

Cobalt-based Metal-Organic Frameworks (MOFs) as spin-selective catalysts

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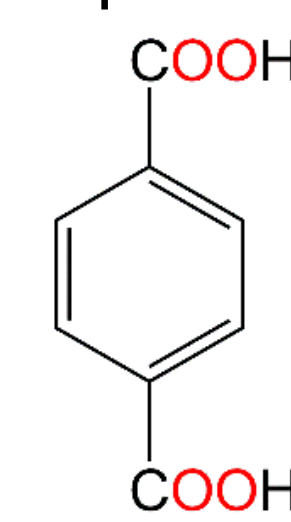
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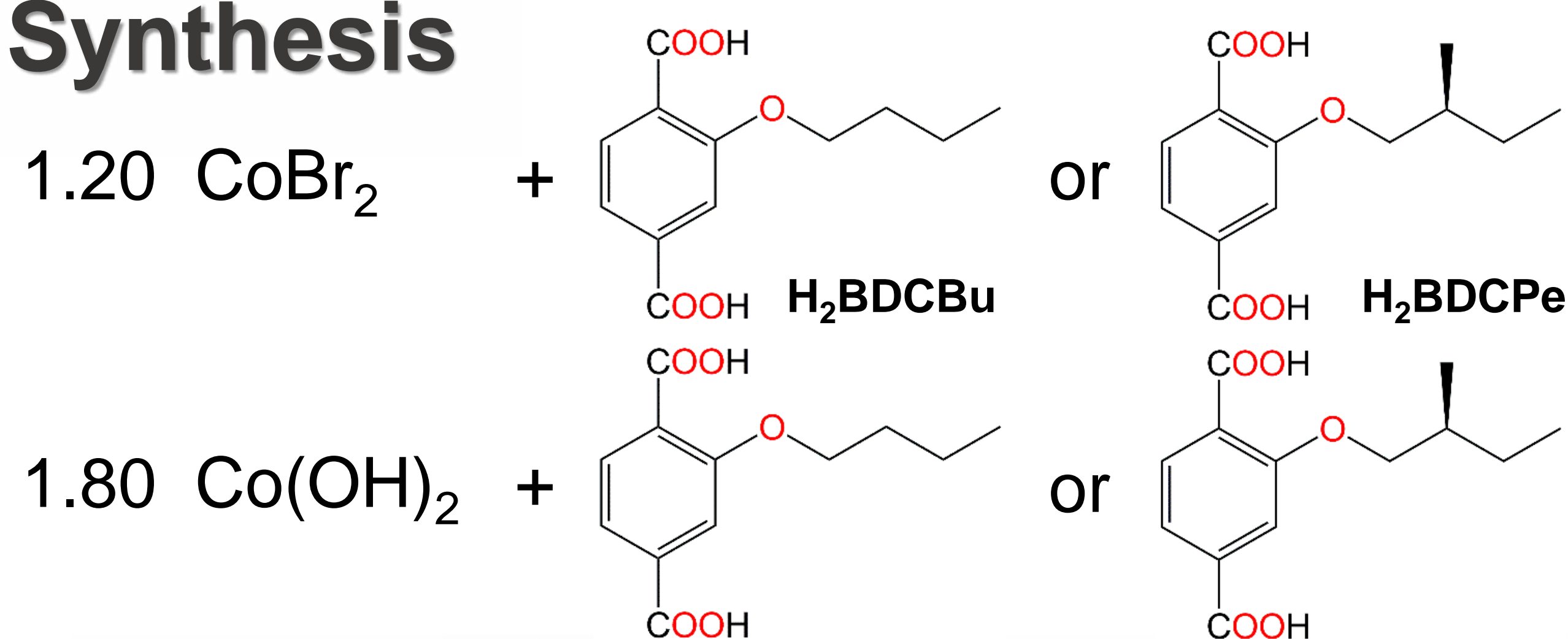


Converting electricity into chemical energy via Electrochemical Water Splitting (EWS) is an eco-friendly method to produce H₂, which can be stored or used as a clean energy alternative to fossil fuels [1]. However, the EWS process is limited by the high overpotential (+1.23 V) [1] needed for the Oxygen 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 [Co₂(OH)₂(BDC)], where H₂BDC is terephthalic acid. Afterwards, we modified H₂BDC with an alkoxy side chain to obtain a chiral ligand (H₂BDCPe) and its achiral analogue (H₂BDCBu). These ligands were incorporated in two types of compounds, obtained by either intercalation with Co(OH)₂ or direct self-assembling from CoBr₂.



