The balance between conductivity and electro-/photo- catalytic performance of guest-incorporated Metal-organic frameworks

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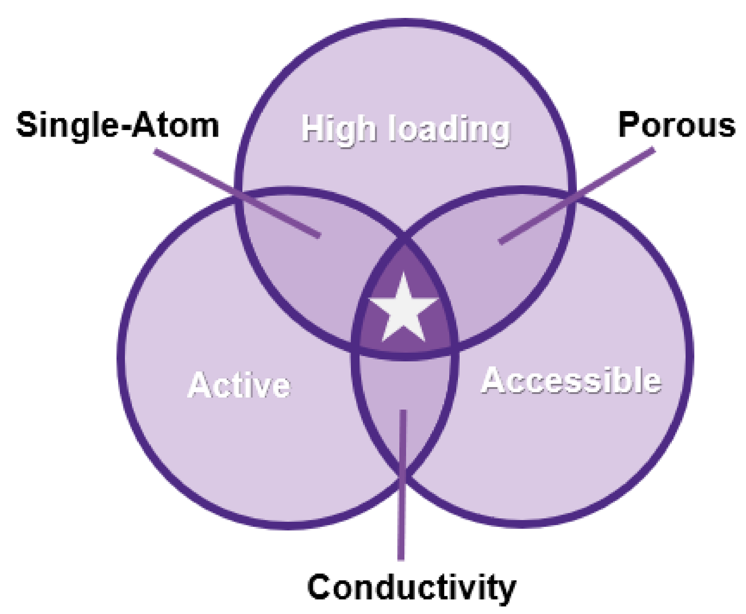
Abstract: The conductivity of porphyrin containing MOFs was enhanced by guest incorporation. After modification, the electrical conductivity and electrocatalytic performance were measured separately. Surprisingly , these MOFs do not require a significant conductivity to generate a noticeable enhancement in electrocatalytic performance. Post-metalization will be used in the future to investigate whether we can achieve the modulation of electrical conductivity and electrochemical performance.

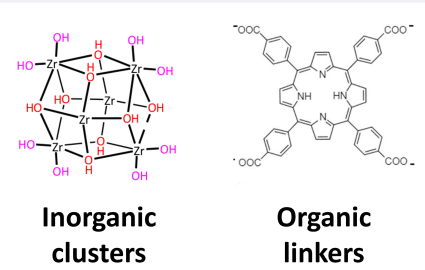
Introduction

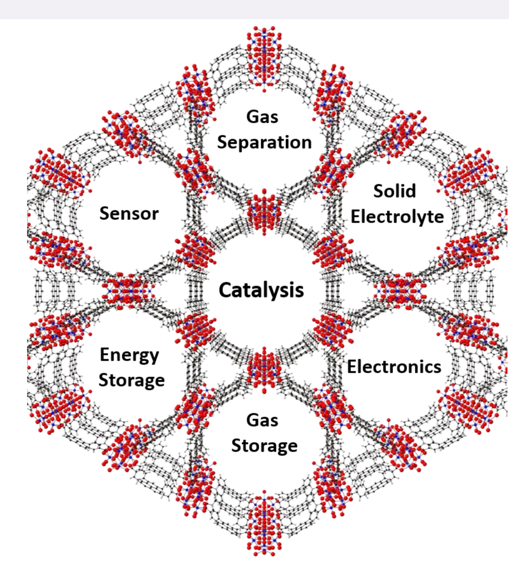


In searching for highly efficient electro-/photo- catalysts, we want to excel in the activity, active-site density (i.e. loading), and the accessibility. We want to not only take advantage of the recyclability of heterogeneous catalysts but also harvest the strength of high loading of active-sites in homogeneous catalysts. In addition, we want to have open space to access all exposed sites to obtain the greatest potential of a given system.

Advantages of Metal Organic Frameworks (MOFs)

- Porous
- Crystalline
- High surface area
- Tunable size/shapes
- Useful tools for fundamental studies
- Different post-synthetic modifications





Drawbacks of Using Pristine MOFs

Most MOFs suffer from their insulating nature when being considered as electrocatalysts

