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Supplementary Information

7-Azaisoindigo as a New Electron Deficient Component of Small Molecule Chromophores for Organic Solar Cells

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1. Device Fabrication Procedures and Performance Data for OPV Devices with P3HT:1–2 Active Layers

1.1. Device Fabrication Procedures

Pre-cleaned ITO-coated glass substrates (Delta Technologies) ($R_s \approx 6\ \Omega/\square$) were UV-ozone cleaned for 15 min immediately prior to use. A layer of poly(3,4-ethylenedioxythiophene:polystyrene sulfonate (Clevios P VP AI 4083) was spin coated onto the ITO substrates and annealed at 150 °C before being placed in an N_2-atmosphere glove box. The active layer solution (10:8 poly(3-hexylthiophene):**1**–**2** by mass, total solid concentration of 18 mg/mL in chlorobenzene) was then deposited by spin coating. The samples were allowed to dry at ambient temperature for 1–2 hours, and then annealed at 100 °C for 20 min. LiF (0.8 nm) and Al (100 nm) were then thermally evaporated onto the substrates at a base pressure of 10^{-6} mbar.

1.2 Device Performance

Table S1 Photovoltaic performance of ITO/PEDOT:PSS/8:10 P3HT:**1**–**2**/LiF/Al bulk heterojunction solar cells.

Compound	[a]V_{oc} (V)	[a]J_{sc} (mA/cm^2)	[a]Fill Factor (%)	[a]PCE (%)	Best PCE (%)
1	0.2 ± 0.1	0.15 ± 0.03	27 ± 1	0.008 ± 0.005	0.016
2	0.25 ± 0.06	0.022 ± 0.005	28 ± 1	0.0015 ± 0.0005	0.002

[a]Averages and standard deviations for each data set were determined from measurements on a minimum of 6 separate devices

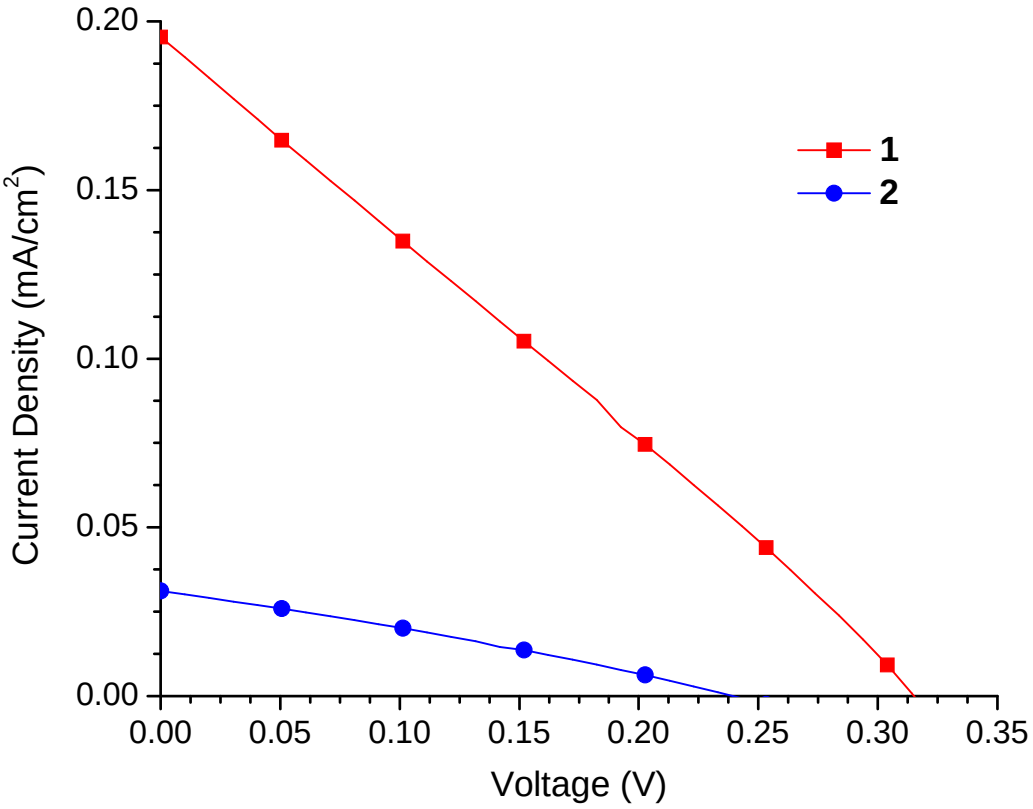


Fig. S1 Current-voltage curves for the most efficient BHJ solar cells based on active layers of P3HT:**1**–**2** (10:8 by mass). All devices were based on the ITO/PEDOT:PSS/P3HT:**1** or **2**/LiF/Al architecture.

