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

Supporting Information

Validation of density functionals for pancake-bonded π-dimers; dispersion is not enough

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Table S1. Full computational test result of DFTs for PLY, $\mathbf{1_2}$ π-dimer.

	E_{int}[b]	E_{int} error	E_{SOMO}	E_{SOMO} error	D_{CC1}[c]	D_{CC1} error	$D_{\alpha\alpha}$	$D_{\alpha\alpha}$ error	Spin[d]
Reference[a]	-11.50		-17.50		3.104		3.092		0.66
APFD	-22.50	-11.00	-19.06	-1.56	3.086	-0.018	3.015	-0.077	0.00
B1B95	-3.88	7.62	-14.95	2.55	3.161	0.057	3.120	0.028	0.00
B1LYP[e]									
O3LYP[e]									
X3LYP	0.59	12.09	-0.46	17.04	4.292	1.188	4.294	1.202	0.99
B3LYP	1.13	12.63	-0.29	17.21	4.499	1.395	4.505	1.413	0.99
B3LYP-D3	-16.18	-4.68	-16.16	1.34	3.181	0.077	3.106	0.014	0.00
B3LYP-D3BJ	-20.12	-8.62	-19.20	-1.70	3.115	0.011	3.042	-0.050	0.00
B3PW91	2.26	13.76	-1.61	15.89	3.846	0.742	3.845	0.753	0.95
B3PW91-D3	-20.98	-9.48	-19.46	-1.96	3.108	0.004	3.021	-0.071	0.00
B3PW91-D3BJ	-25.12	-13.62	-22.82	-5.32	3.034	-0.070	2.961	-0.131	0.00
B97D	-23.30	-11.80	-22.26	-4.76	3.091	-0.013	3.031	-0.061	0.00
B97D3	-25.14	-13.64	-21.98	-4.48	3.110	0.006	3.037	-0.055	0.00
BLYP	1.13	12.63	-9.44	8.06	3.502	0.398	3.472	0.380	0.00
BLYP-D3	-22.40	-10.90	-19.29	-1.79	3.221	0.117	3.140	0.048	0.00
BLYP-D3BJ	-25.70	-14.20	-22.26	-4.76	3.134	0.030	3.068	-0.024	0.00
BMK	-4.53	6.97	-7.79	9.71	3.355	0.251	3.331	0.239	0.78
BMK-D3	-24.14	-12.64	-19.24	-1.74	3.103	-0.001	3.012	-0.080	0.00
BMK-D3BJ	-25.39	-13.89	-18.65	-1.15	3.101	-0.003	3.026	-0.066	0.00
BP86	-2.50	9.00	-15.50	2.00	3.286	0.182	3.250	0.158	0.00
BP86-D3	-27.14	-15.64	-23.13	-5.63	3.135	0.031	3.048	-0.044	0.00
BP86-D3BJ	-30.14	-18.64	-24.94	-7.44	3.078	-0.026	3.011	-0.081	0.00
CAM-B3LYP	0.24	11.74	-1.09	16.41	3.883	0.779	3.885	0.793	0.98
HSE(HSE06)	-1.40	10.10	-5.28	12.22	3.457	0.353	3.444	0.352	0.83
LC-wPBE	-0.36	11.14	-0.89	16.61	3.817	0.713	3.823	0.731	0.99

M05	-3.23	8.27	-1.25	16.25	3.830	0.726	3.826	0.734	0.96
M052X	-10.29	1.21	-14.17	3.33	3.138	0.034	3.089	-0.003	0.64
M052X-D3	-13.79	-2.29	-13.42	4.08	3.155	0.051	3.108	0.016	0.66
M06	-13.64	-2.14	-9.93	7.57	3.294	0.190	3.224	0.132	0.71
M062X	-16.91	-5.41	-18.37	-0.87	3.115	0.011	3.035	-0.057	0.20
M06HF	-21.94	-10.44	-35.10	-17.60	2.931	-0.173	2.829	-0.263	0.00
M06L	-18.54	-7.04	-16.84	0.66	3.161	0.057	3.099	0.007	0.00
M08HX	-20.56	-9.06	-23.69	-6.19	3.033	-0.071	2.953	-0.139	0.00
M11	-13.11	-1.61	-9.03	8.47	3.179	0.075	3.146	0.054	0.89
M11L	-17.09	-5.59	-15.62	1.88	3.198	0.094	3.155	0.063	0.00
MN12SX	-17.36	-5.86	-16.67	0.83	3.161	0.057	3.101	0.009	0.00
MN15	-15.87	-4.37	-17.30	0.20	3.108	0.004	3.041	-0.051	0.24
MN15L	-24.41	-12.91	-17.74	-0.24	3.213	0.109	3.152	0.060	0.00
N12SX	-1.32	10.18	-4.97	12.53	3.480	0.376	3.466	0.374	0.84
PBE0	-1.04	10.46	-3.89	13.61	3.532	0.428	3.526	0.434	0.89
PBE0-D3	-13.91	-2.41	-15.33	2.17	3.144	0.040	3.077	-0.015	0.33
PBE0-D3BJ	-16.21	-4.71	-18.33	-0.83	3.090	-0.014	3.018	-0.074	0.00
PBE	-5.79	5.71	-15.70	1.80	3.278	0.174	3.236	0.144	0.00
PBE-D3	-19.35	-7.85	-19.33	-1.83	3.202	0.098	3.134	0.042	0.00
PBE-D3BJ	-21.54	-10.04	-21.59	-4.09	3.145	0.041	3.080	-0.012	0.00
PW6B95	-6.42	5.08	-14.04	3.46	3.172	0.068	3.132	0.040	0.26
PW6B95D3	-17.91	-6.41	-16.25	1.25	3.143	0.039	3.083	-0.009	0.00
SOGGA11X	-2.91	8.59	-5.01	12.49	3.469	0.365	3.460	0.368	0.87
TPSS	-1.58	9.92	-14.86	2.64	3.245	0.141	3.210	0.118	0.00
TPSS-D3	-20.34	-8.84	-20.32	-2.82	3.144	0.040	3.071	-0.021	0.00
TPSS-D3BJ	-23.15	-11.65	-22.87	-5.37	3.081	-0.023	3.018	-0.074	0.00
WB97XD	-15.23	-3.73	-7.91	9.59	3.258	0.154	3.226	0.134	0.84
PBE-MBD/tier-2	-18.78	-7.28	-21.02	-3.52	3.141	0.037	3.094	0.002	0.00
PBE0-MBD/tier-2	-12.76	-1.26	-18.65	-1.15	3.072	-0.032	3.013	-0.079	0.00

