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Electronic Supplementary Information for:

Covalent modification of surfaces with porous metal-organic materials

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Detailed Experimental Procedures

General Considerations

All reagents and chemicals were purchased from commercial vendors and used without further purification. ^{1}H NMR and ^{19}F NMR spectra were recorded on a Bruker AV 400 MHz spectrometer and the obtained data were analyzed using MestReNova NMR processing software. Infrared (IR) spectra were carried out with a Bruker α II instrument affixed with a diffuse reflectance ATR attachment. Elemental analyses were performed on Thermo Fisher Kα X-ray photoelectron spectroscopy instrument (XPS) at the University of Delaware's Surface Analysis Facility. Time of Flight Secondary Ion Mass Spectrometry spectra and images were recorded using an IONTOF TOF SIMS 5 System housed in the Surface Analysis Facility at the University of Delaware. Powder X-ray diffraction patterns were recorded with Bruker D8 X-ray powder diffractometer with a Cu Kα radiation (1.54 nm) housed in the Advanced Materials Characterization Laboratory at the University of Delaware. Atomic Force Microscopy and NanoIR spectroscopy were recorded using an Anasys Nano IR2 instrument housed in the Advanced Materials Characterization Laboratory at the University of Delaware. AFM images were processed and analyzed using Gwyddion software. Scanning electron microscopy images and energy-dispersive X-ray spectra were taken using an SEM/FIB Auriga 60 housed in the Keck Center for Advanced Microscopy & Microanalysis at the University of Delaware. Mass spectra were obtained using an Acquity UPLC H-class/SQD2 single quadrupole instrument with a 2.5 minute LC-MS analysis program, and analyzed with MassLynx software.

Single-crystal X-ray diffraction

X-ray structural analysis for Mg 5-N_3 calixarene cage and Mg 5-OH calixarene cage: Crystals were mounted using viscous oil onto a plastic mesh and cooled to the data collection temperature. Data were collected on a D8 Venture Photon III diffractometer with Cu-Kα radiation (λ = 1.54178 Å) focused with Goebel mirrors. Unit cell parameters were obtained from fast scan data frames, 1º/s ω, of an Ewald hemisphere. The unit-cell dimensions, equivalent reflections and systematic absences in the diffraction data are consistent with Cm and C2/m for Mg 5-OH calixarene cage. No symmetry higher than triclinic was observed in Mg 5-N_3 calixarene cage. Refinement in the centrosymmetric space group options yielded chemically reasonable and computationally stable results of refinement. The data were treated with multi-scan absorption corrections. [1] Structures were solved using intrinsic phasing methods [2] and refined with full-matrix, least-squares procedures on F 2 . [3]

Each polyhedral structure is located at an inversion center. For Mg 5-OH calixarene cage, the compound molecule is also located at a mirror plane perpendicular to the b-axis. The disordered cell contents of highly porous metal-organic polyhedral (MOP) complexes result in diffraction data that are limited in coverage and resolution. As a result, it is common to have multiple restraints and constraints, and high residuals in the structural model. Presumably disordered solvent molecules were treated as diffused contributions with identities assigned to be chemically reasonable based on the synthesis, and electron counts from the Squeeze results. [4] In Mg 5-OH calixarene cage one phenol and two t-butylphenyl moieties were found disordered in two positions with refined site occupancy ration of 68/32, 62/38, and 60/30, respectively. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions with geometrically calculated positions and with U iso equal to 1.2-1.5 U eq of the attached atom. Atomic scattering factors are contained in the SHELXTL program library. [2] The structures have been deposited at the Cambridge Structural Database under the following CCDC depositary numbers: CCDC 2251521 and 2251522.

Synthesis of *p-tert*-butylthiacalix[4]arene (TC4A): To a 1 L round-bottom flask, p-tert-butylphenol (64.5 g, 0.43 mol), elemental sulfur (27.5 g, 0.86 mol), NaOH (8.86 g, 0.215 mol), and tetraethylene gylcol dimethyl ether (19 mL) were added and stirred under a flow of nitrogen. The mixture was heated to 230 °C over 4 h and held at this temperature overnight. The mixture was allowed to cool to room temperature, yielding a dark-brown solid to which toluene (35 mL) and 4 M H_2SO_4 (78 mL) were added. The flask was then sonicated for 30 min, and the solubilized material was transferred to a separatory funnel. The organic phase was collected, and MeOH (400 mL) was added, precipitating the product as a light-brown powder that could be isolated by vacuum filtration. This process was repeated until all of the initially generated solid was dissolved. The collected product was dried at 120 °C for 24 h prior to use. (Yield: 16.6 g, 21.5 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.60 (s, 4H), 7.64 (s, 8H), 1.22 (s, 36H).

Synthesis of *p-tert*-butylsulfonylcalix[4]arene (SC4A): In a 1 L round-bottom flask, TC4A (7 g, 46.7 mmol) and sodium perborate tetrahydrate (14 g, 91.0 mmol) were added to a mixture of chloroform (210 mL) and acetic acid (350 mL). The resultant solution was heated with stirring at 50 °C for 18 h. After the solution cooled to room temperature, H_2O (300 mL) was added, and the solution was transferred to a separatory funnel. The organic layer was collected, and the solvent was removed via rotary evaporation before an excess of Et_2O was added; the precipitated white solid was collected via vacuum filtration. The product was dried at 120 °C for 24 h prior to use. (Yield: 4.55 g, 55.2 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.98 (s, 2H), 1.27 (m, 9H).

Synthesis of $(Mg_4sc4a)_4(\mu_4\text{-}OH)_4(5\text{-}OH\ isophthalic\ acid)_8)$ [Mg 5-OH]: To a 20 mL scintillation vial, 85 mg SC4A, 100mg $MgCl_2\ 6H_2O$, 60.1mg 5-OH isophthalic acid were added and solvated with 8mL of DMF and 4mL of methanol. The resulting solution was heated at 85° C in a dry bath for 24 hours, after which excess diethyl ether was used to precipitate cage material. The powder was washed several times with diethyl ether, then dried under reduced pressure.

Synthesis of $(Mg_4sc4a)_4(\mu_4\text{-}OH)_4(5\text{-}azido\ isophthalic\ acid)_8$ [Mg 5-N_3)]. To a 20 mL scintillation vial, $Co(NO_3)_2{\cdot}6H_2O$ (145 mg, 0.5 mmol), 5-azide isophthalic acid (68.3 mg, 0.33 mmol), and SC4A (85 mg, 0.1 mmol) were added and solvated in DMF (10 mL). The vial was then heated to 100 °C in a dry bath for 24 hours before cooling slowly to room temperature. Diethyl ether was then added to the reaction mixture to precipitate a tan amorphous solid. The material was then solvent exchanged and washed five times with MeOH at 12-hour intervals before being dried under reduced pressure.

Synthesis of $(Co_4sc4a)_4(\mu_4\text{-}OH)_4(5\text{-}propargyl\ isophthalic\ acid)_8$ [Co (5-ppg)]. To a 20 mL scintillation vial, $Co(NO_3)_2{\cdot}6H_2O$ (145 mg, 0.5 mmol), 5-propargyl isophthalic acid (72.7 mg, 0.33 mmol), and SC4A (85 mg, 0.1 mmol) were added and solvated in DMF (10 mL). The vial was then heated to 100 °C in a dry bath for 24 hours before cooling slowly to room temperature. Diethyl ether was then added to the reaction mixture to precipitate a pink-red amorphous solid. The material was then solvent exchanged and washed five times with MeOH at 12-hour intervals before being dried under reduced pressure.[6]

Synthesis of $[Zr_{12}(\mu_3\text{-}O)_4(\mu\text{-}OH)_{12}(Cp)_{12}(5\text{-}azido\ isophthalic\ acid)_6]Cl_4$ [Zr(N_3)]. To a 20 mL scintillation vial, zirconocene dichloride (150 mg, 0.51 mmol) and 5-azido isophthalic acid (50 mg, 0.24 mmol) were added and solvated with 10 mL of dry DMF. To this, H_2O (1 mL) was added, and the solution sonicated until the solution was homogeneous. The vial was heated to 45 °C in a dry bath and kept at temperature for 10 hours, after which was allowed to cool slowly to room temperature. X-ray quality crystals formed as the reaction progressed. Crystalline material was solvent exchanged 3 times with fresh DMF and three times with chloroform, waiting at least 8 hours between each solvent exchange before being dried under reduced pressure. [6]

Synthesis of $[Zr_{12}(\mu_3\text{-}O)_4(\mu\text{-}OH)_{12}(Cp)_{12}(2,5\text{-}dimethyl\ terephthalic\ acid)_6]OTf_4$ [Zr(diMe)OTf].: To a 20mL scintillation vial, 100 mg (0.17mmol) zirconocene tirflate (Cp_2ZrOTf_2) and 50mg (0.25mmol) 2,5-dimethyl terephthalic acid were combined and solvated with 10 mL of dry DMF and 500uL H_2O. The reaction was allowed to heat in a dry bath at 65° C for 8 hours, after which it was allowed to cool slowly to room temperature. Material was isolated from solution by addition of excess diethyl ether followed by centrifugation and three washes with additional diethyl ether before drying under reduced pressure.[8]

Synthesis of HKUST-1: This material was synthesized according to a previously published method.[5]

Synthesis of ppg-NH_2@HKUST-1: To a 20 mL scintillation vial, 50mg HKUST-1 nanoparticles and 250uL propargyl amine were added and solvated with 10mL of methanol. The resulting mixture was heated at 50° C for 12 hours after which the powder was centrifuged, decanted, and washed with methanol three times, and finally dried under reduced pressure.

Synthesis of 11-azido undecane-1-thiol: This material was synthesized according to a previously published method.[7]

Preparation of azide-functionalized gold surface: This material was cleaned and prepared according to a previously published method.[7]

Preparation of bromide-functionalized gold surface: Pieces of cleaned, gold coated silicon wafer were submerged in a solution of 500uL 11-bromoundecan-1-thiol in 20mL of methanol and allowed to react for 24 hours.

Preparation of carboxylate-functionalized gold surface: Pieces of gold coated silicon wafer were submerged in a solution of 50mg (0.22mmol) 11-mercaptoundecanoic acid in 20mL of methanol and allowed to react for 24 hours.

Representative surface click reaction: To a 20 mL scintillation vial, cage or MOF material (50 mg) was added along with $CuSO_4 \cdot 2.5H_2O$ (2 mg) and sodium ascorbate (6 mg) followed by solvation and sonication in DMF (10 mL). The reaction was allowed to heat at 65 °C for 18 hours. Upon cooling to room temperature, the solution was decanted and the surface was washed 5 times with DMF, the final wash being sonicated in DMF for 5 minutes. The surface was then washed with methanol and dried in a stream of N_2.

Surface alkylation reaction: To a 20 mL scintillation vial Mg 5-OH calixarene cage material (50 mg) was added followed by solvation and sonication in DMF (10 mL). The Br-functionalized gold surface was then submerged in cage solution. The reaction was allowed to heat at 65 °C for 18 hours. Upon cooling to room temperature, the solution was decanted and the surface was washed 5 times with DMF, the final wash being sonicated in DMF for 5 minutes. The surface was then washed with methanol and dried in a stream of N_2.

Surface salt reaction: In a 20 mL scintillation vial, a carboxylate modified gold surface was submerged in a 0.1M aqueous solution of Na_2CO_3 for 30 minutes at room temperature. The surface was then removed, briefly submerged in diH_2O, then submerged in a methanol solution of respective Zr-based cationic cage for 30 minutes. The surface was then removed and gently washed with methanol several times, then dried in an N_2 stream.

