

Supporting Information

Impacts of Linking Units of Porphyrin Dimer Donors on the Performance of Organic Solar Cells

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Materials and Methods

All compounds and solvents were purchased from commercial sources (Aldrich, JK
Chemical and or TCI) and used as received unless otherwise indicated. Column
chromatography with 200-300 mesh silica was used to purify the compounds.

Gel permeation chromatography (GPC): The method involves adding the sample to a
chromatography column filled with gel particles and eluting it with THF.

¹H NMR spectra was conducted on a Bruker AVANCE Digital 500MHz spectrometer
in deuterated chloroform using tetramethylsilane as an internal standard. Matrix-
assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF
MS) data was obtained on a Bruker Daltonics BIFLEX MALDI-TOF Analyzer using
MALDI mode.

UV-Vis-NIR absorption spectra of the films on quartz substrates were measured using a Shimadzu UV-3600 spectrophotometer. Cyclic voltammetry (CV) measurements were carried out on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 50 mV s⁻¹ and against an Ag/AgCl reference electrode with argon-saturated solution of 0.1M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile (CH₃CN). A glass carbon electrode was used as the working electrode. The ferrocene/ferrocenium system (Fc/Fc⁺, 4.8 eV below vacuum level) was used as an internal standard. Under the same experimental conditions, the onset potential of Fc/Fc⁺ was measured to be 0.37 V with respect to the Ag/AgCl reference electrode.

Theoretical calculations were performed to investigate the geometry and frontier molecular orbitals of the three donors by density functional theory (DFT) at the B3LYP/631G(d,p) level. All of the alkyl side chains were replaced with methyl groups to simplify the calculations.

The atomic force microscopy (AFM) measurements of the surface morphology of the active films were conducted on a Nano Scope NS3A system (Digital Instrument).

The electron and hole mobility were measured by using the method of space-charge limited current (SCLC) for electron-only devices with the structure of ITO/ZnO/active layer/ PDIN /Ag and hole-only devices with the structure of ITO/ PEDOT:PSS /active layers/MoO₃/Ag. The electric-field dependent SCLC mobility was estimated using the follow equation:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 \frac{V^2}{L^3} \exp[0.89\gamma \sqrt{\frac{V}{L}}] \quad (1)$$

where J is the current density, L is the film thickness of the active layer, μ_0 is the hole

mobility, ϵ_r is the relative dielectric constant of the transport medium, ϵ_0 is the permittivity of free space (8.85×10^{-12} F m⁻¹), V ($V = V_{appl} - V_{bi}$) is the internal voltage in the device, where V_{appl} is the applied voltage to the device and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

Transient photovoltage (TPV) measurement: Devices were held at open circuit under steady state conditions controlled by a continuous white light bias, and a laser diode is applied to generate an additional amount of charges, causing a small voltage perturbation. After the pulse, the voltage decays back to its steady-state value in a single exponential decay.

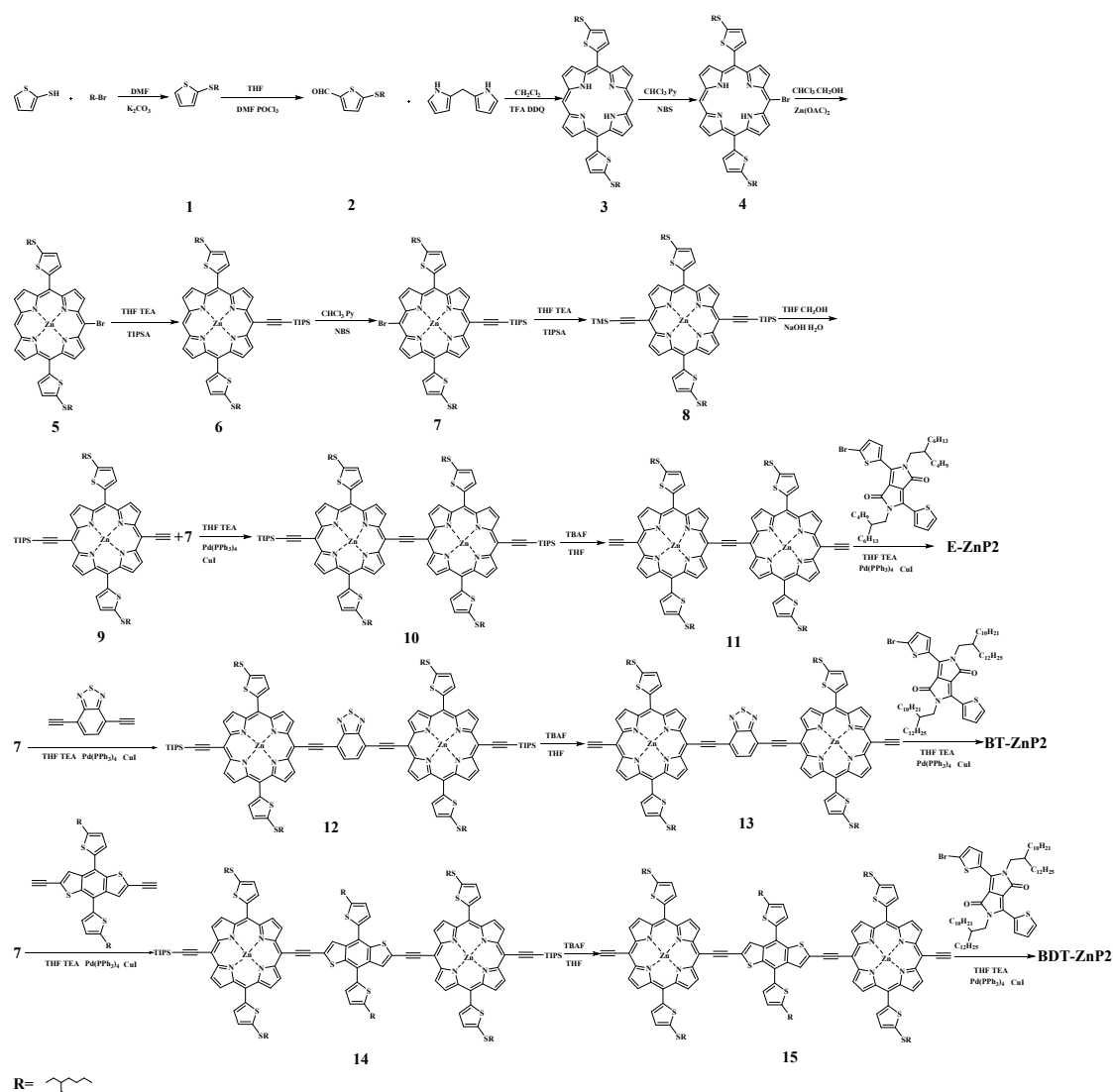
Transient photocurrent (TPC) measurement: Devices were excited with a laser diode. The transient photocurrent response of the devices at short circuit conditions to a pulse from the LED without background illumination. The current traces were recorded on a digital oscilloscope by measuring the voltage drop over a sensor resistor in series with the solar cell.

