I. SUPPORTING INFORMATION

A. Electronic structure calculations

The classification of excited states is the outcome of considerable amount of electronic structure computations on a single PTCDI molecule. DFT and TDDFT calculations were performed in utilizing the Gaussian 09 (Rev. A) program [3], the B3LYP functional [4] and a 6-311G(d,p) basis-set. The optimized ground-state geometry of PTCDI was verified using frequency analysis. Transition partial charges were calculated using TDDFT followed by a natural transition orbital (NTO) analysis [5] .

The effect of electrostatic couplings to the energy shifts (i) was calculated as interaction of partial charge distributions (see e.g. [1, 2] and is included in the diagonal elements $\mathcal{H}_{mm}$ of the standard Frenkel exciton Hamiltonian.

B. Molecular dynamics simulations

MD simulations have been carried in using NAMD program package [6], the AMBER force field [7] and the GAFF parameter sets [8]. A set of 216 PTCDI molecules was considered forming a cubic crystallite of 4.5 nm edge length and with two molecules in the unit cell [9]. Moreover, periodic boundary conditions have been established and the electrostatic interactions were computed using the particle mesh Ewald method [10]. The temperature was increased to 300 K, and 1 ns simulations were carried out. Since no spectral changes could be observed after 0.5 ns of MD simulation, the obtained MD data was considered to be sufficient.

C. Inductive polarisation shifts

In order to include inductive polarisation (ii), many techniques used in quantum chemistry follow an approach, in which only a single molecule is treated quantum mechanically and coupled to the environment, which itself is treated classically (for a recent overview see [11]).

However, since the respective energy shift due to electrostatic coupling was found to be small (<5 meV), in our calculation we neglect the contribution of inductive polarization shifts, which is supposed to be in the same order of magnitude as electrostatic couplings (i).

D. Excitonic coupling

Here, the $\mathcal{J}_{mn}$ were calculated using the molecular coordinates and transition partial charges [1]. Screening can be treated with the so-called *Poisson-transition-charges-from-electrostatic-potential*-method [12] or with methods based on the *polarizable continuum model* and beyond [13]. Recently, some of us demonstrated that a $1/\epsilon$-screening approach, in which $\mathcal{J}_{mn}$ is replaced by $\mathcal{J}_{mn}/\epsilon$, is sufficient as long as only ensemble averages are calculated [2]. Hence, the same approach was used here, yielding maximal values of $\mathcal{J}_{mn}/\epsilon \approx 20$ meV for the MD derived geometry.

E. Modeling of small aggregates

We model a disordered phase by cutting small blocks consisting of 12 molecules out of the 4.5 nm cube. We consider two disordered phases, of which one phase does include π-stacked molecules, and the other does not. The green curve in Fig. 3 is calculated for crystallites which contain (six pairs of each two) π-stacked molecules, the blue curve in Fig. 3 is calculated for thin molecular clusters without π-stacking molecules. The latter model may be considered a model for an amorphous film. The distance in x, y and z-direction between van-der-Waals-shells of neighbored molecules that are positioned in different crystallites/clusters is set to about 2 Å reducing the packing density of films composed of these small crystallites by about 50 %. Of course this kind of model system does not include isotropic orientations of the crystallites, which are likely present in the experiment. But, it includes larger distances between different crystallites due to the smaller packing density, which strongly affects the energy shift.

[1] Madjet, M. E.-A.; Abdurahman, A.; Renger, T. Intermolecular Coulomb Couplings from ab initio Electrostatic Potentials: Application to Optical Transitions of Strongly Coupled Pigments in Photosynthetic Antennae and Reaction Centers. *J. Phys. Chem. B* **2006,** *110,* 17268-17281.
[2] Megow, J.; Renger, T.; May, V. Mixed Quantum-Classical Description of Excitation Energy Transfer in Supramolecular Complexes: Screening of the Excitonic Coupling. *ChemPhysChem* **2014,** *15,* 478-485.
[3] Frisch, M. J. *et al.*, Gaussian 09 Revision A.1 **2009,**

Gaussian Inc. Wallingford CT 2009.
[4] Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994,** *98,* 11623-11627.
[5] Martin, R. L. Natural Transition Orbitals. *J. Chem. Phys.* **2003,** *118,* 4775-4777.
[6] Phillips, J. C.; Braun, R.; Wang, W.; Gumbart, J.; Tajkhorshid, E.; Villa, E.; Chipot, C.; Skeel, R. D.; Kale, L.; Schulten, K. Scalable Molecular Dynamics with

NAMD. *J. Comput. Chem.* **2005, 26,** 1781-1802.

[7] Case, D. A. *et al.*, AMBER **8** (2004), University of California, San Francisco, CA.

[8] Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and Testing of a General AMBER Force Field. *J. Comput. Chem.* **2004, 25,** 1157-1174.

[9] Klebe, G.; Graser, F.; Hädicke, E.; Berndt, J. Crystallochromy as a Solid-State Effect: Correlation of Molecular Conformation, Crystal Packing and Colour in Perylene-3,4:9,10-bis(Dicarboximide) Pigments. *Acta Crystallog. Sect. B* **1989,** *45,* 69-77.

[10] Darden, T.; York, D.; Pedersen, L. Particle Mesh Ewald-an N.Log(N) Method for Ewald Sums in Large Systems. *J. Chem. Phys.* **1993,** *98,* 10089-10092.

[11] Mennucci, B Modeling Environment Effects on Spectroscopies through QM/Classical Models. *Phys. Chem. Chem. Phys.* **2013,** *15,* 6583-6594.

[12] Adolphs, J.; Renger, T. How Proteins Trigger Excitation Energy Transfer in the FMO Complex of Green Sulfur Bacteria. *Biophys. J.* **2006,** *91,* 2778-2797.

[13] Curutchet, C.; Kongsted, J.; Muñoz-Losa, A.; Hossein-Nejad, H.; Scholes, G. D.; Mennucci, B. Photosynthetic Light-Harvesting is Tuned by the Heterogeneous Polarizable Environment of the Protein. *J. Am. Chem. Soc.* **2011,** *133,* 3078-3084.