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Journal of Solid State Chemistry



journal homepage: www.elsevier.com/locate/jssc

Homochiral coordination polymers constructed from aminocarboxylate derivates: Effect of bipyridine on the amidation reaction

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ARTICLE INFO

Article history: Received 11 January 2012 Received in revised form 9 April 2012 Accepted 15 April 2012 Available online 24 April 2012

Keywords: Metal-organic complex Homochiral Amino acid In situ cyclization Nonlinear optical active

ABSTRACT

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1. Introduction

Metal-organic coordination networks have attracted much interest in these decades, because they show numerous inherent advantages over traditional inorganic zeolites. By choice and modification of organic linkers and metal centers, metal-organic coordination networks exhibit varieties of interesting molecular topologies, which permits incorporation of many specific properties [1–8]. Although lots of metal-organic coordination networks have been successfully synthesized so far, it is still a challenge to design and synthesize metal-organic coordination networks with expected structures and properties.

Our interest is focused on the synthesis of homochiral metalorganic polymers, because homochiral polymers show potential applications on enantioselective catalysis [9–14], separations [15–19], and second-order nonlinear optical applications [20–23]. Homochiral coordination polymers can be prepared from chiral ligands and templates, which is a most direct and efficient method [24–28]. Despite the fact that hydrothermal techniques have been used widely in preparation of metal organic complexes, most chiral coordination complexes were obtained using conventional solution synthesis techniques, because the chirality may lost under hydrothermal conditions [29–31]. The natural amino acids are a rich pool of chiral ligands because they: (1) are cheap and readily available; (2) possess several functional groups in one molecule; (3) are relevant to biological systems. Therefore, amino acids are often used to construct new chiral materials [32–37]. Modifying natural amino acids endows the resulting chiral ligands with more structural diversities, as well as fascinating properties, which are helpful for the synthesis of chiral metal–organic polymers with expected functionalities [38–43]. *N*-(2-hydroxybenzyl)-amino acids, which contain terminal and bridging coordination modes that favor the coordination of metal ions, have been used as building blocks in MOF construction [44–46]. However, studies on their analogs synthesized from benzaldehyde derivates without hydroxy group are relatively few [47–50].

In this work, two new amino acid derivates **1a** and **1b** were obtained from L-glutamic acid and used as chiral ligands in constructing homochiral metal–organic complexes. The chirality of ligands retain in the target complexes even under hydrothermal condition. As expected, the metal-organic complexes possess second-order harmonic generation properties due to their chirality.

2. Experimental

2.1. Materials and methods

Commercially available reagents were used as received without further purification. Chiral ligands **1a–1b** were synthesized under

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nitrogen atmosphere. Ligand 2 and complexes 3-7 were synthesized in 25 mL Teflon-lined stainless steel vessels under autogenous pressure. The reactants were stirred homogeneously before heating. ¹H NMR and ¹³C NMR were carried out with Bruker 400 MHz AVANCE III spectrometers. Melting points were obtained on a SGW X-4 microscope without temperature correction. Element analyses were carried out with a Vario EL III element analyzer. Infrared spectra were obtained on a Nicolet Magna 750 FTIR spectrometer. Optical rotation values were measured at the sodium-D line (589 nm) with a SGW-1 polarimeter without temperature correction. Solid-state circular dichroism (CD) spectra were recorded on a I-800 spectropolarimeter (Jasco, Japan). Thermogravimetric analyses (TGA) were performed on a NETZSCH STA449C under nitrogen gas flow at a heating rate of 15 °C min⁻¹ from room temperature to 800 °C. Second harmonic generations (SHG) were measured by using the Kurtz and Perry method [51] with a Nd:YAG laser of 1064 nm wavelength.

2.2. Preparation

2.2.1. (S)-N-(4-cyanobenzoic)-glutamic acid (1a)

