Supporting Information

A pH-stimuli-responsive Eu (III) functionalized metal-organic frameworks hybrid luminescent film for amino acids sensing and anti-counterfeiting

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1. Experimental Section

1.1. Instruments and Characterization.

X-ray diffraction (PXRD) patterns have been acquired using a Bruker D8 ADVANCE diffractometer, employing Cu Kα radiation source (40 mA and 40 kV). Fourier transforms infrared (FTIR) spectra were recorded on a Nexus 912 AO446 infrared spectrum radiometer using KBr as a reference. X-ray photoelectron spectroscopy (XPS) investigation was carried out under ultrahigh vacuum (<10^{-6} Pa) at pass energy of 93.90 eV with an Axis Ultra DLD spectrometer (Kratos, Japan) equipped with an Mg Kα radiation source (1253.6 eV). UV-vis absorption spectra were measured on an Agilent 8453 spectrometer. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 field emission scanning electron microscope operating at 3 kV. Energy dispersive X-ray (EDX) spectra and elemental mapping images were acquired on a scanning electron microscope, operating at 5 kV. Fluorescence spectra were tested at an Edinburgh FLS920 spectrophotometer with a 450 W xenon lamp as the excitation light source using an appropriate cutoff filter. Zeta potentials were conducted on an Anton Paar Litesizer 500. The corresponding Commission Internationale de l'Eclairage (CIE) color coordinates were calculated based on the international CIE standards.

1.2. Preparation of ZnMOF@SA hydrogel.

The uniform suspension of ZnMOF (20 mg) powder was prepared by the ultrasonic method in deionized water (2 mL). Deionized water (20 mL) was heated to boiling, then the sodium alginate (SA) powder (1.0 g) was dissolved to form a SA solution. The homogeneous mixture (ZnMOF@SA) was obtained by dropping the suspension of ZnMOF into the SA solution with continuously stirring for 1 h. Subsequently, the mixture was poured into a purchased mold and cooled to room temperature to shape the ZnMOF@SA hydrogel.
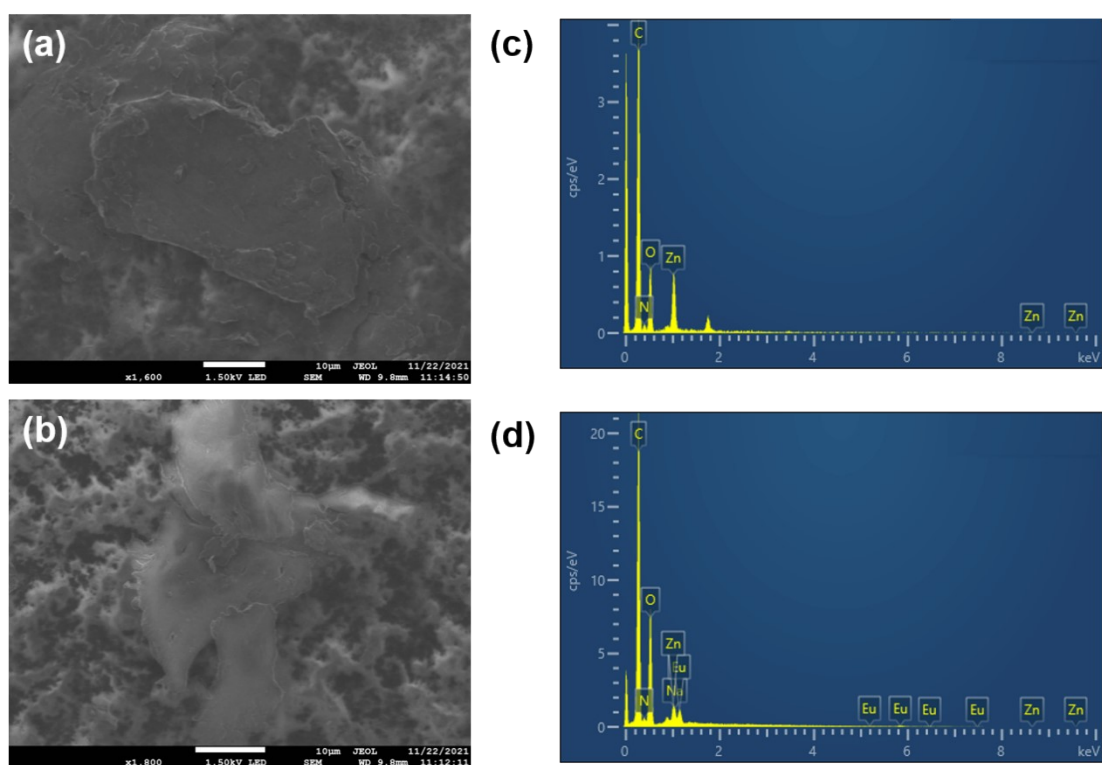
1.3. Preparation of ZnMOF@SA Film

The prepared ZnMOF@SA hydrogel was heated and dried in an oven at 80°C for 2 h to obtain the ZnMOF@SA Film.

2. Supporting Figures and Tables
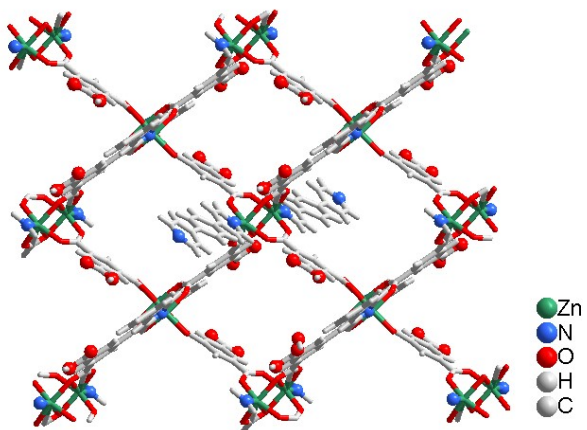
Fig. S1. View of the 2D layered structural unit formed by Zn(II) ions and the ligands.