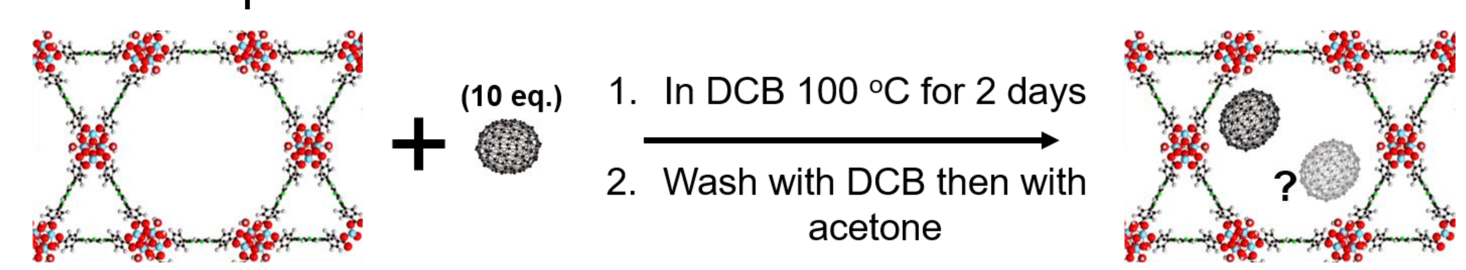
Material	Conductivity (S*cm^{-1})
Metal	> 10^3
Semiconductor	10^3 to 10^{-9}
Insulator (MOFs)	< 10^{-9}

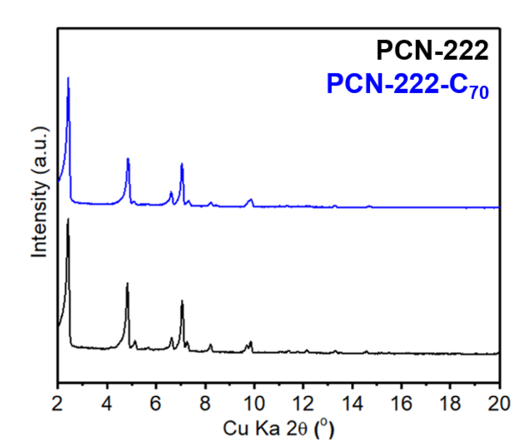
Therefore, many MOFs are used as only the support or being pyrolyzed to afford high catalyst loading and conductivity simultaneously. Herein, we aim to preserve the pristine MOF structure but improved its conductivity through host-guest interactions. However, the insulating nature of most MOFs makes us to ask two key questions:

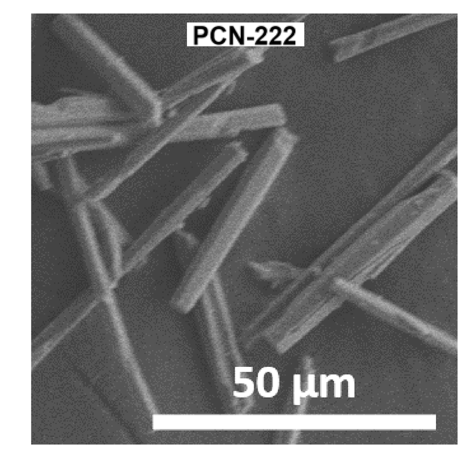
1. How conductive should the MOFs be before diffusion get in the way?
2. With slight increase in conductivity, can the electrocatalytic performance be improved more?

