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Communication

Discovery of Polyoxo-Noble-Metalate-Based Metal-Organic Frameworks

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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.8b13397 • Publication Date (Web): 02 Feb 2019

Downloaded from http://pubs.acs.org on February 2, 2019

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Discovery of Polyoxo-Noble-Metalate-Based Metal-Organic Frameworks

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*Supporting Information

ABSTRACT: Here we report on the synthesis, structure and characterization of the first example of a polyoxo-noble-metalatebased organic framework. This novel class of materials comprises discrete polyoxo-13-palladate(II) (POP) nanocubes $[Pd_{13}O_8(AsO_4)_8H_6]^{8-}$ decorated by four Ba²⁺ ions on each of two opposite faces. These secondary building units (SBUs) are linked to each other via rigid linear organic groups, resulting in a stable 3D polyoxopalladate-metal organic framework (POP-MOF). This novel material exhibits interesting sorption properties as well as catalytic activity.

Polyoxometalates (POMs) are a unique class of discrete, anionic metal oxides, which are generally constructed by early dblock elements such as tungsten, molybdenum, and vanadium in high oxidation states (+4, +5, +6).^[1] POMs are good prospects in the areas of catalysis, molecular electronics, magnetism, and biomedicine due to their unique structural/compositional variety and high thermal stability, combined with the ability to undergo multielectron redox transformations under mild conditions.^[2] Noble metals, such as palladium have shown immense promise as catalysts for many industrially relevant chemical processes.^[3] In 2008 Kortz's group discovered the first polyoxopalladate (POP) and by now >70 members are known.^[4a] POPs are discrete polyanions comprising exclusively Pd²⁺ addenda with external heterogroups (e.g. AsO_4^{3-} , PO_4^{3-} , SeO_3^{2-}) have triggered immense interest among researchers worldwide due to their structural and compositional novelty, stability in solution and applicability as noble metal-based catalysts.^[4]

POPs can be mainly subdivided in two structural categories: the nanocube $[MPd_{12}O_{32}L_8]^{n-}$ and the nanostar $[MPd_{15}O_{40}L_{10}]^{n-}$ (M = central Pd or guest metal ion, L = heterogroup cap).^[4a,5] Recent findings illustrate the structural tuning of these POPs that are accompanied by changes in the central guest ion M,^[5d,6] as well as the ability to synthesize mixed noble metal POPs.^[7] POPs exhibit immense potential as homogeneous catalysts in the oxidation of alcohols, hydrogenation of olefins and water oxidation.^[4a,5a,8,9] In spite of this, the applicability of these materials is hampered by

their low surface areas, catalytic leaching and poor recyclability due to their high solubility.

MOFs are an important class of materials that are characterized by ordered periodic networks of molecular components (metal ions or clusters) that are interconnected in three dimensions by organic linkers leading to stable framework structures with accessible cavities or pores.^[10] The tunable nature of MOFs have made them promising candidate materials for use in the areas of heterogeneous catalysis, gas storage and separation, drug delivery etc.^[10] Some MOFs have been reported containing conventional heteropolytungstates or –molybdates in the cavities.^[11]

Based on all of the above, we decided to synthesize stable heterogeneous MOF-type catalysts by using POPs as secondary building units (SBUs). In this work, we have successfully isolated for the first time a stable POP-based MOF material (POP-MOF), $[Pd_{13}Ba_8O_8(CPA)_8](NO_3)_2 \cdot 3NaCH_3COO \cdot 2NaNO_3 \cdot 70H_2O$ (**JUB-1**, CPA = *p*-carboxyphenylarsonate) that exhibits interesting sorption properties and heterogeneous catalytic activity in microwave assisted Suzuki-Miyaura C – C coupling reactions.



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Figure 1. (a) The polyoxo-13-palladate nanocube $[Pd_{13}O_8(AsO_4)_8H_6]^{8-}$ ($Pd_{13}As_8)^{[4b]}$ (b) Use of *p*-carboxyphenyl-arsonic acid (CPA) as capping group allows to construct an externally functionalized nanocube, $[Pd_{13}O_8(CPA)_8]^{14-}$ ($Pd_{13}(CPA)_8$), which can act as SBU for the construction of 3D MOF-type architectures (this work).

