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

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We report a robust metal-organic framework (MOF) for convenient recovery of Pd(II) from acidic nitric solutions which emulate high-level liquid wastes (HLLW) generated from the reprocessing of spent nuclear fuel. The framework solid (ASUiO-66) was constructed from Zr(IV) ions and the multifunctional linker 2,6-bis(allylsulfanyl)terephthalic acid (H<sub>2</sub>L), and features the well-known UiO-66 topology. Herein the robust Zr(IV)-carboxylate bonds impart structural strength to the host net, while the alkene and thioether units provide for efficient and selective binding of the Pd(II) ions. For example, over 95% of the Pd(II) ions can be adsorbed from a simulated HLLW (1.0 M HNO<sub>3</sub>, containing about 20 different types of metal elements), with Ag(I) being the only other metal ion taken up significantly by the ASUiO-66 sorbent. Moreover, the adsorbed Pd(II) species can be effectively stripped by a dilute solution of thiourea (0.01 M); and the regenerated framework solid can be used for additional cycles of Pd extraction, with the sorption capacity for Pd(II) being little changed (38-41 mg/g). The isotherm adsorption data fit well with the Langmuir model with a saturation capacity of 45.4 mg/g, being equivalent to each octahedral cage in the UiO-66 net containing roughly one Pd(II) ion. In a broader perspective, the alkene and thioether combination could be anchored onto other sorbent systems (e.g., porous polymers and resins) to impart versatile adsorption properties for the retrieval of noble metal ions.

## Introduction

Palladium is widely used in research laboratories and industrial technologies because of its versatile physical and chemical properties. Besides the tens of tons annually consumed in electronics fabrication, palladium is a crucial component in catalytic converters and fuel cell development<sup>1</sup> for the automobile industry; palladium reagents are also indispensable as highly effective catalysts for numerous chemical transformations in pharmaceutical, petroleum and other industrial processes.<sup>2</sup> The large scale and scope of its application, as well as the scarcity of palladium as a precious metal, highlights the recycling of palladium as a strategic issue of economics and sustainability.

In spent nuclear fuels (often in the form of acidic high-level liquid waste, HLLW), Pd(II) species also offer especially strong incentives for separation and recovery among the various fission products.<sup>3</sup> First, palladium exist in appreciable fractions of the spent nuclear fuel, and most of the palladium isotopes therein are non-radioactive or very weakly radioactive. It comprises of stable isotopes <sup>104</sup>Pd (17 wt.%) <sup>105</sup>Pd (29 wt.%) <sup>106</sup>Pd (21 wt.%) <sup>108</sup>Pd (12 wt.%) <sup>110</sup>Pd (4 wt.%) and a radioactive <sup>107</sup>Pd (17 wt.%) isotope, which has a half-life of 6.5×10<sup>6</sup> years. The intrinsic radioactivity of <sup>107</sup>Pd (soft β-emitter with  $E_{max}$  of 35 keV) is very weak and it can be tolerated for many industrial applications. Other platinoid metals present (e.g., Rh and Ru), by comparison, are more radioactive. Second, palladium is potentially detrimental

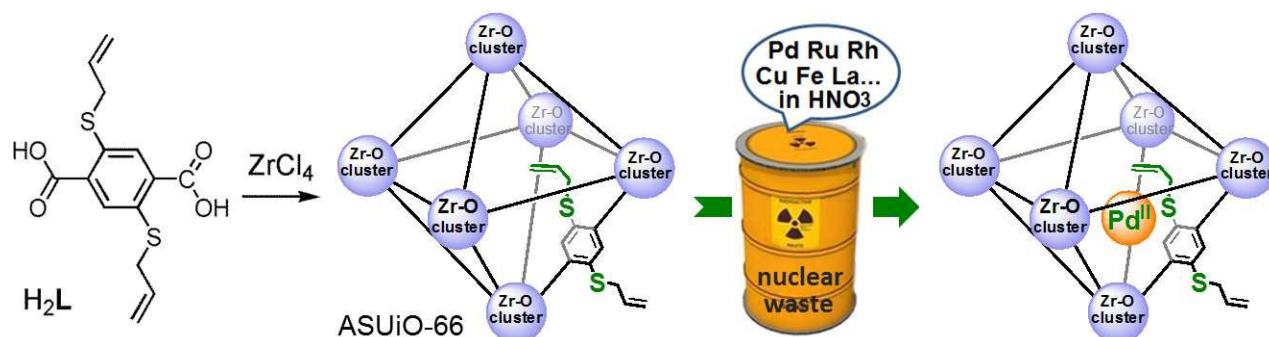
to the commonly used technology of vitrification, which involves melting waste materials into a glass-forming matrix for immobilization purposes; specifically, Pd species tend to form separate phases, and reduces the homogeneity and stability of the vitreous product. Selective removal of Pd therefore bears closely on the topic of nuclear waste storage and management—a topic that begins to attract attention from the field of porous molecular and framework materials.<sup>4</sup>

