Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information:

Comprehensive multi-scale calculations of the electronic properties of PTCDA aggregates: An approach towards a detailed understanding of the static and dynamic spectral characteristics of perylene-based thin films

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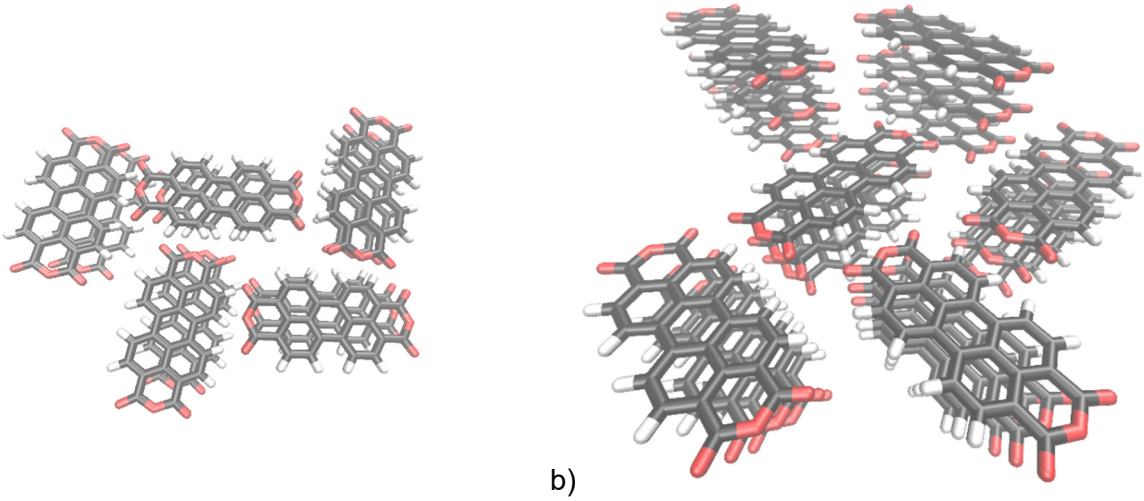
Influence of interactions between out-of-plane stack

Within the paper we analyzed effects resulting from the interaction of two out-of-plane stacks. They indicated that these interactions leave the overall picture unchanged. For this instance, we investigated an in-plane dimer consisting of the both monomers forming the unit cell and a tetramer which consists of two unit cells on top of each other. To check if this picture is changed for larger cluster we computed an in-plane cluster consisting of five monomers in a layer (Figure S1a), a decamer obtained by stacking two pentamers on top of each other, and finally a octadecamer which consisting of three hexamer-in-plane layers (Figure S1b) on top of each other. Due to the size of the clusters the computations had to be performed with the ZINDO/S method, i.e. the energies will be downshifted by about 0.1 eV with respect to the ωB97XD/6-31+G(d) results depicted in Table 3 of the paper. The vertical excitation energies (ΔE), the oscillator strengths (osc) and charge transfer character (qCT) are summarized in Table S1. As for the dimer of the unit cell the lowest states of the pentamer possess high oscillator strengths. This is expected because the monomers form kind of J-aggregates. ZINDO/S predict their excitation energies to 2.67 eV which lies 0.08 eV below the monomer excitation energy. The down shift agrees nicely with splitting of about 0.04 eV which ωB97XD/6-31+G(d) predicts for the splitting within the dimer forming the unit cell (Table 5). Going to the decamer consisting of two pentamers on top of each other the splitting increases considerably but as already mentioned for the tetramer consisting of two unit cells on top of each other the distribution of the intensities switches to the pattern expected for H-aggregates. The same is found if a third layer is taken into account. This supported that the interactions between two or even more stacks do not change the overall picture obtained for one stack.

