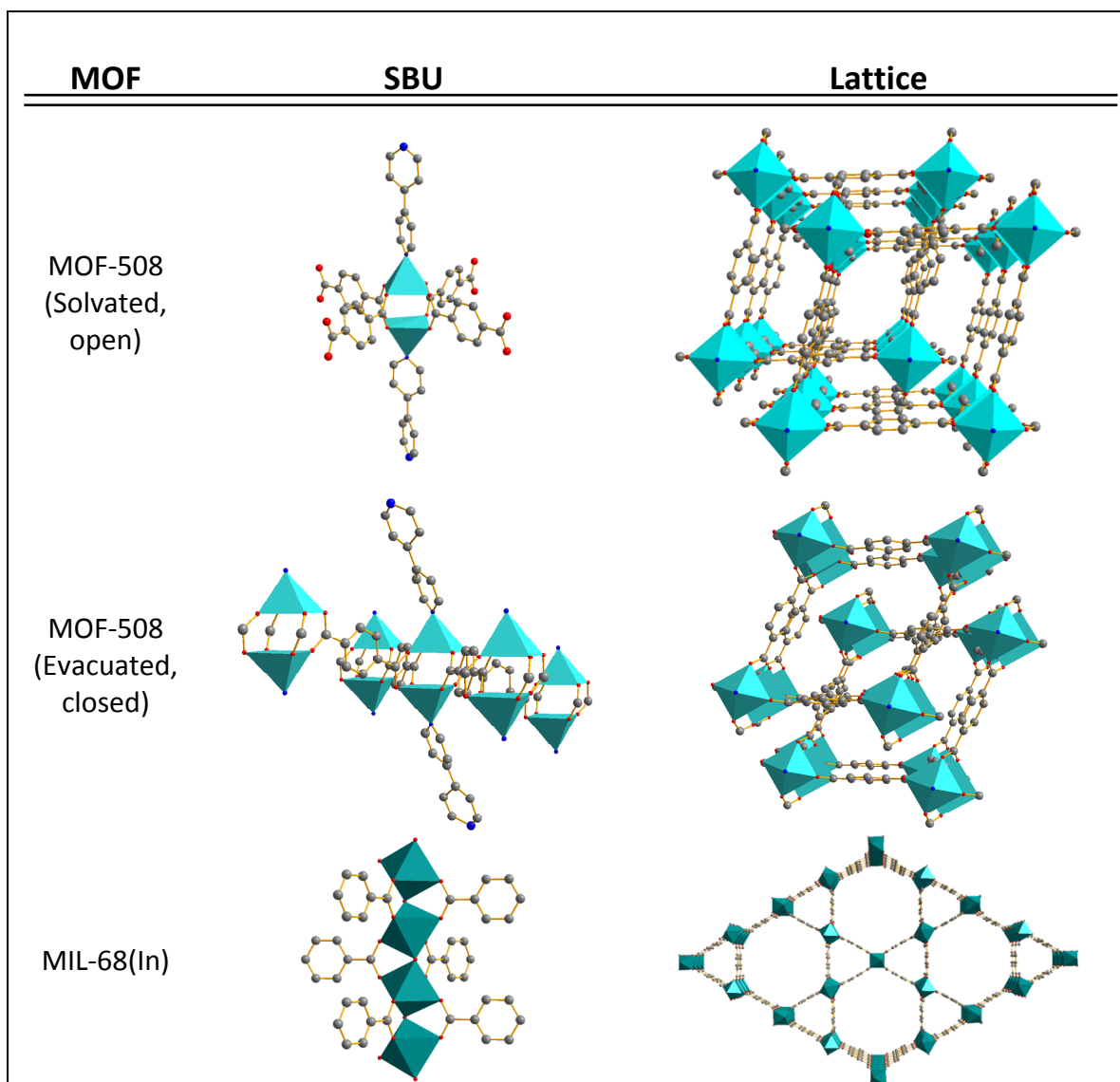


Electronic Supplemental Information for:

Ordered metal nanostructure self-assembly using metal-organic frameworks as templates

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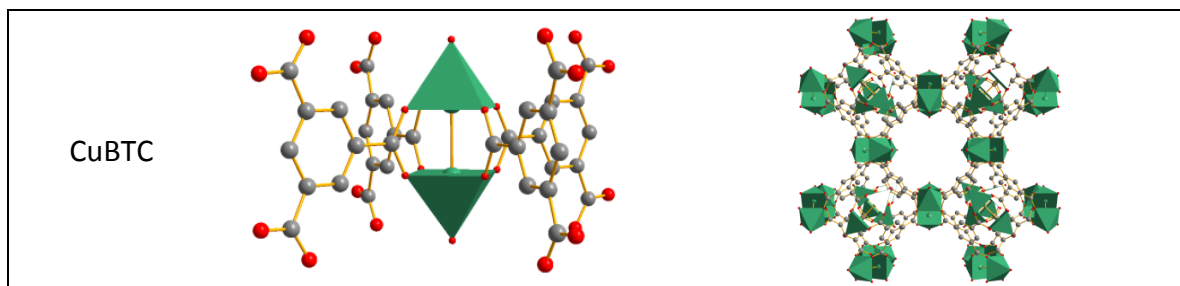


Table S1. Structure of each MOF used in the study, including the secondary building unit (SBU) and the lattice. In the MOF-508 structures the aqua tetrahedra represent zinc ions, the blue spheres are nitrogen, the red spheres are oxygen and the grey spheres are carbon, and these colors for oxygen and carbon are the same in the other MOFs. In MIL-68(In) the teal octahedra represent indium ions and in CuBTC the green tetrahedra represent copper ions.

Methods

MOF Synthesis. All reagents were purchased from Sigma-Aldrich or Acros Organics, and solvents were purchased from Fisher Scientific and used without purification.

