Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Weakly bound PTCDI and PTCDA dimers studied by using MP2 and DFT methods with dispersion correction

Mircea Oltean, George Mile, Mihai Vidrighin, Nicolae Leopold, Vasile Chiş[a]

Babeş-Bolyai University, Faculty of Physics, Kogălniceanu 1, RO-400084, Cluj-Napoca, Romania

Supporting information

---

[a] To whom correspondence should be addressed. E-mail: vasile.chis@phys.ubbcluj.ro

Complete Gaussian09 citation

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; J. A. Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian09*, Revision A.2; Gaussian, Inc.: Wallingford, CT, 2009.

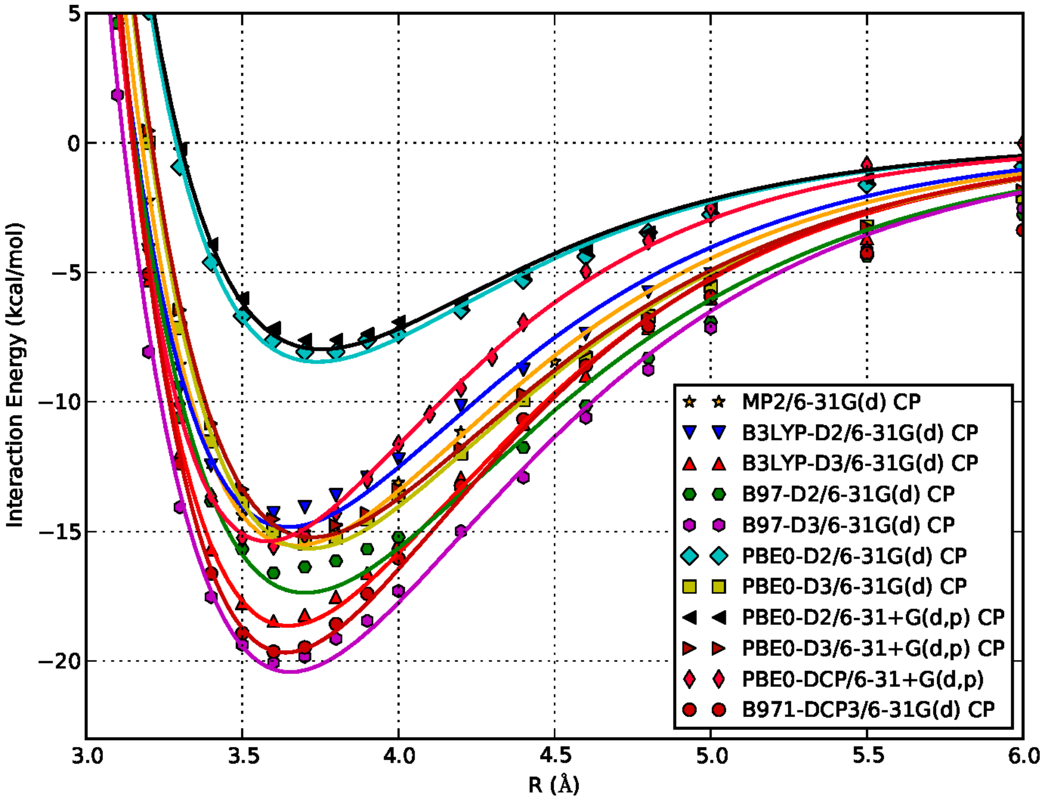

Figure S1. Calculated potential energy curves for the stacked PTCDI dimer at different levels of theory, fitted to a modified-Morse potential function.