Amidst the widely studied methods for retrieving palladium, solid phase extraction methods (e.g., by means of resins,<sup>5</sup> biopolymers<sup>6</sup> and mesoporous silica<sup>7</sup>) presents obvious advantages over solvent extraction, because they are operationally more convenient and pose fewer environmental hazards. Of particular interest are systems workable under strongly nitric acidic conditions, because Pd recovery often involves treatment (e.g., leaching from electronic scrap) by strong HNO<sub>3</sub>. In particular, HLLW solutions invariably contains 1.0-3.0 M HNO<sub>3</sub>, and the chloride ion needs to be strictly excluded, because of its limited miscibility with the molten glass used in the vitrification process. In the industrial setting, anion exchange resins are commonly tested for Pd extraction applications--these entail the formation of PdCl<sub>4</sub><sup>2-</sup> ions for exchange purposes, while resin systems that operate with direct exchange with cationic Pd(II) species in nitric acid solutions have been rarely reported.

In addition, the issue of selectivity often proves challenging, mainly because of the many types of metallic elements present in the HLLW solutions and industrial waste solutions. For example, careful elution steps have to be followed in order to target the desired portions of the eluents for effective separation. Technologies for specific binding and separation of Pd(II) species

persistent Pd(II) uptake properties even under strongly acidic conditions-- properties that are relevant for extracting palladium from high-level liquid waste (HLLW) generated from the reprocessing of nuclear fuel.

## Experimental section



**Scheme 1.** The synthesis of the ASUiO-66 network from molecule  $H_2L$  and  $ZrCl_4$ , and the subsequent use in extracting Pd(II) ions from an acidic solution emulating high-level liquid waste (HLLW). The network is isostructural with UiO-66 and is simplified as an octahedral cage.

under nitric acidic conditions therefore remain a pertinent objective. For this, we look to the growing field of metal-organic frameworks (MOFs),<sup>8</sup> wherein the tunable pore size and functionalities allow for great latitude of design to tackle the issue of selective binding of palladium.

The design here integrates two major advances in the field of porous materials. The first regards the discovery of the highly stable Zr(IV)-based MOF systems.<sup>9</sup> The versatility of this system is attested by its remarkable stability to acids (as well as weak bases),<sup>10</sup> and by the rich array of functionalizations implemented.<sup>11</sup> A inspiring example of practical importance was recently disclosed by Lin and co-workers, in which effective uranium extraction under seawater-like conditions was achieved by a Zr(IV) terphenyldicarboxylate (UiO-68) network equipped with phosphorylurea groups as the binding sites.<sup>12</sup> The second advance refers to the highly specific colorimetric response to Pd(II) species as had been reported of a MOF material (ASMOF-5, AS: allylsulfanyl) based on Zn(II) and molecule  $H_2L$  ( $H_2L$  is drawn in Scheme 1).<sup>13</sup> Therein, the distinct  $\pi$ -donor/acceptor characters of the alkene unit, as well as the thioether group as a soft donor, conjoin to make for selective binding of Pd(II) uptake with fast kinetics. Moreover, alkene and thioether groups are both weak Bronsted bases, which allows them to bind Pd(II) ions even under acidic conditions similar to the HLLW solutions. Zn-based MOFs, however, generally suffer from instability towards water: for example, the ASMOF-5 crystals disintegrate into viscous smears upon contact with aqueous solutions, hampering further testing of sensing or separation applications.

