Supporting Information

Fabrication of molecularly imprinted gold nanoparticles-embedded Fe-MOFs for highly selective SERS detection of 17 β-estradiol in milk

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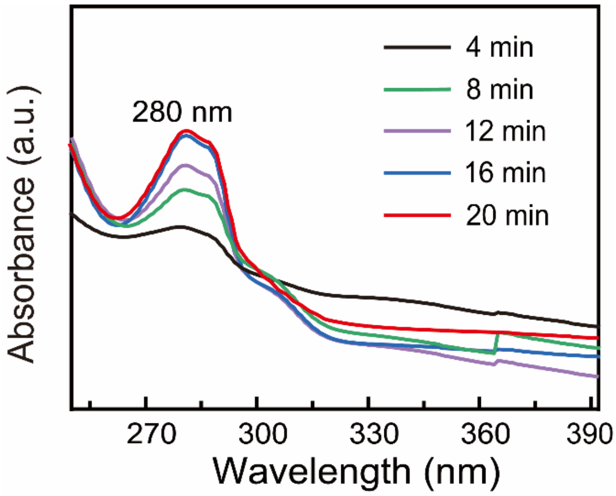

Figure S1. UV-vis spectroscopy of the elution solution. The wavelength of 17β-E2 is located at 280 nm.

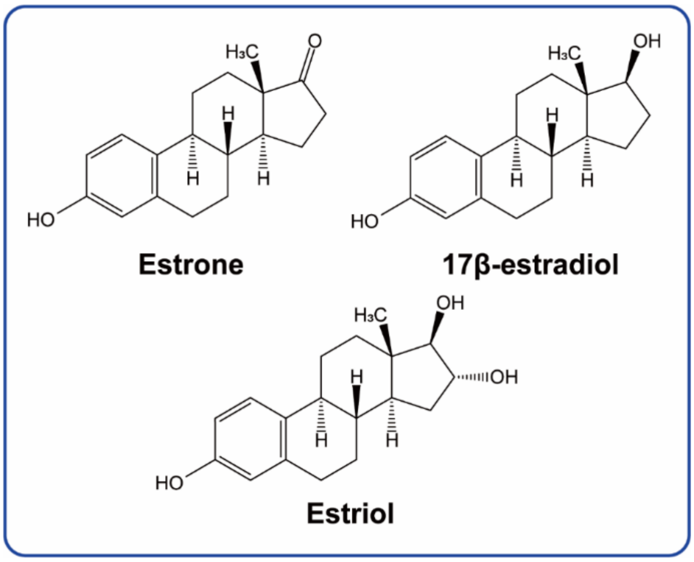

Figure S2. The chemical structure of estrone (E1), 17β-estradiol (17β-E2) and estriol (E3).

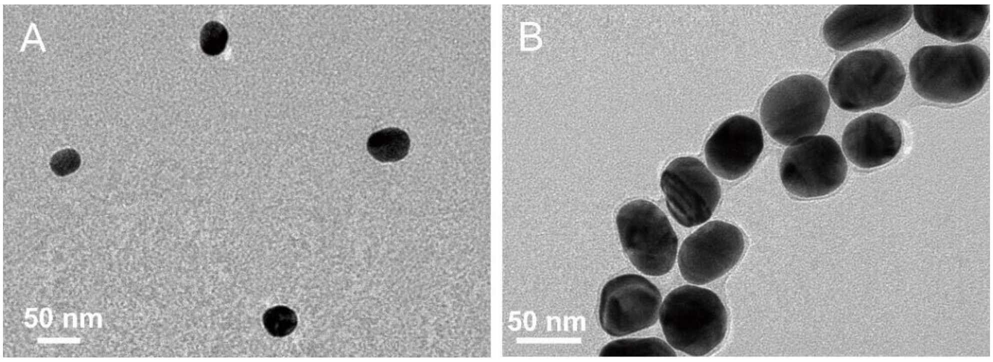

Figure S3. TEM images of (A) AuNPs and (B) core-shell AuNP@MIP-PDA.

