Controlling Visible Light Driven Photoconductivity in Self-Assembled Perylene Bisimide Structures

James J. Walsh, †‡ Jonathan R. Lee, †§ Emily R. Draper, † Stephen M. King, † Frank Jäckel, †§ Martijn A. Zwijnenburg, † Dave J. Adams, †§ and Alexander J. Cowan* †§

†Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, United Kingdom.
‡Stephenson Institute for Renewable Energy, University of Liverpool, Peach Street, Liverpool L69 7ZF, United Kingdom
§Department of Physics, University of Liverpool, Oxford Street, Liverpool L69 7ZE, United Kingdom
ISIS Facility, Rutherford Appleton Laboratory, Science and Technology Facilities Council, Didcot, Oxfordshire OX11 0QX, United Kingdom
*Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom

Supporting Information

ABSTRACT: Alanine-functionalized perylene bisimides (PBI-A) are promising photoconductive materials. PBI-A self-assembles at high concentrations (mM) into highly ordered wormlike structures that are suitable for charge transport. However, we previously reported that the photoconductive properties of dried films of PBI-A did not correlate with the electronic absorption spectra as activity was only observed under UV light. Using transient absorption spectroscopy, we now demonstrate that charge separation can occur within these PBI-A structures in water under visible light. The lack of charge separation in the films is shown by DFT calculations to be due to a large ion-pair energy in the dried samples which is due to both the low dielectric environment and the change in the site of hole-localization upon drying. However, visible light photoconductivity can be induced in dried PBI-A films through the addition of methanol vapor, a suitable electron donor. The extension of PBI-A film activity into the visible region demonstrates that this class of self-assembled PBI-A structures may be of use in a heterojunction system when coupled to a suitable electron donor.

INTRODUCTION

Perylene bisimides (PBIs) are increasingly being explored for use in organic photovoltaic and solar fuel applications due to their large visible extinction coefficients, high chemical and thermal stabilities, and potential synthetic tunability. PBIs are known to self-assemble through π−π-stacking even at very low (<10−5 M) concentrations leading to the formation of aggregates, the structure of which can greatly impact upon the photophysical and photochemical properties of the PBI. However, stacking and subsequent supramolecular structure formation can be difficult to control. One promising approach to controlling aggregation is to develop materials that are able to self-assemble into well-defined structures. We, among others, have recently reported on a class of amino acid appended PBI structures in the literature indicates that a similar loss of visible light activity may also be occurring in other related amino acid appended PBI photoconductive and photocatalytic samples. If visible light photoconductivity could be coupled to the known oxygen tolerance of these self-assembled structures, it...
would represent an important breakthrough in the search for alternative acceptor materials for organic photovoltaics and novel organic photocatalysts.

Transient absorption (TA) spectroscopy has been used extensively to study PBI donor–acceptor systems, providing important insights into the formation and lifetimes of charge separated and excited states. In addition, exciton13 and charge transport14 efficiencies have been measured. Charge separation occurs in oligomeric self-assembled structures and has been shown to be accelerated in closely bound aggregates, with numerous reports of visible light driven charge separation in PBI donor molecules. Here, we present a mechanistic study that explores the factors controlling charge separation both in solution and as a dried film and hence the spectral response of PBI-A. We also demonstrate the viability of the use of these materials in a potential OPV heterojunction, as in the presence of a suitable donor molecule where visible light driven photoconductivity occurs.

