Supplementary Information (SI) for Sustainable Energy & Fuels.

Supporting Information

Band engineering of PTAA hole transporting layer in n-i-p architecture of $MAPbI_3$ based perovskite solar cells

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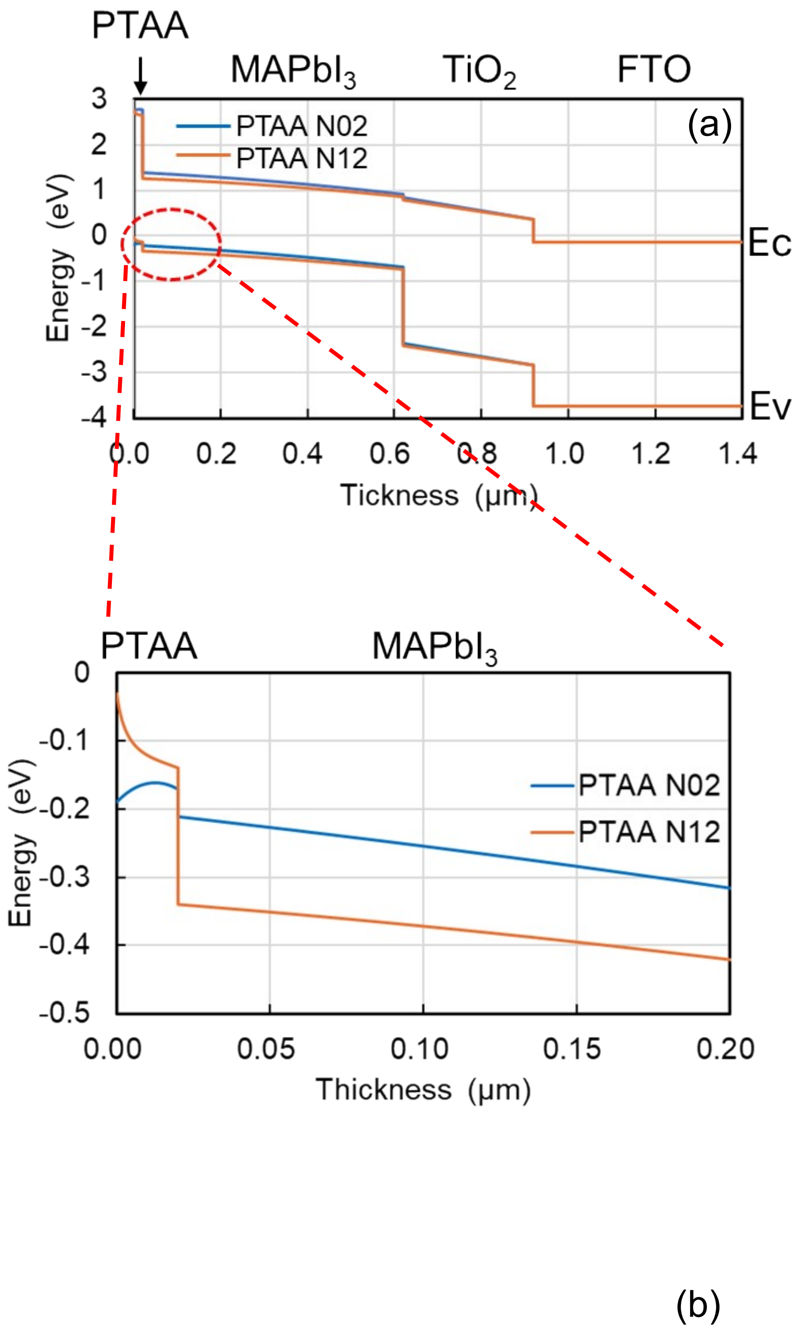


Fig. S1. (a) Energy band diagram of perovskite solar cells with PTAA N02 and N12, as shown in Fig. 1 and (b) valence band maximums between PTAA and $MAPbI_3$.
Conduction band minimums (Ec) and valence band maximums (Ev) were calculated using one-dimensional device simulator SCAPS ver.3.3.05.[1]