X-Ray Photoelectron Spectra (XPS)

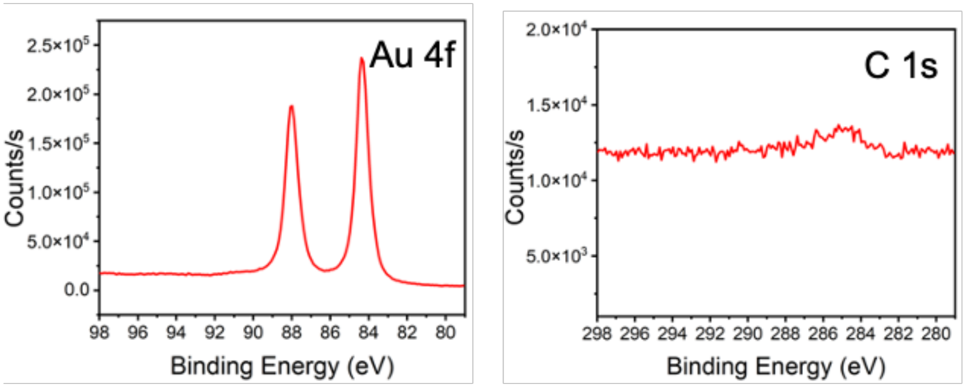

Figure S1. XPS high resolution Au & C spectra for cleaned gold surface.

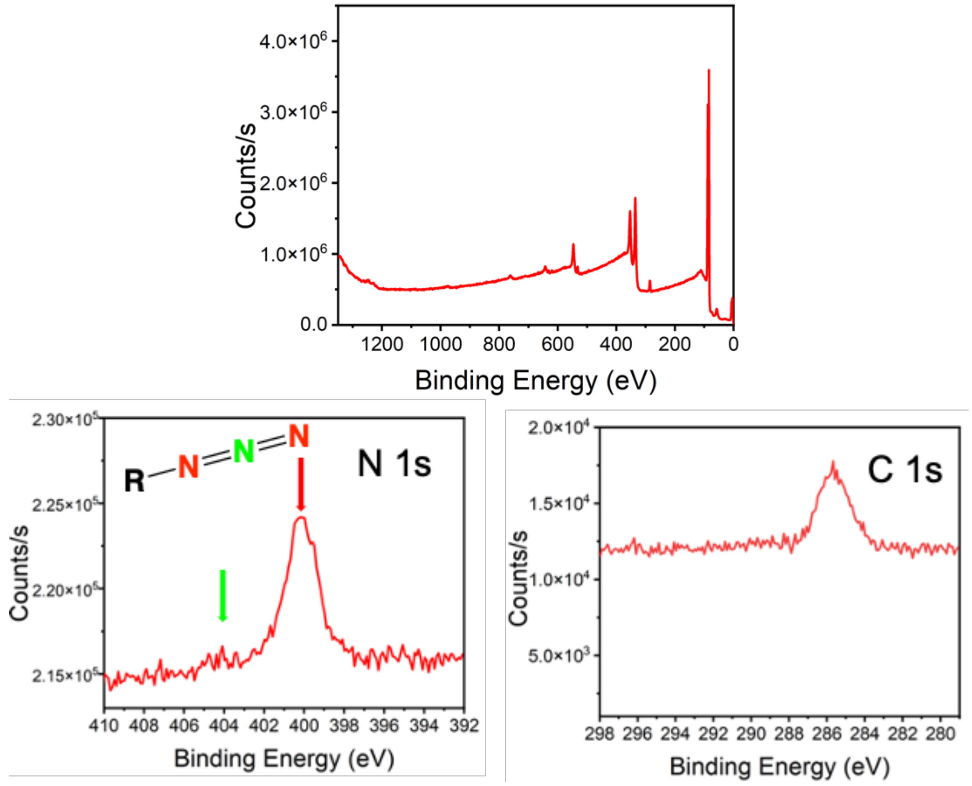

Figure S2. XPS survey spectra and high resolution C & N spectra for azide modified gold surface.

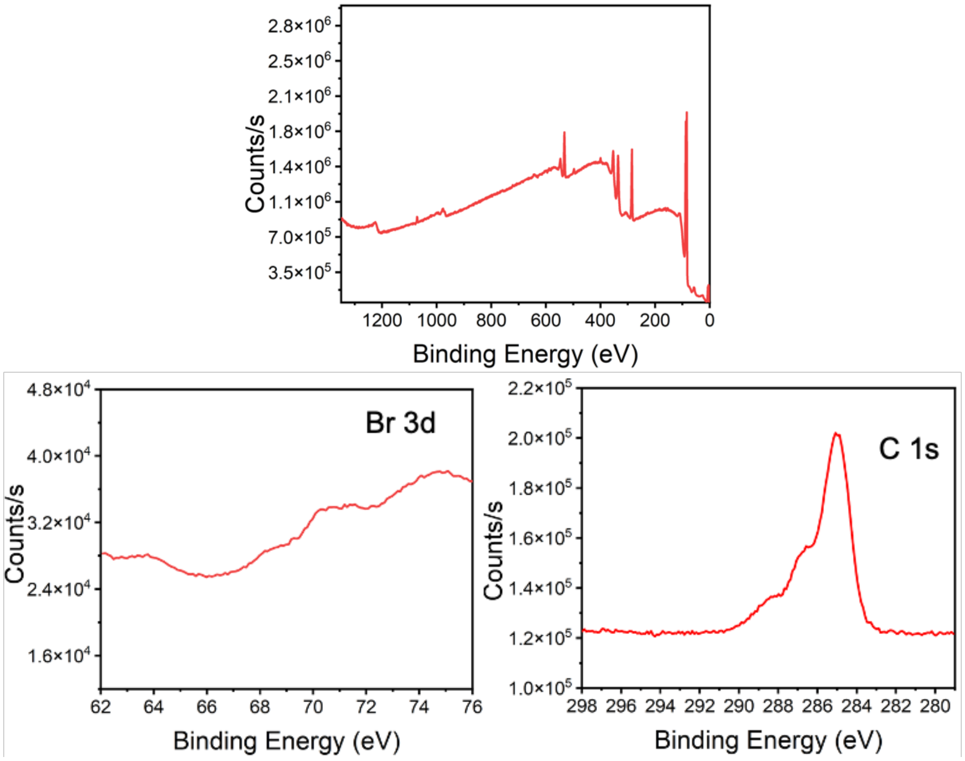

Figure S3. XPS survey spectra and high resolution C & Br spectra for bromide modified gold surface.

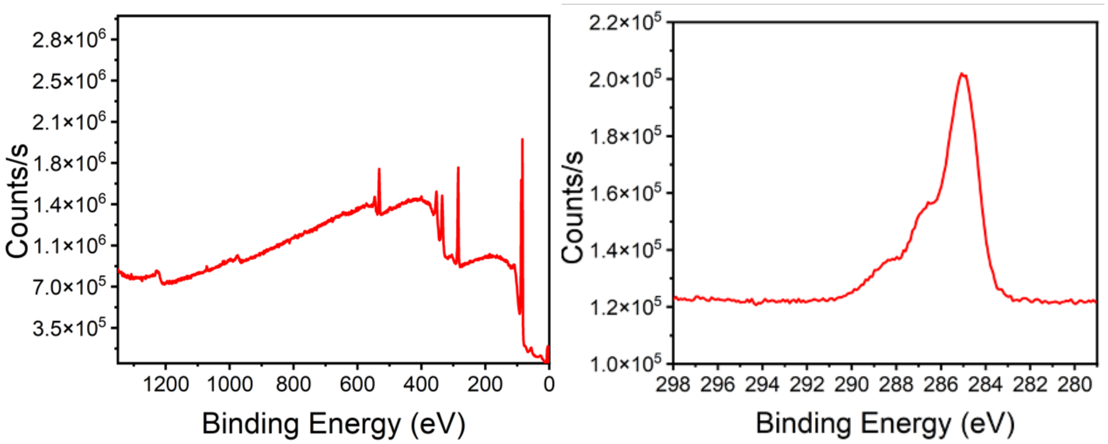

Figure S4. XPS survey spectra and high resolution C spectra for carboxylate modified gold surface.

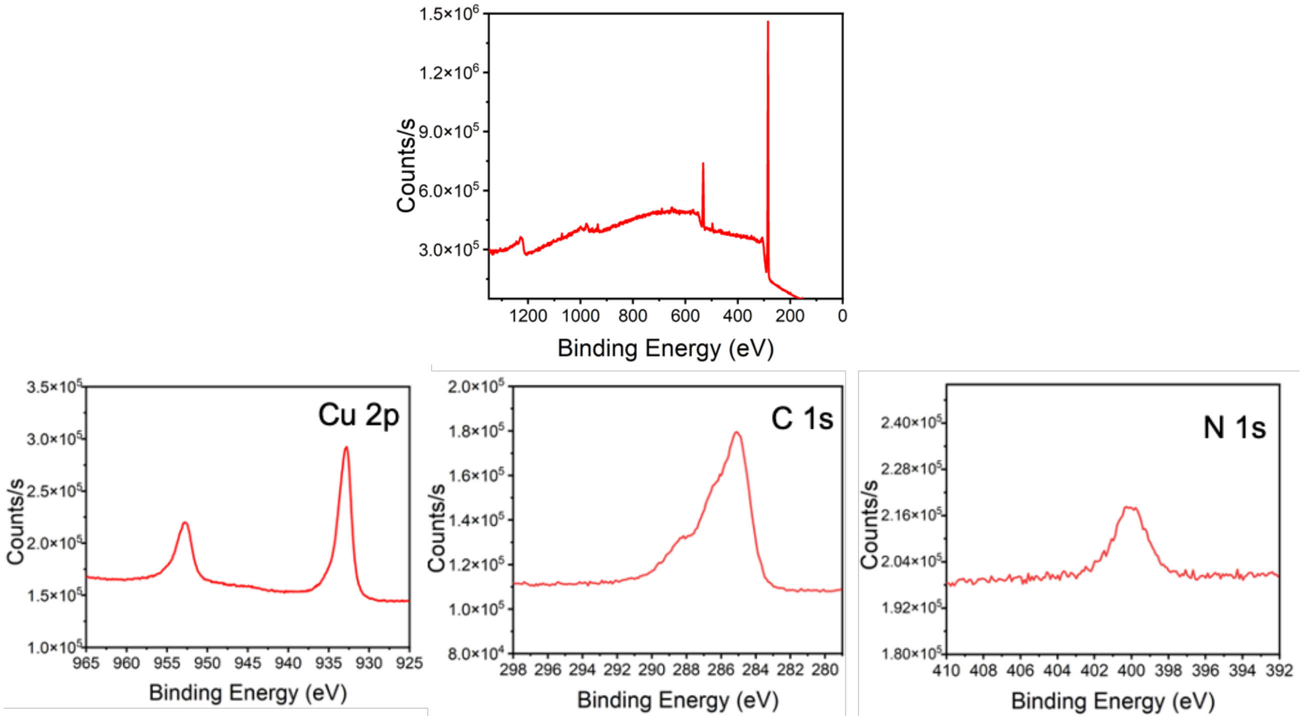

Figure S5. XPS survey spectra and high resolution C, N, & Cu for azide modified surface following click reaction with ppgNH$_2$@HKUST-1.

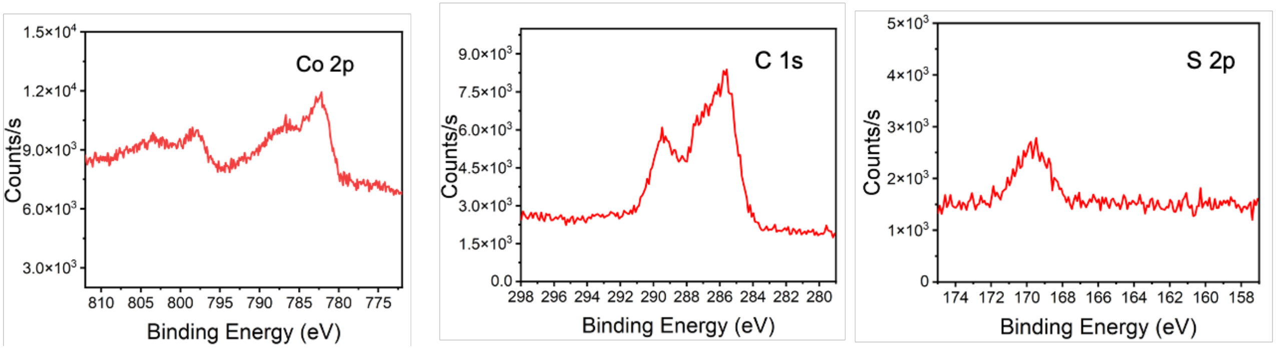

Figure S6. XPS survey spectra and high resolution C, Co, & S spectra for Co 5-ppg calixareneppg cage after click reaction with azide modified gold surface.