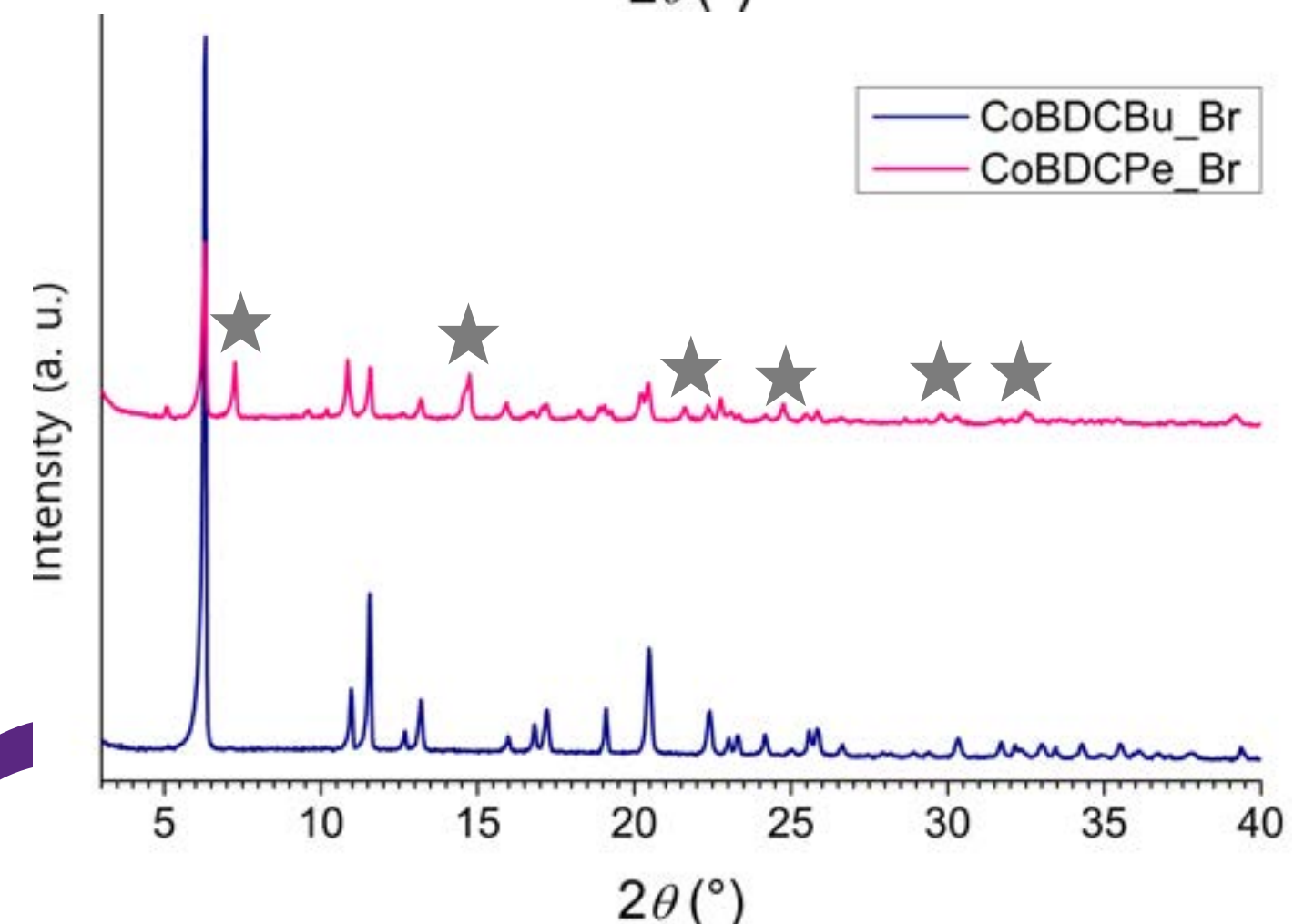
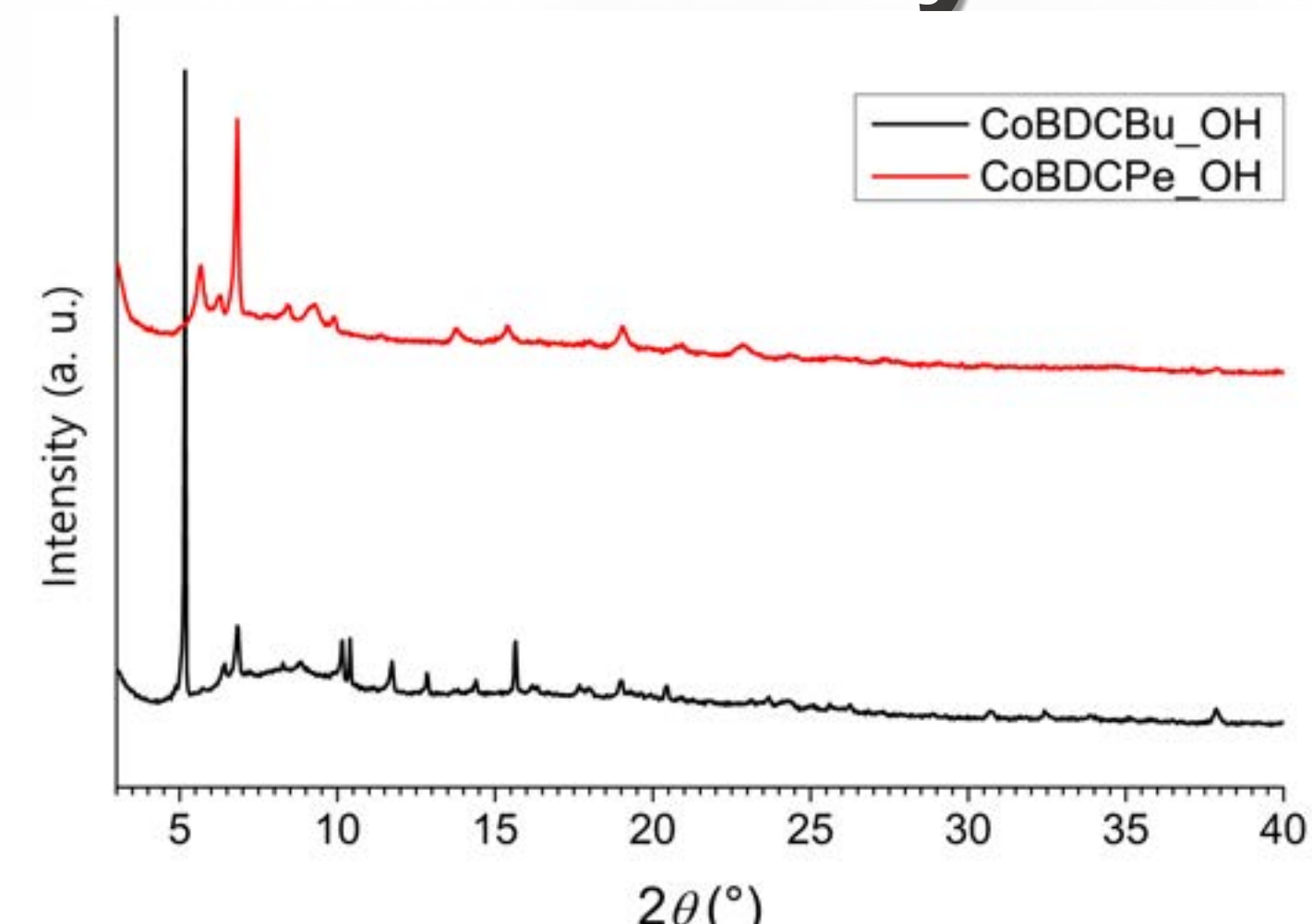
Synthesis



