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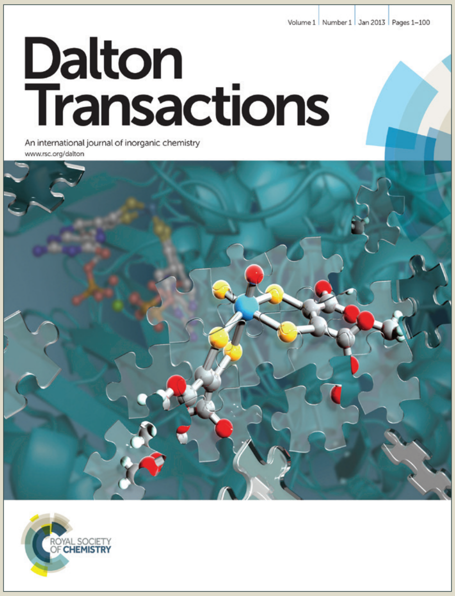

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ARTICLE TYPE

Anion-controlled self-assembly of two NLO-active dinuclear and molecular square Cu(II) enantiomeric pairs: from antiferromagnetic to ferromagnetic coupling†

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Two second-order nonlinear optical (NLO)-active dinuclear and square Cu(II) enantiomeric pairs were obtained via the self-assemblies of enantiopure linear bis-bidentate ligands with different copper(II) salts under the identical reaction conditions. Their magnetic properties are switched from antiferromagnetic to ferromagnetic coupling.

The preparation of enantiopure chiral magnets (ECM) is currently of great interest in the research area of molecule-based magnetic materials because they may show magnetic properties together with other intriguing physical properties such as magneto-chiral dichroism (MChD) effect, second-order nonlinear optical (NLO) activity and ferroelectricity.[1] However, the reported ECMs with circular dichroism (CD) evidence are still scarce mainly owing to difficulties in controlling the chirality of the entire magnetic system.[2] Although it is desirable to obtain ECM utilizing achiral components via spontaneous resolution, which usually leads to a racemic mixture,[3] the self-assembly between paramagnetic metal ions and homochiral ligands has proven to be the most effectual approach to transferring and controlling the chiral information in molecular magnetic system.[1f,g,2]

On the other hand, metallosupramolecular architectures with a distinctive geometry shape, such as molecular polygons (triangle, square, pentagon or hexagon), tetrahedron and other well-defined shapes have attracted much attention during the past decades.[4] They not only bear aesthetically pleasing structures but also have promising applications in host-guest chemistry and magnetic chemistry.[5] Regarding molecular polygons, two types of metal-ligand combinations are often applied for their formations. One is the use of monodentate ditopic ligand with a square-planar metal ion (such as Pt^{2+} and Pd^{2+}), the metal ions and ligands of which are all co-planar.[4d,6] The other is to adopt a rigid bidentate ditopic ligand with an octahedral metal ion (Zn^{2+}, Ni^{2+} and Fe^{2+}, etc.), wherein the ligand strands wrap the metal ions in an interwoven fashion.[4a,b,7] Although such a self-assembly fashion maybe renders an individual single-crystal structure to be chirality, the bulky crystals are a racemate without CD sign.[7,8] Especially, previous studies have shown that the anions play a decisive role in determining the polygon shape.[4b,8] For instance, Dunbar and co-workers demonstrated that the tetrahedral anions BF_4^- and ClO_4^- can act as templates for the formation of molecular squares $[Ni_4(bptz)_4(CHCN)_8]X_8$ (X = BF_4^-, ClO_4^- and bptz = 3,6-bis(2-pyridyl)1,2,4,5-tetrazine, a rigid linear bis-bidentate ligand),[9] whereas the large octahedral anion SbF_6^- results in the exclusive formation of molecular pentagon $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$.[4b] As we are aware, the example that the anions take part in the coordination to the metal ions in the molecular polygon with a linear bis-bidentate ligand has not been reported hitherto. Bearing this in mind, we are interest in the coordination chemistry of enantiopure linear bis-bidentate ligands (+)/(–)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L_S/L_R, Fig. S1, ESI†), which were first used as bridging ligands by our group.[1g,10] We expect to investigate their self-assembly with an octahedral Cu(II) ion and various anions (smaller Cl^- and triangle NO_3^- anions).

