

Extraction of Palladium from Nuclear Waste-like Acidic Solutions by a Metal-Organic Framework with Sulfur and Alkene Functions

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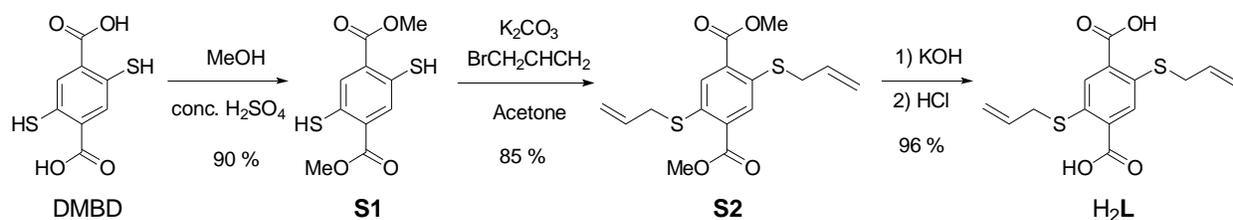
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Supporting Information

General procedure. Starting materials, reagents, and solvents were purchased from Aldrich and used without further purification. The CHN elemental analyses were performed with a Vario Micro CUBE CHN elemental analyzer. The quantification of the metal ions was conducted with a PerkinElmer Optima™ 2100 DV ICP (Inductively Coupled Plasma) optical emission spectrometer. For example, a Pd-loaded ASUiO-66 solid sample (e.g., 2.06 mg) was dissolved in a hot (about 80 °C) HNO₃ (65%)/H₂SO₄ (95%) mixture (v:v=9:1, 0.5 mL). The resultant solution was cooled to rt, and diluted

to 20.0 mL with deionized H₂O. The diluted solution was then subjected to the ICP analysis for the determination of the Pd concentration.

FT-IR spectra were obtained using a Nicolet Avatar 360 FT-IR spectrophotometer. Solution ¹H NMR spectra were recorded on a 400 MHz Bruker superconducting magnet high-field NMR spectrometer at room temperature (rt), with tetramethylsilane (TMS) as the internal standard. Thermogravimetric analyses (TGA) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with a heating rate of 5 °C/min with an empty Al₂O₃ crucible being used as the reference. Powder X-ray diffraction was conducted in the reflection mode at rt on an Inel Equinox 1000 X-ray diffractometer (Inel, France) equipped with CPS 180 detector using monochromated Cu-Kα (λ = 1.5418 Å) radiation. The X-ray tube operated at a voltage of 30 kV and a current of 30 mA. The porosity and surface area analysis was performed using a Quantachrome Autosorb iQ gas sorption analyzer. The activated ASUiO-66 sample (104 mg) was outgassed at 0.03 Torr, heated with a 2 °C/min ramp to 150 °C, and held at 150 °C for 12 hours. The sample was then kept under vacuum until the analysis was run. Pore analysis was performed using N₂ at 77 K (P/P₀ range of 1×10⁻⁵ to 0.995).



Scheme S1. The synthetic steps for 2,6-bis(allylsulfanyl)terephthalic acid (H_2L).

Synthesis of dimethyl 2,5-dimercaptoterephthalate (S1). A 250-ml round-bottom flask were loaded with a magnetic stirring bar, 2,5-dimercapto-1,4-benzenedicarboxylic acid (DMBD, 2.16 g, 9.39 mmol), methanol (100 ml) and concentrated H_2SO_4 (0.5 mL). The flask was then connected to a condenser, and the mixture was refluxed for 48 hours and then cooled back down to room temperature (rt). The reaction mixture was concentrated down to about 50 mL by a rotary evaporator, and then mixed with water (150 mL) to produce a yellowish precipitate that was filtered off by suction, washed extensively with water and dried in air to give the pure product of **S1** (2.19 g, 90 % based on the DMBD). 1H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 2H, CHAr), 4.66 (s, 2H, SHAr), 3.96 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.92, 133.57, 133.48, 129.12, 52.72. FT-IR (KBr pellet, v/cm^{-1}): 3410 (w), 3002(w), 2953 (w), 2535 (w), 1713 (s), 1560 (w), 1434 (m), 1303 (s), 1247 (s), 1136(w), 1090 (s), 954 (m), 823 (m), 777 (m), 632 (w). Chemical analysis of the product $C_{10}H_{10}O_4S_2$ yields the following: calcd [C (46.50%), H (3.90%)]; found [C (46.30%), H (4.05%)].

