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Versatility of Cyclic Triimidazole to Assemble 1D, 2D and 3D Cu(I) Halide Coordination Networks

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KEYWORDS. Cu(I) Halide, Coordination Networks, Cyclic Triimidazole, Crystal Engineering

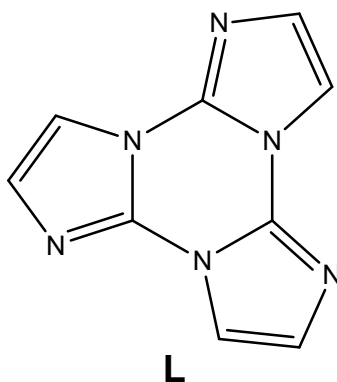
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ABSTRACT

Cyclic triimidazole ($C_9H_6N_6$, **L**), with C_{3h} molecular symmetry and three nitrogen atoms available for coordination, is here successfully employed for the first time in the synthesis of coordination compounds. In particular, by varying the reaction conditions (*e.g.* solvent, temperature, template), seven Cu(I)-halide coordination polymers of different dimensionality are obtained: two 1D polymers, $[CuIL]_n$ (**1**) and $\{[CuIL] \cdot (I_2)_{0.5}\}_n$ (**2**), three 2D nets, $[CuXL]_n$ ($X = I, Br$) (**3-5**), and two 3D networks, $[CuCIL]_n$ (**6**) and $\{[Cu_3L_4]I_3\}_n$ (**7**). Single crystal X-ray diffraction analysis reveals that the structural versatility of both the ligand and the CuX moiety allows to isolate 1D double-stranded stairs in which **L** is monodentate, 2D layers containing either $Cu_2(\mu-X_2)$ or $Cu_2(\mu-X)$ moieties and bidentate **L** ligands, 3D frameworks built up by tridentate **L** linkers and either monodentate or non-coordinating halogen atoms. The 3D frameworks show nets of **srs** and **bor** topologies. The SHG efficiency of powders of **7** (the only non-centrosymmetric derivative of the series) is ten times higher than that of sucrose. Phosphorescent emission of XLCT character is observed for **1** and **6**.

1. INTRODUCTION

Cyclic triimidazole ($C_9H_6N_6$, **L**, Scheme 1) is known since 1973.¹ Despite this, the scarce availability of its precursors, together with tedious synthetic protocols for its isolation, constituted a major impediment in its use. A simple procedure for the preparation of **L** in fairly good yields has been reported only recently,² allowing further investigations on its properties and reactivity. In particular, **L** displays an intriguing photophysical behaviour, being hardly emissive in solution but quite so as crystalline powders ($\Phi = 30\%$), due to concomitant fluorescence and ultralong phosphorescence (τ up to 1 s at room temperature), a behavior that has been associated to the formation of H aggregates through face to face strong π - π interactions in the crystal structure.³ An additional interesting feature of this ligand is the presence, at the vertexes of a regular triangle, of three nitrogen atoms available for coordination to metal ions, this making **L** an appealing tecton for molecular design of coordination compounds.



Scheme 1. Molecular structure of cyclic triimidazole (**L**)

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3 Coordination compounds based on copper(I) halides (CuX, with X = Cl, Br, or I) or
4 pseudohalides and nitrogen-donor ligands are a fascinating class of materials which are known to
5 display a rich structural chemistry, due to the d^{10} electronic configuration of the metal ion, which
6 enables it to adopt a variety of coordination numbers and geometries. Structural motifs spanning
7 from [CuX(L)] monomers, [CuX(L)₂]₂ dimers, [CuX(L)]₄ tetramers, and [CuX(L)]_n polymers
8 have been reported.⁴ These motifs can be reciprocally bridged by nitrogen-donor ligands to give
9 one-, two- or three-dimensional coordination polymers (CPs).⁵⁻⁸ Due to the d^{10} electronic
10 configuration of the metal ion, Cu(I) derivatives may show appealing functional properties
11 influenced by the specific structural features.⁹ As a matter of fact, Cu(I) derivatives with
12 tunable photoluminescence and conductivity properties have attracted considerable
13 attention.¹⁰⁻¹³ In addition, copper(I) coordination compounds with tridentate nitrogen-donor
14 ligands have enjoyed considerable success in bioinorganic chemistry as models for reaction
15 centers in proteins such as those involved in oxygen activation.¹⁴

16
17 Hereafter, we report seven Cu(I) 1D, 2D, and 3D coordination polymers obtained by
18 coupling **L** and CuX (X = I, Br, Cl) under various reaction conditions (changing *e.g.* solvent,
19 temperature, template). In particular, single crystals of [CuIL]_n (**1**), {[CuIL]·(I₂)_{0.5}]_n (**2**),
20 [CuXL]_n (X = I, **3**, **5**; X = Br, **4**), [CuCIL]_n (**6**) and {[Cu₃L₄]I₃]_n (**7**) have been isolated and
21 structurally characterized. The photoluminescent properties of **1** and **6** have been measured
22 both at room and low temperature and the SHG efficiency of powders of **7** (the only non-
23 centrosymmetric derivative of the full series) has been determined by the Kurtz-Perry
24 method.¹⁵

2. EXPERIMENTAL SECTION

2.1. Materials and Methods

All the chemicals and solvents are purchased from Sigma Aldrich and, unless otherwise indicated, used as received. CuI is crystallized by dissolution in a saturated aqueous solution of KI and successive precipitation with water. CuBr and CuCl are purified by grinding in a mortar with sulfuric acid 1 N, followed by washing with water, glacial acetic acid, absolute ethanol and diethyl ether.¹⁶ **L** is synthesized according to the literature.²

Solvothermal syntheses are performed in a sealed 20-mL Teflon-lined reactor, heated (5 °C/min rate) in an oven at 120 °C for 36 h and slowly (0.1 °C/min rate) cooled to 30 °C.

Infrared spectra are collected in ATR mode (compounds **1-4** and **6**) with a Perkin-Elmer Frontier FT-IR spectrometer equipped with an ATR accessory with a diamond/ZnSe crystal or on a Spectrum-100 Perkin Elmer spectrometer (compounds **L** and **7**).

Thermogravimetric analysis (TGA) are performed on a Mettler Toledo TGA/DSC 3+ instrument under dynamic nitrogen (total flow rate 50 cm³/min) with a ramp rate of 5 °C/min in the range 30 – 900 °C. X-ray powder patterns are recorded on a Philips PW1820 diffractometer (CuK_α radiation, $\lambda = 1.5418$), in the 5-50° 2 θ range (with steps of 0.02° and time per step of 2.5 s). Elemental analyses are carried out at the Microanalytical Laboratory of the University of Milan with a Perkin Elmer 2400 instrument.

