Electronic Supplementary Information for

Polaron delocalisation softens electronic and vibrational transitions in conjugated polymers

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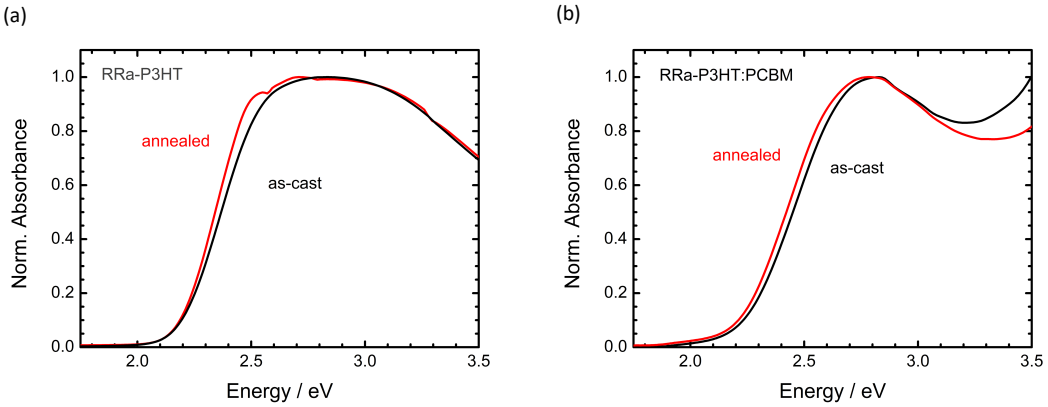

Figure S1: Absorption spectra of neat RRa-P3HT (a) and its blend with PCBM (b). The amorphous polymer's order does not profit from post-deposition thermal annealing.

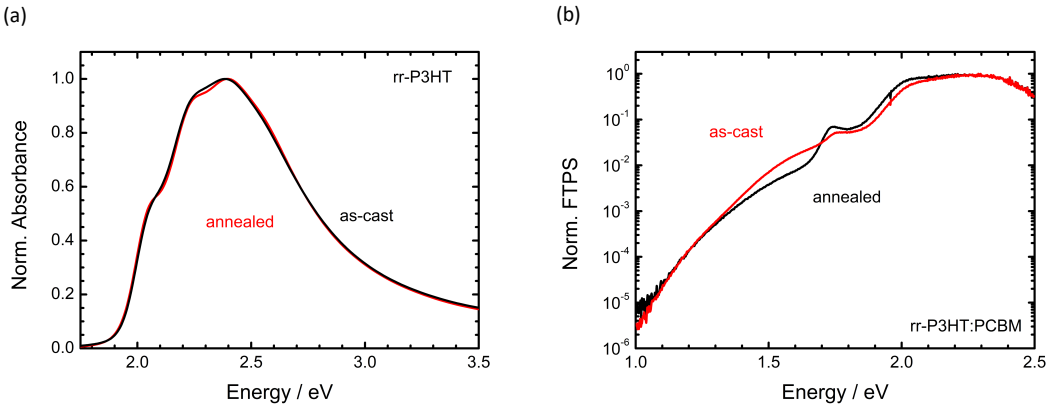

Figure S2: The Absorption spectra of neat rr-P3HT do not exhibit changes upon thermal annealing (a). Despite casting from CF, the polymer forms a highly ordered film already without annealing. The photocurrent spectrum of the rr-P3HT:PCBM blend exhibits distinct changes in the region between 1.3 and 2 eV (b), indicating significantly less disorder after annealing.

