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# **ARTICLE TYPE**

### Controlling the self-assembly of homochiral coordination architectures of Cu<sup>II</sup> by the substitution in amino acid based ligands: synthesis, crystal structures and physicochemical properties

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Through the strategic design of ligands based on amino acids, structural diversity in the chiral coordination architectures of Cu<sup>II</sup> is demonstrated with six new examples: { $[Cu(L-HTyrbenz)_2]CH_3OHH_2O]_n$  (1), { $[Cu(L-HSerbenz)_2]3H_2O]_n$  (2), {[Cu(L- $HTyrthio)_2[H_2O]_n$  (3),  $[Cu(L-HTyr4-pyr)_2(H_2O)]^2H_2O$  (4),  $[Cu(L-HSerthio)_2(H_2O)]$  (5), and  $[Cu(L-Phethio)_2(H_2O)]^3H_2O$  (6) [where 10 L-H<sub>2</sub>Tyrbenz = L-N-(benzyl)-tyrosine, L-H<sub>2</sub>Serbenz = L-N-(benzyl)-serine, L-H<sub>2</sub>Tyrthio = L-N-(methyl-2-thiophenyl)-tyrosine, and L-H<sub>2</sub>Tyr4-pyr = L-N-(methyl-4-pyridyl)-tyrosine, L-H<sub>2</sub>Serthio = L-N-(methyl-2-thiophenyl)-serine and L-HPhethio thiophenyl)-phenylalanine]. For these 1:2 metal-ligand complexes, the availability of a donor atom (either from the phenolic OH group or the carboxylate group of one of the ligands) for bridging between the Cu<sup>II</sup> centers provides the coordination polymers (1-3) while no such availability allows a water molecule to occupy the fifth site around the Cu<sup>II</sup> center for generating hydrogen bonded supramolecular 15 assemblies (4-6). In 1, the coordination polymer is formed via a syn-anti bridging carboxylate showing no role of the phenolic group in its formation. To further emphasize this point, L-tyrosine in 1 was replaced with L-serine to form 2 where an anti-anti bridging by the carboxylate group is observed. On the other hand, the essence in the formation of  $\{[Cu(L-HTyrthio)_2], H_2O\}_n$  (3) lies in the growing of the spiral polymer via the unique phenolic bridging with a distance between two Cu<sup>II</sup> centers of 10.806(9) Å. In changing from L-H<sub>2</sub>Tyrbenz ligand to L-H<sub>2</sub>Tyr4-pyr ligand (1 vs 4), the strong hydrogen bonding of the pyridyl nitrogen with the phenolic group does not <sup>20</sup> allow the latter to bind to Cu<sup>II</sup>. Similarly, in changing from L-H<sub>2</sub>Tyrthio to L-H<sub>2</sub>Serthio (**3** vs **5**) the length of the –CH<sub>2</sub>OH group in the latter is much less than the distance between the two Cu<sup>II</sup> centers to occupy the fifth site and thus a water molecule is coordinated. This is further confirmed by reacting 5 with 2 eq of L-H<sub>2</sub>Tyrthio in methanol to form 3 while the reverse was not possible. All these compounds are characterized by a number of analytical methods, such as elemental analysis, FTIR, UV-Vis and circular dichroism spectroscopy, polarimetry, powder and single crystal X-ray diffraction and thermogravimetric analysis. Photoluminescence properties of all ligands 25 containing the L-tyrosine group and their metal complexes (1, 3 and 4) are compared in the solution at room temperature.

#### Introduction

In the last 15 years, strategic design of diverse coordination architectures have been the subject of immense interest for their <sup>30</sup> diverse structural aesthetics and for their possible roles in various applications, such as catalysis,<sup>1</sup> luminescence,<sup>2-3</sup> molecular separation,<sup>3,4a,4b</sup> gas and liquid adsorption,<sup>4a,4b,5</sup> magnetism,<sup>3,4</sup> etc. The construction of such coordination architectures that include coordination polymers (CPs) and supramolecular assemblies

- <sup>35</sup> depends on coordination bonds and supramolecular interactions, such as hydrogen bonds,  $\pi$ - $\pi$  stacking of aromatic moieties or C-H...O interactions, etc. In CPs coordination bonds provide the major contribution in their constructions while the formation of supramolecular assemblies of higher dimensionality occurs
- <sup>40</sup> through the association of discrete precursors, such as monomers and dimers, by strong supramolecular interactions. Modulation of the contribution of coordination bonds and hydrogen bonds has resulted in numerous diverse (structural and functional) coordination architectures in recent years.<sup>6-12</sup> Thus establishing
- 45 the parameters that control the formation of CPs or supramole-

cular assemblies through chemical modifications in the ligand system will allow one to understand the structure and bonding in <sup>50</sup> these species and to provide further directions in the rational design of improved materials. In this regard, a strategic design of a set of ligands can be a way to do so.

On the other hand, induction of chirality in such networks has been sought due to their usefulness in asymmetric catalysis, chiral <sup>55</sup> recognition and enantiomeric separation, non-linear optics, etc.<sup>13-</sup>

<sup>16</sup> One of the ways to make chiral coordination architectures is the self-assembly of optically pure chiral organic ligands with the metal ions. In addition to their low cost and easy availability, amino acids are also preferred in making chiral ligands due to their abilities to act both as hydrogen bond donors and acceptors and to show different binding modes with the metal centers through various functionalities present in these ligands, e.g., carboxylate, hydroxy, etc.<sup>13-16</sup> One such set of ligands that has been utilized to some extent is the reduced Schiff base ligands of s various amino acids.<sup>17-34</sup> However, their use in making coordination architectures under hydrothermal conditions is

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L-tyrosine is one of the few amino acids with three functional groups (hydroxy, amino and carboxylate) that can provide diverse binding modes (chelating, bridging, etc.); however, a limited <sup>5</sup> number of coordination architectures is reported so far using this amino acid or particularly its Schiff base derivatives.<sup>21,</sup> <sup>23a,23c,25,34,36-38</sup> In our laboratory, using reduced Schiff base ligands of L-tyrosine a systematic study was carried out to show how the formation of CPs or supramolecular assemblies of Cu<sup>II</sup> under 10 non-hydrothermal conditions can be effected by the substitution in it. Further modifications in the ligand using L-phenylalanine and L-serine instead of L-tyrosine provided the concrete support in understanding the formation of supramolecular assemblies over CPs. In doing so, we observed that the presence or absence 15 of a coordinated water molecule at the fifth site around fivecoordinated square pyramidal Cu<sup>II</sup> in all complexes, except 2 where the Cu<sup>II</sup> center is distorted octahedral, due to strategic chemical modifications in the ligand is responsible for the formation of such diverse networks. This is particularly important <sup>20</sup> to note that for the ligand L-H<sub>3</sub>Sersal (where L-H<sub>3</sub>Sersal = L-N-(2-hydroxybenzyl)-serine) and its derivatives, where these act as dianions due to the presence of a 2-hydroxy group, the complexes having a metal to ligand ratio of 1:1 are CPs with coordinated water molecules.<sup>12e</sup> Similarly, the CP reported by Vittal et al.<sup>39</sup> is 25 a 1:1 metal to ligand complex with an alternating bis(phenoxo) core and contains coordinated water molecules. Thus, in the current study the importance of a coordinated water molecule in a

1:2 metal-ligand complex is demonstrated for the first time.

Herein, we report six new Cu<sup>II</sup> complexes as the outcome of work described above: 30 the proposed {[Cu(L- $HTyrbenz_2$ ]·CH<sub>3</sub>OH·H<sub>2</sub>O}<sub>n</sub> (1), {[Cu(L-HSerbenz)<sub>2</sub>]·3H<sub>2</sub>O}<sub>n</sub> (2),  $\{ [Cu(L-HTyrthio)_2] H_2O \}_n$  (3),  $[Cu(L-HTyr4-pyr)_2(H_2O)] 2H_2O \}_n$ (4), [Cu(L-HSerthio)<sub>2</sub>(H<sub>2</sub>O)] (5), and [Cu(L-Phethio)<sub>2</sub>(H<sub>2</sub>O)]<sup>3</sup>H<sub>2</sub>O (6) [where L-H<sub>2</sub>Tyrbenz = L-N-(benzyl)- $_{35}$  tyrosine, L-H<sub>2</sub>Serbenz = L-N-(benzyl)-serine, L-H<sub>2</sub>Tyrthio = L-N-(methyl-2-thiophenyl)-tyrosine, and  $L-H_2Tyr4-pyr = L-N-$ (methyl-4-pyridyl)-tyrosine,  $L-H_2$ Serthio = L-N-(methyl-2thiophenyl)-serine and L-HPhethio = L-N-(methyl-2-thiophenyl)phenylalanine]. Fig. 1 shows the structures of all chiral ligands 40 that are made for this study. All these chiral compounds are structurally characterized by a number of analytical methods,



Fig. 1 Structure of various chiral ligands synthesized and used in this study.



 <sup>1</sup>H NMR spectra of L-Na<sub>2</sub>Tyrbenz, L-Na<sub>2</sub>Serbenz, L-Na<sub>2</sub>Tyrthio, L-Na<sub>2</sub>Tyr4-pyr, L-Na<sub>2</sub>Serthio and L-NaPhethio ligands were obtained in D<sub>2</sub>O solution at 25 °C on a Bruker ARX-400 spectrometer; chemical shifts are reported relative to the residual
 <sup>65</sup> solvent signals. The elemental analysis (C, H, N) was carried out using a Mettler CHNS analyzer; thermogravimetric analysis was carried out from 25 to 500 °C (at a heating rate of 10 °C/min) under dinitrogen atmosphere on a Shimadzu DTG-60. IR spectra were measured in the 4000-400 cm<sup>-1</sup> range on a Perkin-Elmer
 <sup>70</sup> Spectrum I spectrometer with samples prepared as KBr pellets. UV-Vis spectra of the compounds in methanol (a typical concentration of 1 mM) were recorded in an Agilent Technologies Cary60 UV-Vis spectrophotometer using a cuvette

45 such as elemental analysis, FTIR, UV-Vis and circular dichroism

spectroscopy, polarimetry, powder and single crystal X-ray

crystallography and thermogravimetric analysis. Furthermore,

due to the presence of the L-tyrosine group three ligands (L-

H<sub>2</sub>Tyrbenz, L-H<sub>2</sub>Tyrthio and L-H<sub>2</sub>Tyr4-pyr) and their metal

All chemicals and solvents used for synthesis were obtained from

purification. All reactions were carried out under aerobic

55 commercial sources and were used as received, without further

50 complexes (1, 3 and 4) were studied for their photoluminescence

properties in the solution at room temperature.

