

## Article

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# Three Cationic Non-Porous Cu<sup>I</sup>-Coordination Polymers: Structural Investigation and Vapor Iodine Capture

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## ABSTRACT

Three cationic non-porous copper(I) coordination polymers containing bis-pyrazolyl flexible ligands have been prepared and characterized, namely  $\{[\text{Cu}(\mu\text{-bdb})_{1.5}](\text{PF}_6)]_n$  (**1**),  $\{[\text{Cu}(\mu\text{-bpb})_2](\text{PF}_6)]_n$  (**2**) and  $\{[\text{Cu}(\mu\text{-bpmb})_2](\text{PF}_6)]_n$  (**3**) (bdb = 1,4-bis(3,5-dimethylpyrazolyl) methyl)benzene; bpb = 1,4-bis(pyrazolyl)butane; bpmb = 1,4-bis(pyrazolyl) methyl)benzene). All compounds were characterized by IR, PXRD, elemental and thermal analyses, and single-crystal X-ray diffraction. Compound **1**, with methyl-substituted pyrazolyl ligand, forms a chain of alternating rings and ribbons in which the copper(I) centers are three coordinated in distorted trigonal planar geometry. In compounds **2** and **3** copper(I) atoms adopt distorted tetrahedral geometries giving two dimensional sheet structures with 4<sup>4</sup>-**sql** topology. Interestingly, iodine sorption experiments show that colorless crystals of **2** and **3** remain unchanged in the presence of iodine vapors, while the three coordinated compound **1** immediately absorb iodine and turn dark. Anion exchange behavior of compounds **1** and **2** was also investigated both in solution and in solid state.

**Keywords:** Copper(I), coordination polymer, non-porous, gaseous iodine capture, non-coordinating anion.

## INTRODUCTION

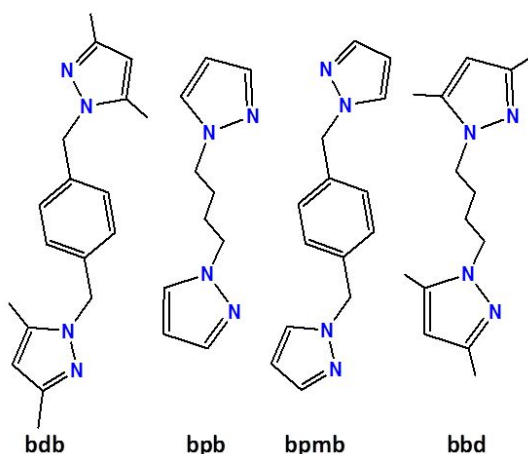
Coordination polymers (CPs) and their unique subclass of metal organic frameworks (MOFs), belong to an interesting category of crystalline materials that is growing exponentially during the past three decades.<sup>1-3</sup> Their structures are composed of organic linkers and metal ions or clusters nodes. Remarkable variety of structures and properties, ease of tailorability and wide range of applications, ranging from gas storage and separation to catalytic processes, electronic devices and biomedicine, made this category of materials one of the most exciting area of research and attracted many scientists.<sup>4-6</sup>

Considering coordination ability of copper atoms, it can be observed that copper(II) ions often form multinuclear Cu-carboxylate clusters through coordination to oxygen atoms of carboxylic ligands.<sup>7-9</sup> On the other hand copper(I) ions often form copper halides aggregates and, among them, especially  $\text{Cu}_n\text{I}_n$  clusters. A variety of copper(I) iodide-based structures with fascinating building blocks have been reported so far.<sup>10-14</sup> The intense investigation in this research field is not only due to this structural variety, but also to the unique properties of copper(I) iodide aggregates, such as luminescence,<sup>14-17</sup> catalytic activity,<sup>18,19</sup> iodine sorption<sup>12,20,21</sup> and others. Despite polymeric structures for copper(I) halides or pseudohalides are well known and investigated, CPs or MOFs made of copper(I) in the presence of non-coordinating anions, such as  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ , and  $\text{SbF}_6^-$ , are still rare and need to be explored more.<sup>22-26</sup> Highly coordinating halides often act as the structure directing factor in the assembly of polymeric copper(I) halide compounds, thus preventing Cu(I) to fully exploit its coordination ability. Hence, the use of non-coordinating anions, allow copper(I) to exhibit variable coordination number and geometry.

Alongside the role of metal ions and coordinating ability of counterions, the structure of coordination polymers are influenced also by other factors, such as the geometry of polydentate linker ligands, crystallization solvent, metal to ligand ratio and synthetic procedure.<sup>27-29</sup> Moreover, factors such as flexibility, steric hindrance, position of donor atoms, spacer group of the linkers and participation of ligands in non-covalent  $\pi\cdots\pi$  stacking interactions and hydrogen bonds also play important roles in the generation of novel structures and properties.<sup>30-32</sup>

Among possible applications for CPs and MOFs attractive is the adsorption of environmentally harmful pollutants.<sup>33-35</sup> In particular capture and isolation of radioactive iodine isotopes from the waste of nuclear power plants is an important subject.<sup>36-38</sup> Because the high fission yield of

iodine, it can spread as volatile species in environment and readily accumulates in the thyroid. The result is the major changes in human metabolic processes and may causes thyroid cancer. Recently, adsorption of iodine into the pores of various MOFs have been reported by many researchers, however, most of such investigations are conducted in solution only.<sup>39-43</sup> Iodine sorption studies in the vapor phase by non-porous coordination polymers are still rare and need to be explored well.<sup>44</sup> Our recent research results show that even non-porous CuI-based coordination polymers can rapidly capture volatile iodine in the gas phase.<sup>45</sup> On the basis of our experience on the design and synthesis of copper(I) coordination polymers,<sup>23,27,46-49</sup> here we investigated the effect of different bispyrazolyl ligands (Scheme 1) on the assembly of non-porous coordination polymers of copper(I) hexafluorophosphate, and characterized three novel compounds. In addition, vapor iodine absorption ability by the synthesized compounds was checked and related to their structure features.



**Scheme 1.** Structure of the bispyrazolyl linker ligands.

## EXPERIMENTAL SECTION

### Materials and Instrumentation

All experiments were carried out in air. The starting materials were purchased from commercial sources and used without further purification;  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  was prepared by published method.<sup>50</sup> The infrared spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded as KBr discs with BOMEN MB102 FT-IR or Perkin Elmer Spectrum two spectrometers. The elemental analyses for C, H

and N were performed on a Costech-ECS 4010 CHNSO analyzer. X-ray powder diffraction patterns were recorded on a Philips X'Pert Pro diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.54184$  Å) in the  $2\theta$  range 5–35(50)°. Simulated XRD powder patterns, based on single crystal X-ray diffraction data, were prepared using Mercury software.<sup>51</sup> Energy dispersive X-ray (EDX) spectroscopy was carried out using an EDX-coupled electron microscope (VEGA 3-TESCAN). Thermogravimetric analyses (TGA) were carried out on a STA PT1600 (Linseis) thermal analyzer between 50 and 600 °C under N<sub>2</sub> atmosphere. UV-Vis spectra were recorded on a Jenway 6715 spectrophotometer in EtOH solution in the range of 300–700 nm.

## Synthetic Procedures

**Preparation of bpmb, bdb, and bpb Ligands:** The ligands were prepared according to published methods.<sup>52–55</sup> Typically, a mixture of pyrazole (1.36 g, 20 mmol) or 3,5-dimethylpyrazole (1.92 g, 20 mmol) and finely powdered potassium hydroxide (2.24 g, 40 mmol) in DMSO (12 mL) were vigorously stirred at 80 °C for 2 h. Then, corresponding dihalides 1,4-bis(chloromethyl)benzene (1.64 g, 10 mmol) or 1,4-dichlorobutane (1.11 mL, 10 mmol) in DMSO (5 mL) was added dropwise to the slurry mixture. The mixture was stirred at 80 °C until completion of the reaction (checked by TLC), cooled to room temperature and then to 0°C in an ice bath. 250 mL of cooled water was poured into the reaction mixture and a precipitate formed immediately, which was collected by filtration, washed with water and dried under vacuum. In the case of bpb, as the product is a liquid, the reaction mixture was poured into water (250 mL) and extracted with chloroform (3×20 mL). The extract was washed with water (2×20 mL) and dried over calcium chloride. After evaporation of chloroform under vacuum, the product was isolated as a yellow oil.

