Supporting Information

Thermal-Induced Twisting and Photoinduced Planarization of Salicylideneaniline in Alcohols

*Karunakaran Ponnusamy, Kannan Ramamurthy, Chellappan Selvaraju**

National Centre for Ultrafast Processes, University of Madras, Chennai 600 113, Tamil Nadu, India.

*E-mail: selvaraj24@hotmail.com

Contents

Figure S9. The fluorescence spectra of SA in methanol and glycerol. (1) Freshly prepared SA in methanol, (2) Freshly prepared SA in glycerol, (3) aged solution of SA in methanol and (4) aged solution of SA in glycerol.

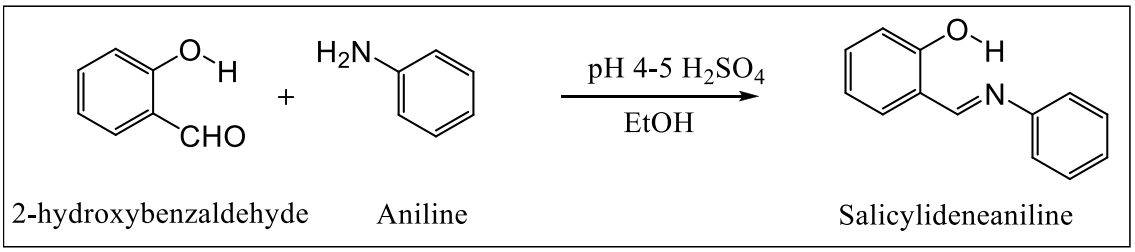
Figure S10. The fluorescence spectra of SA in methanol and glycerol on irradiation with 355 nm laser light. (1) Aged solution of SA in methanol, (2) after 6 min irradiation in methanol, (3) aged solution of SA in glycerol and (4) after 6 min irradiation SA in glycerol.

Table S1. The rate constant for the formation of twisted trans-enol form calculated at different temperatures.

1. Preparation and characterization of Salicylideneaniline (SA)

Aniline (0.91 g, 0.01mol) and 2-hydroxybenzaldehyde (1.27 ml, 0.01mol) were dissolved in 30 ml of dry ethanol, and then few drops of dilute sulfuric acid was added and the mixture was refluxed for 24 h. The solution was cooled to room temperature and poured into 100 ml of ice water. The product was obtained as pale yellow and collected by filtration. The product was washed with cold ethanol and then recrystallized from 85% ethanol-water mixture results in a pale yellow crystalline SA. Yield: 1.91 g, (97%). The **FT-IR** spectrum of SA was shown in **Figure SI-1.** A sharp peak appeared at 1617 cm^{-1} (C=N stretching) indicates the formation of C=N and absence of peak around 1700 cm^{-1} (C=O stretching) indicates the absence of aldehyde functionality. The O-H stretching band was observed at 3453 cm^{-1}. **^{1}H NMR** (400 MHz, DMSO-d_6, TMS) spectrum of SA was shown in **Figure SI-2,** aromatic proton peaks appeared in the range 6.97 (t, 1H), 7.02.–7.30 (m, 3H), 7.30–7.68 (m, 4H), 7.04 (d, 1H), H-C=N peak appeared at 8.96 (s, 1H), the O-H peak appeared at δ ppm 13.13 (br, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6 TMS) spectrum of SA was shown in **Figure SI-3**. δ ppm 114.3, 117.0, 119.6, 119.7,

121.8, 127.4, 129.2, 129.9, 133.0, 133.7, 148.5, the (N=C-H) peak appeared at 160.7, O-H attached carbon peak appeared at δ 164.0. The **ESI mass** spectrum of SA was shown in **Figure SI-4**. MS (ESI): m/z = 198.09 $[M + H]^+$.



Scheme SI-1. Preparation of SA.

