Electronic Supplementary Information for

# Linear Hybrid Siloxane-Based Side Chains for Highly Soluble

# **Isoindigo-Based Conjugated Polymers**

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## 1. Synthesis



Scheme S1. The synthetic route to isoindigo monomers.

### Synthesis of Heptamethylhydroxytrisiloxane (a) $^{1}$

Palladium (10% on carbon, 0.02 eq of Pd) was suspended in a mixture of 1 M phosphate buffer (25 mL, pH = 7) and dioxane (120 mL) in a 500 mL round-bottom flask under a nitrogen atmosphere and cooled to 0 °C with an ice bath. Then a solution of heptamethyltrisiloxane (18.0 g. 75.5 mmol) in dioxane (60 mL) was added dropwise over a period of 20 min. After stirring for 2 h, the ice bath was removed and stirring was continued at room temperature for another 3 h. The Pd/C was removed by filtration and toluene (300 mL) was added to the filtrate. The aqueous layer was separated and extracted with toluene (100 mL). The combined organic phases were then washed with water (3 × 200 mL) and dried with MgSO<sub>4</sub>. Removal of the solvents in vacuo gave the corresponding silanol a in good purity (11.2 g, 80%).

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.05 (s, 1H, OH), 0.14 (s, 6H, HO-Si-(CH<sub>3</sub>)<sub>2</sub>), 0.10 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>-Si), 0.07 ppm (s, 6H, CH<sub>3</sub>)

### Synthesis of Chlorooctamethyltetrasiloxane (b)<sup>1</sup>

Hexamethylcyclotrisiloxane (44.49 g, 0.2 mol) was put in a 1 L round-bottom flask under a nitrogen atmosphere. Chlorodimethylsilane (18.92 g, 0.2mol, 1 eq) and acetonitrile (30 mL) was added, followed by DMF (1.5 mL). This mixture was stirred at room temperature (initially the round bottomed flask became cold). After 80 h, completion of the reaction was confirmed by <sup>1</sup>H-NMR. The reaction mixture was directly purified by vacuum distillation, collecting the colorless oil ( 20 g, 31.5%).

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.70 (sept, 1H, H-Si, 3J = 2.8 Hz), 0.45 (s, 6H, Cl-Si(CH<sub>3</sub>)<sub>2</sub>), 0.20 (d, 6H, H-Si-CH<sub>3</sub>)<sub>2</sub>), 3J = 2.8 Hz), 0.13 ppm (s, 6H, CH<sub>3</sub>), 0.09 (s, 6H, CH<sub>3</sub>).

#### Synthesis of Pentadecamethylheptasiloxane (c)<sup>1</sup>

Chlorooctamethyltetrasiloxane (b) (12.9 g, 51.4 mmol) was dissolved in dry toluene (40 mL, 1 M) in a 250 mL roundbottom flask under a nitrogen atmosphere and cooled in an ice bath. Next pyridine (6 mL, 77.1 mmol) was added over the period of 1 min, followed by the dropwise addition of a solution of Heptamethylhydroxytrisiloxane (a) (51.4 mmol, 1 eq) in dry toluene (40 mL) over the period of 15 min. Afterwards, the ice bath was removed and the mixture was stirred for another 2 h at room temperature. Then water (50 mL) and toluene (50 mL) were added, and the aqueous layer was removed. The organic layer was washed with water ( $2 \times 50$  mL) and dried with MgSO<sub>4</sub>. The solvent was then removed in vacuo, giving the crude silyl hydride as a colorless to slightly yellow oil.

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 4.70 (sept, 3J = 2.8 Hz, 1H, H-Si-(CH<sub>3</sub>)<sub>2</sub>), 0.19 (d, 3J = 2.8 Hz, 6H, H-Si-(CH<sub>3</sub>)<sub>2</sub>), 0.09 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>-Si), 0.09-0.07 (m, 24H, CH<sub>3</sub>), 0.05 ppm (s, 6H, CH<sub>3</sub>).