	pentamer (one layer)			decamer: two pentamer layers			octadecamer three hexamer layers		
state	ΔE	osc.	qCT	ΔE	osc.	qCT	ΔE	osc.	qCT
S1	2.67	1.76	0.05	2.49	0.00	0.14	2.45	0.01	0.28
S2	2.67	1.18	0.05	2.51	0.02	0.15	2.46	0.00	0.24
S3	2.72	0.08	0.02	2.53	0.02	0.14	2.47	0.02	0.22
S4	2.74	0.25	0.03	2.54	0.00	0.16	2.48	0.01	0.31
S5	2.76	2.61	0.06	2.55	0.00	0.08	2.49	0.01	0.19
S6	3.31	0.00	0.47	2.70	0.13	0.33	2.58	0.01	0.13
S7	3.36	0.01	0.45	2.72	4.39	0.41	2.60	0.14	0.25
S8	3.40	0.01	0.50	2.76	0.48	0.50	2.63	0.02	0.20
S9	3.41	0.02	0.66	2.80	0.34	0.53	2.63	0.04	0.31
S10	3.43	0.01	0.56	2.82	2.30	0.51	2.63	0.15	0.12
S11	3.49	0.00	0.25	2.93	0.21	0.86	2.65	0.25	0.26
S12	3.49	0.06	0.26	3.94	0.38	0.86	2.66	0.03	0.18
S13	3.52	0.02	0.19	2.96	0.47	0.78	2.75	0.11	0.80
S14	3.53	0.00	0.10	2.97	0.53	0.79	2.75	1.00	0.57
S15	3.53	0.01	0.21	2.98	0.60	0.81	2.75	1.93	0.69
S16	3.53	0.03	0.22	3.18	0.17	0.92	2.81	0.26	0.72

S17	3.53	0.00	0.15	3.19	0.08	0.91	2.82	0.88	0.53
S18							2.83	2.95	0.58
S19							2.88	0.82	0.74
S20							2.89	1.78	0.63
S21							2.92	0.12	0.78
S22							2.92	0.12	1.00
S23							2.94	1.05	0.65
S24							2.94	0.02	0.92

Table S1: Singlet vertical excitation energies (ΔE) in [eV], the oscillator strengths (osc) and charge transfer character (qCT) of pentamer, decamer and octadecamer depicted in Figure S1. All values were obtained with ZINDO/S.



a) b)

Figure S1: (a) Pentamer in which the momoners are oriented as in a layer of the α-PTCDA crystal. (b) Octadecamer with three layer of the α-PTCDA crystal each containing six PTCDA units

Further out-of-plane stacks characterized by ZINDO/S

ZIndo(S)	hexamer			heptamer			octamer			nonamer		
state	exc. energy [eV]	osc.	qCT	exc. energy [eV]	osc.	qCT	exc. energy [eV]	osc.	qCT	exc. energy [eV]	osc.	qCT
S1	2.476	0.000	0.139	2.474	0.002	0.138	2.473	0.000	0.149	2.472	0.001	0.179
S2	2.509	0.011	0.114	2.498	0.000	0.115	2.491	0.004	0.136	2.486	0.000	0.191
S3	2.576	0.000	0.113	2.545	0.019	0.122	2.525	0.000	0.139	2.513	0.007	0.212
S4	2.682	0.130	0.152	2.620	0.000	0.162	2.580	0.029	0.209	2.554	0.000	0.256
S5	2.810	0.000	0.488	2.725	0.180	0.188	2.659	0.000	0.192	2.614	0.040	0.199
S6	2.848	0.252	0.930	2.826	0.000	0.766	2.759	0.236	0.240	2.693	0.000	0.271
S7	2.867	0.000	0.735	2.847	0.195	0.972	2.833	0.000	0.929	2.785	0.299	0.405
S8	2.930	1.832	0.692	2.874	0.000	0.624	2.847	0.144	0.959	2.836	0.000	0.917
S9	2.960	0.000	0.936	2.930	1.820	0.712	2.884	0.000	0.516	2.849	0.098	0.936
S10	2.967	1.479	0.644	2.948	0.000	0.909	2.930	1.603	0.798	2.893	0.000	0.465
S11	2.990	0.000	0.912	2.965	1.400	0.748	2.948	0.000	0.923	2.930	1.554	0.818
S12	3.042	0.103	0.916	2.983	0.540	0.899	2.959	1.629	0.799	2.946	0.000	0.955
S13	3.076	0.000	0.881	2.994	0.000	0.892	2.976	0.000	0.959	2.959	2.062	0.749
S14	3.093	0.853	0.733	3.034	0.000	0.917	2.986	0.945	0.822	2.974	0.000	0.949

