Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting information

How to interpret absorption and fluorescence spectra of charge transfer states in an organic solar cell

Frank-Julian Kahle[1], Alexander Rudnick[1], Heinz Bässler[2], Anna Köhler[1,2]*

[1] Soft Matter Optoelectronics, University of Bayreuth, 95440 Bayreuth, Germany

[2] Bayreuth Institute of Macromolecular Science (BIMF), University of Bayreuth, 95440 Bayreuth, Germany

*anna.koehler@uni-bayreuth.de

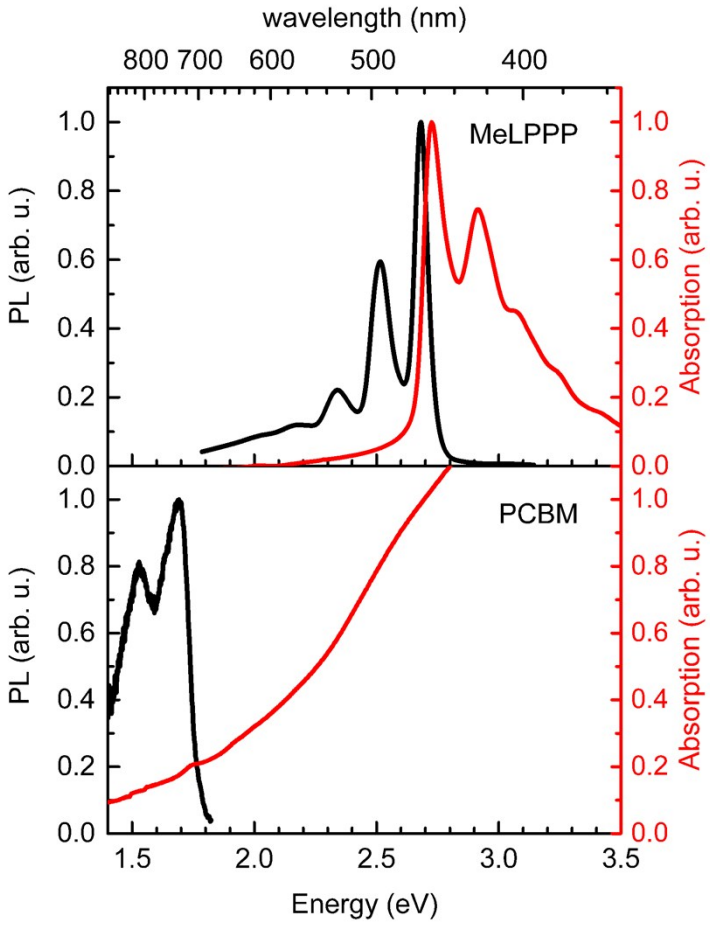

Figure S1: Absorption (red) and emission (black) spectra of pristine MeLPPP (top) and pristine PCBM (bottom) measured in a neat film. For PL spectra, the films were excited at 355 nm and 375 nm, respectively.

