Electronic Supplementary Information

Conformational isomerism involving carboxylate groups of a linker in metal organic frameworks and its distinctive influence on the detection of ketones†

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Calculation of determining solvent molecules squeezed out:

Number of electrons squeezed out = 183.4
Z = 4
Number of electrons squeezed out per unit formula = 183.4/4 = 45.85
Number of electrons in 5 H_2O molecules = 50
Number of electrons squeezed out = 45.85

Support from TGA analysis

%weight loss due to 5 H_2O molecules = (90/516.8) x 100% = 17.4%; this is in good agreement with the experimental value (16%)

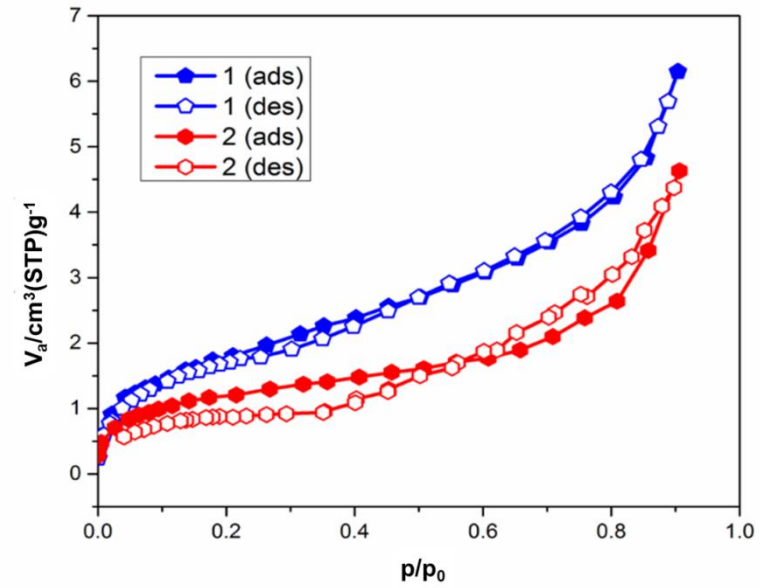


Fig. S1 N_2 gas adsorption-desorption isotherms of **1** and **2** at 77 K.

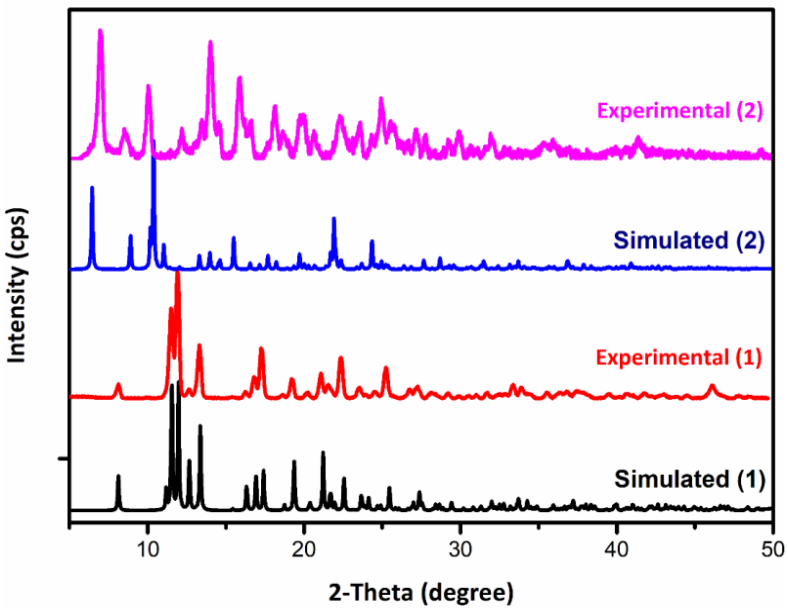


Fig. S2 Simulated and experimental PXRD patterns for **1** and **2**.

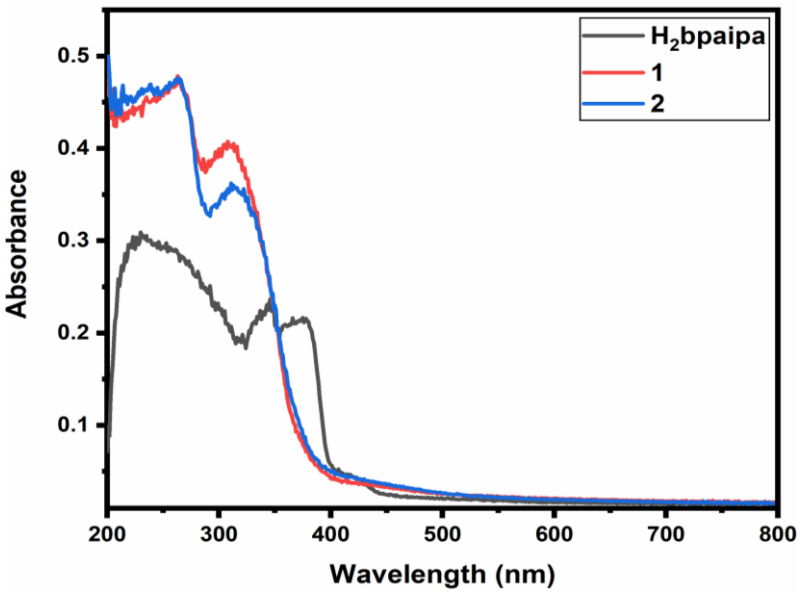


Fig. S3 Solid state diffuse reflectance spectra of **H_2bpaipa**, **1** and **2**.

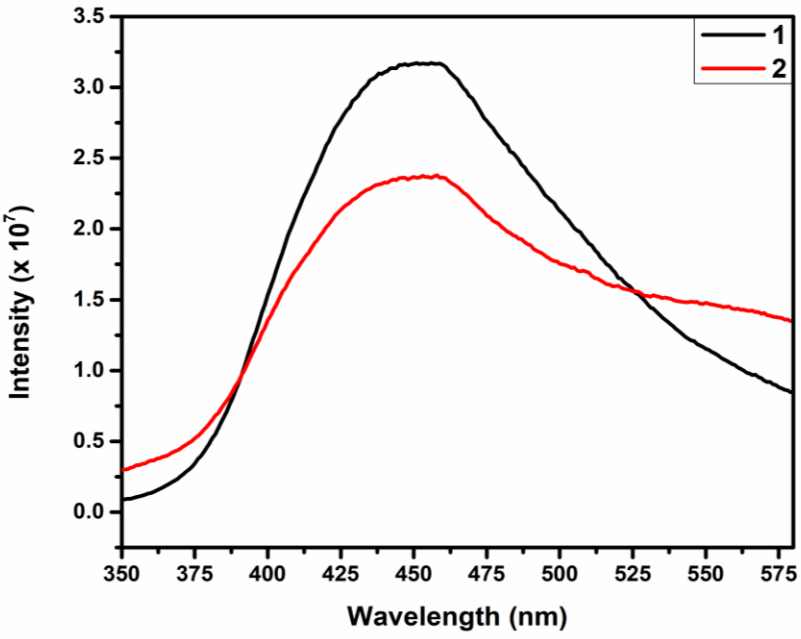


Fig. S4 Luminescence spectra of **1** and **2** in methanol (excitation wavelength: 310 nm).

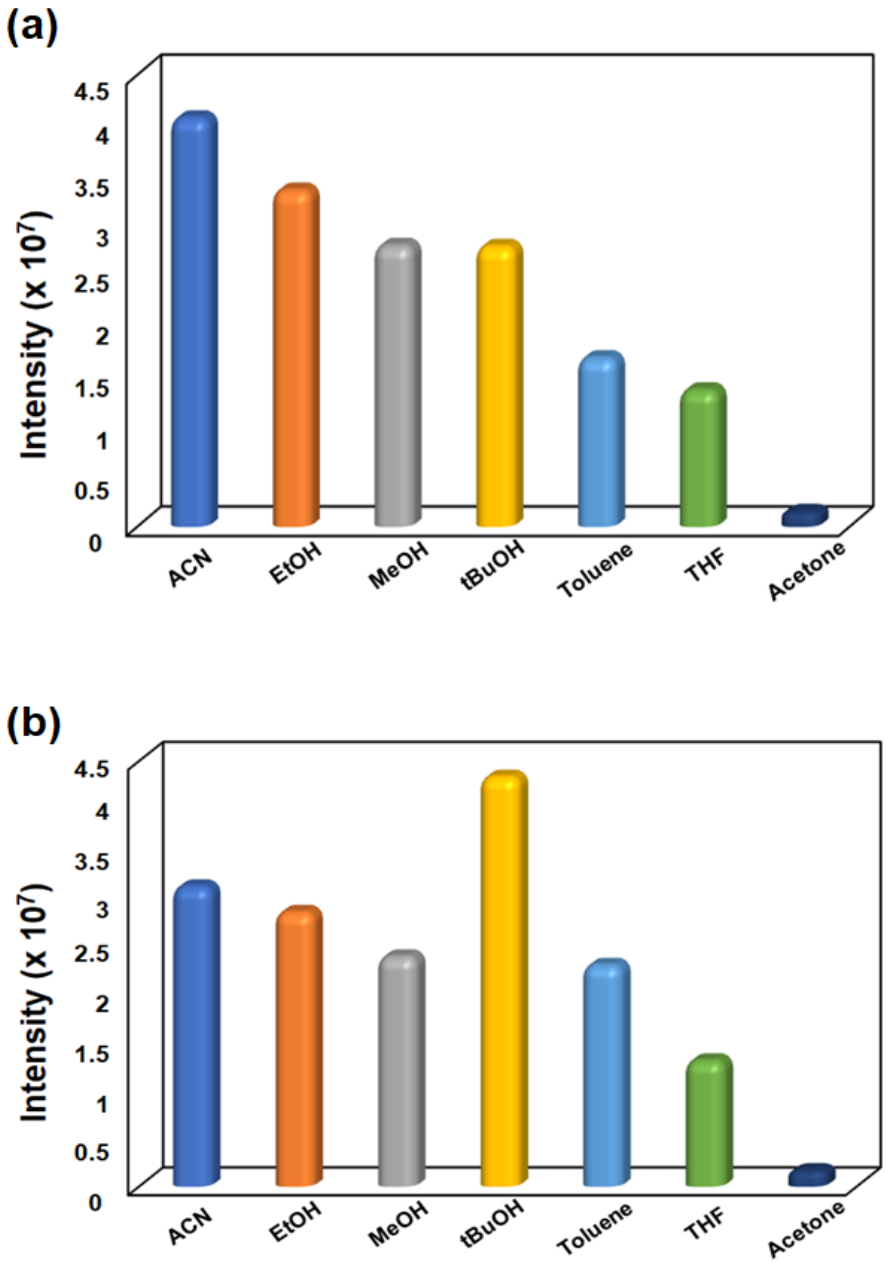


Fig. S5 Sensing of different solvents by (a) **1** and (b) **2**.