L-Glutamic acid (11.7 g, 0.08 mol) was dissolved in an aqueous solution of sodium hydroxide (0.16 mol, 80 mL). A solution of 4-cyanobenzaldehyde (10.5 g, 0.08 mol) in ethanol (40 mL) was added dropwise and then the mixture was cooled to 0 °C. Sodium borohydride (1.0 g, 0.025 mol) was added in small portions and the mixture was stirred at room temperature for 1.5 h. Stirring was continued for 30 min after a second portion of 4-cyanobenzaldehyde (2.1 g, 0.016 mol) was added. Finally, a second portion of sodium borohydride (0.2 g, 4.8 mmol) was added, and the mixture was stirred for another 30 min before it was extracted with diethyl ether to remove excess 4-cyanobenzaldehyde. And then the aqueous layer was acified at 0 °C to pH 3 with concentrated HCl, at which point the compound precipitated as a white powder. The suspension was filtered, and washed with cold water. The white powder was dried under reduced pressure at 50 °C. Yield: 14.7 g (70.0%); Mp. 155–157 °C; $[\alpha]_D^{31.7} = -5.72^{\circ}$ (c 0.005, 0.025 M NaOH). Anal. Calcd. for C₁₃H₁₃N₂O₄ 1a: C 59.54, H 5.38, N 10.68. Found: C 59.23, H 5.44, N 10.61. IR (KBr, cm⁻¹): 3511.38m, 2233.08m, 1716.58s, 1613.60s, 1582.55s, 1488.87w, 1397.04w, 1342.33m, 1277.68m, 1231.26w, 855.35w. ¹H-NMR (400 MHz, DMSO, 20 °C): 1081.81w, δ=13.037(s, 1H, -COOH), 7.799-7.815(m, 2H, H-arom), 7.416-7.795(m, 2H, H-arom), 4.808-4.848(m, 1H, -CH), 4.017-4.141 (m, 2H, -CH₂), 2.499-2.517(m, 2H, -CH₂), 2.286-2.399(m, 2H, -CH₂), 1.956-2.048(m, 1H, -NH) ppm. ¹³C-NMR (400 MHz, DMSO, 22 °C): $\delta = 175.34(-COOH)$, 173.69(-COOH), 143.15(C-arom), 132.85(C-arom), 129.02(C-arom), 119.26(-CN), 110.47(C-arom), 59.31(C-alkyl), 45.14(C-alkyl), 29.25(C-alkyl), 23.04(C-alkyl) ppm.

2.2.2. (S)-N-(4-nitrobenzoic)-glutamic acid (1b)

L-Glutamic acid (14.7 g, 0.1 mol) was dissolved in an aqueous solution of sodium hydroxide (0.2 mol, 100 mL). A solution of 4-nitrobenzaldehyde (15.1 g, 0.1 mol) in methanol (50 mL) was added dropwise and then the mixture was cooled to 0 °C. Sodium borohydride (1.2 g, 0.03 mol) was added in small portions and the mixture was stirred at room temperature for 1.5 h. Stirring was continued for 30 min after a second portion of 4-nitrobenzaldehyde (3.02 g, 0.02 mol) was added. Finally, a second portion of sodium borohydride (0.24 g, 6 mmol) was added, and the mixture was stirred for another 30 min. And then the aqueous layer was acified at 0 °C to pH 3 with concentrated HCl, at which point the compound precipitated as a pale yellow powder. The suspension was filtered, and washed with cold water. The white powder was dried under reduced pressure at 50 °C. Yield: 24 g (85.0%). Mp. 207–208 °C; $[\alpha]_D^{28.6} = -6.46^{\circ}$ (*c* 0.005, 0.025 M NaOH). Anal. Calcd. for C₁₂H₁₄N₂O₆ **1b**: C, 51.06(50.99); H, 5.00(4.96); N, 9.93(9.96). IR (KBr, cm⁻¹): 3505.73 m; 1712.54s; 1614.73s; 1528.56s; 1351.18s; 1270.61m; 1234.72w; 859.24m. ¹H-NMR (400 MHz, DMSO, 27 °C): δ =8.176-8.219(m, 2H, H-arom), 7.500–7.522(m, 2H, H-arom), 4.645-4.882(m, 1H, -CH), 4.039–4.066(m, 2H, -CH₂), 2.499–2.517(m, 2H, -CH₂), 2.310–2.402(m, 2H, -CH₂), 1.978–2.031(m, 1 H, -NH) ppm. ¹³C-NMR (400 MHz, DMSO, 21 °C): δ =175.07(-COOH), 174.56(-COOH), 148.19(C-arom), 147.00(C-arom), 129.61 (C-arom), 124.02(C-arom), 59.95(C-alkyl), 50.38(C-alkyl), 30.88 (C-alkyl), 27.79(C-alkyl) ppm.

