Electronic Supplementary Material (ESI) for ChemComm.

A robust two-dimensional zirconium-based luminescent coordination polymer built on V-shaped dicarboxylate ligand for vapor phase sensing of volatile organic compounds

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Supporting Information

EXPERIMENTAL SECTION

1. Materials and Methods.

All starting reagents used in this study are commercially available and were employed without further purification. The powder X-ray diffractometer analyses were carried out on a Rigaku Ultima-IV unit using Cu Kα radiation ($\lambda = 1.5406$ Å). The data were collected at room temperature in a 2θ range of 3°–40° with a scan speed of 2° min^{-1}. Thermogravimetric analyses of samples were performed using the TA Instruments Q5000 analyzer with nitrogen flow. Samples were heated from room temperature to 600 ℃ at a ramp rate of 10 ℃/min. The infrared spectra were recorded with KBr slices from 4000-400 cm^{-1} using a Nicolet 6700 IR Spectrometer from Thermo Scientific. The photoluminescence study was carried out on a Varian Cary Eclipse spectrophotometer at room temperature.

2. Single Crystal X-ray Diffraction.

Single crystal X-ray diffraction data for **1** were collected on a Bruker PHOTON100 CMOS detector at the Advanced Light Source (ALS) in Lawrence Berkeley National Laboratory, using synchrotron radiation tuned to $\lambda = 0.7749$ Å. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL package.[1] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically using a riding model, except for the water/mu-2-hydroxide hydrogen which could neither be found nor placed and so they were omitted from the refinement, but not the formula. The unresolvable electron density in the structure was removed by SQUEEZE. Displacement parameter restraints were used to model the disorder between O1 and O1', O8, O8' and C8 Summaries of single crystal data are listed in Table S1. CCDC- 1813390 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Synthesis and Structure of compound 1

Synthesis of compound **1**: $ZrCl_4$ (0.1mmol, 0.0233g), H_2sdba (0.1 mmol, 0.0306g), and formic acid (1 mL) in N,N-dimethylformamide(DMF) (6 mL) were ultrasonically dissolved in a 20 mL Pyrex vial. The vial was tightly sealed and placed in an oven heated at 100 ℃ for three days. Then, the vial was removed from the oven and allowed to cool to room temperature. The resulting crystals were collected.

Single-crystal X-ray analysis revealed that compound **1** crystallized in the tetragonal crystal system with the lattice parameters *a* = 23.3559(6) and *b* = 26.7429(8) (Table S1). The asymmetric unit contains three quarters of a Zr^{4+} ion, half of the deprotonated ligand sdba^{2-}, half of a μ_3-O^{2-} atom, half of a μ_3-OH^-, half of a H_2O molecule, and half of a coordinated formate ion. In this structure, there exist two crystallographically-independent Zr atoms (Zr1 and Zr2), which are all eight-coordinated. Each Zr1 ion is coordinated by four carboxylate oxygen atoms from four independent sdba^{2-}ligands, two μ_3-OH$^-$, and two μ_3-O^{2-}. Each Zr2 ion is coordinated to two carboxylate oxygen atoms from two different sdba^{2-} ligands, two μ_3-OH$^-$, two μ_3-O^{2-}, one terminal H_2O or hydroxide (as that site is disordered), and one coordinated formate ion. Six Zr atoms were connected by four μ_3-O atoms， four μ_3-OH$^-$ group，two terminal water molecules, two terminal hydroxide ions, and two formate ions to generate the Zr6 SBU.

Table S1 Crystal data and structure refinement for **1**.

Empirical formula	$C_{58}H_{44}O_{40}S_4Zr_6$
Formula weight	2047.15
Crystal system	tetragonal
Space group	I4/mmm
a/Å	23.3559(6)
b/Å	23.3559(6)
c/Å	26.7429(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	14588.2(9)
Z	4
ρ_{calc}g/cm^3	0.932
R_{int}	0.0722
Data/restraints/parameters	2531/29/155
Goodness-of-fit on F^2	1.127
R_1, wR_2 [I>=2σ (I)]	0.0365, 0.1069
R_1, wR_2 [all data]	0.0490, 0.1149

4. Fluorescence measurements

4.1 Liquid phase fluorescence sensing measurements

The fluorescence properties of **1** suspended in ethanol were investigated following exposure to various solvents. The **1**–ethanol suspension was prepared by sonicating 5 mg of **1** in 3 mL of ethanol for 30 minutes to create a stable suspension. Following sonication, the emission curve for the suspension was collected under 285 nm excitation. 1 mL of the test solvent was then added, and the emission curve was re-collected. The test solvents included H_2O, acetonitrile, methanol, ethanol, 1,4-dioxanane, acetone, DMF, nitrobenzene, 2-nitrotoluene, nitroethane, nitromethane and

1-nitropropane. All samples were well-mixed with a pipet 30 seconds before the emission curve was collected.

4.2 Vapor phase fluorescence sensing measurements

First, 1 ml of each analyte was placed in small glass vials (20ml) for several days to ensure that the equilibrium vapor pressure of each analyte was reached. The samples of **1** were ground into fine powder, and then were stuck on a quartz slide through the use of double-side tape. The initial emission spectrum of solid sample was measured before it was exposed to vapors. Then, the sample slide was exposed to the vapor of analyte in a vial. After the specified exposure time, the slide was taken out from the vial and mounted into the sample holder of the fluorescence spectrophotometer. The sample's fluorescence emission spectrum of was recorded immediately.

4.3 Quantum yield measurements

The quantum yield of solid **1** was collected using a Hamamatsu C11347 Absolute PL Quantum Yield spectrophotometer with integrating sphere under 285 nm excitation by a Xe arc lamp. The internal quantum yield of **1** is 4.0%.

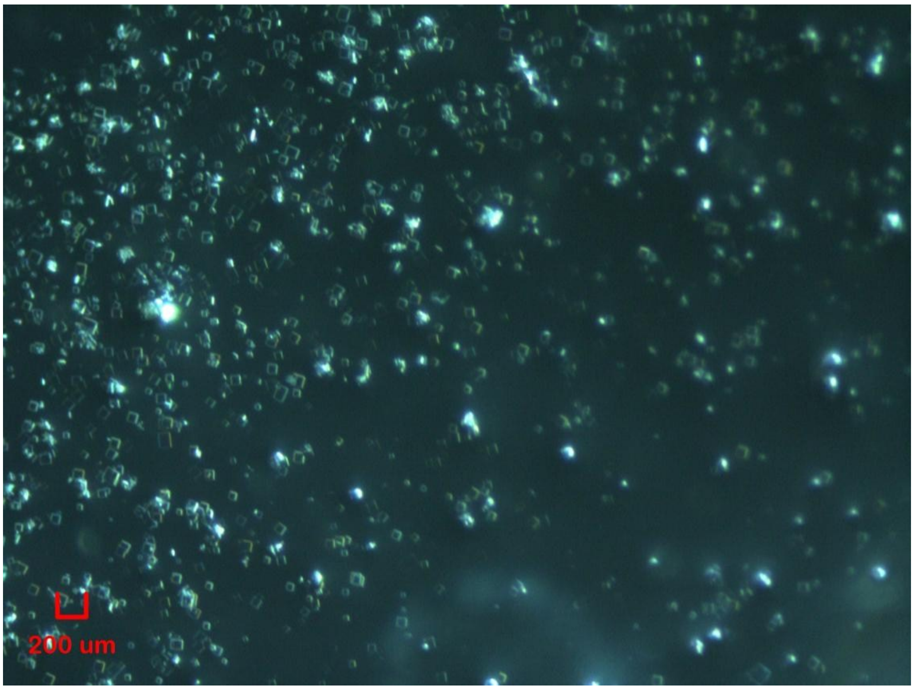

Fig. S1 Optical image of the as-synthesized crystals.

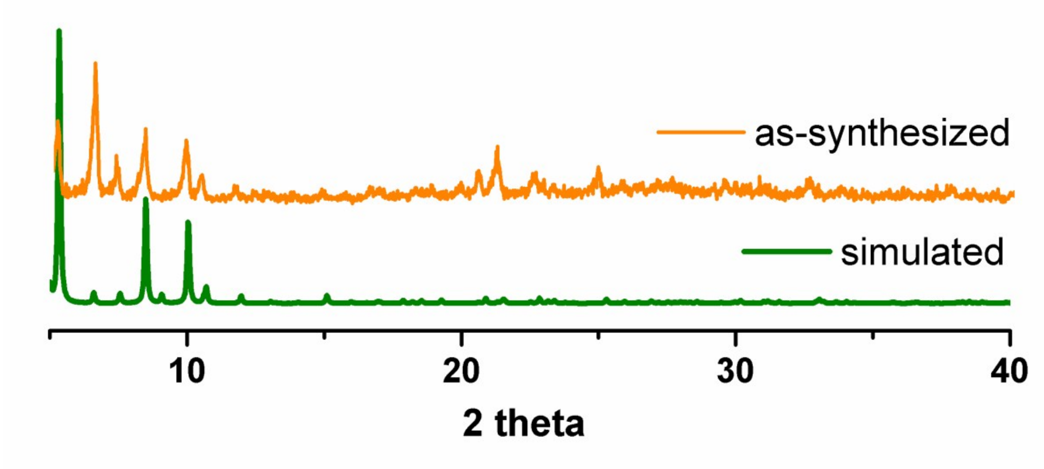

Fig. S2 Comparison of the simulated and experimental PXRD patterns of **1**.

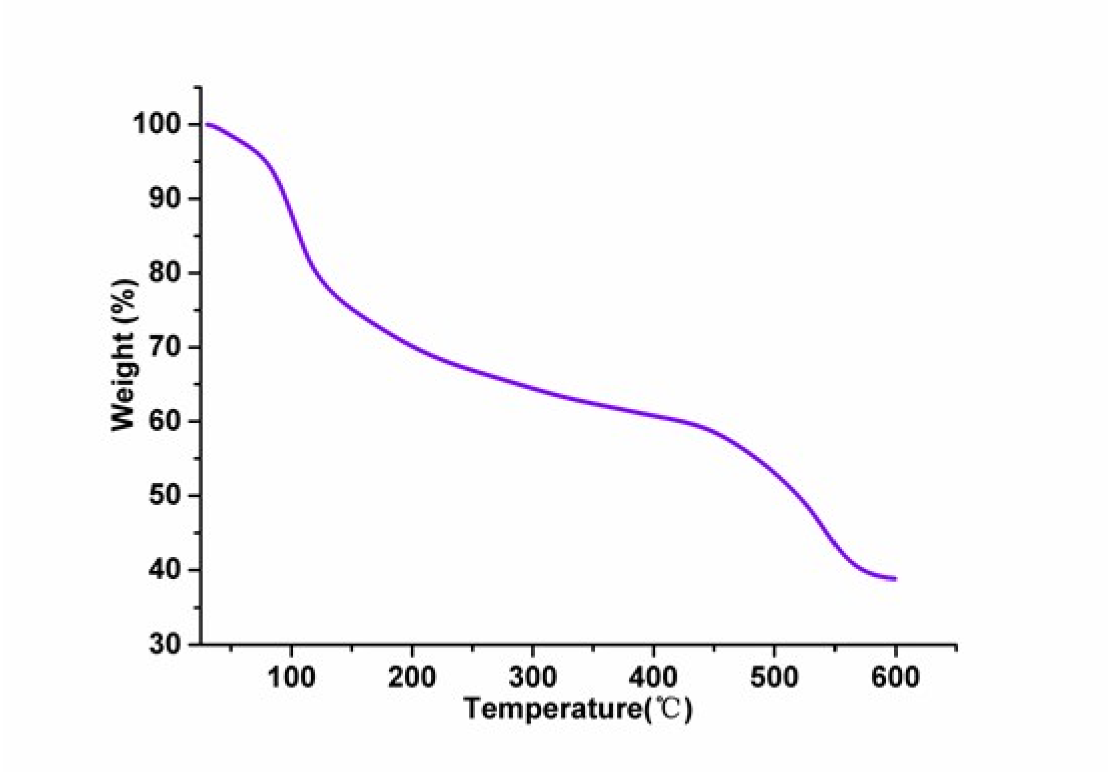

Fig. S3 Thermogravimetric profile of **1** under nitrogen flow.

