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Supporting Information

Benchmark and parameter tuning of hybrid functionals for fast calculation of excitation energies of AIEgens

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Calculation details

All calculation were performed on ORCA 4.1 shared library version installed on a PC (Arch-linux) with Linux kernel 5.5.13.arch1-1 and openmpi 3.1.4 for parallel calculation. The optimization jobs were done under head of input files:

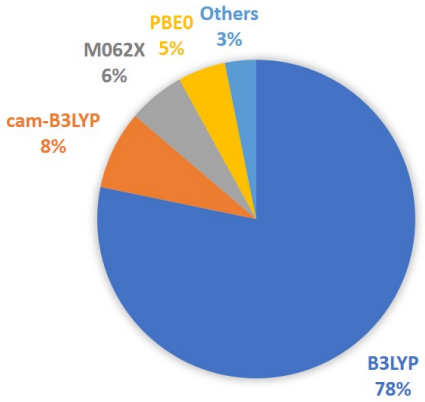
```
! opt BLYP def2-SVP def2/J RI tightSCF grid5 nofinalgrid
```

The TD-DFT calculations for transition energy from ground state to first singlet state were carried out with head of input files (in which XXX denotes different functionals.):

```
! sp XXX def2-SVP def2/J RIJCOSX tightSCF grid5 nofinalgrid
%tddft nroots=20 iroot=1 triplets false tda false end
```

M11, MN15 functionals were not implemented in ORCA. Related calculation was done on NWChem quantum chemistry suite with same settings and calculation level.

Additional figures, schemes and tables



Functionals	No. of results
B3LYP	5460
cam-B3LYP	557
M062X	402
PBE0	339
B3PW91	69
wB97X	65
BHANDHLYP	39
M06	25
X3LYP	10
O3LYP	9
mPW1LYP	2
PW1PW	1
TPSSh	1
M11	0
MN15	0
Total	6979

Figure S1: A rough survey about popularity of different functionals used by general AIE research (on Google scholar, 04/07/2020).

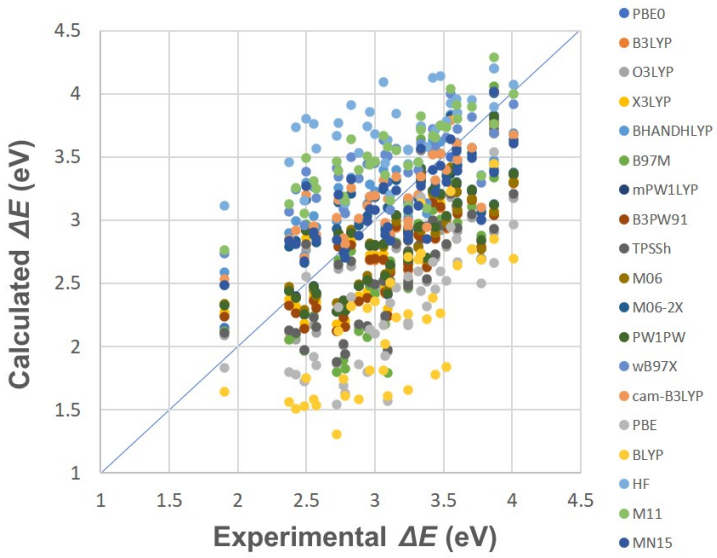
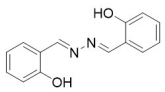
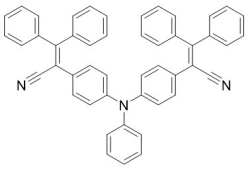


Figure S2: Experimental transition energy versus calculated transition energy from different functionals with def2-SVP basis set.



