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Tunable Electrical Conductivity in Metal-Organic Framework Powders

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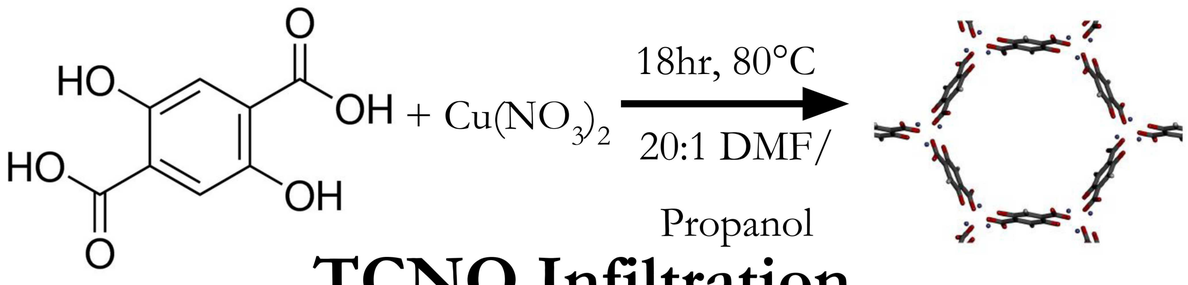
Background & Motivation

Developing novel semiconducting nanomaterials can lead to important advances in conformational electronics, reconfigurable electronics, and sensors. However, current inorganic semiconductors lack synthetic tunability, and semiconducting organic polymers lack in long range order and stability. Metal-organic frameworks (MOFs), a class of nanoporous, crystalline materials composed of organic linkers and metal nodes with synthetic tunability, long range order, and thermodynamic stability, can overcome the challenges perturbing inorganic and organic materials. Due to poor orbital overlap, MOFs are traditionally insulators. However, introduction of redox active guest molecules into the MOF pores can bridge the metal nodes of the MOF, resulting in semiconductivity.

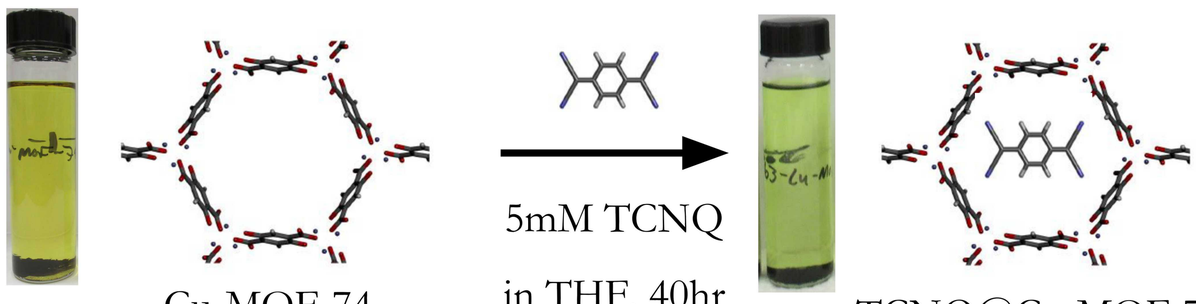
Hypothesis

Introduction of 7,7,8,8-tetracyanoquinodimethane (TCNQ), a conjugated redox active molecule, into Cu-MOF-74 may result in semiconducting behavior by coordinating to its copper nodes.

MOF Synthesis



TCNQ Infiltration



Structures adapted from Shiozawa *et al. Sci. Rep.* **2017**, *7*, 2439.

Conclusion

We synthesized and infiltrated Cu-MOF-74 with TCNQ. The resulting TCNQ@Cu-MOF-74 retained its structure after infiltration and produced conductivity of up to 2.19 x 10^{-3} S/m with a low activation energy of 1.3 meV. Future work includes infiltrating other MOFs, such as X-MOF-74 (X=Fe, Mn, Ni), NOTT-101, MOF-14, and PCN-777.