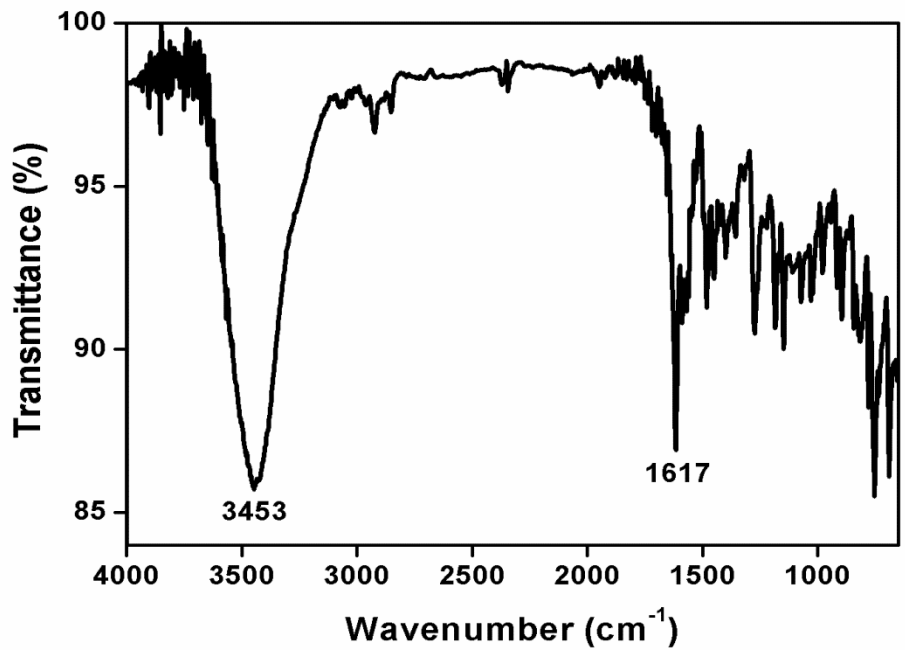


Figure SI-1. FT-IR spectrum of SA.