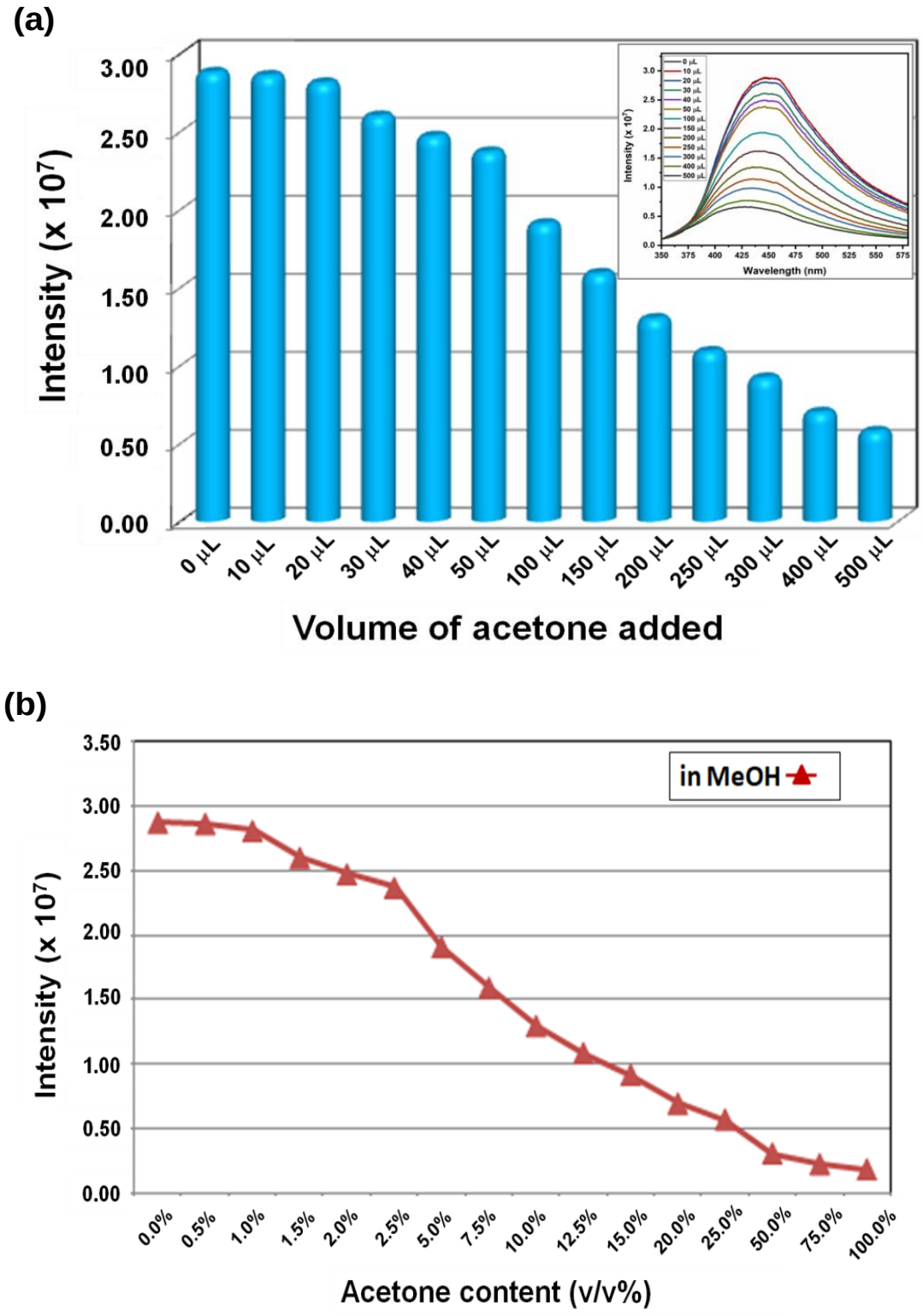


Fig. S6 Sensing of acetone in MeOH by **1**: change of intensity based on incremental addition of acetone (a) intensity vs volume (inset: spectral changes) and (b) intensity vs content in v/v%.

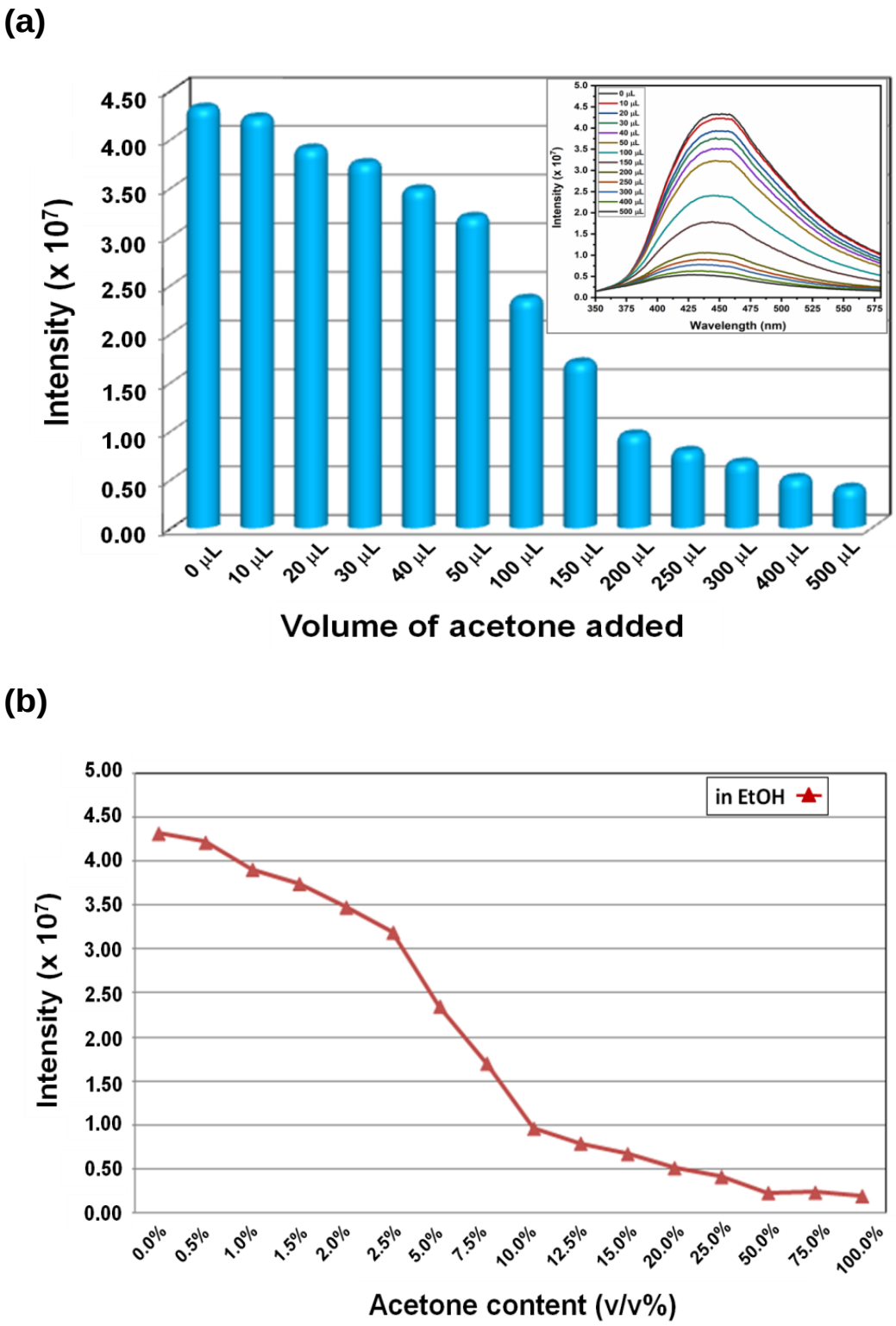


Fig. S7 Sensing of acetone in EtOH by **1**: change of intensity based on incremental addition of acetone (a) intensity vs volume (inset: spectral changes) and (b) intensity vs content in v/v%.

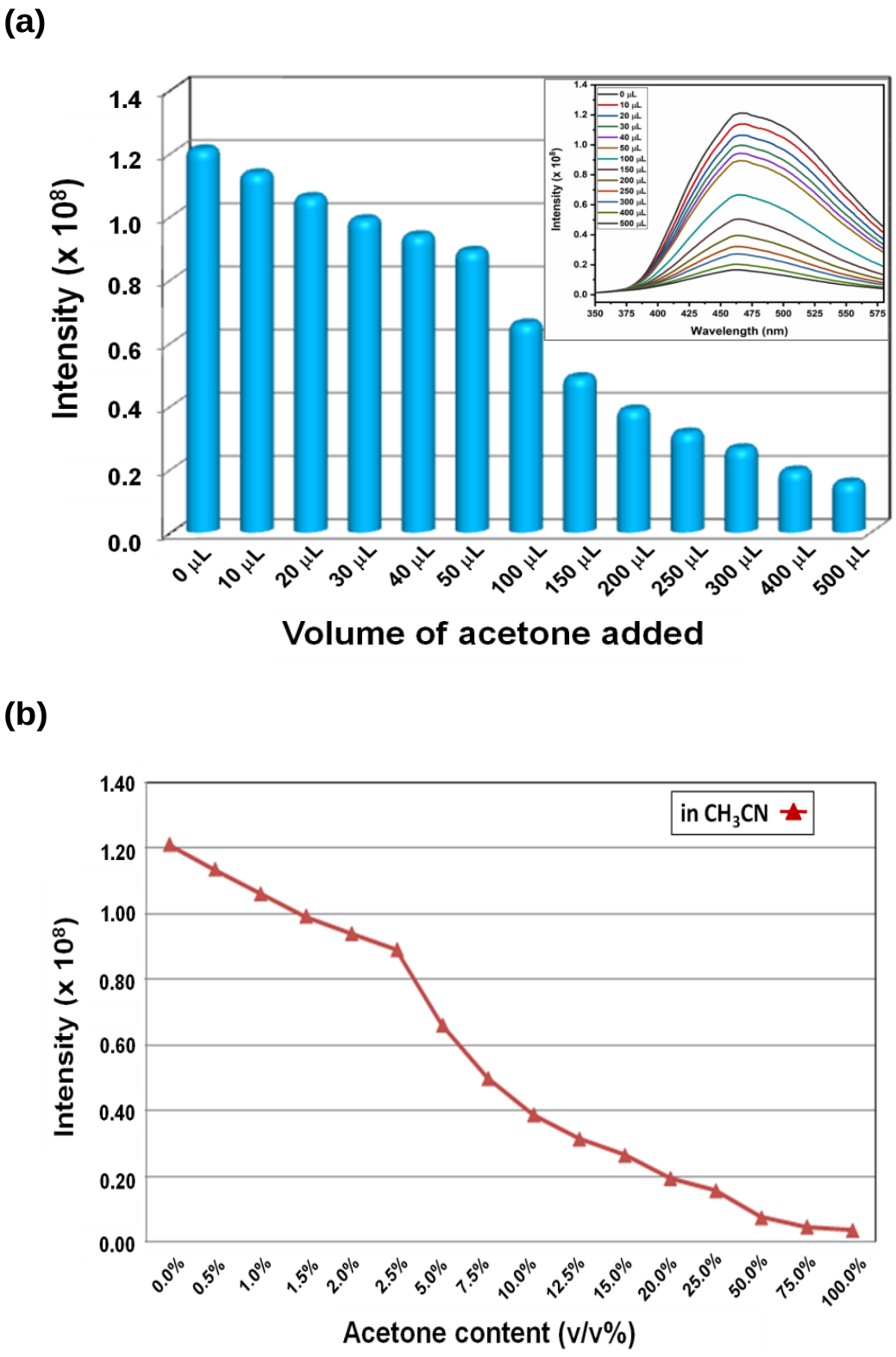


Fig. S8 Sensing of acetone in CH_3CN by **1**: change of intensity based on incremental addition of acetone (a) intensity vs volume (inset: spectral changes) and (b) intensity vs content in v/v%.

