Conjugated Polymer Donor-Molecular Acceptor Nanohybrids for Photocatalytic Hydrogen Evolution

Haofan Yang, Xiaobo Li, Reiner Sebastian Sprick, Andrew I. Cooper

Submitted date: 26/12/2019 • Posted date: 27/12/2019
Licence: CC BY-NC-ND 4.0

Citation information: Yang, Haofan; Li, Xiaobo; Sprick, Reiner Sebastian; Cooper, Andrew I. (2019): Conjugated Polymer Donor-Molecular Acceptor Nanohybrids for Photocatalytic Hydrogen Evolution. ChemRxiv. Preprint. https://doi.org/10.26434/chemrxiv.11418375.v2

A library of 237 organic binary/ternary nanohybrids consisting of conjugated polymers donors and both fullerene and non-fullerene molecular acceptors was prepared and screened for sacrificial photocatalytic hydrogen evolution. These donor-acceptor nanohybrids (DANHs) showed significantly enhanced hydrogen evolution rates compared with the parent donor or acceptor compounds. DANHs of a polycarbazole-based donor combined with a methanofullerene acceptor (PCDTBT/PC$_{60}$BM) showed a high hydrogen evolution rate of 105.2 mmol g$^{-1}$ h$^{-1}$ under visible light ($\lambda > 420$ nm). This DANH photocatalyst produced 5.9 times more hydrogen than a sulfone-containing polymer (P10) under the same conditions, which is one of the most efficient organic photocatalysts reported so far. An apparent quantum yield of hydrogen evolution of 3.0 % at 595 nm was measured for this DANH. The photocatalytic activity of the DANHs, which in optimized cases reached 179.0 mmol g$^{-1}$ h$^{-1}$, is attributed to efficient charge transfer at the polymer donor/molecular acceptor interface. We also show that ternary donor$_A$-donor$_B$-acceptor nanohybrids can give higher activities than binary donor-acceptor hybrids in some cases.

File list (2)

| File Name                                              | Size               | Link                                      |
|--------------------------------------------------------|--------------------|-------------------------------------------|
| DANH_paper_final.pdf                                    | 401.70 KiB         | view on ChemRxiv ➤ download file          |
| Supporting information_DANH_paper.pdf                  | 434.54 KiB         | view on ChemRxiv ➤ download file          |
Conjugated Polymer Donor-Molecular Acceptor Nanohybrids for Photocatalytic Hydrogen Evolution

Haofan Yang, Xiaobo Li,* Reiner Sebastian Sprick and Andrew I. Cooper*

Department of Chemistry and Materials Innovation Factory, University of Liverpool, 51 Oxford Street, Liverpool L7 3NY, U.K.

ABSTRACT: A library of 237 organic binary/ternary nanohybrids consisting of conjugated polymers donors and both fullerene and non-fullerene molecular acceptors was prepared and screened for sacrificial photocatalytic hydrogen evolution. These donor-acceptor nanohybrids (DANHs) showed significantly enhanced hydrogen evolution rates compared with the parent donor or acceptor compounds. DANHs of a polycarbazole-based donor combined with a methanofullerene acceptor (PCDTBT/PC60BM) showed a high hydrogen evolution rate of 105.2 mmol g⁻¹ h⁻¹ under visible light (λ > 420 nm). This DANH photocatalyst produced 5.9 times more hydrogen than a sulfone-containing polymer (P10) under the same conditions, which is one of the most efficient organic photocatalysts reported so far. An apparent quantum yield of hydrogen evolution of 3.0 % at 595 nm was measured for this DANH. The photocatalytic activity of the DANHs, which in optimized cases reached 179.0 mmol g⁻¹ h⁻¹, is attributed to efficient charge transfer at the polymer donor/molecular acceptor interface. We also show that ternary donor-donor-acceptor nanohybrids can give higher activities than binary donor-acceptor hybrids in some cases.

Direct photocatalytic solar hydrogen production promises a technologically simple way to convert solar energy into chemical fuels ¹. To be scalable, however, this approach requires more efficient photocatalysts. Inorganic semiconductor photocatalysts have been explored widely for some time ²,³. Recently, organic photocatalysts have also attracted attention due to potential advantages in terms of tunable composition, structure, and properties ⁴. These organic photocatalysts include polymeric carbon nitride ⁵–⁷, carbon dots ⁸,⁹, conjugated microporous polymers ¹⁰–¹², covalent triazine-based frameworks ¹³,¹⁴ and covalent organic frameworks ¹⁵–¹⁸. However, organic photocatalysts also have some inherent drawbacks, such as strong exciton binding energies, low charge-carrier mobilities, and short charge migration pathlengths. In organic photovoltaics (OPV), these issues have been mitigated by the introduction of donor/acceptor bulk heterojunctions ¹⁹. Such nanoscale blends of a donor and an acceptor ensures that excitons can reach an interface and dissociate into free charge carriers. In principle, this concept should also be transferable to organic polymer photocatalysts.

