Electronic Supplementary Information

Enhanced Light-harvesting of Benzodithiophene Conjugated Porphyrin Electron Donors in Organic Solar Cells

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1. Experimental section

1.1 Materials preparation All the chemicals were analytical grade and used as received without further purification. All the organic solvents used were dried and freshly distilled according to the standard procedures. 5,15-Dibromo-10,20-bis(2-octylundecyl)-Zn(II)porphyrin and dialkoxy-substituted benzo[1,2-b:4,5-b']dithiophene (**BDT**) were synthesized according to the literature methods.[1-3]

1.2 Device Fabrication of OSCs. Indium tin oxide (ITO) coated glass substrates were cleaned prior to device fabrication by sonication in acetone, detergent, distilled water, and isopropyl alcohol. After treated with an oxygen plasma for 5 min, poly (styrene sulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT: PSS) (Bayer Baytron 4083) layer with thickness of 40 nm was spin-coated on the ITO-coated glass substrates at 2500 rpm for 30s, the substrates were subsequently dried at 150°C for 10 min in air and then transferred to a N_2-glovebox. The active layers were spun from solution of donor material: $PC_{71}BM$ at weight ratio of 1:1.2 with an overall concentration of 20 mg/mL in chlorobenzene. The preparing process was operated at 1000 rpm for 60 s. And then the active layer was placed on heating plate at 100 ℃ for 5 min for thermal annealing (TA) or placed in a glass petri dish containing 4.0 mL DCM for 0 or 20 s for solvent vapor annealing (SVA). The thicknesses of active layers were measured by a profilometer and the thickness of the films are approximately 90 nm. Finally, Al (ca. 80 nm) was evaporated with a shadow mask as the top electrode. The effective area was measured to be 16 mm^2.

1.3 Space-charge-limited current (SCLC) mobility measurement The hole-only/electron-only devices used the configurations of ITO/ZnO/Active layer/LiF/Al and ITO/PEDOT/Active layer/MoO_3/Al, respectively. The carrier mobility was measured using the SCLC model at low voltage, which is described by Equation (1):

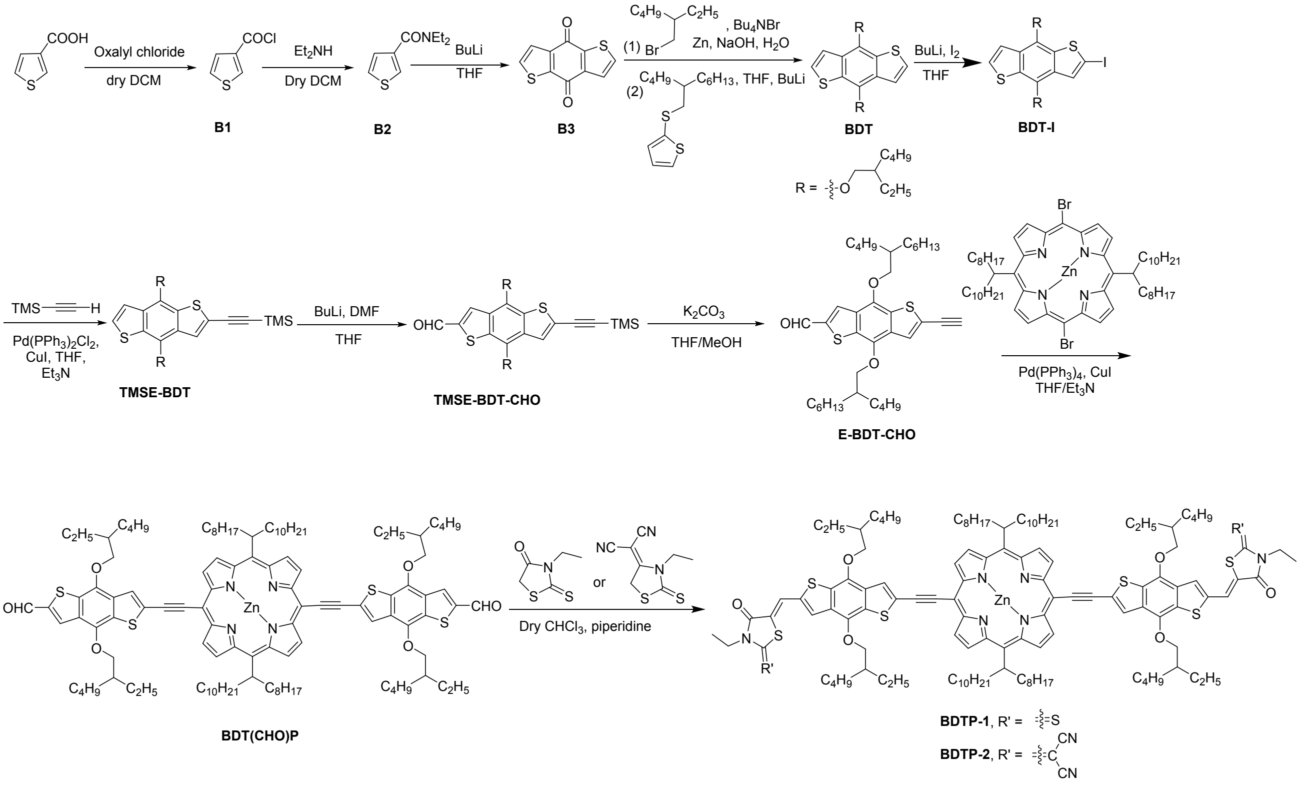
$$J = \left(\frac{8}{9}\right)\varepsilon_r\varepsilon_0\mu\left(\frac{V^2}{L^3}\right) \tag{1}$$

where ε_r is the dielectric constant (assumed to be 3), ε_0 is the permittivity of free space (8.85×10^{-12} $F{\cdot}m^{-1}$);
μ is the electron mobility of the charge carrier; V is voltage drop across the device, which obtained by the applied voltage minus a built-in voltage of ~0.1 V; L (≈100 nm) is the thickness of the active layer.

1.4 Computational Calculation[4] The molecular geometries, the energy levels of frontier molecular orbits, frequencies, excitations and spectra of **BDTP-1** and **BDTP-2** were calculated using density functional theory (DFT) at B3LYP/GENECP (Zn with Lanl2dz basis set and C, H, N, O and S with 6-31G(d) basic set) level using Gaussian 09 Rev D.01.[4] For simplicity of calculation, ethyl or 3-ethylpentane were used as the side-chain substituent.[5] The molecular orbital distributions were plotted with iso-value of 0.02 and 20 excited states were assumed to calculate the computational spectra of molecules using time-dependent (TD)-DFT at the same level.

1.5 Characterization UV-visible spectra were performed at room temperature in quartz cuvettes using a Cary UV-300 spectrophotometer (agilent technologies, USA). The fluorescence spectra were performed at room temperature using a LS55B spectrophotometer (PerkinElmer, USA). The cyclic voltammetry (CV) of film samples were examined using a CHI-600E electrochemical workstation (CH Instrument, USA) and operated at a scan rate of 50 $mV{\cdot}s^{-1}$; and the solvent used was anhydrous acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. The potentials were measured against a Ag/Ag^+ (0.01 M $AgNO_3$) reference electrode; the ferrocene/ferrocenium ion (Fc/Fc^+)

pair was used as the internal standard. The high-resolution mass spectra were characterized from a Bruker Autoflex MALDITOF mass spectrometer. The photovoltaic performance of the devices was measured with a computer-programmed Keithley 2400 source/meter and a Newport's Oriel class A solar simulator, which simulated the AM1.5 sunlight with an energy density of 100 mW cm^{-2} and was certified to the JIS C 8912 standard. External quantum efficiency (EQE) were measured with a 300 W Xenon Lamp (Oriel 6258) as the light source and a Cornerstone 260 Oriel 74125 monochromator with a resolution of 10 nm. The light intensity was calibrated with a NREL-recommended Si detector (Oriel 71030NS), and the short-circuit currents were determined with an Oriel 70310 optical power meter. Atomic force microscopic (AFM) images were acquired using a Veeco Nano Scope IV Multi-Mode AFM system with the tapping mode. Grazing incidence X-ray diffraction (GIWAXS) was performed at BL16B1 beamline of Shanghai Synchrotron Radiation Facility. The sample-to-detector distance is 200 mm and the wavelength of incident X-ray is 0.124 nm. The incidence angle of X ray is 0.10°. And the data were collected by a mar165CCD. The samples used for GIWAXS measurements were prepared by spin-coating the blend solutions onto Si wafers.



Scheme S1 Synthetic pathway of BDT-linked A-π-D-π-A-type porphyrin molecules.

1.6 Synthesis of precursors and targeting molecules

B1 Oxalyl chloride (152.40 g, 1.20 mol) was added very slowly to ice-cooled and stirred dichloromethane (60 mL) solution with thiophene-3-carboxylic acid (76.80 g, 0.60 mol). The afforded mixture was continuous stirred at room temperature and till forming a clear solution (ca. 12h). The solvent and unreacted oxalyl chloride were removed by rotary evaporation to afford B2 as colourless solid. The **B1** was used for next step without further purification.

