Fibrous Film of Two-component Organogel as Sensor to Detect and Distinguish Organic Amines

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Experiment section:

General information. All the raw materials were used without further purification. All the solvents as analytical reagent were purchased from Beijing Chemical Works (Beijing, China), and were used without further purification. Water used throughout all experiments was purified with the Millipore system. Infrared spectra were measured using a Nicolet-360 Fourier transform infrared (FT-IR) spectrometer by incorporating the samples in KBr disks. The UV-vis absorption spectra were obtained using a Mapada UV-1800pc spectrophotometer. Photoluminescence measurements were taken on a Shimadzu RF-5301 Luminescence Spectrometer. Scanning electron microscope (SEM) images were carried out on a Japan Hitachi model SU8020 Scanning electron microscope. The specimens for SEM were prepared by casting film method. Firstly, a small amount of wet gel was transferred in a glass slide, and then solvent was removed in vacuum oven to obtain xerogel film, and then were further coated with a thin layer of gold. The thicknesses of xerogel films were measured by Dektak 150 Stylus Profiler. **C12Ph** and **BPVB** were synthesized by the reported methods.[1, 2]

Preparation of Sensing film: 1. Fibrous film with a thickness of 740 nm: **C12PhBPVB** (1mg) was dissolved in cyclohexane (2 mL) under heating to form clear solution, and then cooled solution of 100 μl was casted on the glass slide (1.3×2.5 cm). The sample was covered by culture dish for slow evaporation of solvent. After 2 h, the slide was transferred into a vacuum oven to further remove solvent. Sensing films for IR spectra on CaF slide were prepared by a similar method. 2. Fibrous film with a thickness of 76 nm: **C12PhBPVB** (1mg) was dissolved in cyclohexane (2 mL) under heating to form clear solution, and then cooled solution of 100 μl was spin coated on glass slide at 1000 rpm for 30 s.

Amine vapors with different concentrations could be achieved by the method reported by L. Zang (Chem. Commun. 2009, 5106-5108).

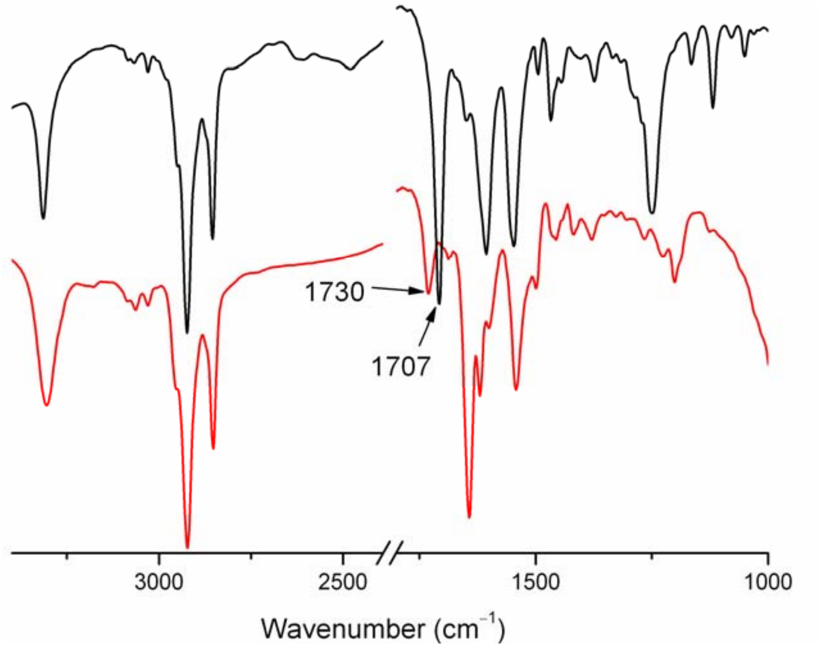

Fig. S1. FT-IR spectra of **C12Ph** in solid state (black) and the cyclohexane xerogel (red) of **C12PhBPVB**.