Dimethyl 2,5-bis(allylsulfanyl)terephthalate (S2). Dimethyl 2,5-dimercaptoterephthalate (**S1**, 0.52 g, 2.01 mmol) and acetone (40 mL) were loaded into a 100 mL two necks round bottom flask charged with magnetic stirring bar. The mixture was bubbled by N_2 for 10 minutes, and then K_2CO_3 (1.21 g, 8.76 mmol), KI (0.07 g, 0.422 mmol) were then added into the reaction mixture under N_2 protection. A mixture of allyl bromide (0.72 g, 5.77 mmol) and acetone (5.0

mL) then injected via cannula under N₂, and the resultant mixture was stirred at rt for 3 hours. The remaining solid (mostly K₂CO₃) was then filtered off, the solvent removed in vacuo, and the yellowish residue was purified by a silica gel plug (silica gel, with 1:2 hexane/dichloromethane as the eluent) to provide a bright yellow crystalline solid (0.58 g, 85% yield based on **S1**). ¹H NMR (400 MHz, CDCl₃): δ 7.89 (s, 2H, CHAr), 5.84-5.91 (m, 2H, CH), 5.17-5.34 (m, 4H, CH₂), 3.94 (s, 6H, CH₃), 3.61-3.62 (d, 4H, SCH₂). ¹³C NMR (100 MHz, CDCl₃): δ 166.08, 136.32, 132.34, 131.08, 129.26, 119.01, 52.53, 35.69. Chemical analysis of the product C₁₆H₁₈O₄S₂ yields the following: calcd [C (56.78%), H (5.36%)]; found [C (56.85%), H (5.28%)].

2,6-bis(allylsulfanyl)terephthalic acid (H₂L). A suspension of dimethyl 2,5-bis(allylsulfanyl)terephthalate (**S2**, 0.56 g, 1.65 mmol) in a KOH solution (3 M, 5 mL) in CH₃OH was stirred at rt overnight in a 10-mL round-bottom flask charged with a magnetic stirring bar. The reaction mixture was then poured into 20 mL of water, and HCl (10%) was then added slowly with vigorous stirring. After the pH value of the mixture became lower than 2, the precipitate was collected by suction filtration and washed with water extensively. Yield: 0.49 g (96%, based on **S2**). The product thus obtained was pure as indicated by NMR and was used for crystal growth without further purification. ¹H NMR (400 MHz, DMSO-*d*₆): δ 13.48 (s, 2H, COOH), 7.79 (s, 2H, CHAr), 5.74-5.82 (m, 2H, CH), 5.13-5.30 (m, 4H, CH₂), 3.64-3.66 (d, 4H, SCH₂). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 167.28, 135.42, 133.50, 132.30, 128.93, 119.09, 34.81. FT-IR (KBr pellet, ν/cm⁻¹): 3435(w), 2997 (m), 2914(m), 2845 (m), 2647 (m), 2557 (m), 1684 (s), 1470 (m), 1412 (m), 1333 (w), 1299 (s), 1244(s), 1088 (m), 930(m), 903(m), 794 (m), 762 (w), 635 (m). Chemical analysis of the product C₁₄H₁₄O₄S₂ yields the following: calcd [C (54.17%), H (4.55%)]; found [C (53.77%), H (4.46%)].

EDTA treatment of Pd-loaded ASUiO-66. A Pd(II)-loaded ASUiO-66 solid (5.0 mg, Pd content: 3.45 %, equivalent to 1.6 μmol of Pd) was stirred with a DI water solution (1.0 mL) of EDTA (ethylenediaminetetraacetic acid, 0.70 mg, 2.4 μmol) at room temperature for 5 hours. After centrifuge, the solid sample was washed by water and dried under vacuum overnight. The color of the solid sample almost no change; and the residual Pd content was found by ICP analysis to be 3.26 % (w/w), as compared with the original value (before treatment) of 3.45 %.

