Supporting Information for:

Revisiting the Half-and-Half Functional

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References

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S1 Statistical Assessments of Ground-State Properties

Table S1: Description of the data sets from GMTKN55 that are used in the present work.[a]

Data Set	Description
	—Barrier Heights—
BH76	Barrier heights of hydrogen transfer, heavy atom transfer, nucleophilic substitution, unimolecular and association reactions
BHPERI	Barrier heights of pericyclic reactions
BHDIV10	Diverse reaction barrier heights
INV24	Inversion/racemization barrier heights
BHROT27	Barrier heights for rotation around single bonds
PX13	Proton-exchange barriers in H_2O, NH_3, and HF clusters
WCPT18	Proton-transfer barriers in uncatalyzed and water-catalyzed reactions
	—Basic Thermochemical Properties—
W4-11	Total atomization energies
G21EA	Adiabatic electron affinities
G21IP	Adiabatic ionization potentials
DIPCS10	Double-ionization potentials of closed-shell systems
PA26	Adiabatic proton affinities, including amino acids
SEI4x4	SIE-related problems
YBDE18	Bond-dissociation energies in ylides
AL2x6	Dimerization energies of AlX_3 compounds
NBPRC	Oligeromizations and H_2 fragmentations of NH_3/BH_3 systems and H_2 activation reactions with PH_3/BH_3 systems
ALK8	Dissociation and other reactions of alkaline compounds
G2RC	Reaction energies of selected G2/97 systems
BH76RC	Reaction energies of the BH76 set
FH51	Reaction energies in various (in)organic systems
TAUT15	Relative energies in tautomers
DC13	13 difficult cases for DFT methods
	—Reaction Energies for Large Systems—
MB16-43	Decomposition energies of artificial molecules
DARC	Reaction energies of Diels-Alder reactions
RSE43	Radical stabilization energies
BSR36	Bond-separation reactions of saturated hydrocarbons
CDIE20	Double-bond isomerization energies in cyclic systems
ISO34	Isomerization energies of small and medium-sized organic molecules
ISOL24	Isomerization energies of large organic molecules
PArel	Relative energies in protonated isomers

[a] Adapted from Table 1 of Ref. 1.

Table S2: Comparison of ground-state error statistics for B3LYP+D3 and CAM-B3LYP+D3.[a]

Functional	Error Statistics (kcal/mol)[b]			
	Mean	MAE	Std. Dev.	Max
B3LYP+D3	−1.15	4.79	3.98	12.92
CAM-B3LYP+D3	−1.64	4.45	4.03	13.75

[a]The B3LYP+D3 and CAM-B3LYP+D3 error statistics are agglomerations of those in Tables S3 and S4, respectively. [b]Versus reference values from GMTKN55.[1]

Table S3: Ground-state error statistics for B3LYP+D3.

Data Set	Error Statistics (kcal/mol)[a]			
	Mean	MAE	Std. Dev.	Max
FH51	1.63	2.77	3.31	9.13
INV24	−0.74	1.00	1.07	3.49
BHPERI	−0.39	0.98	1.29	3.99
TAUT15	−0.46	1.14	1.26	2.13
WCPT18	−1.99	2.15	1.91	5.64
W4-11	−1.97	3.67	5.06	27.59
PArel	−0.04	1.09	1.63	5.14
DARC	3.63	7.84	7.14	9.81
PX13	−4.99	4.99	1.61	8.01
G21EA	−0.48	3.25	3.99	10.61
BSR36	−3.68	3.68	1.99	9.69
MB16-43	−34.12	34.46	19.01	85.51
DC13	3.46	10.38	12.75	27.28
G2RC	1.17	2.79	3.32	8.35
ISOL24	−2.79	6.03	7.94	23.00
NBPRC	1.70	2.42	3.28	9.94
G21IP	2.08	3.76	4.40	11.99
RSE43	−1.74	1.74	0.98	4.49
DIPCS10	1.78	4.41	5.41	12.60
YBDE18	−5.37	5.65	4.00	12.32
BH76	−4.89	4.94	2.83	11.16
SIE4x4	17.66	17.66	9.99	40.19
BH76RC	0.03	2.01	2.58	6.46
AL2X6	−4.23	4.23	0.73	5.38
CDIE20	1.10	1.12	0.57	2.11
PA26	1.93	2.24	2.47	8.63
ISO34	−0.30	1.88	2.75	10.73
BHDIV10	−1.63	2.88	3.05	5.39
ALK8	−1.09	2.29	2.55	5.64
BHROT27	0.36	0.38	0.43	1.26

