[Supplementary Information]

Distorted asymmetric cubic nanostructure of soluble fullerene crystals in efficient polymer:fullerene solar cells

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Experimental Details for Supplementary Information

This part is for the comparison of 1:1 and 1:2 compositions as shown in Figs. S1 and S3. The solutions and films (1:1 and 1:2 compositions) were made in the same way as mentioned in the experimental section. The thickness of blend films was ~175nm and ~170nm for 1:1 and 1:2 compositions, respectively. One set of devices of each composition was annealed at 140ºC for 2hr. The solar cells were fabricated in the same way as described in ref. 18. A quartz substrate (Spectrosil B) was used for the optical absorption measurement of blend films which was performed using an UV-visible absorption spectrophotometer (V-560, Jasco). The x-ray diffractograms of blend films were measured using a reflection mode wide angle x-ray diffraction (WAXD) system (Rigaku, Japan), where the data acquisition time at each angle was maximised in order to get better signal-to-noise ratio because the present films are considerably thinner than conventionally employed thickness of typical polymer films (>1μm) for WAXD measurement. The solar cell measurement was carried out in the same way as mentioned in the experimental section.

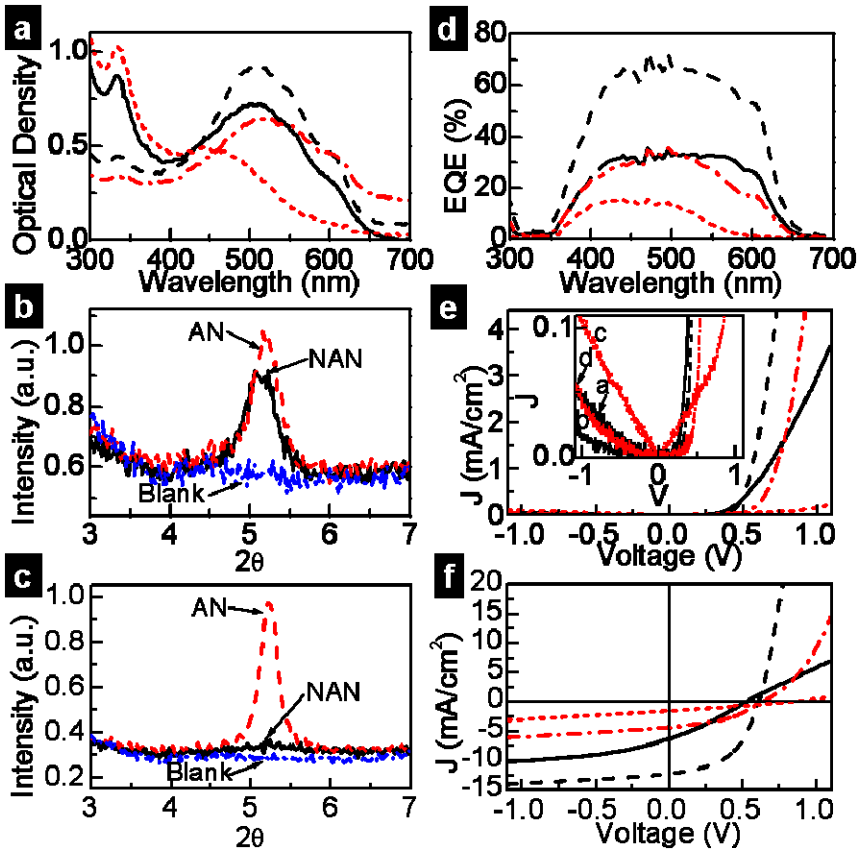

Fig. S1. (a-c) Optical density (a) of P3HT:PCBM blend films: Black solid and dashed lines stand for unannealed and annealed P3HT:PCBM (1:1) blend films, while red short-dashed and dash-dot lines denote unannealed and annealed P3HT:PCBM (1:2) blend films, respectively. (b,c) Reflection mode WAXD patterns of unannealed (NAN) and annealed (AN) P3HT:PCBM blend films: (b) 1:1 and (c) 1:2 compositions, and 'Blank' denotes diffraction patterns for the quartz substrate without the blend film. **(d-f)** EQE (d), dark J-V (e), and light J-V (f) characteristics of solar cells: Black solid and dashed lines stand for not-annealed ('a' in the inset to Fig. S1e) and annealed ('b' in the inset to Fig. S1e) P3HT:PCBM (1:1) blend films, while red short-dashed and dash-dot lines denote unannealed ('c' in the inset to e) and annealed ('d' in the inset to e) P3HT:PCBM (1:2) blend films, respectively. The summary of polymer solar cells (f): (1) unannealed P3HT:PCBM (1:1) device: J_{SC}=6.02mA/cm^2, V_{OC}=0.5V, FF=30.2%, PCE=1.13%; (2) annealed P3HT:PCBM (1:1) device: J_{SC}=12.23mA/cm^2, V_{OC}=0.61V, FF=50%, PCE=4.37%; (3) unannealed P3HT:PCBM (1:2) device: J_{SC}=1.46mA/cm^2, V_{OC}=0.79V, FF=30.1%, PCE=0.41%; (2) annealed P3HT:PCBM (1:2) device: J_{SC}=4.27mA/cm^2, V_{OC}=0.63V, FF=41.3%, PCE=1.31%.