We report herein the construction of two dinuclear and square Cu(II) enantiomeric pairs with the formulae $Cu_2Cl_4L_R/_S2H_2O$ (***R*-1** and ***S*-1** being the isomers containing the L_R and L_S ligands, respectively) and $Cu_4(L_R/_S)_4(NO_3)_8\cdot 11H_2O$ (***R*-2** and ***S*-2**), via the self-assemblies between the different copper(II) salts and either L_R or L_S under the identical reaction conditions. Notably, unlike the reported molecular square complexes with linear bis-bidentate ligands, in which the anions only function as the template,[7,9] the NO_3^- anions take part in the coordination role in ***R*-2** and ***S*-2**. Two Cu(II) enantiomeric pairs represent the first example of homochiral metal complexes whose nuclearity and thereby magnetic exchange are regulated by anions.

The reaction of $CuCl_2\cdot 2H_2O$ with either L_R or L_S (2:1 molar ratio) in $CHCl_3/CH_3CN$ afforded pale-green crystals of ***R*-1** and ***S*-1**, respectively. Interestingly, when $Cu(NO_3)_2\cdot 6H_2O$ was used instead of $CuCl_2\cdot 2H_2O$, deep-blue crystals of ***R*-2** and ***S*-2**, respectively, would be obtained (see ESI†).

X-ray crystallographic analyses revealed that both ***R*-1**/***S*-1** and ***R*-2**/***S*-2** are enantiomeric pairs with chiral space groups *P*1 and *I*4, respectively. Thus only the data obtained from the investigation of ***R*-1** and ***R*-2** are described. ***R*-1** is a chiral dinuclear Cu(II) complex composed of one chiral ligand (L_R), two Cu(II) ions, four Cl^- anions and two H_2O molecules. Each Cu(II) ion is bounded by one pyrazine nitrogen atom (N1 for Cu1 and N3 for Cu2) and one pinene-fused pyridyl nitrogen atom (N2 for Cu1 and N4 for Cu2) of L_R, two Cl^- anions and one H_2O molecule (Fig. 1). Each five-coordinate Cu(II) ion is in a square pyramidal $\{CuN_2Cl_2O\}$ environment with the basal plane defined as N1-N2-Cl1-Cl2 for Cu1 atom and N3-N4-Cl3-Cl4 for Cu2 atom with the O1 and O2 atoms of H_2O molecules occupying the apical sites, respectively. For Cu1, the axial Cu1-O1 distance is 2.394(3) Å and four equatorial bond lengths are 2.039(6), 2.026(6), 20254(6) and 2.249(6) Å for Cu1-N1, Cu1-N2, Cu1-Cl1 and Cu1-Cl2, respectively. The Cu2 atom has the similar coordinate atoms and environment to that of Cu1. Thus the N1 and N3 atoms of the pyrazine ring are equatorially coordinated to the Cu1 and Cu2 atoms in an eq–eq fashion, respectively. Besides, the existence of O–H···Cl hydrogen bonds (Table S2, ESI†) between the coordinated H_2O molecules and the Cl^- anions leads to the formation of two-dimensional supramolecular array in **_R_-1** (Fig. S2, ESI†).

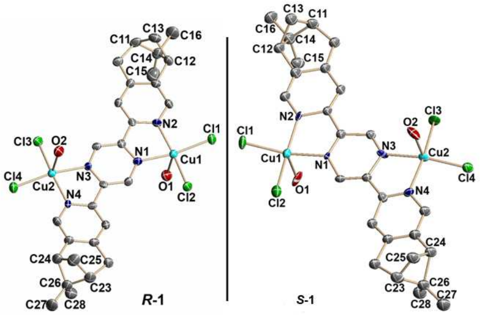

Fig. 1 ORTEP representation (50% probability ellipsoids) and enantiomeric pair of **_R_-1**/**_S_-1**; hydrogen atoms are omitted for clarity.