## Preparation of {[Cu( $\mu$ -bdb)<sub>1.5</sub>](PF<sub>6</sub>)<sub>n</sub>} (1)

A solution of bdb (0.02 g, 0.08 mmol) in CH<sub>3</sub>OH (5 mL) was gently layered on the top of a solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>) (0.015 g, 0.04 mmol) in CH<sub>3</sub>CN (5 mL) in a test tube. Fern leaf-shaped crystals of **1**, suitable for X-ray crystallography, were obtained after a week. They were collected and washed with small amounts of EtOH and Et<sub>2</sub>O and dried in air. (0.021g, 80.7% yield based on Cu). Anal. Calcd for C<sub>27</sub>H<sub>33</sub>CuF<sub>6</sub>N<sub>6</sub>P: C 49.88, H 5.12, N 12.93; Found: C 50.74, H 5.58, N 13.19%.

### Preparation of $\{[\text{Cu}(\mu\text{-bpb})_2](\text{PF}_6)\}_n$ (**2**)

A solution of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (0.2 g, 0.54 mmol) in  $\text{CH}_3\text{CN}$  (25 mL) was added to a solution of bpb (0.2 g, 1.0 mmol) in  $\text{CH}_3\text{CN}$  (25 mL). The reaction mixture was stirred at room temperature for 6 h and the resulting mixture was filtered. Pale blue cubic single crystals of **2** suitable for X-ray crystallography were obtained at room temperature by slow evaporation of the solvent after a week. The crystals were collected and dried in air. (0.17g, 53% yield based on Cu). Anal. Calcd for  $\text{C}_{20}\text{H}_{28}\text{CuN}_8\text{F}_6\text{P}$ : C 40.78, H 4.79, N 19.03; Found: C 40.60, H 4.67, N 19.37%.

### Preparation of $\{[\text{Cu}(\mu\text{-bpmb})_2](\text{PF}_6)\}_n$ (**3**)

A solution of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (0.2 g, 0.54 mmol) in  $\text{CH}_3\text{CN}$  (20 mL) was added to a solution of bpmb (0.254 g, 1.06 mmol) in  $\text{CH}_3\text{CN}$  (20 mL). The reaction mixture was stirred at room temperature for 6 h and then it was filtered. Colorless cubic single crystals of **3** suitable for X-ray crystallography were obtained at room temperature by slow evaporation of the solvent after two weeks. The crystals were collected and washed with small amounts of EtOH and  $\text{Et}_2\text{O}$  and dried in air. (0.31g, 85.0% yield based on Cu). Anal. Calcd for  $\text{C}_{28}\text{H}_{28}\text{CuF}_6\text{N}_8\text{P}$ : C 49.09, H 4.12, N 16.36; Found: C 49.43, H 4.18, N 16.52%.

### Iodine Sorption Study

Crystals of coordination polymers **1-3** and  $\{[\text{Cu}(\mu\text{-bbd})_{1.5}](\text{PF}_6)\}_n$  (refcode **KEZXEU**) and solid iodine were added separately into small vials. The vials were placed into a large vessel, sealed, and heated at 55°C for three different exposure times, 30 min, 50 min and 2 h. Color of the crystals **1** and **KEZXEU** changed immediately to brown, while the color of samples **2** and **3** remained unchanged. The iodine adsorbed samples were collected, washed with cyclohexane, dried in air, and weighed.

### Iodine Release Study

Certain amounts of iodine-adsorbed samples **1-I<sub>2</sub>** and **KEZXEU-I<sub>2</sub>** were suspended in 2 ml of EtOH. The color of the solvent change gradually from light yellow to dark orange. To ensure the completion of the release process, the samples were left in EtOH for 1 day. Solid materials of compounds **1** and **KEZXEU** were recovered by filtration, washed with pure ethanol,  $\text{Et}_2\text{O}$ , dried

in air and identified by FT-IR and PXRD analyses. To determine the iodine content of the samples, released iodine solutions were diluted in 10 ml volumetric flasks and used for UV-Vis spectroscopic measurements at 358 nm.

### Anion Exchange in Solution

Finely powdered samples of **1** and **2** (0.1 mmol) were suspended in 30 mL of aqueous solutions containing, respectively, KSCN (0.005 M), KI (1.0 M), NaClO<sub>4</sub> (1.0 M) and NaBF<sub>4</sub> (1.0 M) and the mixtures were stirred at room temperature for 1 day. The resulting anion-exchanged solids were separated by centrifugation and washed several times with water, EtOH and Et<sub>2</sub>O. After drying in air the exchanged solids were identified by FT-IR and PXRD analysis.

### Anion Exchange in the Solid State

Mixtures of colorless powder of compounds **1** or **2** (0.1 mmol) with, respectively, KSCN, KI, NaClO<sub>4</sub> or NaBF<sub>4</sub> (0.1 mmol) were finely grinded in an agate mortar at room temperature for 30 min. The resulting products were washed several times with water, EtOH and Et<sub>2</sub>O, dried in air and then identified by FT-IR and PXRD analysis.

### X-ray Crystallographic Study

X-ray data were collected on a Bruker Apex II diffractometer using MoK $\alpha$  radiation. The structures were solved using direct methods and refined using a full-matrix least squares procedure based on F<sup>2</sup> using all data.<sup>56</sup> Hydrogen atoms were placed at geometrically estimated positions. Details relating to the crystals and the structural refinements are presented in Table 1. Full details of crystal data and structure refinements, in CIF format, are available as Supplementary Information. CCDC reference numbers 1824721-1824723 for **1**, **2**, and **3**, respectively.

**Table 1.** Crystallographic data and structure refinement details for **1-3**.

Compound	1	2	3
Formula	C <sub>27</sub> H <sub>33</sub> CuN <sub>6</sub> F <sub>6</sub> P	C <sub>20</sub> H <sub>28</sub> CuN <sub>8</sub> F <sub>6</sub> P	C <sub>28</sub> H <sub>28</sub> CuN <sub>8</sub> F <sub>6</sub> P
Formula mass	650.10	589.02	685.09
<i>T</i> (K)	293	293	293
Cryst syst	triclinic	tetragonal	tetragonal
space group	<i>P</i> -1	<i>P</i> 4/ <i>n</i>	<i>P</i> 4/ <i>n</i>
<i>a</i> (Å)	10.3544(8)	12.5954(7)	13.616(3)
<i>b</i> (Å)	11.5905(9))	12.5954(7)	13.616(3)
<i>c</i> (Å)	13.8724(11)	7.9766(9)	7.984(3)
$\alpha(^{\circ})$	70.766(1)	90.	90.
$\beta(^{\circ})$	79.152(1)	90.	90.
$\gamma(^{\circ})$	89.788(1)	90.	90.
<i>V</i> (Å <sup>3</sup> )	1540.8(2)	1265.4(2)	1480.2(9)
<i>Z</i>	2	2	2
<i>D</i> calcd (g cm <sup>-3</sup> )	1.401	1.546	1.537
no. of reflns collected	30990	19496	18442
no. of independentreflns	7366	2079	1685
<i>R</i> <sub>int</sub>	0.033	0.018	0.045
R1[ <i>I</i> > 2σ( <i>I</i> )]	0.0509	0.0378	0.0435
wR <sub>2</sub> (all data)	0.1523	0.1115	0.1246

