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ARTICLE TYPE

# Luminescent [Cu<sub>4</sub>I<sub>4</sub>] Aggregates and [Cu<sub>3</sub>I<sub>3</sub>]-Cyclic Coordination Polymers Supported by Quinolyl-Triazoles

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Quinolyl-1,2,3-triazole ligand supported [Cu<sub>4</sub>I<sub>4</sub>] stair-step aggregates [Cu<sub>4</sub>I<sub>4</sub>(L1)<sub>2</sub>] (1), [Cu<sub>4</sub>I<sub>4</sub>(L2)<sub>2</sub>] (2), [Cu<sub>4</sub>I<sub>4</sub>(L3)<sub>2</sub>] (3), [Cu<sub>4</sub>I<sub>4</sub>(L4)<sub>2</sub>] (4), [Cu<sub>4</sub>I<sub>4</sub>(L5)<sub>2</sub>] (5), and six-membered [Cu<sub>3</sub>I<sub>3</sub>] metallacycle based coordination polymers [Cu<sub>2</sub>I<sub>2</sub>(L6)]<sub>n</sub> (6) and [Cu<sub>2</sub>I<sub>2</sub>(L7)]<sub>n</sub> (7) (ligands are 2-((1*H*-1,2,3-triazol-1-yl)methyl)quinoline (L1), 2-((4-alkyl-1*H*-1,2,3-triazol-1-yl)methyl)quinoline (propyl, butyl and isobutyl) for L2, L3 and L4, respectively) and 2-(1-((quinolin-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl)alcohol (methanol, ethanol and propanol for L5, L6 and L7, respectively) have been prepared and characterized by single-crystal x-ray diffraction (XRD), powder XRD, photoluminescence spectroscopy and thermogravimetric analysis. Complexes 1–5 are stair-step [Cu<sub>4</sub>I<sub>4</sub>] aggregate structures supported by two quinolyl-triazole hybrid ligands. Complexes 6 and 7 are rare cyclic [Cu<sub>3</sub>I<sub>3</sub>] aggregate-based 1-D coordination polymers. All ligands adopt a common tridentate-bridging coordination mode. These complexes are strongly luminescent with yellow emission (500–700 nm) in the solid state.

## Introduction

Transition metal luminescent complexes have been extensively investigated because of their promising emissive triplet excited states and potential applications in sensing, imaging, photo- and electroluminescent devices.<sup>1–6</sup> Luminescent Cu(I) complexes are especially attractive because the metal is cheaper than the precious metals, abundant and the resulting complexes give strong and tunable emissions. Copper(I) iodide complexes, in particular, demonstrate rich photochemical and photophysical behaviours which can be manipulated to some extent by different supporting ligands.<sup>7–13</sup> Nitrogen-heterocycles, phosphine and NHC-carbene ligands have been widely studied with this system.<sup>14–16</sup> Benefitting from the versatility of the copper-catalyzed azide-alkyne cycloaddition (CuAAC) reactions,<sup>17–21</sup> a range of 1,4-disubstituted-1,2,3-triazoles with adjustable electronic and steric properties have been developed for different applications including catalysis and functional molecular assemblies.<sup>22–27</sup> We have used the CuAAC reactions to synthesize pyridine, pyrazole and benzotriazole functionalized 1,2,3-triazole ligands for the preparation of chiral, magnetic and luminescent coordination complexes.<sup>28–33</sup> We herein report seven quinoline substituted 1,2,3-triazoles (L1–L7) with flexible substituent groups and the corresponding copper(I) iodide complexes 1–7. (Scheme 1) These luminescent materials show stair-step [Cu<sub>4</sub>I<sub>4</sub>] clusters and a novel 1-D polymeric propagation of six-membered [Cu<sub>3</sub>I<sub>3</sub>] metallacycles.

