Electronic Supporting Information (ESI) for:

Chromophores of chromophores: A bottom-up Hückel picture of the excited states of photoactive proteins

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Table ESI1: **Experimental and computational energetics.** The vertical detachment energy (VDE), adiabatic detachment energy (ADE), and onset of the first excited state of the neutral (D_1 channel) measured and calculated for phenolate, *p*-methyl-phenolate, *p*-ethyl-phenolate and *p*-vinyl-phenolate (Ph^-, MPh^-, EPh^-, and VPh^-, respectively). The VDE is defined as the vertical difference in energy between the optimised anion ground state geometry and the neutral in this optimized geometry. The ADE is the difference in energy between the optimized anion ground state geometry and the optimized neutral ground state geometry. The D1 channel is calculated as a vertical excitation from the optimized anion ground state geometry to the first doublet excited state of the neutral, using TD-DFT. Calculations were carried out using the B3LYP functional and the aug-cc-pVDZ basis set.

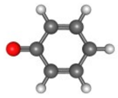
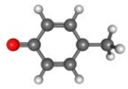
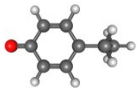
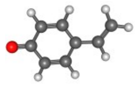
		VDE$_{calc}$	ADE$_{calc}$	D_1 Channel$_{calc}$	VDE$_{exp}$	ADE$_{exp}$	D_1 Channel$_{exp}$
	Ph^-	2.27	2.21	3.28	2.30 ± 0.10	2.27 ± 0.10	3.29 ± 0.10
	MPh^-	2.15	2.07	3.19	2.24 ± 0.10	2.15 ± 0.10	3.21 ± 0.10
	EPh^-	2.18	2.12	3.22	2.23 ± 0.10	2.13 ± 0.10	3.22 ± 0.10
	VPh^-	2.02	1.97	3.11	2.45 ± 0.10	2.31 ± 0.10	3.47 ± 0.10

Figure ESI1: Photoelectron spectra of MPh^-. 3D frequency-resolved photoelectron spectra of MPh^-. All photoelectron spectra are normalised to a unit maximum. The horizontal arrow indicates the onset of the resonance in eV.

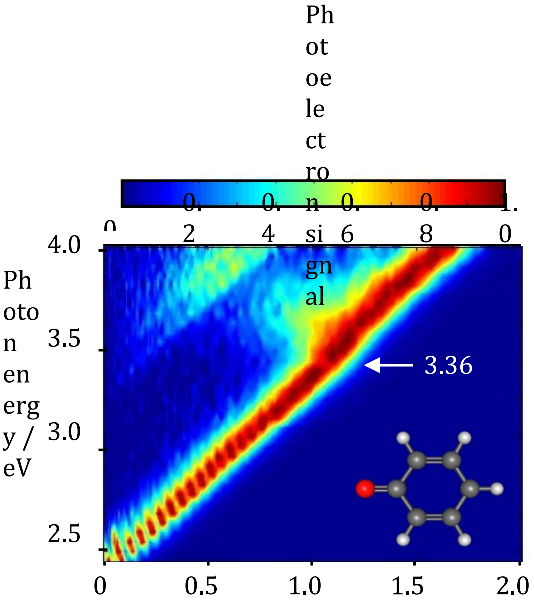


Figure ESI2: Anisotropy across two direct detachment channels. Plots of the experimental (circles) and computed (solid lines) β_2 parameters as a function of the eKE for the D$_0$ and D$_1$ detachment channels for (a) phenolate, (b) MPh$^-$, (c) EPh$^-$, and (d) VPh$^-$. For the D$_0$ channel of EPh$^-$, two calculated PADs are shown, corresponding to the global minimum energy structure (red) and a conformer related by hindered rotation about the single bond (blue). Shaded eKE regions indicate resonance dynamics that change β_2 from the calculated ones The relevant Dyson orbitals used in the calculations are inset and errors associated with the experimental values are indicated.

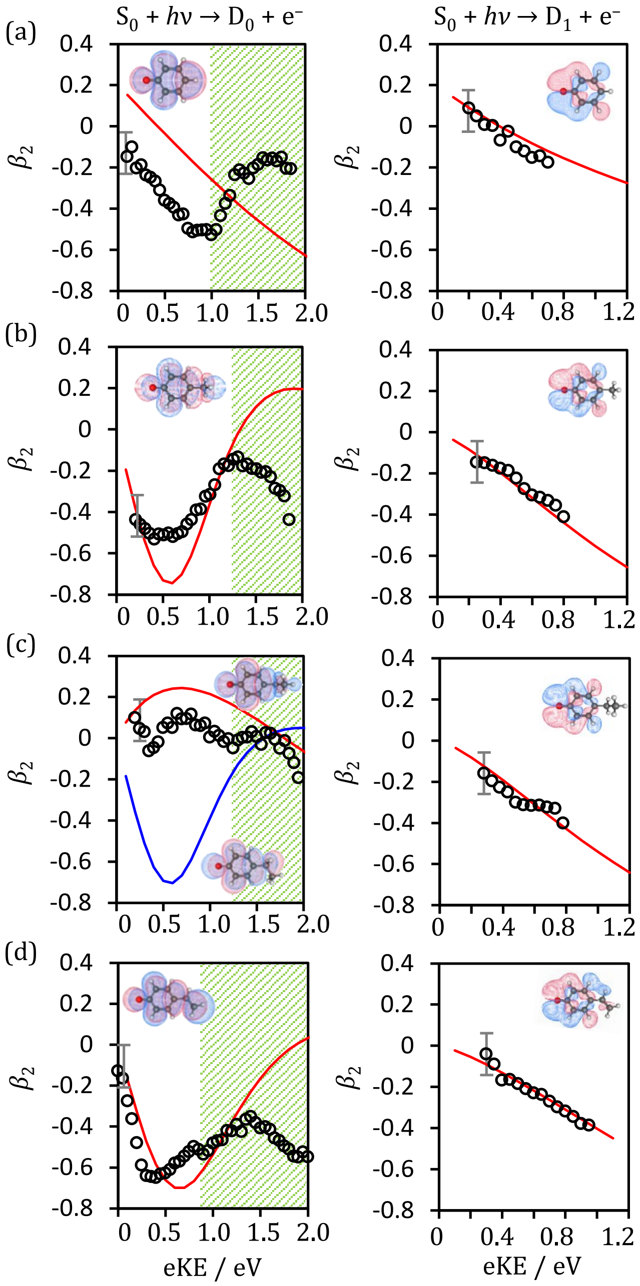


Figure ESI3: Excited states of MPh^- and EPh^-. Energies and relevant molecular orbitals that contribute to the resonance seen experimentally for Ph^-, MPh^- and EPh^-. The augmented function employed in TD-DFT calculations of the neutral excited state leads to significant contributions from very diffuse MOs that are not associated with valence orbitals. For this reason, the augmented function was removed, and the only contributions to the resonance states are shown below.