Supporting Information

Unusual Photoconductive Property of Polyiodide and Enhancement by Catenating with 3-Thiophenemethylamine Salt

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Experimental Section.

Polyiodide Fixed on a Rough Paper. At first, the polyiodide ethanol solution with or without organic molecules was synthesized as follows: 0.1 mL HI (57%) with or without 0.05 mL organic molecule solution was added to 5 mL ethanol, then keep under daylight until the color of solution remain unchanged (Figure S1a, b).[1] Then the solution was dropped on a rough paper (size of 2×2 cm^2) and dried on a hot plate at 50 ^{o}C. Finally, a dark paper was obtained (Figure S1c), which process is reversible through immersing in ethanol as the dissolve of polyiodide (Figure S1d). For comparison, the iodine ethanol solution (0.062g I_2 in 5.1 mL ethanol) with the same I content was also dropped on the rough paper (Figure S1e). Differently, few of iodine was left when the paper was dried (Figure S1f). These results suggest that the polyiodide but iodine can be fixed on rough paper. The UV-Vis absorption spectra of the polyiodide and I_2 ethanol solution (diluted 600 times) are shown in Figure S1g. The classic absorption at 280 nm, 360 nm and 450 nm, which belongs to the the polyiodide ions (I_3^-, I_5^-) were observed for I_2 ethanol solution.[2,3] And the first two of which was observed for the polyiodide solutions. The H^+ is very essential for the stability of polyiodide, as the soluble molecules (aromatic and alkyl) with amino group was added to the original HI solution to decrease the content of H^+ through combining with amino groups, the obtained polyiodide content was decreased (Figure S1g).

Impedance spectroscopy (IS). IS were performed for the polyiodide/paper devices associated with different content of the polyiodide under open-circuit condition with or without illumination. In Figure S3a, two different features similar to the solid solar cells can be observed: one is an arc at high frequency and the other is an arc with a linear part resembling a transmission line (TL) behavior at intermediate frequencies.[4-6] The ohmic serial resistance (R_s) corresponds to the series resistance. The

TL pattern is defined by a straight line, associated to the carrier transport, followed by an arc at lower frequency, which is due to a coupling of chemical capacitance (C_μ) with recombination resistance (R_{rec}). The TL feature could be originated by the transport of electrons through the polyiodide coupled to the recombination between the electrons in one side of the interface (polyiodide) and the holes on the other side of the interface (ITO). The arc at high frequencies can be assigned to a diffusion of holes due to the faster hole transport in the solid phase.[7] As the content of polyiodide increased, the size of these arc decreased and the TL was disappeared, which could be due to the increase of charges and the decrease of recombination resistance (R_{rec}) of electrons (Figure S3a-c). This change was more obviously under illumination, in which the two semicircles were approaching gradually, as the electron Fermi level in the polyiodide increases with the light,[4,8] the transport resistance of electrons through polyiodide becomes smaller, leading to the disappearance of the straight line behavior of the TL. Hence, the equivalent circuit can be simplified to the one shown in Figure S3f. However, at a higher content, these arcs and R_s increases again (Figure S3d), this could be resulting from the increasing of the thickness of polyiodide layer by the surface of existing aggregates, leading to a higher resistance and a low V_{oc} and light-current mentioned above. Most notably, compared to the arcs under dark, Nyquist plots under light has a smaller arc related to R_{rec} of electrons and equal size arc for diffusion of holes.

Synthesis of MATPI1. $C_4H_3SCH_2NH_3I$ (MATPI1) is synthesized according to the literature by a solution reaction of 1 mL of 3-methylaminothiophene, 1.5 mL of hydroiodic acid (HI, 57 wt%), and 10 mL of ethanol in 50 mL round bottomed flask under nitrogen atmosphere at 0 ^oC for 2h with stirring at 400 rpm. The precipitate was recovered by evaporation at 50 ^oC for 2h, washed with diethyl ether three times, and finally dried at 60 ^oC in vacuum oven overnight. 1H NMR (300 MHz, MeOD): (ppm) δ 7.56-7.49 (m, 2 H), 7.20 (d, J = 6.3 Hz, 1 H), 4.16 (s, 2 H). ^{13}C NMR (300 MHz, MeOD): (ppm) δ 134.84 (s), 128.45 (d, J = 10.2 Hz), 126.75 (s), 39.05 (s).

