Supplementary material to: Role of exact exchange in thermally-assisted-occupation density functional theory: A proposal of new hybrid schemes

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TABLES

TABLE S1. Comparison of errors of the reaction energies (in kcal/mol) of the 30 chemical reactions in the NHTBH38/04 and HTBH38/04 sets [1]. For all the TAO-DFT calculations, the optimal θ values given in TABLE I are adopted.

		KS-DFT				TAO-DFT			
Reactions	ΔE_{ref}	B3LYP	B3LYP-D3	PBE0	BHHLYP	B3LYP	B3LYP-D3	PBE0	BHHLYP
$H + N_2O \rightarrow OH + N_2$	-65.08	3.64	3.78	10.20	-10.47	3.81	3.95	10.52	-9.57
$H + FCH_3 \rightarrow HF + CH_3$	-26.64	-0.21	0.24	2.60	-0.96	0.26	0.71	3.09	-0.12
$H + F_2 \rightarrow HF + F$	-103.91	0.22	0.22	0.29	-14.00	0.01	0.01	0.10	-14.21
$CH_3 + FCl \rightarrow CH_3F + Cl$	-52.74	0.20	-0.25	0.08	-5.06	-2.34	-2.79	-1.84	-6.80
$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	-32.65	-2.16	-2.06	-2.24	-5.81	-1.26	-1.15	-1.27	-4.47
$F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$	-26.73	0.42	0.42	0.04	-3.83	1.07	1.07	0.82	-2.75
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	-20.11	0.15	-0.01	-0.80	-0.91	0.24	0.08	-0.73	-0.82
$OH^-\cdots CH_3F \rightarrow HOCH_3\cdots F^-$	-36.24	-1.53	-1.17	-4.00	-1.93	-1.45	-1.09	-3.93	-1.66
$H + N_2 \rightarrow HN_2$	3.97	-7.38	-7.41	-7.11	-6.54	-8.44	-8.46	-8.40	-9.03
$H + CO \rightarrow HCO$	-19.51	-5.68	-5.80	-5.65	-3.84	-6.89	-7.01	-7.13	-6.68
$H + C_2H_4 \rightarrow CH_3CH_2$	-40.03	-1.88	-2.14	-3.42	-4.90	-2.96	-3.22	-4.72	-7.40
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	-26.12	2.68	1.02	-4.34	0.09	0.87	-0.79	-6.46	-4.00
$HCN \rightarrow HNC$	15.05	-1.00	-0.98	-1.19	-2.56	-0.81	-0.79	-0.97	-2.23
$H + HCl \rightarrow H_2 + Cl$	-3.0	-1.50	-1.49	4.28	-2.79	-3.51	-3.51	2.93	-3.66
$OH + H_2 \rightarrow H + H_2O$	-16.1	3.25	3.25	-1.23	6.54	3.09	3.09	-1.56	5.58
$CH_3 + H_2 \rightarrow H + CH_4$	-3.2	2.41	2.38	-1.81	2.52	1.80	1.77	-2.51	1.24
$OH + CH_4 \rightarrow CH_3 + H_2O$	-12.9	0.84	0.86	0.58	4.01	1.30	1.32	0.95	4.34
$OH + NH_3 \rightarrow H_2O + NH_2$	-9.5	-0.44	-0.43	-0.18	1.57	-0.20	-0.19	-0.02	1.68
$HCl + CH_3 \rightarrow Cl + CH_4$	-6.2	0.91	0.89	2.47	-0.27	-1.72	-1.74	0.42	-2.42
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	-16.5	-0.18	0.16	-0.38	3.69	0.26	0.59	-0.04	3.90
$F + H_2 \rightarrow HF + H$	-31.6	1.81	1.81	-1.70	7.63	1.53	1.53	-2.13	6.55
$O + CH_4 \rightarrow OH + CH_3$	5.6	-3.26	-3.23	-2.38	0.94	-3.01	-2.99	-2.17	1.22
$H + PH_3 \rightarrow PH_2 + H_2$	-20.1	-3.71	-3.61	0.33	-3.18	-3.34	-3.23	0.75	-2.45
$H + HO \rightarrow H_2 + O$	-2.4	0.85	0.85	4.19	-3.47	1.22	1.22	4.67	-2.46
$H + H_2S \rightarrow H_2 + HS$	-13.8	-2.32	-2.29	2.79	-2.74	-4.24	-4.21	1.49	-3.70
$O + HCl \rightarrow OH + Cl$	-0.6	-2.35	-2.34	0.08	0.67	-4.73	-4.73	-1.74	-1.20
$NH_2 + CH_3 \rightarrow CH_4 + NH$	-14.4	3.44	3.42	3.03	1.65	3.30	3.28	2.89	1.52
$NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$	-10.8	4.46	4.13	3.99	1.98	4.34	4.01	3.87	1.96
$C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$	-7.0	0.26	0.58	-0.20	2.12	0.46	0.78	-0.02	2.22
$NH_2 + CH_4 \rightarrow CH_3 + NH_3$	-3.3	1.18	1.19	0.66	2.34	1.40	1.40	0.87	2.56
MSE		-0.23	-0.27	-0.03	-1.25	-0.66	-0.70	-0.41	-1.76
MAE		2.01	1.95	2.41	3.63	2.33	2.36	2.63	3.95
rms		2.66	2.61	3.35	4.72	3.05	3.07	3.69	5.00
Max(−)		-7.38	-7.41	-7.11	-14.00	-8.44	-8.46	-8.40	-14.21
Max(+)		4.46	4.13	10.20	7.63	4.34	4.01	10.52	6.55

TABLE S2. The 166 experimentally determined equilibrium bond lengths (in Å) of 136 molecules included in EXTS [2]. Optimized bond lengths are calculated using various methods. For all the TAO-DFT calculations, the optimal θ values given in TABLE I are adopted.