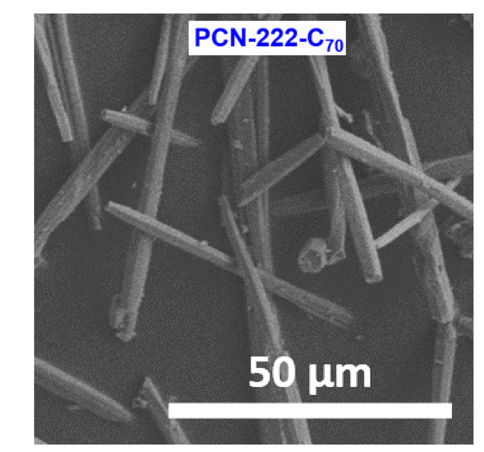
Guest Incorporated MOF

*Results not published

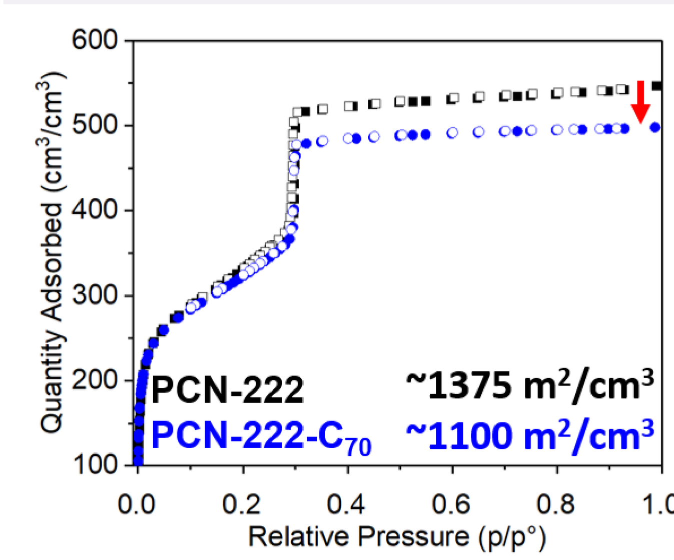


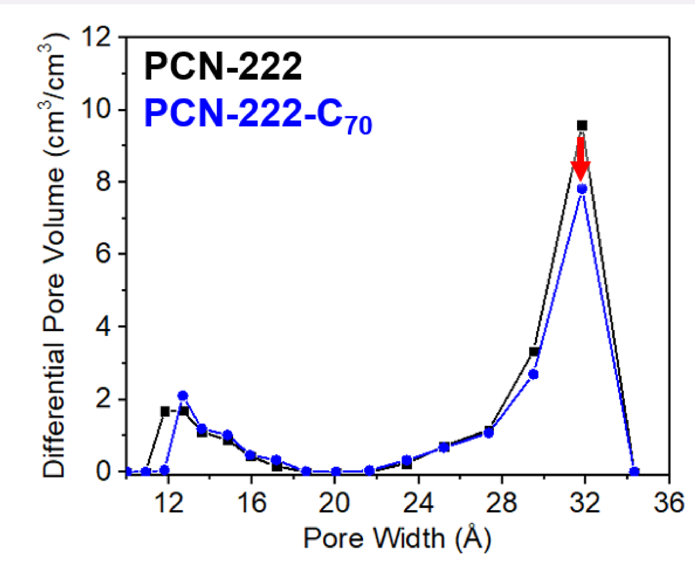




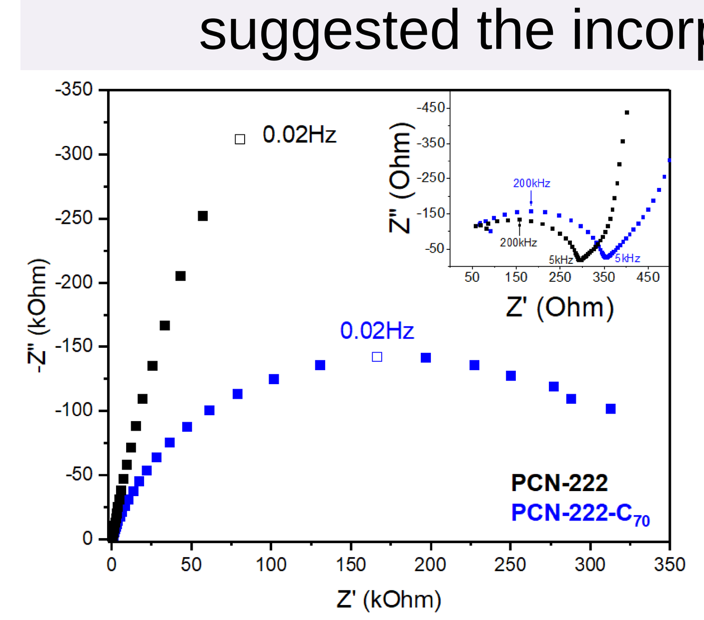


Powder X-Ray Diffraction (PXRD) and Scanning Electron Microscopy (SEM) images suggested preserved crystallinity and morphology respectively



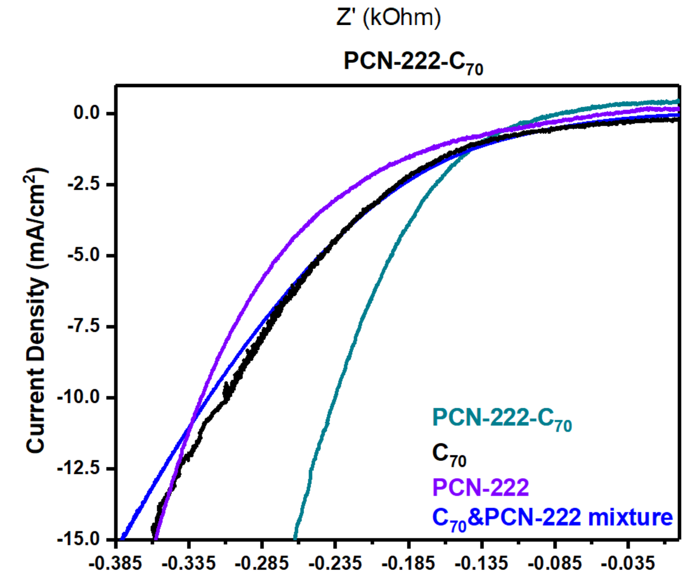


N_2 isotherm with decreased surface area and pore volume suggested the incorporation of guest molecules



Guest-incorporated sample demonstrates reduced charge-transfer resistance, suggesting increased conductivity

