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The Dependence Of The Spectroscopic Properties Of Orcein Dyes On The Hydrogen Bonding From Protic Solvents: Insights From Theory And Experiments

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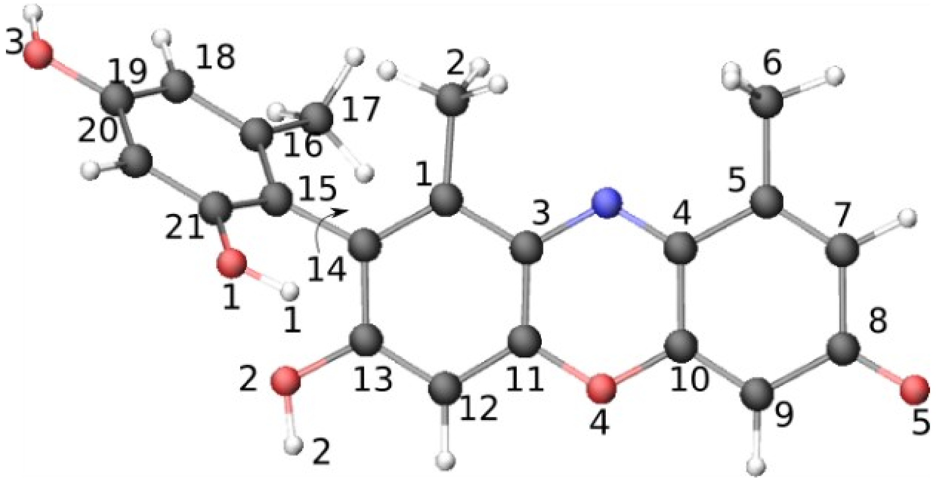

Figure S1. α-HO orcein showing the atom labels reported in Table S1.

	Vac	Acn	MeOH	MeOH
	α-HO	α-HO	α-HO	α-O$^-$
C_1C_2	1.50	1.50	1.50	1.50
C_1C_3	1.41	1.42	1.42	1.44
C_3C_{11}	1.40	1.40	1.40	1.43
C_1C_{14}	1.39	1.39	1.39	1.37
$C_{14}C_{15}$	1.49	1.49	1.49	1.49
$C_{15}C_{16}$	1.40	1.40	1.40	1.40
$C_{16}C_{17}$	1.51	1.51	1.51	1.51
$C_{16}C_{18}$	1.40	1.40	1.39	1.40
$C_{11}O_4$	1.36	1.36	1.36	1.36
C_3N	1.38	1.38	1.38	1.33
C_8O_5	1.23	1.24	1.24	1.26
$C_{13}O_2$	1.36	1.35	1.35	1.26
O_1H_1	0.97	0.97	0.97	0.97
O_2H_2	0.97	0.98	0.97	0.97
$C_{21}O_1$	1.36	1.36	1.37	1.37
$C_{21}C_{15}C_{14}C_{13}$	103.3	98.5	98.5	97.1

Table S1. Main geometrical parameters of protonated α-HO orcein computed in vacuum, acetonitrile and methanol and deprotonated form computed in methanol at the selected CAM-B3LYP-D3/6-31+G(d) level of theory. Bond lengths in Angstrom and angle in degree.

α-HO-(MeOH)$_{10}$	PROTONATED	DEPROTONATED
HB-O1	1.95	1.77
HB-O4	2.05/2.24	2.00/2.15
HB-O5	1.83/1.81	1.74/1.73
HB-N	2.06	2.02
HB-O3	1.69/1.84	1.70/1.83
HB-O2	1.69/1.86	1.70/1.87

Table S2. Bond distances (Å) for the hydrogen interaction between selected α-HO chromophores and methanol molecules in the α-HO-(MeOH)$_{10}$ complex. Atom labels refer to Figure 4 in the main manuscript. Average binding energy is computed equal to 0.37 / 0.41 eV for the protonated / deprotonated complex.