Cu(BTC): Copper(II) nitrate trihydrate (2.9 g, 12 mmol, 1.5 eq.) is dissolved in 25 mL of nanopure water. Trimesic acid (1.68 g, 8 mmol, 1 eq.) is dissolved separately in 25 mL of 200 proof ethanol. The solutions are mixed in a pyrex media jar and capped tightly. The reaction vessel is sealed in a thick-walled PTFE jar for secondary containment, and the apparatus is placed in an oven at 110 °C for 24 hours. The blue crystalline precipitate is filtered and washed 3x with ethanol, 3x with water, and allowed to air dry for 3 days. The reaction yield is 75% based on copper. The crystals are activated under low vacuum (10^{-1} Torr) at 180 °C overnight. Note that Cu(BTC) is very hygroscopic and re-exposure to ambient atmosphere will cause rapid re-adsorption of water vapor. The powder x-ray diffraction pattern is consistent with the literature. Activated Cu(BTC) was found to have a Langmuir surface area of 1352 m²/g.

MOF-508: Zinc(II) nitrate hexahydrate (703 mg, 2.3 mmol, 1 eq.), terephthalic acid (393 mg, 2.3 mmol, 1 eq.), and 4,4'-dipyridyl (185 mg, 1.2 mmol, 0.5 eq.) are dissolved in 200 mL of 1:1 ethanol/DMF in a pyrex media jar. The jar is capped tightly and placed in a 90 °C oven for 24 hours. Upon completion, the white crystalline powder is filtered and washed with 3 x 30 mL DMF then 2 x 30 mL hexanes. The yield as synthesized based on zinc is 82%. The framework is activated under low vacuum (10^{-1} Torr) at 180 °C overnight. Both the as synthesized and activated powder x-ray diffraction patterns are consistent with the literature.²³ Activated MOF-508 was found to have a Langmuir surface area of 592 m²/g.

MIL-68(In): Indium(III) nitrate pentahydrate (2.45 g, 6.3 mmol, 1 eq.) and terephthalic acid (1.2 g, 7 mmol, 1.15 eq.) are dissolved in 30 mL DMF in a pyrex media jar with sonication and heating. The reaction vessel is tightly capped and placed in an oven at 100 °C for 2 days. The MOF precipitates in large (200 µm) crystallites, which are allowed to cool and are then filtered and washed with DMF. Yield based on Indium is 80%. The MOF is activated under low vacuum (10^{-1} Torr) at 180 °C overnight and gives an x-ray powder diffraction pattern consistent with the literature.²² Activated MIL-68(In) was found to have a Langmuir surface area of 956 m²/g.

Ag Infiltration. In a typical infiltration experiment, ~100 mg of the chosen MOF was activated under low vacuum (10^{-1} Torr) at 180 °C for 16 hours, then further evacuated at room temperature on a schlenk apparatus (10^{-2} Torr.) Ag(I) nitrate (256 mg, 1.5 mmol) was dissolved in 500 μ L nanopure water then diluted to 3 mL with 200-proof ethanol to generate a 0.5 M AgNO₃ solution in 5:1 ethanol/water. The Ag salt solution was then cannulated into a glass vial containing the evacuated MOF to generate a slurry. The reaction vessel was backfilled with N₂, sonicated for 2 minutes to ensure thorough mixing, then placed on a shaker and agitated 16 hours at 250 rpm. Following thorough washing to remove excess salt or unbound Ag particles, the samples were reactivated at 180 °C at 10^{-1} Torr for 16 hours. Alternatively, for best results in generating nanowires, reactivation of the Ag@MOF materials is carried out under vacuum at room temperature for 2 days.

TEM sample preparation, electron beam exposure. All MOF samples were suspended in ethanol and sonicated for 30 s. Copper TEM grids with a lacey carbon support film were dipped into the suspension and allowed to dry. The grids were placed in a vacuum chamber with a roughing pump overnight. A JEOL 2010F field-emission TEM operating at 200 kV was used to initiate nanostructure growth and analyze the resulting material morphology. The current density of the electron beam was held constant at 10.3 A/m² when observing nanostructure formation in the MOFs. The current density is minimized to reduce the speed at which the MOFs break down, but sufficiently bright to visualize the break down and coalescence effects in real time.

Ag@MIL-68(In) – Nanowire formation along crystal defects

The nanowire (dark contrast line) shown in Fig. S1 may have formed as a result of a defect. A close-up of the nanowire (Fig. S1 inset), which is 4.3-nm in diameter, reveals silver nanoparticles linked together in a manner similar to a string of pearls. Video S1 shows a nanowire forming as a result of a defect in real time. A corner evident on the left side of this crystal indicates that a change in growth habit is present, possibly a dislocation or a twin. Such defects may provide an environment in which silver can preferentially collect and coalesce.

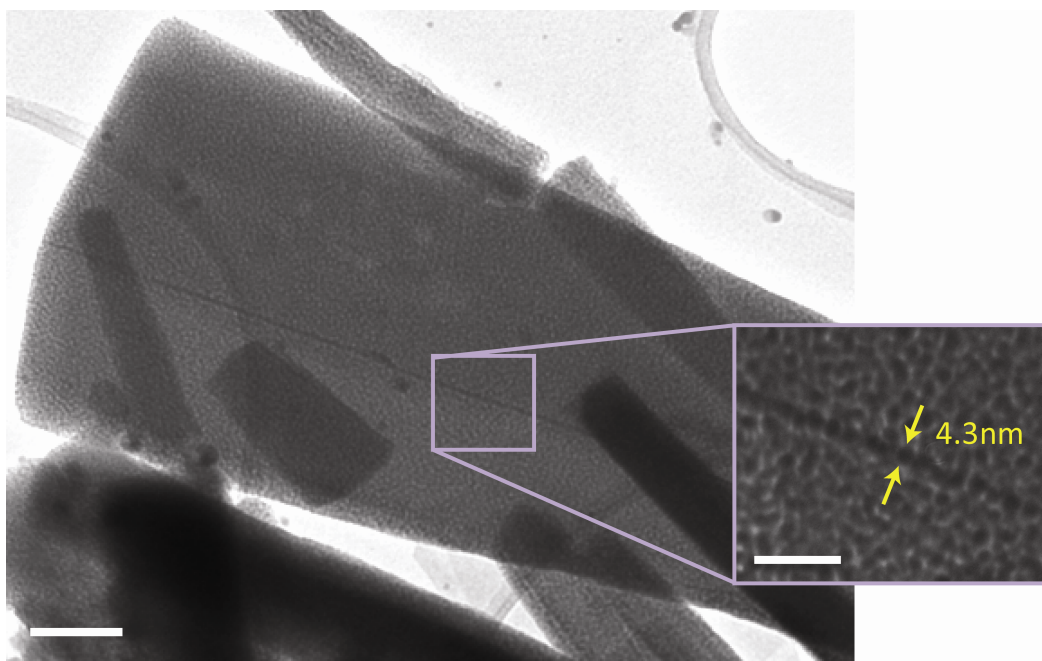


Figure S1. TEM image of Ag@MIL-68(In). The dark contrast line in the center of this MOF is a nanowire, which may have formed as a result of a defect. The scale bar is 50 nm. The inset is a close up of the nanowire. The scale bar is 20 nm.