Device Fabrication: TO-coated glass substrates were cleaned by detergent, deionized water, acetone, and then isopropanol. After cleaned by oxygen plasma for 120 s, 40 nm thick PEDOT:PSS was spin-coated on ITO substrates at 4000 rpm for 30 s. After baked at 150°C for 15 minutes, the substrates were transferred into a nitrogen-filled glove box. The total concentrations of the active materials for all devices were 16 mg/ml. The active layers were prepared using a mixed solvent of chloroform (CF) and 1,8-Diiodooctane (DIO) in a volume ratio of 100:1, and were spin-coated in a nitrogen-filled glove box at 3000 rpm for 30 s. Subsequently, the samples were subjected to

solvent vapor annealing (SVA) by being stored in a petri dish containing dichloromethane (DCM) for 40 seconds. The PDIN layer was deposited by spin casting with a 1% (w/v) solution in methanol at 2000 rpm for 30 s. Finally, 100 nm of Ag was deposited through a shadow mask onto the PDIN layer by thermo evaporation in a vacuum chamber with base pressure of 2×10^{-6} mbar, the effective area was measured to be 0.055 cm². The *J-V* characteristics were measured under AM 1.5 solar simulator (Japan, SAN-EI, XES-40S1) at 100 mW cm⁻² calibrated with a standard Si solar cell, and data were collected using a Keithley 2400 digital source meter. External quantum efficiency (EQE) curves of the encapsulated devices were measured by using an integrated system (Enlitech, Taiwan, China) and a lock-in amplifier with a current preamplifier under short-circuit conditions.

Thermogravimetric analyses (TGA) were carried out with a NETZSCH TG 209 under a nitrogen flow at heating rate of 10 °C/min.

Synthetic Routes



Scheme S1. Synthetic routes of target molecules.

1: Thiophene-2-thiol (6 g, 52 mmol), 1-bromo-2-ethylhexane (12.5 g, 65 mmol) and sodium carbonate (6.9 g, 65 mmol) were dissolved into 50 mL DMF. The mixture was stirred for 1h at 110 °C and cooled to room temperature. Then 200 mL water was added and extracted by ethyl ether twice. The solvent were removed under vacuum, and the residue was purified by silica gel chromatography using hexane as eluent to obtain

compound 1 as light-yellow liquid (11.7 g, yield 90%). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.29 (d, 1H), 7.08 (d, 1H), 6.94 (m, 1H), 2.79 (t, 2H), 1.53-1.24 (m, 9H), 0.87 (m, 6H).

2: To a stirred solution of compound 1 (11.7 g, 59 mmol) in DMF, POCl_3 (13.0 g, 47 mmol) was added dropwise at 0 °C, stirring was continued for 20 min at this temperature. The reaction mixture was warmed to 90 °C and refluxed 2 h, and then it was slowly poured into ice water and neutralized by NaOH to neutrality. After extraction with CHCl_3 , the organic phase was dried over MgSO_4 . The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane (3:1) as light-yellow liquid (7.7 g, yield 72%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.75 (s, 1H), 7.60 (d, 1H), 7.02 (d, 1H), 3.02 (t, 2H), 1.56-0.91 (m, 9H), 0.88 (m, 6H).

3: A solution of compound 2 (7.7 g, 30 mmol) and dipyrromethane (4.4g, 30 mmol) in CH_2Cl_2 (1.8 L) was purged with nitrogen for 30 min, and then trifluoroacetic acid (TFA) (0.18 mL) was added. The mixture was stirred for 12 h at room temperature, and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (10 g) was added. After the mixture was stirred at room temperature for an additional 0.5 h, the reaction was quenched by triethylamine (6 mL). Then the solvent was removed, and the residue was purified by flash column chromatography on silica gel using dichloromethane as the eluent. Recrystallization from CHCl_2 /methanol gave 4 as a purple solid (5.1 g, yield 45%). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 10.28 (s, 2H), 9.38 (d, 4H), 9.32 (d, 4H), 7.75 (d, 2H), 7.215 (d, 2H), 3.15 (d, 4H), 1.82-1.86(m, 2H), 1.50-1.70 (m, 16H), 1.05-0.92 (m, 12H), -3.03 (s, 2H).

4: Compound 3 (5.1 g, 6.68 mmol) was dissolved in 900 ml chloroform with 9 ml pyridine. After the solution was cooled to 0 °C, N-bromosuccinimide (1.2 g, 7.25 mmol) was added and stirred for 30 min. Then the mixture was poured into water, washed with water, dried over anhydrous Na₂SO₄, and concentrated. After the solvent was removed, the residue was purified by flash column chromatography on silica gel using petroleum ether/dichloromethane (3:1) as the eluent. Recrystallization from CHCl₂/methanol gave 5 as a purple solid (2.7 g, yield 49%). ¹H NMR (500 MHz, CDCl₃): δ 10.10 (s, 1H), 9.71 (d, 2H), 9.26 (d, 2H), 9.19 (m, 4H), 7.74 (d, 2H), 7.51 (d, 2H), 3.14 (dd, 4H), 1.85 (m, 2H), 1.72–1.41 (m, 16H), 1.04-0.97 (m, 12H), -2.99 (s, 2H).

