

## Self-Assembly Strategies for Integrating Light Harvesting and Charge Separation in Artificial Photosynthetic Systems

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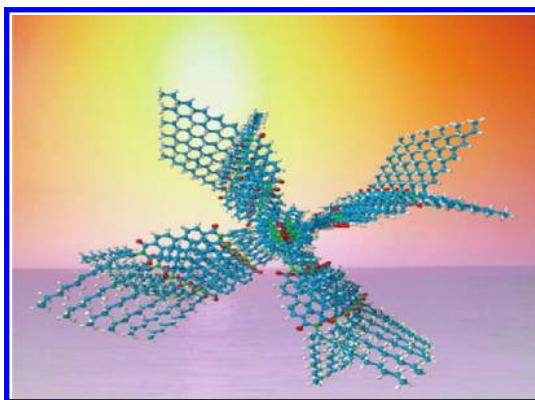
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### CON SPECTUS

In natural photosynthesis, organisms optimize solar energy conversion through organized assemblies of photofunctional chromophores and catalysts within proteins that provide specifically tailored environments for chemical reactions. As with their natural counterparts, artificial photosynthetic systems for practical solar fuels production must collect light energy, separate charge, and transport charge to catalytic sites where multielectron redox processes will occur. While encouraging progress has been made on each aspect of this complex problem, researchers have not yet developed self-ordering and self-assembling components and the tailored environments necessary to realize a fully-functional artificial system.

Previously researchers have used complex, covalent molecular systems comprised of chromophores, electron donors, and electron acceptors to mimic both the light-harvesting and the charge separation functions of photosynthetic proteins. These systems allow for study of the dependencies of electron transfer rate constants on donor–acceptor distance and orientation, electronic interaction, and the free energy of the reaction. The most useful and informative systems are those in which structural constraints control both the distance and the orientation between the electron donors and acceptors. Self-assembly provides a facile means for organizing large numbers of molecules into supramolecular structures that can bridge length scales from nanometers to macroscopic dimensions. The resulting structures must provide pathways for migration of light excitation energy among antenna chromophores, and from antennas to reaction centers. They also must incorporate charge conduits, that is, molecular “wires” that can efficiently move electrons and holes between reaction centers and catalytic sites. The central scientific challenge is to develop small, functional building blocks with a minimum number of covalent linkages, which also have the appropriate molecular recognition properties to facilitate self-assembly of complete, functional artificial photosynthetic systems. In this Account, we explore how self-assembly strategies involving  $\pi$ -stacking can be used to integrate light harvesting with charge separation and transport.

Our current strategy uses covalent building blocks based on chemically robust arylene imide and diimide dyes, biomimetic porphyrins, and chlorophylls. We take advantage of the shapes, sizes, and intermolecular interactions—such as  $\pi$ – $\pi$  and/or metal–ligand interactions—of these molecules to direct the formation of supramolecular structures having enhanced energy capture and charge-transport properties. We use small- and wide-angle X-ray scattering (SAXS/WAXS) from a synchrotron source to elucidate the solution phase structures of these monodisperse noncovalent aggregates. We expect that a greater understanding of self-assembly using  $\pi$ -stacking and molecular designs that combine those features with hydrogen bonding and metal–ligand bonding could simplify the structure of the building blocks for artificial photosynthetic complexes, while retaining their ability to assemble complex, photofunctional structures.



### Introduction

Photosynthetic antenna and reaction center proteins serve as important models for developing

synthetic light harvesting and photochemical charge separation systems.<sup>1,2</sup> A critical step toward integrated artificial photosynthetic systems

is the ability to create large ordered arrays of interactive molecules. Covalent syntheses of large molecular arrays are highly inefficient and costly, thus making self-assembly the method of choice to achieve ordered architectures from functional building blocks. Achieving a functional integrated artificial photosynthetic system requires hierarchical organization at both the molecular and supramolecular level. Covalent synthesis of functional building blocks with well-defined molecular geometries and donor–acceptor distances allows precise control over energy and electron transfer. This is required for the first steps of solar energy conversion because the excited states and initially formed, charge-separated states are thermodynamically and kinetically prone to reactions that convert the stored solar energy to useless heat. Self-assembly, or supramolecular organization, on the other hand, provides a facile mechanism for assembling large numbers of molecules into structures that can bridge length scales from nanometers to macroscopic dimensions. It can also lead to synergistic and *emergent* properties that are not intrinsic to the building blocks themselves.

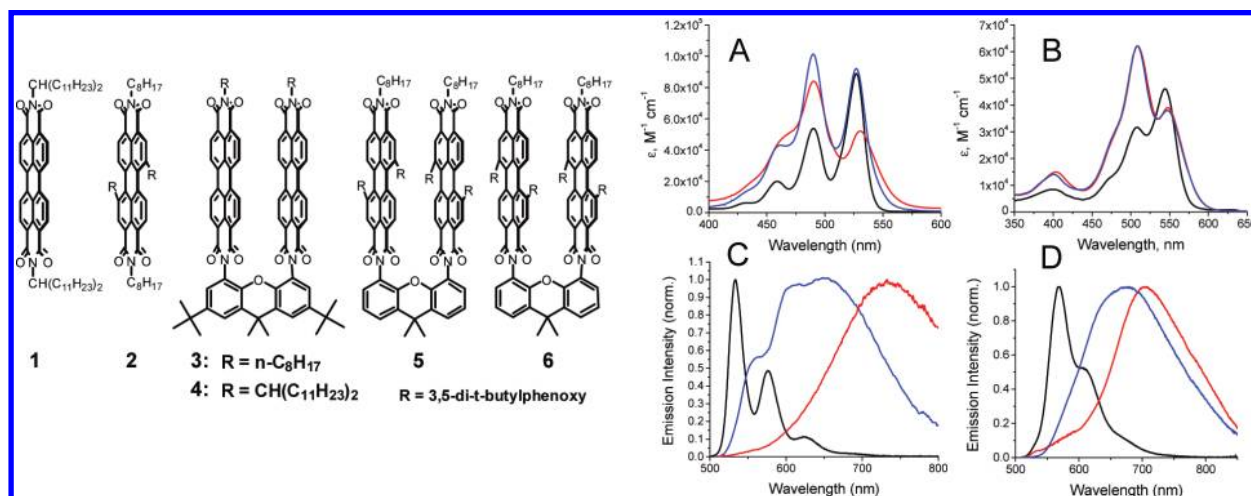
Our current strategy uses covalent building blocks based on chemically robust arylene imide and diimide dyes, as well as biomimetic porphyrins and chlorophylls with particular shapes, sizes, and intermolecular interactions, such as  $\pi$ – $\pi$  and or metal–ligand interactions, to direct the formation of supramolecular structures having enhanced energy capture and charge transport properties. For example, perylene-3,4:9,10-bis(dicarboximide) (PDI, **1** and **2**) and its derivatives have attracted significant interest as active materials for light harvesting,<sup>3</sup> photovoltaics,<sup>4–6</sup> and studies of basic photoinduced charge and energy transfer processes.<sup>7,8</sup> PDI is both photochemically and thermally stable<sup>9</sup> and can be easily modified at its imide nitrogens, as well as at its 1, 6, 7, and 12 “bay” positions. Modifications at these positions tune the electronic properties of PDI resulting in derivatives that absorb light from the near-ultraviolet to the near-infrared region of the spectrum. Moreover, the redox potentials of PDI can be tuned by appropriate substituents resulting in derivatives that are either good electron acceptors<sup>10</sup> or donors.<sup>11</sup> PDI also demonstrates the ability to self-assemble in solution via hydrophobic/hydrophilic interactions as well as by  $\pi$ – $\pi$  stacking.<sup>12</sup>