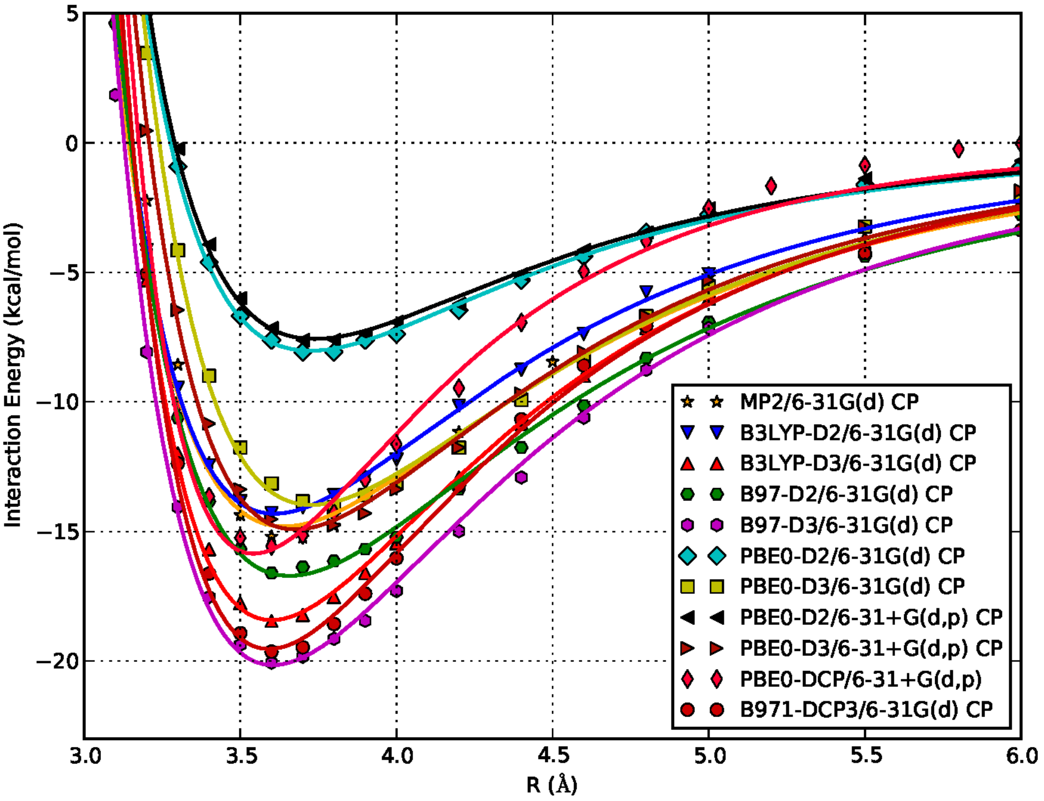

Figure S2. Calculated potential energy curves for the stacked PTCDI dimer at different levels of theory, fitted to a Lennard-Jones potential function.

