

## Supporting information

# Eu(III)-functionalized ZnO@MOFs heterostructures: integration of pre-concentration and efficient charge transfer as ppb-level sensing platform for volatile aldehyde gases in vehicles

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### Experimental Section

#### Materials and Reagents

All chemicals employed were commercially available reagents of analytical grade and used without further purification. Europium chlorides ( $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ ) were prepared by dissolving the  $\text{Eu}_2\text{O}_3$  in excess hydrochloric acid (37.5%) followed by evaporation and crystallization.

#### Measurements

Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2010F electron microscope operated at 200 kV. Powder X-ray diffraction (PXRD) patterns were recorded with a D/max2550VB3+/PC diffractometer under  $\text{CuK}\alpha$  radiation with a 1.5418 Å wavelength and the data were collected within the  $2\theta$  in range of 5–50°. The morphologies of samples were characterized by scanning electron microscopy (SEM, Hitachi S4800, 3 kV) equipped with an energy dispersive X-ray spectrometer (EDS). X-ray photoelectron spectra (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with  $\text{Mg K}\alpha$  radiation ( $h\nu = 1253.6$  eV). Thermogravimetric analysis (TGA) was carried out using a Labsysevo (SETARAM, Franec) system at a heating rate of 5  $\text{K min}^{-1}$  under nitrogen protection. Nitrogen adsorption–desorption isotherms were measured at the liquid nitrogen temperature, using a Nova 1000 analyzer. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. The measurement of metal ion was performed on Perkin Elmer 8300 ICP-OES. UV-Vis spectra are record on Agilent 8453. Luminescence excitation and emission spectra were examined by an Edinburgh FLS920 phosphorimeter. Luminescence lifetime measurements are carried out on an Edinburgh FLS920 phosphorimeter using a microsecond pulse lamp as excitation source. The quantum yield can be defined as the integrated intensity of the luminescence signal divided by the integrated intensity of the absorption signal.

#### The detail and description of experiments

**Synthesis of UiO-MOFs.** A typical synthesis procedure of UiO-MOFs is prepared from the literature using a modified procedure.<sup>14</sup> A mixture of  $\text{H}_2\text{bpydc}$  (0.248 g, 1 mmol),  $\text{ZrCl}_4$  (0.233 g, 1 mmol), glacial acetic acid (2.0 g, 33.33 mmol)

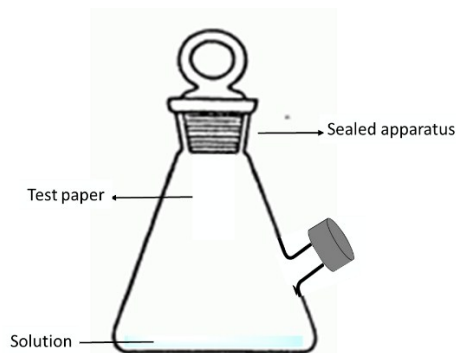
and N,N-dimethyl formamide (DMF, 60 mL) was stirred for 30 min under ambient conditions. Glacial acetic acid here was added to provide better crystallinity of the product. Then the mixture was transferred into a 100 ml Teflon-lined stainless steel container and then heated at 120 °C for 24 h. Cooling to room temperature naturally, the resulting white solid was separated from the mixed dispersion by centrifugation (10000 rpm, 3 min) and washed with DMF and methanol. To remove the organic species encapsulated within the pores of the open framework, the product was washed with methanol via Soxhlet extraction for 24 h, followed by drying at 60 °C under vacuum.

**Synthesis of ZnO.**<sup>16</sup> Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O and LiOH·H<sub>2</sub>O were dissolved together in beakers containing TEG at room temperature by stirring under the protection of nitrogen gas. The molar ration of [LiOH] and [Zn] was fixed at 2 and the [Zn] was fixed at 0.1 M, respectively. After exposed to the air and stirred for 24 h, the ZnO gel can be obtained. Then excess ethyl acetate was added into the TEG solution to precipitate ZnO. The ZnO power was collected by centrifugation at 13000 rpm for 5 min, washed three times with ethyl acetate and dried at 100 °C for 24 h.

**Synthesis of ZnO@Uio-MOFs (ZUM) heterostructures.** The ZnO@Uio-MOFs was prepared by added prepared ZnO (0.05 g, 0.1 g or 0.2 g) in the precursor solution of Uio-MOFs as mention above. The precursor solution is the mixed DMF solution (60 ml) of H<sub>2</sub>bpydc (0.248 g, 1 mmol) and ZrCl<sub>4</sub> (0.233 g, 1 mmol). Then the glacial acetic acid (2.0 g, 33.33 mmol) was added. After 30 minutes of stirring under ambient conditions, the mixture was transferred into a 100 ml Teflon-lined stainless steel container and then heated at 393 K for 24 h. It resulted in a white powdered product after centrifuged at 10000 rpm for 5 min, washed with DMF and methanol and dried at 100 °C for 24 h under vacuum. To remove the organic species encapsulated within the pores of the open framework, the product was washed with methanol via Soxhlet extraction for 24 h.

