Electronic Supplementary Information to:

Porphyrin-Based Ratiometric SERS Sensor for High-Throughput and Ultrasensitive Cadmium Ions Detection

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A. EXPERIMENTAL SECTION

Chemicals and Reagents. Silver nitrate ($AgNO_3$) was purchased from Sigma-Aldrich (St. Louis, Mo, USA). 5,10,15,20-tetrakis (1-methyl-4-pyridinio) porphyrintetra (p-toluenesulfonate) (TMPyP) was obtained from TCI (Shanghai, China). Trisodium citrate and cadmium chloride were acquired from Aladdin Chemistry Co. Ltd. (Shanghai, China). All other chemicals were purchased from Beijing Chemical Reagent Factory (Beijing, China). These reagents were of analytical grade and used as received without further treatment. Deionized water was used throughout the experiments. Phosphate buffer solution (PBS, 0.02 M, and pH = 6.0, 7.0, and 8.0) was prepared using Na_2HPO_4 and NaH_2PO_4.

Preparation of TMPyP-Triggered Ag Aggregates. A silver colloid was synthesized as previously reported.[1] Briefly, an aqueous silver nitrate solution (200 mL, 1.0 mM) was heated to boiling with vigorous stirring, and then an aqueous solution of trisodium citrate (1%, 4 mL) was immediately added into the solution. After heating for another 45 min, the color of mixture changed from pale yellow to greyish-green. The solution was cooled to room temperature with gentle stirring and then stored in dark place. The TMPyP-triggered Ag aggregates were preparation by addition of TMPyP aqueous solution (50 μL, 1 μM) into the Ag NPs colloidal solution (50 μL) with a vortex mixer for 5 seconds.

Real Samples. Rice samples were purchased from the local market and were ground for 30 s using a laboratory-scale mill. Cd^{2+} ions were extracted from crushed rice samples by wet digestion method.[2] Briefly, 0.2 g of the sample powder was heated in 10 mL of concentrated nitric acid, and aliquot of 7-8 mL of a 30% hydrogen peroxide solution was added in batches into the reaction system until no obvious brown smoke was released from the reaction system. And then, 10 mL deionized water was added into the reaction system, and the reaction system

was sustainedly heated until the volume of solution is less than 1 mL. Subsequently, the cooled solution was transferred to a 100 mL volumetric flask, and diluted with PBS (pH=7.0) to volume.

Instruments. UV-vis-NIR absorption spectra were collected on a Persee TU-1901 spectrophotometer. Transmission electron microscopy (TEM) images were acquired with a JEM-2100F TEM operating at 200 kV. Dynamic light scattering (DLS) and zeta-potential were recorded using Nanotrac wave II (Microtrac MRB). SERS spectra were measured by a Raman instrument (Thermo Scientific DXR2) equipped with a laser of 532 nm excitation (5 mW). The Raman spectra were collected with a 50× mirror, and the size of laser spot is about 1 μm on the sample surface. The Raman band of the silicon wafer at 520 cm^{-1} was used to calibrate the spectrometers.