5: To a solution of 4 (2.7 g, 3.3 mmol) in chloroform (250 mL), was added a solution of Zn(OAc)₂ (3.6 g, 17.8 mmol) in methanol (50 mL). The reaction mixture was refluxed for 2h and then washed with water and dried over anhydrous Na₂SO₄. After the solvent was removed, the residue was recrystallized from CHCl₂/methanol gave a purple solid (2.9 g, yield 97%). ¹H NMR (500 MHz, CDCl₃): δ 10.07 (s, 1H), 9.78 (d, 2H), 9.27 (m, 6H), 9.19 (m, 6H), 7.74 (d, 2H), 7.49 (d, 2H), 3.12 (dd, 4H), 1.85 (m, 2H), 1.72-1.41 (m, 16H), 0.98-1.26 (m, 12H).

6: Compound 5 (2.91 g, 3.2 mmol) was dissolved in THF (40 mL), and then triethylamine (20 mL) was added. The mixture was purged with argon for 30 min. Then Pd(PPh₃)₂Cl₂ (245 mg, 0.33 mmol), CuI (67.2 mg, 0.33 mmol), and (triisopropylsilyl)acetylene (1.28 g, 7 mmol) were added. After the mixture was stirred at room temperature for 24 h under Ar, the reaction was quenched with brine. Then the mixture was extracted with dichloromethane, dried with anhydrous Na₂SO₄ and

concentrated. Finally, the residue was purified on column chromatography to afford a purple solid (3.06 g, 95% yield). ¹H NMR (500 MHz, CDCl₃): δ 10.12 (s, 1H), 9.85 (d, 2H), 9.31 (m, 6H), 7.74 (d, 2H), 7.49 (d, 2H), 3.12 (dd, 4H), 1.85 (m, 2H), 1.84-1.45 (m, 37H), 1.26-0.98 (m, 12H).

7: Compound 6 (3.06 g, 3.04 mmol) was dissolved in 200 ml of chloroform and 2 ml of pyridine. After the reaction mixture was cooled to 0 °C, N-bromosuccinimide (623 mg, 3.5 mmol) was added to the reaction mixture and stirred for 30 min. Then the reaction mixture was washed with water, dried over Na₂SO₄, and concentrated. And the residue was purified first by column chromatography on silica gel to give a dark green solid (1.98g, 60 % yield). ¹H NMR (500 MHz, CDCl₃): δ 9.72 (d, 2H), 9.65 (d, 2H), 9.15 (d, 2H), 9.11 (d, 2H), 7.69 (d, 2H), 7.45 (d, 2H), 3.07 (dd, 4H), 1.81 (m, 2H), 1.67–1.43 (m, 37H), 1.02-0.97 (m, 12H).

8: Compound 7 (245mg, 0.225 mmol) was dissolved in THF (30 mL) with triethylamine (15 mL), and then Pd(PPh₃)₂Cl₂ (108mg, 0.18 mmol), CuI (30 mg, 0.18 mmol), and trimethylsilylacetylene (1.26 g, 13 mmol) were added. After the mixture was stirred at 60 °C for 24 h under argon, the reaction was quenched with brine. After the mixture was extracted with chloroform, dried with anhydrous Na₂SO₄ and concentrated. Finally, the residue was purified by column chromatography (silica gel, CH₂Cl₂/petroleum ether (1:4) to afford a dark green solid (206m g, 81% yield). ¹H NMR (500 MHz, CDCl₃): δ 9.74 (d, 2H), 9.67 (d, 2H), 9.15 (d, 2H), 9.13 (m, 6H), 7.69 (d, 2H), 7.40 (d, 2H), 2.92 (dd, 4H), 1.74 (m, 2H), 1.67–1.43 (m, 37H), 1.02-0.93 (m, 12H), 0.62 (s, 9H).

9: Compound 8 (200 mg, 0.177 mmol) was dissolved in THF (15 ml) and MeOH (10 ml). An aqueous solution of NaOH (1 M, 0.9 ml) was added dropwise to the reaction flask and stirred at room temperature for 20 min. Then the reaction mixture was poured into water, extracted with CH₂Cl₂, dried over Na₂SO₄, and evaporated. The residue was purified by column chromatography to give a dark green solid, which was used directly for the next reaction without further purification.

10: After the mixture of compound 9 (176.3 mg, 0.171 mmol) and compound 7 (185.6 mg, 0.171 mmol) in THF (30mL) and triethylamine (15 mL) was purged with argon for 30 min, Pd(PPh₃)₄ (19.6 mg, 0.017 mmol) and CuI (3.14 mg, 0.017 mmol) were added. Then, the mixture was stirred at 60 °C for 24 h under an inert atmosphere. After some routine procedures, the residue was first purified by column chromatography on silica gel and then by gel permeation chromatography (GPC) to give a dark brown solid (285.5mg yield: 82%). ¹H NMR (500 MHz, CDCl₃): δ 10.33 (d, 4H), 9.70 (d, 4H), 9.28 (d, 4H), 9.15 (d, 4H), 7.76 (d, 4H), 7.51 (d, 4H), 3.12 (dd, 8H), 1.84-1.79 (m, 4H), 1.67–1.43 (m, 74H), 1.02-0.93 (m, 24H).

12 and 14: Compound 7 (700 mg, 0.645mmol) and 4,7-Diethynylbenzo[*c*][1,2,5]thiadiazole (53.7mg, 0.29 mmol) or Benzo[1,2-*b*:4,5-*b'*]dithiophene,2,6-Diethynyl-4,8-bis[5-(2-ethylhexyl)-2-thienyl] (181.8 mg, 0.29 mmol) were dissolved in THF (40 mL) with triethylamine (20 mL). Then Pd(PPh₃)₄ (34.6 mg, 0.03 mmol) and CuI (5.7 mg, 0.03 mmol) were added. The mixture was stirred at 60 °C for 48 h under argon protection, then the reaction mixture was poured into water and extracted with CHCl₃ and washed with brine, dried over Na₂SO₄, and

evaporated. The residue was chromatographed on silica gel to isolate the desired product, which was then further purified via GPC to afford compound 12 (439mg, 69% yield) or compound 13 (497mg, 65% yield).

