Supporting information

Morphological Transformation of Pyrazine-based Acene-type Molecules after Blending with Semiconducting Polymers: From Fibers to Quadrilateral Crystals

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General procedure for the synthesis of PBA: Into a stirred solution of compound 1 (3.75 g, 6.0 mmol, synthetic process of 1 was shown in ref[1].) in 150 mL acetic acid was dropwise added compound 2 (0.62 g, 3.0 mmol, purchased from Aldrich chemical company, Inc.) in 60 mL water. The mixture was stirred for 10 h in room temperature and poured into 600 mL water. The mixture was extracted with $CHCl_3$. The organic phase was washed with H_2O. The solution was dried with anhydrous Na_2SO_4. The solvent was removed and added 100 mL CH_2Cl_2, 0.1 g tetrabutylammonium bromide and 10 g $NaIO_4$ 100 mL water. The mixture was stirred for 3 h. The solvent was removed and the precipitated was filtered. The crude product was purified by column chromatography on silica gel with chloroform as the eluent to afford the product as a black solid (1.4 g, 35 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 4H), 7.72 (d, J = 8.8 Hz, 8H), 6.96 (d, J = 8.8 Hz, 8H), 4.05 (t, J = 6.5 Hz, 8H), 1.84 (dd, J = 14.7, 6.9 Hz, 8H), 1.51 (m, 8H), 1.30 (m, 48H), 0.92 (t, J = 6.8 Hz, 12H). MALDI-TOF (m/z): 1345.8 $[M+H]^+$.

Influence of blended insulating polymers on orientation of PBA molecules Fig. S1 shows the diffraction peaks of PBA/insulating polymer blended films after being exposed to CB for 24 h. The position of diffraction peaks at at 2θ=3.9° and 4.3° (d spacing is around 22.63 Å and 20.52 Å, respectively) is the same to that of pure PBA. The weak reflection at 2θ=18.5° appears as well for both PBA/PS blends and PBA/PMMA blends. A new diffraction peak at 2θ=7.8° (d spacing is around 11.32 Å) for PBA/insulating polymer blends should correspond to the secondary diffraction of the crystal plane whose d spacing is 22.63 Å. The appearance of secondary diffraction

indicates that lamellar stacking of the blended films is further improved.[2] Therefore, compared with pure PBA film, the orientation of PBA molecules doesn't change after blending with insulating polymers.

Figure captions

Scheme S1. Synthesis of PBA

Fig. S1 GIXD patterns of PBA and PBA/insulating polymer blends after being exposed to CB for 24 h. Pure PBA film (black line), PBA/PS blended film (red line) and PBA/PMMA blended film (blue line)

Fig. S2 TEM images and SAED patterns of spin-coated thin layers PBA/insulating polymer (2:1 w/w) blends after being exposed to CB vapor for 24 h. The blended polymers are (a) PS and (b) PMMA, respectively. The circles in the TEM images are the selected areas of SAED patterns.

Fig. S3 GIXD patterns of P3BT, P3HT, P3OT, P3DDT and F8BT spin-coated layers prepared under identical condition without post-treatment. The influence of glass substrate on the diffraction patterns at small angle region has been eliminated so as to contrast diffraction intensity for four polythiophenes films. Since no diffraction appears for F8BT spin-coated layer, the original GIXD pattern of F8BT spin-coated layer is shown at the top-right corner.

Scheme S1.

