Supporting Information

An inquisitive fluorescence method for the real-time detection of trace moisture in polar aprotic solvents with the application of water rancidity in foodstuffs

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Table S1. Estimated water amount incorporated in various aprotic solvents for open atmosphere exposure in the absence (A_0) and presence (A_T) of 1% water-spike

Solvent	Exposure time (min)[a]	A_0 (*v*/*v* %)	A_T (*v*/*v* %)	A_T – 1.0 (*v*/*v* %)
Acetone	24	0.11	1.10	0.10
	48	0.28	1.23	0.23
	72	0.43	1.40	0.40
MeCN	24	0.13	1.13	0.13
	48	0.27	1.28	0.28
	72	0.46	1.46	0.46
DMF	24	0.20	1.22	0.22
	48	0.35	1.38	0.38
	72	0.58	1.60	0.60
DMSO	24	0.23	1.22	0.22
	48	0.44	1.41	0.41
	72	0.68	1.66	0.66

[a]Exposure under relative humidity ~75%, temperature ~ 25°C

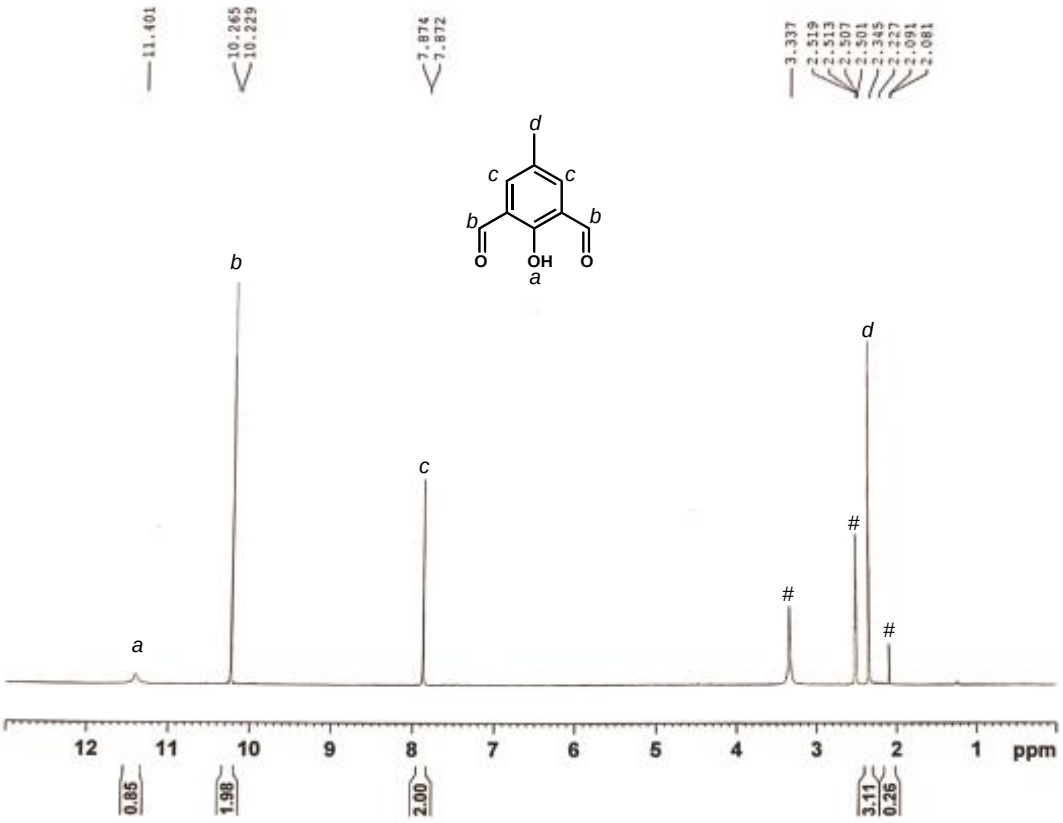

Fig. S1. ^{1}H-NMR spectrum of AH in DMSO-d_6. (Note: # represents the solvent peaks)

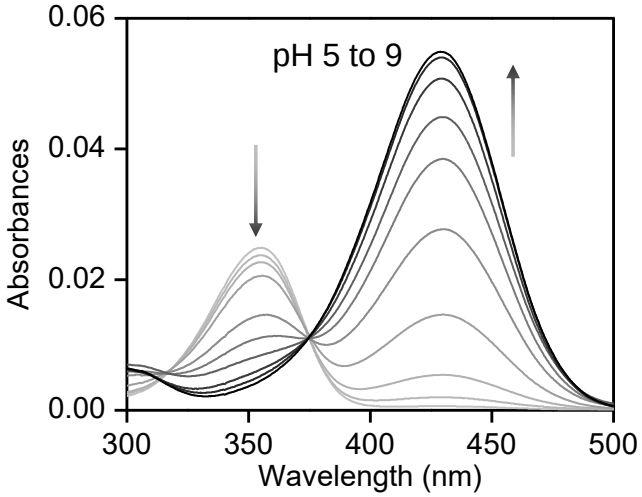

Fig. S2. pH dependent UV-vis absorption spectra of AH (6 μM) in 20 mM HEPES buffer, at 25°C. The pH of buffer solution was adjusted by an addition of NaOH. The increase or decrease of absorbance with increasing pH is depicted by arrows.

