JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
Cite This: J. Am. Chem. Soc. 2019, 141, 3385−3389
pubs.acs.org/JACS

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

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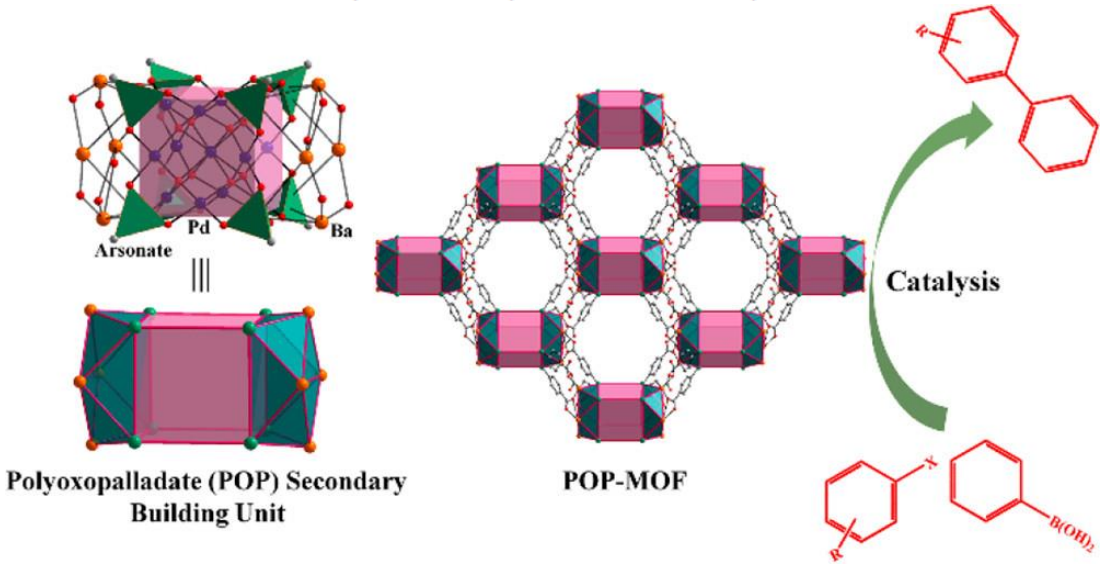

Received: December 15, 2018
Published: February 2, 2019

Jayoti Roy
13-04-2019

In this paper

- CPA^{3-}, p-carboxyphenyl-arsonate capped polyoxopalladate (POP) based metal-organic Framework (MOF) is synthesized.

- $\{Pd_{13}As_8Ba_8O_{68}\}$ unit of cubic-type POP is used as a secondary building units (SBUs) during synthesis of stable MOF.

- This SBUs is connected to eight other such units by the CPA^{3-} linkers to form a 3D cationic open framework.
  The overall structure of $[Pd_{13}Ba_8O_8(CPA)_8](NO_3)_2 \cdot 3NaCH_3COO \cdot 2NaNO_3 \cdot 70H_2O$, JUB-1 is visualized as a body-centered cubic (bcc) arrangement.

- PXRD and sorption studies of JUB-1 is suggested the structural flexibility of MOF.

- JUB-1 is found to be active as the catalyst of Suzuki-Miyaura cross coupling reaction in the presence of polar protic solvent.

Relevance to our group

- Phosphine and thiol protected noble metal nanoclusters
- Atomically precise multimetallic nanoclusters
- Carboxylate, amine protected non noble metal nanoclusters
- Noble metal based metal-organic framework.

7504 *Inorg. Chem.* **2009**, *48*, 7504–7506
DOI: 10.1021/ic900953a

Inorganic Chemistry
Communication

Heteropoly-13-Palladates(II) $[Pd^{II}_{13}(As^{V}Ph)_8O_{32}]^{6-}$ and $[Pd^{II}_{13}Se^{IV}_8O_{32}]^{6-}$