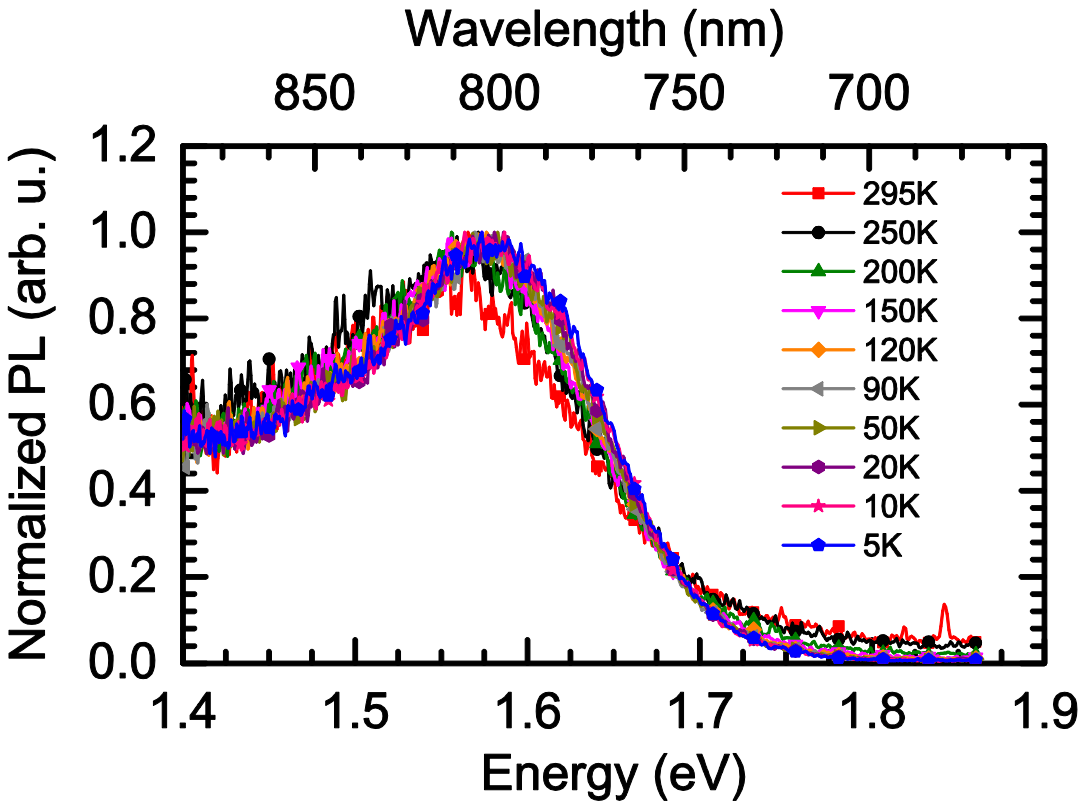

Figure S2: Normalized CT emission spectra from Figure 1c

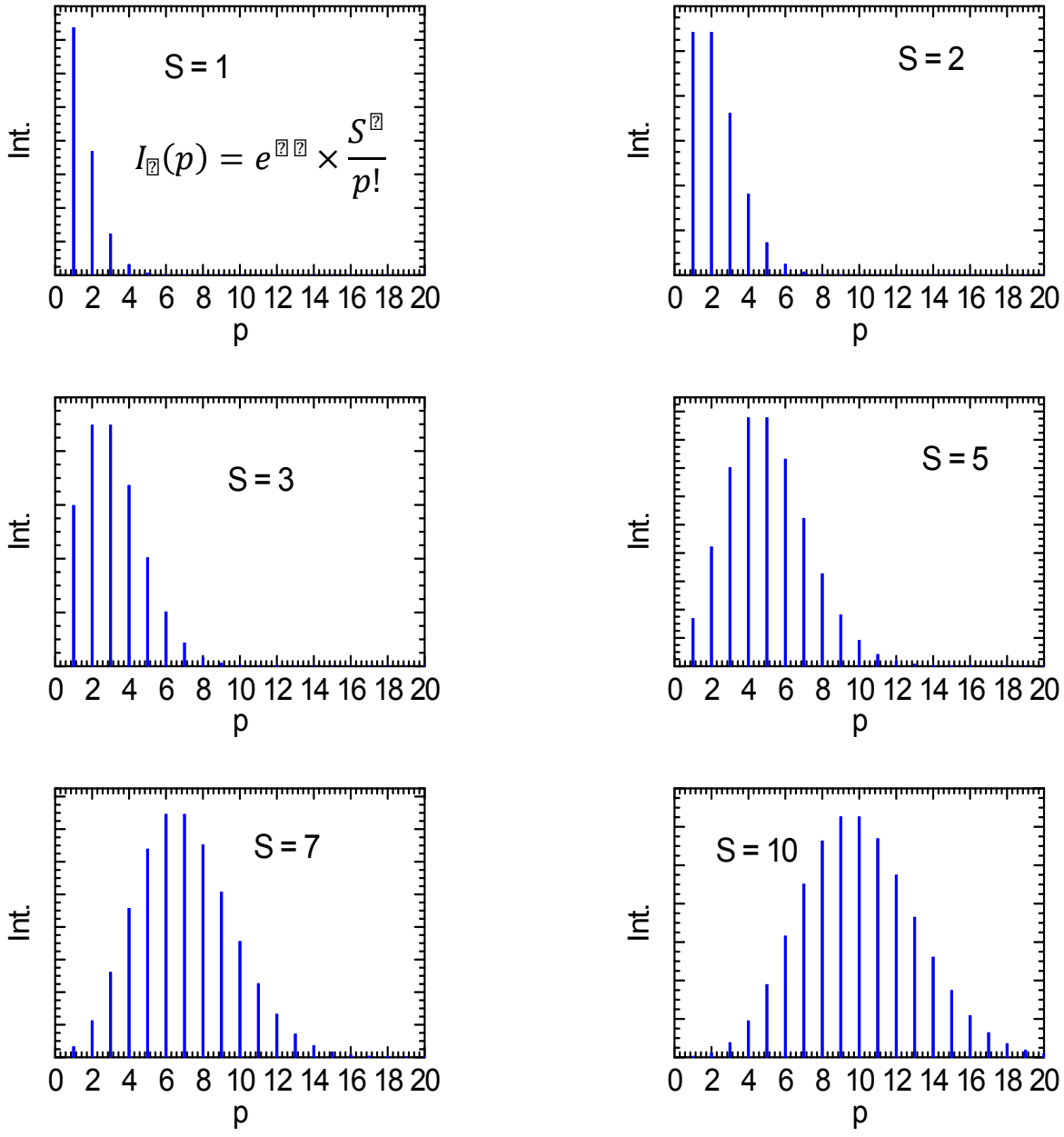

Figure S3: Schematic illustration of how a Poisson distribution becomes a Gaussian one for large values of S (underlying formula is shown in the upper left plot)

