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Faculty of Chemistry

Crystalline Porous Coordination Polymers with Catalytic & Gas Storage Applications

MSc Thesis – Report II

September 7, 2020

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Master Program: Chemistry of Advanced Materials

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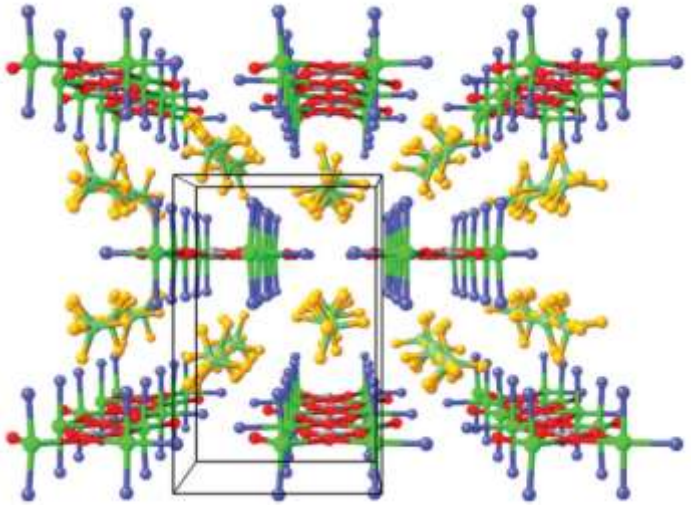
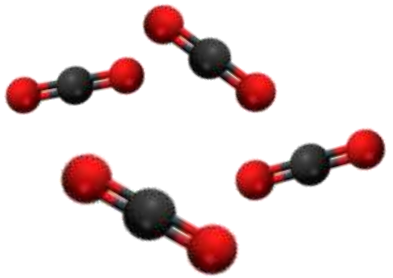
Outline

- Atmospheric CO_2 fixation
- Strategy of synthesis for **P**orous **C**oordination **P**olymers (PCPs)
- Synthesis of Cu-based PCPs with Kagome layers
- Structural and spectral characterization of obtained compounds
- Thermal stability
- Conclusions

