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Chemical sensors based on a Eu (III)-centered Periodic Mesoporous Organosilica hybrid material using picolinic acid as an efficient secondary ligand

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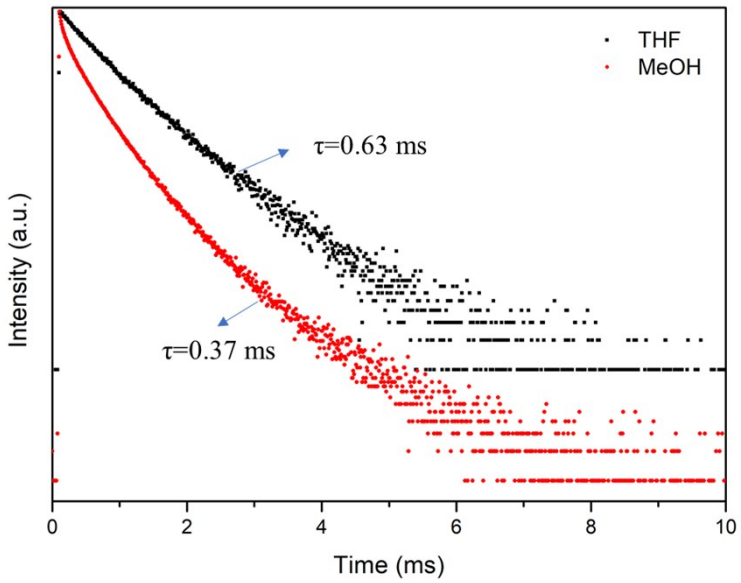

Figure S1 Decay profiles of ePMO@Eu_PA prepared in THF or methanol.

Table S1 CHN analysis results of ePMO and its variant materials.

Sample	C (wt%)	H (wt%)	N (wt%)
ePMO	17.67	2.95	0.14
Am-ePMO	13.43	2.79	3.06
Am-ePMO@o-van	11.51	1.93	5.39
ePMO@Eu_PA	19.42	2.10	5.94

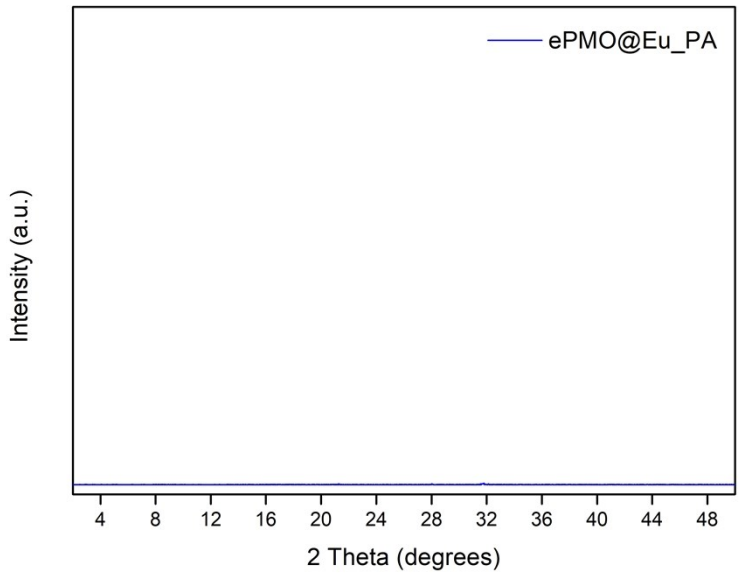

Figure S2 High angle powder XRD pattern of ePMO@Eu_PA.