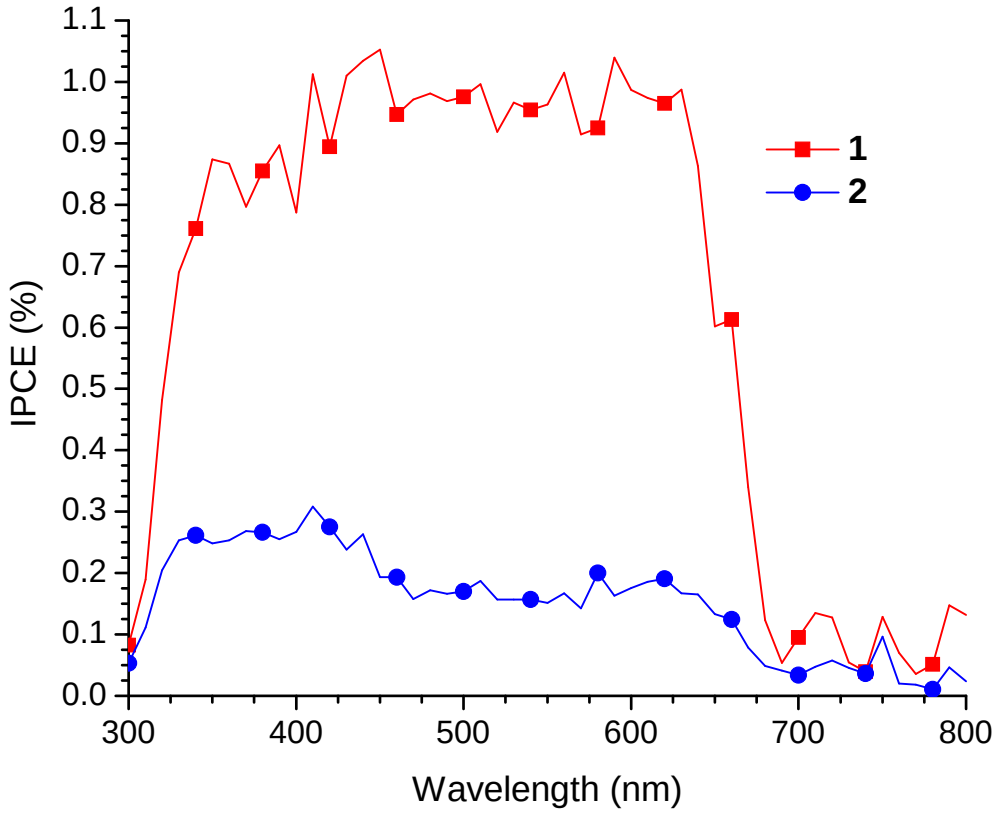


Fig. S2 IPCE spectra of the most efficient BHJ solar cells based on active layers of P3HT:**1**–**2** (10:8 by mass). All devices were based on the ITO/PEDOT:PSS/P3HT:**1** or **2**/LiF/Al architecture.

2. IPCE Spectra of OPV Devices with 2:$PC_{61}BM$ and 4:$PC_{61}BM$ Active Layers

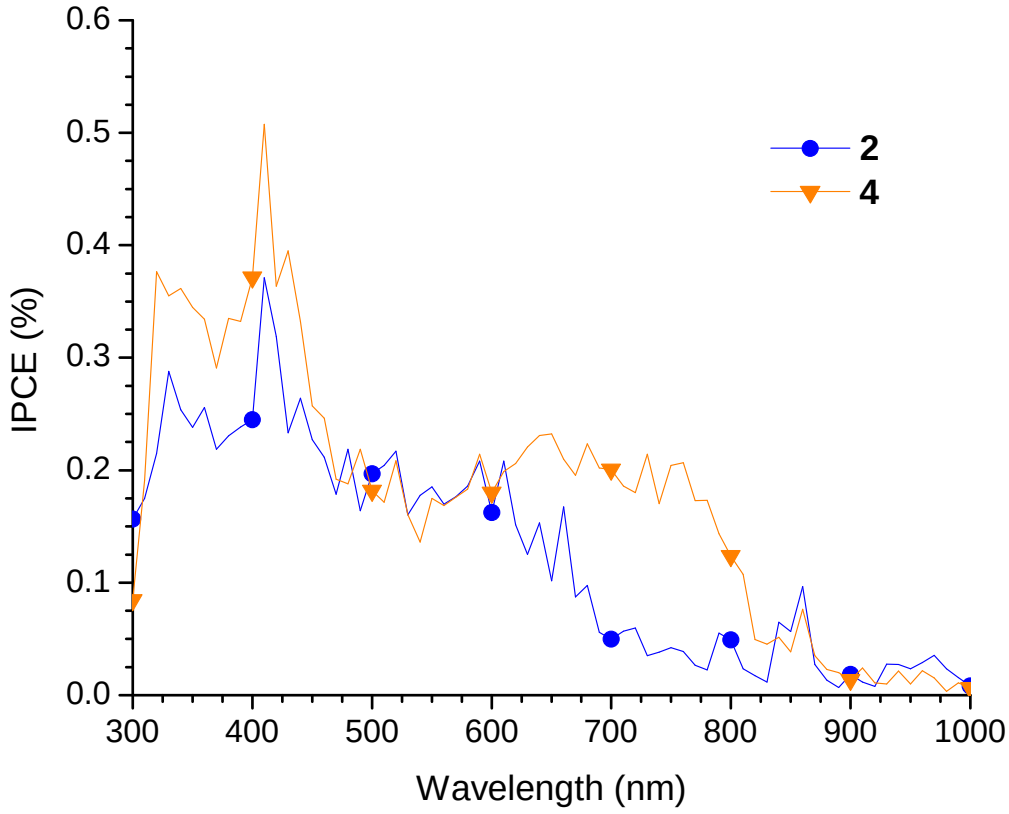
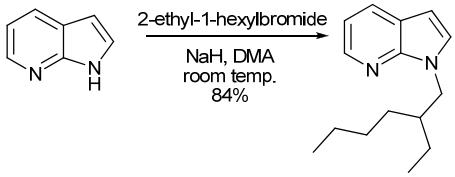


