

Supporting Information

Templating Metastable Pd₂ Carboxylate Aggregates

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A. General Considerations

Materials Solvents were obtained as ACS reagent grade. Unless otherwise noted, all chemicals and solvents were used as received. Ethyl acetate, magnesium sulfate, and dimethyl sulfoxide were obtained from EMD Millipore. Thionyl chloride, potassium iodide, triphenylphosphine, triethylamine, hydrazine monohydrate, dimethyl-5-hydroxyisophthalate, and 5-aminoisophthalic acid were obtained from Alfa Aesar. Diethyl ether (Et₂O), bis(triphenylphosphine)palladium(II) dichloride, 5-nitroisophthalic acid, 1,3,5-benzenetricarbonyl trichloride, copper(II) nitrate trihydrate, tetrafluoroboric acid solution (48% w/w), glucose, methanol, tetrahydrofuran (THF), *N*-methyl-2-pyrrolidone (NMP), peracetic acid solution (39% in acetic acid) and hexanes were obtained from Sigma Aldrich. Silica gel (0.060–0.200 mm, 60 Å for column chromatography), benzene, and *N,N*-dimethylformamide (DMF) were obtained from Acros Organics. Palladium(II) acetate, palladium(II) chloride, zinc nitrate hexahydrate, and copper(I) iodide were obtained from Strem Chemicals. (Trimethylsilyl)acetylene was obtained from Chem Impex. Diisopropylamine, glacial acetic acid, cesium fluoride, 1,3,5-tris(bromomethyl)benzene, and tribromobenzene were obtained from Beantown Chemical. Dichloromethane (CH₂Cl₂), acetonitrile (MeCN), potassium carbonate, and chloroform (CHCl₃) were obtained from Fisher Scientific. Ethanol was obtained from Koptec. Potassium hydroxide and sodium hydroxide were obtained from BDH Analytical Chemicals. *N,N*-dimethylacetamide (DMA) was obtained from TCI. Sodium nitrite and hydrochloric acid were obtained from Macron Chemicals. Sodium bicarbonate was obtained from Aqua Solutions. Pd(PPh₃)₄¹ and 2-*tert*-butylsulfonyl iodosylbenzene (**S11**) were prepared according to literature methods.² NMR solvents was purchased from Cambridge Isotope Laboratories and were used as received. UHP-grade N₂, CO₂, Ar, and He, used in gas adsorption and thermogravimetric measurements, were obtained from Airgas. All reactions were carried out under ambient atmosphere unless otherwise noted.

Characterization Details NMR spectra were recorded on Mercury 300 at 299.92 MHz for ¹H and at 74.98 MHz for ¹³C acquisitions and were referenced against solvent signals: CDCl₃ (7.26 ppm, ¹H; 77.16 ppm, ¹³C) and DMSO-*d*₆ (2.50 ppm, ¹H).³ ¹H NMR data are reported as follows: chemical shift (δ, ppm), (multiplicity: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad), integration). IR spectra were recorded on ATI Mattson Genesis Series FTIR with ATR spectrometer. Spectra were blanked against air and were determined as the average of 64 scans. IR data are reported as follows: wavenumber (cm⁻¹), (peak intensity: s, strong; m, medium; w, weak). Elemental analyses were performed by Atlantic Microlab (Norcross, GA). TGA-MS analyses were performed at a temperature ramp of 20 °C/min on Mettler-Toledo TGA/ DSC 1 with an attached Pfeiffer Vacuum ThermoStar Mass Spectrometer under Ar flow.

X-ray Absorption Details X-ray absorption spectroscopy (XAS) data were collected at the Pd K-edge (~24.3 keV) using the bending magnet beamline of the DuPont-Northwestern-Dow Collaborative Access Team (5-BM-D) at the Advanced Photon Source of Argonne National Laboratory. X-ray energy scans were performed using a Si(111) double-crystal monochromator detuned to 65% of the maximum intensity to reject harmonics. During these measurements, the APS storage ring was run in the top-up mode with the electron beam current at 102 mA. The

vertical size of the beam entering the monochromator was 0.3 mm for maximum energy resolution. The vertical beam size that irradiated the samples was 0.6 mm due to natural beam divergence. The horizontal beam size was set to 10 mm. Samples were prepared by finely dispersing powdered material on Scotch® tape. The XAS data were collected in fluorescence mode using three identical ionization chambers (Oxford Danfysik) operating in their linear regimes. The first ion chamber (I_0) is used to monitor the incident beam intensity. The samples of interest were placed in between the first and second ion chambers (I_T). A Ru metal foil was placed in between the second and third ion chambers (I_{T2}) for energy verification. Each ionization chamber was filled with gas mixtures that absorbed given percentages of the incident beam in order to optimize signal-to-noise ratio, *i.e.*, 10% and 25% absorption in I_0 and I_T respectively (94% N₂/6% Ar in both chambers), and 65% absorption in I_{T2} (100% Ar). XAS data were analyzed using Demeter 0.9.26.

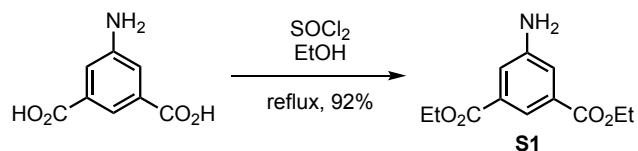
Powder X-ray Diffraction Details Powder X-ray diffraction (PXRD) measurements were carried out on a Bruker D8 Advance Eco X-ray diffractometer (Cu K α , 1.5418 Å; 40 kV, 25 mA) fitted with LynxEye detector. The angular range was measured from 5.00 to 40.00° (2θ) with steps of 0.020° and a measurement time of 0.5 second per step. Simulated PXRD patterns were calculated with Mercury 3.9.

Gas Adsorption Details Gas adsorption isotherms for pressures in the range 0–1.0 bar were measured volumetrically using a Micromeritics ASAP 2020 instrument. Samples were transferred under an N₂ atmosphere to pre-weighed analysis tubes. The samples were evacuated at room temperature until the outgas rate was <10 μ bar/min and further maintained for 16 h. Then the tube was weighed to determine the mass of the activated sample. The tube was transferred to the analysis port of the instrument. UHP-grade (99.999% purity) N₂ and He were used for all adsorption measurements. For all isotherms, both warm and cold free-space measurements were carried out with He; N₂ isotherms were measured at 77 K.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Details ICP-MS measurements were carried out on a PerkinElmer NexION 300D Quadrupole in pulse mode with ASX-520 AutoSampler. The collected data were analyzed by NexIon software Version 1.3. ¹⁰⁸Pd, ⁶⁴Zn and ⁶³Cu concentrations were measured five times to yield the average with ¹⁰³Rh as the internal standard. Calibration curves were made by five different concentrations between 10 and 200 ppb or 5 and 100 ppb (for leaching experiment) with R² > 0.9995; standards were prepared by dilution of analytical standards obtained from BDH Chemicals. Analysis of ion-metathesis samples was accomplished by washing M₃btei (2.0 mg) with MeCN (1.0 mL \times 3) and CHCl₃ (1.0 mL \times 3). The solids were digested in conc. HNO₃ by sonication and diluted with ultrapure water to make 2% HNO₃ solution.

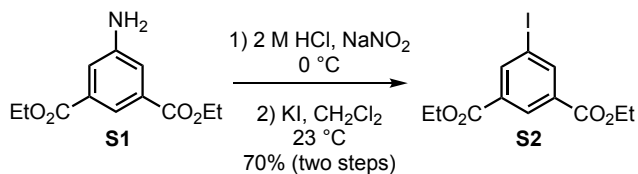
B. Synthesis and Characterization

Synthesis of Diethyl 5-Aminoisophthalate (**S1**)



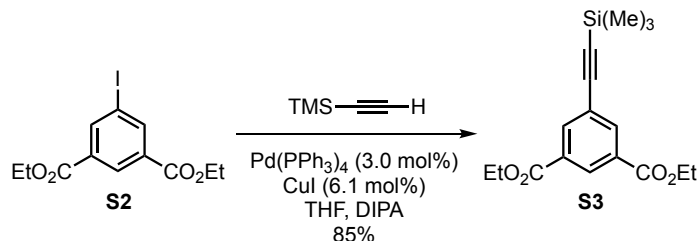
Compound **S1** was prepared according to the following modification of literature methods.⁴ A 500-mL round-bottom flask was charged with 5-aminoisophthalic acid (10.0 g, 55.2 mmol, 1.00 equiv) and EtOH (100 mL). The reaction mixture was cooled to 0 °C and SOCl_2 (12.0 mL, 165 mmol, 3.00 equiv) was added dropwise to the reaction vessel. The resulting mixture was heated at reflux for 5 h. Volatiles were removed *in vacuo* and EtOAc (100 mL) was added to the residue. A saturated aqueous solution of NaHCO_3 (100 mL) was added and the resulting suspension was stirred until the precipitate dissolved. The organic layer was separated and the aqueous layer was extracted with EtOAc (30 mL \times 3). The combined organic layers were dried over Na_2SO_4 . Solvent was removed *in vacuo* to afford 12.0 g of title compound as a white solid (92% yield). ^1H NMR (δ , 23 °C, CDCl_3): 8.06 (t, J = 1.4 Hz, 1H), 7.52 (d, J = 1.4 Hz, 2H), 4.37 (q, J = 7.1 Hz, 4H), 3.91 (bs, 2H), 1.40 (t, J = 7.1 Hz, 6H). IR (cm^{-1}): 3053 (w), 2918 (w), 1639 (w), 1599 (m), 1464 (s), 1395 (s), 1175 (m), 1070 (m), 1026 (m), 845 (m), 685 (s). Recorded ^1H NMR data was identical to that reported in the literature.⁴

Synthesis of Diethyl 5-Iodoisophthalate (**S2**)



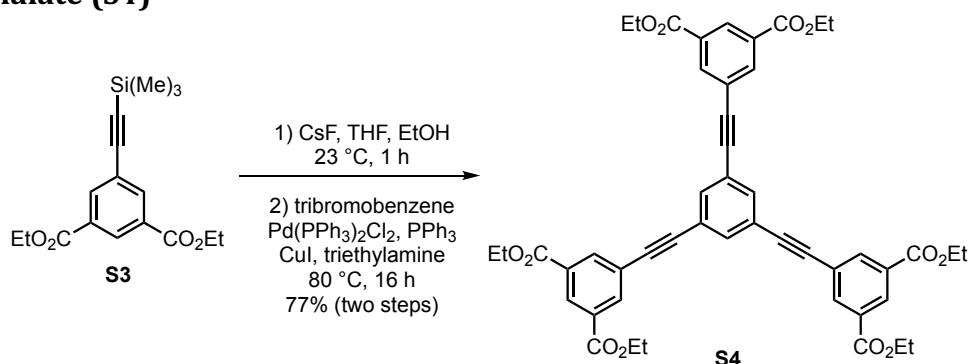
Compound **S2** was prepared according to the following modification of literature methods.⁴ A 500-mL round-bottom flask was charged with compound **S1** (10.0 g, 42.2 mmol, 1.00 equiv) and 2 M HCl (45.0 mL, 90.0 mmol, 2.14 equiv). Sodium nitrite (3.50 g, 50.7 mmol, 1.20 equiv) in H_2O (30 mL) was added dropwise at 0 °C. After stirring at 0 °C for 45 min, a solution of potassium iodide (10.5 g, 63.3 mmol, 1.50 equiv) in H_2O (100 mL) was added dropwise. Dichloromethane (150 mL) was added to the dark-red mixture and the resulting mixture was stirred at 23 °C for 4 h. The layers were separated, the aqueous layer was extracted with dichloromethane (30 mL \times 4), and the combined organic layers were dried over MgSO_4 . Solvent was removed *in vacuo* and the orange residue was purified by SiO_2 chromatography (hexanes/ethyl acetate = 9/1) to afford 10.2 g of title compound as a white solid (70% yield). ^1H NMR (δ , 23 °C, CDCl_3): 8.63 (t, J = 1.4 Hz, 1H), 8.53 (d, J = 1.4 Hz, 2H), 4.41 (q, J = 7.1 Hz, 4H), 1.41 (t, J = 7.1 Hz, 6H). Recorded ^1H NMR data was identical to that reported in the literature.⁴

Synthesis of Diethyl 5-((Trimethylsilyl)ethynyl)isophthalate (**S3**)