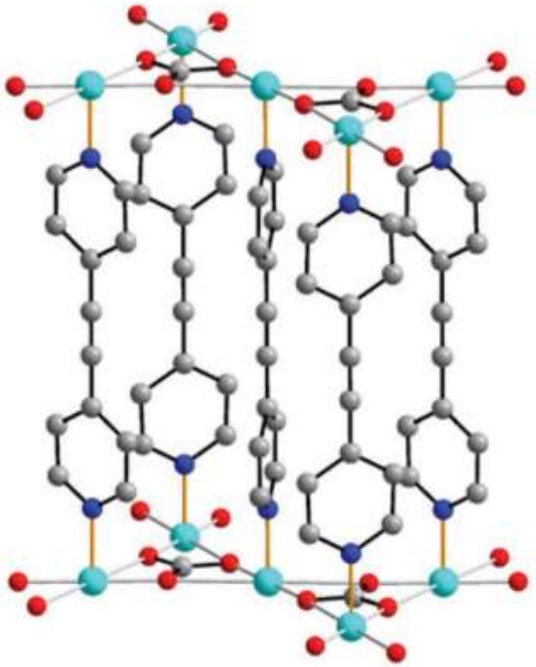
Atmospheric CO_2 fixation





Basic medium

CO_3^{2-}



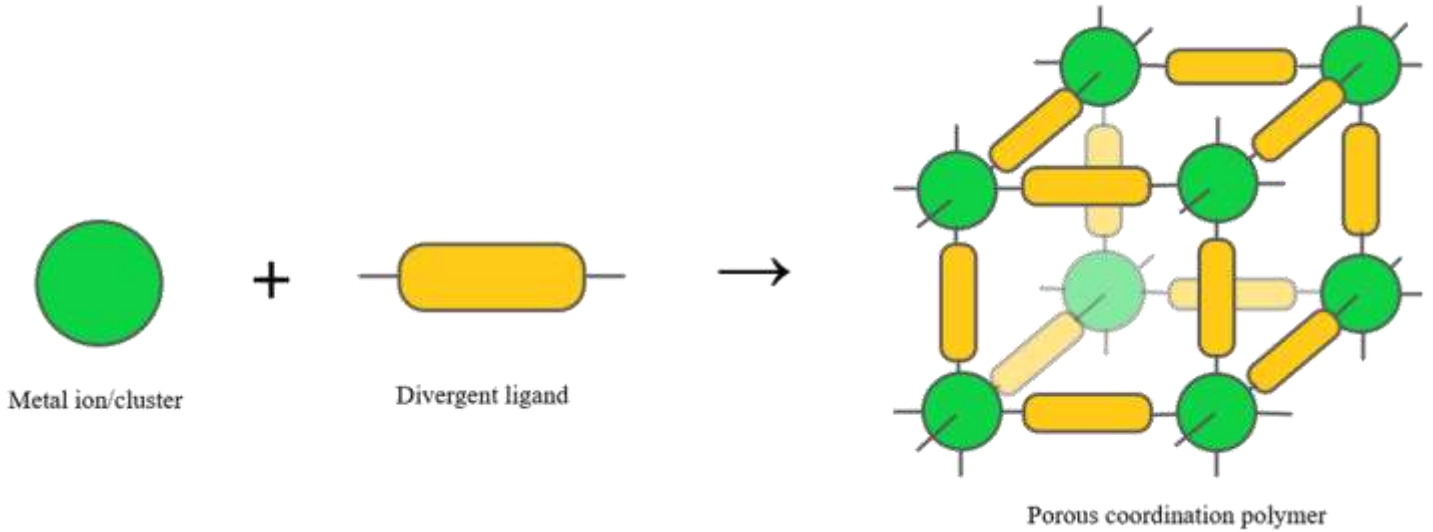
1-D structure

3-D structure

K. Inoue et al., *Dalton Trans.*, 43 (2014), 12974-12981

C.J. Kepert et al., *Dalton Trans.*, 43 (2014), 14766-14771

Strategy of synthesis



Reaction

- Self-assembly
- Room temperature
- Hydrothermal
- Solvothermal

Connectors

- Size
- Stereochemistry (T-shape, trigonal-planar, tetrahedral)

