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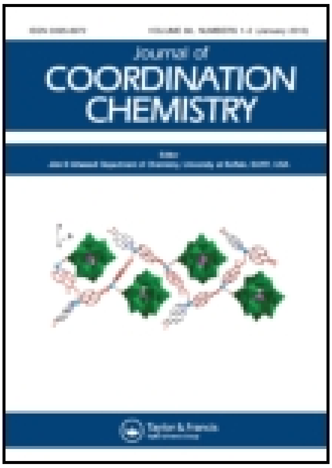

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Three Cu(II) (R)-2-chloromandelato complexes generated from dipyridyl-type ligands with different spacer lengths: syntheses, crystal structures, and ferroelectric properties

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Three Cu(II) (*R*)-2-chloromandelato complexes generated from dipyridyl-type ligands with different spacer lengths: syntheses, crystal structures, and ferroelectric properties

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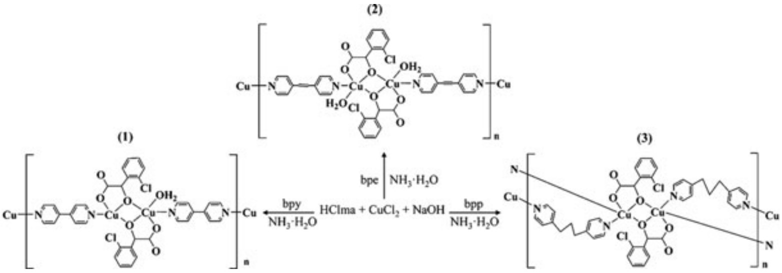

Three Cu(II) complexes, $Cu_2(bpy)(H_2O)(Clma)_2$ (**1**), $Cu_2(bpe)(H_2O)_2(Clma)_2$ (**2**), and Cu(bpp)(Clma) (**3**), were synthesized (HClma = (*R*)-2-Chloromandelic acid, bpy = 4,4′-dipyridine, bpe = 1,2-di(4-pyridyl)ethylene, bpp = 1,3-di(4-pyridyl)propane). Complexes **1**, **2**, and **3** are constructed from 1-D coordination arrays generated from $Cu_2(H_2O)(Clma)_2$, $Cu_2(H_2O)_2(Clma)_2$, and $Cu_2(Clma)_2$ moieties and linked through bpy, bpe, and bpp co-ligands, respectively. **1** and **2** are assembled into 3-D supramolecular networks via O–H···O hydrogen bonds with topology of $(6^3)(6^9{\cdot}8)$ and $(4^{12}{\cdot}6^3)$, respectively, and **3** is assembled into a 3-D architecture through C–H···O hydrogen bonds with topology of $(4^3{\cdot}6^3)(4^3)(4^4{\cdot}6^5{\cdot}8)(4^6{\cdot}6^6{\cdot}8^3)$. Compounds **1**, **2**, and **3** crystallized in acentric space groups *P2₁*, *P1*, and *P2₁*, which exhibit significant ferroelectricity (remnant polarization $Pr = 0.008\ \mu C\ cm^{-2}$, coercive field $Ec = 21.4\ kV\ cm^{-1}$, the spontaneous saturation polarization $Ps = 0.167\ \mu C\ cm^{-2}$ for **1**, $Pr = 0.183\ \mu C\ cm^{-2}$, $Ec = 1.69\ kV\ cm^{-1}$, and $Ps = 0.021\ \mu C\ cm^{-2}$ for **3**). Results from infrared and thermal analyses are also discussed.

Keywords: (*R*)-2-Chloromandelic acid; Dipyridyl-type ligands; Chiral complexes; Ferroelectric properties

1. Introduction

The design and syntheses of functional crystalline-coordination polymers have become a study hotspot as wide applications in the fields of catalysis, host-guest chemistry, gas

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*Corresponding author. Email: zhengcm@nbu.edu.cn storage, and separation are expected [1–4]. Currently, a particular focus on this topic is on chiral metal-organic coordination polymers which possess many important physical properties such as ferroelectricity, pyroelectricity, piezoelectricity, triboluminescence, and nonlinear optical function [5–9]. One of the most effective and direct approaches to obtain chiral complexes is using chiral organic ligands as starting materials [10–13]. (*R*)-2-Chloromandelic acid (HClma) is an α-hydroxycarboxylic ligand with one stereogenic carbon atom and is an important intermediate for the production of clopidogrel, an antiplatelet agent to treat coronary artery and vascular diseases [14, 15]. In recent years, many efforts have been made to develop efficient preparation methods for HClma [16]; however, metal-organic coordination complexes containing HClma are less studied [17–19]. Research into crystalline coordination polymers with various intriguing architectures and topologies have also continued to be studied over the past decades [20–23]. Dipyridyl-type ligands, such as 4,4′-dipyridine (bpy), 1,2-di(4-pyridyl)ethylene (bpe), and 1,3-di(4-pyridyl)propane) (bpp), are widely employed and useful for the preparation of metal-organic coordination polymers with aesthetical structures and intriguing topologies [24–29]. Structure directing effects during the self-assembling, however, remain rather hard to predict. Using different dipyridyl-type ligands (bpy, bpe, and bpp) and maintaining metal and carboxylate starting materials (copper(II) and (*R*)-2-Chloromandelic acid), hard to predict, supramolecular effects in terms of structure direction. Cu(II) ion is widely and successfully used in the field of coordination chemistry due to its magnetic properties and biological activities, for example, Cu(II) is a necessary microelement in the human body [30].

In order to obtain acentric coordination polymers and explore the effect of dipyridyl-type ligands on self-assembly regulation, we have engaged ourselves in the preparation of Cu(III) (*R*)-2-chloromandelato-based complexes and have obtained the three functional polymers, $Cu_2(bpy)(H_2O)(Clma)_2$ (**1**), $Cu_2(bpe)(H_2O)_2(Clma)_2$ (**2**), and Cu(bpp)(Clma) (**3**).