		KS-DFT				TAO-DFT			
Molecule	Experiment	B3LYP	B3LYP-D3	PBE0	BHHLYP	B3LYP	B3LYP-D3	PBE0	BHHLYP
H_2N^-	1.028	1.028	1.028	1.027	1.017	1.027	1.027	1.025	1.015

NO^- ($^3\Sigma^-$)	1.258	1.260	1.260	1.250	1.243	1.258	1.258	1.247	1.239
PO^- ($^3\Sigma^-$)	1.540	1.542	1.542	1.534	1.520	1.539	1.539	1.531	1.515
BeH^+ ($^1\Sigma^+$)	1.312	1.314	1.315	1.319	1.305	1.310	1.311	1.315	1.299
CH^+ ($^1\Sigma^+$)	1.131	1.136	1.136	1.139	1.122	1.135	1.135	1.138	1.120
CN^+ ($^1\Sigma^+$)	1.173	1.172	1.172	1.170	1.160	1.195	1.195	1.188	1.170
H_3^+	0.877	0.880	0.880	0.881	0.873	0.878	0.878	0.879	0.868
H_3O^+	0.976	0.980	0.980	0.977	0.969	0.979	0.979	0.976	0.967
HCO^+	1.097 (CH)	1.095	1.096	1.097	1.088	1.094	1.095	1.095	1.085
	1.105 (CO)	1.101	1.101	1.099	1.088	1.100	1.100	1.099	1.086
MgH^+ ($^1\Sigma^+$)	1.652	1.657	1.657	1.659	1.644	1.653	1.653	1.655	1.641
NO^+ ($^1\Sigma^+$)	1.063	1.056	1.056	1.054	1.041	1.056	1.056	1.053	1.040
NS^+ ($^1\Sigma^+$)	1.440	1.427	1.427	1.422	1.405	1.426	1.426	1.421	1.404
OH^+ ($^3\Sigma^-$)	1.029	1.037	1.037	1.031	1.021	1.036	1.036	1.030	1.019
SiH^+ ($^1\Sigma^+$)	1.504	1.515	1.515	1.518	1.500	1.513	1.513	1.517	1.498
NH_4^+	1.021	1.024	1.024	1.022	1.015	1.023	1.023	1.021	1.013
AlCl ($^1\Sigma^+$)	2.130	2.159	2.159	2.144	2.142	2.156	2.157	2.140	2.137
AlF ($^1\Sigma^+$)	1.654	1.679	1.679	1.672	1.659	1.678	1.678	1.671	1.657
AlH ($^1\Sigma^+$)	1.648	1.661	1.661	1.664	1.646	1.656	1.656	1.658	1.635
AlN ($^3\Pi_i$)	1.786	1.792	1.792	1.788	1.794	1.801	1.801	1.793	1.794
BCl ($^1\Sigma^+$)	1.797	1.719	1.719	1.715	1.707	1.717	1.717	1.713	1.702
BeO ($^1\Sigma^+$)	1.331	1.320	1.320	1.317	1.300	1.329	1.329	1.326	1.310
BeS ($^1\Sigma^+$)	1.742	1.739	1.739	1.736	1.724	1.763	1.764	1.759	1.750
BF ($^1\Sigma^+$)	1.263	1.260	1.260	1.258	1.248	1.260	1.260	1.258	1.247
BF_3	1.307	1.312	1.312	1.307	1.298	1.311	1.311	1.306	1.296
BH ($^1\Sigma^+$)	1.232	1.231	1.231	1.240	1.220	1.228	1.228	1.235	1.213
BN ($^3\Pi$)	1.281	1.317	1.317	1.315	1.300	1.317	1.317	1.314	1.300
C_6H_6	1.390 (CC)	1.391	1.391	1.388	1.382	1.390	1.390	1.386	1.380
	1.086 (CH)	1.082	1.082	1.083	1.074	1.081	1.080	1.082	1.071
CCl_2O	1.177 (CO)	1.173	1.173	1.172	1.161	1.173	1.173	1.172	1.161
	1.737 (CCl)	1.753	1.755	1.734	1.732	1.751	1.753	1.731	1.727
CF_4	1.315	1.324	1.325	1.316	1.305	1.323	1.324	1.315	1.303
CH_2Cl_2	1.766 (CCl)	1.780	1.782	1.761	1.762	1.777	1.780	1.758	1.757
	1.080 (CH)	1.082	1.083	1.084	1.074	1.081	1.082	1.083	1.072
CH_2F_2	1.351 (CF)	1.360	1.361	1.350	1.341	1.359	1.360	1.349	1.339
	1.084 (CH)	1.090	1.091	1.092	1.081	1.088	1.089	1.091	1.078
CH_2O_2 (*trans*)	1.201 (C=O)	1.196	1.196	1.194	1.184	1.196	1.196	1.193	1.183
	1.091 (CH)	1.096	1.097	1.098	1.087	1.095	1.095	1.096	1.084
	1.340 (CO)	1.343	1.344	1.334	1.325	1.342	1.343	1.333	1.323
	0.969 (OH)	0.970	0.970	0.967	0.957	0.969	0.969	0.966	0.955
CH_3Cl	1.086 (CH)	1.084	1.085	1.086	1.077	1.083	1.084	1.085	1.074
	1.778 (CCl)	1.794	1.796	1.771	1.776	1.791	1.794	1.768	1.771
CH_3F	1.086 (CH)	1.089	1.090	1.091	1.082	1.088	1.088	1.089	1.078
	1.383 (CF)	1.389	1.390	1.375	1.369	1.388	1.389	1.374	1.367
CH_4	1.087	1.088	1.088	1.089	1.081	1.086	1.087	1.087	1.078
CHF_3	1.328 (CF)	1.338	1.339	1.329	1.320	1.337	1.338	1.328	1.318
	1.091 (CH)	1.089	1.090	1.091	1.080	1.088	1.089	1.090	1.077
Cl_2 ($^1\Sigma_g^+$)	1.988	2.010	2.010	1.979	1.983	2.012	2.012	1.981	1.986
ClCN	1.629 (CCl)	1.630	1.631	1.620	1.622	1.628	1.629	1.618	1.618
	1.160 (CN)	1.153	1.153	1.152	1.138	1.152	1.152	1.151	1.136
ClF	1.628	1.642	1.642	1.621	1.609	1.642	1.642	1.621	1.609
CO ($^1\Sigma^+$)	1.128	1.124	1.124	1.123	1.112	1.124	1.124	1.122	1.111
CO_2	1.160	1.159	1.159	1.156	1.145	1.158	1.158	1.155	1.144