[a]Versus reference values from GMTKN55.[1]

Table S4: Ground-state error statistics for CAM-B3LYP.

Data Set	Error Statistics (kcal/mol)[a]			
	Mean	MAE	Std. Dev.	Max
FH51	−0.33	2.09	2.71	6.41
INV24	−0.22	1.28	1.94	5.01
BHPERI	2.26	2.29	1.36	4.52
TAUT15	−0.32	0.93	1.04	2.08
WCPT18	−1.42	2.66	2.84	5.16
W4-11	−1.67	3.49	5.86	36.25
PArel	0.10	0.64	1.01	3.45
DARC	−1.62	5.95	7.33	13.41
PX13	−5.67	5.67	2.16	9.22
G21EA	−1.01	3.47	4.01	7.95
BSR36	−4.39	4.39	3.08	14.62
MB16-43	−37.60	38.58	27.32	132.98
DC13	0.93	8.86	11.11	24.91
G2RC	−1.34	3.48	3.66	8.37
ISOL24	−1.33	3.47	4.29	12.77
NBPRC	0.41	2.33	2.82	4.66
G21IP	2.34	3.92	4.50	11.51
RSE43	−1.11	1.11	0.69	3.21
DIPCS10	1.85	4.28	4.94	11.74
YBDE18	−3.75	3.80	2.43	8.22
BH76	−3.08	3.23	2.50	8.63
SIE4x4	13.58	13.58	8.85	34.57
BH76RC	−0.36	1.76	2.12	5.99
AL2X6	−3.38	3.38	0.62	4.19
CDIE20	0.30	0.52	0.69	1.83
PA26	0.04	1.46	1.94	5.14
ISO34	−0.33	1.13	1.68	7.07
BHDIV10	0.18	1.66	1.90	3.49
ALK8	−2.80	3.54	5.14	13.60
BHROT27	0.40	0.43	0.48	1.47

[a] Versus reference values from GMTKN55.[1]

Table S5: Ground-state error statistics for ωB97M-V.

Data Set	Error Statistics (kcal/mol)[a]			
	Mean	MAE	Std. Dev.	Max
BH76	−1.30	1.45	1.42	5.24
BHPERI	0.85	1.07	1.11	4.10
BHDIV10	−1.24	1.37	1.15	3.73
INV24	−0.03	1.28	1.81	5.54
BHROT27	0.07	0.25	0.30	0.67
PX13	−3.31	3.31	1.37	5.44
WCPT18	−1.13	1.81	1.95	5.25
W4-11	−0.76	2.16	4.07	31.30
G21EA	−2.84	3.57	3.40	8.35
G21IP	−0.94	2.98	3.75	8.78
DIPCS10	−4.86	5.36	3.77	10.61
PA26	−1.35	1.83	1.66	4.84
SIE4x4	10.33	10.67	8.34	30.50
YBDE18	−2.63	2.93	2.49	6.87
AL2X6	−1.21	1.21	0.71	1.87
NBPRC	0.40	0.91	1.05	2.18
ALK8	−1.65	2.50	2.62	6.66
G2RC	−0.47	2.15	3.02	10.73
BH76RC	0.40	0.94	1.11	2.69
FH51	−0.08	1.17	1.67	4.58
TAUT15	0.04	0.32	0.46	1.25
DC13	−1.74	5.62	6.93	12.64
MB16-43	−17.79	18.59	13.72	63.41
DARC	13.91	15.51	23.77	51.95
RSE43	−0.82	0.82	0.55	2.60
BSR36	−0.36	0.38	0.21	0.83
CDIE20	−0.22	0.58	0.65	1.28
ISO34	−0.40	0.68	0.80	2.06
ISOL24	−0.18	1.73	2.48	8.13
PArel	0.24	0.59	0.86	2.07

[a] Versus reference values from GMTKN55.[1]

Table S6: Ground-state error statistics for M06-HF.