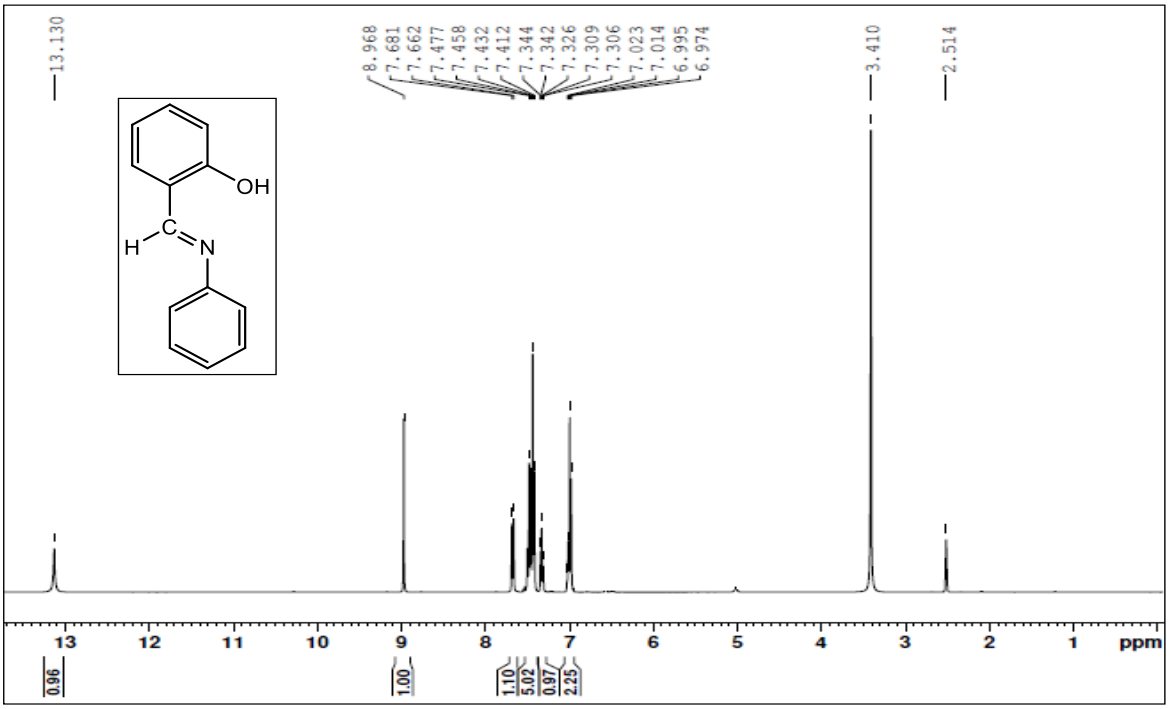


Figure SI-2. ^{1}H NMR spectrum of SA.

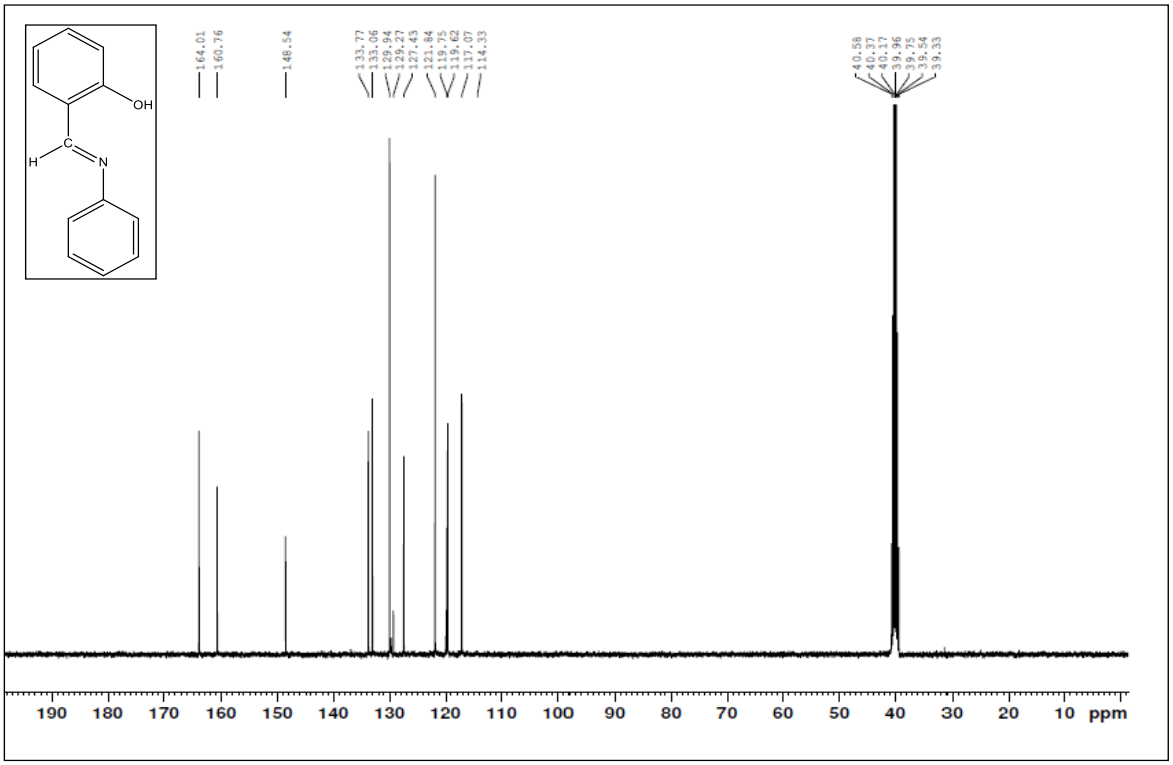


Figure SI-3. ^{13}C NMR spectrum of SA.