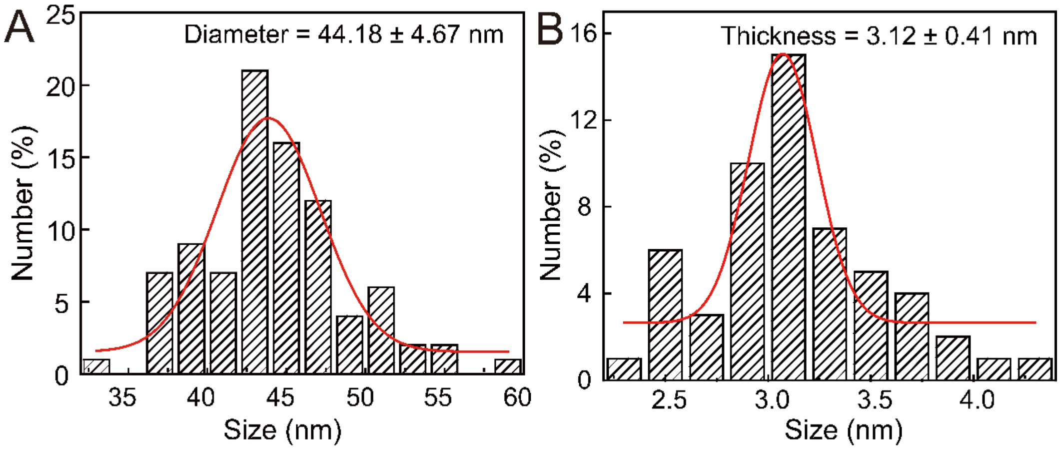

Figure S4. The size distribution of citrate-stabilized AuNPs (A) and the thickness of MIP-PDA shell (B).

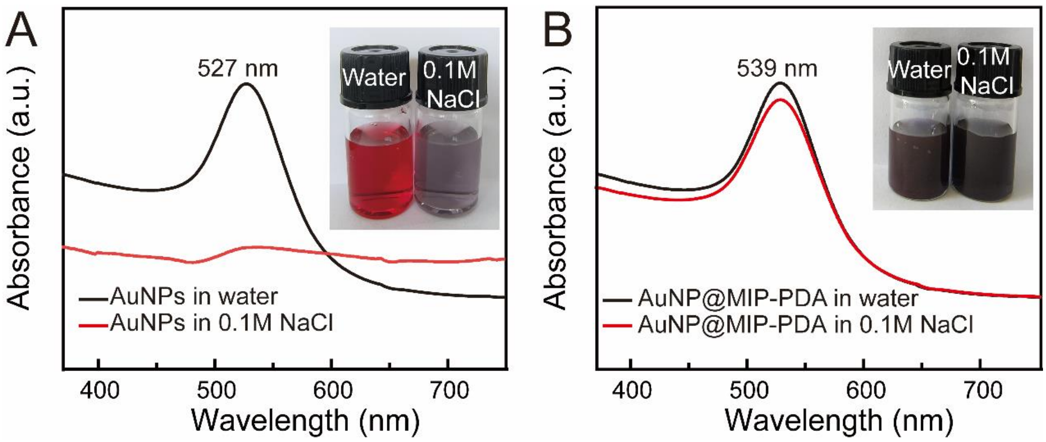

Figure S5. UV–vis spectra of (A) AuNPs and (B) AuNP@MIP-PDA dispersed in water and 0.1 mol/L NaCl. Insets are photographs of different dispersions.

