Electronic Supplementary Material (ESI) for Soft Matter.

Impact of Solution Phase Behaviour and External Fields on Thin Film Morphology: PCBM and RRa-P3HT model system

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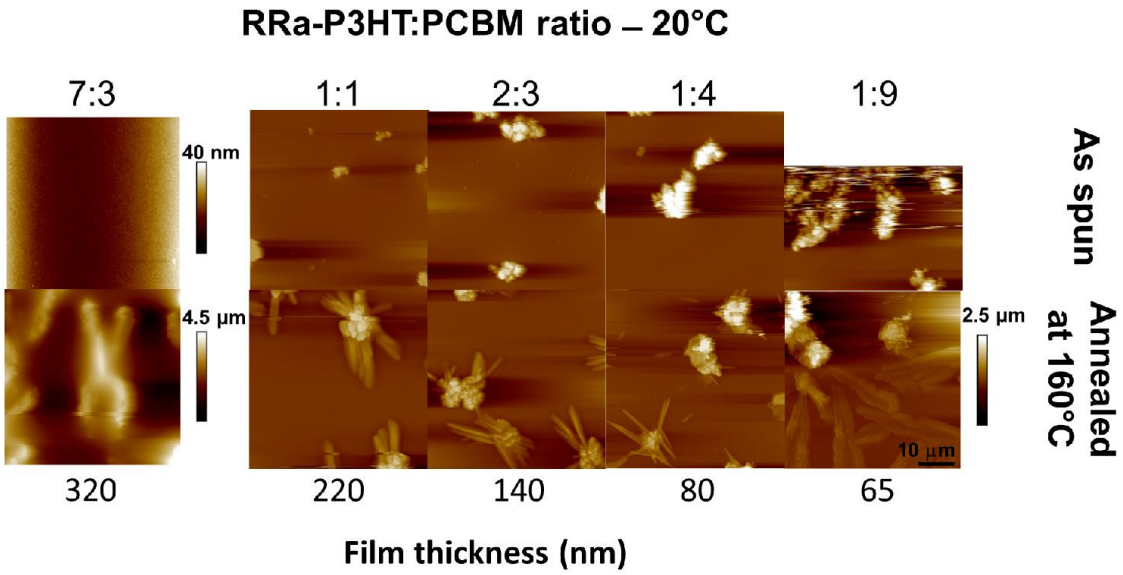

Figure S1. AFM micrographs of RRa-P3HT:PCBM thin films as-spun and annealed at 160°C under vacuum cast from solutions of 30 mg/ml of PCBM in CB prepared at 20°C. The polymer:fullerene ratio is varied and thus the film thicknesses vary accordingly. The other processing parameters are kept the same.

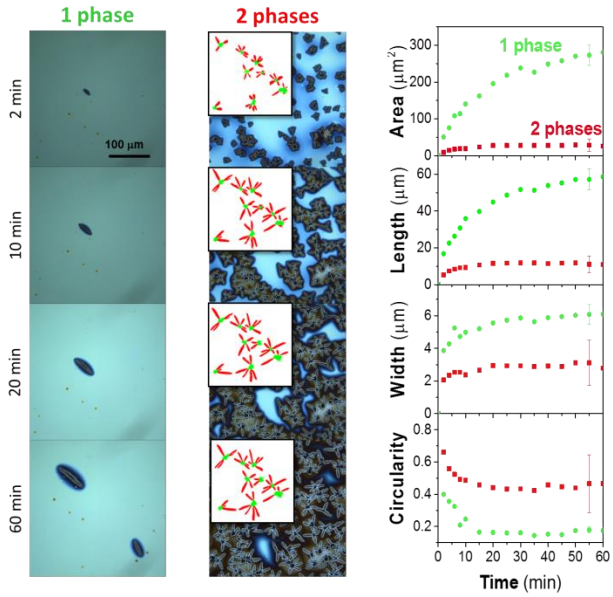

Figure S2. Optical micrographs at different annealing time of RRa-P3HT:PCBM (3:7) cast from solutions at 30 mg/ml of PCBM in CB at 75°C (homogeneous) and 20°C (heterogeneous). The insert represents the thresholding used to analyse the images; the PCBM aggregates from solution are coloured in green while the nucleated needles are coloured in red. The area, length, width and circularity of the needles for both samples is plotted as a function of time.

