Electronic Supplementary Information (ESI)

Temperature-dependent morphology-electron mobility correlations of naphthalene diimide-indacenodithiophene copolymers prepared via direct arylation polymerization

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General measurements and characterization

NMR spectroscopy

NMR spectra were recorded on a Bruker AVANCE III 500 spectrometer (¹H: 500.1 MHz, ¹³C: 125.8 MHz). CDCl₃ (at 30 °C) and C₂D₂Cl₄ (at 120 °C) were used as solvents. The spectra were referenced to the residual solvent peak (CDCl₃: δ (¹H) = 7.26 ppm, δ (¹³C) = 77.0 ppm; C₂D₂Cl₄: δ (¹H) = 5.98 ppm). 2D NMR spectra were recorded to support signal assignment.

SEC measurements

Molecular weights were measured on a Shimadzu system comprising a 5 μ m precolumn and three SDplus columns with pore sizes ranging from 10² to 10⁴ Å (Polymer Standards), connected in series with a RID-20A RI detector and a SPD-M20A photodiode array UV-vis detector (Shimadzu) calibrated with polystyrene standards. CHCl₃ was used as eluent at 40 °C with a flow rate of 1.0 mL min⁻¹.

UV-vis spectroscopy

UV-vis spectra were recorded at 25 °C on a Cary 60 UV-vis (Agilent Technologies) in chloroform solutions (c = 0.02 mg mL⁻¹). Extinction coefficients ε were calculated using the Beer-Lambert law: $\varepsilon = \frac{A}{c*d}$; where A is the absorptivity, d is the optical path length (1 cm) and c is the concentration in mol L⁻¹. Conversion of the concentration into mol L⁻¹ was done using the molecular weight of the repeating unit. Thin film absorption were recorded on the Flame-S UV-vis-spectrometer from Ocean Optics, controlled by the OceanView 1.5.2 software The films were spin coated (1000 rpm, 60 s) from o-DCB solutions.

Cyclic voltammetry

CV measurements were performed at room temperature using a PalmSens4 potentiostat with NBu_4PF_6 (0.1 M) as electrolyte under argon with a scan rate of 50 mV s⁻¹. Films were spin coated (1000 rpm, 60 s) onto ITO substrates as working electrode and measured in dry acetonitrile. A platinum wire was used as counter electrode and a silver wire as reference. The CV curves were plotted against the oxidation potential of ferrocene. CV measurements in solution were done at room temperature in a 0.1 M NBu₄PF₆ *o*-DCB solution using a glassy carbon working electrode.

TGA measurements

TGA measurements were done on a TGA/DSC3+ from Mettler-Toledo within the temperature range 50 °C to 650 °C at a heating rate of 10 K min⁻¹ under N₂.

DSC measurements

DSC measurements were carried out on a DSC 2500 (TA Instruments) under nitrogen atmosphere. Heating and cooling rates were 20 K min⁻¹. The mass of the samples for each measurement was approximately 2-5 mg.

OFET preparation

The samples were fabricated in nitrogen atmosphere. Gold contacts (30 nm) were fabricated on Low alkali 1737F Corning glass substrates using conventional photolithography and thermal evaporation, yielding transistor channels with a length $L = 20 \,\mu\text{m}$ and a width $W = 2 \,\text{mm}$. The semiconducting polymers were dissolved in *o*-dichlorobenzene or toluene at a concentration of 10 mg mL⁻¹, and deposited via spin-coating at 1000 rpm for 30 s in nitrogen atmosphere. After deposition, the residual solvent was removed via vacuum-drying in the case of toluene or annealed at 100 °C for 30 min in nitrogen in the case of *o*-DCB. Then, a layer of Poly(methyl methacrylate) (PMMA) was deposited via spin coating at 1300 rpm for 60 s, yielding a 500 nmthick dielectric layer, and the residual solvent was removed via vacuum drying. Finally, a 40 nm-thick aluminium layer was deposited on the channel area by thermal evaporation through a shadow mask, in order to realize the gate electrodes. The devices were then annealed at different temperatures for 30 min in nitrogen atmosphere. The samples were measured in nitrogen atmosphere using an Agilent B1500A Semiconductor Parameter Analyzer.

PDS

The polymer samples were dissolved in *o*-dichlorobenzene at a concentration of 10 mg mL⁻¹, and deposited on a glass substrate via off-centered spin-coating at 1000 rpm for 60 s. The sample film was placed into a sample holder filled with Fluorinert[™] FC-770 (3 M). The PDS setup uses a 150 W Xenon short-arc lamp (Ushio) which provides light for a monochromator (Oriel Cornerstone, 16 nm FWHM) to achieve a chopped, tunable, monochromatic pump beam. The heat caused through absorption of the pump light in the film changes the refractive index of the Fluorinert[™]. This change is detected by deflecting a diode laser (Thorlabs) whose

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displacement is measured by a position sensitive detector (Thorlabs PDP90A). The magnitude of the deflection is determined by a lock-in amplifier (Amatec SR 7230) and directly correlated to the absorption of the film.