12: ^1H NMR (500 MHz, CDCl_3): δ 10.04 (d, 4H), 9.66 (d, 4H), 9.21 (d, 4H), 9.11 (d, 4H), 8.10 (s, 2H), 7.71 (d, 4H), 7.49 (d, 4H), 3.12 (dd, 8H), 1.84–1.80 (m, 4H), 1.69–1.36 (m, 74H), 1.03–0.89 (m, 24H).

14: ^1H NMR (CDCl_3 + pyridine- d_5): δ 9.68 (dd, 8H), 9.11–8.96 (m, 8H), 7.85 (d, 2H), 7.66 (d, 4H), 7.52 (d, 4H), 7.21 (d, 2H), 7.04 (d, 2H), 3.70 (dd, 8H), 3.08 (d, 4H), 1.81–1.77 (m, 6H), 1.47–1.36 (m, 90H), 0.99–0.77 (m, 36H).

11, 13 and **15:** TBAF (1 M in THF, 0.42 mmol) was added to compound 10 or 12 or 14 (0.14 mmol) in 10 mL of THF at room temperature and then stirred for 5 min. Then, the reaction was quenched with water and the reaction mixture was extracted with chloroform. Purification of the organic layer gives the compound 10 or 12 or 14, which were used directly for the next reaction without further purification.

E-ZnP2: After the solution of compound 10 (224.1 mg, 0.13 mmol) and DPP-Br (279.2 mg, 0.39 mmol) in THF (30 mL) and triethylamine (15 mL) was purged with argon for 30 min, $\text{Pd}(\text{PPh}_3)_4$ (15 mg, 0.013 mmol) and CuI (2.5 mg, 0.013 mmol) were added. Then, the mixture was stirred at 60 °C for 24 h under an argon atmosphere. After some routine procedures, the residue was first purified by column chromatography on silica gel and then by GPC to give a black solid, E-ZnP2 (268.5mg yield: 69%). ^1H NMR (500 MHz, CDCl_3 + pyridine- d_5) δ 10.05 (d, 4H), 9.26 (d, 4H), 9.05–8.94 (m, 8H), 8.73 (d, 2H), 8.57 (d, 2H), 7.94 (d, 4H), 7.63 (d, 4H), 7.23 (d, 4H), 7.00 (d, 2H), 3.66 (dd,

8H), 3.24 (dd, 8H), 1.94–1.61 (m, 28H), 1.25-1.02 (m, 100H), 0.89-0.76 (m, 24H).

MALDI-TOF Mass (m/z): calculated for $C_{170}H_{202}N_{12}O_4S_{12}Zn_2$: 2993.05; found: 2933.12.

BT-ZnP2: Similar to the synthesis method of **E-ZnP2**, give a black solid (296.4mg yield: 60%). MALDI-TOF Mass (m/z): calculated for $C_{226}H_{300}N_{14}O_4S_{13}Zn_2$: 3824.52; found: 4223.68.

BDT-ZnP2: Similar to the synthesis method of **E-ZnP2**, give a black solid (319.2mg yield: 61%). MALDI-TOF Mass (m/z): calculated for $C_{254}H_{338}N_{12}O_4S_{16}Zn_2$: 4267.30; found: 4266.98.

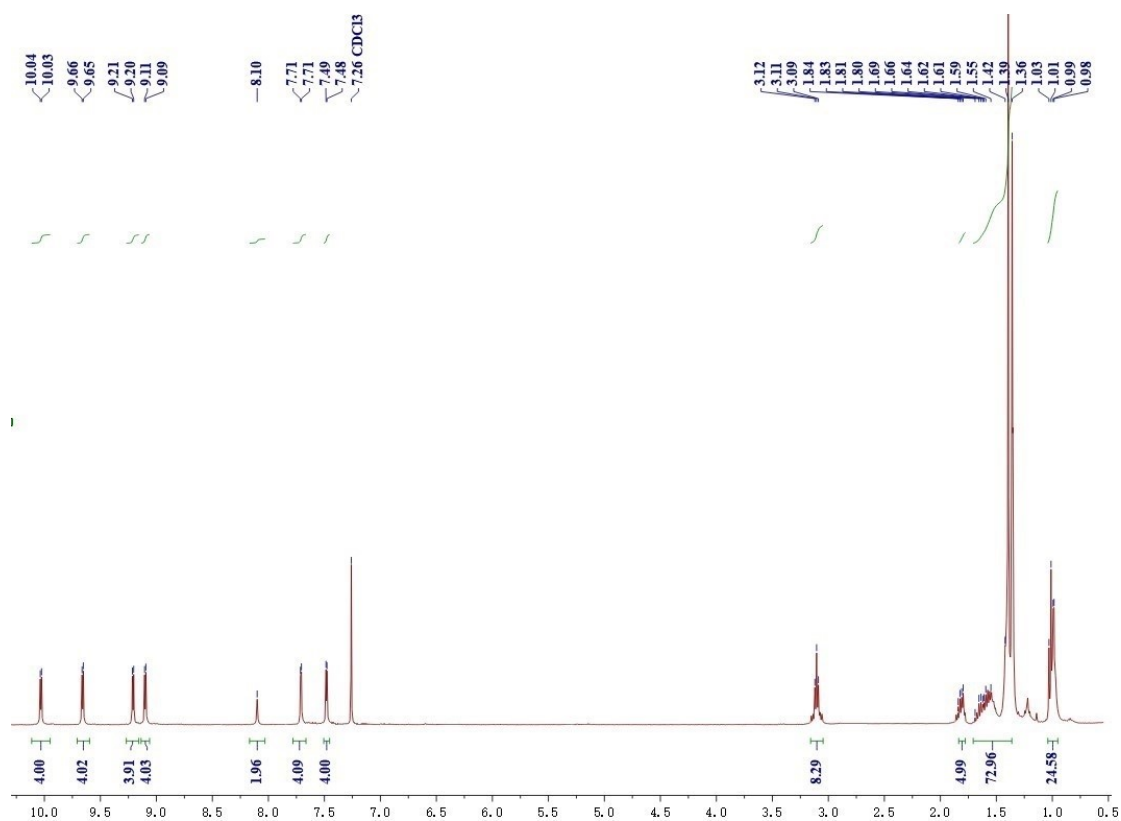


Figure S1. 1H NMR of compound **12** in $CDCl_3$.