The following is for illustrating the ability of EDTA to bind Pd(II) ions. A ground powder sample of PdCl₂ (0.5 mg, 2.8 μmol) was placed DI water (1.0 mL), the mixture was then sonicated for about 2 min to help disperse the powder in water. EDTA (1.2 mg, 4.1 μmol) was then added, and the mixture was stirred at room temperature for 5 hours. A clear yellowish solution was obtained as a result, indicating effective dissolution of PdCl₂.

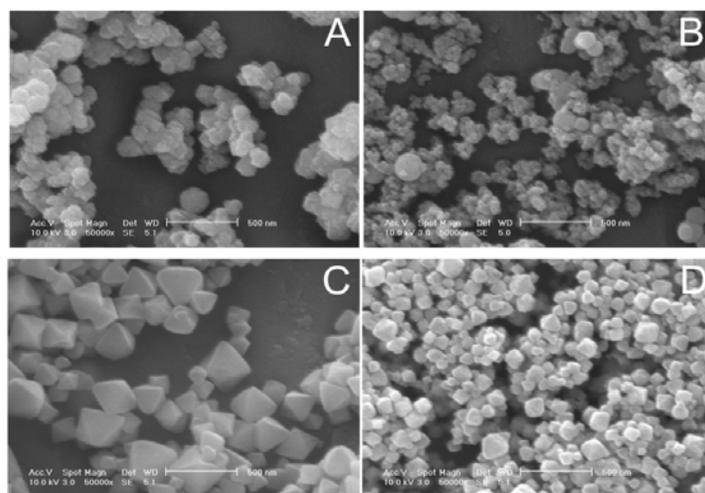
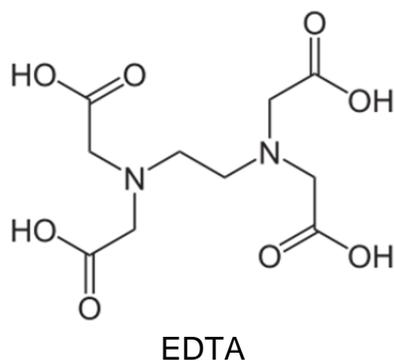


Figure S1. SEM images (5×10^4 magnification) of ASUiO-66 crystallites synthesized in the presence of A) 0, B) 10, C) 30, D) 50 equivalents of acetic acid (scale bar: 500 nm).

