



Supporting Information

for *Macromol. Rapid Commun.*, DOI: 10.1002/marc.201600377

Effect of Broken Conjugation on the Stretchability of Semiconducting Polymers

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1. Experimental methods

Materials

DPP-x polymers used for this work were described in a previous study by Zhao et al.,^[1] including the synthesis method and characterization via NMR, TGA, DSC, AFM, GIXRD and OFET device characterization. Chloroform, *ortho*-dichlorobenzene (ODCB), acetone, isopropyl alcohol (IPA), Zonyl (FS-300), eutectic gallium-indium (EGaIn), and [60]PCBM were obtained from Sigma-Aldrich and used as received. DMSO was purchased from BDH with purity of 99.9%. PEDOT:PSS (Clevios PH1000) was purchased from Heraeus. PDMS (Sylgard 184, Dow Corning) was prepared according to the manufacturer's instructions at a ratio of 10:1 (base:crosslinker) and cured at room temperature for 36 h. For buckling-based experiments, the PDMS were cut into rectangular pieces ($l = 8$ cm, $w = 1$ cm, $h = 0.3$ cm); for crack-onset strain experiments, the rectangular pieces had the dimensions $l = 8$ cm, $w = 1$ cm, $h = 0.15$ cm.

Tensile moduli and crack-onset strains

For the measurements of the mechanical properties, the polymer films were prepared on glass substrates (2.5 cm $\times$ 2.5 cm) by spin-coating. The glass substrates were cleaned by bath sonication of Alconox solution, deionized water, acetone, and isopropanol for 10 min each and dried under compressed air before they were plasma treated for 3 min (30 W, 200 mTorr ambient air). All polymer solutions were prepared by dissolution in chloroform at a concentration of 15 mg mL⁻¹. The solution was stirred at room temperature for 24 h before filtered through a 1 μ m glass microfiber filter. For the measurement of the tensile modulus, three different thicknesses of each polymer sample were prepared by varying the spin speed. The thickness range was controlled to be between 100 nm and 300 nm. The tensile modulus was measured by the

buckling technique, where a film is deposited on an elastic substrate.^[2,3] Upon compression, the rigid film adopts a sinusoidal wrinkling pattern that can be related to the tensile modulus of the film. For the crack-onset strain, all films were prepared to have similar thicknesses, between 150 nm to 200 nm. The polymer films transferred onto unstrained PDMS were then stretched using a computer-controlled linear actuator with a step size of 0.5% strain. Each step was imaged through an optical microscope to observe the generation of cracks. The crack-onset strain of each film was defined as the strain at which the first crack was observed.

Photovoltaic properties

The photovoltaic devices were fabricated with the following architecture: PEDOT:PSS/polymer:PCBM/EGaIn. We first deposited a layer of PEDOT:PSS from an aqueous solution containing 92.9 wt% Clevios PH 1000 (~0.9–1.2 wt% PEDOT:PSS), 7 wt% DMSO, and 0.1 wt% Zonyl fluorosurfactant as the transparent anode. The solution was filtered with a 1 μm glass microfiber syringe filter and then spin-coated at a speed of 500 rpm for 4 min, followed by 2000 rpm for 30 s. The films were subsequently dried at 150 °C for 30 min, resulting in a thickness of ~150 nm. The photoactive layers were deposited from spin-coating at a speed of 500 rpm for 4 min, followed by 2000 rpm for 30 s from mixtures of 1:2 polymer:[60]PCBM (by mass) dissolved in 1:4 chloroform:ODCB at a concentration of 15 mg mL⁻¹. The samples were then immediately placed in a nitrogen-filled glovebox. The electrical contacts were made by depositing EGaIn droplets (extruded by hand from a syringe) as the top contacts. The photovoltaic properties were measured in a nitrogen-filled glovebox using a solar simulator with a 100 mW cm⁻² flux that approximated the solar spectrum under AM 1.5G conditions (ABET Technologies 11016-U up-facing unit calibrated with a reference cell with a KG5 filter). The

current density versus voltage was measured for both dark and under illumination using a Keithley 2400 SourceMeter.

2. Structural characterization of polymers

Detailed characterization for the polymers used in this work has been previously performed and reported by Zhao et al.^[1] The physical properties are reproduced here for convenience. The number-average molar mass and polydispersity were measured by high temperature gel permeation chromatography (GPC) using trichlorobenzene as the eluent at 180 °C and polystyrene for calibration. Decomposition temperatures (T_d) were evaluated by thermal gravimetric analysis (TGA). Melting temperatures (T_m) of DPP-70 and DPP-100 were measured from differential scanning calorimetry (DSC). UV-Vis spectra were taken from dichlorobenzene solutions and spin-coated thin films. The thin films were annealed at 150 °C. E_g^{opt} were calculated from the onset absorption using the equation $E_g^{opt} = 1240/\lambda_{onset}$. HOMO energy levels were obtained from ultraviolet photoemission spectroscopy (UPS) and LUMO energy levels were calculated using the equation $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

Table S1. Physical properties of the DPP polymers, reproduced from Zhao et al.^[1]

	M_n (kDa) / PDI	T_d (°C)	T_m (°C)	λ_{max}^{abs} (nm)		λ_{onset}^{abs} (nm)	E_g^{opt} (eV)	energy levels (eV)	
				solution	film	film		E_{HOMO}	E_{LUMO}
DPP-0	30.7 / 3.61	400		740, 811	725, 789	937	1.32	-4.97	-3.65
DPP-30	23.0 / 3.24	400		729	708	925	1.34	-5.01	-3.67
DPP-50	19.5 / 2.60	399		699	687	915	1.36	-5.08	-3.72
DPP-70	16.9 / 2.20	395	270, 180	645	654	907	1.37	-5.09	-3.72
DPP-100	12.5 / 1.98	390	180	594, 638	595, 637	887	1.40	-5.13	-3.73

3. Crystallographic parameters of the polymers

Table S2. Crystallographic parameters for the polymers used in this work, reproduced from Zhao et al.^[1]

	DPP-0	DPP-30	Polymer DPP-50	DPP-70	DPP-100
Lamellar spacing (Å)	22.28	22.07	21.96	21.75	21.64
Lamellar FWHM (Å ⁻¹)	0.044	0.038	0.039	0.041	0.035
π - π stacking distance (Å)	3.62	3.64	3.65	3.65	3.62
π - π peak FWHM (Å ⁻¹)	0.0844	0.779	0.087	0.0758	0.063

References

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