

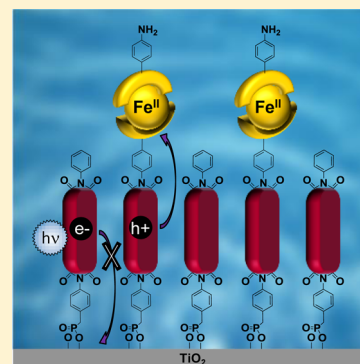
Ultrafast, Light-Induced Electron Transfer in a Perylene Diimide Chromophore-Donor Assembly on TiO₂

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S Supporting Information

ABSTRACT: Surface-bound, perylenediimide (PDI)-based molecular assemblies have been synthesized on nanocrystalline TiO₂ by reaction of a dianhydride with a surface-bound aniline and succinimide bonding. In a second step, the Fe(II) polypyridyl complex [Fe^{II}(tpy-PhNH₂)₂]²⁺ was added to the outside of the film, also by succinimide bonding. Ultrafast transient absorption measurements in 0.1 M HClO₄ reveal that electron injection into TiO₂ by ¹PDI* does not occur, but rather leads to the ultrafast formation of the redox-separated pair PDI^{•+},PDI^{•-}, which decays with complex kinetics ($\tau_1 = 0.8$ ps, $\tau_2 = 15$ ps, and $\tau_3 = 1500$ ps). With the added Fe(II) polypyridyl complex, rapid (<25 ps) oxidation of Fe(II) by the PDI^{•+},PDI^{•-} redox pair occurs to give Fe(III),PDI^{•-} persisting for >400 μ s in the film environment.



Perylenediimide (PDI) dyes are intensely colored with high molar absorptivities and measurable fluorescence quantum yields and lifetimes and have been used as electron-transfer acceptors.^{1,2} They are photostable, oxidatively and reductively stable, and stable in aqueous environments.^{3–16} PDI derivatives have been incorporated into dyad and oligomeric assemblies with ultrafast transient absorption measurements used to investigate excited-state energy and electron transfer and the appearance of transient redox-separated states.^{17–35} The oxidized forms of the dyes have redox potentials that are sufficient to drive water oxidation and excited-state redox potentials sufficient to undergo electron injection into the conduction band of TiO₂.^{36,37}

Given their appealing features, PDI dyes have considerable promise for applications as the dye in dye-sensitized photoelectrosynthesis cells (DSPECs). However, the synthesis of asymmetric PDI derivatives is not well-developed.^{18,38–42} Interfacial PDI structures on TiO₂ and other substrates are generally prepared by vapor deposition,^{43–45} the Langmuir–Blodgett technique,⁴⁶ dip- or spin-coating,^{47–50} an electrostatic layer-by-layer approach,⁵¹ metal phosphonate chemistry,^{52,53} or covalent attachment,^{54,55} with few examples of PDI dyes surface-bound with phosphonate linkers.^{56–58}

We report here the development of a general surface attachment–derivatization synthetic strategy for preparing PDI-based molecular assemblies on oxide surfaces. It is based on covalent attachment of perylene dianhydride precursors to metal oxide surfaces and involves reacting one of the anhydride functional groups with a surface-bound primary amine.^{43,44,59} Reaction of perylene anhydrides with amine bases occurs readily at high temperatures in imidazole melts.^{42,60} A