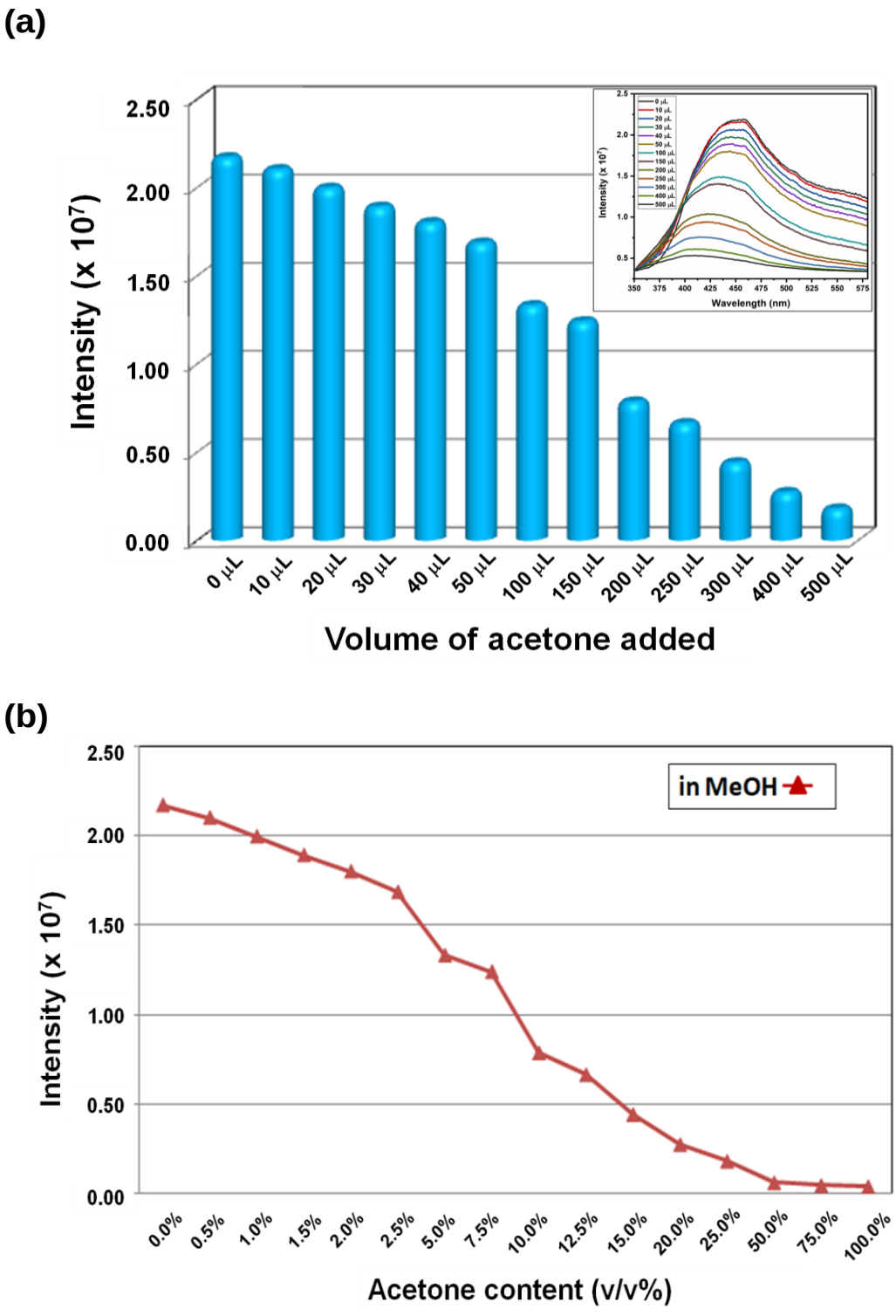
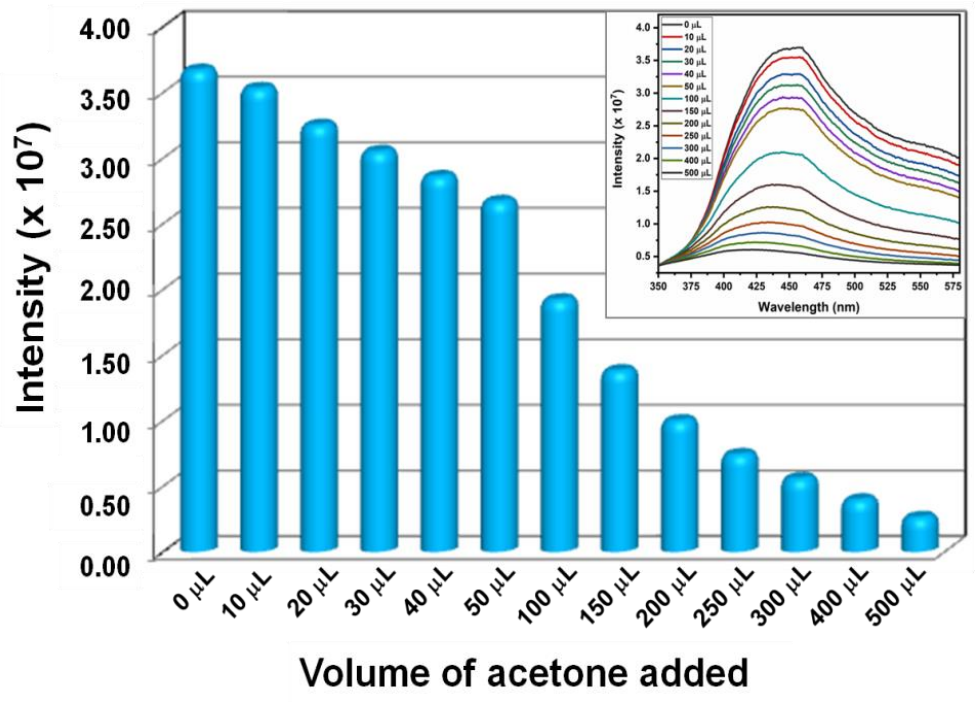


Fig. S9 Sensing of acetone in MeOH by **2**: change of intensity based on incremental addition of acetone (a) intensity vs volume (inset: spectral changes) and (b) intensity vs content in v/v%.

(a)



(b)

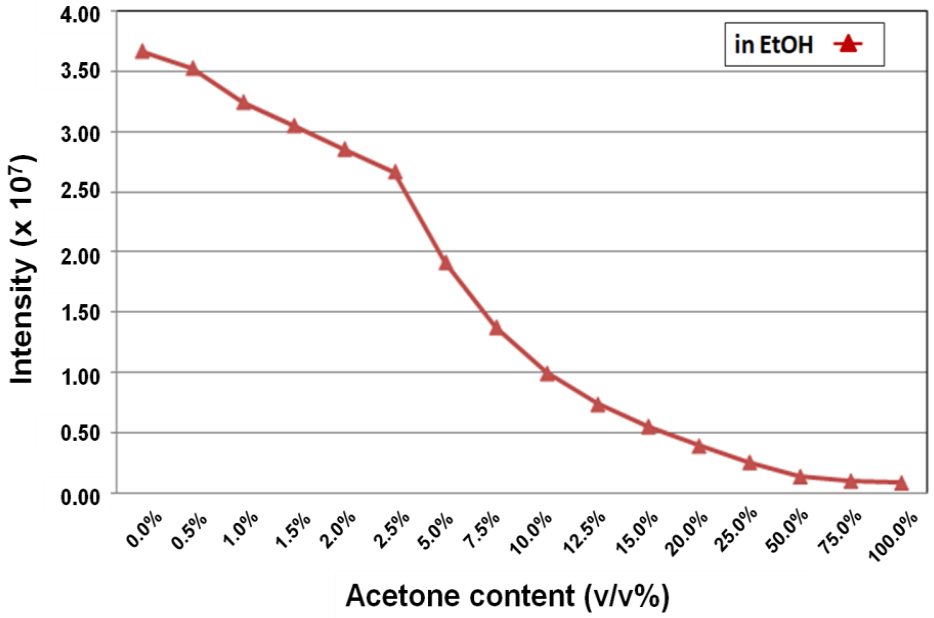


Fig. S10 Sensing of acetone in EtOH by **2**: change of intensity based on incremental addition of acetone (a) intensity vs volume (inset: spectral changes) and (b) intensity vs content in v/v%.

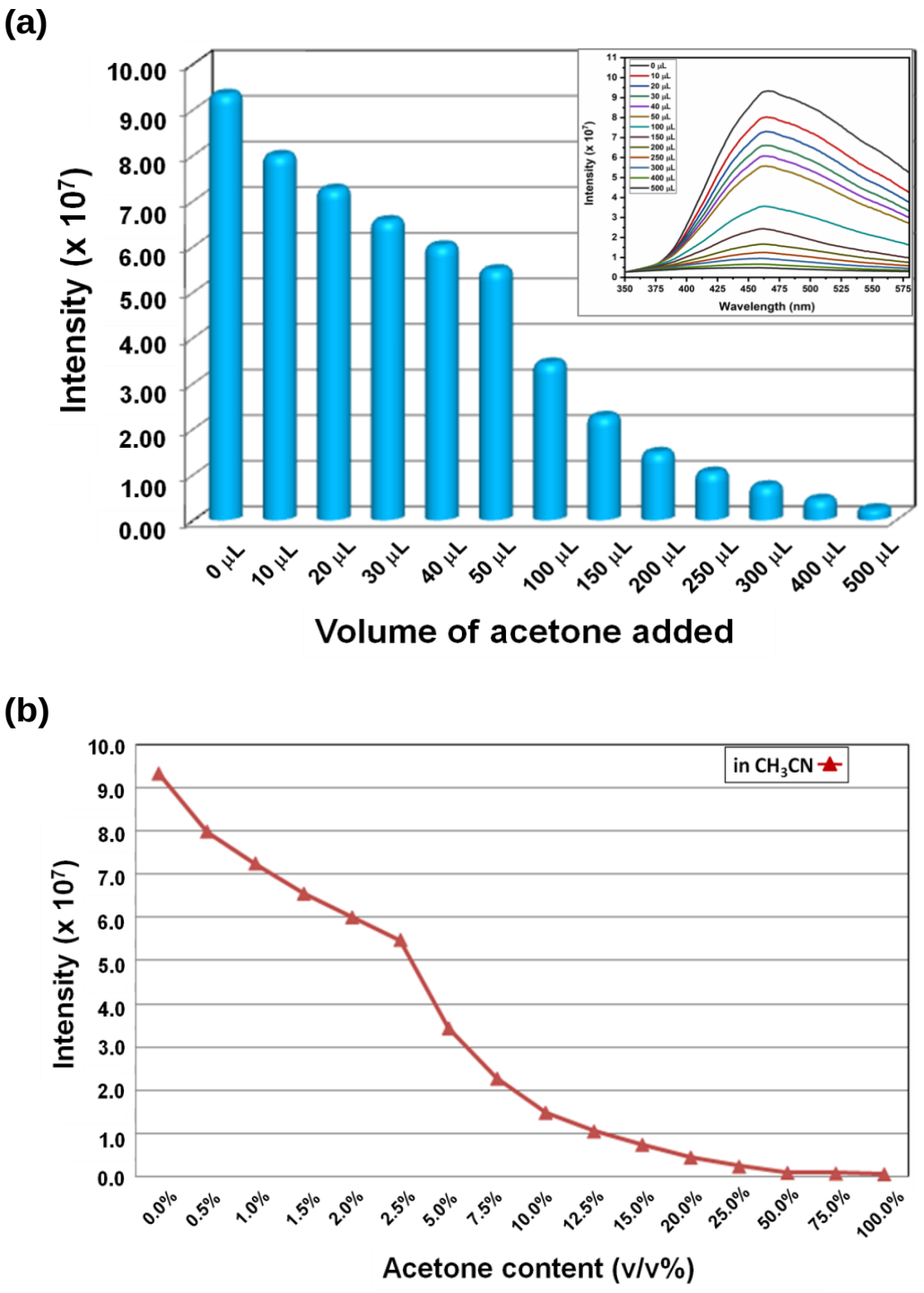


Fig. S11 Sensing of acetone in CH_3CN by **2**: change of intensity based on incremental addition of acetone (a) intensity vs volume (inset: spectral changes) and (b) intensity vs content in v/v%.

