# Supporting Information

# Copolymerization of zinc-activated isoindigo- and naphtalene-diimide based monomers: an efficient route to low bandgap $\pi$ -conjugated random copolymers with tunable properties<sup>†</sup>

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**Methods.** EPR spectra of the anion-radical of the isoindigo-based monomer were recorded on an EMX-plus spectrometer (Bruker Biospin) operating at X-band, and equipped with the high-sensitivity resonator ER 4119 HS-W1. The sample was loaded into a glass capillary (i.d.=0.85 mm, Blaubrand, intraMark). Acquisition parameters were microwave frequency of 9.44 GHz, microwave power of 1 mW, receiver gain of  $1 \times 10^4$ , modulation frequency of 100 kHz, modulation amplitude of 0.5 G, time constant of 10.24 ms, conversion time of 40.96 ms, 16 scans, 1024 data points, sweep width of 20 G, and temperature of 295 K.

Two-dimensional transmission XRD measurements were performed using a Bruker D8 Discover diffractometer operating at 1.6 kW. The diffractometer is equipped with a Cu Twist tube, Ni filter ( $\lambda = 1.5418$  Å), point focusing PolyCap<sup>TM</sup> system for parallel beam generation, and 0.3 mm PinHole collimator for the incident beam. Free standing films were investigated with the X-ray perpendicular to the films. The diffraction patterns were recorded with a VÅNTEC-500 area detector using a sample-to-detector distance of 155 mm.

<sup>1</sup>H NMR spectra were recorded on a Bruker Avance III 500 spectrometer operating at 500.13 MHz for <sup>1</sup>H using a 5 mm <sup>1</sup>H/<sup>13</sup>C/<sup>19</sup>F/<sup>31</sup>P gradient probe. The samples were measured in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> as solvent at 120°C. The spectra were referenced on the residual solvent peak ( $\delta$ (<sup>1</sup>H) = 5.98 ppm).

GPC measurements were carried out on an Agilent 1100 Series (Agilent, USA) normaltemperature size exclusion chromatograph, equipped with refractive index detector and one column PL Gel MIXED-B (Polymer Laboratories, UK). Trichlorobenzene (TCB) was used as eluent for measurements at 60°C and chloroform was used as eluent for measurements at 40°C; the flow rate was 1 mL/min in both cases. Number average molecular weights (Mn) and polydispersity indexes (PDI) of obtained polymers were determined based on calibration with polystyrene standards obtained from Polymer Standards Service (PSS, Germany).

UV/Vis spectra were recorded at room temperature  $(22 \pm 2 \, ^{\circ}C)$  on a Cary 6000i spectrophotometer (Varian). Spectral bandwidth was 1 nm. Fluorescence spectra were recorded at room temperature  $(22 \pm 2 \, ^{\circ}C)$  on a Fluorolog 3 spectrofluorometer (HORIBA Jobin-Yvon) with an excitation wavelength of 385 nm. Spectral bandwidth was 0.5 nm for both excitation and emission monochromator. UV/Vis and fluorescence measurement were carried out with 1 cm standard quartz cuvettes.

Mass spectra were recorded on Maldi TOF Autoflex speed LRF, Bruker Daltonik.

#### **Synthetic procedures:**

All reagents and starting materials were purchased from Aldrich and TCI and used without further purification. 6,6-Dibromoisoindigo was prepared according to the literature methods<sup>1</sup>.

# Synthesis of (E)-6,6'-dibromo-1,1'-bis(2-octyldodecyl)-[3,3'-biindolinylidene]-2,2'-dione (1)



1-Iodo-2-octyldodecane (5.10 g, 12.5 mmol) was added to a suspension of 6,6'dibromoisoindigo (2.10 g, 5 mmol) and potassium carbonate (6.90 g, 50 mmol) in dimethylformamide (DMF) (100 mL). The mixture was heated to 100 °C for 24 h. After cooling to room temperature, the mixture was transferred to a separatory funnel, extracted with diethyl ether and then washed with water. The ether phase was dried over MgSO4. Removal of the solvent gave a crude product, which was purified by silica-gel column chromatography using a mixture of hexane:dichloromethane (1:1) as eluent to obtain compound **4** (4.06 g, 83%). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra correspond to reported one.<sup>2</sup>

