

## Supporting Information

# Disorder in P3HT Nanoparticles Probed by Optical Spectroscopy on P3HT-*b*-PEG Micelles

Patrick Beer<sup>1</sup>, Paul M. Reichstein<sup>2</sup>, Konstantin Schötz<sup>3</sup>, Dominic Raithe<sup>1</sup>, Mukundan Thelakkat<sup>2,4,5</sup>, Jürgen Köhler<sup>1,3,5</sup>, Fabian Panzer<sup>3</sup>, Richard Hildner<sup>1,6\*</sup>

<sup>1</sup> *Spectroscopy of Soft Matter, University of Bayreuth, 95440 Bayreuth, Germany*

<sup>2</sup> *Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany*

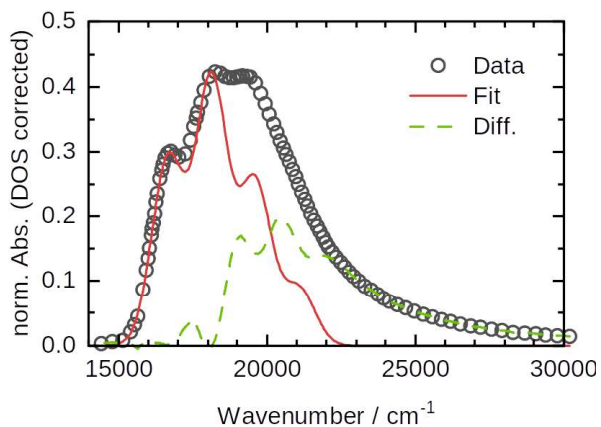
<sup>3</sup> *Soft Matter Optoelectronics, University of Bayreuth, 95440 Bayreuth, Germany*

<sup>4</sup> *Bavarian Polymer Institute, University of Bayreuth, 95440 Bayreuth, Germany*

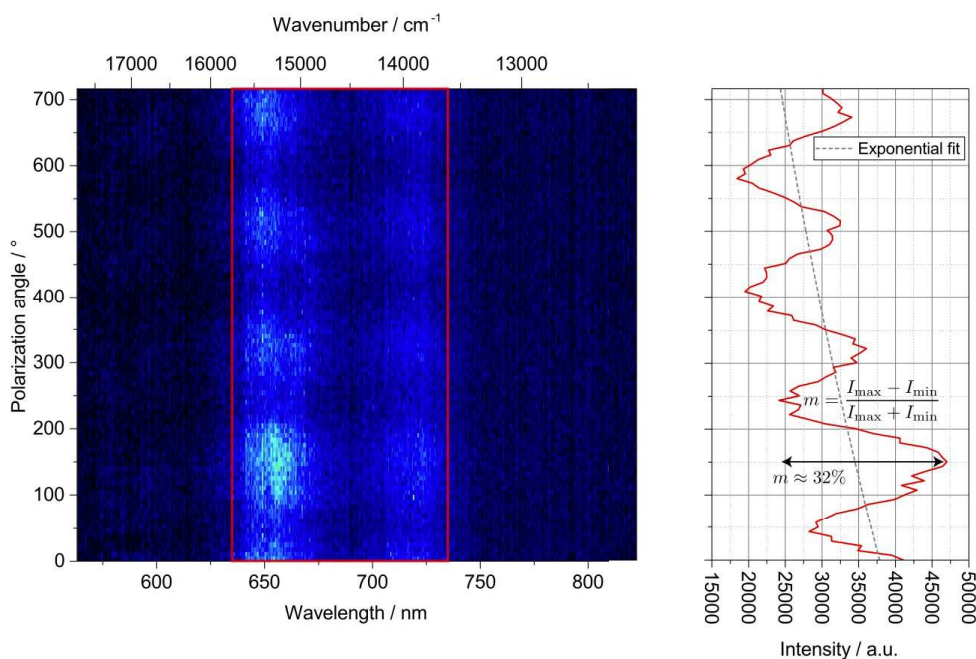
<sup>5</sup> *Bayreuther Institut für Makromolekülforschung (BIMF), University of Bayreuth, 95440 Bayreuth, Germany*

<sup>6</sup> *Zernike Institute for Advanced Materials, University of Groningen, 9747 AG Groningen, The Netherlands*

