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Supplementary Information

Tris(4-(1-phenyl-1H-benzo[d]imidazole)phenyl)phosphine oxide for Enhanced Mobility and Restricted Traps in Photovoltaic Interlayers

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Materials

All organic synthetic reactions were performed under nitrogen atmosphere with corresponding starting materials purchased from commercial suppliers. Solvents applied to the reactions were used after drying with the well-established methods. Isolation of molecules was conducted through flash column chromatography using 230–400 Mesh sized silica gel, and the final products were purified by sublimation steps. In the course of compounds and device preparation, the appropriate materials if accessible in the market were supplied reasonably.

Synthesis of BIPO, TIPO and TBIT

Synthesis of 4-bromo-N-(2-(phenylamino)phenyl)benzamide²⁶

Here, N-phenyl-o-phenylenediamine (21.0 g, 114.0 mmol) was slowly added into a solution of 4-bromobenzoyl chloride (25.0 g, 114.0 mmol) in N,N-dimethylacetamide

(155 mL), and the mixture was stirred for 1 h at room temperature. After the addition of water, the precipitated solid was filtered off and washed with water and methanol. The solid was dried under reduced pressure conditions and recrystallised from a mixture of N,N-dimethylformamide (DMF)–water (7 : 1) and washed with water to obtain the product (31.4 g, 75 %): ¹H nuclear magnetic resonance (NMR) (300 MHz, CD2Cl2, δ): 8.33 (s, 1H), 8.19–8.16 (d, 1H), 7.56–7.51 (m, 4H), 7.32–7.20 (m, 5H), 6.91–6.82 (m, 3H), 5.73 ppm (s, 1H).

Synthesis of 2-(4-bromophenyl)-1-phenyl-1H-benzo[d]-imidazole²⁶

Here, 4-bromo-N-(2-(phenylamino)phenyl)benzamide (3) (31.4 g, 85.5 mmol) was stirred for 16 h in acetic acid (100 mL) under reflux. The solvent was evaporated to obtain the product (27.9 g, 93%): ¹H NMR (300 MHz, CD_2Cl_2 , δ): 7.86–7.83 (m, 1H), 7.56–7.55 (m, 3H), 7.48 (s, 4H), 7.37–7.28 ppm (m, 5H).

Synthesis of bis(1-phenyl-1H-benzo[d]imidazole)phenyl-phosphine oxide (BIPO) (Fig. S1- S3)²⁶

The material was purified via column chromatography (ethyl acetate/MeOH 20:1) to obtain the product (1.2 g, 15%): ¹H NMR (300 MHz, CD_2Cl_2, δ): 7.70–7.69 (d, 2H), 7.62–

7.54 (m, 19H), 7.37–7.30 ppm (m, 10H); ¹³C NMR (500 MHz, CDCl₃, δ): 149.10, 141.15, 135.52, 134.72, 131.83, 131.81, 131.77, 130.28, 130.23, 130.20, 130.15, 128.27, 127.53, 127.43, 127.13, 126.84, 126.74, 125.48, 122.08, 121.47, 118.28, 108.79 ppm; ³¹P NMR (500 MHz, CDCl₃, 300 K, δ) 29.56 ppm; HRMS (FAB⁺): calculated for C₄₄H₃₁N₄OP , 662.2235; found, (M+H) 663.2310.

Synthesis of tris(4-(1-phenyl-1H-benzo[d]imidazole)phenyl) phosphine oxide (TIPO) (Fig. S4-S6)

Here, (4-Bromophenyl)-1-phenyl-1H-benzo[d]imidazole (4) (10.0 g, 28.6 mmol) was dissolved in anhydrous tetrahydrofuran (100 mL) in a nitrogen atmosphere and was cooled to -78 °C in a dry ice/acetone bath. Thereafter, n-Butyl lithium (11.8 mL, 29.5 mmol, 2.5 M in hexane) was slowly added dropwise to give a yellow solution that was thickened to form a slurry. The temperature was not allowed to rise above -70 °C during the addition process. After stirring for 1 h at -78 °C, trichlorophenylphosphine (5) (1.23 g, 8.94 mmol) was also added. The reaction solution was returned to the ambient temperature and was then stirred for 12 h. The mixture was extracted with 1,2-dichloromethane. The combined organic phases were dried (MgSO₄) and concentrated under reduced pressure to give a crude compound, which was dissolved in 1,2-

dichloromethane (100 mL) and 30% aqueous H_2O_2 (20 mL) was then added to the solution. The mixed solution was stirred for 1 h at room temperature. The mixture was extracted with 1,2-dichloromethane. The organic and aqueous portions in the mixed solution were separated, the aqueous portion was extracted with dichloromethane two times, and the combined organic layer was dried over MgSO₄. Afterwards, the solvent was evaporated. The material was purified via column chromatography (ethyl acetate/MeOH 20:1) to obtain the product (3.33 g, 42%): ¹H-NMR (300 MHz, CD₂Cl₂, δ): 7.70–7.69 (d, 3H), 7.61–7.58 (m, 6H), 7.57–7.54 (m, 15H), 7.37–7.30 (m, 15H); ¹³C NMR (500 MHz, CDCl₃, δ): 150.85, 143.11, 135.52, 137.57, 136.69, 133.83, 133.45, 132.62, 131.84, 131.76, 130.04, 129.36, 129.26, 128.88, 127.39, 123.73, 123.05, 119.87, 110.61 ppm MS(FAB⁺): calculated for C₅₇H₃₉N₆OP, 854.2923; found, (M⁺) 855.3004.

