Supporting information

Unambiguous determination of molecular packing in crystalline donor domains of small molecule solution processed solar cell devices using routine X-Ray diffraction techniques.

Aurélien Viterisi,[,a] Núria F. Montcada,[a] Challuri Vijay Kumar,[a] Francesc Gispert-Guirado,[b] Eddy Martin,[a] Eduardo Escudero,[a] and Emilio Palomares*[,a, c]*

[a] Institute of Chemical Research of Catalonia (ICIQ).Avda. Països Catalans, 16. Tarragona. E-43007. Spain.

[b] Universitat Rovira i Virgili. Avda. Països Catalans, 26. Tarragona. E-43007. Spain

[c] Catalan Institution for Advanced Studies and Research (ICREA) Passeig Lluís Companys, 23, Barcelona 08010, Spain

Experimental

Reagents: SQ was synthesized following reported procedures.[1] High purity shiny greenish crystals of SQ were obtained with purity superior to 99% by HPLC. $PC_{70}BM$ was purchased from Solenne (Solenne BV, the Netherlands) and used without further purification. High purity (HPLC gradient grade, 99.9%) $CHCl_3$ and CH_2Cl_2 were used for the active layer deposition. MoO_3 (99.999%) was purchased from Sigma-Aldrich.

Crystallization experiments: Single crystals of SQ were grown in crystallization tubes (0.5×20 cm) by slow diffusion of Hexane or MeOH in a concentrated solution of SQ in $CHCl_3$. Single crystals of the Pbcn phase were isolated from the reaction vessel in the final condensation step of the SQ synthesis.

Thin film Fabrication: Substrates (Optical grade cover slide or Indium Tin Oxide (ITO) 5 Ohm/square (PSiOTec, Ltd., UK) sodalime glass substrates) were first rinsed with acetone to remove the residual photoresist layer. The substrates were then placed in a teflon holder and sequentially sonicated in acetone (1 × 10 min) and isopropanol (2 × 10 min), and finally dried under a flow of nitrogen. The ITO substrates where ozone-treated in a UV-ozone cleaner for 30 min. in ambient atmosphere, and subsequently coated in air with a layer of filtered (0.45 μm, cellulose acetate) solution of Poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS, HC Starck Baytron P) (4500 rpm 30 seconds followed by 3500 rpm 30 seconds) or used for the evaporation of a MoO_3 layer. The PEDOT:PSS films were dried at 120 ºC under inert atmosphere for 15 min.

The MoO_3 layer was deposited by thermal evaporation in an ultra high vacuum chamber

(1×10^{-6} mbar) at a rate of 0.3 Å/s (thickness: 8 nm). Following fabrication, the films were maintained under a nitrogen atmosphere and stored in the dark until used.

Active layers were spin-coated (2000 rpm) in air either over glass substrates, ITO, MoO_3, or over the PEDOT:PSS layer, from a 20 mg/ml (total concentration) solution of SQ and $PC_{70}BM$ (1:3 w/w ratio) or from a 15 mg/ml solution of SQ (deposition volume 50µL). Films of SQ:$PC_{70}BM$ blends spin coated from $CHCl_3$ had an average thickness of 100 nm while those spin coated from DCB thinner than 50 nm. Films of pristine SQ were 80 nm thick on average.

The thickness of the active layer films was measured with a stylus profilometer Ambios Tech. XP-1, from a scratch made in the centre of the substrate.

Solvent vapour annealing: The solvent vapour-annealing step (SVA) was carried out directly after deposition of the active layer by exposing the films to saturated vapours of solvent at room temperature. The SVA vessel consisted of a modified petri dish, where several holes (approx. 0.5 cm diameter) were drilled in the bottom part and held tightly with Teflon tape over another petri dish filled with 10 ml of CH_2Cl_2 (figure S1).

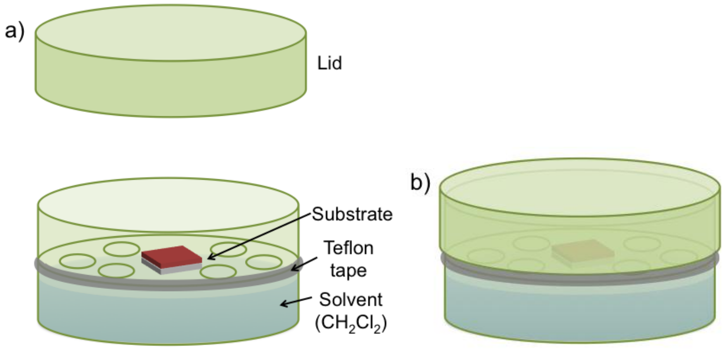

Figure S1. Scheme of the Solvent annealing vessel used for small substrates annealing, a) vessel showed open, b) vessel showed closed

The system was filled 5 min. prior to the SVA step to ensure the atmosphere was saturated with solvent. The substrates were exposed to the solvent vapours at room temperature from 1 min. to 10 min. by placing them in the solvent vessel and keeping the lid on top of the petri dish over the whole annealing process (Figure S1b).