Additional images of Ag nanowires in MOF-508

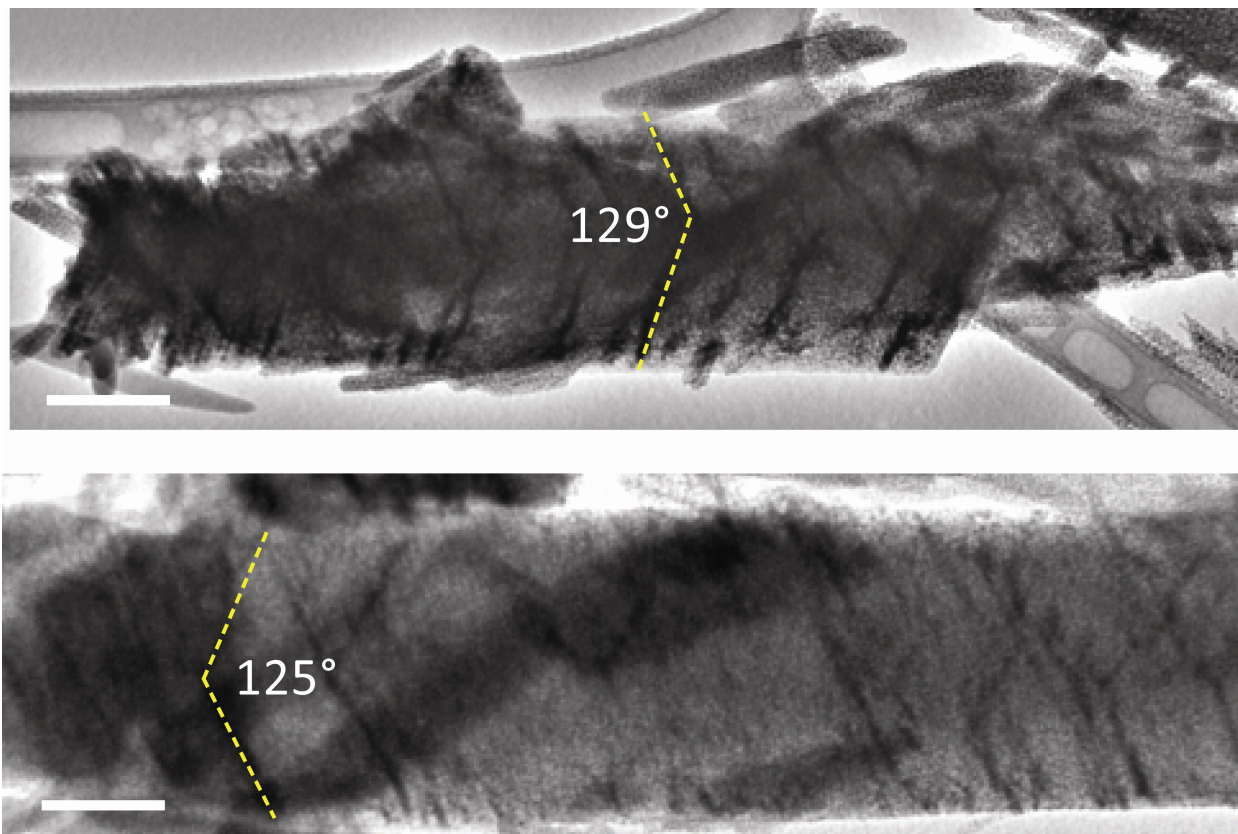


Figure S2. Silver nanowire formation in MOF-508. Nanowires that are oriented 125° relative to each other are shown in the above TEM images. Nanowires are the dark contrast lines in the images. The scale bars are 100 nm.

