

Construction of Chiral One-dimensional Chains via Mononuclear Chiral Precursors and Circular Dichroism Properties^①

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ABSTRACT One-dimensional (1D) chiral chain complexes [CuLSCu(Pydc)] (**2S**) and [CuLRCu(Pydc)] (**2R**) (LS = (E)-3-(((**1S,2S**)-2-(((E)-3-oxo-3-(4-pyridin-4-yl)phenyl)propylidene)amono)-1,2-diphenyl)imino)-1-(4-(pyridin-4-yl)phenyl)butan-1-one) and LR = (E)-3-(((**1R,2R**)-2-(((E)-3-oxo-3-(4-pyridin-4-yl)phenyl)propylidene)amono)-1,2-diphenyl)imino)-1-(4-(pyridin-4-yl)phenyl)butan-1-one and Pydc = 2,6-pyridinedicarboxylic acid) have been synthesized via mononuclear chiral enantiomer precursors CuLS (**1S**) and CuLR (**1R**). Their different chiral configurations of **1S**, **1R**, **2S** and **2R** were determined by single-crystal X-ray diffraction analyses and further characterized by elemental analyses, infrared spectra (IR), powder X-ray diffraction (PXRD), thermal gravimetric analyses (TGA) and circular dichroism spectra (CD).

Keywords: mononuclear chiral precursors, 1D chiral chain, circular dichroism spectra;

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1 INTRODUCTION

Recently, the design and construction of chiral metal organic-frameworks (MOFs) or chiral coordination polymers (CCPs) have received tremendous attention because of intriguing structures and diverse topologies as well as important applications in separation, asymmetric catalysis, recognition, nonlinear optics, and so on^[1-3]. However, the rational design and synthesis of coordination complexes with unique structures and functions still remain a challenge. Among them, the design and construction of CCPs are different from traditional coordination polymers (CPs). Until now, several synthetic strategies have been explored for the construction of CCPs. Usually, these CCPs can be synthesized by the introduction of chiral organic ligands as linkers to assemble with the metal centers^[4-6]. In addition, chiral templates to induce the generation of chiral compounds or achiral starting materials without any chiral auxiliaries via

spontaneous resolution are also a common way^[7-12]. The most effective and straightforward method is the application of chiral ligands, which will ensure the chirality of the resultant network structures^[13-15]. Many studies have been working on the synthesis of CCPs based on the use of 1,2-diphenylethylenediamine derivatives because these polymers are naturally chiral and exhibit excellent coordination with various coordination modes to metal atoms. The chiral carbon atoms in the skeleton are extensively employed as a series of excellent building blocks for the assembly of inorganic-organic hybrid compounds with charming structural^[16-20]. These chiral 1,2-diphenylethylenediamine derivatives were useful in organic synthesis, such as highly enantioselective silylcyanation of aliphatic and aromatic aldehydes^[21], asymmetric hydrogenation of ketones with polymer chiral ligands^[22], and transfer hydrogenation of activated ketones^[23].

Herein, the chiral 1,2-diphenylethylenediamine derivatives

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ligand (LR and LS) to assemble with Cu(II) metal salts, enantiomer chiral mononuclear building blocks **1S** and **1R** were successfully obtained. Enantiomer one-dimensional chiral chain **2S** and **2R** based on correspondent mononuclear chiral precursors **1S** and **1R** under solvothermal conditions have been synthesized.

2 EXPERIMENTAL

2.1 Materials and physical measurements

All reagents were commercially available without further purification. LS and LR were synthesized according to the reported procedure^[24-26]. Infrared (IR) spectra were obtained in the 400~4000 cm⁻¹ range using a Bruker ALPHA FT-IR Spectrometer. Elemental analyses were performed on a PerkinElmer model 2400 analyzer. The solid state CD spectra were recorded on a J-815 spectropolarimeter. Powder X-ray diffraction (PXRD) measurements were carried out on a Bruker D₈ Advance X-ray diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). Thermal gravimetric analyses (TGA) were taken on a Mettler-Toledo thermal analyzer under a N₂ atmosphere at a heating rate of 10 °C min⁻¹.

UV-vis absorption spectra were recorded using a Jasco V-530 instrument.

