

CHIRAL NICKEL(II) METAL-ORGANIC FRAMEWORKS (MOFs) AS SPIN-SELECTIVE CATALYSTS

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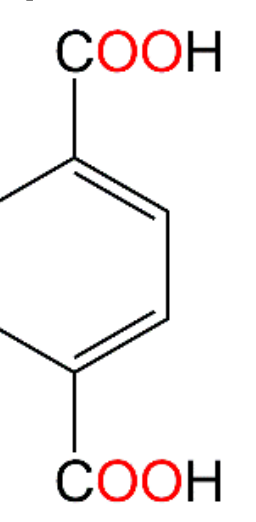
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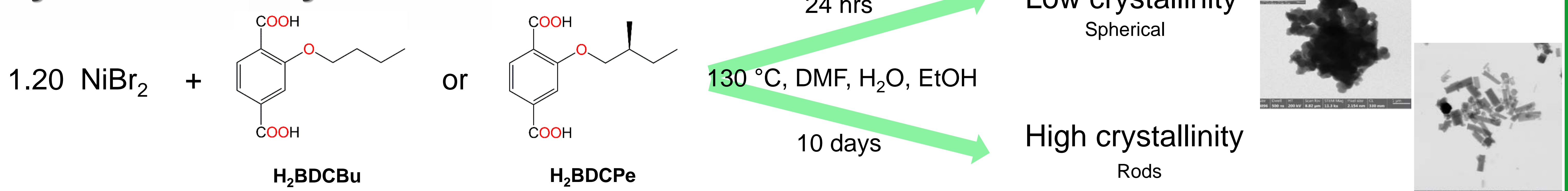


Converting electricity into chemical energy via Electrochemical Water Splitting (EWS) is an eco-friendly method to produce H₂, which can be stored or used as a clean energy alternative to fossil fuels [1]. However, the EWS process is limited by the high overpotential (+1.23 V) [1] needed for the Oxygen Evolution Reaction (OER). To address these challenges, catalysts are indispensable; yet commercial electrolyzers often rely on costly and rare elements like Pt, Ir and Ru. A new approach to reduce the OER overpotential leverages the spin-polarized currents produced by enantiomerically pure catalysts (CISS effect) [1] to favour the generation of triplet O₂ (S = 1) while preventing the

formation of by-products with S = 0, such as H₂O₂. In this work we synthesized chiral MOFs as spin-selective catalysts for the OER using a cheaper and more abundant metal source. Building on recent work of Yuan et al. [2], we first prepared layered compound [Ni₂(OH)₂(BDC)], where H₂BDC is terephthalic acid. Afterwards, we modified H₂BDC introducing an alkoxy side chain, obtaining a chiral ligand and its achiral analogue: H₂BDCPe and H₂BDCBu. Finally, these ligands were incorporated in two families of compounds based on low and high degree of crystallinity, produced by hydrothermal synthesis with NiBr₂.