Synthesis of MATPI2. The MATPI2 is fabricated as follows: 0.1 mL 3-methylaminothiophene (98%, Shanghai Shaoyun Technol-ogy Ltd.), 0.2 mL hydroiodic acid (HI 57 wt %, Aldrich) and 10 mL ethanol

(99.9%) in 20 mL round bottomed flask with constant stir-ring for 48 h at room temperature. It can be observed that solution was changed gradually from colorless to dark brown. Then solution was dried in the air at 40 °C and a dark brown crystal was obtained. 1H NMR (300 MHz, MeOD): (ppm) δ 7.61-7.50 (m, 2 H), 7.23 (d, J = 5.0 Hz, 1 H), 4.18 (s, 2 H). ^{13}C NMR (300 MHz, MeOD): (ppm) δ 134.81 (s), 128.45 (d, J = 10.2 Hz), 126.75 (s), 39.05 (s).

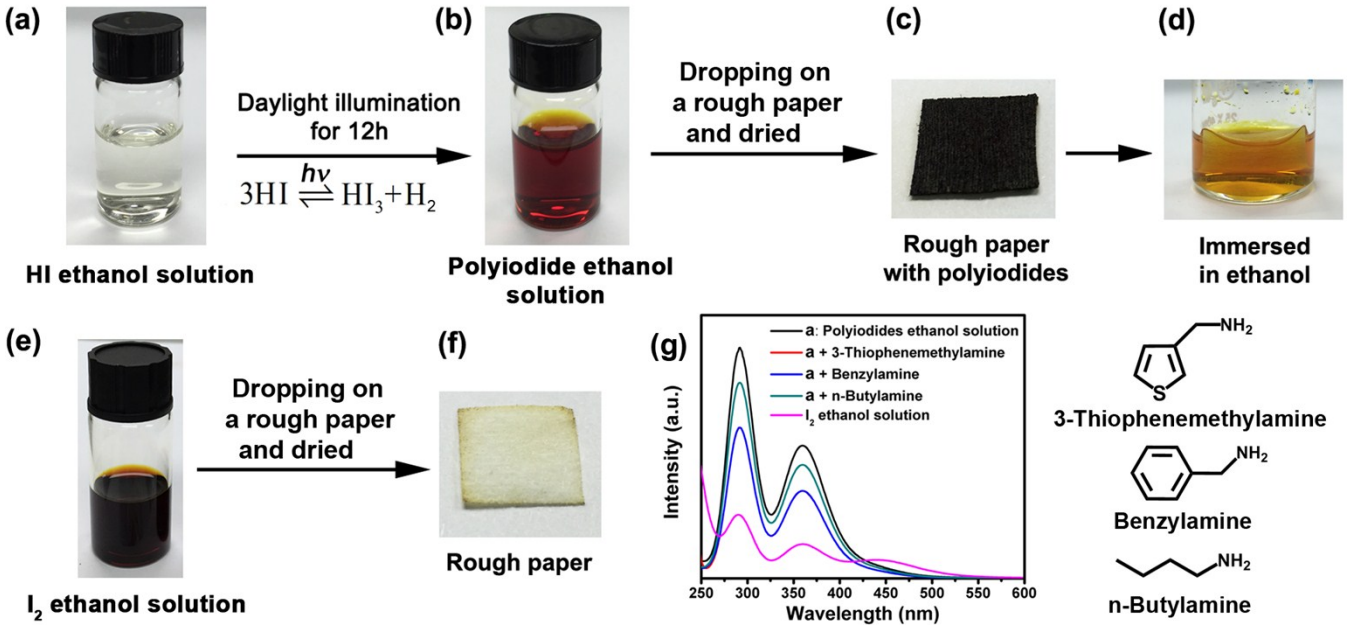


Figure S1. (a) HI ethanol solution; (b) HI ethanol solution with polyiodide ions; (c) Rough paper with polyiodide and (d) was immersed in ethanol; (e) I_2 ethanol solution (the content of I is the same with HI ethanol solution); (f) Dried rough paper treated by I_2 ethanol solution; (g) The absorption spectra of the I_2 ethanol solution and polyiodide ethanol solution with or without organic molecules (3-thiophenemethylamine, Benzylamine and n-Butylamine).

