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New Journal of Chemistry

Complexation behaviour of caffeic, ferulic and *p*-coumaric acids towards aluminium cation: a combined experimental and theoretical approach

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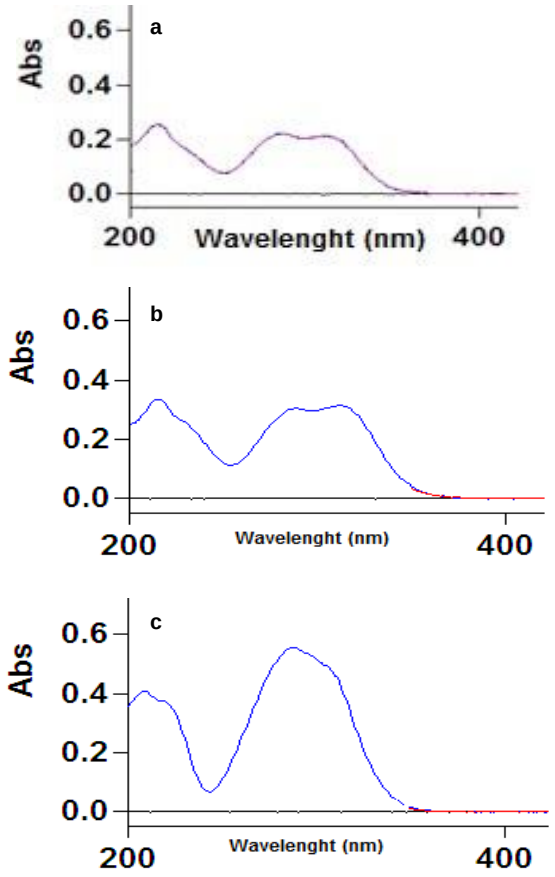

Figure S1. UV absorption spectra of caffeic acid (a), ferulic acid (b) and *p*-coumaric acids (c).

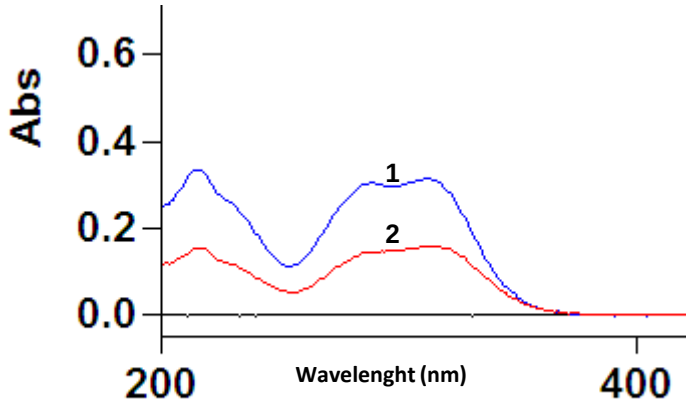

Figure S2. UV spectra at pH=3.5 of 0.1 mM ferulic acid free (line 1) and of the complexes formed between ligands and $AlCl_3$ 0.1 mM (line 2).

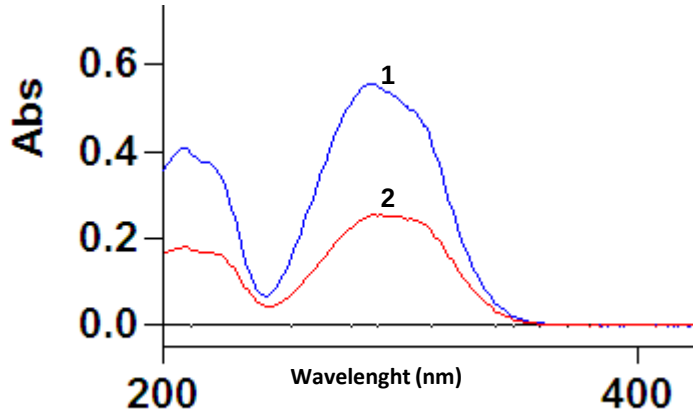

Figure S3. UV spectra at pH=3.5 of 0.1 mM *p*-coumaric acid free (line 1) and of the complexes formed between ligands and $AlCl_3$ 0.1 mM (line 2).

