Electronic Supporting Information for

From fluorogen to fluorophore by elucidation and suppression of ultrafast excited state processes of a Schiff base

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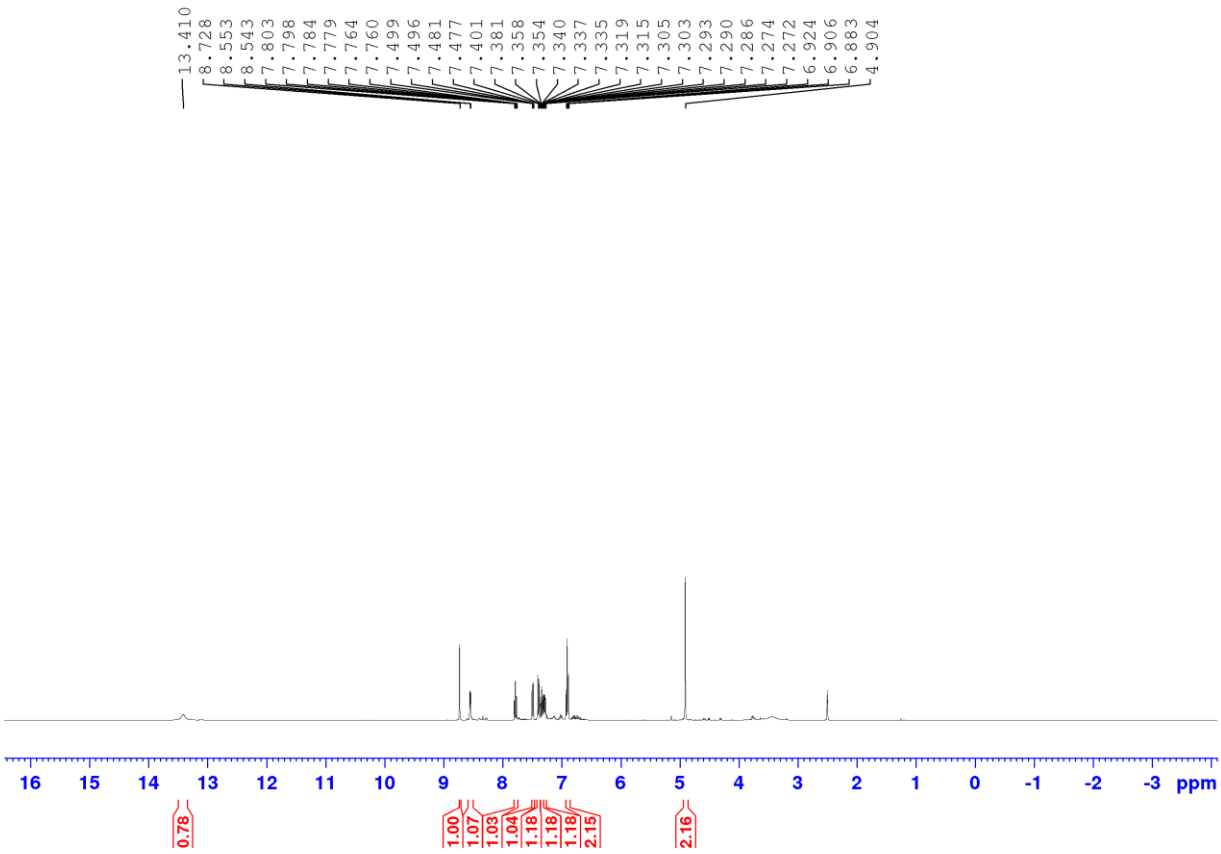
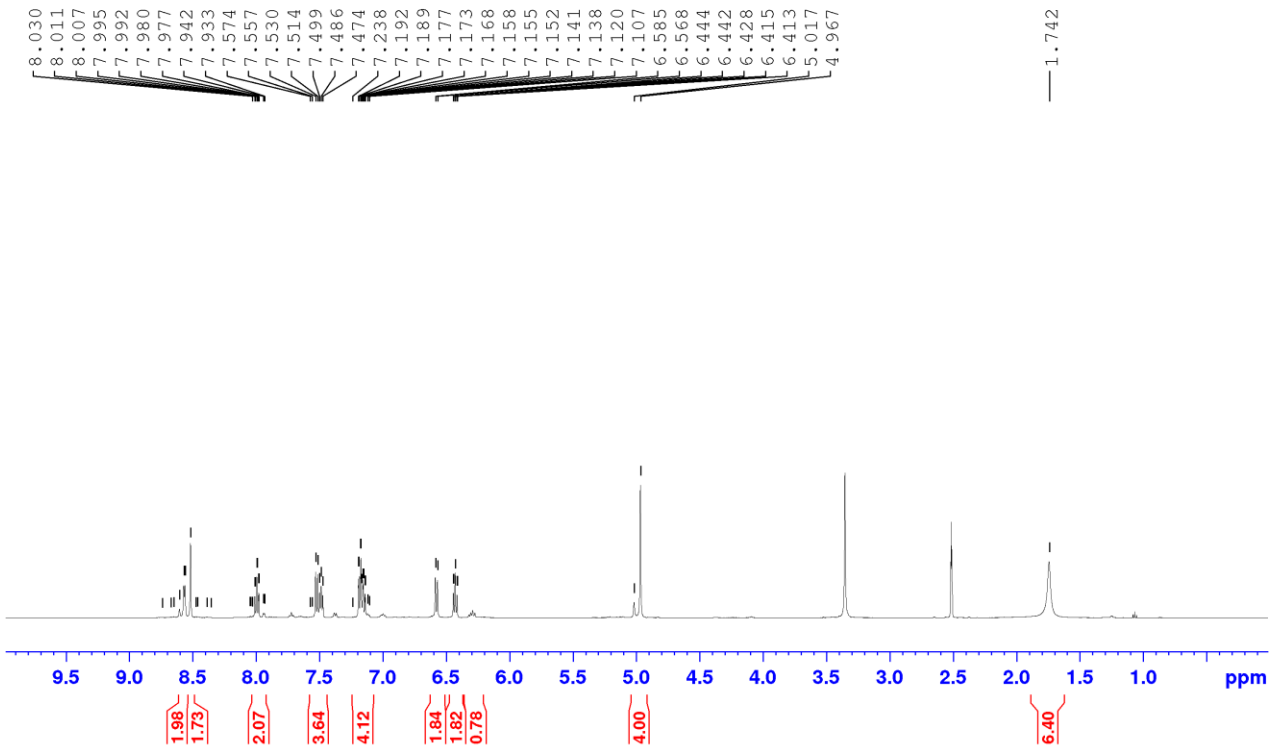
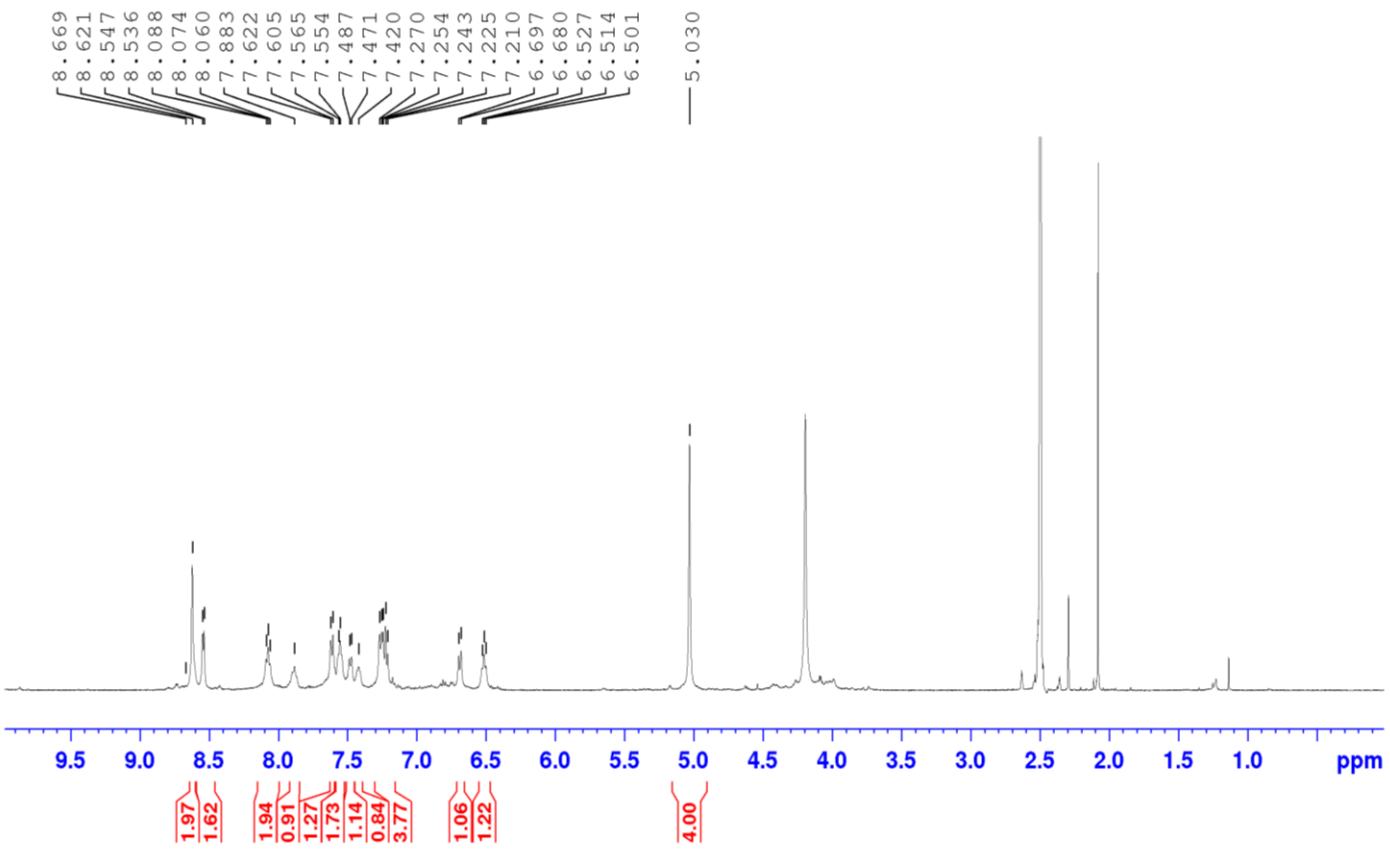
1. NMR Spectra of the Compounds