#### Synthesis of IID-C<sub>5</sub> (d1)

Under ice bath, sodium hydrogen (0.29 g, 7.4 mmol) was added to a solution of 6,6'-dibromoisoindigo (1.3 g, 3.1 mmol) dissolved in anhydrous DMF (25 mL). After 20 minutes, 1-bromo hexene (1.1g, 7.4 mmol) was injected through a septum under nitrogen. The mixture was stirred for 3 h at room temperature and then poured into water (200 mL). The organic phase was extracted by  $CH_2CI_2$ , washed with brine, dried over MgSO<sub>4</sub>. The crude product was washed with MeOH (100 mL) three times. Isolated yield = 1.27g (73.6 %) as a deep red solid. <sup>1</sup>H-NMR (600 MHz, CDCI<sub>3</sub>):  $\delta$  9.07 (d, J = 10.3 Hz, 2H), 7.16 (dd, J = 10.3 Hz, 2.2 Hz, 2H), 6.92 (d, J = 2.5 Hz, 2H), 5.86-5.79 (m, 2H),

5.09-5.02 (m, 4H), 3.75 (t, J = 9 Hz, 4H), 2. 17-2.13 (m, 4H), 1.82-1.77 (m, 4H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) : δ 167.74, 145. 63, 137.07, 132.59, 131.19, 126.79, 125.21, 120.36, 115.78, 111.30, 39. 69, 30.98, 26.40.

### Synthesis of IID-C<sub>6</sub> (d2)

The synthetic procedure is similar as described for IID-C<sub>5</sub> (d1). Isolated yield = 1.55g (75.8 %). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  9.06 (d, J = 10.6 Hz, 2H), 7.16 (dd, J = 10.6 Hz, 2.4 Hz, 2H), 6.92 (d, J = 2.5 Hz, 2H), 5.81-5.74 (m, 2H), 5.03-4.96 (m, 4H), 3.72 (t, J = 8.8 Hz, 4H), 2.13-2.09 (m, 4H), 1.72-1.66 (m, 4H), 1.55-1.45 (m,4H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  167.72, 145. 68, 138.0.7, 132.60, 131.18, 126.76, 125.16,120.38, 115.43, 111.29, 40.02, 33.26, 26.72, 26.12.

#### Synthesis of IID-C<sub>7</sub> (d3)

The synthetic procedure is similar as described for IID-C<sub>5</sub> (d1). Isolated yield = 1.56g (72.8 %). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  9.07(d, J = 10.3 Hz, 2H), 7.17 (dd, J = 10.3 Hz, 2.5 Hz, 2H), 6.91 (d, J = 2.4 Hz, 2H), 5.81-5.74 (m, 2H), 4.99-4.92 (m, 4H), 3.73(J = 9 Hz, 4H), 2.06-2.03(m, 4H), 1.71-1.66 (m, 4H), 1.47-1.37 (m, 8H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) :  $\delta$  167.72, 145.71, 138.53, 132.63, 131.17, 126.74, 125.15, 120.40, 114.64, 111.29, 40.16, 33.54, 28.45, 27.19, 26.37.

### Synthesis of IID-C<sub>5</sub>-Si<sub>7</sub> (e1)

IID-C<sub>5</sub> (d1) (1 g, 1.8 mmol) was dissolved in anhydrous toluene (20 mL) under a nitrogen atmosphere. Pentadecamethylheptasiloxane (C) (2.4 g, 4.4 mmol) was injected through a septum, followed by the addition of a drop (50  $\mu$ L) of Karstedt's catalyst (platinumdivinyltetramethyl-siloxane complex in xylene, 3wt%). The resulting mixture was stirred at 50 °C under nitrogen till complete consumption of compound 1, which was monitored by TLC. The solution was directly subjected to silica gel chromatography using Ethyl acetate/hexane (1:50 – 1:200) as an eluent, yielding dark red oil = 0.98g (34.6%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  9.08 (d, J = 10.3 Hz, 2H), 7.16 (dd, J = 10.3, 2.4 Hz, 2H), 6.91 (d, J = 2.4 Hz, 2H), 3.71(t, J = 9 Hz, 4H), 1.71-1.64 (m, 4H), 1.43-1.32 (m, 8H), 0.54-0.52 (m, 4H), 0.08-0.03 (m, 90H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  167.69, 145.77, 132.60, 131.21, 126.71, 125.10, 120.40, 111.25, 40.23, 30.69, 27.12, 22.96, 18.17, 1.76, 1.74, 1.16, 1.12, 1.10, 1.06, 1.04, 1.01, 0.99, 0.14.