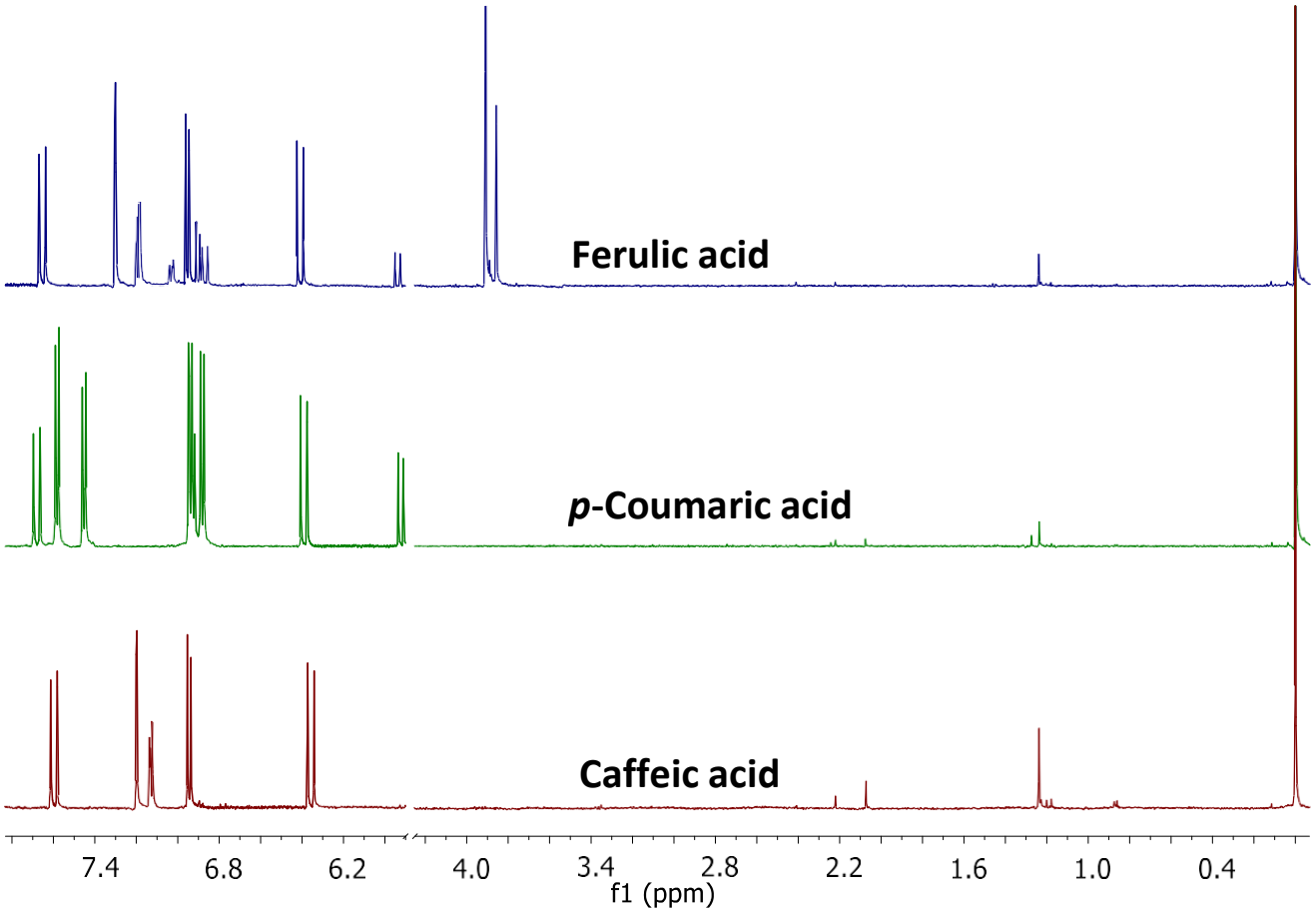

Figure S4. 1D ^{1}H-NMR spectra of caffeic, *p*-coumaric and ferulic acid at pH 3.5.