Determination of detection limit and quantification limit for acetone in 1 and 2 in MeOH, EtOH and CH_3CN:

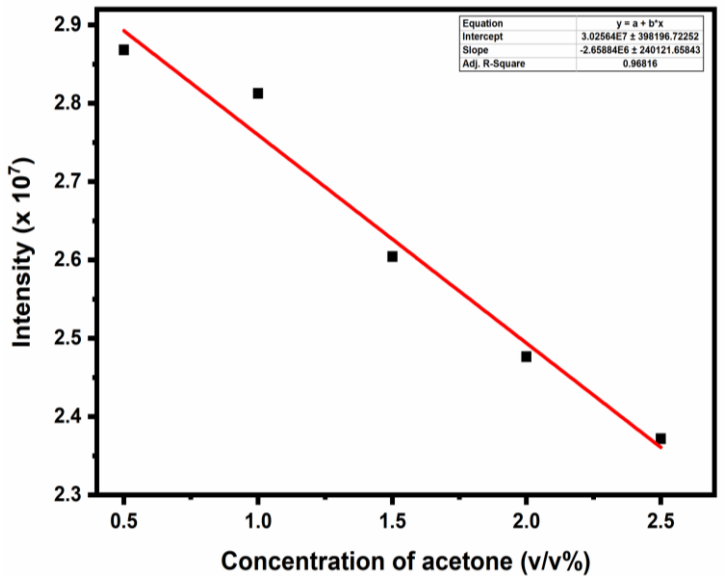


Fig. S12 Determination of detection limit through fitting of the linear region of fluorescence intensity of **1** in MeOH upon incremental addition of acetone to it at λ_{em} = 447 nm (upon λ_{ex} = 310 nm) (R^2 = 0.968).

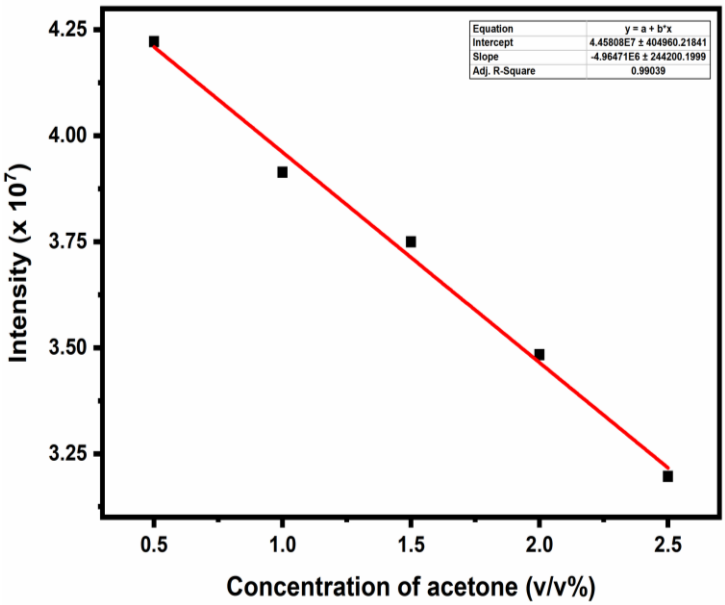


Fig. S13 Determination of detection limit through fitting of the linear region of fluorescence intensity of **1** in EtOH upon incremental addition of acetone to it at λ_{em} = 447 nm (upon λ_{ex} = 310 nm) (R^2 = 0.99).

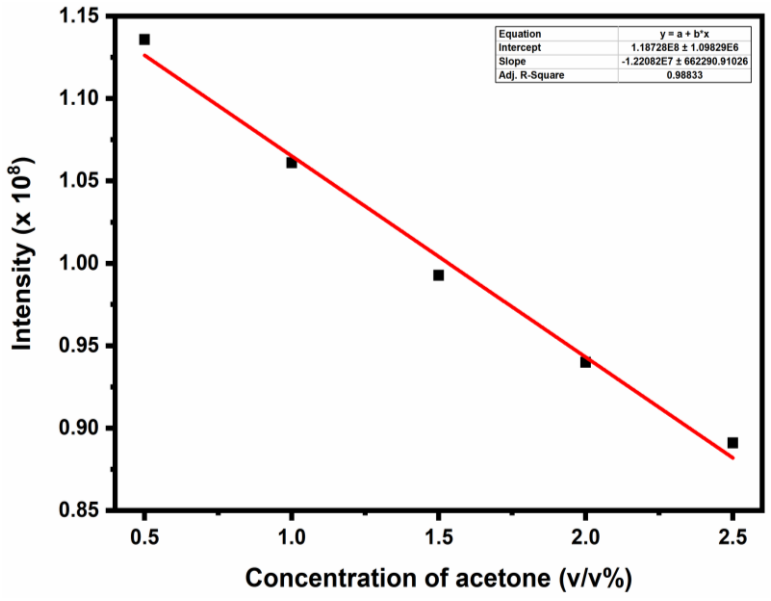


Fig. S14 Determination of detection limit through fitting of the linear region of fluorescence intensity of **1** in CH_3CN upon incremental addition of acetone to it at λ_{em} = 447 nm (upon λ_{ex} = 310 nm) (R^2 = 0.988).

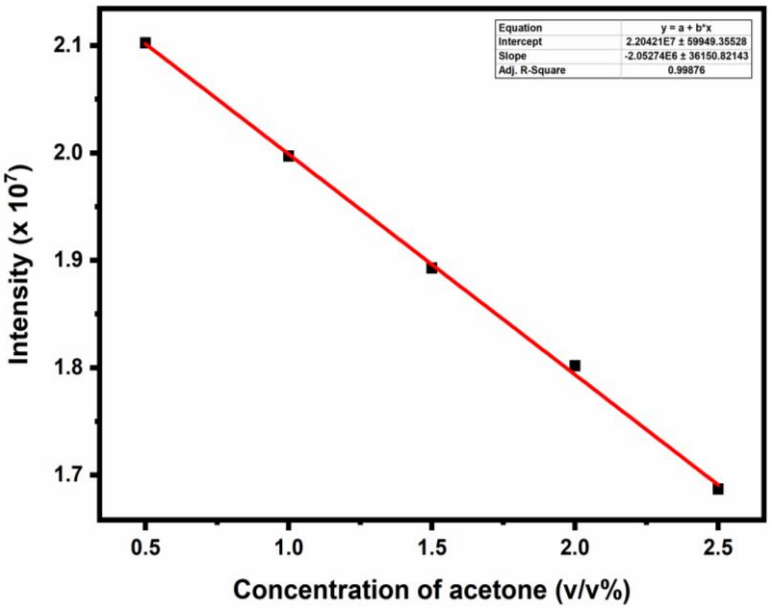


Fig. S15 Determination of detection limit through fitting of the linear region of fluorescence intensity of **2** in MeOH upon incremental addition of acetone to it at λ_{em} = 447 nm (upon λ_{ex} = 310 nm) (R^2 = 0.998).

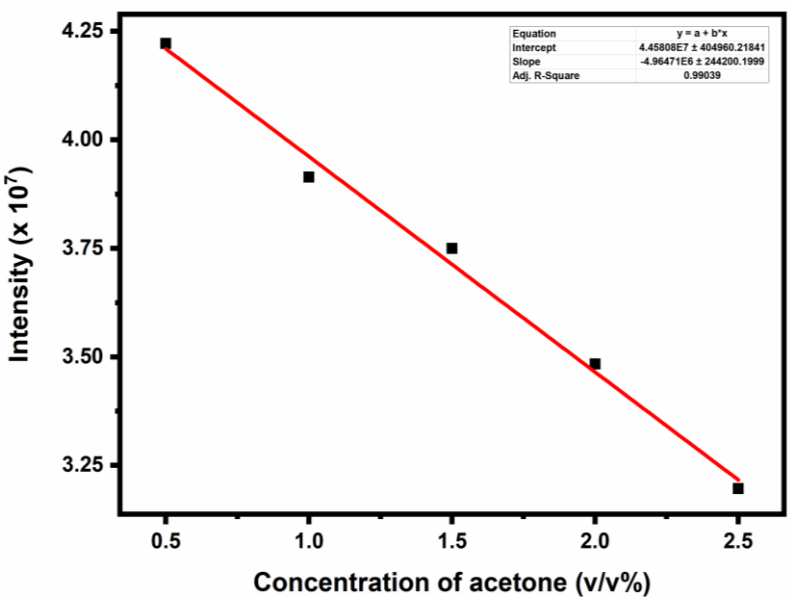


Fig. S16 Determination of detection limit through fitting of the linear region of fluorescence intensity of **2** in EtOH upon incremental addition of acetone to it at λ_{em} = 447 nm (upon λ_{ex} = 310 nm) (R^2 = 0.99).

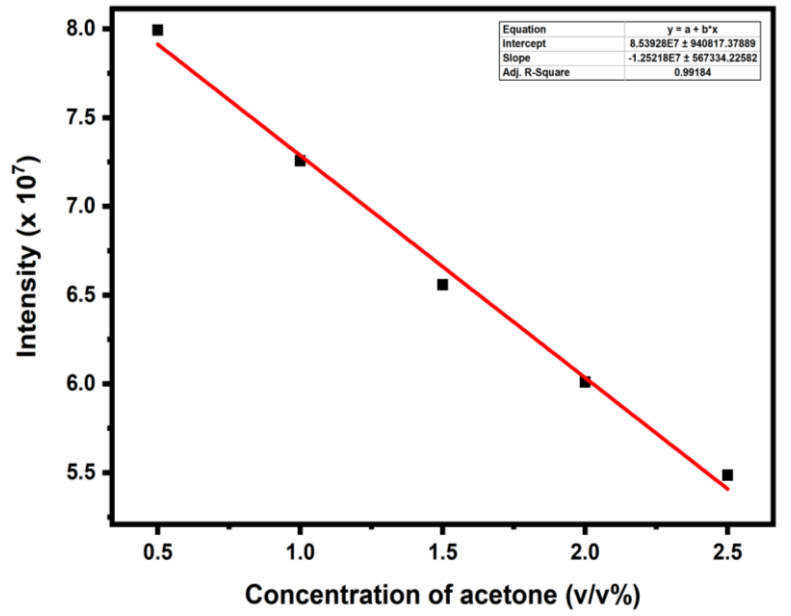


Fig. S17 Determination of detection limit through fitting of the linear region of fluorescence intensity of **2** in CH_3CN upon incremental addition of acetone to it at λ_{em} = 447 nm (upon λ_{ex} = 310 nm) (R^2 = 0.991).

Table S1. Calculation of detection limits for **1** and **2**.

S. No.	Blank readings (1)	Fluorescence intensity (x 10^7)
1.	Reading#1	2.81588
2.	Reading#2	2.67100
3.	Reading#3	2.54067
4.	Reading#4	2.78164
5.	Reading#5	2.72620
6.	Standard Deviation (σ)	1064425

S. No.	Blank readings (2)	Fluorescence intensity (x 10^7)
1.	Reading#1	2.21565
2.	Reading#2	2.39779
3.	Reading#3	2.36071
4.	Reading#4	2.77988
5.	Reading#5	2.27562
6.	Standard Deviation (σ)	2208715

Detection limit was calculated using the following equation:
Detection limit (LoD) = 3σ/m
Where 'σ' is the calculated standard deviation from five blank measurements and 'm' is the slope obtained from the plot of fluorescence emission with increasing concentration of acetone.

Compound	Solvent medium	LOD (v/v%)
1	CH_3CN	0.26
1	MeOH	1.2
1	EtOH	0.63
2	CH_3CN	0.53
2	MeOH	3.23
2	EtOH	1.34

Table S2. Comparison of detection limits for **1** and **2** with those reported in the literature.