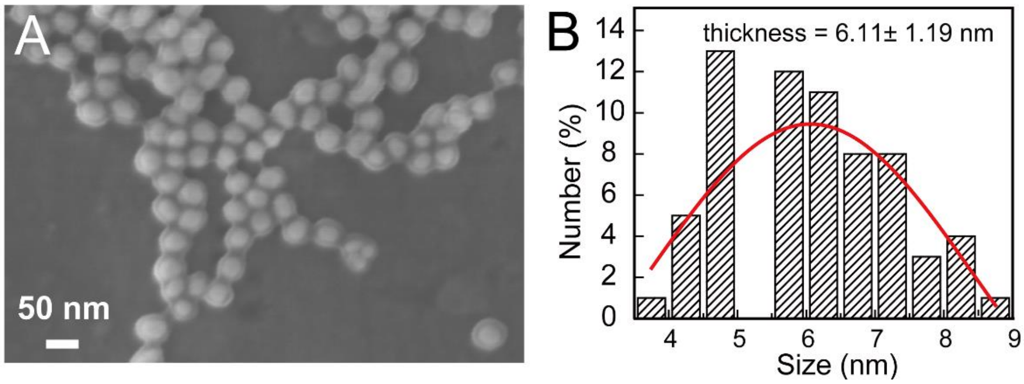

Figure S6. (A) SEM image of AuNP@PDA-MIP fabricated after coating AuNPs with 0.1 mg/mL DA for 40 min. (B) The size distribution of PDA-MIP shell thickness.

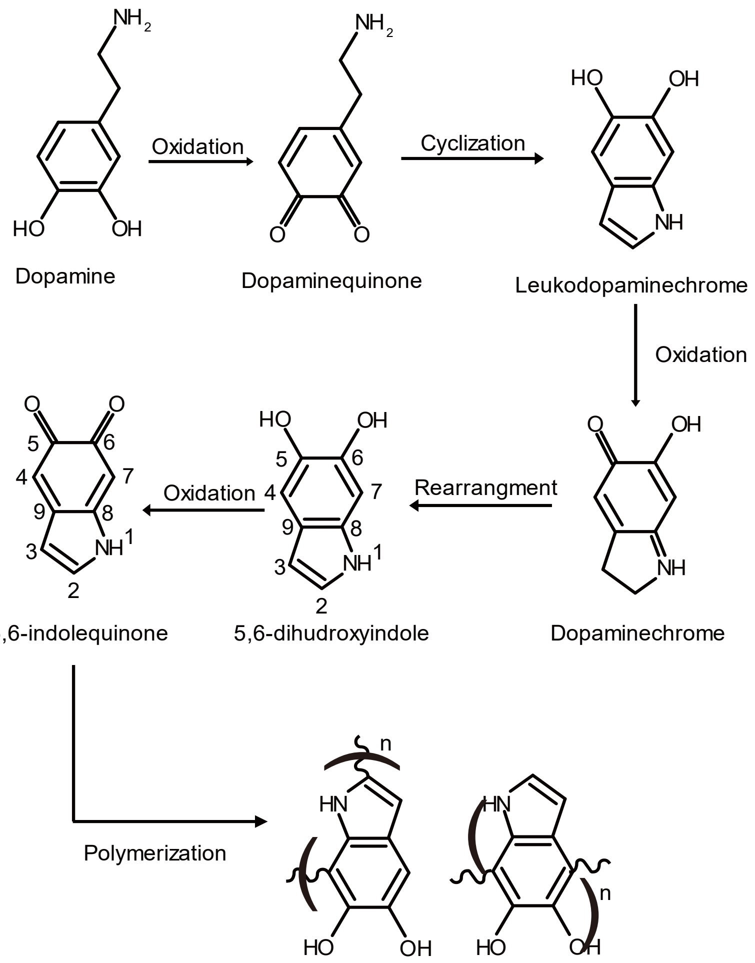

Figure S7. The self-polymerization process of DA in aqueous solution.

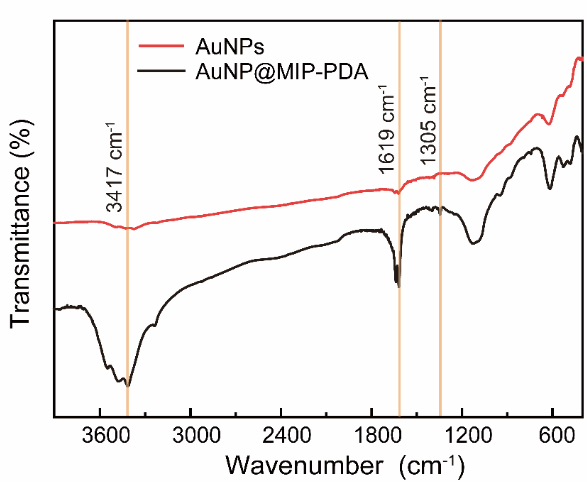

Figure S8. FT-IR spectra of AuNPs and AuNP@MIP-PDA.