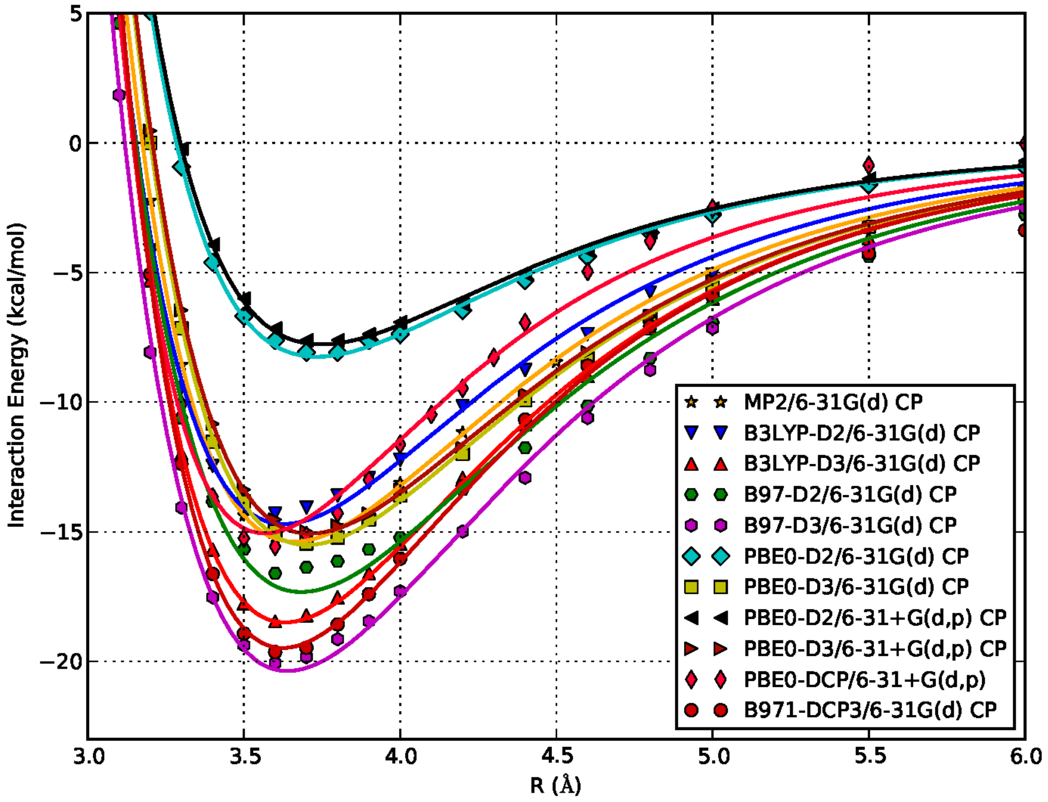

Figure S3. Calculated potential energy curves for the stacked PTCDI dimer at different levels of theory, fitted to a Buckingham potential function.

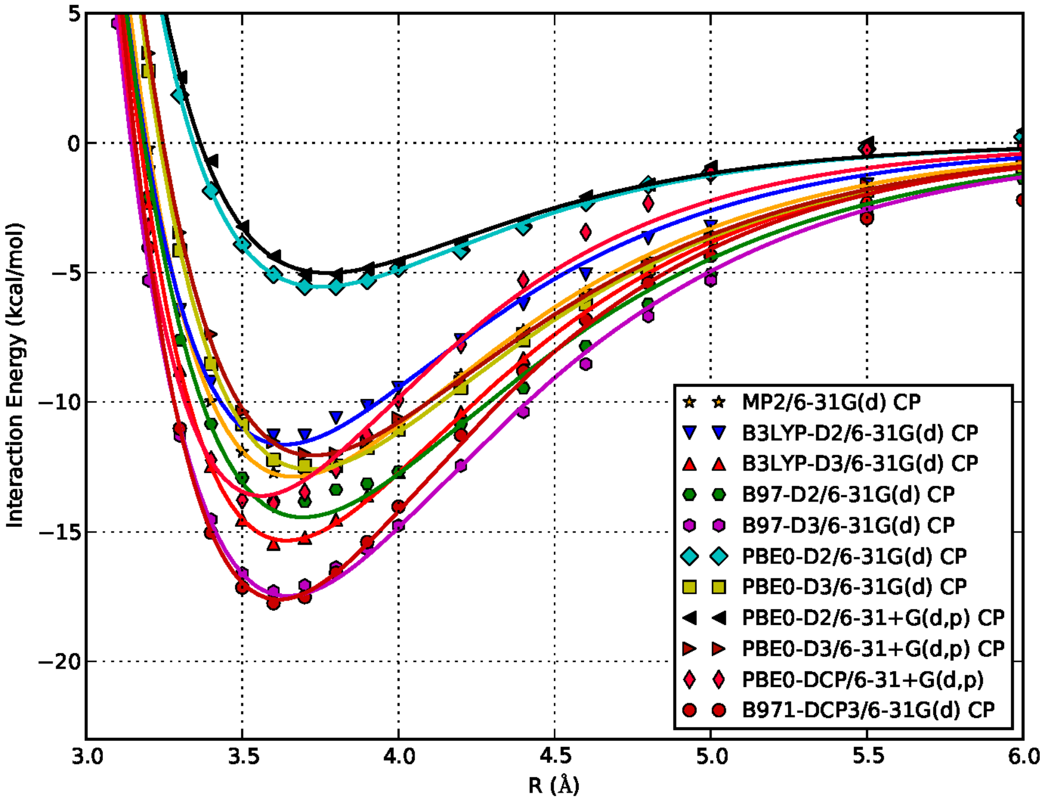

Figure S4. Calculated potential energy curves for the stacked PTCDA dimer at different levels of theory, fitted to a modified-Morse potential function.

