Supporting Information

Effect of Crystallinity in Small Molecular Weight Organic Heterojunction Solar Cells

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1. Syntheses and Characterization of Compounds

1-1. Materials and instrumentations

$^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded with JEOL JNM-ECX 400 spectrometers at ambient temperature by using tetramethylsilane as an internal standard. High-resolution electrospray ionization time-of-flight (HR-ESI-TOF) and High-resolution fast atom bombardment (HR-FAB) were measured by a JEOL JMS-700 MStation spectrometer. UV/Vis spectra were measured with a JASCO UV/Vis/NIR spectrophotometer V-570.

1-2. Single crystal X-ray diffraction analysis

The crystals were mounted in Litho Loops (purchased from Protein Wave). The diffraction data was collected at 103 K with a Rigaku VariMaxRAPID/a imaging plate diffractometer with graphite-monochromated Cu-Kα radiation or with a Rigaku Mercury-8 diffractometer with graphite-monochromated Mo-Kα radiation equipped with a CCD detector. The diffraction data were processed with CrystalStructure of the Rigaku program, solved with the SIR-97 program$^{[1]}$ and refined with the SHELX-97 program.$^{[2]}$
1-3. Synthesis

Scheme S1. Synthetic scheme of BPc-pre-2

Ethyl 4,7-dihydro-8,8-dimethyl-4,7-ethano-3-ido-2H-isindole-1-carboxylate (2)

A solution of ethyl 4,7-dihydro-8,8’-dimethyl-4,7-ethano-2H-isindole-1-carboxylate 1 (2.29 g, 9.3 mmol), benzyltrimethylammonium dichloroiodate (BTMA•ICl2) (3.41 g, 9.8 mmol) and CaCO3 (1.96 g, 19.6 mmol) in CH2Cl2 (100 ml) and MeOH (35 ml) was refluxed for 3 h. After cooling to room temperature, the precipitate was filtrated. The filtrate was washed with aqueous NaHSO3, water and brine, dried over Na2SO4. After removal solvent, the residue was purified by silica gel column chromatography (CH2Cl2) and crystallization from CHCl3/hexane gave 2 as white solid in 89% yield (3.1 g, 8.3 mmol). 1H NMR (400 MHz, CDCl3): δ 8.46 (brs, 1H, -NH), 6.52-6.46 (m, 2H, olefin), 4.35 (dq, 1H, J = 10.8, 7.1 Hz, -CO2Et), 4.27 (dq, 1H, J = 10.8, 7.1 Hz, -CO2Et), 3.81 (m, 1H, bridge head), 3.53 (m, 1H, bridge head), 1.39 (dd, 1H, J = 11.8, 2.6
Hz, bridge), 1.36 (t, 2H, J = 7.1 Hz, -CO$_2$Et), 1.23 (dd, 1H, J = 11.8, 2.6 Hz, bridge), 1.05 (s, 3H, -Me), 0.72 (s, 3H, -Me); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 160.74, 137.49, 136.57, 136.53, 135.96, 135.01, 121.10, 60.17, 46.91, 43.17, 37.71, 35.26, 30.70, 30.22, 14.64; HRMS (ESI) m/z calcd. for C$_{13}$H$_{18}$INO$_2$Na [M+Na$^+$]: 394.0280; Found for 394.0280.

**Ethyl 4,7-dihydro-8,8-dimethyl-4,7-ethano-3-iodo-2-Boc-isoidole-1-carboxylate (3)**

To a solution of 2 (2.94 g, 7.9 mmol) and N, N-dimethyl-4-aminopyridine (DMAP) (50 mg) in dry-CH$_2$Cl$_2$ (50 ml) was added di-tert-butyl dicarbonate (Boc$_2$O) (2.2 ml, 9.5 mmol) under an Ar atmosphere. After stirring for 2 h, the solvent was concentrated under a reduced pressure. The residue was purified by alumina column chromatography (CHCl$_3$) and silica gel column chromatography (CH$_2$Cl$_2$) to give 3 as pale yellow oil in quant., which was then used for next reaction without further purification. $^1$H NMR (400 MHz, CDCl$_3$): δ 6.46 (m, 2H, olefin), 4.37-4.24 (m, 2H, CO$_2$Et), 3.70 (m, 2H, bridge head), 3.55 (m, 2H, bridge head), 1.59 (s, 9H, Boc), 1.39 (dd, 1H, J = 11.9, 2.7 Hz, bridge), 1.35 (t, 3H, J = 7.1 Hz, CO$_2$Et), 1.24 (dd, 1H, J = 11.9, 2.7 Hz, bridge), 1.04 (s, 3H, Me), 0.72 (s, 3H, Me); $^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz) [typical signals]: δ 160.01, 149.29, 140.68, 138.26, 135.33, 122.94, 85.14, 65.49, 60.47, 46.82, 42.65, 37.37, 35.51, 30.59, 30.03, 27.99, 27.72, 14.61.