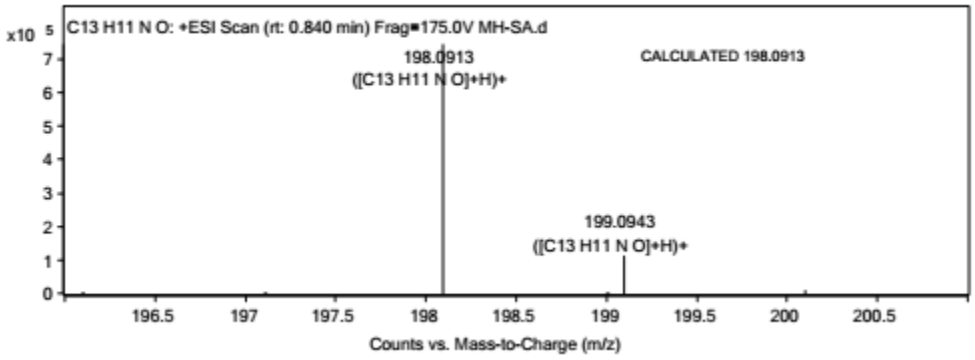


Figure SI-4. ESI mass spectrum of SA.

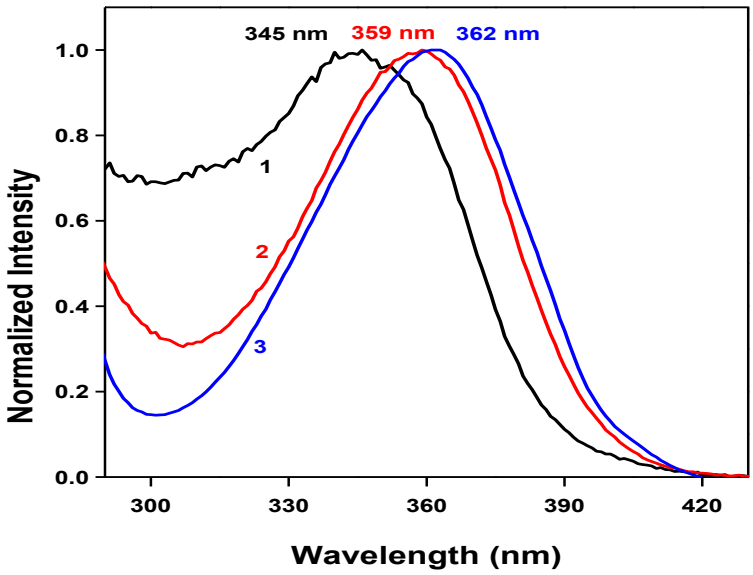


Figure S1. Excitation spectra of freshly prepared solution of SA in methanol monitored at 530 nm (1) and aged solution of SA monitored at 530 nm (2) and 444 nm (3).

