Electronic Supplementary Information (ESI)

Influence of synthetic pathway, molecular weight and side chains on properties of indacenodithiophene-benzothiadiazole copolymers made by direct arylation polycondensation

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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) at 30 °C. CDCl₃ was used as solvent. The spectra were referenced to the residual solvent peak (δ (¹H) = 7.26 ppm, δ (¹³C) = 77.0 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 corresponding repeating unit.

Photoluminescence

PL spectra were recorded at 25 °C with a xenon flash lamp and a Czerny Turner monochromator in chloroform solutions (c = 0.02 mg mL^{-1}).

IR spectroscopy

IR spectra were obtained at 25 °C on a FTS 165 spectrometer (BIO-RAD) equipped with a Golden Gate single ATR accessory from LOT-Oriel GmbH.

DFT calculations

The frontier orbitals of P10 and P16 have been analysed for a single chain segment of the respective polymer in gas phase. The chain segments were structurally optimised before calculating the orbital energies. The DFT calculations have been performed with the M06-2X hybrid functional¹ and cc-pVTZ basis set² within the Gaussian 16 program suite.³ The given

orbital energies were the respective Kohn-Sham energies and the orbitals were visualised using the VMD software⁴.

The excitation wavelengths ℓ for P10 and P16 have been calculated with time-dependent DFT. To this end, the polymer was modelled via three chain segments. The side chains were cut after the first alkyl segment to keep the computational load manageable. The calculations were performed in Gaussian 16³ using the M06-2X hybrid functional¹ and 6-311G^{**} basis set.^{5,6} The experimental solution of chloroform was modelled using the polarisable continuum model^{7,8} as implemented in Gaussian. The chosen solvent was chloroform ($\varepsilon = 4.7$).

Cyclic voltammetry

CV measurements were performed at room temperature using a PalmSens4 potentiostat with NBu4PF6 (0.1M) 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.

FSC measurements

FSC measurements were done with a Mettler Toledo Flash DSC 1 equipped with an intracooler and nitrogen purge. A thin film was spin-coated from a 5 g L⁻¹ chlorobenzene solution directly on the backside of the FSC chip. The sample was first heated by 4000 K s⁻¹ to 300 °C to delete the thermal history and was then aged at different temperatures (30-140 °C) for 30 minutes.

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 polymer was dissolved in *o*-dichlorobenzene at a concentration of 5 mg mL⁻¹, and deposited via off-centered spin-coating at 1000 rpm for 60 s. After deposition, the residual solvent was removed via vacuum-drying. Then a layer of CYTOP was deposited via spin coating at 4000 rpm for 90 s, yielding a 550 nm-thick dielectric layer, and the residual solvent was removed via vacuum drying. Finally, a 40 nm-thick aluminum 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 100 °C in ambient for 2h. The samples were measured in nitrogen atmosphere using an Agilent B1500A Semiconductor Parameter Analyzer.

GIWAXS

Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at the SAXS/WAXS beamline at the Australian Synchrotron. Measurements were performed in vacuum, with an in-vacuum PILATUS 2M detector (Dectris) placed ~ 0.63 cm downstream from the sample. A photon energy of 15.2 keV was used, with the sample to detector distance calibrated using a silver behenate standard. Further details of data analysis can be found in previous work.⁹

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 150W 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 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.

Optimization of Route A



	entry	R ¹	solvent	[M]/M	T/°C	cat/P-ligand mol%	M _n /M _w ^a kg mol⁻¹	D^a	Yield ^b /%
Route A	\$1 ^{c,d}	Ph_6	mesitylene	0.1	80	5/20	24/99	4.1	88
	S2	Ph_6	mesitylene	0.1	80	2/-	-	-	-
	S 3	Ph ₆	chlorobenzene	0.1	100	5/20	8/14	1.7	82
	S 4	Ph_6	chlorobenzene	0.4	100	5/20	16/78	4.8	87
	S 5	Ph_6	chlorobenzene	0.25	100	2/8	19/96	5.2	81
_	S6	Ph ₈	DMAc	0.1	100	5/20	-	-	-

^aFrom SEC in chloroform with PS calibration; ^bisolated yield after Soxhlet extraction with acetone, ethyl acetate and chloroform; ^cgelation after 24 hours; ^da slight excess of BTBr₂ of 5 mol% was used.

