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Electronic Supplementary Information

π–π stacking Interactions between Polyaromatic Hydrocarbon Sheets beyond Dispersion

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Table 1S. Comparison of interaction energies ΔE(kcal/mol) and inter monomer distances R of the optimized stacked dimers of benzene to pentacene using different methods and basis sets.

Method [a]	Basis	ΔE	R (Å)
Benzene dimer			
MP2	SV(P)	-2.848	3.800
SOS-MP2	SV(P)	-1.281	3.808
CCSD(T)	SV(P)	-1.543	3.931[b]
DFT/B3LYP-D3	SV(P)	-2.280	3.807
Naphthalene dimer			
SOS-MP2	SV(P)	-3.794	3.800
CCSD(T)	SV(P)	-4.183	3.800
DFT/B3LYP-D3	SV(P)	-5.107	3.735
Anthracene dimer			
SOS-MP2	SV(P)	-6.730	3.721
CCSD(T)	SV(P)	-7.264	3.651[c]
DFT/B3LYP-D3	SV(P)	-8.051	3.710
Tetracene dimer			
SOS-MP2	SV(P)	-9.900	3.680
SOS-MP2	def2-TZVP	-11.256	3.719
SOS-MP2-F12	cc-pVDZ-F12	-9.410	3.719[b]
DFT/B3LYP-D3	SV(P)	-11.022	3.703
DFT/B3LYP-D3	def2-TZVP	-9.474	3.803
Pentacene dimer			
SOS-MP2	SV(P)	-13.186	3.657
SOS-MP2	def2-TZVP	-14.908	3.696
SOS-MP2-F12	cc-pVDZ-F12	-12.608	3.696[b]
DFT/B3LYP-D3	SV(P)	-14.022	3.691
DFT/B3LYP-D3	def2-TZVP	-12.122	3.803

[a] Geometries were optimized with the same method as used for the energy calculations unless specified differently.
[b] SOS-MP2/def2-TZVP geometry.
[c] From potential energy curve fitting of CCSD(T) data in the distance R. Remaining geometry fixed from SOS-MP2/def2-TZVP geometry.

Table 2S. BSSE corrected and uncorrected interaction energies and average for the acene dimer series using the SOS-MP2/SV(P) approach in comparison with SOS-MP2(F12)/cc-pVDZ-F12 results. All values are in kcal/mol.

Dimer	ΔEuncorr.[a]	ΔE_{BSSE}(corr.)	ΔE(aver.)	ΔE
		SOS-MP2/SV(P)		SOS-MP2(F12)
Benzene	-1.281	0.792	-0.245	-1.340
Naphthalene	-3.794	-0.370	-2.082	-3.730
Anthracene	-6.730	-1.354	-4.042	-6.461
Tetracene	-9.900	-2.520	-6.210	-9.410
Pentacene	-13.186	-3.813	-8.499	-12.608

[a] See Table 1S

Table 3S. BSSE corrected and uncorrected interaction energies for the acene dimer series using the DFT/B3LYP approach in combination with the SV(P) and def2-TZVP basis sets. All values are in kcal/mol.

Dimer	ΔEuncorr.[a]		ΔE_{BSSE}(corr.)	
	SV(P)	def2-TZVP	SV(P)	def2-TZVP
Benzene	-2.280	-1.690	-1.054	-1.462
Naphthalene	-5.107	-4.216	-3.176	-3.909
Anthracene	8.051	-6.832	-5.439	-6.449
Tetracene	-11.022	-9.474	-7.754	-9.014
Pentacene	-14.022	-12.122	-10.068	-11.584

[a] From Table 1, 2 and Table 1S

Table 4S. Interaction energies Δ*E*, optimized inter monomer distances R for restricted and unrestricted calculations of the stacked dimers of heptacene and decacene.[a]