RESULTS AND DISCUSSION

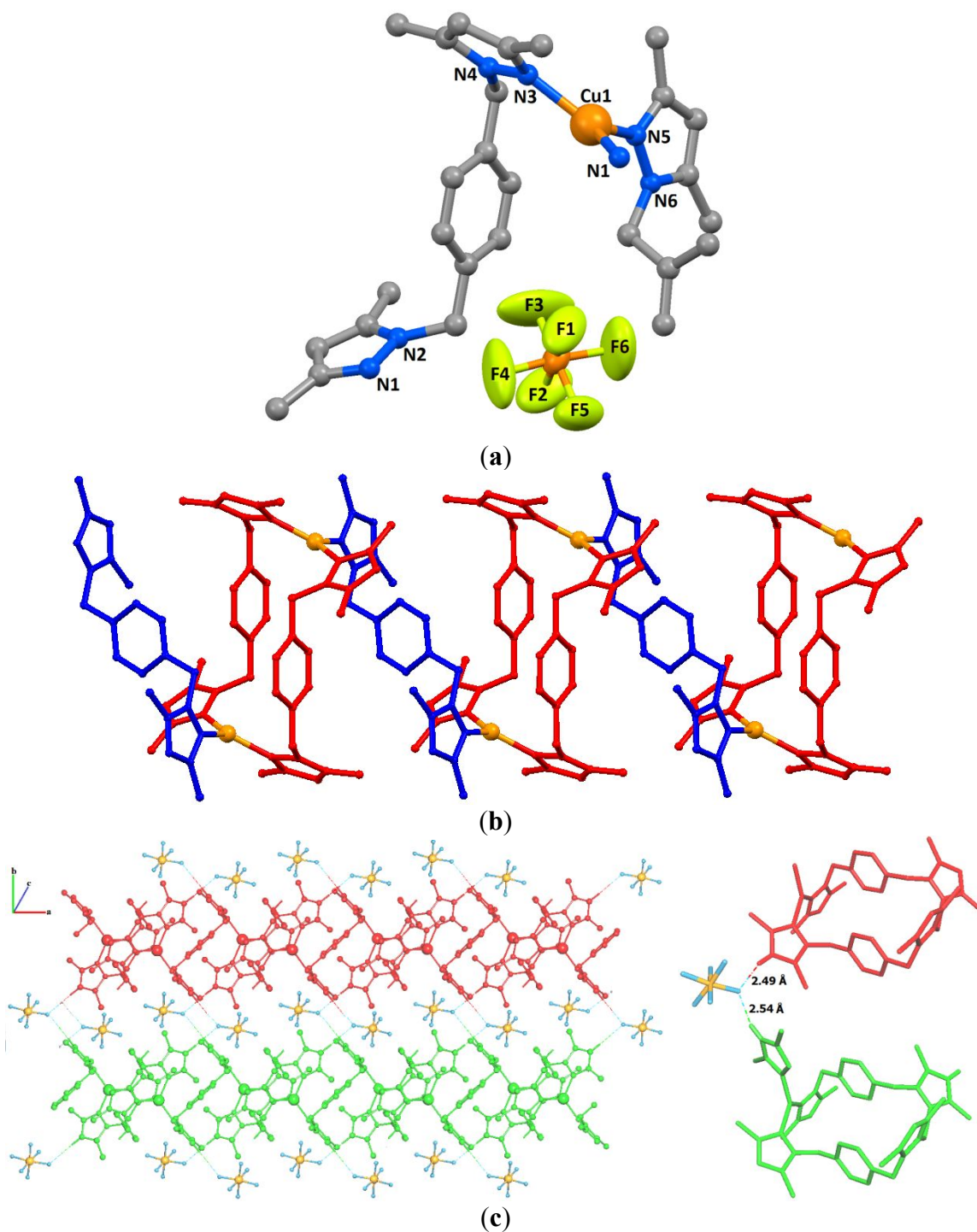
**Synthesis of Complexes 1-3.** We set out to investigate the structural influence of the ligand geometry on the topology of the resultant copper(I) coordination polymers. For this purpose, we have prepared three bidentate pyrazolyl-based ligands and tuned their structures by varying the spacer group and pyrazolyl ring substituents (Scheme 1). In addition, we also used our related reported structure, {[Cu(μ-bbd)<sub>1.5</sub>](PF<sub>6</sub>)}<sub>n</sub> (refcode **KEZXEU**), for comparison.<sup>23</sup> To accurately evaluate the effect of the geometry of the linkers on the structure of the assembled products, and to avoid side effects of the counter anion, we have used Cu(I) salt of the non-coordinating hexafluorophosphate (PF<sub>6</sub><sup>-</sup>) anion. The reactions of [Cu(CH<sub>3</sub>CN)<sub>4</sub>][PF<sub>6</sub>] with bpb, bdb and bpmb ligands in the 1:2 molar ratio produced three novel compounds which are almost stable in air and moisture. Characterization by elemental analyses, FT-IR spectroscopy, PXRD and single-crystal X-ray diffraction show one and two-dimensional polymeric structures for the three compounds.



## Description of the Crystal Structures

### $\{[\text{Cu}(\mu\text{-bdb})_{1.5}](\text{PF}_6)]_n$ (**1**)

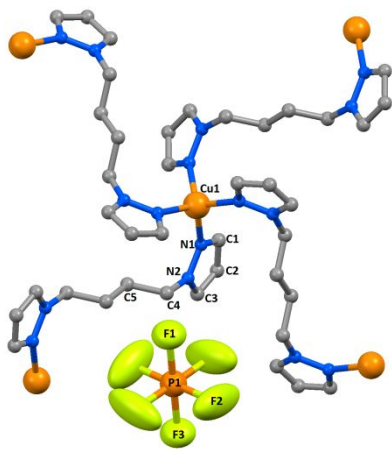
Compound **1** crystallizes in the triclinic *P*-1 space group with *Z*=2 (Table 1). Among all the ligands considered in this work (Scheme 1) the bdb present in compound **1** results less flexible and more sterically hindered being the two pyrazolyl groups spaced by the  $-\text{CH}_2\text{-Ph-CH}_2-$  linker and decorated by methyl groups. As a result, the structure of **1** is a 1D coordination polymer consisting of a sequence of metallocyclic rings and ribbons. The asymmetric unit of **1** contains one Cu(I) ion, one and a half  $\mu\text{-bdb}$  ligand and a  $\text{PF}_6^-$  counter ion (Figure 1a). Each copper atom is coordinated by three pyrazolyl nitrogen atoms from three  $\mu\text{-bdb}$  ligands to form a slightly distorted trigonal planar  $\text{CuN}_3$  environment with N–Cu–N angles and Cu–N bond distances in the ranges  $117.17(9)\text{--}124.20(9)^\circ$  and  $1.978(2)\text{--}1.998(2)$  Å, respectively (Table S1). Although the ligands in the structure of **1** and  $\{[\text{Cu}(\mu\text{-bbd})_{1.5}](\text{PF}_6)]_n$  (**KEZXEU**) are different, the overall structures are similar. Both are 1D, containing three coordinated copper centers and alternating rings and ribbons along the chains. Two crystallographically different types of  $\mu\text{-bdb}$  ligands have been observed in the structure of **1**. The ones that form the ribbons of the chains (blue color in Figure 1b) are centrosymmetric with (Cu)N–to–N(Cu) distance of 9.22 Å, and consequently the dihedral angle between the mean planes of two pyrazolyl rings is  $0^\circ$ . The other ligand form the  $[\text{Cu}_2(\mu\text{-bdb})_2]^+$  metallocycles and is shown in red color in Figure 1b. In this case, the dihedral angle between two pyrazolyl rings is  $66.01^\circ$  and the (Cu)N–to–N(Cu) distance is 8.38 Å. Due to the different linker lengths, two types of  $\text{Cu}\cdots\text{Cu}$  distances have been observed in the 1D structure of **1**. The  $\text{Cu}\cdots\text{Cu}$  separation in the ring motifs is shorter (8.26 Å) than the one between the rings (10.19 Å) as also observed in the structure of **KEZXEU**, where, however, such  $\text{Cu}\cdots\text{Cu}$  distances are shorter of about 2 Å.<sup>23</sup> The chains run along the  $[1\ 0\ 0]$  direction and pack with an *AAA* sequence. Disordered  $\text{PF}_6^-$  counter-anions remain uncoordinated and are located in the space between the chains.



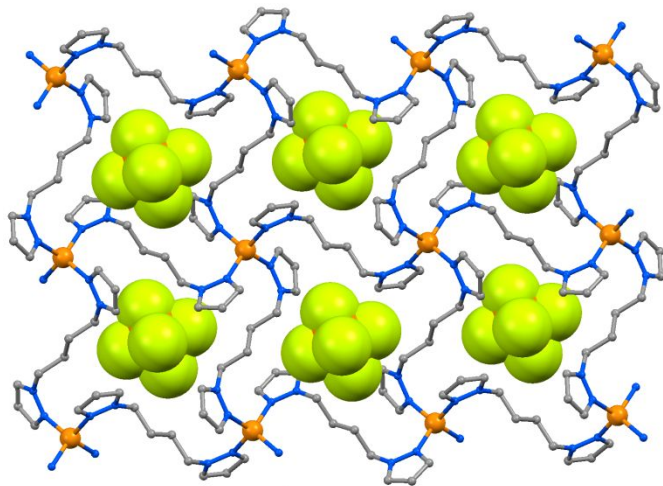
**Figure 1.** Crystal structure of **1**: a) Asymmetric unit with a labeling scheme for non-C, H atoms. b) 1D chain containing a sequence of metalocyclic rings (red) and ribbons (blue). c) Packing of the chains with PF<sub>6</sub><sup>-</sup> anions (left) and a closer view of the non-classic C-H...F interactions (right).