Data Set	Error Statistics (kcal/mol)[a]			
	Mean	MAE	Std. Dev.	Max
BH76	0.80	2.35	3.22	13.28
BHPERI	−1.94	2.80	2.86	5.99
BHDIV10	−1.56	3.21	3.86	8.03
INV24	−0.37	3.81	4.81	12.21
BHROT27	0.01	0.90	1.28	4.25
PX13	−14.41	14.41	6.39	27.03
WCPT18	−1.11	3.90	4.52	9.05
W4-11	−5.11	6.35	9.30	48.50
G21EA	−1.72	3.60	4.66	13.99
G21IP	1.43	5.54	7.46	28.38
DIPCS10	2.90	6.83	8.48	16.89
PA26	−2.53	3.87	3.94	9.11
SIE4x4	1.45	4.09	4.72	9.39
YBDE18	1.92	5.00	5.53	11.38
AL2X6	4.43	4.43	1.84	7.22
NBPRC	−2.46	3.54	4.84	15.59
ALK8	2.12	6.22	8.66	17.46
G2RC	−0.65	5.69	7.13	14.43
BH76RC	0.40	0.94	1.11	2.69
FH51	−0.28	3.69	4.69	12.20
TAUT15	1.44	2.70	2.85	5.90
DC13	−5.68	12.92	16.38	34.45
MB16-43	75.49	75.49	33.62	144.49
DARC	12.80	14.22	20.96	47.51
RSE43	3.04	3.15	1.83	9.04
BSR36	−7.24	7.24	5.89	22.80
CDIE20	−1.18	1.31	0.87	2.35
ISO34	−0.31	2.45	3.13	8.75
ISOL24	1.60	4.32	5.63	16.38
PArel	0.13	2.05	3.23	8.01

[a] Versus reference values from GMTKN55.[1]

Table S7: Ground-state error statistics for BLYP+D3.

Data Set	Error Statistics (kcal/mol)[a]			
	Mean	MAE	Std. Dev.	Max
BH76	−9.10	9.10	4.53	24.52
BHPERI	−4.31	4.31	2.10	10.64
BHDIV10	−5.22	6.17	4.92	12.21
INV24	−1.61	2.26	2.60	8.22
BHROT27	0.19	0.42	0.54	1.33
PX13	−8.88	8.88	1.75	12.96
WCPT18	−5.77	5.77	2.54	11.38
W4-11	4.94	7.45	9.25	38.42
G21EA	−2.18	4.79	5.12	11.07
G21IP	−1.87	4.71	5.26	12.18
DIPCS10	−6.15	8.01	6.76	13.78
PA26	1.72	2.66	3.14	8.93
SIE4x4	25.00	25.00	13.15	52.64
YBDE18	−5.59	7.36	7.53	19.17
AL2X6	−5.63	5.63	1.58	9.02
NBPRC	1.77	3.12	4.20	12.01
ALK8	−2.37	2.93	2.91	7.77
G2RC	4.68	5.76	5.30	16.05
BH76RC	1.00	3.08	4.18	12.69
FH51	3.59	4.58	4.87	17.82
TAUT15	−0.70	1.71	1.89	3.25
DC13	5.63	15.31	17.00	32.76
MB16-43	−34.69	37.35	26.69	94.19
DARC	7.36	9.72	7.43	13.80
RSE43	−2.70	2.70	1.38	6.98
BSR36	−2.64	2.64	1.53	7.86
CDIE20	1.23	1.24	0.42	1.73
ISO34	−0.57	2.64	3.70	11.38
ISOL24	−3.80	8.65	11.16	28.57
PArel	−0.47	1.68	2.58	8.43

[a] Versus reference values from GMTKN55.[1]

Table S8: Ground-state error statistics for B(20)LYP+D3.