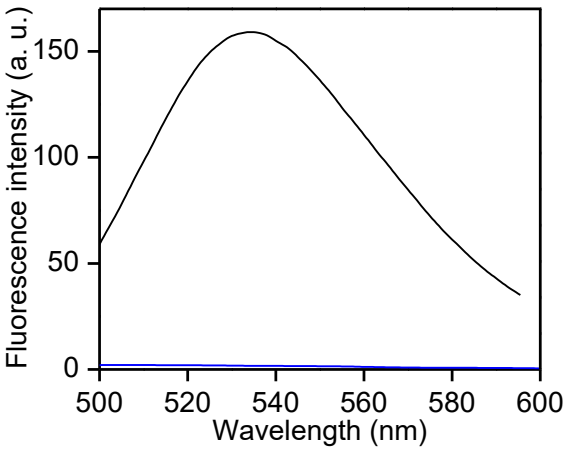

Fig. S3. Fluorescence emission spectra of AH (0.5 μM) in the absence (blue) and presence (black) of KOH (10 μM) in water. Excitation wavelengths: 350 nm (blue) and 440 nm (black).

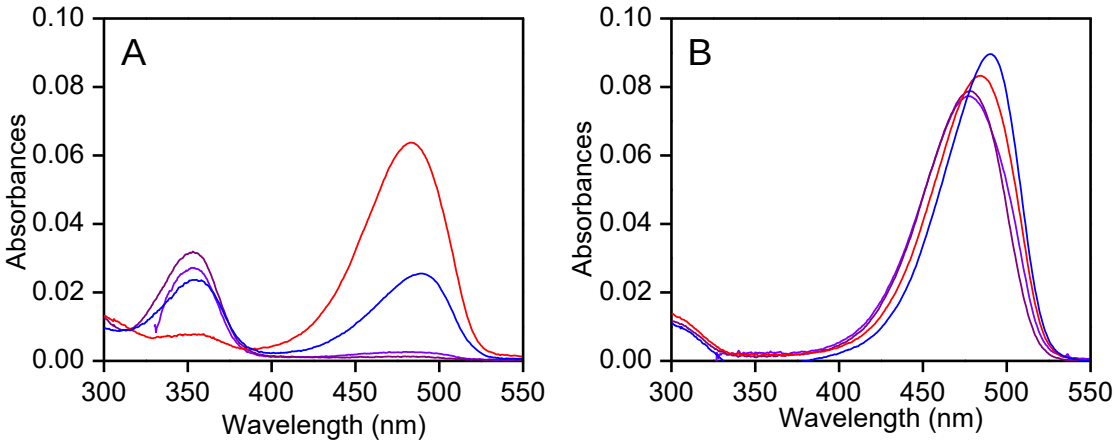

Fig. S4. Different aprotic solvent dependent UV-vis absorption spectra of AH (6 μM) in (A) the absence and (B) presence of KOH (15 μM) at 25°C: violet, acetone; purple, MeCN; red, DMF and blue, DMSO.

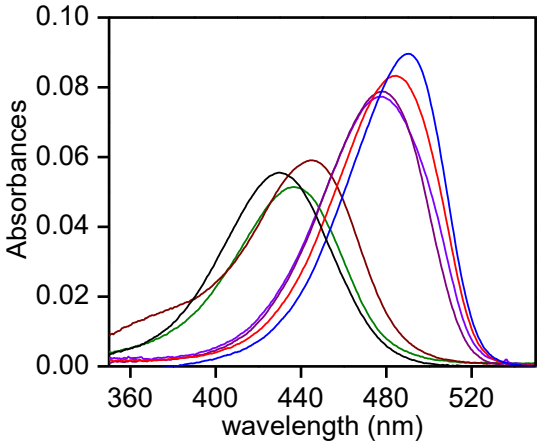

Fig. S5. Different protic solvent dependent UV-vis absorption spectra of AH (6 μM) in presence of KOH (15 μM) at 25°C: black, water; green, methanol; brown, ethanol. The spectra for aprotic solvents are shown for comparison (violet, acetone; purple, MeCN; red, DMF; blue, DMSO).

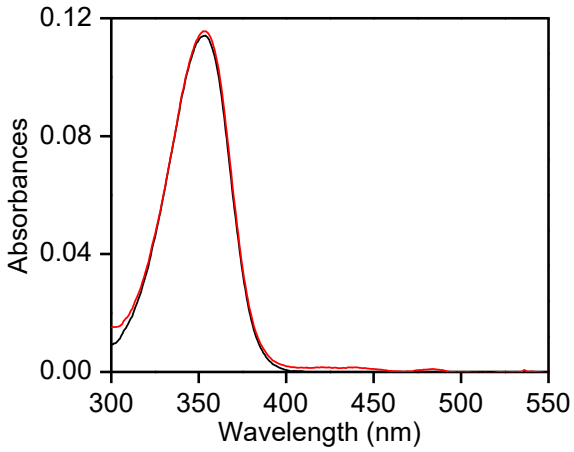

Fig. S6. UV-vis absorption spectra of AH (10 μM) in the absence (black) and presence of TEA (1 mM) (red) in THF medium at 25°C.

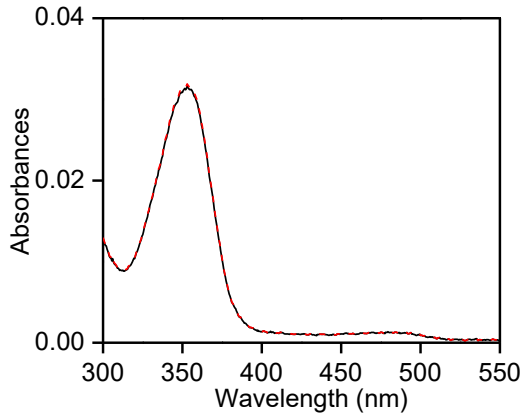

Fig. S7. UV-vis absorption spectra of AH (6 µM) in the absence (black) and presence of 1% (*v*/*v*) water (red, broken line) in MeCN medium at 25°C.