Method[b]	Basis	ΔE (kcal/mol)	R (Å)
Heptacene dimer			
SOS-RMP2	SV(P)	-20.663	3.297
	def2-TZVP	-25.226	3.323
SOS-UMP2	SV(P)	-12.830	3.707
	def2-TZVP	-16.752	3.712
RDFT/B3LYP-D3	SV(P)	-23.319	3.328
	def2-TZVP	-18.651	3.374
UDFT/B3LYP-D3	SV(P)	-25.64	3.459
	def2-TZVP	-22.217	3.553
Decacene dimer			
SOS-RMP2	SV(P)	-48.639	3.359
	def2-TZVP	-55.288	3.388
SOS-UMP2	SV(P)	-19.515	3.666
RDFT/B3LYP-D3	SV(P)	-50.771	3.410
	def2-TZVP	-45.911	3.448
UDFT/B3LYP-D3	SV(P)	-38.239	3.450
	def2-TZVP	-33.564	3.526

[a] Geometries were optimized with the same method as used for the energy calculations.
[b] Restricted and spin unrestricted calculations are denoted by the prefix R and U, respectively.

Table 5S. BSSE uncorrected interaction energies ΔE and displacement vectors R_1, R_2 and R_3[a] for the optimized slipped-parallel dimers in the series of benzene to pentacene using the SOS-MP2 and DFT/B3LYP-D3 methods and the def2-TZVP basis set.

Dimer	Method	ΔE (kcal/mol)	R_1 (Å)	R_2 (Å)	R_3 (Å)
benzene	SOS-MP2	-2.490	3.626	1.564	0.977
	DFT/B3LYP-D3	-2.699	3.614	1.570	0.979
naphthalene	SOS-MP2	-6.585	3.409	1.314	0.987
	DFT/B3LYP-D3	-6.061	3.466	1.381	1.007
anthracene	SOS-MP2	-11.347	3.359	1.266	1.179
	DFT/B3LYP-D3	-9.590	3.426	1.348	1.061
tetracene	SOS-MP2	-16.259	3.323	1.242	1.173
	DFT/B3LYP-D3	-13.162	3.414	1.366	1.079
pentacene	SOS-MP2	-21.492	3.300	1.231	1.191
	DFT/B3LYP-D3	-16.832	3.399	1.320	1.204

[a] See Scheme 2 for the definition of the displacements.

Table 6S. Interaction energies ΔE and inter monomer distances R of the sandwich structures pyrene to coronene circum-2 using SOS-MP2 and DFT/PBE-D3 methods and selected basis sets.

Method	Basis	ΔE (kcal/mol)	R (Å)[a]
Pyrene dimer			
SOS-MP2	SV(P)	-9.082	3.657
DFT/PBE-D3	SV(P)	-9.822	3.735
Coronene dimer			
SOS-MP2	SV (P)	-17.603	3.589
SOS-MP2	def2-TZVP	-19.666	3.633
DFT/PBE-D3	SV(P)	-16.328	3.713
DFT/PBE-D3	def2-TZVP	-14.331	3.805
HBC dimer			
SOS-MP2	SV(P)	-40.118	3.548
SOS-MP2	def2-TZVP	-41.269	3.586
DFT/PBE-D3	SV(P)	-31.468	3.686
DFT/PBE-D3	def2-TZVP	-27.928	3.778
Coronene circum-1 dimer			
SOS-MP2[c]	SV(P)	-63.373	3.509
SOS-MP2[c]	Def2-TZVP	-61.744	3.551
DFT/PBE-D3	SV(P)	-42.350	3.677
DFT/PBE-D3	def-TZVP	-37.500	3.771
Coronene circum-2 dimer			
SOS-MP2	SV(P)	-138.738	3.475
DFT/PBE-D3	SV(P)	-80.730	3.66
DFT/PBE-D3	def2-TZVP	-71.633	3.754

[a] See Scheme 2.

Table 7S. BSSE uncorrected and corrected interaction energies and average for the sandwich dimer series from pyrene to coronene circum-2 using the SOS-MP2 and DFT/PBE-D3 approaches.