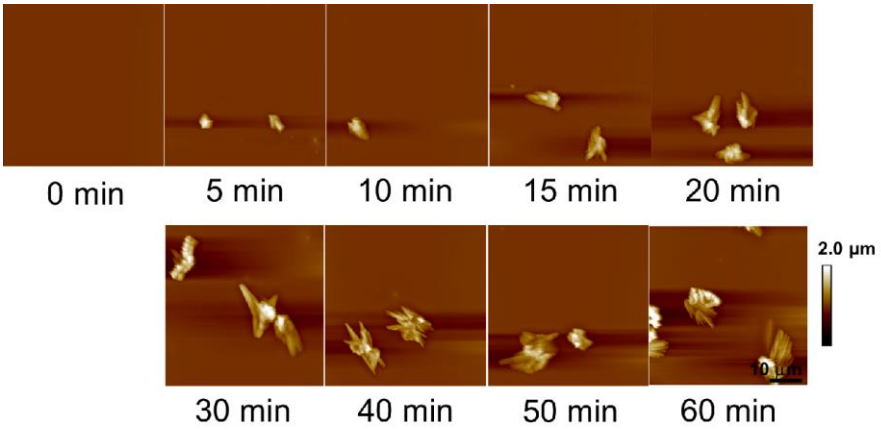

Figure S3. AFM micrographs of samples 1:1 RRa-P3HT:PCBM thin films cast from 30 mg/ml PCBM in CB solutions prepared at 20°C on silicon substrate treated with UVO for 15 min. The samples are annealed for different times.

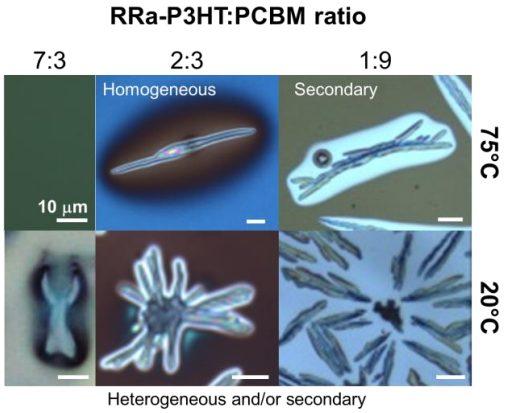

Figure S4. High magnification images of the optical micrographs presented in Figure 4 of the main paper. The scale bars represent 10 µm.

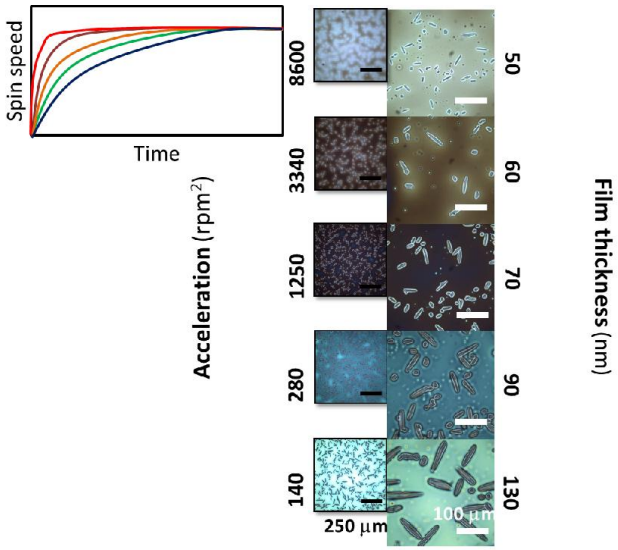

Figure S5. Optical micrographs of 3:7 RRa-P3HT:PCBM thin films cast from 13 mg/ml PCBM in CB solutions prepared at 25°C on silicon substrate treated with UVO for 60 min. The acceleration of the spin coater was varied between 8600 and 140 rpm^2 leading to film thicknesses between 50 and 130 nm. The spin speed was kept at 4000 rpm for all the samples. The samples were annealed at 160°C under vacuum.