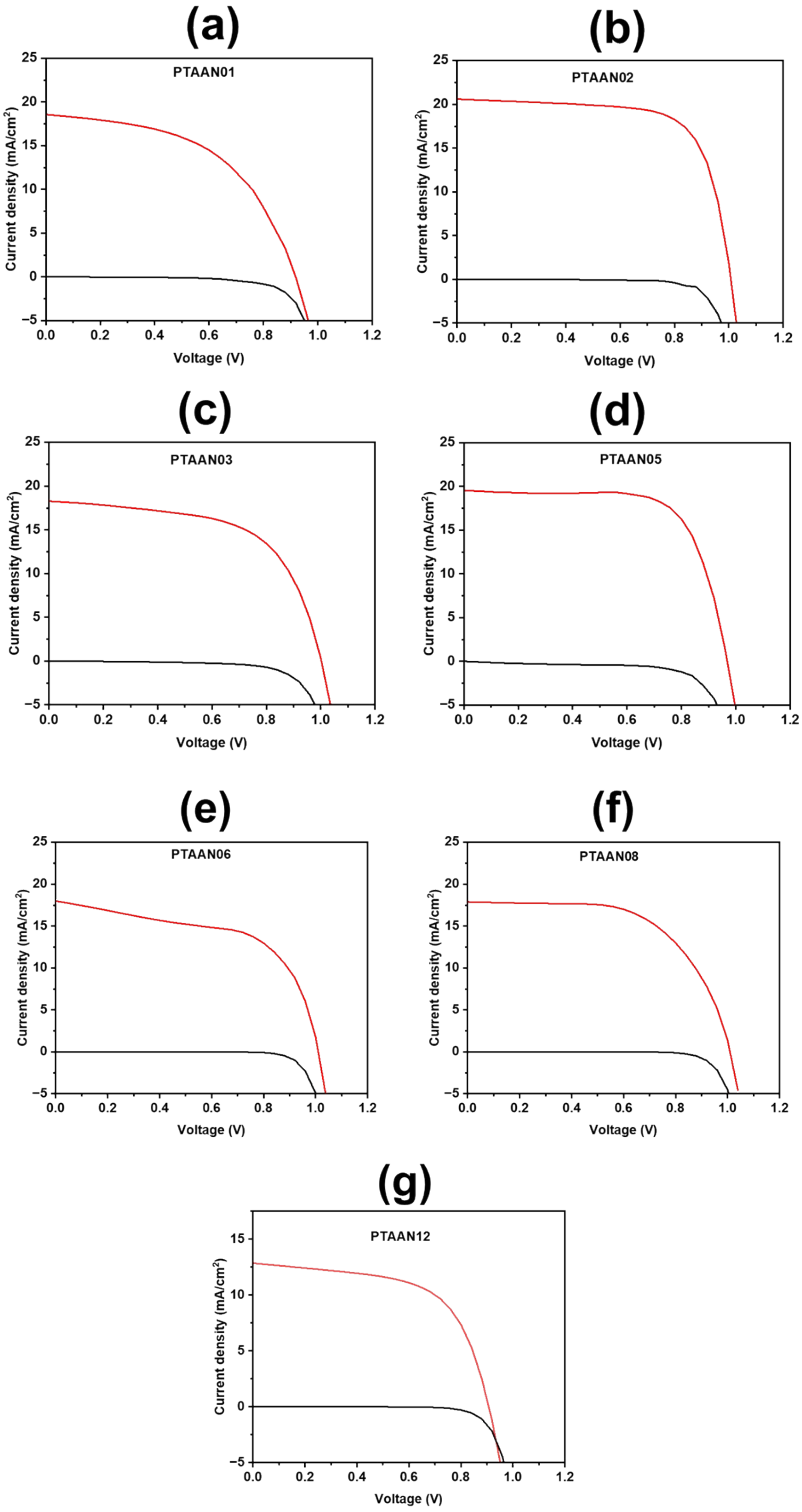


Fig. S2. (a)-(g) J-V characteristics of PSC in this study having different PTAA as HTMs with device architecture FTO/c-TiO_2/m-TiO_2/$MAPbI_3$/HTM/Au.

