Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Intrinsic fluorescence from firefly oxyluciferin monoanions isolated *in vacuo*

Christina Kjær, Jeppe Langeland, Steen Brøndsted Nielsen

Contents

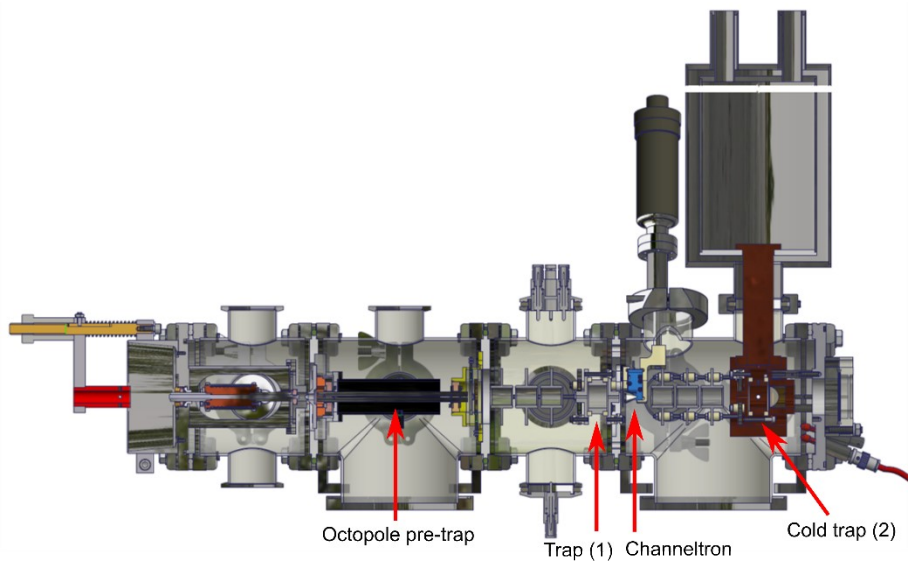


Fig. S1.
Schematic drawing of the LUNA2 setup.

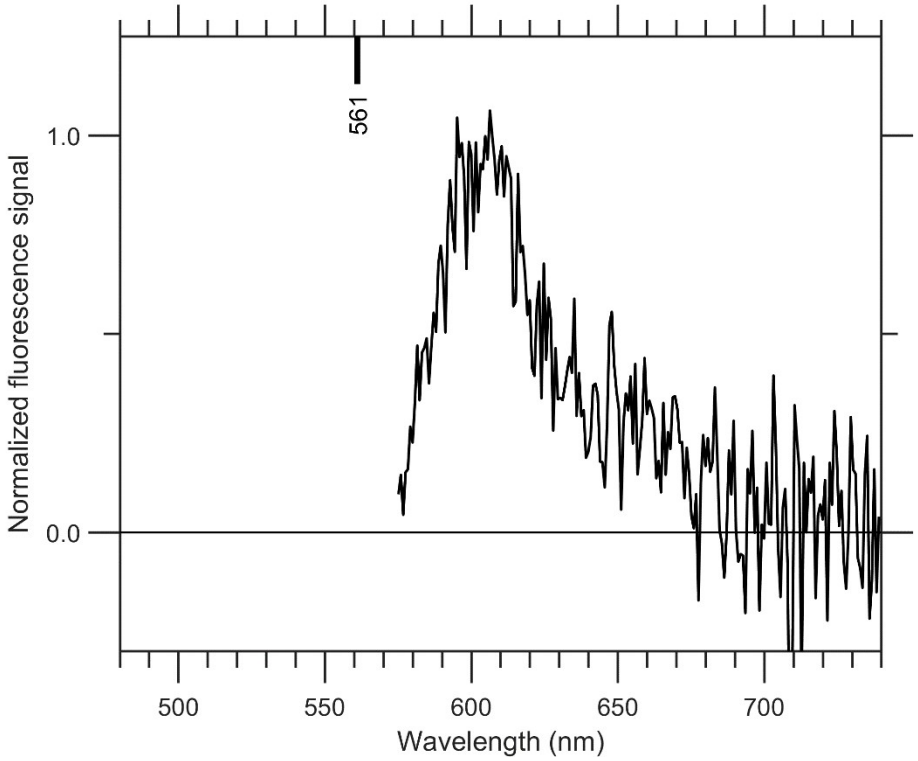


Fig. S2.

Gas-phase fluorescence spectrum of **dm-OL**$^-$ obtained at 300 K. The excitation wavelength was 561 nm. **dm-OL**$^-$ was dissolved in MeOH for electrospray ionization.