Compound **S3** was prepared according to the following modification of literature methods.⁵ A 250-mL Schlenk flask was charged with compound **S2** (9.00 g, 25.9 mmol, 1.00 equiv), tetrakis(triphenylphosphine)palladium(0) (0.900 g, 0.779 mmol, 0.0301 equiv), copper(I) iodide (0.300 g, 1.58 mmol, 0.0610 equiv), THF (45.0 mL), and diisopropylamine (45.0 mL). The resulting mixture was degassed by three freeze-pump-thaw cycles and was then cooled to 0 °C. A 25-mL Schlenk flask was charged with (trimethylsilyl)acetylene (9.90 mL, 71.5 mmol, 2.76 equiv). The (trimethylsilyl)acetylene was degassed by three freeze-pump-thaw cycles and was transferred to the reaction mixture (0 °C) via cannula. The reaction mixture was allowed to warm to 23 °C at which temperature it was stirred for 15 h. At this time, solids were removed by filtration and were washed with hexanes (90 mL). The filtrate was concentrated to give dark-yellow oil, which was purified by SiO₂ chromatography (hexanes/ethyl acetate = 8/2) to afford 7.01 g of title compound as a light-yellow solid (85% yield). ¹H NMR (δ, 23 °C, CDCl₃): 8.60 (t, *J* = 1.7 Hz, 1H), 8.28 (d, *J* = 1.7 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 4H), 1.42 (t, *J* = 7.1 Hz, 6H), 0.27 (s, 9H). Recorded ¹H NMR data was identical to that reported in the literature.⁴

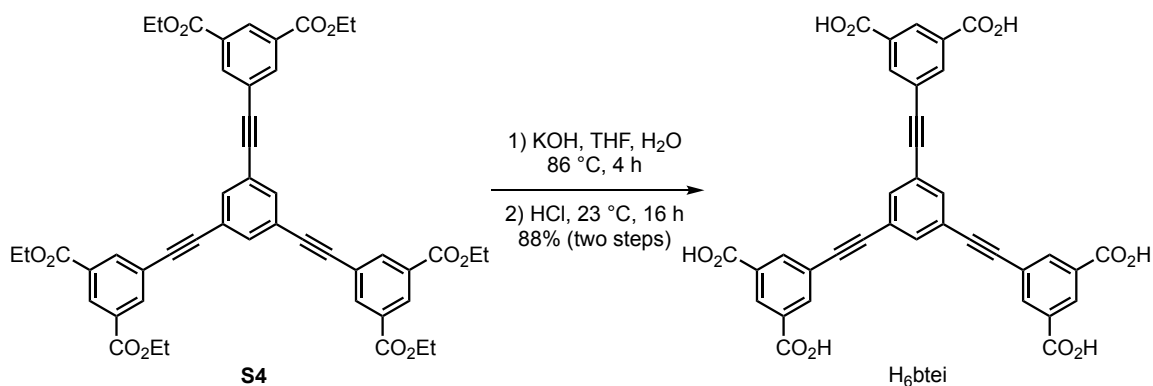
Synthesis of Hexaethyl 5,5',5''-(Benzene-1,3,5-triyltris(ethyne-2,1-diyl))-triisophthalate (**S4**)



Compound **S4** was prepared according to the following modification of literature methods.⁵⁻⁶ A 100-mL round-bottom flask was charged with compound **S3** (2.07 g, 6.52 mmol, 1.00 equiv), THF (25 mL), and EtOH (12.5 mL). Cesium fluoride (1.00 g, 6.58 mmol, 1.01 equiv) was added to the reaction mixture and the reaction was stirred at 23 °C for 1 h. At the time, the solids were removed by filtration and washed with CH₂Cl₂ (10 mL). The filtrate was concentrated *in vacuo* in a 100-mL Schlenk flask. To this reaction vessel was added tribromobenzene (0.430 g, 1.37 mmol, 0.208 equiv),

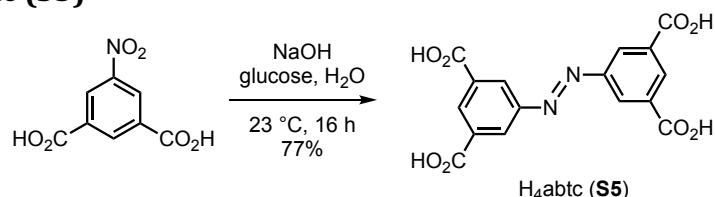
bis(triphenylphosphine)palladium(II) dichloride (0.100 g, 0.142 mmol, 0.0216 equiv), triphenylphosphine (0.0765 g, 0.292 mmol, 0.0448 equiv), and triethylamine (50 mL). The resulting mixture was degassed by three freeze-pump-thaw cycles before CuI (0.0550 g, 0.289 mmol, 0.0443 equiv) was added. The reaction vessel was sealed under an N₂ atmosphere and heated to reflux for 16 h. At this time, volatiles were removed *in vacuo*, the dark-yellow residue was taken up in chloroform (100 mL) and washed with water (75 mL). The layers were separated, the aqueous layer was extracted with chloroform (30 mL × 4), the combined organic layer was dried over MgSO₄, and solvent was removed *in vacuo* to afford dark-yellow solids. The crude solids were purified by SiO₂ chromatography (hexanes/ethyl acetate = 8/2) to afford 0.851 g of title compound as a light-yellow solid (77% yield based on tribromobenzene). ¹H NMR (δ, 23 °C, CDCl₃): 8.66 (t, *J* = 1.6 Hz, 3H), 8.38 (d, *J* = 1.6 Hz, 6H), 7.74 (s, 3H), 4.44 (q, *J* = 7.1 Hz, 12H), 1.44 (t, *J* = 7.1 Hz, 18H). Recorded ¹H NMR data was identical to that reported in the literature.⁴

Synthesis of 5,5',5''-(Benzene-1,3,5-triyltris(ethyne-2,1-diyl))trisisophthalic Acid (H₆btei)



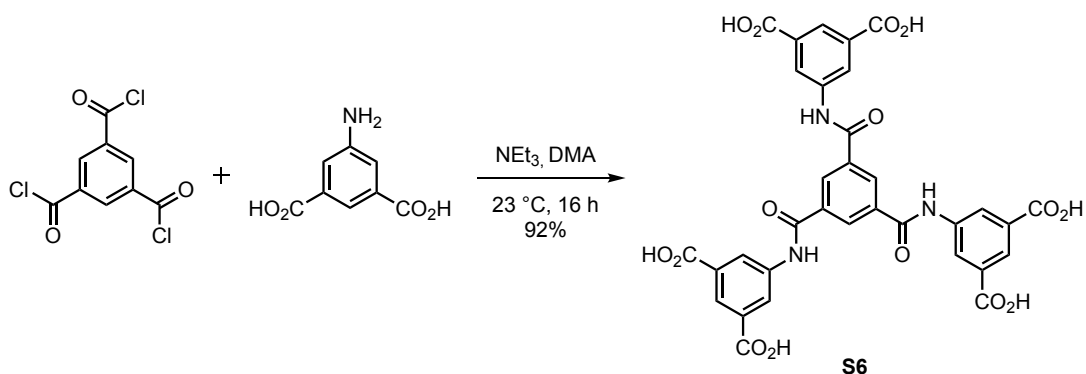
H₆btei was prepared according to the following modification of literature methods.⁶ A 100-mL round-bottom flask was charged with compound **S4** (0.600 g, 0.740 mmol, 1.00 equiv), THF (12 mL), and 1M KOH solution (18 mL). The resulting solution was heated to reflux for 4 h. After this time, 12 M HCl was added until pH = 1 and the reaction mixture was stirred at 23 °C for 16 h. Solids were collected and washed with H₂O to afford 0.418 g of title compound as an amber solid (88% yield). ¹H NMR (δ, 23 °C, *d*₆-DMSO): 13.64 (bs, 6H), 8.48 (t, *J* = 1.6 Hz, 3H), 8.32 (d, *J* = 1.6 Hz, 6H), 8.01 (s, 3H). Recorded ¹H NMR data was identical to that reported in the literature.⁶

Synthesis of H₄abtc (S5)



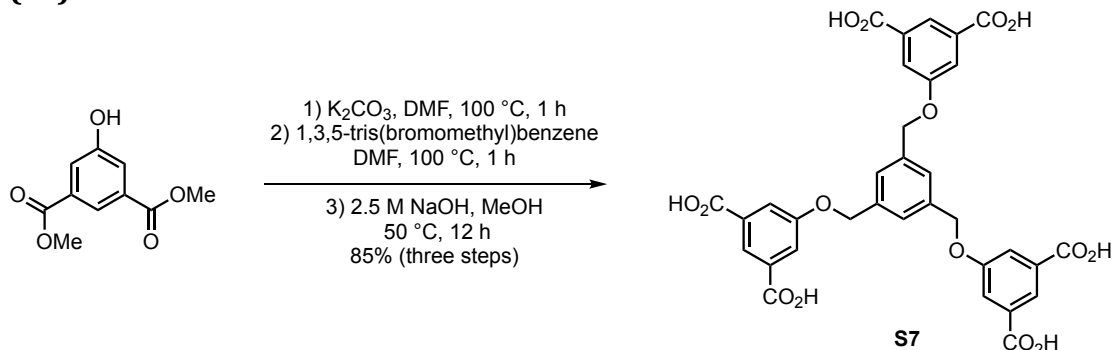
Compound **S5** (H₄abtc) was prepared according to literature methods.⁷ A 250-mL round-bottom flask was charged with 5-nitroisophthalic acid (4.75 g, 22.5 mmol, 1.00 equiv), NaOH (12.5 g, 313 mmol, 13.9 equiv), and H₂O (63 mL). The reaction mixture was stirred at 60 °C for 1 h. A solution of glucose (25.0 g, 139 mol, 6.18 equiv) in H₂O (37 mL) was prepared at 60 °C and was slowly added to the reaction mixture. The brown mixture was cooled to 23 °C and air was bubbled through the reaction mixture for 16 h. At this time, the reaction mixture was cooled to 0 °C, and solids were isolated by filtration. The solids were dissolved in H₂O (50 mL) and the aqueous solution was acidified with conc. HCl to pH < 1. The resulting solids were isolated by filtration, washed with H₂O, and dried at 120 °C to afford 3.09 g of title compound as an orange solid (77% yield). ¹H NMR (δ, 23 °C, *d*₆-DMSO): 8.64 (s, 2H), 8.63 (s, 4H). Recorded ¹H NMR data was identical to that reported in the literature.⁸

Synthesis of 5,5',5''-((Benzene-1,3,5-tricarbonyl)tris(azanediyl))trisophthalic Acid (S6)



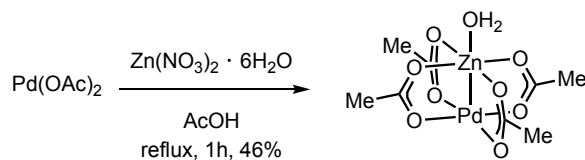
Compound **S6** was prepared according to the following modification of literature methods.⁹ A 250-mL round-bottom flask was charged with 5-aminoisophthalic acid (2.08 g, 11.5 mmol, 3.05 equiv), triethylamine (1.68 mL, 12.1 mmol, 3.21 equiv), and DMA (25 mL) under an N₂ atmosphere. 1,3,5-Benzenetricarbonyl trichloride (1.00 g, 3.77 mmol, 1.00 equiv) was added dropwise and the reaction mixture was stirred at 23 °C for 16 h. At this time, H₂O (150 mL) was added and the solids were collected by filtration and washed with acetone, H₂O, MeOH, and Et₂O to afford 2.42 g of title compound as a yellow solid (92% yield). ¹H NMR (δ, 23 °C, *d*₆-DMSO): 13.33 (bs, 6H), 8.84 (s, 3H), 8.73 (d, *J* = 1.4 Hz, 6H), 8.26 (t, *J* = 1.4 Hz, 3H). Recorded ¹H NMR data was identical to that reported in the literature.⁹

Synthesis of 5,5',5''-((Benzene-1,3,5-triyltris(methylene))tris(oxy))trisophthalic Acid (S7)