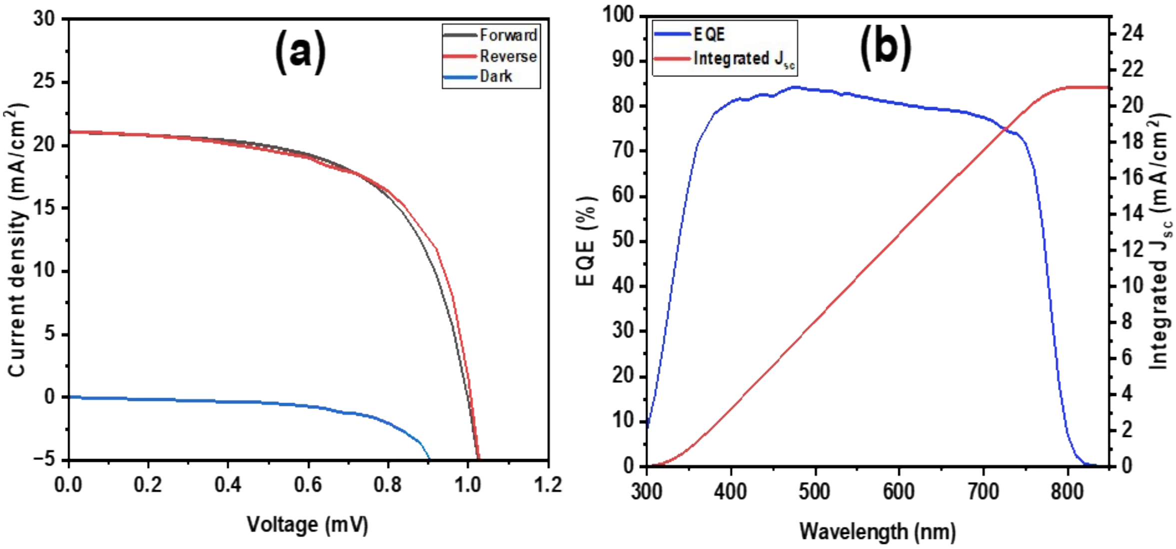


Fig. S3. (a) J-V characteristics of best PSC in this study having PTAA HOMO level at -5.39 eV with device architecture FTO/c-TiO2/m-TiO_2/$MAPbI_3$/PTAAN03/Au (b) External quantum efficiency spectrum and integrated short circuit current density of PTAAN02 device.

Materials and Instrumentations

Most of reagents were purchased from Tokyo Chemical Industry Co., Ltd, except N,N'-diphenylbenzidine derivative (Compound A below), Dibromo compound (Compound B below), mixed xylene, acetone and methanol.

N,N'-diphenylbenzidine derivatives and dibromo compound were synthesized in-house using known methods. Mixed xylene, acetone and methanol were purchased from Daishin Chemical Co.,Ltd.

1H NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) spectrometer.

NMR chemical shifts are reported in ppm relative to the internal standard TMS (δ = 0 ppm), and in addition to the protons of the compound, protons from residual chloroform (δ = 7.25 ppm) and water (δ = 1.53 ppm) are also observed. GPC characterization was carried out in a Waters Alliance GPC system.

Synthesis of PTAA derivatives

Compound A (45.42 g, 108mmol) , Comound B (47.54 g, 108 mmol), $Pd_2(dba)_3$ (0.495g, 0.54mmol), Amphos (0.573 g, 2.16 mmol), Sodium tert-Butoxide (38.36 g, 400 mmol) and a stirrer were placed in a 1000 mL two-neck flask equipped with a reflux condenser, and the atmosphere in the system was replaced with nitrogen while stirring at room temperature using a magnetic stirrer. Thereafter, mixed xylene (600 ml) was added, and the oil bath was heated to 135-140° C. (solution temperature in the flask: 130° C.) with stirring, and the reaction was carried out for 2 hours.

A mixture of mixed xylene (80 ml) solution of bromobenzene (6.80 g, 43.3 mmol) was added dropwise to the reaction solution, and the reaction was continued for 2 hours, for a total of 4 hours, thereby terminating the reaction of the terminal amino groups of the polymer.

