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

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A series of defect-free n-type copolymers poly(naphthalene diimide-*alt*-indacenodithiophene) P(NDI-IDT) comprising alternating naphthalene diimide (NDI) and indacenodithiophene (IDT) units is prepared using atom-economic direct arylation polycondensation (DAP). Copolymers with varying molecular weights up to $M_{n,SEC} = 113 \text{ kg mol}^{-1}$ are obtained in high yield and used to investigate the optical, thermal and electrical properties as a function of chain length. Two weak endotherms are seen in differential scanning calorimetry experiments at 68 °C and 180–220 °C, depending on molecular weight, which are ascribed to side chain ($T_{m,1}$) and main chain ($T_{m,2}$) melting, respectively. Thin-film morphologies are weakly crystalline for annealing temperatures below $T_{m,2}$, with organic field-effect (OFET) mobilities being on the order of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Under these conditions very low Urbach energies (E_U) between 28 and 30 meV are found. However, thermal annealing above $T_{m,2}$ results in amorphous morphologies with hypsochromically shifted optical spectra, strongly increased E_U and complete loss of mobility. In comparison to the well-investigated bithiophene analogue PNDIT2, P(NDI-IDT) thin films are significantly less crystalline, and solutions lack the typical features of aggregation. This is ascribed to the additional bulky hexylphenyl side chains of P(NDI-IDT) that hamper main chain ordering and aggregate formation and thus, interchain charge hopping. With intrachain transport being limited as well, field-effect electron mobilities are limited to $\sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and mostly independent of chain length. These results demonstrate the importance of both intra- and interchain transport to electron mobility for NDI main chain copolymers.

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Introduction

Conjugated polymers are useful materials for high-performance organic electronic devices^{1–3} such as organic solar cells (OSCs)^{4,5} or organic field-effect transistors (OFETs).^{4,6} Especially donor-acceptor copolymers have emerged as modular systems due to versatile tailoring of their structural and electronic properties by suitable selection of donor and acceptor blocks.^{7–9} In the last decade, one focus has been the development of new n-type polymers for OSCs and OFETs.^{10–14} Many of these n-type conjugated polymers are based on naphthalene diimide (NDI), perylene diimide (PDI) or bithiophene imide (BTI).^{10,15–17} A prominent and well-known representative is the naphthalene diimide bithiophene copolymer P(NDIT2), which exhibits intriguing optical and electrical properties.^{16,18,19} Thus, it has been widely employed in all-polymer solar cells (all-PSCs) yielding power conversion efficiencies (PCEs) up to 10%.^{20–22} Moreover, derivatization of P(NDIT2) as lead structure upon variation of

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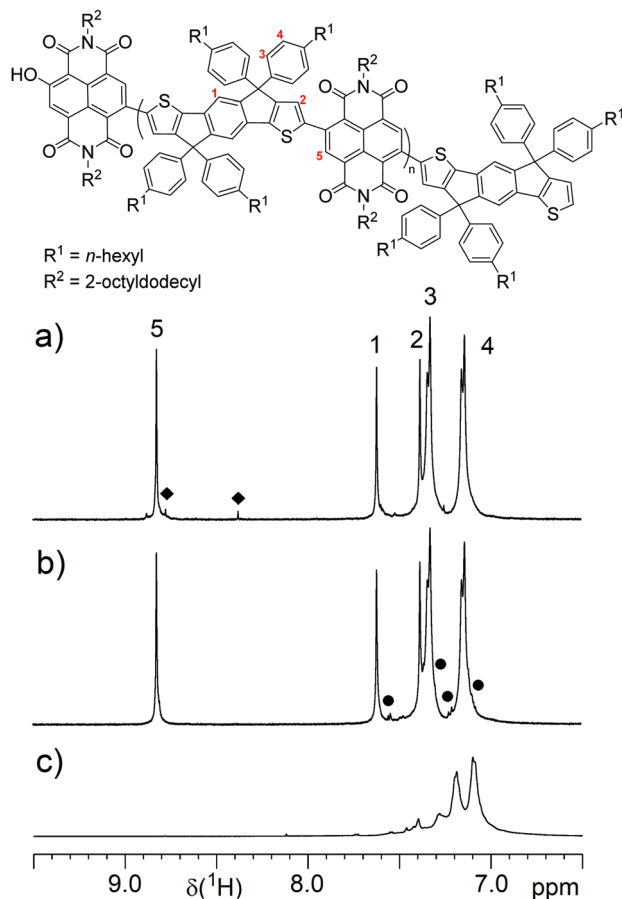


Fig. 1 ^1H NMR spectra of (a) **P7** and (b) **P6**. (c) depicts the ^1H NMR spectrum of model compound $\text{Ph}_8\text{-PIDT}$. Squares and dots mark signals of the $-\text{NDI-OH}$ and the $-\text{IDT-H}$ end groups, respectively.