2.2.3. N-(4-Cyanobenzoic)-5-oxoproline (2)

A mixture of **1a** (59.5 mg, 0.25 mmol) and H₂O (5 mL, 0.28 mol) was sealed in a 25 mL Teflon lined stainless steel container and heated at 80 °C for 48 h. After the mixture was cooled slowly to ambient temperature, colorless prism-shaped crystals of **2** were obtained. The crystals were filtered, washed with distilled water, and dried at ambient temperature. A suitable crystal was selected for single-crystal X-ray diffraction studies. The yield was 61.5% (37.4 mg) based on **1a**. Anal. Calcd. for $C_{13}H_{11}N_2O_3$ **2**: C 63.93, H 4.95, N 11.47. Found: C 64.27, H 4.90, N 11.55. IR (KBr pellet, cm⁻¹): 2515.29m, 2235.02m, 1721.67s, 1630.44s, 1467.55m, 1420.85m, 1362.05m, 1280.08m, 1225.89s, 1172.64w, 988.84w, 866.33m, 654.64m.

2.2.4. $[Cu(cbg)(H_2O)_2]_n$ (3)

A mixture of $Cu(CH_3COO)_2 \cdot 2H_2O$ (100 mg, 0.5 mmol), **1a** (59.5 mg, 0.25 mmol), and NaOH (10 mg, 0.25 mmol) in H₂O (5 mL, 0.28 mol) was sealed in a 25 mL Teflon lined stainless steel container and heated at 80 °C for 48 h. After the mixture was cooled slowly to ambient temperature, blue needle-shaped crystals of **3** were obtained. The crystals were filtered, washed with distilled water, and dried at ambient temperature. A suitable crystal was selected for single-crystal X-ray diffraction studies. The yield was 48.9% (44.0 mg) based on **1a**. Anal. Calcd. for $C_{13}H_{16}CuN_2O_6$ **3**: C 43.39, H 4.48, N 7.79. Found: C 43.49, H 4.37, N 7.81. IR (KBr pellet, cm⁻¹): 3458.51m, 3239.82m, 2227.72m, 1653.80s, 1612.84s, 1549.27s, 1416.41m, 1381.98s, 1323.70m, 984.19w, 857.43w.

2.2.5. $[Cu(cbop)_2(4,4'-bipy)(H_2O)]_n$ (4)

A mixture of copper carbonate (29.2 mg, 0.25 mmol), **1a** (59.5 mg, 0.25 mmol), and 4,4'-bipyridine (39 mg, 0.25 mmol) in H₂O (5 mL, 0.28 mol) was sealed in a 25 mL Teflon lined stainless steel container and heated at 80 °C for 48 h. After the mixture was cooled slowly to ambient temperature, blue prism-shaped crystals of **4** were obtained. The crystals were filtered, washed with distilled water, and dried at ambient temperature. A suitable crystal was selected for single-crystal X-ray diffraction studies. The yield was 22.5% (40.8 mg) based on **1a**. Anal. Calcd. for $C_{36}H_{32}CuN_6O_7$ **4**: C 59.71, H 4.45, N 11.60. Found: C 59.58, H 4.35, N 11.54. IR (KBr pellet, cm⁻¹): 3387.90m, 2228.48m, 1672.56s, 1606.67s, 1413.72m, 1275.86m, 809.77m, 639.10w.

2.2.6. { $[Cu(nbop)_2(4,4'-bipy)] \cdot 4H_2O]_n$ (5)

A mixture of copper carbonate (29.2 mg, 0.25 mmol), **1b** (70.5 mg, 0.25 mmol), and 4,4'-bipyridine (39 mg, 0.25 mmol) in H_2O (5 mL, 0.28 mol) was hated at 120 °C for 12 h. After the mixture was cooled slowly to ambient temperature, blue prism-shaped crystals of **5** were obtained. The crystals were filtered, washed with distilled water, and dried at ambient temperature. A suitable crystal was selected for single-crystal X-ray diffraction studies. The yield was 30.6% (62.5 mg) based on **1b**. Anal. Calcd.

for $C_{34}H_{38}CuN_6O_{14}$ **5**: C 49.91, H 4.68, N 10.27. Found: C 49.58, H 4.48, N 10.15. IR (KBr pellet, cm⁻¹): 3445.32m, 1676.09s, 1610.40s, 1520.32m, 1414.39m, 1347.03s.