Entry	MOFs	Analyte	Solvent medium	LOD (vol%)	Ref.[$]
1.	$[Zn_5(L)_4(H_2tpim)_2(FA)_4(H_2O)_2]_n$, $[Zn(L)(H_2tpim)]_n$	Acetone	DMF	10 25	7
2.	Cd(5-aip)L·3DMA; L = 3,5-di(pyridine-4-yl)-4*H*-1,2,4-triazol-4-amine	Acetone	DMA	1.812*	10
3.	$[Cu(tpp)\cdot H_2O]_{2n}$	Acetone	H_2O	0.0842	11a
4.	$[Zn(L)(bpdc)]\cdot 1.6H_2O$, $[Cu_2(L)(Hbptc)_2]$; L = 1,4-di(1*H*-imidazol-4-yl)benzene	Acetone	DMF	0.0478 0.0465	11b
5.	$[Cd(Tipb)(pta)_{0.5}(H_2O)(NO_3)]\cdot(DMF)_x(H_2O)_y$ $[Cd(Tipb)(mta)]\cdot(DMF)_x(H_2O)_y$	Acetone	CH_3CN	0.084 0.075	11c
6.	$[Zn_2(TPC4A)(DMF)(H_2O)_4]\cdot 3H_2O$	Acetone	EtOH	5	11f
7.	$[Zn_2(2,5\text{-}PDC)(H_2O)_2]\cdot H_2O/Tb^{3+}$	Acetone	H_2O	55[#]	11g
8.	$[Cd_3(L')_2(BTB)_2(H_2O)]\cdot DMF\cdot H_2O$; L' = 1,3-di(1*H*-imidazol-4-yl)benzene	Acetone	CH_3CN	0.122	11e
9.	[Eu(BTC)]	Acetone	1-propanol	N.R.	9
10.	$[Eu_2(\mu_2\text{-}pzdc)(\mu_4\text{-}pzdc)(\mu_2\text{-}ox)(H_2O)_4]\cdot 8H_2O$	Acetone	MeOH	N.R.	11d
11.	$[Eu(BTB(H_2O)_2\cdot(solvent)]_n$, [Eu(BTB)]	Acetone	EtOH	0.3 0.01	11h
12.	$\{[Zn(bpaipa)]\cdot DMF\cdot 2H_2O\}_n$ **(1)** $\{[Zn(bpaipa)]\cdot 5H_2O\}_n$ **(2)**	Acetone	MeOH EtOH CH_3CN MeOH EtOH CH_3CN	1.2 0.63 0.26 3.23 1.34 0.53	This work

LOD units for these sensors are in *mM and [#]ppm. [$]These reference numbers are as cited in the main text.
N.R.= not reported.

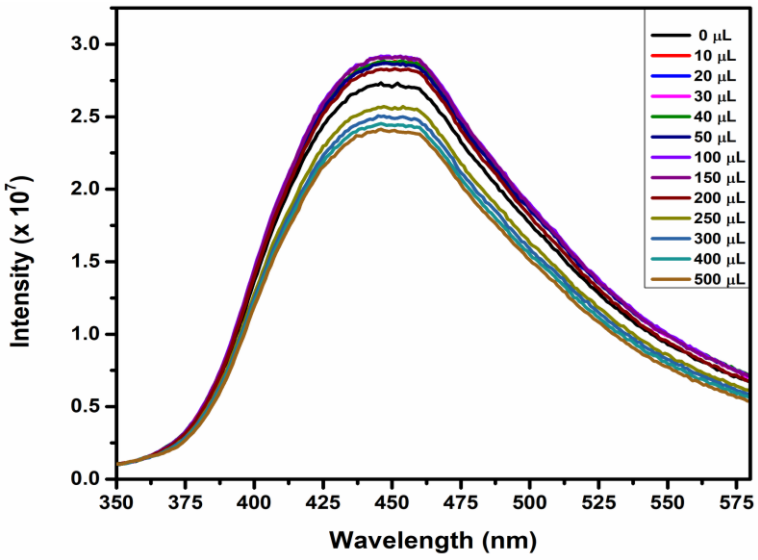


Fig. S18 Emission spectra of **1** (dispersed in methanol) upon incremental addition of 20 mM acetone solution.

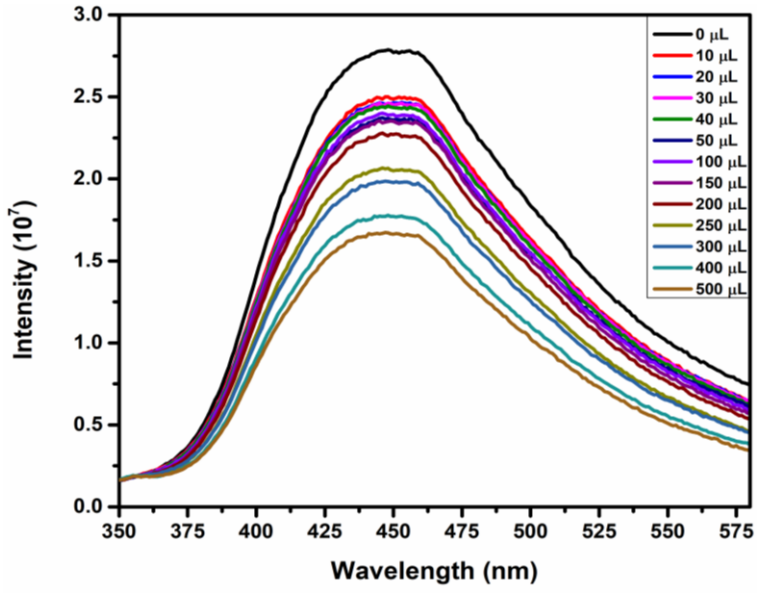


Fig. S19 Emission spectra of **1** (dispersed in methanol) upon incremental addition of 20 mM acetophenone solution.

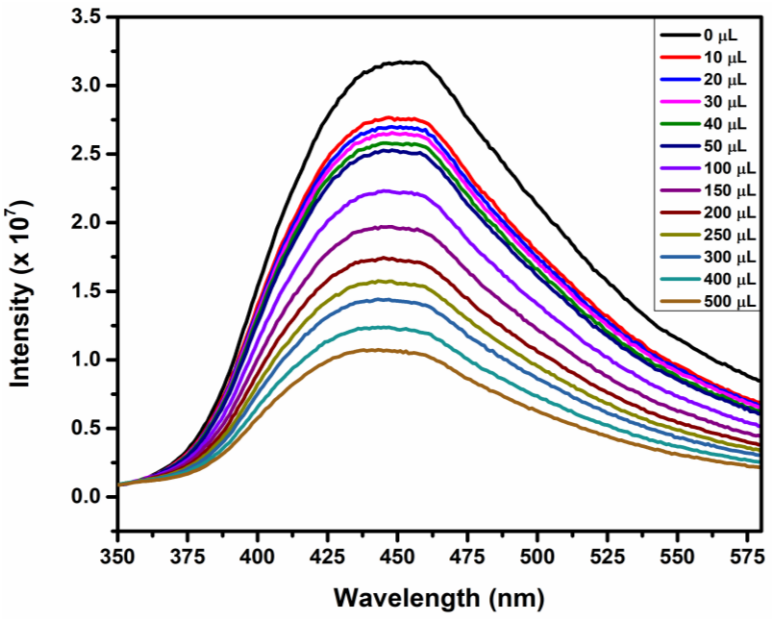


Fig. S20 Emission spectra of **1** (dispersed in methanol) upon incremental addition of 20 mM acetylacetone solution.

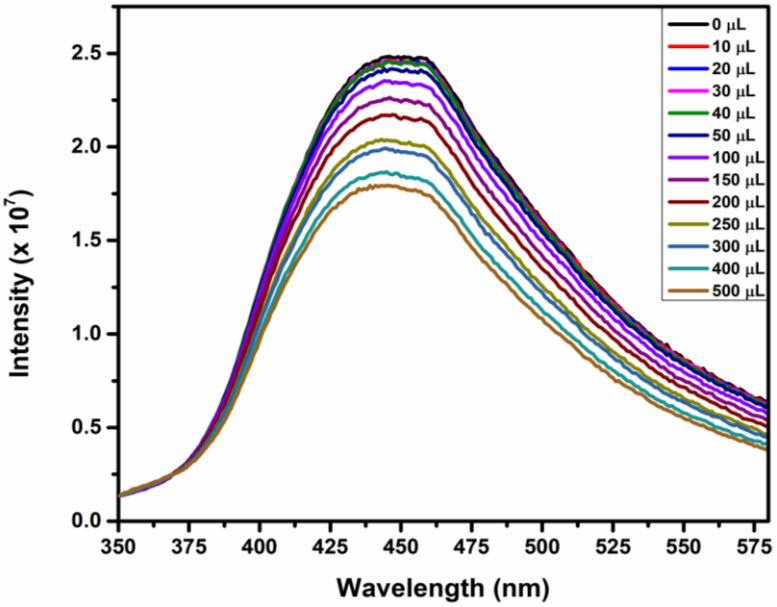


Fig. S21 Emission spectra of **1** (dispersed in methanol) upon incremental addition of 20 mM mesityl oxide solution.

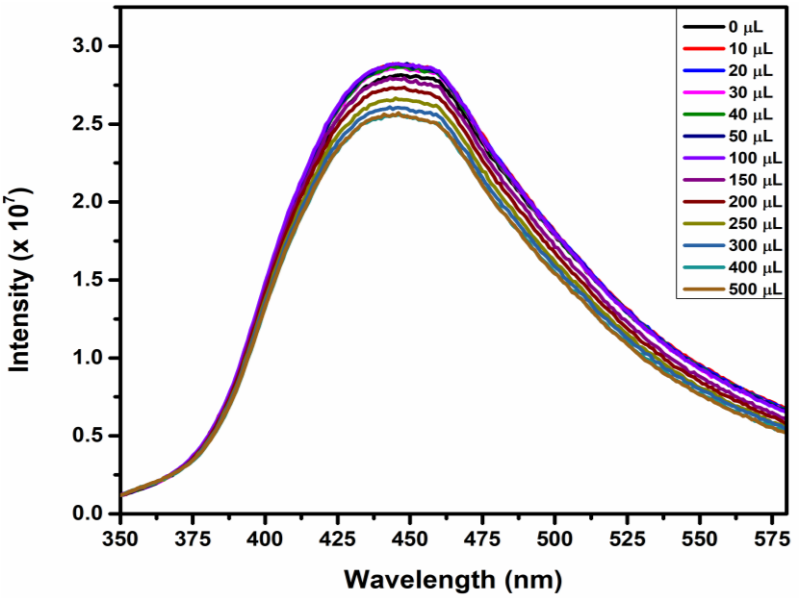


Fig. S22 Emission spectra of **1** (dispersed in methanol) upon incremental addition of 20 mM cyclohexanone solution.

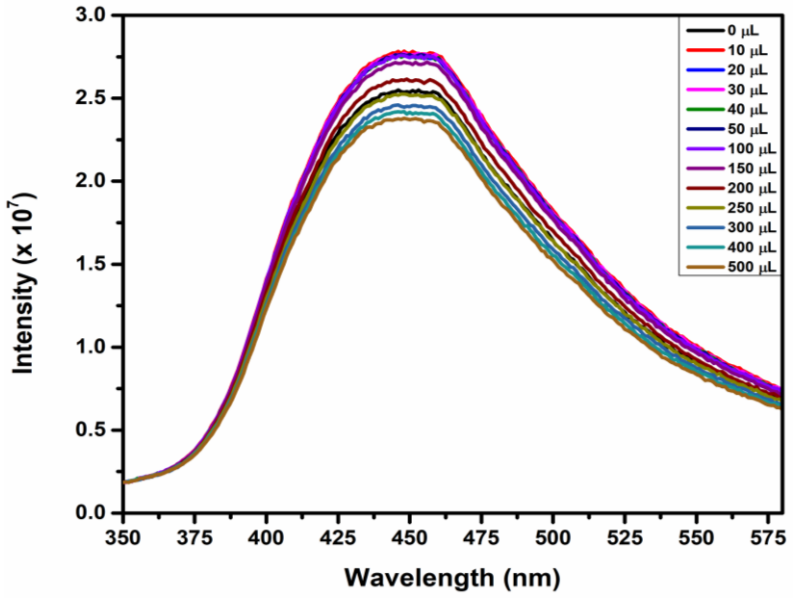


Fig. S23 Emission spectra of **1** (dispersed in methanol) upon incremental addition of 20 mM cyclopentanone solution.