NMR data of C12-IDT monomer



C12-IDT ¹H NMR (500 MHz, CDCl₃): δ 7.27 (s, 2H; 2), 7.25 (d, 4.8 Hz, 2H; 5), 6.96 (d, 4.8 Hz, 2H; 6), 1.97 and 1.84 (2 x m, 8H; 9), 1.3-1.05 (72H; 11-19), 0.88 (t, 7.6 Hz, 12H; 20), 0.84 ppm (m, 8H; 10). ¹³C NMR (125 MHz, CDCl₃): δ 155.1 (7), 153.2 (1), 141.7 (4), 135.6 (3), 126.1 (5), 121.7 (6), 113.1 (2), 53.7 (8), 39.1 (9), 31.9 (18), 30.0 (11), 29.6-29.3 (12-17), 24.2 (10), 22.7 (19), 14.1 ppm (20).

NMR data of C12-PIDTBT



C12-PIDTBT (P10) ¹H NMR (500 MHz, CDCl₃): δ 8.11 (6), 7.93 (22), 7.42 (2), 2.12 and 1.98 (9), 1.4-0.9 (10-19), 0.83 ppm (20). ¹³C NMR (125 MHz, CDCl₃): δ 156.4 (7), 153.7 (1), 152.7 (23), 143.6 (4), 141.4 (5), 136.2 (3), 126.2 (21), 124.6 (22), 122.0 (6), 113.5 (2), 54.3 (8), 39.2 (9), 31.9 (18), 30.1 (11), 30.0-29.2 (12-17), 24.3 (10), 22.7 (19), 14.1 ppm (20).

NMR data of PIDTBT



PIDTBT ¹H NMR (500 MHz, CDCl₃): δ 8.05 (6), 7.82 (22), 7.53 (2), 7.28 (10), 7.11 (11), 2.59 (13), 1.61 (14), 1.4-1.1 (15-19), 0.87 ppm (20). ¹³C NMR (125 MHz, CDCl₃): δ 156.8 (7), 153.8 (1), 152.4 (23), 143.3 (4), 142.2 (5), 141.8 (9), 141.5 (12), 135.5 (3), 128.4 (11), 128.0 (10), 126.1 (21), 124.7 (22), 123.1 (6), 117.7 (2), 63.2 (8), 35.6 (13), 31.9 (18), 31.4 (14), 30.0-29.2 (15-17), 22.7 (19), 14.1 ppm (20).

NMR data of P(K-alt-TBT)



P(K-*alt*-**TBT)** ¹H NMR (500 MHz, CDCl₃): δ 7.85 (d, 3.4 Hz, 2H; 6), 7.78 (s, 2H; 2), 7.77 (d, 8.0 Hz, 4H; 10), 7.70 (s, 2H; 17), 7.15 (d, 8.0 Hz, 4H; 11), 7.10 (d, 3.4 Hz, 2H; 7), 2.50 (d, 4H; 13), 1.56 (m, 4H; 14), 1.4 - 1.1 (64H; 16 x CH₂ of R¹), 0.86 ppm (12H; 2 x CH₃ of R¹). ¹³C NMR (125 MHz, CDCl₃): δ 197.2 (8), 152.3 (16), 148.8 (12), 141.5 (4), 140.5 (5), 140.3 (1), 134.2 (9), 131.7 (3), 130.0 (10), 129.5 (11), 129.4 (2), 129.0 (7), 128.2 (6), 125.5 (15), 125.3 (17), 40.6 (13), 39.4 (14), 33.0, 31.9, 29.9, 29.5, 29.3, 29.2, 26.4 and 22.6 (CH₂ of R¹), 14.1 ppm (CH₃).