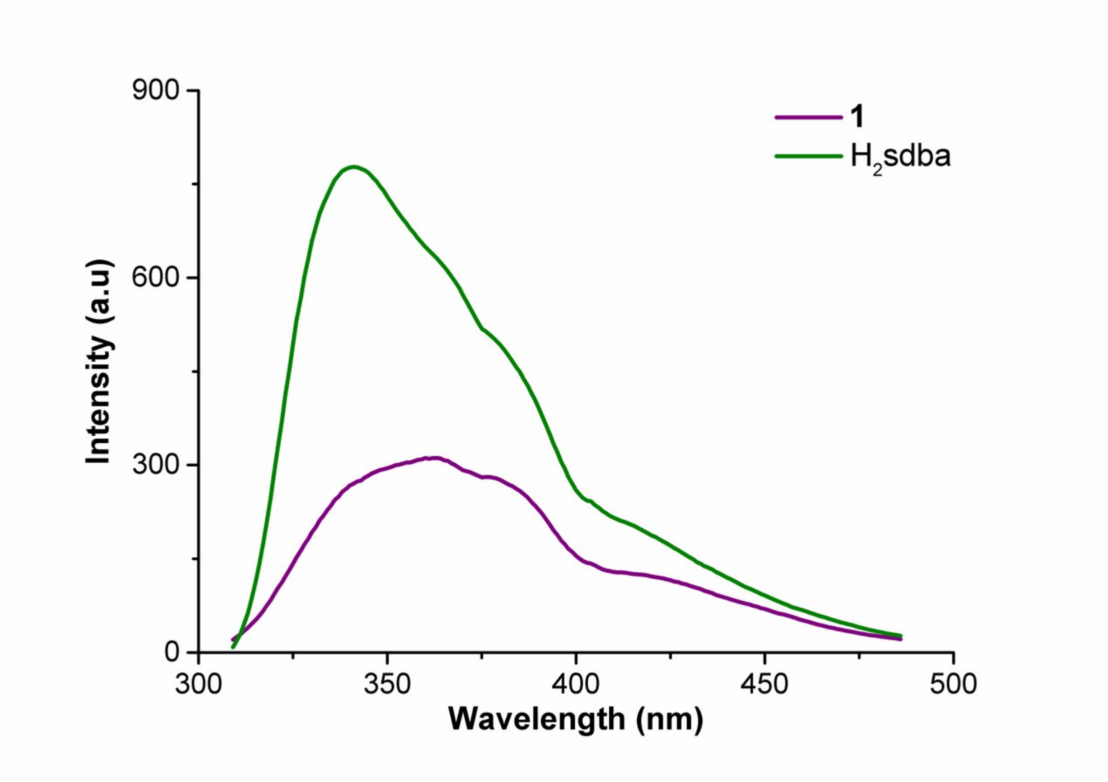

Fig. S4 Emission spectra of H_2sdba and **1** excited at 285 nm.

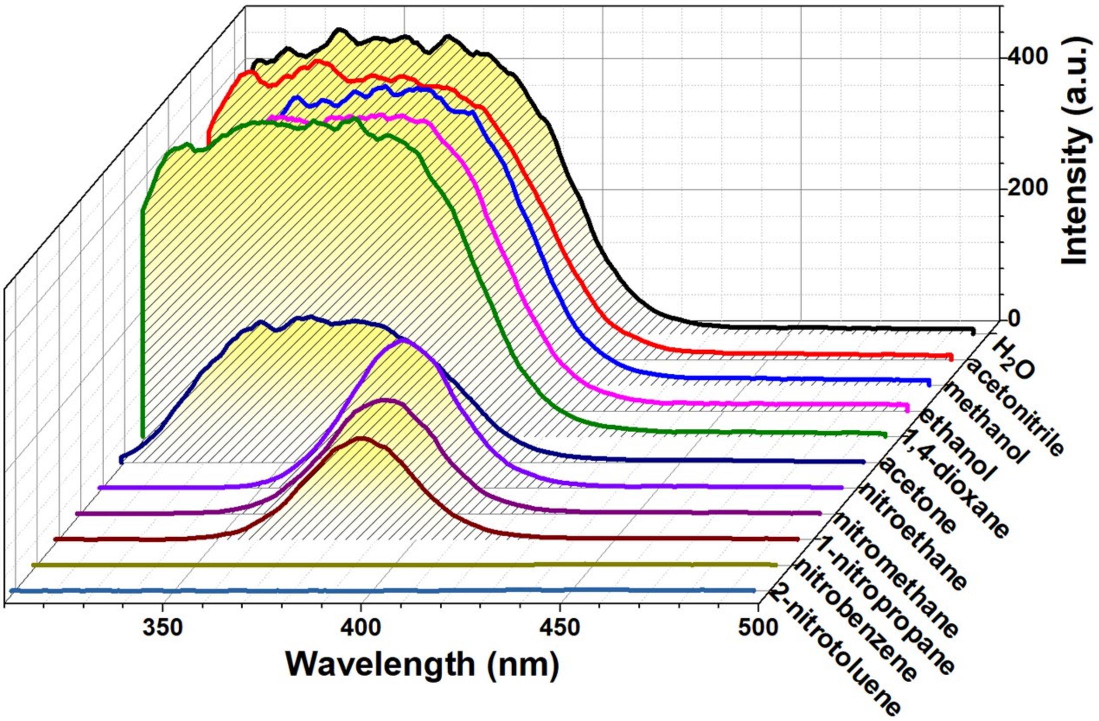

Fig. S5 Fluorescence response of suspensions of **1** in ethanol following exposure to various organic solvents and water.

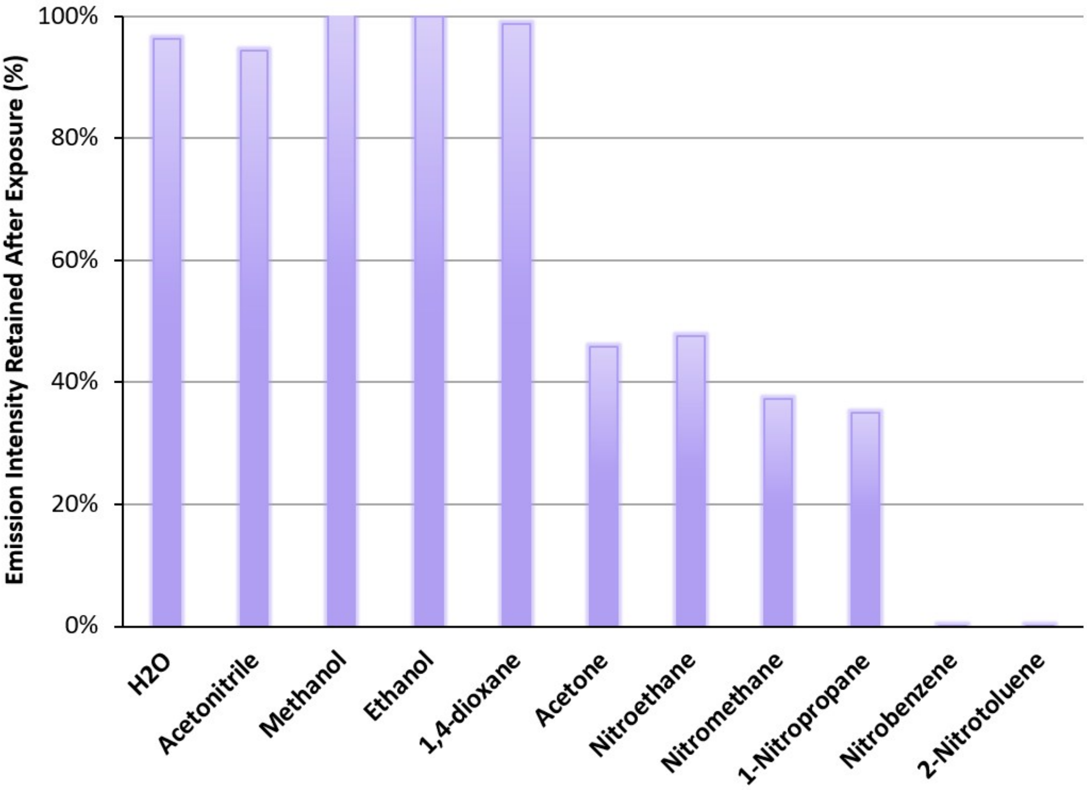

Fig. S6 Percent of emission intensities of **1** suspended in ethanol that were retained following exposure to various solvents, normalized to the emission retained in a suspension of **1** in ethanol following exposure to additional ethanol.

Table S2 Saturated vapor pressure for each of the analytes at room temperature (25 °C).

Analytes	**Abbreviation**	**Vapor Pressure (in mmHg)**
nitrobenzene [L][2]	NB	0.2416
2-nitrotoluene [L]	NT	0.1602
2,4-dinitrotoluene [S]	2,4-DNT	1.44×10^{-6}
toluene [L]	TO	28
ethylbenzene [L]	Et-BZ	9.53
1,3,5-trimethylbenzene [L]	TMB	2.49
nitroethane [L]	NE	20.93
nitromethane [L]	NM	36.7
1-nitropropane [L]	NP	7.5

[a] L: liquid at room temperature; S: solid at room temperature

[b] 1mmHg=1.2468×10^{3} ppm.

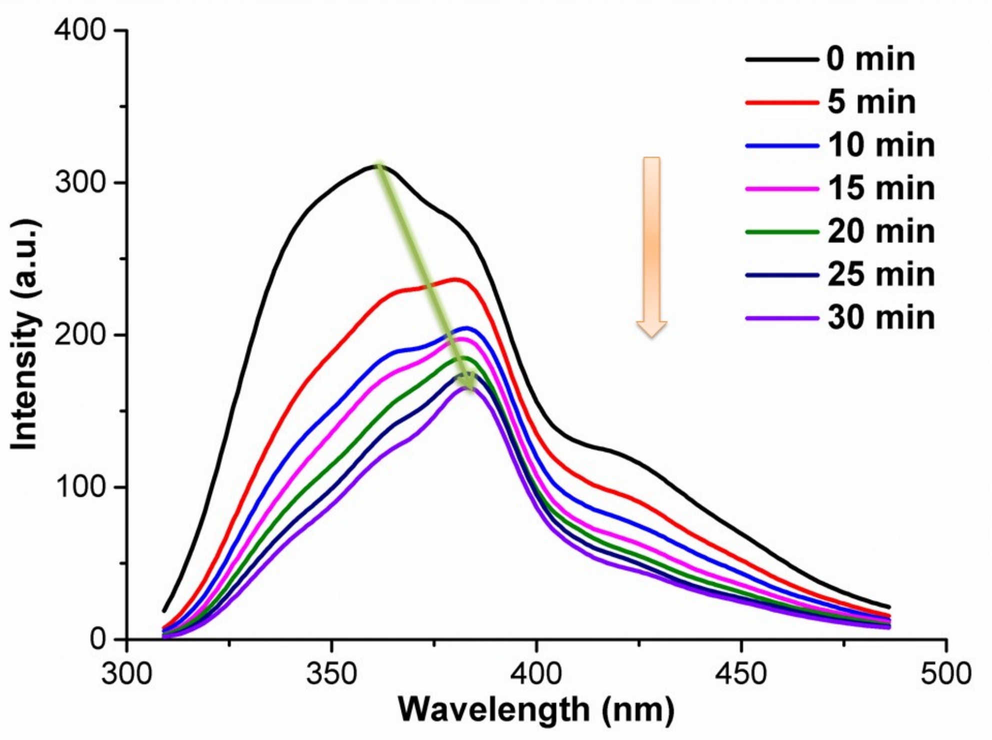

Fig. S7 PL emission spectra of **1** and the same sample after 30 min exposure to 2-nitrotoluene at different time intervals at room temperature.