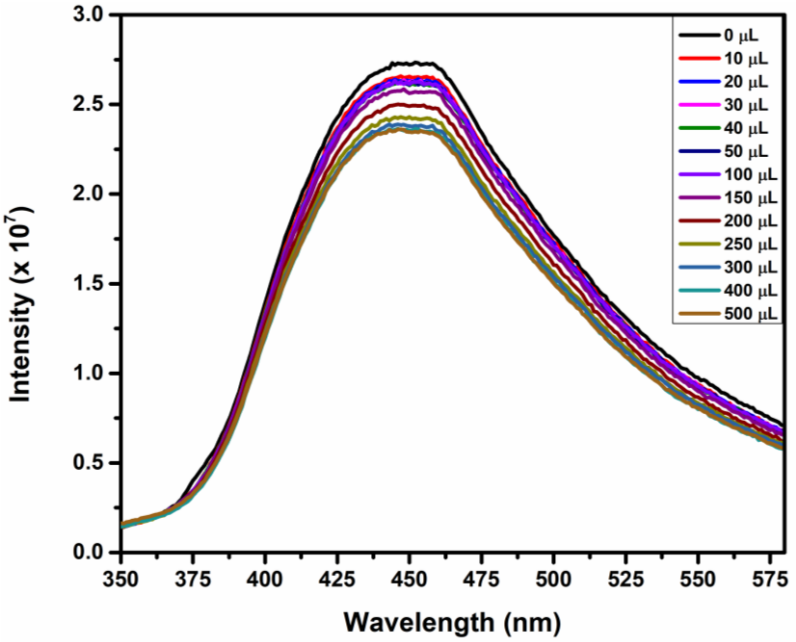


Fig. S24 Emission spectra of **1** (dispersed in methanol) upon incremental addition of 20 mM 3-pentanone.

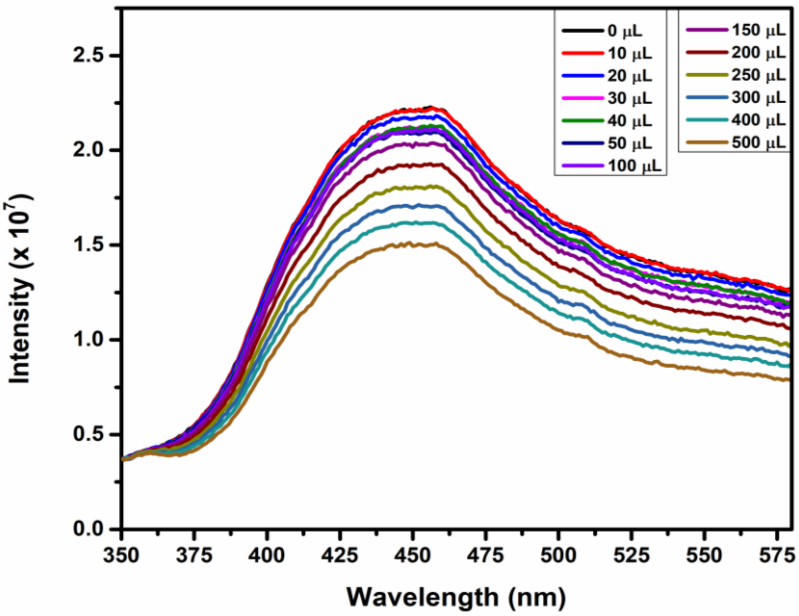


Fig. S25 Emission spectra of **2** (dispersed in methanol) upon incremental addition of 20 mM acetone solution.

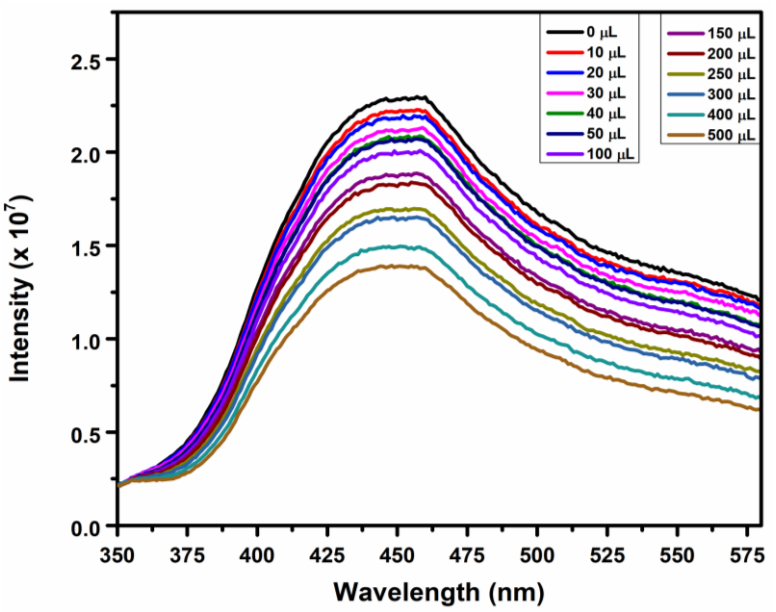


Fig. S26 Emission spectra of **2** (dispersed in methanol) upon incremental addition of 20 mM acetophenone solution.

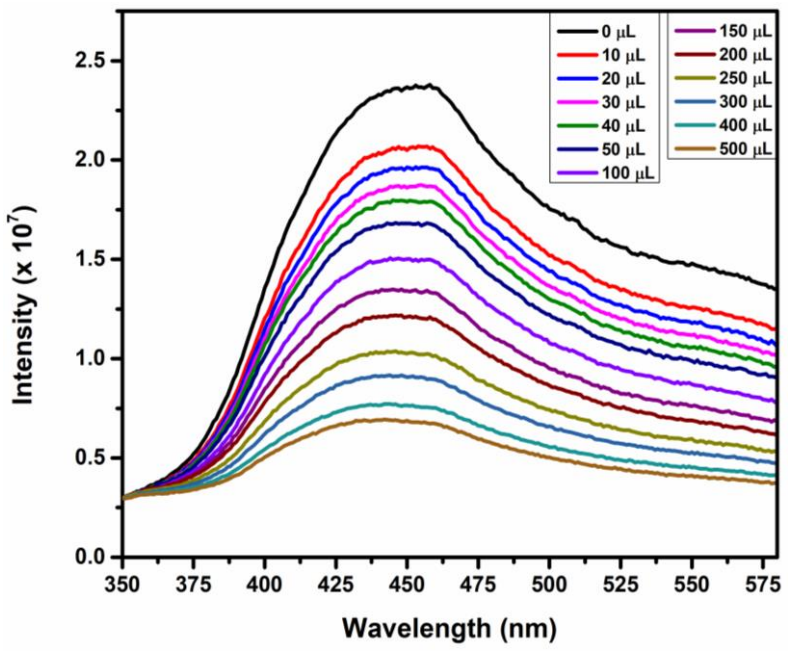


Fig. S27 Emission spectra of **2** (dispersed in methanol) upon incremental addition of 20 mM acetylacetone solution.

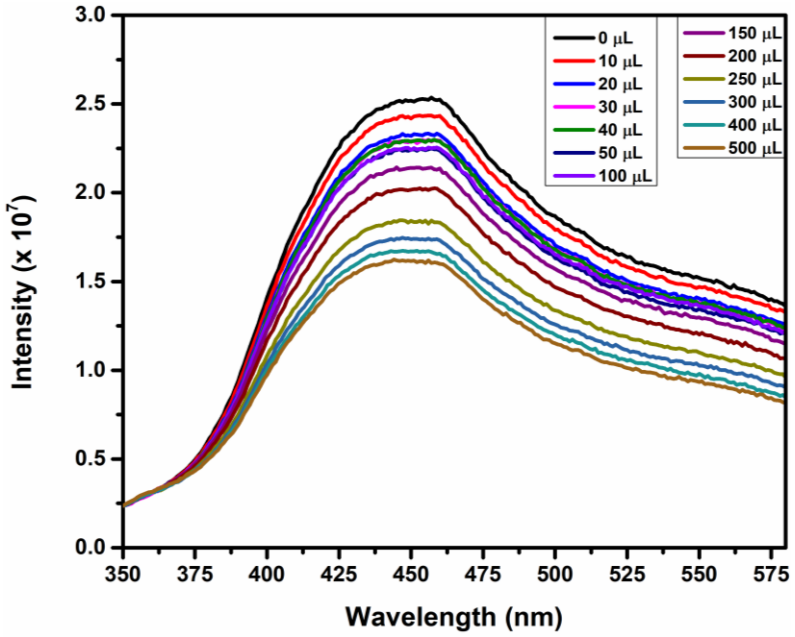


Fig. S28 Emission spectra of **2** (dispersed in methanol) upon incremental addition of 20 mM mesityl oxide solution.

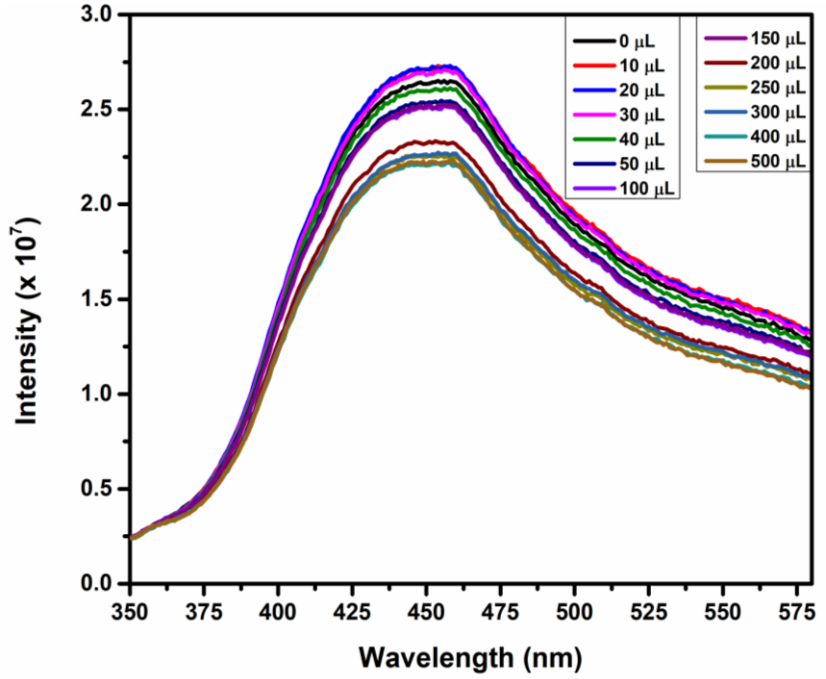


Fig. S29 Emission spectra of **2** (dispersed in methanol) upon incremental addition of 20 mM cyclohexanone solution.