Dimer	ΔEuncorr.[a]	ΔE_{BSSE}(corr.)	ΔE(aver.)
		SOS-MP2/SV(P)	
Pyrene	-9.082	-2.339	-5.711
Coronene	-17.603	-6.221	-11.912
HBC	-40.118	-18.313	-29.215
Coronene circum-1	-63.373	-33.299	-48.336
Coronene circum-2	-138.738	-81.270	-110.004
		SOS-MP2/def2-TZVP	
Pyrene	-10.471	-6.856	-8.663
Coronene	-19.666	-13.093	-16.380
HBC	-41.269	-26.835	-34.052
Coronene circum-1	-61.744	-42.064	-51.904
		DFT/PBE-D3/SV(P)	
Pyrene	-9.822	-7.182	-
Coronene	-16.328	-12.594	-
HBC	-31.468	-25.039	-
Coronene circum-1	-42.350	-34.4736	-
Coronene circum-2	-80.730	-67.093	-
		DFT/PBE-D3/def2-TZVP	
Pyrene	-8.521	-8.046	-
Coronene	-14.331	-13.7174	-
HBC	-27.928	-26.899	-
Coronene circum-1	-37.500	-36.418	-
Coronene circum-2	-71.633	-69.976	-

[a] From Table 6S

Table 8S. Interaction energies ΔE and displacement vectors R_1 and R_2 and R_3[a] for the optimized slipped-parallel dimers in the series of pyrene to coronene circum-2 using the SOS-MP2 and DFT-D3 methods and the SV(P) basis set.

Dimer	Method	ΔE (kcal/mol)	R1 (Å)	R2 (Å)
Pyrene	SOS-MP2	-14.115	3.330	1.522
	DFT/PBE-D3	-12.383	3.523	1.530
Coronene	SOS-MP2	-27.279	3.243	1.424
	DFT/PBE-D3	-19.105	3.641	1.494
HBC	SOS-MP2	-58.325	3.201	1.459
	DFT/PBE-D3	-38.061	3.499	1.583
Coronene	SOS-MP2	-88.586	3.134	1.422
circum-1	DFT/PBE-D3	-51.537	3.354	1.426
Coronene	SOS-MP2	-186.658	3.117	1.438
circum-2	DFT/PBE-D3	-94.313	3.436	1.492

[a] See Scheme 2. Due to the use of C_{2h} symmetry R_3 is always zero.

Table 9S. Interaction energies ΔE and displacement vectors R_1 and R_2[a] for the optimized slipped-parallel dimers in the series of pyrene to coronene circum-2 using the SOS-MP2 and DFT/PBE-D3 methods and the def2-TZVP basis set.

Dimer	Method	ΔE (kcal/mol)	R1 (Å)	R2 (Å)
Pyrene	SOS-MP2	-14.891	3.410	1.524
	DFT/PBE-D3	-10.456	3.620	1.447
Coronene	SOS-MP2	-26.774	3.314	1.438
	DFT/PBE-D3	-16.955	3.617	1.474
HBC	SOS-MP2	-54.997	3.275	1.465
	DFT/PBE-D3	-33.139	3.629	1.583
Coronene	SOS-MP2	-80.203	3.211	1.441
circum-1	DFT/PBE-D3	-42.932	3.466	1.430
Coronene	SOS-MP2	-	-	-
circum-2	DFT/PBE-D3	-80.195	3.341	1.438

[a] See Scheme 2. Due to the use of C_{2h} symmetry R_3 is always zero.

Table 10S. BSSE uncorrected and corrected interaction energies and average for the slipped parallel dimer series from pyrene to coronene circum-2 using the SOS-MP2 and DFT/PBE-D3 approaches.

