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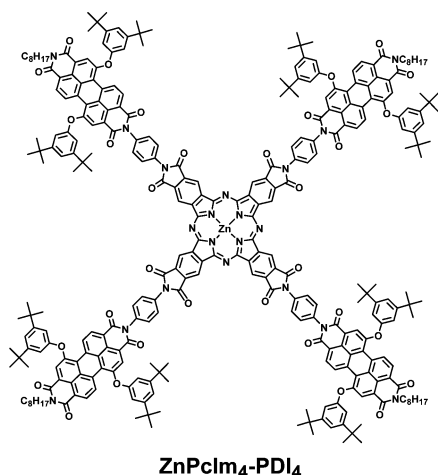
Ultrafast Aggregate-to-Aggregate Energy Transfer within Self-assembled Light-Harvesting Columns of Zinc Phthalocyanine Tetrakis(Perylene-3,4,9,10-bis(dicarboximide))

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Light harvesting in photosynthetic antenna proteins involves a series of highly efficient ultrafast energy transfers between spectroscopically different populations of chlorophylls.^{1,2} Several strategies have been employed to mimic this natural energy transfer process, including polymers,³ dendrimers,⁴ and porphyrin arrays linked by covalent bonds^{5,6} or by self-assembly.^{7–10} In all of these systems, excitation energy transfer occurs from one molecule to another, while very few of them involve energy or electron transfer from one very strongly interacting chromophore aggregate to another such aggregate.^{11,12} Phthalocyanines are known to have significant π – π interactions and form H aggregates easily.^{13,14} Here we report a covalent zinc phthalocyanine perylene-3,4,9,10-bis(dicarboximide) derivative (ZnPcIm₄–PDI₄) in which the individual molecules self-assemble into long fibrous structures in which the ZnPcIm₄ and PDI molecules both stack in register with the same components in an adjacent covalent building block. In this light-harvesting system ultrafast energy transfer occurs from the aggregated peripheral PDI chromophores to the core ZnPcIm₄ aggregate followed by exciton migration between ZnPcIm₄ chromophores with times approaching 100 fs.



ZnPcIm₄–PDI₄ was prepared by refluxing phthalocyanine-2,3,9,10,16,17,23,24-octacarboxytetraanhydride^{15,16} with *N*-octyl-*N'*-(4-aminophenyl)-1,7(3',5'-di-*tert*-butylphenoxy)perylene-3,4:9,10-bis-(dicarboximide)⁹ in pyridine for 48 h followed by chromatographic purification on silica gel and size exclusion columns. The corresponding ZnPcIm₄ reference molecule is terminated by *n*-octyl groups on its imides. The MALDI-TOF mass spectrum of ZnPcIm₄–PDI₄ shows peaks at multiples of the $m/z = 4795$ parent ion up to 33565, which are assemblies of seven molecules. This spectrum provides direct evidence for the strong tendency of ZnPcIm₄–PDI₄ to aggregate.

Face-to-face aggregation of ZnPcIm₄–PDI₄ is evidenced by its electronic absorption spectra, Figure 1. The spectra show that the

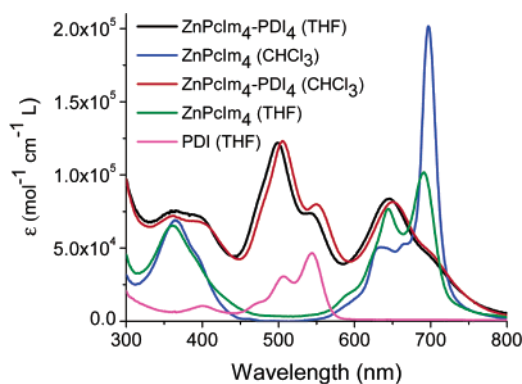


Figure 1. UV–vis absorption spectra.

aggregated molecule absorbs strongly from 300 to 700 nm, making it an ideal system to harvest polychromatic light. The absorption spectra in both THF and CHCl₃ show two broad bands near 500 and 645 nm due to PDI and ZnPcIm₄, respectively, which are both strongly blue-shifted relative to those of the corresponding monomers. Positioning the transition dipoles of two identical chromophores in a parallel, stacked geometry results in exciton coupling of the two transition dipoles causing the lowest-energy electronic transition of the dimer to split into two bands, with the higher-energy band having enhanced oscillator strength.¹⁷ Our previous studies^{9,18} and those of others^{19,20} have revealed that PDI readily forms H-aggregates. The broad band near 645 nm is also characteristic of zinc phthalocyanine H-aggregates.¹⁵ Thus, the electronic absorption spectra strongly support a stacked structure.