## **$\{[\text{Cu}(\mu\text{-bpb})_2]\text{PF}_6\}_n$ (**2**)**

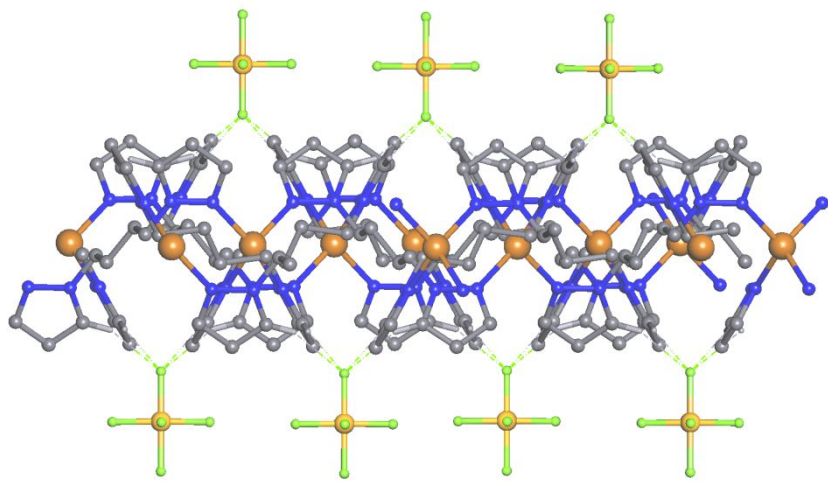
Compound **2** crystallizes in the tetragonal  $P4/n$  space group with  $Z=2$  (Table 1). Single-crystal X-ray diffraction analysis reveals that **2** contain cationic two dimensional  $[\text{Cu}(\mu\text{-bpb})_2]^+$  motifs and  $\text{PF}_6^-$  counter anions (Figure 2). The Cu atom is coordinated by four nitrogen atoms from bpb ligands, giving a  $\text{CuN}_4$  moiety with the N–Cu–N bond angles ranging from 96.74(8) to 116.19(4) Å (Table S1). Deviations from ideal tetrahedral geometry can be specified by  $\tau_4$  parameter<sup>57</sup> which has values of 1.00 and zero for perfect tetrahedral and square planar geometries, respectively. Calculated  $\tau_4$  value of 0.905 for copper ions in **2** represents a deviation from ideal tetrahedral towards square planar geometry, suggesting a distorted tetrahedral geometry for the copper centers. The Cu–N distance is 2.0765(14) Å, comparable to those found in the literature<sup>58,59</sup> and longer than those found in the structure of **1** (1.978(2)-1.998(2) Å). Each copper atom is connected to four adjacent Cu(I) atoms by  $\mu\text{-bpb}$  ligands to form an infinite cationic 2D sheet with **4<sup>4</sup>-sql** topology. The 2D sheets contain centrosymmetric 36-membered  $[\text{Cu}_4(\text{bpb})_4]$  metallocyclic units (Figure 2b) and extend in the crystallographic  $ab$  plane. The layers are perfectly superimposed along  $[0\ 0\ 1]$  direction and disordered  $\text{PF}_6^-$  counter-anions found place at the center of metallocycles and between adjacent layers. There are no significant interactions between  $\text{PF}_6^-$  anions and copper(I) centers. However, closer inspection shows that there are weak C–H $\cdots$ F contacts between not disordered axial fluorine atoms of  $\text{PF}_6^-$  anions and CH atoms of pyrazolyl rings (Figure 2c). Details of the hydrogen bonding geometry are given in Table S2. No remarkable short contacts or  $\pi\cdots\pi$  interactions were found between adjacent sheets.



(a)



(b)



(c)

**Figure 2.** Crystal structure of **2**: a) Coordination environment around copper(I) atom with labeling scheme for the asymmetric unit part. b) View down *c* of a single layer with **4<sup>4</sup>-sql** net and space-filling representation of the PF<sub>6</sub><sup>−</sup> anions. c) View down *a* of a single layer and PF<sub>6</sub><sup>−</sup> anions evidencing the weak C-H⋯F hydrogen bonds.

All the μ-bpb ligands are centrosymmetric and crystallographically equivalent exhibiting an *anti-anti-anti* conformation for the C–C bonds of the  $-(CH_2)_4-$  spacer. The torsion angles NNCC, NCCC, and CCCC, along the ligand, are -86.1(2), -178.35(16) and 180.00(16), respectively, while the dihedral angle between the mean planes of the pyrazolyl rings is 0°. As a result, the (Cu)N⋯N(Cu) ligand length is 7.85 Å. The Cu⋯Cu distance along the μ-bpb ligand is 8.906 Å, which is longer than those observed in the structure of  $\{[Cu(\mu-bbd)_{1.5}](PF_6)]_n$  (6.255 and 8.527 Å).<sup>23</sup> The longer Cu⋯Cu separation in **2** can be due to the fully extended *anti-anti-anti* conformation of the bpb with respect to the *gauche-anti-anti* and *gauche-anti-gauche* conformations of the bbd ligands in **KEZXEU**.

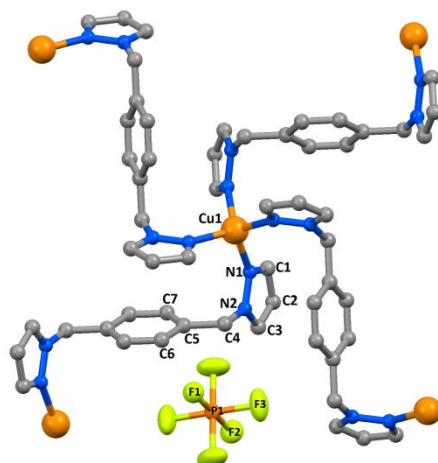
### $\{[Cu(\mu-bpmb)_2](PF_6)]_n$ (**3**)

Single-crystal X-ray diffraction analysis reveals that the same as **2**, compound **3** crystallizes in the tetragonal *P4/n* space group with *Z*=2 (Table 1). The bpmb linker in the structure of **3** is similar to the bdb (compound **1**) without the methyl substituents on the pyrazolyl groups (see Scheme 1). Compound **3** is a cationic 2D coordination polymer in which the coordination sites at the copper atoms are occupied by four nitrogen atoms of four μ-bpmb linkers in a CuN<sub>4</sub> coordination environment. The N–Cu–N bond angles are comprised in a smaller range [101.12(9)-113.80(7)°], compared to the values observed in **2**. Calculated  $\tau_4$  value of 1.03 for copper(I) centers show almost an ideal tetrahedral geometry. The copper atoms are connected to four adjacent Cu(I) atoms by μ-bpmb ligands, forming an infinite cationic 2-D sheet with **4<sup>4</sup>-sql** topology. The structure is shown in Figure 3 and the atoms of the asymmetric unit, containing one copper ion and half ligand (centrosymmetric), are labelled. The dihedral angle between two pyrazolyl rings is 0° and the (Cu)N–to–N(Cu) distance is 8.78 Å. The Cu⋯Cu distance (9.63 Å) in the 2D structure of **3** is in between the values observed in **1** (8.26, 10.19 Å).

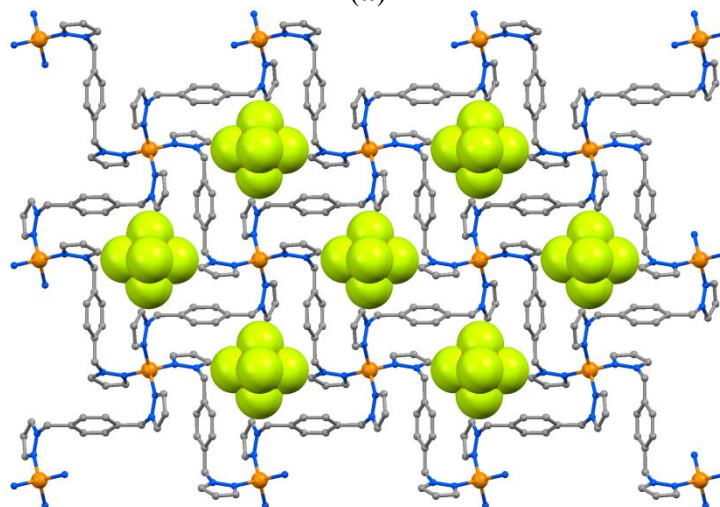
The Cu–N distance is 2.074(2) Å, comparable to that found in the structure of **2** and longer than those found in the structure of **1** [1.980(3)-1.998(4) Å] and **KEZXEU** [1.983(2)-2.0022(19) Å].