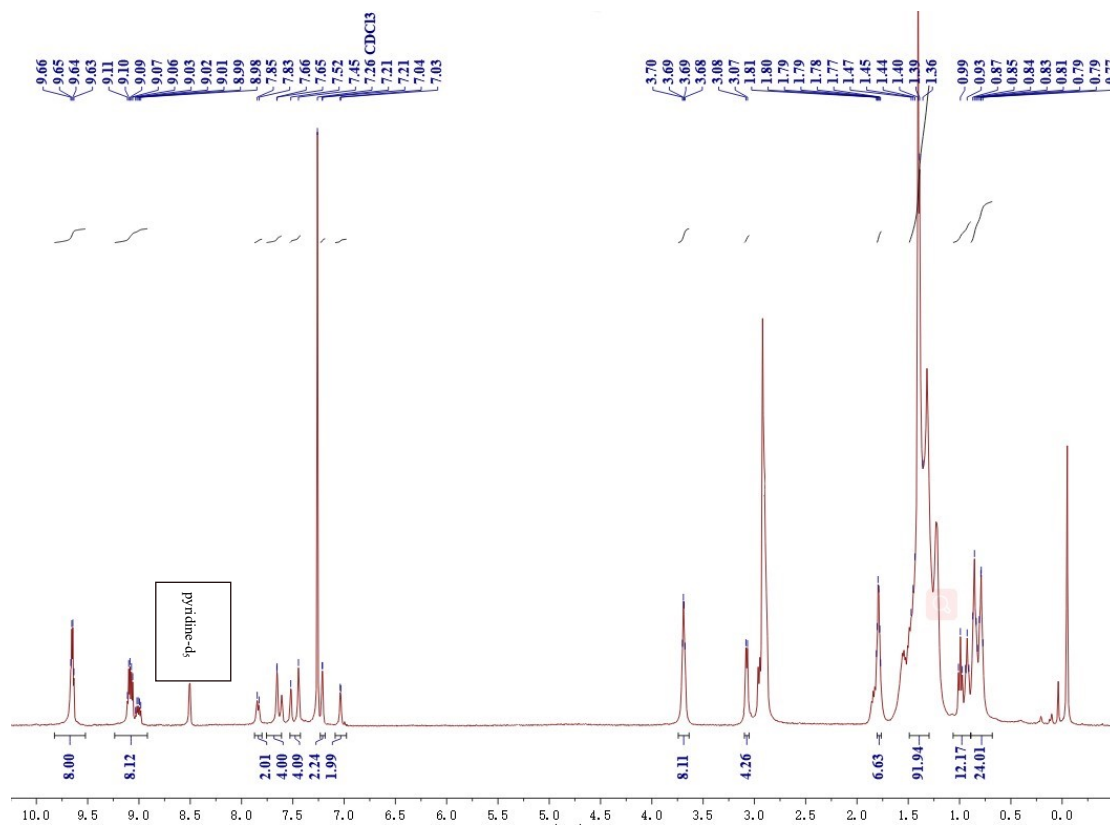


Figure S2. ^1H NMR of compound **14** in CDCl_3 + pyridine- d_5 .

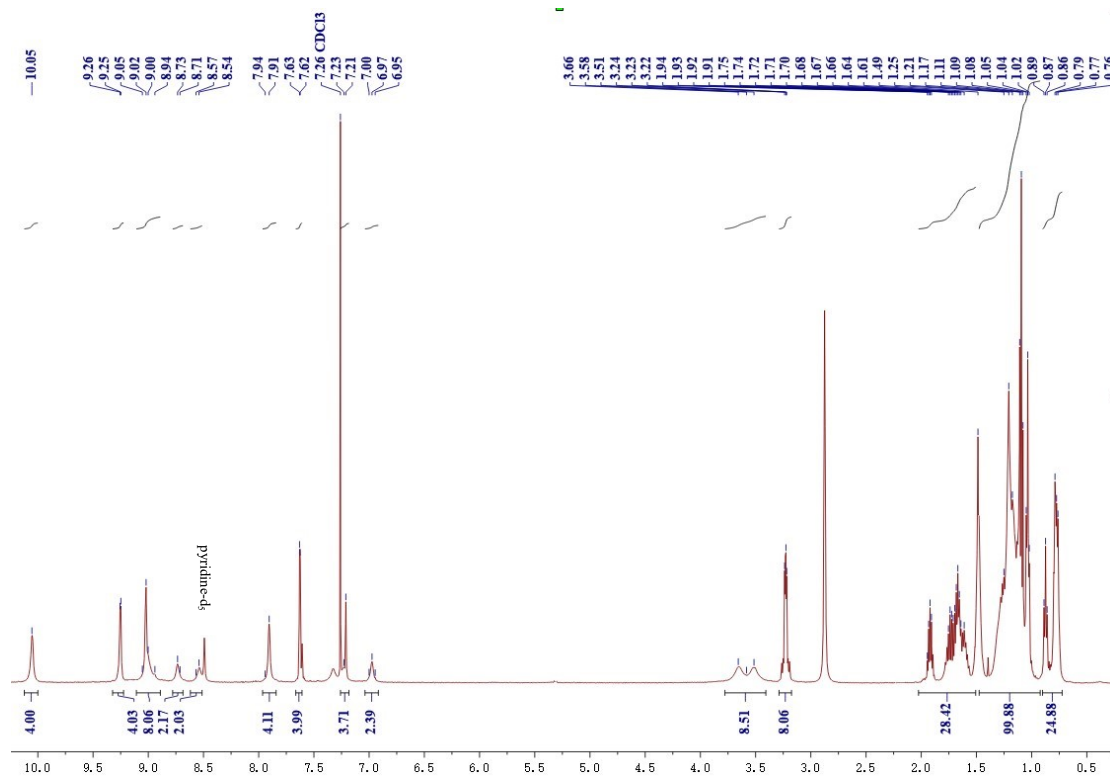


Figure S3. ^1H NMR of compound **E-ZnP2** in CDCl_3 + pyridine- d_5 .

