Supporting Information

1. Experimental Methods

Materials. PBI-Y was synthesized as previously reported.[1,2] Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), L-tyrosine, butylamine, *o*-Xylene (reagent grade, ≥98%), Triton-X100 and imidazole were purchased from Sigma-Aldrich. Indium tin oxide (ITO)-coated glass substrates were purchased from Zhuhai Kaivo Optoelectronic Technology Co., LTD (R_s ≤10 Ω/□ T_r ≥83%). PM6 and Y6C12 were received from Brilliant Matters. SnO_2 was purchased from Alfa Aesar. All commercial reagents were used as received.

Solution preparation. PBI-Y solutions were prepared at a concentration of 0.5 mg/mL. For butylamine solutions, the solutions were left to mix for 1 hour. For NaOH solutions, the **PBI-Y** was dissolved in distilled water and 1 molar equivalent of sodium hydroxide (0.1 M, aqueous). The solutions were stirred overnight until all the gelator had dissolved. SnO_2 nanoparticle solution (15% in H_2O colloidal dispersion) was diluted with deionized water and ethanol in a volumetric ratio of 1:2.5:1.5, and 1 v/v% of Triton X-100 was added. The solution was shaken for 20 minutes before filtering with 0.45 μm poly(vinylidene difluoride) (PVDF) filters (Biomed Scientific). Solutions of PM6 and Y6C12 were prepared in *o*-xylene at concentrations of 14.6 and 17.4 mg/mL, respectively. These solutions were heated at 50°C for 16 hours before mixing in 1:1 v/v ratios (1:1.2 w/w). Blend bulk heterojunction solutions were shaken for 10 minutes prior to spin- or slot-die coating.

Fabrication of solar cells. For spin-coated and slot-die coated solar cells, ITO-coated glass was cleaned by submerging in detergent and deionized water, acetone, and isopropanol, respectively, with ultrasonification for 15 minutes in each solvent. The substrates were then dried over a stream of compressed air before being treated with O_2 plasma (Ossila UV Ozone Cleaner) for 15 minutes.

For spin-coated devices, the SnO_2 precursor solution was spin-coated at 4000 rpm for 30 seconds in air and at room temperature, before being annealed after casting at 200°C in air for 30 minutes. **PBI-Y** was then spin-coated on top at 4000 rpm for 30 seconds in air and at room temperature. The substrates were then annealed after casting at 100°C in air for 10 minutes. The PM6/Y6C12 was spin-coated at 1000 rpm in air and at room temperature for 30 seconds and annealed after casting in air at 100°C for 10 minutes. Molybdenum trioxide was then deposited by thermal evaporation (~$3x10^{-6}$ mbar) before deposition of the silver electrodes by thermal evaporation (~$3x10^{-6}$ mbar) using a shadow mask, forming 0.14 cm^2 active area devices.

For slot-die coated devices, a FOM Technologies shear coater equipped with a 13 mm wide shim was used. The substrate to die head distance was 0.1 mm gap for all layers. For SnO_2, the ITO substrates were kept on the bed of the slot-die coater heated at 50°C, with a coating speed of 20 cm/min and a pump rate of 10 μL/min. The substrates were then annealed after casting at 200°C in air for 30 minutes. **PBI-Y** was slot-die coated with a coating speed of 50 cm/min and a syringe flow of 100 μL/min. The temperature of the bed of the slot-die coater was 30°C. The substrates were annealed after casting at 100°C in air for 10 minutes. The PM6/Y6C12 blend was coated at a coating speed of 100 cm/min and a flow rate of 20 μL/min. The temperature of the slot-die coater head was 40°C and the bed was kept at 50°C, as previously reported.[3] The substrates were annealed after casting at 100°C for 10 minutes. To complete the OPV devices, silver and MoO_x were thermally deposited using a shadow mask with 10 cm cut-outs for large substrates, forming 0.12 cm^2 active area devices.