2.2 Synthesis of LS and LR

A solution of (**1S,2S**)-1,2-diphenylethane-1,2-diamine or (**1R,2R**)-1,2-diphenylethane-1,2-diamine (0.42 g, 2.0 mmol) in MeOH (10 mL) was added dropwise to a stirred solution of 1-(4-(pyridin-4-yl)phenyl)butane-1,3-dione (0.98 g, 4.0 mmol) in MeOH (20 mL). The resulting mixture was heated at reflux for 2 h. After cooling to room temperature and rotary evaporation, ligand LS or LR has been prepared easily, which was purified by column chromatography (SiO₂, hexane-EtOAc 4:1 with 5% MeOH). The enantiomer LS and LR were respectively isolated as a yellow solid (LS, 0.84 g, ca. 84%; LR, 0.87 g, ca. 85%). IR(solid, cm⁻¹) of LS and LR: 3866 (m), 3743 (vs), 3032 (vs), 1771 (s), 1590(s), 1434 (vs), 1325 (vs), 1399(vs), 1195 (vs), 1069 (s), 859 (ms), 544 (m). ¹H NMR(400MHz, CDCl₃) LS and LR: 12.53 (1H), 8.63 (2H), 8.16 (1H), 7.91 (1H), 7.69 (1H), 7.54(2H), 7.51(1H), 7.22(3H), 7.09(2H), 5.72(1H), 4.92 (1H) and 2.09(3H). The schematic diagrams of structures of LS and LR are shown in Fig. 1.

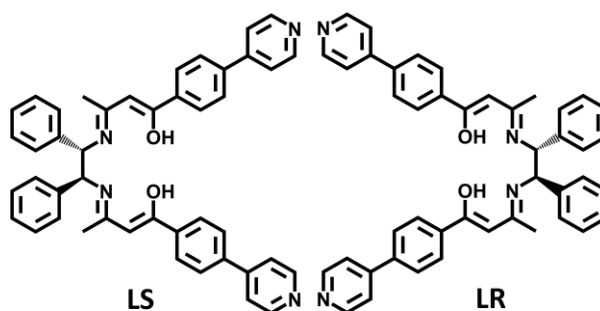


Fig. 1. Structures of LS and LR

2.3 Preparation of 1S and 1R

A solution of Cu(OAc)₂·2H₂O (19.9 mg, 0.10 mmol) in MeOH (5 mL) was added to a solution of LS or LR (69.1 mg, 0.10 mmol) in MeOH (5 mL) at room temperature. A pale green suspension formed upon stirring the reaction mixture for 30 min. The product was separated by filtration and washed with MeOH (5 mL). After drying in vacuo, **1S** (45.0 mg, ca. 80%) or **1R** (47.0 mg, ca. 82%) was obtained as a red solid, respectively. IR (solid, cm⁻¹) 3052w, 3027w, 1589s, 1496s, 1440s, 1025w, 817m, 777s, 707w. Anal. Calcd. of **1S** for C₄₄H₃₆CuN₄O₂: C, 73.77; H, 5.07; N, 7.82%. Found: C, 73.76; H, 5.08; N, 7.82%. Anal. Calcd. of **1R** for C₄₄H₃₆CuN₄O₂: C, 73.77; H, 5.07; N, 7.82%. Found: C, 73.76;

H, 5.08; N, 7.82%.

2.4 Preparation of 2S and 2R

Mononuclear chiral precursors **1S** or **1R** (71.6 mg, 0.1 mmol), Cu(OAc)₂·2H₂O (19.9 mg, 0.10 mmol), Pydc (16.7 mg, 0.1 mmol) and MeOH (5 mL) were added into a Teflon-lined autoclave that was heated under autogenous pressure at 100 °C for 72 h followed by slow cooling to room temperature. The resulting needle-shaped crystals **2S** (48.5 mg, 55%) or **2R** (50.3 mg, 57%) were isolated by filtration, respectively. IR (solid, cm⁻¹) 3058w, 2919w, 1648s, 1590m, 1488s, 1442s, 1035w, 829m, 769s, 703w. Anal. Calcd. for **2S** C₁₀₅H₉₂Cu₄N₁₀O₁₆: C, 62.93; H, 4.63; N, 6.99%. Found: C, 62.82; H, 4.71; N, 6.96%. Anal. Calcd. for **2R**

C₁₀₂H₈₀Cu₄N₁₀O₁₃: C, 64.22; H, 4.23; N, 7.34%. Found: C, 64.16; H, 4.31; N, 7.31%.

