Supporting information for:

A Comprehensive Benchmark of Association (Free) Energies for Realistic Host-Guest Complexes

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Table S1: ΔE obtained with all tested functionals for the S30L set. The two body dispersion contribution $\Delta E^{(2)}_{disp}$ is included in ΔE, the three body dispersion $\Delta E^{(3)}_{disp}$ is given independently. In case of S30L-CI counter ions were included for the complexes indicated with a "CI".

	PW6B95-D3	TPSS-D3	B3LYP-D3	PBE-D3	ωB97xD3	$\Delta E^{(3)}_{disp}$
1	-32.08	-33.011	-35.09	-29.77	-33.18	1.83
2	-21.72	-21.798	-23.01	-19.43	-21.78	1.27
3	-26.17	-22.047	-27.92	-19.97	-21.47	1.95
4	-21.07	-19.900	-21.78	-19.28	-20.35	0.74
5	-35.19	-34.818	-38.05	-30.85	-34.66	2.28
6	-31.38	-33.556	-35.85	-24.15	-24.86	1.88
7	-34.93	-35.952	-39.58	-31.63	-35.39	1.99
8	-39.73	-41.283	-45.35	-36.46	-41.00	2.22
9	-34.98	-37.468	-37.46	-30.58	-32.14	3.30
10	-36.05	-38.339	-38.77	-31.33	-33.67	3.61
11	-43.42	-46.703	-46.94	-37.95	-39.25	5.12
12	-42.88	-46.069	-46.48	-37.16	-39.19	5.07
13	-28.82	-26.917	-30.18	-25.77	-31.55	2.93
14	-31.32	-29.294	-33.21	-26.90	-33.00	3.04
15	-18.17	-22.362	-21.21	-21.41	-15.91	0.33
16	-24.51	-27.923	-26.92	-25.20	-20.09	0.49
17	-32.92	-32.803	-36.87	-33.29	-37.22	1.05
18	-21.41	-22.039	-25.73	-22.25	-24.58	1.03
19	-16.64	-16.468	-17.26	-16.91	-19.11	1.63
20	-20.18	-19.875	-21.45	-20.50	-23.75	2.33
21	-28.98	-27.347	-30.95	-26.81	-32.54	3.42
22	-33.89	-37.786	-38.52	-38.80	-37.39	0.11
23	-58.67	-57.312	-50.45	-67.86	-64.47	-0.26
24	-139.23	-133.727	-143.77	-132.30	-146.92	5.88
25	-33.17	-35.672	-37.78	-29.71	-34.39	2.70
26	-33.14	-35.709	-37.80	-29.80	-34.50	2.74
27	-84.41	-83.021	-87.67	-82.67	-89.02	2.33
28	-80.68	-79.641	-83.44	-79.02	-84.80	1.92
29	-54.79	-53.830	-56.00	-54.77	-56.77	0.52
30	-50.59	-50.187	-52.96	-50.40	-52.60	0.73
23-CI	-63.11	-71.391	-69.46	-72.44	-65.68	-0.05
24-CI	-74.16	-68.629	-77.60	-55.23	-81.44	5.77
25-CI	-35.82	-35.672	-37.78	-31.20	-35.68	2.30
26-CI	-35.62	-35.709	-37.80	-34.31	-35.50	1.90
27-CI	-34.63	-34.458	-37.83	-34.31	-39.34	2.49
28-CI	-29.41	-29.701	-32.40	-29.44	-33.74	2.53
29-CI	-47.18	-44.473	-49.07	-44.18	-46.72	0.49
30-CI	-47.70	-45.667	-51.08	-44.71	-46.46	1.01

Table S2: $\Delta E_{el}^{semiemp}$ obtained with all tested semiempirical methods for the S30L set. The two body dispersion contribution $\Delta E_{disp}^{(2)}$ is included. In case of S30L-CI counter ions were included for the complexes indicated with a "CI".

