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Synthesis and characterization of benzobisthiazole based polymers as donor materials for organic solar cells

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Materials and instrumentation

All solvents and reagents were purchased from Sigma-Aldrich or Acros Organics and used as received or purified according to standard procedures.

Absorption spectra were measured on Avantes AvaSpec-2048 optical fiber spectrometer. The optical spectra of thin films were recorded using 2-channel AvaSpec-2048-2 optical fiber spectrometer integrated inside the glove box.

AFM images were obtained using a NTEGRA PRIMA instrument (NT-MDT, Russia).

Cyclic voltammetry measurements were performed for thin films (150–250 nm) of polymer **P1** deposited on a glassy carbon disc electrode following the previously reported procedure.[1]

The thermal properties of the polymers were investigated by thermal gravimetry analysis (TGA) using a METTLER TOLEDO TGA/DSC 3+ instrument (Mettler-Toledo AG, Analytical, Switzerland) under nitrogen with a heating rate of 15 ºC min^{-1}.

Synthesis

Polymer P1

The monomers **1** (0.300 g, 0.206 mmol) and **2** (0.125 g, 0.206 mmol) were introduced into a 50 mL round-bottom three necked flask equipped with a condenser. Anhydrous toluene (20 mL), bis(dibenzylideneacetone)palladium(0) (6 mg, 5% mol) and tri(*o*-tolyl)phosphine (6 mg, 10% mol) were added. The reaction mixture was deaerated and heated at reflux. The polycondensation reaction was terminated by addition of excess of trimethyl(thiophen-2-yl)stannane and then bromobenzene when the average molecular weight of polymer did not increase within 3-4 h. Then the reaction mixture was cooled down to room temperature and crude polymer was precipitated by addition of 100 mL of methanol. The polymer was then subjected to Soxhlet extraction with acetone, hexane, dichloromethane, and chlorobenzene. The chlorobenzene fraction was concentrated on rotary evaporator to ~20 mL and polymer **P1** was obtained by precipitating with 50 mL of methanol followed by drying in vacuum. The total yield of the r **P1** was 54%. M_w = 58 kDa, M_w/M_n = 1.7.

Polymer P2

Polymer **P2** was synthesized and purified according the procedure given for polymer **P1** from compound **1** (0.300 g, 0.206 mmol) and compound **3** (0.072 g, 0.206 mmol). Yield = 65%. M_w= 62 kDa, M_w/M_n=1.5

Device fabrication

The conjugated polymer **P1** (10 mg) or **P2** (8 mg) and $PC_{71}BM$ (8-16 mg) were dissolved together in 1 mL of 1,2-dichlorobenzene while stirring in air at 70°C for 12 h. The blend solutions were filtered through a 0.45 μm PTFE syringe filter and subjected to blade-coating (ZAA 2300 Automatic Film Applicator, Zehntner GmbH Testing Instruments, Switzerland) on the top of the annealed PEDOT:PSS (Clevios HTL) films deposited on the patterned ITO electrodes. The active layer thickness was varied from 110 to 200 nm by changing the speed of blade movement. The obtained films were transferred immediately inside the glove box and thermally annealed in an argon atmosphere at 95 °C for 10 min. The top electrode comprising Mg (30 nm) and Al (60 nm) was deposited by thermal evaporation at the pressure ~ 4×10^{-6} mbar in a vacuum chamber integrated inside the MBraum glove box. The active area of photovoltaic cells was ~ 30 mm^2 as it was defined by a shadow mask.

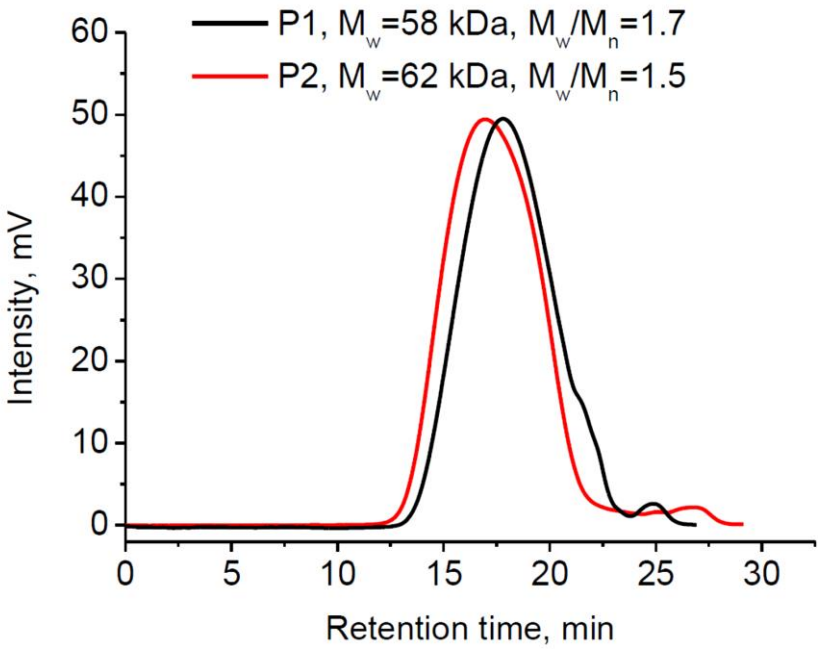

Figure S1 GPC chromatogram of conjugated polymers **P1** and **P2**. Conditions: chlorobenzene 0.5 mL/min, 80°C, GPC Pheneomenex Luna - phenogel 5μ column (0.78×30 cm).