[a]Reference MR-AQCC values are taken from Ref.8 in main text. [b]All energies are in kcal/mol, E_{int} is defined by Equation (1) in the main text. [c]All distances are in Å. [d]Total Mulliken spin densities of a monomer in a dimer. [e] This DFT did not produce a geometry similar to the reference structure.

Table S2. Full computational test result of DFTs for $\mathbf{2_2}$ π-dimer.

	E_{int}[b]	E_{int} error	E_{SOMO}	E_{SOMO} error	D_{SS1}[c]	D_{SS1} error
Reference[a]	-7.00		-18.80		2.870	
APFD	-10.34	-3.34	-31.20	-12.40	2.614	-0.256
B1B95	-1.81	5.19	-28.27	-9.47	2.630	-0.240
B1LYP	2.74	9.74	-20.73	-1.93	2.713	-0.157
O3LYP	0.18	7.18	-21.89	-3.09	2.727	-0.143
X3LYP	-0.08	6.92	-22.21	-3.41	2.714	-0.156
B3LYP	0.27	7.27	-21.78	-2.98	2.725	-0.145
B3LYP-D3	-7.09	-0.09	-24.27	-5.47	2.723	-0.147
B3LYP-D3BJ	-9.30	-2.30	-25.72	-6.92	2.702	-0.168
B3PW91	-1.21	5.79	-26.69	-7.89	2.651	-0.219
B3PW91-D3	-10.03	-3.03	-29.26	-10.46	2.652	-0.218
B3PW91-D3BJ	-12.02	-5.02	-30.56	-11.76	2.633	-0.237
B97D	-11.34	-4.34	-24.78	-5.98	2.806	-0.064
B97D3	-14.65	-7.65	-26.07	-7.27	2.774	-0.096
BLYP	-4.59	2.41	-20.49	-1.69	2.850	-0.020
BLYP-D3	-13.26	-6.26	-24.19	-5.39	2.840	-0.030
BLYP-D3BJ	-15.22	-8.22	-25.73	-6.93	2.806	-0.064
BMK	-0.80	6.20	-52.46	-33.66	2.621	-0.249
BMK-D3	-9.17	-2.17	-51.37	-32.57	2.625	-0.245
BMK-D3BJ	-9.67	-2.67	-52.01	-33.21	2.604	-0.266
BP86	-7.87	-0.87	-26.56	-7.76	2.748	-0.122
BP86-D3	-16.69	-9.69	-29.33	-10.53	2.748	-0.122
BP86-D3BJ	-18.19	-11.19	-30.22	-11.42	2.726	-0.144
CAM-B3LYP	4.69	11.69	-25.83	-7.03	2.596	-0.274
HSE(HSE06)	-3.39	3.61	-28.28	-9.48	2.631	-0.239
LC-wPBE	6.42	13.42	-58.86	-40.06	2.453	-0.417
M05	-4.92	2.08	-30.67	-11.87	2.619	-0.251
M052X	-4.11	2.89	-54.44	-35.64	2.559	-0.311

