Molecular Packing of Amphiphilic Nanosheets Resolved by X-ray Scattering

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Supporting Information

ABSTRACT: Molecular packing in light harvesting 2D assemblies of photocatalytic materials is a critical factor for solar-to-fuel conversion efficiency. However, structure—function correlations have yet to be fully established. This is partly due to the difficulties in extracting the molecular arrangements from the complex 3D powder averaged diffraction patterns of 2D lattices, obtained via in situ wide-angle X-ray scattering. Here, we develop a scattering theory formalism and couple it with a simple geometrical model for the molecular shape of chromophore 9-methoxy-*N*-(sodium hexanoate)perylene-3,4-dicarboximide (MeO-PMI) used in our study. This generally applicable method fully reproduces the measured diffraction pattern including the asymmetric line shapes for the Bragg reflections and yields the molecular packing arrangement within a 2D crystal structure with a remarkable degree of detail. We find an approximate edge-centered herringbone structure for the PMI fused aromatic rings and ordering of the carboxypentyl chains above and below the nanosheets. Such a packing arrangement differs from the more symmetric



face-to-face orientation of the unsubstituted PMI rings. This structural difference is correlated to our measurement of the reduced catalytic performance of MeO-PMI nanosheets as compared to the mesoscopically similar unsubstituted PMI assemblies.

INTRODUCTION

Amphiphilic perylene monoimide (PMI) compounds, containing ionizable groups, have the ability to self-assemble into 2D nanostructures, which gel and develop strong diffraction peaks in the presence of charge-screening ions. These systems have been suggested as bioinspired photocatalytic scaffolds for water splitting reactions due to their ability to support mobile excitons, propagating along the $\pi - \pi$ stacking direction of the nanostructures.^{1,2} The highly ordered nature of the nanostructures allows in-depth analysis of how different crystal packing arrangements impact the catalytic ability of such materials, a feature not possible for amorphous assemblies.³ It is known that the electronic and self-assembly properties of rylene-based compounds can be controlled by addition of substituent groups at different locations on the aromatic core.^{3–8} This provides an opportunity to create a library of different amphiphilic PMIs, which assemble into distinct crystalline packing arrangements with corresponding unique photophysical and catalytic properties. In order to establish a clear structure-property relationship, small- and wide-angle X-ray scattering techniques (SAXS and WAXS) are vital methods for elucidating the structure of 2D PMI materials, which typically do not form 3D single crystals. Furthermore, single crystal data would not necessarily replicate the assembly state in solution; hence, in situ solution WAXS experiments are of primary interest for studying such

materials as it removes the risk of structural modifications caused by environment change. The development of X-ray scattering theory based models will allow for an improved understanding of the crystal structures of self-assembled 2D nanostuctures and facilitate the discovery of photocatalytic scaffolds with superior properties.

In the current work we construct an approach for analyzing the in situ and ex situ WAXS patterns of 2D molecular assembly nanostructures through the example of 9-methoxy-*N*-(sodium hexanoate)perylene-3,4-dicarboximide (MeO-PMI). Furthermore, we investigate the light harvesting capacity and photocatalytic activity of this molecular assembly in solution with a transition-metal-based catalyst.

EXPERIMENTAL METHODS

Synthesis and Catalysis. MeO-PMI was synthesized by Buchwald–Hartwig type coupling of 9-bromo-*N*-(methyl hexanoate)perylene-3,4-dicarboximide with dry methanol with subsequent hydrolysis by sulfuric acid (see Supporting Information, Section 1). See Supporting Information, Section

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Figure 1. (a) Pictures of vials containing 1 mM MeO-PMI monomer dissolved in DMSO (left) and assembled nanostructure in water (7.25 mM, right). (b) Normalized UV–vis absorbance spectra for MeO-PMI in DMSO (1 mM) blue and in water (7.25 mM) red. (c) AFM height mode image of MeO-PMI spin-coated from 8.7 mM aqueous solution onto freshly cleaved mica. (d) Height line cut of AFM image in part c (blue line). (e) Cryo-TEM of 8.7 mM aqueous solution. (f) SAXS data with Porod analysis and minima sensing the thickneess of the nanosheets.

