

# Supporting Information

## Morphology change and improved efficiency in organic photovoltaics via hexa-*peri*-hexabenzocoronene templates

Henk H. Dam,<sup>a‡</sup> Kuan Sun,<sup>a‡</sup> Eric Hanssen,<sup>b</sup> Jonathan M. White,<sup>a</sup> Tomasz Marszalek,<sup>c</sup> Wojciech Pisula,<sup>c</sup> Jens Czolk,<sup>d</sup> Jens Ludwig,<sup>d</sup> Alexander Colsmann,<sup>d</sup> Marina Pfaff,<sup>e</sup> Dagmar Gerthsen,<sup>e</sup> Wallace W. H. Wong,<sup>a\*</sup> David J. Jones.<sup>a\*</sup>

<sup>a</sup>School of Chemistry, Bio21 Institute, The University of Melbourne, 30 Flemington Road, Parkville, Victoria. 3010, Australia.

<sup>b</sup>Advanced Microscopy Facility, Bio21 Institute, The University of Melbourne, 30 Flemington Road, Parkville, Victoria 3010, Australia

<sup>c</sup>Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany.

<sup>d</sup>Lichttechnisches Institut, Karlsruhe Institute of Technology, Engesserstrasse 13, Karlsruhe 76131, Germany.

<sup>e</sup>Laboratorium für Elektronenmikroskopie, Engesserstraße 7, Karlsruhe 76131, Germany.

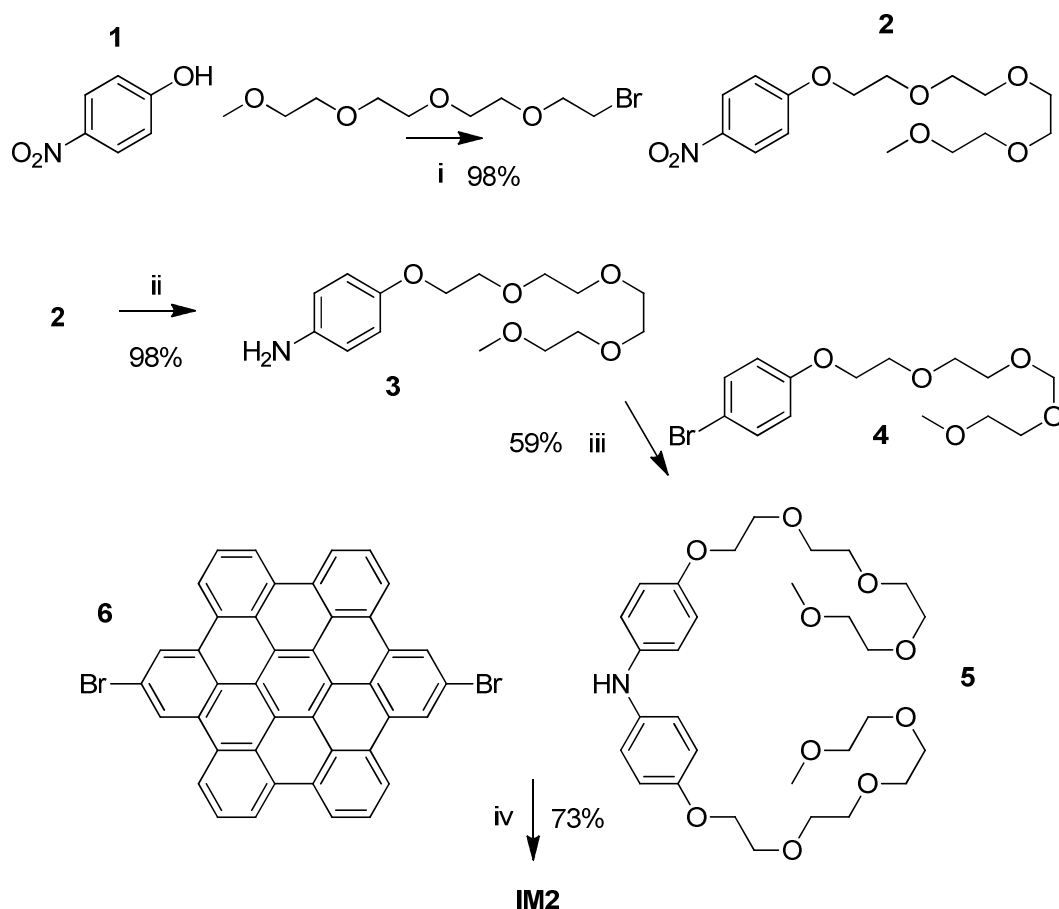
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## General methods

All reactions were performed by using anhydrous solvent under an inert atmosphere unless stated otherwise.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy were carried out by using either a Varian Inova-400 (400 MHz), a Varian Inova-500 (500 MHz) or a Bruker Avance III (600 MHz) instrument. Mass spectra were recorded with a MALDITOF MS Bruker Reflex (DCTB as matrix) or a Finnigan hybrid LTQ-FTICR mass spectrometer (Finnigan, LTQ-FT, Bremen, Germany). IR spectra were obtained on a Perkin–Elmer Spectrum One FTIR spectrometer. The spectra were measured in the wave number range of 4000–650  $\text{cm}^{-1}$ . The spectra were collected by cumulating 8 scans at a resolution of 4  $\text{cm}^{-1}$ . Size Exclusion Chromatography was performed using Bio-Beads® S-X1, 200–400 Mesh obtained from Bio-Rad laboratories Inc. Elemental analyses were obtained commercially through CMAS, Victoria. Column chromatography was carried out on Merck silica gel 60 (230–400 mesh). Dimethylformamide (DMF), methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), methanol (MeOH), Toluene, Chloroform ( $\text{CHCl}_3$ ), Ethanol (EtOH), Ether, dioxane, Tetrahydrofuran (THF), NaOH, HCl, *p*-toluene sulfonyl chloride, Tris(dibenzylidene-acetone) dipalladium(0) ( $\text{Pd}_2(\text{dba})_3$ ), Tri-*tert*-butyl-phosphonium tetra-fluoroborate (97%) ( $\text{HP}(t\text{-Bu})_3\text{BF}_4$ ), 1,1'-bis(diphenylphosphino)-ferrocene (97%) (dppf), bis(pinacolato)diboron (99%), tetraethylammonium hydroxide, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), potassium acetate, trifluoromethanesulfonic acid (triflic acid), and [1,1'-Bis(diphenylphosphino)-Ferrocene]dichloropalladium(II) complex with dichloromethane (1:1) ( $\text{Pd}(\text{dppf})\text{Cl}_2\cdot\text{CH}_2\text{Cl}_2$ ) were obtained from Sigma-Aldrich. All chemicals were used as received. All other precursors and reagents are commercially available. Compound **2** was synthesized according to a modified procedure from literature,<sup>1</sup> compounds **4**<sup>2</sup> and **6**<sup>3</sup> have been described in literature. Interface modifier **IM1** was also prepared using methods described in the literature.<sup>4</sup>

## Synthesis



**Scheme S1.** Synthetic routes towards amphiphilic hexabenzocoronene **IM2**. Reagents and conditions (i)  $\text{K}_2\text{CO}_3$ , DMF, 6 h, 90 °C, 98%; (ii)  $\text{H}_2(\text{g})$ , Pd(C) 10%, Ethanol, 18 h, 24 °C, 98%; (iii) NaOtBu,  $\text{Pd}_2(\text{dba})_3$ , dppf, Toluene, 5 h, 110 °C, 59%; (iv)  $\text{NaO}^t\text{Bu}$ ,  $\text{Pd}_2(\text{dba})_3$ ,  $\text{HP}^t\text{Bu}_3\text{BF}_4$ , Toluene, 48 h, 110 °C, 73%.

**1-[4-nitrophenoxy]-3,6,9-trioxononanethylmethylether (2):** 1-bromo-3,6,9-trioxononanethylmethylether (4.504 g, 16.61 mmol), *p*-nitrophenol **1** (2.311 g, 16.61 mmol), and  $\text{K}_2\text{CO}_3$  (6.887 g, 49.83 mmol) were stirred at 90°C in 25 mL DMF for 6 h. The volatiles were removed under reduced pressure at 90°C. The crude product was dissolved in NaOH (aq) (50 mL, 0.5 M) and the product was extracted with  $\text{CH}_2\text{Cl}_2$  (3 × 30 mL). The combined organic layers were washed with  $\text{H}_2\text{O}$  (4 × 40 mL) and dried with  $\text{MgSO}_4$ . Evaporation of the volatiles at reduced pressure gave **2** as a slightly colored oil (5.158 g, 98%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.19 (d,  $J$  = 9.4, 2H, Ph), 6.98 (d,  $J$  = 9.3, 2H, Ph), 4.22 (t,  $J$  = 4.7, 2H,  $\text{ArOCH}_2$ ), 3.89 (t,  $J$  = 4.8, 2H,  $\text{ArOCH}_2\text{CH}_2$ ), 3.73 – 3.71 (m, 2H,  $\text{OCH}_2$ ), 3.69-3.63 (m, 8H,  $\text{OCH}_2$ ), 3.55-3.53 (m, 2H,

$\text{CH}_2\text{OCH}_3$ ), 3.37 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 163.91, 141.56, 125.84, 114.62, 71.94, 70.93, 70.62, 70.53, 69.38, 68.26, 59.03.  $R_f$  = 0.34 (EtOAc).

