Supporting Information

Enhanced interface adhesion with a polymeric hole transporter enabling high-performance air-processed perovskite solar cells

Yu Zhao,‡ Yangyang Liu,‡ Zhijun Ren, Yiran Li, Yaoyao Zhang, Fan-Cheng Kong, Tianxiao Liu, Xiaoyu Shi, Yunjie Dou, Lingyuan Wang, Feifei Wang, Xiangliang Guo, Yi Cao, Wei Wang, Philip C. Y. Chow, Shangshang Chen*

1. Synthesis details

Synthesis of Poly-DCPA



2,8-dibromo-5,11-dihydroindolo[3,2-b]carbazole (compound 1): cyclohexane-1,4-dione (1.00 g, 8.92 mmol) was dissolved in ethanol (60 ml, 1027.5 mmol), then (4-Bromophenyl)hydrazine hydrochloride (3.98 g, 17.8 mmol) and sodium acetate (1.46 g, 17.8 mmol) were added subsequently. The mixture was stirred at 50°C for 1 hour. After completion of the reaction, the mixture was cooled down to 0°C and filtered. The solid powder was added to a mixture of sulfuric acid (4 ml, 75.0 mmol) and acetic acid (40 ml, 699.4 mmol), and stirred at 0°C for 5 minutes. Then, it was stirred for 1 hour at 30°C and subsequently at 70°C for another 1 hour. Afterward, it was cooled to room temperature and poured into ice water with stirring. The greenish solid was filtered off, washed with water and EtOH to a neutral pH, and dried. Finally, a pure 2,8-dibromo-5,11-dihydroindolo[3,2-b] carbazole (1.03 g, yield 28%) was obtained.

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.29 (s, 2H), 8.47 (d, *J* = 2.0 Hz, 2H), 8.22 (s, 2H), 7.53 – 7.39 (m, 4H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 139.87, 135.49, 127.96, 124.42, 122.93, 122.24, 112.38, 109.60, 101.28.



Tetraethyl((2,8-dibromoindolo[3,2-b]carbazole-5,11-diyl)bis(butane-4,1-

diyl))bis(phosphonate) (compound 2): compound 1 (1.00 g, 2.41 mmol) was dissolved in 1,4dibromobutane (8 ml, 67 mmol), then tetrabutylammonium bromide (0.298 g, 0.926 mmol) and 50% KOH aqueous solution (5.6 ml, 50 mmol) were added subsequently. The mixture was stirred at 60°C for 16 hours, and then cooled to 0°C. The yellow powder was filtered off and washed with water to neutral pH and dried finally. The yellow powder was mixed with triethyl phosphite (88 ml, 510 mmol) and stirred at 110° C overnight. After reaction completed, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (EA: MeOH, 10: 1, v/v) to give 1.53 g (yield 79%) of yellow powder.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 1.9 Hz, 2H), 7.93 (s, 2H), 7.56 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 4.38 (t, *J* = 7.1 Hz, 4H), 4.09 – 3.97 (m, 8H), 2.04 (p, *J* = 7.1 Hz, 4H), 1.74 (d, *J* = 3.5 Hz, 4H), 1.26 (q, *J* = 6.9 Hz, 16H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 140.25, 136.19, 128.61, 124.40, 123.07, 122.31, 110.92, 109.79, 99.13, 61.61, 61.55, 42.95, 29.58, 29.43, 26.19, 24.78, 20.55, 20.50, 16.47, 16.41.



Poly-tetraethyl(indolo[3,2-b]carbazole-5,11-diylbis(butane-4,1-diyl))bis(phosphonate)

(compound 3): compound 2 (0.5 g, 0.626 mmol) was dissolved in 8ml DMF to prepare a solution of component 2 monomer. Ni(COD)₂ (0.21 g, 0.752 mmol), 2,2'-bipyridine (0.12 g, 0.752 mmol) and cyclooctadiene (0.10 ml, 0.752 mmol) were dissolved in 2 ml DMF and then stirred at 80°C for 30 minutes. Compound 2 monomer solution was added dropwise via cannula, and the mixture was stirred at 80°C for 12 hours, then cooled down to room temperature and 1M HCl was added to adjust the pH to 1-2. The resulting precipitate was isolated by filtration. The polymer was then dissolved in dichloromethane and washed successively with 200 ml hot 0.01 M EDTA solution (pH = 3-4), 200 ml hot 0.01 M EDTA solution (pH = 8-9), and 200 ml water. The polymer was then dried under vacuum to give 0.225 g of brown solid (yield 56%).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 10.3 Hz, 2H), 8.12 (s, 2H), 7.88 (s, 2H), 7.48 (t, *J* = 2.0 Hz, 2H), 4.48 (s, 4H), 4.02 – 3.93 (m, 8H), 2.11 (s, 4H), 1.77 (s, 4H), 1.22 – 1.14 (m, 16H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 128.64, 109.82, 99.18, 61.66, 61.59, 43.03, 26.29, 24.89, 16.49, 16.43. GPC analysis (DMF vs. PS): M_n = 6123 Da, M_w = 7608 Da, PDI = 1.24.