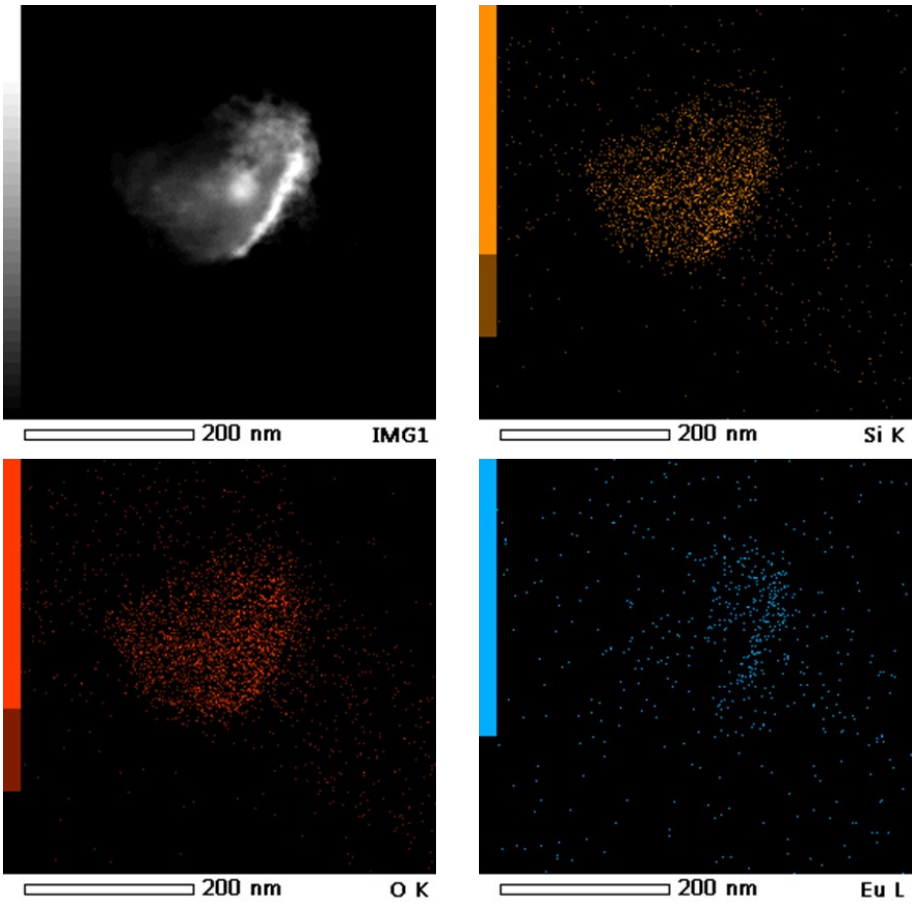

Figure S3 TEM-EDX mapping of ePMO@Eu_PA for the following elements: Si, O, Eu (from top to bottom, left to right).

