Electrical Conductivity and Morphology Changes of HKUST-1 single crystals and thin films upon exposure to TCNQ

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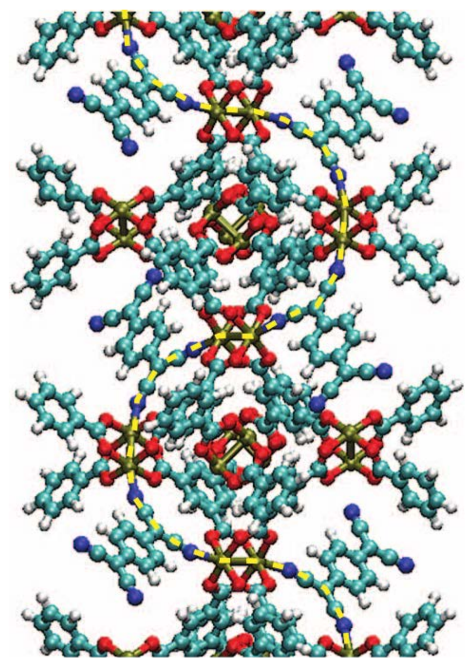
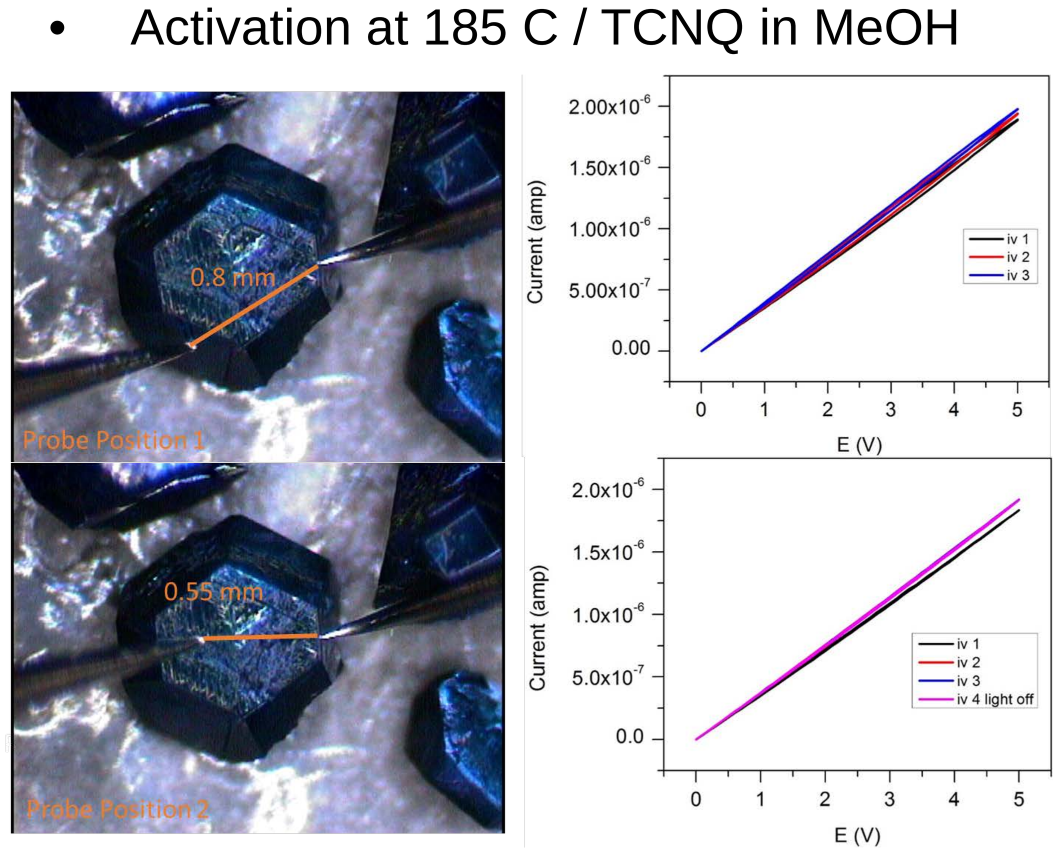
Introduction: TCNQ@Cu_3BTC_2