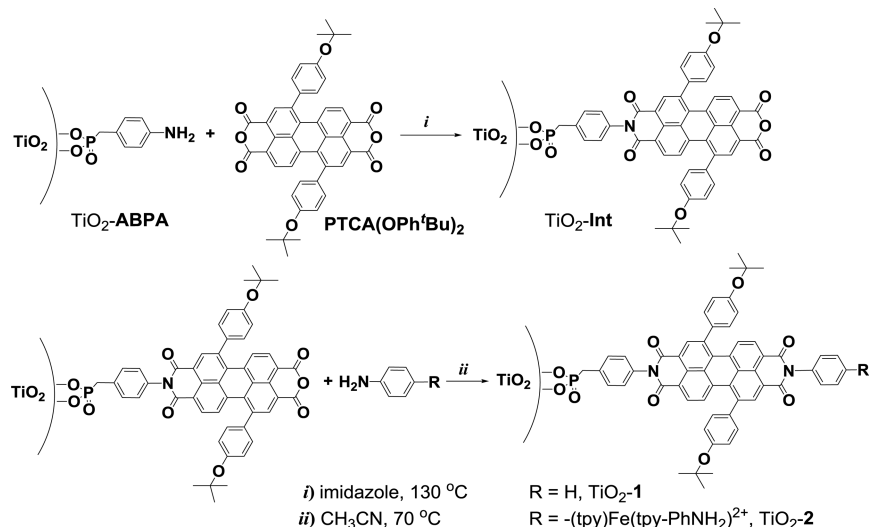
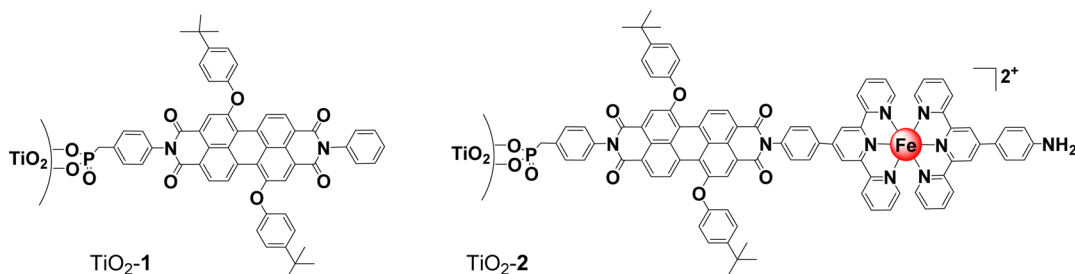
molecular assembly is formed in a second step by utilizing the second anhydride to react with a primary amine group. We also report on the application of ultrafast transient absorption spectroscopy to investigate the electron-transfer dynamics that occur following PDI excitation in surface assemblies on TiO₂.

The synthetic strategy, applied to nanoparticle metal oxide thin-film electrodes of TiO₂ (15–20 nm diameter, 2–3 μ m thick films), is shown in Scheme 1. The first step involved surface binding of 4-aminobenzyl phosphonic acid (ABPA) by soaking electrodes in ABPA/CH₃OH solutions for at least 3 h.⁶¹ The surface binding step leaves the primary amine functional group exposed on the surface, available for surface reaction. The TiO₂-ABPA derivatized electrodes were then immersed for 5–10 min in a nitrogen-purged imidazole melt (130 °C) containing 1,7-(4-*tert*-butylphenoxy)perylene-3,4:9,10-tetracarboxylic dianhydride, PTCA(OPh_tBu)₂. Reaction between the surface-bound amine and one of the anhydride functional groups of PTCA(OPh_tBu)₂ was used to attach the perylene by succinimide bonding, as shown in Scheme 1. Following perylene attachment to the surface, a second amine-anhydride reaction was used for further derivatization with either aniline to give TiO₂–PDI assembly, TiO₂–I, or the redox-active Fe(II) complex, [Fe^{II}(tpy-PhNH₂)₂]²⁺ (tpy-PhNH₂ is 4-([2,2':6',2''-terpyridin]-4'-yl)-aniline) to give Fe(II)-derivatized assembly TiO₂–I–PDI–(N-Ph-

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Scheme 1. Stepwise Synthesis of PDI Assemblies on Nanocrystalline TiO_2 Chart 1. Structures of PDI-Based Assemblies $\text{TiO}_2\text{-1}$ and $\text{TiO}_2\text{-2}$ 

$(\text{tpy})\text{Fe}^{\text{II}}(\text{tpy-PhNH}_2)_2^{2+}$, $\text{TiO}_2\text{-2}$ (Chart 1). Further synthetic details are given in the Supporting Information.

The stepwise syntheses of assemblies $\text{TiO}_2\text{-1}$ and $\text{TiO}_2\text{-2}$ were monitored by ultraviolet (UV)–visible measurements, Figure 1. There was no visible absorption above the TiO_2 background for surface-bound 4-aminobenzyl phosphonic acid as expected for this UV absorber. Addition of the perylene dianhydride, PTCA(OPhtBu)_2 , in the second step gave intermediate **Int**, a surface-bound perylene anhydride as evidenced by the appearance of a perylene absorption in the

