Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Benzothiadiazole-triphenylamine as efficient exciton blocking layer in small molecule based organic solar cells

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Experimental section

Device preparation:

ITO (≈140 nm) coated BK-7 glass substrates (Luminescence Technology Corp., Taiwan), with a sheet resistance of approx. 15 Ω/sq., were patterned by a positive lithography process. Patterned ITO glass substrates were cleaned in an ultrasonic bath using acetone and isopropanol followed by blow-drying with Nitrogen (N_2) gas. In a cluster deposition system, which is directly connected to the N_2 glove box, commercial MoO_3 (Sigma-Aldrich) was thermal evaporated (at a rate of 0.3 Å/s) on the patterned ITO glass substrates. A solution of BTD-TPA$_2$ in chlorobenzene was spin-coated on top of the MoO_x layer with spin speed of 4000 rpm. The devices were subsequently transferred into the cluster system for the deposition of the other layers: DBP (Luminescence Technology Corp., Taiwan) was deposited at 0.3 Å/s, C_{70} (Sigma-Aldrich, Germany) was deposited at a growth rate of 0.5 Å/s, and Silver (Ag, AES pump ApS, Denmark) at 1 Å/s by thermal evaporation at a base pressure of 5×10^{-7} mbar, deposited without breaking the vacuum between the layers. Water-cooled quartz crystal oscillators were used to control the deposition rate and thickness of the evaporated layers. Shadow masks were used to define the active cell area of OSCs, which in this case was approx. 2 mm^2.

Hole only devices (HODs) were fabricated with the following device structure:

ITO/ MoO_3(10 nm)/BTD-TPA$_2$ (different thicknesses)/DBP (20 nm)/ Ag (100 nm).

The current density-voltage (*J-V*) characteristics of the fabricated OSCs were measured in ambient air with a voltage sweep from +2 to -1 V using a source measure unit (Keithley 2400, Keithley

Instruments Inc., USA). A class AAA solar simulator (Sun 3000, Abet Technologies Inc., USA) with the lamp intensity of 100 mW/cm^2 was used for illumination. In order to generate a statistical basis, 6 cells were measured for each of the investigated device types. External quantum efficiency (EQE) measurements were performed by irradiating the samples with a 150W Xenon lamp through a Monochromator (VIS-NIR Newport Cornerstone 1/4m) followed by fiber coupling into a Mitoyo FS-70 microscope in air. A Silicon photodiode (Hamamatsu S2386-44 K) was used to measure the incident power. EQE measurements were performed directly after measuring the J-V characteristics in air and the devices were un-encapsulated.

Photoluminescence (PL) intensity measurements of the structure: Quartz/MoO_3 (10nm)/ BTD-TPA_2 (different thicknesses)/DBP (20 nm), were performed in air through a microscope objective (Nikon EPlan 50X 0.75 EPI) of a fluorescence microscope (Nikon Eclipse ME600) having a mercury short arc lamp with a filtered excitation wavelength centered between 330 nm to 380 nm as light source. For the sensitive EQE measurements, the light of a quartz halogen lamp (50 W) is chopped at 140 Hz and coupled into a Newport Cornerstone 260 1/4m monochromator. The resulting light beam is focused onto the photovoltaic device of which the short-circuit current is fed to a current pre-amplifier connected to a lock-in amplifier (Signal Recovery 7280 DSP). The time constant of the lock-in amplifier was chosen to be 1 s and the amplification of the pre-amplifier was increased to resolve low photocurrents. The external quantum efficiency is determined by dividing the photocurrent of the OSCs by the flux of incoming photons, which was obtained using a calibrated silicon (Si) and indium-gallium-arsenide (InGaAs) photodiode.