Synthesis of 2-(4-cyanophenyl)-1-phenyl-1H-benzo[d]-imidazole

Additionally, (4-Bromophenyl)-1-phenyl-1H-benzo[d]imidazole (10.0 g, 28.6 mmol) and CuCN (6.0 g, 65.8 mmol) were dissolved in 30 mL of DMF, and the solution was refluxed at 150 °C. After the resulting solid was filtered, it was extracted with chloroform. The solution was dried using anhydrous MgSO₄ and the solvent was evaporated. The crude product was purified via column chromatography (hexane / ethyl acetate 2:1) to obtain

the product. (4.5 g, 53%); ¹H-NMR (300 MHz, CD₂Cl₂, δ): 7.74 – 7.71 (d, 1H), 7.64– 7.61 (d, 2H), 7.59–7.57 (m, 5H), 7.39–7.31 (m, 5H).

Synthesis of 2,4,6-tris(4-(1-phenyl-1H-benzo[d]imidazole) phenyl)-1,3,5triazine (TBIT) (Fig. S7-S9)

Furthermore 2-(4-cyanophenyl)-1-phenyl-1H-benzo[d]-imidazole (3.0 g, 10.1 mmol) was dissolved in 20 mL of chloroform. Trifluoromethanesulfonic acid (6.1 g, 40.8 mmol) was added and stirred for 1 h at 0 °C, followed by stirring for 12 h at room temperature. The ammonia water was added to the solution at 0 °C. After the crude product was extracted with chloroform, it was dried using anhydrous MgSO₄. The purification was carried out via column chromatography (chloroform/ethyl acetate 10:1) to obtain the product (2.2 g, 25%): ¹H-NMR (300 MHz, CD2Cl2, δ): 8.73–8.70 (d, 6H), 7.91–7.89 (d, 3H), 7.84–7.81 (d, 6H), 7.61–7.57 (m, 9H); ¹³C NMR (500 MHz, CDCl₃, δ): 151.68, 150.24, 142.91, 137.48, 136.27, 135.81, 134.41, 132.24, 130.43, 129.98, 129.36, 128.00, 127.30, 125.70, 124.45, 123.70, 120.33, 118.78, 112.77, 111.03 ppm MS(FAB⁺): calculated for C₆₀H₃₀N₉, 885.3328; found, (M⁺) 886.3434.

Instrumentation

The ¹H NMR spectra were recorded at 300 or 500 MHz with reference to CD_2Cl_2 (δ 5.32), and low-/high-resolution mass spectra (LRMS and HRMS, respectively) were measured using a positive-ion FAB spectrometer. Ultraviolet-visible (UV-Vis) absorption and photoluminescence (PL) spectra were recorded in dichloromethane using a Shimadazu UV-2201 spectrophotometer and a Perkin-Elmer LS50B fluorescence spectrometer, respectively. Thermogravimetric analysis (TGA) was performed on a TA instruments 2100 TGA analyser under the flow of nitrogen gas at a rate of 10 °C/min. Differential scanning calorimetry (DSC) was measured using a TA DSC 2010 device under anhydrous conditions. Cyclic voltammetry (CV) measurement was performed on CH instruments CHI 1000 with a three-electrode cell, which are Ag/AgCl as reference electrode, Pt as counter electrode, and carbon as working electrode, in a nitrogen bubbled 0.1 M tetrabutylammonium perchlorate (TBAP) solution in methylene dichloride with a scan rate of 50 mV/s at room. The highest occupied molecular orbital (HOMO) level was calculated using the equations: $E_{HOMO} = -(E_{onset} \circ x - ferrocene_{onset}) - 4.8 \text{ eV}$, where E_{onset} ox is the onsets of the oxidation potential, respectively. Ferrocene_{onset} is the onset oxidation potential of ferrocene (0.43 eV), which was used as a reference. The current densityvoltage-luminance (J-V-L) characteristics and electroluminescence (EL) spectra were

characterised using a source measure unit (Keithley 238) and a spectro-radiometer (Minolta CS-2000).



Fig. S1. ¹H NMR data of bis(1-phenyl-1H-benzo[d]imidazole)phenyl-phosphine oxide (BIPO).