Data Set	Error Statistics (kcal/mol)[a]			
	Mean	MAE	Std. Dev.	Max
BH76	−4.88	4.91	2.80	11.84
BHPERI	0.30	1.30	1.70	4.94
BHDIV10	−1.00	2.65	3.01	5.70
INV24	−0.75	0.94	1.03	3.09
BHROT27	0.32	0.35	0.41	1.28
PX13	−4.19	4.19	1.41	6.40
WCPT18	−1.65	1.96	1.93	5.41
W4-11	−6.83	7.09	5.93	30.35
G21EA	−4.12	4.93	4.11	10.77
G21IP	−1.65	4.05	4.56	9.24
DIPCS10	−5.26	6.73	6.09	14.68
PA26	2.02	2.41	2.64	8.87
SIE4x4	17.69	17.69	9.95	40.41
YBDE18	−6.70	6.92	4.17	14.10
AL2X6	−5.51	5.51	0.77	6.42
NBPRC	1.91	3.51	4.08	10.91
ALK8	−4.18	4.91	5.28	13.82
G2RC	1.77	3.18	3.33	7.88
BH76RC	0.20	2.10	2.59	5.74
FH51	1.75	2.83	3.38	10.77
TAUT15	−0.81	1.18	1.22	2.37
DC13	4.24	12.81	16.35	32.40
MB16-43	−48.61	48.61	21.61	114.86
DARC	5.62	8.84	7.25	11.68
RSE43	−1.35	1.35	0.90	4.10
BSR36	−5.53	5.53	3.90	18.58
CDIE20	0.95	0.99	0.52	2.06
ISO34	−0.38	2.08	2.97	11.01
ISOL24	−3.38	6.75	8.72	25.17
PArel	−0.13	1.20	1.76	5.07

[a] Versus reference values from GMTKN55.[1]

Table S9: Ground-state error statistics for B(30)LYP+D3.

Data Set	Error Statistics (kcal/mol)[a]			
	Mean	MAE	Std. Dev.	Max
BH76	−3.14	3.27	2.39	10.96
BHPERI	1.46	1.65	1.29	3.69
BHDIV10	0.48	1.83	2.35	4.83
INV24	−0.02	1.07	1.53	4.24
BHROT27	0.41	0.43	0.42	1.45
PX13	−2.28	2.28	1.40	4.48
WCPT18	0.03	1.75	1.99	3.26
W4-11	−12.00	12.05	7.64	39.09
G21EA	−5.01	5.72	4.13	10.62
G21IP	−1.58	4.09	4.62	9.87
DIPCS10	−4.82	6.29	6.39	16.02
PA26	2.32	2.59	2.58	9.06
SIE4x4	14.16	14.16	8.48	34.35
YBDE18	−6.44	6.44	2.38	10.75
AL2X6	−4.43	4.43	0.56	5.30
NBPRC	1.45	3.13	3.56	8.47
ALK8	−3.38	4.69	5.61	14.08
G2RC	0.19	2.66	3.10	7.81
BH76RC	−0.18	2.33	2.86	6.57
FH51	0.66	2.13	2.81	9.34
TAUT15	−0.77	1.04	1.01	2.48
DC13	2.94	11.76	14.89	30.11
MB16-43	−46.61	46.61	23.78	127.55
DARC	2.77	7.62	7.23	8.68
RSE43	−0.83	0.83	0.71	2.82
BSR36	−5.28	5.28	3.86	18.36
CDIE20	0.76	0.82	0.57	1.97
ISO34	−0.19	1.73	2.54	10.44
ISOL24	−2.42	5.37	6.76	18.37
PArel	0.06	1.06	1.47	4.72

[a] Versus reference values from GMTKN55.[1]

Table S10: Ground-state error statistics for B(40)LYP+D3.

