

Supporting Information
for
Experimental Observation of Metal-Organic Framework-Polymer Interaction
Forces and Intercalation

Joseph M. Palomba, ‡,¹ Verda Saygin, ‡,² Keith A. Brown, *,^{2,3}

1. Soldier Protection Directorate, U.S. Army Combat Capabilities Development Command Soldier Center, Natick, MA, 01760, United States
2. Department of Mechanical Engineering, Boston University, 110 Cummington Mall, Boston, Massachusetts 02215, United States
3. Physics Department and Division of Materials Science and Engineering, Boston University, 590 Commonwealth Avenue, Boston, Massachusetts 02215, United States

*Correspondence to be addressed to brownka@bu.edu

‡These authors contributed equally to this work

Experimental

Materials. All chemicals and solvents were purchased from chemical suppliers Sigma Aldrich, TCI, and Alfa Aesar and used without further purification. Four polymers used were polyvinylidene difluoride (PVDF, $M_w = 530\text{k g/mol}$, Sigma Aldrich), polyethylene oxide (PEO, $M_w = 4\text{k g/mol}$, Alfa Aesar), polystyrene-block-polybutadiene-block-polystyrene (SBS, 30% styrene, Sigma Aldrich - # 432490), and polyisobutylene (PIB, $M_w = 500\text{k g/mol}$, Sigma Aldrich). Tipless atomic force microscopy (AFM) cantilevers were purchased from NANOSENSORS (Neuchatel, Switzerland), product code TL-NCH (125 μm long, 42 N/m force constant). Silicon surfaces used in this study were cut to 1 cm^2 squares and cleaned by sonication in methanol (15 min) and plasma cleaned in an UV-ozone chamber (15 min) before surface functionalization or spin coating polymers.

ZIF-8 Synthesis. Large crystals of ZIF-8 were grown using a previously demonstrated method.¹ Zinc(II) acetate hydrate and agar were dissolved in water with heating and stirring such that final concentration of Zn and agar were 5 mM and 1 wt%. An equal volume of dimethyl formamide (DMF) was added to aqueous solution under stirring and the resulting solution was poured into 10 cm \times 1 cm test tubes filling them two-thirds (~ 5 mL). The tubes were covered with parafilm and allowed to gel at room temperature for 2 hours. A solution of 2-methylimidazole (conc. = 2 M) was prepared in 1:1 mixture of water and DMF and poured on top of agar gel (~ 2 mL) per tube. The test tubes were covered with parafilm and allowed to diffuse and react for 48 hours.

The crystals in the agar gel were scooped from test tube with spatula, first removing and discarding the thin top layer of precipitate, then the rest of the gel was divided into three layers (top, middle, and bottom). The bottom layer had the largest particles and was used for this study. The gel was dissolved in excess DMF and ZIF-8 particles were separated by centrifuge (4000 rpm, 10 min). The particles were then washed 3 \times in DMF and 3 \times in methanol to remove all starting materials and solvent from pores of the MOF. The resulting powder was dried at 80 $^\circ\text{C}$ for 12 hours.

Attachment of ZIF-8 to AFM Cantilever. Tipless tapping mode cantilevers with ~ 42 N/m force constants and ~ 330 kHz primary vibrational resonance were used for preparation of MOF-tipped cantilever. First, the probe was mounted in the AFM. Next, a glass slide was prepared with MOF crystals at one end and nanoliter-scale drops of two-component epoxy (Devon 2 ton epoxy) at the other end which was mixed immediately prior to the experiment. Once prepared, the probe was positioned over a nanoliter-scale epoxy drop using the built-in optical microscope and the AFM system was used to execute a force-indentation curve to deposit a picoliter-scale drop of mixed epoxy at the end of the cantilever. The mass of loaded epoxy on the cantilever was measured using inertial mass sensing.² Finally, a MOF crystal was identified using the built-in optical microscope and the probe was engaged on the chosen particle. The cantilever was then left for 24 hours to allow the epoxy to cure and then rinsed with isopropanol. The product of this process was an attached MOF crystal at the end of the cantilever.