α-HO-(MeOH)	d(Å)	BE (eV)	HOMO	LUMO	H-L	ΔE$_{H-L}$
α-HO	/	/	-7.35 (-3.18)	-2.05(-6.12)	5.30 (2.95)	0
Deprot.	/	/	-6.17	-1.51	4.66	-0.64
HB-N	2.03	0.35	-7.38 (-3.32)	-2.20 (-6.12)	5.17 (2.79)	-0.13 (-0.16)
Deprot.	1.99	0.39	-6.21	-1.66	4.56	
HB-CO	1.78	0.46	-7.46 (-3.29)	-2.19 (-6.23)	5.27 (2.94)	-0.03 (-0.01)
Deprot.	1.71	0.45	-5.61	-1.60	4.00	
HB-O	2.04	0.25	-7.40	-2.11	5.29	-0.01
Deprot.	1.95	0.25	-6.21	-1.58	4.64	
HB-OH	1.93	0.35	-7.39 (-3.21)	-2.08 (-6.13)	5.31 (2.93)	+0.01 (-0.02)
Deprot.	1.73	0.51	-6.28	-1.60	4.68	

Table S3. Bond distances (d, Å) and binding energies (BE, eV) for the hydrogen interaction in the protonated and deprotonated α-HO-(MeOH) complexes, together with HOMO, LUMO, HOMO-LUMO energy gap (H-L) and energy shift of H-L upon MeOH complexation (ΔE$_{H-L}$, eV) at the CAM-B3LYP-D3 level of theory. The electronic structure data of naked α-HO are also reported - the data in parenthesis refer to B3LYP-D3/6-31+(d) level of theory. Structure labels refer to Figure 4 in the main manuscript.

α-HO	**Transition**	**λ (nm)**	**E (eV)**	**f**	**Composition**
Vac	$S_0 \rightarrow S_1$	387	3.20	0.53	H → L (87%) +
	$S_0 \rightarrow S_3$	323	3.84	0.24	H-3 → L (74%)
ACN	$S_0 \rightarrow S_1$	410	3.02	0.75	H → L (90%)
	$S_0 \rightarrow S_3$	343	3.62	0.22	H-3 → L (82%) + H-5 → L (8%)
MeOH	$S_0 \rightarrow S_1$	410	3.02	0.75	H → L (92%)
	$S_0 \rightarrow S_3$	353	3.62	0.22	H-3 → L (82%)

Table S4. Excitation energies (eV), wavelengths (nm), oscillator strengths and transition character of α-HO in vacuum, acetonitrile and methanol at the CAM-B3LYP-D3/6-31+G(d) level of theory. The composition in terms of MO excitations is reported for contributions larger than 10%.

Functional	**Transition**	**λ(nm)**	**E (eV)**	**f**	**Composition**
ωB97X-D	$S_0 \rightarrow S_1$	411 (408)	3.02 (3.04)	0.73 (0.73)	H → L(90%)
	$S_0 \rightarrow S_3$	342 (340)	3.63 (3.65)	0.24 (0.24)	H-3 → L(80%) + H-5 → L(8%)
B3LYP	$S_0 \rightarrow S_2$	457	2.71	0.48	H → L (71%) + H-3 →L (13%)
	$S_0 \rightarrow S_5$	402	3.08	0.28	H-3 → L (73%) + H-2 → L (16%) + H → L (10%)
HSE0	$S_0 \rightarrow S_2$	447	2.77	0.52	H → L (66%) + H-1 → L (21%) + H-3 → L (11%)
	$S_0 \rightarrow S_5$	394	3.15	0.33	H-3 → L (86%) + H → L (9%)
M06	$S_0 \rightarrow S_1$	447	2.77	0.55	H → L (88%)
	$S_0 \rightarrow S_4$	393	3.15	0.29	H-3 → L (83%) + H → L (9%) + H-2 → L (6%)
M06-2X	$S_0 \rightarrow S_1$	407	3.04	0.74	H → L (89%)
	$S_0 \rightarrow S_3$	336	3.68	0.21	H-3 → L (76%) + H-1 → L (13%)
BHandHLYP	$S_0 \rightarrow S_1$	391	3.17	0.85	H → L (94%)
	$S_0 \rightarrow S_2$	328	3.78	0.18	H-3 → L (86%) + H-4 → L (5%)
PBE0	$S_0 \rightarrow S_1$	449	2.76	0.34	H → L (76%) + H-1 → L (17%) + H-3 → L (6%)
	$S_0 \rightarrow S_2$	437	2.84	0.22	H-1 → L (82%) + H → L (13%)
	$S_0 \rightarrow S_4$	388	3.19	0.30	H-3 → L (97%)
BMK	$S_0 \rightarrow S_1$	416	2.98	0.70	H → L (90%)
	$S_0 \rightarrow S_3$	354	3.50	0.17	H-1 → L (65%) + H-3 → L (32%)

Table S5. Excitation energies (eV), wavelengths (nm), oscillator strengths (u.a.) and the composition in terms of MOs of α-HO in methanol using the 6-31+G(d) basis set (in parenthesis the values computed with the 6-311++G(d,p) basis set) and different DFT functionals.