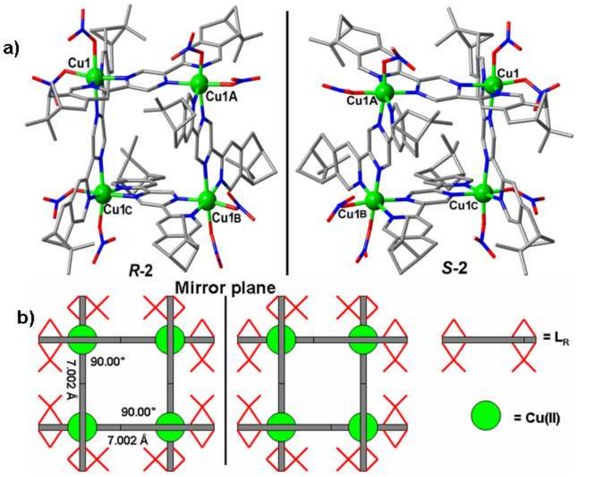

Fig. 2 (a) The mirror-symmetrical molecular structures of **_R_-2**/**_S_-2**; Cu = green, N = blue, O = red, C = gray; hydrogen atoms and lattice water molecules are omitted for clarity; (b) Schematic representation of binding fashion of L_R and L_S with Cu(II) ion in **_R_-2**/**_S_-2**.

While **_R_-2** crystallizes in the chiral space group *I*4 of tetragonal symmetry and its asymmetric unit contains one Cu(II) ion, two monodentate NO_3^- anions along with one pinene-fused pyridine fragment and one pinene-fused pyridyl pyrazine fragment from L_R (Fig. S3, ESI†). As depicted in Fig. 2a, **_R_-2** possesses crystallographic C_4 symmetry. Four crystallographically equivalent Cu(II) ions and four L_R form a molecular square in which each Cu(II) ion occupies the square vertices and each L_R ligand spans one side wrapping two Cu(II) ions in an interwoven fashion (Fig. 2b). Each Cu(II) ion is in a $\{CuN_4O_2\}$ environment and octahedrally coordinated to four nitrogen atoms from two different L_R moieties and to two oxygen atoms of two monodentate NO_3^- anions. The axial Cu–N and Cu–O distances are 2.191 and 2.122 Å, respectively, which are longer than the residual Cu–N/O distances (in the range of 1.947(5)–2.083(5) Å). So, the coordination configuration of the Cu^{2+} ions in **_R_-2** is an elongated octahedron. Four neighbouring Cu···Cu distances are all 7.002 Å with the four Cu···Cu···Cu vertex angles being 90º, indicating a perfect molecular square (Fig. 2b and Fig. S4, ESI†). Indeed, the shape of the molecular structure for **_R_-2** seems to be a molecular square box with one water molecule (O9w) and 0.4 water molecule (O2w) occupying the centres of two entrances to **_R_-2** square box up and down (Fig. S5, ESI†). To the best of our knowledge, **_R_-2** not only is the first enantiopure molecular square complex with CD evidence but also presents the first example of the molecular square complexes based on linear bis-bidentate ligands with the anion being coordinated to the metal ions. Due to the coordination of the NO_3^- anions, the intermolecular interactions of NO_3–O (lone pair)···π (pyrazine ring) were found in **_R_-2** (Fig. S6, ESI†),[11] thus giving the two-dimensional supramolecular array in **_R_-2** (Fig. S7, ESI†).

