ADVANCED ENERGY MATERIALS

Supporting Information

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Long-Lived Charges in Y6:PM6 Bulk-Heterojunction Photoanodes with a Polymer Overlayer Improve Photoelectrocatalytic Performance

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Methods

Chemicals: ZnO nanoparticles were synthesized and dispersed in methanol following a reported method.[1] 2,2'-((2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2",3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (Y6) and poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)] (PM6) were purchased from 1-Material.

Photoanode fabrication: ITO substrates were cleaned by ultrasonication in deionized (DI) water, acetone, and isopropyl alcohol, sequentially. After additional oxygen plasma treatment, ZnO nanoparticles were spin-coated twice on the ITO substrates in ambient air. Y6:PM6 blend solution (1.2:1 weight ratio, 15 mg mL^{-1} in chloroform and 0.5 vol% 1-chloronaphtalene) was spin-coated on the ZnO layer, then the films were annealed at 100 °C for 60 s inside an N_2-filled glove box. To deposit the PM6 film on the Y6:PM6 film, the PM6 film was fabricated by dropping PM6 solution (15 mg mL^{-1} in chlorobenzene and 1 vol% 1,8-diiodooctane) on the DI water contained in a petri dish. PM6 film thickness can be controlled

by the concentration of PM6 solution and the size of the petri dish. PM6 film thickness was measured by Alpha Step surface profiler. Then, the PM6 film on water was transferred on the Y6:PM6 film, showed high uniformity over the various substrates, as described in previous reports.[2, 3] Epoxy resin was applied on the edge of substrates, and they dried overnight in ambient air.

Spectroscopic analyses: Absorption spectra were collected from a UV–vis spectrometer by Agilent Technologies (Cary 60). The steady state PL spectra were recorded using a home-build system by integrating Andor DU420A-BEX2-DD camera (Oxford instrument), KY193 spectrograph (Oxford instrument) and AvaSphere-50 integrating sphere (AVANTES). Collimated Laser Diode Module (CPS532, THORLABS) was used as excitation source at 532 nm. AvaLight-CAL -Mini (AVANTES) was used to calibrate and measure their absolute intensity.

Transient absorption spectroscopy: Helios spectrometer (Spectra Physics, Newport Corp.) was used to measure the broadband pump-probe femtosecond transient absorption spectra and kinetics for thin film samples. Ultrafast laser pulses (800 nm, 100 fs duration) were generated by a 1 kHz Ti:sapphire regenerative amplifier (Solstice, Spectra Physics, Newport Corp.). One portion of the 800 nm pulse was directed to an optical parametric amplifier (TOPAS Prime, Spectra-Physics) and a frequency mixer (Niruvis, Light Conversion) to tune the visible pump pulses at various wavelengths. The pump pulses were modulated at a frequency of 500 Hz by a mechanical chopper. The rest of the 800 nm pulse was routed onto a mechanical delay stage with a 6 ns time window and directed through a non-linear crystal (sapphire for the visible region and YAG for the NIR region) to generate a white light probe ranging from 400 to 1600 nm. The probe pulse was split into two by a neutral density filter. One portion of the probe pulse served as the reference and was directly sent to the fiber-optic coupled multichannel spectrometers (CCD and InGaAs sensors). The rest of the probe pulse together with the pump pulse were focused onto the same spot on the samples with a beam size of around 0.5 mm^2 before sending it to the spectrometer. To compensate the fluctuations, the measured spectrum was normalized to the reference spectrum and averaged for several scans to achieve a good signal-to-noise ratio. Data analysis was performed with the commercialized Surface Xplorer software.

Photoinduced absorption spectroscopy: PIA analysis was carried out on a modified microsecond−second TA spectroscopy set-up. A high-power LED (LEDENGIN, 365 nm) was used as the excitation source, which was driven by a high-precision DC power supply (TTi QL564P). The LED was directed to the sample through a liquid light guide. Light pulses were generated via a MOSFET transistor (STMicroelectronics STF8NM50N) and the gate was modulated by the DAQ card (National Instruments, USB-6361). All data were sampled without previous amplification using the DAQ card. Excitation fluences were measured with a digital power meter (Thorlabs PM100), using a silicon photodiode power sensor (Thorlabs S120UV). Photoelectrochemical cell configuration for PIA analysis was same as described in the next section.

Photoelectrochemical characterization: Photoelectrochemical characterization of organic photoanodes was carried out in a cappuccino cell (a compact chamber made from polyether ether ketone with a small light window) with a three-electrode configuration: a Ag/AgCl (sat'd KCl) as a reference electrode, a Pt mesh as a counter electrode, and the organic photoanode as a working electrode. The electrolytes were 0.1 M borate buffer (pH 8.1), 0.2 M AA in 0.1 M borate buffer (pH 5.5), and 0.2 M Na_2SO_3 in 0.1 M borate buffer (pH 8.1). LSV were recorded by the NOVA software with the scan rate of 10 mV s^{-1}, and the applied potential was controlled by an Autolab potentiostat (PGSTAT 12) under AM 1.5G illumination calibrated by a silicon photodiode. Applied potentials versus the reference electrode were converted to RHE using the Nernst equation: E_{RHE} (V) = $E_{Ag/AgCl}$ (V) + 0.059 × pH + 0.197. The operating area of the organic photoanode was 0.385 cm^2. The external quatum efficiency (EQE) was measured using an xenon lamp coupled with a monochromator (OBB-2001, Photon Technology International). EQE was calcuated dividing photogenerated electron flux by incident photon flux, by measuring the photocurrent at the monochromated light and the monochromated light intensity at different wavelength. Accumulated hydrogen amounts are measured by the clark electrode (unisense). Theoretical hydrogen amounts determined by dividing measured photogenerated charges by 2*F*, where *F* is Faraday's constant, 96485 C mol^{-1}.