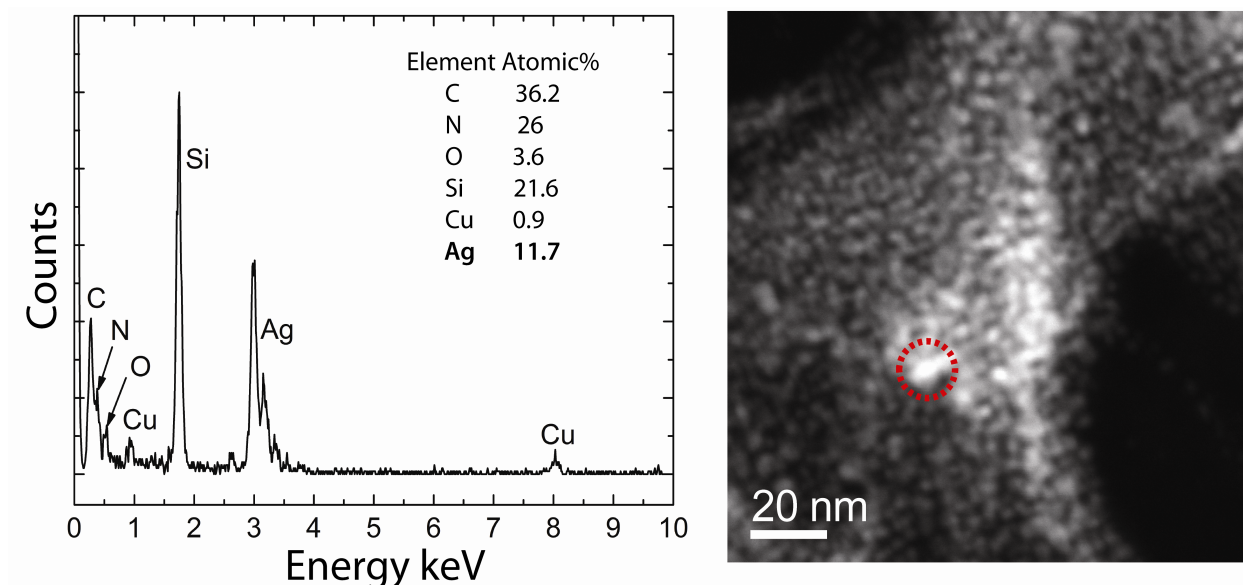


Figure S3. STEM EDS spectrum, left, of an individual silver nanoparticle (red dotted circle in the righthand figure) in Ag@Cu(BTC). Copper is present likely due to surrounding Cu nanoparticles and is only a small percentage of the overall spectrum. Silicon, nitrogen, carbon and oxygen are all present due to the silicon nitride TEM grid or from the decomposed MOF material.

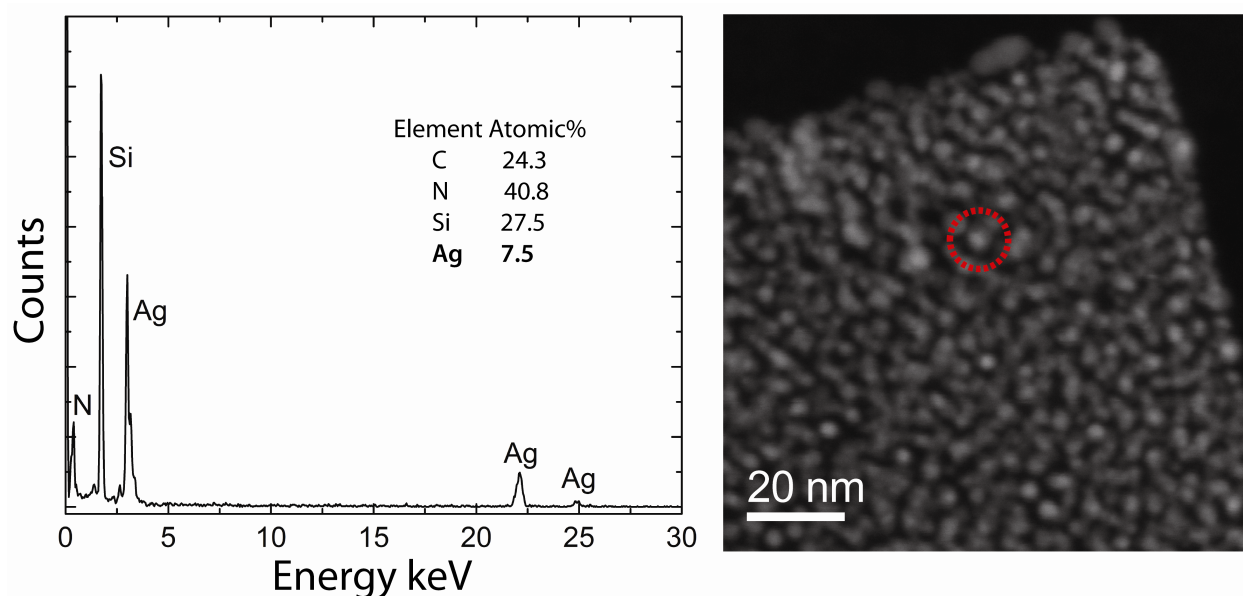


Figure S4. STEM EDS spectrum, left, of an individual silver nanoparticle (red dotted circle in the right figure) in Ag@MIL-68(In). Silicon, nitrogen, carbon and oxygen are all present due to the silicon nitride TEM grid or from the decomposed MOF material. However, indium was not observed.

TEM Information

A JEOL 2010F field-emission TEM operating at 200 kV was used to initiate nanostructure growth and to analyze the resulting material morphology. The current density of the electron beam was held constant at 10.3 A/m² when observing nanostructure formation in the MOFs. The current density was minimized to reduce the speed at which the MOFs break down, but still sufficiently bright enough to visualize the break down and coalescence effects in real time.

Calculating local heating using Bethe's formula

Bethe's formula for calculating irradiation cross sections modified for electrons is:

$$-\frac{dE}{dS} = \frac{\rho Z}{JA} * \frac{10^4}{1.18 \left(\frac{E}{J}\right)^{1/2} + 0.147 \left(\frac{E}{J}\right)} \quad (\text{eV/nm})$$

$$J = 11.53 \text{ (eV)}$$

E is the energy of the electron from the beam in eV, S is the path length of the electron through the material in nm. Z , A , and J are the average atomic number, average atomic weight, and mean excitation energy, respectively.¹ The amount of silver loading in each MOF was known from elemental analysis of the infiltrated materials and included in the in the average atomic number and atomic weight. The density, ρ , of the MOF was estimated to be 1 g/cm³, which was calculated for MOF-5.² The thermal conductivity of the MOF was estimated to be 0.3 W/Km based on theoretical values reported for MOF-5. The energy that was deposited in the material from the electron beam was used to calculate the local heat generated using COMSOL. The predicted temperature rise was ~10 K.

Additional evidence supporting this conclusion comes from differential scanning calorimetry (DSC) experiments reported previously.³ DSC shows silver within the framework does not crystallize until temperatures reach at least 200 °C. At these temperatures the framework remains intact.