**Bipyrrrole 5**

A mixture of 3 (19.6 g, 42 mol) and copper (19.8 g) in dry-DMF (100 ml) was heated at 110 °C for 10 h under argon atmosphere. The reaction mixture was cooled to room temperature, filtered through Celite to remove the copper, then washed with CH$_2$Cl$_2$. The organic phase was washed with 1 M HCl, water and brine, dried over Na$_2$SO$_4$, the solvent was concentrated to give crude N-Boc bipyrrrole 4. A mixture of crude 4 and conc. HCl (100 ml) in EtOAc (400 ml) was stirred for 12 h at room temperature and quenched with water. The mixture was extracted with
EtOAc. The combined organic layer was washed with sat. NaHCO₃, water and brine, and dried over Na₂SO₄, and the solvent was concentrated. The crude product was purified by silica gel column chromatography (5% EtOAc/CH₂Cl₂) to give 5 as white solids in 76% yield (7.70 g, 15.8 mmol). ¹H NMR (400 MHz, CDCl₃): δ 8.50 (brs, 2H, -NH), 6.60-6.50 (m, 4H, olefin), 4.42-4.25 (m, 4H, CO₂Et), 3.84 (m, 4H, bridge head), 1.48-1.26 (m, 4H, bridge), 1.37 (t, 6H, J = 7.3 Hz, CO₂Et), 1.09 (s, 3H, Me), 0.76 (s, 3H, Me); ¹³C NMR (CDCl₃, 100 MHz): δ 161.71, 137.84, 136.22, 134.69, 127.87, 127.77, 118.92, 116.25, 60.05, 46.55, 43.49, 37.75, 34.80, 30.74, 30.25, 14.58; HRMS (ESI) m/z calcd. for C₃₀H₃₇N₂O₄ [M+H⁺]: 489.27533; Found for 489.27740.

Bipyrrrole 6

Under Ar atmosphere, a solution of 5 (2.7 g, 3.9 mmol) and NaOH (2.0 g) in ethylene glycol (30 ml) was heated at 170 °C. After being stirred for 90 min, the reaction mixture was cooled to room temperature then saturated aqueous NaHCO₃ was added. The mixture was extracted with EtOAc and the separated organic layer was washed with water and brine, dried over Na₂SO₄. The solvent was removed under a reduced pressure to obtain the black residue. It was purified by silica gel column chromatography (CH₂Cl₂) to give 6 as pale blue solid in 64% (0.86 g, 2.5 mmol) which was then used for next reaction without further purification. ¹H NMR (400 MHz, CDCl₃): δ 7.39 (brs, 2H, -NH), 6.59-6.47 (m, 4H, olefin), 6.46 (d+d, 2H, J = 1.8 Hz, α-H), 3.79-3.74 (m, 2H, bridge head), 3.22 (d, 2H, J = 6.0 Hz, bridge head), 1.44 (dd, 2H, J = 11.5, 3.2 Hz, bridge), 1.33 (dd, 2H, J = 11.5, 2.3 Hz, bridge), 1.05 (s, 3H, Me), 0.78 (s, 3H, Me); ¹³C NMR (CDCl₃, 100 MHz): δ 136.93, 134.91, 129.71, 123.85, 123.38, 116.27, 116.02, 109.49, 46.13, 44.08, 37.23, 34.55, 30.93, 30.69; HRMS (ESI) m/z calcd. for C₂₄H₂₉N₂ [M+H⁺]: 345.23307; Found for 345.23316.

Bipyrrrole 7
POCl₃ (1.1 mL, 11.7 mmol) was added to a mixture of 6 (0.86 g, 2.5 mmol) and DMF (7.0 ml) in CH₂Cl₂ (20 ml) at 0 °C under an Ar atmosphere. The mixture was then reflux and stirred for 1h. The mixture was poured into aqueous sodium acetate (1.5 g / 20 ml of water) and reflux for another 1 h. After cooling to room temperature, the mixture was extracted with CH₂Cl₂. The combined organic layer was washed with a saturated solution of Na₂CO₃, water, and brine. The solution was then dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was rinsed with MeOH to provide 7 in 79% yield (0.79 g, 1.98 mmol) as a yellow powder. ¹H NMR (CDCl₃, 400 MHz) δ 10.97 (brs, 2H, -NH-), 9.61 (s, 2H, -CHO), 6.62-6.57 (m, 4H, olefin), 4.02 (m, 2H, bridge head), 3.73 (m, 2H, bridge head), 1.51 (dd, 2H, J = 12.2, 3.1 Hz, bridge), 1.39 (dd, 2H, J = 12.2, 2.4 Hz, bridge), 1.13 (s, 6H, -CH₃), 0.81 (s, 6H, -CH₃) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 176.8, 144.32, 135.601, 134.98, 129.60, 127.18, 123.14, 45.76, 43.13, 37.78, 35.20, 31.56, 30.70 ppm; HRMS (FAB) m/z calcd. for C₂₆H₂₉N₂O₂ [M+H⁺]: 401.2224; Found for 402.2219.