**1-[4-Bromophenoxy]-3,6,9-trioxononanethylmethylether (4):** 1-bromo-3,6,9-trioxononanethylmethylether (4.173 g, 15.39 mmol), *p*-bromophenol (2.663 g, 15.39 mmol), and  $\text{K}_2\text{CO}_3$  (6.381 g, 46.17 mmol) were stirred at 90°C in 25 mL DMF for 6 h. The volatiles were removed under reduced pressure at 90°C. The crude product was purified by column chromatography, first eluent  $\text{CH}_2\text{Cl}_2$  which elutes unreacted *p*-bromophenol, the product was eluted with EtOAc giving **4** as a slightly colored oil (4.773 g, 89 %).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.36 (d,  $J$  = 9.0, 2H, Ph), 6.79 (d,  $J$  = 9.0, 2H, Ph), 4.09 (t,  $J$  = 4.8, 2H,  $\text{ArOCH}_2$ ), 3.84 (t,  $J$  = 4.9, 2H,  $\text{ArOCH}_2\text{CH}_2$ ), 3.72 – 3.70 (m, 2H,  $\text{OCH}_2$ ), 3.68-3.63 (m, 8H,  $\text{OCH}_2$ ), 3.54 (t, 2H,  $J$  = 4.9,  $\text{CH}_2\text{OCH}_3$ ), 3.37 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 157.81, 132.05, 116.35, 112.81, 71.803, 70.703, 70.486, 70.474, 70.379, 69.486, 67.568, 58.877.  $R_f$  = 0.38 (EtOAc).

**1-[4-aminophenoxy]-3,6,9-trioxononanethylmethylether (3):** 1-[4-nitrophenoxy]-3,6,9-trioxononanethylmethylether **2** (4.097 g, 12.99 mmol) was dissolved in 40 mL ethanol in a round bottom flask, and Pd(C) 10% (0.040 g) was added. A balloon containing  $\text{H}_2$  (g) was mounted on top of the flask and the mixture was stirred at 24°C for 18 h. The crude product was filtered over Celite and the volatiles were removed under reduced pressure giving 3.600 g of a brown oil which slowly crystallizes up on standing. This oil was subjected to column chromatography (EtOAc) giving **3** as a colorless oil (1.161 g, 44%) and a fraction with an estimated purity of 95% product as a slightly colored oil (1.984 g, 54%), both crystallize up on standing.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.76 (d,  $J$  = 8.9, 2H, Ph), 6.63 (d,  $J$  = 8.8, 2H, Ph), 4.05 (t,  $J$  = 4.1, 2H,  $\text{ArOCH}_2$ ), 3.81 (t,  $J$  = 5.1, 2H,  $\text{ArOCH}_2\text{CH}_2$ ), 3.73 – 3.70 (m, 2H,  $\text{OCH}_2$ ), 3.69-3.63 (m, 8H,  $\text{OCH}_2$ ), 3.54 (t, 2H,  $J$  = 4.9,  $\text{CH}_2\text{OCH}_3$ ), 3.41 (s br, 2H,  $\text{NH}_2$ ), 3.37 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 151.98, 140.31, 116.37, 115.94, 72.01, 70.84, 70.70, 70.69, 70.59, 69.98, 68.23, 59.10. MS ESI:  $m/z$  = 300.1805  $[\text{M}+\text{H}]^+$ , calculated  $m/z$  = 300.1806. Elemental analysis: calculated for  $\text{C}_{15}\text{H}_{25}\text{NO}_5$ , C 60.18%, H 8.42%, N 4.68%, O 26.72%; found C 60.27%, H 8.58%, N 4.51%, O 26.50%. IR ( $\text{cm}^{-1}$ ); 3410 (N-H stretch), 3344 (N-H stretch), 2882 (C-H stretch), 1100 (C-O stretch).  $R_f$  = 0.18 (EtOAc).

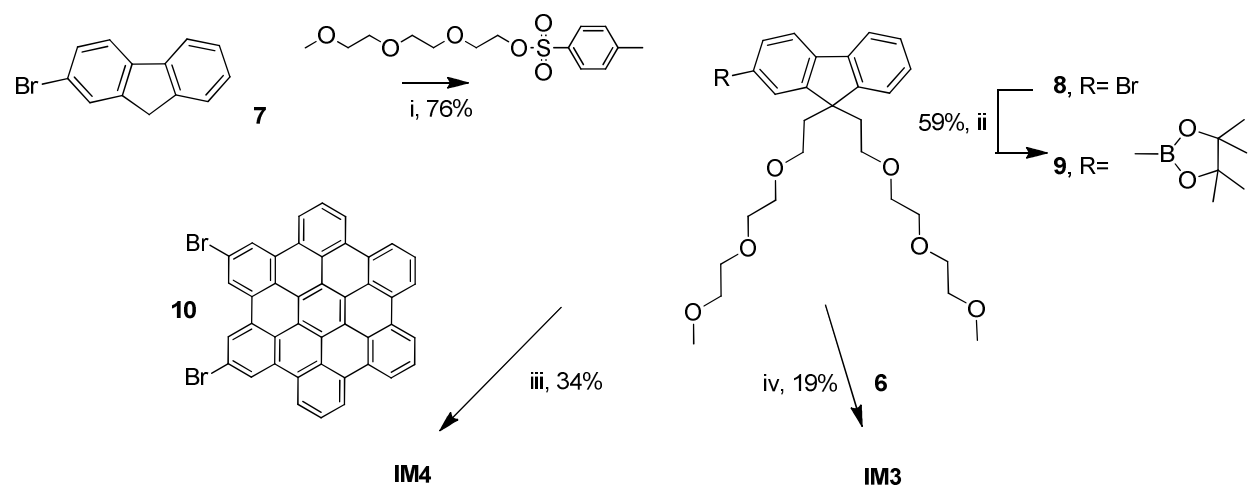
***N,N*-bis-phenoxy-3,6,9-trioxononanethylmethylether (5):** 1-[4-Bromophenoxy]-3,6,9-trioxononanethylmethylether **4** (0.624 g, 1.786 mmol) and 1-[4-aminophenoxy]-3,6,9-trioxononanethylmethylether **3** (0.510 g, 1.786 mmol) were placed in an oven dried schlenk tube and heated at 60°C under vacuum for 3h (drying of **3** and **4** by dissolving in 10 mL dry toluene with activated

molecular sieves 3Å for 72h<sup>5</sup> did result in lower yields of this reaction). After allowing the mixture to cool to 24°C NaOtBu (0.515 g, 5.36 mmol) was added followed by dry Toluene (10 mL) and the resulting mixture was purged with N<sub>2</sub> (g) for 20 min. Pd<sub>2</sub>(dba)<sub>3</sub> (0.041 g, 0.0446 mmol), and dppf (0.050 g, 0.0890 mmol) were added and the resulting mixture was stirred at 110°C for 5 h. After cooling the mixture to 24°C it was filtered over Celite. Evaporation of the volatiles under reduced pressure gave 0.961 g black oil. The crude product was purified by column chromatography (EtOAc) giving **5** as a slightly colored oil (0.613 g, 59 %). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 6.91 (d, J = 8.8, 4H, Ph), 6.83 (d, J = 8.8, 4H, Ph), 4.09 (t, J = 4.6, 4H, ArOCH<sub>2</sub>), 3.83 (t, J = 5.1, 4H, ArOCH<sub>2</sub>CH<sub>2</sub>), 3.72 (t, J = 4.3, 4H, OCH<sub>2</sub>), 3.69-3.64 (m, 16H, OCH<sub>2</sub>), 3.54 (t, J = 5.0, 4H, CH<sub>2</sub>OCH<sub>3</sub>), 3.37 (s, 6H, OCH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ = 150.77, 135.47, 116.88, 116.68, 113.13, 112.98, 69.34, 68.20, 68.02, 67.33, 67.26, 67.19, 65.49, 65.38, 65.26, 56.39. MS ESI m/z = 604.3092 [M + Na]<sup>+</sup>, calculated m/z = 604.3092. Elemental analysis: calculated for C<sub>30</sub>H<sub>47</sub>NO<sub>10</sub>, C 61.94%, H 8.14%, N 2.41%, O 27.50%; found C 61.92%, H 8.33%, N 2.28%, O 27.35%. IR (cm<sup>-1</sup>); 3347 (N-H stretch), 2871 (C-H stretch), 1100 (C-O stretch). R<sub>f</sub> = 0.10 (EtOAc).

Compound **5** is sensitive to oxidation in air and turns black on standing in air. In contrary to the product the oxidized species does not elute in EtOAc with SiO<sub>2</sub> as stationary phase in column chromatography and can be separated as such, the product can be stored at 24 °C under N<sub>2</sub>(g) for at least 7 days.

