

Multivariate Stratified Metal-Organic Frameworks: Diversification Using Domain Building Blocks

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1. General methods

Powder X-ray diffraction patterns were collected using a Bruker AXS D8 Discover powder diffractometer at 40 kV, 40 mA for Cu K α ($\lambda = 1.5406 \text{ \AA}$) with a scan speed of 0.20 sec/step from 3 to 45° at a step size of 0.02°. The data were analyzed using the EVA program from the Bruker Powder Analysis Software package. The simulated powder patterns were calculated using Mercury 3.8 based on MOF crystal structures.

^1H NMR spectra were obtained using Bruker Avance III 300/400/500 MHz spectrometers. Chemical shifts are in parts per million (ppm) using the residual solvent peak (CDCl_3 , $\text{DMSO}-d_6$, or D_2O) as references. MOF samples were digested with $\text{DMSO}-d_6$ and a small amount of hydrofluoric acid 48%, or K_3PO_4 and D_2O .

Scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS) analyses were conducted using ZEISS Sigma 500 VP scanning electron microscope equipped with Oxford Aztec X-EDS. Samples were dispersed in ethanol, and drop cast on TEM grids (Ted Pella Inc 200 mesh carbon film copper grids Catalog No. NC0733370). The TEM grids were dried under ambient conditions before SEM-EDS studies. An STEM sample holder was used to mount the TEM grids. Secondary electron images and EDS data of the samples were collected at a working distance of 8.5 mm and an accelerating voltage of 20 kV. The EDS was acquired using 1024 channels from 0 to 20 keV. Elemental maps were collected for 10-15 minutes with a pixel dwell time of 100 μs and a pixel resolution of 1024x1024. Zirconium maps and line-scans were obtained using the Zr L α 1 line intensity at 2.0 keV. Hafnium maps and line-scans were obtained using the Hf M α 1 line intensity at 1.6 keV. Iodine maps and line-scans were obtained using the I L α 1 intensity at 3.9 keV.

Transmission electron microscopy (TEM) images used to determine size distributions of MOF crystallites were collected on an FEI Morgagni 268 operated at 80 kV with an AMT side mount CCD camera system. TEM images of NPs and NPs \subset MOF composites were collected on a JEOL JEM-2100F equipped with a Gatan Orius camera operated at 200 kV or a Hitachi 9500 ETEM equipped with a Gatan Orius camera operated at 300 kV. High angle annular dark field (HAADF) imaging and scanning transmission electron microscopy - energy dispersive X-ray spectroscopy (STEM-EDS) studies were conducted on a JEOL JEM-2100F. The EDS was acquired using 1024 channels from 0 to 20 keV. Elemental maps were collected for 10-15 minutes with a pixel dwell time of 100 μs and a pixel resolution of 1024x1024. Zirconium maps and line-scans were obtained using the Zr K α 1 line intensity at 15.7 keV. Hafnium maps and line-scans were obtained using the Hf M α 1 line intensity at 1.6 keV. Palladium maps and line-scans were obtained using the Pd L α 1 line intensity at 2.8 keV. Chlorine maps were obtained using the Cl K α 1 line intensity at 2.6 keV. Copper maps were obtained using the Cu L α 1 line intensity at 0.9 keV. Selenium maps were obtained using the Se K α 1 line intensity at 11.2 keV. Silver maps were obtained using the Ag L α 1 line intensity at 3.0 keV. Gold maps were obtained

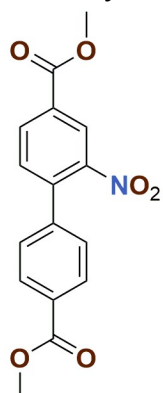
using the Au $L\alpha_1$ line intensity at 9.7 keV. Samples were dispersed in ethanol or acetonitrile, and drop cast on TEM grids (Ted Pella Inc 200 mesh carbon film copper grids Catalog No. NC0733370, or Ni grids for $Cu_{2-x}Se@UiO-67(Zr)@UiO-67(Hf)$). The TEM grids were dried under ambient conditions before TEM and STEM-EDS analyses.

Solution UV/vis spectra of Au and Ag nanoparticles were collected on an Agilent 8453 UV/Vis spectrometer equipped with deuterium and tungsten lamps. Solution UV/vis/NIR extinction spectrum of $Cu_{2-x}Se$ nanoparticles were collected on a Cary 5000 spectrophotometer (Agilent Inc.). UV/vis extinction spectra of NPs@MOF samples were collected on a CRAIC QDI 2010 microspectrophotometer. Samples dispersed in ethanol was drop cast on glass slides, and dried under ambient conditions to form a sample film. Spectra were collected on a $19 \times 19 \mu m^2$ sampling area.

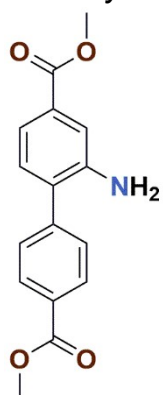
2. Syntheses and characterization of MOF ligands

Dimethyl 2-nitro-1, 1'-biphenyl-4,4'-dicarboxylate (**1**)

Compound **1** was synthesized according to literature conditions.¹

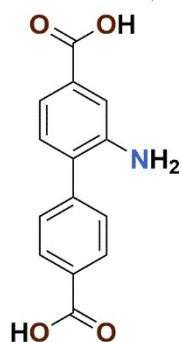


Dimethyl 2-amino-1, 1'-biphenyl-4,4'-dicarboxylate (**2**)



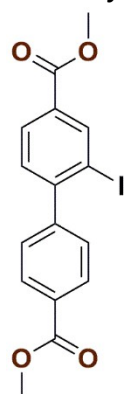
To a 100 mL schlenk flask equipped with a stir bar, were added compound **1** (710 mg, 2 mmol), 10 wt. % palladium on carbon (70 mg) and ethyl acetate (30 mL). The schlenk flask was quickly evacuated on a schlenk line and then backfilled with argon gas. This evacuation and backfill process was repeated for 3 times. The schlenk flask was then evacuated and attached to a H₂ balloon. The reaction mixture was stirred at room temperature under H₂ atmosphere and monitored via thin layer chromatography (TLC). After 6 hours, the reaction was stopped by removing Pd catalyst via vacuum filtration through a celite cake. The filtrate was concentrated *in vacuo* to yield light yellow solid compound **2** (570 mg, 93%). Compound **2** was used without further purification. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (m, 2H), 7.55 (m, 2H), 7.48 (dd, J = 7.9, 1.4 Hz, 1H), 7.45 (d, J = 1.4 Hz, 1H), 7.18 (d, J = 7.9 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.86 (s, 2H).

2-Amino-1, 1'-biphenyl-4,4'-dicarboxylic acid (**3**)



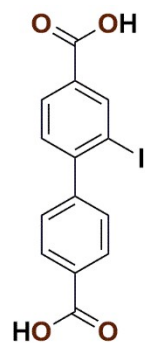
Compound **3** was synthesized using compound **2** as starting material based on literature conditions.¹ ¹H NMR (500 MHz, DMSO-*d*₆) δ 12.83 (s, 2H), 8.01 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 1.5 Hz, 1H), 7.20 (dd, J = 7.5, 1.5 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 5.17 (s, 2H).

Dimethyl 2-iodo-1, 1'-biphenyl-4,4'-dicarboxylate (4**)**



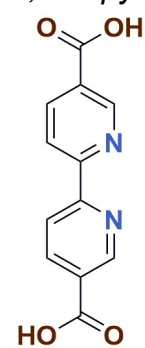
Compound **2** (790 mg, 2.77 mmol) was suspended and stirred in 15% hydrochloric acid (10 mL). NaNO₂ (220 mg, 3.2 mmol) dissolved in H₂O (3 mL) was added dropwise to the suspension at 0 °C. After stirring at 0 °C for 10 min, NaI (500 mg, 3.3 mmol) dissolved in H₂O (3 mL) was added dropwise to the reaction mixture. The reaction was then heated in oil bath at 60 °C for 20 min. Upon cooling down to room temperature, the reaction mixture was poured into iced water (50 mL). The aqueous solution was extracted with ethyl acetate (150 mL, 3x). The combined organic phase was washed with 10% Na₂SO₃ (50 mL, 2x) and brine (50 mL, 1x). The organic phase was dried over Na₂SO₄ and concentrated *in vacuo* to obtain the crude product. The crude product was purified via silica gel column chromatography (hexanes:DCM = 1:1) to yield off-white solid compound **4** (600 mg, 54%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.50 (d, *J* = 1.6 Hz, 1H), 8.06 (m, 3H), 7.52 (m, 3H), 3.90 (s, 6H).

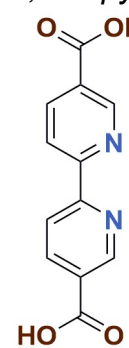
2-Iodo-1, 1'-biphenyl-4,4'-dicarboxylic acid (5**)**



Compound **4** (600 mg, 1.50 mmol) was dissolved in a 1:1 mixture of THF/MeOH (30 mL). To the solution of compound **4**, was added 1 M NaOH aqueous solution (15 mL). The reaction mixture was stirred at room temperature for 24 hours and then concentrated *in vacuo* to remove THF and MeOH. The aqueous residue was then acidified with 1 M HCl solution until the pH of solution reached ~2 and a white slurry formed. The slurry was stirred for 30 min. After vacuum filtration, solid precipitate was collected and washed with water (150 mL, 3x). The off-white solid was dried under vacuum to obtain compound **5** (500 mg, 90%). Compound **5** was used without further purification. ¹H NMR (500 MHz, DMSO-*d*₆) δ 13.21 (s, 2H), 8.48 (d, *J* = 2.0 Hz, 1H), 8.02 (m, 3H), 7.48 (m, 3H).

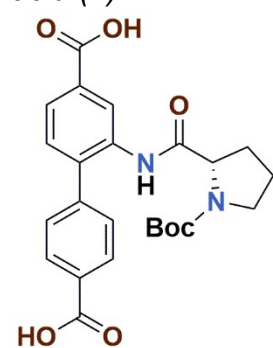
2,2'-Bipyridine-5,5'-dicarboxylic acid (6)

 Compound **6** was synthesized according to literature conditions.²



(S)-2-(1-(tert-butoxycarbonyl)pyrrolidine-2-carboxamido)-1,1'-biphenyl-4,4'-dicarboxylic acid (7)

Compound **7** was synthesized according to literature conditions.³



3. Syntheses and characterization of stratified MOFs

Synthesis of UiO-67(Zr) seed crystallites

0.4 M solution of $\text{Zr}(\text{O}^i\text{Pr})_4$ in CH_3COOH was prepared by mixing $\text{Zr}(\text{O}^i\text{Pr})_4$ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH_3COOH (1 mL). A 0.02 M solution of 1, 1'-biphenyl-4,4'-dicarboxylic acid ($\text{H}_2\text{-BPDC}$) in DMF was prepared by heating a mixture of $\text{H}_2\text{-BPDC}$ (19.4 mg, 0.08 mmol) and DMF (4 mL) on a stir plate at 150 °C until complete dissolution. To a 20 mL Pyrex vial were added in sequence CH_3COOH (0.3 mL), 0.4 M $\text{Zr}(\text{O}^i\text{Pr})_4$ solution (0.05 mL, 0.02 mmol), DMF (4 mL) and 0.02 M $\text{H}_2\text{-BPDC}$ solution (1 mL, 0.02 mmol). The vial was tightly capped and heated at 65 °C for 0.5 h in an isothermal oven to yield turbid suspension. The suspension was centrifuged at 10000 rpm for 2 min to obtain white precipitate. The precipitate was washed with fresh DMF (4 mL, 4x) and used immediately for the next step.

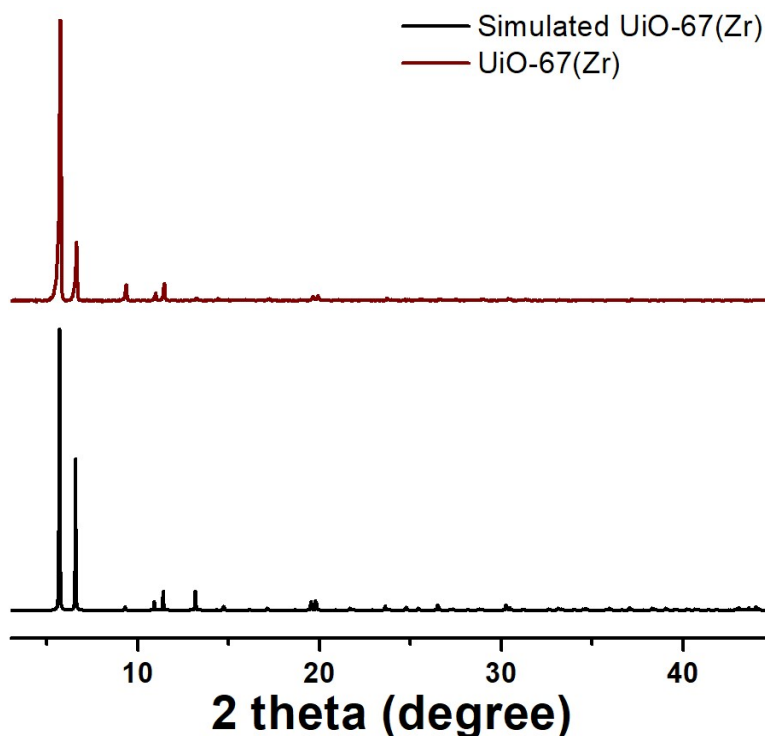


Figure S3.1 Simulated PXRD pattern of UiO-67(Zr) (black) and experimental PXRD pattern of as-synthesized UiO-67(Zr) seed crystallites (red).

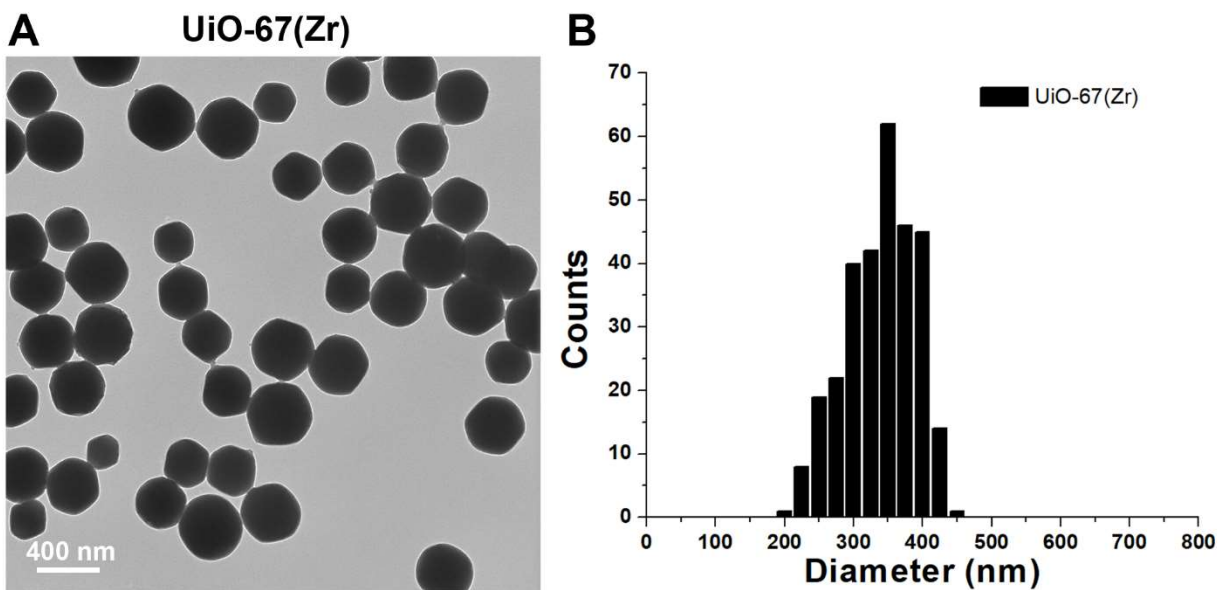


Figure S3.2 TEM image (A) and size distribution (B) of **UiO-67(Zr)** seed crystallites having an average diameter of 351 ± 51 nm (based on 300 counts).

Synthesis of **UiO-67(Zr)**⊂**UiO-67(Hf)**

A 0.02 M solution of H₂-BPDC in DMF was prepared by heating a mixture of H₂-BPDC (19.4 mg, 0.08 mmol) and DMF (4 mL) on a stir plate at 150 °C until complete dissolution. Hf(OⁱPr)₄•PrOH (19 mg, 0.04 mmol) and CH₃COOH (0.7 mL) was mixed in a 20 mL Pyrex vial. After the mixture was sonicated for 3 min, DMF (3.2 mL) and 0.02 M H₂-BPDC solution (2 mL, 0.04 mmol) was added. The mixture was vortexed and incubated at 65 °C in an isothermal oven for 1 h. The reaction suspension was then centrifuged at 10000 rpm for 2 min to obtain white precipitate and clear supernatant. The clear supernatant was carefully collected in a 20 mL Pyrex vial. UiO-67(Zr) seed crystals (*vide supra*) was dispersed in 1 mL DMF and added to the vial. The mixture was stirred with a magnetic stir bar (60 rpm) at 25 °C. After 19 hours the reaction suspension was centrifuged at 10000 rpm for 2 min to obtain white precipitate product. The product was then washed with fresh DMF (4 mL, 4x).

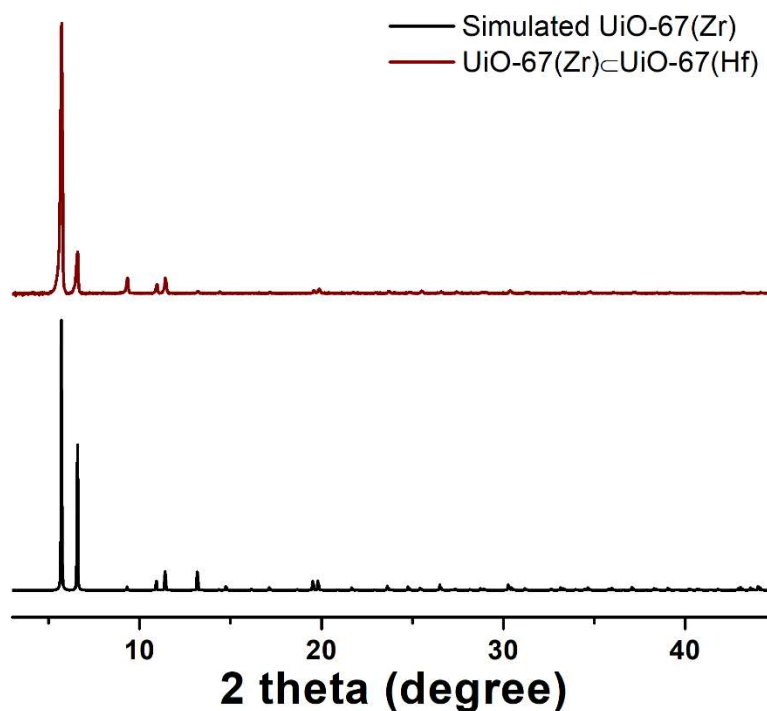
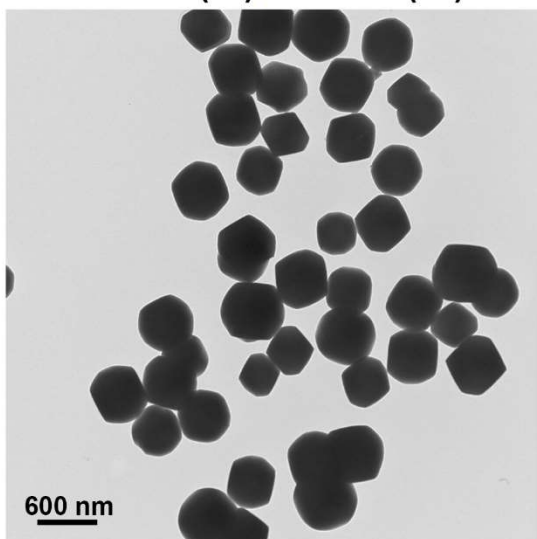


Figure S3.3 Simulated PXRD pattern of UiO-67(Zr) (black) and experimental PXRD pattern of as-synthesized **UiO-67(Zr)**⊂**UiO-67(Hf)** (red).

A UiO-67(Zr)⊂UiO-67(Hf)



B

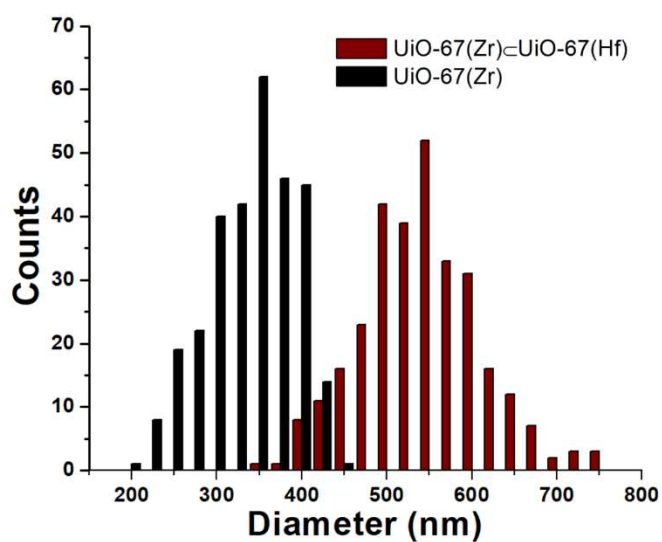


Figure S3.4 TEM image of **UiO-67(Zr)⊂UiO-67(Hf)** crystallites having an average diameter of 555 ± 70 nm (A); Size distributions (based on 300 counts) of **UiO-67(Zr)** seed crystallites (Figure S3.2) (black), and **UiO-67(Zr)⊂UiO-67(Hf)** crystallites (red) (B).

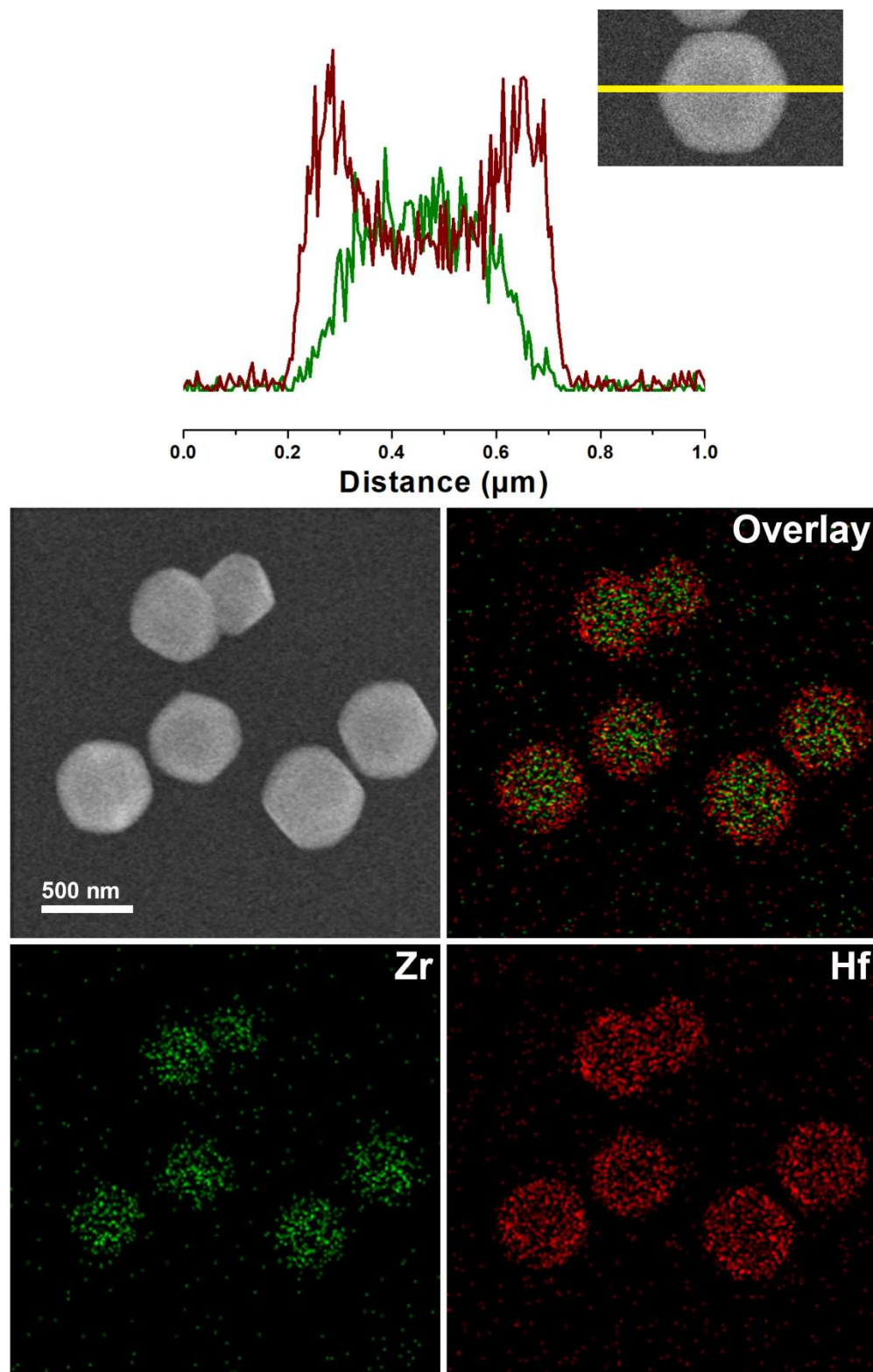


Figure S3.5 SEM-EDS line-scan and mapping data of **UiO-67(Zr)/UiO-67(Hf)** (Zr, green; Hf, red).