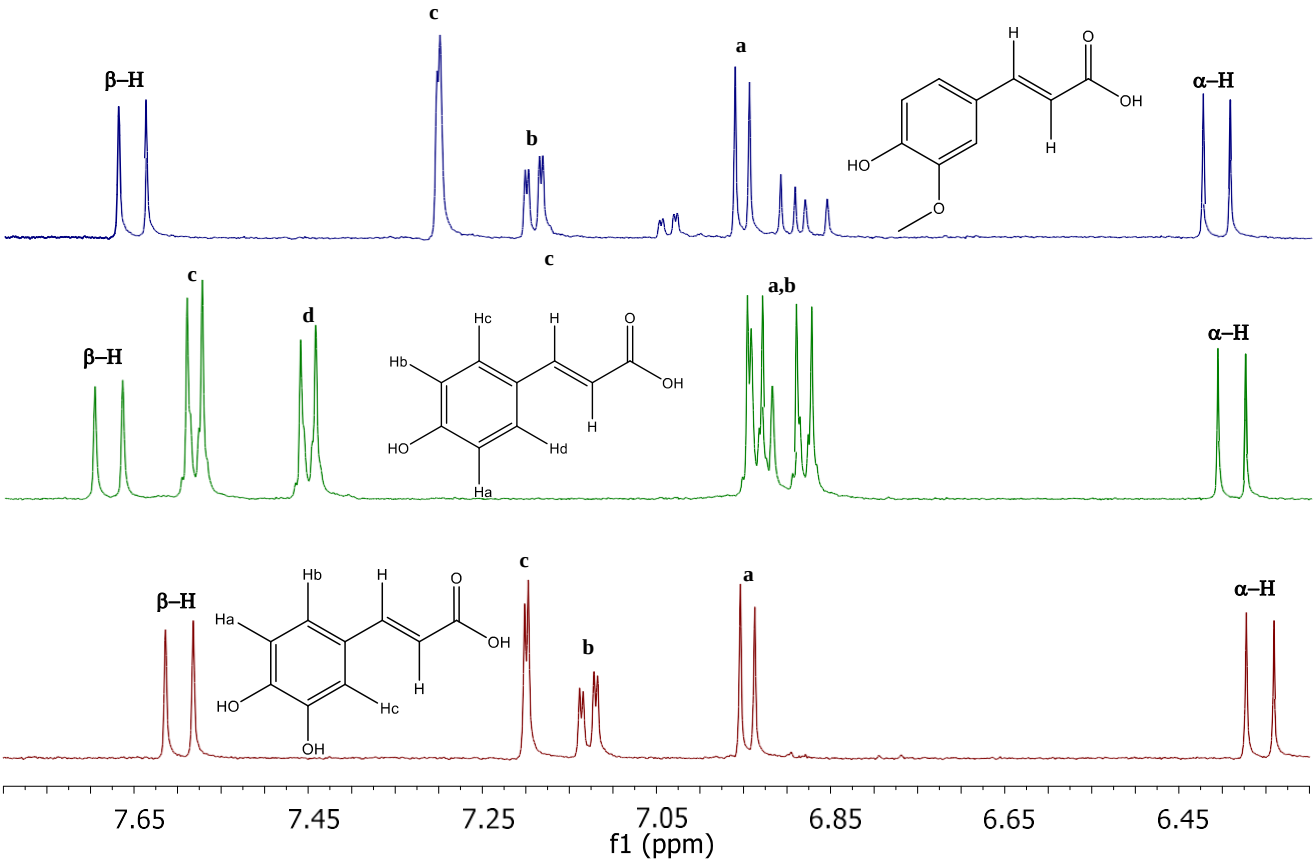

Figure S5. 1D ^{1}H-NMR spectra of ferulic, *p*-coumaric and caffeic acids at pH 3.5 in the 6.3-7.8 ppm spectral range.

