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Electronic Supplementary Information (ESI)

for

A four-fold interpenetrated metal-organic framework as fluorescent sensor for volatile organic compounds

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Materials and measurements

All the solvents and reagents were obtained commercially and used as received. The infrared (IR) spectra were recorded on a TENSOR 27 OPUS (Bruker) Fourier transform infrared (FT-IR) spectrometer using KBr pellets within the 4000−400 cm^{-1} region. Elemental analysis (C, H, N) was performed on a Perkin-Elmer 240C elemental analyzer. Thermal gravimetric analysis (TGA) was carried out on a Rigaku standard TG-DTA analyzer in air atmosphere with a heating rate of 10 °C/min from ambient temperature to 700 °C using an empty Al_2O_3 crucible as the reference. All fluorescence measurements were performed on a Hitachi F-4500 fluorescence spectrophotometer equipped with a plotter unit. Surface areas were measured by nitrogen adsorption and desorption at 77 K using a Bel Japan Inc. model BELSOPR-mini II analyzer and the samples were degassed at 180 ^{o}C for 3 h under vacuum (10^{-5} bar) before analysis. The transient fluorescence decay curves were measured on the PLS 920 (EDINBURGH, UK). The Powder X-ray diffraction (PXRD) spectra were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA with a Cu-target tube and a graphite monochromator. Simulation of the PXRD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the Internet at http://www.iucr.org.

Preparation of complex 1

A mixture of $Cd(NO_3)_2·4H_2O$ (0.04 mmol, 12.34 mg), H_2bpdc (0.02 mmol, 4.84 mg), TPPE (0.01 mmol, 6.4 mg) in DMF-H_2O solvent (5 mL, v/v=4:1) was sealed in a 10 mL vial and heated at 95 ^{o}C for 4 days. The reaction vessel was then cooled to room temperature and pale-yellow block crystals were obtained, which were collected by filtration after washing with DMF. The yield was ca. 52% estimated based on Cd(II). Anal. calcd for **1**, $C_{74}H_{50}Cd_2N_4O_9$: C, 65.15; H, 3.70; N, 4.11%. Found: C, 64.78; H, 3.80; N, 3.73%. FT-IR (KBr pellets, cm^{-1}): 3434 (s), 2928 (w), 1663 (s), 1656 (s), 1600 (w), 1589 (m), 1300 (w), 1225 (m), 853 (m), 812 (m), 771 (m), 737 (w), 682 (m), 595 (w), 511 (w), 428 (w).

Activation of Cd-MOF (1a)

The as-synthesized sample of **1** was immersed into EtOH for 3 days, with the EtOH refreshed every 24h. After the removal of EtOH by centrifuging, the EtOH-exchanged sample was dried at 80°C under vacuum for 24 h to yield activated **1** (denoted as **1a**) and then was ground into powder and used for fluorescence measurements.

Preparation of 1a⊃VOCs

Finely ground **1a** sample (3 mg) were soaked into individual VOCs liquid (3.0 mL) treated by ultrasonication for 30 min and then aged for 3 days to form a stable suspension before fluorescence study.

X-ray Crystallography

X-ray single-crystal diffraction data for **1** was collected on a Rigaku SCX-mini diffractometer with graphite monochromatic Mo-Kα radiation (λ = 0.7173 Å) by ω scan mode. The program SAIN[1] was used for the integration of the diffraction profiles. The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined with

SHELXL (semi-empirical absorption corrections were applied using SADABS program).[2] The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The remained solvent molecules in the channels of **1** were disordered and could not be modeled properly, and the contribution of their electron density was removed by the SQUEEZE routine in PLATON.[3]

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

Formula	$C_{74}H_{50}Cd_2N_4O_9$
Fw	1363.98
Crystal system	Triclinic
Space group	*P*-1
Temperature (K)	293
a (Å)	13.849(3)
b (Å)	14.724(3)
c (Å)	22.987(5)
α (°)	88.25(3)
β (°)	74.38(3)
γ (°)	87.86(3)
V (Å^3)	4510.1(17)
Z	2
μ (mm^{-1})	0.515
Dc (g/cm^3)	1.004
R(int)	0.0925
GOF on F^2	0.903
R_1[a] ［I>2σ(I)］	0.0721(9097)
wR_2[b] ［I>2σ(I)］	0.1982(20264)

