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Supplementary Information

Solution Processed Small Molecule Bulk Heterojunction Organic Photovoltaics Based on a Conjugated Donor-Acceptor Porphyrin

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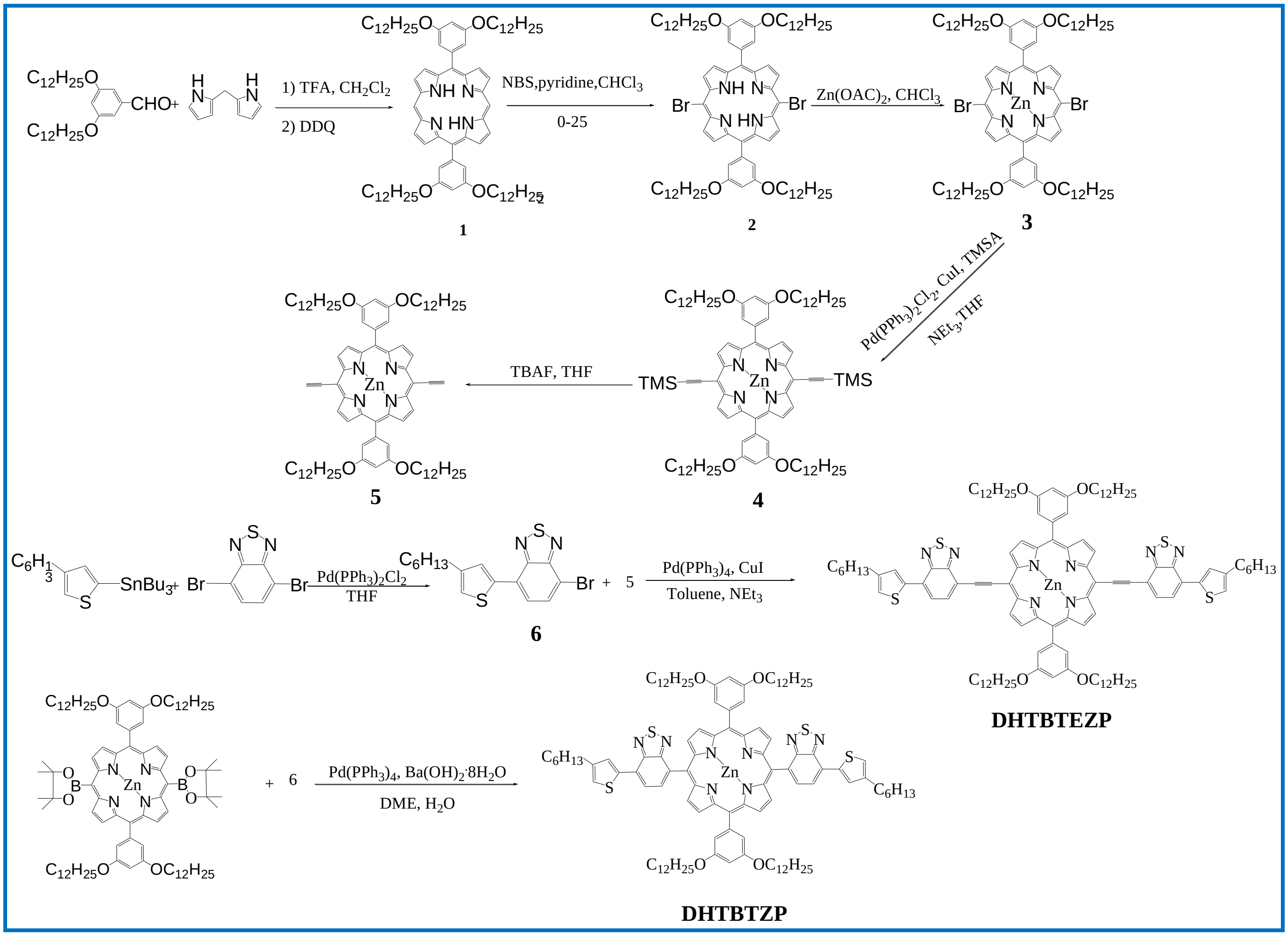

