



Doping of Metal-Organic Frameworks Towards Electronics

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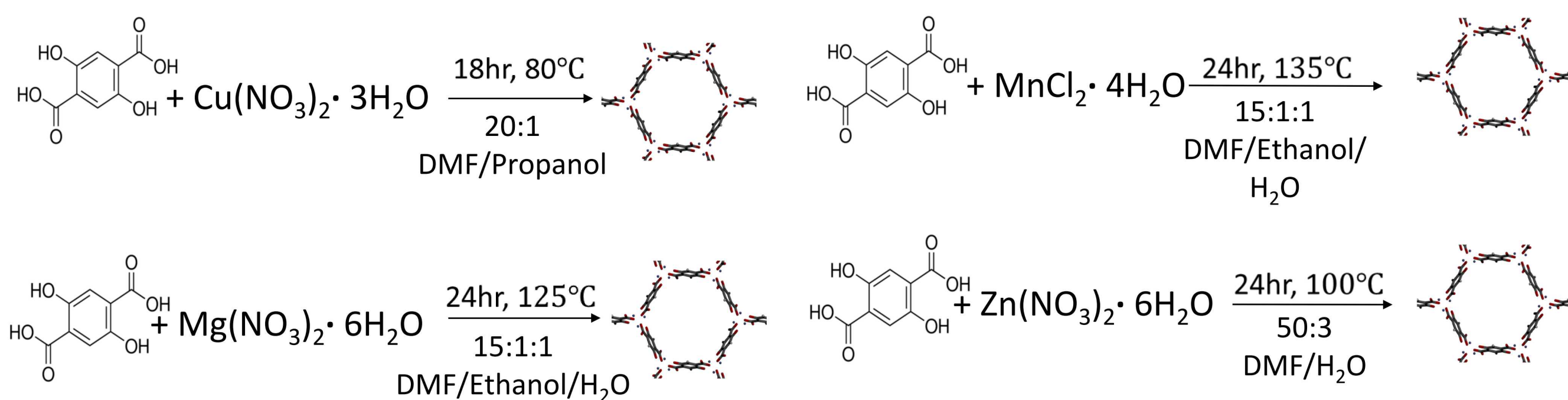
Background

Metal-organic frameworks (MOFs) are a class of nanoporous, crystalline materials composed of metal ions or clusters coordinated to multitopic organic linkers. 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 semiconductive behavior. Establishing novel semiconducting nanomaterials from MOFs could be implemented in a diverse array of electronic components, including electronic devices, reconfigurable electronics, and sensors.