2. Experimental setup

2.1. *Materials and physical measurements*

All chemicals and solvents were commercial products of regent grade and used without purification. Powder X-ray diffractions (PXRDs) were carried out with a Bruker D8 Focus X-ray diffractometer using Cu target and Ni filter (λ = 1.54056 Å) and recorded the diffraction pattern of the sample under room temperature with the range of 2θ between 5° and 50° to identify the synthetic products as well as to check phase purity. FT-IR spectra in the region 4000–400 cm^{-1} were recorded at room temperature at pressed KBr disks on a Shimadzu FT-IR-8900 spectrometer. Thermogravimetric (TG) measurements were performed under a flow of nitrogen gas from room temperature to 900 °C at a heating rate of 10 °C min^{-1} using a Seiko Extra 6000 TG/DTA 6300 apparatus. Single-crystal data were collected on a Rigaku R-Axis Rapid IP X-ray diffractometer using Mo target (λ = 0.71073 Å). The ferroelectric properties of the solid-state sample were measured by a pellet of powdered sample using a Premier II ferroelectric tester at room temperature and the sample was immerged in insulating oil.

2.2. *Synthesis of $[Cu_2(bpy)(H_2O)(Clma)_2]_n$ (1)*

One milliliter (1 M) NaOH and 0.085 g (0.5 mM) $CuCl_2{\cdot}2H_2O$ were added to an aqueous ethanol solution containing 0.186 g (1.0 mM) (*R*)-2-Chloromandelic acid under stirring. The above solution turned into light blue suspension after addition of another aqueous ethanol solution containing 0.078 g (0.5 mM) 4,4′-dipyridine (bpy). The resulting suspension turned into a dark blue solution after adding 2 mL (1 M) $NH_3{\cdot}H_2O$. Then the mixture (pH 8.92) was filtered off. Slow evaporation of the filtrate at room temperature for several days gave green block crystals of **1** (yield: 82%, on the basis of the initial $CuCl_2{\cdot}2H_2O$ input). The product-phase purity was checked according to powder X-ray pattern compared with the simulated PXRD based on the single crystal data (figure S1, see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.939074). Anal. Calcd for $C_{26}H_{20}N_2Cu_2O_7Cl_2$ (670.44): C, 46.58; H, 3.01%. Found: C, 46.02; H, 3.62%. IR spectrum (KBr pellet, ν/cm^{-1}): 3404(m), 3068(w), 2926(w), 1610(s), 1359(s), 1076(m), 1032(m), 814(m), 756(m), 723(w).

2.3. *Synthesis of $[Cu_2(bpe)(H_2O)_2(Clma)_2]_n$ (2)*

Complex **2** was prepared analogous to **1** except that 0.091 g (0.5 mM) 1,2-di(4-pyridyl)ethylene (bpe) was used in place of bpy; the pH of the mixture was 9.33 and yielded a few green block crystals and many blue impurities. The product phase purity of green crystals was checked according to the experimental PXRD. Anal. Calcd for $C_{28}H_{24}N_2Cu_2O_8Cl_2$ (714.49): C, 47.07; H, 3.39%. Found: C, 47.35; H, 3.62%. IR spectrum (KBr pellet, ν/cm^{-1}): 3365(m), 3097(w), 2885(w), 1670(s), 1640(s), 1609(s), 1428(s), 1328(m), 1304 (m), 1093(m), 1068(m), 1031(m), 835(m), 802(m), 753(m), 555(m).

2.4. *Synthesis of $[Cu(bpp)(Clma)]_{2n}$ (3)*

Complex **3** was prepared analogously to **1** except that 0.099 g (0.5 mM) 1,3-di(4-pyridyl) propane) (bpp) was used in place of bpy; the pH of the mixture was 8.94 and yielded green block crystals (yield: 75%, on the basis of the initial $CuCl_2{\cdot}2H_2O$ input). The product phase purity was checked according to the experimental PXRD. Anal. Calcd for $C_{42}H_{38}N_2Cu_2O_6Cl_2$ (892.76): C, 56.51; H, 4.29%. Found: C, 56.04; H, 4.62%. IR spectrum (KBr pellet, ν/cm^{-1}): 3064(w), 2859(w), 1647(s), 1617(s), 1428(s), 1327(m), 1074(m), 1030(m), 805(m), 764(m), 709(m).

2.5. *X-ray crystallography*

Suitable crystals were selected and the measurements were carried out on a Rigaku R-Axis Rapid IP X-ray diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) for **1**–**3**. The reflection intensities in an appropriate θ range (3.04–27.46 for **1**, 3.03–27.45 for **2**, 3.06–27.47 for **3**) were collected at 295 K using the ω scan technique. The data are corrected for *Lp* and absorption effects. The structures of **1** and **3** were solved by direct methods and **2** was done by the Patterson method. SHELXS-97 and SHELXL-97 are used for structure solution and refinement [31, 32]. After several cycles of refinement, all non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least-squares and all hydrogens associated with carbon atoms are geometrically generated. The hydrogens from water were placed by difference Fourier map. A summary of the key crystallographic information is given in table 1 and the main data of bond distances and angles are shown in tables S1–S3.

Table 1. Summary of crystal data, data collection, structure solution, and refinement details for 1–3 ($T = 293(2)$).

