

# 1 Experimental methods

*Trans ortho-, meta- and para-coumaric acid* (hereafter referred to as *oCA*, *mCA* and *pCA*) were purchased from Aldrich and used without further purification.

The experimental setup has been described before.<sup>[1-3]</sup> Briefly, deprotonated chromophore anions were generated by electrospray ionisation of solutions of the coumaric acids dissolved in MeOH with a few drops of NH<sub>3</sub>, mass-selected by a quadrupole and guided into a hexapole trap. The anions were released from the trap at a rate of 20 Hz and focussed into the photoionization region of a collinear velocity-map imaging (VMI) spectrometer where they were intersected by nanosecond laser pulses with  $\lambda = 364 - 315$  nm and energy  $\sim 5$  mJ, generated by frequency-doubling the output of a Nd:YAG pumped dye laser. Electrons were accelerated towards a gated, position-sensitive detector where they were imaged using a CCD (charge-coupled device) camera. Laser-only images were subtracted from images recorded following the interaction of the laser light with the anions, to eliminate background counts arising from scattered laser light. The resulting photoelectron images were processed using the pBasex method.<sup>[4]</sup> The VMI spectrometer was calibrated by recording the photoelectron spectrum of I<sup>-</sup> and has a resolution of  $\sim 5\%$ .

## 2 Deprotonation site

In a combined action spectroscopy computation study, Rocha-Rinza and coworkers sought to determine whether *pCA*<sup>-</sup> was deprotonated at the phenol group or carboxylic acid group, when generated by electrospray ionisation.<sup>[5]</sup> The two  $pK_a$  values for *pCA*<sup>-</sup> in aqueous solution are around 4.4 and 9.0 for deprotonation at the carboxylic acid and phenol groups, respectively, indicating that deprotonation occurs at the carboxylic acid group in aqueous solution. Rocha-Rinza and coworkers found identical action spectra for *pCA*<sup>-</sup> and methyl-substituted derivatives, but analysis of the photodissociation pathways led to the conclusion that the chromophore was formed in its phenoxide form. A separate theoretical study concluded that the maxima in the experimental action spectra were consistent with the calculated vertical excitation energy of the first  $\pi \rightarrow \pi^*$  transition in the phenoxide form of *pCA*<sup>-</sup> (3.0 eV).<sup>[6]</sup> The VDE measurements we report in this paper support the conclusion that coumaric acids are formed in their phenolate forms during the electrospray ionisation process.

### 3 Computational methods and results

The geometric and electronic structures of the molecules were calculated using the Gaussian09 suite of programmes.<sup>[7]</sup> The geometric structures of the phenolate ( $O^-$ ) and carboxylate ( $COO^-$ ) forms of the deprotonated coumaric acid chromophores, and corresponding neutral radicals, were optimised using the B3LYP hybrid functional<sup>[8-11]</sup> and the aug-cc-pVTZ basis set.<sup>[12-17]</sup> Frequency calculations were performed to confirm that minima in the potential energy surface were reached.

Vertical detachment energies (VDEs) were determined using the electron propagator theory (EPT) method with the outer valence Green's function (OVGF)<sup>[18,19]</sup> propagator and a 6-311++G(3df,3pd) basis set.<sup>[20-22]</sup> We have already benchmarked this approach against the high-resolution photoelectron spectrum of the phenoxide anion and shown that it yields good results for the deprotonated green fluorescent protein chromophore anion.<sup>[3]</sup> Moreover, the maximum in the 364 nm (3.41 eV) photoelectron spectrum of  $pCA^-$  (2.9 – 3.0 eV) (Fig. 2 in the main text) is in good agreement with our calculated VDE for the phenolate form of  $pCA^-$  (3.0 eV) and with calculations carried out by Zuev *et al.* for  $pCA^-$  (2.92 eV)<sup>[6]</sup> and Gromov *et al.* for the deprotonated methyl-4-hydroxycinnamate thio ester analogue (2.90 eV)<sup>[23]</sup> and the experimental VDE reported for the methyl coumarate chromophore anion.<sup>[24]</sup>

Vertical excitation energies (VEEs) of the singlet excited electronic states of the phenolate deprotonated coumaric acid chromophores were calculated using the CAM-B3LYP/6-311++G(3df,3pd) method. The long-range corrected version of B3LYP using the Coulomb Attenuating Method (CAM)<sup>[25]</sup> was chosen for its potential to describe excited states with charge-transfer character and because it has been shown to yield reasonably good results for the phenolate form of the  $pCA^-$  anion.<sup>[26]</sup> Our VEEs are similar to those calculated for the analogous methyl coumarates<sup>[26]</sup> and are consistent with action spectra of the methyl coumarates.<sup>[26]</sup> Our value for  $pCA^-$  lies within the range of VEEs calculated by Zuev *et al.*<sup>[6]</sup> and Uppsten and Durbej<sup>[27]</sup>.