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

Table S2. Bond lengths [Å] and angles [°] for complex **1.**

Cd(1)-O(5)	2.277(5)	Cd(2)-N(2)#2	2.309(6)
Cd(1)-O(1)	2.305(4)	N(2)-Cd(2)#7	2.309(6)
Cd(1)-O(9)	2.353(5)	Cd(2)-N(1)#3	2.321(5)
Cd(2)-O(7)	2.361(14)	N(1)-Cd(2)#6	2.321(5)
Cd(2)-O(3)#4	2.388(4)	Cd(1)-N(4)	2.332(5)
Cd(2)-O(4)#4	2.323(5)	Cd(1)-N(3)#1	2.363(5)
Cd(2)-O(8)	2.263(5)	O(5)-Cd(1)-N(4)	135.09(19)
O(5)-Cd(1)-O(1)	85.10(19)	O(5)-Cd(1)-O(9)	87.6(2)
O(1)-Cd(1)-N(4)	139.64(17)	O(5)-Cd(1)-N(3)#1	104.2(2)
O(1)-Cd(1)-O(9)	93.28(17)	O(1)-Cd(1)-N(3)#1	91.78(19)
N(4)-Cd(1)-O(9)	86.28(18)	O(9)-Cd(1)-N(3)#1	167.52(19)
N(4)-Cd(1)-N(3)#1	82.5(2)	O(1)-Cd(1)-O(2)	52.76(16)
O(5)-Cd(1)-O(2)	136.61(18)	O(9)-Cd(1)-O(2)	85.37(16)
N(4)-Cd(1)-O(2)	87.07(16)	O(5)-Cd(1)-O(6)	52.14(18)
N(3)#1-Cd(1)-O(2)	88.64(18)	N(4)-Cd(1)-O(6)	84.29(18)
O(1)-Cd(1)-O(6)	135.72(18)	N(3)#1-Cd(1)-O(6)	88.8(2)
O(9)-Cd(1)-O(6)	95.45(19)	N(2)#2-Cd(2)-N(1) #3	87.6(2)
O(2)-Cd(1)-O(6)	171.24(16)	O(8)-Cd(2)-N(1)#3	96.5(2)
O(8)-Cd(2)-N(2)#2	141.5(2)	N(2)#2-Cd(2)-O(4)#4	100.8(2)
O(8)-Cd(2)-O(4)#4	198.4(2)	O(8)-Cd(2)-O(7)	54.5(4)
N(1)#3-Cd(2)-O(4)#4	143.31(19)	N(1)#3-Cd(2)-O(7)	118.8(15)
N(2)#2-Cd(2)-O(7)	90.1(5)	O(8)-Cd(2)-O(3)#4	125.8(2)
O(4)#4-Cd(2)-O(7)	97.1(16)	N(1)#3-Cd(2)-O(3)#4	89.13(18)
N(2)#2-Cd(2)-O(3)#4	92.5(2)	O(7)-Cd(2)-O(3)#4	152.1(15)
O(4)#4-Cd(2)-O(3)#4	55.17(17)		

Symmetry Codes: #1 x-1,y,z; #2 x,y+2,z; #3 x-1,y+2,z; #4 x,y+1,z+1; #5 x,y-1,z-1; #6 x+1,y-2,z; #7 x,y-2,z; #8 x+1,y,z