### Synthesis of IID-C<sub>6</sub>-Si<sub>7</sub> (e2)

The synthetic procedure is similar as described for e1. Isolated yield = 0.74g (31.6 %). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  9.08 (d, J = 10.3 Hz, 2H), 7.16 (dd, J = 10.5, 2.4 Hz, 2H), 6.91 (d, J = 2.2 Hz, 2H), 3.71(t, J = 8.8 Hz, 4H), 1.72-1.65 (m, 4H), 1.43-1.32 (m, 12H), 0.55-0.52 (m, 4H), 0.08-0.03 (m, 90H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) :  $\delta$  167.71, 145.77, 132.63, 131.18, 126.72, 125.12, 120.41, 111.27, 40.28, 33.03, 27.33, 26.71, 23.11, 18.19, 1.76, 1.75, 1.16, 1.12, 1.10, 1.06, 1.04, 1.01, 0.99, 0.14.

#### Synthesis of IID-C<sub>7</sub>-Si<sub>7</sub> (e3)

The synthetic procedure is similar as described for e1. Isolated yield = 0.67g (33.2 %). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  9.07 (d, J = 10.3 Hz, 2H), 7.16 (dd, J = 10.3, 2.4 Hz, 2H), 6.91 (d, J = 2.3 Hz, 2H), 3.71(t, J = 9 Hz, 4H), 1.70-1.64 (m, 4H), 1.43-1.30 (m, 16H), 0.54-0.52 (m, 4H), 0.08-0.03 (m, 90H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>) :  $\delta$  167.69, 145.76, 132.61, 131.19, 126.71, 125.10, 120.40, 111.25, 40.26, 33.29, 29.67, 27.41, 26.96, 23.15, 18.21, 1.76, 1.16, 1.12, 1.06, 1.04, 1.02, 0.99, 0.15.

#### Synthesis of PIID-C<sub>m</sub>-Si<sub>7</sub> (m = 5-7)

Typical Procedure for Stille Polymerization and Polymer Purification: Tris(dibenzylidenacetone)dipalladium (0.0048mol) and tri(o-tolyl) phosphine (0.0192 mmol) were added to a solution of IID- $C_m$ -Si<sub>7</sub> (0.12 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.12 mmol) in anhydrous chlorobenzene (10 mL) under nitrogen. The solution was subjected to three cycles of evacuation and admission of nitrogen. The mixture was then heated to 130 °C or 48 h. After cooled to room temperature, the mixture was poured into methanol and stirred for 2 h. A black precipitate was collected by filtration. The product was purified by washing with methanol, acetone, and hexane in turn with a Soxhlet extractor. We mainly collected the products extracted by hexane.

(PIID-C<sub>5</sub>-Si<sub>7</sub>). Isolated yield = 30% - 33%. Mn = 5.3 kDa, Mw =7.9 kDa, PDI = 1.5.

For C64H120N2O14S2Si14: C, 48.09; H, 7.51; N, 1.75; S,4.07. Found: C, 48.73; H, 7.23; N, 1.74; S,4.37.

(PIID-C<sub>6</sub>-Si<sub>7</sub>). Isolated yield = 51% - 54%. Mn = 8.1 kDa, Mw = 17.3 kDa, PDI = 2.1.

For C66H124N2O14S2Si14: C, 48.74; H, 7.63; N, 1.72; S,3.97. Found: C, 49.58; H, 7.41; N, 1.83; S,4.19.