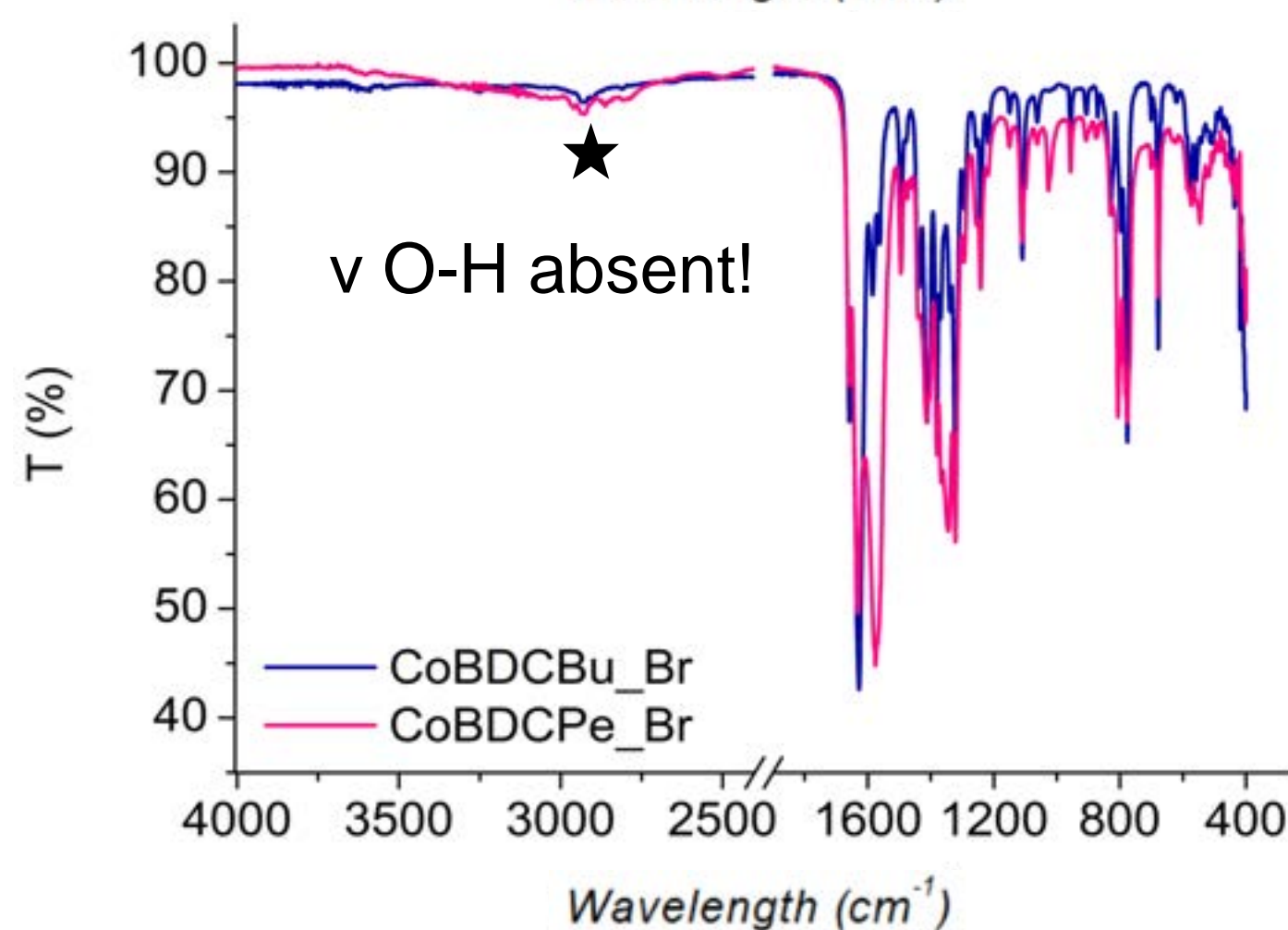