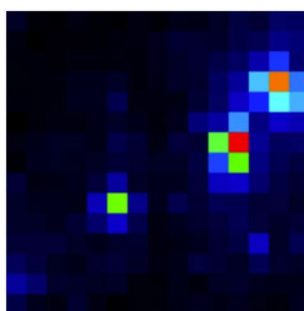
\* Corresponding author: r.m.hildner@rug.nl



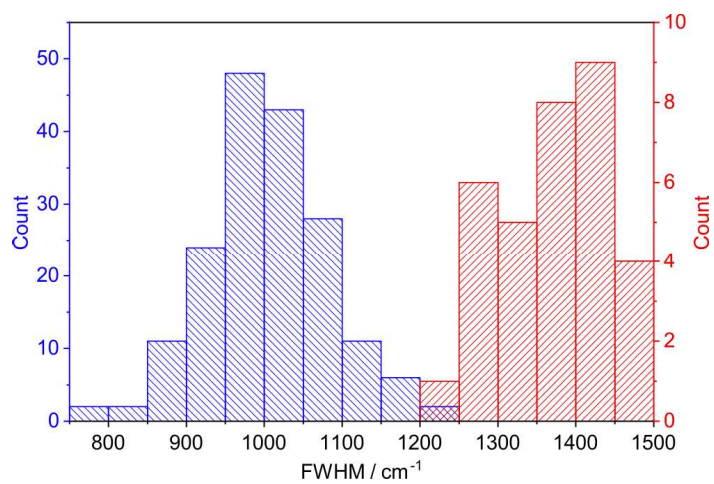
**Figure S1:** Fit of the modified Franck-Condon-progression (red solid, see Eq. 1 in the Materials and Methods sections of the main text) to the absorption spectrum of the P3HT-b-PEG micelles in aqueous solution (grey circles). The lowest-energy  $A_1$  transition is located at  $16660\text{ cm}^{-1}$ , the energy of the effective vibrational mode is  $1470\text{ cm}^{-1}$ , the line width is  $540\text{ cm}^{-1}$ , and the Huang-Rhys parameter was set to 1.05. The extracted free exciton bandwidth is  $710\text{ cm}^{-1}$ . The green dashed line is the residual between data and fit and reflects some contribution of amorphous P3HT to the total absorption of micelles.