Scheme1. Synthetic routines of DHTBTEZP and DHTBTZP

Experimental section

Synthesis

Materials: Tetrahydrofuran (THF) and toluene were distilled from sodium-benzophenone under nitrogen prior to use. Triethylamine (NEt_3), dimethoxyethane (DME), $CH_2Cl_2$and $CHCl_3$ were distilled from CaH_2 prior to use. All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co. and used as received. All manipulations involving air-sensitive reagents were performed under an atmosphere of Ar or N_2. 3,5-di(dodecyloxy)benzaldehyde, dipyrromethane and

5,15-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin zinc were synthesized according to literature methods.[1-3]

5,15-Bis(3,5-di(dodecyloxy)phenyl)porphyrin 1. A solution of 3,5-di(dodecyloxy)benzaldehyde (2.304 g, 4.86 mmol) and dipyrromethane (700 mg, 4.86 mmol) in CH_2Cl_2 (500mL) was purged with nitrogen for 30 min, and then trifluoroacetic acid (TFA) (0.25 mL) was added. The mixture was stirred for 12h at room temperature, and then 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.8 g) was added. After the mixture was stirred at room temperature for an additional 2h, the reaction was quenched by adding triethylamine (5 mL). The solvent was removed, and the residue was purified by flash column chromatography on silica gel using dichloromethane as the eluent. Recrystallization from $CHCl_3$/methanol gave a purple solid. ^1H NMR (300 MHz, $CDCl_3$): δ 10.30 (s, 2H), 9.39 (d, *J*=4.6 Hz, 4H), 9.18 (d, *J*=4.6 Hz, 4H), 7.42 (s, 4H), 6.91 (s, 2H), 4.13 (t, *J*=6.6 Hz, 8H), 1.93 (m, 8H), 1.47 (m, 8H), 1.24 (m, 64H), 0.83 (m, 12H), -3.2 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.67, 147.02, 145.31, 143.16, 131.46, 131.13, 119.07, 114.64, 105.16, 101.12, 68.47, 67.94, 31.92, 29.68, 29.62, 29.47, 29.45, 29.34, 26.16, 25.60, 22.68, 14.09. Mass (MALDI-TOF): Obs. 1200.2; Calcd. for $C_{80}H_{118}N_4O_4$: 1199.8. UV-vis (CH_2Cl_2), λ_{max}=406 nm.

5,15-Dibromo-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin 2. N-Bromosuccinimide (274 mg, 1.54 mmol) was added to a chloroform (700mL) solution containing porphyrin 1 (840 mg, 0.7 mmol) and pyridine (35 mL) at 0℃, and the mixture was stirred for 30 min. Then the mixture was allowed to warm up to room temperature and then stirred for 4h. After the reaction was quenched by addition of acetone, the mixture was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed, and the residue was purified by flash column chromatography on silica gel using petroleum ether/dichloromethane (3:1) as the eluent. Recrystallization from $CHCl_3$/methanol gave a purple solid. ^1H NMR (300 MHz, $CDCl_3$): δ 9.59 (d, *J*= 4.8 Hz, 4H), 8.95 (d, *J*=4.8 Hz, 4H), 7.31 (s, 4H), 6.89 (s, 2H), 4.13 (t, *J*= 6.6 Hz, 8H), 1.85 (m, 8H), 1.46 (m, 8H), 1.24 (m, 64H), 0.83 (m, 12H), -3.2 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.40, 143.06, 121.31, 114.46, 103.60, 101.24, 68.44, 34.04, 32.85, 31.90, 29.70, 29.66, 29.62, 29.54, 29.44, 29.37, 29.33, 28.77, 28.19, 26.11, 22.69, 14.11, 14.09. MS Mass (MALDI-TOF): Obs. 1358.1; Calcd. for $C_{80}H_{116}Br_2N_4O_4$: 1357.6. UV-vis (CH_2Cl_2), λ_{max}=424 nm.