SERS Detection. Various concentrations of Cd^{2+} ions solutions were obtained via serial dilutions of the stock $CdCl_2$ solution (1.0×10^{-6} M) with PBS (pH=7). 100 μL of as-prepared TMPyP-triggered Ag aggregates were mixed with 100 μL of different concentrations of Cd^{2+} ions solutions. The error bars represent standard deviations based on four independent measurements. The data acquisition time was 5 s with three accumulations.
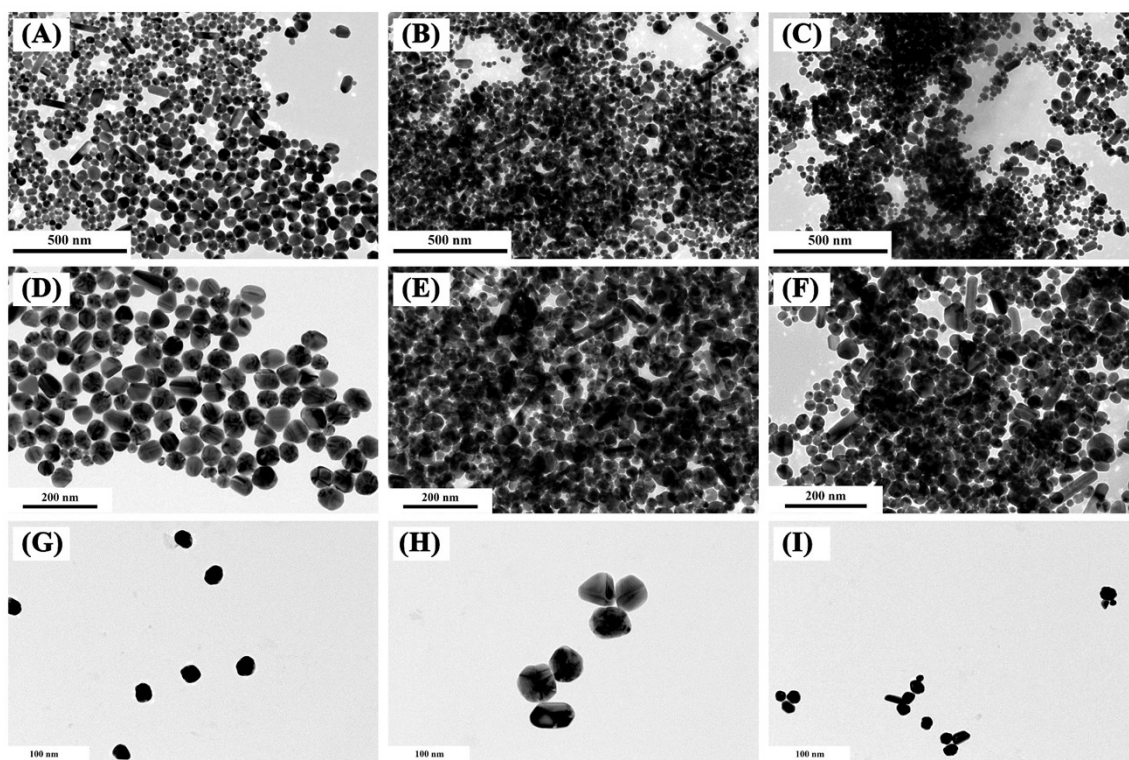
B. Additional Figures.

Fig. S1 TEM images of (A) and (D) Ag NPs, (B) and (E) TMPyP-triggered Ag aggregates, and (C) and (F) TMPyP-triggered Ag aggregates after addition of Cd^{2+} ions. The TEM images were performed for the diluted samples, and trimers were clearly observed for TMPyP-triggered Ag aggregates (Fig. S1H and S1I).
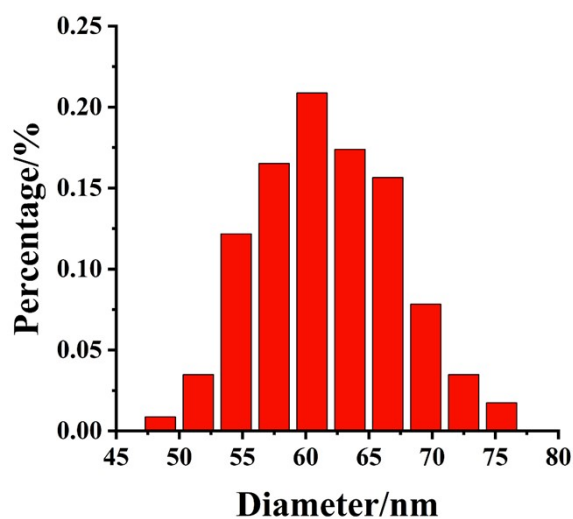

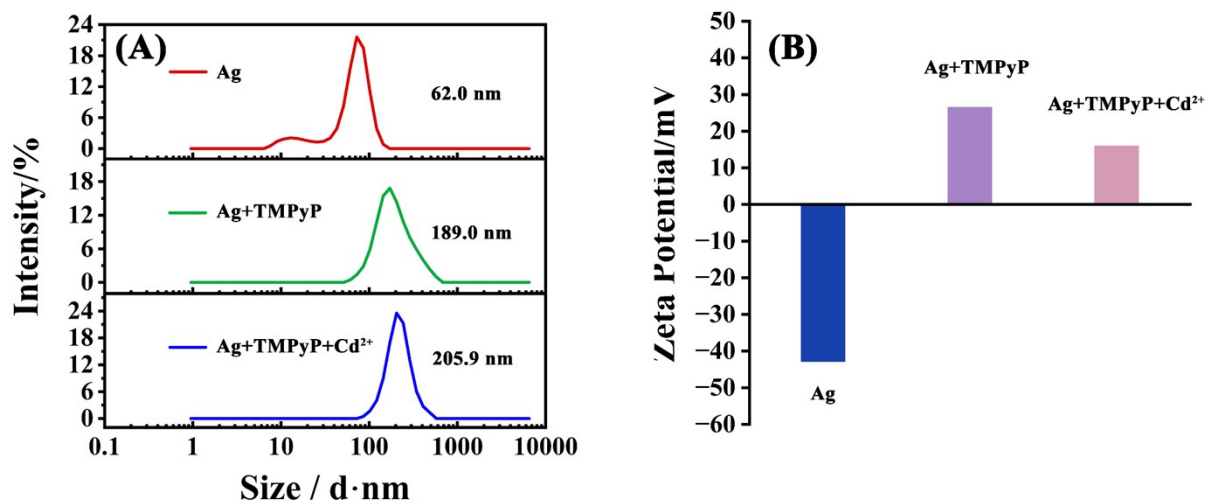**Fig. S2** The particle size distribution histogram of Ag NPs.