Fig. S2. SEM images of ZnMOF (a, b) and EDS energy spectra of ZnMOF (c) and **1@SA** (d).
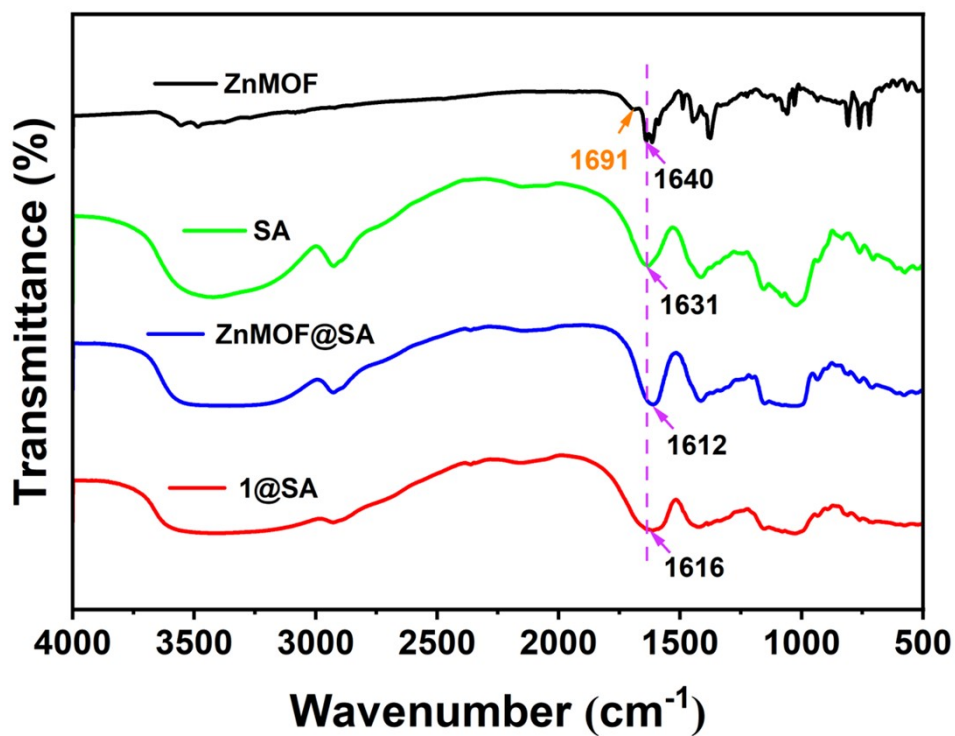
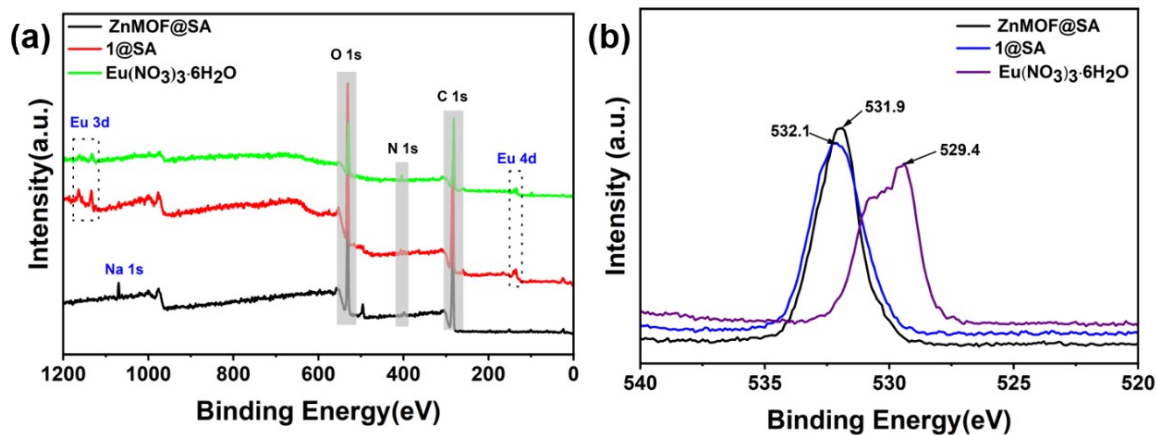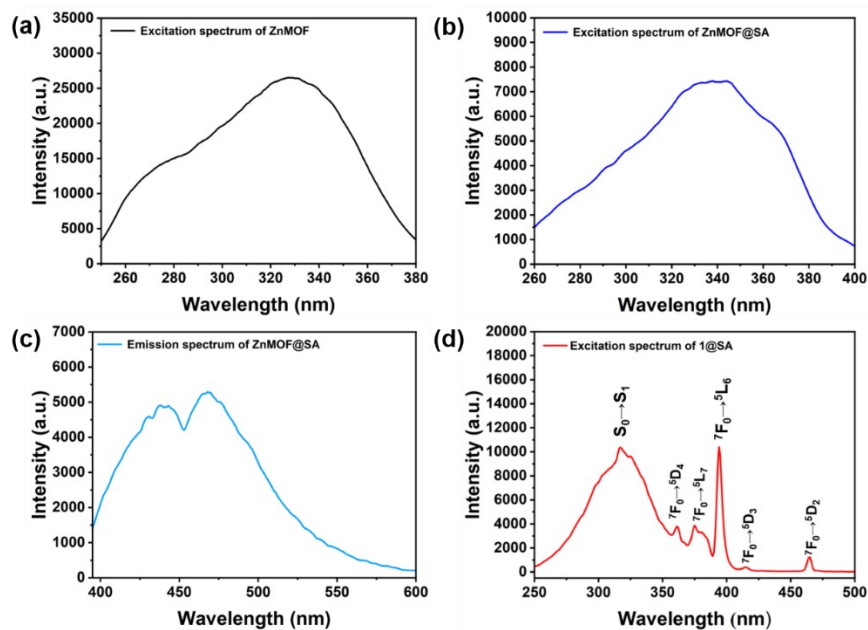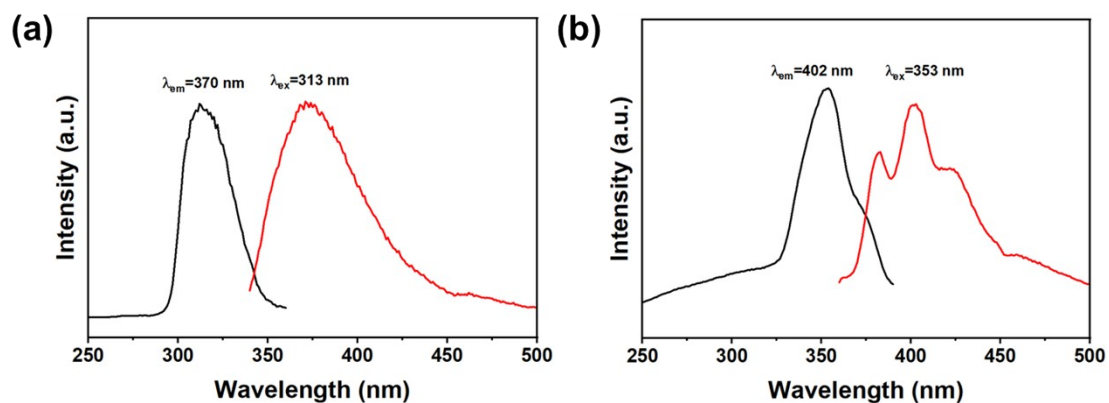**Fig. S3.** The FT-IR spectra of ZnMOF, SA, ZnMOF@SA, and **1@SA**.
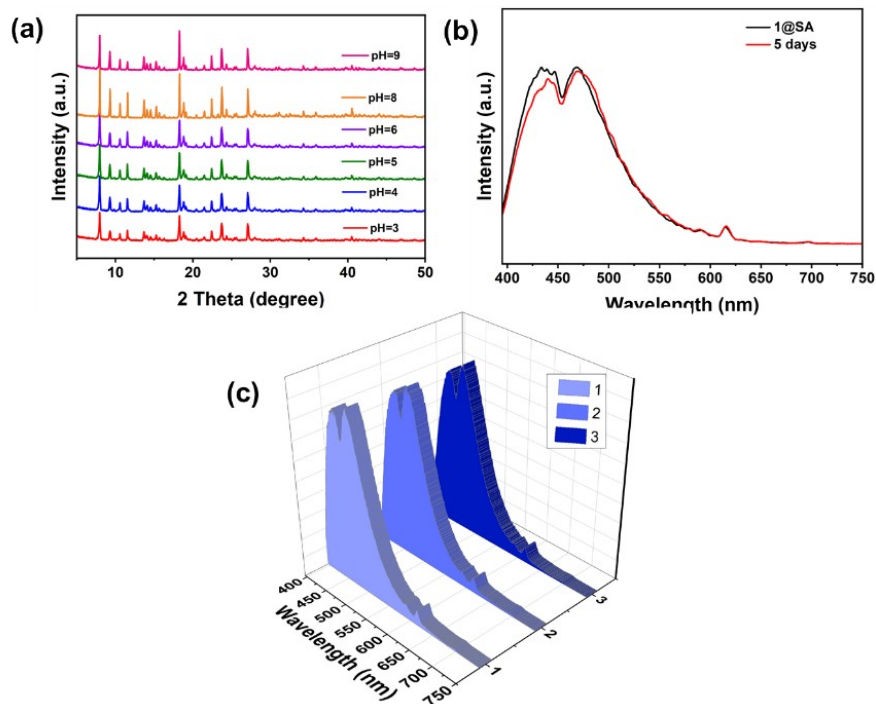

