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Synthesis and photovoltaic properties of novel (X-DADAD)$_n$ conjugated polymers with fluorene and phenylene blocks

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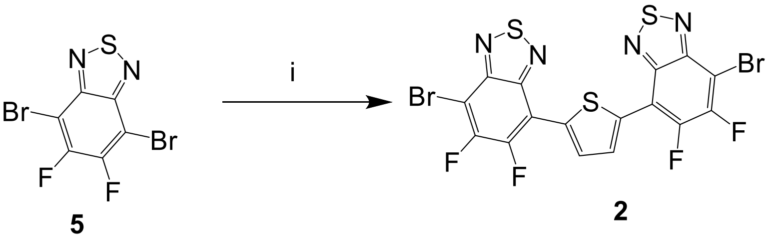
Materials and instrumentation

All solvents and reagents were purchased from Sigma-Aldrich or Acros Organics and used as received or purified according to standard procedures. Acceptor [70]PCBM with a purity of 99% was purchased from Sigma-Aldrich, and PEDOT:PSS from Heraues Clevios. Compounds **1**,[S1] **3**[SError! Bookmark not defined.] and **4**[S2] were obtained as reported previously. Absorption spectra were measured on an Avantes AvaSpec-2048 optical fiber spectrometer. The optical spectra of thin films were recorded with an AvaSpec-2048-2 two-channel optical fiber spectrometer integrated into a glove box. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE 500 instrument.

Synthesis



Scheme S1 *Reagents and conditions*: i, 2,5-bis(trimethylstannyl)thiophene, Pd(PPh$_3$)$_4$, toluene, reflux.

Synthesis of compound **5**

Compound **5** was prepared in accordance with the previously reported procedure.[S3]

Synthesis of compound **2**

Compound **5** (5.6 g, 17 mmol) and 2,5-bis(trimethylstannyl)thiophene (1.74 g, 4.2 mmol) were placed under an inert atmosphere in a two-necked flask equipped with a reflux condenser. Toluene (50 ml) and tetrakis(triphenylphosphine)palladium(0) (10 mg) were then added. The mixture was heated under reflux for 24 h, and then the solvent was removed by evaporation under reduced pressure. The precipitate formed was collected by filtration and washed with methanol. The compound was then purified by vacuum sublimation (10^{-3} mbar). The yield of red crystalline powder of compound **2** was 30%.

^{1}H NMR (CDCl$_3$, 500 MHz) δ: 8.37 (s, 2H). ^{19}F NMR (CDCl$_3$) δ: −120.04 (d, 2F), −125.13 (d, 2F). Found (%): C, 33.01; H, 0.35; N, 9.62; S, 16.52. Calc. for $C_{16}H_2Br_2F_4N_4S_3$ (%): C, 33.01; H, 0.35; Br, 27.45; F, 13.05; N, 9.62; S, 16.52.