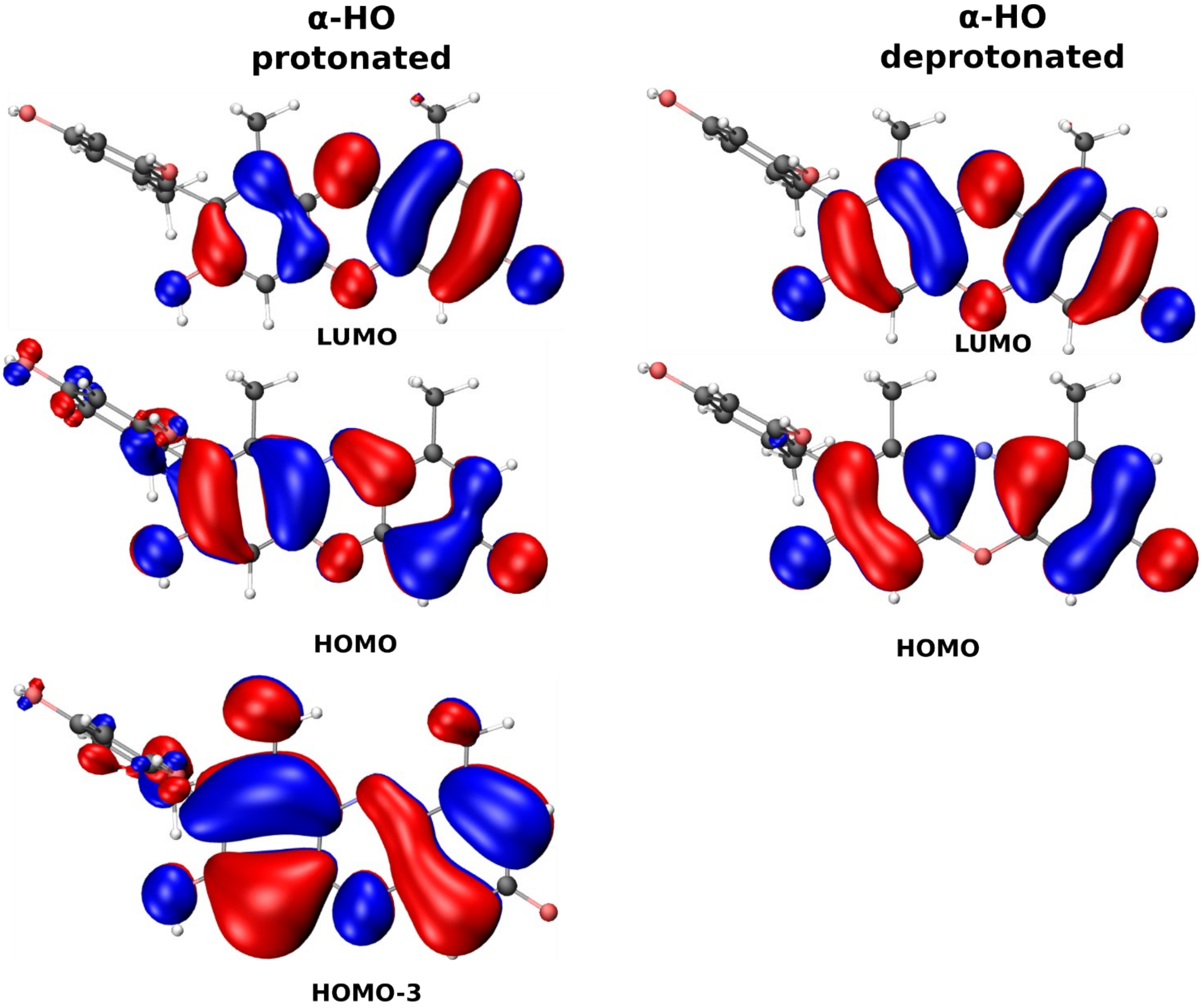

Figure S2. Isodensity plots (cutoff 0.025 e bohr^{-3}) of frontier orbitals for α-OH orcein naked in the protonated (left) and deprotonated (right) forms.