For more demanding applications of metal detection and recovery under water/acidic conditions, the more stable systems of Zr(IV)-based MOFs offer clear advantages. Here we integrate the functional linker  $H_2L$  into a robust Zr(IV)-based framework (designated as ASUiO-66; Scheme 1), so as to better utilize the effective alkene-Pd(II) and thioether-Pd(II) interactions for applications under more stringent conditions. Most notably, we discovered that the ASUiO-66 material exhibits selective and

The general procedures are included in the ESI.

**Microcrystalline sample of ASUiO-66.**  $ZrCl_4$  (433 mg, 1.86 mmol), acetic acid (3.42 g, 57.0 mmol; about 30 molar equivalents to  $ZrCl_4$ ), and DMF (N,N-dimethylformamide; 37.5 mL) were mixed in a beaker and sonicated for about 5 min to give a clear solution. The solution was then evenly divided into thirty 8-mL glass vials. Into each vial was then added a DMF (1.25 mL) solution of  $H_2L$  (19.2 mg, 0.0618 mmol, synthesis known<sup>13</sup>). The vials were then sealed by Teflon caps, and placed in a pre-heated oven at 120 °C for 24 hours. After being slowly cooled down (0.1 °C/min) to rt, the resultant bright yellow precipitates (from all 30 vials) were combined and collected by centrifugation, washed with DMF (35 mL x 2, each stirred at rt for 0.5 h),  $CH_3OH$  (35 mL x 2, each stirred at rt for 0.5 h), and then air-dried at 50 °C overnight. The as-made sample thus obtained (706 mg, 74% yield based on  $ZrCl_4$ ) was revealed by scanning electron microscopy (SEM) to consist of distinct octahedral crystallites measuring about 200-400 nm. Similar yields can be obtained with different amounts of acetic acid added (i.e., as a modulator), but the crystallites become smaller and of less regular shapes (Fig. S1). For the ensuing experiments, all the ASUiO-66 samples were prepared using 30 equivalents of acetic acid. The as-made ASUiO-66 sample can be dissolved in a mixture of 48% HF solution (one drop) and  $DMSO-d_6$  (2.0 mL) for solution  $^1H$  NMR measurement, which indicates the molar ratio of formic acid/DMF/acetic acid to be about 1/3.0/4.0 (Fig. S2). Elemental analyses on the as-made sample found [C (34.27%), H (4.63%), N (1.76%)]; A fitting formula can be determined to be  $Zr_6O_4(OH)_2(L)_5(HCOOH)(DMF)_3(CH_3COOH)_4(H_2O)_{21}$  (mw 2831), which gives a calculated profile as [C (34.42%), H (4.69%), N (1.37%)].

**Activated microcrystalline sample of ASUiO-66.** A thimble (e.g., made from folded filter paper) containing the as-made ASUiO-66 solid (200 mg) was loaded into the main chamber of a Soxhlet extractor which was subsequently fitted with a condenser

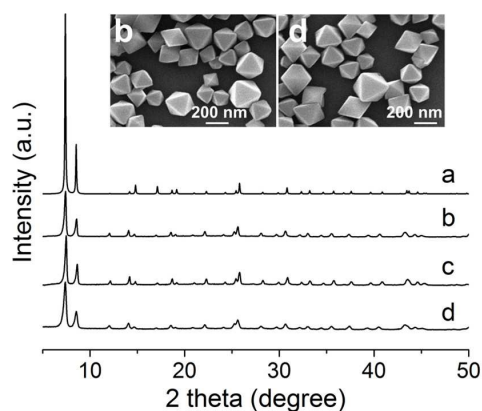
and a 250-mL round-bottom flask containing methanol (150 mL). After the solvent was heated by an oil bath (100 °C) for 4 days, the filter paper was taken out and the solid dried in air to give the activated ASUiO-66 sample. Elemental analysis (CHN) found [C (30.08%), H (4.60%)], a fitting formula can be determined to be  $Zr_6O_4(OH)_2(L)_5(H_2O)_{32}$  which gives a calculated profile as [C (30.05%), H (4.61%)]. Solution  $^1H$  NMR (Fig. S2; the solid was dissolved as above) and IR measurements (e.g., absence of the C=O stretching at  $1656\text{ cm}^{-1}$ ; Fig. S3) also verified the removal of the DMF guest.