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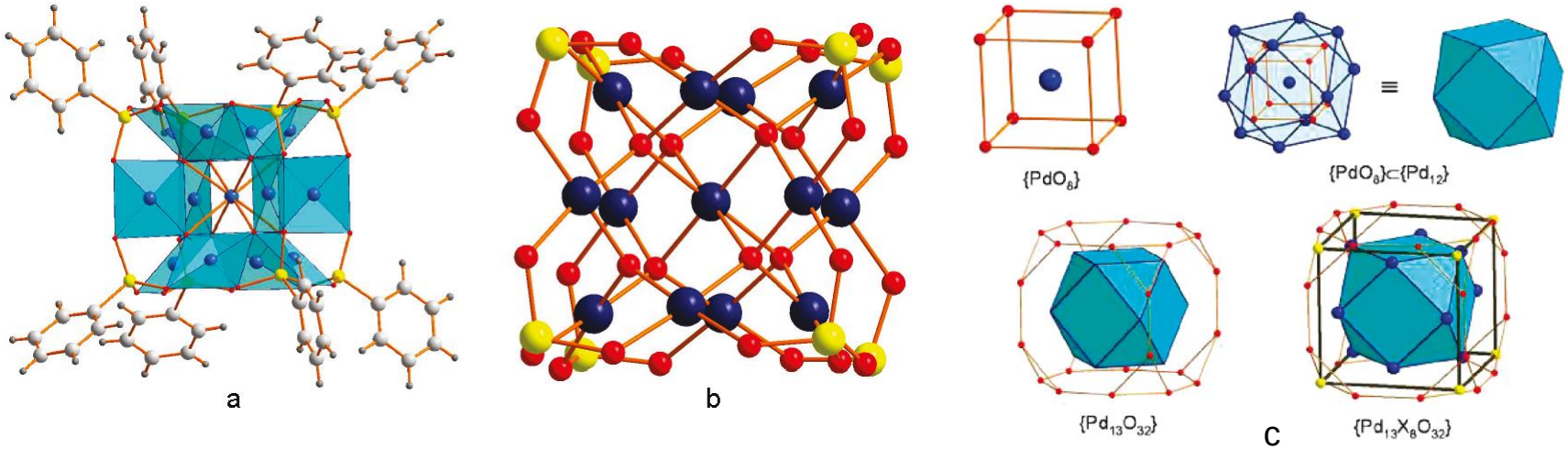


(a) Combined polyhedral/ball-and-stick representation of 1.
(b) Ball-and-stick structure of 2. Color code: Pd, blue; As and Se, yellow; O, red.

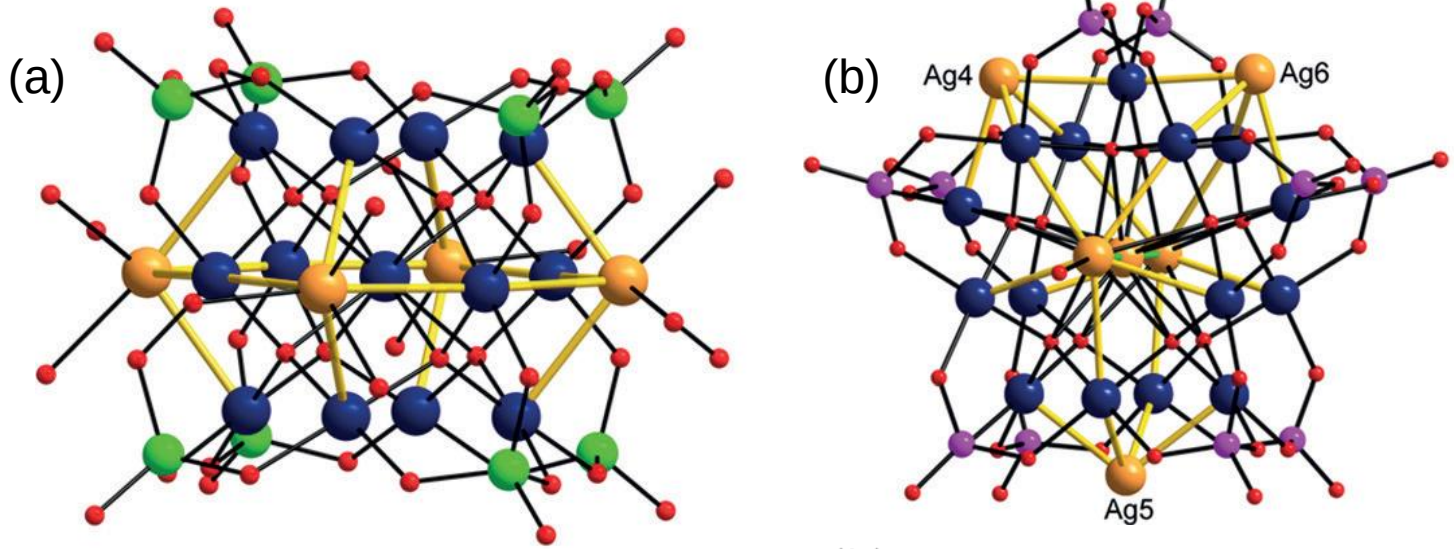
(c) Structural representation of 1 in terms of Platonic and Archimedean solids. Color code: Pd, blue; As, yellow; O, red.

