

Convenient Detection of Pd(II) by a Metal–Organic Framework with Sulfur and Olefin Functions

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Supporting Information

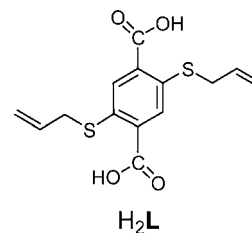
ABSTRACT: A highly specific, distinct color change in the crystals of a metal–organic framework with pendant allyl thioether units in response to Pd species was discovered. The color change (from light yellow to orange/brick red) can be triggered by Pd species at concentrations of a few parts per million and points to the potential use of these crystals in colorimetric detection and quantification of Pd(II) ions. The swift color change is likely due to the combined effects of the multiple functions built into the porous framework: the carboxyl groups for bonding with Zn(II) ions to assemble the host network and the thioether and alkene functions for effective uptake of the Pd(II) analytes (e.g., via the alkene–Pd interaction). The resultant loading of Pd (and other noble metal) species into the porous solid also offers rich potential for catalysis applications, and the alkene side chains are amenable to wide-ranging chemical transformations (e.g., bromination and polymerization), enabling further functionalization of the porous networks.

The major discovery here is a single-crystal system of a metal–organic framework (MOF)¹ that exhibits a highly specific response to Pd(II) species: the nearly colorless crystal turns orange-red even at Pd concentrations as low as a few parts per million. The significance of this observation is rooted in both the practical issue of detection of Pd and other noble metals and the fundamental explorations of functionalizing of porous solid-state materials. As a method for screening Pd species, this discovery is much cheaper and more convenient than instrumental methods [e.g., atomic absorption spectroscopy, inductively coupled plasma (ICP) mass spectrometry, and X-ray fluorescence]; it even rivals fluorescent sensing methods in regard to operational convenience. While these widely studied methods are best suited for liquid phase/solution sensing systems,² the current MOF system as a colorimetric and solid-state sensor is especially easy to use: one simply places the single crystal in the analyte solution and follows the color change of the single crystal for screening/detection. In addition, the solid-state platform offers the potential for use in the retrieval of noble metals.

This example of effective Pd sensing also stands out among the major advances in utilizing MOF materials for sensing applications. In general, the well-defined pore size/geometry and flexible chemical functionality of MOFs offer great potential for sensing³ and separation⁴ applications. One current thrust of applied research is focused on their luminescent properties,⁵ and significant advances have been documented in the sensing of small-molecule analytes (e.g., organic nitro compounds⁶ and other analytes⁷). By comparison, the sensing of Pd and other noble-metal species, in spite of its great importance in industrial and environmental settings, remains largely unexplored in the field of MOFs, even though increasing efforts are being directed toward the loading and sensing of metal species using MOF matrices.^{7d,8} One major challenge here is developing a functionalized MOF system that effectively takes up and interacts with metal species. For example, one needs to have a host network equipped with functional groups that specifically interact with the target analytes of metal species. In spite of fast developments in research on functionalized MOFs, a system that exhibits specific sensing of Pd (or other noble metals) has not been demonstrated (although a MOF with pyridinyl donors for Pd uptake is known^{8h}).

The key design element in the present case is the conjoint thioether and alkene functions built into the side-chain structures of 2,5-dithioalloyterephthalic acid (H₂L; Chart 1). The advantages of such a multifunctional building block are obvious: the sulfur-conjugated aromatic core features intense photoluminescence (PL), providing the potential for sensing;

Chart 1



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moreover, the alkene unit, with its distinct π -donor and π -acceptor characters, tends to bind noble-metal species preferentially, thus facilitating the metal uptake process for fast response in sensing applications. Since noble-metal ions [e.g., Pd(II), Pt(II)] are chemically soft species that also interact significantly with the sulfur (thioether) function, the resultant quenching of the PL of the aromatic core was expected to be substantial. The triggering of the orange-red color, which turned out to be surprisingly specific for Pd species, is thus the result of a combination of rational design and serendipity in our larger exercises of functionalizing MOFs.

