Environmental and complexation effects on the structures and spectroscopic signatures of organic pigments relevant for cultural heritage: the case of Alizarin and Alizarin-Mg(II)/Al(III) complexes. SUPPORTING INFORMATION

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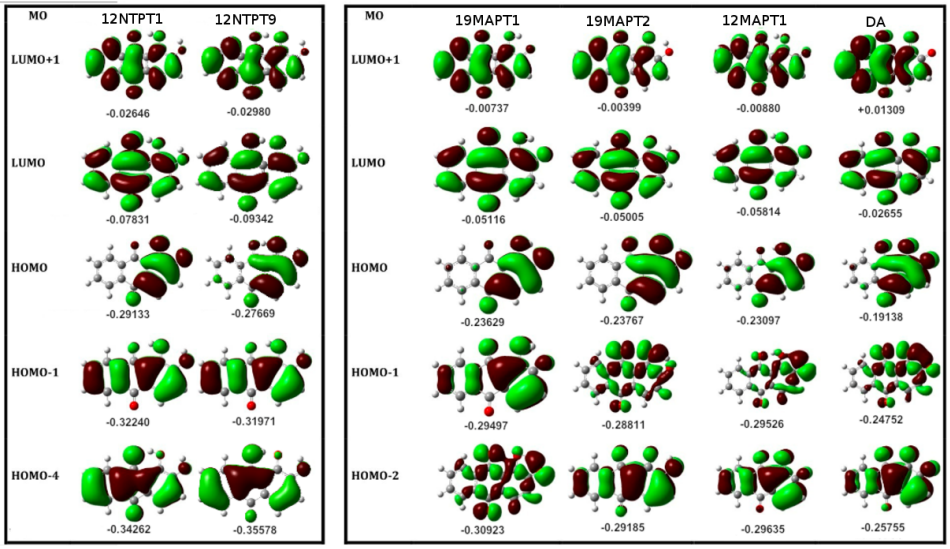

Fig. 1 Frontier molecular orbitals (plots with isovalue threshold of 0.02 and relative energy positions in a.u.) for neutral (left frame) and anionic (right frame) alizarin.

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Table 1 Excited state properties of neutral, mono- and di-deprotonated alizarin in methanol solution, computed at the TD-CAM-B3LYP/aug-N07D//C-PCM level within the non-equilibrium solvation regime. Vertical excitation energies (VE) [eV], absorption wavelengths (λ [nm]) and oscillator strengths (f) are reported along with the most important molecular orbitals (MOs) involved in the transitions

Tautomer	MOs	VE [eV]	λ [nm]	State	f
1,2NT-PT1	H-3→L+1	5.64	220	S_{10}	0.00
	H→L+2	5.62	221	S_9	0.21
	H-1→L+1	5.35	232	S_8	0.58
	H→L+1	4.91	252	S_7	0.31
	H-4→L	4.72	263	S_6	0.17
	H-2→L	4.26	291	S_5	0.09
	H-5→L	3.90	318	S_4	0.00
	H-1→L	3.81	325	S_3	0.03
	H-3→L	3.47	357	S_2	0.00
	H→L	3.36	369	S_1	0.20
1,9MA-PT1	H→L+5	5.01	247	S_{10}	0.20
	H-5→L	4.90	253	S_9	0.11
	H→L+3	4.74	262	S_8	0.00
	H-3→L	4.56	271	S_7	0.00
	H-4→L	4.55	273	S_6	0.08
	H-1→L	4.11	301	S_5	0.29
	H→L+1	-	-	S_5	-
	H-6→L	3.77	329	S_4	0.0
	H→L+2	3.74	331	S_3	0.01
	H-1→L	-	-	S_3	-
	H-2→L	3.45	359	S_2	0.00
	H→L	2.78	446	S_1	0.25
1,9MA-PT2	H→L+4	4.99	248	S_{10}	0.14
	H-4→L	4.90	253	S_9	0.10
	H→L+2	4.77	260	S_8	0.00
	H→L+3	-	-	S_8	-
	H-3→L	4.55	272	S_7	0.06
	H-6→L	4.54	273	S_6	0.00
	H→L+1	4.14	299	S_5	0.04
	H-2→L	3.76	330	S_4	0.02
	H-5→L	3.70	335	S_3	0.00
	H-1→L	3.19	388	S_2	0.00
	H→L	2.82	440	S_1	0.27
1,2MA-PT1	H-5→L	4.90	253	S_{10}	0.32
	H→L+5	4.78	259	S_9	0.00
	H→L+2	4.66	266	S_8	0.00
	H→L+3	-	-	S_8	-
	H-4→L	4.47	277	S_7	0.08
	H-6→L	4.08	304	S_6	0.00
	H→L+1	3.96	313	S_5	0.43
	H-2→L	-	-	S_5	-
	H-3→L	3.78	328	S_4	0.00
	H-2→L	3.58	346	S_3	0.01
	H-1→L	3.49	355	S_2	0.00
	H→L	2.45	506	S_1	0.21
DA	H→L+3	4.39	282	S_{10}	0.00
	H→L+7	-	-	S_{10}	-
	H→L+6	4.37	284	S_9	0.04
	H-6→L	4.27	291	S_8	0.00
	H-3→L	3.97	313	S_7	0.00
	H→L+2	3.84	324	S_6	0.00
	H→L+3	-	-	S_6	-
	H-4→L	3.83	324	S_5	0.00
	H-2→L	3.59	345	S_4	0.01
	H→L+1	3.28	378	S_3	0.02
	H-1→L	2.84	436	S_2	0.00
	H→L	2.37	523	S_1	0.44