Polymer Spin Coating. 1 cm^2 silicon wafer chips were cleaned by sonication in methanol (15 min), dried under an N_2 flow, and plasma cleaned in an UV-ozone chamber (15 min) before

surface functionalization or spin coating polymers. For spin coating of PIB and SBS samples, the silicon wafers were further treated with hexamethyldisilazane (HMDS) to create a hydrophobic surface. For HMDS treatment, the wafers were removed from UV-ozone treatment and placed in a 100 mL screw-top glass jar with 10 μ L of HMDS dropped on the bottom of the jar (not directly on the wafer chip). The jar was sealed and heated on a hotplate set to 70 $^{\circ}$ C for 1 hour. The wafers were removed from jar and washed with methanol and dried under an N₂ stream.

The prepared wafers were used for spin coating immediately after preparation (<1 hour). The general procedure for spin coating films was to drop 100 μ L of 1 wt% solution of polymer onto the wafer chip, spin the wafer at 500 rpm for 30 s to spread the liquid, ramp to high speed over 10 s, and finally spin at high speed for 30 s. The details of solvent choice and maximum speed varied based on the polymer and are listed in Table S1.

Table S1. Spin coating details for polymers.

Polymer	Solvent	Maximum Speed (rpm)
PVDF	DMF	5,000
PEO	Ethanol	5,000
SBS	Toluene	1,000
PIB	Toluene	2,000

Nanoindentation. Nanoindentation was performed at ambient conditions using an Asylum Research MFP-3D Infinity AFM system. Prior to any nanoindentation experiment, the probe was calibrated on a clean untreated silicon wafer chip. For both the MOF-tipped probe and the silica bead-tipped probe, the resonance frequency of the cantilever was recorded to confirm the attached tip (MOF or bead) was still intact. Nanoindentation curves were taken by engaging the cantilever on a desired surface with the following settings: 0.3 V repulsive set point, 3 μ m/s speed, and 10 kHz sampling rate. The force-distance curves were taken on a 6 x 6 grid that spanned 50 x 50 μ m², which ensured that the nanoindenter was engaged on different locations of the sample for each measurement. A minimum of 3 grids were taken on each sample.

Powder X-ray Diffraction (PXRD). PXRD data was collected at room temperature using a Proto AXRD Benchtop diffractometer running at 30 kV, 20 mA for Cu K α (λ = 1.5418 \AA) and a Dectris Mythen 1K silicon strip detector (1280 channels), with a Ni filter, a 0.5 mm divergence slit, a step size of 0.015 $^{\circ}$ in 2 θ , and a 2 θ range of 5-40 $^{\circ}$ at room temperature. The sample was prepped in a plastic sample holder with shallow (0.5 mm) depth and a knife edge anti-scatter slit was used to block low angle scattering and set near flush with sample holder surface.

Scanning Electron Microscopy (SEM). SEM images were collected at room temperature using a Thermo Fisher Scientific Quattro ESEM at a voltage of 30 kV, working distance of 10 mm, and a working pressure of 1.0 \times 10⁻³ Pa. ZIF-8 powder samples were prepared on carbon tape adhered to aluminum sample holder. Cantilever samples were prepared by fastening the end of the cantilever to an aluminum sample holder using a simple, custom-built screw clamp.

Spectroscopic Ellipsometry. The average thickness of each polymer sample was measured using Variable Angle Spectroscopic Ellipsometer (VASE, J.A. Woollam) at room temperature. The ellipsometer was first calibrated using a Si wafer chip. All the measurements are taken from 500 to 1500 nm wavelength, with 20 rev/measurements and at 65°, 70°, and 75°. The data was then fitted using a Cauchy material model using the WVASE ellipsometer software.

