

Electronic Supplementary Information

Imide-Free Electron-Deficient Electrolytes with Adjustable Cathode-Modifying Capabilities Achieved by Side Chains Engineering for Efficient Organic Solar Cells

Guiting Chen,^{*a} Long Wang,^b Hongli Wu,^b Long Li,^a Baitian He,^{*a} Chuanbo Dai^a and Zhicai He^{*b}

^aNortheast Guangdong Key Laboratory of New Functional Materials, Guangdong Rare Earth Photofunctional Materials Engineering Technology Research Centre, School of Chemistry and Environment, Jiaying University, Meizhou 514015, P.R. China.

^bInstitute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P.R. China.

*Corresponding author. Email: zhicaihe@scut.edu.cn, cgt_jy@126.com, baitian-he@foxmail.com.

Experimental section

1. Materials

All of the reagents and solvents employed to synthesize materials were purchased from Energy Chemical, Bide Pharmatech Co., Ltd. and Shanghai Haohong Scientific Co., Ltd., and used as received without further purification. Active layer materials including D18, Y6 and L8-BO were purchased from Derthon Optoelectronic Materials Science Technology Co., Ltd. PEDOT:PSS (CLEVIOS™ P VP AI 4083) was purchased from Heraeus Deutschland GmbH & Co. KG.

2. Synthesis

N-(8-bromooctyl)-6-bromoisatin (**1**): 6-Bromoisatin (3.81 g, 16.9 mmol), 1,8-dibromooctane (23.0 g, 84.5 mmol), anhydrous K₂CO₃ (7.00 g, 50.7 mmol) and anhydrous DMF (40 ml) were added to a 150 ml of three-neck flask under nitrogen. The reaction was heated to 70 °C and stirred for 8 hours. The reaction was mixed with distilled water when cooled to room temperature. The aqueous layer was extracted with CH₂Cl₂ for three times. The combined organic layer was washed with distilled water and brine, followed by drying over anhydrous MgSO₄. The solvent was distilled and the residue was purified by column chromatography on silica gel [petroleum ether/CH₂Cl₂ (1/1, v/v) as eluent]. Compound **1** (5.81 g, 82.4%) was afforded as an orange solid after drying in a vacuum oven. ¹H NMR (500 MHz, CDCl₃) δ: 7.47-7.45 (d, *J* = 7.9 Hz, 1H), 7.28-7.26 (d, *J* = 8.3 Hz, 1H), 7.06 (s, 1H), 3.71-3.68 (t, *J* = 7.3 Hz, 2H), 3.41-3.39 (t, *J* = 6.8 Hz, 2H), 1.88-1.82 (m, 2H), 1.70-1.66 (m, 2H), 1.46-1.32 (m, 8H). ¹³C NMR (126 MHz, CDCl₃) δ: 182.29, 157.96, 151.78, 133.53, 126.83,

126.41, 116.26, 113.71, 40.38, 33.88, 32.64, 28.92, 28.53, 27.96, 27.12, 26.67.

N-(8-bromooctyl)-6-(4-pentylphenyl)isatin (**2**): Compound **1** (3.00 g, 7.19 mmol), 4-pentylbenzeneboronic acid (1.52 g, 7.91 mmol), K₂CO₃ aqueous solution (2M, 7.20 ml, 14.4 mmol), Pd(PPh₃)₄ (416 mg, 0.360 mmol) and tetrahydrofuran (THF) (30 ml) were mixed in a 100 ml of three-neck flask under nitrogen, which was refluxed for 12 hours. After cooled to room temperature, the mixture was evaporated, followed by mixing with CH₂Cl₂. The organic layer was washed with distilled water and brine before dried over anhydrous MgSO₄. The organic solvent was distilled, and the crude product was purified by column chromatography on silica gel [petroleum ether/CH₂Cl₂ (3/1, v/v) as eluent] and then dried to give **2** (2.63 g, 75.5%) as an orange solid. ¹H NMR (500 MHz, CDCl₃) δ: 7.64-7.62 (d, *J* = 7.8 Hz, 1H), 7.54-7.52 (d, *J* = 8.1 Hz, 2H), 7.32-7.29 (m, 3H), 7.04 (s, 1H), 3.77-3.75 (t, *J* = 7.2 Hz, 2H), 3.39-3.36 (t, *J* = 6.8 Hz, 2H), 2.69-2.66 (t, *J* = 7.7 Hz, 2H), 1.85-1.80 (m, 2H), 1.74-1.70 (m, 2H), 1.67-1.64 (m, 2H), 1.44-1.31 (m, 12H), 0.92-0.89 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ: 183.01, 158.88, 151.82, 151.73, 144.79, 136.97, 129.35, 127.28, 125.95, 122.32, 116.25, 108.60, 40.25, 35.76, 33.99, 32.78, 31.58, 31.14, 29.08, 28.66, 28.10, 27.44, 26.86, 22.62, 14.12. HR-MS (MALDI-TOF) *m/z*: [M + H]⁺ calcd for C₂₇H₃₄BrNO₂, 485.18, found, 485.57.

