

Supporting Information

Assembly of Gold Nanorods Functionalized by Zirconium-based Metal–Organic Frameworks for Surface Enhanced Raman Scattering

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Experimental Section

Chemicals and materials

All the reagents were used without further purification. Hexadecyltrimethylammonium bromide (CTAB, >99.0%), hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$, 99.995% trace metals basis), silver nitrate (AgNO_3 , >99.99%), ascorbic acid (BioUltra, $\geq 99.99\%$), sodium oleate (NaOL, >98.0%), sodium borohydride (NaBH_4 , 99%), zirconium (IV) tert-butoxide ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Zr}$), benzoic acid ($\text{C}_7\text{H}_6\text{O}_2$, $\geq 99\%$), acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, 99%), N,N-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, 99.5%), 1,3,6,8-tetrakis(p-benzoic acid)pyrene ($\text{C}_{44}\text{H}_{26}\text{O}_8$, $\geq 95\%$), mPEG-SH ($M_n \approx 6000$ Da) and 4'-mercapto-[1,1'-biphenyl]-4-carbonitrile ($\text{C}_{13}\text{H}_9\text{NS}$, 97%) were purchased from Sigma-Aldrich Co. Ltd.

Hydrochloric acid (HCl, 37 wt. % in water), methanol (CH₄O, 99%), ethanol (C₂H₆O, 99%), 1-propanol (C₃H₈O, 99%) and acetone (C₃H₆O) were purchased from Macklin Chemical Reagent Co., Ltd. All the solutions were prepared in ultrapure water (18.2 MΩ·cm).

Synthesis of Au nanorod

The HAuCl₄ (5 mL, 0.5 mM) was firstly added to CTAB (5 mL, 200 mM) solution, and then 0.6 mL of 10 mM NaBH₄ was injected rapidly under vigorous stirring (1000 rpm) to prepare the seed solution. The solution changes the color from yellow to brownish yellow and was aged at room temperature for 1 h before use.

To prepare the growth solution, 2.8 g CTAB and 493.6 mg NaOL were dissolved in 100 mL of warm water (~50 °C). After cooling to 30 °C, the solution was added with 9.6 mL of 4 mM AgNO₃ solution and kept undisturbed for 10 min. Then, 100 mL of 1 mM HAuCl₄ was added and stirred for 90 min until the solution became colorless. 0.6 mL of 12.1 M HCl was then introduced to adjust the pH, after which 0.5 mL of 0.064 M ascorbic acid (AA) was added. Finally, 160 μL of seed solution above was injected into the growth solution and the mixture was stirred for 30 s and left undisturbed overnight for Au nanorod growth. The final products were separated via centrifugation at 7,500 rpm for 30 mins followed with purification treatment yielding Au nanorod@CTAB.

Au nanorod PEGylations

The synthesized Au nanorod@CTAB were centrifuged and re-dispersed in 50 mL deionized water, and the concentrations of Au nanorod and CTAB were adjusted to 1 nM and 1 mM, respectively. 500 μL of 10 mg/mL thiolated methoxyl-polyethylene glycol (CH₃O(CH₂CH₂O)_nCH₂CH₂SH, Mn≈6000 Da) (mPEG-SH) was added to the Au nanorod@CTAB solution and left to react overnight under slowly stirring. The mixture was centrifuged and re-dispersed in 50 mL ethanol (90%) to remove the residual CTAB. 300 μL mPEG-SH was then added to the solution and stirred overnight again. To remove excess mPEG-SH, the Au nanorod@mPEG was

centrifuged once, with dispersion in ethanol or DMF as required.

The synthesis of Au nanorod@MOF

According to the procedure reported, the Zr_6 node was firstly synthesized. 300 mL 1-propanol and 15 mL of zirconium (IV) tert-butoxide (80 wt%) were mixed and stirred for 10 min. 100 g benzoic acid was added followed by 20 min of ultrasonication. The mixture was further stirred and heated at reflux overnight, obtaining stratified products with clear supernatant and white bottom sediment. Excess 1-propanol was removed by heating under vacuum, resulting in the crystallization of a white solid product. The solid product was fully washed with 1-propanol and then dried under vacuum at room temperature yielding Zr_6 node.