Noble Metalates

International Edition: DOI: 10.1002/anie.201608122
German Edition: DOI: 10.1002/ange.201608122

Discrete Silver(I)-Palladium(II)-Oxo Nanoclusters, $\{Ag_4Pd_{13}\}$ and $\{Ag_5Pd_{15}\}$, and the Role of Metal–Metal Bonding Induced by Cation Confinement

Peng Yang, Yixian Xiang, Zhengguo Lin, Zhongling Lang, Pablo Jiménez-Lozano, Jorge J. Carbó, Josep M. Poblet, Linyuan Fan, Changwen Hu, and Ulrich Kortz**

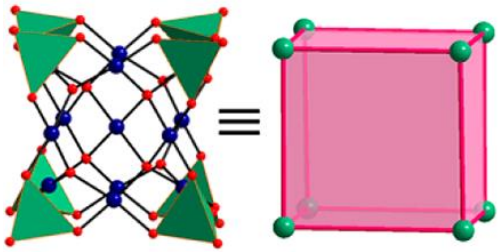


(a) Ball-and-stick representations of Ag_4Pd_{13} in side view Pd dark blue, Ag orange, As green, O red; Ag–Pd interaction, yellow bond

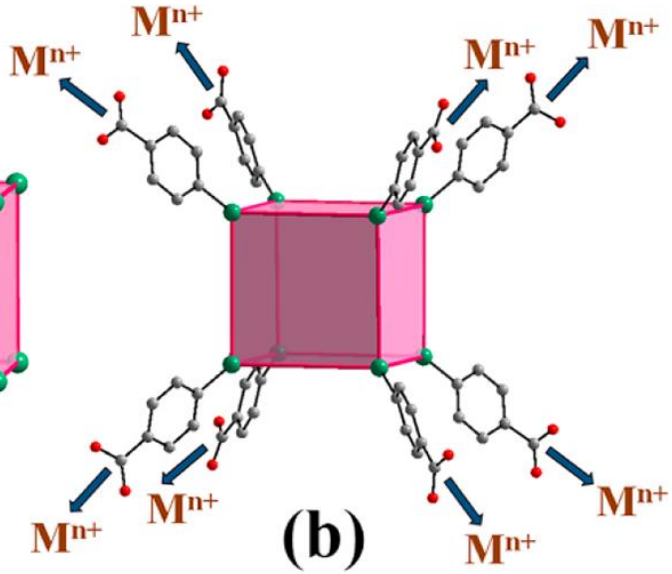
(b) Ball-and-stick representations of Ag_5Pd_{15} in top view Pd dark blue, Ag orange, P fuchsia, O red; Ag–Pd interaction, yellow bond; Ag–Ag interaction, green bond

Peng Yang *et al*., Angew. Chem. Int. Ed. 2016, 55, 15766 –15770

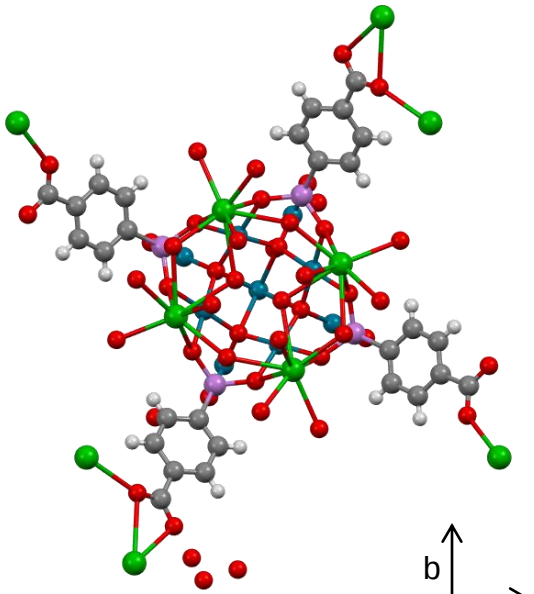
Structure of polyoxo-13-palladate nanocube



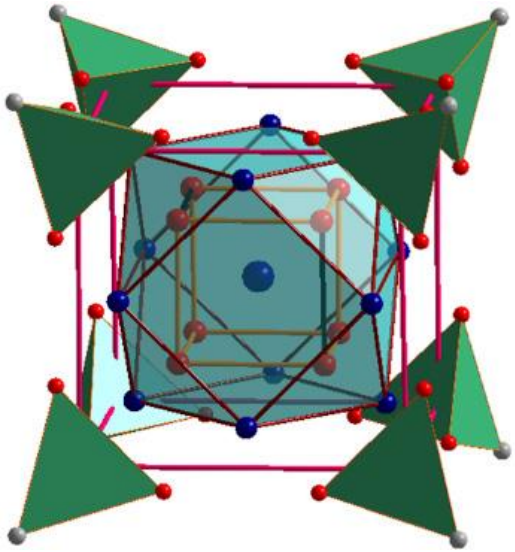
(a)