higher catalyst loading in combination with the addition of a phosphine-ligand facilitates nucleophilic substitution of NDI-Br chain ends by pivalate, leading to NDI-OH end groups (after hydrolysis) and accordingly low molar mass.^{18,26,53}

High temperature ^1H NMR measurements at 120 °C in $\text{C}_2\text{D}_2\text{Cl}_4$ allow to prove this end group by a characteristic signal⁵³ at 8.38 ppm for the proton *ortho* to the OH group (Fig. 1a). Without the usage of the P-ligand the polymers contain predominantly $-\text{IDT-H}$ end groups (Fig. 1b and Fig. S2, ESI[†]). $\text{Ph}_8\text{-PIDT}$ is a model compound for IDT-IDT homocouplings. The signals from the phenyl rings do not overlap with P(NDI-IDT) signals and their appearance in the P(NDI-IDT) spectrum should indicate such defects. Fortunately, the ^1H NMR signals of the P(NDI-IDT) backbone are well separated, but apart from end group signals, additional signals that indicate structural defects are absent. We therefore conclude that P(NDI-IDT) is defect-free, which is in accordance with similar NDI copolymers made by DAP.^{18,26,53,54} Detailed ^1H and ^{13}C NMR analyses are provided in the ESI[†] (Fig. S1–S4).

Optoelectronic and thermal properties

The UV-vis spectra of P(NDI-IDT) in dependence of molecular weight are shown in Fig. 2a and b.

In chloroform solution, the polymers are characterized by a pronounced $\pi\text{-}\pi^*$ band at 395 nm and a broad charge transfer (CT) band at 728 nm with an absorption edge at 818 nm and a slight vibronic shoulder around 650 nm. Neither molecular weight nor the nature of the end groups influence the shape of the absorption spectra. In contrast, the molar extinction coefficients are strongly dependent on molecular weight (Table 2).⁶¹ Compared to P(NDIT2), the absorption maximum of the low energy band exhibits a bathochromic shift of 35 nm (Fig. 2b), that can be attributed to the stronger donor strength of the IDT building block compared to bithiophene. However, the relative intensity of the CT band is lower, pointing to a reduced electronic interaction between NDI and IDT.^{23,26} To investigate the optical properties in more detail we chose polymer **P3** with a medium molar mass of $\sim 60 \text{ kg mol}^{-1}$ (Fig. 2c and d). The solvent has a moderate impact on absorbance. The vibronic shoulder of the CT band is most pronounced in the non-polar solvent toluene. In polar solvents such as tetrahydrofuran (THF) and dichloromethane (DCM) the CT band is slightly blueshifted (Fig. 2c). High-temperature UV-vis spectra do not show significantly altered spectra (Fig. S6, ESI[†]). All these results are consistent with highly soluble copolymers that feature weak aggregation in solution. This is different to the optical behavior of P(NDIT2) and is caused by the additional side chains of P(NDI-IDT) located at IDT which hamper ordering processes.⁶²

Thin film absorption and the influence of the annealing temperature is displayed in Fig. 2d. As spun films show spectra qualitatively similar to those of toluene solutions but with bathochromic shifts of around 40 nm. The spectral shift and the increased intensity of the CT band is attributed to conformational changes/planarization of the polymer backbone as well as chain-chain interactions during film formation. Thermal annealing below main chain melting (*cf.* Fig. 4) at temperatures of 100–150 °C slightly changes CT band intensity. Annealing at 250 °C, which is above T_{m2} , however, reduces CT band intensity as well as causes a hypsochromic shift of 16 nm. Additionally, a new band with low intensity and of unknown nature around 850 nm appears. The onset of the absorption band is used to determine the optical bandgap of **P1–P4**. The spectra reveal an optical bandgap for P(NDI-IDT) of 1.57 eV in solution and a slightly smaller band gap of 1.50 eV in film. The electrical band gaps extracted from cyclic voltammetry (CV), are about 1.85 eV in film and 1.69 eV in solution, respectively (Fig. 3 and Table 3).

Compared to CV measurements in solution with a calculated HOMO of -5.32 eV , the determination from film CV results in a lower lying HOMO energy level of -5.56 eV (Table 3 and Fig. 3). However, the reduction onset $E(\text{Red})$ in solution and film are similar yielding comparable LUMO energy levels of -3.63 eV and -3.71 eV , respectively. The calculated LUMOs are slightly less negative than reported values for P(NDIT2)^{23,26,38} and reflect the stronger donor character of IDT in comparison to bithiophene.