B2 Dichloromethane (200 mL) solution with **B1** was slowly added to ice-cooled mixture of dichloromethane (200 mL) and diethyl-amine (125.00 mL, 1.20 mol). The resulted solution was stirred at room temperature for 0.5 h and then washed by water for 3 times. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed by reduced pressure. The crude product was purified by flash silica-gel column chromatography using chloroform as eluent to afford **B2** as pale-yellow oil (0.56 mol, 92%) ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.49 (s, 1H), 7.33 (d, 1H), 7.19 (d, 1H), 3.40 (m, 4H), 1.20 (t, 6H).

B3 N-butyllithium (40 mL, 2.5 M) was dropwise added into ice-cooled THF (100 mL) with **B2** (0.1 mol, 18.3 g) within 30 min under an inert atmosphere. The resulted solution was stirred at room temperature for 0.5 h. The resulted solution was poured into ice water (250 mL) and stirred for additional 6 hours. The mixture was filtrated and washed by water (100 mL), methanol (25 ml) and hexane (25 mL) to afford **B3** as yellow solid (17.0 g, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.76 (d, 2 H), 7.96 (d, 2 H).

BDT The mixture of **B3** (2.20 g, 10.0 mmol), NaOH (6.00 g, 150.0 mmol) and zinc powder (1.43 g, 22.0 mmol) in water (30 mL) was heated to reflux for 1 h. 2-Ethylhexyl bromide (11.59 g, 60.0 mmol) and tetrabutylammonium bromide (catalytic amount) were added into the reacting solution and continue to reflux for 4 h. The mixture was washed by ice-cooled water and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed by reduced pressure. The crude product was purified by silica-gel column chromatography using hexane as eluent to afford BDT1 as colourless oil (2.01 g, 40 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.45-7.49 (d, J = 5 Hz, 2H), 7.31-7.35 (d, J = 5 Hz, 2H), 3.83-3.96 (m, 4H), 1.49-1.63 (m, 2H), 1.09-1.37 (m, 16H), 0.71-0.89 (m, 12H).

BDT-I BuLi (1 mL, 2.5 mmol, 2.5 M, 1.07 equivalent) was added dropwise to **BDT** (2.33 mmol, 1 equivalent) in dry THF (20 mL) over 50 min at −78 °C under nitrogen atmosphere. The mixture was stirred for 30 min at -78 °C. And iodine (0.7 g, 2.75 mmol, 1.18 equivalent) in dry THF (5 mL) was injected to the solution by syringe. The reaction was stirred for 15 min and quenched with water. The solution was washed by water and extracted by dichloromethane. The dried organic phase was concentrated with rotary evaporator. And the crude product was purified by silica gel column chromatography with hexane as eluent to obtain pure product **BDT-I**. (Yield, 74%). ^{1}H NMR (400 MHz, ppm, $CDCl_3$): 7.64 (s, 1H), 7.45-7.44 (d, J = 4, 1H), 7.41-7.39 (d, J = 8 Hz, 1H), 4.15-4.13 (m, 4H), 1.80-1.78 (m, 2H), 1.65-1.25 (t, 16 H), 1.03-0.94 (m, 12H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$): δ 143.3, 143.2, 131.5, 130.3, 130.2, 126.5, 120.2, 40.7, 40.6, 30.4, 29.2, 23.2, 14.2, 14.2, 11.4.

TMSE-BDT. The compound **BDT-I** (10.00 mmol, 1 equivalent) in THF (30 mL) and triethylamine (15 mL) was degassed and backfilled with nitrogen for at least three times. Bis(triphenylphosphine) palladium (II) dichloride (0.20 mmol, 2 mol% equivalent) and copper(I) iodide (0.20 mmol, 2 mol% equivalent) were added to the flask. The mixture was bubbling with nitrogen for half hour. And trimethylsilyl acetylene (100.00 mmol, 10 equivalent) was injected into the flask via syringe. The mixture was stirred at 50 °C for 3 hours and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column with to obtain pure **TMSE-BDT**. (Yield, 86%). ^{1}H NMR (400 MHz, ppm, $CDCl_3$): 7.65 (s, 1H), 7.44-7.43 (d, J = 4, 1H), 7.40-7.38 (d, J = 8 Hz, 1H), 4.15-4.13 (m, 4H), 1.80-1.78 (m, 2H), 1.65-1.25 (t, 16 H), 1.03-0.94 (m, 12H), 0.27 (s, 9H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$): 143.3, 143.2, 131.5, 130.3, 130.2, 126.5, 120.2, 93.9, 92.1, 40.7, 40.6, 30.4, 29.2, 23.2, 14.2, 14.2, 11.4, 0.01.

TMSE-BDT-CHO BuLi (2.8 mmol, 1 equivalent) was added into the flask dropwise to **TMSE-BDT** (2.8 mmol, 1 equivalent) in dry THF (15 mL) at −78 °C under nitrogen atmosphere. The solution was stirred at −78 °C for 1 h and DMF (2.8 mmol, 1 equivalent) was added in to the solution in one portion. The reaction was stirred for 1 hour at room temperature, and then quenched by water. The solution was washed and then extracted by dichloromethane. The solvent was removed by reduced pressure to obtain the crude product **TMSE-BDT-CHO**.

E-BDT-CHO The **TMSE-BDT-CHO** and K_2CO_3 (2.8 mmol, 1 equivalent) were dissolved in mixture of THF (15 mL) and methanol (8 mL). The mixture was stirred for 3 h at room temperature and then washed by water and extracted by dichloromethane. The crude product was concentrated and purified by silica gel column chromatography using dichloromethane/hexane (3:1, v/v) as eluent to obtain the pure product TB-BDT1-CHO (Yield, 76%). ^{1}H NMR (400 MHz, ppm, $CDCl_3$): δ 10.14 (s, 1H), 8.19 (s, 1H), 7.68 (s, 1H), 4.28-4.20 (m, 4H), 3.57 (s, 1H), 1.88-1.83 (m, 2H), 1.75-1.25 (t, 16 H), 1.08-0.95 (m, 12H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$): δ 143.3, 143.2, 131.5, 130.3, 130.2, 126.5, 120.2, 93.9, 73.5, 40.7, 40.6, 30.4, 29.2, 23.2, 14.2, 14.2, 11.4.

BDT(CHO)P The mixture of **E-BDT-CHO** (0.70 mmol) and 5,15-Dibromo-10,20-bis(2-octylundecyl)-Zn(II)porphyrin (0.30 mmol) in THF (30 mL) and Et_3N (15 mL) were degassed with nitrogen for 30 min. $Pd(PPh_3)_4$ (0.04 mmol) and CuI (0.04 mmol) were added and the solution was continued to stir at 60 °C for 12 h under nitrogen. The solvent was concentrated under reduced pressure, and the solid residue was purified by preparative thin layer chromatography using a $CHCl_3$/hexane (1:1) mixture as eluents. Recrystallization from $CHCl_3$/methanol gave **BDT(CHO)P** as a green solid. (Yield, 82%). ^{1}HNMR (400 MHz, ppm, $CDCl_3$): 10.17 (s, 2H), 9.77-9.65 (m, 8H), 8.27 (s, 2H), 8.04 (s, 2H), 5.23 (s, 2H), 4.43-4.42 (d, J = 4 Hz, 4H), 4.36-4.35 (d, J = 4 Hz, 4H), 2.96-2.94 (m, 4H), 2.76-2.73 (m, 4H), 1.96 (m, 4H), 1.95-0.77 (m, 124H).

General Synthetic procedure for BDTP-1 and BDTP-2

The precursor **BDT(CHO)P** (0.13 mmol) and 3-ethylrhodanine or 2-(1,1-dicyanomethylene)-3-ethylrhodanine (0.13 mmol) in dry $CHCl_3$ (30 mL) were added piperidine (catalytic amount) and the solution was stirred at 60 °C for 12 h under nitrogen atmosphere. The reaction was quenched by adding water (30 mL) and extracted with $CHCl_3$. The dried organic layer was concentrated under reduced pressure and the crude product was purified by silica gel thin layer chromatography using $CHCl_3$/hexane as eluent and recrystallized from a mixture of $CHCl_3$ and methanol to get the final product.

BDTP-1 Brown solid. (Yield, 82%). ^{1}HNMR (400 MHz, ppm, $CDCl_3$): 9.70-9.55 (m, 8H), 7.84 (s, 4H), 7.74 (s, 2H), 5.25 (s, 2H), 4.36 (s, 8H), 4.20 (s, 4H), 3.01 (s, 4H), 2.77 (s, 4H), 1.99 (m, 4H), 1.97-1.09 (m, 118 H), 0.78 (m, 12H). HR-MALDI-TOF (m/z) calculated for BDTP-1: FOUND $[M+H]^+$ = 2185.0361, TRUE $[M+H]^+$ = 2185.0250, ERROR = 5.0507 ppm.