(b)



(C)



(d)

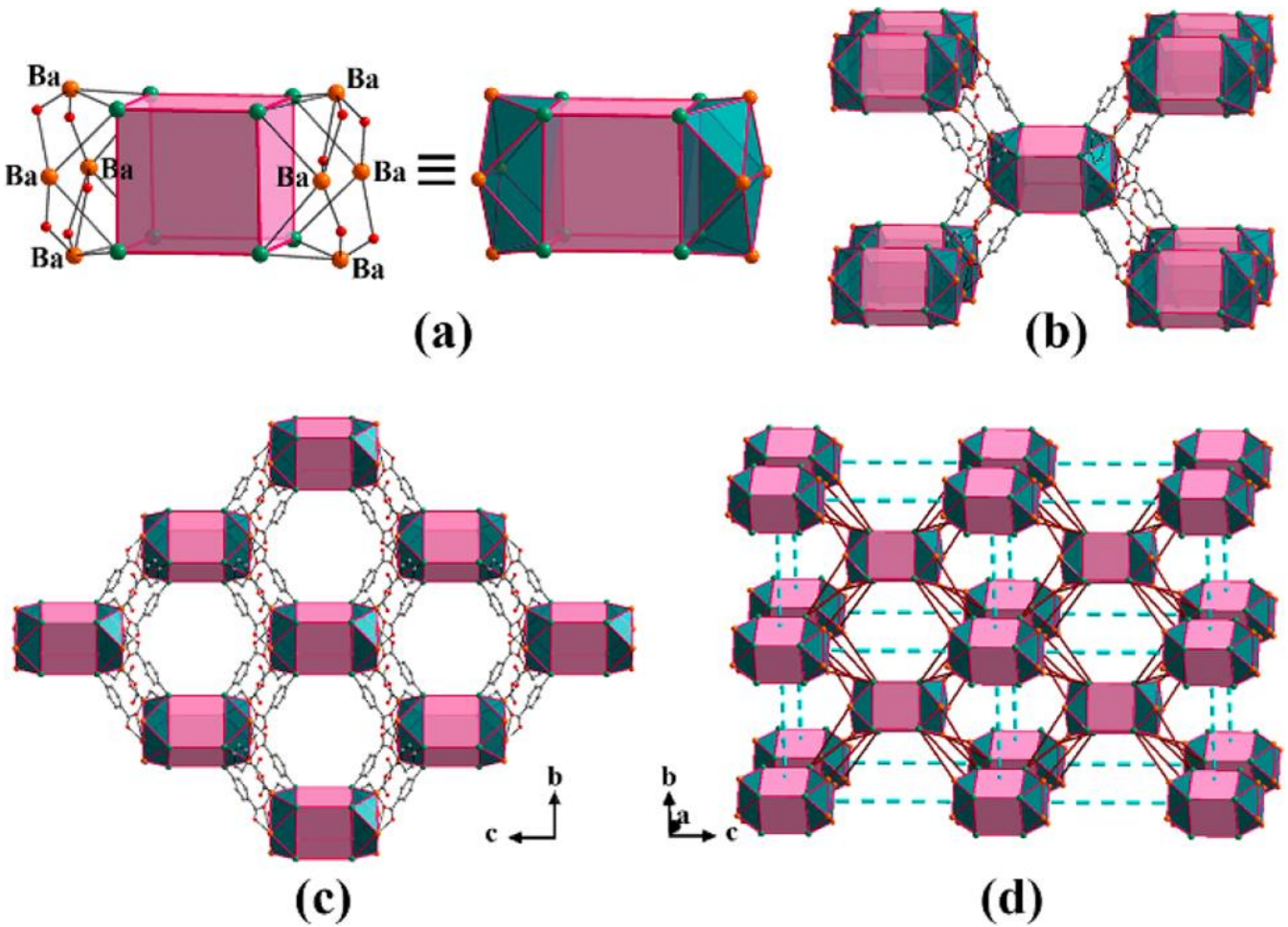
(a) Polyoxo-13-palladate nanocube $[Pd_{13}O_8(AsO_4)_8H_6]^{8-}$

(b) The use of p-carboxyphenyl-arsonic acid (CPA) as capping group allows constructing an externally functionalized nanocube, $[Pd_{13}O_8(CPA)_8]^{14-}$ ($Pd_{13}(CPA)_8$), which can act as an SBU for the construction of 3D MOF-type architectures

(c) Crystal structure of POP along c - direction.