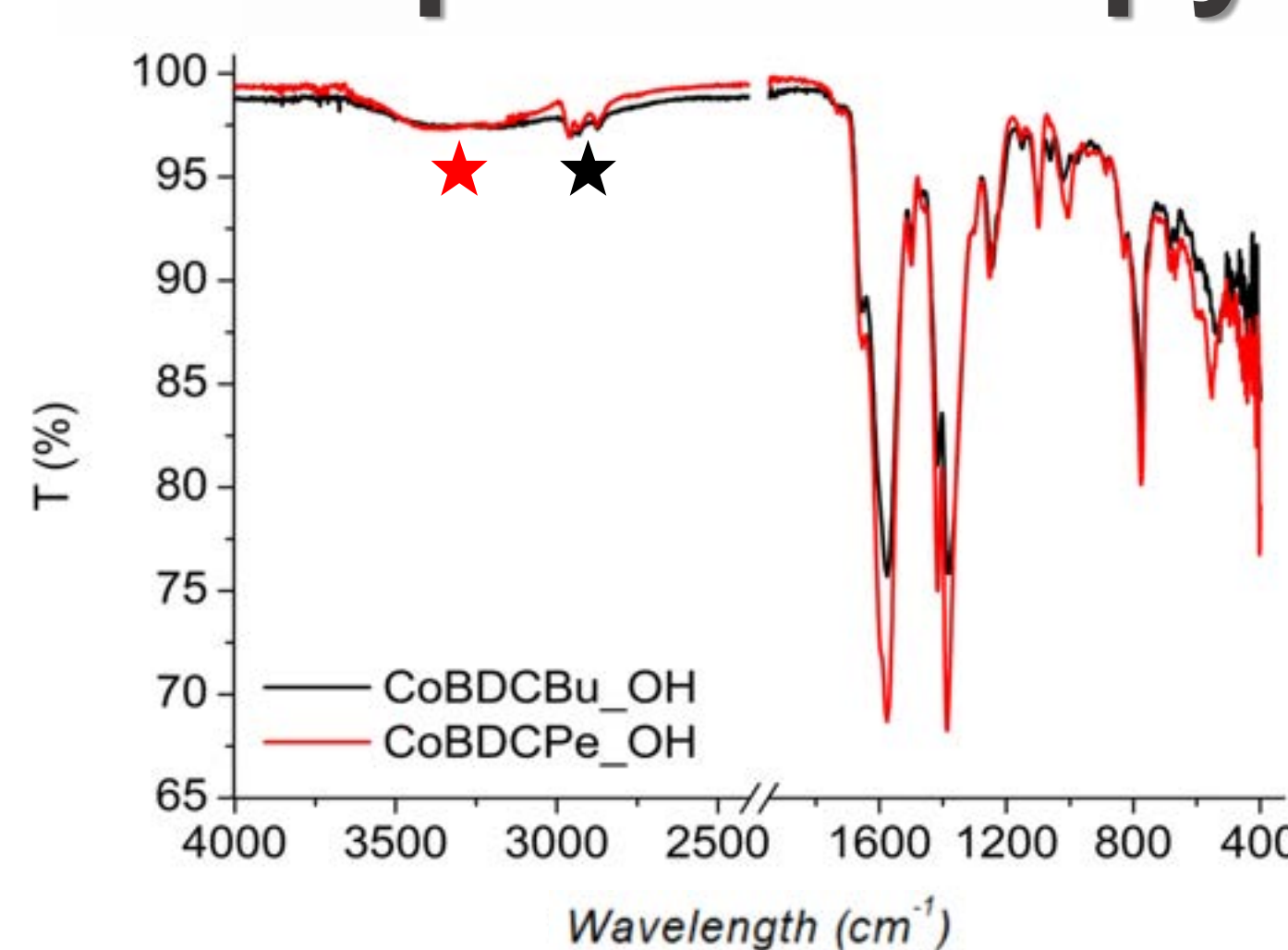
Elemental Analysis (EA)