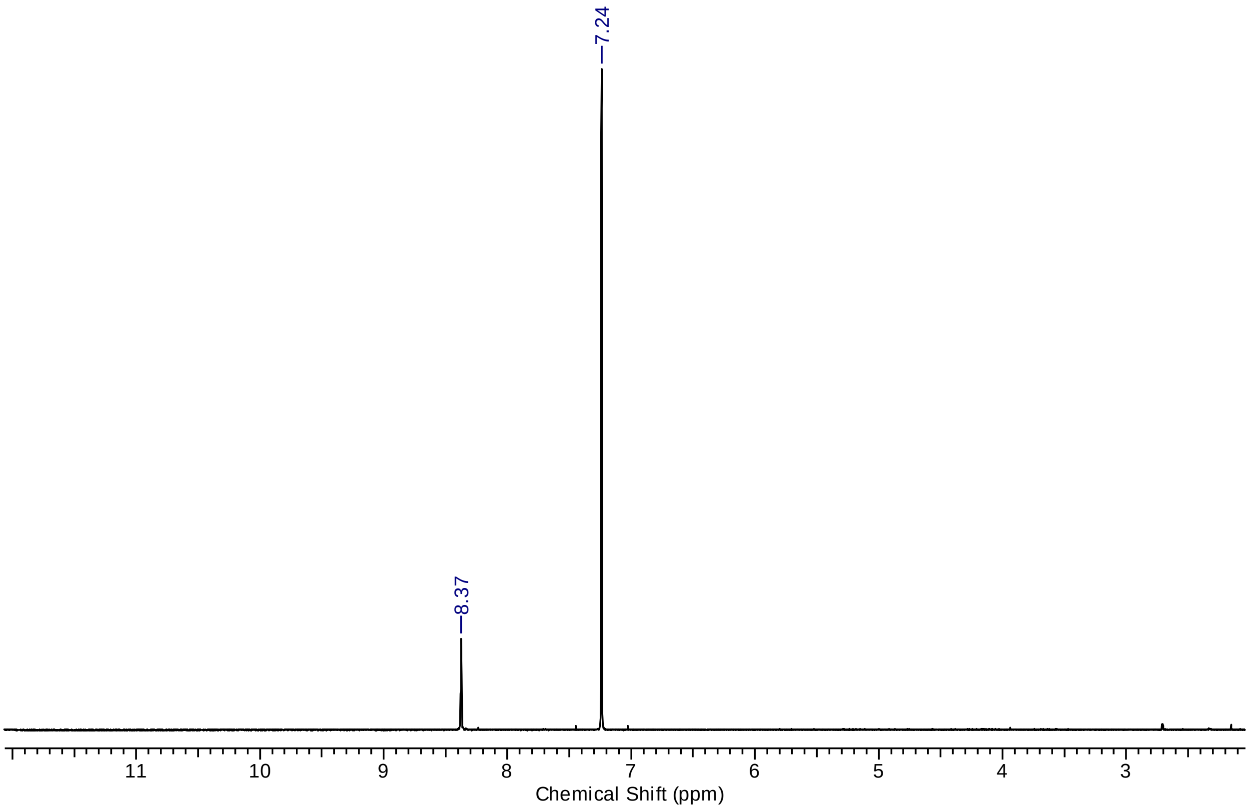


Figure S1 ^{1}H NMR spectrum of compound **2**.