M052X-D3	-4.83	2.17	-54.60	-35.80	2.560	-0.310
M06	-8.50	-1.50	-30.53	-11.73	2.647	-0.223
M062X	-5.43	1.57	-52.72	-33.92	2.587	-0.283
M06HF	-2.10	4.90	-57.48	-38.68	2.495	-0.375
M06L	-11.48	-4.48	-25.25	-6.45	2.813	-0.057
M08HX	-5.38	1.62	-51.73	-32.93	2.586	-0.284
M11	-1.48	5.52	-55.25	-36.45	2.524	-0.347
M11L	-11.08	-4.08	-30.31	-11.51	2.690	-0.180
MN12SX	-7.26	-0.26	-29.54	-10.74	2.664	-0.206
MN15	-5.41	1.59	-47.71	-28.91	2.634	-0.236
MN15L	-12.89	-5.89	-28.35	-9.55	2.784	-0.086
N12SX	-3.84	3.16	-30.52	-11.72	2.599	-0.271
PBE0	-2.96	4.04	-28.98	-10.18	2.614	-0.256
PBE0-D3	-7.74	-0.74	-29.97	-11.17	2.616	-0.254
PBE0-D3BJ	-8.82	-1.82	-30.72	-11.92	2.606	-0.264
PBE	-10.07	-3.07	-27.59	-8.79	2.730	-0.140
PBE-D3	-14.58	-7.58	-28.73	-9.93	2.731	-0.139
PBE-D3BJ	-15.77	-8.77	-29.79	-10.99	2.717	-0.153
PW6B95	-2.71	4.29	-26.61	-7.81	2.650	-0.220
PW6B95D3	-6.73	0.27	-27.82	-9.02	2.648	-0.222
SOGGA11X	0.50	7.50	-31.11	-12.31	2.578	-0.292
TPSS	-6.23	0.77	-23.94	-5.14	2.762	-0.108
TPSS-D3	-12.61	-5.61	-26.22	-7.42	2.761	-0.109
TPSS-D3BJ	-13.87	-6.87	-27.21	-8.41	2.745	-0.125
WB97XD	-1.72	5.28	-30.06	-11.26	2.574	-0.296
PBE-MBD/tier-2	-14.01	-7.01	-29.97	-11.17	2.711	-0.159
PBE0-MBD/tier-2	-7.01	-0.01	-31.93	-13.13	2.593	-0.277

[a]Reference MR-AQCC values are taken from Ref.10 in main text. [b]All energies are in kcal/mol, E_{int} is defined by Equation (1) in main text. [c]All distances are in Å.

Table S3. Full computational test result of DFTs for $\mathbf{3_2}$ π-dimer.

	E_{int}[b]	E_{int} error	E_{SOMO}	E_{SOMO} error	D_{SS1}[c]	D_{SS1} error
Reference[a]	-27.70		-90.20		2.571	
APFD	-49.89	-22.19	-101.13	-10.93	2.468	-0.103
B1B95	-37.57	-9.87	-101.90	-11.70	2.464	-0.107
B1LYP	-26.97	0.73	-81.38	8.82	2.542	-0.029
O3LYP	-27.09	0.61	-87.96	2.24	2.520	-0.051
X3LYP	-30.18	-2.48	-82.88	7.32	2.546	-0.025
B3LYP	-28.95	-1.25	-81.45	8.75	2.556	-0.015
B3LYP-D3	-38.76	-11.06	-81.88	8.32	2.563	-0.008
B3LYP-D3BJ	-43.99	-16.29	-86.90	3.30	2.538	-0.033
B3PW91	-35.76	-8.06	-94.65	-4.45	2.494	-0.077
B3PW91-D3	-46.90	-19.20	-94.13	-3.93	2.505	-0.066
B3PW91-D3BJ	-52.23	-24.53	-99.33	-9.13	2.482	-0.089
B97D	-38.90	-11.20	-75.14	15.06	2.639	0.068
B97D3	-46.48	-18.78	-80.52	9.68	2.611	0.040
BLYP	-28.75	-1.05	-70.32	19.88	2.669	0.098
BLYP-D3	-40.57	-12.87	-72.25	17.95	2.677	0.106
BLYP-D3BJ	-45.99	-18.29	-77.91	12.29	2.643	0.072
BMK	-35.09	-7.39	-105.50	-15.30	2.454	-0.117
BMK-D3	-45.94	-18.24	-105.21	-15.01	2.463	-0.108
BMK-D3BJ	-48.54	-20.84	-109.72	-19.52	2.442	-0.129
BP86	-38.19	-10.49	-85.40	4.80	2.589	0.018
BP86-D3	-49.48	-21.78	-85.88	4.32	2.601	0.030
BP86-D3BJ	-53.89	-26.19	-89.99	0.21	2.577	0.006
CAM-B3LYP	-29.32	-1.62	-96.50	-6.30	2.454	-0.117
HSE	-40.91	-13.21	-98.49	-8.29	2.477	-0.094
LC-wPBE	-36.77	-9.07	-167.56	-77.36	2.342	-0.229
M05	-31.48	-3.78	-105.77	-15.57	2.450	-0.121
M052X	-44.36	-16.66	-108.19	-17.99	2.434	-0.137