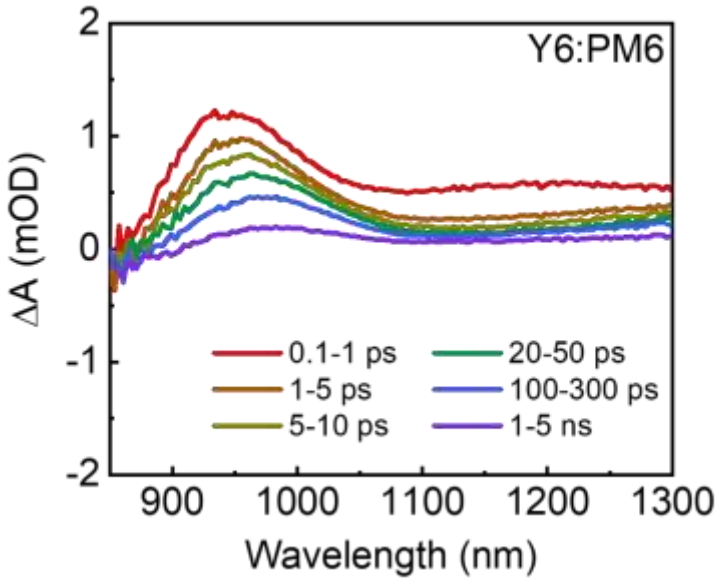

Figure S1. Transient absorption spectra of Y6:PM6 film in near-infrared probe region pumped at the wavelength of 365 nm (fluence: 10 μJ cm^{-2}).

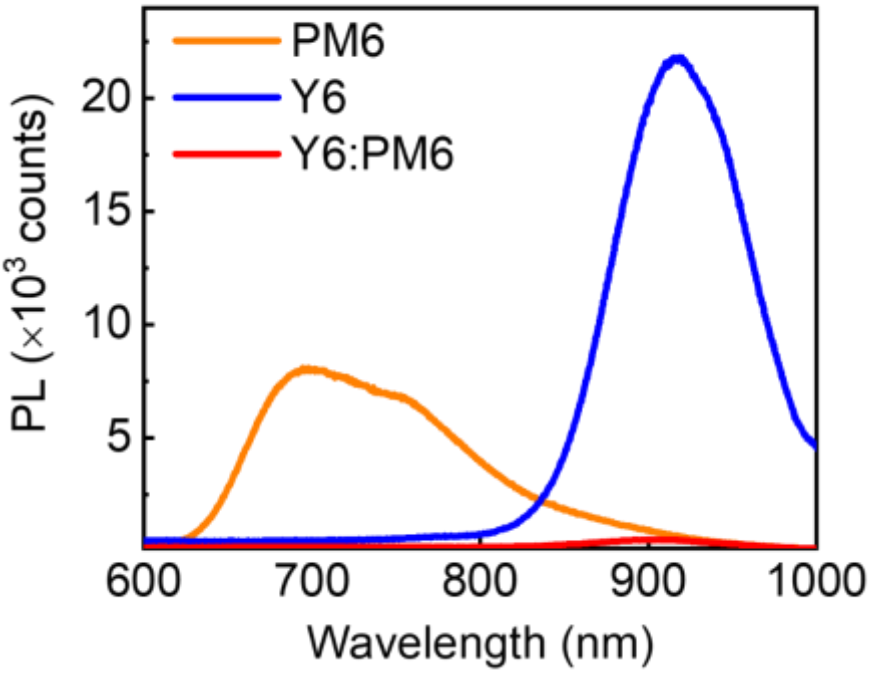

Figure S2. Steady state photoluminescence spectra (normalized to absorbed photon amounts at 532 nm pump wavelength) of neat PM6, neat Y6, and Y6:PM6 film.

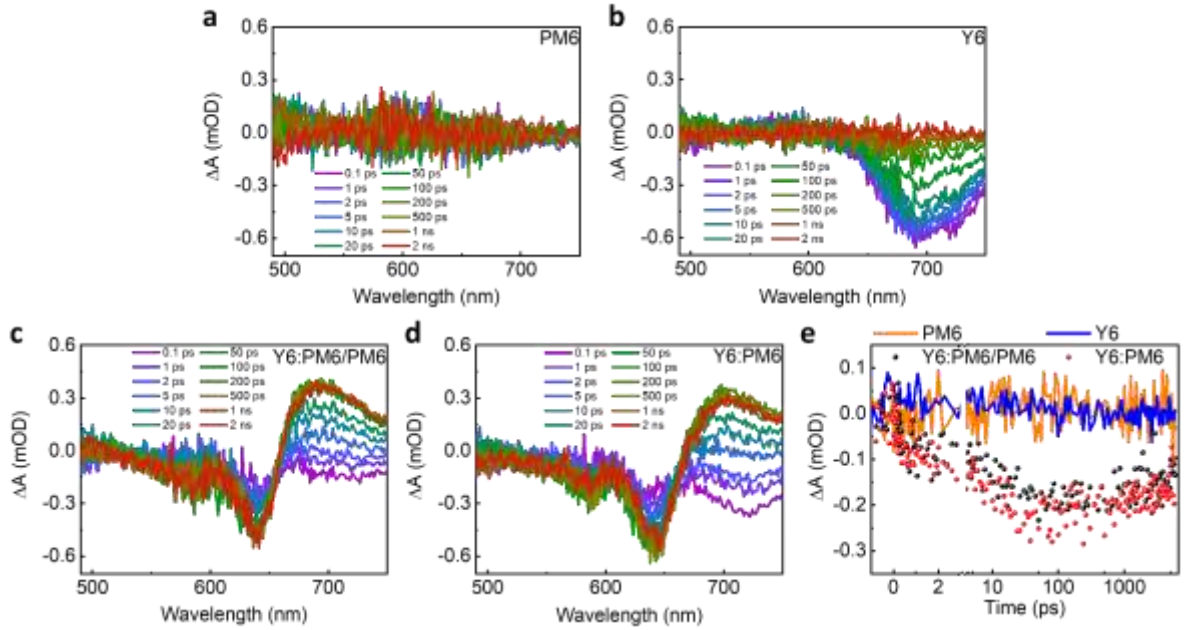

Figure S3. Transient absorption spectra of (**a**) neat PM6, (b) neat Y6, (c) Y6:PM6/PM6, (d) Y6:PM6 film in visible probe region pumped at the wavelength of 750 nm (fluence: 10 μJ cm^{-2}), and (**e**) corresponding kinetics probed at 580 – 590 nm.

