Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information to

A spectroscopic assessment of static and dynamic disorder in a film of a polythiophene with a planarized backbone

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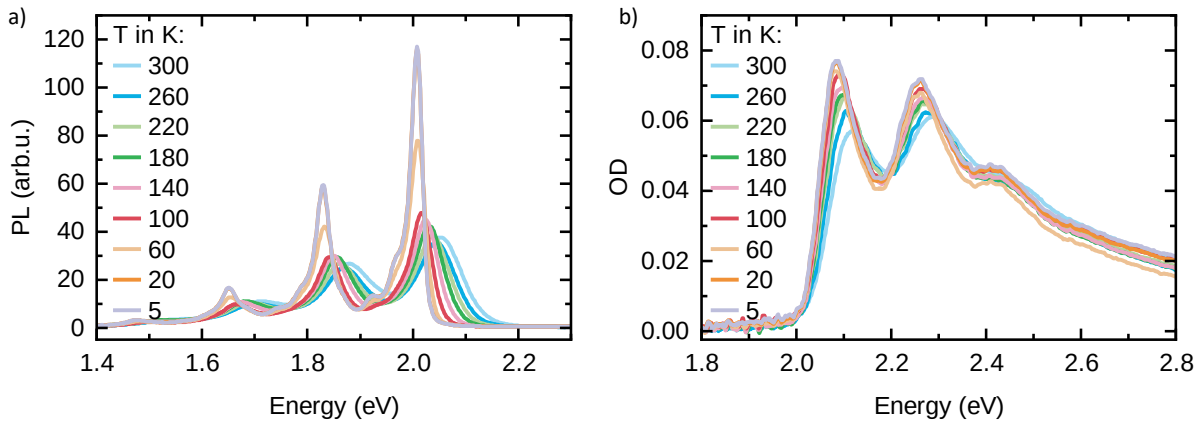

Figure S1: Temperature-dependent measurements of (a) PL and (b) Optical Density of the PDOPT thin film.

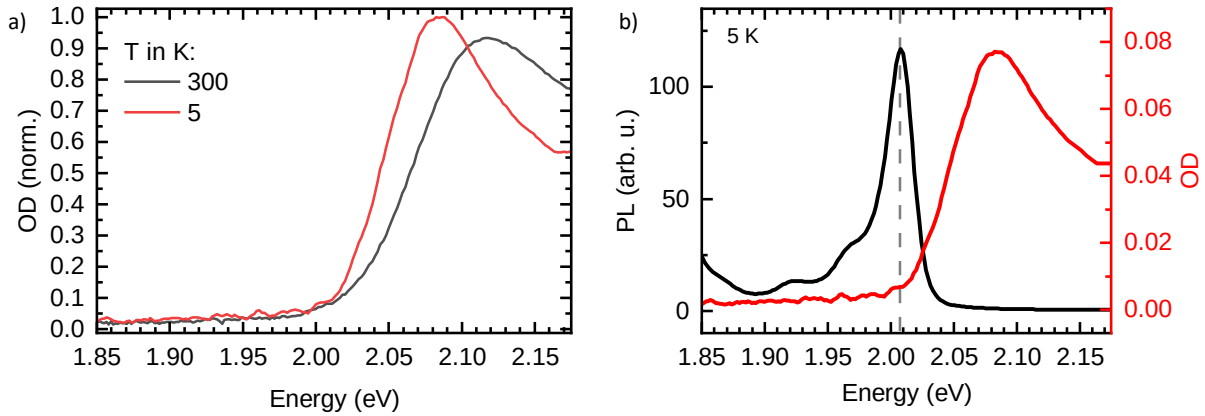

Figure S2: (a) Magnified range of the absorption onset at 300 K and 5 K. (b) PL and absorption at 5 K plotted on the same energy axis. The dashed line indicates the energetic position of the 0-0 PL peak extracted from the FC-analysis.