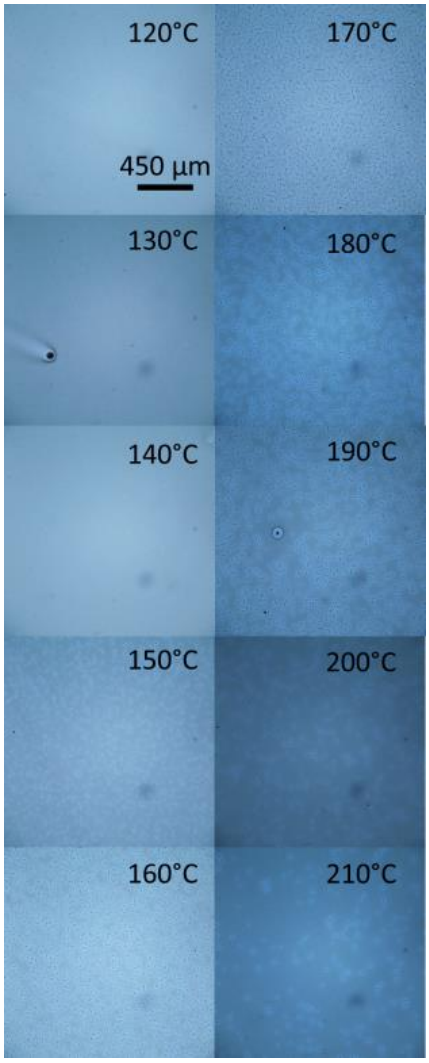

Figure S6. Optical micrographs of 3:7 RRa-P3HT:PCBM samples cast from 10 mg/ml PCBM in CB and annealed for 60 min at different temperatures.

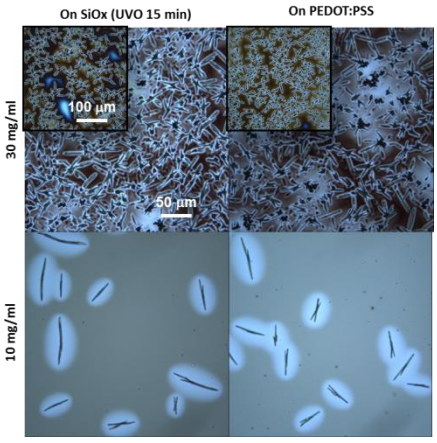

Figure S7. Optical micrographs of 3:7 RRa-P3HT:PCBM thin films cast from 10 and 30 mg/ml PCBM in CB solutions prepared at 25°C on silicon substrate treated with UVO for 15 min and on PEDOT:PSS (PEDOT:PSS - Clevios PVP. AL 4083 from Heraeus - was filtered using a 0.2 µm hydrophilic filter onto the clean silicon wafer, and spin coated at 3000 RPM for 2 minutes and then further dried at 140 °C under vacuum for 1 hour).