**EXPERIMENTAL METHODS**

**Materials.** PBI-alanine (PBI-A, [N,N′-di(−alanine)-perylene-3,4,9,10-tetracarboxylic acid bisimide]) was synthesized as previously described.3 PBI-A solutions were prepared at a concentration of 25 mg/mL (47 mM) using an equimolar quantity of dilute aqueous NaOH (0.1 M) to dissolve the solid and then made up to 25 mg/mL with distilled water. Solutions were left stirring overnight to ensure all the solid had dissolved. To make films, 25 μL of PBI-A solution were drop-cast onto either a glass microscope slide using a 5 × 5 mm mask or a precleaned fluorine tin oxide electrode (FTO, TEC-15, Pilkington). Tetrabutylammonium hexafluorophosphate (TBA PF6, Sigma-Aldrich) was recrystallized from ethanol prior to use. Acetonitrile (CH3CN, VWR, spectroscopic grade) and methanol (MeOH, Sigma, HPLC grade) were used as received. Milli-Q water was used throughout.

**Steady-State Spectroscopy.** UV/vis absorption data were obtained using a Shimadzu 2550 UV/vis spectrophotometer using cells of various path lengths suitable to the range of concentrations studied. Spectroelectrochemistry (SEC) was performed on films of PBI-A cast onto FTO as the working electrode. The films were doctor-bladed and allowed to dry in air in the dark; the edges of the film were then sealed with epoxy resin (Loctite Hysol 3422 A+B) and allowed to dry overnight in the dark. SEC was performed in a quartz cell using 0.1 M TBA PF6 in argon-purged acetonitrile as the supporting electrolyte, a Pt wire as the counter electrode, and a Ag wire as the pseudoreference electrode. A PalmSens3 potentiostat was used for SEC measurements. Fluorescence spectra were collected using a PerkinElmer Fluorescence Spectrometer LS55 using cells of various path lengths suitable to the range of concentrations studied.

**Photoconductivity Measurements.** Photoconductivity was measured using a two-electrode measurement. Films were prepared on microscope slides between two silver electrodes spaced 3 mm apart, with a contact to a copper wire being made using silver paste (RS Electronics). Prior to use, the film was dried in air overnight, and then epoxy resin was placed over the silver electrodes, which was again left to dry overnight. Samples were then sealed in a 1 × 2 cm quartz cuvette with a B24 adapter (Starna) and septum through which the wires could pass and be either left in air, purged with argon, or purged with argon presaturated with MeOH vapor as described in the text. A 365 or 523 nm LED (LED Engin) powered by a TTI QLS64P power supply was used, and the incident light intensity on the sample was 1 mW/cm². A PalmSens’ potentiostat was used for all photoconductivity measurements employing linear sweep voltammetry from −2 to +2 V at 50 mV/s.

**Femtosecond and Microsecond Transient Absorption (fsTA and μsTA) Spectroscopies.** Femtosecond TA spectroscopy was carried out using a PHAROS laser (Light Conversion, Ltd.) operating at 10 kHz coupled to an ORPHEUS optical parametric amplifier (Light Conversion, Ltd.) in tandem with a LYRA harmonic generator (Light Conversion, Ltd.) to produce the desired wavelength for sample excitation. The pump beam intensity was adjusted with a neutral density filter so as to achieve approximately equal photon fluxes at different wavelengths. Typical pulse energies were on the order of 10 nJ. The pump wavelength was tuned to either UV (365 nm) or visible (490 nm) as needed. In contrast to the 523 nm LED used for photoconductivity measurements (see above), 490 nm was chosen as the visible pump wavelength to remove laser scatter in a region of spectral interest. A portion of the PHAROS output was also split off to either UV (365 nm) or visible (490 nm) as needed. The probe beam was focused to a spot size of ~100 μm diameter on the sample and was overlapped completely by the pump beam. Spectra were acquired with a HELIOS transient absorption spectrometer (Ultrafast Systems, LLC). The time resolution of the setup is ~400 fs. Measurements were performed by randomly stepping the
Figure 1a. The spectrum is dominated by the $S_0 \rightarrow S_1$ electronic transition, composed of a series of closely spaced vibronic modes (vibronic states given in brackets). Spectral fitting (Figure S1) reveals the presence of three transitions at 566 (0–0’), 504 (0–1’), and 467 (0–2’) nm, with the greatest contribution from the (0–1’) mode, indicating extensive H-aggregation and cofacial interactions, which will aid the formation of conductive pathways. 