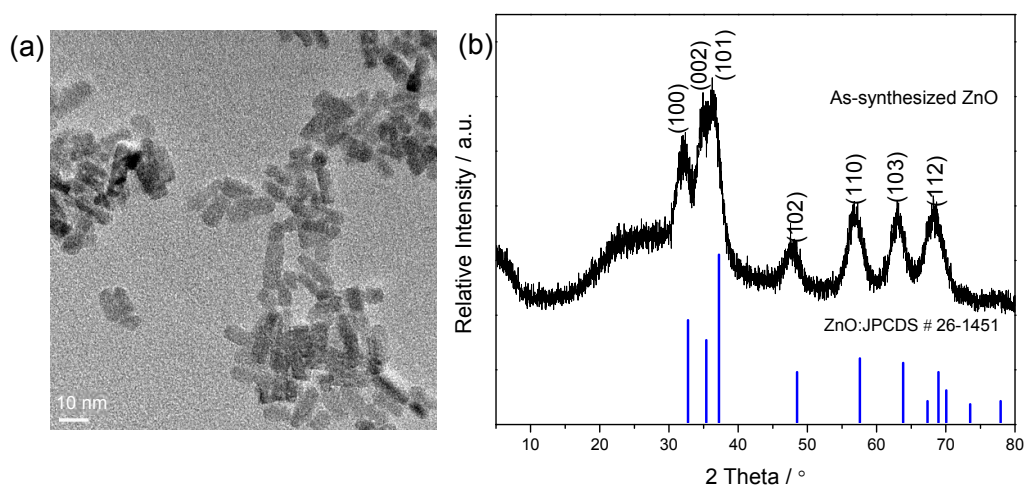
**Preparation of Eu<sup>3+</sup> functionalized Uio-MOFs (Eu<sup>3+</sup>@Uio-MOFs) and ZnO@Uio-MOFs heterostructures (Eu<sup>3+</sup>@ZUM).** Eu<sup>3+</sup>@Uio-MOFs and Eu<sup>3+</sup>@ZUM were prepared by immersing the Uio-MOFs or ZUM solid (100 mg) in 20 ml ethanol solutions of chloride salts of Eu<sup>3+</sup> (10<sup>-4</sup> mmol). After stirring the mixture at room temperature for 24 h, the solid was then filtered off and soaked in 15 ml ethanol. After 24 h, the supernatant was decanted and replaced by fresh ethanol. This procedure was repeated two times to guarantee that the physically adsorbed EuCl<sub>3</sub> salt is removed. Finally, the product was collected by filtration and dried at 60 °C under vacuum. The yield of the Eu<sup>3+</sup>@ZUM product based on ZUM was 92%.

**PL detection of polluted volatile components.** Eu<sup>3+</sup>@ZMH test paper was prepared for vapor detecting experiments by immersing a filter paper (1.0 cm<sup>2</sup> × 2.0 cm<sup>2</sup>) in the ethanol of Eu<sup>3+</sup>@ZUM and drying it at room temperature. Then the test paper was placed onto wall of a 10 mL sealed glass vial that contains 2 mL solvent vapor of every volatile component, as shown below.

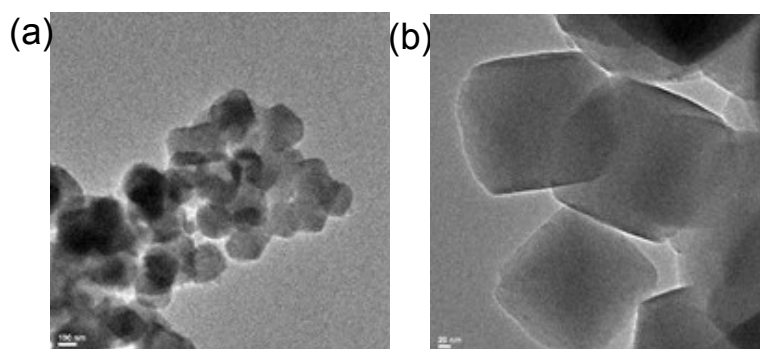


Then the concentration of vapor in the apparatus was determined by indirect method using head space-gas

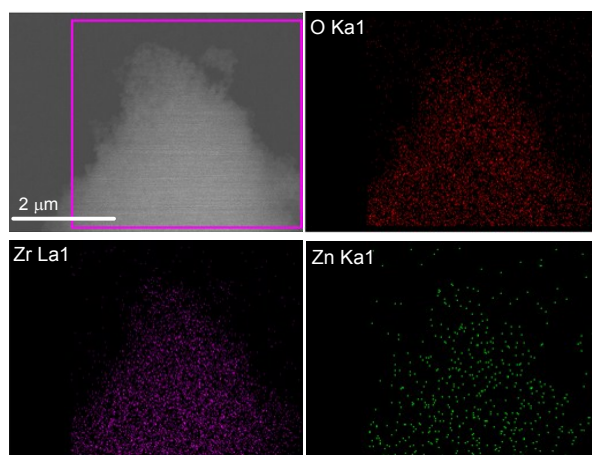
chromatography/mass spectrometry (HS-GC/MS) which can be described as  $C=(C_0V_0-C_1V_1)/V$ , where  $C_0$  and  $C_1$  are the concentration of aldehydes in aqueous solution before and after volatilizing;  $V_0$  and  $V_1$  are the injection volume;  $V$  is the volume of the homemade apparatus for vapor adsorption in our work. It is worth noting that the test paper should not run into the solution. The PL spectra of the test paper were measured after exposed to the vapors for 30 min.



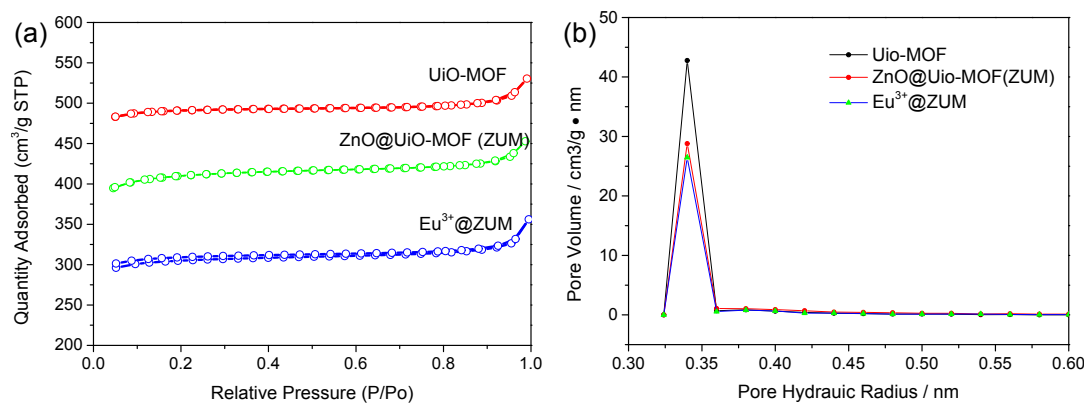
**Fig. S1** (a) TEM image and (b) PXRD pattern of ZnO nanoparticles, with synthetic molar ratios  $[\text{LiOH}]/[\text{Zn}]$  for the samples of 2.



