Supplementary Information

Nano-Structuring Polymer/Fullerene Composites through the Interplay of Conjugated Polymer Crystallization, Block Copolymer Self-Assembly and Complementary Hydrogen Bonding Interactions

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[6, 6]-Phenyl-C61-butyric acid (PCBA). Acetic acid (50 mL) and HCl (30 mL) were added to a solution of [6,6]-Phenyl-C61-butyric acid methyl ester (PCBM) (510 mg, 0.560 mmol) in 100 mL of o-dichlorobenzene, and the solution was refluxed for 18 h. After the solvent was removed under reduced pressure, the residue was treated with methanol and then filtered to give 490 mg PCBA as a black powder (yield 97.6%). $^1$H NMR (300.13 MHz, CDCl$_3$/d$_6$-DMSO/CS$_2$): $\delta$ (ppm) = 2.05-1.98 (-CH$_2$-, m, 2H), 2.30 (-CH$_2$-, t, $J = 7.5$ Hz, 2H), 2.78-2.73 (-CH$_2$-, m, 2H), 7.39-7.29 (Ph-H, m, 3H), 7.76 (Ph-H, d, $J = 7.2$ Hz, 2H),
[6, 6]-Phenyl-C61-butyric acid N-(6-aminopyridin-2-yl) amide (PCBP). In a dry Schlenk flask was added PCBA (200 mg, 0.223 mmol) and CH$_2$Cl$_2$ (40 mL) under nitrogen. To this solution was added 1-chloro-N, N, 2-trimethylpropenylamine (0.04 mL, 0.268 mmol). The reaction mixture was stirred at r.t. for 4 h resulting in a homogeneous solution, and then evaporated to provide the corresponding acid chloride that was dissolved in 40 mL CHCl$_3$ and used directly in the next step. To a solution of 2, 6-diaminopyridine (674 mg, 4.460 mmol) in CH$_2$Cl$_2$ (40 mL) was added the solution of acid chloride in CH$_2$Cl$_2$ dropwise over 30 min. The reaction mixture was stirred at r.t. overnight, and then quenched with MeOH. The solvent was evaporated under reduced pressure and the residue was washed with excess MeOH to remove the unreacted 2, 6-diaminopyridine. PCBP was purified by flash chromatography on silica gel (CH$_2$Cl$_2$/EtOAc, 20:1) as a dark brown powder (160 mg, 73% yield).

1H NMR (300.13 MHz, CDCl$_3$): δ (ppm) = 2.26-2.31 (-CH$_2$-, m, 2H), 2.55 (-CH$_2$-, t, J = 7.5 Hz, 2H), 2.93-2.98 (-CH$_2$-, m, 2H), 4.26 (-NH$_2$-, s, 2H), 6.24 (Pyr-H, d, J = 6.9 Hz, 1 H), 7.41-7.57 (m, 6H), 7.92-7.95 (Ph-H, m, 2H). HRMS (ESI): Calcd. for C$_{76}$H$_{18}$N$_3$O, 988.1450 [M+], 989.1483 for [M+H]; found, 988.1471 [M+], 989.1490 [M+H].

1-Hexylisoorotic acid (S2). Isoorotic acid (6.41 mmol, 1 g) was suspended in hexamethyldisilazane (HMDS) (40.2 mmol, 8.4 mL), and trimethylchlorosilane (TMSCl) (13.46 mmol, 2.0 mL) was added. The mixture was refluxed in a pressure vessel at 120 °C for 4 h until the mixture appeared clear. The reaction vessel was cooled to room temperature, and then 1-bromohexane (64.1 mmol, 9 mL) was added. The mixture was then heated to 100 °C for 48 h. The solvent was then removed under reduced pressure, and the residue was stirred with 10 mL of ice water and 10 mL of glacial acetic acid for 20 min. The precipitate formed was collected by filtration and washed with copious cold water and hexanes to afford 1.4 g product as pale-grey solids (yield 91%). 1H NMR (300.13 MHz, CDCl$_3$): δ (ppm) = 0.89 (-CH$_3$, t, 3H), 1.32 (br, 6 H), 1.75 (-CH$_2$CH$_3$, t, 2H), 3.89 (NCH$_2$-, t, 2H), 8.50 (C=CH, s, 1H), 9.84 (-CONHCO-, s, 1H), 12.21 (-COOH, s, 1H). 13C NMR (75.48 MHz, CDCl$_3$): δ (ppm) = 165.4, 163.3, 153.1, 149.5, 102.2, 50.7, 31.29, 29.1, 26.1, 22.5, 14.1.