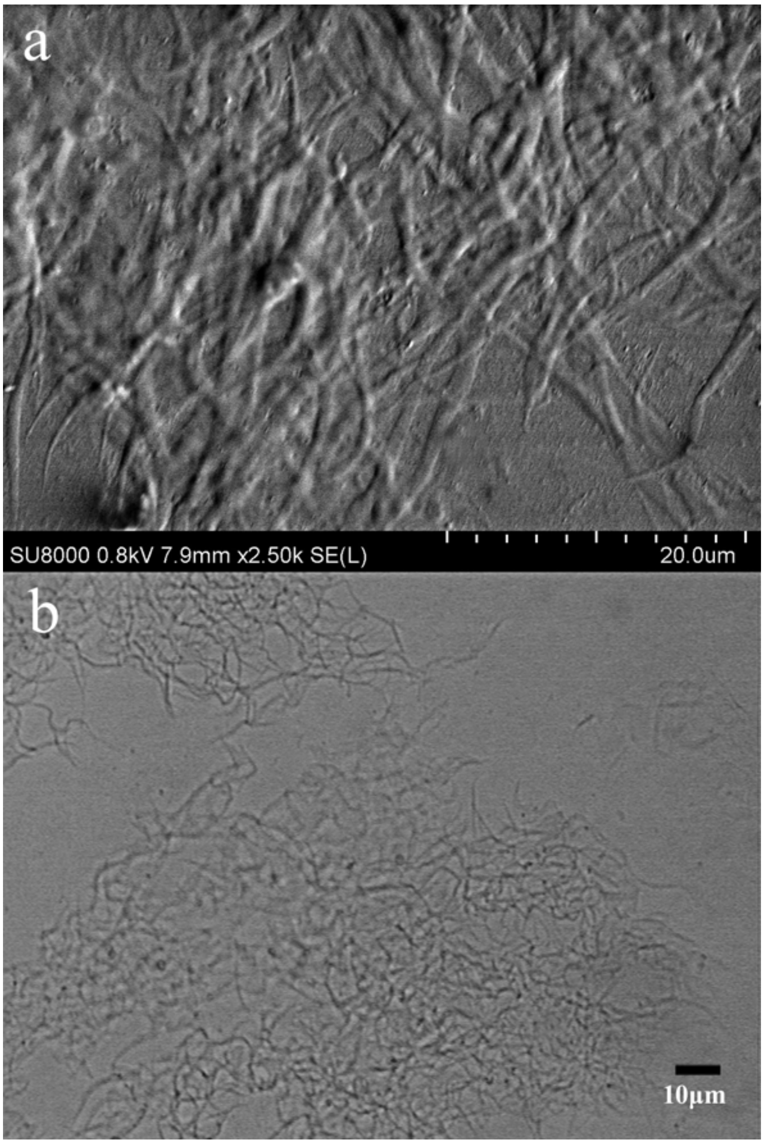

Fig. S2. SEM (a) and light microscope (b) images of xerogel film from cyclohexane.

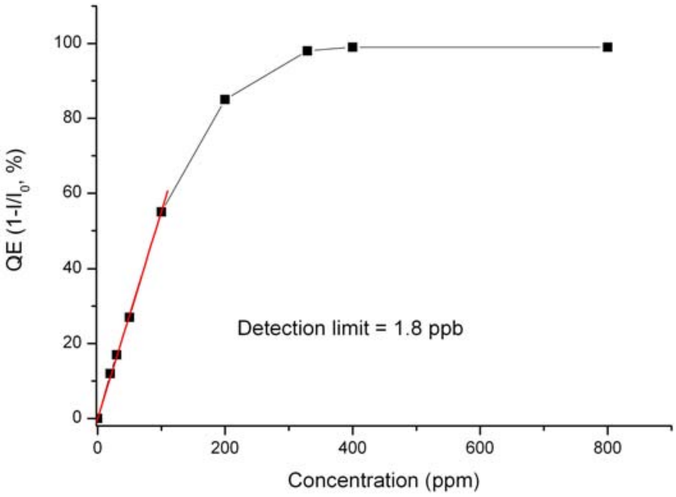

Fig. S3. Fluorescence quenching efficiency (1–I/I$_0$) of xerogel film (a thickness of 740 nm) as a function of the vapor pressure of aniline. The intensity was monitored at 550 nm. λ_{ex} = 360 nm.