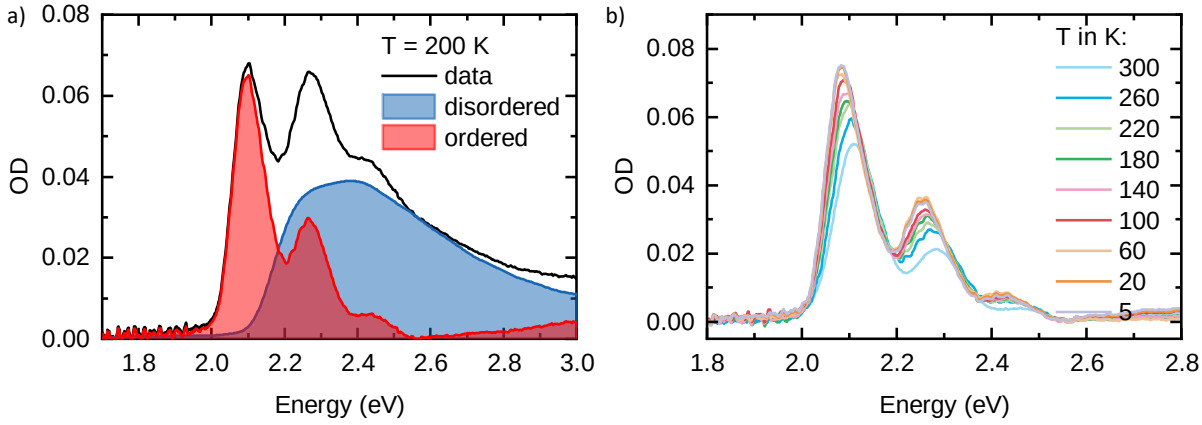

Figure S3: (a) example of the spectral decomposition of the absorption at 200 K (black line) into absorption from non-aggregated chains (blue area) and from aggregated chains (red area). The spectrum of the non-aggregated chains is obtained from temperature-dependent absorption measurements of PDOPT in a THF solution.(b) extracted absorption spectra of the aggregated chains.

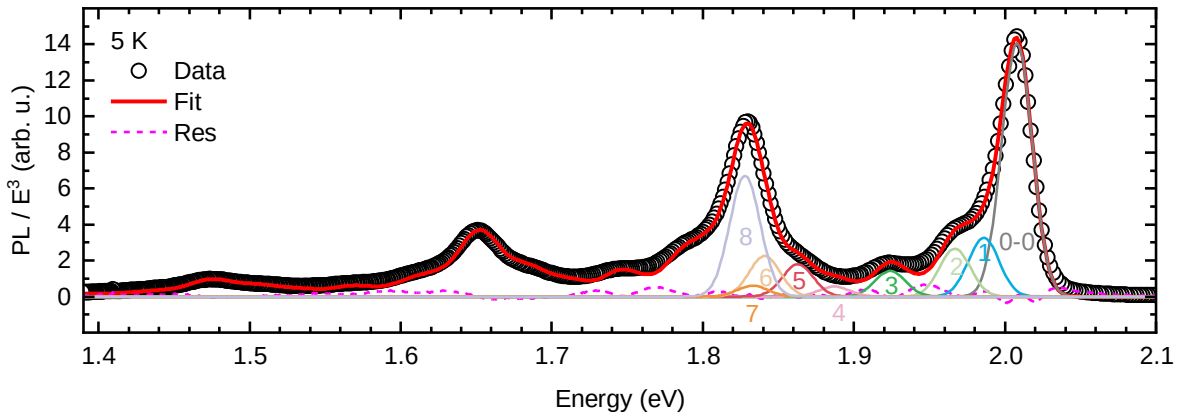

Figure S4: Franck-Condon-fit of the PL spectrum at 5 K on an extended spectral range.