2, for $Na_2[Mo_3S_{13}]$ ·5H₂O synthesis and Supporting Information, Section 3, for hydrogen production experiments.

Wide-Angle X-ray Scattering (WAXS) and Small-Angle X-ray Scattering (SAXS). X-ray measurements were performed at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) 5ID-D station at the Advanced Photon Source (APS). An X-ray energy of 12.00 keV corresponding to a wavelength of 1.033 Å was selected using a double-crystal monochromator. Data were collected simultaneously across three Rayonix CCD detectors. Sample-todetector distances were 201 mm for WAXS, 1013 mm for MAXS, and 8500 mm for SAXS. The scattered intensity was recorded in the interval 0.002 < q < 3.147 Å⁻¹. The wavevector transfer is defined as $q = (4\pi/\lambda) \sin(2\theta/2)$, where 2θ is the scattering angle. Exposure time was 1 s. Samples of 7.25 mM MeO-PMI were oscillated with a syringe pump during exposure to prevent beam damage. Background samples containing water or 50 mM NaCl were also collected in order to perform background subtractions.

Grazing-Incidence Wide-Angle X-ray Scattering (GI-WAXS). Data were collected at APS station 8ID-E. The beam energy was 7.35 keV, sample-to-detector distance 212 mm, and the incident angle 0.2°. Samples were prepared by drop-casting 30 μ L of MeO-PMI (7.25 mM) solution onto a clean glass substrate. The solutions were allowed to dry in air overnight. X-ray scattering was measured using a Dectris Pilatus 1M detector. 2D data were processed using GIXSGUI.⁹ Pixel-by-pixel corrections have been applied for Pilatus and Rayonix detectors: $I_{corrected} = I_{raw}E_mE_dFC_sP^{-1}$, where E_m and E_d are medium and detector efficiency correction (which includes absorption correction), flat-field correction F removes sensitivity variation among the pixels, C_s is the solid angle

correction, and P is the polarization correction, which is horizontal in these experiments.

Atomic Force Microscopy (AFM). AFM characterization was performed at Northwestern's NUANCE Facility using a Bruker Dimension ICON atomic force microscope at ambient conditions. Tapping mode was utilized with single-beam silicon cantilevers with nominal oscillation frequency of 300 kHz. Solutions of 7.25 mM MeO-PMI were spin-coated (10 μ L) on freshly cleaved mica substrates at 2000 rpm.

Ultraviolet–Visible Absorbance Spectroscopy. Absorbance spectroscopy on chromophore amphiphile (CA) solutions (7.25 mM) was performed at the NUANCE Facility in a 0.05 mm path length, closed demountable quartz spectrophotometer cell (Starna Cells) using a Shimadzu UV-1800 spectrophotometer.

Cryogenic Transmission Electron Microscopy (Cryo-TEM). Cryo-TEM imaging was performed on a JEOL 1230 microscope at the NUANCE Facility, operating at 100 kV. A 6.5 μ L droplet of 8.7 mM MeO-PMI was placed on either a lacey carbon copper grid or a C-flat grid (CF-4/2-4C-25, Electron Microscopy Science). The grid was held by tweezers mounted on a Vitrobot Mark IV equipped with a controlled humidity and temperature environment. The temperature was set to 24 °C, and humidity was held at 90%. The specimen was blotted and plunged into a liquid ethane reservoir cooled by liquid nitrogen. The vitrified samples were transferred to a Gatan 626 cryo-holder through a cryo-transfer stage cooled by liquid nitrogen. During observation of the vitrified samples, the cryo-holder temperature was maintained below -180 °C. The images were recorded with a CCD camera.



Figure 2. (a) GIWAXS reciprocal space data of drop-cast dry sample. q_z is the out-of-plane component of the scattering vector, and the in-plane component is $q_r = \sqrt{q_x^2 + q_y^2}$. (b) Reciprocal space schematic representation of a form factor (red cylinder) at a particular reciprocal lattice vector \vec{G}_{ir} . Parallelogram outlined by dashed blue lines represents unit cell in reciprocal space.

