Supramolecular Packing Controls H₂ Photocatalysis in Chromophore Amphiphile Hydrogels

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ABSTRACT: Light harvesting supramolecular assemblies are potentially useful structures as components of solar-to-fuel conversion materials. The development of these functional constructs requires an understanding of optimal packing modes for chromophores. We investigated here assembly in water and the photocatalytic function of perylene monomide chromophore amphiphiles with different alkyl linker lengths separating their hydrophobic core and the hydrophilic carboxylate headgroup. We found that these chromophore amphiphiles (CAs) self-assemble into charged nanostructures of increasing aspect ratio as the linker length is increased. The addition of salt to screen the charged nanostructures induced the formation of hydrogels and led to internal crystallization within some of the nanostructures. For linker lengths up to seven methylenes, the CAs were found to pack into 2D crystalline unit cells within ribbon-shaped nanostructures, whereas the nine methylene CAs assembled into long nanofibers without crystalline molecular packing. At the same time, the different molecular packing arrangements after charge screening led to different absorbance spectra, despite the identical electronic properties of all PMI amphiphiles. While the crystalline CAs formed electronically coupled H-aggregates, only CAs with intermediate linker lengths showed evidence of high intermolecular orbital overlap. Photocatalytic hydrogen production using a nickel-based catalyst was observed in all hydrogels, with the highest turnovers observed for CA gels having intermediate linker lengths. We conclude that the improved photocatalytic performance of the hydrogels formed by supramolecular assemblies of the intermediate linker CA molecules likely arises from improved exciton splitting efficiencies due to their higher orbital overlap.

INTRODUCTION

The integration of light-harvesting nanostructures and fuel-producing catalysts is an interesting goal to develop materials with the capacity to generate solar fuels.1 Natural photosynthetic systems have attained this level of efficiency through colocalization of light-harvesting arrays of π-conjugated chromophores with catalytic reaction centers.2 While natural photosystems can be coupled to proton-reduction catalysts to efficiently convert sunlight directly into hydrogen (H₂),3−5 synthetic materials have also been utilized in solid-state photoconductors6−9 and organic photovoltaic devices10−14 to collect photogenerated charges at electrodes. Self-assembled gels could facilitate the light-driven water splitting reaction within a hydrated environment harboring chromophore−catalyst interactions.12,13 A host of supramolecular, π−π stacked materials have been reported,14 with many studies finding that differences in molecular packing alter light harvesting or energy transport within supramolecular materials.15−21

We reported recently on photocatalysis using charged chromophore amphiphiles (CAs) containing perylene monomide (PMI) moieties and carboxylate groups that assemble into ribbon-shaped nanostructures in water (see Scheme 1).1 The choice of chromophore was based on PMI’s high thermal, chemical, and acid stability as well as strong visible-light absorbance.22 PMI derivatives have found use in covalent dyads23,24 and small supramolecular assemblies25,26 to promote electron−hole separation, a necessary mechanistic step for efficient fuel generation. Interestingly, we found that both gelation of aqueous solutions and internal crystallization within the nanoribbons occur simultaneously by simply adding monovalent, divalent, or polyvalent salts that screen repulsive electrostatic interactions. These CA hydrogels could photo-
sensitize aqueous H₂ evolution in the presence of a watersoluble, cationic nickel proton reduction catalyst, visible light, and ascorbic acid as a source of electrons and protons.

The identification of advantageous packing arrangements to move energy to a catalyst is a crucial parameter for the development of efficient solar-to-fuel conversion supramolecular materials. In this work we have synthesized a series of seven CA molecules to probe the impact of molecular packing on photocatalytic hydrogen production. The structures of supramolecular assemblies formed by these molecules have also been characterized by electron microscopy, X-ray scattering, and UV/vis spectroscopy.

### RESULTS AND DISCUSSION

The PMI derivatives studied here are designated as Ln, where n is the number of methylenes between the imide and the terminal carboxylic acid. These CAs were prepared by the condensation of perylene monoanhydride (PMA) and commercially available or synthetically accessible ω-amino-carboxylic acids (Scheme 1). Conversion of the carboxylic acid to the methyl ester vastly improved solubility of each molecule in organic solvents and enabled purification via recycling gel permeation chromatography (rGPC) (Figure S1). Once purified, we could regenerate the carboxylic acids using sulfuric acid to hydrolyze the ester.

