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Excited-State Equilibration over 30 Å in a Platinum(II) Quinolinolate–Bridge–Platinum(II) Porphyrin Complex

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Long-range triplet excited-state equilibration occurs over a nanometric distance between platinum(II) 8-quinolinolate (²Ptq₂ = 1.87 eV) and platinum(II) tetrathienylporphyrin (²PtTPP = 1.89 eV). The equilibrium is mediated by a fluorene–thiophene–fluorene bridge (²FTF = 1.92 eV) and is characterized by a double-exponential decay (τ₁ = 39 ± 4 ps; τ₂ = 351 ± 15 ps) that suggests the participation of three separate excited states: ²Ptq₂, ²FTF, and ²PtTPP, respectively. Numerical simulation of the dual equilibrium allowed for estimation of the individual rate constants for each of the reversible steps (kₚ = 3.9 × 10⁹−4.1 × 10¹⁰ s⁻¹). As a result of rapid triplet-state equilibration, almost 50% of the excited-state energy is directed from the PtTPP chromophore toward Ptq₂, in spite of a small endothermic barrier (0.03 eV).

The design of photonic systems that allow control over excited-state energy is important for the construction of molecular-level optical devices.¹ Over the last 2 decades, numerous examples based on polyperyridine complexes of ruthenium(II) and osmium(II) have been investigated because of their intriguing electrooptical properties.² Similarly, complexes containing rhenium(I) and copper(I) that display long-lived triplet excited states have also been studied.³ In order to enforce a linear arrangement of the chromophores and ensure vectorial energy migration in light-active systems,⁴ terpyridyl-type moieties have become the ligands of choice for the aforementioned metal centers.

Because of their square-planar geometry and large spin–orbit coupling,⁵ ⁶ platinum(II) complexes bearing low-energy intraligand excited states have the potential to become useful building blocks in the preparation of linear photoactive systems. Particularly attractive are materials based on platinum(II) 8-quinolinolate (Ptq₂), which have received interest because of efficient phosphorescence,⁷ singlet oxygen formation,⁸ and near-IR electroluminescence.⁹ Nevertheless, the triplet state behavior of Ptq₂-based photonic assemblies has not yet been evaluated. Herein we report the first preparation and photophysical study of Ptq₂-based multichromophoric systems 1a–c (Figure 1), which exhibit exclusive intraligand (π−π*) excited states. By carefully matching the triplet energy levels of the individual components, we were able to achieve equilibration of the photogenerated excited state over 30 Å on an ultrafast time scale. This report constitutes the first example of thermal equilibration over a 30 Å distance,⁴²bc.¹⁰ which could pave the road to macroscopic photonic applications.

The platinum quinolinolate chromophore was connected to platinum(II) meso-tetrathienylporphyrins (PtTPPs) by means of conjugated oligomers in systems 1b and 1c. The PtTPP unit was selected because of its well-known photophysical properties and widespread use in photonic materials¹² but mostly because its lowest electronic excited state


is thermally accessible from the lowest electronic state of Ptq2. Because the triplet excited states of Ptq2 and PtTPP are virtually isoenergetic (1Ptq2 = 1.87 eV; 3PtTPP = 1.89 eV),11 we decided to investigate the different scenarios for triplet energy behavior by introducing major differences in the alignment of the triplet energy of the bridge with respect to the platinum centers. In 1b, the triplet level of the quaterfluorene bridge (1F4 = 2.18 eV)13 lies high above those of PtTPP and Ptq2, which limits their electronic communication to superexchange-based interactions.14 On the other hand, the triplet level of the fluorene–thiophene–fluorene (FTF) bridge in 1c lies only slightly above those of PtTPP and Ptq2 (1FTF = 1.92 eV). Recently, we have reported that the triplet state of FTF can be populated to a small extent by thermal equilibration with PtTPP, which could lead to thermal equilibration over the entire molecule in 1c.15

The triplet excited-state behavior of 1a–c was investigated by time-resolved photoluminescence and by transient absorption spectroscopy techniques. The UV–vis spectra of 1b and 1c in the visible region are largely dominated by the PtTPP chromophore because of its high oscillator strength (Figure 1c, left). Importantly, the spectra show features typical for the independent chromophores, which indicated that no significant electronic interactions took place between the connecting units.

