Electronic Supplementary Information for:

A Novel Melting Behavior of Poly(3-alkylthiophene)s Cocrystals: Premelting and Recrystallization of Component Polymers

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1. Thermal analysis on cocrystals composed of P3BT and a different P3HT

P3HT with Mw = 42.1 K and H-T regioregularity = 98% was purchased from Rieke Metals Inc.. The pure P3HT sample and P3HT/P3BT blend with 1:1 weight ratio were prepared by solution casting. P3HT has a melting temperature at 239 ^{o}C. P3HT/P3BT cocrystal shows two endothermic and two exothermic peaks in Fig. S-1.

2. Gaussian fit on (100) peak of HB11 cocrystal

HB11-230, which was obtained by thermal annealing at 230 ^{o}C, has a (100) peak similar to pristine HB11, was selected as an example. We assume that the (100) peak of HB11-230 is a superposition of the (100) peaks of P3HT, HB11 and P3BT. The (100) peak of HB11-230 is subsequently fitted by three Gaussian peaks corresponding to the P3HT, HB11and P3BT (100) peak positions as shown in Fig. S-2. The areas of the three peaks are 158, 953 and 81, respectively. The overlapped area of the diffraction peaks for P3HT/HB11 and HB11/P3BT are 102 and 50, respectively. Thus, the fractions of pure P3HT and P3BT crystals in the HB11 blend are approximately 5%–15% and 3%–8%, respectively. It should be noted that the fractions of pure P3HT and P3BT crystals should be overestimated, since pure P3HT and P3BT samples also show similar (100) peaks which can be fitted by three Gaussian peaks. The DSC heating curve in Fig. 3 reveals the heat fusion of melting transition in the pure P3HT sample is approximately 11–16 J/g. Even if the fraction of P3HT crystal in HB11 is 15%, the value (16 J/g×15% = 2.4 J/g) is not adequate for the heat fusion of the former endothermic peak in HB11: 15.6 J/g$_{(P3HT)}$ (g$_{(P3HT)}$ denotes the weight of P3HT component in HB11). The Gaussian fitting analysis demonstrates

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that cocrystal, not the pure P3HT crystal, is responsible for the former endothermic peak.

3. DSC cooling curves of P3HT, P3BT and their blends

As shown in Fig. S-3, all the blends show two exothermal peaks, which indicate that the component polymer chains have different thermal properties and undergo different crystallization processes. This could help to explain why the blends come into blended crystals after thermal treatment.

4. Space charge limited current (SCLC) study on hole mobility of cocrystals and blended crystals

Hole transportation properties of the cocrystals and blended crystals were investigated on a hole-only device with indium tin oxide (ITO)/active polymer/Au architecture (see Fig. S-4). The polymer active layer was obtained by solution casting method as described in "Sample Preparation" section. 0.2 mL of solution was used for each cast. The film thickness is 1.5–2.5 μm measured by Atomic force microscopy (AFM, Agilent 5500). The films of blended crystals were obtained by thermal treatment at 260 °C in a glove box under a nitrogen atmosphere. Subsequently, 70 nm of Au were evaporated onto the samples to form top electrodes. The electrical measurement was carried out with a Keithley-2400 source meter in a nitrogen atmosphere. The hole mobilities of the samples were obtained by using SCLC model and calculated according to the following equation[1]:

$$\ln(I/(V - V_{bi})^2) = \ln(9\varepsilon_0\varepsilon\mu_h S/(8L^3)) + 0.89\beta((V - V_{bi})/L)^{1/2}$$

where I is the hole current, V the voltage, ε_0 the permittivity of free space, ε the relative permittivity (we assume it is equal to 3), μ_h the hole mobility, S the area of the active layer, L the active layer thickness and β the field activation factor. The built-in voltage (V_{bi}) is –0.4 eV, which is created from the work function difference between ITO (4.8 eV) and Au (5.2 eV).