Mass spectrum analysis

Mass spectrum of terephthalic acid (nominal mass 166 m/z) has two primary fragmentations. The first corresponds to the 100% mass peak at 149 m/z (-17) resulting from the loss of a hydroxyl. The second is loss of a full carboxyl group at 121 m/z (-45). (The signal at 65 m/z is the result of an unknown rearrangement.) Therefore the first bonds to break are between the carbon and aromatic ring and the carbon oxygen bonds, which are located near the O-M-O bonds, where the silver is stabilized. NIST standard electron ionization at 70 eV.⁴

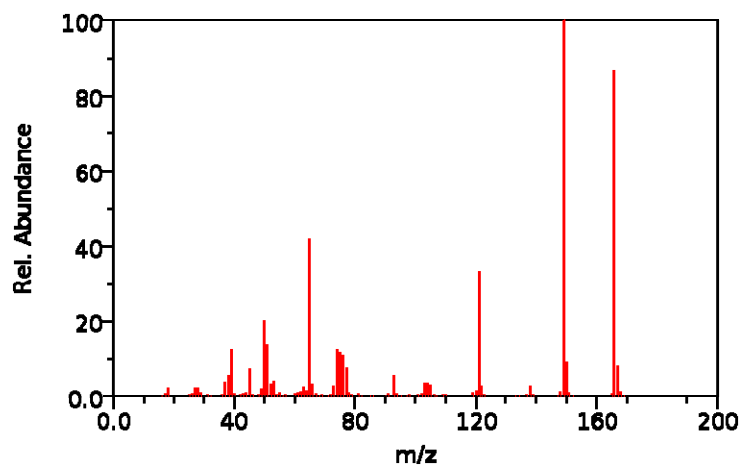


Figure S5. Fragmentation pattern of terephthalic acid.

FTIR studies

Using FTIR to probe the sample before and after silver infiltration it was found that the O-M-O bending modes near 525 cm^{-1} , which are strongly coupled to the arene vibrational modes, are perturbed by the inclusion of Ag clusters. Interaction with the Ag likely acts to decouple the M-O modes as further evidenced by slight shifts in the arene stretching modes near 1600 cm^{-1} . The one exception is Cu(BTC). The lack of an observable O-Cu-O bend or wag makes the assignment of how the Ag interacts difficult, however, there is a much larger perturbation of the arene stretches in Ag@Cu(BTC) than in the other two materials. One possible explanation is the presence of strongly adsorbed and coordinated water which alters the accessible environment of the Ag with respect to MIL-68(In) and MOF-508, which have much weaker adsorption of ambient guests. The spectra were reported previously but have been reassigned here.³

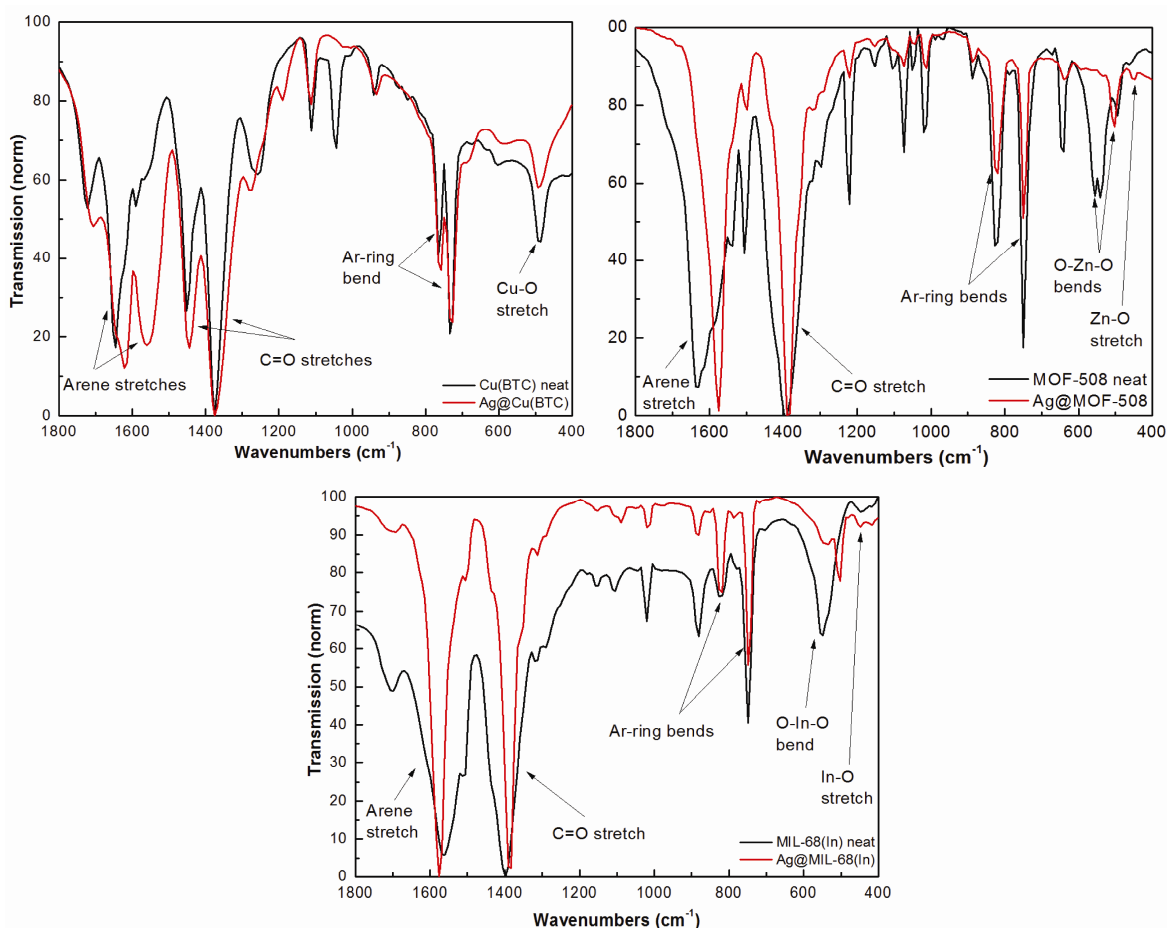


Figure S6. FTIR analysis of the MOFs before and after silver infiltration.

Micro Raman analysis

Micro Raman spectroscopy was done using a 532 nm laser. Terephthalic acid, unexposed MOF-5 and exposed MOF-5 were analyzed. MOF-5 has the same linker, terephthalic acid, as MOF-508 and therefore similar vibrational modes. After exposure to the electron beam the MOF has broken down and no vibrational modes are found that corresponded to modes from the terephthalic acid or unexposed MOF-5. This supports the mass spectroscopy results that suggest the aromatic ring is separated from the metal center. The carbon likely rearranges to form diamond and graphitic-like carbon, which is indicated by the peaks centered at 1337 cm^{-1} and 1609 cm^{-1} .^{5,6} This remaining carbonaceous material is an important component in synthesis process of the silver nanostructures because it acts as a barrier limiting further coalescence.

