

## Supplementary Information: Synthesis of a Surface Mounted Metal-Organic Framework on Gold Using a Au-Carbene Self-Assembled Monolayer Linkage

Esther Frederick,<sup>†,a</sup> Travis W. Shaw,<sup>a</sup> Matthew G. Frith<sup>††,a</sup> and Steven L. Bernasek<sup>\*,a,b</sup>

<sup>a</sup> Department of Chemistry, Princeton University, Princeton, NJ, 08544, UA

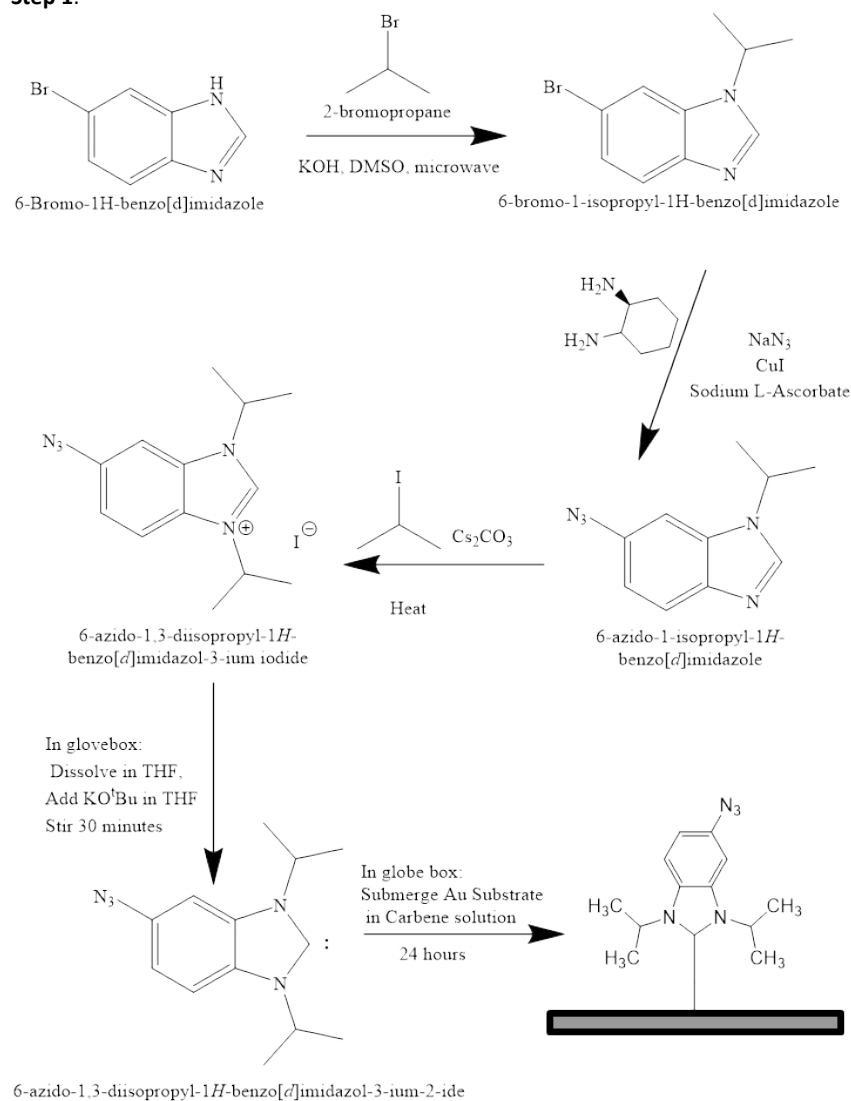
<sup>b</sup> Science Division, Yale-NUS College, 138527, Singapore

<sup>†</sup> Present Address: Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, 92093, United States

<sup>††</sup> Present Address: X-Ray Science Division, Argonne National Laboratory, Argonne, IL, 60439, USA

### SI 1: Experimental Methods – Carbene Synthesis

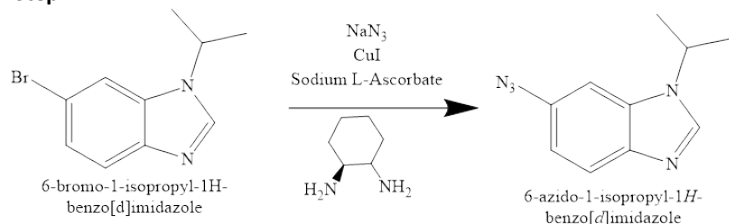
#### Step 1:



