# Continuous multi-channel sensing of volatile acid and organic amine gases using a fluorescent self-assembly system

Xinhua Cao[a, b*], Qianqian Ding[a], Yiran Li[a], Aiping Gao[a], Xueping Chang[a]

[a]College of Chemistry and Chemical Engineering &Henan Province Key laboratory of Utilization of Non-metallic Mineral in the South of Henan, Institute for Conservation and Utilization of Agro-bioresources in Dabie Mountains，Xinyang Normal University, Xinyang 464000, China

[b]State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, P.R. China

*Email - caoxhchem@163.com

**Synthesis of gelator 1**
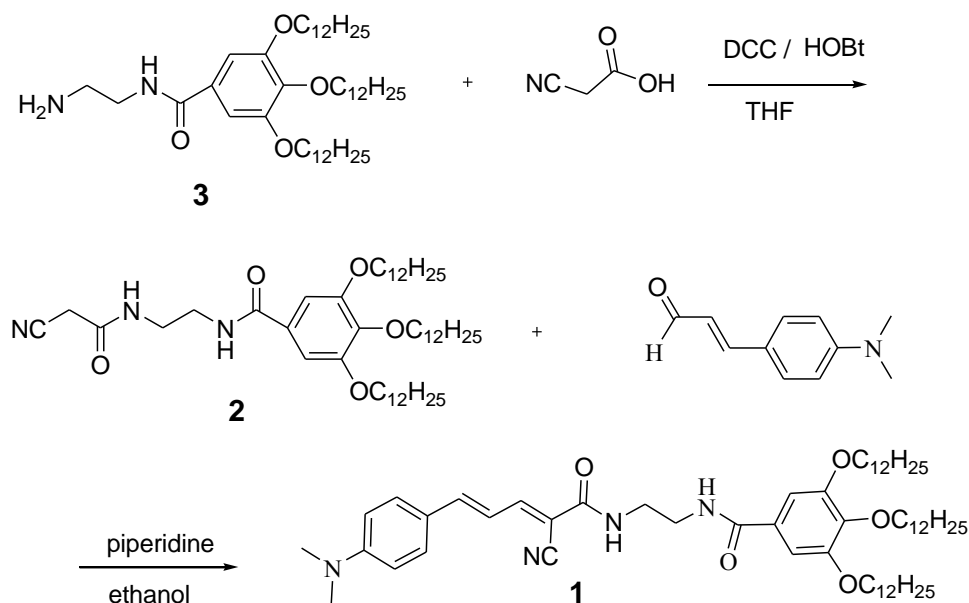


**Compound 1** was synthesized according to literature 1.

**Synthesis of 2**: Compound **3** (1.5 g, 2.09 mmol), cyanoacetic acid (0.18 g, 2.09 mmol), N,N'-dicyclohexylcarbodiimide (1.16 g, 5.65mmol), 1-hydroxybenzotriazole (0.76 g, 5.65 mmol) were mixed in anhydrous THF (80 mL). The reaction mixture was stirred for 12 h under a nitrogen atmosphere at room temperature. After the reaction was over, the solvent was removed under reduced pressure and the residue was subjected to column chromatography (dichloromethane/methanol: 60/1, v/v as eluent) on silica gel to give **2** as a white powder. Yield 83 %；^{1}HNMR (600 MHz, CDCl$_3$): 7.15 (s, 1H), 6.97 (s, 2H), 6.66 (s, 1H), 4.01(m, 6H), 3.62 (d, $J$ = 4.2 Hz, 2H), 3.55 (d, $J$ = 4.2 Hz, 2H), 3.37 (s, 2H), 1.82-1.71 (m, 6H), 1.47 (m, 6H), 1.33-1.26

(m, 45H), 0.88 (t, $J$ = 7.2 Hz, 9H), $^{13}$CNMR (150 MHz, CDCl$_3$): 162.5, 152.7, 144.0, 105.7, 32.0, 29.7, 29.5, 26.2, 22.8, 14.2. HRMS calculated for C$_{48}$H$_{86}$N$_3$O$_5$ [M+H]$^+$ 784.6567, found: 784.6582.