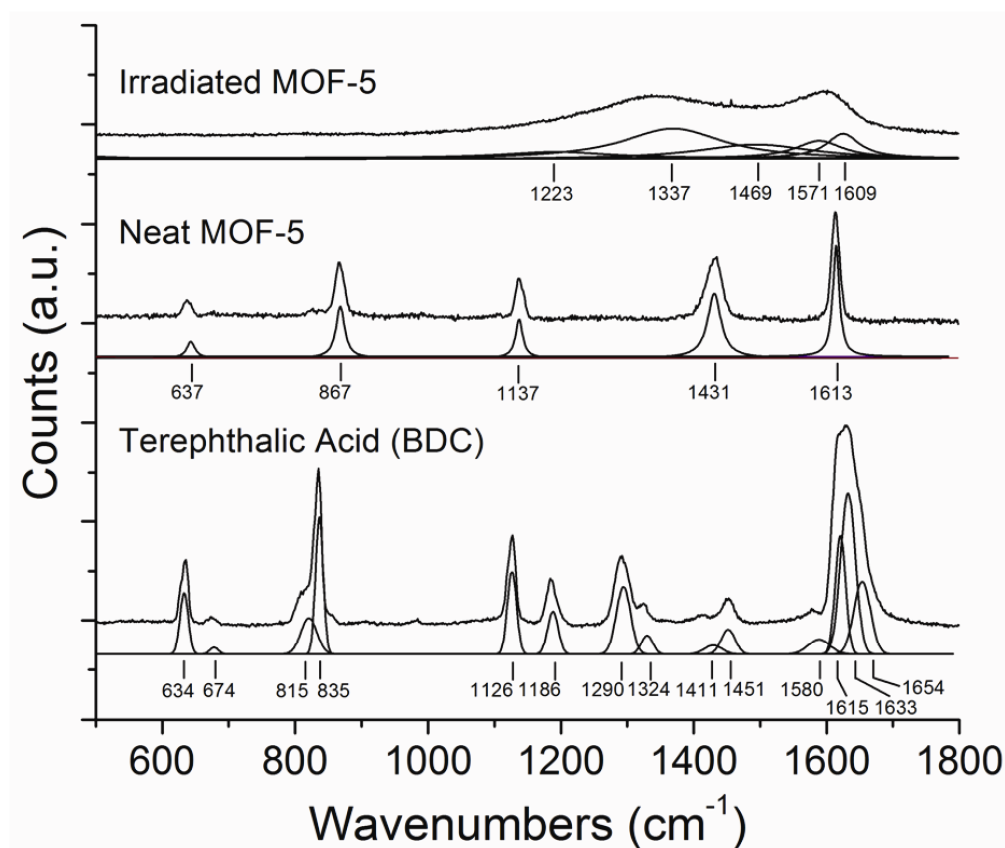


Figure S7. Raman spectra of terephthalic acid, neat MOF-5 and irradiated MOF-5.