Characterization. Optical absorption spectra were recorded using a UV-vis spectrometer (Agilent Technologies Cary 60) at room temperature. The film thickness was estimated by employing an Alpha-Step D-500 stylus profiler (KLA Instruments). Current density-voltage (*J*-V) measurements were performed in inert conditions using a Keithley 2400 source measure unit at AM 1.5G simulated solar light (Newport, Model 92251A-1000) with an irradiation intensity of 100 mW cm^{-2}, which was measured by a calibrated silicon solar cell and a readout meter (Newport, Model 91150V). Atomic force microscopy (AFM) measurements were performed by using a TT-2 AFM (AFM Workshop, USA) in the tapping mode and WSxM software with a 0.01-0.024 Ohm/cm Sb (n) doped Si probe with a reflective back side aluminum coating.

2. Supplementary Figures and Tables

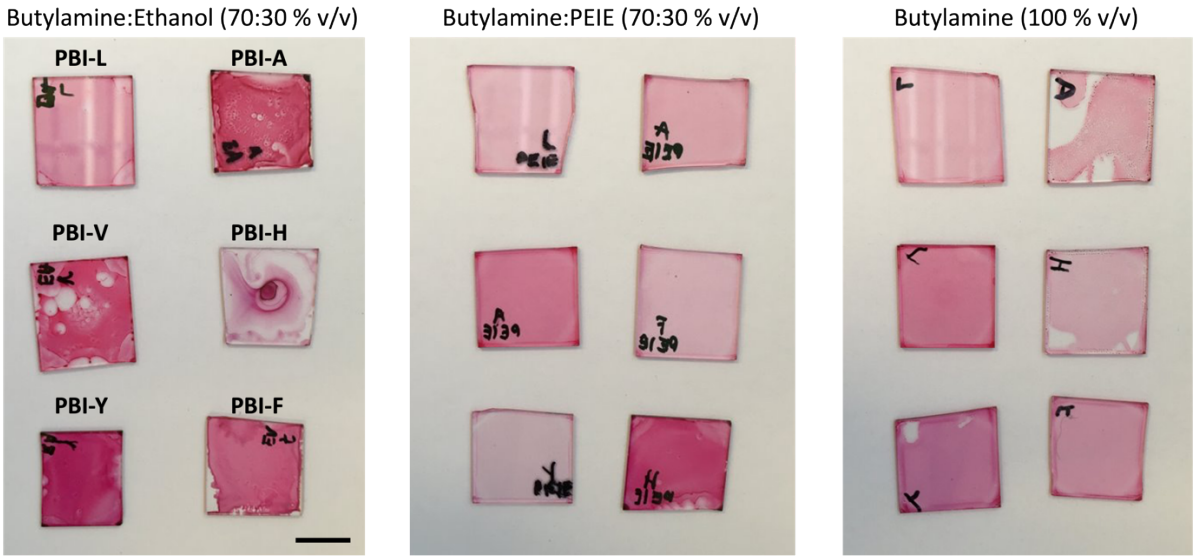

Figure S1. Screening of 6 amino acid functionalized PBIs prepared at a concentration of 0.5 mg/mL in different butylamine-based solvent systems. All films were spin-coated onto plasma-cleaned glass in air and at room temperature. Scale bar represents 1 cm.

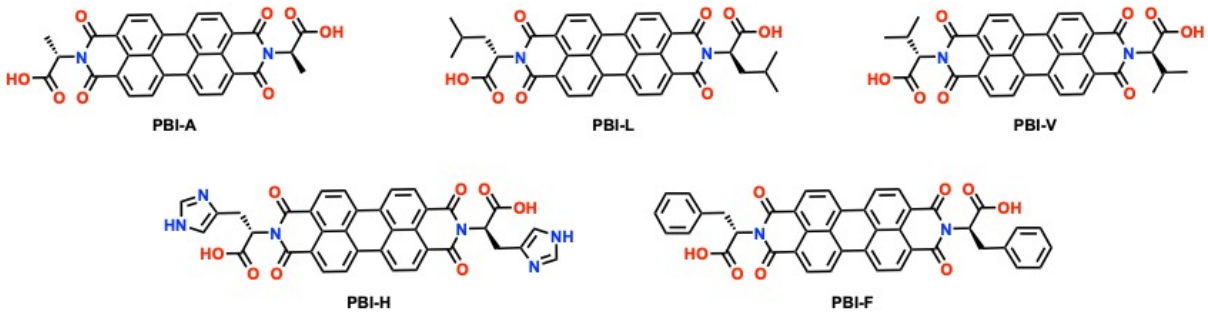

Figure S2. Chemical structures of **PBI-A, PBI-L, PBI-V, PBI-H** and **PBI-F.**

Table S1. Summary of photovoltaic device metrics of the spin-coated devices made using **PBI-Y** dissolved in a butylamine:ethanol mixture (70:30 %v/v).[a,b]

