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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 (^{3}Ptq$_2$ = 1.87 eV) and platinum(II) tetraphenylporphyrin (^{3}PtTPP = 1.89 eV). The equilibrium is mediated by a fluorene–thiophene–fluorene bridge (^{3}FTF = 1.92 eV) and is characterized by a double-exponential decay ($\tau_1 = 39 \pm 4$ ps; $\tau_2 = 351 \pm 15$ ps) that suggests the participation of three separate excited states: ^{3}Ptq$_2$, ^{3}FTF, and ^{3}PtTPP, respectively. Numerical simulation of the dual equilibrium allowed for estimation of the individual rate constants for each of the reversible steps ($k_{ET} = 3.9 \times 10^9$–4.1×10^{10} s^{-1}). As a result of rapid triplet-state equilibration, almost 50% of the excited-state energy is directed from the PtTPP chromophore toward Ptq$_2$, 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 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 (Ptq$_2$), which have received interest because of efficient phosphorescence,[7] singlet oxygen formation,[8] and near-IR electroluminescence.[9] Nevertheless, the triplet state behavior of Ptq$_2$-based photonic assemblies has not yet been evaluated. Herein we report the first preparation and photophysical study of Ptq$_2$-based multichromophoric systems **1a**−**c** (Figure 1), which exhibit exclusive intraligand ($\pi-\pi^*$) 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 (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 materials[12] but mostly because its lowest electronic excited state

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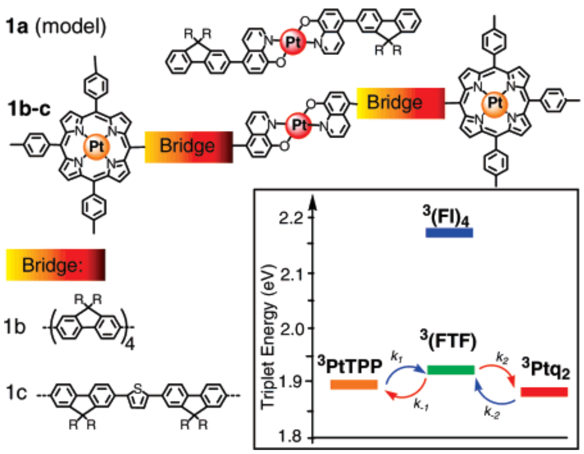

Figure 1. Structures of **1a**–**c**. Inset: Schematic representation of the triplet energy alignment in **1b** and **1c**.[11]

is thermally accessible from the lowest electronic state of Ptq_2. Because the triplet excited states of Ptq_2 and PtTPP are virtually isoenergetic ($^3Ptq_2 = 1.87$ 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 ($^3F_4 = 2.18$ eV)[13] lies high above those of PtTPP and Ptq_2, 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 Ptq_2 ($^3FTF = 1.92$ 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 2A, 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 ($\lambda_{max} = 670$ 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 Ptq_2 absorption), complex **1b** displayed a phosphorescence lifetime of $\tau = 29.24 \pm 0.09$ 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 ($\tau = 50$ μs; $\Phi_{Ph} = 4.6\%$)[16] indicated that little communication between PtTPP and Ptq_2 takes place through the quaterfluorene bridge. On the other hand, it appeared that the quasi-isoenergetic triplet states in **1c** allow effective PtTPP–FTF–Ptq_2 thermal equilibration to occur. Here, a large part of the ^{3}PtTPP excited-state energy seemed to be directed toward the less emissive Ptq_2 center ($\Phi_{Ph} = 0.80\%$ and $\tau = 3.22 \pm 0.01$ 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).

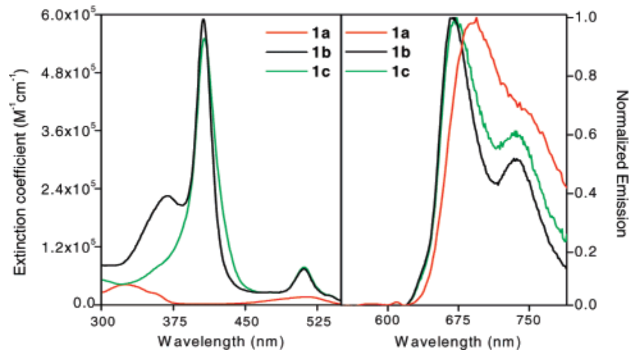

Figure 2. Left: UV–vis spectra of **1a**–**c** in toluene (1 μM). Right: Room-temperature emission spectra upon excitation at 510 nm in degassed toluene.