Cuboid-type POPs, such as the first member ever discovered, $[Pd_{13}O_8(AsO_4)_8H_6]^{8-}$ (Pd₁₃As₈),^[4b] comprise a central Pd²⁺ ion surrounded by a distorted cuboctahedral Pd₁₂ cluster, which is capped by eight arsonate groups forming a distorted cubic shell. Thus, the POP nanocubes have eight latent points of extension in three-dimensional space through the arsonate caps (Figure 1a). Therefore, we envisaged that if we could make use of this fact and connect Pd₁₃As₈ with rigid linear organic linkers such as *p*carboxyphenyl-arsonate ((OOC-C₆H₄-AsO₃)³⁻, CPA), wherein the arsonate group would cap the eight corners of the 13-palladate cube and the carboxyl group in the *para* position would coordinate with other metal ions, we might be able to isolate an eight-connected 3D open framework (Figure 1b).

In this endeavor, we synthesized CPAH₃ using a modified procedure (see ESI) $^{[12]}$ and reacted it with $Pd(OAc)_2$ in a sodium acetate solution (0.5 M, pH 7) at 50 °C, maintaining the pH at \sim 8.2 in-between with aq. NaOH and subsequently layering the resulting solution with aq. Ba(NO₃)₂ solution. After a few days, red block crystals of JUB-1 were isolated, which were washed with cold water and acetonitrile and air dried (~55% yield based on Pd). Single crystal X-ray diffraction revealed that the asymmetric unit of JUB-1 is made up of five crystallographically distinct Pd^{2+} ions, two CPA^{3-} moieties, two Ba^{2+} ions and two μ_4 -O atoms, which leads to a cationic framework $[Pd_{13}Ba_8(\mu_4 O_{8}(CPA)_{8}^{2+}$ (Figures 2 and S1), the charge being balanced by two extra-framework nitrate anions (as calculated from elemental analysis). The twelve outer Pd2+ ions of each nanocube possess the expected square-planar coordination geometry, being bridged by two μ_4 -O²⁻ ions and two oxygens of the arsonate group of CPA³⁻, resulting in a distorted cuboctahedral arrangement with the vertices of the cuboctahedron occupied by the twelve Pd²⁺ ions (Pd - O = 1.965(6) - 2.060(6) Å) (Table S1). The center of the cuboctahedron is occupied by a Pd²⁺ ion that is coordinated to eight μ_4 -O²⁻ ions (Pd – O = 2.329(6) – 2.380(6) Å), consistent with earlier work.^[5b] The cuboctahedron is further capped by eight arsonate groups belonging to eight CPA³⁻ ions resulting in a distorted cube (with arsonates as the vertices) that encapsulates the distorted cuboctahedron (Figure S2). One of the pairs of opposite faces of the outer distorted cube is decorated by tetranuclear $(Ba^{2+})_4$ clusters that are connected to the cube through coordination of the Ba²⁺ ions with oxygens of two adjacent arsonate groups (Figure 2a). The Ba²⁺ ions are joined to each other through μ_2 -H₂O and μ_2 -O of the carboxylate group of the CPA3- anion to form a cyclic tetranuclear cluster (Ba - O = 2.676(7) - 2.957(7) Å) (Figure S3). Thus, the composite {Pd₁₃As₈Ba₈O₆₈} unit can be considered to be an 8-connected SBU with 16 points of extension (hexadecahedron) (Figure 2a),



which is further connected to eight other such units by the CPA³⁻ linkers (Figure 2b) to form a 3D cationic open framework with channels along the crystallographic 'a' direction (Figure 2c) that accommodate the nitrate counter anions and guest molecules. The channels are ~1.2 nm in diameter. The overall structure of **JUB-1** can be visualized as a body-centered cubic (*bcc*) arrangement (Figure 2d).