RESULTS AND DISCUSSION

MeO-PMI is bright red and fluorescent when dissolved in disassembling organic solvents such as DCM or DMSO but appears brownish after assembly in water (Figure 1a). The absorbance of the monomer shows a broad featureless band centered around 520 nm, which undergoes a significant blueshift in water, indicating the formation of a strongly Haggregated species (Figure 1b, see also Figure S7). AFM imaging of MeO-PMI spin-coated on a freshly cleaved mica from aqueous solution reveals the presence of well-defined nanosheets with widths on the order of 100 nm and heights of roughly 2.0 nm (Figure 1c,d). Cryogenic transmission electron microscopy (cryo-TEM) confirms the sheet morphology (Figure 1e). Solution SAXS data (Figure 1f) has a Porod slope of -2, characteristic of 2D objects,^{10,11} and minima corresponding to a 2.1 nm thickness, consistent with the AFM results.

To evaluate the potential catalytic activity of MeO-PMI nanosheets, proton reduction samples were prepared by addition of a cationic polymer (polydiallyldimethylammonium chloride) to an 8.7 mM aqueous solution. A solution of sacrificial electron donor (1.7 M ascorbic acid) and 3.5 μM Na₂[Mo₃S₁₃]·5H₂O catalyst was added. The samples were subsequently purged with argon for 10 min and placed on an illumination source for 18 h. The headspace of each vial was examined using gas chromatography to determine the amount of hydrogen gas produced. The MeO-PMI produced 0.62 μ mol of H_2 , which corresponds to a catalyst turnover number (TON) of 178 \pm 75. MeO-PMI samples were compared to the previously studied system of unsubstituted PMI amphiphile which produced 5.85 μ mol of H₂ under the same experimental conditions, corresponding to an order of magnitude more H₂ produced and a TON of 1695 \pm 314.¹ We attribute this difference in hydrogen production ability between PMI and MeO-PMI to different crystal structures formed by each species, as discussed later. It is known that the crystal packing of these photocatalytic materials greatly influences the hydrogen production by changing the materials ability to support longlived excited states.² As such, it is important to determine the different crystal structures adopted by various substituted and unsubstituted PMIs with a high degree of accuracy to better understand their effect on the material properties.

MeO-PMI nanosheets form 2D crystal lattices in freshly prepared solutions even without the addition of charge screening ions. This is a behavior different from the amphiphile with no substituent at the 9-position¹ and can be attributed to a substantially larger electric dipole moment for the MeO-PMI monomer (see below). 2D MeO-PMI nanosheets exhibit multiple diffraction features both in the ex situ grazing incidence wide-angle X-ray scattering (GIWAXS) of the dropcast films on glass substrates and in solution WAXS experiments. We develop a model that reproduces all peaks in the GIWAXS and the WAXS diffraction patterns in peak position and intensity. Furthermore, the analysis replicates the asymmetric line shapes for the diffraction peaks from PMI assemblies in solutions, observed via WAXS. The unusual asymmetric peak shape was previously observed for diffraction from graphite flakes with small surface absorbed molecules and is characteristic for randomly oriented 2D crystals.¹²⁻¹⁵ Our method extends the WAXS analysis to the case of assembly of large, complex molecules and allows extraction of structural information with a remarkable degree of detail not previously possible. It should be noted that solution WAXS contains all the information to reconstruct the 2D crystal structure, and analysis can be applied to it standalone, independent of the GIWAXS. We will proceed with the analysis of both cases in sequence.

