

Supporting Information

Linear-Shaped Low-Bandgap Asymmetric Conjugated Donor Molecule for Fabrication of Bulk Heterojunction Small-Molecule Organic Solar Cells

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S1.1: Synthesis of intermediate 4,7-dibromobenzothiadiazole (2)

In a 250 ml two-neck flask, 2,1,3-benzothiadiazole (1) (10 g, 73.44 mmol) and 19.87 ml (13.34 g, 164.88 mmol) of 48% HBr were transferred and degassed for 10 min, followed by slow addition of 11.13 g of Br₂ (34.62 ml, 216.65 mmol) at 150 °C. Immediately after adding Br₂, the reaction mixture starts precipitating, which is significantly assisted by further addition of 40 ml HBr and heating at the same temperature for the next 2 h. The reaction mixture was then filtered and treated with DI water several times to obtain an off-white precipitate. To remove the excess bromine from the crude, an aqueous sodium thiosulfate (10%) solution was used until the neutral pH point. The dried crude was then transferred to a beaker containing 200 ml ethyl alcohol and allowed to crystallize at room temperature. White needle-like crystals (20.8 g, yield= 96%) were obtained from the recrystallization process in a mixed solution of ethyl alcohol and chloroform. ¹H NMR (400 MHz, CDCl₃, ppm): 7.75 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): 153.1, 132.4, 113.9. MS, m/z; calculated for [C₆H₂Br₂N₂S]⁺:293.973, found 293.971.

S1.2: Synthesis of monomer 4,7-dithienyl-2,1-3-benzothiadiazole (4)

Intermediate 2 (3.0 g, 10.21 mmol) was dissolved in dry tetrahydrofuran (THF; 120 ml) and purged with nitrogen for 10 min before adding 2-(tributylstannyl)thiophene (11.43 g, 30.63 mmol), followed by 3 mol% PdCl₂(PPh₃)₂. The resultant reaction mixture was heated to reflux temperature for 24 h. The cooled reaction mixture was then poured into a separating funnel and rinsed with dichloromethane (DCM) and DI water multiple times. The obtained organic layer was transferred to a beaker and dried with portion-wise addition of anhydrous MgSO₄ before concentrating with a rotary evaporator. The obtained product was preabsorbed on silica gel to prepare a slurry and purified by the column chromatography technique, where hexane and ethyl acetate (10:1) were used as the eluents. The chromatograms were collected and dried to obtain the pure product (2.30 g, yield=75%) as shiny red crystals. ¹H NMR (400 MHz, CDCl₃, ppm):7.91 (dd, 2H), 7.67 (s, 2H), 7.25 (dd, 2H), 7.01 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): 152.7, 139.1, 128.2, 127.4, 126.9, 126.5, 125.7. MS, m/z; calculated for [C₁₄H₈N₂S₃]⁺:299.985, found 299.984.

S1.3: Synthesis of 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (5)

Compound 5 was synthesized under dark conditions by dissolving monomer 4 (2.5 g, 8.32 mmol) in 80 ml of absolute CHCl₃ at 0 °C under an inert atmosphere. After complete mixing, about 3.70 g (20.8 mmol)

of NBS was added, and the reaction mixture was stirred overnight. The reaction was quenched with a small volume of DI water, and the red precipitate was filtered off and washed with excess water repeatedly. Then dry crude was first dissolved in a small portion of ethyl alcohol and then recrystallized from a solution of ethyl alcohol and chloroform to obtain dark red crystals (2.17 g, yield= 57%). ^1H NMR (400 MHz, CDCl_3 , ppm): 7.81 (d, $J = 4.4$, Hz, 2H), 7.79 (s, 2H), 7.16 (d, 3.92 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): 154.6, 138.9, 127.6, 127.1, 126.7, 125.2, 124.9. MS, m/z ; calculated for $[\text{C}_{14}\text{H}_6\text{Br}_2\text{N}_2\text{S}_3 + \text{H}]^+$: 458.803, found 458.807.