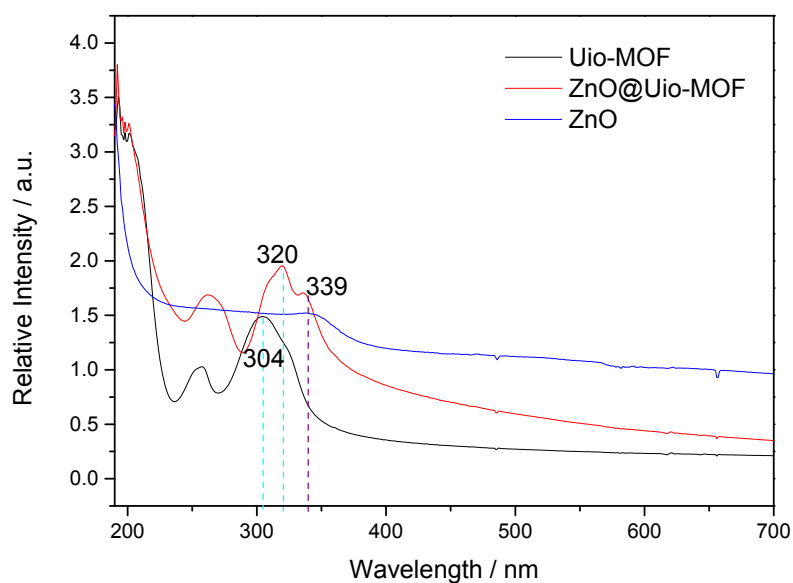
**Fig. S2** TEM images of UiO-MOFs under the solvothermal synthesis conditions at low (100 nm) (a) and high (50 nm) (b) magnifications, respectively.



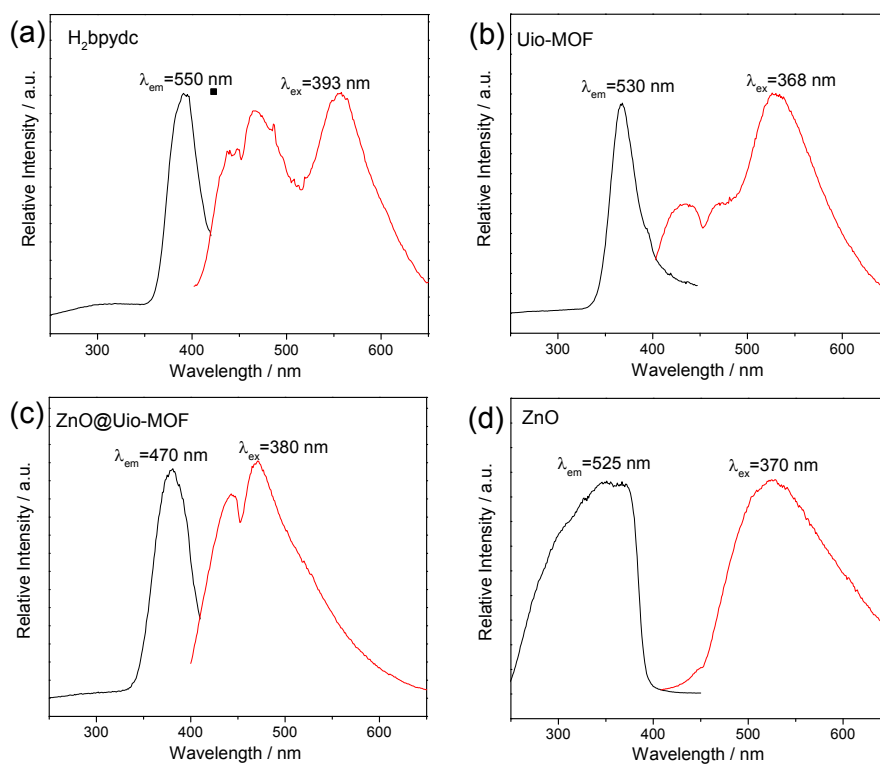
**Fig. S3** EDS mapping of O, Zr and Zn in ZnO@UiO-MOF (ZUM).



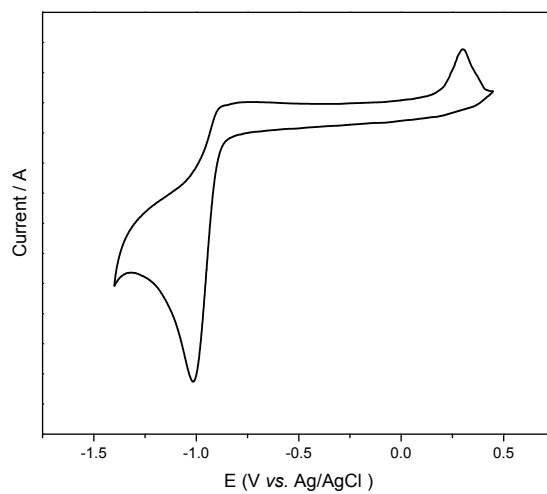
**Fig. S4** N<sub>2</sub> adsorption-desorption isotherms (a) and pore size distributions (b) of UiO-MOF, ZnO@UiO-MOF (ZUM), and Eu<sup>3+</sup>@ZUM.