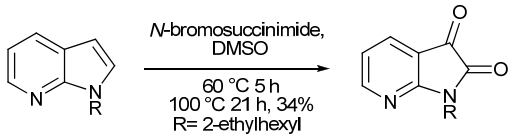
Fig. S3 IPCE spectra of the most efficient BHJ solar cells based on active layers of **2** or **4**:$PC_{61}BM$ (60:40 by mass). All devices were based on the ITO/PEDOT:PSS/**2** or **4**:$PC_{61}BM$/LiF/Al architecture.

3. Detailed Synthetic Procedures



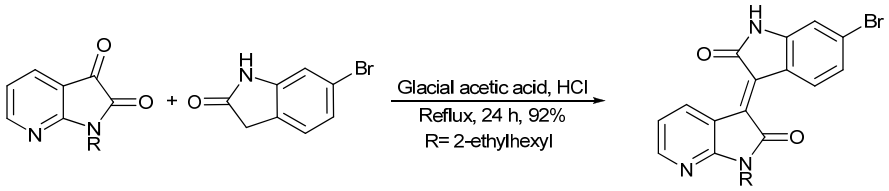
This procedure was carried out according to a previous literature report.[1] 7-Azaindole (355 mg, 3.00 mmol) was dissolved in 10 mL of dimethylacetamide (DMA). NaH (98.2 mg, 4.09 mmol) was added and the reaction was stirred for 30 min under N_2. 2-Ethyl-1-hexylbromide (679 mg,

3.51 mmol) was dissolved in 2 mL of DMA and added slowly to the reaction mixture via syringe and the reaction mixture was stirred for 18 hours at room temperature. The reaction mixture was quenched with H_2O and extracted with DCM; the combined organic phases were washed with deionized water, dried over $MgSO_4$ and concentrated under reduced pressure. The crude 1-(2-ethylhexyl)-7-azaindole was purified by column chromatography on silica gel (eluent: DCM) and dried under high vacuum to yield a clear viscous liquid (579 mg, 83.7%). ^{1}H NMR (500 MHz, $CDCl_3$ δ, ppm): 8.32 (dd J_1 = 1.2 Hz, J_2 = 4.6 Hz 1H), 7.89 (dd J_1 = 1.4 Hz, J_2 = 7.8 Hz 1H), 7.19 (d J = 3.4 Hz 1H), 7.01-7.05 (m 1H), 6.45 (d J = 3.4 Hz 1H), 4.19 (d J = 7.4 Hz 2H), 1.92-2.02 (m 1H), 1.20-1.35 (m 9H), 0.82-0.91 (m 6H)

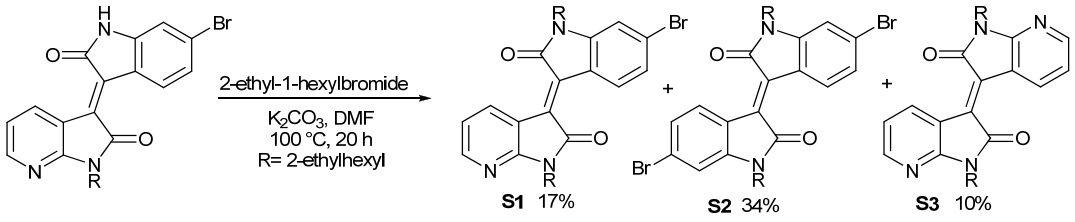


This procedure was adapted from a previous literature report.[1] 1-(2-Ethylhexyl)-7-azaindole (1.02 g, 4.45 mmol) was dissolved in 20 mL of dry DMSO under N_2. *N*-bromosuccinimide (1.60g mg, 8.98 mmol) was added to the flask and the reaction mixture was stirred at 60 °C while sparging with N_2. After 5 hours the temperature was increased to 100 °C and the reaction mixture was heated while sparging with N_2 for 21 hours. The reaction mixture was quenched with 100 mL of H_2O and extracted with DCM. The combined organic phases were washed with deionized water, dried over $MgSO_4$ and concentrated under reduced pressure. The crude 1-(2-ethylhexyl)-7-azaisatin was purified by column chromatography on silica gel (eluent: 1:3 ethyl acetate : hexanes) and dried under high vacuum to yield a yellow-orange solid (395 mg, 34%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 8.35 (dd J = 5.2; 1.6 Hz, 1H), 7.72, (dd J = 7.3; 1.6 Hz,