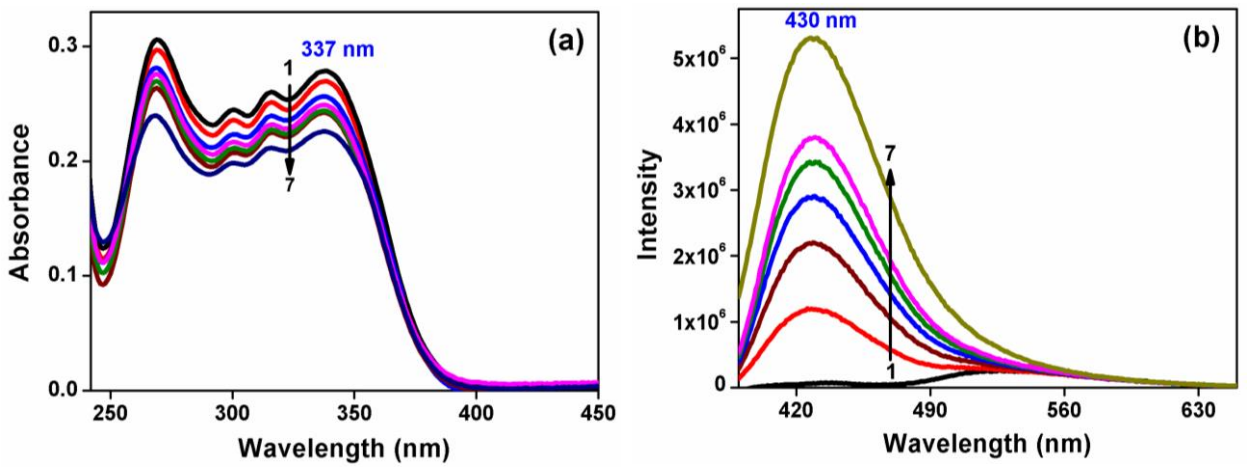


Figure S2. Absorption (a) and Fluorescence spectra (b) of SA in ethanol kept at 323 K for 1) 0 min, 2) 30 min, 3) 60 min, 4) 90 min, 5) 120 min, 6) 150 min and 7) after keeping the solution at room temperature for 24 h.

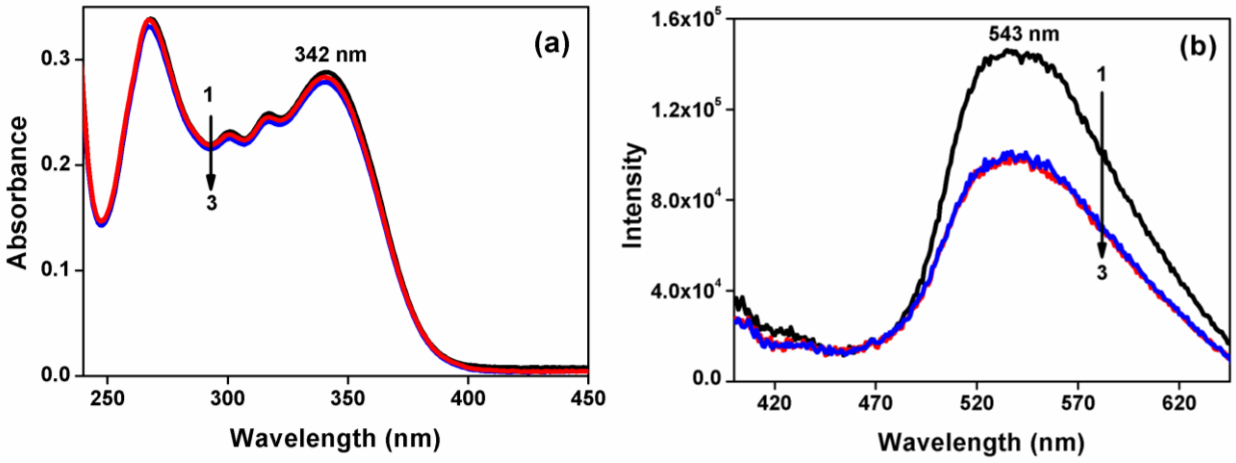


Figure S3. Absorption (a) and Fluorescence (b) spectra of SA in hexane kept at 323 K for 1) 0 min, (2) 60 min and (3) 120 min.