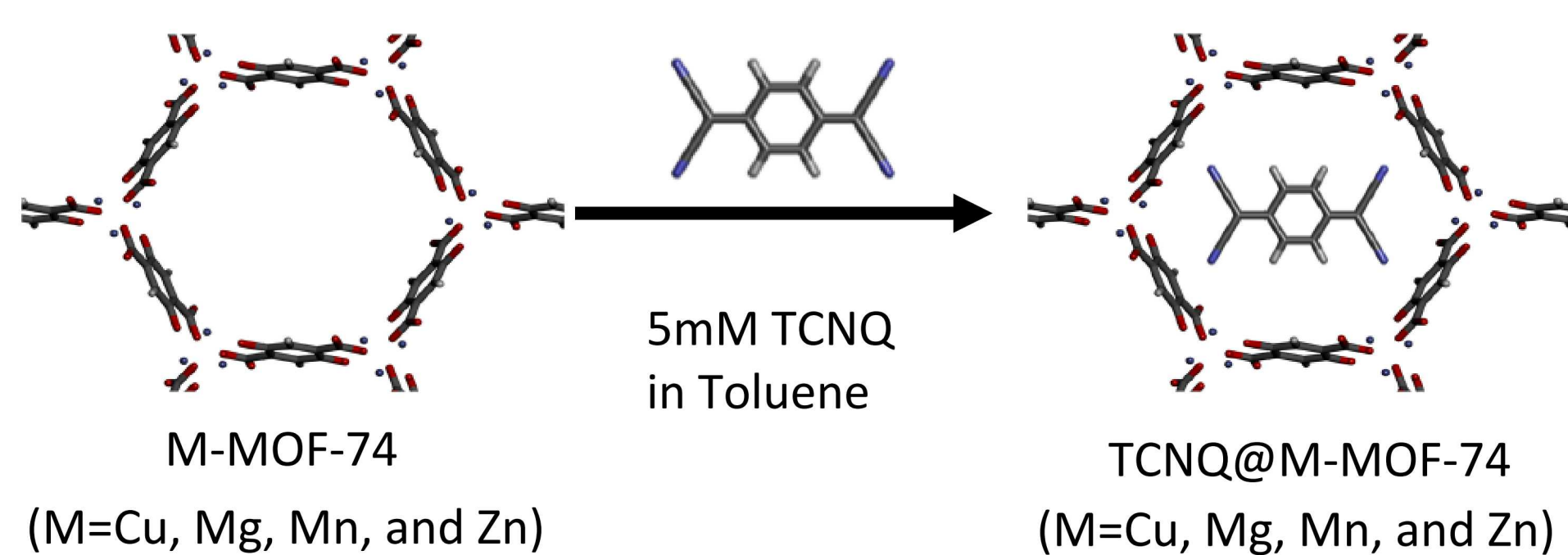
Hypothesis

Infiltration of 7, 7, 8, 8-tetracyanoquinodimethane (TCNQ), a conjugate redox-active guest molecules, into M-MOF-74s (M=Cu, Mg, Mn, Zn), may result in tunable electrical conductivity through coordination of TCNQ to the subunits of the metal nodes.