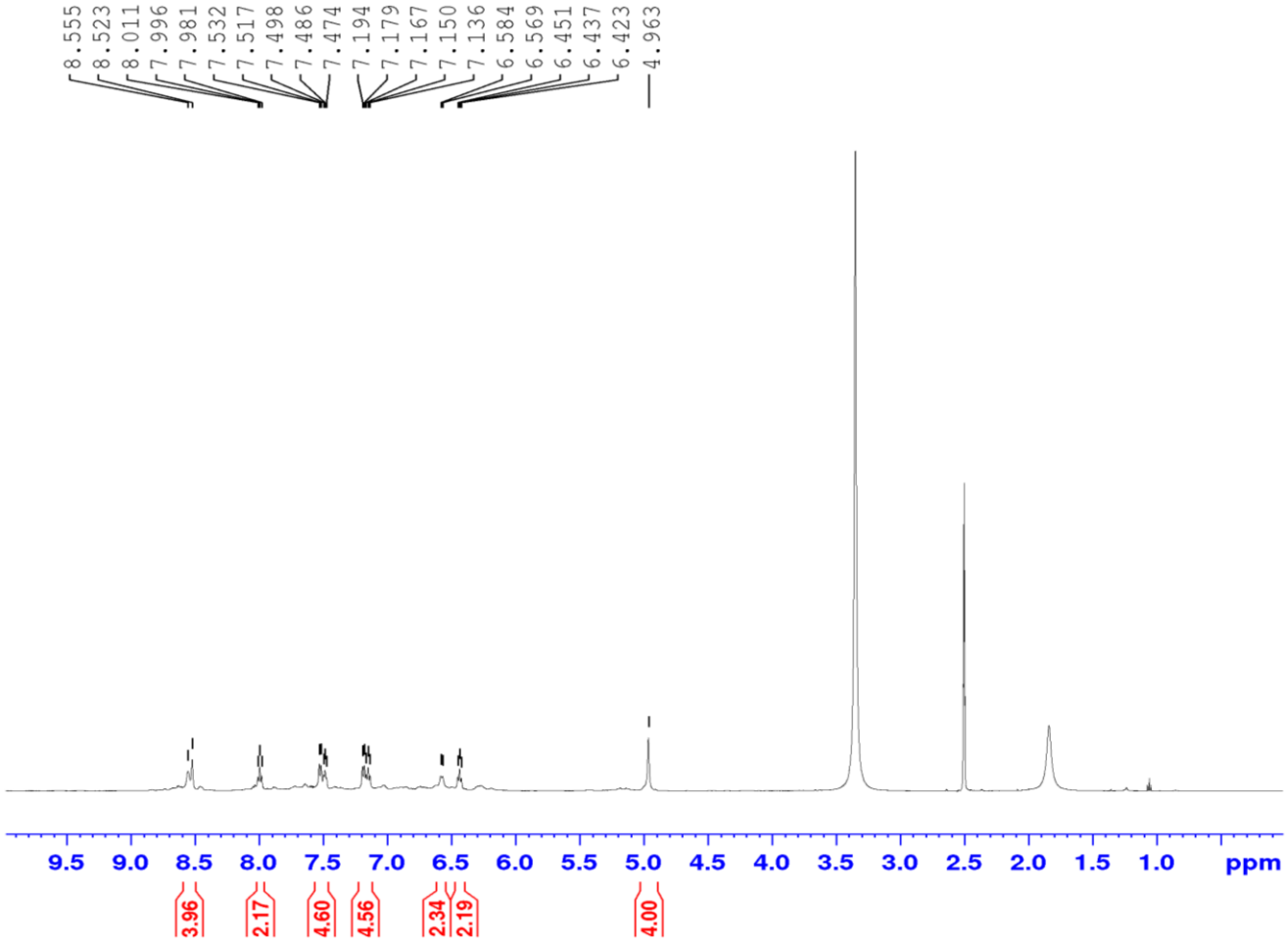
(a) salampy (500 MHz, DMSO) : 6.8-8.5 (8H, m, Ph), 4.9 (2H, s, methylene), 13.4 (1H, br s, OH), 8.7 (1H, s, benzylidenimin)



(b) Znsalampy (bridged) (500 MHz, DMSO) : 6.4-8.5 (16H, m, Ph), 5.0 (4H, s, methylene), 8.6 (2H, s, benzylidenimin), 6.4 (1H, qt, methine), 1.74 (6H, br s, CH_3)



(c) Znsalampy (unbridged) (500 MHz, DMSO) : 6.5- 8.5 (16H, m, Ph), 5.03 (4H, s, methylene), 8.6 (2H, s, benzylidenimin)

