

**Electronic Supplementary information for:**

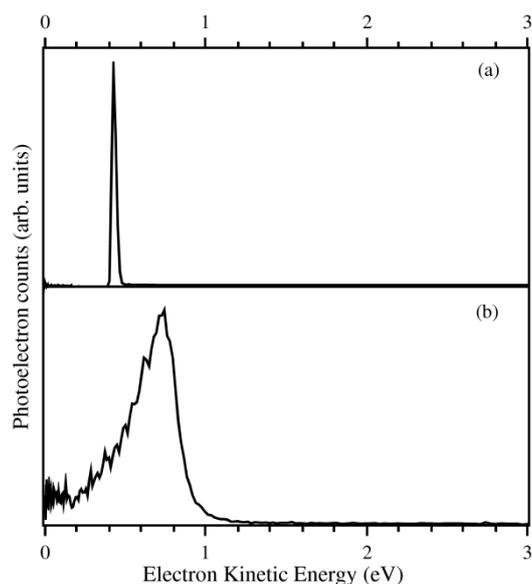
**Photoelectron spectroscopy of the model GFP chromophore anion**

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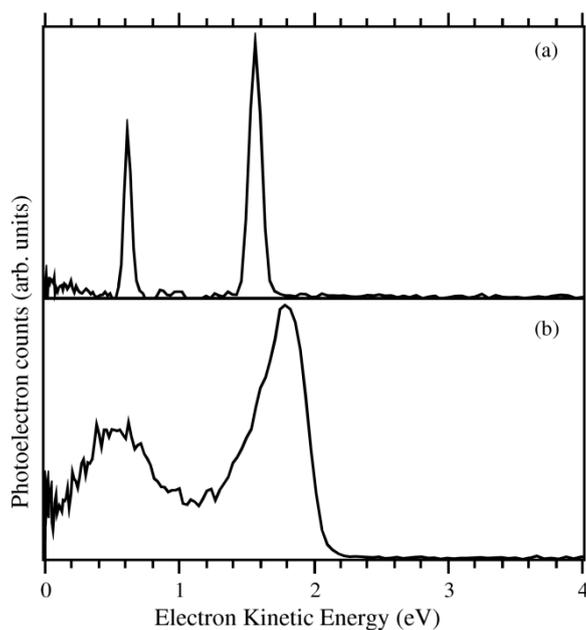
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### **Calibration of photoelectron spectra**

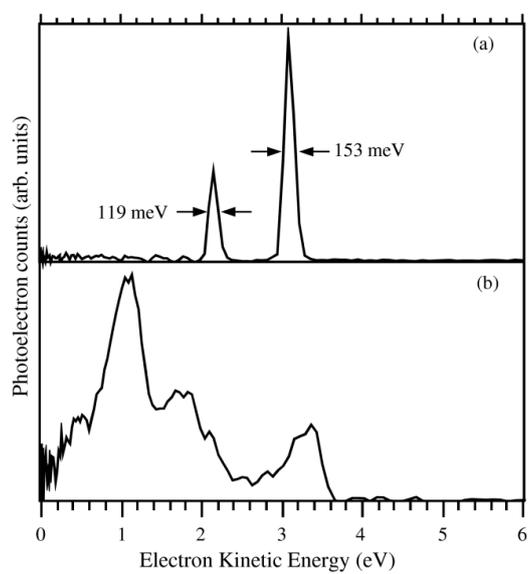
Collected photoelectron (PE) spectra and detachment wavelengths have been calibrated using the well-known photodetachment from iodide ( $\Gamma^-$ ). Figures S1 to S3 show the PE spectra of  $\Gamma^-$  at 355 nm, 268.1 nm and 201.5 nm respectively, as well as the collected PE spectra of  $\text{HBDI}^-$  at those wavelengths. Calibration images were collected before and after the PE spectra of  $\text{HBDI}^-$ . Our detector resolution is  $\sim 5\%$ , as indicated in S3(a).