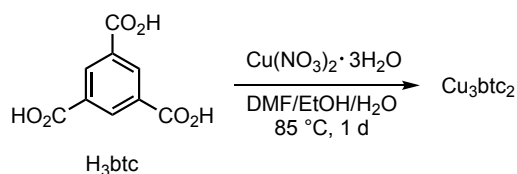
Compound **S7** was prepared according to the following modification of literature methods.¹⁰ A 1-L round-bottom flask was charged with dimethyl-5-hydroxyisophthalate (6.35 g, 30.2 mmol, 7.49 equiv), potassium carbonate (13.0 g, 94.1 mmol, 23.4 equiv), and DMF (125 mL) and the reaction mixture was heated at 100 °C for 1 h. At this time, 1,3,5-tris(bromomethyl)benzene (1.44 g, 4.03 mmol, 1.00 equiv) and DMF (5 mL) was added and the reaction mixture was heated to 100 °C for 1 h. At this time, H_2O (400 mL) was added to the reaction mixture and the resulting white solids were isolated by filtration and washed with cold water. The solids were taken up in MeOH (125 mL) and a sodium hydroxide was added as a 2.0 M aqueous solution (30.0 mL, 60.0 mmol, 14.9 equiv). The reaction mixture was heated to 50 °C for 12 h. The reaction mixture was cooled to the mixture was acidified by conc. HCl until pH < 1. The solids were filtered and washed with cold H_2O to afford 2.25 g of the title compound (85% yield). ^1H NMR (δ , 23 °C, d_6 -DMSO): 8.10 (s, 3H), 7.75 (s, 6H), 7.60 (s, 3H), 5.28 (s, 6H). Recorded ^1H NMR data was identical to that reported in the literature.¹⁰

Synthesis of $\text{PdZn}(\text{OAc})_4 \cdot \text{H}_2\text{O}$



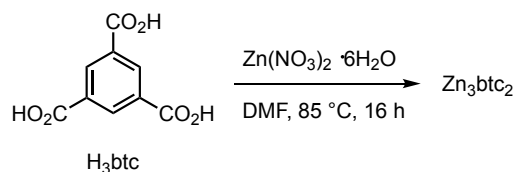
$\text{PdZn}(\text{OAc})_4 \cdot \text{H}_2\text{O}$ was prepared according to literature methods.¹¹ A 10-mL round-bottom flask was charged with $\text{Pd}(\text{OAc})_2$ (0.100 g, 0.445 mmol, 1.00 equiv), zinc acetate hexahydrate (0.135 g, 0.454 mmol, 1.02 equiv), and glacial acetic acid (3 mL). The resulting mixture was heated to reflux for 1 h. After this time, the reaction mixture was allowed to stand at 23 °C for 16 h and brown crystals formed. Solids were collected and washed with cold benzene and hexanes to afford 0.087 g of title compound as yellow crystals (46% yield). The PXRD pattern obtained for $\text{PdZn}(\text{OAc})_4 \cdot \text{H}_2\text{O}$ matched the pattern simulated for single-crystal X-ray diffraction (Figure S13).

Synthesis of Cu₃btc₂



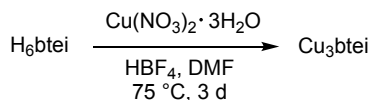
Cu₃btc₂ was prepared according to literature methods.¹² A 150-mL thick-walled vessel was charged with H₃btc (1.50 g, 7.14 mmol, 1.00 equiv), copper(II) nitrate trihydrate (3.00 g, 12.4 mmol, 1.74 equiv), DMF (25 mL), EtOH (25 mL), and water (25 mL). The resulting mixture was sonicated until a homogeneous solution was obtained and the reaction solution was allowed to stand at 85 °C for 1 d. At this time, the hot mother liquor was decanted and the obtained crystalline solids were washed with DMF (20 mL × 2) and dichloromethane (20 mL × 2). The solids were soaked in dichloromethane for 6 d and the solvent was refreshed two times per day. Solvent was removed *in vacuo* to afford 2.53 g of the title compound as a purple solid. The PXRD pattern of synthesized Cu₃btc₂ was consistent with reported data.¹²

Synthesis of Zn₃btc₂



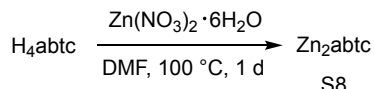
Zn₃btc₂ was prepared according to literature methods.¹³ A 48-mL thick-walled vessel was charged with H₃btc (0.316 g, 1.50 mmol, 1.00 equiv), zinc nitrate hexahydrate (0.682 g, 2.29 mmol, 1.53 equiv), and DMF (40 mL). The resulting mixture was sonicated until a homogeneous solution was obtained and the reaction solution was allowed to stand at 85 °C for 16 h. At this time, the reaction was cooled to 23 °C and solvent was decanted. The crystalline solids were washed with DMF (20 mL × 2) to afford 74.0 mg of title compound as a white solid. The PXRD pattern of synthesized Zn₃btc₂ was consistent with reported data.¹³

Synthesis of Cu₃btei



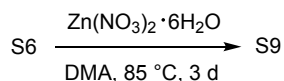
Cu₃btei was prepared according to literature methods.⁶ A 1-dram vial was charged with H₆btei (10.0 mg, 0.0156 mmol, 1.00 equiv), copper(II) nitrate trihydrate (30.0 mg, 0.124 mmol, 7.95 equiv), one drop of HBF₄ solution (48% w/w), and DMF (1.5 mL). The reaction mixture was sonicated until a homogeneous solution was obtained and the reaction solution was allowed to stand at 75 °C for 3 d. At this time, the reaction was cooled to 23 °C and solvent was decanted. The crystalline solids were washed with DMF (0.5 mL × 3) to afford 19.2 mg of title compound as a blue solid. The PXRD pattern of synthesized Cu₃btei was consistent with reported literature data.⁶

Synthesis of Zn₂abtc (**S8**)



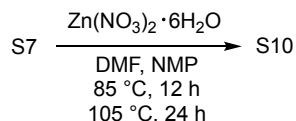
Zn₂abtc was prepared according to the following modification of literature methods.¹⁴ A vial was charged with H₄abtc (35.8 mg, 0.100 mmol, 1.00 equiv), zinc nitrate hexahydrate (89.2 mg, 0.300 mmol, 3.00 equiv), and DMF (2.5 mL). The reaction mixture was sonicated until a homogeneous solution was obtained and the reaction solution was allowed to stand at 100 °C for 1 d. At this time, the reaction was cooled to 23 °C and solvent was decanted. The crystalline solids were washed with DMF (1.0 mL × 3) to afford title compound as an orange solid. The PXRD pattern of synthesized Zn₂abtc was consistent with reported literature data.¹⁴

Synthesis of Zn₃(**S6**) (**S9**)



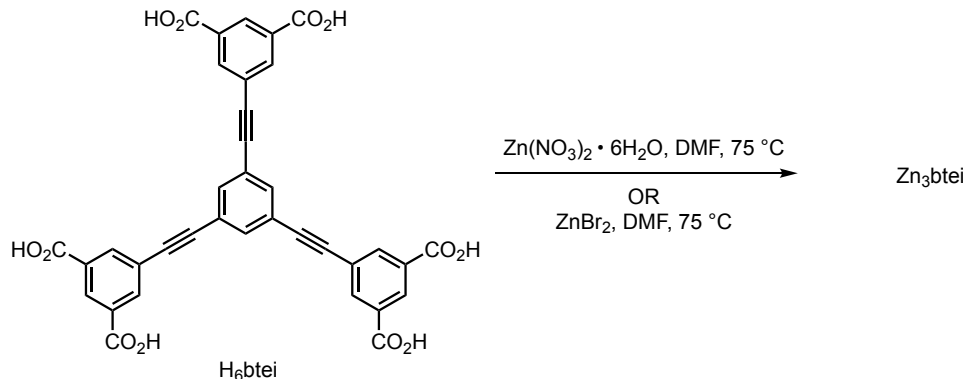
Compound **S9** was prepared according to literature methods.¹⁵ A vial was charged with compound **S6** (50.0 mg, 0.0715 mmol, 1.00 equiv), zinc nitrate hexahydrate (170 mg, 0.571 mmol, 7.99 equiv), and DMA (3.5 mL). The reaction mixture was sonicated until a homogeneous solution was obtained and the reaction solution was allowed to stand at 85 °C for 3 d. At this time, the reaction was cooled to 23 °C and solvent was decanted. The crystalline solids were washed with DMA (1.0 mL × 3) to afford title compound as a colorless solid. The PXRD pattern of synthesized **S9** was consistent with reported literature data.¹⁵

Synthesis of Zn₃(**S7**) (**S10**)



Compound **S10** was prepared according to the following modification of literature methods.¹⁰ A vial was charged with compound **S7** (18.0 mg, 0.0273 mmol, 1.00 equiv), zinc nitrate hexahydrate (12.0 mg, 0.0403 mmol, 1.48 equiv), NMP (1.0 mL), and DMF (1.0 mL). The reaction mixture was sonicated until a homogeneous solution was obtained and the reaction solution was allowed to stand at 85 °C for 12 h and then 105 °C for 24 h. At this time, the reaction was cooled to 23 °C and solvent was decanted. The crystalline solids were washed with DMF (1.0 mL × 3) to afford title compound as a colorless solid. The PXRD pattern of synthesized **S10** was consistent with reported literature data.¹⁰

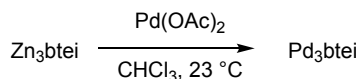
Synthesis of Zn₃btei



Microcrystalline Zn₃btei was prepared according to the following modification of literature methods.¹⁷ A 1-dram vial was charged with H₆btei (8.00 mg, 0.0125 mmol, 1.00 equiv), zinc nitrate hexahydrate (12.0 mg, 0.0403 mmol, 3.22 equiv), and DMF (0.5 mL). The reaction mixture was sonicated until a homogeneous solution was obtained and the reaction solution was allowed to stand at 75 °C for 2 d. At this time, the reaction was cooled to 23 °C and solvent was decanted. The crystalline solids were washed with DMF (0.5 mL × 3) to afford 7.90 mg of title compound as an amber solid. The PXRD pattern of synthesized Zn₃btei was consistent with reported literature data.¹⁶

Crystalline Zn₃btei was prepared according to literature methods.⁶ A 2-dram vial was charged with H₆btei (10.0 mg, 0.0156 mmol, 1.00 equiv), zinc bromide (30.0 mg, 0.133 mmol, 8.53 equiv), and DMF (1.5 mL). The reaction mixture was sonicated until a homogeneous solution was obtained and the reaction solution was allowed to stand at 75 °C for 3 d. At this time, the reaction was cooled to 23 °C and solvent was decanted. The crystalline solids were washed with DMF (1.5 mL × 3) to afford 7.40 mg of title compound as amber solids. Elemental Analysis (EA) for [Zn₃(btei)(H₂O)₉(C₃H₇NO)_{1.7}(CHCl₃)_{1.35}]: calcd. C, 39.83; H, 3.41; N, 1.86; Cl, 11.22; found C, 39.25; H, 2.78; N, 1.86; Cl, 11.14. The PXRD pattern of synthesized Zn₃btei was consistent with reported literature data.⁶

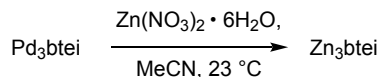
Transmetalation of Zn₃btei



Zn₃btei was soaked in CHCl₃ for 3 d or 28 d and the solvent was refreshed three times per day. Pd(OAc)₂ was purified prior to use. Pd(OAc)₂ was dissolved in CHCl₃, filtered through Celite, and CHCl₃ was removed under vacuum. A 0.5-dram vial was charged with Zn₃btei (7.4 mg), Pd(OAc)₂ (2 mg), and chloroform (0.5 mL) and the Pd solution was refreshed weekly. Elemental Analysis (EA) for [Pd_{2.25}Zn_{0.75}(btei)(H₂O)₁₃(C₃H₇NO)_{0.6}(CHCl₃)_{0.4}]: calcd. C, 38.18; H, 3.57; N, 0.70; Cl, 3.57; found C, 37.03; H, 2.64; N, 0.71; Cl, 3.47.

Transmetalation reactions between other MOFs and Pd(OAc)₂ were conducted using similar procedures.

Back-Exchange of Pd₃btei with Zn(II)

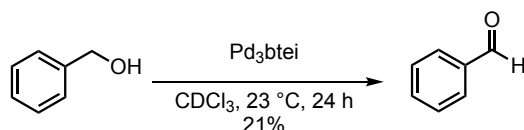


A 0.5-dram vial was charged with Pd₃btei (7.40 mg), zinc nitrate hexahydrate (50.0 mg) and MeCN (0.5 mL) and the mixture was allowed to stand for 7 d.

Digestion of Pd₃btei with AcOH

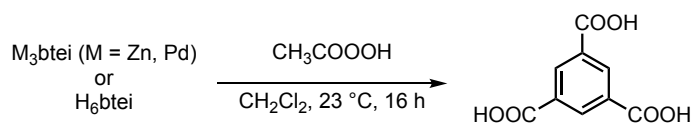
A 1-dram vial was charged with Pd₃btei (5.0 mg) and AcOH (1.0 mL). After sonication at 23 °C for 3 min, the solution was discarded. The solids were washed with MeOH (0.5 mL x 3) and the volatiles were removed *in vacuo*. ¹H NMR of the solids corresponded to that of H₆btei.