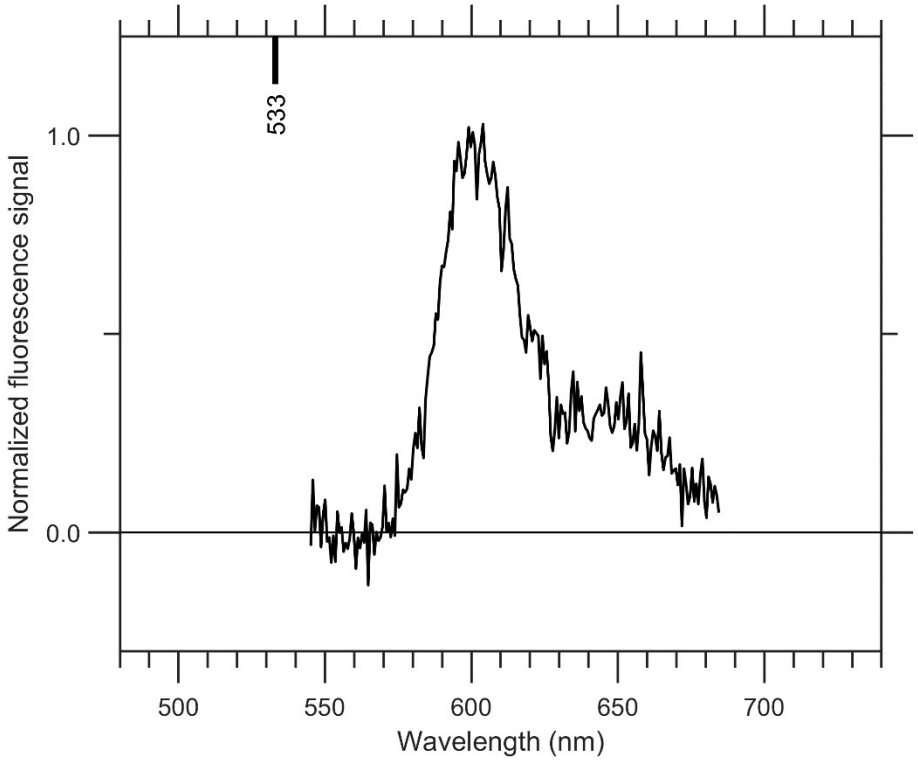


Fig. S3.

Gas-phase fluorescence spectrum of **dm-OL**$^-$ obtained at 100 K. The excitation wavelength was 533 nm. **dm-OL**$^-$ was dissolved in MeOH for electrospray ionization.

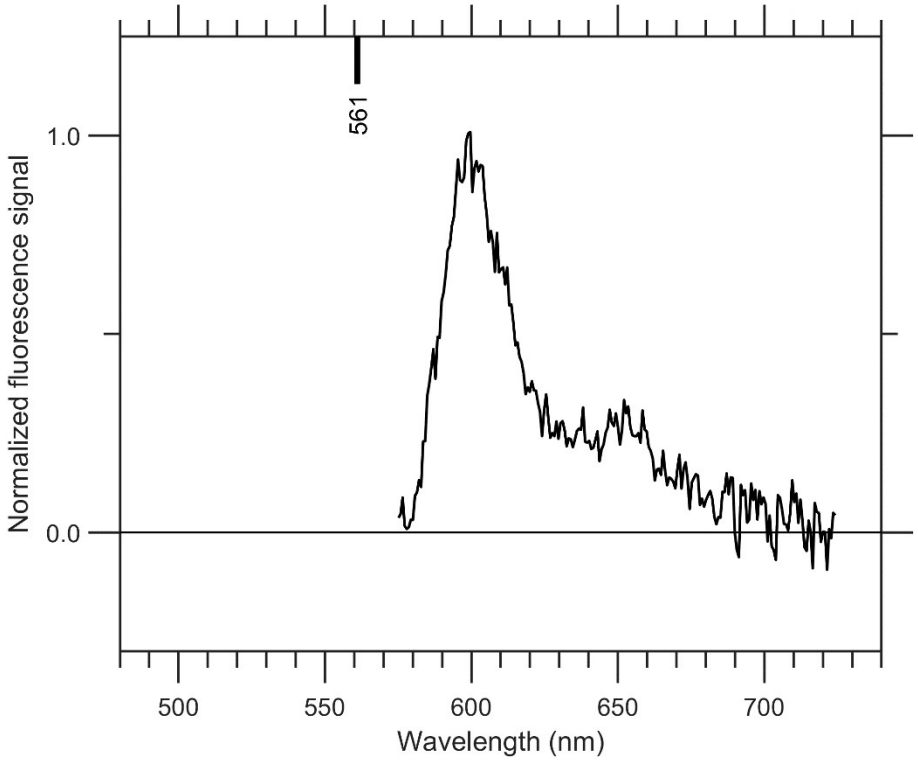


Fig. S4.