Comparison with the UV/vis spectrum of PBI-A at low concentration ($10^{-7}$ M) indicates that a high level of aggregation between the PBI units occurs at 47 mM (Figure S2). The $S_0 \rightarrow S_2$ transition is also apparent for the PBI-A film in the UV with a maximum at ca. 360 nm. Previous structural analyses have demonstrated the PBI aggregates in the dried films are in the form of long one-dimensional wormlike micelle structures. In line with our past study, excitation into the $S_0 \rightarrow S_1$ transition (523 nm LED) of the PBI-A film under an argon atmosphere is seen to lead to negligible change in the electrical resistance of the sample (Figure 1b), while excitation of the $S_0 \rightarrow S_2$ transition (365 nm) leads to a large decrease in resistance with the sample showing an Ohmic response indicating that the samples are photoconductive under UV light. This result confirms that long-range charge transport through the extended $\pi \rightarrow \pi$ stacked structure of the dried PBI-A film is possible and that the lack of photocconductivity following $S_0 \rightarrow S_1$ excitation may be due to a lack of initial charge separation or the presence of only short-lived charge-separated states.

In order to examine the potential roles that supramolecular structure and solvent have in controlling charge separation, we initially studied the self-assembled PBI-A structures in solution. It is well understood that the nature of the aggregates formed in PBI solutions is highly dependent upon the PBI concentration. Spectroelectrochemistry (SEC) of the PBI-A solution (47 mM) at pH 9, the concentration used for preparing the PBI-A films, both UV/vis and fluorescence measurements indicate that significant PBI-A aggregation has occurred evidenced by the quenching of the monomer type fluorescence at 652 nm (Figure S2b, S2c), and the increase in the contribution of the (0–1’) transition of the UV/vis spectrum. Spectroelectrochemistry (SEC) of the reduced film is also shown in Figure 1a and is typical of a reduced PBI species. Viscosity measurements of the solution indicate the presence of large-scale aggregates (Figure S4), attributed to wormlike micelles, in agreement with the previous analysis of the dried sample by SEM and XRD which identified that the facially stacked aggregates had a PBI separation of ca. 3.5 Å with structures on the micron scale. Further confirmation of the presence of similar structures in both the solution studies and the dried films is achieved using small angle neutron scattering (SANS). The scattering from the solution sample could be fitted to a wormlike chain model (as the Kratky–Porod flexible cylinder model in the SasView software package (https://www.sasview.org, Figure S5). We have successfully used this model for other related systems. The fit suggests that the system contains structures with a radius of $6.4 \pm 0.1$ nm, with a Kuhn length of $10.1 \pm 1.3$ nm.
The TA spectra of PBI-A solutions at 47 mM using both UV (365 nm) and visible (490 nm) excitation indicate that the excited state species present after 1 ps are very similar, showing a loss of the aggregated ground state (504, ca. 560 nm) and a long-lived broad positive band at 725 nm with shoulders at ca. 540, ca. 625, and 818 nm (Figures 2, 3). The newly formed intermediate species under both UV and visible light excitation correlates well with both the previously reported spectrum of the PBI•−A in solution5 and of the electrochemically generated PBI•−A in a dried film (541, 723, 806, ca. 635 nm (sh), Figure 1b) indicating that excitation of either the S0−S1 or S2−S3 transition leads to the formation of a charge-separated state with the electron localized on the PBI core. The broadness of the PBI radical feature may indicate a degree of charge migration within the aggregate with previous studies noting a broadening of spectral features in aggregated PBIs.11,29