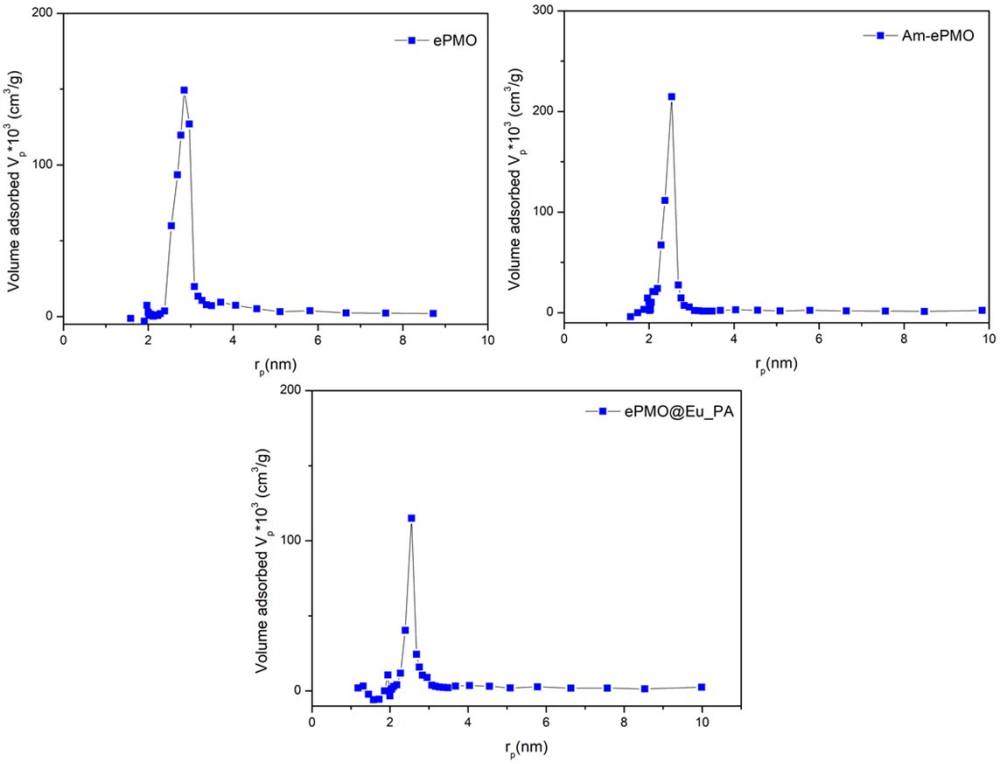

Figure S4 BJH pore size distribution of PMO materials: ePMO, Am-ePMO and ePMO@Eu_PA (from top to bottom).

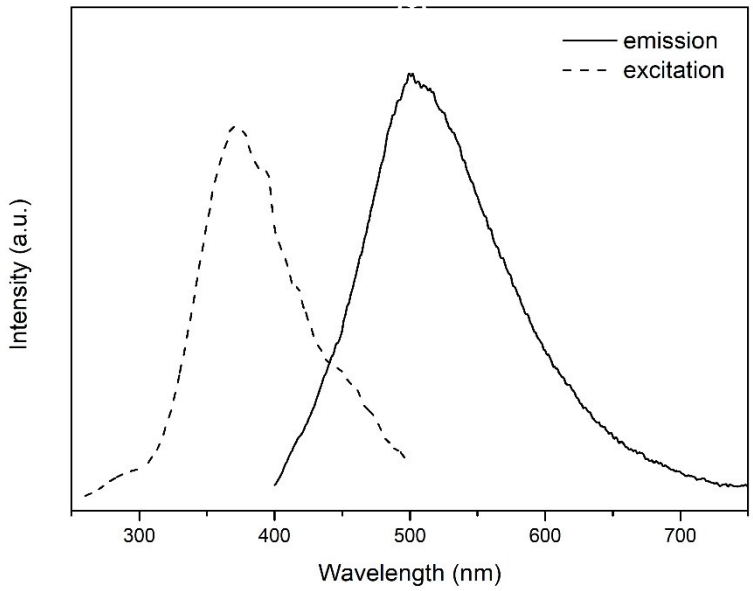

Figure S5 RT combined excitation-emission spectrum of Am-ePMO@o-van (the dashed line represents the excitation spectrum. The continuous line represents the emission spectrum).

Table S2 Assignment of peaks labeled in Figure 2 (in the main text).

Label	Wavelength (nm)	Transitions
	Excitation	
a	277	$\pi^*\leftarrow\pi$
b	316	$^5H_3\leftarrow{}^7F_0$
c	359	$^5D_4\leftarrow{}^7F_0$
d	375	$^5L_7\leftarrow{}^7F_0$
e	392	$^5L_6\leftarrow{}^7F_0$
	Emission	
f	578	$^5D_0\rightarrow{}^7F_0$
g	591	$^5D_0\rightarrow{}^7F_1$
h	615	$^5D_0\rightarrow{}^7F_2$
i	649	$^5D_0\rightarrow{}^7F_3$
j	699	$^5D_0\rightarrow{}^7F_4$