The Zr_6 node powder (18.2 mg) was dispersed in a mixture of DMF (7.5 mL) and glacial acetic acid (1.82 mL). Then, 0.3 mL of Au nanorod@mPEG was added and the dispersion was vigorously stirred. The H_4TBAPy linker solution in DMF (0.1~0.8 mL, 2 mg/mL) was injected slowly with a syringe pump (0.05 mL/min) and the solution was left stirring overnight. To remove excess reagents, the products were centrifuged and washed thrice in DMF and solvent was exchanged to acetone after the third centrifugation. After ultrasonic dispersion, the solution was left undisturbed at room temperature for 12 hours and the prepared Au nanorod@Zr-MOF was separated by centrifugation, and re-dispersed in acetone or methanol.

Fabrication of random stacking Au nanorod

10.0 μ L of fresh prepared Au nanorod@mPEG suspension was dropped on a Si wafer treated with piranha solution using a pipette. After natural drying, the disordered Au nanorod substrate was prepared.

Fabrication of ordered array Au nanorod

Large-area arrays of vertically aligned Au nanorod was fabricated as follows. By centrifugation and re-dispersion twice, the concentration of Au nanorod and CTAB of stock solutions were adjusted to 10 nM and 1 mM, respectively. 10.0 μ L of fresh

prepared Au nanorod suspension was dropped on a Si wafer treated with piranha solution using a pipette. The droplet was allowed to evaporate on the wafer in a sealed petri dish containing a saturated K_2SO_4 solution. Then the sealed petri dish was placed in an incubator with temperature set at 30 °C. The evaporation process lasted over 72 hours.

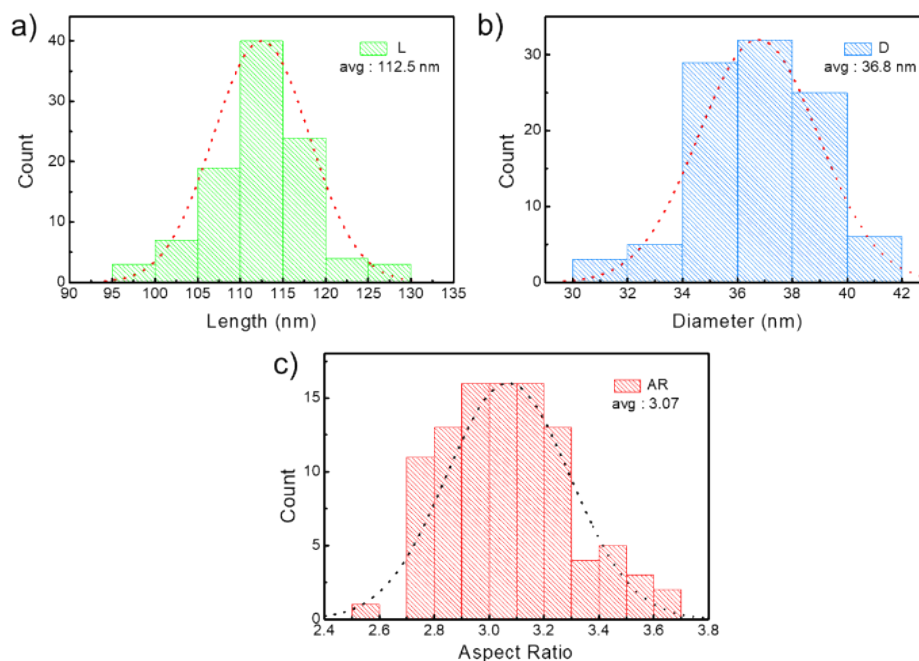


Figure S1 The length (a), diameter (b) and aspect ratio (c) distribution of synthesized Au nanorods.

Charaterization

The samples morphology was characterized by TEM (JEOL, JEM-2100F) operated at 100 kV and HRTEM (JEM-3000F) operated at 300 kV. Extinction spectra were recorded on a UV-3600 spectrophotometer (Shimadzu). All the Raman spectra were collected using a confocal micro-Raman spectrometer (Renishaw InVia Reflex) with a 785-nm laser. The typical integration time was 10 s and the excitation power was kept at 0.1 mW without any observable heating effect.