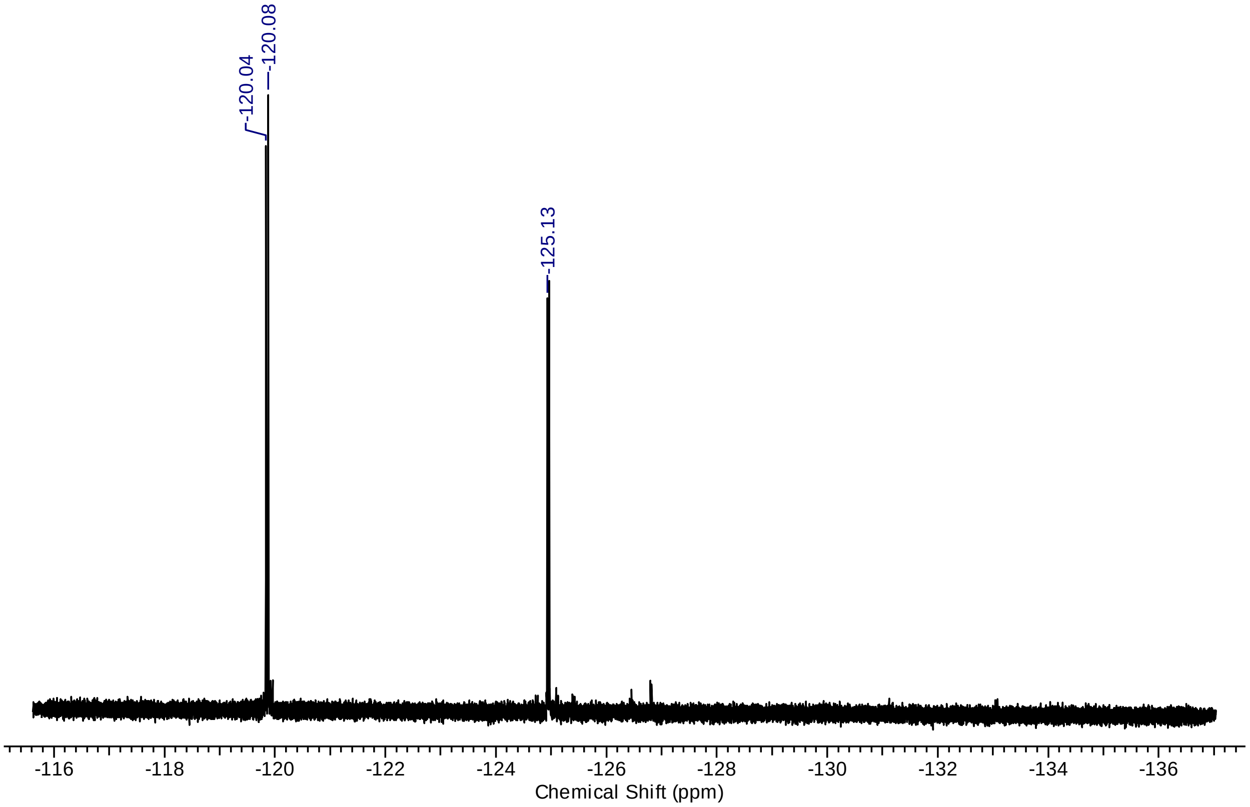


Figure S2 ^{19}F NMR spectrum of compound **2**.

Thermal properties

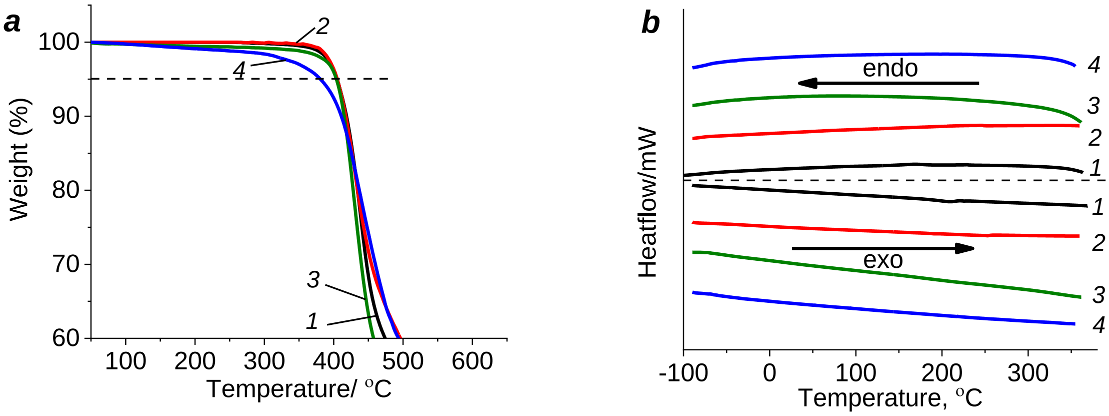


Figure S3 (*a*) TGA and (*b*) DSC curves (heating rate of 15°C min^{-1}, N_2) for conjugated polymers **P1**–**P4** (curves *1*–*4*).