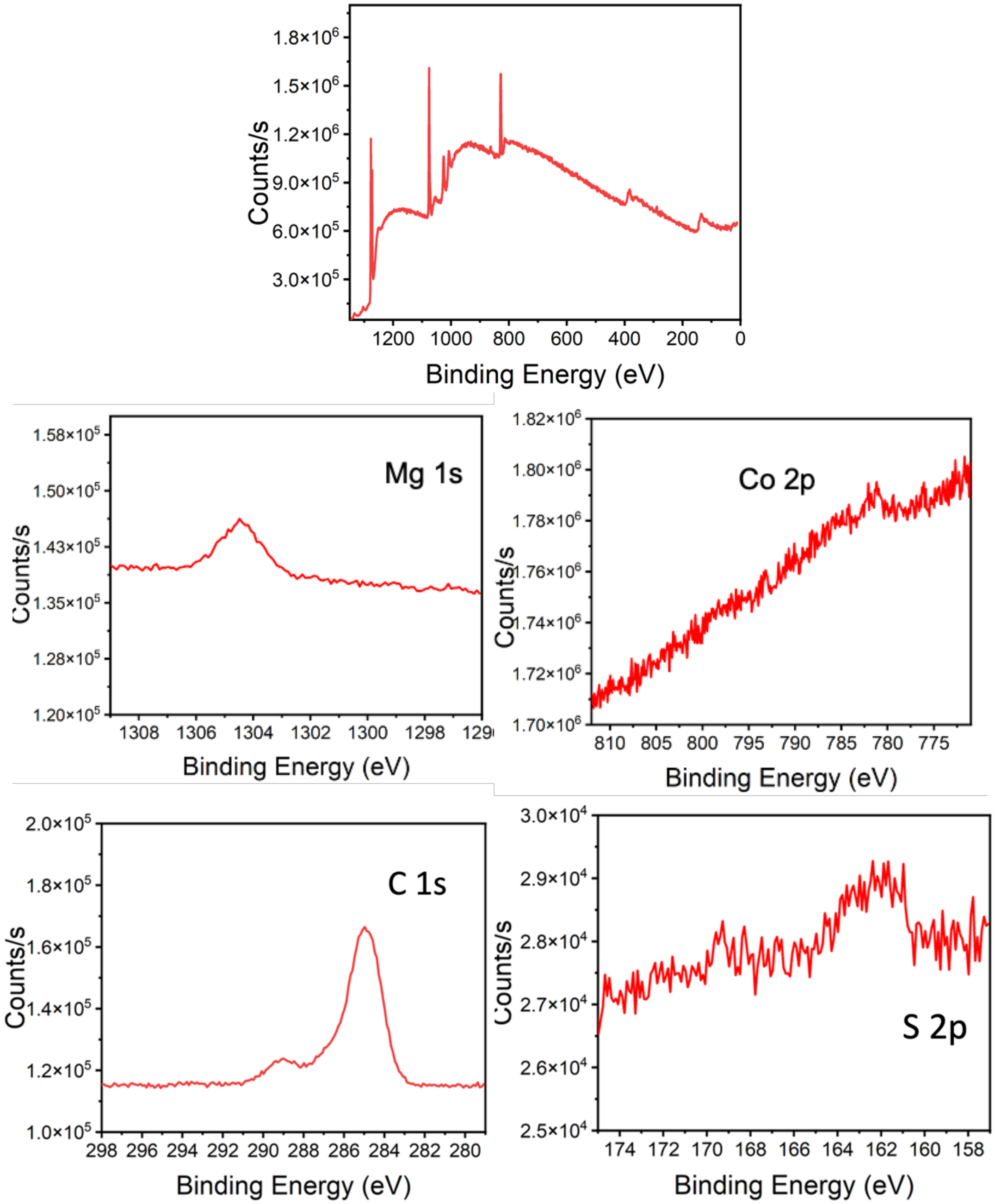

Figure S7. XPS survey spectra and high resolution Mg, Co, C, & S spectra for Co 5-ppg calixareneppg cage after click reaction with azide modified gold surface followed by click reaction with Mg 5-N3 calixarene cage.

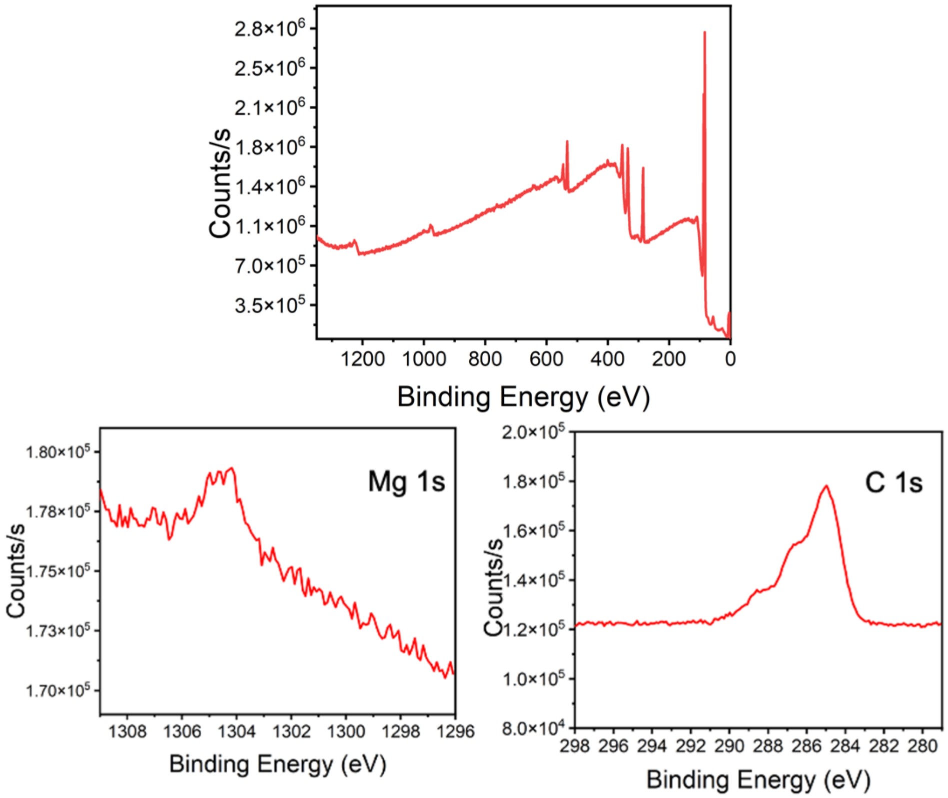

Figure S8. XPS survey spectra and high resolution Mg & C spectra for Mg 5-OH calixarene cage after SN2 reaction with bromide modified gold surface.

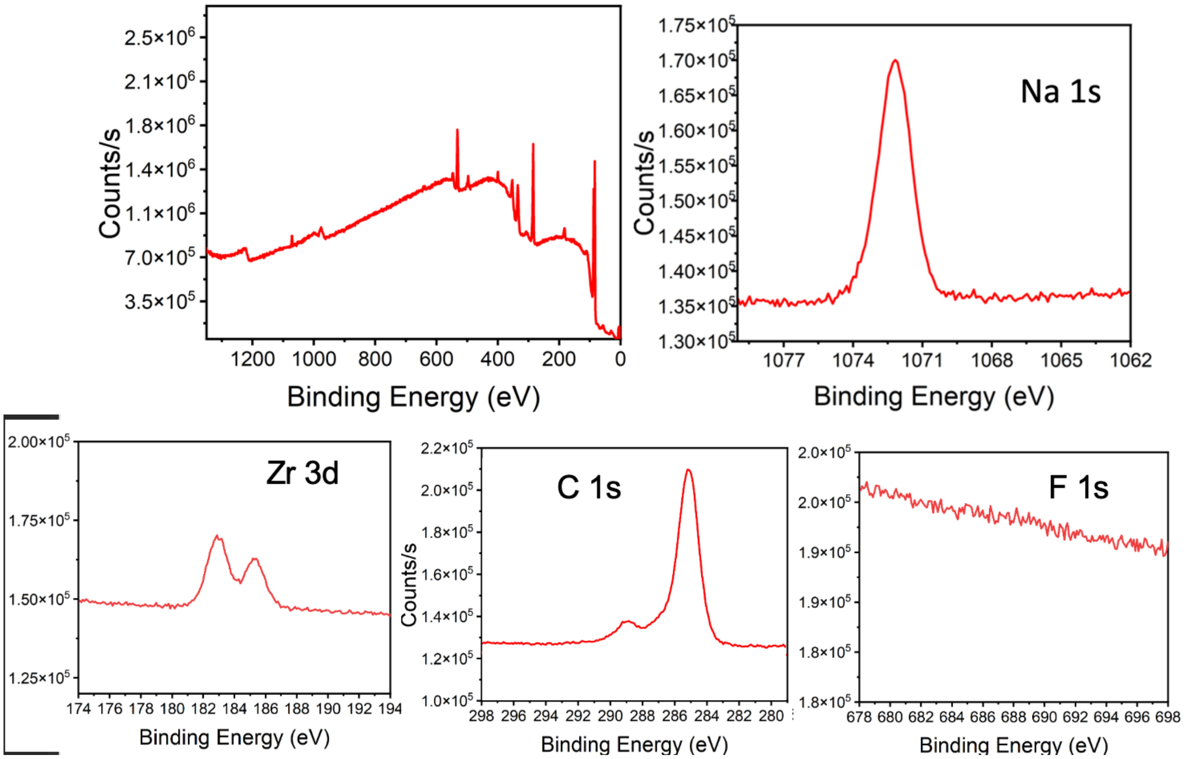

Figure S9. XPS survey spectra and high resolution Na, Zr, C, & F spectra for Zr diMe OTf cage after ion exchange reaction with carboxylate modified gold surface.

^{1}H & ^{19}F NMR Spectra

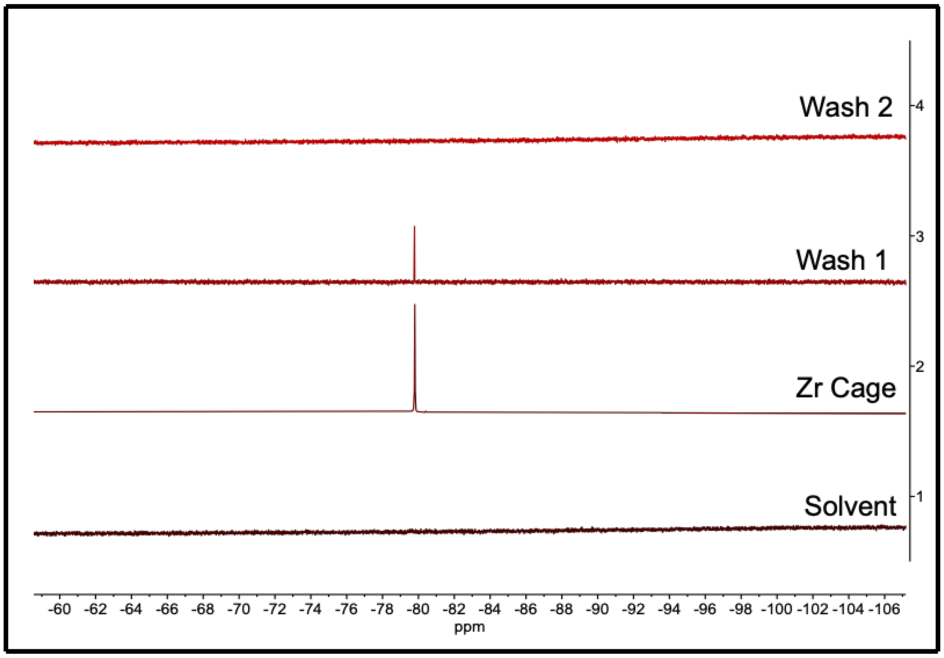

Figure S10. ^{19}F NMR spectra of MeOD (bottom), Zr diMe OTf cage in MeOD (second bottom), MeOD wash 1 after ion exchange reaction with surface (second top), and wash 2 after ion exchange reaction with surface (top).