BDOPV-P: Benzo[1,2-*b*:4,5-*b'*]difuran-2,6(3H,7H)-dione (0.330 g, 1.74 mmol), compound **2** (1.85 g, 3.82 mmol), *p*-toluenesulfonic acid (TsOH) (100 mg, 0.526 mmol) and HOAc (40 ml) were added to a 100 ml of three-neck flask under nitrogen, followed by refluxing for 24 hours. When cooled to room temperature, the mixture was poured into distilled water. The filter residue from suction filtration was washed with methanol, and purified by column chromatography on silica gel [petroleum ether/CH₂Cl₂ (1/2, v/v) as eluent]. BDOPV-P (1.41 g, 72.0%) was given as a dark solid after recrystallization from THF and drying in a vacuum oven. ¹H NMR (400 MHz, CDCl₃) δ: 9.06-9.04 (m, 4H), 7.55-7.53 (d, *J* = 8.1 Hz, 4H), 7.27-7.25 (m, 6H), 6.92 (s, 2H), 3.83-3.80 (t, *J* = 7.1 Hz, 4H), 3.41-3.38 (t, *J* = 6.8 Hz, 4H), 2.65-2.61 (t, *J* = 8.0 Hz, 4H), 1.89-1.82 (m, 4H), 1.78-1.71 (m, 4H), 1.68-1.61 (m, 4H), 1.48-1.34 (m, 24H), 0.93-0.89 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ: 167.65, 167.60, 151.71, 147.11, 146.73, 144.20, 137.26, 136.45, 131.20, 129.22, 127.06, 126.92, 125.49, 121.24, 120.15, 110.79, 106.58, 40.24, 35.81, 34.11, 32.87, 31.69, 31.22, 29.24, 28.78, 28.22, 27.64, 27.05, 22.70, 14.19. HR-MS (MALDI-TOF) *m/z*: [M + H]⁺ calcd for C₆₄H₇₀Br₂N₂O₆, 1122.36, found, 1122.90.

BDOPV-1: BDOPV-P (0.260 g, 0.232 mmol) and (CH₃)₃N (2M in THF, 2.9 ml, 5.80 mmol) were mixed with CHCl₃ (30 ml) in a 150 ml of three-neck flask under nitrogen. The reaction was stirred for 5 days, during which DMF was added to dissolved the precipitate. The solution was concentrated and added dropwise into 200 ml of ethyl acetate, and the precipitate was collected by filtration. The resulted solid

was dissolved in 2 ml of DMF, which was added dropwise into 200 ml of ethyl acetate again, followed by filtration to afford the target material BDOPV-1 (0.154 g, 53.6%) as a dark solid after drying in a vacuum oven. ^1H NMR (500 MHz, DMSO- d_6) δ : 7.95-6.81 (m, 16H), 3.82-3.77 (m, 4H), 3.24 (br, 4H), 3.02-2.98 (m, 18H), 2.62 (br, 4H), 1.64-1.59 (m, 12H), 1.31 (br, 24H), 0.88 (br, 6H).

BDOPV-2: BDOPV-P (0.240 g, 0.214 mmol) and $(\text{CH}_3\text{CH}_2)_3\text{N}$ (2.17 g, 21.4 mmol) were mixed with CHCl_3 (30 ml) in a 150 ml of three-neck flask under nitrogen. The reaction was heated to 55 °C and stirred for 5 days, during which DMF was added to dissolve the precipitate. The solution was concentrated and added dropwise into 200 ml of ethyl acetate, and the precipitate was collected by filtration. The resulted solid was dissolved in 2 ml of DMF, which was added dropwise into 200 ml of ethyl acetate again, followed by filtration to afford the target material BDOPV-2 (0.136 g, 48.0%) as a dark solid after drying in a vacuum oven. ^1H NMR (400 MHz, DMSO- d_6) δ : 7.95-7.20 (m, 16H), 3.80-3.72 (m, 4H), 3.19-3.05 (m, 16H), 2.61-2.60 (m, 4H), 1.62-1.59 (m, 12H), 1.30-1.21 (m, 24H), 1.13-1.12 (m, 18H), 0.89-0.86 (m, 6H).

3. Instruments and characterization

^1H NMR and ^{13}C NMR spectra were acquired on a Bruker AV-500 spectrometer with tetramethylsilane as an internal reference. Matrix-assisted laser-desorption/ionization time-of-flight mass spectra (MALDI-TOF MS) were performed on a Bruker BIFLEXIII TOF mass spectrometer. TGA curves were recorded on a NETZSCH TG 209 analyzer with a heating rate of 10 °C min^{-1} and a nitrogen flow rate of 30 mL min^{-1} . UV-vis absorption spectra were given on a HP 8453 spectrophotometer. CV data were obtained on a CHI600D electrochemical workstation. A standard three-electrodes cell composed of a Pt working electrode, a Pt wire counter electrode and a SCE reference electrode was employed, and the electrolyte solution was an anhydrous solution of 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphates (Bu_4NPF_6) in acetonitrile.