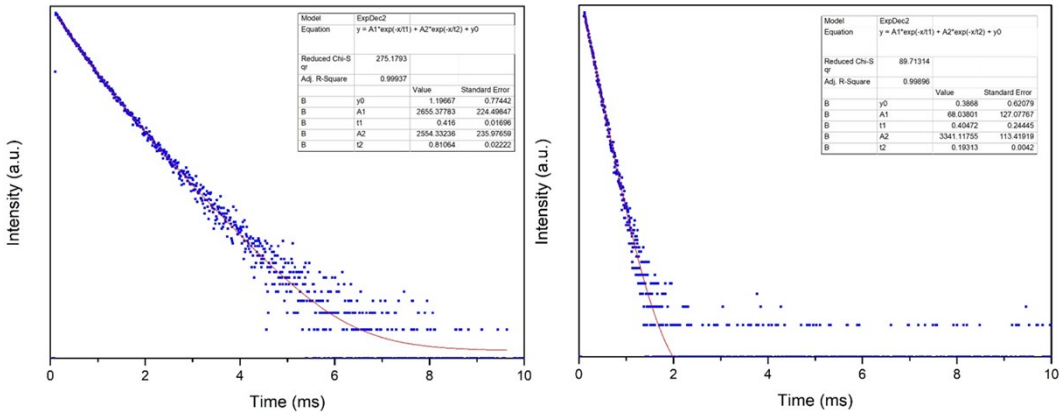

Figure S6 Left: decay profile of ePMO@Eu_PA in solid-state form; right: decay profile of ePMO@Eu_PA in aqueous suspension.

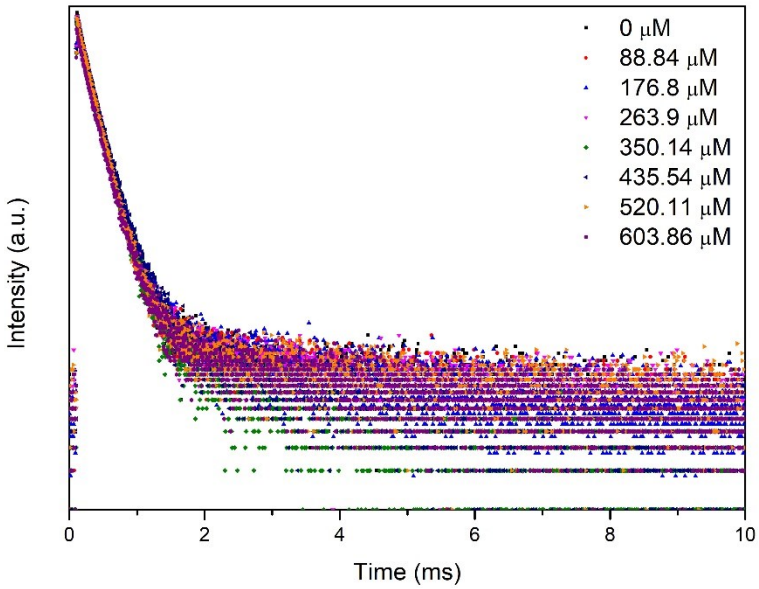

Figure S7 Luminescence decay times of an aqueous suspension of ePMO@Eu_PA

observed at different concentrations of Fe^{3+}.

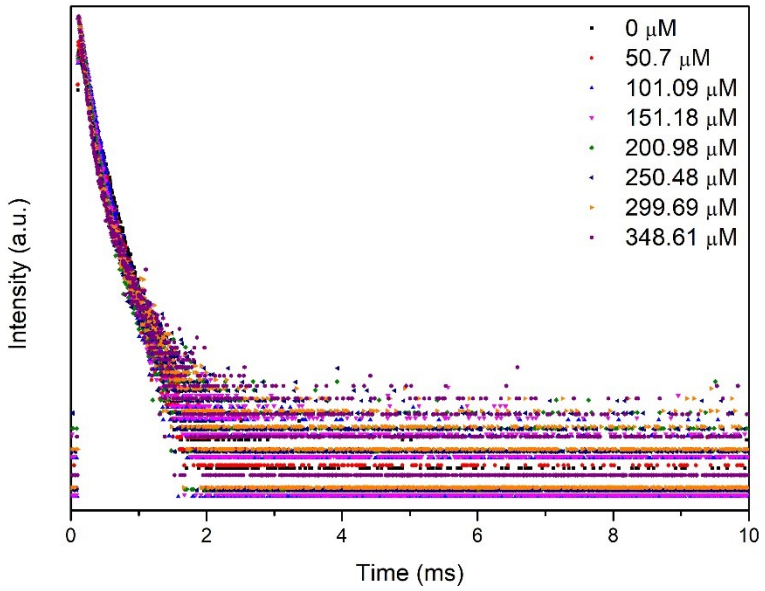

Figure S8 Luminescence decay times of an aqueous suspension of ePMO@Eu_PA observed at different concentrations of Co^{2+}.