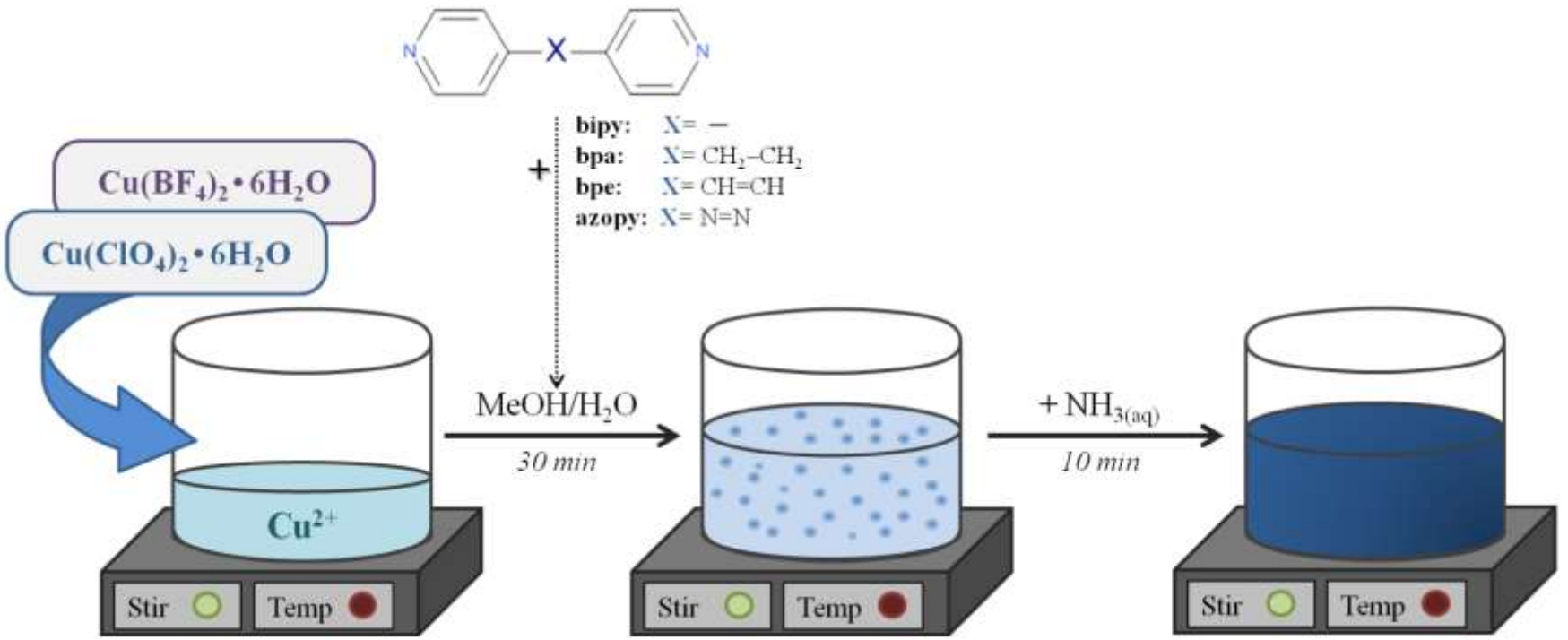
Linkers

- Shape
- Size
- Rigidity
- Charge

Auxiliary

- Counter ions
- Nonbonding guests
- Template molecules

Synthesis of Cu-based PCPs with Kagomé layers



$\{[Cu_3(CO_3)_2(L)_3](Y)_2\}_n$

1. L = bpa, Y=ClO_4 **3.** L = bpe, Y=ClO_4 **5.** L = bipy, Y=ClO_4 **7.** L = azopy, Y=ClO_4

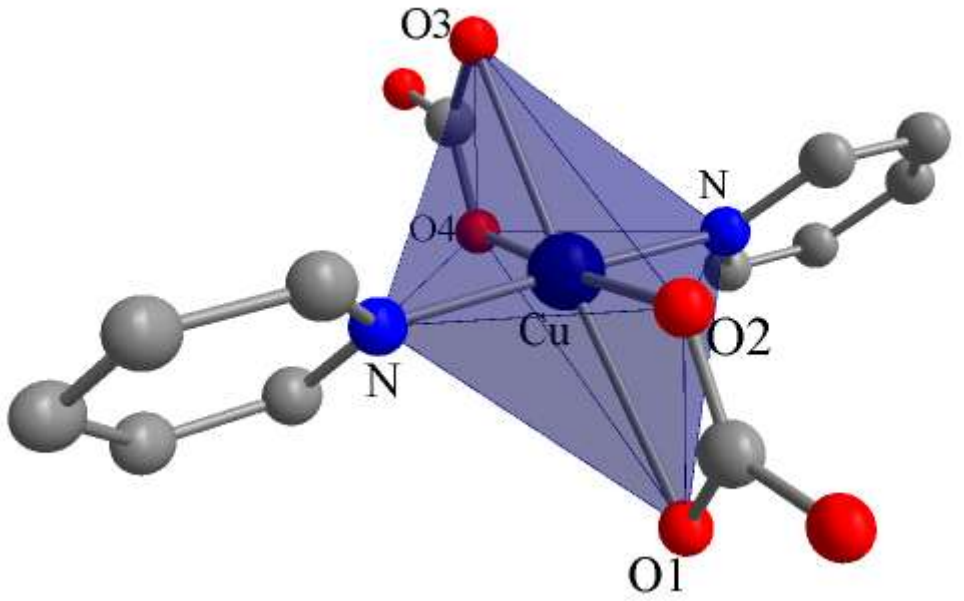
2. L = bpa, Y=BF_4 **4.** L = bpe, Y=BF_4 **6.** L = bipy, Y=BF_4 **8.** L = azopy, Y=BF_4

Structural characterization

***Copper* (II)**

Coordination number = 6

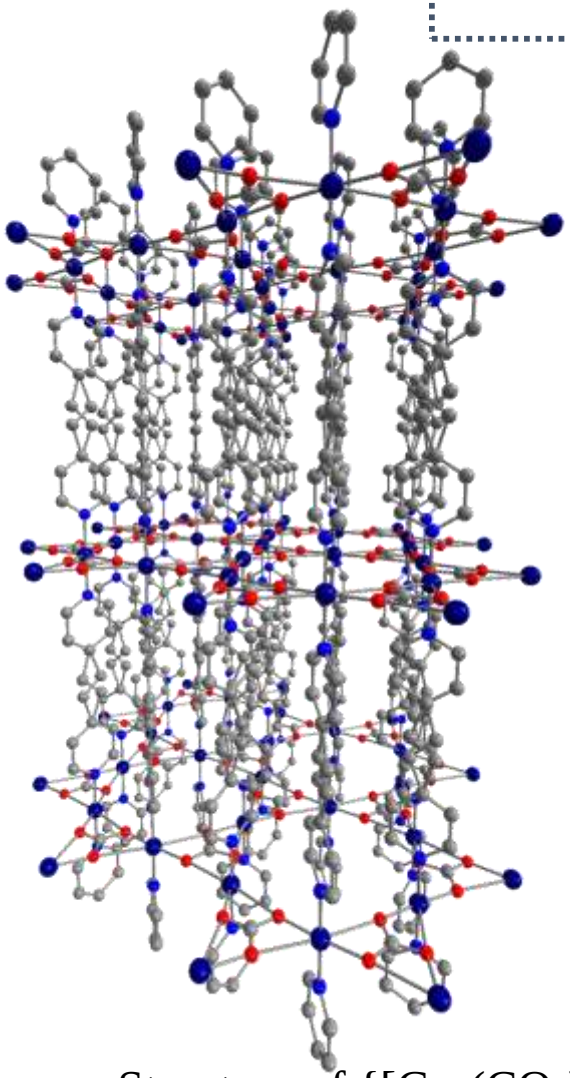
Geometry: distorted octahedron



Specific bond lengths (Å)	
Cu – O(1)	2.721(9)
Cu – O(2)	1.959(7)
Cu – O(3)	2.650(4)
Cu – O(4)	1.968(8)
Cu – N	1.998(5)

Atoms	Angle (º)	Atoms	Angle (º)
O(1) – Cu – O(2)	53.1(3)	**O(2) – Cu – N**	90.0(1)
O(2) – Cu – O(3)	120.5(3)	**O(4) – Cu – N**	90.0(1)
O(3) – Cu – O(4)	54.9(2)	**O(1) – Cu – N**	89.2(1)
O(1) – Cu – O(4)	131.5(3)	**O(3) – Cu – N**	90.8(1)