4. Fabrications and measurement of OSCs

ITO-coated glass substrates were cleaned carefully with deionized water, acetone and isopropanol successively. Whereafter, the substrates were dried at 150 °C for 10 min, followed by being treated in a UV-ozone cleaner. Then the PEDOT:PSS aqueous solution was spin-coated on top of the ITO substrates, which were then placed on an annealing table at 150 °C for 20 min to form anode interface layers of about 40 nm. The aforesaid substrates were transferred into an N_2 atmosphere glove box (Vacuum Atmosphere Co.). The D18:Y6 (1:1.6 w/w, total 12 mg/ml concentration) was dissolved in chloroform via stirring at 65 °C for 4 h, which was spin-coated on the PEDOT:PSS layers immediately after heating at 110 °C for 10 min, followed by

solvent vapor annealing with chloroform for 1 min to form active layers with nominal thickness around 110 nm. As for the D18:L8-BO system, the D18:L8-BO (1:1.5 w/w, total 13 mg/ml concentration) was dissolved in chloroform via stirring at 65 °C for 4 h, which was spin-coated on the PEDOT:PSS layers immediately after heating at 110 °C for 10 min, followed by solvent vapor annealing with CS₂ for 1 min to form active layers with nominal thickness around 100 nm. The PM6:Y6 (1:1.2 w/w, total 16 mg/ml concentration) was spin-coated on the PEDOT:PSS layers from chloroform solution with 0.5% (v/v) chloronaphthalene as the additive, followed by annealing at 100 °C for 10 min to form active layers with nominal thickness around 100 nm. Basing on this, BDOPV-1 and BDOPV-2 (both dissolved in TFE at 0.5 mg/ml concentration) solutions were spin-coated on the active layers severally after MeOH treatment on the active layers, forming CILs of ca 7 nm thickness. The thickness of CILs were tested by a step profiler. PDINN was spin-coated from its MeOH solution with 1 mg/ml concentration. At last, metallic Ag were thermal-evaporated on top of the CILs in a vacuum chamber to generate cathodes with 100 nm thickness. The active areas of OSC devices were all 0.04 cm². The *J-V* characteristics were acquired using a Keithley 2400 Source Measure Unit under 1 sun, AM 1.5 G illumination provided by a 3A solar simulator. The illumination intensity of solar simulator was around 100 mW cm⁻² as determined by a mono-crystal silicon reference cell. The EQE spectra were recorded on a solar cell-photodetector responsivity measurement system that was calibrated with a certified mono-crystal silicon reference cell.

Supporting figures

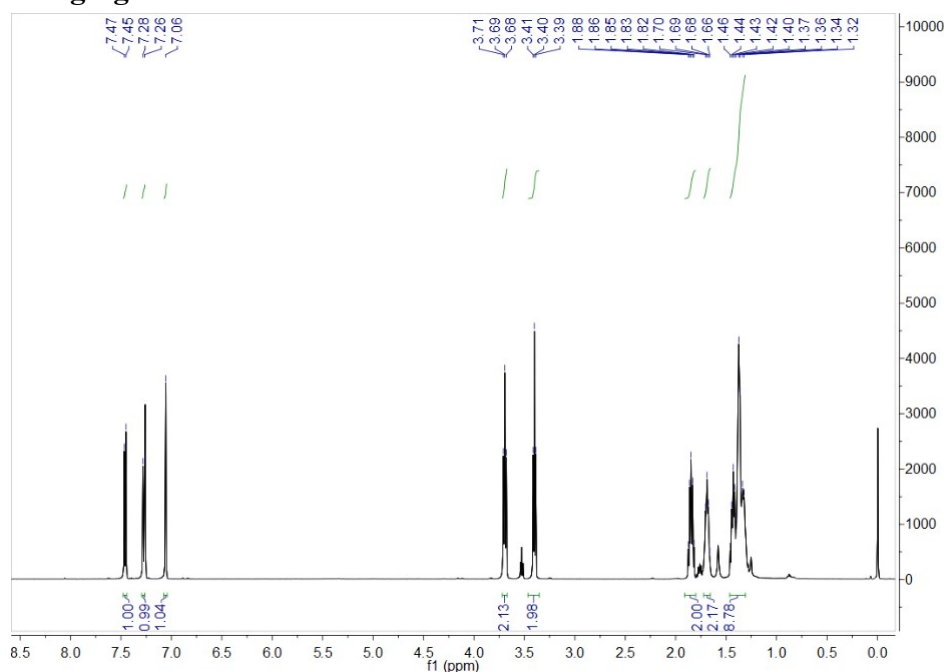


Fig. S1 ¹H NMR spectrum of compound 1.