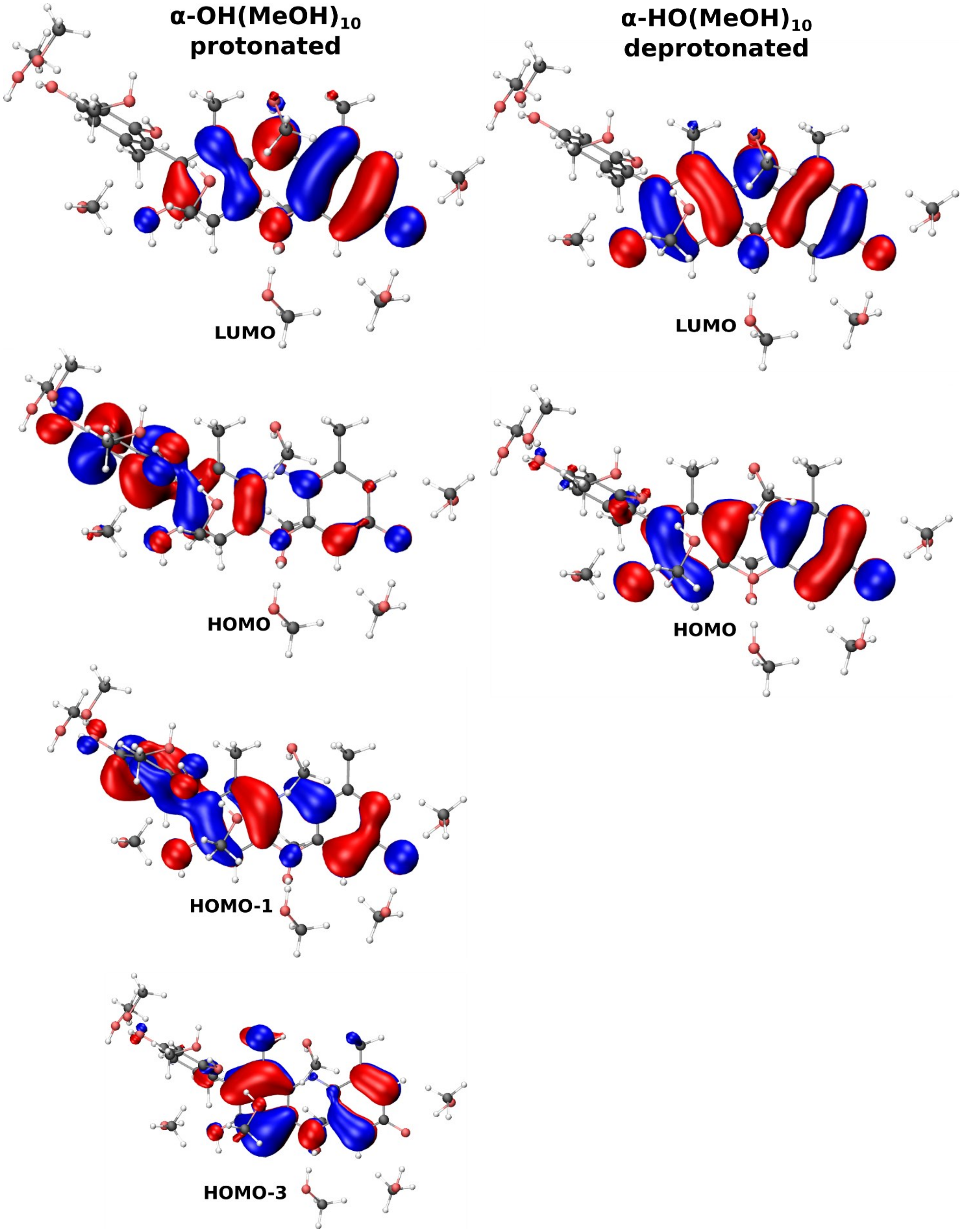

Figure S3. Isodensity plots (cutoff 0.025 e bohr^{-3}) of frontier orbitals for α-HO orcein complexed with 10 methanol molecules in the protonated (left) and deprotonated (right) forms.