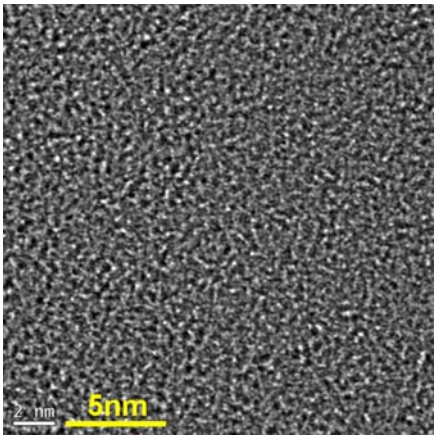

Fig. S2. Typical FE-TEM image of pristine P3HT film of which thickness is ~100 nm.

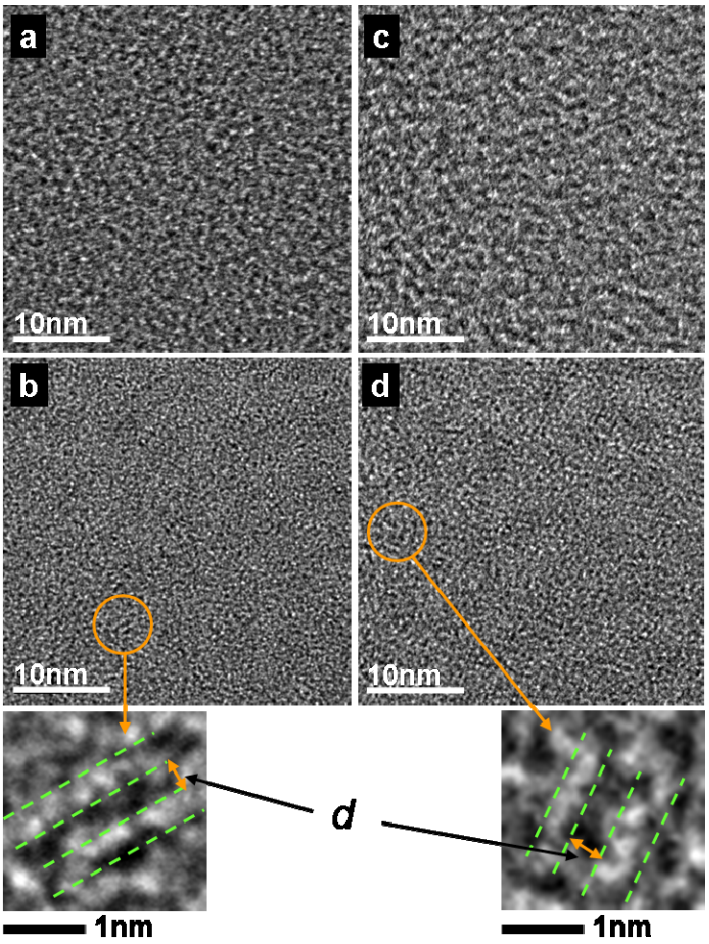

Fig. S3. FE-TEM images focusing on the P3HT nanocrystals: Unannealed (a) and annealed (b) P3HT:PCBM (1:1) blend films, and unannealed (c) and annealed (d) P3HT:PCBM (1:2) blend films. '*d*' in the enlarged images (bottom) shows the spacing between P3HT nanocrystal domains: The average observed '*d*' value was very slightly bigger for 1:1 composition than for 1:2 composition, which might be the effect of (not-well-ordered and/or very little) PCBM molecules/aggregates inserted in between P3HT crystal domains.

