## SUPPORTING INFORMATION

for

# SERS of molecules that do not adsorb on Ag surfaces: a metal-organic framework-based functionalization strategy

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#### **Characterization of ZIF-8/FON**

X-ray Diffraction (XRD)



Figure S - 1. Grazing-incidence XRD pattern of ZIF-8 film grown on Ag FON and simulated pXRD pattern of bulk ZIF-8. The coincidence of the film peaks with the reflections in the simulated pattern confirms that the single phase is ZIF-8.

SEM



Figure S - 2. SEM of as made ZIF-8 film on FON (a) and the sample after exposure to pyridine (b) and benzene (c). No cracking was observed beyond what was obviously induced by the electron beam.

#### **SERS** Apparatus

A schematic diagram for the Raman spectrometer is shown in Figure S-3. Spectra were recorded using 785 nm excitation from a Ti:sapphire laser (Spectra Physics model 3900) coupled to a solid state 532 nm pump laser (Millennia, Spectra Physics). A 785 nm bandpass filter and neutral density filters were used to reject stray pump laser light and attenuate the output power at

785 nm to ~1 mW. The excitation laser was focused to a ~1 mm spot on the sample, held in a flow cell. Scattered light was collected in 180° backscattering geometry and passed through a 785 nm notch filter before entering the spectrometer The collected signal was analyzed using an ACTON 2300i Czerny–Turner monochromater with a 600 grooves/mm grating, and captured with a LN<sub>2</sub>-cooled back-illuminated CCD (Spec-10 400B). The setup's spectral resolution was 6 cm<sup>-1</sup>. Integration time for all SERS spectra was 10 s. During sensing experiments using continuous dosing of vapors, spectra were acquired every 2 min.



Figure S - 3. Schematic of Raman spectrometer. 785 nm laser light (shown here in green) was focused onto the sample through a series of mirrors and prisms. Raman scattered light was collected in backscattering geometry.

#### Adsorption/Desorption of benzene by SERS

The kinetics of benzene adsorption and desorption in a ZIF-8-coated FON were measured as described in the main text by acquiring a SERS spectrum every two minutes while benzene vapor was dosed to the sample flow cell. Figure S-4 shows the intensity of the 992 cm<sup>-1</sup> ring breathing mode of benzene as the sample is initially under N<sub>2</sub> flow at time = 0. At "on", benzene vapor is introduced, and the peak intensity rises and saturates rapidly, within 6 minutes. At "off" the sample flow cell is purged with N<sub>2</sub> and the benzene signal decays slowly as the benzene desorbs (described in Figure 5B in the main text). In general, vapor adsorption was observed to occur much more rapidly than desorption for all analytes.



Figure S - 4. Peak intensity at 992 cm<sup>-1</sup> as a function of time showing the adsorption of benzene, introduced to a ZIF-8-coated FON at "on". Slow desorption of benzene occurs after the flow cell is purged with  $N_2$  at "off".

#### **Calculation of Benzene Layer Thickness**

In the main text, we describe the dependence of the benzene SERS signal intensity on benzene partial pressure for a bare FON (Figure 4c). We speculate that the appearance of this this signal is due to a layer of liquid benzene that forms of the surface of the FON (shown schematically in Figure S-5). This appears to only form when the FON is in a closed flow cell under constant flow. We do not observe SERS signal when we incubate a bare FON in benzene vapor and subsequently acquire a spectrum. To test if this is a reasonable hypothesis, we calculated what thickness of liquid benzene would be required to account for the observed SERS signal from saturated benzene flow over a bare FON. We have calculated this thickness by comparing the signal intensity at 992 cm<sup>-1</sup> observed with saturated benzene (BZ) vapor ( $p/p_0 = 1$  in Figure 4c) to the signal intensity at 1584 cm<sup>-1</sup> observed from monolayer of benzenethiol (BT) adsorbed on an identical FON surface. In each case the intensity was normalized by the number of scatterers and the normal Raman cross section of the given mode (at 785 nm excitation). Because the same apparatus was used (identical spot size and collection efficiency) we can compare the two signals by:

$$\frac{I(BZ)}{N_{BZ}\sigma_{BZ}} = \frac{I(BT)}{N_{BT}\sigma_{BT}}$$
(S.1)