Gas-phase fluorescence spectrum of **dm-OL**$^-$ obtained at 100 K. The excitation wavelength was 561 nm. **dm-OL**$^-$ was dissolved in MeOH for electrospray ionization.

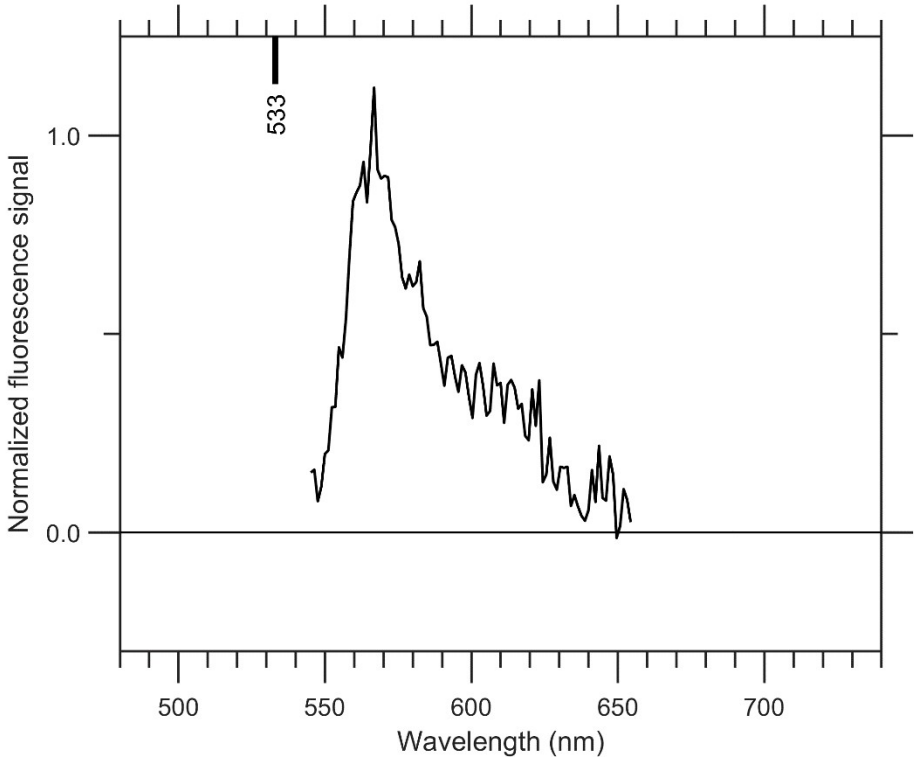


Fig. S5.

Gas-phase fluorescence spectrum of **OL**$^-$ obtained at 300 K. The excitation wavelength was 533 nm. **OL**$^-$ was dissolved in MeOH for electrospray ionization.

