Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information (ESI)

A luminescent metal-organic framework constructed by a tetraphenylethene-based ligand for sensing volatile organic compounds

Materials and measurements. Tetrakis[4-(4-carboxyphenyl)phenyl]ethene (H_4TCPPE)[1] and (*S*)-5,6-dimethyl-2-(pyrrolidin-2-yl)-1*H*-benzimidazole (Dmpbim)[2] were prepared according to literature method. The elemental analyses were performed in a PE240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets. The powder XRD patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer. Thermal analyses were performed in nitrogen in the temperature range 25–600 ^{o}C with a heating rate of 10 ^{o}C min^{-1} on a TGA-DTA V1.1b Inst 2100 instrument. Fluorescence spectra were recorded on a Perkin-Elmer LS55 spectrofluorometer. The fluorescence absolute quantum yields (Φ_{fl}) of the samples were determined with a Horiba Jobin Yvon Fluorolog-3 spectrofluorimeter. Time-resolved fluorescence measurements were performed using a Life-Spec-ps fluorescence lifetime analytical spectrometer (Edinburgh Instruments). The adsorption isotherms were measured at 298 K for CO_2 and 77 K for N_2 using a Micrometric ASAP2020M system and ultra-pure gases (99.999%).

Preparation of 1. A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.050 mmol, 0.0149g), H_4TCPPE (0.005 mmol, 0.0042 g), Dmpbim (0.015 mmol, 0.0032g), 2 mL dimethylacetamide (DMAC) and 1 mL ethanol was mixed into a 10 mL screw capped vial. After applying ultrasound for 20 minutes, the vial was heated at 120 °C for 2 days, and then cooling to room temperature, pale-yellow plate crystals of **1** were obtained (yield: 46% based on H_4TCPPE). IR (KBr, cm^{-1}): 3023(w), 2926(w), 1607(s), 1528(m), 1404(s), 1263(w), 1184(w), 1000(m), 780(s), 701(w), 658(w), 586(w), 490(w). Dmpbim maybe play a role of chelating agent. Without Dmpbim, the white microcrystallines were characterized unsuccessfully.

Preparation of activated 1. The as-synthesized **1** crystals were washed three times with DMAC, and then were suspended in fresh CH_2Cl_2 at ambient lab conditions for two days, over which time the supernatant was decanted and replenished with fresh CH_2Cl_2 two times to remove adsorbed solvent molecules. At the end of the last decantation cycle, the crystals were collected and heated at 50 °C under high vacuum for 2 h, giving the activated **1** sample. Anal. Calcd for $C_{27}H_{16}O_4Zn$: C, 69.03; H, 3.43%. Found: C, 68.38; H, 3.69%. IR (KBr, cm^{-1}): 3426(w), 3027(w), 2354(w), 1666(m), 1619(s), 1513(m), 1406(s), 1175(w), 1115(w), 1022(m), 838(w), 763(s), 748(w), 456(m).

Treatment of activated 1 with VOC. The activated **1** sample was exposed in each vapour of nitrobenzene (NB) and 2,4-dinitrotoluene (DNT), and soaked into each other VOC liquids for 1 week, resulting in the formation of activated **1** with VOC. Subsequently, the sample was collected and dried with tissue for further characterization.

Crystallographic analysis. Data collection for complex **1** was carried out on a Saturn 70 CCD diffractometer. Hemisphere of data was collected in the θ range of 3.44-27.66 for **1**. The data were integrated using the Siemens SAINT program,[3] with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Empirical absorption and extinction corrections were applied. The structures were solved by direct method and refined on F^2 by full-matrix least squares using SHELXTL.[4] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were put in calculated positions and refined isotropically with the isotropic vibration parameters related to the non-hydrogen atoms to which they are bonded. The solvent molecules are highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. These solvent molecules were removed using the SQUEEZE routine of PLATON and the structure was then refined again using the data generated.[5]

Table S1. Crystallographic data for compound **1**.