Electrically conductive metal-organic frameworks are potentially useful for a variety of applications, such as in sensors, optoelectronic devices, and electrocatalytic devices. However, reliable methods are still lacking for synthesizing conducting MOFs, either *de novo*, or from known insulating MOFs. Infiltration of tetracyanoquinodimethane (TCNQ) into the pores of $[Cu_3BTC_2]_n$ (BTC = benzene-1,3,5-tricarboxylate) has been shown to increase the conductivity of $[Cu_3BTC_2]_n$ by six orders of magnitude.[1] To determine the generality of this method, we have investigated the environmental factors which govern the high conductivity, such as solvent, infiltration time, and activation temperature. We have also expanded the scope of the investigation beyond thin films to large single crystals of $[Cu_3BTC_2]_n$

Conductivity Measurements on MOF Single Crystals

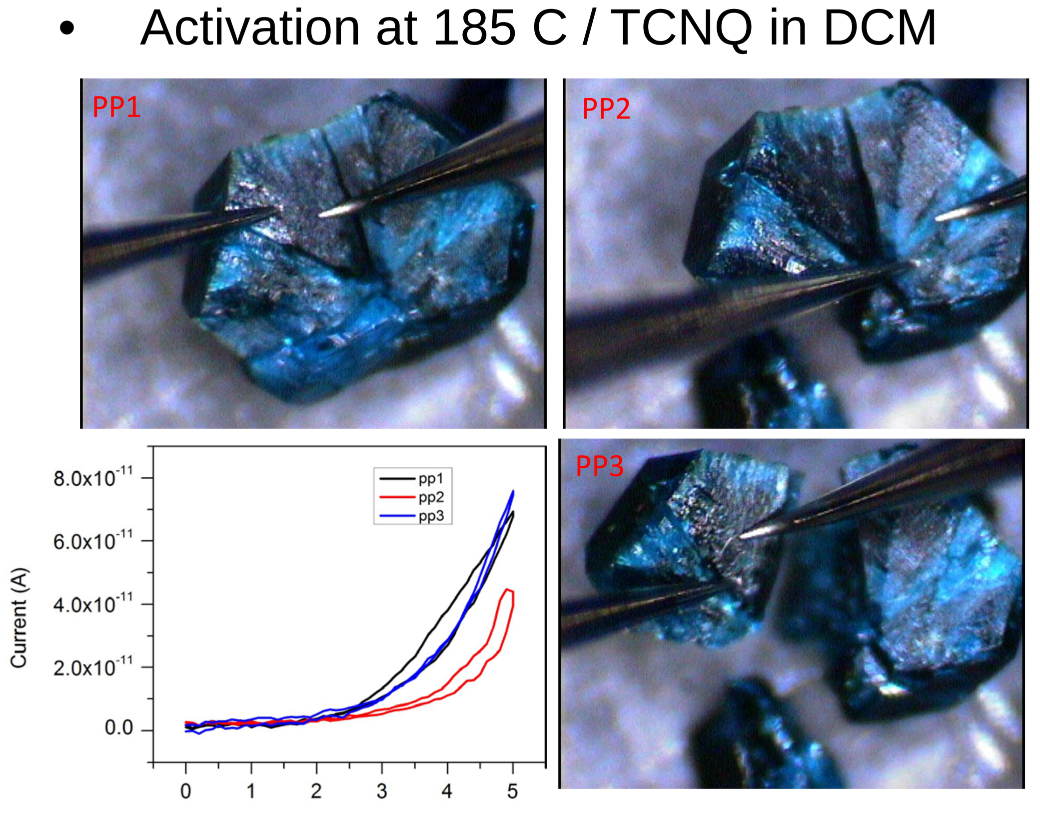
- Activation at 185 C / TCNQ in MeOH



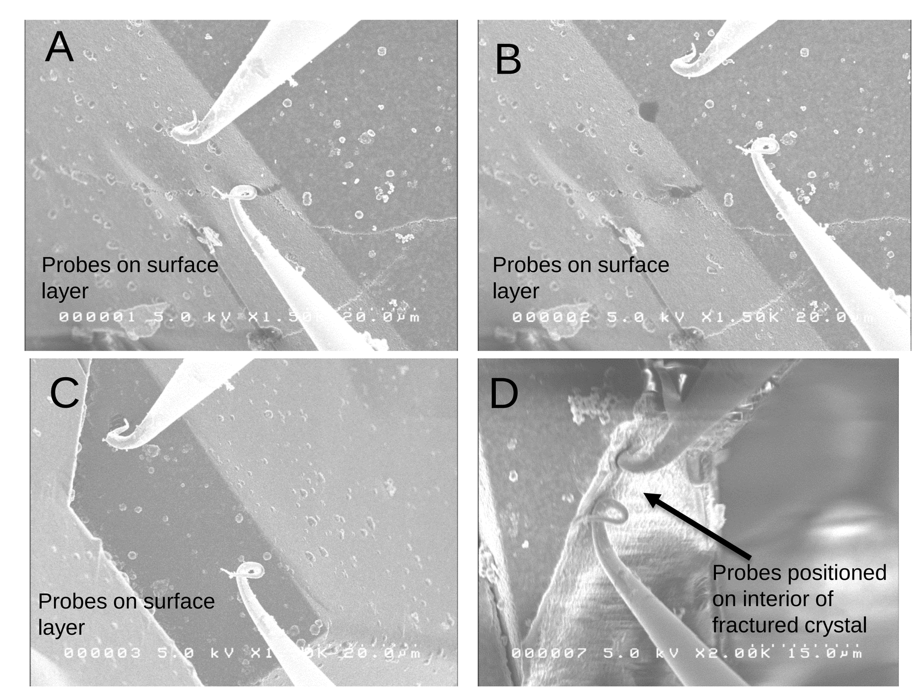
Large (~ 1 mm diameter) $[Cu_3BTC_2]_n$ crystals were grown following a literature procedure.[2] After soaking in EtOH, the large crystals were activated at 185 ° C under vacuum. Samples were then exposed to a saturated solution of TCNQ in MeOH (~ 1 mM). I-V curves were collected using a 2-probe station. High ohmic conductivity was observed

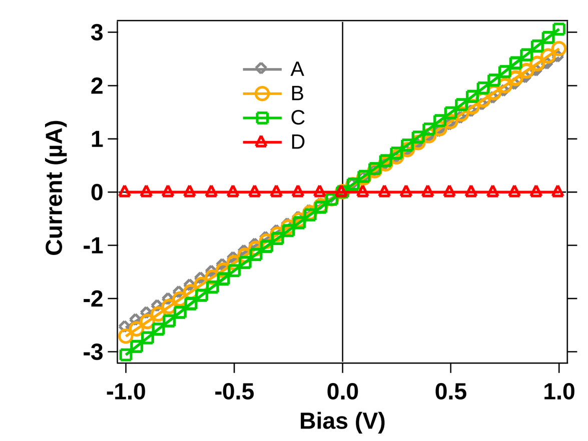
- Activation at 185 C / TCNQ in DCM

Crystals that were also infiltrated with a 5 mM solution of TCNQ in DCM. Images at right show electrical probes making contact to the interior of a fractured crystal. Interior of the crystal showed higher conductivity than the surface. Darker region of the crystal seems to correlate with increased conductivity.