**Synthesis of 1**: Compound **2** (1.0 g, 1.25 mmol), 4-dimethylaminocinnamaldehyde (0.22 g, 1.25 mmol) and piperidine (catalytic amount) were added to ethanol (30 mL). The above solution was heated to refluxing overnight. After the reaction was over, the large amount of precipitate were appeared, and filtered. The filter cake was washed with ethanol for three times. The light red product **1** was obtained with the yield of 65 %; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J$ = 11.4 Hz, 1H), 7.47 (d, $J$ = 8.4 Hz, 2H), 7.14 (d, $J$ = 15.0 Hz, 1H), 7.10 (s, 1H), 7.81 (t, $J$ = 6.0 Hz, 1H), 7.04 (d, $J$ = 12.0 Hz, 1H), 7.00 (s, 2H), 6.74 (s, 3H), 4.02 (t, $J$ = 6.6 Hz, 4H), 3.96 (t, $J$ = 6.6 Hz, 2H), 3.65-3.62 (m, 4H), 3.07 (s, 6H), 1.82-1.70 (m, 6H), 1.48-1.42 (m, 6H), 1.33-1.23 (m, 45H), 1.44-1.25 (m, 30H), 0.86 (t, $J$ = 7.2 Hz, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 168.0, 154.7, 153.1, 132.1, 130.7, 118.2, 116.8, 112.0, 105.6, 73.6, 69.2, 40.2, 32.0, 29.8, 29.7, 29.6, 29.5, 26.3, 26.2, 22.8, 14.2; HRMS calculated for C$_{59}$H$_{97}$N$_4$O$_5$ [M+H]$^+$ 941.7459, Found: 941.7443.
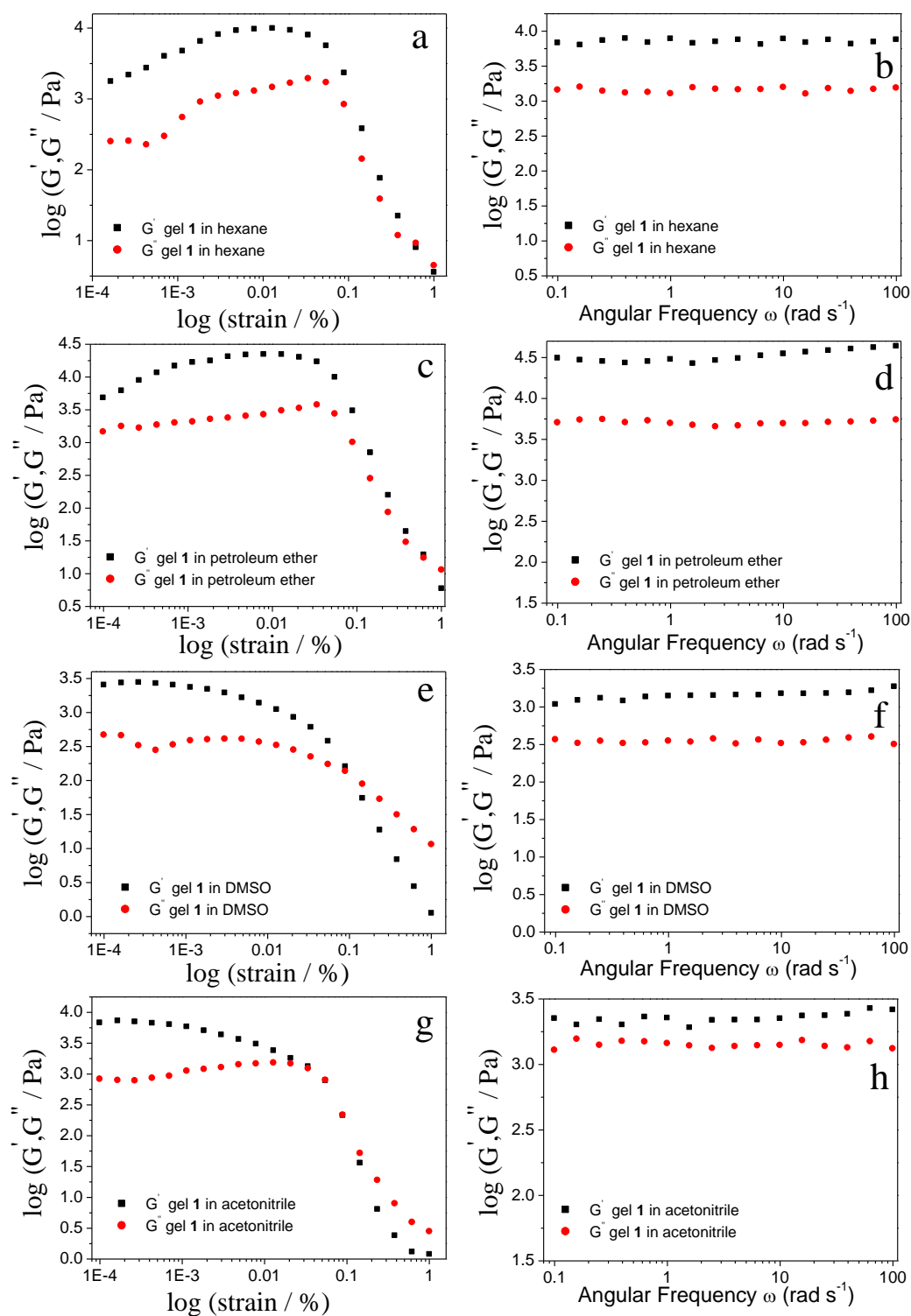
**Fig. S1**. Dynamic oscillatory data for gels **1** in hexane, petroleum ether, DMSO and acetonitrile at the CGC at 20 ºC: a) strain sweep of the gels at a frequency of 6.28 rad s⁻¹; b) frequency sweep of the gels at a strain of 0.01 %.
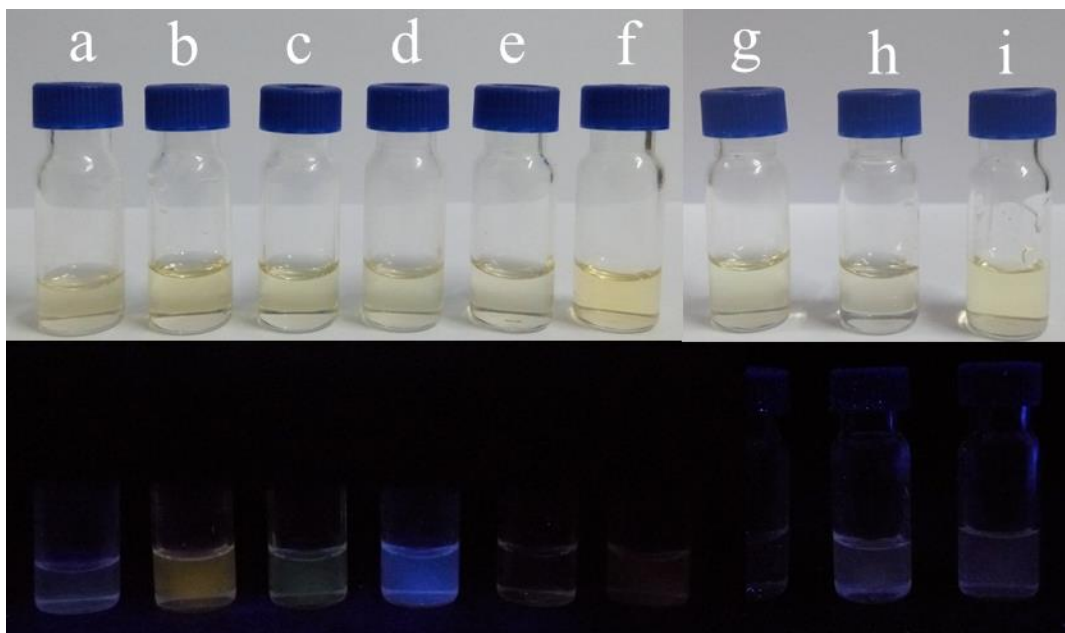
**Fig. S2** Visual changes in color for compound **1** in different solvents (10⁻⁵ M)： a) for CH₂Cl₂; b) for DMF; c) for THF; d) for acetate ether; e) for hexane; f) for methanol; g) for petroleum ether; h) for DMSO and i) for acetonitrile. The upper and lower were under daylight and 365 nm UV lamp, respectively.
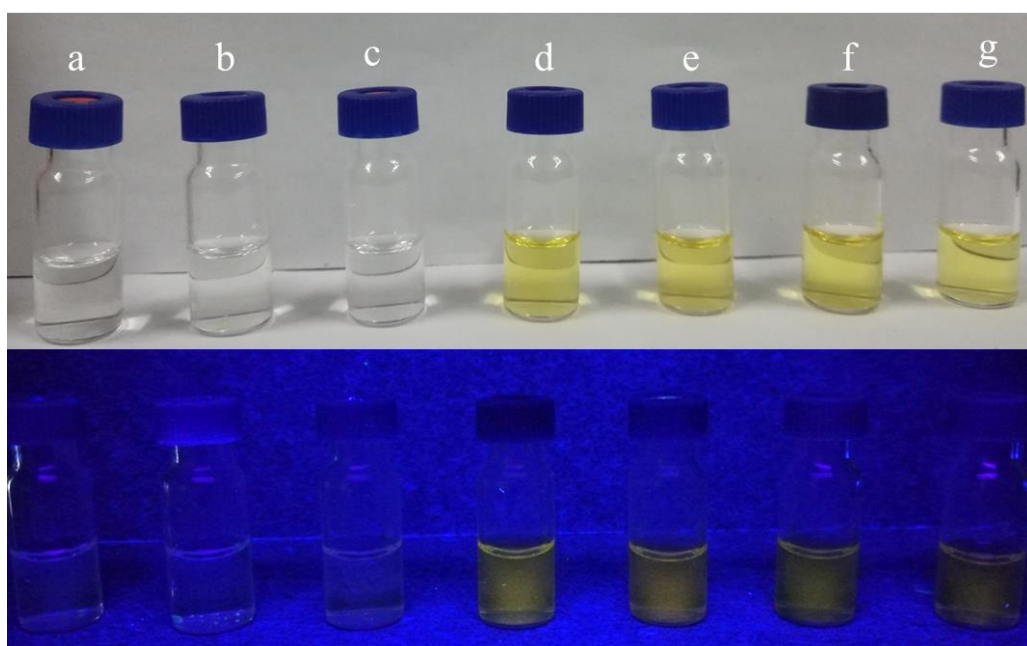