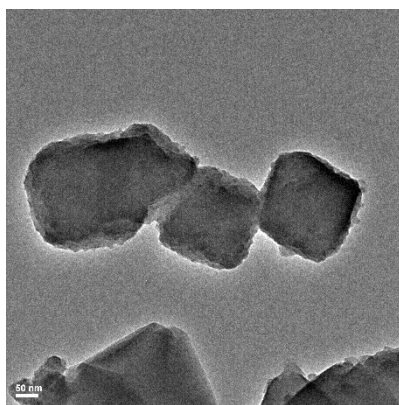
**Fig. S5** UV-Vis absorption spectra of suspended ZnO, UiO-MOF and ZnO@UiO-MOF in aqueous solution.



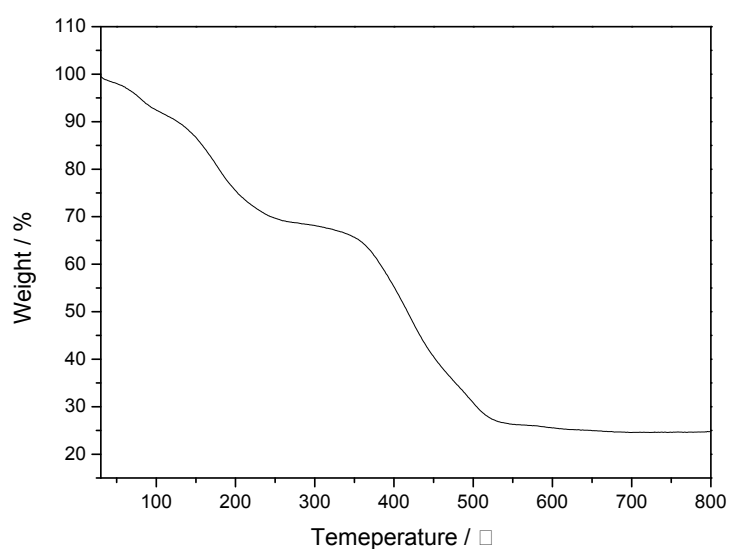
**Fig. S6** Room-temperature PL spectra of as-prepared H<sub>2</sub>bpydc (a), UiO-MOFs (b), ZnO@UIO-MOFs (c) and ZnO (d) in the solid state.



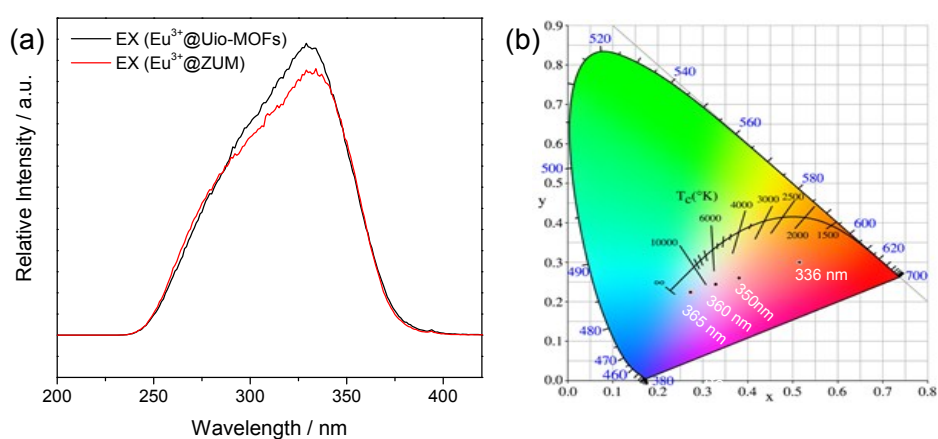
**Fig. S7** Cyclic voltammograms of UiO-MOFs at a scan rate of 100 mV/s against Ag/AgCl electrode.



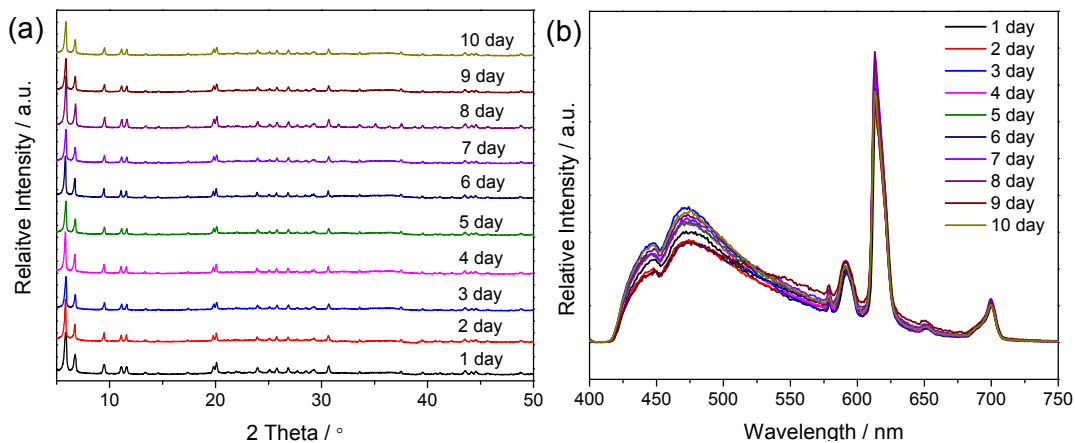
**Fig. S8** The typical TEM images of  $\text{Eu}^{3+}$ @ZUM.