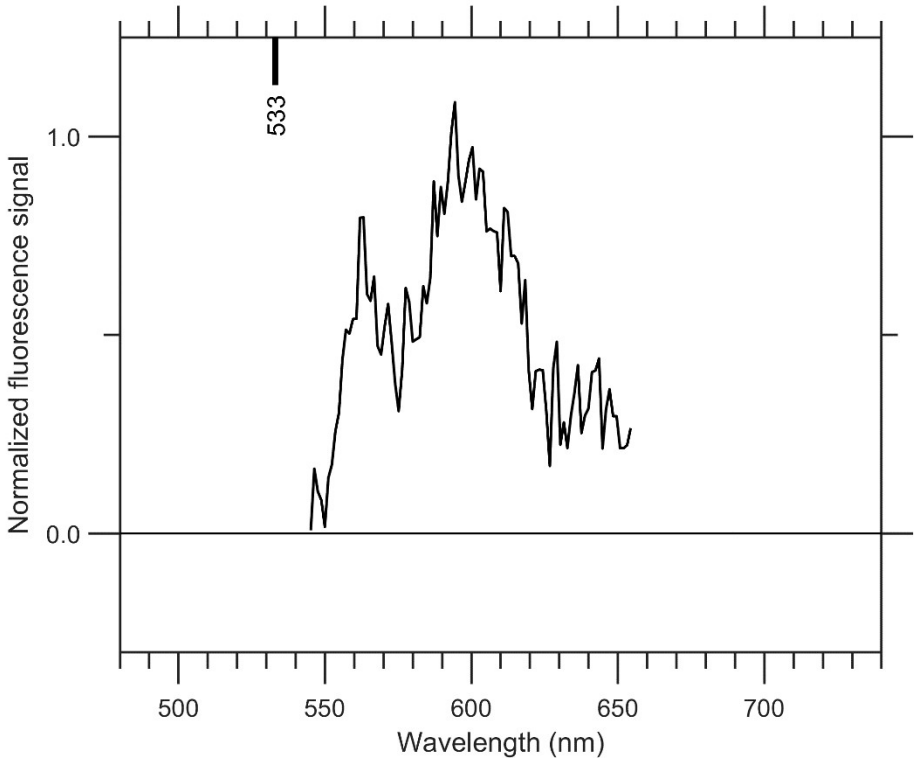


Fig. S6.

Gas-phase fluorescence spectrum of **OL**$^-$ obtained at 100 K. The excitation wavelength was 533 nm. **OL**$^-$ was dissolved in MeCN for electrospray ionization.

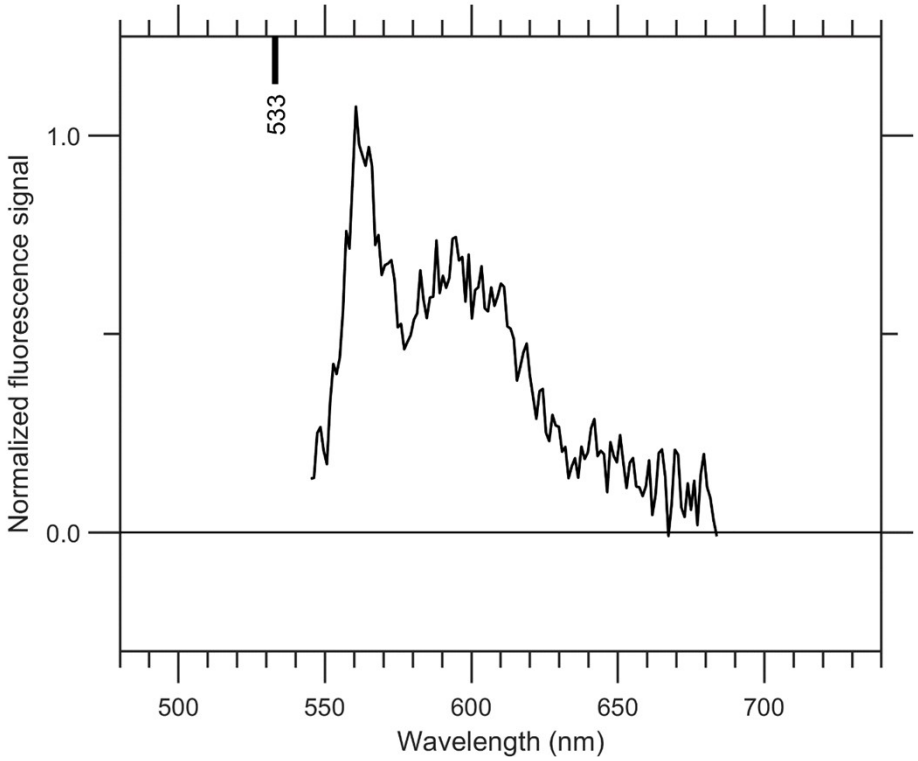


Fig. S7.

Gas-phase fluorescence spectrum of **OL**$^-$ obtained at 100 K. The excitation wavelength was 533 nm. **OL**$^-$ was dissolved in MeOH for electrospray ionization.