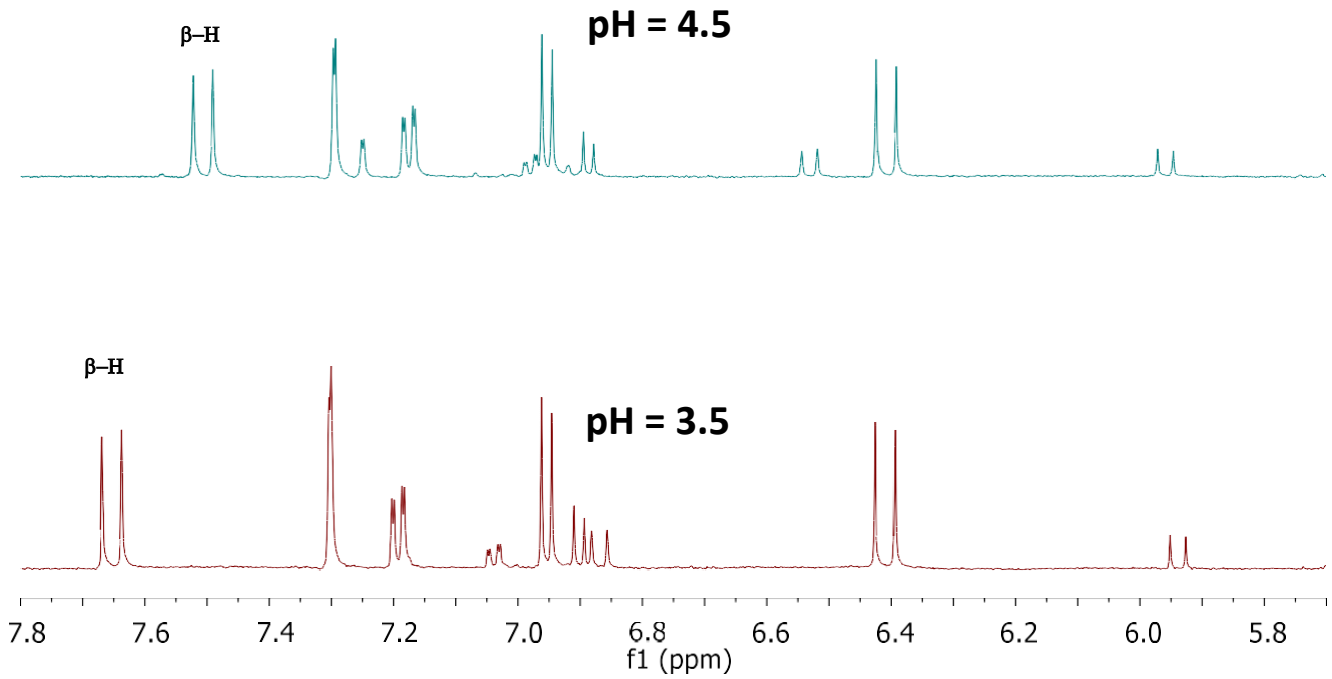

Figure S6. ^{1}H-NMR spectra of ferulic acid at different pH.