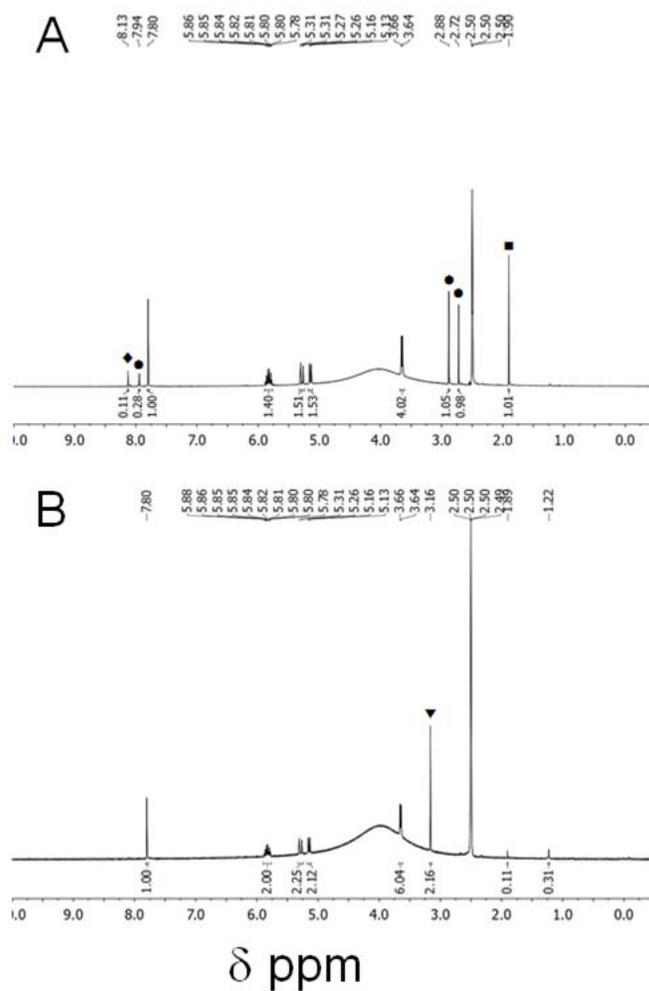


Figure S2. Solution ^1H NMR spectra of (A) an as-made ASUiO-66, and (B) an activated ASUiO-66 sample. Both were dissolved in a mixture of HF/DMSO- d_6 . The hump around 4.0 ppm is from H₂O. Peak labelling: \blacklozenge , HCOOH; \bullet , DMF; \blacksquare , CH₃COOH; \blacktriangledown , CH₃OH.

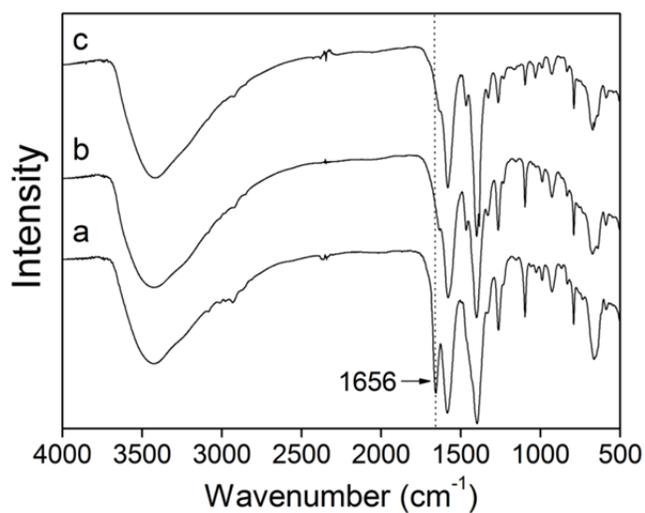


Figure S3. The IR spectra of (a) as-made ASUiO-66 (the 1656 peak arises from the C=O stretching of the DMF guests); (b) activated ASUiO-66; (c) sample of (a) after 5 cycles of adsorption and stripping.

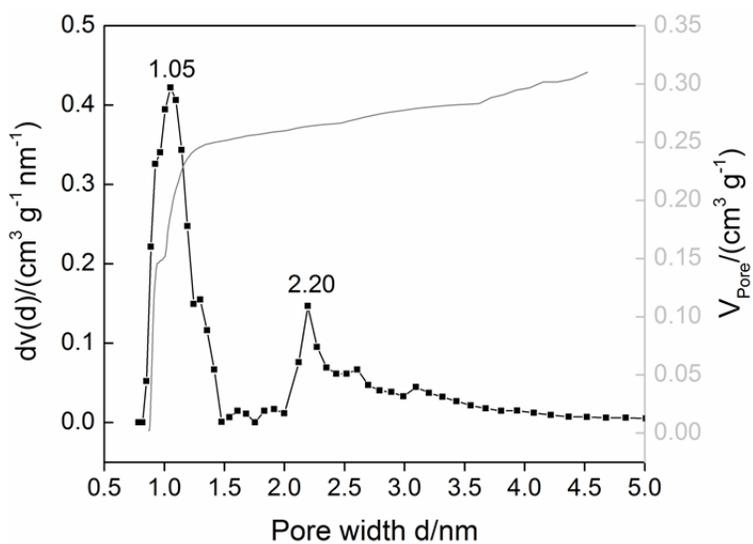


Figure S4. Pore size distribution and pore volume of an activated ASUiO-66 sample (N₂ gas at 77 K; DFT model).

