Supplementary Information

An accuracy improved ratiometric SERS sensor for rhodamine 6G in chili powder using metal-organic frameworks support

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S1 Preparation optimization of Au-MBA@Ag NRs

10 μL 4-MBA ethanol solution (0.1mM) was added to 1 mL Au NRs, and incubated at room temperature overnight. After centrifuged at 12000 rpm for 10 min, the solution was dispersed into 3 mL CTAC (0.02 M). 4, 6, 8, 10, 12, 14 μL $AgNO_3$ (0.1 M), and 16. 24, 32, 40, 48, 56 μL AA (0.1 M) correspondingly were added to it respectively, stirred for 1 min, 65 °C water bath for 2.5 h, a series of Au-MBA@Ag NRs solutions with different silver shell thickness from blue-green to orange were obtained, centrifuged at 10000 rpm for 10 min, washed in water, and finally dispersed in 1 mL water. 50 μL R6G solution (10 μM) was added to 100 μL of the above Au-MBA@Ag NRs solutions, then detect Raman intensity to evaluate the SERS performances of Au-MBA@Ag NRs prepared with different amounts of $AgNO_3$.

S2 Optimization of preparation of MOFs based SERS substrate

1-6 mL MIL-88B-NH_2 aqueous dispersion (1 mg/mL) was mixed with 1 mL Au-MBA@Ag NRs/PSS with the preparation ratio (volume ratio, v/v) changed at 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, respectively. Then, the dispersion was shaken at room temperature for 30 min following with three times of water washing. Finally, the obtained MOFs based SERS substrate of AMAPM was dispersed in 1-6 mL water to and store at 4 °C.

S3 Optimization of the amount of AMAPM

A certain volume of AMAPM aqueous dispersion (1 mg/mL) was added to 1 mL R6G (1 μM) and constant volume to 2 mL. After 60 min shaking at room temperature, the dispersion was centrifuged at 8000 rpm for 10 min. Then, 300 μL of supernatant was take to determine the fluorescence intensity and calculate the adsorption efficiency according to the following formula:

$$R = \frac{F_0 - F_1}{F_0} \times 100\%$$

where R is the adsorption efficiency, F_0 and F_1 are the initial fluorescence intensities of R6G and after adsorption, respectively.

S4 Optimization of the adsorption time of AMAPM

250 μL AMAPM aqueous dispersion (1 mg/mL) was added to 1 mL R6G (1 μM)

and shaked at room temperature for 20-120 min, respectively. After a centrifugation at 8000 rpm for 10 min, 300 μL of supernatant was take to determine the fluorescence intensity and calculate adsorption efficiency.

S5 Optimization of pH

The pH of 1 μM R6G was adjusted to 3-9 with dilute hydrochloric acid or sodium hydroxide solution. 250 μL AMAPM aqueous dispersion (1 mg/mL) was added to 1 mL of R6G (1 μM) with different pH and shaking for 60 min at room temperature. After a centrifugation at 8000 rpm for 10 min, 300 μL of supernatant was take to determine the fluorescence intensity to calculate adsorption efficiency. Meanwhile, the precipitate was dispersed in 50 μL water for SERS measurement to calculate the ratio of I_{1363}/I_{1077} for SERS performance evaluation.

S6 Optimization of ion strength

The ionic strength of 1 μM R6G was adjusted to 0-0.10 mol/L with 1 M NaCl solution and the pH was adjusted to 5. 250 μL of AMAPM (1 mg/mL) was added to 1 mL of R6G with different ionic strengths and shaking for 60 min at room temperature. After a centrifugation at 8000 rpm for 10 min, 300 μL of supernatant was take to determine the fluorescence intensity to calculate the adsorption efficiency. Meanwhile, the precipitate was dispersed in 50 μL water for SERS measurement to calculate the ratio of I_{1363}/I_{1077} for SERS performance evaluation.

