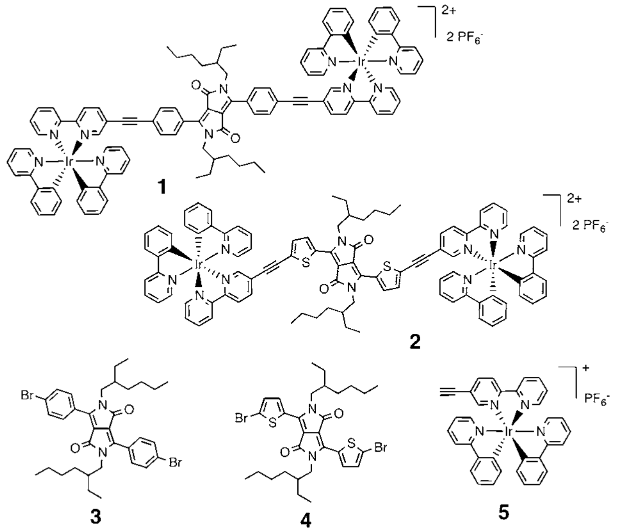

Figure 1 presents the absorption and photoluminescence spectra of **1** and **2** recorded in acetonitrile at room temperature directly compared to that from the corresponding synthetic DPP precursors **3** and **4** as well as that of the Ir(III) terminal acetylene synthon **5**. The corresponding spectral maxima and extinction coefficients are collected in Table S1. Immediately obvious are the substantial red shifts (~1500 cm^{-1}) in the lowest energy $\pi-\pi^*$ absorption bands exhibited by **1** and **2**

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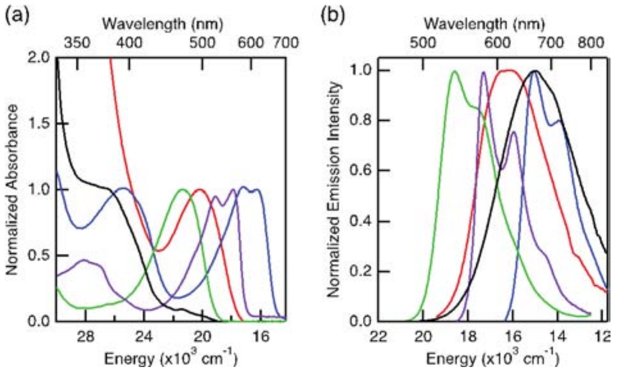

Figure 1. Normalized absorption (a) and corrected photoluminescence (b) spectra for **1** (red), **2** (blue), **3** (green), **4** (purple), and **5** (black) in acetonitrile solution. Each emission spectrum was generated by exciting on the red edge of the lowest energy absorption band.

with respect to their synthetic precursors **3** and **4**, illustrating the importance of the π-extension achieved as a result of coordination-induced planarization of the bpy substituents.[19] This is further supported through DFT calculations where the HOMO and LUMO orbitals responsible for the lowest energy electron transition clearly extend through both terminal bpy subunits, illustrated for **1** in Figure 2. The photoluminescence from **1** and **2**, obtained through excitation into the lowest energy absorption band, is characteristic of strongly quenched singlet fluorescence emanating from the DPP portion of each molecule as evidenced through quantum yields and lifetimes. In **1**, the quantum yield decreases to 0.003 ± 0.0003 (from 0.95 ± 0.019 in **3**), and for **2**, the quantum yield decreases to 0.16 ± 0.0032 (from 0.77 ± 0.0154 in **4**). Similarly, the fluorescence lifetime of **1** and **2** ($\tau \sim < 1$ ns) is substantially quenched relative to both DPP synthons ($\tau \sim 6-7$ ns in **3** and **4**) and the model Ir(III) charge transfer chromophore **5** ($\tau = 80$ ns).

