

Supporting Information

Radical Polymers as Interfacial Layers in Inverted Hybrid Perovskite Solar Cells

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- 1. Synthesis of PTMA-BP**
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1. Synthesis of PTMA-BP

All reagents were purchased from Sigma-Aldrich, and used as received unless otherwise specified. Poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) was synthesized according to previously developed synthetic methods.¹⁻² 4-benzoylphenyl methacrylate was synthesized according to previously reported procedure by Yu and coworkers.³ The benzophenone moiety is relatively transparent to visible light, and can be used as a mean to photo-crosslink the macromolecular chains.

1.1 Synthesis of poly{(2,2,6,6-tetramethyl-4-piperidinyloxy methacrylate)-co-(4-benzoylphenyl methacrylate)} (PTMPM-BP)

In a 250 mL reaction flask containing a Teflon-coated magnetic stir bar, 4.5 g of 2,2,6,6-tetramethyl-4-piperidinyloxy methacrylate or TMPM (20 mmol), 535 mg of benzoylphenyl methacrylate (2 mol), 10 mg of azobisisobutyronitrile (AIBN, 0.06 mmol), and 100 mL of toluene were allowed to mix. After removing dissolved gases by three freeze–pump–thaw cycles, the reaction was heated to 70 °C and allowed to react for a period of 24 hours under inert conditions. After this time, the solution was cooled to room temperature and concentrated (to a total volume of 5 mL) using a rotary evaporator. The solution was added dropwise to 500 mL of n-hexane at 0 °C to yield PTMPM-BP as a white precipitate. The solid powder was filtered and dried in vacuum to yield 3.75 g of the desired product. Due to the presence of amine functional sites, a proper evaluation of the molecular weight of the material using SEC was not possible.

1.2 Oxidation of PTMPM-BP to poly{(2,2,6,6-tetramethyl-4-piperidinyloxy methacrylate)-co-(4-benzoylphenyl methacrylate)} (PTMA-BP)

To a stirring solution of 500 mg of PTMPM-BP in 5 mL of dichloromethane, a solution of 1 g (5.8 mmol) of meta-chloroperbenzoic acid (m-CPBA) in 15 mL of dichloromethane was

poured. The reaction mixture immediately gained an orange color resulting from the formation of the nitroxide functionalities. The reaction was allowed to proceed for 15 minutes, and it was then repeatedly washed with saturated aqueous sodium bicarbonate. The organic layer was then evaporated to a small volume (2-3 mL) and precipitated in n-hexane at 0 °C. The residue was collected and dried in vacuum to yield 400 mg of PTMA-BP ($M_n = 25.9 \text{ kg mol}^{-1}$, $D = 2.7$) as characterized in **Figure S1** by using ^1H NMR.