A mixed xylene (80 ml) solution of diphenylamine (14.66 g, 86.8 mmol) was added dropwise to the reaction solution, and the reaction was continued for 2 hours, for a total of 6 hours, thereby terminating the reaction of the terminal bromo groups of the polymer.

An antisolvent of 1350 mL of acetone and 150 mL of water was stirred, and the reaction solution was slowly poured into it to precipitate a solid. After stirring for 1 hour, the solid was separated by filtration. 1000 mL of methanol was added to the separated solid, and the mixture was stirred for 30 minutes. The solid was again separated by filtration and vacuum dried (100° C, 8 hours) to obtain a primary solid.

The primary solid was dissolved in 1200 mL of toluene by heating and washed twice with 400 mL of water in a separatory funnel. Anhydrous sodium sulfate was added to the organic layer and stirred at room temperature for 5 minutes, after which the reaction solution was filtered, and the filtrate was collected. Thereafter, as a clay adsorption treatment, 66.6 g of activated clay was added to the filtrate, which was then heated to 100°C and stirred for 50 minutes, after which the reaction solution was filtered by hot filtration and the filtrate was collected. This clay adsorption treatment was carried out a total of 6 times.

After six rounds of clay adsorption, the filtrate was concentrated to 400 mL using an evaporator. The concentrated solution was dropped into an antisolvent of 1350 mL acetone and 150 mL water, and the precipitated solid was separated by filtration. 1000 mL of methanol was added to the precipitated solid and stirred, and the solid was separated again by filtration and vacuum dried (100°C, 8 hours) to obtain the polymer (24.2 g, Yield: ca. 32%) as a yellow solid.

The synthesized polymer was measured using Gel permeation chromatography(GPC), and weight-average molecular weight (Mw) and number-average molecular weight (Mn) were calculated using polystyrene conversion.

Mw=66.2kDa, Mn=49.7kDa (molecular weight distribution 1.33)

^{1}H NMR (600 MHz, Chloroform-d) : δ =7.45(s, 4H), 7.41(d, 4H), 7.35(d, 4H), 7.07-6.85(m, 6H), 6.85-6.91(m, 10H), 2.34(s, 6H), 2.02(s, 12H)

As an example, the synthetic scheme for PTAA-N06 is shown in Fig. S4. ^{1}H NMR spectra are shown in Fig. S5.

