Supporting Information for Article

Minimal Auxiliary Basis Set Approach for the Electronic Excitation Spectra of Organic Molecules

Zehao Zhou,[†] Fabio Della Sala,[‡] and Shane M. Parker[*,†]

†*Department of Chemistry, Case Western Reserve University*

10900 Euclid Ave, Cleveland, OH 44106, USA

‡*Center for Biomolecular Nanotechnologies, Istituto Italiano di Tecnologia, Via Barsanti 14,*

73010 Arnesano (LE), Italy

¶*Institute for Microelectronics and Microsystems (CNR-IMM), Via Monteroni, Campus*

Unisalento, 73100 Lecce, Italy

E-mail: shane.parker@case.edu

2D structures of the molecules in EXTEST42 and TUNE20 are shown in Fig. S1. The coordinate files for all geometries are available online.[1,2]

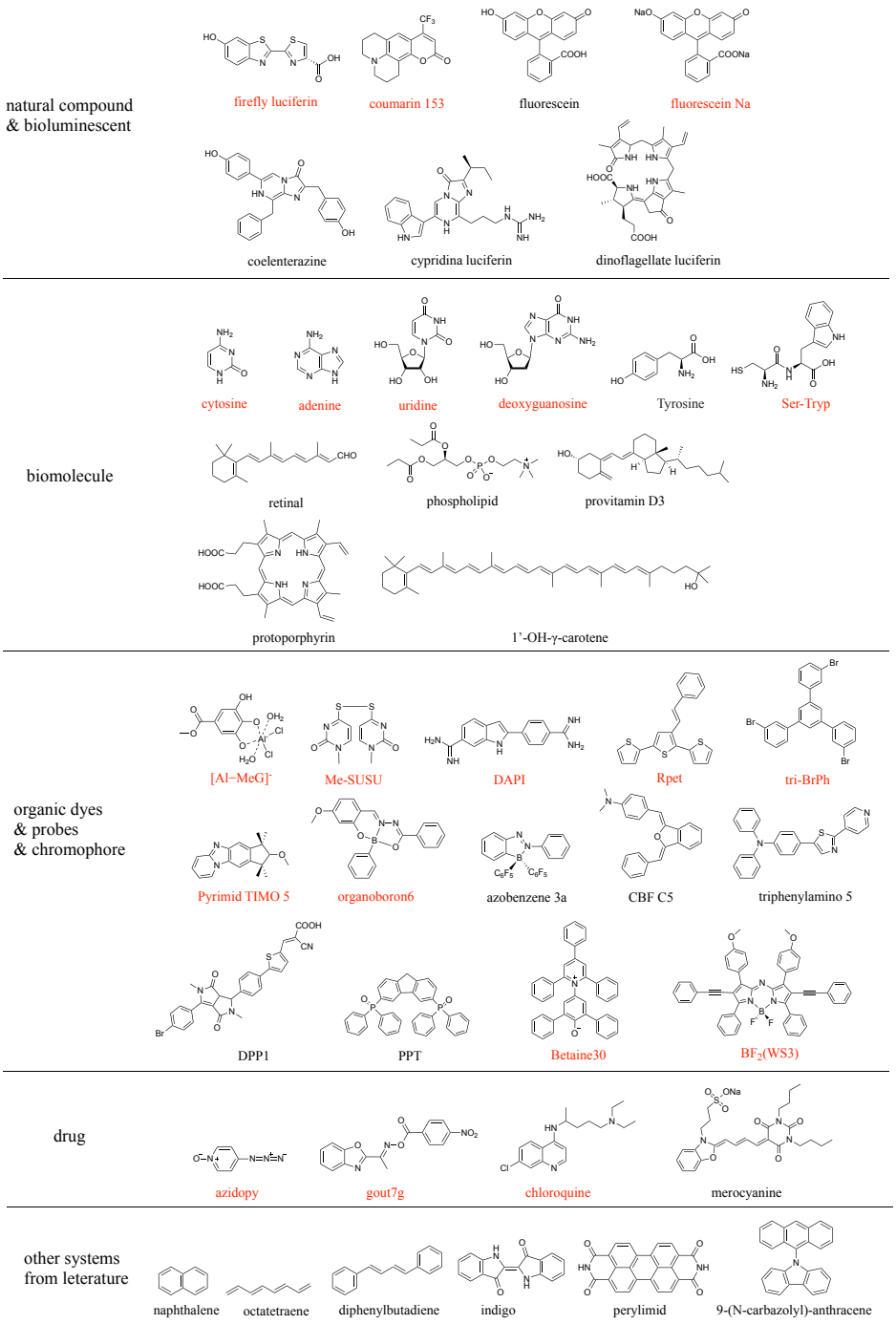

Figure S1: 2D structures of molecules in EXTEST42 set. TUNE20 set is composed of molecules with red names.

The detailed results from scanning θ from 0.05 to 10 for each individual molecule in TUNE20 are shown in Fig. S2