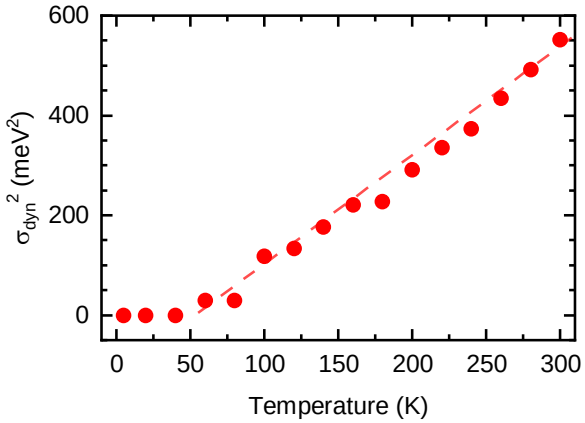

Figure S5: Contribution of the dynamic disorder (squared) to the line width of the absorption spectra as a function of temperature.

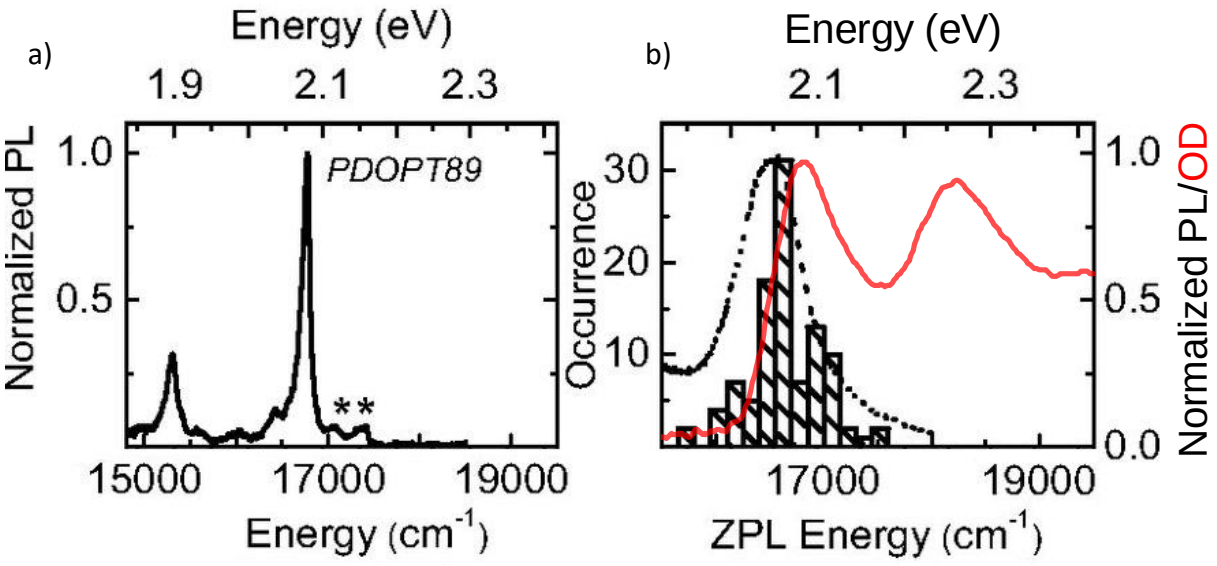

Figure S6: a) Single-chain spectrum of PDOPT from the same batch as the material used in this study, embedded in n-hexadecane. Asterisks denote additional weak zero phonon lines from the same single PDOPT chain. b) Distribution of spectral positions of the zero phonon lines. Dashed lines are low-temperature ensemble PL spectra of the corresponding matrix-isolated PDOPT sample (in n-hexadecane). Adapted with permission from D. Raithel, L. Simine, S. Pickel, K. Schötz, et al., *P Natl Acad Sci USA* **2018,** *115*, 2699, Copyright 2018 National Academy of Sciences [1]

Table S1: Full parameters of the Franck-Condon-Analysis of the PL spectra. (Corresponding vibrational energies are S1: 22 meV, S2: 41 meV, S3: 84 meV, S4: 121 meV, S5: 145 meV, S6: 167 meV, S7: 175 meV, S8: 180 meV.