Cathode Interlayer	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
SnO_2	0.82 ± 0.003 (0.82)	23.84 ± 0.05 (23.90)	69.2 ± 0.2 (70.2)	13.6 ± 0.1 (13.7)
SnO_2/**PBI-Y**	0.78 ± 0.002 (0.78)	24.40 ± 0.2 (24.50)	54.0 ± 0.3 (54.5)	10.3 ± 0.1 (10.4)

[a] Values reported are average of 10 best devices

[b] ± Standard deviation. Champion devices performance in parentheses.

Table S2. Summary of photovoltaic device metrics of the spin-coated devices made using **PBI-Y** dissolved in a butylamine:PEIE mixture (70:30 %v/v).[a,b]

Cathode Interlayer	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
SnO_2	0.79 ± 0.002 (0.79)	19.41 ± 0.2 (19.62)	66.5 ± 0.7 (68.1)	10.2 ± 0.04 (10.3)
SnO_2/**PBI-Y**	0.79 ± 0.006 (0.80)	20.50 ± 0.4 (21.12)	64.3 ± 0.2 (65.7)	10.7 ± 0.3 (10.4)

[a] Values reported are average of 10 best devices

[b] ± Standard deviation. Champion devices performance in parentheses.

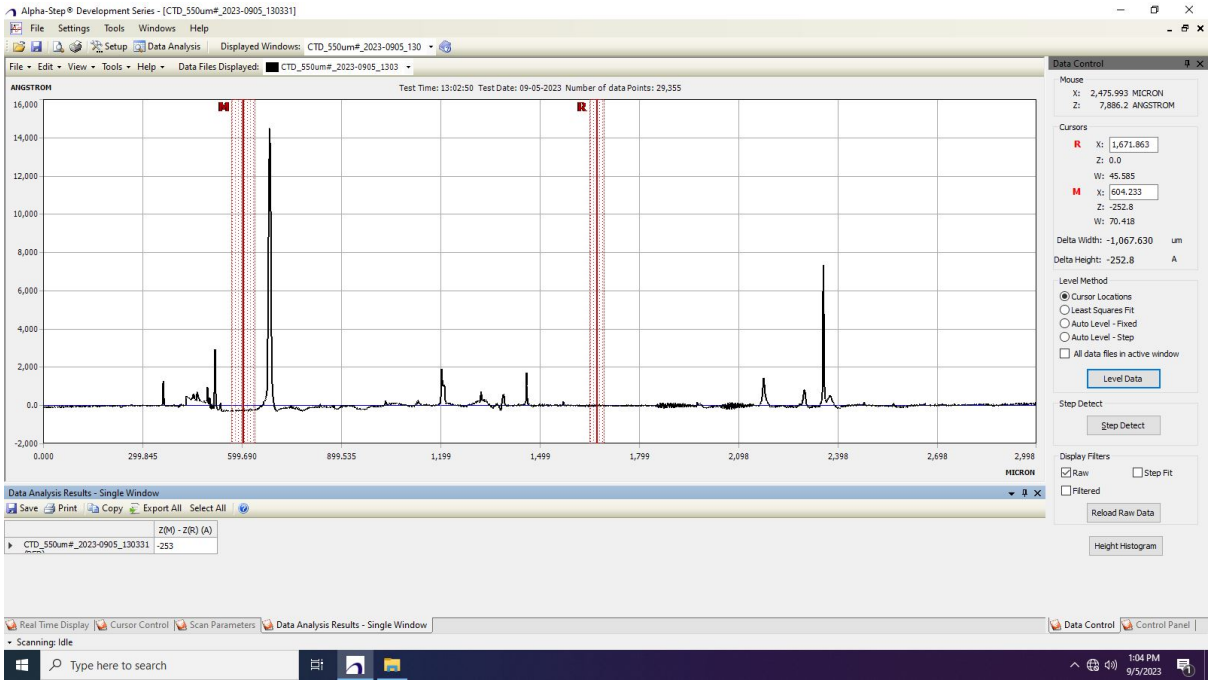

Figure S3. Thickness measurements by profilometer for glass/SnO_2/**PBI-Y** films (spin-coated). Films were cast at a concentration of 5 mg/mL in air and at room temperature.