VDEs to the lowest lying electronically excited states of the neutral radicals,  $D_1$ , were determined by first calculating the  $D_1 - D_0$  VEEs at the optimised geometries of the anions and adding these values to the calculated VDEs (Table S8), giving values of 4.219, 3.887, 3.885 and 4.392 eV for  $oCA^-$ ,  $s-trans\ mCA^-$ ,  $s-cis\ mCA^-$  and  $pCA^-$ , respectively.

Photoelectron spectra of phenolate deprotonated coumaric acid chromophores were calcu-

lated using ezSpectrum 3.0.<sup>[28]</sup> These calculations require the equilibrium geometries, harmonic frequencies and normal mode vectors of the deprotonated coumaric acid anions and corresponding neutral radicals as input and these were obtained from the B3LYP/aug-cc-pVTZ calculations performed using Gaussian09. The Franck-Condon overlap integrals were calculated in ezSpectrum using the parallel normal mode approximation. The vibrational temperature of the anions was assumed to be 300 K and the minimum intensity threshold was set to 0.001. The maximum number of vibrational quanta in the anion and radical were limited to 4 and 6, respectively, and the vibrational energy in the anion state was capped at 0.3 eV. The resulting stick spectra were convoluted with instrumental profiles with HWHM in the range 10 – 21 meV, corresponding to 5% eKE resolution at the 0-0 transition.

VDEs, VEEs and oscillator strengths plotted in Fig. 2 of the paper for  $mCA^-$  are the averages of those for the *s-cis* and *s-trans* forms.

Table S1: Z-matrix of the B3LYP/aug-cc-pVTZ optimised geometries used to calculate the VDE, VEEs and FC spectra for the phenolate form of  $o\text{CA}^-$ ,  $\phi_a = 0^\circ$ .

Atom Number	Symbol	NA	NB	NC	Bond	Angle	Dihedral
1	C						
2	C	1			1.376901		
3	C	2	1		1.413400	123.156291	
4	C	3	2	1	1.466713	119.396305	0.003409
5	C	4	3	2	1.449034	115.045071	-0.008216
6	C	5	4	3	1.369817	122.899318	0.008453
7	H	2	1	6	1.085956	119.326900	-179.997355
8	H	5	4	3	1.083477	116.082032	-179.993144
9	C	3	2	1	1.425977	117.567073	-179.997260
10	H	9	3	2	1.087914	115.024266	0.000307
11	C	9	3	2	1.362831	129.681225	-179.998791
12	H	11	9	3	1.077044	120.850104	-0.000773
13	C	11	9	3	1.441381	120.100865	179.999311
14	O	13	11	9	1.384124	112.298803	179.985512
15	H	14	13	11	0.966139	104.338021	-179.987785
16	O	13	11	9	1.224506	129.161490	0.013454
17	H	6	5	4	1.085893	119.485576	179.997078
18	H	1	2	3	1.082138	120.979287	179.999592
19	O	4	3	2	1.255043	123.643511	-179.987715

Table S2: Z-matrix of the B3LYP/aug-cc-pVTZ optimised geometries used to calculate the VDE for the carboxylate form of  $o\text{CA}^-$ ,  $\phi_a = 0^\circ$ .

Atom Number	Symbol	NA	NB	NC	Bond	Angle	Dihedral
1	C						
2	C	1			1.388370		
3	C	2	1		1.394943	122.207686	
4	C	3	2	1	1.477399	118.103603	-0.001360
5	C	4	3	2	1.454316	117.275058	0.003259
6	C	5	4	3	1.363103	121.771607	-0.003363
7	H	2	1	6	1.082547	119.164797	179.998988
8	H	5	4	3	1.081068	116.048715	179.997513
9	C	3	2	1	1.440257	118.226452	179.999147
10	H	9	3	2	1.085578	115.173004	0.000000
11	C	9	3	2	1.347236	128.696276	180.000000
12	H	11	9	3	1.077054	122.404829	0.000000
13	C	11	9	3	1.474613	119.269758	180.000000
14	O	13	11	9	1.356464	111.320301	179.999150
15	H	14	13	11	0.968230	106.902780	-179.999222
16	O	13	11	9	1.209870	126.395130	0.000862
17	H	6	5	4	1.081792	120.498680	-179.998856
18	H	1	2	3	1.081270	119.608948	-179.999733
19	O	4	3	2	1.241905	122.648947	179.996384

Table S3: Z-matrix of the B3LYP/aug-cc-pVTZ optimised geometries used to calculate the VDE, VEEs and FC spectra for the phenolate form of  $mCA^-$ ,  $\phi_a = 0^\circ$ .

