Electronic Supplementary Material (ESI) for Analyst.

Electronic supplementary information

A simple colorimetric sensor for the detection of moisture in organic solvents and building materials: applications in rewritable paper and fingerprint imaging

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1. Materials and Instrument

All the chemicals used were analytical grade reagents and were used without further purification. Quinizarin (1,4-dihydroxy-9,10-anthraquinone) and Tetrabutylammonium fluoride([n-Bu_4NF]) were purchased from Sigma Aldrich. All the solvents were purified by standard distillation method. UV-Vis absorption spectra were recorded on an Evolution 201 UV-Vis Spectrophotometer while emission spectra were recorded on a Cary Eclipse fluorescence spectrophotometer using quartz cells of 1.0 cm path length. ^{19}F-NMR was measured on a Magritek spinsolve, 43 MHz with DMSO-d6. TMS used as an internal standard.

2. General procedure for spectroscopic measurements

2.1 UV-Vis absorption titration of 1 with Fluoride Ion.

For UV-Vis absorption study, fluoride ion concentration required for the formation of **1.F** from **1** was systematically determined by titration of **1** with [n-Bu_4NF] anion. For each titration, 0.025mM solution of **1** was prepared by diluting 0.1mL (0.5mM) stock solution to 2 mL by adding 1.9 mL of respective solvents such as dry acetone, acetonitrile, THF and DMSO.

2.2 Fluorescence emission titration of 1 with Fluoride Ion.

For emission study, fluoride ion concentration required for the formation of **1.F** from **1** was systematically determined by fluorescence titration of **1** with [n-Bu_4NF] anion. For each titration, 0.025mM solution of **1** was prepared by diluting 0.1mL (0.5mM) stock solution to 2 mL by adding 1.9 mL of respective solvents such as dry acetone, acetonitrile, THF and DMSO.

The final n-Bu_4NF concentration required for the formation of **1.F** was determined both for absorption and emission titrations as shown in following table S1.

Table S1:
Estimated F^-ion concentration required for the formation of **1.F** in each solvent.

Solvents	**Concentration of 1**	**The concentration of F^- ion required for the complete 1.F formation**
Acetone	0.025 mM	1.090 mM
Acetonitrile	0.025 mM	0.234 mM
THF	0.025 mM	0.379 mM
DMSO	0.025 mM	0.306 mM

2.3 UV-Vis absorption titration of 1.F with water

For the UV-Vis absorption study of **1.F** with water, 2 mL solution of **1.F** prepared by using different dry solvents such as acetone, acetonitrile, THF and DMSO, was titrated against the different amount of water (0- 2.594 wt %) at RT

2.4 Fluorescence emission titration of 1.F with water

For the emission study of **1.F** with water, 2 mL solution of **1.F** prepared by using different dry solvents such as acetone, acetonitrile, THF and DMSO, was titrated against the different amount of water (0- 2.594 wt %) at RT.

2.5 Reversibility experiments.

Reversibility experiment of the **1.F** solution in acetonitrile was performed with the alternative addition of water and molecular sieves. For this experiment, approx. 2 gm of activated molecular sieves (4Å pore size) was added to the water spiked solution of **1.F**. The water molecules were removed by activated molecular sieves within few seconds and the solution turned back to **1**. Then fluoride ion (in excess) was again added to the same solution to induce the formation of **1.F** for further water detection. This process was repeated many times.

2.6 Effect of temperature

The effect of temperature on receptor **1.F** in the presence and also in absence of water was studied. UV-Vis absorption spectrum was monitored at 470 nm at a different temperature range (10-80 ◦C) by taking the solution of **1.F** (1 = 0.025 mM and F = 0.234 mM) in acetonitrile.

2.7 Time-dependent study

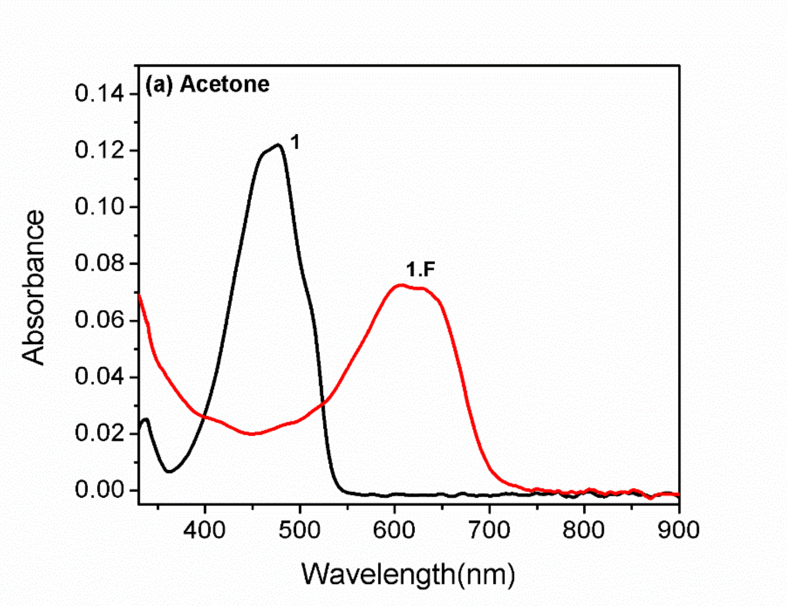
Time-dependent study with water on receptor **1.F** (1 = 0.025 mM and F = 0.234 mM) was performed. UV-Vis absorption and emission spectra in the presence (1.157 wt %) and absence of water at 470 nm and 550 nm, respectively was monitored for 30 minutes at RT.

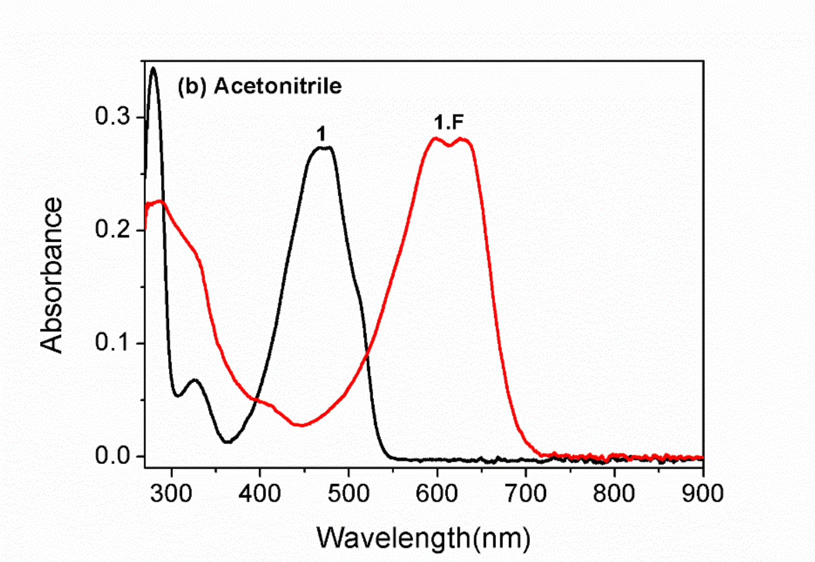
2.8 Test paper preparation

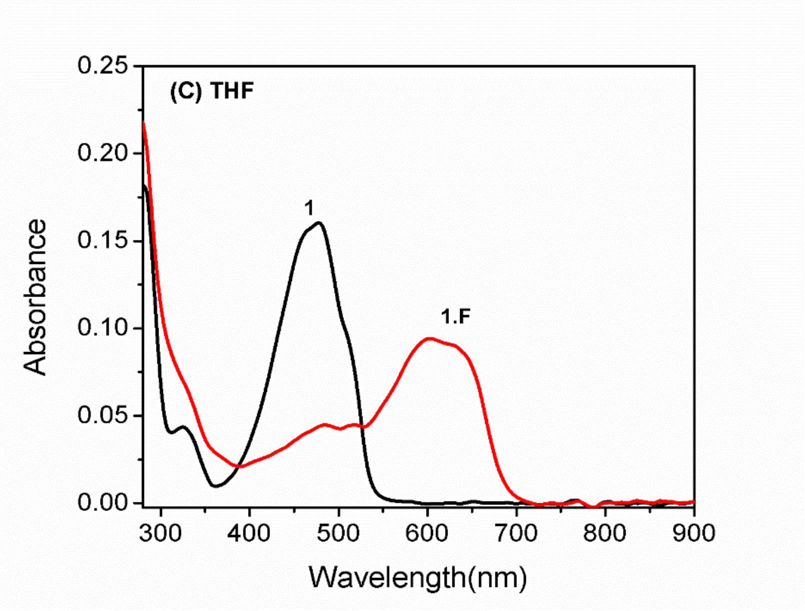
Test paper incorporated with **1.F** was prepared by using cellulose-based filter paper. The filter paper was immersed in the 10 ml solution of **1** (10^{-2} M) with an excess of Fluoride ion in dry acetone for overnight. The wet paper was then allowed to dry at 40 °C under the moisture-free condition. This blue color paper incorporated with **1.F** was used for studies.