Powdered active layers preparation: Large area (50 cm^2) thin films of SQ:$PC_{70}BM$ (1:3) or pristine SQ were deposited on round shaped glass substrates (typically on the outer side of pre-cleaned petri dishes (8 cm diameter)) using the same conditions as those used for processing active layers. 6 petri dishes of each active layer type were necessary to provide sufficient powder material. Spin coating was carried from SQ:$PC_{70}BM$ (1:3) 20 mg/mL (total concentration) solutions and from SQ (15 mg/mL) solutions at 2000 rpm. An approximate 300 µL volume of solution was deposited by syringe by pushing the desired volume of solution through a 0.2 µm PTFE filter over the substrate. The resulting layers had an average thickness of 130 nm. The SQ:$PC_{70}BM$ and pristine SQ films were subsequently submitted to SVA for 2h and 1h30 respectively (see figure S2 for a schematic of “powdered” layer preparation). These long SVA times are required to allow for maximum crystallite growth and so to increase the signal to noise ratio in the diffractogram. They have been determined experimentally to give a similar ratio between the two crystalline phases as in the active layer. Figure S7 shows diffractograms of powdered layers of pristine SQ solvent annealed for longer time and thermally annealed. The SVA step was carried out in in a sealed vessel (1 L volume) filled with CH_2Cl_2 (200 ml) (figure S3).

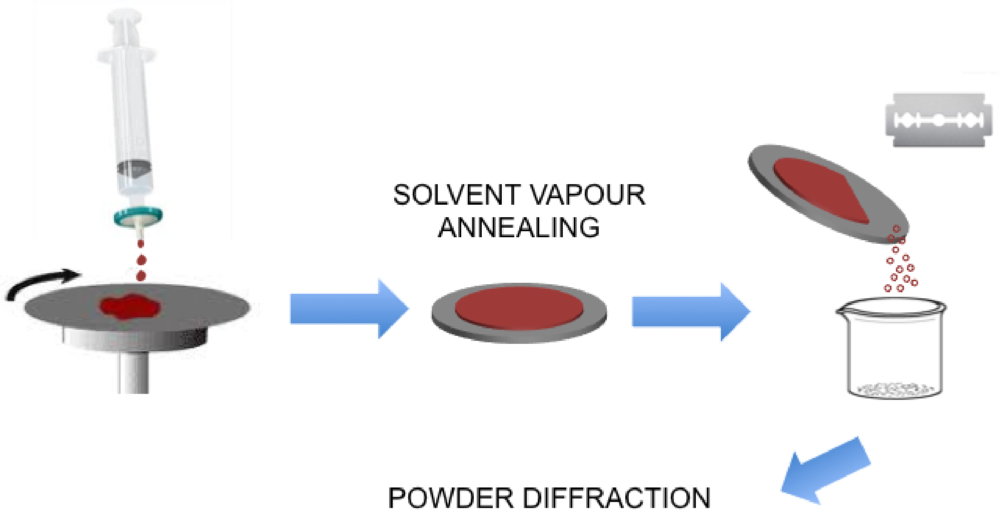

Figure S2. Schematics of powdered active layer preparation

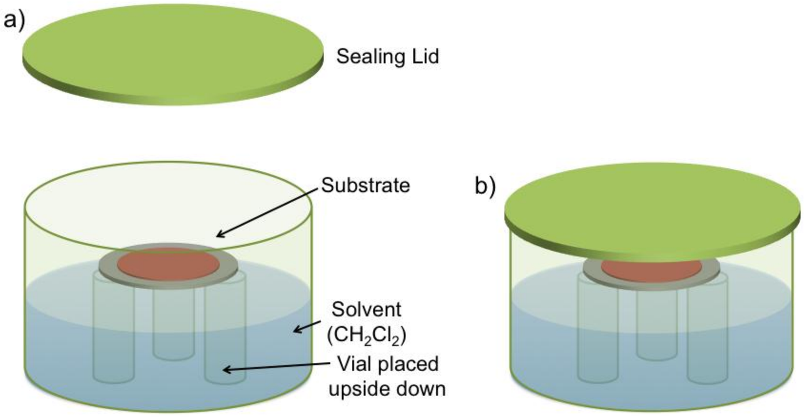

Figure S3. Scheme of the Solvent annealing vessel used for large substrates annealing, a) vessel showed open, b) vessel showed closed