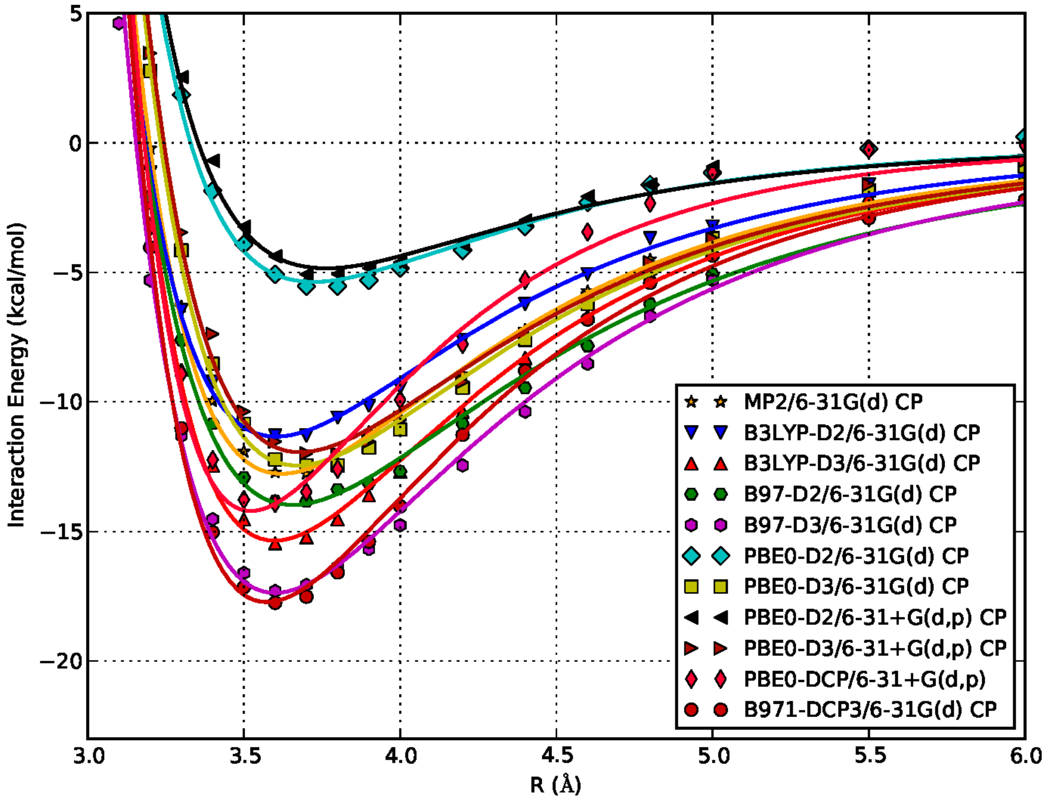

Figure S5. Calculated potential energy curves for the stacked PTCDA dimer at different levels of theory, fitted to a Lennard-Jones potential function.