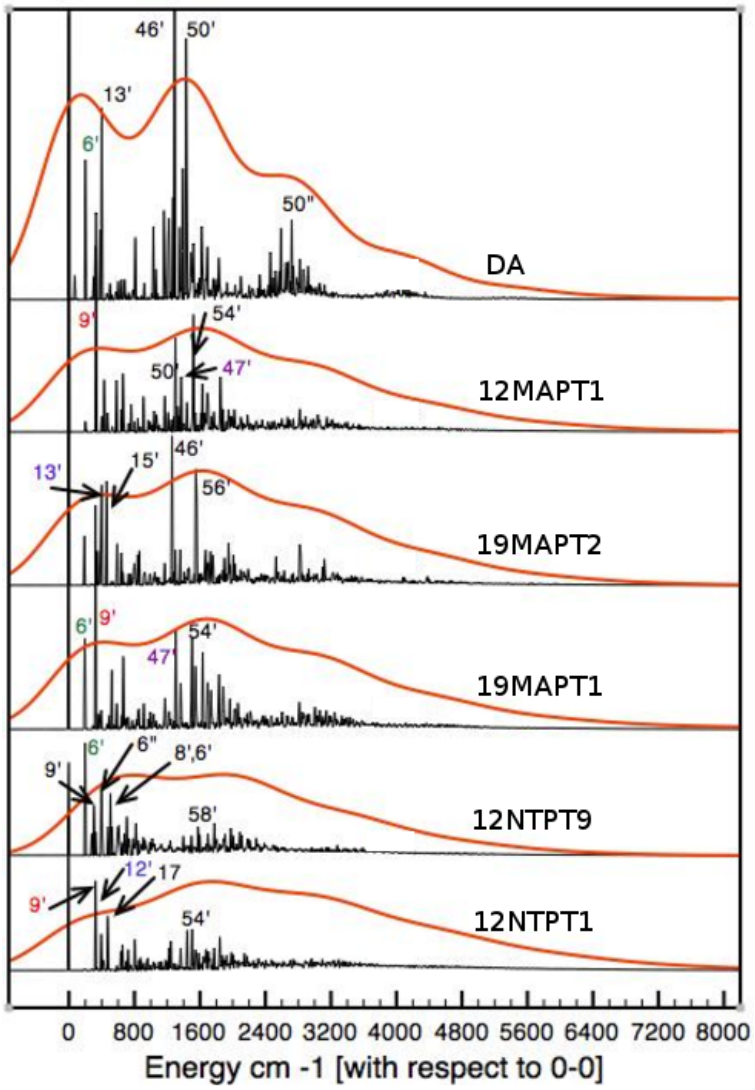

Fig. 2 Vibrational contributions to the $S_1 \leftarrow S_0$ electronic transition of the neutral (1,2NT-PT1, 1,2NT-PT9), monoanionic (1,9MA-PT1, 1,9MA-PT2, 1,2MA-PT1) and dianionic (DA) forms of alizarin in metanol solution. Spectra are shown in an energy scale relative to the transition origin ($< 0|0 >$) and most important vibronic contributions are marked by mode number.