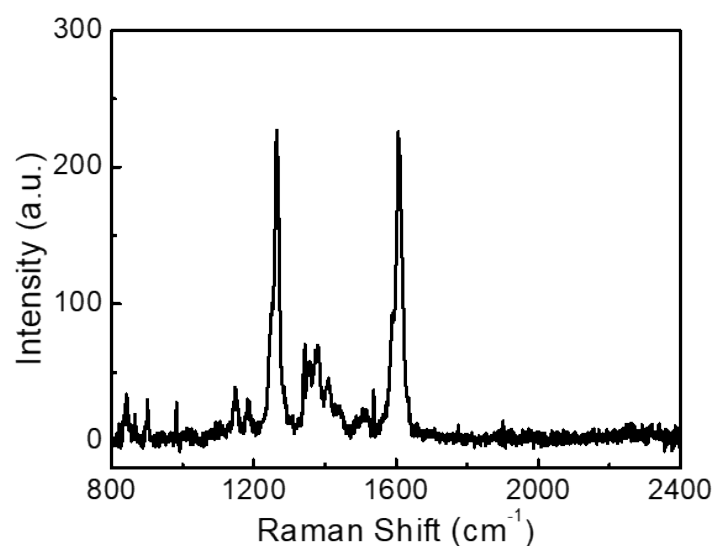


Figure S2 Raman spectrum of Zr-MOF in powder form.

The EF calculation

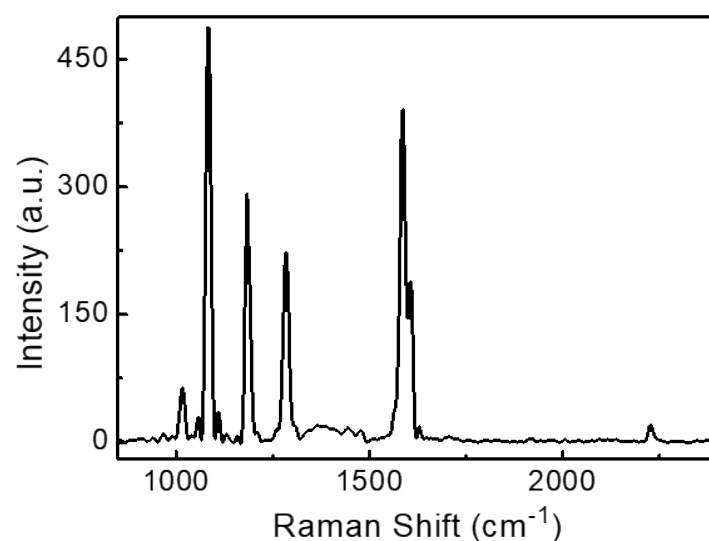


Figure S3 The Raman spectra of BPTCN.

The EF can be calculated based on the following equation:

$$EF = (I_{\text{sers}}/I_{\text{ref}})(N_{\text{ref}}/N_{\text{sers}})$$

where I_{sers} and I_{ref} are the Raman intensities of BPTCN molecules on the SERS-active substrate and under non-SERS condition, respectively. N_{sers} and N_{ref} are the number of BPTCN molecules absorbed on the SERS-active substrate and powder sample under laser illumination, respectively. The values of N_{sers} and N_{ref} can be estimated by the concentration of surface species or powder sample in the corresponding sampling

areas. The laser in the setup was focused on a spot with a diameter of $d = (\lambda/NA) \times 1.22 = 1.28 \mu\text{m}$. The penetration depth of the 785 nm laser beam is about $2 \mu\text{m}$. The average surface density of BPTCN molecule in densely packed monolayer is about one BPTCN molecule per $1.05 \times 10^{-18} \text{ m}^2$. N_{serS} is estimated to be 1.22×10^6 . For N_{ref} , the sampling volume is the illuminated volume of laser spot $V_{\text{illu}} = 2.57 \mu\text{m}^3$ and $N_{\text{ref}} = V_{\text{illu}} \rho R / Mr = 8.87 \times 10^9$ (R is Avogadro constant, ρ is the BPTCN density of 1.21 g/cm^3 , Mr value is 211.28 g/mol). Specifically, in the case of Raman band at 1083 cm^{-1} , the EF of BPTCN molecules on Au nanorod@Zr-MOF substrate was calculated to be 4.7×10^5 .