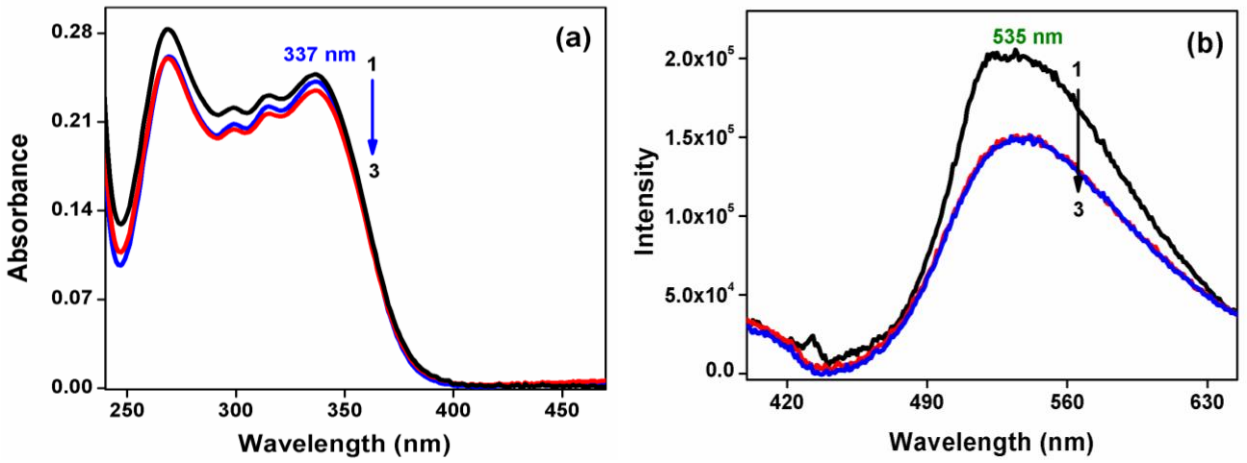


Figure S4. Absorption (a) and Fluorescence (b) spectra of SA in acetonitrile kept at 323 K for (1) 0 min, (2) 60 min and (3) 120 min.

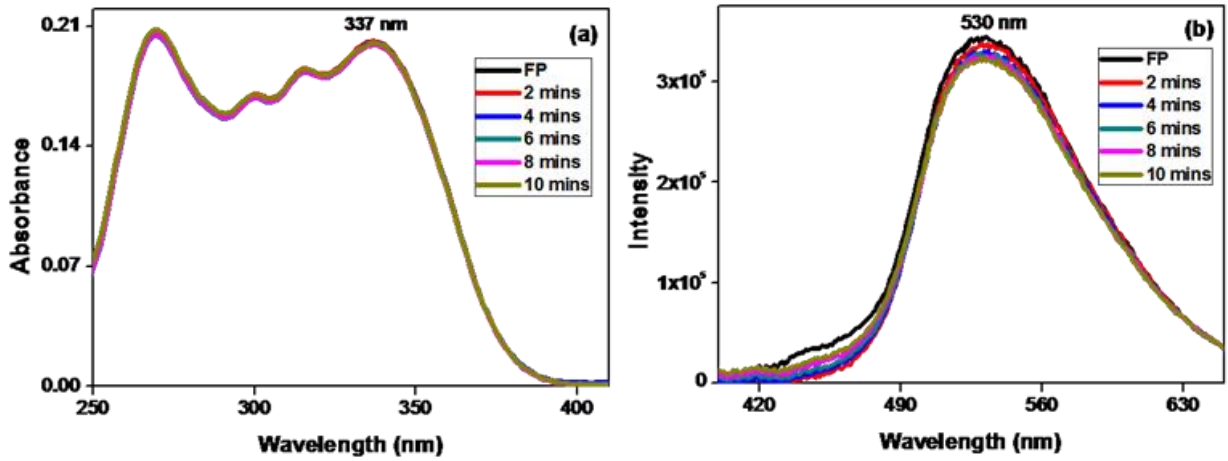


Figure S5. Absorption (a) and fluorescence (b) spectrum of freshly prepared solution SA in methanol at different laser irradiation (λ = 355 nm) time.

