

Evaluation of Anion-Exchange Properties for a Series of Crystalline Porous Coordination Polymers

MSc Thesis – Report III

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Master Program: Chemistry of Advanced Materials

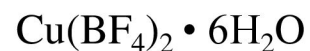
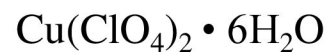
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Outline

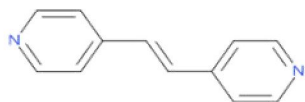
- ❖ **Cu-based Metal Organic Frameworks (MOFs)**
- ❖ **Anion exchange studies**
 - Low concentration of anions
 - Concentration variation
 - High concentration of anions
- ❖ **Conclusions**

Cu-based MOFs

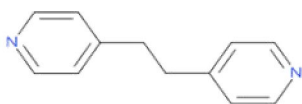
Metal salts



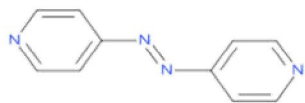
Ligands



1,2-bis(4-pyridyl)ethylene (bpy)

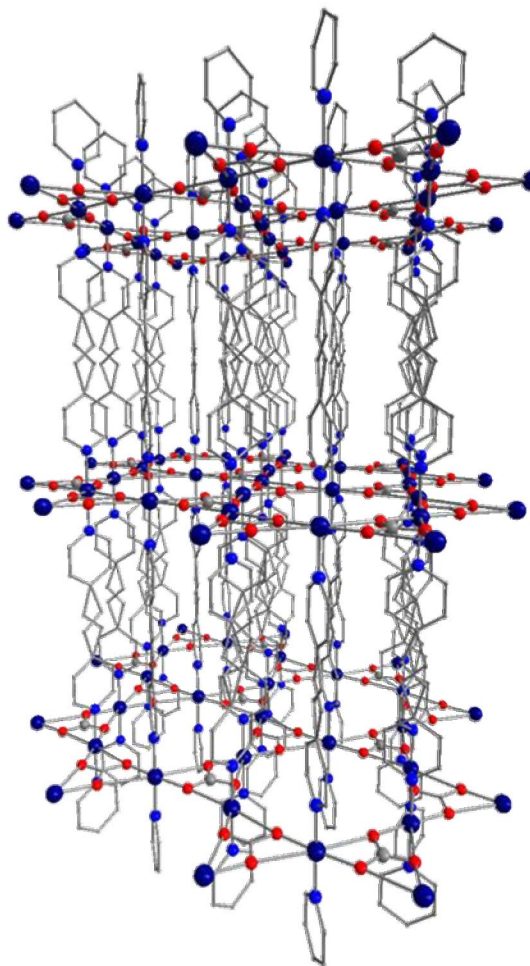


1,2-bis(4-pyridyl)ethane (bpe)



4,4'-azopyridine (azopy)

+ CO₂ (atm)