The reduced PBI and the PBI-A ground state bleach are observed to partially recover at the same rate (Figures S6, S7) with kinetics that can be fitted to a minimum of three exponential components (τ1 = ca. 1 ps, τ2 = 17 (±0.9) ps and τ3 = 257 (±16) ps at ca. 820 nm, 490 nm excitation). A singular value decomposition analysis did not identify any additional spectral features beyond that of the PBI-A ground state and the reduced PBI, and it is proposed that the triexponential fit represents a parametrization of the dispersive kinetics, indicating that multiple recombination pathways exist in the supramolecular structure. It is also notable that a significant (ca. 10%) concentration of the photogenerated reduced PBI persists beyond 3.2 ns. The formation of such a long-lived radical anion also supports the hypothesized anion migration through the PBI structure. Alternatively, the lack of charge recombination may indicate that the localization of the cation is preventing charge carrier recombination. It is therefore important that the nature of the electron donor site is identified.

Based upon the oxidation (E_{OX} = 0.80 V_{Ag/AgCl}) and reduction (E_{RED} = −0.56 V_{Ag/AgCl}) potentials of PBI-A at ca. pH 9 measured by square-wave voltammetry (Figure S8), and the reported oxidation potentials of alanine (ca. 0.4−0.65 V_{Ag/AgCl})22,30 in basic solution and the PBI core of similar materials (ca. 1.3−1.5 V)31,32 it is proposed that the amino acid substituent can act as an electron donor, with the PBI core being the acceptor unit following photoexcitation of the solution. Furthermore, we observe no spectral features that are readily assignable to a PBI radical cation in Figure 2, supporting our assignment of the alanine unit as the electron donor.32,33 As the spectrum of oxidized alanine is expected to be outside the spectral window of this study,34 we are unable to ascertain how the oxidized alanine group evolves with time. Therefore, we assign the photochemically generated transient with features at 540, ca. 625, and 818 nm to PBI•−A−' (where A' is an alanine residue following initial oxidation of undefined state).

To further aid the spectral assignment, DFT calculations have been carried out to study the excess electron and hole localization and thus radical anion and cation formation, as well as to predict the PBI-A reduction potentials. Initially, we examined a neutral, a singly deprotonated, and a doubly deprotonated PBI-A molecule in water, Table S1. In the case of neutral PBI-A in water, an excess electron and hole are both predicted to localize on the PBI core. However, at the experimental pH studied (pH 9), the carboxylic acid of the alanine group is expected to be deprotonated. Calculations show that deprotonation leads to localization of the hole on the deprotonated alanine group(s), while the radical anion is still predicted to involve localization of the excess electron on the PBI core. This is all in-line with predictions of the redox potentials of free alanine and unsubstituted PBI, given in Table S1, which show an excellent correlation to the measured redox potentials, quoted above. The oxidation potential of neutral free alanine in water (6.18 V vs. vacuum and 1.62 vs. Ag/AgCl) is predicted to lie significantly more positive than that of unsubstituted PBI (5.75 vs. vacuum and 1.20 vs. Ag/AgCl) and thus is harder to oxidize. Deprotonated free alanine in contrast has a significantly smaller oxidation potential (4.80 vs. vacuum and 0.31 vs. Ag/AgCl) and is thus easier to oxidize than unsubstituted PBI. This different localization of excess electron and hole could potentially have a positive effect on suppressing electron-hole recombination by moving them onto different “sublattices” and may be a further contributing factor behind the long-lived PBI•− state. DFT calculations also allow us to predict the energy required to make a pair of charge-separated states, i.e., a radical cation and radical anion separated by a large distance, commonly referred to as the quasiparticle or transport gap in extended solids but below discussed as the ion pair energy. The energy required to generate a pair of charge-separated states, radical ions, for a deprotonated PBI-A in water is calculated to be of the order of 2 eV (see Table S2). In practice, stacking in solids or supramolecular aggregates will further slightly reduce this value (and that calculated for Na2PBI-A below) by several hundred meV as a result of hybridization of the frontier orbitals of the different molecules; nonetheless, as shown below, the calculations agree well with the observed experimental behavior. This relatively small (ca. 2 eV) ion pair energy for deprotonated PBI-A in solution means visible light excitation (528 nm, 2.35 eV) into the S0−S1 transition should be able to photoionize the excited state into charge-separated states. Experimentally, the Gibbs energy of photoinduced electron transfer in a donor–acceptor system35,36 can also be estimated using eq 1, which takes into account the donor and acceptor electrochemical redox potentials, the Coulombic interactions (C) between the two ions, and their the difference in solvation energies between the system of interest and the solvent that E_{OX} and E_{RED} were measured in (S). Indeed, in water at pH 9 we estimate an ion pair energy of ca. 1.3 eV, and we calculate that a large driving force exists for charge transfer from the lowest energy singlet excited state (ΔG_{ET} ~ −1 eV, see Table S3 for full details), in agreement with the TA observations of
efficient charge separation and the DFT calculations outlined above.