T (K)	$E_{0\text{-}0}$ (eV)	S1	S2	S3	S4	S5	S6	S7	S8	σ (meV)	α
300	2.05590	0.129	0.083	0.195	0.069	0.073	0.179	0.073	0.629	37.46	1.103
280	2.05156	0.129	0.083	0.195	0.069	0.073	0.179	0.073	0.629	35.92	1.103
260	2.04738	0.129	0.101	0.195	0.069	0.073	0.179	0.073	0.629	34.03	1.092
240	2.04344	0.129	0.101	0.195	0.069	0.073	0.179	0.073	0.629	32.38	1.092
220	2.03964	0.129	0.122	0.195	0.069	0.090	0.179	0.073	0.610	30.47	1.075
200	2.03640	0.129	0.137	0.184	0.069	0.090	0.179	0.073	0.610	28.87	1.075
180	2.03444	0.129	0.180	0.178	0.069	0.126	0.179	0.073	0.589	26.79	1.075
160	2.03100	0.163	0.238	0.159	0.069	0.148	0.179	0.073	0.574	23.44	1.075
140	2.02786	0.173	0.238	0.159	0.069	0.148	0.179	0.073	0.557	22.61	1.075
120	2.02332	0.201	0.238	0.173	0.069	0.158	0.179	0.073	0.534	20.59	1.089
100	2.01938	0.250	0.282	0.157	0.069	0.158	0.179	0.073	0.534	17.42	1.120
80	2.01460	0.268	0.260	0.147	0.062	0.167	0.179	0.048	0.534	14.87	1.1208
60	2.01072	0.268	0.242	0.131	0.058	0.147	0.179	0.048	0.534	12.60	1.1208
40	2.00866	0.268	0.218	0.113	0.044	0.143	0.179	0.048	0.534	10.82	1.1208
20	2.00794	0.260	0.212	0.113	0.044	0.143	0.179	0.048	0.534	10.15	1.1208
5	2.00794	0.260	0.212	0.113	0.044	0.143	0.179	0.048	0.534	10.15	1.1208

Table S2: Full parameters of the Franck-Condon-Analysis of the absorption spectra. (Corresponding vibrational energies are S1: 22 meV, S2: 41 meV, S3: 84 meV, S6: 167 meV, S7: 175 meV, S8: 180 meV. Satisfying fits were obtained without modes 4 and 5, i.e., S4 and S5 were set to zero.)

T (K)	$E_{0\text{-}0}$ (eV)	S1	S2	S3	S6	S7	S8	σ (meV)
300	2.09826	0.231	0.22	0.158	0.131	0.016	0.184	37.08
280	2.09486	0.231	0.22	0.163	0.161	0.016	0.184	36.25
260	2.09186	0.231	0.22	0.180	0.184	0.016	0.184	35.45
240	2.08946	0.231	0.22	0.180	0.184	0.016	0.184	34.58
220	2.08686	0.231	0.22	0.180	0.184	0.016	0.184	34.03
200	2.08506	0.231	0.22	0.180	0.184	0.016	0.184	33.37
180	2.08346	0.231	0.22	0.180	0.184	0.016	0.184	32.41
160	2.08346	0.231	0.22	0.180	0.184	0.016	0.184	32.30
140	2.08166	0.231	0.22	0.180	0.184	0.016	0.184	31.62
120	2.08126	0.231	0.22	0.180	0.184	0.016	0.174	30.93
100	2.08046	0.231	0.22	0.188	0.184	0.016	0.182	30.67
80	2.07786	0.231	0.22	0.208	0.184	0.016	0.182	29.19
60	2.07526	0.231	0.22	0.208	0.184	0.016	0.214	29.19
40	2.07566	0.231	0.22	0.208	0.176	0.016	0.206	28.68
20	2.07486	0.231	0.22	0.208	0.176	0.016	0.206	28.68
5	2.07486	0.231	0.22	0.208	0.176	0.016	0.188	28.68