CS ($^1\Sigma^+$)	1.535	1.532	1.532	1.529	1.516	1.531	1.531	1.528	1.514
CS_2	1.553	1.554	1.554	1.549	1.541	1.553	1.553	1.547	1.539
F_2 ($^1\Sigma_g^+$)	1.412	1.394	1.394	1.373	1.357	1.394	1.394	1.372	1.356
F_2O	1.405	1.398	1.399	1.377	1.361	1.397	1.398	1.376	1.359
F_2S	1.587	1.609	1.609	1.594	1.580	1.608	1.608	1.593	1.578
F_2Si	1.590	1.614	1.615	1.607	1.593	1.613	1.614	1.606	1.591
F_3HSi	1.562 (SiF)	1.582	1.581	1.576	1.563	1.580	1.580	1.574	1.561
	1.447 (SiH)	1.454	1.452	1.458	1.444	1.451	1.450	1.455	1.439
H_2 ($^1\Sigma_g^+$)	0.741	0.743	0.743	0.745	0.737	0.741	0.741	0.743	0.732
H_2CCCH_2	1.076 (CH)	1.083	1.083	1.084	1.075	1.082	1.082	1.082	1.072
	1.308 (CC)	1.300	1.300	1.299	1.292	1.299	1.299	1.298	1.289
H_2CS	1.611 (CS)	1.606	1.607	1.600	1.592	1.607	1.607	1.600	1.592
	1.086 (CH)	1.087	1.088	1.089	1.079	1.086	1.086	1.087	1.076
H_2O	0.958	0.961	0.961	0.958	0.950	0.960	0.960	0.957	0.948
H_2S	1.336	1.342	1.342	1.341	1.331	1.340	1.340	1.339	1.327
H_2Si	1.514	1.522	1.522	1.525	1.509	1.518	1.518	1.519	1.501
HCCCN	1.062 (CH)	1.062	1.063	1.065	1.056	1.061	1.061	1.063	1.053
	1.206 (C≡C)	1.201	1.201	1.200	1.187	1.200	1.200	1.200	1.186
	1.376 (CC)	1.368	1.368	1.368	1.371	1.367	1.367	1.366	1.367
	1.161 (C≡N)	1.155	1.155	1.154	1.139	1.154	1.154	1.153	1.139
HCCH	1.061 (CH)	1.062	1.062	1.064	1.055	1.060	1.061	1.062	1.052
	1.203 (CC)	1.196	1.196	1.197	1.186	1.195	1.195	1.195	1.183
HCl ($^1\Sigma^+$)	1.275	1.281	1.281	1.278	1.270	1.279	1.279	1.276	1.267
HCN	1.065 (CH)	1.066	1.066	1.068	1.059	1.065	1.065	1.066	1.056
	1.153 (CN)	1.146	1.146	1.145	1.133	1.145	1.145	1.144	1.132
HCP	1.066 (CH)	1.070	1.071	1.073	1.063	1.069	1.069	1.071	1.060
	1.540 (CP)	1.533	1.533	1.530	1.517	1.532	1.532	1.529	1.516
HF ($^1\Sigma^+$)	0.917	0.922	0.922	0.918	0.910	0.921	0.921	0.917	0.908
HNC	0.994 (NH)	0.997	0.997	0.997	0.988	0.996	0.996	0.995	0.986
	1.169 (NC)	1.164	1.164	1.164	1.152	1.164	1.164	1.163	1.151
HOCl	0.964 (OH)	0.967	0.967	0.964	0.954	0.966	0.966	0.963	0.952
	1.689 (OCl)	1.699	1.700	1.675	1.665	1.699	1.699	1.674	1.663
LiCl ($^1\Sigma^+$)	2.021	2.022	2.022	2.018	2.012	2.018	2.019	2.013	2.010
LiF ($^1\Sigma^+$)	1.564	1.572	1.572	1.570	1.558	1.569	1.570	1.568	1.554
LiH ($^1\Sigma^+$)	1.596	1.589	1.590	1.598	1.584	1.584	1.584	1.591	1.577
MgO ($^1\Sigma^+$)	1.749	1.739	1.739	1.732	1.722	1.763	1.763	1.755	1.736
MgS ($^1\Sigma^+$)	2.143	2.149	2.149	2.136	2.131	2.199	2.199	2.182	2.177
N_2 ($^1\Sigma_g^+$)	1.098	1.091	1.091	1.090	1.078	1.091	1.091	1.089	1.077
N_2O	1.127 (NN)	1.121	1.121	1.118	1.101	1.121	1.121	1.118	1.100
	1.185 (NO)	1.182	1.183	1.174	1.170	1.182	1.182	1.173	1.169
NaCl ($^1\Sigma^+$)	2.361	2.372	2.376	2.365	2.359	2.372	2.375	2.363	2.363
NaF ($^1\Sigma^+$)	1.926	1.933	1.934	1.929	1.914	1.931	1.932	1.926	1.911
NaH ($^1\Sigma^+$)	1.887	1.876	1.877	1.885	1.871	1.876	1.876	1.884	1.874
NF ($^3\Sigma^-$)	1.317	1.316	1.316	1.301	1.294	1.315	1.315	1.300	1.292
NH ($^3\Sigma^-$)	1.036	1.040	1.040	1.038	1.028	1.039	1.039	1.036	1.025
NH_3	1.012	0.998	0.998	0.997	0.990	0.997	0.997	0.995	0.987
O_2 ($^3\Sigma_g^-$)	1.208	1.203	1.203	1.192	1.179	1.203	1.203	1.191	1.177
O_3	1.272	1.251	1.252	1.236	1.219	1.253	1.253	1.237	1.220
OCS	1.147 (CO)	1.155	1.155	1.152	1.138	1.155	1.155	1.151	1.138
	1.561 (CS)	1.563	1.563	1.558	1.555	1.561	1.562	1.556	1.552
P_2 ($^1\Sigma_g^+$)	1.893	1.888	1.888	1.880	1.864	1.888	1.888	1.880	1.869
PF ($^3\Sigma^-$)	1.590	1.609	1.609	1.599	1.586	1.608	1.609	1.598	1.585