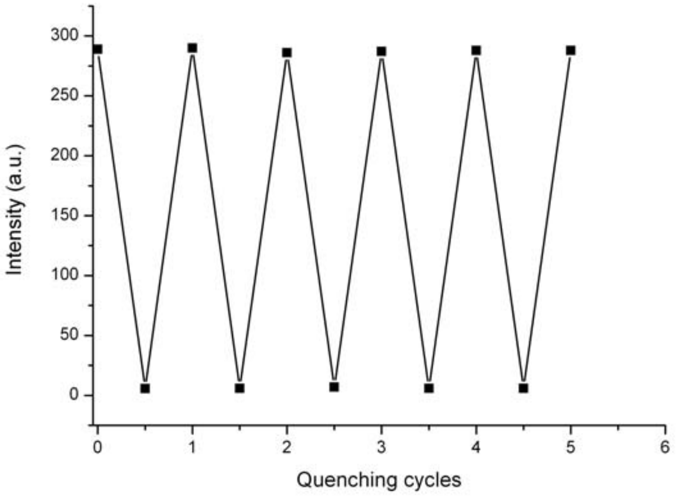

Fig. S4. Five continuous cycles of quenching-recovery were tested for the xerogel film (a thickness of 740 nm) upon exposure to the saturated vapor (329 ppm) of aniline. The quenching was performed by exposing the film towards aniline vapor for 30 s, and the recovery of fluorescence was done by blowing with a gas blower for 2 min. The intensity was monitored at 550 nm. λ_{ex} = 360 nm.