Treatment of Pd₃btei with BnOH



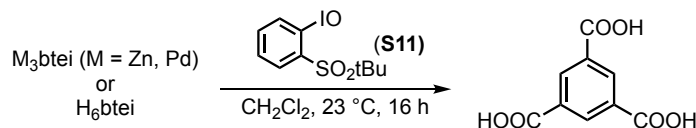
An NMR tube was charged with Pd₃btei (6.30 mg, 0.00677 mmol, 1.00 equiv), benzyl alcohol (2.00 μL, 0.0192 mmol, 2.84 equiv), mesitylene (2.00 μL, 0.0145 mmol, 2.14 equiv), and CDCl₃ (0.45 mL). The reaction mixture was agitated using a mechanical shaker for 24 h at 23 °C. At this time, benzaldehyde was detected by ¹H NMR and the yield was determined to be 21% by integration against the resonances of mesitylene.

General Procedure for Oxidation with Peracetic Acid



A one-dram vial was charged with Pd₃btei (0.00445 mmol, 1.00 equiv), peracetic acid (39% in acetic acid, 8.08 μL, 0.0472 mmol, 10.6 equiv), and CH₂Cl₂ (0.30 mL). After stirring at 23 °C for 16 h, solution turned light yellow and most of the solids dissolved. Water (0.30 mL) was added and the aqueous layer was collected and filtered. [C₉H₅O₆]⁻ was observed by mass spectrometry (ESI negative, calc: 209.0081; expt m/z: 209.0087). Similar experiments were conducted with Zn₃btei and H₆btei using peracetic acid. [C₉H₅O₆]⁻ was observed by mass spectrometry in each of these experiments.

General Procedure for Oxidation with 2-*Tert*-butylsulfonyl Iodosylbenzene (**S11**)

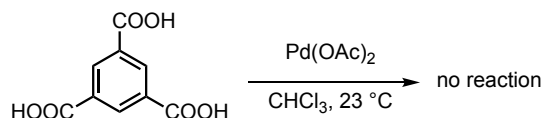


A one-dram vial was charged with Pd_3btei (0.00445 mmol, 1.00 equiv), hypervalent iodine reagent **S11** (15.0 mg, 0.0441 mmol, 9.90 equiv), and CH_2Cl_2 (0.30 mL). After stirring at $23\text{ }^\circ\text{C}$ for 16 h, solution turned light yellow and some of the solids remained undissolved. DCM was decanted and water (0.30 mL) was added and the solution was filtered. $[\text{C}_9\text{H}_5\text{O}_6]^-$ was observed by mass spectrometry (ESI negative, calc: 209.0085; expt m/z : 209.0087). Similar experiments were conducted with Zn_3btei and $H_6\text{btei}$ using **S11**. $[\text{C}_9\text{H}_5\text{O}_6]^-$ was observed by mass spectrometry in each of these experiments.

General Procedure for CS_2 Experiment

A one-dram vial was charged with Pd_3btei (2.0 mg), CS_2 (0.01 mL), and CH_2Cl_2 (0.5 mL). The reaction mixture was allowed to sit for 1 h at $23\text{ }^\circ\text{C}$. At this time, the reaction solvent was decanted and IR spectra were recorded for the remaining solids. Similar experiments were conducted with Zn_3btei and $\text{Pd}(\text{OAc})_2$ using CS_2 . For $\text{Pd}(\text{OAc})_2$, the reaction was allowed to air dry prior to acquisition of the IR spectrum.

Attempt to Directly Synthesize Pd_3btei under Cation Exchange Conditions



A 20-mL vial was charged with $\text{Pd}(\text{OAc})_2$ (60.0 mg, 0.267 mmol, 4.01 equiv), $H_3\text{btc}$ (14.0 mg, 0.0666 mmol, 1.00 equiv), and CHCl_3 (15.0 mL). After standing at $23\text{ }^\circ\text{C}$ for 24 h, solvent was removed *in vacuo* to afford white and orange solids. PXRD analysis of the solids did not display any of the signals attributable to $M_3\text{btei}$ frameworks.

C. Supporting Data

C.1 Coordinates of Optimized Structures

Table S1. Coordinates for optimized geometry of Pd(OAc)₂.

Atom	X	Y	Z
O	1.756794	1.087321	0.019089
O	-1.756708	-1.087420	-0.019125
C	2.430258	-0.000395	0.018232
C	-2.430303	0.000161	-0.018173
O	1.756668	-1.087876	0.019087
O	-1.756838	1.087754	-0.019085
C	3.926593	0.000022	-0.014726
H	4.261525	0.020976	-1.058672
H	4.313085	0.889949	0.487586
H	4.313509	-0.907879	0.453627
C	-3.926666	-0.000140	0.014902
H	-4.261542	-0.005236	1.059062
H	-4.313646	0.901003	-0.466402
H	-4.313223	-0.897111	-0.474553
Pd	0.000036	0.000047	-0.000039

Table S2. Coordinates for optimized geometry of Pd₂(OAc)₄.

Atom	X	Y	Z
O	-1.456793	1.432494	-1.147017
O	1.455459	-1.447963	-1.142675
O	-1.438447	-1.463812	-1.144355
O	1.442007	1.448162	-1.144394
C	-1.853951	1.828375	-0.002515
C	-1.834874	-1.859626	0.000712
C	1.856609	-1.838020	0.002689
C	1.832426	1.850038	0.000600
O	-1.458304	1.432559	1.142832
O	-1.438991	-1.463457	1.145610
O	1.455278	-1.446397	1.147295
O	1.440523	1.449852	1.145462
C	-2.930161	-2.905455	-0.001983
H	-3.898581	-2.398783	-0.087877
H	-2.816829	-3.568131	-0.862644
H	-2.917012	-3.473802	0.929734
C	-2.901375	2.922323	0.000154
H	-2.398032	3.890144	0.108973
H	-3.456259	2.922075	-0.939658
H	-3.576293	2.795439	0.849480
C	2.965438	-2.869471	0.001071
H	3.927498	-2.349662	-0.077670
H	2.955336	-3.441608	0.930524
H	2.865164	-3.530128	-0.862725
C	2.864652	2.958321	-0.001990
H	2.345843	3.920708	-0.083297
H	3.435762	2.949774	0.928117
H	3.526140	2.856121	-0.864943
Pd	-0.000448	-0.006211	1.309424
Pd	0.000640	-0.007323	-1.309043

Table S3. Coordinates for optimized geometry of Pd₃(OAc)₆.

Atom	X	Y	Z
Pd	1.619339	-0.929252	0.014006
C	-0.063527	-2.607519	1.868932
O	1.046467	-2.409266	1.293111
O	-1.174028	-2.047058	1.620059
C	-2.270779	1.267057	-1.892147
O	-1.528187	2.119232	-1.320660
O	-2.364702	0.027496	-1.640214
C	-3.178158	1.797375	-2.984445
H	-3.445016	0.997916	-3.678150
H	-4.097632	2.174483	-2.521305
H	-2.696088	2.623911	-3.510415
C	-0.077932	-3.658332	2.961265
H	0.912599	-3.758400	3.408479
H	-0.821832	-3.403082	3.719043
H	-0.361423	-4.620238	2.518104
Pd	-0.000013	1.867439	-0.000017
C	-2.277021	1.349145	1.834966
O	-2.651907	0.290927	1.246865
O	-1.243670	2.042684	1.594708
C	0.063702	-2.607749	-1.868759
O	1.174224	-2.047313	-1.619923
O	-1.046320	-2.409312	-1.293058
C	0.078015	-3.658857	-2.960809
H	-0.911720	-3.756345	-3.410385
H	0.824469	-3.405920	-3.716824
H	0.357531	-4.621458	-2.516624
C	-3.159641	1.823424	2.972363
H	-2.972965	1.191910	3.848399
H	-2.939589	2.861650	3.225049
H	-4.211469	1.708379	2.698582
Pd	-1.619309	-0.929275	-0.014030
C	2.276994	1.349213	-1.835011
O	2.651813	0.290911	-1.247027
O	1.243674	2.042783	-1.594697
C	3.159490	1.823504	-2.972499
H	2.970243	1.194055	-3.849485
H	2.941442	2.862654	-3.223146
H	4.211357	1.705552	-2.700179
C	2.270730	1.267241	1.892075
O	2.364612	0.027680	1.640159
O	1.528161	2.119436	1.320574
C	3.178091	1.797565	2.984386
H	4.097347	2.175156	2.521209
H	2.695803	2.623787	3.510655
H	3.445334	0.998013	3.677832

Table S4. Coordinates for optimized geometry of Pd₄(OAc)₈.

Atom	X	Y	Z
Pd	1.643894	-0.726051	0.128975
Pd	-0.725647	-1.642710	-0.128703
Pd	-1.643790	0.726026	0.128793
Pd	0.725698	1.642585	-0.129296
O	2.199496	-2.944158	0.075640
O	0.092868	-3.525427	-0.532630
C	1.340545	-3.761549	-0.336568
C	1.782990	-5.173964	-0.677347
O	1.339982	-0.922483	2.127993
O	-0.598143	-2.046739	1.846620
C	0.375170	-1.633647	2.549387
C	0.395146	-2.040605	4.001783
O	-2.943249	-2.199346	-0.073016
O	-3.526350	-0.092614	0.532529
C	-3.761316	-1.340595	0.337805
C	-5.173848	-1.784247	0.676451
O	-0.923277	-1.339405	-2.127671
O	-2.048761	0.597931	-1.846353
C	-1.635613	-0.375424	-2.548849
C	-2.043237	-0.396502	-4.001006
O	-2.198990	2.944228	0.075132
O	-0.092521	3.525349	-0.533871
C	-1.339934	3.761728	-0.337071
C	-1.783936	5.173694	-0.677711
O	-1.339834	0.923139	2.127728
O	0.598198	2.047376	1.845869
C	-0.375115	1.634578	2.548758
C	-0.394969	2.041926	4.001035
O	2.943264	2.199337	-0.073843
O	3.526381	0.092845	0.532471
C	3.761353	1.340724	0.337106
C	5.173617	1.784709	0.676411
O	0.923190	1.338644	-2.128160
O	2.048909	-0.598401	-1.846209
C	1.635827	0.374746	-2.548964
C	2.042833	0.395228	-4.001298
H	2.648444	-5.451693	-0.071525
H	0.965270	-5.883195	-0.531376
H	2.077761	-5.199939	-1.732946
H	-0.623503	-2.155149	4.377749
H	0.906786	-3.006735	4.082960
H	0.950199	-1.309207	4.592756
H	-5.459815	-2.632143	0.049787
H	-5.193613	-2.108635	1.723475
H	-5.880214	-0.959918	0.557107
H	-2.165488	0.621470	-4.376231

H	-1.308548	-0.946286	-4.592853
H	-3.005486	-0.915541	-4.081841
H	-0.956626	5.878793	-0.572620
H	-2.123464	5.188501	-1.719946
H	-2.622415	5.465116	-0.040828
H	0.623681	2.157116	4.376798
H	-0.906954	3.007916	4.081828
H	-0.949578	1.310536	4.592420
H	5.880258	0.960555	0.557465
H	5.459727	2.632630	0.049840
H	5.192710	2.109167	1.723420
H	1.304457	0.939098	-4.594051
H	3.001797	0.920093	-4.083542
H	2.171058	-0.622701	-4.374589

C.2 Optimization of Transmetalation Chemistry

Table S5. Examination of cation metathesis in btc-supported networks.