P(NDI-IDT) shows excellent thermal stability with a degradation temperature greater than 440 °C (Fig. S7, ESI[†]). The thermal properties were further investigated by differential



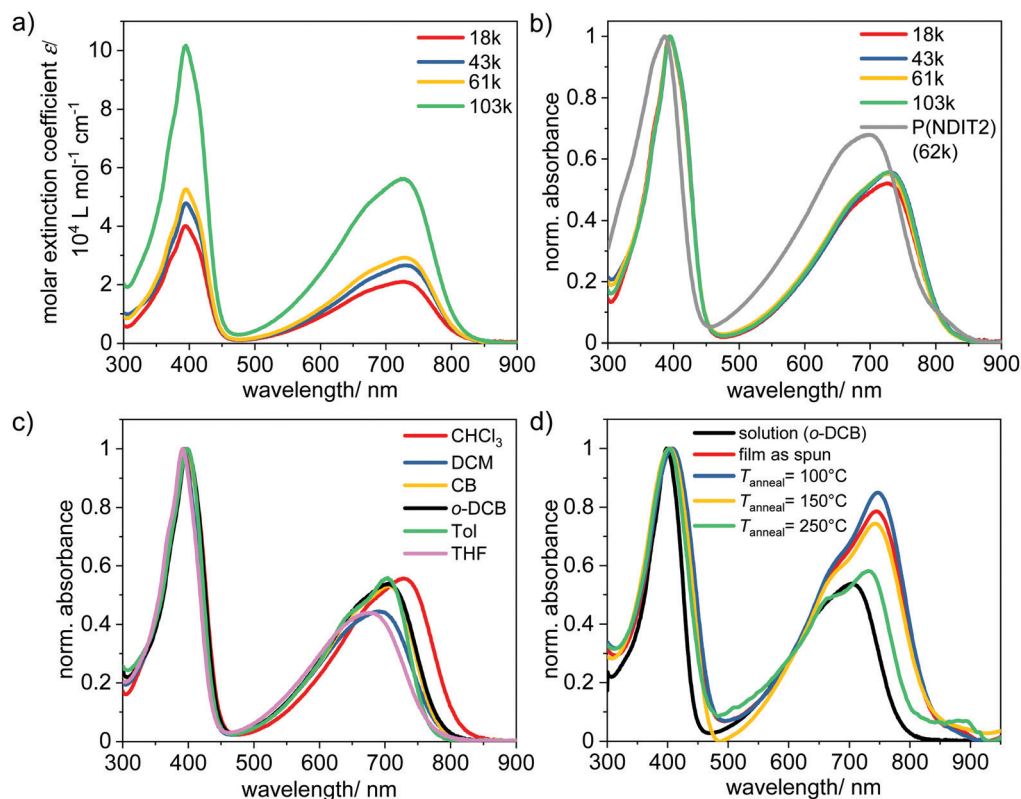


Fig. 2 Molar extinction coefficient (a) and normalized (b) UV-vis spectra of P(NDI-IDT) of different MW (M_n in g mol^{-1}) in chloroform solution at room temperature. Solvent dependent (c) and film (d) UV-vis spectra of **P3** ($M_n = 61 \text{ kg mol}^{-1}$).

Table 2 Summary of optical and thermal properties of selected samples

Entry	M_n/M_w^a (kg mol^{-1})	$\lambda_{\text{abs,max}}^b$ (nm)	$\epsilon_{\text{abs,max}}^b$ ($10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$)	T_{m1}^c ($^{\circ}\text{C}$)	T_{m2}^c ($^{\circ}\text{C}$)	T_c^c ($^{\circ}\text{C}$)	ΔH_{m2}^c (J g^{-1})	ΔH_c^c (J g^{-1})
P1	18/25	394/726	21	68	183	178	4.03	4.58
P2	43/86	395/731	27	65	202	191	1.90	1.76
P3	61/113	395/728	29	66	207	196	0.79	0.72
P4	103/516	394/726	56	69	213	201	0.64	0.84

^a From SEC in CHCl_3 . ^b Measured in chloroform at room temperature; molar extinction coefficient was calculated from maximum wavelength of the low-energy band (see non-italic values). ^c DSC measured with 20 K min^{-1} under N_2 .

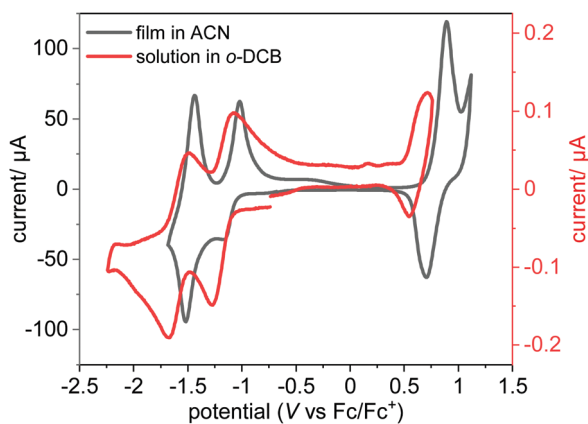


Fig. 3 Cyclic voltammograms of P(NDI-IDT) as film deposited on an ITO substrate in a 0.1 M NBu_4PF_6 acetonitrile solution (black) and in a 0.1 M NBu_4PF_6 o-DCB solution (red) at a scan rate of 50 mV s^{-1} .