The mobility of cocrystals and blended crystals are compared in Fig. S-4. For the blended crystals, HB21 and HB11 have relatively lower hole mobility with a factor of 0.14 and 0.61 compared with that of the corresponding cocrystals. The hole mobility for HB21 blended crystals is actually close to the one of the P3HT film which was annealed at 260 °C. We infer that the decreased hole mobility for HB21 and HB11 blended crystals should be attributed to the dilute effect resulting from the relatively lower hole mobility of P3HT crystals. When the weight fraction of P3HT in the blends decreases to 0.33 (i.e., HB12 blended crystals), a substantially increased hole mobility which is comparable to HB21 cocrystals is obtained. The result shown here has demonstrated that cocrystallization of P3ATs could provide an effective way to tune the hole mobility of the blends, which gives not only significantly higher hole mobility than that of the corresponding blended crystals, but also homogeneous property at any scales.
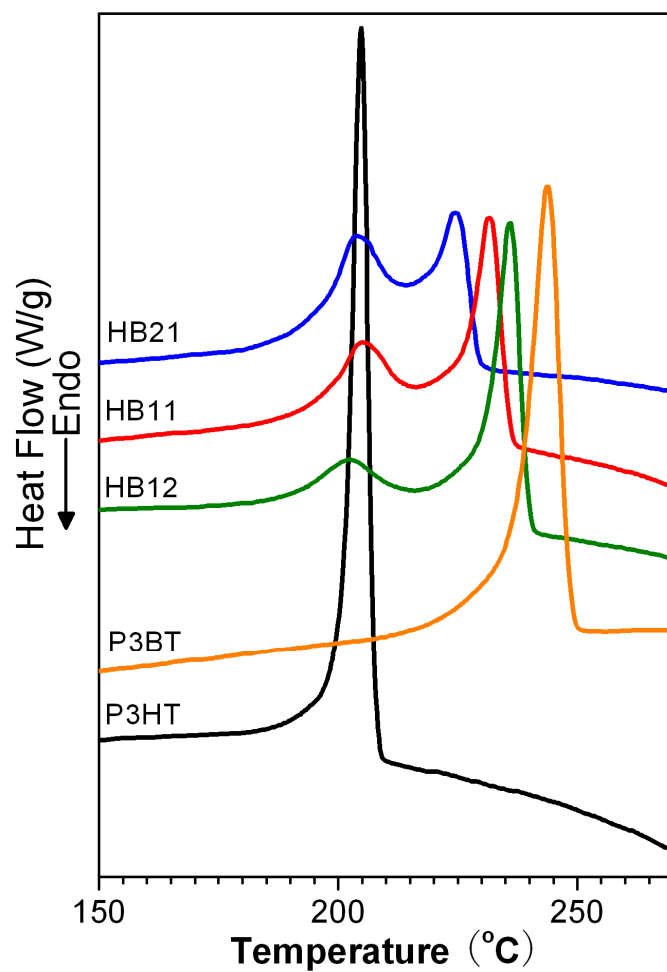
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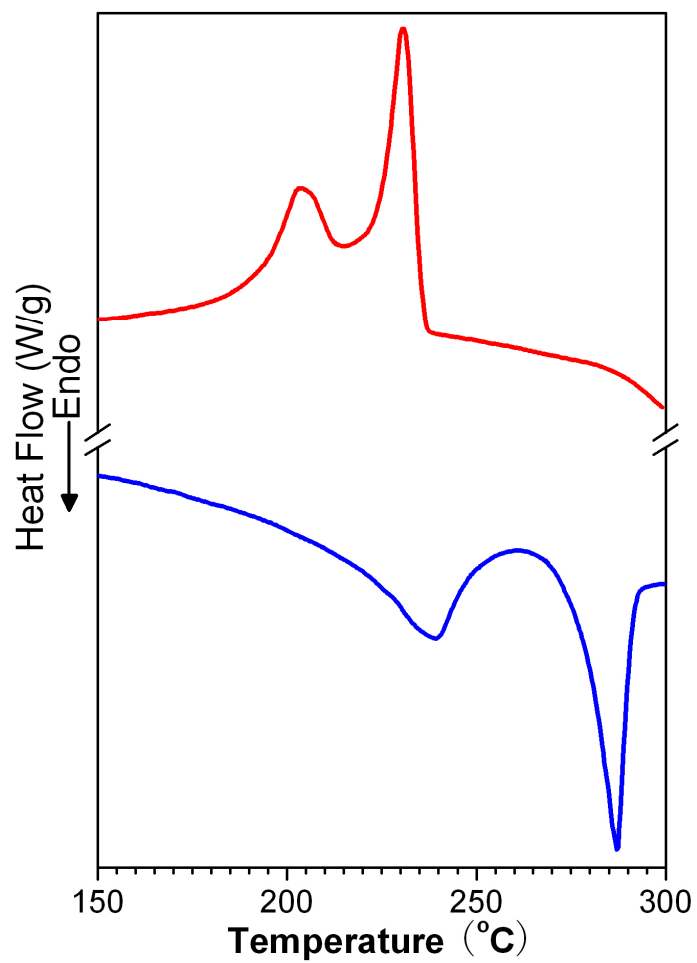
Fig. S-1. DSC heating and cooling curves of P3HT and P3BT cocrystal with 1:1 weight ratio. The heating and cooling rate is 10 $^{\circ}$C/min.
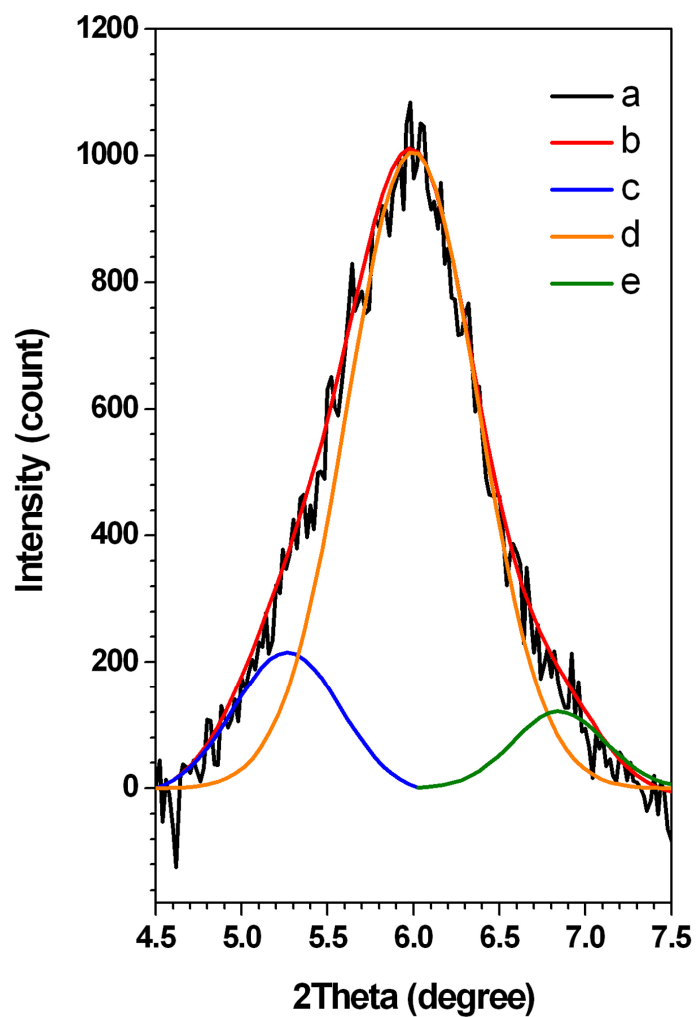
Fig. S-2. (a) Initial curve and (b) Gaussian fitting result of (100) peak in HB11-230 XRD profile with baseline subtraction; Gaussian fitting: (c) P3HT (100) peak, (d) HB11 (100) peak and (e) P3BT (100) peak for HB11-230.