In studies of supramolecular assemblies in solution, it is important to establish direct relationships between structure and observed function. It has been recently demonstrated that small- and wide-angle X-ray scattering (SAXS/WAXS) from monodisperse noncovalent aggregates using a synchrotron source is a powerful tool for the elucidation of their solution-

phase structures.<sup>13–17</sup> We have used the Advanced Photon Source at Argonne National Laboratory to determine the *solution* structures of supramolecular assemblies at concentrations typical of optical and EPR spectroscopic measurements used to characterize their function. Guinier analysis of the scattering data provides at a minimum the radius of gyration of the complex,  $R_g$ , an estimate of its molecular weight (provided appropriate standards are available), and more importantly, a gauge of the polydispersity of the aggregates.<sup>18,19</sup> In favorable cases, if the assemblies are nearly monodisperse, further analysis of the SAXS/WAXS data using atomic pair distance distribution functions (PDFs) and simulated annealing procedures can be performed to obtain structures in solution with a resolution approaching 2–3 Å for molecular weights up to about 50 kD.<sup>19</sup> For example, using these techniques we have previously obtained structures of complex oligomeric arylene diimide assemblies having molecular weights up to 28 kD.<sup>15–17,20</sup> New computational approaches allow SAXS/WAXS data to be interpreted in terms of coordinate models<sup>13,14,21</sup> and molecular dynamics simulations<sup>22,23</sup> and can be used to refine the structures of self-assembled systems.<sup>24</sup>

## Photophysical Consequences of Self-Assembly

The photophysical properties of molecules containing multiple identical chromophores are strongly dependent on the relative orientation and distance between the adjacent chromophores. The zero-order molecular exciton model<sup>25</sup> predicts that coupling of the transition dipole moments creates two new exciton states. For cofacially stacked chromophores having parallel transition moments (*H*-aggregates) the transition from the ground state to the higher energy exciton state is fully allowed, while the transition to the lower exciton state is forbidden. Extension of this model to include vibronic coupling modifies the selection rules for the zero-order exciton states.<sup>26–31</sup> These points are illustrated by comparing the photophysics of PDI monomers **1** and **2** to a series of covalent, cofacially oriented,  $\pi$ -stacked PDI dimers, **3–6** (Figure 1).<sup>32</sup> Since the transition dipole of PDI lies along its N–N axis,<sup>33</sup> and the transition dipoles of the PDI molecules are near parallel in these dimers, the exciton models that include vibronic coupling predict the selective enhancement observed in the 0–1 vibronic bands for these dimers (Figure 1A,B). On the other hand, **3–6** display emission spectra that are significantly red-shifted relative to those of monomers **1** and **2** (Figure 1C,D). These excimer-like spectra are indicative of significant electronic coupling between the  $\pi$  systems of the adjacent PDI



**FIGURE 1.** Chemical structures of **1–6**. Absorption spectra in  $\text{CHCl}_3$  of (A) **1** (black), **3** (red), and **4** (blue); (B) **2** (black), **5** (red), and **6** (blue). Emission spectra in  $\text{CHCl}_3$  of (C) **1** (black), **3** (red), and **4** (blue); (D) **2** (black), **5** (red), and **6** (blue).

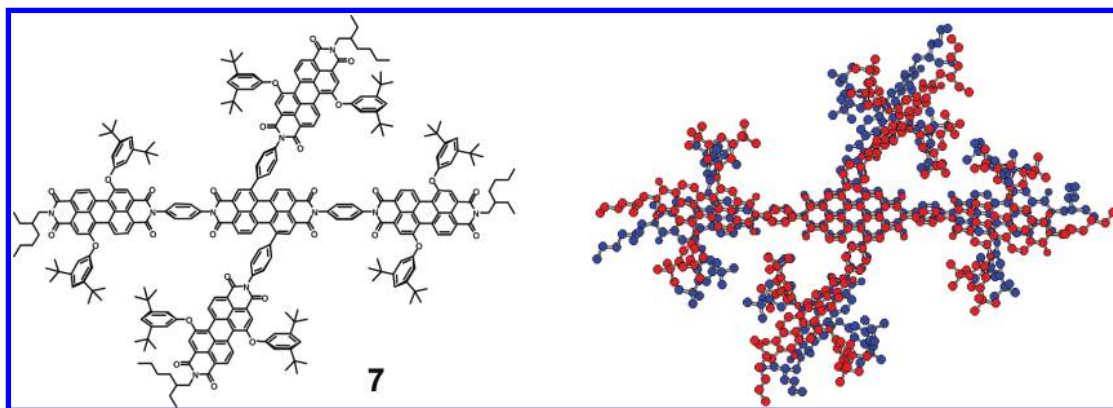
molecules. Placing sterically unencumbered *n*-octyl groups on the imide nitrogen atoms at the end of the PDI chromophores not attached to the xantheno spacer results in **3** having near optimal  $\pi$ -stacking leading to formation of a low energy excimer-like state (Figure 1C). On the other hand, substituting the more sterically demanding 12-tricosanyl group on the imides causes deviations from the optimum that result in an excimer-like state having a higher energy in **4** (Figure 1C). By comparison, dimers **5** and **6** have two isomers, whose photophysical properties depend on the ability of the phenoxy groups at the 1,7-positions to modify the  $\pi$  stacking of the PDI molecules. In general, disruption of optimal  $\pi$ -stacking by steric interactions of the phenoxy side groups in **5** and **6** results in excimer-like states that are higher in energy than that of **3** in a manner similar to that of **4**.

## Energy Transport in Self-Assembled Systems

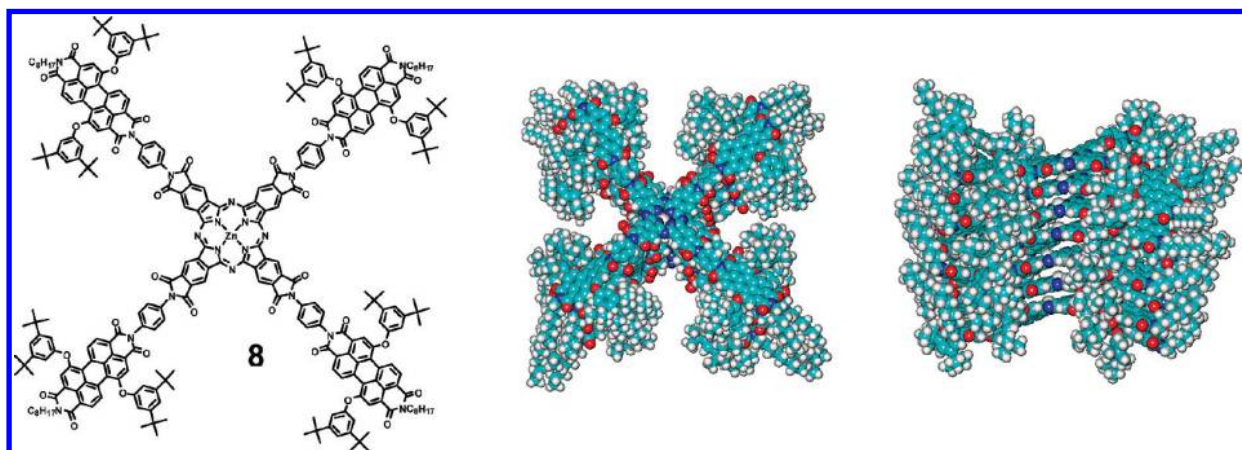
An antenna, or light-harvesting molecule, is one which increases the cross-section for absorption of solar energy without undergoing charge separation itself. Following photoexcitation of an antenna chromophore array, a series of one or more energy transfer steps occurs, which funnels the excitation energy to a site at which charge separation occurs. Covalent light-harvesting chromophoric arrays designed to funnel energy to a central site often involve significant synthetic complexity.<sup>34</sup> We have reported on several multichromophore PDI building blocks that self-assemble in solution and on surfaces into supramolecular light-harvesting arrays.<sup>15,35</sup> For example, in building block **7** a central PDI chromophore is decorated with four additional PDI molecules, two each at its imide nitrogen atoms and one each at the 1 and 7 positions to produce a saddle-shaped molecule ( $\text{PDI}_5$ ). This molecule self-as-