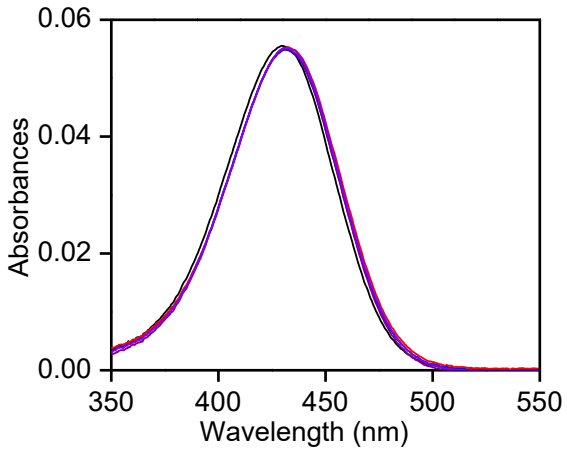

Fig. S8. UV-vis absorption of AH (6 μM) in the presence of KOH (15 μM) and 10% (*v*/*v*) different aprotic solvents in water at 25°C: violet, acetone; purple, MeCN; red, DMF; blue, DMSO. The spectrum in the absence of aprotic solvent is depicted in black.

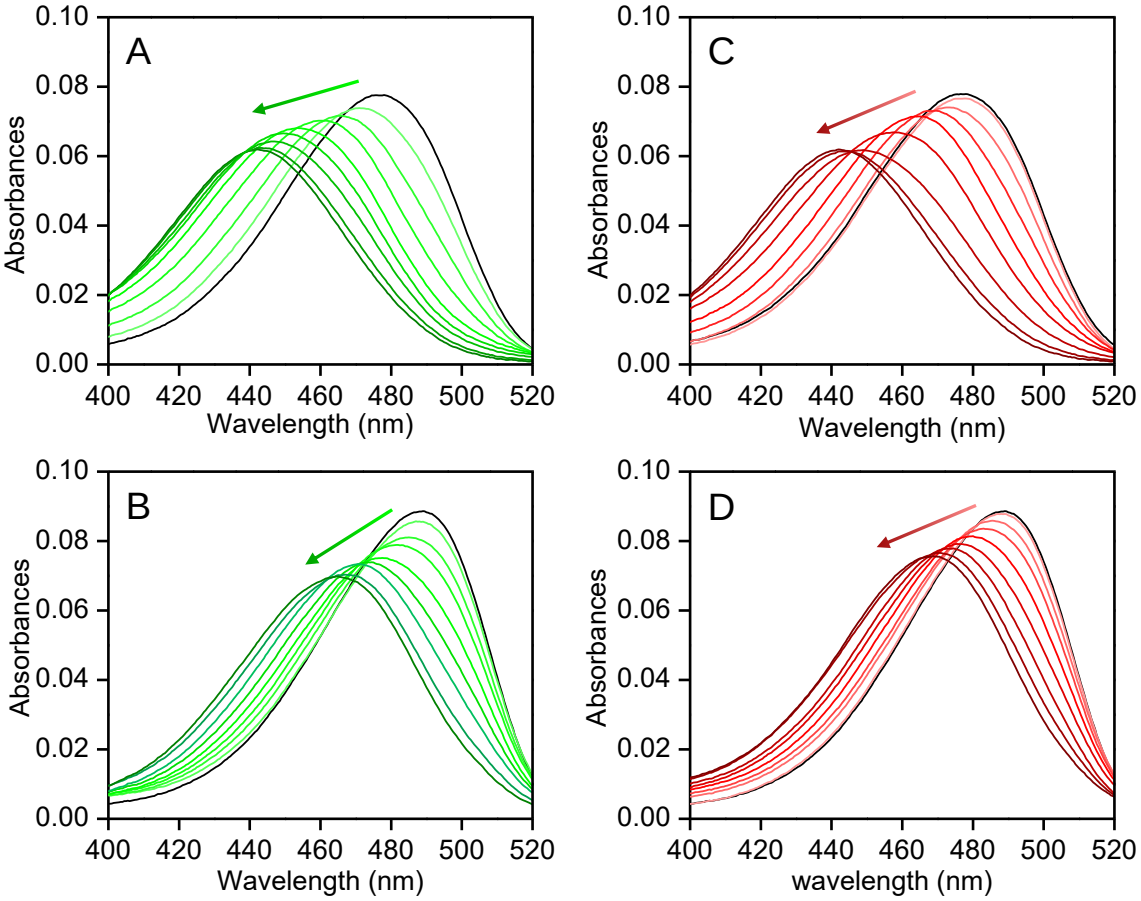

Fig. S9. UV-vis absorption spectra of AH (6 μM) in the presence of KOH (15 μM) under various amount of (A,B) methanol% or (C,D) ethanol% (*v*/*v*) in (A,C) MeCN or (B,D) DMSO medium (methanol% at 25°C: 1.0, 3.0, 6.0, 9.0, 12.0, 15.0, 18.0, 23.0; ethanol%: 1.0, 2.0, 5.0, 8.0, 12.0, 16.0, 20.0, 25.0). (A–D) The gradual spectral blue shift with increasing alcohol% is depicted by arrow. The spectra in the absence of alcohol are shown in black.

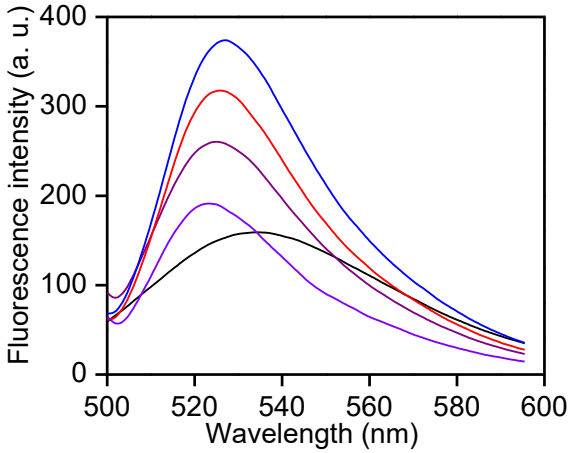

Fig. S10. Fluorescence emission spectra of AH (0.5 μM) in the presence of KOH (10 μM) in various aprotic solvents at 25°C: black, water; violet, acetone; purple, MeCN; red, DMF; blue, DMSO. Excitation wavelengths: 440 nm for water and 485 nm for aprotic solvents.