2.2.7. { $[Cd(nbop)_2(4,4'-bipy)] \cdot 2H_2O_n(6)$

A mixture of cadmium carbonate (43.1 mg, 0.25 mmol), **1b** (70.5 mg, 0.25 mmol), and 4,4'-bipyridine(39 mg, 0.25 mmol) in H_2O (5 mL, 0.28 mol) was sealed in a 25 mL Teflon lined stainless steel container and heated at 100 °C for 24 h. After the mixture was cooled slowly to ambient temperature, pale yellow prism-shaped crystals of **6** were obtained. The crystals were filtered, washed with distilled water, and dried at ambient temperature. A suitable crystal was selected for single-crystal X-ray diffraction studies. The yield was 21.0% (43.6 mg) based on **1b**. Anal. Calcd. for C₃₄H₃₄CdN₆O₁₂ **6**: C 49.14, H 4.12, N 10.11. Found: C 49.18, H 3.54, N 10.07. IR (KBr pellet, cm⁻¹): 3421.34m, 1677.45s, 1659.26s, 1591.70s, 1519.79s, 1448.35w, 1414.63m, 1347.46s, 1297.32w, 1218.68w, 814.28m, 708.26m, 627.58m.

2.2.8. $[Ni(nbop)_2(4,4'-bipy)(H_2O)_2]_n$ (7)

A mixture of nickel carbonate (33.3 mg, 0.25 mmol), **1b** (70.5 mg, 0.25 mmol), and 4,4'-bipyridine(39 mg, 0.25 mmol) in H₂O (5 mL, 0.28 mol) was sealed in a 25 mL Teflon lined stainless steel container and heated at 120 °C for 12 h. After the mixture was cooled slowly to ambient temperature, green prism-shaped crystals of **7** were obtained. The crystals were filtered, washed with distilled water, and dried at ambient temperature. A suitable crystal was selected for single-crystal X-ray diffraction studies. The yield was 29.1% (56.5 mg) based on **1b**. Anal. Calcd. for C₃₄H₃₄N₆NiO₁₂ **7**: C 52.53, H 4.41, N 10.81. Found: C 52.48, H 4.29, N 10.80. IR (KBr pellet, cm⁻¹): 3314.65m, 1669.52s, 1608.17s, 1516.30m, 1418.05m, 1401.41m, 1343.35s, 1305.34m, 732.62w.

2.3. Single-crystal X-ray diffraction

X-ray data of **2–7** were collected on a Rigaku Mercury CCD/AFC diffractometer using graphite monochromated Mo K_{α} radiation (λ (Mo K_{α}) 0.71073 Å) at 293(2) K. Data were reduced with *CrystalClear* version 1.3. These structures were solved by direct methods and refined by full-matrix least-squares techniques on F² using *SHELXTL*-97 [52]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically. Crystal data, as well as details of the data collection and refinement for the complexes are summarized in Tables 1 and 2.

3. Results and discussion

3.1. Synthesis

Ligands (*S*)-*N*-(4-cyanobenzoic)-glutamic acid (**1a**) and (*S*)-*N*-(4-nitrobenzoic)-glutamic acid (**1b**) were obtained from condensation of one equivalent of sodium glutamate and one equivalent of corresponding aldehyde in water/alcohol solution, followed by in situ reduction of the unstable imine bond via sodium borohydride (Scheme 1). Acidifying the solution with hydrochloric acid at low temperature precipitated the products from water. Strong peaks at approximately 1717, 1614, 1583 cm⁻¹ in the IR spectra of **1a** and **1b** suggest the presence of carboxyl groups. Reduction of the imine group is supported by the ¹H NMR chemical shift at about 2.0 ppm, which indicates the presence of a secondary amine group. Although racemization was observed during the synthesis process of analogous ligands [46], ligands **1a** and **1b** preserve the S-configuration of L-glutamic acid testified by optical rotation and solid-state CD spectrum (Fig. 1(A)).

Table 1

Crystallographic data and structural refinements for 2-4.