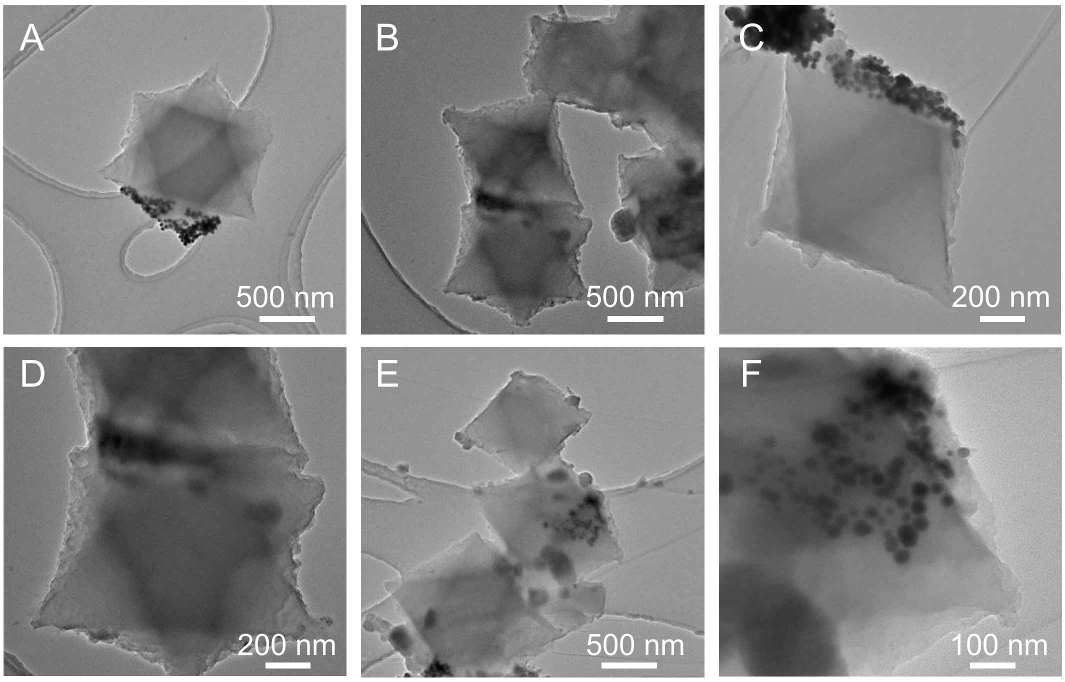

Figure S9. (A-F) TEM images from different views of AuNP@MIP-PDA@MIL-101(Fe) fabricated with 9 mL of AuNP@MIP-PDA in the absence of acetic acid.