Fig. S4. XPS spectra (a) and O 1s XPS (b) for ZnMOF@SA, **1@SA**, and $Eu(NO_3)_3 \cdot 6H_2O$.

Fig. S5. Excitation spectra of (a) ZnMOF, (b) ZnMOF@SA (λem = 470 nm), and (d) **1@SA** (λem = 615 nm). (c) The emission spectrum of ZnMOF@SA (λex = 365 nm).


Fig. S6. The emission (red line) and excitation (black line) spectra of H_3BTC (a) and bpbenz (b).
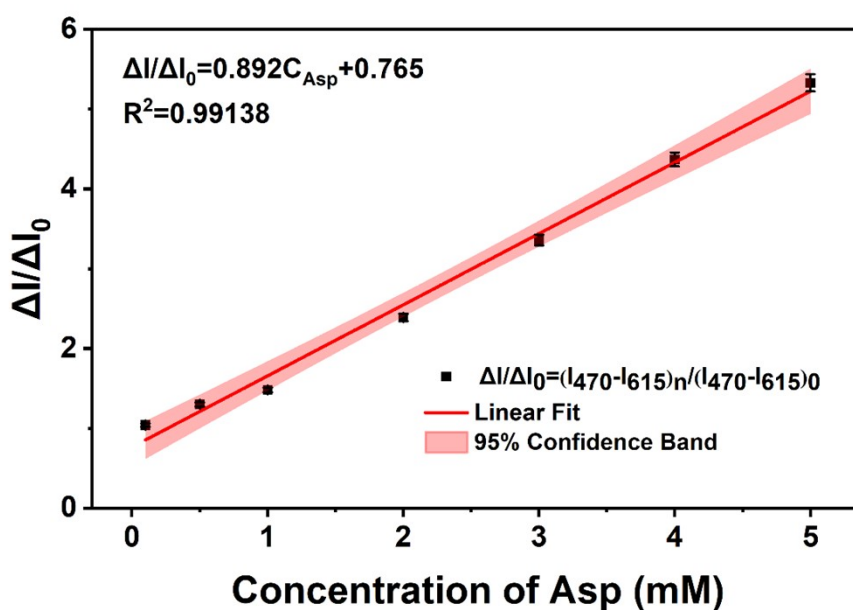
Fig. S7. (a) PXRD patterns of ZnMOF in different pH values. (b) The fluorescence changes of **1@SA** before and after 5 days in the air at room temperature. (c) Emission spectra of different batches of **1@SA** prepared by the same method. (λex = 365 nm)
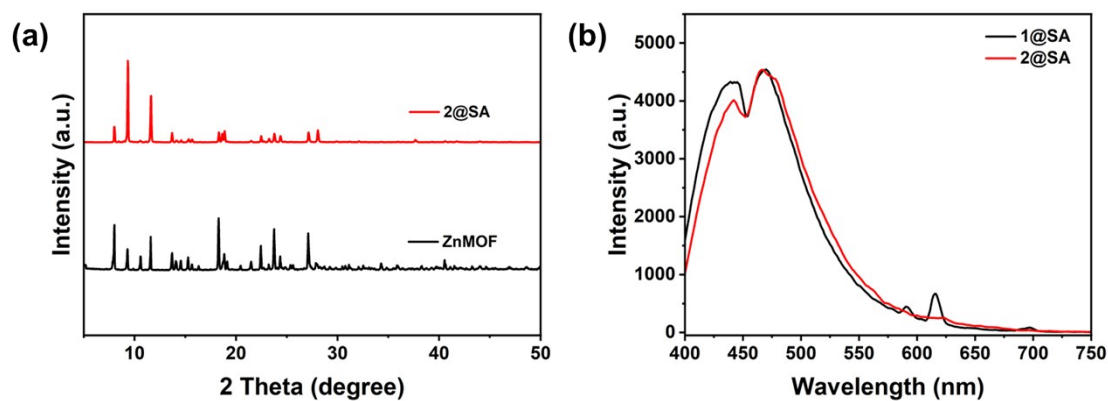