Experimental section

Materials and methods

- of path length 10 mm. Emission spectra were obtained using a 75 Perkin Elmer Fluorimeter (LS55) with a cuvette of 10 mm path length. For photoluminescence spectra, 0.5 mM methanolic solutions of the compounds were prepared. Optical rotations were recorded using Anton Paar Modular circular Polarimeter (MCP
- 300). Measurements were carried out using a glass cell with 50 <sup>80</sup> mm path length. CD spectra were recorded on a Chirascan spectropolarimeter (Applied Photo-physics, Leatherhead, Surrey, UK) using quartz cuvettes with a 2 mm path length. ESI mass spectrometry was performed using either Waters HRMS instrument or Thermo Scientific LTQ XL LC-MS instrument for <sup>85</sup> the 50-2000 amu range.

#### Synthesis of L-H<sub>2</sub>Tyrbenz

To a solution of 500 mg of L-tyrosine (2.8 mmol) and 220 mg of NaOH (5.6 mmol) in 14 mL of a methanol:water mixture (v/v <sup>90</sup> 1:1) was added 0.28 mL (2.8 mmol) of benzaldehyde. The resulting solution was refluxed for 1h. The yellow reaction mixture was brought to room temperature prior to addition of 105 mg of NaBH<sub>4</sub> (4.8 mmol) at 0 °C. The solution was stirred until the yellow color disappeared. The pH of the solution was <sup>95</sup> adjusted to 5 using (~2 mL) glacial acetic acid and stirred for half an hour. A white precipitate was filtered, washed with water and air dried. Yield: 350 mg (47%). HRMS (ESI-TOF): m/z calcd for [(L-H<sub>2</sub>Tyrbenzl)H]<sup>+</sup>, 272.1287; found, 272.1278. M.pt. 263 °C. <sup>1</sup>H NMR (D<sub>2</sub>O): δ 2.62 (d, 2H), 3.17 (t, 1H), 3.41 (d, 1H), 3.60 <sup>100</sup> (d, 1H), 6.43 (d, 2H), 6.83 (d, 2H), 7.16 – 7.28 (m, 5H). Selected

FTIR peaks (KBr, cm<sup>-1</sup>): 3174(s), 3011(w), 2827(w), 2747(w), 1603(w), 1580(br), 1516(s), 1437(m), 1396(s), 1253(s), 1106(s), 828(s), 743(s), 697(s). Specific rotation  $[\alpha]_{\rm D}^{20} = +12.50$  (0.018%, H<sub>2</sub>O).

#### Synthesis of L-H<sub>2</sub>Serbenz

It was prepared following the procedure described for L- $H_2Tyrbenz$  except 500 mg (4.7 mmol) of L-serine was used instead of L-tyrosine. In this case, the resulting yellow Schiff <sup>10</sup> base solution was refluxed for 8 h. A white precipitate was filtered, washed with water and air dried. Yield: 300 mg (32%). HRMS (ESI-TOF): m/z calcd for [(L-H<sub>2</sub>Serbenz)H]<sup>+</sup>, 196.0973; found, 196.0970. M.pt. 219 °C. <sup>1</sup>H NMR (D<sub>2</sub>O):  $\delta$  2.51 (t, 2H), 3.00 (t, 1H), 3.42 (d, 1H), 3.58 (d, 1H), 6.30 (d, 2H), 6.69 (d, 15 2H), 7.20 (d, 2H), 7.91 (d, 2H). Selected FTIR peaks (KBr, cm<sup>-1</sup>): 3245(br), 3197(s), 3063(s), 1625(s), 1596(s), 1534(s), 1471(s), 1455(w), 1276(s), 1201(s), 1080(s), 758(s), 648(w). Specific rotation [ $\alpha$ ]  $_D^{20} = +14.77$  (0.018%, H<sub>2</sub>O).

#### 20 Synthesis of L-H<sub>2</sub>Tyrthio

It was prepared following the procedure described for L-H<sub>2</sub>Tyrbenz except 0.26 mL (2.8)mmol) of 2thiophenecarboxyaldehyde was used instead of benzaldehyde. In this case, the resulting yellow Schiff base solution was refluxed 25 for 3 h. A white precipitate was filtered, washed with water and air dried. Yield: 581 mg (76%). HRMS (ESI-TOF): m/z calcd for [(L-H<sub>2</sub>Tyrthio)H]<sup>+</sup>, 278.1785; found, 278.0851. M.pt. 248 °C. <sup>1</sup>H NMR (D<sub>2</sub>O): δ 2.59 (d, 2H), 3.16(t, 1H), 3.61 (d, 1H), 3.75 (d, 1H), 6.38 (d, 2H), 6.76-6.85 (m, 4H), 7.18 (d, 1H). Selected FTIR  $_{30}$  peaks (KBr, cm<sup>-1</sup>): 3435(br), 3178(s), 3006(w), 2692(w), 2624(w), 1581(br), 1517(s), 1436(s), 1393(s), 1262(s), 1105(s), 821(s), 717(m), 533(s). Specific rotation  $[\alpha]_D^{20} = -2.27 (0.018\%)$ , H<sub>2</sub>O).

#### 35 Synthesis of L-H<sub>2</sub>Tyr4-pyr

It was prepared following the procedure described for L- $H_2$ Tyrbenz except 0.26 mL (2.8 mmol) of 4pyridinecarboxyaldehyde was used instead of benzaldehyde. In this case, the resulting yellow Schiff base solution was stirred for 40 6 h. A white precipitate was filtered, washed with water and air dried. Yield: 670 mg (89%). HRMS (ESI-TOF): m/z calcd for  $[(L-H_2Tyr4-pyr)H]^+$ , 273.1239; found, 273.1245. M.pt. 250 °C. <sup>1</sup>H NMR (D<sub>2</sub>O):  $\delta$  2.64 - 3.68 (m, 2H), 3.13 (t, 1H), 3.50 (d, 1H),

3.71 (d, 1H), 6.43 (d, 2H), 6.83 (d, 2H), 7.17 (d, 2H), 8.30 (d, 45 2H). Selected FTIR peaks (KBr, cm<sup>-1</sup>): 3161(br), 2808(w), 2359(w), 1614(s), 1518(s), 1449(m), 1385(s), 1332(s), 1234(w), 1104(s), 872(s), 801(s), 573(m). Specific rotation  $[\alpha]_D^{20} = +9.09$ (0.018%, H<sub>2</sub>O).

#### 50 Synthesis of L-H<sub>2</sub>Serthio

It was prepared following the procedure described for  $L-H_2Tyrbenz$  except 500 mg (4.7 mmol) of L-serine and 0.45 mL (4.7 mmol) of thiophenecarboxyaldehyde was used instead of L-tyrosine and benzaldehyde, respectively. In this case, the

<sup>55</sup> resulting yellow Schiff base solution was stirred for 3 h at room temperature. A white precipitate was filtered, washed with water and air dried. Yield: 445 mg (42%). HRMS (ESI-TOF): m/z calcd for [(L-H<sub>2</sub>Serthio)Na]<sup>+</sup>, 224.1292; found, 224.0357. M.pt. 216.9 °C. <sup>1</sup>H NMR (D<sub>2</sub>O): δ 3.05 (t, 1H), 3.56 (d, 2H), 3.75 (d, 1H), 60 3.87(d, 1H), 6.87-6.89 (m, 2H), 7.22-7.23 (dd, 2H). Selected FTIR peaks (KBr, cm<sup>-1</sup>): 3251(br), 3079(w), 2989(w), 2424(w), 1622(s), 1567(s), 1479(s), 1443(m), 1368(s), 1328(s), 1214(s), 1160(s), 1086(s), 855(s), 722(s), 545(s). Specific rotation [α]  $_{\rm D}$ <sup>20</sup> = -22.73 (0.018%, H<sub>2</sub>O).

#### Synthesis of L-HPhethio

It was prepared following the procedure described for L-H<sub>2</sub>Tyrbenz except 500 mg (3 mmol) of L-phenylalanine and 0.28 mL (3 mmol) of thiophenealdehyde was used instead of L-<sup>70</sup> tyrosine and benzaldehyde, respectively. In this case, the resulting yellow Schiff base solution was reflux for 24 h. A white precipitate was filtered, washed with water and air dried. Yield: 362 mg (46%). HRMS (ESI-TOF): m/z calcd for [(L-HPhethio)Na]<sup>+</sup>, 284.1655; found, 284.0726. M.pt. 227 °C. <sup>1</sup>H <sup>75</sup> NMR (D<sub>2</sub>O):  $\delta$  2.69-2.76 (m, 2H), 3.20 (t, 1H), 3.63 (d, 1H), 3.79 (d, 1H), 6.81 (d, 1H), 6.83-6.86 (m, 1H), 7.06 (d, 2H), 7.12 (d, 1H), 7.18-7.20 (m, 3H). Selected FTIR peaks (KBr, cm<sup>-1</sup>): 3418(br), 3179(s), 3010(w), 2806(w), 2689(w), 1603(w), 1586(br), 1515(s), 1438(m), 1397(s), 1346(s), 1252(s), 1106(s), <sup>80</sup> 827(s), 746(m), 550(s). Specific rotation [ $\alpha$ ] D <sup>20</sup> = +30.40 (0.018%, H<sub>2</sub>O).

#### Synthesis of ${[Cu(L-HTyrbenz)_2] CH_3OH H_2O]_n (1)}$

In a 10 mL round bottom flask, 25 mg (0.092 mmol) of L-<sup>85</sup> H<sub>2</sub>Tyrbenz and 5 mg (0.092 mmol) of KOH were dissolved in 3 mL methanol. To this was added 11.5 mg (0.046 mmol) of CuSO<sub>4</sub>5H<sub>2</sub>O with stirring. The reaction mixture turned blue and was stirred for 6 h. After filtering off the K<sub>2</sub>SO<sub>4</sub> precipitate, the blue filtrate was evaporated to dryness to obtain the product. <sup>90</sup> Yield: 24 mg (75%). Anal. Calc. (%) for C<sub>33</sub>H<sub>38</sub>N<sub>2</sub>O<sub>8</sub>Cu (MW 653.5): Calc. C, 58.76; H, 5.81; N, 4.28. Found: C, 59.13; H, 5.80; N, 4.29. Selected FTIR peaks (KBr, cm<sup>-1</sup>): 3269(s), 3019(w), 2931(w), 1634(s), 1592(w), 1514(s), 1454(m), 1359(m), 1271(w), 1240(s), 1171(w), 806, 701. UV-Vis [ $\lambda_{max}$ , nm]: 204, <sup>95</sup> 225, 278, 590. Specific rotation [ $\alpha$ ] D<sup>20</sup> = +56.0 (0.025%, CH<sub>3</sub>OH).