Regardless of the excitation wavelength, the steady-state emission spectra of 1b and 1c displayed the typical PtTPP-based phosphorescence (λmax = 670 and 740 nm; Figure 2B, right). However, 1b and 1c showed significant differences in lifetimes and quantum yields of emission. Upon excitation at 510 nm (the PtTPP Q band and Ptq2 absorption), complex 1b displayed a phosphorescence lifetime of τ = 29.24 ± 0.09 μs and a quantum yield of 4.3%, while for 1c, a lifetime of 12.69 ± 0.05 μs and a quantum yield of 1.7% were determined. The fact that 1b exhibited emission properties similar to those of the parent PtTPP (τ = 50 μs; Φph = 4.6%)16 indicated that little communication between PtTPP and Ptq2 takes place through the quaterfluorene bridge. On the other hand, it appeared that the quasi-isoenergetic triplet states in 1c allow effective PtTPP–FTF–Ptq2 thermal equilibration to occur. Here, a large part of the 3PtTPP excited-state energy seemed to be directed toward the less emissive Ptq2 center (Φph = 0.80% and τ = 3.22 ± 0.01 μs recorded for the model compound 1a). To explore this hypothesis further, we employed nanosecond transient absorption spectroscopy with excitation at 510 nm (Figure 3).

For 1b, typical nanosecond transient features associated with PtTPP were observed with a lifetime consistent with the recorded phosphorescence decay, τ = 29.3 ± 0.2 μs. Interestingly, 1c also displayed spectral features associated with PtTPP but with less intense absorption and significantly faster decay kinetics (τ = 8.2 ± 0.1 μs) than 1b.17 The fact that complex 1c displayed almost exclusively spectral features from 3PtTPP is in accordance with the higher

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**Figure 1.** Structures of 1a–c. Inset: Schematic representation of the triplet energy alignment in 1b and 1c.11

**Figure 2.** Left: UV–vis spectra of 1a–c in toluene (1 μM). Right: Room-temperature emission spectra upon excitation at 510 nm in degassed toluene.

**Figure 3.** Transient absorption spectra of 1a–c 200 ns after excitation at 510 nm. Inset: Decay trace of 1c at 460 nm (3PtTPP absorption).

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(17) A comparison between 1b and 1c under the same photon flux and optical density revealed about half the intensity for the spectral features of the latter.
extinction coefficient of this species. However, the substantial reduction in the lifetime strongly suggests that fast equilibration between $^3$PtTPP and a shorter-lived excited state occurs within the duration of the laser pulse in the nanosecond experiment (~7 ns).

The excited-state dynamics of $1c$ was also investigated by femtosecond transient absorption spectroscopy, where the effective intersystem crossing of PtTPP (ISC $\sim 1$ ps) allowed for direct probing of the triplet excited states. Upon selective excitation of PtTPP at 400 nm, rapid changes in the $^3$PtTPP absorption band of $1c$ were observed as a result of equilibration (Figure 4). In contrast to simple thermal equilibration processes, the excited-state dynamics of $1c$ was characterized by a double-exponential function ($\tau_1 = 39 \pm 4$ ps; $\tau_2 = 351 \pm 15$ ps), which agreed with the proposed equilibration of three separate excited states, i.e., $^3$PtTPP, $^3$FTF, and $^3$Ptq. Interestingly, the introduction of $^3$Ptq as an accessible excited state to both $^3$PtTPP and $^3$FTF results in a considerable increase in the excited-state energy transfer from PtTPP. Numerical simulation of the double-equilibration kinetic decay allowed for estimation of the individual rate constants for each of the reversible energy-transfer processes between $^3$PtTPP, $^3$FTF, and $^3$Ptq. Similar equilibrium concentrations for $1a$ and $1c$ were adapted from ref 15, which describes in detail the equilibration between PtTPP and the FTF bridge.

Supporting Information Available: Synthesis and characterization of compounds $1a$–$c$ and their precursors, lifetime fits, time-resolved and low-temperature emission spectra for $1a$–$c$, and numerical assessment of the thermal equilibration process. This material is available free of charge via the Internet at http://pubs.acs.org.

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