Mathematically, the procedure used in the manuscript to obtain the fit in Figure 5b is equivalent to performing one multi-mode fit, taking both modes into account simultaneously, according to[1]

$$rPL(E) = \frac{PL(E)}{E} \propto \sum_{m_i} \prod_i \frac{S^{m_i}}{m_i!} e^{-S_i} \cdot \Gamma \cdot \delta\left(E - \left(E_0 - \sum_i m_i \hbar\omega_i\right)\right) \quad (7)$$

with the number of modes, *i*, ranging from 0 to 1 in our case. We used $\hbar\omega_0 = 10\ meV$ and $\hbar\omega_1 = 165\ meV$. The number of overtones, m_i, was running from 0 to 20 for m_0, and from 0 to 1 for m_1. In equation (7) we again considered the electronic transition moment M to be dependent on energy, i.e. $M = \frac{V\Delta\mu}{h\nu} = \frac{V\Delta\mu}{E}$. The resulting fit, according to equation (7) is shown in Figure S4. Just like the fit presented in Figure 5a, it gives an excellent match to the experimental data. Also, the values for S_i and $\hbar\omega_i$ are in line with the values obtained from the method presented in the paper, therefore validating that both approaches are equivalent.

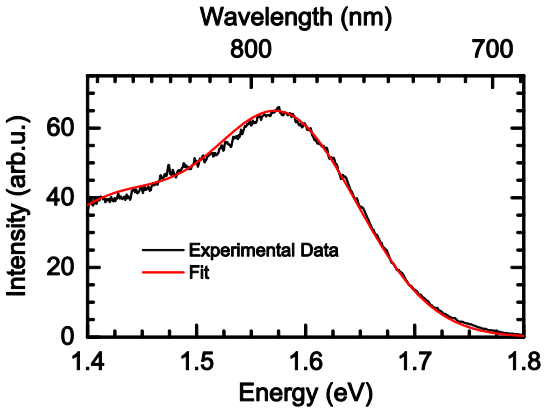

Figure S4: Franck-Condon fit with two vibronic modes according to eq. (7) with $\hbar\omega_0 = 10\ meV$ and $\hbar\omega_1 = 165\ meV$ of the 90K reduced PL recorded after a delay of 90ns with respect to the excitation pulse

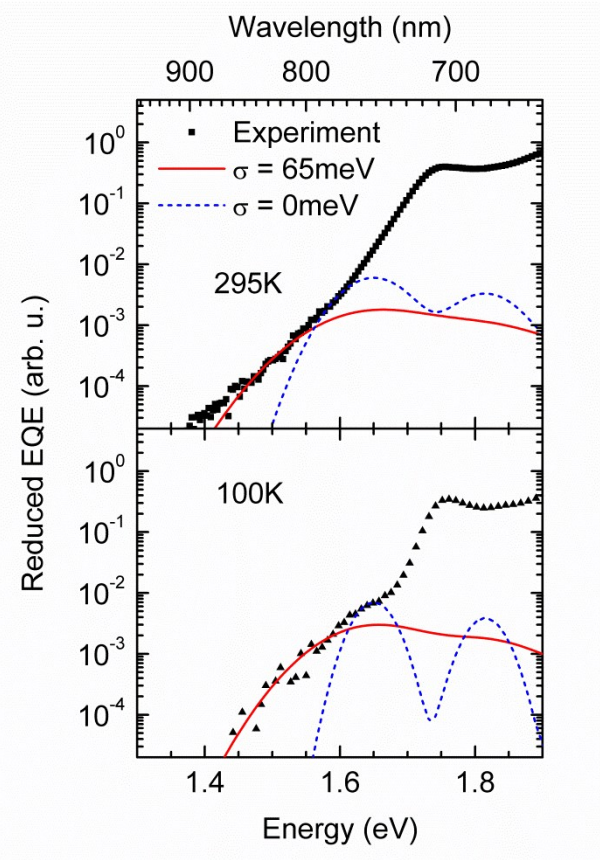

Figure S5: Reduced EQE (symbols) of a MeLPPP:PCBM blend at room temperature and at 100 K, along with MLJ fits with (solid line) and without (dashed line) disorder. The fit parameters are listed in Table 3 of the manuscript.

References

1. P. K. H. Ho, J. S. Kim, N. Tessler and R. H. Friend, *J Chem Phys*, 2001, **115**, 2709-2720.