**Figure SI 1.** Synthetic scheme for 6-bromo-1-isopropyl-1H-benzo[d]imidazole

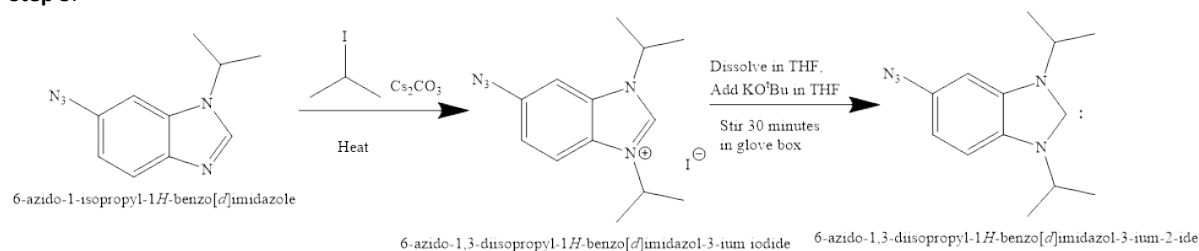
was successfully synthesized by microwave reaction of a 1:1:1.5 ratio of 6-Bromo-1H-benzo[d]imidazole, 2-bromopropane and KOH as adapted from a 1-isopropylbenzimidazole reaction by Lopyrev et al.<sup>1</sup> <sup>1</sup>H NMR matched calculated expected values.

### Step 2:



**Figure SI 2.** Synthetic scheme for 6-azido-1-isopropyl-1H-benzo[d]imidazole. 6-bromo-1-isopropyl-1H-benzo[d]imidazole was successfully converted to 6-azido-1-isopropyl-1H-benzo[d]imidazole using a 1:0.12:2:0.2 ratio of 6-Bromo-1H-benzo[d]imidazole, CuI, NaN<sub>3</sub>, trans-N,N'-dimehyl-1,2-cyclohexyldiamine and sodium L-ascorbate in a 7:3 solution of EtOH:H<sub>2</sub>O as adapted from literature.<sup>2</sup> The product was purified using distillation and column chromatography. The chemical structure of the product was verified with <sup>1</sup>H NMR in CHCl<sub>3</sub>, with trace impurities below baseline observed.

### Step 3:

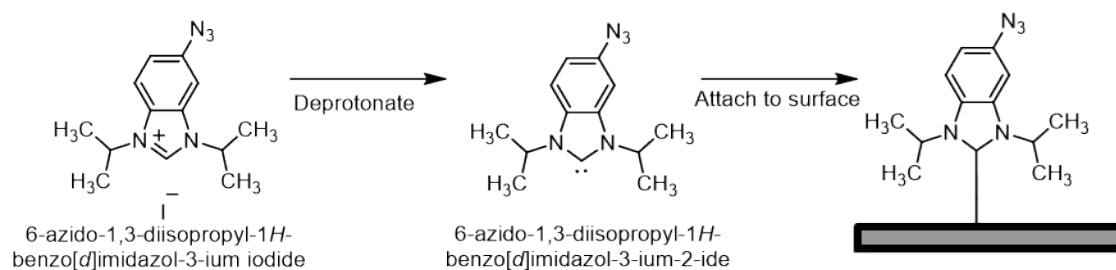


**Figure SI 3.** Synthetic scheme for imidazolium salt and corresponding carbene. 6-azido-1,3-isopropyl-1H-benzo[d]imidazole imidazole was successfully converted to 6-azido-1,3-isopropyl-1H-benzo[d]imidazole-3-ium iodide salt by refluxing a 1:25:2:1 ratio of 6-azido-1H-benzo[d]imidazole, 2-iodopropane and Cs<sub>2</sub>CO<sub>3</sub> as adapted from Crudden et al.<sup>3</sup> <sup>1</sup>H NMR was used to verify the product. Imidazolium salt was introduced into the glovebox and deprotonated using potassium t-butoxide according to published methods<sup>3</sup> to form the carbene solution used for surface functionalization. The surface characterization conducted post-functionalization indicated the successful formation of the carbene.