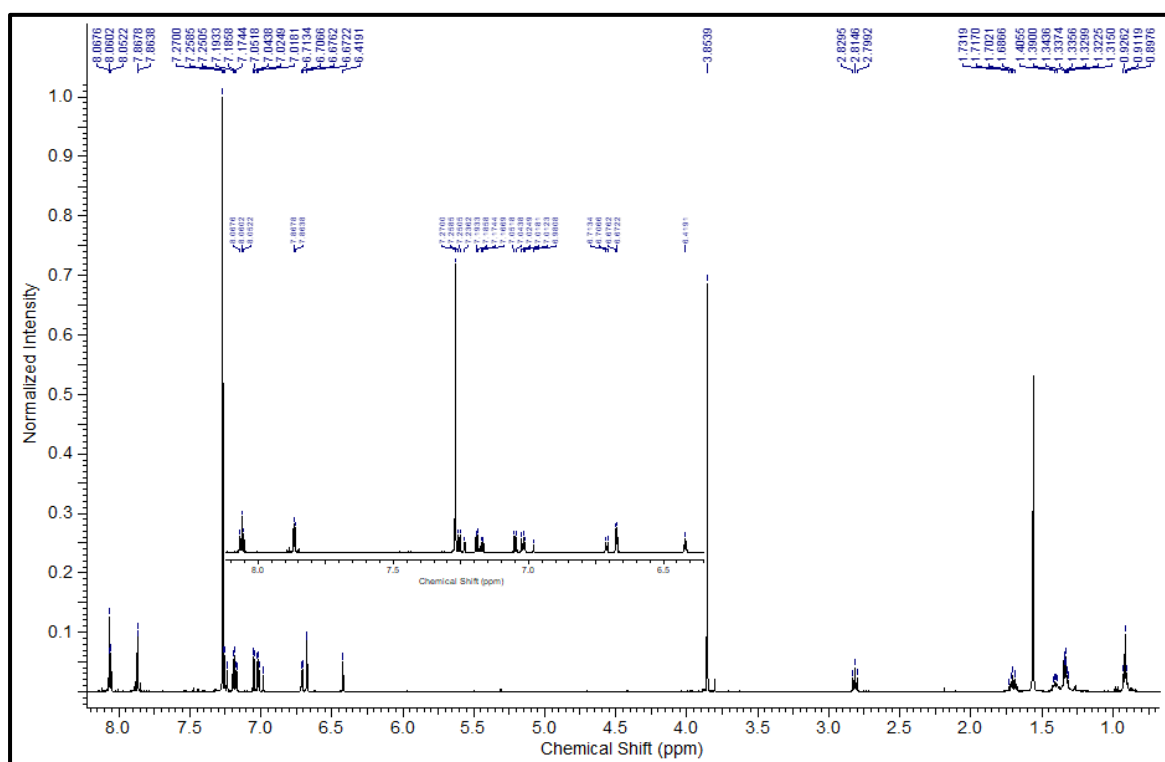


Figure S1. ^1H NMR spectrum of the MBTR molecule.