2.9 Method for calculating detection limit

The Limit of detection (LOD) was calculated by using formula = (3 x σ)/slope
Where σ = Standard deviation of the blank sample.


(a) Acetone
1
1.F
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Absorbance
400
500
600
700
800
900
Wavelength(nm)


(b) Acetonitrile
1
1.F
0.3
0.2
0.1
0.0
Absorbance
300
400
500
600
700
800
900
Wavelength(nm)


(C) THF
1
1.F
0.25
0.20
0.15
0.10
0.05
0.00
Absorbance
300
400
500
600
700
800
900
Wavelength(nm)

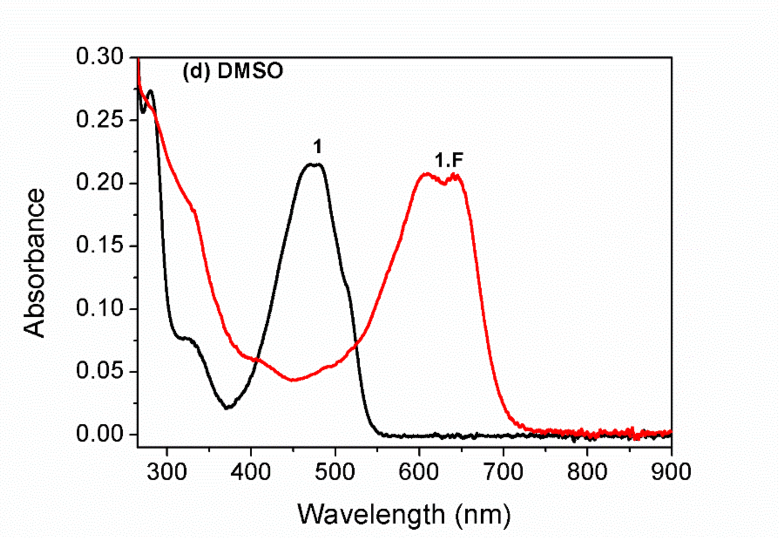
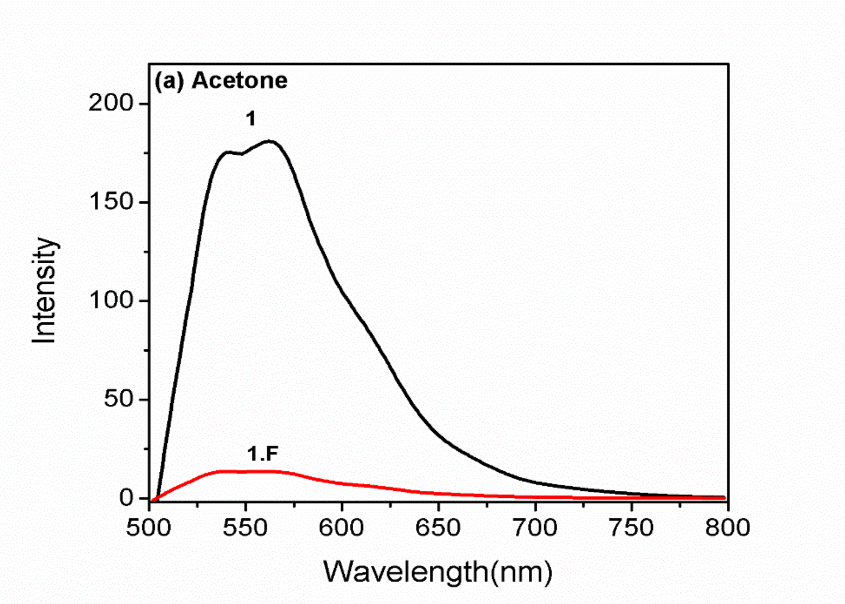


Figure S1: The UV-Vis absorption spectra for **1** (0.025mM) and **1** with Fluoride in (a) acetone (b) acetonitrile (c) THF and (d) DMSO respectively.



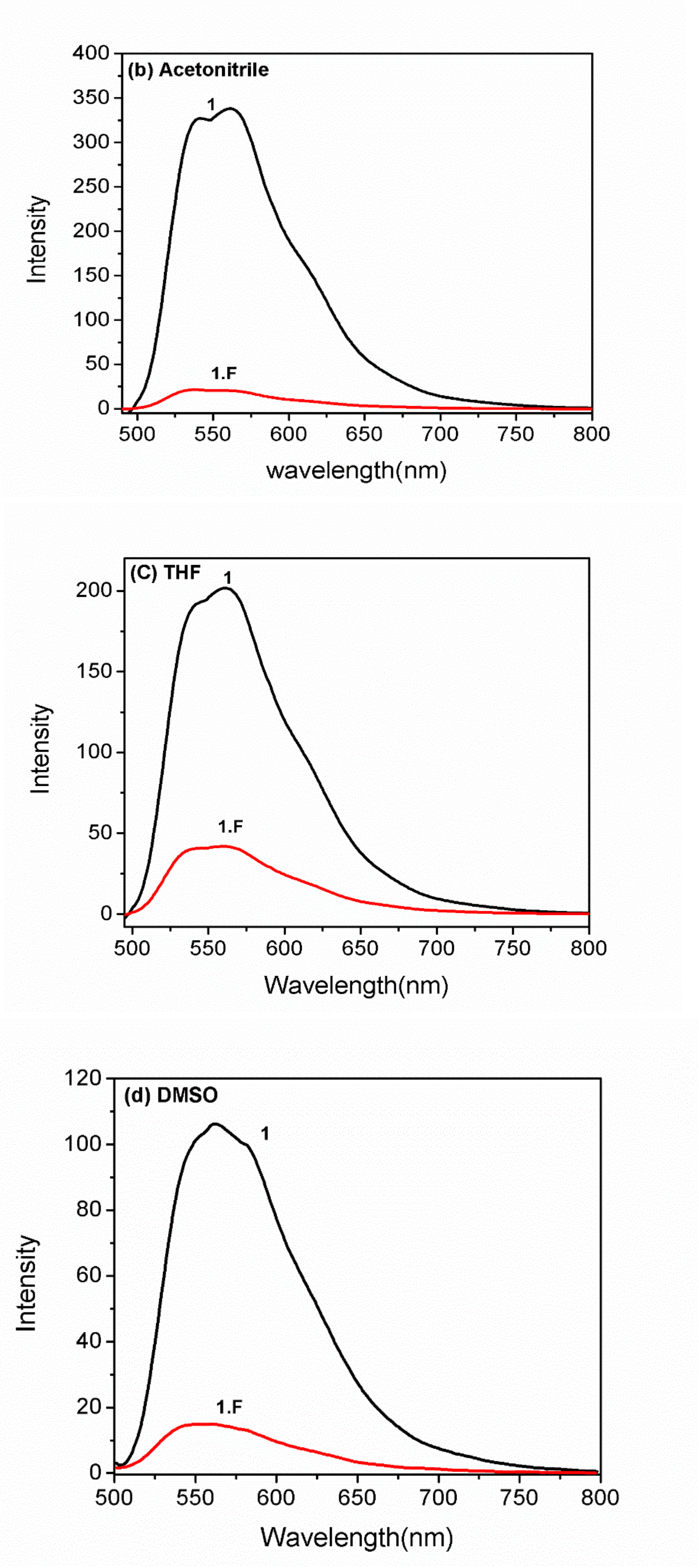
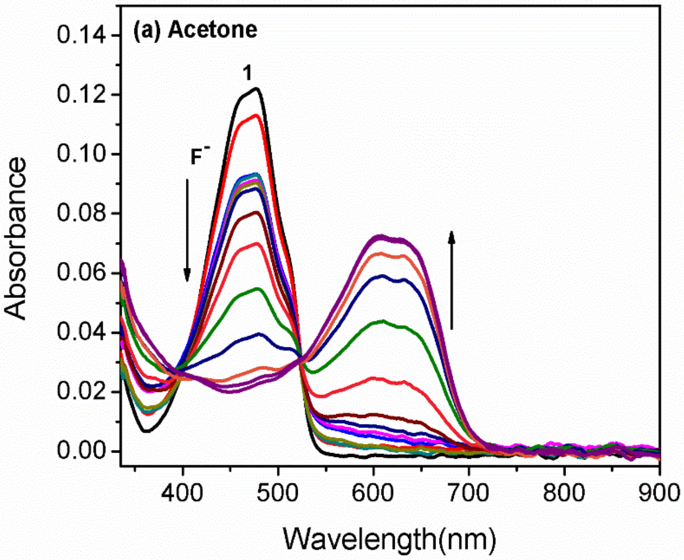
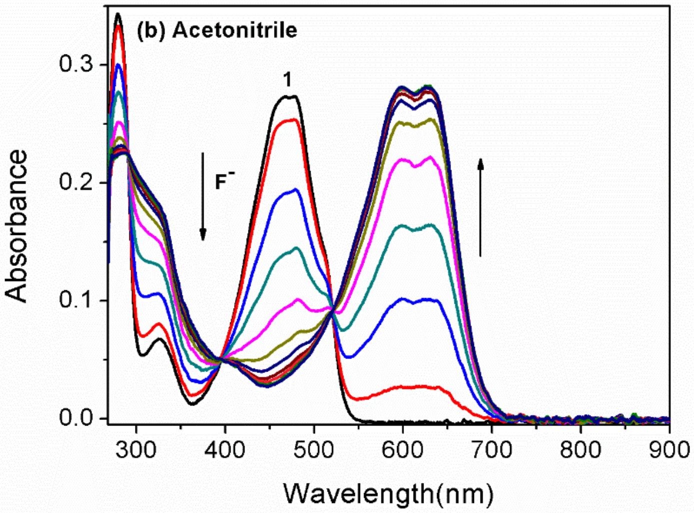
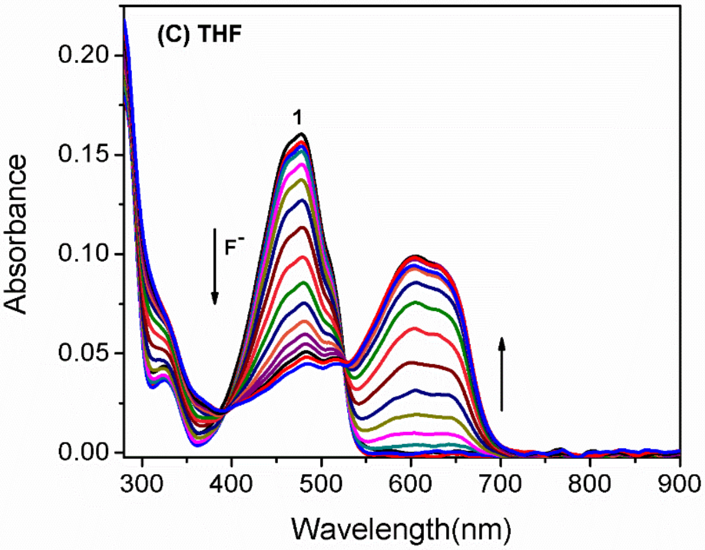


