

Supporting Information for

The Impact of Thermal Treatment On The Performance of Benzo[1,2-b:4,5-b']difuran-Based Organic Solar Cells

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1. Experimental part

1.1. Materials

Toluene was dried over P₂O₅ and freshly distilled prior to use. Other reagents and solvents were purchased commercially as analytical-grade quality and used without further purification.

1.2. Characterization

¹H NMR spectra was recorded using a Bruker AV-400 spectrometer, with tetramethylsilane (TMS) as the internal reference, chemical shifts were recorded in ppm. The UV-Vis absorption spectra were recorded on the SHIMADZU UV-2450 spectrophotometer. For the film state measurements, the three small molecules solution in chloroform were drop-cast on quartz plates. Optical bandgap was calculated from the onset of the absorption band.

1.3. Electrochemistry

In voltammetry measurements, the cathodic polarization of working electrode leads to increase of energy of electrons inside the electrode material. As soon as the energy

of electrons in the working electrode reaches the LUMO energy level of material in solution the exchange of electrons across the electrode/electrolyte interface might happen, which results in the measured current increase. Oppositely, the anodic polarization of working electrode leads to decrease of the energy of electrons in the working electrode. In analogy with LUMO energy level, the achieving of HOMO energy of material in solution should cause the exchange of electrons accompanied by the appearance of detectable currents. The absence of synchronization between the energy levels of electrons in electrode and in the material in solution results in absence of detectable currents in a certain potential ranges (so called capacitive regions). Therefore, the voltammetry is tool towards the assessment of energy levels of material in solution. Being a pulse voltammetry method SWV allows decrease significantly the capacitive contribution into the entire redox responses, which leads to precise measurement of the half wave potentials of redox processes.

However, it should be stressed, that the energy levels assessed from voltammetry measurements might be rationalized only as comparative characteristics. Obviously, the environment of a real photovoltaic device is significantly different from the environment of material of study in electrochemical measurements. Moreover, the working electrode material and electrolyte composition dramatically affects the voltammetric responses. Therefore, the correct comparison of electrochemical energetics of different materials can be carried out only if the electrochemical data has been measured in the same condition.

SWV has been utilized to comparative assess the energy levels of developed materials. As soon as all developed compounds were insoluble in acetonitrile, platinum electrode was modified by drop casting of chloroform solution of appropriate compounds and was used as working electrode in acetonitrile-based

electrolyte. As a result of electrode reaction compounds of study underwent redox transfers and became charged products leaking into the electrolyte. Thus the working electrode has been recovered by polishing and modified with compounds of study each time before the electrochemical measurement.

1.4. Atomic force microscopy (AFM)

Measurements were done with a Digital Instrument Nanoscope IIIa equipped with a type G scanner (Digital Instrument Inc., Santa Barbara, CA, USA). The measurements were done in tapping mode and in air using a Micro Masch NSC 15 silicon cantilever.

1.5. Computational details

Geometries of molecule B1 was performed with the Gaussian package using the B3LYP functional in combination with the cc-pvdz basis set. Alkyl chains have been replaced by a methyl group to reduce computational times. To determine the absorption spectra of the three molecules, the 20 first excited states were calculated with the Dalton package⁴ using the CAM-B3LYP functional⁵ in combination with the aug-cc-pvdz basis set. We chose to use the CAM-B3LYP functional in order to properly describe the charge separation inherent to all donor-acceptor systems.

1.6. Fabrication and characterization of organic solar cells

The solar cells were fabricated in the configuration of the traditional sandwich structure with an indium tin oxide (ITO) glass anode and LiF/Al cathode. Poly(3,4-

ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron P4083, Germany) was filtered through a 0.45 μm filter and spin coated at 3000 rpm for 60 s on the ITO electrode. Subsequently, the PEDOT: PSS film was baked at 120 $^{\circ}\text{C}$ for 30 min in the air to give a thin film with a thickness of 40 nm. A blend of the three small molecules and PC₆₁BM were dissolved in chloroform (CF), and spin-cast at 3500 rpm for 40 s onto the PEDOT:PSS layer. The substrates were then dried at 120 $^{\circ}\text{C}$ for 10 min. The thickness of the photoactive layer is in the range of 105-120 nm measured by Dektak surface profilometer. The cathode LiF (0.6 nm) capped with Al (90 nm) was thermal evaporated under a shadow mask in a base pressure of ca. 5×10^{-6} mbar. The device active area of the OSCs is 4 mm². J-V curves were recorded with a Keithley 2400 Source Meter under AM 1.5G illumination with an intensity of 100 mW/cm² from a solar simulator (Model SS50A, Photo Emission Tech., Inc.).

1.7. Photoluminescence (PL) spectroscopy

PL spectra of thin films were recorded using an Oriel liquid light guide and a Shamrock SR 303i spectrograph coupled to a Newton EMCCD silicon detector. The films were excited using a blue PMM-208G-VT laser pump (4 mW/cm²) with a wavelength of 405 nm.