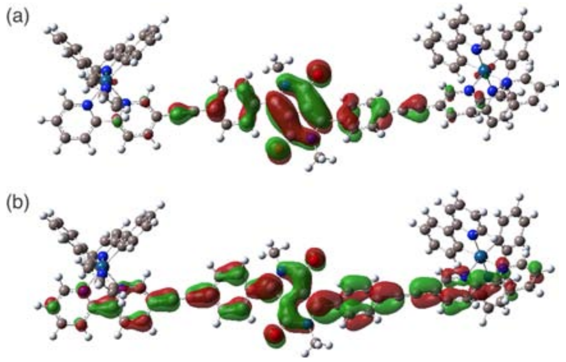

Figure 2. DFT-calculated isodensity plots of the HOMO (a) and LUMO (b) orbitals of the geometry optimized ground state of **1** in an acetonitrile dielectric continuum. The long aliphatic chains were replaced by methyl groups.

In N-coordinated DPP-based metal complexes, it has been shown that the fluorescence quantum efficiencies were enhanced (in most cases) with respect to the "free" DPP ligand with little effect on the corresponding lifetimes.[16] These data correlated well with relative distortion from the planarity observed in the crystal structures; the more planar, the higher the fluorescence quantum efficiency. In **1** and **2**, which are not N-bound, metal coordination to the distal bpy subunits results in strong quenching of the DPP-based singlet fluorescence implying that there is strong electronic coupling between the Ir(III) centers and the DPP subunit in both molecules. This likely results from strong conjugation across the entire DPP backbone as illustrated by the DFT calculations in Figure 2. These calculations also imply that there is no effective electronic communication to the nitrogen substituents resident on the DPP structure.

While it is commonplace for Ir(III)-based metal–organic chromophores to exhibit photoinduced electron transfer chemistry, cyclic voltammetry data illustrate that the metal complex associated redox potentials (determined in **5**) actually bracket those of the DPP subunit in each case, Table S2. For both **1** and **2**, the driving force for oxidative and reductive electron transfer from the lowest energy excited singlet state is endothermic (~0.4 V for **1** and 0.3–0.4 V for **2**) as calculated using the Rehm–Weller expression with E_{00} estimated from the fluorescence emission maxima. Therefore, no charge shift chemistry is expected from the excited states of **1** and **2** as long as the excitation selectively targets the DPP moiety at low energies. In essence, the origin of fluorescence quenching in these molecules can be tentatively assigned to singlet–triplet intersystem crossing promoted by the two iridium internal heavy atoms resident in each structure. Similar phenomena have been previously observed in structurally similarly mononuclear Ir(III) complexes[18] as well as those bearing extended aromatic cores.[20]

More clear-cut evidence for triplet state production in **1** and **2** emerged from nanosecond transient absorption spectroscopy. In both instances, selective excitation of the DPP subunit at long wavelengths resulted in the generation of long-lived transient signals ($\tau \approx 3$ μs) with large absorption amplitudes in the red and ground state bleaching in regions featuring the largest DPP singlet absorptions, Figure 3. Note that related long lifetime features were not observed in the corresponding experiments performed on **3** and **4**. Both oxidative and reductive spectroelectrochemical experiments were performed