#### Synthesis of {[Cu(L-HSerbenz)<sub>2</sub>]<sup>3</sup>H<sub>2</sub>O}<sub>n</sub> (2)

In a 10 mL round bottom flask, 12 mg (0.065 mmol) of <sup>100</sup> CuSO<sub>4</sub>·5H<sub>2</sub>O was dissolved in 1 mL water. To this was added a clear solution of L-KHSerbenz prepared by using 25 mg (0.13 mmol) of L-H<sub>2</sub>Serbenz and 7 mg (0.13 mmol) of potassium hydroxide in 2 mL of water. The reaction mixture turned blue and was stirred for 3h. A blue precipitate was filtered off, washed <sup>105</sup> with water and air dried. Yield: 23 mg (71%). Anal. Calc. (%) for C<sub>20</sub>H<sub>30</sub>N<sub>2</sub>O<sub>9</sub>Cu (MW 506.11): Calc. C, 47.47; H, 5.98; N, 5.54. Found: C, 46.71; H, 5.81; N, 5.37. Selected FTIR peaks (KBr, cm<sup>-1</sup>): 3375(br), 3277(s), 1623(s), 1496(w), 1457(m), 1372(m), 1358(s), 1345(w), 1278(m), 1146(w), 1079(s), 972(m), 753(w), <sup>110</sup> 694(s). UV-Vis [ $\lambda_{max}$ , nm]: 205, 254, 589. Specific rotation [ $\alpha$ ] D <sup>20</sup> = +51.0 (0.025%, CH<sub>3</sub>OH).

#### Synthesis of {[Cu(L-HTyrthio)<sub>2</sub>]<sup>·</sup>H<sub>2</sub>O}<sub>n</sub> (3)

It was prepared following the procedure described for 2 except L-<sup>115</sup> KHTyrthio, prepared by using 25 mg (0.09 mmol) of L-H<sub>2</sub>Tyrthio and 5 mg (0.09 mmol) of potassium hydroxide in 2 mL of water, was used instead of L-KHSerbenz. A purple precipitate was filtered off, washed with water and air dried. Yield: 24 mg (84%). Anal. Calc. (%) for  $C_{28}H_{30}N_2O_7S_2Cu$  (MW 634.22): Calc. C, 53.03; H, 4.77; N, 4.42. Found: C, 52.57; H, 4.68; N, 4.26. s Selected FTIR peaks (KBr, cm<sup>-1</sup>): 3371(br), 3252(w), 3220(w), 1636(w), 1614(m), 1603(m), 1515(s), 1445(m), 1376(m), 1269(s), 1108(w), 881(m), 846, 714. UV-Vis [ $\lambda_{max}$ , nm]: 229, 279, 585. Specific rotation [ $\alpha$ ]  $_D^{20} = +46.0$  (0.025%, CH<sub>3</sub>OH).

#### <sup>10</sup> Synthesis of [Cu(L-HTyr4-pyr)<sub>2</sub>(H<sub>2</sub>O)]<sup>2</sup>H<sub>2</sub>O (4)

It was prepared following the procedure described for **2** except L-KHTyr4-pyr, prepared by using 25 mg (0.092 mmol) of L-H<sub>2</sub>Tyr4-pyr and 5 mg (0.09 mmol) of potassium hydroxide in 2 mL of water, was used instead of L-KHSerbenz. A green <sup>15</sup> precipitate was filtered off, washed with water and air dried. Yield: 20 mg (61%). Anal. Calc. (%) for C<sub>30</sub>H<sub>37</sub>N<sub>4</sub>O<sub>9.5</sub>Cu (MW 668.5): Calc. C, 53.85; H, 5.53; N, 8.38. Found: C, 53.71; H, 5.46; N, 8.50. Despite our best effort, the CHN data could be fit with 2.5 water molecules. Selected FTIR peaks (KBr, cm<sup>-1</sup>): <sup>20</sup> 3434(br), 3237(s), 1644(s), 1612(s), 1517(s), 1453(s), 1379(s), 1264(s), 1088(s), 980(s), 798. UV-Vis [ $\lambda_{max}$ , nm ] 224, 259, 282, 600. Specific rotation [ $\alpha$ ] D<sup>20</sup> = +96.0 (0.025%, CH<sub>3</sub>OH).

#### Synthesis of [Cu(L-HSerthio)<sub>2</sub>(H<sub>2</sub>O)] (5)

<sup>25</sup> It was prepared following the procedure described for **2** except L-KHSerthio, prepared by using 25 mg (0.113 mmol) of L-H<sub>2</sub>Serthio and 6.5 mg (0.113 mmol) of potassium hydroxide in 2 mL of water, was used instead of L-KHSerbenz. A blue precipitate is filtered off, washed with water and air dried. Yield: <sup>30</sup> 18 mg (66%). Anal. Calc. (%) for C<sub>16</sub>H<sub>22</sub>N<sub>2</sub>O<sub>7</sub>S<sub>2</sub>Cu (MW 482.05): Calc. C, 39.86; H, 4.60; N, 5.81. Found: C, 40.16; H, 4.42; N, 5.75. Selected FTIR peaks (KBr, cm<sup>-1</sup>): 3327(br), 3212(m), 1642(m), 1629(s), 1444(s), 1421(w), 1391(m), 1348(w), 1300(w), 1216(w), 1099(w), 1016(m), 716(s), 673(w). <sup>35</sup> UV-Vis [ $\lambda_{max}$ , nm]: 235, 276, 586. Specific rotation [ $\alpha$ ] D<sup>20</sup> = +74.0 (0.025%, CH<sub>3</sub>OH).

#### Synthesis of [Cu(L-Phethio)<sub>2</sub>(H<sub>2</sub>O)]<sup>-</sup>4H<sub>2</sub>O (6)

It was prepared following the procedure described for **2** except L-<sup>40</sup> KPhethio, prepared by using 25 mg (0.096 mmol) of L-HPhethio and 5 mg (0.09 mmol) of potassium hydroxide in 2 mL of water, was used instead of L-KHSerbenz. A purple precipitate was filtered off, washed with water and air dried. Yield: 15 mg (46.5%). Anal. Calc. (%) for For  $C_{28}H_{38}N_2O_9S_2Cu$  (MW 674.28):

<sup>45</sup> Calc. C, 49.8; H, 5.68; N, 4.15. Found: C, 49.2; H, 5.5; N, 4.0. Selected FTIR peaks (KBr, cm<sup>-1</sup>): 3375(br), 3277(s), 1623(s), 1496(w), 1457(m), 1372(m), 1358(s), 1345(w), 1278(m), 1146(w), 1079(s), 972(m), 753(w), 694(s). UV-Vis [λ<sub>max</sub>, nm]: 212, 235, 275, 582. Specific rotation [α]  $_{\rm D}$ <sup>20</sup> = +62.0 (0.025%, <sup>50</sup> CH<sub>3</sub>OH).

#### Conversion of 5 to 3

In a 10 mL round bottom flask, 30 mg (0.12 mmol) of **5** was dissolved in 3 mL methanol. To this was added 35 mg (0.06 <sup>55</sup> mmol) of L-H<sub>2</sub>Tyrthio with stirring. The reaction mixture was stirred for 24 h. After filtering off the white precipitate (confirmed to be H<sub>2</sub>Serthio by FTIR spectroscopy), the blue filtrate was evaporated to dryness to obtain **3**. Yield: 24 mg

(60%). Based on the comparison of the FTIR and PXRD data of <sup>60</sup> the product, it was confirmed that the product isolated was **3**.

Single crystal X-ray data collection and refinements Following the practices of this laboratory published earlier,<sup>12a</sup> initial crystal evaluation and data collection were performed on a 65 Kappa APEX II diffractometer equipped with a CCD detector (with the crystal-to-detector distance fixed at 60 mm) and sealedtube monochromated MoKa radiation using the program APEX2.<sup>40</sup> For each sample, three sets of frames of data were collected with  $0.30^{\circ}$  steps in  $\omega$  and an exposure time of 10 s 70 within a randomly oriented region of reciprocal space surveyed to the extent of 1.3 hemispheres to a resolution of 0.85 Å. By using the program SAINT<sup>40</sup> for the integration of the data, reflection profiles were fitted, and values of  $F^2$  and  $\sigma(F^2)$  for each reflection were obtained. Data were also corrected for Lorentz and 75 polarization effects. The subroutine XPREP<sup>40</sup> was used for the processing of data that included determination of space group, application of an absorption correction (SADABS)<sup>40</sup>, merging of data, and generation of files necessary for solution and refinement. The crystal structures were solved and refined using <sup>80</sup> SHELX 97.<sup>41</sup> In each case, the space group was chosen based on systematic absences and confirmed by the successful refinement of the structure. Furthermore, Flack parameters of all the structures confirmed the correct absolute configurations. Positions of most of the non-hydrogen atoms were obtained from direct methods solution. Several full-matrix least-85 A squares/difference Fourier cycles were performed, locating the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters except where mentioned. In order to obtain reasonable thermal <sup>90</sup> parameters compared to other atoms, the lowest residual factors and optimum goodness of fit with convergence of refinement, adjustments to the structures of 4 and 5 were done accordingly. In 4, the occupancy factor of the lattice water molecule O6 was adjusted to 0.5. In 5, one of the thiophene rings was modelled for 95 the 2-fold disorder, where the S1, C6, C7 and C8 atoms were allowed to occupy at two different sites (S1A/S1B, C6A/C6B, C7A/C7B and C8A/8B with final occupancy factors 0.605 and 0.395, respectively); all atoms in the ring were refined isotropically with further constraints to have the expected bond 100 lengths and thermal parameters. In each structure, all hydrogen atoms were placed in ideal positions and refined as riding atoms individual with isotropic displacement parameters. Crystallographic parameters and basic information pertaining to data collection and structure refinement for all compounds are <sup>105</sup> summarized in Table 1. All figures were drawn using Olex2<sup>42</sup> and MERCURY 3.043 and hydrogen bonding parameters were generated using PLATON.44 The final positional and thermal parameters of the non-hydrogen atoms for all structures are listed in the CIF files (ESI<sup>†</sup>). 110

#### **Powder X-ray studies**

Data were recorded on a Rigaku Ultima IV diffractometer equipped with a 3 KW sealed tube Cu K $\alpha$  X-ray radiation (generator power settings: 40 kV and 40 mA) and a DTex Ultra <sup>115</sup> detector using parallel beam geometry (2.5° primary and secondary solar slits, 0.5° divergence slit with 10 mm height limit

slit). For each sample, a fine powder was packed on a glass sample holder that was placed on the sample rotation stage (120 rpm) attachment. The data were collected over an angle range  $5^{\circ}$  to  $50^{\circ}$  with a scanning speed of  $1^{\circ}$  per minute with  $0.02^{\circ}$  step.