Table S2. Polymer film thickness measurements taken with ellipsometer

Polymer	Average thickness (nm)
PVDF	105 ± 3
PEO	110 ± 0.4
SBS - A	873 ± 5
SBS - B	144 ± 2
PIB	811 ± 6

Tapping Mode AFM Imaging. AFM topographic images of the polymer surfaces were taken at ambient conditions using an Asylum Research MFP-3D Infinity AFM (Oxford Instruments) using TAP300AI-G probes (Budget Sensors). Tapping mode topographic images were taken with 256 points and lines, a 550 mV setpoint, and a 0.5 Hz scan rate to investigate the roughness of the prepared polymer samples. Figure S7 shows height maps from 20 × 20 μm² scans of PVDF, PEO, SBS, and PIB.

Table S3. Polymer film roughness measurements determined with AFM topography imaging

Polymer	Roughness (nm)
PVDF	6.6
PEO	6.3
SBS - A	1.2
SBS - B	1.5
PIB	2.8

Experimental Results

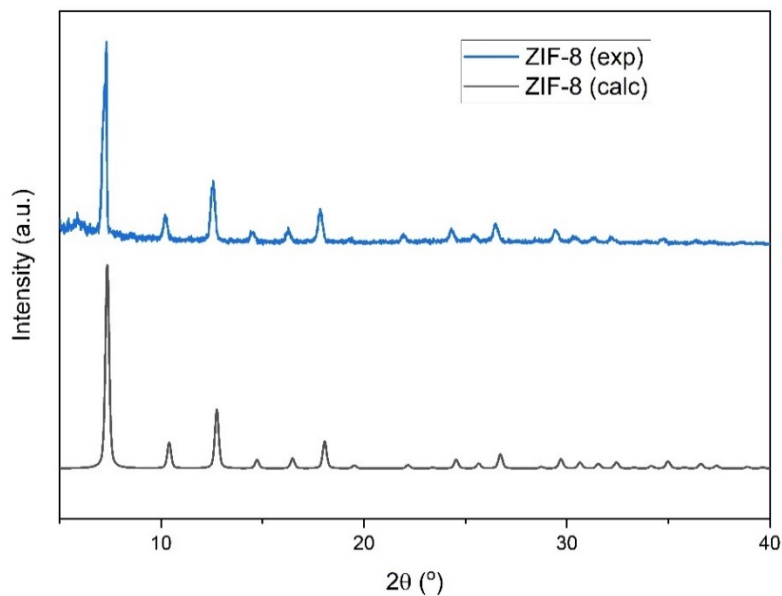


Figure S1. PXRD pattern of ZIF-8 used for AFM cantilever, from bottom of agar gel synthesis (top) compared to calculated pattern from crystal structure.