**Fig. S1** Photoelectron spectra of  $\Gamma^-$  (a) and  $\text{HBDI}^-$  (b) collected at 355 nm.



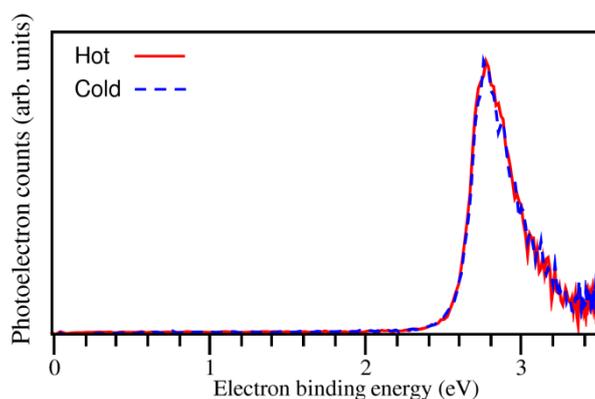
**Fig. S2** Photoelectron spectra of  $\Gamma^-$  (a) and  $\text{HBDI}^-$  (b) collected at 268.1 nm.



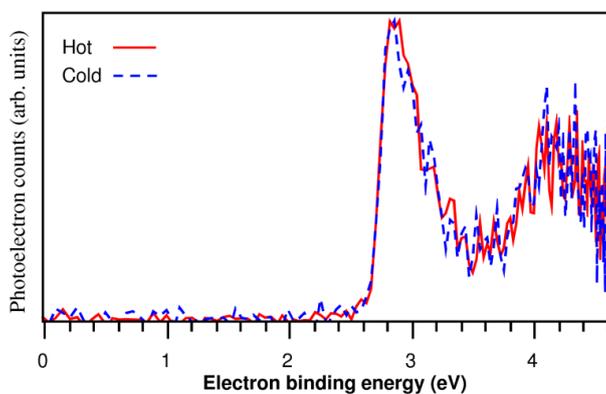
**Fig. S3** Photoelectron spectra of  $\Gamma^-$  (a) and  $\text{HBDI}^-$  (b) collected at 201.5 nm. Indicated in (a) are the full-width at half maximum, yielding a detector resolution of  $\sim 5\%$ .

### Effect of internal energy on photoelectron spectra

The amount of internal energy the ions possess can be varied by changing the trapping conditions in our ring electrode trap. Spectra at approximately room temperature are obtained by using Helium as a buffer gas and keeping all trapping voltages as low as feasible. Using heavier buffer gasses leads to considerable heating of ions, and we have performed experiments using air as a buffer gas, which increases momentum transfer to the ions by a factor of  $\sim 6$  and leads to ion temperatures several hundred K above room temperature. Photoelectron spectra collected under these two conditions appear identical, as shown in Figures S4 and S5, and yield identical values for the vertical and adiabatic detachment energy ( $VDE$  and  $ADE$ , respectively) within our 0.1 eV error margin.



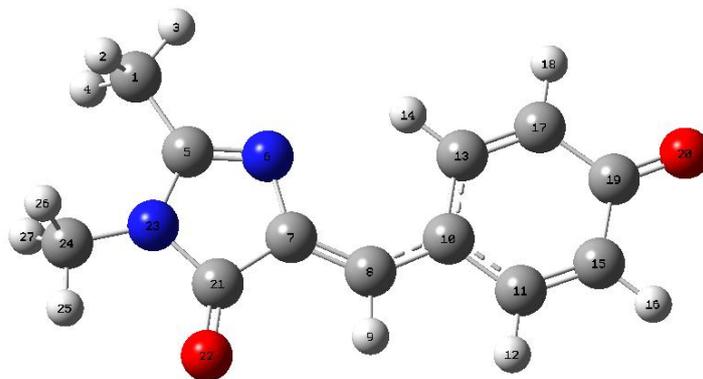
**Fig. S4** Photoelectron spectra of HBDI<sup>-</sup> collected at 3.496 eV photon energy (355nm) and different amounts of internal energy. The obtained  $VDE$  and  $ADE$  are identical.



**Fig. S5** Photoelectron spectra of HBDI<sup>-</sup> collected at 4.63 eV photon energy (268.1 nm) and different amounts of internal energy. The obtained  $VDE$  and  $ADE$  are identical.

### Details of electronic structure calculations

All calculations were carried out using the Gaussian09 software package.<sup>1</sup> The HBDI anion geometry was optimised using the CAM-B3LYP functional<sup>2</sup> and aug-cc-pVDZ basis set. The optimised structure is shown in Figure S6 with atomic coordinates given in table S1.