#### **5 Results and discussion**

#### Synthesis

Out of the six ligands used in this study, three (L-H<sub>2</sub>Tyrthio, L-H<sub>2</sub>Tyr4-pyr and L-H<sub>2</sub>Serthio) are new. A general methodology was developed to synthesize the ligands. In all cases, the sodium salt of the respective L-amino acid and the appropriate aldehyde were stirred or refluxed depending upon the reactivity of the aldehyde to obtain the respective Schiff base. One can correlate the reaction conditions with respect to the substitution in the 15 aldehyde; however, it was not the case for several of these and thus optimized conditions were obtained through design of experiments. The Schiff base was further reduced using sodium borohydride. The desired products were obtained by the addition of glacial acetic acid to the sodium salt of the reduced Schiff 20 bases of the L-amino acids (as shown in Scheme S1, ESI†). <sup>1</sup>H NMR (Figs. S1-S6, ESI†) and FTIR (Figs. S7-S12, ESI†) spectra of all the ligands are reported.

Metal complexes were synthesized via a two-component selfassembly reaction of CuSO<sub>4</sub>5H<sub>2</sub>O and the respective <sup>25</sup> monopotassium salt of the ligand in a 1:2 ratio under ambient conditions; the solvent for the reaction was chosen based on the solubility of the product and the by-product K<sub>2</sub>SO<sub>4</sub>. Unlike all other compounds, **1** was found to be moderately soluble in water. For **1**, the reaction was carried out in methanol to separate the by-

- <sup>30</sup> product via filtration allowing its isolation by evaporating the filtrate under reduced pressure. On the other hand, for **2**, **3**, **4**, **5** and **6** water was chosen as the reaction solvent in which the byproduct  $K_2SO_4$  was soluble to obtain these as direct precipitates. Interestingly, in the absence of any additional ancillary ligands
- <sup>35</sup> the isolation of divalent metal (Co<sup>II</sup> and Zn<sup>II</sup>) complexes with a metal to ligand ratio of 1:2 for tyrosine have been reported<sup>38</sup> while [Cu(L-Ph-Tyr)(phen)(ClO<sub>4</sub>)]<sup>21</sup> (where L-Ph-Tyr = L-N-(benzyl)-tyrosine, which is abbreviated as L-H<sub>2</sub>Tyrbenz in the present work, and phen = 1, 10-phenanthroline) is a 1:1 complex.
  <sup>40</sup> Similarly, for the ligand L-H<sub>3</sub>Sersal and its derivatives that act as dianion due to the presence of 2-hydroxy group, the 1:1 metalligand complexes are obtained;<sup>12e, 39</sup> thus these complexes are

#### 45 Description of the structures

CPs with coordinated water molecules.

Crystals of 1-5 suitable for the single crystal X-ray study were grown from the slow evaporation of the respective methanolic solution: 1 in 10 days, 2 in 7 days, 3 in 5 days, 4 in 7 days and 5

- <sup>50</sup> in 3 days. Despite numerous attempts, crystals of **6** suitable for data collection could not be obtained; however, a comparison of its spectroscopic data (UV-vis, CD and FTIR) with those of **4** and **5** indicates their structural similarities (*vide infra*).
- Compound 1 and 2 crystallize in the chiral monoclinic space 55 group  $P2_1$  and orthorhombic space group  $P2_12_12_1$ , respectively. The asymmetric unit of 1 and 2 consists of one Cu<sup>II</sup> center surrounded by two ligands (L-HTyrbenz and L-HSerbenz,

respectively) and two lattice solvents (one methanol molecule and one water molecule) and three water molecules, respectively. 60 Both are carboxylato-bridged 1D coordination polymers but the difference in geometry around the Cu<sup>II</sup> center arises from the substitution in the ligand. As shown in Fig. 2a, the Cu<sup>II</sup> center in 1 has a distorted square pyramidal geometry with a coordination environment of O<sub>3</sub>N<sub>2</sub> type - out of the four equatorial sites two 65 are occupied by the nitrogen atoms (N1 and N2) of the amine groups whereas the other two are occupied by the oxygen atoms (O3 and O5) of the carboxylates of two ligands, and the apical site is occupied by the oxygen atom (O4') of the carboxylate of the ligand bound to the adjacent metal center. The carboxylate 70 group of one ligand binds in a monodentate fashion (with oxygen atom O3) while the carboxylate group of the second ligand (with oxygen atoms O4 and O5) bridges in a syn-anti fashion between two Cu<sup>II</sup> centers forming the 1D coordination polymer chain (see Fig. 3a). On the other hand, the Cu<sup>II</sup> center in 2 (see Fig. 2b) has a 75 distorted octahedral geometry having the sixth position occupied by the hydroxymethyl group of one of the ligands (Cu<sup>II</sup>-OH bond

length: 2.723(1) Å).



<sup>80</sup> Fig. 2 Coordination environment around Cu(II) in (a) 1 and (b) 2.

Unlike 1, the bridging carboxylate group of the ligand in 2 that forms the 1D coordination polymer chains as shown in Fig 3b is in an anti-anti binding mode between two Cu<sup>II</sup> centers. Examples 85 of carboxylate bridging by L-tyrosine or L-tyrosine based ligands to form 1D CPs are limited in the literature:  ${Co(L-tyrosine)}_{n}^{38}$  $\{Zn(L-tyrosine)\}_{n}^{38}[Cu(L-tyrosine)_2]_{n}^{45} \{[Zn(L-tyrosine)_2(H_2O)]\}$  $(H_2O)_{n}^{45}$  and  $\{[Cu_2(L-HTyrsal)_2(H_2O)](H_2O)\}_n^{39}$  (where L- $H_2$ Tyrsal = L-N-(2-hydroxybenzyl)-tyrosine); unlike the first four <sup>90</sup> complexes where the carboxylate group bridges between the Cu<sup>II</sup> or Zn<sup>II</sup> centers, respectively, the last one with the L-tyrosine based Schiff base ligand the carboxylate group bridges the bis(phenoxo)dicopper units in the polymeric structure. In 1, the Cu-N<sub>amine</sub> bond distances are 2.015(3) Å and 2.022(3) Å, 95 comparable to 2.022(3) Å reported for [Cu(L-Ph-Tyr)(phen)(ClO<sub>4</sub>)];<sup>21</sup> however, the Cu-O<sub>(monodentate carboxylate)</sub> distance in [Cu(L-Ph-Tyr)(phen)(ClO<sub>4</sub>)], 1.958(3) Å, is comparable to one of the Cu-O(bridged carboxylate) distances of



Fig. 3 Comparison of the carboxylate bridging in the polymeric structures of (a) 1 and (b) 2.

- 1.957(3) Å in 1 but is slightly longer than the Cu-O<sub>(monodentate</sub> carboxylate) bond of 1.931(3) Å in 1. For 1, the bond angle O<sub>(carboxylate)-</sub>Cu-N<sub>(amine)</sub> for each ligand is 82.68(14)° and 84.76(16)°, which are similar to that of 83.25(9)° in [Cu(L-Ph-<sup>10</sup> Tyr)(phen)(ClO<sub>4</sub>)]. The selected bond distances and bond angles for 1 and 2 are listed in Tables S1 and S2 (ESI<sup>+</sup>), respectively. Moreover, the involvement of the phenolic group in the ligands for the hydrogen bonding network is very different in these complexes compared to 1. The 1D CP chains in 1 are involved in 15 extensive intermolecular hydrogen bonding with the lattice water and methanol molecules giving rise to a 2D supramolecular array. Out of the two phenolic groups (O1 and O6) of the L-HTyrbenz ligands in 1, one (O6) is involved in connecting the 1D chains to generate the 2D network. In this hydrogen bonding network, 20 there are two sets: (a) between the oxygen atom (O7) of the lattice methanol molecule and -OH (O1) of the phenol group (O---O distance: 2.672(6) Å) and the uncoordinated oxygen atom (O2) of the monodentate carboxylate of the ligand (O---O distance: 2.667(8) Å) as shown in Fig. S13, (ESI<sup>+</sup>), and (b)
- <sup>25</sup> between the oxygen atom (O8) of the lattice water molecule and oxygen atom (O5) of the bridged carboxylate (O---O distance: 2.985(8) Å) as well as the oxygen atom (O6) of the phenol part of the ligand (O---O distance: 2.652(8) Å). O8 is also hydrogen bonded to the oxygen atom (O7) of the lattice methanol molecule
- <sup>30</sup> (O---O distance: 3.049(7) Å). Thus the O8 atom, which acts as a donor (bifurcated) as well as acceptor, connects the two 1D chains through O6 (see Fig. 4) forming a R<sub>4</sub><sup>4</sup>(29) motif.<sup>46</sup> This 29-membered ring consists of four donor atoms (O6, O8, O6', O8'), four acceptor atoms (O5, O8, O5', O8') and some part of
- $_{35}$  the ligand skeleton. In {Co(L-tyrosine)}\_n, and {Zn(L-tyrosine)}\_n, the phenolic –OH is deprotonated and thus the phenoxo group coordinates with another metal center.  $^{38}$  In [Cu(L-tyrosine)\_2]\_n and

 $\{[Zn(L-tyrosine)_2(H_2O)](H_2O)\}_n$ , the phenolic -OH group is directly hydrogen bonded to the uncoordinated oxygen atom of carboxylate group.45 40 the monodentate In {[Cu<sub>2</sub>(L- $HTyrsal_{2}(H_{2}O)$ ]  $(H_{2}O)_{n}$ , the phenolic -OH group is involved in both intrachain and interchain hydrogen bonding. It connects one of the oxygen atom of the bridging carboxylate groups to the lattice water molecule to form the 1D chain. For the interchain 45 hydrogen bonding, the lattice water molecule and the phenolic -OH groups are involved.<sup>39</sup> In **1**, the Cu<sup>II</sup>...Cu<sup>II</sup> distance is 5.833(6) Å, which is similar to that (5.763(6) Å) found in {[Cu<sub>2</sub>(L- $HTyrsal_{2}(H_{2}O)](H_{2}O)_{n}$  though the Cu<sup>II</sup> centers in the latter are part of the bis(phenoxo) moieties that alternates in the CP chain; <sup>50</sup> this distance is much shorter (4.93(7) Å) in  $[Cu(L-tyrosine)_2]_n$ due to the ant-anti bridging mode of the carboxylate group. On the other hand, the Cu...Cu distance in 2 is 5.495(3) Å.