Table 3 Summary of electrochemical properties

	$\lambda_{\text{abs,onset}}^a$ (nm)	$E_{g,\text{opt}}^c$ (eV)	$E_{g,\text{el}}^c$ (eV)	E_{ox} (V)	E_{red} (V)	$E_{\text{red}}^{1/2}$ (V)	HOMO ^d (eV)	LUMO ^d (eV)
Film ^a	824	1.50	1.85	0.76	-1.09	-1.10	-5.56	-3.71
Solution ^b	789	1.57	1.69	0.53	-1.12	-1.17	-5.32	-3.63

^a Films were spin coated on ITO substrate (1000 rpm, 60 s) from o-DCB solutions. ^b In o-DCB solution at r.t. ^c Determined from absorption onset. ^d Calculated as followed HOMO = $[E_{\text{ox}} + 4.8] \text{ eV}$ and LUMO = $[-E_{\text{red}}^{1/2} - 4.8] \text{ eV}$.

scanning calorimetry (DSC) as a function of molecular weight (Table 2 and Fig. S8, ESI[†]). **P1–P4** exhibit weakly semicrystalline behavior seen by two broad and weak endothermic transitions depending on molecular weight. Both transitions are most distinct in **P1** with lowest MW (Fig. 4a and Fig. S8, ESI[†]).



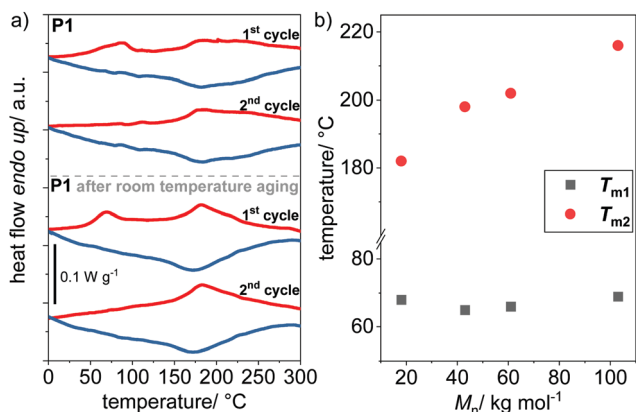


Fig. 4 (a) DSC curves of **P1** ($M_n = 18 \text{ kg mol}^{-1}$). First and second cycles were measured under N_2 with 10 K min^{-1} before and with 20 K min^{-1} after room temperature aging; (b) side chain T_{m1} and main chain T_{m2} melting transitions in dependence of M_w .

T_{m1} around 68 °C vanishes in the second heating cycle and reappears in the first heating cycle after the sample was stored at room temperature for several weeks. In analogy to P3HT,⁶³ we hypothesize that T_{m1} arises from side chain melting and T_{m2} from main chain melting (Fig. 4b). Apparently the rather high density of side chains of P(NDI-IDT) allows for some ordering, and thus, for the appearance of an endothermic peak in the DSC traces not seen with P(NDI2). The mixed structure of side

chains and their rather random orientation may cause the slow crystallization over a time scale much larger than that of the DSC experiment.

Charge transport properties

Organic field-effect transistor (OFET) devices with a top-gate bottom-contact configuration were fabricated to investigate the electron transport properties of P(NDI-IDT). The devices show n-channel behaviour and were optimized by screening the solvent for spin coating, annealing temperature, contact engineering and channel length (Fig. 5 and Fig. S9, S10, ESI†). While the solvent seems to have a minor influence on the transfer characteristic curves, the annealing temperature has a greater impact (Fig. 5a and b). Annealing of the devices at moderate temperatures, up to 150 °C , is necessary to enhance their performance, but is deleterious for annealing temperatures that approach T_{m2} (Fig. 5b and Table 4).

The charge mobilities of the optimized OFET devices in the saturation regime ($V_d = 40 \text{ V}$) are in the order of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Table 5). The reduction of the channel length from 20 to $5 \mu\text{m}$ resulted in a correct scaling of currents, suggesting that contact resistance is not a limiting factor for the estimated field-effect mobility. The current as well as electron mobility increases with increasing molecular weight up to $M_n = 61 \text{ kg mol}^{-1}$ and afterwards slightly decreases for the highest MW sample **P4** (Fig. 5c and d).