NMR data of P11



P11 ¹H NMR (500 MHz, CDCl₃): δ 8.00 (6), 7.84 (17), 7.39 (2), 7.28 (10), 7.08 (11), 2.48 (13), 2.00 (18), 1.61 (14), 1.4-1.1 (CH₂), 0.87 ppm (CH₃). ¹³C NMR (125 MHz, CDCl₃): δ 159.1 (7), 156.4 (1), 152.5 (16), 142.3 (5), 140.4 (4, 9, 12), 135.2 (3), 129.3 (11), 126.5-124 (10, 15, 17), 122.0 (6), 115.2 (2), 53.0 (8), 40.1 (13), 39.4 (14), 33.2, 31.9, 31-29, 26.5 (all CH₂), 24.8 (18), 22.7 (CH₂), 14.1 ppm (CH₃).

NMR spectra of C12-PIDTBT via DAP



Figure S1¹H (a) and ¹³C NMR spectrum (b) of C12-PIDTBT (P10) (solvent: CDCl₃).



Figure S2 ¹H (a) and ¹³C NMR spectrum (b) of C12-IDT (solvent: CDCl₃).

NMR spectra of PIDTBT via DAP



Figure S3 ¹H (a) and ¹³C NMR spectrum (b) of Ph₈-PIDTBT from DAP (solvent: CDCl₃).



Figure S4 ¹H NMR spectrum of **Ph₆-PIDTBT** (entry **P3**; solvent: $CDCl_3$). The numbering corresponds to the formula of PIDTBT except for the C₆ alkyl chain with 13 - 18.

Syntheses of Ph₆IDT and model compounds

Synthesis of $Ph_{6}IDT$. To a solution of 1-bromo-4-hexylbenzene (400 mg, 1.65 mmol, 3 eq) in 3 mL THF at -78 °C was added *n*-butyl lithium (0.7 mL, 1.77 mmol, 2.5 M, 3.2 eq). After stirring at -78 °C for 1h, 2,5-di(thiophen-2-yl)-1,4-phenylenebis[(4-hexylphenyl)methanone] (342 mg, 0.55 mmol, 1 eq) in 4 mL THF was added slowly. The reaction mixture was stirred overnight and then quenched with sat. sodium chloride solution, extracted with ethyl acetate and dried over magnesium sulfate. The solvent was removed under vacuum. Under inert gas atmosphere the crude product was dissolved in 6 mL dry dichloromethane and BF₃*OEt₂ (1.4 mg, 1.3 mL, 9.9 mmol, 18 eq) was added. After stirring for 2 h at room temperature the reaction mixture was quenched with ethanol and water, extracted with chloroform and dried over magnesium sulfate. The solvent was removed under vacuum and the crude product was recrystallized from petroleum ether to afford Ph₆IDT as off-white solid (210 mg, 0.23 mmol, 42 %). ¹H NMR (500 MHz, CDCl₃): δ 7.43 (s, 2H; 2), 7.23 (d, 4.8 Hz, 2H; 5), 7.15 (d, 8.2 Hz, 8H; 10), 7.05 (d, 8.2 Hz, 8H; 11), 6.99 (d, 4.8 Hz, 2H; 6), 2.55 (t, 7.7 Hz, 8H; 13), 1.58 (m, 8H; 14), 1.4-1.2 (24H; 15-17), 0.88 ppm (t, 7.6 Hz, 12H; 18). ¹³C NMR (125 MHz, CDCl₃): δ 155.9 (7), 153.4 (1), 142.1 (9), 141.3 (12), 141.2 (4), 135.1 (3), 128.3 (11), 127.9 (10), 127.3 (5), 123.1 (6), 117.5 (2), 62.7 (8), 35.6 (13), 31.7 (16), 31.3 (14), 29.1 (15), 22.6 (17), 14.1 ppm (18).

Scheme S1 Synthesis of model compounds 1 and 2.