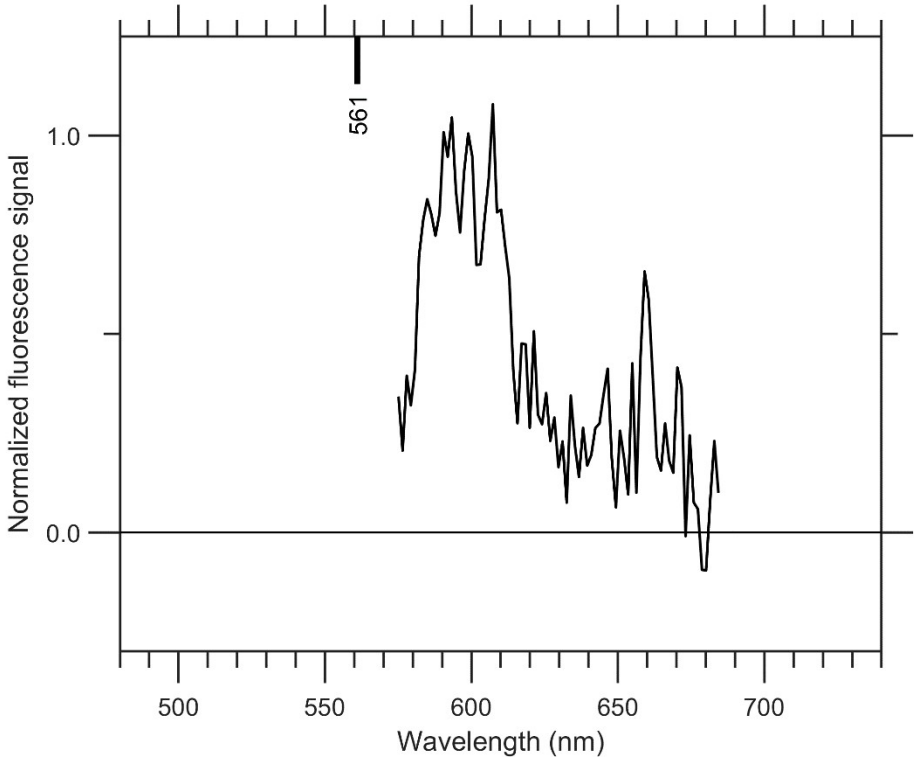


Fig. S8.

Gas-phase fluorescence spectrum of **OL**$^-$ obtained at 100 K. The excitation wavelength was 561 nm. **OL**$^-$ was dissolved in MeCN for electrospray ionization.

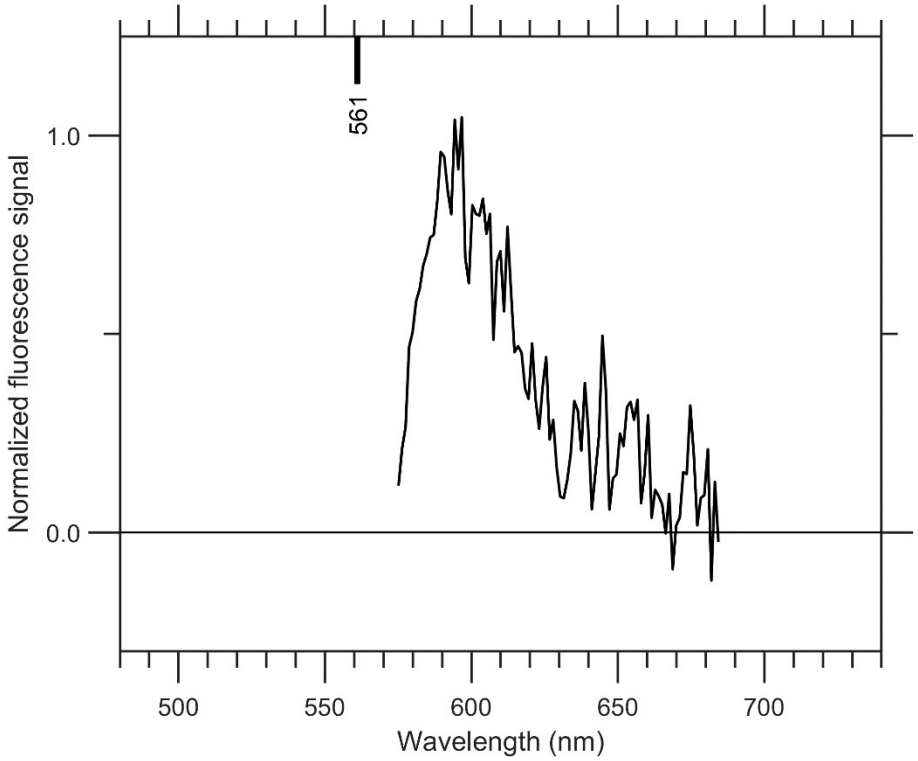


Fig. S9.

Gas-phase fluorescence spectrum of **OL**$^-$ obtained at 100 K. The excitation wavelength was 561 nm. **OL**$^-$ was dissolved in MeOH for electrospray ionization.