Synthesis of **UiO-67(Hf)** seed crystallites

A 0.02 M solution of H₂-BPDC in DMF was prepared by heating a mixture of H₂-BPDC (19.4 mg, 0.08 mmol) and DMF (4 mL) on a stir plate at 150 °C until complete dissolution. Hf(O^{*i*}Pr)₄•PrOH (76 mg, 0.16 mmol) and CH₃COOH (2.8 mL) was mixed in a 40 mL pyrex vial. After the mixture was sonicated for 3 min, DMF (13.8 mL) and 0.02 M H₂-BPDC solution (8 mL, 0.16 mmol) was added. The mixture was vortexed and allowed to react at 25 °C. After 24 h, the reaction suspension was centrifuged to obtain white precipitate. The precipitate was washed with fresh DMF (16 mL, 4x), dispersed in 2 mL DMF and used immediately as seeds to prepare stratified MOFs.

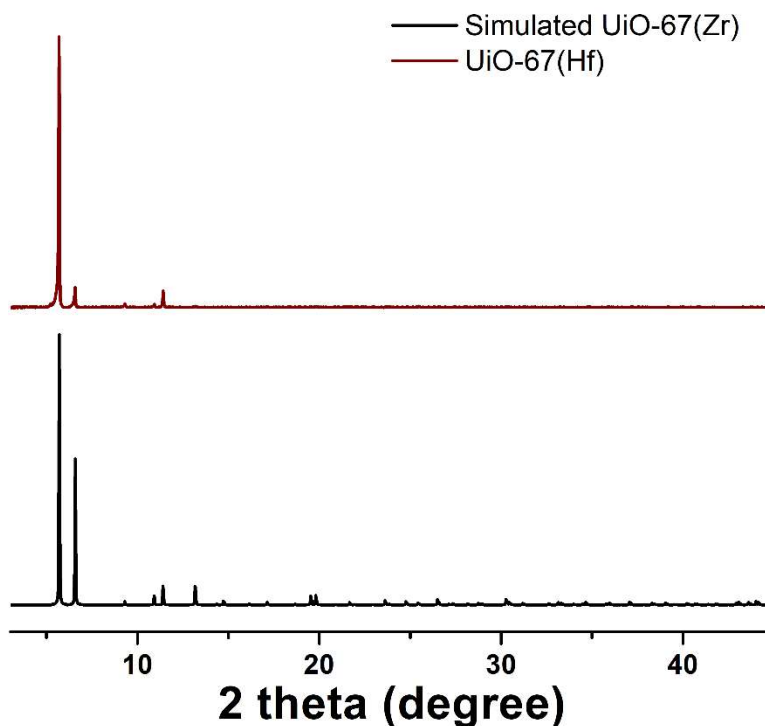


Figure S3.6 Simulated PXRD pattern of UiO-67(Zr) (black) and experimental PXRD pattern of as-synthesized **UiO-67(Hf)** seed crystallites (red).

Synthesis of UiO-67(Hf)⊂UiO-67(Zr)

0.4 M solution of $\text{Zr}(\text{O}^i\text{Pr})_4$ in CH_3COOH was prepared by mixing $\text{Zr}(\text{O}^i\text{Pr})_4$ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH_3COOH (1 mL). A 0.02 M solution of $\text{H}_2\text{-BPDC}$ in DMF was prepared by heating a mixture of $\text{H}_2\text{-BPDC}$ (19.4 mg, 0.08 mmol) and DMF (4 mL) on a stir plate at 150 °C until complete dissolution. To a 20 mL Pyrex vial were added in sequence CH_3COOH (0.6 mL), 0.4 M $\text{Zr}(\text{O}^i\text{Pr})_4$ solution in CH_3COOH (0.1 mL, 0.04 mmol), DMF (3 mL) and 0.02 M $\text{H}_2\text{-BPDC}$ solution (2 mL, 0.04 mmol). The vial was tightly capped and vortexed for 10 seconds. The reaction was allowed to proceed at room temperature for 50 min, at which point, a murky suspension was formed. After centrifugation at 10,000 rpm to remove the precipitate, supernatant was collected in a new 20 mL vial. To the supernatant was added 1 mL of DMF suspension of UiO-67(Hf) seed crystals prepared previously (*vide supra*). The mixture was stirred with a magnetic stir bar (60 rpm) at room temperature for 18 hrs. After centrifugation at 10,000 rpm, white precipitate was collected and washed with DMF (16 mL, 4x).

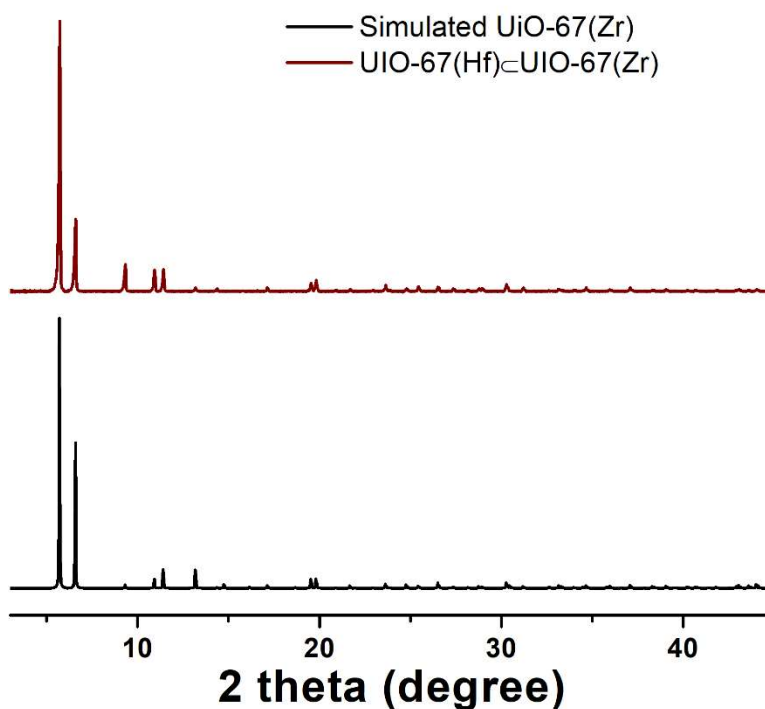


Figure S3.7 Simulated PXRD pattern of **UiO-67(Zr)** (black) and experimental PXRD pattern of as-synthesized **UiO-67(Hf)⊂UiO-67(Zr)** (red).

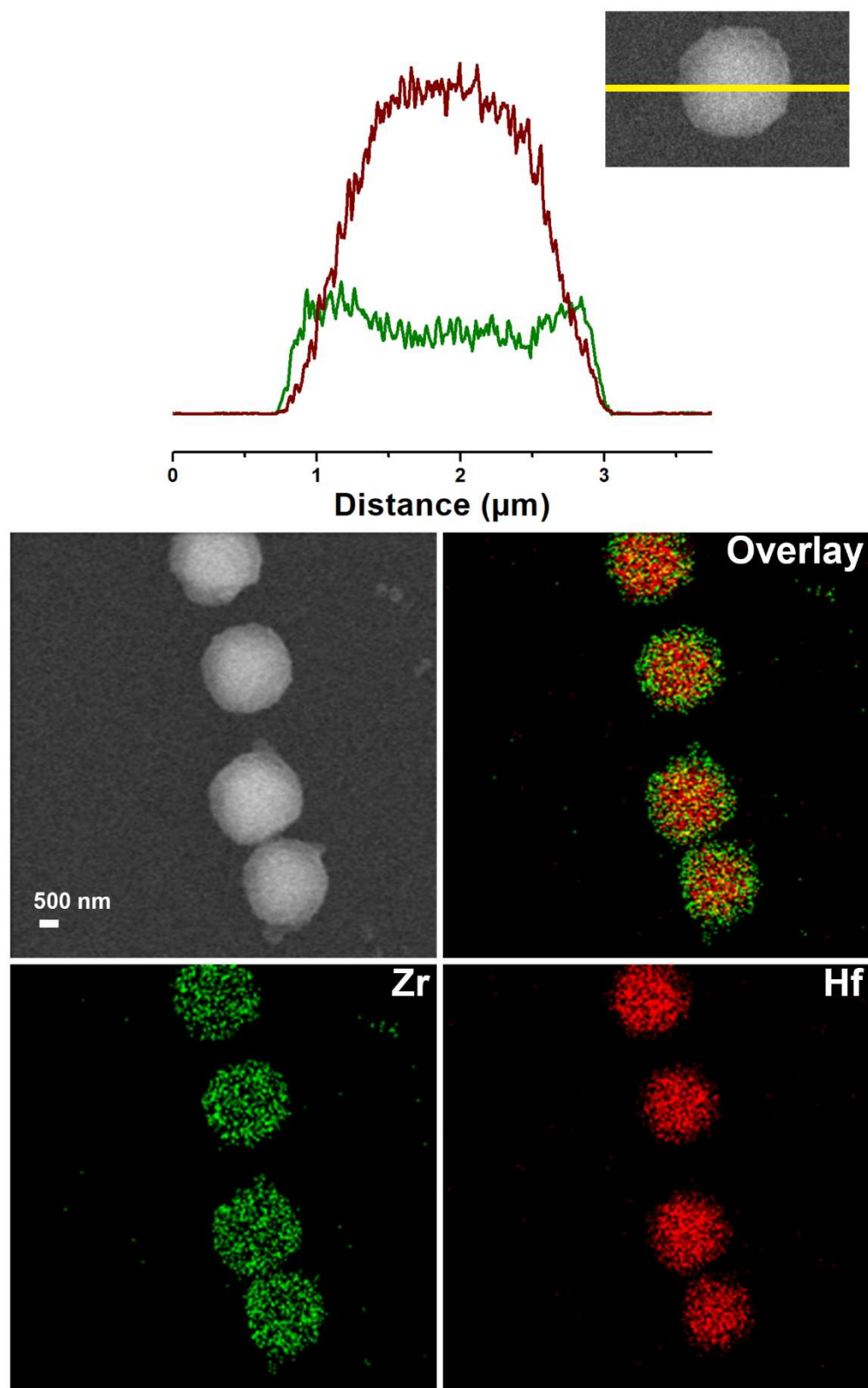


Figure S3.8 SEM-EDS line-scan and mapping data of **UiO-67(Hf)@UiO-67(Zr)** (Zr, green; Hf, red).

Synthesis of **I-UiO-67(Zr)** seed crystallites

0.4 M solution of $\text{Zr}(\text{O}^i\text{Pr})_4$ in CH_3COOH was prepared by mixing $\text{Zr}(\text{O}^i\text{Pr})_4$ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH_3COOH (1 mL). 0.015 M solution of 2-iodo-1, 1'-biphenyl-4,4'-dicarboxylic acid ($\text{H}_2\text{-I-BPDC}$) in DMF was prepared by dissolving $\text{H}_2\text{-I-BPDC}$ (16.2 mg, 0.045 mmol) in DMF (3 mL). To a 40 mL Pyrex vial were added in sequence CH_3COOH (1.05 mL), 0.4 M $\text{Zr}(\text{O}^i\text{Pr})_4$ solution (0.15 mL, 0.06 mmol), DMF (9 mL) and 0.015 M $\text{H}_2\text{-I-BPDC}$ solution (3 mL, 0.045 mmol). The vial was tightly capped and heated at 65 °C in an isothermal oven for 3.5 h to yield turbid suspension. The suspension was centrifuged at 10000 rpm for 2 min to obtain white precipitate. The precipitate was washed with fresh DMF (16 mL, 4x).

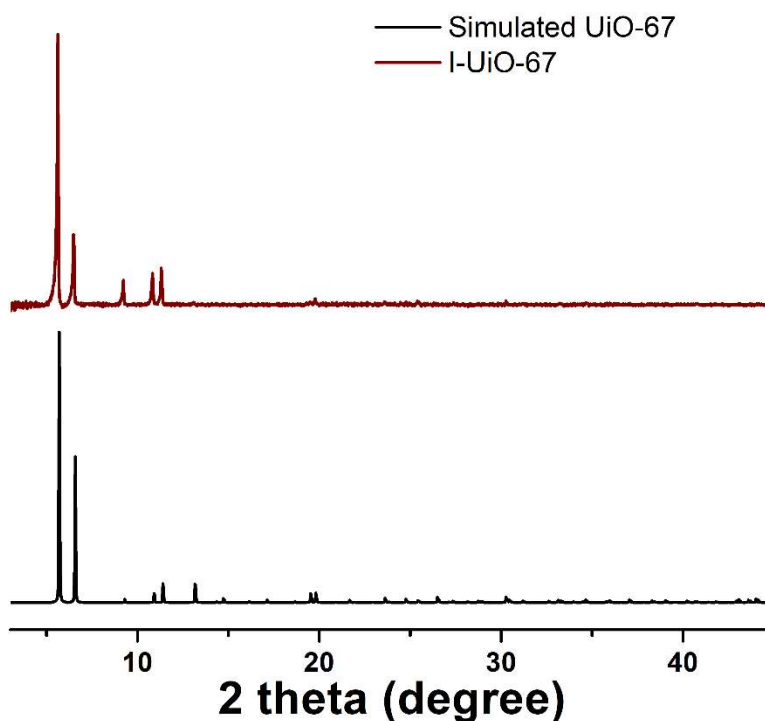


Figure S3.9 Simulated PXRD pattern of UiO-67(Zr) (black) and experimental PXRD pattern of as-synthesized **I-UiO-67(Zr)** seed crystallites (red).

Synthesis of *I*-UiO-67(Zr)⊂UiO-67(Hf)

0.02 M solution of H₂-BPDC in DMF was prepared by heating a mixture of H₂-BPDC (19.4 mg, 0.08 mmol) and DMF (4 mL) on a stir plate at 150 °C until complete dissolution. Hf(O^{*i*}Pr)₄•PrOH (19 mg, 0.04 mmol) and CH₃COOH (0.7 mL) was mixed in a 20 mL Pyrex vial. After the mixture was sonicated for 3 min, DMF (3.2 mL) and 0.02 M H₂-BPDC solution (2 mL, 0.04 mmol) was added. The mixture was vortexed and incubated at 65 °C in an isothermal oven for 50 min. The reaction suspension was then centrifuged at 10000 rpm for 2 min to obtain white precipitate and clear supernatant. The clear supernatant was carefully collected in a 20 mL Pyrex vial. *I*-UiO-67(Zr) seed crystals previously (*vide supra*) prepared was added to the supernatant in the vial. The mixture was allowed to react at 25 °C for 14 h. The reaction suspension was centrifuged at 10000 rpm for 2 min to obtain white precipitate product. The product was then washed with fresh DMF (16 mL, 4x) and dispersed in 5 mL fresh DMF.

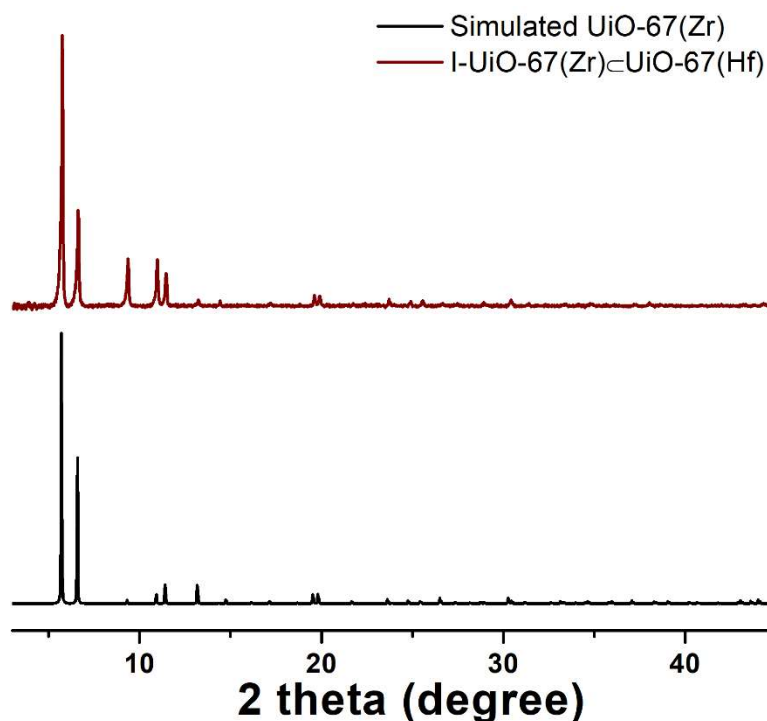


Figure S3.10 Simulated PXRD pattern of **UiO-67(Zr)** (black) and PXRD pattern of as-synthesized ***I*-UiO-67(Zr)⊂UiO-67(Hf)** (red).

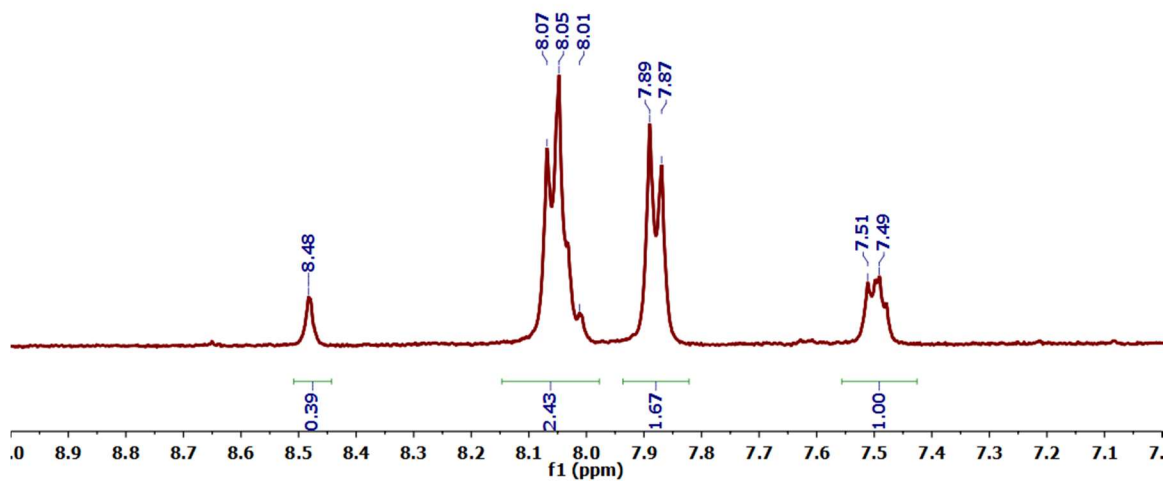


Figure S3.11 ^1H NMR of acid digested I-UiO-67(Zr)⊂UiO-67(Hf) in DMSO- d_6 showing an approximate I-BPDC : BPDC ratio of 1:1.25.

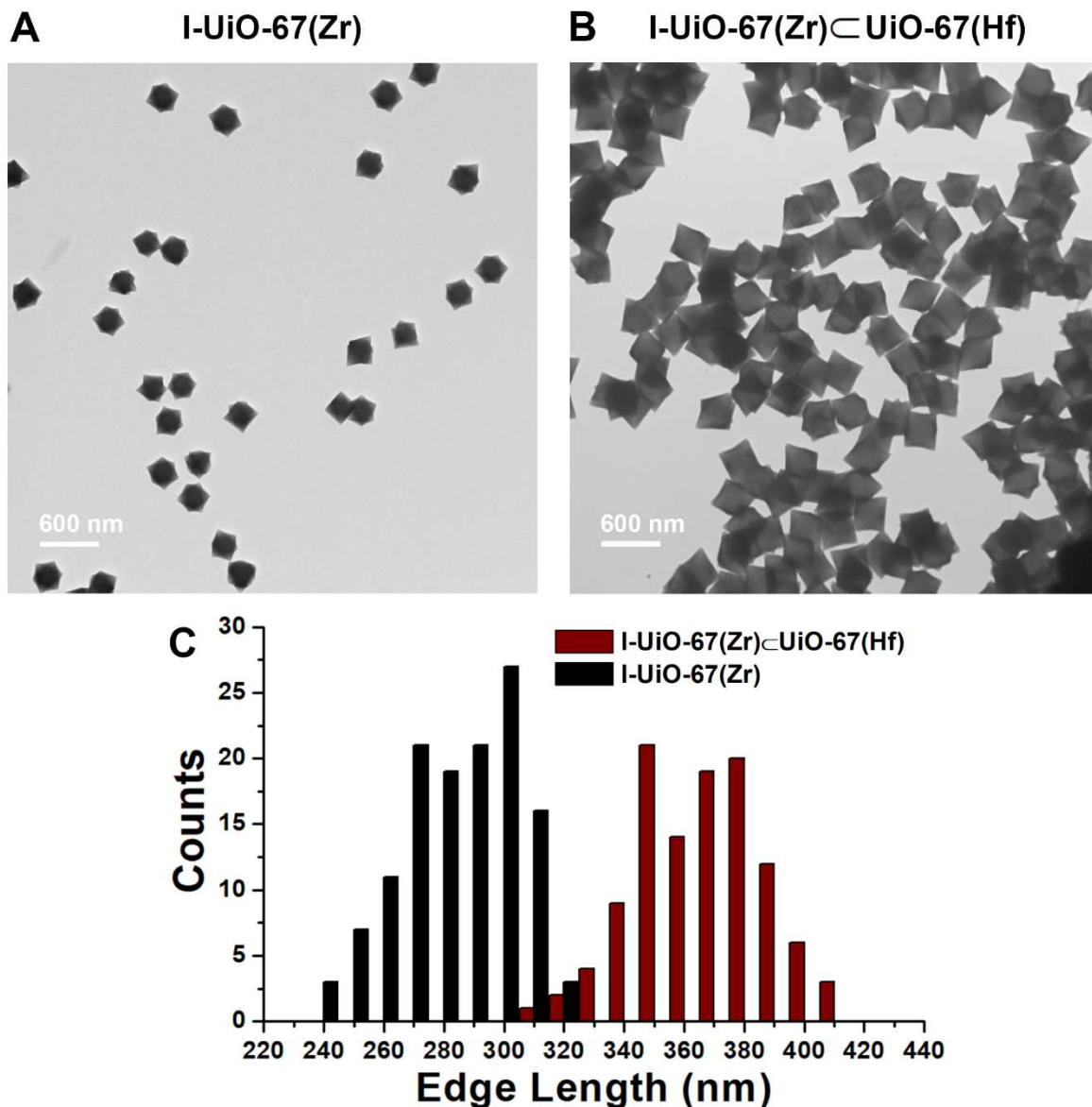


Figure S3.12 TEM image of octahedral **I-UiO-67(Zr)** seed crystallites with an average edge length of 290 ± 19 nm (A); TEM image of octahedral **I-UiO-67(Zr)⊂UiO-67(Hf)** crystallites with an average edge length of 371 ± 20 nm (B); size distributions (based on 100 counts) of I-UiO-67(Zr) seed crystallites (black) and **I-UiO-67(Zr)⊂UiO-67(Hf)** crystallites (red) (C).

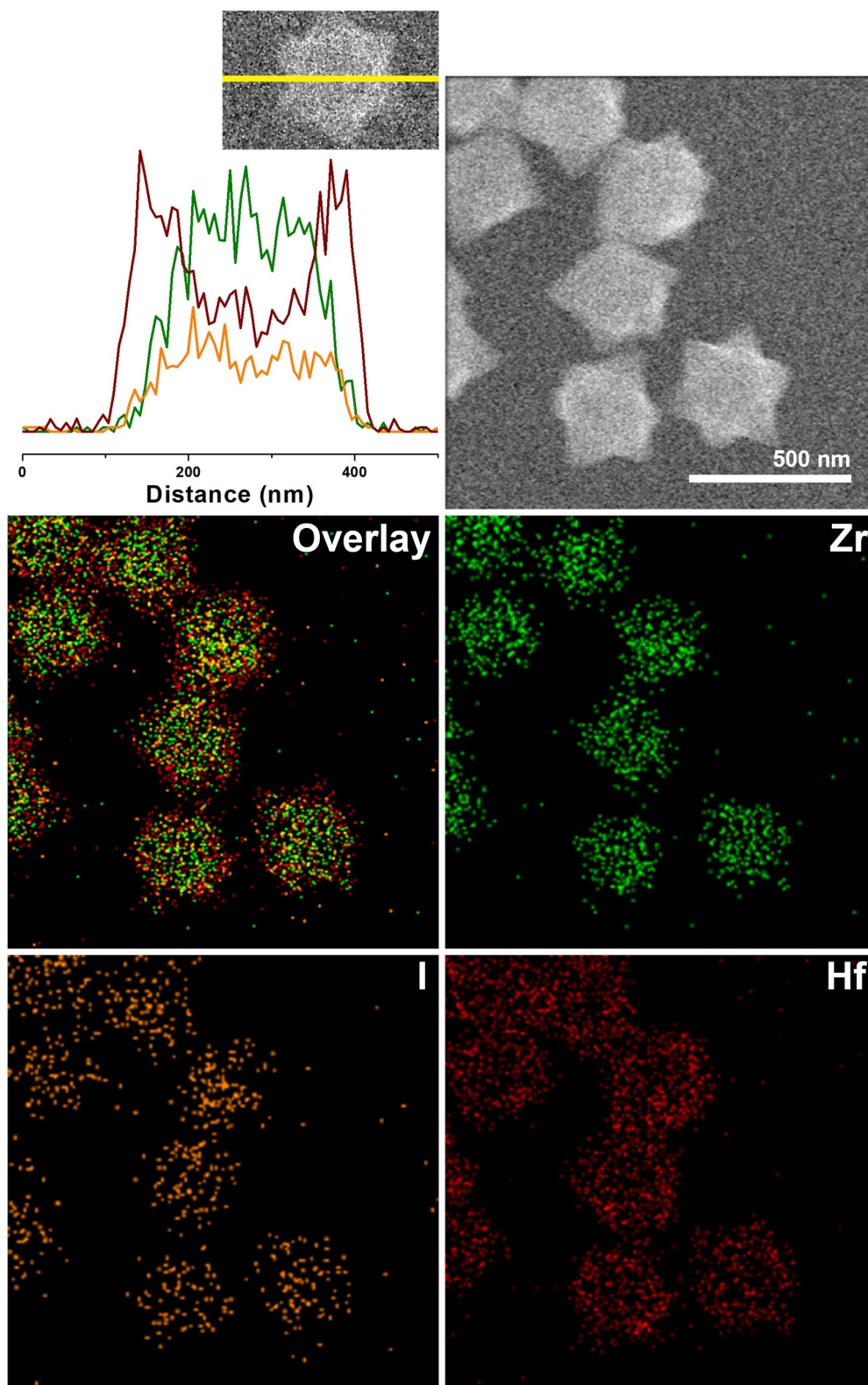


Figure S3.13 SEM-EDS line-scan and mapping data of I-UiO-67(Zr)@UiO-67(Hf) (Zr, green; I, orange; Hf, red).