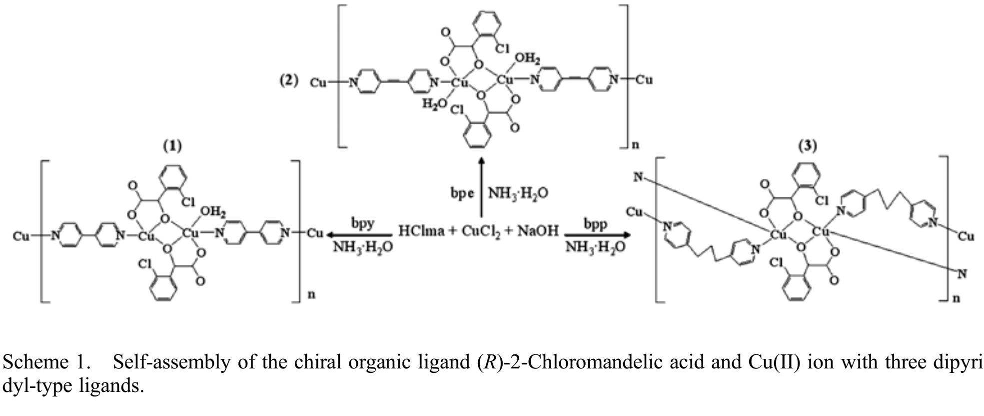
Param	**1**	**2**	**3**
Empirical formula	$C_{26}H_{20}N_2Cu_2O_7Cl_2$	$C_{28}H_{24}N_2Cu_2O_8Cl_2$	$C_{42}H_{38}N_4Cu_2O_6Cl_2$
Formula weight	670.44	714.49	892.76
Crystal habit, color	Green, block	Green, block	Green, block
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*P2₁*	*P1*	*P2₁*
a (Å)	12.612(3)	8.001(2)	9.332(2)
b (Å)	7.824(2)	8.019(2)	13.227(3)
c (Å)	13.305(3)	13.718(3)	16.381(3)
α (°)	90	92.93(3)	90
β (°)	104.90(3)	103.40(3)	91.85(3)
γ (°)	90	118.61(3)	90
Volume ($Å^3$)	1270.4(5)	738.0(4)	1992.2(7)
Z	2	1	2
Density (calculated, $g\,cm^{-3}$)	1.753	1.608	1.488
Measured reflections	12413	7273	18,674
Independent reflections	5616	5485	8767
Reflection with $I \geq 2\sigma(I)$	3267	3410	6470
F (0 0 0)	676	362	916
Crystal size (mm)	0.25 × 0.13 × 0.10	0.35 × 0.26 × 0.25	0.41 × 0.25 × 0.21
θ Range for data collection (°)	3.04–27.46	3.03–27.45	3.06–27.47
R_{int}	0.0768	0.0479	0.0505
Number of parameters	353	379	505
Goodness-of-fit on F^2	1.154	1.089	1.117
R_1, wR_2 $[I \geq 2\sigma(I)]^a$	0.0516, 0.1081	0.0581, 0.1242	0.0352, 0.0779
R_1, wR_2 (all data)^a	0.1214, 0.1637	0.1057, 0.1698	0.0646, 0.1121
$\delta\rho_{max}$, $\delta\rho_{min}$ ($e\,Å^{-3}$)	1.186, −1.148	0.786, −0.964	0.644, −0.776

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, and $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. For **1**, $a = 0.0251$ and $b = 4.5415$. For **2**, $a = 0.0537$ and $b = 0.9919$. For **3**, $a = 0.0318$ and $b = 1.2218$.

3. Results and discussion

3.1. *Syntheses*

Under ammonia condition, $CuCl_2{\cdot}2H_2O$, (*R*)-2-Chloromandelic acid, and NaOH reacted with three different spacer lengths dipyridyl-type ligands, 4,4′-dipyridine, 1,2-di(4-pyridyl) ethylene, and 1,3-di(4-pyridyl)propane), resulting in the formation of $Cu_2(bpy)(H_2O)(Clma)_2$ (**1**), $Cu_2(bpe)(H_2O)_2(Clma)_2$ (**2**), and Cu(bpp)(Clma) (**3**), respectively. The above reactions are shown in scheme 1. All complexes are stable in air and insoluble in water, methanol, ethanol, and acetone at room temperature.



Scheme 1. Self-assembly of the chiral organic ligand (*R*)-2-Chloromandelic acid and Cu(II) ion with three dipyridyl-type ligands.

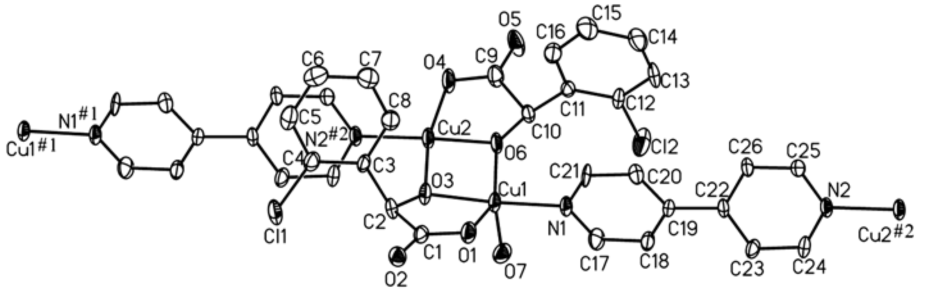


Figure 1. ORTEP view of $Cu_2(bpy)(H_2O)(Clma)_2$ (**1**) with ellipsoids at 45% probability; hydrogens were omitted for clarity.

3.2. *Description of the crystal structures*

3.2.1. $Cu_2(bpy)(H_2O)(Clma)_2$ (1). Compound **1** crystallizes in a chiral space group $P2_1$ and the asymmetric unit consists of two Cu(II) ions (Cu(1) and Cu(2)), two (*R*)-2-Chloromandelato (Clma) ligands, one 4,4′-dipyridine (bpy) ligand, and one coordinated water molecule. Both Clma ions function as terminal ligands and display a $\eta^2\mu_2$ bridging fashion with two oxygen atoms from a carboxylic and a hydroxyl groups chelating one Cu(II) atom, and the hydroxyl O atom also bridging another Cu(II) atom. As illustrated in figure 1, the two center atoms (Cu(1) and Cu(2)) adopt different coordination geometries. Cu(1) is in a CuO_4N coordination environment, coordinated by four O atoms from two Clma ions and one water molecule, and one N atom from one bpy ligand. Cu(2) is coordinated by three O atoms from two Clma ions and one N atom from one bpy ligand forming a square CuO_3N chromophore. In other words, the adjacent two polyhedrons share one base. The Cu–O/N bond length of Cu(1) in the basal plane falls in the range 1.927(5)–1.985(6) Å, and the axial position is 2.224(4) Å. The cisoid angles subtended at the Cu(1) ion fall in the range 77.9(2)°–100.1(3)° and transoid ones are 147.7(3)° and 175.9(4)°, exhibiting significant distortion from the corresponding value for a regular square pyramid (theoretical value: 90° and 180°). Towards the apical O atom, the Cu(1) atom is shifted by 0.262 Å from the basal plane. According to Addison's definition [33], the τ value for the Cu(1) coordination environment is 0.47 ($\tau = 0$ and 1 for a regular square pyramid and a regular trigonal bipyramid, respectively). The distance from Cu(2) ion to the basal O/N atoms falls in the range 1.891(5)–1.981(6) Å. The cisoid and transoid O–Cu–O/N bond angles over the range 80.4(2)°–98.9(3)° and 164.9(1)°–176.0(3)°, respectively (table S1), indicate a slight deviation of the coordination tetragon from an ideal one. In each cluster unit, the distance from Cu(1) to Cu(2) is 2.973(2) Å.