2.2. Synthesis of 1D [CuIL]_n (**1**)

A saturated aqueous solution of KI is added to solid CuI. The resulting mixture is filtered and transferred into a vial. **L** (15 mg, 0.076 mmol) dissolved in CH₃CN (2 mL) is added to 4 mL of this solution. The vial is kept closed at room temperature for one night, producing colorless needle-shaped crystals which are separated from the solution and dried over filter

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3 paper. The crystals display a higher stability in the solid state (where crystallinity is
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5 preserved at least 1 week) than in the mother liquor (where loss of crystallinity occurs in few
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7 days). Anal. Calc. for $C_9H_6CuIN_6$ (%): C, 27.81; H, 1.56; N, 21.62. Found: C, 27.63; H, 1.61; N,
8
9 21.82.
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12 13 14 **2.3. Synthesis of 1D $\{[CuIL] \cdot 0.5(I_2)\}_n$ (2)**

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16 In a glass beaker, $Cu(NO_3)_2 \cdot 3H_2O$ (24 mg, 0.098 mmol) and KI (33 mg, 0.199 mmol) are
17
18 stirred in boiling CH_3CN (20 mL) for 10 minutes; then L (20 mg, 0.103 mmol) and 4,4'-
19
20 bipyridine (5 mg, 0.033 mmol) are added and allowed to react for 20 minutes at the same
21
22 temperature. The formation of an unidentified yellow precipitate is observed. After
23
24 filtration, the dark brown solution is transferred into an open vial and slowly evaporated at
25
26 room temperature to afford brown crystals of **2**.
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31 32 **2.4. Synthesis of 2D $[CuIL]_n$ (3)**

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34 In a closed vial, a solution of CuI (24 mg, 0.126 mmol) dissolved in CH_3CN (4 mL) is added
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36 to a solution of L (24 mg, 0.121 mmol) in CH_3CN (4 mL). After few months at room
37
38 temperature, the formation of colourless crystals of **3** contaminated by trace amounts of **1** is
39
40 observed. Single crystals of **3** suitable for X-ray diffraction analysis are manually separated.
41
42 Anal. Calc. for $C_9H_6CuIN_6$ (%): C, 27.81; H, 1.56; N, 21.62. Found: C, 27.98; H, 1.57; N, 21.38.
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45 46 47 **2.5. Synthesis of 2D $[CuBrL]_n$ (4)**

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49 In a Teflon beaker, solid L (22 mg, 0.111 mmol) and CuBr (16 mg, 0.111 mmol) are
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51 suspended in a CH_3CN/DMF (4 mL, 3:1 v:v) solution. The mixture is heated under
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53 solvothermal conditions according to the ramp described in the Materials and Methods
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3 section, producing colourless crystals of **4** (Yield 47%). Anal. Calc. for $C_9H_6CuI_2N_6$ (%): C,
4 31.64; H, 1.77; N, 24.60. Found: C, 31.55; H, 1.73; N, 24.44.
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8 **2.6. Synthesis of 2D [CuIL]_n (5)**

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10 **5** is obtained as a by-product in the synthesis of compound **7** (Section 2.8 and Scheme 2).
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12 Single crystals of **5** suitable for X-ray diffraction analysis are manually separated.
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15 **2.7. Synthesis of 3D [CuCIL]_n (6)**

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17 In a Teflon beaker, solid CuCl (10 mg, 0.101 mmol) and **L** (20 mg, 0.101 mmol) are added
18
19 to CH_3CN (3 mL) and DMF (1 mL). The mixture is then heated under solvothermal
20
21 conditions according to the ramp described in the Materials and Methods section. **6** is formed
22
23 as either amber/brown single crystals, or beige powders (PXRD evidences) directly in the
24
25 Teflon beaker (Yield 70%). Alternatively, **6** can be obtained by solvothermal reaction of CuI
26
27 or CuBr with **L** by using CH_2Cl_2 (1 mL), CH_3CN (2 mL) and DMF (1 mL) as solvent mixture.
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31 Anal. Calc. for $C_9H_6CuI_2N_6$ (%): C, 36.74; H, 2.04; N, 28.28. Found: C, 36.43; H, 2.18; N,
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33 27.54.
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39 **2.8. Synthesis of 3D {[Cu₃L₄]I₃}_n (7)**

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41 Solid $Cu(BF_4)_2 \cdot xH_2O$ (12 mg, 0.051 mmol, calculated based on the anhydrous salt formula),
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43 KI (9 mg, 0.054 mmol), and **L** (10 mg, 0.051 mmol) are placed in a Teflon beaker and suspended
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45 in CH_3CN (3 mL). The mixture is heated at 70 - 72 °C upon stirring on an electric hob for 20
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47 min, giving a light brown solution which is filtered. After few weeks at room temperature, the
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49 formation of colorless crystals of **7** with the shape of truncated trigonal pyramid (Figure S1) is
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51 observed. Upon gradual evaporation of the mother liquor, colorless crystals of different shape
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3 and identified by single crystal X-ray analysis as **5** are found in the same beaker. Anal. Calc. for
4 $C_9H_6CuI_2N_6$ (%): C, 31.70; H, 1.77; N, 24.65. Found: C, 32.60; H, 1.98; N, 25.43.
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7 **2.9 Crystallographic Studies**

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10 Diffraction measurements for **1**, **6** (150 K), **2-4** (293 K) and **7** (100 K) are run on a Bruker
11 SMART APEX-II CCD area-detector diffractometer equipped with a Mo X-ray tube, a graphite
12 monochromator and an Oxford Cryosystems Cryostream 700Plus cryostat. X-ray diffraction data
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14 for compounds **5** and **7** (293 K) are collected on an Xcalibur E diffractometer equipped with a
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16 CCD area detector, a Mo X-ray tube and a graphite monochromator. Final unit cell dimensions
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18 are obtained and refined on an entire data set. The intensities are corrected for Lorentz and
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20 polarization effects as well as for empirical absorption based on the multi-scan technique. The
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22 structures are solved by direct methods and refined by full-matrix least-squares fitting on F^2 with
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24 the programs SHELXS97 and SHELXL2014/2016, respectively.^{17,18} Non-hydrogen atoms, apart
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26 iodide ions in compound **7**, are refined anisotropically. All hydrogen atoms are placed in
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28 geometrically calculated positions and subsequently refined using a riding model. In compound
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30 **7**, the iodide anions are found from a difference Fourier map as disordered in different
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32 positions and have been refined isotropically with a combined occupancy to provide the
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34 charge balance. Low temperature X-ray diffraction does not allow to significantly improve
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36 the description of the iodide anions. The accessible empty volume in **7** is calculated by the
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38 software PLATON.¹⁹ The figures have been produced using the softwares Mercury²⁰ and
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3. RESULTS AND DISCUSSION