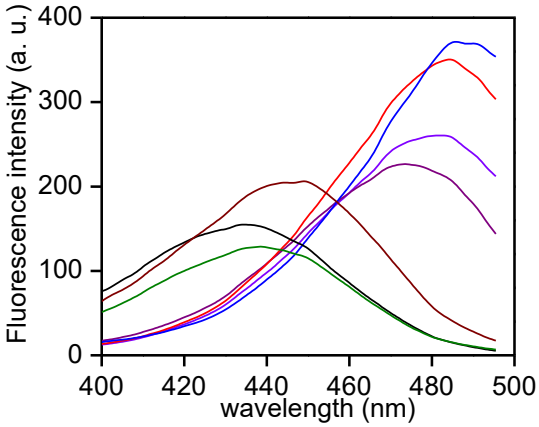

Fig. S11. Fluorescence excitation spectra of AH (0.5 μM) in the presence of KOH (10 μM) in various solvents at 25°C: black, water; green, methanol; brown, ethanol; violet, acetone; purple, MeCN; red, DMF; blue, DMSO. Emission wavelength was 525 nm.

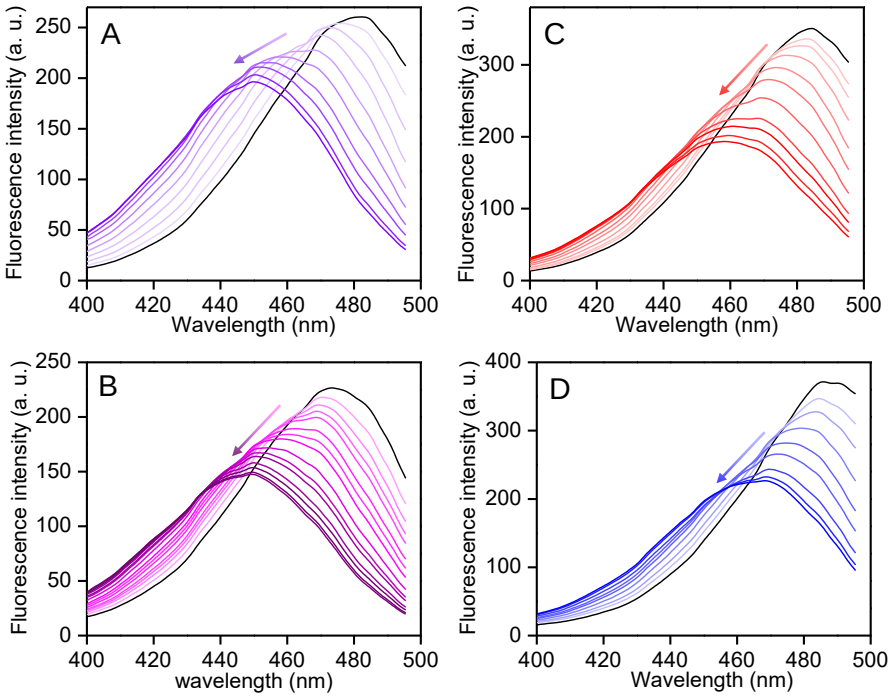

Fig. S12. Fluorescence excitation spectra of AH (0.5 μM) in the presence of KOH (10 μM) under various water% (*v*/*v*) in different solvent system: (A) acetone (water%: 0.1, 0.3, 0.6, 1.1, 1.8, 3.0, 4.5, 8.0 and 11.5); (B) MeCN (water%: 0.1, 0.2, 0.3, 0.4, 0.6 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 4.7 and 5.5); (C) DMF (water%: 0.2, 0.4, 0.8, 1.5, 2.5, 4.0, 6.5, 8.0, 10.0 and 12.0) and (D) DMSO (water%: 0.5, 1.0, 2.0, 3.5, 5.0, 7.5, 10.0 and 11.4). (A–D) The spectra in the absence of water are shown in black. The gradual blue shift for the excitation intensity with increasing water% are depicted by arrows. Emission wavelength was 525 nm.

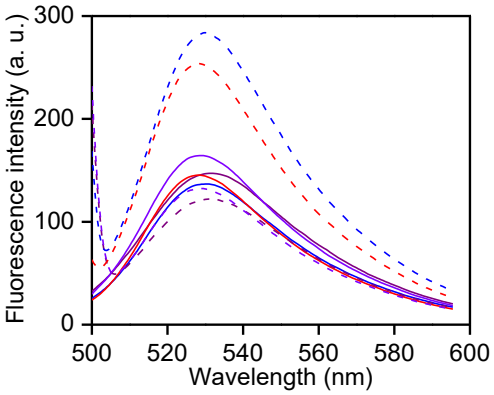

Fig. S13. Excitation wavelength dependent fluorescence emission spectra of AH (0.5 μM) in the presence of KOH (10 μM) and various water% (*v*/*v*) in different aprotic solvents at 25°C: (violet) 1.1% water in acetone; (purple) 1.0% water in MeCN; (red) 1.5% water in DMF and (blue) 3.5% water in DMSO. Excitation wavelengths were 440 nm (solid lines) and 485 nm (broken lines).