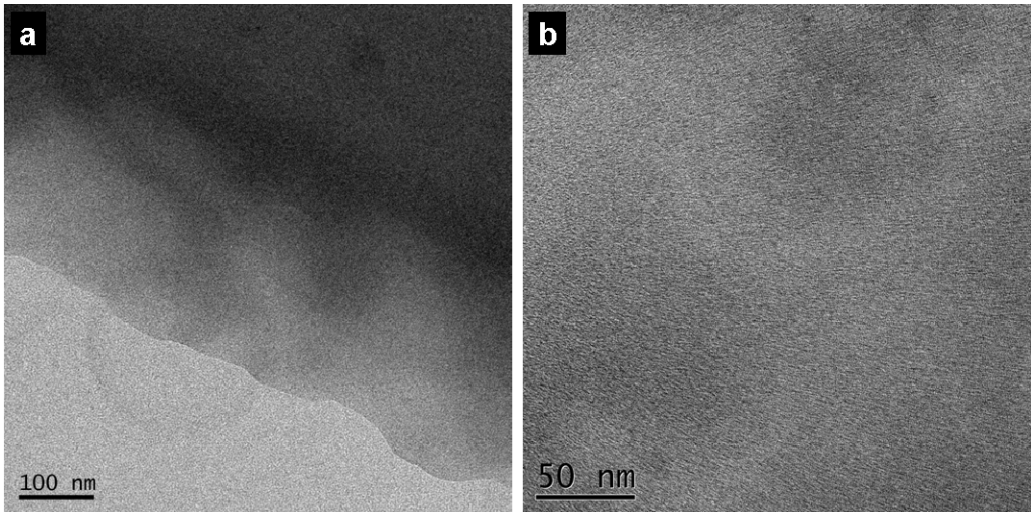

Fig. S4. Example of low magnification FE-TEM images to find any P3HT nanofibrils: Scale bar = 100nm (a) and 50nm (b). However, no particular nanofabrils are observed despite searching several positions randomly.

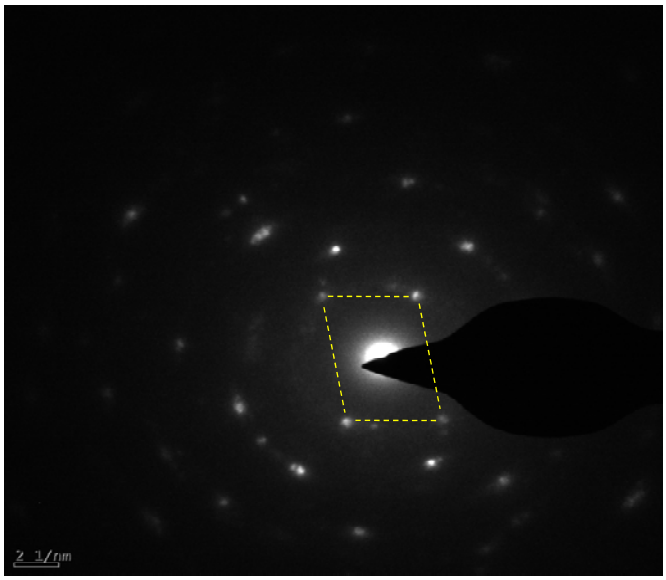

Fig. S5. Full image of SAED pattern for the PCBM nanocrystals in the annealed P3HT:PCBM (1:1) blend film (refer to the part of SAED pattern in Fig. 2b in the main manuscript).