## SI 2: Experimental Methods: Surface Functionalization and SurMOF formation.

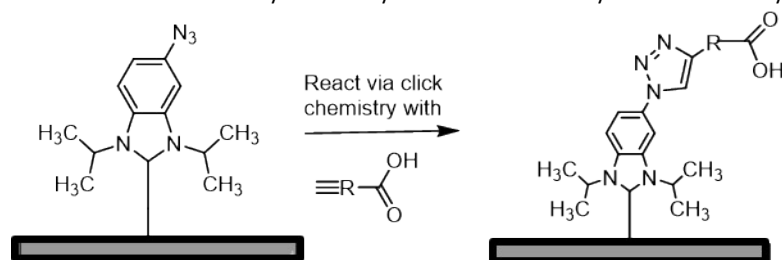
**Preparation of Gold Substrate:** Au substrates were prepared by thermal deposition (Edwards 306A Thermal Evaporator) of a 30 nm Ti adhesion layer, followed by 200 nm Au on a clean Si(100) wafer (p-type, 0.001-0.005 ohm•cm, University Wafer).

**SAM Synthesis:** The carbene-Au functionalization procedure developed by Crudden<sup>3</sup> was adapted to form azide terminated SAMs that allowed for modification of the surface functionalization via click chemistry.



**Figure SI 4.** Schematic of carbene SAM functionalization on Au. A clean, freshly prepared gold sample in a glass sample jar was placed in the glovebox. The carbene solution was diluted to 1 mM in toluene and ~8 mL solution was added via pipette to completely submerge the substrate. The container was closed with a glass stopper to avoid solution evaporation. After 12 hours, the first solution was removed via pipette (taking care not to touch the surface) and fresh solution was added and allowed to sit for another 12 hours. Samples were cleaned with THF using a 15 mL rinse followed by 15 minutes of sonication. Surfaces were characterized via XPS and ellipsometry to confirm successful deposition and surface uniformity.

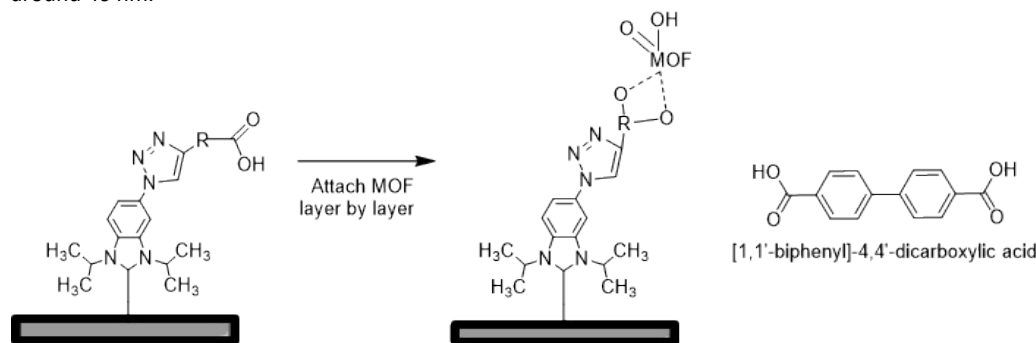
**Modification of the SAM surface chemistry to form carboxylic acid terminated SAM:** The azide capped SAM was functionalized with carboxylic acid alkynes via click chemistry to form a carboxylic acid terminated substrate.



**Figure SI 5.** Schematic of SAM post-modification via click chemistry.

All aqueous solutions were prepared using Millipore (MQ) H<sub>2</sub>O (18.2 MΩ·cm). A 3 mL aliquot of Millipore H<sub>2</sub>O was added to 2 mL of a 0.01 M undecynoic acid (Sigma-Aldrich, Slovakia, Germany, 95%) DMSO solution. To this solution, 0.2 mL of a 0.1 M aqueous CuSO<sub>4</sub> (Sigma-Aldrich, Japan, ≥ 99%) and 0.4 mL of 1 M aqueous sodium ascorbate (Sigma-Aldrich, China, ≥ 98%) were added. The resulting solution was stirred for 3 minutes and then poured over the carbene-Au substrates in a glass bottle and covered. Samples sat for ~24 hours and were then cleaned using a 15 mL rinse followed by 15 minutes of sonication in THF twice and MQ H<sub>2</sub>O once.