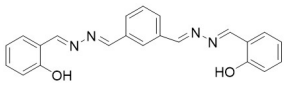
No. 18

$\Delta E_{Exp.}$	3.42 eV
B3LYP	3.13 eV
M062X	3.53 eV
PBE-40	3.48 eV
BLYP-40	3.47 eV



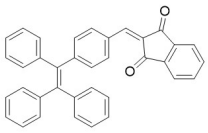
No. 34

$\Delta E_{Exp.}$	2.94 eV
B3LYP	2.39 eV
M062X	3.03 eV
PBE-40	2.89 eV
BLYP-40	2.90 eV



No. 24

$\Delta E_{Exp.}$	2.96 eV
B3LYP	2.68 eV
M062X	3.18 eV
PBE-40	3.11 eV
BLYP-40	3.09 eV



No. 36

$\Delta E_{Exp.}$	3.07 eV
B3LYP	2.42 eV
M062X	2.93 eV
PBE-40	2.80 eV
BLYP-40	2.91 eV

Figure S3: Some typical ESIPT and ICT systems and the calculation transition energy from corresponding methods.

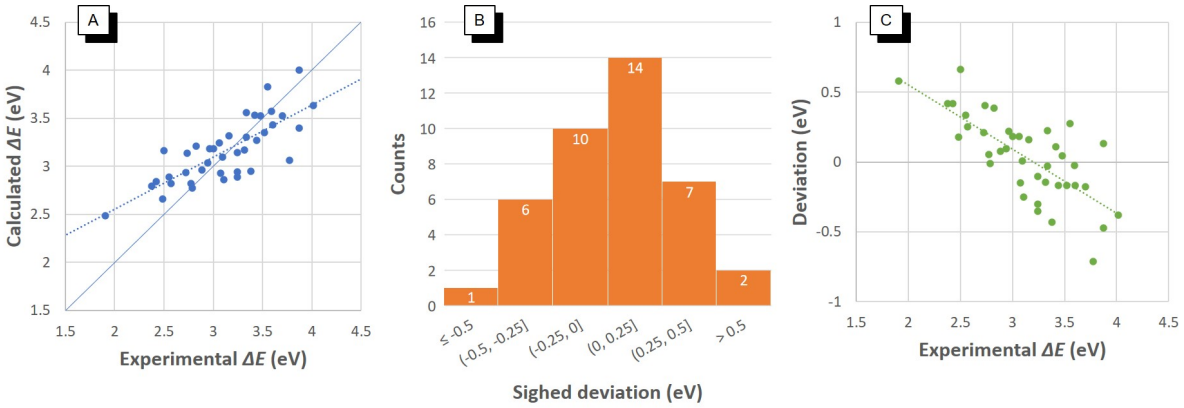


Figure S4: (A) Experimental transition energy versus calculated transition energy, (B) histogram of sighed deviation and (C) calculation deviation distribution to experimental transition energy from M062X functional with def2-SVP basis set.

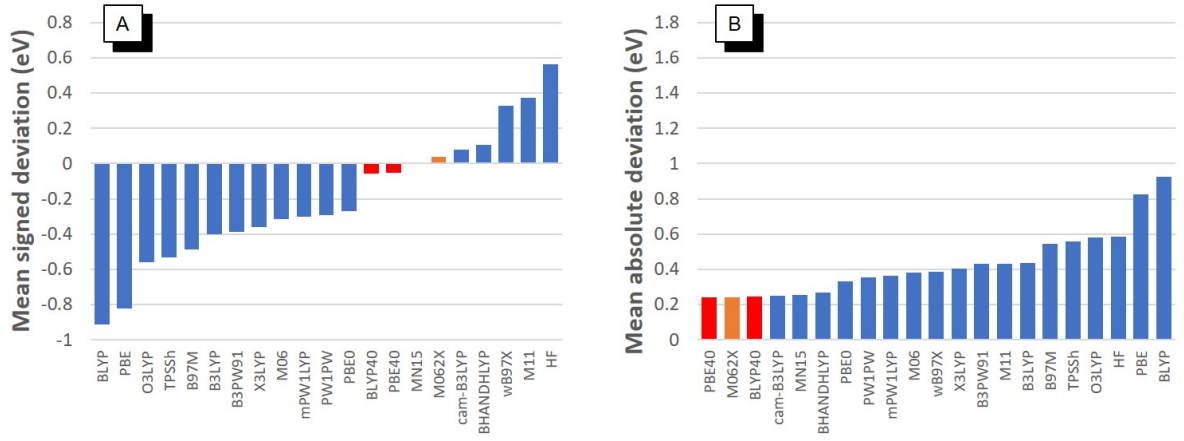


Figure S5: MSD and MAD of functionals including PBE40 and BLYP40.