where I where is the signal intensity for the measured mode (992 cm<sup>-1</sup> for BZ and 1584 cm<sup>-1</sup> for BT), N is the number of scatterers and  $\sigma$  is the normal Raman cross section of the chosen mode. The normal Raman cross sections have been reported for BZ at 992 cm<sup>-1</sup> ( $\sigma_{BZ} = 3.4 \times 10^{-29} \text{ cm}^2$ ) and for BT at 1584 cm<sup>-1</sup> ( $\sigma_{BT} = 8.9 \times 10^{-30} \text{ cm}^2$ ) using 785 nm excitation.<sup>1</sup> For the BT monolayer,  $N_{BZ}$  depends on the spot size, s, and the surface density of molecules,  $\rho_{surf}$  (6.8 x  $10^{14} \text{ cm}^{-2}$ ) by:

$$N_{BT} = s\rho_{surf} \tag{S.2}$$

For the benzene case, we assumed a liquid layer of uniform thickness, such that the number of scatterers is determined by:

 $N_{BZ} = \frac{st\rho_{liq}N_A}{M_w} \square$  (S.3) where *s* is the the spot size, *t* is the film thickness,  $\rho_{liq}$  is the density of liquid benzene (0.877 g·cm<sup>-3</sup>),  $N_A$  is Avogadro's number (6.022 x 10<sup>23</sup> mol<sup>-1</sup>), and  $M_W$  is the molecular weight of benzene (78.11 g·mol<sup>-1</sup>). Substituting equations S.2 and S.3 into S.1 yields:

$$\frac{I(BZ)M_W}{st\rho_{liq}N_A\sigma_{BZ}} = \frac{I(BT)}{s\rho_{surf}\sigma_{BT}}$$
(S.4)

Because <sup>*s*</sup> appears in the denominator on both sides of Eqn S.4, the spot size can be eliminated from the calculation. Substituting in the measured intensities of I(BZ) = 1044 counts·mW<sup>-1</sup>·s<sup>-1</sup> for the bare FON with saturated benzene vapor (p/p<sub>o</sub> = 1) and I(BT) = 149 counts·mW<sup>-1</sup>·s<sup>-1</sup> for the bare FON and BT monolayer as well as the other known values, we calculate t = 1.8 nm.



Figure S - 5. Schematic diagram of proposed 1.8 nm liquid benzene layer (red) forming on the surface of Ag FON.

### Quartz Crystal Microbalance (QCM) Gravimetry

QCM was used to compare the amount of vapor absorbed by ZIF-8 films of two different thicknesses. These experiments were performed using a Maxtek RQCM (Inficon). Gold-coated quartz crystals (25 MHz, Inficon) were coated with ZIF-8 using the same procedure used for Ag FONs. On one crystal, a thin film of ZIF-8 was grown as described in the main text. On a separate crystal, the ZIF-8 procedure was repeated a total of five times (cycles) to grow a film five times as thick. Figure S - 6 shows the amount of mass gained by the one cycle (thin) and five cycle (thick) ZIF-8 films and the non-functionalized crystal upon exposure to 80% pyridine vapor. The non-functionalized crystal shows a small mass increase of 50 ng/cm<sup>2</sup>. This corresponds very well to the mass expected for a monolayer of chemisorbed pyridine molecules

oriented perpendicular to the substrate (53 ng/cm<sup>2</sup>). The thin ZIF-8 film gains a significantly larger amount of mass (4.1  $\mu$ g/cm<sup>2</sup>) due to its ability to adsorb vapor. The thick crystal gains 15  $\mu$ g/cm<sup>2</sup>, or 3.7 times as much mass as the thin crystal, indicating that the vapor sorption scales with film thickness. We believe that this confirms our hypothesis that sorption occurs throughout the thickness of the film, consistent with adsorption at grain boundaries or a similar site that propagates perpendicular to the substrate. If adsorption only occurred on the top surface of the ZIF-8 film, then the thick and thin films would show nominally the same mass increase which should also be similar to the "bare QCM" sample.



Figure S - 6. QCM data showing the mass increase upon exposing the samples depicted schematically on the right to 80% pyridine vapor: blue) bare Au-coated QCM crystal, red) one cycle ZIF-8 film, black) five cycle ZIF-8 film. At time = 0 the samples are under  $N_2$  flow. Pyridine vapor is introduced at "on" and purged with  $N_2$  at "off".

Reference:

<sup>1.</sup> Aggarwal, R. L., Farrar, L. W., Diebold, E. D., Polla, D. L., *J. Raman Spectrosc.* **2009**, *40*, 1331-1333.