	2	3	4
Empirical formula Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°)	$\begin{array}{c} C_{13}H_{11}N_2O_3 \\ Orthorhombic \\ P_2_{12}2_1 \\ 5.071(2) \\ 13.152(6) \\ 17.641(8) \\ 90 \\ 90 \\ 90 \\ 90 \end{array}$	C ₁₃ H ₁₆ CuN ₂ O ₆ Monoclinic P2 ₁ 7.2547(14) 7.3221(11) 13.748(3) 90 100.432(13) 90	$\begin{array}{c} C_{36}H_{32}CuN_6O_7\\ Monoclinic\\ C2\\ 27.967(12)\\ 5.779(2)\\ 22.193(9)\\ 90\\ 114.499(6)\\ 90\end{array}$
$V(Å^3)$	1176.5(9)	718.2(2)	3264(2)
Z Formula weight $D_c (g \text{ cm}^{-3})$ $\mu(\text{mm}^{-1})$ $\Lambda (Å)$ Temperature (K) R_{int} $R_1^a, wR_2^b(I > 26(I))$	$\begin{array}{c} 4 \\ 243.24 \\ 1.373 \\ 0.100 \\ 0.71073 \\ 293(2) \\ 0.0345 \\ R_1 {=} 0.0440, \\ wR_2 {=} 0.1049 \end{array}$	$\begin{array}{c} 2\\ 359.82\\ 1.664\\ 1.552\\ 0.71073\\ 293(2)\\ 0.0413\\ R_1{=}0.0482,\\ wR_2{=}0.1036 \end{array}$	$\begin{array}{c} 4 \\ 724.22 \\ 1.474 \\ 0.730 \\ 0.71073 \\ 293(2) \\ 0.0264 \\ R_1 = 0.0426, \\ wR_2 = 0.0915 \end{array}$
R_1 , wR_2 (all data)	$R_1 = 0.0565,$ $wR_2 = 0.1124$	$R_1 = 0.0640,$ $wR_2 = 0.1178$	$R_1 = 0.0500,$ $wR_2 = 0.0975$
Flack parameter GOF	1.040	0.00 (2) 1.053	-0.005 (11) 1.069

^a $R = \sum (||F_o| - |F_c||) / \sum |F_o|.$

^b $wR = \{\sum w[(F_o^2 - F_c^2)^2] / \sum w[(F_o^2)^2] \}^{0.5} \dots$

Table 2

Crystallographic data and structural refinements for 5-7.

	5	6	7
Empirical formula Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°)	C ₃₄ H ₃₈ CuN ₆ O ₁₄ Orthorhombic P2 ₁ 2 ₁ 2 ₁ 11.129(7) 17.624(11) 19.353(12) 90 90	C ₃₄ H ₃₄ CdN ₆ O ₁₂ Monoclinic P2 ₁ 11.759(7) 8.819(5) 18.246(11) 90 104.066(10) 90	C ₃₄ H ₃₄ N ₆ NiO ₁₂ Monoclinic C2 15.444(11) 11.308(7) 10.076(7) 90 104.115(9) 90
$V(Å^3)$	3796(4)	1835.4(18)	1706(2)
Z Formula weight $D_c (g cm^{-3})$ $\mu(mm^{-1})$ $\lambda (Å)$ Temperature (K) R_{int} $R_1^a, wR_2^b (I > 26(I))$	$\begin{array}{c} 4 \\ 818.24 \\ 1.432 \\ 0.650 \\ 0.71073 \\ 293(2) \\ 0.1124 \\ R_1 = 0.0911, \\ wR_2 = 0.2208 \end{array}$	2 831.07 1.504 0.665 0.71073 293(2) 0.0452 R_1 =0.0429, wR_2 =0.0946	2 777.38 1.513 0.643 0.71073 293(2) 0.0326 R_1 =0.0402, wR_2 =0.0746
R_1 , wR_2 (all data)	$R_1 = 0.1550,$ $wR_2 = 0.2838$	$R_1 = 0.0583,$ $wR_2 = 0.1018$	$R_1 = 0.0501,$ $wR_2 = 0.0799$
Flack parameter GOF	-0.03 (3) 1.052	-0.03 (3) 0.990	0.002 (14) 1.003

^a $R = \sum (||F_o| - |F_c||) / \sum |F_o|.$

^b $wR = \{\sum w[(F_o^2 - F_c^2)^2] / \sum w[(F_o^2)^2] \}^{0.5} \dots$

Complex $[Cu(cbg)(H_2O)_2]_n$ (**3**) was obtained as a pure phase by reacting copper acetate with **1a** and sodium hydroxide under hydrothermal condition. Single crystal X-ray diffraction analysis reveals that complex **3** is a 1D infinite structure.

4,4'-Bipyridine is often used as bridge ligand in constructing metal-organic frameworks. A new chiral 2D network would be expected when 4,4'-bipyridine was introduced into complex **3**.



R = -NO₂ 1b

Scheme 1. Preparation of ligands 1a and 1b.