Fig. S8. (a) The PXRD patterns of ZnMOF and **2@SA**. (b) The fluorescence spectra of **1@SA** and **2@SA** under the excitation of 365 nm.
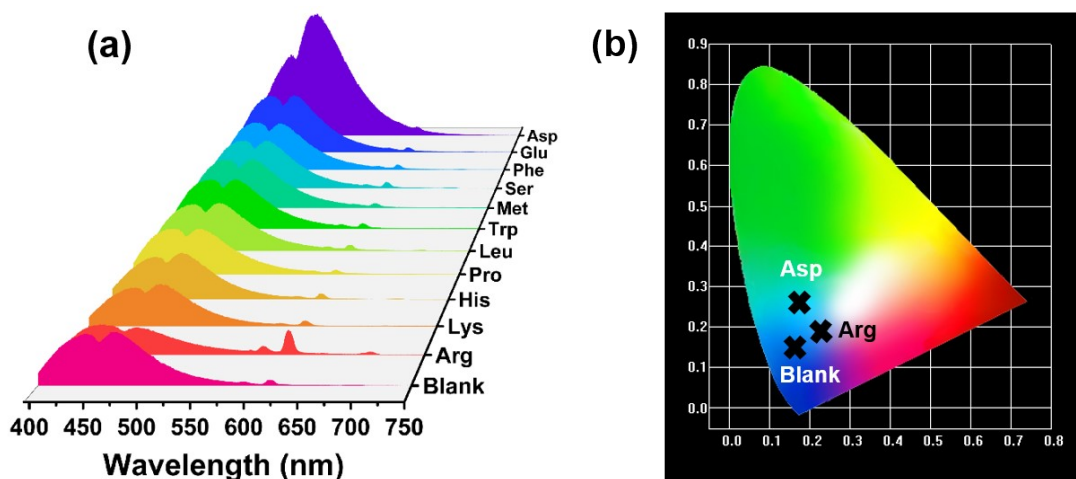
Fig. S9. Fluorescence spectra of **1@SA** in 10 mM different amino acids solution (a) and the corresponding CIE coordinates of **1@SA** in Arg or Asp solution (b).

$\Delta I/\Delta I_0 = 0.892 C_{Asp} + 0.765$
$R^2 = 0.99138$

$\Delta I/\Delta I_0 = (I_{470} - I_{615})_n / (I_{470} - I_{615})_0$
Linear Fit
95% Confidence Band