Structural characterization



Structure of $\{[Cu_3(CO_3)_2(L)_3](Y)_2\}_n$

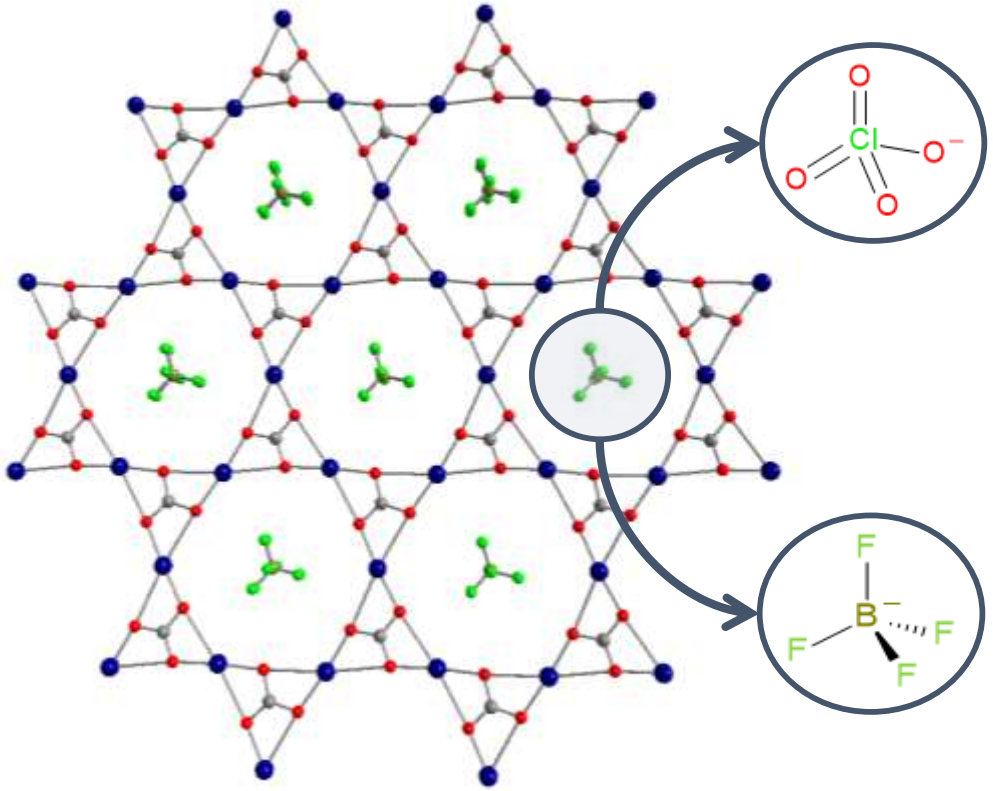
-anions omitted for clarity

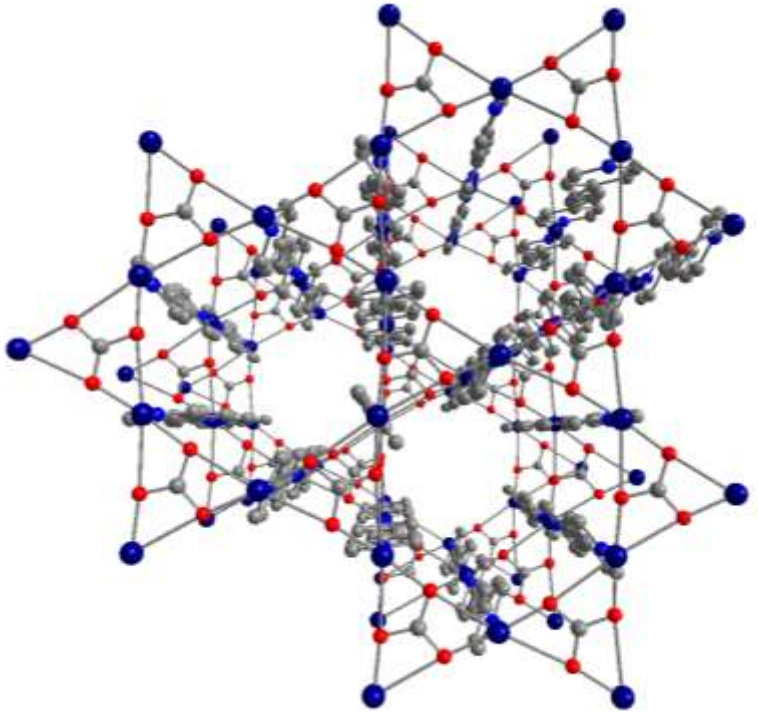
Crystallographic data

Compound	1	3	4	8
Crystal system	hexagonal	hexagonal	hexagonal	hexagonal
Space group	P-6	P-6	P-6	P-6
a (Å)	9.739(7)	9.297(5)	9.275(3)	9.279(6)
b (Å)	9.739(7)	9.297(5)	9.275(3)	9.279(6)
c (Å)	13.367(1)	13.364(8)	13.371(4)	12.960(7)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	120	120	120	120
Volume (Å^3)	1098.1(1)	1000.4(1)	996.2(7)	966.6(1)