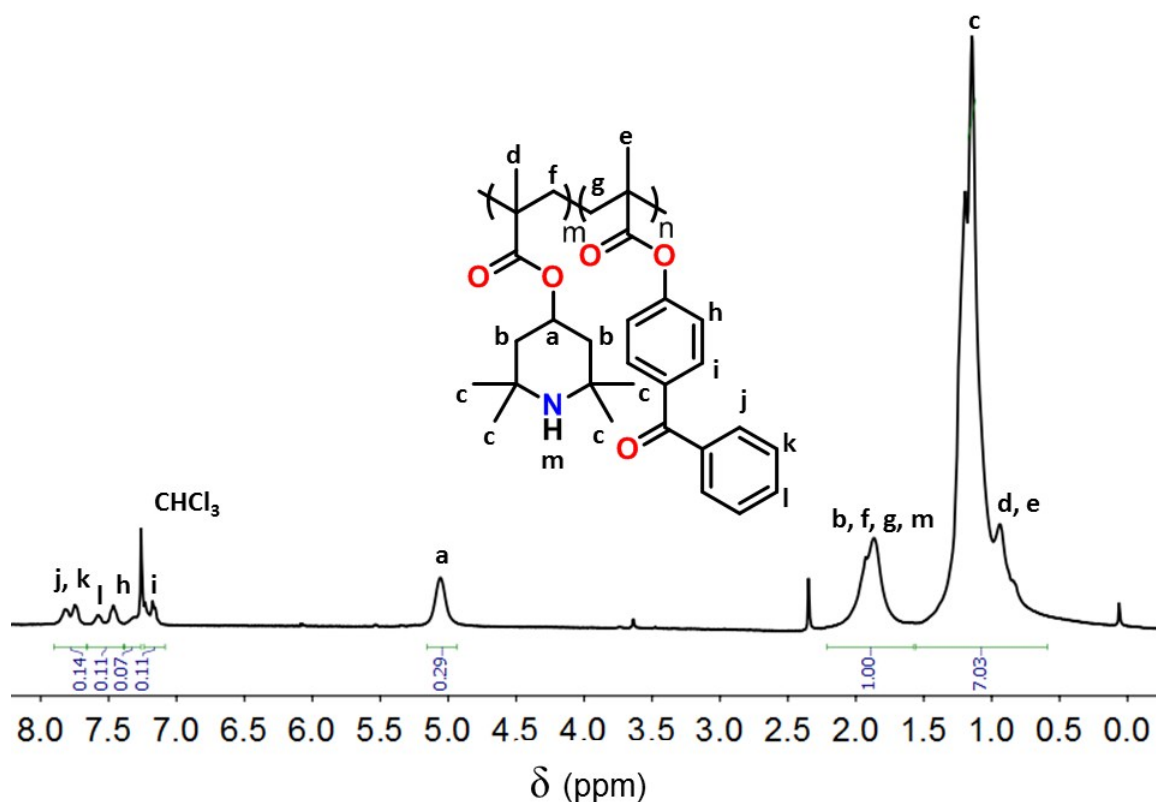


Figure S1. ^1H NMR of PTMPM-BP in CDCl_3 . The ratio of the total aromatic protons (0.43, 10 H per unit) to the peak at 5.0 ppm, corresponding to the piperidine moieties (0.29, 1 H per unit), can be used to determine that the benzophenone moieties are present at 15% (on a molar basis).

2. Characteristics of PTMA-BP

As evident from the figures given below, 90% conversion of the amine units to radical nitroxides was observed. As the amine units form 85% of the structural repeat units, it is calculated that 76.5% of the repeat units in PTMA-BP copolymers contain nitroxide radical sites, which is comparable to standard PTMA samples synthesized at laboratory conditions.⁴

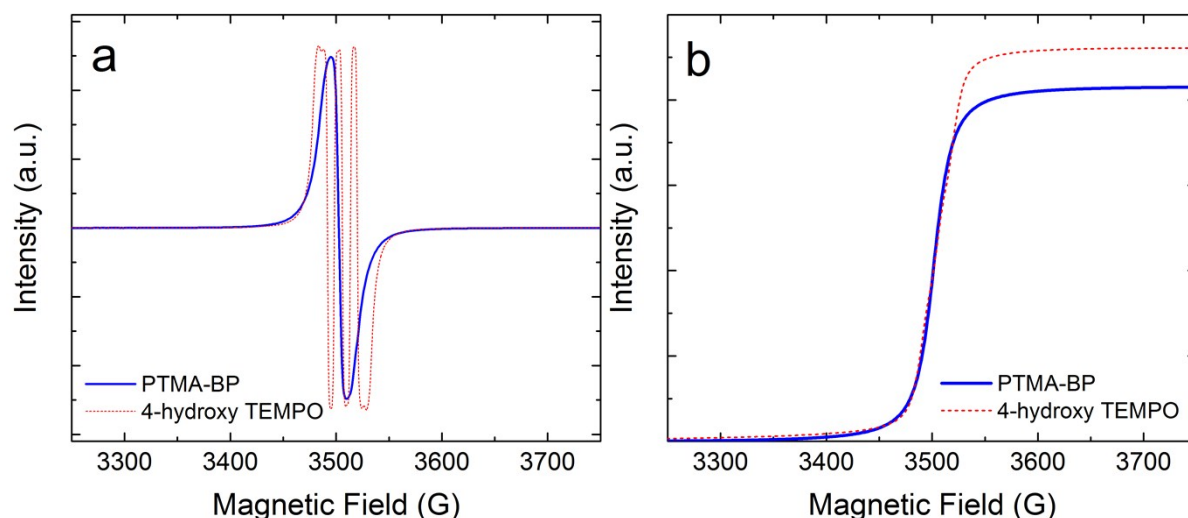


Figure S2. a) EPR spectroscopy data and the b) integrated representation of this data for the small molecule standard, 4-hydroxy TEMPO, and the PTMA-BP. The small molecule data demonstrate hyperfine splitting, the peaks of which broaden into a more Lorentzian shaped curve for the PTMA-BP polymer. The use of equimolar amounts of TEMPOL (2 mg mL⁻¹) and PTMA-BP (5.75 mg mL⁻¹) in toluene solutions show that the radical content is ~90% for the radical polymer. As only 85% sites in PTMPM-BP were the amine entities, the final radical content for the polymer is 76.5% among the repeat units, which is comparable to standard PTMA synthesized in laboratories.