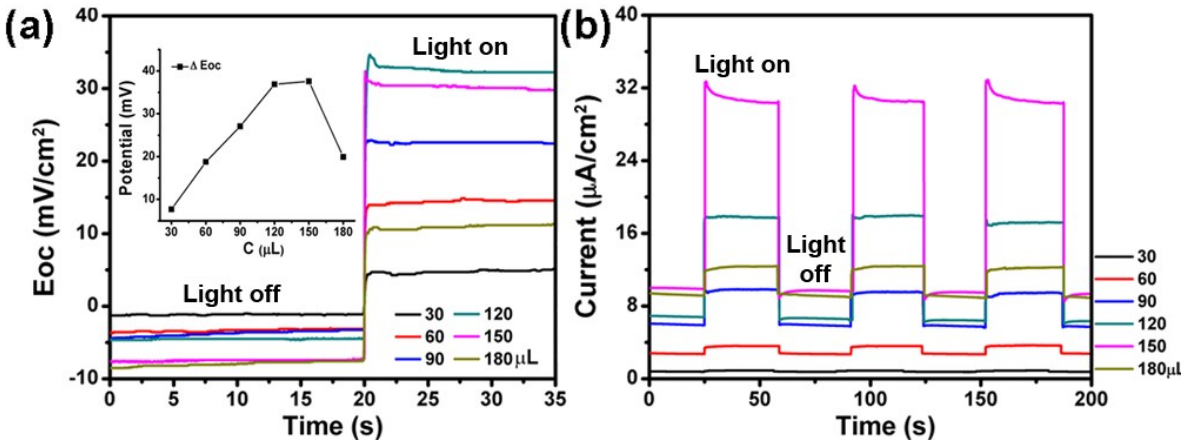


Figure S2. (a) Open-Circuit Potential with different content of polyiodide (Inset is the curve of ΔEoclight-dark and polyiodide content). (b) Corresponding time dependence of the photocurrent rise and decay of the device under periodic illumination of a flashlight. The bias is 0.1 V.