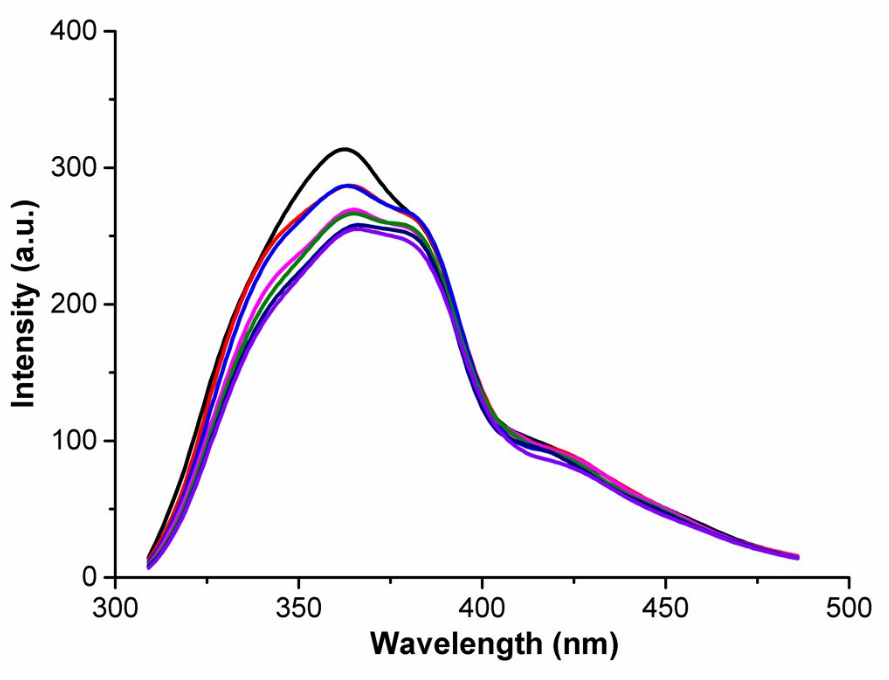

Fig. S8 PL emission spectra of **1** and the same sample after 30 min exposure to 2,4-dinitrotoluene at different time intervals at room temperature.

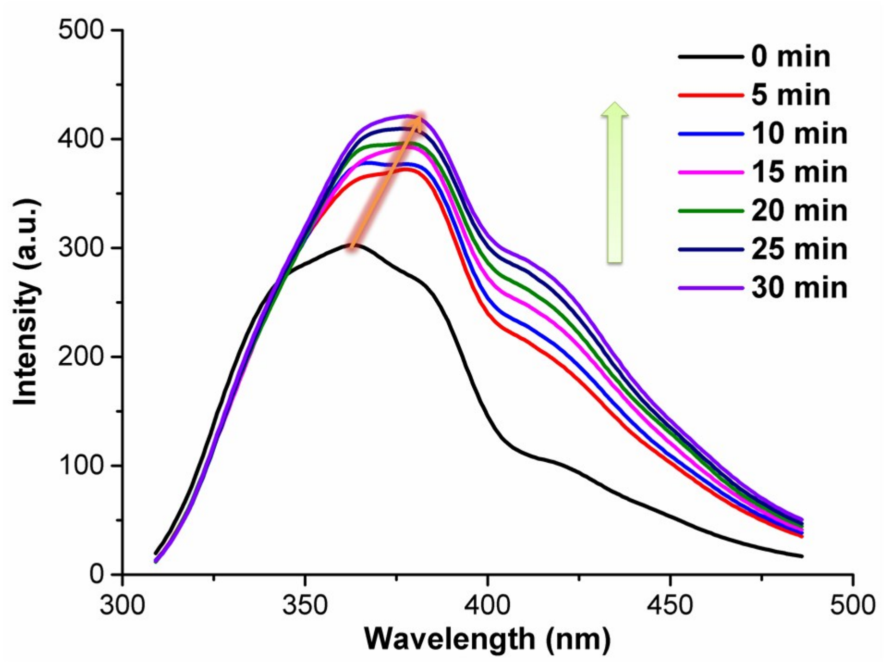

Fig. S9 PL emission spectra of **1** and the same sample after 30 min exposure to toluene at different time intervals at room temperature.

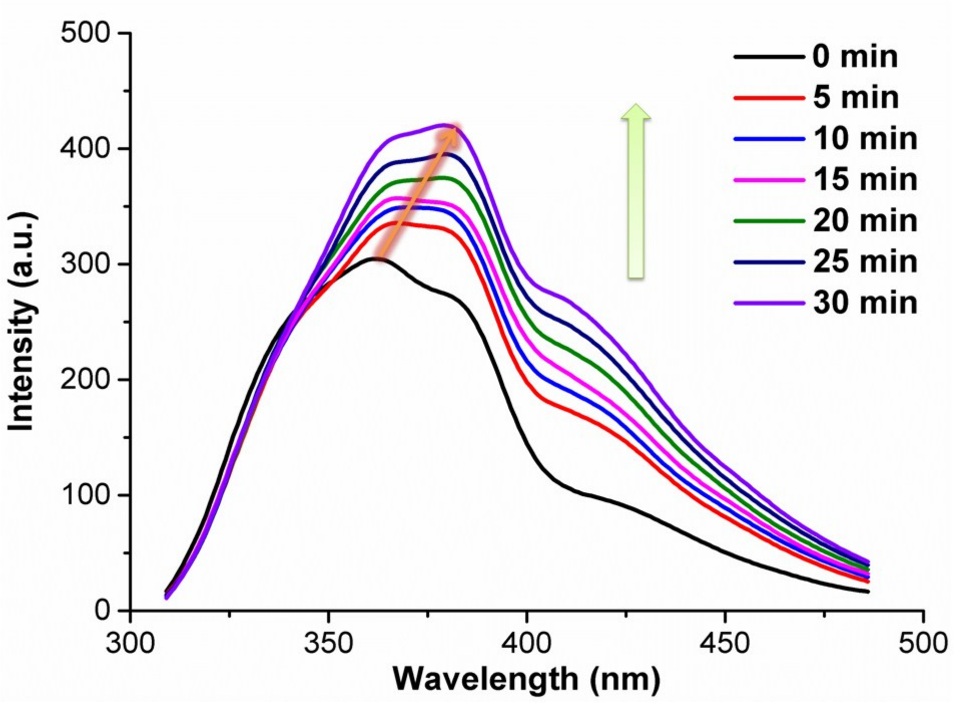

Fig. S10 PL emission spectra of **1** and the same sample after 30 min exposure to ethylbenzene at different time intervals at room temperature.

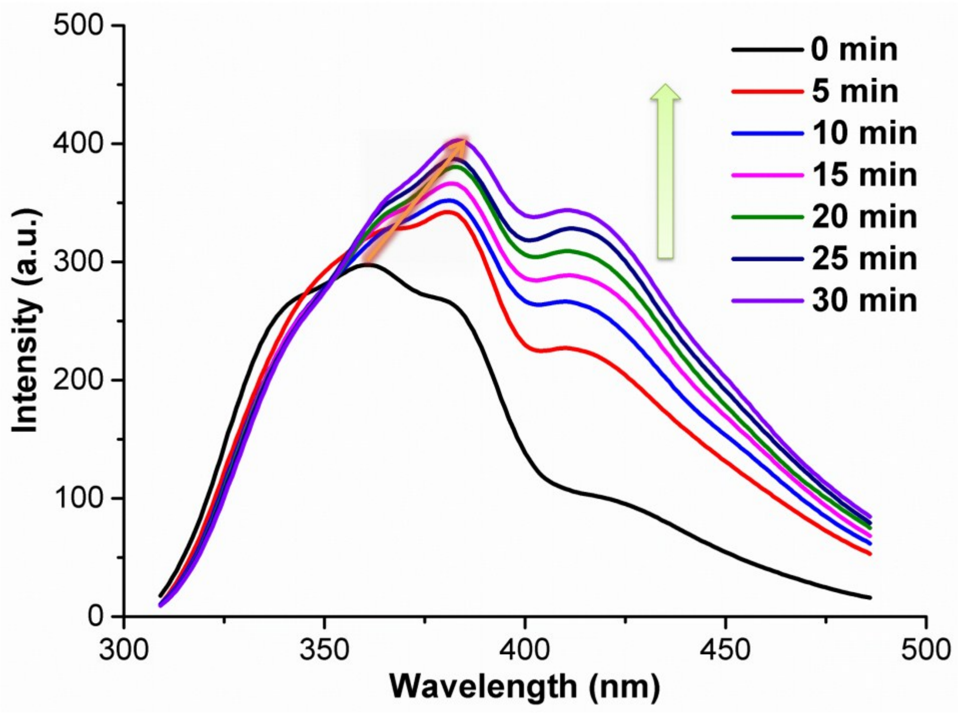

Fig. S11 PL emission spectra of **1** and the same sample after 30 min exposure to 1,3,5-trimethylbenzene at different time intervals at room temperature.

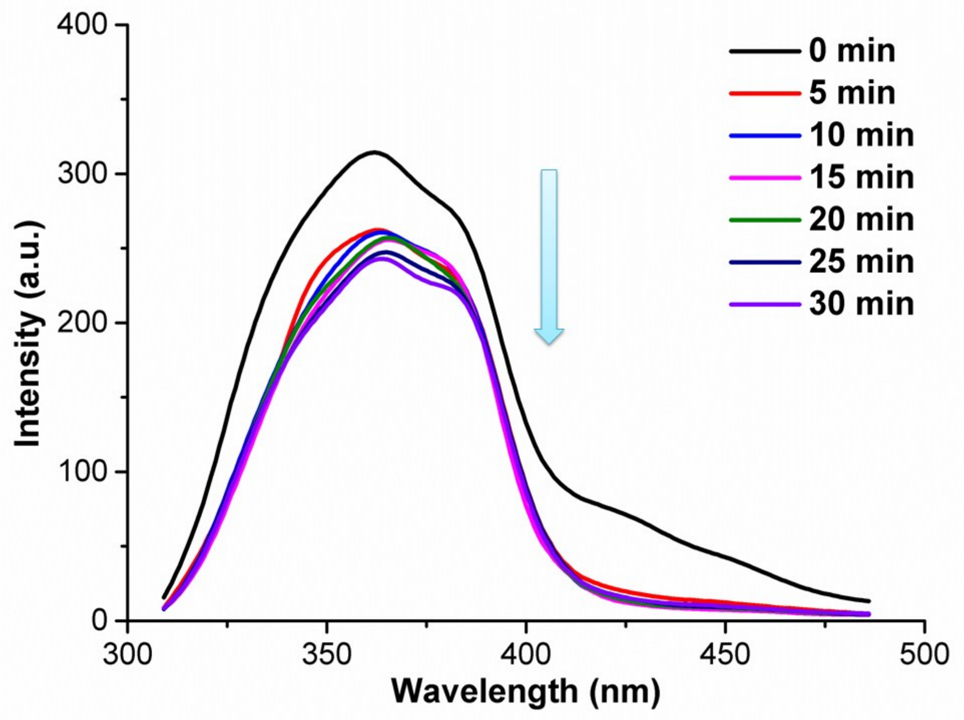

Fig. S12 PL emission spectra of **1** and the same sample after 30 min exposure to nitromethane at different time intervals at room temperature.

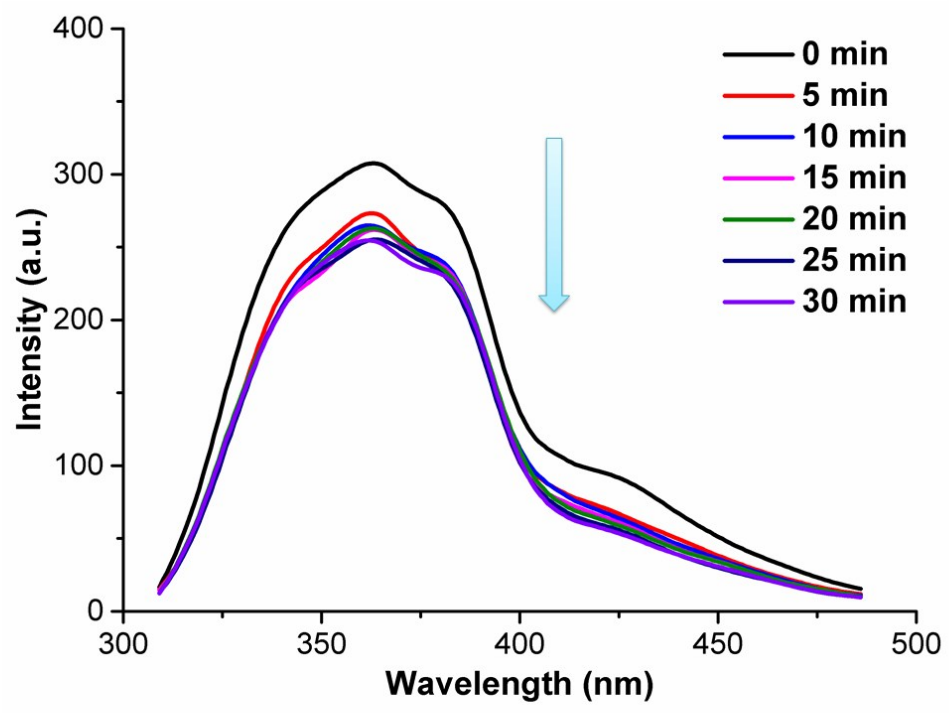

Fig. S13 PL emission spectra of **1** and the same sample after 30 min exposure to nitroethane at different time intervals at room temperature.