Structural characterization

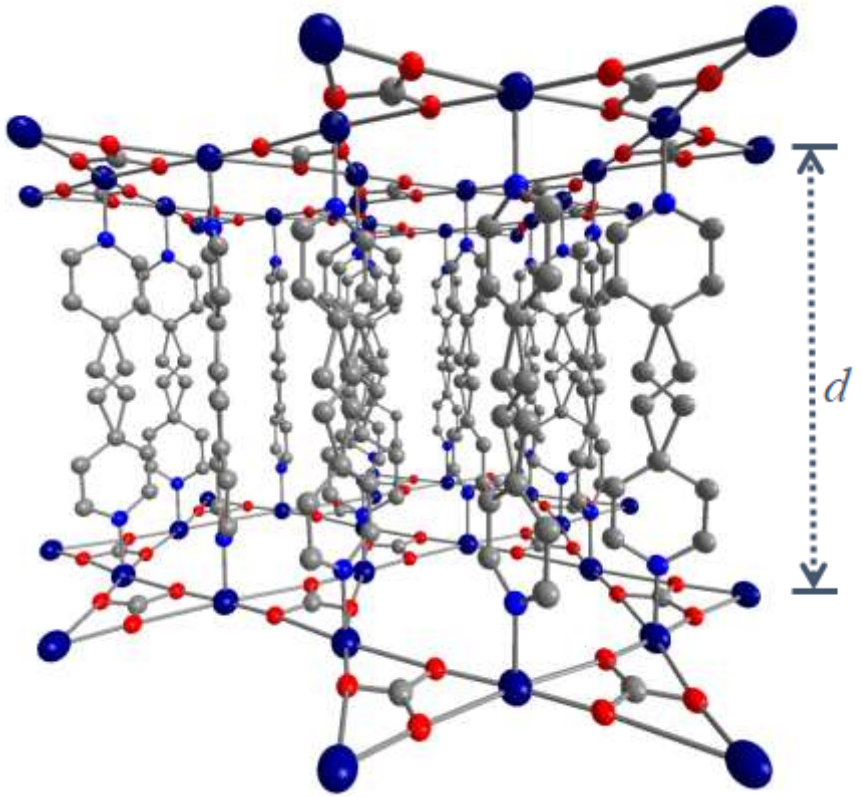
Kagomé layer

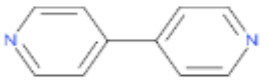
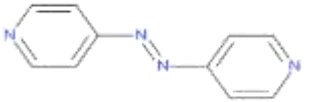
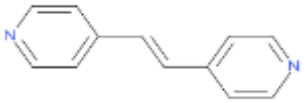
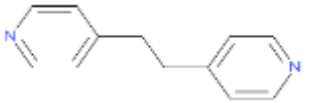




Hexagonal channels
along *c*-axis

Structural characterization

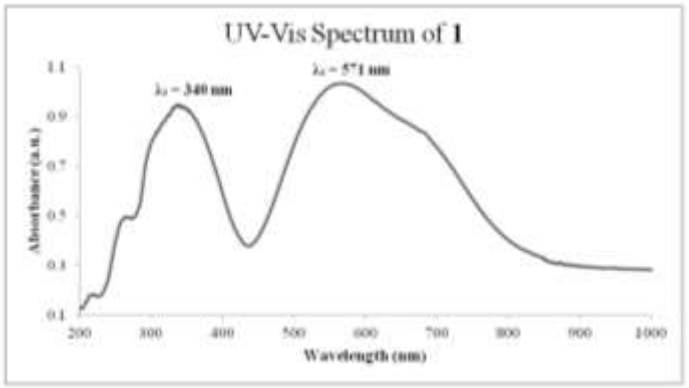


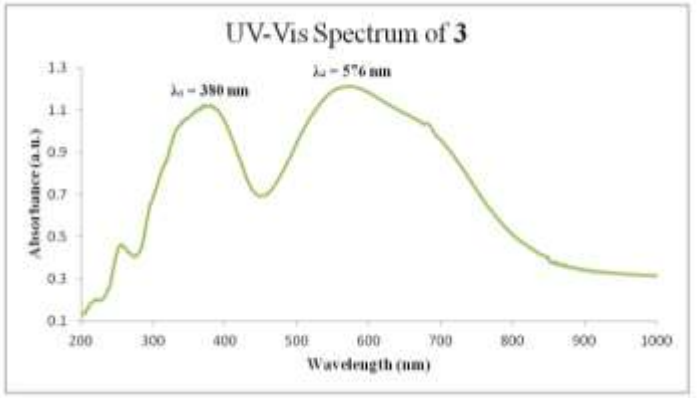
Ligand	Interlayer distance (Å)
 4,4’-bipyridyl	11.104
 4,4’-azopyridine	12.987
 1,2-bis(4-pyridyl)ethylene	13.365
 1,2-bis(4-pyridyl)ethane	13.367
 1,2-bis(4-pyridyl)acetylene	13.603*

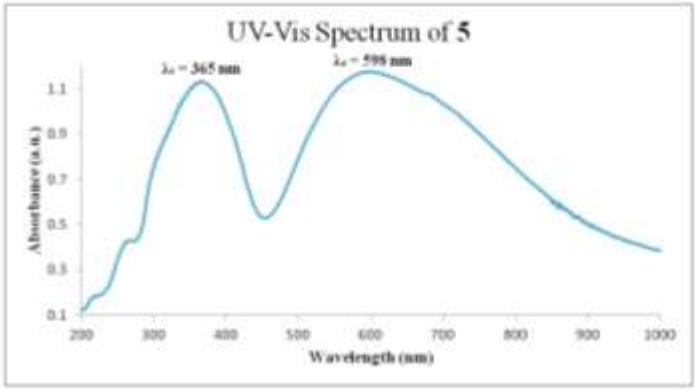
*C.J. Kepert et al., *Dalton Trans.*, 43 (2014), 14766-14771