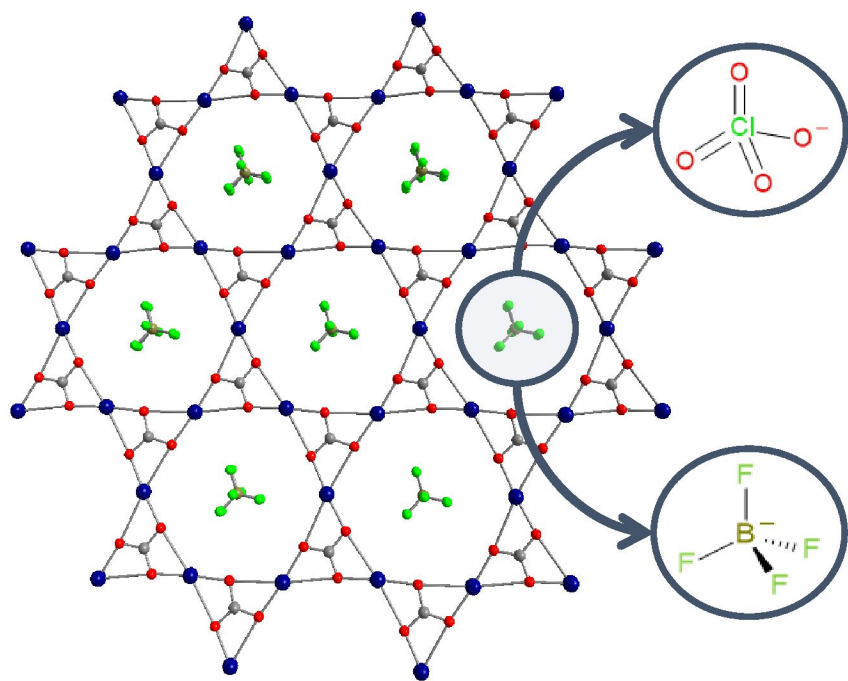


Structure of $\{[\text{Cu}_3(\text{CO}_3)_2(\text{L})_3](\text{Y})_2\}_n$

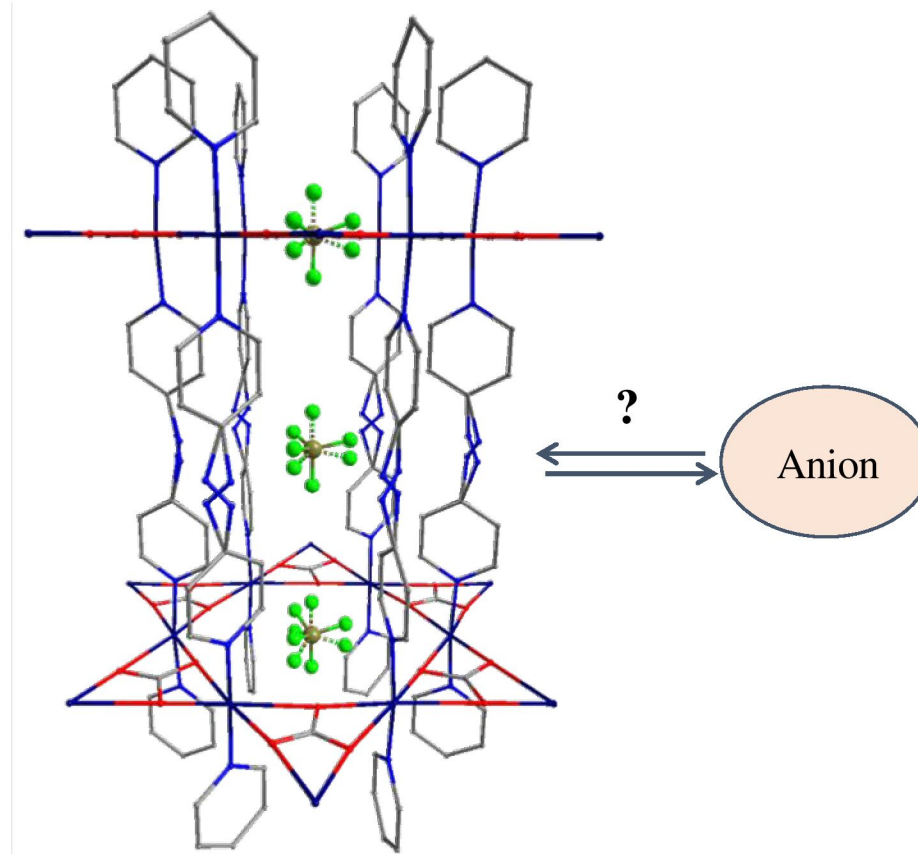
anions omitted for clarity

	L	Y
MB-1	bpy	ClO_4^-
MB-2	bpy	BF_4^-
MB-3	bpe	ClO_4^-
MB-4	bpe	BF_4^-
MB-5	azopy	ClO_4^-
MB-6	azopy	BF_4^-