Reacting H_2L and $\text{Zn}(\text{NO}_3)_2$ in DEF/methanol produced large cubic crystals of ASMOF-5 (AS = allylthio) in high yield and purity. X-ray diffraction (XRD) [data sets were obtained from as-made and HgCl_2 -treated samples; see the Supporting Information (SI) for details] showed ASMOF-5 to be isorecticular with the prototypical MOF-5 (Figure 1),⁹ a well-known network

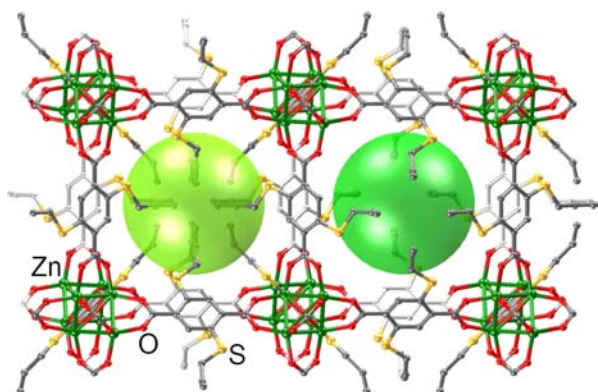


Figure 1. Two face-sharing unit boxes in the single-crystal structure of ASMOF-5. The disorder of the phenyl rings and side chains is not shown. The large spheres inside the boxes highlight the pores and the side chains, which are oriented such that only one of the two unit boxes (here, the left one) contains the side chains.

system that has been functionalized with many other side-chain groups.^{8e,10} ASMOF-5 adopts the same space group as MOF-5 ($Fm\bar{3}m$); however, the phenyl rings are tilted by $\sim 17^\circ$ from the positions in MOF-5 and thus are disordered over two symmetry-equivalent positions, and the side chains are disordered over the four positions of the benzene core (see the SI for crystallographic details). The spatial distribution of the side chains as revealed in the low-temperature (100 K) XRD data sets is noteworthy: in each face-sharing pair of unit boxes, only one is occupied by the side chains, while the other is not (Figure 1). The activated ASMOF-5 sample displayed typical type-I N_2 adsorption isotherms at 77.4 K, with a BET surface area of $618 \text{ m}^2/\text{g}$ and a micropore volume of $0.231 \text{ cm}^3/\text{g}$ (Figure S1 in the SI).

Upon immersion in an acetonitrile solution of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.25% w/w), the ASMOF-5 crystals turned from light yellow into dark brick-red within several minutes (Figure 2), indicating a significant interaction between the framework solid and the $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ guest (as-made and activated samples behaved similarly). The Raman spectrum of the Pd(II)-treated crystals revealed a distinct peak around 372 cm^{-1} (Figure S2), corresponding to Pd(II)-olefin stretch frequencies reported earlier.¹¹ The powder XRD (PXRD) patterns of the $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ -treated crystals indicated that the original host framework retained its crystalline order (Figure 3), although usable single-crystal data sets could not be obtained

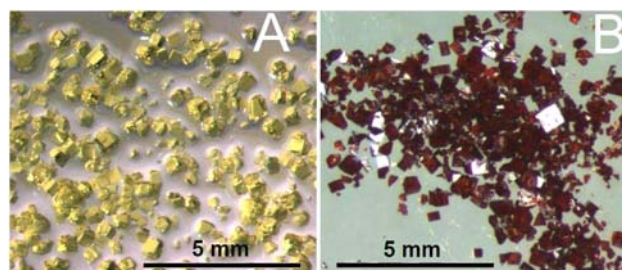


Figure 2. Photographs of ASMOF-5 powder samples: (A) activated crystals in acetonitrile; (B) activated crystals after immersion in an acetonitrile solution of PdCl_2 (0.25% w/w) for 10 min at room temperature.