Here, we designed a library of donor-acceptor nanohybrids (DANHs) photocatalysts that combine conjugated polymer donors with either fullerene/non-fullerene molecular acceptors (Fig. 1). We then evaluated their photocatalytic hydrogen evolution performance. To our knowledge, organic nanoparticles consisting of conjugated polymer donors and molecular acceptors have not been reported for direct photocatalytic hydrogen evolution using a catalyst suspension. Organic nanoparticles composed of a single conjugated polymer were developed previously for photocatalytic hydrogen production ²⁰–²², but those photocatalysts showed rapid deactivation (in less than 2 hours) after a high initial hydrogen evolution rate of 52.4 mmol g⁻¹ h⁻¹ (17 µmol h⁻¹). By comparison, the organic DANHs photocatalysts reported here show both increased hydrogen evolution rates (up to 179.0 mmol g⁻¹ h⁻¹) and enhanced photocatalytic stability (sustained H₂ production for at least 18 hours).
We studied five conjugated polymer donors (D1–D5) and four molecular acceptors (A1–A4) (Fig. 1a-b). Water dispersible DANHs were prepared using nano-precipitation strategy, as shown in Fig. 1c. A tetrahydrofuran (THF) solution containing the polymer donor and the molecular acceptor was injected into water with continuous sonication, followed by the evaporation of the THF (detailed procedures in Supporting Information). Colloidal solutions of DANHs were obtained (Fig. 1c) after THF removal. It is well known that the composition ratio between donor-acceptor is critical for photovoltaic performance. Likewise here for photocatalysis, we screened a broad range of relative donor-to-acceptor ratios to give a total DANH library of 237 samples. The photocatalytic hydrogen evolution performance of this library was then screened using high-throughput parallel 48-sample photocatalysis screen, as introduced previously by our group. Fig. 2 plots the sacrificial photocatalytic hydrogen evolution rate for A1-4/D1-D5 DANH combinations as a function of donor/acceptor composition ratios (w/w %). The photocatalytic performance of the DANHs is strongly dependent on this ratio.
Fig. 2. Sacrificial photocatalytic hydrogen production activities for the various combinations of polymer donors and molecular acceptors: (a) A1/Dn; (b) A2/Dn; (c) A3/Dn, and; (d) A4/Dn, plotted as a function of the acceptor weight fraction that was added in the nanoprecipitation process (100 % corresponds to the pure acceptor nanoparticle). Testing conditions: catalyst concentration = 20–100 µg mL⁻¹ (0.1–0.5 mg in 5 mL water); ascorbic acid (0.04 M); Pt loading based on total mass of donor and acceptor: (3 wt. % using a stock solution of H₂PtCl₆, 8 wt. % in water); light source = solar simulator, 1 sun; irradiation time = 2 hours. The hydrogen evolution rate is proportional to the area of the circles (for scale, the maximum hydrogen evolution rate found was 171.4 mmol g⁻¹ h⁻¹ for 70.6:29.4 w/w % DANH of A1/D4 (Fig. 2d).

DANHs combinations that involved A3 showed little improvement in hydrogen evolution rate (HER) with respect to the pure donor polymers or molecular acceptors (Fig. 2c). By contrast, combinations involving A2 showed synergies at acceptor ratios in the range 70–80 w/w, particular for polymer D1 (Fig. 2b). However, much higher HERs were observed for DANHs that included A1 (Fig. 2a) and A4 (Fig. 2d). The most promising combinations were found to be A1/D1 and A1/D2 (Fig. 2a) and A4/D1, and A4/D2 (Fig. 2d).

For the A1 series, the highest performance, 142.9 mmol g⁻¹ h⁻¹, was observed for A1/D1 DANHs at a mass ratio of 70.6/29.4. This HER is 71 times higher than the HER for the pure acceptor, A1 (2.0 mmol g⁻¹ h⁻¹), and 357 times higher than the pure polymer donor, D1 (0.4 mmol g⁻¹ h⁻¹), respectively, showing a strong synergistic effect in these DANHs. The results of a more exhaustive search of the variation of HER with A1/D1 composition are shown in Fig. S1, which substantiates the conclusions of the high-throughput screening (i.e., around 70 w/w % A1 gives the maximum HER). Combining polymer D1 with PC70BM (A2) (Fig. 2b) or [60]IPB (A3) (Fig. 2c) gives the same compositional trend in HER (a maximum at around 70–80 w/w % acceptor), but the HERs are much lower than observed for PC60BM (A1) (Fig. 2a).

Recently, high-performing non-fullerene based molecular acceptors have surpassed the most efficient fullerene acceptors for organic photovoltaics, which inspired us to prepare DANH photocatalysts using ITIC-2F (A4) as non-fullerene based acceptor. As shown in Fig. 2d, A4/D1 (70.6 wt. % A4) exhibited the highest HER of 171.4 mmol g⁻¹ h⁻¹ among the combinations in this library.

The coprecipitation of both donor and acceptor is important for the HER: physical mixtures of A1 and D1 nanoparticles (detailed procedures in Supporting Information) showed significantly lower HERs compared with the A1/D1 and A4/D1 DANHs (Fig.
activities 23 and 18 times lower, respectively, when \( A1 \) mass ratio is 70.6 \%, suggesting that the formation of donor-acceptor junctions is essential. This was supported by photoluminescence results that show complete quenching for both \( A1/D1 \) and \( A4/D1 \) DANHs, which results from efficient charge transfer. By contrast, physical mixtures of the donors and acceptors showed incomplete quenching as a result of the poor junction formation (Fig. 3).

![Emission spectrum of (a) A1/D1 NADHs under 375 nm excitation and (b) A4/D1 NADHs under 600 nm excitation, compared with their physical mixture counterparts (A1+D1 and A4+D1). Measurements were carried out at ambient temperature in aqueous solution.](image)

We also studied the effect of ascorbic acid concentration, cocatalyst type, and cocatalyst loading on the HER for the \( A1/D1 \) NADH (70.6 wt. \% \( A1 \)). The HER could be further improved to 179.0 mmol g\(^{-1}\) h\(^{-1}\) from 142.9 mmol g\(^{-1}\) h\(^{-1}\) (screening conditions) by using 0.2 M ascorbic acid and 3\% Pt loading (Fig. S3). Platinum was found to be the most efficient co-catalyst of a range of \( \beta \) catalyst precursors that were studied (Fig. S4). We also tried to tune the morphology and size of the \( A1/D1 \) DANHs by introducing surfactants during nanoprecipitation (Fig. S5), but this was found to markedly decrease the HER. No appreciable hydrogen generation could be detected for \( A1/D1 \) (70.6 wt. \% \( A1 \)) in the absence scavenger (ascorbic acid), Pt, or light irradiation.