Dimer	ΔEuncorr.[a]	ΔE_{BSSE}(corr.)	ΔE(aver.)
		SOS-MP2/SV(P)	
Pyrene	-14.115	-3.228	-8.672
Coronene	-27.279	-9.631	-18.455
HBC	-58.325	-26.140	-42.232
Coronene circum-1	-88.586	-43.243	-65.915
Coronene circum-2	-186.658	-101.155	-143.906
		SOS-MP2/def2-TZVP	
Pyrene	-14.891	-9.663	-12.277
Coronene	-26.774	-17.796	-22.285
HBC	-54.997	-37.089	-46.043
Coronene circum-1	-80.203	-55.719	-67.961
		DFT/PBE-D3/SV(P)	
Pyrene	-12.383	-9.232	-
Coronene	-19.105	-15.500	-
HBC	-38.061	-30.350	-
Coronene circum-1	-51.289	-40.155	-
Coronene circum-2	-95.177	-78.630	-
		DFT/PBE-D3/def2-TZVP	
Pyrene	-10.456	-9.833	-
Coronene	-16.955	-16.164	-
HBC	-33.139	-31.777	-
Coronene circum-1	-42.932	-41.328	-
Coronene circum-2	-80.195	-76.985	-

[a] From Table 8S and Table 9S

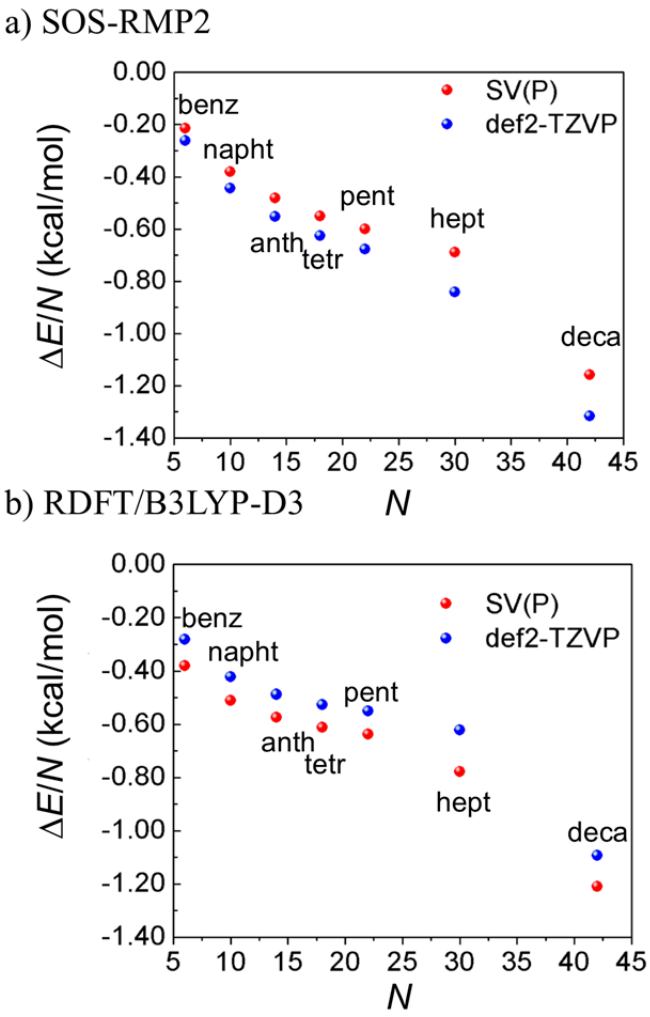

Figure 1S: Interaction energies Δ*E/N* (*N* is the numbers of C atoms in the monomer) for the series of benzene to decacene sandwich dimers in dependence of *N* for the a) SOS-RMP2 and b) the RDFT/B3LYP-D3 methods using the SV(P) and def2-TZVP basis sets.