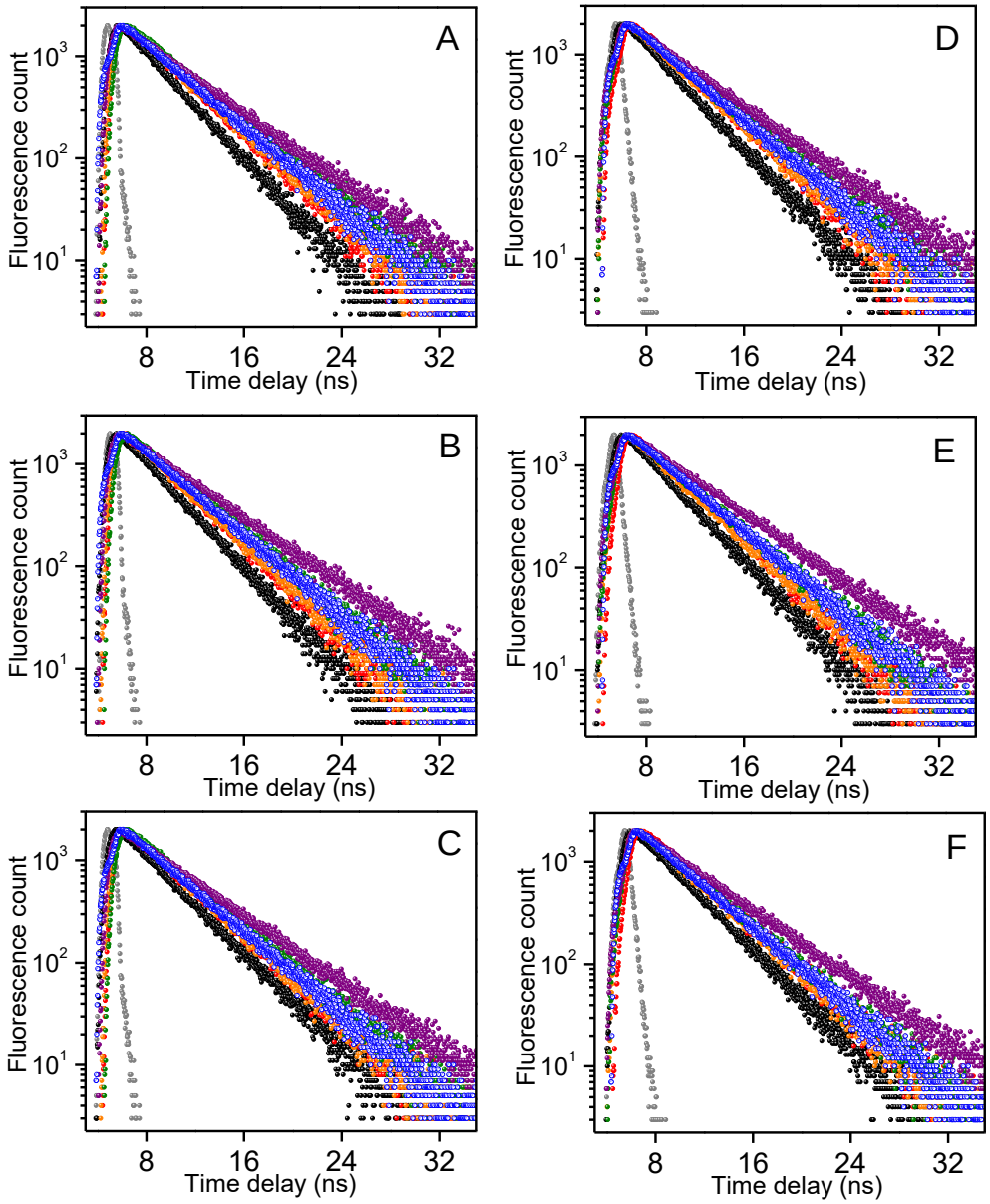

Fig. S14. Excitation wavelength dependent fluorescence transients of AH (6 μM) in the presence of KOH (15 μM) in different solvents under various water% (*v*/*v*): (A,D) MeCN (red, 1.0; orange, 2.0; green, 4.0; purple, 8.0), (B,E) DMF (red, 1.5%; orange, 3.0%; green, 7.0%; purple, 13%), (C,F) DMSO (red, 1.5%; orange, 3.0%; green, 7.0%; purple, 13%). Excitation wavelengths were (A–C) 450 nm and (D–F) 490 nm. The fluorescence transient in the absence of water and pure water medium are depicted in black and blue, respectively, for comparison. The fluorescence collected at 525 nm. The scattering profile is shown in grey.