	C	H	N
A	36.18	3.76	4.89
B	33.78	3.88	3.66
C	35.55	4.19	2.39
D	33.33	3.81	2.29

Powder X-ray Diffraction

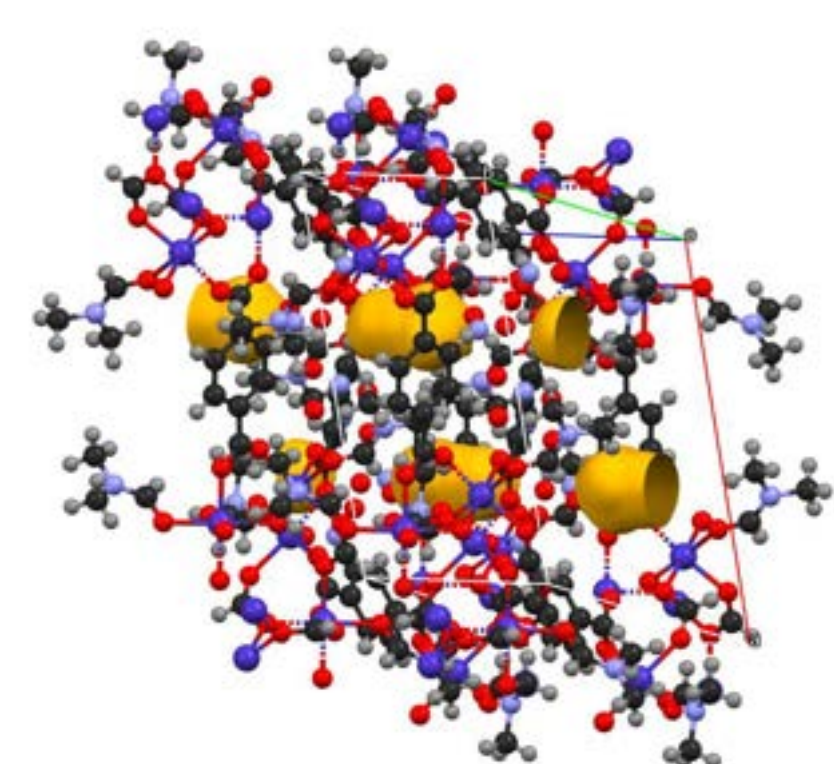
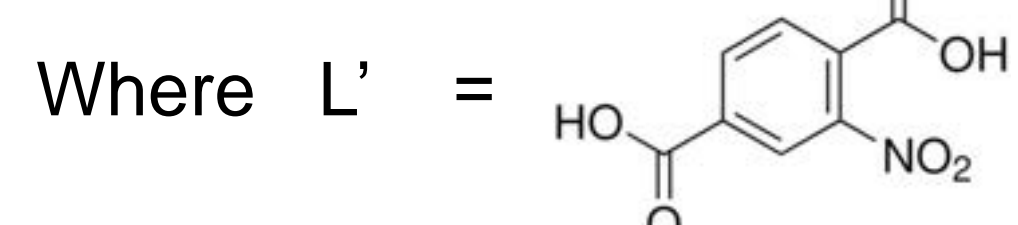
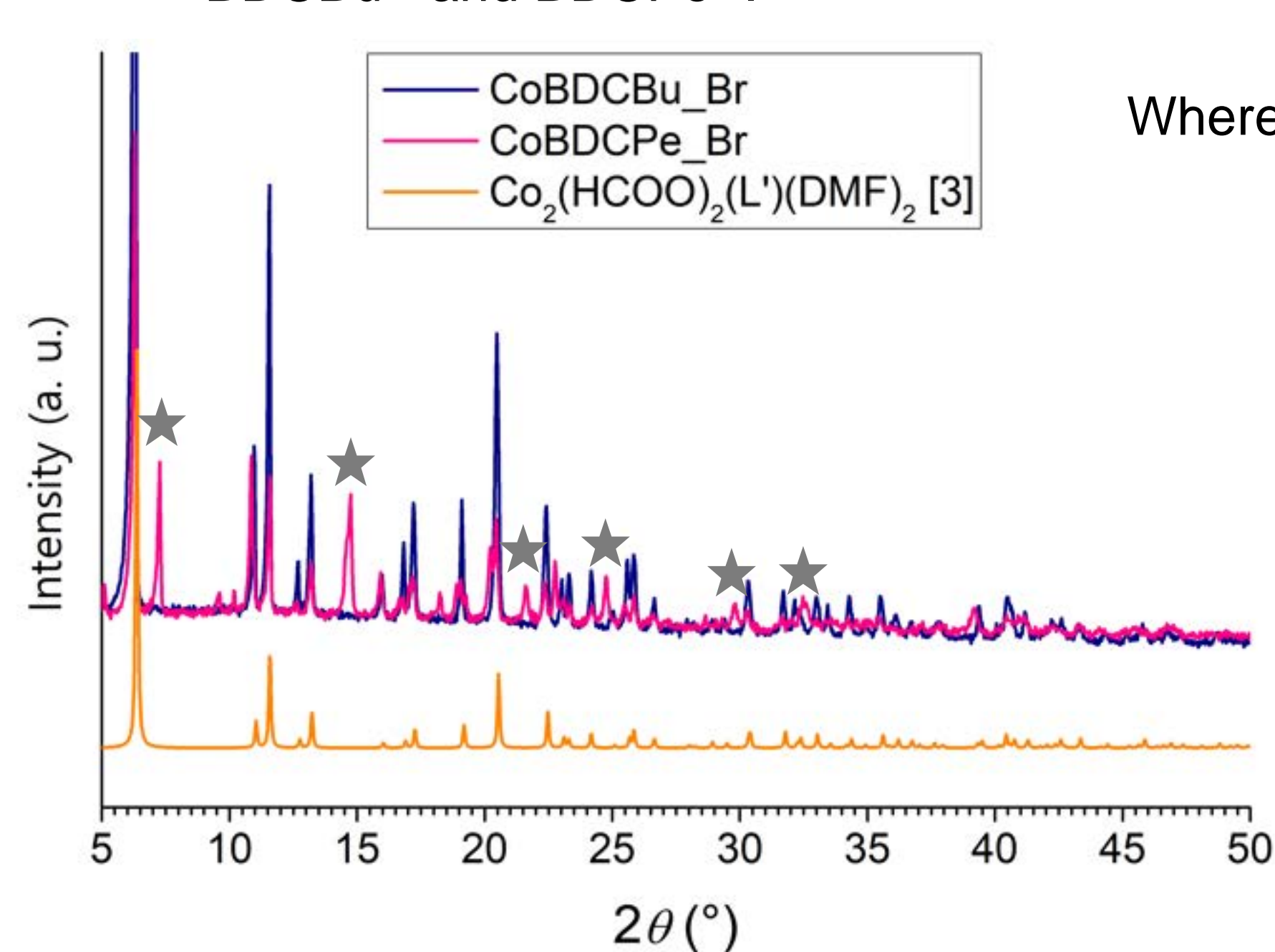


