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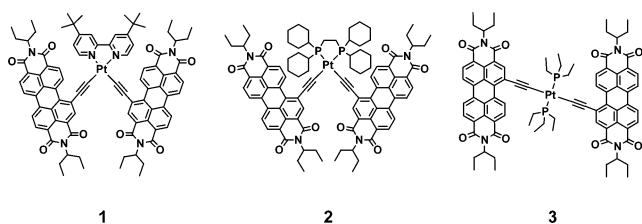
Accessing the Triplet Excited State in Perylenediimides

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Perylenediimides (PDIs) continue to emerge as quintessential chromophores in a variety of photofunctional materials.^{1,2} In addition to their desirable visible light-harvesting and impressive fluorescence properties, PDIs have established niche applications in chemical sensing,³ organic field-effect transistors,^{4,5} light-emitting diodes,⁶ and photovoltaics (PVs).^{5,7} Given recent reports highlighting how polymeric PV performance is enhanced by utilizing long-lived triplet excited states in the photoinduced charge separation step,^{8,9} access to the PDI triplet state clearly represents a desirable goal for solar energy conversion using these molecules. Despite recent attempts,¹⁰ the PDI triplet state remains accessible only through bimolecular sensitization¹¹ or in sophisticated molecular architectures involving a cascade of nonradiative steps.^{2,12–14} Here, we designed molecules **1–3** in an effort to efficiently generate the triplet state of PDI following photoexcitation in three distinct Pt^{II} square planar structures. The platinum–acetylide motif was selected as this combination is known to induce strong spin–orbit coupling facilitating a rapid ($k_{\text{isc}} > 10^{11} \text{ s}^{-1}$) singlet \rightarrow triplet intersystem crossing in the appended organic chromophore.^{9,15} Structures **2** and **3** examine the influence of *cis*- vs *trans*-PDI–acetylide ligation whereas **1**, which inherently possesses a more complex electronic structure, assesses the consequence of positioning a triplet charge transfer (³CT) excited state energetically proximate to the PDI triplet.



Complete synthetic and structural characterization details of **1–3** are provided as Supporting Information (SI). Briefly, treatment of PDI–CC–TMS¹⁶ with NaOH in methanol produced the terminal acetylene (PDI–CCH) which was reacted with the appropriate Pt(II) chloride precursor in CH₂Cl₂ in the presence of *i*-Pr₂NH and CuI, affording high yield (>75%) chloride-to-acetylide metathesis in each case. All compounds were structurally characterized by NMR, MALDI-MS, and elemental analysis.

Figure 1 presents the absorption spectra of **1**, **2**, and **3** as well as the absorption and emission spectra of the PDI acetylide precursor, PDI–CCH. All three Pt^{II} complexes exhibit absorptions dominated by the π – π^* transitions of the PDI moiety with maxima between 570 and 573 nm ($\epsilon \approx 65\,500$ – $68\,000 \text{ M}^{-1} \text{ cm}^{-1}$). These absorptions are significantly red-shifted relative to that of the PDI–CCH chromophore (529 nm, $\epsilon = 80\,000 \text{ M}^{-1} \text{ cm}^{-1}$), as is typically observed when a conjugated terminal acetylene produces the corresponding Pt–acetylide chromophore.^{15,17} Surprisingly, the extinction coefficients of **1–3** are not double that of the PDI–

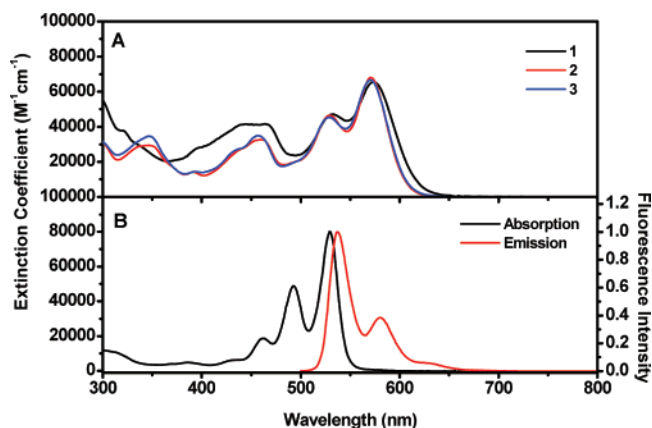


Figure 1. (A) Absorption spectra of **1**, **2**, and **3**. (B) Absorption and fluorescence spectra of PDI–CCH. All spectra were collected in CH₂Cl₂.

CCH; however, integration of each absorption spectrum yielded the expected 2:1 ratio (based on number of PDIs) for complexes **2** and **3** relative to PDI–CCH. A significant increase in extinction coefficient is observed for **1** in the 375–500 nm region which results from the overlapping CT transition, thereby rendering a greater than 2:1 integrated absorption ratio relative to PDI–CCH. PDI–CCH exhibits strong fluorescence ($\Phi = 0.91$) centered at 537 nm with a lifetime of 4.53 ns, Figure S1. Upon ligation via an acetylide bridge in the bay region to Pt^{II}, the fluorescence is quantitatively quenched in **1–3**, and unfortunately, no corresponding phosphorescence could be detected in the visible or near-IR region under degassed conditions. However, all three complexes sensitize ¹O₂ emission at 1270 nm in aerated CH₂Cl₂ with visible light excitation, Figure S2. This result indirectly suggests that the lowest energy excited state in these molecules can be assigned to a triplet. It also stands to reason that the excited state in **1** is likely similar to that in **2** and **3** due to a lack of any photoluminescence emanating from these samples. Hence, nanosecond transient absorption spectroscopy was used to establish the nature of the lowest triplet state in **1–3**.