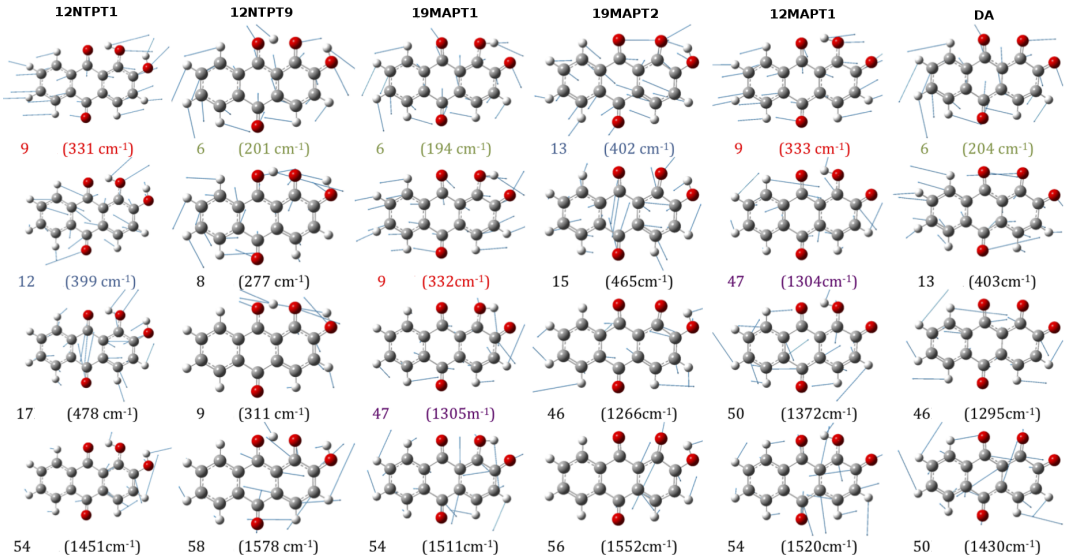

Fig. 3 Normal modes related to the most important vibronic contributions (see figure 2) for neutral (1,2NT-PT1, 1,2NT-PT9), monoanionic (1,9MA-PT1, 1,9MA-PT2, 1,2MA-PT1) and dianionic (DA) forms of alizarin in methanol solution. Similarities between molecular vibrations for different systems are emphasised by caption colors.

Table 2 Most intense vibrational contributions to free Alizarin $S_1 \leftarrow S_0$ electronic transition. Energy and intensities of single vibronic contributions for neutral (1,2NTPT1, 1,2NTPT9), monoanionic (1,9MA-PT1, 1,9MA-PT2, 1,2MA-PT1) and dianionic (DA) forms of alizarin in metanol solution. The absolute energy of (<0|0>) transition and relative energies of the three most intense transition from funtamental state to the single overtones <0|n>

Neutral (1,2NT-PT1)

Transition	label	Energy [cm^{-1}]	Intensity
<0|0>	0	24 405	$0.3372*10^7$
9^1	9	331	$0.1947*10^7$
12^1	12	398	$0.4241*10^6$
17^1	17	478	$0.1173*10^7$
54^1	54	1451	$0.7673*10^6$

Neutral (1,2NT-PT9)

Transition	label	Energy [cm^{-1}]	Intensity
<0|0>	0	19 773	$0.2015*10^7$
6^1	6	201	$0.2439*10^7$
9^1	9	311	$0.1084*10^7$
6^2	6^2	402	$0.1476*10^7$
$8^1,6^1$	8,6	478	$0.5654*10^6$
58^1	58	1578	$0.5071*10^6$

Monoanion (1,9MA-PT1)

Transition	label	Energy [cm^{-1}]	Intensity
<0|0>	0	20 340	$0.7498*10^7$
6^1	6	194	$0.1976*10^7$
9^1	9	331	$0.4865*10^7$
47^1	47	1304	$0.2075*10^7$
54^1	54	1510	$0.1462*10^7$

Monoanion (1,9MA-PT2)

Transition	label	Energy [cm^{-1}]	Intensity
<0|0>	0	20 728	$0.9805*^7$
13^1	13	402	$0.2172*10^7$
15^1	15	465	$0.2255*10^7$
46^1	46	1267	$0.3134*10^7$
56^1	56	1552	$0.2508*10^7$

Monoanion (1,2MA-PT1)