Template Network	Pd Source	Temp / °C	Solvent	Result
Zn ₃ btc ₂	Pd(O ₂ CCF ₃) ₂	23	CHCl ₃	Pd black after 5 d
Zn ₃ btc ₂	Pd(OAc) ₂	55	CHCl ₃	Pd black after 2 d
Zn ₃ btc ₂	Pd(OAc) ₂	80	MeCN	Pd black after 1 d
Zn ₃ btc ₂	PdCl ₂	80	MeCN	Pd black after 1 d
Zn ₃ btc ₂	Pd(O ₂ CCF ₃) ₂ (DMSO) ₂	23	CHCl ₃	Pd black after 3 d
Zn ₃ btc ₂	[Pd(MeCN) ₄][(BF ₄) ₂]	23	CHCl ₃	Pd black after 4 d
Zn ₃ btc ₂	Pd(OAc) ₂	23	CHCl ₃	35% exchange after 20 d
Cu ₃ btc ₂	Pd(OAc) ₂	23	CHCl ₃	<1% exchange after 150 d
Cu ₃ btc ₂	Pd(OAc) ₂	23	MeOH	Pd black after 3 h
Cu ₃ btc ₂	Pd(OAc) ₂	23	EtOH	Pd black after 3 h
Cu ₃ btc ₂	Pd(OAc) ₂	23	DMF	Pd black after 5 h
Cu ₃ btc ₂	Pd(OAc) ₂	75	DMF	Pd black after 1 h
Cu ₃ btc ₂	Pd(OAc) ₂	80	MeCN	Pd black after 2 d
Cu ₃ btc ₂	PdCl ₂	23	MeOH	Pd black after 5 h
Cu ₃ btc ₂	PdCl ₂	23	EtOH	Pd black after 7 h
Cu ₃ btc ₂	PdCl ₂	23	DMF	Pd black after 7 h
Cu ₃ btc ₂	PdCl ₂	75	DMF	Pd black after 1 h
Cu ₃ btc ₂	Pd(O ₂ CCF ₃) ₂	23	CHCl ₃	Pd black after 5 d
Cu ₃ btc ₂	Pd(OAc) ₂	55	CHCl ₃	Pd black after 2 d
Cu ₃ btc ₂	Pd(OAc) ₂	80	MeCN	Pd black after 1 d
Cu ₃ btc ₂	PdCl ₂	80	MeCN	Pd black after 1 d
Cu ₃ btc ₂	Pd(O ₂ CCF ₃) ₂ (DMSO) ₂	23	CHCl ₃	Pd black after 3 d
Cu ₃ btc ₂	[Pd(MeCN) ₄][(BF ₄) ₂]	23	CHCl ₃	Pd black after 4 d

Table S6. Examination of cation metathesis in btei-supported networks.

Template Network	Pd Source	Temp / °C	Solvent	Result
Zn ₃ btei (crystalline)	Pd(O ₂ CCF ₃) ₂	23	CHCl ₃	Pd black after 5 d
Zn ₃ btei (microcrystalline)	Pd(O ₂ CCF ₃) ₂	23	CHCl ₃	Pd black after 5 d
Cu ₃ btei	Pd(OAc) ₂	23	CHCl ₃	20% exchange after 56 d

Table S7. Examination of cation metathesis in other networks.

Template Network	Pd Source	Temp / °C	Solvent	Result
Zn ₃ abtc (S8)	Pd(OAc) ₂	23	CHCl ₃	54 % 161 d
S9	Pd(OAc) ₂	23	CHCl ₃	46 % 161 d
S10	Pd(OAc) ₂	23	CHCl ₃	29 % 161 d

C.3. Characterization of Exchanged Materials

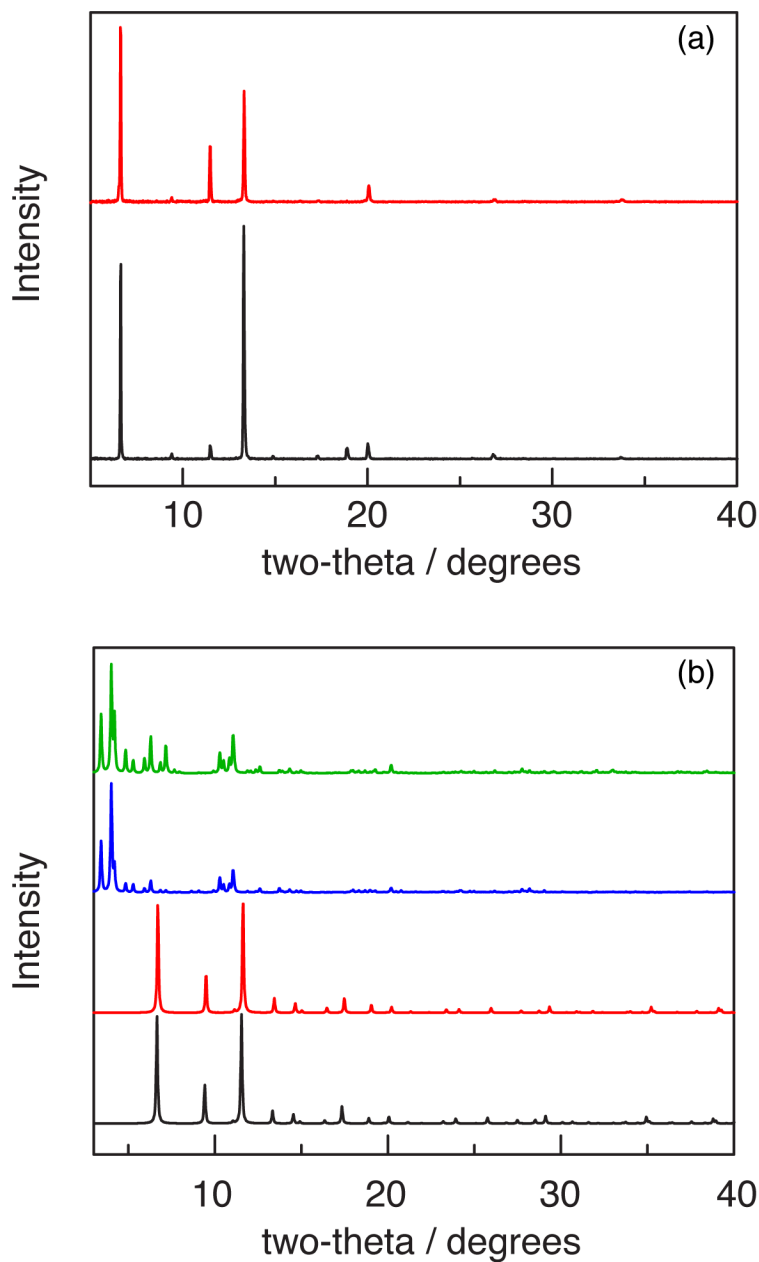


Figure S1. (a) PXR D patterns for Zn₃btc₂ (—) and for Pd-exchanged material (—). (b) Simulated PXR D of Pd substituted MIL-101 structure (trigonal prismatic Pd₃ nodes, —), simulated PXR D of MIL-100 (Cr₃(btc)₂, —), simulated PXR D of Cu₃(btc)₂ (—), and simulated PXR D of Zn₃(btc)₂ (—).

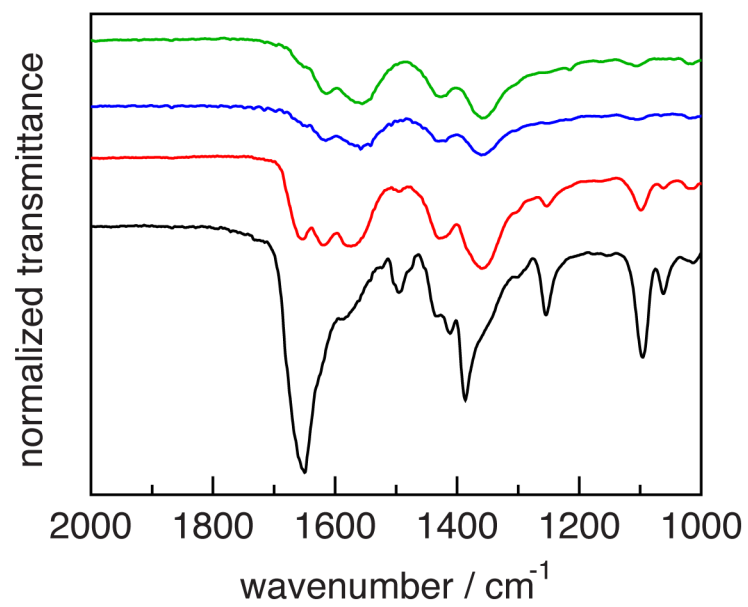


Figure S2. IR spectra of Zn₃btei in DMF (—), Zn₃btei in CHCl₃ for 1 hour (—), Zn₃btei in CHCl₃ for 1 day (—), and Zn₃btei in CHCl₃ for 3 days (—).

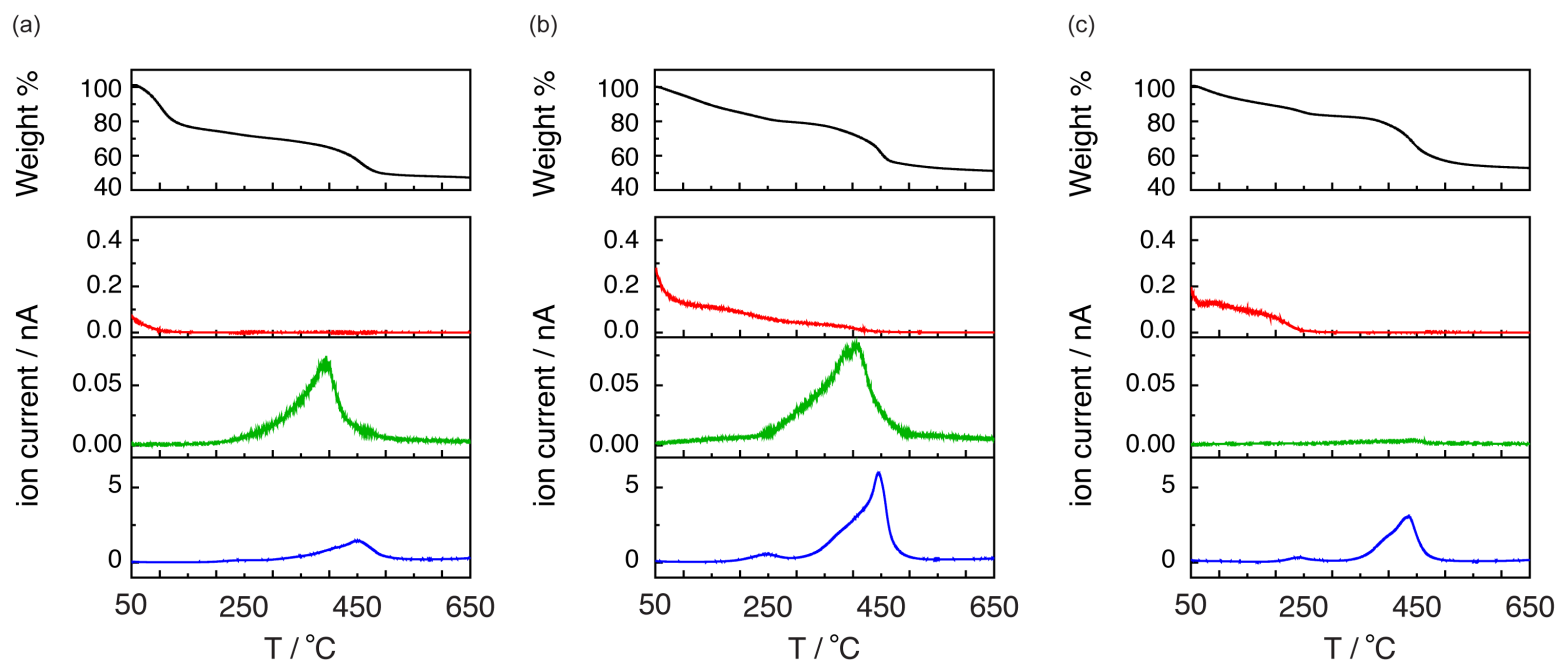
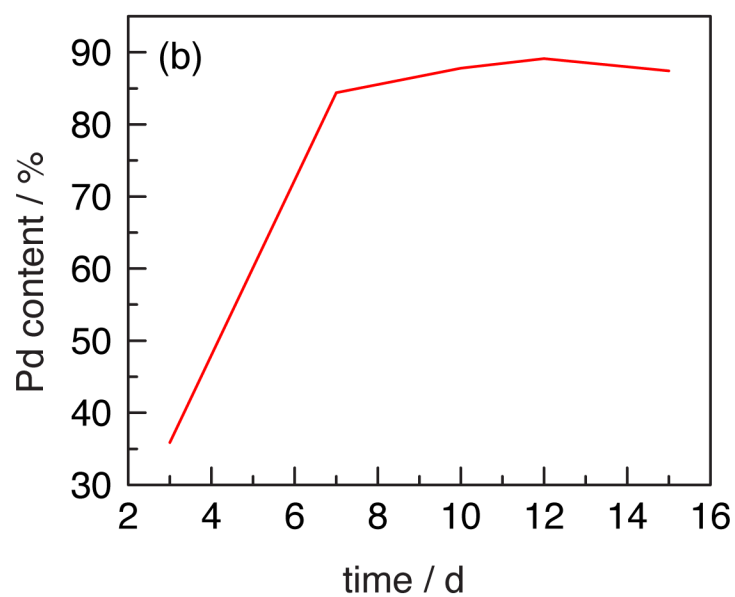
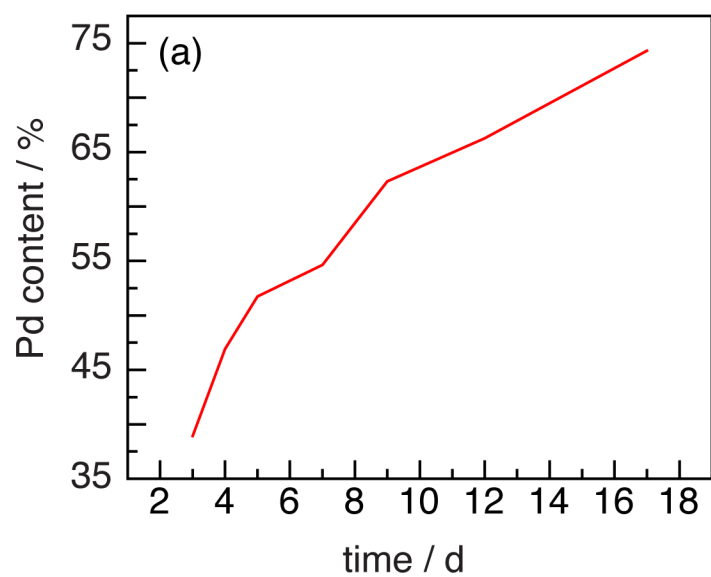


Figure S3. TGA-MS spectra (—) of Zn_3btei exchanged in CHCl_3 for (a) 1 h; (b) 1 d; and (c) 28 d. Mass loss was attributed to CHCl_3 (—), DMF (—), and CO_2 (—).