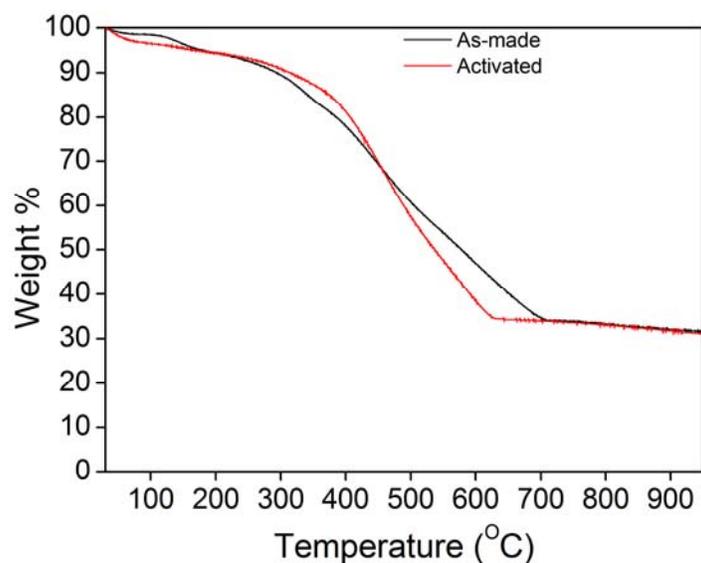


Figure S5. Thermogravimetric analysis (TGA) plots of an as-made ASUiO-66 (black line) and the activated ASUiO-66 sample (red line).

Table S1. The Pd weight percentages in a sample of ASUiO-66 in different cycles of loading and stripping.

ASUiO-66 samples	Weight %	ASUiO-66 samples	Weight %
cycle 1: Pd(NO ₃) ₂ -loaded	3.86	cycle 1: Pd(NO ₃) ₂ - depleted	0.59
cycle 2: Pd(NO ₃) ₂ -loaded	3.04	cycle 2: Pd(NO ₃) ₂ - depleted	0.99
cycle 3: Pd(NO ₃) ₂ -loaded	3.89	cycle 3: Pd(NO ₃) ₂ - depleted	1.27
cycle 4: Pd(NO ₃) ₂ -loaded	3.46	cycle 4: Pd(NO ₃) ₂ - depleted	0.94
cycle 5: Pd(NO ₃) ₂ -loaded	3.90	cycle 5: Pd(NO ₃) ₂ - depleted	1.33

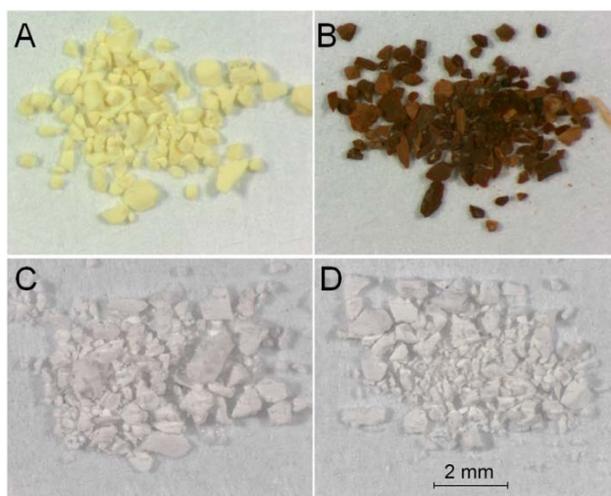


Figure S6. Photographs of (a) an as-made ASUiO-66 powder sample; (b) sample (a) after being shaken with the simulated HLLW for one hour; (c) an as-made UiO-66 powder sample; (d) sample (c) after being shaken with the simulated HLLW for one hour.