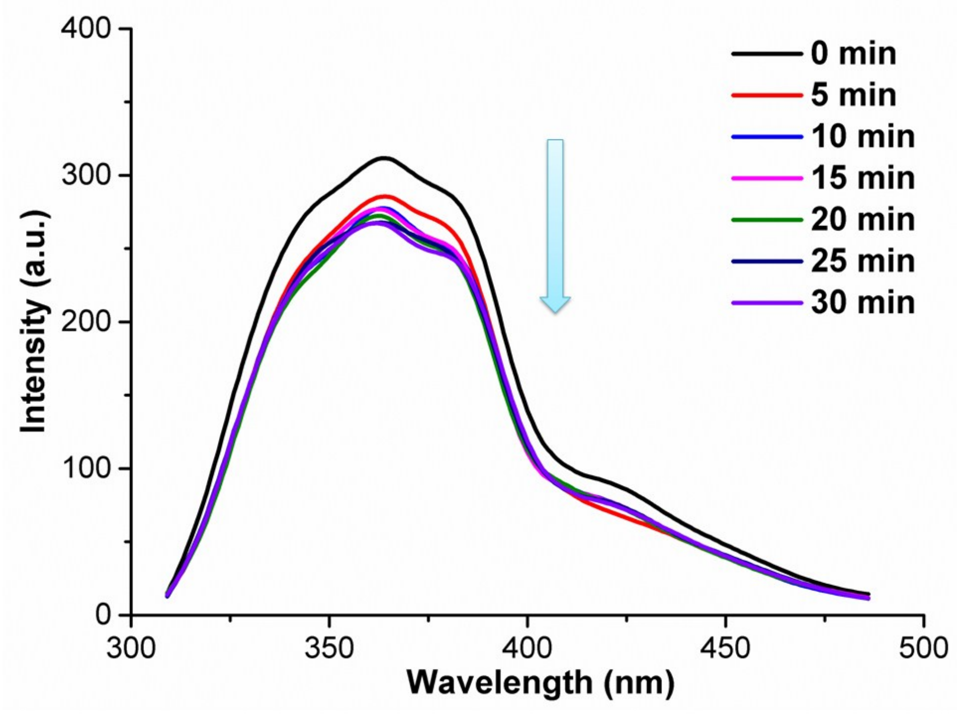

Fig. S14 PL emission spectra of **1** and the same sample after 30 min exposure to 1-nitropropane at different time intervals at room temperature.

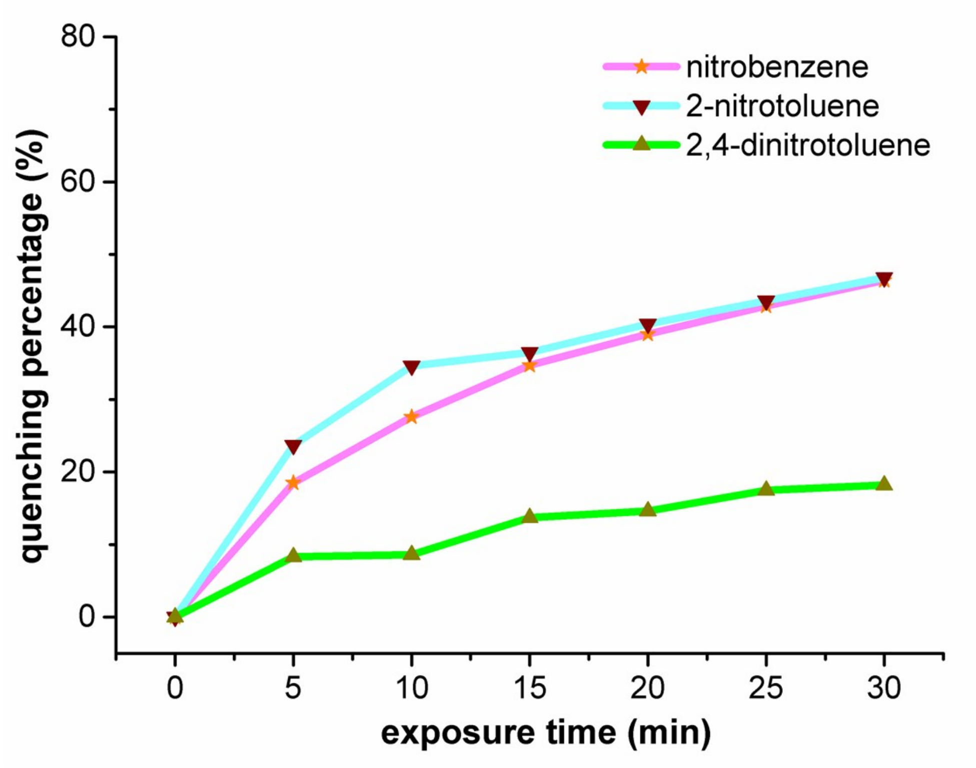

Fig. S15 Fluorescence percentage quenching graphs for **1** upon exposure to Group A analytes.

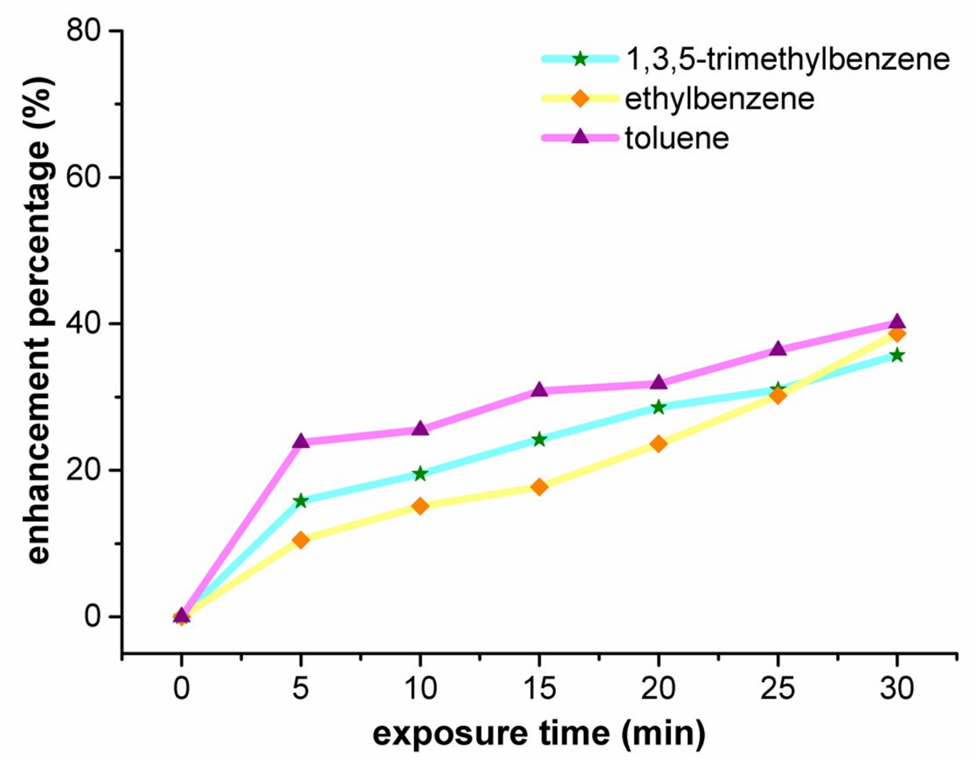

Fig. S16 Fluorescence percentage quenching graphs for **1** upon exposure to Group B analytes.

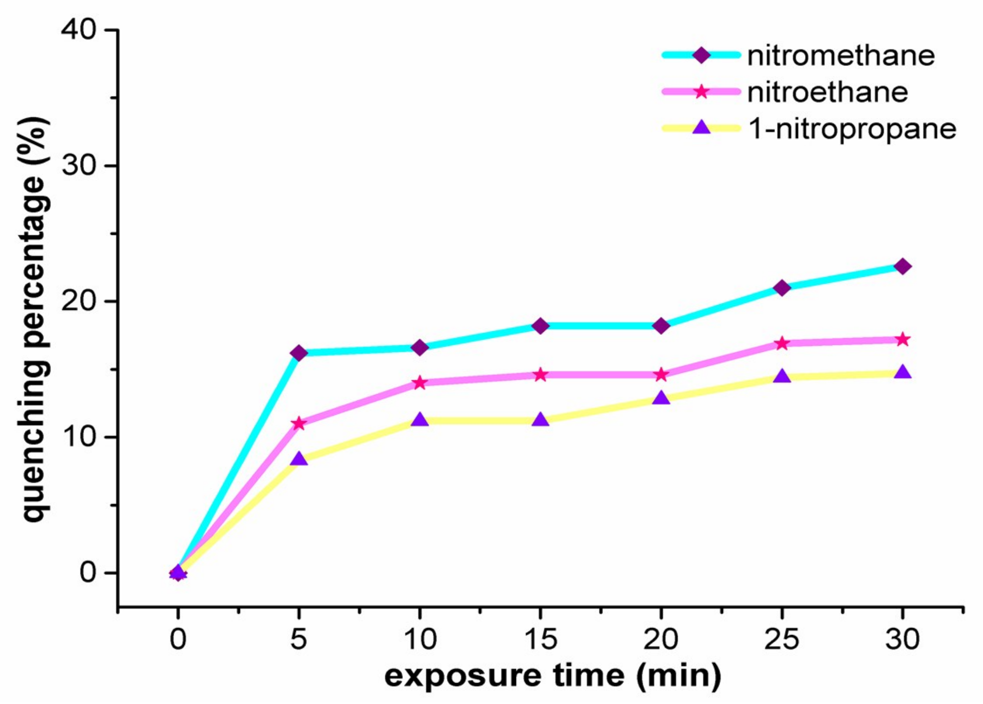

Fig. S17 Fluorescence percentage quenching graphs for **1** upon exposure to Group C analytes.