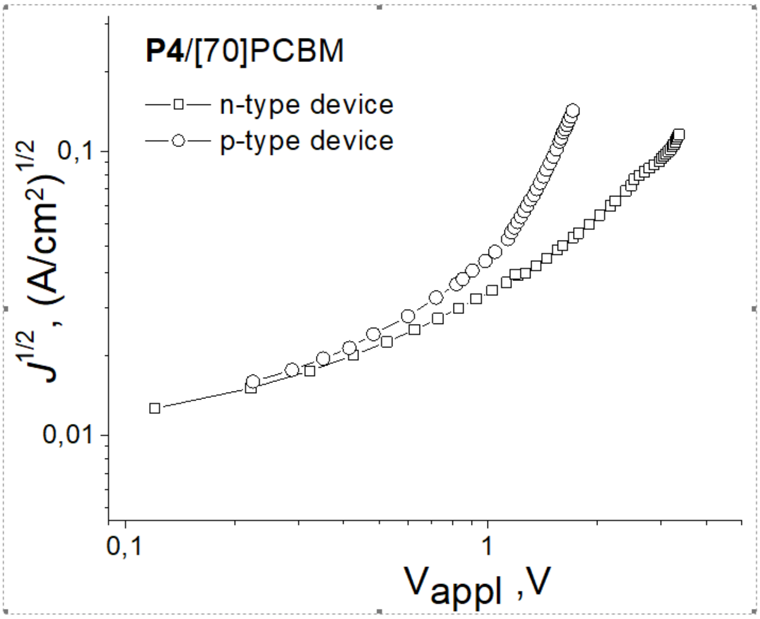


Figure S4 $J^{1/2}$–V plots for electron-only and hole-only devices based on **P4**/[70]PCBM.

Thermal properties

The thermal properties of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a METTLER TOLEDO TGA/DSC 3+ instrument in a nitrogen atmosphere at a heating rate of 10 ºC min^{-1}.

Cyclic voltammetry measurements

Cyclic voltammetry measurements were performed for thin films (150–250 nm) deposited on a glassy carbon disc electrode (d = 5 mm, BAS Inc.) by drop casting from 1,2-dichlorobenzene. The measurements were carried out in a three electrode electrochemical cell using a 0.1 M Bu_4NPF_6 solution in acetonitrile as a supporting electrolyte, a platinum wire as a counter electrode and a silver wire immersed in a 0.01 M $AgNO_3$ solution in 0.1 M TBAP (MeCN) as a reference Ag/Ag$^+$ electrode. Ferrocene was used as an internal standard. The electrolyte solution was purged with argon before measurements. Voltammograms were recorded on an ELINS P-20X instrument at room temperature with a potential sweep rate of 50 mV s^{-1}.

Fabrication of photovoltaic devices

The polymer (5–15 mg) and [70]PCBM (5–15 mg) were dissolved together in 1,2-dichlorobenzene (1 ml) with stirring at room temperature for 48 h. The resulting solution was filtered through a 0.45 mm PTFE syringe filter and spin-coated at 400–1000 rpm for 150 s over annealed PEDOT:PSS films deposited on patterned ITO electrodes. The obtained films were immediately transferred inside the glove box. The top electrode, composed of Mg and Al, was deposited by thermal evaporation at a pressure below 4 × 10^{-6} mbar in a vacuum chamber integrated into the MBraun glove box. The size of the active area in photovoltaic cells was ~0.3 cm^2, since it was defined by the shadow mask.

Characterization of organic solar cells

The current–voltage (*J–V*) characteristics of the devices were obtained under simulated 100 mW cm^{-2} AM1.5 solar irradiation provided by a KHS Steuernagel solar simulator integrated into the MBraun glove box. The illumination intensity was checked each time before measurements using a calibrated silicon diode with a known spectral response. The *J–V* curves were recorded in an inert atmosphere using a Kethley 2400 source–measurement unit. The active areas of all devices were measured with good accuracy immediately after the *J–V* measurements to estimate the short circuit current density. The obtained J_{SC} values were confirmed by integrating the external quantum efficiency (EQE) spectra against the standard AM1.5G spectrum. The EQE spectra were measured in an inert atmosphere using a specially designed setup (LOMO instruments, Russia).

References

S1 I. E. Kuznetsov, P. M. Kuznetsov, M. I. Ustinova, K. E. Zakirov, P. A. Troshin and A. V. Akkuratov, *Phys. Status Solidi A*, 2021, **218**, 2000816, doi: 10.1002/pssa.202000816.

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S3 J. Kim, M. H. Yun, G.-H. Kim, J. Lee, S. M. Lee, S.-J. Ko, Y. Kim, G. K. Dutta, M. Moon, S. Y. Park, D. S. Kim, J. Y. Kim and C. Yang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7523, doi: 10.1021/am500891z.