

Supporting Information

Visualizing Order in Dispersions and Solid State Morphology with CryoTEM and Electron Tomography: P3HT:PCBM Organic Solar Cells

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This file contains:

1. P3HT crystallization in the absence and presence of PCBM, Figure S1.
2. Time-resolved crystallization of P3HT as revealed by cryo-TEM, Figure S2.

1. P3HT crystallization in absence and presence of PCBM

The absence or presence of PCBM can have an effect on the crystallization of P3HT. During the crystallization experiments presented in the paper, the PCBM is either completely dissolved or forms nanocrystals, as indicated by the diffuse band in the electron diffraction spectrum at $d = 0.46$ nm ($q = 13.6$ nm⁻¹) in Figure 1d. Hence, the potential role of PCBM as nucleation sites for P3HT nanowires can never be completely excluded. However, in our experiment it is not expected to play a significant role.

A much more pronounced effect is the effect of PCBM on the crystallization kinetics. Our data in Figure S1 shows the crystallization kinetics of P3HT in the absence and presence of PCBM, followed by the UVvis absorption spectra. Two solutions of P3HT 1m% in toluene and P3HT:PCBM, 1:1, 1m% in toluene were crystallized over 7 days. The red shift of the spectrum with $\lambda_{\text{max}} = 445$ nm to two maxima at 570 nm and 612 nm can be attributed to an increase in conjugation length of the polymer, and an increase in interchain coupling, both resulting from the aggregation of P3HT in solution. This red shift is completed already after 1 day in the case of the P3HT dispersion and takes significantly longer in the case of the P3HT:PCBM dispersion. This can be explained by adsorption of PCBM molecules at the P3HT chain and nanowire surface, which makes crystallization slower and more difficult.

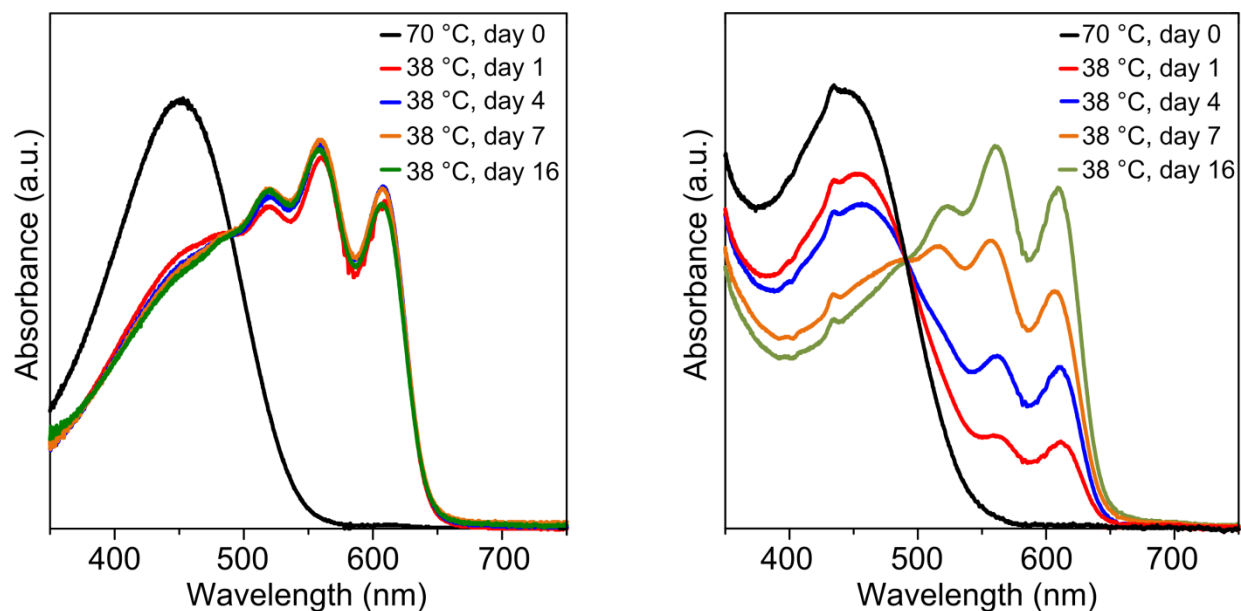


Figure S1: Absorption spectrum of (left) P3HT 1m% in toluene and (right) P3HT:PCBM, 1:1, 1m% in toluene changing with aggregation time under identical conditions.

2. Time-resolved crystallization of P3HT as revealed by cryoTEM

Figure S2 shows cryo-transmission electron microscopy images (cryo-TEM) of the crystallization of P3HT nanowires isothermally at 38 °C in a P3HT:PCBM blend 1:1, 1 mass % in toluene. This temperature was chosen to induce crystallization at a concentration where solar cells can be processed without trapping the P3HT in a gel phase. This intermediate temperature has the consequence that the crystallization is retarded as compared to other reports.¹⁻⁶ Initially (0 days), no crystalline structure can be observed in both the low and high magnification images. There are some large scale, black regions with indicate enrichment of P3HT and PCBM at certain locations. After 1 day, crystalline fragments start to appear randomly distributed throughout the sample. These fragments show the 1.7 nm lamellar stacking of phase I P3HT. The number of lamella in the stack is limited to 3-5. In the overall image these fibers showing the lamellar stacks are clearly visible and often curved. P3HT crystals are generally quite rigid and their curvature at this stage is due to small crystalline segments that are connected by more amorphous regions. The wires that are oriented with the lamellar stacks perpendicular to the electron beam are not visible. This is probably due to the limited thickness of the wires at this point, which limits the contrast as compared to the solvent background. After 4 days of crystallization, the images show elongated darker regions and inside those regions, relatively larger and thicker crystalline P3HT, as compared to the previous timepoint. The darker regions are amorphous P3HT and PCBM that are enriched around the crystalline segments. From 7 days onward, these darker regions become smaller and more concentrated around the crystalline P3HT nanowires that are now visible under multiple orientations. This indicates that the crystalline nanowires have become thicker, which is also shown by some of the lamellar stacks that have now become significantly thicker (+8 lamella), although some thinner sections are also visible.