PH ($^3\Sigma^-$)	1.422	1.427	1.427	1.427	1.414	1.425	1.425	1.424	1.410
PH_3	1.413	1.418	1.418	1.419	1.406	1.416	1.416	1.416	1.401
PN ($^1\Sigma^+$)	1.491	1.481	1.481	1.478	1.461	1.480	1.480	1.477	1.460
S_2 ($^3\Sigma_g^-$)	1.889	1.903	1.903	1.886	1.877	1.902	1.902	1.885	1.878
S_2O	1.884 (SS)	1.894	1.895	1.878	1.865	1.898	1.898	1.881	1.871
	1.456 (SO)	1.460	1.460	1.451	1.434	1.461	1.461	1.452	1.436
SCS	1.553	1.554	1.554	1.549	1.541	1.553	1.553	1.547	1.539
SiO ($^1\Sigma^+$)	1.510	1.512	1.512	1.507	1.492	1.511	1.511	1.506	1.491
SiS ($^1\Sigma^+$)	1.929	1.938	1.938	1.930	1.918	1.938	1.938	1.930	1.921
SO ($^3\Sigma^-$)	1.481	1.488	1.488	1.478	1.463	1.487	1.487	1.477	1.461
SO_2	1.431	1.437	1.437	1.429	1.412	1.436	1.436	1.429	1.411
B_2H_6	1.314 (BH ×2)	1.311	1.313	1.314	1.305	1.309	1.310	1.311	1.300
	1.184 (BH ×4)	1.185	1.186	1.190	1.179	1.183	1.184	1.187	1.174
cyclopropane	1.501 (CC)	1.504	1.505	1.498	1.493	1.503	1.504	1.496	1.490
	1.083 (CH)	1.081	1.081	1.082	1.073	1.079	1.080	1.080	1.070
C_2^- ($^2\Sigma_g^+$)	1.268	1.258	1.258	1.259	1.248	1.262	1.262	1.261	1.249
NH^- ($^2\Pi_i$)	1.047	1.041	1.041	1.039	1.029	1.039	1.039	1.038	1.026
AlH^+ ($^2\Sigma^+$)	1.602	1.621	1.621	1.617	1.605	1.614	1.614	1.610	1.593
Cl_2^+ ($^2\Pi_{3/2g}$)	1.892	1.908	1.908	1.883	1.877	1.908	1.908	1.882	1.877
CO^+ ($^2\Sigma^+$)	1.115	1.108	1.108	1.106	1.093	1.108	1.108	1.105	1.092
HCl^+ ($^2\Pi_i$)	1.315	1.323	1.323	1.320	1.310	1.322	1.322	1.318	1.307
He_2^+ ($^2\Sigma_u^+$)	1.081	1.145	1.145	1.132	1.106	1.143	1.143	1.130	1.103
HF^+ ($^2\Pi_i$)	1.001	1.013	1.013	1.006	0.997	1.012	1.012	1.004	0.995
N_2^+ ($^2\Sigma_g^+$)	1.116	1.105	1.105	1.102	1.092	1.105	1.105	1.103	1.092
NH^+ ($^2\Pi_r$)	1.070	1.078	1.078	1.076	1.063	1.077	1.077	1.074	1.060
NH_3^+	1.014	1.025	1.025	1.023	1.016	1.024	1.024	1.022	1.013
O_2^+ ($^2\Pi_g$)	1.116	1.105	1.105	1.098	1.083	1.105	1.105	1.097	1.082
PF^+ ($^2\Pi_r$)	1.500	1.519	1.519	1.511	1.497	1.518	1.518	1.510	1.495
H_2O^+ ($^2B_1$)	0.999	1.005	1.005	1.001	0.992	1.004	1.004	1.000	0.990
AlS ($^2\Sigma^+$)	2.029	2.045	2.046	2.031	2.029	2.071	2.071	2.049	2.049
BeCl ($^2\Sigma^+$)	1.797	1.802	1.802	1.798	1.795	1.800	1.800	1.796	1.791
BeF ($^2\Sigma^+$)	1.361	1.364	1.364	1.362	1.352	1.363	1.363	1.361	1.351
BeH ($^2\Sigma^+$)	1.343	1.341	1.341	1.349	1.334	1.336	1.336	1.343	1.325
BO ($^2\Sigma^+$)	1.205	1.200	1.200	1.199	1.187	1.200	1.200	1.198	1.186
BS ($^2\Sigma^+$)	1.609	1.610	1.610	1.607	1.598	1.610	1.611	1.607	1.599
CCl ($^2\Pi_{1/2}$, $^2\Pi_{3/2}$)	1.645	1.654	1.654	1.642	1.641	1.649	1.649	1.638	1.635
CF ($^2\Pi_r$)	1.272	1.272	1.272	1.265	1.256	1.271	1.271	1.264	1.254
CH ($^2\Pi_r$)	1.120	1.122	1.122	1.124	1.110	1.120	1.120	1.122	1.106
CH_3	1.076	1.078	1.078	1.079	1.071	1.076	1.077	1.077	1.067
ClO ($^2\Pi_i$)	1.570	1.576	1.576	1.559	1.560	1.571	1.571	1.554	1.554
CN ($^2\Sigma^+$)	1.172	1.162	1.162	1.160	1.146	1.163	1.163	1.160	1.146
CP ($^2\Sigma^+$)	1.562	1.553	1.553	1.549	1.537	1.558	1.558	1.552	1.541
H_2N ($^2B_1$)	1.025	1.027	1.027	1.026	1.016	1.026	1.026	1.024	1.013
HO	0.970	0.974	0.974	0.971	0.961	0.973	0.973	0.969	0.959
HOO	0.971 (OH)	0.975	0.976	0.972	0.960	0.974	0.975	0.971	0.959
	1.331 (OO)	1.324	1.324	1.307	1.300	1.323	1.323	1.306	1.298
MgCl ($^2\Sigma^+$)	2.199	2.221	2.221	2.208	2.205	2.218	2.219	2.205	2.203
MgF ($^2\Sigma^+$)	1.750	1.769	1.769	1.763	1.750	1.768	1.768	1.761	1.747
MgH ($^2\Sigma^+$)	1.730	1.742	1.743	1.742	1.729	1.734	1.735	1.733	1.716
NO ($^2\Pi_r$)	1.151	1.145	1.145	1.139	1.128	1.144	1.144	1.139	1.126
NO_2 ($^2A_1$)	1.195	1.190	1.190	1.182	1.170	1.190	1.190	1.182	1.169
NS ($^2\Pi_r$)	1.494	1.490	1.490	1.484	1.471	1.489	1.489	1.483	1.469

OP ($^2\Pi_r$)	1.474	1.477	1.477	1.471	1.455	1.476	1.476	1.470	1.454
SF ($^2\Pi_{3/2}$, $^2\Pi_{1/2}$)	1.601	1.614	1.614	1.599	1.587	1.612	1.612	1.597	1.585
SH ($^2\Pi_i$)	1.345	1.346	1.346	1.345	1.335	1.344	1.344	1.343	1.331
SiCl ($^2\Pi_r$)	2.058	2.083	2.084	2.066	2.067	2.078	2.078	2.060	2.060
SiF ($^2\Pi_r$)	1.601	1.625	1.625	1.617	1.605	1.623	1.623	1.615	1.602
SiH ($^2\Pi_r$)	1.520	1.528	1.528	1.531	1.515	1.525	1.525	1.527	1.509
SiN ($^2\Sigma^+$)	1.572	1.566	1.566	1.562	1.550	1.575	1.575	1.568	1.555
HCO	1.119 (CH)	1.123	1.123	1.123	1.112	1.120	1.121	1.120	1.107
	1.175 (CO)	1.171	1.171	1.168	1.158	1.171	1.171	1.168	1.157
MSE		0.003	0.003	-0.002	-0.012	0.003	0.003	-0.002	-0.014
MAE		0.008	0.008	0.008	0.013	0.008	0.008	0.008	0.015
rms		0.013	0.013	0.012	0.017	0.013	0.014	0.013	0.019
Max(−)		-0.078	-0.078	-0.082	-0.090	-0.080	-0.080	-0.085	-0.095
Max(+)		0.065	0.065	0.051	0.025	0.063	0.063	0.049	0.035

TABLE S3. Non-hydrogen transfer barrier heights (in kcal/mol) of the NHTBH38/04 set [1]. For all the TAO-DFT calculations, the optimal θ values given in TABLE I are adopted.