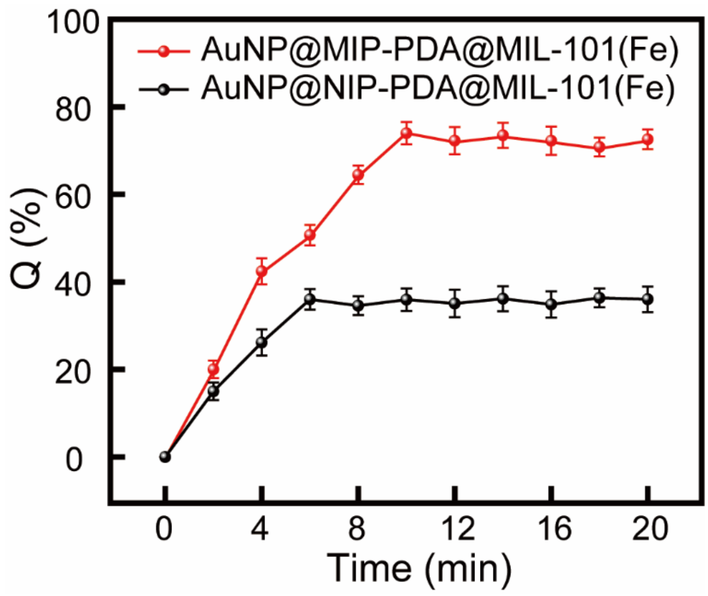

Figure S10. The plots of adsorption efficiency *vs.* time for AuNP@MIP-PDA@MIL-101(Fe) and AuNP@NIP-PDA@MIL-101(Fe) after adsorption of 2.0×10^{-8} mol/L 17β-E2, respectively. Integration time: 40 s; laser power: 40 mW.

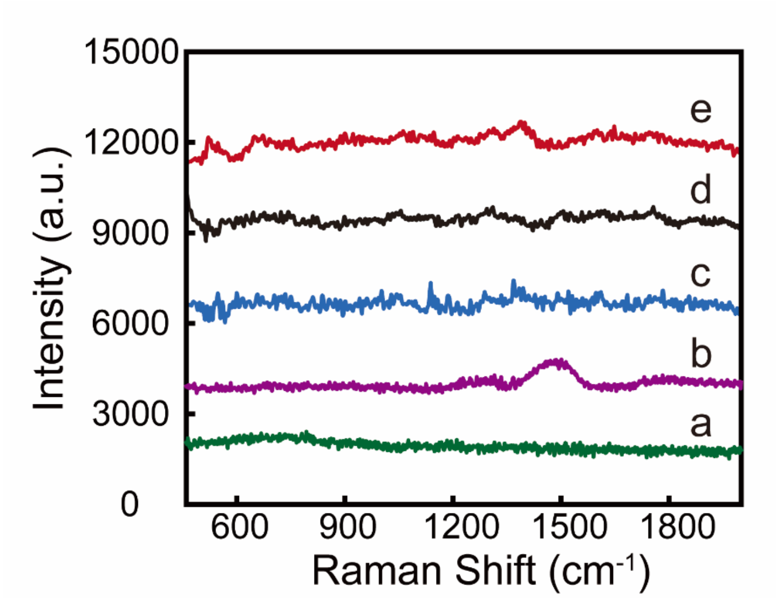

Figure S11. Normal Raman spectra of (a) AuNPs, (b) AuNP@MIP-PDA, (c) MIL-101(Fe), (d) AuNP@NIP-PDA@MIL-101(Fe) and (e) AuNP@MIP-PDA@MIL-101(Fe). Integration time: 40 s; laser power: 40 mW.

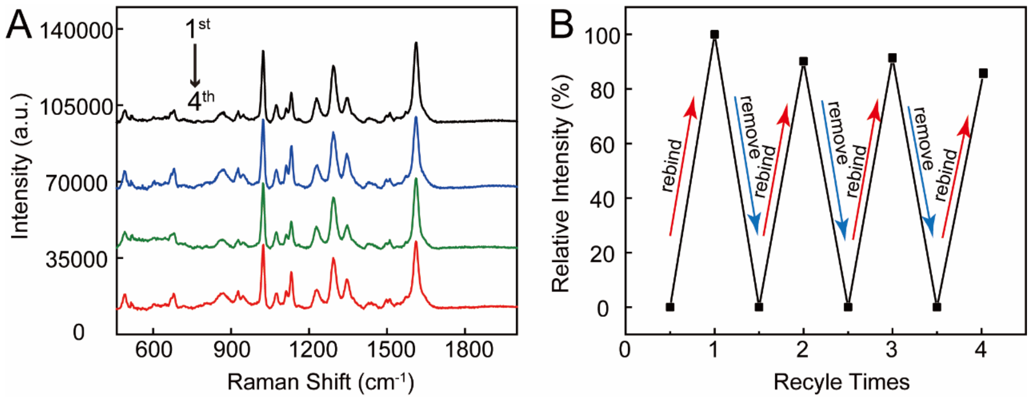

Figure S12. (A) SERS spectra of AuNP@MIP-PDA@MIL-101(Fe) upon four cycles of elution and recombination of 1.0×10^{-8} mol/L 17β-E2. (B) The corresponding responses by monitoring SERS intensity of the bands at 1611 cm^{-1}. Integration time: 40 s; laser power: 40 mW.