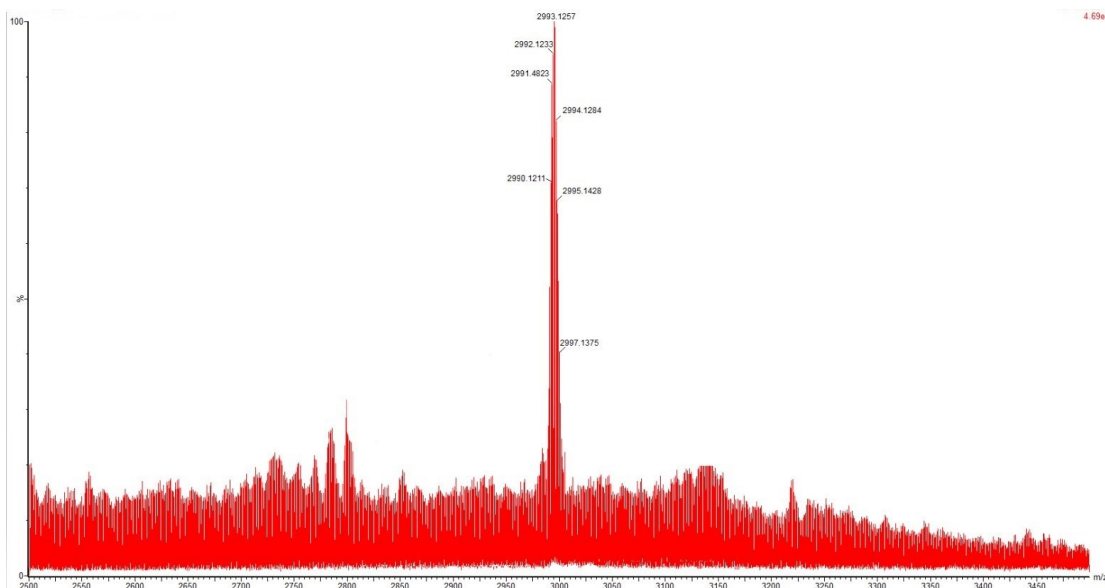


Figure S4. Mass (MALDI-TOF) spectrum of **E-ZnP2**.

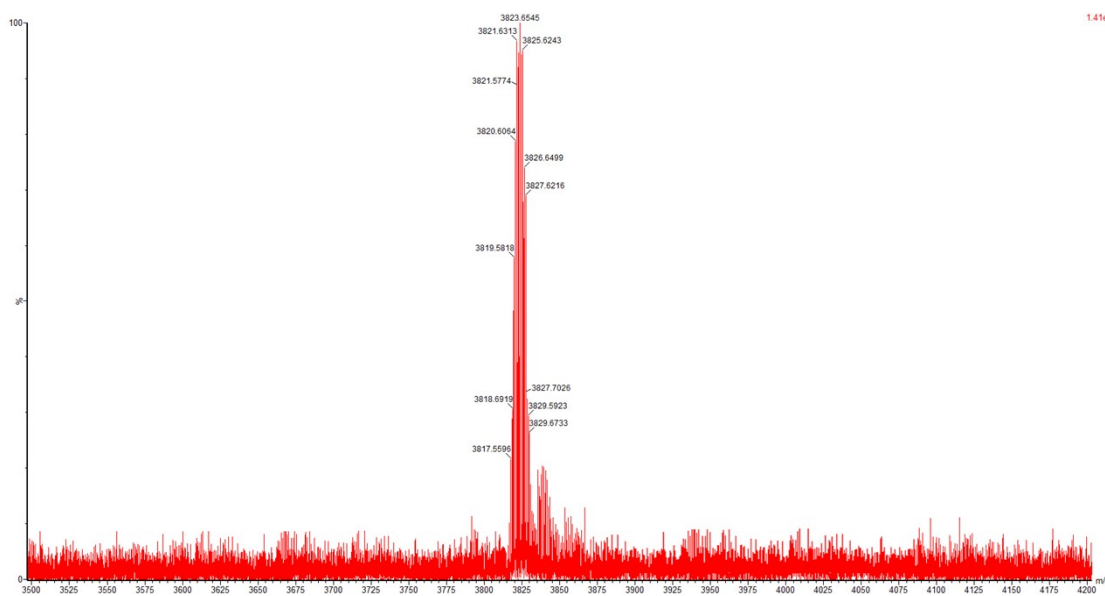


Figure S5. Mass (MALDI-TOF) spectrum of **BT-ZnP2**.