As **1** was prepared in a slightly more basic solution, the proton α-OH from Clma ligand was removed and the resulting α-O^- links two Cu(II) ions as a μ^2-bridge forming a $Cu_2(Clma)_2$ node. **1** features 1-D chains $[Cu_2(H_2O)(bpy)(Clma)_2]_n$ generated from $Cu_2(H_2O)(Clma)_2$ moieties bridged by bpy ligands along the [001] direction. Parallel to (100), the chain close to the near one leading to the distance from the center metal Cu(2) to $O5^{\#1}$ ($\#1 = -x + 1, y - 0.5, -z + 1$) atom from the adjacent chain to be 2.921 Å. As a result, no water molecule coordinates with Cu(2) atom for the short distance of Cu(2) and $O5^{\#1}$ which is different from Cu(1). The chains are held together by O–H···O hydrogen bonds between water molecule and carboxyl groups ($O2^{\#2}$ and $O5^{\#1}$, $\#2 = -x + 2, y - 0.5, -z + 1$)

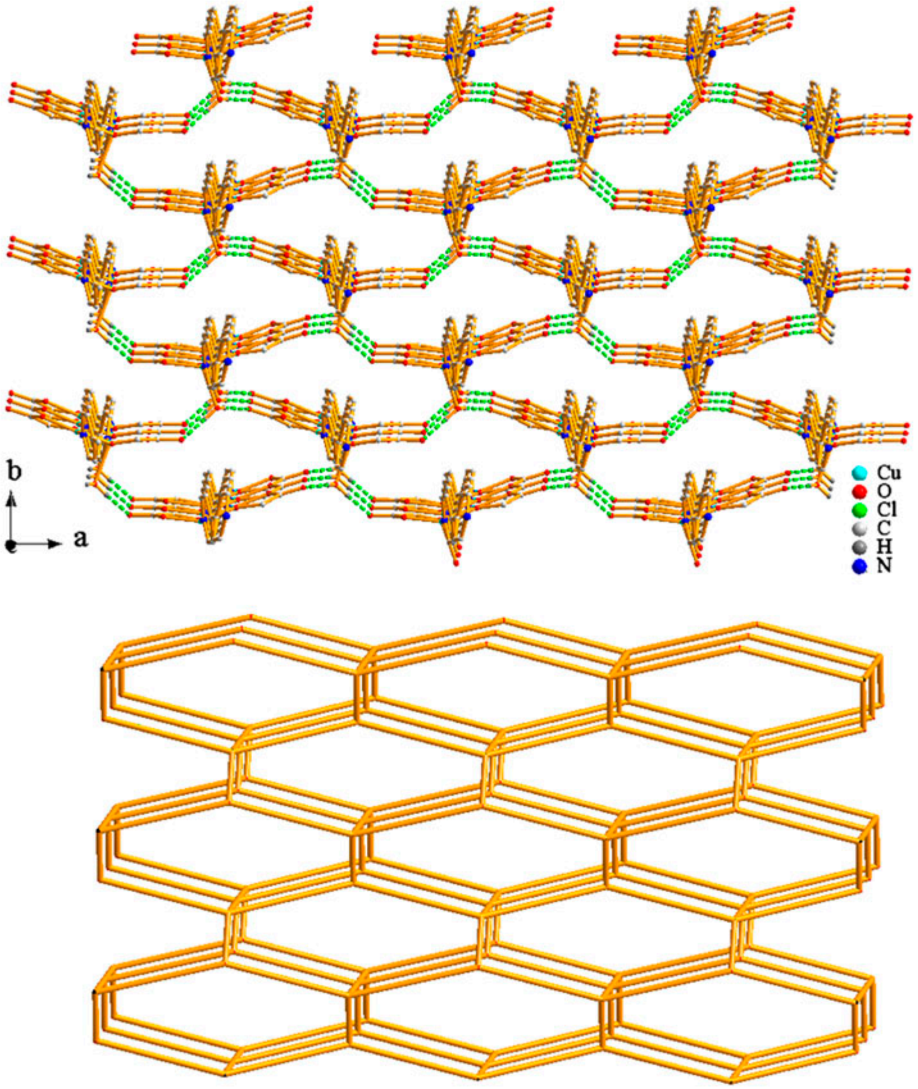


Figure 2. 3-D $[Cu_2(H_2O)(bpy)(Clma)_2]_n$ framework formed by O–H···O hydrogen bonds (a) along with the corresponding topological nets (b) in **1**. For clarity, the majority of hydrogens were omitted.

forming 3-D supramolecular networks (table S1). According to the topology, both Clma and bpe ligands can be treated as twofold connector simplified into a stick. So the Cu_2 units could be considered as five-connected nodes with $(6^9 \cdot 8)$ and a “long” schläfli notation $6 \cdot 6 \cdot 6 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 8_6$ which connected three water molecules, two other Cu_2 centers via coordination bonds, bridging ligand bpy, and O–H···O hydrogen bonds. The water molecule acts as three-connected nodes with (6^3) net and a “long” schläfli notation $6_3 \cdot 6_3 \cdot 6_3$ linking three dinuclear Cu_2 units. Therefore, the resulting 3-D supramolecular network can be described as (3,5)-connected dinodal net topology of $(6^3)(6^9 \cdot 8)$ (figure 2).

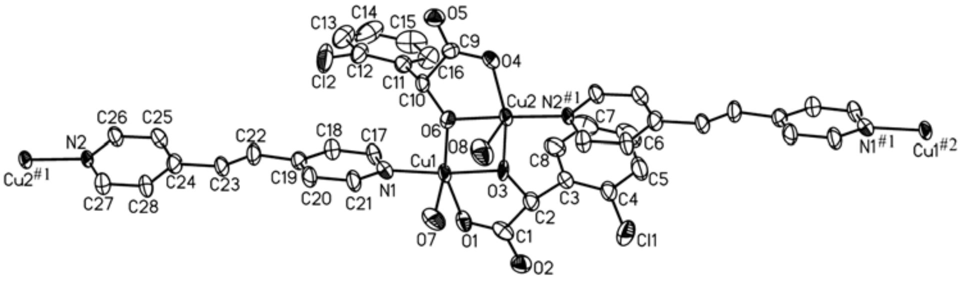


Figure 3. ORTEP view of Cu$_2$(bpe)(H$_2$O)$_2$(Clma)$_2$ (**2**) with ellipsoids at 45% probability; hydrogens were omitted for clarity.