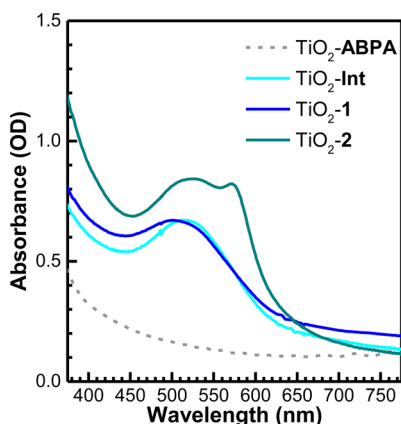


Figure 1. UV–visible absorption spectra obtained during stepwise assembly formation of **1** and **2** on *nano* TiO_2 . The spectra were obtained on dry films aligned perpendicular to the spectrophotometer beam in air at room temperature.

visible at $\lambda_{\text{max}} = 515$ nm, Figure 1. There is evidence for a π stacking interaction on the surface between PDI groups by the considerable broadening of the absorption manifolds and by a change in the relative absorptivities of the vibronic progressions. A related behavior is observed in polar solvents of the dye which gives rise to one-dimensional (1D), PDI-stacked structures.^{62–64}

In the final assembly-forming reaction, the exposed anhydride functional group in **Int** was allowed to react with either 0.1 mM aniline or $[\text{Fe}(\text{tpy-PhNH}_2)_2]^{2+}$ by soaking the slide in a 70 °C acetonitrile solution for 10 min. Addition of aniline in the third stage of assembly formation to form $\text{TiO}_2\text{-1}$, Figure 1, induced minimal spectral changes. Addition of Fe(II) to **Int** to give $\text{TiO}_2\text{-2}$, Figure 1, resulted in a new metal-to-ligand charge transfer (MLCT) absorption feature at $\lambda_{\text{max}} = 575$ nm as well as a slight red-shift in the perylene absorptions by ~ 15 nm. There was no evidence for surface binding of $[\text{Fe}(\text{tpy-PhNH}_2)_2]^{2+}$ to the underivatized TiO_2 films. Surface binding of Fe(II) to the exterior of the dyes is robust without loss over extended soaking times consistent with linkage by succinimide bond formation as illustrated in Scheme 1.

On the basis of UV–visible spectral comparisons and relative solution absorptivities, we estimate the extent of Fe(II) surface loading per surface perylene unit to be $\sim 50 \pm 10\%$. The less than 1:1 surface coverage in Fe(II) is presumably the result of the relatively large ~ 14 Å diameter of the Fe(II) polypyridyl complex relative to the surface perylene units. With partial loading, unreacted anhydride groups are present at the surfaces of the films which, under the conditions of our experiments in aqueous solutions, are hydrolyzed to the corresponding acids.