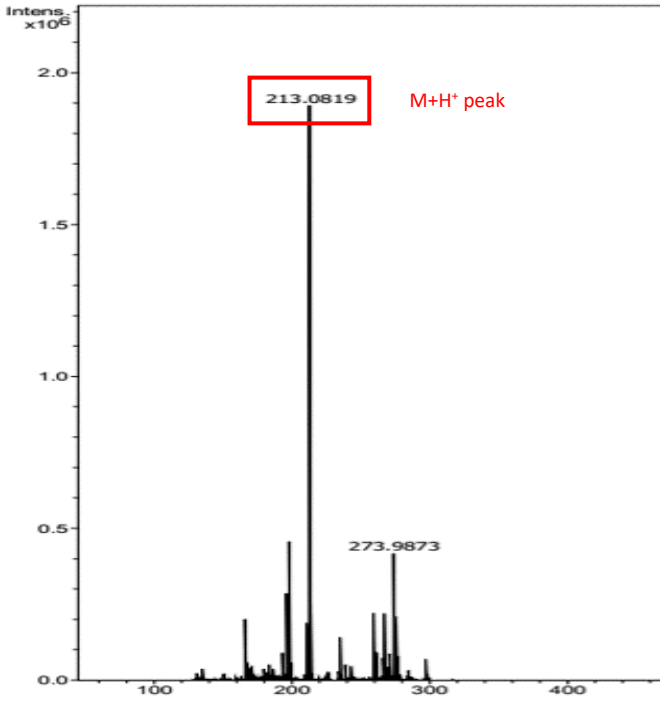


(d) Alsalampy^{+} (500 MHz, DMSO) : 6.5- 8.5 (16H, m, Ph), 4.96 (4H, s, methylene), 8.0 (2H, t, benzylidenimin)

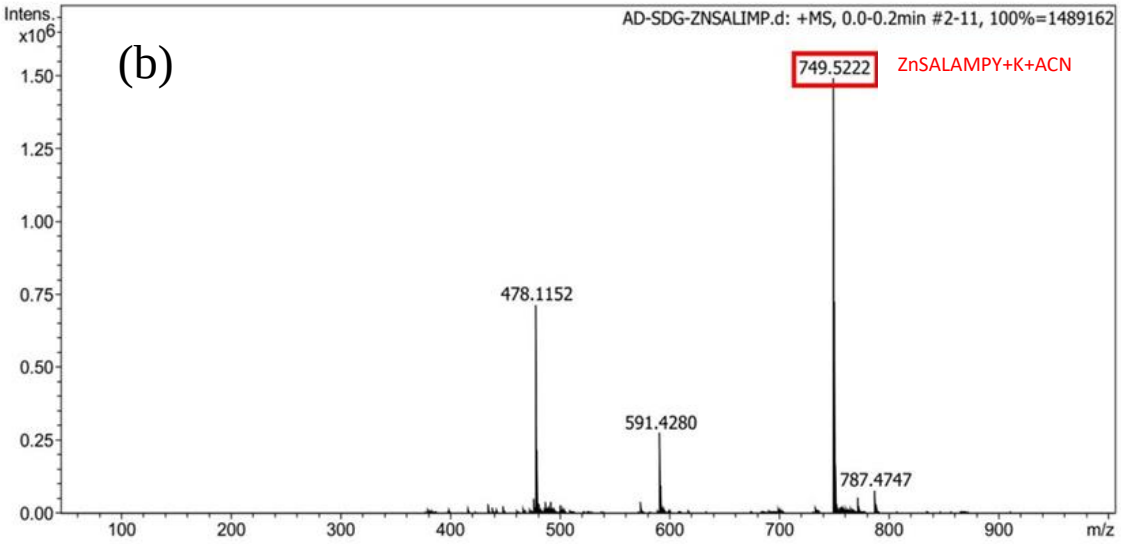
Figure S1. NMR spectra of (a) salampy (b) Znsalampy (bridged) (c) Znsalampy (unbridged) (d) Alsalampy^{+}

2. ESI-MS Spectra of the Compounds

(a)



(b)