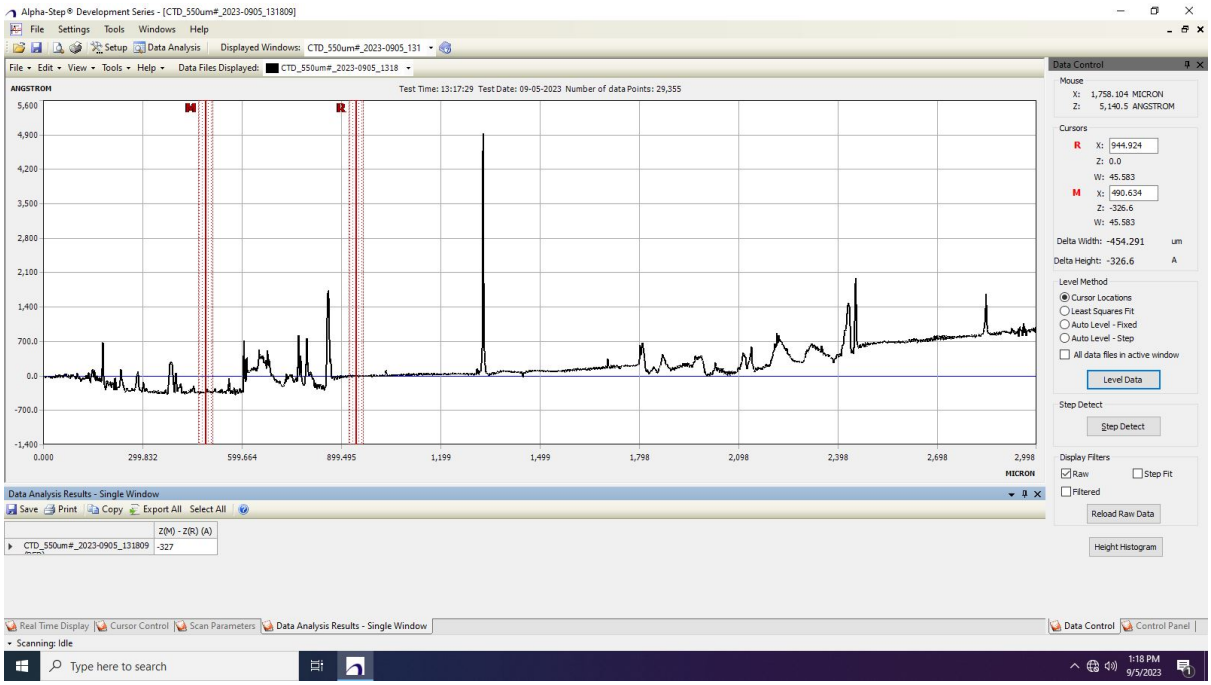

Figure S4. Thickness measurements by profilometer for glass/SnO_2/**PBI-Y** films (slot-die coated). Films were cast at a concentration of 5 mg/mL in air and at room temperature.

Table S3. Summary of photovoltaic device metrics of spin-coated devices made from **PBI-Y** deposited from a 3 mg/mL solution in butylamine.

Cathode Interlayer	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
SnO_2/**PBI-Y**	0.78 ± 0.001	21.52 ± 0.39	62.8 ± 0.68	10.6 ± 0.2

Table S4. Summary of photovoltaic device metrics of the spin-coated devices.[a,b]

Cathode Interlayer	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
SnO_2	0.82 ± 0.003 (0.82)	23.21 ± 0.6 (23.45)	63.2 ± 0.5 (65.2)	12.4 ± 0.2 (12.5)
SnO_2/**PBI-Y**	0.80 ± 0.002 (0.80)	23.72 ± 0.5 (24.47)	65.7 ± 0.3 (64.9)	12.4 ± 0.2 (12.8)

[a] Values reported are average of 10 best devices

[b] ± Standard deviation. Champion devices performance in parentheses.