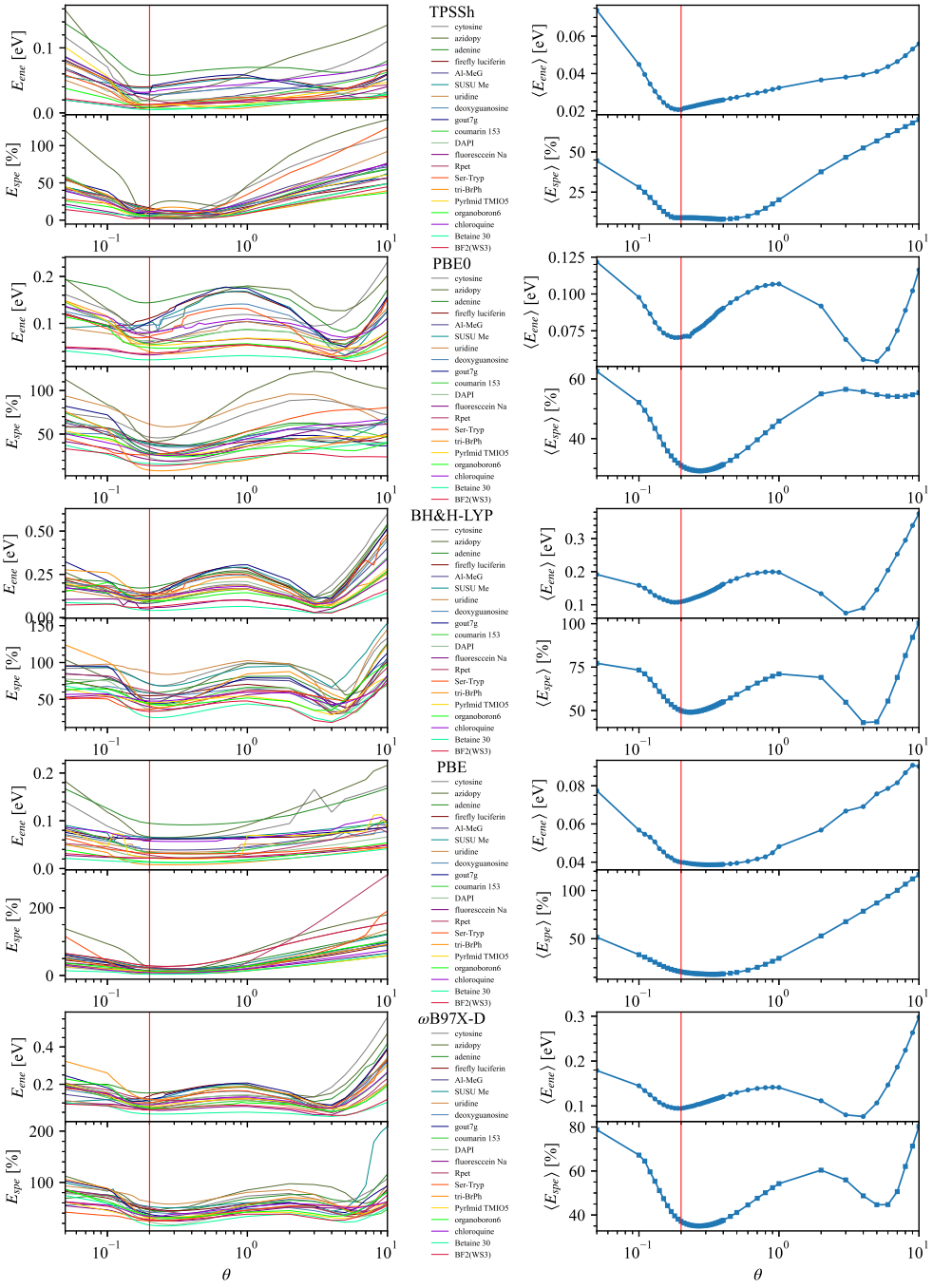

Figure S2: The E_{ene} and E_{spe} against θ for molecules in TUNE20 with def2-SVP and the TPSSh, PBE0, BH&H-LYP, PBE and ωB97X-D density functionals. The system-averaged values are shown on the right. The vertical red line indicates the chosen global value of $\theta = 0.2$.

Table SI lists the S_1 energies of the EXTEST42 predicted by PBE0 with standard TDDFT/def2-TZVP, and the S_1 deviation of sTDDFT/def2-TZVP, TDDFT-ris/def2-TZVP and TDDFT/def2-SVP. In the case of state flipping, a star mark denotes that instead of the S_1 state, the state closest to TDDFT S_1 state is compared (the state with largest association value $j(i)$ in Eq. (12) in main paper). Table SI also reports E_{ene} for sTDDFT and TDDFT-ris for each individual molecule in the last two columns. The last row reports the mean absolute error (MAE) of S_1 energies and E_{ene}, only including molecules where both sTDDFT and TDDFT-ris have correct S_1 state (no star mark).

Table SI: With PBE0, the S_1 energies of the EXTEST42 by standard TDDFT/def2-TZVP, and the S_1 deviation of sTDDFT, TDDFT-ris and TDDFT/def2-SVP. Star mark demotes a state flipping.