The active layers were scratched off the petri dishes using very sharp razor blades and placed between two layers of polyethylene thin film held tightly in Bruker sample holder ring (ref number: C79298A3244D81) for θ-2θ transmission diffraction analysis.

X-Ray diffraction: XRD measurements on thin films were carried out in the Bragg-Brentano θ-θ configuration on a Bruker-AXS D8-Discover diffractometer with parallel incident beam (Göbel mirror), a vertical theta-theta goniometer, a XYZ motorized stage mounted on an Eulerian cradle, an incident and diffracted beam Soller slits, a 0.02º receiving slit and a scintillation counter as a detector. Cukα (kα$_1$+kα$_2$) radiation was obtained from a copper X-ray tube operated at 40 kV and 40 mA. Diffraction pattern were recorded over an angular 2theta range of 1º to 25º. The data were collected with an angular step of 0.05º at 10 sec per step.

GIXRD measurements were performed with the same system equipped with a 500μm beam collimator and a HI-STAR area detector (multiwire proportional counter of 30x30 cm with 1024x1024 pixel) and GADDS software (General Area Diffraction System). A Helium beam path (SAXS extension) was placed between the sample and the detector to reduce air scattering at low angles. The direct X-ray beam was stopped by a beam stop placed directly on the detector surface. The detector was kept at a distance of 30 cm from the sample and the incident X-ray beam was set at an angle of ω=0.5º with the sample surface, determined experimentally to be below the critical angle for total external reflection. The collected frames (2D XRD pattern) cover a range from 0.9 to 9.2º 2θ with the detector placed at 0º. The exposure time was of 300s per frame.

XRD measurements on powdered active layers were carried out in the Bragg-Brentano θ-2θ configuration on a Bruker D8 Advance Series diffractometer, with a vertical 2theta-theta goniometer, a Kα1 germanium monochromator, fixed divergence slit and diffracted beam radial soller and a VÅNDTEC single photon counting PSD detector. XRD patterns were recorded over an angular 2theta range of 4º to 40º with a step size of 0.016º at 16 sec per step.

Diffractograms and refinement data:

Least square refinements were carried out with the TOPAS software V4.2, 2009, Brüker AXS GmbH, Karlsruhe, Germany.