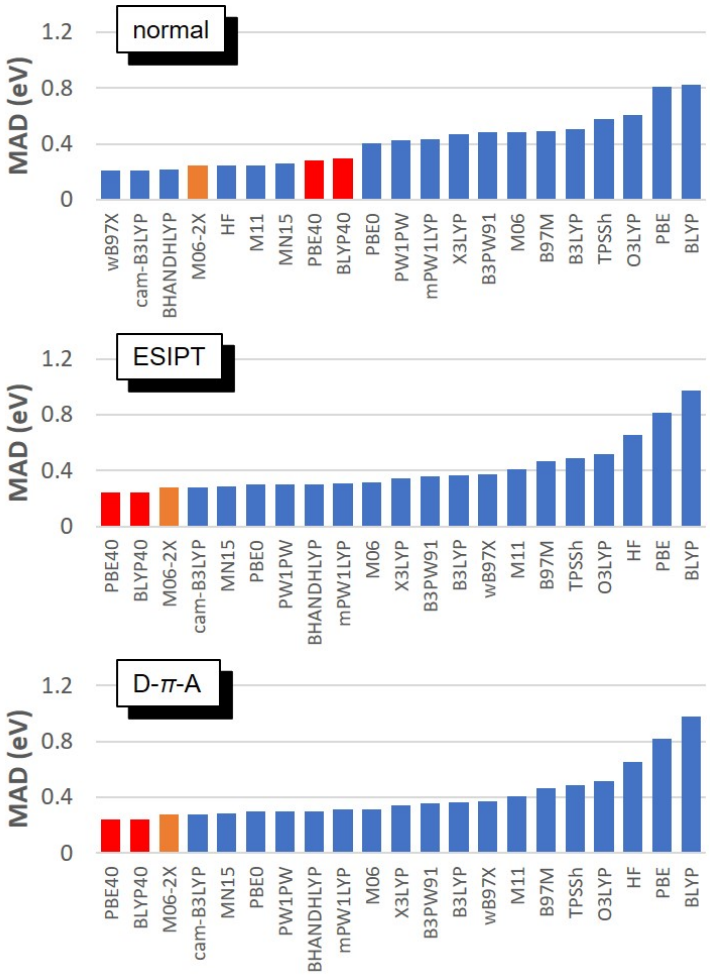


Figure S6: MAD of functionals including PBE40 and BLYP40 in different subsets.

Table S1: MAD (eV) of calculation under different methods with def2-SVP basis set in total and different subsets.

Methods	total	Normal	ESIPT	D-π-A
M062X	0.241086	0.243078	0.259129	0.246543
cam-B3LYP	0.248617	0.211839	0.259212	0.29157
BHANDHLYP	0.267162	0.215903	0.292237	0.320799
PBE0	0.332308	0.404754	0.287492	0.276886
PW1PW	0.355527	0.425169	0.287983	0.312411
mPW1LYP	0.362037	0.434971	0.29764	0.314319
M06	0.379461	0.485659	0.301434	0.312921
wB97X	0.387921	0.209032	0.364257	0.568816
X3LYP	0.404762	0.468167	0.332924	0.356983
B3PW91	0.429609	0.483228	0.347363	0.390176
B3LYP	0.436824	0.504199	0.355259	0.385329
B97M	0.544136	0.493450	0.454112	0.579572
TPSSh	0.55674	0.579049	0.481304	0.532546
O3LYP	0.581079	0.605045	0.510635	0.553813
HF	0.583045	0.246598	0.659381	0.855763
PBE	0.824205	0.811968	0.809756	0.797716
BLYP	0.92555	0.826131	0.982148	0.930732
M11	0.430185	0.247978	0.62777	0.406182
MN15	0.25449	0.261663	0.271397	0.286384

Table S2: MAD (eV) and MSD (eV) of calculation under single-parameterized functionals with def2-SVP basis set and varied HF fraction (a).