Next, time-course photocatalytic hydrogen evolution rates for \( A1/D1 \) NADHs were investigated. \( A1/D1 \) NADHs showed an initial HER of 105.2 mmol g\(^{-1}\) h\(^{-1}\) (120.9 \( \mu \)mol h\(^{-1}\)) in the first 2 hours under visible light illumination (\( \lambda > 420 \) nm) using condition 1 (Fig. 4a). Similar initial rates were observed for the other two sets of reaction conditions, which had different ascorbic acid concentrations and Pt loadings (Fig. 4a). The hydrogen evolution activity decreased over time, but the NADHs were still active after 18 hours photocatalysis, with a rate of 37.8 mmol g\(^{-1}\) h\(^{-1}\) over the last 4 hours. Therefore, the \( A1/D1 \) DANH both exhibits excellent \( H_2 \) production rates and has much better stability compared with previously reported pure polymer nanoparticle photocatalysts\(^{20–22}\), which show activity for only 1, 4 and 11 hours, respectively. The catalyst mass used here (1.15 mg) is also higher than for earlier studies (around 0.05 and 0.33 mg polymer)\(^{20,21}\). At lower catalysis loadings, even higher hydrogen evolution rates of 247.8 mmol g\(^{-1}\) h\(^{-1}\) and 383.4 mmol g\(^{-1}\) h\(^{-1}\) were observed for 0.23 mg and 0.115 mg of \( A1/D1 \) NADHs (70.6 wt. \% \( A1 \)), respectively (Fig. S6). Of course, for practical applications, the amount of hydrogen produced per unit area irradiated is the most important parameter, and hence such low catalyst loadings are less useful.

Compared to \( \text{P}10 \), one of the most efficient organic photocatalysts developed by our group\(^{28}\), the \( A1/D1 \) DANH catalyst was almost 6 times more active in terms of mass-normalized rate over 8 hours (85.0 mmol g\(^{-1}\) h\(^{-1}\) for \( A1/D1 \) versus 14.3 mmol g\(^{-1}\) h\(^{-1}\) for \( \text{P}10 \) under the same conditions) (Fig. 4b). An apparent quantum yield (AQY) of 3.02 \% was obtained at long wavelength of 595 nm (Fig. 4c), which places these \( A1/D1 \) DANHs among the most efficient photocatalysts for sacrificial hydrogen evolution in suspension-based systems (Table S1). The AQYs recorded at 420, 490 and 515 nm were 3.72\%, 3.43\%, and 3.16\%, respectively (Fig. 4c). These three similar AQY yields are consistent with the relatively flat UV-vis spectra of the sample in this spectral range (Fig. 4c).

Phase separation from solution was observed after photocatalysis (Fig. S7a-b), which might suggest that this is a primary cause for loss of HER over time. SEM characterizations of the \( A1/D1 \) samples before and after photocatalysis supported particle aggregation (Fig. S8). The \( A1/D1 \) samples were collected after photocatalysis and redissolved into THF solvent for characterization by UV-vis and \( ^1H \) NMR spectroscopy. No obvious changes occurred before and after photocatalysis (Fig. S9). We therefore suggest that the observed rate loss for \( A1/D1 \) is due to the aggregation of the DANHs during photocatalysis, rather than chemical decomposition. In support of this interpretation, \( A4/D1 \) samples exhibited a HER of 77.7 mmol g\(^{-1}\) h\(^{-1}\) in the first 2 hour (Fig. 4b) but experienced a great loss of photocatalytic activity during irradiation. We observed that the \( A4/D1 \) DANHs aggregated much more quickly than the \( A1/D1 \) samples (Fig. S7c-d), perhaps explaining the more rapid deactivation. Note also that no such deactivation occurs over 8 hours for \( \text{P}10 \), which is not nanoparticulate.
Fig. 4. (a) Time course of hydrogen production for A1/D1 NADHs and a bulk, pure conjugated polymer, P10, irradiated by 300 W Xe lamp fitted with a $\lambda > 420$ nm filter using 1.15 mg of the catalyst. Condition 1: 0.1 M ascorbic acid and 9 wt. % Pt; condition 2: 0.2 M ascorbic acid and 9 wt. % Pt; condition 3: 0.2 M ascorbic acid and 3 wt. % Pt. Half circle points represent the beginning of the next run after degassing. (b) Time course of hydrogen production for A1/D1 NADH, A4/D1 NADH, and bulk P10 irradiated by 300 W Xe lamp fitted with a $\lambda > 420$ nm filter using 1.15 mg of catalysts under condition 1. Half circle points represent the beginning of the next run after degassing. (c) UV-vis spectra and AQY of A1/D1 measured with monochromatic LED light at 420, 495, 515 and 595 nm, respectively. UV-vis spectrum of pure A1 and D1 nanoparticles are plotted with dashed lines (Intensity rescaled for clarity). (d) Hydrogen evolution rate of A1/D3:D5 ternary nanohybrids of various compositions. Catalyst concentrations: 0.3, 0.23 and 0.14 mg in 5 mL water; ascorbic acid: 0.04 M; Pt loading: 3 wt. %; light source = solar simulator; irradiation time = 2 hours. Inset: HOMO and LUMO band levels of donors and acceptors.

Finally, we extended these binary donor-acceptor nanohybrids to ternary donor$_A$-donor$_B$-acceptor nanohybrids (donor$_A$ : donor$_B$ = 1 : 1), and evaluated the photocatalytic activities using our high throughput photocatalysis screening platform. Compared to A1/D1 and A1/D2 binary DANHs, A1/D1:D2 ternary DANHs did not show enhanced photocatalytic activity (Fig. S10a). Ternary A1/D2:D3, A1/D2:D5, A1/D3:D4 and A1/D4:D5 also showed no improvement (Fig. S10b-h). However, intriguingly, in the presence of both D3 and D5, the hydrogen production rate of A1/D3:D5 was significantly improved. A1/D3:D5 reached a HER of 87.1 mmol g$^{-1}$ h$^{-1}$, which is much higher than the rate obtained for binary A1/D3 (1.6 mmol g$^{-1}$ h$^{-1}$) or A1/D5 (5.4 mmol g$^{-1}$ h$^{-1}$) DANHs with the same compositions (Fig. 4d). Enhancement to the performance was also accomplished in A1/D2:D4 DANHs (Fig. S11). This shows that ternary donor$_A$-donor$_B$-acceptor compositions may outperform binary systems for photocatalysis in the future, raising an interesting multicomponent optimization challenge.

