

Supplementary information

Vapour printing: Patterning of the optical and electrical properties of organic semiconductors in one simple step

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Evolution of the beta phase of PFO with time upon vapour printing.

As the β -phase corresponds to an extended conformation of the polymer chains, one may follow the formation of the β -phase by estimating the corresponding increases in polarisability, α .³¹ For wavelengths at which the material is transparent, the following equation can be derived:^{38,39}

$$\frac{\alpha_t}{\alpha_0} \cong \frac{n_t^2 - 1}{n_0^2 - 1} \times \frac{\rho_0}{\rho_t} \cong \frac{n_t^2 - 1}{n_0^2 - 1} \times \frac{d_t}{d_0} \quad \text{Eq. 1}$$

In other words, since the change in density, ρ , can be estimated from the relative change in d and the variations in n are deduced from the ellipsometric data (Fig. S2), the increase in polarisability due to the formation of the β -phase of PFO can be estimated from Eq. 1. Fig. S2a shows the variation of the polarisability with exposure time, which follows a profile that can be described by an Avrami equation of the general form.^{33,40}

$$\frac{\alpha_t}{\alpha_0} = A_0 \times (1 - A_1 \times e^{-Kt^n}) \quad \text{Eq. 2}$$

Interestingly, the fit to the experimental data yields an Avrami coefficient $n \sim 2$, which phenomenologically agrees with the fact that the planarisation of the polymer chains induced by the β -phase formation can be considered a two dimensional process. The

final polarisability of the β -phase dried film after seven minutes of vapour printing is some 10% higher compared to the as spin-coated film. Alternatively, if Eq. 1 is expressed in terms of the Fraser fraction f of aligned polymer segments,³⁹ we can estimate a final increase in f (assuming $f_0=0$) of about 20% for the β -phase (see Fig. S2c).

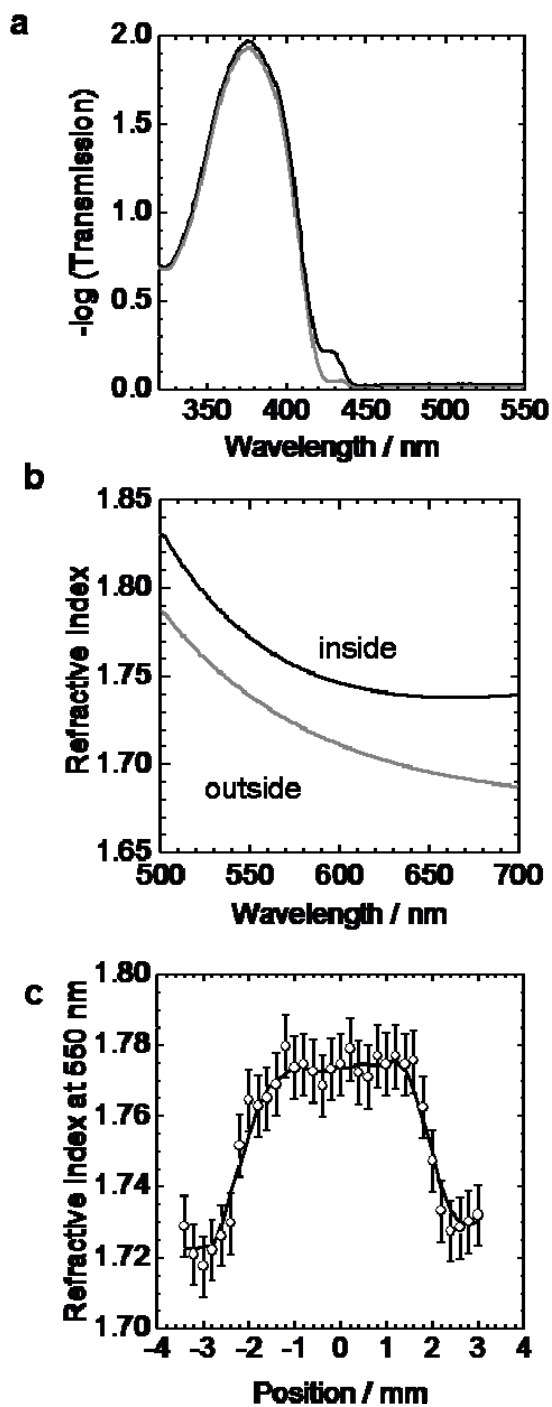


Fig. S1. (a) Absorbance spectra of PFO thin films before (grey) and after chlorobenzene vapour exposure (black). (b) Refractive index of PFO thin films before (grey) and after chlorobenzene vapour exposure (black). (c) Profile of the refractive index measured across a vapour-printed β -phase dot (*c.f.* Fig. 1c in main text). The refractive index was deduced by fitting ellipsometry measurement maps using a Cauchy dispersion law.