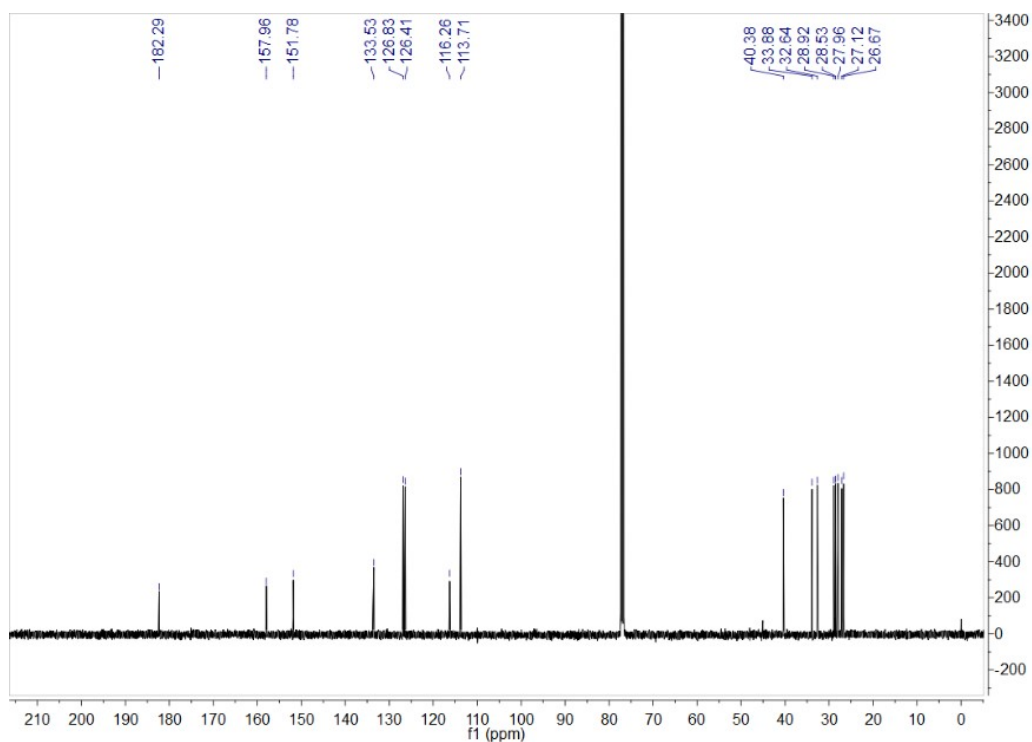


Fig. S2 ¹³C NMR spectrum of compound 1.

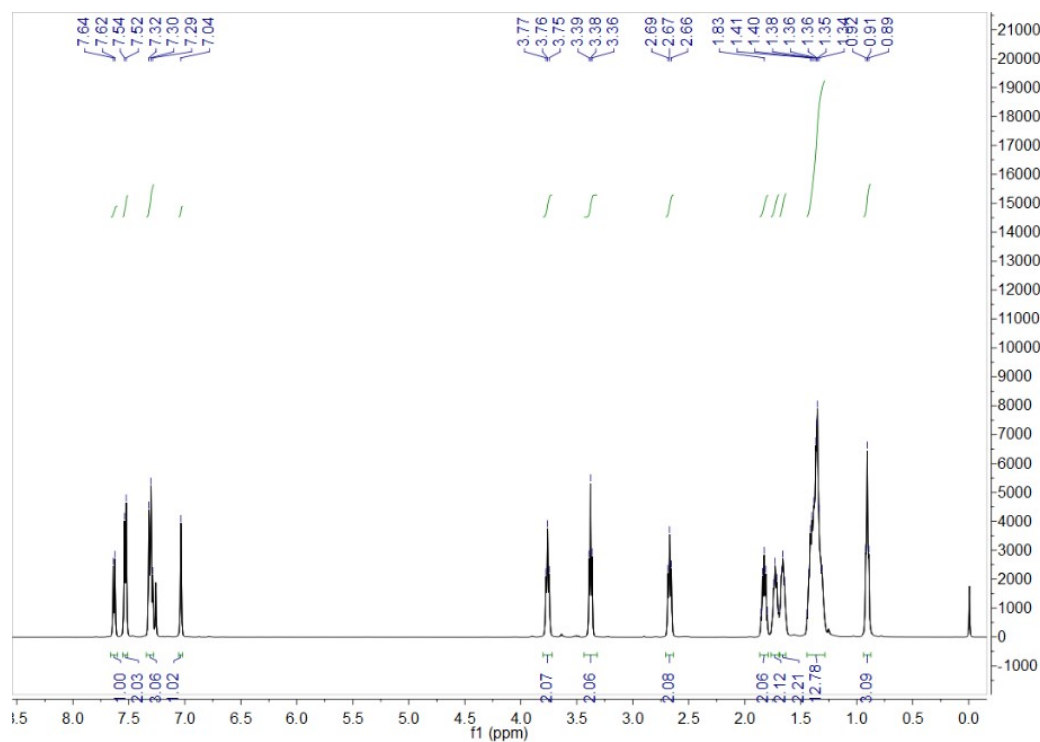


Fig. S3 ¹H NMR spectrum of compound 2.