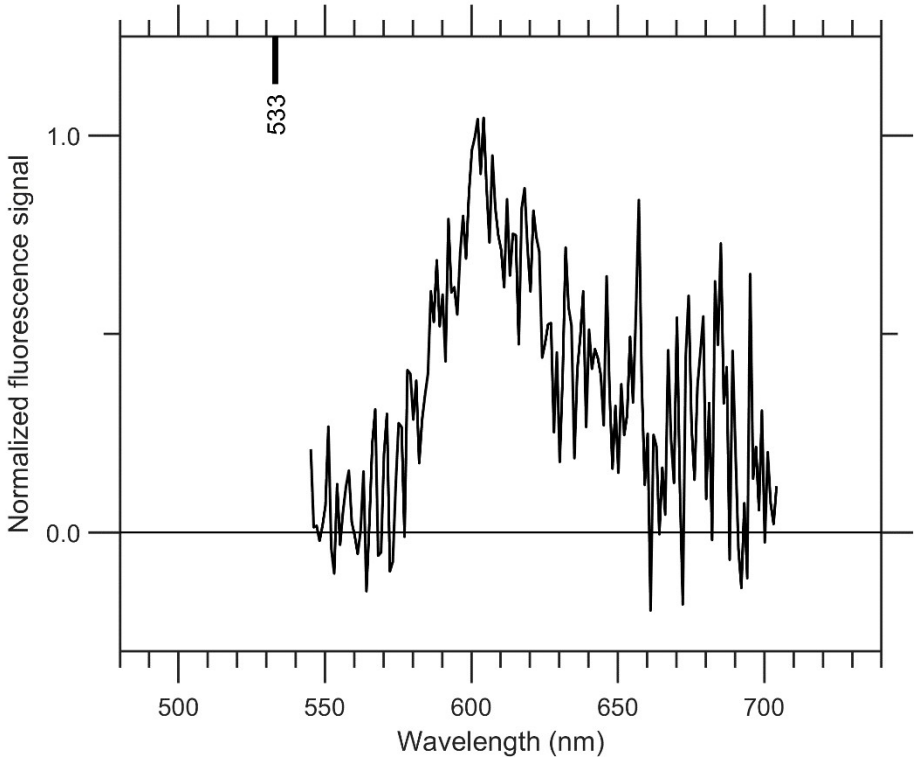


Fig. S10.

Gas-phase fluorescence spectrum of **dm-OL**$^-$ obtained at 300 K. The excitation wavelength was 533 nm. **dm-OL**$^-$ was dissolved in MeOH for electrospray ionization.

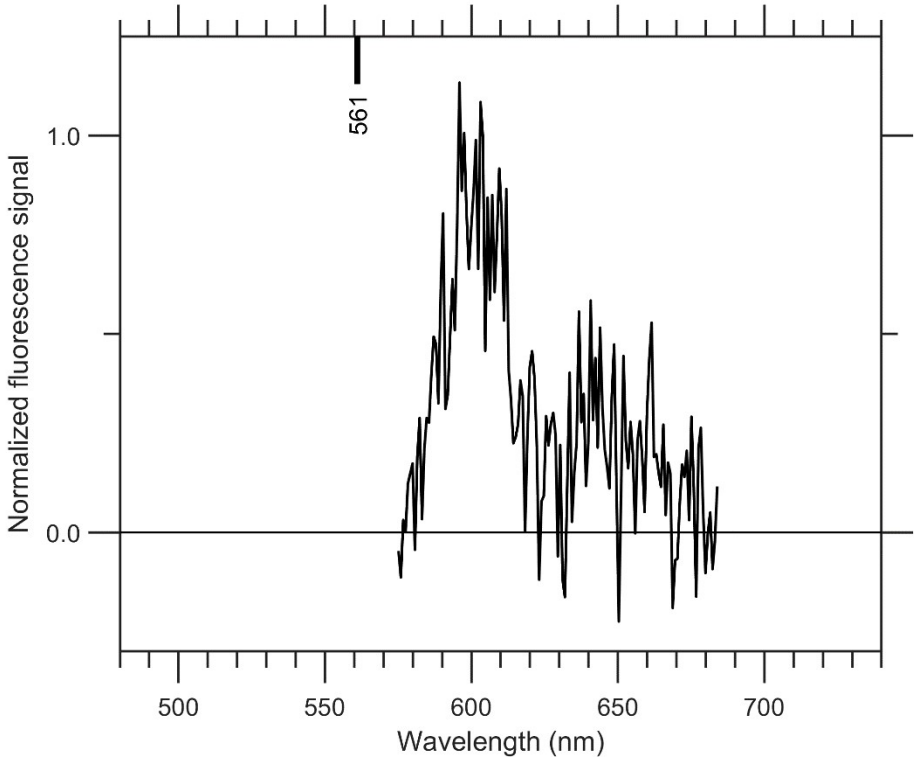


Fig. S11.