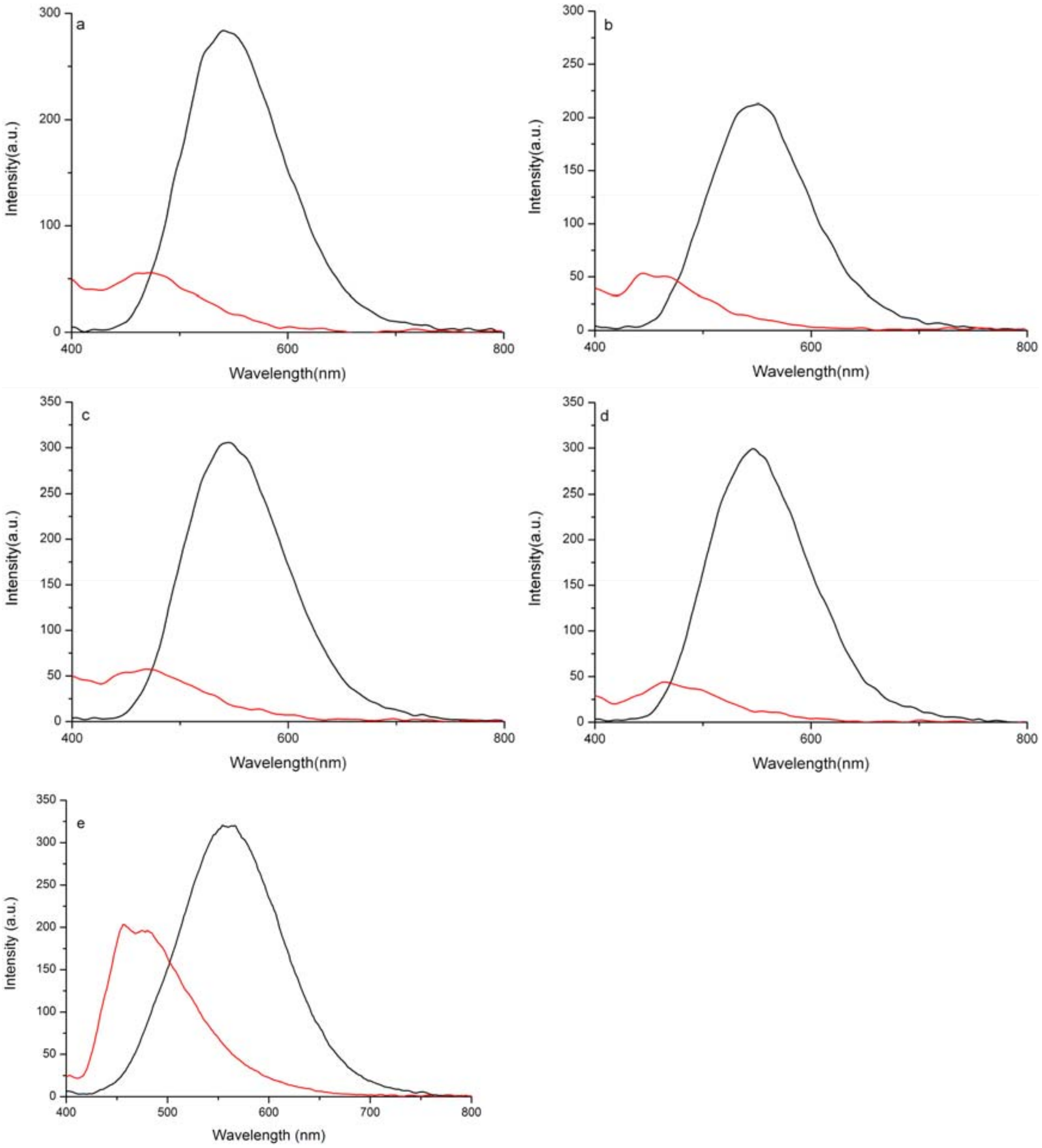

Fig. S5. Fluorescence spectra of the xerogel film (a thickness of 740 nm) before (black) and after (red) exposing to the saturated vapors of (a) dibutylamine, (b) dipropylamine, (c) tributylamine, (d) triethylamine, and (e) NH_3 for 30 s at 16 °C. $\lambda_{ex} = 360$ nm.

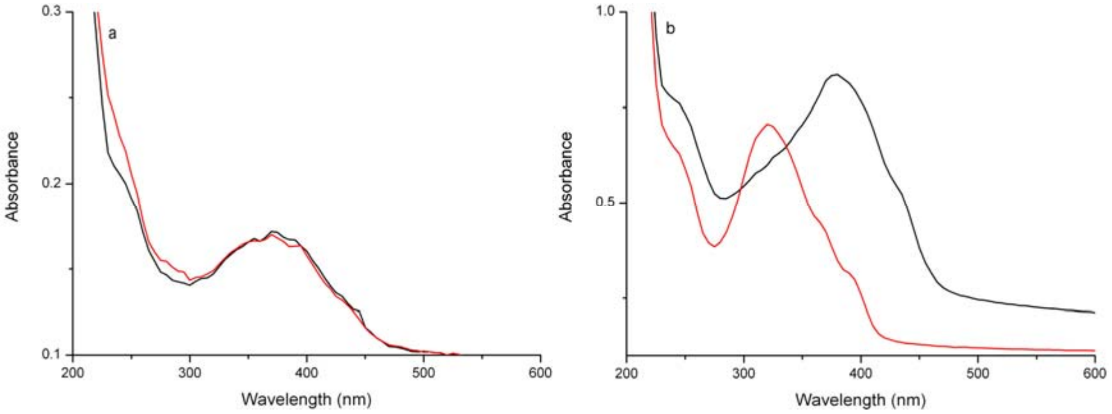

Fig. S6. Absorption spectra of xerogel films before (black) and after (red) exposing to the saturated vapor of (a) aniline and (b) n-butylamine for 30 s.

