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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 (³Ptq₂ = 1.87 eV) and platinum(II) tetraphenylporphyrin (³PTPP = 1.89 eV). The equilibrium is mediated by a fluorene-thiophene-fluorene bridge (³FTF = 1.92 eV) and is characterized by a double-exponential decay (t₁ = 39 ± 4 ps; t₂ = 351 ± 15 ps) that suggests the participation of three separate excited states: ³Ptq₂, ³FTF, and ³PTPP, respectively. Numerical simulation of the dual equilibrium allowed for estimation of the individual rate constants for each of the reversible steps (kₑ₇ = 3.9 × 10¹⁰−4.1 × 10¹⁰ s⁻¹). As a result of rapid triplet-state equilibration, almost 50% of the excited-state energy is directed from the PTTP 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 polypyridine complexes of rhenium(I) 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 (³Ptq₂), 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 ³a–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,²b,c,¹⁰ which could pave the road to macroscopic photonic applications.

The platinum quinolinolate chromophore was connected to platinum(II) meso-tetraphenylporphyrins (³PTPPs) by means of conjugated oligomers in systems ³b and ³c. The PTTP 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 (³Ptq₂ = 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 (¹F₂ = 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 phospholuminescence 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 (λ_max = 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; Φ_ph = 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 (Φ_ph = 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 ³PtTPP 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 ³PtTPP 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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(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.
The excited-state dynamics of 3 FTF was also investigated by femtosecond transient absorption spectroscopy, where the effective intersystem crossing of PtTPP (ISC 1 ps) allowed for direct probing of the triplet excited states. Upon selective excitation of PtTPP at 400 nm, rapid changes in the PtTPP absorption band of 3 FTF were observed as a result of equilibration (Figure 4). In contrast to simple thermal equilibration processes, the excited-state dynamics of 3 FTF was characterized by a double-exponential function \((\tau_1 = 39 \pm 4 \text{ ps}; \tau_2 = 351 \pm 15 \text{ ps})\), which agreed with the proposed equilibration of three separate excited states, i.e., PtTPP, 3 FTF, and 3 Ptq. Interestingly, the introduction of 3 Ptq as an accessible excited state to both 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 PtTPP, 3 FTF, and 3 Ptq: \(k_1 = 3.9 \times 10^9 \text{ s}^{-1}, k_{-1} = 4.1 \times 10^{10} \text{ s}^{-1}, k_2 = 2.3 \times 10^{10} \text{ s}^{-1}, \) and \(k_{-2} = 1.1 \times 10^{10} \text{ s}^{-1}\). Similar equilibrium concentrations for PtTPP, 3 FTF, and 3 Ptq were adapted from ref 15, which describes in detail the equilibration between PtTPP and the FTF bridge.

In summary, we report the incorporation of Ptq complexes into multichromophoric assemblies that exhibit dramatically distinct photophysical behavior depending on the triplet energy of the conjugated electronic spacer. A long-range double equilibration was obtained in the case of system 3c with quasi-isoenergetic components. The platinum porphyrin centers act as light antennae that transmit the energy toward the center of the molecule in spite of a slightly endothermic barrier. Overall, the equilibration across the molecule (30 Å center-to-center distance) is remarkably efficient. To the best of our knowledge, this is the first example of triplet excited-state equilibration taking place so efficiently over a long distance. The described strategy may prove useful in the design of photoactive molecular systems.

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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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References

(18) The values for \(k_1\) and \(k_{-1}\) were adapted from ref 15, which describes in detail the equilibration between PtTPP and the FTF bridge.