These observations indicate stronger Cu–N bonds for three coordinated copper(I) centers and nitrogen atoms of 3,5-dimethyl substituted pyrazolyl rings.

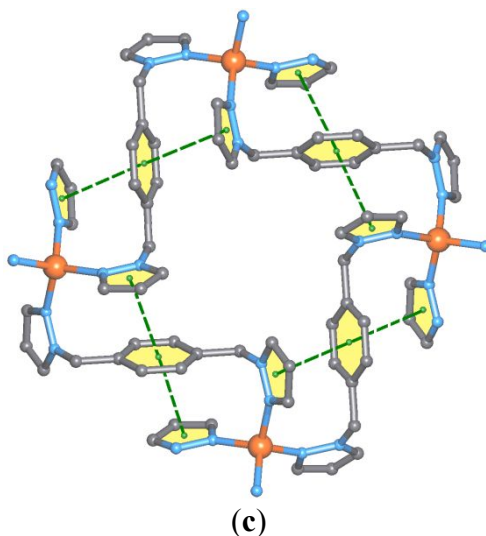
The 2D sheets extend in the crystallographic *ab* plane and pack as AAA along the *c* axis, forming 1D channels across the 2D sheets that accommodate the PF<sub>6</sub><sup>−</sup> counterions. In contrast to the structure of **1**, **2**, and **KEZZEU**,<sup>23</sup> significant  $\pi\cdots\pi$  stacking interactions occur in **3** (Figure 3c). The conformation of the bpmb ligands are such as to bring one pyrazolyl ring of a ligand into close proximity of a phenyl ring of an adjacent bpmb ligand belonging to the same layer, with a centroid $\cdots$ centroid distance of 3.647(2) Å and a dihedral angle of 6.88(17)° between the two rings.<sup>60</sup> In addition, weak C–H $\cdots$ F hydrogen interactions have also been observed between one of the fluorine atoms of the PF<sub>6</sub><sup>−</sup> anions and H atoms of the pyrazolyl rings (Table S2).<sup>61–64</sup>



(a)



(b)



**Figure 3.** Crystal structure of **3**: a) Coordination environment around copper(I) atom with labelling scheme for the asymmetric unit part. b) View down *c* of a single layer with **4<sup>4</sup>-sql** net and space-filling representation of the PF<sub>6</sub><sup>-</sup> anions. c) Intra-layer  $\pi\cdots\pi$  stacking interactions between two pyrazolyl and one phenyl rings belonging to three different bpmb ligands.

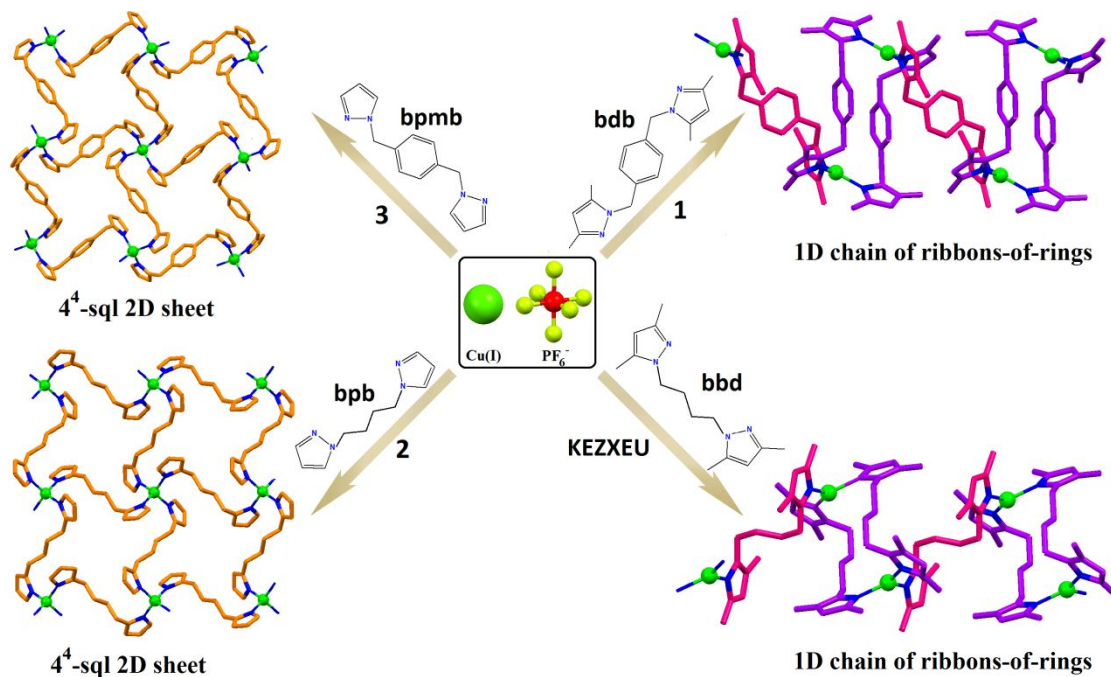
### Effect of the Geometry of the Linker Ligands

Tuning the structure of the linkers by varying the steric hindrance of pyrazolyl rings and/or the flexibility of the spacer groups show interesting and remarkable effect on the assembled coordination polymers. The bdb and bbd linkers with methyl decorated pyrazolyl rings (see Scheme 1), form one-dimensional polymeric structures composed of three coordinate copper centers in a trigonal planar geometry, while the bpmb and bpb linkers with un-substituted pyrazolyl groups, resulted in almost similar 2D structures with four coordinated copper centers. Changing the spacer group from a  $-(\text{CH}_2)_4-$  to  $-\text{CH}_2-\text{Ph}-\text{CH}_2-$  displays no meaningful effect on the structure of the resultant polymers (Scheme 2).

Preference towards trigonal planar geometry by copper atoms in the structures of **1** and **KEZXEU** and towards the four-coordinate tetrahedral one in the structures of **2** and **3** is most likely due to the large steric hindrance induced by the 3,5-dimethylpyrazole rings of the bpb and bpmb ligands. Moreover, the results clearly show the much more crucial role of the steric hindrance of the pyrazolyl ring in orienting the final Cu(I) coordination compared to the effect induced by the different nature of the pyrazolyl spacer groups. In the presence of non-coordinating anions, such as PF<sub>6</sub><sup>-</sup>, copper centers show their intrinsic nature to select three- or four-coordinate geometry depending on the steric hindrance of the ligands.



Interestingly, a significant relation between the structure of the coordination polymers and their ability to capture volatile iodine was observed. So, the 1D structures with three coordinate Cu(I) atoms act as an iodine sorbent, while 2D structures with four coordinate copper centers show no ability of iodine sorption.



**Scheme 2:** Schematic view of the effect of the different bis-pyrazolyl ligands on the structure of cationic copper(I) coordination polymers.