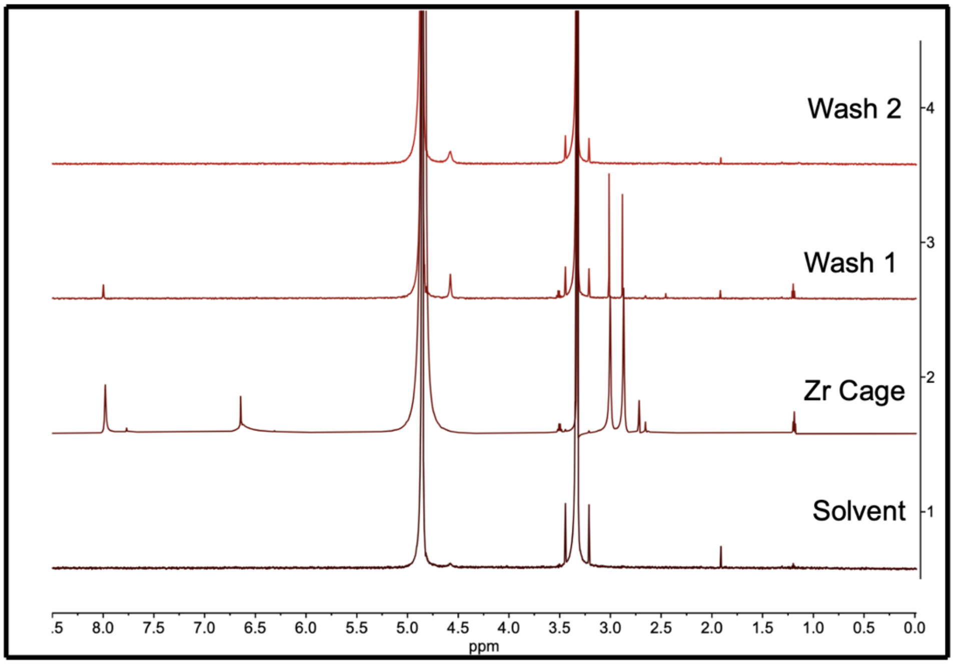

Figure S11. ^{1}H NMR spectra of MeOD (bottom), Zr diMe OTf cage in MeOD (second bottom), MeOD wash 1 after ion exchange reaction with surface (second top), and wash 2 after ion exchange reaction with surface (top).

Crystal Structures & Crystallographic Tables

Table S1. Crystal data and structure refinement details.

Compound	Mg 5-N_3 calixarene cage	Mg 5-OH calixarene cage
Sum Formula	$C_{346}H_{492}Mg_{16}N_{64}O_{126}S_{16}$	$C_{336}H_{476}Mg_{16}N_{38}O_{128}S_{16}$
Moiety Formula	$C_{224}H_{204}Mg_{16}N_{24}O_{84}S_{16}$, 40[$C_3H_7NO$], 2[$CH_3OH$],	$C_{224}H_{212}Mg_{16}O_{92}S_{16}$, 2($C_2H_6N$), 36[$C_3H_7NO$]
Formula Weight, g/mol	8465.93	7997.44
Temperature, K	120.0	120.0
Crystal system	triclinic	monoclinic
Space group	P-1	C2/*m*
Cell dimensions		
a, Å	20.535(2)	48.792(2)
b, Å	20.545(2)	16.3286(8)
c, Å	28.071(3)	26.4064(12)
α, °	93.156(4)	90
β, °	95.625(5)	97.66(5)
γ, °	112.500(4)	90
Volume, Å^3	10834(2)	20850(3)
Z	1	2
ρ_{calc}, g/cm^3	1.298	1.274
μ/mm^{-1}	1.718	1.739
F(000)	4472.0	8460.0
Reflections collected	128812	90748
Independent reflections	30347	19883
Data/restraints/parameters	30347/3134/1605	19883/2581/849
Goodness-of-fit	1.022	1.020
R [I>=2σ (I)] R_1/wR_2	0.1267/0.3420	0.1020/0.2818
R indexes [all data] R_1/wR_2	0.1378/0.3535	0.1110/0.2904
CCDC	2251521	2251522

Powder X-Ray Diffraction Patterns (PXRD)

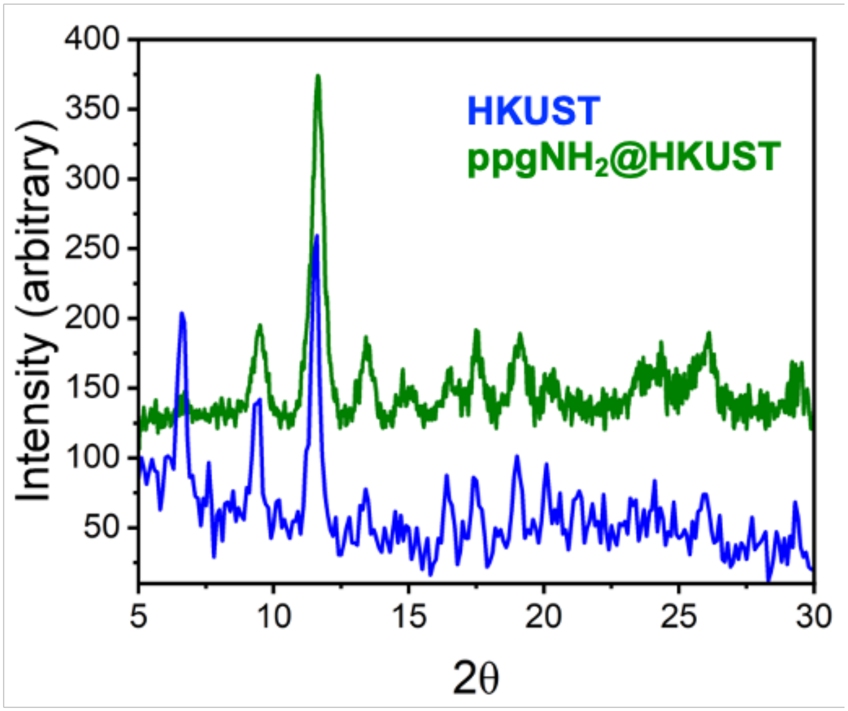

Figure S12. Stacked PXRD patterns of HKUST 1 nanoparticles (blue) and $ppgNH_2$@HKUST-1 (green.)

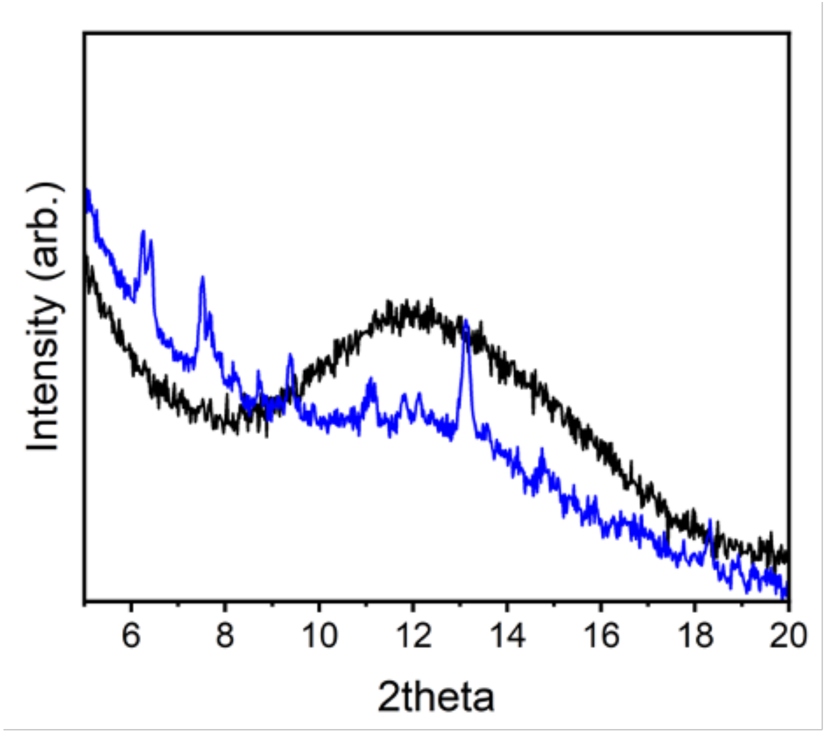

Figure S13. Grazing incidence diffraction patterns of black: HKUST-1 solvothermally grown on $ppgNH_2$ modified surface after click reaction with azide gold surface; and blue: HKUST-1 nanoparticles introduced to $ppgNH_2$ modified surface after synthesis.

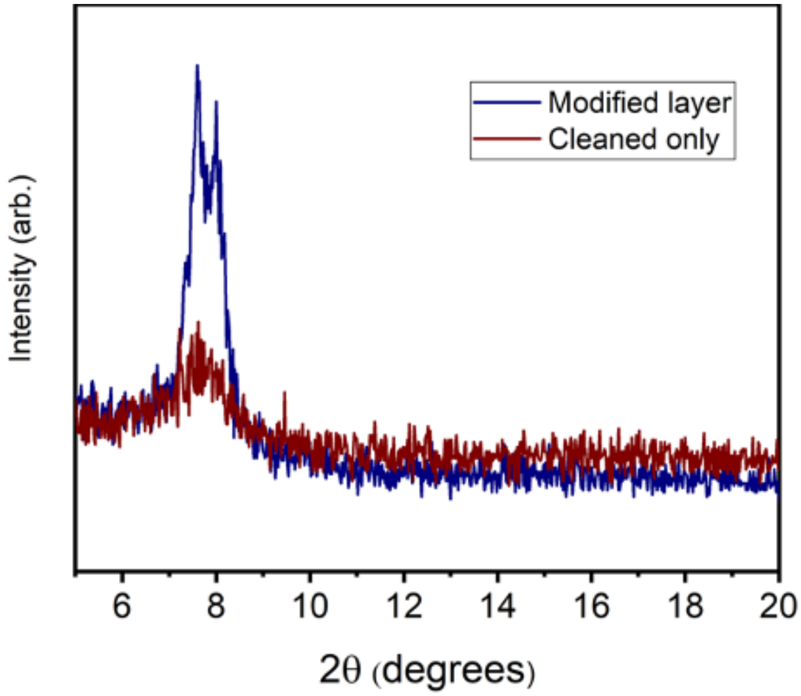

Figure S14. PXRD patterns of Co 5-ppg calixarene cage crystalized out of DMF on top of a cleaned, unmodified surface (red), and on an azide-modified surface after a click reaction with Co 5-ppg calixarene cage (blue).

Infrared Spectra (IR)

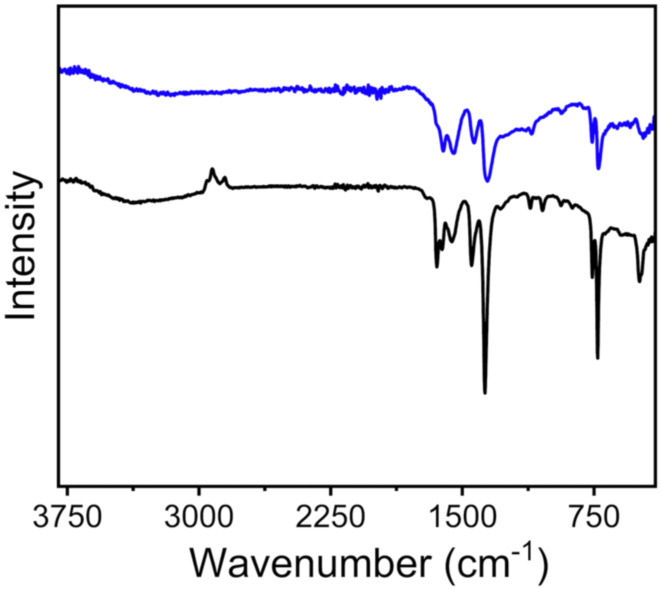

Figure S15. Infrared spectra of HKUST 1 nanoparticles (black) and ppgNH$_2$@ HKUST 1 (blue).