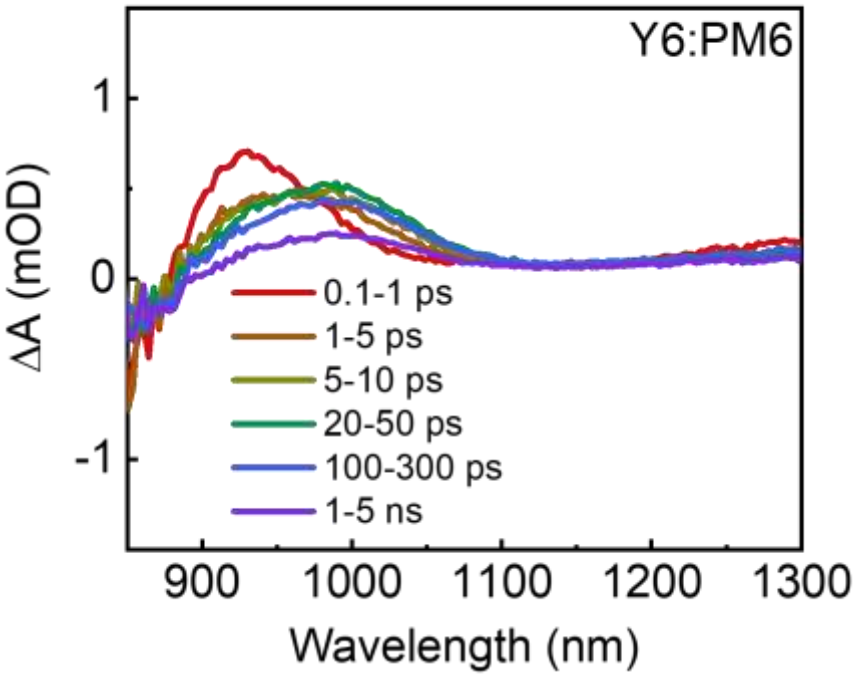

Figure S4. Transient absorption spectra of Y6:PM6 film in near-infrared probe region pumped at the wavelength of 750 nm (fluence: 5 μJ cm^{-2}).

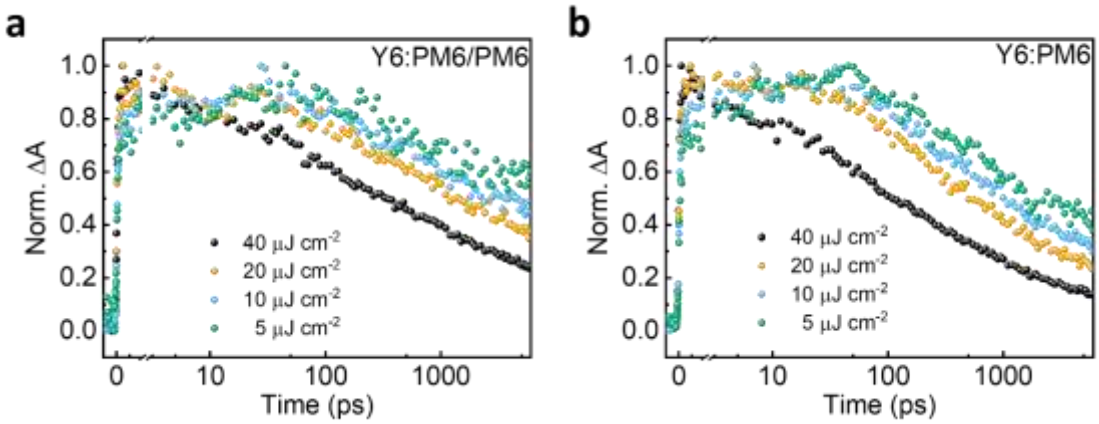

Figure S5. Normalized transient absorption kinetics of (a) Y6:PM6/PM6 and (b) Y6:PM6 film probed at 980 – 1000 nm depending on the pump fluences (at the pump wavelength of 750 nm). The decay half-time is 358, 1403, 2996, and > 6000 ps (103, 545, 1096, and 2196 ps) under the pump fluence of 40, 20, 10, and 5 μJ cm^{-2}, respectively, in Y6:PM6/PM6 (in Y6:PM6).

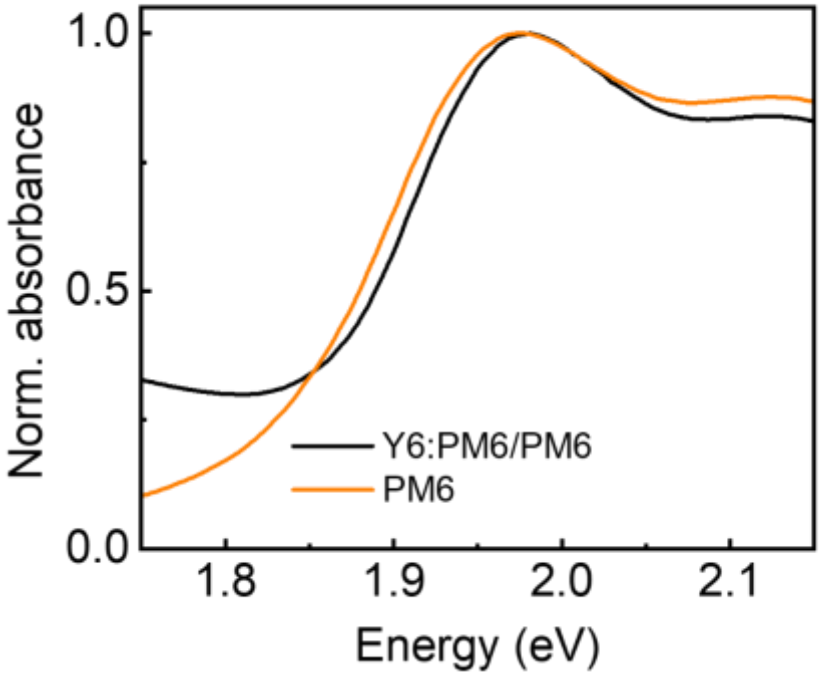

Figure S6. Normalized absorption spectra of Y6:PM6/PM6 and neat PM6 film as a function of energy.