Poly-DCPA: compound 3 (0.05 g) was dissolved in 10 ml dichloromethane and bromotrimethylsilane (0.05 ml) was added dropwise to it slowly. The mixture was stirred at 25 °C for 12 hours and then 20 ml methanol was added and stirred for 4 hours. The solution was concentrated and dropped into ether to precipitate for 3 times, and brown powder was obtained (35 mg, yield 85%). It should be noted that phosphonate groups may not fully convert to phosphonic acid during the hydrolysis process. However, Poly-DCPA is not soluble in common GPC solvents like DMF and THF, and direct molecular weight determination via GPC is not feasible. Given that the hydrolysis reaction occurs exclusively at the phosphate side chains, we can reasonably estimate the molecular weight (M_n) of Poly-DCPA to be approximately 5260 Da based on the calculated polymerization degree of **compound 3**. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.50 (s, 2H), 8.24 (d, *J* = 1.9 Hz, 2H), 7.88 (s, 2H), 7.45 (s,

2H), 4.33 (s, 4H), 1.18 (d, *J* = 1.7 Hz, 13H).

¹³C NMR (101 MHz, Methanol- d_4) δ 62.67, 32.57, 31.74, 30.62, 30.28, 29.99, 23.28, 14.35.

Synthesis of DCPA



Tetraethyl(indolo[3,2-b]carbazole-5,11-diylbis(butane-4,1-diyl))bis(phosphonate): 5,11dihydroindolo[3,2-b]carbazole (1.00 g, 3.90 mmol) was dissolved in 1,4-dibromobutane (10.0 ml, 83.9 mmol), then tetrabutylammonium bromide (0.599 g, 1.86 mmol) and 50 % KOH aqueous solution (8.96 ml, 80.9 mmol) were added subsequently. The mixture was stirred at 60°C for 16 hours, and then cooled to 0°C. The yellow powder was filtered off and washed with water to neutral pH and dried finally. The yellow powder was mixed with triethyl phosphite (45.0 ml, 260 mmol) and stirred at 110°C overnight. After the reaction completed, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (pure EA) to give 1.84 g of yellow powder (yield 74%).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 7.7 Hz, 2H), 8.00 (s, 2H), 7.52 – 7.44 (m, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 4.43 (t, *J* = 7.1 Hz, 4H), 4.11 – 3.95 (m, 8H), 2.07 (t, *J* = 7.3 Hz, 4H), 1.80 – 1.73 (m, 8H), 1.24 (t, *J* = 7.1 Hz, 12H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 141.56, 135.95, 125.79, 122.86, 120.26, 118.17, 108.30, 98.75, 61.61, 61.54, 42.83, 29.73, 29.58, 26.24, 24.83, 20.59, 20.55, 16.44, 16.38.



DCPA: compound 4 (0.05 g) was dissolved in 10 ml dichloromethane and bromotrimethylsilane (0.05 ml) was added dropwise to it slowly. The mixture was stirred at 25 °C for 12 hours and then 20 ml methanol was added and stirred for 4 hours. The solution was concentrated and dropped into ether to precipitate for 3 times, and yellow powder was obtained (36 mg, yield 87%).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.45 – 8.19 (m, 4H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 2H), 4.48 (s, 4H), 1.93 (q, *J* = 7.2 Hz, 4H), 1.59 (d, *J* = 10.6 Hz, 8H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 141.66, 136.00, 126.16, 122.72, 122.65, 120.88, 118.26, 109.29, 99.86, 42.76, 29.97, 29.82, 27.91, 21.04.

The NMR spectra related to the synthesis of DCPA and Poly-DCPA can be found in Figures S17 to S29.

2. Supporting Figures and Tables



Figure S1. Contact angle measurements of (a) DCPA and (b) Poly-DCPA solutions (1 mg ml⁻¹, chloroform/MeOH=1:1, v/v) on ITO glass substrates. Contact angle measurements of perovskite precursor solution on the ITO glass substrates coated with (c) DCPA and (d) Poly-DCPA .



Figure S2. The thermogravimetry analysis result of DCPA and Poly-DCPA.



Figure S3. CV curves of DCPA and Poly-DCPA. Inset shows the CV curve of Ferrocene internal standard.



Figure S4. (a) Synthesis route of Poly-DCBr (M_n : 2756 Da, M_w : 4365 Da). (b) XPS In 3d spectra of bare ITO, Poly-DCBA- and Poly-DCPA-coated ITO substrates.