Fig. S10. The linear fitted curve showing $\Delta I/\Delta I_0$ versus Asp concentration, $\lambda ex = 365$ nm.
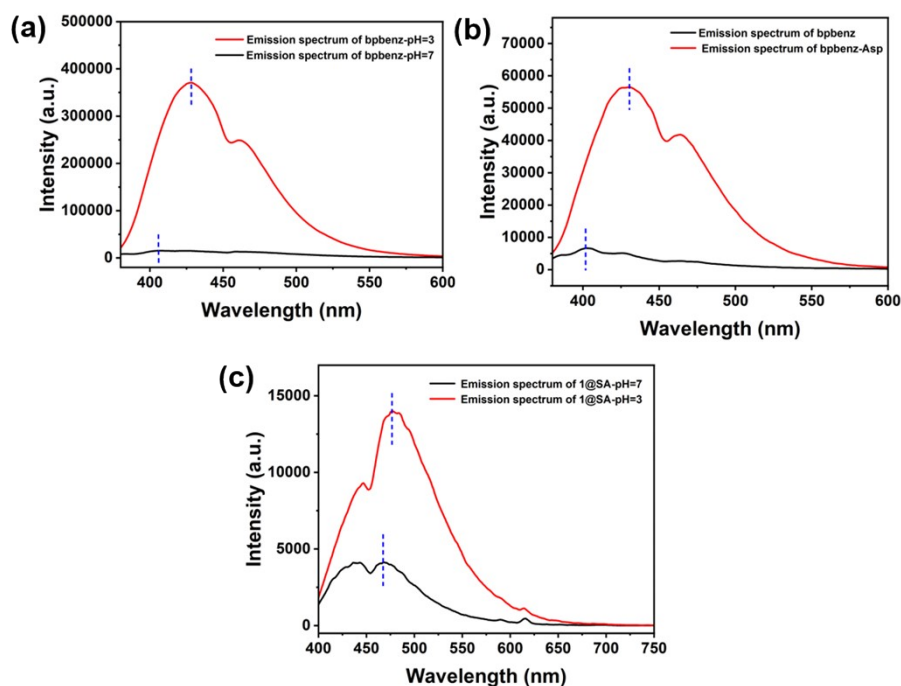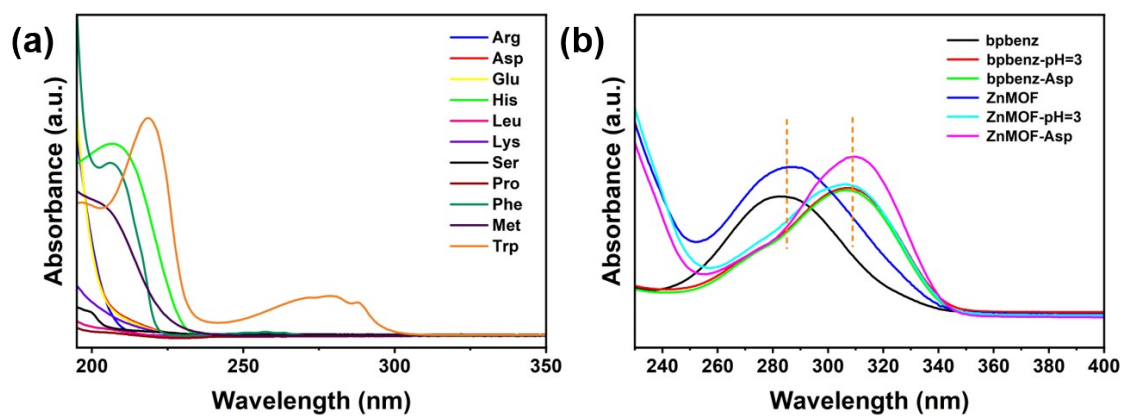
Fig. S11. The emission spectra of bpbenz (a) and **1@SA** (c) in different pH solutions and the emission spectrum of bpbenz in Asp solution (b). (λex=365 nm).
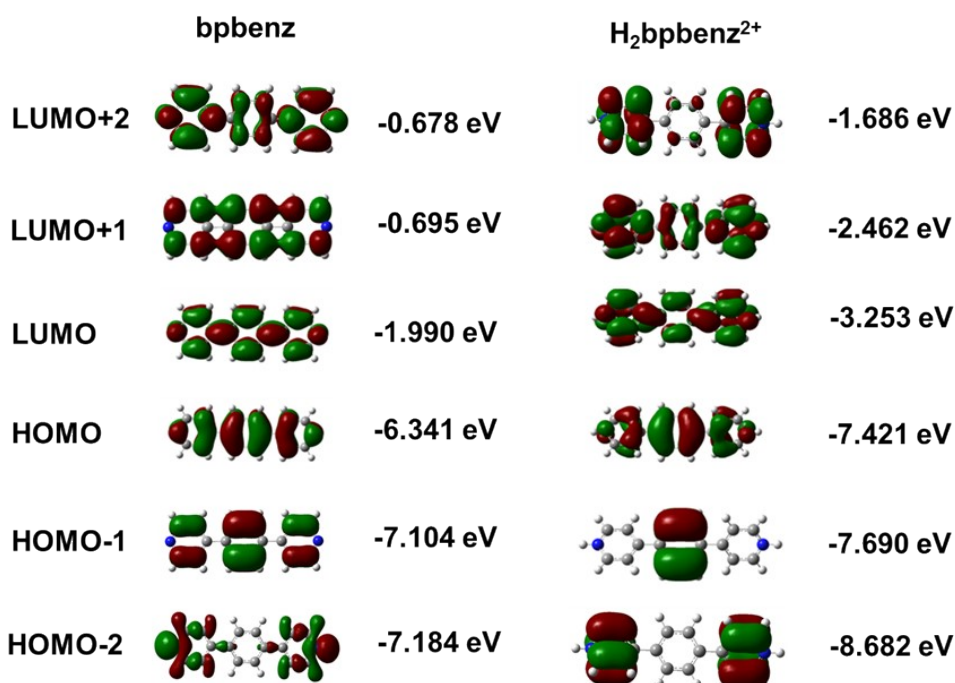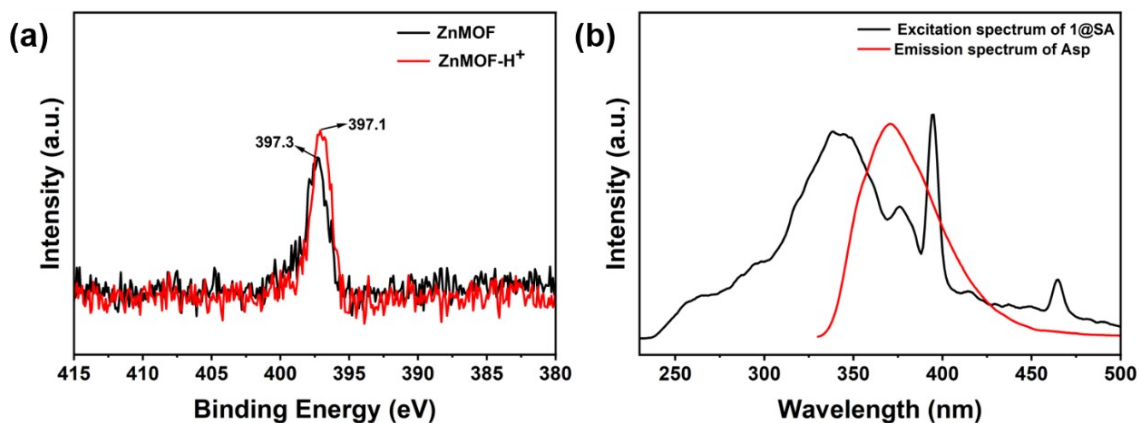

Fig. S12. The frontier molecular orbitals of bpbenz and $H_2bpbenz^{2+}$. The orbitals were obtained by the density functional theory (DFT) calculation based on the b3lyp/6-31g + G(d, p) level.
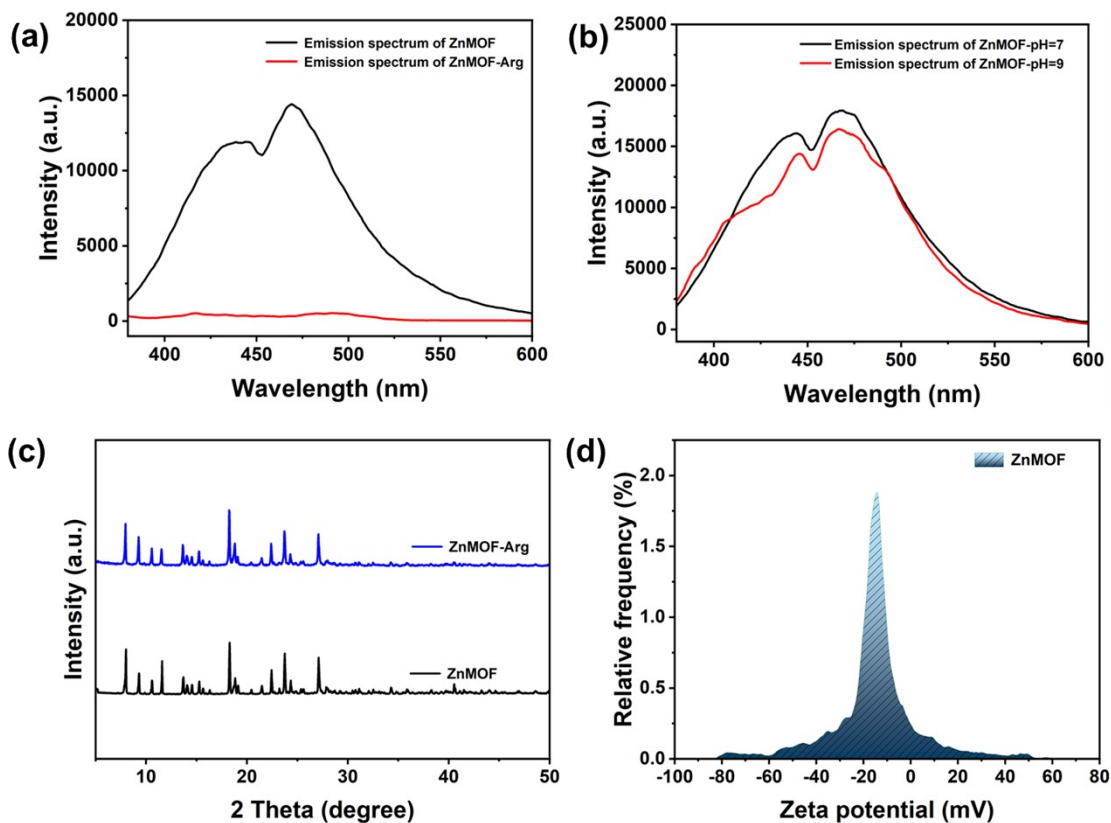
Fig. S13. The UV-vis absorption of various amino acid aqueous solution (a) and bpbenz and ZnMOF in different solutions (b).