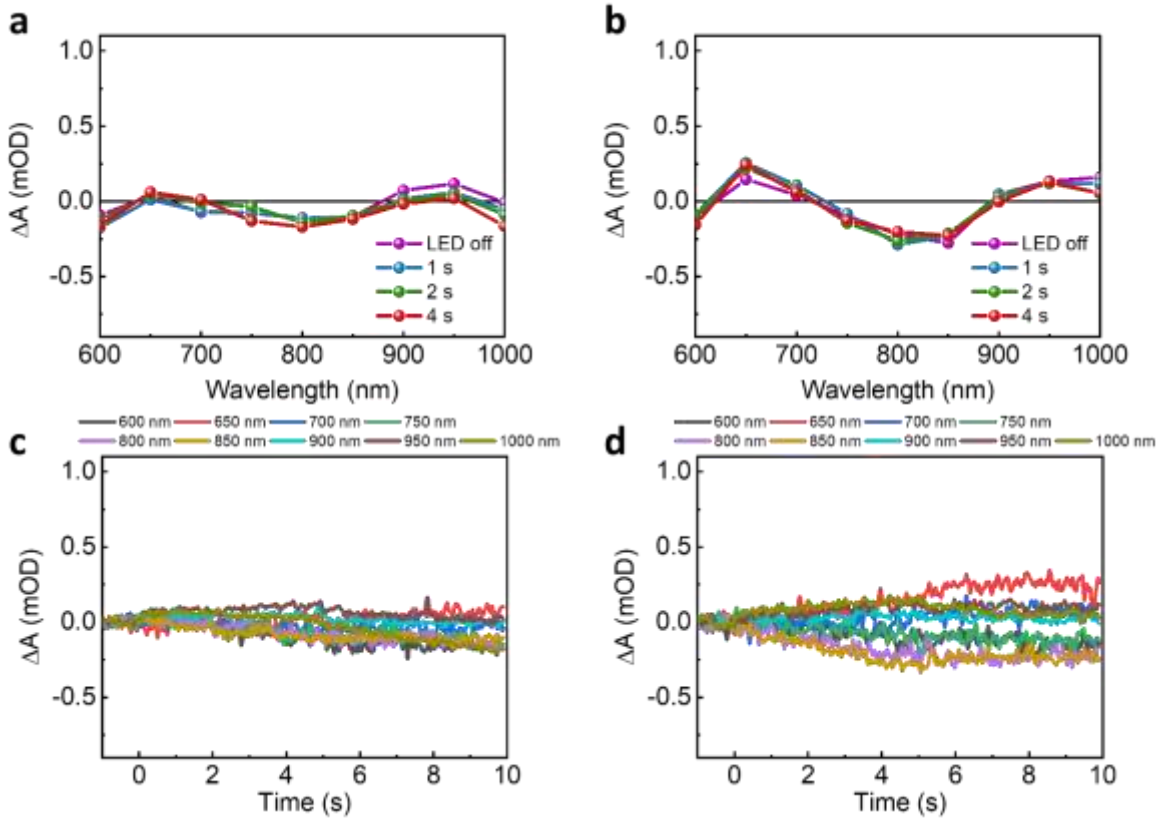

Figure S7. Photoinduced absorption (PIA) spectra of (a) the Y6:PM6/PM6 and (b) the Y6:PM6 photoanodes in 1 M borate buffer (pH 8.1) without external bias and at different time delays after the LED (40 mW cm^{-2} at 365 nm) is off. PIA kinetics of (c) the Y6:PM6/PM6 and (d) the Y6:PM6 photoanodes probing at 600 – 1000 nm.