Figure S5. IR spectra of Poly-DCPA powder and scratched Poly-DCPA/perovskite mixture.



Figure S6. AFM height images (1 μm by 1 μm) of a) DCPA and b) Poly-DCPA-coated ITO substrates.



Figure S7. Pseudo-color plots of the femtosecond transient absorption spectra of perovskite film based on (a) DCPA and (b) Poly-DCPA. Corresponding fs-transient kinetics traces (c) at the respective GSB signals of the perovskite films based on DCPA and Poly-DCPA. Solid lines represent the best fit for the kinetic traces, and inset shows the fitting results.



Figure S8. XRD patterns of the perovskite films deposited on DCPA and Poly-DCPA.



Figure S9. SEM images of ITO/DCPA/PVSK surface (a) and ITO/Poly-DCPA/PVSK surface (b). SEM images of buried interface of the perovskite films based on the DCPA (c) and Poly-DCPA (d) interfacial layer.



Figure S10. Reverse and forward J-V sweeping curves of the Poly-DCPA-based champion cell.



Figure S11. Statistical analysis on photovoltaic parameters of PSCs based on DCPA and Poly-DCPA.



Figure S12. The *J-V* curves of PSCs based on different thickness of (a) DCPA and (b) Poly-DCPA layers.



Figure S13. The device PCEs versus the thickness of DCPA and Poly-DCPA layers.



Figure S14. Schematic illustration of EL mapping characterization setup.



Figure S15. *I-V* characteristic curve of the Poly-DCPA-based perovskite module (aperture area: 12.24 cm²).



Figure S16. Optical image of the module dead area obtained with a metallographic microscope.



Figure S17. The step profiler curve of scratched Poly-DCPA layer on ITO.



Figure S18. ¹H NMR (400 MHz, (CD₃)₂SO) spectrum of compound 1.



Figure S19. ¹³C NMR (101 MHz, (CD₃)₂SO) spectrum of compound 1.



Figure S20. ¹H NMR (400 MHz, CDCl₃) spectrum of compound 2.



Figure S21. ¹³C NMR (101 MHz, CDCl₃) spectrum of compound 2.



Figure S22. ¹H NMR (400 MHz, CDCl₃) spectrum of compound 3.



Figure S23. ¹³C NMR (101 MHz, CDCl₃) spectrum of compound 3.



Figure S24. ¹H NMR (400 MHz, CDCl₃) spectrum of compound 4.



Figure S25. ¹³C NMR (101 MHz, CDCl₃) spectrum of compound 4.



Figure S26. ¹H NMR (400 MHz, CDCl₃) spectrum of Poly-DCPA.



Figure S27. ¹³C NMR (101 MHz, CDCl₃) spectrum of Poly-DCPA.



Figure S28. ¹H NMR (400 MHz, (CD₃)₂SO) spectrum of DCPA.



Figure S29. ¹³C NMR (101 MHz, (CD₃)₂SO) spectrum of DCPA.

Sample	<i>A</i> ₁	<i>t</i> ₁ (ns)	<i>A</i> ₂	<i>t</i> ₂ (ns)	t _{ave} (ns)
DCPA	1129.17	7.74	969.11	387.36	378.72
Poly-DCPA	914.48	10.16	989.22	514.21	505.17

Table S1. Summary of the fitting parameters for the TRPL spectra using the bi-exponential decay function $y = y_0 + A_1 exp(-x/t_1) + A_2 exp(-x/t_2)$, $t_{ave} = (A_1 t_1^2 + A_2 t_2^2)/(A_1 t_1 + A_2 t_2)$.

Table S2. The photovoltaic parameters of the PSCs based on DCPA and Poly-DCPA.

HTL	V _{oc} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
DCPA	1.11	25.0	79.4	22.0
	(1.05±0.04)	(23.9±0.8)	(74.4±3.7)	(19.7±1.6)
Poly-DCPA	1.17	25.4	83.6	24.9
	(1.15±0.01)	(24.9±0.4)	(81.1±1.8)	(23.5±0.9)

HTL	Thickness (nm)	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
DCPA	1	1.10	24.5	77.7	20.8
	2	1.11	25.0	79.4	22.0
	3	1.10	25.1	78.4	21.7
	4	1.09	24.7	77.6	20.9
	5	1.12	24.2	76.8	20.8
	6	1.13	24.2	76.8	19.4
	10	1.14	24.1	57.6	15.8
Poly DCPA _	3	1.17	25.0	81.5	23.8
	7	1.17	25.4	83.6	24.9
	10	1.17	25.4	83.4	24.8
	14	1.18	25.1	82.7	24.5
	17	1.16	25.5	83.5	24.6
	20	1.18	25.4	81.5	24.3
	35	1.18	24.2	81.2	23.2

Table S3. Device parameters based on different thickness of DCPA and Poly-DCPA layers.