Synthesis and characterization of: 4,4'-(2,1,3-Benzothiadiazole-4,7-diyl)bis(N,N-diphenylaniline) **(BTD-TPA$_2$):**

4,7-dibromobenzo[c][1,2,5]thiadiazole (0,1 g; 0.34 mmol), 4-(diphenylamino)phenyl)boronic acid (0,2 g; 0,7 mmol), K_2CO_3 (2M, 4 mL) and $Pd(PPh_3)_4$ (35 mg, 0,03 mmol) were dissolved in THF (20 mL). The reaction mixture was then stirred at reflux in the dark for 12 h, then was let cool down and poured into water. The organic layer was dried over $MgSO_4$, concentrated and the residue mixture was purified by column chromatography on silica with CH_2Cl_2/hexane = 3:1 as eluent to obtain the product as a bright orange solid (203 mg, Y= 96%). ^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 7.95-7.93 (m; 4H, PhH); 7.81 (s, 2H, benzodithiazole); 7.37-7.33 (m, 8H, PhH); 7.23-7.12 (m, 16H, PhH). MS (MALDI-TOF): m/z calculated for $C_{42}H_{30}N_4S$: 622.219; found: 622.210.

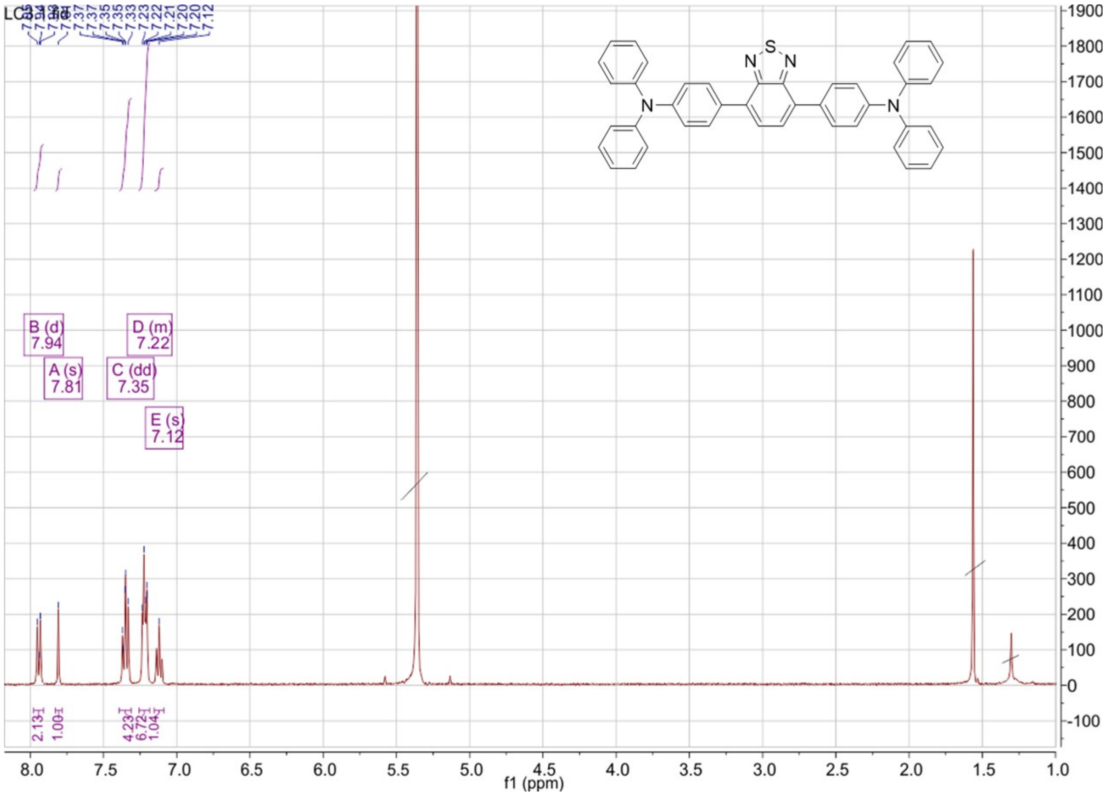

Figure S1. ^{1}H-NMR spectrum of BTD-TPA$_2$ recorded in CD_2Cl_2.