IR spectroscopy



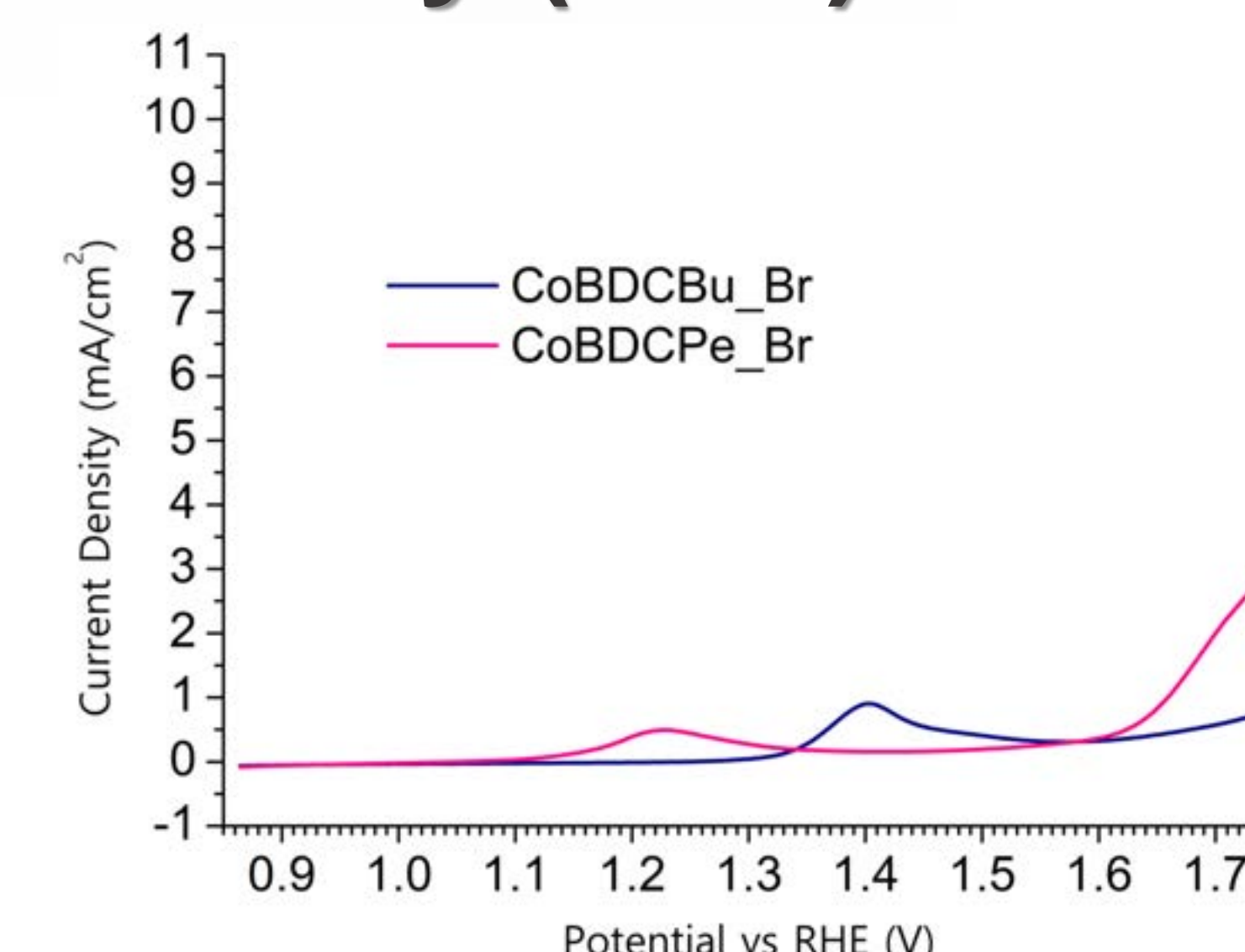
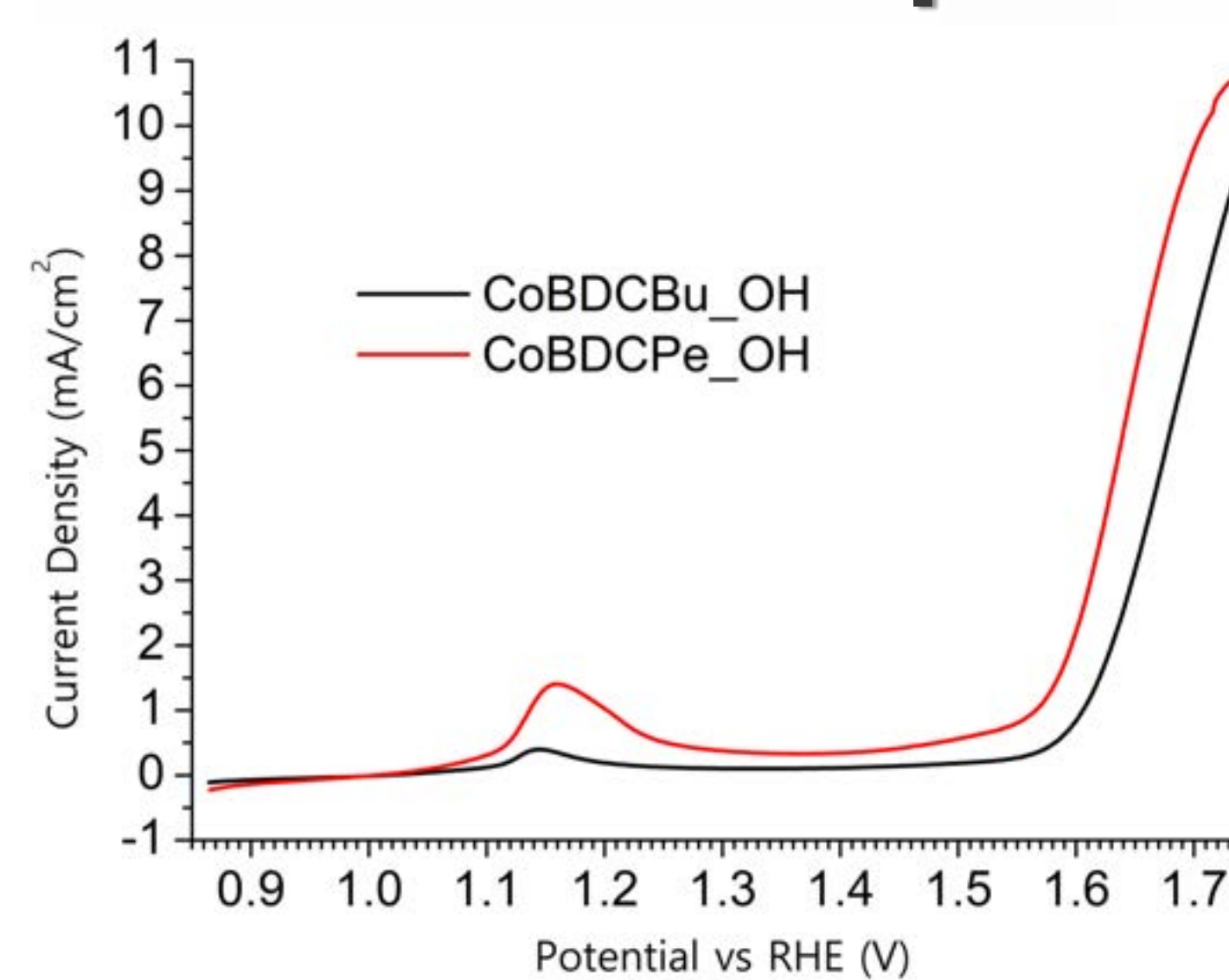
- ★ v O-H hydrogen-bonded
- ★ v modes C-H aliphatic
- ★ v C-C aryl (in-ring)
- ★ v_{as} COO⁻
- ★ v_s COO⁻
- ★ v C-O alkyl aryl ethers (sidechain)
- ★ δ_{out of plane} C-H aryl