We investigated the structure of CA assemblies in aqueous solution to determine how linker length variations altered nanostructure morphologies and molecular packing. The molecules in the homologous series are insoluble in water in their protonated form, but are soluble at least up to 11.5 mM concentrations with 1 equiv of NaOH. The CA assemblies formed by the water-soluble carboxylates were imaged using cryogenic transmission electron microscopy (cryo-TEM) to capture their solution-state morphologies (Figure 1a−g). L1 and L2 molecules assembled into ribbons hundreds of nanometers to micrometers in length (Figure 1a). In contrast, L3 and L4 formed small nanostructures of various widths that did not have a distinct morphology (Figure 1c, d, respectively). L5 formed a mixture of thin and wide ribbons, while L7 showed exclusively thin ribbons in water (Figure 1e, f, respectively). Lastly, microscopy of L9 revealed micrometer-long nanostructures less than 10 nm in width (Figure 1g). The CA assembly morphologies clearly change by simply varying the linker length, with two dominant trends: increasing the linker length beyond one methylene reduces nanostructure dimensions, while increasing the linker length from five to nine methylenes results in increasing nanostructure aspect ratio.

We obtained small-angle X-ray scattering (SAXS) on bulk solutions of CA assemblies to explore the impact of salt on CA assembly. SAXS provides quantitative, solution-state data regarding the size and shape of 10−100 nm nanostructures. With 50 mM NaCl and without salt, CA solutions displayed scattering slopes between −1 and −2 in the low q regime, indicative of 1D nanostructures with 100-nm-scale features (Figure 2a and Figure S2). The scattering from L1 through L7 molecules was fit to a parallelepiped form factor model, approximating nanostructures as long, flat nanoribbons (Figure S3 and Table S1). Interestingly, L9 can be modeled as thin ribbons or elliptical cylinders with diameters less than 10 nm, suggesting that this CA packs differently from others in the series.

To investigate molecular packing within nanostructures, we obtained wide-angle X-ray scattering (WAXS) data on CA assemblies. We obtained small-angle X-ray scattering (SAXS) on bulk solutions of CA assemblies to explore the impact of salt on CA assembly. SAXS provides quantitative, solution-state data regarding the size and shape of 10−100 nm nanostructures. With 50 mM NaCl and without salt, CA solutions displayed scattering slopes between −1 and −2 in the low q regime, indicative of 1D nanostructures with 100-nm-scale features (Figure 2a and Figure S2). The scattering from L1 through L7 molecules was fit to a parallelepiped form factor model, approximating nanostructures as long, flat nanoribbons (Figure S3 and Table S1). Interestingly, L9 can be modeled as thin ribbons or elliptical cylinders with diameters less than 10 nm, suggesting that this CA packs differently from others in the series.

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solutions gelled with poly(diallyl dimethylammonium chloride) (PDDA). L1–L7 displayed three diffraction peaks between 0.6 and 2.0 Å⁻¹ (Figure 2b), a consequence of diffraction by a crystalline 2D oblique unit cell. These three peaks represent the \( a^* \), b*, and (a + b)* vectors that define the inverse-space 2D oblique lattice unit cell. Despite having identical aromatic and ion functionalizations, the unit cell dimensions differed between L1–L4 and L5/L7 (Table 1, Tables S2 and S3). Specifically, the edge-to-edge chromophore distance (\( a \) vector) increases from 7.8 Å for L1–L4 to 8.6 Å for L5/L7 while the height (\( b \) vector), comparable to \( \pi-\pi \) stacking distances, decreases from 3.8 Å for L1–L4 to 3.6 Å for L5/L7. Furthermore, many of the CAs display the same three diffraction peaks even without screening ions (Figure S4) and with NaCl instead of PDDA (Figure S5 and Table S4). The data suggest that the crystallographic unit cell dimensions are intrinsic to the supramolecular assembly in water and are not altered by the screening salt. We previously observed a similar lack of specificity to salt identity on L5 crystalline packing, suggesting amorphous packing within these nanostructures.