Table S5. Summary of photovoltaic device metrics of the spin-coated devices using 0.1 M NaOH (aq) as the base.[a,b]

Cathode Interlayer	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
SnO_2	0.82 ± 0.003 (0.82)	23.21 ± 0.6 (23.45)	63.2 ± 0.5 (65.2)	12.4 ± 0.2 (12.5)
SnO_2/**PBI-Y** (NaOH)	0.77 ± 0.002 (0.77)	23.12 ± 0.1 (23.27)	57.3 ± 0.2 (57.5)	10.2 ± 0.07 (10.3)

[a] Values reported are average of 10 best devices

[b] ± Standard deviation. Champion devices performance in parentheses.

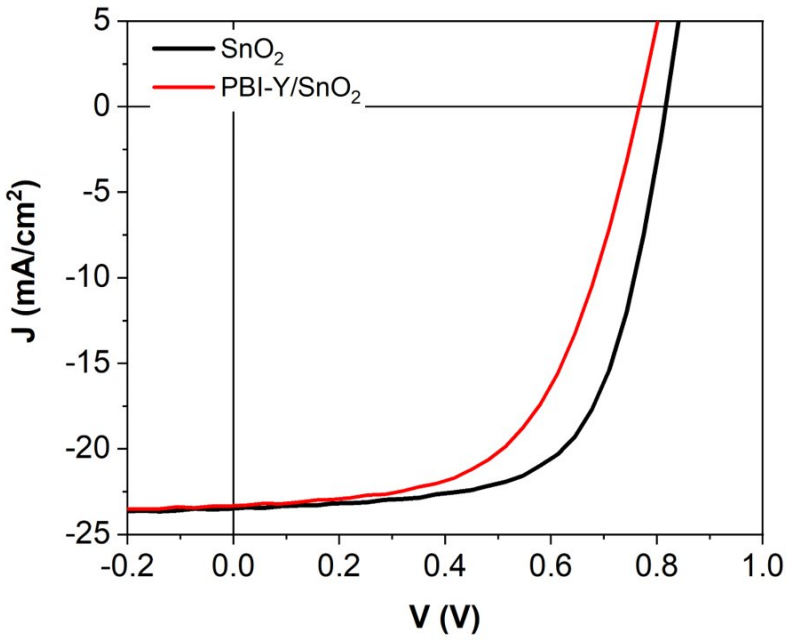

Figure S5. *J-V* curves of slot-die coated SnO_2/**PBI-Y** devices using 0.1 M NaOH (aq) (red) compared to reference with SnO_2 only.

Table S6. Summary of photovoltaic device metrics of the slot-die coated devices.[a,b]

Cathode Interlayer	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
SnO_2	0.80 ± 0.004 (0.80)	22.11 ± 0.4 (22.45)	65.2 ± 0.3 (66.3)	9.2 ± 0.3 (9.4)
SnO_2/**PBI-Y**	0.78 ± 0.005 (0.78)	22.3 ± 0.3 (22.8)	60.2 ± 0.3 (61.2)	10.4 ± 0.1 (10.6)

[a] Values reported are average of 10 best devices

[b] ± Standard deviation. Champion devices performance in parentheses.

Table S7. Summary of photovoltaic device metrics of the spin-coated devices using **PBI-Y** alone as the electron transport layer.

Cathode Interlayer	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
PBI-Y	0.72	20.17	25.44	3.69

References

1. E. R. Draper, L. J. Archibald, M. C. Nolan, R. Schweins, M. A. Zwijnenburg, S. Sproules and D. J. Adams, *Chem. Eur. J.*, 2018, **24**, 4006–4010.

2. D. McDowall, B. J. Greeves, R. Clowes, K. McAulay, A. M. Fuentes-Caparrós, L. Thomson, N. Khunti, N. Cowieson, M. C. Nolan, M. Wallace, A. I. Cooper, E. R. Draper, A. J. Cowan and D. J. Adams, *Adv. Energy Mater.*, 2020, **10**, 2002469.

3. M. R. Niazi, H. Zhao, R. M. Lamarche, R. Munir, S. Trudel, J. Hu and G. C. Welch, *Adv. Mater. Interfaces*, 2022, **9**, 2201363.