Cu-based MOFs



Kagomé layer in ab -plane

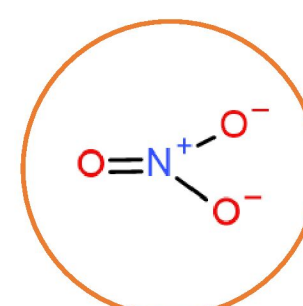
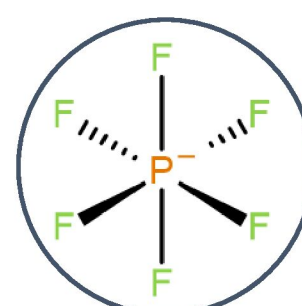
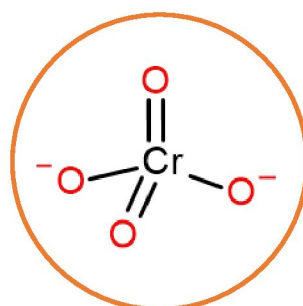
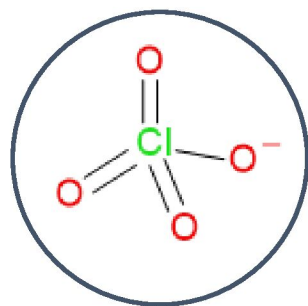
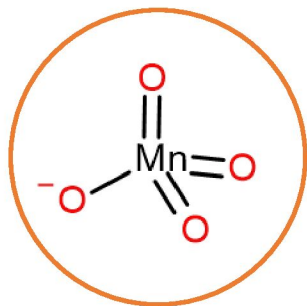


Hexagonal channels along c -axis

Anion exchange studies

Selection:

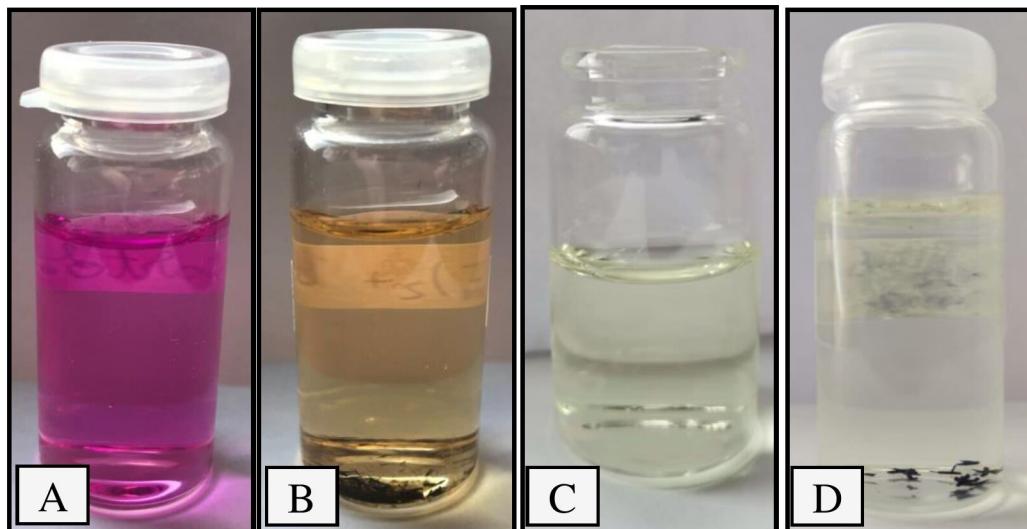
- 1) Anions with same geometry and same charge
- 2) Anions with same geometry and different charge
- 3) Anions with different geometry and same charge