**Pd(II) sorption isotherm measurement.** Nine sample solutions (each being 5.0 mL) with Pd (in the form of  $Pd(NO_3)_2$ ) concentrations of 30.5, 61, 81, 102, 152, 203, 254, 305 and 355 mg/L in 3.0 M  $HNO_3$  were prepared. To each solution was added an ASUiO-66 powder (as-made, 10.0 mg); the mixture was sonicated at rt for about 2 min, and then shaken at 300 rpm for 1.0 hour using a IKA KS 501 Digital Orbital shaker. After the sorbent solid was separated by centrifugation, the concentration of the residual Pd in the supernatant was determined by ICP-AES.

## Results and Discussions

### Characterization of ASUiO-66 crystallites.

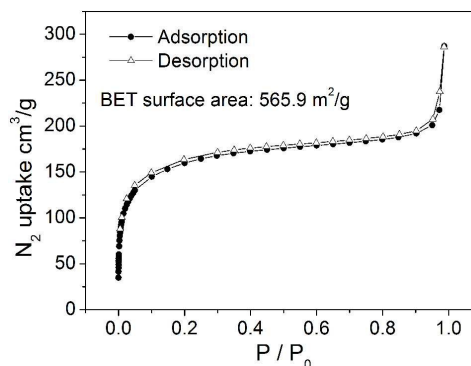
Powder X-ray diffraction (PXRD) indicates that the ASUiO-66 (made from  $H_2L$  and  $ZrCl_4$ ) framework (Fig. 1) to be isostructural with the reported UiO-66, which is based on  $Zr_6O_4(OH)_4$  clusters linked by the 1,4-benzenedicarboxylate struts.<sup>9</sup> The structure features a face-centered cubic arrangement of the Zr-O clusters, and thus contains tetrahedral and octahedral cages in 2:1 ratio (e.g., see Scheme 1). Scanning Electron Microscopy (SEM) measurements indicate that the solid sample of ASUiO-66 uniformly consists of regular-shaped, octahedral crystallites on the scale of 200 nm (insets of Fig. 1). The crystalline morphology thus observed is also consistent with other isorecticular Zr-MOF crystals reported.<sup>11b, 11e</sup> As per  $N_2$  sorption studies at 77 K, the activated ASUiO-66 sample displayed type-I gas adsorption isotherms (Fig. 2) with a specific surface area of ca  $566\text{ m}^2/\text{g}$  and a micropore volume of  $0.31\text{ cm}^3/\text{g}$  (see also the



**Fig. 1** PXRD patterns: (a) calculated from the single-crystal structure of UiO-66; (b) as-made ASUiO-66; (c) activated ASUiO-66; (d) the sample of (b) after 5 cycles of Pd(II) loading and stripping. Insets: SEM images of samples (b) and (d).

pore size distribution in Fig. S4).

Thermogravimetric (TG, see Fig. S5) analyses point to significant ligand deficiency with regards the idealized composition of  $Zr_6O_4(OH)_4(L)_6$ . For example, the residual weight ( $ZrO_2$ , mw 123) at the end of TGA is 31.5%; while the remaining weight for the guest-free state (e.g., at  $200^\circ\text{C}$  after the departure of DMF) is 94.5%, corresponding to the formula  $Zr_6O_4(OH)_2(L)_5$ . This composition can also be fitted to the CHN elemental analysis data [C (30.08%), H (4.60%)] from an activated sample: e.g.,  $Zr_6O_4(OH)_2(L)_5(H_2O)_{32}$  gives a calculated profile as [C (30.05%), H (4.61%)], with the added water content likely contributed by atmospheric moisture. Ligand deficiency is



**Fig. 2** The  $N_2$  sorption isotherm at 77 K for an activated ASUiO-66 sample.

commonly observed in the UiO series of Zr-MOFs, with the associated structural features (e.g., with regards charge balance) well discussed in the literature.<sup>14</sup> Here we focus on the metal uptake properties enabled by the allyl-sulfur side chains within this robust porous framework.