Fig. S14. (a) The XPS spectra of N 1s electron of ZnMOF without and with acid treatment. (b) The excitation spectrum of **1@SA** and emission spectrum of Asp.

Fig. S15. The emission spectra of ZnMOF in Arg solution (a) and different pH solutions (b) under the excitation of 365 nm. (c) The PXRD patterns of ZnMOF without and with the Arg treatment. (d) The zeta potential of ZnMOF.
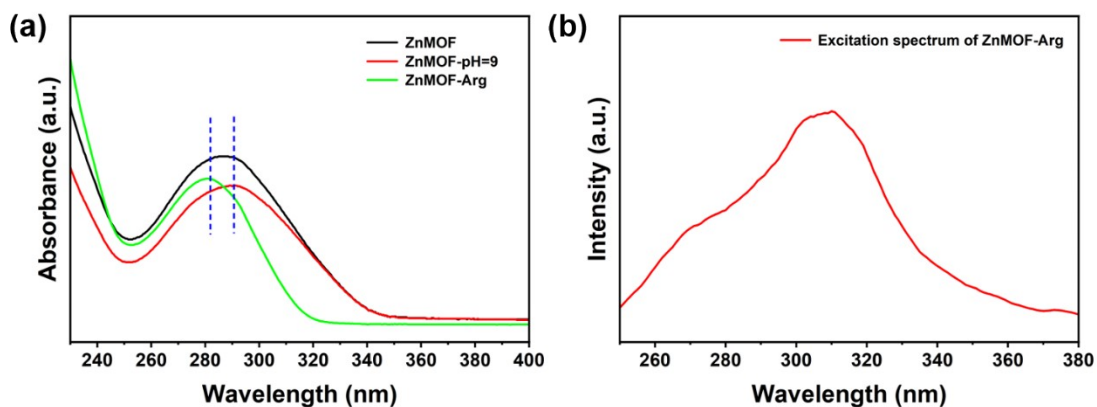
Fig. S16. (a) The UV-vis absorption of ZnMOF in an alkaline environment and Arg solution. (b) The excitation spectrum of ZnMOF in Arg solution.
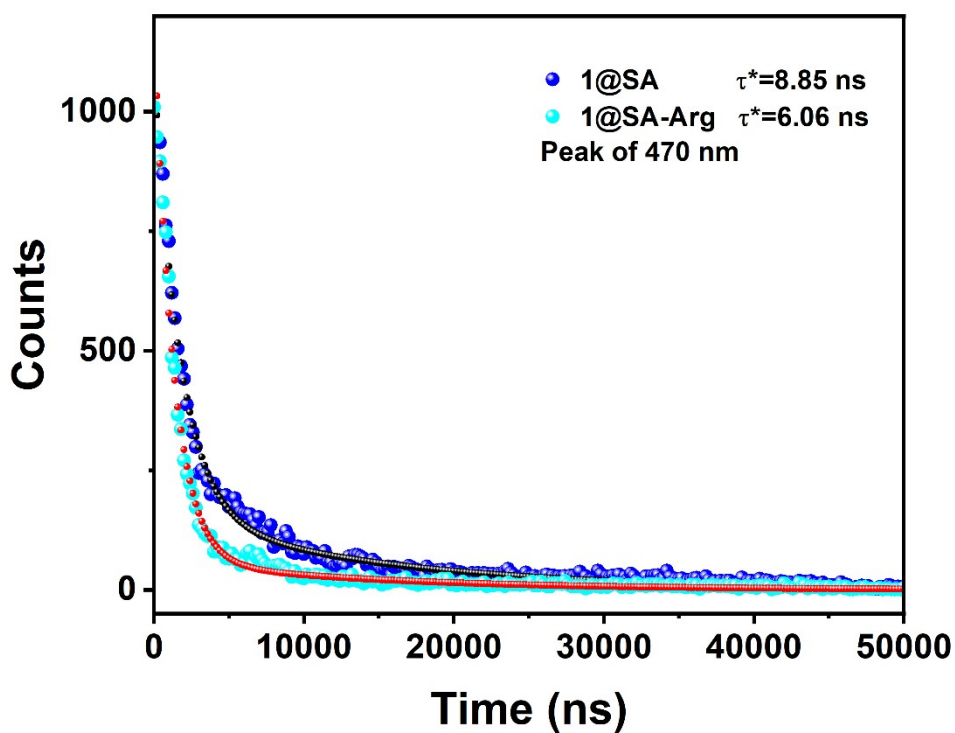
Fig. S17. Lifetime decay curves of the **1@SA** at 470 nm in the absence and presence of Arg.
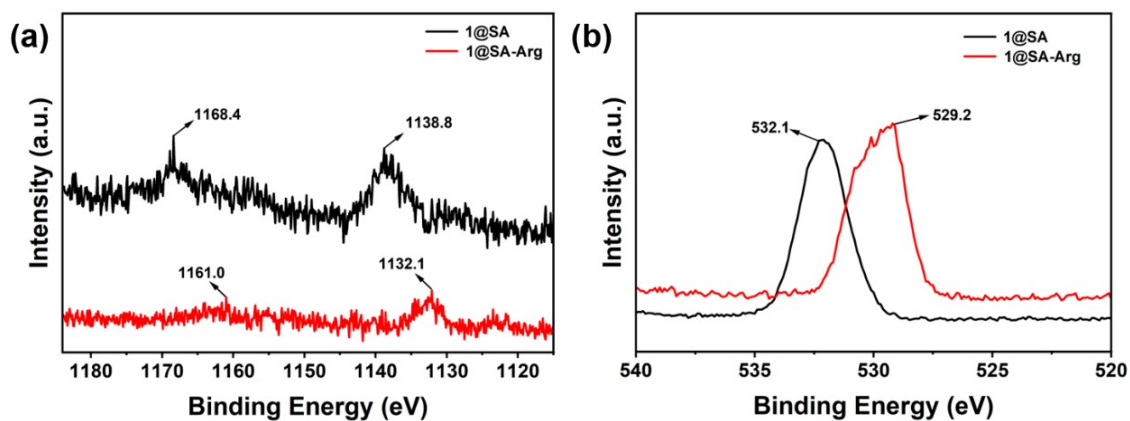