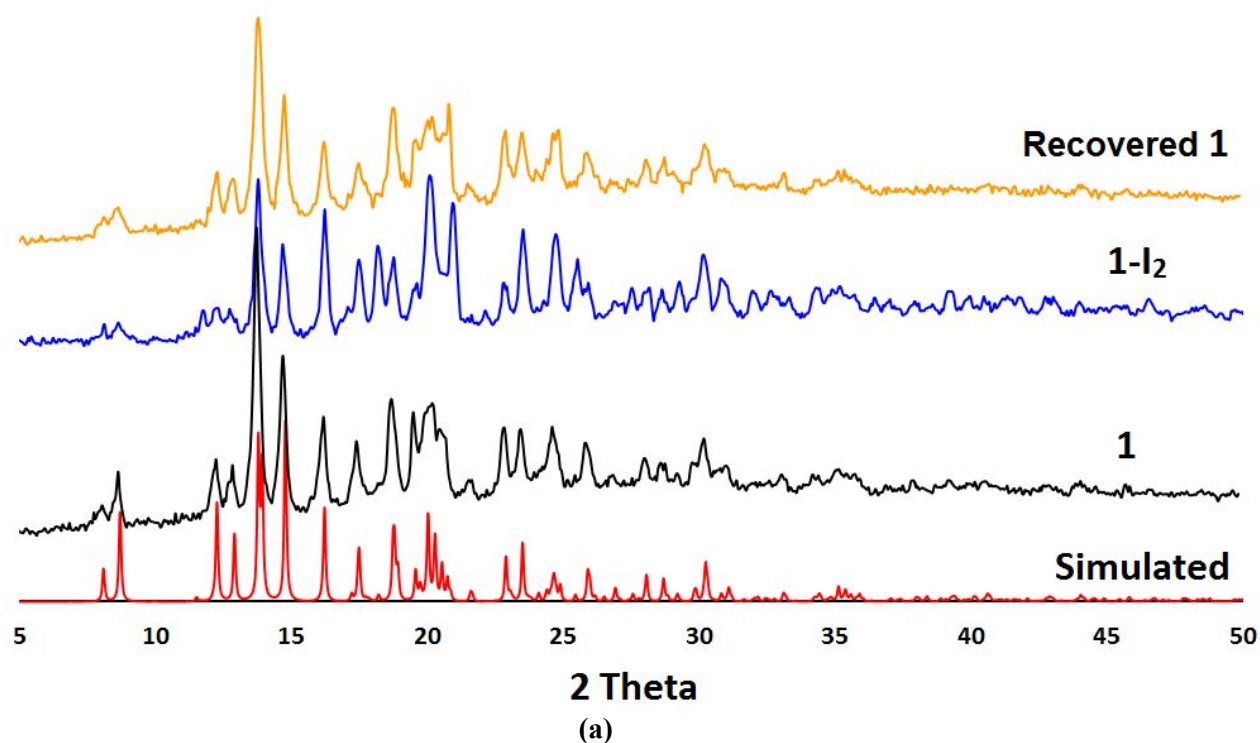
### Spectroscopic Characterization

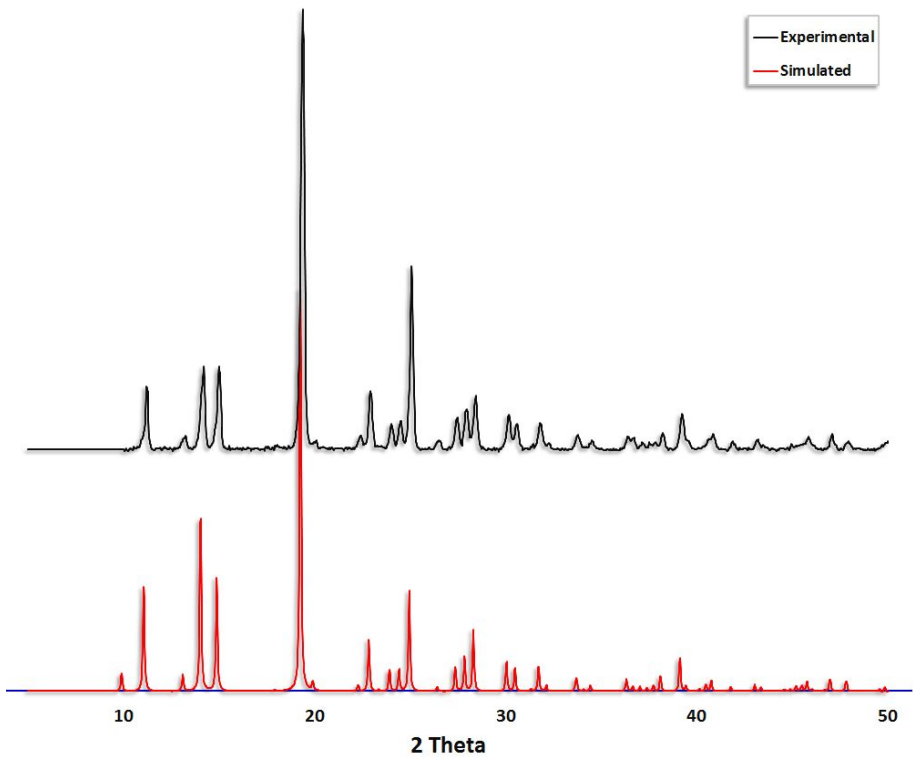
Infrared spectra of coordination polymers **1**, **2** and **3** are shown in Figure S1. Stretching vibration of C=N bonds, typical of the pyrazolyl rings, are present at 1551 (bdb in **1**), 1513 (bpb in **2**) and 1519 (bpmb in **3**)  $\text{cm}^{-1}$ . The location of the peaks depends on the type of substituents on the pyrazolyl rings. In compound **1**, where the pyrazolyl rings bring two methyl substituents, this vibration is shifted to higher wavenumber with respect to the values found for compounds **2** and **3** containing un-substituted pyrazolyl rings. The peaks with weak to medium intensity at 3142 (bdb in **1**), 3149 (bpb in **2**) and 3135 and 3150  $\text{cm}^{-1}$  (bpmb in **3**) are assigned to the stretching vibration of aromatic C-H bonds of the coordinated ligands. Symmetric and asymmetric stretching vibrations of the methylene ( $-\text{CH}_2-$ ) and methyl ( $-\text{CH}_3$ ) groups are observed in the



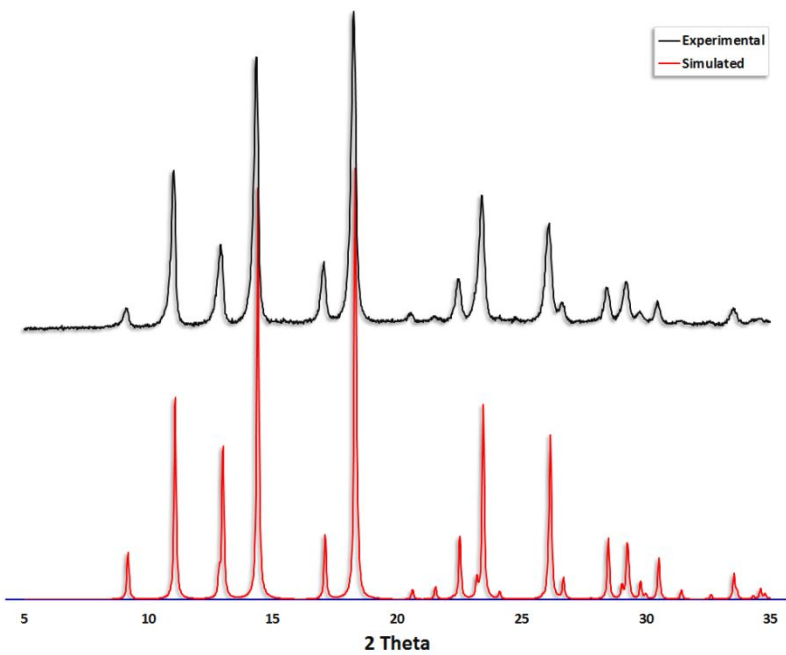
region of 2866-2950  $\text{cm}^{-1}$ . The infrared spectra of the compounds also show two sharp bands at 557 and 845 (multiple or broad)  $\text{cm}^{-1}$ , attributed to the vibration bands of  $\text{PF}_6^-$  counter anion.<sup>24</sup>

Experimental and simulated powder X-ray diffraction (PXRD) patterns of the samples are shown in Figures 4. The results show suitable phase purity of the bulk materials.

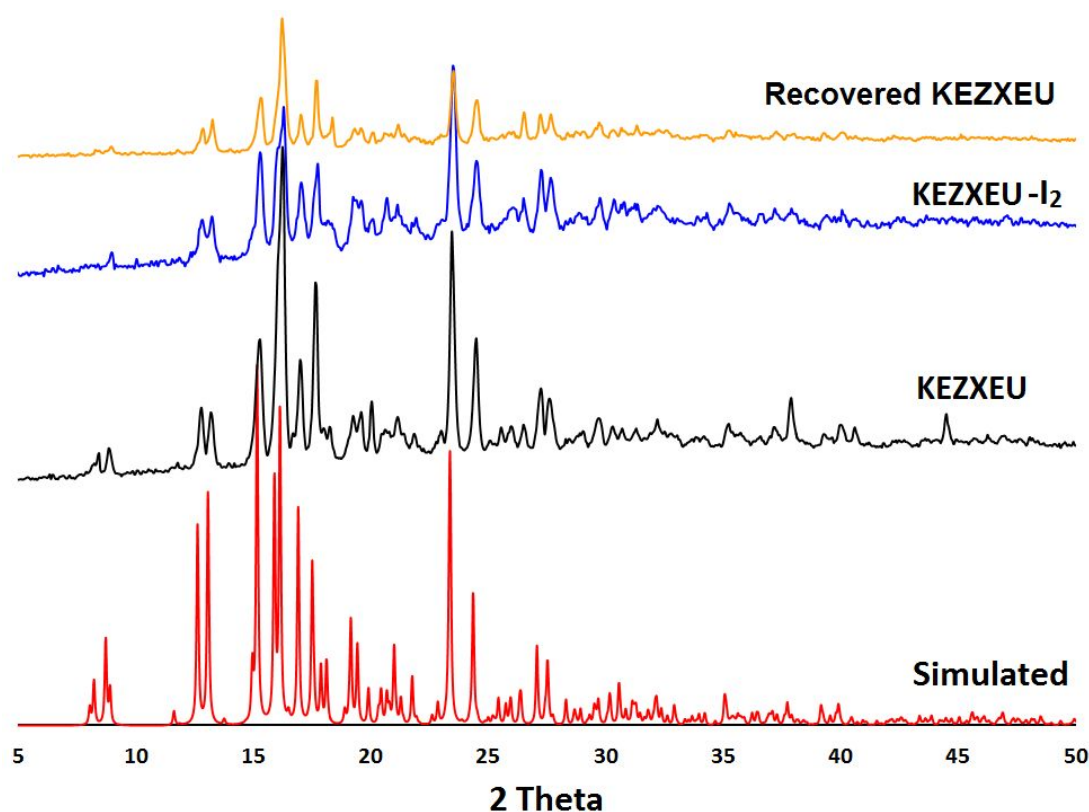




(b)