***p*-bis-(*N,N*-bis-phenoxy-3,6,9-trioxononanethylmethylether)-hexabenzocoronene (IM2):** Compound **5** (1.57 g, 2.7 mmol), HBC **6** (0.835 g, 1.23 mmol), and NaOtBu (0.472 g, 4.91 mmol) were placed in an oven dried schlenk tube under N<sub>2</sub> (g) atmosphere. The mixture was dried under vacuum at 60°C for 3h (drying of **5** by dissolving in 10 mL dry toluene with activated molecular sieves 3Å for 72h<sup>5</sup> did result in lower yields of this reaction). Dry toluene (20 mL) was added and the resulting mixture was ultrasonicated for 2h at 24°C followed by purging the mixture with N<sub>2</sub> (g) for 20 min. Pd<sub>2</sub>(dba)<sub>3</sub> (0.112 g, 0.123 mmol), and HP(tBu)<sub>3</sub>BF<sub>4</sub> (0.142 g, 0.491 mmol) were added and the resulting mixture was stirred at 110°C for 48 h. The crude product was filtered over silica with Hyflo gel on top using CH<sub>2</sub>Cl<sub>2</sub> followed by EtOAc, which eluted an impurity. The product was filtered of using CH<sub>2</sub>Cl<sub>2</sub>/MeOH 10:1. The solvent was removed and the product was precipitated from CH<sub>3</sub>CN giving **IM2** as a red powder (1.513 g, 73 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.69 (d, J = 8.1, 4H, ArHBC), 8.46 (s, 4H, ArHBC), 8.39 (d, J = 8.0, 4H, ArHBC), 7.76 (t, J = 7.8, 4H, ArHBC), 7.34 (d, J = 8.9, 8H, PhN), 7.02 (d, J = 9.0, 8H, PhN), 3.95 (t, J = 5.0, 8H, ArOCH<sub>2</sub>), 3.81 (t, J = 4.5, 8H, ArOCH<sub>2</sub>CH<sub>2</sub>), 3.76-3.65 (m, 34H, OCH<sub>2</sub>), 3.56 (t, J = 4.9, 8H, CH<sub>2</sub>OCH<sub>3</sub>), 3.37 (s, 12H, OCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 155.34, 146.60, 141.39, 130.73, 129.56, 129.33,

126.86, 125.83, 124.67, 121.26, 121.07, 119.47, 119.30, 115.76, 113.64, 72.01, 70.93, 70.75, 70.71, 70.60, 69.96, 67.82, 67.13, 59.10. MS ESI:  $m/z = 1704.74336$   $[M+Na]^+$ , calculated  $m/z = 1704.74212$ . Elemental analysis: calculated for  $C_{102}H_{108}N_2O_{20}$ , C 72.84%, H 6.47%, N 1.67%, O 19.02%; found C 72.33%, H 6.46%, N 1.55%, O 19.33%. IR ( $cm^{-1}$ ); 2866 (C-H stretch), 1100 (C-O stretch).  $R_f = 0.10$  (EtOAc).



**Scheme S2.** Synthetic routes towards amphiphilic hexabenzocoronenes **IM3** and **IM4**. Reagents and conditions (i) NaH, DMF, 18h, 24°C, 76%; (ii) KOAc, bis(pinacolato)diboron, dioxane, Pd(dppf)Cl<sub>2</sub>, 18 h, 90 °C, 59%; (iii) Et<sub>4</sub>NOH, Pd(PPh<sub>3</sub>)<sub>4</sub>, Toluene, 72 h, 110 °C, 32%; (iv) Et<sub>4</sub>NOH, Pd<sub>2</sub>(dba)<sub>3</sub>, HP(tBu)<sub>3</sub>BF<sub>4</sub>, Toluene, 72 h, 90 °C, 19%.

**di-Bromo-Hexabenzocoronene (10):** A mixture of 1,1':2',1''-Terphenyl, 4,4''-dibromo-3',4',5',6'-tetraphenyl<sup>6</sup> (0.700 g, 1.01 mmol), DDQ (1.377 g, 6.07 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was cooled to 0°C. Triflic acid (0.537 mL, 6.07 mmol) was slowly added and the resulting mixture was stirred for 3 h at 0°C. Saturated K<sub>2</sub>CO<sub>3</sub> (aq) was added and the mixture was filtered over Celite and sequentially washed with H<sub>2</sub>O and acetone. The volatiles were removed under reduced pressure giving a red solid. The crude product was purified by soxhlet extraction with MeOH for 18 h followed by CH<sub>2</sub>Cl<sub>2</sub> for 6 h giving **6** as a red compound (0.405 g, 59%). MALDI-TOF MS:  $m/z = 678.108$   $[M+H]^+$ , 679.111, 680.100, 681.089, 682.097, 683.095 peaks are in accordance with the simulated mass spectrum. IR ( $cm^{-1}$ ); 1577, 1358, 852, 786, 755, 740.

**2-Bromo-9,9-bis-(1-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethyl)-fluorene (8):** 2-bromofluorene (3.00 g, 12.24 mmol) was dissolved in anhydrous DMF (50 mL) and NaH (1.33 g, 33.29 mmol, 60 %w/w dispersion in mineral oil) was added under a N<sub>2</sub>(g) atmosphere. The resulting mixture was stirred at 24°C for 30 minutes. Subsequently, 1-(*p*-tosylsulfonyl)-3,6,9-trioxodecane (9.66 g, 30.35 mmol) was added

and the solution was stirred for 18h. The reaction was quenched with H<sub>2</sub>O (60 mL) and the product was extracted with CH<sub>2</sub>Cl<sub>2</sub>. (2 × 50 mL). The combined organic fractions were washed with H<sub>2</sub>O (2 × 60 mL), brine (60 mL) and dried with MgSO<sub>4</sub>. Evaporation of the volatiles under reduced pressure gave 9.47 g red oil. The crude product was purified by column chromatography (EtOAc) to give **8** as a slightly orange oil (5.00 g, 76 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.65-7.63 (m, 1H, Ar), 7.54 (t, J = 1.8, 1H, Ar), 7.53 (s, 1H, Ar), 7.46 (dd, J = 1.8, 6.3, 1H, ArH), 7.40-7.38 (m, 1H, ArH), 7.34-7.32 (m, 2H, ArH), 3.53 – 3.51 (m, 4H, OCH<sub>2</sub>), 3.49 – 3.46 (m, 4H, OCH<sub>2</sub>), 3.39 (t, J = 4.9, 4H, OCH<sub>2</sub>), 3.34 (s, 6H, OCH<sub>3</sub>), 2.76 (m, 4H, CCH<sub>2</sub>CH<sub>2</sub>O), 2.35 (m, 4H, CCH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ = 151.21, 148.53, 139.43, 139.37, 130.37, 127.77, 127.46, 126.58, 123.15, 121.10, 119.88, 71.83, 70.40, 69.96, 66.89, 58.95, 51.50, 39.55. MS ESI: m/z = 561.16498 [M+Na]<sup>+</sup>, calculated m/z = 561.16497. IR (cm<sup>-1</sup>); 2870 (C-H stretch), 1103 (C-O stretch). R<sub>f</sub> = 0.38 (EtOAc).

**2-pinacolatoboron-9,9-bis-(1-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethyl)-fluorene (9):** compound **8** (2.95 g, 5.48 mmol), bis(pinacolato)diboron (1.391 g, 5.48 mmol), and potassium acetate (1.882 g, 19.18 mmol) were mixed with anhydrous dioxane (20 mL) and purged with N<sub>2</sub>(g) for 20 min. Pd(dppf)Cl<sub>2</sub> CH<sub>2</sub>Cl<sub>2</sub> (0.149 g, 0.183 mmol) was added and the resulting mixture was stirred at 90°C for 18h. The reaction product was taken up in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and H<sub>2</sub>O (30 mL). The organic layer was washed with H<sub>2</sub>O/Brine (1/1) (3 × 40 mL). The organic layer was dried with MgSO<sub>4</sub>. Evaporation of the volatiles under reduced pressure gave 3.442 g black oil. The crude product was purified by column chromatography (EtOAc) to give **9** as a slightly colored oil (2.03 g, 59 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.83-7.79 (m, 2H, Ar), 7.07-7.66 (m, 2H, Ar), 7.43-7.41 (m, 1H, Ar), 7.35-7.30 (m, 2H, Ar), 3.52 – 3.50 (m, 4H, OCH<sub>2</sub>), 3.47 – 3.45 (m, 4H, OCH<sub>2</sub>), 3.39 (t, J = 4.2, 4H, OCH<sub>2</sub>), 3.33 (s, 6H, OCH<sub>3</sub>), 3.19 (t, J = 4.2, 4H, OCH<sub>2</sub>), 2.77-2.65 (m, 4H, CCH<sub>2</sub>CH<sub>2</sub>O), 2.47-2.35 (m, 4H, CCH<sub>2</sub>), 1.39 (s, 12H, CCH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ = 149.55, 148.03, 143.45, 140.31, 134.18, 129.26, 127.95, 127.32, 123.26, 120.32, 119.20, 83.90, 71.95, 70.55, 70.04, 67.09, 59.07, 51.15, 39.70, 25.06. MS ESI: m/z = 607.34148 [M+Na]<sup>+</sup>, calculated m/z = 607.34186. IR (cm<sup>-1</sup>); 2871 (C-H stretch), 1105 (C-O stretch). R<sub>f</sub> = 0.36 (EtOAc).