1H), 6.96-6.99 (m 1H), 3.65 (dd J_1 = 7.1; 1.3 Hz, 2H), 1.90 (m 1H), 1.10-1.40 (m 10H), 0.70-0.90 (m 7H)



This procedure was adapted from previously reported literature procedure.[2] 1-(2-Ethylhexyl)-7-azaisatin (308 mg, 1.45 mmol) and 6-bromo-2-oxindole (369 mg, 1.42 mmol) were dissolved in 12 mL of glacial acetic acid. Concentrated hydrochloric acid (0.1 mL) was added to the flask and the reaction mixture was heated at reflux for 24 hours under N_2. The reaction mixture was cooled to room temperature and diluted with 5% aqueous $NaHCO_3$ (w/v). The product was isolated by suction filtration, washed with $NaHCO_3$(aq) three times, H_2O three times and 1:1 EtOH:H_2O three times and dried under high vacuum to yield 1-(2-ethylhexyl)-7-aza-6′-bromoisoindigo as a red-black solid (591.5 mg, 92.3%). ^{1}H NMR (500 MHz, D_6-DMF, δ, ppm): 11.21 (s 1H), 9.43 (d J = 7.8; 1.4 Hz, 1H), 9.19 (d J = 8.6 Hz 1H), 8.32 (dd J_1 = 5.0; 1.4 Hz, 1H), 7.30 (dd J_1 = 8.7; 1.9 Hz, 1H), 7.19 (d J = 1.9 Hz 1H), 7.12-7.15 (m 1H), 3.82 (d J = 7.6 Hz 2H), 2.04 (m 1H), 1.25-1.45 (m 9H), 0.84-0.96 (m 6H)



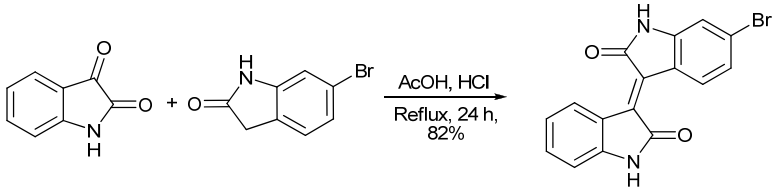
This procedure was adapted from a previously reported synthesis.[2] 1-(2-Ethylhexyl)-7-aza-6′-bromoisoindigo (57.4 mg, 0.126 mmol) was dissolved in 2 mL of dry DMF under N_2. K_2CO_3

(119 mg, 0.859 mmol) was added and the reaction mixture was stirred for 30 min. 2-Ethyl-1-hexylbromide (0.10 mL, 0.56 mmol) was added and the reaction was stirred at 100 °C for 20 hours. The reaction mixture was poured over 50 mL of brine and extracted with DCM. The combined organic phases were washed three times with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting three products were separated by column chromatography on silica gel (eluent: DCM) and dried under high vacuum to yield red-black solids.

1,1′-bis-(2-ethylhexyl)-7-aza-6′-bromoisoindigo (S1): (12.5 mg, 17.0%), ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 9.37 (d *J*= 7.9; 1.3 Hz, 1H), 9.145 (d *J* = 8.6 Hz 1H), 8.21 (d *J* = 5.1; 1.4 Hz, 1H), 7.20 (d *J* = 8.6; 1.7 Hz, 1H), 6.96-6.99 (m 1H), 6.92 (d *J* = 1.6 Hz 1H), 3.79-3.82 (m 2H), 3.60-3.68 (m 2H), 2.02-2.04 (m 1H), 1.82-1.85 (m 1H), 1.25-1.38 (m 19H), 0.79-0.95 (m 15H)

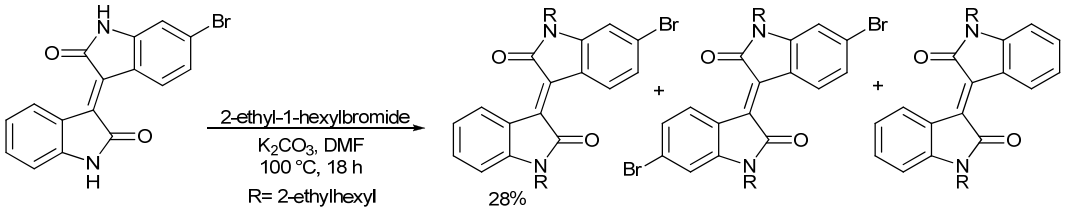
1,1′-bis-(2-ethylhexyl)-6,6′-dibromoisoindigo (S2): (24.1 mg, 33.7%), ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 9.04 (d *J* = 8.6 Hz 2H), 7.17 (d *J* = 8.6; 1.6 Hz, 2H), 6.89 (s 2H), 3.60-3.65 (m 4H), 1.81-1.84 (m 2H), 1.25-1.40 (m 27H), 0.82-0.95 (m 19H)