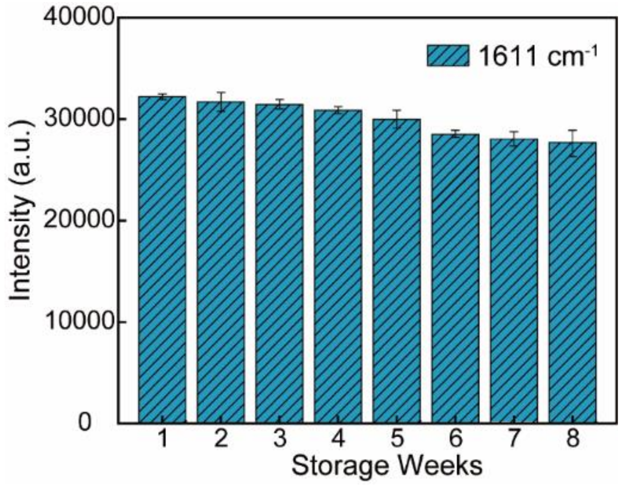

Figure S13. The relationships between SERS intensity at 1611 cm^{-1} and the storage weeks.

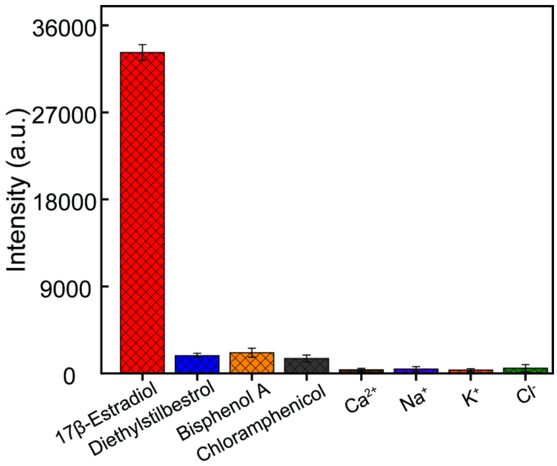

Figure S14. SERS band intensity of 1611 cm^{-1} for 1.0×10^{-8} mol/L 17β-E2, diethylstilbestrol, bisphenol A, chloramphenicol, Ca^{2+}, Na^{+}, K^{+} and Cl^{-}, respectively.

Table S1. Raman and SERS spectral data of 17β-E2 incubated on AuNP@MIP-PDA@MIL-101(Fe).[1-3]

Raman	SERS	Assignments
-	868	ν(C-C)
1002	1024	δ(C-C)
-	1074	ν(C-O)
1125	1131	δ(C-H) ring; γ(C-H)
1143	-	δ(CH_3)
1176	-	γ(CH_3)
1233	1228	γ(C-H) from methyl; δ(C-H) + δ(-OH) + ν(C-C) from phenol groups
1251	-	ν(C-O); ν(C-C) ring
1300	-	δ(-OH)
1338	-	ν(C-C) from phenyl rings; δ(C-H) + δ(-OH) from phenol groups
1430	1428	δ(CH_3)
1589	-	ν(C-C) ring
1621	1611	ν(C-C) ring

ν: Stretching vibration, δ: in-plane bending vibration, γ: out of plane bending vibration.

S1. Calculation of Enhancement Factor (EF).