Fig. S18. The XPS spectra of Eu 3d (a) and O 1s (b) electrons in **1@SA** without and with Arg.
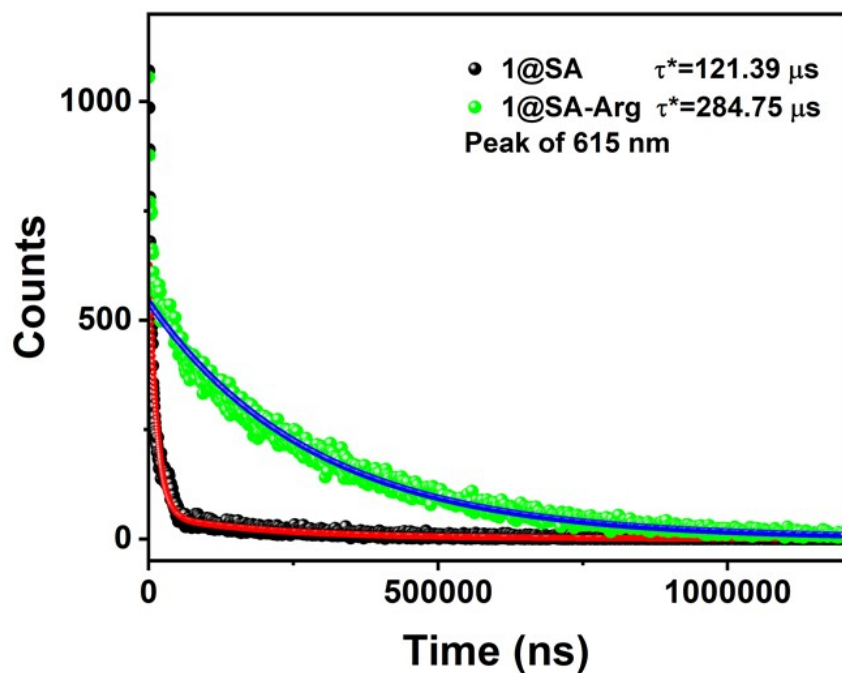
Fig. S19. Lifetime decay curves of **1@SA** at 615 nm in the absence and presence of Arg.
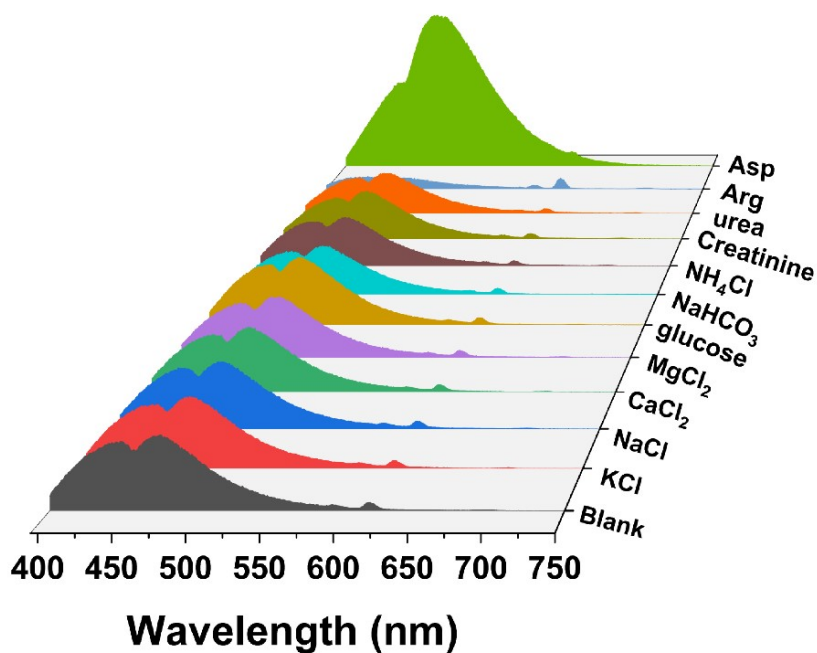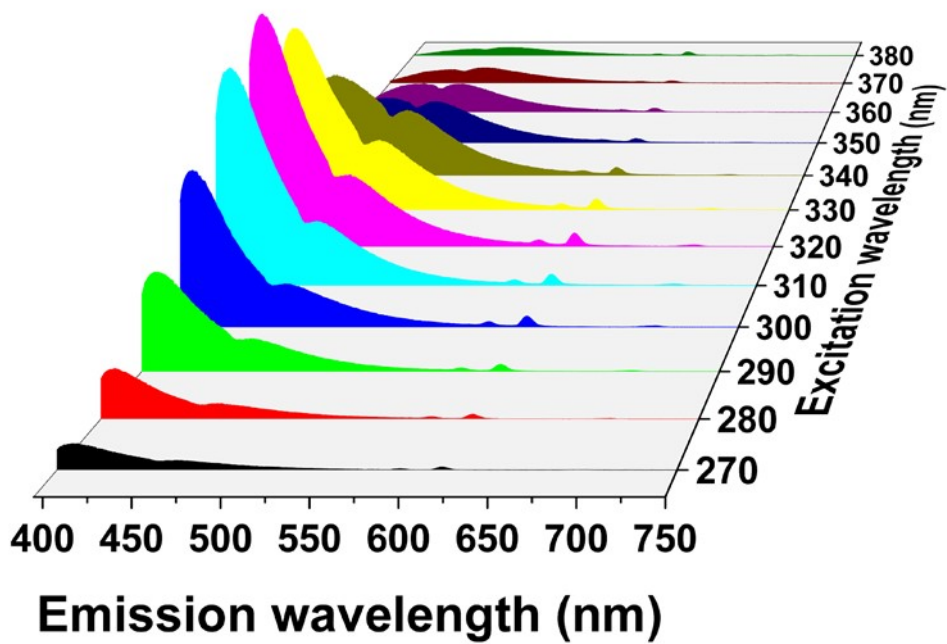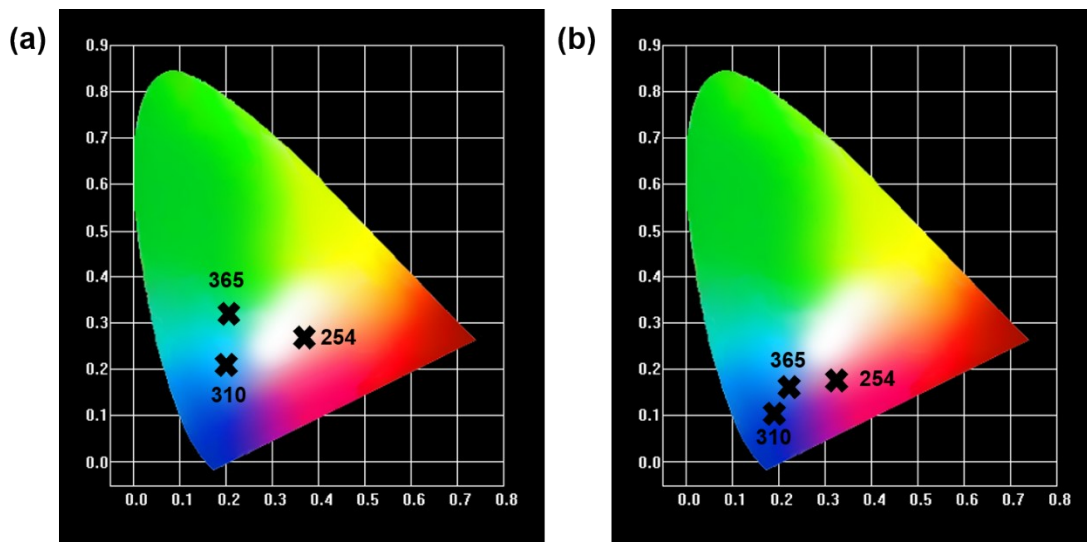

