

Supporting Information

Post-Metalated Zirconium Metal Organic Frameworks as a Highly Potent Bactericide

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Experimental Section:

General Methods. 2,2'-bipyridine-5,5'-dicarboxylic acid (H_2bpydc) and 1, 2, 4, 5-benzenetetracarboxylic acid in addition to all the other reagents and solvents, were purchased from Sigma-Aldrich and used without further purification. The Infrared spectroscopy (IR) spectra were recorded on a FT-IR spectrometer Thermo-Nicolet working in the transmittance mode, in the 450-3950 cm^{-1} range. The free and silver-metalated MOFs were prepared as pellets and analyzed by a JASCO V-570 UV-vis-NIR spectrophotometer. UV-visible spectra of the metalated compounds showed a wide band centered around 450 and 550 nm for UIO-67- $bpydc-Ag$ and UIO-66-COO- Ag , respectively. As for the parent MOF materials, the white powder, indeed, did not absorb in the visible region. Thermogravimetric Analysis (TGA) was performed with Netzsch TG 209 F1 Libra apparatus. The analyses were recorded in N_2 flow from 30 to 800 °C at a heating rate of 3 K. min^{-1} . Powder X-ray diffraction (PXRD) patterns were collected using a Bruker D8 advance X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) at 40 kV, 40 mA (1600 W) using Cu $K\alpha$ radiation ($k = 1.5418 \text{ \AA}$). Scanning electron microscopy (SEM) was performed using a MIRA3 Tescan electron microscope, where the samples were first coated with a thin layer (10 nm) of gold. Nitrogen sorption measurements were carried out at 77 K. Prior to the measurements, the samples were activated under dynamic vacuum at 110°C for 6 hours. Silver concentration was determined using Atomic Absorption Spectroscopy conducted with a thermo elemental analyzer. Approximately 2 mg of the sample were digested

with sonication in a mixture of water (10 mL) and HF (100 μ L). The digested solution was used directly for atomic absorption test.

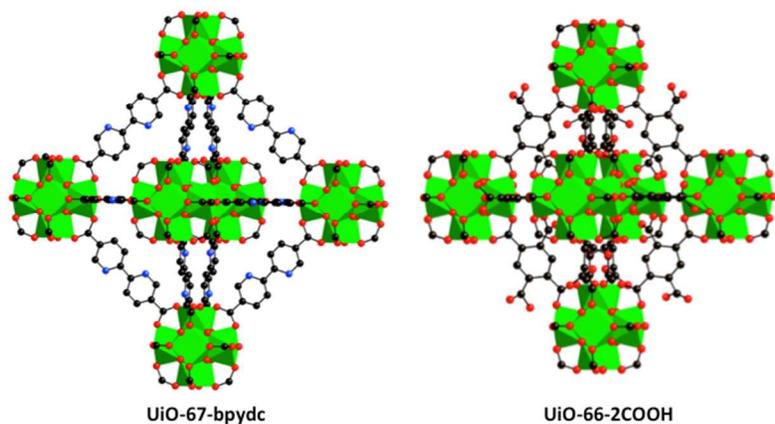


Figure S1. Crystal structures of UiO-67-bpydc and UiO-66-2COOH

Synthesis of UiO-67-bpydc In a 4 mL scintillation vial, H₂bpydc (10 mg, 0.04 mmol) was dissolved in 2 mL N, N-Dimethylformamide and sonicated for 10 minutes. Following sonication, zirconyl chloride octahydrate (ZrOCl₂ · 8H₂O) (13.0 mg, 0.04 mmol) was added to the solution. After 10 minutes further sonication, formic acid (0.7 mL) was added to the solution. The reaction mixture was sonicated for a couple of minutes, and then heated in an oven at 130°C for 24 hours. The resulting white microcrystalline powder was centrifuged and the supernatant discarded.