sembles into an ordered dimeric structure  $(\text{PDI}_5)_2$  in toluene and 2-methyltetrahydrofuran solutions with the PDI molecules approximately parallel to one another primarily due to  $\pi$ - $\pi$  interactions between adjacent PDI chromophores as indicated by SAXS/WAXS measurements (Figure 2). Photoexcitation of  $(\text{PDI}_5)_2$  in solution gives direct evidence of strong  $\pi$ - $\pi$  interactions between the excited PDI chromophore and other PDI molecules nearby based on the observed formation of an excimer-like state in <130 fs having a lifetime of about 20 ns. At higher laser fluences, multiple photoexcitations of the supramolecular dimer leads to fast singlet-singlet annihilation, which occurs with exciton hopping times of about 5 ps, and is comparable to that observed in photosynthetic light-harvesting proteins from green plants.

We have also demonstrated that ultrafast energy transfer can occur readily from one  $\pi$ -stacked supramolecular chromophore assembly to a neighboring assembly followed by ultrafast energy migration within the energy-accepting assembly.<sup>16</sup> We have synthesized a zinc phthalocyanine-octacarboxytetraimide in which all four imide nitrogen atoms are substituted with PDI molecules ( $\text{ZnPcIm}_4$ -PDI<sub>4</sub>, **8**). Appending the electron-withdrawing imide groups to the ZnPc core makes this macrocycle very hard to oxidize, so that electron transfer from  $^1\text{ZnPcIm}_4$  to PDI is energetically uphill. The individual  $\text{ZnPcIm}_4$ -PDI<sub>4</sub> molecules self-assemble into stacked heptamers in solution as evidenced by SAXS/WAXS (Figure 3) and form long fibrous structures in the solid as evidenced by TEM. The  $\text{ZnPcIm}_4$  and PDI molecules both stack in register with the same components in an adjacent covalent building block. Selective laser excitation of the PDI molecules results in ultrafast energy transfer with  $\tau = 1.3$  ps from the stacked peripheral PDI chromophores to the core  $\text{ZnPcIm}_4$  chromophore stack. Exciton hopping between the  $\text{ZnPcIm}_4$  chro-



**FIGURE 2.** Left: chemical structure of PDI<sub>5</sub> (**7**); Right: top view of the structure of (PDI<sub>5</sub>)<sub>2</sub> in toluene obtained using SAXS/WAXS data.



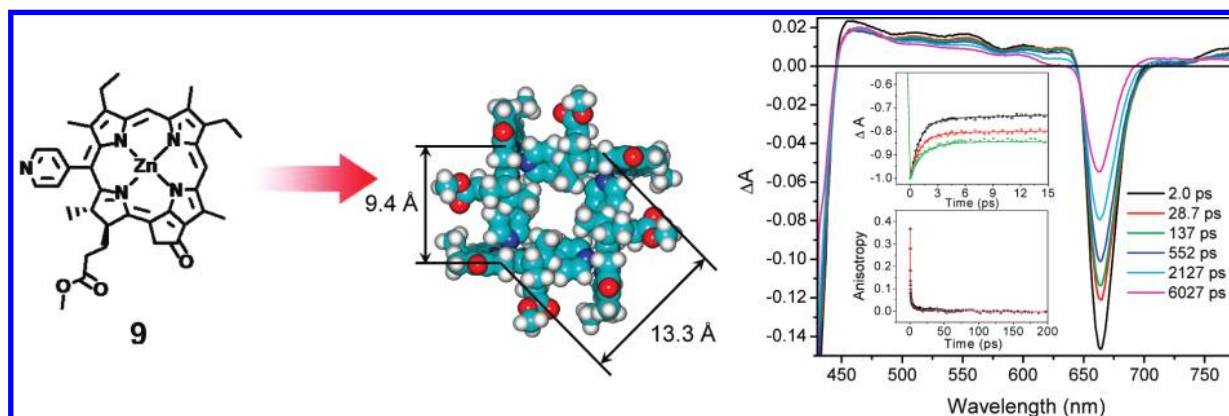
**FIGURE 3.** (Left) Chemical structure of ZnPclm<sub>4</sub>-PDI<sub>4</sub> (**8**); (center) top view and (right) side view of the structure of (ZnPclm<sub>4</sub>-PDI<sub>4</sub>)<sub>7</sub> in toluene obtained using SAXS/WAXS data.

mophores then occurs with  $\tau = 160$  fs, which approaches the vibrational time scale.

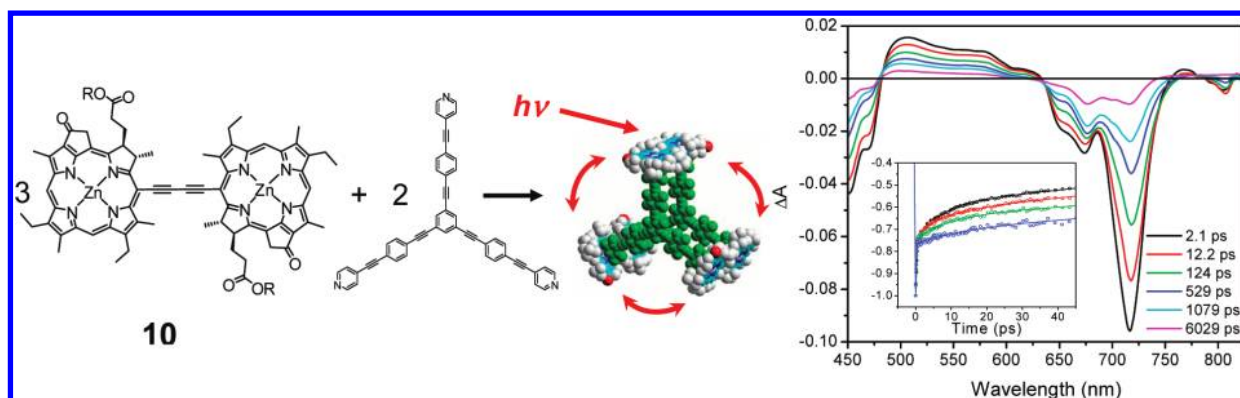
Ever since the crystal structure of the LH-II antenna protein from purple photosynthetic bacteria revealed that its bacteriochlorophylls are arrayed in a ring structure,<sup>36</sup> considerable effort has been invested in making biomimetic chromophore rings, many of which offer insights into the photophysics of energy collection and transfer in these proteins.<sup>37–40</sup> However, a more efficient strategy for multichromophore array construction is desirable for developing artificial photosynthetic systems for solar energy conversion. The 20-position of chlorophyll *a* (Chl *a*) offers a new site for rigid attachment of ligands that can be used to build supramolecular Chl structures based on metal–ligand binding.<sup>41</sup> To explore this strategy we have prepared a zinc 20-(4-pyridyl)chlorophyll (ZC) derivative, **9**, that self-assembles into a cyclic tetramer as evidenced by SAXS/WAXS studies in solution (Figure 4). This cyclic ZC tetramer exhibits an ultrafast intramolecular energy transfer rate of  $(1.3 \text{ ps})^{-1}$  as determined from femtosecond singlet–singlet annihilation and transient absorption anisotropy studies. The larger transition dipole moment for the low-

est energy electronic transition of ZC compared to that of metalloporphyrins increases the rate of Förster (through-space) energy transfer between the Chls. Extension of this self-assembly strategy makes it possible to design and self-assemble larger Chl rings for energy transfer in artificial photosynthetic systems.