1,1′-bis-(2-ethylhexyl)-7,7′-diazaisoindigo (S3): (7.3 mg, 10.2%), ^{1}H NMR (500MHz, $CDCl_3$, δ, ppm): 9.45 (dd J_1 = 4.8; 1.3 Hz, 2H), 8.23 (dd *J* = 5.06; 1.3 Hz, 2H), 6.99-7.02 (m 2H), 3.80-3.81 (m 4H), 2.02-2.05 (m 2H), 1.25-1.41 (m 23H), 0.86-0.94 (m 18H)

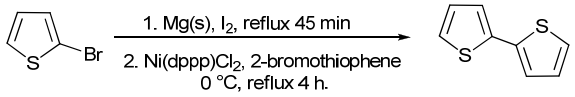


This procedure was adapted from a previous literature report.[2] To a slurry of 6-bromoisatin (131 mg, 0.892 mmol) and 6-bromo-2-oxindole (187 mg, 0.880 mmol) in 5.6 mL of glacial acetic acid

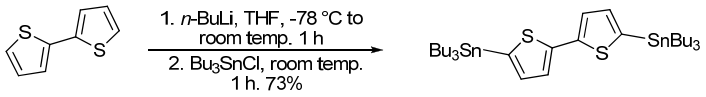
was added 0.05 mL of concentrated hydrochloric acid. The reaction mixture was heated to reflux for 24 hours. The reaction mixture was cooled and the product was isolated by suction filtration. The resulting red-black solid was washed with H_2O three times and EtOH three times and dried under high vacuum to yield 6-bromoisoindigo (246 mg, 82.0%).



This procedure was adapted from a previous literature report.[2] 6-Bromoisoindigo (246 mg, 0.721 mmol), and K_2CO_3 (637 mg, 4.61 mmol) were dissolved in 15 mL of dry DMF under N_2. 2-Ethyl-1-hexylbromide (0.40 mL, 2.25 mmol) was added via syringe and the reaction mixture was stirred at 100 °C for 18 hours. The reaction mixture was poured over 100 mL H_2O and extracted with DCM. The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude 1,1′-(2-ethylhexyl)-6-bromoisoindigo was purified by column chromatography on silica gel (eluent: 3:2 hexane: DCM), and dried under high vacuum to yield a red solid (112 mg, 27.5%). ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): 9.13 (d, *J* = 7.9 Hz 1H), 9.05 (d, *J* 8.52 Hz 1H), 7.35 (t, *J* = 7.5 Hz 1H), 7.15 (d, *J* = 8.4 Hz 1H), 7.04 (t, *J* = 7.6 Hz 1H), 6.88 (s, 1H), 6.76 (d, *J* = 7.7 Hz 1H), 3.56-3.70 (m, 4H), 1.77-1.88 (m, 2H), 1.22-1.45 (m, 18H), 0.82-0.97, (m, 14H)

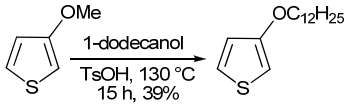


This procedure was adapted from a previous literature report.[3] To Mg turnings (0.9460 g, 0.0201 mol) and trace I_2 in 15 mL of dry THF under N_2 was added 0.5 mL of 2-bromothiophene (2.4 mL, 0.025 mol), to initiate an exothermic reaction. Once the reaction began the remaining 2-bromothiophene was added dropwise and the reaction mixture was stirred at reflux for 45 min. The solution was cooled to room temperature and added via syringe to a solution of Ni(dppp)Cl_2 (17 mg, 0.031 mmol) and 2-bromothiophene (1.95 mL, 0.0120 mol) in 10 mL of dry THF at 0 °C. The mixture was then heated to reflux for 4 hours. The resulting mixture was poured over 50 mL H_2O and extracted with DCM. Dilute aqueous hydrochloric acid was required to break the resulting emulsion. The organic layers were washed with 5% aqueous $NaHCO_3$ (w/v) and brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude 2,2′-bithiophene was purified by column chromatography on silica gel (eluent: hexanes) and dried under high vacuum to yield a white solid (2.642 g, 78.9%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.21 (d, J = 5.1 Hz 1H), 7.18 (d, J = 3.5 Hz 1H), 7.02 (t, J = 3.7 Hz 1H)

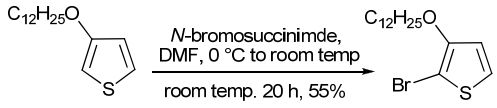


This procedure was adapted from a previous literature report.[4] 2,2′-Bithiophene (53.1 mg, 0.319 mmol), was dissolved in 3 mL of dry THF under N_2. The solution was cooled to –78 °C and *n*-butyllithium (2.5 mol/L in hexanes, 0.29 mL, 0.725 mmol) was added to the solution dropwise. A white precipitate formed and the suspension was warmed to room temperature and stirred for 1 hour. Tributyltin chloride (0.19 mL, 0.70 mmol) was added and the reaction mixture was heated at reflux for 1 hour. The mixture was then cooled to room temperature and 7 mL of hexane was

added. The organic layer was washed with 5% aqueous $NaHCO_3$ (w/v) and water, dried over $MgSO_4$ and concentrated under high vacuum to yield 5,5′-di(tributylstannyl)-2,2′-bithiophene as a viscous green liquid (172 mg, 72.6%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.29 (d, J = 3.33 Hz 1H), 7.05 (d, J = 3.45 Hz 1H), 1.57 (m 7H), 1.34 (m 7H), 1.11 (m, 7H), 0.91 (m 11H)