Powder X-ray diffraction studies (PXRD) on the as-synthesized **JUB-1** indicated that the bulk material obtained was phase-pure as it matched with the simulated PXRD pattern (as obtained from Mercury software version 3.8), (Figure S4). Upon dehydration of

Figure 2. (a) (left figure) The POP nanocubes in **JUB-1** connected to two pairs of tetranuclear Ba²⁺ clusters on opposite faces (Ba = orange balls, arsonate caps = green balls, oxygen = red balls). The overall SBU can be visualized as a hexadecahedron (right figure) (b) The SBU connected to eight other SBUs through the CPA³⁻ anions. (c) The 3D structure of **JUB-1** showing channels along the crystallographic 'a' direction. d) The *bcc* topological framework in **JUB-1**.

JUB-1 by heating at 50 °C in vacuo for 4-5 hours, it was observed from the PXRD pattern that there is partial loss of crystallinity and the reflections become broader and shift towards higher angles. This can be correlated with the loss of water molecules from the pores, thereby leading to a disruption in the long range order. Upon rehydration in an atmosphere of water vapor at room temperature, JUB-1 regains its crystallinity and pore structure as the initial PXRD pattern is regained (Figure S4). Thermogravimetric analysis (TGA) studies reiterated the observations of the PXRD analysis. The TGA curve of the assynthesized JUB-1 indicated an initial weight loss of ~20% that corresponds to the loss of the 70 crystal waters (calc. ~19.8%) (Figure S5). The dehydrated JUB-1, although retaining the overall decomposition characteristics, did not exhibit the initial weight loss in its TGA curve (Figure S6). Upon rehydration, the initial shape of the TGA curve is regained demonstrating the facile nature of the dehydration-rehydration behavior of the material.

Inspired by these observations, we performed N₂, CO₂ and solvent vapor (H₂O, MeOH and EtOH) sorption studies on the dehydrated **JUB-1** at 77, 195 and 298 K, respectively. However, no N₂ or CO₂ uptake was observed, suggesting that activated **JUB-1** is non porous towards the two gases in the applied pressure range (ESI, Figure S7). Water vapor sorption exhibits a negligible water uptake until a partial pressure of 0.5 beyond which there is significant uptake of water vapor (~1000 mL/g at p/p₀ = 0.95) (Figure 3a). This indicates that the pores, which collapse after dehydration, open up at partial pressures of ~0.5 of water vapor leading to an increased adsorption at higher pressures.^[13] Methanol and ethanol sorption isotherms exhibit a

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Figure 3. (a) Water vapor adsorption-desorption isotherm of JUB-1 at 298 K. (b) Methanol and ethanol vapor adsorption-desorption isotherms of JUB-1 at 298 K (the closed and open symbols indicate adsorption and desorption, respectively).

similar increase in uptake at around relative humidity of 50-60% (Figure 3b) and at a relative humidity of 95% both exhibit similar total uptake (~130 mL/g). Significantly higher uptake value for water vapor as compared to methanol or ethanol vapors could be correlated to the higher polarity of water as compared to the alcohols. Thus, the combination of PXRD and sorption results alludes to the flexibility of the structure of **JUB-1**, which can be considered to be a soft porous crystal.^[13h]

Pd2+-based salts or complexes and Pd2+/Pd0 supported on porous matrices have been extensively utilized in recent years as homogeneous and heterogeneous catalysts, respectively, for C-C coupling reactions.^[14] Having made a MOF purely based on Pd²⁺ oxo-clusters as the SBU (JUB-1), we endeavored to investigate the heterogeneous catalytic activity in the Suzuki-Miyaura cross coupling reaction. In a typical reaction, an oven-dried microwave reaction vessel was charged with the aryl halide (0.5 mmol, limiting reagent), phenylboronic acid (0.75 mmol), anhydrous K₂CO₃ (1.5 mmol), dehydrated JUB-1 (2 mol% Pd basis), dry DMF (3mL) and dry MeOH (1mL). The vessel was purged with N₂ for a few minutes, sealed and heated in a microwave reactor at 100 °C (~100 W) for 1.5 h (see ESI Tables S4 and S5 for the optimization of the catalysis conditions). JUB-1 was found to be active as catalyst only in the presence of polar protic solvents. such as DMF, MeOH and EtOH (ESI). This observation can be correlated to the PXRD and sorption studies, wherein polar protic solvents were found to regenerate the porous crystalline nature of JUB-1. With bromobenzene as the model substrate, quantitative conversions were observed from GC analysis after 90 mins without indicating any leaching in the hot filtration experiment (Figure S8a). The UV-visible spectrum of the filtrate after catalysis did not show any peaks corresponding to Pd²⁺ ions in solution, hence indicating negligible leaching if any (Figure S9a).