XRD of neat vs. Ag@MOF

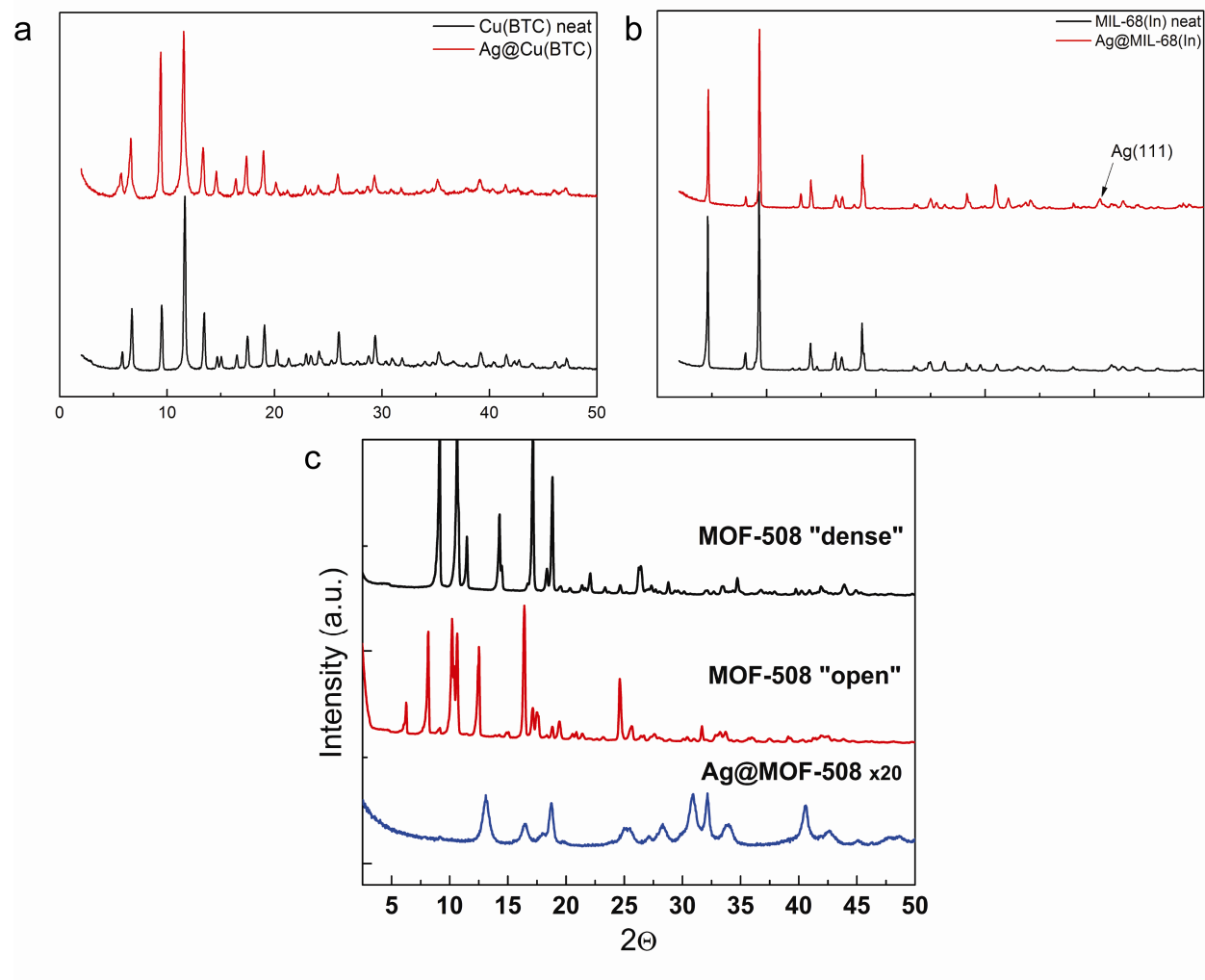


Figure S8. XRD patterns of neat and infiltrated MOFs. a): Cu(BTC); b) MIL-68; c) MOF-508.

Three smaller pores in MOF-508

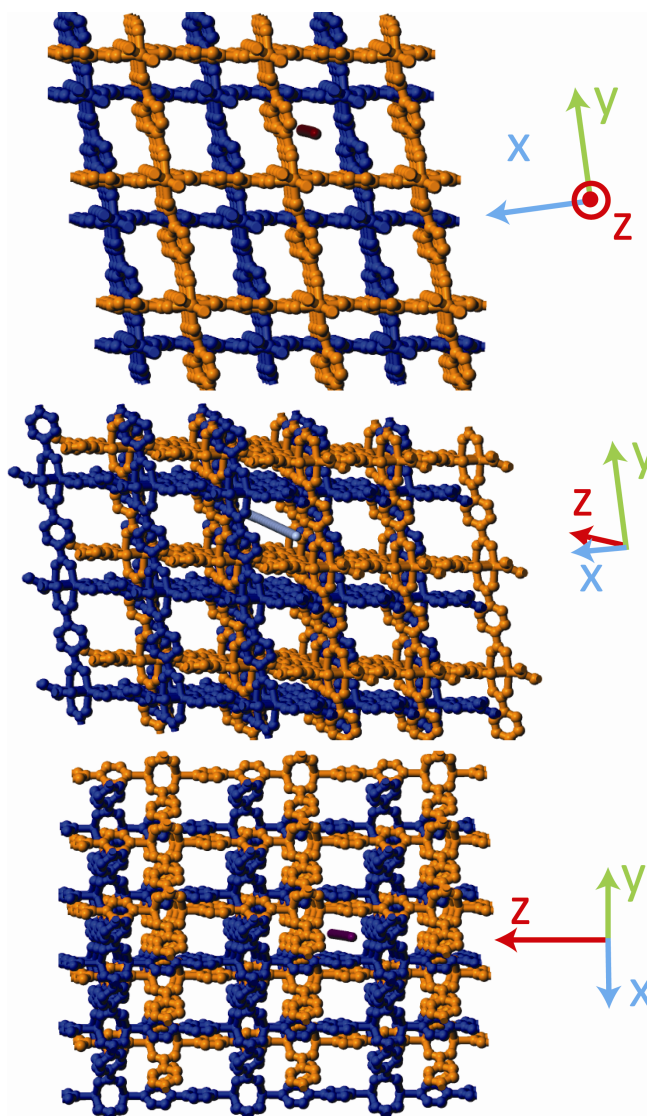


Figure S9. Three smaller pores in MOF-508 are unfavorable for nanowire formation. These pores may be responsible for nanoparticle nucleation.

Pores in evacuated (closed) MOF-508

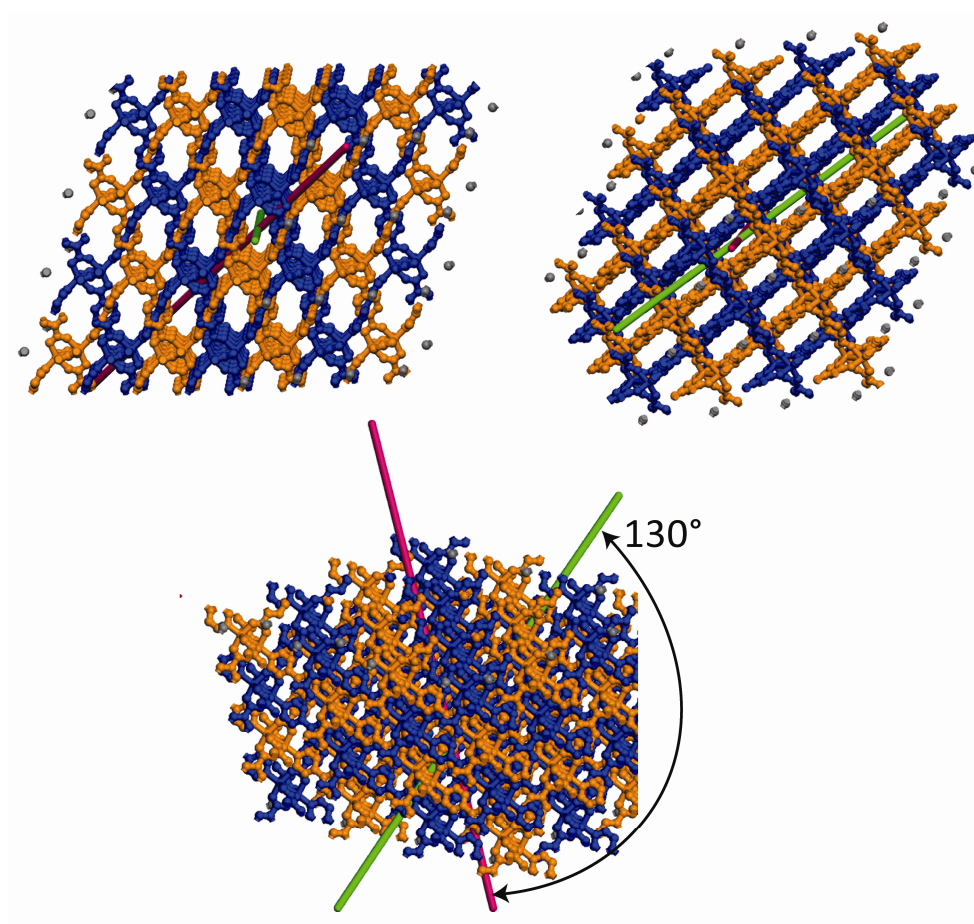


Figure S10. Pores in evacuated MOF-508. The pores that are favorable for nanowire formation are available in both the open and closed forms of the MOF. The pores in the closed framework are in nearly the same orientation as the open framework forming an angle of 130°.