M052X-D3	-44.84	-17.14	-108.05	-17.85	2.434	-0.137
M06	-36.67	-8.97	-101.08	-10.88	2.484	-0.087
M062X	-40.58	-12.88	-106.05	-15.85	2.440	-0.131
M06HF	-47.07	-19.37	-114.79	-24.59	2.385	-0.186
M06L	-39.36	-11.66	-81.10	9.10	2.640	0.069
M08HX	-43.13	-15.43	-108.88	-18.68	2.438	-0.133
M11	-40.71	-13.01	-112.41	-22.21	2.408	-0.163
M11L	-37.13	-9.43	-102.15	-11.95	2.499	-0.072
MN12SX	-36.10	-8.40	-103.84	-13.64	2.472	-0.099
MN15	-38.66	-10.96	-103.41	-13.21	2.459	-0.112
MN15L	-40.91	-13.21	-104.28	-14.08	2.524	-0.047
N12SX	-41.20	-13.50	-103.55	-13.35	2.447	-0.124
PBE0	-41.05	-13.35	-101.58	-11.38	2.459	-0.112
PBE0-D3	-46.84	-19.14	-101.01	-10.81	2.465	-0.106
PBE0-D3BJ	-49.47	-21.77	-103.42	-13.22	2.455	-0.116
PBE	-41.85	-14.15	-88.32	1.88	2.569	-0.002
PBE-D3	-47.24	-19.54	-88.34	1.86	2.574	0.003
PBE-D3BJ	-50.36	-22.66	-91.12	-0.92	2.562	-0.009
PW6B95	-37.14	-9.44	-96.96	-6.76	2.482	-0.089
PW6B95D3	-42.92	-15.22	-98.03	-7.83	2.479	-0.092
SOGGA11X	-34.95	-7.25	-109.71	-19.51	2.423	-0.148
TPSS	-37.92	-10.22	-82.35	7.85	2.602	0.031
TPSS-D3	-45.97	-18.27	-82.35	7.85	2.611	0.040
TPSS-D3BJ	-49.56	-21.86	-85.70	4.50	2.597	0.026
WB97XD	-35.07	-7.37	-104.92	-14.72	2.429	-0.142
PBE-MBD/tier-2	-32.69	-4.99	-106.82	-16.62	2.557	-0.014
PBE0-MBD/tier-2	-33.66	-5.96	-92.74	-2.54	2.446	-0.125

[a]Reference MR-AQCC values are taken from Ref.10 in main text. [b]All energies are in kcal/mol, E_{int} is defined by Equation (1) in main text. [c]All distances are in Å.

Table S4. Full computational test result of DFTs for $\mathbf{4_2}$ π-dimer.

	E_{int}[b]	E_{int} error	D_{CC2}[c]	D_{CC2} error	D_{KN}	D_{KN} error
Reference[a]	-10.10		2.735		3.869	
APFD	-11.40	-1.30	2.563	-0.172	3.515	-0.354
B1B95	-1.09	9.01	2.620	-0.115	3.695	-0.174
B1LYP[d]						
O3LYP[d]						
X3LYP	0.33	10.43	2.736	0.001	3.748	-0.121
B3LYP	1.05	11.15	2.757	0.022	3.756	-0.113
B3LYP-D3	-7.31	2.79	2.692	-0.043	3.748	-0.121
B3LYP-D3BJ	-9.41	0.69	2.650	-0.085	3.745	-0.124
B3PW91	0.38	10.48	2.688	-0.047	3.729	-0.140
B3PW91-D3	-9.17	0.93	2.627	-0.108	3.734	-0.135
B3PW91-D3BJ	-11.57	-1.47	2.587	-0.148	3.727	-0.142
B97D	-12.77	-2.67	2.706	-0.029	3.742	-0.127
B97D3	-12.75	-2.65	2.717	-0.018	3.833	-0.036
BLYP	-1.59	8.51	2.914	0.179	3.806	-0.063
BLYP-D3	-11.00	-0.90	2.801	0.066	3.822	-0.047
BLYP-D3BJ	-13.25	-3.15	2.734	-0.001	3.796	-0.073
BMK	-0.82	9.28	2.586	-0.149	3.699	-0.170
BMK-D3	-8.60	1.50	2.557	-0.178	3.688	-0.181
BMK-D3BJ	-10.18	-0.08	2.550	-0.185	3.679	-0.190
BP86	-4.38	5.72	2.774	0.039	3.756	-0.113
BP86-D3	-13.66	-3.56	2.699	-0.036	3.769	-0.100
BP86-D3BJ	-15.77	-5.67	2.659	-0.076	3.756	-0.113
CAM-B3LYP[d]						
HSE	-2.75	7.35	2.645	-0.090	3.703	-0.166
LC-wPBE	0.39	10.49	3.854	1.119	5.624	1.755
M05	-0.55	9.55	3.283	0.548	3.819	-0.050
M052X	-8.72	1.38	2.484	-0.251	3.627	-0.242