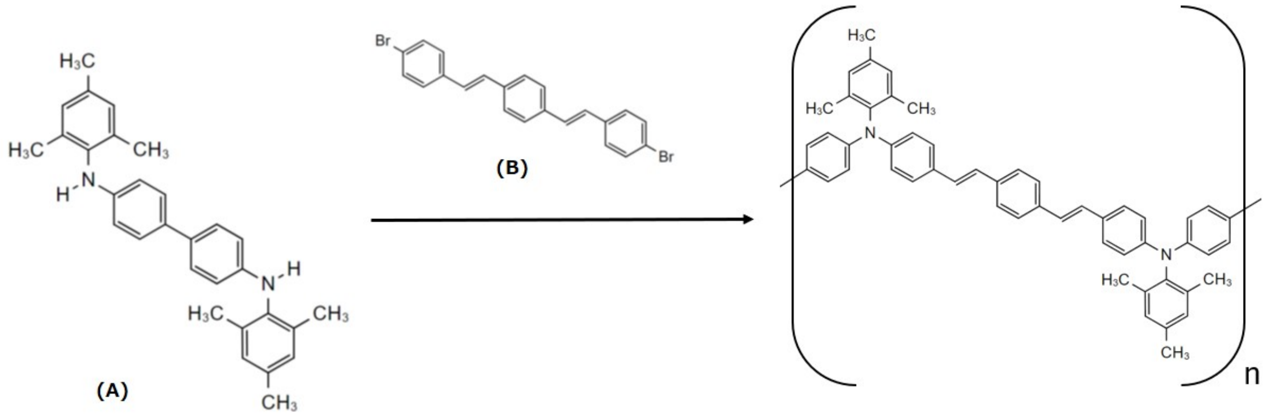
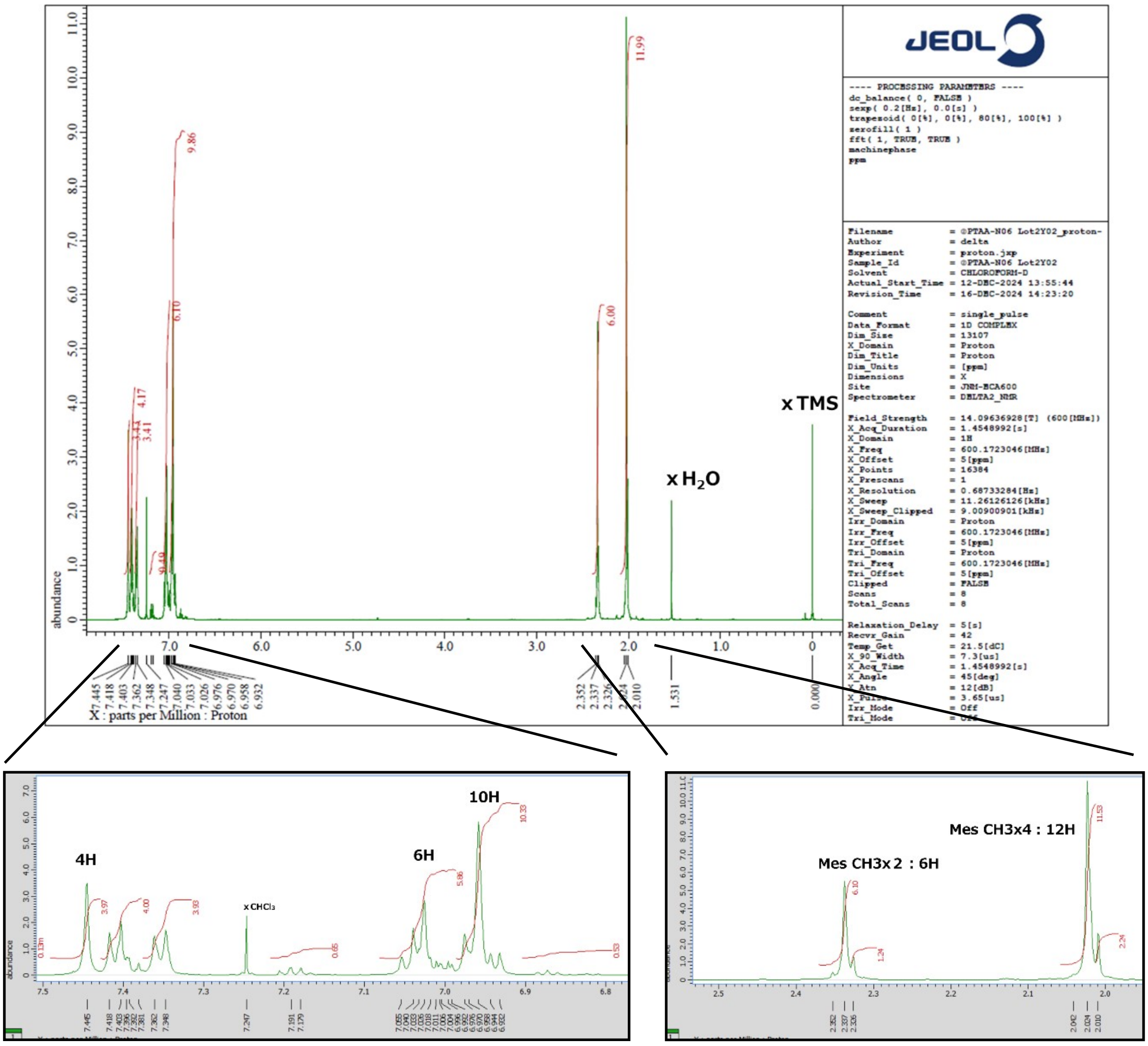


Fig. S4. Synthetic scheme for PTAA-N06



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ppm

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Fig. S5. ^{1}H NMR spectra of PTAA-N06

Reference:

(1) M. Burgelman, P. Nollet, S. Degrave, Modeling Polycrystalline Semiconductor Solar Cells, *Thin Solid Films* **2000**, 361-362, 527–532.

Also, see, http://www.elis.ugent.be/ELISgroups/solar/projects/scaps.html.