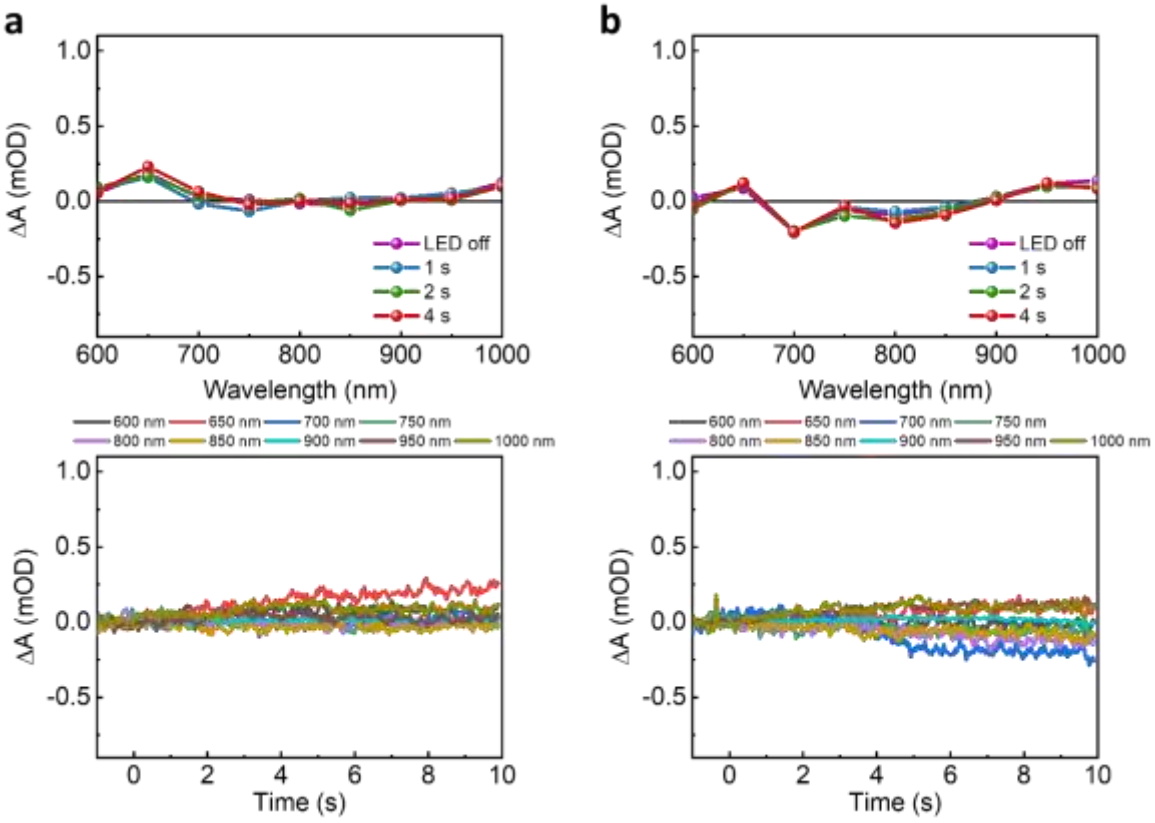

Figure S8. PIA spectra of (a) the Y6:PM6/PM6 and (b) the Y6:PM6 photoanodes in 0.2 M AA in 1 M borate buffer (pH 5.5) without external bias and at different time delays after the LED (40 mW cm^{-2} at 365 nm) is off. PIA kinetics of (c) the Y6:PM6/PM6 and (d) the Y6:PM6 photoanodes probing at 600 – 1000 nm.

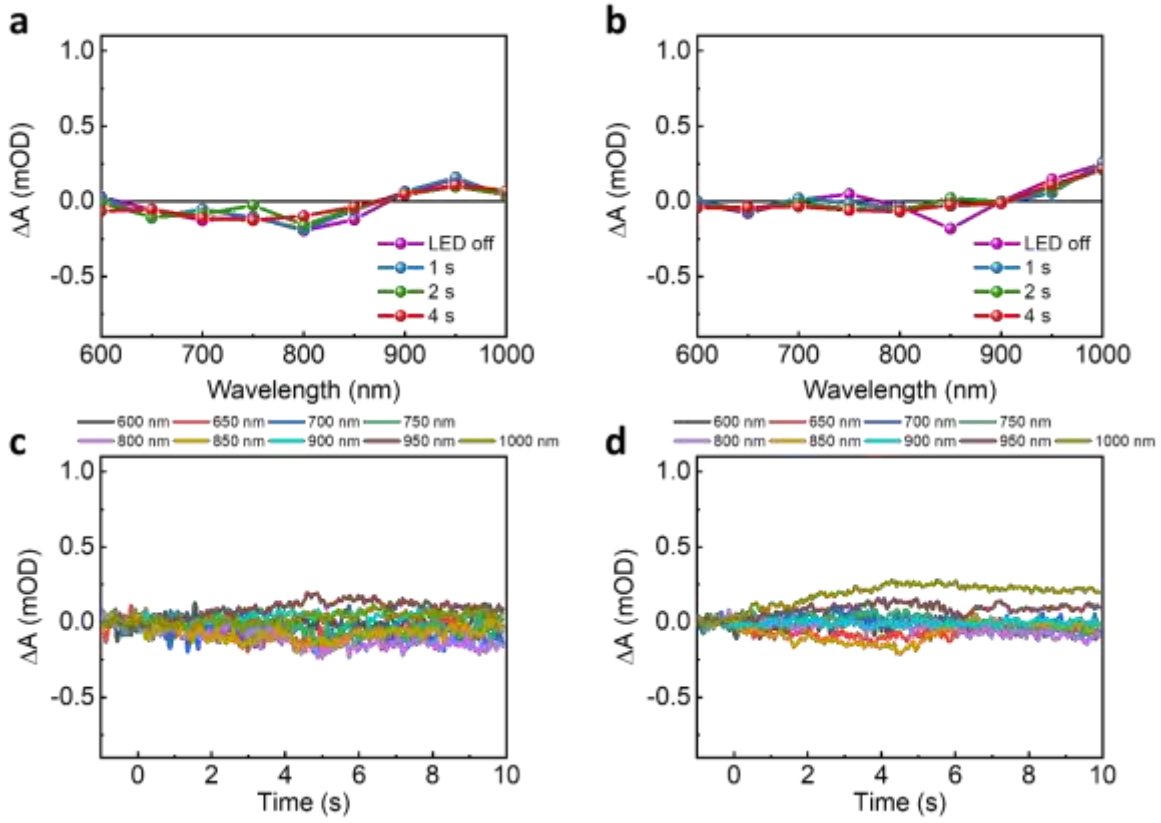

Figure S9. PIA spectra of (a) the Y6:PM6/PM6 and (b) the Y6:PM6 photoanodes in 0.2 M Na_2SO_3 in 1 M borate buffer (pH 8.1) without external bias after the pump LED (40 mW cm^{-2} at 365 nm) off. PIA kinetics of (c) the Y6:PM6/PM6 and (d) the Y6:PM6 photoanodes probing at 600 – 1000 nm.