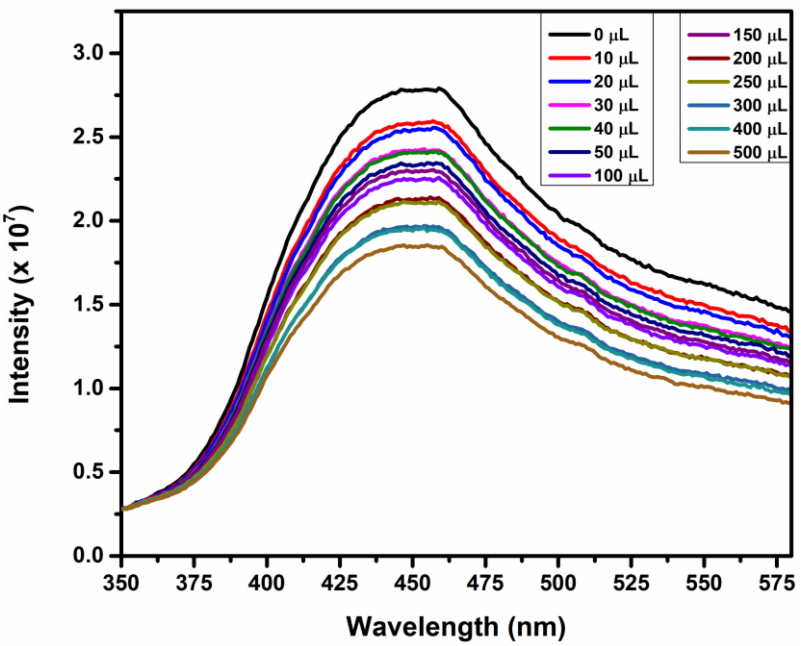


Fig. S30 Emission spectra of **2** (dispersed in methanol) upon incremental addition of 20 mM cyclopentanone solution.

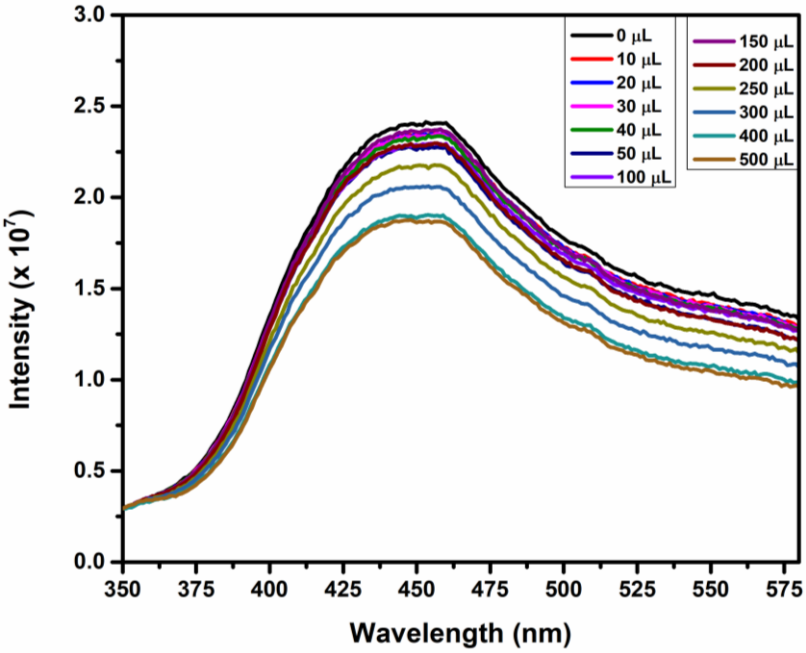


Fig. S31 Emission spectra of **2** (dispersed in methanol) upon incremental addition of 20 mM 3-pentanone solution.

Detection Limit Calculation and Determination of Stern-Volmer Constant

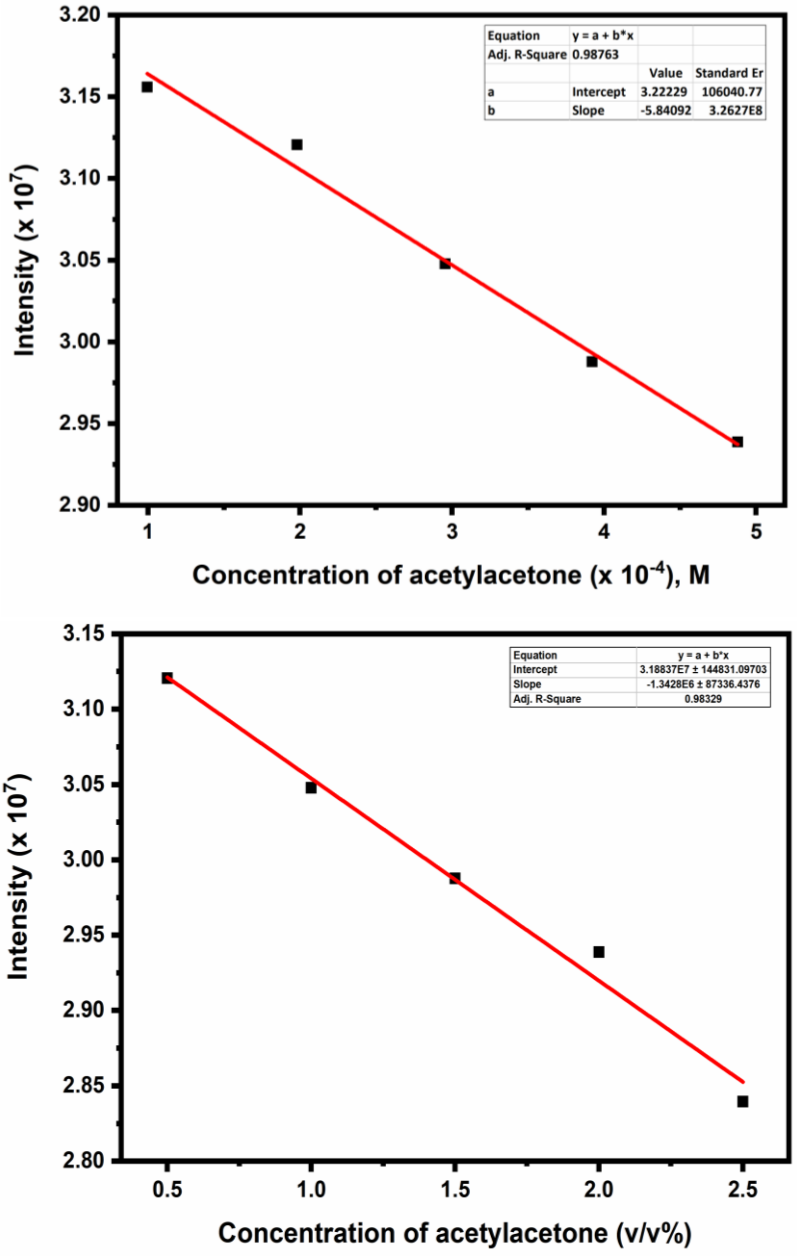


Fig. S32 Determination of detection limit through fitting of the linear region of fluorescence intensity of **1** upon incremental addition of acetylacetone to it at λ_{em} = 447 nm (upon λ_{ex} = 310 nm) (R^2 = 0.987).

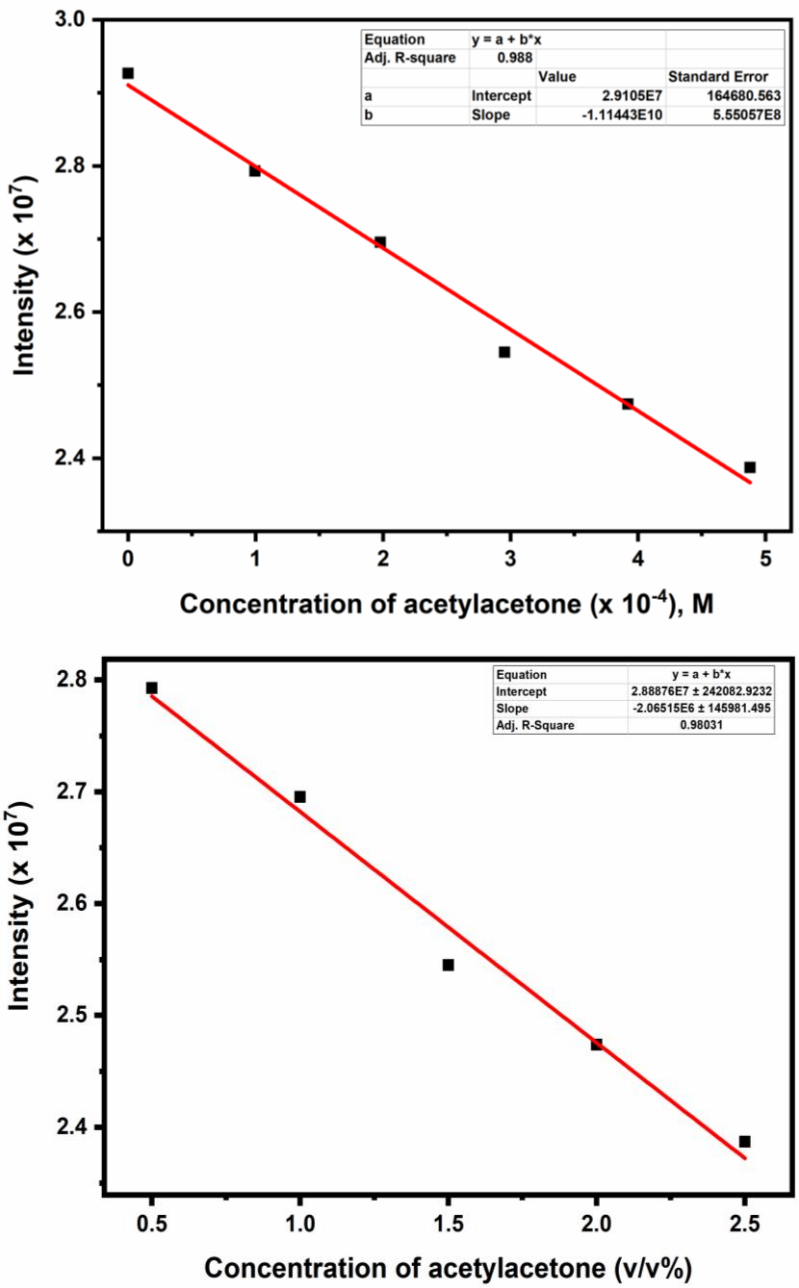


Fig. S33 Determination of detection limit through fitting of the linear region of fluorescence intensity of **2** upon incremental addition of acetylacetone to it at λ_{em} = 447 nm (upon λ_{ex} = 310 nm) (R^2 = 0.988).

Determination of detection limit and quantification limit for acetylacetone in 1 and 2:

Detection limit was calculated using the following equation:
Detection limit (LoD) = 3σ/m
Quantification limit (LoQ) = 10σ/m
Where 'σ' is the calculated standard deviation from five blank measurements and 'm' is the slope obtained from the plot of fluorescence emission with increasing concentration of acetylacetone.

Compound	LOD	LOQ
1	54.7 ppm (546.7 μM), 2.38 v/v%	182.4 ppm 7.93 v/v%
2	59.5 ppm (594.5 μM), 4.94 v/v%	198.4 ppm 16.47 v/v%

Determination of Stern-Volmer constant for acetylacetone in 1 and 2:

The Stern-Volmer equation:
$I_0/I = 1 + K_{SV}[A]$,
Where K_{SV} is the quenching constant (M^{-1}),[A] is molar concentration of the acetylacetone analyte and I_0 and I are the emission intensities of **1**or **2**, before and after addition of acetylacetone analyte, respectively.