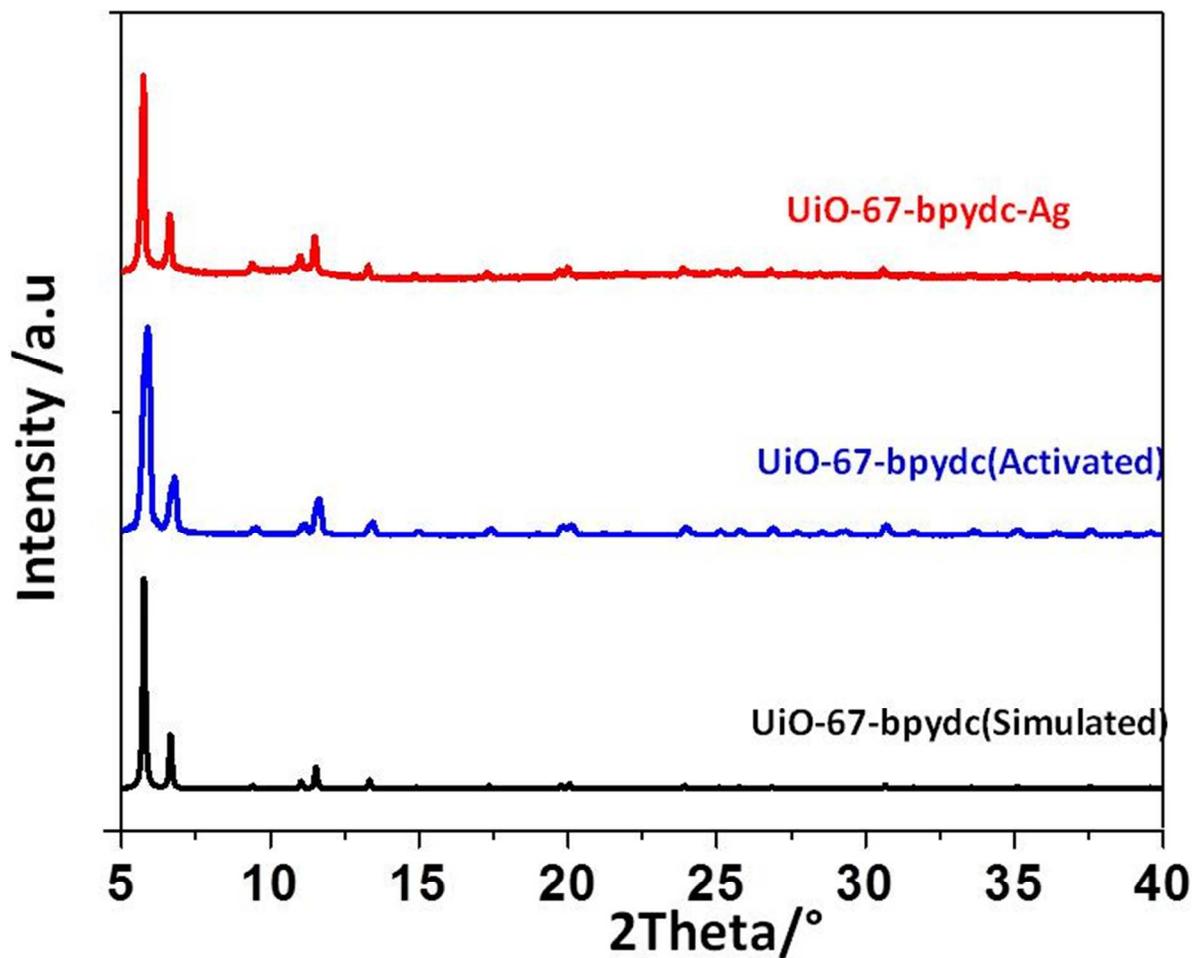


Figure S2. PXRD patterns of the simulated UiO-67-bpydc compared to the activated UiO-67-bpydc and the Ag- metallated UiO-67-bpydc (UiO-67-bpydc-Ag).

N₂ Isotherm of UiO-67-bpydc

The obtained white microcrystalline powder of UiO-67-bpydc was purified by washing with DMF for three days in order to remove the unreacted materials, then the DMF was exchanged with MeOH via solvent exchange process for 3 days (3 times /day). The obtained product was collected and dried under dynamic vacuum at 110 °C for 12 h.