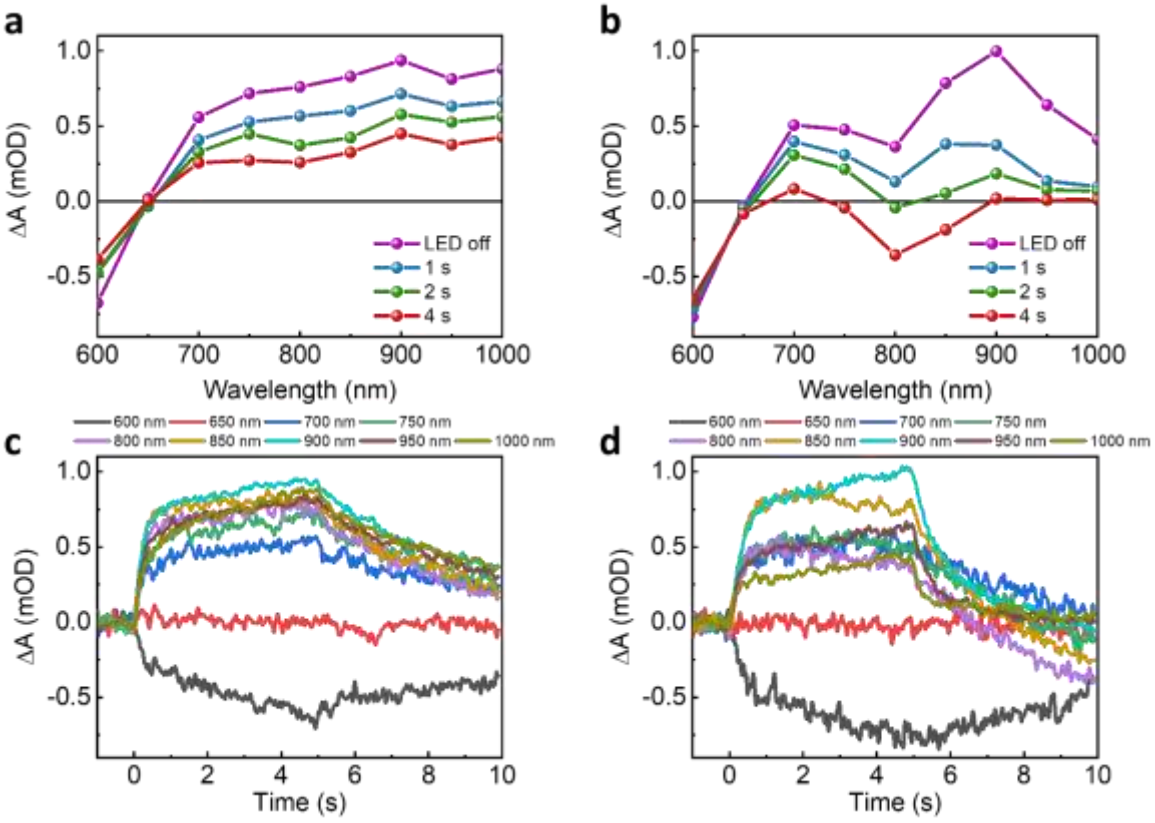

Figure S10. PIA spectra of (a) the Y6:PM6/PM6 and (b) the Y6:PM6 photoanodes in 1 M borate buffer (pH 8.1) at 1.23 V_{RHE} after the pump LED (40 mW cm^{-2} at 365 nm) off. PIA kinetics of (c) the Y6:PM6/PM6 and (d) the Y6:PM6 photoanodes probing at 600 – 1000 nm.

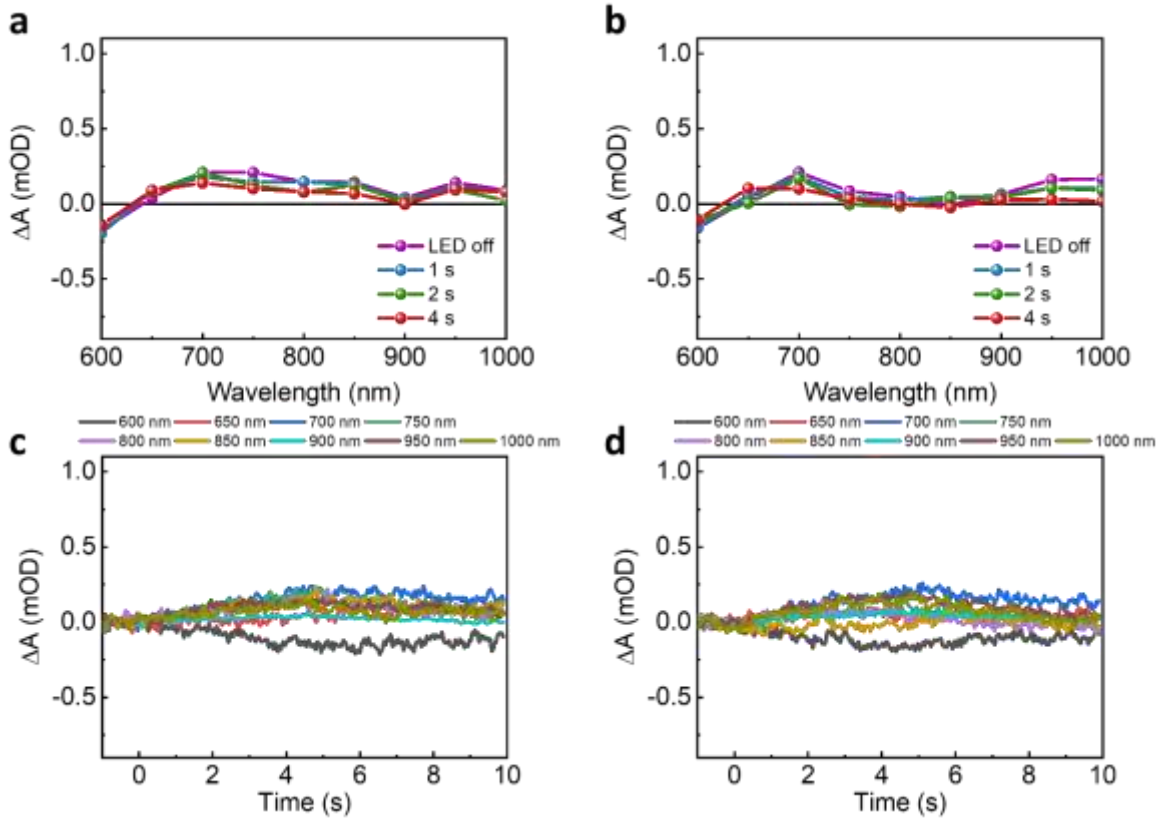

Figure S11. PIA spectra of (a) the Y6:PM6/PM6 and (b) the Y6:PM6 photoanodes in 0.2 M AA in 1 M borate buffer (pH 5.5) at 1.23 V_{RHE} after the pump LED (40 mW cm^{-2} at 365 nm) off. PIA kinetics of (c) the Y6:PM6/PM6 and (d) the Y6:PM6 photoanodes probing at 600 – 1000 nm.