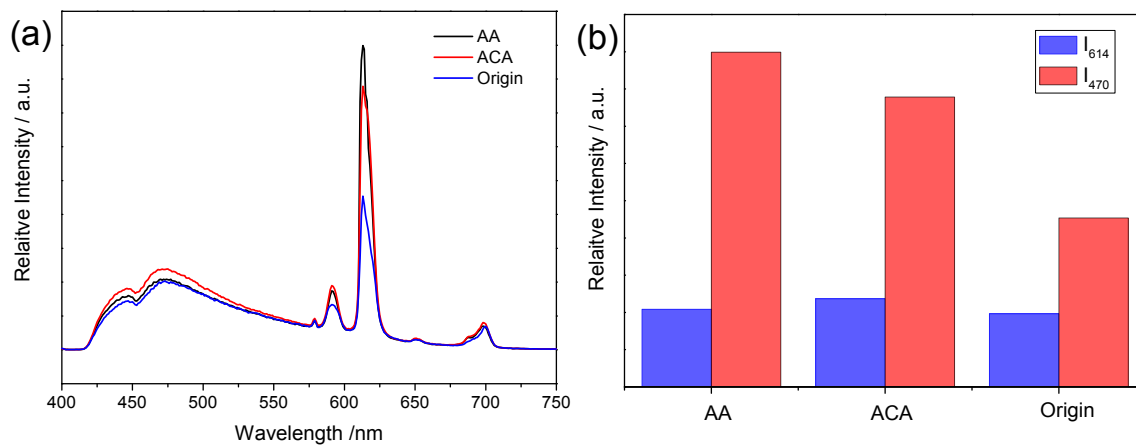
**Fig. S9** Thermal gravimetric analysis (TGA) of  $\text{Eu}^{3+}$ @ZUM under the protection of  $\text{N}_2$ .



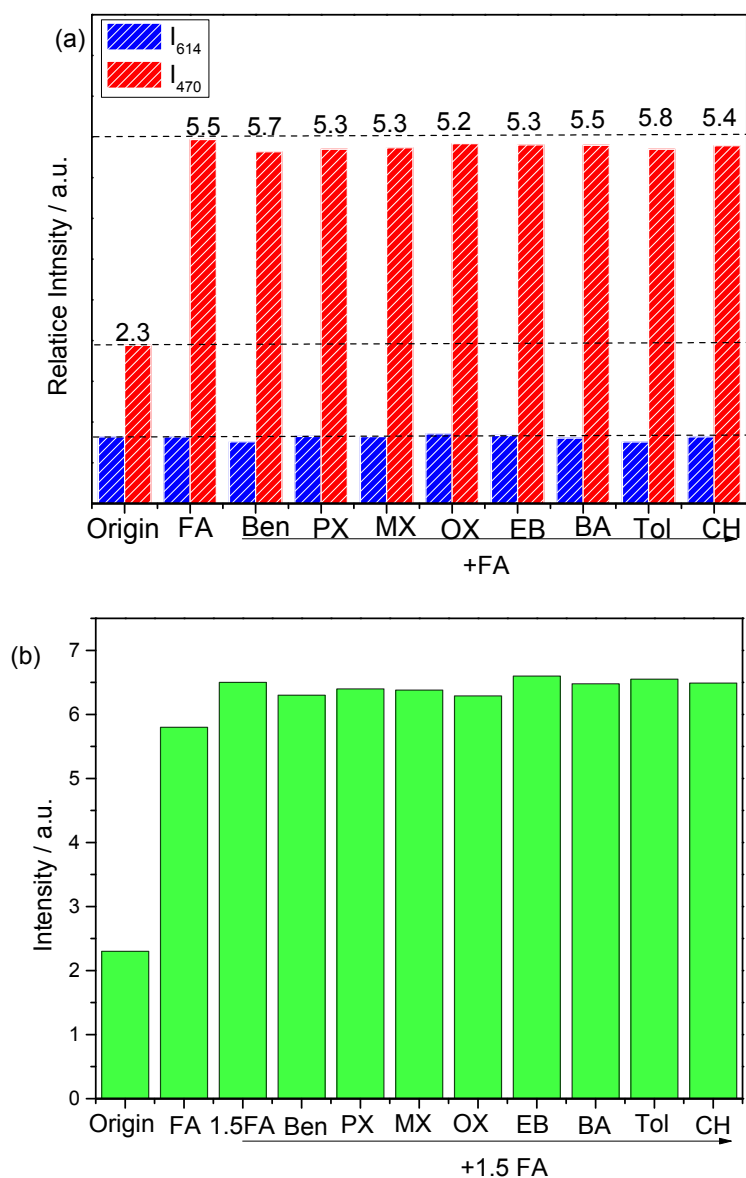
**Fig. S10** (a) Room-temperature excitation spectra of  $\text{Eu}^{3+}$ @Uio-MOFs (black line) and  $\text{Eu}^{3+}$ @ZUM (red line) at 614 nm emission wavelength and (b) The CIE chromaticity coordinates of  $\text{Eu}^{3+}$ @ZUM calculated from the emission spectra shown in Fig. 3, which shows the luminescent color changes with excitation wavelength.



**Fig. S11** Day-to-day structure (a) and PL stability (b) of  $\text{Eu}^{3+}$ @ZUM in the laboratory air (55% relative humidity) under excitation at 365 nm.