	HF-3c	DFTB-D3	PM6-D3	PM6-D3H+	PM6-D3H2	PM6-D3H4	PM7	OM2-D3
1	-30.89	-28.62	-29.42	-29.42	-29.42	-31.53	-38.49	-32.28
2	-21.26	-19.88	-19.64	-19.64	-19.64	-21.75	-26.70	-20.47
3	-20.78	-23.94	-25.74	-24.23	-24.94	-27.85	-32.04	-24.94
4	-19.22	-18.79	-20.17	-18.93	-19.97	-22.28	-24.23	-
5	-34.38	-34.07	-34.92	-34.74	-34.74	-37.03	-45.56	-34.64
6	-25.71	-24.61	-26.04	-26.01	-26.01	-28.14	-35.51	-23.59
7	-39.88	-38.78	-31.20	-31.20	-31.20	-33.31	-49.45	-30.04
8	-45.32	-44.03	-35.17	-35.17	-35.17	-37.28	-57.31	-33.89
9	-37.37	-36.37	-30.39	-30.39	-30.39	-32.50	-57.19	-32.71
10	-39.26	-38.10	-31.82	-31.82	-31.82	-33.92	-60.79	-33.68
11	-39.28	-44.49	-41.49	-41.48	-41.48	-43.59	-75.20	-
12	-39.69	-44.33	-41.69	-41.69	-41.69	-43.80	-75.97	-
13	-28.06	-26.75	-28.17	-27.77	-27.63	-30.27	-35.81	-25.45
14	-29.68	-30.64	-29.90	-29.68	-29.68	-32.01	-36.04	-
15	-38.97	-36.63	-31.82	-31.82	-35.38	-35.56	-4.03	-
16	-52.12	-42.40	-41.36	-41.35	-48.25	-45.79	-8.91	-
17	-28.56	-31.15	-43.63	-42.53	-45.00	-45.74	-45.09	-36.47
18	-20.47	-23.08	-33.03	-32.42	-32.32	-35.14	-34.48	-26.67
19	-16.41	-17.15	-19.66	-21.89	-22.03	-21.77	-19.26	-15.43
20	-19.79	-22.62	-25.62	-27.38	-27.52	-27.72	-25.23	-20.75
21	-27.62	-28.22	-28.12	-28.33	-27.22	-30.23	-33.16	-23.82
22	-39.52	-33.76	-42.37	-42.22	-44.57	-44.47	-49.26	-34.99
23	-66.17	-41.69	-57.24	-58.79	-57.22	-59.35	-72.11	-50.40
24	-144.10	-162.05	-166.42	-164.68	-164.68	-168.53	-183.77	-162.21
25	-34.08	-29.38	-24.33	-24.33	-24.33	-26.44	-50.48	-27.11
26	-34.28	-29.49	-24.11	-24.11	-24.11	-26.22	-50.85	-26.97
27	-92.41	-95.17	-95.32	-94.92	-92.76	-97.43	-112.65	-94.98
28	-88.76	-89.88	-92.37	-91.95	-90.13	-94.48	-110.49	-91.20
29	-68.72	-58.39	-41.06	-49.80	-59.37	-77.21	-53.64	-89.93
30	-65.11	-56.79	-73.22	-46.69	-59.77	-76.41	-53.72	-147.72
23-CI	-72.46	-47.47	-110.74	-55.88	-112.28	-124.59	-68.76	-
24-CI	-64.82	-87.86	-82.35	-81.14	-81.14	-84.60	-83.11	-
25-CI	-37.76	-34.71	-27.86	-27.86	-27.86	-30.10	-50.81	-
26-CI	-37.80	-34.77	-27.57	-27.58	-27.58	-29.82	-51.37	-
27-CI	-38.65	-42.97	-42.85	-42.20	-39.77	-45.09	-58.42	-
28-CI	-33.89	-36.83	-39.59	-38.28	-37.44	-41.83	-56.81	-
29-CI	-71.57	-61.74	-51.78	-47.08	-52.94	-60.20	-41.36	-
30-CI	-81.65	-61.16	-58.02	-55.89	-57.27	-63.58	-42.98	-

Table S3: ΔG_{RRHO} obtained with all tested semiempirical methods for the S30L set. In case of S30L-CI counter ions were included for the complexes indicated with a "CI".