**Fig. S6** Optimised HBDI<sup>-</sup> structure with atomic labels. Coordinates are given in table S1.

Atom	X	Y	Z
1	-3.30911	2.41910	0.00001
2	-3.95274	2.52047	0.88658
3	-2.57526	3.22990	-0.00014
4	-3.95304	2.52040	-0.88635
5	-2.57540	1.12282	-0.00006
6	-1.28840	0.99520	-0.00018
7	-1.02490	-0.38555	-0.00009
8	0.20633	-1.01435	-0.00003
9	0.11523	-2.10425	0.00001
10	1.52224	-0.51525	-0.00001
11	2.61475	-1.43594	0.00003
12	2.38222	-2.50421	0.00004
13	1.85900	0.87580	-0.00006
14	1.04434	1.59770	-0.00012
15	3.91941	-1.03189	0.00006
16	4.73697	-1.75408	0.00008
17	3.15725	1.29838	-0.00003
18	3.40067	2.36209	-0.00008
19	4.28322	0.37541	0.00008
20	5.47161	0.76461	-0.00001
21	-2.27873	-1.11760	-0.00013
22	-2.56122	-2.32056	0.00004
23	-3.24101	-0.09367	0.00006
24	-4.65775	-0.33615	0.00021
25	-4.78714	-1.42408	0.00042
26	-5.14318	0.08231	0.89370
27	-5.14332	0.08197	-0.89336

**Table S1** Atomic coordinates for optimised HBDI<sup>-</sup> structure. Atomic labels are specified in Fig. S6.

All subsequent calculations were carried out using this optimised geometry. The total calculated HF energy for the anion is  $-723.65717 E_h$ , the HF energy of the corresponding neutral in the optimised anion geometry is  $-723.55457 E_h$ . The neutral optimised geometry has a total energy of  $-723.55821 E_h$ . These results yield  $VDE = 2.79$  eV and  $ADE = 2.69$  eV. A time-dependent DFT calculation was carried out to find excited states of the neutral, within the anion optimised geometry. Details of the first four excited states, their excitation energies and orbital contributions are given in table S2. Calculated molecular orbitals for MOs 53 – 57 are shown in the main paper. MO57 is the HOMO in the anion. Dominant contributions are indicated in bold in the table and these correspond to single electron transitions in which an electron is excited from progressively lower MOs. The MOs plotted in the main paper are those of the anion, but the corresponding neutral MOs are qualitatively the same.

Excited State 1: 1.5422 eV	
<b>55B -&gt; 57B</b>	<b>0.86677</b>
55B -> 58B	-0.43085
55B -> 69B	-0.12045
55B -> 74B	-0.10772
Excited State 2: 2.0673 eV	
57A -> 58A	-0.46453
52B -> 58B	0.11354
<b>56B -&gt; 57B</b>	<b>0.84760</b>
56B -> 58B	0.16273
Excited State 3: 2.6250 eV	
54A -> 58A	0.10517
57A -> 61A	0.12854
<b>54B -&gt; 57B</b>	<b>0.92261</b>
54B -> 58B	-0.28467
Excited State 4: 2.7565 eV	
<b>53B -&gt; 57B</b>	<b>0.87034</b>
53B -> 58B	0.42324

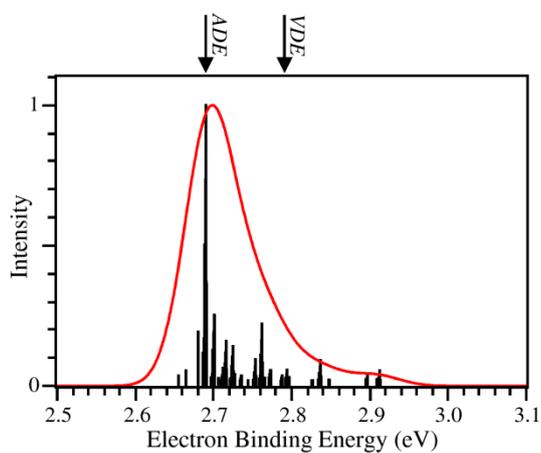
**Table S2** Calculated neutral excited states (in the optimised anion geometry), their excitation energies and orbital contributions. The dominant contribution to each excitation is shown in bold.