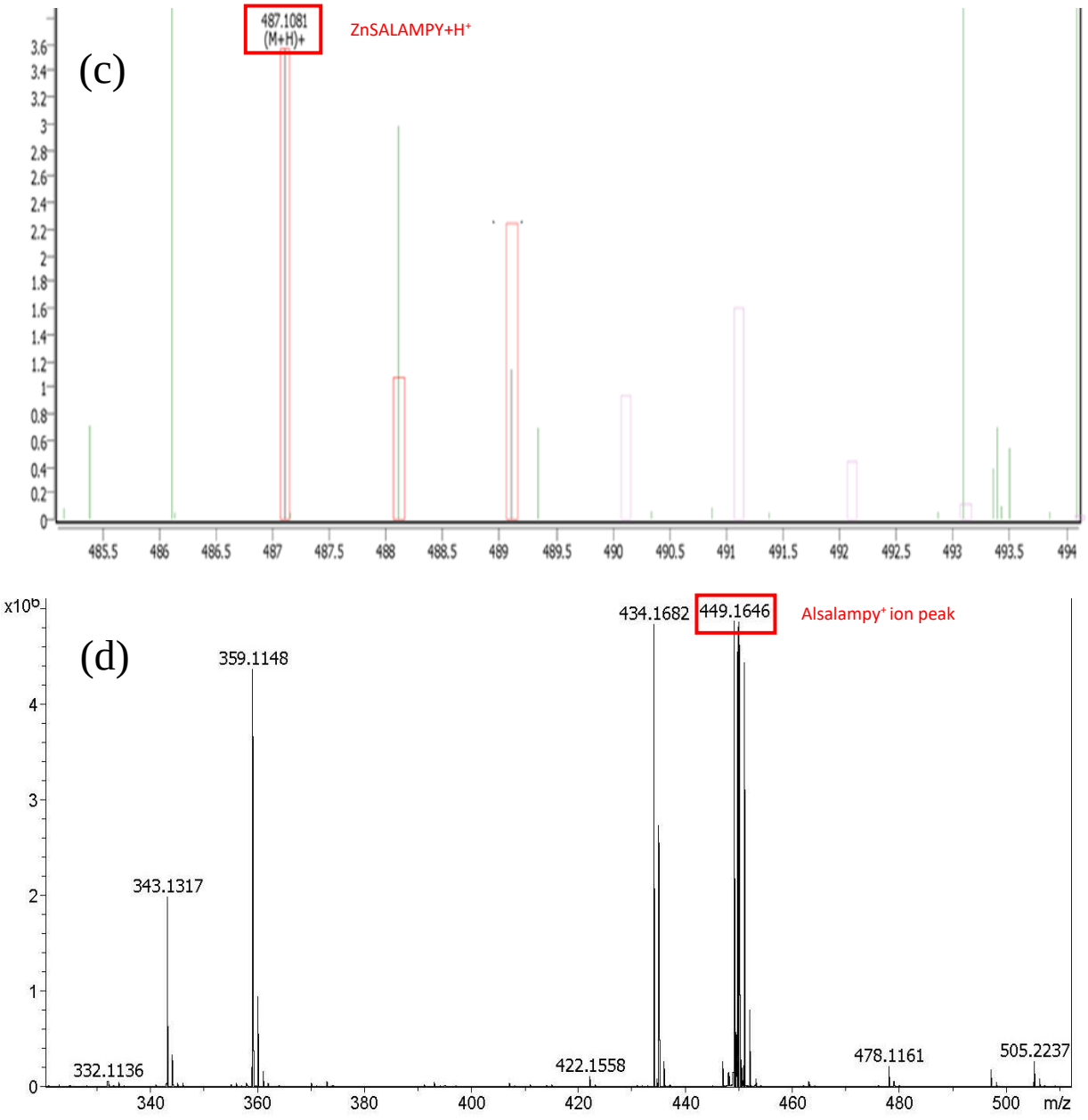


Figure. S2. ESI-MS spectra of (a) salampy (b) Znsalampy (bridged) (c) Znsalampy (unbridged) (d) Alsalampy^{+}

3. Supplementary Note 1: Fundamentals of FOG setup

For probing into the picosecond regime Femtosecond Optical Gating was used. A detailed discussion of the fundamental working principle is provided here.[2] All the compounds were excited using 400 nm light. Laser power and integration times were meticulously controlled so as to obtain the best quality data, without allowing the samples to undergo photodegradation.

A modelocked 100fs Ti: Sapphire (Tsunami, Spectra Physics, USA) having its fundamental at 800nm (1W, 80Mhz repetition rate) and its corresponding second harmonic at 400 nm is used as the source of excitation for all the samples. The sample was excited using only 25 mW of 400 nm light which is kept in a rotating cell. The excitation light is kept at magic angle polarization (using a combination of Glan polarization and Bereck's wave plate) with respect to the gate light in order to take care of rotational anisotropy. The emission signal was upconverted with 800nm gate light using a 0.5 mm thick β-BBO crystal. The upconverted signal is then allowed to pass through a UV bandpass filter to cut out excitation and gate light and finally through a double monochromator (DM2100, CDP, Russia) and directed into a photon counter acting on the principles of PMT (having dark noise < 5cps) was used for signal counting. The IRF recorded by measuring correlation between the gate light and Raman signal of ethanol (400 nm excitation) when fitted using a Gaussian function showed a FWHM of around 275 fs. The decay traces were fitted using a home built program in Igor Pro 6.3 software.