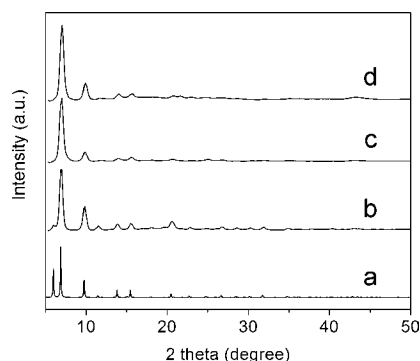


Figure 3. PXRD patterns: (a) calculated from the single-crystal structure of ASMOF-5; (b) as-made ASMOF-5; (c) activated ASMOF-5; (d) ASMOF-5 treated with PdCl_2 fresh out of solution.

from these Pd-treated samples. The intense bluish-green PL of the host framework was completely quenched (Figure S3). ICP elemental analysis of the PdCl_2 -treated ASMOF-5 sample revealed a Zn/Pd ratio of 6.25:1, equivalent to 0.64 Pd(II) ion per unit box. The amount of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ thus uploaded into the allyl-laced framework is significant.

To probe the lower limit of the PdCl_2 concentration that can be detected by the ASMOF-5 crystals, a single-crystal grain of ASMOF-5 ($\sim 0.2 \text{ mm}^3$; as-made or activated) was placed in each of a series of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ solutions (10, 5, 1, 0.5, or 0 ppm in CH_2Cl_2 ; $V \approx 2.0 \text{ mL}$), which were then heated to 80°C in sealed Pyrex glass tubes. Within 1 h, the PL of the ASMOF-5 crystals in all of the Pd solutions were distinctly quenched relative to the one placed in pure CH_2Cl_2 (Figure 4 top), indicating that the emission intensity is highly sensitive: even sub-ppm levels of Pd can be readily detected. The colors of the crystals, by comparison, exhibited a pattern of more gradual variation in correlation with

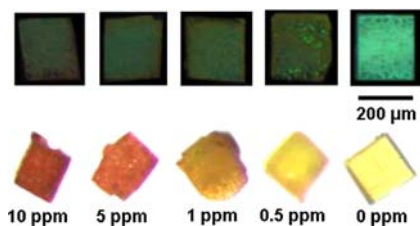


Figure 4. Photographs of the ASMOF-5 crystals under 365 nm UV radiation (top row) and under natural light (bottom row) before and after immersion at 80°C in CH_2Cl_2 solutions of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ at various concentrations (as labeled). Durations of immersion: top row, 1 h; bottom row, 4 h.

the Pd concentration, providing the potential for use in colorimetric determination of Pd concentrations (Figure 4 bottom). For example, after treatment at 80 °C for 4 h, the orange tinge of the crystal in the 0.5 ppm solution was just visible to the eye, while the ones in the more concentrated solutions were increasingly darker in coloration; at 10 ppm and above, the crystals became (dark) brick red.

More interestingly, the change in the color of the ASMOF-5 crystals to orange-red is highly specific to Pd species. Over a very broad range of Pd concentrations (5–1500 ppm), only Pd species trigger the color change to orange-red, and other noble-metal ions [e.g., Pt(II), Ir(III), Ru(III)] and transition-metal ions can be readily distinguished from Pd(II) (Figure 5). Specifically,

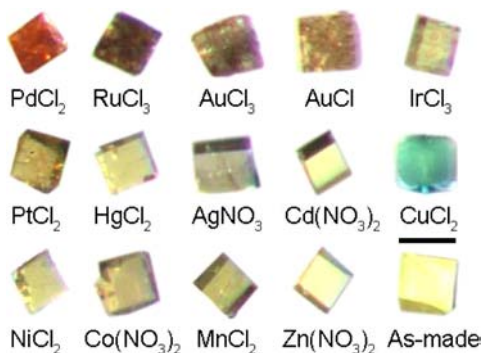


Figure 5. Photographs of ASMOF-5 crystals under natural light before and after immersion (for 0.5 h at 80 °C and then 2 h at rt) in CH_3CN solutions of various metal salts (1.0 mL each, all at 1500 ppm metal ion). The scale bar is 200 μm .

at lower concentrations (e.g., 5.0 ppm), other metal ions generally do not affect much the yellow color of the crystal samples (Figure S4); at higher concentrations (e.g., >1000 ppm), the colors caused by other metal species tend to be brownish-gray, which can easily be distinguished from the orange-red color caused by Pd. On the other hand, the PL of the crystal is quenched by most transition-metal ions and is thus less selective in identifying a specific metal ion (see Figure S5).