2.5 X-ray crystallography

The single-crystal X-ray intensity data were measured at 293 K on a Agilent SuperNova CCD-based diffractometer (CuK α radiation, λ = 1.54184 Å) for **1S**, **1R** and **2S**. After determination of crystal quality and initial tetragonal unit cell parameters, a hemi sphere of frame data was collected. **2R** data were measured at 293 K on a Bruker SMART APEX CCD-based diffractometer (MoK α radiation, λ = 0.71073 Å)^[27]. The structures of **1S** and **1R** were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL97 crystallographic software package with anisotropic displacement parameters for all non-hydrogen atoms^[28]. All H atoms were introduced in calculations using the riding model. The structures of **2S** and **2R** were solved by direct method Olex2 1.2 and refined by full-matrix least-squares on F^2 . Hydrogen atoms were added geometrically and refined using a riding model. The crystal of **1S**

belongs to orthorhombic system, space group $P2_12_12_1$ with a = 8.68270(10), b = 19.7671(3), c = 19.9466(4) Å, γ = 120°, V = 3423.47(9) Å³, Z = 4, D_c = 1.390 Mg·m⁻³, $\mu(\text{MoK}\alpha)$ = 1.256 mm⁻¹, $F(000)$ = 1492, R = 0.0371 and wR = 0.0973. The crystal of **1R** belongs to orthorhombic system, space group $P2_12_12_1$ with a = 8.68270(10), b = 19.7671(3), c = 19.9466(4) Å, V = 3423.47(9) Å³, Z = 4, D_c = 1.390 Mg·m⁻³, $\mu(\text{MoK}\alpha)$ = 1.256 mm⁻¹, $F(000)$ = 1492, R = 0.0371 and wR = 0.0973. The crystal of **2S** belongs to triclinic system, space group $P1$ with a = 9.4824(5), b = 15.7874(8), c = 16.4005(9) Å, α = 87.802(4)°, β = 76.332(5)°, γ = 72.661(5)°, V = 2275.9(2) Å³, Z = 1, D_c = 1.462 Mg·m⁻³, $\mu(\text{MoK}\alpha)$ = 1.669 mm⁻¹, $F(000)$ = 1036, R = 0.0384 and wR = 0.0987. The crystal of **2R** is of triclinic system, space group $P1$ with a = 9.683(3), b = 15.633(5), c = 6.160(5) Å, α = 88.394(4)°, β = 74.459(4)°, γ = 73.459(4)°, V = 2256.2(12) Å³, Z = 1, D_c = 1.423 Mg·m⁻³, $\mu(\text{MoK}\alpha)$ = 1.003 mm⁻¹, $F(000)$ = 982, R = 0.0547 and wR = 0.0864. The selected bond lengths and bond angles are listed in Table 1.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) of **1S**, **1R**, **2S** and **2R**