The transient absorption difference spectra of **1**, **2**, and **3** are presented in Figure 2, panel A, B, and C, respectively, following $450 \pm 2 \text{ nm}$ pulsed laser excitation in CH₂Cl₂ at room temperature; the single-exponential lifetimes measured in each case are indicated on each panel. All major features of the three difference spectra agree remarkably well with each other. Select single wavelength kinetic traces and their respective fits with residuals are provided as SI. The transient spectrum observed in each case appeared promptly within the instrument response so no information could be obtained on the spectral evolution of the transients. The major visible absorption features measured in all three complexes are qualitatively similar and red-shifted relative to bimolecular triplet-state sensitization experiments performed on PDI–CCH using thioxanthone as the sensitizer, Figure S3. Taken together, the

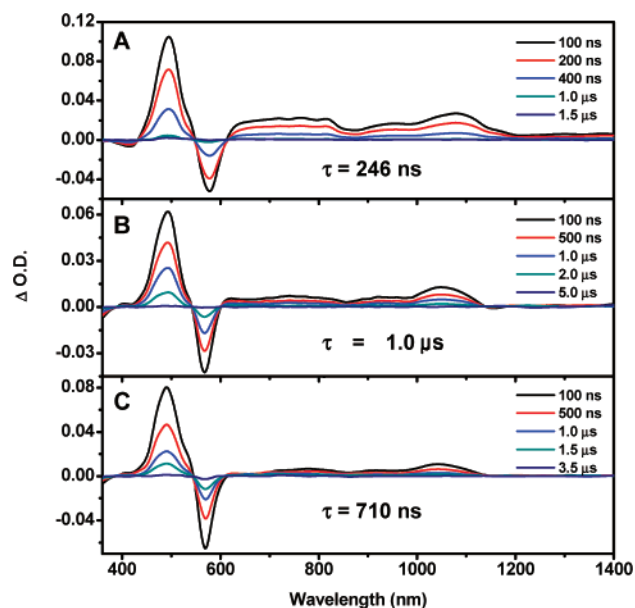


Figure 2. Transient absorption difference spectra of **1** (A), **2** (B), and **3** (C). All transients were collected in deaerated CH_2Cl_2 at room temperature with $\lambda_{\text{ex}} = 450 \text{ nm}$ (2.5–3 mJ/pulse). Single-exponential decay times are indicated within each panel.

experimental data support the conclusion that a long lifetime PDI-localized triplet state is readily accessible and populated in **1–3**.

The transient absorption spectrum of **1** (Figure 2A) does not exhibit features typical of the ^3CT excited state of Pt^{II} diimine chromophores.^{15,17} The difference spectrum in Figure 2A reveals an intense excited state absorption at 495 nm and ground state bleach near 575 nm followed by a broad, less intense absorption between 620 and 880 nm and excited state absorption centered at 1080 nm. These spectral features do not coincide with characteristic PDI singlet state transient absorptions or the associated radical cations or anions. The excited state lifetime of **1** as ascertained by transient absorption kinetics is 246 ns, consistent with the anticipated PDI-localized triplet state parentage.

The corresponding *cis*-disposed phosphine model complex **2** lacking CT excited states exhibits a transient absorption spectrum nearly identical to that of **1**, Figure 2B. The most disparate difference between **1** and **2** is that the excited state lifetime is extended to 1.0 μs in **2**. This increase in lifetime may be accounted for by the lack of a low-lying ^3CT state in **2**, the presence of which may facilitate more efficient excited state deactivation in **1**. Future ultrafast transient absorption measurements will be applied to investigate these processes further. To exclude the possibility of electronic coupling effects between neighboring PDI moieties in **1** and **2**, the corresponding *trans*-disposed model complex **3** was synthesized. Importantly, no quantitative changes occur in the position, shape, relative intensities, and number of transitions in the ground state (Figure 1A) or transient absorption difference spectra (Figure 2C). This observation readily excludes the possibility of intramolecular interactions from neighboring PDI units. Interest-

ingly, the excited state lifetime of **3** ($\tau = 710 \text{ ns}$) lies between that of **1** and **2** which implies that stereochemistry and the nature of the coordinated ligands profoundly influence the excited state dynamics in these PDI-acetylide chromophores.

We have directly observed the triplet state of the PDI chromophore by establishing a Pt^{II} -acetylide linkage in its bay region. The singlet fluorescence of the PDI moieties is quantitatively quenched as a result of this linkage, producing characteristic transient absorption difference spectra with concomitant long lifetimes ranging from 246 ns to 1.0 μs . Each of these nonluminescent compounds readily sensitizes $^1\text{O}_2$ emission in the near-IR when excited with visible light in the presence of dissolved O_2 . The current work represents an efficient starting point toward intramolecularly accessing the long-lived PDI triplet state, proven elusive in the past. Armed with the present strategy, polymer solar cells harnessing the PDI triplet state now appear viable, but its broad application in photonics and photofunctional materials also seems imminent.

Acknowledgment. The authors thank Dr. Xianghuai Wang for helpful discussions. This work was supported by the Air Force Office of Scientific Research (FA9550-05-1-0276), the National Science Foundation (CHE-0719050), the ACS-PRF (44138-AC3), and the BGSU Research Enhancement Initiative.

Supporting Information Available: Synthesis, experimental details, additional kinetic analyses and spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA800333Y