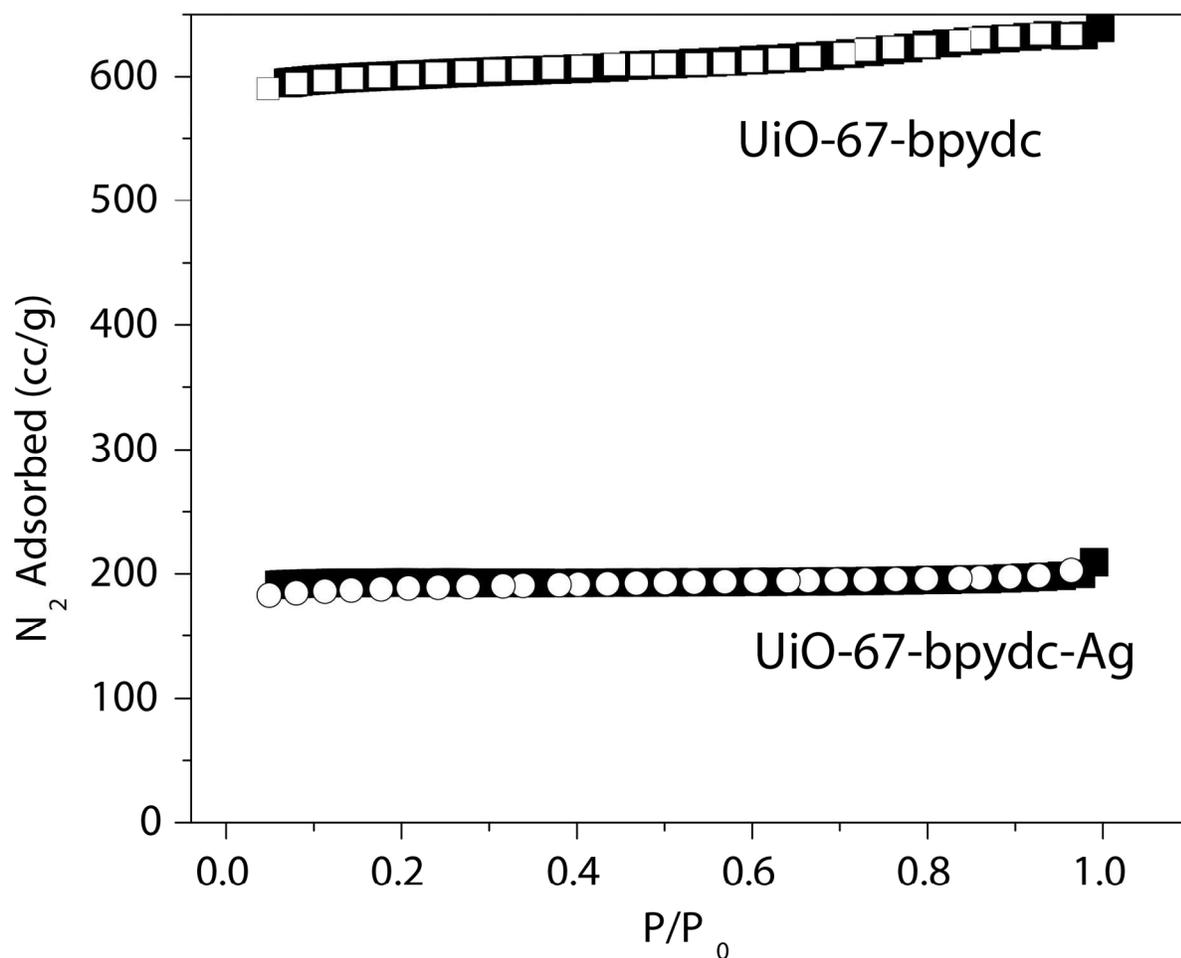


Figure S3. N₂ isotherms at 77 K of UiO-67-bpydc and UiO-67-bpydc-Ag

Synthesis of UiO-66-2COOH In a 20 mL scintillation vial, 1, 2, 4, 5-benzenetetracarboxylic acid (47.0 mg, 0.184 mmol) was dissolved in 4 mL DMF and sonicated for 10 minutes. Following sonication, ZrOCl₂·8H₂O (59.5 mg, 0.184 mmol) was added to the solution. After 10 minutes of further sonication, formic acid (4 mL) was added to the solution. The reaction mixture was sonicated for a couple of minutes, and then heated in an oven at 130°C for 5 hours. The resulting white microcrystalline powder was purified by washing with DMF then with MeOH. The obtained product was collected by centrifugation and dried under dynamic vacuum at 80 °C. In order to ensure that only 2 of the 4 carboxylate binding units are involved in the formation of the mof structure, a Powley refinement was performed based on the UiO-66 model (fig S1).