(PIID-C<sub>7</sub>-Si<sub>7</sub>). Isolated yield = 59% - 62%. Mn = 12.2 kDa, Mw = 26.9 kDa, PDI = 2.2.

For C68H128N2O14S2Si14: C, 49.36; H, 7.74; N, 1.70; S,3.88. Found: C, 50.30; H, 7.50; N, 1.80; S,4.15.

### Synthesis of PIID-Ref

Typical Procedure for Stille Polymerization and Polymer Purification: Tris(dibenzylidenacetone)dipalladium (0.012mol) and tri(o-tolyl) phosphine (0.048 mmol) were added to a solution of IID-Ref (0.30 mmol) and 5,5'bis(trimethylstannyl)-2,2'-bithiophene (0.30 mmol) in anhydrous chlorobenzene (30 mL) under nitrogen. The solution was subjected to three cycles of evacuation and admission of nitrogen. The mixture was then heated to 130 °C or 48 h. After cooled to room temperature, the mixture was poured into methanol and stirred for 2 h. A black precipitate was collected by filtration. The product was purified by washing with methanol, acetone, hexane, and chloroform in turn with a Soxhlet extractor. We mainly collected the products extracted by hexane (PIID-Ref) and chloroform (PIID-Ref-high).

(PIID-Ref). Isolated yield = 5% - 10%. Mn = 19.2 kDa, Mw =82.6 kDa, PDI = 4.3.

(PIID-Ref-high). Isolated yield = 80% - 85%. Mn = 118.4 kDa, Mw = 294.4 kDa, PDI = 2.5.

### 2. General methods

Nuclear magnetic resonance (NMR) spectra were record on an Agilent VNMRS600 (600 MHz) spectrometer. Elemental analysis was performed on a Vario EL instrument. Mass spectra were measured using Matrix-assisted Laser Desorption/Ionization TOF/TOF MS (MALDI-TOF, Autoflex Speed TOF/TOF, Bruker Daltonics). The numberaverage molecular weight (Mn) and polydispersity indices (PDIs) of the polymers were characterized by gel permeation chromatography (GPC) equipped with a Waters 1515 pump and a Waters 2414 differential refractive index detector. A series of three linear Styragel columns (HR0.5, HR2, and HR4; 3.6 × 300 mm) was used at a temperature of 40 °C. The eluent used was tetrahydrofuran at a flow rate of 0.3 mL min<sup>-1</sup>. Cyclic voltammetry (CV) measurements were conducted on a CHI 660 D electrochemical workstation under nitrogen equipped with a threeelectrode system containing Bu4NPF6 (0.1 M) in deoxygenated anhydrous acetonitrile and at a scan rate of 100 mV/s, polymer thin film was coated on surface of Pt disc that acted as the working electrode, another platinum wire was ultilized as the auxiliary electrode, meanwhile an Ag/Ag+ electrode acted as the reference electrode, and ferrocene was selected as the standard. Ultraviolet photoemission spectroscopy (UPS) was conducted on a Photoelectron Spectrometer. Thermo-gravimetric analyses (TGA) were performed on a TA Instruments QS000IR. Differential scanning calorimetry (DSC) analyses were performed on a Instrument DSC Q200 calorimeter. Ultraviolet-Visible-Near infrared (UV-Vis-NIR) spectroscopy was carried out on an Agilent Cary 5000 UV-vis-NIR spectrophotometer with samples in both solution and thin film. The atomic force microscopy (AFM) images were obtained using a SPA300HV instrument. Grazing-incidence-X-ray diffraction (GIXRD) measurements were performed using 9A beamline at the Pohang Accelerator Laboratory (PAL) in Korea.





Figure S1. MALDI-TOF-MS of IID-C5-Si7, IID-C6-Si7, and IID-C7-Si7.

### 4. GPC



Figure S2. GPC results at 40°C with THF as eluent for PIID-C<sub>m</sub>-Si<sub>7</sub> (m = 5-7), PIID-Ref, and PIID-Ref-high.

# 5. CV

All polymers hve similar highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, indicating that the alkyl spacer length did not significantly alter the electronic energy levels of the polymers.