BDTP-2 Brown solid, (Yield, 78 %). ^{1}HNMR (400 MHz, $CDCl_3$): 9.73-9.52 (m, 8H), 7.88-7.81 (m, 2H), 7.70 (s, 4H), 5.25 (s, 2H), 4.39-4.34 (m, 8H), 4.18-4.16 (d, *J*=8 Hz, 4H), 2.83-2.80 (m, 4H), 2.00-1.98 (d, *J*=8 Hz, 4H), 1.97-1.09 (m, 122 H), 0.78 (m, 12H). HR-MALDI-TOF (m/z) calculated for BDTP-2: FOUND $[M+H]^+$ = 2249.0952, TRUE$[M+H]^+$ = 2249.0937, ERROR = 0.6669 ppm.

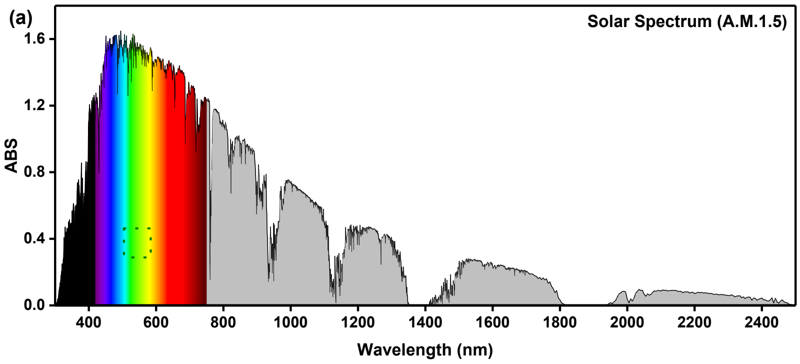


Figure S1. Distribution of solar spectrum (AM. 1.5G).

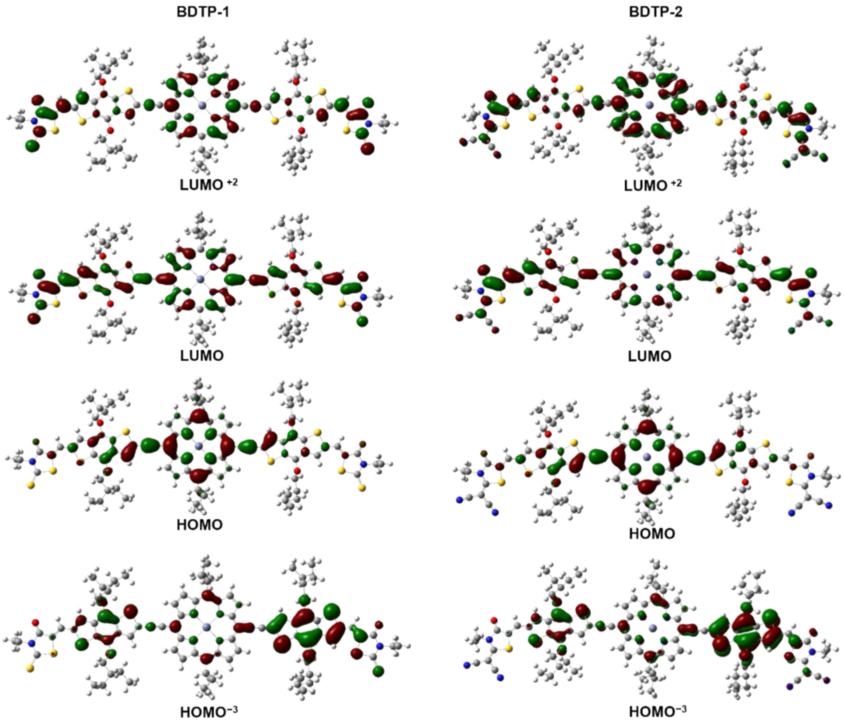


Figure S2. Mainly molecular orbitals involved in the excitations of **BDTP-1** and **BDTP-2** in green spectral absorptions calculated using DFT at the B3LYP/GENECP/LANL2DZ level.

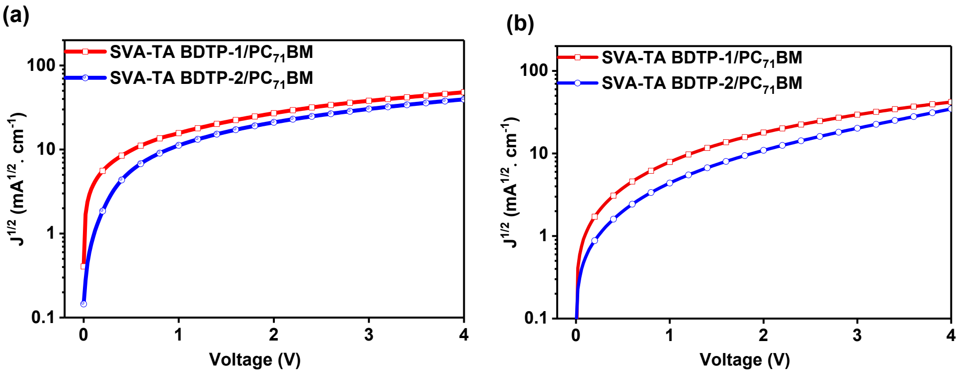


Figure S3. Hole-only mobility (a) and electron-only mobility (b) of SVA-TA BDTP-1/$PC_{71}BM$ and SVA-TA BDTP-2/$PC_{71}BM$ blended films.

Table S1. Selected parameters for the vertical excitation (UV-vis absorption) of the compounds. Electronic excitation energies (eV) and oscillator strengths (*f*), configurations of the low-lying excited states of **BDTP-1**. Calculated by TDDFT//B3LYP/GENECP/LANL2DZ, based on the optimized ground state geometries (No specific solvent was defined in all the calculation).

		TDDFT/B3LYP/ GENECP			
	Electronic transition [a]	Excitation energy	f [b]	Composition [c]	CI [d]
Absorption	$S_0 \rightarrow S_1$	1.64 eV (756 nm)	2.6931	H →L	0.6962
	$S_0 \rightarrow S_6$	2.35 eV (527 nm)	0.4087	H-3 → L	0.5778
				H-2 → L+3	–0.1733
				H-1 → L+1	0.3196
	$S_0 \rightarrow S_{14}$	2.74 eV (453 nm)	0.9142	H-5 → L	–0.2678
				H-4 → L+1	–0.2182
				H-3 →L+1	0.1312
				H-3 →L+2	0.4649
				H-2 →L+3	–0.2952
				H-1→ L+2	0.1139

[a] Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. [b] Oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] Coefficient of the wavefunction for each excitation. The CI coefficients are in absolute values.

Table S2. Selected parameters for the vertical excitation (UV-vis absorption) of the compounds. Electronic excitation energies (eV) and oscillator strengths (*f*), configurations of the low-lying excited states of **BDTP-2**. Calculated by TDDFT//B3LYP/GENECP/LANL2DZ, based on the optimized ground state geometries (No specific solvent was defined in all the calculation).

	TDDFT/B3LYP/ GENECP				
	Electronic transition [a]	Excitation energy	f [b]	Composition [c]	CI [d]
Absorption	$S_0 \rightarrow S_1$	1.59 eV (778 nm)	2.6449	H →L	0.6976
	$S_0 \rightarrow S_6$	2.31 eV (537 nm)	0.4331	H-3 → L	–0.3932
				H-2 → L+3	0.1360
				H-1 → L+1	0.5274
	$S_0 \rightarrow S_{12}$	2.72 eV (455 nm)	0.9549	H-5 → L	–0.2504
				H-4 → L+1	–0.2354
				H-3 →L+1	0.1111
				H-3 →L+2	0.4788
				H-2 →L+3	–0.2970
				H-1→ L+2	0.1117

[a] Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. [b] Oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] Coefficient of the wavefunction for each excitation. The CI coefficients are in absolute values.

Table S3. Parameters of AFM, GIWAXS results of neat, blend-films of **BDTP-1**/$PC_{71}BM$, **BDTP-2**/$PC_{71}BM$.

sample	q100 /nm^{-1}	d /nm	FWHM /nm^{-1}	CL /nm	q200 /nm^{-1}	q300 /nm^{-1}	PCBM/nm^{-1}	q010 /nm^{-1}	d /nm
BDTP-1	3.60	1.75	0.37	16.23	7.06	10.53	--	17.65	0.36
TA **BDTP-1**/$PC_{71}BM$	3.61	1.74	0.68	8.59	6.80	--	13.86	17.65	0.36
SVA-TA **BDTP-1**/$PC_{71}BM$	3.66	1.72	0.64	9.13	6.99	--	13.86	17.65	0.36
BDTP-2	3.60	1.75	0.32	18.26	7.06	10.55	--	17.65	0.36
TA **BDTP-2**/$PC_{71}BM$	3.66	1.72	0.92	6.35	6.74	--	13.86	17.65	0.36
SVA-TA **BDTP-2**/$PC_{71}BM$	3.62	1.74	0.58	10.07	6.93	--	13.86	17.65	0.36

The layer space (d-spacing) is calculated according to d=2π/q, and coherence length is calculated to CL = 2πk/q, k=0.93.