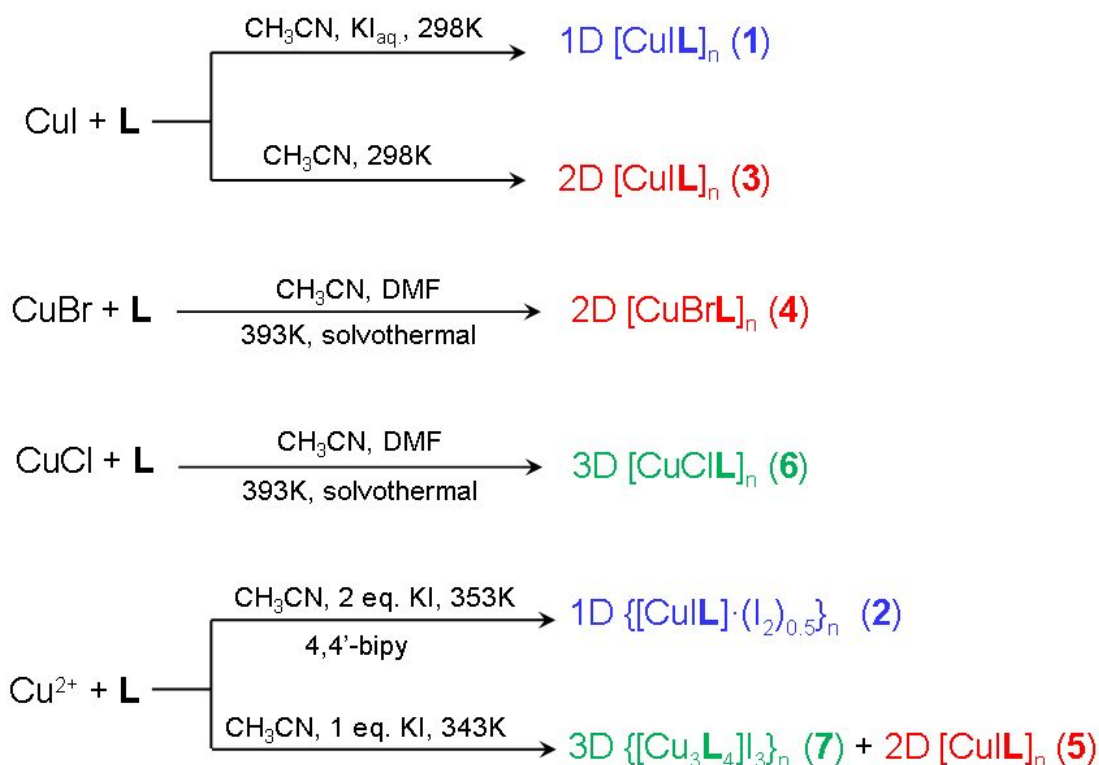
3.1. Synthesis

Since the d^{10} electronic configuration of Cu(I) enforces no stereochemical demands, the coordination sphere of this metal ion (normally four-coordinate) is largely determined by electrostatic and steric requirements. Furthermore, Cu(I) complexes in solution are quite labile to ligand substitution. This means that, when dealing with the synthesis of Cu(I) compounds, slightly different procedures may lead to different derivatives. In addition, the use of ligands having three available coordination sites increases the number of possible structural motifs. For all these reasons, in the present study, various synthetic conditions aimed at obtaining selectively pure compounds have been tested.

By adding at room temperature an acetonitrile solution of **L** to a solution of CuI dissolved in saturated aqueous KI, the 1D double-stranded stair CP **1** is selectively obtained within few hours (Scheme 2). Interestingly, when CuI is dissolved in acetonitrile, crystals of the 2D derivative **3** can be isolated in mixture with **1** after few months. On the contrary, by thermal-assisted *in situ* reduction of an acetonitrile solution of a Cu(II) salt in the presence of excess KI and 4,4'-bipyridine as template,²² the 1D compound **2**, containing clathrated iodine, is obtained. Attempts to obtain **2** by reaction of CuI with **L** in the presence of iodine were unsuccessful. By the same *in situ* reduction of Cu(II) in the presence of stoichiometric KI and in the absence of template, compound **7** can be obtained as small, colorless crystals with the habitus of truncated trigonal pyramid (Figure S1) contaminated by colorless prismatic crystals of **5**.

By solvothermal reaction at 120 °C for 36 h of a suspension of CuBr and **L** in a CH₃CN/DMF solution, the 2D derivative **4** is obtained. When CuCl is reacted under the same solvothermal conditions, the 3D network [CuCl(**L**)]_n **6** is isolated. However, an unidentified microcrystalline

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3 powder is obtained when the same solvothermal reaction is performed using CuI as starting
4 material. On the other hand, when dichloromethane is added to the solvent mixture
5 (CH₃CN/DMF/CH₂Cl₂), compound **6** is isolated by using either CuI or CuBr as starting
6 materials. In these cases, the chloride anion is abstracted from CH₂Cl₂ by reductive
7 dechlorination.²³ To check the purity of compounds **1-7**, powder X-ray diffraction patterns are
8 collected on the synthesized bulk materials and compared with those calculated from the crystal
9 structure, except for **5** that is isolated only in very low amount (see Figs. S2-S7). A good
10 agreement is found for all compounds, apart **2**, which is obtained as dark crystals contaminated
11 by a white powder, despite many attempts to synthesize pure crystals. The obtained materials are
12 also characterized by FT-IR spectroscopy (Figs S8-S14) and thermogravimetric analysis (Fig.
13 S15), showing decomposition temperatures in the range 200-240 °C.
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Scheme 2. Synthetic pathways to isolate the reported compounds.

3.2. Crystal Structure Analysis

For all the compounds, main crystallographic data and selected bond distances and angles are reported in Tables S1 and S2, respectively.

3.2.1. 1D Coordination Polymers: $[\text{CuI}\mathbf{L}]_n$ (1) and $\{[\text{CuI}(\mathbf{L})] \cdot (\text{I}_2)_{0.5}\}_n$ (2)

Single-crystal X-ray diffraction analysis reveals that **1** shows the quite common 1D double-stranded stair motif of $[\text{CuI}]_n$ composition. **1** crystallizes in the monoclinic $P2_1/c$ space group (Table S1). The asymmetric unit contains one **L** molecule, one copper(I) ion and one iodide ion.



Figure 1. Representation of the crystal structure of **1**: (a) The coordination sphere of the Cu(I) ion, with partial labeling scheme. Ellipsoids are represented at 50% probability level. Symmetry codes: #1: $-x, \frac{1}{2}+y, \frac{1}{2}-z$; #2: $-x, y-\frac{1}{2}, \frac{1}{2}-z$. (b) Portion of the double-stranded stair motif running along the [010] crystallographic direction. (c) Portion of the crystal packing viewed in perspective along the c -axis. In (b) and (c) the hydrogen atoms are omitted for clarity.