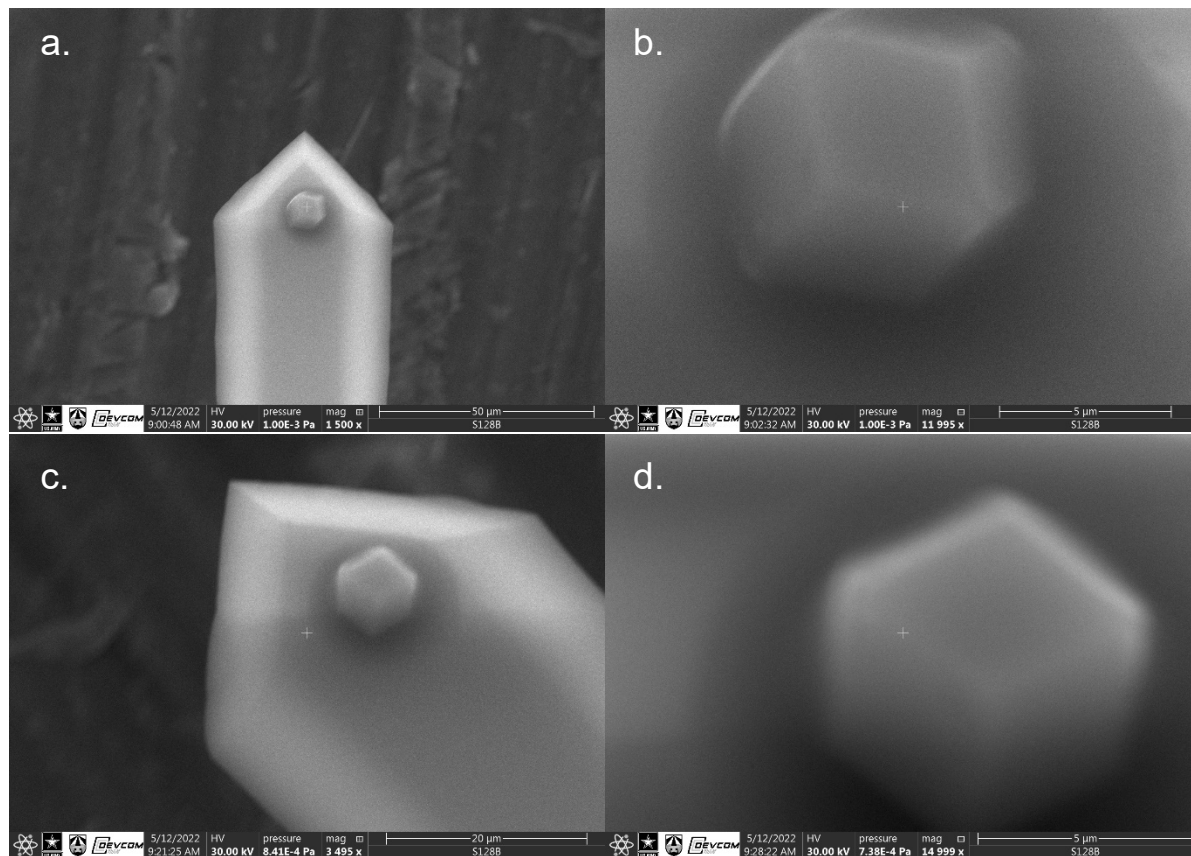


Figure S2. SEM images of ZIF-8 cantilever showing 15° (a-b) and 25° (c-d) tilt angles to show 3D picture of tip.

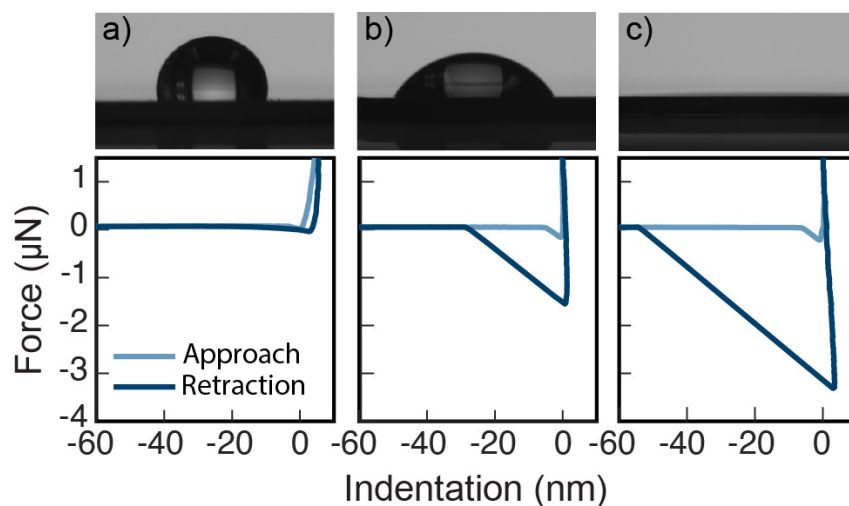


Figure S3. MOF nanoindentation curves on surfaces with water contact angle photographs: (a) fluorosilane-coated, (b) untreated, and (c) plasma-treated silicon.