# (E)-1,1'-bis(2-octyldodecyl)-6,6'-di(thiophen-2-yl)-[3,3'-biindolinylidene]-2,2'-dione (TiIT).



To the solution of compound 1 (4.9 g, 5 mmol) and tributyl(thiophen-2-yl)stannane (4.67 g, 12.5 mmol) in anhydrous tetrahydrofuran (THF, 50 mL) bubbled with nitrogen, tris(dibenzylideneacetone)dipalladium(0) (Pd<sub>2</sub>(dba)<sub>3</sub>) (15 mg) and tri(*o*-tolyl)phosphine (P(*o*-tol)<sub>3</sub>) (30 mg) were added in one portion. The solution was bubbled with nitrogen for another 20 min. The mixture was stirred overnight at 80 °C under nitrogen. Then the mixture was cooled to room temperature and poured into water. The organic phase was extracted by diethyl ether, and then washed with water, dried over MgSO<sub>4</sub>. After the removal of the

solvent under reduced pressure, the solids were purified by silica-gel chromatography with dichloromethane: hexane = 1:2 as the eluent to afford the compound **TiIT** (3.75 g, 76 %).



Figure S1. 500 MHz <sup>1</sup>H NMR spectrum of TiIT (solvent: CDCl<sub>3</sub>)



Figure S2. 125 MHz <sup>13</sup>C NMR spectrum of TiIT (solvent: CDCl<sub>3</sub>)

NMR data of TiIT:



<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 9.19 (d, 2H; 9), 7.42 (dd, 2H; 3), 7.35 (d, 2H; 1); 7.31 (dd, 2H; 10), 7.12 (dd, 2H; 2), 7.00 (d, 2H; 6), 3.71 (d, 4H; 13), 1.95 (m, 2H; 14), 1.45-1.3 (16H; 16, 16', 19, 19'), 1.3-1.15 (48H; 16-18, 16'-18'), 0.86 (12H; 20, 20').

<sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 168.6 (11), 145.7 (7), 144.2 (4), 137.7 (5), 131.9 (12), 130.3 (9), 128.3 (2), 126.0 (1), 124.1 (3), 121.1 (8), 119.2 (10), 105.0 (6), 44.5 (13), 36.4 (14), 31.9 (18, 18'), 31.8 (15, 15'), 30.0 – 29.3 (17, 17'), 26.6 (16, 16'), 22.7 (19, 19'), 14.1 ppm (20, 20').

(E)-6,6'-bis(5-bromothiophen-2-yl)-1,1'-bis(2-octyldodecyl)-[3,3'-biindolinylidene]-2,2'dione (Br-TiIT-Br)



To the solution of the compound TiIT (4.94 g, 5 mmol) in chloroform (30 mL), Nbromosuccinimide (NBS) (1.96 g, 11 mmol) was added in several portions in 2 h at room temperature. After the addition of NBS, the mixture was stirred for another 2 h, and then poured into water. The organic phase was extracted by diethyl ether, washed by water, dried over MgSO<sub>4</sub>. After the purification by silica chromatography with hexane:dichloromethane = 2:1 as the eluent, compound Br-TiIT-Br was obtained (5.27 g, 92%).



Figure S3. 500 MHz <sup>1</sup>H NMR spectrum of Br-TiIT-Br (solvent: CDCl<sub>3</sub>)



Figure S4. 125 MHz <sup>13</sup>C NMR spectrum of Br-TiIT-Br (solvent: CDCl<sub>3</sub>)



<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 9.18 (d, 2H; 9), 7.19 (dd, 2H; 10), 7.14 (d, 2H; 3), 7.06 (d, 2H; 2), 6.86 (d, 2H; 6), 3.69 (d, 4H; 13), 1.91 (m, 2H; 14), 1.45-1.3 (16H; 16, 16', 19, 19'), 1.3-1.15 (48H; 16-18, 16'-18'), 0.86 (12H; 20, 20').

<sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 168.4 (11), 145.7 (7), 145.5 (4), 136.7 (5), 131.9 (12), 131.1 (2), 130.4 (9), 124.2 (3), 121.3 (8), 118.7 (10), 113.0 (1), 104.5 (6), 44.4 (13), 36.3 (14), 31.9 (18, 18'), 31.8 (15, 15'), 30.0 – 29.3 (17, 17'), 26.6 (16, 16'), 22.7 (19, 19'), 14.1 ppm (20, 20').



Figure S5. MALDI-TOF spectrum of Br-TiIT-Br.

### Polymerization

All operations were done in glovebox under inert gas atmosphere. The activated monomer was prepared as follows: **1** (300 mg, 0.262 mmol) was placed in a flask equipped with a magnetic stirrer and a septum. Dry THF (30 mL) and active Zn (2.62 mmol) were added and the mixture was stirred for 1h. Afterwards, mixture was filtrated through 0.2  $\mu$ m PTFE filter and Pd catalyst (1 mg, 0.01 mol%) (1 equivalent of Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> and 1 equivalent of P'Bu<sub>3</sub>) in 1 mL THF was added rapidly. The reaction mixture was quenched with methanol and extracted with CHCl<sub>3</sub>. Organic layer was washed with water, dried over anhydrous MgSO<sub>4</sub>, evaporated under reduced pressure to give the crude polymer.

**Table S1.** Analyses of the GPC data of crude reaction mixtures obtained upon the polymerization of Br-TiIT-Br/Zn at the  $[Br-TiIT-Br/Zn]/[Pd/P^tBu_3]$  ratio of 100/1.

Polymeriz. time	M <sub>n</sub> kg/mol	M <sub>w</sub> kg/mol	Ð	Polymeric fraction, %	Di- mer, %	Mono mer, %	Content of reactive groups in dimer and monomer, %	Conve rsion, %	DP (Mn) by Carothers
1h	4.5	16	3.7	73	20	7	10+7=17	83	6 (6 kg/mol)
2h	9	51	5.9	85	10	5	5+5=10	90	10 (10 kg/mol)
4h	12	125	10.2	92	6	2	3+2=5	95	20 (20 kg/mol)
6h	16	150	9.3						
8h	17	220	13.0						
16h	18	370	20.5						



**Figure S6.** Number average molecular weight versus monomer conversion plot for polymerization of Br-TiIT-Br/Zn at the [Br-TiIT-Br/Zn]/[Pd/P<sup>t</sup>Bu<sub>3</sub>] ratio of 100/1. The sharp increase of the molecular weight only at high monomer conversion is typical for the step-growth polycondensations.

Although exact reason of the suppressed chain-growth behavior (compared to rylenebased monomers) requires further elucidation, it can be proposed that the presence of a double bond in the TiIT monomer may cause a strong coordination of Pd(0) catalyst formed after the reduction elimination step. It is known that olefins are much stronger ligands for transition metals than aryls.<sup>27</sup> This complexation process may prohibit the intramolecular transfer of the catalyst toward the growing chain end (ring-walking)<sup>28</sup> and thus, prevent the *intra*molecular oxidative addition of Pd(0) to C-Br. In this case, an alternative *inter*molecular oxidative addition may be a more favoured process because it involves a direct attack of arylhalides (i.e., another monomer or oligomer having C-Br bonds) onto Pd(0) and thus it does not require for Pd(0) to be mobile.

#### Scheme S1.



Chain-growth





**Figure S7.** Films of PTiIT and PNDIT2 homopolymers as well as P(TiIT-TNDIT) copolymers were prepared on electrodes and their redox behavior was studied by cyclic voltammetry in acetonitrile in the presence of 0.1 M NBu<sub>4</sub>PF<sub>6</sub> as electrolyte at 50 mV•s<sup>-1</sup> scan rate.