3.2.2. Cu$_2$(bpe)(H$_2$O)$_2$(Clma)$_2$ (2). Compound **2** crystallizes in a chiral space group *P1* and the asymmetric unit consists of two Cu(II) ions (Cu(1) and Cu(2)), two (*R*)-2-Chloromandelato (Clma) ligands, one 1,2-di(4-pyridyl)ethylene (bpe), and two coordinated water molecules. The two Clma ions display the same coordination mode with that of **1**. Both Cu cations (Cu(1) and Cu(2)) are coordinated by two Clma ions, one bpe ligand, and one aqua water molecule (figure 3). All the central metal atoms are in a square-pyramidal CuNO$_4$ chromophore with the aqua oxygen atom at the apical position, and the adjacent two square pyramids share one base. Within the coordination sphere, the equatorial Cu–N/O distances fall in the range 1.900(7)–1.947(8) Å for Cu(1) and 1.886(9)–1.963(9) Å for Cu(2), and the axial Cu–O distances are 2.577(4) and 2.581(6) Å for Cu(1) and Cu(2), respectively (table S1). Toward the apical aqua ligand, the Cu atoms are shifted by 0.117 Å for Cu(1) and 0.105 Å for Cu(2) from the basal plane. The cisoid O–Cu–O/N bond angles are over the range 76.4(3)°–99.0(4)° for Cu(1), 77.0(3)°–99.3(4)° for Cu(2), and transoid ones are 158.7(3)° and 174.2(5)° for Cu(1), 158.9(3)° and 175.2(5)° for Cu(2). Additionally, the Cu(1) and Cu(2) atoms with τ values of 0.26 and 0.27 exhibit significant distortion from an ideal square pyramid. In each simple unit, the distance between Cu(1) and Cu(2) is 2.998(1) Å.

Complex **2** is constructed from 1-D coordination arrays [Cu$_2$(H$_2$O)$_2$(bpe)(Clma)$_2$]$_n$ unfolded with Cu$_2$(H$_2$O)$_2$(Clma)$_2$ dinuclear unit connected by bpe ligand in the [011] direction and the proton α-OH from Clma ligand was also removed exhibiting a close similarity to that found in **1**. The resulting chains are held together by O–H···O hydrogen bonds between water molecules and carboxyl groups (O1$^{\#1}$ and O4$^{\#2}$, $\#1 = x - 1$, y, z; $\#2 = x$, $y - 1$) forming 3-D supramolecular networks as shown in figure 4 (table S2). From a topological viewpoint, all the Clma ligands, water molecules and bpe ligands treated as twofold connector simplified into a stick. As a result, the Cu$_2$ units can be regarded as six-connected nodes with ($4^{12}\cdot6^{3}$) and a "long" schläfli notation $4\cdot4\cdot4\cdot4\cdot4\cdot4\cdot4\cdot4\cdot4\cdot4\cdot4\cdot4\cdot6_4\cdot6_4\cdot6_4$ which connected two water molecules, two other Cu$_2$ centers, and two water molecules via coordination bonds, bridging ligand bpe, and O–H···O hydrogen bonds, respectively. The whole topology can be described as six-connected dinodal net topology of ($4^{12}\cdot6^{3}$), different from **1**.

3.2.3. Cu(bpp)(Clma) (3). Compound **3** crystallizes in a chiral space group $P2_1$ and the asymmetric unit consists of two Cu(II) ions (Cu(1) and Cu(2)), two (*R*)-2-Chloromandelato (Clma) ligands, and two 1,3-di(4-pyridyl)propane (bpp) molecules. Both Cu cations (Cu(1)

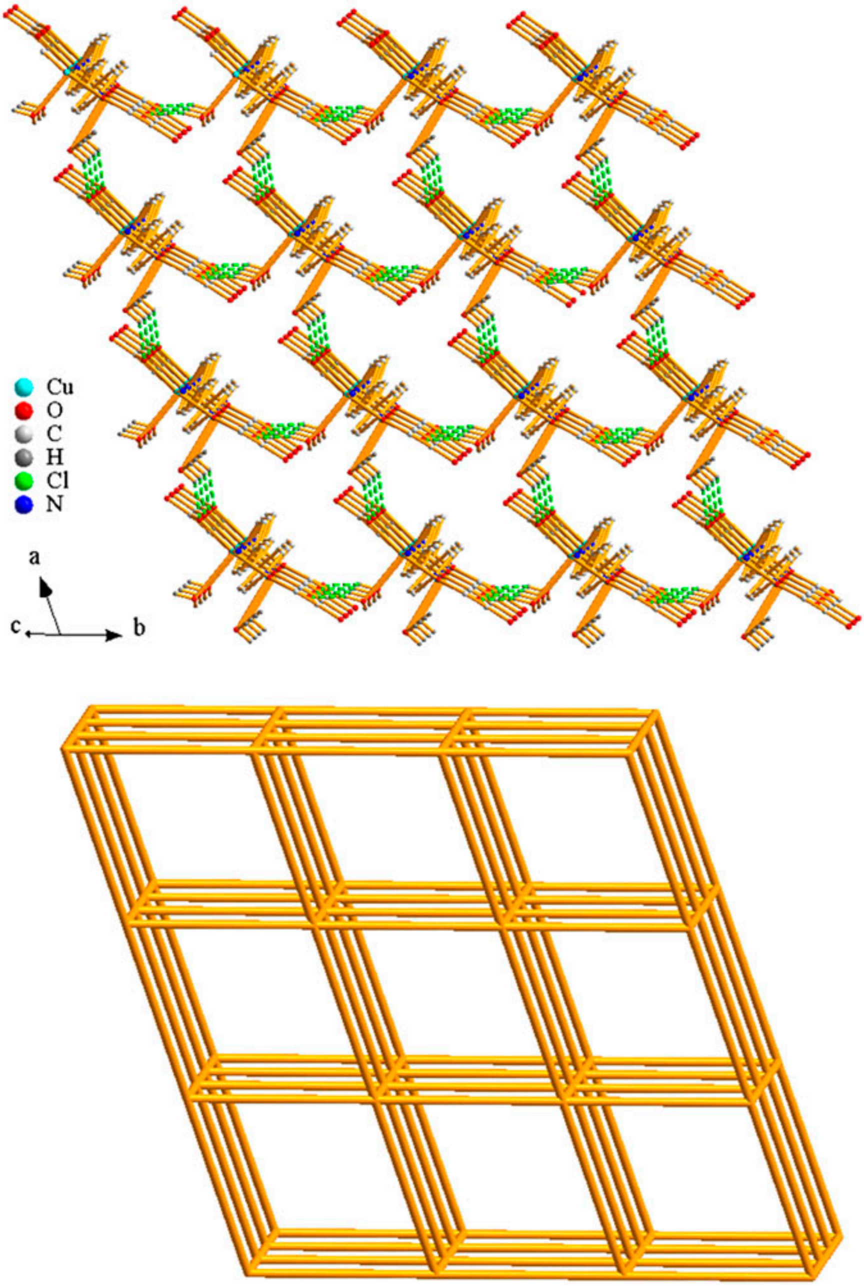


Figure 4. 3-D $[Cu_2(H_2O)_2(bpe)(Clma)_2]_n$ framework formed by O–H···O hydrogen bonds (a) along with the corresponding topological nets (b) in **2**. For clarity, the majority of hydrogens were omitted.