$$\Delta G_{ET} = E_{OX} - E_{RED} - E^* - C + S$$  \hspace{1cm} (1)

It is therefore apparent that the visible light excitation of PBI-A supramolecular structures in solution, which are similar to those employed in dried films, can lead to the formation of long-lived separated charges. TA studies on solid PBI-A films prepared by drying the 47 mM pH 9 solutions on glass slides are now presented to ascertain if the dielectric environment is controlling the activity, Figure 4. Following excitation of the sample at 365 nm (S₀–S₁ transition), we observe the ground state bands being bleached and the formation of a new transient species at ca. 550, ca. 725, and 810 nm, Figure 4a), which shows excellent agreement with both the electrochemically generated spectrum of a PBI**-A** radical in a dried film (Figure 4d) and the transient spectrum recorded for the same system in aqueous solution at pH 9 (Figure 2a) allowing us to assign the transient spectrum recorded for the same system in aqueous solution to the excited state.35,36 Experimentally we can estimate the e−e+ quasiparticle gap, and multiple examples exist for PBI materials such as aqueous solutions, screen the free charge of the excess electron and hole and renormalize (reduce) ion pair energies such as aqueous solutions, screen the free charge of the excess electron and hole and renormalize (reduce) ion pair energies.

The lack of formation of the charge-separated state in solid films may be rationalized through consideration of the effective dielectric constant of the dried PBI-A (film, ε ≈ 3) compared to the solvent dielectric for the solvated PBI-A structures (water, ε ~ 80). Environments with a high relative dielectric permittivity, such as aqueous solutions, screen the free charge of the excess electron and hole and renormalize (reduce) ion pair energies/ quasiparticle gap, and multiple examples exist for PBI materials where charge separation can be controlled by the solvent environment.55,56 Experimentally we can estimate the effect of changing the dielectric environment through the use of eq 1, providing it is assumed that the site of hole and electron localization remains the same. In this case, we estimate a decrease in the driving force for charge separation in the film compared to in solution by ca. 0.7 eV (Table S3). However, while reductive spectroelectrochemistry (Figure 4d) indicates that the electron on the PBI-A film still resides on the PBI core, experiments to identify the site of hole localization on the dried PBI-A film were unsuccessful due to the insulating nature of the nonreduced PBI film. Importantly, DFT calculations on model systems indicate that the site of hole localization in solution and in the solid may be significantly different. As the dried films are prepared from a NaOH (pH 9) PBI solution, we examined two versions of a Na-substituted PBI-A: a single Na⁺PBI-A molecule in the gas phase and a Na⁺PBI-A molecule in the gas phase with two additional coordinated water molecules per sodium cation.
i.e., the simplest possible models of fully and partially dried down Na2PBI-A solutions. Focusing on the radical cation, the hole is predicted in both of these systems to localize for approximately 50% on the two alanine groups and for approximately 50% on the PBI core. In contrast, the excess electron of the radical anion localizes exclusively on the PBI core for both models. Another noticeable difference between Na2PBI-A and (de)protonated PBI-A is that when taking nuclear relaxation into account in the latter the hole typically localizes on one of the two alanine groups while in the case of Na2PBI-A no such symmetry breaking is predicted to occur. Crucially, our calculations indicate that for our model system representing the low dielectric environment of the dried film the ion pair energy has increased from 2 to over 4 eV, a value which is roughly 2 eV greater than the lowest energy excitation rationalizing, in line with the argument above, the experimentally determined lack of visible light charge separation in the solid film, Table S2.