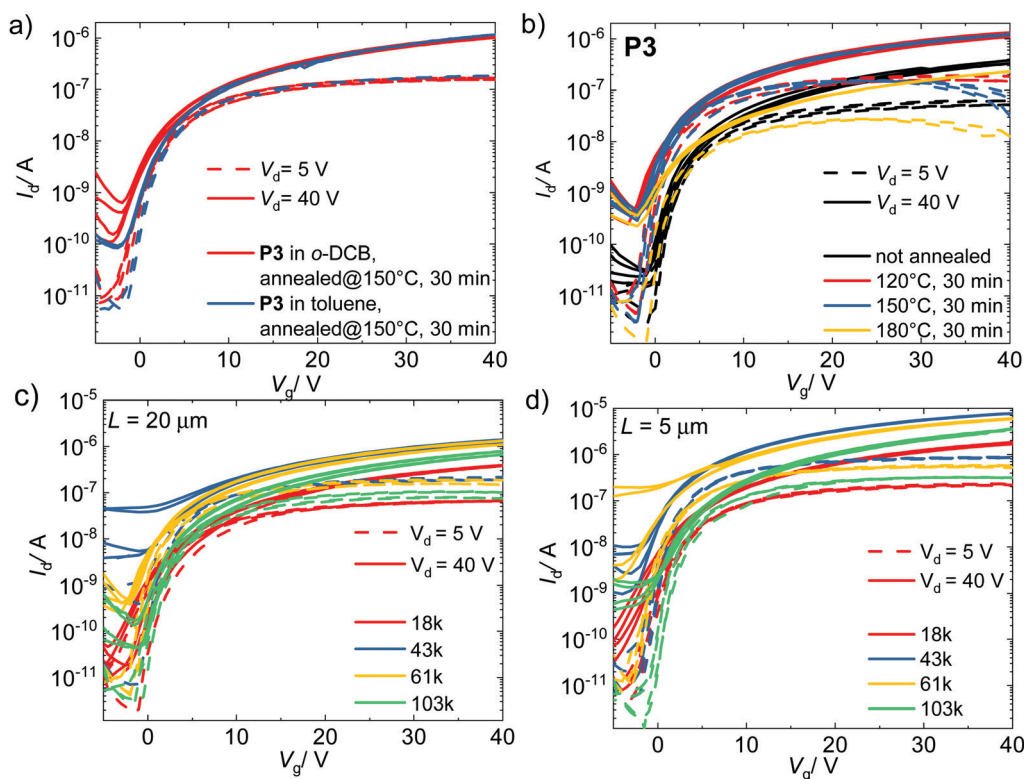


Fig. 5 Optimization of OFET devices. Effect of solvent for spin coating (a) and annealing temperature for **P3** (b). Transfer curves of optimized devices as a function of MW (g mol^{-1}) and channel length (c and d).



Table 4 OFET data of **P3** devices at different annealing temperatures^a

T_{anneal} (°C)	V_{th} ^b (V)	On/off ratio	μ_{sat} ^c (cm ² V ⁻¹ s ⁻¹)
Not annealed	2.8	$\sim 10^3$	1.5×10^{-3}
120	1.9	$\sim 10^4$	3.9×10^{-3}
150	1.7	$\sim 10^4$	4.2×10^{-3}
180	2.5	$\sim 10^3$	5.3×10^{-4}
250 ^d	—	—	—

^a Devices with $L = 20 \mu\text{m}$ were used in all entries. ^b Calculated at $V_{\text{d}} = 5 \text{ V}$ in linear scale. ^c Calculated at $V_{\text{d}} = 40 \text{ V}$. ^d No mobilities could be extracted due to noise in the measurements.

Table 5 OFET characteristics of optimized devices ($T_{\text{anneal}} = 150 \text{ }^\circ\text{C}$) in dependence of MW^a

Entry	$M_{\text{n}}/M_{\text{w}}$ (kg mol ⁻¹)	V_{th} ^b (V)	On/off ratio ^c	μ_{sat} ^d (cm ² V ⁻¹ s ⁻¹)
P1	18/25	1.8	$\sim 10^3$	1.1×10^{-3}
P2	43/86	2.8	$\sim 10^2$	4.4×10^{-3}
P3	61/113	1.9	$\sim 10^3$	3.9×10^{-3}
P4	103/516	3.4	$\sim 10^4$	1.7×10^{-3}

^a Devices with $L = 20 \mu\text{m}$ were used in all entries. ^b Calculated at $V_{\text{d}} = 5 \text{ V}$ in linear scale. ^c Values are similar for $V_{\text{d}} = 5 \text{ V}$ and $V_{\text{d}} = 40 \text{ V}$. ^d Calculated at $V_{\text{d}} = 40 \text{ V}$.