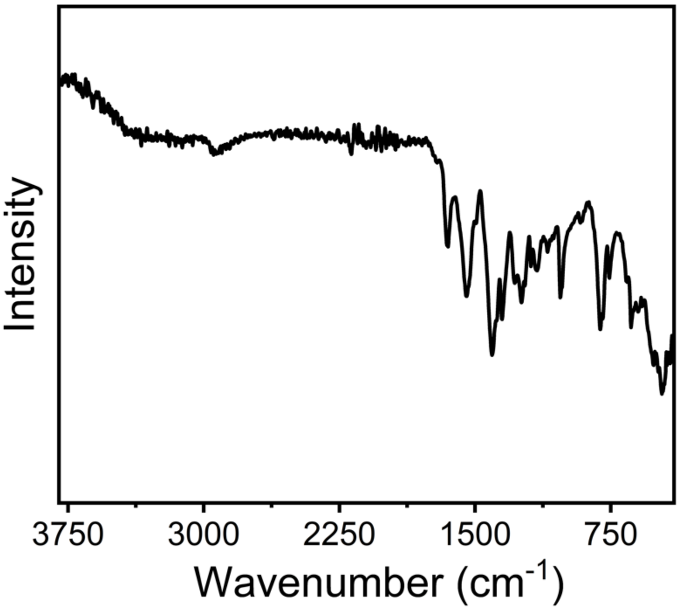

Figure S16. Infrared spectra of Zr diMe OTf cage.

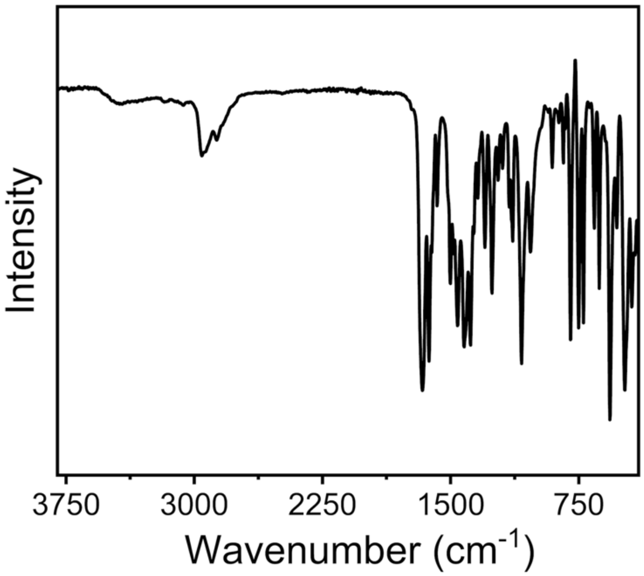

Figure S17. Infrared spectra of Mg 5-OH calixarene cage

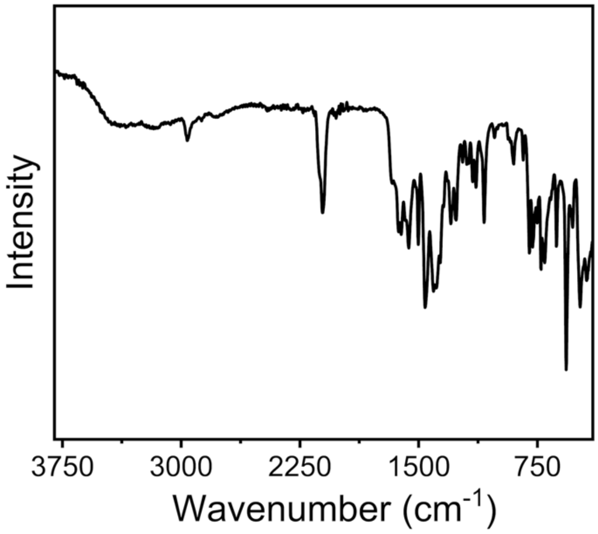

Figure S18. Infrared spectra of Mg 5-N3 calixarene cage.

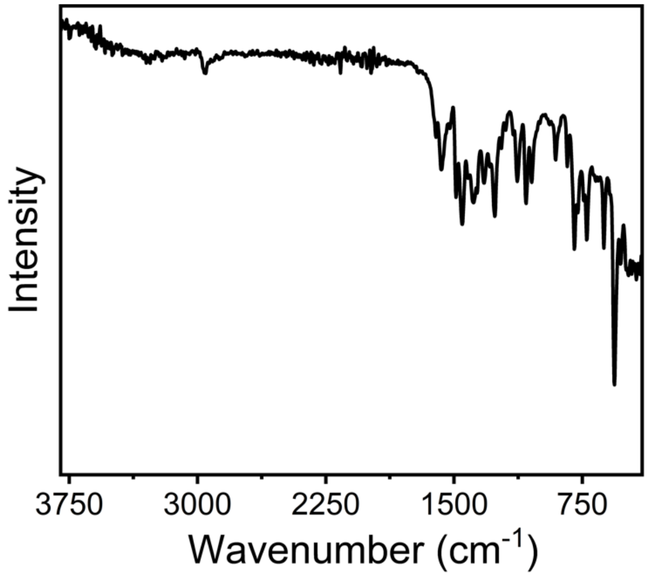

Figure S19. Infrared spectra of Co 5-ppg calixarene cage.

Mass Spectra

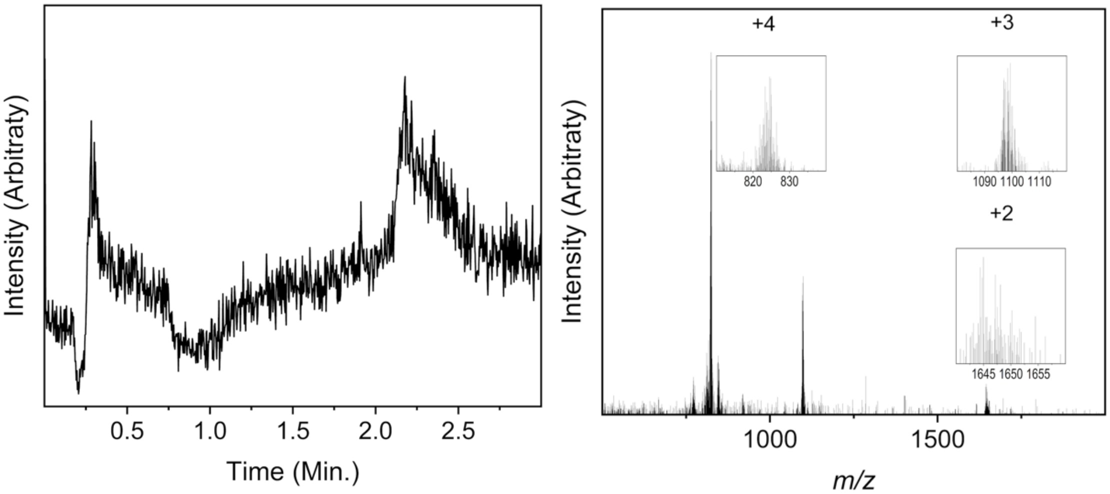

Figure S20. Chromatogram left, and mass spectra, right of Zr diMe OTf cage depicting characteristic 4+, 3+, & 2+ peaks.

Time of Flight Secondary Ion Mass Spectrometry Data (TOF-SIMS)

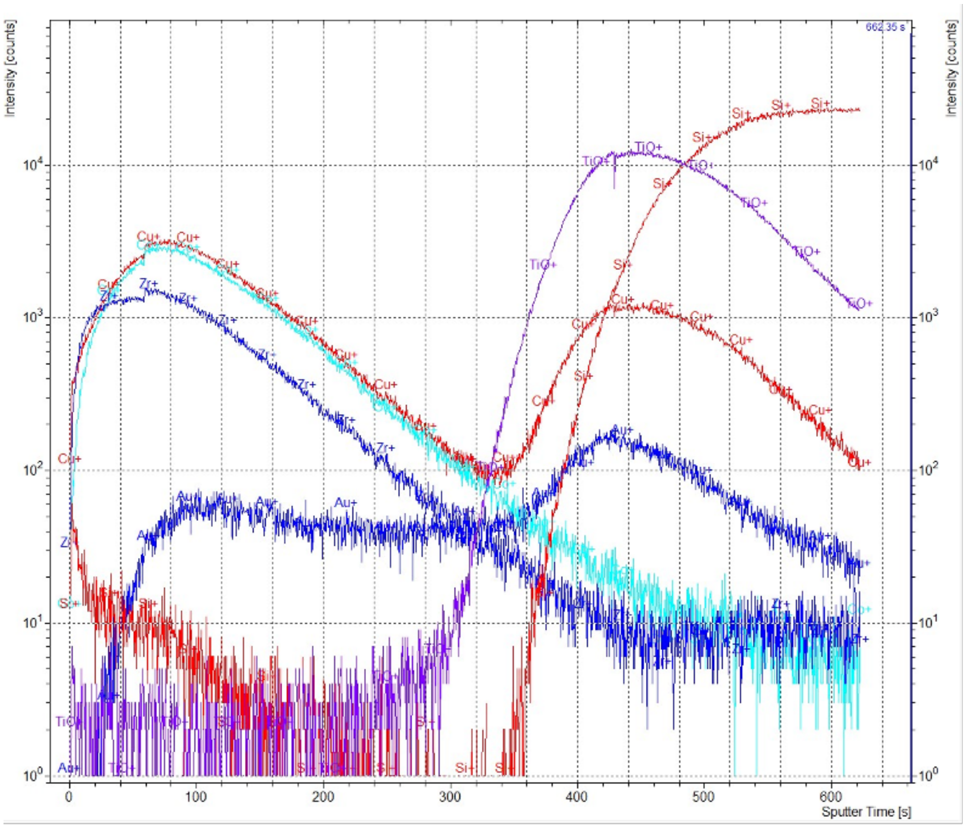

Figure S21. Depth profile of azide functionalized surface after click reaction with first, Co 5-ppg calixarene cage, then Zr N_3 cage. Traces of note include, light blue corresponding to Co, & dark blue corresponding to Zr. Etching was carried out using an O_2+ sputter source.

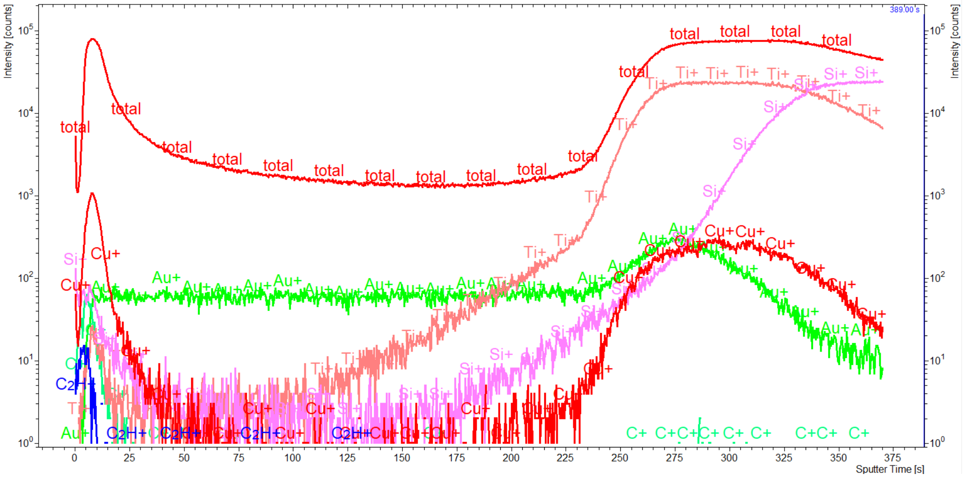

Figure S22. Depth profile of azide functionalized surface after click reaction with ppgNH$_2$ HKUST-1 nanoparticles. Traces of note include, red corresponding to Cu, & dark blue corresponding to C_2H . Etching was carried out using an O_2+ sputter source.