Data Set	Error Statistics (kcal/mol)[a]			
	Mean	MAE	Std. Dev.	Max
BH76	−1.53	2.13	2.43	10.38
BHPERI	2.60	2.60	1.11	4.38
BHDIV10	1.88	2.13	1.97	4.92
INV24	0.70	1.65	2.52	8.32
BHROT27	0.51	0.52	0.46	1.63
PX13	−0.47	1.32	1.46	2.86
WCPT18	1.62	2.16	2.22	6.12
W4-11	−17.05	17.08	10.60	47.65
G21EA	−5.85	6.63	4.45	11.83
G21IP	−1.51	4.26	4.92	10.58
DIPCS10	−4.38	6.54	7.05	17.35
PA26	2.65	2.85	2.64	9.31
SIE4x4	10.72	10.72	7.19	28.39
YBDE18	−6.21	6.21	1.11	8.11
AL2X6	−3.36	3.36	0.65	4.17
NBPRC	0.97	2.93	3.29	6.01
ALK8	−2.59	4.48	6.00	14.29
G2RC	−1.36	2.97	3.52	9.12
BH76RC	−0.55	3.02	3.69	8.22
FH51	−0.43	1.93	2.55	7.87
TAUT15	−0.73	0.93	0.88	2.64
DC13	1.58	11.18	13.89	27.75
MB16-43	−44.20	44.81	28.34	140.14
DARC	−0.12	6.39	7.23	11.60
RSE43	−0.36	0.49	0.59	1.81
BSR36	−5.01	5.01	3.84	18.12
CDIE20	0.58	0.70	0.63	1.87
ISO34	−0.01	1.41	2.18	9.78
ISOL24	−1.47	4.15	4.97	11.56
PArel	0.26	1.01	1.39	4.46

[a] Versus reference values from GMTKN55.[1]

Table S11: Ground-state error statistics for B(50)LYP+D3, which is equivalent to BH&H-LYP+D3.

Data Set	Error Statistics (kcal/mol)[a]			
	Mean	MAE	Std. Dev.	Max
BH76	0.05	2.17	2.82	9.90
BHPERI	4.09	4.09	1.15	6.28
BHDIV10	2.68	2.68	1.92	5.65
INV24	1.35	2.40	3.74	12.60
BHROT27	0.60	0.60	0.61	1.77
PX13	0.95	1.49	1.48	3.11
WCPT18	3.19	3.19	2.40	9.07
W4-11	−20.95	21.00	13.78	62.62
G21EA	−6.67	7.49	4.96	13.73
G21IP	−1.44	4.50	5.40	12.02
DIPCS10	−3.89	7.17	8.00	18.63
PA26	2.99	3.25	2.74	9.66
SIE4x4	7.14	7.14	6.26	22.30
YBDE18	−5.73	5.73	2.00	10.62
AL2X6	−1.21	1.40	1.06	2.22
NBPRC	0.83	2.37	2.61	4.74
ALK8	1.70	4.37	5.31	9.97
G2RC	−2.90	4.17	4.53	12.18
BH76RC	−0.84	3.72	4.69	12.19
FH51	−1.03	1.98	2.43	7.07
TAUT15	−0.25	0.55	0.77	2.48
DC13	−0.13	9.68	11.83	24.60
MB16-43	−31.52	34.33	29.90	120.83
DARC	−2.74	5.46	7.00	13.70
RSE43	−0.30	0.51	0.57	1.35
BSR36	−4.57	4.57	2.53	12.15
CDIE20	0.53	0.66	0.69	1.94
ISO34	0.22	1.26	2.05	9.37
ISOL24	−0.49	3.54	4.41	10.14
PArel	0.51	1.03	1.42	4.20

[a] Versus reference values from GMTKN55.[1]

Table S12: Ground-state error statistics for B(60)LYP+D3.

