

Electronic Supplementary Information

Solvent Assisted Shape Dependent MAPbI₃/Polyfluorene Heterostructures with Larger Surface Area for Improved Photocatalytic H₂ Evolution

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Experimental Section

Materials: Lead Iodide (PbI_2 , 99%), Hydriodic Acid (57 wt% HI in H_2O), Fluorene (99%), 1,6-Dibromohexane (99%), 4-(Dimethylamino)pyridine (99%), were purchased from Sigma-Aldrich. Ferric Chloride Anhydrous (99%) was obtained from Merck, India. Methylammonium Iodide was purchased from Greatcell Solar, Australia. Hypophosphorus Acid (H_3PO_2 , 50% in H_2O) was obtained from Loba Chemie, India. All chemicals were used as received.

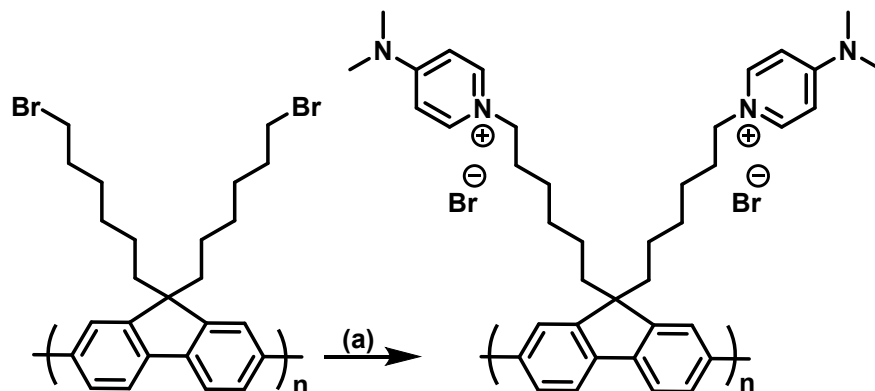
Preparation of MAPI_{HI} powder and MAPI saturated solution: MAPI was synthesized by dissolving MAI and PbI_2 in molar ratio of 1:1 in HI/ H_3PO_2 aqueous solution. Specifically, 15 g PbI_2 was dissolved in 50 mL of HI acid (57 wt% in water), then 5.15 g MAI was slowly added into the solution with vigorous stirring under 80°C . The saturated solution used here was prepared by adding 57 wt% of HI at 50 wt% H_3PO_2 in 5:1(v/v) ratio. The reaction solution with black precipitate was stirred and heated to 100°C for 1h for crystallization to attain the dynamic equilibrium, followed by cooling down to room temperature to obtain the saturated solution containing black MAPI precipitates at the bottom. The MAPI precipitates were separated out from saturated solution by centrifuge, the obtained saturated solution was stored for next photocatalytic measurements, while the precipitates were dried in a vacuum oven at 80°C to get pristine MAPI powder.

Preparation of MAPI_{DMF} : MAPI_{DMF} was prepared by dissolving PbI_2 and MAI in a weight ratio of 3:1 in anhydrous DMF solvent followed by vigorous magnetic stirring at 70°C until a clean bright yellow solution was prepared. Anhydrous toluene was added dropwise in the solution. White precipitate will start to appear, toluene was added till complete precipitate appeared with constant

stirring at 90°C for 3 hours. The reaction mixture was centrifuged with dry ethyl acetate and the precipitate was collected after 3 washes. The precipitate was dried in vacuum oven at 80°C for 12 hours and stored inside the glove box for further use.

Fabrication of $\text{MAPI}_{\text{DMF}}/\text{PF}_{10}$: PbI_2 and MAI were dissolved in a weight ratio of 3:1 in anhydrous DMF solvent followed by vigorous magnetic stirring at 70°C until a clean bright yellow solution was prepared. 10 weight % of polyfluorene was added in the solution and stirred at 70°C for 15 minutes. Anhydrous toluene was added dropwise in the solution. White precipitate will start to appear, toluene was added till complete precipitate appeared with constant stirring at 90°C for 3 hours. The reaction mixture was centrifuged with dry ethyl acetate and the precipitate was collected after 3 washes. The precipitate was dried in vacuum oven at 80°C for 12 hours and stored inside the glove box for further use.

Synthesis of PF: In a 10 mL round bottom flask, the precursor polymer (70 mg), which we had reported earlier (*ACS Sens.* **2018**, 3, 8, 1451–1461), was solubilized in dimethylformamide (2 ml) and then added 4-Dimethylaminopyridine (DMAP) (0.3474 g). The reaction mixture was stirred for 4 days at 80°C in an inert nitrogen gas atmosphere. Later it was cooled to room temperature and poured into diethyl ether to get precipitates. The precipitates were collected and washed multiple times with dichloromethane (DCM) followed by drying at room temperature to get a brown-colored polymer (PF) (Yield = 90%). $^1\text{H NMR}$ (600 MHz, δ , DMSO-d_6): 8.24 (b), 7.95 (b), 7.87 (b), 7.82 (b), 7.46 (b), 7.36 (b), 6.97 (b), 4.05 (b), 3.15 (b), (b), 2.11 (b), 1.53 (b), 1.01 (b), 0.61 (b).