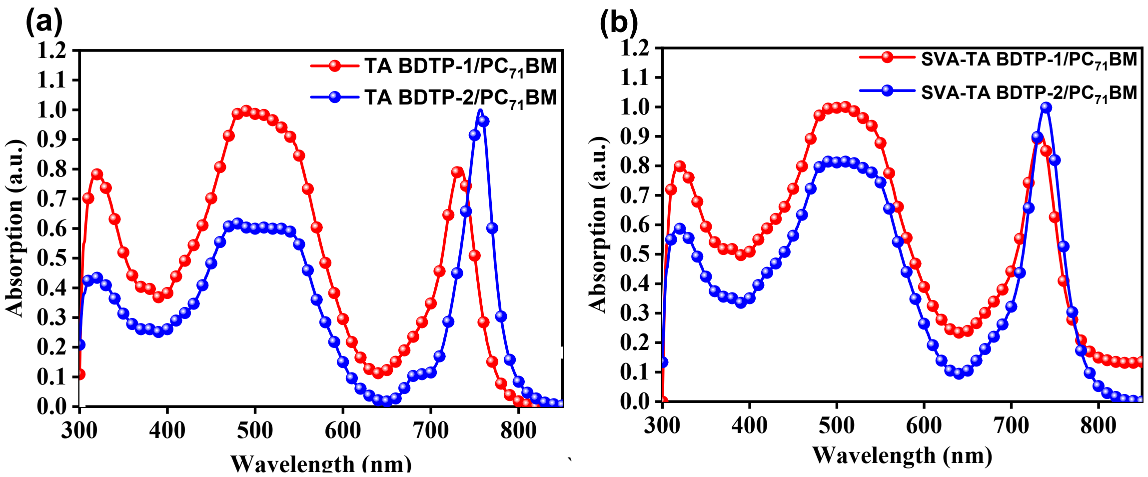


Figure S4. The UV-Vis absorption spectra of blends TA donor/$PC_{71}BM$ (a) and SVA-TA donor/$PC_{71}BM$ (b).

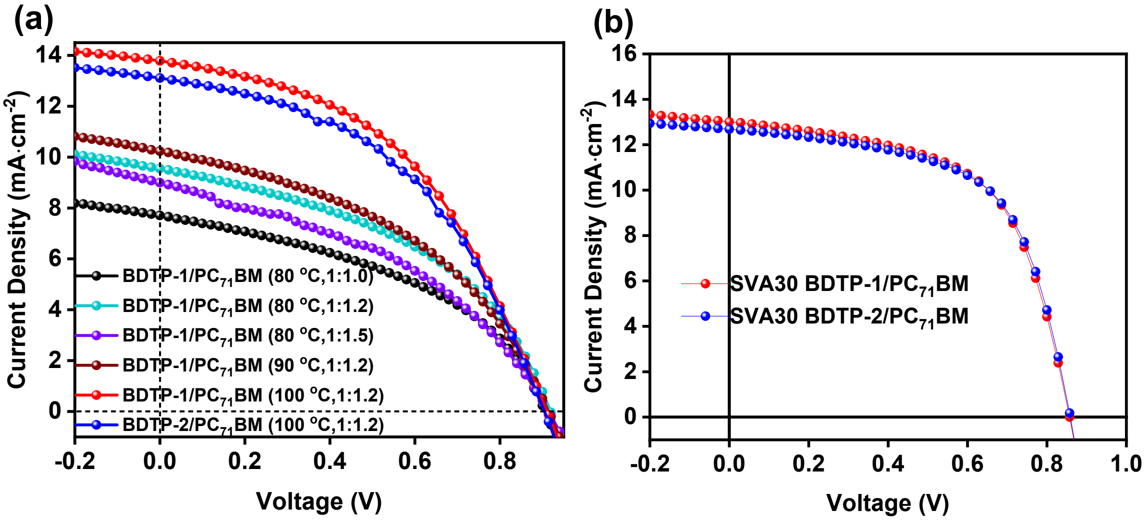


Figure S5. a) J–V curves of the BHJ OSCs under different **BDTP-1**:PC$_{71}$BM weight ratios (1:1.0, 1:1.2, 1:1.5) and thermal annealing temperatures (5 mins); b) J–V curves of the BHJ OSCs using **BDTP-1** (or **BDTP-2**):PC$_{71}$BM (1:1.2) under 30 s solvent vapor annealing

Table S4. Photovoltaic parameters of OSCs using **BDTP-1** and **BDTP-2** as donor materials and PC$_{71}$BM as acceptor.

Samples	Ratio	TA[a]/°C	SVA[b]	V_{OC} (V)	J_{SC} (mA·cm^{-2})	FF (%)	PCE (%)[c]
BDTP-1/PC$_{71}$BM	1:1.0	80	0	0.91 (±0.01)	7.71 (±0.04)	43.20 (±0.01)	3.03 (±0.03)
BDTP-1/PC$_{71}$BM	1:1.2	80	0	0.92 (±0.00)	9.55 (±0.04)	44.20 (±0.01)	3.90 (±0.01)
BDTP-1/PC$_{71}$BM	1:1.5	80	0	0.91 (±0.00)	9.00 (±0.06)	41.30 (±0.01)	3.33 (±0.05)
BDTP-1/PC$_{71}$BM	1:1.2	90	0	0.91 (±0.01)	10.24 (±0.06)	44.10 (±0.01)	4.03 (±0.05)
BDTP-1/PC$_{71}$BM	1:1.2	100	0	0.91 (±0.01)	13.73 (±0.05)	46.41 (±0.01)	5.79 (±0.05)
BDTP-2/PC$_{71}$BM	1:1.2	100	0	0.90 (±0.01)	13.06 (±0.04)	45.71 (±0.01)	5.39 (±0.01)
BDTP-1/PC$_{71}$BM	1:1.2	100	20	0.86 (±0.01)	14.30 (±0.06)	64.22 (±0.01)	7.92 (±0.05)
BDTP-2/PC$_{71}$BM	1:1.2	100	20	0.86 (±0.01)	14.10 (±0.03)	65.03 (±0.01)	7.89 (±0.01)
BDTP-1/PC$_{71}$BM	1:1.2	100	30	0.86 (±0.01)	13.10 (±0.04)	60.51 (±0.01)	6.79 (±0.04)
BDTP-2/PC$_{71}$BM	1:1.2	100	30	0.86 (±0.00)	12.65 (±0.04)	61.42 (±0.01)	6.67 (±0.04)

[a] Thermally annealing in different temperature for 5 min. [b] SVA: Thermally annealed device optionally exposed to DCM vapour. Device structure: ITO/PEDOT:PSS/Donor: PC$_{71}$BM/Ca/Al. The active layers were spin-coated from their chlorobenzene solutions with 2.0 vol% pyridine as additive and the films' thickness are approximately 90 nm. [c] Each value in parenthesis was averaged from 24 devices with standard deviation.

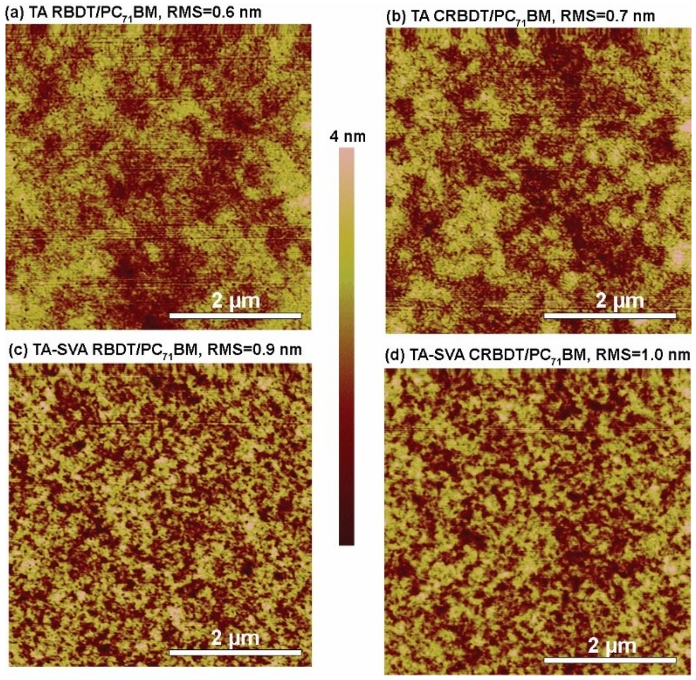


Figure S6. AFM height images of blend films TA **BDTP-1**/PC$_{71}$BM, TA **BDTP-2**/PC$_{71}$BM, TA-SVA **BDTP-1**/PC$_{71}$BM and TA-SVA **BDTP-2**/PC$_{71}$BM.