Hydrothermal Synthesis

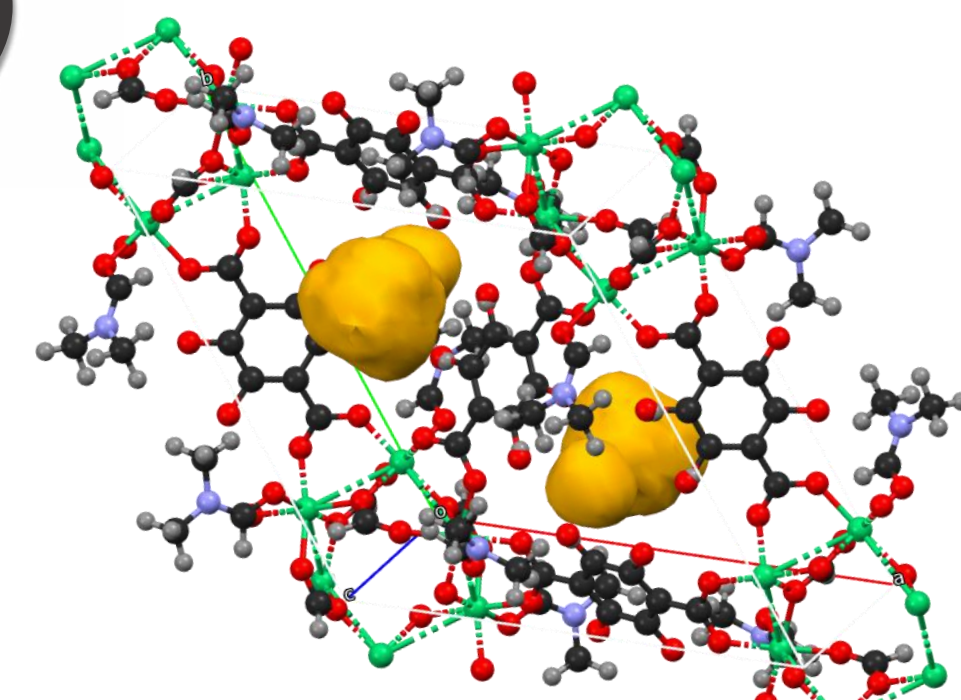


Powder X-ray Diffraction (PXRD)

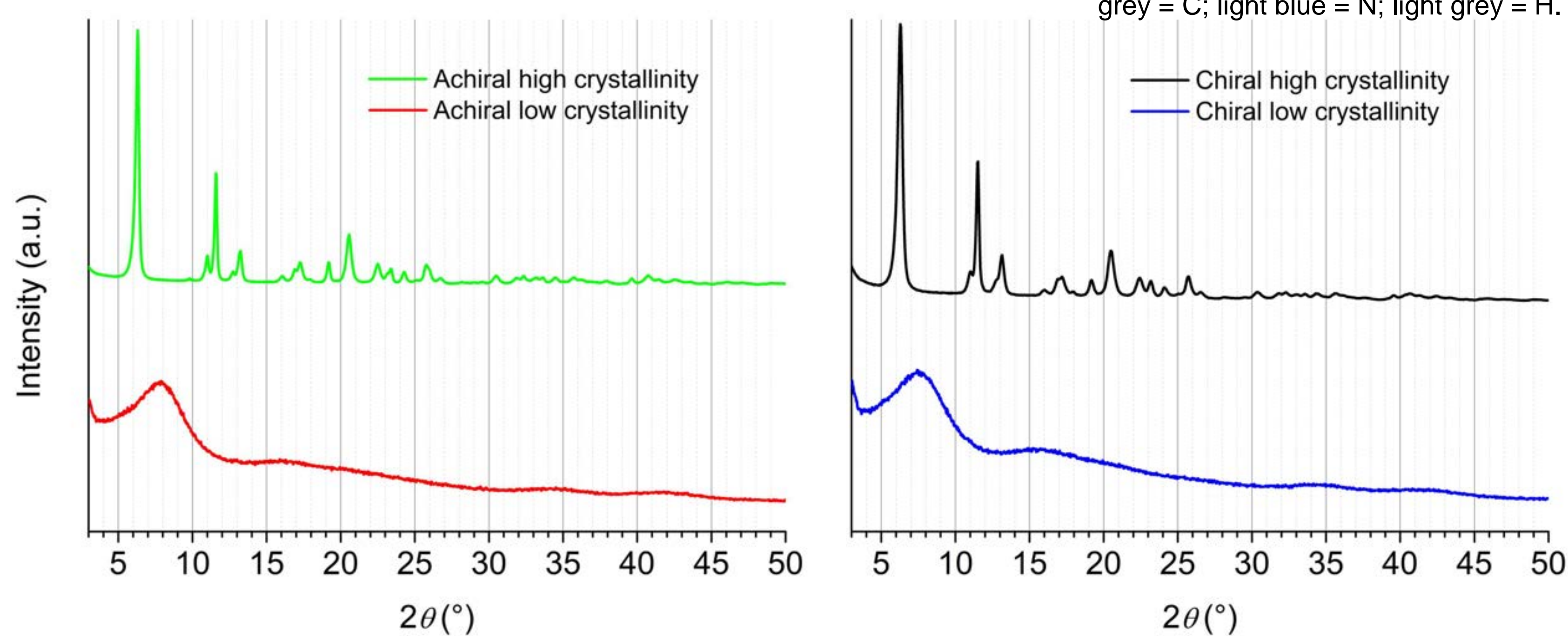
Achiral and Chiral high cryst. were solved → they are 3D-MOFs containing formates, DMF and ligands.