5,15-Dibromo-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin Zinc 3. To a solution of 2 (745 mg, 0.55 mmol) in chloroform (50 mL) was added a solution of $Zn(OAc)_2$ (243 mg, 1.2 mmol) in methanol (12 mL). The reaction mixture was refluxed for 2h, and then washed with water and dried over anhydrous Na_2SO_4. The solvent was removed, and the residue was recrystallization from $CHCl_3$/methanol gave a reddish solid. ^1H NMR (300 MHz, $CDCl_3$): δ 9.70 (d, *J*=4.8 Hz, 4H), 9.06 (d, *J*=4.8 Hz, 4H), 7.30 (s, 4H), 6.86 (s, 2H), 4.12 (t, *J*=6.55 Hz, 8H), 1.88 (m, 8H), 1.46 (m, 8H), 1.25 (m, 64H), 0.85 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.18, 150.60, 150.15, 143.65, 133.60, 133.04, 122.11, 114.53, 105.06, 101.16, 68.45, 31.90, 29.61, 29.60, 29.43, 29.33, 26.08, 22.65, 14.10, 14.06. Mass (MALDI-TOF): Obs. 1421.0; Calcd. for $C_{80}H_{114}Br_2N_4O_4Zn$: 1421.0 . UV-vis ($CH_2Cl_2$), λ_{max}=425 nm.

5,15-Bis(trimethylsilyethynyl)-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin Zinc 4. 3 (710 mg, 0.5 mmol) was dissolved in THF (25mL) and triethylamine (12.5) was added. The mixture was purged with nitrogen for 30 min. Then $Pd(PPh_3)_2Cl_2$ (17.5 mg, 0.025 mmol) , CuI (5 mg, 0.025 mmol) , and trimethylsilyacetylene (200 mg, 2 mmol) were added. After the mixture was stirred at room temperature for 3 days under nitrogen, the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether (1:1) to afford a green solid. ^1H NMR (300 MHz, $CDCl_3$): δ 9.68 (d, *J*=4.6 Hz, 4H), 9.04 (d, *J*=4.6 Hz, 4H), 7.33 (s, 4H), 6.89 (s, 2H), 4.10 (t, *J*=6.4 Hz, 8H), 1.82 (m, 8H), 1.50 (m, 8H), 1.23 (m, 64H), 0.83 (m, 12H), 0.60 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.28, 150.04, 143.75, 132.84, 131.19, 122.57, 114.37, 107.40, 101.89, 101.34, 101.15, 68.43, 31.90, 29.66, 29.63, 29.60, 29.45, 29.38, 29.33, 26.11, 22.67, 14.10. Mass (MALDI-TOF): Obs. 1455.2; Calcd. for $C_{90}H_{132}N_4O_4Si_2Zn$: 1455.6. UV-vis ($CH_2Cl_2$), λ_{max}=436 nm.

5,15-Diethynyl-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin zinc 5. Tetrabutylammonium fluoride (0.72 mL, 1M in THF) was added to a stirred solution of porphyrin 4 (509 mg, 0.35 mmol) in THF (20 mL). After stirring for 5 min, water was added to quench the reaction. The solution was extracted with chloroform, washed with water and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether (1/1) to give a green solid). ^1H NMR (300MHz, $CDCl_3$): δ 9.74 (d, *J*=4.68 Hz, 4H), 9.07 (d, *J*=4.65 Hz, 4H), 7.34 (s, 4H), 6.89 (s, 2H), 4.14 (m, 10H), 1.83 (m, 8H), 1.45 (m, 8H), 1.24 (m, 64H), 0.83 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.35, 152.37, 150.20, 133.04, 131.19, 114.30, 68.42, 31.88, 29.63, 29.58, 29.43, 29.38, 29.30, 26.11, 22.64, 14.05. Mass (MALDI-TOF): Obs. 1311.2; Calcd. for $C_{84}H_{116}N_4O_4Zn$: 1311.2. UV-vis (CH_2Cl_2), λ_{max}=430 nm.