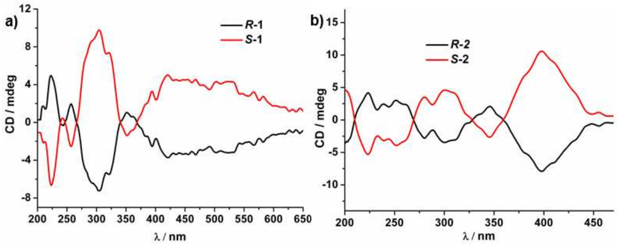

Fig. 3 Solid-state CD spectra of **_R_-1**/**_S_-1** (a) and **_R_-2**/**_S_-2** (b) based on a pressed KCl disk of respective crystals (1% wt).

The mirror-symmetrical CD spectra of both **_R_-1**/**_S_-1** and **_R_-2**/**_S_-2** verified their chiroptical activities and respective enantiomeric natures (Fig. 3). **_R_-1** displays positive Cotton effects at λ_{max} = 221 nm with negative one at λ_{max} = 303 nm, whereas **_S_-1** shows Cotton effects with opposite signals at the same wavelengths. **_R_-2** exhibits positive Cotton effects at λ_{max} = 222 and 345 nm with negative signals at λ_{max} = 301 and 398 nm, whereas **_S_-2** shows Cotton effects with opposite signals at the same wavelengths. Furthermore, the NLO-activities of **_R_-1** and **_R_-2** were ascertained by performing SHG experiments using Kurtz and Perry method.[12] We estimated the second-order NLO effects of **_R_-1** and **_R_-2,** which shows the SHG efficiencies approximately 2 and 2.5 times that of KDP (KH_2PO_4), respectively.

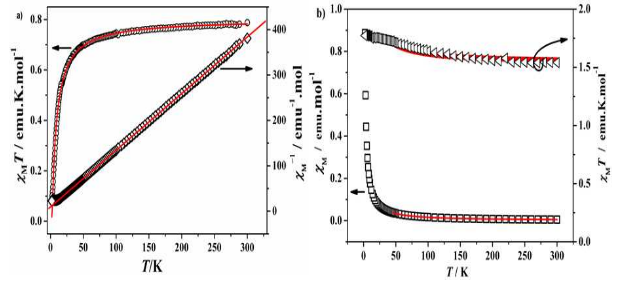

Fig. 4 Temperature dependence of $\chi_M T$ and χ_M^{-1} plots for **_R_-1** (a), $\chi_M T$ and χ_M *vs.* *T* plots for **_R_-2** (b), the solid red lines correspond to the fits.

The magnetic studies have been pursued on ***R*-1** and ***R*-2** in the 300–2 K temperature range with an applied field of 2 kOe. The temperature dependence of $\chi_M T$ product for ***R*-1** is shown in Fig. 4a. Above 100 K, the value of $\chi_M T$ is nearly constant and reaches 0.80 emu·K·mol^{-1} at 300 K, being as expected for two magnetically isolated Cu(II) ions (0.82 emu·K·mol^{-1}, assuming $g = 2.1$). Below 100 K, the value of $\chi_M T$ drastically drops to 0.018 emu·K·mol^{-1} at 2 K. These features are characteristic of the occurrence of an antiferromagnetic interaction between the Cu(II) ions through the pyrazine ring in ***R*-1**. Given that ***R*-1** is a dinuclear structure, its magnetic susceptibility data were analyzed in terms of a simple Bleaney–Bowers expression (1) for a Cu(II) dimer based on the isotropic Hamiltonian $H = -2JS_{Cu1} \cdot S_{Cu2}$. Here, N, K and β constants have their usual significance and J reflects the magnetic coupling through the pyrazine ring.