	1
Formula	$C_{27}H_{16}O_4Zn$
M	469.77
crystal dimensions [mm]	0.34×0.21×0.13
crystal system	Orthorhombic
space group	*Ibam*
a [Å]	36.006(3)
b [Å]	6.0130(5)
c [Å]	31.426(3)
α [°]	90.00
β [°]	90.00
γ [°]	90.00
V [Å^3]	6803.8(10)
Z	8
D_c [g cm^{-3}]	0.917
μ [mm^{-1}]	0.742
F(000)	1920
R_{int}	0.093
T_{max}, T_{min}	24.76, 3.44
GoF on F^2	1.45
R_1, wR_2[a] [$I>2\sigma(I)$]	0.1294, 0.4214
(all data)	10413
$(\Delta\rho)_{\text{max}}$, $(\Delta\rho)_{\text{min}}$/e Å^{-3}	0.94, –1.59

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Emission wavelengths, fluorescence quantum yields and fluorescence lifetimes of **1**, activated **1** and H_4TCPPE.

Sample	**1**	activated **1**	H_4TCPPE
λ_{max} (nm)	461	535	545
Φ_{fl} (%)	7.2	11.3	30.0
τ (ns)	1.5	3.0	3.0

Table S3. Emission wavelengths of activated **1** with various VOCs.

Sample	activated **1** + benzene	activated **1** + *p*-xylene	activated **1** + *m*-xylene	activated **1** + mesitylene
λ_{max} (nm)	512	498	503	493
Sample	activated **1** + hexane	activated **1** + cyclohexane	activated **1** + nitrobenzene	activated **1** + 2,4-dinitrotoluene
λ_{max} (nm)	505	507	520	505

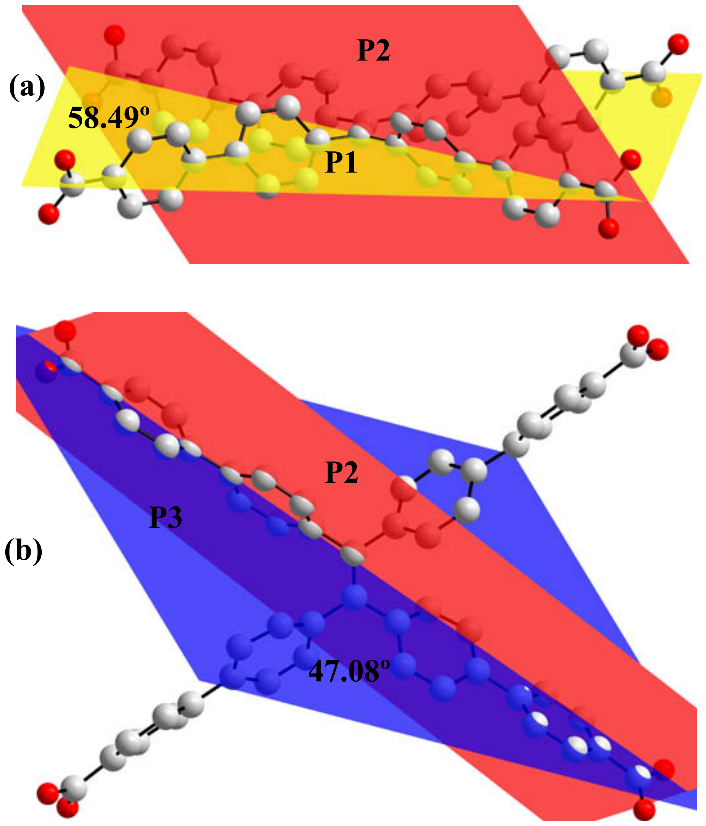

Fig. S1 The dihedral angles are labeled for (a) P1-P2 and (b) P2-P3.