Synthesis of **NH₂-UiO-67(Zr)** seed crystallites

0.4 M solution of Zr(O^{*n*}Pr)₄ in CH₃COOH was prepared by mixing Zr(O^{*n*}Pr)₄ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH₃COOH (1 mL). A 0.02 M solution of 2-amino-1, 1'-biphenyl-4,4'-dicarboxylic acid (H₂-NH₂-BPDC) in DMF was prepared by dissolving H₂-NH₂-BPDC (15.4 mg, 0.06 mmol) in DMF (3 mL). To a 40 mL Pyrex vial were added in sequence CH₃COOH (0.6 mL), 0.4 M Zr(O^{*n*}Pr)₄ solution (0.15 mL, 0.06 mmol), DMF (15 mL) and 0.02 M H₂-NH₂-BPDC solution (3 mL, 0.06 mmol). The vial was tightly capped and heated at 65 °C in an isothermal oven for 16 h to yield turbid yellow suspension. The suspension was centrifuged at 10000 rpm for 2 min to obtain yellow precipitate. The precipitate was washed with fresh DMF (16 mL, 4x) and dispersed in DMF (3 mL).

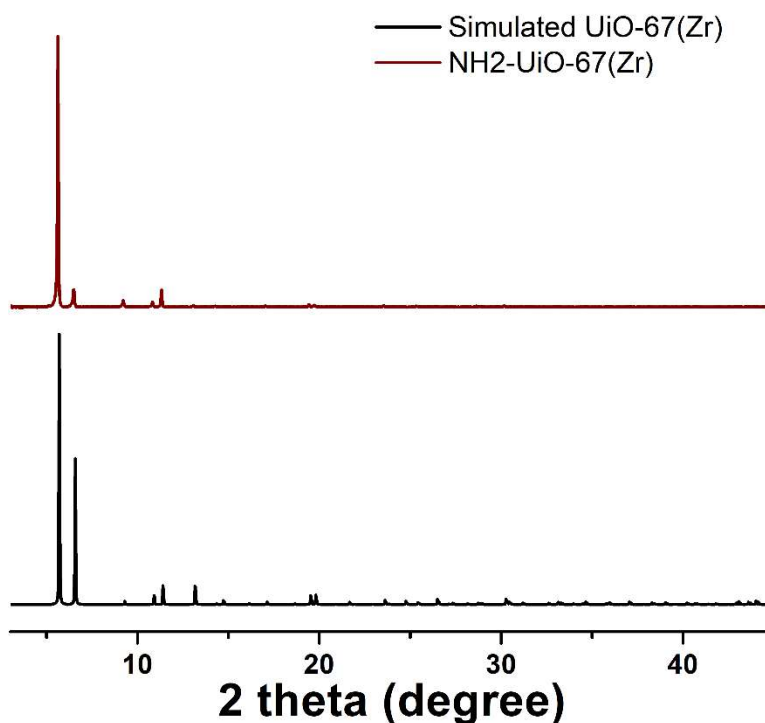


Figure S3.14 Simulated PXRD pattern based on UiO-67(Zr) (black) and experimental PXRD pattern of as-synthesized **NH₂-UiO-67(Zr)** seed crystallites (red).

Synthesis of **NH₂-UiO-67(Zr)**⊂**I-UiO-67(Zr)**

0.4 M solution of Zr(O^{*n*}Pr)₄ in CH₃COOH was prepared by mixing Zr(O^{*n*}Pr)₄ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH₃COOH (1 mL). A 0.015 M solution of H₂-I-BPDC in DMF was prepared by dissolving H₂-I-BPDC (16.2 mg, 0.045 mmol) in DMF (3 mL). To a 20 mL Pyrex vial were added in sequence CH₃COOH (0.30 mL), 0.4 M Zr(O^{*n*}Pr)₄ solution (0.05 mL, 0.02 mmol), DMF (2 mL), 0.015 M H₂-I-BPDC solution (1 mL, 0.015 mmol) and 1 mL of DMF suspension of the NH₂-UiO-67(Zr) seed crystals (*vide supra*). The mixture was stirred with a magnetic stir bar (60 rpm) at 25 °C for 5 h. The suspension was centrifuged at 10000 rpm for 2 min to obtain yellow precipitate. The precipitate was washed with fresh DMF (4 mL, 4x) and used immediately for characterization and further reactions.

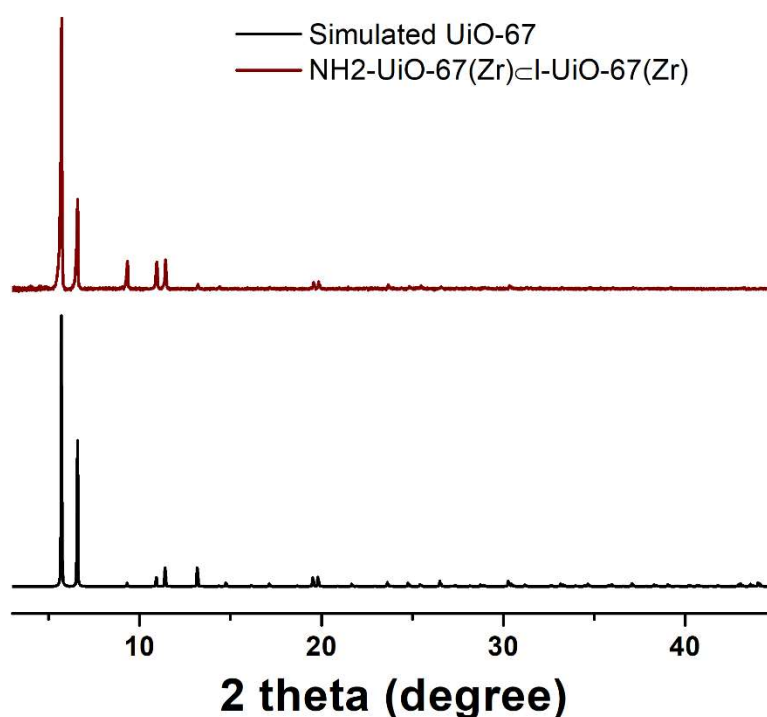


Figure S3.15 Simulated PXRD pattern of UiO-67(Zr) (black) and experimental PXRD pattern of as-synthesized **NH₂-UiO-67(Zr)**⊂**I-UiO-67(Zr)** (red).

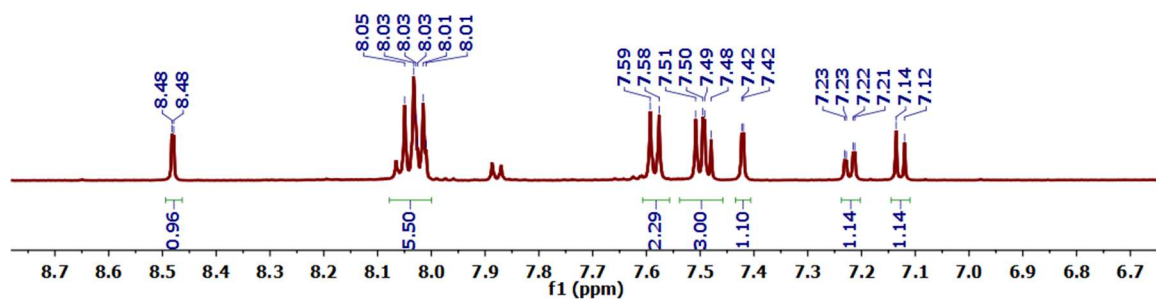


Figure S3.16 ^1H NMR of acid digested $\text{NH}_2\text{-UiO-67(Zr)Cl-UiO-67(Zr)}$ in DMSO-d_6 showing an approximate I-BPDC : $\text{NH}_2\text{-BPDC}$ ratio of 1:1.15.

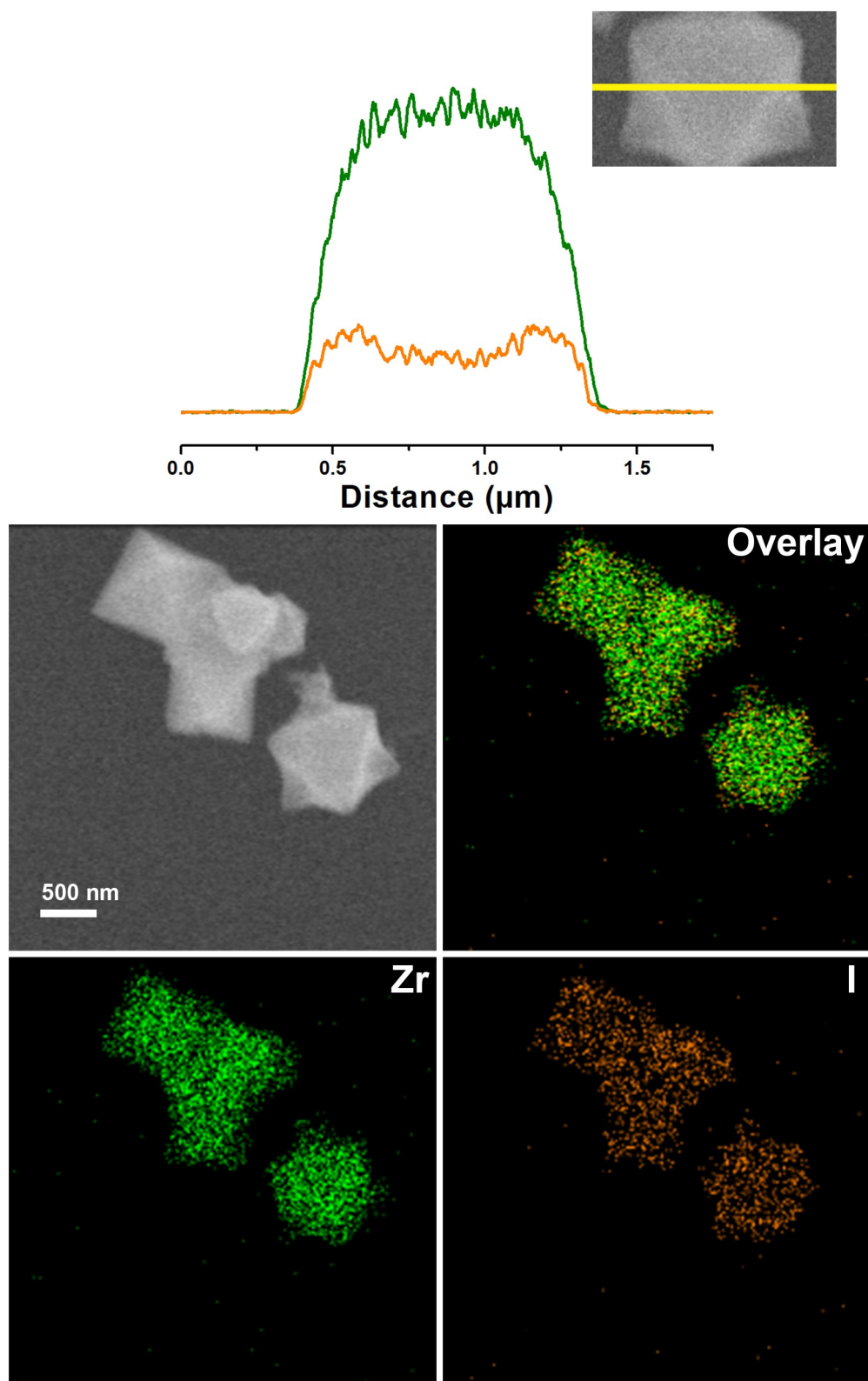


Figure S3.17 SEM-EDS line-scan and mapping data of $\text{NH}_2\text{-UiO-67(Zr)Cl-UiO-67(Zr)}$ (Zr, green; Cl, orange).

*Linker exchange experiment using **NH₂-UiO-67(Zr)** and H₂-I-BPDC*

A 0.015 M solution of H₂-I-BPDC in DMF was prepared by dissolving H₂-I-BPDC (16.2 mg, 0.045 mmol) in DMF (3 mL). To a 20 mL Pyrex vial were added in sequence CH₃COOH (0.35 mL), DMF (2 mL), 0.015 M H₂-I-BPDC solution (1 mL, 0.015 mmol) and 1 mL of DMF suspension of the NH₂-UiO-67(Zr) seed crystals (*vide supra*). The mixture was stirred with a magnetic stir bar (60 rpm) at 25 °C for 5 h. The suspension was centrifuged at 10000 rpm for 2 min to obtain yellow precipitate. The precipitate was washed with fresh DMF (4x) and used immediately for characterization and further reactions.

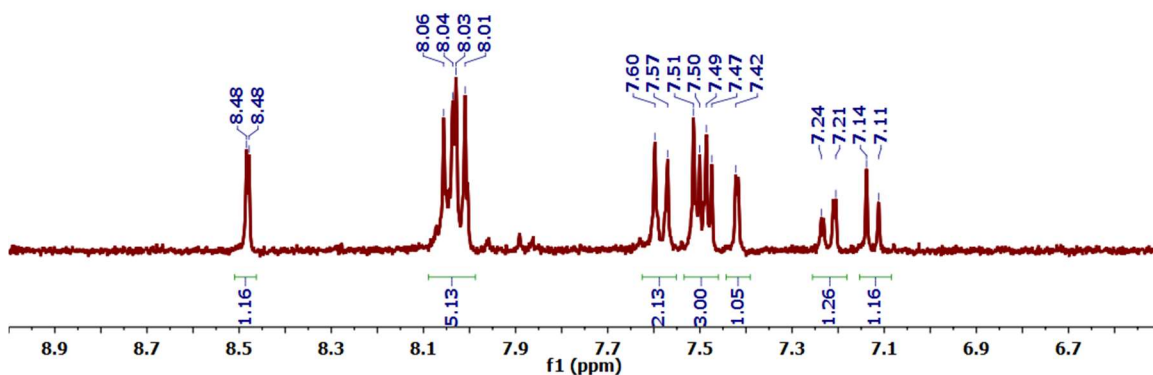


Figure S3.18 ¹H NMR of acid digested **NH₂-UiO-67(Zr)Cl-UiO-67(Zr)** in DMSO-d₆ showing an approximate I-BPDC : NH₂-BPDC ratio of 1:1.2.

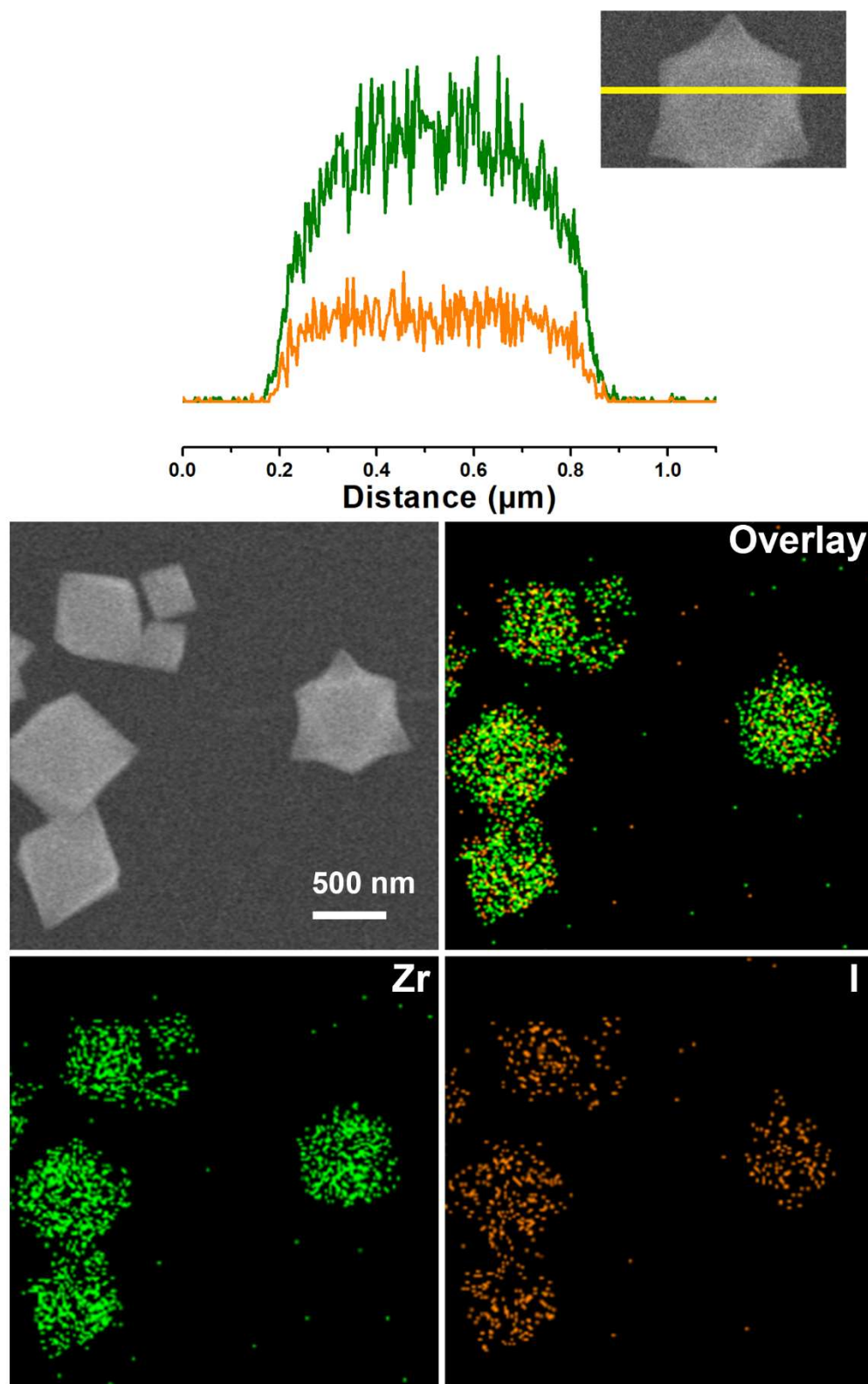


Figure S3.19 SEM-EDS line-scan and mapping data of crystallites formed after a linker exchange reaction between $\text{NH}_2\text{-UiO-67(Zr)}$ and I-BPDC (Zr, green; I, orange).

Synthesis of UiO-67(Zr)⊂UiO-67(Hf)⊂UiO-67(Zr)

0.4 M solution of $\text{Zr}(\text{O}^i\text{Pr})_4$ in CH_3COOH was prepared by mixing $\text{Zr}(\text{O}^i\text{Pr})_4$ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH_3COOH (1 mL). A 0.02 M solution of $\text{H}_2\text{-BPDC}$ in DMF was prepared by mixing $\text{H}_2\text{-BPDC}$ (19.4 mg, 0.08 mmol) with DMF (4 mL) followed by heating on a stir plate at 150 °C until complete dissolution. To a 20 mL Pyrex vial were added in sequence CH_3COOH (0.6 mL), 0.4 M $\text{Zr}(\text{O}^i\text{Pr})_4$ solution in CH_3COOH (0.1 mL, 0.04 mmol), DMF (3 mL) and 0.02 M $\text{H}_2\text{-BPDC}$ solution (2 mL, 0.04 mmol). The vial was tightly capped and vortexed for 10 seconds. The reaction was allowed to proceed at room temperature for 50 min, at which point, a murky suspension was formed. After centrifugation at 10,000 rpm to remove the precipitate, supernatant was collected in a new 20 mL vial. To the supernatant was added UiO-67(Zr)⊂UiO-67(Hf) crystals prepared previously (*vide supra*). The mixture was stirred with a magnetic stir bar (200 rpm) at room temperature for 5.5 hrs. After centrifugation at 10,000 rpm, white precipitate was collected and washed with DMF (16 mL, 4x).

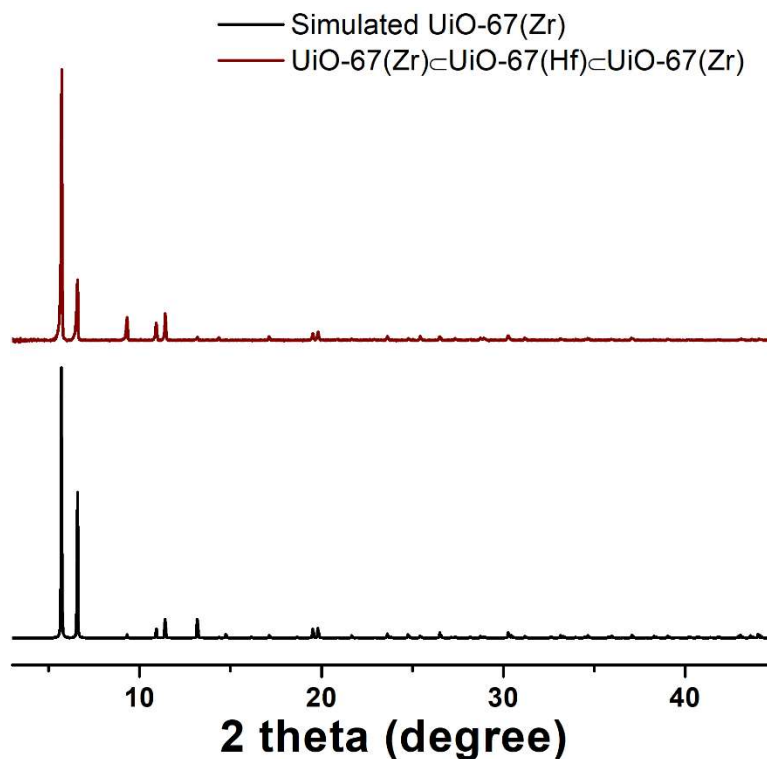


Figure S3.20 Simulated PXRD pattern of UiO-67(Zr) (black) and experimental PXRD pattern of as-synthesized **UiO-67(Zr)⊂UiO-67(Hf)⊂UiO-67(Zr)** (red).

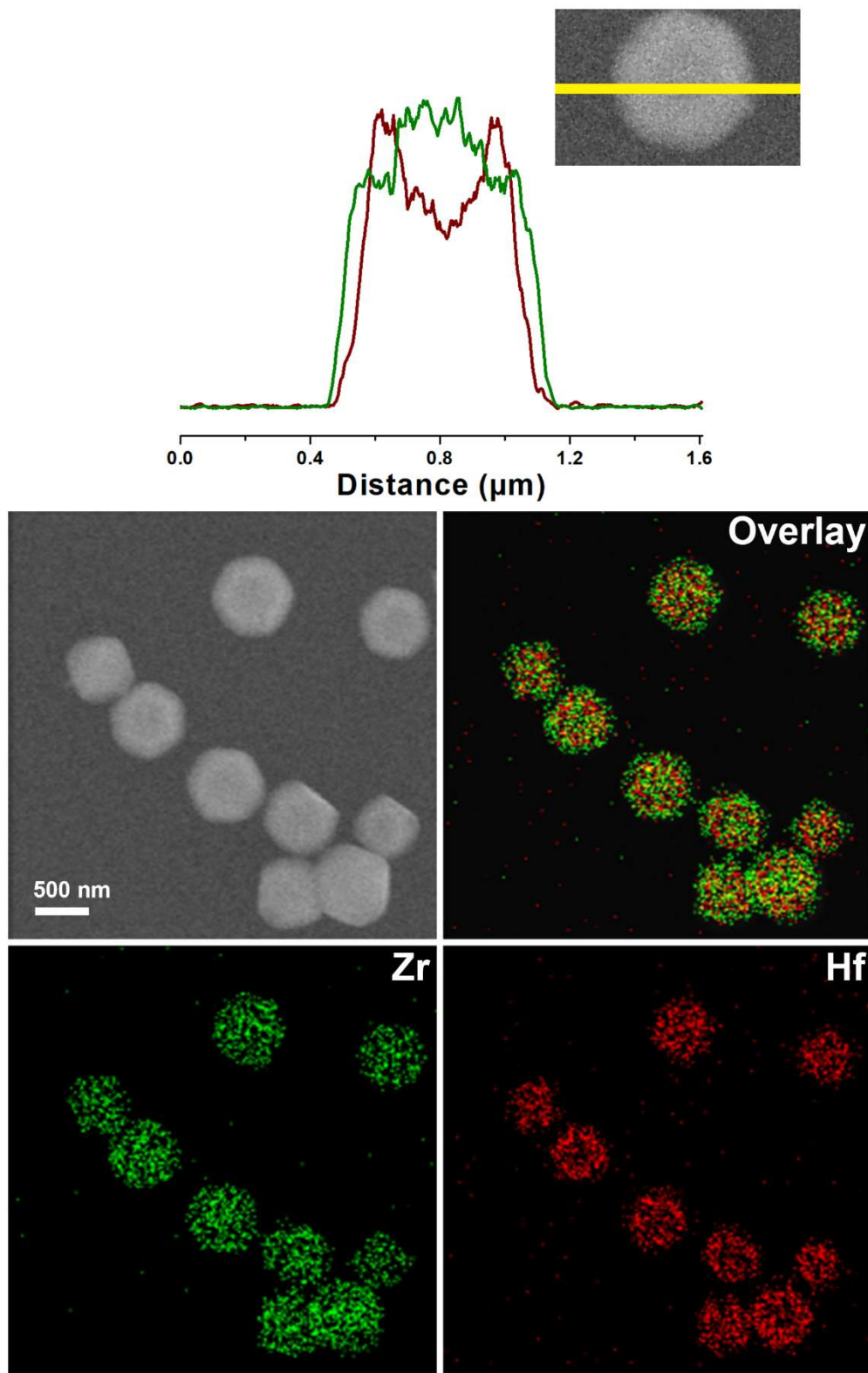


Figure S3.21 SEM-EDS characterization of $\text{UiO-67(Zr)}@\text{UiO-67(Hf)}@\text{UiO-67(Zr)}$ (Zr, green; Hf, red).