### 55 Selective binding of Pd(II) from simulated HLLW.

The remarkable binding selectivity of the ASUiO-66 crystallites for Pd(II) ions is readily seen in a simple treatment of a simulated HLLW, which contains a complex mixture of metal and non-metal species (Table 1) dissolved in strong acids.<sup>15</sup> For example, After being shaken for one hour at rt an ASUiO-66 solid sample (300 mg, containing about 1.0 mmol of the allylthio side chains as the sorbent units) with a SHLLW solution (40 mL, containing about 12.8 mg/0.12 mmol of  $Pd^{2+}$ ), over 95% of the Pd(II) was removed from the solution (as per ICP-AES analysis). Moreover, the concentrations of most other elements remain largely unchanged in the solution, indicating minimum uptake by the ASUiO-66 sorbent. Only Ag and Se were significantly sorbed, with about 85% and 70%, respectively, being removed from the solution after the treatment (see Fig. 3). The selective binding of Pd(II) and Ag(I) can be ascribed to effective metal-alkene interactions and their relatively small hydration energies (the uptake of Se—e.g., in the form of  $H_2SeO_3$  in the HLLW—likely operates through other mechanisms remaining to be identified). For example, the large hydration energies of Rh(III) and Ru(III) apparently obviate effective binding with the alkene groups, even though as platinumoids they often bind alkenes in other solvents. To highlight the importance of allylthio side chains in the observed metal binding, the parent UiO-66 sample<sup>9</sup> was similarly treated



with the SHLLW: the UiO-66 powder showed no darkening of color (see Fig. S6), with no significant changes in the concentrations of the elements in the solution (e.g., that of Pd only changed from 290 ppm to 286 ppm, as ICP analysis).

**Table 1.** Concentrations (mg/L) of the solutes in a Simulated High Level Liquid Waste (in 1.0 M HNO<sub>3</sub>).

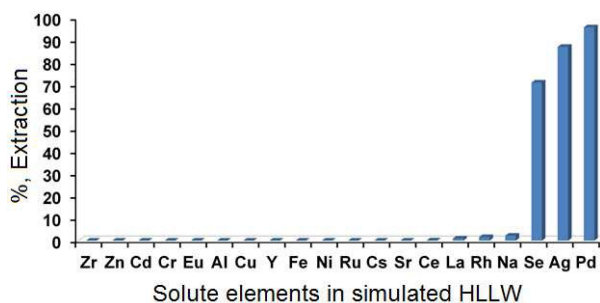
Constituent	Conc.	Constituent	Conc.
AgNO <sub>3</sub>	18.5	Rh(NO <sub>3</sub> ) <sub>3</sub>	87.2
Cd(NO <sub>3</sub> ) <sub>2</sub>	16.6	Ru(NO <sub>3</sub> ) <sub>3</sub>	289.1
Ce(NO <sub>3</sub> ) <sub>3</sub>	548.1	Se <sup>a</sup>	6.9
CsNO <sub>3</sub>	240.7	Sr(NO <sub>3</sub> ) <sub>2</sub>	171.7
Eu(NO <sub>3</sub> ) <sub>3</sub>	30.6	Y <sub>2</sub> O <sub>3</sub>	145.0
La(NO <sub>3</sub> ) <sub>3</sub>	236.3	Zr(NO <sub>3</sub> ) <sub>4</sub>	660.8
Pd(NO <sub>3</sub> ) <sub>2</sub>	319.0	Cr(NO <sub>3</sub> ) <sub>3</sub>	81.8
Ni(NO <sub>3</sub> ) <sub>2</sub>	35.8	Zn(NO <sub>3</sub> ) <sub>2</sub>	17.6
Fe(NO <sub>3</sub> ) <sub>3</sub>	1684.5	Al(NO <sub>3</sub> ) <sub>3</sub>	6.9
NaNO <sub>3</sub>	1083.1	C(NO <sub>3</sub> ) <sub>2</sub>	16.6

<sup>a</sup> In the form of H<sub>2</sub>SeO<sub>3</sub>.