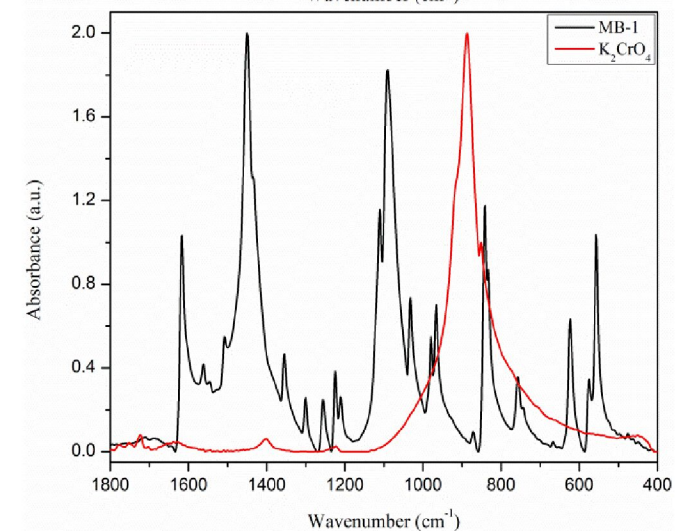
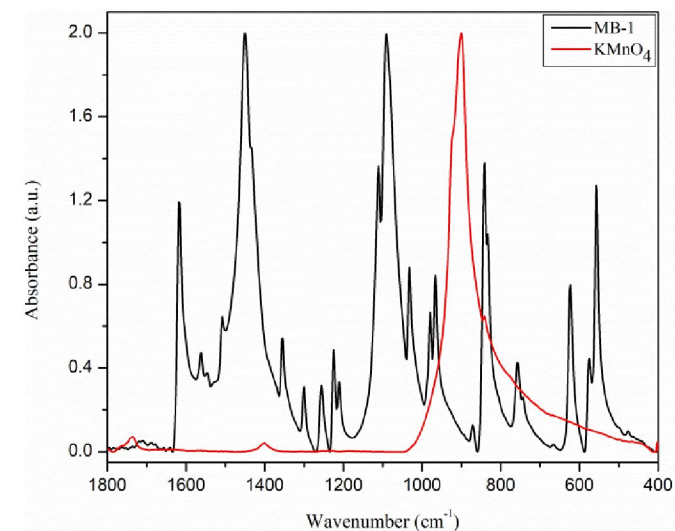
Study:

- A. Low concentration of anions
- B. High concentration of anions

Low concentration of anions

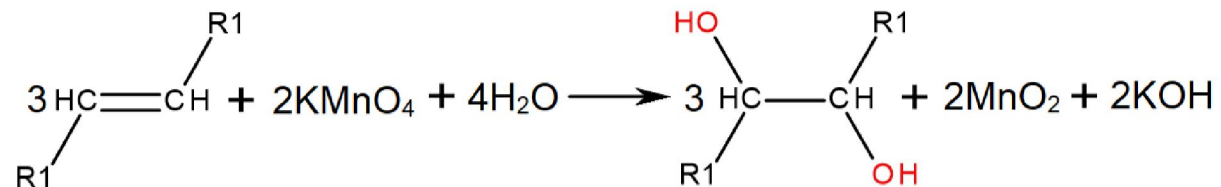


Photographs of 0.1 mM aqueous solution of KMnO_4 (A), compound MB-1 in KMnO_4 0.1 mM after 3 days (B), 0.1 mM aqueous solution of K_2CrO_4 (C), and compound MB-1 in K_2CrO_4 0.1 mM after 3 days (D)