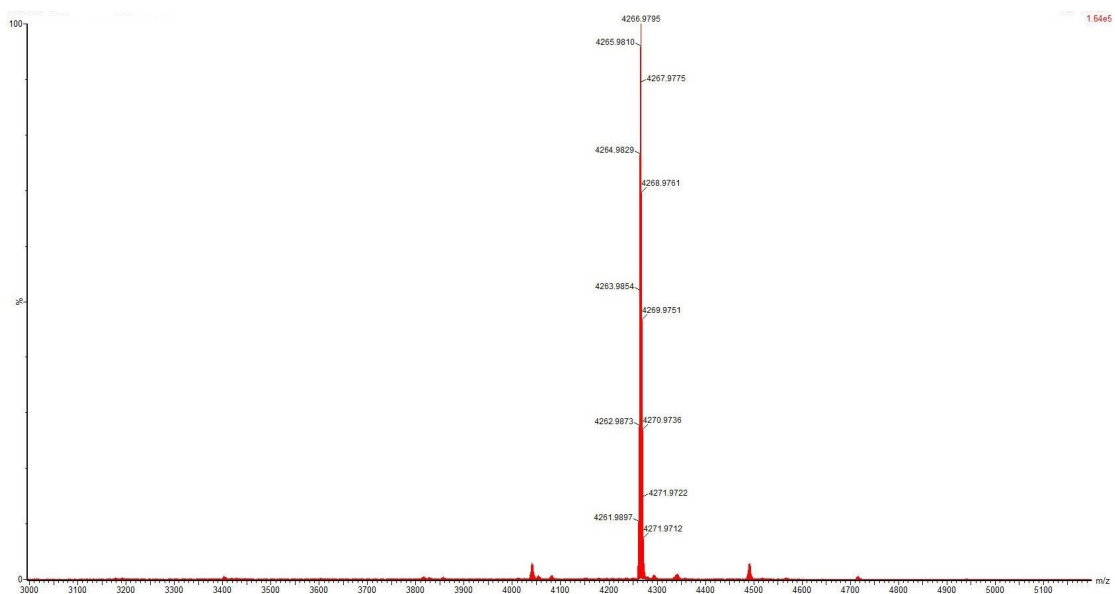


Figure S6. Mass (MALDI-TOF) spectrum of **BDT-ZnP2**.

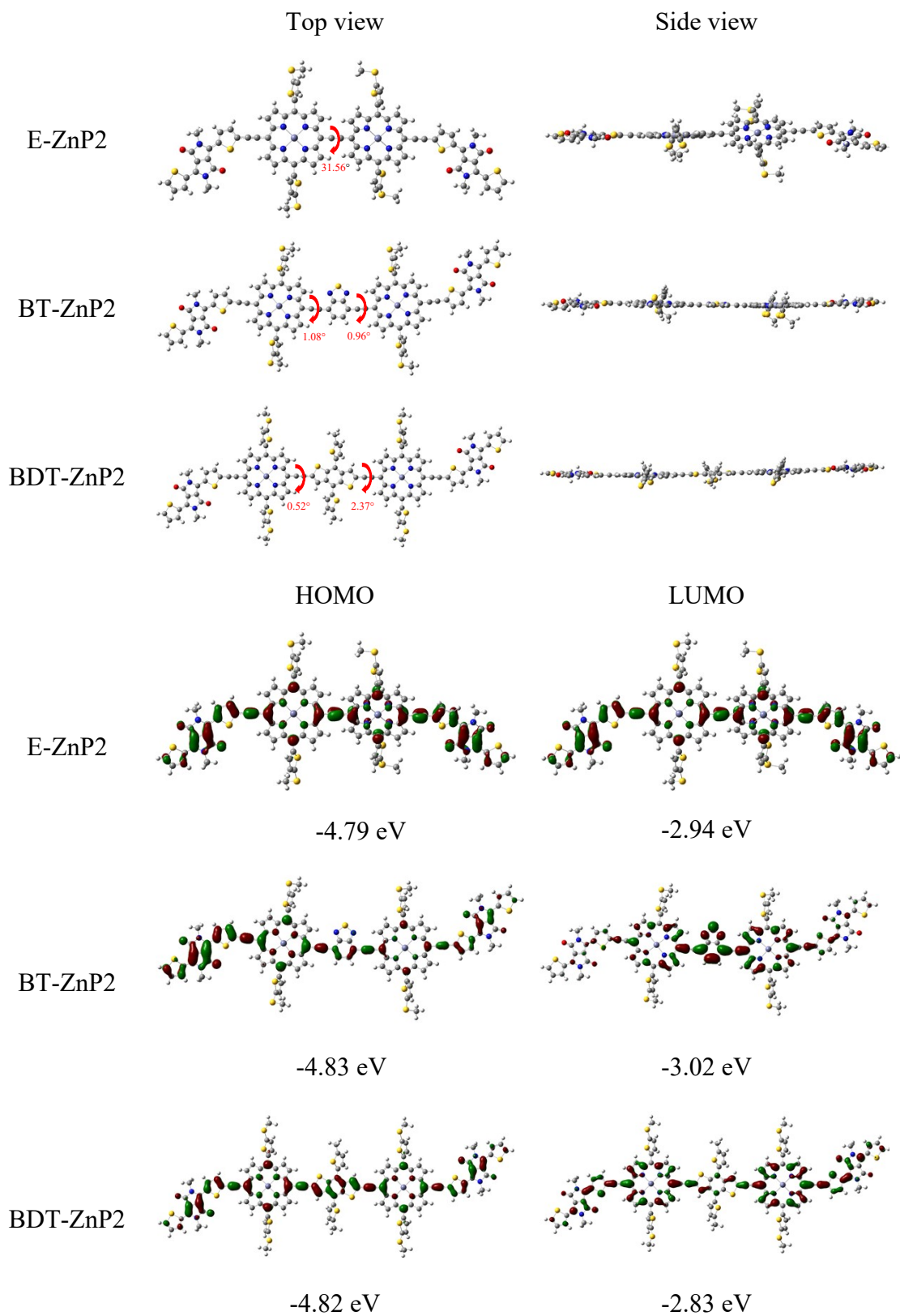


Figure S7. DFT results of the three donors.

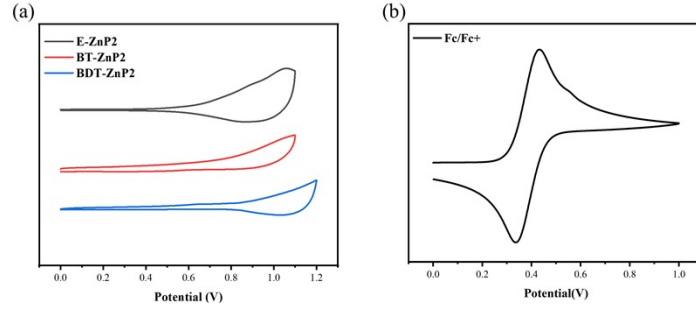


Figure S8. Cyclic voltammograms of (a) the three donors and (b) ferrocene/ferrocenium.