MOF Syntheses

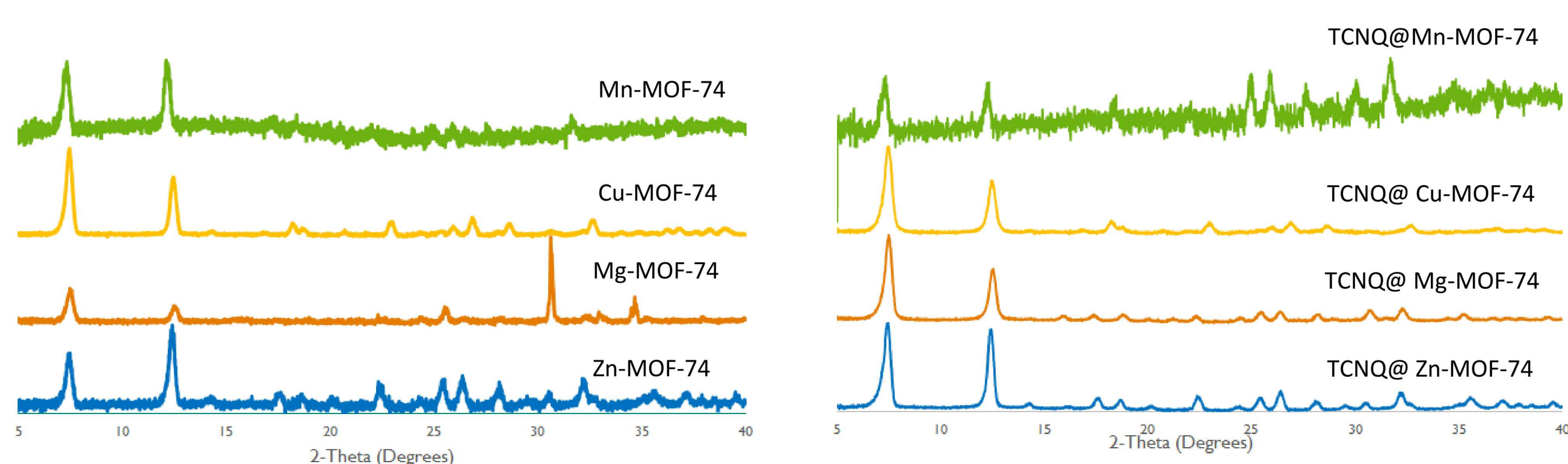


TCNQ Infiltration



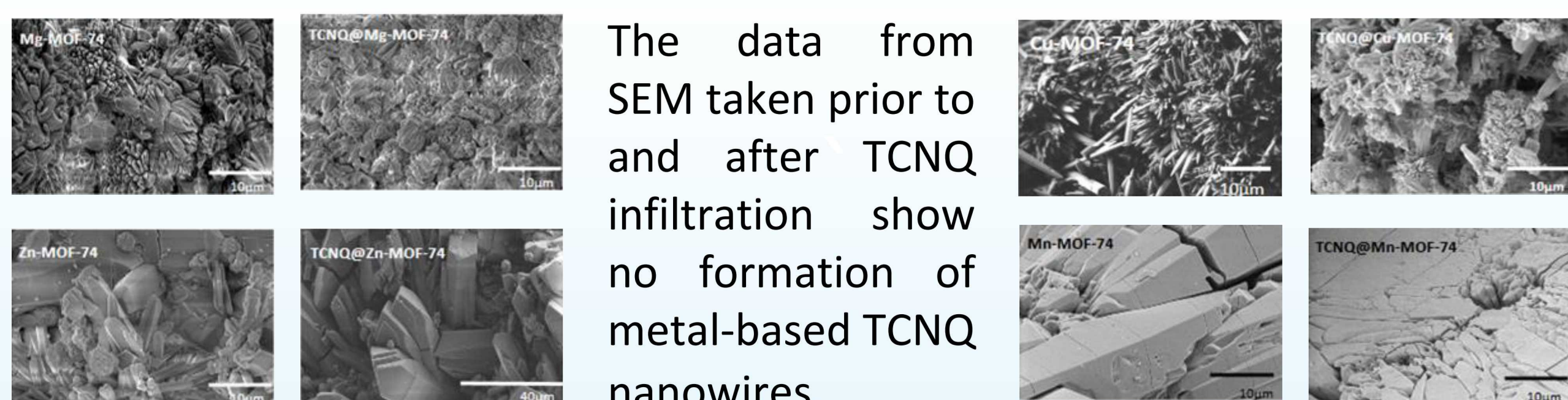
Structures adapted from Shiozawa *et al. Sci. Rep.* **2017**, *7*, 2439.

Powder X-ray Diffraction (PXRD)