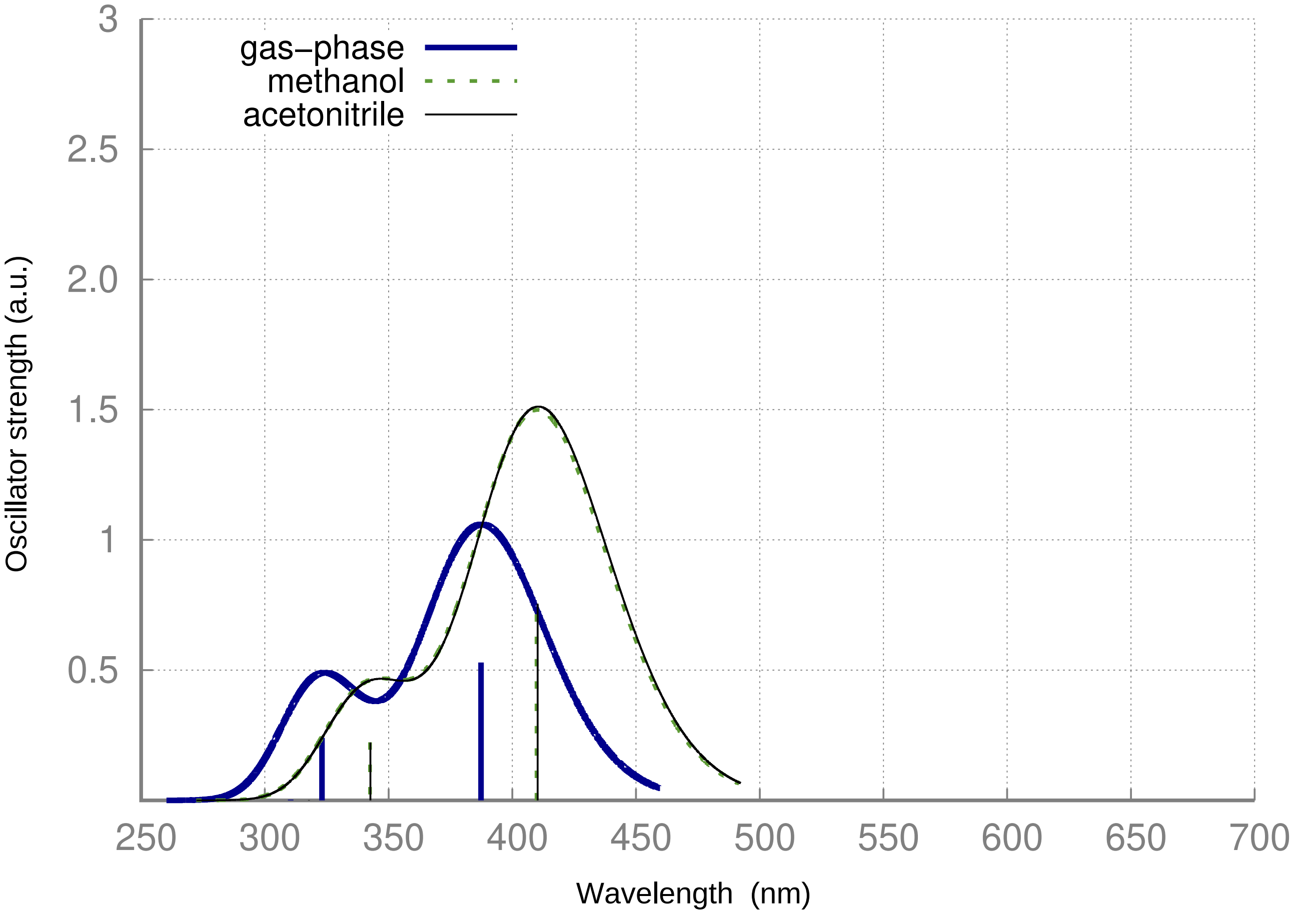

Figure S4. α-HO orcein absorption spectra (Oscillator Strength, a.u., vs Wavelength, nm) computed in vacuo, acetonitrile and methanol at the CAM-B3LYP-D3/6-31+(d) level of theory.