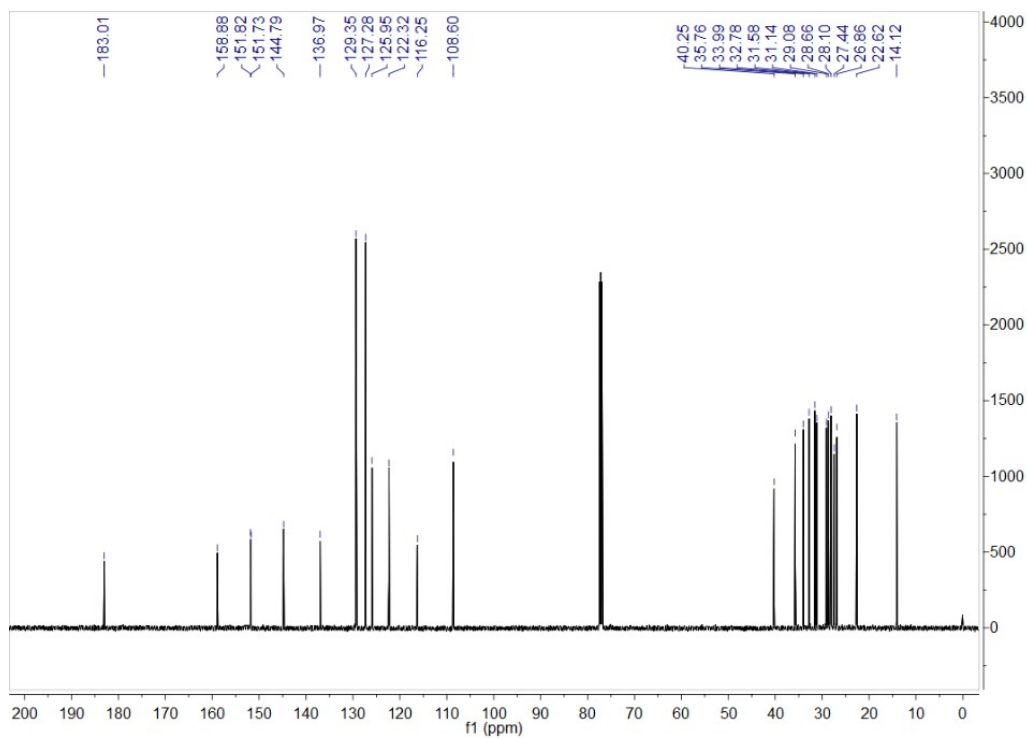


Fig. S4 ^{13}C NMR spectrum of compound **2**.

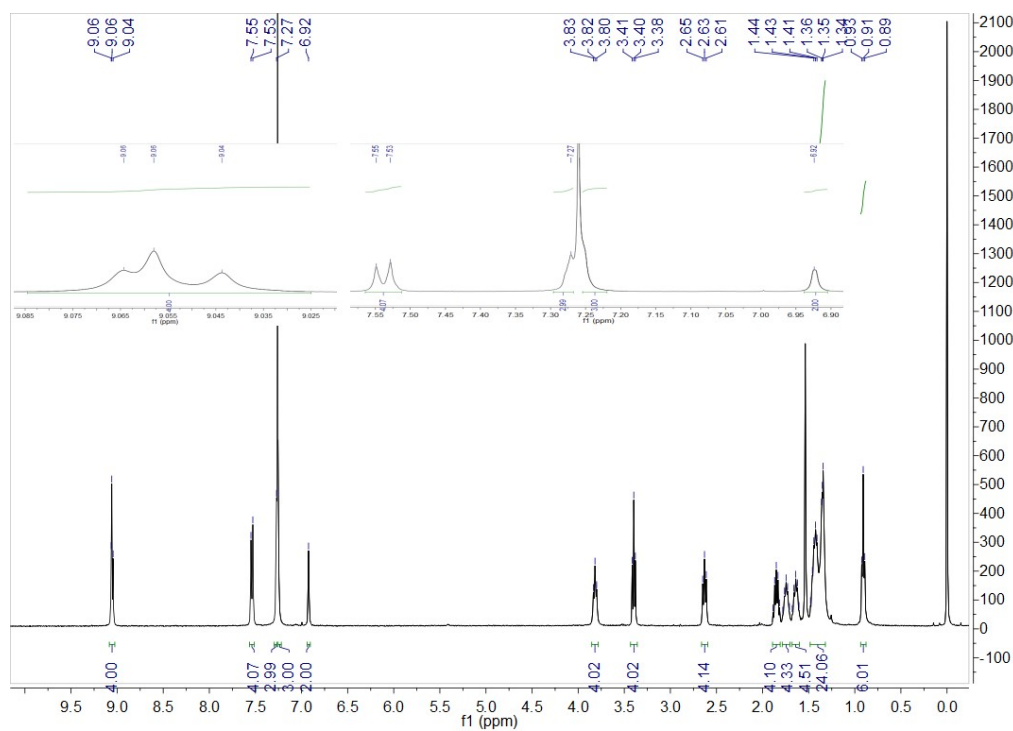


Fig. S5 ^1H NMR spectrum of compound BDOPV-P.

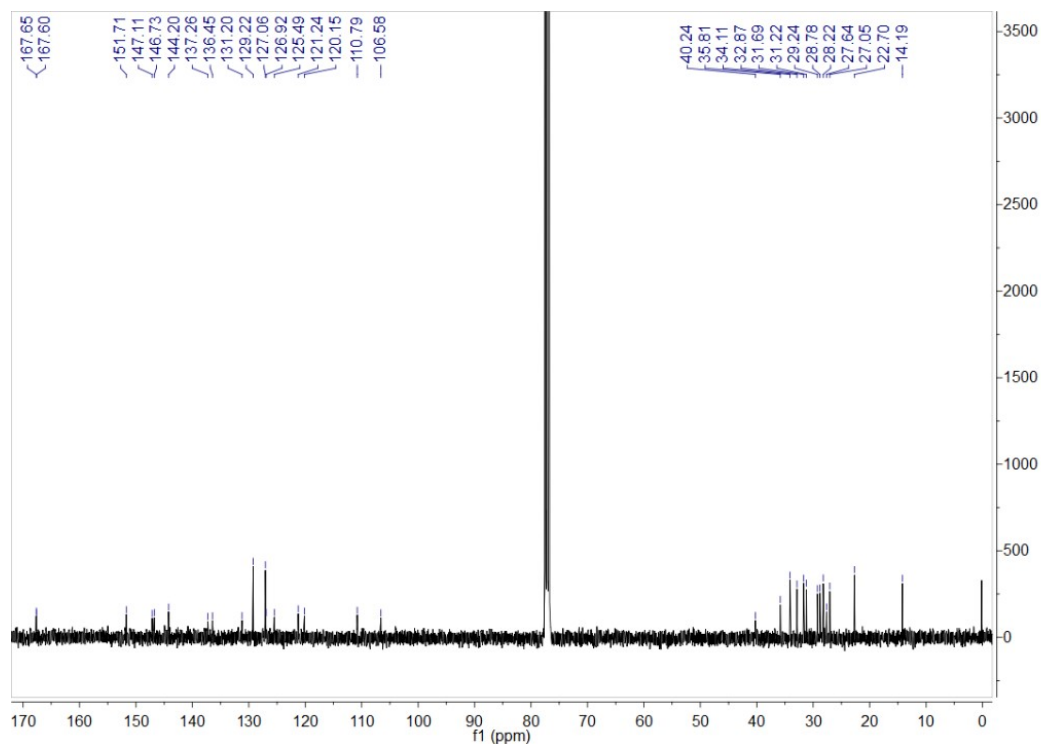


Fig. S6 ^{13}C NMR spectrum of compound BDOPV-P.