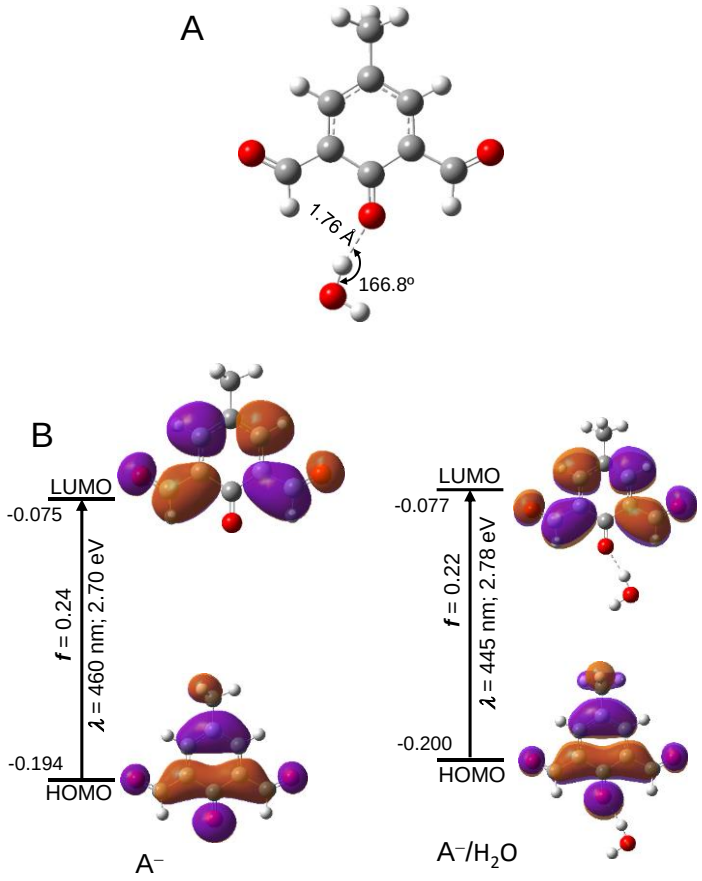

Fig. S15. (A) DFT-optimized structure of A^{-}/H_2O H-bonded complex. The H-bond and its related angle are shown in single broken line and curved lines, respectively; color index: C, gray; O, red and H, white. (B) Frontier molecular orbital profiles (HOMO/LUMO) including various UV-vis absorption parameters of A^{-} (left panel) and A^{-}/H_2O complex (right panel) based on TD-DFT (B3LYP/6-31G++ (3d,3p)) calculations.

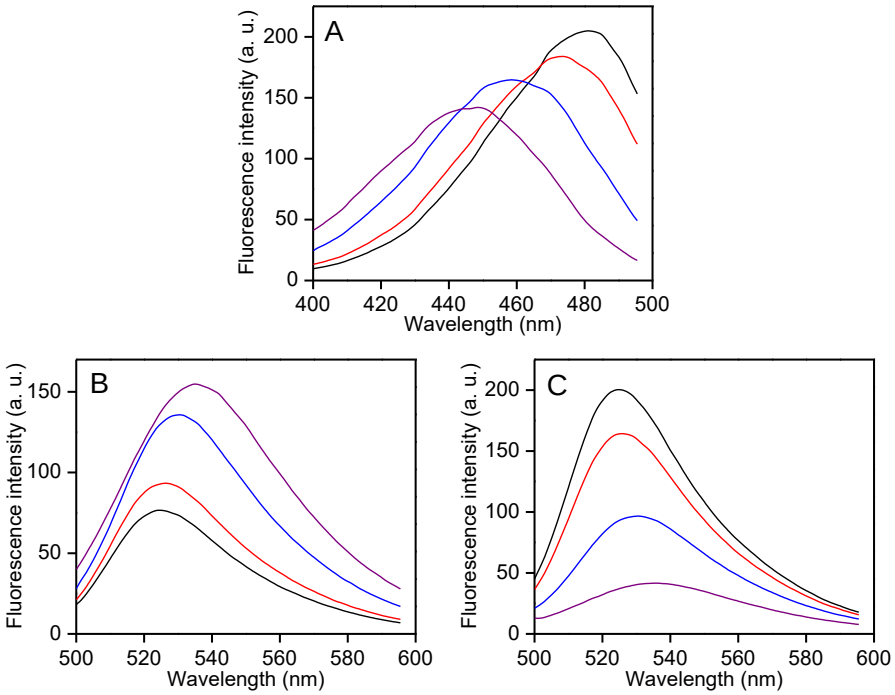

Fig. S16. Fluorescence (A) excitation spectra and (B,C) excitation wavelength dependent (B: 440 nm and C: 485 nm) emission spectra of AH (0.5 μM) in the presence of TEA (1 mM) under various water% (*v*/*v*) in MeCN solvent: water%: red, 0.3; blue, 1.0 and purple, 6.0. The spectra in the absence of water are shown in black. (A) Emission wavelength was 525 nm.