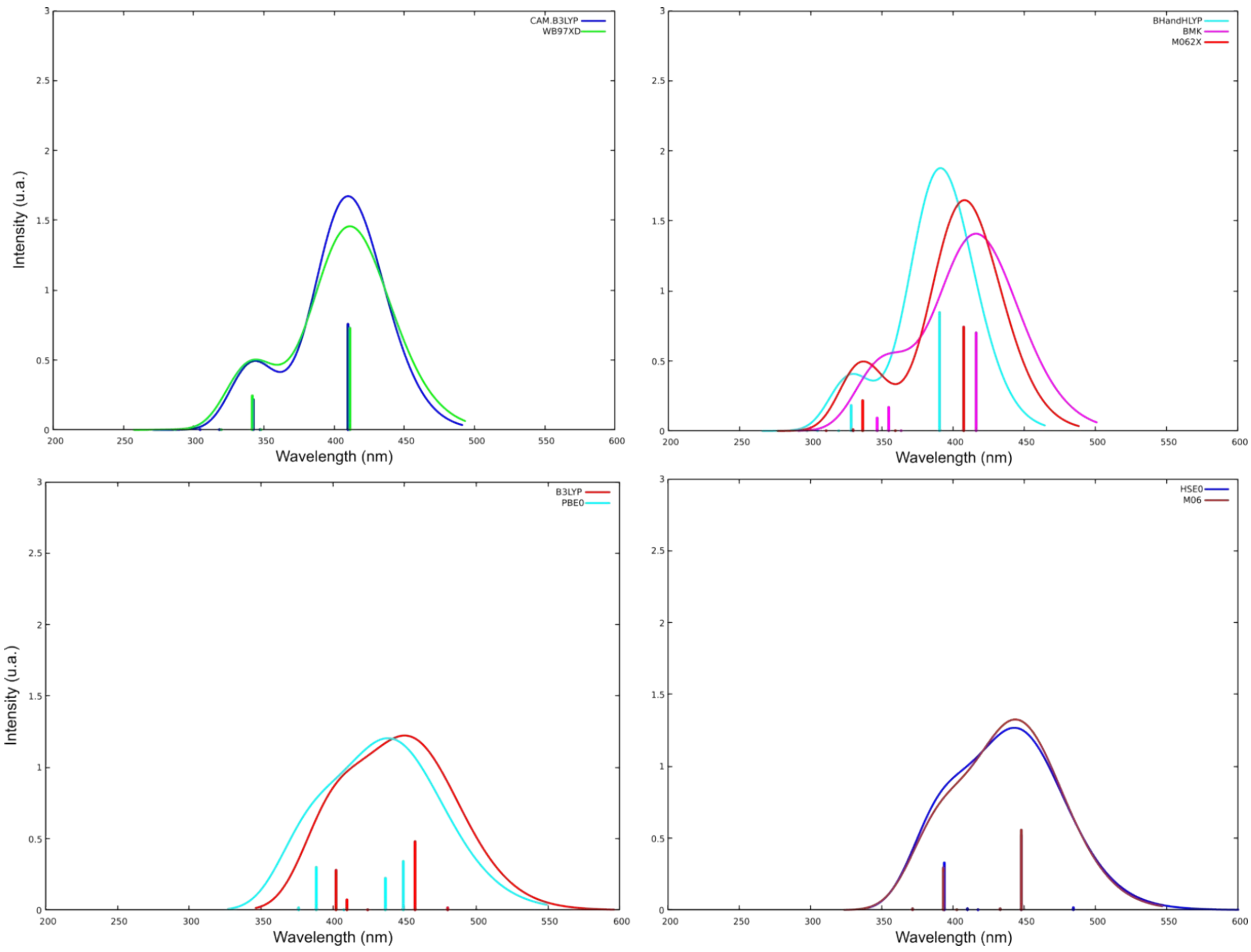

Figure S5. Absorption spectra of α-HO computed with long-range corrected DFT functionals (top) and other hybrid DFT functionals (bottom).