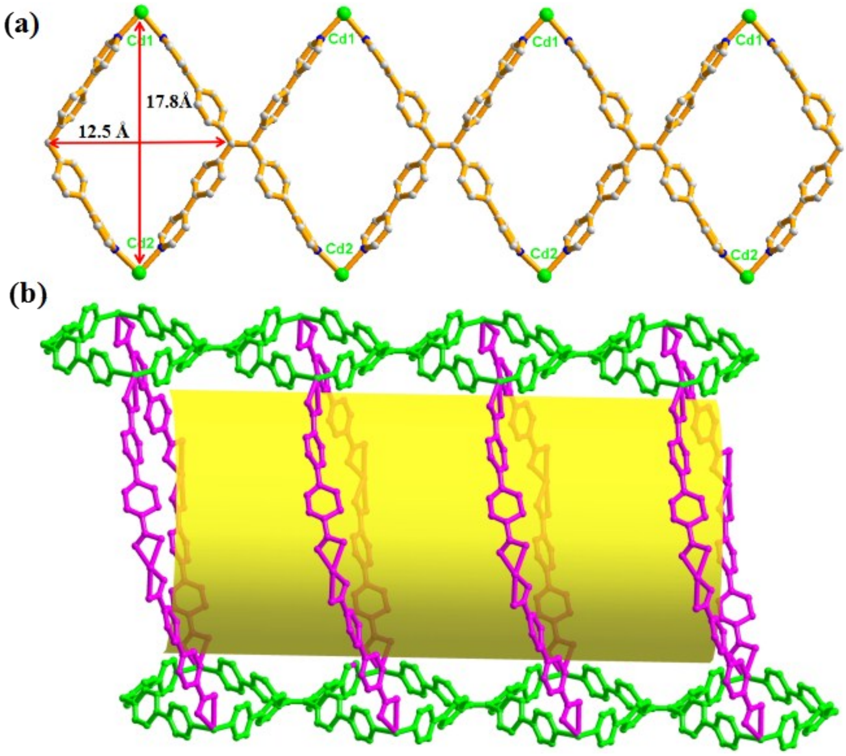

Fig. S1 (a) Schematic presentation of one-dimensional chains in a rhomboic form; (b) Representation of the 1D channel.

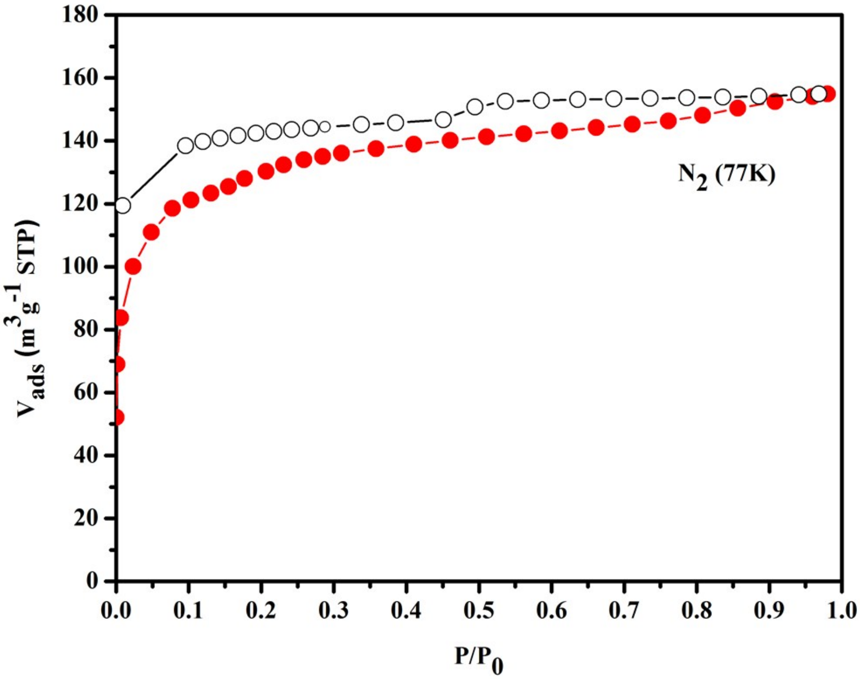

Fig. S2 Gas adsorption and desorption isotherm of **1a** based N_2 sorption data at 77 K.