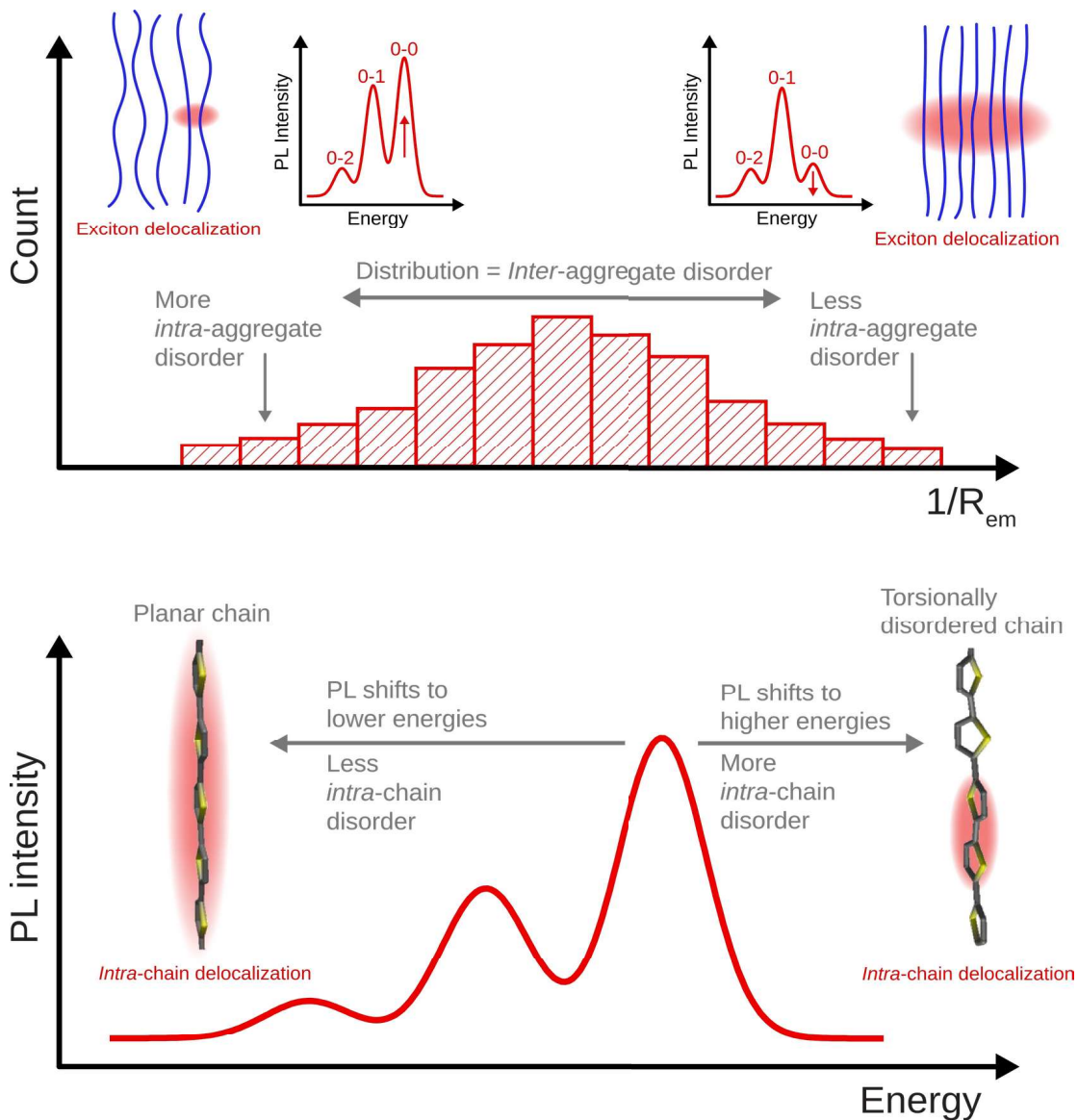
**Figure S2:** Left: Two-dimensional representation of a stack of sequentially recorded PL spectra with the (linear) excitation polarisation rotated by  $7.2^\circ$  after acquisition of each spectrum. Those data were taken from an isolated PL spot, as shown below in the scanning confocal PL image in Fig. S3 measured at low temperature on P3HT-*b*-PEG micelles cast from a 1:300 diluted aqueous solution. Right: PL intensity integrated between about 15750 and 13600  $\text{cm}^{-1}$  (red box, left) as function of the polarisation angle. This signal is not fully modulated, indicating a spatial distribution of absorbing transition dipole moments (projected on the focal plane). This distribution can have two origins: (i) An agglomerate of micelles is measured, in which each micelle's core has a perfectly crystalline P3HT core (i.e., all chains well aligned along one single direction), and the different micelles in the agglomerate are aligned in slightly different directions; (ii) A single micelle is measured, but the P3HT core is composed of several crystalline domains, each with a slightly different orientation. The scanning confocal PL image, Fig. S3, together with typical sizes from crystalline P3HT domains discussed in the main text indicate that we investigate single micelles [option (ii)].