**Fig. S3** Visual changes in color for compound **1** in acetonitrile solvents (10⁻⁴ M) with addition of different acid (1.0

eq.)： a) for TFA; b) for H₂SO₄; c) for HCl; d) for solution **1**; e) for propionic acid; f) for acetic acid; g) for formic

acid. The upper and lower were under daylight and 365 nm UV lamp, respectively.

## Association constant (K) for compound 1 and TFA

The reaction formulation of 1 to TFA can be written as Eq. 1 with the 1:1 ratio, Where B and A

stand for **1** and TFA, respectively.



**Fig. S2** Visual changes in color for compound **1** in different solvents ($10^{-5}$ M)： a) for $CH_2Cl_2$; b) for DMF; c) for THF; d) for acetate ether; e) for hexane; f) for methanol; g) for petroleum ether; h) for DMSO and i) for acetonitrile. The upper and lower were under daylight and 365 nm UV lamp, respectively.



**Fig. S3** Visual changes in color for compound **1** in acetonitrile solvents ($10^{-4}$ M) with addition of different acid (1.0

eq.)： a) for TFA; b) for $H_2SO_4$; c) for HCl; d) for solution **1**; e) for propionic acid; f) for acetic acid; g) for formic

acid. The upper and lower were under daylight and 365 nm UV lamp, respectively.

## Association constant (K) for compound 1 and TFA

The reaction formulation of 1 to TFA can be written as Eq. 1 with the 1:1 ratio, Where B and A

stand for **1** and TFA, respectively.

$$B + A \underset{\longleftarrow}{\overset{K}{\rightleftharpoons}} BA \qquad \text{Eq.1}$$

Therefore, association constant K at room temperature can be determined as the Eq. 2.

$$K = \frac{[BA]_e}{[B]_e\,[A]_e} = \frac{[BA]_e}{([B]_s - [BA]_e)\,([B]_s - [BA]_e)} \qquad \text{Eq.2}$$

Where, [BA] stands for the concentration of the complex; [B] stands for the concentration of **1**; [A] stands for the concentration of **A**; under script e, s stand for states at equilibrium and the beginning, respectively.

$$[BA]_e = \frac{\triangle F_{558\ nm}}{\varepsilon} \qquad \text{Eq.3}$$

Where $\triangle F_{558nm}$ is the fluorescence emission change (Figure 8a), $\varepsilon$ is the illumine coefficient of

complex. Therefore, the association constant (K) of **1** to TFA with the ratio of [TFA]/[**1**] ≤1 and

the illumine coefficient $\varepsilon$ are determined by the fitting of experimental data in Figure 8a by using

equation 4.

$$Y = \frac{x}{K[B]_s\,\varepsilon} + \frac{1}{[B]_s\,\varepsilon} \qquad \text{Eq.4}$$

The two variables (1 / [I$_0$-I]) Vs 1 / [TFA]) were fit very well with the linear fitting: Y = 3.64641E-4 + 5.32298E-9x (y = A + Bx). K was calculated as $6.85 \times 10^4$ M$^{-1}$ according to Eq. 4.