In several recent studies employing supramolecular PBIs as photoconductors and photocatalysts, additional external electron donors (e.g., methanol, diethylamine) have led to visible light activity.55,56 We therefore decided to explore the effect of methanol vapor on the current—voltage response of dried PBI-A films under visible light illumination, Figure 1b. Methanol vapor was employed here as it offers the opportunity to introduce an alternative electron donor (\( E_{ox} \approx -0.4 \) V Ag/AgCl at pH 9)57,58 directly into the solid self-assembled PBI-A film. In the presence of the methanol donor, we observe a large decrease in resistance under visible light illumination (S23 nm, Figure 1b) demonstrating that excitation of the S0 – S1 transition of the dried PBI-A film can induce the sample to become conductive. The TA spectrum of a dried PBI-A film in the presence of methanol vapor confirms that it is indeed possible to form a PBI**–A radical following 490 nm excitation, with the bands of the reduced PBI at 545, 735, and 812 being present within 1 ps and persisting for >3.2 ns, Figures 4c, d. It is therefore apparent that by careful control of the inclusion of a suitable electron donor to the PBI-A that visible light driven charge separation can be enabled, in which the exciton oxidizes methanol, highlighting the feasibility of developing efficient donor–acceptor heterojunctions based on self-assembled amino acid appended PBI acceptors.

**CONCLUSIONS**

Self-assembled structures formed from amino acid PBIs are known to be highly promising photoconductive materials due to their reported oxygen tolerance and ability to form long-range one-dimensional structures both in dried solutions and when gelled. However, a significant issue has been multiple amino acid PBIs have reported photoactivity primarily under UV illumination, despite the UV/vis absorption spectrum extending into the visible region.59,60,61 Here, we use TA spectroscopy to show that PBI**, whose presence is known to correlate to the material showing photoconductivity, can be generated within a PBI-A supramolecular structure in water within 1 ps under both UV (S0–S1) and visible (S0–S1) light excitation. In contrast, when dried films are employed charge separation only occurs under UV illumination due to a destabilization of the charge-separated state in the low dielectric environment and a change in the site of hole localization. In these experiments, it is proposed that the alanine functionality is acting as an electron donor, and this is supported by the observation that the inclusion of a more readily oxidized electron donor (methanol) leads to the switching on of photoactivity under visible light. The differing spectral response of the PBI-A 1-D structures in different dielectric environments represents an important design consideration for the development of these promising materials for use in optoelectronic devices.

**ASSOCIATED CONTENT**

1 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b06222.

Full description of the experimental methods; variable concentration UV/vis and emission spectroscopy experiments; the calculation of the donor–acceptor distance within an aggregated PBI-A sample; SANS data, kinetic fits, and supplementary DFT information (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

*E-mail: a.j.cowan@liverpool.ac.uk.
*E-mail: d.j.adams@liverpool.ac.uk.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

J.J.W. and E.R.D. acknowledge the EPSRC for financial support. J.R.L. acknowledges the School of Physics (University of Liverpool) for a GTA studentship. A.J.C., D.J.A., and M.A.Z. thank the EPSRC for fellowships (EP/K006851/1, EP/L021978/1, and EP/1004424/1 respectively). The Laser Loan Pool of the Central Laser Facility (CLF), part of the UK Science and Technology Facilities Council (STFC), is thanked for the loan of equipment through EP/G03088X/1. Experiments at the ISIS Pulsed Neutron and Muon Source were supported by a beam-time allocation from the STFC (Computational time on ARCHER, the U.K.’s high-performance computing service (via our membership of the U.K.’s HPC Materials Chemistry Consortium, which is funded by EPSRC grant EP/L000202/1), and the EPSRC National Service for Computational Chemistry Software is gratefully acknowledged. This work benefited from the SasView software, originally developed by the DANSE project under NSF award DMR-0520547.