Yellow voids can fit the disordered alkoxy sidechain of BDCBu²⁻ and BDCPe²⁻ BUT only **20/30%** is preserved into the cavities of the structure, while the others are hydrolyzed to OH moieties (confirmed by leaching via NMR).

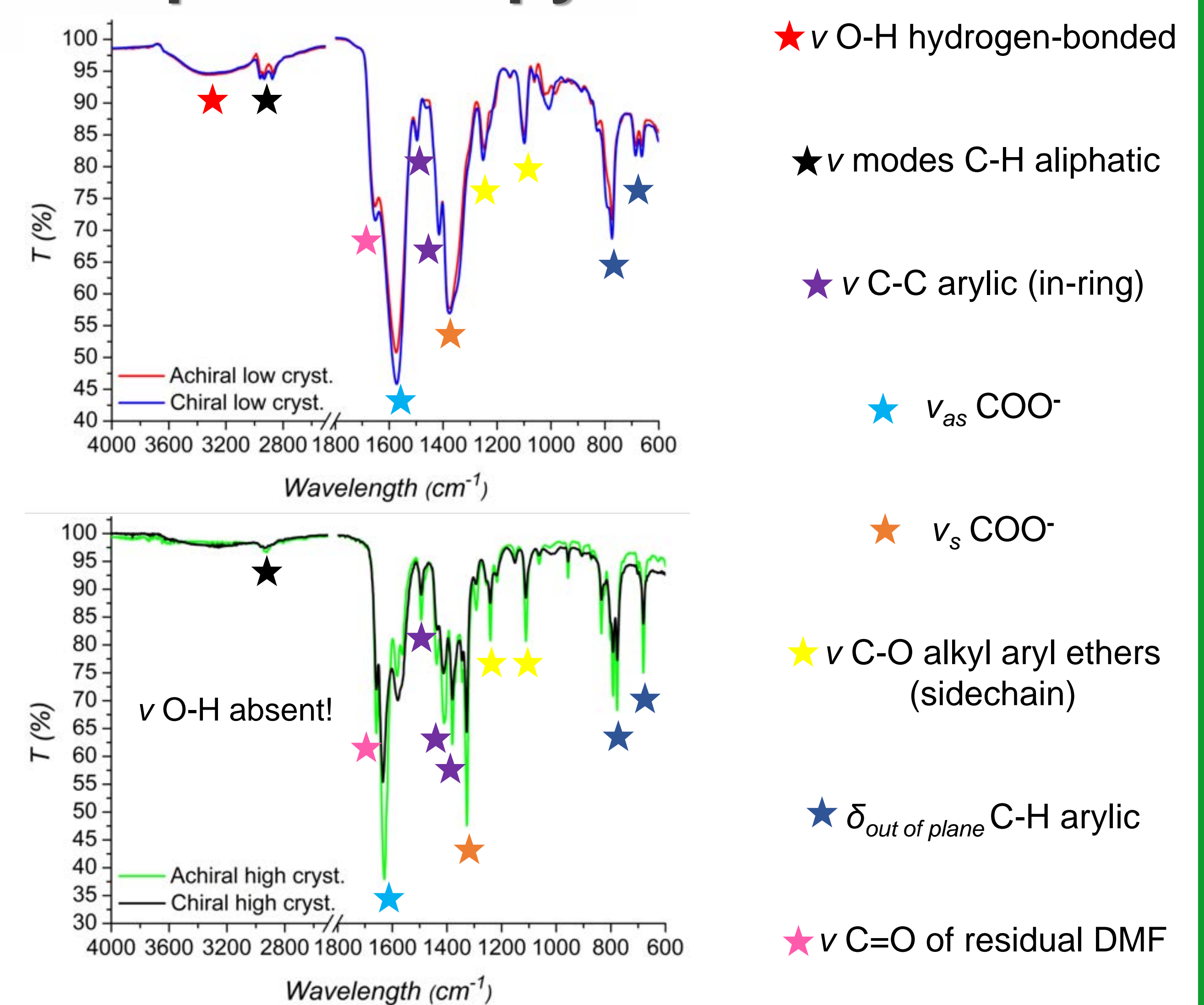
Formula: [Ni₂(HCOO)₂(BDC-OH)_{0.7/0.8}(BDCBu/Pe)_{0.2/0.3}](DMF)