### Stripping of Pd(II) from the loaded ASUiO-66.

The ASUiO-66 sorbent solid thus treated with the simulated HLLW becomes dark-brown (as compared with the light yellow color of the as-made solid, Fig. 4), a color change signifying effective interaction between the Pd(II) ions and the solid host, as had been the colorimetric response to Pd(II) observed of the Zn(II)-L-based framework of ASMOF-5.<sup>13</sup> After being isolated by centrifugation, washed with DI water (30 mL x 3, with stirring at rt for 0.5 h each time), and evacuated overnight to remove the residual water, the Pd-loaded sorbent was found to contain about 3.86% of Pd (by weight, as per ICP-AES analysis).

The Pd species thus taken up by ASUiO-66 can be retrieved,

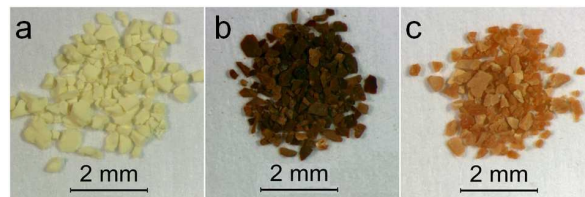


**Fig. 3** Percentages (plotted as a column chart) of the solute elements in a simulated HLLW that are adsorbed by an as-made ASUiO-66 solid (e.g., 95% of the Pd was adsorbed).

and the ASUiO-66 can be reused for additional cycles of metal uptake. In particular, thiourea, with its distinct sulfur donor, proves effective in stripping the Pd(II) species off the ASUiO-66 matrix. In a typical procedure, a Pd-loaded ASUiO-66 solid (244 mg, Pd content: 3.86%, equivalent to 0.088 mmol of Pd) was first stirred with a HNO<sub>3</sub> solution (0.1 M, 44 mL) of thiourea (0.01 M) at 50 °C for 2 h. After the same treatment was applied to the ASUiO-66 sorbent for a second time, the residual Pd content was found to have dropped from 3.86% to 0.59%, with the majority

(i.e., 85%) of the loaded Pd species being stripped off by the thiourea/HNO<sub>3</sub> solution (with the residual 15% of Pd being largely resistant against stripping—e.g., even with stronger thiourea solutions). Concomitantly, the color of the MOF sorbent faded from dark brown to orange in the Pd stripping process (Fig. 4).

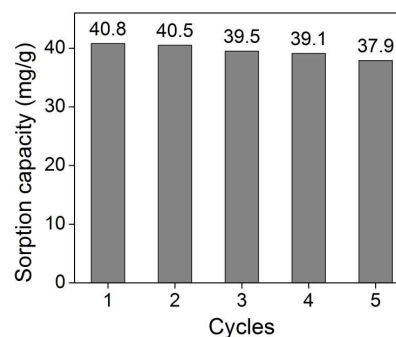
Moreover, the cycle of loading and stripping can be repeated without significant compromise on the uptake and retrieval capabilities (see Table S1). For example, throughout the five rounds tested, the sorption capacity for Pd(II) remains little changed, being within the narrow range of 38–41 mg/g (see Fig. 5). Also persistent throughout the cycles are the regularly shaped, octahedral ASUiO-66 crystallites as revealed by SEM (inset of



**Fig. 4** Photographs of (a) an as-made ASUiO-66 powder sample; (b) sample (a) after being shaken with a simulated HLLW for one hour; (c) sample (b) after being stirred in an HNO<sub>3</sub> (0.1 M) solution of thiourea (0.01 M), in order to strip the loaded Pd(II) ions.

Fig. 1), the IR peaks (Fig. S3), and the PXRD pattern (Fig. 1) indicative of the crystalline phase consistent with the as-made sample. Further examination using solution <sup>1</sup>H NMR (the sample dissolved in HF/DMSO-*d*<sub>6</sub>) indicates that H<sub>2</sub>L molecules remain largely intact, with its peaks dominating the spectra (Fig. S7).