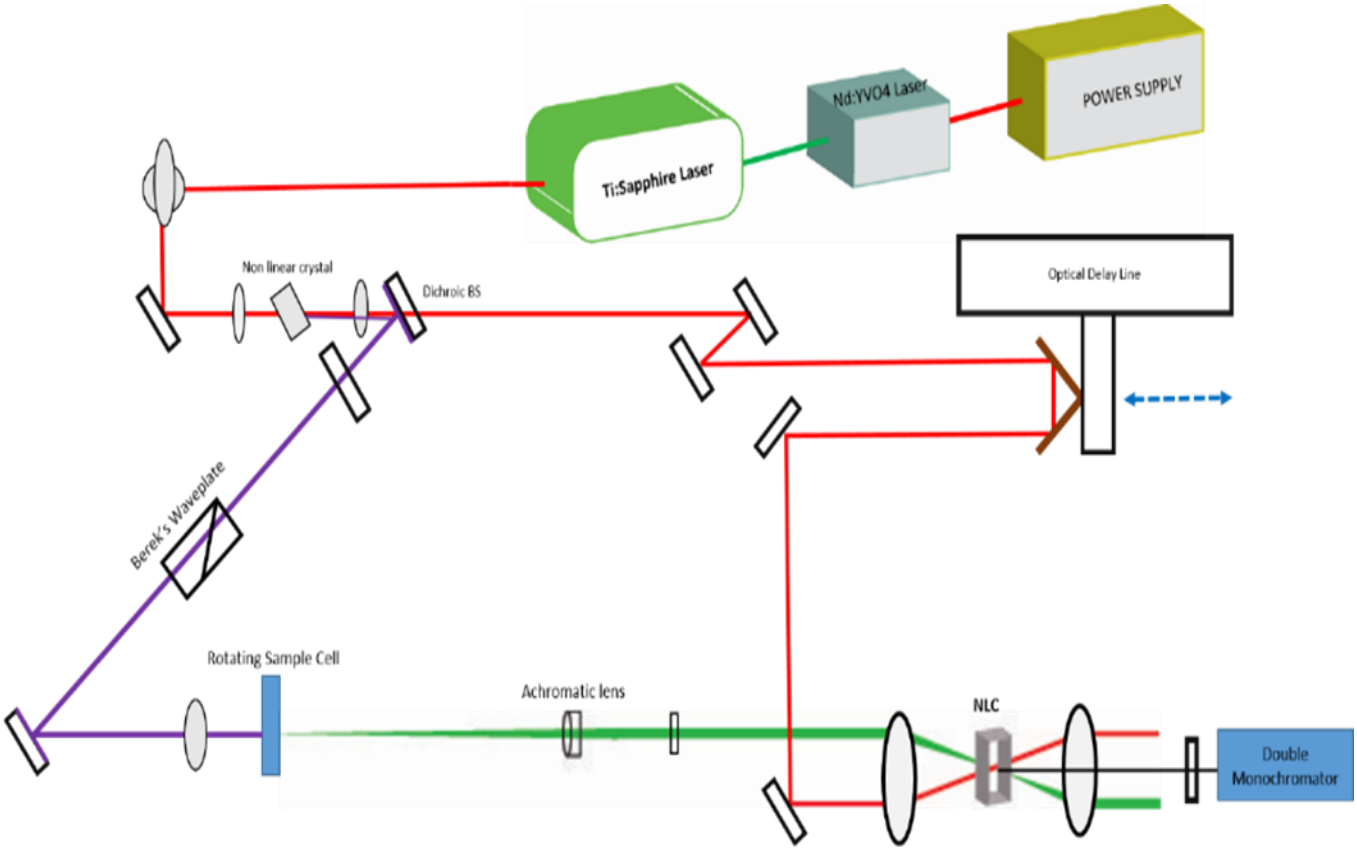


Figure S3. Schematics of FOG set up

4. Wavelength dependent decays of salampy recorded using FOG

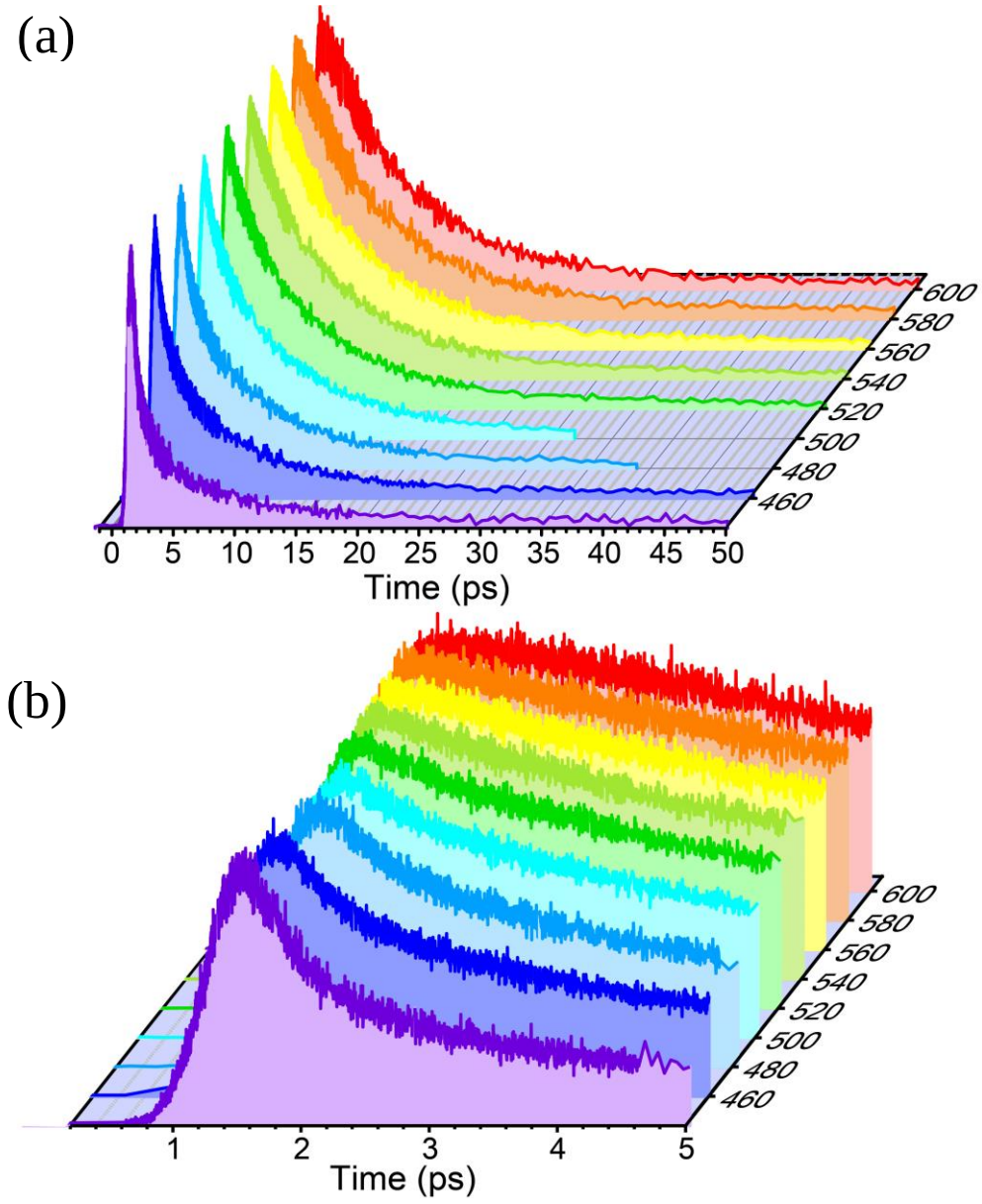


Figure S4. Wavelength dependent fluorescence transients of salampy in MeOH (λ_{ex} = 400 nm) showing the (a) complete decays and (b) decays at initial times, highlighting the ultrafast evolution of the cis keto form from the enol form.