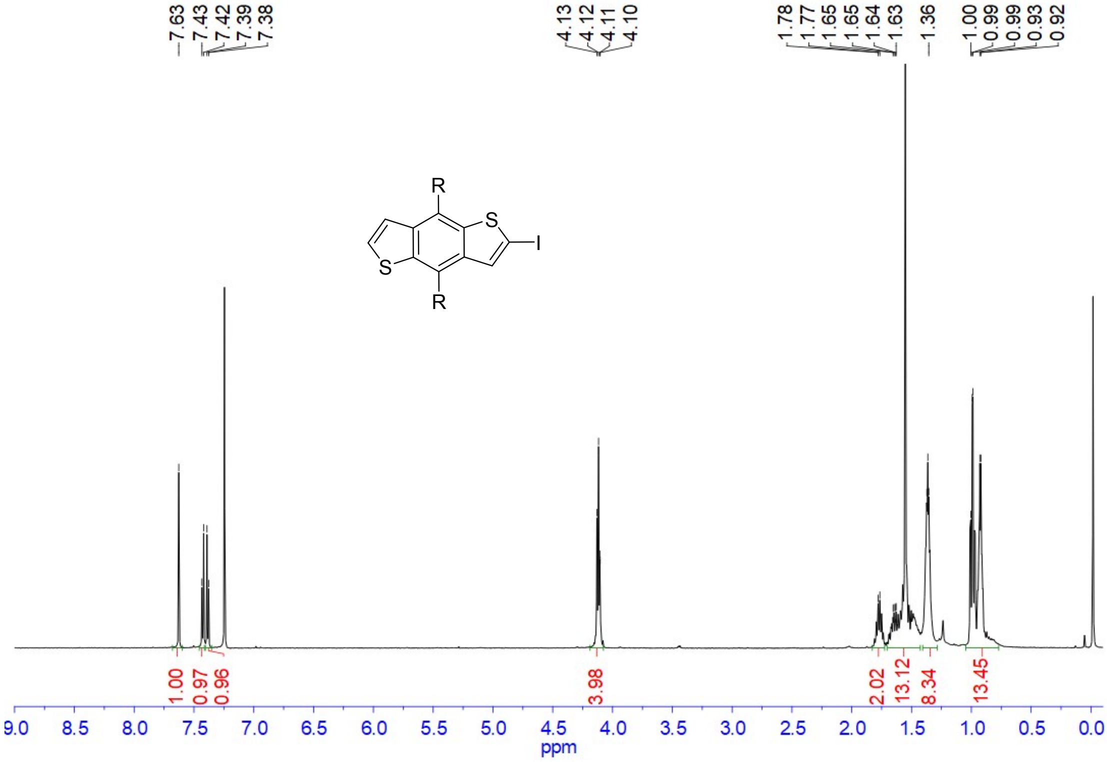


Figure S7. ^{1}H NMR of molecule of compound **BDT-I.**

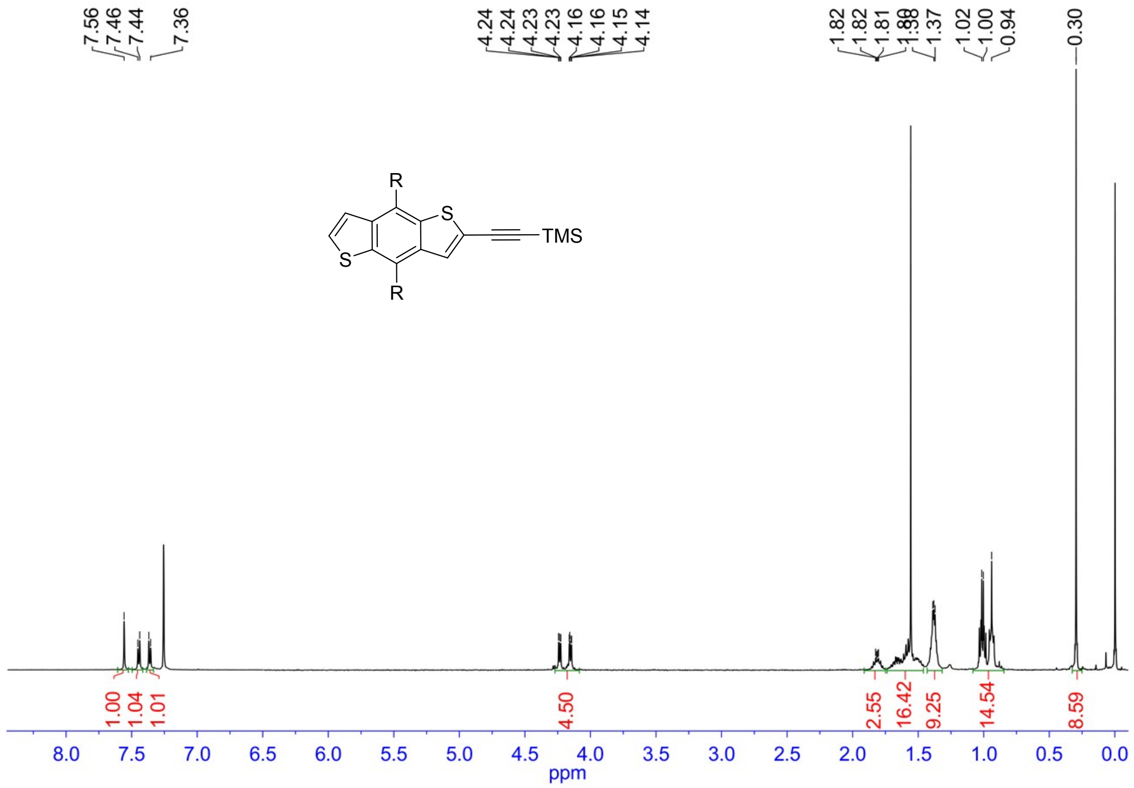


Figure S8. ^{1}H NMR of molecule of compound **TMSE-BDT**.

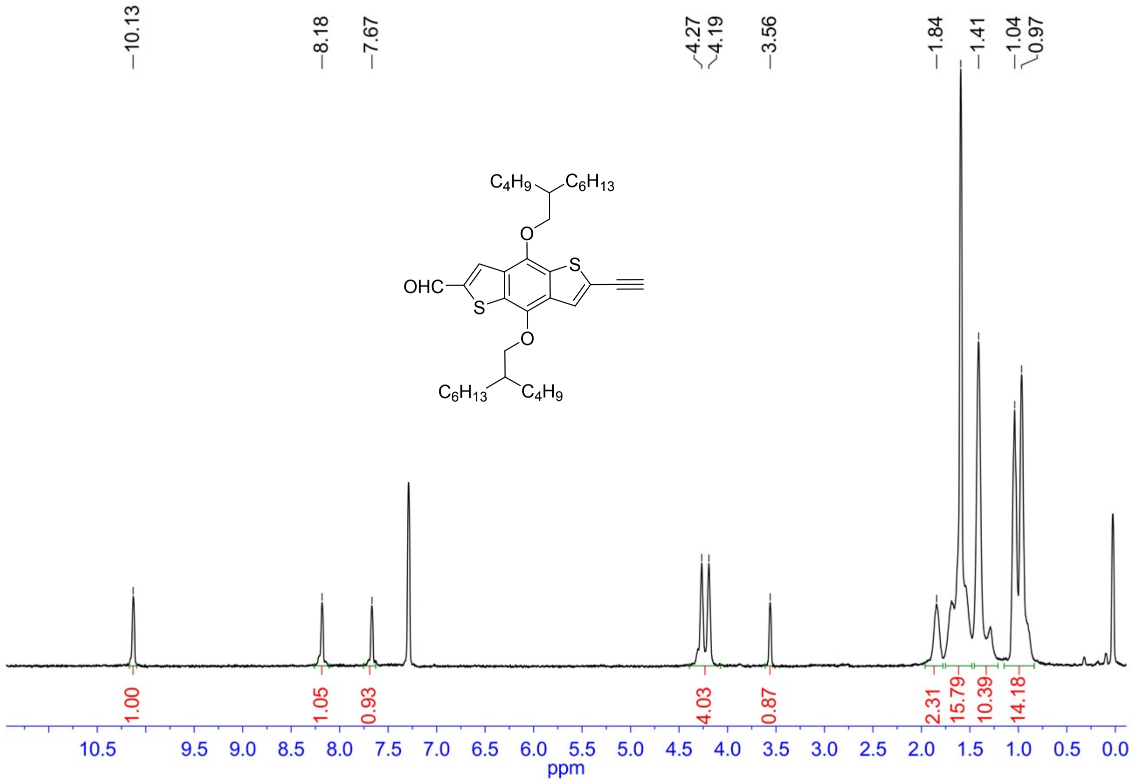


Figure S7. ^{1}H NMR of molecule of compound **E-BDT-CHO**.