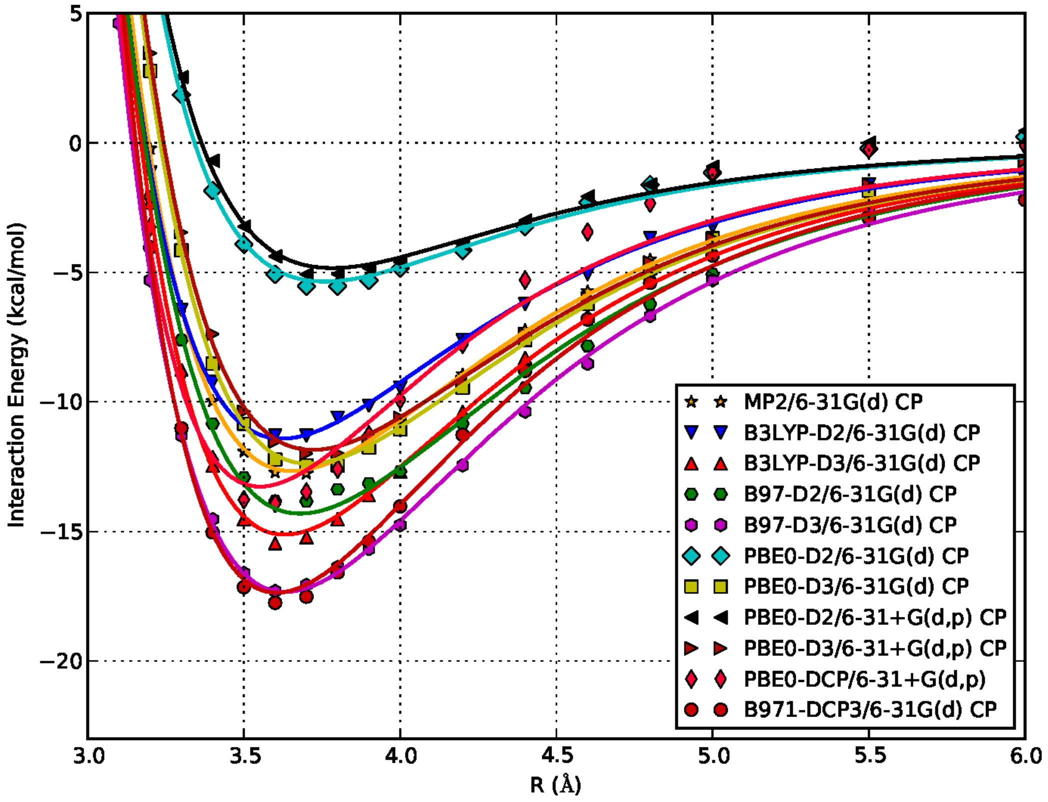

Figure S6. Calculated potential energy curves for the stacked PTCDA dimer at different levels of theory, fitted to a Buckingham potential function.

Table S1. Binding energies, equilibrium distances and fitting parameters for PTCDI and PTCDA dimers with the Murrel-Sorbie potential function

PTCDI									**PTCDA**					
No.	Method	Basis set	D_e (kcal/mol)	R_e(Å)	a_1	a_2	a_3	R^2	D_e (kcal/mol)	R_e(Å)	a_1	a_2	a_3	R^2
1	MP2 CP	6-31G(d)	-16.12	3.708	3.211	2.992	1.005	0.9818	-12.80	3.659	2.040	-0.135	0.284	1.0000
2	B3LYP-D2 CP	6-31G(d)	-14.37	3.610	2.002	-0.027	0.749	0.9998	-11.32	3.625	2.387	0.571	0.696	0.9998
3	B3LYP-D3 CP	6-31G(d)	-18.43	3.626	1.770	-0.436	0.418	1.0000	-15.29	3.637	1.998	-0.216	0.251	0.9999
4	B97-D2 CP	6-31G(d)	-16.56	3.665	2.147	0.909	0.882	0.9997	-13.86	3.686	2.363	1.238	0.864	0.9998
5	B97-D3 CP	6-31G(d)	-20.02	3.629	2.039	0.437	0.498	0.9999	-17.20	3.639	2.332	0.927	0.534	0.9998
6	PBE0-D2 CP	6-31G(d)	-8.09	3.738	2.232	0.416	0.698	0.9999	-5.60	3.761	3.068	1.879	0.678	0.9998
7	PBE0-D3 CP	6-31G(d)	-15.40	3.699	1.831	-0.158	0.351	0.9999	-12.55	3.715	2.128	0.208	0.229	1.0000
8	PBE0-D2 CP	6-31+G(d,p)	-7.63	3.762	2.393	0.881	0.726	1.0000	-5.12	3.797	3.425	3.057	1.228	0.9996
9	PBE0-D3 CP	6-31+G(d,p)	-14.97	3.709	1.898	-0.002	0.341	1.0000	-12.01	3.733	2.430	0.956	0.365	0.9999
10	PBE0-DCP	6-31+G(d,p)	-15.61	3.592	2.060	-0.499	0.224	0.9998	-14.00	3.585	3.650	3.717	1.560	0.9998
11	B971-DCP3 CP	6-31G(d)	-19.69	3.620	1.460	-1.180	0.571	1.0000	-17.78	3.611	1.491	-1.350	0.552	1.0000

Table S2. Binding energies, equilibrium distances and fitting parameters for PTCDI and PTCDA dimers with the modified-Morse potential function

			PTCDI				PTCDA			
No.	Method	Basis set	D_e (kcal/mol)	R_e(Å)	a	R^2	D_e (kcal/mol)	R_e(Å)	a	R^2
1	MP2 CP	6-31G(d)	-14.74	3.647	1.400	0.9704	-12.75	3.664	1.487	0.9998
2	B3LYP-D2 CP	6-31G(d)	-14.83	3.647	1.418	0.9930	-10.19	3.673	1.559	0.9990
3	B3LYP-D3 CP	6-31G(d)	-18.63	3.647	1.388	0.9977	-15.34	3.642	1.481	0.9998
4	B97-D2 CP	6-31G(d)	-17.36	3.702	1.268	0.9911	-14.44	3.695	1.362	0.9961
5	B97-D3 CP	6-31G(d)	-20.43	3.654	1.298	0.9969	-17.48	3.645	1.384	0.9991
6	PBE0-D2 CP	6-31G(d)	-8.46	3.741	1.531	0.9985	-5.56	3.752	1.6986	0.9997
7	PBE0-D3 CP	6-31G(d)	-15.66	3.715	1.355	0.9988	-12.59	3.716	1.4422	0.9999
8	PBE0-D2 CP	6-31+G(d,p)	-7.98	3.753	1.531	0.9988	-5.03	3.774	1.695	0.9993
9	PBE0-D3 CP	6-31+G(d,p)	-15.22	3.722	1.353	0.9991	-12.06	3.727	1.441	0.9998
10	PBE0-DCP	6-31+G(d,p)	-15.38	3.579	1.613	0.9983	-13.61	3.560	1.706	0.9962
11	B971-DCP3 CP	6-31G(d)	-19.67	3.638	1.428	0.9959	-17.62	3.616	1.510	0.9984