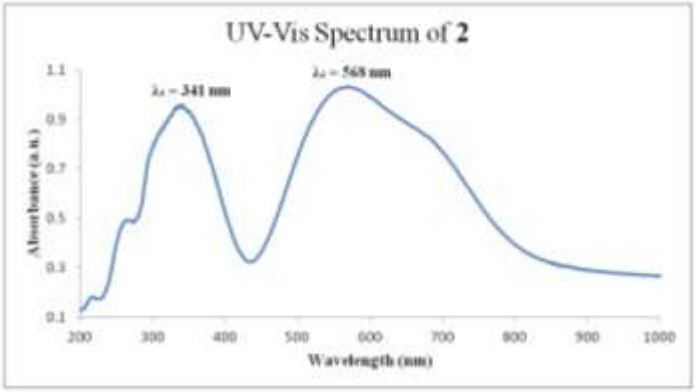
Spectral characterization

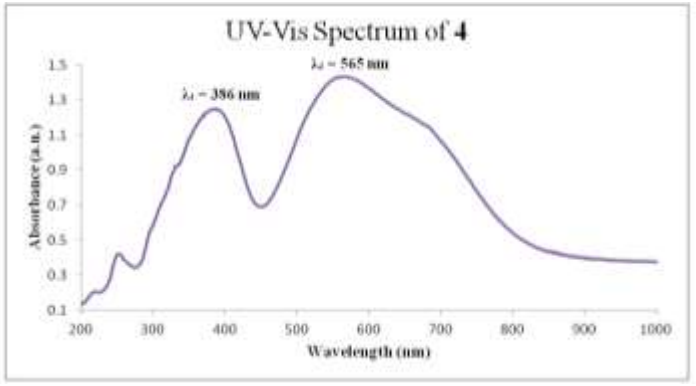
UV-Vis-NIR spectra

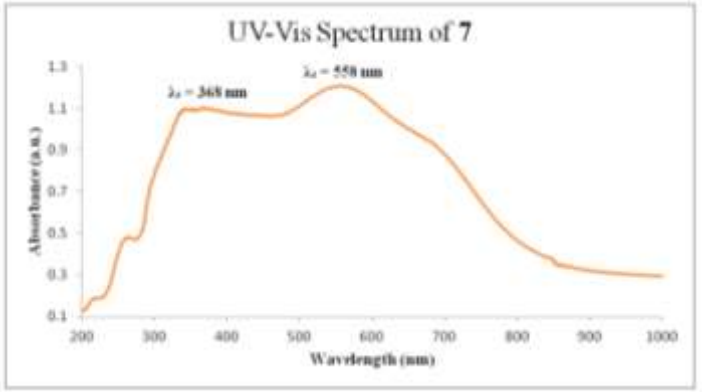




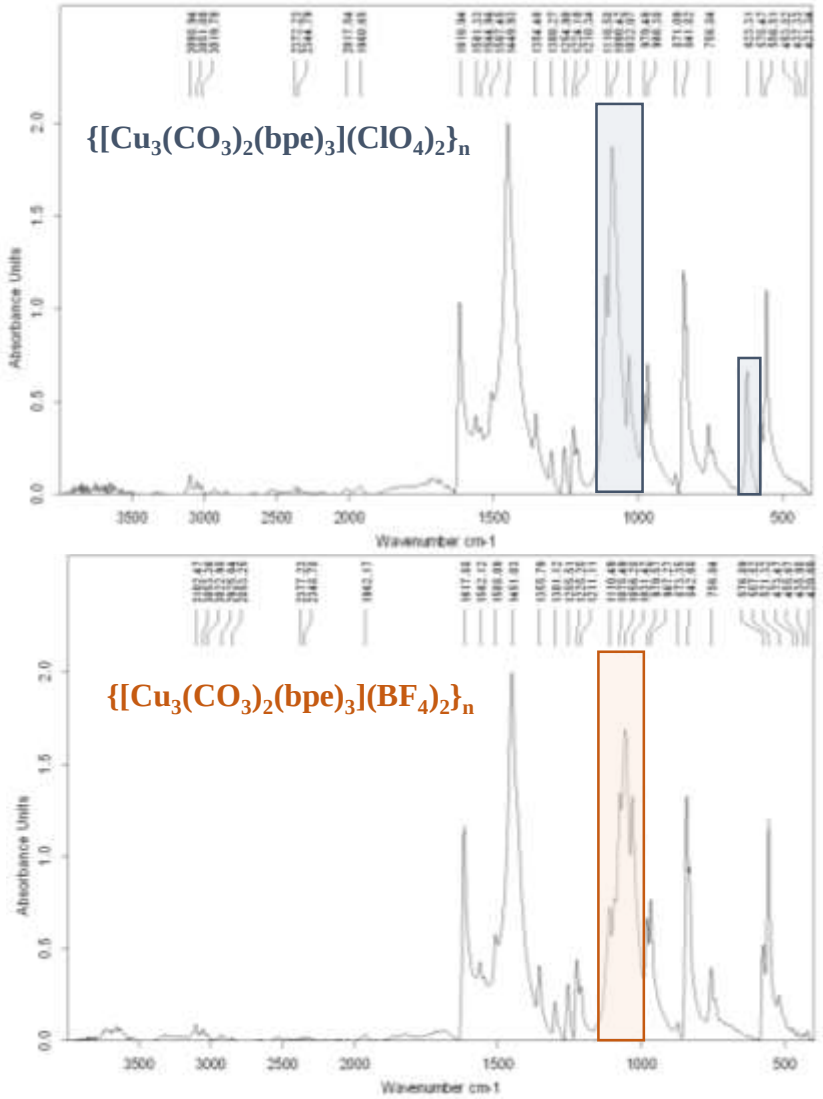








Spectral characterization

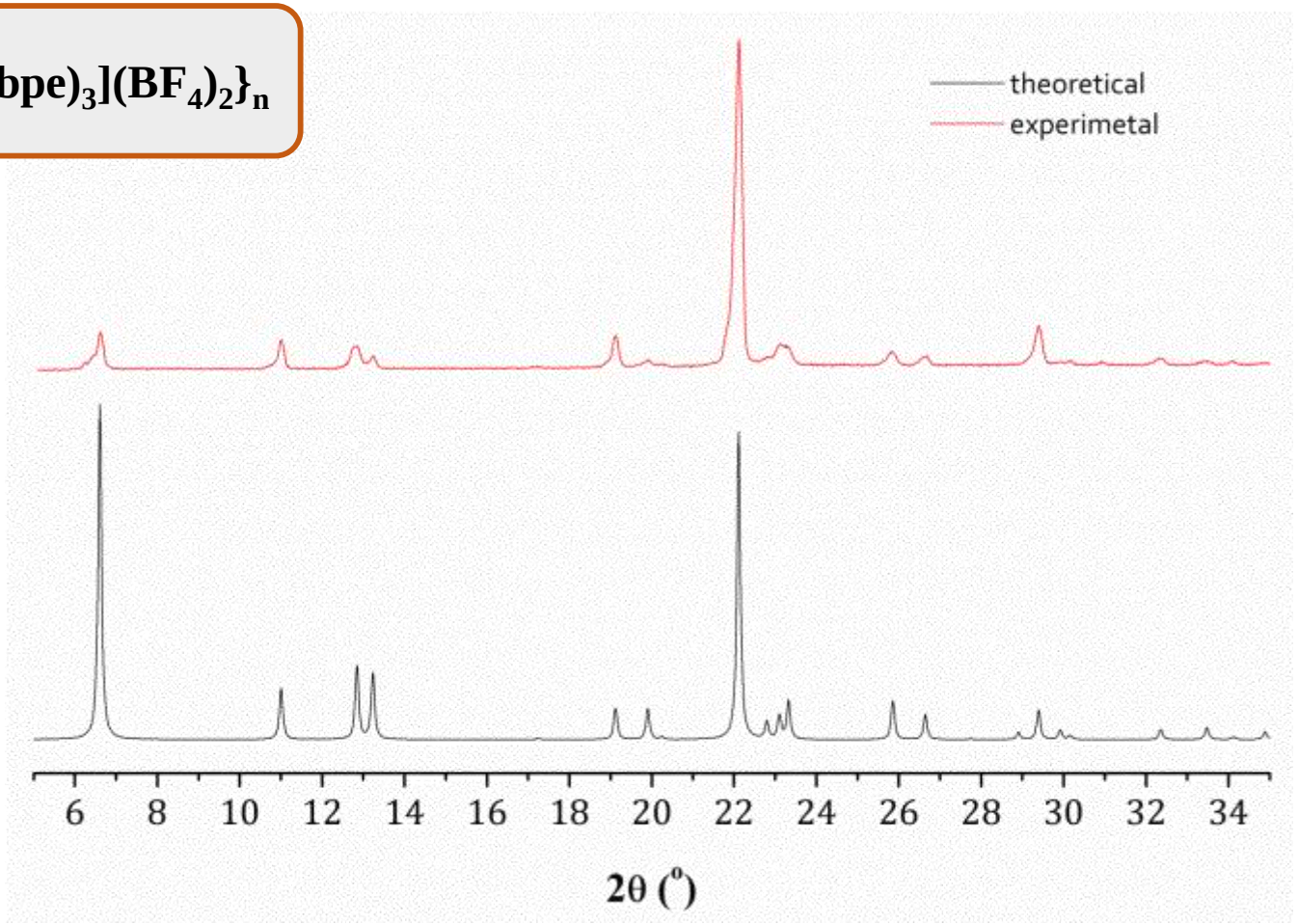


FTIR spectra

Bonds	Compounds						
	1	2	3	4	5	7	8
ν COO^-	1619 (m)	1619 (m)	1616 (m)	1617 (m)	1613 (m)	1608 (m)	1609 (m)
ν C=N ν C=C	1442 (s) 1345 (w) 1235 (w) 840 (m)	1444 (s) 1347 (w) 1236 (w) 875 (m)	1449 (s) 1300 (w) 1254 (w) 871 (m)	1451 (s) 1301 (w) 1255 (w) 873 (m)	1438 (s) 1327 (w) 1228 (m) 820 (s)	1449 (s) 1329 (w) 1237 (w) 861 (m)	1450 (s) 1331 (w) 1237 (w) 862 (m)
ν BF_4^-	–	1054 (s)	–	1075 (s)	–	–	1064 (s)
ν ClO_4^-	1087 (s), 623 (m)	–	1090 (s), 623 (m)	–	1092 (s), 624 (m)	1084 (s), 622 (m)	–
ν Cu-O	546 (m)	547 (m)	556 (m)	557 (m)	481 (w)	576 (m)	578 (m)
ν Cu-N	447 (w)	434 (w)	437 (w)	436 (w)	436 (w)	445 (w)	434 (w)