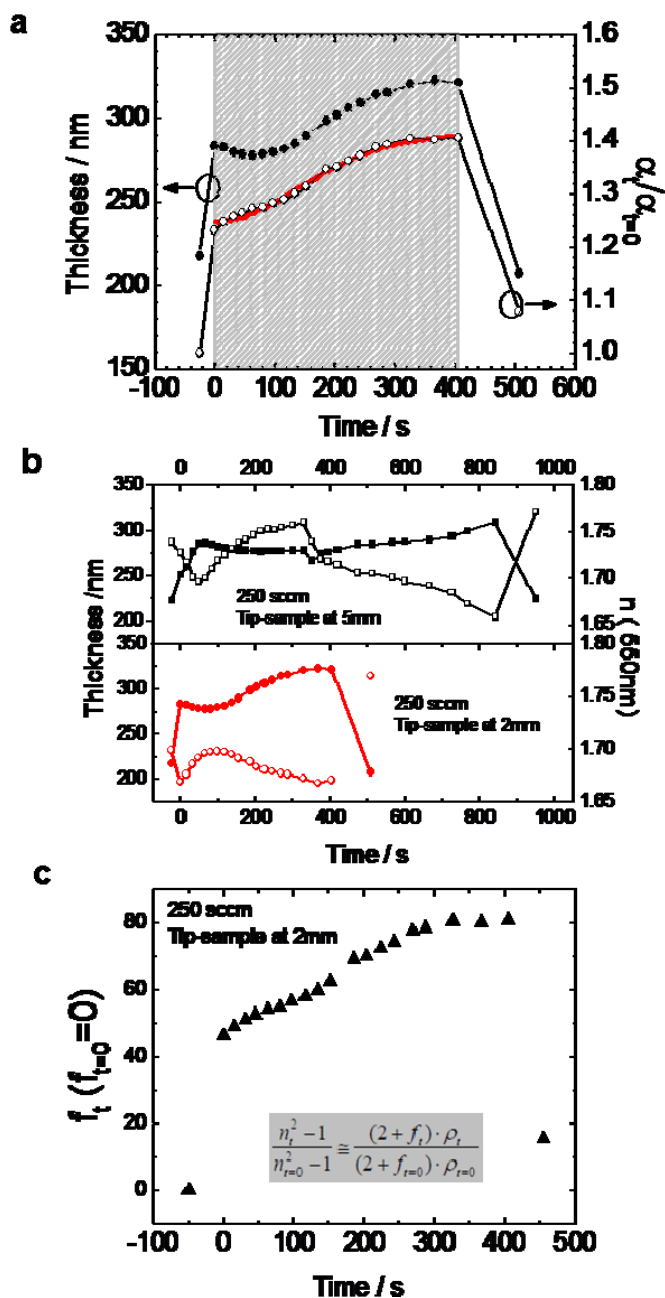


Fig. S2. (a) *In-situ* ellipsometric measurements recorded during vapour printing of the sample displayed in Fig. 1c permitted to follow the evolution of film thickness through a Cauchy analysis (solid circles) and of the polarisability deduced using Eq. 1 (open circles), which could be fitted using Eq. 2, *i.e.*, a generalised Avrami expression (red line); the duration of vapour exposure is indicated by a grey box and the position of the dried film rescaled to longer times for clarity. (b) Evolution of the thickness and refractive index as a film is exposed to the vapour printer. Top panel, for a 5 mm tip-sample distance, bottom panel, 2 mm tip-sample distance. (c) Evolution of the Fraser orientation fraction deduced using the equation in the inset (from Ref. 41).