4-Bromo-7-(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole 6. Under a nitrogen atmosphere, a mixture of 4,7-dibromo-2,1,3-benzothiadiazole (882 mg, 3 mmol), tributyl-(4-hexyl-2-thienyl)-stannane (458 mg, 1 mmol), and $Pd(PPh_3)_2Cl_2$ (42 mg, 0.06 mmol) was dissolved in degassed anhydrous THF (30 mL). The solution was kept at 80°C for 24h. The mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine and then dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (eluent: petroleum/CH_2Cl_2=15:1). Recrystallization from ethanol gave the pure product as yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.83 (d, *J*=7.71 Hz, 1H), 7.69 (d, *J*=7.71 Hz, 1H), 7.06 (s, 1H), 2.71 (t, *J*=7.68 Hz, 2H), 1.73 (m, 2H), 1.3 (m, 6H), 0.92 (t, *J*=7.68 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.79, 151.80, 144.50, 138.08, 132.21, 129.61, 127.36, 125.51, 122.04, 112.05, 31.67, 30.59, 30.43, 29.01, 22.60, 14.06. MS (ESI): m/z=382.8; Calcd. for $C_{16}H_{17}BrN_2S_2$: 381.4. UV-vis (CH_2Cl_2), λ_{max}=415 nm.

5,15-Bis(7-(4-hexyl-thiophen-2-yl)-2,1,3-benzothiadiazole-4-yl-ethynyl)-10,20-bis(3,5-di(dodecyloxy)phenyl)-porphyrin zinc (DHTBTEZP). To a 50mL two necked round-bottom flask were added 5,15-diethynyl-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin Zinc (262 mg, 0.2 mmol), 4-bromo-7-(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (228.6mg, 0.6 mmol), anhydrous toluene (10 mL), and triethylamine (5 mL). The mixture was deoxygenated with N_2 for 30 min. Pd $(PPh_3)_4$ (48 mg, 0.04

mmol) and CuI (8 mg, 0.04 mmol) were added. The mixture was stirred at 80℃ for 3 days. After cooling to room temperature, the mixture was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed, and the residue was purified by HPLC gave a dark green solid. Mass (MALDI-TOF): Obs. 1912.5; Calcd. for $C_{116}H_{148}N_8O_4S_4Zn$, 1912.1.

5,15-Bis(7-(4-hexyl-thiophen-2-yl)-2,1,3-benzothiadiazole)-10,20-bis(3,5-di(dodecyloxy)phenyl)-porphyrin zinc (DHTBTZP). To a 50mL single necked round-bottom flask were added 5,15-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin Zinc (303 mg, 0.2 mmol), 4-bromo-7-(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (228.6mg, 0.6 mmol), $Ba(OH)_2.8H_2O$ (0.08 g, 0.24 mmol), $Pd(PPh_3)_4$ (48 mg, 0.04 mmol), freshly distilled dimethoxyethane (15 mL), and H_2O (0.3 mL). The mixture was deoxygenated via three freeze-pump-thaw degas cycles and stirred at 80℃ for 3 days under an inert atmosphere. After cooling to room temperature, the mixture was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed, and the residue was purified by HPLC gave a purple solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.02 (d, *J*=5.5 Hz, 4H), 8.75 (d, *J*=6 Hz, 4H), 8.49 (d, *J*=7.3 Hz, 1H), 8.42 (d, *J*=7.2 Hz, 1H), 8.34 (d, *J*=7 Hz, 2H), 8.29 (s, 2H), 7.34 (s, 4H), 7.20 (s, 2H), 6.84 (s, 2H), 4.09 (t, *J*=5.0 Hz, 8H), 2.85 (t, *J*=7.6 Hz, 4H), 1.84 (m, 12H), 1.46 (m, 12H), 1.25 (m, 72H), 0.97 (t, *J*=7.0 Hz, 3H), 0.85 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.87, 158.18, 151.50, 150.28, 150.18, 144.62, 144.36, 139.12, 134.35, 132.63, 131.15, 129.73, 127.81, 124.49, 122.03, 121.53, 115.37, 114.29, 101.12, 68.37, 31.86, 31.76, 30.77, 30.59, 29.60, 29.57, 29.54, 29.39, 29.36, 29.28, 29.08, 26.07, 22.67, 22.62, 14.11, 14.04. Mass (MALDI-TOF): Obs. 1862.8; Calcd. for $C_{112}H_{148}N_8O_4S_4Zn$, 1864.1.