Figure S2: The emission spectra for **1** (0.025mM) and **1** with Fluoride ion in (a) acetone (b) acetonitrile (c) THF and (d) DMSO respectively.


(a) Acetone
1
F-
Absorbance
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
400
500
600
700
800
900
Wavelength(nm)


(b) Acetonitrile
1
F-
Absorbance
0.3
0.2
0.1
0.0
300
400
500
600
700
800
900
Wavelength(nm)



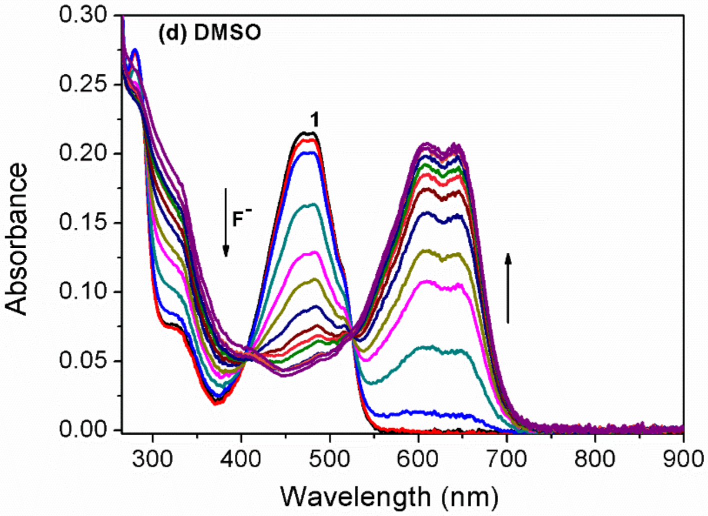
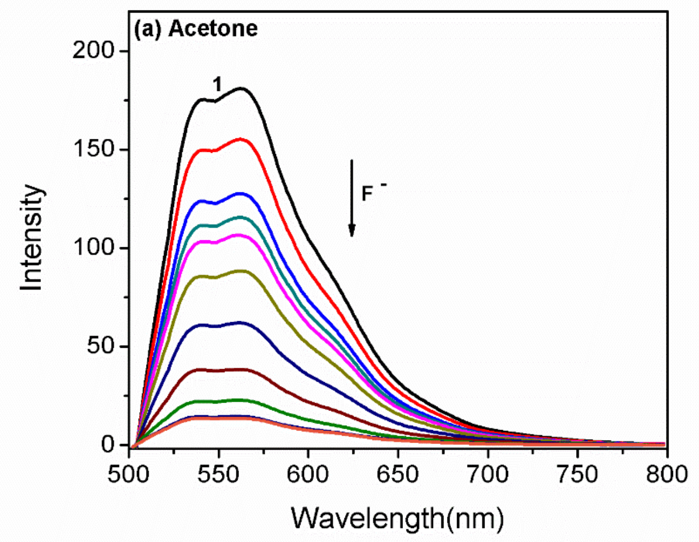
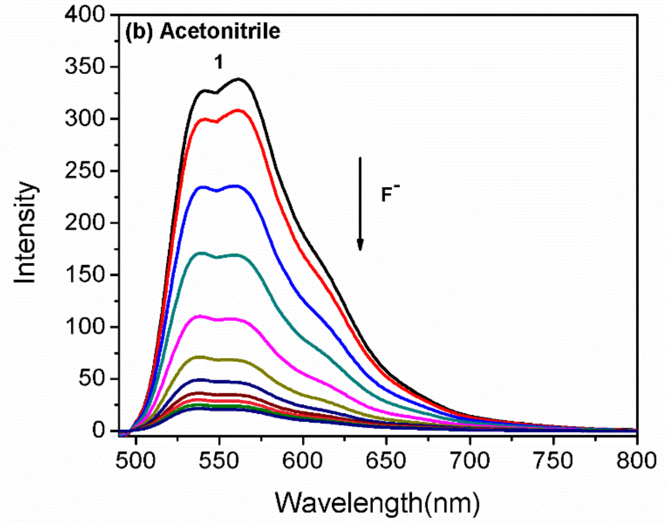
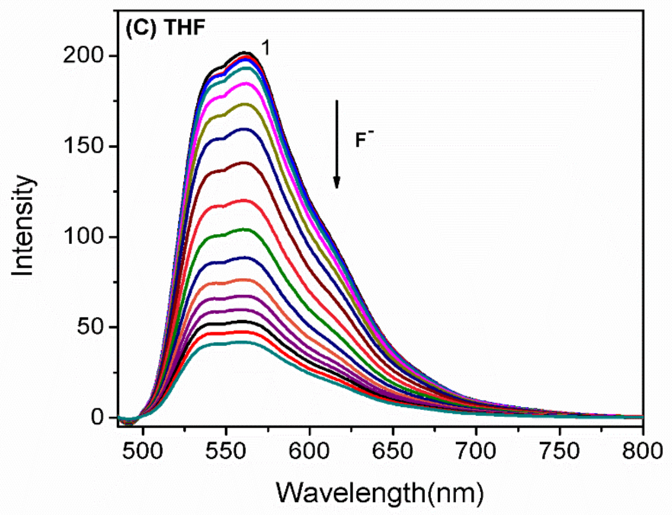


Figure S3: UV-Vis titration for **1** (0.025 mM) in (a) acetone (b) acetonitrile (c) THF and (d) DMSO with different concentration of fluoride [F$^-$] = (a) 0 - 1.09 mM (b) 0 - 0.234 mM (c) 0- 0.379 mM and (d) 0- 0.306 mM respectively.