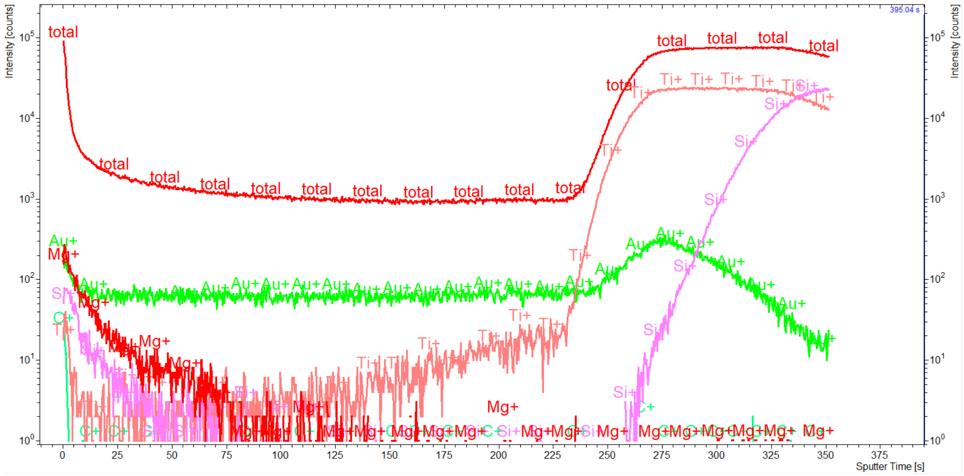

Figure S23. Depth profile of bromide functionalized surface after SN2 reaction with Mg 5-OH calixarene cage. Traces of note include, red corresponding to Mg, & green corresponding to Au. Etching was carried out using an O_2+ sputter source.

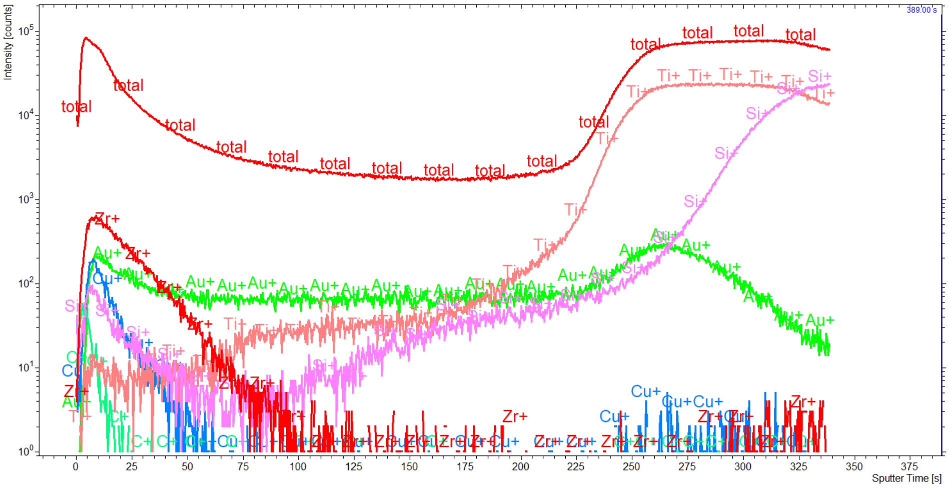

Figure S24. Depth profile of carboxylate functionalized surface after ion exchange reaction with Zr diMe OTf cage. Traces of note include, red corresponding to Zr, & green corresponding to Au. Etching was carried out using an O_2+ sputter source.

Scanning Electron Microscopy Images (SEM)

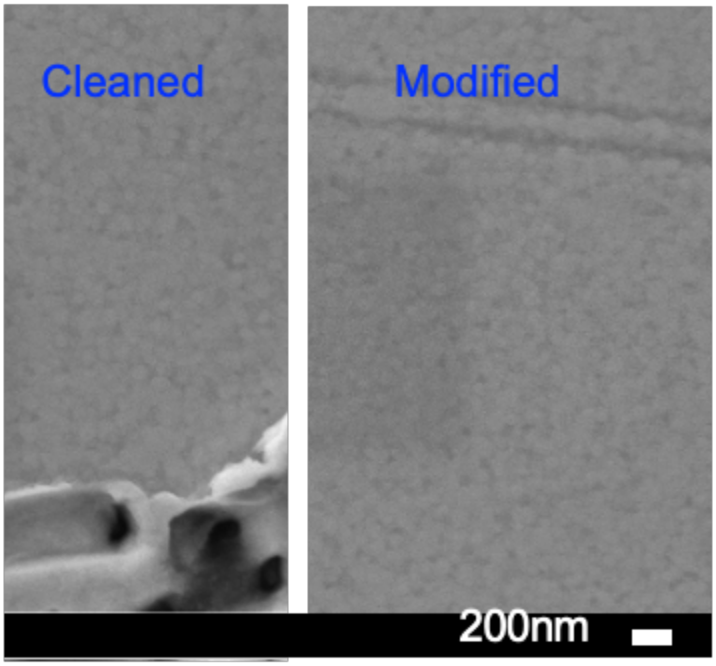

Figure S25. SEM image of cleaned gold surface (left) and azide-modified gold surface (right.)

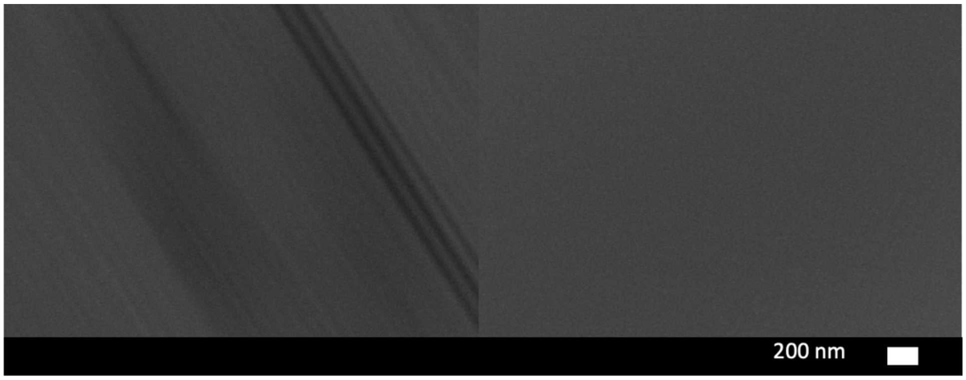

Figure S26. SEM image of bromide-modified gold surface (left) and carboxylate-modified surface (right).

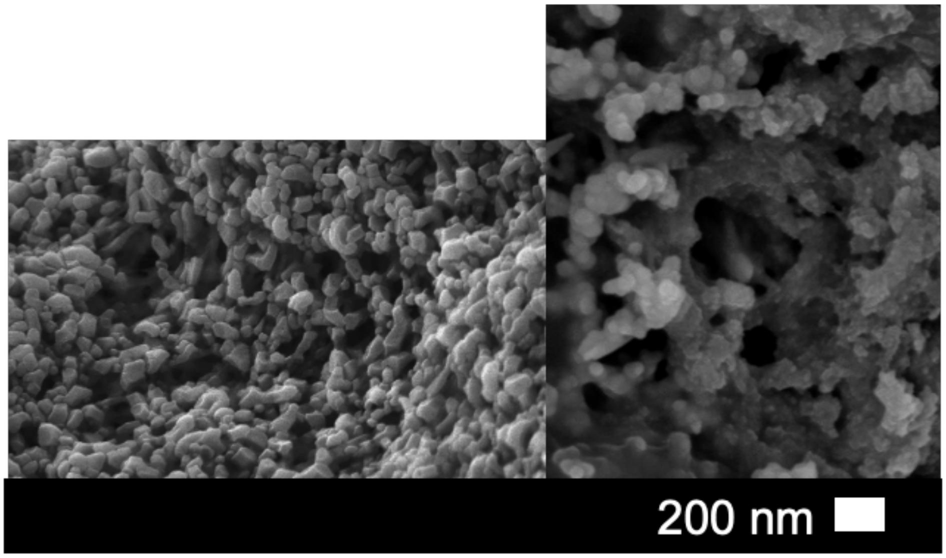

Figure S27. SEM image of HKUST-1 (left) and ppgNH_2 @ HKUST-1 particles (right.)

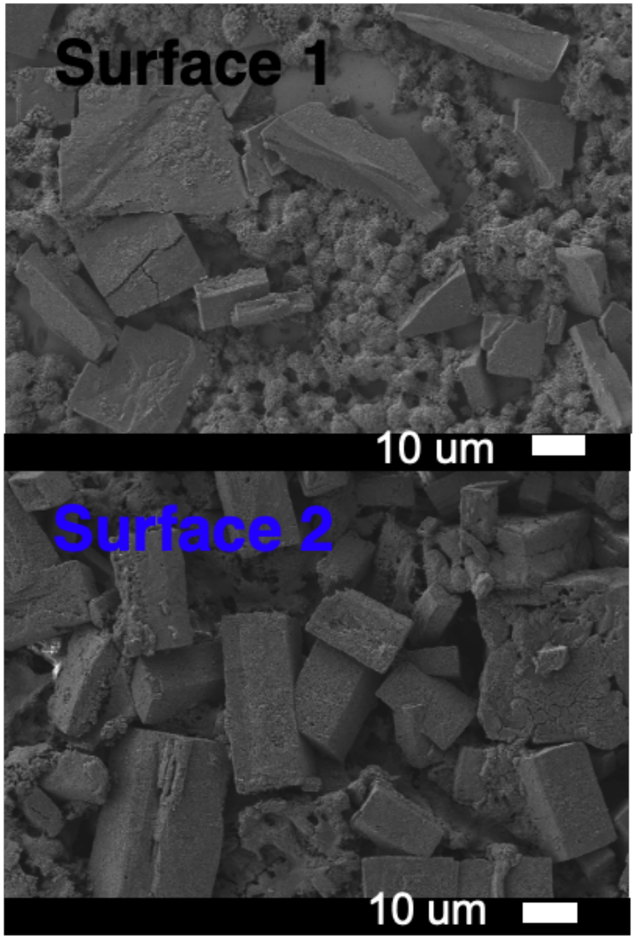

Figure S28. SEM image of HKUST-1 solvothermally grown on ppgNH_2 modified surface after click reaction with azide gold surface (surface 1); and HKUST-1 nanoparticles introduced to ppgNH_2 modified surface after synthesis (surface 2.)

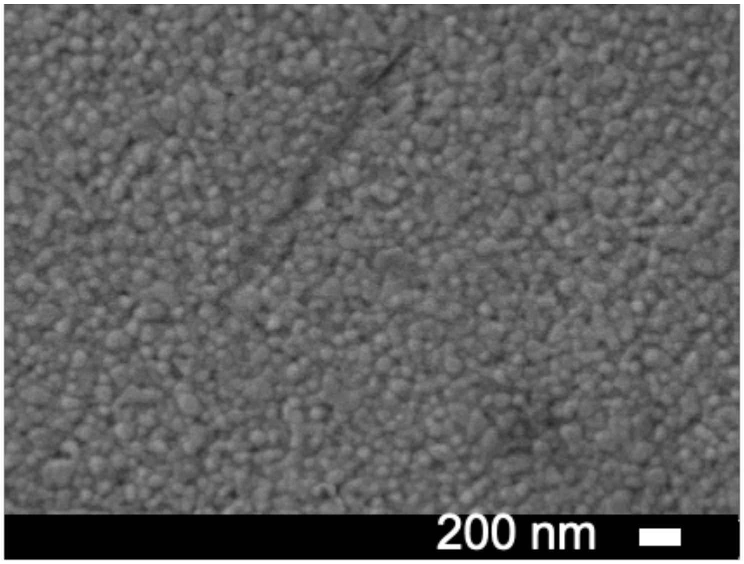

Figure S29. SEM image of ppgNH_2 @ HKUST-1 particles after click reaction with azide-modified surface.