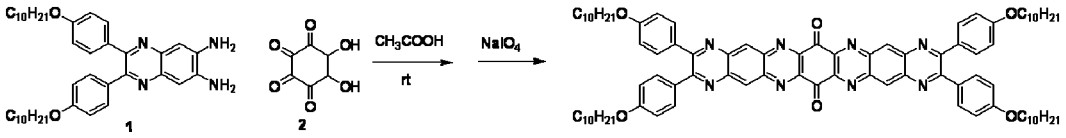


Fig. S1

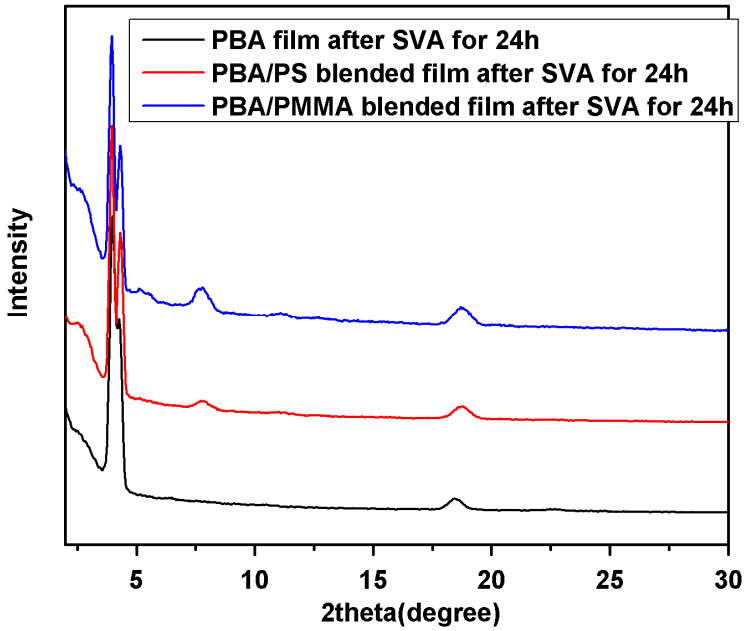


Fig. S2

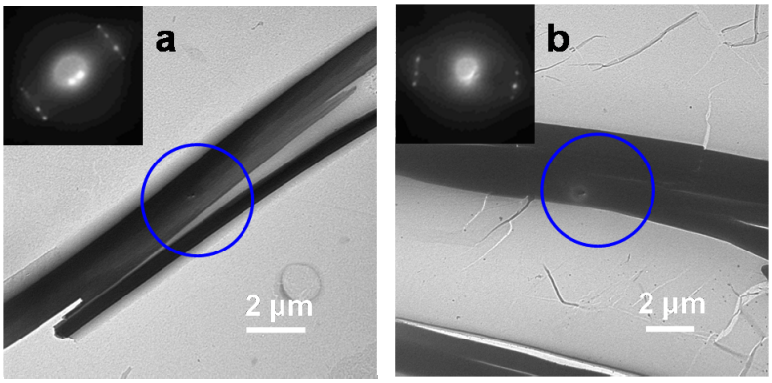
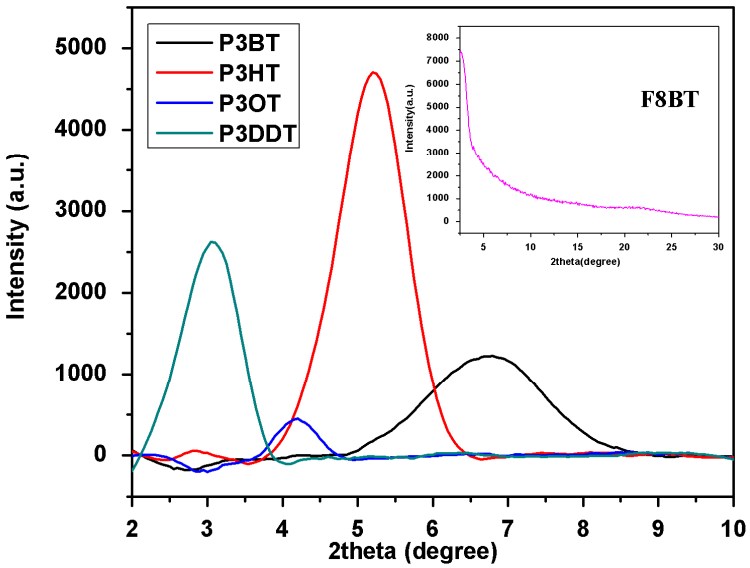


Fig. S3



References

1. M. Wang, Y. Li, H. Tong, Y. Cheng, L. Wang, X. Jing and F. Wang, *Org. Lett.*, 2011, **13**, 4378-4381.

2. L. Ye, S. Zhang, W. Ma, B. Fan, X. Guo, Y. Huang, H. Ade and J. Hou, *Adv. Mater.*, 2012, **24**, 6335-6341.