	HF-3c	DFTB-D3	PM6-D3
1	15.80	14.54	13.35
2	15.01	14.63	14.79
3	16.65	23.12	16.01
4	15.48	15.04	15.22
5	17.46	22.52	15.28
6	15.71	15.42	14.18
7	21.54	22.53	20.91
8	23.87	24.45	21.58
9	16.83	13.59	16.53
10	17.45	13.77	16.56
11	16.59	14.33	18.55
12	17.42	14.36	18.99
13	14.94	14.52	15.82
14	15.52	15.65	15.43
15	17.84	16.41	19.96
16	19.31	16.75	19.61
17	17.18	16.87	16.29
18	16.15	16.13	15.62
19	15.54	14.97	16.63
20	16.50	16.20	16.11
21	16.26	17.46	18.74
22	19.60	19.31	23.78
23	18.27	16.07	17.90
24	21.39	20.77	26.71
25	17.60	18.17	17.95
26	17.84	17.51	16.59
27	15.29	18.30	13.03
28	14.82	17.05	12.16
29	19.54	15.73	16.10
30	20.13	17.18	22.17
23-CI	18.27	16.07	17.90
24-CI	21.39	20.77	26.71
25-CI	17.60	18.17	17.95
26-CI	17.84	17.51	16.59
27-CI	15.29	18.30	13.03
28-CI	14.82	17.05	12.16
29-CI	19.54	15.73	16.10
30-CI	20.13	17.18	22.17

Table S4: ΔG_{solv} obtained with all tested continuum solvation models for the S30L set. In case of S30L-CI counter ions were included for the complexes indicated with a "CI".

	COSMO-RS	12	13	13 fine	14	14 fine	SMD
1		9.04	9.08	9.28	9.31	9.8	12.97
2		4.37	4.34	4.35	4.48	5.18	8.71
3		5.39	5.62	5.51	5.77	6.5	6.62
4		2.99	3.44	2.94	3.35	3.1	5.57
5		6.33	6.47	6.48	6.70	8.91	11.04
6		5.19	5.39	5.50	5.50	7.67	10.39
7		8.02	8.23	8.78	8.33	10.69	10.93
8		10.72	10.88	11.57	11.05	13.84	12.09
9		6.25	5.52	5.75	7.06	8.35	14.68
10		7.23	6.33	6.58	8.05	9.75	16.25
11		11.96	7.80	8.07	11.13	13.08	18.21
12		12.30	7.99	8.21	11.41	14.25	17.71
13		5.89	5.36	5.38	6.08	6.37	6.58
14		6.81	6.16	5.60	6.97	7.28	7.42
15		-1.16	-1.27	-1.18	-0.95	-1.71	-0.31
16		0.71	0.39	0.47	0.89	-0.09	1.48
17		7.90	7.74	7.47	8.09	8.03	12.82
18		3.86	4.08	4.20	4.09	5.33	11.54
19		-1.38	-2.51	-1.08	-1.43	-1.62	0.54
20		-2.56	-3.59	-2.15	-2.55	-2.9	-0.70
21		-9.11	-7.95	-6.15	-8.21	-9.24	3.43
22		11.3	10.78	8.80	11.47	8.78	13.18
23		25.75	25.69	23.96	26.25	23.65	34.76
24		83.85	86.27	89.42	85.54	81.27	88.17
25		3.96	3.17	2.22	3.70	4.86	3.27
26		3.73	3.00	1.85	3.60	4.49	4.20
27		54.33	57.14	59.99	56.09	52.55	48.75
28		54.05	56.79	59.59	55.77	53.26	50.43
29		25.80	27.40	28.60	27.04	26.901	29.74
30		21.46	23.22	24.61	22.97	23.278	23.35
23-CI		27.428	33.92	31.71	34.69	30.94	20.37
24-CI		27.21	28.00	29.32	27.27	27.4	26.43
25-CI		8.10	7.42	7.07	7.96	7.76	7.43
26-CI		7.89	7.25	7.34	7.78	7.51	8.23
27-CI		10.59	10.94	14.12	10.44	10	7.05
28-CI		8.45	8.67	11.44	8.20	8.77	8.19
29-CI		22.08	21.03	19.77	21.63	20.12	16.17
30-CI		26.74	25.74	24.26	26.70	25.08	16.71