	PBE functional		BLYP functional	
HF fraction (a)	MAD	MSD	MAD	MSD
0	0.824205	-0.821380	0.925550	-0.914780
0.25	0.332308	-0.269680	0.366314	-0.307430
0.3	0.295436	-0.214100	0.307717	-0.217860
0.35	0.254579	-0.129140	0.264420	-0.130540
0.4	0.240636	-0.050480	0.246730	-0.056000
0.45	0.245952	0.022642	0.254765	0.011516
0.5	0.260224	0.089943	0.267162	0.106176
0.55	0.284665	0.151560	-	-
0.6	-	-	0.309183	0.191417
0.65	0.334095	0.258233	-	-
1	0.583045	0.562386	0.583045	0.562386

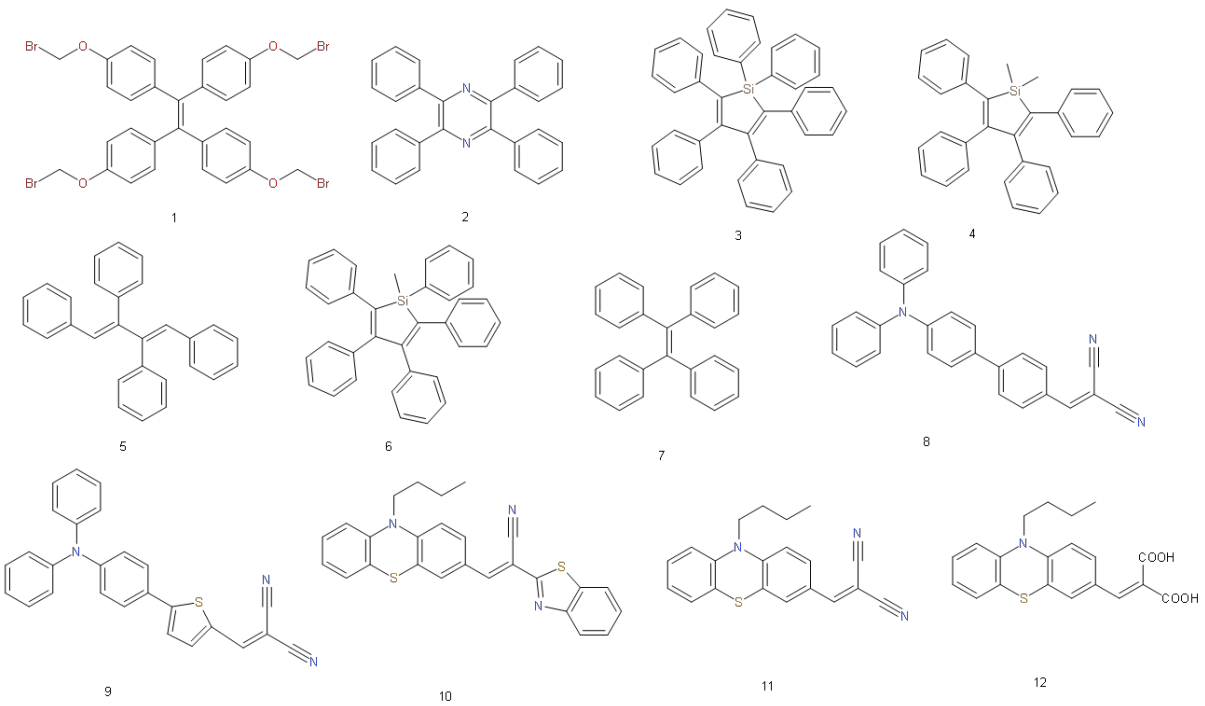


Figure S7: Chemical structures in dataset (1-12).