Transition	label	Energy [cm^{-1}]	Intensity
<0|0>	0	17 833	$0.9030*10^7$
9^1	9	333	$0.4763*10^7$
47^1	47	1303	$0.1978*10^7$
50^1	50	1372	$0.9661*10^6$
54^1	54	1520	$0.2084*10^7$

Dianionic (DA)

Transition	label	Energy [cm^{-1}]	Intensity
<0|0>	0	17 643	$0.3183*^8$
6^1	6	204	$0.3030*^7$
13^1	13	403	$0.3999*^7$
46^1	46	1295	$0.8623*^7$
50^1	50	1430	$0.5504*^7$
50^2	50^2	2861	$0.4725*^6$

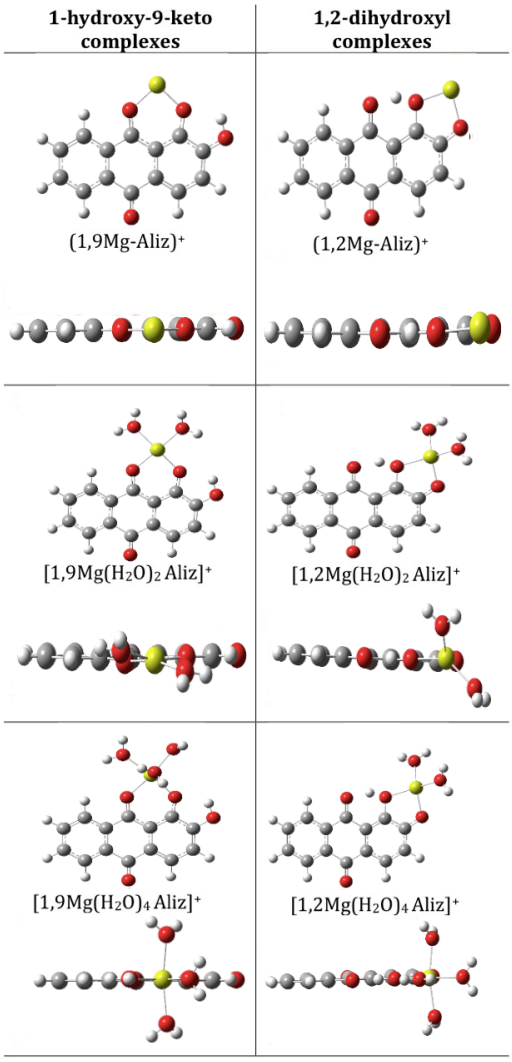

Fig. 4 Equilibrium structures of the Mg-Alizarin complexes in dioxane/water solution. 1-hydroxy-9-keto and 1,2-dihydroxyl Mg-Alizarin complexes with solvent described by CPCM model (1,9Mg-Aliz and 1,2Mg-Aliz) or with *n* water molecules in solvation sphere (1,2Mg$(H_2O)_n$, 1,9Mg$(H_2O)_n$). Both parallel and perpendicular (with respect to molecular plane) views are presented.

Table 3 Ground state equilibrium structures and relative free energy values in dioxane/water solution, for the 1,9 and 1,2 Mg-Alizarin complexes with solvent described by the CPCM model (1,9Mg and 1,2Mg) or with and *n* water molecules in solvation sphere (1,2Mg(H_2O)$_n$, 1,9Mg(H_2O)$_n$). All computations at the CAM-B3LYP/aug-N07D//CPCM level. Bond lengths in Å, angles in degrees, Δ*G* in kJ/mol