Table S3. Binding energies, equilibrium distances and fitting parameters for PTCDI and PTCDA dimers with the Lennard-Jones potential function

			PTCDI							PTCDA						
No.	Method	Basis set	D_e (kcal/mol)	R_e(Å)	a	b	c	d	R^2	D_e (kcal/mol)	R_e(Å)	a	b	c	d	R^2
1	MP2 CP	6-31G(d)	-14.81	3.640	3.46	9.4740	3.83	4.6765	0.9843	-12.78	3.620	3.44	11.1552	3.69	5.6094	0.996
2	B3LYP-D2 CP	6-31G(d)	-14.32	3.609	3.39	10.6652	3.70	4.7976	0.9995	-11.35	3.603	3.38	11.3142	3.59	5.6102	0.9978
3	B3LYP-D3 CP	6-31G(d)	-18.43	3.600	3.49	10.6400	3.91	5.0439	0.9979	-15.36	3.597	3.48	11.1560	3.80	5.6977	0.9946
4	B97-D2 CP	6-31G(d)	-16.72	3.658	3.45	9.7781	3.88	4.3074	0.9968	-13.97	3.656	3.44	10.2651	3.76	4.8170	0.9947
5	B97-D3 CP	6-31G(d)	-20.16	3.604	3.51	10.0527	4.01	4.7332	0.9951	-17.36	3.599	3.50	10.5108	3.89	5.2526	0.9916
6	PBE0-D2 CP	6-31G(d)	-8.03	3.724	3.35	11.0708	3.44	5.2509	0.9992	-5.37	3.723	3.33	12.1411	3.33	6.4079	0.996
7	PBE0-D3 CP	6-31G(d)	-13.97	3.728	3.52	10.0615	3.85	4.8204	0.9957	-12.45	3.669	3.47	10.9241	3.72	5.4835	0.9942
8	PBE0-D2 CP	6-31+G(d,p)	-7.56	3.738	3.35	11.0656	3.42	5.2926	0.9985	-4.84	3.762	3.32	11.9334	3.28	6.1292	0.9973
9	PBE0-D3 CP	6-31+G(d,p)	-14.92	3.676	3.49	10.4036	3.83	4.9392	0.9962	-11.95	3.680	3.47	10.9247	3.71	5.5275	0.9927
10	PBE0-DCP	6-31+G(d,p)	-15.87	3.542	3.51	11.9785	3.79	6.7753	0.9845	-14.21	3.523	3.47	12.7533	3.70	7.3447	0.9847
11	B971-DCP3 CP	6-31G(d)	-19.53	3.592	3.50	11.0178	3.93	5.1558	0.9953	-17.73	3.573	3.50	11.4255	3.86	5.7782	0.9949

Table S4. Binding energies, equilibrium distances and fitting parameters for PTCDI and PTCDA dimers with the Buckingham potential function