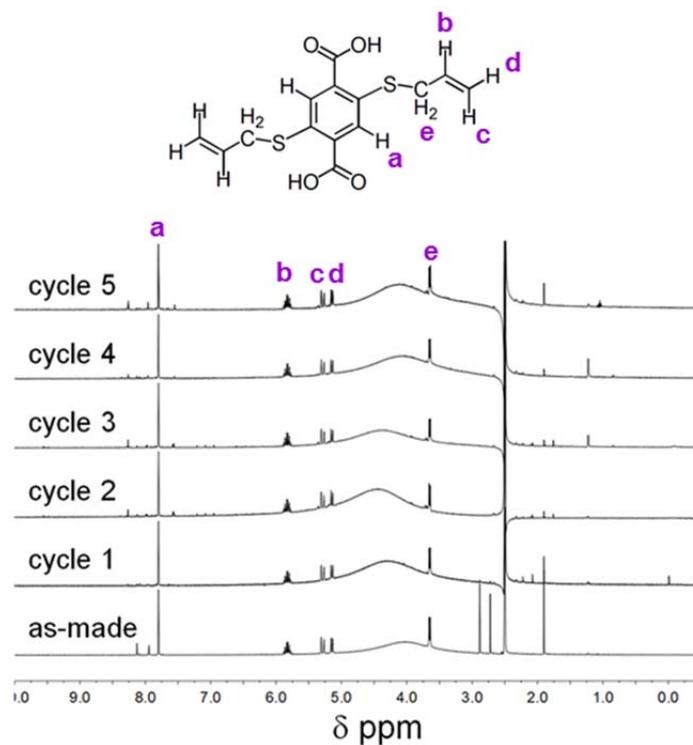


Figure S7. Solution ^1H NMR spectra of an as-made ASUiO-66 sample, and the sample after each of the five cycles of Pd(II) loading and stripping. The samples were dissolved in a mixture of HF/DMSO- d_6 .

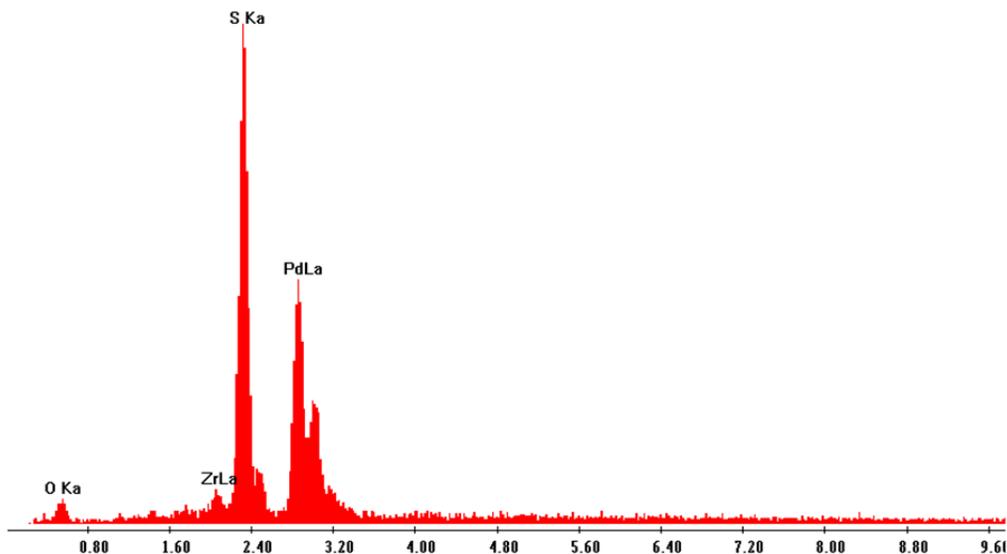
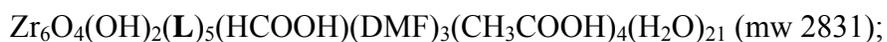


Figure S8. An energy-dispersive X-ray (EDX) spectrum of a solid sample that was first precipitated from the supernatant (i.e., the stripping solution containing the extracted Pd²⁺ ions), and then washed by HNO₃ (65%, at rt). The spectrum indicates PdS as the major component.

Calculation of the Pd/octahedral cage (OC) ratio

Formula unit for as-made ASUiO-66:



Each formula unit contains one octahedral cage (OC), therefore:

$$q_{max} = \frac{45.37 \text{ mg Pd}}{1.0 \text{ g ASUiO66}} = \frac{\frac{45.37}{106.42} \text{ mmol Pd}}{\frac{1.0}{2831} \text{ mol ASUiO66}} = 1.2 \frac{\text{Pd}}{\text{ASUiO66}} = 1.2 \text{Pd/OC}$$