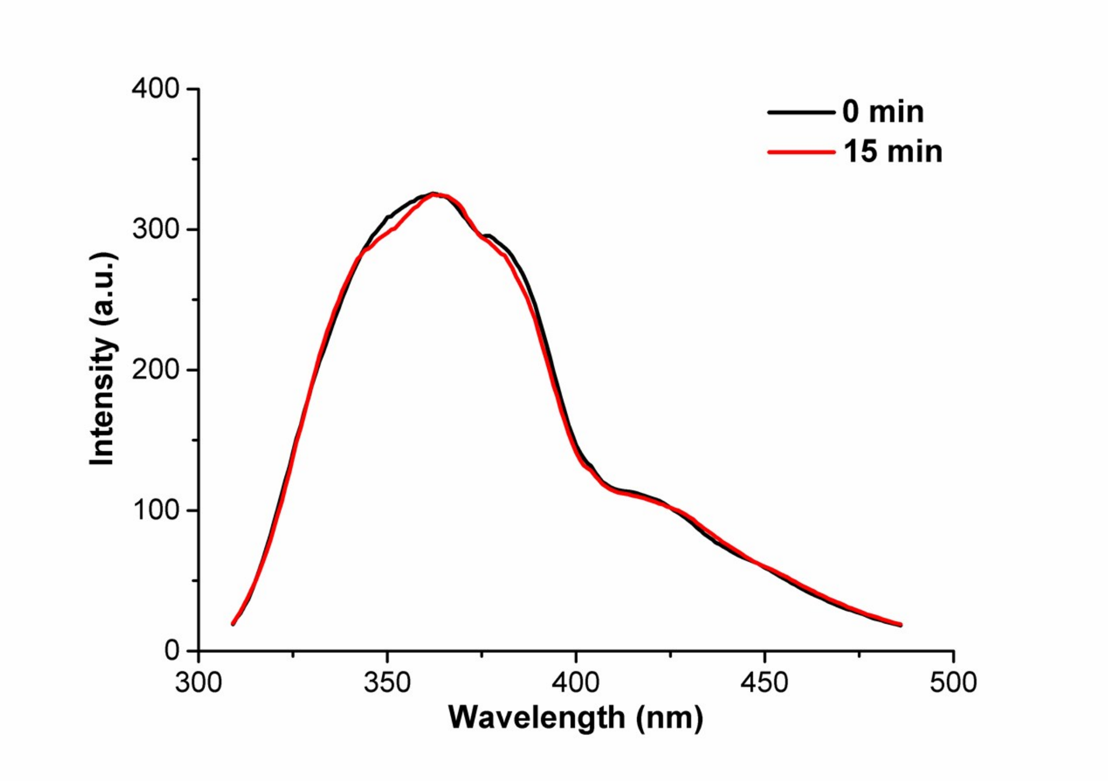

Fig. S18 Fluorescence emission spectrum of **1** after 15 min exposure to air at room temperature.

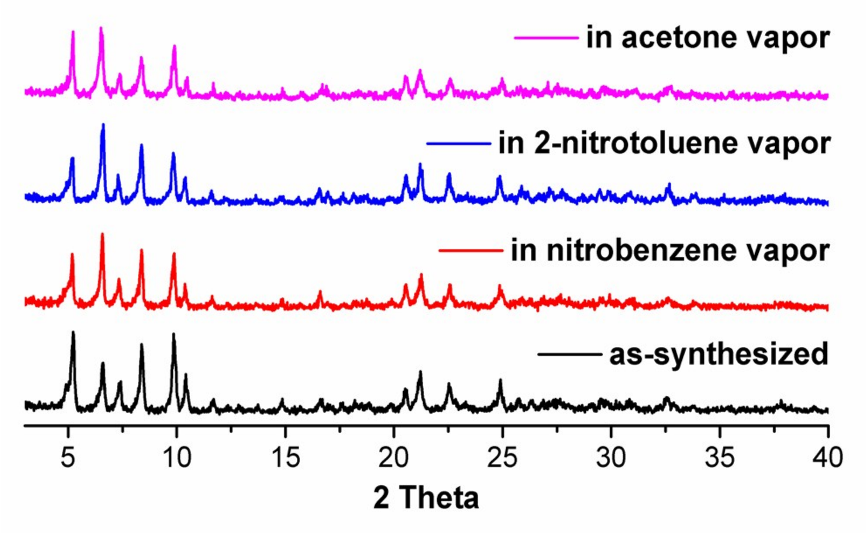

Fig. S19 PXRD patterns of **1** before and after exposure to acetone, nitrobenzene and 2-nitrotoluene vapor.

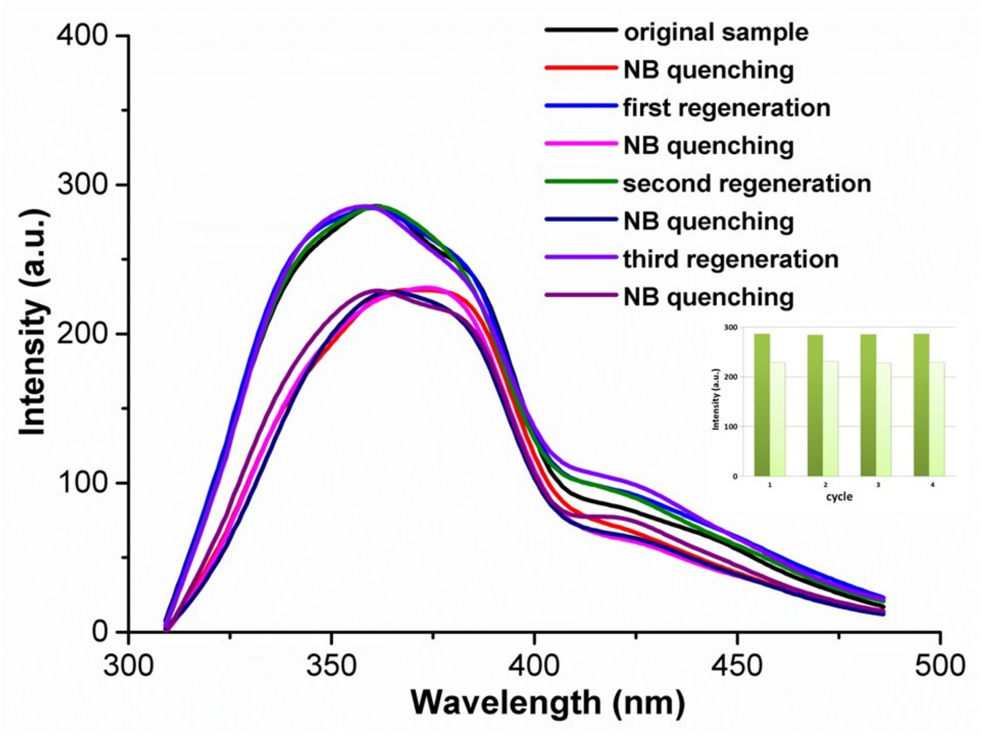

Fig. S20 Emission spectra of **1** in consecutive quenching and regeneration cycles. Dark green bar: emission of sample. Light green bar: emission after exposure to nitrobenzene vapor for 5 min.

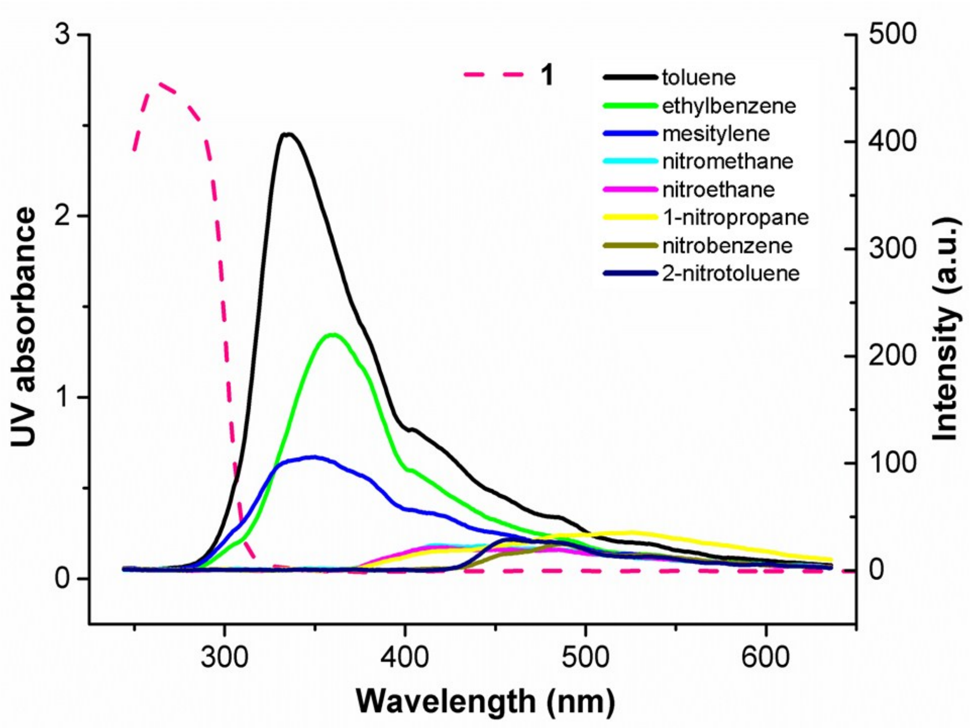

Fig. S21 Emission spectra of Group A-C analytes (solid lines) and UV absorbance of **1** (dashed pink).

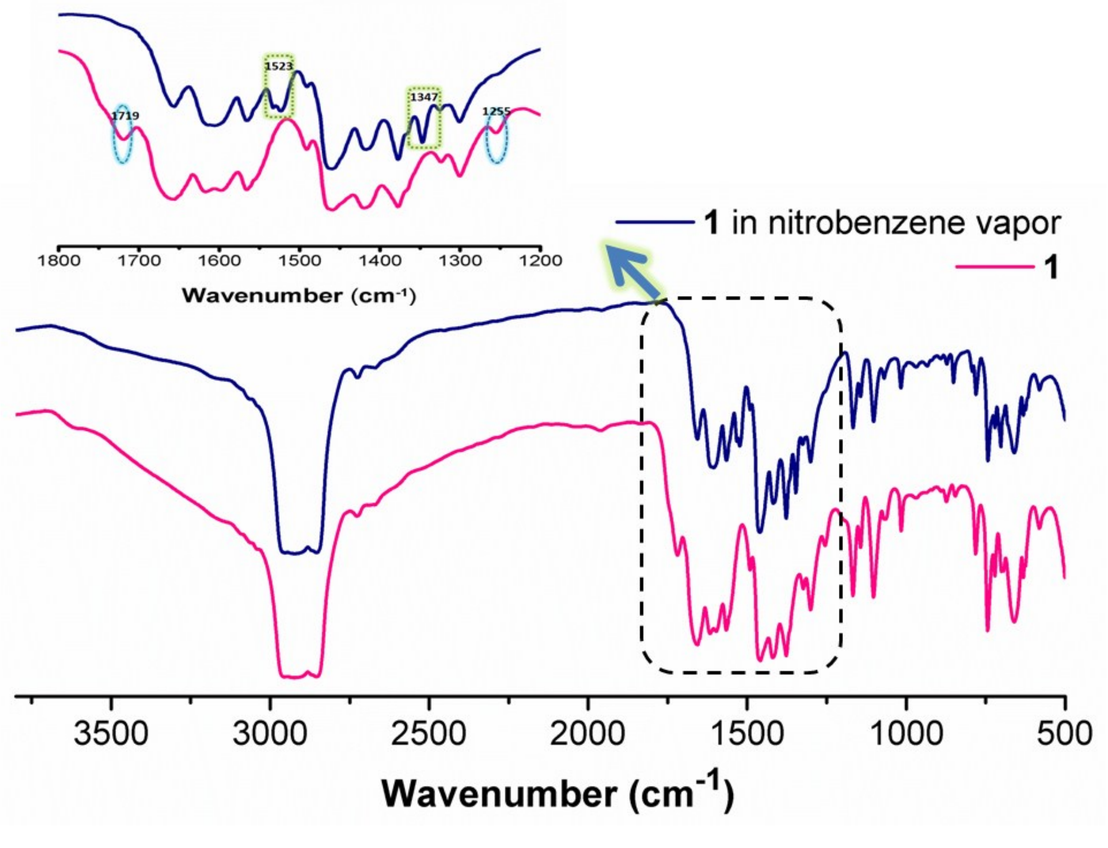

Fig. S22 IR spectra of **1** following exposure to nitrobenzene vapor.