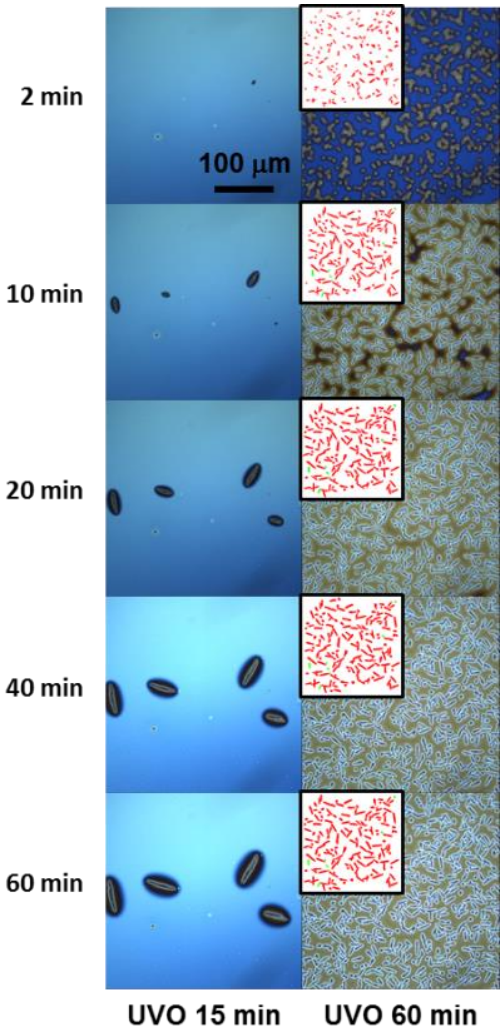

Figure S8. Optical micrographs of 3:7 RRa-P3HT:PCBM thin films cast from a 20 mg/ml PCBM in CB solution prepared at 20°C on substrates exposed to UVO for 15 and 60 min respectively and annealed at 160°C.

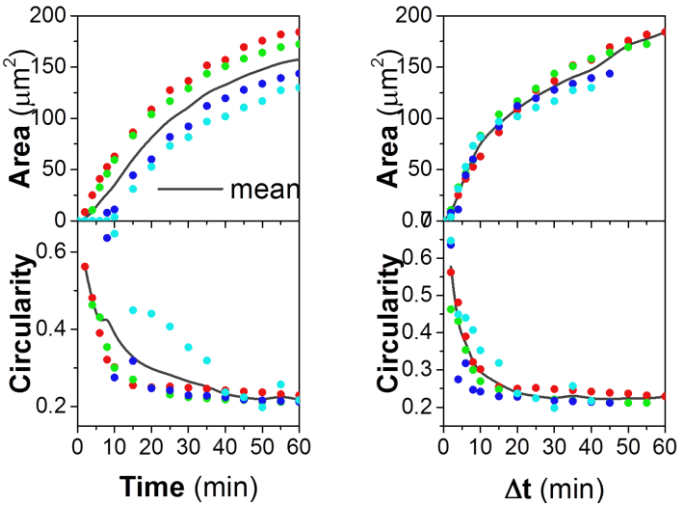

Figure S9. Area and circularity of crystals as a function of time for 3:7 RRa-P3HT:PCBM thin films cast from a 20 mg/ml PCBM in CB solution prepared at 25°C on substrates exposed to UVO for 15 min. In the right panel, the graphs have been rescaled by removing the elapse time before nucleation. We observed as previously[1] that the curves are collapsing on the same curve when the graphs are rescaled to take into account the elapse time before nucleation.