Cu(I) shows a CuI_3N distorted tetrahedral environment (Figure 1a) defined by one of the nitrogen atoms of **L** (N1) and three μ_3 -iodide ions that adopt a distorted trigonal pyramidal geometry [Cu-I: 2.6107(5), 2.7231(4), 2.7716(5) Å and Cu-N: 2.0284(19) Å; the bond angles around copper(I) are in the range 99.16(6)°-129.41(6)°; see Table S2]. The geometrical parameters are in agreement with those reported in the literature for similar structures.^{4,24-27}

The μ_3 -iodide ions generate a $[\text{CuI}]_n$ double-stranded stair decorated on both sides by dangling **L** ligands (Figure 1b). Along the stair, the Cu...Cu nearest neighbor distance is 3.2479(7) Å, longer than the sum of van der Waals radii of Cu(I) ions (2.80 Å),²⁸ indicating no interaction between the metal centers. The dihedral angle between adjacent Cu_2I_2 planar units along the stair is 63.3°. The ligands are tilted with respect to the propagation direction of the stair (the crystallographic b -axis) by 45.3°. On the two sides of the stair, coordinated **L**

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3 ligands stack parallel with a distance of 3.1730(6) Å between their mean planes and a
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5 distance of 4.5090(13) Å between the triazinic centroids. The two columns of L ligands on
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7 the same stair are almost orthogonal to each other, with an angle between the mean planes of
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9 adjacent ligands of different columns of 89.4°. In accordance with the presence of a two-fold
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11 screw axis running along the crystallographic *b*-axis, the arrangement of the L ligands
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13 produces a helical stair with a pitch of 4.5090(6) Å. Adjacent stairs show opposite
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15 handedness, this resulting into a centrosymmetric packing (see Figure 1c). Weak inter-stair
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17 C-H...N intermolecular interactions (3.287, 3.499 Å) involving the uncoordinated nitrogen
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19 atoms of L from adjacent stairs are present. No inter-stair π - π interactions are found.
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27 Compound **2** is obtained by a redox reaction between copper(II) and iodide in the
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29 presence of 4,4'-bipyridine as the template, as described in Section 2.3. To the best of our
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31 knowledge, despite the rich family of 1D double-stranded stairs, there is only one iodine
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33 clathrate [CuI]_n stair analogous to **2**, that, remarkably, was obtained by a similar redox
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35 reaction.²⁹ **2** crystallizes in the triclinic *P*-1 space group (Table S1). The asymmetric unit
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37 contains one Cu(I) ion, one L ligand, one iodide ion and half of an iodine molecule. An Ortep
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39 view of a portion of the crystal structure is shown in Figure 2a. Compound **2** contains a
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41 double-stranded stair motif (Figure 2b) similar to that of **1**. The intra-ladder Cu...Cu nearest
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43 neighbour distances amount to 2.8336(8) Å, close to the sum of the van der Waals radii of
44
45 copper, and 3.6159(9) Å. The ladders run along *a* with a dihedral angle between consecutive
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47 Cu₂I₂ units of 68.2° and a tilt angle for L equal to 81.9° (N-Cu...Cu angle along the *a*-axis).
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51 Furthermore, in **2** dangling ligands on both sides of the ladder are parallel [with distances
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between mean planes and triazinic centroids of 3.1976(9) and 4.2910(9) Å, respectively]. Nearby ladders are connected through $\mu_3\text{-I}\cdots\text{I}_2$ interactions [3.4106(7) Å] generating supramolecular 2D layers (see Figure 2c).

A search in the Cambridge Structural Database (CSD Ver. 5.40 Nov. 2018) for copper(I) iodide compounds showing the 1D double-stranded stair motif found in **1** and **2** produced a list of 48 structures, which are reported, with the relative intrachain Cu \cdots Cu distances, in Table S3. Cu \cdots Cu distances less than the sum of vdW radius of copper (2.80 Å)⁴² are considered important for the optical and electrical properties of 1D polymeric structures,¹² and the range of values found for this parameter, among the 48 structures analysed, extends for more than 1 Å, being comprised between 2.674 and 3.776 Å.

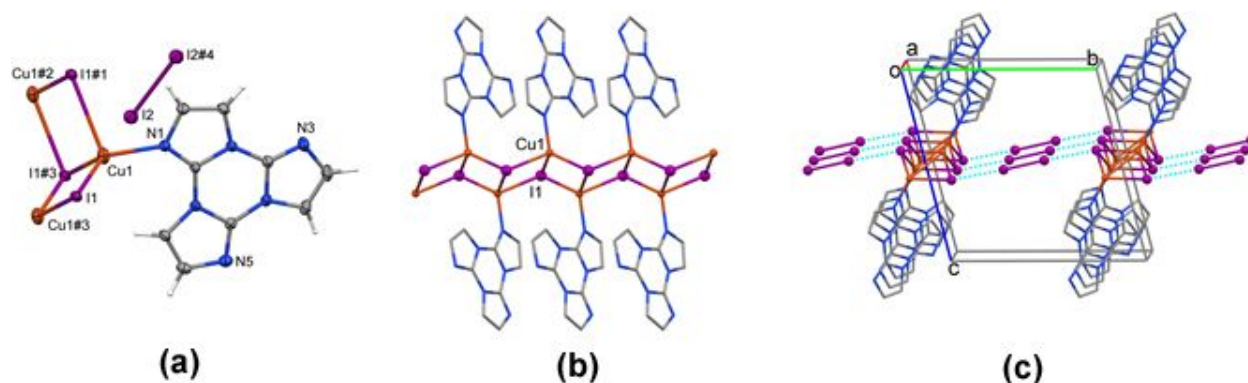
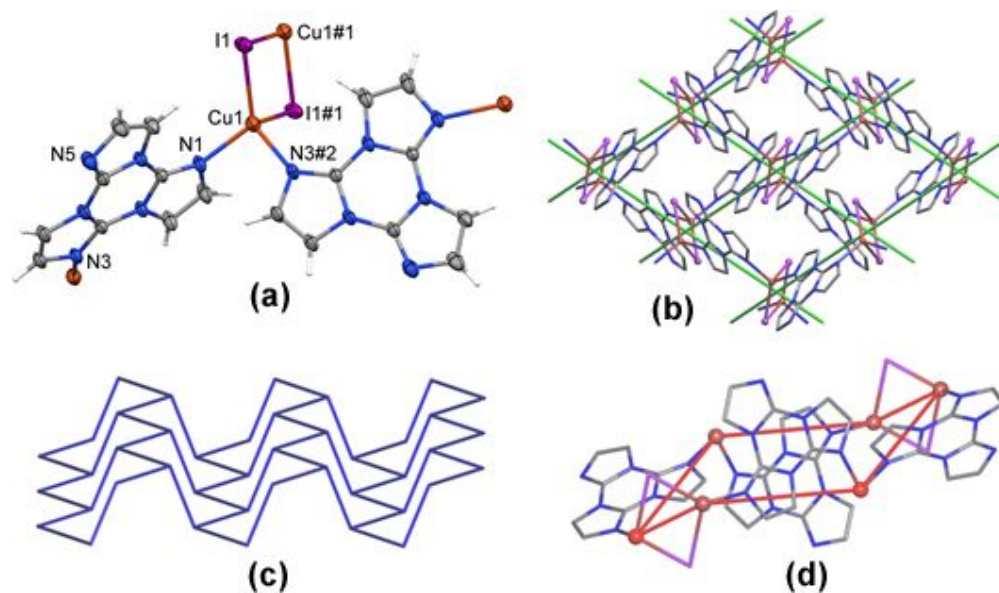