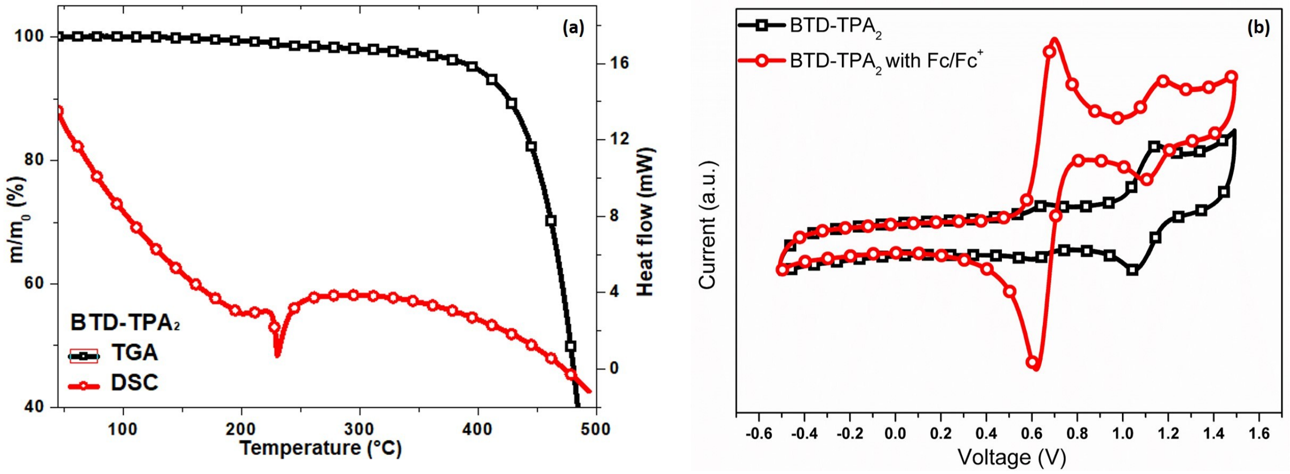

Figure S2. (a) Thermogravimetric analysis (TGA) curves and Differential scanning calorimetry (DSC) recorded for BTD-TPA$_2$, under N_2 atmosphere at a heating rate of 10°C/min; and (b) cyclic voltammogram of BTD-TPA$_2$ in dichloromethane at room temperature [c ~ $1\cdot10^{-3}$ M] with TBAPF [0.1 M] as supporting electrolyte.

Table S1. Summary of the statistical values of PV parameters of the OSCs employing different concentrations of BTD-TPA$_2$ as EBL, calculated on six different samples for each configuration. In bracket, J_{sc} values calculated by integrated EQE spectra.

Concentration BTD-TPA$_2$	**V_{OC} (mV)**	**J_{SC} (mA/cm^2)**	**FF (%)**	**PCE (%)**
40 mM	870 ± 10	6.84 ± 0.9 (6.0)	38.16 ± 3	2.30 ± 0.39
30 mM	930 ± 20	7.96 ± 0.15(7.9)	41.69 ± 1	3.08 ± 0.09
20 mM	940 ± 0	8.53 ± 0.17 (8.5)	54.22 ± 0.3	4.36 ± 0.10
15 mM	940± 0	9.10 ± 0.14 (9.1)	63.28 ± 0.4	5.42 ± 0.08
10 mM	940 ± 0	9.03 ± 0.24 (8.9)	59.18 ± 3	5.04 ± 0.18
5 mM	950 ± 0	7.32 ± 0.19 (7.9)	62.70 ± 0.4	4.35 ± 0.13
2.5 mM	900 ± 5	7.02 ± 0.17 (7.3)	55.63 ± 4	4.17 ± 0.07
1.25 mM	860 ± 0	6.60 ± 0.05 (6.6)	68.40 ± 0.6	3.87 ± 0.01
0 mM	910 ± 4	6.68 ± 0.16 (6.94)	63.82 ± 3.8	3.85 ± 0.20