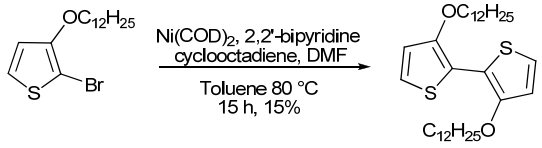


This synthesis was adapted from a previously reported procedure.[5] 3-Methoxythiophene (1.4 mL, 18 mmol) was dissolved in 15 mL of dry toluene. 1-Dodecanol (7.8 mL, 35 mmol) was added, followed by *p*-toluenesulfonic acid (0.33 g, 1.8 mmol). The reaction mixture was heated at reflux under N_2 overnight. The reaction mixture was diluted with 50 mL of DCM and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated to dryness under reduced pressure. The crude 3-dodecyloxythiophene was purified by column chromatography on silica gel (eluent: hexanes, gradient to 25% DCM in hexanes) and concentrated under reduced pressure to yield 2.26 g of a colorless oil. This product was dried under high vacuum to a final yield of 1.82 g (38.8%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.17 (m, 1H), 6.75 (d, J = 5.18 Hz, 1H), 6.23 (t, J = 1.51 Hz, 1H), 3.94 (t, J = 6.53 Hz, 2H), 1.74-1.79(m, 2H), 1.41-1.47 (m, 2H), 1.23-1.36 (m 18H)

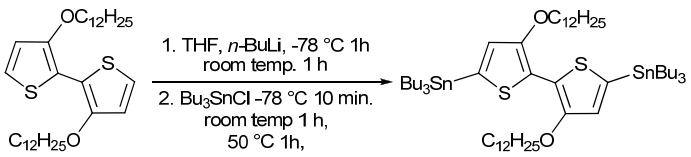


This synthesis was adapted from a previously reported procedure.[5] 3-Dodecyloxythiophene (1.82 g, 6.78 mmol) was dissolved in 15 mL of dry THF. The solution was cooled to 0 °C in an ice bath under N_2. *N*-bromosuccinimide (1.21 g, 6.78 mmol) was added. The reaction mixture was

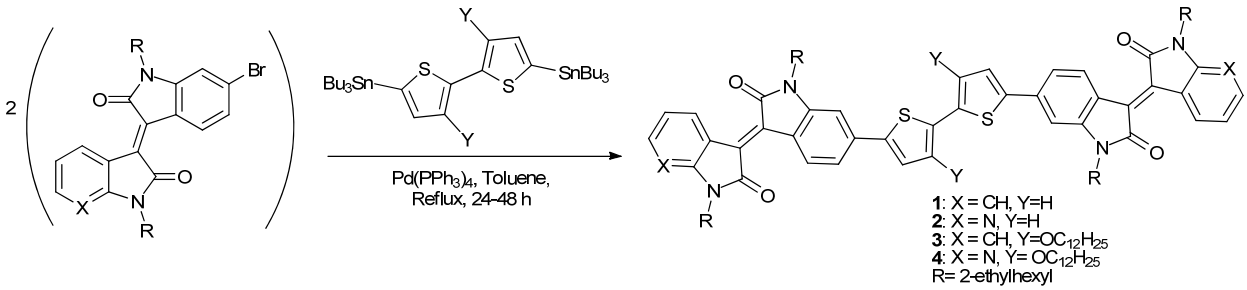
warmed slowly to room temperature, and stirred for 20 hours. The reaction mixture was diluted with 50 mL diethyl ether, washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude 2-bromo-3-dodecyloxythiophene was purified by column chromatography on silica gel (eluent: hexanes), concentrated under reduced pressure and dried under high vacuum to yield an off-white solid (1.29 g, 55%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.18 (d J = 5.95 Hz, 1H), 6.74 (d J = 5.95 Hz, 1H), 4.03 (t, J = 6.57 Hz, 2H), 1.72-1.78 (m, 2H), 1.42-1.47 (m, 2H), 1.23-1.37 (m, 17H)