Figure 2. Representation of the crystal structure of **2**: (a) Portion of the crystal structure showing the coordination sphere of copper(I), with partial labeling scheme. Ellipsoids are represented at 50% probability level. Symmetry codes: #1: $1-x; y; z$; #2: $-x-1; 2-y; 1-z$; #3: $-x; 2-y; 1-z$; #4: $-x; 1-y; 1-z$. (b) Portion of the double-stranded stair running along the [100] crystallographic direction. (c) Portion of the crystal packing viewed in perspective along the crystallographic a -axis. The short $\text{I}\cdots\text{I}_2$ contacts are represented with dashed cyan lines. In (b) and (c) the hydrogen atoms have been omitted for clarity.

3.2.2. 2D Coordination Polymers: [CuIL]_n (**3**), [CuBrL]_n (**4**) and [CuIL]_n (**5**)

Single crystal X-ray diffraction structure determination reveals that compounds **3** and **4** are isomorphous and show a 2D polymeric motif in which **L** behaves as a μ_2, κ^2 -bridging ligand. The two compounds crystallize in the monoclinic $P2_1/n$ space group (Table S1). The asymmetric unit contains one **L** spacer and one CuX (X = Br, I) unit (Figure 3a). The two crystal structures are characterized by the presence of Cu₂(μ -X)₂ dimeric units which are connected by μ -L spacers to give 2D corrugated layers.³⁰ The copper(I) ions are in a distorted tetrahedral environment of the type CuX₂N₂, being coordinated to two halogen atoms [Cu1-Br = 2.3990(14), 2.6076(8) Å; Cu1-I = 2.5687(15), 2.7531(8) Å] and to two nitrogen atoms of two linkers **L** [Cu1-N1 = 2.0821(13), 2.0757(16) Å; Cu1-N3 = 2.0778(15), 2.0598(19) Å, for **3** and **4**, respectively]. Within a single layer, the **L** molecules adopt two different orientations, with a dihedral angle of 64.03° in **3** and 63.98° in **4** (Figure 3b). Each Cu₂(μ -X)₂ unit is connected to four others through four bridging **L** ligands. The layers show a thickness, that is the distance between parallel planes passing through the external hydrogen atoms, of 9.635 Å and 9.185 Å in **3** and **4**, respectively. The layers stack parallel along the [-101] crystallographic direction in ABAB fashion, but are superimposed along the [001] crystallographic direction. From a topological point of view, if the copper atoms are considered as nodes the resulting topology is **hcb** (Figure 3c), resembling that of black phosphorous (chair conformation of the hexagonal windows, Figure 3d). The Cu...Cu edges of the **hcb** net in **3** are equal to 3.324(2) Å (supported by μ -X) and 7.665(5) Å (supported by μ -**L**). In **4** the same distances are equal to 3.106(2) and 7.658(5) Å, respectively. Alternatively,

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3 if the barycenter of the $\text{Cu}_2(\mu\text{-X})_2$ units is taken as nodes the resulting topology is **sql**, with
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5 rhombic windows of edges 8.129 Å long (Figure 3b). Adjacent layers are interconnected
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7 through π - π interactions between **L** molecules with interplanar separations and distances
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9 between the triazinic centroids of 3.3505(4) and 4.458(3) Å for **3** and 3.3497(5) and 4.381(3)
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11 Å for **4**.
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38 **Figure 3.** Representation of the crystal structure of **3** (at the drawing level, the crystal
39 structure of **4** is comparable): (a) Portion of the crystal structure, showing the coordination
40 sphere of Cu1 with partial labeling scheme. Ellipsoids have been represented at 50%
41 probability level. Symmetry codes: #1: $1-x, -y, -z$; #2: $x-1/2, 1/2-y, z-1/2$. (b) Portion of a single
42 layer viewed along the c -axis showing the underlying **sql** net (green). (c) Simplified view of
43 portion of the **hcb** layer. (d) A single hexagonal window (in chair conformation) within a
44 layer. In (b) and (d) the hydrogen atoms have been omitted for clarity.
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49 The crystal structure of **5** reveals a 2D polymeric motif different from that of **3** and **4**. Indeed,
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51 $\text{Cu}_2(\mu\text{-X})_2$ units are present in **3** and **4**, while **5** contains $\text{Cu}_2(\mu\text{-X})$ fragments that give chiral
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53 layers through μ_2 -bridging linkers. **5** crystallizes in the orthorhombic *Pbca* space group (Table
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S1). The asymmetric unit contains one CuI unit and one L molecule (see Figure 4a). The copper(I) ions are in a distorted CuI_2N_2 tetrahedral environment (Figure 4a), being coordinated to bridging iodides and L spacers with Cu-I distances equal to 2.5588(5) and 2.7460(5) Å, and Cu-N distances equal to 2.074(3) and 2.084(3) Å (Table S2). The layer comprises $(\text{CuI})_n$ helical chains running along the *a*-axis, with a Cu...Cu closest distance of 4.5191(6) Å between neighboring Cu atoms separated by I atoms, and a helical pitch of 7.3349(4) Å, equal to the value of the *a*-axis. The bridging L ligands connect the inorganic chains along the crystallographic *b*-axis, with a Cu...Cu separation of 7.6428(9) Å (Figure 4b). The ligands at the same metal center are tilted by an angle of 75.25°. Similarly, to **3** and **4**, the layer topology may be described as **sql** (Figure 4c). The layers, 9.577 Å thick, pack in antiparallel mode along the *c*-axis. Stacking interactions are found between L ligands belonging to neighboring layers with interplanar distance of 3.3581(9) Å and distances between the triazinic centroids of 4.4743(18) Å.