Synthesis of I-UiO-67(Zr)⊂UiO-67(Hf)⊂NH₂-UiO-67(Zr)

0.4 M solution of Zr(O^{*n*}Pr)₄ in CH₃COOH was prepared by mixing Zr(O^{*n*}Pr)₄ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH₃COOH (1 mL). A 0.02 M solution of H₂-NH₂-BPDC in DMF was prepared by dissolving H₂-NH₂-BPDC (10.3 mg, 0.04 mmol) with DMF (2 mL). To a 20 mL Pyrex vial were added in sequence CH₃COOH (0.25 mL), 0.4 M Zr(O^{*n*}Pr)₄ solution (0.05 mL, 0.02 mmol), 3 mL of the DMF suspension of I-UiO-67(Zr)⊂UiO-67(Hf) prepared previously (*vide supra*) and 0.02 M H₂-BPDC solution (1 mL, 0.02 mmol). The vial was tightly capped and allowed to stand at room temperature for 14 hrs. After centrifugation of the resulting suspension at 10000 rpm for 2 min, pale yellow precipitate was obtained. The precipitate was washed with fresh DMF (16 mL, 4x) before characterization.

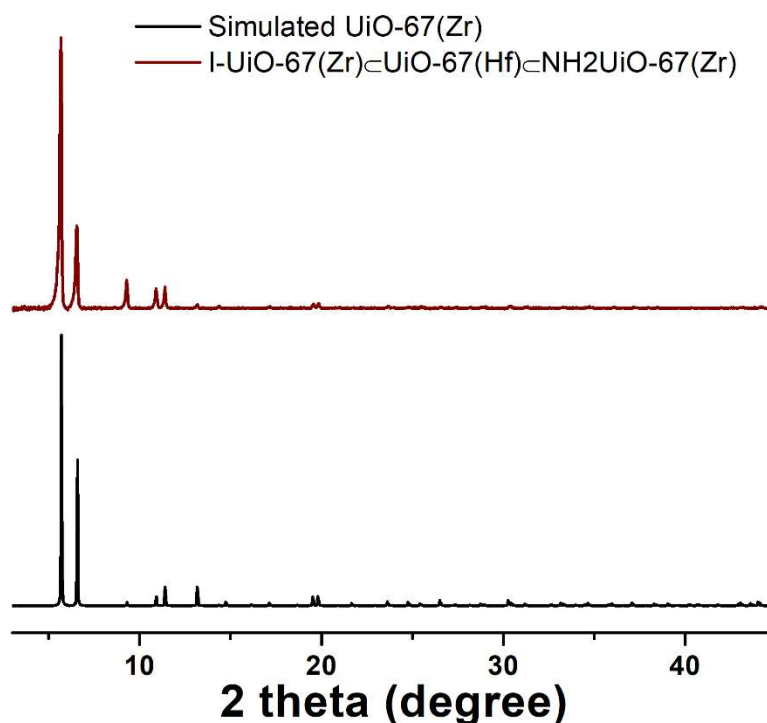


Figure S3.22 Simulated PXRD pattern of UiO-67(Zr) (black) and experimental PXRD pattern of as-synthesized I-UiO-67(Zr)⊂UiO-67(Hf)⊂NH₂-UiO-67(Zr) (red).

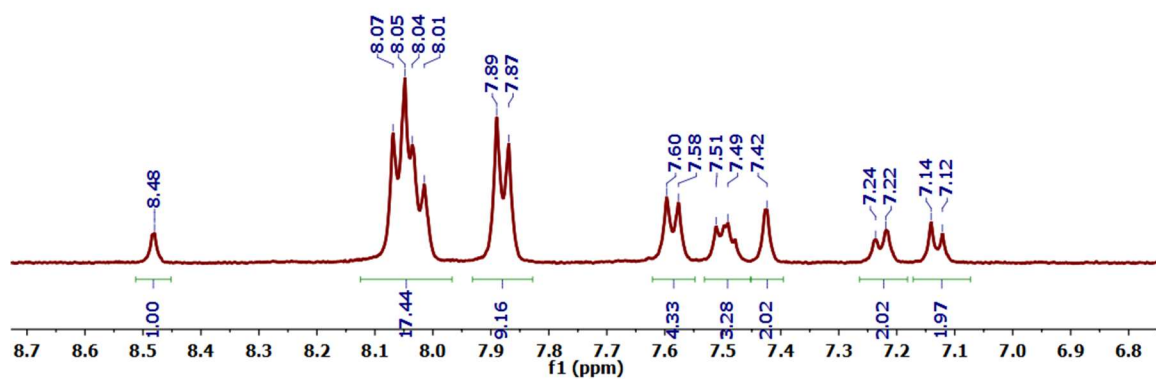


Figure S3.23 ^1H NMR of acid digested $\text{I-UiO-67(Zr)}\text{⌢UiO-67(Hf)}\text{⌢NH}_2\text{-UiO-67(Zr)}$ in DMSO-d_6 showing an approximate I-BPDC : BPDC : $\text{NH}_2\text{-BPDC}$ ratio of 1 : 2.29 : 2.

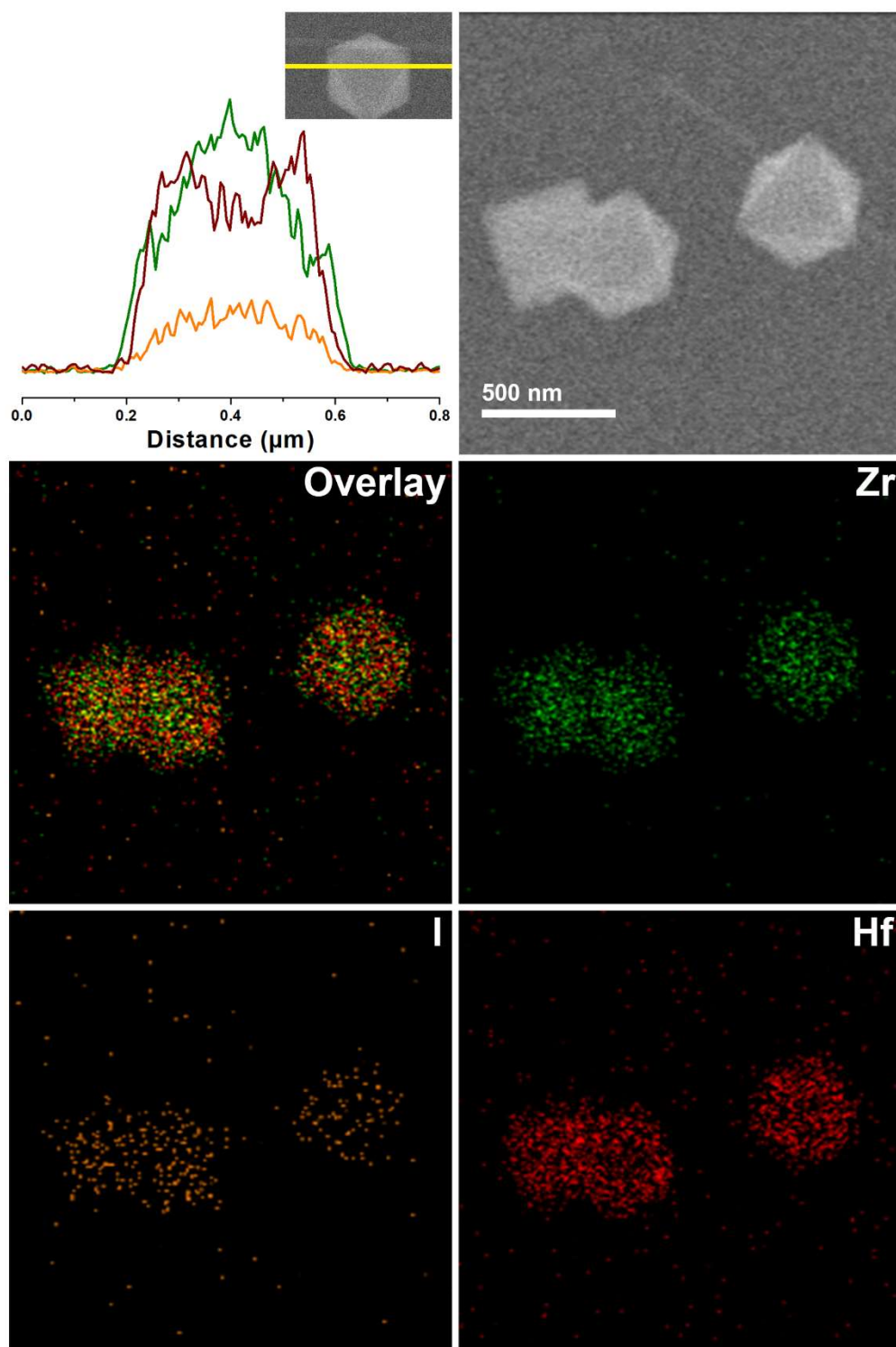


Figure S3.24 SEM-EDS characterization of I-UiO-67(Zr) c UiO-67(Hf) c NH₂-UiO-67(Zr) (Zr, green; I, orange; Hf, red).

Synthesis of **Bpy-UiO-67(Zr)** seed crystallites

Bpy-UiO-67(Zr) seed crystallites were prepared using one of the conditions below.

Condition I: Bpy-UiO-67(Zr) was synthesized using modified literature conditions.⁴ To a 20 mL Pyrex vial was added 2 2'-bipyridine-5 5'-dicarboxylic acid (H₂-BpyDC) (12.2 mg, 0.05 mmol) and 2 mL of DMF. The mixture was sonicated for 30 min to form a suspension. Acetic acid (0.2 mL) and ZrCl₄ (11.7 mg, 0.05 mmol) were then added to the vial. After sonication for 10 min, the vial was placed in a 120 °C oven for 24 hours. The reaction suspension was then centrifuged at 10,000 rpm for 3 min to obtain white precipitate. The precipitate was washed with fresh DMF (16 mL, 4x) and suspended in DMF (1 mL).

Condition II: To a 20 mL Pyrex vial was added ZrCl₄ (9.8 mg, 0.04 mmol), DMF (10 mL), CH₃COOH (0.5 mL) and H₂-BpyDC (9.3 mg, 0.04 mmol). After sonication for 5 min, the vial was placed in a 100 °C for 6.5 hours. The reaction suspension was then centrifuged at 10,000 rpm for 3 min to obtain white precipitate. The precipitate was washed with fresh DMF (16 mL, 4x) and dispersed in DMF (1 mL).

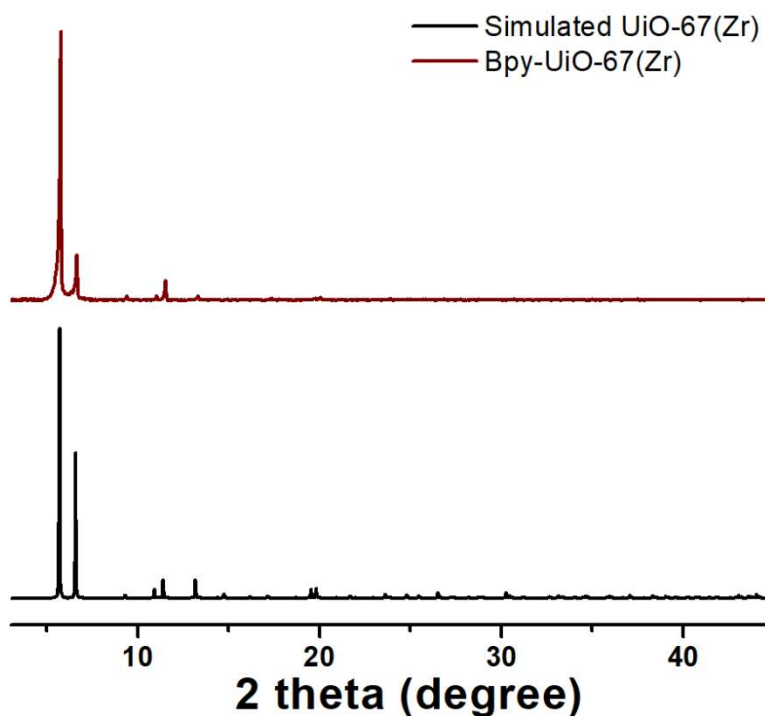


Figure S3.25 Simulated PXRD pattern of UiO-67(Zr) (black) and experimental PXRD pattern of as-synthesized **Bpy-UiO-67(Zr)** seed crystallites (red).

Synthesis of **Bpy-UiO-67(Zr)**⊂**UiO-67(Zr)**

0.4 M solution of $\text{Zr}(\text{O}^i\text{Pr})_4$ in CH_3COOH was prepared by mixing $\text{Zr}(\text{O}^i\text{Pr})_4$ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH_3COOH (1 mL). A 0.02 M solution of $\text{H}_2\text{-BPDC}$ in DMF was prepared by heating a mixture of $\text{H}_2\text{-BPDC}$ (19.4 mg, 0.08 mmol) and DMF (4 mL) on a stir plate at 150 °C until complete dissolution. To a 20 mL Pyrex vial were added in sequence CH_3COOH (0.3 mL), 0.4 M $\text{Zr}(\text{O}^i\text{Pr})_4$ solution in CH_3COOH (0.05 mL, 0.02 mmol), DMF (3 mL) and 0.02 M $\text{H}_2\text{-BPDC}$ solution (1 mL, 0.02 mmol) and DMF suspension of **Bpy-UiO-67(Zr)** (1 mL) prepared previously (condition I, *vide supra*). The mixture was vortexed for 10 seconds and stirred at 200 rpm and room temperature for 2 h. After centrifugation at 10,000 rpm for 3 min, **Bpy-UiO-67(Zr)**⊂**UiO-67(Zr)** was obtained as white precipitate. The precipitate was copiously washed with fresh DMF (4 mL, 4x) and acetonitrile (4 mL, 4x) and suspended in 1 mL acetonitrile.

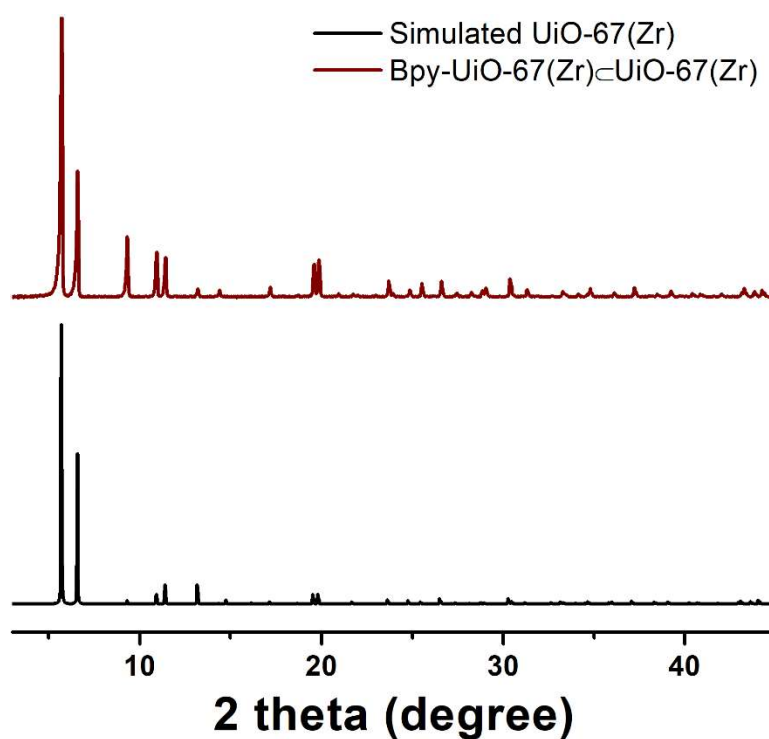


Figure S3.26 Simulated PXRD pattern of UiO-67(Zr) (black) and experimental PXRD pattern of as-synthesized **Bpy-UiO-67(Zr)**⊂**UiO-67(Zr)** (red).

Synthesis of **Bpy-UiO-67(Zr)⊂Pro-UiO-67(Zr)**

0.4 M solution of $\text{Zr}(\text{O}^i\text{Pr})_4$ in CH_3COOH was prepared by mixing $\text{Zr}(\text{O}^i\text{Pr})_4$ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH_3COOH (1 mL). A 0.02 M solution of (S)-2-(1-(tert-butoxycarbonyl)pyrrolidine-2-carboxamido)-1,1'-biphenyl-4,4'-dicarboxylic acid linker (H_2 -Pro-BPDC) in DMF was prepared by dissolving H_2 -Pro-BPDC (36 mg, 0.08 mmol) in DMF (4 mL). To a 20 mL Pyrex vial were added in sequence CH_3COOH (0.4 mL), 0.4 M $\text{Zr}(\text{O}^i\text{Pr})_4$ solution in CH_3COOH (0.1 mL, 0.04 mmol), DMF (7 mL) and 0.02 M H_2 -Pro-BPDC solution (2 mL, 0.04 mmol) and DMF suspension of Bpy-UiO-67(Zr) (1 mL) prepared previously (condition II, *vide supra*). The mixture was vortexed for 10 seconds and stirred with a magnetic stir bar (50 rpm) in a 65 °C oil bath for 5.5 hours. The reaction was cooled down to room temperature and centrifuged at 10,000 rpm for 3 min to obtain Bpy-UiO-67(Zr)⊂Pro-UiO-67(Zr) as a white precipitate. The precipitate was copiously washed with fresh DMF (4 mL, 4x) and acetonitrile (4 mL, 4x) and evacuated under schlenk line vacuum for 2 hours.

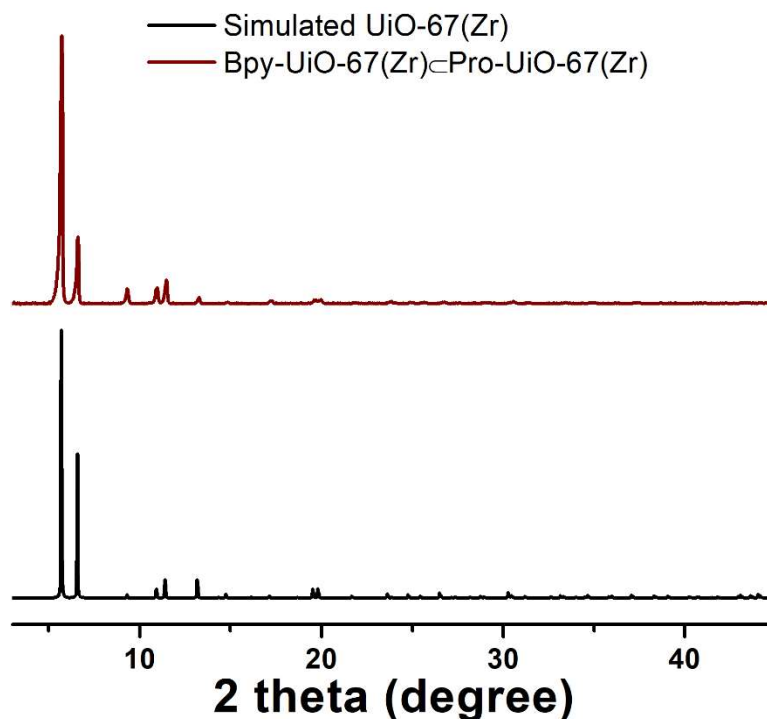


Figure S3.27 Simulated PXRD pattern of UiO-67(Zr) (black) and experimental PXRD pattern of as-synthesized **Bpy-UiO-67(Zr)⊂Pro-UiO-67(Zr)** (red).

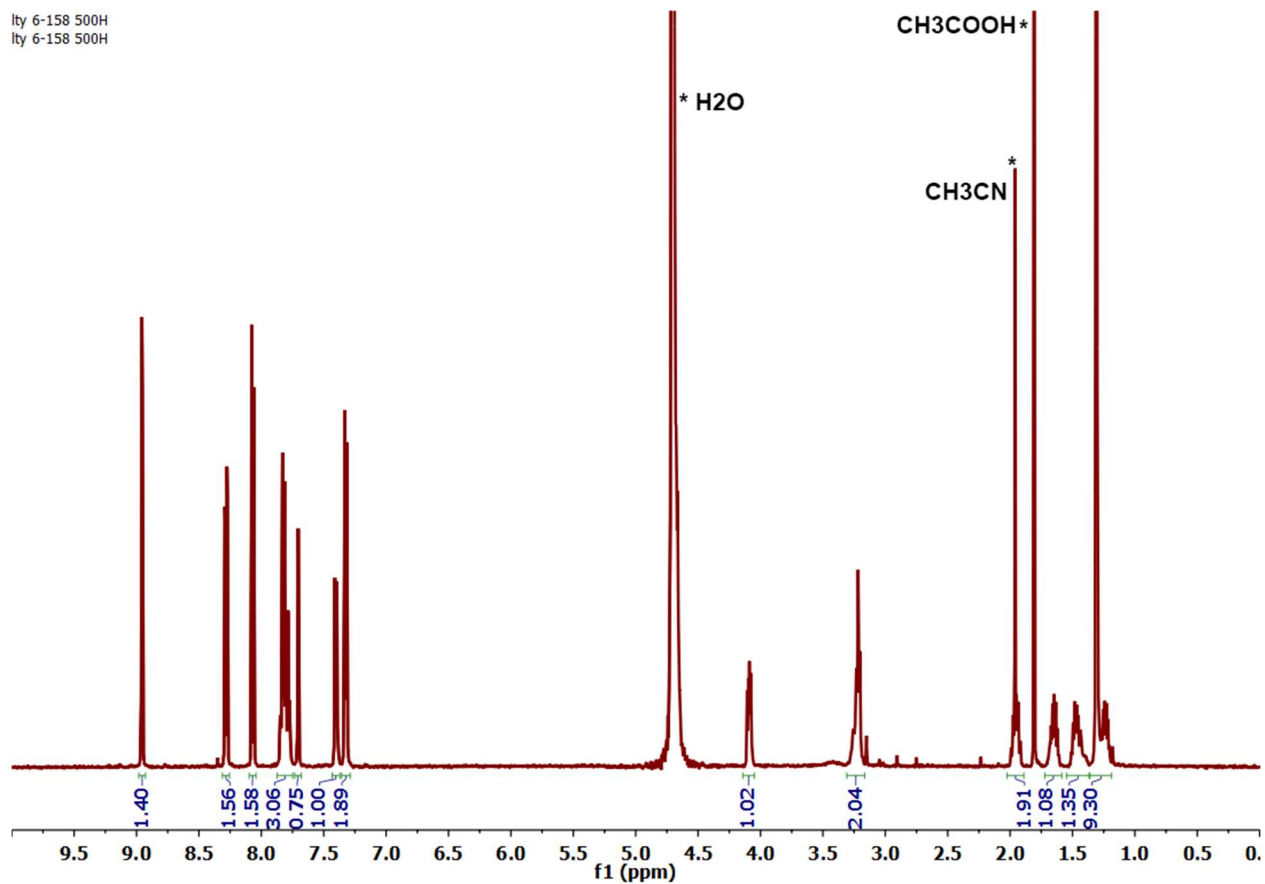


Figure S3.28 ^1H NMR of digested **Bpy-UiO-67(Zr)cPro-UiO-67(Hf)** in $\text{K}_3\text{PO}_4/\text{D}_2\text{O}$ showing an approximate BpyDC : Pro-BPDC ratio of 1:1.25.