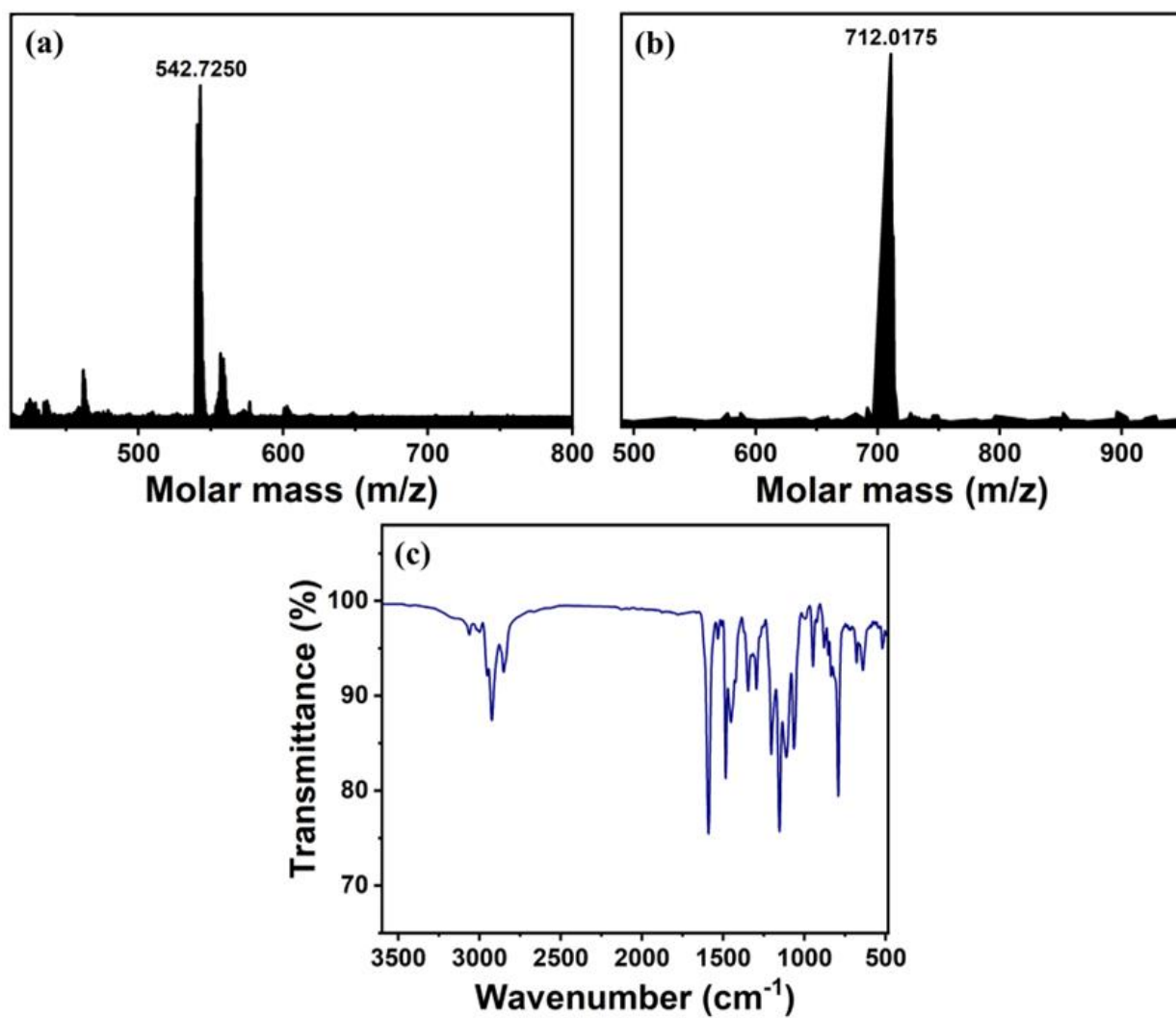


Figure S2. Mass spectroscopy plots of (a) intermediate 7 and (b) MBTR molecule; (c) FTIR spectra of MBTR molecule.