1.8. Synthesis of small molecule B1

Under the protection of nitrogen, the equimolar amount of compound 2 and DPP-Br (0.2 mmol) add to 10 mL of anhydrous toluene, then add Pd(PPh₃)₄ (10 mg), stir the reaction at 110 $^{\circ}\text{C}$ for 48 hours, cool to room temperature, the mixture was poured into 100 mL of methanol for precipitation, filter, and pass the crude product through

silica gel Column (the eluent is petroleum ether: dichloromethane=1:1 (v/v)) to obtain blue solid B1 (237 mg, yield 85%)

^1H NMR (400 MHz, CDCl_3 , ppm): 8.92(s, 2H), 8.64(s, 2H), 7.63(s, 2H), 7.31(s, 2H), 7.26(s, 2H), 7.08(s, 2H), 4.34(d, 4H), 4.02-3.95(d, 8H), 1.84-1.77(m, 6H), 1.53-1.27 (m, 48H), 0.97-0.85(m, 36H).

TOF-MS: m/z =1396.

Anal. Calcd for $\text{C}_{86}\text{H}_{114}\text{N}_4\text{O}_{12}$ (%): C, 74.00; H, 8.23; N, 4.01. Found (%): C, 74.02; H, 8.21; N, 4.03.

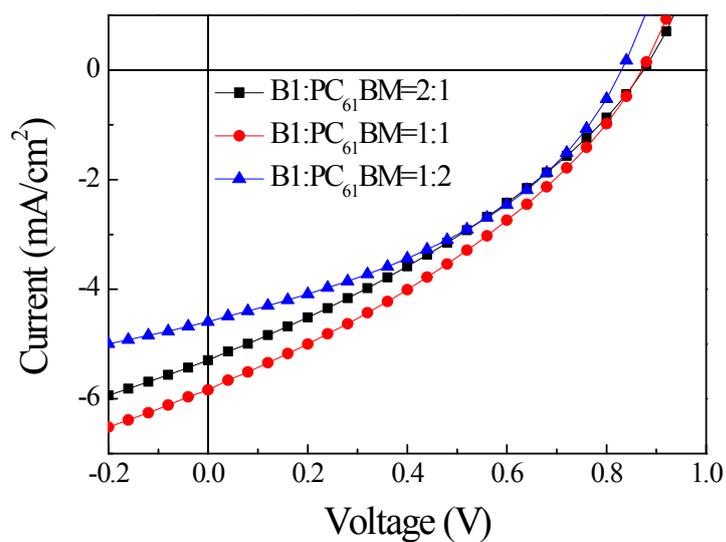


Fig. S1 J-V curves of the PSCs based on B1/PC₆₁BM under illumination of AM1.5G, 100 mW/cm².

Tab. S1 Photovoltaic parameters of the OSCs based on B1/PC₆₁BM (average PCE of 12 devices).

Active layer	V_{oc} (V)	J_{sc} (mAcm ⁻²)	FF (%)	PCE (%)
B1:PC ₆₁ BM=2:1	0.87	5.3	33.0	1.5
B1:PC ₆₁ BM=1:1	0.87	5.8	34.0	1.7
B1:PC ₆₁ BM=1:2	0.83	4.6	40.0	1.5

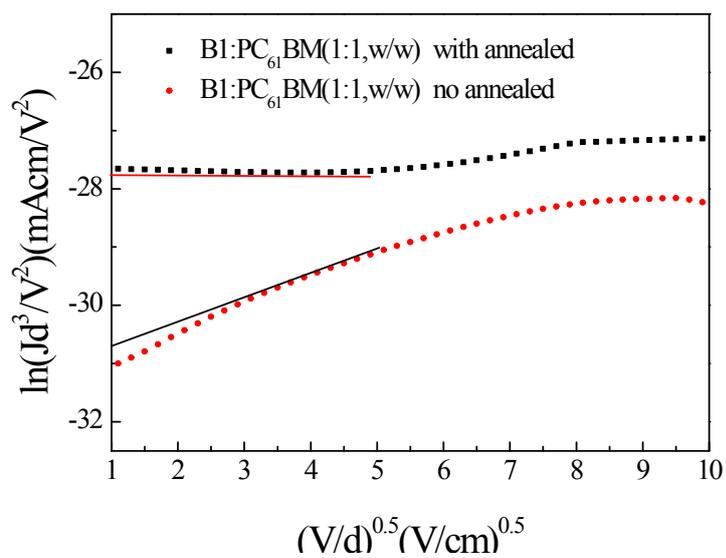


Fig. S2 $\ln(Jd^3 / V^2)$ vs $(V / d)^{0.5}$ plots of the blends of B1/PC₆₁BM for measurement of the hole mobilities by SCLC method.