Bond / Angle	*[1,9Mg]*	*[1,9Mg(H_2O)$_2$]*	*[1,9Mg(H_2O)$_4$]*	Bond/Angle	*[1,2Mg]*	*[1,2Mg(H_2O)$_2$]*	*[1,2Mg(H_2O)*
C(9)=O(11)	1.271	1.263	1.255	C(9)=O(11)	1.251	1.246	1.244
C(1)=O(12)	1.316	1.308	1.302	C(1)=O(12)	1.383	1.380	1.372
C(2)=O(13)	1.344	1.346	1.346	C(2)=O(13)	1.325	1.315	1.308
C(10)=O(14)	1.218	1.219	1.220	C(10)=O(14)	1.218	1.219	1.221
O(12)-Mg	1.870	1.910	1.957	O(12)-H(15)	1.067	1.029	1.013
O(13)-H(16)	0.971	0.972	0.975	O(13)-Mg	1.888	1.918	1.971
O(11)-Mg	1.904	1.951	2.009	O(11)-H(15)	1.401	1.500	1.548
O(12)-H(16)	2.008	1.998	1.965	O(12)-Mg	1.973	2.026	2.102
O(11)-O(12)	2.784	2.747	2.744	O(11)-O(12)	2.404	2.452	2.479
O(12)-O(13)	2.588	2.593	2.578	O(12)-O(13)	2.669	2.636	2.632
C(9)-C(17)-C(1)	121.4	121.6	121.1	C(9)-C(17)-C(1)	118.7	119.1	119.2
O(11)-C(9)-C(17)	123.1	122.9	123.1	O(11)-C(9)-C(17)	119.2	119.7	120.1
C(17)-C(1)-O(12)	126.8	126.6	126.9	C(17)-C(1)-O(12)	120.2	121.0	121.5
C(2)-C(1)-O(12)	114.3	115.0	114.9	C(2)-C(1)-O(12)	116.8	115.8	115.4
C(1)-C(2)-O(13)	117.5	116.9	116.2	C(1)-C(2)-O(13)	118.7	118.3	118.5
O(11)-Mg-O(12)	95.1	90.7	87.5	O(11)-H(15)-O(12)	153.6	151.1	150.2
O(12)-H(16)-O(13)	116.2	117.3	118.6	O(12)-Mg-O(13)	87.4	83.8	80.4
Thermochemistry	*[1,9Mg]*	*[1,9Mg(H_2O)$_2$]*	*[1,9Mg(H_2O)$_4$]*	Thermochemistry	*[1,2Mg]*	*[1,2Mg(H_2O)$_2$]*	*[1,2Mg(H_2O)*
Δ*G* (kJ/mol)	0	0	0	Δ*G* (kJ/mol)	29.4	21.4	25.2

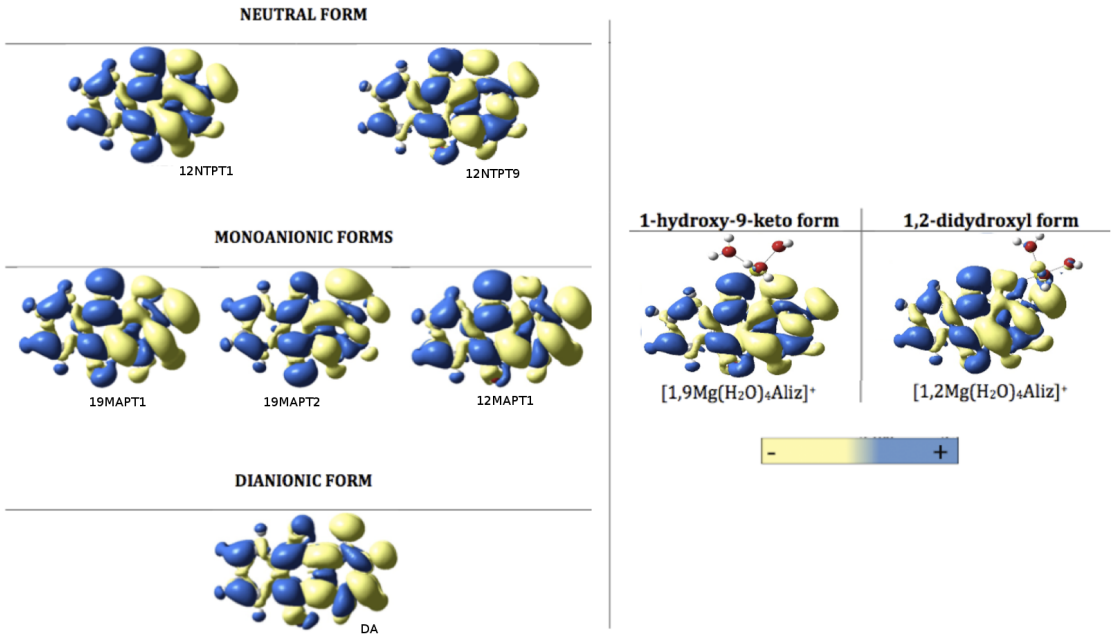

Fig. 5 Changes in electronic density during the HOMO→LUMO transition in free lingand and complexed alizarin (1,9Mg and 1,2Mg forms) in ethanol/water solution, considering up to 4 explicit H_2O molecules. The regions, which have lost electron density as a result of transition, are shown in bright yellow, whereas the darker blue regions gained electron density. ELD densities evaluated with an isovalue threshold of 0.0004.