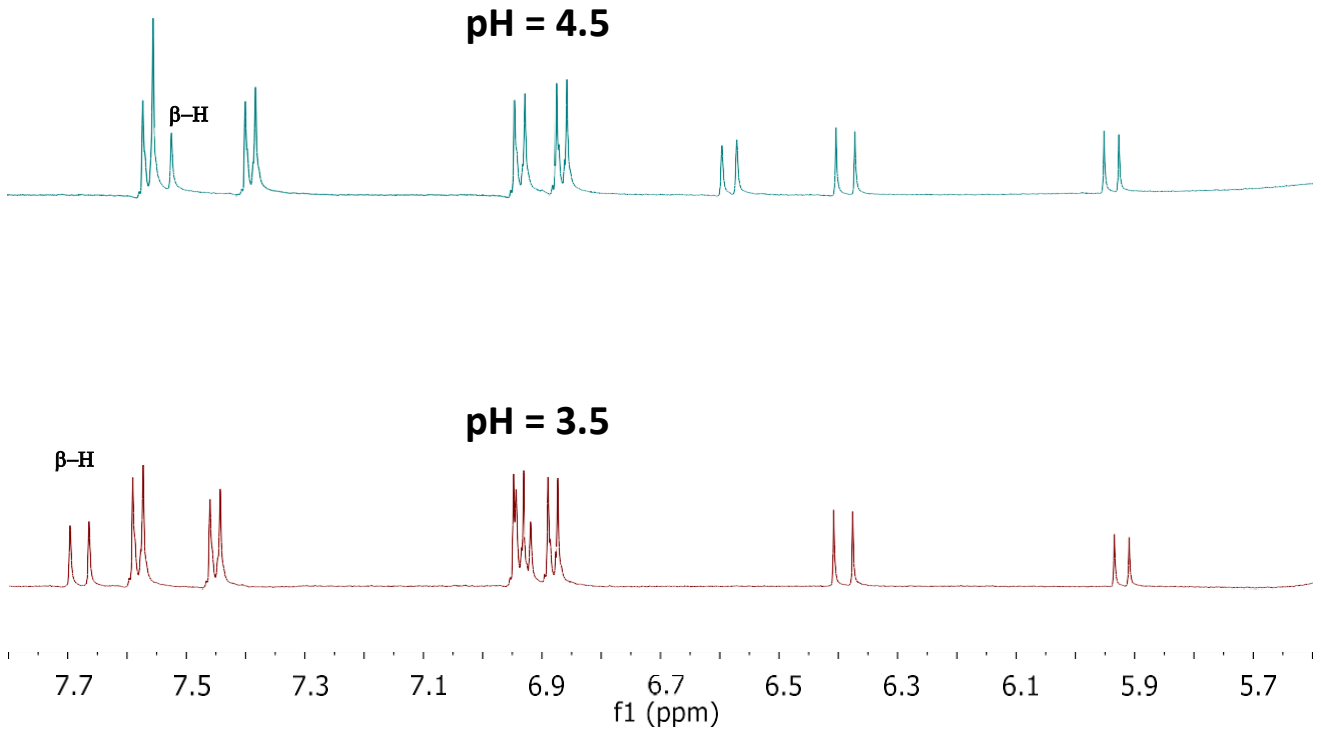

Figure S7. ^{1}H-NMR spectra of *p*-coumaric acid at different pH.