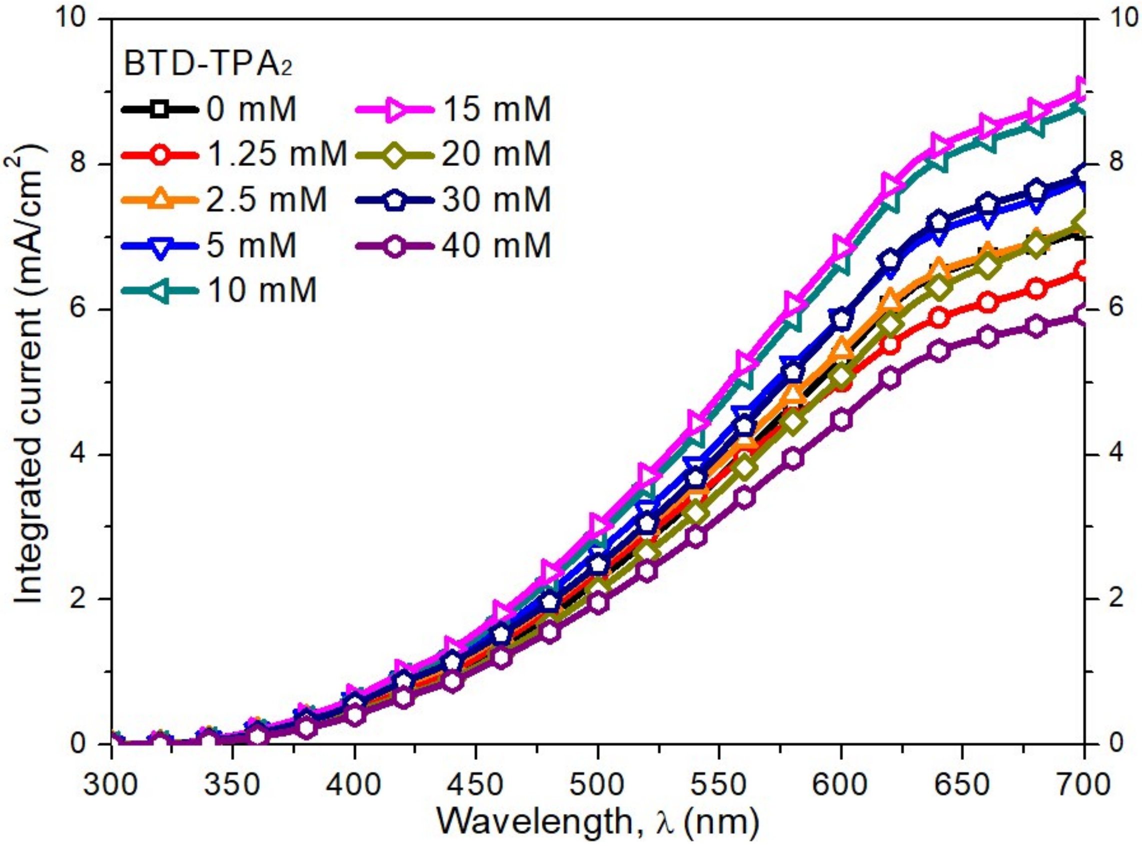

Figure S3. Calculated integrated current derived from Figure 3b.