In order to confirm this, we tested the stability of a PTMA-BP thin film using UV-Vis light absorption spectroscopy. A thin-film of PTMA-BP on a glass substrate was made using drop-casting method. The film was crosslinked under UV light (254 nm) and the UV-Vis spectroscopic data was collected. Further, a blank solution of DMF (at 80 °C) was spin coated on the top of this layer, and after drying, another UV-Vis spectrum was recorded. As evident from the figure given below, the PTMA-BP layer stays stable through the process.

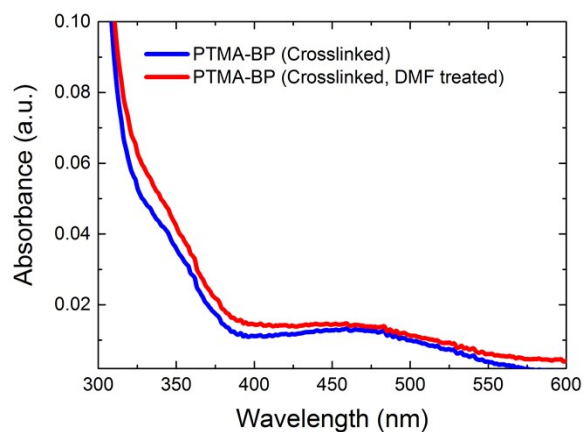


Figure S3. UV-Vis absorption spectra of a thin-film of PTMA-BP on a glass substrate after crosslinking, before and after spin-coating a blank solution of DMF (at 80 °C) on the top of it. The film was drop casted from a CHCl_3 solution of PTMA-BP (10 mg mL^{-1}). The stability of the film is evident from the similar absorption profile of before and after treatment of the film. The slight alterations in the spectra can be related to the minute changes in the orientations of the glass film in the sample holder for data collection or by inclusion of some DMF molecules in the film.

3. J-V characteristics of PSCs

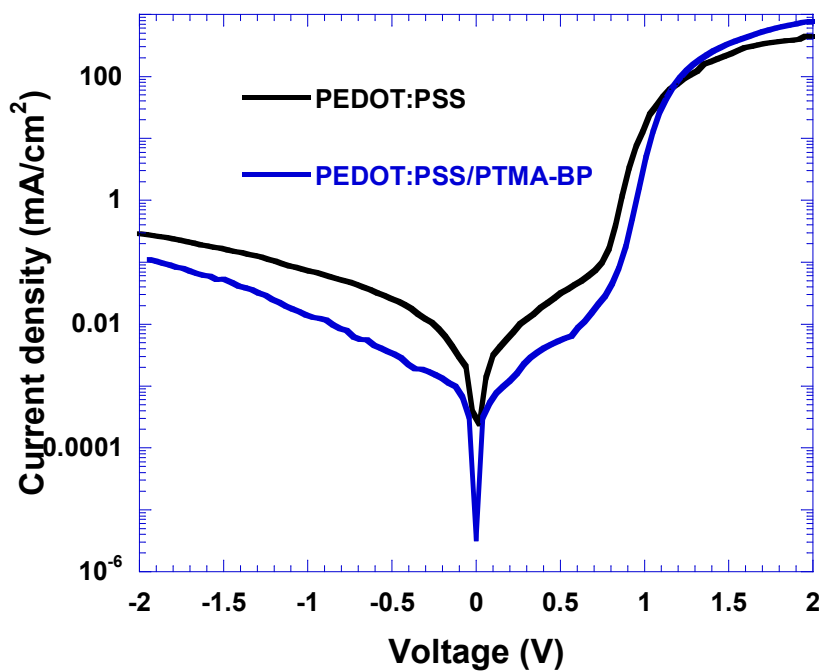


Figure S4. J-V characteristics of the PSCs based on either the PEDOT:PSS HEL or the PEDOT:PSS/PTMA-BP HEL in dark.

Figure S4 shows representative dark J-V curves of PSCs based on PEDOT:PSS and PEDOT:PSS/PTMA-BP HELs. The lower dark current of PSCs incorporated with PTMA-BP layer consists with the enhancement on V_{OC} .