Complex 1S					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu(1)–O(1)	1.9005(18)	Cu(1)–O(2)	1.908(2)	Cu(1)–N(2)	1.930(2)
Cu(1)–N(1)	1.940(2)				
Angle	(°)	Angle	(°)	Angle	(°)
O(1)–Cu(1)–O(2)	89.42(8)	O(1)–Cu(1)–N(2)	167.82(9)	O(2)–Cu(1)–N(2)	93.26(9)
O(1)–Cu(1)–N(1)	93.93(9)	O(2)–Cu(1)–N(1)	168.45(10)	N(2)–Cu(1)–N(1)	85.78(9)
Complex 1R					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu(1)–O(1)	1.9005(18)	Cu(1)–O(2)	1.908(2)	Cu(1)–N(2)	1.930(2)
Cu(1)–N(1)	1.940(2)				
Angle	(°)	Angle	(°)	Angle	(°)
O(1)–Cu(1)–O(2)	89.42(8)	O(1)–Cu(1)–N(2)	167.82(9)	O(2)–Cu(1)–N(2)	93.26(9)
O(1)–Cu(1)–N(1)	93.93(9)	O(2)–Cu(1)–N(1)	168.45(10)	N(2)–Cu(1)–N(1)	85.78(9)
Complex 2S					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu(1)–N(5)	1.904(4)	Cu(1)–N(6)	2.224(4)	Cu(1)–N(4)	1.972(4)
Cu(1)–O(5)	1.999(3)	Cu(1)–O(3)	2.042(4)	Cu(2)–N(1)#1	2.194(4)
Cu(2)–N(10)	1.899(4)	Cu(2)–N(9)	1.976(4)	Cu(2)–O(12)	2.006(3)
Cu(2)–O(10)	2.038(3)	Cu(3)–O(8)	1.892(3)	N(8)–Cu(3)	1.930(4)
Cu(3)–O(7)	1.910(3)	Cu(3)–N(7)	1.926(4)	Cu(4)–O(2)	1.893(3)
Cu(4)–O(1)	1.915(4)	Cu(4)–N(2)	1.926(4)		
Angle	(°)	Angle	(°)	Angle	(°)
N(5)–Cu(1)–N(4)	160.45(16)	N(5)–Cu(1)–O(5)	81.29(16)	N(4)–Cu(1)–O(5)	97.86(16)
N(5)–Cu(1)–O(3)	80.11(16)	N(4)–Cu(1)–O(3)	97.75(16)	O(5)–Cu(1)–O(3)	160.55(14)
N(5)–Cu(1)–N(6)	104.78(16)	N(4)–Cu(1)–N(6)	94.75(16)	O(5)–Cu(1)–N(6)	95.42(16)
O(3)–Cu(1)–N(6)	94.76(16)	N(10)–Cu(2)–N(9)	160.39(17)	N(10)–Cu(2)–O(12)	81.33(16)
N(9)–Cu(2)–O(12)	98.70(16)	N(10)–Cu(2)–O(10)	80.13(16)	N(9)–Cu(2)–O(10)	96.63(16)
O(12)–Cu(2)–O(10)	160.40(14)	N(10)–Cu(2)–N(1)#1	106.64(16)	N(9)–Cu(2)–N(1)#1	92.91(16)
O(12)–Cu(2)–N(1)#1	95.18(15)	O(10)–Cu(2)–N(1)#1	96.18(15)	O(8)–Cu(3)–O(7)	87.56(15)

To be continued

O(8)–Cu(3)–N(7)	174.03(17)	O(7)–Cu(3)–N(7)	94.07(17)	O(8)–Cu(3)–N(8)	93.30(16)
O(7)–Cu(3)–N(8)	167.73(16)	N(7)–Cu(3)–N(8)	86.33(18)	O(2)–Cu(4)–O(1)	87.03(15)
O(2)–Cu(4)–N(2)	175.69(18)	O(1)–Cu(4)–N(2)	93.62(16)	O(2)–Cu(4)–N(3)	93.21(16)
O(1)–Cu(4)–N(3)	175.38(18)				
Complex 2R					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu(1)–N(6)	1.891(5)	Cu(1)–N(5)	1.965(6)	Cu(1)–O(9)	2.007(4)
Cu(1)–O(7)	2.038(5)	Cu(1)–N(7)	2.216(5)	Cu(2)–O(6)	1.896(4)
Cu(2)–O(5)	1.905(4)	Cu(2)–N(3)	1.942(5)	Cu(2)–N(4)	1.947(5)
Cu(3)–N(1)	1.893(5)	Cu(3)–N(10)#1	1.983(5)	Cu(3)–O(3)	1.999(4)
Cu(3)–O(1)	2.017(4)	Cu(3)–N(2)	2.210(5)	Cu(4)–O(11)	1.897(4)
Cu(4)–O(12)	1.897(4)	Cu(4)–N(9)	1.933(5)	Cu(4)–N(8)	1.941(5)
Angle	(°)	Angle	(°)	Angle	(°)
N(6)–Cu(1)–N(5)	158.0(2)	N(6)–Cu(1)–O(9)	81.5(2)	N(5)–Cu(1)–O(9)	98.3(2)
N(6)–Cu(1)–O(7)	79.2(2)	N(5)–Cu(1)–O(7)	96.9(2)	O(9)–Cu(1)–O(7)	159.6(2)
N(6)–Cu(1)–N(7)	105.6(2)	N(5)–Cu(1)–N(7)	96.3(2)	O(9)–Cu(1)–N(7)	96.2(2)
O(7)–Cu(1)–N(7)	95.6(2)	O(6)–Cu(2)–O(5)	88.32(18)	O(6)–Cu(2)–N(3)	176.0(2)
O(5)–Cu(2)–N(3)	92.5(2)	O(6)–Cu(2)–N(4)	93.6(2)	O(5)–Cu(2)–N(4)	173.8(2)
N(3)–Cu(2)–N(4)	85.1(2)	N(1)–Cu(3)–N(10)#1	158.9(2)	N(1)–Cu(3)–O(3)	81.7(2)
N(10)#1–Cu(3)–O(3)	98.9(2)	N(1)–Cu(3)–O(1)	80.7(2)	N(10)#1–Cu(3)–O(1)	95.1(2)
O(3)–Cu(3)–O(1)	160.98(19)	N(1)–Cu(3)–N(2)	109.1(2)	N(10)#1–Cu(3)–N(2)	91.9(2)
O(3)–Cu(3)–N(2)	93.78(19)	O(1)–Cu(3)–N(2)	98.63(19)	O(11)–Cu(4)–O(12)	87.90(18)
O(11)–Cu(4)–N(9)	168.4(2)	O(12)–Cu(4)–N(9)	92.9(2)	O(11)–Cu(4)–N(8)	93.9(2)
O(12)–Cu(4)–N(8)	174.1(2)	N(9)–Cu(4)–N(8)	86.4(2)		