Gas-phase fluorescence spectrum of **dm-OL**$^-$ obtained at 100 K. The excitation wavelength was 561 nm. **dm-OL**$^-$ was dissolved in MeCN for electrospray ionization.

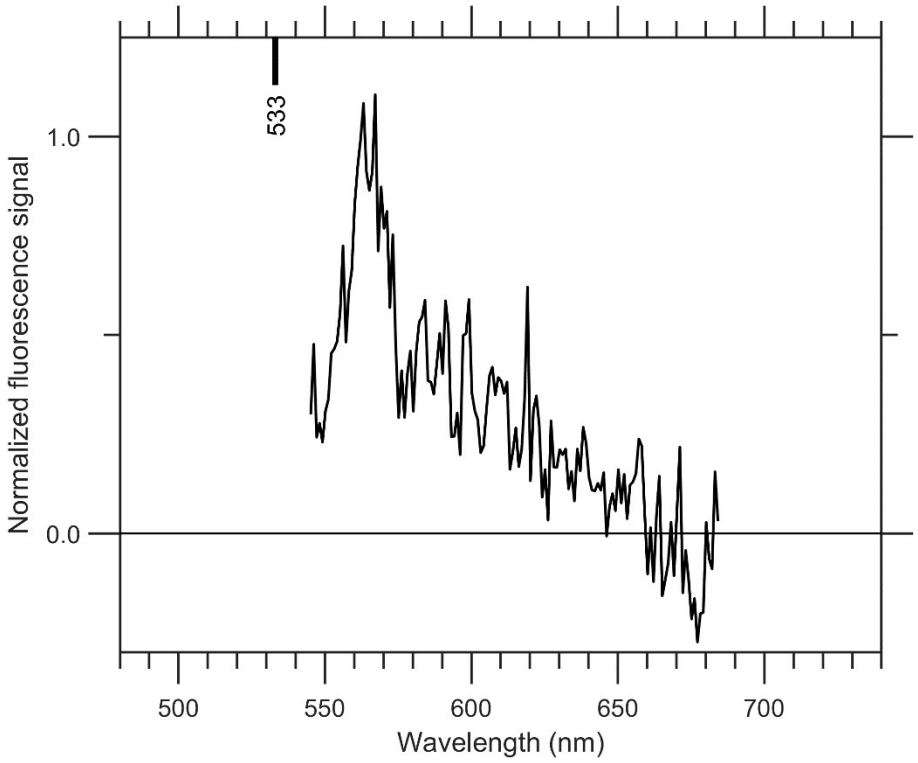


Fig. S12.

Gas-phase fluorescence spectrum of **m-OL**$^-$ obtained at 100 K. The excitation wavelength was 533 nm. **m-OL**$^-$ was dissolved in MeOH for electrospray ionization. The chemical structure is shown in **Fig. S15**.