(a) Acetone
1
F -
Intensity
0
50
100
150
200
500
550
600
650
700
750
800
Wavelength(nm)


(b) Acetonitrile
1
F-
Intensity
0
50
100
150
200
250
300
350
400
500
550
600
650
700
750
800
Wavelength(nm)


(C) THF
1
F-
Intensity
0
50
100
150
200
500
550
600
650
700
750
800
Wavelength(nm)

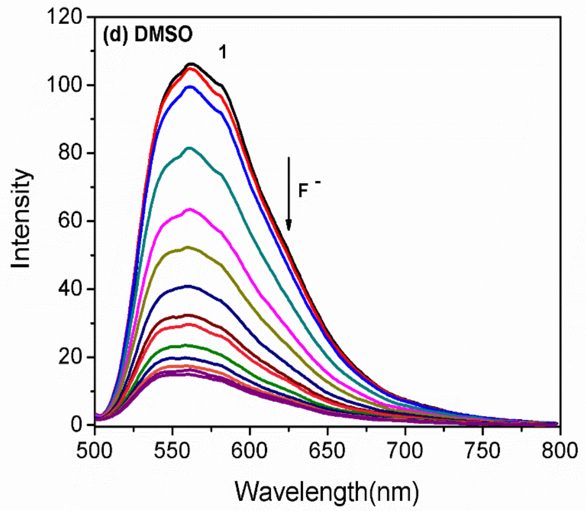
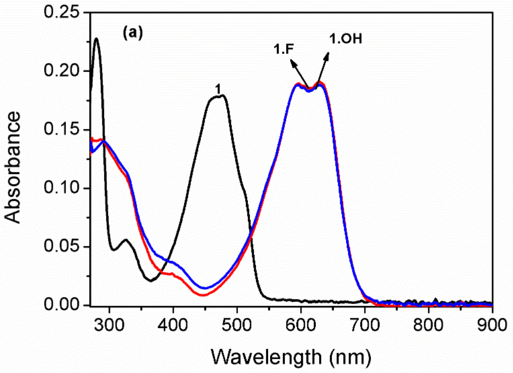


Figure S4: Emission titration for **1** (0.025 mM) in (a) acetone (b) acetonitrile (c) THF and (d) DMSO with different concentration of fluoride [F$^-$] = (a) 0 - 1.09mM (b) 0 - 0.234mM (c) 0- 0.379mM and (d) 0- 0.306mM respectively.



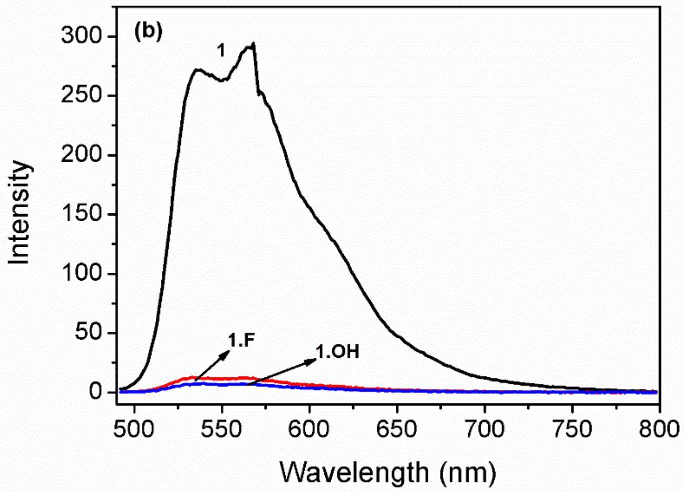


Figure S5: (a) UV-Vis spectra and (b) emission spectra of **1** (0.025mM) with [(nBu$_4$N)]OH and [(nBu$_4$N)]F in acetonitrile.

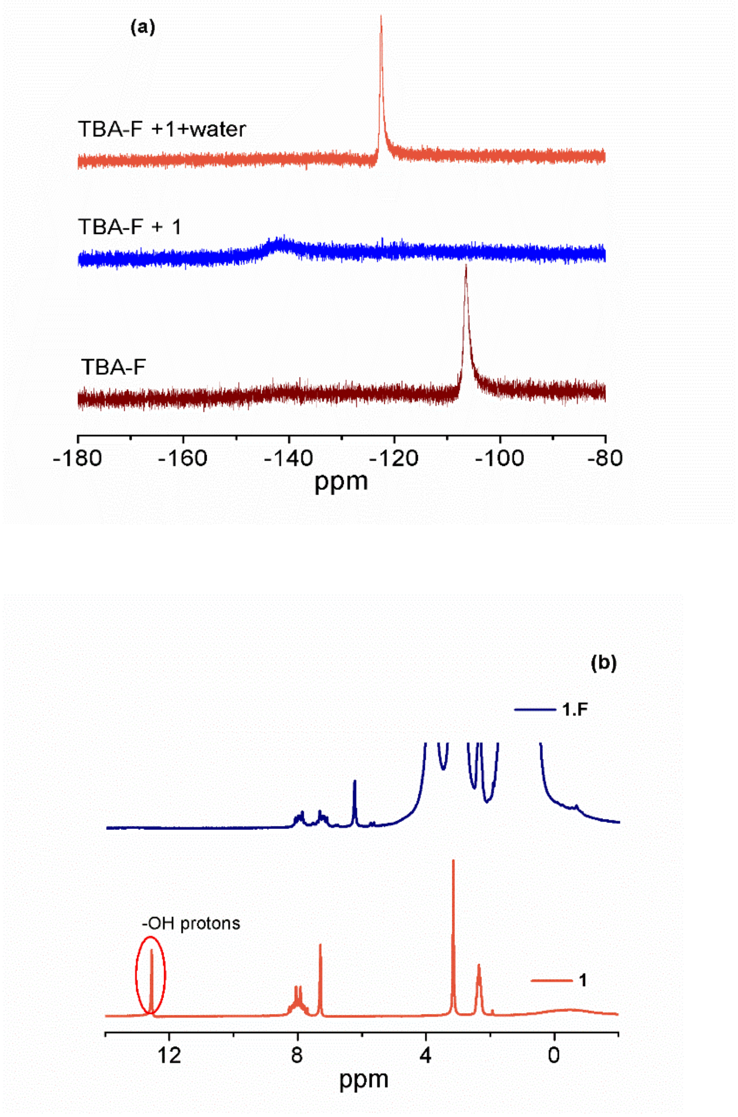
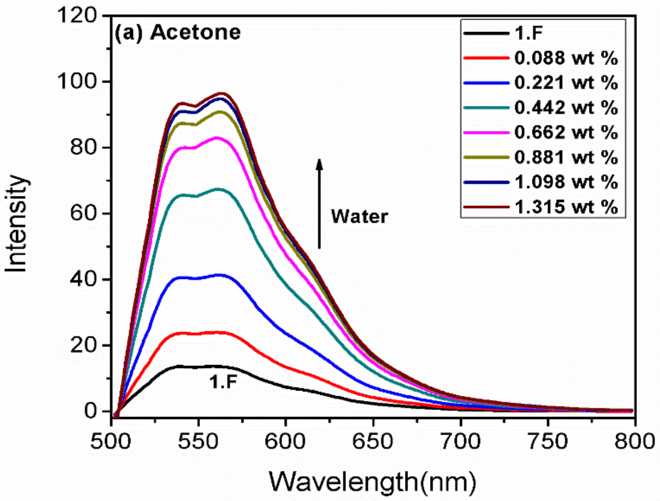
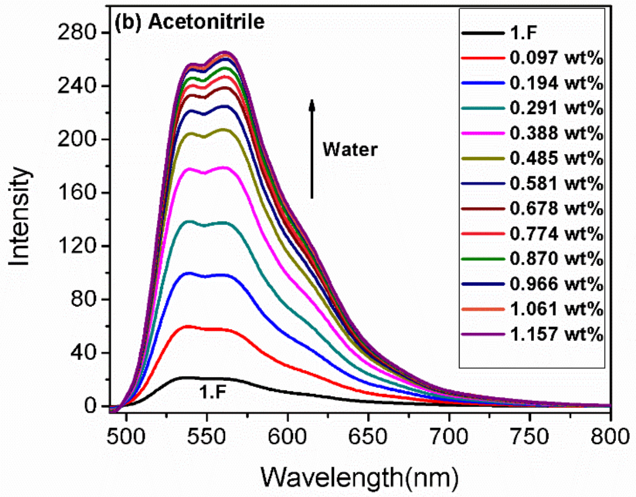
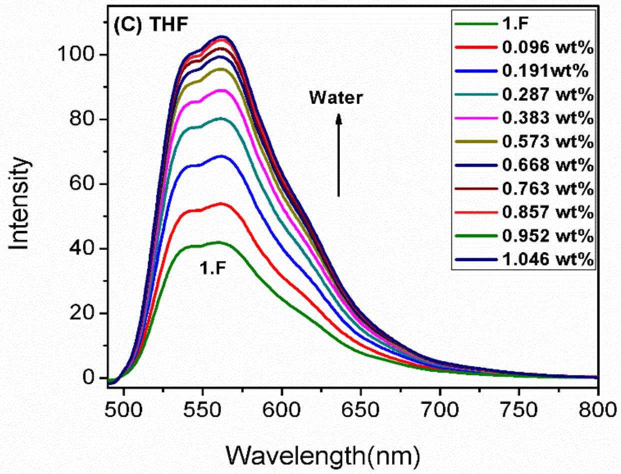


Figure S6: (a) Partial ^{19}F NMR spectrum of [(nBu$_4$N)]F (199 mM), **1**(20 mM) + fluoride ions and **1**(20 mM) +fluoride ions + 35 % water in DMSO-d$_6$. (b) Partial ^{1}H NMR spectrum of **1** (20 mM) and **1** with excess fluoride in DMSO-d$_6$


(a) Acetone
Intensity
Wavelength(nm)
0
20
40
60
80
100
120
500
550
600
650
700
750
800
1.F
0.088 wt %
0.221 wt %
0.442 wt %
0.662 wt %
0.881 wt %
1.098 wt %
1.315 wt %
Water
1.F