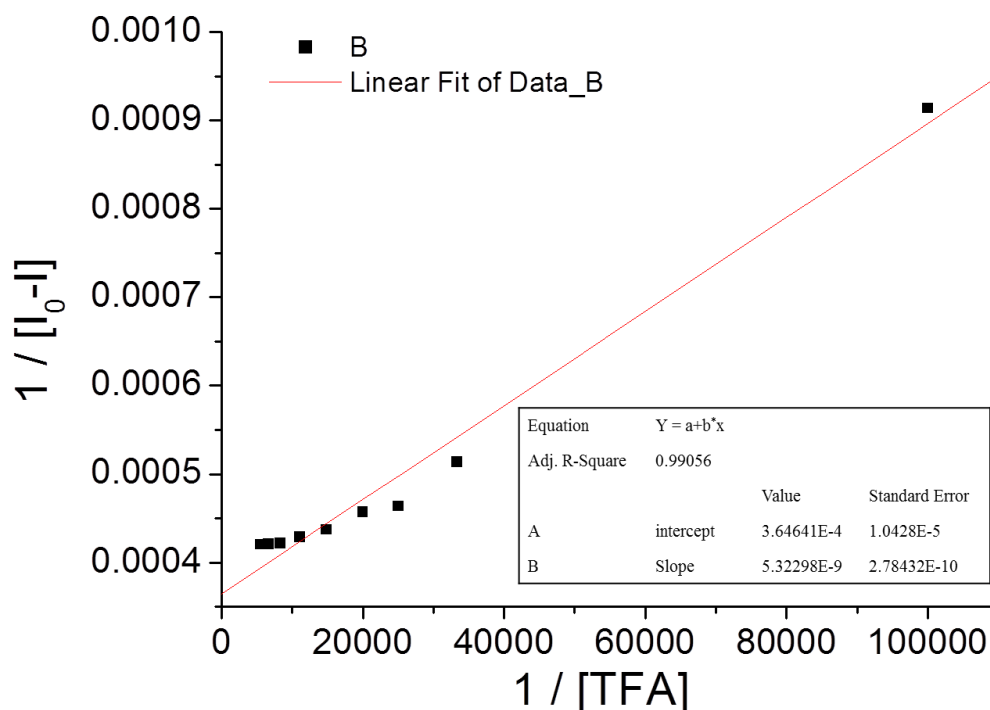| Equation | Y = a+b*x | |
|---|---|---|
| Adj. R-Square | 0.99056 | |
| | Value | Standard Error |
| A | intercept | 3.64641E-4 | 1.0428E-5 |
| B | Slope | 5.32298E-9 | 2.78432E-10 |

**Fig. S4** The linear fitting curve of fluorescence emission change of **1** with the addition of TFA.

## Limit of detection calculation

**Table S1** Detection limit of compound **1** toward TFA in acetonitrile by fluorescence intensity changes at 558 nm

| n | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|----|----|
| Intensity (Xn) | 173.5 | 173.4 | 173.1 | 173.1 | 173.1 | 173.6 | 173.5 | 173.8 | 173.6 | 173.3 | 173.5 |

$X_{average} = 173.41$  $\sigma_{wb} = sqrt(\sum(X_n - X_{average})^2/n) = 0.049918$

The detection limit: $[TFA] = 3\sigma/b = 1.03 \times 10^{-8}$ M
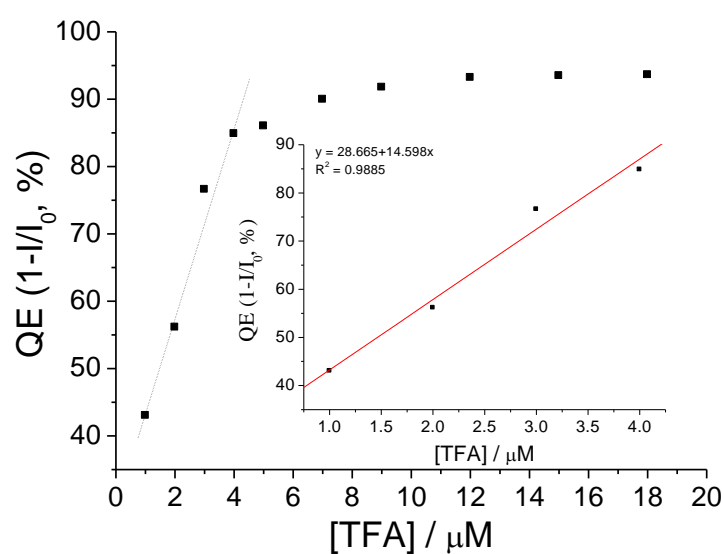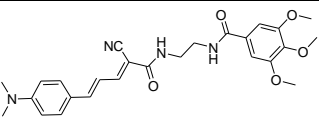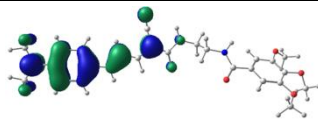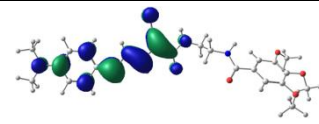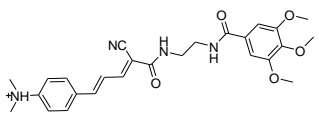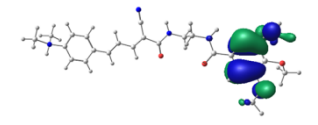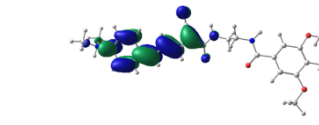


**Fig. S5** The curves of the fluorescence emission intensity at 558 nm versus the concentration of TFA. Inset: Calibrations curve in the concentrations range of 0 to 4 μmol/L of TFA.