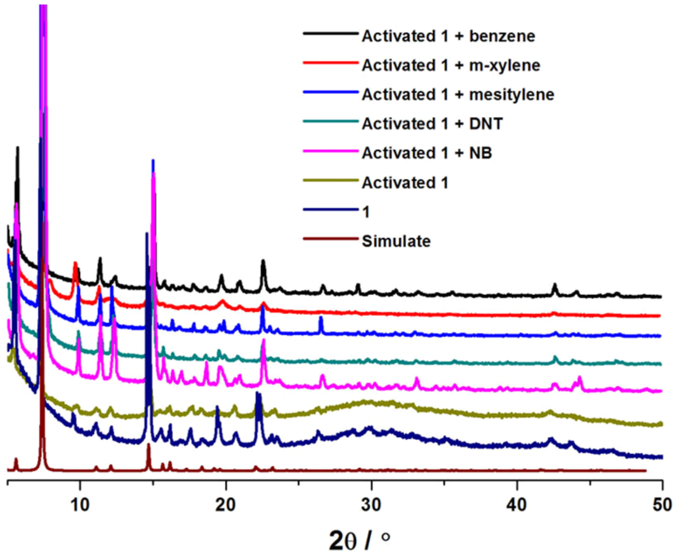

Fig. S2 XRD patterns for **1**, activated **1** and activated **1** with VOCs.

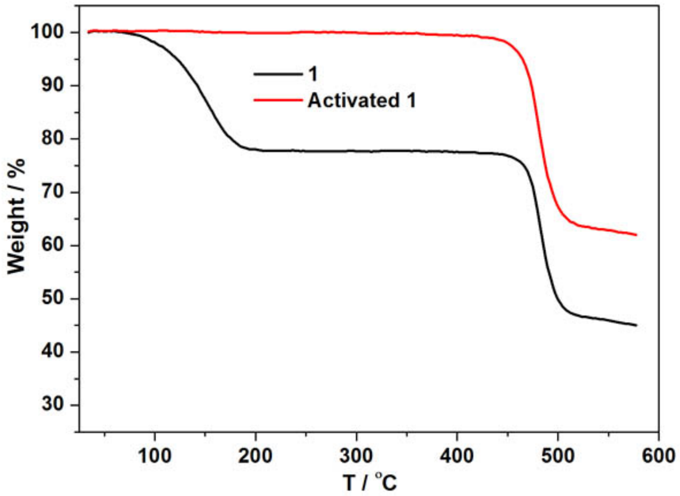

Fig. S3 Thermal analyses for **1** and activated **1**.

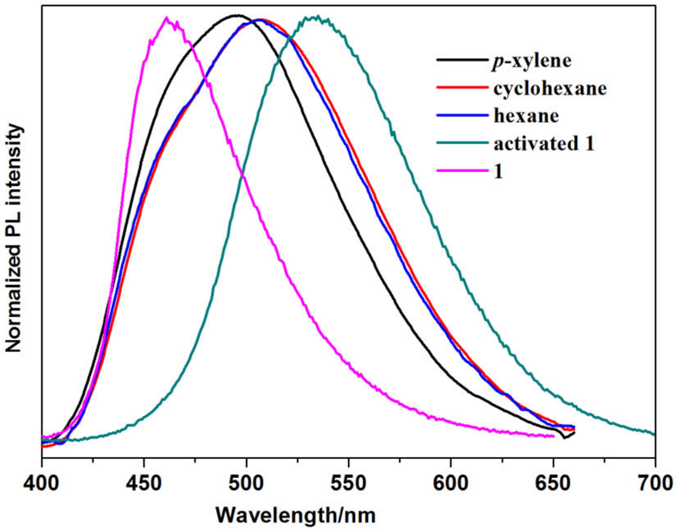

Fig. S4 Emission spectra of activated **1** with *p*-xylene, cyclohexane and hexane guest molecules.

References

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2 E. Lacoste, E. Vaique, M. Berlande, I. Pianet, J.-M. Vincent and Y. Landais, *Eur. J. Org. Chem.* 2007, 167-177.

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4 SAINT, Program for Data Extraction and Reduction, Siemens Analytical X-ray Instruments, Madison, WI, 1994-1996.

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