

## Combining Light-Harvesting and Charge Separation in a Self-Assembled Artificial Photosynthetic System Based on Perylene-3,4,9,10-bis(dicarboximide) Chromophores

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The development of efficient artificial systems for solar energy conversion is important for sustainable energy utilization. Natural photosynthesis relies upon noncovalent interactions between similar chromophores to regulate energy and electron flow, while most artificial antenna arrays and reaction centers employ chemically distinct, covalently linked chromophores and redox cofactors.<sup>1–6</sup> Self-assembly of chromophores at specific distances and orientations to provide particular photophysical or redox functions is critical in both antenna and reaction center proteins and is especially important in producing the special pair primary electron donor.<sup>7,8</sup> Here we show that self-assembly of a covalent antenna array into a larger structure, in turn, induces formation of a functional special pair that undergoes internal charge separation.

We recently reported on a green chromophore, 1,7-bis(pyrrolidin-1-yl)perylene-3,4:9,10-bis(dicarboximide) (5PDI), that has photophysical and redox properties strongly analogous to those of chlorophyll *a*.<sup>9</sup> When two 5PDI chromophores are constrained to a cofacial geometry by attachment of one imide nitrogen atom of each 5PDI to the 4 and 5 positions of a xanthene spacer (*cof*-5PDI<sub>2</sub>), photoexcitation of the dimer in toluene results in quantitative electron transfer from one 5PDI to the adjacent 5PDI in 170 fs because of symmetry breaking in its lowest excited singlet state.<sup>10</sup> On the other hand, 5PDI monomers show no tendency to self-assemble into dimers in toluene.<sup>9</sup> Importantly, the observed symmetry breaking in the lowest excited singlet state of *cof*-5PDI<sub>2</sub> is very similar to that proposed to occur within the photoexcited special pair donor in photosynthetic reaction centers, which results in significant intradimer charge-transfer character.<sup>11,12</sup> We now show that a self-assembling antenna reaction-center array can be prepared by decorating 5PDI with four 1,7-(3',5'-di-*tert*-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (PDI) molecules to give compound **1** (Figure 1; see Supporting Information). This is due to the propensity of PDI molecules to self-assemble into cofacially stacked arrays (H-aggregates).<sup>13,14</sup>

Compound **1** is very stable: it does not show any decomposition upon weeks-long exposure to air and/or room lights, in both the solid state and solution. It was characterized by mass spectrometry, UV–vis spectroscopy, <sup>1</sup>H NMR, and gel permeation chromatography (GPC). The UV–vis absorption of **1** covers the entire visible spectrum (Figure 2A). Cofacial aggregation of **1** in toluene is revealed by the characteristic enhancement of the 0–1 electronic absorption bands of both PDI and 5PDI,<sup>10,13,15</sup> 510 and 640 nm, respectively, due to exciton interactions between the stacked chromophores.<sup>16</sup> Compound **1** is largely disaggregated in chloroform at low concentrations (<10<sup>−4</sup> M) (Figure 2A). GPC on toluene and THF solutions of **1** indicates that dimers of **1** are the dominant species. <sup>1</sup>H NMR shows that the aromatic resonances of 5PDI–PDI<sub>4</sub> in toluene-*d*<sub>8</sub> are shifted upfield by 0.1–0.2 ppm relative to typical resonances of monomeric PDI and 5PDI.<sup>9</sup> Moreover, the chemical shifts and the shape of the PDI aromatic resonances of **1**

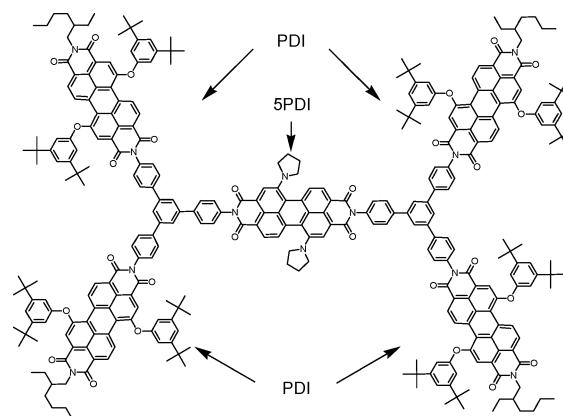


Figure 1. Structure of compound **1**, 5PDI–PDI<sub>4</sub>.