PMI nanosheets lack the rigidity of 3D crystallites, making atom-by-atom diffraction refinement unfeasible. However, we demonstrate that it is possible to use slab models, which emulate reasonably well both the electron density distribution of the lattice basis and degrees of freedom of modified PMI molecule. This assumption validates itself with excellent fits to the experimental data. As will be shown below, the identified structure is not what one would expect by simply juxtaposing $\pi - \pi$ stacked PMI molecular threads side-by-side in rows, but rather an edge-centered herringbone lattice bearing resemblance to other organic herringbone structures observed in thin film¹⁶ and single crystal diffraction.¹⁷⁻²⁰

The GIWAXS pattern of a drop-cast sample manifests rods parallel to the q_z axis (Figure 2a), a distinctive feature of 2D crystals lying flat on a substrate with crystal domains having an azimuthal rotational randomness. Intense spots along the q_z axis (centered at $q_r = 0$) indicate multilayering with a period of 20.6 Å (Figure 2a), close to the height of a single sheet revealed by AFM (Figure 1d) and SAXS minima (Figure 1f). The number of layers in a single specular domain, estimated by the Scherrer equation, is N = 6. However, this spacing period is dependent upon the evaporation conditions of drop-casting and has been observed to vary between 20 and 25 Å. Spin-casting, which



Figure 3. (a) T-shaped projection model of the MeO-PMI. Red arrow indicates dipole moment. (b) In-plane line cut of GIWAXS data and model fit to the data with $R^2 = 0.952$ (see Figure S9 for log plot). Miller indices of diffraction peaks are also shown. Blue dashed line indicates the difference between data and model fit. It is offset for clarity. (c) Projection of the basis onto the plane of the 2D sheet with selected parameters values determined from the analysis. Longer outlined rectangles represent the perylene fused rings, solid rectangles the carboxypentyl chain above the 2D plane, and faded rectangles below. (d) Idealized unit cell with solid and dashed wedges representing carboxypentyl chains above and below the plane of the sheet, respectively. (e) Tilt angles of π - π stacked perylenes (longitudinal and transverse shifts are not shown).

efficiently removes the water between the layers, yields a value of 20.5 Å (see Supporting Information, Section 5).

The diffraction condition for a particular reciprocal lattice vector \vec{G}_i is depicted on Figure 2b. The red cylinder shows schematically the Fourier transform of the electron density of the sheet in reciprocal space at a 2D lattice vector G_i . Nonzero diffraction intensity results when scattering vector \vec{q} intersects the cylinder (generalized Laue condition). The diameter and height of this cylinder are restricted correspondingly by the domain size and the component of the form factor along the normal \vec{n} to the sheet (*h* is the height of the sheet). The latter gives rise to the rods in GIWAXS. To enforce rotational randomness of drop-cast sheets around normal \vec{n} , integration of intensity needs to be carried out only over azimuthal angle ϕ of vector \vec{q} , as rotation of the lattice at fixed \vec{q} is equivalent to fixing the lattice and rotating the vector \vec{q} . On the other hand, in solution WAXS, spherical randomness of nanosheets requires averaging over the solid angle (i.e., over both azimuthal and polar angles) which results in a mapping of the 2D GIWAXS information onto 1D diffraction pattern and coupling of lateral and specular information.

We start with formalizing the model for the GIWAXS data from the nanosheets. The in-plane line cut through the data (Figure 3b, red line) at $q_z \approx 0$, where the scattering vector \vec{q} lies in the plane of the nanosheets, is only sensitive to the 2D projection of the (electron density) structure. From the experimental peak positions, the 2D lattice is determined to be oblique with lattice parameters a = 12.41 Å, b = 8.95 Å, and $\gamma = 89.5^{\circ}$ for MeO-PMI (see Supporting Information, Section 4). From the assigned *hk* Miller indices (vertical dashed lines in Figure 3b) one can see that peaks differing only in the sign of their $h \times k$ product (e.g., 31 and $\overline{31}$) have a small *q* separation. This small peak splitting would disappear if the unit cell were rectangular. However, fixing γ at 90° causes a 50% increase to the value of χ^2 generated by the numerical fitting procedures described below.

As depicted in Figure 3a, the width of an individual PMI molecule is 6.6 Å, while the estimate of π - π stacking distance²¹ is ~4 Å. This together with the lattice constants indicates that the basis (Figure 3c) of the 2D crystal structure (Figure 3d) consists of four molecules. After determining the lattice parameters from the peak positions, deducing the 2D crystal structure then reduces to the task of establishing the arrangement of molecules in the basis from analyzing the intensities and line shapes of the set of diffraction peaks.