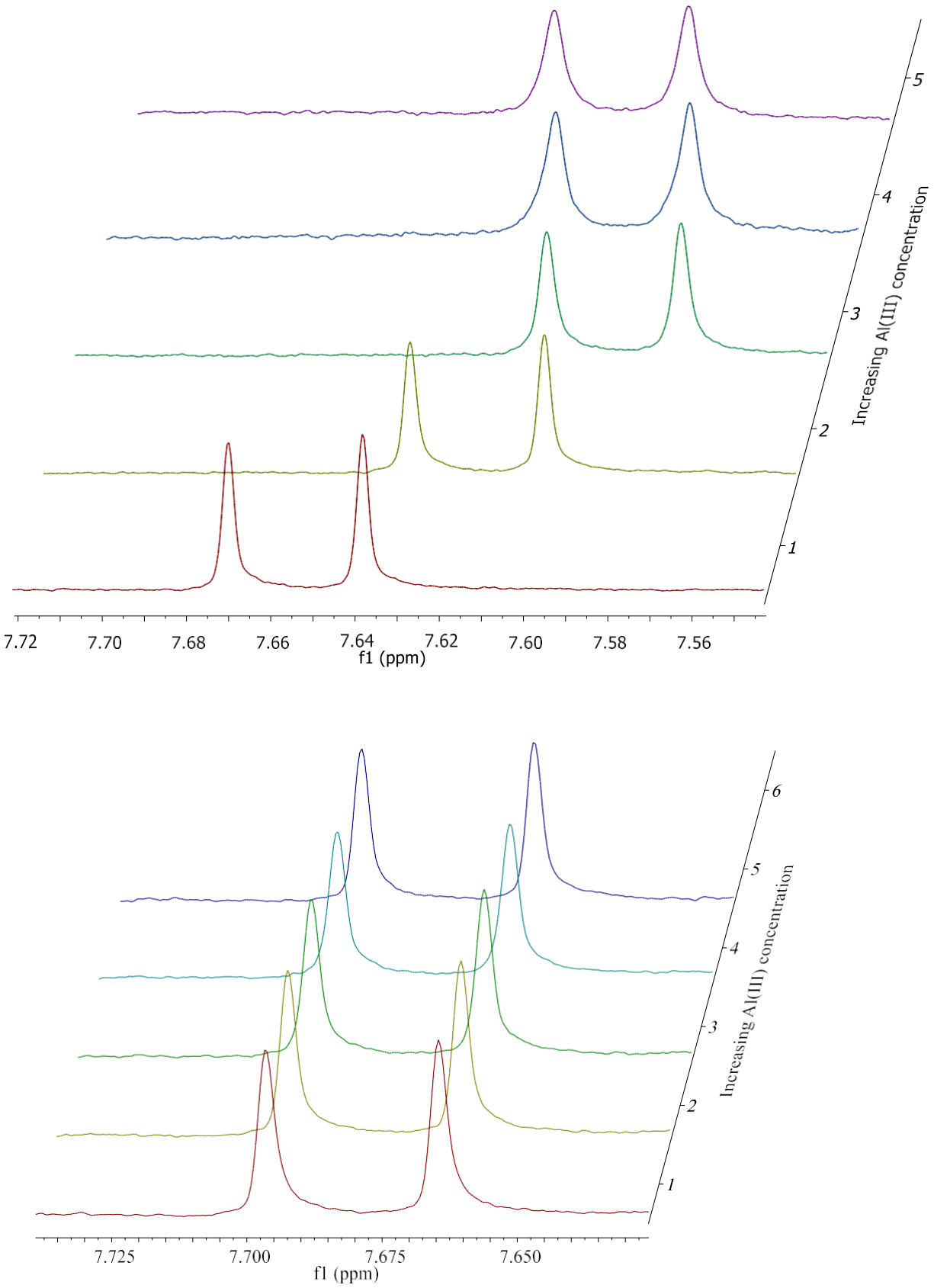

Figure S8. Up-field shift of the ^{1}H-NMR doublet of the β-proton of ferulic and *p*-coumaric acids plotted as a function of increasing concentration of Al^{3+} at pH 3.5.