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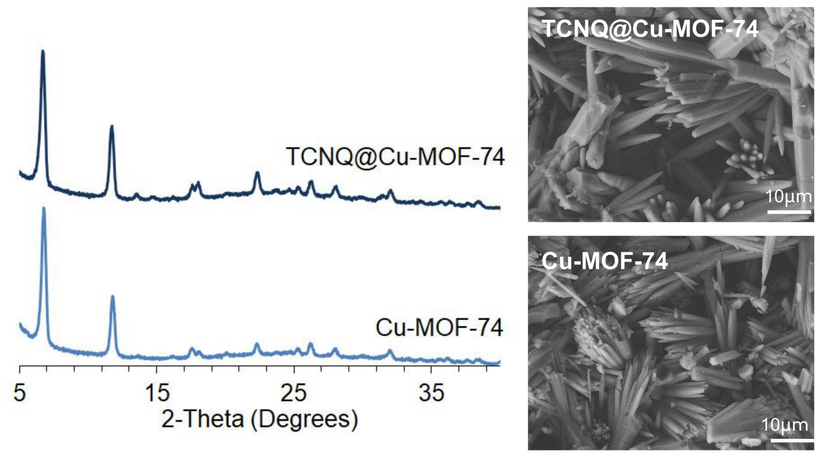
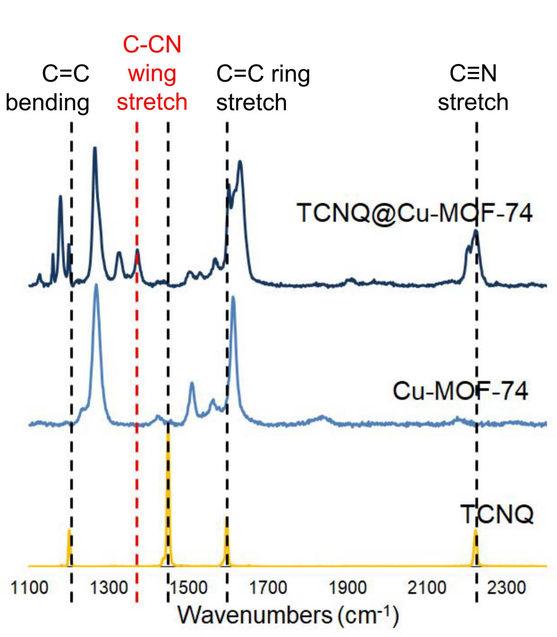
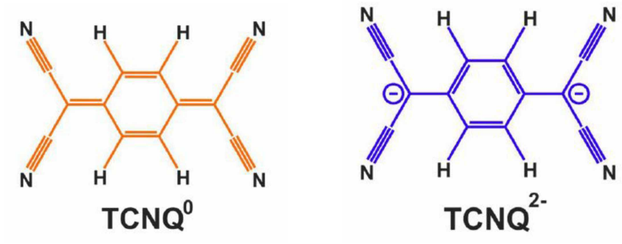
Structural Characterization



The data from powder x-ray diffraction (PXRD) and scanning electron microscopy (SEM) taken prior to and following TCNQ infiltration show the Cu-MOF-74 to have retained its structure.

Raman Spectroscopy

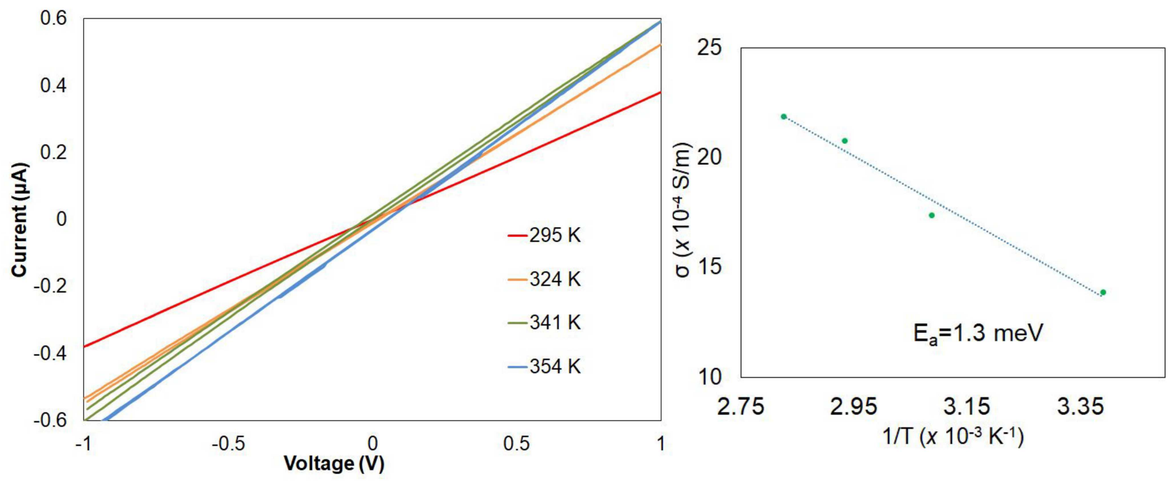




Structures adapted from Shiozawa *et al. Sci. Rep.* **2017**, *7*, 2439.

Raman scans indicate that the TCNQ is coordinating to the open copper sites. The redshift of the C-CN wing stretch and C=C stretch indicates a charge transfer between the copper and TCNQ. This implies orbital overlap, resulting in the semiconductivity of the MOF.

Conductivity Tests



TCNQ@Cu-MOF-74 powder was crushed into a pellet by 3 metric tons of pressure for 2 minutes. The resulting pellet underwent conductivity tests via the two point probe method. The results indicate a maximum conductivity of 2.19 x 10^{-3} S/m at 354 K and an activation energy of 1.3 meV.

TCNQ@Cu-MOF-74 pellet (d=1cm, h=0.0288mm)

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