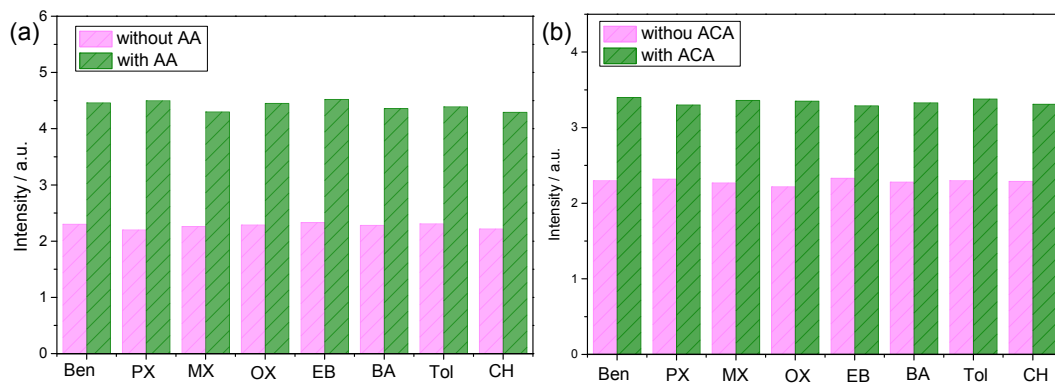


**Fig. S12** The fluorescent response (a) and intensity ( $I_{614}$  and  $I_{470}$ ) of  $\text{Eu}^{3+}$ @ZUM towards AA and ACA under excitation at 365 nm.

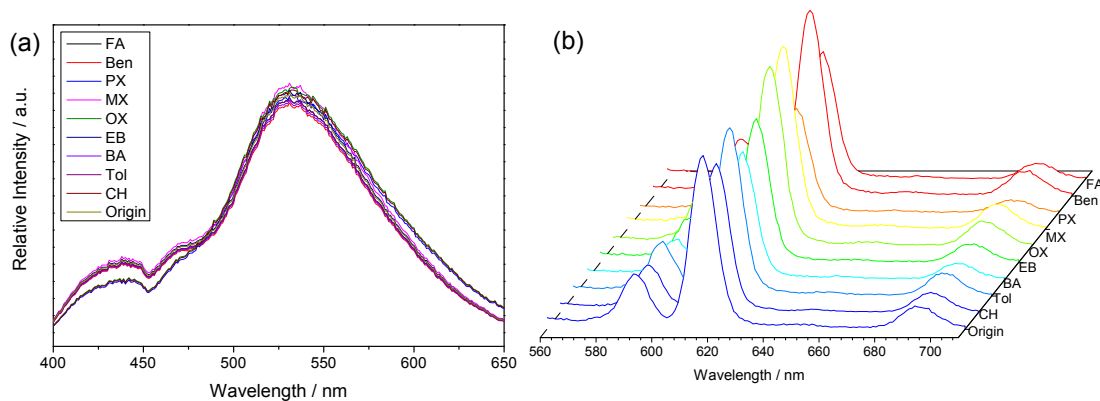


**Fig. S13** (a) The fluorescent response of Eu<sup>3+</sup>@ZUM test paper toward FA (10 ppm) in the presence of other various interfering gases (20 ppm). The inset numbers are the corresponding  $I_{614}/I_{470}$ . (b) The  $I_{614}/I_{470}$  value of Eu<sup>3+</sup>@ZUM test paper toward FA (15 ppm) in the presence of other various interfering gases (20 ppm).

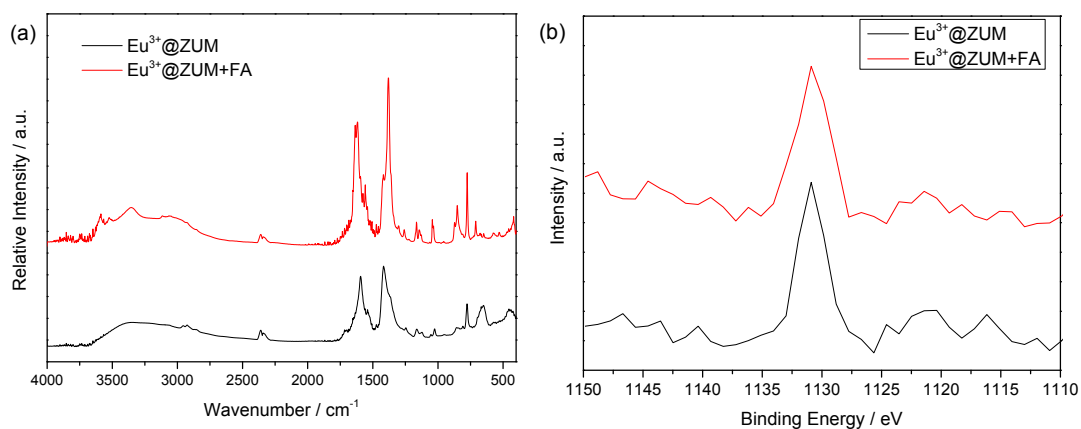




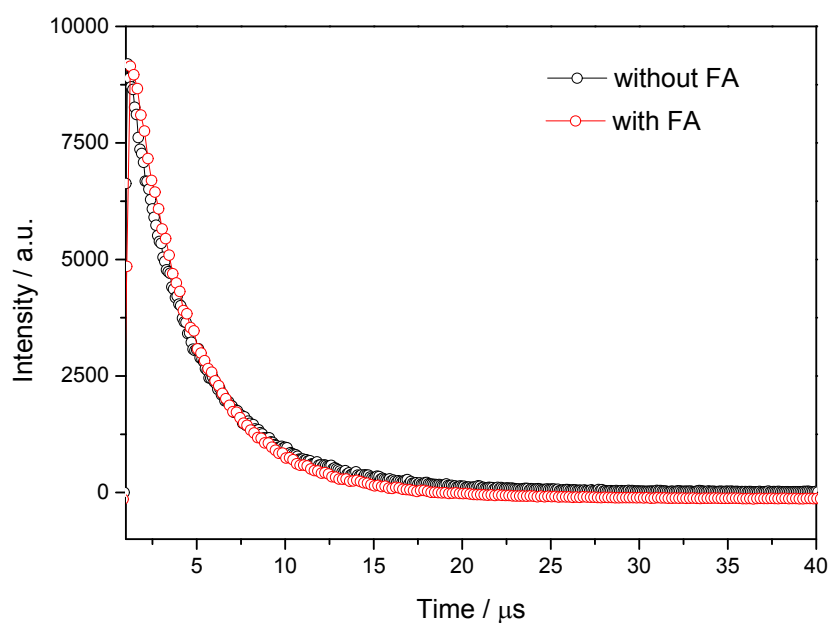
**Fig. S14** The fluorescent response of  $\text{Eu}^{3+}$ @ZUM test paper toward AA (a) and ACA (b) (10 ppm) in the presence of other various interfering gases (20 ppm).