**Building SurMOF:** The carboxylic acid terminated SAMs were further functionalized by layer-by-layer deposition of Cu<sup>2+</sup> metal centers and organic strut ligands using a procedure adapted from Liu et al.<sup>3</sup> Substrates were sequentially dipped in 1 mM ethanol solutions, the first containing 1 mM Cu(CH<sub>3</sub>COO)<sub>2</sub> (Sigma-Aldrich, Germany, ≥ 99%) and the second containing an organic ligand, in this case [1,1'-biphenyl]-4,4'-dicarboxylic acid (bpdc) Sigma-Aldrich, China, ≥ 97%). The substrates were dipped in the first solution for 15 minutes and then dipped in the second solution for 30 minutes with a 2 minute ethanol dip to rinse in between each functionalizing dip. This procedure was repeated 23 times to ensure enough coverage for successful SurMOF formation (Figure SI 8). Characterization measurements were performed using XPS, ellipsometry and XRD. Capping with noble metals was not attempted but can be readily attained by attaching a linker with the appropriate functional group for the desired metal to the MOF. Based upon the 23 cycles, the thickness of the combined SAM and surMOF was estimated to be around 40 nm.



**Figure SI 6.** Schematic of SurMOF functionalization and bpdc ligand used in SurMOF.

### SI 3: Experimental Methods: Surface and SurMOF Characterization

**AFM:** Measurements were obtained in ambient conditions using a Veeco Dimension Nanoman instrument. The instrument was operated in tapping mode using Bruker Model:RTESP Si tips with resonant frequencies in the 323–380 kHz range. Images were processed using the Gwyddion software package.<sup>6</sup> Data was median height matched, scar corrected and the lowest height/phase point was set to 0. When appropriate, the color gradient was chosen to make differences in surface features more readily observable.

**XPS:** Measurements were performed using an Mg K $\alpha$  X-ray source (1253.6 eV) and an electron spectrometer (VG ESCALAB MkII) operated in constant analyzer energy mode using pass energies of 100 and 20 eV for survey and high-resolution scans respectively. Data was analyzed using the commercially available CasaXPS software. A linear baseline was used for s peaks (O

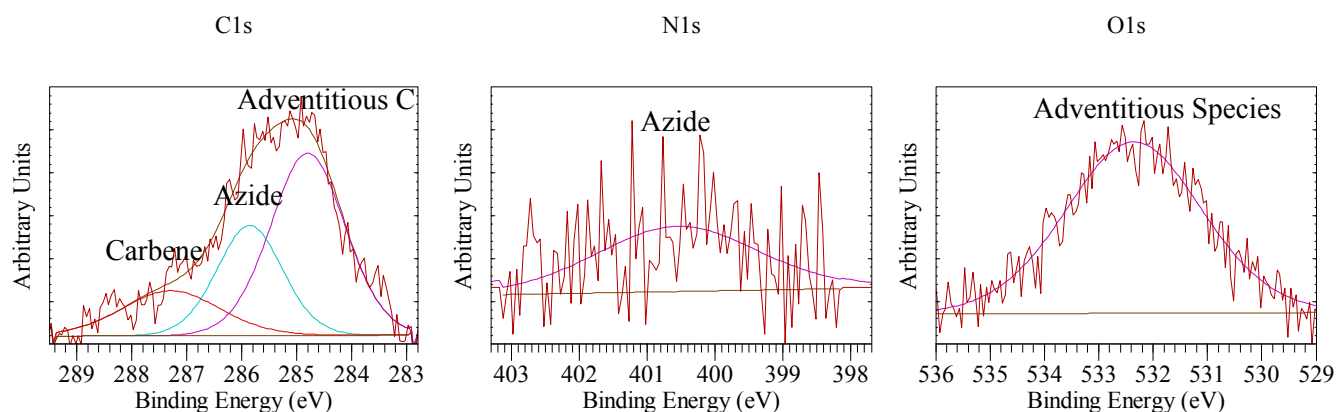
1s, C 1s), while a Shirley baseline was used for all p peaks (P 2P, S 2P, Si 2P). All peaks were calibrated to adventitious carbon at 284.8 eV and fit using a Gaussian-Lorentzian (30). Au 4f doublet peaks were fit using a Shirley baseline, integrated area  $4f^{7/2}:4f_{5/2} = 4:3$  and  $\Delta = 3.67$  eV. Cu 2p doublet peaks were fit using integrated area  $2p^{3/2}:2p^{1/2} = 2:1$  and  $\Delta = 19.9$  eV.