SEM images reveal polycrystalline film on surface of single crystal

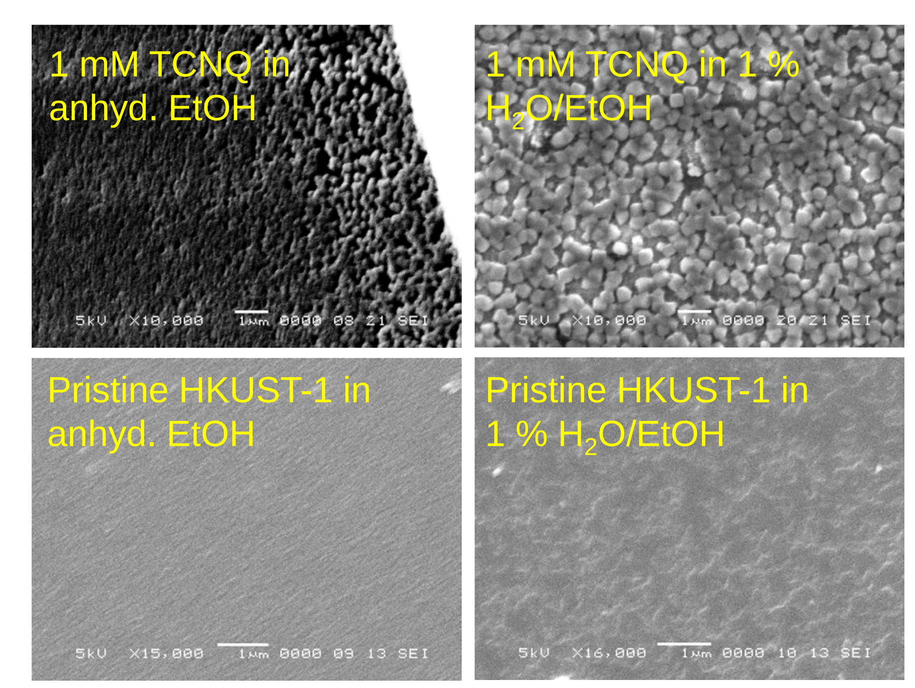




A film is observed on the surface of the crystal when TCNQ is infiltrated using MeOH as the solvent. Electrical measurements show that this film is highly conductive (A-C), whereas the interior of the crystal is not (D).