The microscopy and scattering data indicate the presence of two morphologies within the CA series. Specifically, we observe a ribbon morphology (Figure 3a) capable of crystallization into two different packing arrangements for L1–L7 (Figure 3b–d) and a noncrystalline 1D nanostructure with an elliptical cross section for L9 (Figure 3e). Among the crystalline nanostructures, we observed two different unit cell patterns: a “short-linker” unit cell for L1–L4 and an “intermediate-linker” unit cell for L5 and L7. A similar effect, in which the alkyne substituent alters crystalline packing, has been observed with PDIs.39 As L1 has only one methylene unit, that assembly should be controlled primarily by the interplay between \( \pi-\pi \) stacking and electrostatic repulsion. As the number of methylenes is increased, we expect some additional stabilization due to increased hydrophobicity and van der Waals contacts among the molecules (up to 7 kJ/mol per methylene). The observed change in crystalline packing dimensions between L4 and L5 could reflect a shift in the balance of noncovalent forces due to increased contribution of van der Waals attractions. An additional change from crystalline ribbons for L7 to noncrystalline fibers for L9 is observed, possibly resulting from frustration between the van der Waals cohesion and \( \pi-\pi \) stacking forces. Furthermore, another contribution to ordering frustration is the competition between hydrophobic inter-

Table 1. Peak Positions and Calculated Unit Cell Dimensions for CA Linker Series in Aqueous PDDA Solutions, from WAXSS

| molecule | \( a \) (Å) | \( b \) (Å) | \( \theta \) (deg) | area (Å²) |
|----------|--------|--------|----------|---------|
| L1       | 7.83   | 3.74   | 86.5     | 29.3    |
| L2       | 7.83   | 3.77   | 86.5     | 29.4    |
| L3       | 7.77   | 3.79   | 86.5     | 29.4    |
| L4       | 7.72   | 3.81   | 86.3     | 29.3    |
| L5       | 8.57   | 3.64   | 87.2     | 31.2    |
| L7       | 8.61   | 3.64   | 87.3     | 31.3    |
| L9       | –      | –      | –        | –       |

*aSee Supporting Information for determination of unit cell parameters.

Figure 3. Representation of molecular packing within CA nanostructures. (a) Ribbon with CAs packed into 2D oblique lattice. (b) 2D unit cell with overlaid CA packing. (c) Short-linker and (d) intermediate-linker 2D unit cells with labeled parameters, scaled for comparison. (e) Proposed packing of L9 into a cylinder with an elliptical cross section.

actions among the longest linkers and electrostatic repulsion of the carboxylate groups.

We were interested in determining nanostructure thickness to estimate the chromophore–catalyst distance, since this parameter should be important for the electron transfer processes during photocatalysis. We therefore investigated CA films using grazing incidence X-ray scattering (GIXS), a technique that has been previously used to elucidate CA nanostructure thicknesses by measuring the lamellar packing repeat distance in CA films. These CA samples displayed diffraction peaks in the z-direction as a 1:2:3 ratio of \( q \) values with respect to the primary scattering peak, indicative of a lamellar nanostructure packing (Figure 4). Using the primary scattering peak, we found that the real-space distances increase linearly with linker length (Figure S6), except for L9 which does not form ribbons and is therefore not expected to form a lamellar structure. The lamellar d-spacings correspond to the thickness of the ribbon-shaped nanostructures (the smallest dimension of these structures), allowing us to estimate the distance between the PMI chromophore and the external surface of the nanoscale ribbon where a catalyst molecule might bind (Table 2 and Figure S7; see Supporting Information for calculation). Although these distances appear shorter than expected based on molecular modeling, the alkyl linkers may coil or tilt relative to the nanostructure surface. Tilting between the alkyl imide substituent and aromatic perylene have been reported for other perylene imide systems1,35,36 and may contribute to the off-axis scattering features that appear in L4–L7 films (Figure 3d–f, white arrows and Table S5). The high propensity for these nanostructures to stack on top of one another impeded measurements of single-ribbon thicknesses by atomic force microscopy (Figure S8).
We also observed three grazing-incidence diffraction peaks in the $xy$-plane for $L_1$–$L_7$, indicating that these CA assemblies remain crystalline upon drying. The unit cells of $L_1$–$L_7$ shrink in both dimensions by 7% relative to the gel state, likely due to dehydration (Table S5). In this dry state, $L_9$ showed a peak corresponding to 3.7 Å, consistent with the other PMI $\pi-\pi$ stacking distances, and a very broad feature at 4.6 Å, perhaps due to coiling or packing of the alkyl linkers. This value is comparable to interchain distances ($\sim$4.4 Å) reported between alkyl tails within self-assembled monolayers.33 The persistence of CA crystallinity in both hydrated and dried states could allow us to cast crystalline films for other electronic applications.