To estimate the ZnPcIm₄–PDI₄ aggregate size and shape in solution we performed small-angle X-ray scattering (SAXS) measurements in THF (6×10^{-4} M) using a high-flux synchrotron source, see Supporting Information. Guinier analysis,²¹ Figure S3, reveals that ZnPcIm₄–PDI₄ forms monodisperse aggregates in THF (linear Guinier plot) with a radius of gyration $R_g = 21.1$ Å. The monodisperse character of the ZnPcIm₄–PDI₄ aggregates in THF allows an analysis of the scattering data using a pair distance distribution function (PDF) and a simulated annealing procedure.²² These methodologies show that the SAXS data is best fit to a stack of seven cofacial ZnPcIm₄–PDI₄ molecules with overall dimensions of 6 nm \times 6 nm \times 3 nm, Figure 2, see also Supporting Information.

As the concentration of ZnPcIm₄–PDI₄ is increased, the cylindrical stacks grow to form long fibers. The TEM image, Figure 3, of ZnPcIm₄–PDI₄ shows fibers longer than 1 μ m with different diameters. The smallest discernible fiber diameter in the image is about 5 nm, as indicated by the arrow, which is about the width of a single ZnPcIm₄–PDI₄ molecule. These fibers also form ropes, some of which have helical twists, as can be seen just right of center in the image.

The fluorescence from H-aggregates of zinc phthalocyanine is strongly quenched,¹⁴ while H-aggregates of PDI exhibit an excimer-

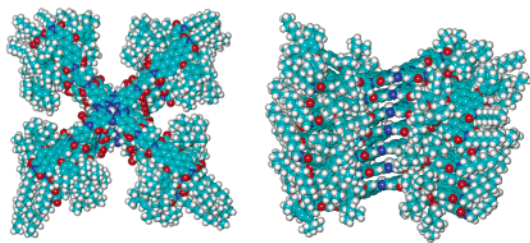


Figure 2. Best fit structure of $(\text{ZnPcIm}_4\text{-PDI}_4)_7$ aggregates from modeling the SAXS data. (Left): Top view. (Right): Side view.

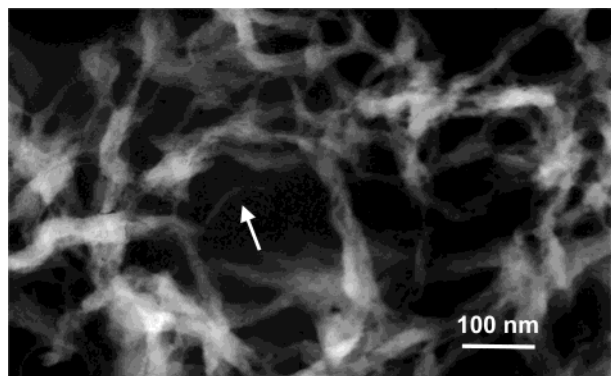


Figure 3. TEM image of $(\text{ZnPcIm}_4\text{-PDI}_4)_n$ aggregates deposited from an *n*-pentanol suspension.