Symmetry transformations used to generate the equivalent atoms: 2S: #1: $x - 2, y, z - 1$, 2R: #1: $x + 2, y, z + 1$

3 RESULTS AND DISCUSSION

3.1 Structures of **1S** and **1R**

Single-crystal X-ray diffraction analysis revealed that complexes **1S** and **1R** in the orthorhombic space group $P2_12_12_1$. ORTEP drawings are shown in Fig. 2. The Cu(II) cations, locating on the center and adopting a square planar arrangement, are both four-coordinated by two oxygen atoms

(O(1), O(2)) and two nitrogen atoms (N(1), N(2)) from one ligand molecule. The Cu–N and Cu–O bond distances in the basal planes of **1S** are 1.930(2), 1.940(2) Å and 1.9005(18), 1.908(2) Å, respectively. The angles O(1)–Cu(1)–N(2) and N(2)–Cu(1)–N(1) are 167.82(9)° and 85.78(9)°. Obviously, the coordination condition of Cu(II) cation in **1R** is the same as in **1S**.

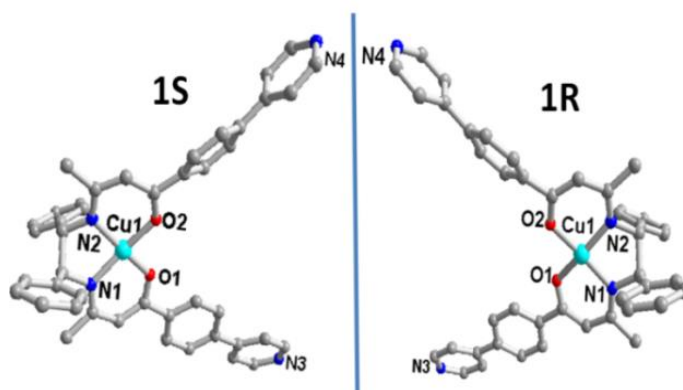


Fig. 2. Coordination environment of Cu(II) center of compounds **1S** and **1R**. The hydrogen atoms are omitted for clarity

3.2 Structures of **2S** and **2R**

Complexes **2S** and **2R** belong to a trigonal space group $P1$, and X-ray single-crystal diffraction analysis reveals the Cu(3) and Cu(4) of **2S** and Cu(2) and Cu(4) of **2R** still keep four-coordinated by two oxygen and two nitrogen atoms from

one ligand LS or LR molecules. The Cu–O and Cu–N bond distances are in the ranges of 1.892(3) ~ 1.915(4) and 1.926(4) ~ 1.947(5) Å, respectively. These values are similar to those in complexes **1S** and **1R**. Detailed bond lengths and bond angles for complexes **2S** and **2R** are provided in Table 2.