	CHCl <sub>3</sub> , 40°C			TCB 60°C			TCB, 150°C		
Ratio	M <sub>n</sub> kg/mol	M <sub>w</sub> kg/mol	Đ	M <sub>n</sub> kg/mol	M <sub>w</sub> kg/mol	Đ	M <sub>n</sub> kg/mol	M <sub>w</sub> kg/mol	Ð
P(TiIT <sub>27</sub> -co- TNDIT <sub>73</sub> )	24	104	4.3	19.3	55	2.8	21.5	55	2.5
P(TiIT <sub>53</sub> -co- PTNDIT <sub>47</sub> )	22.4	117	5.2	14	35.5	2.5	15.2	33	2.1
P(TiIT <sub>75</sub> -co- TNDIT <sub>25</sub> )	33	220	6.6	16.9	68	4.0	15.4	34.7	2.2

 Table S2. GPC data of P(TiIT-co-TNDIT) copolymers

### MALDI-TOF data for P(TiIT) and copolymers

## P(TiIT)



Molecular weight of TiIT repeat unit is 985; the most abundant termination of the polymer is H/H, however H/Br and Br/Br terminations are also present. The most unusual observation is the presence of intense "half repeat unit" peaks with the m/z=494 which we assign to specie shown in the inset; it forms most likely by decomposition at the double bond located in the middle due to high stability of carbene-like structures as shown on the picture.

MALDI-TOF spectra of P(TiIT-co-TNDIT) copolymers are similar to the spectrum of the homopolymer P(TiIT) because of similarity of masses of TiIT and TNDIT repeat units (the latter is heavier only by 4). The most important difference between the homopolymer and copolymers is decreased intensity of the "half repeat unit" peaks which decreases with the increase of the TNDIT content.

# P (TiIT<sub>75</sub>-co-TNDIT<sub>25</sub>)



# P(TiIT<sub>53</sub>-co-TNDIT<sub>47</sub>)



P(TiIT<sub>27</sub>-co-TNDIT<sub>73</sub>)



Overview of all the spectra in the area corresponded to 5-mers and 5.5-mers: the intensity of the "half repeat unit" peak is decreased with the increase of the TNDIT content. In addition, the content of H/Br termination is decreased upon the increase of the TNDIT content.



## XRD results.

To obtain more quantitative data, the relative degree of crystallinity,  $\chi$ , and coherence length of the polymer film before and after thermal annealing were extracted from the XRD curves. The whole curve was fitted using individual Gaussian functions for each diffraction peak and the amorphous broad amorphous hump extending between q =1.1 to 2 A<sup>11</sup> superimposed on a linear background.  $\chi$  values were obtained from the ratio of the total scattering intensity of the (100) peak to that of the sum of the total scattering intensities of the amorphous hump and the (100) peak. The coherence length was extracted from the full width at half maximum, FWHM, of the (100) peak ( $2\pi/FWHM$ ) and the results are summarized in Table 1.

**Table S3.** The relative degree of crystallinity,  $\chi$ , and coherence length of the polymer film before and after thermal annealing derived from the XRD data.

	As-prepared	Annealed
χ (%)	6	18
Coherence length (nm)	5.8	11.2

For a comparison, much higher crystallinity exhibited donor-acceptor PNDIT2 ( $M_n \sim 108$  kg/mol, PDI=2.3):  $\chi$ =59% and the coherence length of 23 nm (Y. Karpov, W. Zhao, I. Raguzin, T. Beryozkina, V. Bakulev, M. Al-Hussein, L. Häußler, M. Stamm, B. Voit, A. Facchetti, R. Tkachov, A. Kiriy. ACS Appl. Mater. Interfaces 2015, 7, 12478).

	M <sub>n</sub> kg/mol	M <sub>w</sub> kg/mol	Đ	<sup>1</sup> H NMR	MALDI- TOF	UV- vis	XRD	CV
P(TiIT)	16.6	59.8	3.6	+	+	+	+	+
P(TiIT <sub>27</sub> -co- TNDIT <sub>73</sub> )	21.5	55	2.5	+	+	+		+
P(TiIT <sub>47</sub> -co- TNDIT <sub>53</sub> )	15.2	33	2.1	+	+	+		+
P(TiIT <sub>75</sub> -co- TNDIT <sub>25</sub> )	15.4	34.7	2.2	+	+	+		+

References.

- 1) Mei, J.; Graham, K. R.; Stalder, R.; Reynolds, J. R. Org. Lett., 2010, 12, 660.
- 2) Zhang, G.; Fu, Y.; Xie, Z.; Zhang, Q. Macromolecules, 2011, 44, 1414.