General characterization methods

The chemical structures of the materials used in this study were identified by ^{1}H NMR and ^{13}C NMR (Bruker AVANCE Digital 300 MHZ spectrometer in deuterated chloroform using tetramethylsilane as an internal standard). Mass Spectrometry (MS) data was obtained on a Bruker Daltonics BIFLEX Ⅲ MALDI-TOF Analyzer using MALDI mode. Thermogravimetric analysis (TGA) measurements were performed on a NETZSCH TG 209 under a nitrogen flow at heating rate of 10 ℃/min. UV-vis absorption spectra were measured using a HP 8453 spectrophotometer. Cyclic voltammetry (CV) was carried out on a CHI660C electrochemical workstation at scan rate of 50 mV s^{-1} in the nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN). A platinum electrode coated with a thin DHTBTEZP film, a Pt wire and a calomel electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. The mobilities of the blend of DHTBTEZP or DHTBTZP with $PC_{71}BM$ were determined by fitting the dark current to the model of the space charge limited current (SCLC). Films were prepared by dissolving DHTBTEZP or DHTBTZP and $PC_{71}BM$ (weight ratio: 1:3) in DCB/CB with 1 vol% pyridine as additives, followed by spin-coating on the top surface of a PEDOT: PSS substrate. The structures of hole-only devices were ITO/PEDOT: PSS (40nm)/active layer/MoO_3 (10nm)/Al, and the electric-field dependent SCLC mobility was estimated using Equation (1).[4]

$$J = \frac{9}{8}\varepsilon\varepsilon_0\frac{E^2}{d}\mu_0 \exp\left(\beta\sqrt{E}\right) \qquad (1)$$

Fabrication and characterization of photovoltaic devices

The ITO-coated glass substrates were cleaned with acetone, detergent, distilled water, and isopropyl alcohol in an ultrasonic bath and then dried overnight in an oven at >70℃. After UV ozone treatment of the ITO substrates for 5 min, 40 nm thick PEDOT: PSS (Bayer Baytron 4083) layer was spin-cast from aqueous solution (3000 rpm for 40 s). The substrates were dried at 130℃ for 20 min in air and then transferred to a N_2-glovebox for spin-casting the blend layers, which were deposited on top of the PEDOT: PSS layer from a 1,2-dichlorobenzene/chlorobenzene (DCB/CB) (1:3) solution with 1 vol% pyridine as additives. All blended ratios of DHTBTEZP or DHTBTZP:$PC_{71}BM$ were 1:3 by weight and the thicknesses of blend layers were average 60±2 nm measured by a profilometer. The ultra-thin PFN layer was subsequently deposited by spin-casting from 0.02% (w/v) solution in methanol (from 2000 rpm for 30 s). Finally, Al (80 nm) were evaporated with a shadow mask as the top electrode. The effective area was measured to be 0.16 cm^2. The current-density–voltage (J–V) characteristics were measured with a Keithley 236 digital source meter under AM 1.5 solar simulator (Oriel model 91192) at 100 mW cm^{-2}. The spectral response was measured with a commercial photo modulation spectroscopic setup (Oriel). A calibrated Si photodiode was used to determine the photosensitivity.