**Figure S3.** CV measurements of PIID- $C_m$ -Si<sub>7</sub> (m = 5-7). **6. UPS** 

UPS results was consistent with CV results.



Figure S4. UPS spectra of PIID-C<sub>m</sub>-Si<sub>7</sub> (m = 5-7).

# 7. TGA and DSC analysis

TGA characterizations were in a nitrogen atmosphere (25 mL min<sup>-1</sup>) at a heating rate of 10 °C min<sup>-1</sup>. DSC characterizations were based on the 2nd heating and cooling processes in a nitrogen atmosphere (25 mL min<sup>-1</sup>) and a heating/cooling rate of 20 °C min<sup>-1</sup>. All polymers exhibited two glass transition temperatures ( $T_g$ ), one corresponding to the flexible side chains (< 0 °C) and another produced by the rigid backbone (> 0°C).<sup>2</sup>



Figure S5. (a) TGA analysis of PIID- $C_m$ -Si<sub>7</sub> (m = 5-7). (b-d) DSC analysis of PIID- $C_m$ -Si<sub>7</sub> (m = 5-7).

### 8. UV-Vis-NIR absorption spectra



Figure S6. UV-Vis-NIR absorption spectra of PIID- $C_m$ -Si<sub>7</sub> (m = 5-7) in dilute solutions and films.

## 9. AFM



Figure S7. AFM height images of PIID- $C_5$ -Si<sub>7</sub> and PIID- $C_6$ -Si<sub>7</sub> films. **10. GIXRD** 



Figure S8. 2D-GIXRD (a) and 1D-XRD (b) patterns of PIID-C<sub>5</sub>-Si<sub>7</sub> and PIID-C<sub>6</sub>-Si<sub>7</sub> films.

### 11. Fabrication and characterization of FETs

BGTC FETs were fabricated to investigate the influence of processing solvents on the device performance. A CYTOP was spin-coated on a gate of *n*-doped Si with a 300 nm-thick SiO<sub>2</sub> dielectric layer. The polymers were dissolved in CF, Tol, Hex, and EA (5 mg/mL) and dropped onto the CYTOP and spin-coated at 3000 rpm for 30 s. The film thickness was about 60-80 nm. The polymer films were annealed at different temperatures (90, 110,130, 150, and 170 °C) for 30 min in glove box. The source and drain electrodes (40 nm-thick Au) were prepared by thermal evaporation, and the channel length (L) and width (W) were 100 and 1000  $\mu$ m, respectively.

To fabricate the flexible BGTC FETs, aluminum metal was evaporated on a polyethylene terephthalate (PET) substrate, which served as a gate electrode. PMMA was used as a dielectric layer. A hexane solution of PIID- $C_7$ -Si<sub>7</sub> (5 mg/mL) was dropped onto PMMA or CYTOP and spin-coated at 3000 rpm for 30 s. The polymer films were annealed at 110 °C for 30 min in glove box. The source and drain electrodes (40 nm-thick Au) were prepared by thermal evaporation, and the channel L and W were 80 and 720 µm, respectively.

To fabricate the flexible BGBC FETs, aluminum metal was evaporated on a PET substrate, which served as a gate electrode. PMMA was used as the dielectric layer. The source and drain electrodes (40 nm-thick Au) were prepared by thermal evaporation, and the channel L and W were 80 and 720  $\mu$ m, respectively. A octane solution of PIID-C<sub>7</sub>-Si<sub>7</sub> (6 mg/mL) was dropped onto PMMA using DIMATIX MDP-3000 inkjet printer and formed a thin film in the channel between the electrodes. The polymer films were annealed at 110 °C for 30 min in glove box.

The electrical properties of all devices were measured by using Keithley 4200-SCS semiconductor parameter analyzer. The mobility was calculated according to the conventional equation at the saturation regime:  $I_{DS}$ = (W/2L)  $\mu$  C<sub>i</sub> (V<sub>G</sub> - V<sub>th</sub>)<sup>2</sup>, where  $I_{DS}$  is the drain current in saturated regime, W/L is the channel width/length, C<sub>i</sub> is the dielectric layer capacitance per unit area, V<sub>G</sub> and V<sub>th</sub> are the gate voltage and the threshold voltage, respectively.