and Cu(2)) are coordinated by two Clma ions and two bpp ligands (figure 5). In the square-pyramidal CuN_2O_3 coordination sphere of the Cu(II) atom, two bpp are occupied in the apical and one of the basal position in the *cis*-conformation. **3** having normal bonding values

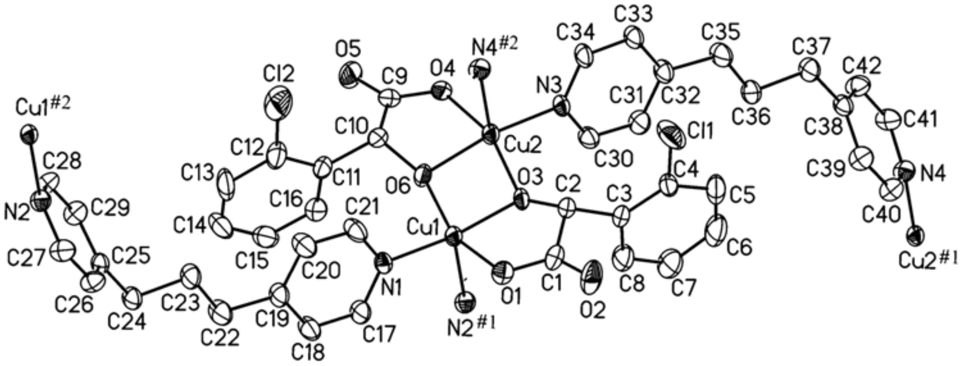


Figure 5. ORTEP view of Cu(bpp)(Clma) (**3**) with ellipsoids at 45% probability; hydrogens were omitted for clarity.

(table S3) with τ values of 0.20 for Cu(1) and 0.11 for Cu(2) exhibit significant distortion from an ideal square pyramid with "4 + 1" coordinate type. In each dinuclear unit, the Cu···Cu separation is 2.984(1) Å.

Complex **3** is a chiral supramolecular network composed of 1-D molecular assemblies connected by pairs of bpp ligands into an interesting double-stranded chain of loops along the *b*-axis, rather than a single-loop chain observed in **1** and **2**. The resulting chains are held together by C–H···O hydrogen bonds forming 3-D supramolecular networks (table S3). Topological analyses of hydrogen bonding interaction such as O–H···O hydrogen bonds are common while C–H···O bonds are rarely reported [34]. Compound **3** is constructed by C–H···O hydrogen bond interactions from 1- to 3-D supramolecular. From a topological viewpoint, one of the Clma ligand connects one dinuclear center Cu_2 via coordination interaction and one bpp through C–H···O hydrogen bond which can be regarded as two-connected nodes simplified into a linker. As a result, the dinuclear metal centers Cu_2 can be regarded as six-connected nodes linking one Clma ligand and five bpp molecules which lead to $(4^6\cdot6^6\cdot8^3)$ nets, and corresponding "long" topological vertex symbols are $4\cdot4\cdot4\cdot4\cdot4\cdot4\cdot6_2\cdot6_2\cdot6_2\cdot6_2\cdot6_2\cdot6_3\cdot8_8\cdot8_8\cdot8_9$. The other Clma ligand acts as five-connected joining one dinuclear center, two bpp ligands, and two Clma molecules, with $(4^4\cdot6^5\cdot8)$ nets and "long" schläfli notation $4\cdot4\cdot4\cdot4\cdot6\cdot6_2\cdot6_3\cdot6_4\cdot6_5\cdot8_{10}$. One of the co-ligands, bpp, joins two Cu_2 centers and two Clma molecules which can be described as four-connected nodes build up a $(4^3\cdot6^3)$ net with a "long" topological vertex symbols $4\cdot6\cdot4\cdot6_3\cdot4\cdot6_4$. The other three-connected nodes bpp ligand connect three Cu_2 centers that lead to a (4^3) net with long vertex symbol $4\cdot4\cdot4$. As a whole, the 3-D supramelcular network can be described as a 3,4,5,6-c net of $(4^3\cdot6^3)(4^3)(4^4\cdot6^5\cdot8)(4^6\cdot6^6\cdot8^3)$ as shown in figure 6.

Bpy (7.708 Å), bpe (9.386 Å), and bpp (10.001 Å) are three different dipyridyl-type molecules with different spacer lengths and different flexibility. Employing the above three ligands afforded different structures in which the numbers of coordination water molecules (1 for complex **1**, 2 for complex **2**, 0 for complex **3**) and a clear decreasing progression of the density of **1**–**3** may be ascribed to two main factors. The first is three dipyridyl-type ligands with different sizes influence the distance of metal dimers (11.037, 13.278, 13.227 Å) to form three different asymmetric units. The second as well as the most important factors is the different flexibility. Many relatively rigid molecules like bpy and bpe are