Fig. 1. CD data of (A) ligand **1b** and (B) complex **6** obtained from a transparent disk made from a mixture of **1b** or **6** (2 mg) and KBr (50 mg).

However, under the same synthetic procedure except addition of 4,4'-bipyridine, only complex **4** with 1D infinite chain was obtained. Besides, **1a** in **4** undergoes in situ cyclization forming a new chiral ligand (S)-*N*-(4-cyanobenzoic)-5-oxoproline (cbop, **2**). Complex **4** can also be synthesized from **1a**, 4,4'-bipyridine, and basic copper carbonate with 1:1:1 mol ratio in water solution.

Ligand **2** can be obtained by directly heating ligand **1a** in water to 80 °C for 48 h. Intramolecular amidation happens to the second amine group and the γ -carboxyl group of **1a**, and forms a stable five-member heterocyclic ring. Intramolecular amidation is confirmed by the peaks at approximate 1722, 1630 cm⁻¹ in the IR spectrum. Intramolecular amidation is a common feature of glutamic acid and its derivates [53], because thermodynamically more stable five-membered structure is achieved by cyclization. Rosseinsky et al. synthesized ligand bgxH₄ and coordinated it with copper and 4,4'-bipyridine. In situ cyclization of the ligand was considered to be the effect of metal ion, which probably acted as a Lewis catalyst [39]. Although the possible role of metal ions in cyclization reaction cannot be excluded completely, we presume metal ions may not be the key factor of in situ ligand condensation, because ligand **1a** keeps its original structure with Cu^{2+} as metal ion, as can be seen from complex **3**. On the other hand, under similar reaction condition without metal ions, condensation of **1a** also happens and yields **2**.

We have speculated that ligand 1a in complex 3 kept its configuration in order to connect neighboring metals with the γ -carboxyl group when no other bridge ligand such as 4,4'-bipyridine was used. In order to find out the main reason of in situ cyclization, complexes 5-7 were synthesized, too, Blue prism crystals of complex **5** were obtained by reacting ligand **1b** with basic copper carbonate and 4,4'-bipyridine at 120 °C for 12 h. To our surprise, although little difference between raw materials, complexes 4 and 5 show absolutely different structures. In complex 5, ligand 1b also experiences in situ cyclization. However, the condensed ligand nbop coordinates metal ions not only with the α carboxyl group but also with the carbonyl group on the five member ring, thus forms a 2D network. Reacted **1b** and 4,4'-bipyridine with either cadmium carbonate or nickel carbonate under hydrothermal conditions, complexes 6 and 7 were crystallized from the reaction mixtures. The coordination mode of complex 6 is similar to that of complex 5. However, despite the difference in metal and ligand, complex 7 shows similar structure to complex 4. These facts indicate that, condensation of glutamic derivate ligands has occurred against the impact of metal and ligand. Crystals of 6 in KBr pellets give clear signals in solid-state CD spectroscopy (Fig. 1(B)), which indicates that the chirality of ligand is preserved in the complex even at temperature up to 100 °C.

Excluding those factors mentioned above, 4,4'-bipyridine may play a key role in the condensation of **1a** or **1b** during the formation of **4-7**. We speculate that the coordination ability of 4,4'-bipyridine is slightly stronger than **1a** or **1b**. Thus, in complexes **4-7**, 4,4'-bipyridine coordinates with metal prior to the chiral ligand, resulting to the condensation of **1a** or **1b**. When 4,4'-bipyridine is absent in the reaction, just as in complex **3**, **1a** or **1b** coordinates with metal ions quickly and maintains its original structure. Adding other auxiliary ligand into the reaction, such as isonicotinic acid, whose coordination ability is even stronger than 4,4'-bipyridine, the product crystals would be the complex constructed from metal and isonicotinic acid. Ligand **1a** or **1b** does not participate in the reaction in that case.