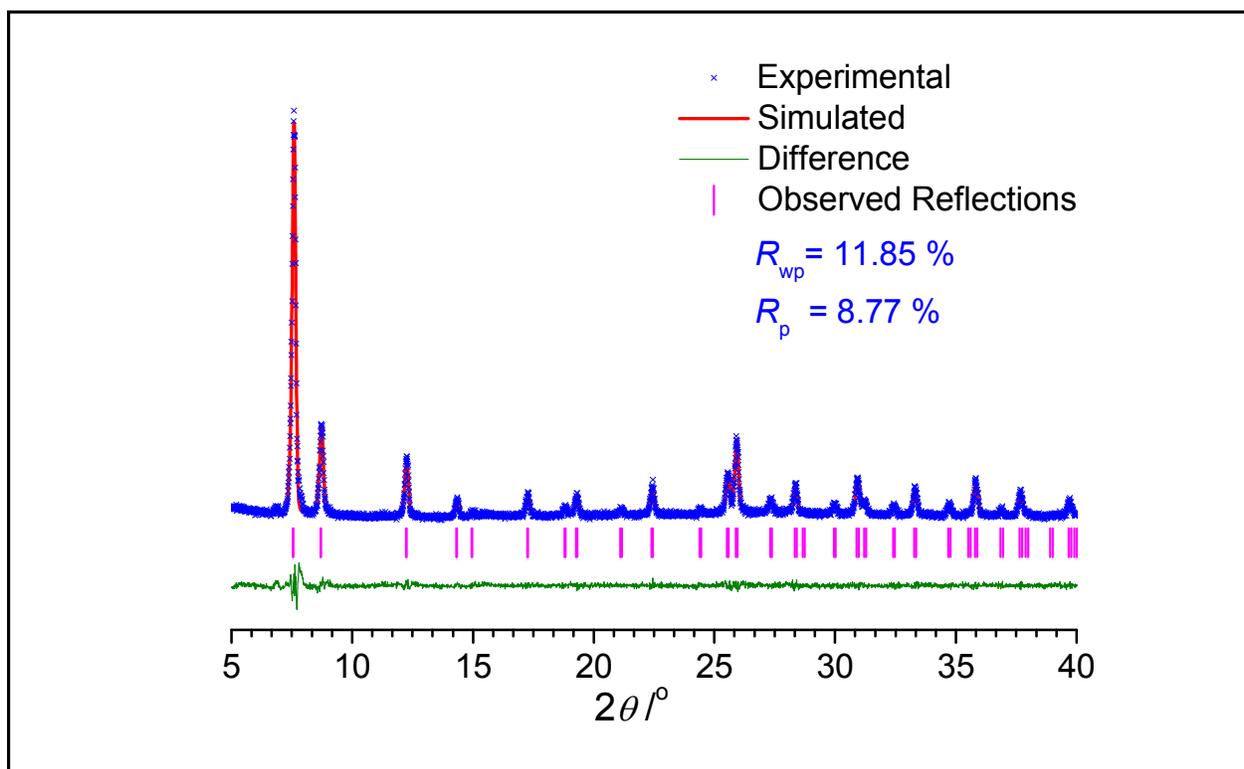


Figure S4. Powley refinement of UiO-66-2-COOH (blue and red: experimental and calculated PXRD patterns, Pink bars: Bragg peak positions, green: $I_{obs}-I_{calc}$ difference ($R_p= 8.77 \%$). The resulting unit-cell parameters are $a = 20.8375 (5) \text{ \AA}$, (cubic, S.G. F23).