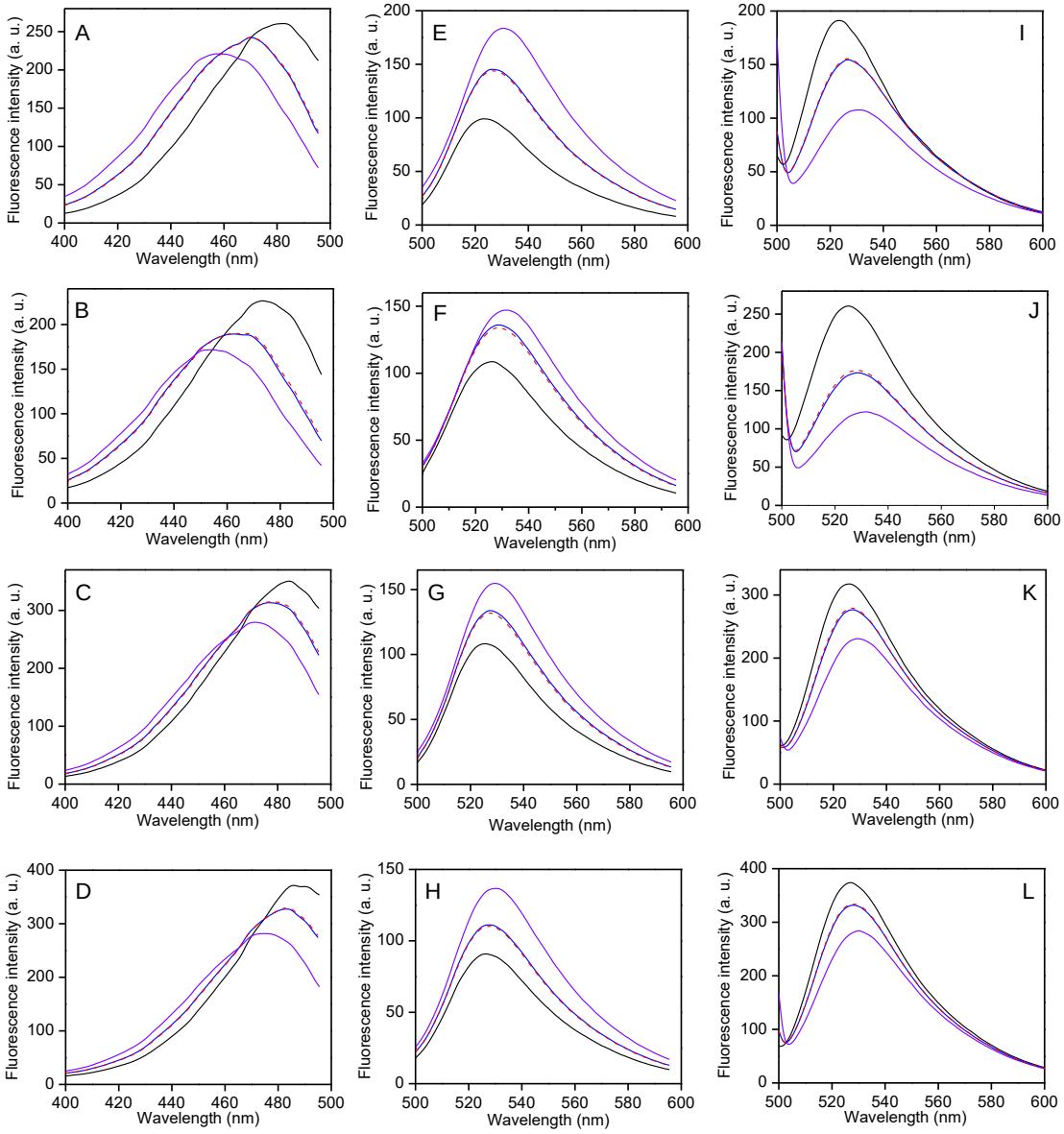

Fig. S17. Fluorescence (A–D) excitation and (E–L) excitation wavelength dependent emission spectra (E–H: 440 nm; I–L: 485 nm) of AH (0.5 μM) in the presence of KOH (10 μM) and different water% (*v*/*v*) in various solvent mediums: (A,E,I) acetone; (B,F,J) MeCN; (C,G,K) DMF; (D,H,L) DMSO. The spectra in the presence of 1.8%, 1.5%, 2.5% and 3.5% water for acetone, MeCN, DMF and DMSO, respectively, (violet), followed by addition of respective same solvents containing identical probe concentration to adjust the water concentrations 0.6%, 0.6%, 0.8% and 1.0% respectively (broken red) are depicted. The spectra in presence of 0.6%, 0.6%, 0.8% and 1.0% for acetone, MeCN, DMF and DMSO, respectively, are shown in blue. The spectra in the absence of water are shown in black for comparison.

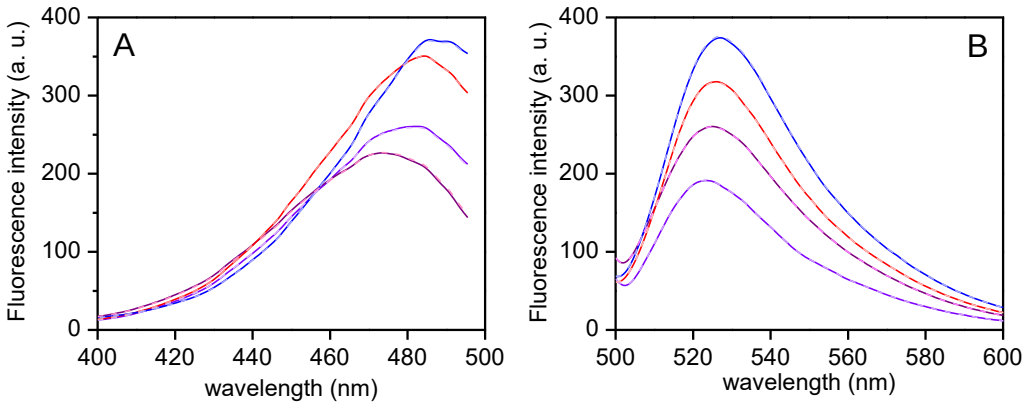

Fig. S18. Fluorescence (A) excitation and (B) emission spectra of AH (0.5 μM) in the presence of KOH (10 μM) in different solvents before (solid lines) and after (broken and corresponding light colour lines) incubation under dry nitrogen in the presence of the 3Å molecular sieves for 12 hr: violet, acetone; purple, MeCN; red, DMF; blue, DMSO. Excitation and emission spectra were recorded for the fixed emission wavelength at 525 nm (A) and excitation wavelength at 485 nm (B), respectively.