Atom Number	Symbol	NA	NB	NC	Bond	Angle	Dihedral
1	C						
2	C	1			1.385750		
3	C	2	1		1.403221	122.401050	
4	C	3	2	1	1.411160	116.505129	0.000000
5	C	4	3	2	1.392524	121.458650	0.000366
6	C	5	4	3	1.386648	120.322080	-0.000504
7	H	2	1	6	1.081269	119.344800	179.998486
8	H	5	4	3	1.081887	118.364514	-180.000000
9	C	3	2	1	1.463307	122.955096	179.999691
10	H	9	3	2	1.089262	119.225354	-179.981230
11	C	9	3	2	1.336325	128.769392	0.018061
12	H	11	9	3	1.084783	122.304152	0.001319
13	C	11	9	3	1.534096	122.445072	-179.999288
14	O	13	11	9	1.254622	114.057463	179.997146
15	O	13	11	9	1.253451	116.462812	-0.003279
16	H	6	5	4	1.082405	119.869139	-180.000000
17	H	1	2	3	1.082191	119.912645	-179.999658
18	O	4	3	2	1.368589	122.288699	-179.998829
19	H	18	4	3	0.964229	109.004881	0.002357

Table S4: Z-matrix of the B3LYP/aug-cc-pVTZ optimised geometries used to calculate the VDE for the carboxylate form of  $mCA^-$ ,  $\phi_a = 0^\circ$ .

Atom Number	Symbol	NA	NB	NC	Bond	Angle	Dihedral
1	C						
2	C	1			1.390970		
3	C	2	1		1.411354	118.076145	
4	C	3	2	1	1.398337	120.031198	0.001624
5	C	4	3	2	1.441163	123.671920	0.002612
6	C	1	2	3	1.386900	122.175309	-0.001708
7	H	1	6	5	1.086067	118.889088	179.997845
8	H	2	1	6	1.080524	120.643087	-180.000000
9	H	4	3	2	1.084467	119.400384	-179.998827
10	C	3	2	1	1.447709	122.532227	-179.997981
11	H	10	3	2	1.085630	115.552518	-180.000000
12	C	10	3	2	1.351681	128.308337	0.000000
13	H	12	10	3	1.079899	122.073853	0.000715
14	C	12	10	3	1.449384	121.390832	-179.999375
15	O	14	12	10	1.379527	111.748597	-179.985290
16	H	15	14	12	0.966585	104.954618	179.987212
17	O	14	12	10	1.217164	128.669744	-0.014057
18	O	5	4	3	1.263200	122.959191	-179.992107
19	H	6	1	2	1.084087	120.357323	179.998831

Table S5: Z-matrix of the B3LYP/aug-cc-pVTZ optimised geometries used to calculate the VDE, VEEs and FC spectra for the phenolate form of  $p\text{CA}^-$ ,  $\phi_a = 0^\circ$ .

Atom Number	Symbol	NA	NB	NC	Bond	Angle	Dihedral
1	C						
2	C	1			1.397754		
3	C	2	1		1.418456	121.404909	
4	C	3	2	1	1.380043	118.389181	0.006136
5	C	4	3	2	1.446125	121.996797	0.011428
6	C	1	2	3	1.374264	120.680788	-0.005852
7	H	1	6	5	1.081738	120.170240	179.989766
8	H	2	1	6	1.080428	118.876773	-179.997950
9	H	4	3	2	1.081893	121.154741	-179.996296
10	C	3	2	1	1.461184	122.593700	-179.992976
11	H	10	3	2	1.084482	115.806638	179.999701
12	C	10	3	2	1.337518	127.357324	0.001325
13	H	12	10	3	1.080328	123.269442	-0.001142
14	C	12	10	3	1.474232	120.315890	179.998108
15	O	14	12	10	1.358188	111.136336	179.992887
16	H	15	14	12	0.968296	106.960682	-179.992850
17	O	14	12	10	1.207725	126.413053	0.007340
18	O	5	4	3	1.251396	121.353661	-179.975462
19	H	6	1	2	1.080982	122.150583	179.996163

Table S6: Z-matrix of the B3LYP/aug-cc-pVTZ optimised geometries used to calculate the VDE for the carboxylate form of  $p\text{CA}^-$ ,  $\phi_a = 0^\circ$ .