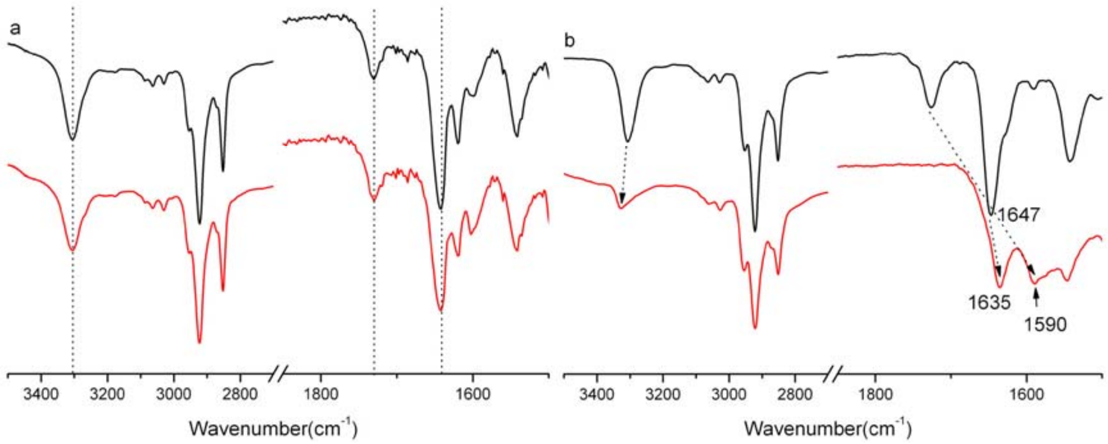

Fig. S7. FT-IR spectra of xerogel film before (black) and after (red) exposing to the saturated vapor of (a) aniline and (b) n-butylamine for 30 s.

Table 1. The HOMO and LUMO energy levels of **C12PhBPVB** and **BPVB**.

Molecule	LUMO (eV)[a]	HOMO (eV)[b]	LUMO (eV)[c]	HOMO (eV)[c]
BPVB	-2.59	-5.62	-2.33	-5.79
C12PhBPVB	-2.70	-5.73	-2.77	-6.17

[a] Electrochemical method was used to obtain the LUMO energy levels by comparing with a external reference, the ferrocene/ferrocenium (Fc/Fc$^+$, 4.8 eV relative to vacuum).[3]

[b] The HOMO energy level was estimated by subtracting E_{gap} (3.03 eV) to E_{HOMO}.

[c] Energy levels of HOMO and LUMO versus vacuum were given after geometrical optimization at the B3LYP/6-31G level of theory.

Table 2. The pK_b and HOMO energy levels of amines and pyridine.

amine	pK_b[a]	HOMO (ev)[b]	amine	pK_b[a]	HOMO (ev)[b]
aniline	9.37	-5.63	dibutylamine	3.35	-5.94
N-methylailine	9.15	-5.44	tributylamine	3.11	-5.60
N,N-dimethylailine	8.93	-5.36	dipropylamine	3.02	-5.76
n-butylamine	3.41	-6.13	triethylamine	3.35	-5.73
NH_3	4.73				

[a] pK_b data of amines are cited from ref. 4. [b] The oxidation potentials of amines and pyridine are cited from ref. 5.

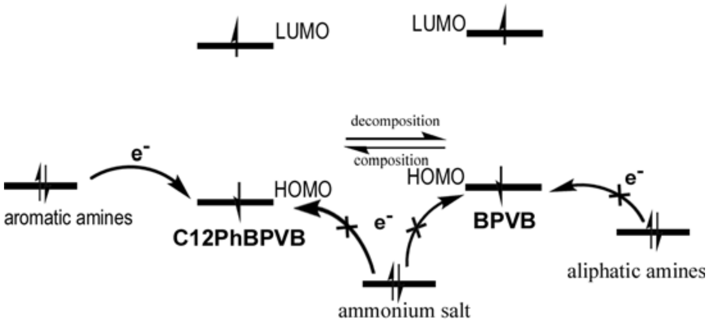

Fig. S8. Energy level diagram of photoinduced electron transfer in the presence of aromatic and aliphatic amines