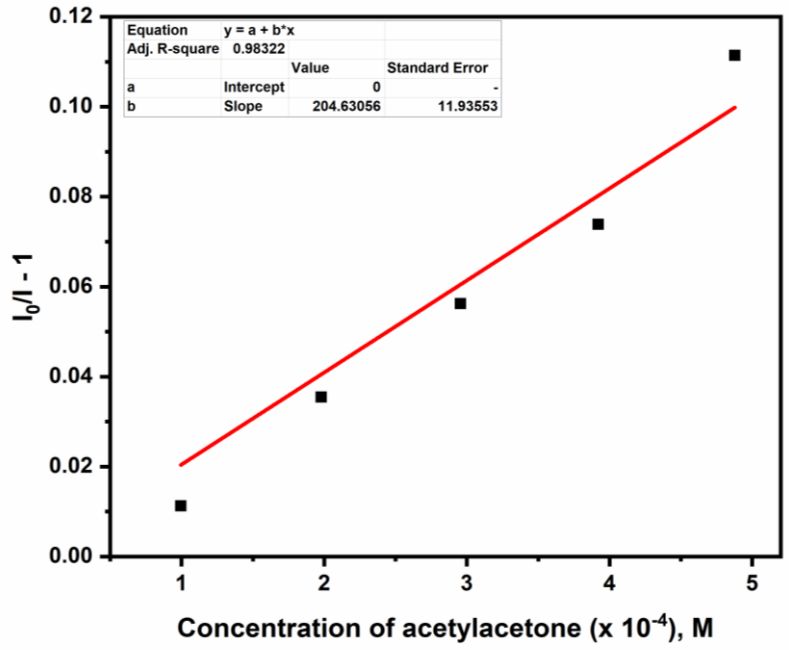


Fig. S34 Stern-Volmer (SV) plot for acetylacetone in **1**. The relative fluorescence intensity is linear with acetylacetone concentration in the range of 1–5 x 10^{-4} M, $I_0/I = 1 + 204.63056$ [Acetylacetone] ($R^2 = 0.983$).

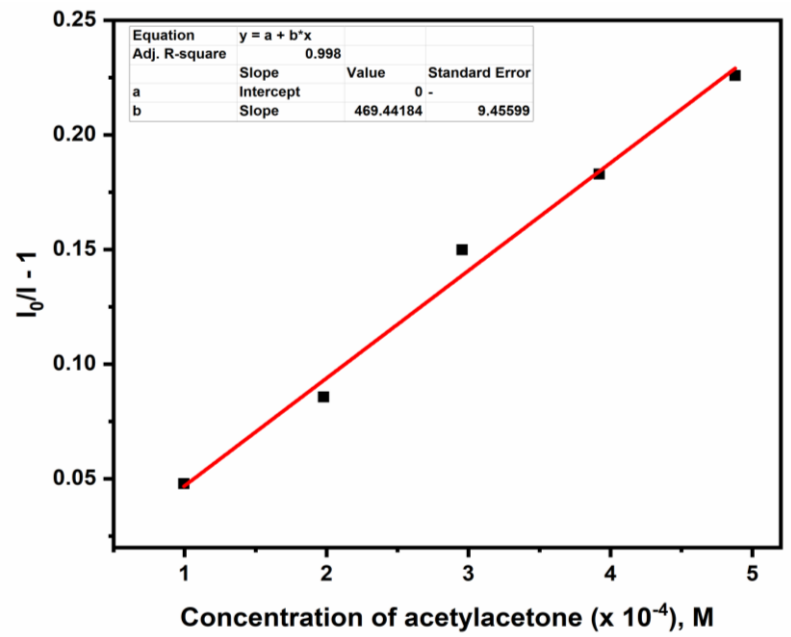


Fig. S35 Stern-Volmer (SV) plot for acetylacetone in **2**. The relative fluorescence intensity is linear with acetylacetone concentration in the range of 1–5 x 10^{-4} M, $I_0/I = 1 + 469.44184$ [Acetylacetone] ($R^2 = 0.998$).

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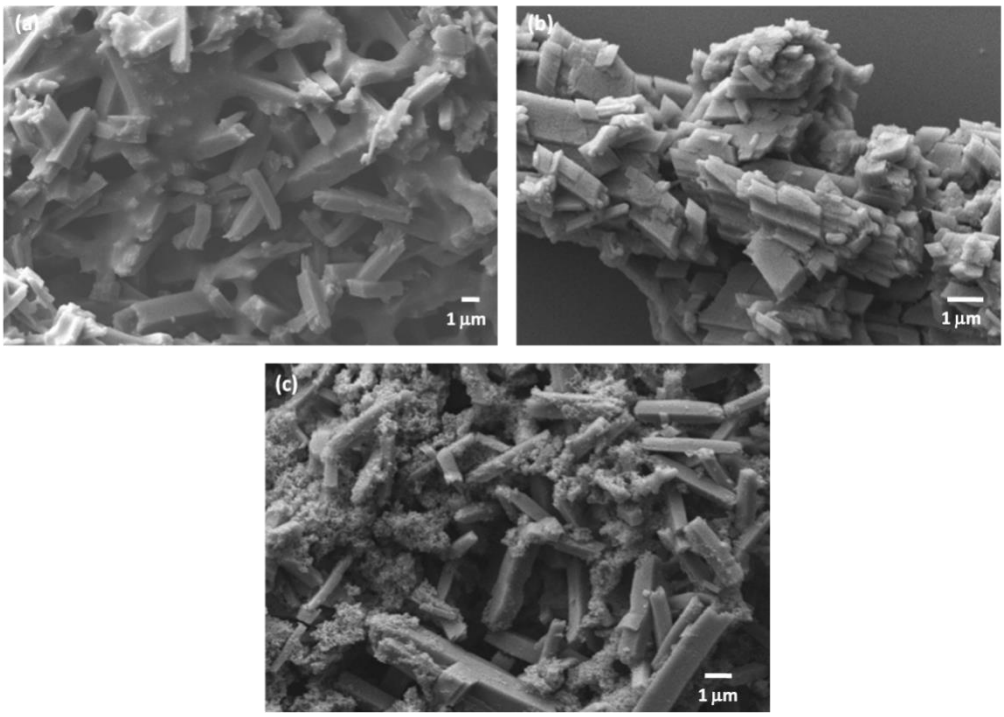

Fig. S36 FESEM images of **1**: before (a) and (b,c) after dipping in different ketones (acetophenone and cyclohexanone, respectively).

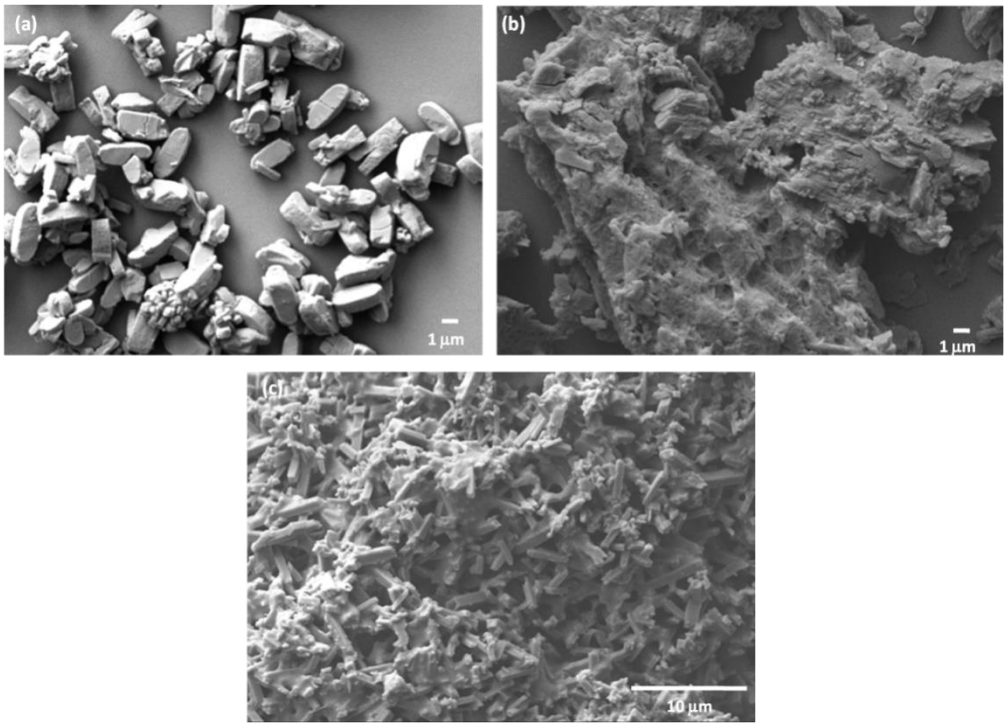

Fig. S37 FESEM images of **2**: before (a) and (b,c) after dipping in different ketones (acetophenone and cyclohexanone, respectively).

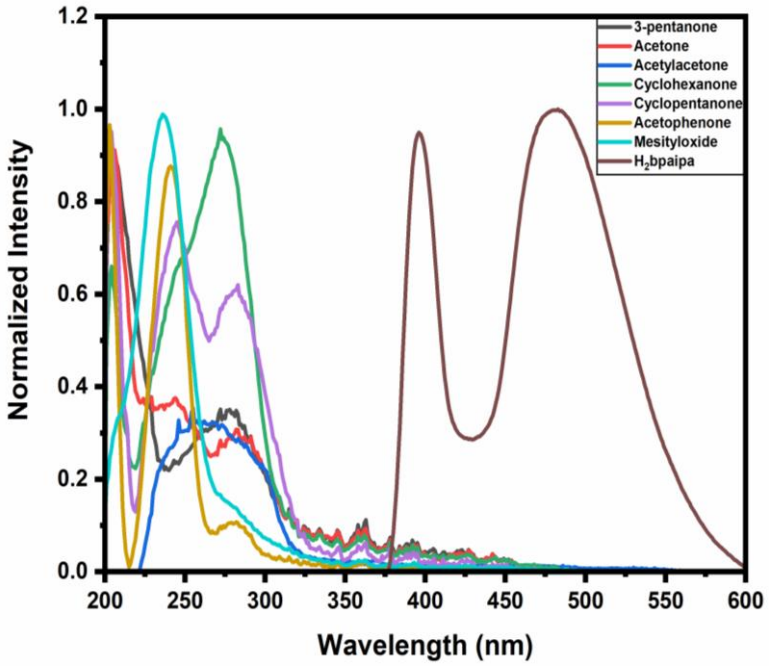

Fig. S38 Spectral overlap of absorption spectra of different ketone analytes and emission spectra of the ligand H_2bpaipa.

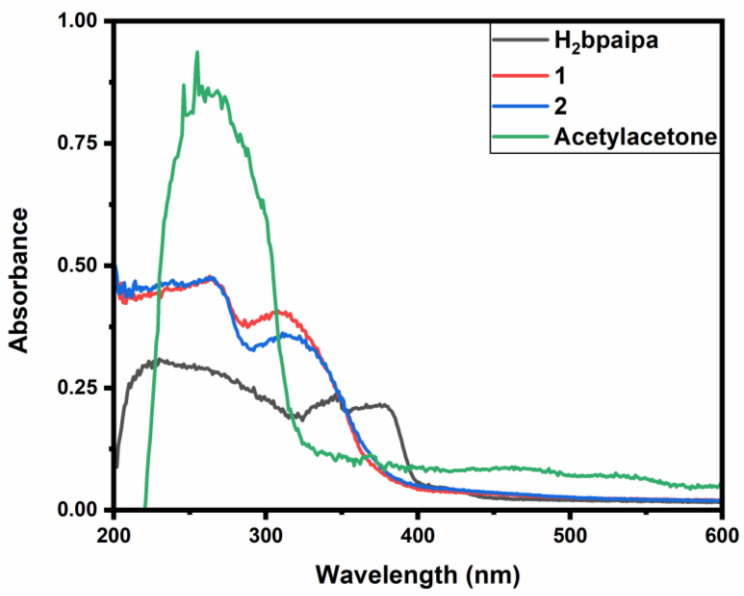

Fig. S39 Spectral overlap of absorption spectra of H_2bpaipa, **1, 2** and acetylacetone.