Continuing this conceptual direction, a butadiyne-linked Chl dimer, **10**, was synthesized and its photophysical properties were studied in toluene. The butadiyne linkage between the 20-positions of the macrocycles results in a new electronic transition polarized along the long axis of the dimer. This transition greatly increases the ability of this dimer to absorb the solar spectrum over a broad wavelength range. Femtosecond transient absorption spectroscopy reveals the relative rate of rotation of the macrocycles around the butadiyne bond joining them as has been observed in related porphyrin systems.<sup>42</sup> Following addition of 3-fold symmetric, metal-coordinating ligands, the Chl dimers self-assemble into prismatic structures in which the dimers comprise the faces of the prisms (Figure 5). These structures were confirmed by SAXS/WAXS measurements in solution. Photoexcitation of the



**FIGURE 4.** (Left) Chemical structure of **9** (ZC); (center) structure of self-assembled ZC tetramer obtained from SAXS/WAXS data in toluene at APS; (right) transient absorption spectra of tetramer in toluene following excitation with 665 nm, 120 fs laser pulses. (Top inset) power dependent transient absorption kinetics of tetramer monitored at 660 nm using 1.00 (black), 0.66 (red), and 0.33 ( $\mu\text{J}$ ) per 665 nm excitation pulse. (Bottom inset) Transient anisotropy kinetics at 555 nm.



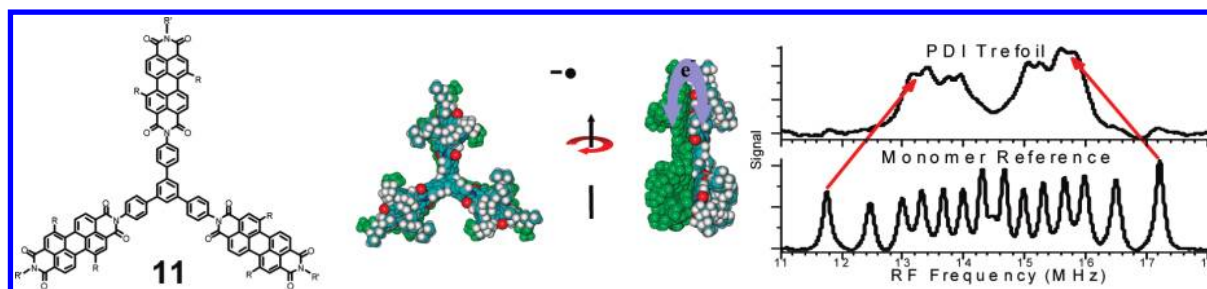
**FIGURE 5.** (Left) 3-Fold symmetric prisms having Chl dimers (**10**) as their faces. Structure determined by SAXS/WAXS. (Right) Transient absorption spectra of the prism in toluene following excitation with 710 nm, 120 fs laser pulses. (Inset) Power-dependent transient absorption kinetics monitored at 721 nm using 1.00 (black), 0.66 (red), 0.33 (green) and 0.11 (blue)  $\mu\text{J}$  per 710 nm excitation pulse.

prismatic assemblies reveals that efficient, through-space energy transfer occurs between the macrocyclic dimers within the prisms. The distance dependence of energy transfer between the faces of the prisms was observed by varying the size of the prismatic assemblies through the use of 3-fold symmetric ligands having arms with different lengths and is somewhat weaker than that predicted by the Förster dipole–dipole model resulting in more efficient energy transfer between the prism faces at longer distances. These results show that self-assembly of discrete macrocyclic prisms provides a useful new strategy for controlling singlet exciton flow in artificial photosynthetic systems.

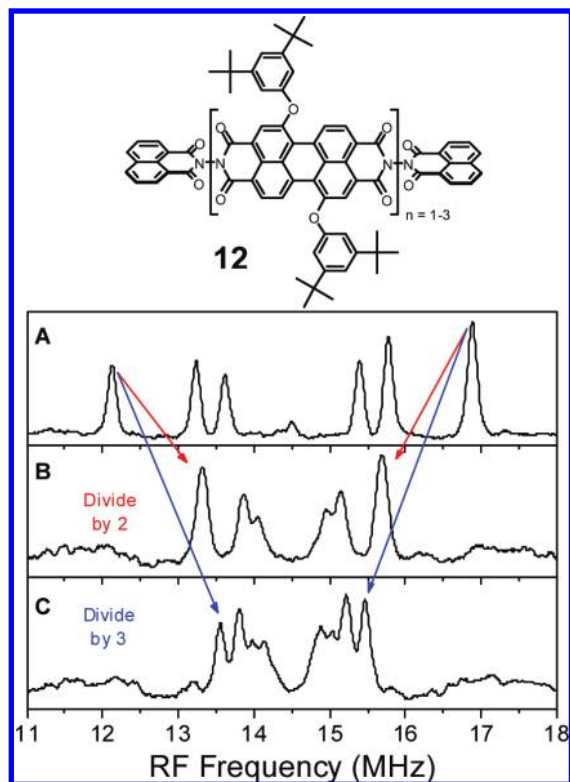
## Photodriven Charge Separation and Transport in Self-Assembled Systems

Strongly interacting  $\pi$ -stacked arrangements of chromophores are found in many biologically important molecules such as the primary electron donor within photosynthetic RC proteins and the base pairs within duplex DNA. In designing systems

for artificial photosynthesis, an important question is how effective are particular self-assembled, noncovalent structures composed of multiple redox chromophores in promoting rapid charge transport between them. To address this question in self-assembled PDI arrays, we have carried out room-temperature, solution-phase EPR and ENDOR studies of the radical anions of a PDI monomer, a covalent, cofacial PDI dimer, and a covalent PDI<sub>3</sub> trefoil molecule, **11**, that self-assembles into  $\pi$ -stacked dimers as determined by SAXS/WAXS (Figure 6, center). Upon one-electron reduction, full sharing of the unpaired electron between two  $\pi$ -stacked, noncovalent PDI molecules in the self-assembled PDI<sub>3</sub> trefoil dimer is revealed by a halving of the hyperfine coupling constants in this species, relative to those of the monomers. Electron hopping on a  $>10^7$  s<sup>-1</sup> time scale occurs in this supramolecular system, which is similar to that observed in covalent, cofacial PDI reference dimer **5**. In contrast, no electron hopping occurs between the covalently linked PDI molecules in the monomeric PDI<sub>3</sub> trefoil.



**FIGURE 6.** (Left) Chemical structure of PDI<sub>3</sub> (**11**); (center) structure of self-assembled (PDI<sub>3</sub>)<sub>2</sub> obtained by SAXS/WAXS; (right) proton ENDOR spectra of the radical anions of (PDI<sub>3</sub>)<sub>2</sub> and a monomeric PDI reference molecule in CH<sub>2</sub>Cl<sub>2</sub>-3% TEA solution at 297 K.