Table S5: Comparison of ΔG_{RRHO} obtained with semi-empirical methods with those obtained from TPSS-D3/def2-TZVP calculations for eight complexes. The MAD and MD is given w.r.t. TPSS-D3.

	TPSS-D3	HF-3c	DFTB-D3	PM6-D3
1	14.4	15.8	16.8	13.3
3	16.8[a]	18.3	23.6	16.0
7	21.4	21.5	21.8	19.1
9	16.8[a]	17.0	18.7	16.8
15	18.3	17.8	16.4	20.0
17	17.4[a]	17.2	17.3	16.3
22	19.2	18.7	16.1	17.9
25	18.1	18.1	18.2	17.9
MAD		0.4	1.6	1.1
MD		0.1	0.3	0.4

[a] Taken from: S. Grimme *Chem. Eur. J.*, **2012**, 18, 9955-9964.

Table S6: Comparison of the reference binding energies ΔE^{emp} for the complexes that were already contained in the S12L set, with the old empirical reference values and binding energies obtained from DFT-SAPT and DQMC calculations. For convenience we also provide PBE-MBD* and PBE-D3+ATM values.

	ΔE^{emp}	$\Delta E^{emp[a]}_{old}$	ΔE (DFT-SAPT)[b]	ΔE (DQMC)[c]	ΔE (PBE-MBD*)[c]	ΔE (PBE-D3+ATM)
1	-29.0	-30.0	-30.00	-27.2	-29.0	-27.9
2	-20.8	-20.4	-19.3	-17.2	-18.8	-18.2
3	-23.5	-24.8	-27.0	-	-	-18.0
4	-20.3	-20.7	-22.0	-	-	-18.5
9	-28.4	-27.9	-33.9	-25.8	-28.3	-27.3
10	-29.8	-29.3	-35.2	-	-	-27.7
17	-33.4	-34.8	-33.0	-33.4	-33.8	-32.2
18	-23.3	-23.2	-21.5	-	-	-21.2
21	-24.2	-22.6	-27.7	-24.1	-27.4	-23.4
27	-82.2	-77.4	-82.4	-81.0	-82.1	-80.3
28	-80.1	-77.1	-78.7	-	-	-77.1

[a] Taken from: T. Risthaus, S. Grimme *J. Chem. Theory Comp.*, **2013**, *9*, 1580–1591.
[b] Taken from: A. Heßelmann, T. Korona *J. Chem. Phys.*, **2014**, *141*, 094107.
[c] Taken from: A. Ambrosetti, D. Alfè, R. A. DiStasio, A. Tkatchenko *J. Phys. Chem. Lett.*, **2014**, *5*, 849–855.