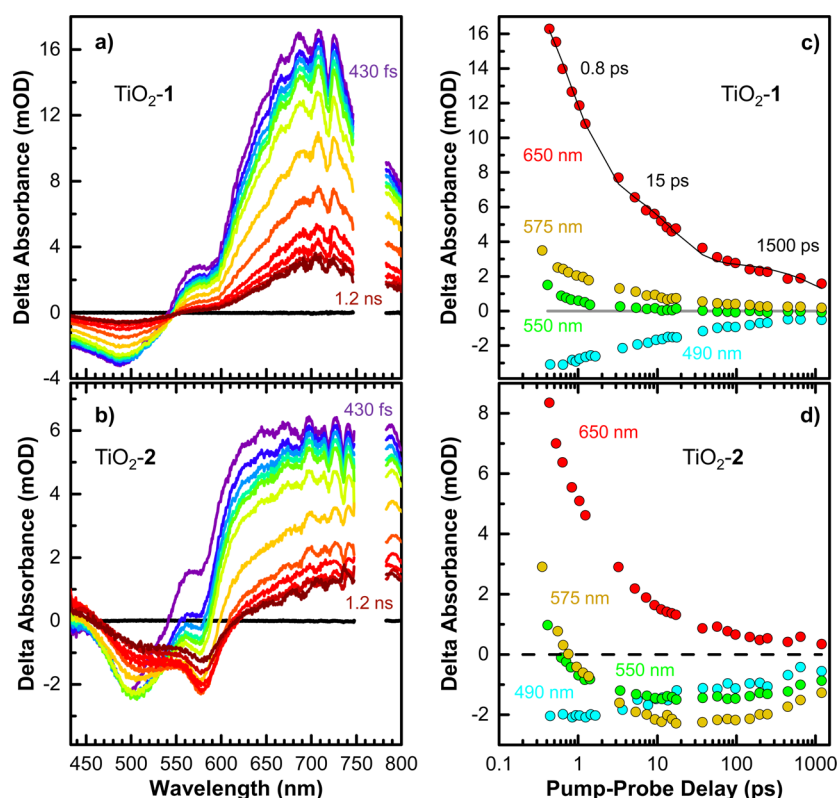


Figure 2. (a) Transient absorption spectra of TiO₂-1 immersed in 0.1 M aqueous HClO₄ at room temperature following $\lambda_{\text{exc}} = 425$ nm, 150 nJ/pulse excitation acquired at the following time delays (in picoseconds): -6.49 (black), 0.43 (violet), 0.65 (indigo), 0.84 (royal blue), 1.08 (aqua), 1.32 (green), 2.0 (light green), 5.0 (orange), 23 (dark orange), 75 (orange-red), 195 (light red), 530 (red), and 1200 (dark red). (b) As for panel a but for TiO₂-2 with the black line corresponding to -6.0 ps. (c) Kinetic traces at 490 nm (cyan circles), 550 nm (green circles), 575 nm (gold circles), and 650 nm (red circles) for TiO₂-1 in 0.1 M HClO₄. A triexponential fit to the 650 nm kinetics transients is shown as the black, solid line through the data with the time constants indicated. (d) As for panel c but for TiO₂-2.

In cyclic voltammograms (CVs) of TiO₂-1 and TiO₂-2 (data not shown) on fluorine-doped tin oxide (FTO)/*in situ* TiO₂ in 0.1 M HClO₄, there was no evidence for perylene oxidation from 0.2 to 1.7 V vs NHE. Scans to reductive potentials were limited to potentials >0.2 V vs NHE in order to avoid background reduction of TiO₂. TiO₂ is a large band gap semiconductor without a significant population of mid-band gap levels with electron transfer constrained to occur by cross-surface site-to-site hopping to and from the underlying FTO electrode.^{65–67} Nevertheless, electrochemical activity of adsorbed organic and inorganic molecules on TiO₂ is routinely observed. The absence of the expected redox couples for the perylene moieties of **1** and **2** when surface-bound to TiO₂ or planar FTO is apparently due to slow electron-transfer kinetics, even at a conductive collector electrode, possibly arising from the inability of the external electrolyte to enter the tightly packed, hydrophobic films for charge compensation.⁵⁸ By contrast, solution-based oxidative and reductive electrochemistry for a carbon-chain-functionalized derivative of **1** (data not shown; 1×10^{-4} M in CHCl₃ with 0.1 M *n*Bu₄PF₆, structure shown in Figure S3) was observed by CV measurements at an FTO working electrode surface-derivatized with [Ru(bpy)₂(P₂bpy)]²⁺ (bpy = 2,2'-bipyridine; P₂bpy = 4,4'-diphosphonic acid-2,2'-bipyridine) as an interfacial redox mediator.^{68–70} PDI-based waves were observed at 1.49 V (PDI^{••/0}), -0.71 V (PDI^{0/•-}), and -0.85 V (PDI^{•-/-2-}) vs NHE.

For TiO₂-2 in 0.1 M HClO₄, a wave for the external, chemically bound - [(NHtpy)Fe^{II}(tpy-PhNH₂)]^{4+/3+} couple was observed at $E_{1/2} = 1.2$ V vs NHE, close to the value of 1.06

V for the Fe(tpy)₂^{3+/2+} couple. The Fe(III/II) wave in **2** is distorted and scan-rate-dependent, consistent with kinetically inhibited electron transfer as found for other molecules surface-bound to TiO₂.⁷¹ The driving force for oxidation of Fe(II) to Fe(III) by the radical cation of perylene is ~0.29 V based on $E^{\circ'}$ values of 1.49 V (PDI^{••/0}) and 1.2 V (Fe^{III/II}) vs NHE.