Further recovery of palladium from the supernatant (i.e., the stripping solution containing the extracted Pd<sup>2+</sup> ions) is



**Fig. 5** Sorption capacities (plotted as a column chart) of Pd(II) in the five cycles of loading and stripping.

convenient. For example, a mixture of the supernatant (10 mL; containing 0.90 mg Pd) and ammonia solution (25%, 0.5 mL; to raise the alkalinity), after being heated at 50 °C for a few minutes, gave a black precipitate that can be collected by filtration. While ICP analysis on the filtrate indicated complete precipitation of the Pd ions; the black solid (water-washed and air-dried), after being dissolved in hot nitric acid (65%), was found by ICP to contain substantially Pd (44%, w/w), together with small amounts of Ag (3.11%, w/w) and Zr (1.15%; w/w). The experimental Pd content (44%) approximated that of Pd(II) thioureate, Pd(HNCSNH<sub>2</sub>)<sub>2</sub>

(Pd fraction: 41.5%), and some Pd-rich components (e.g., PdS) might be present to raise the overall Pd content to the value found.

### Pd(II) sorption isotherm studies.

Adsorption isotherms delineate the adsorption capacity (i.e., the amount of guest adsorbed divided by the sorbent mass) as a function of the guest concentration in the solution (this is equilibrated with the adsorbent phase; under a constant temperature), and are routinely measured to shed light on the underlying adsorption mechanism. For this, sorption isotherm data were obtained by interacting the ASUiO-66 sorbent with Pd(II) solutions (in 3.0 M HNO<sub>3</sub>) of various concentrations (e.g., in the range of 30–355 mg/L). The adsorption data fit well with the Langmuir isotherm model and the isotherm is expressed linearly as:

$$\frac{C_e}{q_e} = C_e \times \frac{1}{q_{max}} + \frac{1}{K_L q_{max}}$$

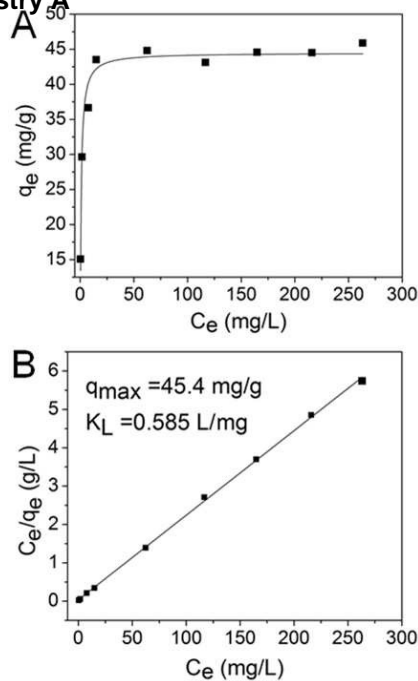
where  $q_e$  (mg/g) is the sorption capacity at equilibrium,  $q_{max}$  (mg/g) is the saturated capacity,  $C_e$  (mg/L) is the Pd concentration in solution at equilibrium and  $K_L$  (L/mg) is a constant related to binding site affinity. Values for  $q_{max}$  and  $K_L$  can be obtained from the slope and y-intercept, respectively, by plotting  $C_e/q_e$  vs.  $C_e$ , as shown in Fig. 6.

The Langmuir model represents the nonlinear sorption and suggests that the Pd(II) uptake occurs on a homogeneous surface by monolayer coverage without interaction between adsorbed metal species.<sup>16</sup> This model is also consistent with the structural uniformity throughout the crystalline MOF sorbent, especially with regards to the pore geometry and the spatial distribution of the allylthio groups as the sorbent sites. The saturated capacity  $q_{max}$  (45.4 mg/g) derived from these measurements indicated a corresponding formula  $Zr_6O_4(OH)_2(L)_5 \cdot 1.2Pd$ , which is equivalent to an approximately 1:1 ratio between the octahedral cage and the Pd(II) ion (see SI for the detailed calculation), and suggests that the Pd(II) ions might be mostly confined in the octahedral voids of the ASUiO-66 host.