M052X-D3	-10.14	-0.04	2.485	-0.250	3.628	-0.241
M06	-5.56	4.54	2.646	-0.089	3.696	-0.173
M062X	-7.97	2.13	2.513	-0.222	3.647	-0.222
M06HF	-18.80	-8.70	2.382	-0.353	3.577	-0.292
M06L	-7.39	2.71	2.745	0.010	3.734	-0.135
M08HX	-9.09	1.01	2.528	-0.207	3.659	-0.210
M11	-2.56	7.54	2.965	0.230	3.744	-0.125
M11L	-9.57	0.53	2.741	0.006	3.748	-0.121
MN12SX	-6.86	3.24	2.672	-0.063	3.740	-0.129
MN15	-7.16	2.94	2.578	-0.157	3.689	-0.180
MN15L	-10.53	-0.43	2.746	0.011	3.794	-0.075
N12SX	-1.21	8.89	2.646	-0.089	3.706	-0.163
PBE0	-2.20	7.90	2.623	-0.112	3.695	-0.174
PBE0-D3	-7.77	2.33	2.599	-0.136	3.694	-0.175
PBE0-D3BJ	-8.90	1.20	2.584	-0.151	3.703	-0.166
PBE	-6.83	3.27	2.752	0.017	3.743	-0.126
PBE-D3	-12.12	-2.02	2.719	-0.016	3.750	-0.119
PBE-D3BJ	-13.29	-3.19	2.684	-0.051	3.745	-0.124
PW6B95	-2.57	7.53	2.634	-0.102	3.702	-0.167
PW6B95D3	-7.15	2.95	2.615	-0.120	3.708	-0.161
SOGGA11X	0.91	11.01	2.624	-0.111	3.731	-0.138
TPSS	-3.96	6.14	2.757	0.022	3.743	-0.126
TPSS-D3	-10.94	-0.84	2.707	-0.028	3.758	-0.111
TPSS-D3BJ	-12.64	-2.54	2.665	-0.070	3.745	-0.124
WB97XD	-4.05	6.05	3.126	0.391	3.846	-0.023
PBE-MBD/tier-2	-13.37	-3.27	2.668	-0.067	3.657	-0.212
PBE0-MBD/tier-2	-7.82	2.28	2.570	-0.165	3.622	-0.247

[a]Reference MR-AQCC values are taken from Ref.11 in main text. [b]All energies are in kcal/mol, E_{int} is defined by Equation (2) in main text. [c]All distances are in Å. [d]This DFT did not produce a geometry similar to the reference structure.

S2. Full results for all systems in figures.