This synthesis was adapted from a previously reported procedure.[5] Bis(cyclooctadienyl)nickel(0) (1.535 g, 5.57 mmol) was dissolved in 15 mL of anhydrous DMF. 2,2′-Bipyridine (0.87 g, 5.6 mmol) and cyclooctadiene (0.45 mL, 3.7 mmol) were added and the reaction mixture was heated at 80 °C for 1 hour. 2-Bromo-3-dodecyloxythiophene (1.29 g, 3.71 mmol) was dissolved in 25 mL of dry toluene and added to the reaction mixture dropwise. The reaction mixture was subsequently stirred overnight at 80 °C. The reaction mixture was diluted with 100 mL of DCM and washed with 10% aqueous hydrochloric acid and water, dried over $MgSO_4$ and concentrated to dryness under reduced pressure. The crude 3,3′-bis(dodecyloxy)-2,2′-bithiophene was purified by column chromatography on silica gel (eluent: hexanes, gradient to 20% DCM in hexanes) and dried under high vacuum to yield a pale yellow solid (0.300 g, 30.2%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.07 (d J = 5.55 Hz, 2H), 6.83 (d J = 5.56 Hz, 2H), 4.09 (t J = 6.52 Hz, 4H), 1.81-1.87 (m 5H), 1.48-1.56 (m 10H), 1.22-1.39 (m 42H)



This synthesis was adapted from a previously reported procedure.[5] 3,3′-Bis(dodecyloxy)-2,2′-bithiophene (230 mg, 0.43 mmol) was dissolved in 5 mL of dry THF and cooled to –78°C, *n*-butyllithium (0.38 mL, 0.95 mmol) was added dropwise and the reaction mixture was stirred at –78 °C for 1 hour. It was then warmed to room temperature and stirred for an additional 1 hour. The reaction mixture was, again, cooled to –78 °C and tributyltin chloride (0.20 mL, 0.95 mmol) was added. The mixture was stirred at –78 °C for 10 min before being warmed to room temperature and stirred for 2.5 hours. The reaction mixture was diluted with 20 mL of ethyl acetate, washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield 5,5′-di(tributylstannyl)-3,3′-bisdodecyloxy-2,2′-bithiophene as a yellow oil (657 mg, 137%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 6.83 (s, 1H), 4.10 (t, J = 6.41 Hz), 1.82-1.88 (m 3H), 1.51-1.67 (m 20H), 1.43-1.50 (m 2H), 1.22-1.39 (m 47H), 1.02-1.17 (m 12H), 0.86-0.94 (m 32H), 0.78-0.82 (m 2H)



5,5′-di(1,1′-bis(2-ethylhexyl)isoindigo)-3,3′-bithiophene (1):[2]

5,5′-di(tributylstannyl)-2,2′-bithiophene (29.2 mg, 0.0392 mmol) was dissolved in 5 mL of dry toluene and degassed using three freeze pump thaw cycles. 1,1′-Bis(2-ethylhexyl)-6-bromoisoindigo (51.4 mg, 0.0909 mmol) and $Pd(PPh_3)_4$ (3.6 mg, 0.0031 mmol) were added to

the solution and the reaction mixture was stirred at reflux for 45 hours. The solvent was removed under reduced pressure and the crude **1** was purified by chromatography on silica gel (eluent: 1:1 DCM: hexanes, gradient to 5:3 DCM: hexanes) and dried under high vacuum to yield a dark purple solid (31.8 mg, 71.5%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 9.20 (d J = 8.4 Hz 2H), 9.15 (d J = 8.0 Hz, 2H), 7.28-7.38 (m 6H), 7.05 (t J = 8.5 Hz 2H), 6.99 (d J = 1.5 Hz 2H), 6.78 Hz (d J = 7.8 Hz 2H), 3.63-3.80 (m 9H), 1.84-1.94 (m 5H), 1.28-1.47 (m 44H), 0.86-1.00 (m 31H). MALDI-TOF MS (m/z): $(M+H)^+$ (calc'd): 1135.6, (found): 1135.7

5,5′-di(1,1′-bis(2-ethylhexyl)-7-azaisoindigo)-2,2′-bithiophene (2):

5,5′-Di(tributylstannyl)-2,2′-Bithiophene (31.7 mg, 0.0426 mmol) was dissolved in 5 mL of freshly degassed (using three freeze pump thaw cycles) dry toluene. 1,1′-Bis(2-ethylhexyl)-7-aza-6′-bromoisoindigo (53.2 mg 0.0939 mmol) and $Pd(PPh_3)_4$ (3.2 mg, 0.0028 mmol) were added and the reaction mixture was stirred at reflux for 48 hours. The solvent was removed under reduced pressure and the crude **2** was purified by column chromatography on silica gel (eluent: DCM) and dried under high vacuum to yield a dark purple solid (34.2 mg, 70.6%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 9.36 (dd J_1 = 7.8; J_2 = 1.3 Hz, 1H), 9.27 (d J = 8.4 Hz 1H), 8.19 (dd J_1 = 4.9; J_2 = 1.2 Hz, 1H), 7.36-7.41 (m 2H), 7.31 (dd J_1 = 8.4; J_2 = 1.5 Hz, 1H), 6.94-6.99 (m 2H), 3.50-3.88 (m 7H), 2.01-2.05 (m 1H), 1.85-1.93 (m 1H), 1.19-1.50 (m 32H), 0.79-1.01 (m 23H). ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) 168.6, 168.0, 162.7, 158.1, 157.9, 157.7, 149.6, 146.2, 143.0, 137.93, 137.88, 136.7, 133.7, 130.9, 130.8, 130.2, 130.0, 125.5, 125.3, 122.6, 120.8, 119.2, 118.8, 116.9, 116.4, 113.1, 104.8, 104.7, 100.0, 57.8, 55.4, 44.2, 43.5, 37.8, 37.4, 30.8, 30.5, 28.9, 28.5, 27.89, 27.88, 26.9, 24.3, 24.27, 23.9, 23.1, 22.7, 17.5, 14.2, 14.18, 12.1, 13.6, 10.8, 10.6, 1.0. MALDI-TOF MS (m/z): $(M+H)^+$ (calc'd): 1137.6, (found): 1137.7