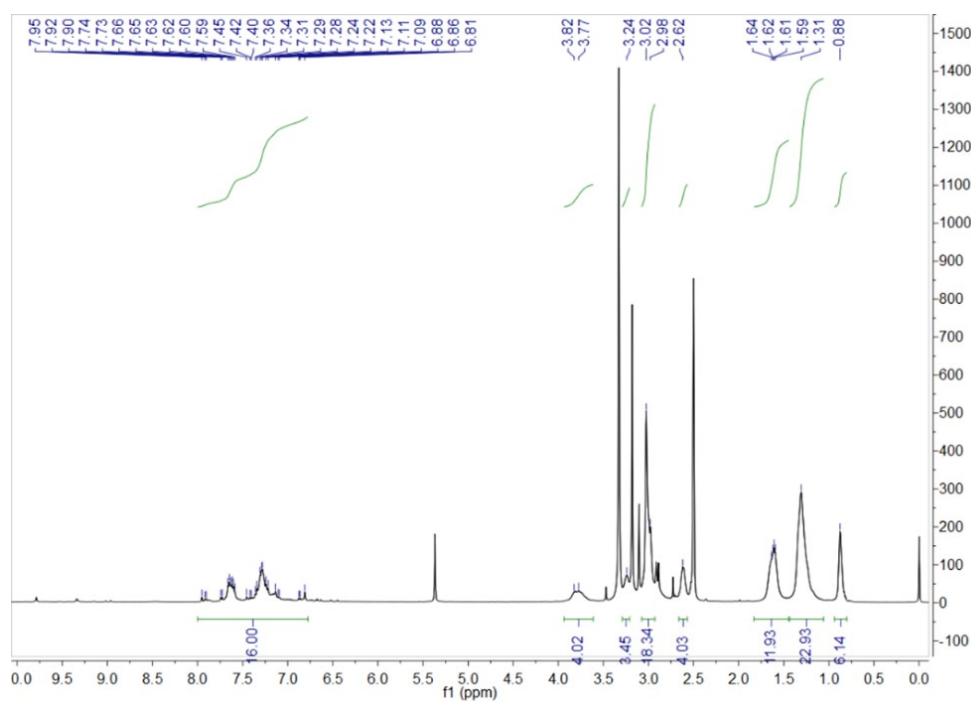


Fig. S7 ^1H NMR spectrum of compound BDOPV-1.

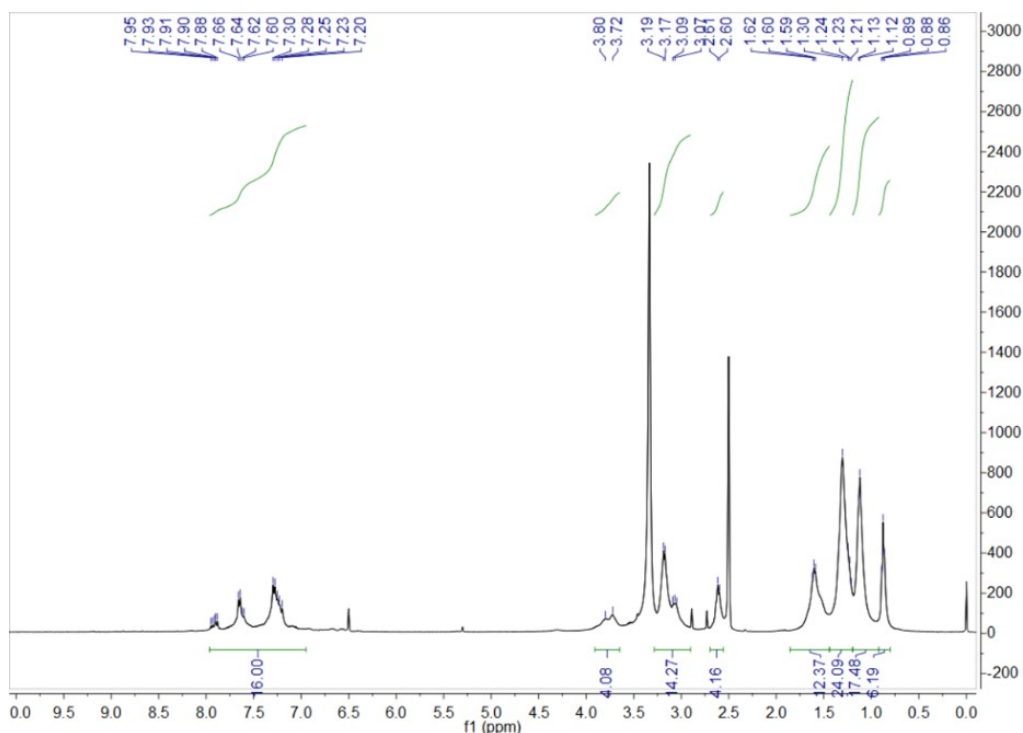


Fig. S8 ^1H NMR spectrum of compound BDOPV-2.