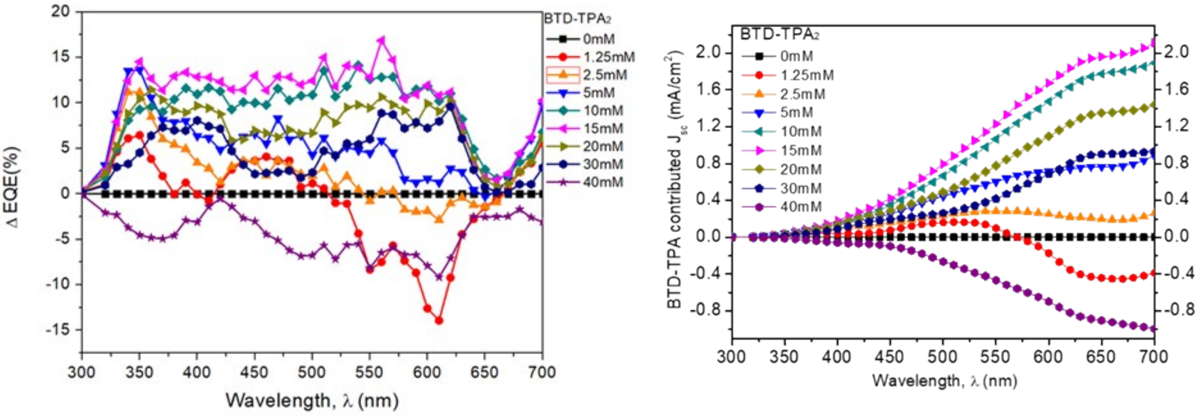

Figure S4. Change in EQE $\{\Delta EQE = EQE_{DBP+BTDTPA_2} - EQE_{DBP}\ (\%)\}$ as function of wavelength for the devices with different concentrations of BTD-TPA$_2$ as EBL and corresponding photocurrent contributed by the BTD-TPA$_2$ as co-donor, which was determined by integrating ΔEQE curve (300-700nm).

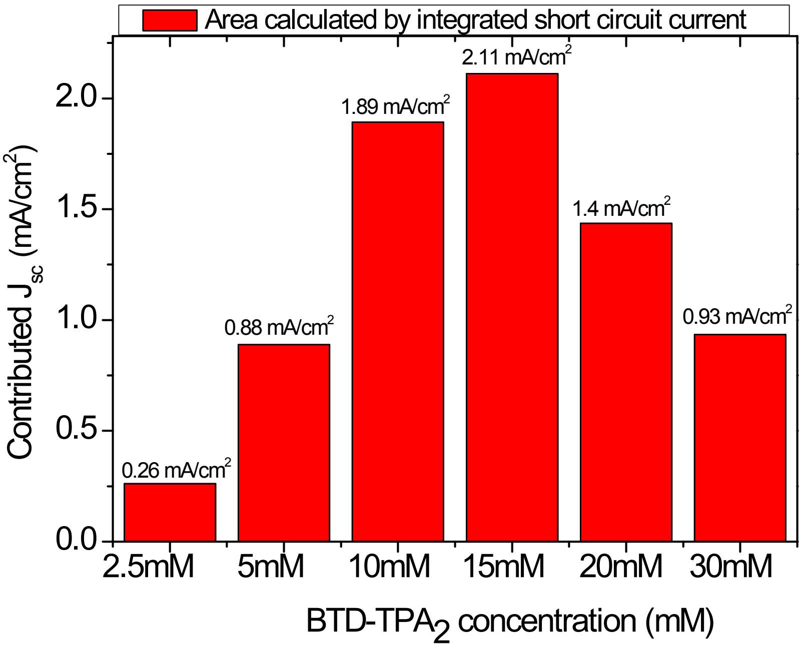

Figure S5. Plot of BTD-TPA$_2$ contributed photocurrent due to co-donor effect as a function of BTD-TPA$_2$ concentration.