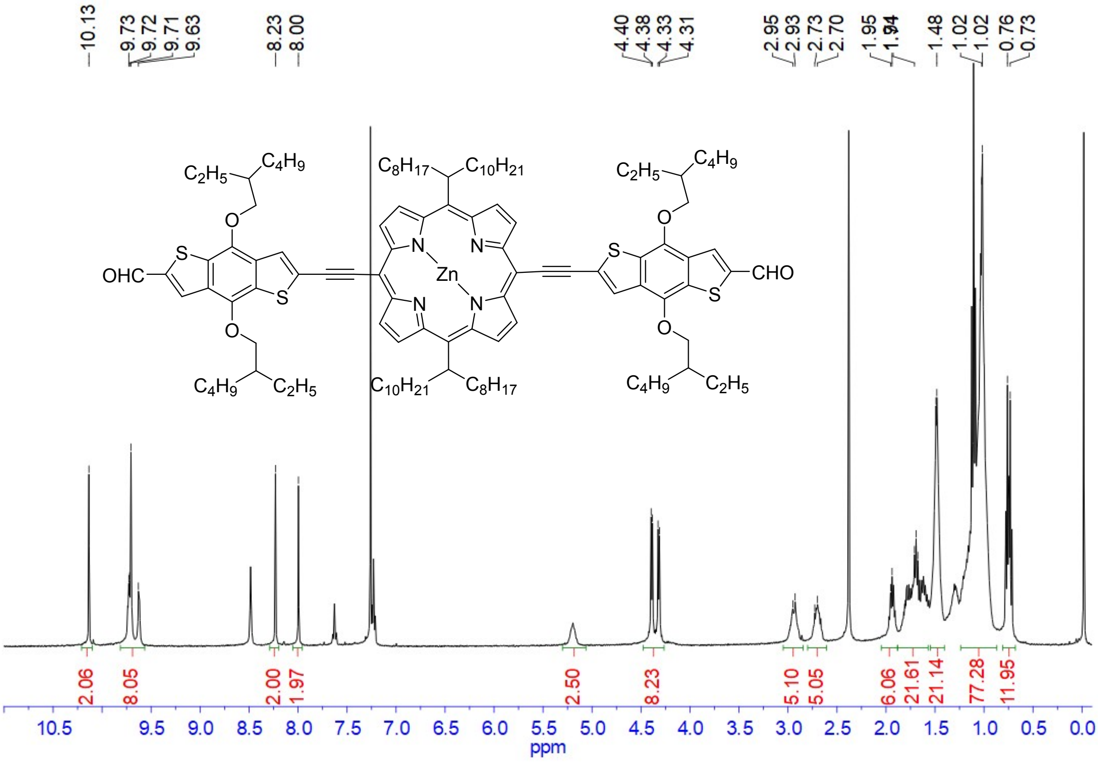


Figure S10. ^{1}H NMR of molecule of compound **BDT(CHO)P**.

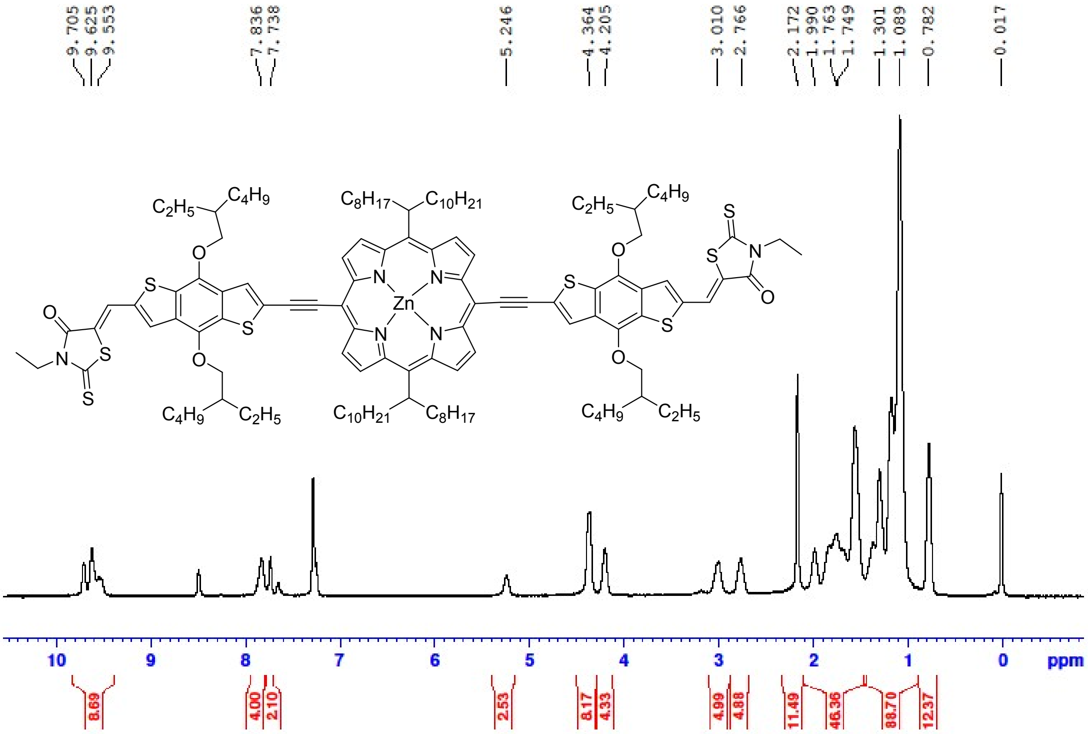
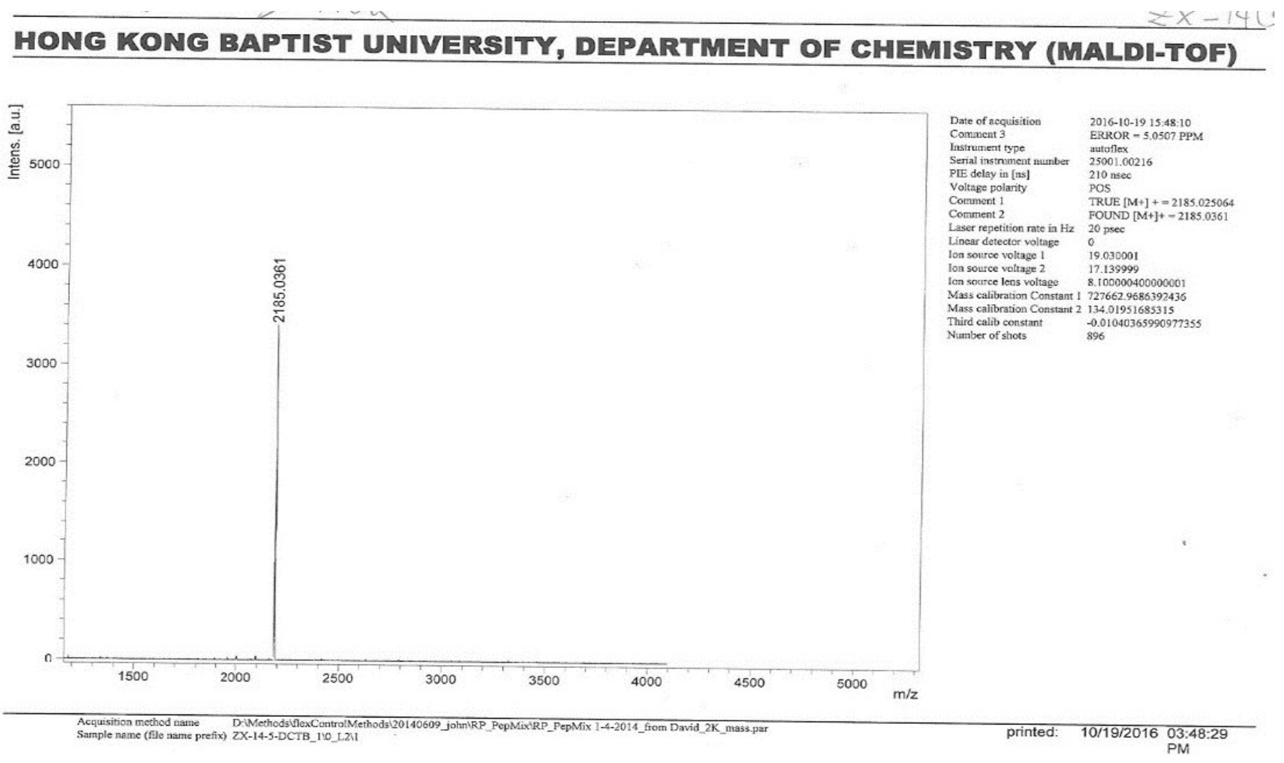


Figure S11. ^{1}H NMR of molecule **BDTP-1**.