In addition to hydrogen bonding, various C-H...O interactions like C26-H12A..O6 and C26-H12B..O4 with a donor-acceptor <sup>55</sup> distances of 2.989(7) Å and 3.102(7) Å, respectively, further strengthens the association of the 1D CPs in **1**. All hydrogen bonding parameters for **1** are listed in Table 2.

In 2, all three lattice solvent molecules (water) forming a triad are involved in connecting these 1D chains through strong 60 hydrogen bonding. However, each set of three lattice water molecules for each 1D chains are not connected to each other. For the hydrogen bonding within each 1D chain (see Fig. S14, ESI<sup>+</sup>), two out of the three lattice water molecules (O1S and O3S) are involved: O3S acts both as a hydrogen bond donor and a 65 hydrogen bond acceptor. As a donor, O3S is hydrogen bonded to -OH (O5) of the -CH<sub>2</sub>OH (O---O distance: 2.915(4) Å) and the uncoordinated oxygen atom (O3) of the monodentate carboxylate of the ligand (O---O distance: 2.858(4) Å). As an acceptor, O3S is hydrogen bonded to the nitrogen (N1) of the amine part of the 70 ligand (N---O distance: 3.516(4) Å). O1S shows a three center bifurcated hydrogen bonding with uncoordinated (O3) and coordinated (O2) oxygen atoms of the monodentate carboxylate (distances: O1S---O3, 3.577(4) Å; O1S---O2, 2.752(4) Å) and oxygen atom (O6) of the bridging carboxylate (O1S---O6 75 distance: 2.864(4) Å) of the ligand. The third lattice water molecule (O2S) plays a very significant role. Although it is not directly involved in the intra-chain hydrogen bonding but as shown in Fig 5, it bridges between the two lattice water molecules O1S and O3S (O2S---O1S distance: 2.953(5) Å) (O2S-80 --O3S distance: 2.865(6) Å) from different triads of different 1D chains to form the inter-chain hydrogen bonding, thus extending

chains to form the inter-chain hydrogen bonding, thus extending the dimensionality. Further reinforcement of the network is by the inter-chain hydrogen bonding between the two oxygen atoms (O1 and O5) of the -CH<sub>2</sub>OH groups of the two ligands coordinated to seach Cu<sup>II</sup> centers and oxygen atom of a lattice water molecule (O1S) (O1---O1S distance: 2.777(4) Å) and the uncoordinated oxygen atom (O3) of the monodentate carboxylate (O5---O3 distance: 2.972(4) Å) of the ligand, respectively. Thus both CH<sub>2</sub>OH groups from two L-HSerbenz ligands are involved in <sup>90</sup> connecting these 1D chains for the overall network in **2**. This is very different from the involvement of the phenolic groups of the L-HTyrbenz in **1**. All these hydrogen bondings in **2** lead to the formation of four different motifs:  $R_3^4(11)$ ,  $R_4^4(11)$ ,  $R_5^4(14)$  and  $R_7^2(10)$ .<sup>46</sup> Both the eleven-membered motifs consist of four



Fig. 4 Two 1D chains connected via lattice water molecules in 1.

acceptor atoms (O1, N1, O2S and O2S'in R<sub>4</sub><sup>4</sup>(11) and O2S, O3S, 5 O5 and N2 in R<sub>3</sub><sup>4</sup>(11)); however, these vary in number of donor atoms (O1S, O3S, O3S' and O1S'in R<sub>4</sub><sup>4</sup>(11) and O3S, O3 and O2S in R<sub>3</sub><sup>4</sup>(11)). The R<sub>5</sub><sup>4</sup>(14) motif comprises of four acceptor atoms (N1, O6, O3S, O1S) and five donor atoms (O3S, O1S, O3, O1S' and O2). The ten-membered ring in R<sub>2</sub><sup>2</sup>(10) has two donor <sup>10</sup> atoms (O6 and O2) and two acceptor atoms (O1S and O1S'). In all these motifs, rest of the ring is made of some portion of the ligand skeleton. All hydrogen bonding parameters for **2** are listed in Table 2.

Compound **3** crystallizes in the monoclinic chiral space group <sup>15</sup>  $P2_1$ . The asymmetric unit of **3** comprises of a pentacoordinated Cu<sup>II</sup> center surrounded by two L-HTyrthio ligands and one lattice water molecule (as shown in Fig. S15, ESI†). The Cu<sup>II</sup> center has a distorted square pyramidal geometry with an O<sub>3</sub>N<sub>2</sub> coordination environment. The four equatorial sites are occupied by the two <sup>20</sup> nitrogen atoms (N1 and N2) of the amine group and two oxygen

atoms (O2 and O4) of the carboxylates of the two ligands. Unlike 1 and 2, both the carboxylates in 3 bind to the metal

Unlike I and Z, both the carboxylates in 3 bind to the metal center in a monodentate fashion. The sulphur atoms in the two thiophene rings of the mononuclear unit point towards each other.

- <sup>25</sup> The apical site is occupied by the phenolic oxygen (O3') of the ligand coordinating to the next metal center (Cu<sup>II</sup>-OH bond length: 2.704(5) Å) generating a spiral 1D coordination polymer (as shown in Fig. 6). The selected bond distances and bond angles for **3** are listed in Tables S1 and S2 (ESI<sup>†</sup>), respectively. This is the selected bond in the selection of the sele
- <sup>30</sup> kind of phenol-bridged coordination polymer is limited in the literature.<sup>47</sup> The other phenolic groups (O6) of the second L-HTyrthio ligand shows a bifurcated hydrogen bonding with oxygen atoms (O4 and O5) of the monodentate carboxylate of the ligand (O6---O4 distance: 3.035(7) Å) (O6---O5 distance:
- <sup>35</sup> 3.018(7) Å) coordinating to Cu<sup>II</sup> of the adjacent coordination polymer. The Cu...Cu distance between two adjacent Cu<sup>II</sup> centers

in a spiral chain is 10.806(9) Å. Each 1D spiral chain is further extended by the intra-chain hydrogen bonding. The oxygen atom(O1S) of the lattice water molecule acts as a hydrogen bond 40 acceptor showing bifurcated hydrogen bonding with the oxygen atom (O3) of the coordinated phenol (O---O distance: 2.672(7) Å) and nitrogen (N2) atom of the amine part of the ligand (O---N distance: 3.009(6) Å). This lattice water molecule (O1S) also acts as a hydrogen bond donor and shows hydrogen bonding with the

<sup>45</sup> oxygen atom (O1) of the carboxylate (O---O distance: 2.730(6) Å) of the ligand. This reinforcement of hydrogen bonding within each spiral chain forms two motifs labeled as R<sub>2</sub><sup>-2</sup>(21) and R<sub>2</sub><sup>-1</sup>(6) (see Fig. S16, ESI†).<sup>46</sup> The 21-membered motif R<sub>2</sub><sup>-2</sup>(21) consists of two donor atoms (O1S and O3) and two acceptor atoms (O5 and O1S). The six-membered motif R<sub>2</sub><sup>-1</sup>(6) consists of O3 as acceptor and O1S and N2 as donor atoms. The remaining parts of both the motifs are made up of some part of the ligand. The lattice water O1S is also involved in inter-chain bifurcated hydrogen bonding with the oxygen atoms (O1 and O2) of the s5 carboxylate of the ligands of the next chain (distances: O1S---O1, 3.195(7) Å; O1S---O2, 2.787(6) Å) (see Fig. 7). All hydrogen bonding parameters for **3** are listed in Table 2.

Compound 4 crystallizes in the monoclinic chiral space group C2. A 2-fold axis that passes through the Cu<sup>II</sup> center and the <sup>60</sup> coordinated water molecule generates the whole molecule from the asymmetric unit. There are two lattice water molecules per mononuclear unit. The Cu<sup>II</sup> center with an  $O_3N_2$  coordination environment has a distorted square pyramidal geometry (see Fig. S17, ESI<sup>†</sup>) where two equatorial sites are occupied by the <sup>65</sup> nitrogen atoms of the amine group and the other two equatorial sites are occupied by the oxygen atoms of the carboxylates of the two ligands. The apical site is occupied by a water molecule (O2). Both the carboxylates bind to the metal center in a monodentate fashion. The selected bond distances and bond angles for



Fig. 5 3D supramolecular array in 2 involving 1D chains and lattice water molecules.



Fig. 6 1D helical structure of 3.

4 are listed in Table S1 and S2 (ESI<sup>†</sup>), respectively. The nitrogen atom (N2) of the pyridyl moiety is hydrogen bonded to the oxygen atom (O1) of the phenol moiety of the second ligand (N--10 -O distance: 2.673(6) Å) and vice-versa, resulting in the formation of a network in the x direction (as shown in Fig. 8, top). Few examples of this kind of hydrogen bonding between phenolic O-H and pyridyl N are also known.<sup>48-49</sup> In the system

<sup>15</sup> with co-crystals of 4,4'-bipyridine-N-monoxide (BPMO) and p-coumaric acid (PCA), the N---O distance 2.689(3) Å and an angle of 175°.<sup>48</sup> In another co-crystal system of resorcinol and methyl ester of acrylic acid, two types of O-H..N bonding is observed (N---O distances: 2.787(4) Å and 2.800(4) Å).<sup>49</sup> The N--O
<sup>20</sup> distances in both the systems are comparable to the N--O distance in 4. The oxygen atom (O2) of the coordinated water molecule is

Table 1 Crystal Structure Data and Refinement Parameters for 1, 2, 3, 4 and 5.

