Supporting Information

Hydrogen-Bonding-Directed Helical Nanofibers in a Polythiophene-Based All-Conjugated Diblock Copolymer

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**Figure S1.** Circular Dichroism (CD) spectrum of P3HT-b-P3HHT (1:1) helical nanofiber solution aged at 20 °C for 12 h.

**Figure S2.** (a-c) TEM and (d-f) AFM images showing the growth process of the P3HT-b-P3HHT (1:1) helical nanofibers in the pyridine solution aged at 20 °C for (a, d) 10 min, (b, e) 1 h, and (c, f) 32 h, respectively. It indicated the helical fibers were formed at the beginning of the aging process and grew longer up to several to tens of micrometers and connected with each other to form a network with the increased aging time.
Figure S3. (a and b) Cryo-TEM images of the P3HT-b-P3HHT (1:1) helical nanofibers yielded in the pyridine solution aged at 20 °C for 12 h.

Figure S4. (a) TEM and (b) AFM images of the P3HT-b-P3HHT (1:1) ordinary nanofibers without helical structures yielded in the pyridine solution aged at 30 °C for 12 h.
Figure S5. UV-vis absorption spectra of P3HT-b-P3HHT thin films cast from (a) pyridine solution heated at 90 ºC for 1 h (original pyridine solution (black line) followed by aging at 30 ºC (red line) and 20 ºC (blue line), respectively.

Figure S6. PL spectra of P3HT-b-P3HHT pyridine solution aged at 20 ºC (black line) and its corresponding thin film (red line).
Figure S7. TEM images of P3HT-\(b\)-P3HHT (1:1) helical nanofibers yielded in the pyridine solution aged at (a) 10 °C and (b) 4 °C for 12 h, respectively.

Figure S8. (a and c) TEM and (b and d) AFM images of P3HT-\(b\)-P3HHT helical nanofibers with different block ratios in pyridine aged at 20 °C for 12 h. The block ratio of P3HT to P3HHT is (a and b) 1:3 and (c and d) 3:1.
Figure S9. (a) The chemical structure of P3HT-\textit{b}-P3THPHT. (b) TEM image of amorphous structure without nanofiber morphology assembled from P3HT-\textit{b}-P3THPHT(1:1).
**Figure S10.** (a) Representative FESEM images of P3HT-\(b\)-P3HHT (1:1) helical nanofibers yielded in pyridine aged at 20 °C for 12 h. (b-f) Superhelix structures formed after injecting different volume of initial P3HT-\(b\)-P3HHT helical fiber solutions to 200 μL methanol solvent. The volume of initial P3HT-\(b\)-P3HHT helical fiber solutions is (b) 30 μL, (c) 20 μL and (d,e,f) 10 μL, respectively. (e and f) The amplified images of the structures in Figure S8d. (g-i) Superhelix structures formed after injecting initial P3HT-\(b\)-P3HHT helical fiber solutions (10 μL) into 200 μL (g) CH\(_2\)Cl\(_2\) and (h and i) hexane solvent, respectively.
Figure S11. (a, c, e) Transfer and (b, d, f) output curves of OFETs fabricated by using ordinary nanofibers of (a and b) P3HT-b-P3HHT (1:1), (c and d) P3HHT, and (e and f) P3HT, respectively.