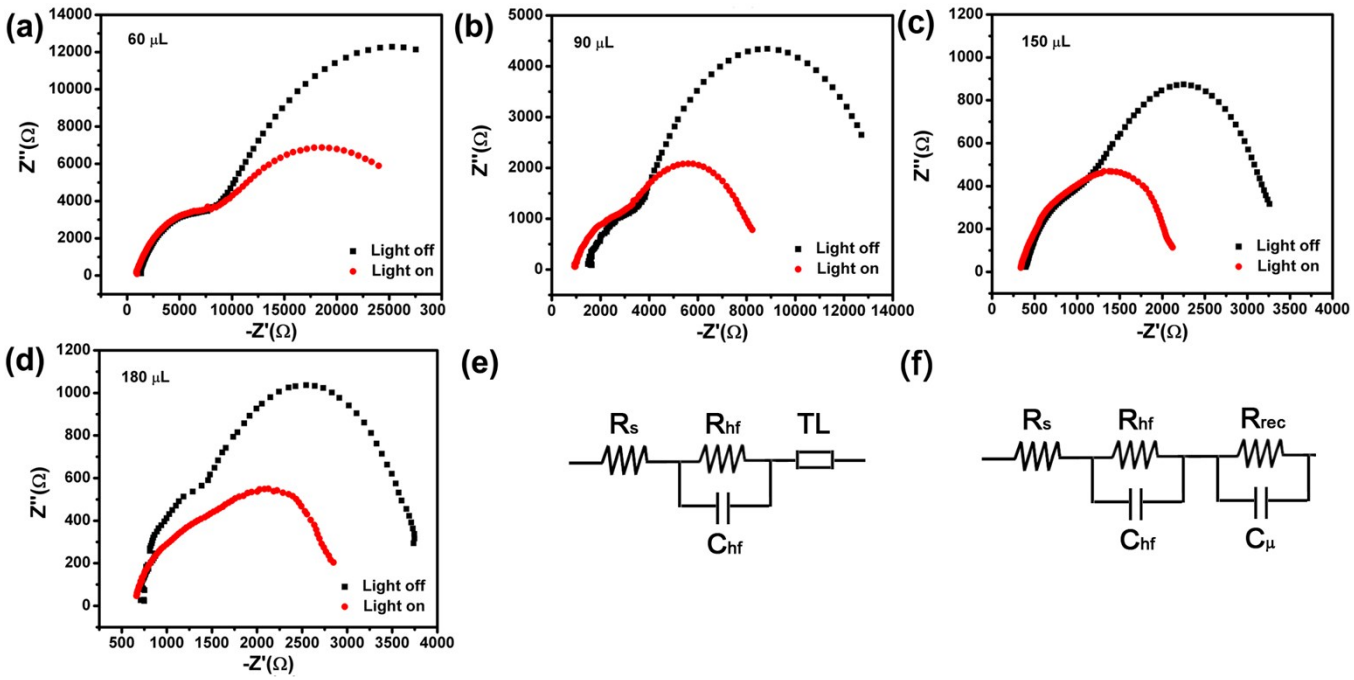
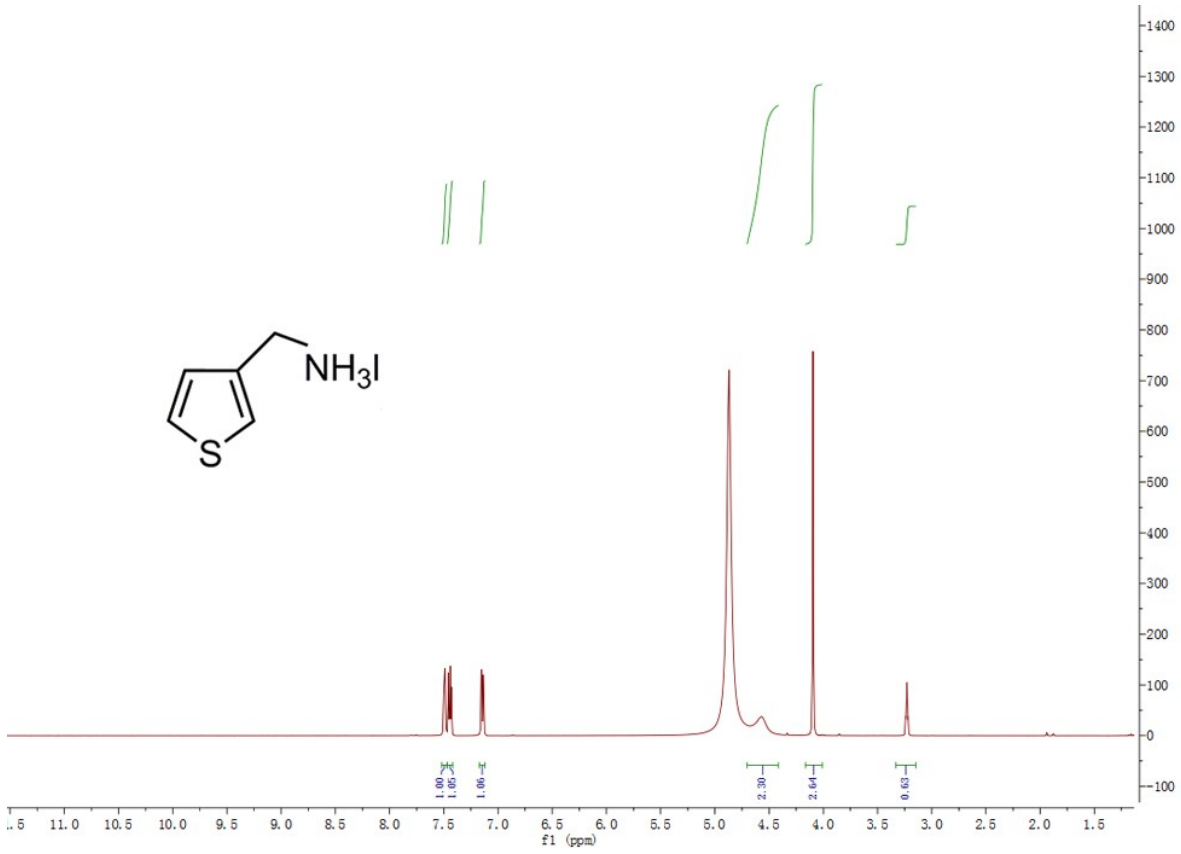