			PTCDI						**PTCDA**					
No.	Method	Basis set	D_e (kcal/mol)	R_e(Å)	a	b	c	R^2	D_e (kcal/mol)	R_e(Å)	a	b	c	R^2
1	MP2 CP	6-31G(d)	-15.38	3.662	47429.25	3.0007	3540.75	0.9998	-12.66	3.654	74387.42	3.2236	2664.27	0.9995
2	B3LYP-D2 CP	6-31G(d)	-14.69	3.63	54125.86	3.0879	3136.09	0.9973	-11.42	3.622	120791.65	3.4461	2153.39	0.9996
3	B3LYP-D3 CP	6-31G(d)	-18.49	3.633	51784.27	2.9912	4115.81	0.9997	-15.13	3.630	80320.22	3.2110	3092.80	0.9992
4	B97-D2 CP	6-31G(d)	-17.32	3.684	26293.95	2.7352	4641.80	0.9937	-14.32	3.680	37591.78	2.9310	3472.54	0.9978
5	B97-D3 CP	6-31G(d)	-20.36	3.640	32516.24	2.7868	5027.54	0.9987	-17.34	3.632	46171.98	2.9745	3880.35	0.9991
6	PBE0-D2 CP	6-31G(d)	-8.26	3.734	84256.50	3.3318	1872.95	0.9997	-5.35	3.758	217725.71	3.7368	1142.83	0.9987
7	PBE0-D3 CP	6-31G(d)	-15.50	3.703	38989.31	2.8977	3932.50	0.9998	-12.38	3.708	56413.14	3.0932	2926.91	0.9994
8	PBE0-D2 CP	6-31+G(d,p)	-7.77	3.748	81212.89	3.3267	1800.10	0.9997	-4.84	3.783	200035.41	3.7180	1070.99	0.9982
9	PBE0-D3 CP	6-31+G(d,p)	-15.06	3.711	37906.67	2.8918	3869.61	0.9999	-11.85	3.720	54355.50	3.0854	2853.96	0.9991
10	PBE0-DCP	6-31+G(d,p)	-15.06	3.566	214023.48	3.5981	2520.77	0.9922	-13.26	3.551	380736.67	3.8425	2059.15	0.9878
11	B971-DCP3 CP	6-31G(d)	-19.49	3.624	70750.39	3.0878	4127.31	0.9984	-17.36	3.604	110159.51	3.2937	3338.37	0.9985

Impact of the dispersion correction scheme on the APEFs parameters

As observed in Figures 1 and 2, the PBE0-D results are mostly affected by the adopted dispersion correction scheme. Thus, the PBE0-D3 binding energies are about 6.9 kcal/mol larger in magnitude, while R_e values are around 0.05 Å shorter than for PBE0-D2. Expectedly, the quality of the used basis sets does not affect considerably the PECs' parameters calculated by using these PBE0-D approaches. Since dispersion correction schemes are independent on the used basis sets, these small variations between the two employed BSs are due to the minor differences between the optimized geometrical parameters at the corresponding level of theory and the differences between the used damping functions.

Considering the deviations from the MP2 (and PBE0-DCP) calculated binding energies, it is clear that D3 correction is imperative when PBE0 functional (with both BSs) is used as a DFT-D type approach while its predecessor D2 seems to be sufficient when it is coupled to B3LYP and B97 functionals.

As seen in Table 1, even though not corrected for BSSE, PBE0-DCP approach predicts a binding energy of -15.61 kcal/mol (MS fitted curve) for PTCDI in excellent agreement with either the more laborious CP corrected MP2 method, with B3LYP-D2, B97-D2 and PBE0-D3 approaches or with previously reported data[54]. The same approach performs also very well for PTCDA, providing binding energies in good agreement with MP2 method. For both derivatives, the inter-monomer equilibrium distance given by the PBE0-DCP approach is significantly lower than the CP corrected values predicted by MP2 and DFT-D methods. Actually, for all the computational methods, the not-CP corrected R_e values, either for PTCDI or PTCDA are closer to the experimental interplanar spacing for planar perylene structures of about 3.5 Å.[137]

Similar analytical PECs have been derived by Lilienfeld and Andrienko[86] for a series of π-π stacked dimers of polyaromatic hydrocarbons. These authors used a DFT-DCP-type approach coupled with a plane-wave basis set, with dispersion calibrated atom centered potentials on C atoms only. For the pyrene dimer they obtained D_e and R_e values of -0.687 eV and 3.630 Å, respectively, by fitting the calculated curves to LJ, Morse and Buckingham potentials. Our results obtained by fitting the PBE0-DCP data with the Buckingham potential are similar: -0.653 eV and 3.566 Å for PTCDI and -0.575 eV and 3.551 Å for PTCDA. Moreover, as seen in Table S4, our Buckingham parameters for the two derivatives, obtained by fitting the PBE0-DCP data ($A=2.14\cdot10^5$, $B=3.598$ and $C=2.52\cdot10^3$ for PTCDI; $A=3.81\cdot10^5$, $B=3.843$ and $C=2.06\cdot10^3$ for PTCDA) are also in line with those obtained for perylene:[86] $A=2.09\cdot10^5$, $B=3.388$ and $C=4.47\cdot10^4$. Thus, PBE0-DCP is again validated as a reliable and fast approach for calculating coarse-grained interaction potentials that can be subsequently fitted to an APEF.