To summarize, high-throughput screening was used to discover both binary and ternary NADHs with sacrificial hydrogen evolution rates that greatly outperform the constituent donors and acceptors. This illustrates that a key principle from the field of organic photovoltaics can be translated into direct photocatalysis using organic materials. Non-fullerene acceptors gave higher photocatalytic performance, which is again relates to recent progress in OPV. Our results imply that catalyst lifetime may be limited by colloidal stability, rather than chemical decomposition, at least for short irradiation times (< 1 day), suggesting the potential to improve catalyst lifetimes in the future.
AUTHOR INFORMATION

Corresponding Author
*e-mail: Xiaobo.li@liverpool.ac.uk; aicooper@liverpool.ac.uk

ACKNOWLEDGMENT

We thank the Leverhulme Trust for studentship via the Leverhulme Research Centre for Functional Materials Design, and Engineering and Physical Sciences Research Council (EPSRC) for financial support under Grant EP/N004884/1. We thank Ni Wang and Chengxi Zhao for helpful discussions.

Keywords: nanocomposites • photocatalysis • hydrogen production • donor acceptor • nanoparticles

REFERENCES

(1) Fujishima, A., & Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature 1972, 238, 37–38. https://doi.org/10.1038/238037a0.

(2) Chen, X.; Shen, S.; Guo, L.; Mao, S. S. Semiconductor-Based Photocatalytic Hydrogen Generation. Chem. Rev. 2010, 110 (11), 6503–6570. https://doi.org/10.1021/cr1001645.

(3) Kudo, A.; Miseki, Y. Heterogeneous Photocatalyst Materials for Water Splitting. Chem. Soc. Rev. 2009, 38 (1), 253–278. https://doi.org/10.1039/b800489q.

(4) Wang, Y.; Vogel, A.; Sachs, M.; Sprick, R. S.; Wilbraham, L.; Moniz, S. J. A.; Godin, R.; Zwijnenburg, M. A.; Durrant, J. R; Cooper, A. I.; et al. Current Understanding and Challenges of Solar-Driven Hydrogen Generation Using Polymeric Photocatalysts. Nat. Energy 2019, 4 (9), 746–760. https://doi.org/10.1038/s41560-019-0456-5.

(5) Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. A Metal-Free Polymeric Photocatalyst for Hydrogen Production from Water under Visible Light. Nat. Mater. 2009, 8 (1), 76–80. https://doi.org/10.1038/nmat2317.

(6) Lin, L.; Yu, Z.; Wang, X. Crystalline Carbon Nitride Semiconductors for Photocatalytic Water Splitting. Angew. Chemie - Int. Ed. 2019, 58 (19), 6164–6175. https://doi.org/10.1002/anie.201809897.

(7) Martin, D. J.; Oiu, K.; Shevlin, S. A.; Handoko, A. D.; Chen, X.; Guo, Z.; Tang, J. Highly Efficient Photocatalytic H2 Evolution from Water Using Visible Light and Structure-Controlled Graphitic Carbon Nitride. Angew. Chemie - Int. Ed. 2014, 53 (35), 9240–9245. https://doi.org/10.1002/anie.201403375.

(8) Martindale, B. C. M.; Joliat, E.; Bachmann, C.; Alberto, R.; Reisner, E. Clean Donor Oxidation Enhances the H2 Evolution Activity of a Carbon Quantum Dot–Molecular Catalyst Photosystem. Angew. Chemie - Int. Ed. 2016, 55 (32), 9402–9406. https://doi.org/10.1002/anie.201604355.

(9) Martindale, B. C. M.; Hutton, G. A. M.; Caputo, C. A.; Reisner, E. Solar Hydrogen Production Using Carbon Quantum Dots and a Molecular Nickel Catalyst. J. Am. Chem. Soc. 2015, 137 (18), 6018–6025. https://doi.org/10.1021/jacs.5b01650.

(10) Kochergin, Y. S.; Schwarz, D.; Achariya, A.; Ichangi, A.; Kulkarni, R.; Eliášová, P.; Vacek, J.; Schmidt, J.; Thomas, A.; Bojdiys, M. J. Exploring the “Goldilocks Zone” of Semiconducting Polymer Photocatalysts by Donor–Acceptor Interactions. Angew. Chemie - Int. Ed. 2018, 57 (43), 14188–14192. https://doi.org/10.1002/anie.201809702.

(11) Wang, Z.; Yang, X.; Yang, T.; Zhao, Y.; Wang, F.; Chen, Y.; Zeng, J. H.; Yan, C.; Huang, F.; Jiang, J. X. Dibenzothiophene Dioxide Based Conjugated Microporous Polymers for Visible-Light-Driven Hydrogen Production. ACS Catal. 2018, 8 (9), 8590–8596. https://doi.org/10.1021/acscatal.8b02607.

(12) Cooper, A. I. Conjugated Microporous Polymers. Adv. Mater. 2009, 21 (12), 1291–1295.
(13) Wang, K.; Yang, L. M.; Wang, X.; Guo, L.; Cheng, G.; Zhang, C.; Jin, S.; Tan, B.; Cooper, A. Covalent Triazine Frameworks via a Low-Temperature Polycondensation Approach. Angew. Chemie - Int. Ed. 2017, 56 (45), 14149–14153. https://doi.org/10.1002/anie.201708548.