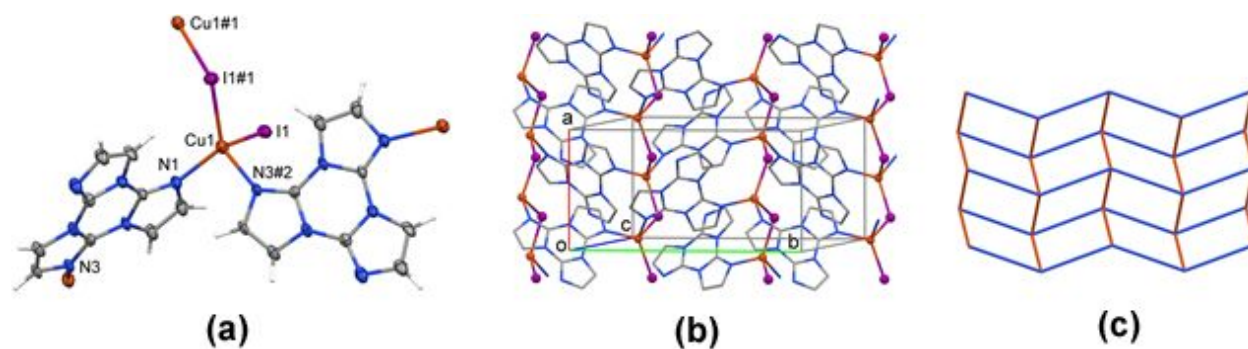


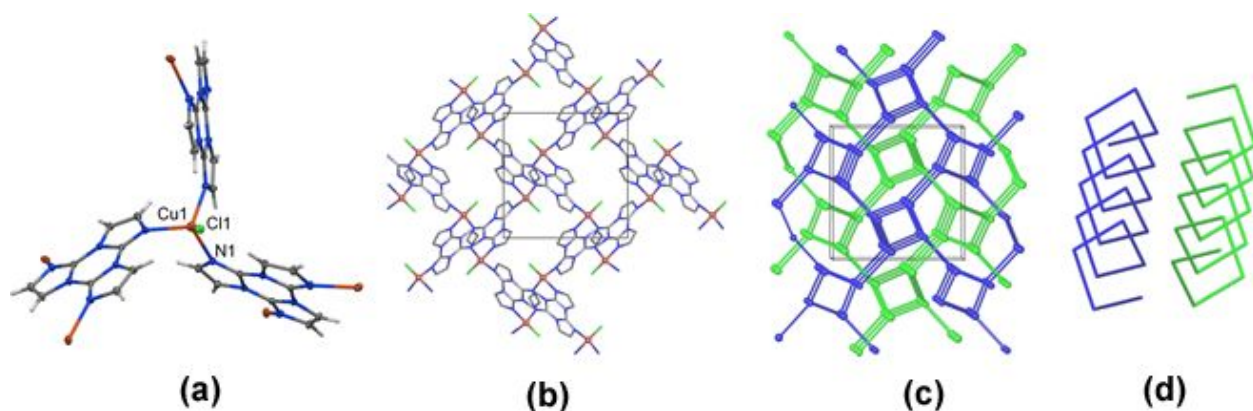
Figure 4. Representation of the crystal structure of **5**: (a) Portion of the crystal structure showing the coordination sphere of Cu1 with partial labeling scheme. Ellipsoids have been represented at 50% probability level. Symmetry codes: #1: $\frac{1}{2}+x$; y ; $\frac{1}{2}-z$; #2: $\frac{1}{2}-x$; $\frac{1}{2}+y$; z . (b) Portion of a 2D layer viewed in perspective along the *c*-axis. (c) Simplified view of portion of the **sql** layer. In (b) the hydrogen atoms have been omitted for clarity.

3.2.3. 3D Coordination Polymers: [CuClL]_n (6) and {[Cu₃L₄]I₃}_n (7)

The crystal structure of **6** belongs to the cubic *Pa*-3 space group, and the asymmetric unit contains one third of **L** and one third of copper and chlorine atoms, all residing on three-fold rotation axes. **L** serves as μ_3 -bridge and coordinates to Cu(I) metal centers through all three nitrogen atoms (Figure 5a), resulting in a 3D network (Figure 5b). Copper(I) ions are in a distorted tetrahedral environment of the CuClN₃ type, being coordinated to the nitrogen atoms of three μ_3 -**L** [Cu-N1 2.1295(13) Å] and a terminal chloride [Cu-Cl1 2.2567(10) Å]. An analysis of the crystal structure reveals that the resulting network is 3-connected with the chiral **srs** (SrSi₂) topology. Both copper(I) ions and μ_3 -**L** spacers act as the 3-connected nodes of the network. To fill the large cavities of the framework, a second identical network is entangled to the first one, to give an overall two-fold interpenetrate structure of class IIa, where the two networks are related by a center of inversion (Figure 5c).^{31,32} The **srs** net is one of the prototypical net characterized by the presence of helical motifs connected to each other. It is a chiral network with helices having the same helicity. The resulting two-fold array is achiral, being formed by two single **srs** nets of opposite chirality (related by a center of inversion) (Figure 5c,d). The interpenetrated framework does not show empty volume. The shortest Cu...Cu separations between copper(I) ions of the same and different nets are 7.814(3) and 6.398(3) Å, respectively. The interpenetrated networks reveal face to face stacking interactions between center-of-symmetry-related ligands, with interplanar separation of 3.3135(3) Å and distance between the triazinic centroids of 3.2892(15) Å. Thermogravimetric analysis (TGA) shows that **6** is stable up to about 240 °C and start to