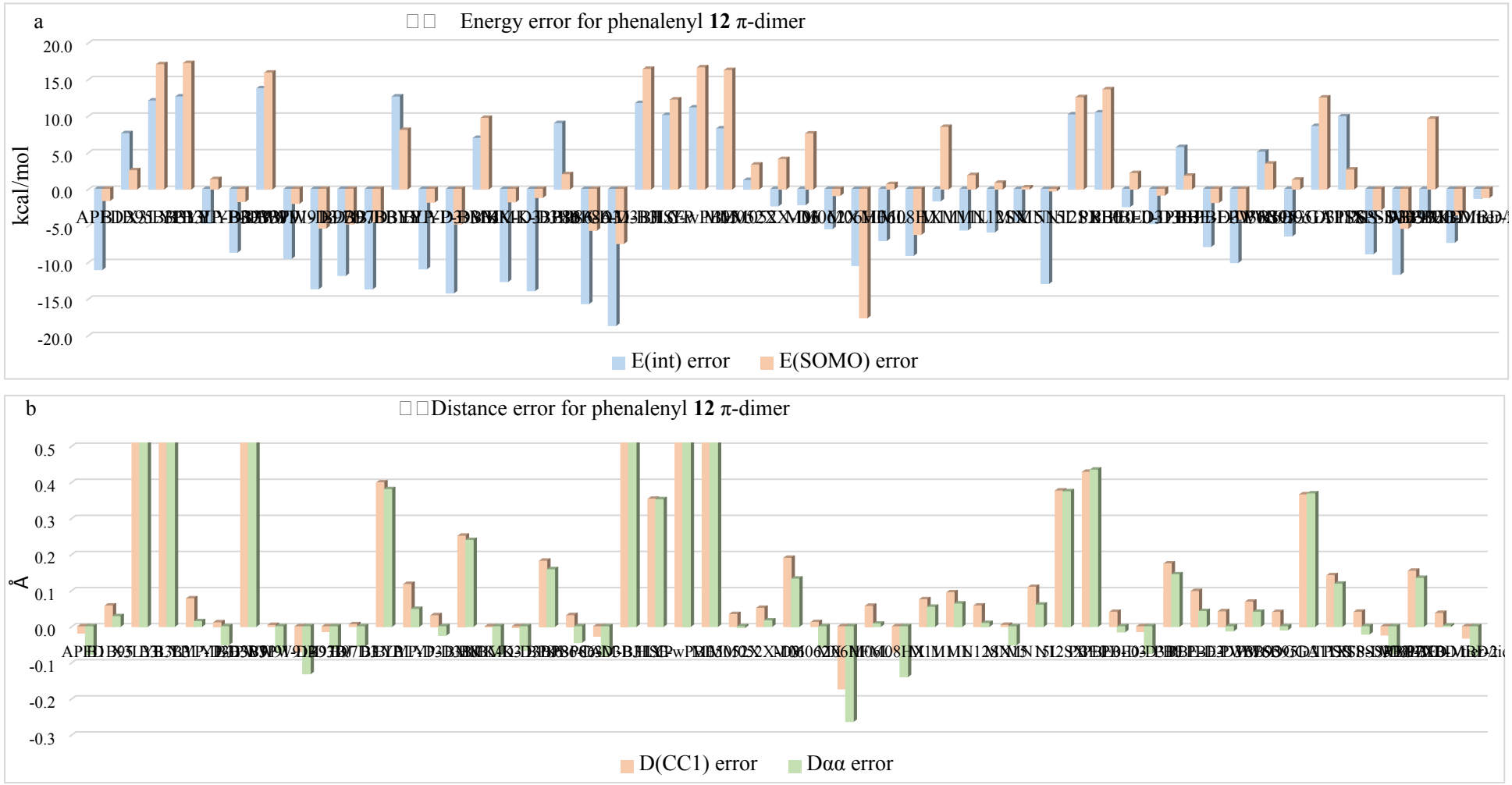

Fig S1. DFT result for PLY $\mathbf{1}_2$ π-dimer. Figure S1a shows the energy errors and Figure S1b shows distance errors compared to the MR-AQCC values. In Figure S1b, maximum Y-axis is set at 0.5 Å and methods including X3LYP, B3LYP, B3PW91, CAM-B3LYP, LC-wPBE, M05 are exceeding this limit, check exact value at Table S1. B1YLP and O3LYP are not shown in this figure because the optimized geometries are not similar to the reference structures.