			KS-DFT				TAO-DFT			
Reactions		ΔE_{ref}	B3LYP	B3LYP-D3	PBE0	BHHLYP	B3LYP	B3LYP-D3	PBE0	BHHLYP
Heavy-atom transfer reactions										
$H + N_2O \rightarrow OH + N_2$	V^f	18.14	11.37	11.02	13.91	15.61	10.93	10.58	13.35	14.05
	V^r	83.22	72.81	72.32	68.79	91.16	72.20	71.71	67.91	88.70
$H + FH \rightarrow HF + H$	V^f	42.18	31.01	30.92	33.74	38.36	31.16	31.07	33.89	38.21
	V^r	42.18	31.01	30.92	33.74	38.36	31.16	31.07	33.89	38.21
$H + ClH \rightarrow HCl + H$	V^f	18.00	12.41	12.34	13.38	16.56	11.85	11.78	12.69	14.94
	V^r	18.00	12.41	12.34	13.38	16.56	11.85	11.78	12.69	14.94
$H + FCH_3 \rightarrow HF + CH_3$	V^f	30.38	21.79	21.25	25.71	29.78	21.70	21.16	25.56	29.02
	V^r	57.02	48.64	47.65	49.75	57.38	48.09	47.10	49.11	55.77
$H + F_2 \rightarrow HF + F$	V^f	2.27	-7.54	-7.72	-4.60	-4.47	-8.02	-8.19	-5.17	-5.58
	V^r	106.18	96.16	95.97	99.02	113.44	95.89	95.71	98.65	112.53
$CH_3 + FCl \rightarrow CH_3F + Cl$	V^f	7.43	-1.58	-2.88	0.79	5.68	-3.02	-4.32	-0.85	2.36
	V^r	60.17	50.96	50.11	53.45	63.48	52.06	51.21	53.72	61.90
Nucleophilic substitution reactions										
$F^- + CH_3F \rightarrow FCH_3 + F^-$	V^f	-0.34	-3.93	-4.91	-2.67	0.33	-4.81	-5.79	-3.75	-2.05
	V^r	-0.34	-3.93	-4.91	-2.67	0.33	-4.81	-5.79	-3.75	-2.05
$F^-\cdots CH_3F \rightarrow FCH_3\cdots F^-$	V^f	13.38	10.23	10.47	11.69	14.62	10.25	10.48	11.73	14.91
	V^r	13.38	10.23	10.47	11.69	14.62	10.25	10.48	11.73	14.91
$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	V^f	3.10	-0.57	-2.14	0.87	3.10	-1.84	-3.42	-0.66	-0.12
	V^r	3.10	-0.57	-2.14	0.87	3.10	-1.84	-3.42	-0.66	-0.12
$Cl^-\cdots CH_3Cl \rightarrow ClCH_3\cdots Cl^-$	V^f	13.61	9.22	9.18	11.29	13.07	9.23	9.19	11.30	13.41
	V^r	13.61	9.22	9.18	11.29	13.07	9.23	9.19	11.30	13.41
$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	V^f	-12.54	-16.55	-17.81	-15.45	-14.09	-17.21	-18.47	-16.30	-16.24
	V^r	20.11	18.26	16.90	19.44	24.36	16.70	15.34	17.62	20.88
$F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$	V^f	2.89	0.31	0.35	1.66	2.49	0.55	0.59	1.96	3.14
	V^r	29.62	26.62	26.66	28.35	33.05	26.22	26.25	27.87	32.62
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	V^f	-2.78	-5.83	-7.07	-4.97	-1.35	-6.37	-7.61	-5.72	-3.45
	V^r	17.33	14.13	13.05	15.94	19.67	13.50	12.42	15.12	17.48
$OH^-\cdots CH_3F \rightarrow HOCH_3\cdots F^-$	V^f	10.96	7.69	7.63	8.82	12.48	7.97	7.91	9.10	12.98
	V^r	47.20	45.46	45.04	49.06	50.65	45.66	45.24	49.27	50.88
Unimolecular and association reactions										
$H + N_2 \rightarrow HN_2$	V^f	14.69	7.47	7.36	8.50	11.04	6.81	6.70	7.69	9.28
	V^r	10.72	10.88	10.79	11.64	13.61	11.28	11.19	12.12	14.34
$H + CO \rightarrow HCO$	V^f	3.17	-0.59	-1.00	0.31	1.46	-1.11	-1.51	-0.33	0.07
	V^r	22.68	24.60	24.32	25.47	24.81	25.29	25.00	26.31	26.27

$H + C_2H_4 \rightarrow CH_3CH_2$	V^f	1.72	-0.18	-0.84	0.67	0.49	-0.67	-1.33	0.06	-0.93
	V^r	41.75	41.73	41.33	44.12	45.42	42.32	41.92	44.81	46.50
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	V^f	6.85	6.00	3.97	4.02	7.78	4.69	2.66	2.48	4.52
	V^r	32.97	29.44	29.07	34.48	33.82	29.95	29.58	35.06	34.64
$HCN \rightarrow HNC$	V^f	48.16	47.38	47.46	46.37	47.92	47.58	47.67	46.60	48.28
	V^r	33.11	33.33	33.39	32.51	35.44	33.34	33.41	32.53	35.45
MSE			-4.57	-5.09	-3.13	0.52	-4.88	-5.39	-3.53	-0.51
MAE			4.69	5.19	3.63	2.21	5.08	5.56	4.18	2.75
rms			5.71	6.14	4.63	2.93	6.02	6.49	5.10	3.29
Max(−)			-11.17	-11.26	-14.43	-6.74	-11.02	-11.75	-15.31	-7.85
Max(+)			1.92	1.64	2.79	7.94	2.61	2.32	3.63	6.35

TABLE S4. Hydrogen transfer barrier heights (in kcal/mol) of the HTBH38/04 set [1]. For all the TAO-DFT calculations, the optimal θ values given in TABLE I are adopted.