The in-plane scattered intensity can be written in a form of the following integral:

$$I(q) \propto \sum_{i} \int_{0}^{2\pi} e^{-(1/2\sigma^{2})(\vec{q} - \vec{G}_{i})^{2}} |F(\vec{q})|^{2} d\phi$$
(1)

where *F* is the form factor of the basis projected onto the plane of the nanosheet, and the summation is over reciprocal 2D lattice vectors \vec{G}_i . The latter is easily expressed in terms of unit cell parameters *a*, *b*, and γ . The first factor of the integrand is a result of a Gaussian approximation to the sum over repeated unit cells within a single domain and is characterized by the spread σ , which is inversely proportional to the domain size.²² This factor imposes the in-plane width constraint in reciprocal lattice (diameter of the red cylinder in Figure 2b). For the mesoscale PMI assemblies in our case, σ is small. Therefore, the form factor of the molecule, with all dimensions less than 2 nm, does not substantially vary in the relevant integration space and can be pulled out of the integral, which then can be resolved analytically, yielding



Figure 4. (a) Solution WAXS experimental and fitted curves with peaks indexed for full range of q values. (b) Expanded view of the (11) peak along with the fit.

$$I(q) \propto 2\pi \sum_{i} e^{-(1/2\sigma^{2})(q^{2}+G_{i}^{2})} B_{0}\left(\frac{qG_{i}}{\sigma^{2}}\right) |F(\vec{G}_{i})|^{2}$$
(2)

where $B_0(x)$ is the modified Bessel function of the first kind. Since $\frac{qG_i}{\sigma^2} \gg 1$ for almost all of the WAXS region, an asymptotic expansion for the Bessel function, $B_0(z) \xrightarrow{z \to \infty} \frac{e^z}{\sqrt{2\pi z}}$, can be used, resulting in

$$I(q) \propto \sum_{i} \frac{\sigma}{\sqrt{qG_i}} e^{-(1/2\sigma^2)(q-G_i)^2} |F(\vec{G}_i)|^2$$
(3)

Since lattice vibrational effects in 2D systems make the Lorentzian distribution a better descriptor of the peak shape than Gaussian, 23,24 we recast expression 3 as

$$I(q) \propto \sum_{i} \frac{\sigma}{\sqrt{qG_{i}}} \frac{1}{1 + \frac{(q-G_{i})^{2}}{\sigma^{2}}} |F(\vec{G}_{i})|^{2}$$
(4)

The Lorentz factor $\frac{1}{\sqrt{qG_i}}$ plays a significant role in WAXS data fitting when the *q*-range is large.

To construct a parametrized projected form factor F for basis, we model each of the four PMI molecules with two rectangular solid boxes: a thin plate for the fused rings²⁵ and a narrow rod for the carboxypentyl chain pinned to the center of the top side of the plate. The form factors for the projections of the plate and chain oriented with their longer projected sides along the *x*-axis (i.e., side *a* of the unit cell) are correspondingly

$$f_p(\vec{q}, \vec{l}_p) = n_p \operatorname{sinc}\left(\frac{q_x l_{p,x}}{2}\right) \operatorname{sinc}\left(\frac{q_y l_{p,y}}{2}\right)$$
(5a)

$$f_c(\vec{q}, \vec{l}_c) = n_c \operatorname{sinc}\left(\frac{q_x l_{c,x}}{2}\right) \operatorname{sinc}\left(\frac{q_y l_{c,y}}{2}\right) e^{iq_x l_{c,x}/2}$$
(5b)

where n_p and n_c are correspondingly the total number of electrons in the plate and carboxypentyl chain and \vec{l}_p and \vec{l}_c are the corresponding sizes of sides. Each of the four plates and rods is given an individual rotational angle α_{τ} around the normal \vec{n} to the 2D lattice sheet, which in the case of the rod models the rotational freedom of the carboxypentyl group about the C–N σ bond. The fitted width of the plate indirectly accounts for the possible tilt of the molecule (polar angle to \vec{n} , Figure 2b). Hence, the basis form factor can be written in the following general form:

$$F(\vec{q}) = \sum_{\tau=1}^{4} f_p [\hat{R}(-\alpha_{p,\tau})\vec{q}, \vec{l}_p] e^{i\vec{q}\cdot\vec{r}_{\tau}} + \sum_{\tau=1}^{4} f_c [\hat{R}(-\alpha_{c,\tau})\vec{q}, \vec{l}_c] e^{i\vec{q}\cdot\vec{r}_{\tau}}$$
(6)

where α is the rotation angle of each individual plate and chain around the normal \vec{n} , \hat{R} is the 2D orthogonal rotation matrix around normal \vec{n} , and r_{τ} are the positions of four molecules of the basis with respect to the origin of the latter. Ab initio DFT (B3LYP) optimization with 6-31G basis for the plate (MeO-PMI with carboxypentyl group replaced by methyl; see Supporting Information, Section 9) indicates a large dipole moment of 8.6 D, thereby strongly favoring an antiparallel arrangement of neighbors. As a comparison, an amphiphile with no substituent at the 9-position has a dipole moment of 6.7 D. This effect is due to the electron-donating ability of the methoxy group to the aromatic system.

The obtained analytical expression for the scattering intensity (eqs 4 and 6) facilitates numerical fitting procedures by allowing deployment of not only local but also global optimization techniques, such as random search²⁶ and differential annealing²⁷ methods. Figure 3b shows the fit to the experimental data with rotational angles and plate width as the sought out fitting parameters (the sides of the rods were fixed to be 1.8 Å (the H–H distance) and 4.8 Å (the projected length of carboxypentyl chain)).

Figure 3c depicts the obtained angles and plate width. Figure 3d shows the idealized unit cell where inferred angles were equalized within $\pm 10^{\circ}$ margin to demonstrate the closest most symmetric 2D lattice, which for the plates is an edge-centered herringbone structure. The inferred $\pi - \pi$ stacking distance and transverse shift are both 3.2 ± 0.2 Å (Figure 3d, orange and purple arrows, respectively). Moreover, the chains themselves arrange in symmetric lattices both above and below the plane of the sheet. This latter ordering further manifests itself in a spot on the GIWAXS pattern (Figure 2a) at $q_r = 0.5 \text{ Å}^{-1}$ and $q_z =$ 0.45 Å⁻¹, corresponding to in-plane spacing $\frac{2\pi}{0.5} = 12.6$ Å and polar angle $\tan^{-1}\left(\frac{0.45}{0.5}\right) = 42^{\circ}$, in good agreement with a =12.4 Å and $180^{\circ} - \angle N - C - (C_4 H_8 COO^-) = 45^{\circ}$ (Figure 3a,d, see Supporting Information, Section 8). Carboxyalkyl chains can affect the geometry of approach of the catalyst to the stacked aromatic rings, which carry the propagating photogenerated electrons.

Simpler models, which either do not take chains into account or fix chain-plate angles, fail to reproduce the combined intensity of the (31) and $(\overline{3}1)$ peaks (see Supporting

Information, Sections 12 and 13). The emergence of a faint rod at $q_r = 0.25$ Å⁻¹ in Figure 2a, corresponding to a doubling of lattice constant *a*, indicates a small distortion that if accounted for would result in further doubling of the basis. However, our model does not consider these effects to avoid overfitting with too large of a number of parameters.

The obtained projected width of 9.1 Å is significantly larger than the actual 6.6 Å width of PMI as a result of tilting of the molecule. The computed tilt angle from geometrical sizes of the molecules is 15.6° ; therefore, the rotational angle between two stacked molecules is 31° (Figure 3e), which is in good agreement with single crystal diffraction and computational results on cognate compounds^{21,28–30} (see Supporting Information, Section 8).