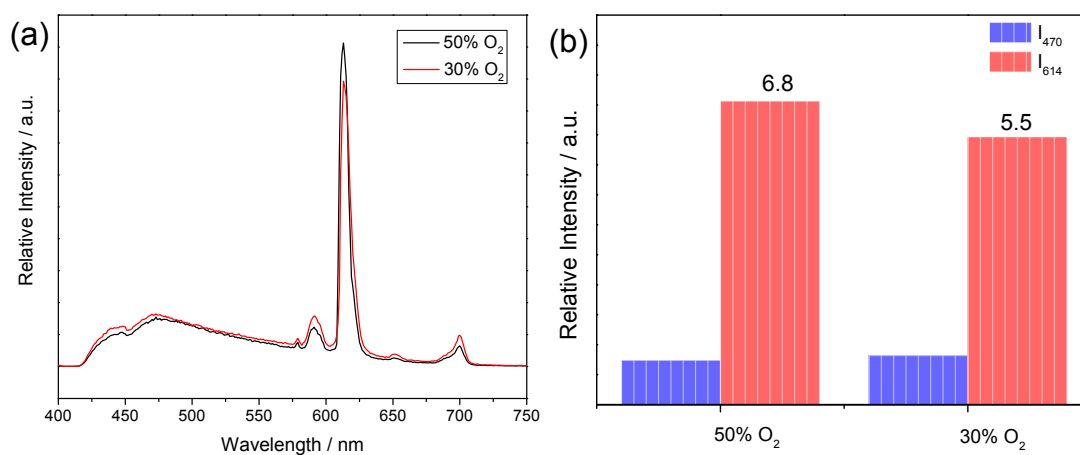
**Fig. S15** The PL emission spectra of Uio-MOFs (a) and  $\text{Eu}^{3+}$ @Uio-MOFs towards various polluting gases in vehicle.



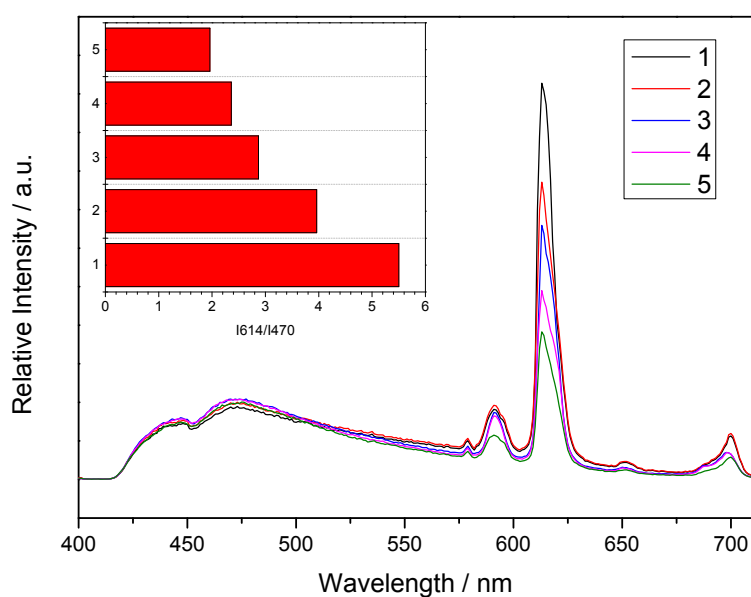
**Fig. S16** The FTIR (a) and Eu 3d XPS spectra of  $\text{Eu}^{3+}$ @ZUM before (black line) and after (red line) exposure to FA.



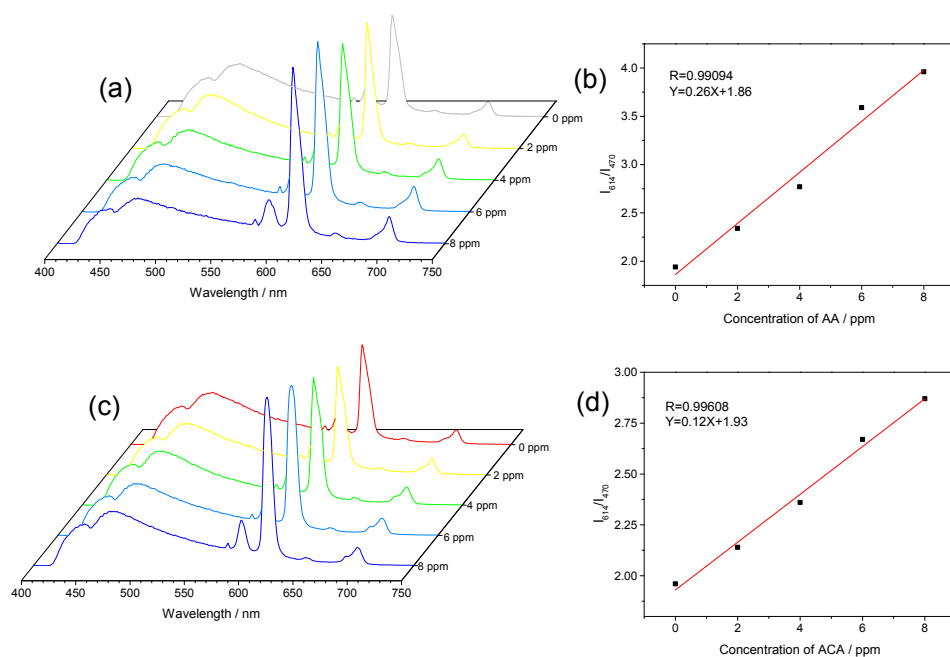
**Fig. S17** Luminescence decay times ( $^5D_0 \rightarrow ^7F_2$ ) of  $\text{Eu}^{3+}$ @ZUM without (black line) and with (red line) FA. The excitation wavelength is 336 nm.