To further assess the degree to which Pd(II) uptake occurs on the outer surface of the solid sample, the Pd-loaded ASUiO-66 solid was treated with a water solution of the strong metal chelator EDTA. Even after being stirred at room temperature for 5 hrs, the Pd content in the ASUiO-66 solid was found by ICP analysis to remain largely unchanged [i.e., before EDTA treatment: 3.45 %; after: 3.26 %]. This experiment indicated that the majority of Pd remains inaccessible to the EDTA chelator, lending additional evidence of Pd(II) being lodged well inside the pores of the ASUiO-66 framework. The key assumption for the above experiment is that EDTA is able to effectively extract accessible Pd(II) species (e.g., those stuck on the outer surface of the ASUiO-66 powder). This assumption is found to be reasonable because a ground solid sample of PdCl<sub>2</sub> became fully dissolved when similarly treated by the EDTA solution (see ESI for more details).

### Conclusions

In conclusion, ASUiO-66, a porous crystalline solid based on a



**Fig. 6** A: The Langmuir adsorption isotherm for ASUiO-66 in a 3.0 M HNO<sub>3</sub> solution. Sorption capacities ( $q_e$ ) plotted against Pd concentrations at equilibrium. B: linear expression of the Langmuir isotherm. Values of saturation sorption capacity ( $q_{max}$ ) and the Langmuir constant ( $K_L$ ), obtained from the slope and y-intercept, respectively, are also shown.

simple and easy-to-make functional linker (L), presents clear potential in the real world application of palladium extraction and recovery. Such a potential is especially highlighted by the remarkable stability and selectivity properties demonstrated herein. In particular, the stability of the current framework solid stems from the robust strong Zr(IV)-carboxylate links, which allows for its repeated use as a sorbent material under the stringent condition of strongly acidic environments. On the other hand, the combined thioether and alkene functions from the side chains of linker L enable the remarkable selectivity of the sorbent solid, allowing for Pd<sup>2+</sup> (and to a lesser degree Ag<sup>+</sup>) to be separated from the complex mixture of the numerous metal species commonly present in nuclear waste (e.g., HLLW).

On the broader front, the combined functions of thioether and alkene can be explored in ion exchange resins and other sorbent systems, so as to transplant similar binding selectivity for the extraction and recycling of palladium. Modifications around the alkene unit (e.g., with fluoro substituents) could also further mitigate the hydrophilicity character of the porous framework, so as to make it even more stable towards acidic conditions, while maintaining its binding affinity for Pd(II) ions. We also believe that selective binding for other noble metals (such as Rh<sup>3+</sup> and Ru<sup>3+</sup>) can be achieved through a judicious screening for an effective combination among the alkene, thioether, carboxylate, amine functions and other donor groups.

### ACKNOWLEDGMENTS

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## Notes

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† Electronic Supplementary Information (ESI) available: Additional SEM and photographic images, solution <sup>1</sup>H NMR spectra, TGA plots, and additional data related to the quantification of Pd and other elements. See DOI: 10.1039/b000000x/

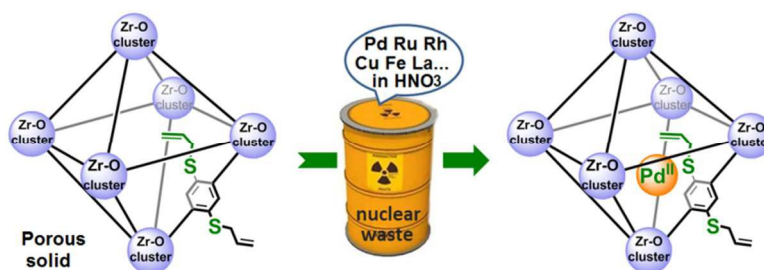
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TOC graphic



Hard-and-soft combo does the trick: hard and robust Zr(IV)-carboxylate nodes build up the net, while soft allyl and sulfur donors selectively extract Pd(II)—from amongst other elements in nuclear wastes.