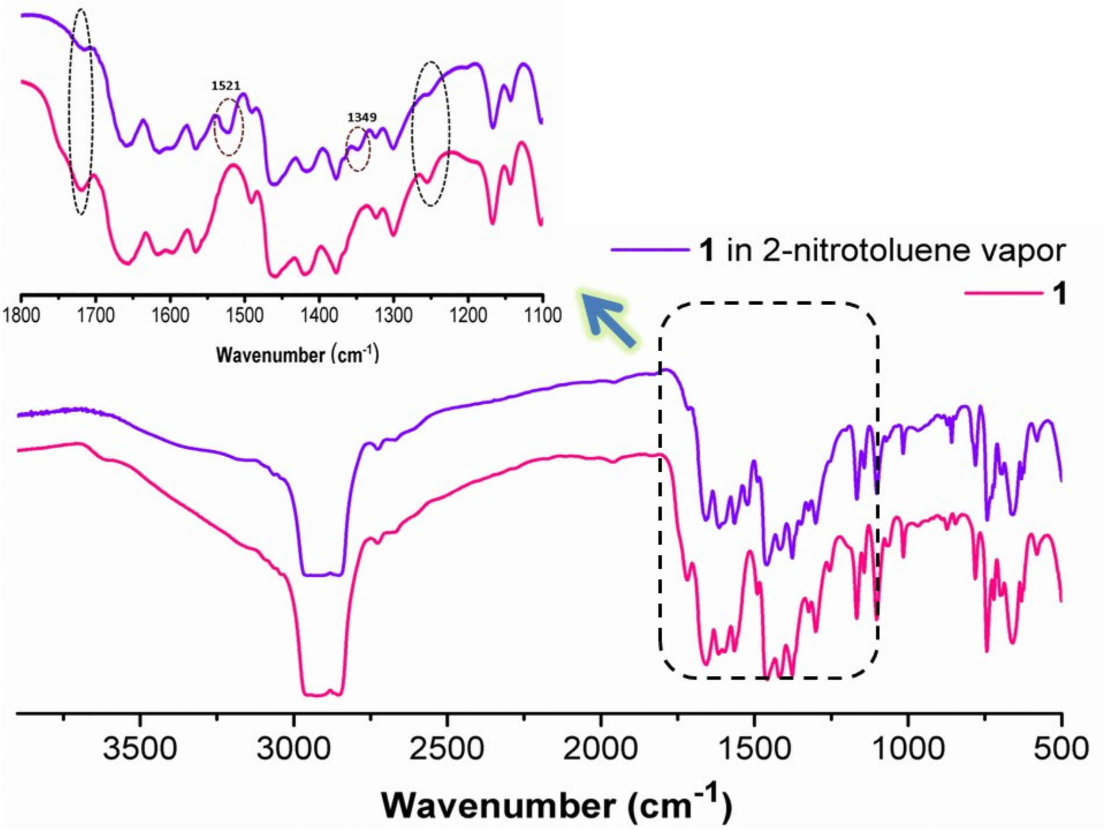

Fig. S23 IR spectra of **1** following exposure to 2-nitrotoluene vapor.

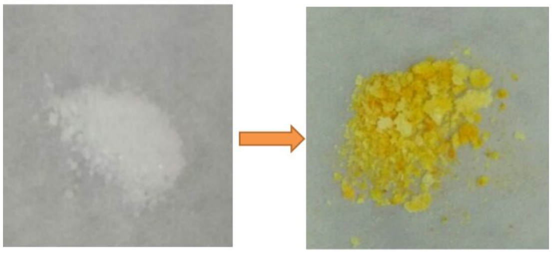

Fig. S24 Illustration of color change of **1** in nitrobenzene vapor

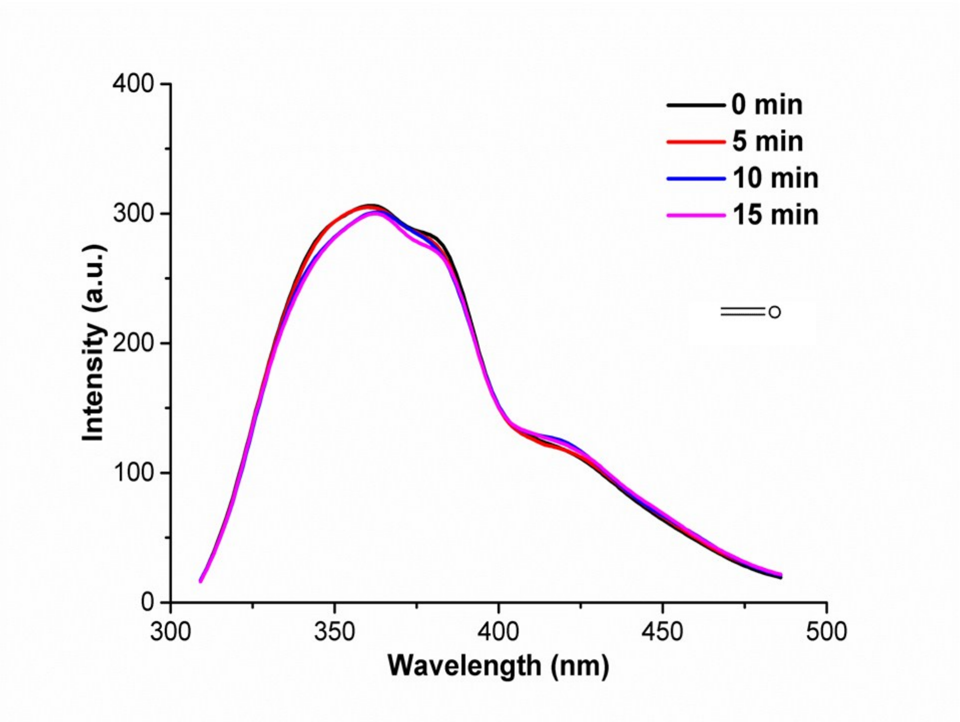

Fig. S25 PL emission spectrum of **1** after 15 min exposure to formaldehyde vapor at room temperature.

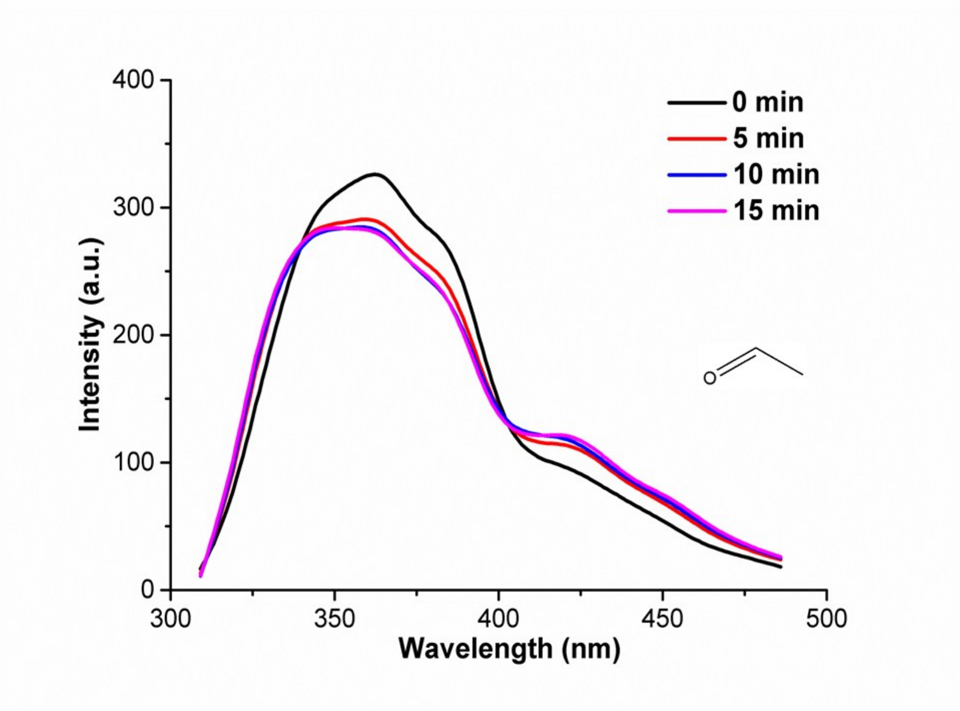

Fig. S26 PL emission spectrum of **1** after 15 min exposure to acetaldehyde vapor at room temperature.

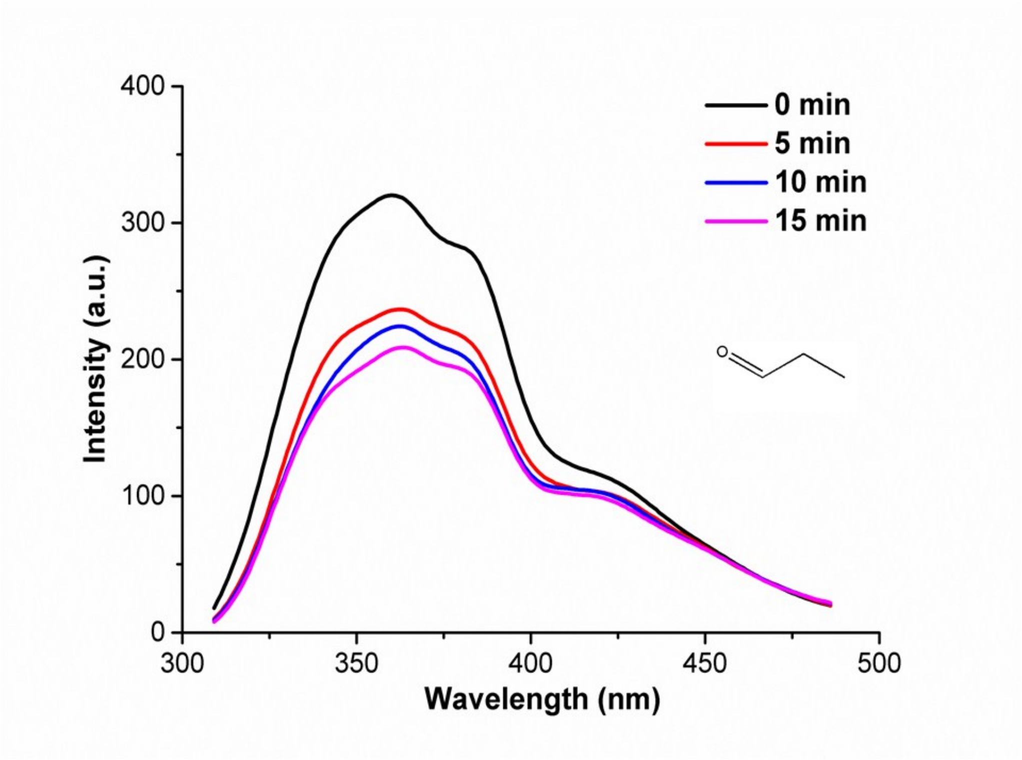

Fig. S27 PL emission spectrum of **1** after 15 min exposure to propionaldehyde vapor at room temperature.

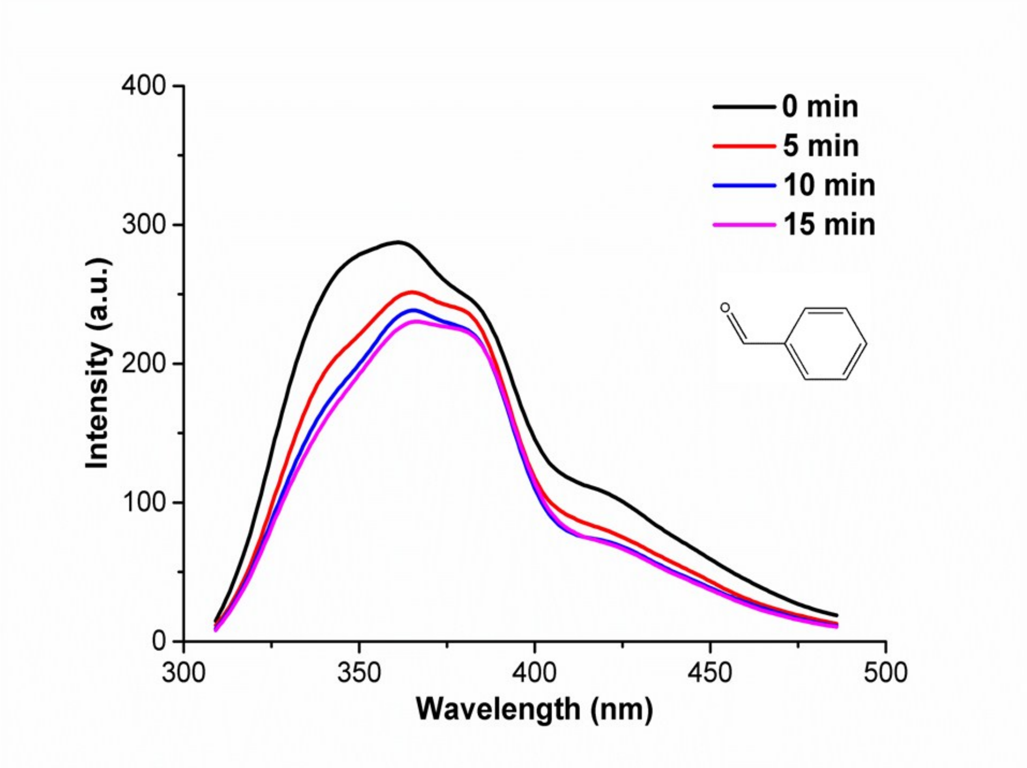

Fig. S28 PL emission spectrum of **1** after 15 min exposure to benzaldehyde vapor at room temperature.