The EF value can be estimated using the following equation:

$$EF = \left(\frac{I_{SERS}}{I_{Raman}}\right) \times \left(\frac{N_{Raman}}{N_{SERS}}\right)$$

where I_{SERS} stands for the intensities of the vibrational mode in the SERS spectra and I_{Raman} stands for the normal Raman spectra of solid 17β-E2. N_{SERS} and N_{Raman} are the number of 17β-E2 molecules adsorbed on the AuNP@MIP-PDA@MIL-101(Fe) substrate and bulk molecules illuminated by the laser focus spot under SERS and normal Raman conditions, respectively. I_{SERS} and I_{Raman} can be obtained from the spectra directly while N_{SERS} and N_{Raman} need to be calculated on the basis of the estimation of the corresponding sample area. N_{SERS} and N_{Raman} can be obtained according to the reported method[4-5].

In this work, 3 μL of 1.0 × 10^{-8} mol/L 17β-E2 solution was dropped onto the AuNP@MIP-PDA@MIL-101(Fe) substrate, which left a spot of ca. 2.72 mm in diameter, following the SERS spectra of 17β-E2 were recorded, and the band 1611 cm^{-1} was selected to calculate the EF. Suppose the molecules uniformly dispersed on the substrate and then the density of the molecules on the substrate was assumed to be 1.0 × 10^{-8} mol/L × 3 μL × N_A /(π × 1.36^2 mm^2). The laser spot has a 10μm diameter and the surface area is about 7.9 ×10^{-5} mm^2, so N_{SERS} value is estimated as following:

$N_{SERS} = 1.0 \times 10^{-8}$ mol/L $\times 3 \times 10^{-6}$ L $\times$ N_A $\times (7.9 \times 10^{-5}/5.8)$=2.45×$10^5$

Taking the laser spot diameter (about 10 μm), the penetration depth (about 2 μm), and the molecule weight of solid 17β-E2 (1.17 g/cm^3) into account, N_{Raman} had a value of 4.06×10^{11} (N_{Raman}=1.17 g cm^{-3} × π × 25 $μm^2$ × 2 μm × N_A / 272.382 g mol^{-1} =4.06×10^{11}) in the detected solid sample area.

All the spectra were normalized for laser power and acquisition time. Raman intensity I_{SERS} is 36052 cnts at the band of 1611 cm^{-1}, and the I_{Raman} is measured to be 1400 cnts. Therefore,

$EF_{17β\text{-}E2}$= (I_{SERS} / I_{Raman}) × (N_{Raman} / N_{SERS}) = (36052 cnts / 1400 cnts) × (4.06×10^{11} mol / 2.45×10^5 mol) = 4.26 × 10^7.

The EF at the band at 1611 cm^{-1} of 17β-E2 can be calculated to be 4.26×10^7 for the AuNP@MIP-PDA@MIL-101(Fe) substrate (**Figure S15**).

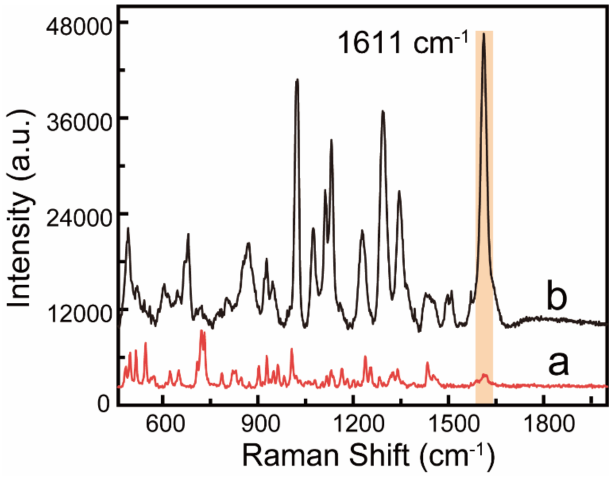

Figure S15. (a) Normal Raman spectrum of solid 17β-E2; (b) SERS spectra of AuNP@MIP-PDA@MIL-101(Fe) substrate after adsorption of 17β-E2 with the concentration of 1.0×10^{-8} mol/L, respectively.

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5. Xia, Z.; Li, D.; Deng, W., Identification and Detection of Volatile Aldehydes as Lung Cancer Biomarkers by Vapor Generation Combined with Paper-Based Thin-Film Microextraction. *Anal Chem* **2021,** *93* (11), 4924-4931.