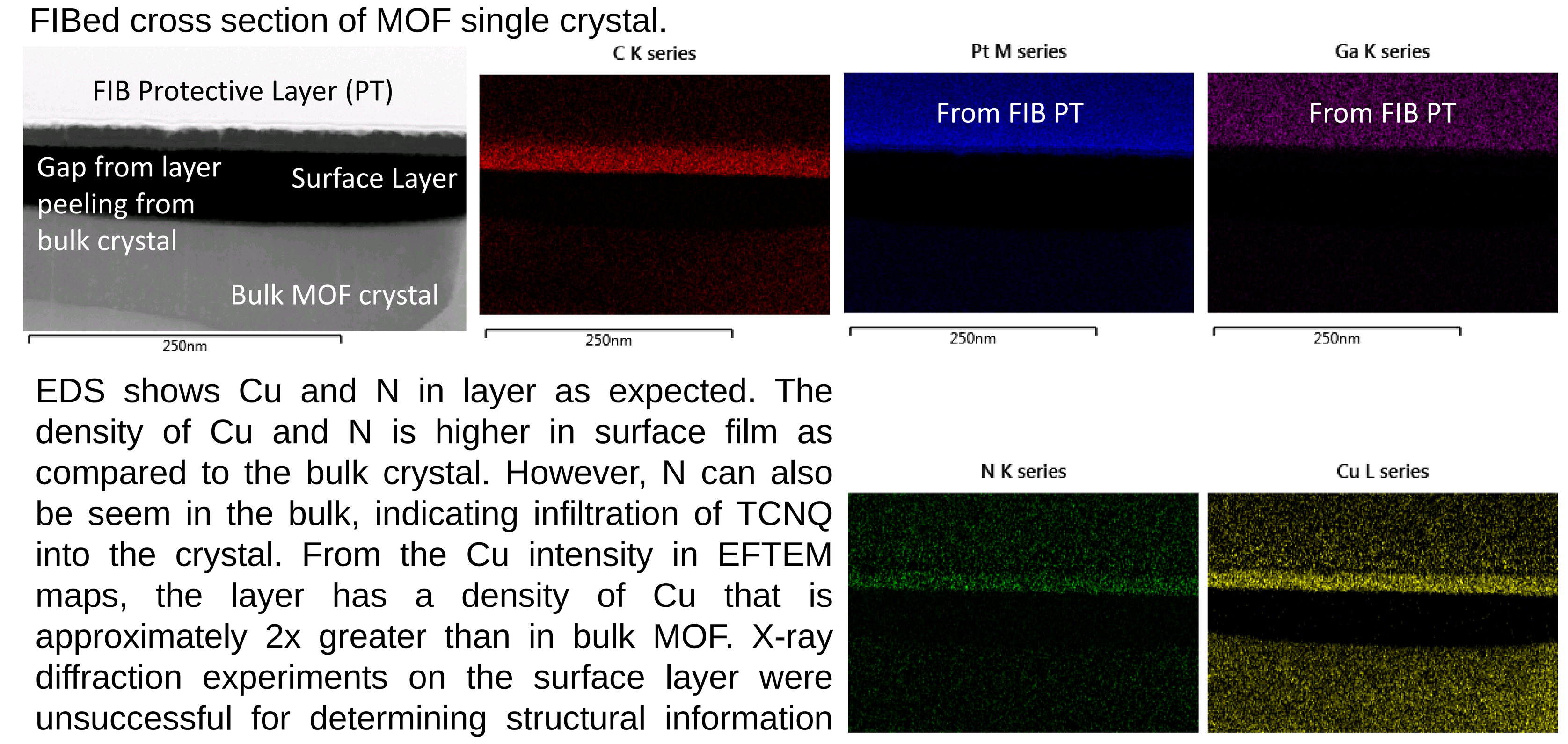
Morphology changes of crystal surface

Single crystals (activated at 180 C) were exposed to solutions of 1 mM TCNQ in either anhydrous or wet EtOH. In both cases, a polycrystalline film is observed to form. Control experiments, (lower images at right) indicate