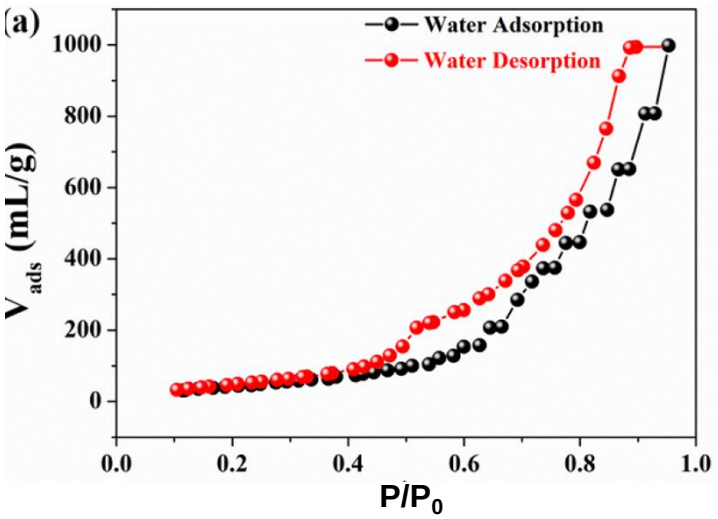
(d) The core building block of **JUB-1** comprises a central Pd^{II} ion surrounded by a O_8 cube, which in turn is encapsulated by a distorted Pd_{12} cuboctahedron, which is surrounded by a distorted cube of eight arsenate caps.

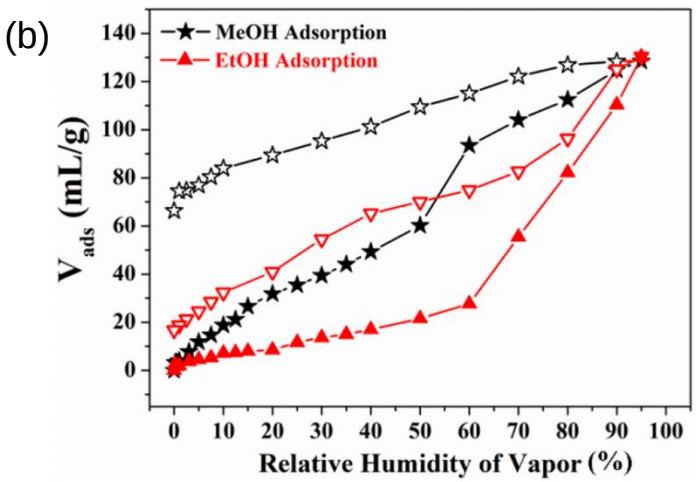
Structure of polyoxopalladate – metal-organic framework $[Pd_{13}Ba_8O_8(CPA)_8](NO_3)_2 \cdot 3NaCH_3COO \cdot 2NaNO_3 \cdot 70H_2O$, JUB-1



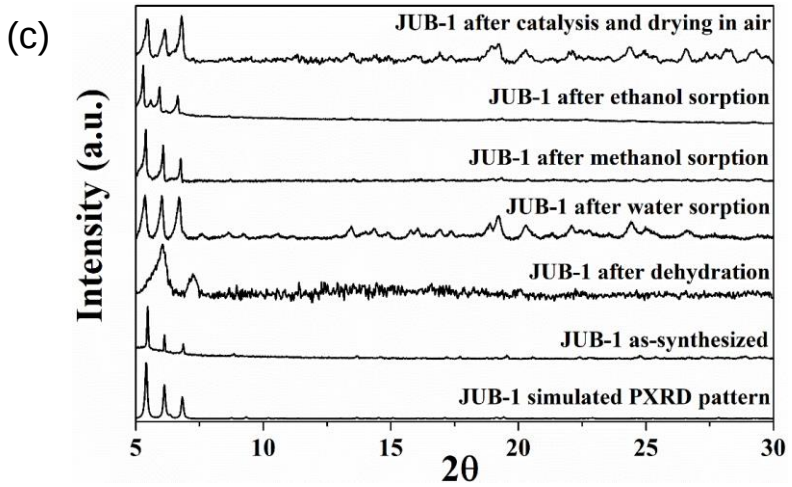
(a) (Left) POP nanocubes in JUB-1 connected to two pairs of tetranuclear Ba^{2+} clusters on opposite faces (Ba = orange balls, arsonate caps = green balls, oxygen = red balls). The overall SBU can be visualized as a hexadecahedron (right). (b) SBU connected to eight other SBUs through the CPA^{3-} anions.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