Scheme S1. Synthesis of PF. (a) 4-Dimethylaminopyridine (DMAP), DMF, 80°C, 4 days.

Characterization

Powder X-ray diffractogram were obtained from Rigaku Micromax-007HF diffractometer equipped with Cu K α 1 irradiation ($\lambda = 1.54184 \text{ \AA}$) at scan rate of 4°/min. Morphology studies were conducted using ZEISS SIGMA 300 FESEM operated at 5kV and JEOL JEM 2010 FETEM operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was executed using a PHI 5000 Versa Probe III automated photoelectron spectrometer (ULVAC-PHI, Japan) with an Al K α X-ray beam (1486.7 eV) at 20 kV, 84 W for the analysis of the chemical compositions. Solid state UV-vis spectra were recorded on a PerkinElmer Lambda-750 UV-vis-near-IR spectrometer equipped with an integrating sphere and BaSO₄ powders were used as a reflectance standard. Photoluminescence spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer. Energy-dispersive X-ray (EDX) spectroscopy (Ametek EDAX

attached on Sigma 300, Zeiss) was used for surface elemental analysis. CH Instruments CHI760D potentiostat was used for Electrochemical measurements.

Photocatalytic measurement. The photocatalytic hydrogen evolution experiments were carried out in a glass vessel coupled with gas chromatograph (Agilent 7820A GC System). A typical process consists of (a) 50 mg of photocatalyst dispersed in 15 ml of MAPI saturated aqueous solution of HI/ H₃PO₂ under constant stirring, (b) degassing the photocatalytic chamber for 30 min, (c) using online gas chromatography to confirm no H₂ was being generated in the reaction chamber in absence of light irradiation and (d) turning on the light source to start the photocatalytic HI splitting reaction with continuous monitoring of the hydrogen generation by gas chromatograph.

Photoelectrochemical measurement: The electrochemical impedance spectroscopy (EIS) and transient photocurrent response curves were performed on the electrochemical workstation (CH Instruments Ins.) in a three-electrode configuration with the assembled photoelectrodes (photocatalysts coated on 1 cm² of carbon paper) as the working electrode, the Ag/AgCl as the reference electrode and the Pt wire as the counter electrode. The EIS experiments were performed in MAPI saturated aqueous HI/H₃PO₂ solution under scan rate of 10 mV s⁻¹.

Table S1. Photophysical and electrochemical properties of polyfluorene.

Sample	E ^{red} _{onset} (V)	E ^{ox} _{onset} (V)	LUMO/HOMO (V)	Optical gap (eV)
PF	-0.46 V	1.56 V	-3.98 V/-6 V	2.02 eV

Visible light source for photocatalytic measurements: The visible light source used here for the experiments is a 50 W with power density of 150 mW/cm² white LED bought from Ledvance Osram. The spectrum of this light source is 420 nm -790 nm.

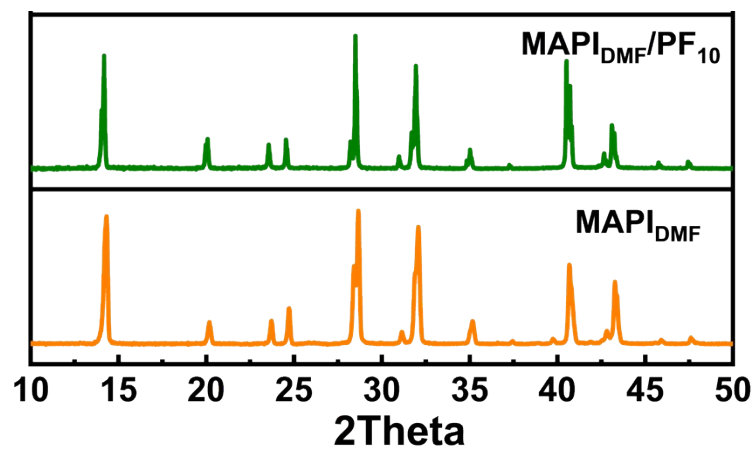


Figure S1. XRD study of MAPI_{DMF} and MAPI_{DMF}/PF₁₀ after 80 hours of HER activities.