Almost the same pattern between chiral and achiral compounds from direct self-assembling besides ★ peaks + comparison with similar pattern found in literature [3] (in orange). Yellow voids can fit the alkoxy sidechain of BDCBu²⁻ and BDCPe²⁻.



Yellow = voids ; blue = Co; red = O; dark grey = C; light blue = N; light grey = H [3].

Linear Sweep Voltammetry (LSV)



	CoBDCBu_Br	CoBDCPe_Br	CoBDCBu_OH	CoBDCPe_OH
E onset vs RHE [V]	1.72	1.62	1.6	1.58
Tafel Slope [mV/dec]	161.7	111.8	101	90.4

Conclusions and future steps

- The composition of CoBDCBu_OH and CoBDCPe_OH can be represented by the general molecular formula [Co₃(OH)₄(BDCBu/Pe)](DMF). Since the metal source is cobalt hydroxide we expect these materials to be 2D layered structure of Co(OH)₂ and the organic linker.
 - PXRD patterns and EA results suggest that CoBDCBu_Br and CoBDCPe_Br structure is more likely a 3D MOF with the following composition: [Co₂(HCOO)₂(BDC-OH)_{0.5}(BDCBu/Pe)_{0.5}](DMF). This means that alkoxy sidechains are hydrolyzed by ~50% and remain as OH moieties (instead of NO₂ groups as reported by Seabra et al. [3]), while ~50% is preserved into the cavities of the structure.
 - Chirality enhance the electrochemical activity for the Water Splitting reaction, in particular, CoBDCPe_OH is the best.
- Future perspectives: structural resolution AND spin-polarization measurements (mc-AFM) of the compounds.

References

- [1] Raveendran et al., *RSC Adv.*, **2023**, 13, 3843-3876.
- [2] Yuan et al., *Nat. Mater.*, **2022**, 21, 673-680.
- [3] V. Seabra et al., *Trans. Metal Chem.* **2025**, 50, 115-125