Fig. S2. ¹³C NMR data of bis(1-phenyl-1H-benzo[d]imidazole)phenyl-phosphine oxide

(BIPO).



Fig. S3. Mass data of bis(1-phenyl-1H-benzo[d]imidazole)phenyl-phosphine oxide

(BIPO).



Fig. S4. ¹H NMR data of tris(4-(1-phenyl-1H-benzo[d]imidazol)phenyl)phosphine oxide

(TIPO).



Fig. S5. ¹³C NMR data of tris(4-(1-phenyl-1H-benzo[d]imidazol)phenyl)phosphine

oxide (TIPO)



Fig. S6. Mass data of tris(4-(1-phenyl-1H-benzo[d]imidazol)phenyl)phosphine (TIPO).



Fig. S7. ¹H-NMR data of 2,4,6-tris(4-(1-phenyl-1H-benzo[d]imidazol)phenyl)-1,3,5-

triazine (TIBT).



Fig. S8. ¹³C-NMR data of 2,4,6-tris(4-(1-phenyl-1H-benzo[d]imidazol)phenyl)-1,3,5-

triazine (TIBT).



TBIT



Fig. S9. Mass data of 2,4,6-tris(4-(1-phenyl-1H-benzo[d]imidazol)phenyl)-1,3,5-triazine (TIBT).



Fig. S10. Solubility test images of BIPO, TIPO, and TBIT small molecules in IPA solvent at room temperature without magnetic bars.



Fig. S11. Cross-Section FE-SEM analysis of (a) Pristine device and (b) device with TIPO

interlayer.







Fig. S12. Density functional theory (DFT) calculated dipole moment of BIPO, TIPO, and TBIT.



Fig. S13. DFT calculated HOMO and LUMO of BIPO, TIPO, and TBIT.



Fig. S14. UV-vis absorption spectra and PL spectra of BIPO with solutions and films, respectively.



Fig. S15. Differential scanning calorimetry (DSC) and thermal gravimetric (TG) analyses

of (a,e) BIPO, (b,f) TIPO, and (c,g) TBIT.



Fig. S16. Cyclic voltammetry measurements of (a) BIPO, (b) TIPO, and (c) TBIT.



Fig. S17. Statistics of (a) V_{OC} , (b) J_{SC} , (c) FF, and (d) PCE distribution for PVSCs with BIPO, TIPO, and TBIT interlayers.



Fig. S18. Dark current density curve of perovskite solar cell with BIPO interlayer (blue), TIPO interlayer (red) and TBIT interlayer (green).



Fig. S19. XRD analysis of BIPO, TIPO and TBIT materials on glass.



Fig. S20. Reflectance analysis of device with BIPO, TIPO, and TBIT interlayer.



Fig. S21. UV-vis spectra of the films with PEDOT:PSS/MAPbI₃/PC₇₀BM/BIPO on ITO substrate (blue) , PEDOT:PSS/MAPbI₃/PC₇₀BM/TIPO on ITO substrate (red), and PEDOT:PSS/MAPbI₃/PC₇₀BM/TBIT (green) on ITO substrate.



Fig. S22. Photos depict the water contact angles of (a) ITO/PC₇₀BM (b) ITO/BIPO (c) ITO/TIPO (d) ITO/TBIT, (e) ITO/PC₇₀BM/BIPO, (f) ITO/PC₇₀BM/TIPO, and (g) ITO/PC₇₀BM/TBIT films.

	Uv-vis, λ_n	_{nax} (nm)	PL, λ _{ma} ,	. (nm)	Eg	номо	LUMO	T _d	Tg	T _m
	solution	film	solution	film	(eV)	(eV)	(eV)	(°C)	(°C)	(°C)
BIPO	311	318	373	389	3.35	7.07	3.72	451	129	277
TIPO	312	315	374	392	3.36	7.01	3.65	525	153	288
TBIT	342	349	418	446	3.04	6.73	3.69	556	188	328

Table S1. Optical, electrical, and physical analyses of the properties of BIPO, TIPO, andTBIT small molecules.

ETL interlayer	V _{OC}	J _{SC}	IPCE	FF	PCE
(Avg.)	[V]	[mA/cm ²]	[mA/cm ²]	[%]	[%]
Pristine	0.935	17.71	17.36	69.71	11.58
BIPO	0.920	17.86	17.94	73.29	12.03
TIPO	0.914	17.94	18.08	74.71	12.23
TBIT	0.918	17.22	17.36	70.14	11.08

Table S2. Average values of the parameters of the inverted perovskite device with various interlayers.

	$R_{S}\left(\Omega ight)$	$\mathrm{R}_{\mathrm{sh}}\left(\Omega ight)$
pristine	46.82	10399.19
BIPO	37.14	299901.11
TIPO	42.95	754992.12
TBIT	57.07	263923.62

 Table S3. Calculated values of series resistance and shunt resistance from dark current density analysis.