Ultrafast time-resolved absorption measurements from 430–800 nm were carried out following 425 nm excitation of TiO₂-1 and TiO₂-2 in aqueous 0.1 M HClO₄. As shown by the results for TiO₂-1 in Figure 2A, at 430 fs, a bleach is observed at 490 nm corresponding to the PDI absorption maximum near 500 nm. An additional, broad absorption feature appears at wavelengths beyond ~550 nm. It arises from excitation of a PDI---PDI pair to give a (PDI---PDI)* exciplex or, given the reactivity behavior described below, an overlap in $\pi \rightarrow \pi^*$ absorptions for a PDI^{•+},PDI^{•-} redox separated (RS) state, eq 1.^{4–8,11,63,72} The latter is supported by the absence of evidence for stimulated emission.

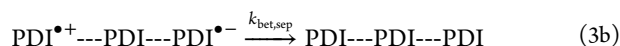
The initial spectral shape following excitation (<10 ps) evolves rapidly to the final exciplex or RS state (Figure S4) due to a structural rearrangement or, perhaps, due to evolution from an initially formed excited state distinct from the exciplex or RS state. As noted above, there is clear evidence in the visible ground-state spectrum for PDI---PDI π -stacking as shown by spectral broadening and the modified vibronic structure for the PDI $\pi \rightarrow \pi^*$ absorptions consistent with excitonic, partially delocalized excitation.⁷³

$$\text{PDI} \cdots \text{PDI} \xrightarrow{h\nu} \text{PDI}^{\bullet-} \cdots \text{PDI}^{\bullet+}(\text{RS}) \xrightarrow{k_{\text{bet}}} \text{PDI} \cdots \text{PDI} \quad (1)$$

As shown in Figure 2C, following 425 nm excitation, decay of both the bleach and positive absorption features occurs simultaneously over three distinct time domains. The kinetics observed at 650 nm were fit to the triexponential decay function in eq 2 with $\tau_1 = 0.8$ ps, $\tau_2 = 15$ ps, and $\tau_3 = 1500$ ps with $A_1 = 0.64$, $A_2 = 0.23$, and $A_3 = 0.13$.

$$I = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} \quad (2)$$

The decay kinetics are complex resulting from multiple relaxation pathways. The rapid, 0.8 ps, dominant (64%) component could arise from a number of processes including structural rearrangement, excited-state evolution, or back electron transfer between $\text{PDI}^{+\bullet}\cdots\text{PDI}^{-\bullet}$ geminate pairs as shown in [eq 1](#). The slower components presumably arise from back electron transfer between nongeminate, PDI-separated radical cation–radical anion pairs formed by rapid hole or electron hopping away from the initial site of excitation, [eq 3a](#), followed by slower back electron transfer, [eq 3b](#) ($k_{\text{bet,sep}}$). In 1D columnar structures formed in solutions of PDI with zinc porphyrin, Zn(Por), traps are known to undergo facile, intrastrand electron transfer with redox separation rates to the porphyrin following excitation of $(0.71 \text{ ps})^{-1}$.⁶³

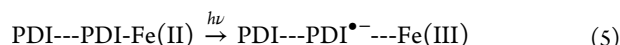
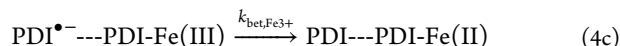
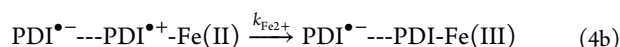
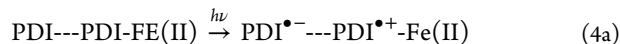


In the kinetic data, there is no evidence for injection into the nanocrystalline TiO₂ substrate by PDI^{0/•-} even though it is relatively strongly reducing with $E^{\circ'} = -0.71$ V vs NHE in CHCl₃ for the PDI^{0/•-} couple with $E_{\text{cb}} \sim -0.1$ V vs NHE at pH 1 for the TiO₂ conduction band.⁷⁴ As for electrochemical oxidation of PDI, the absence of injection may be due to the inability of the π -stacked films to achieve charge balance by rapid ion migration, perhaps with a role for disorder and redox trapping within the films. It is also possible that the driving force for photoinjection may be smaller than expected because the $E^{\circ'}$ estimate obtained from the solution-based analogue of **1** in CHCl₃ may be significantly different than the true $E^{\circ'}$ value for the perylene portion of assemblies **1** and **2** on TiO₂ in aqueous 0.1 M HClO₄.