**Contact angle goniometry:** Data was collected at ambient conditions. A drop of Millipore water ( $\sim 2 \mu\text{L}$ ) was placed on the sample surface to form a sessile drop from which the contact angle was measured by a Theta Optical Tensiometer (KSV Instruments, Finland).

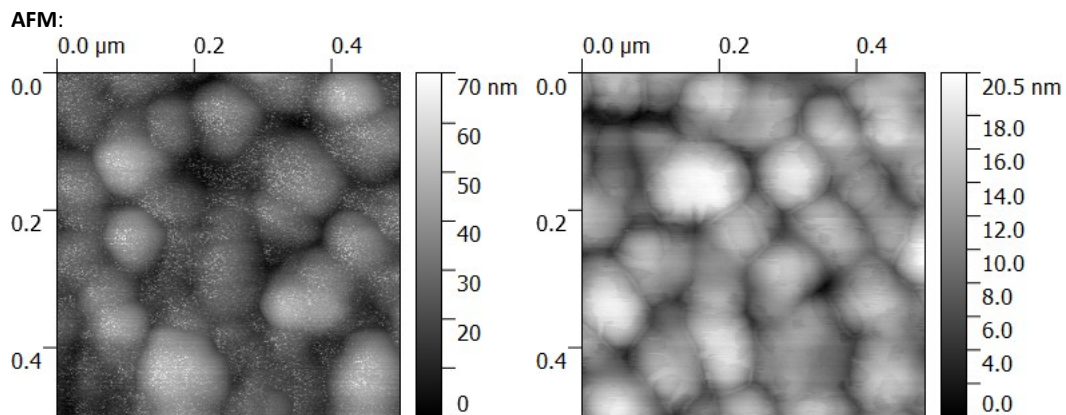
**Ellipsometry:** Measurements were made with an LSE Stokes Ellipsometer (Gaertner Scientific Corp., USA) using a helium-neon laser (633 nm) source at a fixed incident angle of  $70^\circ$ . The refractive index of silicon and organic layer was taken to be 3.85 and 1.5 respectively. A number of points across the sample were measured to assure uniformity.

**Grazing incidence XRD:** Measurements were made using a Bruker D8 Discover X-Ray Diffractometer equipped with Soller slits<sup>5</sup> and a Cu K $\alpha$  radiation source. The x-rays were incident on the surface at  $0.5^\circ$ , with a scan rate of 0.2/min from 2 to 40  $2\theta$  and collected overnight ( $\sim 16$  hours).