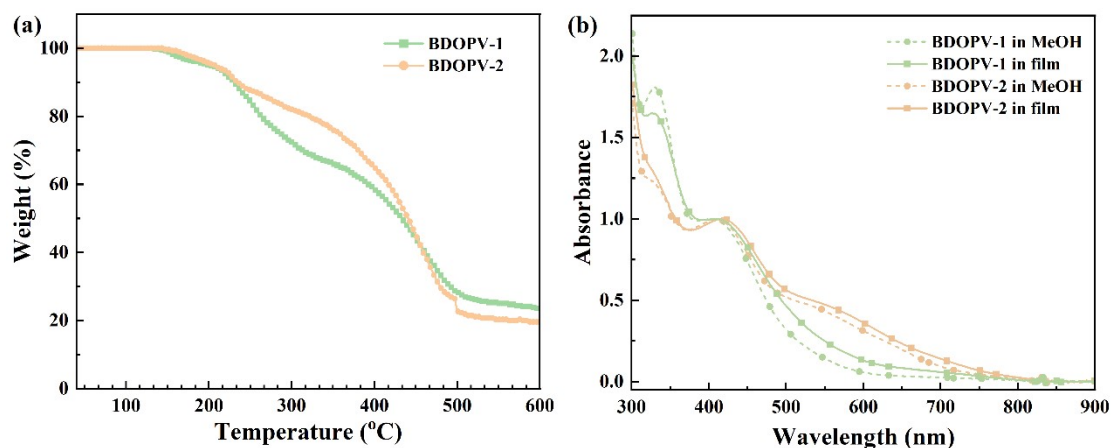


Fig. S9 (a) TGA curves and (b) UV-vis absorption spectra of CIMs.

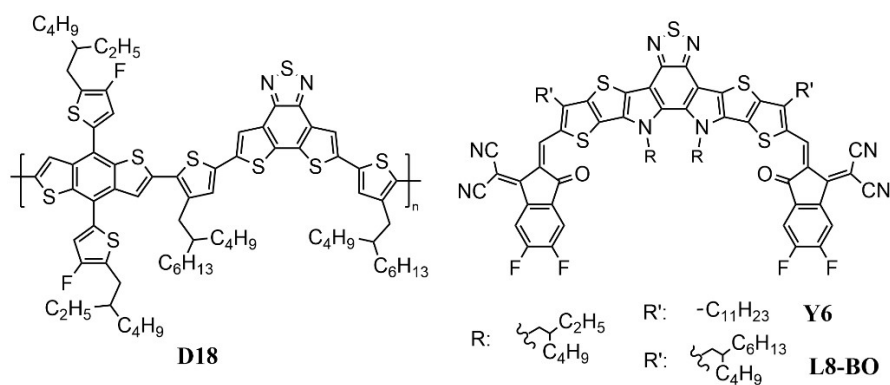


Fig. S10 The structures of donor and acceptors in the studied OSCs.

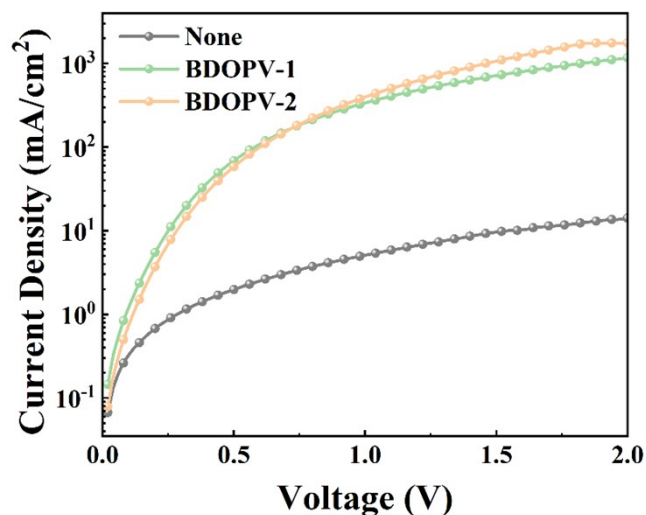


Fig. S11 The J - V curves of Y6-based electron-only devices.

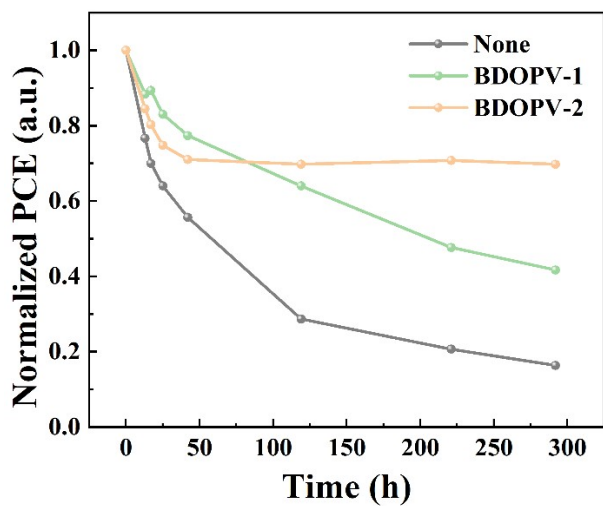


Fig. S12 The PCE-storage time curves of D18:Y6-based OSCs.