that the formation of the film is depend on the presence of TCNQ. PXRD of the crushed single crystals showed only reflections associated with pristine HKUST-1.



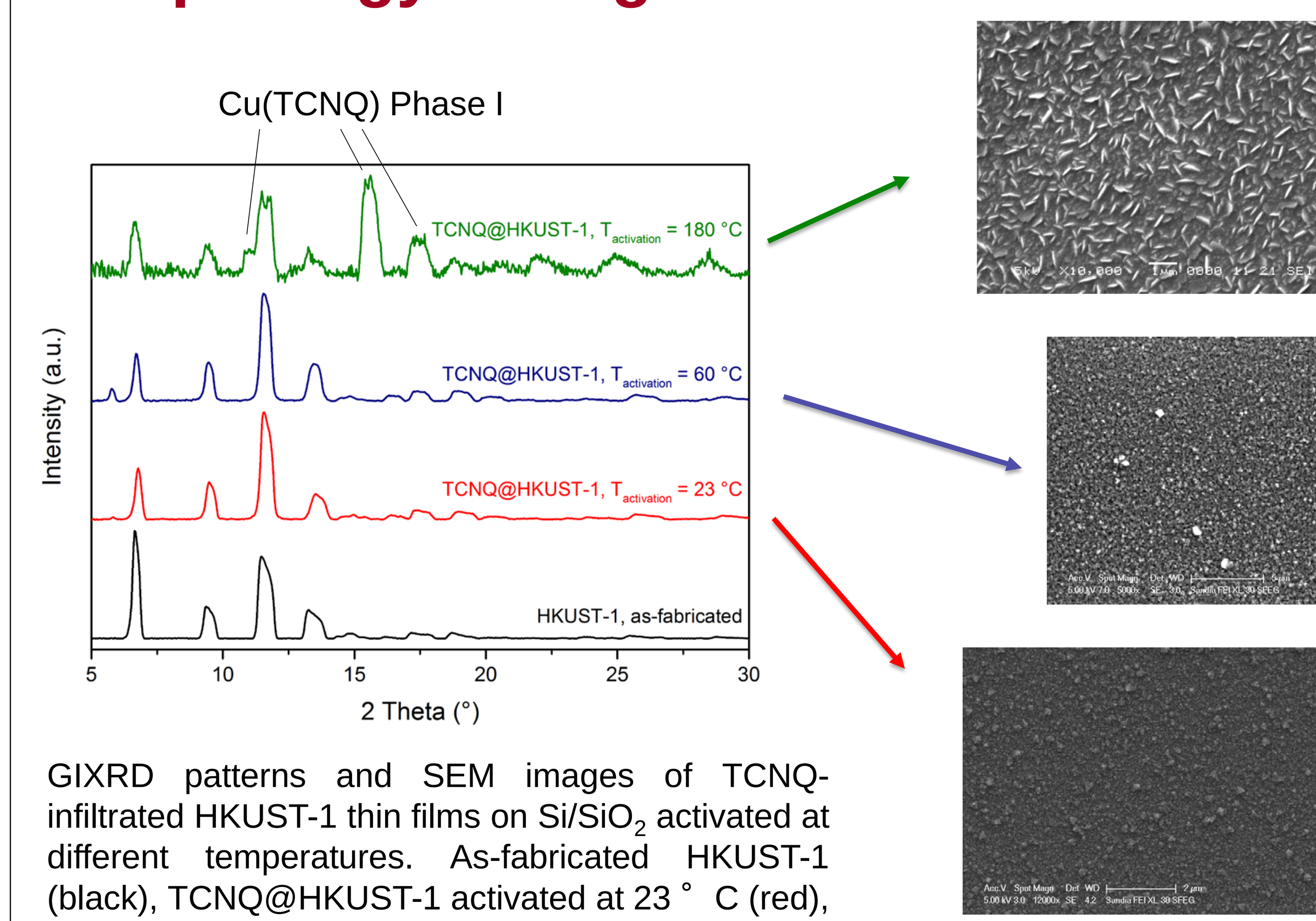
TEM/EDS Analysis of Film on Crystal Surface

FIBed cross section of MOF single crystal.