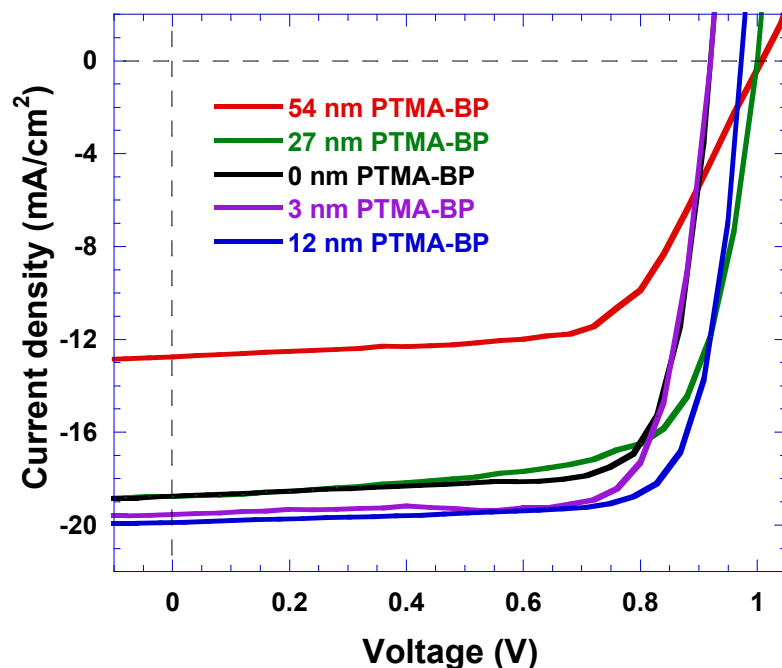


Figure S5. J-V characteristics of the PSCs based on the PEDOT:PSS/PTMA-BP HELs with different thickness of the PTMA-BP layers.

The PTMA-BP thin films with different thickness values were cast from toluene precursor solutions with the concentrations of 0.5, 2, 5 and 10 mg/mL by using the same rotational frequency of 6,000 rpm and followed by the annealing at 80 °C for and illuminating at 254 nm UV light for 10 minutes. As shown in **Figure S5**, the J-V characteristics of the PSCs based on PEDOT:PSS/PTMA-BP HEL versus the thickness of PTMA-BP thin layers exhibit an obvious thickness dependence. As the thickness of PTMA-BP thin layer is increased, the V_{OC} first is increased from ~ 0.91 V to ~ 1.00 V and then remained at the same value. Moreover, the J_{SC} is also increased and then decreased, even rapidly dropping to ~ 12.76 mA/cm². These device performance parameters are summarized in **Table S1**. A certain thickness of PTMA-BP thin layer was required to achieve the enhancement on V_{OC} when the PTMA-BP could fully cover the PEDOT:PSS layer and form a better band alignment.

Table S1. Device Performance Parameters of the PSCs based on either the PEDOT:PSS HEL or the PEDOT:PSS/PTMA-BP HEL

Thickness of PTMA-BP (nm)	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF	PCE (%)	R _S (Ω)	R _{SH} (kΩ)
0	0.91	18.75	0.78	13.33	74.07	22.17
3	0.92	19.55	0.78	14.01	74.32	24.25
12	0.99	19.89	0.77	15.08	74.63	30.16
27	1.00	18.77	0.71	13.30	93.46	34.53
54	1.00	12.76	0.65	8.24	416.67	19.89