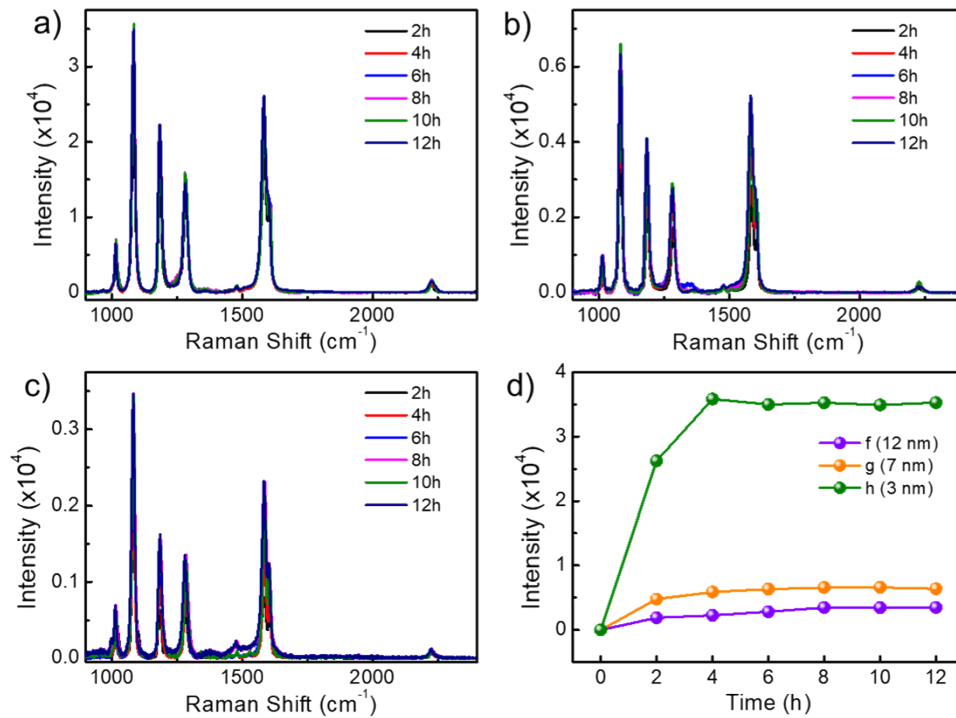


Figure S4 Raman spectra of BPTCN collected at every 2 h interval when different Au nanorod@Zr-MOF samples with 3, 7, 12 nm-MOF shell were employed as SERS substrates (a-c) and the corresponding SERS intensities at 1083 cm^{-1} vs. the incubation time (d).