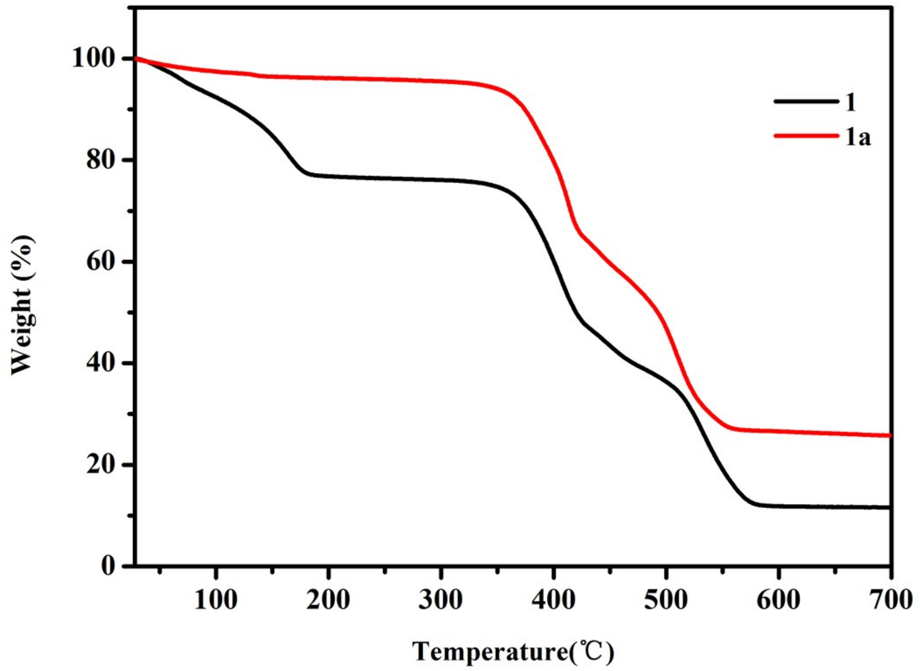

Fig. S3 Thermogravimetric curve of complex **1** and **1a** under air atmosphere.

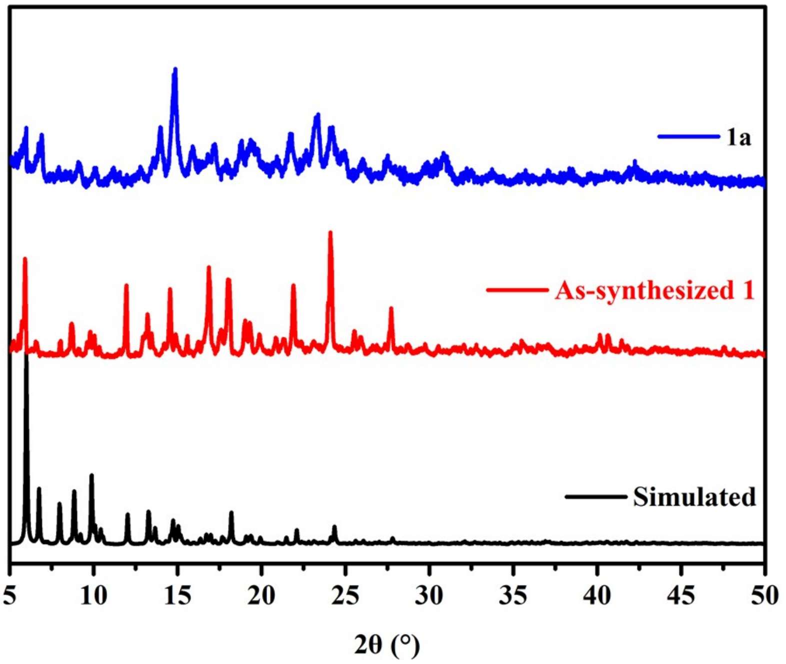

Fig. S4 The PXRD of **1a** (blue), as-synthesized **1** (red) and the calculated pattern (black) from the crystal structure of **1**.