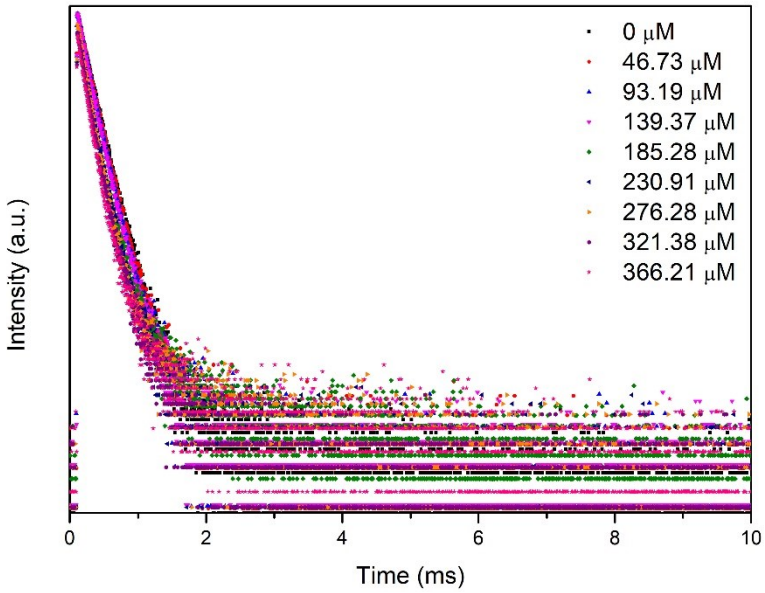

Figure S9 Luminescence decay times of an aqueous suspension of ePMO@Eu_PA observed at different concentrations of Cu^{2+}.

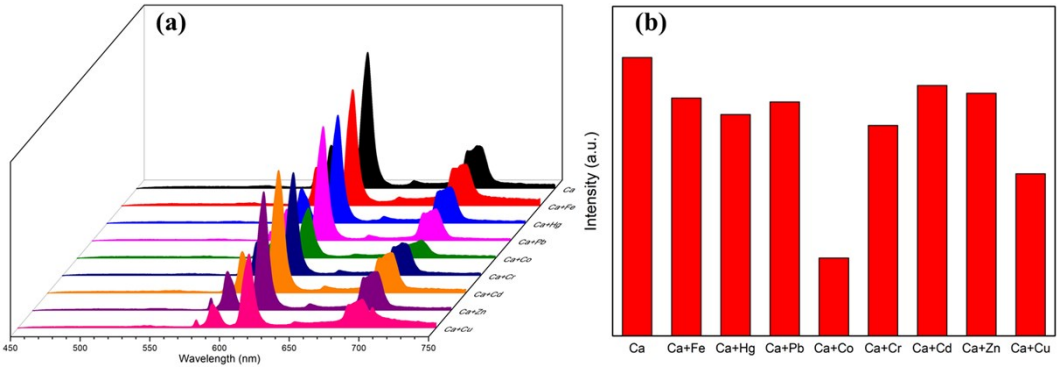

Figure S10 (a) Emission spectra and (b) emission intensity of the $^5D_0 \rightarrow {}^7F_2$ transition peak of ePMO@Eu_PA in the presence of Ca^{2+} and competing ions. (The mixed solution contains: 1 mg ePMO@Eu_PA /1 mL water; 20 µL Ca^{2+} (1000 ppm) and 20 µL competing ions (1000 ppm)).

S1. Limit of Detection (LOD) for Ca^{2+}, Fe^{3+}, Co^{2+} and Cu^{2+}

The blank suspensions were prepared by immersing 1 mg of ePMO@Eu_PA in 1 mL water (LOD calculation for Fe^{3+}, Co^{2+} and Cu^{2+}). The blank suspension for Ca^{2+} was prepared by immersing 1 mg of ePMO@Eu_PA in 200 µL water. The suspensions with different metal ion concentrations were prepared by adding different volume of metal ion nitrate solutions (1000 ppm) to the blank suspensions for the determination of limit of detection.