Data Set	Error Statistics (kcal/mol)[a]			
	Mean	MAE	Std. Dev.	Max
BH76	1.27	2.75	3.47	13.08
BHPERI	4.85	4.85	1.69	7.64
BHDIV10	4.47	4.47	2.39	8.77
INV24	2.17	3.24	4.73	16.64
BHROT27	0.72	0.73	0.62	1.99
PX13	2.85	2.85	1.69	5.33
WCPT18	4.54	4.54	3.02	11.93
W4-11	−26.51	26.56	17.29	80.56
G21EA	−7.43	8.34	5.66	15.58
G21IP	−1.36	4.76	6.03	14.95
DIPCS10	−3.54	8.07	9.10	19.94
PA26	3.41	3.80	3.02	10.01
SIE4x4	4.06	4.42	5.49	16.78
YBDE18	−5.81	5.81	3.36	14.27
AL2X6	−1.22	1.69	1.23	2.45
NBPRC	−0.05	2.99	3.64	6.34
ALK8	−1.02	5.24	6.87	14.60
G2RC	−4.41	5.77	5.44	15.44
BH76RC	−1.25	4.72	5.94	16.73
FH51	−2.63	3.16	3.20	11.74
TAUT15	−0.67	0.85	0.84	2.96
DC13	−1.30	10.80	13.60	24.52
MB16-43	−38.38	42.70	41.07	165.10
DARC	−6.00	6.07	7.26	17.61
RSE43	0.42	0.64	0.64	1.61
BSR36	−4.45	4.45	3.83	17.61
CDIE20	0.25	0.52	0.75	1.79
ISO34	0.33	1.09	1.78	8.25
ISOL24	0.37	2.28	3.03	8.92
PArel	0.68	1.36	1.87	4.86

[a] Versus reference values from GMTKN55.[1]

Table S13: Ground-state error statistics for B(70)LYP+D3.

Data Set	Error Statistics (kcal/mol)[a]			
	Mean	MAE	Std. Dev.	Max
BH76	2.48	3.65	4.17	17.97
BHPERI	5.96	5.96	2.22	10.64
BHDIV10	5.65	5.65	2.99	11.28
INV24	2.90	4.06	5.86	20.87
BHROT27	0.82	0.84	0.72	2.31
PX13	4.37	4.37	1.85	7.01
WCPT18	5.88	5.88	3.52	14.78
W4-11	−30.98	31.10	20.68	97.77
G21EA	−8.17	9.13	6.40	17.55
G21IP	−1.28	5.13	6.73	18.14
DIPCS10	−3.12	8.95	10.33	21.21
PA26	3.83	4.35	3.30	10.46
SIE4x4	0.85	4.48	5.32	11.12
YBDE18	−5.64	5.89	4.95	18.24
AL2X6	−0.15	1.18	1.55	3.09
NBPRC	−0.60	3.39	4.18	7.84
ALK8	−0.25	5.80	7.34	14.70
G2RC	−5.91	7.42	6.59	19.35
BH76RC	−1.59	5.61	7.15	21.14
FH51	−3.73	4.09	3.92	16.86
TAUT15	−0.65	0.83	0.90	3.11
DC13	−2.79	11.29	14.36	26.90
MB16-43	−35.05	44.24	48.27	177.48
DARC	−8.99	8.99	7.29	20.68
RSE43	0.73	0.94	0.78	1.99
BSR36	−4.15	4.15	3.85	17.34
CDIE20	0.10	0.53	0.82	1.83
ISO34	0.49	1.18	1.81	7.37
ISOL24	1.28	2.95	3.79	10.50
PArel	0.90	1.54	2.28	7.06

[a] Versus reference values from GMTKN55.[1]

S2 TD-DFT Excitation Energies

Table S14: Vertical excitation energies and errors in TD-DFT calculations using different functionals.[a]