3.2. Structure descriptions

The coordination mode and the crystallographic data of **3** are exhibited in Figs. 2 and 3 and Table 1, respectively. Complex 3 crystallizes in $P2_1$ chiral space group. In complex **3**, the copper (II) ions are five-coordinated with four oxygen atoms and one nitrogen atom to form a slightly distorted square-pyramidal geometry (Fig. 2). Ligand **1a** retains the coordination ability of L-glutamic acid and acts as a tridentate ligand with the amino group and α -carboxyl group to chelating Cu²⁺ ion, and γ -carboxyl group coordinating another Cu^{2+} ion. The bond length of Cu-N is 2.017(4) Å, which is parallel to that reported by Vittal [44] using **1a** analog as ligand (Cu-N=1.978 Å), while the bond lengths of Cu–O (1.897(4)-1.902(4) Å) is shorter than those in Cu-**1a** analog (1.921-1.969 Å). The two remaining coordination sites of Cu²⁺ are occupied by water molecules. The bond distance between metal center and coordination water molecules at the planar position of square pyramid is 1.959(4) Å, and the distance at the axial position is slightly longer (2.396(4) Å). Two neighboring Cu^{2+} ions are bridged by **1a** to form a one-dimensional infinite left-handed helical chain along the *a*-axis (Fig. 3). The successful in situ reduction of the imine in the ligand is evident from the



Fig. 2. The ORTEP diagram of complex 3 with a numbering scheme.



Fig. 3. (A) Packing of the 1D chain polymer. Hydrogen atoms have been omitted for clarity. (B) Chiral helix of complex **3**.

C(6)-N(1) distance (1.495 Å) when compared with usual C–N amine bonds (1.47–1.50 Å). In addition to the asymmetric center at atom C(6), the coordination of the ligand to the metal ion gives rise to an asymmetric secondary nitrogen atom N(1) with R-absolute configuration, which is a subsequent induction of the neighboring homochiral carbon center.

X-ray diffraction analysis reveals that complex 4 is a monoclinic C2 space group and also exhibits slightly distorted squarepyramidal five-coordinate geometry. In complex **4**, each Cu^{2+} ion is coordinated by two nitrogen atoms from 4,4'-bipyridine (Cu-N=2.05(2) Å), two oxygen atoms from the condensed ligand **2** (Cu–O=1.95(2) Å), and one water molecule (Cu–O=2.18(4) Å) (Fig. 4 and Table 1). The four planar positions are occupied by 4,4'-bipyridine and ligand **2**, and the water molecule binding at the apex completes the coordination sphere. The amine group of ligand 2 loses its coordination property because it is a tertiary amine. As a result, ligand 2 coordinates to metal ion only with the oxygen atom from α -carboxyl group. The neighboring Cu²⁺ ions are bridged by 4,4'-bipyridine to form a 1D infinite chain along *c*-axis in complex **4** (Fig. 5). The crystals of ligand **2** can be isolated as pure colorless prism. The isolated ligand 2 crystallizes in orthorhombic $P2_12_12_1$ space group (Fig. 6 and Table 1).

Complex **5** crystallizes in an orthorhombic $P2_12_12_1$ space group. The coordination mode and the crystallographic data of complex **5** are exhibited in Figs. 7 and 8 and Table 2, respectively.



Fig. 4. The ORTEP diagram of complex 4 with a numbering scheme.



Fig. 5. Packing of the 1D chain polymer of complex **4**. Hydrogen atoms have been omitted for clarity.

In complex **5**, each Cu^{2+} ion is coordinated by two nitrogen atoms from 4,4'-bipyridine and three oxygen atoms from 1b to form a distorted square pyramidal structure. Ligand 1b also experiences in situ cyclization and the cyclized ligand nbop maitains the S-configuration of 1b, just as in complex 4. The ligand nbop coordinates with Cu²⁺ by two modes. One nbop coordinates with metal ion in a single non-bridge mode only by α -carboxyl group. The bond distance of Cu–O is 1.970(6) Å. The other two nbop act as bidentate linkers bridging neighboring metals with α -carboxyl group and the carbonyl group on the five membered ring to form a 1D infinite chain along *b* axis. The Cu–carboxyl bond distance is 1.963(6) Å, while the Cu-carbonyl group distance is 2.399(6) Å. At the same time, two bipyridine molecules also link the neighboring metal ions to form a 1D chain along *a* axis (Cu-N=1.995-2.025(6) Å), thus resulting in a 2D network structure. The four planar positions of square pyramid are occupied by 4,4'-bipyridine and carboxyl groups from nbop. The carbonyl group on the five member ring occupies the axial position. As can be seen from the structure of complex 5, nbop coordinates metals by carbonyl group of the heterocyclic ring, although the Cu-O bond is relatively weak. This result reverses our previous speculation that glutamic derivates keep their carboxyl side chains in order to bridge adjacent metals.