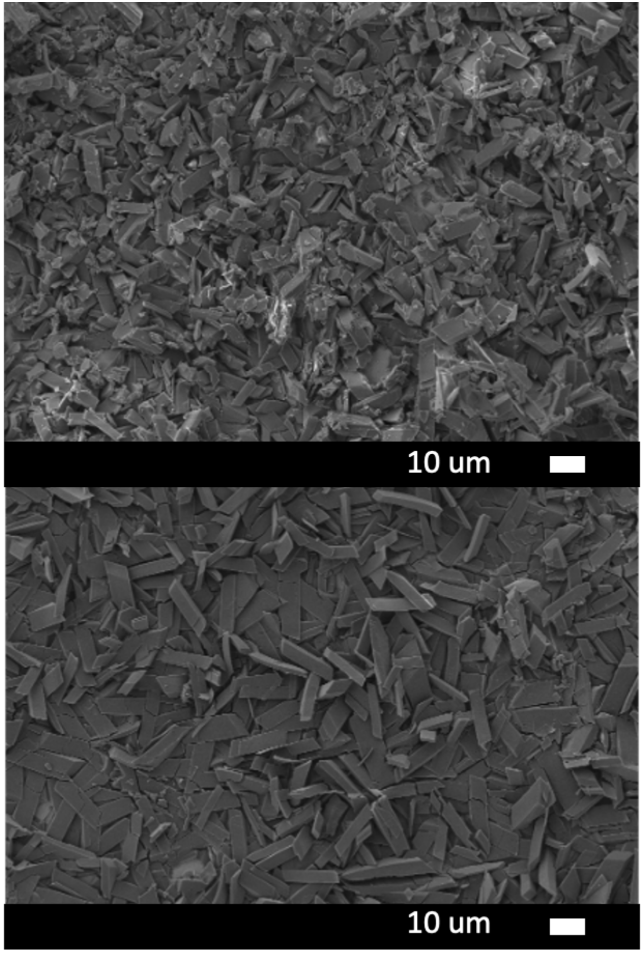

Figure S30. SEM image of Co 5-ppg calixarene cage crystalized out of DMF on top of a clean, unmodified gold surface (top), and on top of an azide modified surface after click reaction with Co 5-ppg calixarene cage (bottom.)

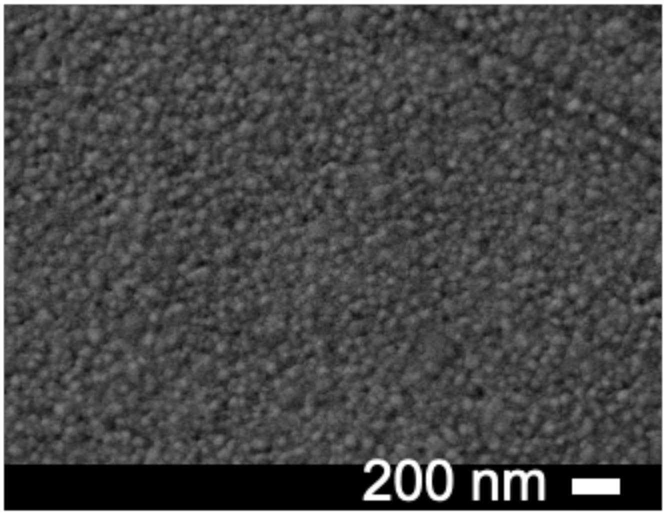

Figure S31. SEM image of azide modified surface following click reaction with first Co 5-ppg calixarene cage followed by Mg 5-N3 calixarene cage.

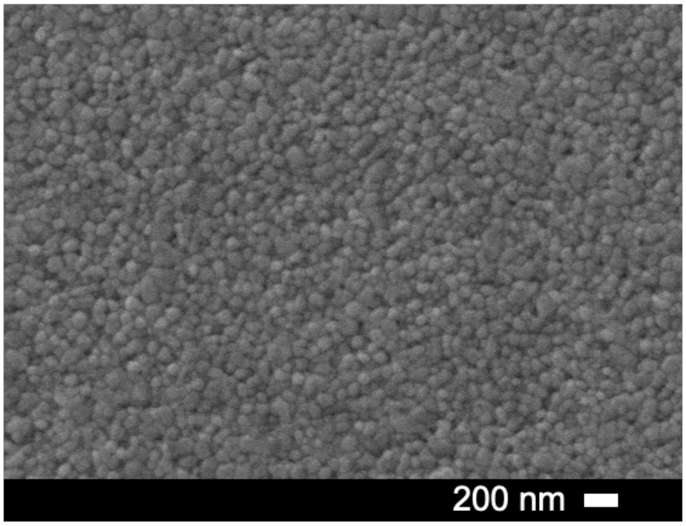

Figure S32. SEM image of bromide modified surface following SN2 reaction with Mg 5-OH calixarene cage.

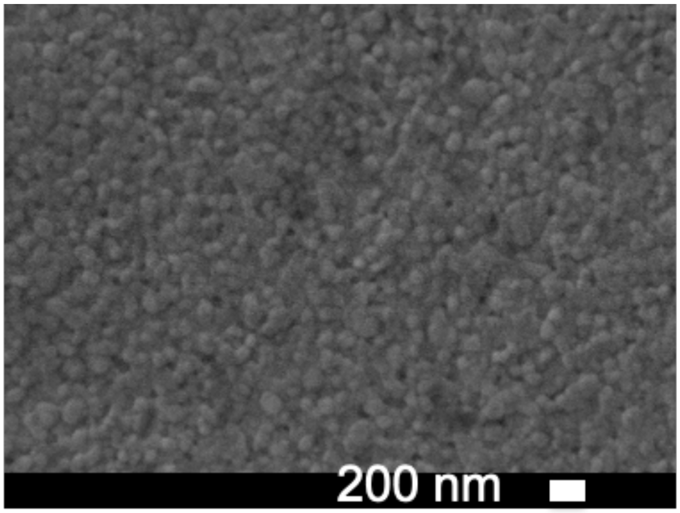

Figure S33. SEM image of carboxylate modified surface following an ion exchange reaction with Zr diMe OTf cage.

Atomic Force Microscopy Images (AFM)

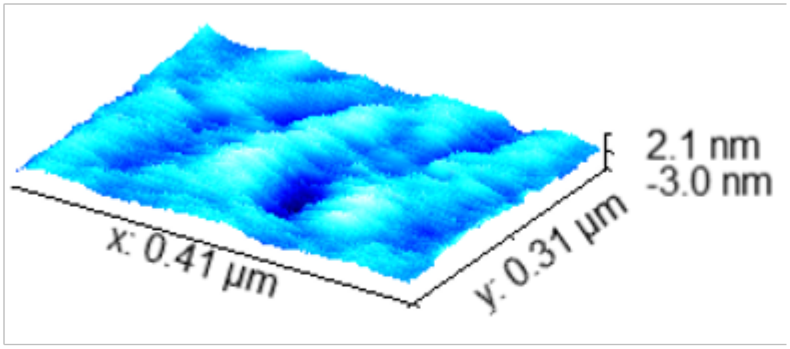

Figure S34. AFM image of cleaned gold surface.

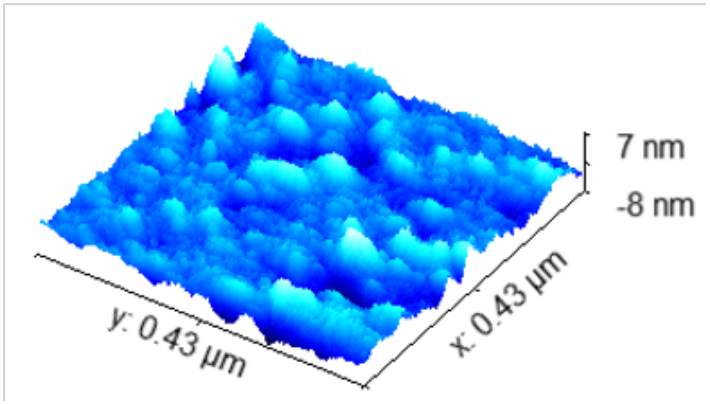

Figure S35. AFM image of azide modified gold surface.

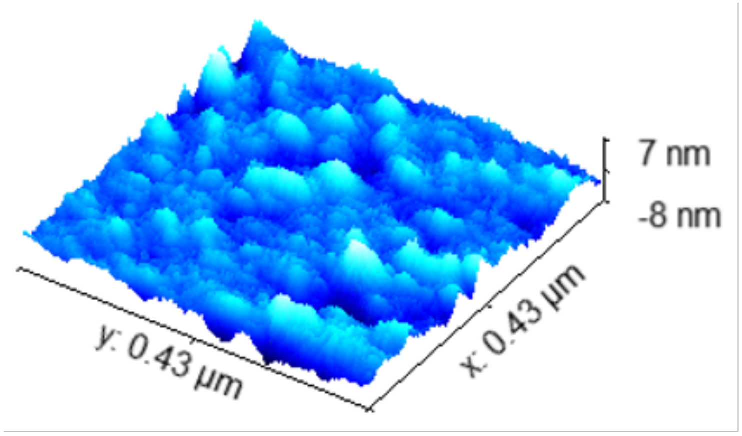

Figure S36. AFM image of bromide modified gold surface.

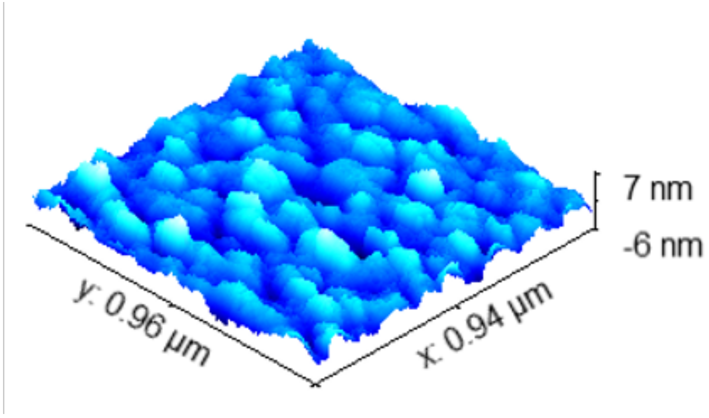

Figure S37. AFM image of carboxylate modified gold surface.

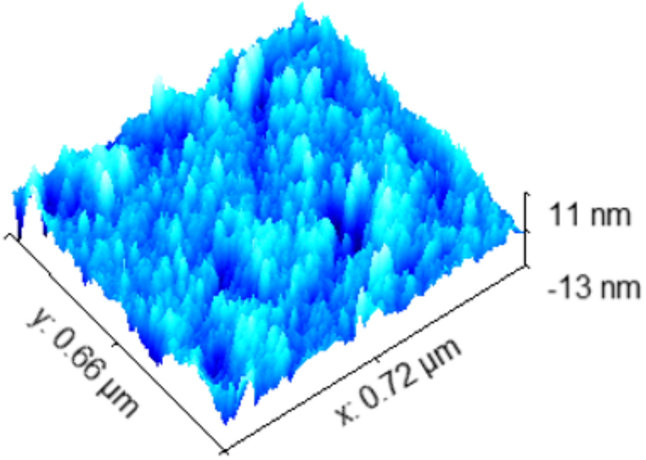

Figure S38. AFM image of azide modified surface following click reaction with $ppgNH_2$ @ HKUST-1 particles.