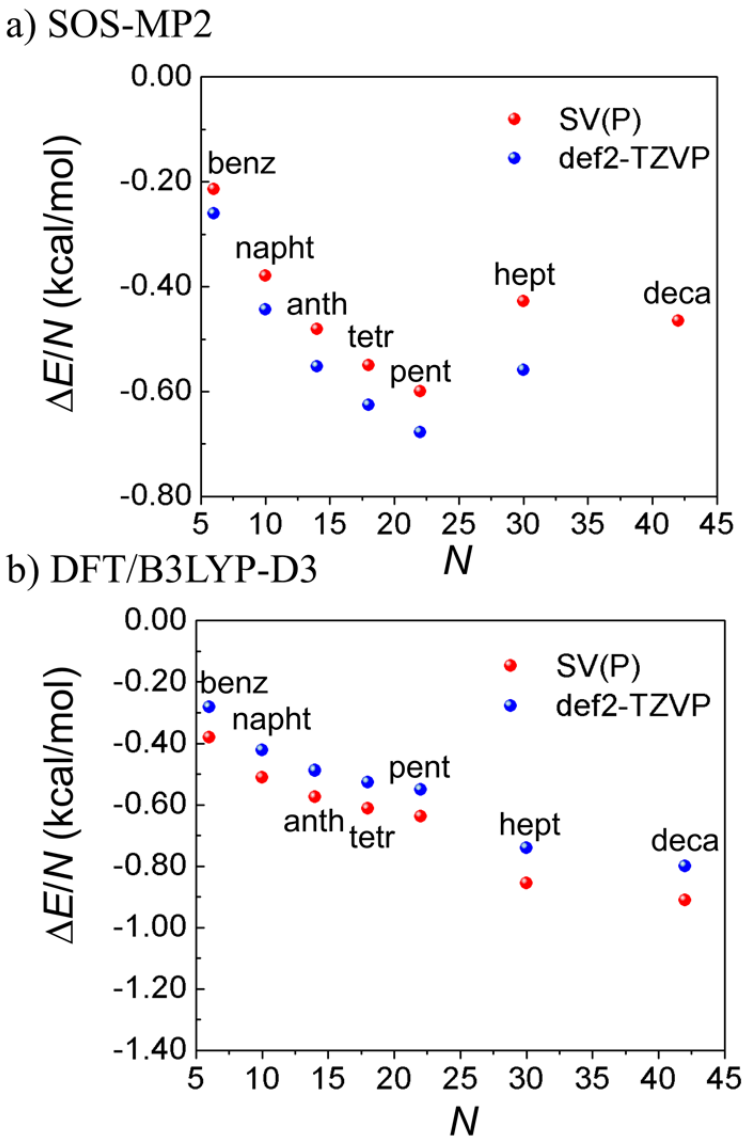

Figure 2S: Interaction energies Δ*E*/*N* (*N* is the numbers of C atoms in the dimer) for the series of benzene to decacene sandwich dimers in dependence of *N* for the a) SOS-MP2 and b) the DFT/B3LYP-D3 methods using the SV(P) and def2-TZVP basis sets. Restricted (SOS-RMP2 and RDFT) results are shown up to pentacene, unrestricted calculations (SOS-UMP2 and UDFT/B3LYP) have been used for the heptacene and decacene dimers.