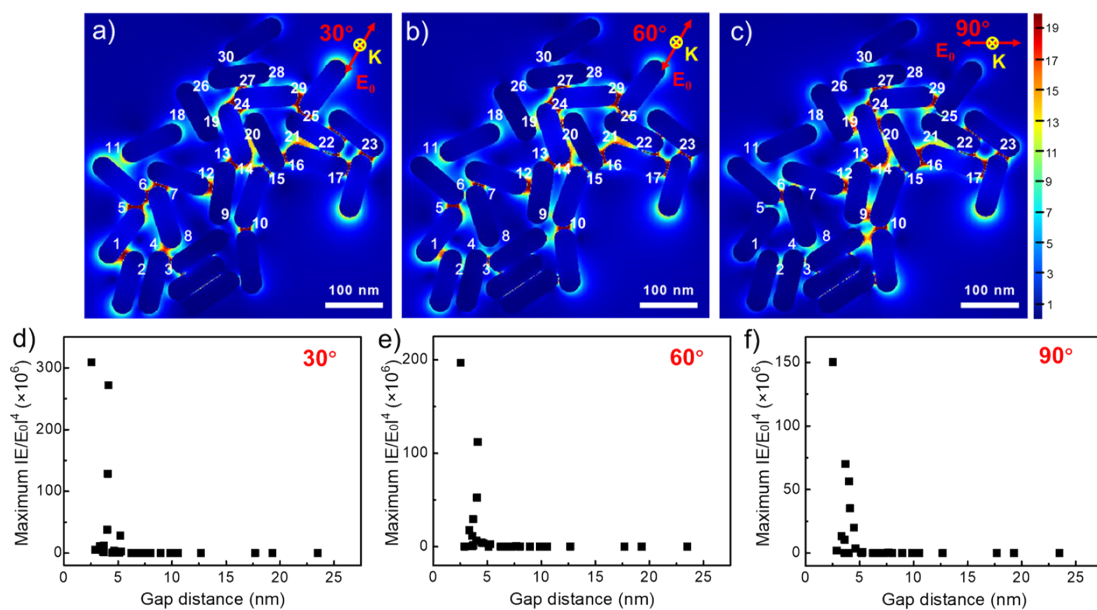


Figure S5 Electric field distribution of Au nanorods with incident light polarization angle of 30° (a), 60° (b), 90°(c) and corresponding statistical analysis of maximum electric field enhancement factor ($|E/E_0|^4$) vs. gap distance over 30 spots (d-f). E denotes the electric field vector and K denotes the wavevector.

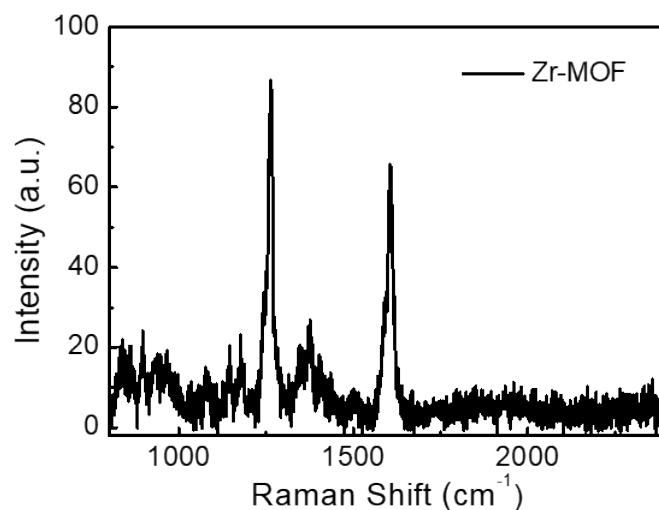


Figure S6 Raman spectrum of BPTCN (2×10^{-6} M) using porous MOF as substrate.

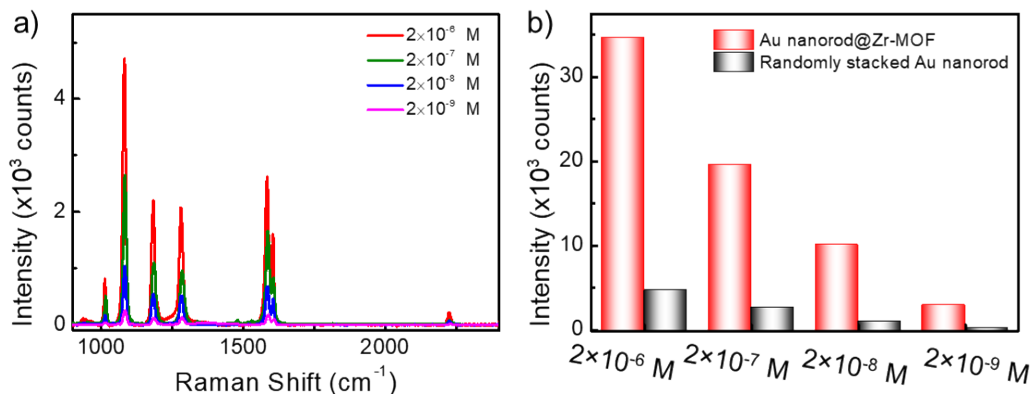


Figure S7 Raman spectra of BPTCN at different concentrations using randomly stacked Au nanorod as SERS substrate (a). The Raman intensities (1083 cm^{-1}) diagram of BPTCN measured with Au nanorod@Zr-MOF and randomly stacked Au nanorods substrates.