Figures S4a and S4b. (a) Plot of $\text{Pd}(\text{OAc})_2$ exchange into Zn_3btei that was pre-soaked in CHCl_3 for 28 d. (b) Plot of $\text{Pd}(\text{NO}_3)_2$ exchange into Zn_3btei that was pre-soaked in CHCl_3 for 28 d.

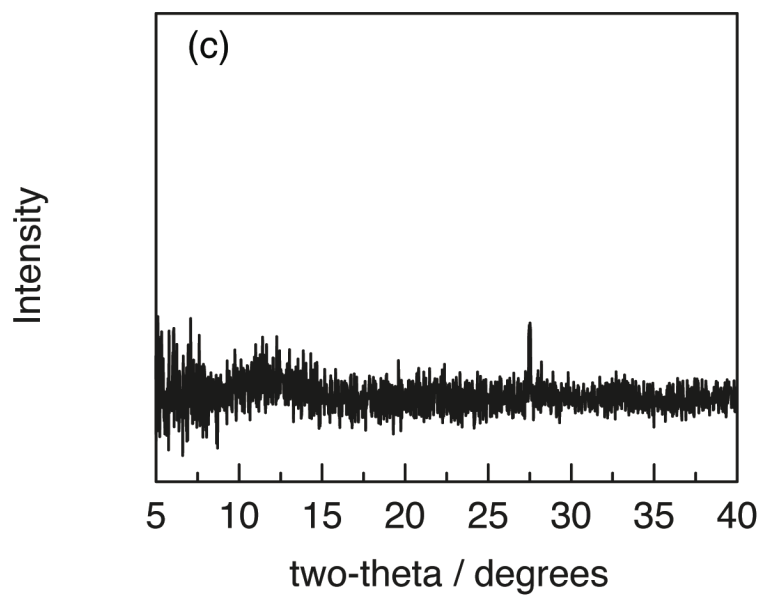


Figure S4c. PXRD pattern of material obtained following $\text{Pd}(\text{NO}_3)_2$ exchange with Zn_3btei .

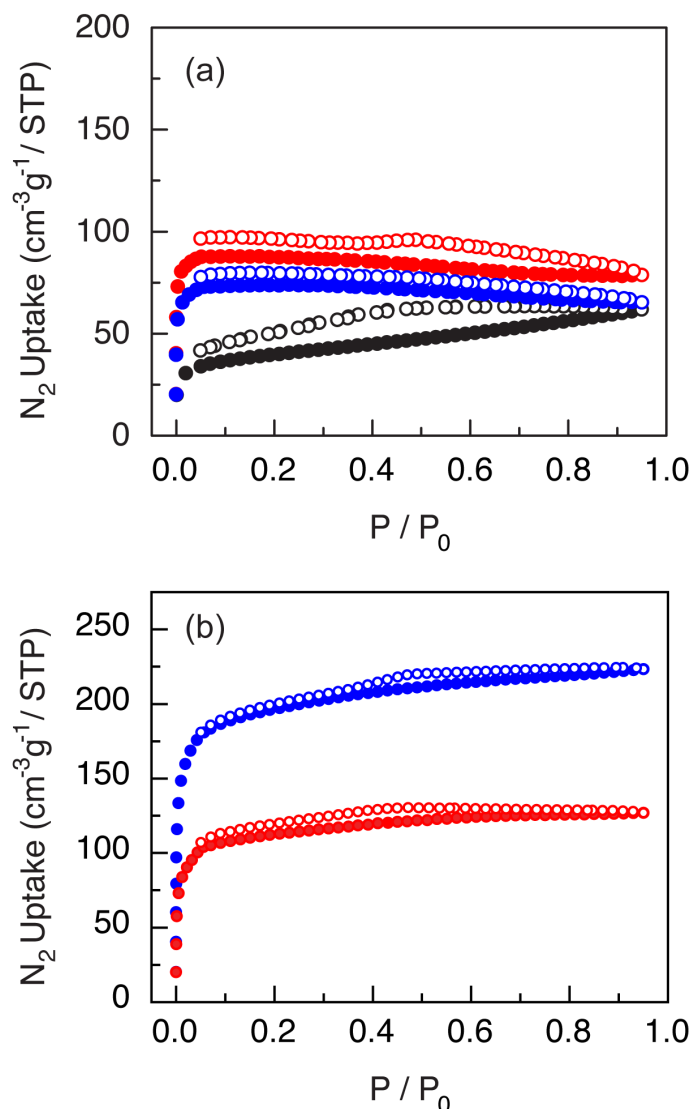


Figure S5. N₂ adsorption isotherms for Zn₃btei and Pd₃btei at different conditions. Supercritical CO₂ activation and heating (45 °C) were incapable of access higher gas uptake capacity. N₂ adsorption isotherms collected at 77 K (a) for Zn₃btei that was activated by vacuum twice at 23 °C (adsorption (●;●), desorption (○;○)) and by supercritical CO₂ (adsorption (●), desorption (○)); (b) for Pd₃btei that was activated at 45 °C for 16 h (adsorption (●), desorption (○)); and, for Pd₃btei that was activated by supercritical CO₂ (adsorption (●), desorption (○)).

Samples	BET surface area (m ² /g)	Langmuir surface area (m ² /g)
Zn ₃ btei/23 °C-1	348	386
Zn ₃ btei/23 °C-2	N/A	175
Zn ₃ btei/supercritical CO ₂	290	325
Pd ₃ btei/45 °C	741	858
Pd ₃ btei/supercritical CO ₂	425	493

C.4. Single-Crystal X-Ray Diffraction

The single crystal X-ray diffraction experiment was conducted using synchrotron radiation ($\lambda = 0.41328 \text{ \AA}$) equipped with a Pilatus3 X CdTe 1M detector and an Oxford cryostream cooling device operating at 100 K at NSF's ChemMatCARS Sector 15 of Advanced Photon Source (APS) housed at Argonne National Laboratory (ANL). Data were collected as a series of phi scans. Indexing was performed using Bruker APEX3. Data integration and reduction were performed using SaintPlus. Absorption correction was performed by multi-scan method implemented in SADABS. Space group was determined using XPREP implemented in APEX3. Structures were solved using SHELXT and refined using SHELXL-2017 (full-matrix least-squares on F^2) with OLEX2 interface program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. Despite using synchrotron radiation, the best crystal sample diffracted only up to 1.12 \AA resolution after many attempts. EXYZ and EADP commands were used to refine the partially exchanged Zn site. Considering that large accessible voids with this structure accommodate heavily disordered solvent molecules, solvent mask in OLOEX2 was thus employed to process the refinement. Crystal data and structure refinement conditions are shown in Table S8.

Table S8. Crystal data and structure refinement for Pd₃btei.

<i>Crystal data</i>	
Chemical formula	0.02(C ₁₁₅₂ H ₃₈₄ O _{460.8} Pd _{19.41} Zn _{76.59})
Fw (g/mol)	597.24
Temperature (K)	100(2)
Crystal system, space group	Cubic, <i>Fm-3m</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	43.149(5), 43.149(5), 43.149(5)
α , β , γ (°)	90, 90, 90
<i>V</i> (Å ³)	80337(27)
<i>Z</i>	48
Radiation type	Synchrotron, $\lambda = 0.41328$ Å
μ (mm ⁻¹)	0.268
Crystal size (mm)	0.02 × 0.02 × 0.02
<i>Data collection</i>	
Diffractometer	Pilatus3 X CdTe 1M
Absorption correction	Multi-scan, <i>SADABS</i>
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	139206, 1544, 1121
<i>R</i> _{int}	0.128
$\sin(\theta/\lambda)_{\max}$ (Å ⁻¹)	1.12
<i>Refinement</i>	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.043, 0.134, 1.06
No. of reflections	1544
No. of parameters	99
H-atom treatment	H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.0638P)^2 + 222.7243P]$ where $P = (F_o^2 + 2F_c^2)/3$
r_{\max} , r_{\min} (e Å ⁻³)	0.26, -0.19

C.5. EXAFS Analysis

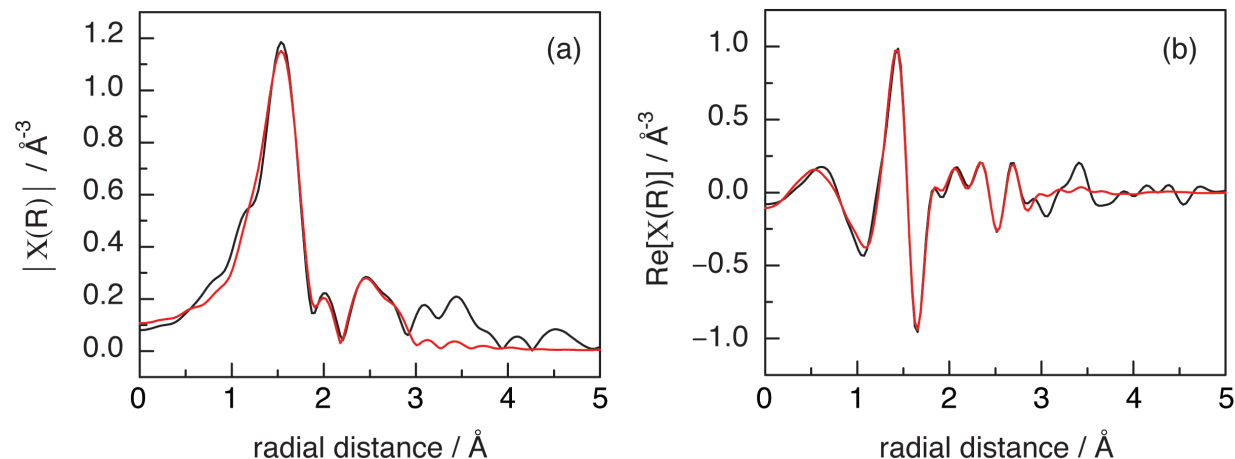


Figure S6. EXAFS Pd K-edge data (window range 1.0 Å – 3.3 Å) for Pd₃btei; experimental data (—) and fit (—) using the FEFF9 code. Fourier transforms (FT) of the Pd K-edge EXAFS data measured on the sample following 86% Pd exchange. Left: the FT moduli; right: real parts of the FTs. The metal–metal interaction around Pd is dominated by the Pd–Pd ones at 2.72 ± 0.03 Å.

Table S9. EXAFS data analysis of Pd₃btei. N, coordination number. S_0^2 , amplitude reduction factor. R, the distance between absorber and scatterer; σ^2 , the Debye-Waller factor; ΔE_0 , the energy shift. R-factor is 0.008.