Also, an ICP-MS analysis on the filtrate after catalysis revealed a Pd content of only ~0.5 ppm, which further indicates that leaching is negligible (ESI). Further, an elemental analysis (Pd, Ba and As) of JUB-1 after catalysis indicated a Pd : As : Ba molar ratio of 13 : 8.4 : 8.2, which is consistent with the molecular formula of JUB-1 (ESI). The catalyst JUB-1 also exhibited recyclability with no significant loss in activity over four reaction cycles (Figure S9b). Following this, various substituted bromo- and chlorobenzenes were utilized as substrates along with phenylboronic acid to study the scope of JUB-1 as a catalyst (Table S6). High conversions $(\sim 88 - 100\%)$ were observed for bromobenzenes, with those functionalized with electron-withdrawing groups exhibiting higher yields, as expected.^[14a] For the substituted chlorobenzenes, comparatively lower yields were observed since the activation of C-Cl bonds is more difficult than C-Br bonds.^[14a] However, a quantitative yield was observed for the nitro-substituted chlorobenzene (Figures S10). The catalyst was also found to be stable as observed from PXRD, IR, XPS and TEM analysis of the catalyst after the catalysis (Figures S4, S11, S12 and S13). The catalytic activity was found to be comparable to other known Pdbased catalysts under microwave conditions (ESI Table S7). However, JUB-1 being a palladium-oxo cluster-based MOF has the advantage over other reported catalysts of not requiring additional support matrices in order to act as a heterogeneous catalyst. Since Suzuki-Miyaura cross-coupling reaction involves Pd(0) as the catalytically active site,^[15a] we propose a mechanism involving in situ partial reduction of the polypalladate moiety of JUB-1 under the catalytic conditions (ESI Figure S14). MeOH has been known to reduce Pd²⁺ to Pd(0) at high temperatures.^[15b] This was confirmed by XPS studies on JUB-1 catalyst, which indicated a partial reduction of the palladate moieties when the catalyst, after catalysis, was isolated and dried under vacuum. Upon re-exposure to air, the reduced Pd centers are re-oxidized (see XPS, ESI Figure S12). We envisage that JUB-1 is stable enough to such partial oxidation-reductions (see PXRD, Figure S4). Similar mechanistic observations have been reported before.^[15c-e] Thus, JUB-1 could be considered as an efficient precatalyst in the Suzuki-Miyaura cross coupling reaction.^[15c,f,g]

In conclusion, we have isolated the first polyoxo-noblemetalate-based MOF, with the discrete, cuboid polyoxopalladate (POP) Pd₁₃ as key building block (SBU). To date, the number of MOFs based on noble metals (e.g. Pd) is very small, which highlights the importance of our work.^[16] This work represents the discovery of a fundamentally novel class of materials that paves the way for the full utilization of the entire class of discrete polyoxopalladates (POPs), as well as polyoxoaurates, of different shape, size, and composition,^[4-7] as building blocks for stable 3D framework materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: . X-ray crystallographic file in CIF format for **JUB-1** (CIF) Synthetic methods, TGA analysis, PXRD, IR spectra, XPS spectra, TEM studies and the catalytic studies for **JUB-1** (PDF)

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The authors declare no competing financial interests.

ACKNOWLEDGMENT

U.K. thanks the German Research Council (DFG, KO-2288/26-1), Jacobs University, and CMST COST Action CM1203 (PoCheMoN) for support. D.T. and M.W. thank the German Research Council (DFG) for financial support for the X-ray diffraction setup (INST 1841154-1FUGG). Figures 1 and 2 were generated by Diamond, Version 3.2 (copyright Crystal Impact GbR).

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