Synthesis of model compound **1**. Compound **Ph₆IDT** (200 mg, 0.2 mmol, 1 eq), 4,7-dibromo-2,1,3-benzothiadiazole (972 mg, 3.3 mmol, 15 eq), potassium carbonate (91.4 mg, 0.7 mmol, 3 eq) and pivalic acid (22.5 mg, 0.2 mmol, 1 eq) were weight into a Schlenk tube and dissolved in 4.4 mL degassed mesitylene. Then Pd₂dba₃ (10.1 mg, 5 mol%) and P(*o*-anisyl)₃ (15.5 mg, 20 mol%) were added. After stirring for 24 h at 100 °C the reaction mixture was allowed to cool to room temperature, diluted with petroleum ether, filtered and the solvent was removed under vacuum. The crude product was purified by column chromatography (petroleum ether:dichloromethane, 1:1) to afford **1** as dark red crystals (75 mg, 56 µmol, 26 %). ¹H NMR (500 MHz, CDCl₃): δ 8.00 (s, 2H; 6), 7.77 (d, 7.7 Hz, 2H; 21), 7.62 (d, 7.7 Hz, 2H; 20), 7.54 (s, 2H; 2), 7.26 (d, 7.9 Hz, 8H; 10), 7.11 (d, 7.9 Hz, 8H; 11), 2.57 (t, 7.7 Hz, 8H; 13), 1.60 (m, 8H; 14), 1.4-1.2 (24H; 15-17), 0.87 ppm (t, 7.6 Hz, 12H; 18). ¹³C NMR (125 MHz, CDCl₃): δ 156.8 (7), 153.7 (1, 23), 151.4 (24), 143.8 (4), 141.7 (9, 12), 141.1 (5), 135.5 (3), 132.2 (21), 128.5 (11), 127.9 (10), 127.4 (19), 124.5 (20), 123.5 (6), 117.9 (2), 111.6 (22), 63.2 (8), 35.6 (13), 31.7 (16), 31.3 (14), 29.1 (15), 22.6 (17), 14.0 ppm (18).

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Synthesis of model compound **2**.¹⁰ Compound **1** (29 mg, 21.8 μmol, 1 eq), caesium carbonate (17 mg, 52.3 μmol, 2.4 eq) were weight into a Schlenk tube and dissolved in 27 μL degassed cyclohexanol. Then Pd₂dba₃ (0.2 mg, 1 mol%) and tris(2,4-di-*tert*-butylphenyl) phosphite (**3**) (0.6 mg, 4 mol%) were added and stirred for 16 h at 120 °C. After cooling to room temperature the reaction mixture was extracted with dichloromethane, washed with water and dried over magnesium sulfate. The solvent was removed under vacuum to afford **2** as red solid (21 mg, 17.9 μmol, 82 %). ¹H NMR (500 MHz, CDCl₃): δ 8.04 (s, 2H; 6), 7.87 (d, 8.7 Hz, 2H; 22), 7.83 (d, 7.1 Hz, 2H; 20), 7.58 (dd, 8.7 Hz, 7.1 Hz, 2H; 21), 7.53 (s, 2H; 2), 7.26 (d, 8.4 Hz, 8H; 10), 7.10 (d, 8.4 Hz, 8H; 11), 2.57 (t, 7.7 Hz, 8H; 13), 1.60 (m, 8H; 14), 1.4-1.2 (24H; 15-17), 0.86 ppm (t, 7.6 Hz, 12H; 18). ¹³C NMR (125 MHz, CDCl₃): δ 156.6 (7), 155.6 (23), 153.7 (1), 151.9 (24), 143.3 (4), 141.8 (5, 9), 141.6 (12), 135.5 (3), 132.2 (21), 129.6 (21), 128.4 (11), 128.2 (19), 128.0 (10), 124.4 (20), 123.6 (6), 119.6 (22), 117.8 (2), 63.2 (8), 35.6 (13), 31.7 (16), 31.3 (14), 29.1 (15), 22.6 (17), 14.1 ppm (18).

NMR spectra of monomer Ph_6IDT



Figure S5 ¹H (a) and ¹³C NMR spectrum (b) of Ph_6IDT (solvent: CDCl₃).

NMR spectra of model compound 1



Figure S6 ¹H (a) and ¹³C NMR spectrum (b) of compound $\mathbf{1} - BT$ -Br end group model (solvent: CDCl₃).

NMR spectra of model compound 2



Figure S7 ¹H (a) and ¹³C NMR spectrum (b) of compound 2 - BT-H end group model (solvent: CDCl₃).

NMR spectra of P(K-alt-TBT)



Figure S8 ¹H (a) and ¹³C NMR spectrum (b) of **P(K-***alt***-TBT)**. The dots mark signals of the –TBT-H end group (solvent: $CDCl_3$).