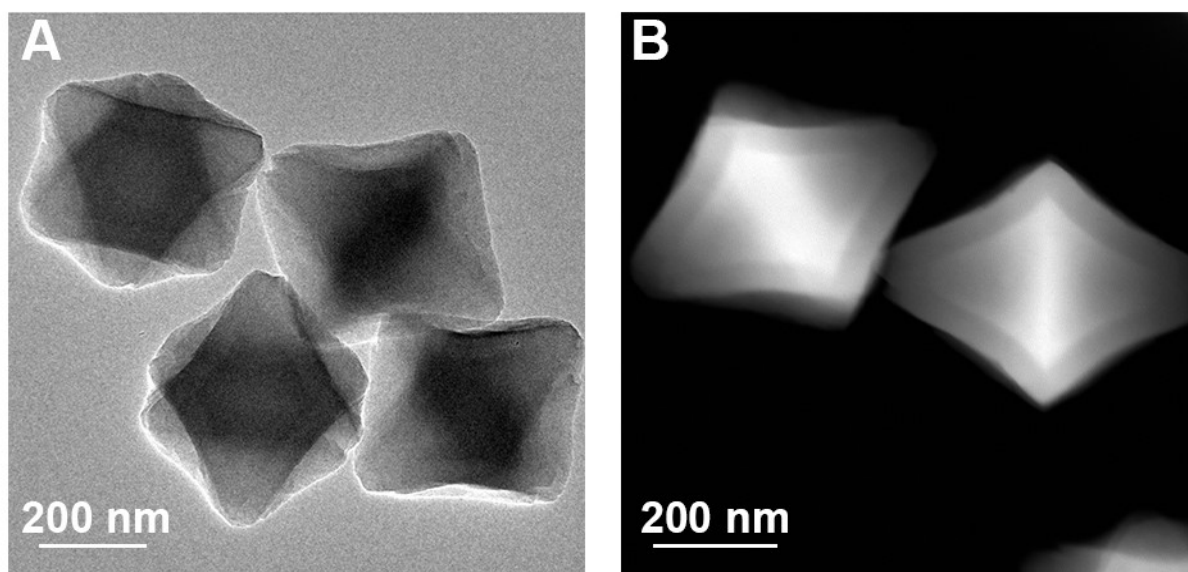


Figure S3.29 TEM image (A) and STEM-HAADF image (B) of **Bpy-UiO-67(Zr)cPro-UiO-67(Zr)**.

UiO-67(Zr) metalation control experiment

Bis(acetonitrile)dichloropalladium(II) (15.6 mg, 0.06 mmol) was dissolved in 3 mL acetonitrile in a 4 mL pyrex vial. The Bis(acetonitrile)dichloropalladium(II) solution was then mixed with 1 mL acetonitrile suspension of UiO-67(Zr) (~ 3 mg, ~0.009 mmol BPDC). The mixture was placed at room temperature for 24 hours. After centrifugation at 10,000 rpm for 2 min and copiously wash with acetonitrile (6 mL, 6x), white precipitate was collected and examined by STEM-EDS.

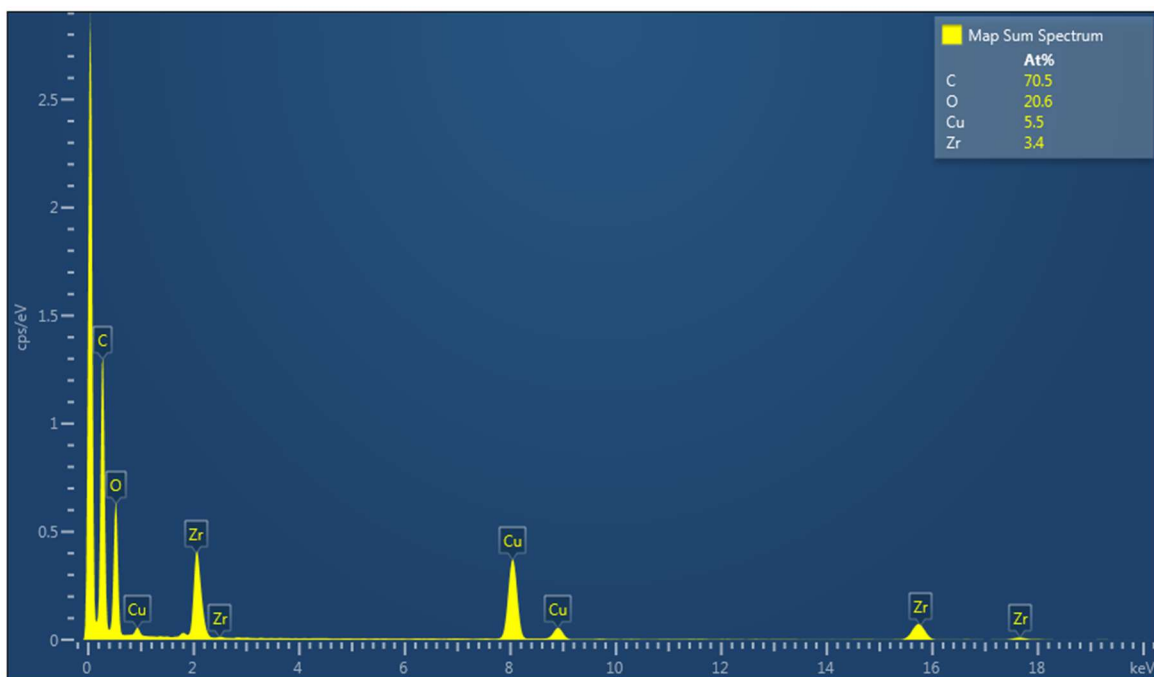
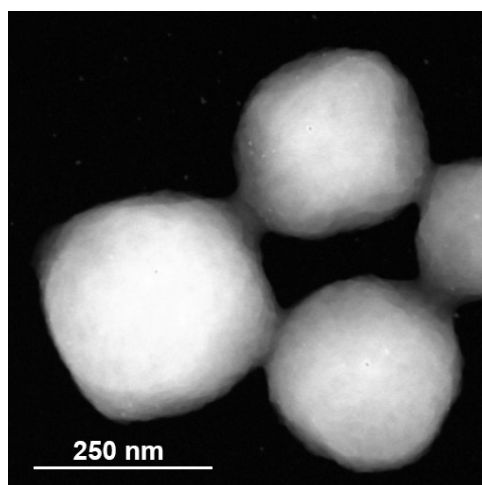


Figure S3.30 STEM-HAADF Image of UiO-67(Zr) (top) and EDS sum spectrum (bottom) of the entire image area after soaking with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ solution and thorough washing.

Pro-UiO-67(Zr) metalation control experiment

0.4 M solution of $\text{Zr}(\text{O}^n\text{Pr})_4$ in CH_3COOH was prepared by mixing $\text{Zr}(\text{O}^n\text{Pr})_4$ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH_3COOH (1 mL). A 0.02 M solution of $\text{H}_2\text{-Pro-BPDC}$ in DMF was prepared by dissolving $\text{H}_2\text{-Pro-BPDC}$ (18 mg, 0.04 mmol) in DMF (2 mL). To a 20 mL Pyrex vial were added in sequence CH_3COOH (0.2 mL), 0.4 M $\text{Zr}(\text{O}^n\text{Pr})_4$ solution (0.05 mL, 0.02 mmol), DMF (4 mL) and 0.02 M $\text{H}_2\text{-Pro-BPDC}$ solution (1 mL, 0.02 mmol). The vial was tightly capped and heated at 65 °C for 9 hours in an isothermal oven to yield turbid suspension. The suspension was centrifuged at 10000 rpm for 2 min to obtain Pro-UiO-67(Zr) as off-white precipitate. The precipitate was washed with fresh DMF (4 mL, 4x) and acetonitrile (4 mL, 4x), and then evacuated under vacuum for 1 h.

Bis(acetonitrile)dichloropalladium(II) (2.6 mg, 0.01 mmol) was dissolved in 1 mL acetonitrile in a 4 mL pyrex vial. The Bis(acetonitrile)dichloropalladium(II) solution was then mixed with 0.5 mL acetonitrile suspension of Pro-UiO-67(Zr) (~ 4 mg, ~0.007 mmol BPDC). The mixture was placed at room temperature for 24 h. After centrifugation at 10,000 rpm for 2 min and copiously wash with acetonitrile (6 mL, 6x), white precipitate was collected and examined by STEM-EDS.

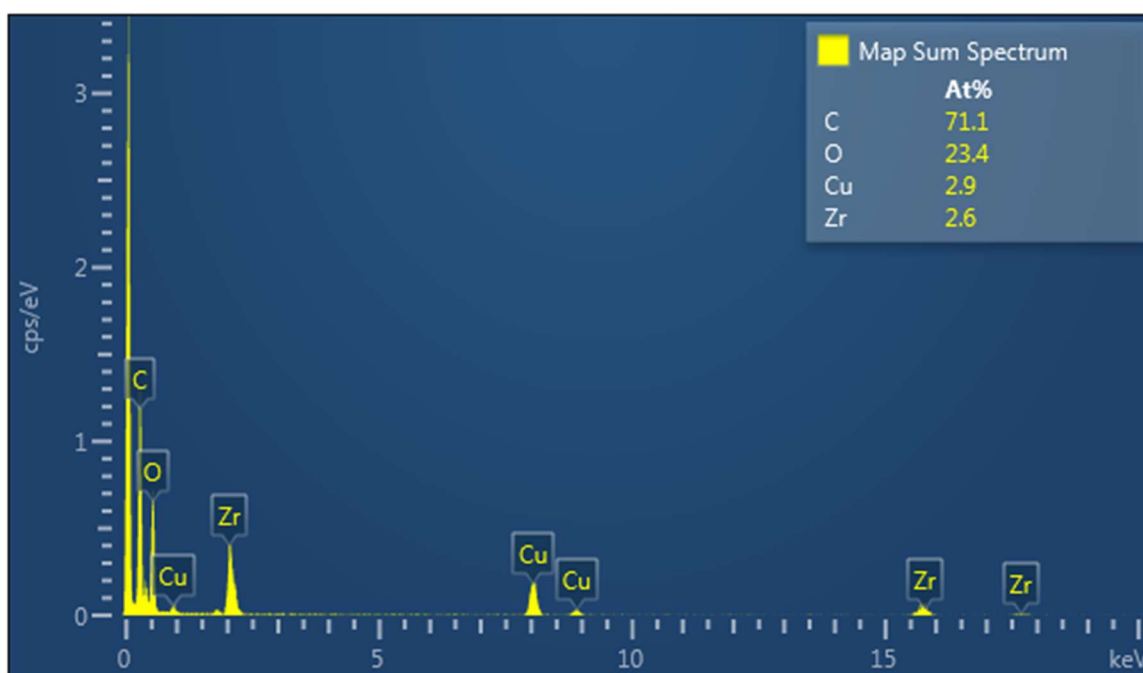
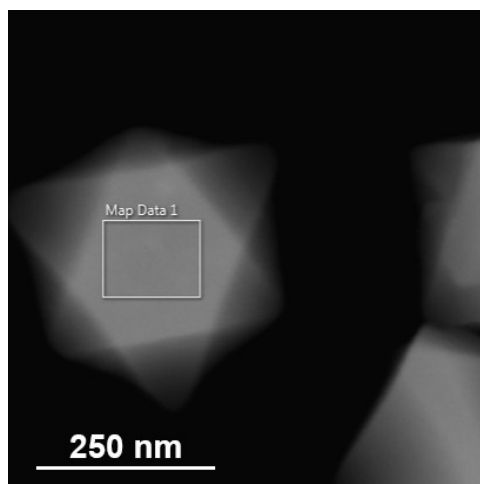


Figure S3.31 STEM-HAADF Image of **Pro-UiO-67(Zr)** (top) and EDS sum spectrum (bottom) of the surveyed area after soaking with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ solution and thorough washing.

Synthesis of *BpyPd-UiO-67(Zr)*⊂*UiO-67(Zr)*

Bis(acetonitrile)dichloropalladium(II) (10.4 mg, 0.04 mmol) was dissolved in 3 mL acetonitrile in a 4 mL Pyrex vial. The Bis(acetonitrile)dichloropalladium(II) solution was then mixed with 1 mL acetonitrile suspension of *Bpy-UiO-67(Zr)*⊂*UiO-67(Zr)* (~0.033 mmol *BpyDC*) prepared previously (*vide supra*). The mixture was placed at room temperature for 24 h. After centrifugation at 10,000 rpm for 2 min and copiously wash with acetonitrile (6 mL, 6x), yellow precipitate was collected.

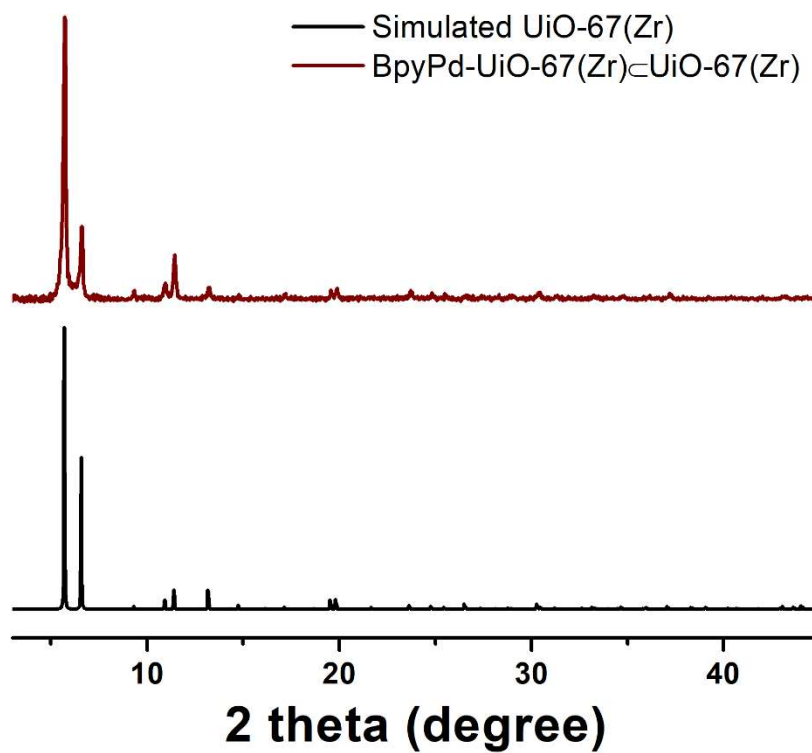


Figure S3.32 Simulated PXRD pattern of *UiO-67(Zr)* (black) and experimental PXRD pattern of as-synthesized ***BpyPd-UiO-67(Zr)*⊂*UiO-67(Zr)*** (red).

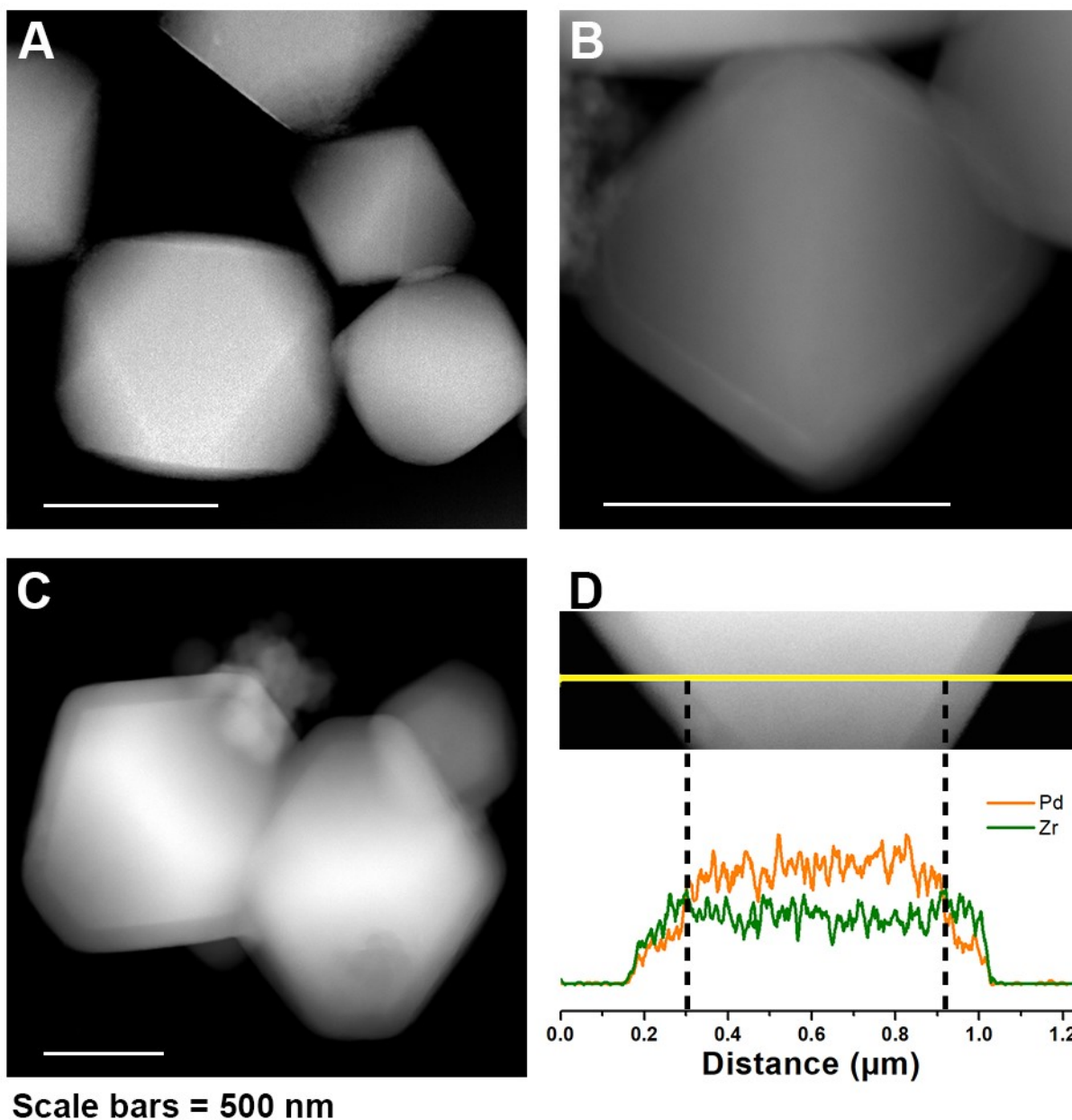
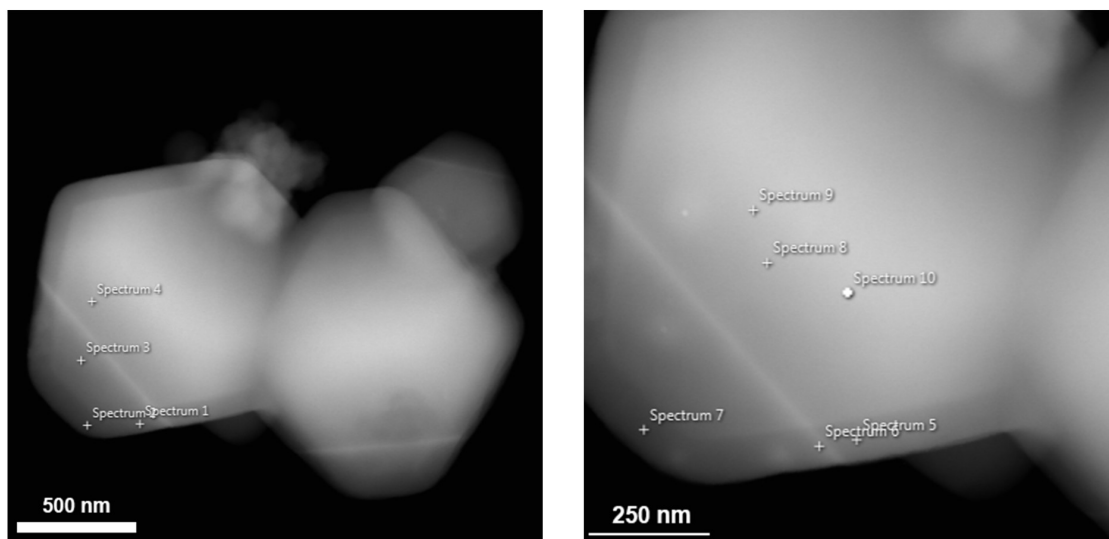


Figure S3.33 STEM-HAADF images of **Bpy-UiO-67(Zr)** (A), **Bpy-UiO-67(Zr)⊂UiO-67(Zr)** (B), and **BpyPd-UiO-67(Zr)⊂UiO-67(Zr)** (C); STEM-EDS line-scan data of **BpyPd-UiO-67(Zr)⊂UiO-67(Zr)** (D).



Site number	Site Location	Zr/Pd Ratio
1	Shell	1: 0.201
2	Shell	1: 0.206
3	Core	1: 0.535
4	Core	1: 0.725
5	Shell	1: 0.222
6	Shell	1: 0.211
7	Shell	1: 0.199
8	Core	1: 0.831
9	Core	1: 0.819
10	Core	1: 0.989

Figure S3.34 Zr:Pd ratios at different points in a **BpyPd-UiO-67(Zr)** crystal determined from STEM-EDS spectra using Zr K α 1 at 15.7 keV and Pd L α 1 at 2.8 keV.

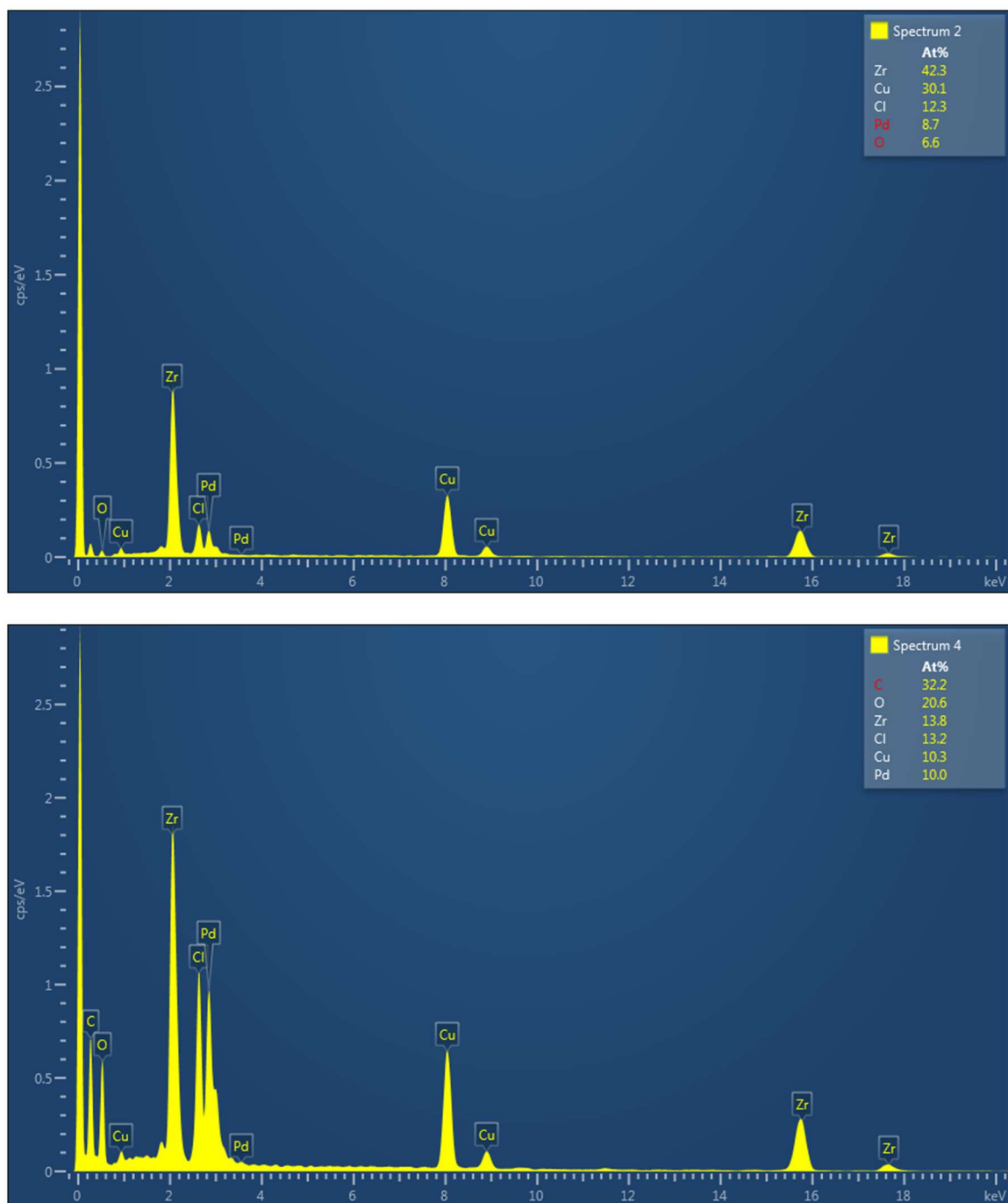


Figure S3.35 Representative EDS spectra of outer stratum (top, spectrum for site 2 in Figure S3.34) and inner stratum (bottom, spectrum for site 4 in Figure S3.34).

Synthesis of *BpyPd-UiO-67(Zr)*⊂*Pro-UiO-67(Zr)*

Bpy-UiO-67(Zr)⊂*Pro-UiO-67(Zr)* (34.4 mg, containing ~ 0.03 mmol bipyridine linker) was suspended in 1 mL acetonitrile. Bis(acetonitrile)dichloropalladium(II) (7.5 mg, 0.031 mmol) dissolved in acetonitrile (6 mL) was added to the MOF suspension. The mixture was allowed to react at room temperature for 24 h and then centrifuged at 10,000 rpm for 2 min. The yellow precipitate was collected and profusely washed with acetonitrile (6 mL, 6x).