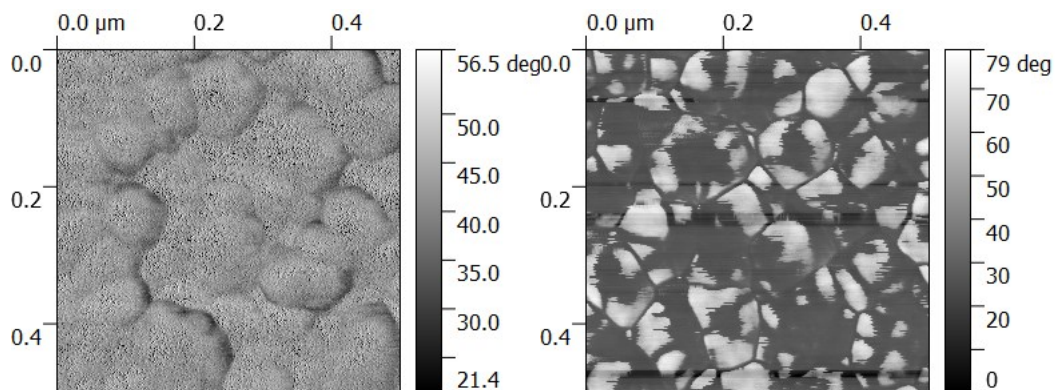
## SI 4: Experimental Data



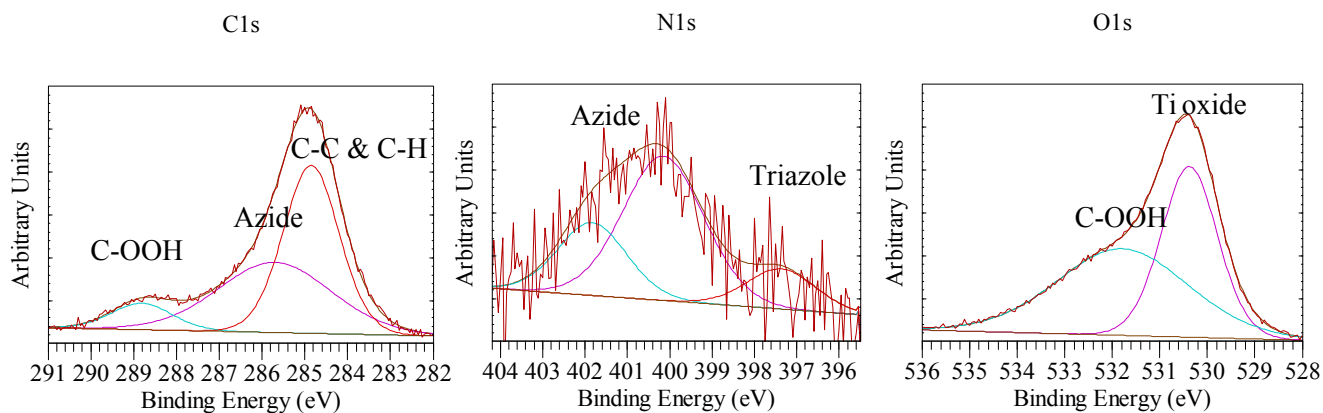
**Figure SI 7.** XPS spectra of carbene linked SAM on Au.



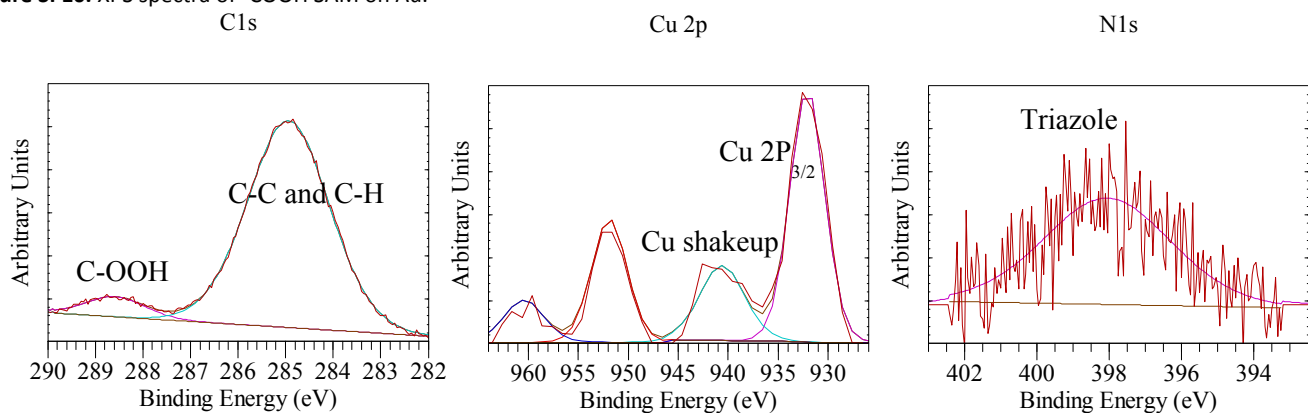
**Figure SI 8.** 500 nm AFM height images of clean Au (left) and Au with  $-\text{COOH}$  terminated SAM (right). Height images taken of bare substrate and after  $-\text{COOH}$  SAM surface modification both displayed round islands of 20-25 nm presumed to be island areas characteristic of the Au sample. However, the functionalized Au substrate had a RMS of 3 nm as opposed to the RMS of 10 nm for the bare substrate. The RMS decrease indicated greater uniformity attributed to SAM functionalization.