(c)



(d)

**Figure 4.** Observed (black) and calculated from single-crystal structure (red) powder X-ray diffraction patterns for compounds; a) **1**, b) **2**, c) **3**, and d) **KEZXEU**. PXRD patterns of iodine adsorbed samples of **1**-I<sub>2</sub> and **KEZXEU**-I<sub>2</sub> (blue) and recovered **1** and **KEZXEU** (orange).

### Iodine Sorption and Release

Most of the investigations on iodine sorption have been performed using porous coordination polymers or metal-organic frameworks but in solution only.<sup>39-43</sup> However, iodine sorption studies in the gas phase by non-porous coordination polymers are still rare and need to be explored well.<sup>44</sup> Kawano et. al., reported CuI-based 3D porous coordination networks with outstanding feature of iodine sorption in the gas phase<sup>12</sup> and, by crystallographic evidence, showed both chemi- and physi-sorption of iodine in these porous coordination networks. Our recent research revealed iodine capture feature of non-porous Cu<sub>n</sub>I<sub>n</sub>-based coordination polymers in the gas phase.<sup>45</sup> Herein, we have explored this property by non-porous cationic Cu(I) CPs not containing copper-iodide clusters moieties. Analysis of the structures by Platon<sup>65</sup> confirms no accessible void for guest molecules.

Fixed iodine vapor pressure strategy was employed, and vials containing colorless crystals of compounds **1-3** and that of the already reported structure  $\{[\text{Cu}(\mu\text{-bbd})_{1.5}](\text{PF}_6)\}_n$ <sup>23</sup> were left in a capped vessel containing crystals of iodine and then heated at 55 °C for three different exposure times, 30 min, 50 min and 2 h (Table S3). Monitoring by naked eye revealed that the color of samples **1** and **KEZXEU** immediately changed to deep brown, while that of samples **2** and **3** remained unchanged. Photographs of the samples before and after vapor iodine sorption are shown in Figure 5. Surprisingly, compounds having similar crystal structures, indifferently with respect to the ligands, behave in the same way. Hence, **1** and **KEZXEU**, with the same 1D chain structure and trigonal geometry of the copper atoms, showed vapor I<sub>2</sub> adsorption. On the contrary, no iodine adsorption was evidenced for **2** and **3**, with 2D structures and tetrahedral copper atoms. On the other hand, none of the four compounds showed the ability to adsorb iodine in cyclohexane solution.

To evaluate the maximum amount of volatile iodine adsorbed by **1** and **KEZXEU**, the adsorbed crystals, taken after a given exposure time, were washed with cyclohexane to remove deposited iodine on their surface, dried and weighed. After 2h of exposure time the maximum of adsorbed I<sub>2</sub> was reached for both samples and, as determined gravimetrically, it was of 47.0 and 58.2 wt % for **1** and **KEZXEU**, respectively (Table S3). In terms of moles this means that 1.20 and 1.33 moles of I<sub>2</sub> are adsorbed *per* formula unit of **1** and **KEZXEU**, respectively.

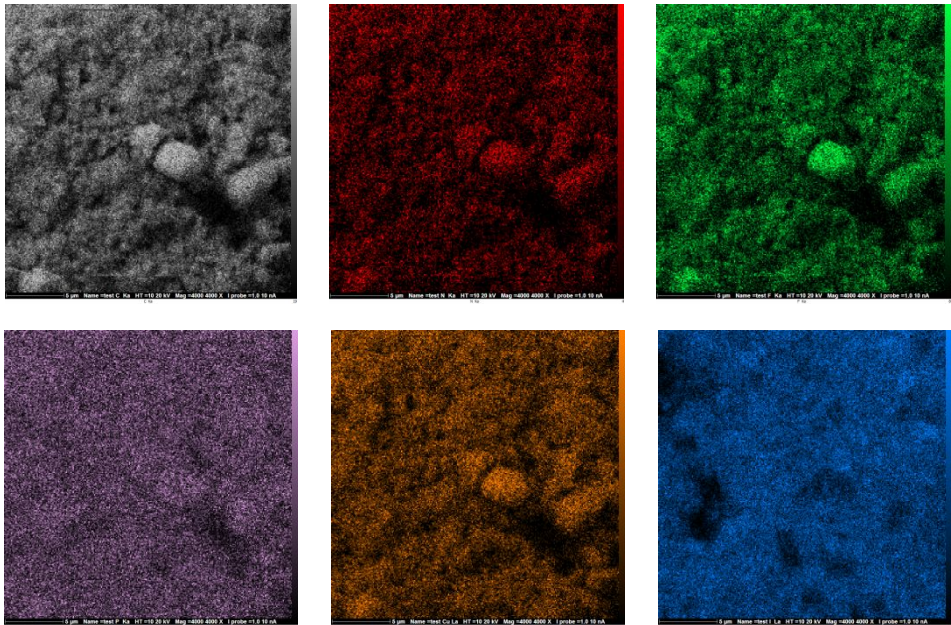


**Figure 5.** Photographs of samples of compounds **1-3** and **KEZXEU** before and after iodine sorption.

To investigate the vapor iodine uptake process in **1** and **KEZXEU**, IR spectra and PXRD patterns on adsorbed samples **1-I<sub>2</sub>** and **KEZXEU-I<sub>2</sub>** were acquired. FT-IR spectra of **1** and **1-I<sub>2</sub>** are almost the same (Figure S1 a,b). PXRD patterns of **1-I<sub>2</sub>** and **KEZXEU-I<sub>2</sub>** were recorded and compared with that of the relative pristine materials, and no substantial differences were found (Figure 4a,d). These may confirm that the structures of the two compounds are maintained during iodine sorption process. Thermal stability of the compounds before and after I<sub>2</sub> sorption was also investigated by thermogravimetry under nitrogen atmosphere. The results (Figure S2) showed that the structures are stable up to about 250 °C and start to collapse at higher

temperatures, except for **1** that is stable up to about 200 °C. Comparison between the thermogravimetric traces of **1** and **1-I<sub>2</sub>** showed that iodine release occurs at temperature close to the decomposition point of **1**. To understand whether thermal iodine release from **1-I<sub>2</sub>** can be attained with retention of the framework, powder of **1-I<sub>2</sub>** was heated at 200°C for 20 min in N<sub>2</sub> atmosphere. A color change from brown to yellow was visible after the first 5 min (Figure S3a) while the FT-IR spectrum, acquired on the sample heated for 20 min, (Figure S3 b) is comparable to that of the pristine samples. These results confirm that iodine in **1-I<sub>2</sub>** can be thermally released at 200°C without destruction of the framework. The TG trace of **KEZXEU-I<sub>2</sub>** show that iodine release occurs at lower temperatures (ca. 110°C) with respect to the decomposition temperature of **KEZXEU**. This may imply a weaker interaction of iodine molecules with the structure of **KEZXEU** compared to that of **1**. The results are consistent with faster release of adsorbed iodine from **KEZXEU-I<sub>2</sub>** in pure EtOH (*vide infra*).

In order to get a better insight on the iodine sorption behavior, energy dispersive X-ray (EDX) analyses have also been performed on **1-I<sub>2</sub>** and **KEZXEU-I<sub>2</sub>**. The EDX maps reveal uniform distribution of adsorbed iodine over the samples (Figure 6). Moreover, EDX elemental analysis predict average iodine content of about 51 and 60 wt% for **1-I<sub>2</sub>** and **KEZXEU-I<sub>2</sub>**, respectively, (Figure S4) which are almost consistent with the values obtained gravimetrically (Table S3).