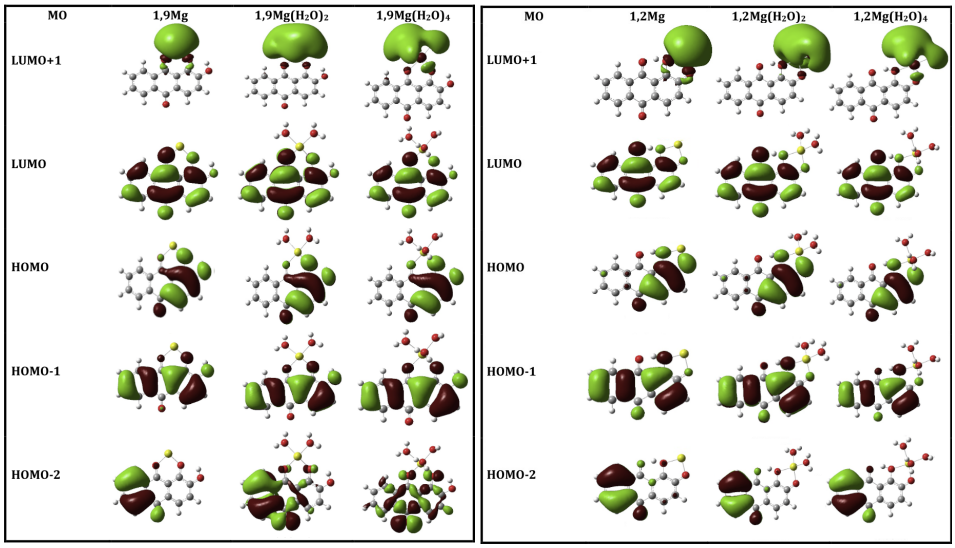

Fig. 6 Frontier molecular orbitals (plots with isovalue threshold of 0.02 and relative energy positions in a.u.) for Alizarin Mg-complexes (1,9Mg and 1,2Mg forms) in ethanol/water solution, considering up to 4 explicit H_2O molecules.

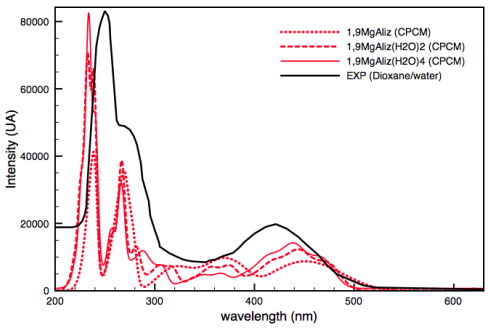

Fig. 7 Vibrationally resolved electronic spectra for complexed 1,9Mg-Alizarin in dioxane/water solution, considering effect of adding up to 4 water molecules.

Table 4 Excited state properties of 1,9 and 1,2 Mg-Alizarin complexes in dioxane/water solution, with solvent described by the CPCM model (1,9Mg and 1,2Mg) or with and 2 water molecules in solvation sphere (1,2Mg(H_2O)$_2$, 1,9Mg(H_2O)$_2$, computed at the TD-CAM-B3LYP/aug-N07D//CPCM level within the non-equilibrium solvation regime. Vertical excitation energies (VE) [eV], absorption wavelengths (λ [nm]), oscillator strengths (f) and dipole moment (μ [Debyee]) are reported along with the most important molecular orbitals (MOs) involved in the transitions.

1,2Mg Aliz

Band	MOs	VE [eV]	λ [nm]	State	μ^a [D]	f
III	H-1→L+2	5.45	227	S_{12}	20.78	0.26
	H-6→L+1	5.42	228	S_{11}	6.49	0.04
	H-3→L+2	5.34	232	S_{10}	16.76	0.00
II	H→L+2	4.84	256	S_9	1.42	0.50
	H-1→L+1	4.83	257	S_8	23.40	0.00
	H-4→L	4.62	268	S_7	19.91	0.35
	H-5→L	4.25	292	S_6	21.94	0.00
	H-2→L	4.04	307	S_5	15.72	0.13
	H-1→L	3.78	328	S_4	19.86	0.17
	H→L+1	3.36	369	S_3	3.42	0.01
	H-3→L	3.31	374	S_2	16.66	0.00
I	H→L	3.15	393	S_1	24.00	0.09