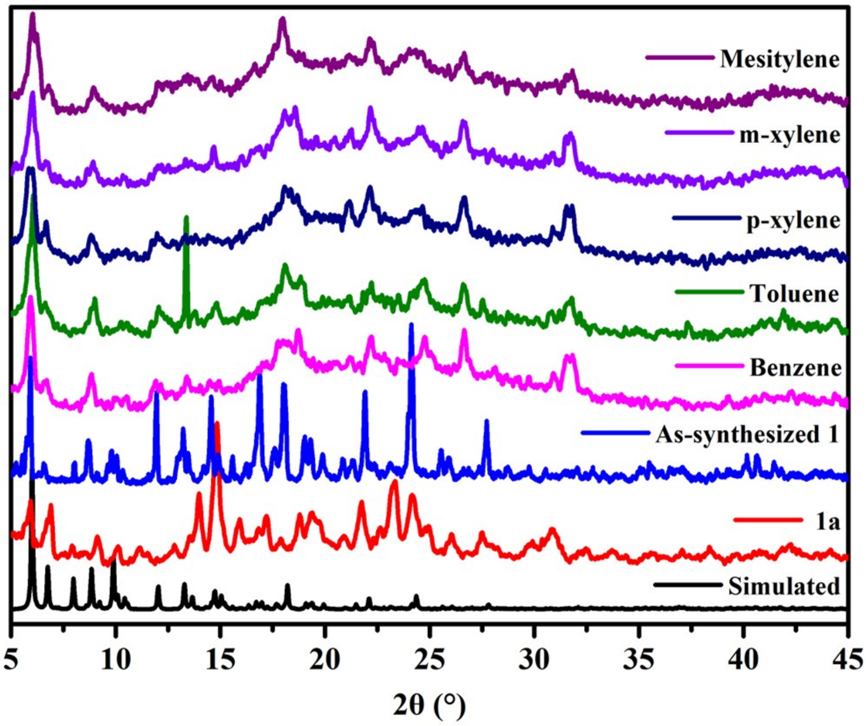

Fig. S5 Comparison of PXRD patterns for **1**, **1a** and **1a**⊃VOCs.

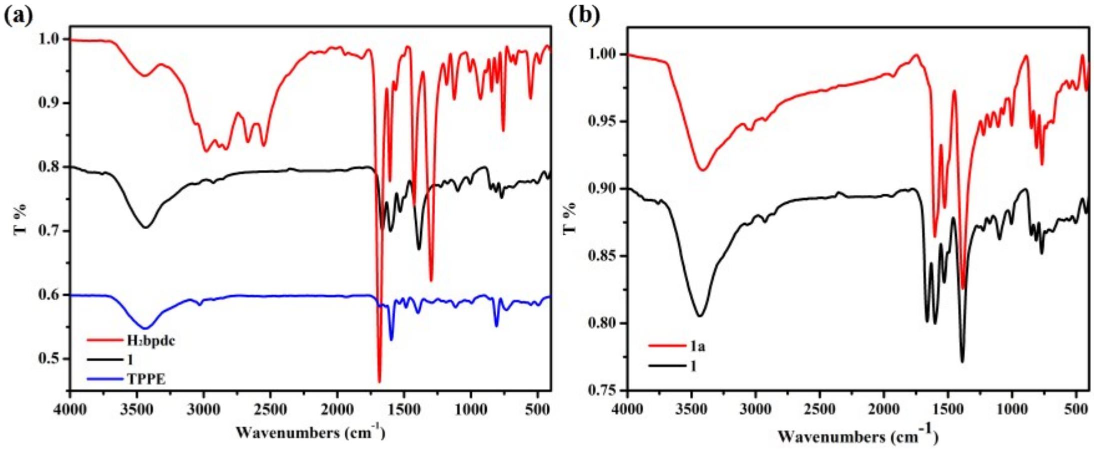

Fig. S6 (a) FT-IR comparison of free H_2bpdc, TPPE and **1;** (b) FT-IR comparison of **1** and **1a**.