(a)





Iodine release was also investigated in polar EtOH and non-polar CCl<sub>4</sub> solvents. The results show faster iodine release in polar EtOH with respect to CCl<sub>4</sub>. Probably, the interactions of iodine species with the polar molecules of EtOH provides sufficient energy to overcome the weak supramolecular interactions between adsorbed iodine molecules and the skeleton of the coordination polymers and set off the release of iodine by the polar solvent.<sup>66,67</sup> Photographs of iodine release tests in ethanol and of recovered solid materials of compounds **1** and **KEZXEU** are shown in Figure S5. The iodine release from **1**-I<sub>2</sub> and **KEZXEU**-I<sub>2</sub> in EtOH was also monitored by time-dependent UV-Vis measurements (Figure S5) following the increase in the intensity of the band at 358 nm. The results show faster release of iodine from **KEZXEU**-I<sub>2</sub> with respect to **1**-I<sub>2</sub> confirming what observed in the TG analysis. Moreover, UV-Vis quantitative analysis of the iodine content of **1**-I<sub>2</sub> and **KEZXEU**-I<sub>2</sub> obtained at 2 h exposure time gave values of 45.0 and 62.0 wt%, respectively, which are almost consistent with that obtained gravimetrically and comparable to that reported for porous coordination networks.<sup>12</sup>

Encapsulation of iodine by MOFs and CPs could be ascribed to various supramolecular interactions between iodine and ligand moieties, such as,  $\pi \cdots \text{I}$  and  $\text{O/N/C-H} \cdots \text{I}$  hydrogen bonding<sup>66,67</sup> or to interaction of iodine with open coordination sites in the skeleton of the structures.<sup>68</sup> Another way to iodine capture is the formation of I–I halogen bond between  $\text{I}_2$  molecules and  $[\text{CuI}]_n$  moieties in the structure of copper iodide-coordination networks.<sup>12</sup> In the present work, as compounds **2** and **3** with 2D sheet structures, that are containing aromatic rings and C–H groups, show no tendency to capture iodine, the most rational factor for iodine capture by the 1D CPs **1** and **KEZXEU** may be assigned to the presence of three coordinated trigonal planar copper atoms with open coordination sites.

### Anion Exchange Properties of **1** and **2**

As revealed by the crystal structure analyses of **1-3**, the hexafluorophosphate anions are loosely connected to the cationic skeleton of the structures through weak  $\text{C-H} \cdots \text{F}$  interactions. To investigate whether the  $\text{PF}_6^-$  anions can be exchanged by other anions, anion exchange reactions were carried out on **1** and **2** as representative of 1D and 2D structural type, respectively. Anion exchange processes were investigated both in solution and in the solid state and the anion-exchanged products were identified by FT-IR and PXRD techniques. Hence, a certain amount of finely powdered samples of **1** or **2** were added to aqueous solutions containing, respectively,  $\text{SCN}^-$  (0.005 M),  $\text{I}^-$ ,  $\text{ClO}_4^-$  or  $\text{BF}_4^-$  (1 M) and the resulting mixtures were stirred at room temperature for one day. The results show that  $\text{PF}_6^-$  anions of **1** or **2** were replaced only by the strongly coordinating  $\text{SCN}^-$  anion (Figure S1 a, c; **1-SCN** and **2-SCN**). The presence of  $\text{SCN}^-$  in the anion-exchanged products is established from the appearance of a sharp band at  $2113 \text{ cm}^{-1}$ , which is assigned to the CN stretching mode of the thiocyanate groups<sup>23</sup> and the disappearance of vibrations bands due to  $\text{PF}_6^-$  anions in the FT-IR spectra. Anion exchange experiments in the solid state were also investigated by grinding certain amount of **1** or **2** with solid KSCN, KI,  $\text{NaClO}_4$  and  $\text{NaBF}_4$  in an agate mortar (molar ratio 1:1). Anion exchange in the solid state for **2** is the same as that in solution and only  $\text{SCN}^-$  is able to replace  $\text{PF}_6^-$ . Differently, the  $\text{PF}_6^-$  anions in the structure of **1** were also replaced by iodide ions (Figure S1 b). This phenomenon could be put in relation to the presence of an additional accessible coordination site on the three coordinated copper(I) centers in the structure of **1**. The anions  $\text{ClO}_4^-$  and  $\text{BF}_4^-$  resulted not able to



replace  $\text{PF}_6^-$  in **1** and **2** either in solution or in the solid state, this may be due to their weakly coordinating character. To investigate structural change during anion exchange process, PXRD analyses were performed on anion-exchanged products **1**-SCN, **1**-I, and **2**-SCN (Figure S6). The results indicate structural change during anion exchange. Concerning the anion exchange product **1**-I in the solid state, the results show structural transformation to a corresponding CuI coordination polymer  $[\text{CuI}(\mu\text{-bdb})]_n$  (**ACITAK**)<sup>45</sup> (Figure S6 a).

## CONCLUSION

We reported the facile syntheses of three cationic Cu(I) coordination polymers with flexible bispyrazolyl linker ligands and investigated the effect of the geometry of the linkers on their structures and iodine sorption behavior. Due to the known structure-directing effects of halides and pseudo-halides on the structure of Cu(I) CPs, non- or weakly-coordinating  $\text{PF}_6^-$  anion has been selected as counter anion. Crystal structure analysis on the isolated compounds show no clear effect of the pyrazolyl spacer groups but an evident influence of pyrazolyl ring steric hindrance. The relation of the structures with their capability in the capture of volatile iodine is also attractive. Ligands containing methyl-substituted bulky pyrazolyl rings form low dimensional coordination polymers of three coordinated copper centers and are good iodine sorbents. Ligands with non-substituted rings give rise to higher dimensional CPs with four coordinated copper centers with any ability of iodine sorption. Therefore, the results show that even non-porous copper(I) coordination polymers have potential application in sorption of gaseous iodine and that such ability can be tuned by changing the coordination geometry of copper(I) ions.

## SUPPORTING INFORMATION AVAILABLE

Selected bond lengths (Å) and bond angles (°) for compounds **1-3** (Table S1) and hydrogen bonds for compounds **2** and **3** (Table S2); Gravimetric and UV-Vis determination of iodine contents for compounds **1** and **KEZXEU** in different  $\text{I}_2(\text{g})$  exposure time (Table S3). FT-IR spectra for complexes and anion exchanged products (Figures S1,S3), TGA curves (Figure S2), EDX spectra and iodine contents information for iodine-adsorbed samples (Figure S4),

Photographs of iodine release tests (Figure S5), PXRD patterns for anion exchanged products (Figure S6). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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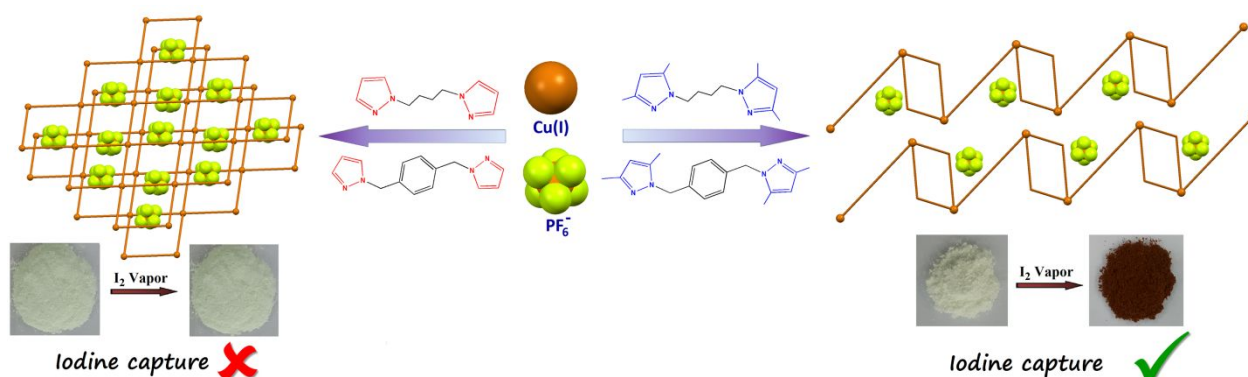
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## Three Cationic Non-Porous Cu<sup>I</sup>-Coordination Polymers: Structural Investigation and Vapor Iodine Capture

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Ligands containing methyl-substituted bulky pyrazolyl rings form low dimensional coordination polymers of three coordinated copper centers and are good iodine sorbents. Ligands with non-substituted rings give rise to higher dimensional CPs with four coordinated copper centers without any ability of iodine sorption.