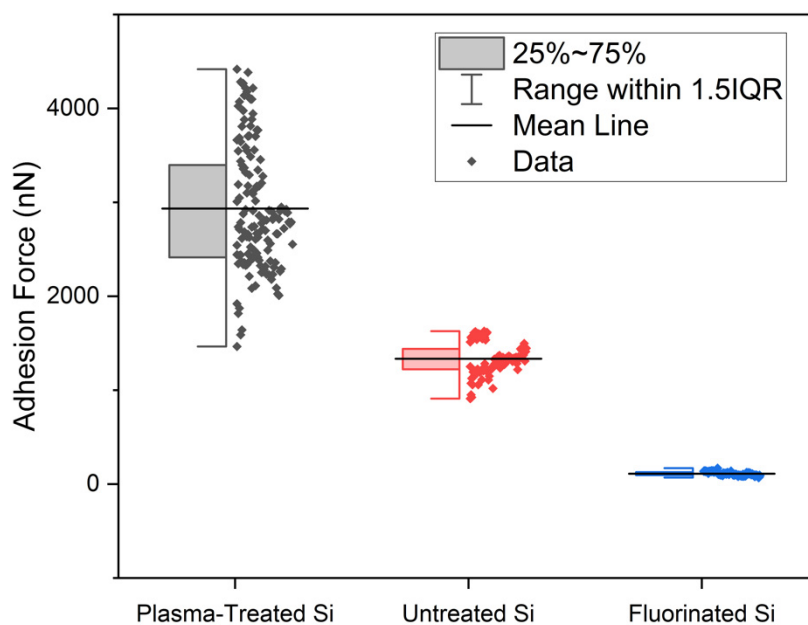


Figure S4. Box and whisker plots including all data points of adhesion force measured by the MOF-tipped probe on different Si surfaces. Each box represents the middle 50% of data and the whiskers represents +/- an additional 1.5 interquartile range (includes 99.3% of data). Each experimental condition depicts >108 measurements.

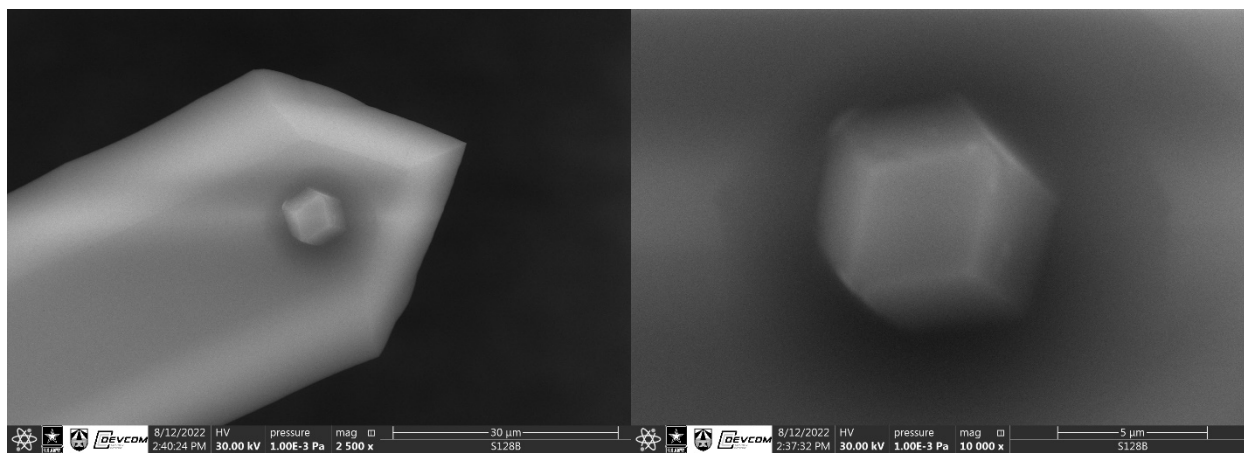


Figure S5. SEM images of ZIF-8 cantilever after all nanoindentation experiments.