Fig. S3 (A) Dynamic light scattering analysis and (B) zeta potential of Ag NPs before and after addition of TMPyP (10^{-6} M), and TMPyP-triggered Ag aggregates in the presence of Cd^{2+} (10^{-6} M). It was found that the hydrodynamic diameter of Ag NPs is around 62.0 nm, which is corresponding to the monodispersed state. However, the hydrodynamic diameter of Ag NPs increases to 189.0 nm after the addition of TMPyP, indicating the formation of TMPyP-triggered Ag aggregates. The hydrodynamic diameter of TMPyP-triggered aggregates slightly increases from 189 to 205 nm after addition of Cd^{2+} ions, indicating that the further aggregation of Ag NPs.
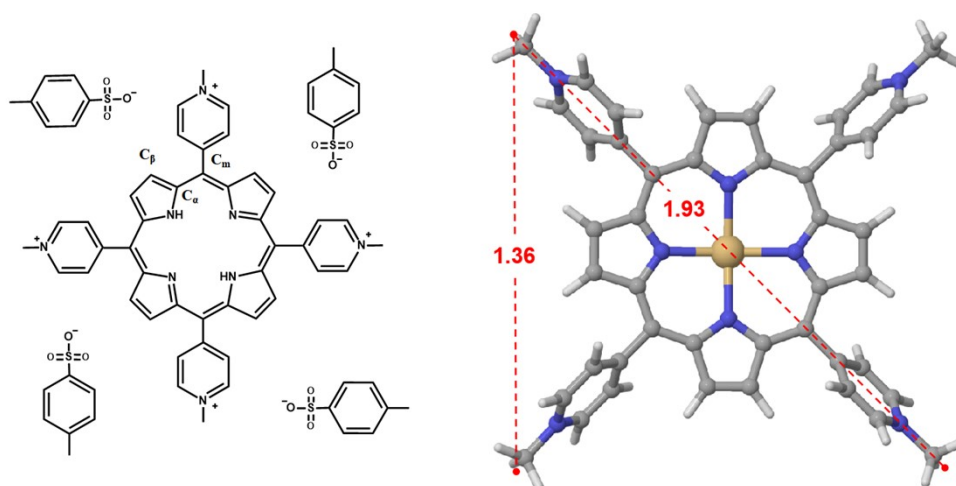

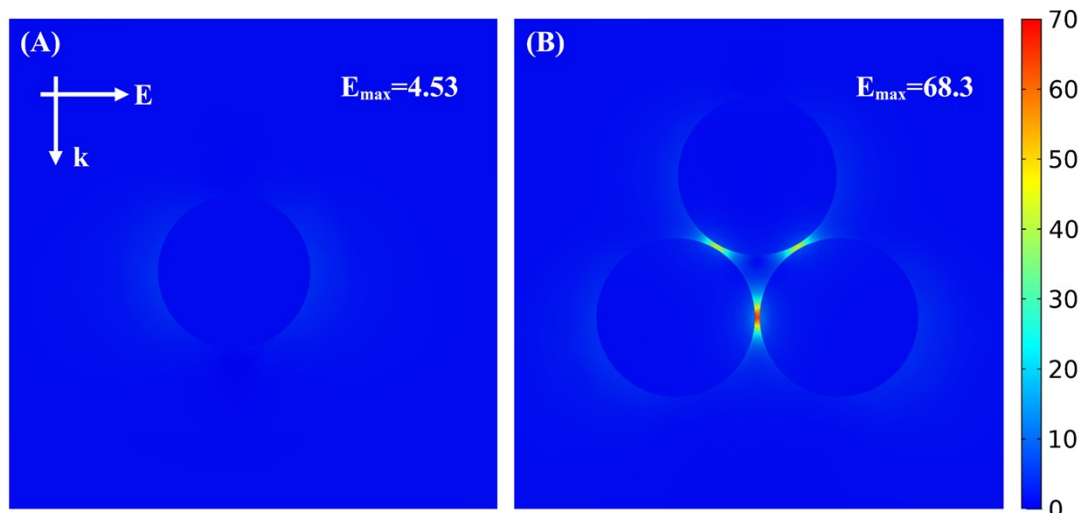**Fig. S4** Structure diagram of TMPyP molecule.