**p-bis-(9,9-bis-(1-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethyl)-fluorene)-hexabenzocoronene (IM3):** Fluorene **9** (0.515 g, 0.882 mmol), was dissolved in toluene (10 mL), HBC **6** (0.200 g, 0.294 mmol) and Et<sub>4</sub>NOH (0.200 mL, 20% wt in H<sub>2</sub>O) were added and the resulting mixture was purged with N<sub>2</sub>(g) for 20 min. Pd<sub>2</sub>(dba)<sub>3</sub> (0.054 g, 0.059 mmol) and HP(tBu)<sub>3</sub>BF<sub>4</sub> (0.068 g, 0.235 mmol) were added and the resulting mixture was stirred at 90°C for 72h. The mixture was filtered over Celite and the volatiles were



evaporated under reduced pressure giving 0.930 g of a red compound. This was subjected to column chromatography, impurities were eluted with EtOAc and the product was eluted with CHCl<sub>3</sub>/MeOH (15/1) and was obtained as a yellow sticky solid (0.110 g) after evaporating of the volatiles under reduced pressure. The product was further purified by precipitation from EtOAc giving **IM3** as a yellow powder (0.080 g, 19 %). <sup>1</sup>H NMR (2 mM, 500 MHz, CDCl<sub>3</sub>) δ = 8.74 (s b, 4H, Ar-HBC), 8.59 (s b, 4H, Ar-HBC), 8.39 (s b, 4H, Ar-HBC), 8.11 (s, 2H, Ar-Flu), 7.98-7.93 (m, 4H, Ar-Flu), 7.90 (d, J = 7.1, 2H, Ar-Flu), 7.68 (t b, 4H, Ar-HBC), 7.63 (d, J = 7.1, 2H, Ar-Flu), 7.53 (t, J = 7.4, 2H, Ar-Flu), 7.48 (t, J = 6.3, 2H, Ar-Flu), 3.55 – 3.51 (m, 18H, OCH<sub>2</sub>), 3.46 – 3.39 (m, 18H, OCH<sub>2</sub>), 3.25 (s, 12H, OCH<sub>3</sub>), 3.24-3.18 (m, 4H, CCH<sub>2</sub>CH<sub>2</sub>O), 3.10-3.05 (m, 4H, CCH<sub>2</sub>CH<sub>2</sub>O), 2.82-2.70 (m, 8H, CCH<sub>2</sub>). <sup>13</sup>C NMR (64 mM, 125 MHz, CDCl<sub>3</sub>) δ = 150.12, 149.45, 141.26, 140.44, 139.85, 137.27, 129.46, 128.88, 128.82, 127.68, 127.53, 125.43, 123.61, 122.92, 121.98, 120.76, 120.67, 120.28, 119.17, 119.01, 118.79, 71.95, 70.72, 70.60, 67.64, 59.05, 51.71, 40.11. MS ESI: m/z = 1458.64080, [M<sup>+</sup>] calculated m/z = 1458.63584. Elemental analysis: calculated for C<sub>102</sub>H<sub>108</sub>N<sub>2</sub>O<sub>20</sub>, C 72.84%, H 6.47%, N 1.67%, O 19.02%; found C 72.33%, H 6.46%, N 1.55%, O 19.33%. IR (cm<sup>-1</sup>); 2865 (C-H stretch), 1101 (C-O stretch). R<sub>f</sub> = 0.60 CHCl<sub>3</sub>/MeOH (10/1), R<sub>f</sub> = 0.49 CHCl<sub>3</sub>/MeOH (15/1)

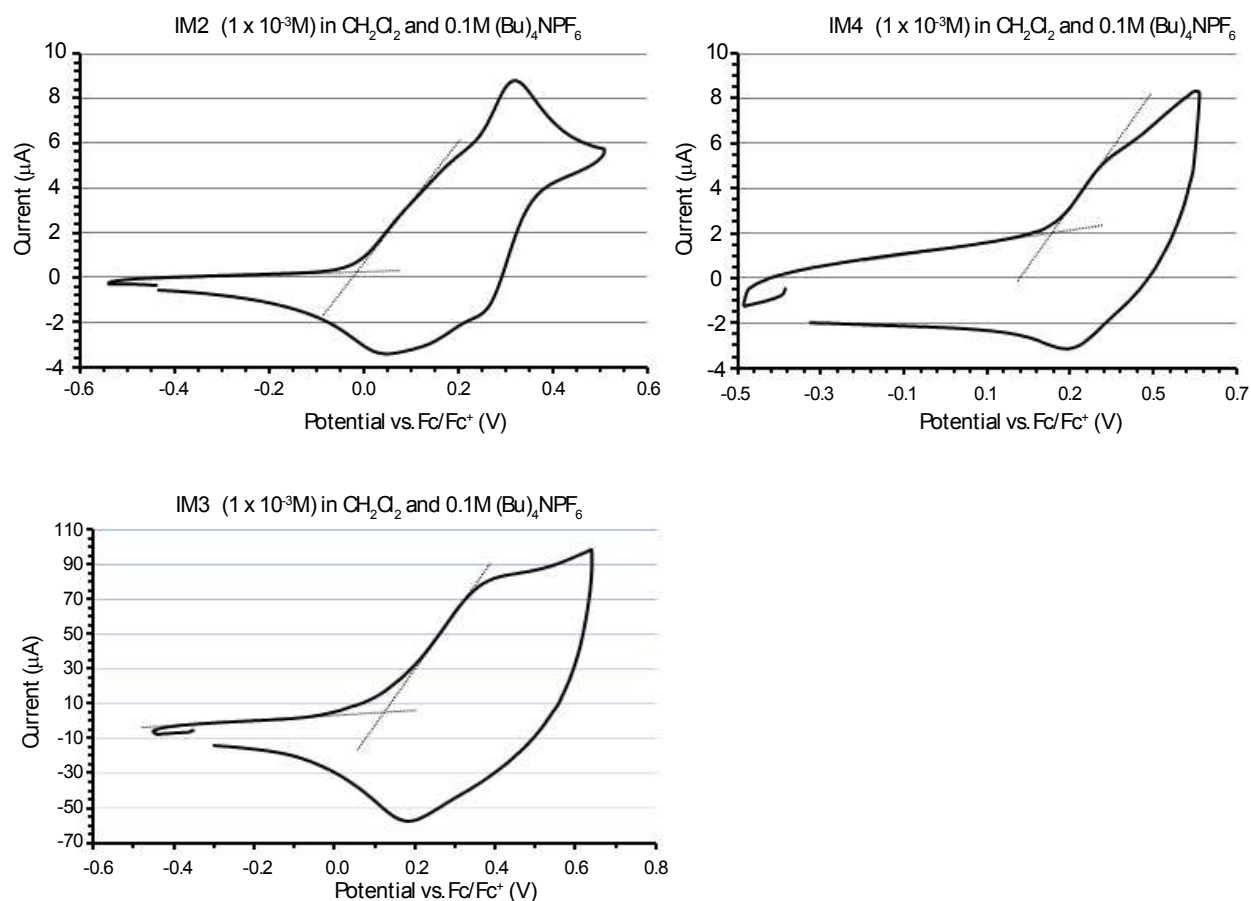
**o-bis-(9,9-bis-(1-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethyl)-fluorene)-hexabenzocoronene**

**(IM4):** Fluorene **9** (0.258 g, 0.441 mmol) was dissolved in toluene (10 mL) and HBC **10** (0.120 g, 0.176 mmol) was added and the resulting mixture was ultrasonicated for 2.5h. Et<sub>4</sub>NOH (0.100 mL, 20% wt in H<sub>2</sub>O) was added and the resulting mixture was purged with N<sub>2</sub>(g) for 20 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (0.034 g, 0.030 mmol) was added and the mixture was stirred at 110°C for 72h. The mixture was filtered over Celite and the volatiles were evaporated under reduced pressure giving 0.370 g of a red compound. The crude product was purified with Size Exclusion Chromatography, eluent Toluene giving **IM4** as a red solid (0.087 g, 34%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.71 (s b, 2H, Ar-HBC), 8.57 (s b, 2H, Ar-HBC), 8.48 (d b, J = 7.4, 2H, Ar-HBC), 8.24 (s b, 6H, Ar-HBC), 8.10 (s, 2H, Ar-Flu), 8.06 (d, J = 7.7, 2H, Ar-Flu), 8.01 (d, J = 7.6, 2H, Ar-Flu), 7.94 (d, J = 6.8, 2H, Ar-Flu), 7.66 (d, J = 7.12, 2H, Ar-Flu), 7.59-7.48 (m, 4H and 4H, Ar-HBC and Ar-Flu), 3.55 – 3.51 (m, 16H, OCH<sub>2</sub>), 3.47 – 3.41 (m, 16H, OCH<sub>2</sub>), 3.28-3.22 (m, 4H, CCH<sub>2</sub>CH<sub>2</sub>O), 3.24 (s, 12H, OCH<sub>3</sub>), 3.12-3.10, (m, 4H, CCH<sub>2</sub>CH<sub>2</sub>O), 2.86-2.72 (m, 8H, CCH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 150.26, 149.52, 141.27, 140.47, 140.11, 137.57, 129.73, 129.56, 129.23, 129.18, 129.12, 129.03, 127.76, 127.56, 125.72, 125.62, 123.87, 123.72, 123.68, 123.35, 122.14, 121.17, 120.92, 120.83, 120.35, 119.57, 119.47, 119.43, 119.32, 118.99, 71.97, 70.76, 70.63, 70.39, 67.71, 59.08, 51.81, 40.23. MS ESI: m/z = 1458.64389 [M]<sup>+</sup>, calculated m/z = 1458.63584. Elemental analysis: calculated for C<sub>102</sub>H<sub>108</sub>N<sub>2</sub>O<sub>20</sub>, C