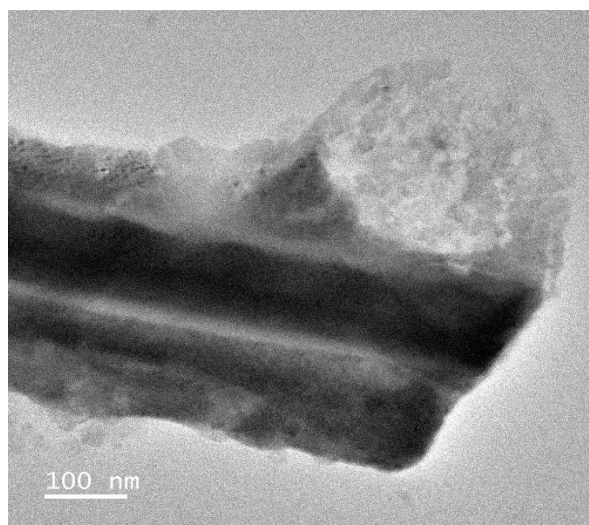


Figure S2. TEM image of MAPI_{DMF}/PF₁₀.

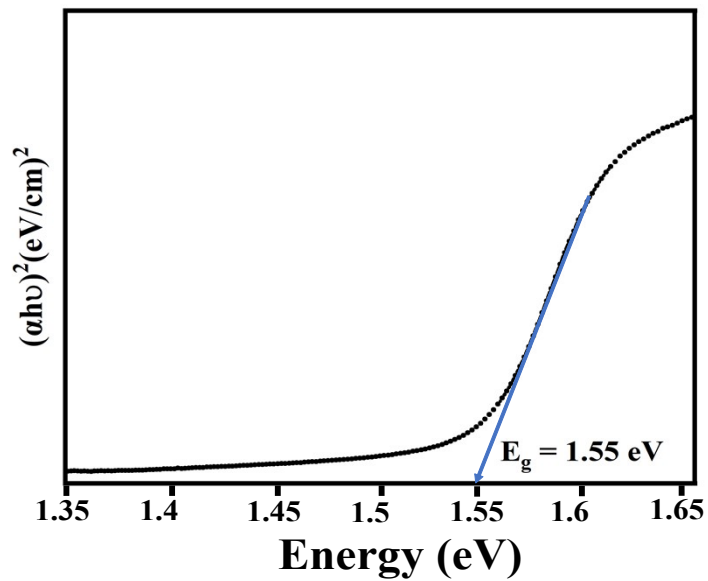


Figure S3. Band gap of pristine MAPI_{DMF} calculated from Tauc plot.

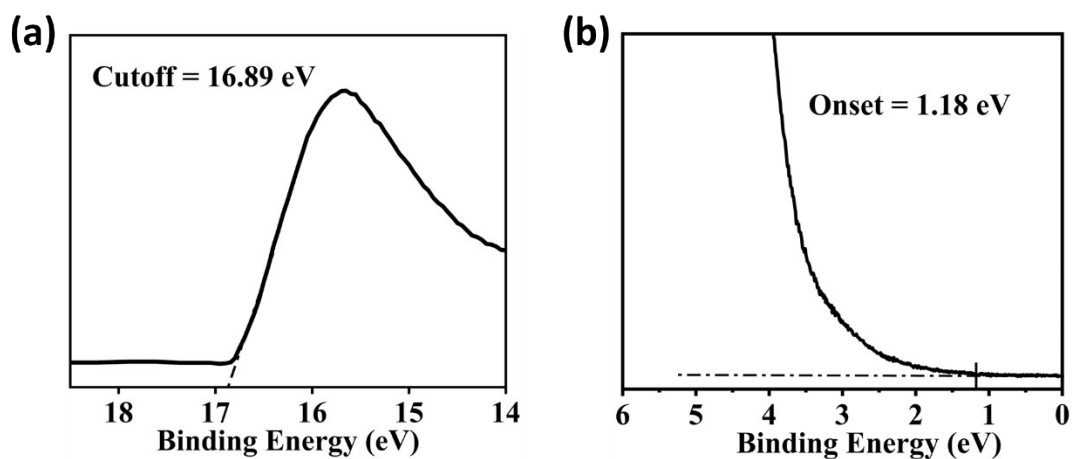


Figure S4. UPS spectra of MAPI_{DMF}.

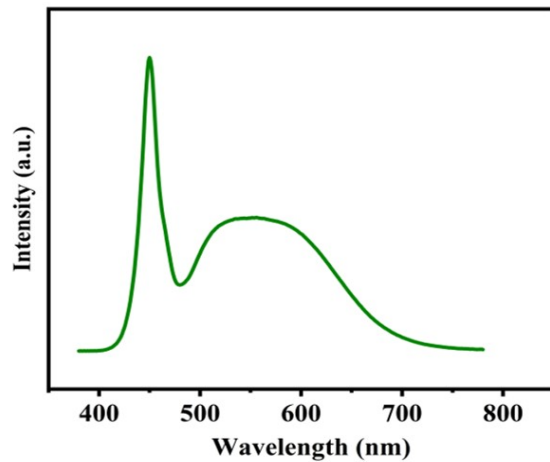


Figure S5. Electroluminescence of white LED light source.

