

### Supplementary information

Fig. S1: Absorption spectra of pristine PFO polymer films prepared by dip-coating (solid line) or casting (dashed line), and a PFO/8 wt% PEO/silica film (dotted line). The spectra of the PFO/8 wt% PEO/silica film shows strong 0-0 vibronic transitions of the extended-conjugation  $\beta$ -phase at 406 and 436 nm, respectively, and a broad featureless peak centred at  $\sim$ 380 nm assigned to the 0-1 transition of the glassy  $\alpha$ -phase. This spectrum generally resembles that of pristine PFO film prepared by casting and containing aggregates (dashed line), and is dissimilar to that of the disordered PFO film prepared by dip-coating (solid line). The presence of PFO aggregates in the PFO/8 wt% PEO/silica film is also evident from the noticeable red-shift of the absorption features,  $>10$  nm, compared to dip-coated PFO films (solid line) and PFO-incorporated Brij-56-directed silica films (Fig. 5 in paper), associated with the increased conjugation length of PFO chains in the aggregated domain.