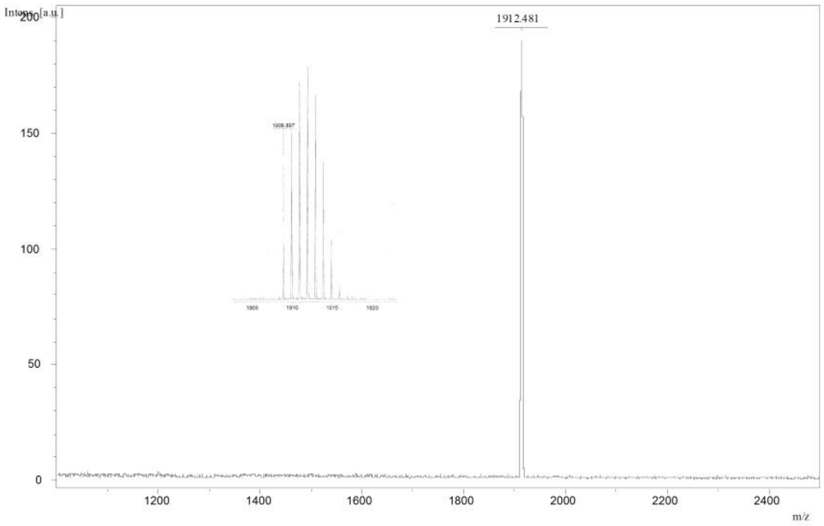

Figure S1. Mass spectrum (Maldi-TOF) of DHTBTEZP.

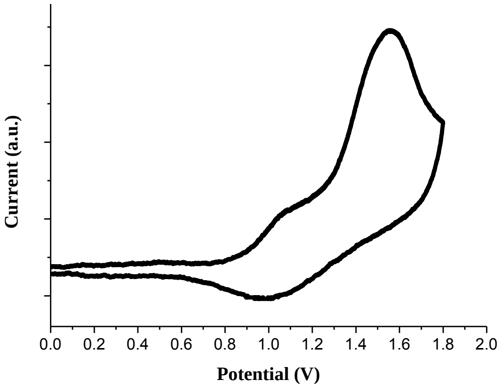

Figure S2. Cyclic voltammograms of the DHTBTEZP films coated on platinum electrodes in 0.1 mol L^{-1} Bu_4NPF_6 CH_3CN solutions.

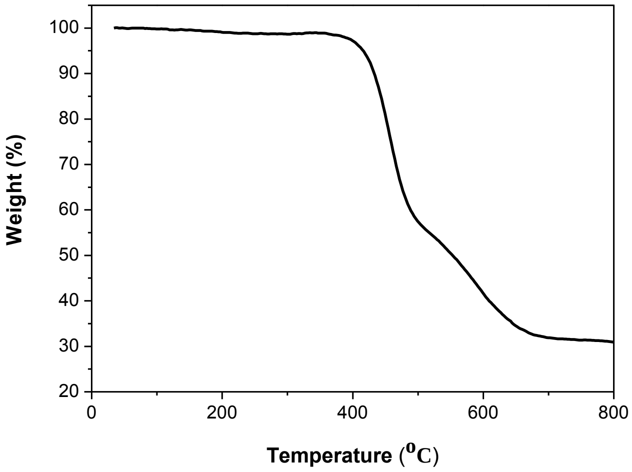

Figure S3. TGA of DHTBTEZP.

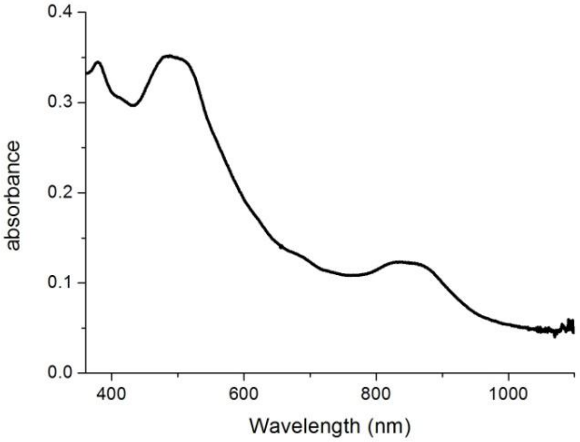

Figure S4. UV-vis absorption spectrum the DHTBTEZP/$PC_{71}BM$ blend (weight ratio: 1:3) film.

Reference

[1] W. R. Li, K. C. Kao, Y. C. Yo, C. K. Lai, *Helv. Chim. Acta.*, 1999, **82**, 1400.

[2] H. Lee, J. S. Lindsey, *Tetrahedron.*, 1994, **50**, 11427.

[3] G. H. Alison, A. K. Matthew, M. I. Peter, J. T. Michael, *J. Am. Chem. Soc.*, 1998, **120**, 12676-112677.

[4] P. W. M. Blom, M. J. M. deJong, M. G. vanMunster, *Phys. Rev. B.*, 1997, **55**, R656.