Compound	1	2	3	4	5
Chemical Formula Formula Weight	C <sub>33</sub> H <sub>38</sub> CuN <sub>2</sub> O <sub>8</sub> 654.19	$\begin{array}{c} C_{20}H_{30}CuN_2O_9\\ 506.00\end{array}$	C <sub>28</sub> H <sub>30</sub> CuN <sub>2</sub> O <sub>7</sub> S <sub>2</sub> 634.2	C <sub>30</sub> H <sub>36</sub> CuN <sub>4</sub> O <sub>9</sub> 660.17	$\begin{array}{c} C_{16}H_{22}CuN_2O_7S_2\\ 482.01\end{array}$
Temperature (K)	260(2)	296(2)	296(2)	250(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1$	$P2_{1}2_{1}2_{1}$	$P2_1$	<i>C</i> 2	$P2_{1}$
a (Å)	12.7195(19)	9.2543(6)	10.2891(10)	12.0163(8)	10.6279(19)
b (Å)	9.7533(14)	10.0380(8)	9.0692(9)	7.7380(5)	7.9827(14)
c (Å)	14.170(2)	23.8749(19)	14.9871(17)	17.1859(14)	23.447(4)
a (°)	90	90	90	90	90
β (°)	115.087(9)	90	91.668(7)	107.324(2)	94.130(3)
γ (°)	90	90	90	90	90
Ζ	2	4	2	2	4
V (Å <sup>3</sup> )	1592.1(4)	2217.9(3)	1397.9(3)	1525.49(19)	1988.6(6)
Density (mg/cm <sup>3</sup> )	1.365	1.515	1.507	1.437	1.610
$\mu$ (mm <sup>-1</sup> )	0.739	1.039	0.980	0.776	1.349
F (000)	686	1060	658	690	996
Theta (°) Range	1.59 to 25.26	1.71 to 25.14	1.98 to 25.14	2.48 to 25.04	1.92 to 24.96
for Data Coll. Reflections Collected	15183	13150	8182	5711	17388
Independent Reflections	5589	3868	4273	2469	6862
Reflections with $I > 2\sigma(I)$ )	4668	3282	3435	2291	4195
R <sub>int</sub>	0.0435	0.0506	0.0435	0.0322	0.0768
No. of Parameters refined	407	309	371	218	514
GOF on F <sup>2</sup>	0.936	0.916	0.941	0.936	1.002
Final $R_1^a/wR_2^b$ (I >2 $\sigma$ (I))	0.0378/0.0762	0.0341/0.0616	0.0411/0.0776	0.0336/0.0691	0.0590/ 0.1251
$R_1/wR_2$ (all data)	0.0507/0.0831	0.0480/0.0675	0.0582/0.0858	0.0378/0.0711	0.1118/ 0.1490
Flack Parameter	0.027(9)	0.014(10)	0.011(13)	0.022(11)	-0.001(13)
Largest diff. peak	0.249	0.284	0.283	0.182	0.578
and hole $(e^{A^{-3}})$	and -0.245	and -0.315	and -0.309	and -0.196	and -0.729

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| \Sigma |F_{o}|. {}^{b}wR_{2} = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w(F_{o}^{2})^{2}]^{1/2}, \text{ where } w = 1/[\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP], P = (F_{o}^{2} + 2F_{c}^{2}) / 3$ 

hydrogen bonded to the uncoordinated oxygen atom (O4) of the monodentate carboxylate of the ligand (O---O distance: 2.743(4) Å) to have the network propagated in the y direction, as shown in Fig. 8, bottom. The 2D assembly in **4** has extensive hydrogen to bonding thus forming a network with variable pore sizes. One of the lattice water molecules (O5) connects the phenolic oxygen atoms (O1) of the ligand via hydrogen bonding (O5---O1 distance: 2.934(6) Å). The other lattice water molecule (O6) is hydrogen bonded to the nitrogen (N1) of the amine (N---O 15 distance: 3.182(7) Å) as well as to the coordinated oxygen (O3) and uncoordinated oxygen atom (O4) of the monodentate carboxylate of the ligand (O6---O3 distance: 2.719(8) Å; O6---O4 distance: 3.146(8) Å). The C-H...O interactions C2-H2A..O5, 20 C5-H5..O4 and C11-H11...O6 with donor-acceptor distances 3.410(5) Å, 3.371(6) Å and 3.358(8) Å, respectively, provide an additional strength to the network. Various hydrogen bondings lead to two kinds of motif formation in 4: R<sub>4</sub><sup>4</sup>(61) and R<sub>3</sub><sup>5</sup>(49).<sup>46</sup> The 61- membered motif R<sub>4</sub><sup>4</sup>(61) consists of four acceptor atoms 25 (O1, O1', O1'', O1''') and four donor atoms (N2, N2', N2'', N2''') whereas 49-membered motif R<sub>3</sub><sup>5</sup>(49) consists of five acceptor atoms (O2, O5, O5', O5'', O5''') and three donor atoms(O4, O1 and O1'). Again, in both the cases the motifs were completed by the ligand skeletons. All hydrogen bonding 30 parameters for **4** are listed in Table 2. Compound 5 crystallizes in the monoclinic chiral space group  $P2_1$ . The asymmetric unit of 5 consists of two independent molecules (see Fig. S18, ESI<sup>†</sup>). Each mononuclear unit consists of a pentacoordinated Cu<sup>II</sup> center bound to two L-HSerthio s ligands. The Cu<sup>II</sup> center has a distorted square pyramidal geometry with an O<sub>3</sub>N<sub>2</sub> coordination environment; two equatorial



Fig. 7 Inter-chain hydrogen bonding in **3** involving the lattice water molecule (two chains are shown with different colors).

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- <sup>10</sup> sites are occupied by the nitrogen atoms of the amine group whereas the other two equatorial sites are occupied by the carboxylate oxygens of the ligands. The apical site is occupied by a water molecule. Both the carboxylates binds to the metal center in a monodentate fashion. The selected bond distances and bond
  <sup>15</sup> angles for 5 are listed in Tables S1 and S2 (ESI<sup>†</sup>), respectively. The two independent molecules in the asymmetric unit not only differ in the arrangement of sulphur atoms in the two thiophene rings (in one molecule these point towards each other whereas in the other molecule these point away from each other), see Fig.
  <sup>20</sup> S18 (ESI<sup>†</sup>) but also vary in their hydrogen bonding interactions.
- Each molecule forms a unique 1D supramolecular chain via intermolecular hydrogen bonding as shown in Fig. 9. In the first 1D chain, the two oxygen atoms (O6 and O7, respectively) of the  $-CH_2OH$  of one mononuclear unit shows an intermolecular
- <sup>25</sup> hydrogen bonding with the uncoordinated oxygen atoms (O5 and O3, respectively) of the carboxylates of the next mononuclear units in an intermolecular fashion (O6---O5 distance: 2.686(12) Å; O7---O3 distance: 2.687(12) Å). The oxygen atom (O1) of the coordinated water molecule shows intermolecular hydrogen
- <sup>30</sup> bonding with two coordinated oxygen atoms (O2 and O4) of the two carboxylates of two different molecules (O1---O2 distances: 2.868(11) Å and O1---O4 distance: 2.918(11) Å, respectively). The nitrogens (N2 and N1) of the amine part of the ligands of one mononuclear unit are hydrogen bonded to the oxygen atom (O1)
  <sup>35</sup> of the coordinated water and oxygen atom (O6) of the -CH<sub>2</sub>OH
- part of the ligand of the next unit respectively (distances: N2---O1, 3.240(12) Å; N1---O6, 3.014(13)Å). These hydrogen bondings lead to the formation of four motifs:  $R_3^{2}(6)$ ,  $R_2^{2}(8)$ ,  $R_2^{2}(4)$  and  $R_2^{2}(9)$ .<sup>46</sup> All four motifs consist of two acceptor atoms
- <sup>40</sup> (O1 and O1'in  $R_3^2(6)$ ; O1 and O1' in  $R_2^2(8)$ ; O1 and O1'in  $R_2^2(4)$ and N1 and N2 in  $R_2^2(9)$ ) and two donor atoms (O2 and O7 in

 $R_2^2(8)$ ; O7 and O7' in  $R_2^2(4)$  and O1 and O6 in  $R_2^2(9)$  except the six-member  $R_3^2(6)$  motif which consists of three donor atoms (O2, O3 and O3'). Like all the motifs, these also consist of some 45 part of the ligands. In addition to the hydrogen bonding interactions observed in the first 1D chain, for the second 1D chain the coordinated water molecule (O8) shows hydrogen bonding with the oxygen atom (O12) of the -CH<sub>2</sub>OH of the ligand (O8---O12 distance: 2.962(12) Å). Similar to the first 50 chain, the oxygen atoms (O14 and O11) of the -CH<sub>2</sub>OH of two ligands coordinated to same metal center are hydrogen bonded to the uncoordinated oxygen atoms (O10 and O13, respectively) of the carboxylate of the adjacent molecules in an intermolecular fashion (O14---O10 distance: 2.630(14) Å; O11--- O13 distance: 55 2.725(13) Å). These hydrogen bondings give rise to three motifs within this chain: two  $R_2^2(10)$  and one  $R_2^2(12)$ .<sup>46</sup> All motifs consist of two donor atoms (O17 and O18 in  $R_2^2(10)$ ; O13 and O10 in  $R_2^2(12)$ ) and two acceptor atoms (N3 and N4 in  $R_2^2(10)$ ; O18 and O17 in  $R_2^{(2)}(12)$  along with some parts of the ligands. 60 All hydrogen bonding parameters for 5 are listed in Table 2.

#### Effect of the substitution on the ligands

- In this study, a systematic change in the reduced Schiff base <sup>65</sup> derivatives of L-amino acid ligands has been used to investigate the formation of products under similar reaction conditions. Clearly, the coordination of a water molecule to the Cu<sup>II</sup> center is controlled by the nature of substitution present in the ligand. This in turn forms either the CPs (1, 2 and 3) with a general formula 70 {[ML<sub>2</sub>]·Y}<sub>n</sub>, or the supramolecular assemblies (4, 5 and 6) with a general formula [ML<sub>2</sub>(H<sub>2</sub>O)]'Y, where L is the ligand and Y represents the lattice solvent molecules. Their formation is purely based on the coordination chemistry of a 1:2 metal to ligand complex. After having four sites occupied by two ligands the fifth 75 site around Cu<sup>II</sup> is occupied by the donor atom (either from the phenolic OH group or the carboxylate group) that is available in 1-3 while a water molecule occupies in 4-6. In {[Cu(L-
- $HTyrbenz)_2$ ]  $CH_3OH H_2O_{n}$  (1), the coordination polymer is formed via bridging carboxylate showing no role of the phenolic  $R_{00}$  group in its formation. To further emphasize this point, Ltyrosine was replaced with L-serine to form another CP, {[Cu(L-HSerbenz)\_2]  $3H_2O_{n}$  (2).