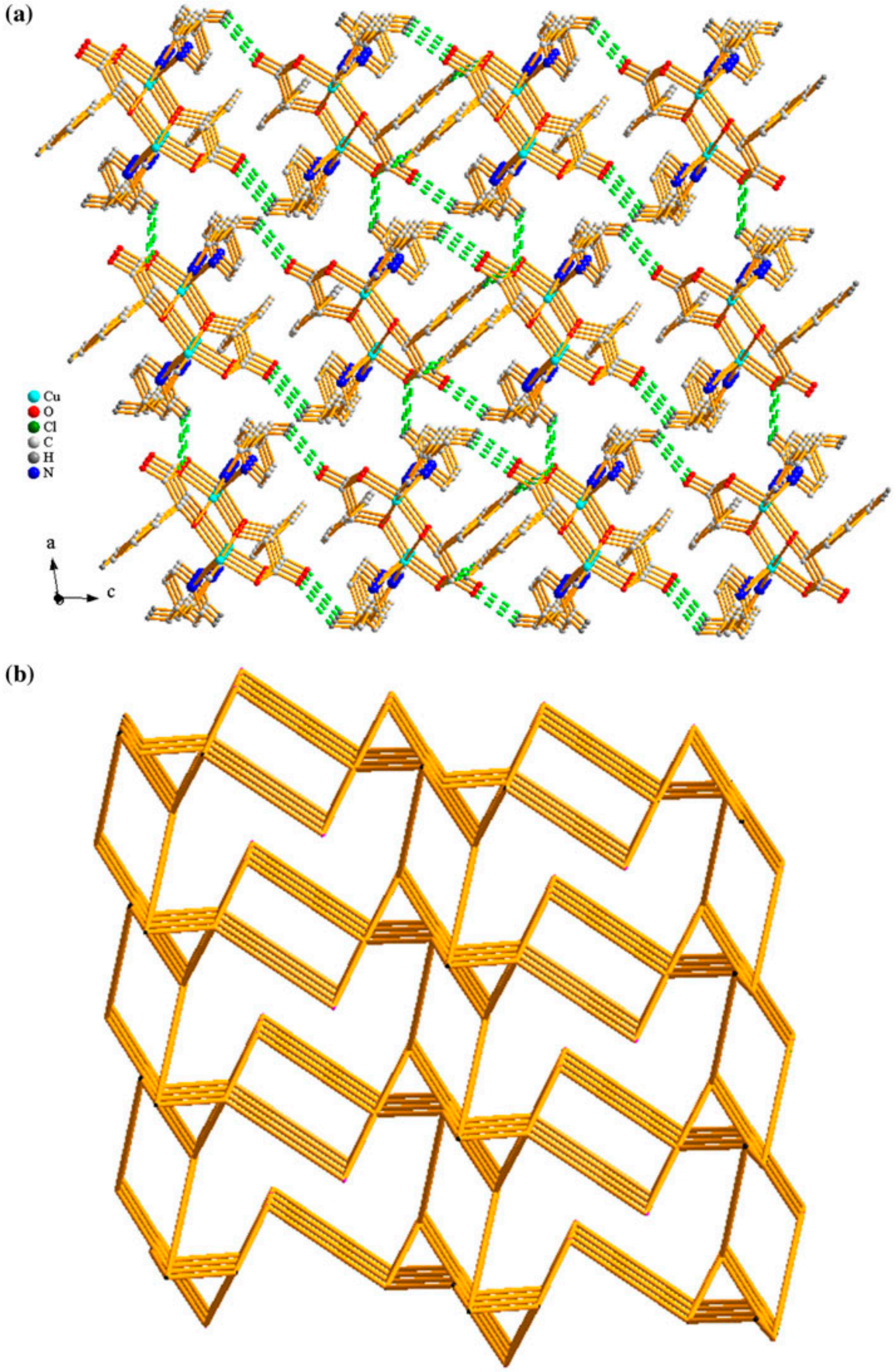


Figure 6. 3-D [Cu(bpp)(Clma)]$_{2n}$ framework formed by C–H···O hydrogen bonds (a) along with the corresponding topological nets (b) in **3**. For clarity, the majority of hydrogens were omitted.

common resulting in single-stranded chains, while flexible components, such as bpp, bte (1,2-bis(1,2,4-triazol-1-yl)ethane), and btp(1,3-bis(1,2,4-triazol-1-yl)propane), are easier to form double-stranded chains in the assembling of structures [35–37].

3.3. *Infrared spectra*

The infrared spectra (figure S2) of **1** and **2** show characteristic broad bands from 3100 to 3600 cm^{-1} due to the absorption from O–H stretching vibrations of the water molecules. The C–H vibrations from benzene ring and methane are observed at 3054–3068 and 2878–2926 cm^{-1} for **1**, respectively (3056–3097 and 2888–2933 cm^{-1} for **2**, 3024–3064 and 2859–2940 cm^{-1} for **3**). The asymmetric (ν_{as}) absorptions of carboxyl groups are observed at 1610 cm^{-1} for **1** (1609 cm^{-1} for **2**, 1617 cm^{-1} for **3**), while the symmetric (ν_s) ones are centered at 1359 cm^{-1} for **1** (1328 cm^{-1} for **2**, 1327 cm^{-1} for **3**), and the values of ($\nu_{as} - \nu_s$) = 251 cm^{-1} for **1** (281 cm^{-1} for **2**, 290 cm^{-1} for **3**) indicate the mono-mode of carboxyl groups [38] which is consistent with the single-crystal X-ray diffraction. Two sharp and medium-strong peaks (1640 and 1670 cm^{-1}) in **2** can be ascribed to C=C stretching vibrations from bpe ligand. The medium-strong vibrations around 1076 and 1032 cm^{-1} for **1** (1068 and 1031 cm^{-1} for **2**, 1074 and 1030 cm^{-1} for **3**) correspond to the C–O stretching of hydroxyl groups. The sharp and middle peaks at 723 and 814 cm^{-1} for **1** (720 and 802 cm^{-1} for **2**, 709 and 805 cm^{-1} for **3**) can be assigned to C–Cl vibration of Clma ligands. The =C–H bending vibration out-plane on the aromatic rings at 756, 753, and 764 cm^{-1} for **1**–**3**, respectively, corresponds to a para-position substitution.

3.4. *Thermal analyses*

The thermal behaviors of **1**–**3** have been measured from 30 to 900 °C in a flowing N_2 atmosphere (figure S3). Compound **1** displays good thermal stability over 30–110 °C. Afterwards, sample **1** undergoes the first weight loss (2.62%) in good agreement with the value of 2.69% calculated from the release of one mole-coordinated water molecule per formula unit. Upon heating (150–630 °C), the dehydrate intermediate "Cu_2(bpy)(Clma)$_2$" experiences a framework collapse as shown by the TG curve which displays bursting weight loss. Upon further heating, the sample weight remains almost unchanged. The brick-red residue of 21.24% collected at 900 °C corresponds to the value of 21.34% calculated for one mole Cu_2O.