(14) Kuecken, S.; Acharjya, A.; Zhi, L.; Schwarze, M.; Schomäcker, R.; Thomas, A. Fast Tuning of Covalent Triazine Frameworks for Photocatalytic Hydrogen Evolution. Chem. Commun. 2017, 53 (43), 5854–5857. https://doi.org/10.1039/c7cc01827d.

(15) Vyas, V. S.; Haase, F.; Stegbauer, L.; Savasci, G.; Podjaski, F.; Ochsenfeld, C.; Lotsch, B. V. A Tunable Azine Covalent Organic Framework Platform for Visible Light-Induced Hydrogen Generation. Nat. Commun. 2015, 6, 1–9. https://doi.org/10.1038/ncomms9508.

(16) Wang, X.; Chen, L.; Chong, S. Y.; Little, M. A.; Wu, Y.; Zhu, W. H.; Clowes, R.; Yan, Y.; Zwiijnenburg, M. A.; Sprick, R. S.; et al. Sulfone-Containing Covalent Organic Frameworks for Photocatalytic Hydrogen Evolution from Water. Nat. Chem. 2018, 10 (12), 1180–1189. https://doi.org/10.1038/s41557-018-0141-5.

(17) Pachfule, P.; Acharjya, A.; Roese, J.; Langenhahn, T.; Schwarze, M.; Schomäcker, R.; Thomas, A.; Schmidt, J. Diacetylene Functionalized Covalent Organic Framework (COF) for Photocatalytic Hydrogen Generation. J. Am. Chem. Soc. 2018, 140 (4), 1423–1427. https://doi.org/10.1021/jacs.7b11255.

(18) Bi, S.; Yang, C.; Zhang, W.; Xu, J.; Liu, L.; Wu, D.; Wang, X.; Han, Y.; Liang, Q.; Zhang, F. Two-Dimensional Semiconducting Covalent Organic Frameworks via Condensation at Arylmethyl Carbon Atoms. Nat. Commun. 2019, 10 (1), 1–10. https://doi.org/10.1038/s41467-019-10504-6.

(19) Scharber, M. C.; Sariciftci, N. S. Efficiency of Bulk-Heterojunction Organic Solar Cells. Prog. Polym. Sci. 2013, 38 (12), 1929–1940. https://doi.org/10.1016/j.progpolymsci.2013.05.001.

(20) Wang, L.; Fernández-Terán, R.; Zhang, L.; Fernandes, D. L. A.; Tian, L.; Chen, H.; Tian, H. Organic Polymer Dots as Photocatalysts for Visible-Light-Driven Hydrogen Generation. Angew. Chemie - Int. Ed. 2016, 55 (40), 12306–12310. https://doi.org/10.1002/anie.201607018.

(21) Pati, P. B.; Damas, G.; Tian, L.; Fernandes, D. L. A.; Zhang, L.; Pehlivan, I. B.; Edvinsson, T.; Araujo, C. M.; Tian, H. An Experimental and Theoretical Study of an Efficient Polymer Nano-Photocatalyst for Hydrogen Evolution. Energy Environ. Sci. 2017, 10 (6), 1372–1376. https://doi.org/10.1039/c7ee00751e.

(22) Tseng, P. J.; Chang, C. L.; Chan, Y. H.; Ting, L. Y.; Chen, P. Y.; Liao, C. H.; Tsai, M. L.; Chou, H. H. Design and Synthesis of Cycloplatinated Polymer Dots as Photocatalysts for Visible-Light-Driven Hydrogen Evolution. ACS Catal. 2018, 8 (9), 7766–7772. https://doi.org/10.1021/acscatal.8b01678.

(23) Ameri, T.; Min, J.; Li, N.; Machui, F.; Baran, D.; Forster, M.; Schottler, K. J.; Dolfen, D.; Scherf, U.; Brabec, C. J. Performance Enhancement of the P3ht/Pcbm Solar Cells through Nir Sensitization Using a Small-Bandgap Polymer. Adv. Energy Mater. 2012, 2 (10), 1198–1202. https://doi.org/10.1002/aenm.201200219.

(24) Schubert, S.; Delaney, J. T.; Schubert, U. S. Nanoprecipitation and Nanoformulation of Polymers: From History to Powerful Possibilities beyond Poly(Lactic Acid). Soft Matter 2011, 7 (5), 1581–1588. https://doi.org/10.1039/c0sm00862a.

(25) Bai, Y.; Wilbraham, L.; Slater, B. J.; Zwiijnenburg, M. A.; Sprick, R. S.; Cooper, A. I. Accelerated Discovery of Organic Polymer Photocatalysts for Hydrogen Evolution from Water through the Integration of Experiment and Theory. J. Am. Chem. Soc. 2019, 141 (22), 9063–9071. https://doi.org/10.1021/jacs.9b03591.

(26) Zhao, W.; Li, S.; Yao, H.; Zhang, S.; Zhang, Y.; Yang, B.; Hou, J. Molecular Optimization Enables over 13% Efficiency in Organic Solar Cells. J. Am. Chem. Soc. 2017, 139 (21), 7148–7151. https://doi.org/10.1021/jacs.7b02677.

(27) Hou, J.; Inganas, O.; Friend, R. H.; Gao, F. Organic Solar Cells Based on Non-Fullerene Acceptors. Nat. Mater. 2018, 17 (2), 119–128. https://doi.org/10.1038/NMAT5063.

(28) Sachs, M.; Sprick, R. S.; Pearce, D.; Hillman, S. A. J.; Monti, A.; Guilbert, A. A. Y.; Brownbill, N. J.; Dimitrov, S.; Shi,
X.; Blanc, F.; et al. Understanding Structure-Activity Relationships in Linear Polymer Photocatalysts for Hydrogen Evolution. *Nat. Commun.*, 2018, 9 (1), 1–11. https://doi.org/10.1038/s41467-018-07420-6.
Conjugated Polymer Donor-Molecular Acceptor Nanohybrids for Photocatalytic Hydrogen Evolution

Haofan Yang, Xiaobo Li,* Reiner Sebastian Sprick and Andrew I. Cooper*

Department of Chemistry and Materials Innovation Factory, University of Liverpool, 51 Oxford Street, Liverpool L7 3NY, U.K.