Flexibility of the structure of POP-MOF, (JUB-1)



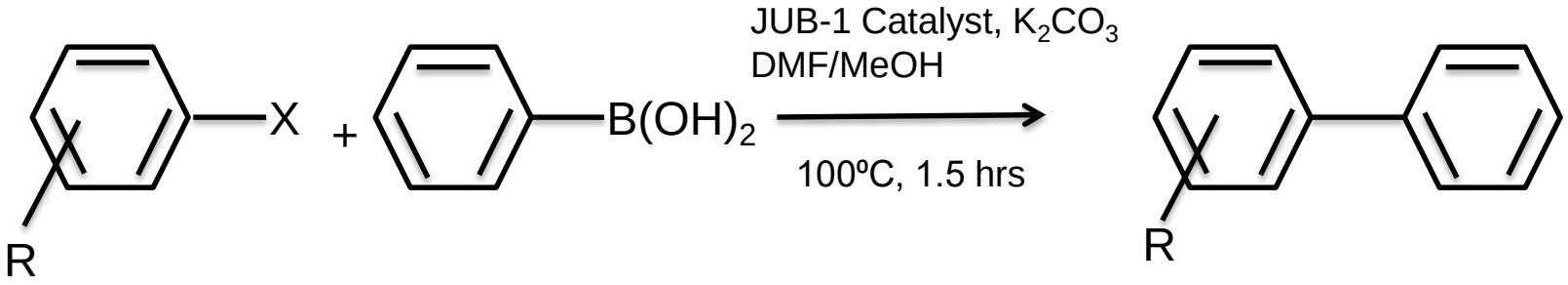


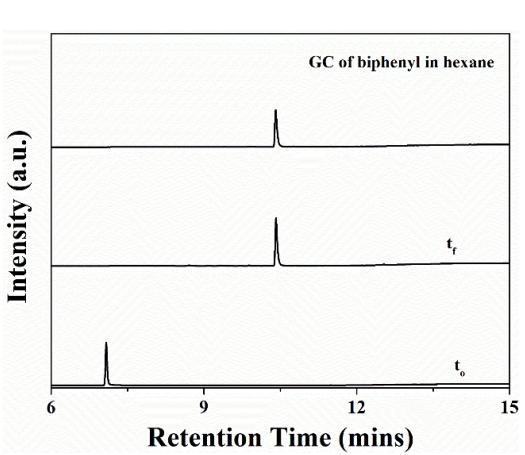
(a) Water vapor adsorption−desorption isotherm of JUB-1 at 298 K. (b) Methanol and ethanol vapor adsorption−desorption isotherms of JUB-1 at 298 K (the closed and open symbols indicate adsorption and desorption, respectively).

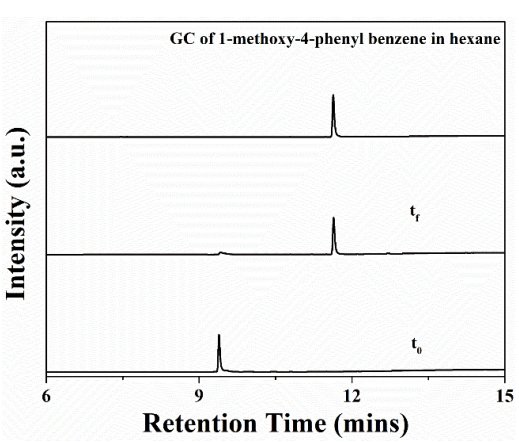


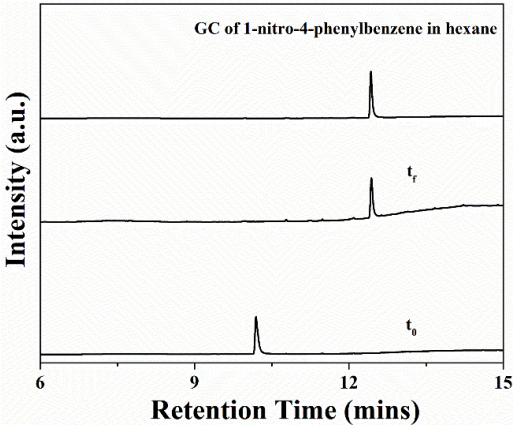
(c) Powder X-ray diffraction studies on **JUB-1**.