The N(3) and N(4) nitrogen atoms without coordination in complex **1S** or **1R** are bound to two Cu(II) atoms to generate a one-dimensional structure (Fig. 3). The local coordination geometry around the connected Cu(II) center in **2S** or **2R** conforms to a square base pyramidal five-coordinate geometry. The Cu(II) metal center is bound to three N atoms from two nitrogen atoms without coordination of pyridine and a pydc ligands, two oxygen and one N atoms from the pydc ligand and one N atom located in the plane, whilst the two bound N atoms from pyridine are situated in the plane

and N atoms from pyridine are situated in the axial positions. The equatorial Cu–N and Cu–O bond distances fall in the ranges of 1.899(4)~1.972(4) and 1.999(3)~2.042(4) Å, respectively. However, the apical Cu–N bonds are in the range of 2.194(4)~2.244(4) Å. Using Addison's model^[29, 30], τ is 100 for the ideal trigonal bipyramidal (TBP) but 0 in the square base pyramidal (SP) geometry. $\tau = 0.006(\text{Cu1})$ and $0.003(\text{Cu2})$ for **2S** and $\tau = 0.026(\text{Cu1})$ and $0.034(\text{Cu3})$ for **2R**, indicating that the Cu(II) coordination geometry is close to be SP geometry.

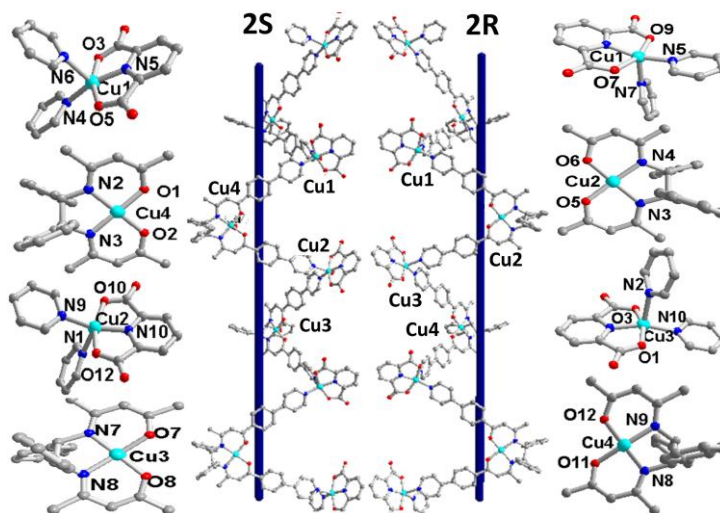


Fig. 3. Perspective drawings of compounds **2S** and **2R**. The hydrogen atoms are omitted for clarity

3.3 PXRD studies and TGA analysis

PXRD was employed to check the phase purity. As shown in Fig. 4 (left), the major peaks of complexes **1S**, **1R**, **2S** and **2R** displayed in the experimental patterns were consistent with the simulated patterns obtained according to the single-crystal diffraction data, which confirmed the phase of the bulk samples are pure.

TGA was conducted to investigate the thermal stability of

complexes **1S**, **1R**, **2S** and **2R**. As shown in Fig. 4 (right), **1S** and **1R** show the same TGA curve and displayed no obvious weight loss below 385 °C. The TGA for **2S** shows a weight loss of 5.2% (calculated 5.6%) before 100 °C, which is associated with the loss of methanol and H₂O molecule. **2R** exhibited no obvious weight loss before 320 °C. **2S** and **2R** have a similar decomposition temperature at 320 °C.

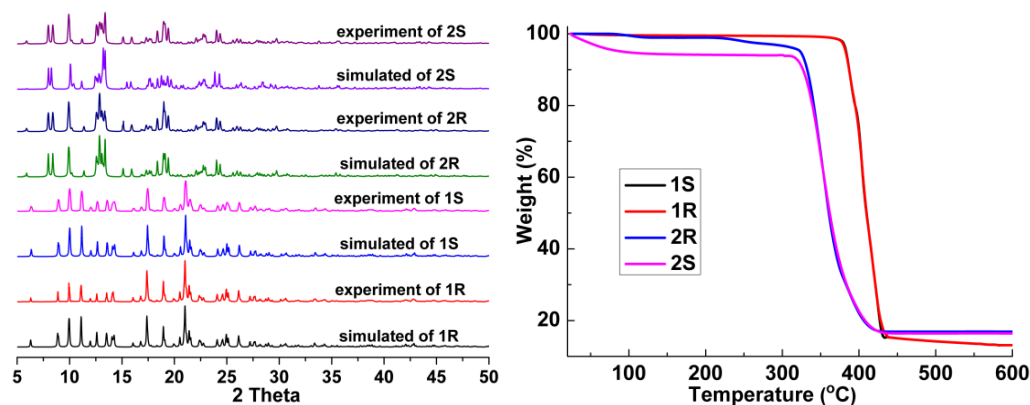


Fig. 4. PXRD patterns (left) and TGA curves (right) of **1S**, **1R**, **2S** and **2R**