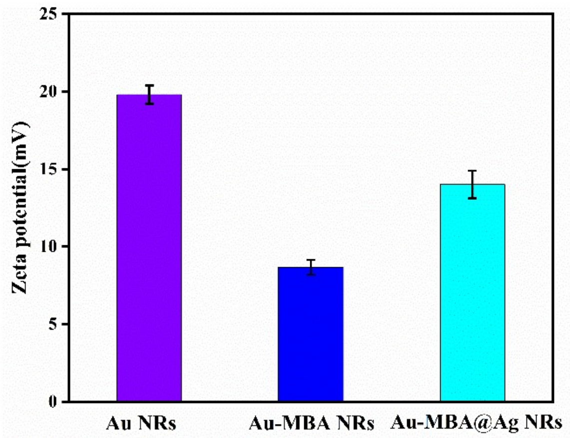

Figure S1 Zeta potential of Au NRs, Au-MBA NRs, Au-MBA@Ag NRs prepared by 6 μL $AgNO_3$ (0.1 M) and 24 μL AA (0.1 M).

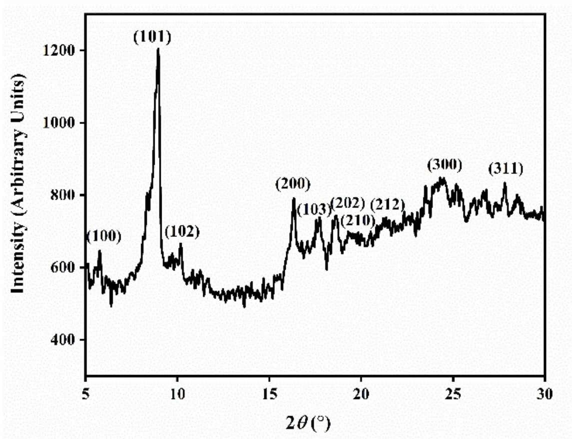

Figure S2 XRD patterns of MIL-88B-NH_2 (5-30°)

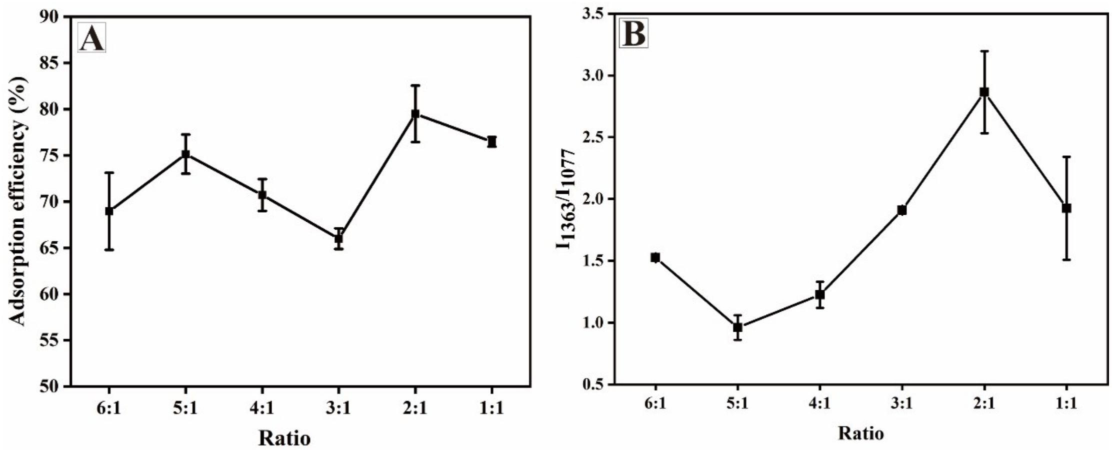

Figure S3 Effect of preparation ratio of functionalized MOFs on adsorption efficiency (A) and SERS performance (B) of R6G.