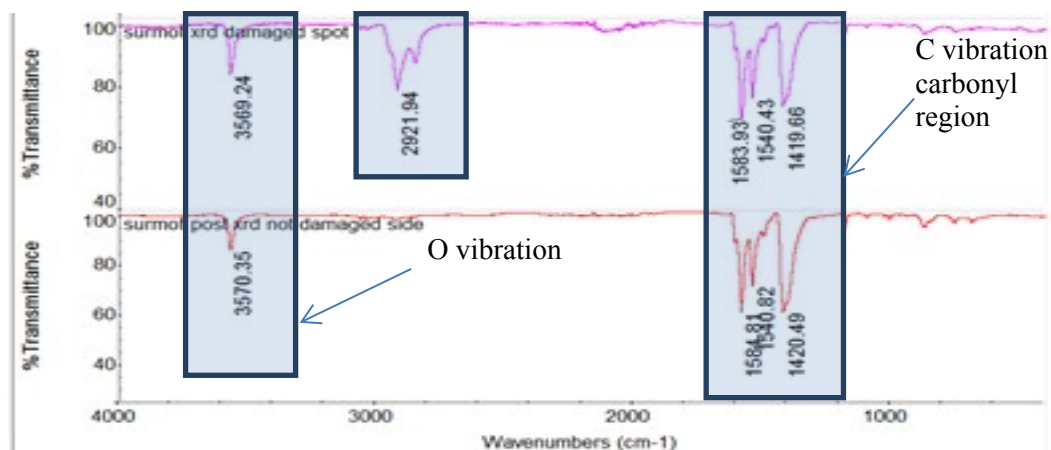
**Figure SI 9.** 500 nm AFM phase images of clean Au (left) and Au with -COOH terminated SAM (right). Phase images after surface functionalization displayed a visible change, which was attributed to areas of different chemical composition due to surface functionalization, with an increase of RMS to 16 from a RMS of 5 on the bare substrate indicating a greater variation in chemical composition across the surface.



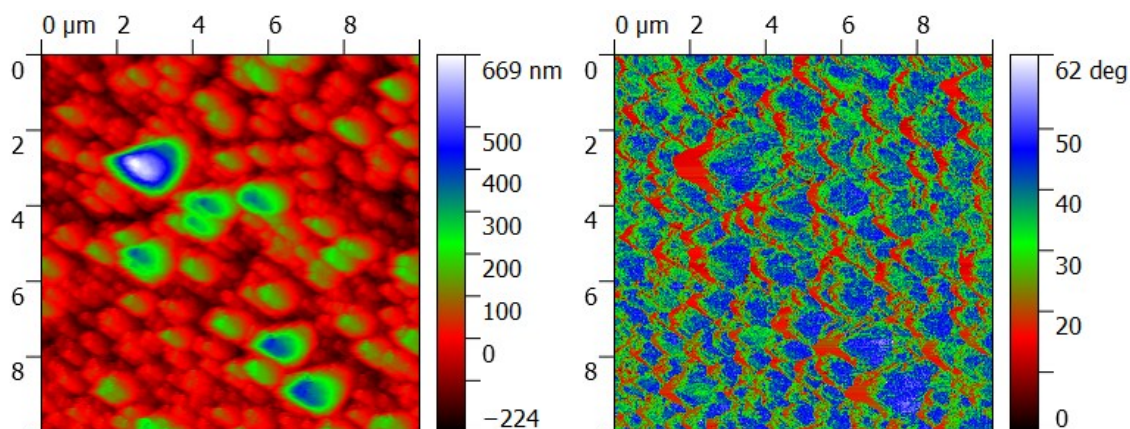
**Figure SI 10.** XPS spectra of -COOH SAM on Au.



**Figure SI 11.** XPS spectra of surMOF on Au.



**Figure SI 12.** ATR-FTIR spectra of surMOF sample post-XRD. Comparison of XRD exposed region (top) and non-XRD exposed region (bottom) of the same sample display the presence of a new peak at  $2921\text{ cm}^{-1}$  in the XRD exposed areas.



**Figure SI 13.**  $10\text{ }\mu\text{m}$  AFM height, RMS  $112\text{ nm}$  (left) and phase, RMS  $10.18\text{ deg}$  (right) of surMOF sample. Most features in  $10\text{ }\mu\text{m}$  height scans were  $100\text{ nm}$  high by  $\sim 500$  wide. Larger features were attributed to areas of preferential crystallization, likely due to surface/SAM defects. Phase images displayed an irregular core-shell structure. Red areas in the phase image corresponded to lower heights in the height image and were attributed to areas without surMOF. Irregularly shaped blue centers were surrounded by a green shell indicating that the edges of the islands have a different chemistry than the centers.

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