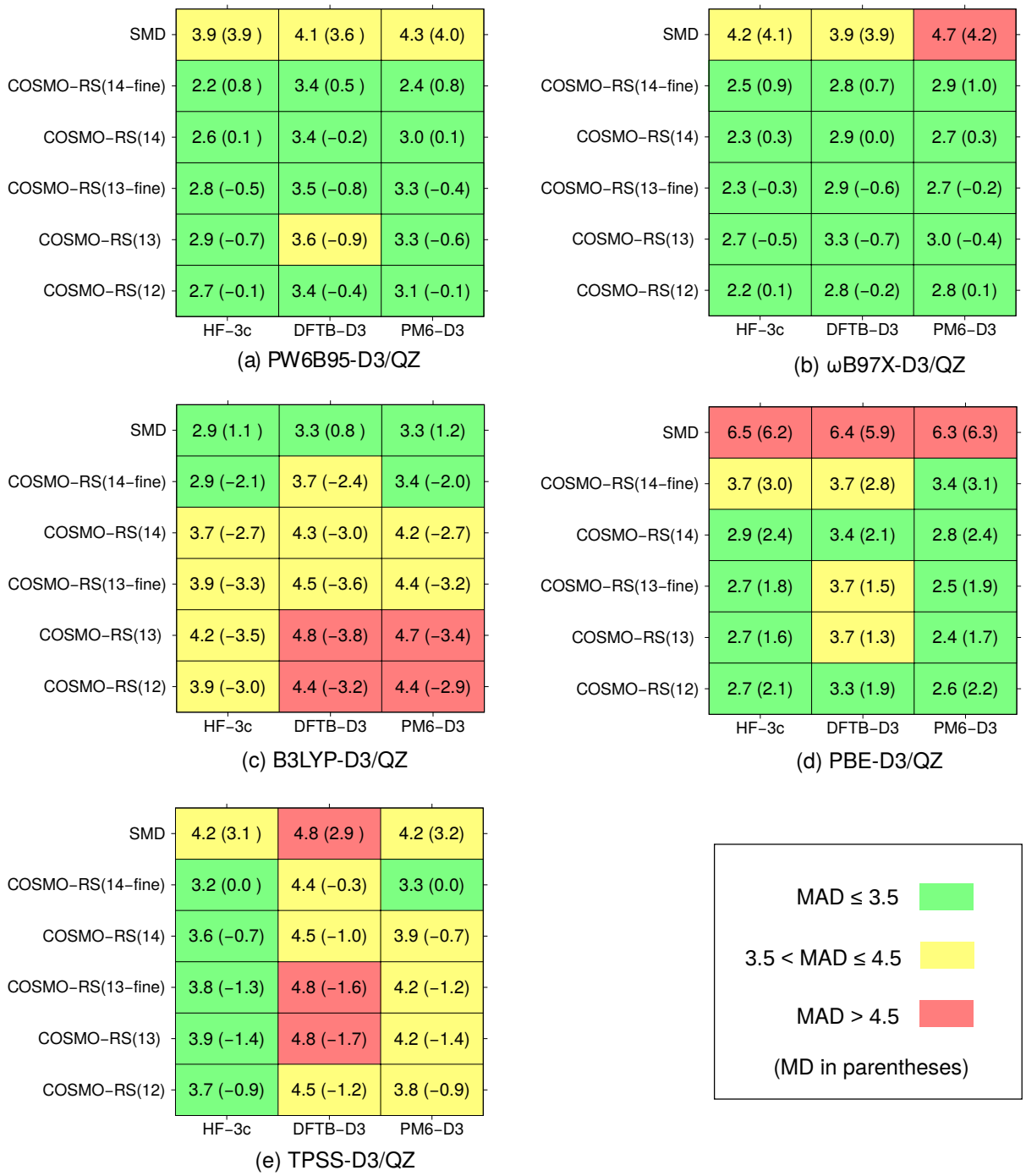

Figure S1: MADs (and MDs) for several combination of functionals (PW6B95-D3, B3LYP-D3, TPSS-D3 and PBE-D3 for ΔE), semi-empirical methods for frequencies (HF-3c, DFTB-D3 and PBE-D3 for ΔG^{T}_{RRHO}), and continuum solvation models (SMD and COSMO-RS with several parametrizations for $\Delta\delta G_{solv}$) w.r.t. to experimental ΔG_a for the S30L test set without the charged system **23** to **30**. The three body dispersion contribution $\Delta E^{(3)}_{disp}$ is included in ΔE.