Path	N	S_0^2	R / Å	$\sigma^2 / \text{Å}^2$	$\Delta E_0 / \text{eV}$
Pd–O	4.00	1.018	2.01 ± 0.01	0.0051	8.45 ± 1.25
Pd–Pd	1.00	1.018	2.72 ± 0.03	0.0103	8.45 ± 1.25
Pd–C	4.00	1.018	2.94 ± 0.03	0.0034	8.45 ± 1.25
Pd–O	4.00	1.018	3.14 ± 0.04	0.0088	8.45 ± 1.25

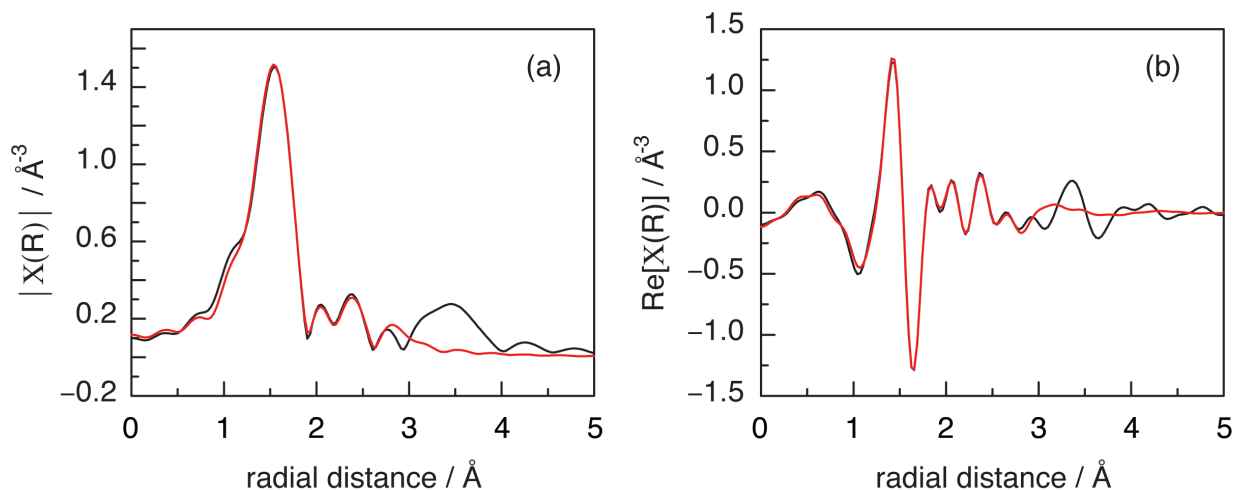


Figure S7. EXAFS Pd K-edge data (window range 1.0 Å – 3.0 Å) for PdZn(OAc)₄(H₂O); experiment data (—) and fit (—) using the FEFF9 code. Left: the FT moduli; right: real parts of the FTs.

Table S10. EXAFS data analysis of PdZn(OAc)₄ · H₂O. N, coordination number. S₀², amplitude reduction factor. R, the distance between absorber and scatterer; σ², the Debye-Waller factor; ΔE₀, the energy shift. R-factor is 0.005.

Path	N	S ₀ ²	R / Å	σ ² / Å ²	ΔE ₀ / eV
Pd–O	4.00	1.022	2.01 ± 0.01	0.0024	9.21 ± 1.27
Pd–Zn	1.00	1.022	2.61 ± 0.05	0.0107	9.21 ± 1.27
Pd–C	2.00	1.022	2.92 ± 0.03	0.0015	9.21 ± 1.27
Pd–C	2.00	1.022	2.98 ± 0.03	0.0015	9.21 ± 1.27
Pd–O	2.00	1.022	3.07 ± 0.04	0.0086	9.21 ± 1.27
Pd–O	2.00	1.022	3.13 ± 0.04	0.0086	9.21 ± 1.27

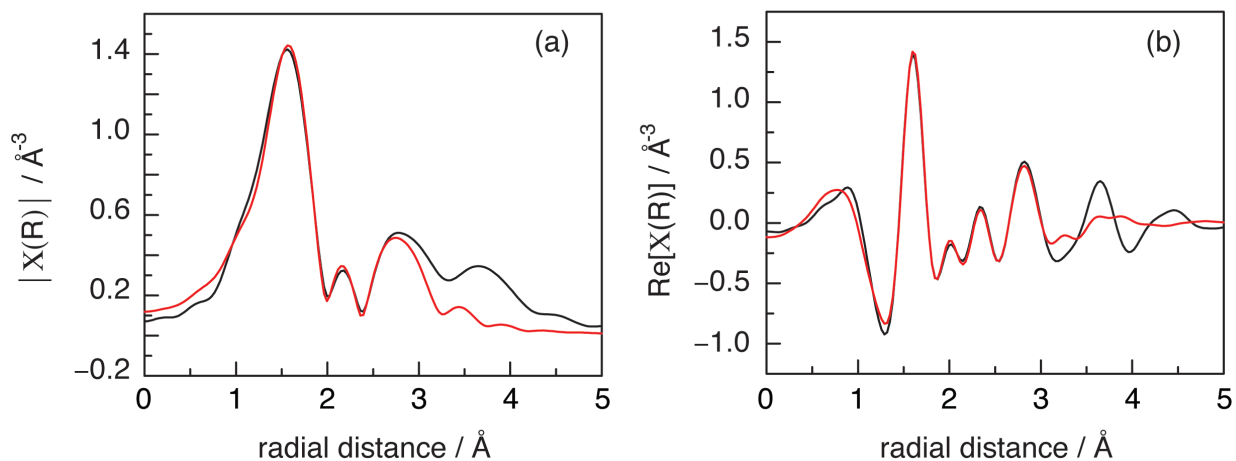


Figure S8. EXAFS Zn K-edge data (window range 1.0 \AA – 3.3 \AA) for PdZn(OAc)₄ · H₂O; experiment data (—) and fit (—) using the FEFF9 code. Left: the FT moduli; right: real parts of the FTs.

Table S11. EXAFS data analysis of PdZn(OAc)₄ · H₂O. N, coordination number. S_0^2 , amplitude reduction factor. R, the distance between absorber and scatterer; σ^2 , the Debye-Waller factor; ΔE_0 , the energy shift. R-factor is 0.014.

Path	N	S_0^2	R / \AA	$\sigma^2 / \text{\AA}^2$	$\Delta E_0 / \text{eV}$
Zn-O	2.00	0.976	2.05 ± 0.03	0.0074	8.97 ± 2.38
Zn-O	2.00	0.976	2.08 ± 0.03	0.0074	8.97 ± 2.38
Zn-Pd	1.00	0.976	2.61 ± 0.07	0.0055	8.97 ± 2.38
Zn-C	4.00	0.976	3.03 ± 0.09	0.0032	8.97 ± 2.38
Zn-O	4.00	0.976	3.23 ± 0.08	0.0035	8.97 ± 2.38

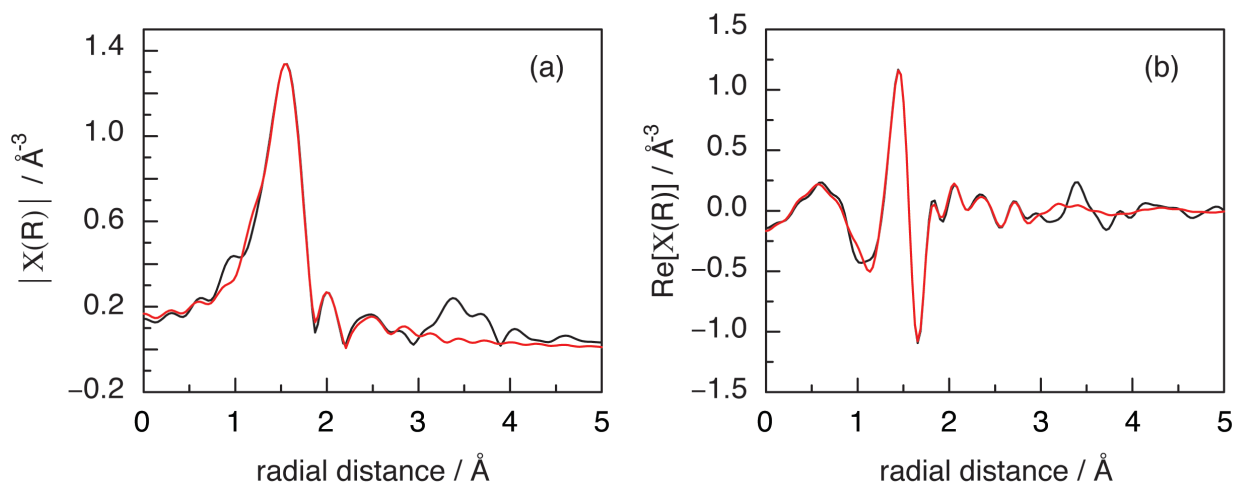


Figure S9. EXAFS Pd K-edge data (window range 1.0 Å – 3.3 Å) for (PdZn)_{1.5}btei; experiment data (—) and fit (—) using the FEFF9 code. Fourier transforms (FT) of the Pd K-edge EXAFS data measured on the sample following 50% Pd exchange. Left: the FT moduli; right: real parts of the FTs.

Table S12. EXAFS data analysis of (PdZn)_{1.5}btei. N, coordination number. S₀², amplitude reduction factor. R, the distance between absorber and scatterer; σ², the Debye-Waller factor; ΔE₀, the energy shift. R-factor is 0.016.

Path	N	S ₀ ²	R / Å	σ ² / Å ²	ΔE ₀ / eV
Pd-O	4.00	1.037	2.01 ± 0.01	0.0034	6.11 ± 1.50
Pd-Zn	0.50	1.037	2.65 ± 0.07	0.0097	6.11 ± 1.50
Pd-Pd	0.50	1.037	2.70 ± 0.07	0.0097	6.11 ± 1.50
Pd-C	4.00	1.037	2.96 ± 0.03	0.0052	6.11 ± 1.50
Pd-O	4.00	1.037	3.16 ± 0.07	0.0149	6.11 ± 1.50

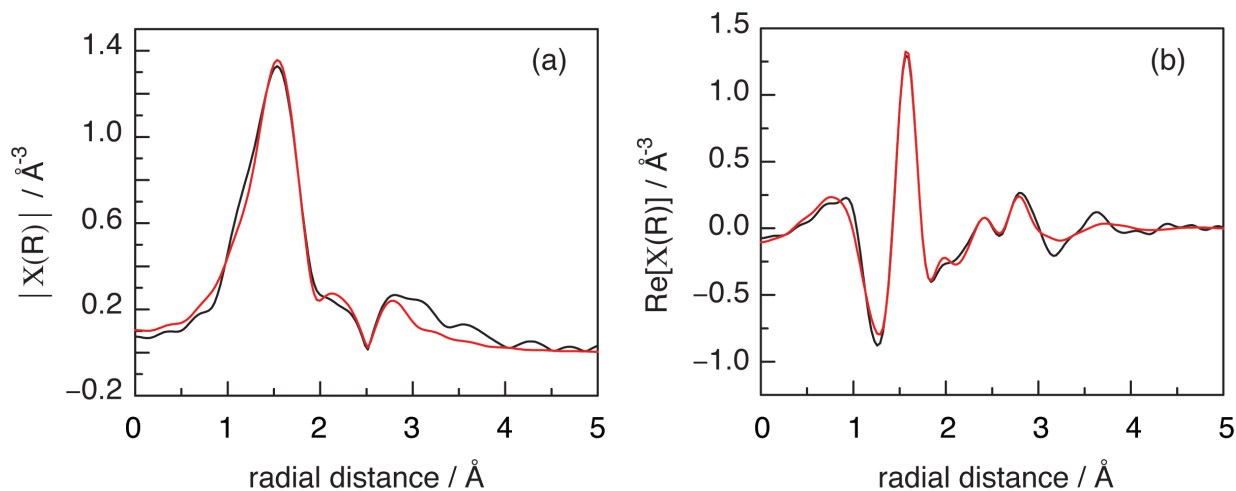


Figure S10. EXAFS Zn K-edge data (window range 1.0 \AA – 3.8 \AA) for $(\text{PdZn})_{1.5}\text{bte}$ i; experiment data (—) and fit (—) using the FEFF9 code. Fourier transforms (FT) of the Pd K-edge EXAFS data measured on the sample following 50% Pd exchange. Left: the FT moduli; right: real parts of the FTs.

Table S13. EXAFS data analysis of $(\text{PdZn})_{1.5}\text{bte}$ i. N, coordination number. S_0^2 , amplitude reduction factor. R, the distance between absorber and scatterer; σ^2 , the Debye-Waller factor; ΔE_0 , the energy shift. R-factor is 0.020.