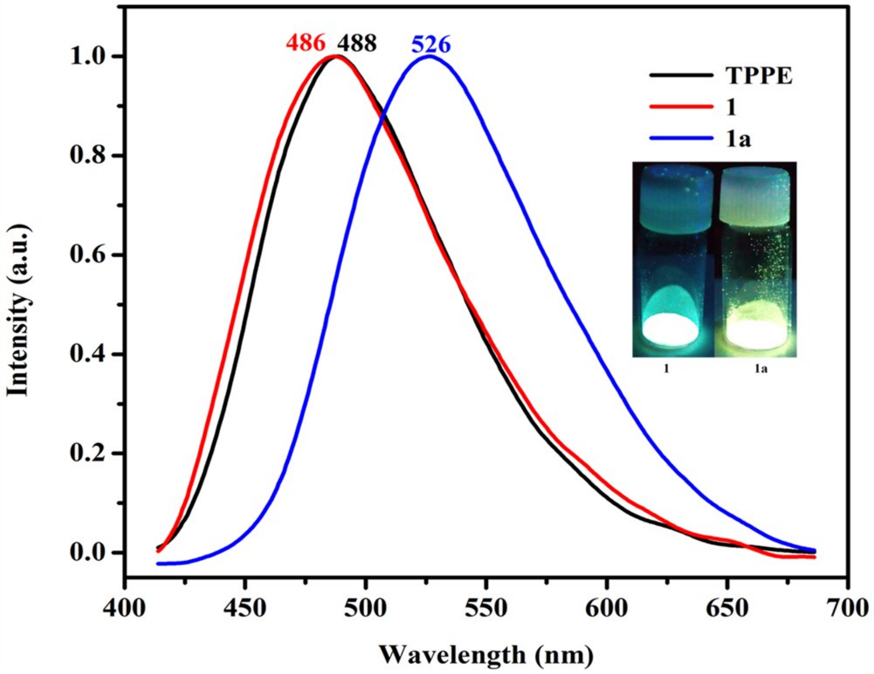

Fig. S7 Solid-state emission spectra of tppe, **1** and **1a** (λ_{ex} = 380 nm). Inset: **1** and **1a** under the irradiation of 365 nm UV-lamp.

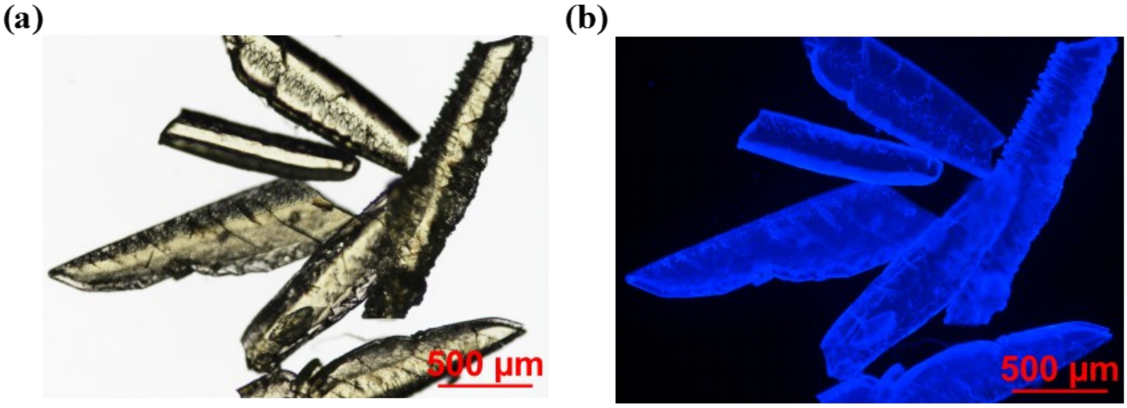

Fig. S8 Microscope images of freshly synthesized crystals of complex **1:** (a) under ambient light; (b) under the UV light (365 nm).

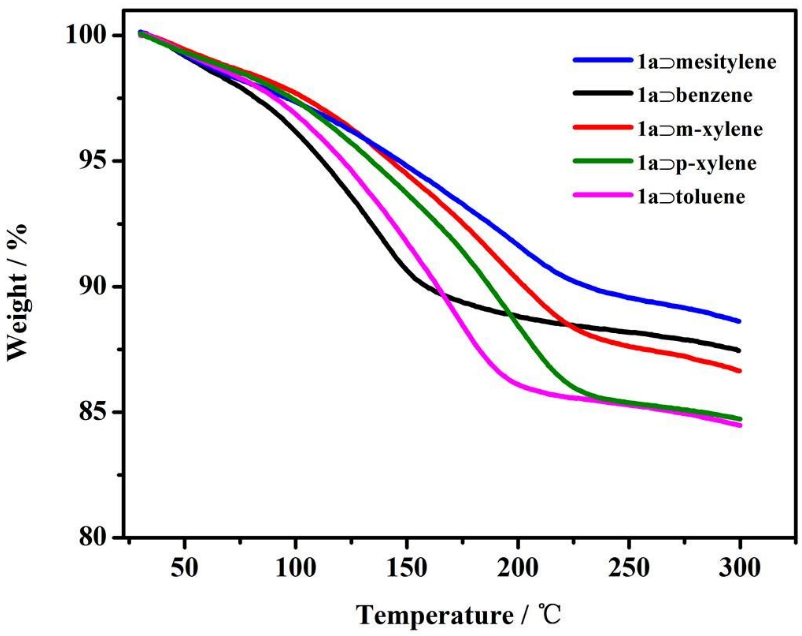

Fig. S9. The TGA curves of the soaked samples of **1a** in different volatile organic compounds of benzene, toluene, m-xylene, p-xylene, and mesitylene under heating rate of 10℃/min under air atmosphere. The mass loss in the first step corresponds to the removal of guest molecules.