Table of Contents

1. Experimental section

1.1 Materials

1.2 Synthesis of DANHs

1.3 Characterization methods

1.4 High throughput photocatalysis measurements

1.5 Hydrogen evolution kinetic experiments

1.6 Apparent quantum yield measurements

2. Supporting figures

3. Supporting table
Experimental Section

1.1 Materials
Poly[N-9’-heptadecanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)] (D1),
poly[(9,9-di-n-octylfluorene-alt-bithiophene), poly[(9,9-di-n-octylfluorenyl-2,7-diy]-co-bithiophene] (D2),
poly[(9,9-di-n-octylfluorene-alt-benzothiadiazole)] (D3), poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-
phenylenevinylene] (D4), poly(3-hexylthiophene-2,5-diyl) (D5), [6,6]-phenyl-C61-butyric acid methyl
ester (A1), [6,6]-phenyl-C71-butyric acid methyl ester (A2), indene-C60-propionic acid butyl ester (A3)
and 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-6,7-difluoro-indanone))-5,5,11,11-tetrakis(4-
hexylphenyl)-dithieno[2,3-d:2’,3’-d’]-s-indaceno[1,2-b:5,6-b’]dithiophene (A4) were obtained from
Ossila (U.K). Poly(sodium 4-styrenesulfonate), poly(styrene-alt-maleic acid) sodium salt solution,
sodium dodecyl sulfate (SDS), ascorbic acid (AA), hexachloroplatinic acid solution (8 wt. % in water)
and tetrahydrofuran (THF inhibitor-free) were purchased from Sigma-Aldrich. Metal precursors were
obtained from commercial suppliers Sigma-Aldrich, TCI and Alfa Aesar. The deionized water was
purified using a Milli-Q System ($\rho = 15 \text{ M}\Omega$). All chemicals were used as received without further
purification.

1.2 Synthesis of DANHs
The donor and acceptor materials were dissolved in anhydrous THF with a concentration of 0.2
mg mL$^{-1}$ and 1 mg mL$^{-1}$, respectively, serving as stock solution. A volume of 1 mL of the donor
and the acceptor stock solutions was mixed together and sonicated for a few minutes. Next, 0.5 mL of this
mixture was added rapidly into a vial containing 5 mL of deionized water under continuous sonication
for around 10 seconds. All samples were placed in a cover-free sample holder on a hot plate at
130 °C for 5 hours to completely evaporate the residual THF. For the preparation of pure donor or
acceptor nanomaterials, all procedures were the same except that 1 mL of donor or acceptor stock
solution was used.

1.3 Characterization methods
SEM Measurements were carried out on Hitachi S-4800 cold field emission scanning electron
microscope (FE-SEM). Images were collected at working voltage of 10 kV and a working distance of
3.4 mm using a combination of upper and lower secondary electron detectors. Samples was dropped
on silica wafer before imaging. $^1$H NMR spectra were recorded at 400 MHz using a Bruker Avance
400 NMR spectrometer. The UV-visible absorption spectra and steady-state photoluminescence
spectra were measured on a Shimadzu UV-2550 UV-Vis spectrometer and an Edinburgh Instruments
LS980-D2S2-STM spectrometer, respectively. Samples with good aqueous dispersibility were
synthesized by a moderate evaporation method (heating overnight at 60 °C with stirring) and diluted
with an appropriate amount of water to keep the sample concentration at 0.01 mg mL$^{-1}$ before
measuring the spectrum.

1.3 High throughput photocatalysis measurement
Before photocatalysis, certain amounts of 1 M ascorbic acid solution and hexachloroplatinic acid
solution were added into vial (volume = 12 ml) containing 5 ml of above prepared DANHs aqueous
solution. The photocatalytic H$_2$ production activities were then evaluated using a high-throughput
degas-irradiation-analysis system. Specifically, after purging with nitrogen for 3 hours in a Sweigher
robot (Chemspeed Technologies), the vials were capped with piercable caps using a capper tool a
nitrogen atmosphere. Next, up to 48 vials were illuminated using a solar simulator (A4.5G, Class AAA,
IEC/JIS/ASTM, 1440 W xenon, 12 × 12 in., MODEL:94123A) for 2 hours. The samples were rotated
and rocked on their sides during irradiation. Gaseous products were injected via a transfer line
equipped with headspace injector and the H$_2$ production was analyzed using an Agilent HS-GC (Fig
S2c) equipped with a flame ionization detector (FID) and a 5 Å molecular sieve column (temperature:
45 °C).

1.4 Hydrogen evolution kinetics experiments
Kinetic measurements were conducted in a 69 mL quartz flask. Catalysts (normally 1.15 mg for
A1/D1) were dispersed into 0.1 M ascorbic acid water solution (25 mL) with diluted hexachloroplatinic
acid solution as a platinum precursor (3% to 9% loading). After bubbling with N$_2$ for 30 min to remove
O$_2$, the reaction mixture was illuminated with a 300 W Newport Xe light-source (Model: 6258, Ozone
free) using a 420 nm cut-off filter. The light source was cooled by water circulating through a metal
jacket. Gas samples were taken out by using a gas-tight syringe and run on a Bruker 450-GC gas
chromatograph. Hydrogen was detected with a thermal conductivity S3 detector referencing against
standard gas with a known concentration of hydrogen. Any hydrogen dissolved in the reaction mixture was not measured and the pressure increase generated by the evolved hydrogen was neglected in the calculations. After the photocatalysis experiment, samples were recovered by washing with water and centrifuging twice at 14000 rpm for 15 min.