ZX-14

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Ion source lens voltage 8.100000400000001
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Mass calibration Constant 2 134.01951685315
Third calib constant -0.01040365990977355
Number of shots 896

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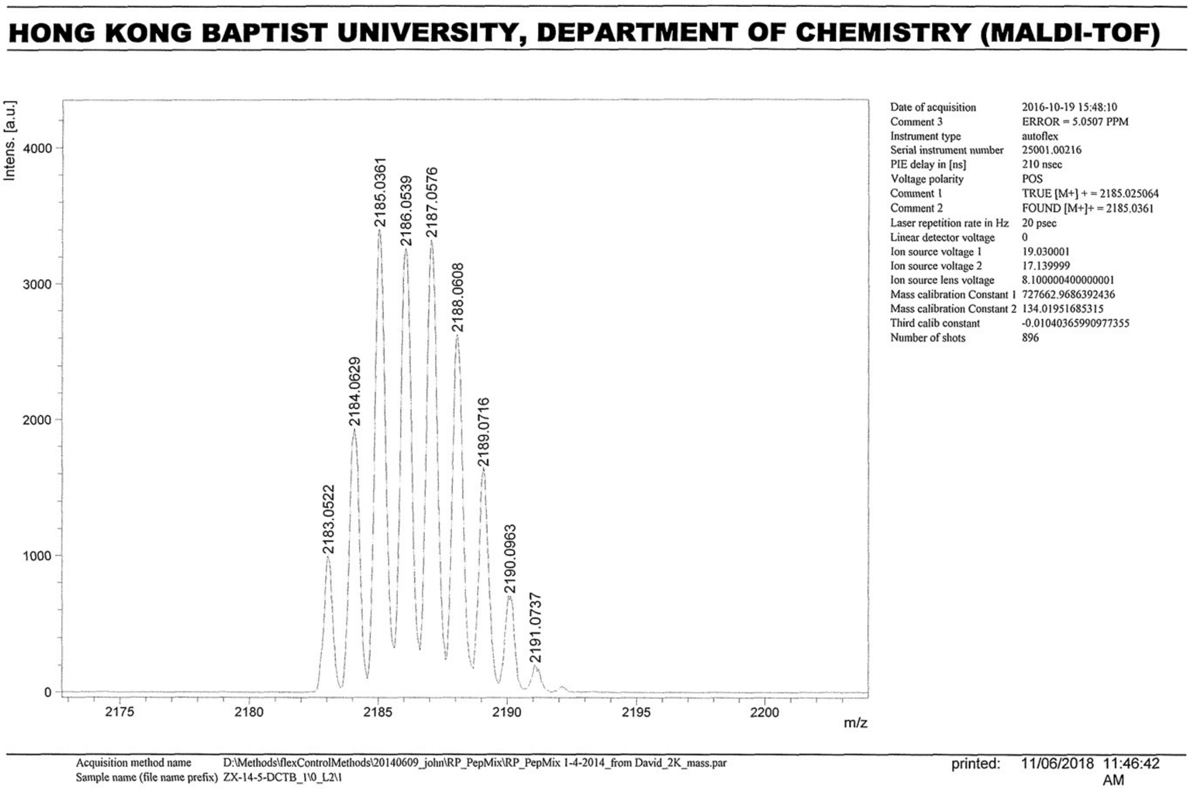
Figure S12. HR-MALDI-TOF-MS spectrum of molecule **BDTP-1**.



HONG KONG BAPTIST UNIVERSITY, DEPARTMENT OF CHEMISTRY (MALDI-TOF)

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Linear detector voltage 0
Ion source voltage 1 19.030001
Ion source voltage 2 17.139999
Ion source lens voltage 8.100000400000001
Mass calibration Constant 1 727662.9686392436
Mass calibration Constant 2 134.01951685315
Third calib constant -0.01040365990977355
Number of shots 896

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Figure S13. Isotopic resolution of the HR-MALDI-TOF-MS main peak of molecule **BDTP-1**.

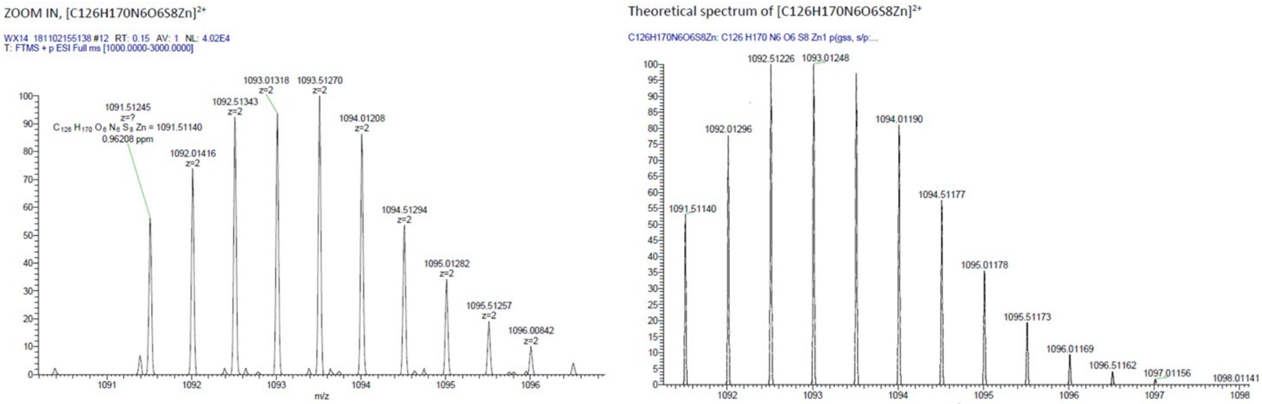


Figure S14. Found and theoretic spectra of HR-ESI-MS of molecule **BDTP-1**.

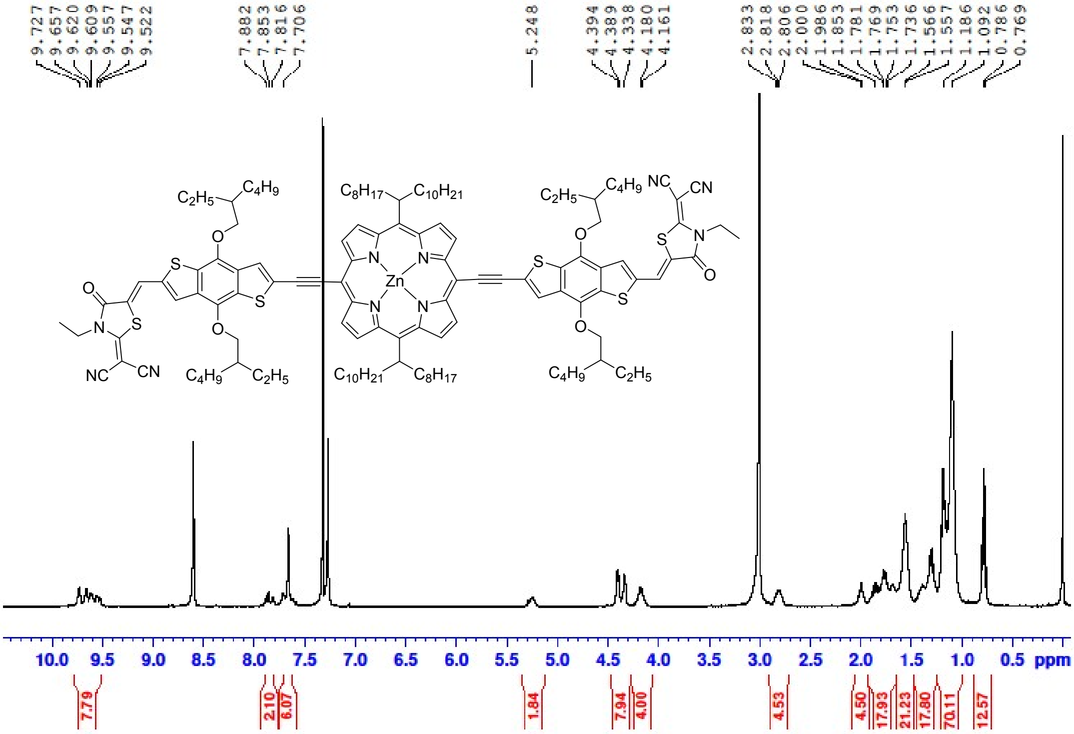
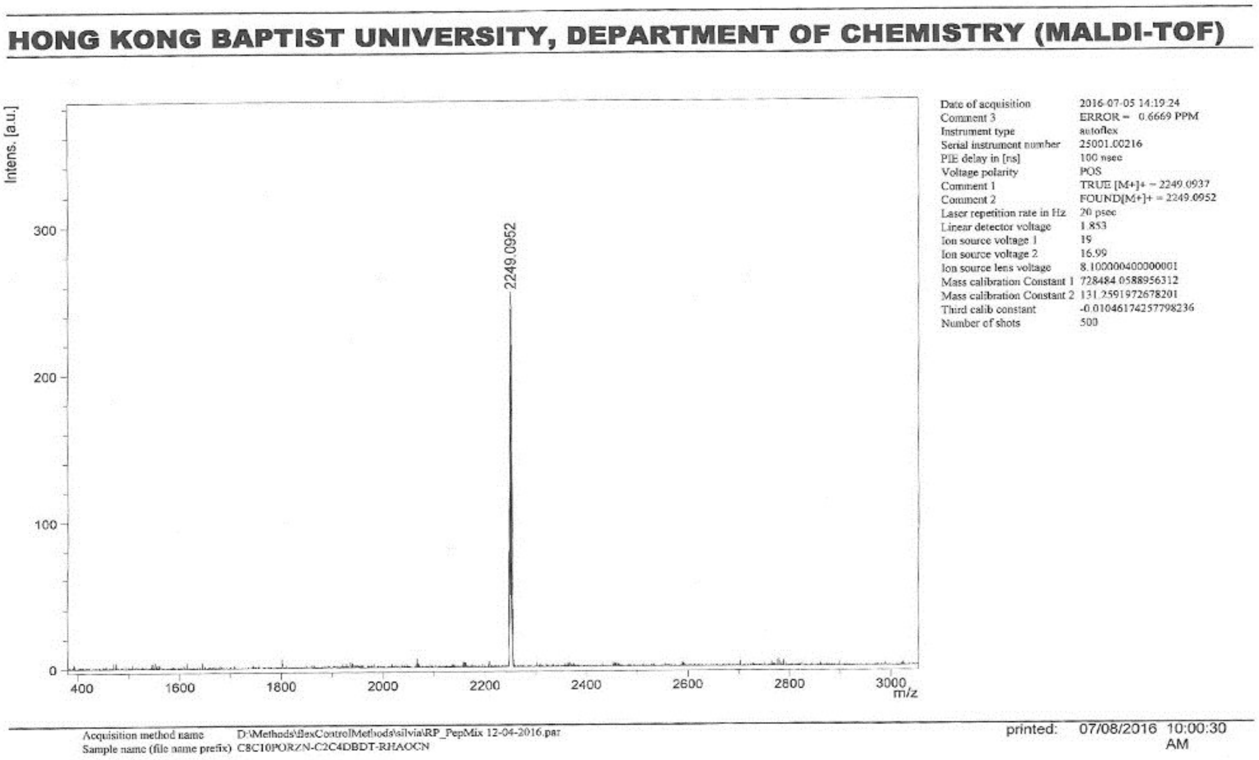