(b) Acetonitrile
Intensity
Wavelength(nm)
0
40
80
120
160
200
240
280
500
550
600
650
700
750
800
1.F
0.097 wt%
0.194 wt%
0.291 wt%
0.388 wt%
0.485 wt%
0.581 wt%
0.678 wt%
0.774 wt%
0.870 wt%
0.966 wt%
1.061 wt%
1.157 wt%
Water
1.F


(C) THF
Intensity
Wavelength(nm)
0
20
40
60
80
100
500
550
600
650
700
750
800
1.F
0.096 wt%
0.191wt%
0.287 wt%
0.383 wt%
0.573 wt%
0.668 wt%
0.763 wt%
0.857 wt%
0.952 wt%
1.046 wt%
Water
1.F

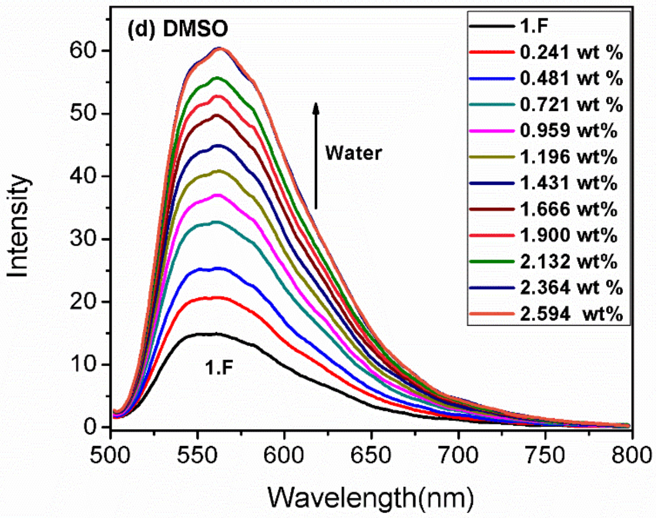


Figure S7: Emission titration for (a) **1.F** in acetone with 0-1.315 wt % of water content (b) **1.F** in acetonitrile with 0-1.157 wt % of water content (c) **1.F** in THF with 0-1.046 % of water content (d) **1.F** in DMSO with 0 -2.594 wt % of water content.

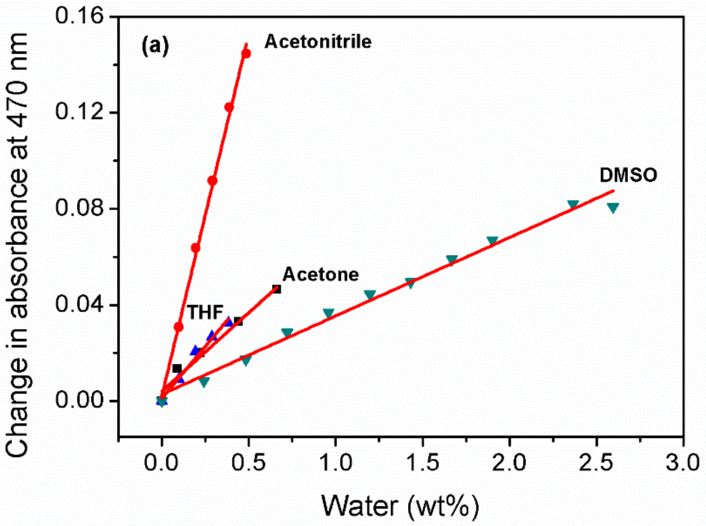


Figure S8: Calibration Curve of **1.F** with water in acetone, acetonitrile, THF and DMSO in a low-water-content region below 3.0 wt%

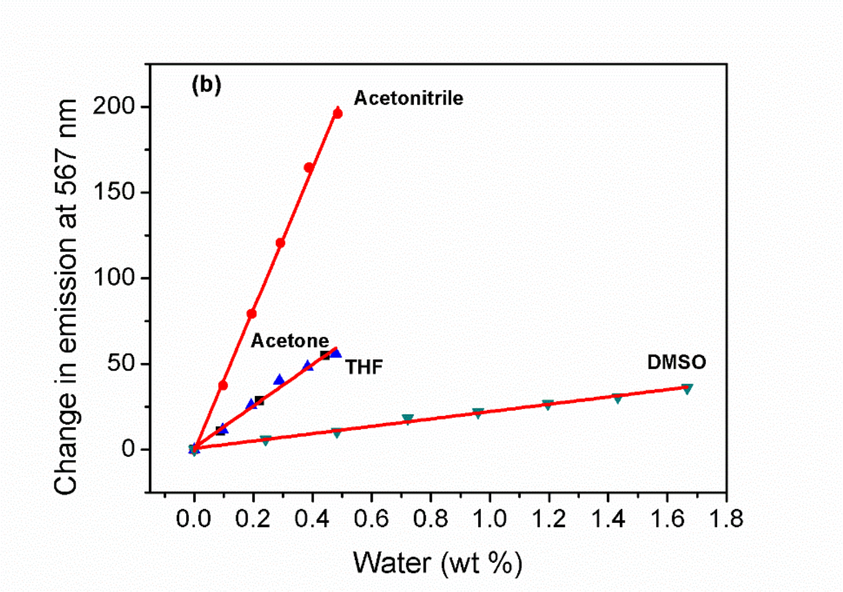
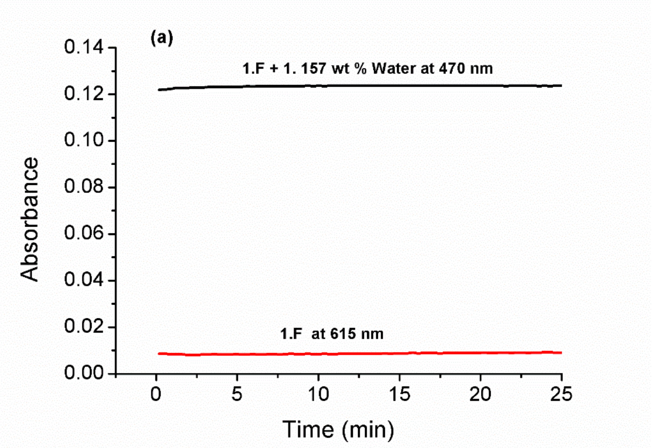


Figure S9: Calibration Curve of **1.F** with water in acetone, acetonitrile, THF and DMSO in a low-water-content region below 1.8 wt%



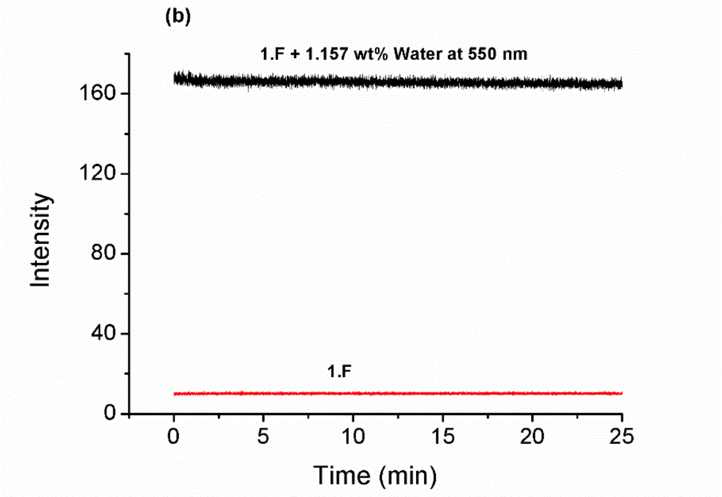


Figure S10: Time dependent (a) colorimetric change (b) fluorogenic change of **1.F** (0.025mM) with 1.157 wt % of water in acetonitrile.