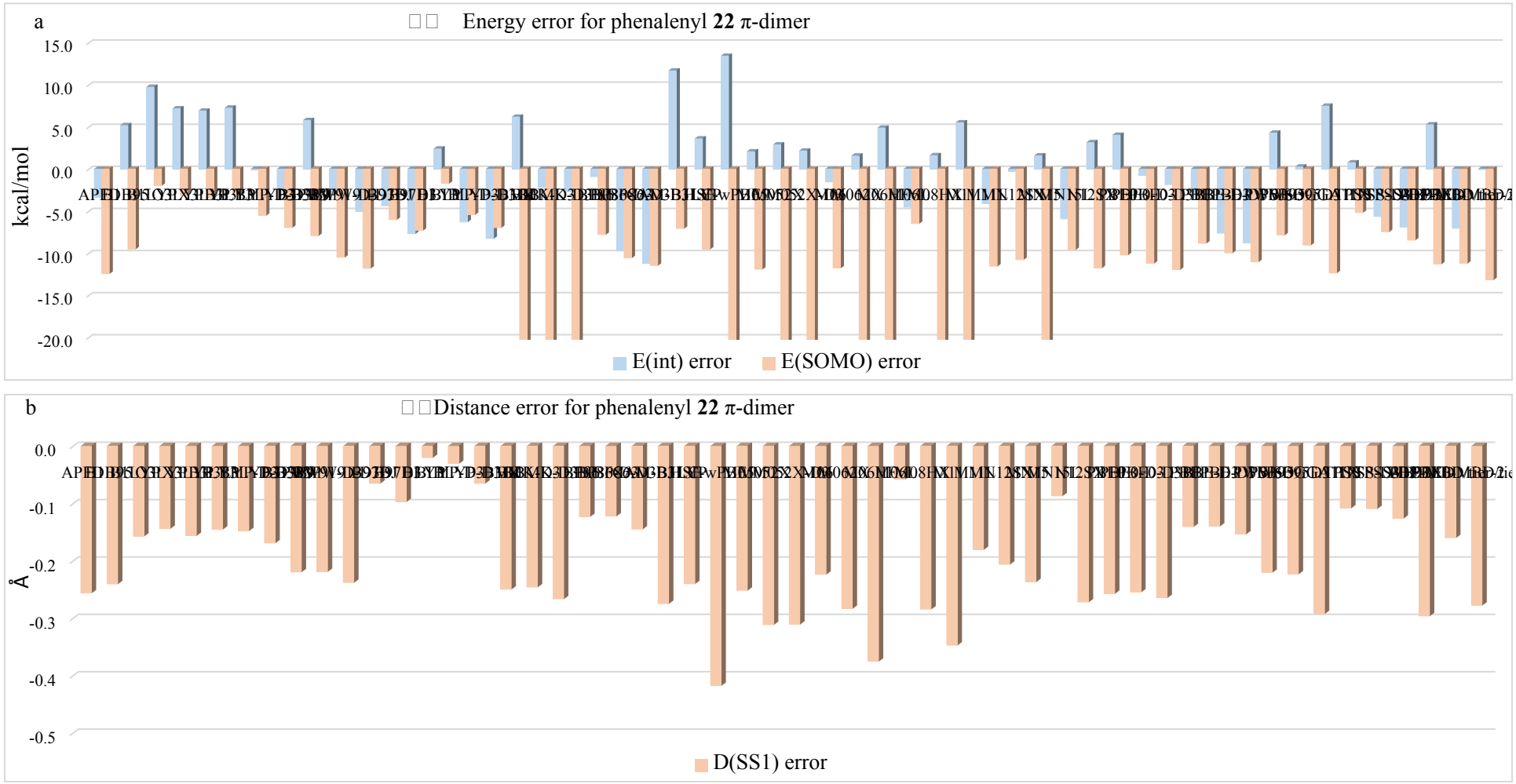

Fig S2. DFT result for $\mathbf{2_2}$ π-dimer. Figure S2a shows the energy errors and Figure S2b shows distance errors compared to the MR-AQCC values. In Figure S2a, minimum Y-axis is set at -20 kcal/mol and methods including BMK, BMK-D3, BMK-D3BJ, LC-wPBE, M05-2X, M05-2X-D3, M06-2X, M06HF, M08HX, M11, MN15 exceed the limit in E_{SOMO}. The exact E_{SOMO} values of these methods can be found at Table S2.

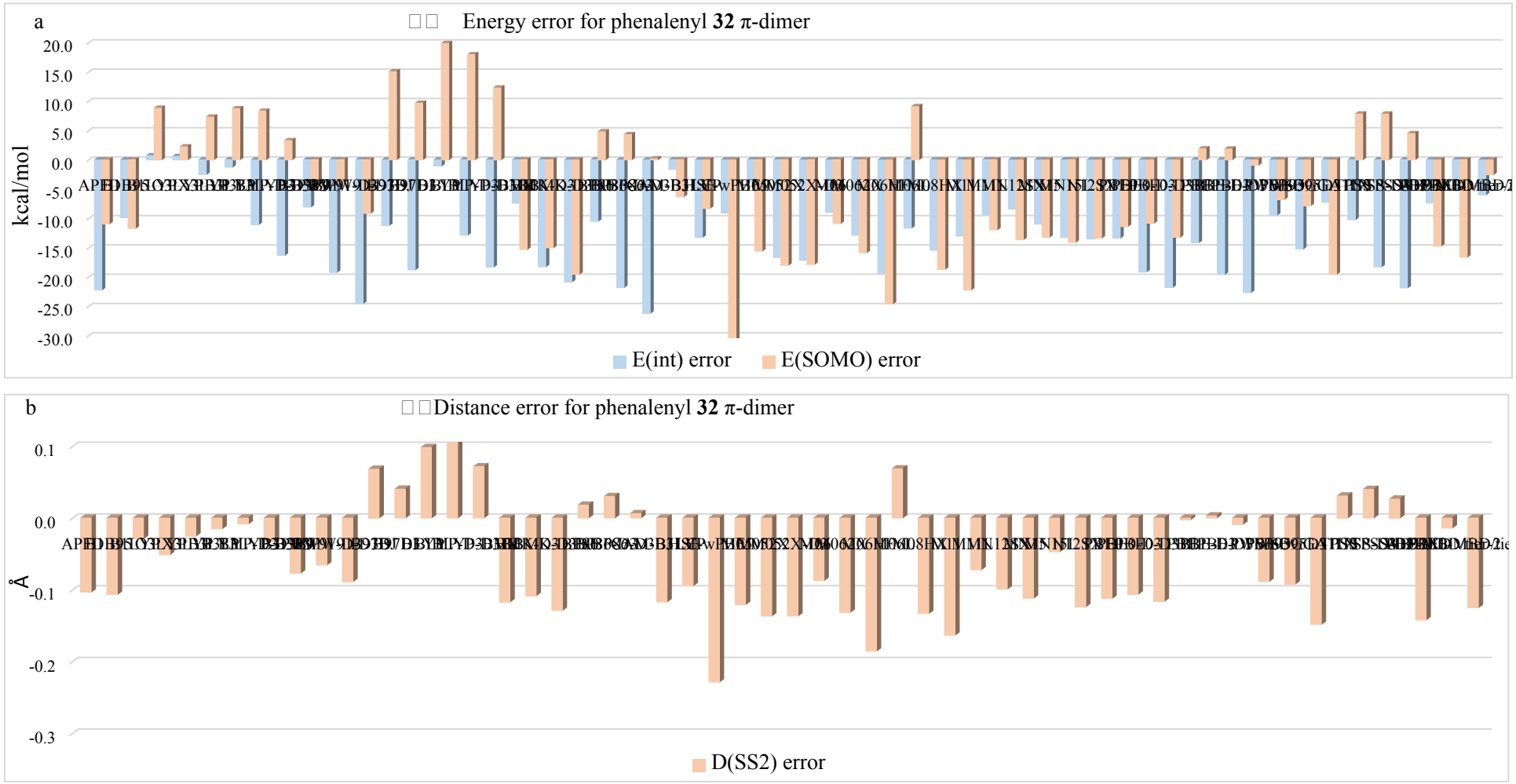

Fig S3. DFT result for $\mathbf{3_2}$ π-dimer. Figure S3a shows the energy errors and Figure S3b shows distance errors compared to the MR-AQCC values. In Figure S3a, minimum Y-axis is set at -30 kcal/mol and E_{SOMO} value for LC-wPBE is -77.36 kcal/mol which exceeds the limit.