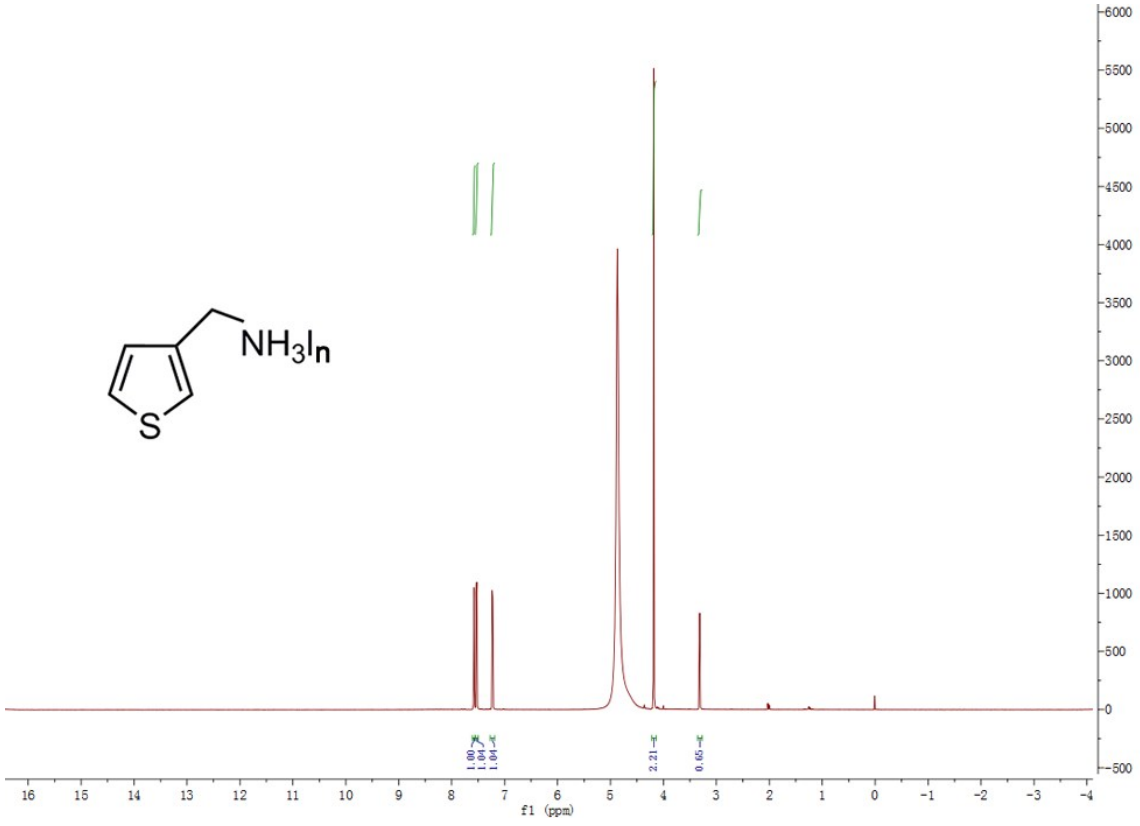