Figure S15. ^{1}H NMR of molecule **BDTP-2**.



HONG KONG BAPTIST UNIVERSITY, DEPARTMENT OF CHEMISTRY (MALDI-TOF)

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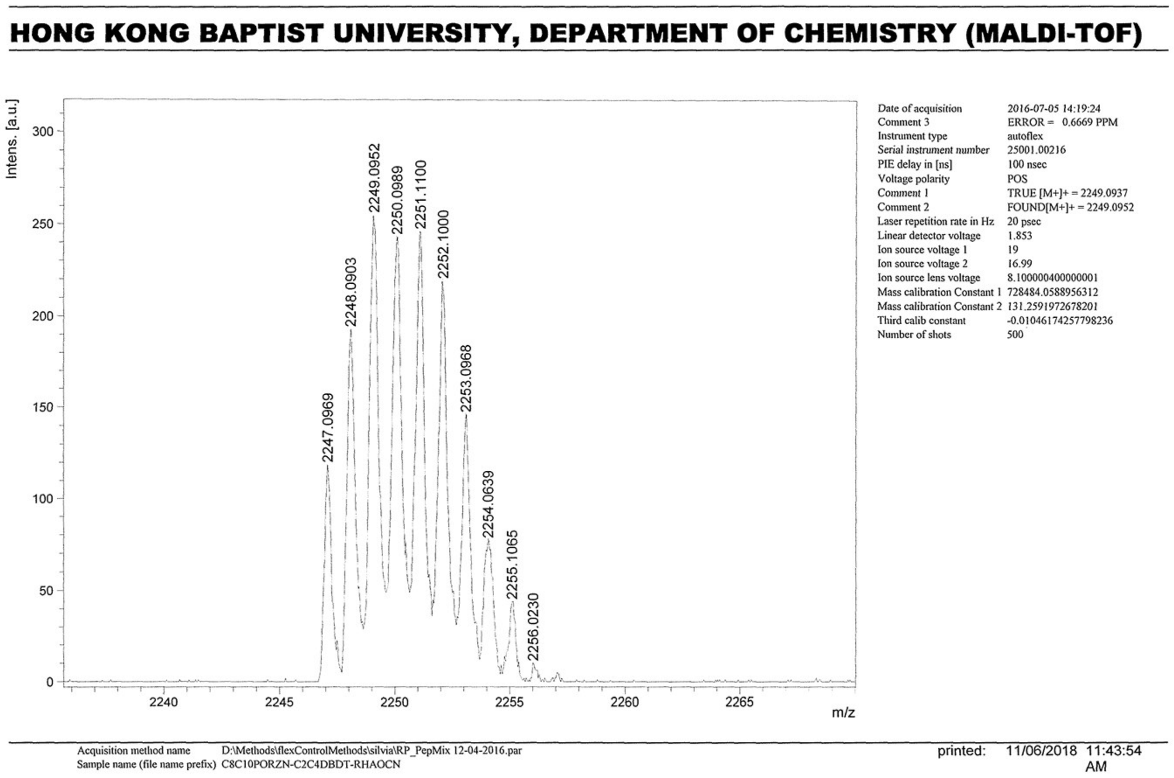
Comment 2	FOUND[M+]+ = 2249.0952
Laser repetition rate in Hz	20 psec
Linear detector voltage	1.853
Ion source voltage 1	19
Ion source voltage 2	16.99
Ion source lens voltage	8.10000040000001
Mass calibration Constant 1	728484.0588956312
Mass calibration Constant 2	131.2591972678201
Third calib constant	-0.01046174257798236
Number of shots	500

Acquisition method name D:\Methods\flexControlMethods\silvia\RP_PepMix 12-04-2016.par
Sample name (file name prefix) C8C10PORZN-C2C4DBDT-RHAOCN

printed: 07/08/2016 10:00:30 AM

Figure S16. HR-MALDI-TOF-MS spectrum of molecule **BDTP-2**.



HONG KONG BAPTIST UNIVERSITY, DEPARTMENT OF CHEMISTRY (MALDI-TOF)

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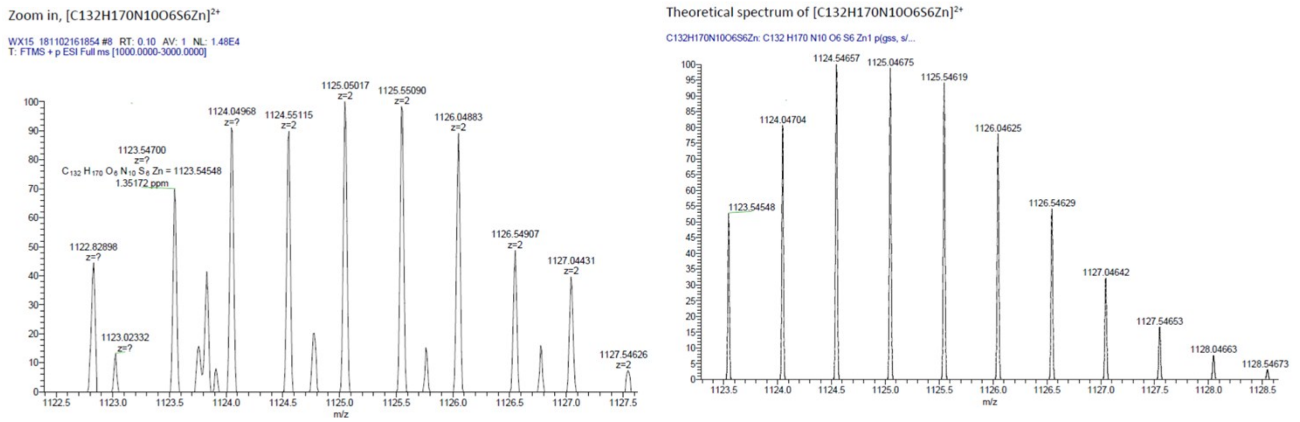
Comment 2	FOUND[M+]+ = 2249.0952
Laser repetition rate in Hz	20 psec
Linear detector voltage	1.853
Ion source voltage 1	19
Ion source voltage 2	16.99
Ion source lens voltage	8.100000400000001
Mass calibration Constant 1	728484.0588956312
Mass calibration Constant 2	131.2591972678201
Third calib constant	-0.01046174257798236
Number of shots	500

Acquisition method name D:\Methods\flexControlMethods\silvia\RP_PepMix 12-04-2016.par
Sample name (file name prefix) C8C10PORZN-C2C4DBDT-RHAOCN

printed: 11/06/2018 11:43:54 AM

Figure S17. Isotopic resolution of the HR-MALDI-TOF-MS main peak of molecule **BDTP-2**.



Zoom in, $[C_{132}H_{170}N_{10}O_6S_6Zn]^{2+}$

Theoretical spectrum of $[C_{132}H_{170}N_{10}O_6S_6Zn]^{2+}$

Figure S18. Found and theoretic spectra of HR-ESI-MS of molecule **BDTP-2**.

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