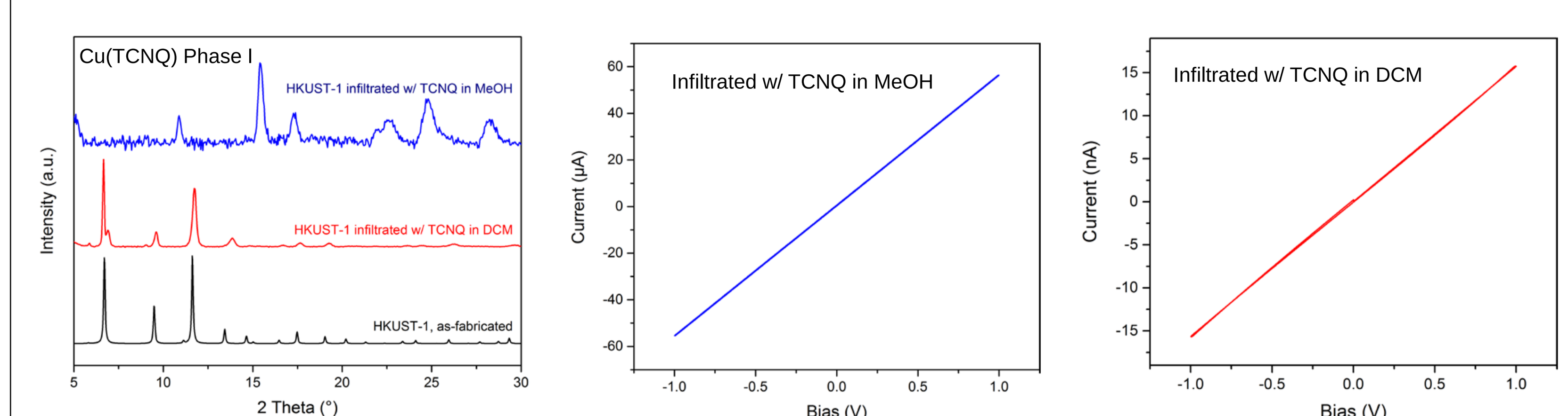


EDS shows Cu and N in layer as expected. The density of Cu and N is higher in surface film as compared to the bulk crystal. However, N can also be seem in the bulk, indicating infiltration of TCNQ into the crystal. From the Cu intensity in EFTEM maps, the layer has a density of Cu that is approximately 2x greater than in bulk MOF. X-ray diffraction experiments on the surface layer were unsuccessful for determining structural information due to lack of diffracting lines or spots.

Morphology changes of MOF thin film



GIXRD patterns and SEM images of TCNQ-infiltrated HKUST-1 thin films on Si/SiO_2 activated at different temperatures. As-fabricated HKUST-1 (black), TCNQ@HKUST-1 activated at 23 ° C (red), 60 ° C (blue), and 180 ° C (green).



GIXRD patterns of pristine and TCNQ-infiltrated HKUST-1 thin films on Si/SiO_2 (actiavation at 100C). While the sample infiltrated w/ DCM (red) maintained the crystal structure of the pristine MOF (black), infiltration w/ MeOH caused a transformation to Cu(TCNQ)[3]. Both films show ohmic conductivity; however, the film that maintained the HKUST-1 structure was much more resistive. This is consistent with the observations on the single crystals.

Conclusions and Future Work

- Infiltration of the canonical MOF HKUST-1 with TCNQ molecules gives rise to electrical conductivity. However, activation temperature and infiltration conditions must be chosen carefully to avoid triggering a phase transition to CuTCNQ material, which is not porous though highly conductive.
- The target of future work is to define the conditions at which pristine HKUST-1 can be infiltrated with TCNQ to obtain an electrically conducting material yet maintaining the structural integrity and hence the properties of the MOF

References

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3) Heintz, R. A.; Zhao, H.; Ouyang, X.; Grandinetti, G.; Cowen, J.; Dunbar, K. R. *Inorg. Chem.* **1999**, *38* (1), 144–156.

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