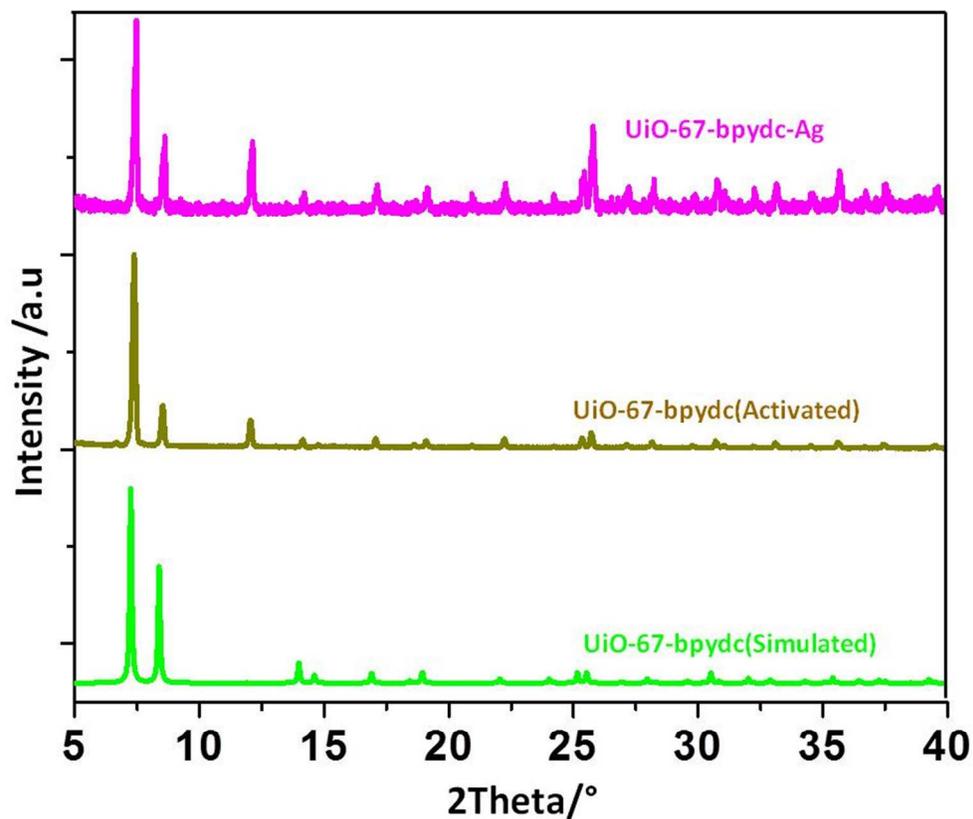


Figure S5. PXRD patterns of the simulated UiO-66-2-COOH compared to the activated UiO-66-2-COOH and the Ag- metallated UiO-66-2-COOH (UiO-66-2-COO-Ag).

N₂ Isotherm of UiO-66-2-COOH

The obtained white microcrystalline powder of UiO-66-2-COOH was purified by washing with DMF for three days in order to remove the unreacted materials, then the DMF was exchanged with MeOH via solvent exchange process for 3 days (3 times /day). The obtained product was collected and dried under dynamic vacuum at 100 °C for 12 h.