1.5 Apparent quantum yield measurements
The apparent quantum yield for the photocatalytic \( \text{H}_2 \) evolution was measured using a \( \lambda = 420 \text{ nm} \) LED (129.5 mW), \( \lambda = 490 \text{ nm} \) LED (97.1 mW), \( \lambda = 515 \text{ nm} \) LED (65.7 mW) and \( \lambda = 595 \text{ nm} \) LED (115.0 mW) controlled by an IsoTech IPS303DD power supply. For the measurement, 6 vials of A1/D1 sample, prepared by nano-precipitation strategy, were mixed together and then diluted to 25 mL with deionized water. Then, 440 mg of ascorbic acid (0.1 M) and diluted hexachloroplatinic acid (9% loading) were added before illuminating with LED. The light intensity was measured with a ThorLabs S120VC photodiode power sensor controlled by a ThorLabs PM100D Power and Energy Meter Console and the apparent quantum yield was estimated using the equation below:

\[
AQY = 2 \times \frac{\text{moles of hydrogen evolved}}{\text{moles of incident photons}} \times 100\%
\]
Supporting figures

Figure S1. Photocatalytic hydrogen production rate for A1/D1 NADHs as a function of A1 fraction. Conditions: Catalyst concentration: 20–100 µg mL⁻¹ (0.1-0.5 mg in 5 mL water); ascorbic acid: 0.04 M; Pt loading: 3% wt. % (using H₂PtCl₆ 8 wt. % in water); light source: solar simulator, 1 sun; irradiation time: 2 hours.

Figure S2. H₂ production rate of A1/D1 and A1+D1 as a function of A1 fraction. Conditions: catalysts concentration: 20–100 µg mL⁻¹ (0.1-0.5 mg in 5 mL water); ascorbic acid: 0.04 M; Pt loading: 3 wt. % (using H₂PtCl₆ 8 wt. % in water); light source: solar simulator; irradiation time: 2 hours.
Figure S3. (a) Effect of ascorbic acid concentration on H₂ production rate under solar simulator irradiation. Catalyst concentration: 46 or 34 µg mL⁻¹ (0.23 or 0.17 mg in 5 mL water); ascorbic acid: 0.02–0.5 M; Pt loading: 3 wt. % (using H₂PtCl₆ 8 wt. % in water); light source: solar simulator; irradiation time: 2 hours. (b) Amount of Pt loading effect on H₂ production rate under solar simulator. Catalyst concentration: 46 or 34 µg mL⁻¹ (0.23 or 0.17 mg in 5 mL water); ascorbic acid: 0.04 M; Pt loading: 0.5%–9% (using H₂PtCl₆ 8 wt. % in water); light source: solar simulator; irradiation time: 2 hours.

Figure S4. H₂ production rate for A1/D1 NADHs using various metal precursors. Catalyst concentration: 46 µg mL⁻¹ (0.23 in 5 mL water); ascorbic acid: 0.04 M; metal loading: 3%; light source: solar simulator; irradiation time: 2 hours.
**Figure S5.** Effect of surfactants with different concentration on the H₂ production rate for A1/D1 (70.6% A1). Conditions: catalysts concentration: 46 µg mL⁻¹ (0.23 in 5 mL water); ascorbic acid: 0.04 M; Metal loading: 3 wt. %; light source: solar simulator; irradiation time: 2 hours. Surfactant 1: SDS, surfactant 2: Poly(sodium 4-styrenesulfonate) and surfactant 3: Poly(styrene-alt-maleic acid) sodium salt solution.

**Figure S6.** Time course of (a) mass-normalized and (b) non mass-normalized H₂ production of A1/D1 NADHs. Conditions: ascorbic acid: 0.1 M; Pt loading: 9% Pt; light source: 300 W Xe light source fitted with a λ > 420 nm filter. Half circle points represent the beginning of next measurement after degassing.
Supporting Table

Table S1. Photocatalytic performance of various reported organic photocatalysts. Note that the HER (and AQY) depends on the irradiation source and experimental set-up, and hence these values can only be compared in a qualitative sense.

| Materials               | HER (mmol g⁻¹ h⁻¹) | AQY (%) | Journal and publication year | Reference |
|-------------------------|--------------------|---------|------------------------------|-----------|
| DBTD-CMP₁               | 9.2 (λ > 420 nm)   | 0.2% (500 nm) | ACS Catal. 2018              | [2]       |
| FS-COF                  | 10.1 (λ >420 nm)   | 0.6% (600 nm) | Nat. Chem. 2018              | [3]       |
| FS-COF+dye              | 16.3 (λ >420 nm)   | 2.2% (600 nm) | Nat. Commun. 2019            | [4]       |
| g-C₆N₂-COF              | 4.1 (λ >420 nm)    | 3.2% (520 nm) | Nat. Commun. 2019            | [4]       |
| Polymer dots PIFDTBT/g-C₃N₄ | 0.58 (λ >400 nm)   | ~0.5% (500 nm) | Appl. Catal. B Environ. 2019 | [5]       |
| CTF-BT/Th               | 6.6 (λ >420 nm)    | ~2.5% (500 nm) | Angew. Chem. Int. Ed. 2019   | [6]       |
| DA-HM                   | 4.14 (λ >420 nm)   | ~2% (500 nm)  | Angew. Chem. Int. Ed. 2018   | [7]       |
| g-C₃N₄-MF₁₀₀            | 3.6 (λ >420 nm)    | ~4% (500 nm)  | Nano Energy 2019             | [8]       |
| P3/CN                   | 13 (λ = 420~780 nm)| ~1.5% (630 nm) | Adv. Funct. Mater. 2018      | [9]       |
| Polymer dots PFFTQ-PtPy₁₅ | 12.7 (λ >420 nm)   | 0.4% (515 nm) | ACS Catal. 2018              | [10]      |
| Polymer dots PFODTBT    | 63 (λ >420 nm)     | 0.6% (550 nm) | Energy Environ. Sci. 2017    | [11]      |
| Pt-PVP-Tp-COF           | 8.4 (λ >420 nm)    | 0.6% (475 nm) | Angew. Chem. Int. Ed. 2019   | [12]      |
| Polymer dots PBT₂/g-C₃N₄ | 0.93 (λ >400 nm)   | 0.8% (550 nm) | J. Mater. Chem. A 2019      | [13]      |
| P10                     | 3.2 (λ >420 nm)    | 11.6% (420 nm) | Nat. Commun. 2018            | [14]      |
| Ter-CTF-0.7             | 19.3 (λ >420 nm)   | 14.78% (550 nm) | ACS Catal. 2019 | [15] |
| This work A1/D1 DANHs  | 105.2 (λ >420 nm)  | 3.16% (515 nm) |                         |           |
Figure S7. Image of aqueous A1/D1 reaction solution in a 69 mL flask (a) before and (b) after the photocatalysis experiment (19 hours irradiation). Also, aqueous A4/D1 reaction solution (a) before and (b) after photocatalysis experiment (10 hours irradiation).