Compared to the above-described GIWAXS, the peaks in the solution WAXS experiments for 2D lattices exhibit only slightly shifted peak positions but have characteristic asymmetric line shapes arising from the 3D randomness of the orientation of the nanosheets²³ (Figure 4). This is mathematically equivalent to solid angle averaging of rods located at 2D reciprocal lattice vectors \vec{G}_i . Figure 2b gives a qualitative understanding of the phenomenon: as the magnitude of \vec{q} increases, the $|\vec{q}| = \text{const}$ sphere intersects the nonzero form factor region (red cylinder, q_{\min}) and scattering intensity starts to rise sharply as both the form factor (due to movement toward the reciprocal lattice point G_i) and the surface area cut by the cylinder increase. The width of the rise, which is of the order of σ , contains the information regarding the domain size. After passing the maximum point (which is not necessarily at G_i because of the combination of the mentioned two factors), a long tail emerges, even beyond $G_i + \sigma_i$ as there are still corners of the cylinder with higher q_z values that intersect the $|\vec{q}| = \text{const}$ sphere. Therefore, the decrease of scattered intensity in the tail is both due to moving away from the G_i position as well as the reduced form factor at higher q_z . It is possible to show that peak shift and high-q tail width are nonlinear combinations of h and σ_{i} with only a weak dependence on G_i (see Supporting Information, Section 7). Spherically averaged intensities for solution WAXS can be expressed as

$$I(q) \propto \sum_{i} \int_{0}^{2\pi} \int_{0}^{\pi} e^{-(1/2\sigma^{2})(\vec{q}-\vec{G}_{i})^{2}} |F(\vec{q})|^{2} \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi$$

$$\tag{7}$$

where angle θ is the polar angle of \vec{q} with respect to normal \vec{n} . If in solution there is a preferential orientation of nanosheets (e.g., because of solvent flow through a narrow capillary), the integration range of ϕ and θ would be arcs (possibly weighted) smaller than 2π and π , respectively. However, by assuming that the domains are sufficiently large, the exponential factor will essentially confine the nonvanishing region of the integrand within the tight vicinity of the reciprocal lattice vector, thereby allowing the extension of the integration limits to those in eq 7. Within that region the in-plane variation of the form factor F can be neglected, resulting in

$$I(q) \propto \sum_{i} \int_{0}^{2\pi} \int_{0}^{\pi} e^{-(1/2\sigma^{2})(\vec{q} - \vec{G}_{i})^{2}} |F(\vec{G}_{i}, q_{z})|^{2} \sin \theta \, d\theta \, d\phi$$
(8)

We carry out the ϕ integration as before, reducing the integral to only an integration over θ . The out-of-plane resolution of solution WAXS does not allow refinement of density profile along the normal \vec{n} in sufficient detail to distinguish between the perylene plate and carboxypentyl chain; hence, one can use a single slab model to describe the electron density profile along the normal \vec{n} , which is a simple sinc function in reciprocal space as in eqs 5. This simplifying assumption decouples projected and normal components of the form factor, resulting in

$$I(q) \propto \sum_{i} |F_{\parallel}(\vec{G}_{i})|^{2} \int_{0}^{\pi} e^{-(1/2\sigma^{2})(q\sin\theta - G_{i})^{2}} \sigma \sqrt{\frac{2\pi \sin \theta}{G_{i}q}} \times |F_{\perp}(q \cos \theta)|^{2} d\theta$$
(9)

where F_{\parallel} is given by eq 6 and $F_{\perp}(q) = \operatorname{sinc}\left(q\frac{h}{2}\right)$ where *h* is the electron density weighted height of the sheet. The integration in eq 9 can be performed numerically by using algebraic summation procedure to make it computationally efficient for multiparameter fitting (see Supporting Information, Section 6). Figure 4a shows the fit to the solution WAXS experimental curve for MeO-PMI. The obtained angles are in agreement with our GIWAXS analysis; however, the lattice is slightly larger: a = 12.88 Å, b = 9.24 Å, $\gamma = 89.8^{\circ}$ which can be attributed to electrostatic screening of charges and dipoles in water and increased entropy of the system.