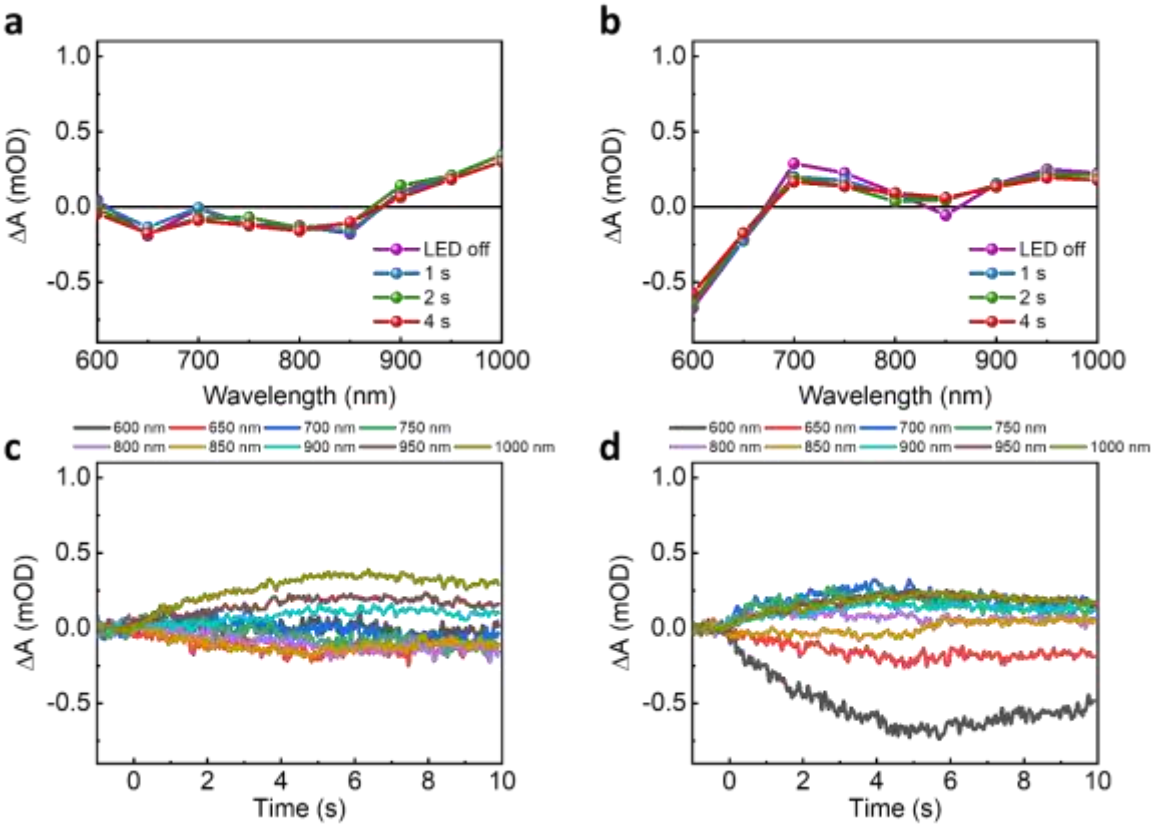

Figure S12. PIA spectra of (a) the Y6:PM6/PM6 and (b) the Y6:PM6 photoanodes in 0.2 M Na_2SO_3 in 1 M borate buffer (pH 8.1) at 1.23 V_{RHE} after the pump LED (40 mW cm^{-2} at 365 nm) off. PIA kinetics of (c) the Y6:PM6/PM6 and (d) the Y6:PM6 photoanodes probing at 600 – 1000 nm.

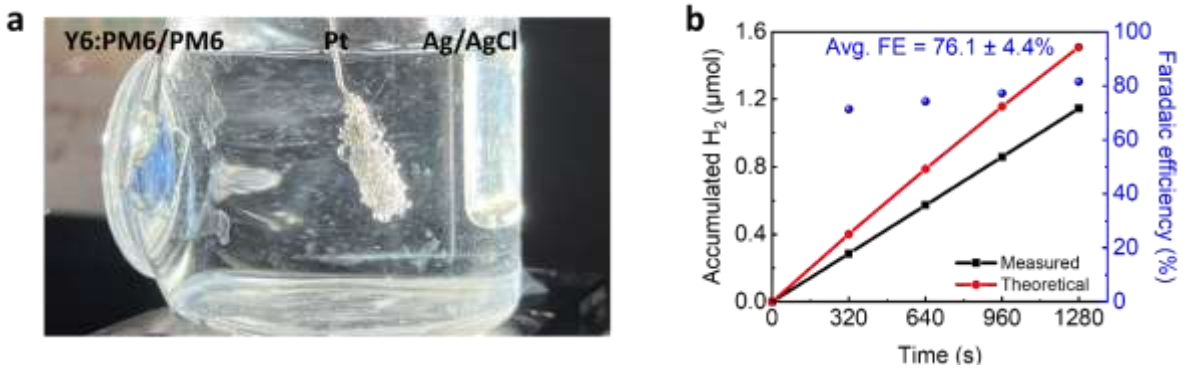

Figure S13. (a) A digital photograph of a photoelectrochemical cell with a three-electrode configuration: the Y6:PM6/PM6 photoanode as a working electrode, a Pt mesh as a counter electrode (coupled hydrogen evolution), and a Ag/AgCl as a reference electrode. (b) Comparison of measured and theoretical hydrogen evolution amounts from the Pt counter electrode at 1.23 V_{RHE} in 0.2 M AA in 1 M borate buffer under continuous 1 sun illumination, and corresponding Faradaic efficiency. Accumulated hydrogen amounts are measured by the clark electrode (unisense). Theoretical hydrogen amounts determined by dividing measured photogenerated charges by 2*F*, where *F* is Faraday's constant, 96485 C mol^{-1}.