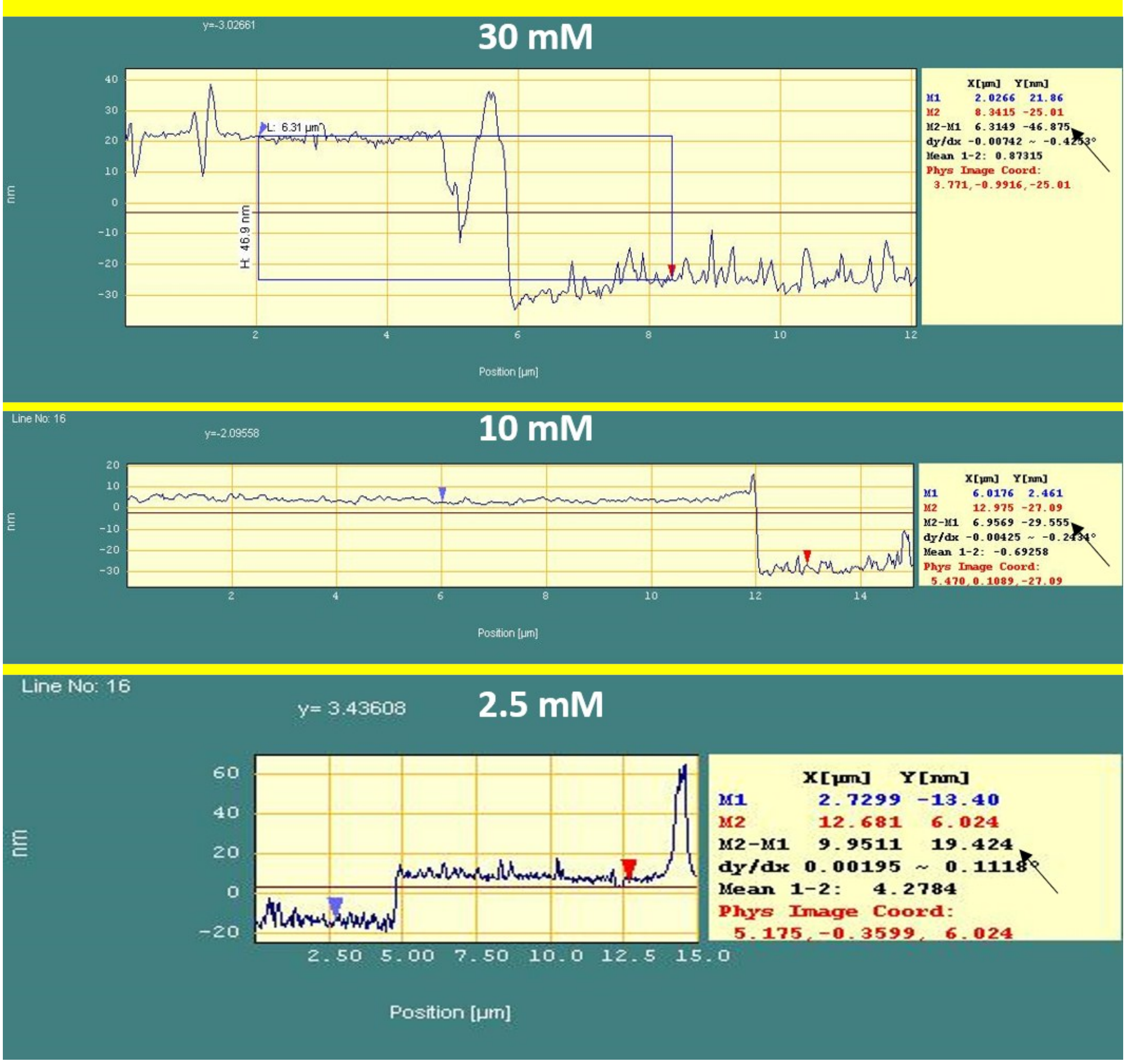

Figure S6. Representative images relative to thickness estimation by AFM, BTD-TPA$_2$ film deposited by spin-coating on top of MoO$_x$ layer.

Table S2. Thickness measured by AFM for each concentration of BTD-TPA$_2$ film deposited by spin-coating on top of MoO$_x$ layer. (solution prepared in chlorobenzene, spin-coating parameters: 4000 rpm, 2000 rpms^{-1}).

Concentration BTD-TPA$_2$	**Thickness (nm)**
40 mM	65
30 mM	45
20 mM	40
15 mM	35
10 mM	30
5 mM	25
2.5 mM	20
1.25 mM	15

Table S3. Summary of photovoltaic parameters of the organic solar cells employing two different concentrations of BTD-TPA$_2$ (15mM and 20mM) as donor and as DBP co-donor using the device architecture: ITO/MoO$_3$(10 nm)/BTD-TPA$_2$(40 or 35 nm)/DBP (0-20 nm)/C$_{70}$(30 nm)/BCP (10 nm)/Ag (100 nm).

Donor configuration	V_{oc} **(mV)**	J_{sc}**(mA/cm^2)**	**FF (%)**	**PCE (%)**
BTD-TPA$_2$ (40 nm)/DBP (0 nm)	930	4.94	52.74	2.44
BTD-TPA$_2$ (35 nm)/DBP (0 nm)	870	4.81	55.63	2.34
BTD-TPA$_2$ (40 nm)/DBP (5 nm)	940	8.01	55.51	4.19
BTD-TPA$_2$ (35 nm)/DBP (5 nm)	940	6.51	58.36	3.59
BTD-TPA$_2$ (0 nm)/DBP (20 nm)	900	6.69	64.86	3.91

