Ag⁺-sensitized lanthanide luminescence in Ln³⁺ postfunctionalized metal-organic framework and Ag⁺ sensing

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Experimental Section

Materials and instrumentation: The salts of $Ln(NO_3)_3 \cdot 6H_2O$ were prepared by dissolving the corresponding lanthanide oxide compounds in excess nitric acid followed by evaporation and crystallization. Pyromellitic acid (98 %) was purchased from Adamas and used directly without further purification. All the other starting materials and reagents were all AR and used as purchased. The crystalline phases of the products were determined by X-ray powder diffraction patterns (XRD) using a Rigaku D/max-Rb diffractometer equipped with Cu anode. Nitrogen adsorption/desorption isotherms were measured at liquid nitrogen temperature using a Nova 1000 analyzer. The UV-Vis study was performed on an Agilent 8453 UV-Vis spectrophotometer. Measurement of Al^{3+} , Ln^{3+} and Ag^+ ions was performed on an X-7 series inductively coupled plasma-mass spectrometer (ICPMS) (Thermo Elemental, Cheshire, UK). Photoluminescence spectra and luminescence lifetimes (τ) were examined by an Edinburgh FLS920 spectrophotometer.

Typical procedure for synthesis of MIL-121: The compound MIL-121 was prepared by hydrothermal reaction of $Al(NO_3)_3 \cdot 9H_2O$ (1.2 g, 3.2 mmol) and pyromellitic acid (noted H₄btec, 0.4 g, 1.6 mmol) in 5 mL of deionized water at 210 °C for 24 h. The starting pH value was 1.41 and 0.26 at the end of the reaction. It resulted in a white powdered product, which was filtered off, washed with deionized water, and dried at 80 °C for 12 h in vacuum.¹ To remove the organic species encapsulated within the pores of the open framework, the samples was activated by Soxhlet extraction in methanol for 24 h and then dried at 80 °C under vacuum overnight.

Ln³⁺@MIL-121 preparation: MIL-121 (100 mg) was soaked in aqueous solutions of $Ln(NO_3)_3 \cdot 6H_2O$ (10 mL, 1mmol) for 24 h. The solid was then separated from the mixed dispersion by centrifugation, and extensively washed with water to remove residual Ln^{3+} cations on the surface. Subsequently, the resulted white powder was dried under vacuum at room temperature.

Ag⁺/Ln³⁺@MIL-121 (Ln³⁺= Sm³⁺, Dy³⁺, Nd³⁺, Yb³⁺, Er³⁺) preparation: Ag⁺/Ln³⁺@MIL-121 was prepared by stirring the mixture of MIL-121(100 mg), Ln(NO₃)₃·6H₂O (1 mmol) and AgNO₃ (1 mmol) in 10 mL H₂O. After one day of soakage under dark condition, the solid was then separated from the mixed dispersion by centrifugation, extensively washed with water, and dried at room temperature under vacuum.

Luminescence-sensing experiment: 3 mg of Sm³⁺@MIL-121 were simply immersed in the aqueous solutions of $M(NO_3)_z$ (10⁻² mol·L⁻¹, 3 mL) at room temperature (M^{z+} = Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, Mn²⁺, Fe³⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺, Zn²⁺, Cd²⁺, Pb²⁺).² The mixtures were then sonicated for 30 min to form the metal ion-incorporated suspension for luminescent measurements.



Figure S1 Representative structure of MIL-121, with open non-coordinated -COOH sites for the subsequent incorporation of Ln^{3+} cations.



Figure S2 FTIR spectra of MIL-121.



Figure S3 N₂ adsorption-desorption isotherms of MIL-121.



Figure S4 UV-Vis spectra of the fine suspensions of powdered MIL-121, Sm^{3+} @MIL-121 and Ag⁺/Sm³⁺@MIL-121 with H₂O as dispersing solvent. The absorption band at 297 nm is assigned to π - π * transitions of the ligands in MIL-121.

compounds	Al ³⁺	Sm ³⁺	Ag^+	Dy ³⁺	Al·In·Ag	
compounds	(ppm)	(ppm)	(ppm)	(ppm)	AI. LII. Ag	
Sm ³⁺ @MIL-121	13.84	7.01			2:1	
Ag ⁺ /Sm ³⁺ @MIL-121	12.88	3.78	5.42		3.4:1:1.4	
Dy ³⁺ @MIL-121	12.70			6.51	2:1	
Ag+/Dy3+@MIL-121	10.62		4.46	2.99	3.6:1:1.5	

Table S1 The ICPMS results of Ln^{3+} @MIL-121 and Ag⁺/Ln³⁺@MIL-121 (Ln = Sm, Dy)



Figure S5 Excitation and emission spectra of MIL-121.



Figure S6 Excitation spectra of Sm³⁺@MIL-121 (black line) and Ag⁺/Sm³⁺@MIL-121 (red line) monitored at 603 nm.



Figure S7 Excitation spectra of Dy³⁺@MIL-121 (black line) and Ag⁺/Dy³⁺@MIL-121 (red line) monitored at 575 nm.



Figure S8 NIR emissions of (a) Ag⁺/Nd³⁺@MIL-121, (b) Ag⁺/Yb³⁺@MIL-121, and (c) Ag⁺/Er³⁺@MIL-121



Scheme S1 Illustration of the fluorescence enhancement of Ln³⁺@MIL-121 by Ag⁺.

Compounds	$\lambda_{ex}/\lambda_{em}$	Luminescence lifetimes
Compounds	(nm)	(µs)
Sm ³⁺ @MIL-121	320/603	18.0
Ag ⁺ /Sm ³⁺ @MIL-121	320/603	97.6
Dy ³⁺ @MIL-121	325/575	8.5
Ag ⁺ /Dy ³⁺ @MIL-121	325/575	41.9

Table S2 Luminescence lifetimes of Ln³⁺@MIL-121 and Ag⁺/Ln³⁺@MIL-121 (Ln = Sm, Dy).



Figure S9 (a) The emission spectra of $Ag^+/Sm^{3+}@MIL-121$ monitored at different excitation wavelength, and the inset shows its orange and white photoluminescence colors with 320 and 340 nm UV excitations using a Xe lamp as the excitation source; (b) the CIE chromaticity diagram of $Ag^+/Sm^{3+}@MIL-121$ excited at different wavelength.

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Samples	$\lambda_{ex} (nm)$	CRI	CCT(K)	CIE(x,y)
Ag ⁺ /Sm ³⁺ @MIL-121	340	81.3	4038	(0.3560, 0.2910)
Ag ⁺ /Sm ³⁺ @MIL-121	350	59.7	10370	(0.2822, 0.2772)
Ag+/Dy3+@MIL-121	325	80.1	5583	(0.3305, 0.3390)

Table S3 Color Properties of Ag⁺/Ln³⁺@MIL-121 (Ln = Sm, Dy) Samples



Figure S10 PXRD patterns of the Sm³⁺@MIL-121 after immersing in aqueous solutions containing various metal ions.



Figure S11 Fluorescent spectra of Sm³⁺@MIL-121 in the presence of different concentrations of Ag⁺ in aqueous solution (λ_{ex} =320 nm). Inset: linear relationship of fluorescence intensity at 603 nm as a function of Ag⁺ concentrations.

References

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