Poly(3-hexylthiophene)-b-Poly(3-(6'-dimethyl-tert-butyldiphenyl) hexylthiophene) (P2). Two three-necked round-bottomed flasks (250 mL and 50 mL) equipped with stopcocks and septa were flame dried under high vacuum and cooled to room temperature under N$_2$. Monomer M1 (1.48 g, 3.972 mmol) and LiCl (168 mg, 3.972 mmol) was placed in the 250 mL flask under N$_2$, and then evacuated under high vacuum to remove any residual water and oxygen. After adding dry THF (40 mL) into the flask via a syringe, the solution was cooled to 0 °C. A 2 M solution of i-PrMgCl in THF (2 mL, 3.972 mmol) was added via syringe and the mixture was stirred at 0 °C for 30 min (solution 1). In the other 50 mL flask, 0.2 g (0.397 mmol) 2,5-dibromo-3-(6'-dimethyl-tert-butyldiphenyl)hexylthiophene was first reacted with 0.2 mL i-PrMgCl in the
presence of 20 mg LiCl (0.397 mmol) in 10 mL THF (solution 2) to yield M2. Solution 1 was heated up to 35 °C and Ni(dppp)Cl2 catalyst (10.76 mg, 0.0397 mmol), which was suspended in 5 mL dry THF, was added in one portion. The reaction mixture was stirred at 35 °C for 15 min, an aliquot was withdrawn with a syringe and injected into a methanol solution to give P1 for SEC analysis (RI, CHCl3, 1 mL/min: $M_n = 35,300, M_w = 42,400, PDI = 1.2$). Solution 2 containing M2 was then transferred to solution 1 via a cannula. The resulting red solution was stirred at 35 °C for 40 min before 0.5 mL EtMgCl solution (2M in THF) was added. The polymer was isolated by precipitation into MeOH and successively washed by Soxhlet extraction using methanol, acetone, and chloroform. The polymer was recovered by precipitation of the chloroform solution into methanol and dried under high vacuum to give a black solid (0.86 g, 89%). $^1$H NMR (300.13 MHz, CDCl3): $\delta$ (ppm) = 0.041 (O-(tBu)Si(CH3)2), 0.90-0.94, 1.25-1.71, 2.81 (hexyl-H’s, methylene-H’s and tBu-H’s), 3.61 (-OCH2CH2-), 6.98 (Th-H). SEC (RI, CHCl3 1 mL/min): $M_n = 42,700, M_w = 50,800, PDI = 1.2$.

Poly(3-hexylthiophene)-b-Poly(3-(6'-hydroxyl)hexylthiophene) (P3). In a 100 mL Schlenk flask was added 750 mg polymer P2 and 100 mL THF under N2. The solution became clear after stirring at 60 °C for ca. 30 min. Tetrabutylammonium fluoride (TBAF) solution (2 mL, 2M in THF) was then added dropwise via syringe. The reaction mixture was kept stirring at 60 °C for 8 h and concentrated under reduced pressure to ca. 5 mL. P3 was recovered as a black solid by precipitation into a mixture of methanol and acetone (1/1, vol/vvol) and dried under vacuum overnight (650 mg, 88%). $^1$H NMR (300.13 MHz, CDCl3): $\delta$ (ppm) = 0.92, 1.25-1.71, 2.04, 2.81 (hexyl-H’s and methylene-H’s), 3.66 (-OCH2CH2-), 6.98 (Th-H). SEC (RI, CHCl3 1 mL/min): $M_n = 35,900, M_w = 48,300, PDI = 1.3$.