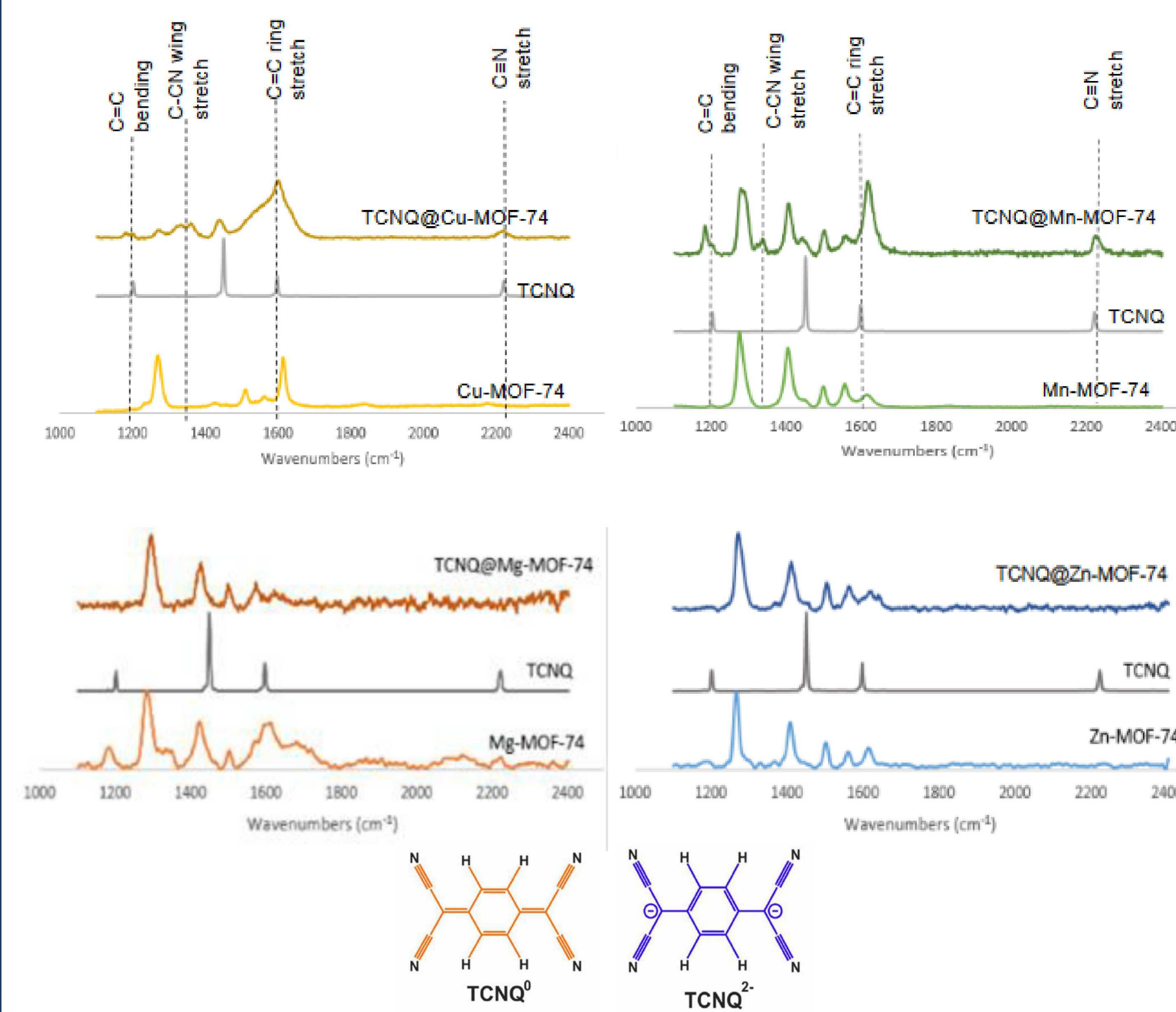


Crystallinity retained after TCNQ infiltration of MOF powders

Scanning Electron Microscopy (SEM)