Figure S9. Transfer curves of FETs with optimized PIID-C<sub>m</sub>-Si<sub>7</sub> (m = 5-7) films prepared by spin coating.



Figure S10. Output curves of FETs with optimized PIID-C<sub>m</sub>-Si<sub>7</sub> (m = 5-7) films prepared by spin coating.



Figure S11. Transfer curves of FETs with PIID-Ref and PIID-Ref-high films prepared by spin coating.



Figure S12. Air stability of PIID-C7-Si7-based FETs fabricated from different solvents. (RH = 30-70%)



Figure S13. Transfer and output curves of flexible PIID-C<sub>7</sub>-Si<sub>7</sub>-based BGCT FET arrays prepared by spin coating.



**Figure S14.** Transfer curves of flexible PIID-C<sub>7</sub>-Si<sub>7</sub>-based BGCT FET arrays after bending. (a) equal bending/recovering times in different curvature radii. (b) different bending/recovering times in curvature radii of 9 mm.



Figure S15. Transfer and output curves of the flexible PIID-C7-Si7-based BGBC FETs prepared by inkjet printing.

**Table S1.** Physical properties of PIID- $C_m$ -Si<sub>7</sub> (m = 5-7).

Polymers	M <sub>n</sub> /PDI [kDa] <sup>a</sup>	λ <sub>max</sub> <sup>sol</sup> [nm] <sup>b</sup>	λ <sub>max</sub> film [nm] <sup>c</sup>	E <sub>g</sub> <sup>opt</sup> [eV] <sup>d</sup>	Е <sub>номо</sub> [eV] <sup>е</sup>	E <sub>LUMO</sub> [eV] <sup>e</sup>	E <sub>g</sub> <sup>CV</sup> [eV] <sup>e</sup>	Е <sub>номо</sub> <sup>ups</sup> [eV] <sup>f</sup>	T <sub>d</sub> [℃] <sup>g</sup>
PIID-C <sub>5</sub> -Si <sub>7</sub>	5.3/1.5	649	706,642	1.61	-5.44	-3.73	1.71	-5.84	379
PIID-C <sub>6</sub> -Si <sub>7</sub>	8.1/2.1	657	712,644	1.60	-5.43	-3.72	1.71	-5.87	395
PIID-C7-Si7	12.2/2.2	659	714,649	1.61	-5.42	-3.73	1.69	-5.89	394

<sup>*a*</sup>Measured by GPC using polystyrene standard and tetrahydrofuran as the eluent at 40 °C. <sup>*b*</sup>From polymer solutions (10<sup>-5</sup> M in chloroform). <sup>*c*</sup>From chloroform–processed polymer films on quartz glass. <sup>*d*</sup>E<sub>g</sub><sup>opt</sup> = 1240/ $\lambda_{onset}$  (in film). <sup>*e*</sup>E<sub>HOMO</sub> = – (4.75 + Eox onset), E<sub>LUMO</sub> = – (4.75 + E red onset) and E<sub>g</sub><sup>CV</sup> = E<sub>LUMO</sub> – E<sub>HOMO</sub>. <sup>*f*</sup>Estimated from the Ultraviolet photoelectron spectroscopy. <sup>*g*</sup>The 5% weight loss temperatures.