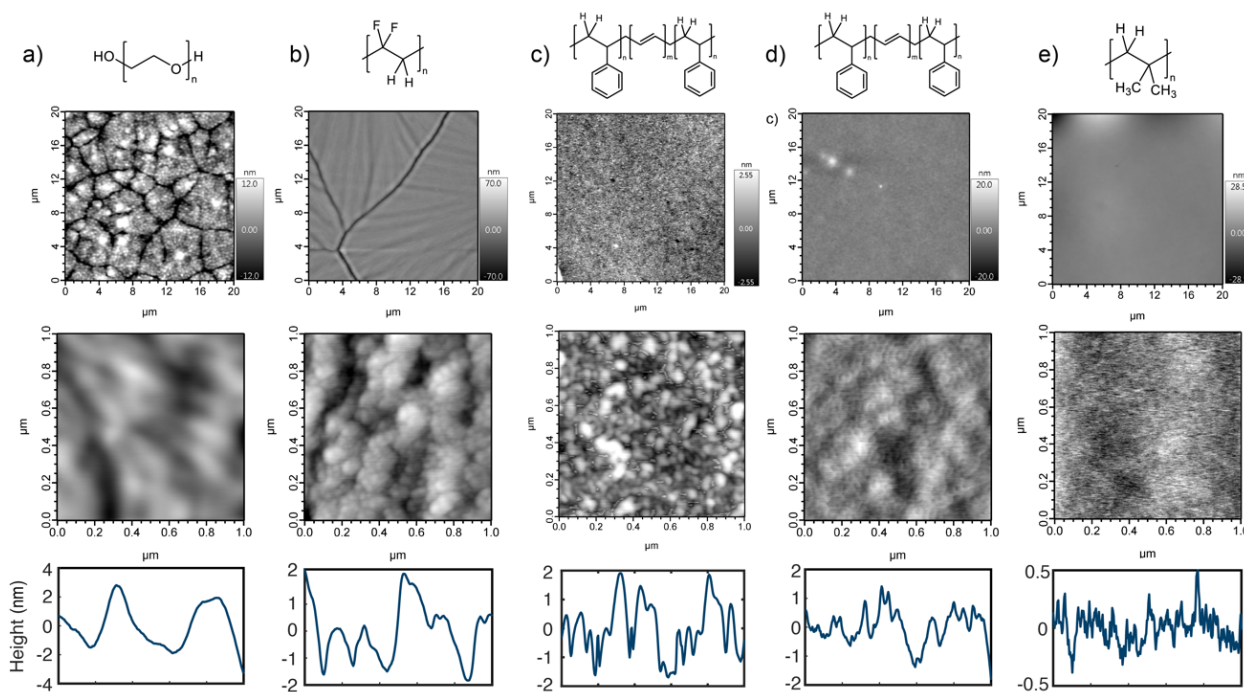


Figure S6. AFM topographic images of a) PVDF, b) PEO, c) thin SBS, d) thick SBS and e) PIB surfaces.