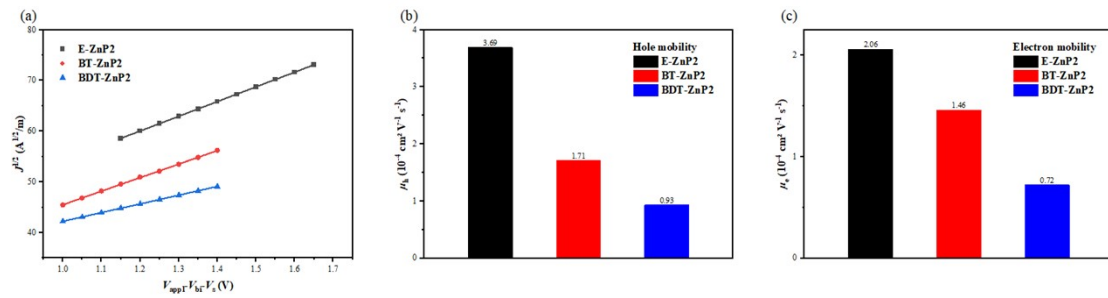


Figure S9. (a) J - V characteristics in the dark for electron-only devices. (b) Hole mobilities and (c) electron mobilities of the optimized devices.

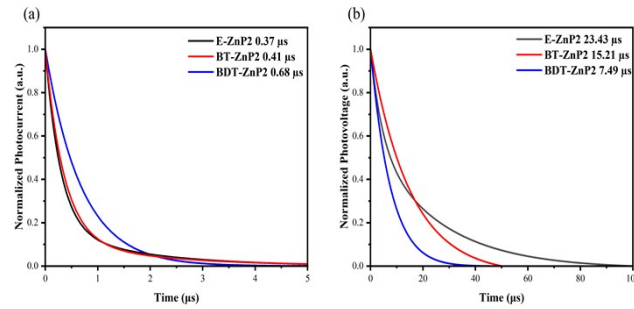


Figure S10. (a) TPV and (d) TPC tests of the optimized devices.

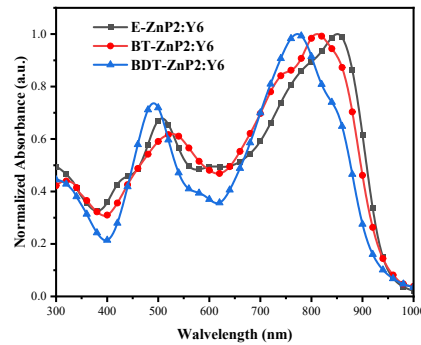


Figure S11. UV-vis absorption spectra of the blend films.

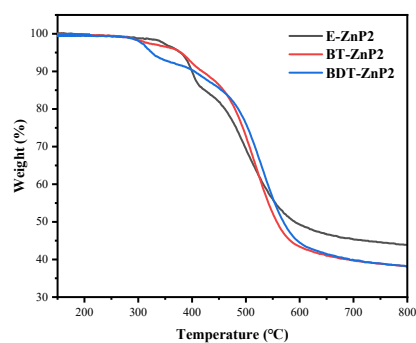


Figure S12. TGA thermogram of compounds under inert atmosphere at a scan rate of 10 °C/min.

Table S1. Photovoltaic performance of the solar cells with different mixture rate.

Active layer	D:A	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
E-ZnP2:Y6	1.5:1	0.65	8.85	40.73	2.34
	1:1	0.66	9.01	37.58	2.24
	1:1.5	0.66	8.64	35.07	2.00
BT-	1.5:1	0.66	7.53	40.56	2.01
ZnP2:Y6	1:1	0.67	7.83	39.53	2.07
	1:1.5	0.66	7.67	39.62	2.00
BDT-ZnP2:	1.5:1	0.68	4.12	28.15	0.79
Y6	1:1	0.69	4.41	27.58	0.84
	1:1.5	0.68	4.46	26.47	0.80

Table S2. Photovoltaic performance under different postprocessing methods.

Active layer	Conditions	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
E-ZnP2:Y6	As-cast	0.65	8.85	40.73	2.34

=1.5:1	DIO	0.63	20.25	57.83	7.38
	DIO+SVA	0.63	23.23	65.89	9.64
BT-	As-cast	0.67	7.83	39.53	2.07
ZnP2:Y6	DIO	0.65	12.92	45.28	3.80
=1:1	DIO+SVA	0.66	15.02	45.69	4.53
BDT-ZnP2:	As-cast	0.69	4.41	27.58	0.84
Y6 =1:1	DIO	0.67	7.69	38.28	1.97
	DIO+SVA	0.65	8.46	39.47	2.17

Table S3. Photovoltaic parameters of the optimized devices based on different acceptors.

Donors	Acceptors	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
E-ZnP2	Y6	0.63	23.23	65.89	9.64
	IDIC	0.72	8.58	54.03	3.34
	L8-BO	0.66	13.87	49.23	4.51
BT-ZnP2	Y6	0.66	15.02	45.69	4.53
	IDIC	0.75	7.84	34.57	2.03
	L8-BO	0.68	7.83	38.66	2.06
BDT-ZnP2	Y6	0.65	8.46	39.47	2.17
	IDIC	0.73	5.42	29.08	1.15
	L8-BO	0.68	5.38	41.33	1.51

Table S4. Photovoltaic parameters of the optimized devices based on different electron transports layers (ETLs).

Active layers	ETLs	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
E-ZnP2:Y6	PDIN	0.63	23.23	65.89	9.64
	PDINO	0.63	22.89	64.87	9.35
	PFN-Br	0.62	22.18	66.27	9.11
BT-ZnP2:Y6	PDIN	0.66	15.02	45.69	4.53
	PDINO	0.66	13.95	46.74	4.30
	PFN-Br	0.65	14.19	46.07	4.25
BDT-ZnP2:Y6	PDIN	0.65	8.46	39.47	2.17
	PDINO	0.65	9.09	34.54	2.04
	PFN-Br	0.66	7.88	37.49	1.95

Table S5. The parameters of the pure films obtained from contact angle measurements.

Sample	Contact angle (°)		Surface tension (mN m ⁻¹)	χ
	H ₂ O	EG		
E-ZnP2	88.17	69.17	21.69	0.002
BT-ZnP2	97.57	72.01	18.71	0.122
BDT-ZnP2	77.38	69.51	27.16	0.359
Y6	89.97	68.74	21.27	-