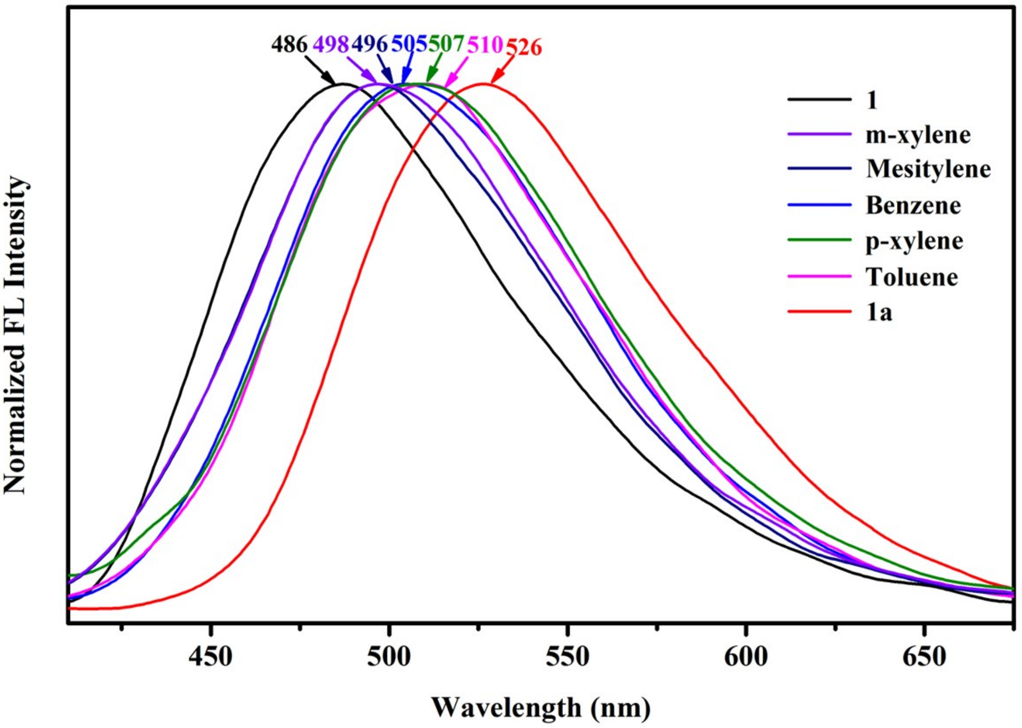

Fig. S10. Normalized emission spectra of **1**, **1a** and **1a**⊃VOCs. (excited at 380 nm)