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3 decompose losing 66% of weight up to 390 °C, probably due to the loss of **L**, leaving 33% of
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6 CuCl as residue (calc. 33.3 %) (Fig. S15).
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9 A search in the ToposPro²¹ database (TTD) for known examples of MOFs with the **srs**
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11 topology gave a list of more than 500 structures, 67 of which contain copper and 20, in
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13 particular, Cu(I) ions (see Table S4). Among these latter 20 structures, five contain ligands
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15 with a triazinic core similar to **L** (DEJGIJ,³³ SADLIT,³² SAQSAF,³⁴ SAQSEJ,³⁴ SAQSIN³⁴) and
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17 one a three donor imidazol ligand (MOXKOA)³⁵.
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44 **Figure 5.** Representation of the crystal structure of **6**: (a) Portion of the crystal structure showing
45 the coordination sphere of Cu1, with partial labeling scheme. Ellipsoids have been represented at
46 50% probability level. (b) Portion of a single 3-connected 3D network of **srs** topology. (c, d)
47 Simplified view showing two-fold interpenetration of two **srs** networks of opposite chirality. In
48 (b) the hydrogen atoms have been omitted for clarity.
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52 Compound **7** crystallizes in the cubic space group $F-43c$ (Table S1). The asymmetric unit
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54 contains one quarter of Cu(I) atom, one third of **L** linker, and one quarter of iodide anion, since
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3 Cu(I) and I⁻ reside on a four-fold rotation axis and L on a three-fold one. The iodide anions are
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5 strongly disordered and, despite an X-ray data collection performed at 100 K, it has not been
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7 possible to individuate a unique position in the crystal structure. The Cu(I) ion shows a
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9 tetrahedral CuN₄ coordination with a Cu-N distance of 2.065(6) Å (Figure 6a). The
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11 coordination positions are all occupied by L ligands, differently from the previous compounds
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13 where the halide anions are involved in the coordination to copper(I). In contrast to **6**, the
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15 copper(I) ions in **7** act as 4-connected nodes, while L acts as a 3-connected one in both
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17 networks. In **7**, the resulting crystal structure is a 3D network with a (3,4)-connected
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19 topology of **bor** type,³⁶ which combines tetrahedral and triangular building blocks (Figure 6b,
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21 c).³⁷ This interesting topology is quite uncommon among MOF structures and only 14
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23 examples have been found in the ToposPro database (TTD), which show 7 single and 7 2-fold
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25 interpenetrated nets. Among the 14 structures, listed in Table S5, 4 contain ligands that have
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27 similarities with L, being 1,3,5-triazine substituted molecules (FEWWUB,³⁸ TOYLOT³⁹ and
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29 WUHHEN⁴⁰) and 1,3,5-tris(1-imidazolyl)benzene (XILLEL).⁴¹
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40 The cationic 3D network of **7** possesses two types of cavities with diameter of *ca* 5.4 Å and
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42 11.0 Å (taking into account the van der Waals radii of the atoms decorating the cavities
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44 walls), which provide a total potential solvent/anion accessible volume of 3959 Å³ (40%,
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46 Figure 6d). The bigger cavities are interconnected by channels with a diameter of at least 2.6
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48 Å (Figure 6d). The iodide anions are disordered in these cavities, whose size is bigger than
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50 the van der Waals radius of iodine (2.20 Å).⁴²
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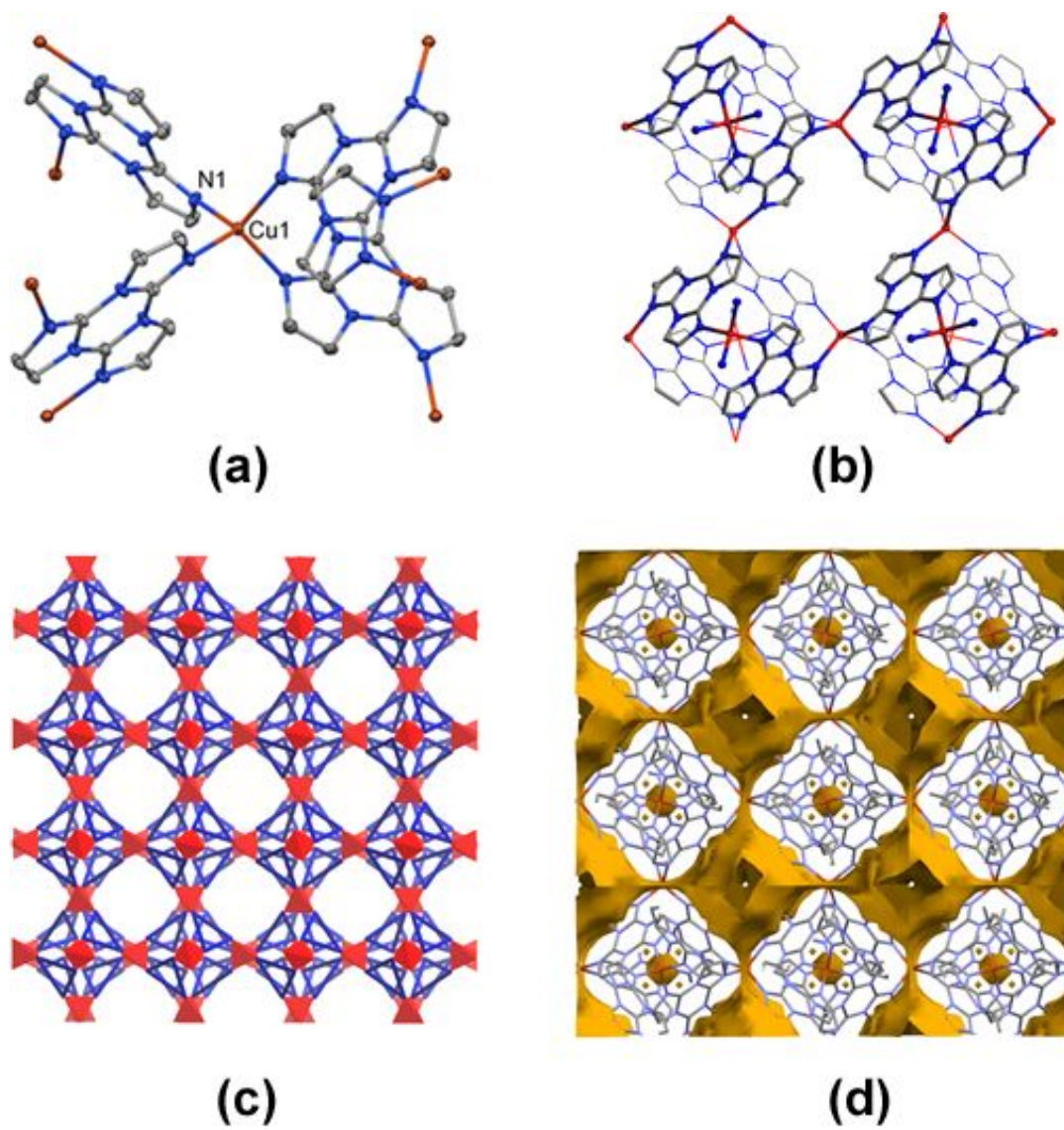
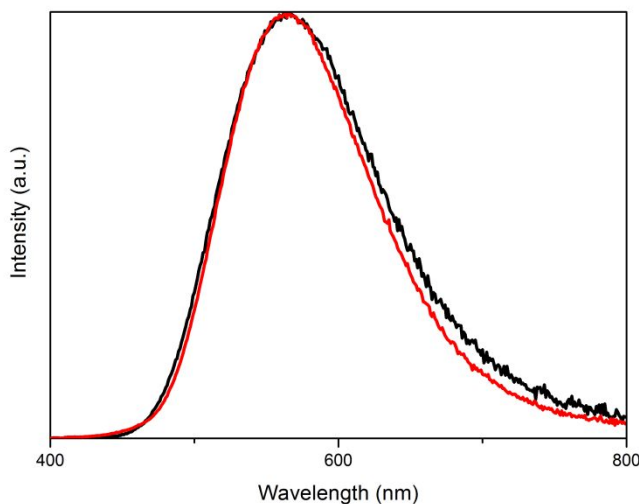


Figure 6. Representation of the crystal structure of **7**: (a) Portion of the crystal structure, showing the coordination sphere of copper(I), with partial labelling scheme. The thermal ellipsoids have been represented at 30% probability level. (b) Portion of the 3D network. (c) The tetrahedral and triangular building blocks of the **bor** topology. (d) Potential solvent/anion accessible volume. In (a), (b) and (d) the hydrogen atoms have been omitted for clarity.