$$\chi_M = \frac{2Ng^2\beta^2}{KT} \times \frac{1}{3 + e^{-2J/KT}} \qquad (1)$$

The best fit provides the following parameters: $J = -4.05$ cm^{-1}, $g = 2.07$ with the agreement factor R of 1.35×10^{-4}. Additionally, a fit to the magnetic data by the Curie–Weiss law $\chi_M = C/(T-\theta)$ in the whole temperature range gives $C = 0.80$ emu·K·mol^{-1} and $\theta = -7.67$ K. The negative J and θ values also confirm the overall antiferromagnetic interaction between the two Cu(II) ions in ***R*-1**. Usually, two magnetic interaction paths can result in the antiferromagnetic coupling in the Cu–μ–pyrazine–Cu magnetic systems with an eq–eq coordination fashion of the N and Cu atoms (Fig. S8, ESI†). One is the spin-polarization mechanism via π-bonds with a small J value, and the other is the direct σ-type N···N interaction (dσ-nσ exchange path) with a larger J value (J >16 cm^{-1}).[13] Considering the small J value of ***R*-1**, we believe that the antiferromagnetic interactions in ***R*-1** mainly result from the spin-polarization mechanism.[14]

The magnetic property of ***R*-2** in the form of $\chi_M T$ *vs.* T plot is depicted in Fig. 4b. The $\chi_M T$ value is 1.55 emu·K·mol^{-1} at 300 K, corresponding very well to the expected value for four isolated Cu(II) ions (1.65 emu·K·mol^{-1}, assuming $g = 2.1$). Upon cooling, the $\chi_M T$ product increases gradually up to 1.78 emu·K·mol^{-1} at 2 K, indicating the existence of intramolecular ferromagnetic coupling. The magnetic data were fitted over the temperature range 50–300 K using an exchange expression (2) derived from the Hamiltonian $H = g\beta S - (JS_{Cu1} \cdot S_{Cu1A} + JS_{Cu1A} \cdot S_{Cu1B} + JS_{Cu1B} \cdot S_{Cu1C} + JS_{Cu1C} \cdot S_{Cu1})$ for a square arrangement of four identical metal centres with $S = 1/2$, where all parameters have their usual meaning.

$$\chi_M = \frac{2N}{kT} g^2\beta^2[5\exp(2J/kT)+3]/[5\exp(2J/kT) + 10 + \exp(-4J/kT)] \qquad (2)$$

The fit gives the parameter values: $J = +5.78$ cm^{-1}, $g = 2.02$ and $R = 1.95 \times 10^{-4}$. Moreover, a good fit to the magnetic data by the Curie–Weiss law $\chi_M = C/(T-\theta)$ leads to $C = 1.57$ emu·K·mol^{-1} and $\theta = 2.89$ K. The positive J and θ values also confirm the overall intramolecular ferromagnetic coupling between four Cu(II) ions. The coupling constant J is obviously larger than those of two Cu(II) [2×2] grid-like complexes (J = +1.04 and 0.97 cm^{-1}),[15a] but comparable to that of the [2×2] square grid Cu(II) complex with a $Cu_4(\mu\text{–}O)_4$ core (J = 6.2 cm^{-1}).[15b] The strict Orthogonality of the 3 $d_{x^2-y^2}$ magnetic orbitals of the Cu(II) ions is responsible for the ferromagnetic coupling in ***R*-2**.[15,16]

In summary, the dinuclear and square Cu(II) enantiomeric pairs have been synthesized using the linear bis-bidentate chiral ligands L_S/L_R and the copper(II) salts with different anions under the same reaction conditions, which demonstrates the effect of the anions on the nuclearity of the Cu(II) enantiomeric pairs. The square Cu(II) enantiomeric pair is the first example of enantiopure molecular square complexes. Moreover, they provide the first example of magnetic exchange switching from antiferromagnetic to ferromagnetic in enantiopure polynuclear molecular magnetic systems with NLO-activity.

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Two NLO-active dinuclear and molecular square Cu(II) enantiomeric pairs were obtained via the self-assemblies of enantiopure linear bis-bidentate ligands with different copper(II) salts under the identical reaction conditions. Their magnetic properties are switched from antiferromagnetic to ferromagnetic coupling.