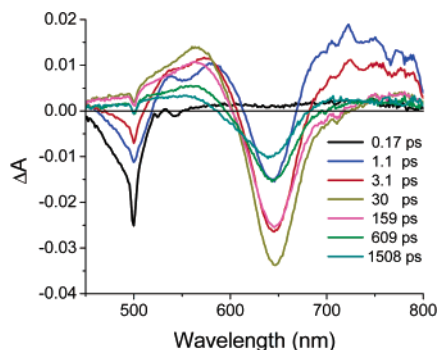


Figure 4. Transient absorption spectra of $(\text{ZnPcIm}_4\text{-PDI}_4)_7$ in THF.

like emission near 700 nm with quantum yields of 15–30%.¹⁸ When $(\text{PDI})_7$ within $(\text{ZnPcIm}_4\text{-PDI}_4)_7$ is selectively excited at 500 nm, where the absorbance of $(\text{ZnPcIm}_4)_7$ is very small, there is no emission from $(\text{PDI})_7$. This implies that the excimer-like emission of $(\text{PDI})_7$ is quenched by $(\text{ZnPcIm}_4)_7$. PDI has a reversible one-electron reduction potential of -0.53 V vs SCE,⁹ while ZnPcIm_4 undergoes one-electron reduction at -0.45 V vs SCE and does not oxidize at potentials < 1.5 V vs SCE. Thus, both PDI and ZnPcIm_4 are very good electron acceptors, so that photoinduced electron transfer between ZnPcIm_4 and PDI is thermodynamically unfavorable. When $(\text{ZnPcIm}_4\text{-PDI}_4)_7$ is excited with a 100-fs, 500-nm laser pulse, the bleach of the 500-nm ground-state absorption band of $(\text{PDI})_7$ occurs with the laser flash due to the selective formation of $^1*(\text{PDI})_7$. The decay of $^1*(\text{PDI})_7$ occurs with $\tau = 1.3$ ps as indicated by the recovery of the bleach at 500 nm, Figure 4, and is accompanied by the bleach of the 645-nm ground-state absorption band of $(\text{ZnPcIm}_4)_7$ with $\tau = 1.3$ ps due to the formation of $^1*(\text{ZnPcIm}_4)_7$. The fact that the time constants for the decay of $^1*(\text{PDI})_7$ and the formation of $^1*(\text{ZnPcIm}_4)_7$ are the same indicates that energy transfer from $^1*(\text{PDI})_7$ to $(\text{ZnPcIm}_4)_7$ within $(\text{ZnPcIm}_4\text{-PDI}_4)_7$ is quantitative. The lifetime of the lowest-excited singlet state of monomeric ZnPcIm_4 (in CHCl_3) is 2.5 ns, see Supporting Information. However, the decay of $^1*(\text{ZnPcIm}_4)_7$ within

$(\text{ZnPcIm}_4\text{-PDI}_4)_7$ is biexponential with $\tau = 1.1$ ps (0.5) and 260 ps (0.5). The residual bleach at 645 nm and the small positive absorption features at $\lambda > 750$ nm at long times are due to formation of $^3*\text{ZnPcIm}_4$. The amplitude of the 1.1-ps component is laser power dependent and is due to singlet–singlet annihilation,¹⁸ while the 260-ps component is characteristic of aggregated Zn phthalocyanines²³ as well as our ZnPcIm_4 reference, see Supporting Information. The annihilation lifetime, τ_a , can be used to estimate the exciton hopping time between ZnPcIm_4 sites within the $(\text{ZnPcIm}_4\text{-PDI}_4)_7$ aggregate. Assuming random hopping between equally spaced nearest neighbors on a linear chain, $\tau_a = N(N-1)\tau_{\text{hop}}/6$, where N is the number of sites and τ_{hop} is the exciton lifetime at each site.²⁴ Using this model, if $\tau_a = 1.1$ ps and $N = 7$, then $\tau_{\text{hop}} = 160$ fs. A comparison between τ_{hop} and the 260-ps exciton lifetime implies that energy transfer can occur through large $\text{ZnPcIm}_4\text{-PDI}_4$ aggregates before significant excited-state decay occurs.

Our results suggest that large artificial light-harvesting systems can be achieved by self-assembly of $\text{ZnPcIm}_4\text{-PDI}_4$ building blocks.

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Supporting Information Available: Synthetic and spectroscopic details. This material is available free of charge via the Internet at <http://www.pubs.acs.org>

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