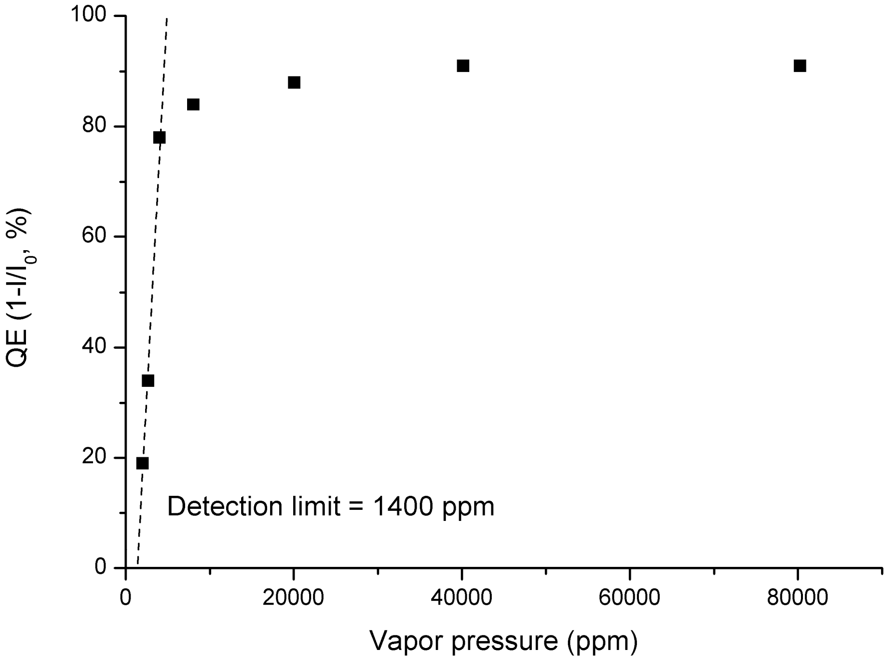

Fig. S9. Fluorescence quenching efficiency (1–I/I$_0$) of xerogel film (a thickness of 740 nm) as a function of the vapor pressure of *n*-butylamine. The intensity was monitored at 550 nm. λ_{ex} = 360 nm.

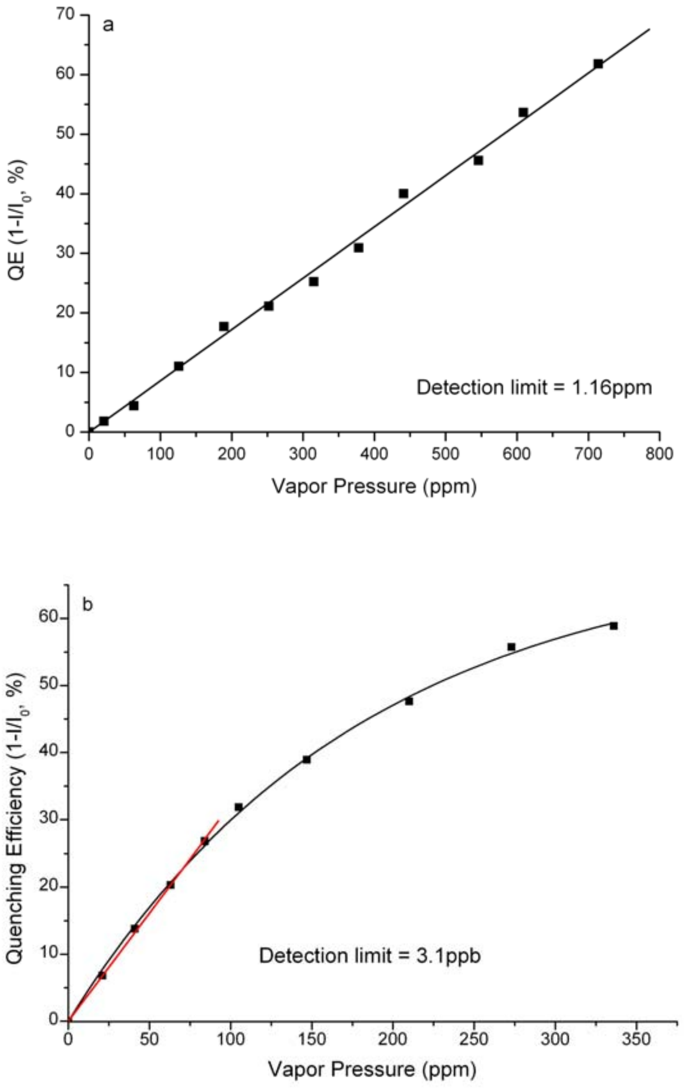

Fig. S10. Fluorescence quenching efficiency ($1-I/I_0$) of xerogel film (a thickness of 76 nm) as a function of the vapor pressure of (a) *n*-butylamine and (b) tributylamine. The intensity was monitored at 550 nm. λ_{ex} = 360 nm.