**Table S2**. HOMOs and LUMOs Distributions of complex **Ir** ([Ir(bt)2(acac)] and [Ir(pba)2(Phen)]PF$_6$

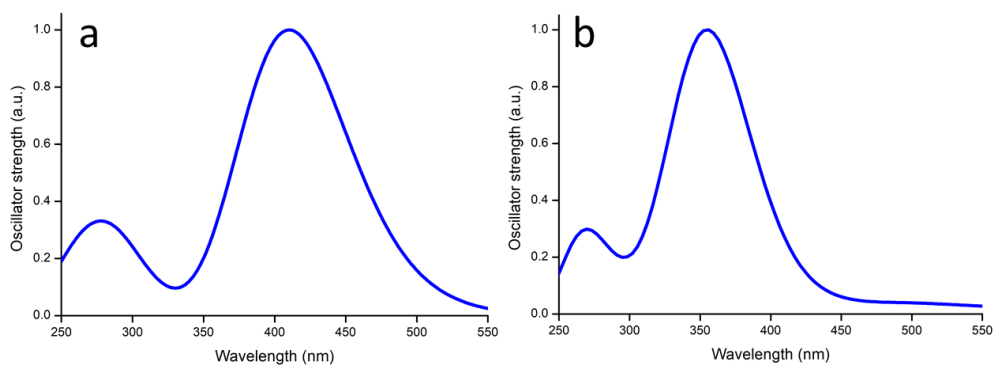| Molecule | HOMO | LUMO |
|----------|------|------|
|  1 |  -5.59 eV |  -2.5 eV |
|  1-H$^+$ |  -7.29 eV |  -5.61 eV |

**Fig. S6** The absorption spectra of compound **1** and complex **1-TFA** obtained from the DFT calculation: a) for compound **1** b) for complex **1-TFA**.

**The association constant (K) for TEA and complex 1-TFA**

The detailed procedure was similar that association constant (K) for compound 1 and TFA

The two variables $(1 / [I-I_0])$ Vs $1 / [TEA]$) were fit very well with the linear fitting: $Y = 5.58431E-4 + 1.38671E-8x$ ($y = A + Bx$). K was calculated as $4.027 \times 10^4$ $M^{-1}$ according to Eq. 4.
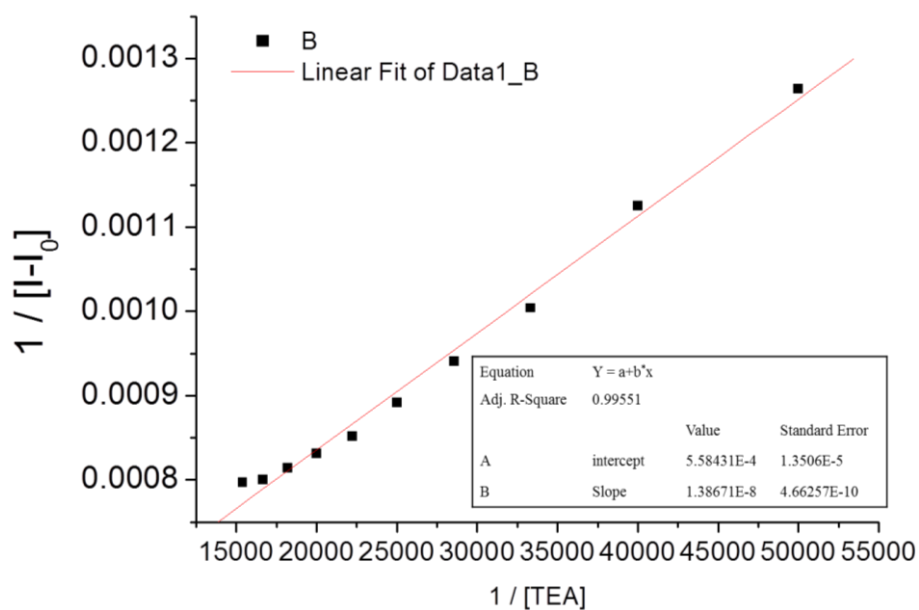


**Fig. S7** The linear fitting curve of fluorescence emission change of complex **1-TFA** with the addition of TEA.

# Limit of detection calculation

**Table S3** Detection limit of complex **1-TFA** toward TEA in acetonitrile by fluorescence intensity changes at 560 nm

| n | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Intensity (Xn) | 173.4 | 173.2 | 173.0 | 173.3 | 173.5 | 173.8 | 173.2 | 173.2 | 173.3 | 173.6 | 173.3 |

$X_{average} = 173.31$    $\sigma_{wb} = \text{sqrt}(\sum(X_n - X_{average})^2/n) = 0.1113$