The domain size estimate, by the Scherrer formula,²² for the sheets in solution is substantially larger than that in drop-cast form, 456 Å vs 274 Å, pointing to a high level of stability of MeO-PMI 2D sheets in solution. The fitted thickness of the sheet is 14 Å, a value smaller than 21 Å obtained by SAXS and GIWAXS. This is due to the fact that carboxypentyl chains are half as dense in numbers per unit area on each side of the sheet because of antiparallel geometry of perylene plates (WAXS senses electron density weighted average height in our model), and also due to the hydrated cationic counterion spacer inbetween the 2D layers which is present in drop-casted film for GIWAXS, but is not crystallographically correlated with the 2D lattice to make it contribute to solution WAXS. Overall, the presented general approach for 2D molecular crystals reveals the molecular packing in the MeO-PMI assemblies. In particular, we show that the fused aromatic ring plates pack in an edge-centered herringbone lattice, which is substantially different from the face-to-face packing arrangement of these plates in assembly of unsubstituted PMI. This difference is likely the origin of the reduced hydrogen production in the presence of MeO-PMI as compared to the case of unsubstituted PMI, as discussed next.

The general principle of the photoactivity of the PMI-based assemblies involves absorption of a photon to create a bound electron-hole pair on the same molecule [Frenkel exciton (FE)], which subsequently undergoes charge separation such that the electron and hole reside on different molecules. The hydrogen production is mediated by the relocation of the photogenerated electrons via these charge-separated excitons to the proton reducing catalyst $([Mo_3S_{13}]^{2-})$. The charge transfer between adjacent PMI molecules depends upon the extent of nearest-neighbor HOMO-HOMO and LUMO-LUMO overlaps, which are quantified by the charge transfer integrals for electron and hole, t_e and t_h .^{2,31,32} The distortions from the faceto-face parallel stacking (unsubstitued PMI) to the tranversely shifted nearest-neighbor arrangements (MeO-PMI) should render these overlap integrals small, and possibly of opposite signs, thereby also reducing the width of charge separated (CT) band of states which is of the order of $4|t_e + t_h|$. Furthermore, the narrow and blue-shifted peak in the UV-vis spectrum

(Figure 1b), which is without accompanying red-shifted secondary peak, in contrast to PMI, suggests that the ratio of the energy separation between FE state and CT band of states to the width $4|t_e + t_h|$ is larger for MeO-PMI than for PMI.² This reduces the mixing between the CT band of states and FE state, thereby preventing efficient charge separation, and as a consequence lowers the catalytic activity of MeO-PMI scaffold.

CONCLUSION

Molecular packing of PMI photocatalytic nanostructures is a key parameter controlling catalytic yield. The presented general approach for extracting the molecular packing details in 2D molecular crystals from WAXS patterns established the ordering modes of aromatic and chain fragments of MeO-PMI. The diffraction theory successfully reproduced the asymmetric line shape of diffraction peaks in solution WAXS by incorporating the form factor of the basis and yielded the electron density averaged height of the sheet in situ. Approximate edge centered herringbone arrangement of aromatic rings is further revealed, with large transverse shift and significant tilt of the molecules. Information on domain size was demonstrated to be contained in the low q shoulder of the peaks, while the high q shoulder had a nonlinear coupling of the height and domain size. We showed that the diffraction peaks in solution WAXS are shifted from the positions of reciprocal lattice vectors. This approach is applicable to crystalline 2D structures both in bulk solutions and at interfaces and is adaptable for testing detailed theory-based atomic-scale models.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b11391.

Synthesis of MeO-PMI, Na₂[Mo₃S₁₃]-SH₂O, hydrogen production experiments, peak matching for unit cell parameter deduction, X-ray reflectivity and grazing incidence X-ray scattering, numerical integration procedure for WAXS intensity, WAXS peak position shifts and shoulder widths estimation, tilt angle deduction and scattering from tilted chains, molecular orbitals and partial charges of the monomer, cyclic voltammetry, UV–vis spectra for various concentrations of MeO-PMI, WAXS sensitivity to structural details, statistical errors on GIWAXS fitted parameters (PDF)

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Notes

The authors declare no competing financial interest.

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