Interference from other metal species was also investigated. Such tests indicated that the presence of a significant amount of other metal species (up to a 1:1 molar ratio with Pd) generally did not perturb the occurrence of the orange-red color induced by Pd (Figure S6). Only Ru(III) appeared to interfere, with the orange-red color indicative of Pd being largely obscured. Such tolerance is not especially high but is more than sufficient for quick screening in special cases where other metal species tend to be absent or low (e.g., detection of residual Pd in pharmaceuticals made from Pd-catalyzed protocols).

To highlight the role of the alkene unit in facilitating the color change in ASMOF-5, comparative Pd uptake experiments were conducted for ASMOF-5, the reported SESMOF-5 (in which the linker side chain is $\text{CH}_3\text{SCH}_2\text{CH}_2\text{S}-$),¹² and unfunctionalized MOF-5. Because of the side-chain similarities (thioether) and differences (alkene vs thioether), the comparison of ASMOF-5 and SESMOF-5 is especially pertinent for teasing out the role of the alkene function. A single crystal sample of ASMOF-5, SESMOF-5 and MOF-5 was thus each placed in a saturated solution of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1.0 mL, room temperature): while the ASMOF-5 crystal instantaneously takes on a brick-red color, the color change in the SESMOF-5 remains barely visible even after 3 hours; the MOF-5 crystal exhibits no color change, but

becomes translucent instead (Figure 6). The much slower and less intense color change observed for SESMOF-5 (compared

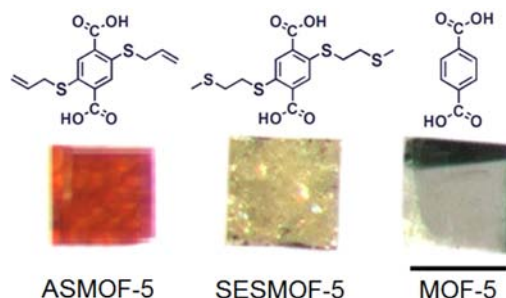


Figure 6. (top) Structures of the linker building blocks in ASMOF-5, SESMOF-5, and MOF-5 and (bottom) photographs of the corresponding crystals under natural light after immersion (for 5 min at 80 °C and then 3 h at rt) in saturated CH_3CN solutions of $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1.0 mL each, ~0.25% w/w). The scale bar is 200 μm .

with ASMOF-5) points to an essential contribution from the alkene unit in bringing about the distinct color change in ASMOF-5; apparently, such a role is fulfilled in conjunction with other functional groups (i.e., the sulfur and carboxylate units) in the ASMOF-5 structure, as typical alkene–Pd(II) complexation by itself does not normally lead to the orange-red color observed in the case of ASMOF-5. Further study in characterizing the interaction between Pd(II) and the host network should shed light on the origin of the coloration of Pd-loaded ASMOF-5.

In a larger sense, the speedy uptake of Pd and other noble-metal species into MOF structures opens new doors for catalytic and sensing applications because of the unique reactivities of noble metals. The present ASMOF system, however, suffers from instability, as is often observed for Zn-based MOFs. Although as-made samples are stable in air for days, activated and Pd-loaded samples degrade in air within a few hours, as indicated by PXRD (Figure S7). As a quick and inexpensive method for screening Pd species, ASMOF-5 (especially the more stable as-made crystals) should be of potential use. For wider-ranging applications in catalysis and sensing, more robust MOFs based on harder metal ions [e.g., Al(III), Zr(IV)] should offer the advantage of better stability compared with ASMOF-5.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental methods and additional data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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