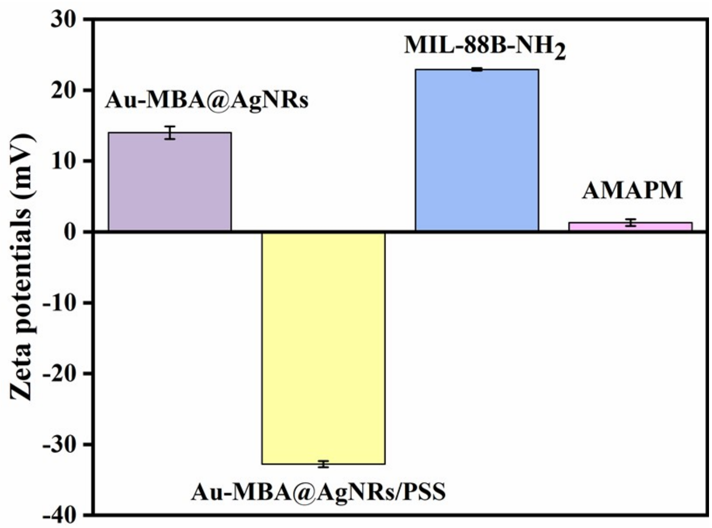

Figure S4 Zeta potentials of Au-MBA@Ag NRs, Au-MBA@Ag NRs/PSS, MIL-88B-NH_2 and

AMAPM.

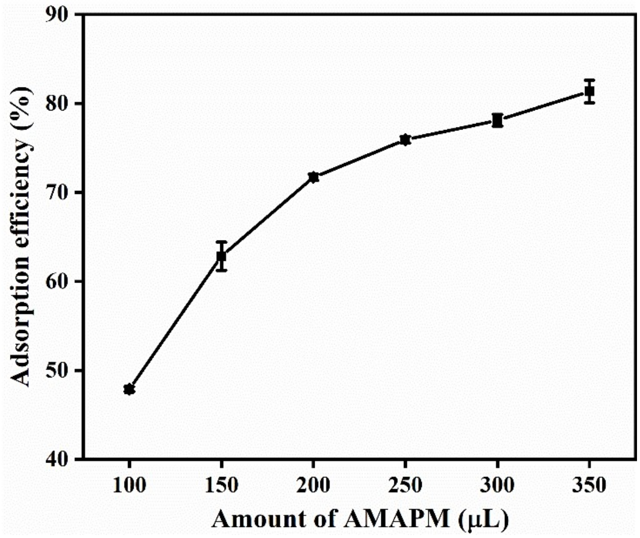

Figure S5 Effect of AMAPM amount on adsorption efficiency of R6G.

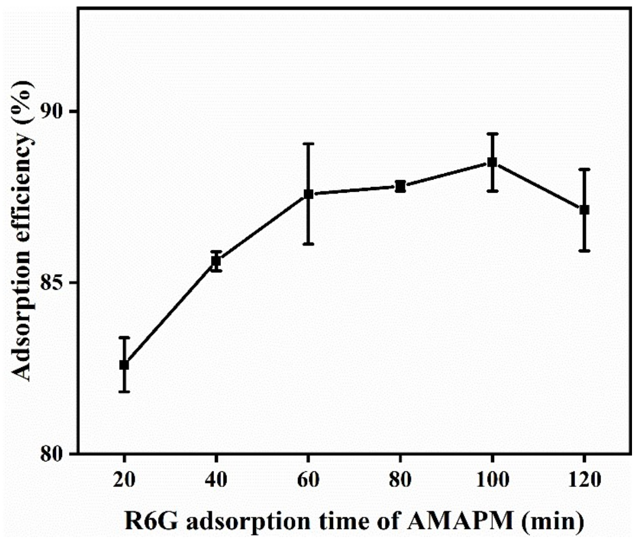

Figure S6 Effect of R6G adsorption time of AMAPM for the adsorption efficiency of R6G.