Electrolyte: 0.1 M TBAPF6 in DCM; Working: MOF-Modified FTO Electrode; Reference: Ag/AgCl sat. KCl; Counter: Pt

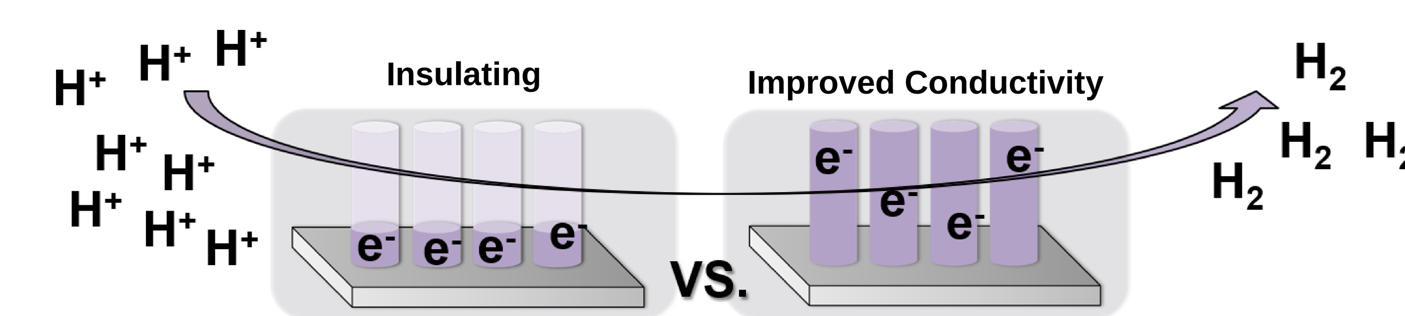


PCN-222-C_{70} out-performed the control samples, including C_{70}, PCN-222, and C_{70}&PCN-222 mixture

Deposition mixture: Sonicate the mixture of Nafion+MOF+IPA+H_2O then drop-cast on glassy carbon electrode; Counter: carbon; Measurement Conditions: 0.5 M H_2SO_4 , 1600 RPM, LSV: 2 mV/s

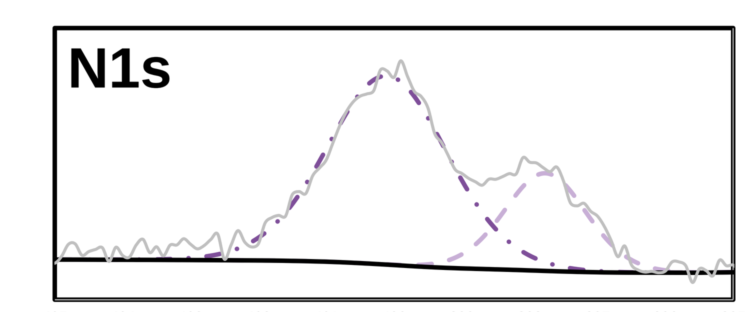
Conclusions

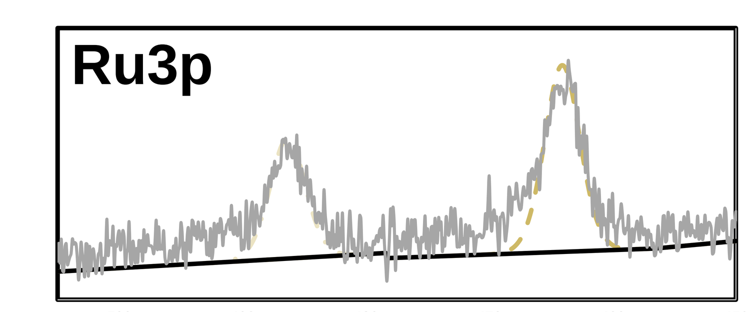
1. We can engender electronic conductivity in MOFs with retention of MOF porosity
2. The magnitude of MOF electronic conductivity can be engineered by changing the electron donors and acceptors
3. Increased conductivity boosts electrochemical performance



Future Directions

1. Acquire greater synthetic control for incorporating guests to the desired places suggested by the computational predictions
2. Metalize the porphyrin to fine tune conductivity
3. Functionalize the fullerene to fine tune conductivity
4. Compare the conductivities and electrochemical performance





Ru 3p peaks with binding energy of 464.08 eV and 496.35 eV suggests potential Ru-N interactions

References & Acknowledgements

1. Goswami, S. et al. Chem. Sci. 2018, 9, 4477-4481.

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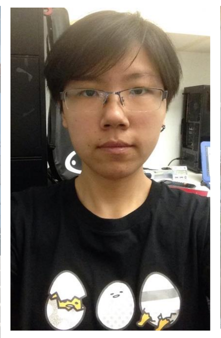

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