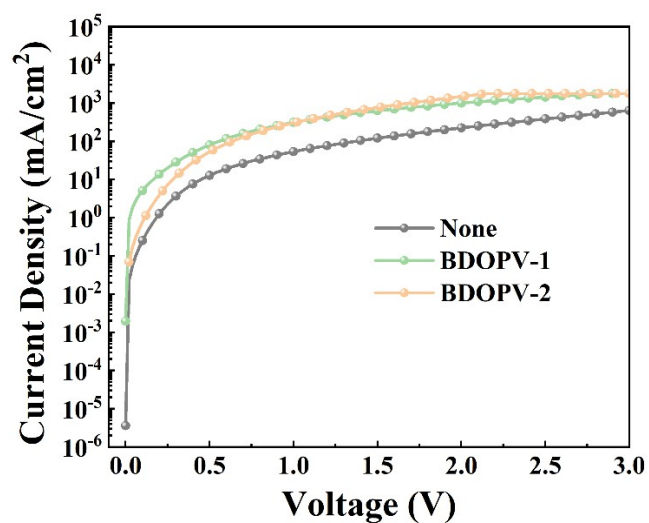


Fig. S13 The J - V curves of D18:Y6-based electron-only devices.

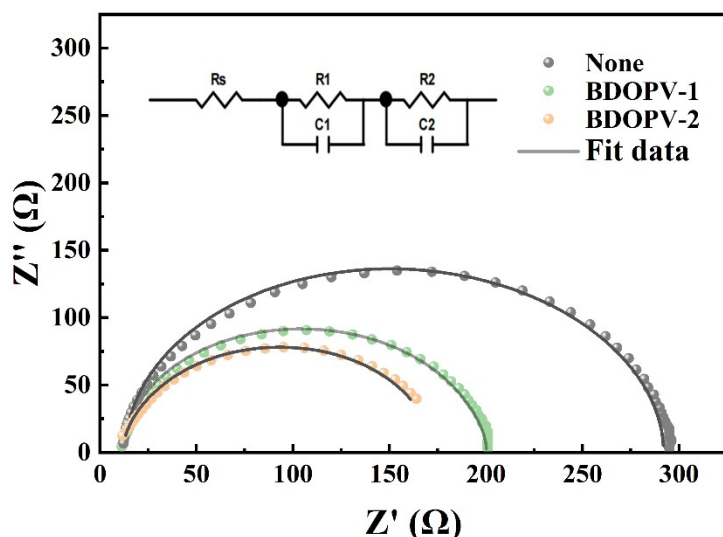


Fig. S14 The EIS Nyquist plots of OSCs with different CILs. Inset: the equivalent-circuit model employed for fitting the EIS data.

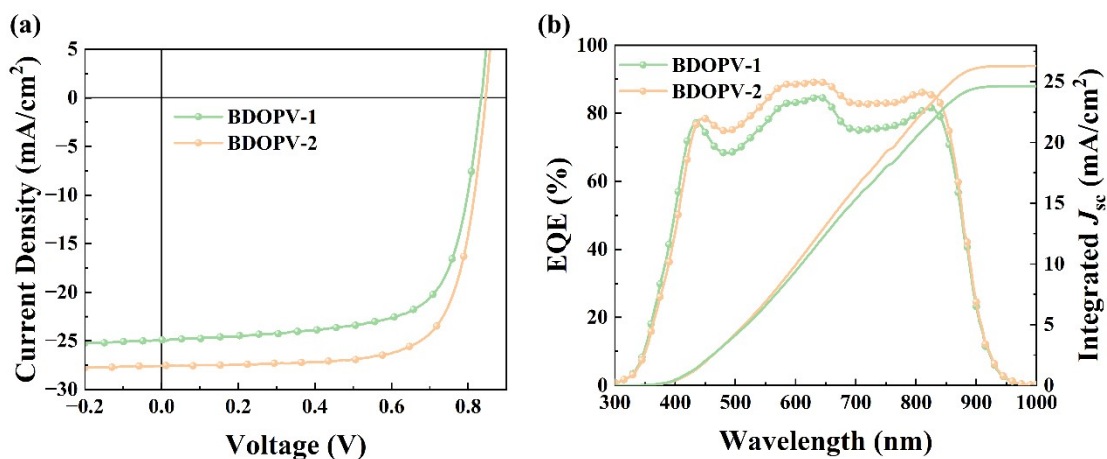


Fig. S15 The (a) J - V curves under AM 1.5 G illumination at 100 mW cm^{-2} , and (b) EQE spectra and integrated J_{sc} s of PM6:Y6-based OSCs with different CILs.

Table S1 Photovoltaic Parameters of PM6:Y6-Based OSCs with Different CILs under AM 1.5 G Illumination at 100 mW cm^{-2}

CIL	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	Integral J_{sc} (mA cm^{-2})
BDOPV-1	0.834	24.91	69.54	14.45 ^a (13.85 ± 0.39) ^b	24.64
BDOPV-2	0.845	27.57	72.91	16.99 ^a (16.53 ± 0.27) ^b	26.30

^aThe values of optimal devices. ^bThe average values and standard deviations obtained from at least six individual devices.