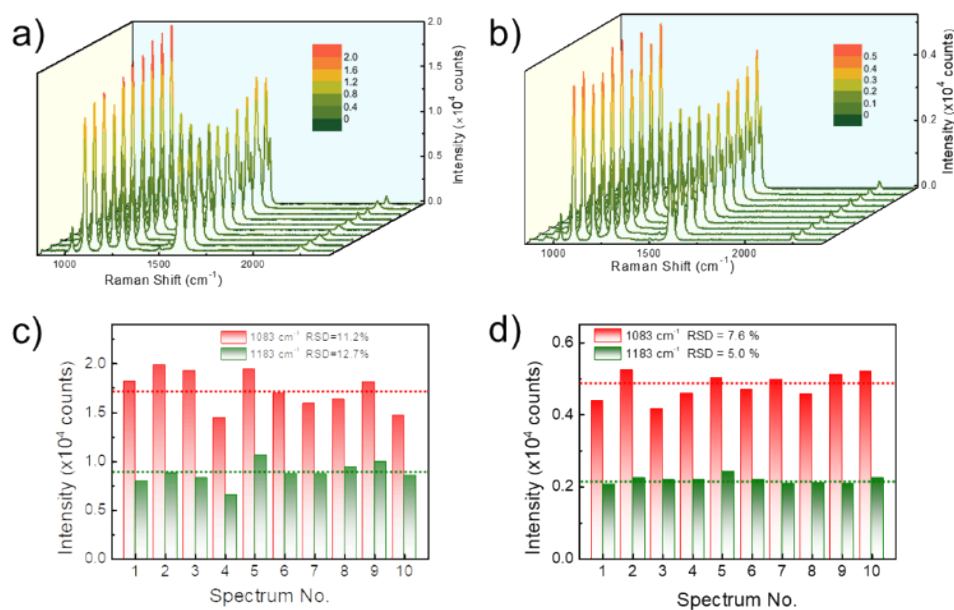


Figure S8 Raman spectra (a) of BPTCN ($2 \times 10^{-6}\text{ M}$) randomly collected at ten different spots and the corresponding SERS intensities (b) at 1083 cm^{-1} and 1183 cm^{-1} on ordered array Au nanorod. Raman spectra (c) of BPTCN ($2 \times 10^{-6}\text{ M}$) randomly collected at ten different spots and the corresponding SERS intensities (d) at 1083 cm^{-1} and 1183 cm^{-1} on random stacking Au nanorod.

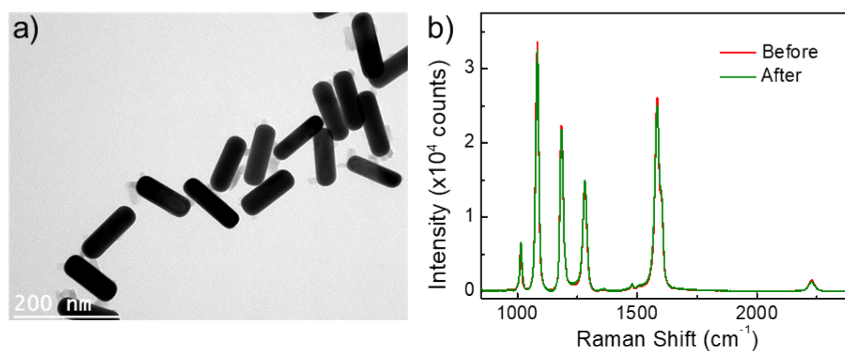


Figure S9 TEM image (a) and Raman spectra of BPTCN using Au nanorod@Zr-MOF after annealing in air for 4h and immersion in 3.5 wt% NaCl solution for one week.