Figure S3. (a) (b) (c) (d) Representative Nyquist plots of a simple device with different content of polyiodides under dark (black) and a flashlight illumination employing (red) with short-circuit over the frequency range of 0.1 Hz to 100 kHz. (e) Complete equivalent circuit to fit the impedance spectra. (f) Simplified equivalent circuit to fit the impedance spectra for the case of electron transport resistance in polyiodides much lower than recombination resistance.


NH3I
S
1.00
1.05
1.06
2.30
2.64
0.63
f1 (ppm)


NH3In
S
1.00
1.04
1.04
2.21
0.65
f1 (ppm)

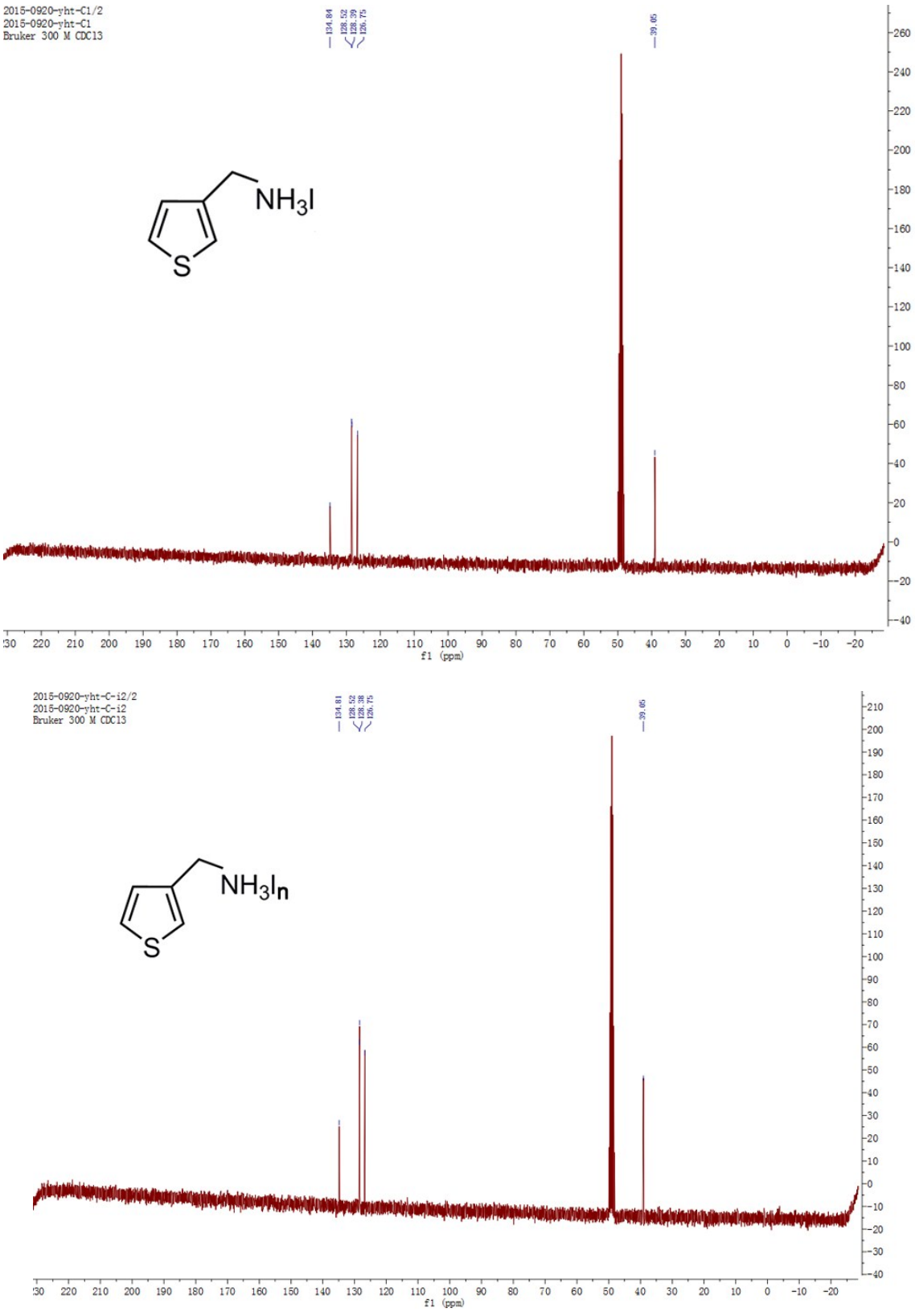


Figure S4. ^{1}H NMR and ^{13}C NMR of MATPI1 and MATPI2.

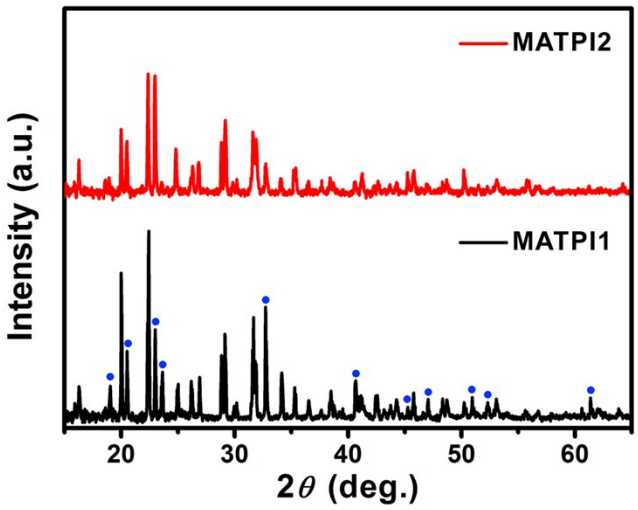


Figure S5. X-ray diffraction pattern for MATPI2 and MATPI1 powder at -20 °C temperature.