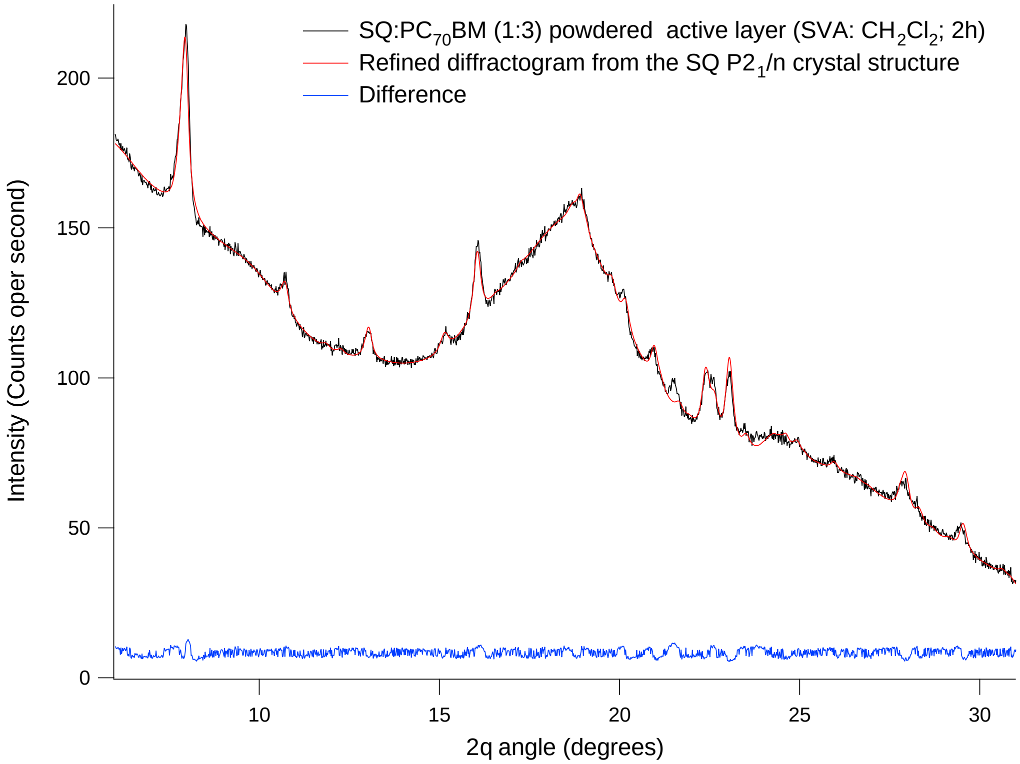

Figure S4. Profile refinement of the SQ:$PC_{70}BM$ powdered active layer diffractogram. R factors: R_{exp}= 0.86, R_{wp}= 1.21, goodness of fit (GOF)= 1.42; refined unit cell parameters were a=6.211(2) Å, b=16.372(7) Å, c=14.826(4) Å, β=92.75(2)º

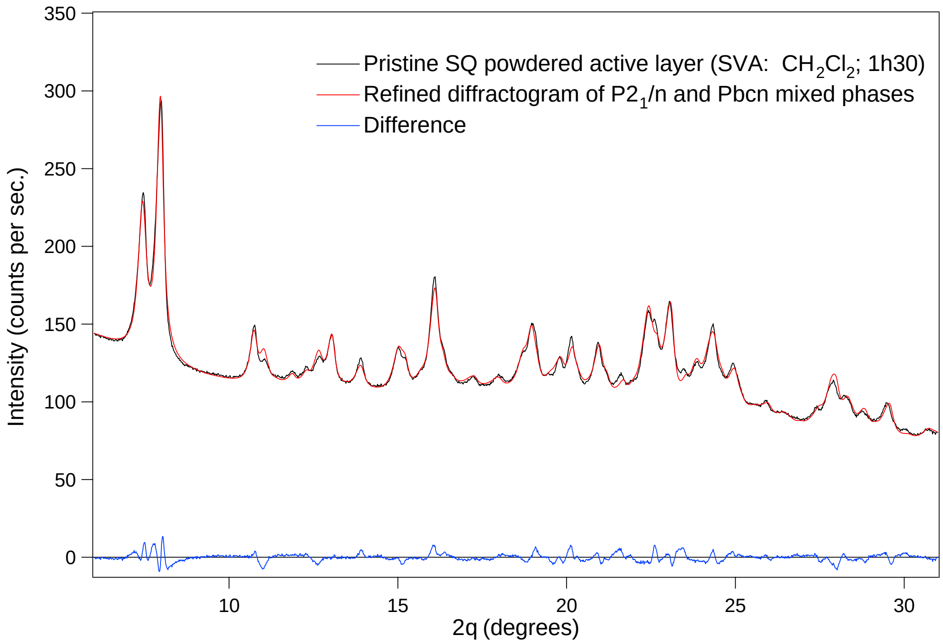

Figure S5. Pristine SQ solvent annealed powdered active layer diffractogram and refined diffractogram of $P2_1/n$ and Pbcn mixed phases. R factors: R_{exp}= 0.80, R_{wp}= 3.79, GOF= 4.76, accounting for a 54:46 ratio of $P2_1/n$:Pbcn phases respectively with refined cell parameters a=6.1892(12) Å, b=16.3403(41) Å, c=14.8160(27)Å, β=92.714(14)º for the $P2_1/n$ fraction and a=15.3620(40), b=18.1846(73), c=10.8174(32) for the Pbcn fraction.