72.84%, H 6.47%, N 1.67%, O 19.02%; found C 72.33%, H 6.46%, N 1.55%, O 19.33%. IR ( $\text{cm}^{-1}$ ); 2867 (C-H stretch), 1103 (C-O stretch).  $R_f = 0.03$   $\text{CH}_3\text{CN}/\text{MeOH}$  (10/1),  $R_f = 0.65$   $\text{CHCl}_3/\text{MeOH}$  (10/1)

#### Measurement of HOMO levels of IM2-IM4 via cyclic voltammetry.

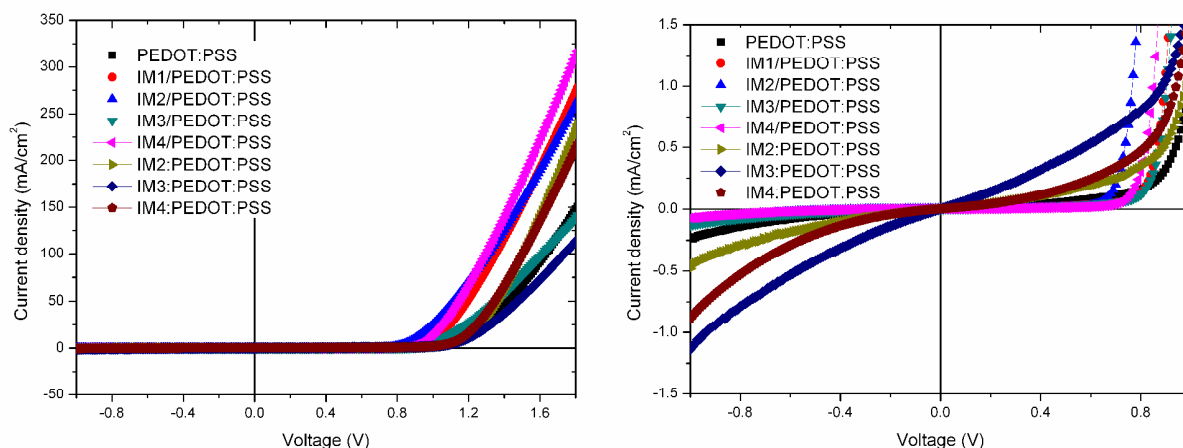
The HOMO levels of **IM2**, **IM3**, and **IM4** were measured using cyclic voltammetry (Figure S1) and are respectively -4.78eV, -4.91eV, and -5.07eV. Cyclic voltammograms (CVs) were recorded in 0.1 M  $\text{Bu}_4\text{NPF}_6$  electrolyte in  $\text{CH}_2\text{Cl}_2$  under inert atmosphere by purging the electrochemical cell with argon for 30 min. A glassy carbon electrode was used as the working electrode with a  $\text{Ag}/\text{AgCl}$  reference electrode and a platinum counter electrode. The oxidation onset in the CV was used to estimate the highest occupied molecular orbital (HOMO) energy of the compounds using ferrocene as the internal reference. The ferrocene/ferrocenium redox couple was set at -4.8 eV against vacuum. Therefore, the HOMO energy is given by the following equation.  $E_{\text{HOMO}} = -(\text{oxidation onset potential} + 4.8) \text{ eV}$



**Figure S1.** Cyclic voltammetry graphs of **IM2**, **IM3**, and **IM4**.

## Bulk heterojunction solar cell devices

All the fabrication and characterization processes were carried out in air. Patterned indium tin oxide (ITO) glasses were washed in the following order by detergent, deionized water, acetone, and 2-propanol using ultrasonication and, subsequently, UV/ozone-treated. PEDOT:PSS was spin-coated on top (8000 rpm) and the resulting layer was annealed (150 °C for 10 min) in air. After cooling down to room temperature, a solution consisting of re-crystallized FHBC (8 mg) and PCBM (16 mg) in chlorobenzene (1 ml) was spin-coated on top (1000 rpm) in air. The films were transferred to a thermal evaporator where 1 nm LiF and 100 nm aluminum were deposited through a shadow mask (active area of 0.10 cm<sup>2</sup>) at a base pressure of  $1 \times 10^{-6}$  torr. No thermal annealing was carried out. Film thickness was determined with a Veeco Dektak 150+ Surface Profiler. The thicknesses of the photoactive layers were optimized to 60 - 70 nm. The solar cells were illuminated at 100 mW cm<sup>-2</sup> using 1 kW Oriel solar simulator with an AM 1.5G filter in air and J-V curves were measured using a Keithley 2400 source meter. For accurate measurement, the light intensity was calibrated using a reference silicon solar cell (PVmeasurements Inc.) certified by the National Renewable Energy Laboratory. Series resistance ( $R_s$ ) and shunt resistance ( $R_{sh}$ ) were derived from dark currents by taking the reciprocal of the slopes at 1.5 and 0 V, respectively.



**Figure S2.** Dark J-V curves of PEDOT:PSS, IM:PEDOT:PSS, and IM/PEDOT:PSS layers.

**Table S1.** Bulk heterojunction solar cell device data

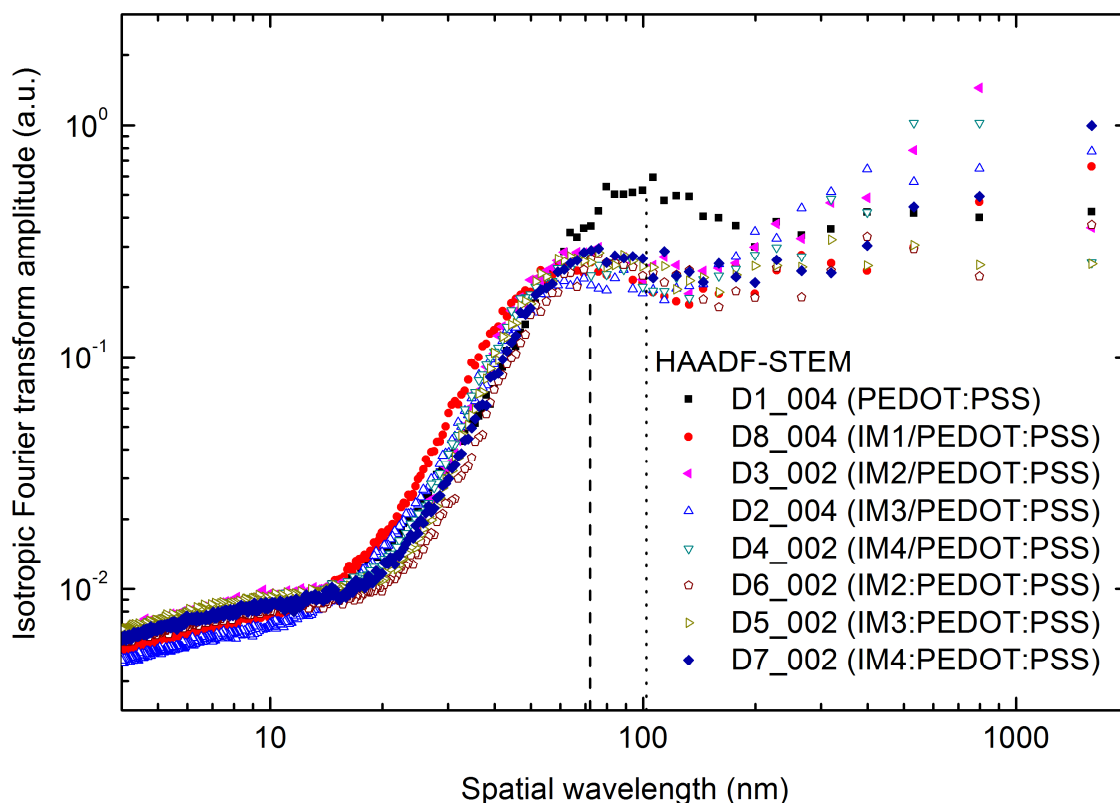
Interlayer material	Sample ID	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)	Z-value	p-value
PEDOT:PSS	130423_15-32_cell1.txt	0.94	-2.41	48.43	1.1		
	130423_15-32_cell2.txt	0.93	-2.46	56.44	1.29		
	130423_15-32_cell3.txt	0.92	-1.93	56.14	0.99		
	130423_15-32_cell4.txt	0.92	-1.6	54.4	0.8		
	130423_15-32_cell5.txt	0.91	-1.63	54.21	0.8		
	130423_15-32_cell6.txt	0.92	-1.83	55.03	0.93		
	<b>Mean</b>	<b>0.92</b>	<b>-1.98</b>	<b>54.11</b>	<b>0.99</b>		
	<b>Stdev</b>	<b>0.01</b>	<b>0.38</b>	<b>2.92</b>	<b>0.19</b>		
IM1/ PEDOT:PSS	T1_cell1.txt	0.95	-2.06	64.11	1.26		
	T1_cell2.txt	0.94	-1.86	61.95	1.08		
	T1_cell3.txt	0.92	-1.87	58.43	1.01		
	T1_cell4.txt	0.94	-1.94	64.88	1.18		
	T1_cell5.txt	0.94	-1.77	64.75	1.08		
	T1_cell6.txt	0.93	-2.32	64.14	1.38		
	<b>Mean</b>	<b>0.94</b>	<b>-1.97</b>	<b>63.04</b>	<b>1.17</b>	<b>3.13</b>	<b>0.17%</b>
	<b>Stdev</b>	<b>0.01</b>	<b>0.20</b>	<b>2.49</b>	<b>0.14</b>		
IM2/ PEDOT:PSS	S3_cell1.txt	0.81	-2.72	59.67	1.31		
	S3_cell2.txt	0.81	-2.65	61.12	1.31		
	S3_cell3.txt	0.81	-2.12	66.08	1.13		
	S3_cell4.txt	0.81	-2.03	59.83	0.98		
	S3_cell5.txt	0.82	-2.27	65.97	1.23		
	S3_cell6.txt	0.82	-2.55	63.72	1.33		
	<b>Mean</b>	<b>0.81</b>	<b>-2.39</b>	<b>62.73</b>	<b>1.22</b>	<b>4.02</b>	<b>0.00%</b>