### **Simulation of Photoelectron Spectra**

In order to gain some insight into the nature of the photodetachment from the  $S_0$  to the neutral  $D_0$  state, and to clarify the relationship between the experimental  $VDE$  and theoretical  $VDE$ , we have simulated the photoelectron spectrum. Anion and neutral geometries were optimised using CAM-B3LYP/Aug-cc-pVDZ methods<sup>2</sup> and frequencies in the respective optimised geometries calculated. All calculations were carried out using Gaussian09.<sup>1</sup> The  $ADE$  was calculated as 2.69 eV. Full dimensional harmonic Franck-Condon factors were calculated using ezSpectrum and the Duschinsky rotations formalism.<sup>3,4</sup> An initial anion temperature of 300 K was assumed and vibrational excitation limited to 1 quantum in the initial state and 4 quanta in the final state, all combination bands were included. Also shown is a convolution of the calculated stick spectrum with a Gaussian instrument response function (FWHM = 0.1 eV).

The predominant transition is calculated to be the vibrational origin,  $v'' = 0 \leftarrow v' = 0$  (i.e. the  $ADE$ ). The calculated  $VDE = 2.79$  eV, as indicated in Fig. S7. Hence, assuming no spectral width, the observed maximum in the photoelectron spectrum would correspond to the  $ADE$  rather than  $VDE$  and would imply that the reported experimental  $ADE$  is actually  $\sim 0.1$  eV too low, further increasing the disagreement with high level theory. However, when convoluted with a Gaussian instrument response function, the spectral maximum shifts towards the  $VDE$  as shown in Fig. S7. The actual spectral width measured experimentally suggests that there is more width observed experimentally than simulated. This could be due to a number of factors including temperature, the true spectral resolution of the spectrometer and of course the fact that in the present case, the level of theory used to simulate the photoelectron spectrum is rather low compared to other high-level electronic structure calculations. Regardless, all these factors would suggest that the experimentally observed  $VDE$  will lie between the theoretical  $ADE$  and  $VDE$  and will be likely to be quite close to the theoretical  $VDE$  with a maximum deviation of  $<0.1$  eV, which is within the quoted error bars. It seems unlikely that the experimental spectral maximum is much higher than the theoretical  $VDE$  (which is calculated to be 2.54 eV). We once again stress that the level of theory employed here is

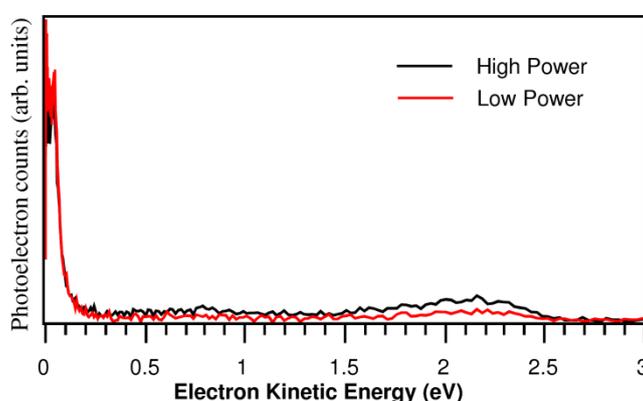
significantly lower than that of previous calculations and it would be of interest to simulate the spectrum using the higher level of theory, although this is beyond the scope of the current experimental work.



**Fig. S7** Simulated photoelectron spectra for photodetachment from the anion ground to the neutral ground state, at 300 K and with vibrational excitation limited to 1 quantum in the initial and 4 quanta in the final state. Shown in red is a convolution of the stick spectrum with a Gaussian instrument response function with FWHM = 0.1 eV.

### Power dependence of 480 nm spectrum

To determine whether the observed exponential tail between  $0.1 \text{ eV} < eKE < 0.2 \text{ eV}$  arises from multiphoton effects, we have collected the photoelectron spectrum at 480 nm at two different pulse energies,  $65 \mu\text{J pulse}^{-1}$  (“high power”) and  $20 \mu\text{J pulse}^{-1}$  (“low power”). The resulting spectra are shown in Fig. S8. No dependence of the exponential tail on laser power is observed. We thus conclude that it arises from a single photon process. Multiphoton processes are clearly identified at higher kinetic energies in the spectrum. The feature at  $\sim 2.2 \text{ eV}$  corresponds to 2-photon detachment into the neutral ground state.



**Fig. S8** Photoelectron spectrum of HBDI<sup>-</sup> collected at 480 nm with differing laser powers. The exponential tail at low  $eKE$  prevails in both spectra.

## References

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4. This work was conducted using the resources of the iOpenShell Center for Computational Studies of Electronic Structure and Spectroscopy of Open-Shell and Electronically Excited Species (<http://iopenshell.usc.edu>) supported by the National Science Foundation through the CRIF:CRF program.