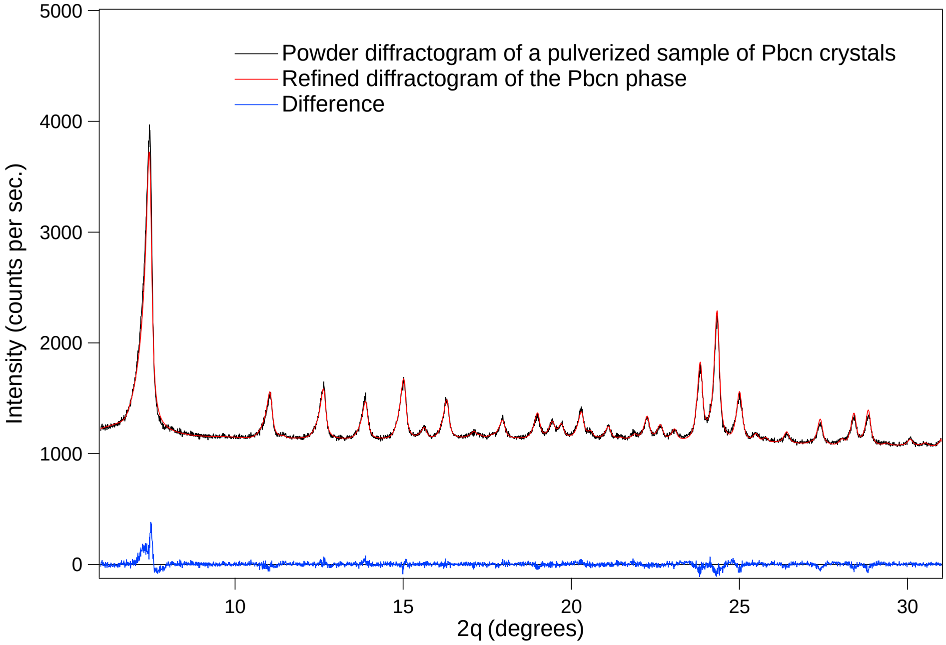

Figure S6. Powder diffractogram of a pulverized sample of Pbcn crystals (black line) and fitted diffractogram from the Pbcn phase using Rietveld refinement routines (red line), R factors: R_{exp}= 6.36, R_{wp}= 8.42, GOF= 1.32 with refined cell parameters a=15.3627(11), b=18.1917(21), c=10.82561(89).

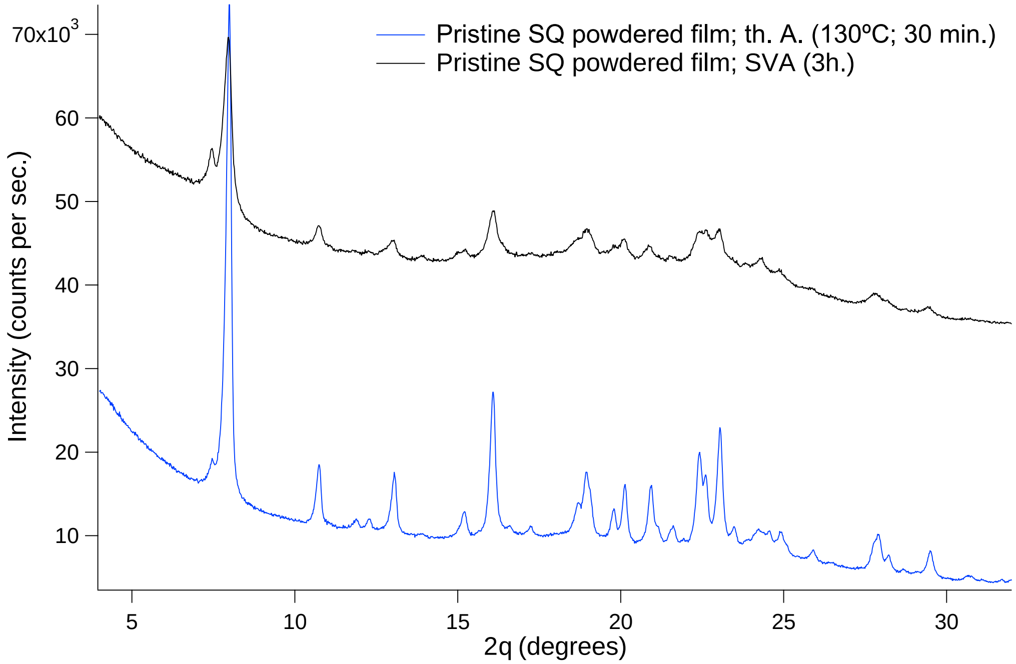

Figure S7. Pristine SQ powdered active layer diffractograms deposited form CHCl$_3$ and submitted to a different annealing process.

References

1. M. Tian, M. Furuki, I. Iwasa, Y. Sato, L. S. Pu and S. Tatsuura, *J. Phys. Chem. B*, 2002, **106**, 4370.