5. Time Resolved Emission Spectra (TRES) of salampy

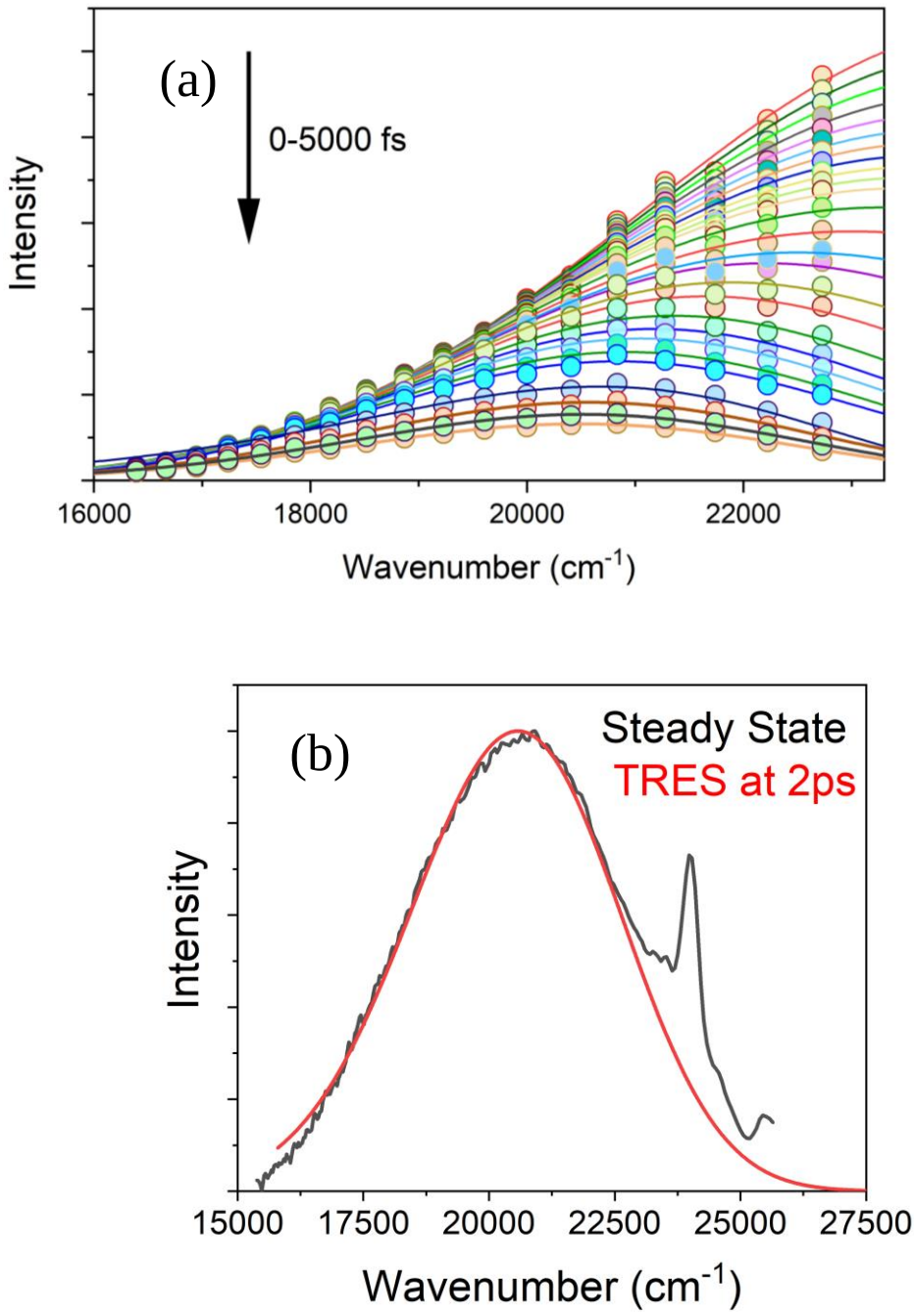


Figure S5. (a) TRES of salampy in MeOH upto 5 ps (b) overlaid steady state emission spectra and TRES at 2 ps of neutral salampy showing convergence

6. Time evolution of fluorescence of of salampy$^-$