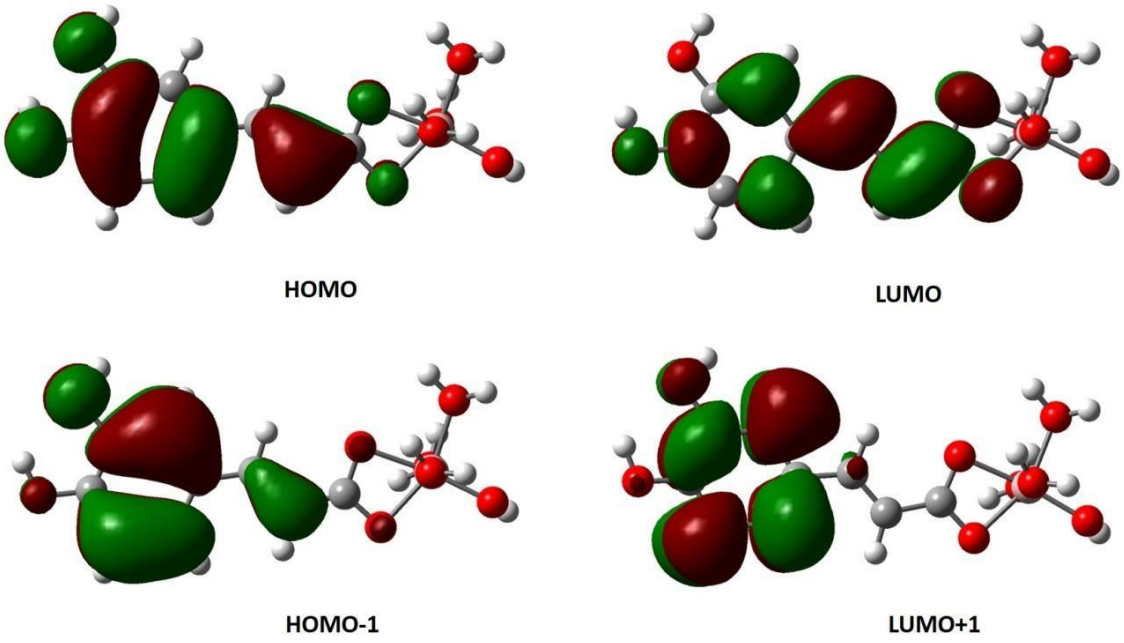

Figure S9. Four “Gouterman’s orbitals” of the lowest energy caffeic acid complex.

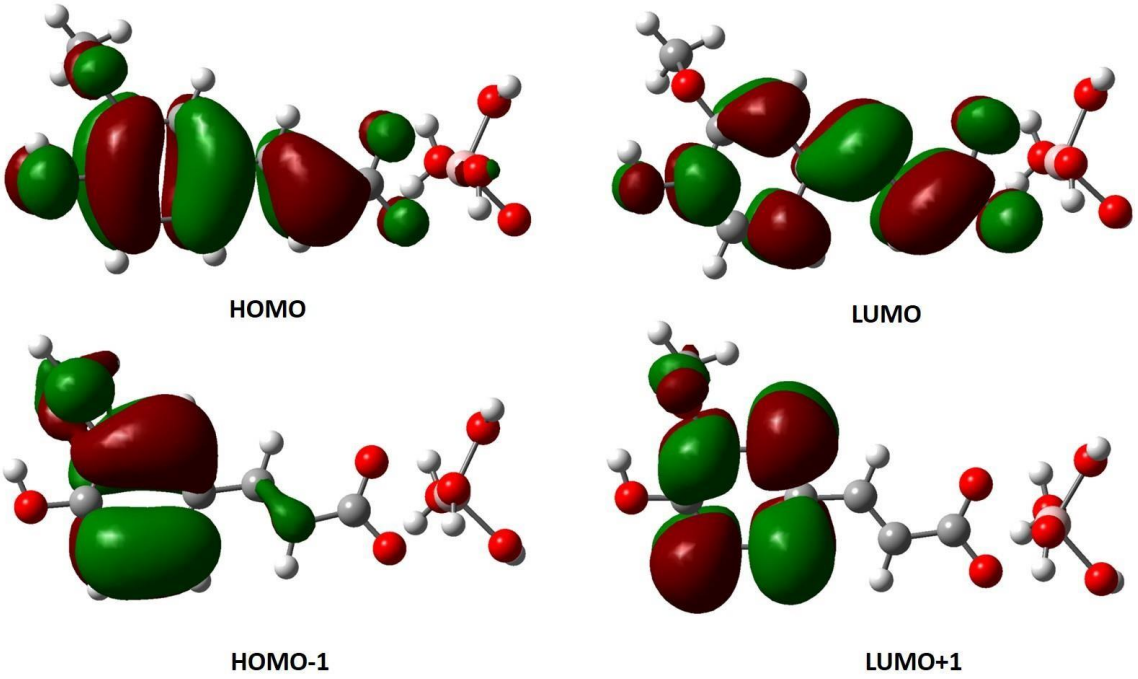

Figure S10. Four “Gouterman’s orbitals” of the lowest energy ferulic acid complex.