GIWAXS

The GIWAXS experiments were performed using a SAXSLAB laboratory setup (Retro-F) (Copenhagen, Denmark) equipped with an AXO microfocus X-ray source (Dresden, Germany) and an AXO multilayer X-ray optics (ASTIX) as a monochromator for Cu-K_{α} radiation ($\lambda = 0.15418$ nm). A DECTRIS PILATUS3 R 300 K detector (Daettwil, Switzerland) was used to record the 2D WAXS patterns. The measurements were performed in reflection geometry in vacuum at room temperature and at the angle of incidence of 0.16° being above the critical angles of the polymers, the sample to detector distance was around 89 mm. The detector images were converted into the reciprocal space maps of scattering patterns with two components, q_z and q_r , being perpendicular and parallel to the sample surface, respectively. On account of the special geometry of measurements, a certain area of the reciprocal space along the q_z axis was not accessible and appeared as a blank arc. Two additional blank vertical strips arose at the positions where two of three adjacent parts of the detector meet, and were inactive regions of the detector.

NMR data of P(NDI-IDT)



¹H NMR (500 MHz, CDCl₃): δ 8.75 (21), 7.54 (2), 7.27 (6,10), 7.10 (11), 4.09 (v br, 26), 2.58 (13), 1.98 (27), 1.61 (14), 1.4-1.1 (CH₂), 0.95-0.8 (CH₃). End groups: *NDI-OH* -12.9 (OH), 8.70 (21"), 8.35 (21'), *IDT-H* - 7.48 (2', 2"), 7.27 (6'), 7.16 (10'), 7.06 (11'), 7.02 ppm (5').

¹H NMR (500 MHz, C₂D₂Cl₄, 120°C): δ 8.82 (21), 7.62 (2), 7.28 (6), 7.33 (10), 7.15 (11), 4.15 (v br, 26), 2.65 (13), 2.07 (27), 1.69 (14), 1.5-1.2 (CH₂), 1.0-0.8 (CH₃). End groups: *NDI-OH* -12.8 (OH), 8.77 (21''), 8.38 (21'), *IDT-H* - 7.55 (2', 2''), 7.37 (6'), 7.22 (10'), 7.11 (11'), 7.08 ppm (5').

¹³C NMR (125 MHz, CDCl₃,): δ 162.6 (24,25), 156.4 (7), 153.7 (1), 144.9 (4), 142.9 (20), 141.6 (9,12), 139.9 (5), 136.3 (21), 135.7 (3), 128.4 (11), 128.0 (10), 127.6 (23), 125.7 (6), 125.1 (22), 122.5 (19), 118.0 (2), 63.2 (8), 45.2 (26), 36.5 (27), 35.6 (13), 31.9, 31.8, 31.4, 30.1, 29.6, 29.3, 29.2, 26.6, 22.6 (all CH₂), 14.1 ppm (CH₃).

NMR spectra



Figure S1 1 H NMR spectrum of P4 in CDCl₃ at 30°C (a) and in C₂D₂Cl₄ at 120°C (b).



Figure S2 TOCSY spectrum of P5 in $CDCl_3$ with assigned correlations between IDT-H end group signals. * marks ¹³C satellite signals of $CHCl_3$.



Figure S3 ¹³C NMR spectrum of P4 in CDCl₃.



Figure S4 HSQC spectrum (region) of P4 in CDCl₃.

Size exclusion chromatography



Figure S5 SEC curves of P(NDI-IDT) samples in chloroform.



High temperature UV-vis spectra

Figure S6 High temperature UV-vis spectra in chlorobenzene (a) and chloroform (b) of P3.

Thermogravimetric analysis



Figure S7 Thermograms of P(NDI-IDT) in N₂.



Additional DSC data

Figure S8 DSC curves of P(NDI-IDT) for $M_n = 43 \text{ kg mol}^{-1}$ (a), $M_n = 61 \text{ kg mol}^{-1}$ (b) and $M_n = 103 \text{ kg mol}^{-1}$ (c). First and second cycles were measured under N₂ with 10 K min⁻¹ before and with 20 K min⁻¹ after room temperature aging.

Additional OFET data



Figure S9 Influence of the solvent (a, c, e) and annealing temperature (b, d, f) on the transfer curves of OFET devices with **P1**, **P2** and **P3**.



Figure S10 Comparison of the transfer curves of P3 between OFETs with and without SAM.



Additional GIWAXS data

Figure S11 1D scattering curves of **P3** annealed at 120 °C (green line) and at 250 °C (blue line). The scattering curves were extracted by a complete azimuthal integration of the 2D GIWAXS patterns in Figure 7a and 7c, respectively. The red lines are fitting of the experimental scattering curves. The background scattering was fitted using a power law dependence of intensity on the scattering vector $q: I_{background} = I_0 \cdot q^{-n}$ Fitting of the scattering signals was used to find the area A below the (100) peaks, which resulted in $A = 6.96 \cdot 10^{-5}$ for **P3** annealed at 120 °C and $A = 3.8 \cdot 10^{-6}$ for **P3** annealed at 250 °C. The corresponding fitted Lorentzian peaks of the (100) crystal reflections are shown in the Figure inset. As the area below the diffraction peaks is proportional to the degree of crystallinity of the samples, it is evident that annealing at 250 °C entailed a dramatic decrease in the sample crystallinity.