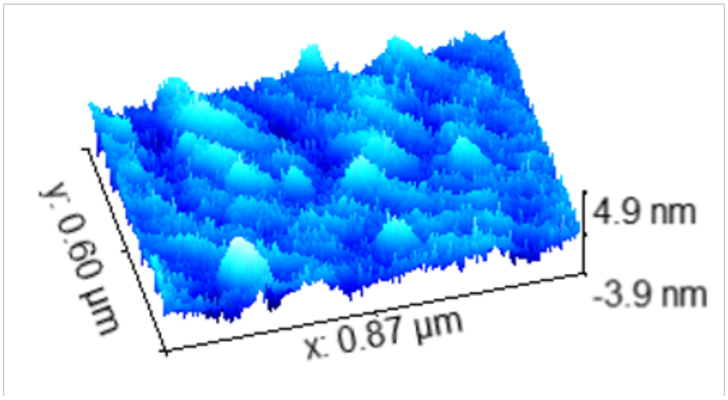

Figure S39. AFM image of azide modified surface following click reaction with Co 5-ppg calixarene cage.

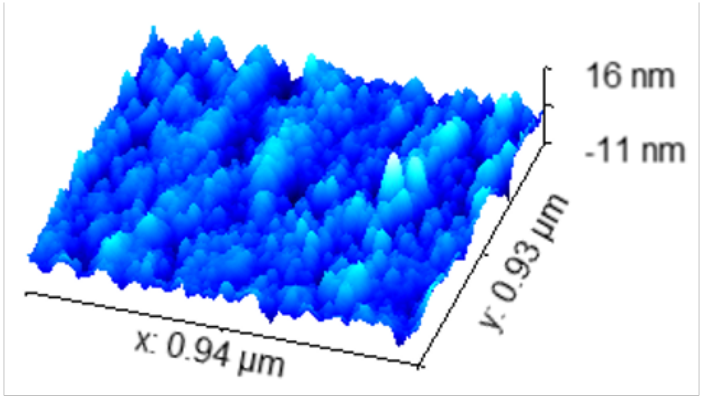

Figure S40. AFM image of azide modified surface following click reaction with Co 5-ppg calixarene cage followed by Mg 5-N3 calixarene cage.

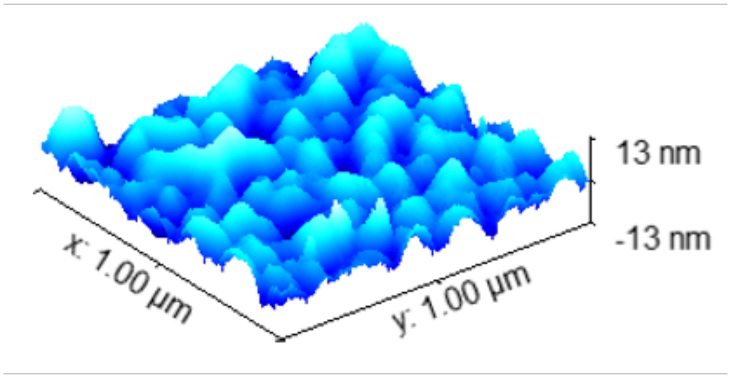

Figure S41. AFM image of bromide modified surface following SN2 reaction with Mg 5-OH calixarene cage.

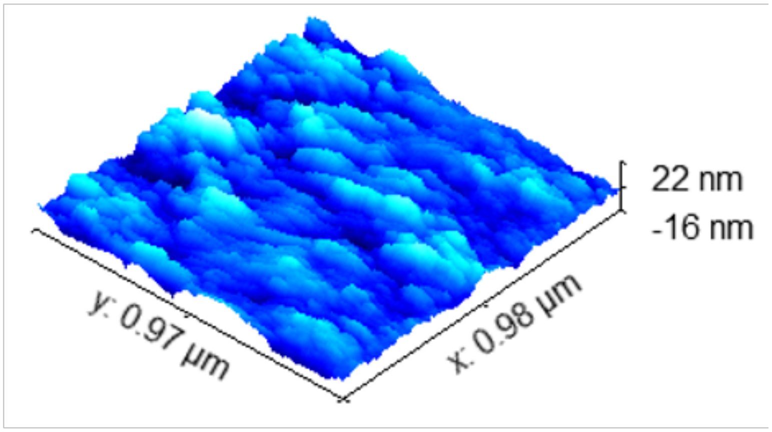

Figure S42. AFM image of carboxylate modified surface following ion exchange reaction with Zr diMe OTf cage.

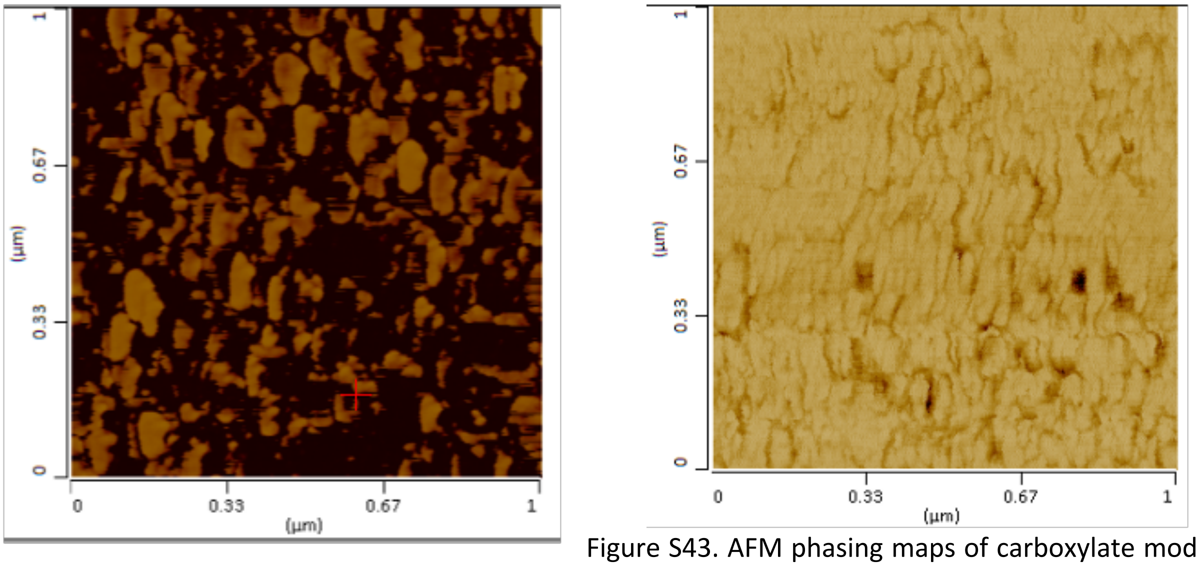

Figure S43. AFM phasing maps of carboxylate modified surface before (left), and after (right) ion exchange reaction with Zr diMe OTf cage.

NanoIR Spectra

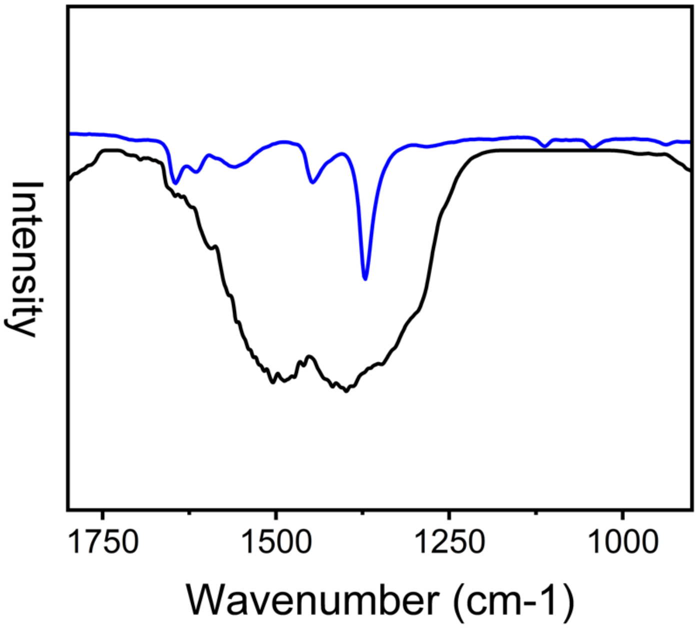

Figure S44. NanoIR spectra of ppgNH₂ @ HKUST-1 on azide modified gold surface stacked with ppgNH₂ @ HKUST-1 bulk IR spectra.

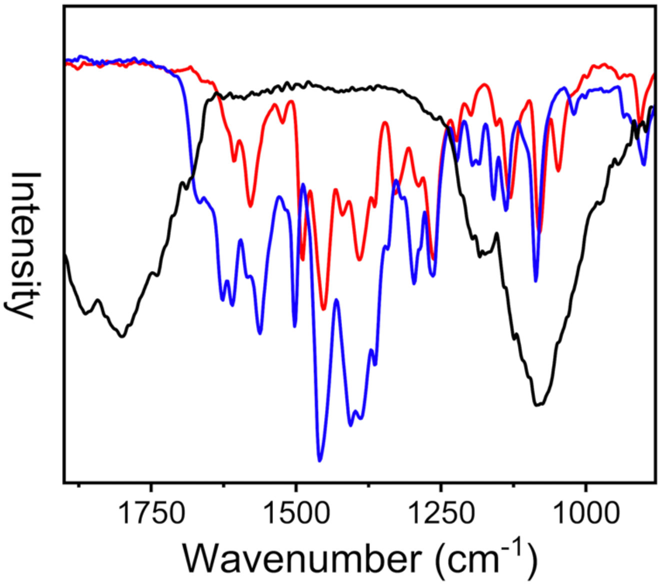

Figure S45. NanoIR spectra of clicked Co 5-ppg calixarene cage on azide modified gold surface followed by clicked Mg 5-N3 calixarene cage (black) stacked Co 5-ppg calixarene (red) and Mg 5-N3 calixarene (blue) bulk IR spectra.

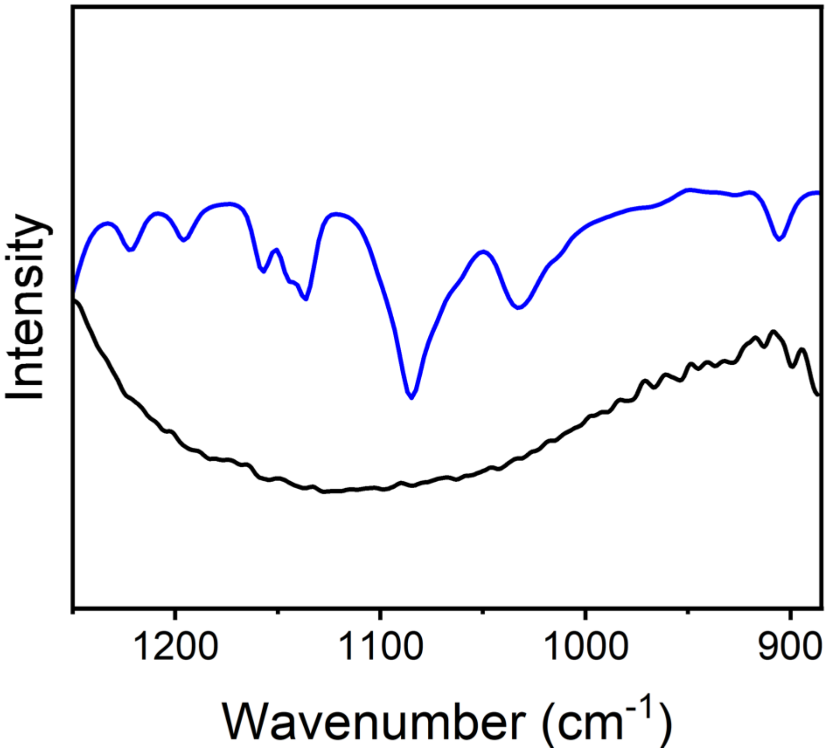

Figure S46. NanoIR spectra of Mg 5-OH calixarene cage on bromide modified gold surface (black) stacked with Mg 5-OH calixarene cage bulk IR spectra (blue).

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