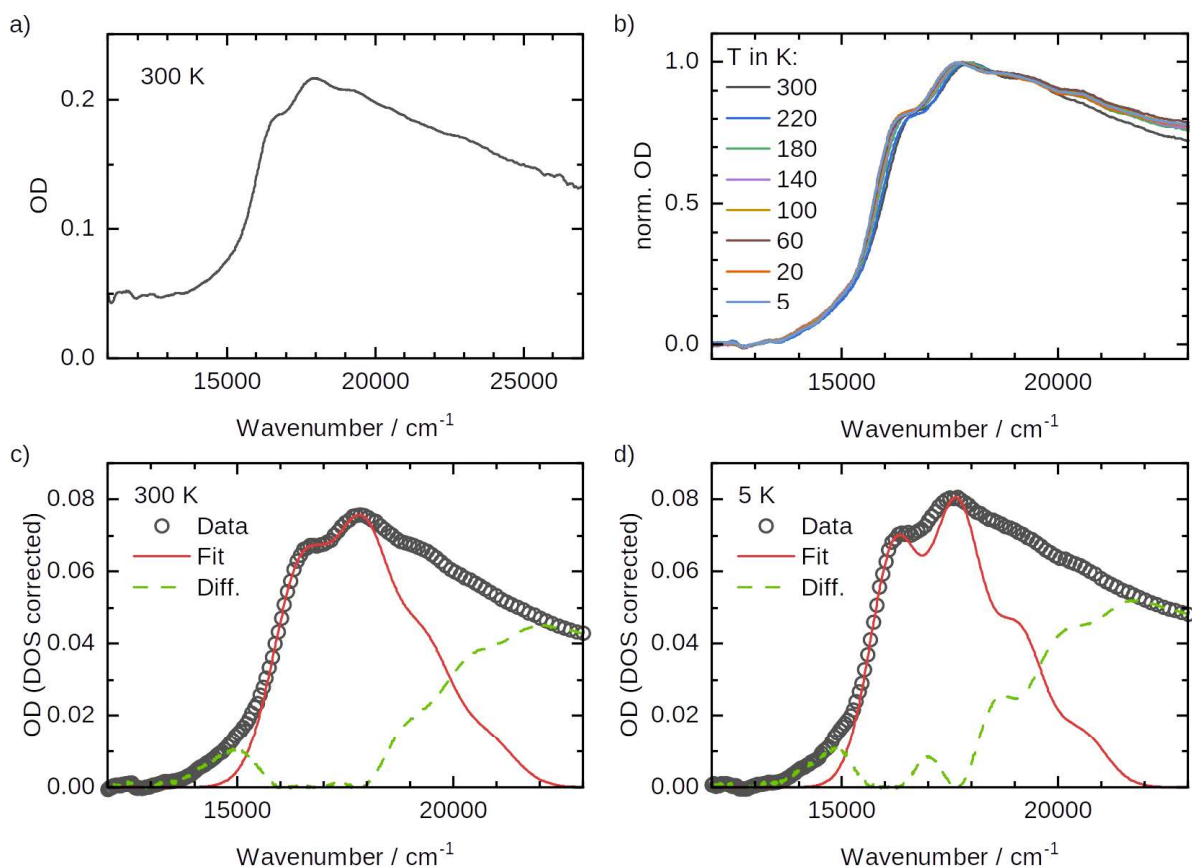
**Figure S3:** Scanning confocal PL image of P3HT-*b*-PEG micelles at 1.5 K, cast from aqueous solution. The PL intensity is colour-coded and the image size is  $15 \times 15 \mu\text{m}$ . Several diffraction-limited spots with relatively homogeneous PL intensities are found, indicating that each spot corresponds to a single micelle.



**Figure S4:** Distributions of the line widths of the 0-0 PL peaks of PL spectra of P3HT-*b*-PEG micelles at RT (red) and LT (blue), see also Fig. 2 of the main text.



**Figure S5:** Illustration of the effect of disorder on the shape of PL spectra of H-aggregates. Top: Influence of intra- and inter-aggregate on the inverse peak emission ratio  $1/R_{em}$  and the (inter-chain) exciton delocalisation of disordered H-aggregates. Bottom: Shifts of the PL spectrum of isolated, non-interacting chains as function of intra-chain torsional disorder. See main text for details.



**Figure S6:** a) As-measured absorption of the P3HT thin film at 300 K. b) Temperature-dependent offset-corrected and normalized absorption of the P3HT thin films from 300 K to 5 K. c,d) Fit of a modified Franck-Condon-Progression (see Eq. 1 in the Materials and Methods section of the main text) to the absorption at 300 K (c) and 5 K (d). For both fits, the Huang-Rhys parameter was set to 1.05 (equal to the fitting in Fig. S1), the energy of the effective vibrational mode was 1435 cm<sup>-1</sup>. The position of the lowest-energy A<sub>1</sub> peak is 16460 cm<sup>-1</sup> at 300 K, and 16230 cm<sup>-1</sup> at 5 K. The line widths are 645 cm<sup>-1</sup> and 572 cm<sup>-1</sup>, correspondingly. The exciton bandwidth is 200 cm<sup>-1</sup> for both temperatures. The deviations between fit and data around 15000 cm<sup>-1</sup> are probably caused by residual scattering.

The temperature-dependent reduction in line width in the film results from a smaller homogeneous line width towards low temperature as well as from a smaller inhomogeneous line width due to lesser degree of disorder at 5 K (partial chain planarisation). Comparing the line width of the A<sub>1</sub> peak for the film and the micelles at RT (Fig. S1), we find that the micelles feature a slightly narrower line width, indicating overall a smaller degree of inter-aggregate disorder for the P3HT-aggregates in micelles.