			KS-DFT				TAO-DFT			
Reactions		ΔE_{ref}	B3LYP	B3LYP-D3	PBE0	BHHLYP	B3LYP	B3LYP-D3	PBE0	BHHLYP
$H + HCl \rightarrow H_2 + Cl$	V^f	5.7	-0.77	-0.94	2.94	1.71	-2.11	-2.29	1.45	-0.92
	V^r	8.7	3.73	3.55	1.66	7.50	4.40	4.22	1.52	5.74
$OH + H_2 \rightarrow H + H_2O$	V^f	5.1	0.51	0.20	-0.02	6.81	-0.24	-0.55	-1.00	4.82
	V^r	21.2	13.35	13.05	17.31	16.37	12.76	12.46	16.66	15.34
$CH_3 + H_2 \rightarrow H + CH_4$	V^f	12.1	8.73	8.21	6.89	11.76	7.84	7.32	5.85	9.62
	V^r	15.3	9.52	9.03	11.90	12.43	9.25	8.75	11.56	11.58
$OH + CH_4 \rightarrow CH_3 + H_2O$	V^f	6.7	1.92	1.04	1.62	9.60	1.13	0.26	0.58	7.45
	V^r	19.6	13.97	13.08	13.94	18.49	12.73	11.84	12.53	16.01
$H + H_2 \rightarrow H_2 + H$	V^f	9.6	4.22	4.17	5.63	6.44	3.86	3.81	5.19	5.53
	V^r	9.6	4.22	4.17	5.63	6.44	3.86	3.81	5.19	5.53
$OH + NH_3 \rightarrow H_2O + NH_2$	V^f	3.2	-2.62	-3.49	-2.27	7.61	-3.72	-4.59	-3.66	4.86
	V^r	12.7	7.32	6.44	7.41	15.54	5.97	5.09	5.85	12.68
$HCl + CH_3 \rightarrow Cl+ CH_4$	V^f	1.7	-1.59	-2.64	-2.49	1.86	-3.13	-4.18	-4.27	-1.55
	V^r	7.9	3.70	2.67	1.24	8.32	4.79	3.76	1.51	7.06
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	V^f	3.4	-1.05	-2.18	-1.23	6.87	-1.86	-2.98	-2.29	4.64
	V^r	19.9	15.63	14.17	15.66	19.68	14.39	12.93	14.25	17.24
$F + H_2 \rightarrow HF + H$	V^f	1.8	-6.03	-6.33	-4.90	1.20	-6.78	-7.08	-5.82	-0.54
	V^r	33.4	23.76	23.46	28.40	25.17	23.29	22.99	27.92	24.51
$O + CH_4 \rightarrow OH + CH_3$	V^f	13.7	6.78	6.14	7.16	15.33	5.97	5.33	6.14	13.32
	V^r	8.1	4.44	3.78	3.94	8.79	3.38	2.72	2.71	6.51
$H + PH_3 \rightarrow PH_2 + H_2$	V^f	3.1	-1.09	-1.44	0.35	1.32	-1.59	-1.93	-0.26	-0.17
	V^r	23.2	22.72	22.28	20.12	24.60	21.85	21.41	19.09	22.39
$H + HO \rightarrow H_2 + O$	V^f	10.7	4.14	3.93	7.13	7.53	3.70	3.49	6.60	6.55
	V^r	13.1	5.69	5.48	5.33	13.40	4.88	4.67	4.33	11.41
$H + H_2S \rightarrow H_2 + HS$	V^f	3.5	-0.58	-0.98	1.05	2.00	-1.62	-2.02	-0.01	-0.19
	V^r	17.3	15.54	15.11	12.06	18.54	16.42	15.99	12.30	17.32
$O + HCl \rightarrow OH + Cl$	V^f	9.8	0.96	0.81	2.22	12.23	-1.01	-1.16	0.01	8.43
	V^r	10.4	3.90	3.75	2.74	12.16	4.32	4.16	2.36	10.23
$NH_2 + CH_3 \rightarrow CH_4 + NH$	V^f	8.0	6.13	5.25	5.05	10.45	5.11	4.23	3.85	8.10
	V^r	22.4	17.09	16.23	16.42	23.20	16.21	15.35	15.36	20.99
$NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$	V^f	7.5	8.20	6.77	6.89	12.13	7.14	5.71	5.65	9.74
	V^r	18.3	14.54	13.43	13.70	20.96	13.60	12.50	12.58	18.58
$C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$	V^f	10.4	8.73	7.40	7.26	14.85	7.73	6.40	6.04	12.31
	V^r	17.4	15.47	13.82	14.45	19.73	14.27	12.62	13.06	17.09
$NH_2 + CH_4 \rightarrow CH_3 + NH_3$	V^f	14.5	11.27	10.23	9.87	17.14	10.32	9.27	8.71	14.75
	V^r	17.8	13.39	12.34	12.50	18.10	12.22	11.17	11.14	15.48
s-trans cis-$C_5H_8 \rightarrow$ *s-trans cis*-C_5H_8	V^f	38.4	38.77	38.58	35.57	44.72	38.30	38.11	35.00	43.40
	V^r	38.4	38.77	38.58	35.57	44.72	38.30	38.11	35.00	43.40
MSE			-4.48	-5.12	-4.60	0.58	-5.20	-5.84	-5.55	-1.43
MAE			4.56	5.14	4.60	2.48	5.20	5.84	5.55	2.40

rms	5.10	5.62	4.88	3.11	5.79	6.34	5.80	3.15
Max(−)	-9.64	-9.94	-7.77	-8.23	-10.81	-10.96	-9.79	-8.89
Max(+)	0.70	0.18	-0.61	6.32	-0.10	-0.29	-1.85	5.00

TABLE S5. Interaction energies (in kcal/mol) of the S22 set [3]. The counterpoise corrections are used to reduce the basis set superposition errors. Monomer deformation energies are not included. For all the TAO-DFT calculations, the optimal θ values given in TABLE I are adopted.