3.4 UV-Vis and CD spectra

The solution spectra of **1S** (1×10^{-5} M), **1R** (1×10^{-5} M), **2S** (1×10^{-5} M) and **2R** (1×10^{-5} M) were recorded in CH_2Cl_2 between 200 and 600 nm (Fig. 5). **1S** and **1R** exhibit three peaks at about 225, 250 and 350 nm, and **2S** and **2R** also show three peaks at about 230, 260 and 360 nm, respectively. The band at 350 nm was attributed to the $\pi\text{-}\pi^*$ transition of the azomethine chromophore and the two other bands at higher energy region 250 and 230 nm were attributed to the $\pi\text{-}\pi^*$ transition of the benzene ring. Compared to the free ligands **1S** and **1R**, the absorption peaks of **2S** and **2R** have slight red-shift probably assigned to the coordination of ligands pydc to Cu ion to form a 1D spiral structure. Solid circular dichroism (CD) spectra measured in KCl pellets for **1S**, **1R**, **2S** and **2R** confirm the enantiomeric nature of the optically active (Fig. 5). Complexes **1S** and **2S** exhibit

positive Cotton effects at 250, and 330 nm, and negative dichroic signals at 300 and 410 nm. As predicting, enantiomer complexes **1R** and **2R** display Cotton effects with opposite signs at the corresponding wavelengths. Good mirror symmetry of CD spectra confirmed the optical activity and enantiomeric nature of complexes **1S**, **1R** and **2S**, **2R**. Similar to UV-vis absorption, the difference of CD spectra of **1S/1R** and **2S/2R** is mainly due to the formation of 1D spiral structure which makes the larger intensity CD signal for **2S/2R**. The similar square-planar copper(II) complexes with Schiff bases derived from (S,S)-(+)-cyclohexane-1,2-diamine and calixsalen have similar circular dichroism^[31-33]. The two pair of Cotton peaks: 410, 330 nm and 300, 250 nm correspond to the exciton coupling states the $\pi\text{-}\pi^*$ transition of azomethine chromophore of ligand and the $\pi\text{-}\pi^*$ transition of benzene ring, respectively.

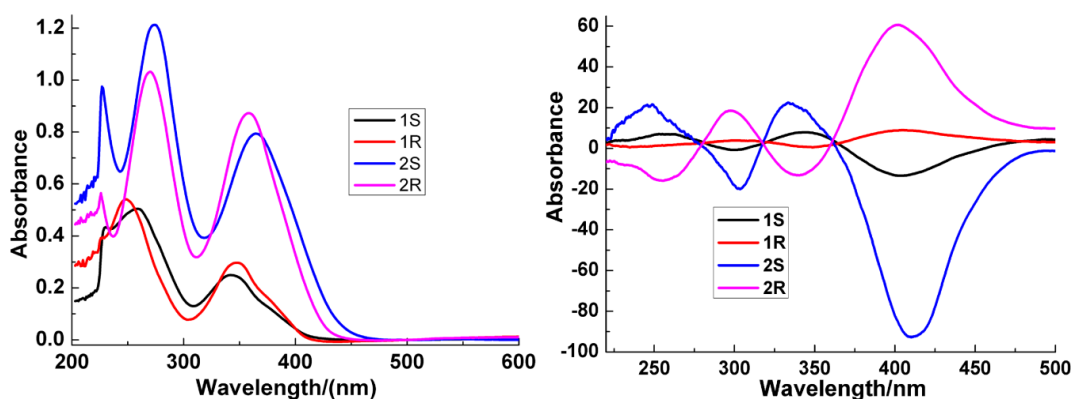


Fig. 5. UV-Vis spectrogram of **1S**, **1R**, **2S** and **2R** in CH_2Cl_2 (left) and CD spectra of **1S**, **1R** and **2S**, **2R** in KCl pellets (right)

4 CONCLUSION

Two 1D enantiomer chiral chains **2S** and **2R** based on correspondent mononuclear enantiomer chiral precursors **1S** and **1R** have been synthesized. Single-crystal X-ray diffraction analyses and CD spectra for complexes **1S**, **1R**

and **2S**, **2R** were successfully carried out, respectively, conforming their optical and enantiomeric nature activities. Moreover, this work will provide a favorable idea for the further design of chiral coordination polymer with novel structures and properties.

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