Gross and collaborators[96] have obtained the APEF for the interaction between the pentacene and CO molecules by fitting the PBE-vdW calculated interaction energies (in the attractive part of the potential) with a Lennard-Jones potential of general form. Their exponents (b and d) are very close to the standard 12-6 LJ potential. Our exponents, obtained by fitting all the calculated points are between 9.15 and 12.76 and between 4.30 and 7.06, respectively (see Table S3) for both PTCDs. Such deviations from the exact “12-6” values are normally expected, depending on the shape and size of the interacting entities[59,123] and on the effects of the electrostatic contributions.

Dispersion energies for PTCDI and PTCDA

As shown in Figures 1 and 2, different DFT-D approaches provide quantitatively different binding energies. In order to investigate further this effect we present in Fig.S7 the dispersion energies as a function of the inter-monomer distance for the two kind of analyzed dimers, calculated using the B3LYP-D3, B97-D3 and PBE0-D3 methods with the BS1 basis set.

These energies have been obtained by subtracting twice the intramolecular dispersion energy calculated at the same level of theory from the total dispersion energy of the dimer.

As observed in Fig. S7, for an inter-monomer distance of 3 Å, B97-D3 method provides significantly more (attractive) dispersion interactions than the other two used methods while the three approaches converge at large inter-monomer separation (6.0 Å). Thus, for PTCDI they are -3.23, -3.11 and -2.81 kcal/mol for B97-D3/BS1, B3LYP-D3/BS1 and PBE0-D3/BS1, respectively, while for PTCDA the corresponding values are: -3.09, -3.00 and -2.70 kcal/mol.

By fitting the dependencies of the dispersion energies calculated with the three functionals for both dimers, we estimated the dispersion energies at the corresponding minimum of the potential: -39.57, -34.38 and -24.03 kcal/mol for PTCDI and -37.52, -32.77 and -22.14 kcal/mol for PTCDA. Thus, the ratios of these energies and the corresponding binding energies (see Tables 1 and 2) are between 1.56 (for PTCDI with PBE0-D) method and 2.18 (for PTCDA with B97-D method).

Very similar contributions of the dispersion energies to binding, calculated by SAPT(DFT) method have been reported for different sheet graphite models.[123,137] Moreover, the ratios of the binding energies of PTCDI and PTCDA and the ratios of the corresponding dispersion energies are also very similar. Thus, the former ratios are: 1.05, 1.06 and 1.09 for B97, B3LYP and PBE0 functionals, while for the second ratio the corresponding values are: 1.16, 1.21 and 1.23. Clearly, the order of the dispersion energies is mirrored in the total interaction energies and it can also be concluded that H structures of the two dimers are predominantly bound by dispersion interactions.

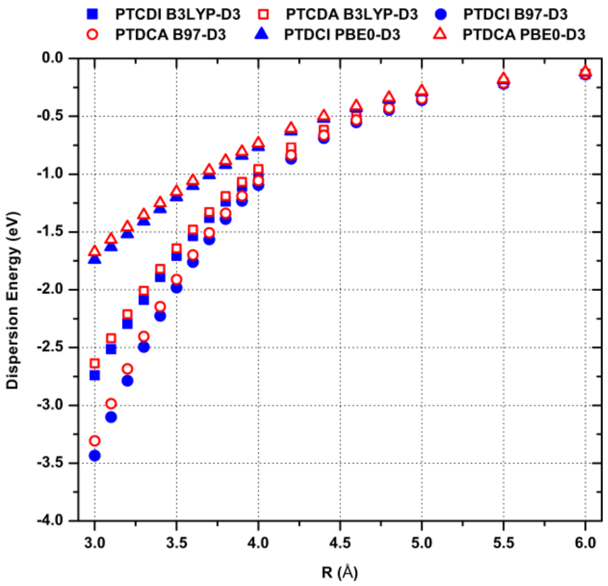

Fig.S7 Dispersion energies for PTCDI and PTCDA dimers calculated as a function of inter-monomer distance at B3LYP-D3/6-31G(d), B97-D3/6-31G(d) and PBE0-D3/6-31G(d) levels of theory