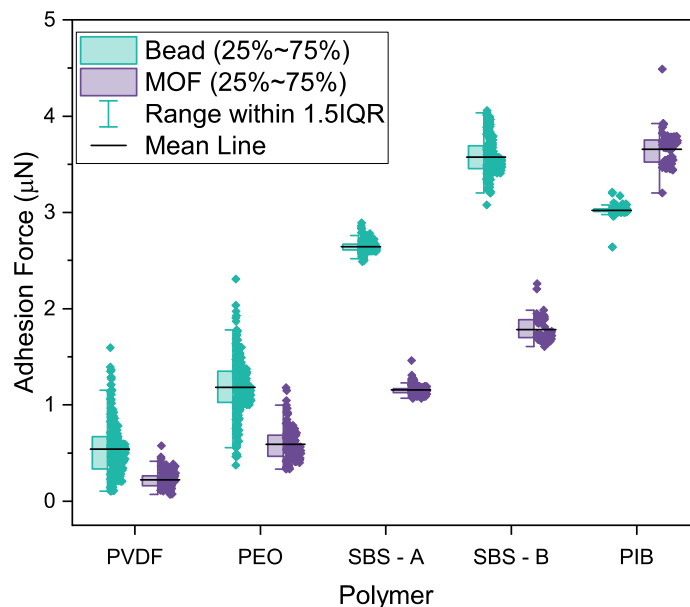


Figure S7. Box and whisker plots including all data points of adhesion force measured by both the silica bead (teal) and MOF (purple)-tipped probes on different polymer. Each box represents the middle 50% of data and the whiskers represents \pm an additional 1.5 interquartile range (includes 99.3% of data). Each experimental condition depicts > 200 measurements.

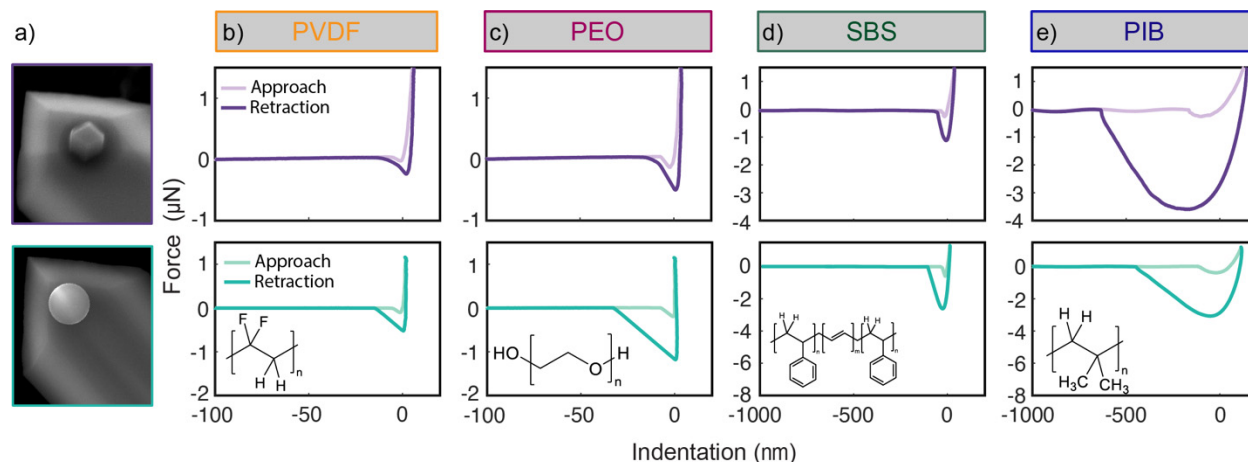


Figure S8. a) SEM images of the MOF-tipped cantilever (top) and the bead-tipped cantilever (bottom). (b-e) Force-indentation curves on surfaces PVDF, PEO, SBS and PIB, respectively with the MOF-tipped cantilever on the top row and with the bead-tipped cantilever on the bottom row.

References

- Saliba, D.; Ammar, M.; Rammal, M.; Al-Ghoul, M.; Hmadeh, M., Crystal Growth of ZIF-8, ZIF-67, and Their Mixed-Metal Derivatives. *J. Am. Chem. Soc.* **2018**, 140, 1812-1823.
- V. Saygin, B. Xu, S. Andersson, K.A. Brown, "Closed-Loop Nanopatterning of Liquids with Dip-Pen Nanolithography", *ACS Applied Materials & Interfaces*, **2021**, 13, 14710-14717.