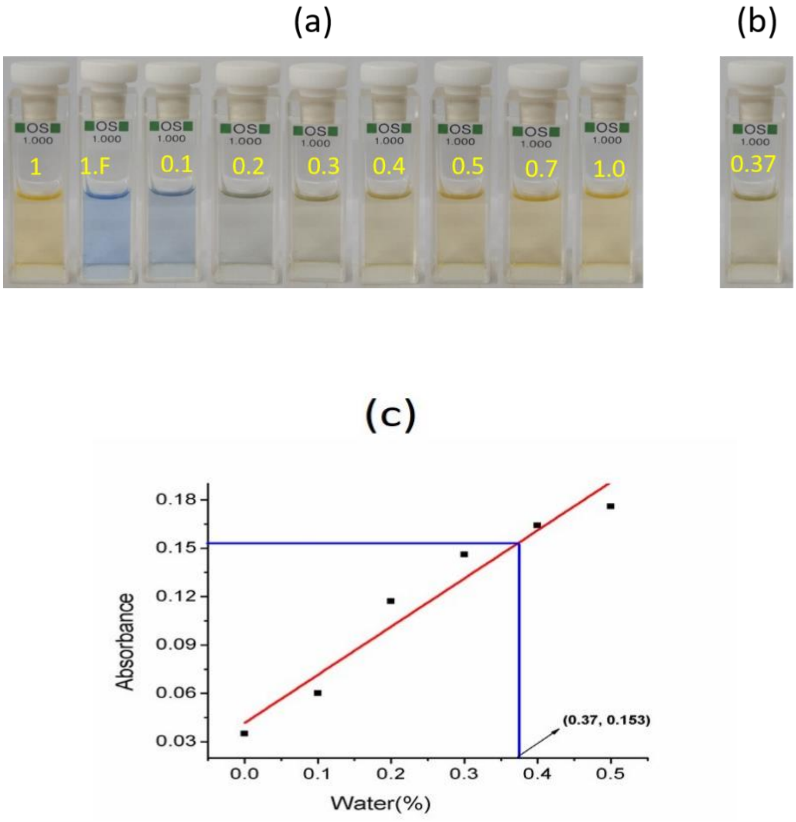


Figure S11: (a) **1.F** (0.025mM) solutions with spiked water (wt %) at 0.1, 0.2, 0.3, 0.4, 0.5, 0.7 and 1.0 respectively in acetonitrile. (b) Determination of unknown quantity of water from **1.F** solution. (c) Calibration curve for the determination of unknown quantity for water (wt %) present in the solution of **1.F** in acetonitrile.

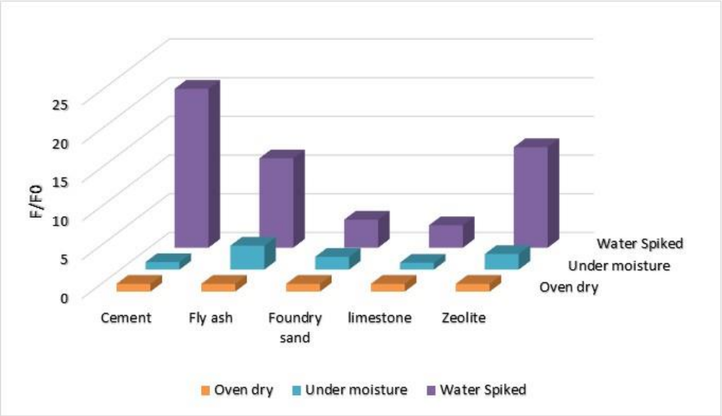


Figure S12: Change in emission intensities of **1.F** in presence of various raw building materials in dry acetonitrile [**1.F**] = 0.025mM.

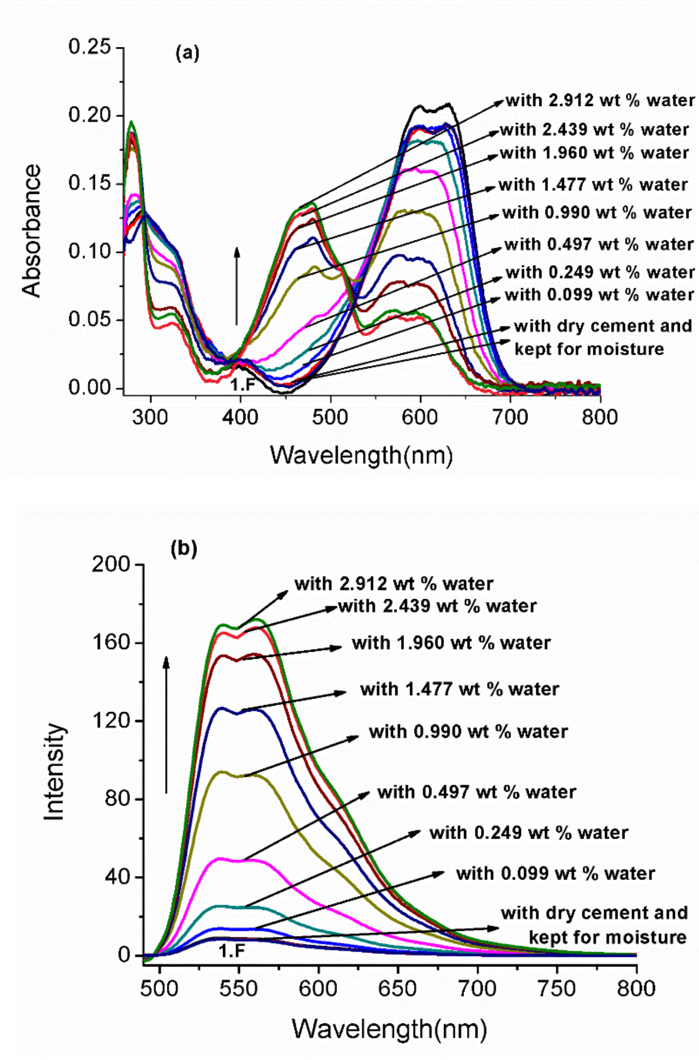


Figure S13: (a) Absorption spectra of **1.F** (0.025mM) with oven dry cement spiked with different % of water and placed under moisture for 1hr at RT in acetonitrile. (b) emission spectra of **1.F** (0.025mM) with oven dry cement spiked with different % of water and placed under moisture for 1hr at RT in acetonitrile.

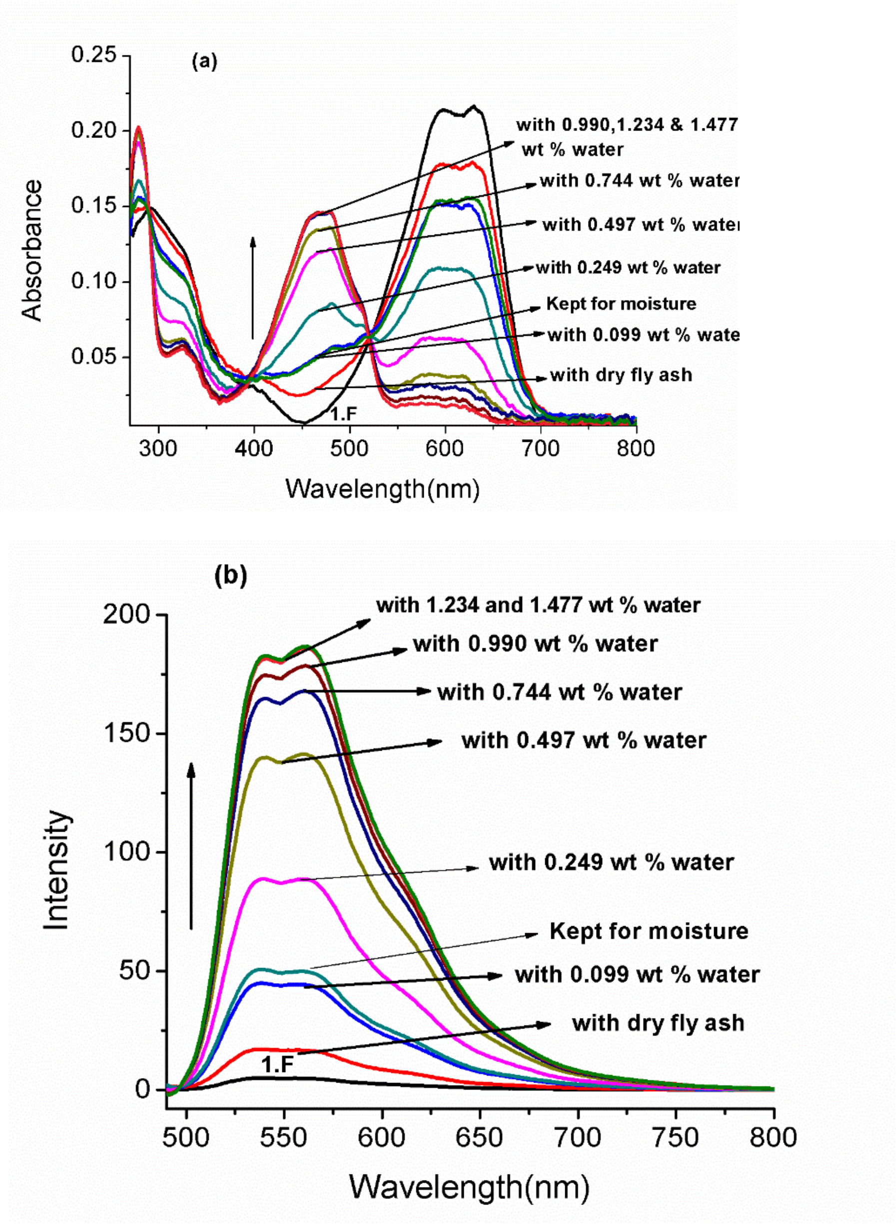


Figure S14: (a) Absorption spectra of **1.F** (0.025mM) with oven dry flyash spiked with different % of water and placed under moisture for 1hr at RT in acetonitrile. (b) emission spectra of **1.F** (0.025mM) with oven dry flyash spiked with different % of water and placed under moisture for 1hr at RT in acetonitrile.