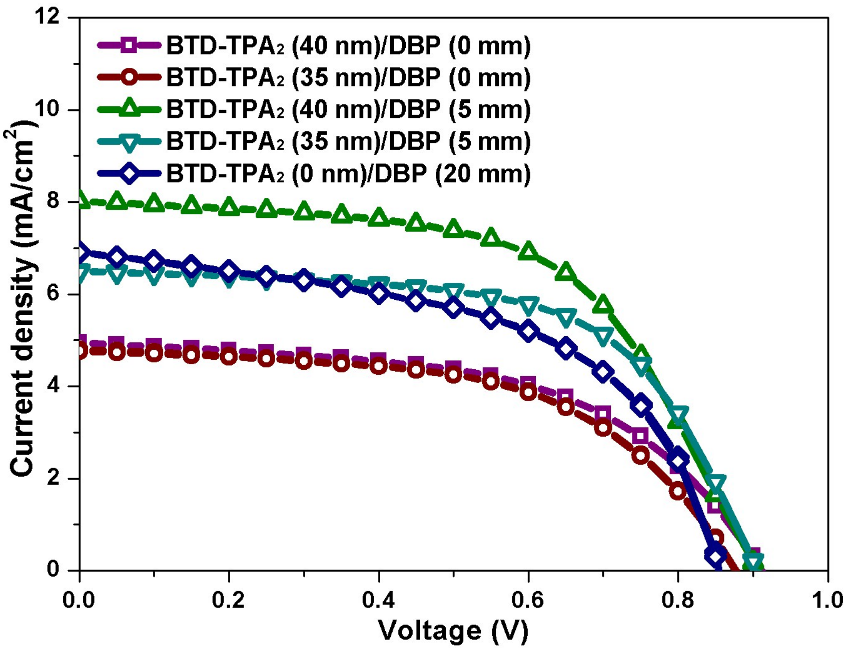

Fig. S7. *J-V* characteristics of organic solar cells fabricated with BTD-TPA$_2$ employed as donor and DBP as co-donor, deposited from two different concentrations.

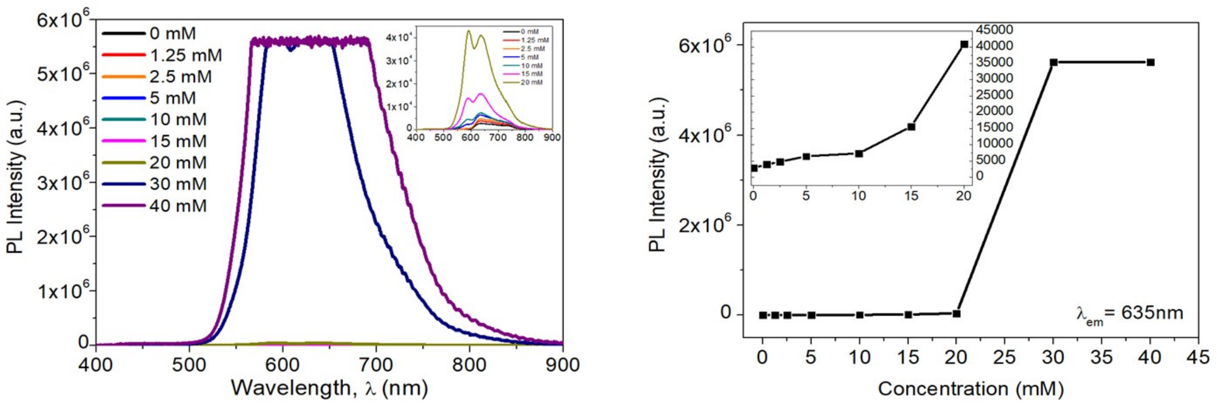

Figure S8. Left) Photoluminescence measurements of the layer stack: Quartz/ MoO_x (10 nm)/BTD-TPA_2/ DBP (15 nm), with the thicker layers (30 and 40 mM, i.e. 45 and 65 nm thick layers) of BTD-TPA_2, exceeding the measurable range, inset shows the PL emission of 0-20mM concentration, Right), Plot of PL intensity of DBP at λ_{em} =635 nm as a function of BTD-TPA_2 concentration.