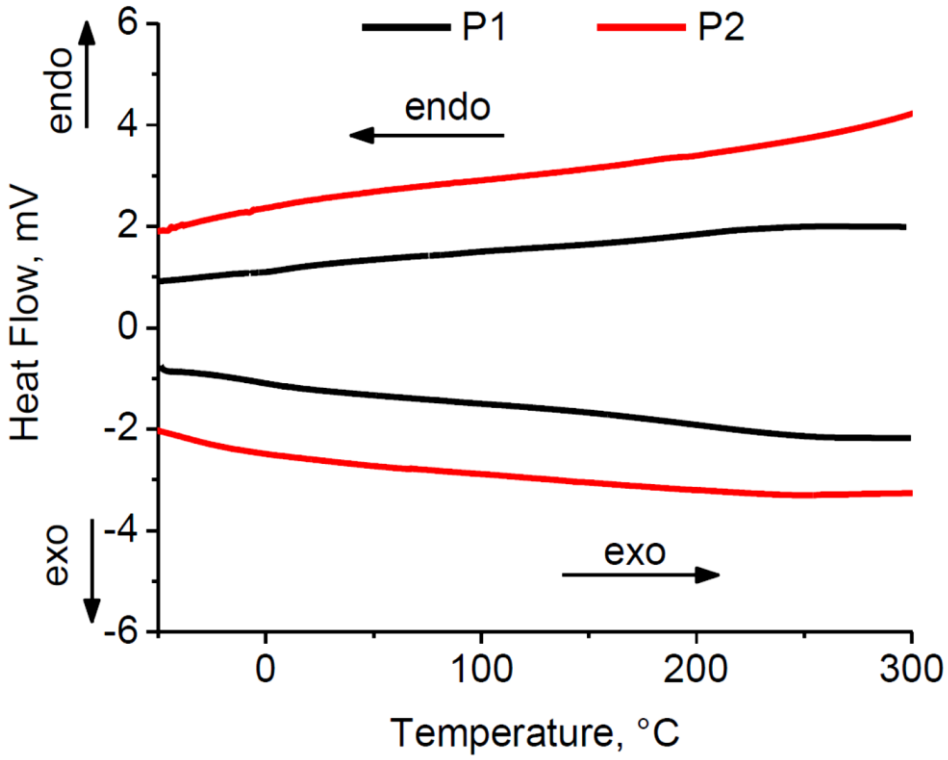

Figure S2 DSC curves (heating rate of 10°C min^{-1} under N_2) of conjugated polymers **P1** and **P2**.

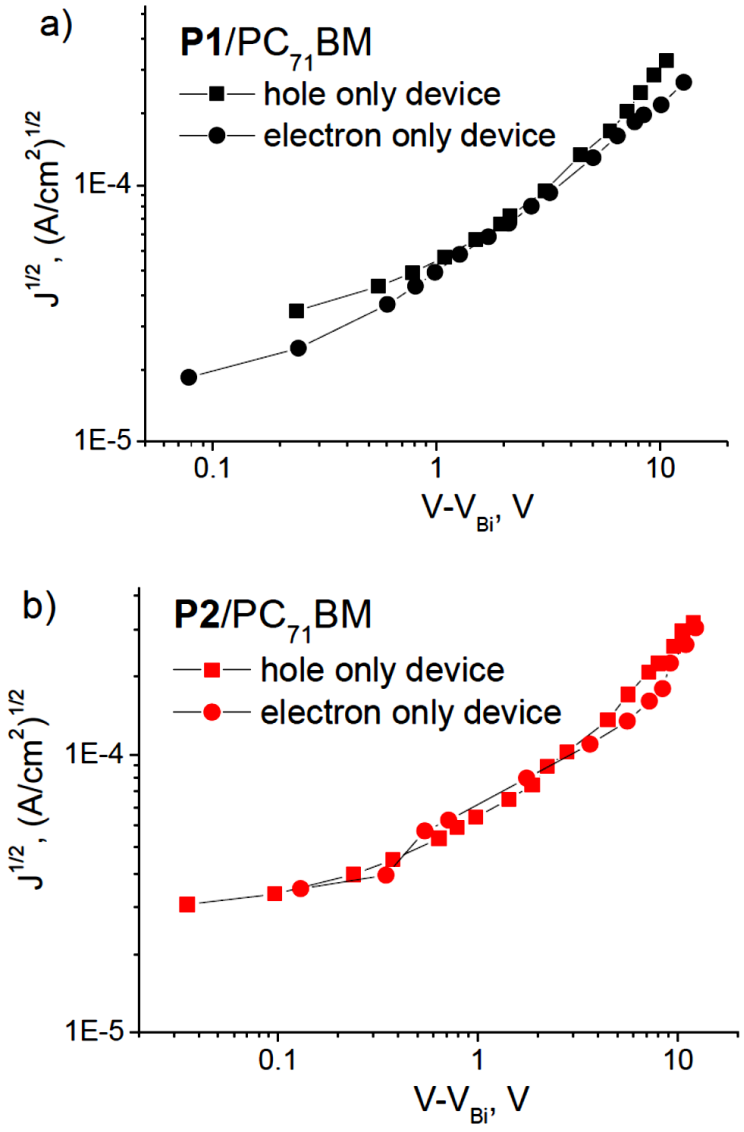

Figure S3 $J^{1/2}$-V plots of electron-only and hole-only devices based on **P1**/$PC_{71}BM$ *(a)* and **P2**/$PC_{71}BM$ *(b)* blends.

References

1. A. V. Akkuratov, F. A. Prudnov, L. N. Inasaridze, and P. A. Troshin, *Tetrahedron Lett.*, 2017, **58**, 97.