In changing from L-H<sub>2</sub>Tyrbenz ligand to L-H<sub>2</sub>Tyr4-pyr ligand (1 vs 4), the strong hydrogen bonding of the pyridyl nitrogen with <sup>85</sup> the phenolic OH does not allow the latter to bind to Cu<sup>II</sup>. The structural assortment of compounds such as 4 can be accredited to the presence and position of the hetero atom in the ring. For example, as reported earlier the use of L-H<sub>2</sub>tyr-2pyr with Cu<sup>II</sup> results in the formation of a supramolecular assembly [Cu(L-<sup>90</sup> Htyr2-pyr)<sub>2</sub>].<sup>50</sup> But the environment around Cu<sup>II</sup> and the hydrogen bonding interactions present in the 4 is distinctly different from the supramolecular array in [Cu(L-Htyr2-pyr)<sub>2</sub>]. In 4, Cu<sup>II</sup> is pentacoordinated with an O<sub>3</sub>N<sub>2</sub> environment, whereas in [Cu(L-Htyr2-pyr)<sub>2</sub>], hexacoordinated Cu<sup>II</sup> is surrounded by an <sup>95</sup> O<sub>2</sub>N<sub>4</sub> environment. In both the cases, the nitrogen of the amine and oxygen of the carboxylate of the ligand bind to the metal center. In addition to that, the pyridyl nitrogens also coordinate to

the  $Cu^{II}$  in case of  $[Cu(L-Htyr2-pyr)_2]$  whereas in 4, the fifth

coordination of the Cu<sup>II</sup> center is completed by a water molecule.



Fig. 8 Hydrogen bondings in x (top) and y (bottom) directions for the formation of the 2D supramolecular network in 4. Other lattice water molecule (O6) is omitted for clarity.

In [Cu(L-Htyr2-pyr)<sub>2</sub>] the supramolecular assembly grows through the hydrogen bonding which involves the phenolic OH, oxygens of the carboxylates and the lattice solvent (water) molecules. In **4**, the above mentioned hydrogen bonding do exist <sup>10</sup> along with another typical hydrogen bonding between the pyridyl nitrogen and the phenolic –OH of the ligand (*vide supra*). Thus the 2-pyr derivative forms a polymeric structure because no such pyr..HO(phenol) hydrogen bonding is possible. Similarly, in

changing from L-H<sub>2</sub>Tyrthio to L-H<sub>2</sub>Serthio (**3** vs **5**) the length of <sup>15</sup> the –CH<sub>2</sub>OH group in the latter is much less than the distance between the two Cu<sup>II</sup> centers to occupy the fifth site and thus a water molecule is coordinated. Thus the essence in the formation of {[Cu(L-HTyrthio)<sub>2</sub>]<sup>-</sup>H<sub>2</sub>O}<sub>n</sub> (**3**) lies in the growing of the spiral polymer via the unique phenolic bridging with a distance between <sup>20</sup> two Cu<sup>II</sup> centers of 10.806 Å. This is further confirmed by established by PXRD (see Fig. S21, ESI<sup>†</sup>) while the reverse was not possible. To further illustrate the significance of the phenolic part, the L-Tyrosine part in the ligand L-H<sub>2</sub>tyrthio is supplanted <sup>25</sup> with L-Phenylalanine and the resultant ligand L-HPhethio gives [Cu(L-Phethio)<sub>2</sub>(H<sub>2</sub>O)]<sup>3</sup>H<sub>2</sub>O (**6**). Although the crystal structure of **6** is not obtained even after several attempts, the values for the carboxylate stretching frequencies in its FTIR spectrum advocates the presence of monodentate carboxylatebridged CP formation.<sup>45,53</sup> The absence of the phenolic -OH group in L-Phethio further insinuate the formation of any phenolic bridged CP, thus confirming **6** to be a supramolecular assembly and not a CP.

reacting 5 with 2 eq of L-H<sub>2</sub>Tyrthio in methanol to form 3 as



Fig. 9 Two independent 1D supramolecular chains in 5 (Chain 1: top; Chain 2: bottom).

#### 5 Powder X-ray data analysis

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To confirm whether the single crystal structure corresponds to the bulk material or not, powder X-ray diffraction patterns were recorded for **1-5** at room temperature. The experimental and a simulated (from the single crystal data) patterns were similar to

- <sup>10</sup> simulated (from the single crystal data) patterns were similar to each other (see Figs. S19-S23, ESI<sup>†</sup>). Powder pattern of **6** was also recorded to check the crystalline nature of the compound (see Fig. S24, ESI<sup>†</sup>). The patterns obtained confirm that the single crystal and bulk material are the same. It also confirms the <sup>15</sup> phase purity of the bulk sample.
- UV-Vis and Circular Dichroism (CD) spectroscopy

UV-Visible and CD studies were carried using ~1 mM <sup>20</sup> methanolic solution of **1-6**. In the visible part of the spectra for **1-6**, major peaks are at 590 nm ( $\varepsilon = 159 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}$ ), 589 nm ( $\varepsilon = 144 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}$ ), 585 nm ( $\varepsilon = 200 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}$ ), 600 nm ( $\varepsilon = 174 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}$ ), 586 nm ( $\varepsilon = 152 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}$ ) and 582 nm ( $\varepsilon = 153 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}$ ) and 582 nm ( $\varepsilon = 153 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}$ ), respectively (as shown in Fig. 10a). These <sup>25</sup> peaks are due to the d-d transition in Cu<sup>II</sup> (<sup>2</sup>E<sub>g</sub> to <sup>2</sup>T<sub>2g</sub>).<sup>51</sup> In the CD spectrum (400-700 nm) for **1**, the positive Cotton effect is observed at 445 and 632 nm. The corresponding peaks for other

D-HA	r(D-H) (Å)	r(HA) (Å)	r(DA) (Å)	∠D-HA (°)	Symmetry
1					
O1-H2O7	0.82	1.86	2.672(6)	168	x,-1+y,z
O6-H5O8	0.82	1.84	2.652(8)	171	1-x,-1/2+y,-z
O8-H12CO7	0.75	2.31	3.049(7)	169	
O8-H12DO5	0.87	2.17	2.985(8)	157	-x,1/2+y,-z
O7-H51O2	0.82	1.86	2.667(8)	167	
С5-Н20Об	0.93	2.53	3.263(8)	136	1-x,-1/2+y,-z
C10-H26BO5	0.97	2.43	3.317(6)	152	-x,1/2+y,-z
2					
O1-H1O1S	0.82	1.96	2.777(4)	171	-x,-1/2+y,1/2-z
O1S-H1SBO6	0.85	2.03	2.864(4)	167	-x,-1/2+y,1/2-z
N1-H1AO3S	0.98	2.56	3.516(4)	165	-1+x,y,z
N2 -H2O2S	0.98	2.10	3.078(5)	172	-1/2+x,1/2-y,-z
O1S-H1SAO2	0.85	1.91	2.752(4)	171	1/2-x,1-y,1/2+z
O2S-H2SBO1S	0.85	2.11	2.953(5)	173	1-x,-1/2+y,1/2-z
O2S-H2SAO3S	0.86	2.01	2.865(6)	177	
O5-H5O3	0.82	2.24	2.972(4)	149	-1/2+x,1/2-y,-z
O3S-H3SBO3	0.85	2.05	2.858(4)	159	
O3S -H3SAO5	0.85	2.10	2.915(4)	161	1+x,y,z
C13-H13BO4	0.97	2.44	3.322(5)	151	1/2+x,3/2-y,-z
3					
O1S-H1SBO1	0.85	1.90	2.730(6)	166	1-x,1/2+y,1-z
N2-H2O1S	0.98	2.23	3.009(6)	135	1-x,1/2+y,1-z
O1S-H1SAO1	0.86	2.57	3.195(7)	131	1+x,y,-1+z
O1S-H1SAO2	0.86	1.95	2.787(6)	165	1+x,y,-1+z
O3-H3O1S	0.82	1.87	2.672(7)	167	x,y,1+z
O6-H6O4	0.84	2.24	3.035(7)	156	-1+x,y,z
O6-H6O5	0.84	2.29	3.018(7)	145	-1+x,y,z
4					
N1-H106	0.98	2.35	3.182(7)	142	-1/2+x,1/2+y,z
O1-H1AN2	0.82	1.87	2.673(6)	164	1/2-x,-1/2+y,1-z
O2-H2O4	0.84	1.91	2.743(4)	171	-1/2+x,1/2+y,z
O5-H5AO1	0.87	2.07	2.934(6)	172	
O6-H6AO4	0.84	2.33	3.146(8)	164	x,-1+y,z
O6-H6BO3	0.84	1.94	2.719(8)	154	1/2-x,-1/2+y,-z
C2-H2AO5	0.93	2.55	3.410(5)	154	1/2+x,1/2+y,z
C5-H5O4	0.93	2.47	3.371(6)	162	-1/2+x,-1/2+y,z
C11-H11O6	0.93	2.48	3.358(8)	157	x,1+y,z
5					
N1-H106	0.98	2.18	3.014(13)	142	1-x,-1/2+y,1-z
O1-H1CO4	0.85	2.11	2.918(11)	158	1-x,-1/2+y,1-z
O1-H1DO2	0.85	2.03	2.868(11)	167	1-x,1/2+y,1-z
N2-H2O1	0.98	2.40	3.240(12)	143	1-x,1/2+y,1-z
Об-НбО5	0.82	1.87	2.687(12)	173	1-x,-1/2+y,1-z

07-Н703	0.82	1.92
O8-H8CO12	0.85	2.28
O14-H14AO10	0.82	1.84
O11-H11O13	0.82	1.92
C1-H1FO7	0.97	2.40
C17-H17AO10	0.97	2.57



Fig. 10 a) UV spectra and b) CD spectra for 1-6 in wavelength range from 400 to 700 nm.

550

Wavelength (nm)

600

650

700

500

400

b)

450

complexes are as follows: **2**, 453 and 653 nm; **3**, 434 and 650 nm; **4**, 453 and 671 nm; **5**, 459 and 658 nm; **6**, 454 and 657 nm. For **1**, the negative Cotton effect is observed at 537 nm. The 10 corresponding peaks for other complexes are as follows: **2**, 522 nm; **3**, 524 nm; **4**, 523 nm; **5**, 527 nm; **6**, 520 nm (as shown in

- nm; **3**, 524 nm; **4**, 533 nm; **5**, 527 nm; **6**, 530 nm (as shown in Fig. 10b). The peaks in the range of 520-540 nm are due to d-d transitions.<sup>52</sup> In the UV region of the spectra of **1-6** (200 to 400 nm), the
- In the 6.V region of the spectra of 16 (200 to 400 hm), the peaks at around 200 nm (π-π\*) and 225 nm (n-π\*) are due to the ligand. The peaks within the range of 250-275 nm in various spectra are due to the various substitutions in the aldehyde part of the ligands (as shown in Fig. 11a).