Molecule	Transition Type	Benchmark (eV)[b]	TD-DFT Error (eV)					
			B(10)LYP	B3LYP	B(30)LYP	BH&H-LYP	B(60)LYP	B(70)LYP
Dipeptide	CT	8.07	−2.25	−1.76	−1.03	−0.62	−0.34	−0.12
	CT	7.18	−1.52	−1.03	−0.55	0.07	0.30	0.52
	L	5.62	−0.10	−0.07	0.06	0.30	0.42	0.55
	L	5.79	−0.50	−0.02	0.12	0.37	0.49	0.61
β-dipeptide	CT	9.13	−2.64	−1.87	−0.99	−0.71	−0.17	0.37
	CT	7.99	−1.67	−0.79	−0.50	−0.32	−0.21	−0.04
	L	5.40	0.14	0.26	0.36	0.53	0.65	0.78
	L	5.10	0.28	0.46	0.58	0.9	1.01	1.13
Naphthalene	L	4.88	−0.64	−0.50	−0.38	−0.2	−0.14	−0.10
	L	4.46	−0.10	0.01	0.11	0.28	0.35	0.42
Tetracene	L	2.90	−0.60	−0.47	−0.35	−0.16	−0.09	−0.02
	L	3.52	−0.18	−0.05	0.05	0.21	0.27	0.32
Pentacene	L	2.35	−0.59	−0.46	−0.36	−0.17	−0.10	−0.04
	L	3.27	−0.60	−0.06	−0.07	0.18	0.23	0.28
Hexacene	L	1.95	−0.65	−0.47	−0.36	−0.18	−0.12	−0.06
	L	3.09	−0.93	−0.08	−0.43	−0.15	−0.07	0.01
PP	L	4.85	−0.30	−0.09	0.10	0.33	0.43	0.50
	L	5.13	−0.36	−0.17	−0.22	0.06	0.16	0.26
	CT	5.47	−1.19	−0.89	−0.63	−0.14	0.86	1.21
	CT	5.94	−1.66	−1.30	−0.71	0.02	1.02	1.19
DMABN	L	4.25	−0.01	0.19	0.37	0.68	0.80	0.92
	CT	4.56	−0.08	0.08	0.22	0.44	0.53	0.59
PA-2	L	5.92	−0.13	−0.04	0.03	0.16	0.21	0.25
PA-3	L	4.95	−0.24	−0.14	−0.05	0.11	0.18	0.24
PA-4	L	4.41	−0.39	−0.28	−0.18	0.00	0.08	0.15
PA-5	L	4.27	−0.73	−0.61	−0.50	−0.31	−0.22	−0.14
CO	L	10.23	−0.22	−0.20	−0.10	0.63	0.97	1.31
	L	9.88	−0.53	−0.16	−0.20	0.13	0.13	0.14
	L	8.51	−0.20	−0.12	−0.06	0.06	0.11	0.15
H_2CO	L	3.94	−0.14	−0.09	−0.03	0.08	0.13	0.20
HCl	CT	8.23	−0.74	−0.57	−0.49	−0.23	−0.11	0.01

[a]Full linear response TD-DFT. [b]From Ref. 2.

Table S15: Errors in K-edge transition energies in comparison to benchmark values.[a]

Molecule	Element	TD-B(α)LYP Error (eV)[b]					Benchmark
		$\alpha = 30$	$\alpha = 40$	$\alpha = 50$	$\alpha = 60$	$\alpha = 70$	(eV)[c]
Acetaldehyde	C	−7.08	−4.49	−1.95	0.22	2.95	286.30
	O	−6.58	−2.40	1.69	5.71	9.65	531.14
Acetic Acid	C	−10.34	−7.61	−4.98	−2.42	2.13	288.69
	O	−9.25	−5.20	−1.20	2.76	6.68	531.95
Acetone	C	−8.31	−5.84	−3.43	−1.08	1.22	286.80
	O	−10.41	−6.61	−2.86	0.86	4.54	531.30
Benzaldehyde	C	−10.72	−7.07	−4.61	−1.97	0.26	287.70
	O	−10.45	−6.59	−2.78	0.96	4.66	531.00
Benzamide	C	−10.84	−8.07	−5.39	−3.35	−0.27	288.09
Dimethyl Carbonate	C	−9.60	−6.51	−3.37	−1.07	1.64	290.33
	O	−10.16	−6.24	−2.37	1.47	5.27	532.93
Diphenyl Carbonate	O	−10.34	−6.39	−2.51	1.33	5.12	532.93
Diphenyl Urea	O	−10.46	−6.39	−2.40	1.53	5.41	532.50
Phenylalanine	C	−7.51	−4.72	−2.04	0.58	3.17	285.10
	O	−7.53	−3.14	1.23	5.27	9.22	532.20
	N	−9.15	−5.35	−0.59	1.93	6.42	401.20
Terephthaldehyde	C	−10.28	−8.43	−5.66	−3.00	−0.42	288.20
	O	−10.18	−6.30	−2.49	1.25	4.95	530.60
Tyrosine	C	−5.62	−2.93	−0.33	0.48	3.01	285.10
Urea	C	−8.06	−5.62	−3.24	−0.93	1.33	289.53
	O	−9.97	−5.96	−2.01	1.90	5.77	532.50
Mean		−9.18	−5.80	−2.44	0.59	3.94	
MAE		9.18	5.80	2.72	1.91	4.01	