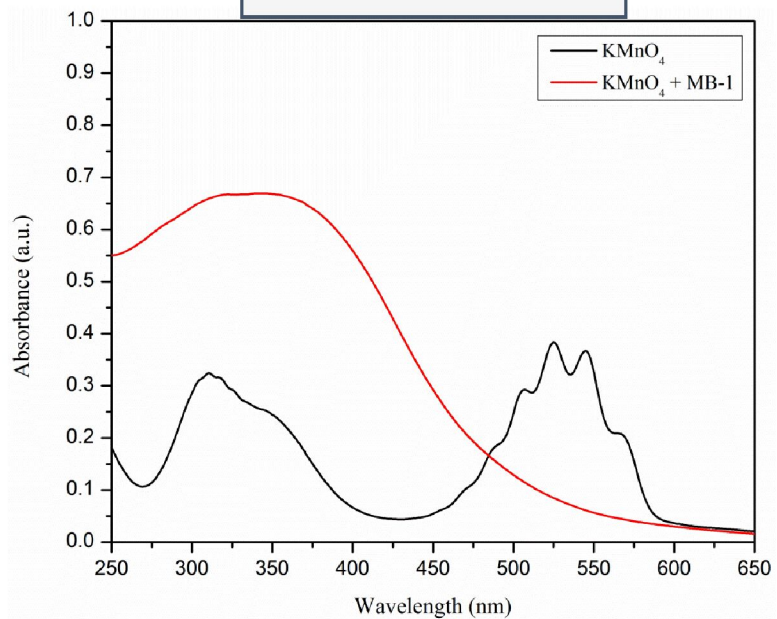


Low concentration of anions

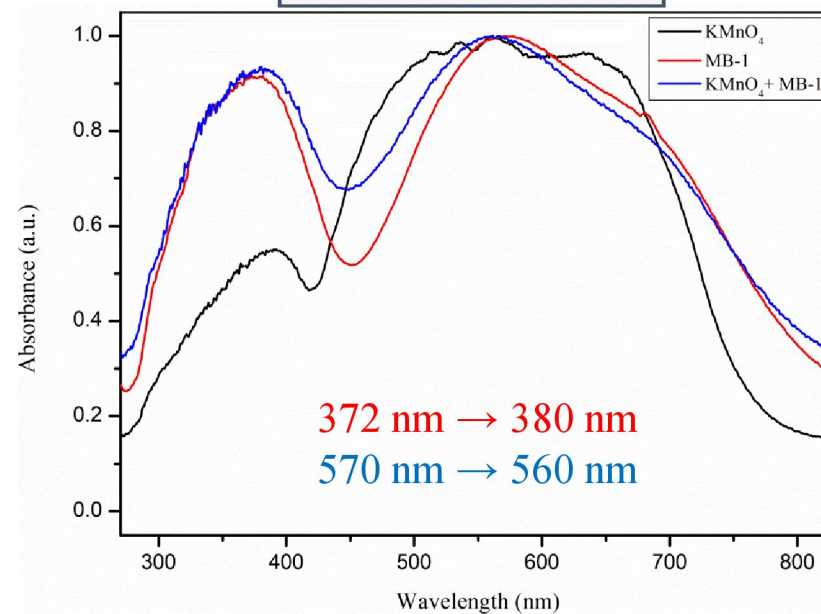
Oxidation of ethylene derivate ligand to vicinal diol