Absorbance spectra for the CA assemblies were measured in solutions that disfavor self-assembly and in the gel state under the same charge-screening conditions used in the X-ray studies. When molecularly dissolved in DMSO, $L_1$–$L_9$ display identical absorbance patterns with a maximum at 485 nm (Figure S9), indicating that the CAs are electronically identical. This is consistent with previous reports of an orbital node at the imide nitrogen that decouples the PMI core from the surrounding environment present within the nanostructures.34,35

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Table 2. Peak Positions and Calculated Unit Cell Dimensions for CA Linker Series in Dry Films, from GIXS

| molecule | PMI–Surface Distance (Å) | $a$ (Å) | $b$ (Å) | $\theta$ (deg) | area ($Å^2$) |
|----------|--------------------------|---------|---------|---------------|-------------|
| $L_1$    | 3.10                     | 7.53    | 3.63    | 86.5          | 27.3        |
| $L_2$    | 3.25                     | 7.46    | 3.67    | 85.9          | 27.3        |
| $L_3$    | 4.00                     | 7.54    | 3.65    | 86.4          | 27.5        |
| $L_4$    | 4.25                     | 7.41    | 3.63    | 85.9          | 26.8        |
| $L_5$    | 4.5                      | 8.15    | 3.51    | 87.7          | 28.6        |
| $L_7$    | 5.55                     | 8.23    | 3.52    | 87.2          | 28.9        |
| $L_9$    | 9.25                     |         |         |               |             |

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We observed in water solutions highly blue-shifted absorbance maxima for $L_1$–$L_7$ (Figure 5), consistent with strong electronic coupling within H-aggregates arising from cofacial $\pi-\pi$ stacking.24 This blue shift is consistent with a decoupling of the photogenerated exciton from lattice vibrational states.33 $L_1$ and $L_2$ displayed nearly overlapping absorbance spectra with maxima at 424 nm. In contrast, $L_3$ and $L_4$ derivatives exhibit absorbance maxima between 472 and 476, near the absorbance maxima of nonscreened assemblies (Figure S10). We also observed shoulders at 424 nm, which are the same as the blue-shifted maxima of $L_1$ and $L_2$ spectra. These shoulders likely represent absorbance by the crystalline assemblies observed by WAXS and GIXS. The low intensity of the shoulders suggests that many of the $L_3$ and $L_4$ molecules are not actually in a crystalline environment, possibly due to disorder within nanostructures. The $L_5$ and $L_7$ derivatives showed very similar spectra, with maxima at 440 nm, also consistent with relatively high electronic coupling among PMI moieties, although not as strongly coupled as $L_1$–$L_4$ spectra. In contrast, $L_9$ showed a broad, red-shifted spectrum (with respect to the monomeric species), possibly due to translational offsets between adjacent $\pi-\pi$ stacked PMI cores.

Interestingly, we observed an additional red-shifted peak at 570 nm for $L_5$ and $L_7$ but not $L_1$–$L_4$. From our proposed molecular packing, we expect all the PMI transition dipole moments to be parallel to one another, which excludes the possibility of J-aggregation commonly associated with red-shifted peaks. Similar red-shifted peaks have been previously reported for crystals of symmetric perylene diimides (PDIs) that also cannot form J-aggregates.17 These red-shifted features...
are a consequence of variations in HOMO–HOMO overlap among cofacially packed PDIs. The degree of in-phase orbital overlap has been found to depend strongly on the transverse and longitudinal translations between crystalline PDI molecules that appear when the imide substituent is varied.35,36 Therefore, in our crystalline assemblies of L5 and L7, the appearance of the red-shifted peak is likely due to a greater degree of in-phase HOMO–HOMO orbital overlap relative to L1–L4. This increased overlap is consistent with closer π–π stacking of L5 and L7, but we cannot exclude the contribution from translations of the molecular positions within the crystals. Furthermore, it has been shown that differences in orbital overlap within PDI crystals increases the crystals’ abilities to create free charges upon photoexcitation, likely due to greater exciton-splitting abilities.37 We therefore expect the observed differences in orbital overlap to alter the exciton-splitting capabilities of our crystalline assemblies formed from the various PMI molecules.