Following 425 nm photoexcitation of $\text{TiO}_2\text{-2}$ in 0.1 M HClO_4 , the rapid initial spectral evolution described above for $\text{TiO}_2\text{-1}$ was observed. It was followed by spectral changes consistent with capture of the oxidative equivalent in the initially formed $\text{PDI}^{\bullet+}\text{---PDI}^{\bullet-}$ pair by electron transfer from the Fe(II) complex, [Figure 2](#). The Fe(II) complex is exposed to the external solution and is electroactive. At 430 fs following excitation, the initial $\text{PDI}^{\bullet+}$ bleach feature at ~ 500 nm appears in the transient absorption difference followed by the appearance of a second bleach feature arising from loss of the Fe(II) MLCT absorption at 575 nm. Its appearance is accompanied by a loss in $\text{PDI}^{\bullet+}$ absorbance on the high-energy side of the 650 nm $\text{PDI}^{\bullet+}$, $\text{PDI}^{\bullet-}$ absorption band on the same time scale. The Fe(II) bleach and loss of the $\text{PDI}^{\bullet+}$ absorbance are enhanced over time at the expense of the $\text{PDI}^{\bullet+}$ bleach feature. Absorbance changes with time for both exhibit complex kinetics with the Fe(II) bleach feature most prominent by ~ 25 ps and diminished to half intensity by 1.2 ns. Direct excitation of the Fe(II) complex at 425 nm was apparently minimal given

the absence of a prominent Fe MLCT bleach at the earliest observation time.

These observations and literature precedents^{72,73,75} are consistent with excitation to give the $\text{PDI}^{\bullet+}, \text{PDI}^{\bullet-}$ redox pair in **eq 1**, followed by electron-transfer oxidation of chemically linked Fe(II) by $\text{PDI}^{\bullet+}$, **eq 4a**, to give $\text{PDI}^{\bullet-} \cdots \text{PDI-Fe(III)}$, **eq 4b**. The absence of Fe(III) at the first observation time following excitation precludes direct, light-driven oxidation by charge transfer to PDI, **eq 5**.



Following the initial transient spectral changes, back electron transfer between $\text{PDI}^{\bullet-}$ and Fe(III) is relatively slow, eq 4c, occurring with complex kinetics which extend past 400 μs (data not shown). Similar recombination kinetics on the microsecond time scale are observed for **1**. Electron recombination in room-temperature, aqueous solution PDI, Zn(Por) 1D structures, $\text{PDI}^{\bullet-}\text{---Zn(Por)}^{\bullet+} \rightarrow \text{PDI---Zn(Por)}$, is biphasic with ultrafast, $k_{\text{CR1}} = (5.0 \text{ ps})^{-1}$, and nanosecond, $k_{\text{CR2}} = (2200 \text{ ps})^{-1}$, components.⁶³ For an adsorbed PDI derivative on WO_3 ,⁷⁶ back electron transfer from $\text{WO}_3(\text{e}^-)$ to $\text{PDI}^{+\bullet}$ is also slow, occurring on the microsecond time scale perhaps because of a disordered structure with the oxidative and reductive equivalents at spatially separated trap sites.

Our results point to a general strategy for stepwise assembly of molecular components directly on nanocrystalline oxide interfaces where ultrafast formation of surface-bound $\text{PDI}^{\bullet-}$ --- $\text{PDI}^{\bullet+}$ pairs occurs following visible excitation into the broadened π, π^* manifold of the dye. The transient absorption results with an added, external Fe(II) hole trap provide evidence for a relatively rich photodriven reactivity in perylene assemblies on TiO_2 in 0.1 M HClO_4 despite the apparent lack of photoinjection. Oxidative equivalents are delivered rapidly to chemically linked Fe(II) leading to formation of $-(\text{NHtpy})\text{-Fe}^{\text{III}}(\text{tpy-PhNH}_3)]^{4+}$ on the periphery. There is evidence for π -stacking in the films and a resistance to oxidation or reduction of PDI, presumably due to inhibited counterion equilibration.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcclett.5b02194.

Chemical structures of $\text{Fe}^{\text{II}}(\text{tpy-PhNH}_2)_2$ and solubilized PDI derivatives, UV–visible absorption spectrum for $\text{Fe}^{\text{II}}(\text{tpy-PhNH}_2)_2$ in CH_3CN , and normalized transient absorption spectra ([PDF](#))

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Notes

The authors declare no competing financial interest.

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