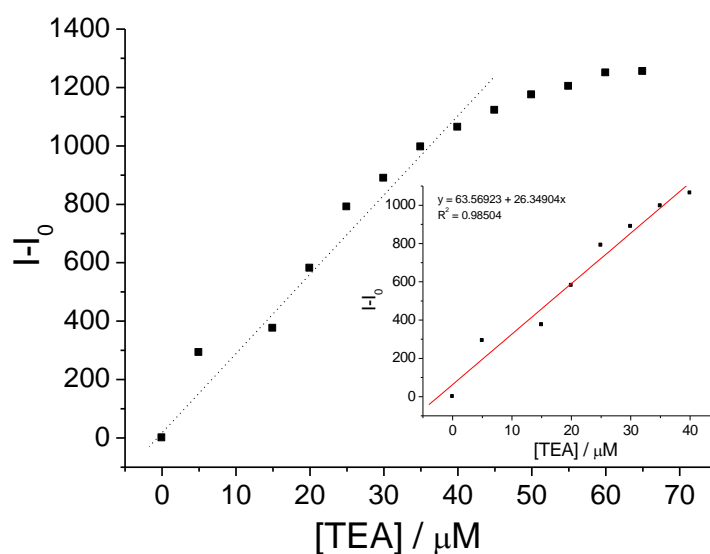The detection limit: $[TEA] = 3\sigma/b = 1.27 \times 10^{-8}$ M



**Fig. S8** The curves of the fluorescence emission intensity at 560 nm of 1-TFA versus the concentration of TEA. Inset: Calibrations curve in the concentrations range of 0 to 40 μmol/L of TEA.

# Limit of detection calculation

**Table S4** Detection limit of xerogel **1** toward TFA by fluorescence intensity changes at 619 nm

| n | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Intensity (Xn) | 44.68 | 44.66 | 44.63 | 44.59 | 44.52 | 44.55 | 44.52 | 44.55 | 44.59 | 44.64 | 44.59 |

$X_{average} = 44.59$    $\sigma_{wb} = \text{sqrt}(\sum(X_n - X_{average})^2/n) = 0.002736$

The detection limit: $[TFA] = 3\sigma/b = 3.2$ ppb
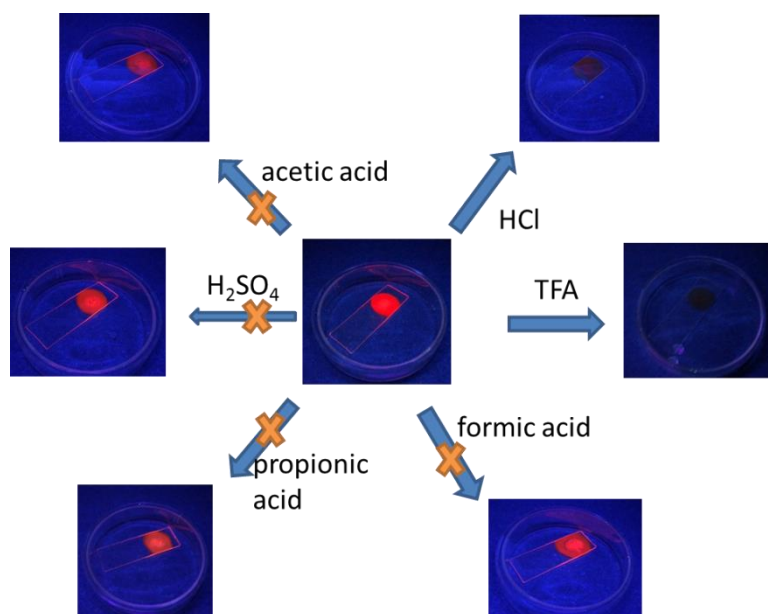
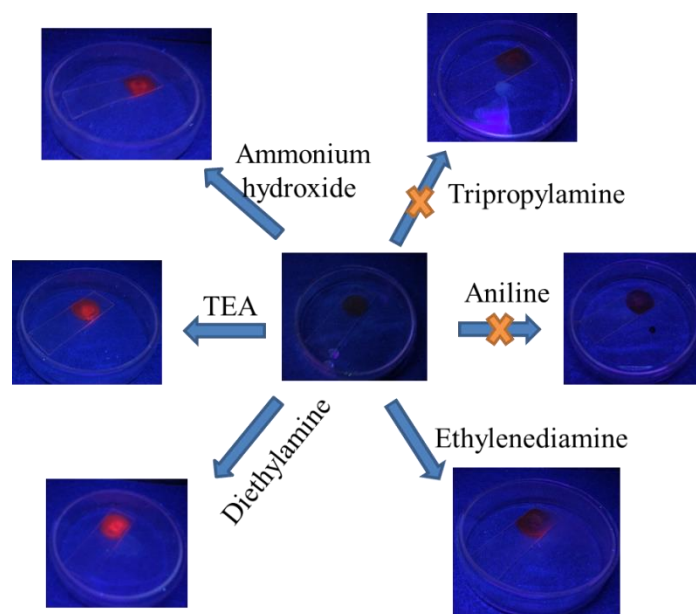**Fig.S9** Images of xerogel **1** from hexane with sensing different acids.