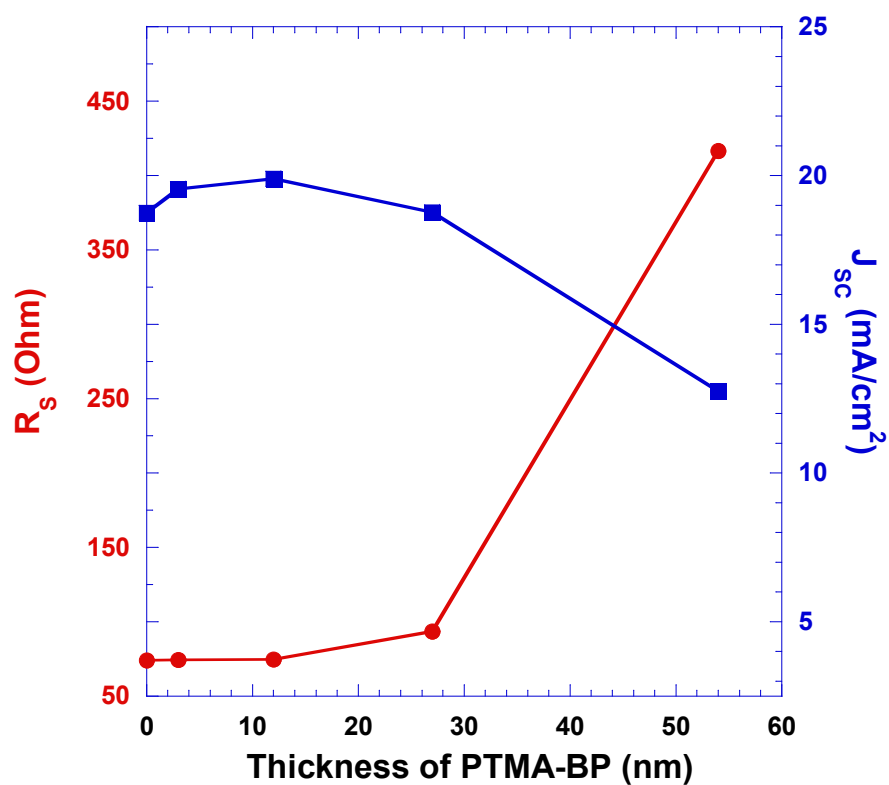


Figure S6. Thickness dependence of the PTMA-BP layer on the R_s and J_{sc} of PSCs.

The series resistance (R_s) of PSCs based on PEDOT:PSS/PTMA-BP HELs varied with the thickness of the PTMA-BP layers, and this value was estimated by calculating the reciprocal of slope at open circuit condition (i.e., at $J = 0 \text{ mA cm}^{-2}$) from **Figure S6**. As shown in **Figure S6**, the R_s and J_{SC} values of the PSCs present the inverse tendencies with each other with increasing PTMA-BP layer thickness. The R_s of the PSCs is related to the resistance of the PTMA-BP layers because the only difference is the thickness of PTMA-BP thin layer. The J_{SC} was inhibited by the high resistance for a thick PTMA-BP layer while the charge transport could be realized through tunneling effect for a thin PTMA-BP layer, implying that the enhancement on J_{SC} for thin PTMA-BP layer resulted from the suppressed surface recombination on PTMA-BP layer.

4. Time-resolved photocurrent measurements

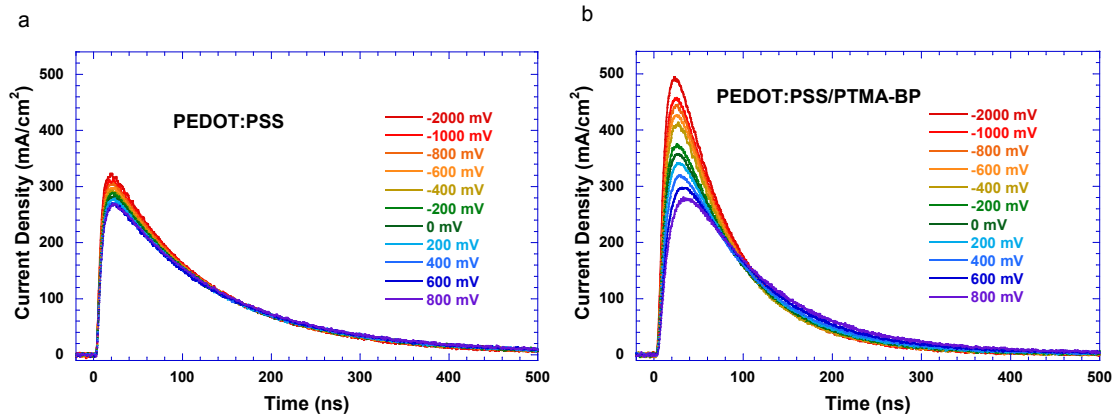


Figure S7. TPC curves of PSCs based on a) PEDOT:PSS and b) PEDOT:PSS/PTMA-BP HELs at different applied voltage biases.

Figure S7a and **Figure S7b** display the voltage dependence on TPC of the PSCs based on PEDOT:PSS and PEDOT:PSS/PTMA-BP HELs, respectively, under the same input laser energy. The maximum transient photocurrent increases with the applied bias (reverse) and the maximum transient photocurrent of PSCs based on PEDOT:PSS/PTMA-BP bilayer is higher than that of

pristine PSCs under the same bias. The faster decay of the transient photocurrent of PSCs incorporated with PTMA-BP thin layer implies a more efficient charge extraction than that of pristine PSCs.

References

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