Overall, the MW dependence of mobility is rather limited. In general, electron mobilities are up to three orders of magnitude lower than the reported values for P(NDIT2).²⁶

In order to better understand the OFET behaviour as a function of the annealing temperature, we first carried out photothermal deflection spectroscopy (PDS) on thin films of **P3** and P(NDIT2) as reference. This sensitive technique provides insight into the electronic order of polymer thin films. Thereby, the bandgap edge absorption of polymer films is measured to extract the so-called Urbach energy U_{E} . U_{E} is known to be related to the degree of energetic disorder of the material and hence is typically associated with the charge transport properties.^{41,42,64,65} The thin films were prepared analogously to the OFET fabrication process. P(NDI-IDT) **P3** exhibits a sharp sub-band gap absorption and an extracted value $U_{\text{E}} = (29.3 \pm 0.9) \text{ meV}$ ($T_{\text{anneal}} = 120 \text{ }^\circ\text{C}$). The value is comparable to P(NDIT2) which exhibits $U_{\text{E}} = (30.6 \pm 0.9) \text{ meV}$ (Fig. 6 and Table 6). Further experiments in which the influence of annealing temperature on the energetic disorder were investigated, show that annealing at temperature higher than $150 \text{ }^\circ\text{C}$ is detrimental for the energetic order of the material (Table 6). Interestingly, the lowest Urbach energy ($28.2 \pm 1.0 \text{ meV}$) could be extracted from the absorption of the **P3** as spun thin film, which is one of the lowest reported values for conjugated polymers (Fig. 6).^{42,66} These observations clearly show that U_{E} alone cannot grasp the complexity of charge transport process in a polymer thin film. While U_{E} can help to understand the relation between thin film morphology and energetic order of optically probed states, the accessibility of such states along the channel of a transistors through an efficient percolative path is a requirement for high carrier mobility. The presence of bulky hexylphenyl side chains at the IDT unit, hindering solution aggregation, as well as crystallization and overall

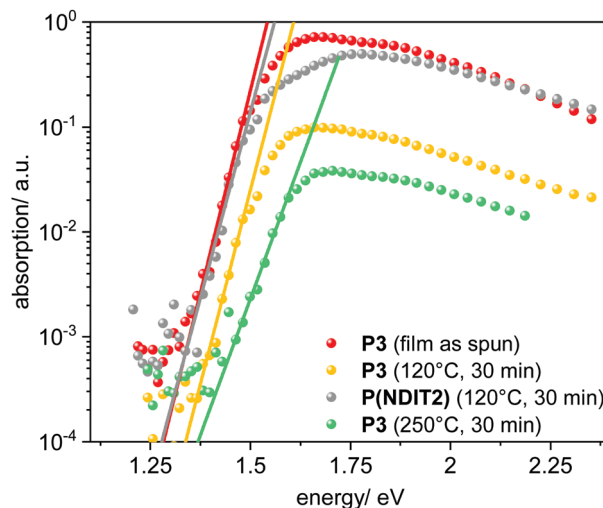


Fig. 6 Comparison between the absorption of **P3** ($M_{\text{n}} = 61 \text{ kg mol}^{-1}$) and P(NDIT2) ($M_{\text{n}} = 62 \text{ kg mol}^{-1}$) thin films in dependence of the annealing temperature; measured by photothermal deflection spectroscopy. The solid line displays the corresponding exponential fits for extraction of the Urbach energy U_{E} . Films were spin-coated (1000 rpm, 60 s) from *o*-DCB solutions.

Table 6 Urbach energy of **P3** and P(NDIT2) in dependence of annealing temperature^a

Entry	T_{anneal} ^a (°C)	U_{E} (meV)
P3	Not annealed	28.2 ± 1.0
P3	120	29.3 ± 0.9
P3	250	41.7 ± 2.9
P(NDIT2)	120	30.6 ± 2.0

^a Films were spin-coated (1000 rpm, 60 s) from *o*-DCB solutions and annealed at the given temperature for 30 min under argon.

interconnectivity in thin films, can have a drastic effect on morphology and interchain transport. The latter plays a dominant role in the case of highly localized states, as is typical of NDI-based co-polymers, where intrachain transport is not effective.^{67,68}

GIWAXS measurements

To gain further information about the molecular packing of P(NDI-IDT), grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed on thin films of **P3**. The films were prepared using the conditions for the best OFET device with $T_{\text{anneal}} = 120 \text{ }^\circ\text{C}$ (below main chain melting) and, in comparison, for annealing above main chain melting at $T_{\text{anneal}} = 250 \text{ }^\circ\text{C}$. The results are illustrated in Fig. 7a–d. The sample annealed at $120 \text{ }^\circ\text{C}$ shows a low degree order suggesting a liquid crystalline organization rather than a crystalline one. The observed (100) and (200) peaks at $q = 0.334 \text{ } \text{\AA}^{-1}$ and $q = 0.668 \text{ } \text{\AA}^{-1}$ allowed determining the interchain d_{100} -spacing along the side chain direction being $18.81 \text{ } \text{\AA}$. The azimuthal distribution of the (100) peak clearly indicates a preferential edge-on orientation (Fig. 7a and b). Furthermore, the 2D GIWAXS image and the 1D scattering curves extracted from it