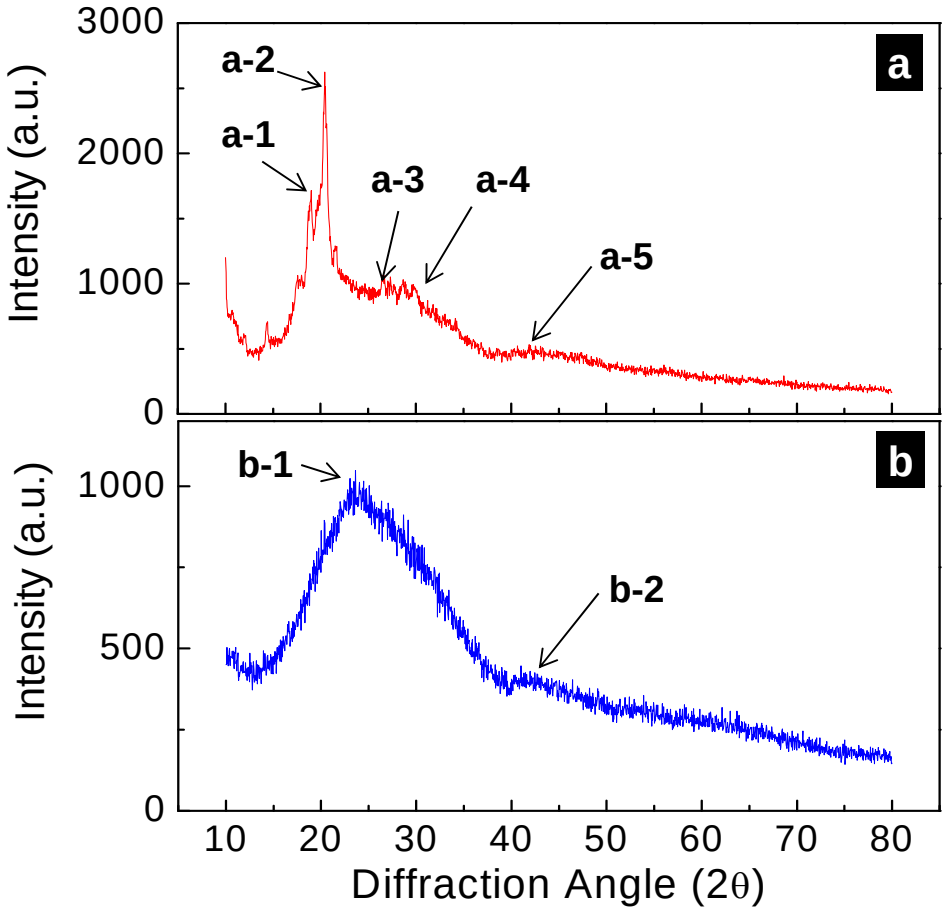

Fig. S6. Wide angle x-ray diffraction patterns of annealed films (140 ^{o}C for 2hr) coated on glass substrates: (a) pristine PCBM film and (b) P3HT:PCBM (1:1) blend film. The average d-spacing values are 0.47nm (a-1), 0.44nm (a-2), 0.37nm (a-3), 0.31nm (a-4), 0.22nm (a-5), 0.38nm (b-1), and 0.22nm (b-2). Here we think that the broad b-1 peak has a complex signal including reflected beams from the substrate.

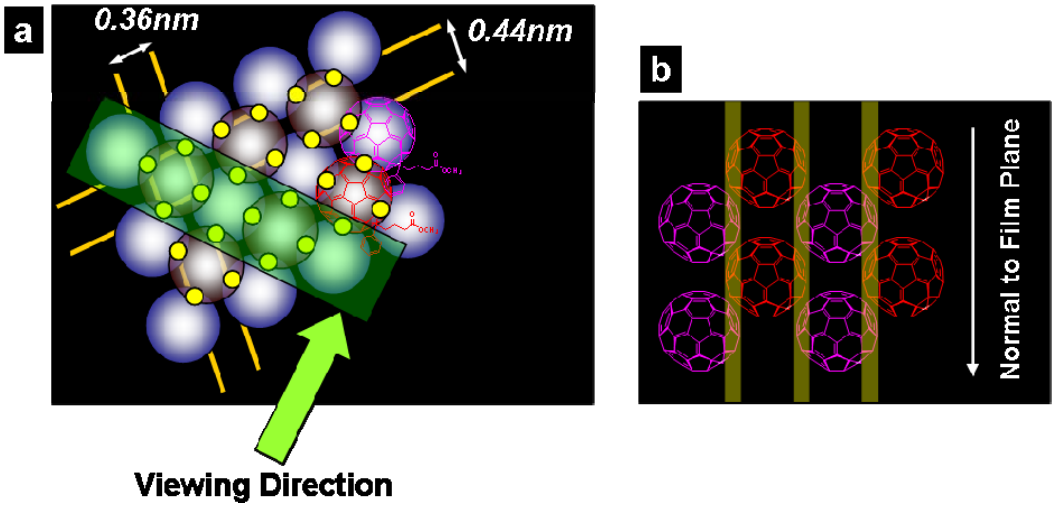

Fig. S7. Schematic illustration of vertical stacking (b) of PCBM molecules in which the viewing direction was selected as given in (a) in order to give better visibility of the stacking geometry. The close contact parts of stacked PCBM molecules are highlighted in yellow bars in (b), whilst they are marked in yellow dots in (a). Note that the attached soluble group to PCBM is not shown in (b) for clear schematic image and the top view (a) is remade from Fig. 2c in the main manuscript. We think that imaging just PCBM molecules (not crystals) would not deliver a clear but a blur image because of delocalized electron density around PCBM molecule. We also note that the wall thickness of fullerene is about 0.35nm based on its inner and outer diameters (see http://www.sesres.com/PhysicalProperties.asp), which supports that the measured TEM spots come from the molecular stacking as mentioned here.