[a]TD-DFT calculations use full linear response. [b]Errors calculated as the difference between the TD-DFT value and the reference value. [c]From Ref. 3.

Table S16: Errors in S_1 excitation energies for donor–acceptor complexes, in comparison to CIS(D) benchmarks.

Molecule	ΔE[CIS(D)] (eV)[a]	TD-DFT Error (eV)[b]				
		B3LYP	B(30)LYP	B(40)LYP	BHHLYP	B(60)LYP
4T-TCNQ	1.13	0.34	0.40	0.48	0.59	0.74
4T-F2TCNQ	0.98	0.53	0.56	0.61	0.68	0.78
4T-F4TCNQ	0.88	0.67	0.68	0.71	0.75	0.82
AT-TCNQ	1.40	−0.17	−0.06	0.07	0.24	0.44
AT-F2TCNQ	1.21	−0.11	−0.03	0.09	0.24	0.42
AT-F4TCNQ	1.06	−0.14	−0.06	0.05	0.20	0.38
DMeO-BTBT-TCNQ-Re	1.39	−0.40	−0.15	0.11	0.38	0.67
DMeO-BTBT-F2TCNQ-Re	1.20	−0.34	−0.11	0.13	0.25	0.67
DMeO-BTBT-F4TCNQ-Re	1.03	−0.25	−0.04	0.18	0.56	0.68
DTBDT-TCNQ	1.42	−0.18	0.00	0.19	0.41	0.65
DTBDT-F2TCNQ	1.18	−0.10	0.07	0.25	0.45	0.67
DTBDT-F4TCNQ	1.03	0.00	0.15	0.30	0.48	0.67
Naphthalene-F2TCNQ	2.01	−0.67	−0.47	−0.26	-0.03	0.21
Naphthalene-F4TCNQ	1.81	−0.54	−0.36	−0.17	0.04	0.26
STB-TCNQ	1.78	-0.17	−0.04	−0.68	0.32	0.53
STB-F2TCNQ	1.63	−0.08	0.03	0.17	0.34	0.54
STB-F4TCNQ	1.52	0.06	0.15	0.26	0.40	0.56
Npe-TCNQ	1.63	−0.38	−0.22	−0.03	0.19	0.42
Npe-F2TCNQ	1.47	−0.33	−0.19	−0.01	0.19	0.42
Npe-F4TCNQ	1.30	−0.10	−0.01	0.11	0.27	0.45
Tetracene-TCNQ	0.61	0.07	0.10	0.17	0.28	0.43
Tetracene-F2TCNQ	0.76	0.19	0.20	0.24	0.32	0.44
Mean		−0.10	0.03	0.14	0.34	0.54
MAE		0.26	0.18	0.24	0.34	0.54

[b]Reference excitation energies computed at the CIS(D)/aug-cc-pVTZ level (this work). [a]Errors calculated as the difference between the TD-DFT value and the CIS(D) reference value.