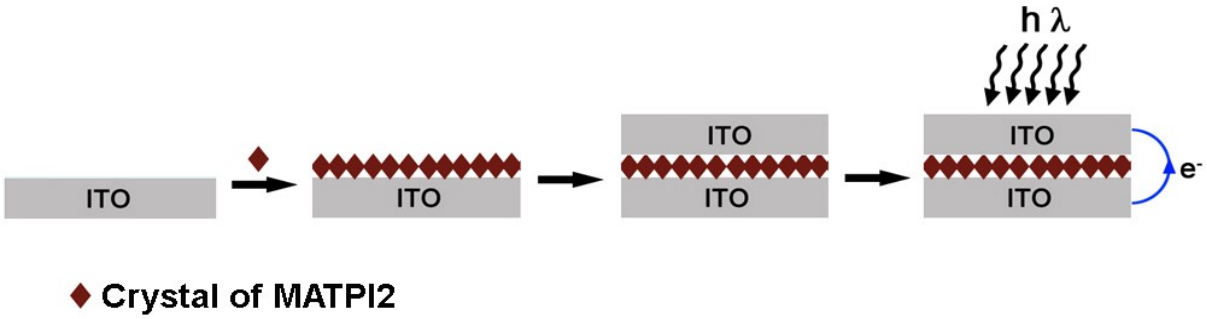


Figure S6. The structure of a simple device for MATPI2.

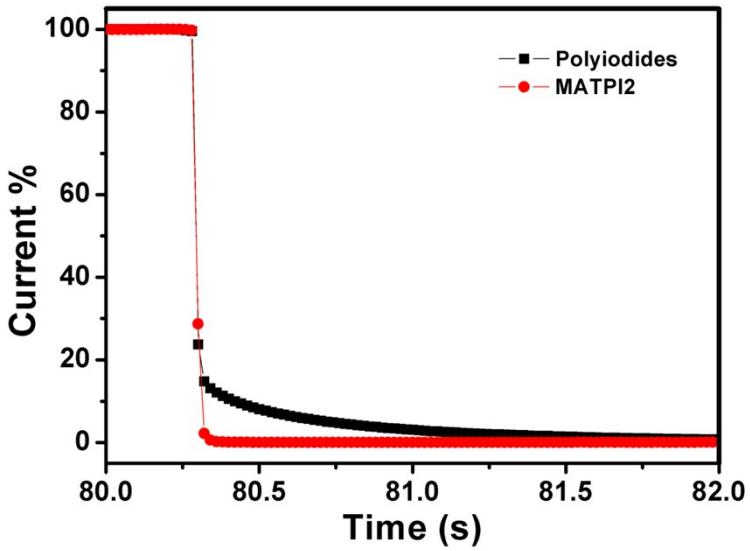


Figure S7. The decay curve of current with time (40 ms and 720 ms for the polyiodides and MATPI2 devices respectively as the current reduced by 97% of light current).