Compound **2** displays similar TG behavior with **1**. The observed weight loss for the first step decomposition in the temperature range 50–80 °C reaches 4.59% corresponding to the calculated value (5.04%) for the removal of two mole-coordinated water molecules per formula unit. The lower dehydration temperature of sample **2** may be attributed to the longer distance between Cu(II) and oxygen atoms from water molecules (2.577 and 2.581 Å), in contrast with that in sample **1** (2.224 Å). The dehydrate intermediate "Cu_2(bpe)(Clma)$_2$" remains stable from 80 to 160 °C. Upon heating (160–600 °C), the intermediate undergoes a framework collapse which is remarkably similar to sample **1** as shown by the TG curves. Upon further heating, the sample weight decreases very slowly. The final brick-red residue of 20.03% collected at 900 °C is assumed to be Cu_2O (20.75%).

Compound **3** displays a different thermal decomposition course with **1** and **2**. The title complex displays good thermal stability in the range of 30–150 °C. Upon further heating, the sample undergoes an abrupt weight loss, a gradual diminishing and no weight loss over the temperature ranges 150–350, 350–600, and 600–900 °C, respectively, as shown by the TG curve. The black residue of 16.49% collected at 900 °C is assumed to be the mixture of Cu and C.

3.5. *Ferroelectric properties*

Complexes **1**–**3** crystallize in chiral space groups $P2_1$, $P1$, and $P2_1$ associated with the point group C_2, C_1, and C_2 which may possess ferroelectric properties. Unfortunately, the ferroelectric behaviors of polymer **2** were not investigated due to the low yield. The electrical hysteresis loop of **1** and **3** were recorded at room temperature, using powder samples in

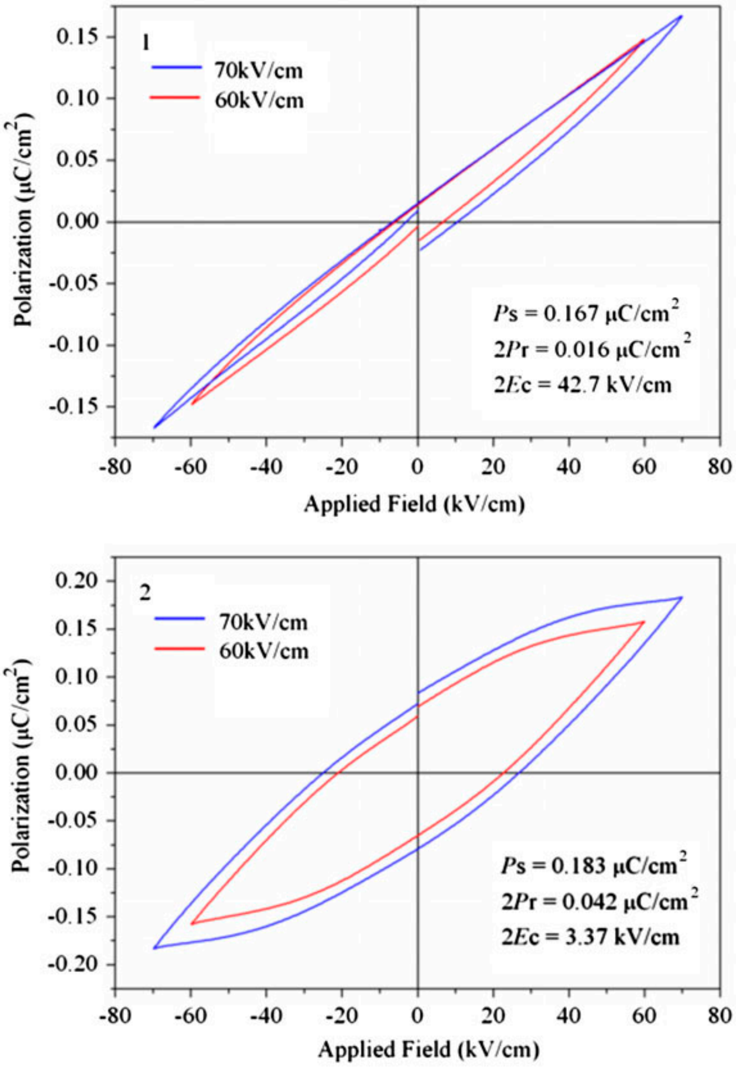


Figure 7. Electric hysteresis loops for a pellet obtained from powdered samples of **1** and **3**, respectively.

pellets (figure 7). Experimental results indicate typical ferroelectric feature with a remnant polarization (*P*r) of ca. 0.008 μC cm^{-2} for **1** (0.021 μC cm^{-2} for **3**) and coercive field (*E*c) of ca. 21.4 kV cm^{-1} for **1** (1.69 kV cm^{-1} for **3**). The spontaneous saturation polarization (*P*s) is ca. 0.167 μC cm^{-2} for **1** (0.183 μC cm^{-2} for **3**), which is lower than that of a typical ferroelectric compound (e.g. $NaKC_4H_4O_6{\cdot}4H_2O$, Rochelle salt; usually *P*s = 0.25 μC cm^{-2}).

4. Conclusion

Three Cu(II) coordination polymers, $Cu_2(bpy)(H_2O)(Clma)_2$ (**1**), $Cu_2(bpe)(H_2O)_2(Clma)_2$ (**2**) and Cu(bpp)(Clma) (**3**), have been obtained by solution-based methods. Compounds **1**–**3** feature 1-D chains based on bridging ligands bpy, bpe and bpp with different spacer lengths and unfolded with $Cu_2(H_2O)(Clma)_2$, $Cu_2(H_2O)_2(Clma)_2$, and $Cu_2(Clma)_2$ dinuclear units, respectively. **1** and **3** exhibit significant ferroelectric effects which findings provide a new impetus for the construction of novel ferroelectric (*R*)-2-Chloromandelic acid based coordination materials. **1**–**3** were obtained using chiral (*R*)-2-Chloromandelic acid ligand which may provide an avenue for the construction of useful crystal chiral drugs.

Supplementary material

Crystallographic data for **1–3** deposited with the Cambridge Crystallographic Data Center, CCDC-972490 (**1**), 972491 (**2**) and 972489 (**3**). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 (0) 1223-336033; Email: deposit@ccdc.cam.ac.uk]. PXRD patterns, infrared spectra and TG curves of **1**, **2** and **3** are shown in figures S1–S3 and tables containing main data of bond distances and angles are described in tables S1, S2 and S3 for **1**, **2** and **3**, respectively.

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