S15	3.179	0.000	0.863	3.061	0.132	0.889	3.003	0.000	0.885	2.975	0.169	0.961
S16	3.181	0.222	0.839	3.085	0.000	0.890	3.028	0.001	0.920	2.992	0.798	0.823

Electron-hole plots for the trimer out-of-plane stack

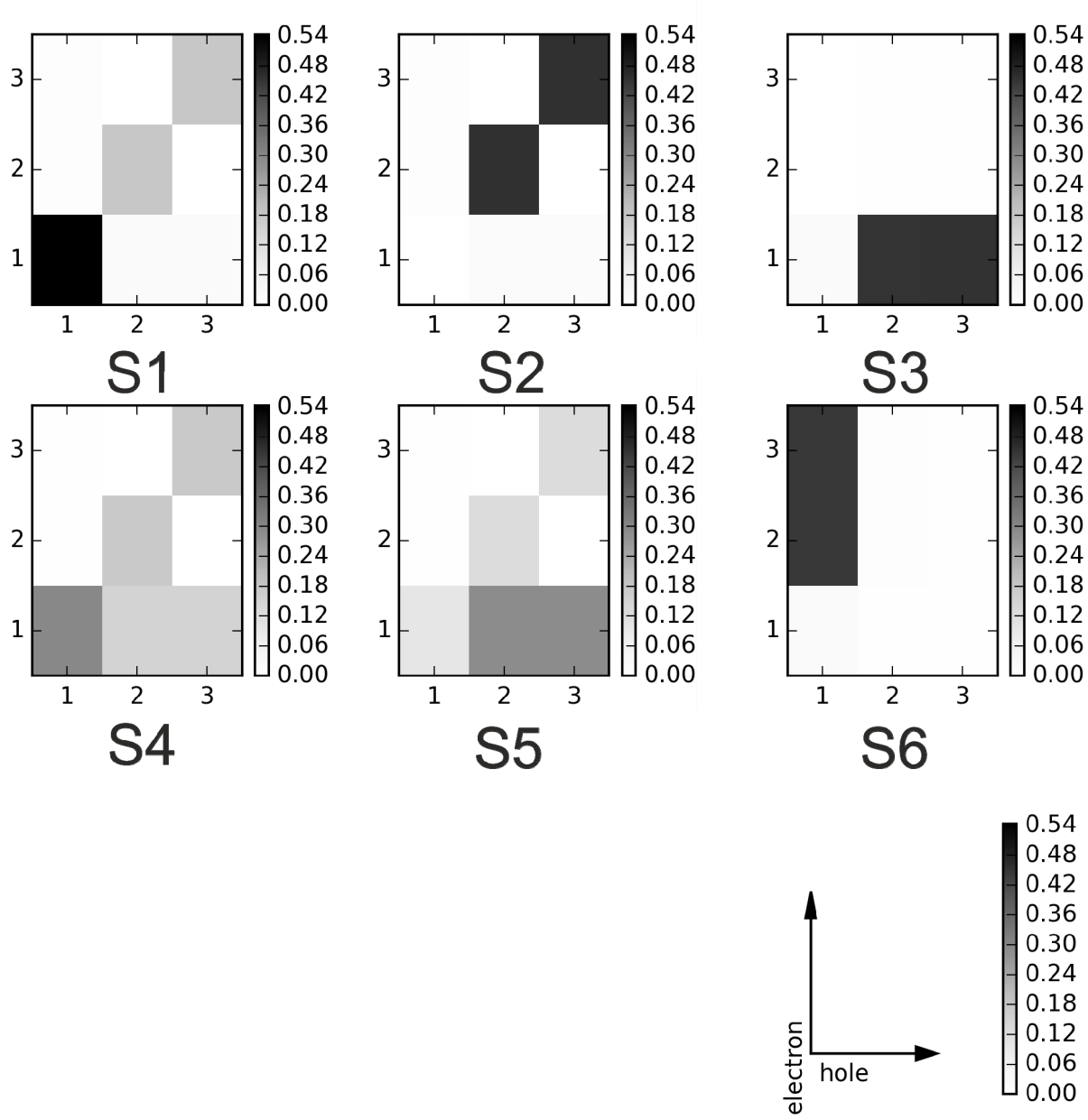


Figure S2: The electron-hole correlation plots of the Omega matrices for the first six singlet states are given. The results are obtained for the out-of-plane trimer stack calculated with TD-ωB97XD//6-31+G(d).

Influence of surface relaxation effects

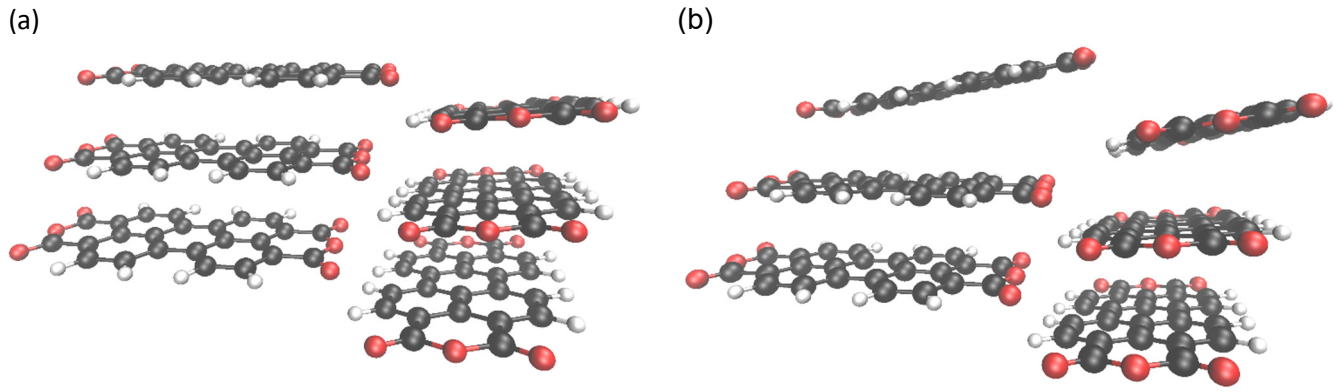


Figure S3: (a) Hexamer cut out of the surface of the QM/MM cluster in which the upper two layers were allowed to relax. (b) corresponding non-distorted hexamer

	non-distorted hexamer			distorted hexamer (surface relaxation)		
state	ΔE	osc.	qCT	ΔE	osc.	qCT
S1	2.48	0.01	0.16	2.31	0.41	0.08
S2	2.51	0.01	0.10	2.34	0.47	0.03