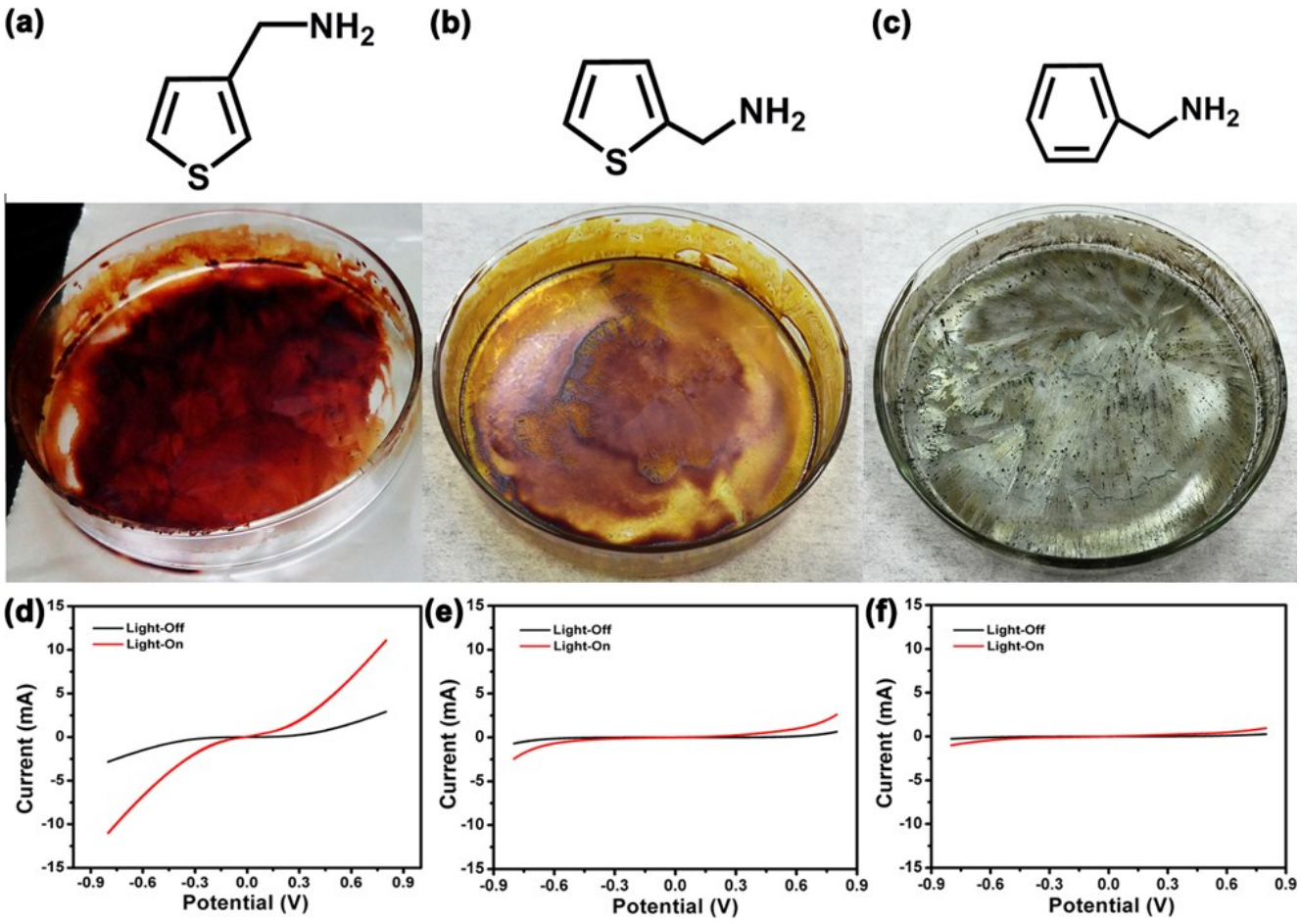


Figure S8. (a) (b) (c) are the appearance of products obtained from 3-methylaminothiophene, 2-methylaminothiophene and benzylamine; (d) (e) (f) are the corresponding CV curves of the devices under dark and 1 sun illumination.

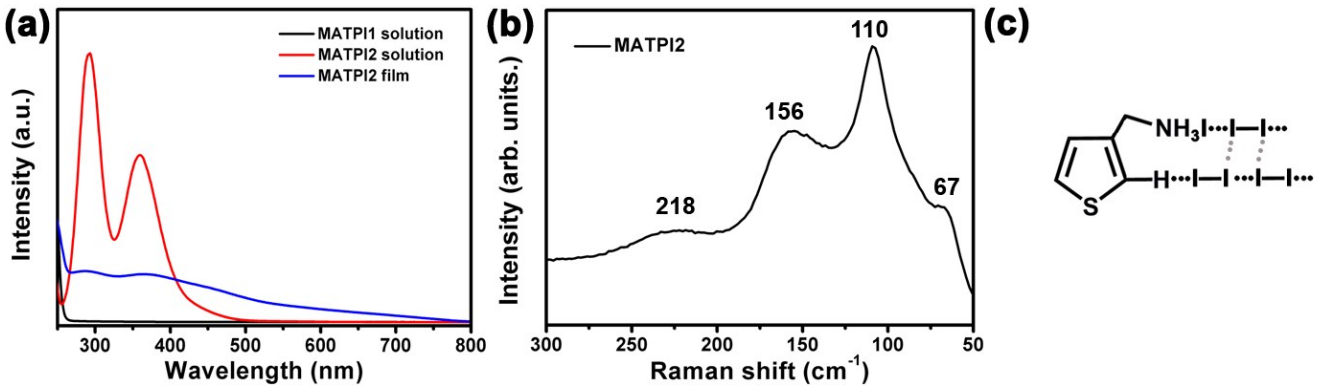


Figure S9. (a) The absorption spectra of the MATPI2, MATPI1 ethanol solution and MATPI2 thin-film spin coated from ethanol solvent. (b) Proposed interaction between polyiodide and MATPI1 Structure. (c) Raman spectra of MATPI2.

Reference:

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