			S_1 (eV)	S_1 error (eV)			E_{ene} (eV)	
Classes	No. Molecules	N_{atm}	TDDFT	sTDDFT	TDDFT-ris	def2-SVP	sTDDFT	TDDFT-ris
natural compound &bioluminescent	1 firefly luciferin	26	3.82	-0.19	-0.10	0.11	0.204	0.101
	2 coumarin 153	36	3.30	-0.23	-0.06	0.07	0.234	0.054
	3 fluorescein	37	2.83	-0.19	-0.10	-0.10	0.241	0.046
	4 fluoresccein Na[3]	37	2.24	-0.25	0.00	-0.07	0.252	0.033
	5 coelenterazine[4]	53	2.72	-0.25	-0.08	0.00	0.264	0.043
	6 cypridina luciferin	57	3.52	-0.25	-0.04	0.08	0.255	0.057
	7 DFL luciferin	83	2.87	-0.26	0.00	0.08	0.269	0.052
biomolecule	8 Cytosine	13	4.74	-0.06	-0.12	0.06	0.285	0.073
	9 Adenine	15	5.02	-0.06	-0.11	-0.02	0.224	0.130
	10 Tyrosine	24	4.95	-0.13	-0.15	0.10	0.249	0.048
	11 Uracil	29	4.78	-0.08	-0.12	-0.01	0.248	0.066
	12 Guanine	32	4.87	-0.09	-0.15	0.10	0.258	0.085
	13 Ser-Tryp	38	4.56	-0.18	-0.09	0.11	0.267	0.063
	14 retinal	49	2.93	-0.21	-0.06	0.05	0.229	0.047
	15 phospholipid	52	5.55	0.11*	-0.15	-0.01	0.366	0.047
	16 provitamin D_3	72	4.32	-0.14	-0.10	0.10	0.244	0.039
	17 protoporphyrin	76	2.18	-0.32	-0.06	0.02	0.246	0.036
	18 1'-OH-γ-carotene	99	1.90	-0.22	-0.06	0.04	0.272	0.033
organic dyes &chromophore	19 [Al−MeG]$^-$[5]	28	3.97	-0.18	-0.06	0.08	0.263	0.054
	20 SUSU Me[6]	28	4.23	-0.18	-0.11	0.10	0.209	0.086
	21 DAPI[7]	36	3.54	-0.17	-0.05	0.08	0.246	0.059
	22 Rpet[8]	37	3.05	-0.13	-0.13	0.10	0.209	0.068
	23 tri-BrPh[9]	42	4.19	-0.20	-0.07	0.06	0.232	0.041
	24 PyrImid TMIO5[10]	43	3.47	-0.20	-0.07	0.08	0.239	0.050