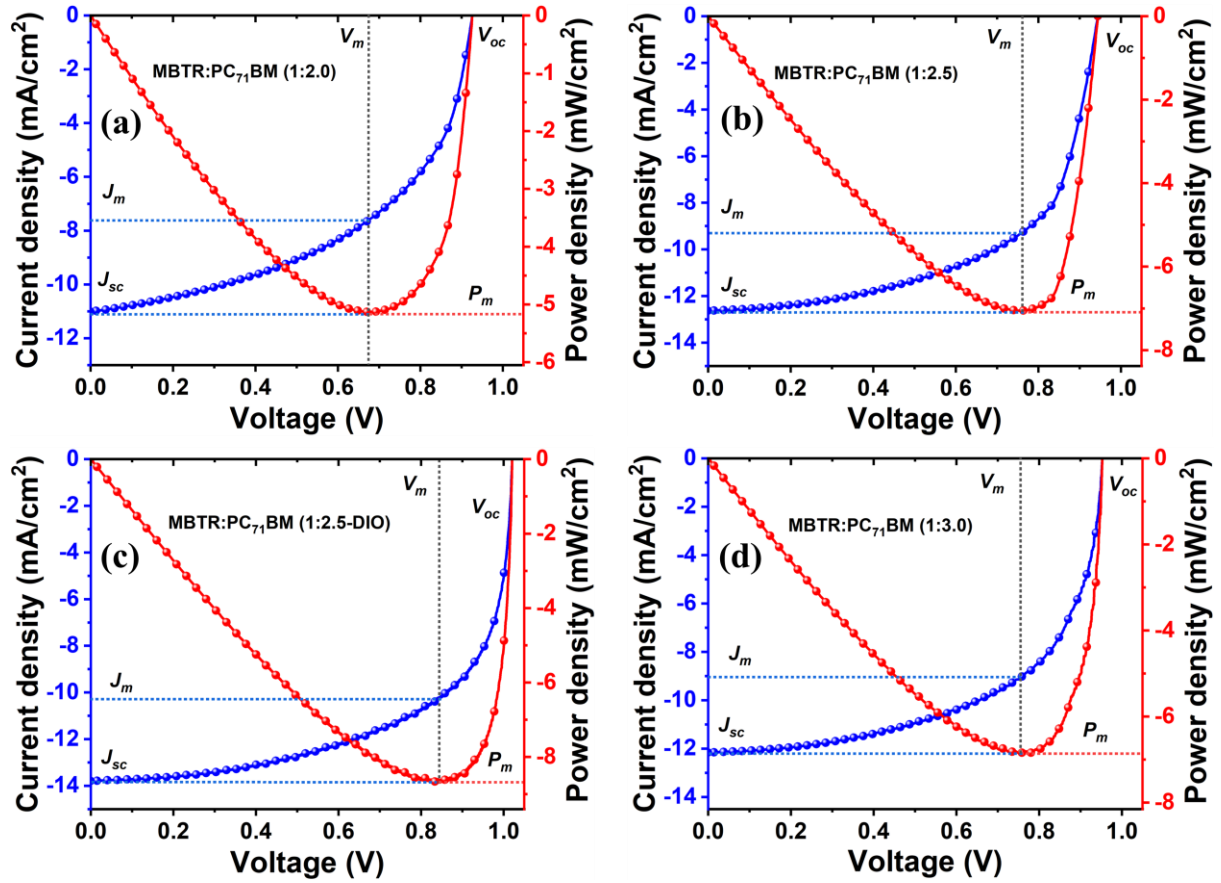


Figure S3. 4th quadrant I-V characteristics of BHJ OSCs with different w/w% ratio of MBTR:PC₇₁BM; (a) MBTR:PC₇₁BM (1:2.0), (b) MBTR:PC₇₁BM (1:2.5), (c) MBTR:PC₇₁BM (1:2.5) with DIO and (d) MBTR:PC₇₁BM (1:3.0).

S.2 FF of BHJ OSCs

The accuracy of FF for organic devices is investigated by the fourth quadrant I-V characteristics of MBTR:PC₇₁BM with the varying donor: acceptor (w/w% ratio) content under the illumination of 1.5 A.M. at 100 mW/cm². FF is characterized as maximum electrical power (P_m) from the solar device at the maximum voltage (V_m) and current (J_m) associated to the product of V_{oc} and J_{sc} [1-3]. The FF is calculated from the expression:

$$FF = \frac{V_m J_m}{V_{oc} J_{sc}} \times 100$$

where $P_m = V_m J_m$

The PCE can be expressed by the following equation:

$$PCE = \frac{FF V_{oc} J_{sc}}{P_{light}}$$

The P_m is calculated with the help of the fourth quadrant I-V curve using the equation as 5.15 mW/cm², 7.05 mW/cm², 8.77 mW/cm² and 6.82 mW/cm² for MBTR:PC₇₁BM (1:2.0), MBTR:PC₇₁BM (1:2.5), MBTR:PC₇₁BM (1:2.5) with DIO and MBTR:PC₇₁BM (1:3.0).

References

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