[a] Ground state Dipole moment = 19.55D

1,9Mg Aliz

Band	MOs	VE [eV]	λ [nm]	State	μ^d [D]	f
III	H-5→L+1	5.37	231	S_{12}	5.38	0.03
	H-1→L+2	5.26	236	S_{11}	18.25	0.35
	H-3→L+2	5.22	238	S_{10}	14.55	0.00
	H-1→L+1	4.89	253	S_9	0.71	0.00
II	H-4→L	4.72	263	S_8	19.65	0.23
	H-4→L	4.58	271	S_7	19.24	0.21
	H-5→L	4.37	284	S_6	20.57	0.00
	H-2→L	3.96	313	S_5	18.39	0.12
	H→L+1	3.64	340	S_4	2.44	0.00
	H-1→L	3.42	362	S_3	17.93	0.16
	H-3→L	3.19	388	S_2	14.70	0.00
I	H→L	2.81	441	S_1	18.53	0.17

[d] Ground state Dipole moment = 18.40D

1,2Mg(H_2O)$_2$

Band	MOs	VE [eV]	λ [nm]	State	μ^b [D]	f
III	H-6→L	5.61	221	S_{11}	30.53	0.00
	H→L+6	5.54	224	S_{11}	20.63	0.44
	H-1→L+2	5.42	228	S_{10}	24.03	0.15
	H-3→L+2	5.37	231	S_9	19.58	0.00
II	H-4→L	4.78	259	S_8	24.48	0.38
	H→L+1	4.62	268	S_7	6.12	0.05
	H→L+2	4.59	270	S_6	22.39	0.41
	H-2→L	4.13	300	S_5	18.17	0.12
	H-5→L	4.12	301	S_4	24.32	0.00
	H-1→L	3.82	324	S_3	22.80	0.13
	H-3→L	3.36	369	S_2	19.31	0.00
I	H→L	3.09	401	S_1	26.74	0.11

[b] Ground state Dipole moment = 22.07D

1,9Mg(H_2O)$_2$

Band	MOs	VE [eV]	λ [nm]	State	μ^e [D]	f
III	H-7→L	5.65	219	S_{12}	23.04	0.00
	H→L+4	5.44	228	S_{11}	20.99	0.46
	H-3→L+2	5.28	235	S_{10}	17.00	0.02
	H-1→L+2	5.25	236	S_9	21.29	0.43
	H→L+1	4.77	260	S_8	4.33	0.00
II	H-4→L	4.74	261	S_7	20.79	0.25
	H→L+2	4.55	272	S_6	23.08	0.14
	H-5→L	4.23	293	S_5	23.15	0.00
	H-2→L	4.11	302	S_4	20.70	0.12
	H-1→L	3.51	354	S_3	20.40	0.11
	H-3→L	3.26	380	S_2	17.31	0.00
I	H→L	2.86	433	S_1	20.88	0.21

[e] Ground state Dipole moment = 20.78D

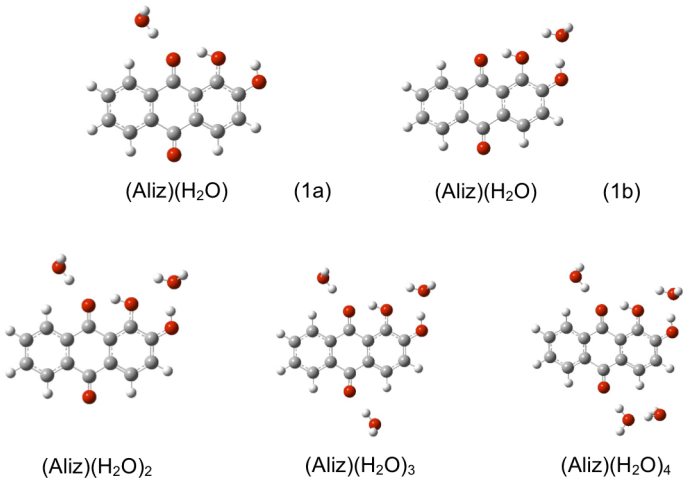

Fig. 8 Equilibrium structures of the neutral Alizarin with solvent described by mixed dicrete-continuum model, namely CPCM plus n=(1-4) water molecules in a solvation sphere.