5,5′-di(1,1′-bis(2-ethylhexyl)isoindigo)-2,2′-[(5,5′-bisdodecyloxy)bithiophene] (3):

5,5′-Di(tributylstannyl)-3,3′-bisdodecyloxy-2,2′-bithiophene (210.7 mg, 0.1893 mmol) was dissolved in 13 mL of dry toluene and degassed using three freeze pump thaw cycles. 1,1′-Bis(2-ethylhexyl)-6-bromoisoindigo (215.0 mg, 0.3801 mmol) and $Pd(PPh_3)_4$ (12.9 mg, 0.0112 mmol) were added and the reaction mixture was stirred at reflux for 20 hours. The solvent was removed under reduced pressure and the crude **3** was purified by column chromatography on silica gel (eluent: 1:1 DCM:hexanes, gradient to 3:2 DCM:hexanes) and dried under high vacuum to yield a dark blue solid (147.2 mg, 51.7%). ^{1}H NMR (500 MHz, CD_2Cl_2, δ ppm): 9.20 (d J = 8.4 Hz 1H), 9.14 (d, J = 7.9 Hz), 7.35 (t, J = 7.7 Hz 1H), 7.30 (d, J = 8.4 Hz 1H), 7.26 (s, 1H), 7.01-7.04 (m, 2H), 6.82 (d, J = 7.89 Hz 1H), 4.26 (t, J = 7.44 Hz 2H), 3.63-3.78 (m 4H), 1.84-2.01 (m, 4H), 1.56-1.66 (m, 2H), 1.17-1.50 (m 35H), 0.80-1.04 (m 16H). ^{13}C NMR (500 MHz, CD_2Cl_2, δ ppm) 168.5, 168.2, 153.4, 146.0, 145.1, 139.0, 137.9, 132.6, 121.9, 120.9, 115.8, 103.8, 72.3, 44.3, 44.02, 44.01, 44.0, 43.0, 37.8, 37.6, 31.9, 30.8, 30.7, 29.73, 29.67, 29.5, 29.4, 28.8, 28.7, 27.8, 26.1, 24.2, 24.1, 23.1, 22.7, 19.6, 13.90, 13.86, 13.8, 10.6, 10.5, 0.8. MALDI-TOF MS (m/z): (M^+): (calc'd): 1503.98, (found): 1504.0

5,5′-di(1,1′-bis(2-ethylhexyl)-7-azaisoindigo)-2,2′-[(3,3′-bisdodecyloxy)bithiophene] (4):

5,5′-Di(tributylstannyl)-3,3′-bisdodecyloxy-2,2′-bithiophene (106.3 mg, 0.0955 mmol) was dissolved in 13 mL of dry toluene and degassed using three freeze pump thaw cycles. 1,1′-Bis(2-ethylhexyl)-7-aza-6′-bromoisoindigo (115.5 mg 0.2039 mmol) and $Pd(PPh_3)_4$ (6.4 mg, 0.00554 mmol) were added and the reaction was stirred at reflux for 20 hours. The solvent was removed under reduced pressure and the crude **4** was purified by column chromatography on silica gel (eluent: DCM, gradient to 1% methanol in DCM) and concentrated under high vacuum to yield a dark blue solid (125.3 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 9.36 (d J = 7.70 Hz, 1H),

9.25 (d, *J* = 8.43 Hz 1H), 8.19 (d *J* = 4.93 Hz 1H), 7.31 (d *J* = 8.03 Hz 1H), 7.20 (s, 1H), 6.97 (m 2H), 4.24 (t *J* = 6.44 Hz 2H), 3.83 (d, *J* = 7.11 Hz 2H), 3.71-3.76 (m 2H), 2.02-2.10 (m 1H), 1.87-2.00 (m 3H), 1.54-1.66(m 10H), 1.20-1.48 (m 43H), 0.80-1.02 (m 22H). ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm), 168.8, 168.2, 157.6, 153.4, 149.4, 146.2, 139.1, 138.7, 136.6, 133.8, 130.8, 129.6, 120.5, 118.5, 118.1, 116.6, 116.3, 113.1, 104.0, 72.2, 44.2, 43.4, 37.8, 37.5, 31.9, 30.9, 30.5, 29.72, 29.69, 29.61, 28.8, 28.5, 26.1, 24.2, 23.9, 23.13, 23.10, 22.7, 14.1, 10.9, 10.6, 1.04. MALDI-TOF MS: (M^+): (calc'd): 1505.97, (found): 1506.0

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