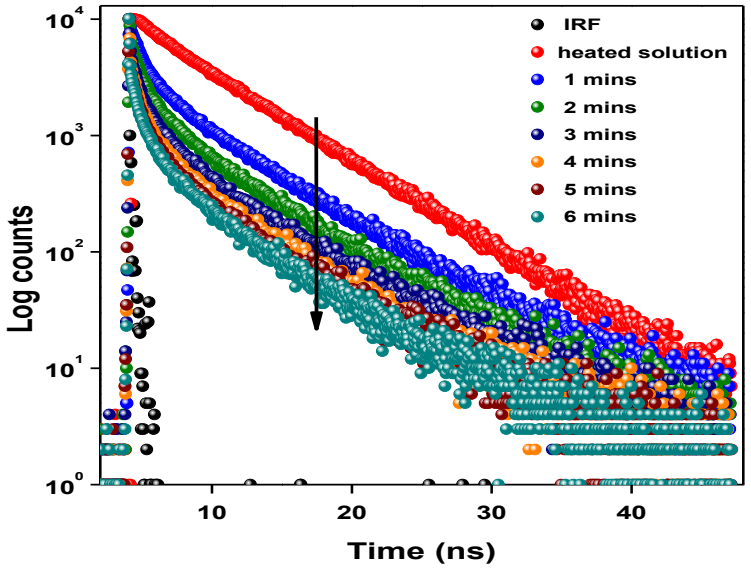


Figure S6. The fluorescence decay of SA in methanol monitored at 440 nm (λ_{exc} = 375 nm) at different laser irradiation (λ = 355 nm) time.

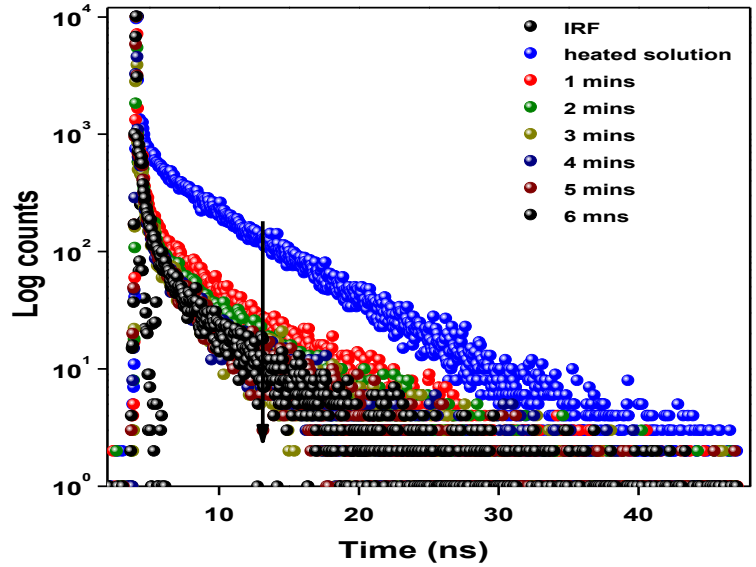


Figure S7. The fluorescence decay of SA in methanol monitored at 530 nm (λ_{exc} = 375 nm) at different laser irradiation (λ = 355 nm) time.

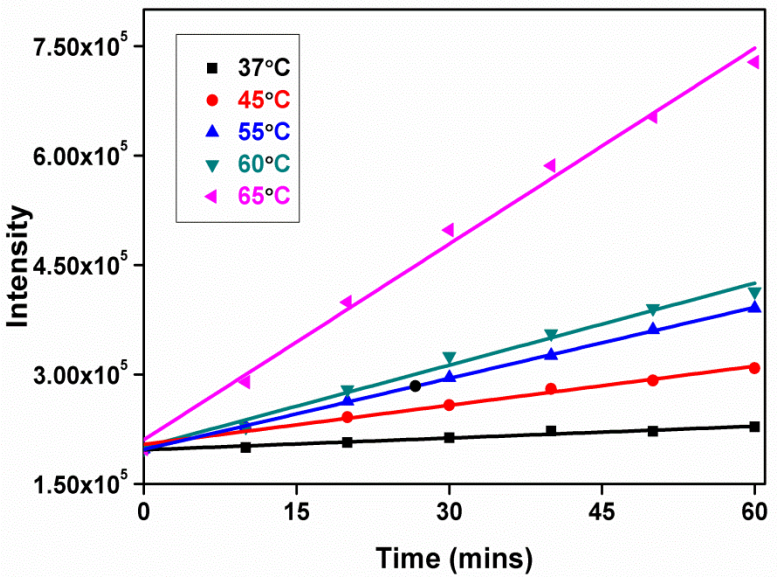


Figure S8: Plot of fluorescence intensity of twisted trans-enol form with time at different temperatures.