**Table S2.** Crystallographic parameters of PIID- $C_m$ -Si<sub>7</sub> (m = 5-7) films.

Solvent	CF	Tol	Hex
PIID-C5-Si7			
π–π spacing [Å]	3.61	3.60	3.60
Lamellar spacing [Å]	34.06	34.34	33.56
in-plane fwhm [Å-1]	0.073	0.065	0.092
in-plane CL (Å)	olane CL (Å) 86.07		68.30
PIID-C <sub>6</sub> -Si <sub>7</sub>			
π–π spacing [Å]	3.61	3.61	3.62
Lamellar spacing [Å]	36.38	37.14	37.16
in-plane fwhm [Å-1]	0.085	0.079	0.098
in-plane CL (Å)	73.92	79.53	64.11
PIID-C7-Si7			
π–π spacing [Å]	3.61	3.60	3.62
Lamellar spacing [Å]	35.32	35.12	35.80
in-plane fwhm [Å <sup>-1</sup> ]	0.093	0.084	0.099
n-plane CL (Å) 67.56		74.80	63.47

Table S3. Charge transport performance of PIID- $C_m$ -Si<sub>7</sub> (m = 5-7)-based BGTC FETs.

Solvent	CF	Tol	Hex	EA
PIID-C <sub>5</sub> -Si <sub>7</sub>				
Average mobility [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	0.27	0.29	0.19	0.16
Max mobility [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	0.31	0.32	0.22	0.18
l <sub>on/off</sub>	10 <sup>5</sup> -10 <sup>6</sup>			
V <sub>th</sub> [V]	1.1	2.7	2.7	1.6
PIID-C <sub>6</sub> -Si <sub>7</sub>				
Average mobility [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	0.62	0.65	0.47	0.32
Max mobility [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	0.81	0.82	0.53	0.35
I <sub>on/off</sub>	10 <sup>6</sup> -10 <sup>7</sup>	10 <sup>6</sup> -10 <sup>7</sup>	10 <sup>5</sup> -10 <sup>6</sup>	10 <sup>5</sup> -10 <sup>6</sup>
V <sub>th</sub> [V]	4.4	1.7	2.1	5.0
PIID-C7-Si7				
Average mobility [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	1.09	1.38	1.01	0.79
Max mobility [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	1.24	1.58	1.12	0.87
l <sub>on/off</sub>	10 <sup>6</sup> -10 <sup>7</sup>			
V <sub>th</sub> [V]	1.2	4.0	2.6	3.3

Year Materials Max mobility Device structure Ref Solvents [cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>] IIDDT 2011 0.79 chloroform Bottom-gate/top-contact 3a 2012 IIDDT-C3 3.62 1,1,2,2-tetrachloroethane Bottom-gate/top-contact 3b 2011 PII2T-Si 2.48 chloroform Bottom-gate/top-contact 3c 2015 PII2F-C<sub>9</sub>Si 3.4 chloroform Bottom-gate/top-contact 3d

**Table S4.** The mobility of reported isoindigo-based conjugated polymers modified with branched alkyl side chains and branched hybrid siloxane-based side chains.



**12.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of monomers and polymers.





<sup>1</sup>H NMR spectra of (b).



<sup>1</sup>H NMR spectra of IID-C<sub>5</sub>.



<sup>&</sup>lt;sup>1</sup>H NMR spectra of IID-C<sub>6</sub>.



<sup>13</sup>C NMR spectra of IID-C<sub>6</sub>.



<sup>1</sup>H NMR spectra of **IID-C**<sub>7</sub>.



<sup>13</sup>C NMR spectra of IID-C<sub>7</sub>.



<sup>1</sup>H NMR spectra of IID-C<sub>5</sub>-Si<sub>7</sub>.





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9.5

-8 -6 -4 -2 -0

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<sup>&</sup>lt;sup>1</sup>H NMR spectra of IID-C<sub>6</sub>-Si<sub>7</sub>.



<sup>13</sup>C NMR spectra of IID-C<sub>6</sub>-Si<sub>7</sub>.



<sup>1</sup>H NMR spectra of IID-C<sub>7</sub>-Si<sub>7</sub>.



<sup>13</sup>C NMR spectra of IID-C<sub>7</sub>-Si<sub>7</sub>.



<sup>1</sup>H NMR spectra of PIID-C<sub>5</sub>-Si<sub>7</sub>.



<sup>1</sup>H NMR spectra of PIID-C<sub>6</sub>-Si<sub>7</sub>.



<sup>1</sup>H NMR spectra of **PIID-C<sub>7</sub>-Si**<sub>7</sub>.

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