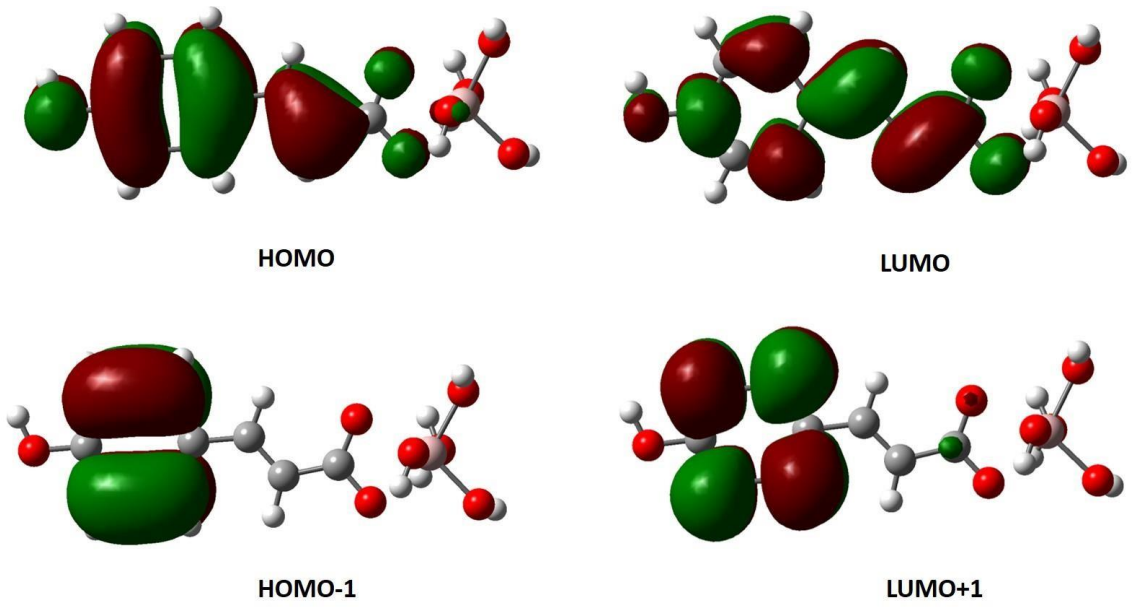

Figure S11. Four “Gouterman’s orbitals” of the lowest energy *p*-coumaric acid complex.

Table S1. Main excitation energies (ΔE), oscillator strengths (f) and MO contribution (%) computed for free ligands , calculated at (TD)-M052X/6-31G* level of theory, in aqueous solution.

Acids		**MO contribution**	**ΔE**		**f**
	Bands		**nm**	**eV**	
Caffeic	S1	H→L (70%)	277	4.48	0.704
	S2	H-1→L(53%); H→L+1 (45%)	213	5.83	0.572
	S3	H-4→L (50%);H-1→L+1(41%9	195	6.36	0.211
	S4	H-> L+5 (63%); H-1 →L+1 (27%)	177	7.00	0.119
Ferulic	S1	H→L (70%)	279	4.44	0.683
	S2	H-1→ L (54%); H→L+1 (46%)	214	5.60	0.669
	S3	H-1→L+1(44%); H-5→L	194	6.38	0.186
	S4	(24%) H-1→L+1(36%);	178	6.94	0.163
***p*-Coumaric**	S1	H→L (70%)	273	4.53	0.7596
	S2	H-1	204	6.08	0.3435
	S3	→L(60%);H→L+1(37%) H-	192	6.46	0.2929
	S4	1→L+1(46%)	175	7.08	0.3097