Fig. S5 Spatial maps of electric field distribution of Ag monomer and trimer with the 532 nm excitation. The incident direction and the polarization are shown in the corresponding images.
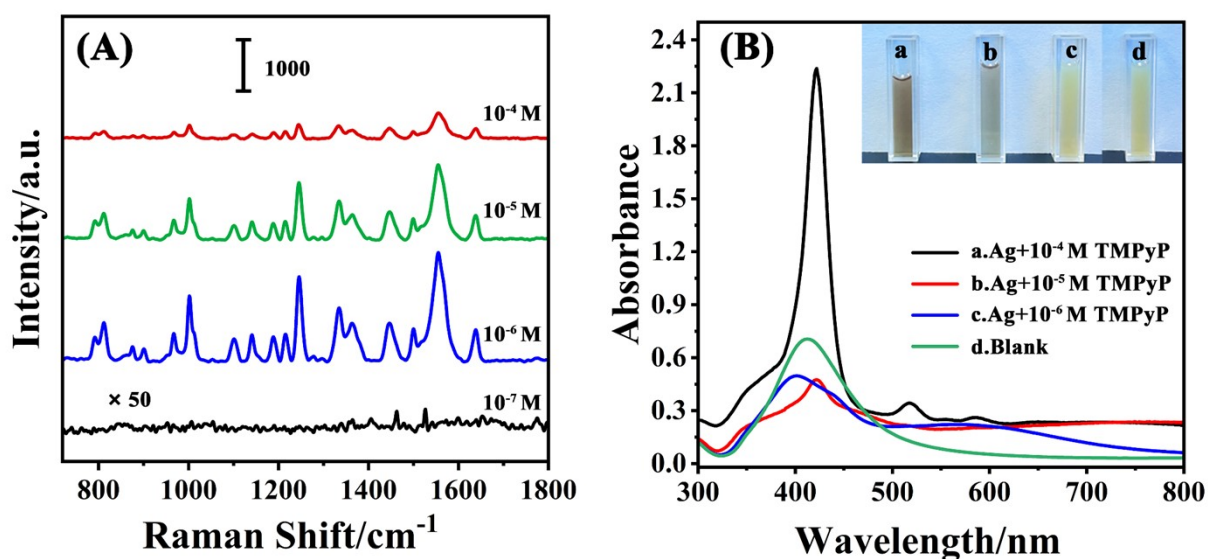