In order to explore the impact of both chromophore–catalyst distance and packing arrangements on photocatalysis, we investigated light-driven proton reduction from CA gels, similar to our previously described procedure. Briefly, gels were prepared in sealed glass vessels by the addition of aqueous PDDA solutions (5 wt %) to aqueous CA solutions (11.5 mM before dilution). CA-PDDA gels were aged overnight prior to mixing with the sacrificial electron donor ascorbic acid (0.85 M, pH 4) and a water-soluble P2N2 nickel catalyst (19.5 μM; see Figure S11 for structure). As expected, the CA gels surrounded by this highly screened solution retain the previously described molecular packing within the nanostructures (Figure S12). After 18 h of illumination, the amount of H2 present in the headspace was measured via gas chromatography (GC). We observed that L5 and L7 produced significantly more H2 than the molecules with either shorter or longer linker lengths (Figure 6).

Interestingly, we observed anomalously high H2 photosensitization by the L3 relative to the other short linkers (L1, L2, and L4). In contrast to the other CA-PDDA materials, which form gels, L3 formed a fine red precipitate upon the addition of PDDA. SEM of the precipitate showed the precipitate to have nanostructured features similar to the other gels (Figure S13). Dilution with aqueous ascorbic acid resuspended some of this material to give an orange suspension surrounding the red solid (Figure S14). While photocatalysis with this material afforded 367 turnovers of H2, localization of the suspension back into the precipitate via centrifugation yielded approximately 240 turnovers (Figure S15), which is more consistent with H2 produced by L2 and L4 (187 and 188, respectively). It appears that the dispersed suspension can capture more of the incident light than the solid precipitate at the bottom of the tube or the other CA-PDDA gels. We observed that L1–L4, having the shortest chromophore–surface distances, yielded similar and low TONs. While short distances may favor electron transfer, charge recombination could also be favorable at these distances. Therefore, the photocatalytic activity at short distances does not appear to be dominated by the chromophore–catalyst distance. However, L5 photosensitized more H2 than L7, due to the smaller distance between the PMI core and catalyst for L5. Since L4 and L5 appear to have very similar chromophore–surface distances (see Table 2), we were surprised to observe such large differences in H2 production. As discussed previously, L5 and L4 crystallize into different unit cells. This change in molecular packing of L5 was accompanied by a red-shifted absorbance peak, indicative of relatively higher in-phase HOMO–HOMO orbital overlap within that assembly. This suggests that the two systems may adopt different pathways after absorption of a photon. We expect the mechanism of photocatalytic H2 evolution to proceed by formation of a photogenerated exciton, followed by electron transfer from excess ascorbate in solution (330 times relative to CA and 24 000 times relative to catalyst) to give a PMI radical anion. For H2 to be produced, the Ni catalyst must be reduced two times by CA radical anions and receive two protons from solution. Higher in-phase orbital overlaps between molecules has been shown in PDI crystals to result in higher photoconductivities.37 It has been hypothesized that the increase in photogenerated charge carrier collection is due to increased exciton splitting efficiencies from higher orbital overlap.36 Since L5 has a higher orbital overlap than L4, it should also have a higher exciton splitting ability to generate the free charges needed for the electron transfer events required for H2 production. Therefore, future efforts to maximize solar-to-fuel conversion would benefit from a focus on improving orbital overlaps between CA molecules.

The supramolecular assemblies formed by L9 molecules in water, which did not reveal any crystallinity in solution, yielded the lowest values of catalytic turnovers of the homologous series studied here. While the absence of crystalline peaks makes it difficult to determine the molecular packing geometry, fluorescence measurements showed an emission maximum at 680 nm (Figure S16), comparable to known PMI excimers.24 The low-energy excimer states formed in L9 assemblies may function as low-energy trap states that could lower H2 photosensitization yields. Furthermore, the L9 chromophore–surface distance, at ~9 Å, may also limit electron transfer to and from the aggregated PMI cores.

### CONCLUSIONS

Varying the linker length connecting conjugated cores and ionizable groups in chromophore amphiphiles has very significant and not easily predictable consequences on their supramolecular structure and photocatalytic performance. Increasing the linker length results in changes to both the nanoscale morphology and molecular packing arrangements. The molecular packing for linkers of five and seven methylenes...
showed the highest in-phase HOMO–HOMO orbital overlap, resulting in greater exciton-splitting capabilities to boost turnover numbers in photocatalytic hydrogen production. We conclude that exciton splitting within supramolecular materials for photocatalytic reactions will be critical in the development of integrated scaffolds for solar-to-fuel conversion.

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