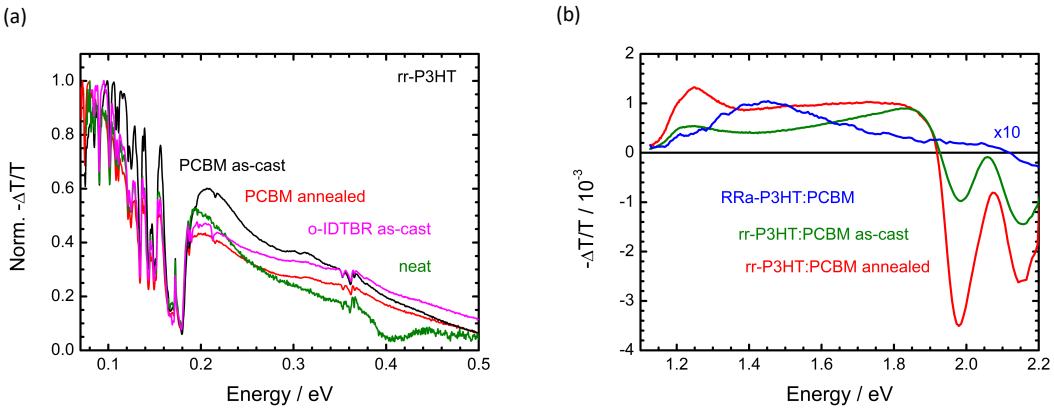

Figure S3: Photoinduced absorption spectra in the MIR spectral range of selected films containing rr-P3HT (a). The neat polymer, as well as the blend with the electron acceptor o-IDTBR offer a peak of the PIA band at low energy – comparable to the annealed P3HT:PCBM film. The PIA spectra in the NIR in (b) were obtained using the chopper-wheel set-up. Additional to the absorption bands, the ground state bleach is observable above 2.0 eV. Upon annealing, the low energy band around 1.2 eV for rr-P3HT shifts to the blue (revealing a shoulder at 1.23 eV attributed to the PCBM anion).

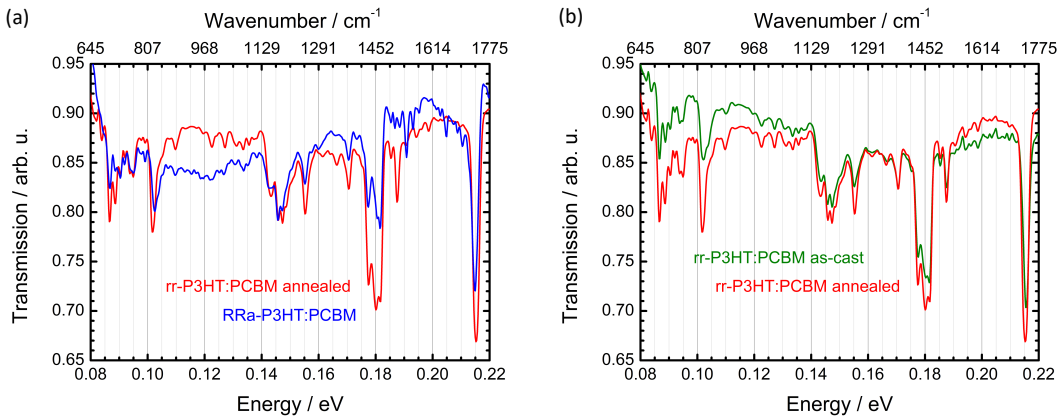

Figure S4: Comparison of direct transmission spectra of P3HT films including the RRa-variant (a) and rr-P3HT as-cast (b). The spectra are largely identical, but the peak around 102 meV follows the crystallinity trend established in the main text. Additionally, minor changes can be observed around 0.18 eV –mostly between the RRa- and rr-variant in (a).

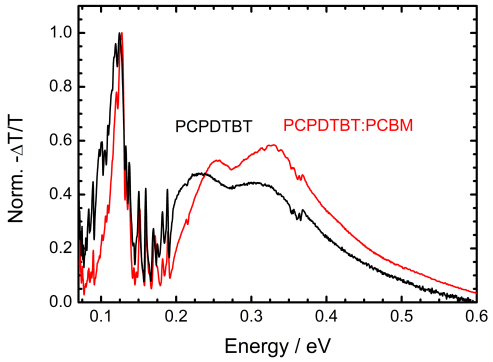

Figure S5: The normalised PIA spectrum of neat PCPDTBT and its blend with PCBM (no additive) illustrates the red-shift for larger polymer chain disorder analogous to the main text.