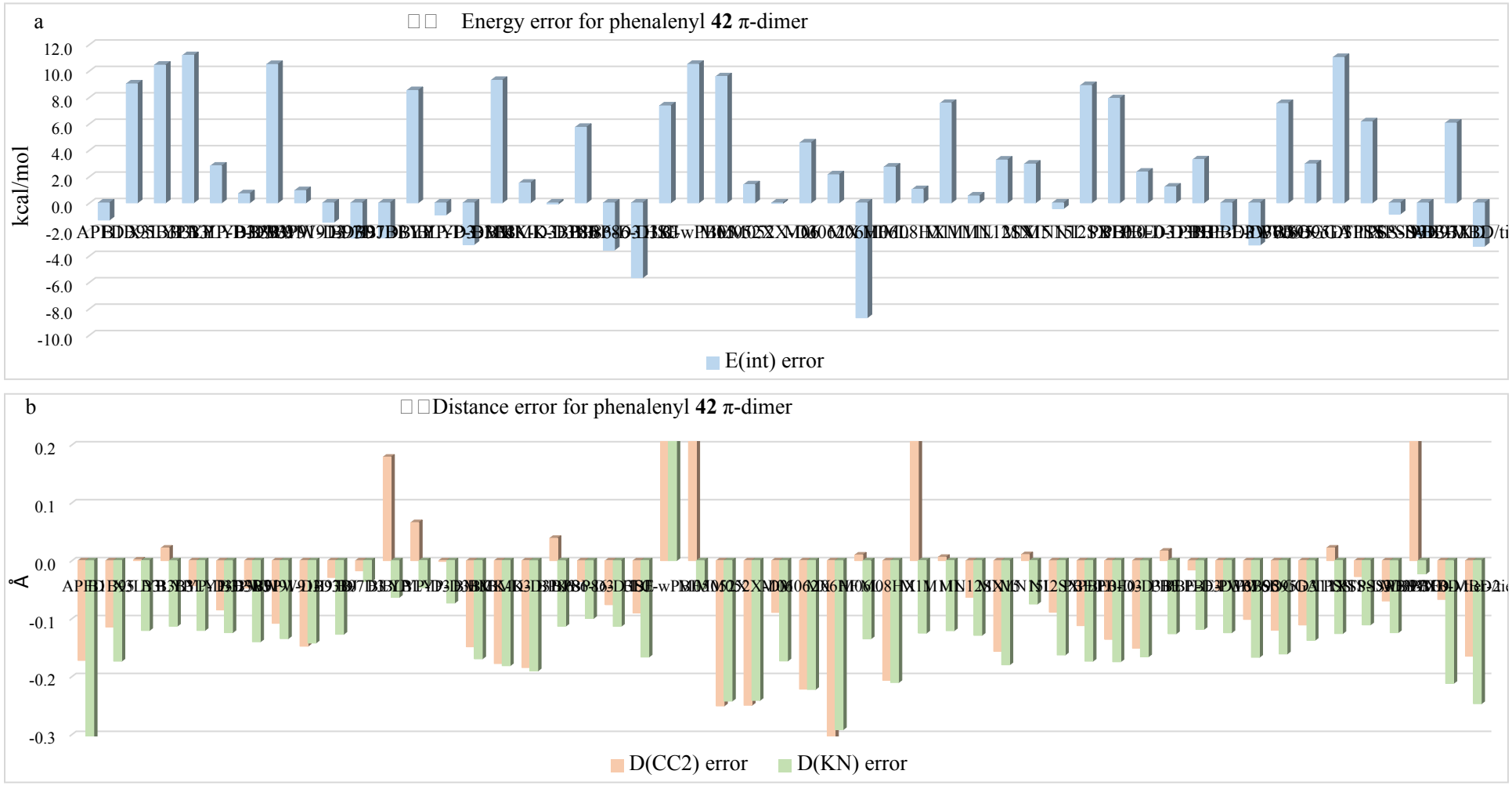

Fig S4. DFT result for $\mathbf{4_2}$ π-dimer. Figure S4a shows the energy errors and Figure S4b shows distance errors compared to the MR-AQCC values. In Figure S4b, minimum Y-axis is set at -0.3 Å and the maximum Y-axis is set at Å. Methods including APFD, LC-wPBE, M05, M06HF, M11, WB97XD exceed the limit. The exact distance error values of these DFTs can be found at Table S4. B1LYP, O3LYP and CAM-B3LYP are not shown in this figure because the optimized geometries are not similar to the reference structures.

S3. Additional computational details including D3(BJ) on selected DFTs.

Not all DFTs have dispersion correction terms available in Gaussian G16 A03 version. We selected the following DFTs with different dispersion corrections including D, D3 and D3BJ:

DFTs with D: APF, B97, WB97X.

DFTs with D3: B3LYP, B3PW91, B97, BLYP, BMK, BP86, M052X, PBE, PBE0, PW6B95, TPSS.

DFTs with D3BJ: B3LYP, B3PW91, BLYP, BMK, BP86, PBE, PBE0, TPSS.