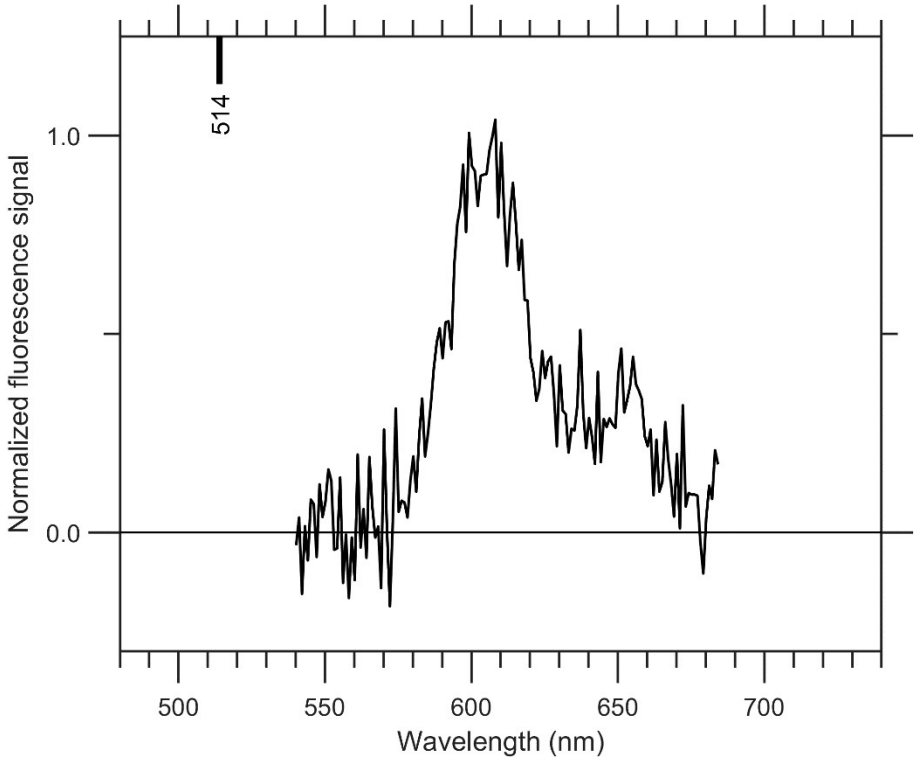


Fig. S13.

Gas-phase fluorescence spectrum of **dm-OL**$^-$ obtained at 100 K. The excitation wavelength was 514 nm. **dm-OL**$^-$ was dissolved in MeOH for electrospray ionization.

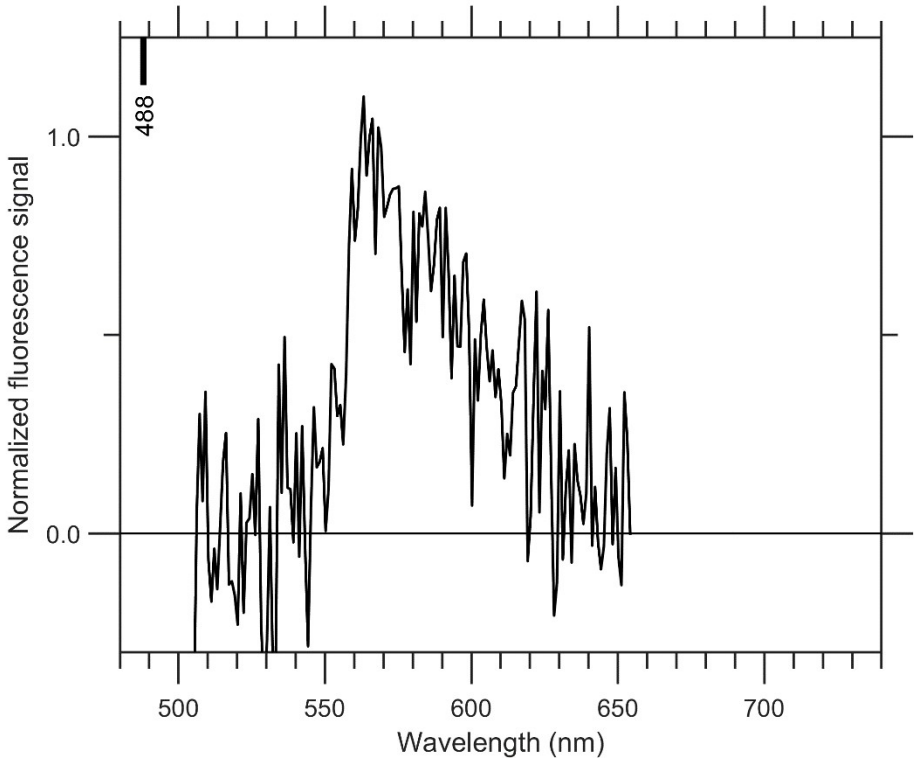
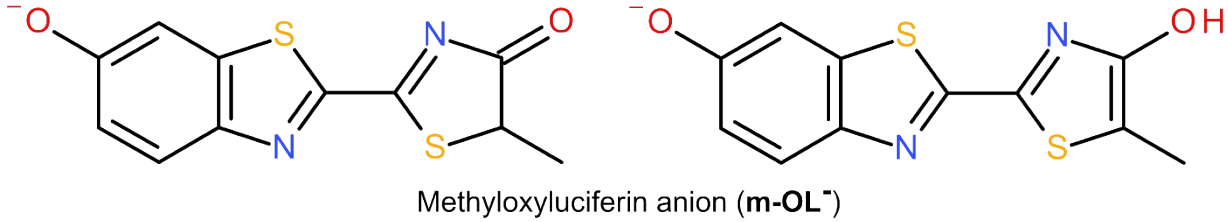


Fig. S14.

Gas-phase fluorescence spectrum of **OL**$^-$ obtained at 100 K. The excitation wavelength was 488 nm. **OL**$^-$ was dissolved in MeOH for electrospray ionization.



Methyloxyluciferin anion (**m-OL**$^-$)

Fig. S15.

Chemical structures of **m-OL**$^-$ (keto and enol forms).