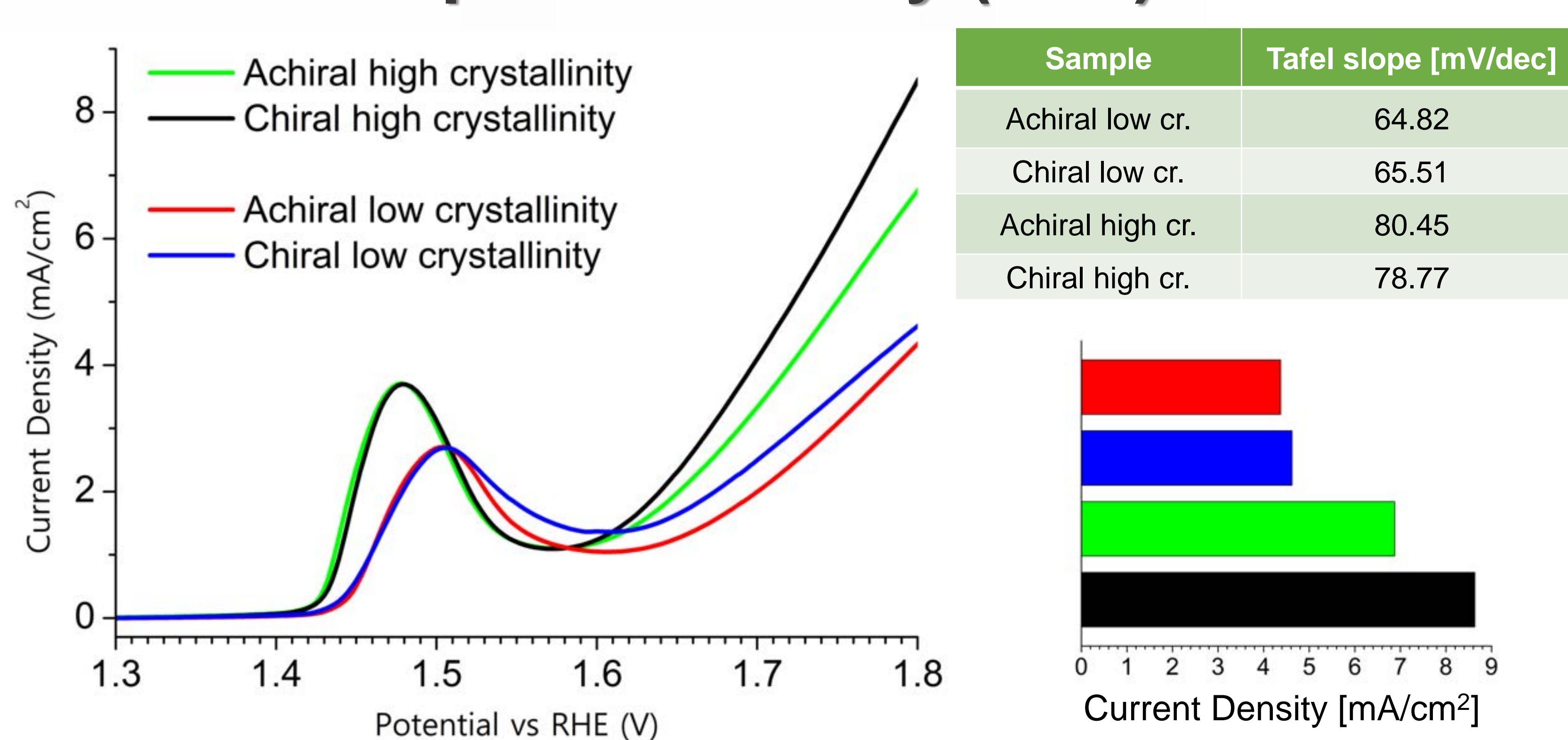
Yellow = voids ; green = Ni; red = O; dark grey = C; light blue = N; light grey = H.