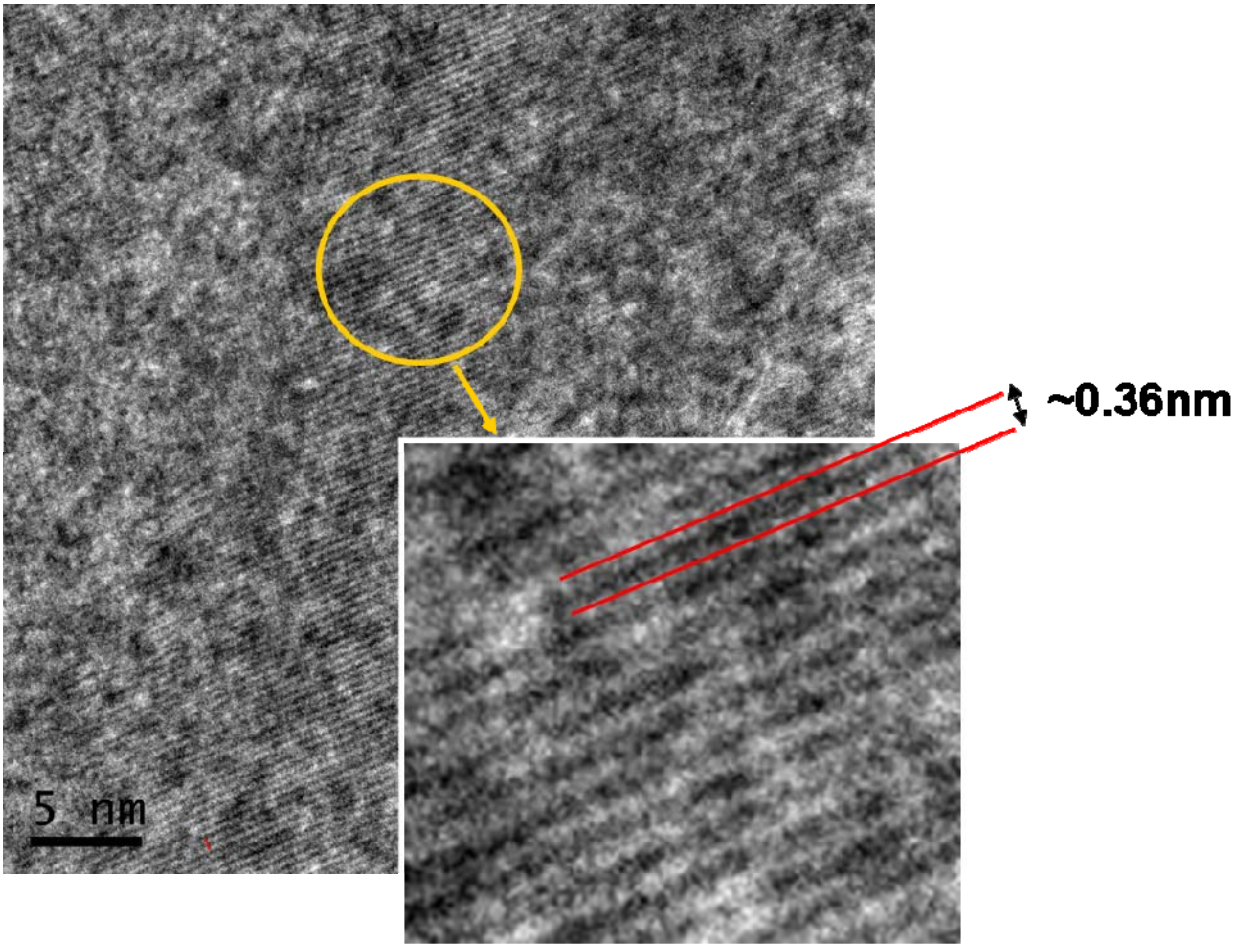

Fig. S8. FE-TEM image exhibiting the formation of ordered PCBM nanocrystals in the different position of annealed P3HT:PCBM (1:1) blend film from Fig. 2b in the main manuscript. Note that the degree of order in this image is a bit poorer than that in Fig. 2b.