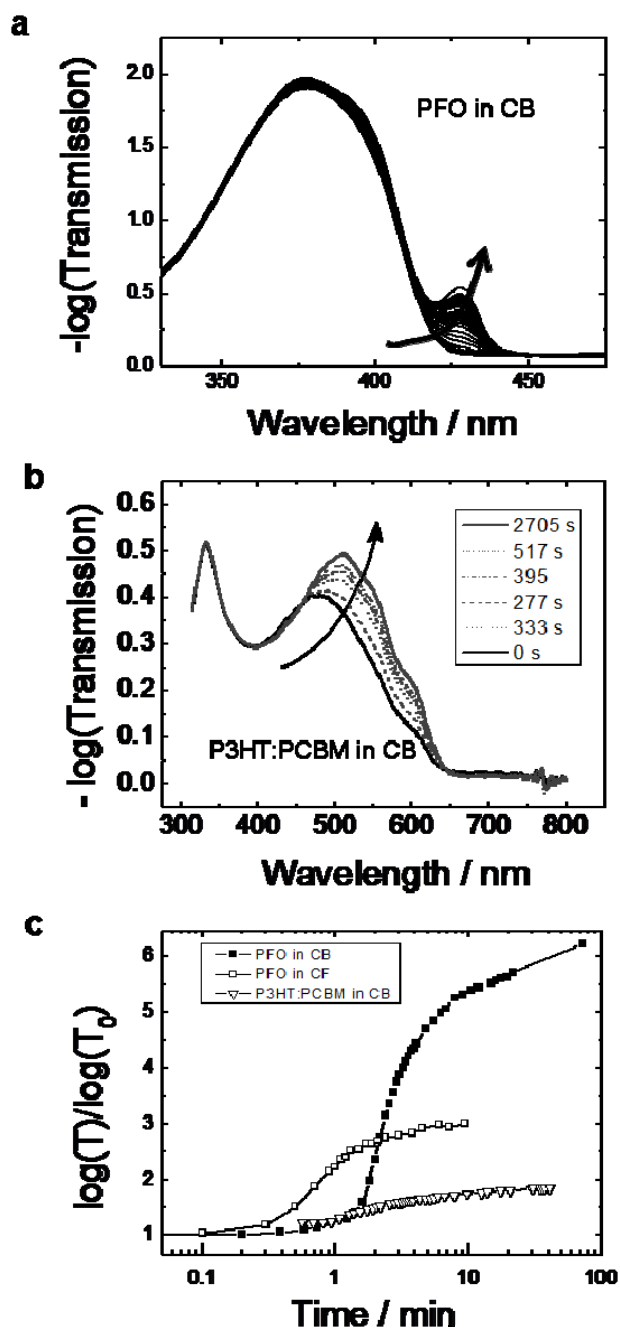


Fig. S3. Real time measurements of the change in absorption of PFO (a) and P3HT:PCBM (b) when vapour-annealed using chlorobenzene. The appearance of the beta-phase peak in PFO (at 430 nm) and the long wavelength shoulder in P3HT (at 615 nm) are summarised in (c) where the effect of changing chlorobenzene by chloroform is also shown. The uptake of solvent clearly varies depending on the specific material and solvent. For PFO, it changes from 1 to 5 minutes when going from chloroform to chlorobenzene. For P3HT:PCBM, ca. two minutes are required when exposed to chlorobenzene.