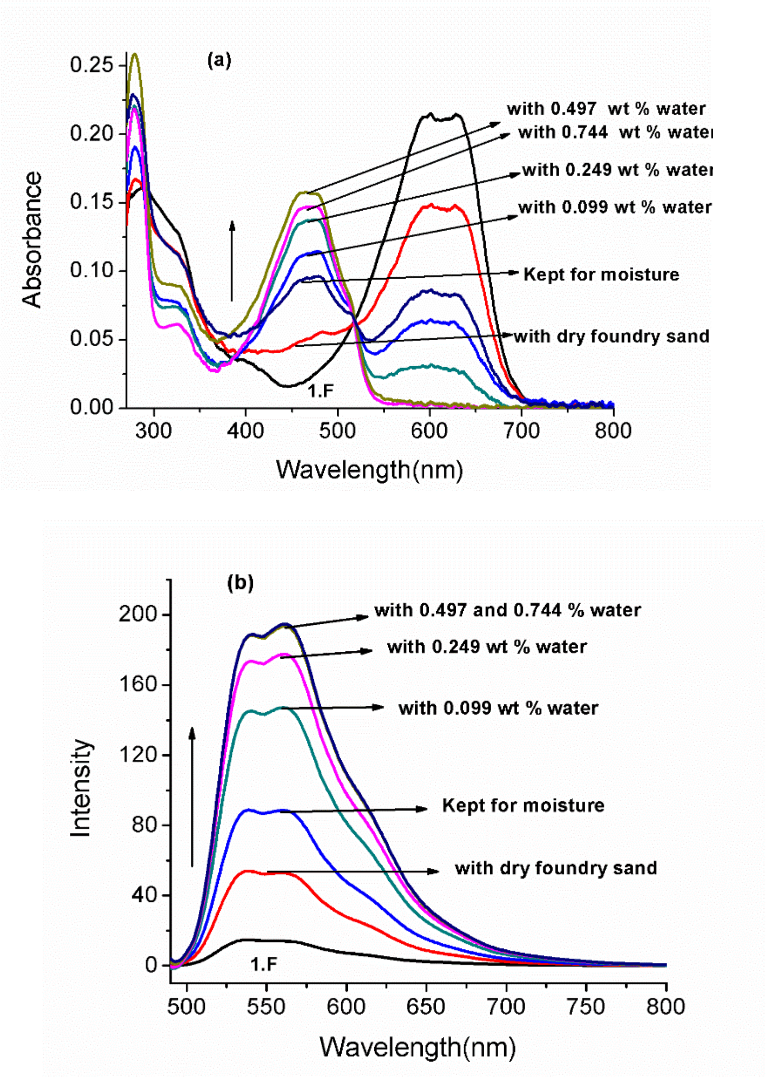


Figure S15: (a) Absorption spectra of **1.F** (0.025mM) with oven dry foundry sand spiked with different % of water and placed under moisture for 1hr at RT in acetonitrile. (b) emission spectra of **1.F** (0.025mM) with oven dry foundry sand spiked with different % of water and placed under moisture for 1hr at RT in acetonitrile.

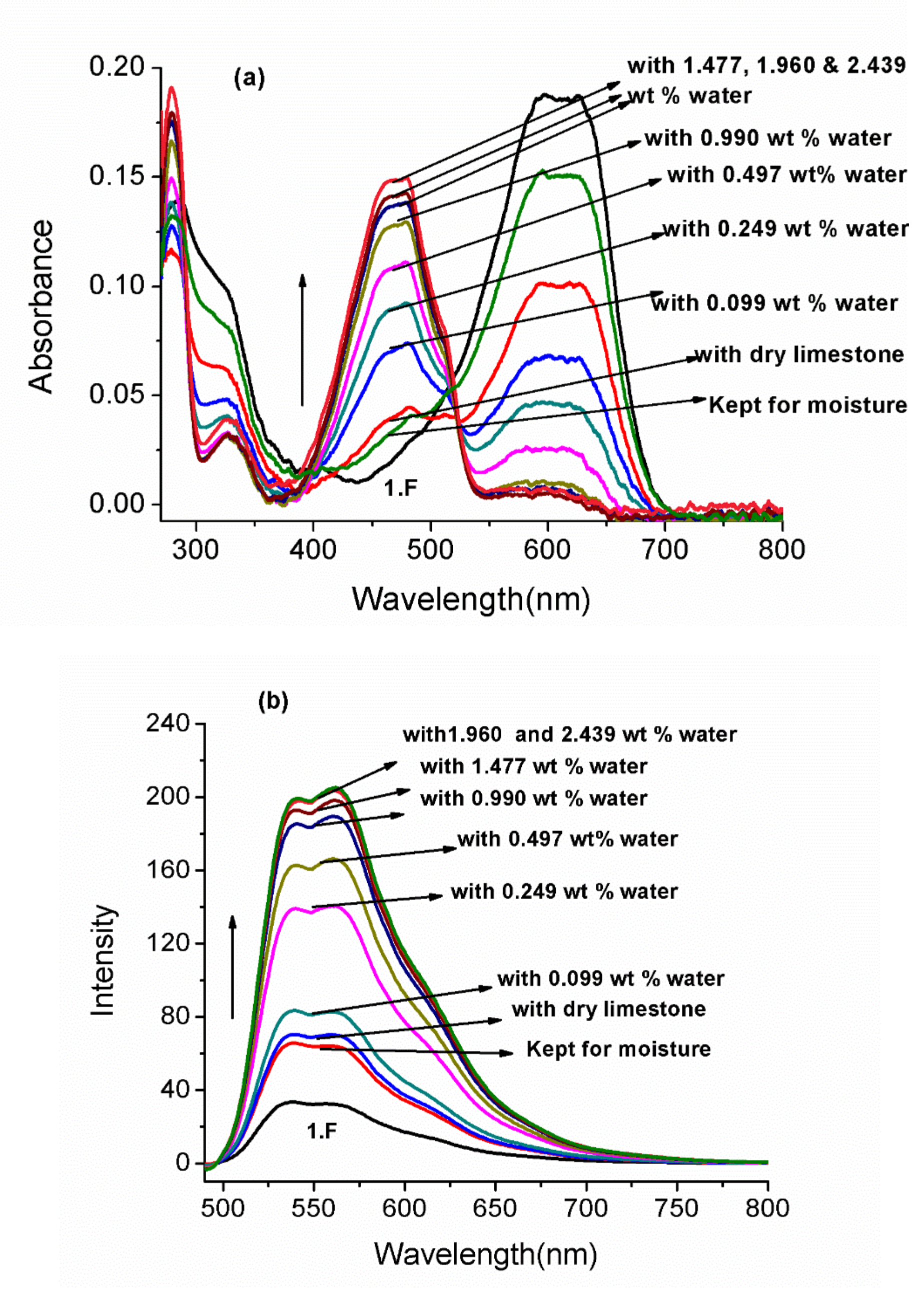
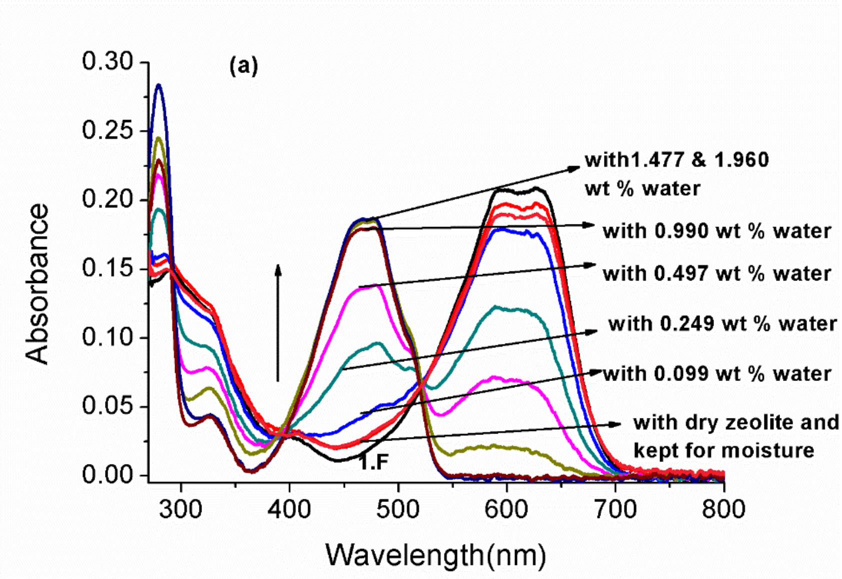


Figure S16: (a) Absorption spectra of **1.F** (0.025mM) with oven dry lime stone spiked with different % of water and placed under moisture for 1hr at RT in acetonitrile. (b) emission spectra of **1.F** (0.025mM) with oven dry lime stone spiked with different % of water and placed under moisture for 1hr at RT in acetonitrile.