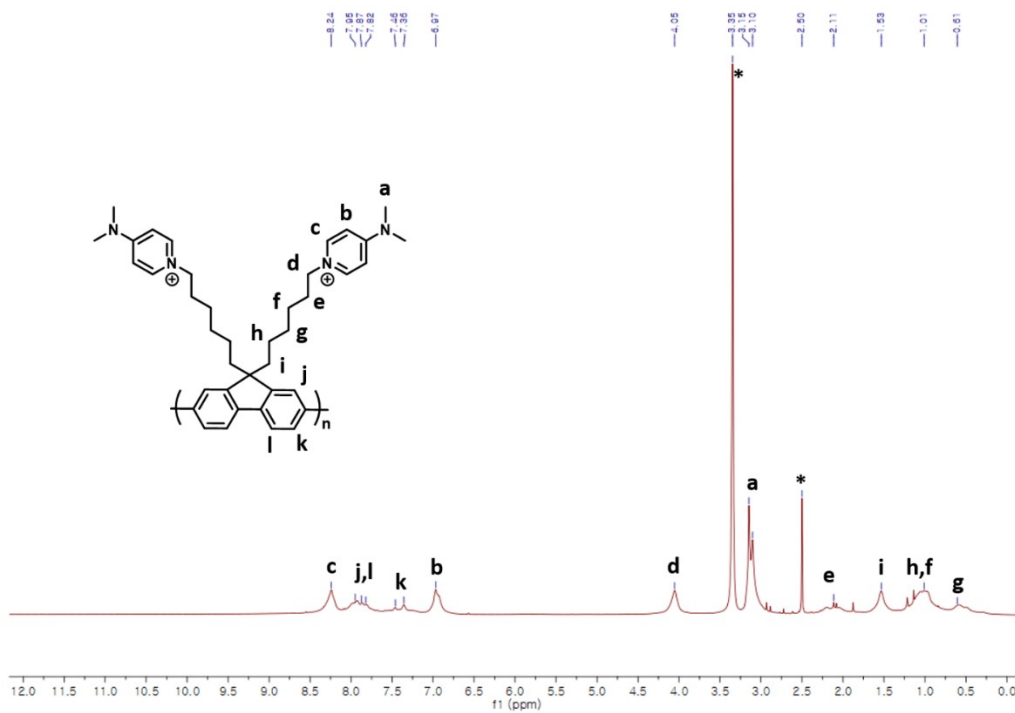


Figure S6. ¹H NMR spectra of PF.

Table S2. A summary of the performance and experimental parameters of reported halide perovskite photocatalysts for H₂ evolution.

MHP Catalyst	Co-catalyst	Light source	Activity	Reference cited in main Article
MAPbI ₃	Pt	($\lambda \geq 475$ nm) 100 mW/cm ²	57 $\mu\text{mol g}^{-1} \text{h}^{-1}$	13
MAPbI ₃	CoP	100 mW /cm ² , AM 1.5 G	786 $\mu\text{mol g}^{-1} \text{h}^{-1}$	16
MAPbI ₃	RGO	120 mW/cm ² $\lambda \geq 420$ nm	939 $\mu\text{mol g}^{-1} \text{h}^{-1}$	45
MAPbI ₃	TiO ₂ /Pt	200 mW/cm ² $\lambda \geq 420$ nm	1784 $\mu\text{mol g}^{-1} \text{h}^{-1}$	14
MAPbI ₃	NiCoB	$\lambda \geq 420$ nm, 100 mW/cm ²	2625 $\mu\text{mol g}^{-1} \text{h}^{-1}$	19
MAPbI ₃	Black P	$\lambda \geq 420$ nm, 100 mW/cm ²	3742 $\mu\text{mol g}^{-1} \text{h}^{-1}$	18
BA ₂ MA ₃ Pb ₄ I ₁₃	Pt	AM 1.5G, 100 mW/cm ²	3948 $\mu\text{mol g}^{-1} \text{h}^{-1}$	25
MAPbI ₃	Polyfluorene	$\lambda \geq 420$ nm, 150 mW/cm ² , 50 W	6200 $\mu\text{mol g}^{-1} \text{h}^{-1}$	This work
MAPbI ₃	Carbonized polymer dot	$\lambda \geq 420$ nm, 100 mW/cm ²	11497 $\mu\text{mol g}^{-1} \text{h}^{-1}$	17
MAPbI ₃	MoS ₂	280 W, $\lambda \geq$ 420 nm, 100 mW/cm ²	30 000 $\mu\text{mol g}^{-1} \text{h}^{-1}$	15