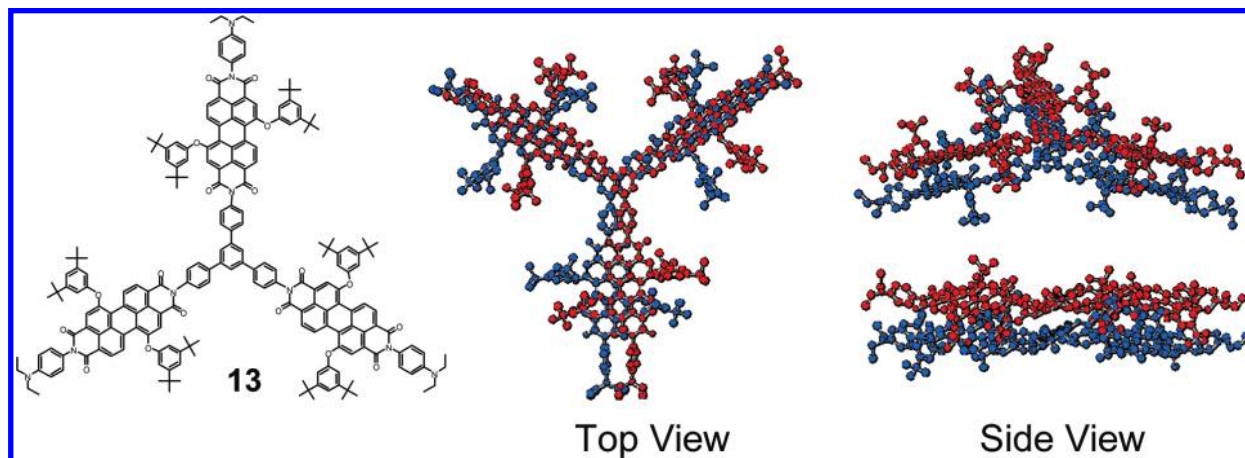
**FIGURE 7.** <sup>1</sup>H-ENDOR spectra of the radical anions of **12** ( $n = 1$ ) (A), **12** ( $n = 2$ ) (B), and **12** ( $n = 3$ ) (C) in DMF with ~1 to 4% TEA (w/w), at 290 K.

We have recently compared this behavior with that of a linear covalent series of PDI monomers, dimers, and trimers directly linked via N–N bonds, **12**.<sup>43</sup> In these molecules, the  $\pi$  systems of the PDI molecules are oriented nearly perpendicular to one another. One-electron chemical reduction of these species yields stable radical anions in which the electron rapidly hops between the PDI units. This is particularly striking in the case of the trimer in which its hyperfine splittings are nearly three times less than those of the corresponding monomer (Figure 7), as predicted for rapid hopping on a time scale that is faster than the  $10^7 \text{ s}^{-1}$  RF frequency used to induce the nuclear spin transitions.<sup>44,45</sup> Importantly, we have found that the electronic properties of the bonds that link the PDI molecules are critical to achieving rapid electron hopping

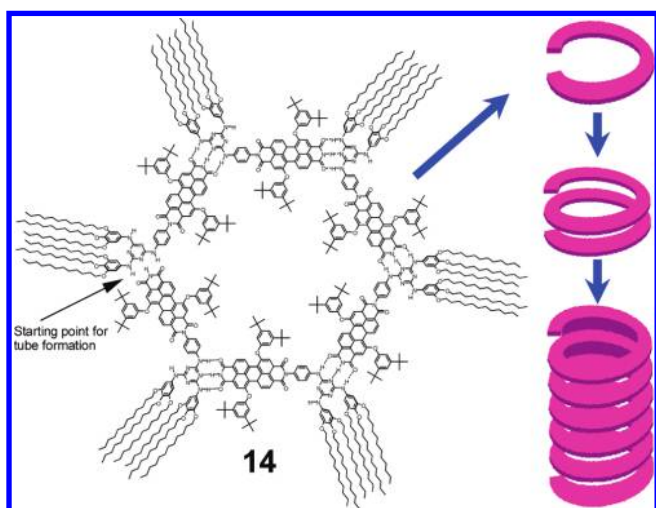
between them. For example, the naphthalene-1,8-dicarboximide (NMI) end-caps on the trimer proved essential to achieving an electronic equivalence of each PDI, so that each PDI is bound at both ends to another imide group through a N–N bond, and thus each PDI has essentially identical redox potentials. Attaching a phenyl or an alkyl group to the terminal nitrogen atoms of the PDIs at the ends of the trimer localizes the electron on the central PDI.

In a more highly functionalized version of the PDI<sub>3</sub> trefoil described above, we have studied the influence of  $\pi$ -stacking on photoinduced electron transfer.<sup>20</sup> The donor–acceptor unit is a DEA–PDI pair, **13**, (DEA = *N,N*-diethylaniline; PDI = perylene-3,4:9,10-bis(dicarboximide)), in which the 4-position of DEA is covalently attached to the nitrogen atom of one imide of PDI. One, two, or three DEA–PDI units are attached to the para position of one of the phenyl groups of 1,3,5-triphenylbenzene using the other PDI imide group to form (DEA–PDI) <sub>$n=1-3$</sub> . These molecules demonstrate an increasing tendency to self-assemble into  $\pi$ -stacked dimers in solution in the order (DEA–PDI)  $\ll$  (DEA–PDI)<sub>2</sub> < (DEA–PDI)<sub>3</sub> (Figure 8). Photoinduced electron transfer in both the monomers and self-assembled dimers was studied by femtosecond transient absorption spectroscopy. The charge separation and charge recombination time constants are found to be independent of  $\pi$ -stacking aptitudes, while the transient spectral features differ significantly upon dimerization. The electronic interactions imposed by  $\pi$ -stacking appear to change the energies of the ground, excited, and ionic states of DEA–PDI to a similar extent, which results in similar energies for charge separation and recombination within the monomers and dimers.

In a more complex system, a PDI-based electron donor–acceptor monomer was designed to self-assemble using the synergistic effects of  $\pi$ – $\pi$  stacking, nanosegregation, and hydrogen bonding, **14**.<sup>46</sup> Using SAXS/WAXS techniques, the resulting assemblies were found to consist of twelve monomers arranged in a hydrogen-bonded, two-turn helix (Figure 9). These cyclic arrays grow to lengths of about 1  $\mu\text{m}$  and form bundles of tubular structures in the solid



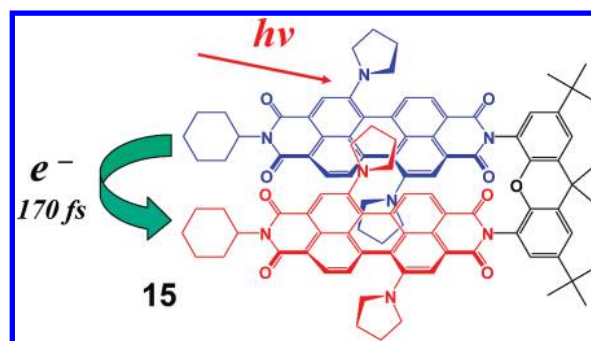
**FIGURE 8.** (Left) Chemical structure of structure of (DEA-PDI)<sub>3</sub> (**13**); (center) view along the stacking direction (top) and at both axes 90° to that direction (side).



**FIGURE 9.** Chemical structure of structure of **14** and its progressive self-assembly into helical nanotubes using a combination of hydrogen bonding and  $\pi$ - $\pi$  stacking.

phase. Assembly is solvent dependent, with methylcyclohexane inducing assembly and tetrahydrofuran disrupting it. The solution phase photophysics of the dodecamer were probed by UV-vis, time-resolved fluorescence, and femtosecond transient absorption spectroscopies, revealing that formation of the dodecamer introduces an ultrafast electron transfer pathway from the tris(*n*-dodecyloxy)aniline donor group to the adjacent PDI acceptor that is hydrogen-bonded to it. This interaction is not present in the monomer, so that the longer donor-acceptor distance in the monomer results in an electron transfer rate that cannot compete with decay of <sup>1</sup>PDI.