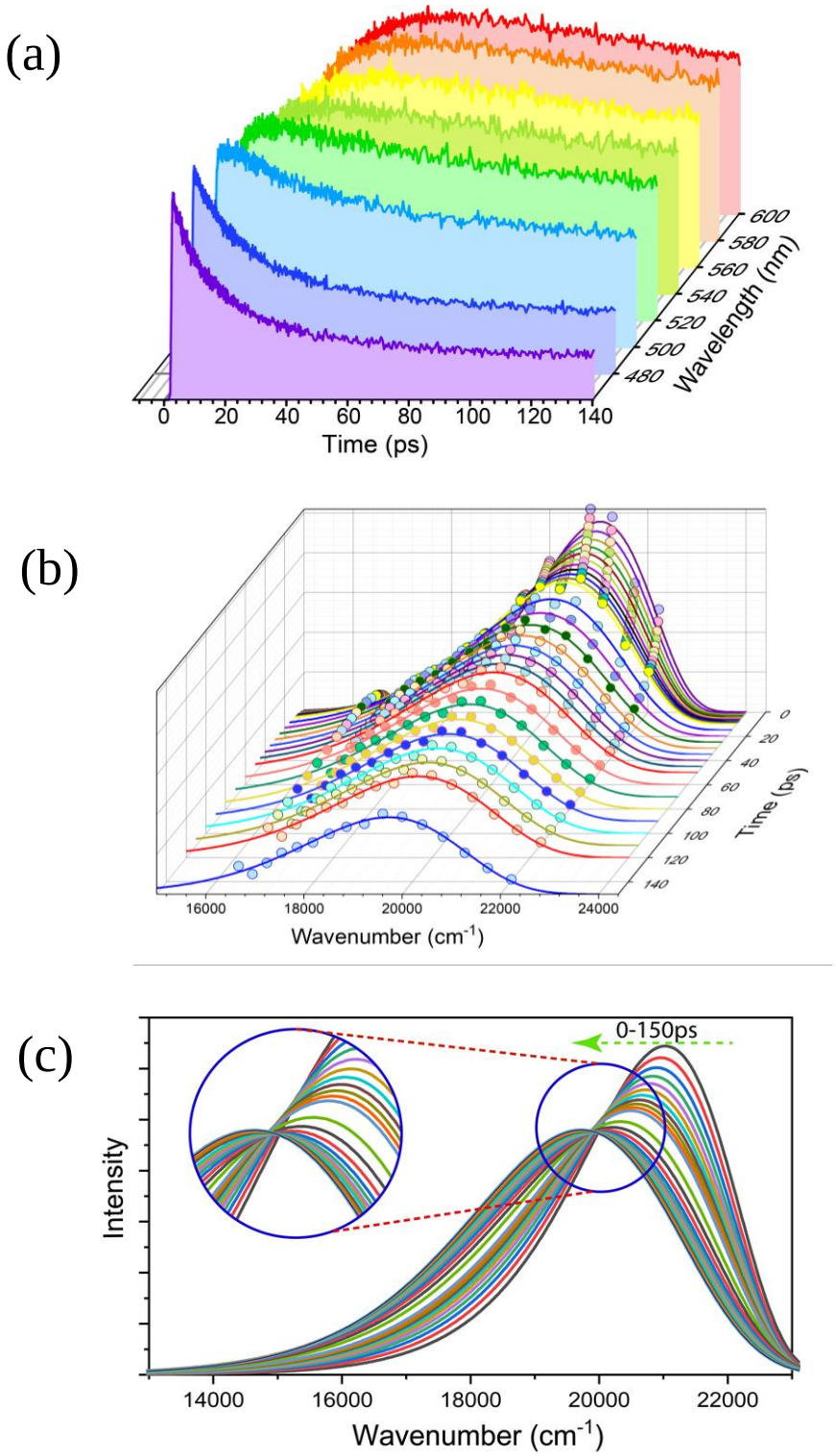


Figure S6. (a) Wavelength dependent fluorescence transients (λ_{ex} = 400 nm), (b) Time Resolved Emission Spectra (TRES) and (c) Time Resolved Area Normalized Emission Spectra (TRANES) of anionic salampy$^-$ in MeOH.