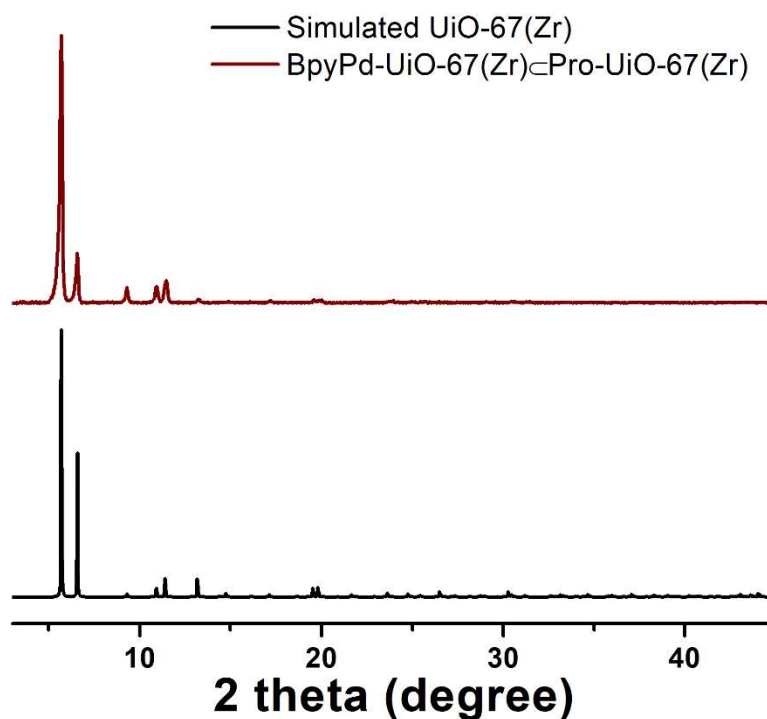


Figure S3.36 Simulated PXRD pattern of UiO-67(Zr) and experimental PXRD pattern of as-synthesized *BpyPd-UiO-67(Zr)*⊂*Pro-UiO-67(Zr)* (red).

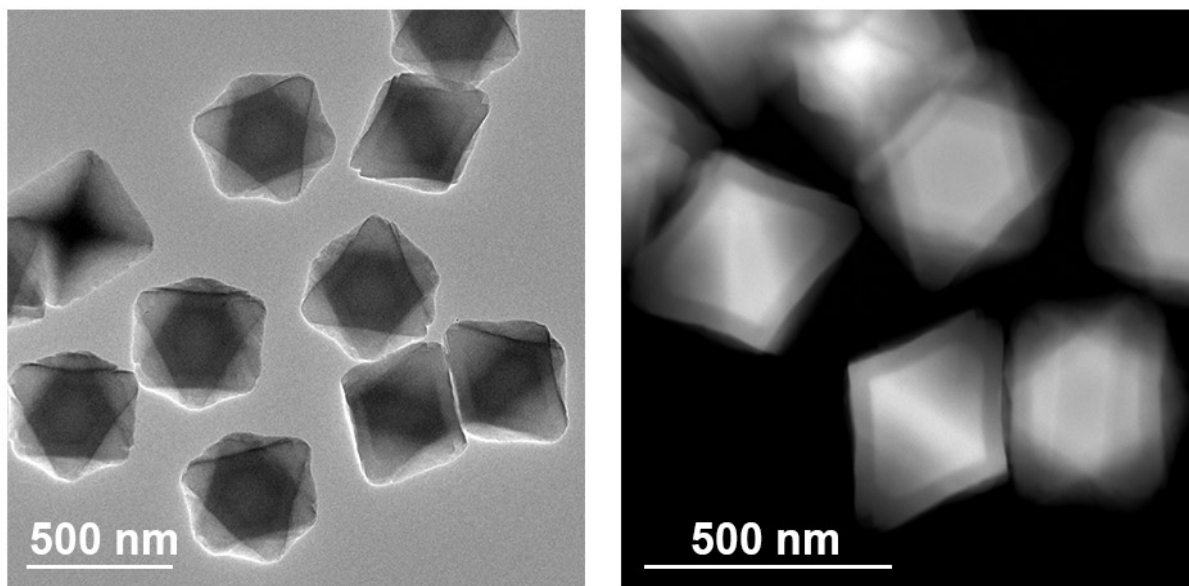


Figure S3.37 TEM and STEM-HAADF images of **BpyPd-UiO-67(Zr)@Pro-UiO-67(Zr)**.

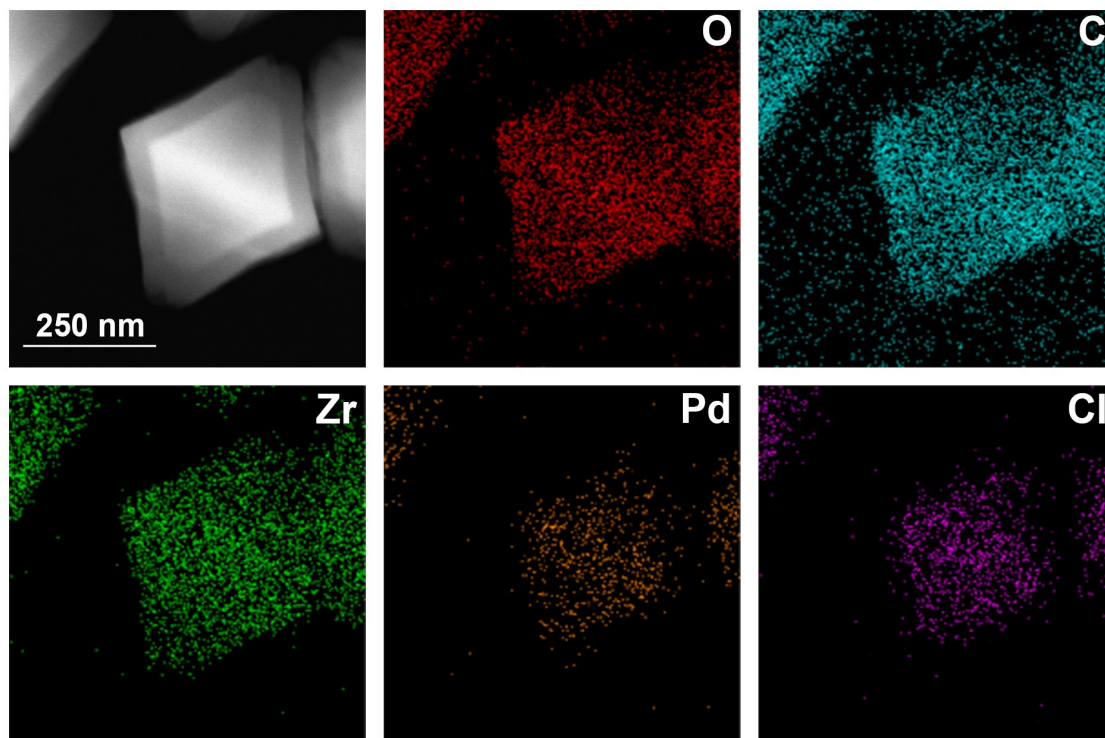


Figure S3.38 STEM-EDS mapping data of **BpyPd-UiO-67(Zr)@Pro-UiO-67(Zr)**.

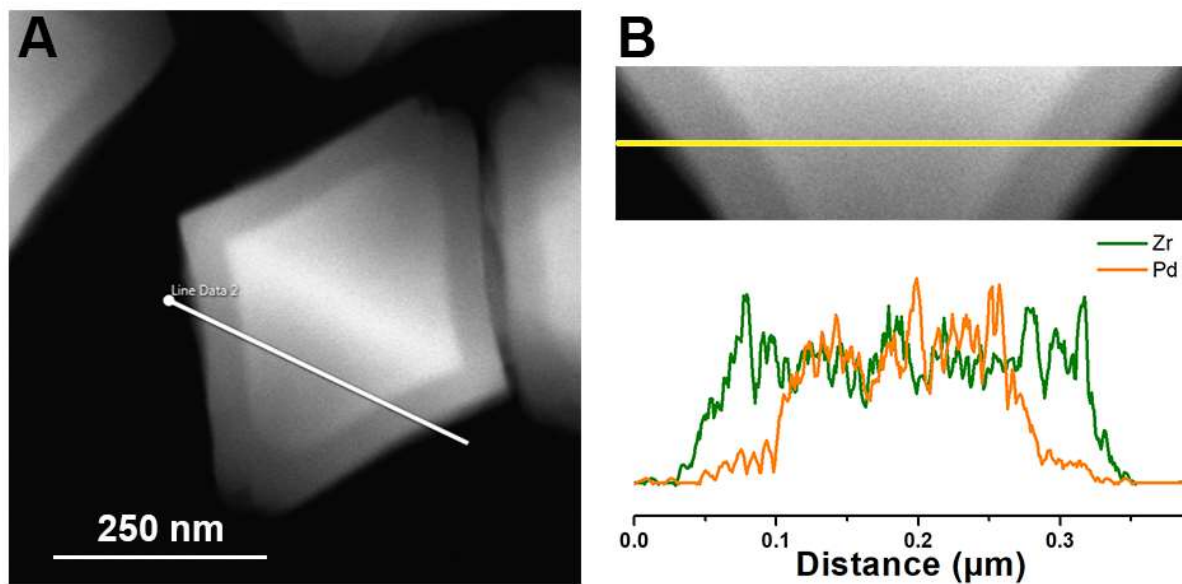
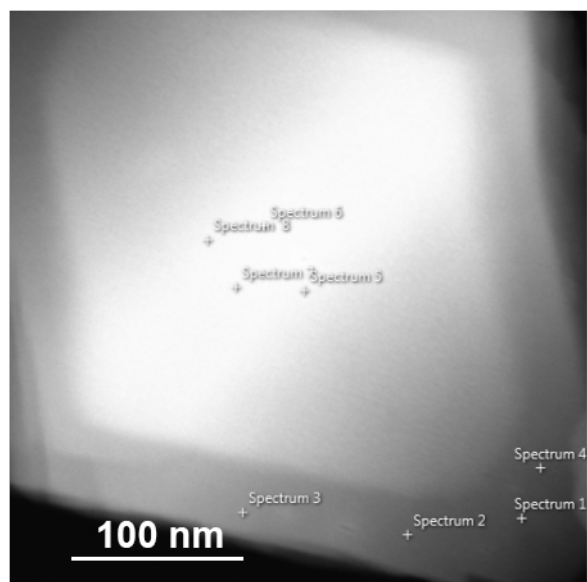


Figure S3.39 STEM-EDS line-scan data of **BpyPd-UiO-67(Zr)@Pro-UiO-67(Zr)**.



Site number	Point Location	Pd/Zr Ratio
1	Shell	0:1
2	Shell	0:1
3	Shell	0.08:1
4	Shell	0:1
5	Core	0.62:1
6	Core	0.85:1
7	Core	0.84:1
8	Core	0.75:1

Figure S3.40 Pd:Zr ratios at different points in a **BpyPd-UiO-67(Zr)** crystal determined from STEM-EDS spectra using Zr K α 1 at 15.7 keV and Pd L α 1 at 2.8 keV.

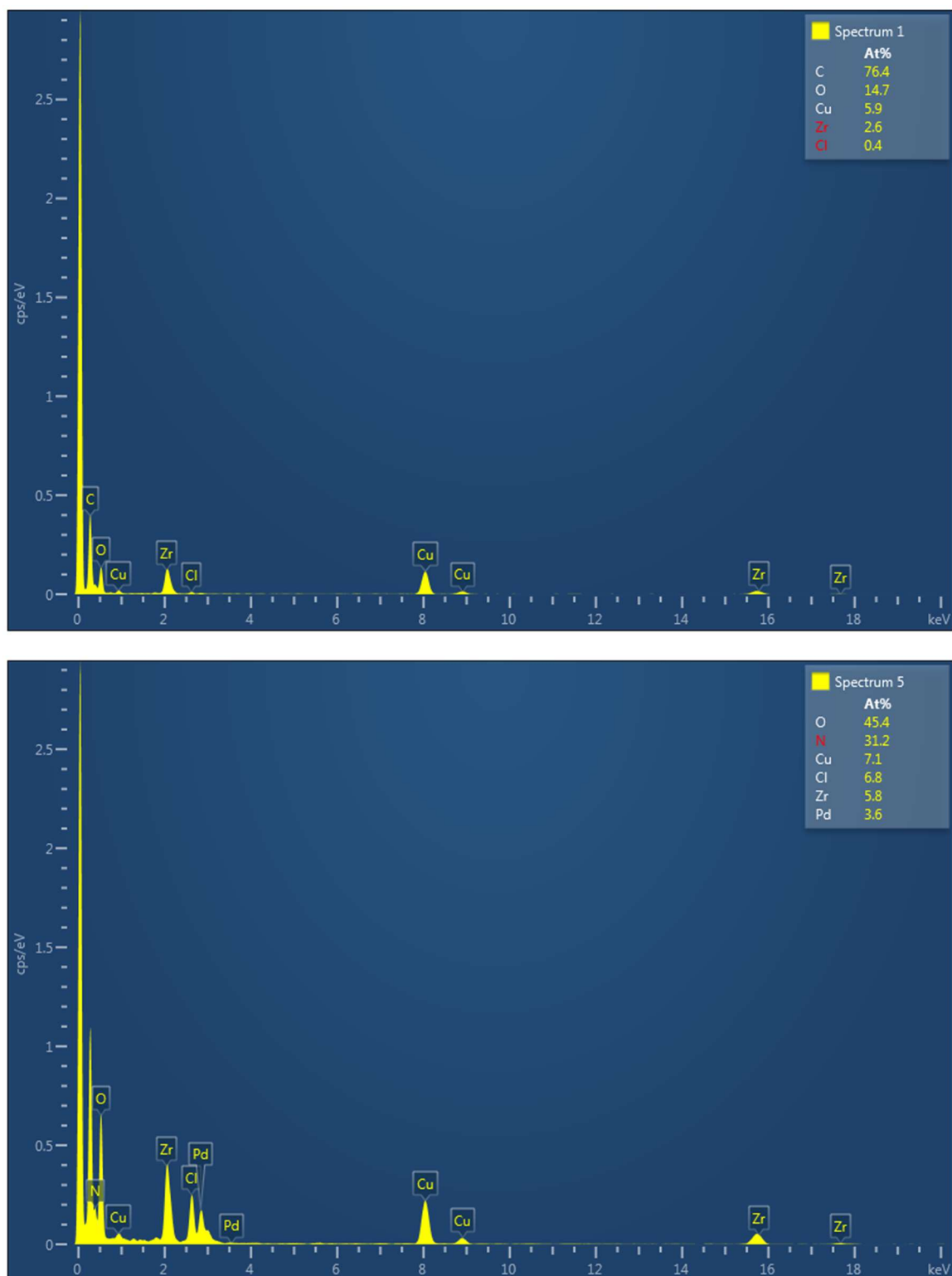


Figure S3.41 Representative EDS spectra of outer stratum (top, spectrum of site 1 in Figure S3.40) and inner stratum (bottom, spectrum of site 5 in Figure S3.40).

4. Nanoparticle syntheses and characterization

Methods and materials

Hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.999%), sodium citrate tribasic dihydrate (citrate, $\geq 99\%$), copper(II) sulfate hexahydrate ($\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$, $> 99.995\%$), selenium dioxide (SeO_2 , $> 99.5\%$), ascorbic acid (70% technical grade), polyvinylpyrrolidone (PVP, average molecular weight 10 kDa) were purchased from Sigma Aldrich (St. Louis, MO). Absolute ethanol (EtOH) was purchased from Thermo Fisher Scientific (Pittsburgh, PA). All chemicals were used as received with no additional purification unless otherwise noted. NANOpure[®] (Thermo Scientific, $> 18.2 \text{ M}\Omega \cdot \text{cm}$) water was used in the preparation of all aqueous solutions. All purchased chemicals were used without further purification except where otherwise noted.

Prior to use, all glassware and Teflon stir bars were washed in aqua regia and rinsed with copious amounts of water prior to oven drying. *Caution: aqua regia is highly toxic and corrosive, and should only be used with proper personal protective equipment and training. Aqua regia should be handled only inside a fume hood.*

Synthesis of citrate capped Au nanoparticles

AuNPs were synthesized using a modified Frens procedure. In a 1 L, three-neck round-bottom flask containing a stir bar, 500 mL of aqueous HAuCl_4 (1 mM) solution was prepared. The solution was heated to vigorous reflux while stirring until a rapid drip rate was achieved (drip rate \sim one/s). Meanwhile, a 50 mL aqueous solution of 30 mM citrate was prepared. This citrate solution was rapidly added to the refluxing HAuCl_4 solution. After addition, the reaction mixture changed from yellow, to colorless, to black, to purple-red within 1 min. The resulting AuNP solution was allowed to reflux for 5 min before it was removed from heat. This mixture was cooled to room temperature. Prior to use, AuNPs were filtered using a poly(vinylidene fluoride) (PVDF) filter membrane with a pore size of $0.45 \mu\text{m}$ (25 mm GD/XP disposable filters, Whatman, Inc.). Immediately after filtration, the AuNPs were concentrated by separating 1 mL aliquots into 1.5 mL centrifuge tubes and centrifuging the solution at 20 000 rcf for 5 min (Eppendorf 5424 centrifuge). The supernatant was removed, and another 1 mL aliquot of filtered NPs was added and centrifuged once more. The supernatant was removed.

Ligand exchange of Au nanoparticles with 55 kDa PVP

A 3 mL of aqueous 10 kDa PVP (5 mM) solution was prepared. Meanwhile, purified AuNP solutions were distributed to 500 μ L aliquots in 1.5 mL centrifuge tubes for ligand exchange. 200 μ L aliquots of PVP solution and 800 μ L of water were added in the centrifuge tubes containing purified NPs. This mixture was then placed on a temperature controlled mixer for 4 h at 1000 rpm and 25 $^{\circ}$ C (Eppendorf R Thermomixer). After at least 6 hours, the NP solutions were washed a total of 5 times. Here, washing indicates centrifuging the sample and removing all supernatant followed by resuspension in water. The final purified NP sample was suspended in water for sample characterization. To prepare DMF solution of Au nanoparticles used in MOF encapsulation reactions, the aqueous solution was lyophilized to remove water and the residue was dissolved in DMF.

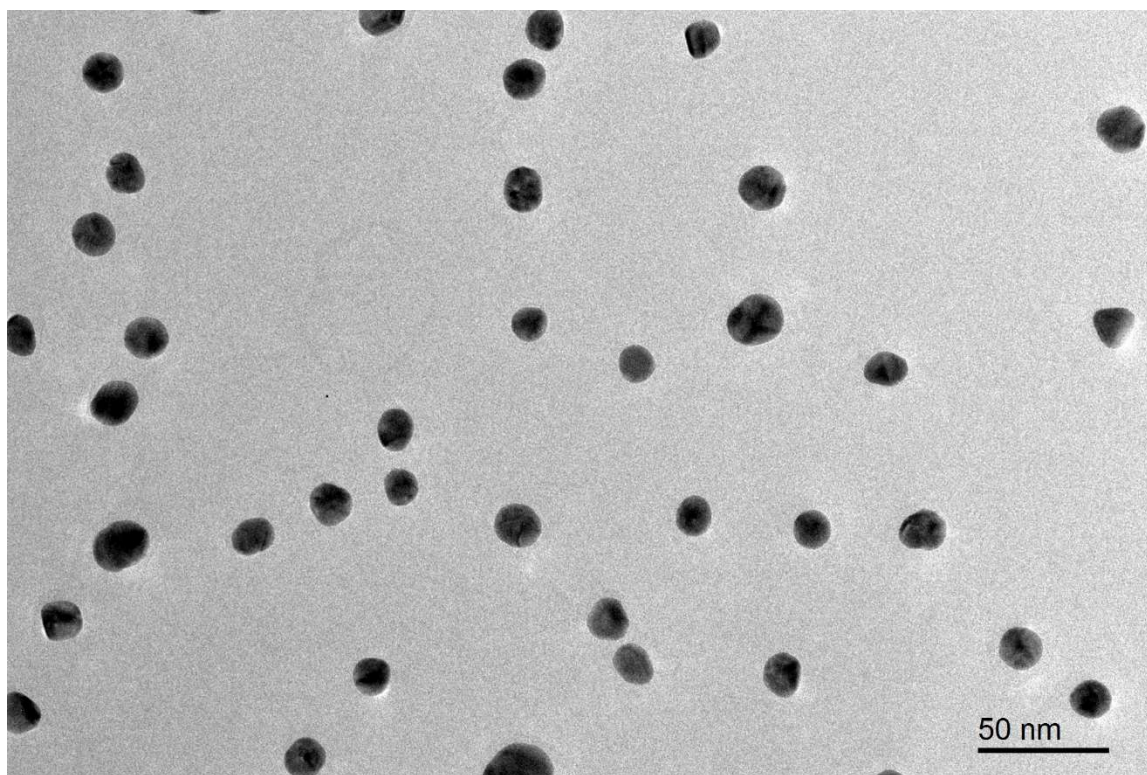


Figure S4.1 TEM images of 13 nm 55 kDa PVP capped Au nanoparticles.

40 kDa PVP capped Ag nanoparticles

40 nm 40 kDa PVP capped Ag nanoparticles was purchased from VWR as a dried powder (#103369-674 NanoXact Silver Nanospheres, Dried Powder). Ag nanoparticles were dissolved in DMF before MOF encapsulation reactions.

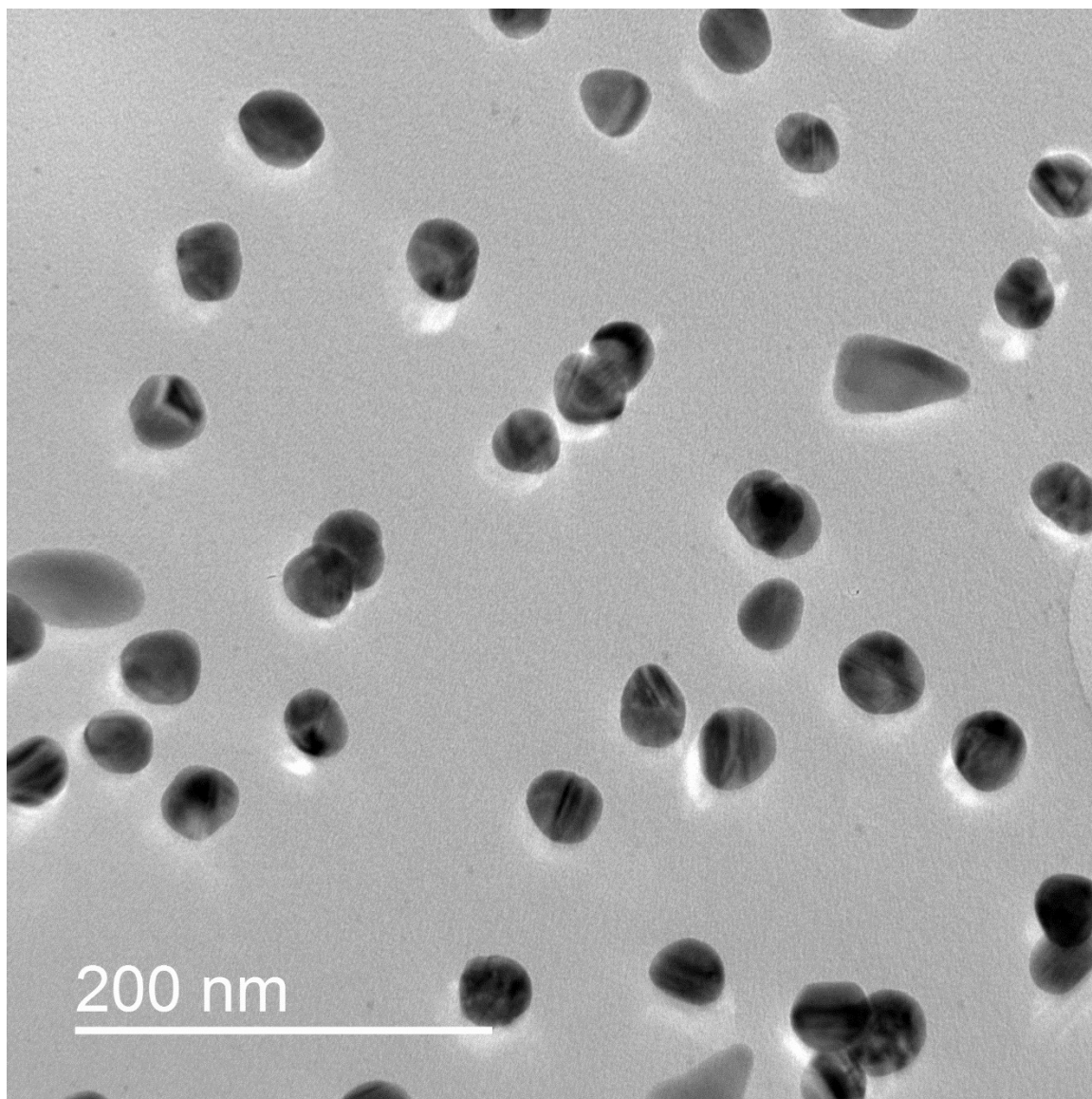


Figure S4.2 TEM image of 40 nm Ag nanoparticles capped with 40 kDa PVP.