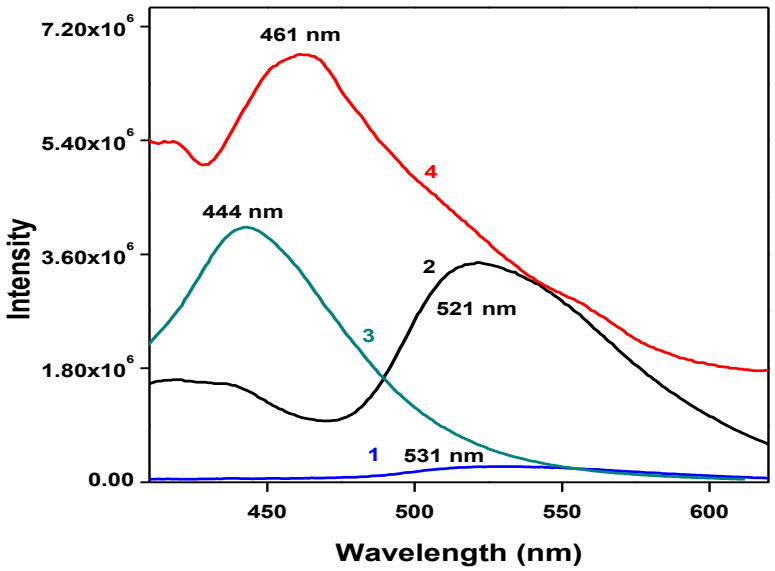


Figure S9. The fluorescence spectra of SA in methanol and glycerol. (1) Freshly prepared SA in methanol, (2) Freshly prepared SA in glycerol, (3) aged solution of SA in methanol and (4) aged solution of SA in glycerol.

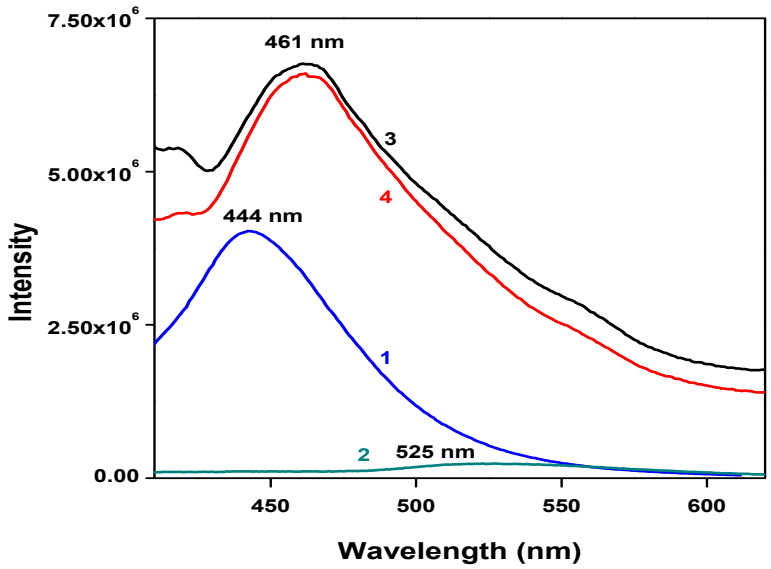


Figure S10. The fluorescence spectra of SA in methanol and glycerol on irradiation with 355 nm laser light. (1) Aged solution of SA in methanol, (2) after 6 min irradiation in methanol, (3) aged solution of SA in glycerol and (4) after 6 min irradiation SA in glycerol.

Table S1. The rate constant for the formation of twisted trans-enol form calculated at different temperatures.

S. No.	Temperature (K)	Rate constant (s^{-1})
1	310	466
2	318	1425
3	328	3166
4	333	3964
5	338	8969