UV-Vis on solution



UV-Vis on solid



KMnO₄ concentration variation

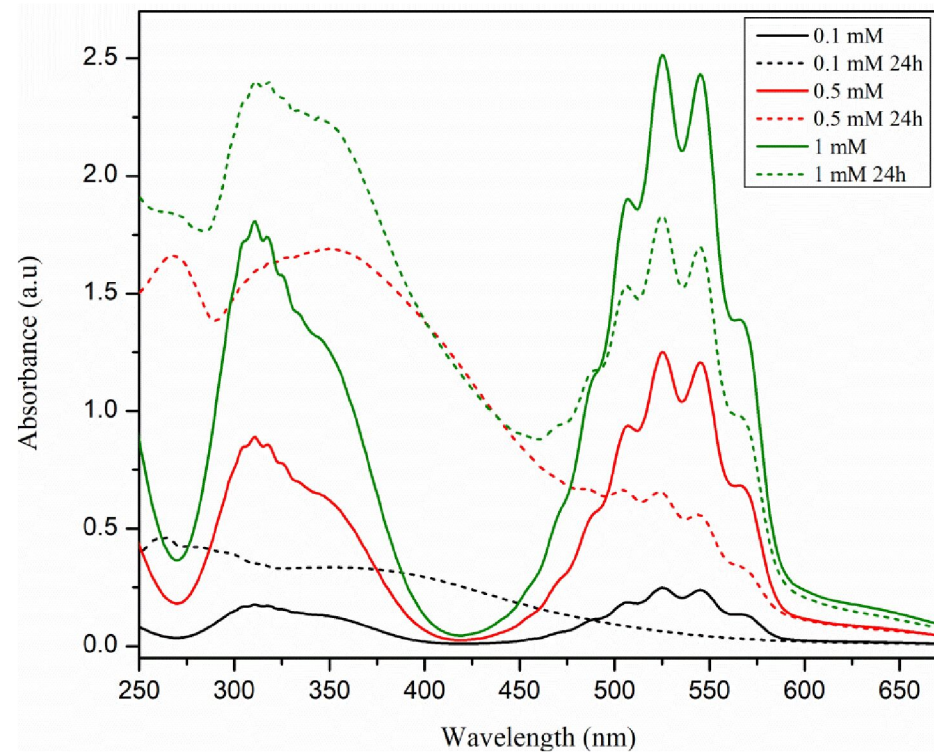


Initial series of KMnO₄ solutions



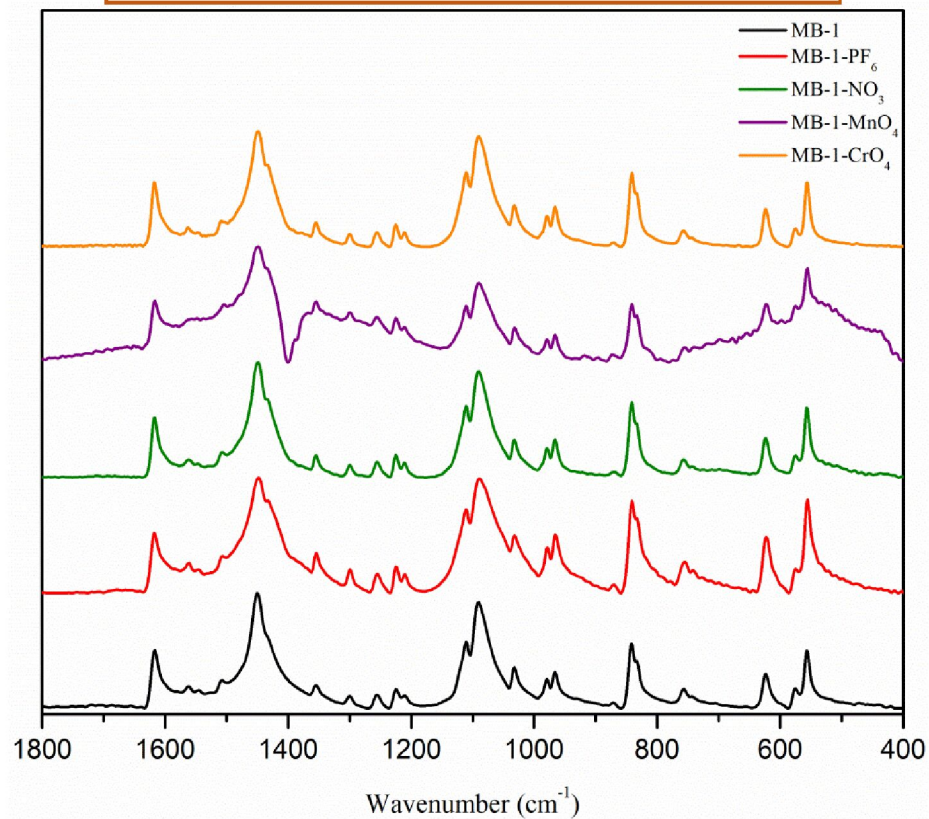
KMnO₄ solutions after 24h of contact with MB-1