Synthesis of 55 kDa PVP capped Cu_{2-x}Se ($x=0.75$) nanoparticles

Cu_{2-x}Se NPs were synthesized at room temperature under ambient atmosphere according to a modified literature procedure.⁵ 10 mL of aqueous 55 kDa PVP (50 mM) solution dissolved in NANOpure water was added in a glass vial containing a stir bar. 500 μL of aqueous SeO_2 (0.25 M) solution was added followed by a quick injection of 200 μL of aqueous 1.13 M ascorbic acid. The clear yellow solution turned red after the reduction of SeO_2 to form Se seeds. 10 minutes later, 500 μL of aqueous CuSO_4 (0.50 M) solution was added into the red solution. The solution was stirred for 15 seconds until the color turned a darker brown to allow Cu^{2+} ions to diffuse into the Se lattices before a quick injection of 300 μL of aqueous 1.13 M ascorbic acid. The solution was left stirring for at least 6 hours to allow for the reaction to complete. The green colored solution was then purified by diluting with more NANOpure water in a 50 mL Falcon tube and centrifuged in an Eppendorf 5804R centrifuge with a fixed angle rotor (FA-45-6-30) (Eppendorf, Inc.) at a force of 16,000 rpm at 20 °C for 15 min. The supernatant solution was discarded and the pellet was diluted with NANOpure water for another 15 minute centrifugation. The purification process was repeated once and resuspended in NANOpure water. After the final purification, the NPs were lyophilized overnight (Labconco Freezone 6, Materials Characterization Laboratory, University of Pittsburgh Department of Chemistry), and the dried NP powder was characterized dry and resuspended in ethanol for MOF encapsulation reactions.

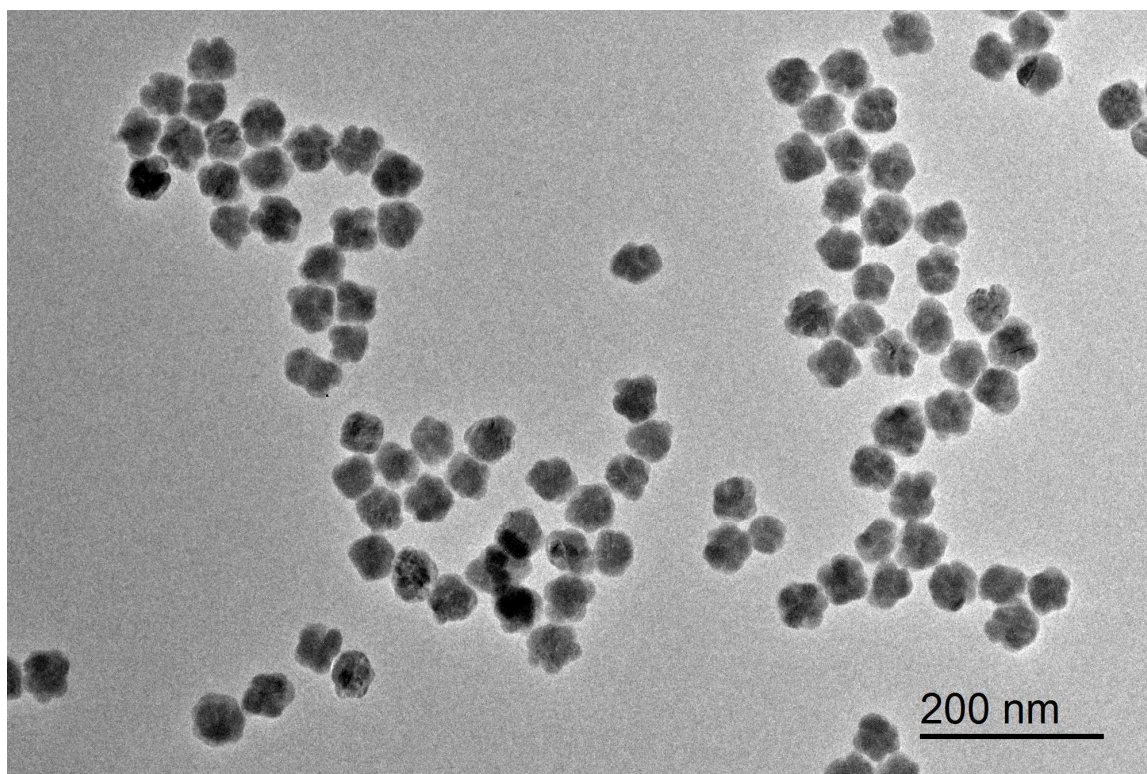


Figure S4.3 TEM image of Cu_{2-x}Se nanoparticles capped with 55 kDa.

5. Syntheses and characterization of NPs@MOF composites

Synthesis of **Au@UiO-67**

0.4 M solution of $\text{Zr}(\text{O}^i\text{Pr})_4$ in CH_3COOH was prepared by mixing $\text{Zr}(\text{O}^i\text{Pr})_4$ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH_3COOH (1 mL). A 0.02 M solution of $\text{H}_2\text{-BPDC}$ in DMF was prepared by heating a mixture of $\text{H}_2\text{-BPDC}$ (19.4 mg, 0.08 mmol) and DMF (4 mL) on a stir plate at 150 °C until complete dissolution. DMF solution of 13 nm Au nanoparticles capped with 55 kDa PVP was prepared such that the optical density was 0.132 at 521 nm upon dilution by 25 times. To a 20 mL Pyrex vial were added in sequence CH_3COOH (0.3 mL), 0.4 M $\text{Zr}(\text{O}^i\text{Pr})_4$ solution (0.05 mL, 0.02 mmol), DMF (4 mL) and 0.02 M $\text{H}_2\text{-BPDC}$ solution (1 mL, 0.02 mmol), Au nanoparticle solution (0.2 mL). The vial was tightly capped and heated at 65 °C in an isothermal oven for 30 min to yield pink turbid suspension. The suspension was centrifuged at 10000 rpm for 2 min to obtain pink precipitate. The precipitate was washed with fresh DMF (16mL, 4x) and used immediately for the next step.

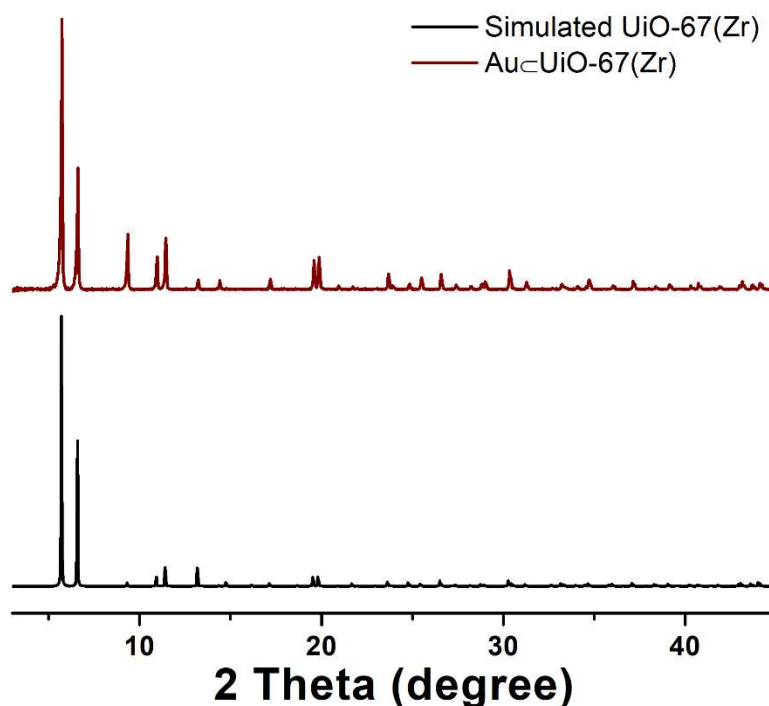


Figure S5.1 Simulated PXRD pattern of UiO-67(Zr) (black) and PXRD pattern of as-synthesized **Au@UiO-67(Zr)** (red).

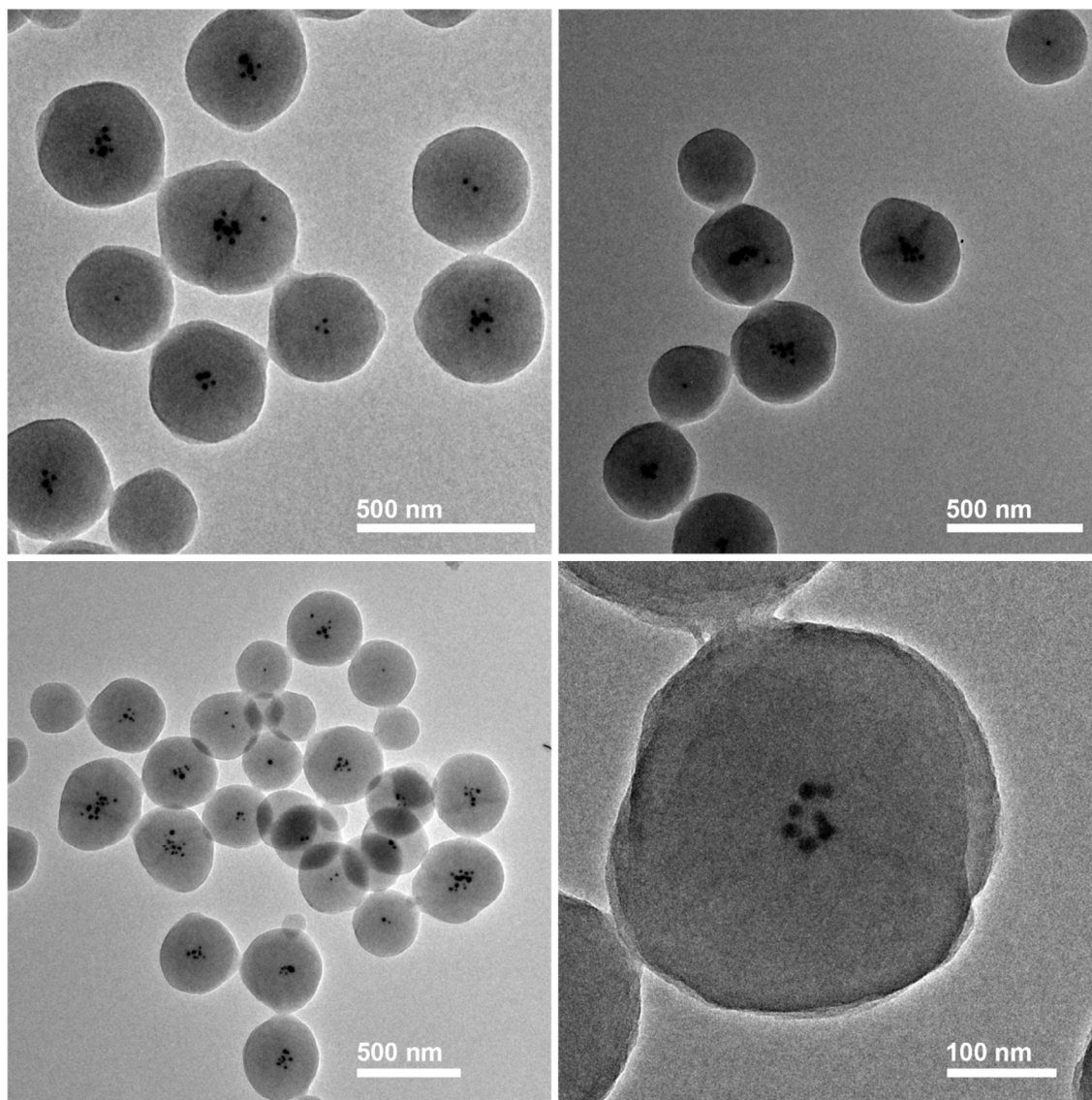


Figure S5.2 TEM images of **AucUiO-67(Zr)**.

Synthesis of **Au \subset UiO-67(Zr) \subset UiO-67(Hf)**

0.02 M solution of H₂-BPDC in DMF was prepared by heating a mixture of H₂-BPDC (19.4 mg, 0.08 mmol) and DMF (4 mL) on a stir plate at 150 °C until complete dissolution. Hf(OⁱPr)₄•PrOH (19 mg, 0.04 mmol) and CH₃COOH (0.7 mL) was mixed in a 20 mL Pyrex vial. After the mixture was sonicated for 3 min, DMF (3.2 mL) and 0.02 M H₂-BPDC solution (2 mL, 0.04 mmol) was added. The mixture was vortexed and incubated at 65 °C in an isothermal oven for 50 min. The reaction suspension was then centrifuged at 10000 rpm for 2 min to obtain white precipitate and clear supernatant. The clear supernatant (3 mL) was used to disperse Au \subset UiO-67(Zr) prepared previously (*vide supra*) by vortexing and sonication. The reaction was allowed to proceed at 25 °C without stirring for 19 hours. the reaction suspension was centrifuged at 10000 rpm for 2 min to obtain pink precipitate. The product was then washed with fresh DMF (16mL, 4x) before further characterization or reactions.

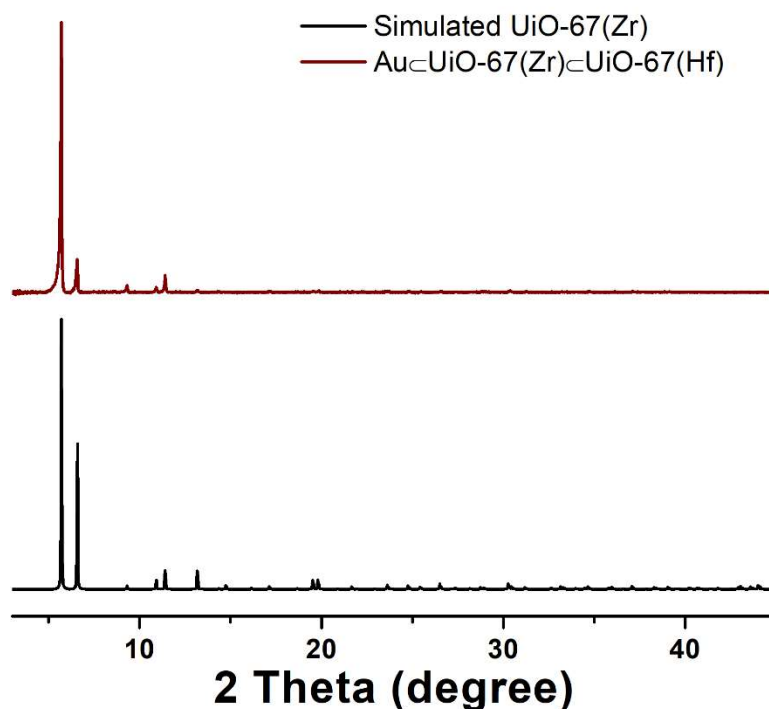


Figure S5.3 Simulated PXRD pattern of UiO-67(Zr) (black) and experimental PXRD pattern of as-synthesized **Au \subset UiO-67(Zr) \subset UiO-67(Hf)** (red).

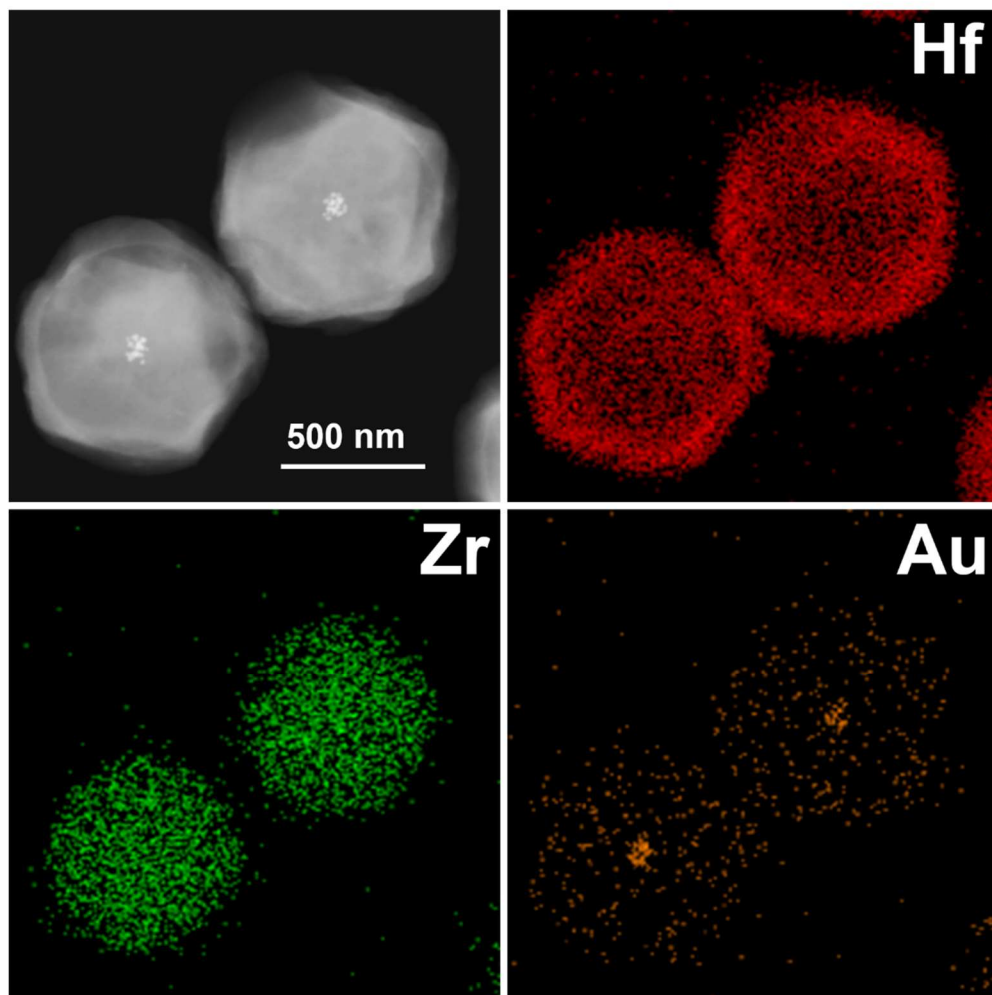


Figure S5.4 STEM-EDS characterization of $\text{Au}@ \text{UiO-67}(\text{Zr})@ \text{UiO-67}(\text{Hf})$.

Synthesis of **Ag@UiO-67(Zr)**

0.4 M solution of $\text{Zr}(\text{O}^i\text{Pr})_4$ in CH_3COOH was prepared by mixing $\text{Zr}(\text{O}^i\text{Pr})_4$ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH_3COOH (1 mL). A 0.02 M solution of $\text{H}_2\text{-BPDC}$ in DMF was prepared by heating a mixture of $\text{H}_2\text{-BPDC}$ (19.4 mg, 0.08 mmol) and DMF (4 mL) on a stir plate at 150 °C until complete dissolution. DMF solution of 40 nm Ag nanoparticles capped with 40k PVP was prepared such that the optical density was ~0.37 at 439 nm upon dilution by 10 times. To a 20 mL Pyrex vial were added in sequence CH_3COOH (0.3 mL), 0.4 M $\text{Zr}(\text{O}^i\text{Pr})_4$ solution (0.05 mL, 0.02 mmol), DMF (1.6 mL), 0.02 M $\text{H}_2\text{-BPDC}$ solution (1 mL, 0.02 mmol) and Ag nanoparticle solution (0.8 mL). The vial was tightly capped and heated at 65 °C for 15 min in an isothermal oven to yield turbid suspension. The suspension was centrifuged at 10000 rpm for 2 min to obtain dark yellow precipitate. The precipitate was washed with fresh DMF (16mL, 4x) and used immediately for the next step.

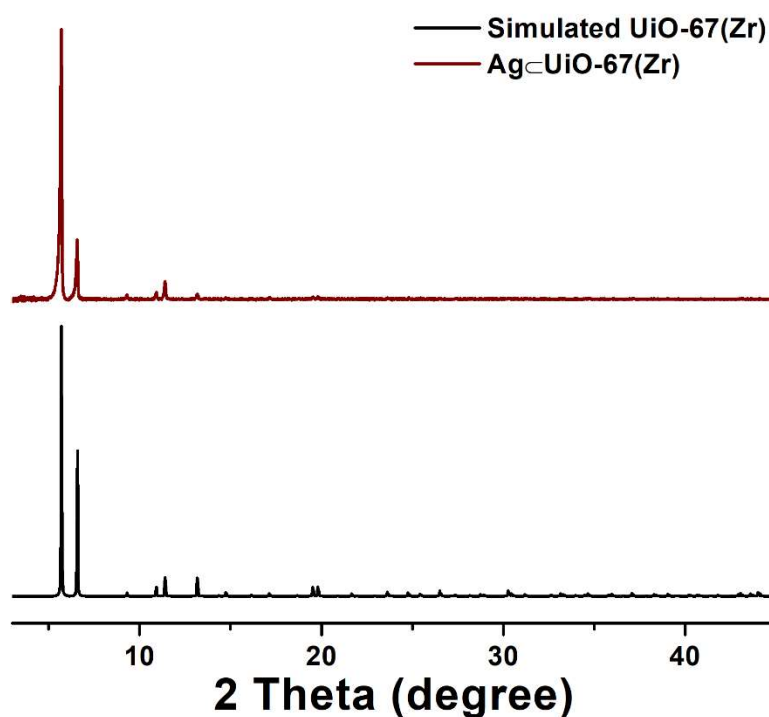


Figure S5.5 Simulated PXRD pattern based on **UiO-67(Zr)** crystal structure and PXRD pattern of as-synthesized **Ag@UiO-67(Zr)** (red).

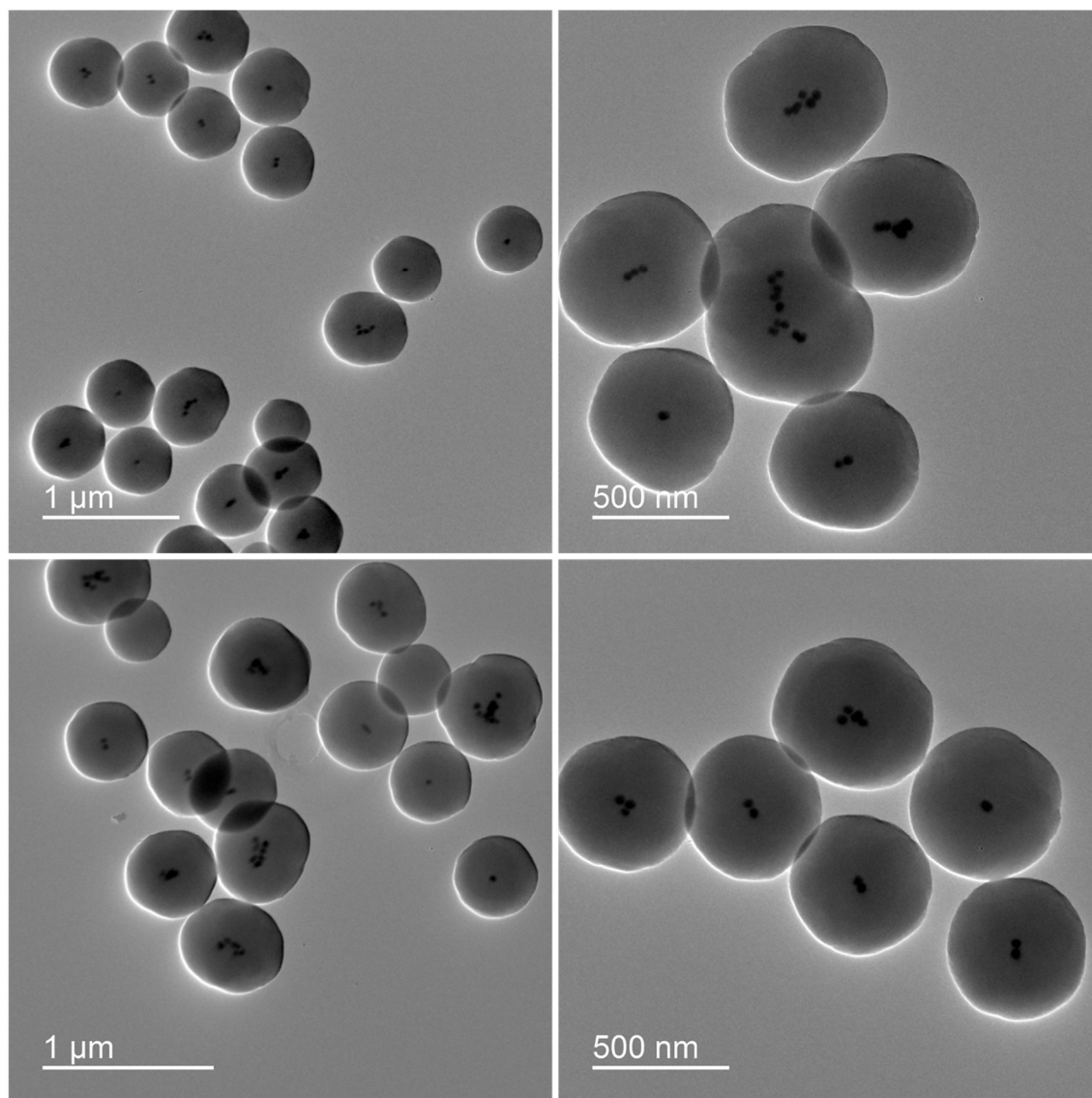


Figure S5.6 TEM images of **Ag@UiO-67(Zr)**.