2.686(12)	154	1-x,1/2+y,1-z
2.962(12)	138	2-x,-1/2+y,-z
2.630(14)	160	2-x,1/2+y,-z
2.725(13)	169	2-x,-1/2+y,-z
3.166(15)	136	1-x,1/2+y,1-z
3.335(15)	136	1-x,1/2+y,-z

3.335(15)
136
1-x,1/2+y,-z
In the CD spectrum of 1 (200-400 nm), the positive Cotton effect is observed at 217, 240 and 273 nm. The corresponding peaks for other complexes are as follows: 2, 210 and 234 nm; 3, 200 and 246 nm; 4, 260 nm; 5, 200 and 251 nm; 6, 200 and 285 nm. For 1, the negative Cotton effect is observed at 200 nm and 25 224 nm. The corresponding peaks for other complexes are as follows: 2, 200 nm; 3, 224 nm; 4, 217 and 277 nm 5, 229 nm; 6, 227 and 285 nm (as shown in Fig. 11b).

#### FT-IR spectroscopy

30

The IR spectra of **1-6** (see Figs. S25-S30, ESI<sup>†</sup>) were recorded in solid state using KBr pellets. In the FT-IR spectra of **1-6**, the broad peak in the range of 3300-3400 cm<sup>-1</sup> is due to the lattice water molecules. The peak at 3269 cm<sup>-1</sup> (**1**), 3252 cm<sup>-1</sup> (**3**) and 35 3269 cm<sup>-1</sup> (**4**) is due to phenolic –OH of the ligands. The sharp peak observed at 3237 cm<sup>-1</sup> (**4**), 3257 cm<sup>-1</sup> (**5**) and 3277 cm<sup>-1</sup>(**6**) is due to coordinated water molecule. The hydroxyl peak of the –CH<sub>2</sub>OH for **2** and **5** appears at 3111 cm<sup>-1</sup> and 3212 cm<sup>-1</sup>, respectively. The peaks in the range of 2930-2950 cm<sup>-1</sup> are for the 40 N-H of amine part of the complexes. The presence of two types of asymmetric and symmetric stretches for the carboxylate group in **1** and **2** are well in accordance with the presence of two types of carboxylate binding modes (monodentate and bridging) in **1** and **2**. The various FTIR peaks for the carboxylates in **1-6** are 4s listed in Table S3 (ESI<sup>†</sup>).

The stretching frequency for the C-O is observed at 1240 cm<sup>-1</sup> (1), 1278 cm<sup>-1</sup> (2), 1244 cm<sup>-1</sup> (3), 1264 cm<sup>-1</sup> (4), 1254 cm<sup>-1</sup> (5) and 1278 cm<sup>-1</sup> (6). In the spectrum of 3, the peaks at 1198 cm<sup>-1</sup> and 714 cm<sup>-1</sup> are due to C=S and C-S present in the thiophene <sup>50</sup> ring of the ligand. The corresponding peaks for 5 appear at 1177 cm<sup>-1</sup> and 716 cm<sup>-1</sup>, respectively.<sup>54</sup>

#### Thermogravimetric analyses

<sup>55</sup> Thermal stabilities of **1-6** were studied as a function of temperature in the range of 25-500 °C (see Fig. S31, ESI<sup>†</sup>). Since **1**, **2** and **3** are CPs, their profiles show thermal stabilities up to 200 °C with an initial loss of the lattice solvent molecules at around 100 °C. For **1**, it is a three step weight loss profile. The <sup>60</sup> first weight loss of 4.96% between 50-120 °C corresponds to loss of two lattice water molecule (ca. 5.2%). The second step showing weight loss of 15.4% between 120-220 °C indicates loss of three lattice water molecules along with loss of a CO<sub>2</sub> molecule from the ligand (ca. 14.9%). The third step showing <sup>65</sup> weight loss of 50.1% between 220-400 °C indicates loss of the Cu-ligand complex (ca. 51.9%). For **2**, it is a two step weight loss profile. The first weight loss of 10.2% between 50-100 °C corresponds to loss of three lattice water molecule (ca. 10.7%). The second step showing weight loss of 64.7% between 100 °C corresponds to loss of three lattice water molecule (ca. 10.7%).

200-400 °C indicates loss of the ligand (ca. 69.4%). For **3**, it is a three step weight loss profile. The first weight loss of 4.2% between 50-170 °C corresponds to loss of two lattice water molecules (ca. 4.2%). The second step showing weight loss of

- 5 12.9% between 160-230 °C indicates loss of a thiophene molecule (ca. 13.4%). The third step showing weight loss of 39.1% between 230-400 °C indicates loss of left over ligand (ca. 36.4%). Each of 4 and 6 shows loss of both lattice as well as coordinated solvent molecules at around 150 °C. For 4, it is a four
- <sup>10</sup> step weight loss profile. The first weight loss of 10.03% between 50-110 °C corresponds to loss of four uncoordinated water molecules (ca. 9.96%). The second step showing weight loss of 6.7% between 110-200 °C indicates loss of one uncoordinated and one coordinated water molecules (ca. 6.3%). The third step 15 showing weight loss of 35.2% between 200-330 °C indicates loss of a tyrosine molecule and a copper atom (ca. 33.8%). The fourth step showing weight loss of 11.9% between 330-400 °C indicates loss of a pyridyl group (ca. 12.5%). The TGA profile of **5**, shows



Fig. 11 a) UV spectra and b) CD spectra for 1-6 in wavelength range from 200 to 400 nm.

it to be highly stable till 200°C thus confirming the presence of strong hydrogen bonding. The weight loss of 69.82% between <sup>25</sup> 202-304 °C corresponds to loss of the coordinated water molecule and the ligand (ca. 67.1%). For **6**, it is a three step weight loss

profile. The first weight loss of 3.44% between 50-150 °C corresponds to loss of one water molecule (ca. 2.87%). The second step showing weight loss of 6.01% between 150-190 °C <sup>30</sup> indicates loss of three more water molecules (ca. 8.6%). The third step showing weight loss of 59.7% between 200-400 °C indicates further degradation of the compound.

#### **Photoluminescence properties**

All tyrosine based ligands show good fluorescence as tyrosine <sup>35</sup> itself is a natural fluorophore. All the ligands were excited at 270 nm to show emission at 310 nm for L-NaHTyrbenz, 318 nm for L-NaHTyrthio and 324 nm for L-NaHTyr4-pyr. In the presence of Cu(II) ions the fluorescence due to the ligands is quenched as can be seen in the emission spectra of **1**, **3** and **4** (Fig 12). This is

<sup>40</sup> due to the fact that a transition-metal center can persuade the nonradiative deactivation of adjoining photoexcited fluorophore by dexter type energy transfer between the orbitals of appropriate energy of Cu<sup>II</sup> and the respective fluorophores.<sup>55</sup>



45 Fig. 12 Emission spectra of L- NaHTyrbenz, L-NaHTyrthio, L-NaHTyr4pyr, 1, 3 and 4.

#### Conclusions

In this article we have demonstrated that the formation of diverse chiral coordination architectures can be controlled by the strategic 50 substitution on the reduced Schiff base ligands of amino acids.  $({[Cu(L-HTyrbenz)_2]CH_3OHH_2O]_n}$ Those {[Cu(L-(1),  $HSerbenz_2$   $3H_2O_n(2)$  and  $\{[Cu(L-HTyrthio)_2]H_2O_n(3)\}$ which do not have any coordinated water moelcule are 1D CPs but their formation is through different functionalities of the 55 ligand (a syn-anti bridging carboxylate and hydroxy group of the L-tyrosine part of the ligand in 1 and 3, respectively, and an antianti bridging carboxylate group of L-serine part of the ligand in 2). On the other hand, each of the three complexes ([Cu(L-HTyr4-pyr)<sub>2</sub>(H<sub>2</sub>O)] 2H<sub>2</sub>O (4), [Cu(L-HSerthio)<sub>2</sub>(H<sub>2</sub>O)] (5), and 60 [Cu(L-Phethio)<sub>2</sub>(H<sub>2</sub>O)] 3H<sub>2</sub>O (6)) that contains a coordinated water molecule are supramolecular assemblies via extensive hydrogen bonding. Thus the involvement of the phenolic -OH group in the ligands derived from L-Tyrosine in a coordination bond is dictated by the substitution on the N atom of the ligand.

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For the methylthiophenyl containing ligands, the phenolic group in L-HTyrthio is long enough to bridge the two Cu<sup>II</sup> centers in **3** but the much shorter length of the -CH<sub>2</sub>OH group in L-HSerthio is responsible for the formation of **5**. Furthermore, the s significance of the phenolic part is observed when the L-Tyrosine

- part in the ligand L-H<sub>2</sub>tyrthio is exchanged with L-Phenylalanine and the resultant ligand L-HPhethio gives 6. Therefore, these ligands are found to play an important role in determining the coordination architectures with diverse physico-chemical
- <sup>10</sup> properties as determined by a number of analytical methods, such as FTIR, Fluorescence, UV-Vis and circular dichroism spectroscopy, polarimetry, powder and single crystal X-ray diffraction and thermogravimetric analysis. Based on the results presented in the paper, we are currently conducting further work <sup>15</sup> involving other substitutions on the ligands to showcase the generalization of this scheme.

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#### Notes and references

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<sup>†</sup>Electronic Supplementary Information (ESI) available: Crystallographic data of the structures **1**, **2**, **3**, **4** and **5** in CIF format (CCDC no. 993632-993636, respectively). NMR and FTIR spectra for the ligands, additional figures related to crystal structures of **1**, **2**, **3**, **4** and **5**, PXRD patterns,

- 35 FTIR spectra, and TGA scans for 1-6. Selected bond distances and angles of 1, 2, 3, 4 and 5. See DOI: 10.1039/b000000x/
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#### Table of Contents – artwork and synopsis



<sup>5</sup> In this paper we report six chiral ligands based on L-tyrosine, L-serine and L-phenylalanine and their homochiral Cu<sup>II</sup> complexes to study the effects of various substitutions in the ligands on the formation of diverse coordination architectures. This has allowed us to identify the factors involved in controlling the formation of either coordination polymers or supramolecular assemblies.