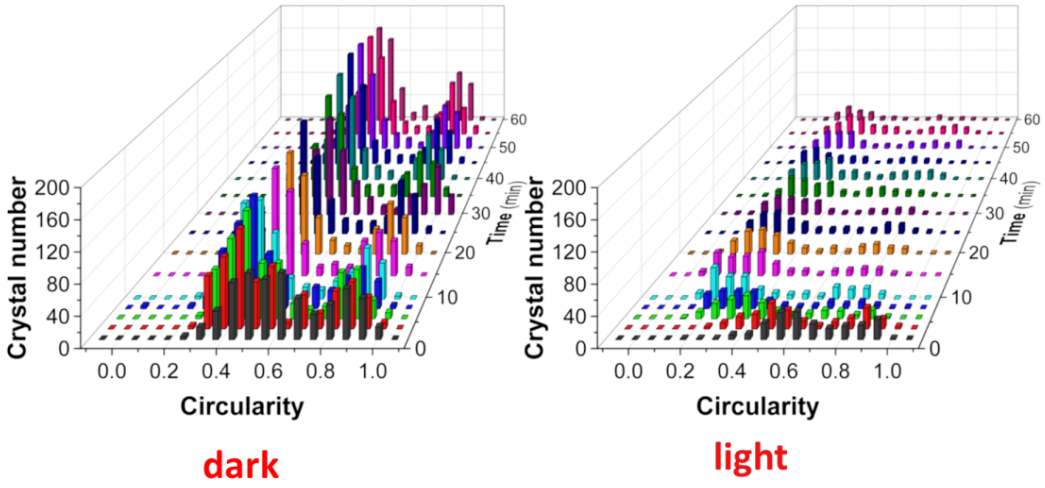

Figure S10. Crystal number as a function of the crystal circularity for 3:7 RRa-P3HT:PCBM thin films cast from a 20 mg/ml PCBM in CB solution prepared at 25°C on substrates exposed to UVO for 60 min and annealed under light or kept in dark. The optical micrographs at different annealing time are presented in Figure S12.

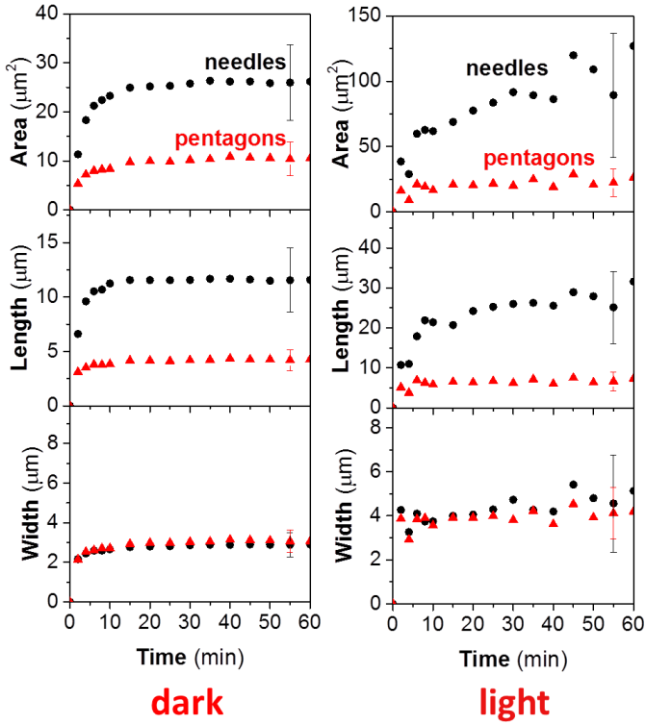

Figure S11. Area, length and width of crystals as a function of time for 3:7 RRa-P3HT:PCBM thin films cast from a 20 mg/ml PCBM in CB solution prepared at 25°C on substrates exposed to UVO for 60 min and annealed under light or kept in dark. The optical micrographs at different annealing time are presented in Figure S12.