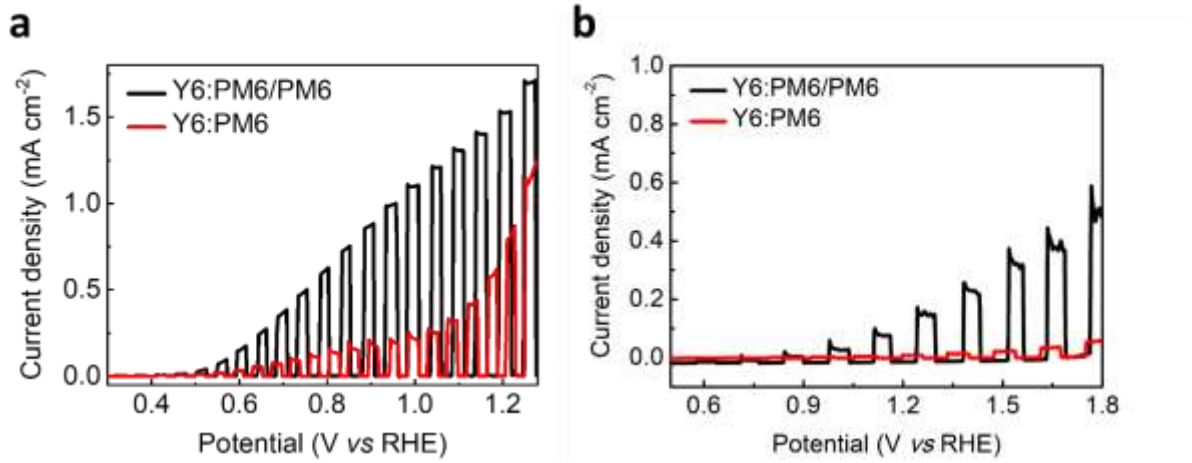

Figure S14. Linear sweep voltammetry scans of the Y6:PM6/PM6 and the Y6:PM6 photoanode in (a) 0.2 M Na_2SO_3 in 1 M borate buffer (pH 8.1) and (b) 0.5 M H_2O_2 in 0.5 M NaOH (pH 13) under chopped 1 sun illumination.

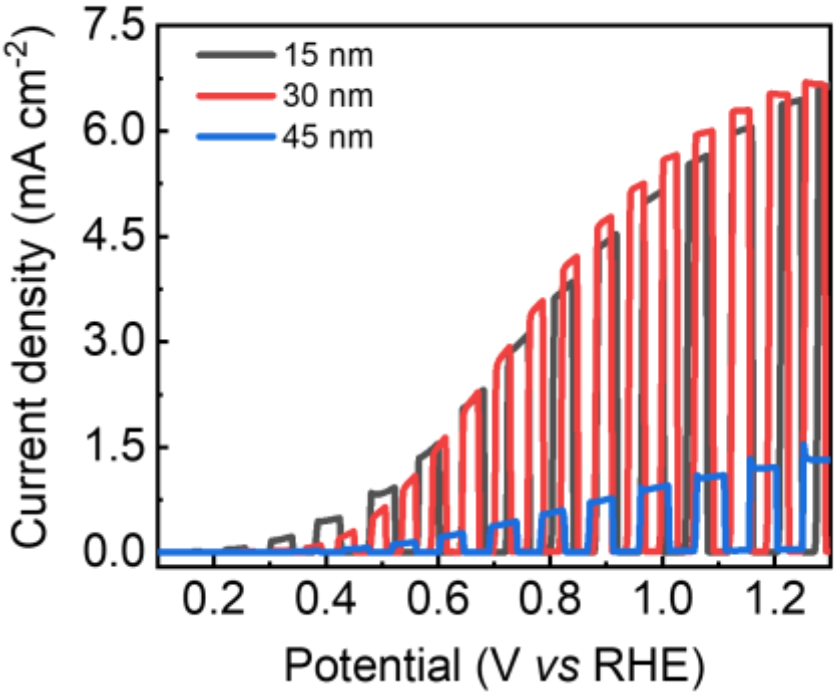

Figure S15. Linear sweep voltammetry scans of the Y6:PM6/PM6 photoanodes with different thicknesses of the PM6 overlayer in 0.2 M AA in 1 M borate buffer (pH 5.5) under chopped 1 sun illumination.

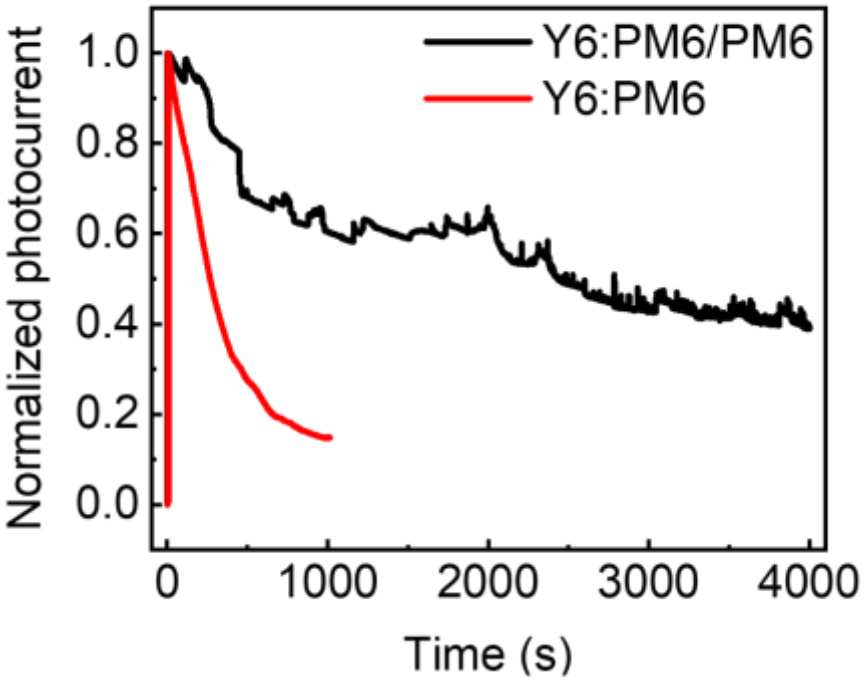

Figure S16. Normalized chronoamperometry curves under 1 sun illumination in 0.2 M AA in 1 M borate buffer at 1.23 V_{RHE}. The measurements were carried out without stirring.

Supplementary References

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[2] T. H. Lee, R. R. Rao, R. A. Pacalaj, A. A. Wilson, J. R. Durrant, *Adv. Energy Mater.* **2022,** *12*, 2103698.

[3] T. H. Lee, W.-W. Park, S. Y. Park, S. Cho, O.-H. Kwon, J. Y. Kim, *Sol. RRL* **2021**, *5*, 2100326.