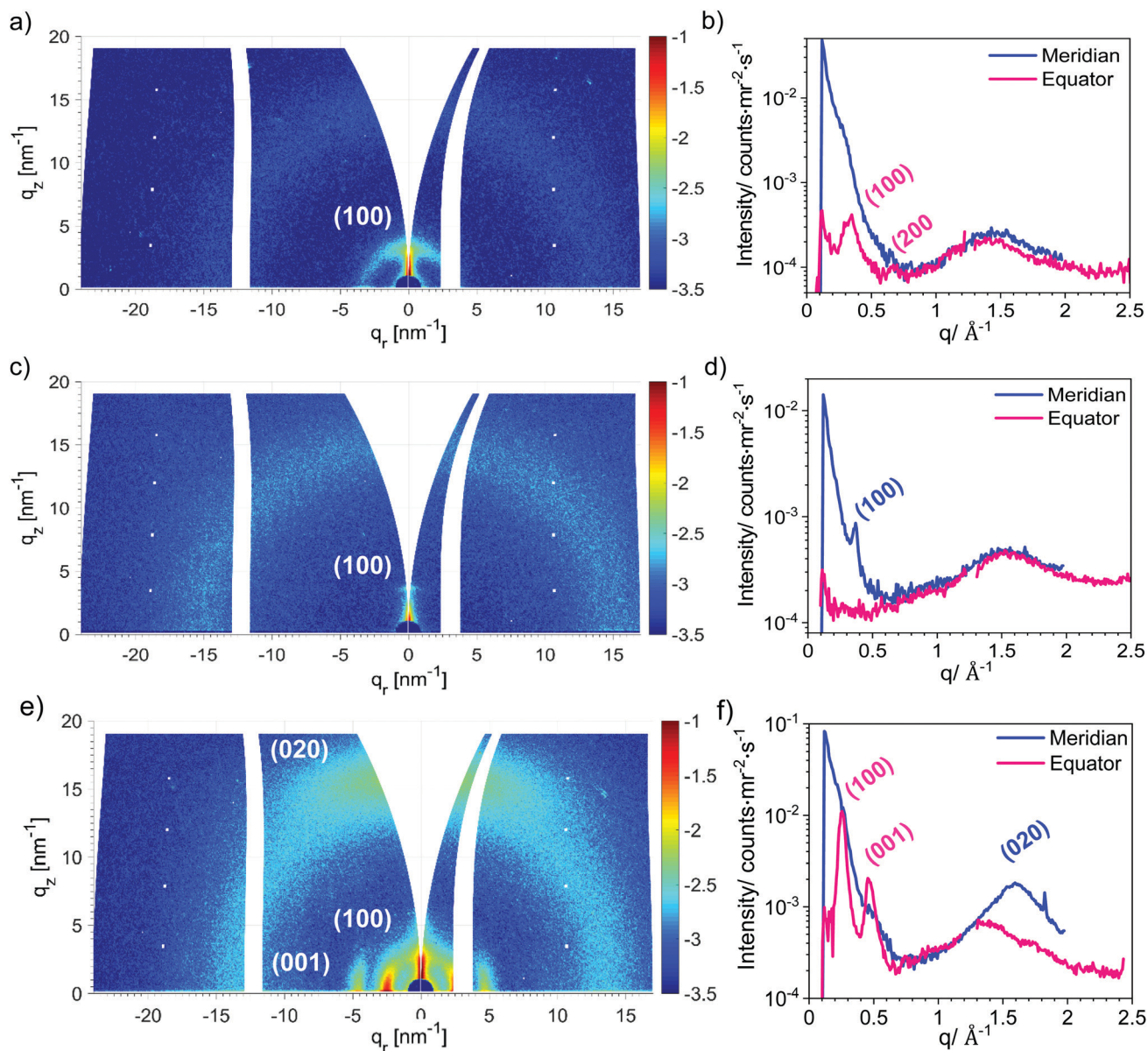


Fig. 7 GIWAXS patterns and 1D GIWAXS profiles of **P3** thin films annealed at 120 °C (a and b) and at 250 °C (c and d) as well as of P(NDIT2) thin film annealed at 120 °C (e and f).

along meridian and equator do not show any prominent π - π stacking peaks (Fig. 7a and b). Such observation confirms the drastic effect of the molecular structure on the π - π stacking disorder, introducing energetic barriers to interchain transport of electrons through the films. Upon annealing at 250 °C (Fig. 7c and d) the material evidences a solely edge-on orientation and a significantly reduced molecular ordering, as the area below the (100) peak decreased by about 20 times (see ESI,† Figure S11), with a slightly decreased d_{100} -spacing. The dependence of the annealing temperature on the molecular ordering complies with the previously discussed reduction of the CT absorption band and can partly explain the diminished mobilities for annealing above 150 °C.