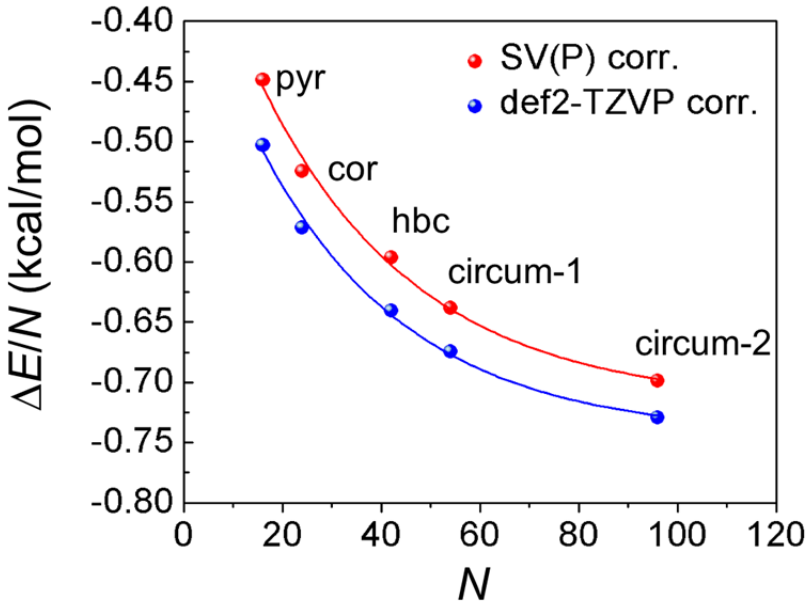

Figure 3S: DFT/PBE-D3 interaction energies Δ*E*/*N* (*N* is the numbers of C atoms in the monomer) for the sandwich dimers of pyrene to coronene circum-2 in dependence of *N* using the SV(P) and def2-TZVP basis sets.

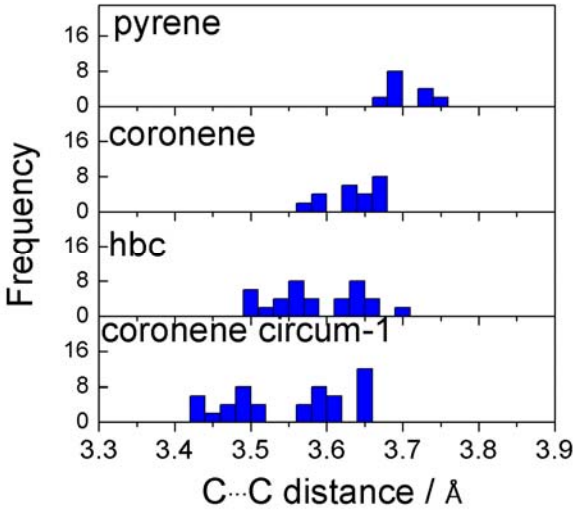

Figure 4S. Histograms of perpendicular interring distances for different sandwich structures computed using the SOS-MP2/def2-TZVP approach.

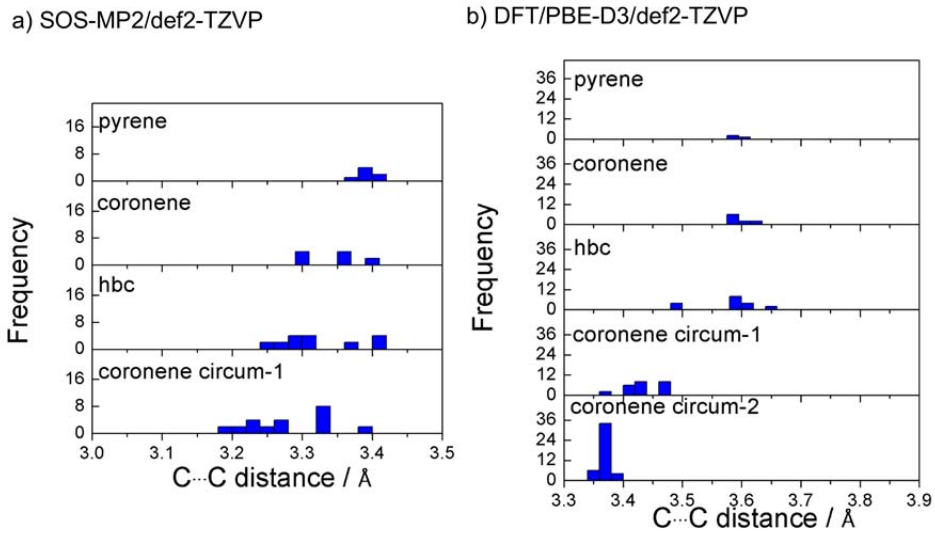

Figure 5S. Histograms of perpendicular interring distances for different slipped parallel structures in C_{2h} symmetry using a) the SOS-MP2/def2-TZVP and b) the DFT/PBE-D3/def2-TZVP method.