Poly(3-hexylthiophene)-b-Poly(3-(6'-(1-hexylisoorotic acid amido))hexylthiophene) (P3HT-b-P3IOAT). In a 25 mL three-neck flask equipped with a condenser and septa was added 246 mg (1.02 mmol) 1-N-hexylisoorotic acid and 2 mL thionyl chloride under nitrogen, and the solution was refluxed for 8 h to give the corresponding acid chloride. The excess SOCl2 was removed under vacuum and the residue was dissolve in 10 mL of dry CHCl3 and the solvent was removed under reduced pressure remove residual SOCl2. In the other 250 mL Schlenk flask was added 200 mg P3 and 30 mL CHCl3 under nitrogen. The reaction mixture was kept stirring at 60 °C for 20 min until all polymer dissolved and then triethylamine (0.3 mL) was added into the polymer solution. The acid chloride was dissolved in 15 mL CHCl3 and transferred into the polymer solution via cannula. The reaction was kept at 60 °C for another 8 h and concentrated under reduced pressure to ca. 5 mL. The crude polymer was isolated by precipitation into methanol and successively Soxhlet extracted using methanol, acetone, and chloroform. The chloroform solution was concentrated and precipitated into MeOH to give P3HT-b-P3IOAT as a black solid (200 mg, 78%). $^1$H NMR (300.13 MHz, CDCl3): $\delta$ (ppm) = 0.92, 1.25-1.71,
2.80 (hexyl-H’s and methylene-H’s), 3.77 (-COOCH₂-), 4.29 (NCH₂-), 6.98 (Th-H), 8.19 (C=CH-). SEC (RI, CHCl₃ 1 mL/min) at 35 °C: $M_n = 27,200$, $M_w = 43,500$, $PDI = 1.6$; at 55 °C: $M_n = 32,100$, $M_w = 47,900$, $PDI = 1.5$.

**Figure S1.** UV-Vis absorption spectra of **P3HT-b-P3IOAT** in chlorobenzene (10 mg/mL) with addition of various amounts of acetone (vol./vol.) and aged at room temperature for 14 h. All spectra were taken by diluting corresponding original solutions with identical mixed solvents to a final **P3HT-b-P3IOAT** concentration of 0.025 mg/mL.
Figure S2. UV-Vis absorption spectra of P3HT-b-P3IOAT NFs (black); pre-formed P3HT-b-P3IOAT NFs with subsequent addition of PCBP (40 wt.%, red); composite NFs in-situ formed from P3HT-b-P3IOAT/PCBP (10/4, wt./wt.) mixture solution (blue); pre-formed P3HT-b-P3IOAT NFs with subsequent addition of PCBP (80 wt.%, green); and composite NFs in-situ formed from P3HT-b-P3IOAT/PCBP (10/8, wt./wt.) mixture solution (brown). NFs are formed by addition of acetone to chlorobenzene solutions (1/5, vol./vol.) of polymer or polymer/PCBP mixtures (10 mg/mL of polymer in chlorobenzene) and aged for 14 h. All spectra are normalized at 488 nm. All spectra were taken by diluting corresponding original solutions with identical mixed solvents to a final P3HT-b-P3IOAT concentration of 0.025 mg/mL.
Figure S3. I-V curves (under simulated AM1.5 G irradiation) of different devices employing P3HT-b-P3IOAT/PCBP composite nanofibers under different blending conditions measured after thermal annealing at 110 °C for various times: (A) pre-formed P3HT-b-P3IOAT NFs with subsequent addition of PCBP (40 wt.%); (B) composite NFs in-situ formed from P3HT-b-P3IOAT/PCBP (10/4, wt./wt.) mixture solution; (C) pre-formed P3HT-b-P3IOAT NFs with subsequent addition of PCBP (80 wt.%); (D) composite NFs in-situ formed from P3HT-b-P3IOAT/PCBP (10/8, wt./wt.) mixture solution.
Figure S4. Atomic force microscopy (AFM) height images (2 µm × 2 µm) of as-cast (left column), optimized (150 °C, 15 min, middle column) and aged (110 °C, 112 h, right column) devices employing only P3HT-b-P3IOAT NFs (A-C); pre-formed P3HT-b-P3IOAT/PCBP composite NFs at 10/4 (D-F) and 10/8 (G-I) weight ratios; and in-situ formed P3HT-b-P3IOAT/PCBP composite NFs at 10/4 (J-L) and 10/8 (M-O) weight ratios. Scale bars in all: 200 nm.