**REFERENCES**

(1) Neuteboom, E. E.; Meskers, S. C. J.; Van Hal, P. A.; Van Duren, J. K. J.; Meijer, E. W.; Janssen, R. A. J.; Dupin, H.; Poutois, G.; Cornil, J.; Lazzaroni, R.; et al. Alternating Oligo(p-phenylene vinylene) Donor Acceptor Materials. Chem. Rev. 2016, 120, 18479 – 18484.

(2) Chen, S.; Jacobs, D. L.; Xu, J.; Li, Y.; Wang, C.; Zang, L. 1D Nanofiber Composites of Perylene Diimides for Visible-Light-Driven Hydrogen Evolution from Water. RSC Adv. 2014, 4, 48486–48491.

(3) Würthner, F.; Saha-Müller, C. R.; Fimmel, B.; Ogi, S.; Leowanawat, P.; Schmidt, D. Perylene Bisimide Dye Assemblies as Archetype Functional Supramolecular Materials. Chem. Rev. 2016, 116, 962–1052.
(24) Ahlrichs, R.; Bär, M.; Häsler, M.; Horn, H.; Köhlmel, C. Electronic Structure Calculations on Workstation Computers: The Program System Turbomole. Chem. Phys. Lett. 1989, 162, 165–169.
(25) Furche, F.; Ahlrichs, R.; Hättig, C.; Klopper, W.; Sierka, M.; Weigend, F. Turbomole. WIREs Comput. Mol. Sci. 2014, 4, 91–100.
(26) Ambrosek, D.; Marcinia, H.; Lochbrunner, S.; Tatchen, J.; Li, X.-Q.; Wüthener, F.; Kühn, O. Photophysical and Quantum Chemical Study on a J-Aggregate Forming Perylene Bisdime Monomer. Phys. Chem. Chem. Phys. 2011, 13, 17649–17657.
(27) Raeburn, J.; Mendoza-Cuenca, C.; Cattoz, B. N.; Little, M. A.; Terry, A. E.; Cardoso, A. Z.; Griffiths, P. C.; Adams, D. J. The Effect of Solvent Choice on the Gelation and Final Hydrogel Properties of Fmoc–Diphenylalanine. Soft Matter 2015, 11, 927–935.
(28) Draper, E. R.; Mears, L. L. E.; Castilla, A. M.; King, S. M.; McDonald, T. O.; Akhtar, R.; Adams, D. J. Using the Hydrolysis of Anhydrides To Control Gel Properties And Homogeneity in pH-Triggered Gelation. Soft Matter 2015, 11, 9536–9537.
(29) van der Boom, T.; Hayes, R. T.; Zhao, Y.; Bushard, P. J.; Weiss, E. A.; Wasielewski, M. R. Charge Transport in Photofunctional Nanoparticles Self-Assembled from Zinc 5,10,15,20-Tetrakis-(perylenediimide)porphyrin Building Blocks. J. Am. Chem. Soc. 2002, 124, 9582–9590.
(30) Almedahi, T.; Herlem, G.; Cattey, H.; Blondau-Patissier, V.; Gharbi, T. Electroosmosis of Poly(alanine)-Like Peptides in Concentrated Alamine Based Electrolytes. Characterization Coupled to DFT Study and Application to pH Proton Reson. J. Phys. Chem. C 2014, 118, 25041–25050.
(31) Ronconi, F.; Syriagnis, Z.; Bonasera, A.; Prato, M.; Argazzi, R.; Caramori, S.; Cristino, V.; Bignozzi, C. A. Modification of Nano-crystalline WO3 with a Dicationic Perylene Bisdime: Applications to Molecular Level Solar Water Splitting. J. Am. Chem. Soc. 2015, 137, 4630–4633.