MIL-68(In) oriented perpendicular to the 1-D pores

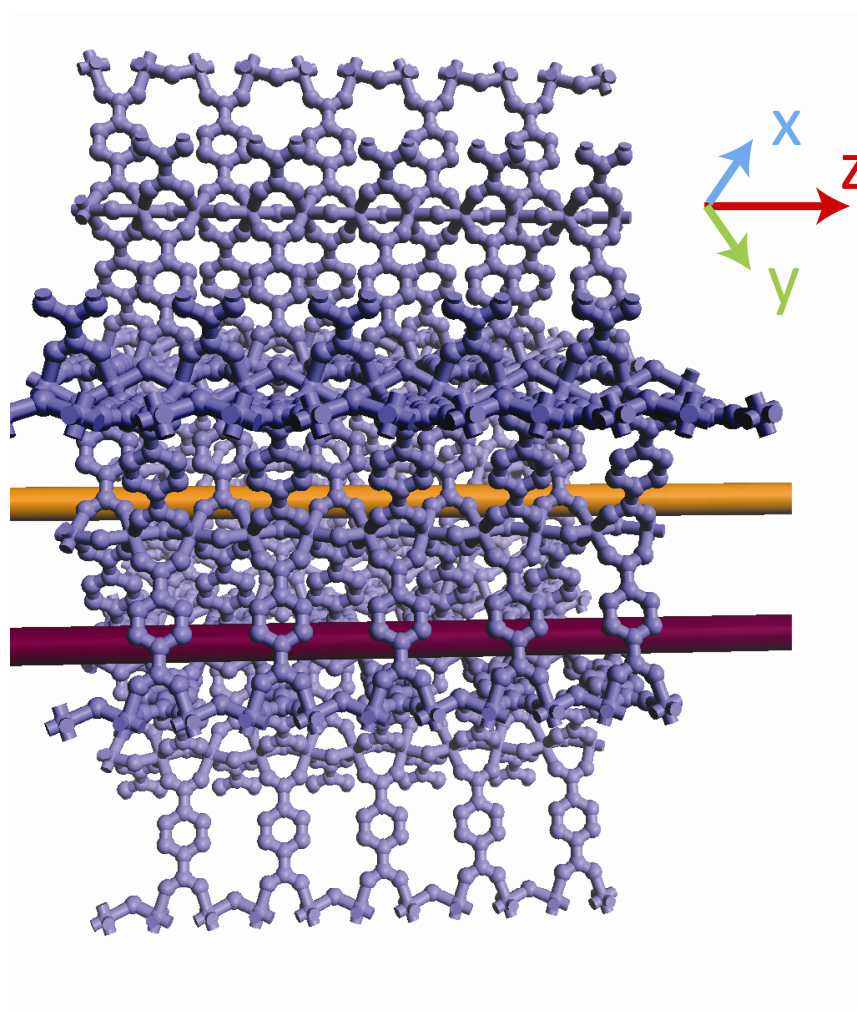


Figure S11. MIL-68(In) oriented perpendicular to the one-dimensional pores. The structure of MIL-68(In) does not favor inter-pore diffusion of silver. The aromatics are aligned along the pore wall making it difficult for silver to move from pore to pore.

Silver nanoparticle diffusion in MOF-508

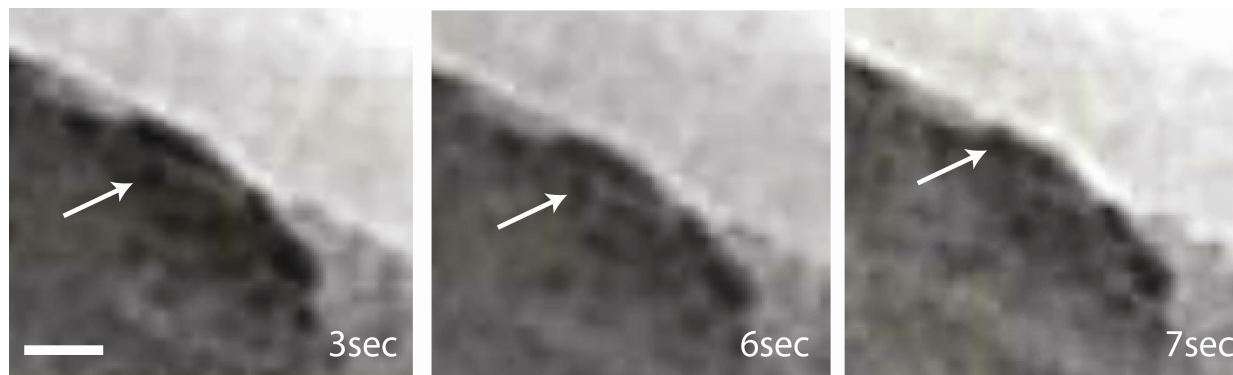


Figure S12. Silver nanoparticle mobility in MOF-508. After silver has coalesced in MOF-508 to form nanoparticles a few nanometers in diameter, they are still mobile. Three frames from video S3 shows a nanoparticle diffusing.

Videos

Video S1: Breakdown and silver coalescence in MIL-68(In)

Video S2: Breakdown and silver coalescence in MIL-68(In) showing twin defect nanowire formation

Video S3: Breakdown and silver coalescence in MOF-508

References

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