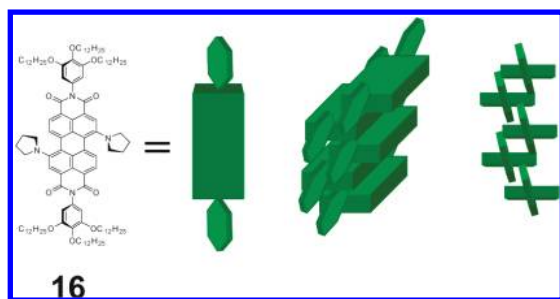
In an effort to develop more robust biomimetic electron donor-acceptor systems we synthesized a covalent cofacial dimer of 1,7-bis(pyrrolidin-1'-yl)perylene-3,4,9,10-bis(dicarboximide) (5PDI),<sup>11</sup> a green chromophore with an intense absorption at 686 nm, having both electronic and redox properties that are remarkably similar to those of Chl *a*.<sup>47</sup> Ultrafast



**FIGURE 10.** Chemical structure of structure of 5PDI<sub>2</sub> (**15**).

transient absorption spectroscopy following excitation of 5PDI<sub>2</sub>, **15** (Figure 10) with 700 nm, 100 fs laser pulses shows that quantitative intradimer electron transfer occurs within **15** in toluene with  $\tau = 170$  fs followed by charge recombination to ground state with  $\tau = 220$  ps. The symmetry breaking mechanism leading to rapid charge separation in **15** is most likely due to rotation of a pyrrolidine ring about the C-N bond joining it to the PDI core following photoexcitation,<sup>48</sup> leading to greater charge transfer character in the excited state, thus making the photoexcited 5PDI molecule a better electron donor, while the adjacent 5PDI molecule serves as the acceptor.

Given our observation that placing two "Chl-like" 5PDI chromophores in a face-to-face configuration, **15**, leads to quantitative photoinduced charge separation, we reasoned that this same chromophore would be an excellent candidate for eliciting photochemical charge separation in a self-assembled, supramolecular system. The 5PDI chromophore does not have an intrinsic strong tendency to form aggregates, however, in contrast to PDI and its derivatives. This is due to steric hindrance to stacking imposed by the pyrrolidine rings at the 1 and 7 positions. We initially decided to apply well-known strategies used to produce discotic liquid crystals to induce



**FIGURE 11.** Chemical structure of **16** and structure of  $5\text{PDI}_5$  that is consistent with the SAXS/WAXS data. The structural model of  $5\text{PDI}_5$  accounts for the steric demand of the trialkoxyphenyl groups, whose  $\pi$  systems have about a  $78^\circ$  dihedral angle relative to that of the  $5\text{PDI}$  core chromophore. Lateral slippage of  $5\text{PDI}$  cores still permits  $H$ -aggregation.

assembly, where long alkyl chains are appended to aromatic core molecules to promote stacking through nanosegregation. Thus, we appended tris(*n*-dodecyloxy)phenyl groups to both imide nitrogens of  $5\text{PDI}$  to give **16**, a molecule that self-assembles into ordered supramolecular pentamers (**16**)<sub>5</sub> at  $10^{-4}$  M in methylcyclohexane (MCH) based on SAXS/WAXS measurements and displays a liquid crystalline phase (Figure 11).<sup>49</sup> Transient absorption measurements carried out in MCH show that symmetry breaking in the excited singlet state of (**16**)<sub>5</sub> occurs within the 130 fs instrument response time of the experiment, which produces a  $5\text{PDI}^{+\bullet}-5\text{PDI}^{-\bullet}$  radical ion pair on an adjacent pair of  $5\text{PDI}$  molecules within (**16**)<sub>5</sub> that recombines with  $\tau = 1.05$  ns.

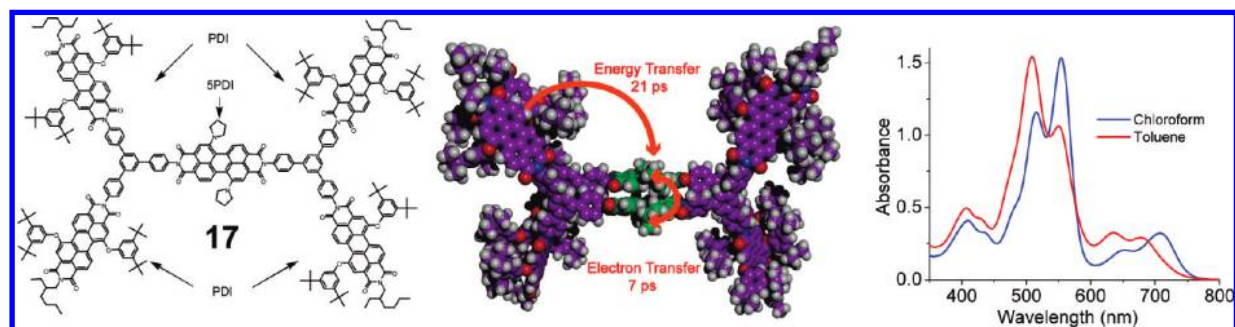
On the basis of our experience with using self-assembly to induce a face-to-face geometry within (**16**)<sub>5</sub> that promotes charge separation, we decided to use the self-assembly properties of PDI to bring two  $5\text{PDI}$  molecules close to one another as well as providing a light-harvesting antenna array. We have reported the synthesis and characterization of **17**, which self-assembles into  $\pi$ -stacked dimers (**17**)<sub>2</sub> in solution as revealed by SAXS/WAXS (Figure 12).<sup>17</sup> This dimeric array demonstrates that self-assembly of a robust PDI-based artificial light-harvesting antenna structure induces self-assembly of a functional special pair of  $5\text{PDI}$  molecules that undergoes ultrafast, quantitative charge separation. The structure consists of four PDI molecules attached to a single  $5\text{PDI}$  core, which self-assembles to form (**17**)<sub>2</sub> in toluene. Femtosecond transient absorption spectroscopy shows that energy transfer from (PDI)<sub>2</sub> to ( $5\text{PDI}$ )<sub>2</sub> occurs with  $\tau = 21$  ps, followed by excited state symmetry breaking of  $^1(5\text{PDI})_2$  to produce  $5\text{PDI}^{+\bullet}-5\text{PDI}^{-\bullet}$  quantitatively with  $\tau_{\text{CS}} = 7$  ps. The ion pair recombines with  $\tau_{\text{CR}} = 420$  ps. Electron transfer occurs only in the dimeric system, and does not occur in the disassembled monomer, thus mimicking both antenna and special pair function in photosynthesis. The charge separation observed in (**17**)<sub>2</sub> is an example of

emergent behavior that does not occur when monomeric **17** is photoexcited.