Fig. S20. Fluorescence spectra of **1@SA** in different serum species solutions (10 mM).

Fig. S21. Emission spectra of **1@SA** at different excitation wavelengths.
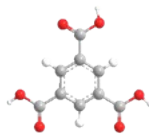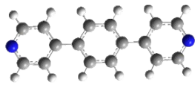

Fig. S22. The CIE coordinates of **1@SA** in Asp (a) and Arg (b) solution under different exciting wavelengths.

Table S1. Excitation and emission level transitions of Eu^{3+} ions.

	Transitions	Wavelength (nm)	Energy gap(eV)
	$^7F_0 \rightarrow ^5D_4$	361	3.43
	$^7F_0 \rightarrow ^5L_7$	375	3.31
	$^7F_0 \rightarrow ^5L_6$	394	3.15
	$^7F_0 \rightarrow ^5D_3$	415	2.99
	$^7F_0 \rightarrow ^5D_2$	465	2.67
Eu^{3+}	$^7F_0 \rightarrow ^5D_1$	535	2.32
	$^5D_0 \rightarrow ^7F_0$	579	2.14
	$^5D_0 \rightarrow ^7F_1$	591	2.10
	$^5D_0 \rightarrow ^7F_2$	615	2.02
	$^5D_0 \rightarrow ^7F_3$	653	1.90
	$^5D_0 \rightarrow ^7F_4$	696	1.78

Energy = 1240/λ (eV)

Table S2. Summary of S_1 and T_1 energy level (eV) of H_3BTC and bpbenz calculated by the time dependent density functional theory (TD-DFT) method.

	H_3BTC	bpbenz
Optimized molecular structure		
S_1 (eV)	4.67	3.99
T_1 (eV)	2.66	1.93

Table S3. Analysis report of the EDS energy spectra of ZnMOF and **1@SA**.

Material	Element	Weight %
ZnMOF	C	58.82
	N	9.61
	O	18.23
	Zn	13.34
1@SA	C	49.68
	N	3.53
	O	22.03
	Eu	21.52
	Zn	3.23

Table S4. Summary of transition type, energy, oscillator strength (f) and the contribution (%) of bpbenz and $H_2bpbenz^{2+}$ calculated by the time dependent density functional theory (TD-DFT) method.

Molecule	Transition	Energy (eV)	f	Type	%
bpbenz	$S_1 \rightarrow S_0$	3.99	1.1300	HOMO→LUMO	97.5
$H_2bpbenz^{2+}$	$S_1 \rightarrow S_0$	3.73	0.9635	HOMO→LUMO	99.3

Table S5. Summary of decay lifetime of **1@SA** without and with Arg.

Sample	1@SA	1@SA-Arg	Sample	1@SA	1@SA-Arg
λ_{ex} (nm)	365	365	λ_{ex} (nm)	365	365
λ_{em} (nm)	470	470	λ_{em} (nm)	615	615
τ_1 (ns)	1.73	1.28	τ_1 (µs)	13.31	284.75
A_1	931.18	1134.73	A_1	616.86	541.59
Percentage (%)	41.24	62.52	Percentage (%)	42.70	100
τ_2 (ns)	13.85	14.0	τ_2 (µs)	201.91	/
A_2	165.67	62.43	A_2	54.58	/
Percentage (%)	58.76	37.48	Percentage (%)	57.3	/
X^2	0.973	1.151	X^2	1.003	0.861

$[\tau^* = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)]$

Table S6. The results of recovery experiments.

Samples	No.	Spiked (mM)	Measured (mM)	Recovery (%)	RSD (%)
Asp	1	0.5	0.483	96.6	2.61
	2	1	0.989	98.9	2.96
	3	3	3.202	105.7	4.78
Arg	1	0.05	0.048	95.5	2.83
	2	0.3	0.315	104.9	3.12
	3	0.5	0.461	92.2	5.17