## **Electronic Supporting Information**

Luminescence spectroscopy of oxazine dye cations isolated in vacuo

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Fig S1. Photoinduced dissociation mass spectra of CV<sup>+</sup> (top) and BCB<sup>+</sup> (bottom).



Fig S2. Yield of daughter ions from CV<sup>+</sup> (m/z 262) as a function of laser power for three daughter ions with m/z 218 (top), 233 (middle) and 245 (bottom). The excitation wavelength was 500 nm. The lines are fits to the function  $b \cdot x^a$  and the *a*-parameter gives the number of photons needed to cause the dissociation to give the respective daughter ion. Saturation occurs at high laser power for m/z 233 and 245 (middle and bottom) so the data point at maximum laser power has been omitted in the fit.



Fig S3. Yield of daughter ions from BCB<sup>+</sup> (m/z 282) as a function of laser power for two daughter ions with m/z 238 (top) and 253 (bottom). The laser wavelength was in both cases 560 nm. The lines are fits to the function  $b \cdot x^a$  and the *a*-parameter gives the number of photons needed to cause the dissociation to give the respective daughter ion. Saturation occurs at high laser power for m/z238 (top) so the two data points at highest laser powers have been omitted in the fit.



Fig S4. Yield of daughter ions *versus* laser wavelength for (a) CV<sup>+</sup> and (b) BCB<sup>+</sup>. These spectra are not corrected for the number of photons absorbed.



Fig S5. Luminescence spectra of  $CV^+$  obtained after photoexcitation at three different wavelengths. A notch filter matching the excitation wavelength is used for blocking the laser light before reaching the spectrometer. The excitation wavelength at 560 nm is in the emission band so the notch filter also blocks the emitted photons. The full width at half maximum of the blocking region of the 561 nm notch filter is 18 nm. The spectra were measured with a spectrometer entrance slit width of 1250  $\mu$ m.



Fig S6. Gas-phase luminescence spectra of  $Ox-170^+$  obtained at four different spectral resolutions determined by the spectrometer entrance slit width (312 µm, 625 µm, 1250 µm and 2500 µm). In all cases the excitation wavelength was 560 nm.