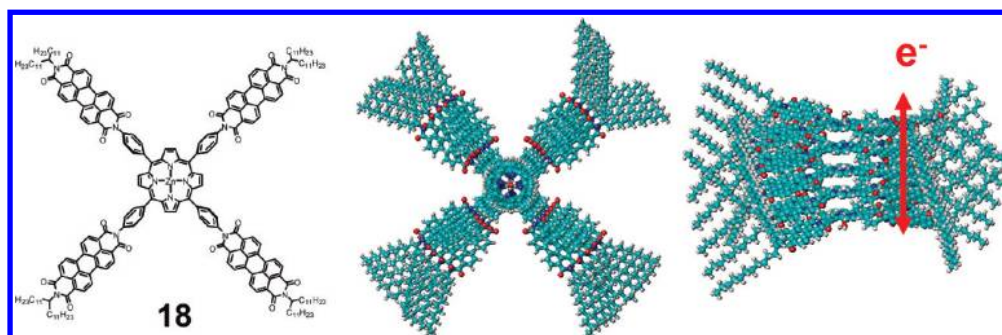
We have also explored self-assembling building blocks containing both electron donors and acceptors, which provide advantages for promoting charge separation and transport in artificial photosynthetic systems. A bichromophoric electron donor–acceptor molecule composed of a zinc tetraphenylporphyrin (ZnTPP) donor surrounded by four PDI acceptors (ZnTPP–PDI<sub>4</sub>) was synthesized, **18**.<sup>50</sup> The properties of this molecule were compared to a reference molecule having ZnTPP covalently bound to a single PDI (ZnTPP–PDI). In toluene, ZnTPP–PDI<sub>4</sub> self-assembles into nearly monodisperse assemblies comprising five molecules arranged in a columnar stack, (ZnTPP–PDI<sub>4</sub>)<sub>5</sub> (Figure 13) as determined using SAXS/WAXS. The nearly monodisperse nature of this assembly contrasts sharply with our previously reported ZnTPP–PDI<sub>4</sub> derivatives having 1,7-bis(3,5-di-*t*-butylphenoxy) groups on the PDI acceptors and provides a significant improvement in structural order.<sup>35</sup> The ZnTPP–PDI reference molecule does not aggregate. Femtosecond transient absorption spectroscopy shows that laser excitation of both ZnTPP–PDI and (ZnTPP–PDI<sub>4</sub>)<sub>5</sub> results in quantitative formation of ZnTPP<sup>+\bullet</sup>–PDI<sup>-\bullet</sup> radical ion pairs in a few picoseconds. The transient absorption spectra of (ZnTPP–PDI<sub>4</sub>)<sub>5</sub> also show that the PDI<sup>-\bullet</sup> radical anion interacts strongly with adjacent PDI molecules and suggests that the electron migrates within the columnar stack. Corresponding evidence for migration of the hole through the columnar stack of ZnTPP molecules could not be obtained as a result of the much higher absorptivity of PDI<sup>-\bullet</sup> relative to that of ZnTPP<sup>+\bullet</sup> in the spectral region probed. Charge recombination occurs more slowly within (ZnTPP–PDI<sub>4</sub>)<sub>5</sub> ( $\tau = 4.8$  ns) than it does in ZnTPP–PDI ( $\tau = 3.0$  ns) producing mostly ground state as well as a modest yield of  $^3\text{PDI}$ . Our results provide evidence that control over the donor–acceptor geometry in segregated, self-assembled stacks of electron donor–acceptor molecules can lead to efficient charge transport relevant to their applications in artificial photosynthetic systems and organic photovoltaics.

The ZnTPP electron donor in (ZnTPP–PDI<sub>4</sub>)<sub>5</sub> has an excited singlet state energy that is approximately 0.25 eV lower than that of PDI. In addition, ZnTPP is relatively easy to oxidize. To preserve a larger fraction of the total photon energy absorbed by the self-assembled donor–acceptor building block, we have modified the structure described above to incorporate a central pyrene (Py) electron donor to which four PDI acceptors are covalently bound (Py–PDI<sub>4</sub>, **19**).<sup>51</sup> This arrangement results in coplanarity of the  $\pi$  systems of both Py and the PDI molecules. The terminal imide of each PDI is functionalized with a long branched aliphatic hydrocarbon tail to ensure

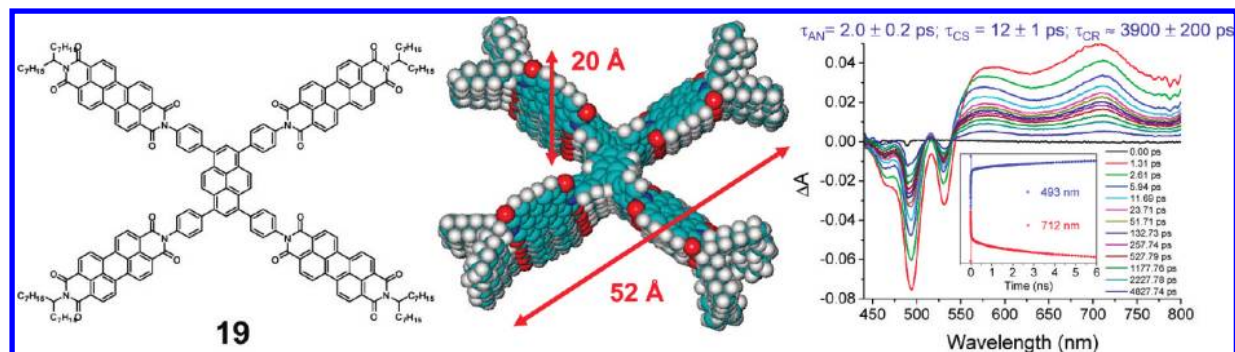




**FIGURE 12.** Chemical structure of **17** (left), the best fit structure of  $(17)_2$  from modeling the SAXS/WAXS data (center), and the UV-vis spectra showing dimerization in toluene (monomers in  $\text{CHCl}_3$ ) and excellent solar spectral coverage (right).



**FIGURE 13.** (Left) Chemical structure of  $\text{ZnTPP-PDI}_4$  (**18**), (center) top view, and (right) side view of the structure of  $(\text{ZnTPP-PDI}_4)_5$  in toluene obtained using SAXS/WAXS data. The hydrocarbon “swallowtails” are tilted out of plane relative to PDI chromophores.

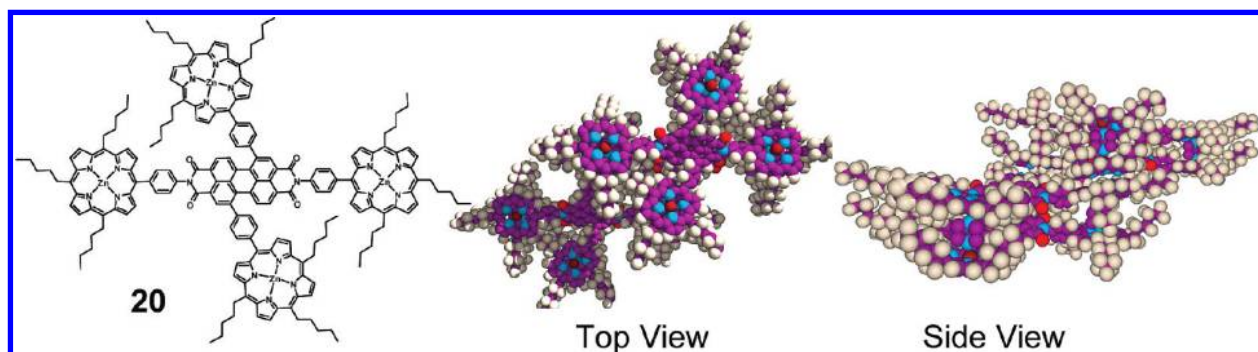


**FIGURE 14.** Left: chemical structure of  $\text{Py-PDI}_4$  (**19**); Center: top view of the structure of  $(\text{Py-PDI}_4)_5$  in toluene obtained using SAXS/WAXS data. Right: Transient absorption spectra and kinetics.

good solubility. Coplanarity allows the  $\text{Py-PDI}_4$  building blocks to self-assemble into structures in which the molecules are arranged in a cofacial configuration (*H*-type aggregate). The self-assembly process is driven primarily by intermolecular  $\pi$ - $\pi$  interactions between adjacent PDI chromophores and produces nearly monodisperse cofacially stacked columnar arrays of five  $\text{Py-PDI}_4$  molecules (Figure 14). Selective photoexcitation of PDI within  $(\text{Py-PDI}_4)_5$  results in rapid electron transfer from Py to  $^1\text{PDI}$ . The transient spectra once again show evidence of charge sharing among the stacked PDI molecules in  $(\text{Py-PDI}_4)_5$  as indicated by the broadening of the  $\text{PDI}^*$  band at 600–800 nm.