	<b>Stdev</b>	<b>0.01</b>	<b>0.29</b>	<b>2.93</b>	<b>0.14</b>		
<b>IM3/ PEDOT:PSS</b>	S2_cell1.txt	0.91	-2.66	65.41	1.58		
	S2_cell2.txt	0.9	-2.36	64.69	1.37		
	S2_cell3.txt	0.91	-2.35	58.62	1.25		
	S2_cell4.txt	0.9	-2.18	64.77	1.27		
	S2_cell5.txt	0.9	-2.09	63.62	1.2		
	S2_cell6.txt	0.91	-2.55	65.61	1.52		
	<b>Mean</b>	<b>0.91</b>	<b>-2.37</b>	<b>63.79</b>	<b>1.37</b>	<b>5.94</b>	<b>0.00%</b>
	<b>Stdev</b>	<b>0.01</b>	<b>0.22</b>	<b>2.63</b>	<b>0.15</b>		
<b>IM4/ PEDOT:PSS</b>	I6_cell1.txt	0.85	-2.55	61.08	1.33		
	I6_cell2.txt	0.83	-2.34	55.83	1.08		
	I6_cell3.txt	0.83	-2.53	63.87	1.34		
	I6_cell4.txt	0.79	-2.49	50.36	0.99		
	I6_cell5.txt	0.8	-2.41	63.02	1.21		
	I6_cell6.txt	0.8	-2.51	63.66	1.28		
	<b>Mean</b>	<b>0.82</b>	<b>-2.47</b>	<b>59.64</b>	<b>1.21</b>	<b>3.70</b>	<b>0.02%</b>
	<b>Stdev</b>	<b>0.02</b>	<b>0.08</b>	<b>5.44</b>	<b>0.14</b>		
<b>IM2: PEDOT:PSS</b>	S9_cell1.txt	0.93	-2.62	52.83	1.29		
	S9_cell2.txt	0.91	-2.49	49.98	1.13		
	S9_cell3.txt	0.91	-2.18	50.44	1		
	S9_cell4.txt	0.89	-1.94	46.02	0.79		
	S9_cell5.txt	0.89	-1.81	44.74	0.72		
	S9_cell6.txt	0.87	-1.78	44.35	0.68		
	<b>Mean</b>	<b>0.90</b>	<b>-2.14</b>	<b>48.06</b>	<b>0.94</b>	<b>-0.55</b>	<b>58.23%</b>
	<b>Stdev</b>	<b>0.02</b>	<b>0.36</b>	<b>3.49</b>	<b>0.25</b>		

IM3: PEDOT:PSS	T7_cell1.txt	0.95	-2.25	50.05	1.07		
	T7_cell2.txt	0.94	-2.27	49.49	1.06		
	T7_cell3.txt	0.94	-1.72	48.76	0.79		
	T7_cell4.txt	0.93	-1.53	46.81	0.67		
	T7_cell5.txt	0.93	-1.81	48.95	0.82		
	T7_cell6.txt	0.94	-2.06	49.09	0.95		
	<b>Mean</b>	<b>0.94</b>	<b>-1.94</b>	<b>48.86</b>	<b>0.89</b>	<b>-1.48</b>	<b>13.89%</b>
	<b>Stdev</b>	<b>0.01</b>	<b>0.30</b>	<b>1.10</b>	<b>0.16</b>		
IM4: PEDOT:PSS	T9_cell1.txt	0.94	-2.43	53.68	1.22		
	T9_cell2.txt	0.93	-2.13	52.44	1.04		
	T9_cell3.txt	0.92	-1.87	49.08	0.84		
	T9_cell4.txt	0.93	-1.85	50.44	0.87		
	T9_cell5.txt	0.93	-1.99	50.11	0.93		
	T9_cell6.txt	0.93	-2.12	51.45	1.01		
	<b>Mean</b>	<b>0.93</b>	<b>-2.07</b>	<b>51.20</b>	<b>0.99</b>	<b>-0.09</b>	<b>92.83%</b>
	<b>Stdev</b>	<b>0.01</b>	<b>0.21</b>	<b>1.67</b>	<b>0.14</b>		

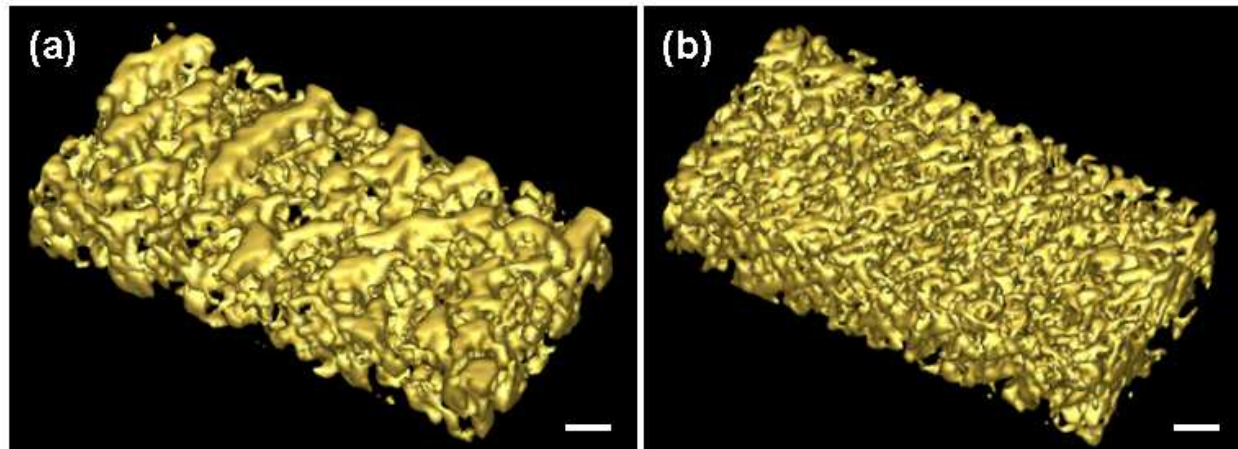
## High-angle angular dark-field scanning transmission electron microscope (HAADF STEM) studies

For quantitative analysis of the domain size and phase separation within FHBC:PCBM active layers depending on the interface modification, two-dimensional fast Fourier transform (2D FFT) was applied to the HAADF STEM images. Squared sections of 830 by 830 pixels with a resolution of 1.923 nm/pixel for HAADF STEM images were used. The 2D FFT images were angular averaged to get a one dimensional isotropic representation of the images. The spatial wavelengths were calculated by taking the inverse of the spatial frequencies given by the 2D FFT.

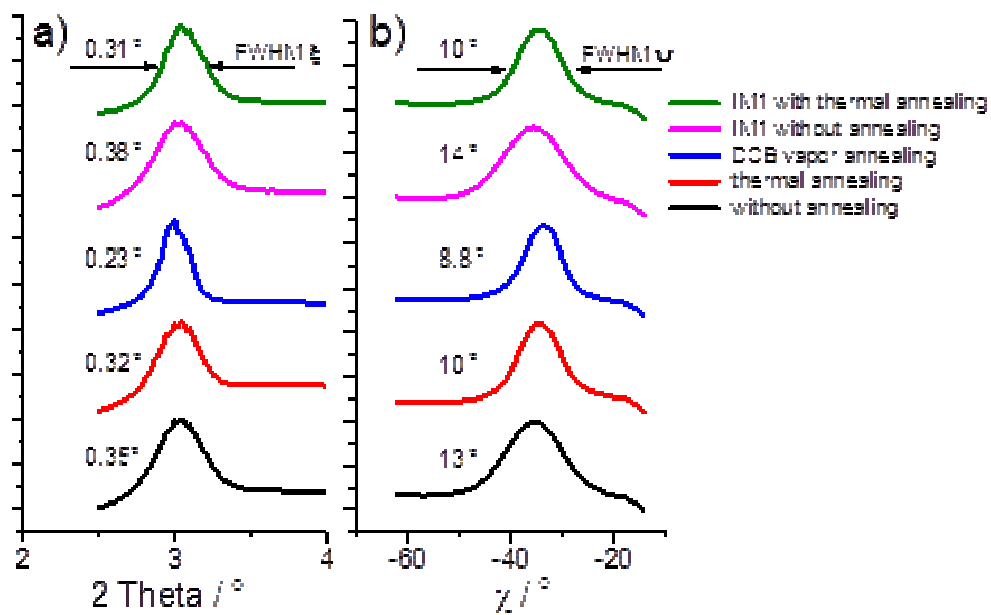


**Figure S3.** Radially averaged two-dimensional discrete Fourier transform of the respective HAADF STEM images. As guide to the eye, the spatial wavelengths of the peaks in the isotropic Fourier transform amplitude are highlighted. The mean phase separation within the layers was estimated by dividing the spatial wavelength in half.