These cryo-TEM images show that P3HT first appears as thin crystalline fragments and then grow out to long crystalline nanowires. Although the growth of P3HT crystals is generally described as one-dimensional growth,⁶ the cryo-TEM images show fast growth along the fiber length and very slow growth along the lamellar stacking direction in time.

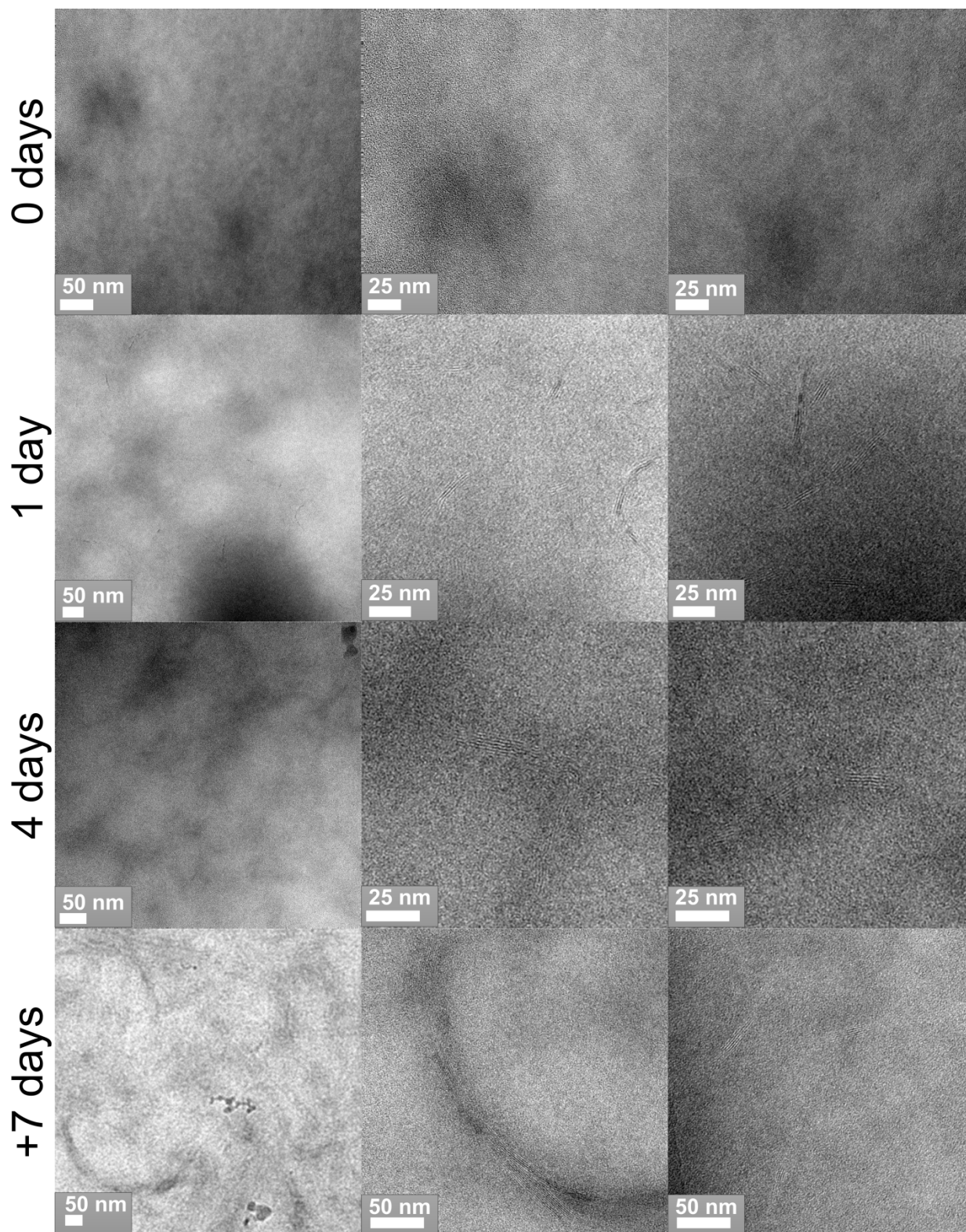


Figure S2: Cryo-TEM images showing in detail the growth of P3HT nanowires in a 1 mass % P3HT:PCBM 1:1 blend in toluene. Thin crystalline segments of about 25 nm, already clearly showing 3-5 lamellar (100) stacking distances of 1.7 nm, grow out to +100 nm long crystalline nanowires containing +8 lamellar distances, indicating strong anisotropic growth.

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