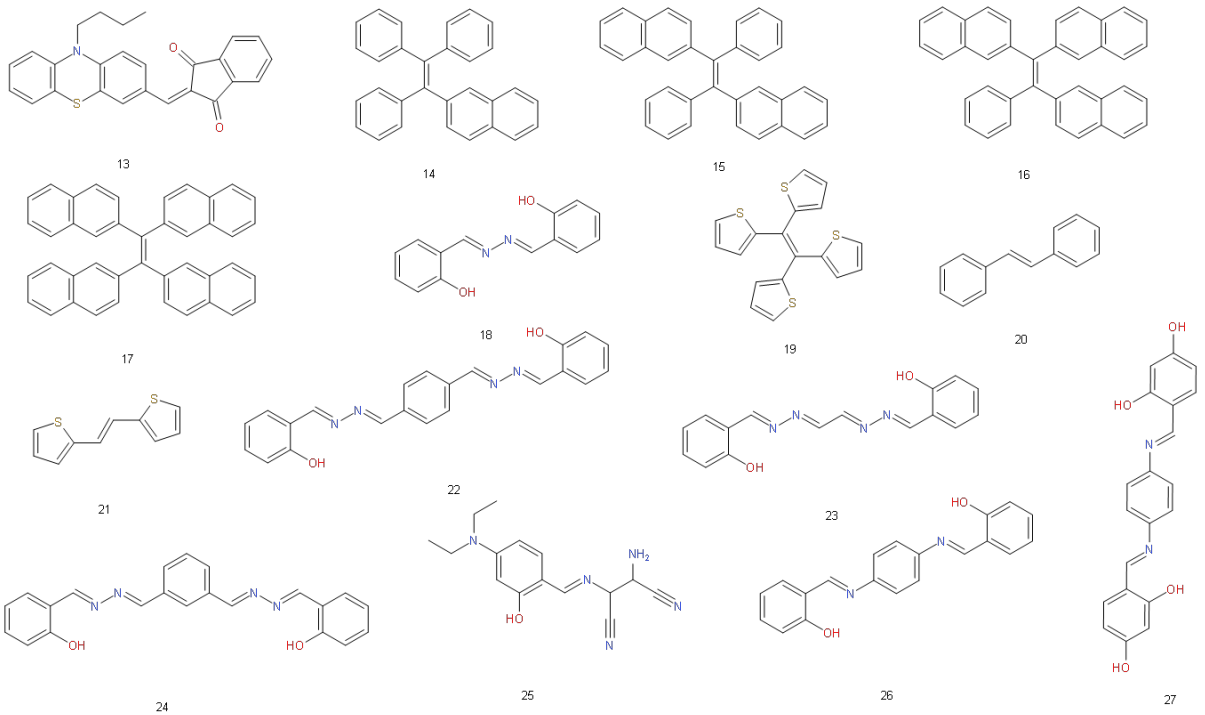


Figure S8: Chemical structures in dataset (13-27).