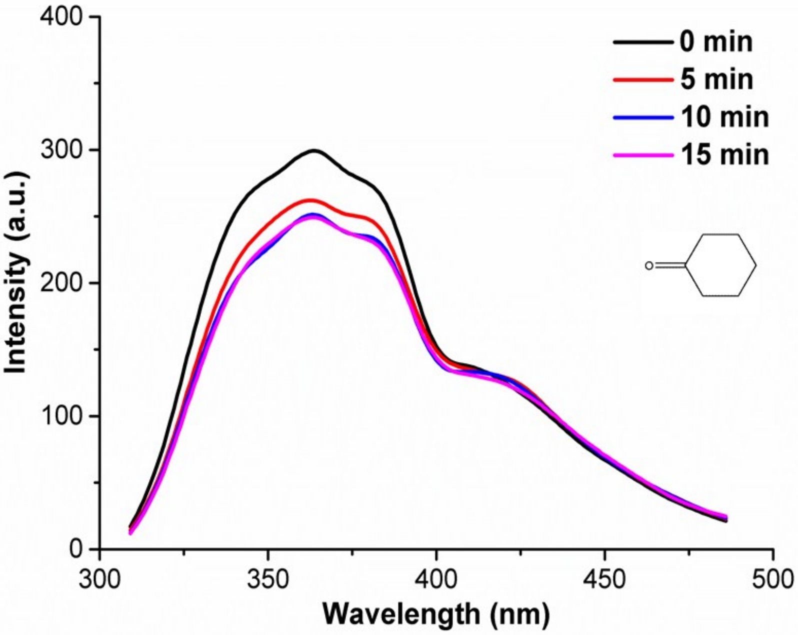

Fig. S29 PL emission spectrum of **1** after 15 min exposure to cyclohexanone vapor at room temperature.

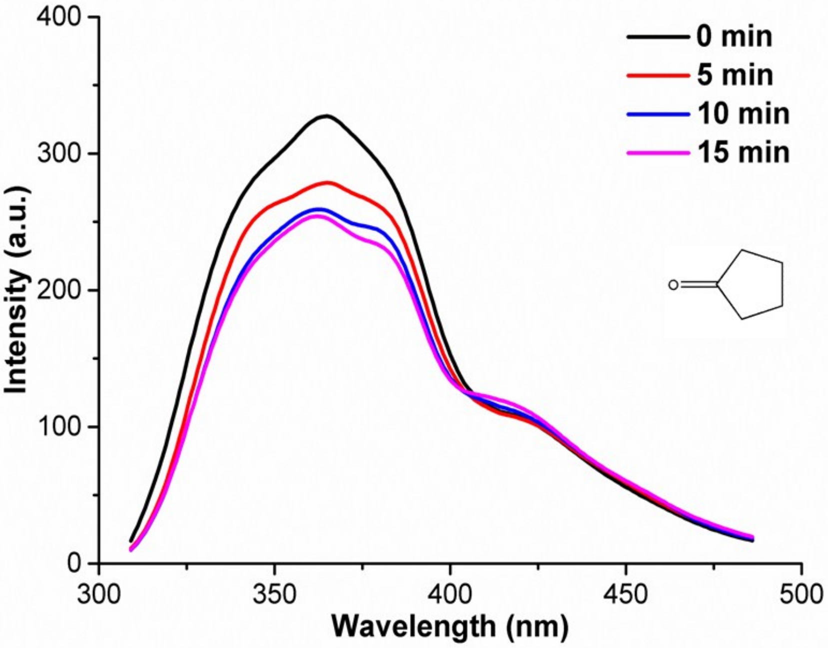

Fig. S30 PL emission spectrum of **1** after 15 min exposure to cyclopentanone vapor at room temperature.

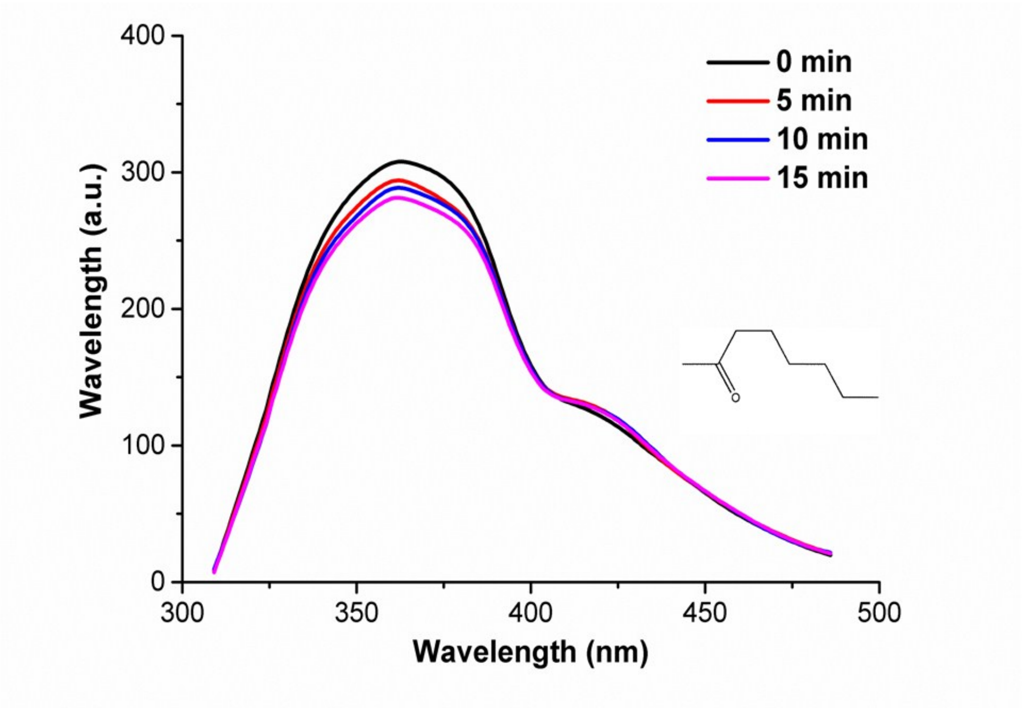

Fig. S31 PL emission spectrum of **1** after 15 min exposure to 2-octanone vapor at room temperature.

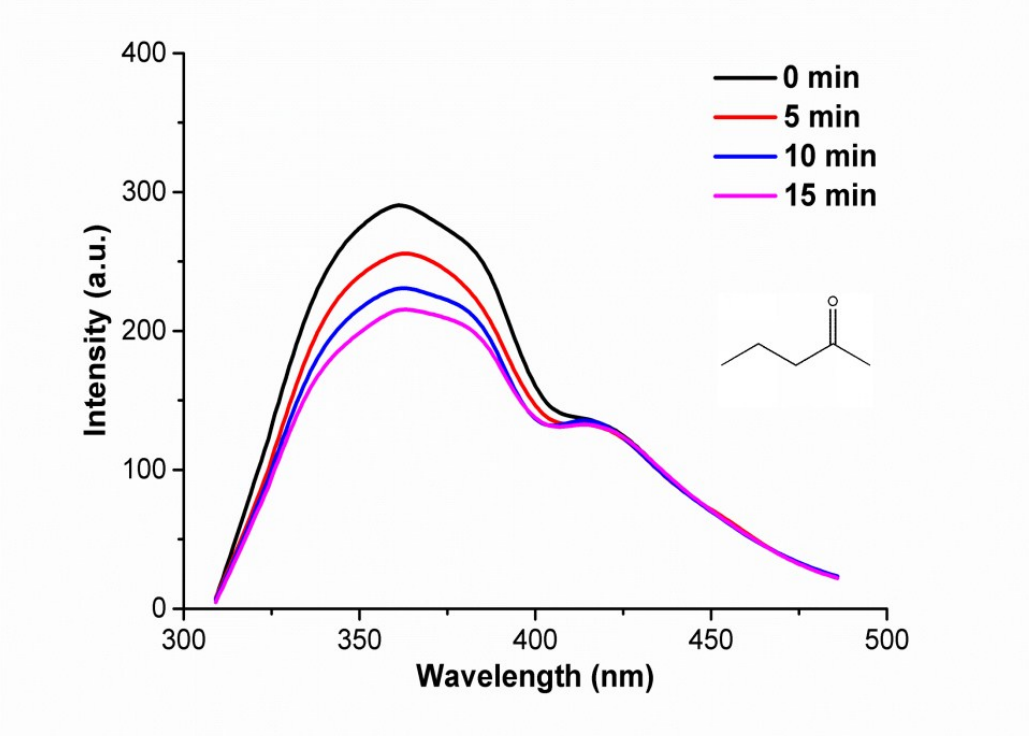

Fig. S32 PL emission spectrum of **1** after 15 minutes exposure to 2-pentanone vapor at room temperature.

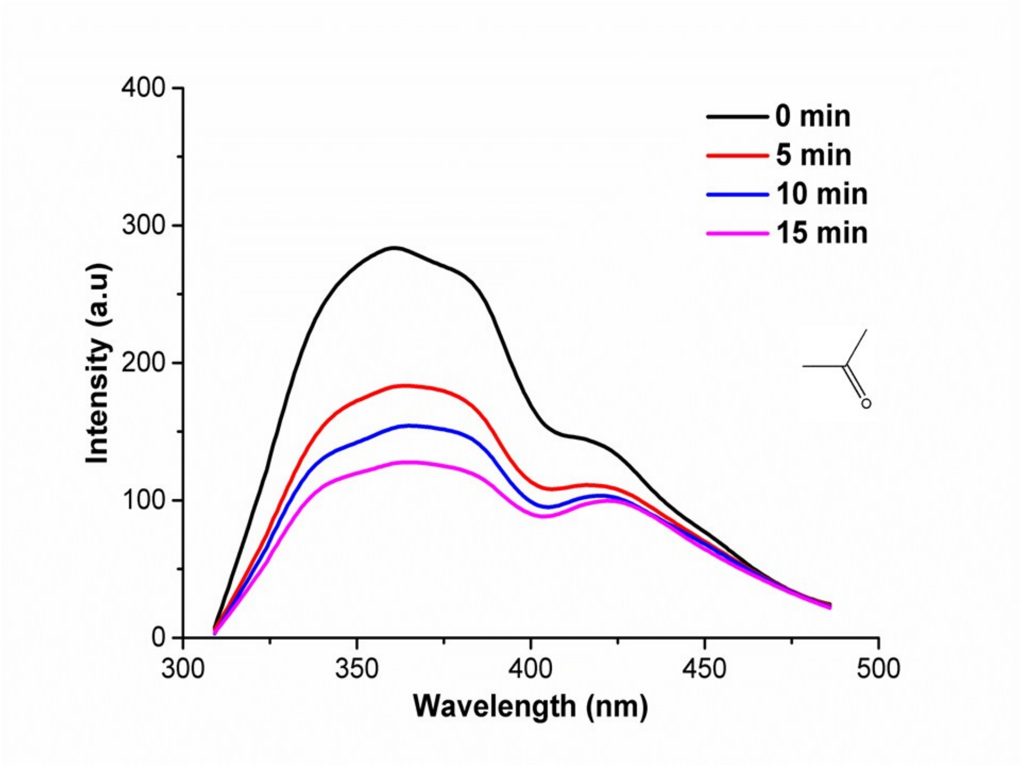

Fig. S33 PL emission spectrum of **1** after 15 min exposure to acetone vapor at room temperature.