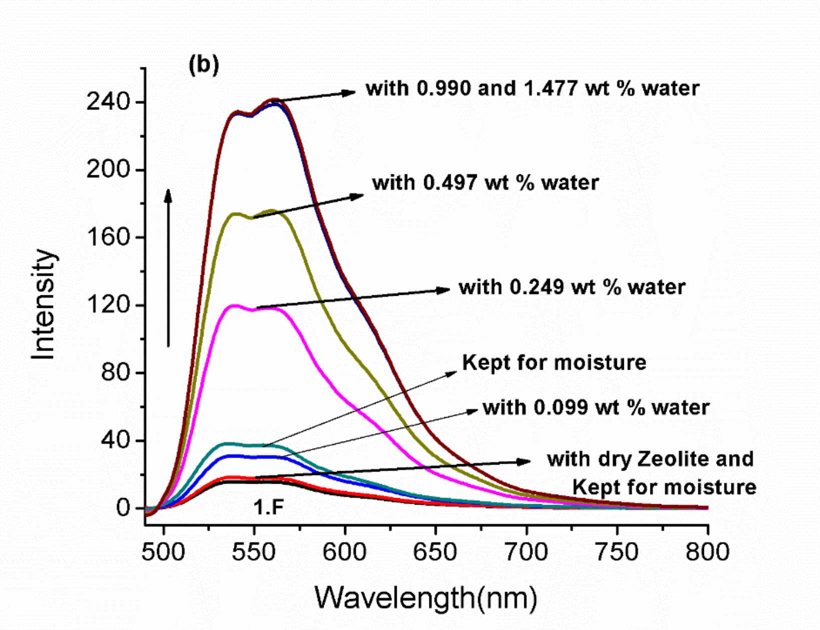


Figure S17: (a) Absorption spectra of **1.F** (0.025mM) with oven dry zeolite spiked with different % of water and placed under moisture for 1hr at RT in acetonitrile. (b) Emission spectra of **1.F** (0.025mM) with oven dry zeolite spiked with different % of water and placed under moisture for 1hr at RT in acetonitrile.

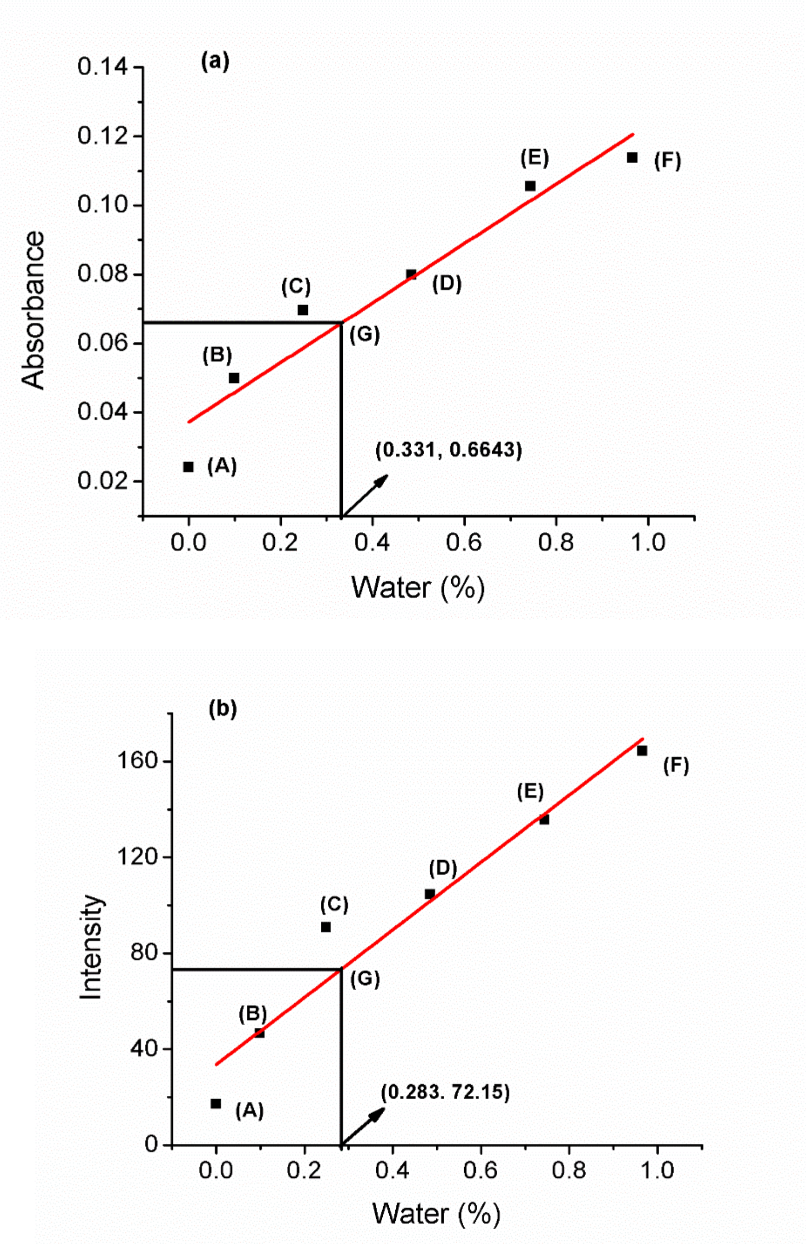


Figure S18: (a) Absorption and (b) emission study for the determination of the unknown quantity of water % present in flyash after placed it under moisture during conduct experiment.
Here
A: **1.F** (0.025mM) + 50 mg oven dry fly ash taken in acetonitrile.
B: **1.F** (0.025mM) + 50 mg fly ash with 0.099 wt % water spiked in acetonitrile.
C: **1.F** (0.025mM) + 50 mg fly ash with 0.249 wt % water spiked in acetonitrile.
D: **1.F** (0.025mM) + 50 mg fly ash with 0.485 wt % water spiked in acetonitrile
E: **1.F** (0.025mM) + 50 mg fly ash with 0.744 wt % water spiked in acetonitrile
F: **1.F** (0.025mM) + 50 mg fly ash with 0.966 wt % water spiked in acetonitrile
G: approx. 0.3 % of water examined flyash after kept under moisture.

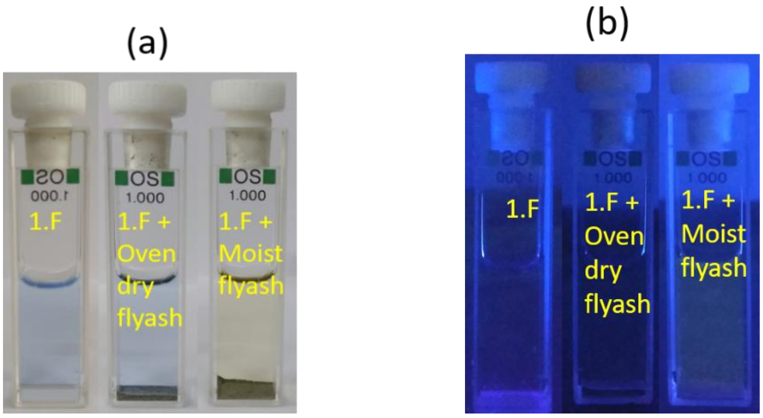


Figure S19: (a) Color change (b) Fluorescence response of **1.F** (0.025mM) with flyash in acetonitrile observed through naked eye and under UV light respectively.

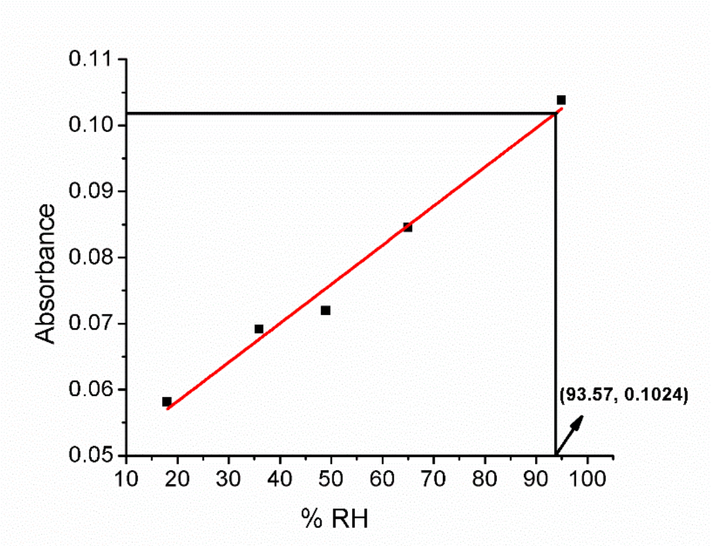


Figure S20: Calibration curve for the determination of the unknown quantity of moisture (93.57% RH) present in the solution of **1.F** (0.025mM) in dry acetonitrile kept in open environment.