**BPc-pre-2**

TiCl₄ (5.48 mL, 50 mmol) was added dropwise to a solution of Zn dust (6.54 g) and CuCl (0.40 g, 4.0 mmol) in THF (200 mL) at room temperature under an Ar atmosphere, and the mixture was heated under reflux for 2 h. Subsequently a solution of 7 (0.80 g, 2.0 mmol) in THF (200 mL) was added dropwise to the boiling reaction mixture over 1 h. The mixture was then heated to reflux for another 1 h. After cooling to 0 °C, a aqueous solution of K₂CO₃ (200 mL) was added dropwise over 30 min. After filtration the precipitate was washed with CH₂Cl₂, the combined organic layer was then dried with Na₂SO₄, and the solution was removed under
reduced pressure. The crude product was purified by silica gel column chromatography (CH$_2$Cl$_2$) and recrystallized from CH$_2$Cl$_2$/MeOH to give **Bpc-pre-2** as a blue powder in 20\% (148 mg, 0.20 mmol). $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) $\delta$: 9.76 (s, 4H, *meso*, mixed isomers), 7.22-7.11 (m, 8H, olefin), 5.93-5.87 (m, 4H, bridge head), 4.97-4.93 (m, 4H, bridge head), 2.09-1.96 (m, 4H, bridge), 1.82-1.62 (m, 4H, bridge), 1.51-1.45 (m, 12H, -CH$_3$), 0.65-0.54 (m+brs, 14H, -CH$_3$+-NH) ppm; $^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz) $\delta$ (mixture of isomers and typical signals): 151.54, 143.22, 139.74, 138.13, 136.13, 131.0, 110.51, 49.63, 44.16, 40.76, 40.35, 31.43, 31.39, 31.33 ppm; UV (CH$_2$Cl$_2$) $\lambda_{max}$ ($\varepsilon$): 375 (118242, sh), 384 (138465), 569 (34899), 616 (23950), 650 (31291); HRMS (FAB) $m/z$ calcd. for C$_{52}$H$_{55}$N$_4$ [M+H$^+$]: 735.4421; Found for 735.4433.
1-4. Analytical data

Fig. S1. $^1$H and $^{13}$C NMR spectra of 2 in CDCl$_3$. 

[Image of NMR spectra]
Fig. S2. $^1$H and $^{13}$C NMR spectra of 3 in CDCl$_3$. 
Fig. S3. $^1$H and $^{13}$C NMR spectra of 5 in CDCl$_3$. 
Fig. S4. $^1$H and $^{13}$C NMR spectra of 6 in CDCl$_3$. 
Fig. S5. $^1$H and $^{13}$C NMR spectra of 7 in CDCl$_3$. 
Fig. S6. $^1$H and $^{13}$C NMR spectra of BPc-pre-2 in CD$_2$Cl$_2$. 
Fig. S7. Crystal structure of BPC-pre-2. Thermal ellipsoid represent for 50% probability.

Crystallographic date: C$_{52}$H$_{54}$N$_4$$\cdot$4(C$_6$H$_5$Cl), M = 1185.26, triclinic, space group P -1, $a = 9.7677(3)$ Å, $b = 12.2522(3)$ Å, $c = 13.5414(3)$ Å, $\alpha = 93.7274(7)^\circ$, $\beta = 93.7976(7)^\circ$, $\gamma = 97.7976(7)^\circ$, $V = 1553.66(7)$ Å$^3$, Z = 1, T = 103 K, $R_I = 0.0565$ (for $I > 2\sigma(I)$), $R_wR_f = 0.1489$ (for all data), GOF = 1.132.
2. Other supporting figures

Figure S8. TG analysis for BPC-pre-2.

Figure S9. FT-IR spectra of the BPC-pre-2 film before and after annealing at 200 °C for 10 min.
Figure S10. J–V curves for OPV cells with BPe film converted from BPe-pre-2 (-2 V to 2V).

Figure S11. The J-V characteristic of Al/LiF:PCBM/LiF/Al device.