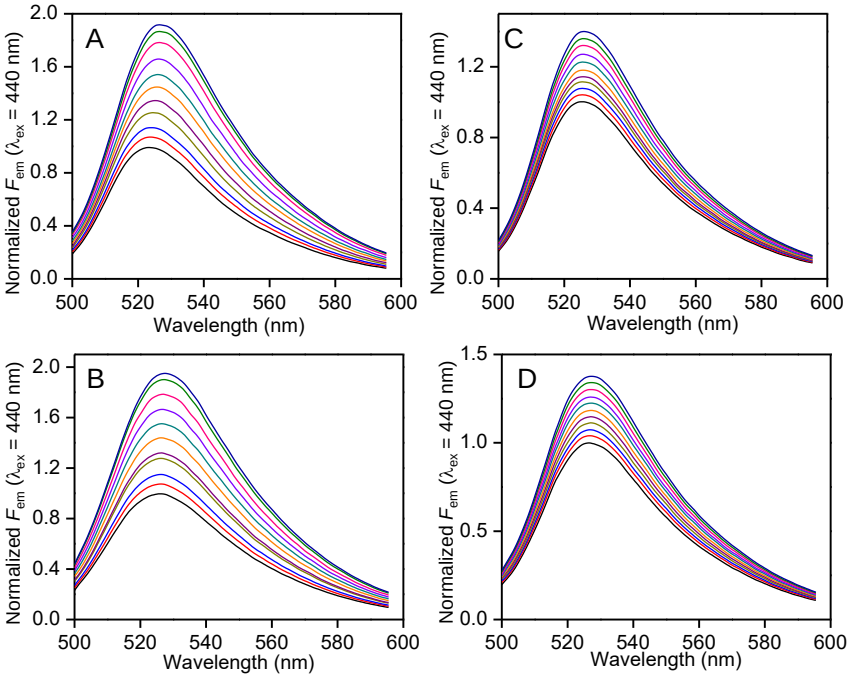

Fig. S19. Normalized fluorescence emission spectra of AH (0.5 μM) in the presence of KOH (10 μM) in different aprotic solvents after open atmosphere exposure under 75% (±5%) relative humidity at 25°C (±1°C): (A) acetone; (B) MeCN; (C) DMF and (D) DMSO. (A–D) The solvent was exposed for different time intervals (in min): (red) 12; (blue) 24; (dark yellow) 36; (purple) 48; (orange) 60; (dark cyan) 72; (violet) 84; (pink) 96; (green) 108 and (dark blue) 120. The spectra without the exposure are depicted in black. For the normalization of emission spectra, each emission spectrum for the excitation at 440 nm was divided by the maximum intensity value in the absence of water, the resultant spectrum was further divided by the extent of emission intensity decrease factor with respect to zero water condition for the excitation at 485 nm.

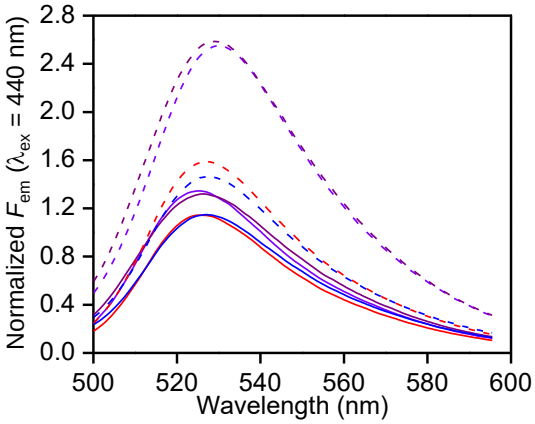

Fig. S20. Normalized fluorescence emission spectra of AH (0.5 μM) in the presence of KOH (10 μM) in different aprotic solvents (violet, acetone; purple, MeCN; red, DMF; blue, DMSO) after the open atmosphere exposure for 48 min (relative humidity 75% (±5%)) at 25°C (±1°C) (solid lines) without and (broken lines) with 1% (*v*/*v*) water-spikes. For the normalization of emission spectra, each emission spectrum for the excitation at 440 nm was divided by the maximum intensity value in the absence of water, the resultant spectrum was further divided by the extent of emission intensity decrease factor with respect to zero water condition for the excitation at 485 nm.

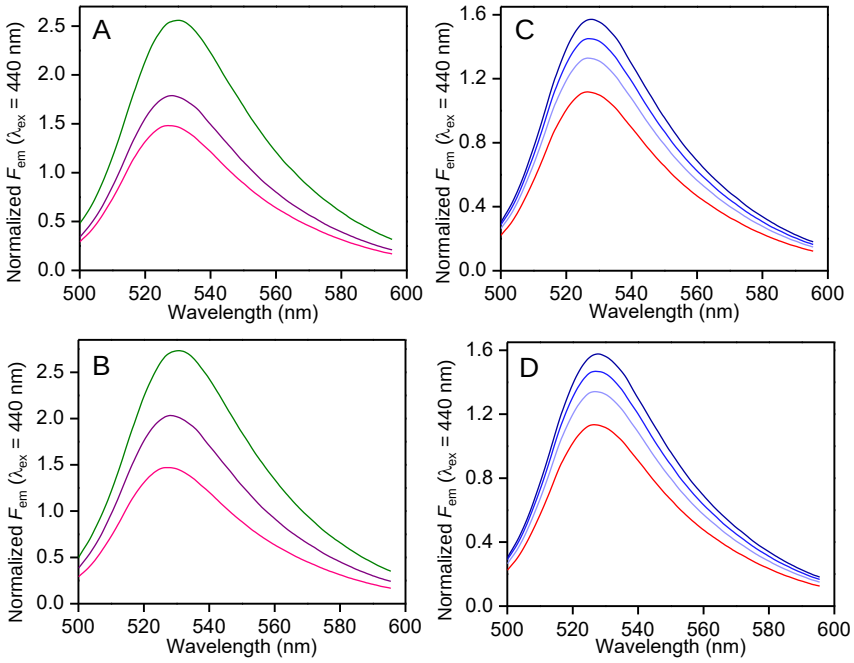

Fig. S21. Normalized fluorescence emission spectra of AH (0.5 μM) in the presence of KOH (10 μM) in 100 mL DMSO containing various amount of different food samples: (A) butter: (red) 10 g, (purple) 20 g and (green) 40 g; (B) cheese: (red) 4 g, (purple) 10 g and (green) 20 g; (C) ghee: 100 g in the absence (red) and the presence of different external added water-spikes (light blue, 0.5%; blue, 1.0%; dark blue, 1.5% (v/v)); (D) coconut oil: 100 g in the absence (red) and the presence of different external added water-spikes (light blue, 0.5%; blue, 1.0%; dark blue, 1.5% (*v*/*v*)). (A–D) The spectra were reordered for the DMSO medium after separating it from the food sample solution. For the normalization of emission spectra, each emission spectrum for the excitation at 440 nm was divided by the maximum intensity value in the absence of water, the resultant spectrum was further divided by the extent of emission intensity decrease factor with respect to zero water condition for the excitation at 485 nm.