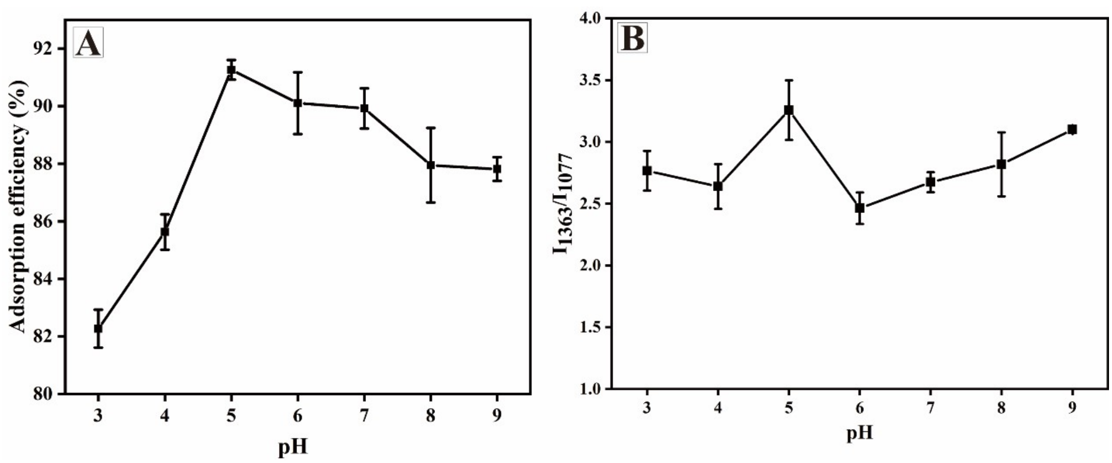

Figure S7 Effect of pH on adsorption efficiency (A) and SERS performance (B) of R6G.

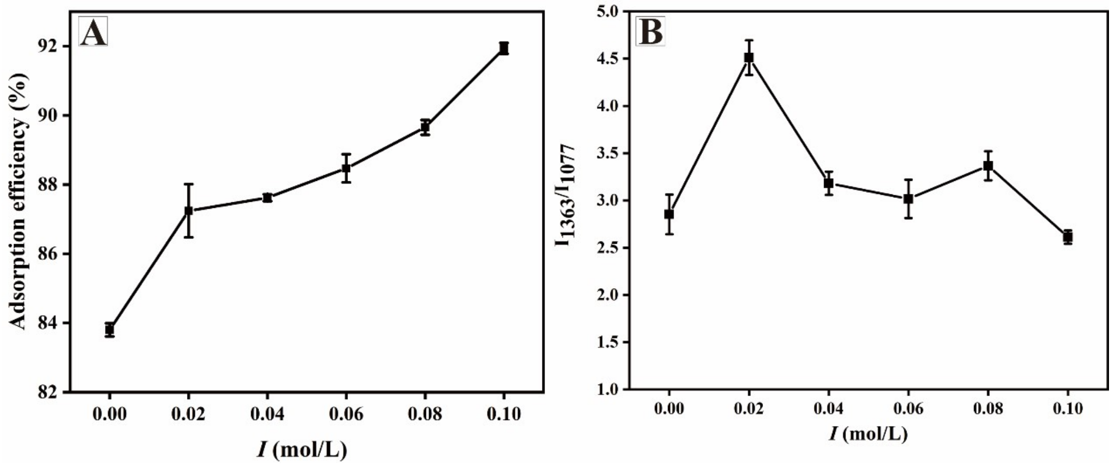

Figure S8 Effect of ion strength (*I*) on adsorption efficiency (A) and SERS performance (B) of R6G.

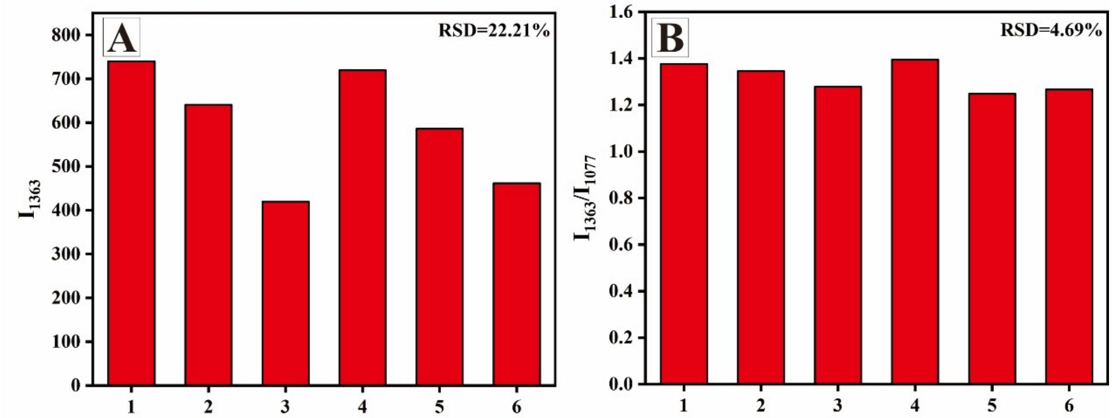

Figure S9 (A) I_{1363} and (B) I_{1363}/I_{1077} obtained in 6 detections of R6G (80 nM).