	25 organoboron6[11]	44	3.11	-0.16	-0.08	0.02	0.246	0.049
	26 azobenzene 3a[12]	46	2.83	-0.27	-0.03	0.02	0.224	0.085
	27 DBF C5[13]	47	2.74	-0.20	-0.03	0.02	0.246	0.030
	28 triphenylamino 5[14]	49	2.85	-0.22	-0.05	0.07	0.226	0.072
	29 DPP1[15]	55	2.06	-0.27	-0.03	0.04	0.240	0.040
	30 PPT[16]	69	4.35	-0.16	-0.10	0.13	0.233	0.079
	31 Betaine 30	72	1.57	-0.29	-0.04	0.03	0.275	0.022
	32 BF_2(WS3)[17]	92	1.84	-0.30	-0.03	0.02	0.258	0.035
drug	33 azidopy[18]	14	3.44	-0.17	-0.07	0.02	0.211	0.073
	34 gout7g[19]	35	3.68	-0.33	-0.00*	0.05	0.251	0.092
	35 chloroquine	48	3.88	-0.21	-0.08	0.09	0.232	0.073
	36 merocyanine	70	2.95	-0.17	-0.07	0.07	0.267	0.048
other systems from literature	37 naphthalene[20]	18	4.37	0.05	-0.04*	0.09	0.180	0.068
	38 octatetraene[20]	18	3.98	0.01	0.08	0.09	0.207	0.066
	39 diphenylbutadiene	30	3.46	0.08	0.04	0.07	0.223	0.042
	40 indigo[20]	30	1.99	0.19	0.02	0.07	0.201	0.050
	41 perylimid	40	2.05	0.22	0.00	0.06	0.236	0.038
	42 (N-cbz)-anthracene[20]	44	2.88	0.23	0.00	0.02	0.224	0.049
	MAE (eV)			0.188	0.068	0.063	0.242	0.058

Fig. S3 shows the two-dimensional scans for naphthalene with PBE0/def2-SVP against auxiliary basis exponent of C and H.

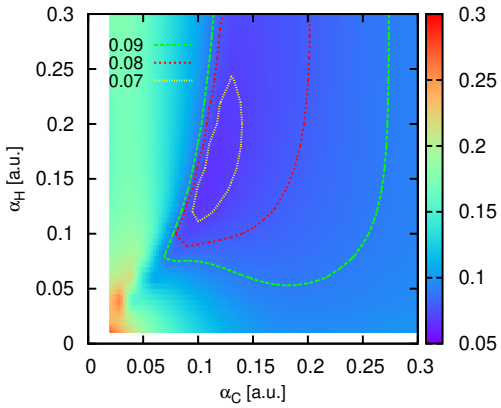

Figure S3: Two-dimensional scan of E_{ene} as a function of α_C and α_H for naphthalene for the PBE0 functional and def2-SVP basis set. Errors are in eV.

UV absorption spectra for each individual molecule in EXTEST42 with the PBE0 density functional and the def2-TZVP basis set are shown in S4.