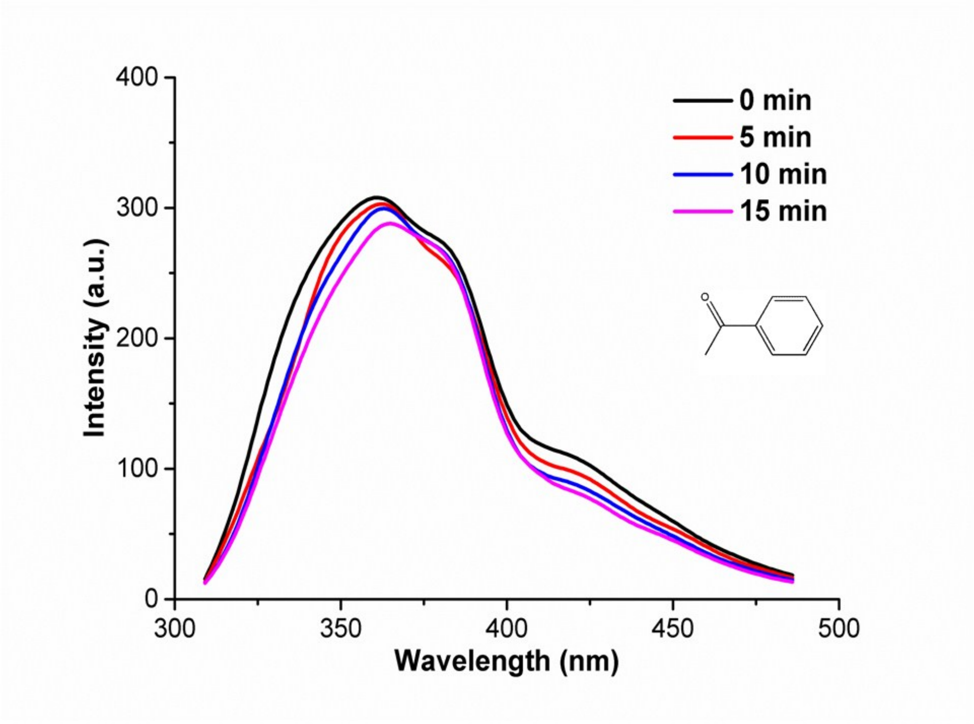

Fig. S34 PL emission spectrum of **1** after 15 min exposure to acetophenone vapor at room temperature.

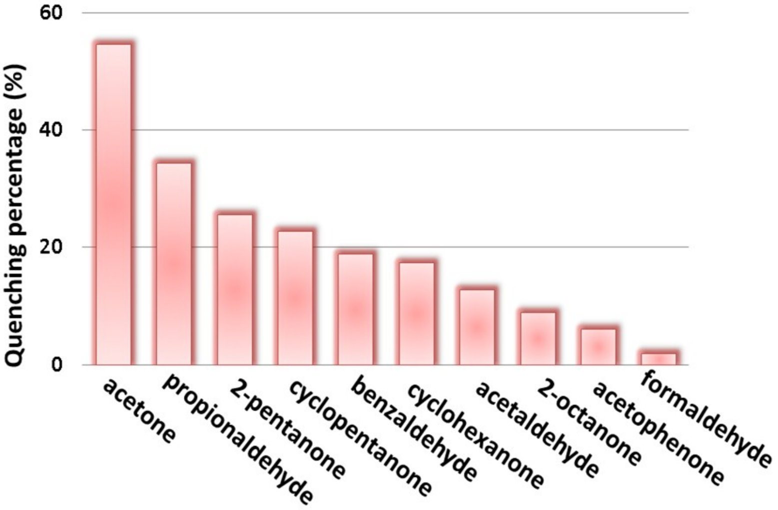

Fig. S35 A summary of the emission intensity change of **1** after exposure to aldehydes and ketones for 15 min at room temperature.

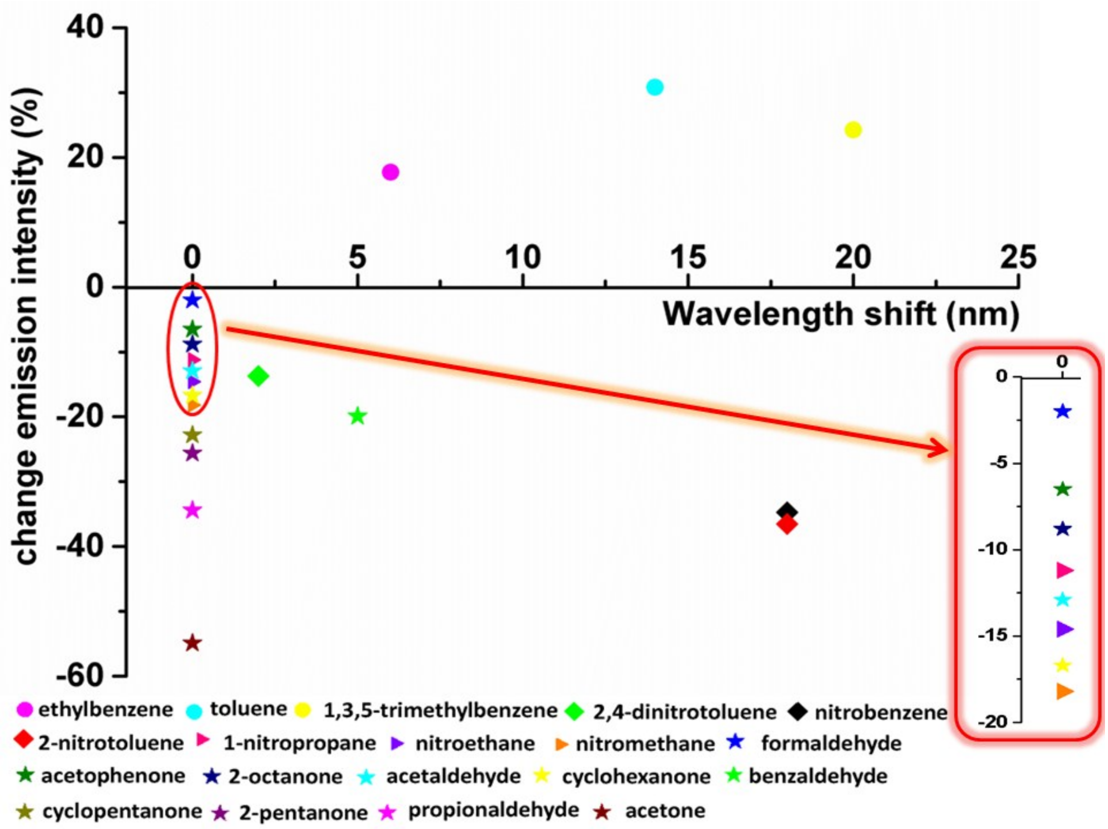

Fig. S36 A two-dimensional map based on the fluorescence response of **1** toward different analytes. Data were taken after exposure to analyte vapor 15 min.

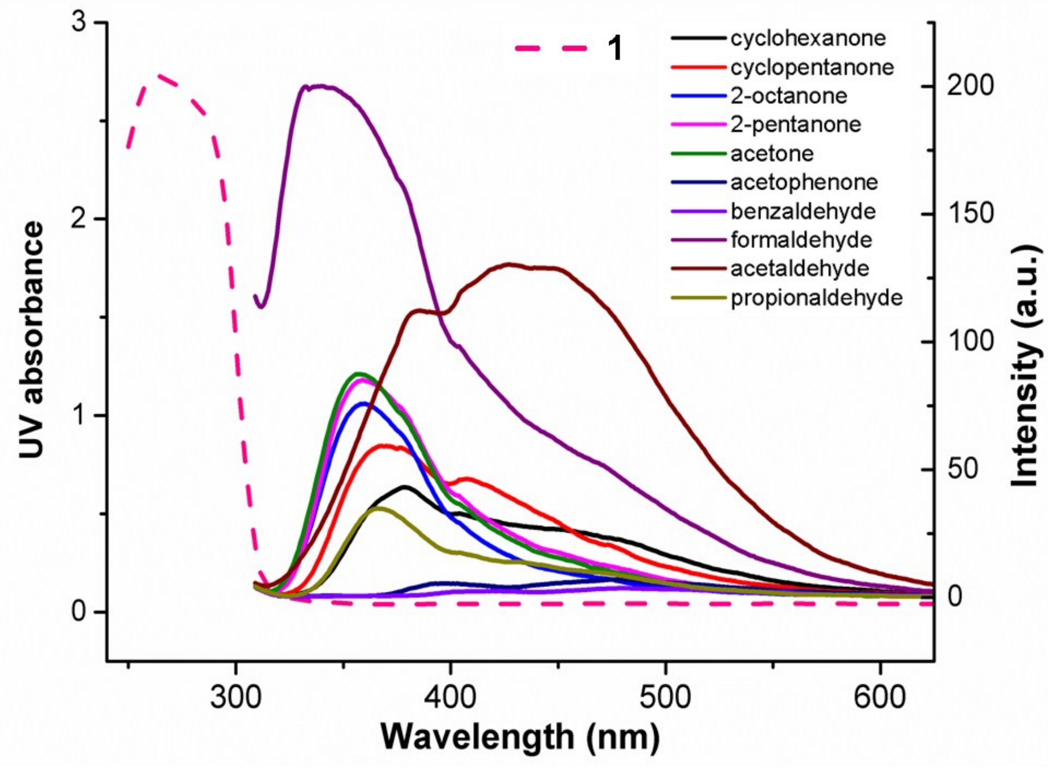

Fig. S37 Emission spectra of aldehydes and ketones (solid lines) and UV absorbance of **1** (dashed pink).

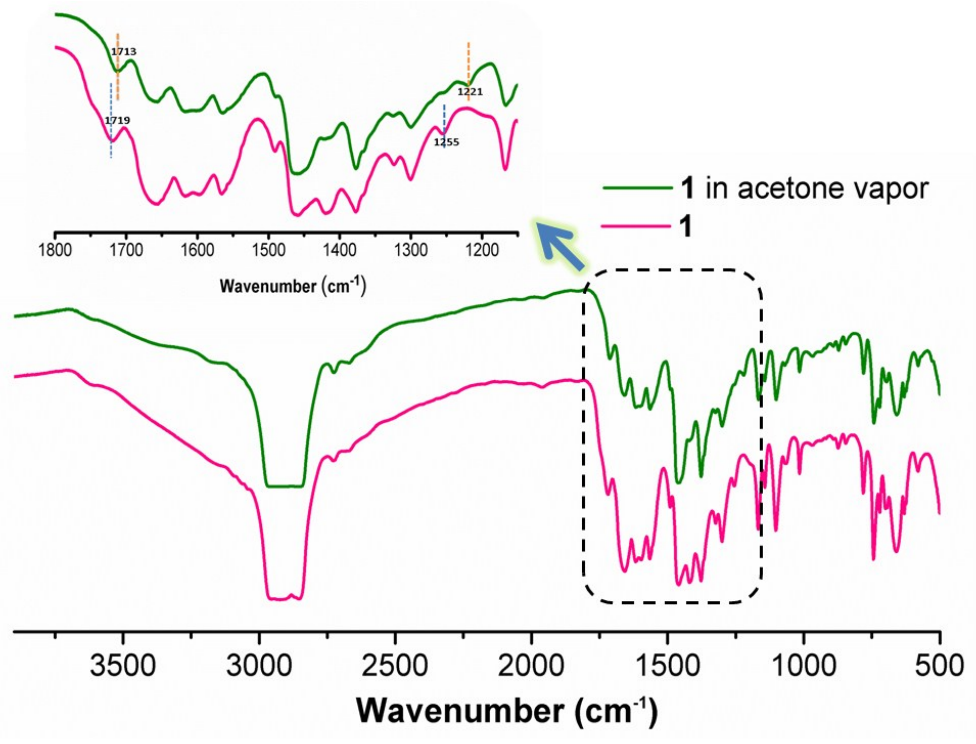

Fig. S38 IR spectra of **1** following exposure to acetone vapor.

References

1. (a) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3–8; (b) G. M. Sheldrick, SHELXTL Ver. 2014/7, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.

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