## Transmission electron microscopy (TEM) and TEM tomography



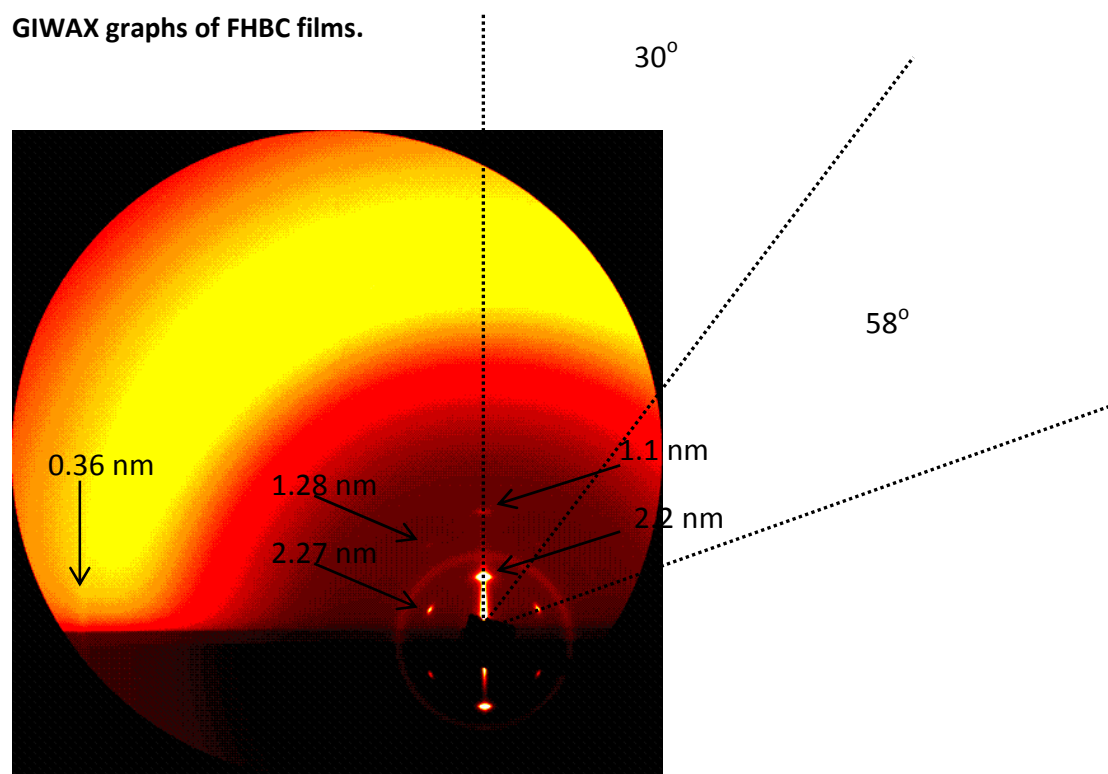
**Figure S4.** Computer models constructed from TEM tomograms of FHBC:PCBM thin films on (a) PEDOT:PSS and (b) IM3/PEDOT:PSS. The scale bar is 50 nm.



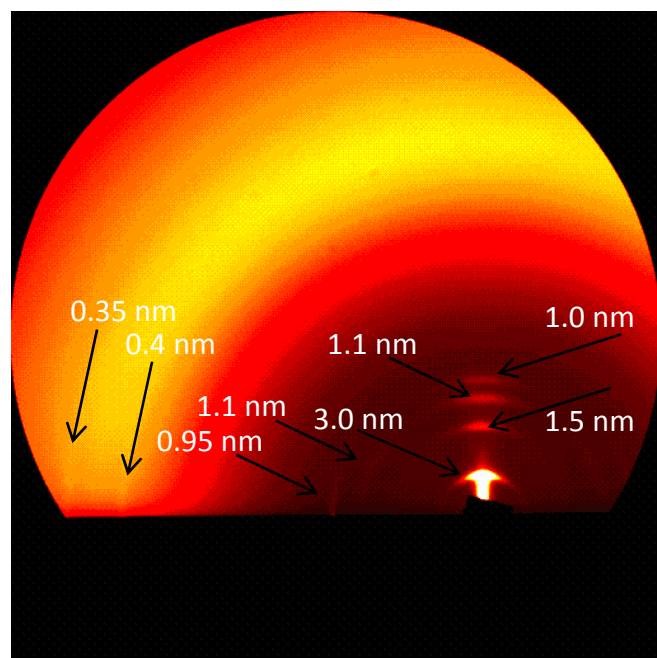
**Figure S5.** a) Radial and b) azimuthal integration of the 010 reflection indicated in Figure 6a and the corresponding FWHM values.



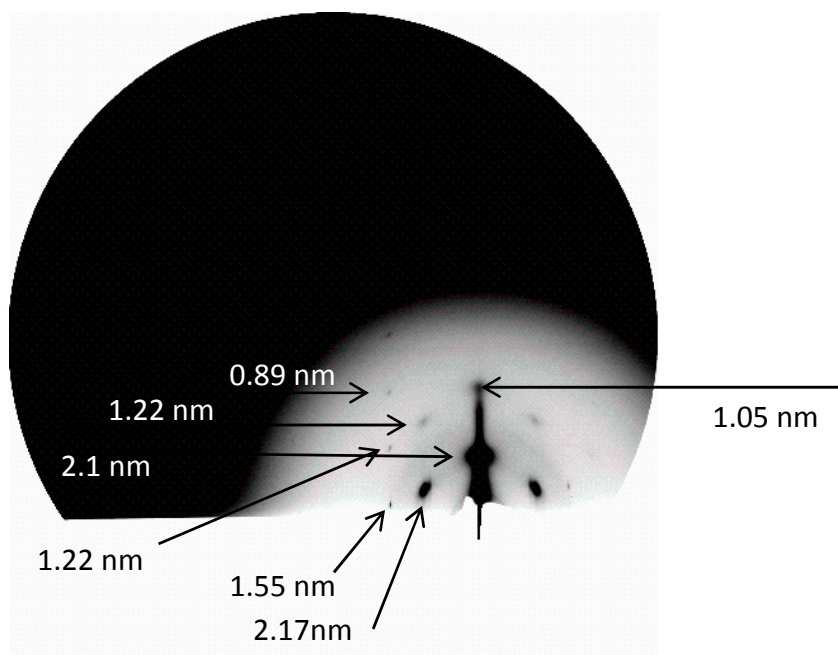
GIWAX graphs of FHBC films.



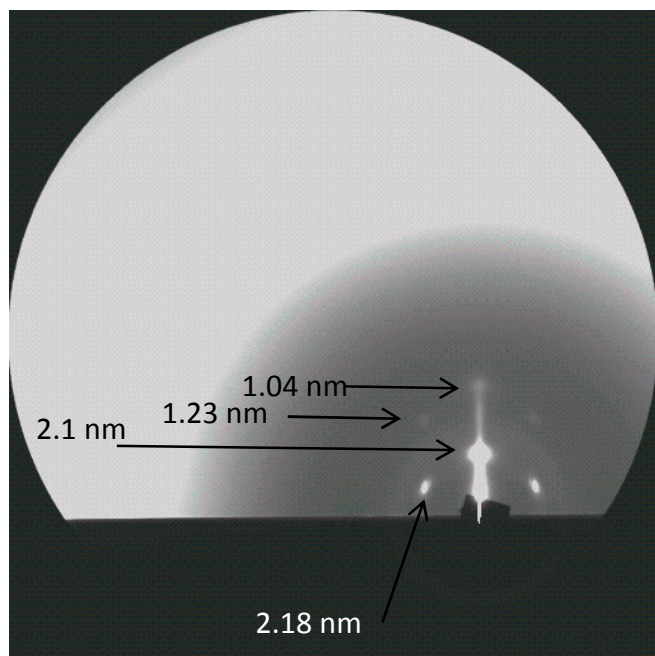
**Figure S6.** FHBC/PEDOT:PSS/glass, the FHBC layer is vapor annealed with dichlorobenzene for 24h followed by annealing at  $150^\circ\text{C}$  for 30s.



**Figure S7.** FHBC/IM1/PEDOT:PSS/glass, the FHBC layer is vapor annealed with dichlorobenzene for 24h followed by annealing at  $150^\circ\text{C}$  for 30s.