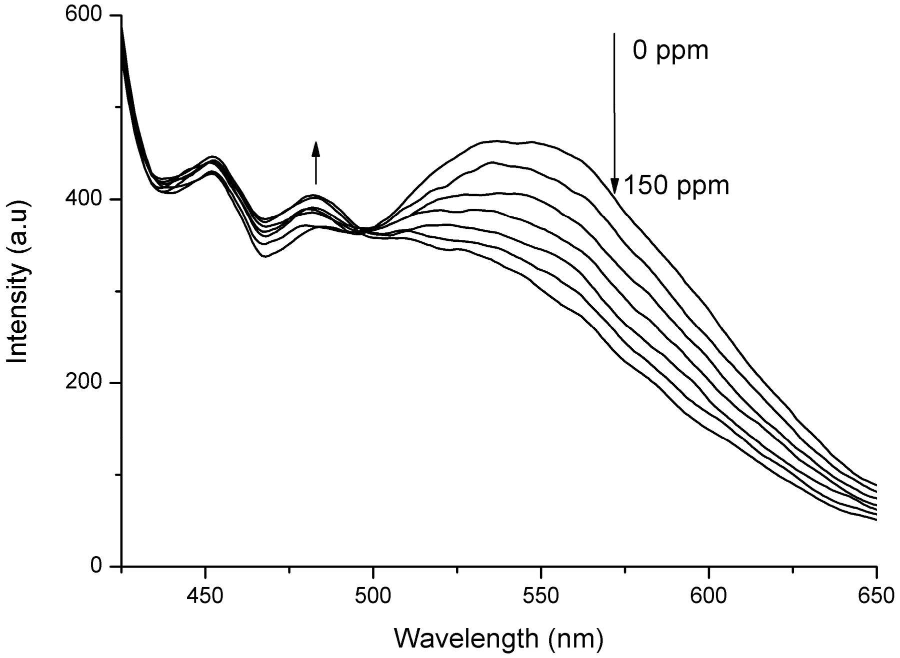

Fig. S11. Fluorescence spectra of the xerogel film (a thickness of 76 nm) in the presence of different of tributylamine. λ_{ex} = 360 nm.

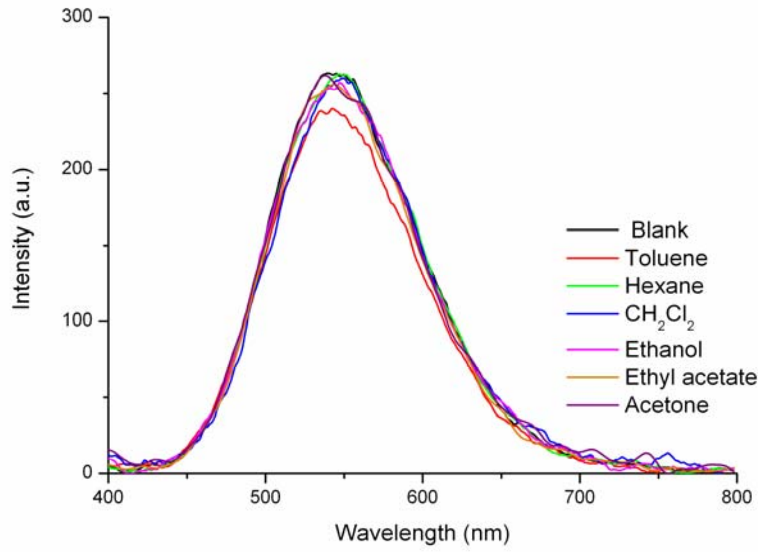

Fig. S12. Fluorescence spectra of the xerogel films (a thickness of 740 nm) upon exposure to the saturated vapors of common organic solvents with a response time of 30 s at 16 °C. λ_{ex} = 360 nm.

Reference:

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