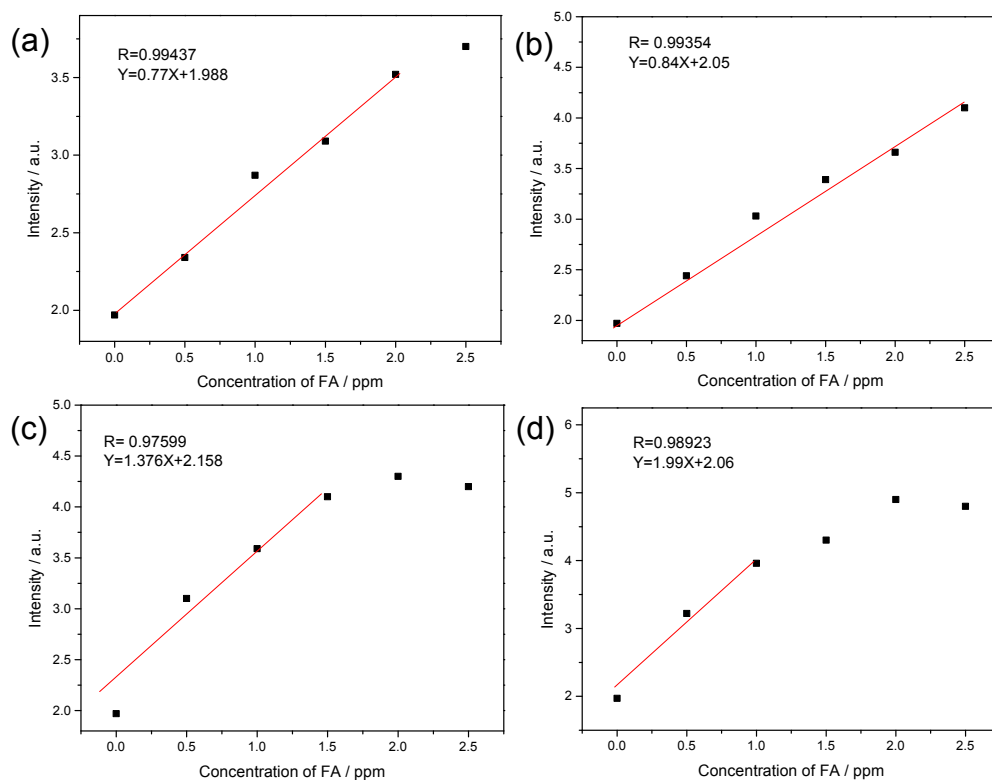
**Fig. S18** The PL emission spectra (a) and intensities ( $I_{614}$  and  $I_{470}$ ) of  $\text{Eu}^{3+}$ @ZUM test paper under the different concentration of  $\text{O}_2$ .



**Fig. S19** The PL emission spectra of  $\text{Eu}^{3+}$ @ZUM test paper in the presence of FA for five consecutive detection,  $\lambda_{\text{ex}}=365$  nm. The inset is the corresponding intensities of  $I_{614}/I_{470}$ .



**Fig. S20** The PL emission spectra (a) and the linear fitted curve showing  $I_{614}/I_{470}$  vs. FA concentration (b) of  $\text{Eu}^{3+}$ @ZUM towards AA and the PL emission spectra (c) and the linear fitted curve showing  $I_{614}/I_{470}$  vs. FA concentration (d) of  $\text{Eu}^{3+}$ @ZUM towards ACA. The The excitation wavelength is 365 nm.



**Fig. S21** The linear fitted curve showing  $I_{614}/I_{470}$  vs. FA concentration for the Eu<sup>3+</sup>@ZUM test paper at the temperature of 35 °C (a), 45 °C (b), 55 °C (c) and 65 °C (d).

**Table S1** The element content on Uio-MOFs, ZnO@Uio-MOFs (ZUM) and Eu<sup>3+</sup>@ZUM determined by ICP-OES studies.

Samples	Zr (ppm)	Zn (ppm)	Eu (ppm)
Uio-MOF	46.8	--	--
ZnO@Uio-MOF (ZUM)	41.4	5.726	--
Eu <sup>3+</sup> @ZUM	38.25	4.56	0.628

**Table S2** Absolute quantum yield ( $\phi$ ) and luminescence lifetime ( $\tau$ ) of Uio-MOFs and ZnO@Uio-MOFs (ZUM) at room temperature.

Samples	$\phi$ (%)	$\tau$ ( $\mu$ s)	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm)
Uio-MOF	35.68	54.92	368	530
ZnO@Uio-MOF (ZUM)	21.91	23.42	380	470

**Table S3** Calculated RSD of the sensing method at the temperature from 25 °C to 65 °C in the concentration of 0.5 and 1 ppm.

Temperature (°C)	Concentration (ppm)	relative standard deviation (RSD)
25	0.5	1.1±0.5
	1	2.3±0.2
35	0.5	1.8±0.6
	1	1.6±0.3
45	0.5	2.4±0.6
	1	1.7±0.9
55	0.5	3.1±0.7
	1	1.4±0.2
65	0.5	2.8±0.2
	1	3.3±0.8