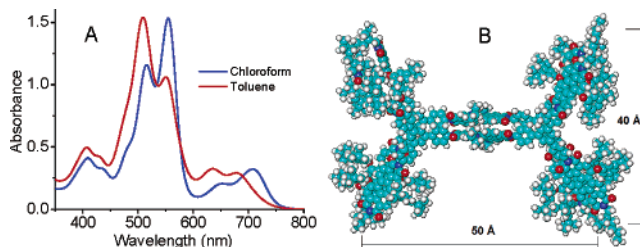
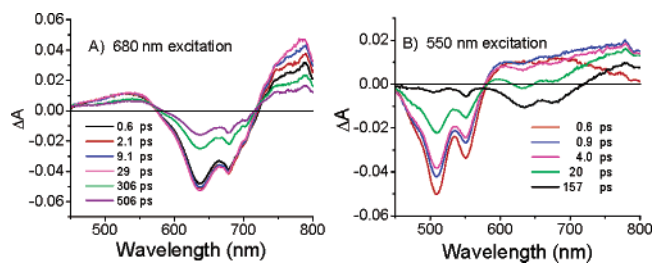


Figure 2. (A) UV–vis spectra of **1**. (B) Structure of (5PDI–PDI<sub>4</sub>)<sub>2</sub> that best fits the SAXS data in toluene.

in toluene-*d*<sub>8</sub> are independent of concentration in the range 6 × 10<sup>−5</sup> to 1 × 10<sup>−3</sup> M, which is consistent with the dominance of a single species.<sup>17,18</sup>

To elucidate the aggregate structure, we performed small-angle X-ray scattering (SAXS) measurements on 10<sup>−4</sup> to 10<sup>−5</sup> M toluene solutions of **1** using a high-flux synchrotron source (Advanced Photon Source at Argonne National Laboratory). Guinier analysis<sup>19,20</sup> (Figure S8) reveals that **1** forms aggregates that are essentially monodisperse (linear Guinier plot) with a radius of gyration, *R*<sub>g</sub> = 18.0 Å. The analysis of the scattering data using both a pair distance distribution function and a simulated annealing procedure<sup>20</sup> (Figures S9–S11) shows that the dimensions of 5PDI–PDI<sub>4</sub> aggregates are approximately 50 × 40 × 7 Å<sup>3</sup> and their shape can be fit to the overall twofold symmetry of the 5PDI–PDI<sub>4</sub> structure. The dimensions and shape of the reconstructed aggregate (see Supporting Information) confirm that a cofacially stacked 5PDI–PDI<sub>4</sub> dimer is the best fit to the experimental data in toluene (Figure 2B).

Femtosecond transient absorption spectroscopy is used to probe the photophysics of self-assembled (5PDI–PDI<sub>4</sub>)<sub>2</sub> at 10<sup>−5</sup> M in toluene. Selective excitation of (5PDI)<sub>2</sub> with a 680-nm, 100-fs laser pulse results in the appearance of a positive spectral feature at 750–800 nm in the transient absorption spectrum of (5PDI–PDI<sub>4</sub>)<sub>2</sub>



**Figure 3.** Transient absorption spectra of **1** in toluene.

(Figure 3A). The rise and decay of this band occur with  $\tau = 7$  and 420 ps, respectively, the decay time being identical to the recovery of the ground state bleach at 640 nm. Both time constants are significantly shorter than the  $\tau = 4.5$  ns lifetime of  $^1\text{5PDI}$ .<sup>9</sup> Both the transient spectra and kinetics of  $(\text{5PDI-PDI}_4)_2$  in toluene are very similar to those observed for *cof*- $5\text{PDI}_2$ .<sup>10</sup> Specifically, the transient absorption spectra in Figure 3A are assigned to  $5\text{PDI}^{*+} - 5\text{PDI}^{*-}$  on the basis of spectroelectrochemical data obtained for each ion,<sup>10</sup> while the charge separation ( $\tau_{\text{CS}} = 7$  ps) and charge recombination ( $\tau_{\text{CR}} = 420$  ps) time constants for  $(\text{5PDI})_2$  within  $(\text{5PDI-PDI}_4)_2$  are somewhat longer than those observed earlier for *cof*- $5\text{PDI}_2$  ( $\tau_{\text{CS}} = 0.17$  ps,  $\tau_{\text{CR}} = 220$  ps). This may be attributed to a slightly different geometry of the cofacial 5PDI pair in  $(\text{5PDI-PDI}_4)_2$  vs that present in *cof*- $5\text{PDI}_2$ . Electron transfer from  $(\text{5PDI})_2$  to PDI or  $(\text{PDI})_2$  does not take place, as the spectroscopic features due to both  $\text{PDI}^{*-}$  and  $(\text{PDI})_2^{*-}$  (700–750 nm)<sup>13,21</sup> as well as the bleach due to ground-state depletion of PDI or  $(\text{PDI})_2$  were not observed.