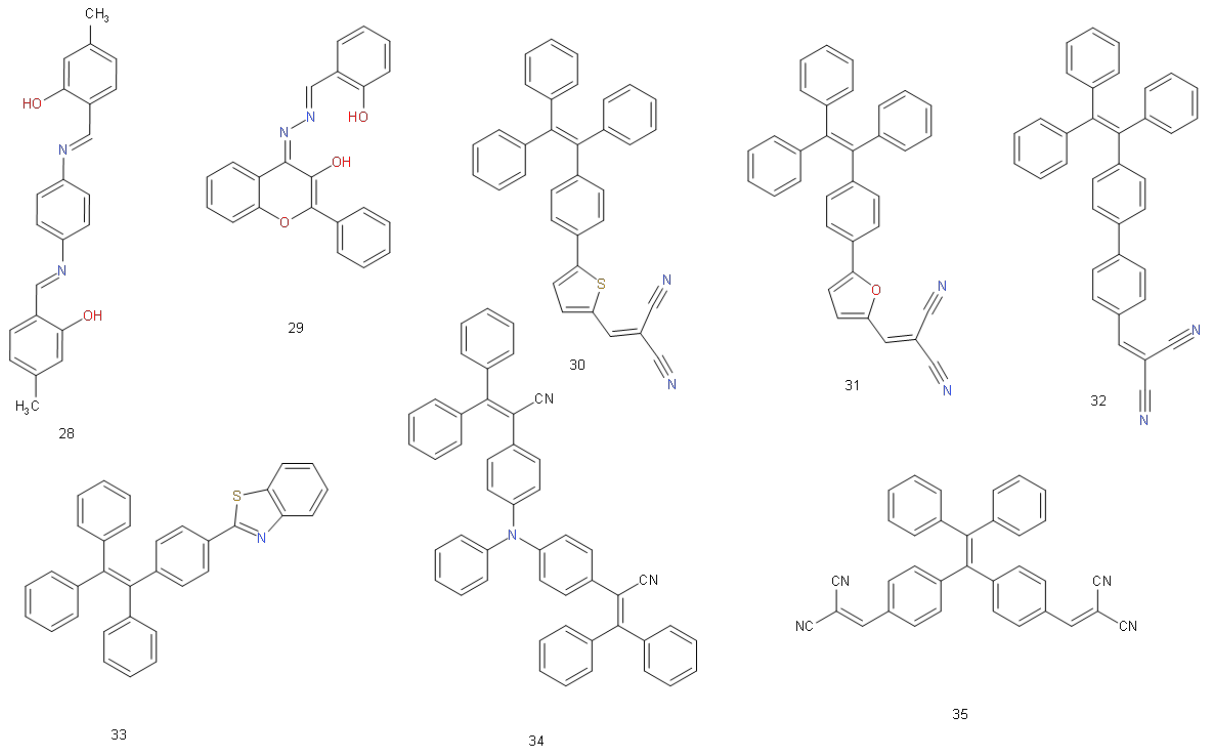


Figure S9: Chemical structures in dataset (28-35).

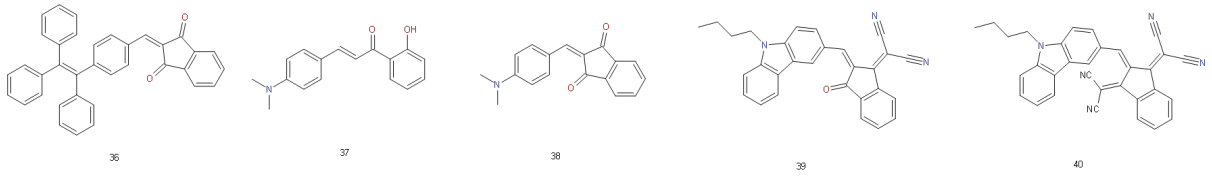


Figure S10: Chemical structures in dataset (36-40).

Table S3: Experimental transition energy data and type labels for compounds in tested dataset.

compounds	experimental (eV)	type
1	3.870967742	normal
2	3.550295858	normal
3	3.773584906	normal
4	3.314917127	normal
5	3.592814371	normal
6	3.243243243	normal
7	4.013377926	normal
8	2.721088435	D-π-A
9	2.48447205	D-π-A
10	2.569593148	D-π-A
11	2.553191489	D-π-A
12	3.06122449	D-π-A
13	2.424242424	D-π-A
14	3.703703704	normal
15	3.603603604	normal
16	3.519061584	normal
17	3.438395415	normal
18	3.418803419	ESIPT
19	3.10880829	normal
20	3.870967742	normal
21	3.333333333	normal
22	3	ESIPT
23	2.962962963	ESIPT
24	3.47826087	ESIPT
25	2.733485194	ESIPT D-π-A
26	3.157894737	ESIPT
27	3.243243243	ESIPT
28	3.243243243	ESIPT
29	3.38028169	ESIPT
30	2.784222738	D-π-A
31	2.771362587	D-π-A
32	3.092783505	D-π-A
33	3.333333333	D-π-A
34	2.941176471	D-π-A
35	3.076923077	D-π-A
36	2.884615385	D-π-A
37	2.823529412	ESIPT D-π-A
38	2.5	D-π-A
39	2.376237624	D-π-A
40	1.904761905	D-π-A