We have also explored the inverse strategy in which metal-ligand binding of zinc porphyrins is used to assemble

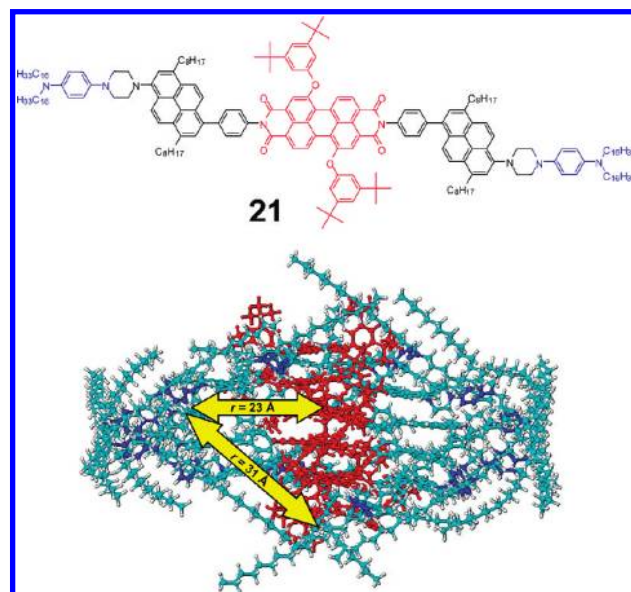
a multichromophore array based on a  $(\text{Z3PN})_4\text{PDI}$  building block, **20**, consisting of four zinc 5-phenyl-10,15,20-tri(*n*-pentyl)porphyrins (Z3PN) attached to the 1,7,*N,N'*-positions of PDI.<sup>52</sup> Using a combination of metal-ligand binding with the bidentate ligand 1,4-diazabicyclo[2.2.2]octane (DABCO) and  $\pi$ - $\pi$  stacking,  $(\text{Z3PN})_4\text{PDI}$  forms a supramolecular assembly,  $[(\text{Z3PN})_4\text{PDI}]_2\text{-DABCO}_4$ , in toluene solution. The structure of this hierarchical assembly (Figure 15) was characterized using solution-phase SAX/WAXS and demonstrates both efficient light harvesting and facile charge separation and transport using multiple pathways. The dynamics of energy and charge transport within this system were compared to those of two model compounds, *N,N'*- $(\text{Z3PN})_2\text{PDI}$  and 1,7- $(\text{Z3PN})_2\text{PDI}$ . The symmetry of the lowest unoccupied molecular orbital of PDI



**FIGURE 15.** (Left) Chemical structure of structure of  $[[(\text{Z3PN})_4\text{PDI}]_2\text{-DABCO}_4]_2$  (**20**). Views are along the stacking direction (top) and an axis  $90^\circ$  to that direction (side).

results in significantly different electronic couplings between Z3PN and PDI when they are connected at the 1,7-positions versus the  $N,N'$ -positions of PDI. This results in two distinct pathways for electron transfer in  $(\text{Z3PN})_4\text{PDI}$ .

Our results described above show that self-assembly of arylene imide and diimide chromophores can produce photo-functional assemblies in which electron transfer through non-covalent, cofacially stacked PDI molecules is rapid. However, the  $(\text{ZnTPP-PDI})_4$ ,  $(\text{Py-PDI})_4$ , and  $[[(\text{Z3PN})_4\text{PDI}]_2\text{-DABCO}_4]_2$  assemblies described above do not have sufficiently long radical ion pair lifetimes for long distance charge transport through the noncovalent  $\pi$ -stacked PDI (or ZnTPP or Z3PN) molecules to be competitive with charge recombination. To remedy this problem, we have recently synthesized a donor-acceptor triad building block consisting of a PDI chromophoric acceptor, an aminopyrene primary donor (APy), and a diaminobenzene secondary donor (DAB) that remains monomeric in toluene, **21**, and self-assembles into a helical hexamer in methylcyclohexane as shown by SAXS/WAXS (Figure 16).<sup>53</sup> This assembly is the size of a small protein ( $\sim 18$  kD), and has PDI acceptors  $\pi$ -stacked upon one another with about a  $35^\circ$  dihedral angle between them, while the DAB donors are not associated. Time-resolved EPR spectroscopy of photogenerated  $\text{DAB}^{+\bullet}\text{-APy-PDI}^{-\bullet}$  within **21** shows that both the spin-spin exchange ( $2J$ ) and dipolar ( $D$ ) interactions of the radical ion pair decrease dramatically when **21** assembles into the helical hexamer (Figure 16). Analysis of these results shows that the average distance between the radical ions of the radical ion pair formed within the helical hexamer is 31 Å, whereas the through-bond DAB-PDI distance within the building block is only 23 Å. This data shows that the electron migrates through the  $\pi$ -stacked PDI acceptors much faster than the 40 ns charge recombination time of  $\text{DAB}^{+\bullet}\text{-PDI}^{-\bullet}$ . This is the first example of noncovalent secondary charge transport in a  $\pi$ -stacked system being competitive with charge recombination. This behavior is important for developing both



**FIGURE 16.** DAB-APy-PDI-APy-DAB monomer (**21**), and the structure (side view) of its self-assembled hexamer in methylcyclohexane as determined by SAXS/WAXS.

artificial photosynthetic systems and organic photovoltaics for solar energy conversion.

## Concluding Remarks

The field of artificial photosynthesis has developed in parallel with that of supramolecular chemistry. Yet, the fundamental requirements for photoinduced charge transport in self-assembled systems remain poorly understood. The preparation and characterization of new covalent building blocks that both initiate photoinduced charge separation and promote long distance charge transport by self-assembling into extended noncovalent structures is needed to build functional systems. In addition, the development of antenna-reaction center systems in which self-assembly of the antenna elicits formation of a reaction center capable of separating charge for times sufficiently long to promote long distance charge transport is an important step to integrate multiple tasks for artificial photosynthesis. Achieving these goals will require a

knowledge of how self-assembly using  $\pi$ -stacking can be combined with hydrogen bonding and metal–ligand bonding to simplify the structure of the building blocks, and yet retain the overall ability to assemble complex, photofunctional structures.

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**Michael R. Wasielewski** was born in Chicago in 1949 and received his B.S. (1971) and Ph.D. (1975) degrees from the University of Chicago. He was a postdoctoral fellow at Columbia University, after which he began his career at Argonne National Laboratory, ultimately becoming the Group Leader of the Molecular Photonics Group. In 1994, he joined the faculty of Northwestern University, where he is currently Professor of Chemistry and Director of the Argonne-Northwestern Solar Energy Research (ANSER) Center, which is a DOE Energy Frontier Research Center. He also holds a joint appointment in the Center for Nanoscale Materials at Argonne. His research centers on light-driven charge transport in molecules and nanoscale materials for solar energy conversion as well as spin dynamics of multispin organic molecules, materials for molecule-based optoelectronics and spintronics, and time-resolved optical and EPR spectroscopy.

#### FOOTNOTES

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