Energy transfer from  $(\text{PDI})_2$  to  $(\text{5PDI})_2$  is demonstrated by selective excitation of  $(\text{5PDI-PDI}_4)_2$  with 550-nm, 100-fs laser pulses, which results in the immediate bleach of the 510-nm absorption band of  $(\text{PDI})_2$  followed by recovery of this bleach with  $\tau = 21$  ps, while the  $(\text{5PDI})_2$  ground-state absorption at 640–680 nm bleaches with  $\tau = 21$  ps (Figure 3B). Given that the lifetime of  $^1(\text{PDI})_2$   $\tau_{\text{F}} = 23$  ns,<sup>14</sup> the energy transfer efficiency  $\phi = \tau_{\text{F}}/(\tau_{\text{F}} + \tau) \cong 1$ . The residual longer-lived PDI species observed at  $t = 157$  ps is most likely due to a small amount of residual  $\text{PDI}_4$ - $5\text{PDI}$  monomer that is present in equilibrium with the dimer. Energy transfer from PDI to 5PDI within the monomer is slower than that in the dimer because of poorer Förster overlap in the monomer. Efficient singlet-singlet energy transfer from  $(\text{PDI})_2$  to  $(\text{5PDI})_2$  within  $(\text{5PDI-PDI}_4)_2$  is expected because of the lower energy of  $^1(\text{5PDI})_2$  relative to that of  $^1(\text{PDI})_2$ , as well as the significant overlap of the  $(\text{PDI})_2$  fluorescence<sup>14</sup> and  $(\text{5PDI})_2$  absorption bands.<sup>10</sup> Following energy transfer from  $^1(\text{PDI})_2$  to  $(\text{5PDI})_2$ , the bleach at 640–690 nm and the positive absorption change at 750–800 nm both decay with  $\tau = 420$  ps, matching the charge recombination time constant observed when  $(\text{5PDI})_2$  in  $(\text{5PDI-PDI}_4)_2$  is directly excited at 680 nm. Thus, both the transient spectra and kinetics following energy transfer show that electron transfer occurs within  $(\text{5PDI})_2$  to yield  $5\text{PDI}^{*+} - 5\text{PDI}^{*-}$ . Photoexcitation at shorter wavelengths (e.g., 400 nm, see Supporting Information) also leads to quantitative electron transfer within  $(\text{5PDI})_2$ . Thus, the PDI chromophore not only serves to enforce self-assembly of the system by  $\pi$ -stacking, but also performs the role of the light-harvesting antenna, funneling energy toward the lower energy 5PDI core.

The quantitative electron transfer observed between the two 5PDI molecules in  $(\text{5PDI-PDI}_4)_2$  is a function of their close proximity in the self-assembled dimer. At low concentrations in chloroform, compound **1** is largely disaggregated. Under these conditions, the concentration is too low for accurate transient absorption measurements, and therefore time-resolved fluorescence spectroscopy is used to determine whether the lifetime of 5PDI is shortened because

of competitive electron transfer. A  $10^{-5}$  M chloroform solution of **1** exhibits strong fluorescence from 5PDI having a 4.5-ns lifetime, similar to that of monomeric 5PDI,<sup>9</sup> while fluorescence from a  $10^{-5}$  M solution of **1** in toluene is strongly quenched. The monomeric 5PDI fluorescence observed in chloroform rules out a significant electron transfer pathway in that solvent. As a whole, the data strongly support the idea that a preformed 5PDI dimer is necessary for electron transfer to occur.

Thus,  $(\text{5PDI-PDI}_4)_2$  mimics the primary events occurring in the photosynthetic reaction center: efficient energy capture due to the excellent spectral coverage, energy funneling toward the electron transferring core unit, and, finally, excited-state symmetry breaking resulting in ultrafast charge separation, which is a property of placing two identical 5PDI molecules next to one another to form a special pair structure. The ability to self-assemble identical or very similar chromophores, demonstrating energy funneling and electron transfer, can greatly simplify the design of an artificial reaction center. Research aimed at the incorporation of  $(\text{5PDI-PDI}_4)_2$  into larger self-assembling ordered arrays is currently underway.

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**Supporting Information Available:** Experimental details, including synthesis, SAXS, and photophysical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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