Limit of detection (LOD) was calculated using the plots of concentration versus and fluorescence intensity in Figure 5. Limit of detection was calculated using the below equation.

$$LOD = 3\sigma/k$$

Where σ stands for the standard deviation of 3 blank fluorescence intensities, k stands for the slope of the graph (S-V curve). Here, k can be calculated by using Stern–Volmer (S-V) equation: $I_0/I = K_{SV}c+1$. The fitted curves and calculated LOD results are displayed in Figure 5 and Table 1 in the main text.

S2. Recyclability and stability of ePMO@Eu_PA

Given the importance of recyclability in practical applications, a fast and simple method of recycling as metal ion sensor (Co^{2+} was selected as an example) as well as pH sensor was measured.

For the metal ion sensing experiment, ePMO@Eu_PA was soaked in the Co^{2+} solution for a few minutes for the first quenching experiment. Afterward, the powder of ePMO@Eu_PA was centrifuged and washed several times with distilled water and dried at 80°C. The recovered solid was collected and then used in the successive quenching experiments (four times). For the pH sensing experiment, the recyclability was examined by cyclic detection of pH at pH 7.73 and 10.23. After each treatment, the sample was centrifuged and washed with distilled water, and finally dried in an oven at 80°C.

After each experiment, the recovered sample (in solid-state) was placed under a UV lamp (302 nm illumination) to observe the color change. Eventually, the final

recovered samples were characterized by PXRD and DRIFTs to evaluate the stability of ePMO@Eu_PA.

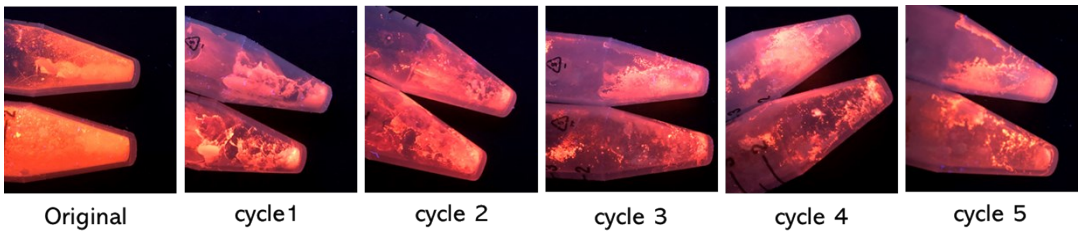

Figure S11 Photographs taken under a UV lamp (302 nm illumination) of ePMO@Eu_PA in solid state (top: Co^{2+} sensing; bottom: pH sensing, pH values are 7.73, 10.23, 7.73, 10.23 and 7.73 from left to right, corresponding to cycle 1-5, respectively.)

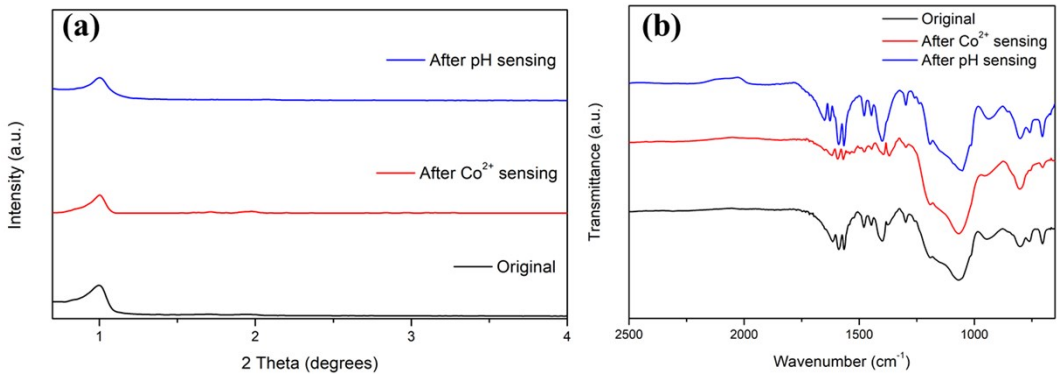

Figure S12 PXRD patterns and DRIFT spectra of ePMO@Eu_PA after different treatments.