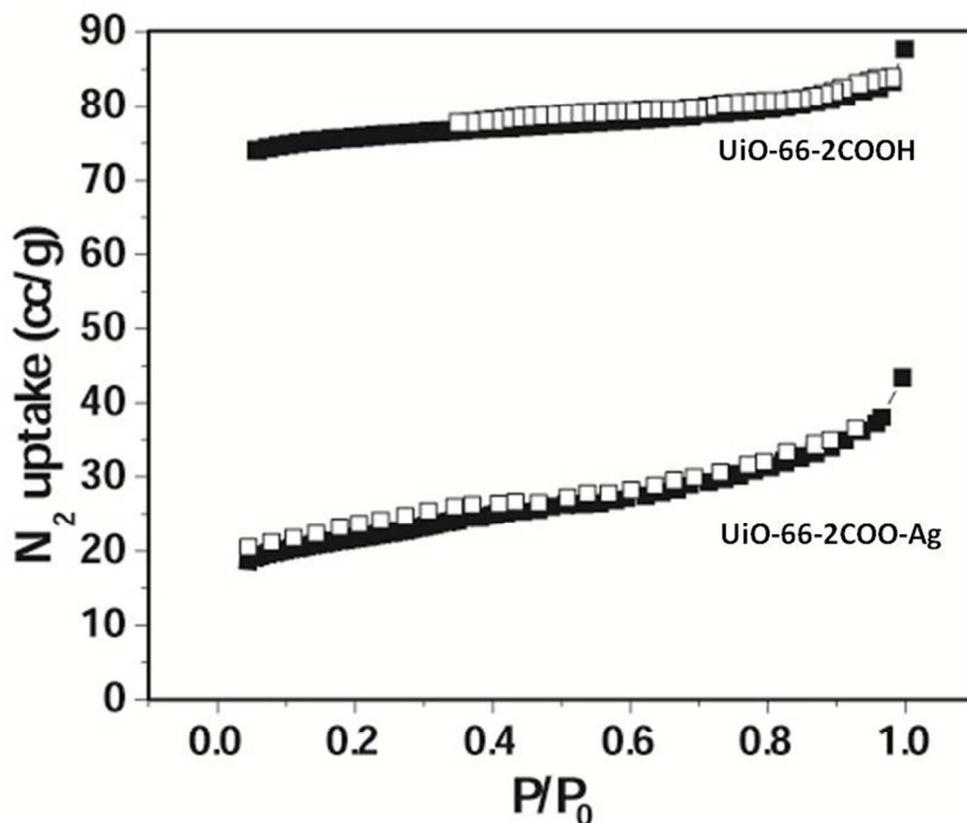


Figure S6. N₂ isotherms at 77 K of UiO-66-2-COOH and UiO-66-2-COO-Ag

Synthesis of UiO-67-bpydc-Ag In a 20 mL scintillation vial, silver nitrate (AgNO₃) (40 mg) was dissolved in MeOH (10 mL) by sonication for 10 minutes. UiO-67-bpydc (20 mg) was then added to the silver solution. The reaction mixture was then stirred on a hot plate at 50°C for 20 hours. The resulting brownish microcrystalline powder was centrifuged and the supernatant discarded. The solids were washed with MeOH for two days, and the solution was exchanged with fresh MeOH two times per day. The solids were collected by centrifugation and dried under dynamic vacuum at 110 °C.

Synthesis of UiO-66-2COO-Ag In a 20 mL scintillation vial, silver nitrate (AgNO₃) (40 mg) was dissolved in MeOH (10 mL) by sonication for 10 minutes. UiO-66-2-COOH (20 mg) was then added to the silver solution. The reaction mixture was then stirred on a hot plate at 50°C for 20 hours. The resulting

brownish microcrystalline powder was centrifuged and the supernatant discarded. The solids were washed with MeOH for two days, and the solution was exchanged with fresh MeOH two times per day. The solids were collected by centrifugation and dried under dynamic vacuum at 110 °C.



Figure S7. UiO-66-2-COOAg (left) and UiO-67-bpydc-Ag (right) suspended in MeOH.

Scanning Electron Microscopy:

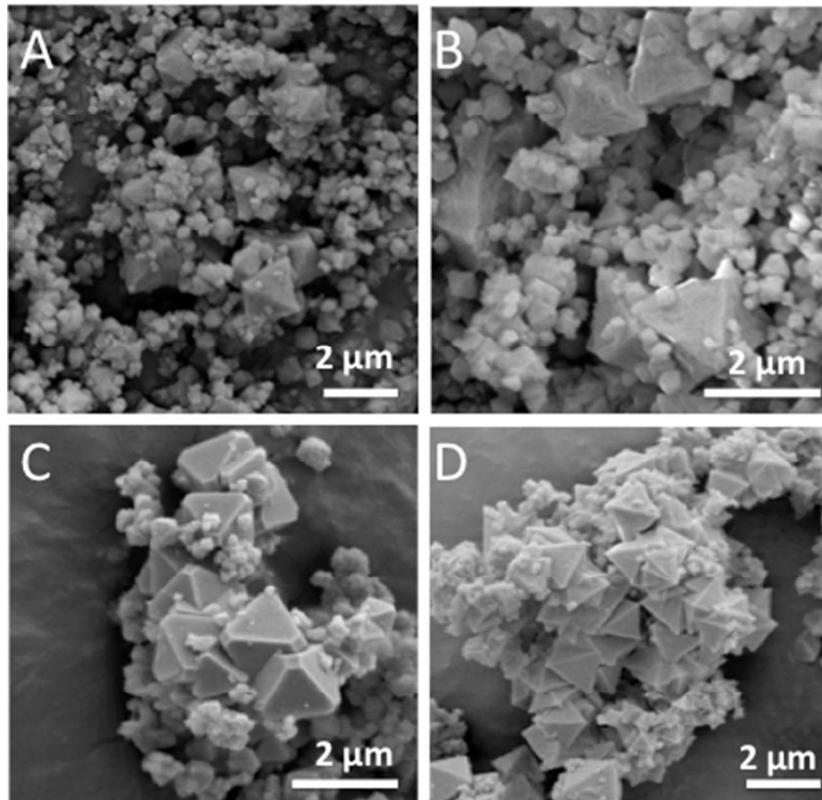


Figure S8. SEM images of UiO-67-bpydc (A), UiO-67-bpydc-Ag (C), UiO-66-2COOH (B), UiO-66-2COO-Ag (D).

Silver release from UiO-66-2COOAg and UiO-67-bpydc-Ag over 24 h:

The concentration of silver released from UiO-66-2COOAg and UiO-67-bpydc-Ag crystals was determined using Atomic Absorption Spectroscopy (AAS) conducted with a thermo elemental analyzer. Six reaction mixtures composed of 2 mg of UiO-67-bpydc-Ag were suspended in 2 ml of a solution of LB Broth. The mixtures were left to stir for 30 min, 1h, 3h, 6h, 12h and 24h and then the mixtures were centrifuged and AAS was performed on the supernatant which was diluted 100 times. The obtained values are shown in figure S9. Both MOFs exhibit continuous release of silver cations which can explain their high antibacterial activity.

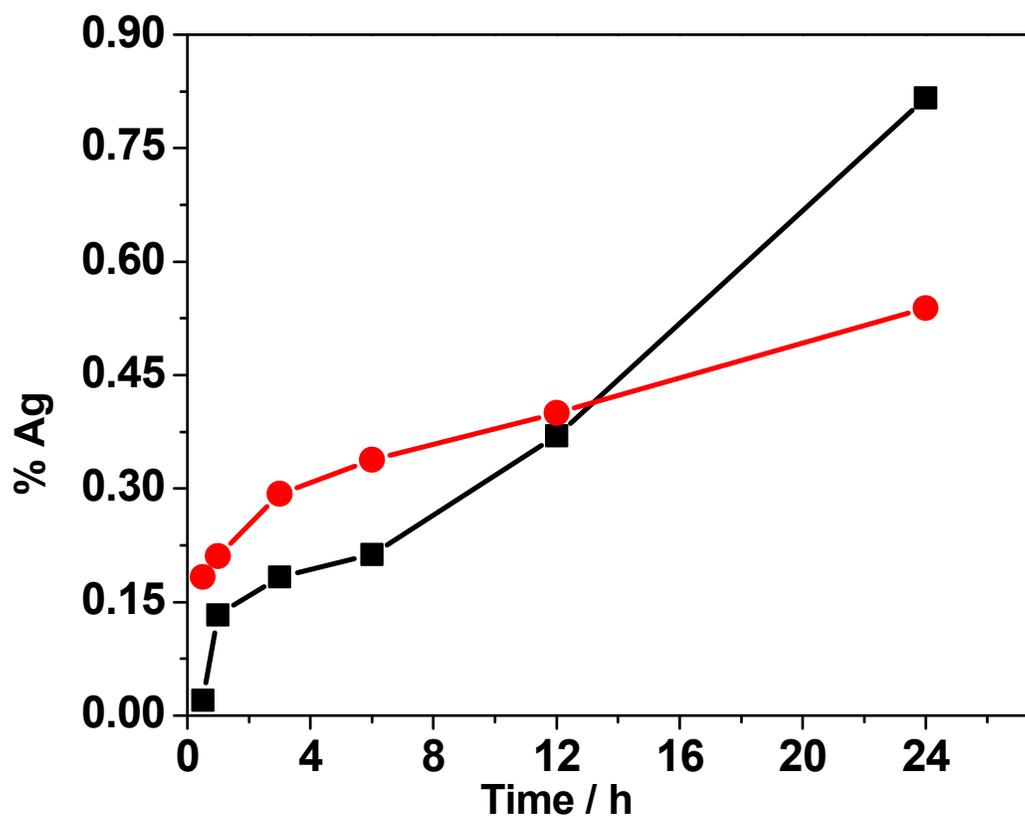


Figure S9. Percent of silver cations released from UiO-66-2COOAg (red) and UiO-67-bpydc-Ag (black) over 24 h.