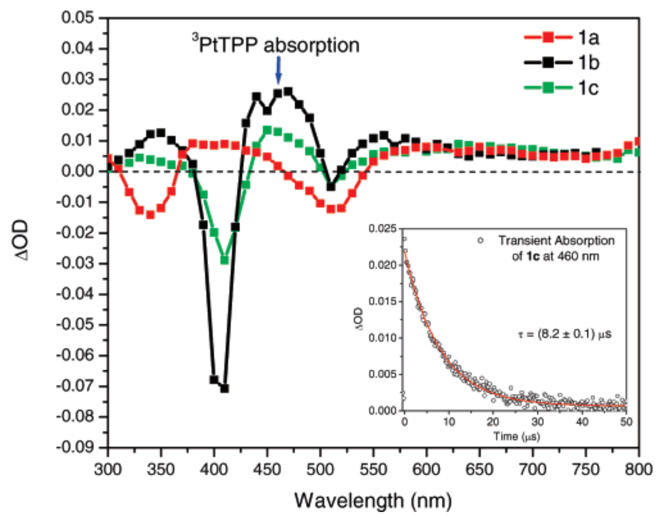

Figure 3. Transient absorption spectra of **1a**–**c** 200 ns after excitation at 510 nm. Inset: Decay trace of **1c** at 460 nm (^{3}PtTPP absorption).

For **1b**, typical nanosecond transient features associated with ^{3}PtTPP were observed with a lifetime consistent with the recorded phosphorescence decay, $\tau = 29.3 \pm 0.2$ μs. Interestingly, **1c** also displayed spectral features associated with ^{3}PtTPP but with less intense absorption and significantly faster decay kinetics ($\tau = 8.2 \pm 0.1$ μs) than **1b**.[17] The fact that complex **1c** displayed almost exclusively spectral features from ^{3}PtTPP 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.

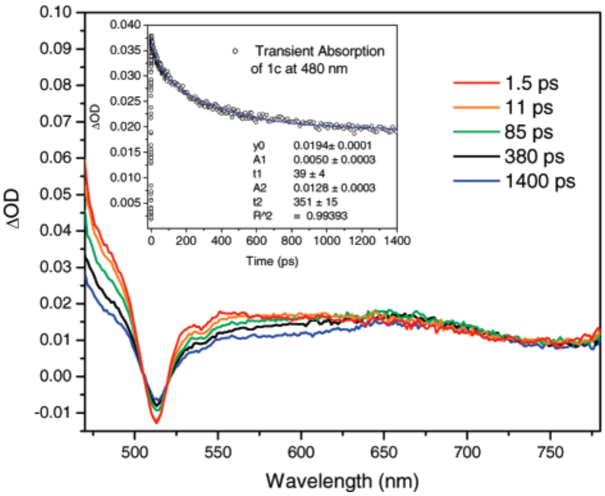

Figure 4. Femtosecond spectral evolution of **1c** (λ_{exc} = 400 nm). Inset: Decay trace at 480 nm showing the thermal equilibration process.

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 ~ 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,[2b,c,10] 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$_2$. Interestingly, the introduction of ^{3}Ptq$_2$ 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.[15] 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$_2$:[18] $k_1 = 3.9 \times 10^9$ s^{-1}, $k_{-1} = 4.1 \times 10^{10}$ s^{-1}, $k_2 = 2.3 \times 10^{10}$ s^{-1}, and $k_{-2} = 1.1 \times 10^{10}$ s^{-1}.[11] Similar equilibrium concentrations for ^{3}PtTPP and ^{3}Ptq$_2$ were estimated, which is in agreement with the independent steady-state luminescence spectroscopic observations.

The nature of the double thermal equilibration was further supported by low-temperature luminescence spectroscopy measurements in glassy MeTHF matrixes. Upon excitation at 510 nm (the PtTPP Q band and Ptq$_2$ absorption), two lifetime components ($\tau_1 = 12.9 \pm 0.4$ μs; $\tau_2 = 105.4 \pm 0.7$ μs) were observed for both **1b** and **1c** at 77 K. The phosphorescence emission was resolved by the time-gating technique, which allowed assignment of the two components to phosphorescence from Ptq$_2$ (short lifetime) and emission from PtTPP (long lifetime) in agreement with literature reports and the emission spectra of **1a**.[19] Additionally, changes in the emission spectra were observed depending on the wavelength of excitation in agreement with the relative contributions of Ptq$_2$ and PtTPP to the absorption at a specific wavelength. For example, the emission spectra of **1b**−**c** displayed more intense Ptq$_2$ phosphorescence spectral features upon excitation at 480 nm, where this chromophore presents maximum contribution to the overall absorption profile.[11] From these observations, it was concluded that Ptq$_2$ and PtTPP behave as independent chromophores at 77 K in both **1b** and **1c**[20] and that the equilibration process proposed for **1c** is strongly activated by temperature.

In summary, we report the incorporation of Ptq$_2$ 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 **1c** 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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