Suzuki-Miyaura cross coupling reaction of JUB-1



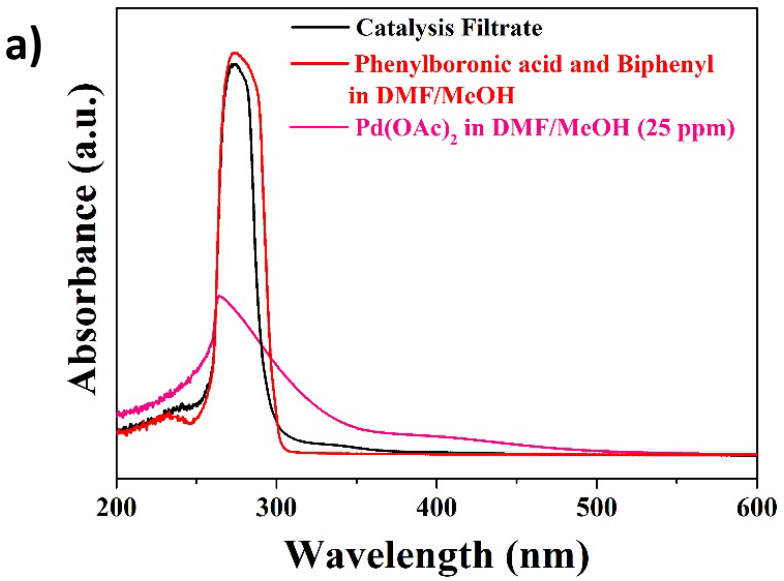


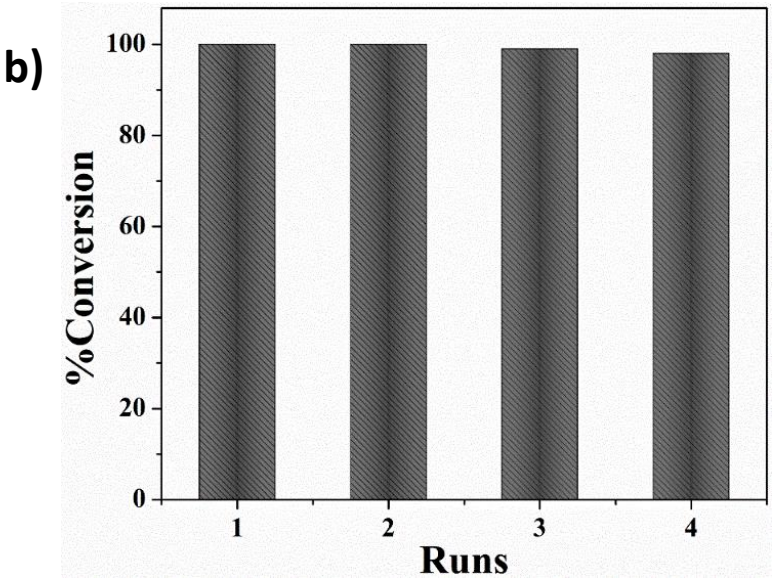




The GC spectra of the catalytic reaction (Reaction of (a) bromobenzene; (b) 4-nitrobromobenzene; (c) 4-bromoanisole; with phenyl boronic acid) without adding catalyst
(t_0 = initial aliquot and t_f = final aliquot after reaction)
as compared to the GC spectra of biphenyl derivetive product in hexane solvent.

Stability of polyoxopalladate – metal-organic framework (JUB-1)