		KS-DFT				TAO-DFT			
Complex [Symmetry]	ΔE_{ref}	B3LYP	B3LYP-D3	PBE0	BHHLYP	B3LYP	B3LYP-D3	PBE0	BHHLYP
Hydrogen bonded complexes									
$(NH_3)_2$ [C_{2h}]	-3.17	-2.19	-3.11	-2.77	-2.56	-2.79	-3.71	-3.46	-3.91
$(H_2O)_2$ [C_s]	-5.02	-4.49	-5.23	-4.92	-4.96	-5.10	-5.84	-5.63	-6.30
Formic acid dimer [C_{2h}]	-18.61	-17.29	-19.61	-18.86	-18.90	-18.71	-21.04	-20.52	-21.96
Formamide dimer [C_{2h}]	-15.96	-13.97	-16.54	-15.27	-15.32	-15.31	-17.88	-16.83	-18.19
Uracil dimer [C_{2h}]	-20.65	-17.87	-21.20	-19.16	-19.46	-19.16	-22.48	-20.64	-22.21
2-pyridoxine·2-aminopyridine [C_1]	-16.71	-13.72	-17.63	-15.35	-14.57	-15.19	-19.09	-17.05	-17.79
Adenine·thymine WC [C_1]	-16.37	-12.82	-17.05	-14.50	-13.94	-14.46	-18.69	-16.40	-17.60
MSE		2.02	-0.55	0.81	0.97	0.82	-1.75	-0.58	-1.64
MAE		2.02	0.57	0.88	1.05	0.88	1.75	0.58	1.64
Dispersion complexes									
$(CH_4)_2$ [D_{3d}]	-0.53	0.40	-0.52	-0.04	0.16	-0.01	-0.93	-0.51	-0.78
$(C_2H_4)_2$ [D_{2d}]	-1.51	0.51	-1.61	-0.35	-0.04	-0.27	-2.39	-1.25	-1.88
Benzene·CH_4 [C_3]	-1.50	0.82	-1.43	-0.08	0.33	0.08	-2.17	-0.92	-1.41
Benzene dimer [C_{2h}]	-2.73	3.84	-2.19	1.80	3.06	2.31	-3.72	0.03	-0.76
Pyrazine dimer [C_s]	-4.42	2.56	-3.71	0.52	1.57	1.05	-5.22	-1.22	-2.15
Uracil dimer [C_2]	-10.12	-0.86	-10.03	-3.29	-2.76	-2.76	-11.92	-5.49	-7.26
Indole·benzene [C_1]	-5.22	4.81	-3.74	2.02	3.69	2.82	-5.72	-0.28	-1.27
Adenine·thymine stack [C_1]	-12.23	1.46	-11.01	-2.14	-0.95	-1.04	-13.51	-5.04	-6.93
MSE		6.48	0.50	4.59	5.41	5.06	-0.92	2.95	1.98
MAE		6.48	0.53	4.59	5.41	5.06	0.92	2.95	2.13
Mixed complexes									
Ethene·ethine [C_{2v}]	-1.53	-0.64	-1.70	-1.18	-0.94	-1.15	-2.21	-1.76	-2.13
Benzene·H_2O [C_s]	-3.28	-1.21	-3.53	-2.21	-1.86	-2.02	-4.34	-3.14	-3.68
Benzene·NH_3 [C_s]	-2.35	-0.08	-2.44	-1.03	-0.64	-0.87	-3.22	-1.93	-2.44
Benzene·HCN [C_s]	-4.46	-1.93	-4.68	-3.28	-2.92	-2.81	-5.55	-4.28	-4.94
Benzene dimer [C_{2v}]	-2.74	1.02	-2.67	-0.28	0.30	0.03	-3.67	-1.43	-2.07
Indole·benzene T-shape [C_1]	-5.73	-0.50	-5.43	-2.36	-1.52	-2.07	-6.99	-4.23	-5.32
Phenol dimer [C_1]	-7.05	-2.94	-7.19	-4.18	-4.05	-4.19	-8.45	-5.64	-6.96
MSE		2.98	-0.07	1.80	2.22	2.01	-1.04	0.68	-0.06
MAE		2.98	0.18	1.80	2.22	2.01	1.04	0.74	0.39
MSE		3.95	-0.02	2.50	2.98	2.74	-1.22	1.10	0.18
MAE		3.95	0.43	2.52	3.01	2.76	1.22	1.49	1.42
rms		5.17	0.59	3.62	4.22	3.98	1.37	2.40	1.98
Max(−)		0.53	-1.00	-0.25	-0.29	-0.10	-2.43	-1.91	-3.35
Max(+)		13.69	1.48	10.09	11.28	11.19	-0.40	7.19	5.30

TABLE S6. Singlet-triplet energy gap [$E_{\mathrm{T}} - E_{\mathrm{S}}$] (in kcal/mol) of n-acene as a function of the acene length, calculated using various hybrid functionals in spin-unrestricted KS-DFT and TAO-DFT. For all the TAO-DFT calculations, the optimal θ values given in TABLE I are adopted. The experimental data (uncorrected for zero-point vibrations, thermal vibrations, etc.) are taken from Refs. [4–7], the DMRG data are taken from Ref. [8], and the CCSD(T)/CBS data are taken from Ref. [9].

					KS-DFT				TAO-DFT			
n	Expt.	DMRG/cc-pVDZ	DMRG/STO-3G	CCSD(T)/CBS	B3LYP	B3LYP-D3	PBE0	BHHLYP	B3LYP	B3LYP-D3	PBE0	BHHLYP
2	61.0	61.0	61.5	65.83	62.65	62.64	62.59	62.96	60.58	60.57	60.17	58.79
3	43.1	44.0	45.9	48.21	41.78	41.81	41.31	41.40	40.44	40.47	39.81	38.77
4	29.3	31.9	34.7	33.49	27.70	27.75	26.99	26.50	27.27	27.31	26.60	25.74
5	19.8	23.4	26.7	25.27	17.87	17.92	16.95	18.41	18.74	18.78	18.10	17.35
6		17.5	21.0	17.71	10.93	10.97	10.90	15.01	13.31	13.34	12.71	11.99
7				13.40	7.31	7.33	8.23	14.23	9.89	9.92	9.34	8.60
8			14.2	9.20	5.78	5.78	7.31	15.02	7.73	7.75	7.21	6.43
9				7.00	5.35	5.34	7.39	16.89	6.30	6.32	5.81	4.99
10			11.6	4.64	5.57	5.56	8.12	18.48	5.30	5.31	5.08	3.99
11				3.65	6.24	6.23	9.35	18.65	4.56	4.57	4.12	3.27
12			10.7		7.25	7.23	10.76	18.57	3.99	4.00	3.97	2.73
13									3.53	3.54	3.62	2.30
14									3.15	3.16	2.78	1.95
15									2.85	2.86	2.51	1.70
16									2.61	2.61	2.28	1.59
17									2.39	2.40	2.09	1.35
18									2.22	2.22	1.93	1.21
19									2.08	2.08	1.78	1.12
20									1.95	1.95	1.67	1.02
21									1.83	1.83	1.57	0.94
22									1.73	1.73	1.49	0.88
23									1.64	1.64	1.39	0.75
24									1.56	1.56	1.33	0.77
25									1.49	1.49	1.24	0.70
26									1.42	1.42	1.15	0.65
27									1.36	1.36	1.14	0.66
28									1.31	1.30	1.10	0.64
29									1.25	1.26	1.08	0.61
30									1.21	1.21	1.03	0.56

TABLE S7. Vertical ionization potential (in eV) for the lowest singlet state of n-acene as a function of the acene length, calculated using various hybrid functionals in spin-unrestricted TAO-DFT. For all the TAO-DFT calculations, the optimal θ values given in TABLE I are adopted. The experimental data are taken from the compilation in Ref. [10], and the CCSD(T)/CBS data are taken from Ref. [11].