(32) Lindquist, R. J.; Phelan, B. T.; Reynal, A.; Margulies, E. A.; Shoer, L. E.; Durrant, J. R.; Wasielewski, M. R. Strongly Oxidizing Perylene-3,4-Dicarboximides for Use in Water Oxidation Photocatalysis. J. Am. Chem. Soc. 2014, 136, 4009–4013.
(33) Wüthener, F.; Sautter, A.; Schmid, D.; Weber, P. J. A. Fluorescent and Electroactive Cyclic Assemblies from Perylene Tetracarboxylic Acid Bisdime Ligands and Metal Phosphane Triflates. Chem.—Eur. J. 2001, 7, 894–902.
(34) Natarajan, S.; Britto, S. A. M. A.; Ramachandran, E. Growth, Thermal, Spectroscopic, and Optical Studies of L-Alaninum Maleate, a New Organic Nonlinear Optical Material. Cryst. Growth Des. 2006, 6, 137–140.
(35) Wu, Y.; Young, R. M.; Frasconi, M.; Schneebeli, S. T.; Spenst, P.; Gardiner, D. M.; Brown, K. E.; Wüthener, F.; Stoddart, J. F.; Wasielewski, M. R. Ultras Fast Photoinitiated Symmetry-Breaking Charge Separation and Electron Shaking in Perylenediimide Molecular Triangles. J. Am. Chem. Soc. 2015, 137, 13236–13239.
(36) Nowak-Król, A.; Fimmel, B.; Son, M.; Kim, D.; Wüthener, F. Photoinitiated Electron Transfer (PET) Versus Excimer Formation in Supramolecular P/N-Heterojunctions of Perylene Bisdime Dyes and Implications for Organic Photovoltaics. Faraday Discuss. 2015, 185, 507–527.
(37) Datar, A.; Balakrishnan, K.; Zang, L. One-Dimensional Self-Assembly of a Water Soluble Perylene Diimide Molecule by Ph Triggered Hydrogelation. Chem. Commun. 2013, 49, 6894–6896.
(38) Weingarten, A. S.; Kazantzis, R. V.; Palmer, L. C.; McClendon, M.; Kolonow, A. R.; Samuel, A. P. S.; Kiebala, D. J.; Wasielewski, M. R.; Stupp, S. I. Self-Assembly Hydrogel Scaffolds for Photocatalytic Hydrogen Production. Nat. Chem. 2014, 6, 964–970.
(39) Berr, M. J.; Wagner, P.; Fischbach, S.; Vaneski, A.; Schneider, J.; Suska, A. S.; Rogach, A. L.; Jäckel, F.; Feldmann, J. Hole Scavenger
Redox Potentials Determine Quantum Efficiency and Stability of Pt-Decorated Cds Nanorods for Photocatalytic Hydrogen Generation.

Appl. Phys. Lett. 2012, 100, 223903.

(40) Chen, S.; Li, Y.; Wang, C. Visible-Light-Driven Photocatalytic H2 Evolution from Aqueous Suspensions of Perylene Diimide Dye-Sensitized Pt/TiO2 Catalysts. RSC Adv. 2015, 5, 15880–15885.

(41) Chen, S.; Wang, C.; Bunes, B. R.; Li, Y.; Wang, C.; Zang, L. Enhancement Of Visible-Light-Driven Photocatalytic H2 Evolution from Water Over g-C3N4 through Combination with Perylene Diimide Aggregates. Appl. Catal., A 2015, 498, 63–68.

■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published to the Web on August 12, 2016, with an error in the TOC/abstract graphics. This was corrected in the version published to the Web on August 17, 2016.