Fig. S6 (A) UV-vis absorption spectra of Ag NPs in the presence of different concentration of TMPyP. Inset shows the corresponding optical pictures of Ag NPs solution. (B) SERS spectra of TMPyP with different concentration. In the presence of high concentration TMPyP (10^{-4} M), the absorption peak corresponding to Ag NPs disappeared and only the typical absorption for TMPyP was observed, indicating the precipitation of Ag aggregates. Besides, the optical picture of Ag NPs with 10^{-4} M TMPyP exhibits the bulk color of the TMPyP, further indicating that the precipitation of Ag aggregates in the presence of high concentration TMPyP.
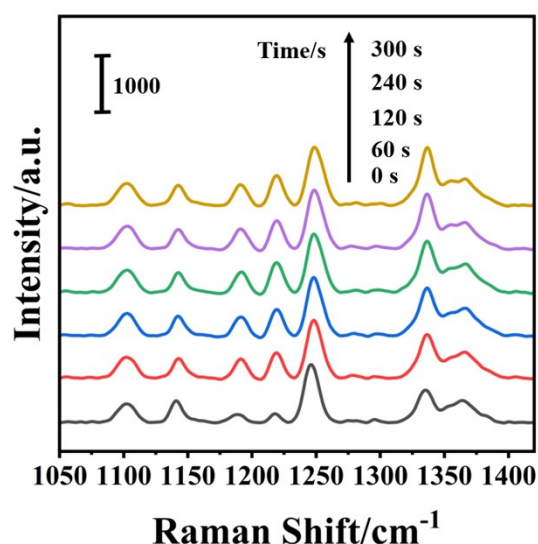
Fig. S7 SERS spectra of time-dependent change in the presence of Cd^{2+} ions (10^{-6} M).
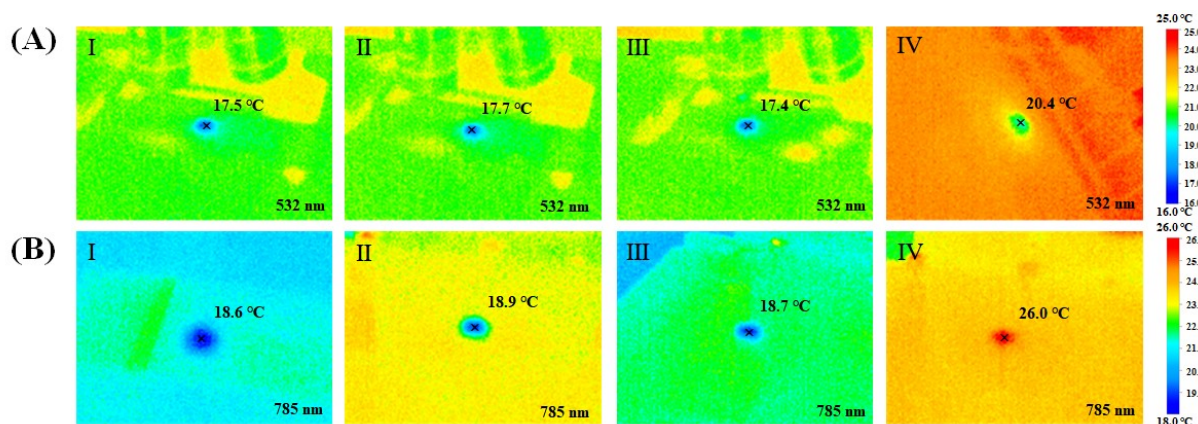

Fig. S8 IR thermal photos of TMPyP solution and TMPyP-triggered Ag aggregates solution under (A) 532 nm and (B) 785 nm lasers irradiation for 200 s. Inset labels represent the IR thermal photos of solution before (I and III) and after (II and IV) irradiation with corresponding lasers. With the irradiation of 532 nm laser, the system temperature of TMPyP solution risen by 0.2 degrees, but the system temperature of TMPyP-triggered Ag aggregates solution risen by 3 degrees. This temperature rise behavior is more evident with the irradiation of 785 nm laser than that of 532 nm laser. Obviously, the TMPyP-triggered Ag aggregates generate a non-radiative photothermal effect to increase the system temperature of solution. It should be noted that the local temperature around the Ag aggregates is much higher than the system temperature of the solution, accelerating the coordination reaction between Cd^{2+} ions and porphyrin core.

Table S1 The assignments of Raman and SERS bands for TMPyP.

Raman shift/ cm^{-1}	SERS/ cm^{-1}	Assignment
968	965	v (C_α - C_β) or v (C_α - C_m)
1003	1000	v (Pry)
1101	1100	δ (C_β - H)
1141	1138	v (C_α - C_β)
1188	1188	v (N - CH_3)
1217	1214	δ (Pry) or v (N - C_α)
1246	1245	δ (C_m - Pry)
1336	1332	v (C_α - N)
1365	1358	v (C_α - N)
1448	1451	v (C_α - C_m) + v (C_α - C_β) or Pyr, v (C - C)
1500	1498	v (C_β - C_β)
1556	1552	v (C_β - C_β)
1637	1635	δ (Pry)

v: stretching vibration; δ: bending vibration; Pry: N-methylpyridyl group.

Table S2 Comparison of different methods for Cd^{2+} ions detection.

Detection method	Linear range	LOD	Response time	Ref.
SERS	0.1 nM-1 µM	0.1 nM	200 s	This work
Colorimetric assay	Not available	5 µM	Not available	3
UV-vis spectroscopy	0-11.5 µM	72 nM	20 min	4
UV-vis spectroscopy	0.2-1 µM	0.2 µM	8 min	5
Electrochemistry	0.0063-1.07 µM	1.79 nM	Not available	6
Electrochemistry	0.1-10 µM	10 nM	5 min	7
Fluorescence	0.2-10 µM	0.1 µM	Not available	8
Colorimetric and fluorescent detection	0-100 µM	73 nM	Not available	9

References

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