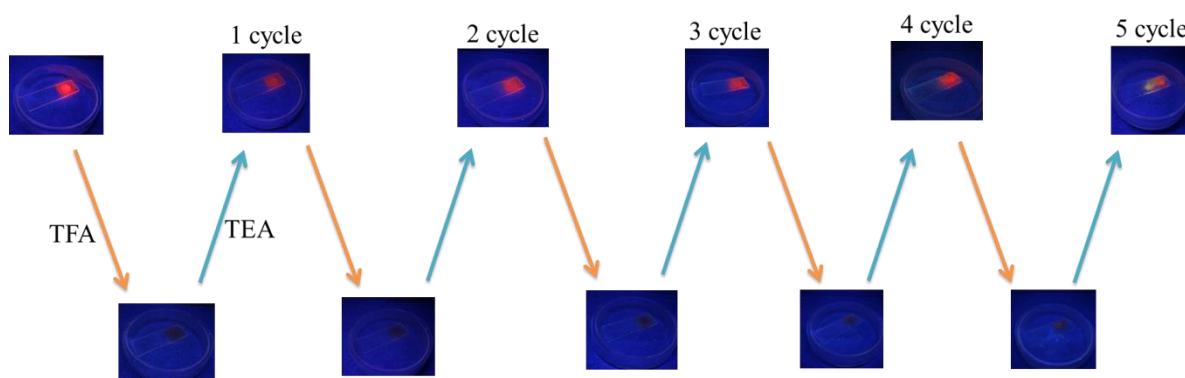**Fig.S10** Images of xerogel **1-TFA** from hexane with different amines.



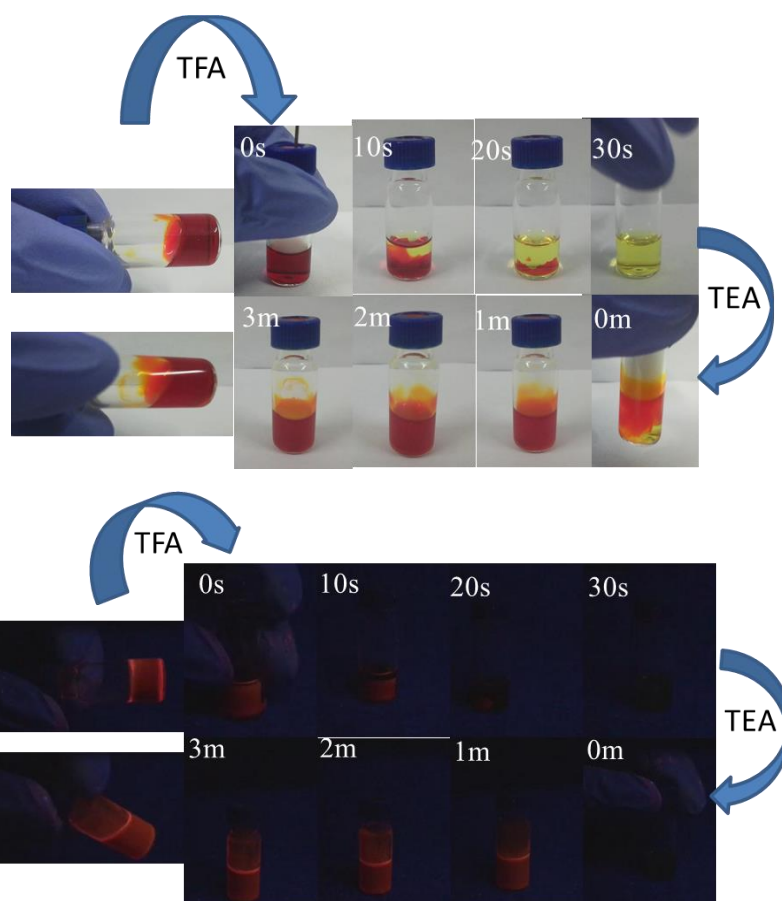**Fig.11** Images of xerogel **1** from hexane with sensing TFA and TEA in turn for five cycle

times.

**Fig. S12** The change of organogel **1** in hexane under addition of TFA and TEA in turn.

**Reference:**

1. Xue, P. C.; Ding, J. P.; Shen, Y. B.; Gao, H. Q.; Zhao, J. Y.; Sun, J. B.; Lu, R. Aggregation-Induced Emission Nanofiber as a Dual Sensor for Aromatic Amine and Acid Vapor. *J. Mater. Chem. C* **2017**,5, 11532-11541.