Complex **6** crystallizes in a monoclinic $P2_1$ space group with coordination mode similar to that of complex **5** (Fig. 9, Table 2). Each Cd^{2+} ion is coordinated by five oxygen atoms from three nbop ligands and two nitrogen atoms from 4,4'-bipyridine to form an approximate pentagonal bipyramidal geometry. Ligand nbop coordinates to Cd^{2+} with two modes. Two of them act

as tridentate linkers bridging neighboring metals with α -carboxyl group and the carbonyl group on the five membered ring to form a 1D infinite chain. The Cd–carboxyl bond distances is 2.367(4)–2.441(4) Å, and the bond length of Cd–carbonyl group is 2.396(4) Å. The third nbop coordinates metal ion only with the oxygen atoms of carboxyl group (Cd–O=2.339(4)–2.438(3) Å). Furthermore, 4,4'-bipyridine bridges the neighboring Cd²⁺ and connects the 1D chain to form a new 2D network (Cd–N=2.35 (3) Å).

Different from complex **6**, complex **7** crystallizes in a monoclinic C2 space group with coordination mode similar to that of complex **4** (Fig. 10, Table 2). Each Ni^{2+} ion is coordinated by four oxygen atoms and two nitrogen atoms forming an octahedral geometry. Two of the oxygen atoms come from two condensed



Fig. 6. The ORTEP diagram of ligand 2 with a numbering scheme.

ligands nbop (Ni–O=2.061 Å), and the other two come from water molecules (Ni–O=2.089). 4,4'-Bipyridine bridges neighboring metal ions to form a 1D infinite chain structure.

3.3. SHG properties

In ligands **1a** and **1b**, the amino group of glutamic acid was modified with substituted phenyl groups, which help to construct Π -conjugated systems in these compounds. At the same time, the cyano- or nitro- group on the 4-position of the phenyl, accompanied with the amino group from glutamic acid, acting as the acceptor and the donor of electron respectively, forms a good donor-II-acceptor system. Besides, the chirality of glutamic acid ensures ligands **1a** and **1b** crystallizing in noncentrosymmetric space groups, which is an essential requirement for SHG response. Therefore, **1a** and **1b** would be expected to possess second-order nonlinear effect. On the other hand, reducing the imine bond will result in the decrease of conjugation, leading to a lower second harmonic generation (SHG) response. Using the methods proposed by Kurtz and Perry, the SHG efficiencies of 1a and 1b were estimated. The experimental results indicate that the SHG responses of both are about 1.1 times as high as that of potassium dihydrogen phosphate (KDP). Preliminary SHG measurement of the complexes constructed from 1a and 1b reveals that complexes 6 and 7 display SHG responses close to that of KDP. The decrease in SHG responses may due to disorder of the dipole arrangement in the complexes.

4. Conclusions

In summary, two new chiral aminocarboxlate derivates **1a** and **1b** have been synthesized and used as ligands in constructing homochiral metal organic complexes **3–7**. All these complexes synthesized under hydrothermal conditions were proved to be optically pure. Complex **3** is a 1D helical infinite chain bridged by ligand **1a**. Complexes **4–7** possess 1D and 2D structures respectively, in which the chiral ligands **1a** and **1b** experience in situ intramolecular amidation. For the ligand condensation, competitive coordination



Fig. 7. The ORTEP diagram of complex 5 with a numbering scheme.



Fig. 8. Packing of the 2D polymer of complex 5 viewed along the c axis. Hydrogen atoms have been omitted for clarity.



Fig. 9. Ball and stick representation of the coordination spheres of Cd ions in complex 6. The hydrogen atoms are omitted for clarity.



Fig. 10. Ball and stick representation of the coordination spheres of Ni ions in complex 7. The hydrogen atoms are omitted for clarity.

of 4,4'-bipyridine may be the main factor. The optical properties of the ligands and the complexes have also been measured. Moderate SHG responses are observed in ligands 1a-1b and complexes 6-7. The decrease in SHG responses of the mteal complexes may due to disorder of the dipole arrangement.

Supplementary material

CCDC-804067 (for 2),-804068 (for 3), -804069 (for 4), -804070 (for 5), -804071 (for 6), -804072 (for 7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from. The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by grants from the 973 Program (2007CB815301), the National Science Foundation of China (20733003, 20871114 and 20801055), the Science Foundation of CAS (KJCX2-YW-H20) and of Fujian Province (2009HZ0006-1, 2006L2005).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2012.04.025.

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