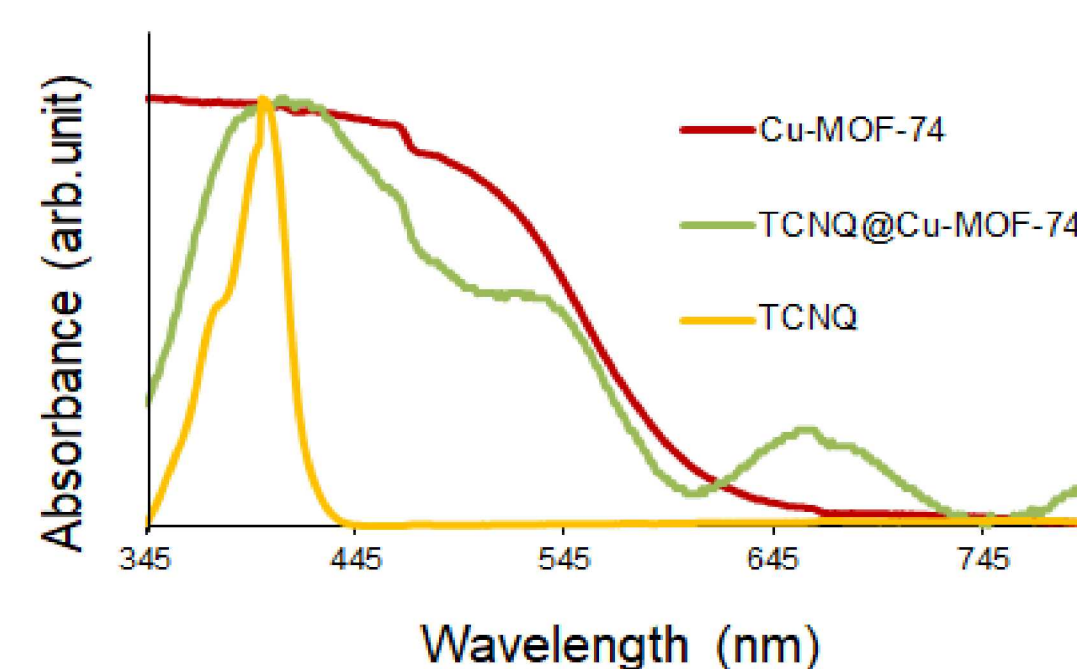
Raman Spectroscopy



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

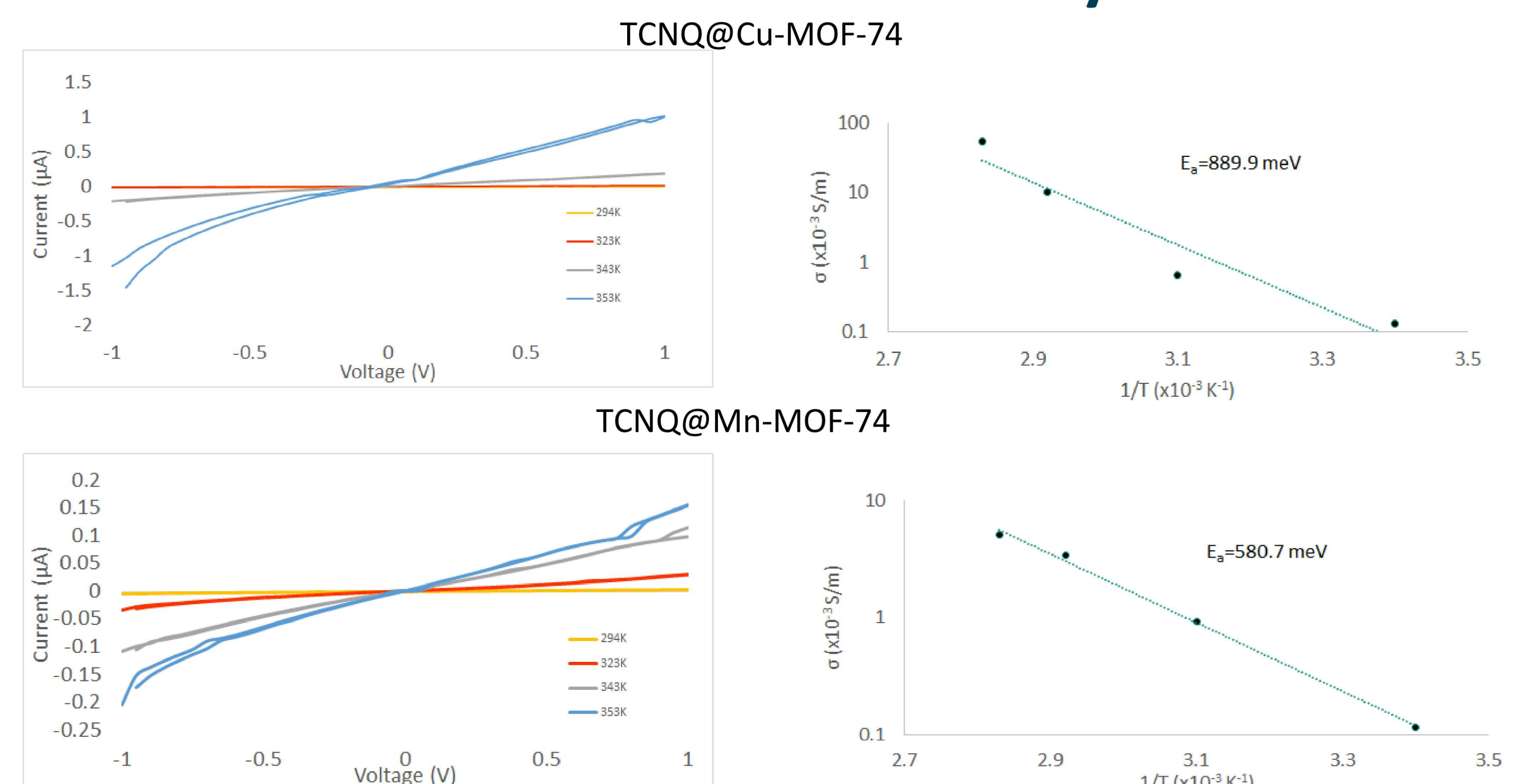
Raman scans indicate TCNQ coordination to the open copper and manganese sites. The C-CN wing stretch shift to 1365 cm^{-1} , C=C ring stretch at 1600 cm^{-1} , C=C bending at 1200 cm^{-1} , and evidence of C≡N stretch at 2230 cm^{-1} indicate bonding between the metal and TCNQ. The formation of the TCNQ@MOF-74 salt and resulting charge transfer gives rise to the semi-conductivity of the doped MOF.

UV-vis Absorbance



After TCNQ infiltration, a peak at 660 nm appears, suggesting a charge transfer complex forms between the Cu-MOF-74 and TCNQ. This peak is notably the result of a low energy electronic transition not observed in the un-doped MOF. We expect similar results with Mn-MOF-74.

Electrical Conductivity



TCNQ@M-MOF-74 powder were 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 for TCNQ@Cu-MOF-74 indicate a maximum conductivity of $5.40 \times 10^{-2}\text{ S/m}$ at 353 K and an activation energy of 889.9 meV. The TCNQ@Mn-MOF-74 results indicate a maximum conductivity of $5.02 \times 10^{-3}\text{ S/m}$ at 353 K and an activation energy of 580.7 meV. This conductivity is on the same order of magnitude as that of TCNQ@Co-MOF-74 MOF in the literature.

Conclusions

We synthesized and infiltrated the insulator of Cu-MOF-74 and Mn-MOF-74 with TCNQ. The resulting TCNQ@Cu-MOF-74 and TCNQ@Mn-MOF-74 salts retained their macrostructure after infiltration while sustaining a significant change in local and long range electronic properties. The doped Cu-MOF-74 and Mn-MOF-74 materials produced conductivities of up to $5.40 \times 10^{-2}\text{ S/m}$ and $5.02 \times 10^{-3}\text{ S/m}$ with activation energies of 889.9 meV and 580.7 meV, respectively.

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