3.3. Photoluminescent and NLO behavior

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3 Although all compounds, except for **2**, XRPD and EA analyses show a good degree of
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6 purity, only **1** and **6** could be isolated with the high purity grade required for
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9 photoluminescence characterization.

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11 Crystals of compound **1** display, at room temperature, an unresolved emission at 568 nm
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13 ($\tau = 31.02 \mu\text{s}$, see SI) which is only very slightly blue-shifted ($\lambda_{\text{em}} = 564 \text{ nm}$, $\tau = 47.14 \mu\text{s}$) at 77
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16 K (Figure 7). The long lifetimes, the absence of vibrational structure, the long Cu...Cu nearest
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19 neighbor distance in the crystal structure [3.248 \AA , significantly longer than the sum of van
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22 der Waals radii of Cu(I) ions, 2.80 \AA] and the blue shift at low temperature point to a triplet

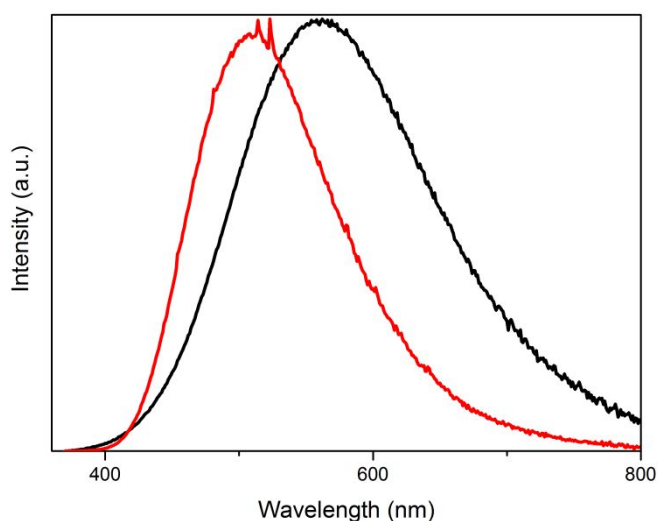


45 state of XLCT character at the origin of the emissive behavior of **1**.

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47 **Figure 7.** Normalized Emission spectra of crystals of **1** at 298 K (black solid line, $\lambda_{\text{exc}} = 300$
48 nm) and 77 K (red line, $\lambda_{\text{exc}} = 300 \text{ nm}$).
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52 A similar interpretation can be formulated for **6**, which displays a room temperature
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55 photoluminescent behavior (Figure 8) comparable to that of **1**, though characterized by a
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more complex and faster decay: an unresolved emission is observed at 560 nm, best fitted with a triexponential decay ($\tau_1 = 0.176 \mu\text{s}$, 13%; $\tau_2 = 1.41 \mu\text{s}$, 24%; $\tau_3 = 6.67 \mu\text{s}$, 63%, see SI).



However, differently from **1**, a more pronounced (47 nm) blue-shift is found going to 77 K ($\lambda_{\text{em}} = 513 \text{ nm}$), together with a large increase of the average lifetime (best fitted with a biexponential, $\tau_1 = 207 \mu\text{s}$, 99%; $\tau_2 = 3.78 \text{ ms}$, 1%, see SI).

Figure 8. Normalized emission spectra of crystals of **6** at 298 K (black solid line, $\lambda_{\text{exc}} = 350 \text{ nm}$) and 77 K (red line, $\lambda_{\text{exc}} = 350 \text{ nm}$).

Among all compounds, only **7** crystallizes in a non-centrosymmetric space group, the necessary requirement to observe non-zero second order nonlinear optical (NLO) properties in the solid state.⁴³ Its second harmonic generation (SHG) response, measured by the Kurtz–Perry technique working at 1907 nm, results in 10 times that of the standard sucrose.

4. Conclusions

The versatility of cyclic triimidazole **L** as potential ligand to build up coordination polymers is here explored for the first time. Seven new Cu(I) CPs have been prepared and structurally characterized, ranging from 1D chains to 3D coordination networks in which **L** is either monodentate or bi- and tridentate bridging. The reported structures comprise two 1D double-stranded stairs, **1** and **2**, that enrich the large family of Cu(I) 1D compounds with potentially interesting physical properties. Inside this family, compound **2** is the second reported example of iodine clathrate derivative. Among the three 2D derivatives **3-5**, **5** is particularly interesting due to the chiral nature of its layers which, however, pack in a centrosymmetric arrangement. Similarly, compound **6** contains chiral **srs** nets that give an achiral framework through two-fold interpenetration of nets of opposite chirality. The only non-centrosymmetric derivative, **7**, which shows a 3D net of **bor** topology, gives an SHG response 10 times that of the standard sucrose. The versatility of the Cu(I)/**L** pair is further demonstrated by the observation that CPs **1**, **3** and **5** are supramolecular isomers.^{44,45} Photophysical measurements on compounds **1** and **6** reveal a room temperature phosphorescence in the 510-565 nm range, imputable to ³XLCT transitions.

ASSOCIATED CONTENT

Supporting Information

1
2
3 Experimental section describing the photoluminescence properties measurement. Images of
4 selected single crystals of **7** (Figure S1). Powder X-ray diffraction patterns of compounds **1-7**
5 (Figures S2-S7), IR spectra of **L** and compounds **1-7** (Figures S8-14) and TGA traces of
6 compounds **3, 4, 6** and **7** (Figure S15). Photophysical characterization results (Figures S16-S21).
7 Main crystallographic data and crystal structure determination details for **1-7** (Table S1). Main
8 bond distances and angles in the crystal structures of **1-7** (Table S2). Analyses of structures
9 extracted from CSD showing $[\text{Cu}_2\text{I}_2]_n$ a double stranded 1D motif (Table S3), Cu(I) based **srs**
10 topology (Table S4) and **bor** topology (Table S5). The Supporting Information is available free
11 of charge on the ACS Publications website at DOI: [10.1021/acs.cgd.XXXX](https://doi.org/10.1021/acs.cgd.XXXX). Cif files for **1-7**
12 were deposited in the Cambridge Structural Database with CCDC deposition numbers 1858423-
13 1858430.
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Versatility of Cyclic Triimidazole to Assemble 1D, 2D and 3D Cu(I) Halide Coordination Networks

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Synopsis

1
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3 Seven novel Cu(I)-halide coordination polymers are successfully synthesized by exploiting
4 the structural versatility of the cyclic trimidazole ligand ($C_9H_6N_6$). Single-crystal X-ray
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9 diffraction reveals that the compounds display 1D, 2D and 3D coordination networks.