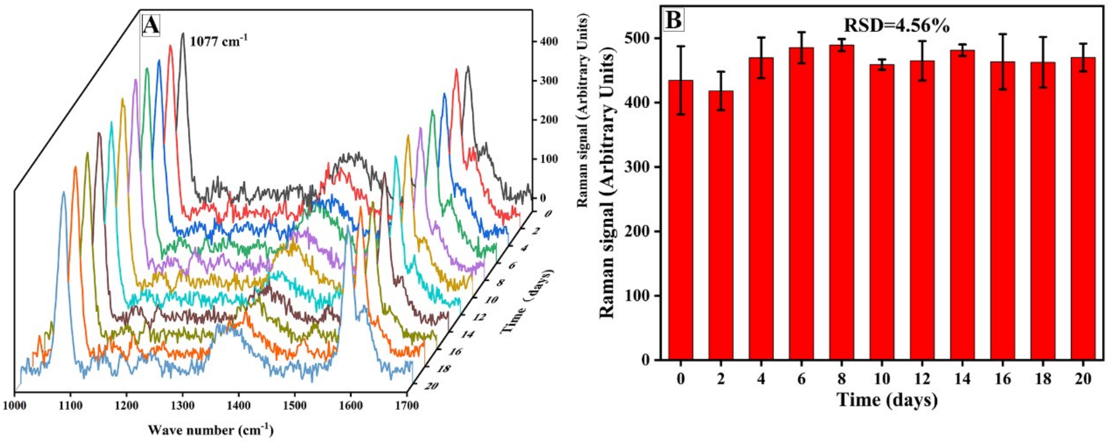

Figure S10 (A) The SERS spectra and (B) the SERS signals intensity at 1077 cm^{-1} of AMAPM SERS substrate stored at 4 °C for different days.

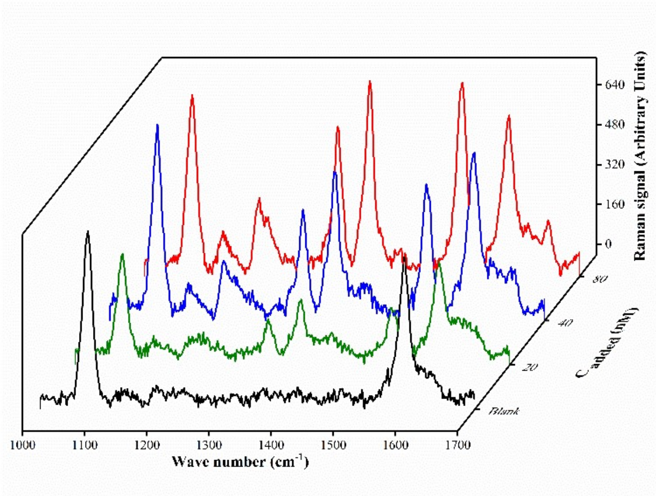

Figure S11 The actual SERS spectra of the real sample and spiked samples of chilli powder.

Table S1 Comparison of analytical performances of various detection methods of R6G.

Methods	Nanopaticles	Linear Range	LOD (nM)	Reference
UV-Vis	-	5-900 ng/mL	4.99	1
HPLC-Vis	-	10-1000 μg/mL	4.97	2
Fluorescence	AIE-MIPs-1	0-10 μM	260	3
SERS	Au/DW	10^{-7}-10^{-3} M	100	4
SERS	Ag NWs network	10^{-7}-10^{-6} M	100	5
SERS	GO/Ag/PSi	10^{-7}-10^{-4} M	100	6
SERS	Fe_3O_4@Au@MIL-100(Fe)	10^{-9}-10^{-5} M	1	7
SERS	AMAPM	5-320 nM	2.29	This work

References

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