S3	2.63	0.02	0.13	2.54	0.02	0.09
S4	2.66	0.04	0.16	2.58	0.02	0.10
S5	2.79	1.07	0.85	2.79	2.80	0.25
S6	2.81	1.67	0.71	2.84	1.29	0.34
S7	2.84	0.86	0.51	2.90	0.00	1.00
S8	2.91	0.05	0.97	2.99	0.10	0.97
S9	2.96	0.06	0.97	3.01	0.19	0.91
S10	2.98	0.09	0.94	3.03	0.04	0.98
S11	2.98	0.69	0.72	3.05	0.02	0.96
S12	3.02	0.29	0.89	3.06	0.02	0.95
S13	3.03	0.04	0.98	3.08	0.06	0.93
S14	3.04	0.19	0.95	3.12	0.00	0.96
S15	3.10	0.04	0.91	3.15	0.20	0.88
S16	3.16	0.03	0.98	3.15	0.04	0.93
S17	3.17	0.01	0.88	3.17	0.11	0.90
S18	3.18	0.08	0.82	3.18	0.06	0.89
S19	3.22	0.17	0.92	3.23	0.01	0.91
S20	3.23	0.01	0.94	3.25	0.00	1.00

Table S2: Vertical excitation energies (ΔE) in [eV], oscillator strengths (osc), and charge transfer character (qCT) of a hexamer taken from the crystal in comparison to a hexamer that includes surface relaxation. All values were obtained with ZINDO/S.