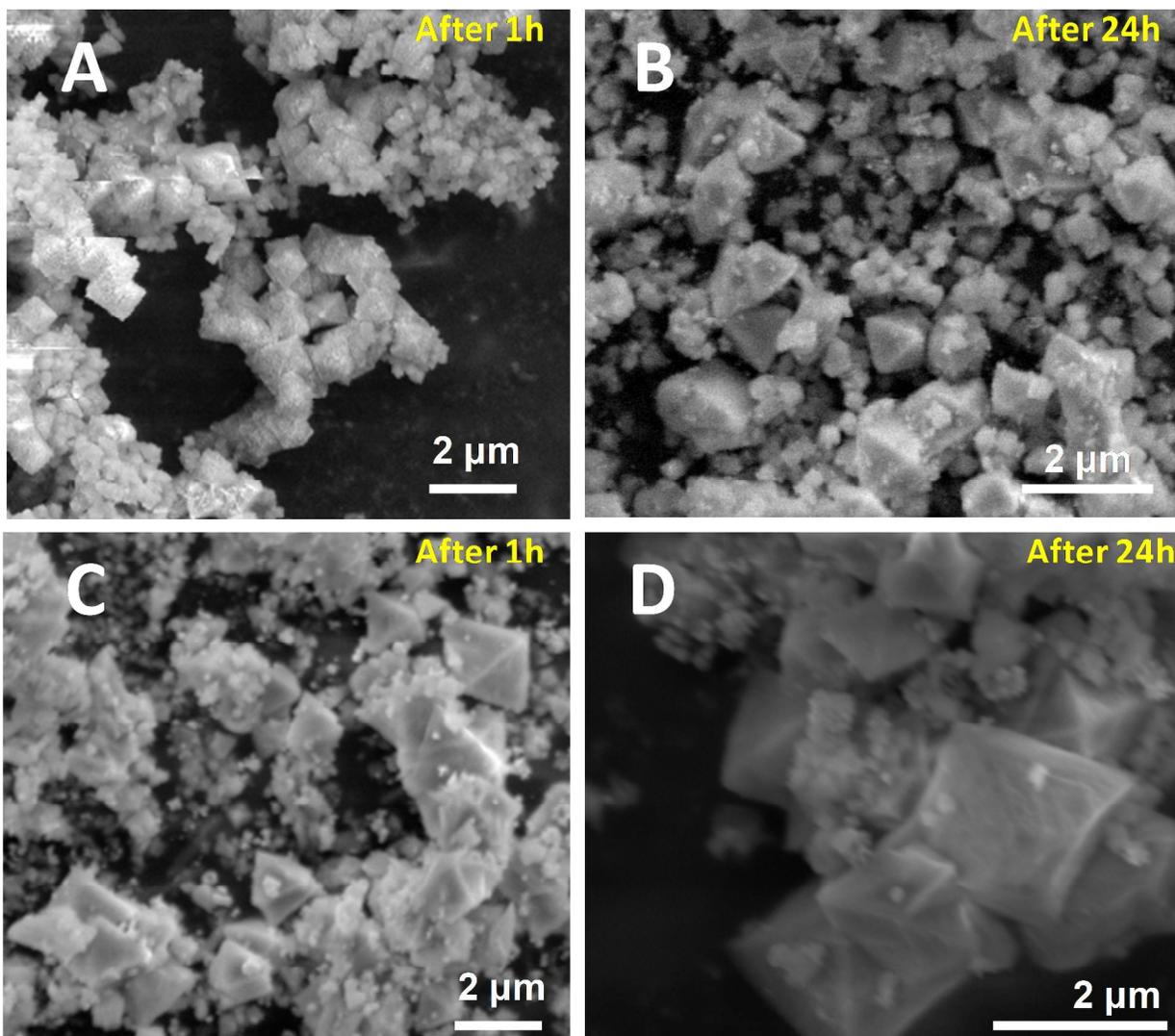


Figure S10. SEM images of UiO-67-bpydc-Ag (A and B) and UiO-66-2COO-Ag (C and D) after dispersion in LB Broth solution for 1h and 24 h.