Path	N	S_0^2	R / \AA	$\sigma^2 / \text{\AA}^2$	$\Delta E_0 / \text{eV}$
Zn-O	4.00	1.019	2.01 ± 0.01	0.0063	8.05 ± 1.14
Zn-O	1.00	1.019	2.18 ± 0.01	0.0063	8.05 ± 1.14
Zn-Pd	0.50	1.019	2.60 ± 0.06	0.0072	8.05 ± 1.14
Zn-Zn	0.50	1.019	2.90 ± 0.06	0.0051	8.05 ± 1.14
Zn-C	4.00	1.019	3.11 ± 0.06	0.0228	8.05 ± 1.14

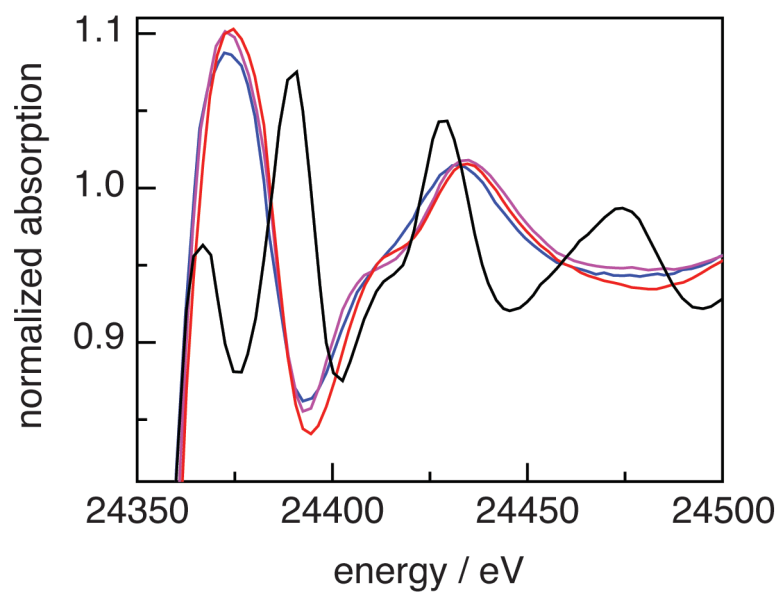
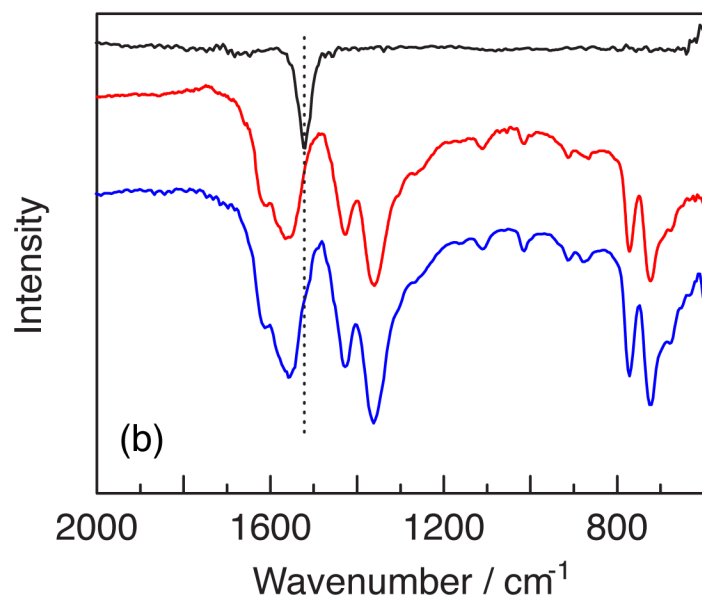
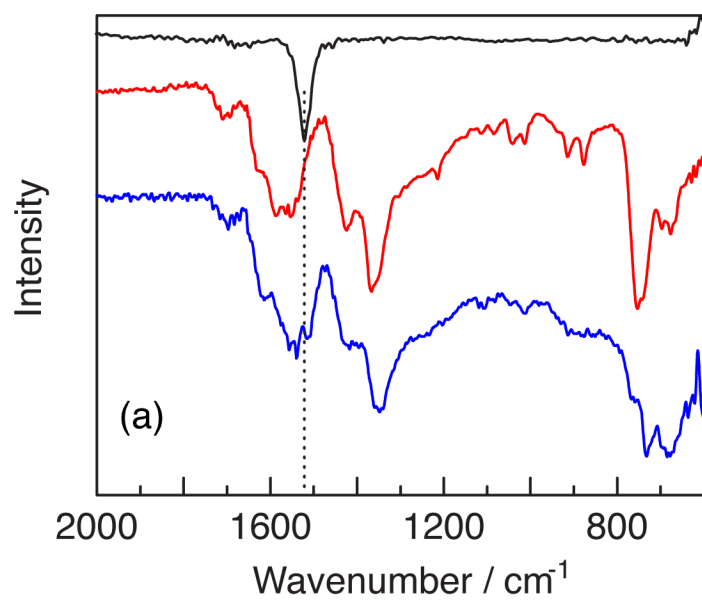


Figure S11. XANES spectra of Pd₃btei (—), Pd(OAc)₂ (—), PdZn(OAc)₄ · H₂O (—), and Pd(0) (—). The edge energy in Pd(II) species is higher than that in Pd(0), which is inconsistent with reduction of the Pd₂ sites upon transmetalation.



Figures S12a and S12b. IR spectra of (a) CS₂ (—), Pd₃btei (—), and Pd₃btei treated with CS₂ (—); (b) CS₂ (—), Zn₃btei (—), and Zn₃btei treated with CS₂ (—).

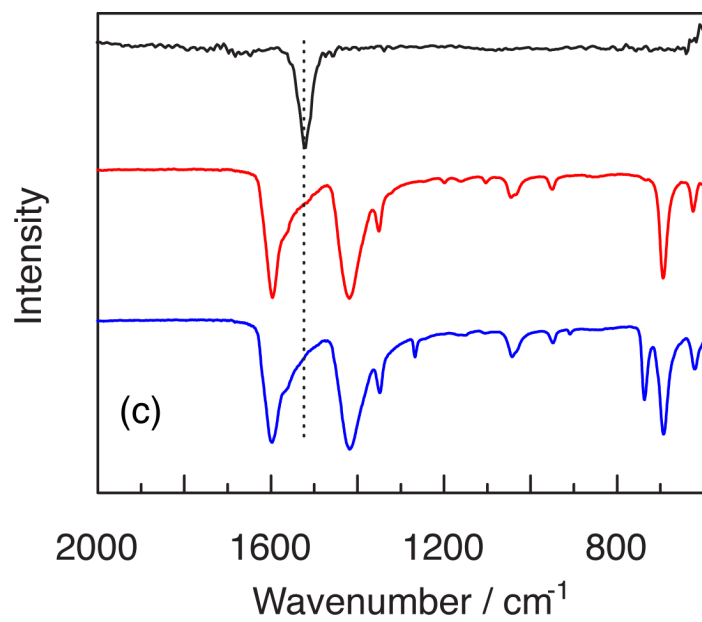


Figure S12c. IR spectra of CS₂ (—), Pd(OAc)₂ (—), and Pd(OAc)₂ treated with CS₂ (—).

C.6. Additional Data

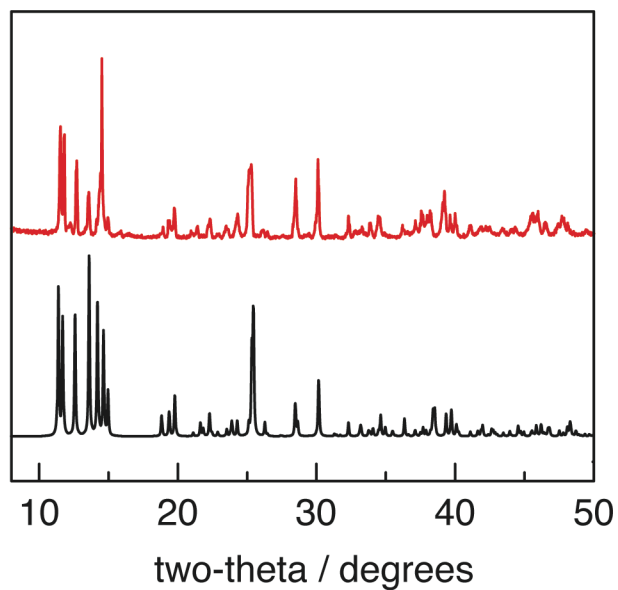


Figure S13. Calculated (—) and Experimental (—) PXR D pattern of $\text{PdZn}(\text{OAc})_4 \cdot \text{H}_2\text{O}$.

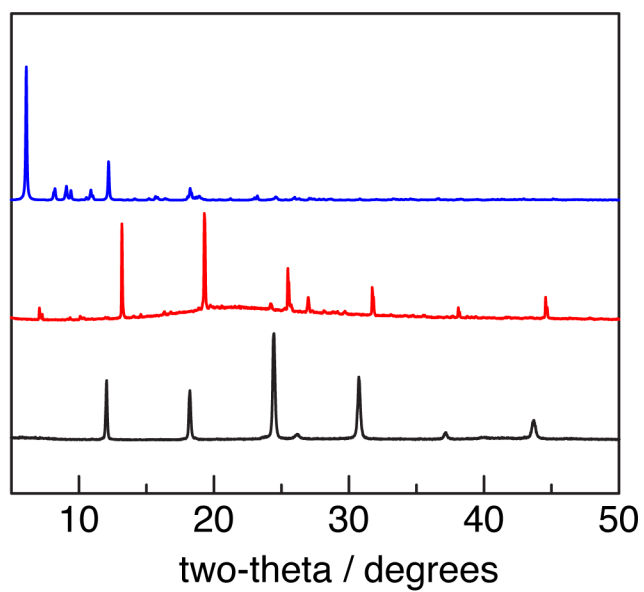


Figure S14. PXRd patterns of calculated **S8** (—), as-synthesized **S8** (—), and Pd-exchanged **S8** (—).

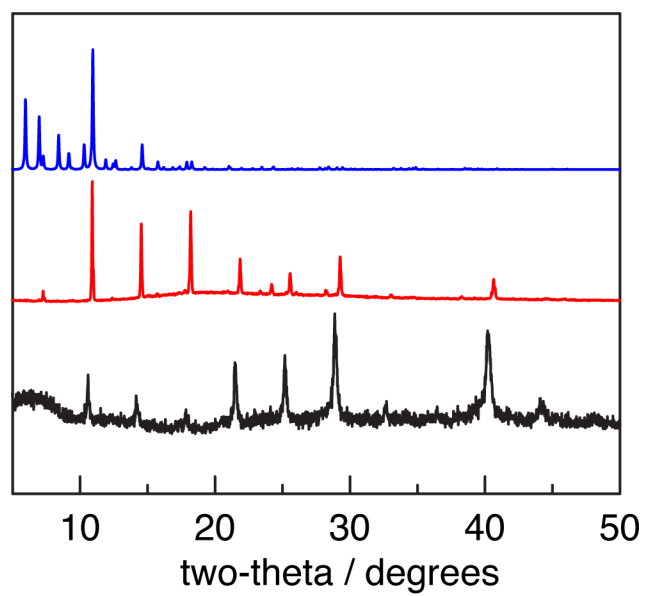


Figure S15. PXRd pattern of calculated **S9** (—), as-synthesized **S9** (—), and Pd-exchanged **S9** (—).

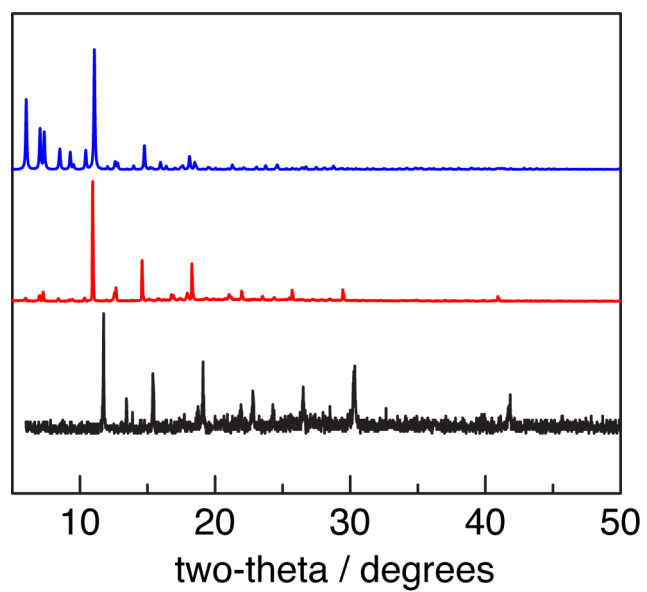


Figure S16. PXRD pattern of calculated **S10** (—), as-synthesized **S10** (—), and Pd-exchanged **S10** (—).

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