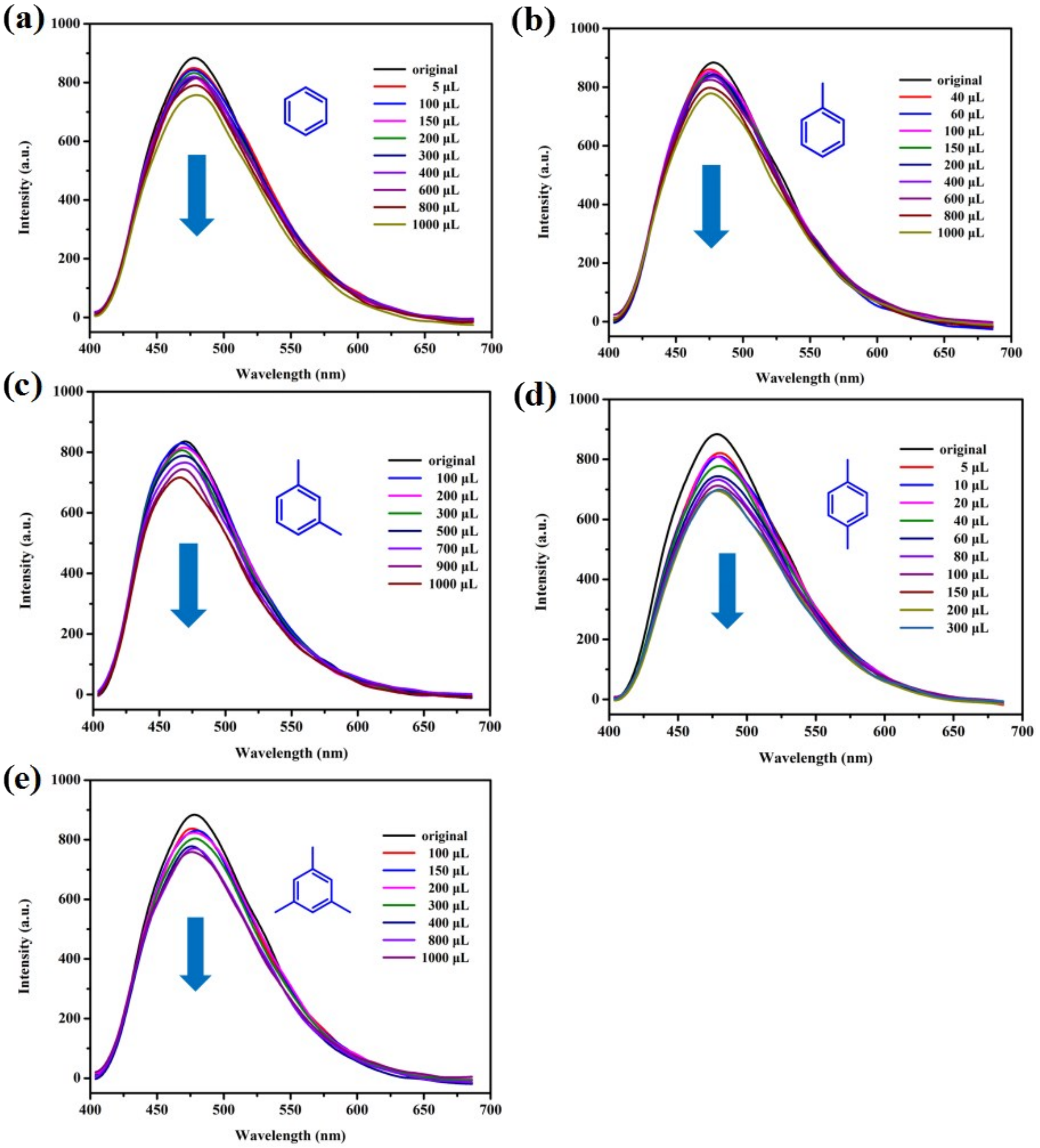

Fig. S11. Fluorescence titration of **1a** dispersed in DMF solution of benzene (a), toluene (b), *m*-xylene (c), *p*-xylene (d), and mesitylene (e) with different concentrations (λ_{ex} = 380 nm).

Table S3. 1a⊃VOCs measured by elemental analysis.

1a with guest molecule	**Atom% (product)**[a]					
	C		**H**		**N**	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
1a⊃benzene	63.80	68.56	3.85	4.2	3.25	3.59
1a⊃toluene	65.16	69.56	4.60	4.55	3.48	3.41
1a⊃m-xylene	65.58	68.57	4.37	4.48	3.53	3.55
1a⊃p-xylene	65.82	68.72	4.62	4.51	3.43	3.53
1a⊃mesitylene	63.23	67.72	4.39	4.35	3.73	3.69

[a] **Atom%, determined by elemental analysis.**

Table S4. Emission wavelengths, fluorescence quantum yields and fluorescence lifetimes of **1**, **1a** and TPPE.

Sample	**TPPE**	**1**	**1a**
λ_{max} (nm)	488	486	526
Φ_{fl} (%)	57.2	53.8	63.3
τ (ns)	1.82	2.94	4.54

Table S5. Emission wavelengths and fluorescence quantum yields of **1a ⊃ VOCs**.

Sample	**1a⊃Toluene**	**1a⊃*p*-xylene**	**1a⊃Benzene**
λ_{max} (nm)	510	508	505
Φ_{fl} (%)	64.5	71.8	72.5
Sample	**1a⊃Mesitylene**	**1a⊃*m*-xylene**	
λ_{max} (nm)	495	497	
Φ_{fl} (%)	59.4	70.9	

References

1. *SAINT Software Reference Manual*; Bruker AXS: Madison, WI, 1998.
2. (a) Sheldrick, G. M. SHELXTL NT, *Program for Solution and Refinement of Crystal Structures*, Version 5.1; University of Gttingen: Germany, 1997. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, 64, 112−122.
3. Spek, A. L. *J. Appl. Crystallogr.* **2003**, 36,7−13.