Figure S9 ¹H NMR spectrum (region) of **P(K**-*alt*-**TBT)** before (bottom) and after phenyl end capping (top). The dots mark signals of the –TBT-H end group and the squares the phenyl signals of the formed –TBT-Ph end group. The –TBT-H signals are disappeared (solvent: CDCl₃).

Reaction control of route B by UV-vis and IR spectroscopy



Figure S10 Reaction control of Me/Ph₂₀-PIDTBT (**P12**) via route B by UV-vis (a) and IR (b) spectroscopy.



Figure S11 Reaction control of Ph_{20}/Ph_{20} -PIDTBT (**P13**) via route B by UV-vis (a) and IR (b) spectroscopy.

NMR spectra of P11



 $\begin{array}{ccc} \textbf{13} & \textbf{14} \\ \textbf{R}^1 = \textbf{CH}_2 \text{-} \textbf{CH}(\textbf{C}_8\textbf{H}_{17})\textbf{C}_{10}\textbf{H}_{21} \end{array}$



Figure S12 ¹H (a) and ¹³C NMR spectrum (b) of P11 (solvent: $CDCl_3$).

NMR spectra of P13



Figure S13 ¹H (a) and ¹³C NMR spectrum (b) of **P13** from polymer analogous synthesis (solvent: CDCl₃).

SEC curves



Figure S14 Comparison of SEC curves of PIDTBT via route A (P9) and via route B (P11-P13).

CV measurements



Figure S15 Cyclic voltammograms of **P1** and **P10** as film deposited on an ITO substrate in a 0.1 M NBu₄PF₆ acetonitrile solution (a, b) and in a 0.1 M NBu₄PF₆ *o*-DCB solution (c, d) at a scan rate of 50 mV s⁻¹. b) and d) show the enlarged region of oxidation onsets.

		E(Ox)	κ ^{onset} abs / nm	E _g / eV	HOMO ^b / eV	LUMO ^b / eV	ΔΗΟΜΟ (CV)/ meV	ΔLUMO (CV)/ meV
filma	P1	0.35	715	1.73	-5.15	-3.46	50	0
	P10	0.30	733	1.69	-5.10	-3.46		0
colution	P1	0.09	707	1.76	-4.89	-3.13	30	-1
Solution	P10	0.06	721	1.72	-4.86	-3.14		

Table S2 Summary of e	lectrochemical	properties.
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^aFilms were spin coated on ITO substrate (1000 rpm, 60 s); ^bCalculated as followed E(HOMO) = E(Ox) + 4.8 eV and E(LUMO) = E(HOMO) + E_g. $E^{1/2}(Fc/Fc+) = 0.58$ V in ACN and 0.79 V in *o*-DCB, respectively.

TGA and DSC curves



Figure S16 TGA thermograms of PIDTBT in N₂.



Figure S17 DSC curves of PIDTBT via DAP (route A) in dependence on molecular weight (a) and in dependence on side chain pattern and synthetic method. **P8** ($R = Ph_8$), **P1**, **P3** ($R = Ph_6$) and **P10** ($R = C_{12}H_{25}$) were made via DAP (route A); **P13** ($R = Ph_{20}/Ph_{20}$) via route B. Measured under N₂ with 20 K min⁻¹.



Figure S18 Comparison of DSC curves of PIDTBT with alkylphenyl (**P1**, **P5**) and aliphatic (**P10**) side chains on IDT unit. Measured under N_2 with 20 K min⁻¹

Transfer and output curves of FET measurements



Figure S19 Transfer and output curves for the realized OFETs based on a-b) P5, c-d) P8, e-f) P9.



Figure S20 Transfer and output curves for the realized OFETs based on a-b) P1, c-d) P3.



Figure S21 Transfer (a) and output (b) curve for the realized OFETs based on P10.



Figure S22 Transfer and output curves for the realized OFETs based on a-b) P12, c-d) P13.

Photothermal deflection spectroscopy



Figure S23 Absorption of Ph_6 -PIDTBT (**P1**) and C12-PIDTBT (**P10**) films; measured by photothermal deflection spectroscopy. The solid line displays the exponential fit for extraction of the Urbach energies U_E .

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