In order to investigate the difference of ordering between P(NDI-IDT) and P(NDIT2), the GIWAXS measurements of a

P(NDIT2) film annealed at 120 °C were carried out (Fig. 7e and f). In contrast to the edge-on orientation of P(NDI-IDT), P(NDIT2) exhibits a predominant face-on orientation. In addition, a (020) diffraction peak corresponding to the π - π stacking distance of 3.94 Å can be monitored suggesting a significantly higher crystalline order than that in P(NDI-IDT).

Experimental

Materials and methods

All starting materials were purchased from commercial sources and used without further purification unless otherwise specified. All reactions were carried out in flame dried glassware and under dry inert gas atmosphere. Compounds Ph₆IDT, NDIBr₂



and the model compound Ph₈-PIDT were synthesized according to published protocols.^{59,60,69}

Detailed information about instrumentation and experimental procedures are described in the ESI.† SEC curves of the samples P1–P7 are shown in Fig. S5.

Synthetic procedures

General synthetic procedure for synthesis of P(NDI-IDT) via DAP (P6). Ph₆IDT (141.1 mg, 155.5 μmol, 1 eq.), NDIBr₂ (153.2 mg, 155.5 μmol, 1 eq.), pivalic acid (15.9 mg, 155.5 μmol, 1 eq.) and potassium carbonate (64.5 mg, 466.6 μmol, 3 eq.) were placed in a vial and dissolved in 0.62 mL degassed mesitylene. Then Pd₂dba₃ (2.8 mg, 2 mol%) were added under argon and stirred for 48 h at 80 °C. After cooling to room temperature, the mixture was diluted with chloroform, precipitated into methanol and purified by Soxhlet extraction with acetone, ethyl acetate and chloroform. The chloroform fraction was filtered through a silica gel plug and dried overnight in a vacuum oven at 50 °C to afford a dark green solid. Yield: 243 mg (90%).

Conclusions

We have presented a robust and atom-economic friendly protocol to prepare highly soluble alternating copolymers made from naphthalene diimide (NDI) and indacenodithiophene (IDT) via direct arylation polycondensation. Detailed molecular characterizations indicate that P(NDI-IDT) is defect-free. Molecular weights (MWs) up to $M_{n,SEC} = 113 \text{ kg mol}^{-1}$ can be tuned by an appropriate adjustment of reaction conditions. The optical behaviour of the polymers indicate weakly aggregated chains. In solution, the absorption spectra are almost independent of temperature and moderately influenced by the type of solvent. Thermal annealing of thin films above 150 °C results in hypsochromically shifted spectra and reduced intensity of the CT band. While molar extinction coefficients and thermal properties do depend on MW, absorption onset and maximum of the charge transfer band are not affected by MW. DSC shows two weak and broad endothermic transitions which are ascribed to side chain and main chain melting. Optimization of the OFET devices reveal that annealing is important to boost performance, but it is deleterious at temperatures above 150 °C, where films lose their weak crystallinity. Electron mobilities are moderate and mostly independent of MW for as spun films and entirely vanish for thermal annealing above main chain melting. Urbach energies are very low for as spun films but rather higher after thermal annealing above main chain melting. GIWAXS reveals a very weakly crystalline morphology of films after spin coating and an almost entirely amorphous morphology after thermal annealing above main chain melting. Taken together, both low Urbach energies as well as a semicrystalline morphology with chain–chain contacts are required for efficient charge transport. The latter is not possible in P(NDI-IDT) films, as the additional and bulky hexylphenyl side chains do not allow for significant solution aggregation and crystallization in thin films. These results emphasize the importance

of interchain transport for high carrier mobility, especially if intrachain transport alone is not efficient as is the case with P(NDIT2). Side chain variation at the IDT monomer may allow control over aggregation for P(NDI-IDT) to capitalize on its very low Urbach energies as well as on fibrillar morphologies commonly seen with P(NDIT2).

Author contributions

D. Adameczak synthesized the polymers and characterized them by SEC, UV-vis and PL spectroscopy, cyclic voltammetry, TGA as well as DSC analyses. D. Adameczak wrote the first draft of the manuscript. B. Passarella and M. Caironi characterized the polymers in organic field-effect transistors. H. Komber performed high-temperature NMR spectroscopy and evaluated the data. D. Becker-Koch and Y. Vaynzof performed PDS experiments. O. Dolynchuk carried out the GIWAXS measurements and evaluated the data. S. Schmidt synthesized P(NDIT2). M. Sommer designed and supervised the work. All authors were involved in revising the manuscript.

Conflicts of interest

There are no conflicts to declare.

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