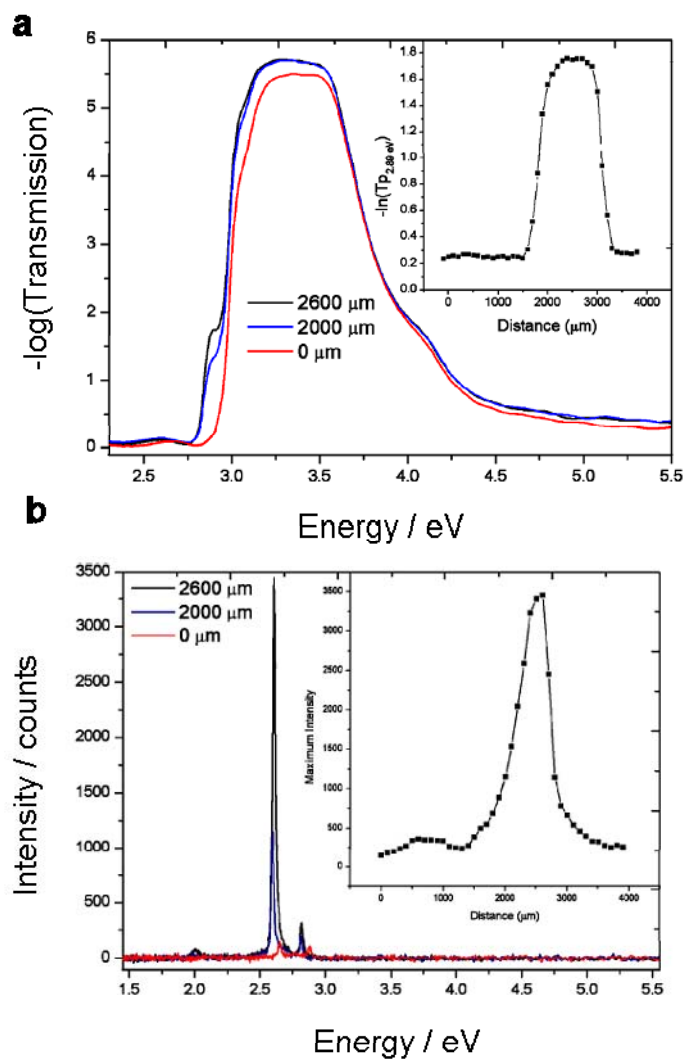


Fig. S4. (a) Absorption spectra and profile (inset) for a PFO waveguide fabricated using vapour printing. The different absorption curves correspond to different positions in the profile. (b) Waveguided spectra and profile (inset) measured at the edge of the sample.

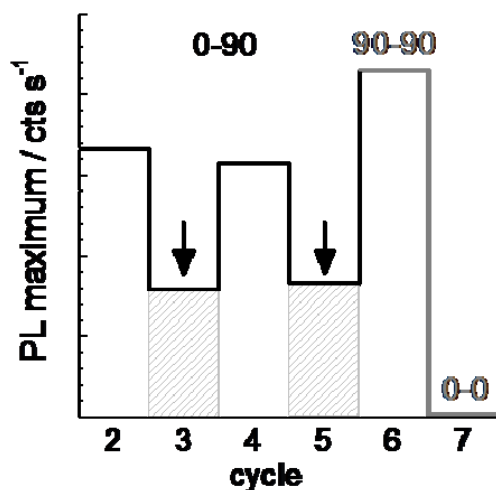


Fig. S5. Variation of the waveguided PL (440 nm) at the edge of the interferometer when pressure is applied (indicated by arrows and grey shaded area). The last two cycles show that the waveguided PL is highly polarised.

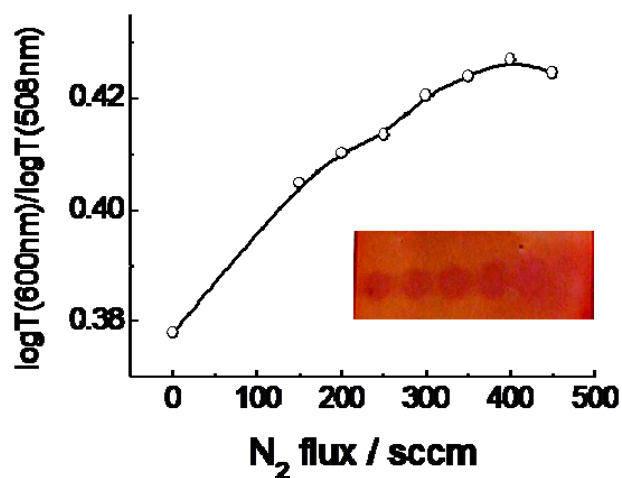


Fig. S6. The relative heights of the long wavelength shoulder and the maximum of absorption for a P3HT:PCBM film exposed to different N₂ fluxes for 10 seconds using a nozzle with inner diameter ca. 250 μm (see inset picture).

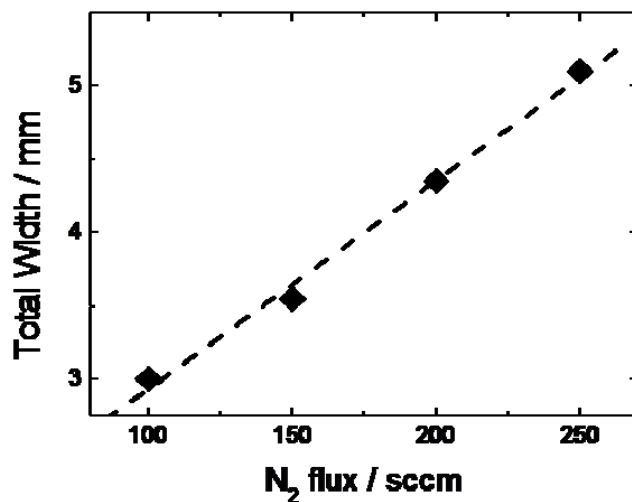


Fig. S7. Total width of features, w , obtained using vapour printing (nozzle inner diameter ca 250 μm) as a function of the nitrogen flux.