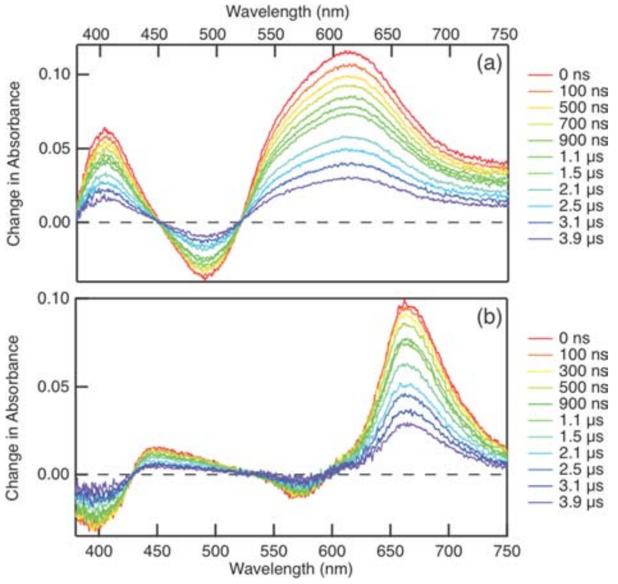

Figure 3. Transient absorption difference spectra measured as a function of various delay times in argon saturated acetonitrile solution: (a) **1** following 540 nm excitation (~2 mJ/pulse, 5–7 ns fwhm). (b) **2** following 640 nm excitation (~1.5 mJ/pulse, 5–7 ns fwhm). Each difference spectrum represents an average of 20 transients.

on **2** in order to approximate the transient absorption signal that would potentially arise from a photoinduced charge-separated state, Figure S8. The resultant spectra of both oxidized and reduced **2** are distinctly different from the long-lived species observed in transient absorption experiments (Figure 3b), again suggesting that the species observed in the transient absorption is indeed the DPP-localized triplet state rather than an electron transfer product with an unusually long charge recombination rate. The long lifetimes observed in the transient absorption experiments were significantly quenched in the presence of dissolved dioxygen (Figures S6 and S7) with the concomitant sensitization of $^1O_2$ photoluminescence centered at 1270 nm, Figure S5, indirectly implying a triplet excited state manifold being responsible for the transient signals observed in **1** and **2**, Figure 3. These observations prompted us to examine the near-IR region to ascertain whether **1** or **2** produces any DPP-centered phosphorescence, which has yet to be observed from the general class of DPP chromophores. Unfortunately, no such emission signals could be acquired at room temperature, but experiments performed at 77 K in 9:2 butyronitrile/propionitrile glasses successfully yielded near-IR photoluminescence in **1**, Figure 4, thereby representing the first observation of phosphorescence from a DPP-bearing chromophore. The uncorrected emission maximum of **1** was centered at 950 nm whereas the analogous experiments performed for **2** failed to produce any signals in the near-IR attributable to phosphorescence.

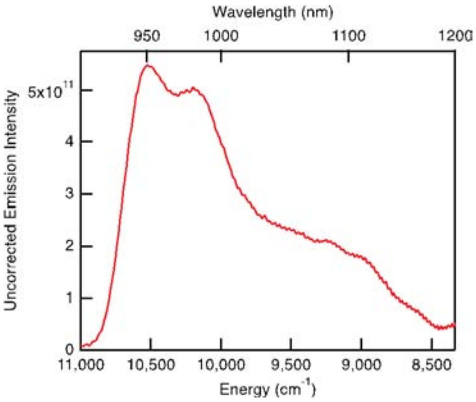

Figure 4. Uncorrected phosphorescence spectrum of **1** at 77 K recorded in a 9:2 butyronitrile/propionitrile glass (λ_{ex} = 500 nm). An 850-nm-long pass filter was used to remove all residual singlet fluorescence artifacts.

This manuscript described the first examples of DPP-containing coordination compounds and illustrated how the photophysics of this important chromophore can be substantially altered as a result of imposing this structural motif. The bpy-DPP-bpy linker resulted in DPP chromophores exhibiting extended π-conjugation and substantially red-shifted absorption and fluorescence spectra resulting from coordination-induced planarization on both ends of the molecule. The singlet state photophysics normally associated with the DPP moiety gives way to triplet state dominated photophysics in the metal−organic assemblies **1** and **2**, as evidenced by strong singlet state quenching, the generation of long-lived absorption transients in the red, the sensitization of $^1O_2$ photoluminescence, and in the case of **1**, near-IR phosphorescence at low temperatures. In addition to their molecular photophysics that may be exploited in a range of optical-based applications, the light-harvesting properties of metal−organic DPP molecules are of particular interest as dyes for incorporation into next generation photovoltaics.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete synthetic details; structural characterization; computational approaches; and additional spectroscopic, electrochemical, and spectroelectrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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