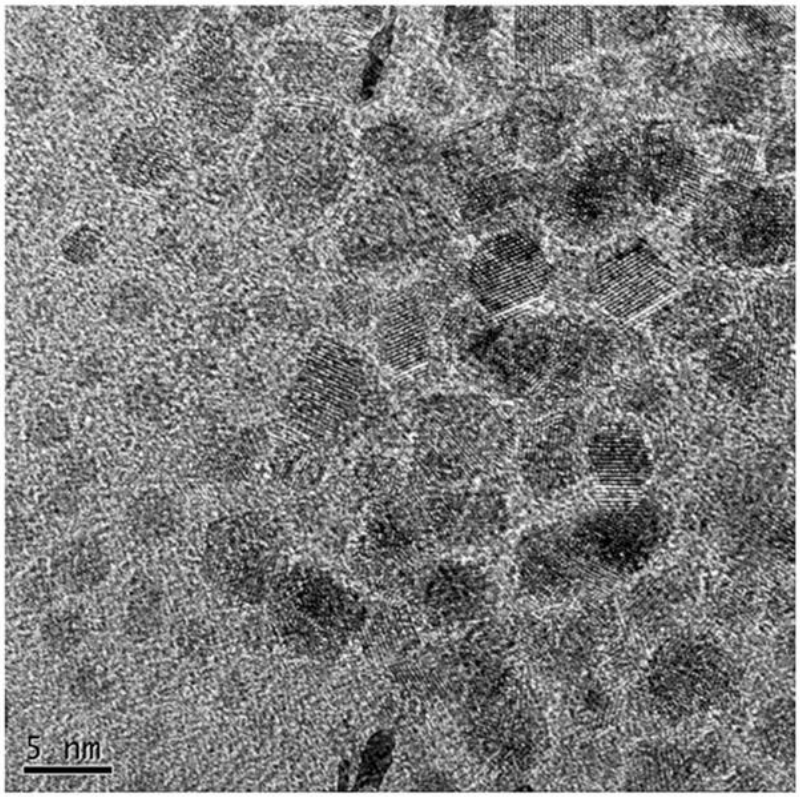


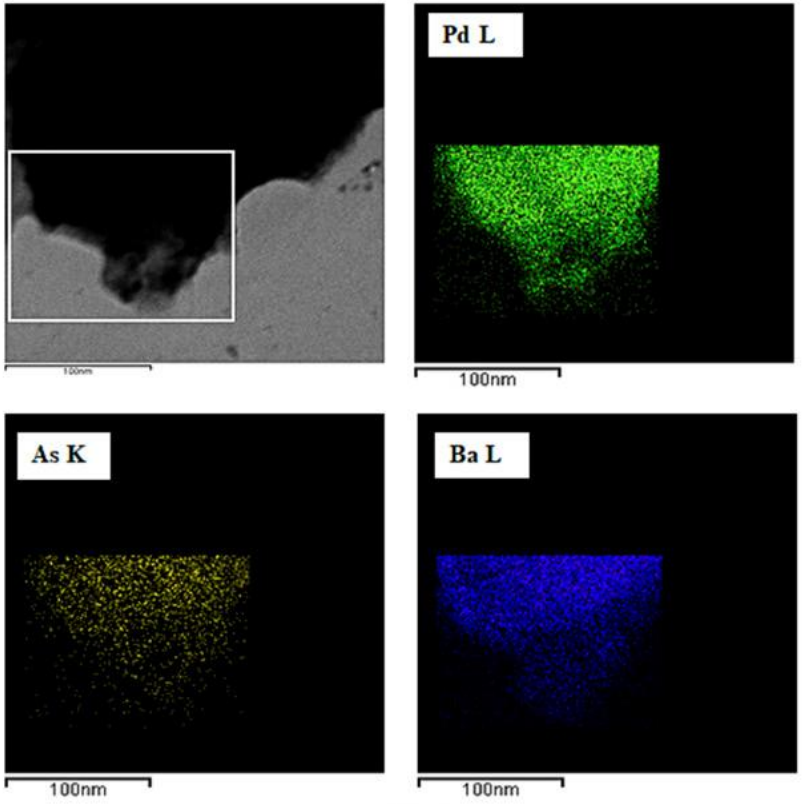


(a) UV-Visible spectra of the filtrate after catalysis (bromobenzene as substrate), phenylboronic acid and 4,4'-biphenyl in a solvent mixture of DMF/MeOH and $Pd(OAc)_2$ in a solvent mixture of DMF/MeOH.

(b) Figure depicts the recyclability of the **JUB-1** as a catalyst for the Suzuki-Miyaura coupling reaction

TEM study





(a) TEM image of **JUB-1** particles after catalysis, (b) EDX mapping of **JUB-1**. TEM images of **JUB-1** after catalysis show that nanoparticles of **JUB-1** are formed with particle sizes ranging from 4-5 nm.
The particles are uniformly shaped and the observation of lattice fringes indicates the crystalline nature of **JUB-1**. EDXA mapping indicates a uniform distribution of the elements (Pd, Ba and As).

Conclusion

- First example of polyoxo-palladate (POP) based metal-organic framework (MOF) with discrete, cuboid Pd_{13} as a key building block (SBU).
- JUB-1 is very small noble metal based MOFs.
- From PXRD and sorption results alludes to the flexibility of the structure of JUB-1, which can be considered to be as a permanently porous third generation coordination polymer and a soft porous crystal.
- JUB-1 is found to be active as the catalyst for Suzuki-Miyaura cross-coupling reaction in the presence of polar protic solvents, such as DMF, MeOH, EtOH.

Thank You