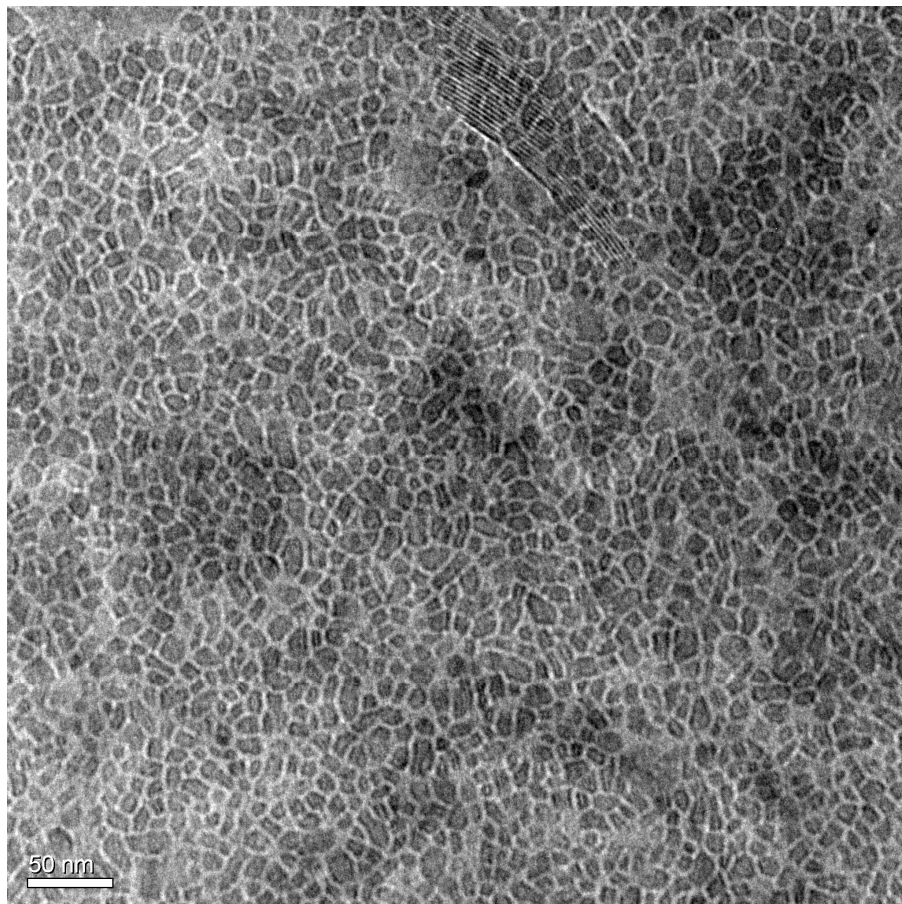


**Figure S8.** FHBC/IM2/PEDOT:PSS/glass, the FHBC layer is vapor annealed with dichlorobenzene for 24h followed by annealing at 150°C for 30s.



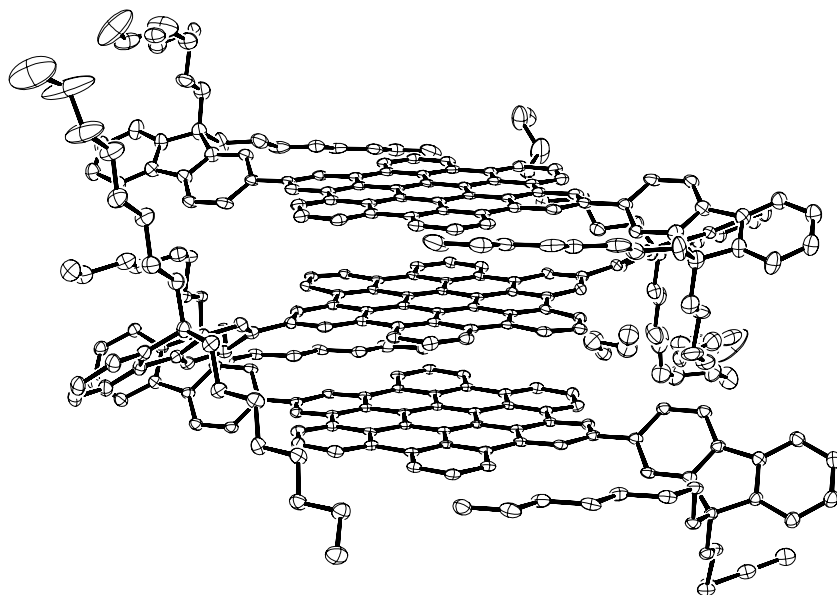
**Figure S9.** FHBC/IM4/PEDOT:PSS/glass, the FHBC layer is vapor annealed with dichlorobenzene for 24h followed by annealing at 150°C for 30s.

TEM bright field image of FHBC film.



**Figure S10.** High-resolution bright field TEM image of a FHBC film on **IM1**/PEDOT:PSS substrate after vapor + thermal annealing, which was exposed to dichlorobenzene vapor for 24h followed by thermal annealing at 150°C for 30s. The scale bar is 50 nm.

## Single Crystal Data for FHBC

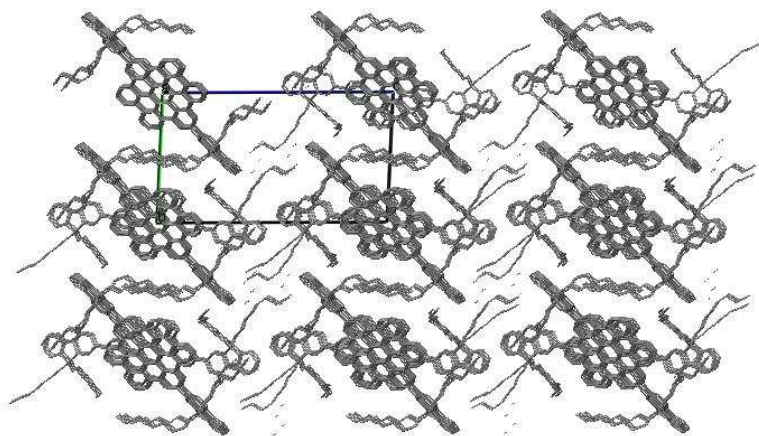


**Figure S11.** Thermal ellipsoid structure of **FHBC**.

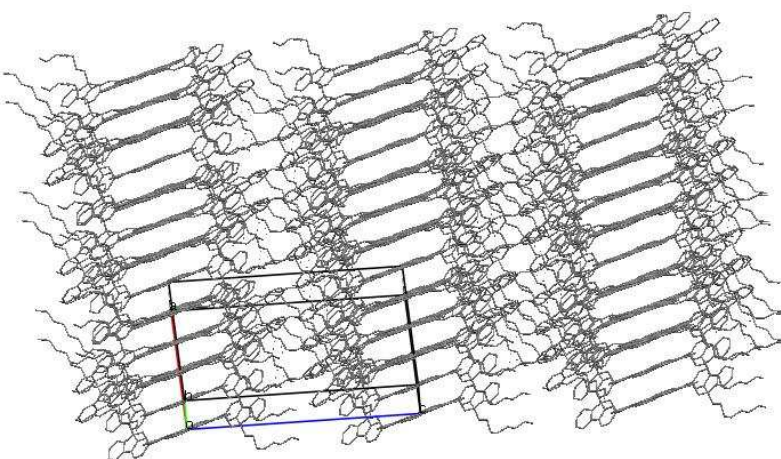
**Crystallography.** Intensity data were collected with an Oxford Diffraction SuperNova CCD diffractometer using Cu-K $\alpha$  radiation (graphite crystal monochromator  $\lambda = 1.54184$ ). The temperature during data collection was maintained at 130.0(1) using an Oxford Cryostream low temperature device

Crystal data for **FHBC** C<sub>200</sub>H<sub>193</sub>.3(CH<sub>2</sub>Cl<sub>2</sub>),  $M = 2851.31$ ,  $T = 130.0(2)$  K,  $\lambda = 1.5418$ , Triclinic, space group P-1,  $a = 17.2331(8)$ ,  $b = 17.2446(7)$ ,  $c = 27.9818(14)$  Å,  $\alpha = 92.121(4)^\circ$ ,  $\beta = 91.996(4)^\circ$ ,  $\gamma = 112.639(4)^\circ$ ,  $V = 7658.7(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.235$  Mg M<sup>-3</sup>,  $\mu(\text{Cu-K}\alpha) = 1.458$  mm<sup>-1</sup>,  $F(000) = 3030$ , crystal size 0.43 x 0.28 x 0.04 mm. 62862 reflections measured, 30176 independent reflections ( $R_{\text{int}} = 0.06$ ) the final  $R$  was 0.1280, [ $I > 2\sigma(I)$ ] and  $wR(F^2)$  was 0.3971 (all data).

The asymmetric unit consists of one unique molecule of FHBC which is  $\pi$ -stacked above and below to two half molecules which sit on crystallographic inversion centres, the three  $\pi$ -systems are close to parallel. The interplanar spacings are ca. 3.42 and 3.04 Å and the corresponding centroid to centroid distances between the central hexabenzocoronene ring and the two flanking molecules are 4.141 and 4.498 Å respectively indicating a certain amount of slippage of the  $\pi$ -stacked ring systems. The structure contains three molecules of dichloromethane, which is disordered. The structure consists of columnar stacks of the hexabenzocoronene rings extending down the  $a$ -axis.



**Figure S12.** Crystal packing diagram of FHBC extending down the *a*-axis



**Figure S13.** Crystal packing diagram of FHBC viewing down the *a*-*b* direction

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