Atom Number	Symbol	NA	NB	NC	Bond	Angle	Dihedral
1	C						
2	C	1			1.385160		
3	C	2	1		1.405905	120.704196	
4	C	3	2	1	1.402439	117.272322	0.000000
5	C	4	3	2	1.389250	121.633118	0.000000
6	C	5	4	3	1.388655	120.583221	0.000000
7	H	1	2	3	1.083083	119.451486	-180.000000
8	H	2	1	6	1.080314	119.775570	180.000000
9	H	4	3	2	1.085359	118.760210	-180.000000
10	C	3	2	1	1.463206	123.961566	180.000000
11	H	10	3	2	1.086222	116.540445	-180.000000
12	C	10	3	2	1.336441	127.818200	0.000000
13	H	12	10	3	1.085219	121.697278	0.000000
14	C	12	10	3	1.534476	123.511223	-180.000000
15	O	14	12	10	1.255941	113.850852	179.999328
16	O	14	12	10	1.252298	116.712770	-0.002449
17	O	5	4	3	1.378864	121.648829	180.000000
18	H	6	5	4	1.081036	119.866342	180.000000
19	H	17	5	4	0.961999	108.543400	0.000000

Table S7: B3LYP/aug-cc-pVTZ energies (in Hartrees) of the phenolate ( $O^-$ ) ( $\phi_a = 0^\circ$ ) and carboxylate ( $COO^-$ ) forms of  $oCA^-$ ,  $mCA^-$  and  $pCA^-$ . The differences,  $E_{COO^-} - E_{O^-}$ , are in eV.

Chromophore		$E_{O^-}$	$E_{COO^-}$	$E_{COO^-} - E_{O^-}$
$oCA^-$		-573.136343	-573.121717	0.398
$mCA^-$	<i>s-trans</i>	-573.124694	-573.119919	0.130
	<i>s-cis</i>	-573.124737	-573.120317	0.120
$pCA^-$		-573.141579	-573.117255	0.662

Table S8: EPT/6-311++G(3df,3pd) calculated vertical detachment energies (VDEs) in eV and pole strengths (in parentheses) of the phenolate ( $O^-$ ) and carboxylate ( $COO^-$ ) forms of  $oCA^-$ ,  $mCA^-$  and  $pCA^-$  presented in Fig. 1 in the main text.

Chromophore		VDE ( $O^-$ )	VDE ( $COO^-$ )
$oCA^-$		2.943 (0.881)	4.900 (0.888)
$mCA^-$	<i>s-trans</i>	2.723 (0.878)	4.954 (0.887)
	<i>s-cis</i>	2.713 (0.878)	4.930 (0.887)
$pCA^-$		3.002 (0.878)	4.684 (0.888)

Table S9: CAM-B3LYP/6-311++G(3df,3pd) vertical excitation energies in eV, oscillator strengths,  $f$  (in parentheses), and main configurations of the first two transitions with oscillator strengths  $f \geq 0.03$  for the phenolate forms of  $oCA^-$ ,  $mCA^-$  and  $pCA^-$  (with  $\phi_a = 0^\circ$ ).

Chromophore		$1^1\pi\pi^*$		$2^1\pi\pi^*$	
		VEE ( $f$ )	configuration	VEE ( $f$ )	configuration
$oCA^-$		3.238 (0.398)	0.70(43-46)	4.628 (0.120)	0.46(41-46) + 0.48(43-52)
$mCA^-$	<i>s-trans</i>	2.461 (0.053)	0.70(43-44)	4.113 (0.523)	0.68(41-44)
	<i>s-cis</i>	2.446 (0.034)	0.70(43-44)	4.151 (0.307)	0.61(41-44)
$pCA^-$		3.444 (0.913)	0.69(43-45)	4.333 (0.101)	0.67(43-51)

Table S10: EPT/6-311++G(3df,3pd) calculated vertical detachment energies (VDEs) in eV and pole strengths (in parentheses) of the phenolate ( $O^-$ ) forms of  $oCA^-$ , *s-cis*  $mCA^-$  and  $pCA^-$  in their twisted conformations with  $\phi_a = 90^\circ$  and  $\phi_b = 90^\circ$ , compared with those for the planar forms (Fig. 1 in the main text).

Chromophore	VDE ( $O^-$ )	VDE ( $O^-$ )	VDE ( $O^-$ )
	planar	$\phi_a = 90^\circ$	$\phi_b = 90^\circ$
$oCA^-$	2.943 (0.881)	2.744 (0.885)	2.541 (0.886)
<i>s-cis</i> $mCA^-$	2.713 (0.878)	2.548 (0.883)	2.527 (0.886)
$pCA^-$	3.002 (0.878)	2.672 (0.882)	2.512 (0.884)

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