Fig. S-3. DSC cooling curves of P3HT, P3BT and their blends. The cooling rate is 10 °C/min. The curves are off set from baseline for clarity.
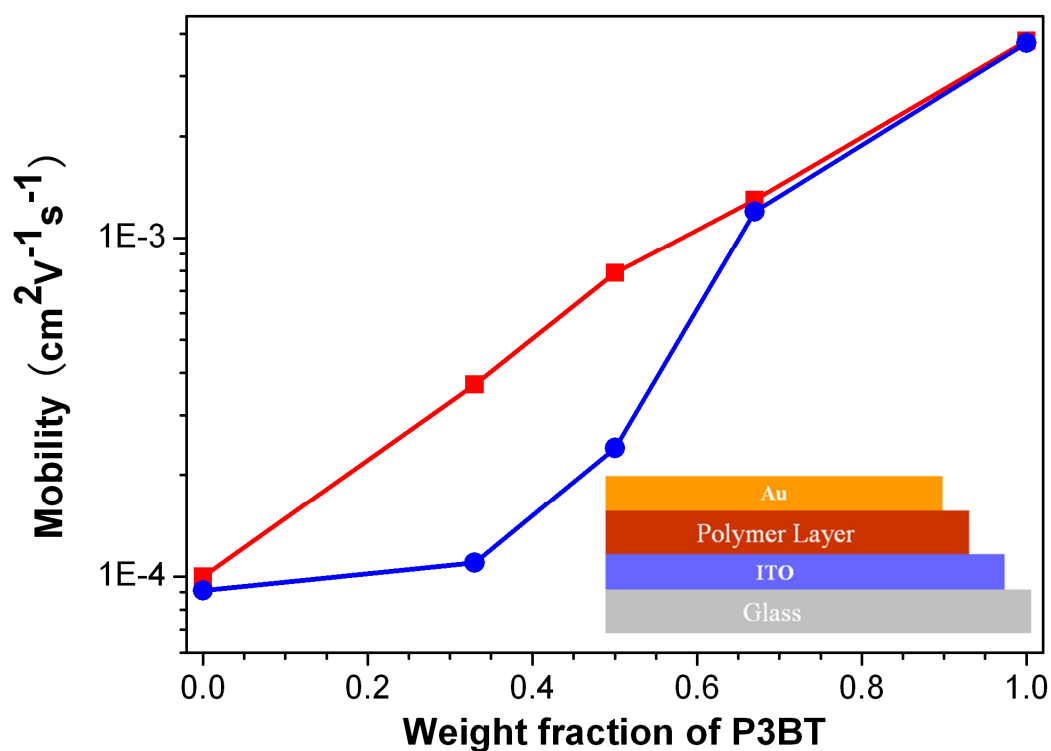
Fig. S-4. Average values of hole mobility: P3HT, P3BT and the cocrystals, which were prepared by solution casting method (red square); P3HT, P3BT and the blended crystals, which were prepared by thermal treatment at 260 °C (blue circule). The insert illustrates the hole-only device architecture.

References

1.   V. D. Mihailetchi, J. Wildeman and P. W. M. Blom, *Phys. Rev. Lett.*, 2005, **94**, 126602.