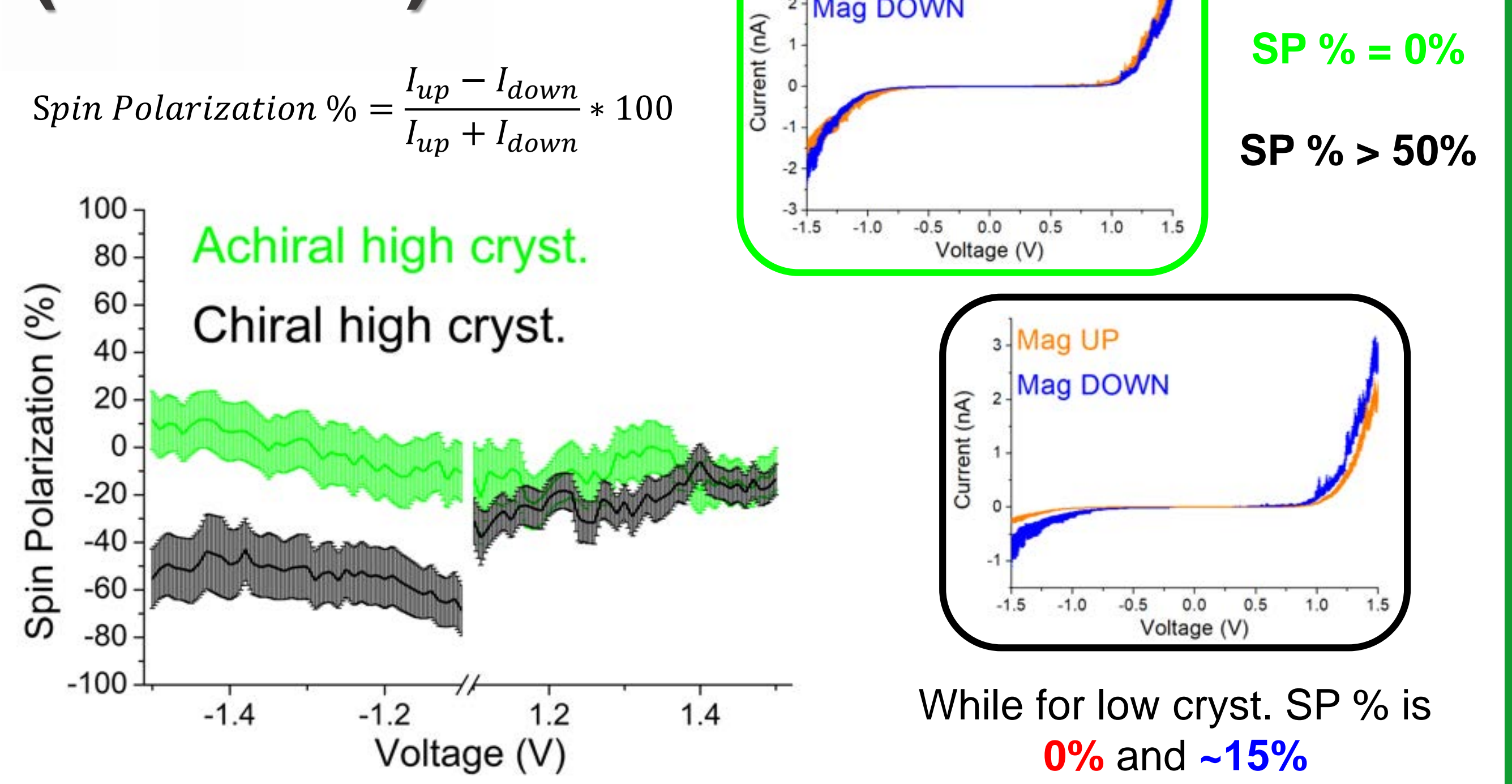
IR spectroscopy



Linear Sweep Voltammetry (LSV)



Spin Polarization measurements (mc-AFM)



Conclusions and future steps

- The current densities increase as crystallinity increases (red vs green for Achiral and blue vs black for Chiral)
- More importantly, Chirality enhance the electrochemical activity for the Water Splitting reaction compared to their Achiral counterparts. Especially, Chiral with high crystallinity is the best one → Chirality plays a fundamental role in OER
- The Spin Polarization is clearly influenced by the crystallinity of the material
- For the future: measuring how much O₂ is produced by using a rotating disk electrode

References

- [1] Raveendran et al., *RSC Adv.*, **2023**, 13, 3843-3876.
- [2] Yuan et al., *Nat. Mater.*, **2022**, 21, 673-680.