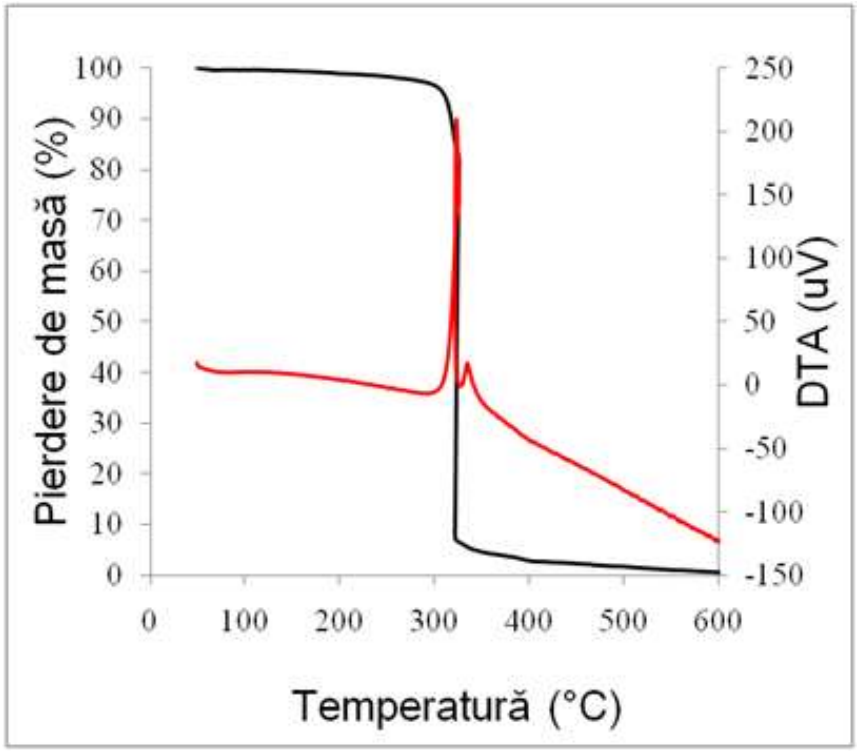
Powder X-ray diffraction

$\{[Cu_3(CO_3)_2(bpe)_3](BF_4)_2\}_n$

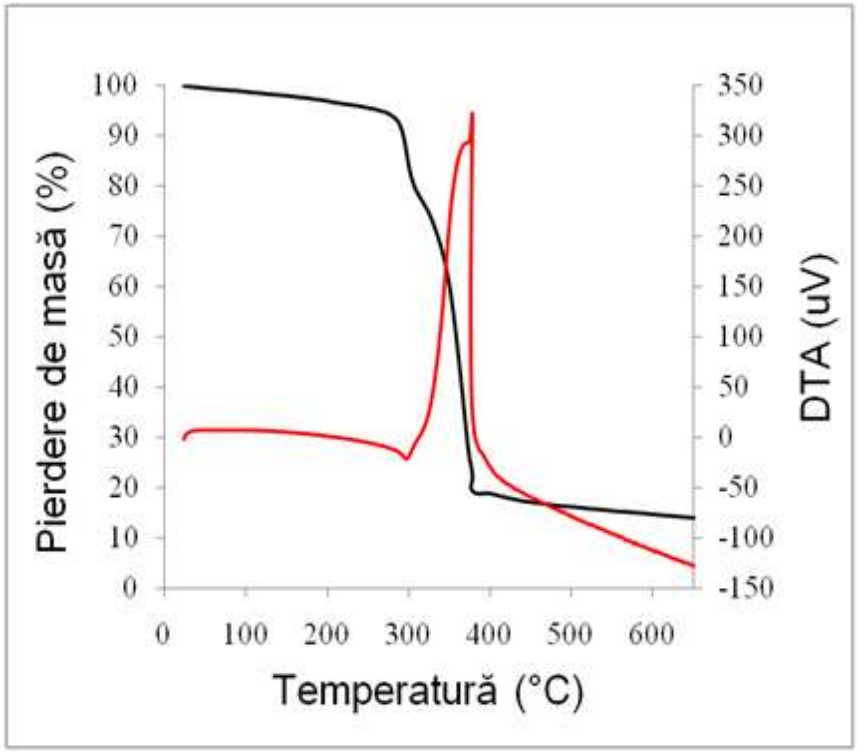


Thermal Analysis

$\{[Cu_3(CO_3)_2(bpe)_3](ClO_4)_2\}_n$



$\{[Cu_3(CO_3)_2(bpe)_3](BF_4)_2\}_n$



Conclusions

- A series of 3-D isostructural Cu(II)-based coordination polymers consisting of 2-D Cu(CO_3) Kagomé lattices were obtained.
- Different spectroscopic techniques, such as FTIR and UV-Vis in solid state, single crystal and powder X-ray diffractions, as well as thermal analysis were used to characterize the obtained compounds.
- The single crystal X-ray diffraction revealed, through direct fixation of atmospheric CO_2, the formation of Kagomé layers which are linked one to another via bypiridine-based ligands. The 2-D Cu(CO_3) Kagomé layers are stacked directly over each other to form hexagonal channels along the *c*-axis.
- The influence of various exo-bidentate diamine ligands on the distance between Kagomé layers was investigated.
- The thermal decomposition shown a thermal stability up to approximately 300 °C in the case of $\{[Cu_3(CO_3)_2(bpe)_3](ClO_4)_2\}_n$ and $\{[Cu_3(CO_3)_2(bpe)_3](BF_4)_2\}_n$.

Thank you for your attention!