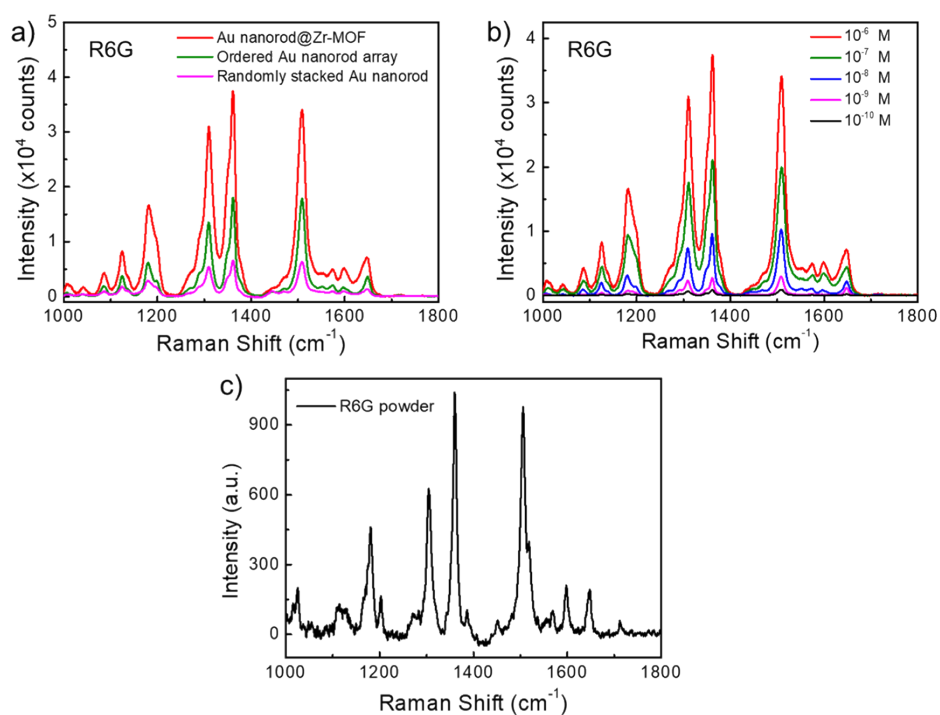


Figure S10 Raman spectra of R6G (10^{-6} M) using Au nanorod@Zr-MOF structures, ordered Au nanorod arrays, and randomly stacked Au nanorods as SERS substrates (a). Raman spectra of R6G with different concentrations using Au nanorod@Zr-MOF as substrate (b). Control Raman spectra of R6G powder (c).

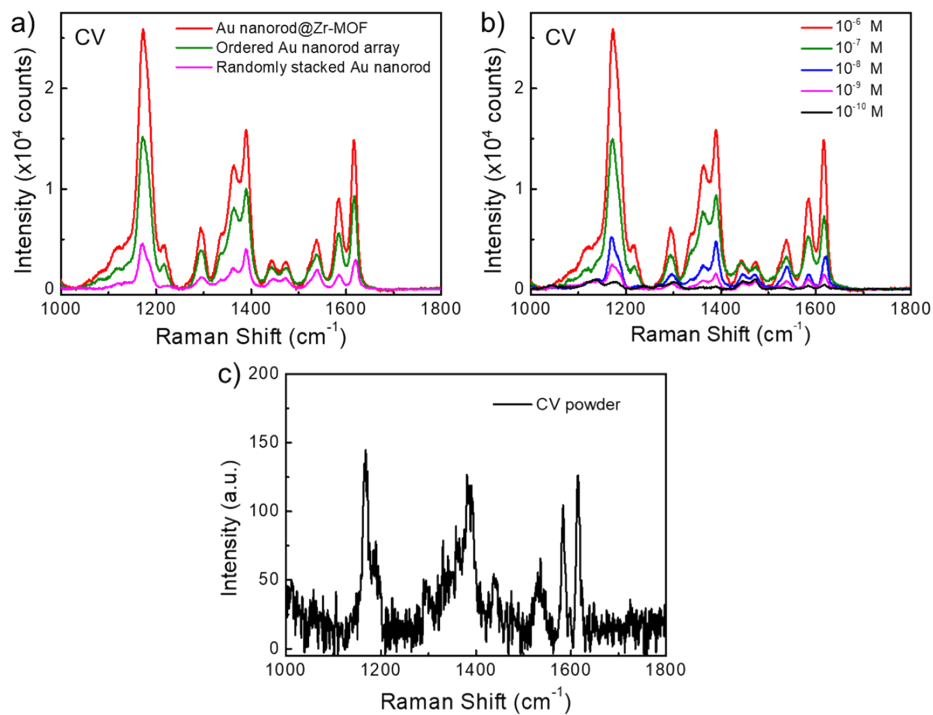


Figure S11 Raman spectra of CV (10^{-6} M) using Au nanorod@Zr-MOF structures, ordered Au nanorod arrays, and randomly stacked Au nanorods as SERS substrates (a). Raman spectra of CV with different concentrations using Au nanorod@Zr-MOF as substrate (b). Control Raman spectra of CV powder (c).