The spectroscopic measurements of Engel et al.[46,47] and Alonso et al.[45] were performed for single crystals so that surface relaxation effects can be excluded as reason for the increased

intensities of the lower states. Nevertheless, we checked the influence of surface relaxation or defects on the electronic structure of α-PTCDA because CT states localized at the surface may be final point of the photo-induced relaxation processes. The computations started from the large cluster used within the QM/MM computations (Figure 2 of the paper). The lower part of this cluster was fixed while the upper two layers were allowed to relax to mimic surface relaxation effects. The relaxation was performed with the OPLS-force field. From the relaxed part of the cluster, we cut a stacked hexamer and computed the corresponding states using again ZINDO/S. The corresponding values are summarized in Table S2 (distorted cluster) together with the values obtained for the corresponding non-distorted hexamer cluster. The rmsd-value between both clusters is 3.5 Å. This distortion induces a redshift of the lowest states by about 0.15 eV. Even more important, in the distorted cluster the two lowest states gain considerable intensity. The question remains if the distortions pushes the CT states below the Frenkel states. Table S2 indicates that this does not happen. Also in the distorted cluster, the Frenkel states lie well below the CT states. Additionally, previous works already predicted that for larger longitudinal or transversal shift of both monomers with respect to each other a crossing of both Frenkel states happens but also indicated that the relative order of Frenkel and CT states is not changed.

	hexamer(rel)			**trimer(tilted & twisted)**		
state	ΔE	osc.	qCT	ΔE	osc.	qCT
S1	2.31	0.41	0.08	2.32	0.42	0.03
S2	2.34	0.47	0.03	2.58	0.02	0.07
S3	2.54	0.02	0.09	2.84	1.77	0.28
S4	2.58	0.02	0.10	2.96	0.03	0.99
	trimer(tilted)			**trimer(cryst)**		
state	ΔE	osc.	qCT	ΔE	osc.	qCT
S1	2.54	0.02	0.11	2.51	0.01	0.11
S2	2.69	0.00	0.06	2.66	0.00	0.06
S3	2.88	1.93	0.45	2.85	1.78	0.44
S4	3.02	0.62	0.78	2.97	0.00	0.97

Table S3: Vertical excitation energies (ΔE) in [eV], oscillator strengths (osc.), and charge transfer character (qCT) of the relaxed hexamer (Table 5) and model systems to reveal the reasons for the increased oscillator strengths of the lowest states. All values were obtained with ZINDO/S.

To investigate whether inter- or intramolecular distortions are responsible for the increased oscillator strengths we varied the distortion from the relaxed hexamer to a trimer cut out of the crystal structure. The results are given in Table S3. Table S3 only contains the values for the four lowest states because we are mainly interested in the two lowest states that gained intensity in the relaxed hexamer. Going from the relaxed hexamer to one of the two involved trimers the number of states is halved, i.e. only one of the two lowest states remains. Consequently, for the trimer only the lowest state possesses intensity which was the case for the two lowest states of the hexamer. However, the increased intensity of the lowest state remains in the trimer. Table S3 only includes the values obtained for the right trimer (Figure

S3) because the values for both trimers indicated in Figure S3 do not differ considerably. Within the relaxed trimer both lower monomers adopt the crystal geometry while the upper monomer is tilted upwards (Figure S3 inter-molecular distortion). Additionally, the anhydride moiety is slightly twisted out of the molecular plane (intra-molecular distortion). Removing the latter distortion by replacing the upper monomer by a flat one which is still tilted upwards the oscillator strength of the lowest band nearly vanishes indicating that the increased intensity found for the relaxed structure result from the intramolecular distortion rather than from the intermolecular one. This is in line with our discussion about the influence of intra- and inter-monomer vibration effects given in the paper. As in the not-distorted aggregates the lowest states are Frenkel-type states while CT-type states appear at higher energies.