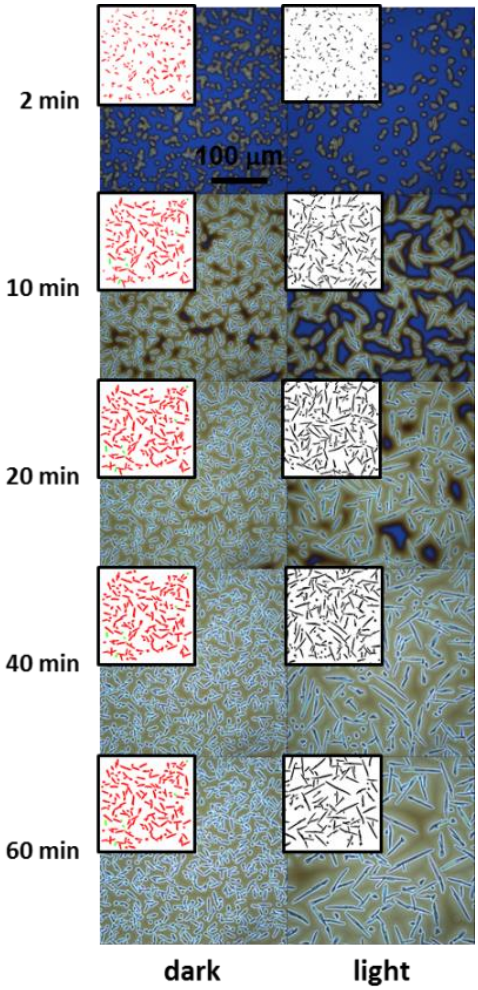

Figure S12. Optical micrographs of 3:7 RRa-P3HT:PCBM thin films cast from a 20 mg/ml PCBM in CB solution prepared at 20°C on substrates exposed to UVO for 60 min and annealed at 160°C in the dark and under light exposure respectively.

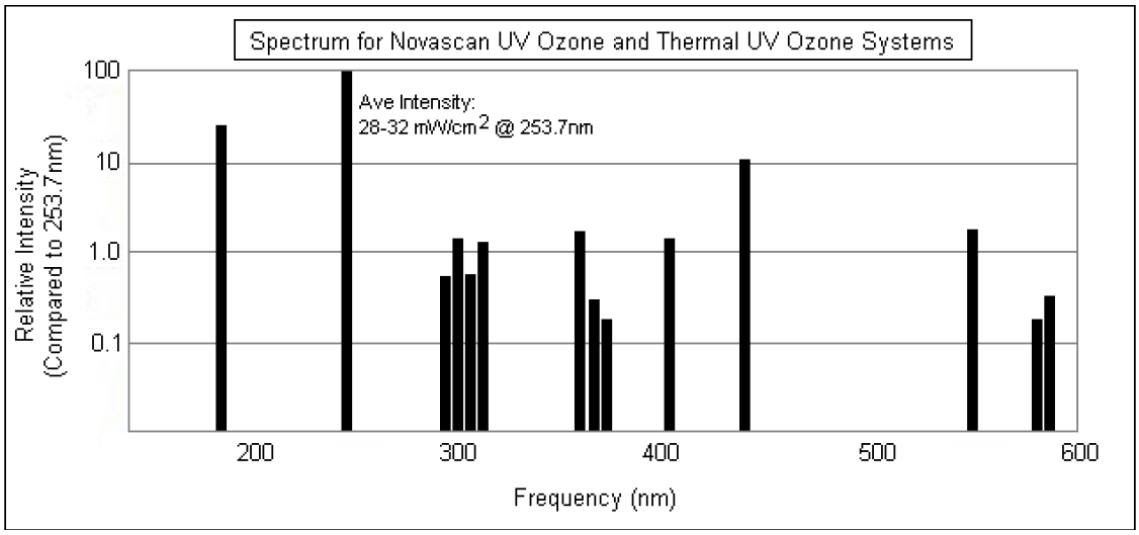

Figure S13. Spectrum of UV lamp of the Novascan UV ozone cleaner.

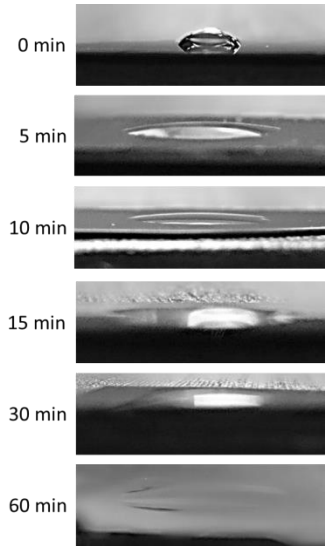

Figure S14. Water contact angle measurement as a function of UVO time exposure.

1 D. Môn, A. M. Higgins, D. James, M. Hampton, J. E. Macdonald, M. B. Ward and J. Rawle, *Phys. Chem. Chem. Phys.*, 2015, **17**, 2216-2227.