UV-Vis on KMnO₄ solutions 0.1-1 mM

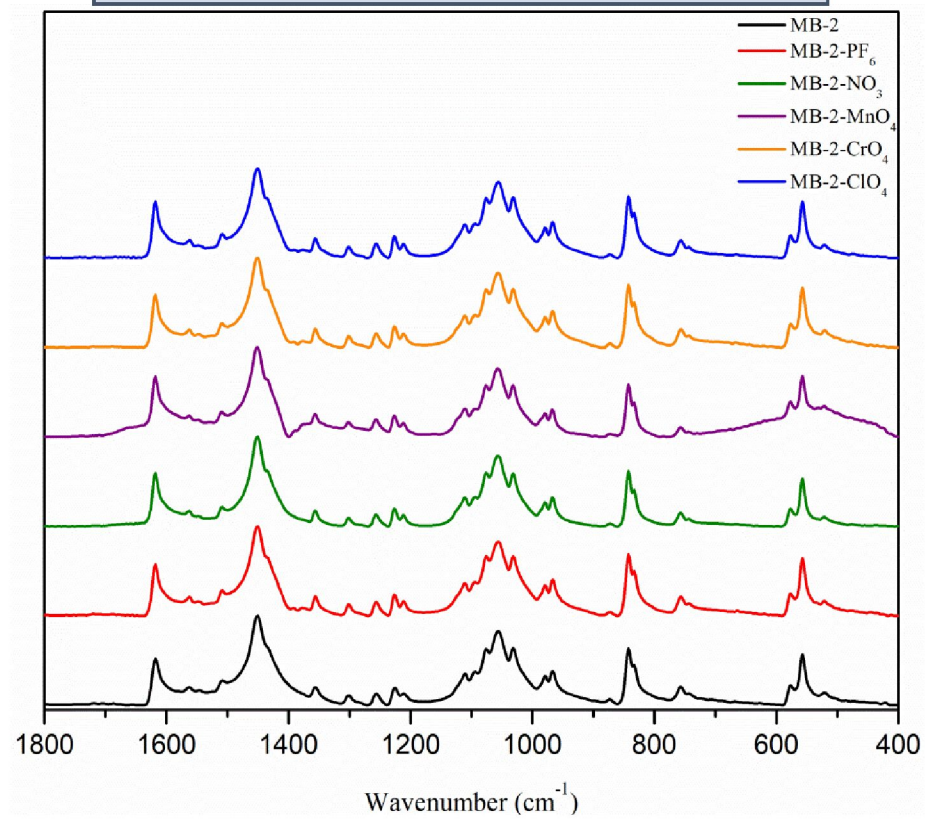


High concentration of anions

FTIR spectra of MB-1 immersed in solutions of different anions



FTIR spectra of MB-2 immersed in solutions of different anions



Conclusions

- ❖ The potential anion-exchange properties of Cu-based coordination polymers were investigated, using both low and high concentration of anions.
- ❖ FTIR spectroscopy and UV-Vis spectroscopy on solid and solution were used to investigate the exchange. It was revealed that at room temperature and atmospheric pressure no anion-exchange occurred, when NO_3^- , PF_6^- , CrO_4^- , or ClO_4^- were employed, regardless of the concentrations used.
- ❖ In the case of MnO_4^- , both visual changes and modifications in the IR and UV-Vis spectra of the compound and solution occurred.
- ❖ These modifications can be explained in terms of chemical oxidation of the 1,2-bis(4-pyridyl)ethylene ligand with permanganate to vicinal diol, chemical transformation supported as well by the presence of colloidal manganese(IV) that is produced following the reaction.
- ❖ The resulting modification of the ligand may be classified as a chemical post-synthetic modification occurred in the presence of MnO_4^- .

Thank you for your attention!