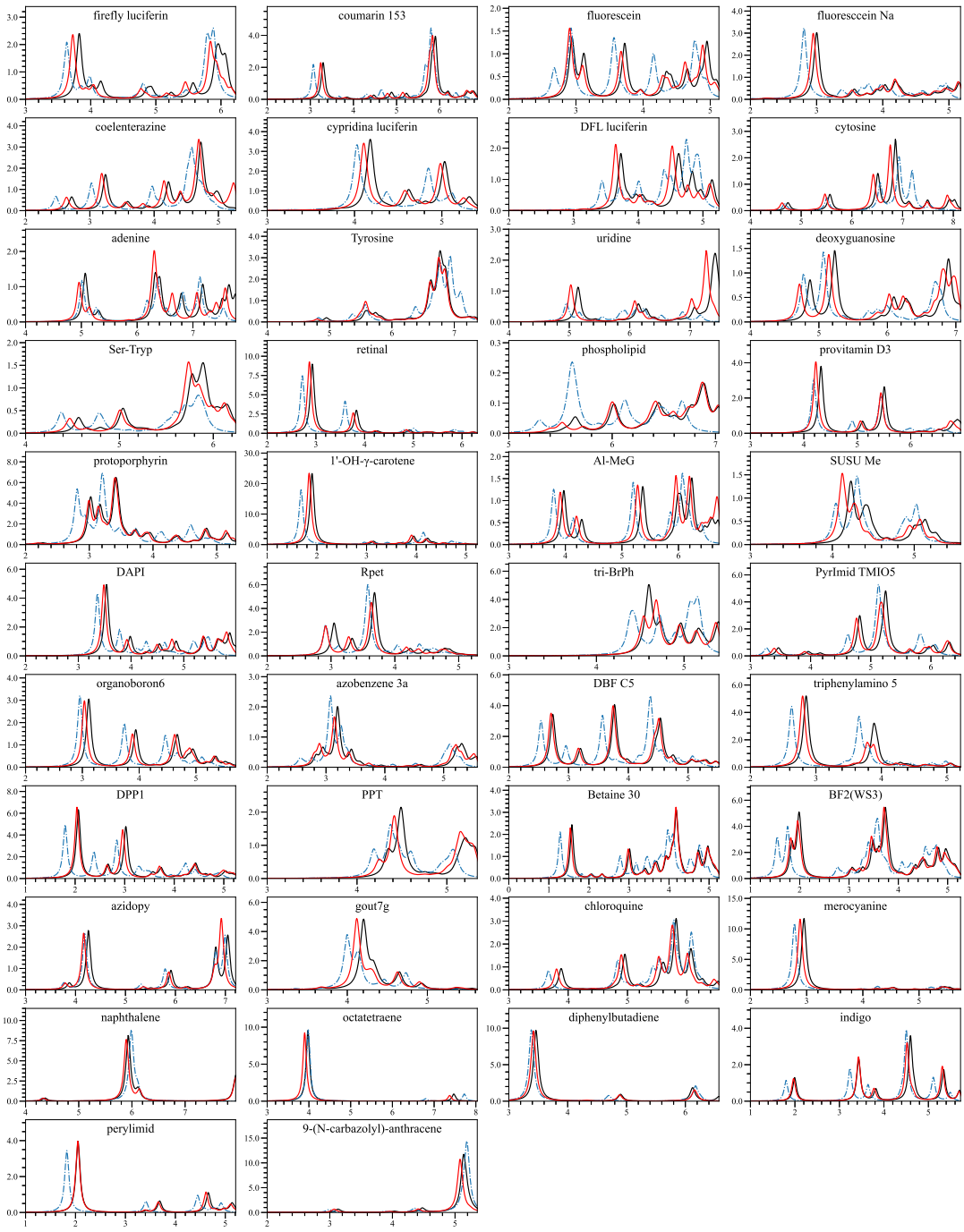

Figure S4: The UV spectra simulated by TDDFT(black solid line), TDDFT-ris (red solid line) and sTDDFT (blue dashed line) for EXTEST42 with PBE0/def2-TZVP. Spectra were plotted using Lorentzian broadening with FWHM = 0.1 eV.

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