			TAO-DFT			
n	Expt.	CCSD(T)/CBS	B3LYP	B3LYP-D3	PBE0	BHHLYP
2	8.14	8.24	7.52	7.52	7.60	7.34
3	7.44	7.47	6.74	6.74	6.82	6.55
4	6.97	6.95	6.20	6.20	6.28	6.02
5	6.59	6.57	5.82	5.82	5.91	5.63
6		6.43	5.55	5.55	5.63	5.36
7			5.35	5.35	5.44	5.16
8			5.20	5.20	5.28	5.00
9			5.07	5.07	5.16	4.87
10			4.97	4.97	5.07	4.77
11			4.89	4.89	4.97	4.68
12			4.81	4.81	4.92	4.61
13			4.75	4.75	4.86	4.54
14			4.69	4.69	4.78	4.49
15			4.64	4.64	4.73	4.43
16			4.59	4.59	4.68	4.39
17			4.55	4.55	4.64	4.35
18			4.51	4.51	4.60	4.31

19	4.48	4.48	4.57	4.28
20	4.45	4.45	4.54	4.25
21	4.42	4.42	4.51	4.22
22	4.39	4.39	4.48	4.19
23	4.36	4.36	4.46	4.17
24	4.34	4.34	4.43	4.14
25	4.32	4.32	4.41	4.12
26	4.30	4.30	4.39	4.10
27	4.28	4.28	4.37	4.08
28	4.26	4.26	4.35	4.07
29	4.24	4.24	4.34	4.05
30	4.23	4.23	4.32	4.03

TABLE S8. Vertical electron affinity (in eV) for the lowest singlet state of n-acene as a function of the acene length, calculated using various hybrid functionals in spin-unrestricted TAO-DFT. For all the TAO-DFT calculations, the optimal θ values given in TABLE I are adopted. The experimental data are taken from the compilation in Ref. [10], and the CCSD(T)/CBS data are taken from Ref. [12].

			TAO-DFT			
n	Expt.	CCSD(T)/CBS	B3LYP	B3LYP-D3	PBE0	BHHLYP
2	-0.20	-0.48	-0.83	-0.83	-0.77	-1.05
3	0.53	0.28	0.04	0.04	0.11	-0.17
4	1.07	0.82	0.64	0.64	0.72	0.43
5	1.39	1.21	1.07	1.07	1.15	0.86
6		1.47	1.38	1.38	1.46	1.17
7			1.61	1.61	1.70	1.41
8			1.79	1.79	1.87	1.59
9			1.93	1.93	2.01	1.73
10			2.04	2.04	2.12	1.85
11			2.14	2.14	2.23	1.95
12			2.22	2.22	2.30	2.03
13			2.30	2.30	2.37	2.10
14			2.36	2.36	2.45	2.17
15			2.42	2.42	2.51	2.23
16			2.47	2.47	2.56	2.28
17			2.52	2.52	2.61	2.33
18			2.56	2.56	2.65	2.37
19			2.60	2.60	2.69	2.41
20			2.63	2.63	2.72	2.44
21			2.67	2.66	2.76	2.47
22			2.70	2.69	2.79	2.50
23			2.72	2.72	2.82	2.53
24			2.75	2.75	2.84	2.56
25			2.77	2.77	2.87	2.58
26			2.80	2.80	2.89	2.61
27			2.82	2.82	2.91	2.63
28			2.84	2.84	2.93	2.64
29			2.86	2.85	2.95	2.66
30			2.87	2.87	2.97	2.68

TABLE S9. Fundamental gap (in eV) for the lowest singlet state of n-acene as a function of the acene length, calculated using various hybrid functionals in spin-unrestricted TAO-DFT. For all the TAO-DFT calculations, the optimal θ values given in TABLE I are adopted. The experimental data are taken from the compilation in Ref. [10], and the CCSD(T)/CBS data are taken from Refs. [11, 12].

			TAO-DFT			
n	Expt.	CCSD(T)/CBS	B3LYP	B3LYP-D3	PBE0	BHHLYP
2	8.34	8.72	8.35	8.35	8.37	8.39
3	6.91	7.19	6.70	6.70	6.70	6.73
4	5.90	6.13	5.56	5.56	5.56	5.59
5	5.20	5.37	4.75	4.75	4.75	4.78
6		4.96	4.17	4.17	4.17	4.19
7			3.74	3.74	3.74	3.75
8			3.41	3.41	3.41	3.41
9			3.15	3.15	3.15	3.14
10			2.93	2.93	2.95	2.92
11			2.75	2.75	2.75	2.74
12			2.59	2.59	2.62	2.58
13			2.45	2.45	2.49	2.44
14			2.33	2.33	2.33	2.31
15			2.22	2.22	2.22	2.21
16			2.12	2.12	2.12	2.12
17			2.03	2.03	2.03	2.02
18			1.95	1.95	1.95	1.94
19			1.88	1.88	1.88	1.87
20			1.81	1.81	1.81	1.81
21			1.75	1.75	1.75	1.74
22			1.69	1.69	1.69	1.69
23			1.64	1.64	1.64	1.63
24			1.59	1.59	1.59	1.59
25			1.55	1.55	1.54	1.54
26			1.50	1.50	1.50	1.49
27			1.46	1.46	1.46	1.46
28			1.42	1.42	1.42	1.42
29			1.39	1.39	1.39	1.38
30			1.36	1.36	1.36	1.35

TABLE S10. Symmetrized von Neumann entropy for the lowest singlet state of n-acene as a function of the acene length, calculated using various hybrid functionals in spin-restricted TAO-DFT. For all the TAO-DFT calculations, the optimal θ values given in TABLE I are adopted.

	TAO-DFT			
n	B3LYP	B3LYP-D3	PBE0	BHHLYP
2	0.10	0.10	0.13	0.35
3	0.26	0.26	0.31	0.62
4	0.50	0.50	0.58	0.96
5	0.81	0.81	0.90	1.33
6	1.14	1.14	1.23	1.72
7	1.45	1.45	1.55	2.10
8	1.74	1.74	1.85	2.47
9	2.01	2.01	2.14	2.83
10	2.28	2.27	2.42	3.19
11	2.54	2.54	2.70	3.54

12	2.81	2.80	2.98	3.90
13	3.07	3.07	3.26	4.26
14	3.35	3.34	3.55	4.62
15	3.62	3.61	3.83	4.97
16	3.89	3.89	4.11	5.33
17	4.16	4.16	4.40	5.69
18	4.43	4.43	4.68	6.05
19	4.70	4.70	4.97	6.41
20	4.97	4.97	5.25	6.77
21	5.24	5.24	5.54	7.12
22	5.51	5.51	5.82	7.48
23	5.78	5.78	6.11	7.84
24	6.05	6.05	6.39	8.20
25	6.32	6.32	6.67	8.56
26	6.59	6.59	6.96	8.91
27	6.86	6.86	7.24	9.27
28	7.13	7.13	7.53	9.63
29	7.40	7.40	7.81	9.99
30	7.67	7.67	8.10	10.35