Figure S8. SEM images of A1/D1 (a) before and (b) after the photocatalysis experiment and equivalent images under high magnification (scale bar: 100 nm) (c) before and (d) after experiment.
Figure S9. Absorption spectrum of A1/D1 before and after photocatalysis experiment (a) in water and (b) in THF. (c) $^1$H NMR of A1/D1 before (top) and after (down) photocatalysis experiment.

Figure S10. Hydrogen production rates for various ternary systems with different compositions. Catalyst concentration: 60, 46 and 28 µg mL$^{-1}$ in 5 mL water; ascorbic acid: 0.04 M; Pt loading: 3 wt. %; light source: solar simulator; irradiation time: 2 hours.
Figure S11. \( \text{H}_2 \) production rate for A1/D2D4 ternary NADH system. Conditions: catalysts concentration: 60, 46 and 28 \( \mu \text{g mL}^{-1} \) in 5 mL water; ascorbic acid: 0.04 M; Pt loading: 3 wt. %; light source: solar simulator; irradiation time: 2 hours.

References

[1] T. Ameri, J. Min, N. Li, F. Machui, D. Baran, M. Forster, K. J. Schottler, D. Dolfen, U. Scherf, C. J. Brabec, \textit{Adv. Energy Mater.} \textbf{2012}, \textit{2}, 1198–1202.

[2] Z. Wang, X. Yang, T. Yang, Y. Zhao, F. Wang, Y. Chen, J. H. Zeng, C. Yan, F. Huang, J. X. Jiang, \textit{ACS Catal.} \textbf{2018}, \textit{8}, 8590–8596.

[3] X. Wang, L. Chen, S. Y. Chong, M. A. Little, Y. Wu, W. H. Zhu, R. Clowes, Y. Yan, M. A. Zwijnenburg, R. S. Sprick, et al., \textit{Nat. Chem.} \textbf{2018}, \textit{10}, 1180–1189.

[4] S. Bi, C. Yang, W. Zhang, J. Xu, L. Liu, D. Wu, X. Wang, Y. Han, Q. Liang, F. Zhang, \textit{Nat. Commun.} \textbf{2019}, \textit{10}, 1–10.

[5] W. Zhou, T. Jia, D. Zhang, Z. Zheng, W. Hong, X. Chen, \textit{Appl. Catal. B Environ.} \textbf{2019}, \textit{259}, 118067.

[6] W. Huang, Q. He, Y. Hu, Y. Li, \textit{Angew. Chemie - Int. Ed.} \textbf{2019}, \textit{58}, 8676–8680.

[7] H. Ou, X. Chen, L. Lin, Y. Fang, X. Wang, \textit{Angew. Chemie - Int. Ed.} \textbf{2018}, \textit{57}, 8729–8733.

[8] H. Che, C. Liu, G. Che, G. Liao, H. Dong, C. Li, N. Song, C. Li, \textit{Nano Energy} \textbf{2019}, \textit{104273}.

[9] F. Yu, Z. Wang, S. Zhang, H. Ye, K. Kong, X. Gong, J. Hua, H. Tian, \textit{Adv. Funct. Mater.} \textbf{2018}, \textit{28}, 1–13.

[10] P. J. Tseng, C. L. Chang, Y. H. Chan, L. Y. Ting, P. Y. Chen, C. H. Liao, M. L. Tsai, H. H. Chou, \textit{ACS Catal.} \textbf{2018}, \textit{8}, 7766–7772.

[11] P. B. Pati, G. Damas, L. Tian, D. L. A. Fernandes, L. Zhang, I. B. Pehlivan, T. Edvinsson, C. M. Araujo, H. Tian, \textit{Energy Environ. Sci.} \textbf{2017}, \textit{10}, 1372–1376.

[12] J. Ming, A. Liu, J. Zhao, P. Zhang, H. Huang, H. Lin, Z. Xu, X. Zhang, X. Wang, J. Hofkens, et al., \textit{Angew. Chemie - Int. Ed.} \textbf{2019}, \textit{18458–18462}.

[13] W. Zhou, T. Jia, H. Shi, D. Yu, W. Hong, X. Chen, \textit{J. Mater. Chem. A} \textbf{2019}, \textit{7}, 303–311.

[14] M. Sachs, R. S. Sprick, D. Pearce, S. A. J. Hillman, A. Monti, A. A. Y. Guilbert, N. J. Brownbill, S. Dimitrov, X. Shi, F. Blanc, et al., \textit{Nat. Commun.} \textbf{2018}, \textit{9}, 1–11.

[15] L. Guo, Y. Niu, S. Razzaque, tan, S. Jin, \textit{ACS Catal.} \textbf{2019}, \textit{9}, 9438–9445.