Synthesis of $\text{Ag}@ \text{UiO-67}(\text{Zr})@ \text{UiO-67}(\text{Hf})$

0.02 M solution of $\text{H}_2\text{-BPDC}$ in DMF was prepared by heating a mixture of $\text{H}_2\text{-BPDC}$ (19.4 mg, 0.08 mmol) and DMF (4 mL) on a stir plate at 150 °C until complete dissolution. $\text{Hf}(\text{O}^i\text{Pr})_4 \cdot \text{PrOH}$ (19 mg, 0.04 mmol) and CH_3COOH (0.7 mL) was mixed in a 20 mL Pyrex vial. After the mixture was sonicated for 3 min, DMF (3.2 mL) and 0.02 M $\text{H}_2\text{-BPDC}$ solution (2 mL, 0.04 mmol) was added. The mixture was vortexed and incubated at 65 °C in an isothermal oven for 50 min. The reaction suspension was then centrifuged at 10000 rpm for 2 min to obtain white precipitate and clear supernatant. The clear supernatant (3 mL) was used to disperse $\text{Ag}@ \text{UiO-67}(\text{Zr})$ prepared previously (*vide supra*) by vortexing and sonication. The reaction was allowed to proceed at 25 °C without stirring for 8 h. the reaction suspension was centrifuged at 10000 rpm for 2 min to obtain yellow precipitate. The product was then washed with fresh DMF (16mL, 4x) before further characterization or reactions.

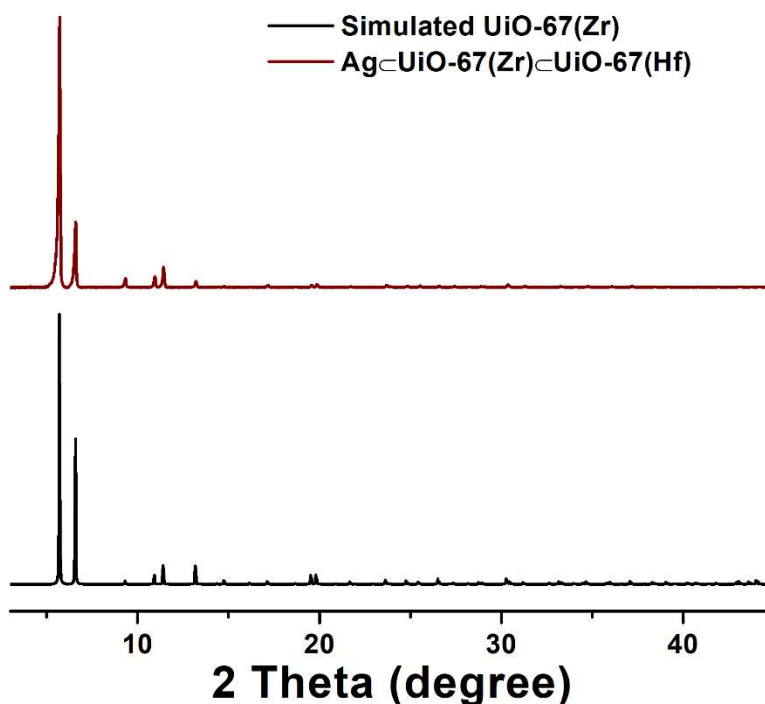


Figure S5.7 Simulated PXRD pattern based on UiO-67(Zr) crystal structure (black) and PXRD pattern of as-synthesized $\text{Ag}@ \text{UiO-67}(\text{Zr})@ \text{UiO-67}(\text{Hf})$ (red).

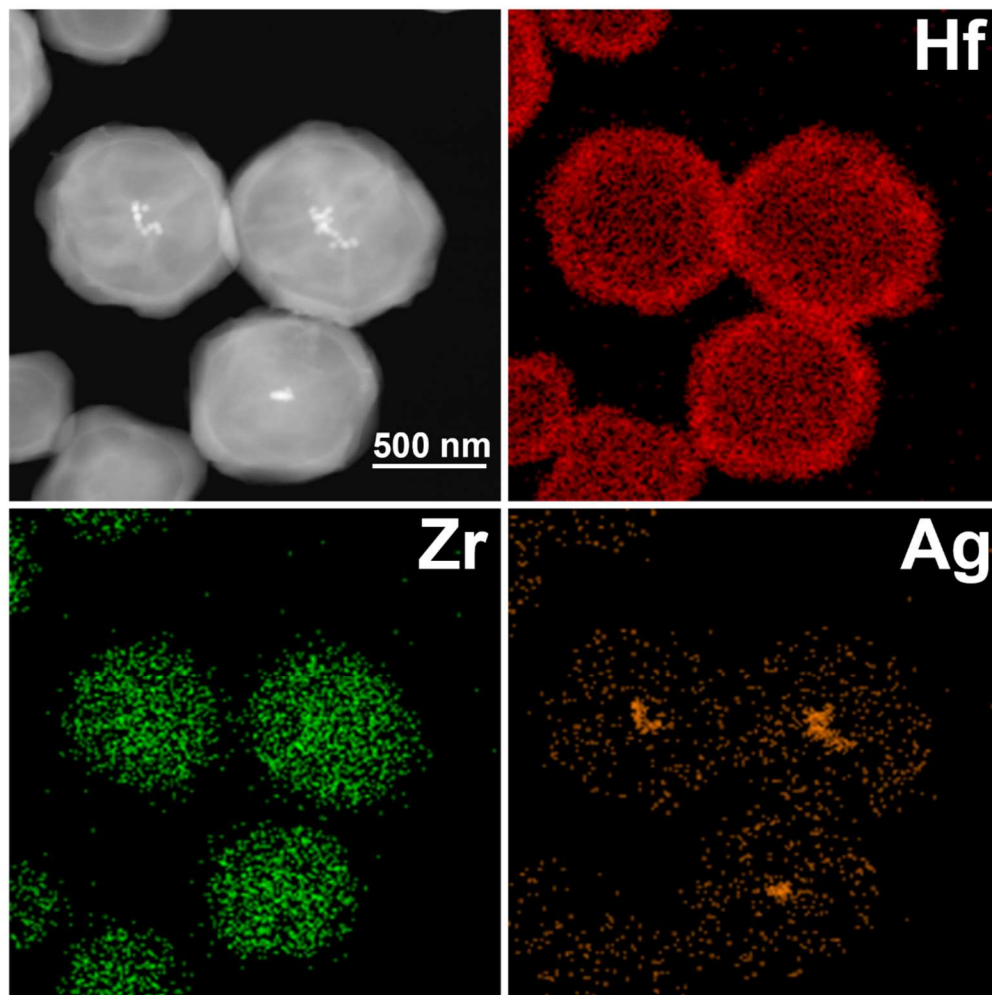


Figure S5.8 STEM-EDS characterization of $\text{Ag} \subset \text{UiO-67}(\text{Zr}) \subset \text{UiO-67}(\text{Hf})$.

Synthesis of $\text{Cu}_{2-x}\text{Se}@\text{UiO-67}(\text{Zr})$

0.4 M solution of $\text{Zr}(\text{O}^i\text{Pr})_4$ in CH_3COOH was prepared by mixing $\text{Zr}(\text{O}^i\text{Pr})_4$ 70 wt. % in *n*-propanol (187.2 mg, 0.4 mmol) with CH_3COOH (1 mL). A 0.02 M solution of $\text{H}_2\text{-BPDC}$ in DMF was prepared by mixing $\text{H}_2\text{-BPDC}$ (19.4 mg, 0.08 mmol) with DMF (4 mL) followed by heating on a stir plate at 150 °C until complete dissolution. EtOH solution of 50 nm Cu_{2-x}Se nanoparticles capped with 55 kDa PVP was prepared with optical density 0.2 at 1085 nm. To a 20 mL Pyrex vial were added in sequence CH_3COOH (1.2 mL), 0.4 M $\text{Zr}(\text{O}^i\text{Pr})_4$ solution (0.2 mL, 0.08 mmol), DMF (4 mL), 0.02 M $\text{H}_2\text{-BPDC}$ solution (4 mL, 0.08 mmol), and Cu_{2-x}Se nanoparticle EtOH solution (optical density ~ 0.20 at 1085 nm, 8 mL). The reaction was tightly capped and allowed to reaction at room temperature for 40 min to yield turbid suspension. The suspension was centrifuged at 10000 rpm for 2 min to obtain dark green precipitate. The precipitate was washed with fresh DMF (16mL, 4x) and used immediately for the next step.

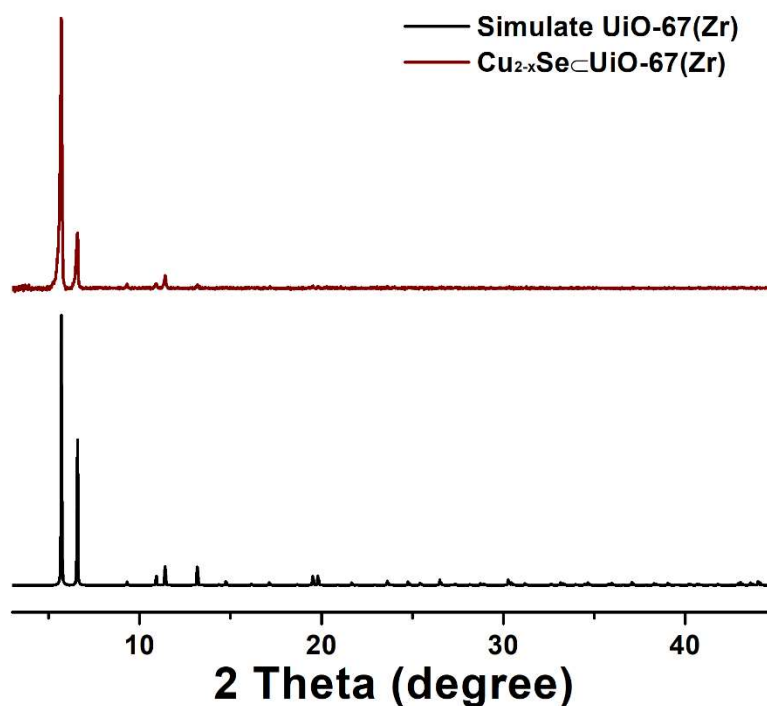


Figure S5.9 Simulated PXRD pattern based on UiO-67(Zr) crystal structure and PXRD pattern of as-synthesized $\text{Cu}_{2-x}\text{Se}@\text{UiO-67}(\text{Zr})$ (red).

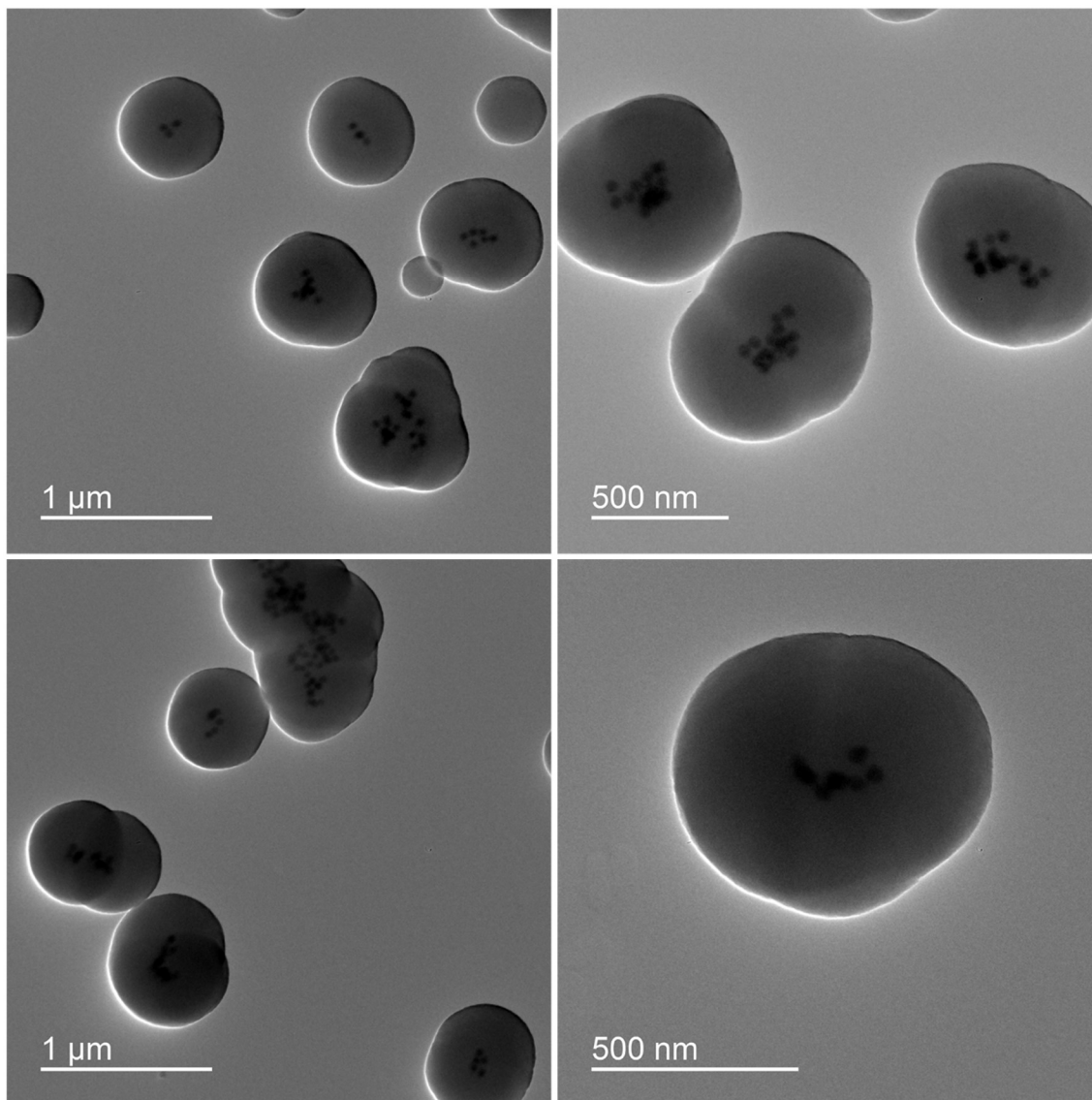


Figure S5.10 TEM images of $\text{Cu}_{2-x}\text{Se}@ \text{UiO}-67(\text{Zr})$.

Synthesis of $\text{Cu}_{2-x}\text{Se}@\text{UiO-67}(\text{Zr})@\text{UiO-67}(\text{Hf})$

0.02 M solution of $\text{H}_2\text{-BPDC}$ in DMF was prepared by heating a mixture of $\text{H}_2\text{-BPDC}$ (19.4 mg, 0.08 mmol) and DMF (4 mL) on a stir plate at 150 °C until complete dissolution. $\text{Hf}(\text{O}^i\text{Pr})_4 \cdot \text{PrOH}$ (19 mg, 0.04 mmol) and CH_3COOH (0.7 mL) was mixed in a 20 mL Pyrex vial. After the mixture was sonicated for 3 min, DMF (3.2 mL) and 0.02 M $\text{H}_2\text{-BPDC}$ solution (2 mL, 0.04 mmol) was added. The mixture was vortexed and incubated at 65 °C in an isothermal oven for 50 min. The reaction suspension was then centrifuged at 10000 rpm for 2 min to obtain white precipitate and clear supernatant. The clear supernatant (3 mL) was used to disperse $\text{Cu}_{2-x}\text{Se}@\text{UiO-67}(\text{Zr})$ prepared previously (*vide supra*) by brief vortexing and sonication. The reaction was allowed to proceed at 25 °C without stirring for 6 h. the reaction suspension was centrifuged at 10000 rpm for 2 min to obtain grey precipitate. The product was then washed with fresh DMF (16mL, 4x) before further characterization or reactions.

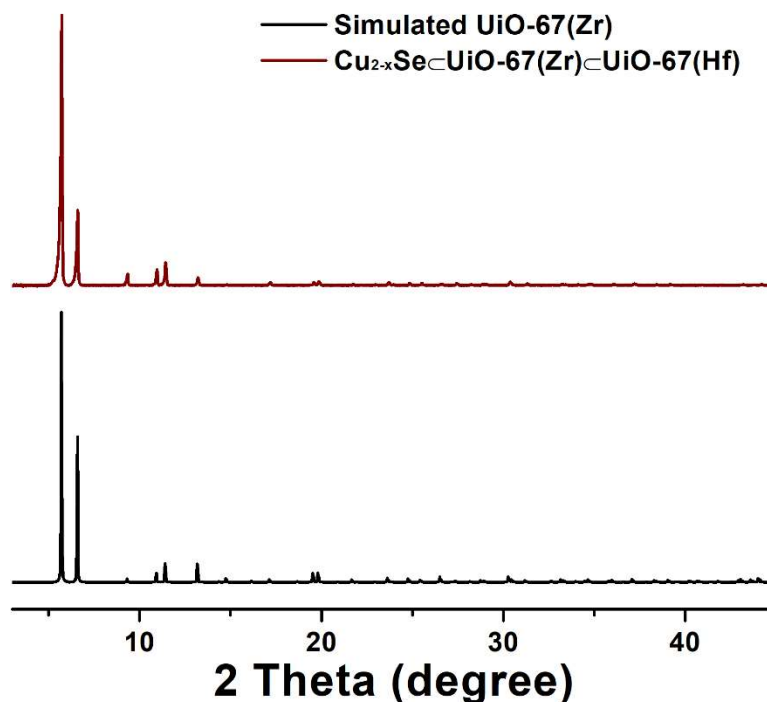


Figure S5.11 Simulated PXRD pattern based on UiO-67(Zr) crystal structure and PXRD pattern of as-synthesized $\text{Cu}_{2-x}\text{Se}@\text{UiO-67}(\text{Zr})@\text{UiO-67}(\text{Hf})$ (red).

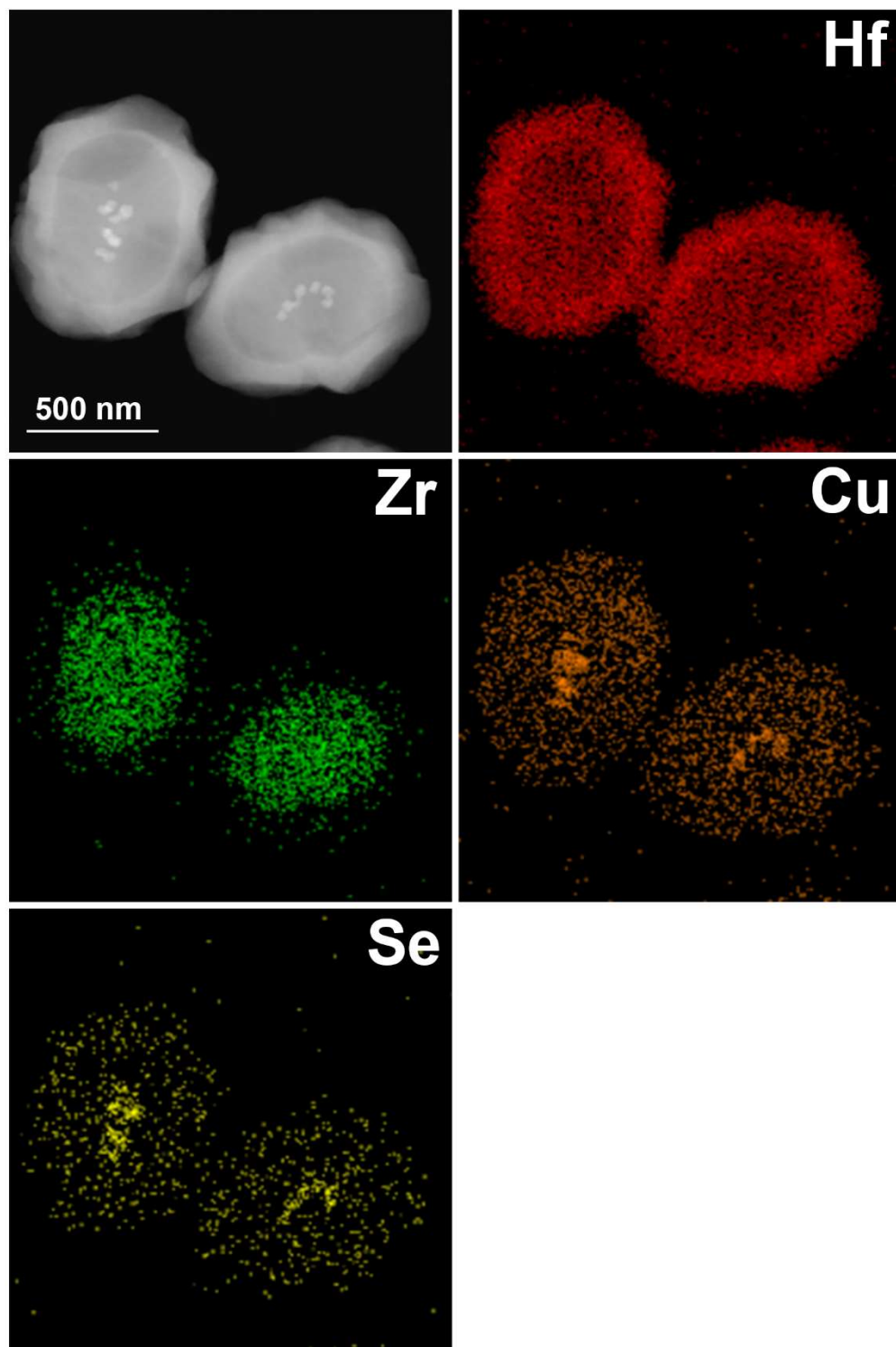


Figure S5.12 STEM-EDS characterization of $\text{Cu}_{2-x}\text{Se}@ \text{UiO-67}(\text{Zr})@ \text{UiO-67}(\text{Hf})$.

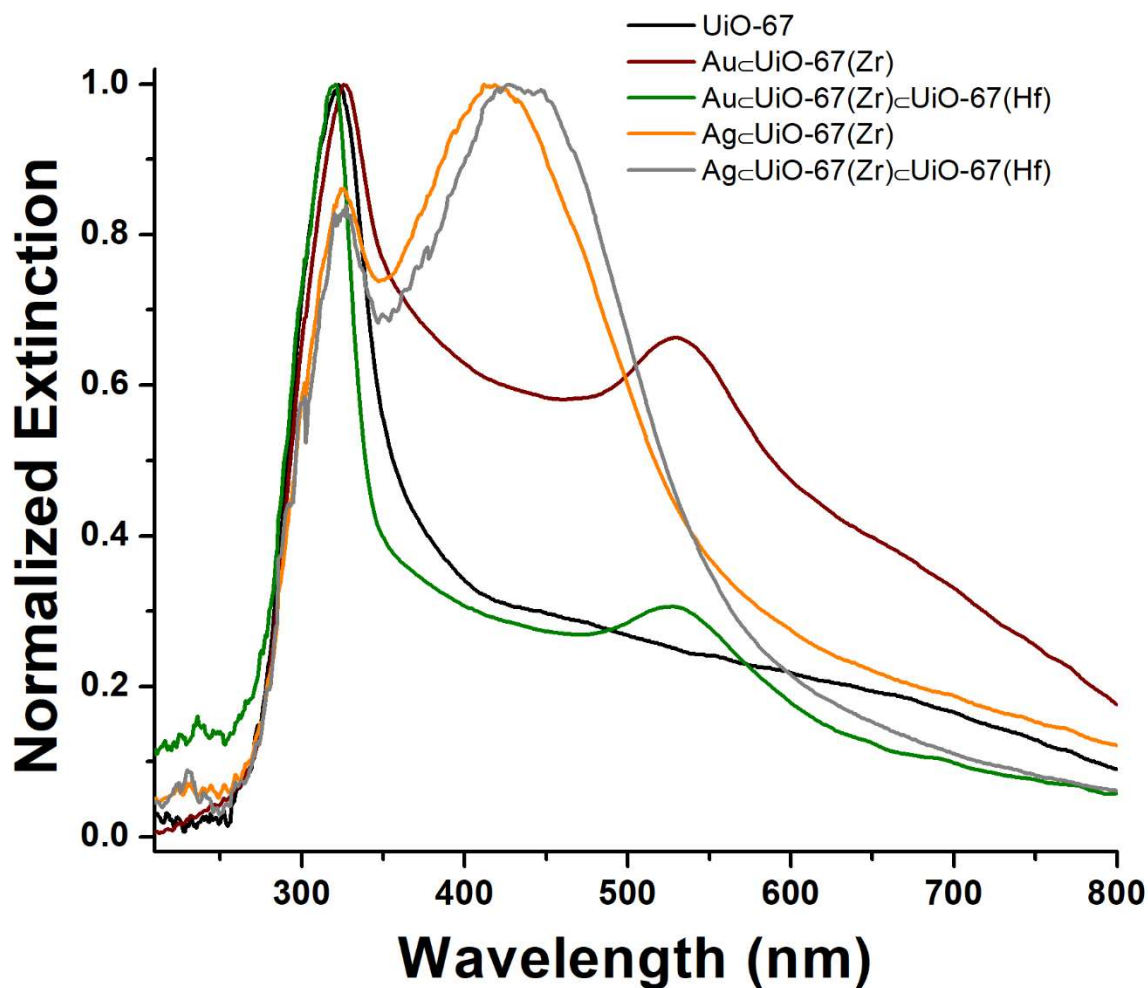


Figure S5.13 Extinction spectra of **UiO-67(Zr)** (black), **Au⊂UiO-67(Zr)** (red), **Au⊂UiO-67(Zr)⊂UiO-67(Hf)** (green), **Ag⊂UiO-67(Zr)** (orange) and **Ag⊂UiO-67(Zr)⊂UiO-67(Hf)** (grey) samples drop cast on glass slides.

6. References

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