&lt;&lt;Scheme 1 Here&gt;&gt;

**Scheme 1** The chemical structures and coordination modes of ligands L1–L7 in complexes 1–7.

## Experimental section

### General details

All starting chemicals were used as received. Elemental analyses were performed on a thermo electron corporation flash EA 1112 series analyzer. Infrared spectra were obtained on a Perkin Elmer Spectrum 2000 FT-IR spectrometer from samples in KBr disc. Electrospray ionization mass spectra (ESI-MS) were recorded in positive ion mode using a Shimadzu LCMS-IT-TOF mass spectrometer. NMR spectra were measured at room temperature using JEOL 500 MHz NMR spectrometer. Powder X-ray diffraction data were collected on a Bruker AXS GADDS X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). Thermogravimetric analyses (TGA) were carried out in an air stream using a TA Instruments TGA Q500 analyzer with a heating rate of 10 °C/min. Photoluminescence was measured using a Perkin Elmer LS55 luminescence spectrophotometer. During the luminescent measurements, an attenuator set at 1 % T was used for all the complexes 1–7 due to their strong solid-state emissions.

### General procedure for ligand synthesis

&lt;&lt;Scheme 2 Here&gt;&gt;

**Scheme 2** Synthetic routes to ligands via one-pot CuAAC click reactions.

*Sodium azide is potentially explosive. Only micro-scaled*

reactions may be performed, and all operations must be handled with necessary precautionary measures. 2-(Chloromethyl) quinoline hydrochloride (428 mg, 2 mmol), Na<sub>2</sub>CO<sub>3</sub> (210 mg, 2 mmol), NaN<sub>3</sub> (156 mg, 2.4 mmol), alkyne (4 mmol) and CuI (23 mg, 0.12 mmol) were placed in a reaction tube containing a mixed solvent CH<sub>3</sub>OH/H<sub>2</sub>O (1:1, 4 mL). The reaction was stirred at 50°C for 24 h on a MultiMax reactor. The alkynes, ethynyltrimethylsilane, 1-pentyne, 1-hexyne, 4-methyl-1-pentyne, propargyl alcohol, 3-butyn-1-ol and 4-pentyn-1-ol, were used in the synthesis of ligands L1–L7, respectively. (Scheme 2) After the reaction, the mixture was extracted three times with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered, concentrated and purified by column chromatography on silica. The structures of the ligands were confirmed by NMR spectroscopy and ESI-MS.

2-((1*H*-1,2,3-triazol-1-yl)methyl)quinoline (L1), C<sub>12</sub>H<sub>10</sub>N<sub>4</sub>, 210.24. Yield: 274 mg, 65%. ESI-MS (*m/z*, %): [L1+H]<sup>+</sup> (211, 100). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500.2 MHz) δ 8.20 and 8.18 (d, 1H, *J* = 9 Hz), 8.14 and 8.12 (d, 1H, *J* = 8 Hz), 7.84 and 7.82 (d, 1H, *J* = 9 Hz), 7.79–7.76 (m, 2H), 7.74 (s, 1H, triazole), 7.61–7.58 (m, 1H), 7.31 and 7.30 (d, 1H, *J* = 9 Hz) and 5.92 (s, 2H, quinolyl-CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.8 MHz) δ 154.4, 147.0, 138.6, 134.5, 130.8, 128.7, 127.9, 127.8, 127.6, 124.4 and 119.9 (quinolyl and triazole groups) and 55.7 (quinolyl-CH<sub>2</sub>-triazole).

2-[(4-Propyl-1*H*-1,2,3-triazol-1-yl)methyl]-quinoline (L2), C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>, 252.32. Yield: 363 mg, 72%. ESI-MS (*m/z*, %): [L2+H]<sup>+</sup> (253, 100). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500.2 MHz) δ 8.30 and 8.28 (d, 1H, *J* = 9 Hz), 8.01 and 7.99 (d, 1H, *J* = 9 Hz), 7.94 and 7.92 (d, 1H, *J* = 9 Hz), 7.79, 7.78 and 7.76 (t, 1H, *J* = 8 Hz), 7.67 (s, 1H, triazole), 7.63, 7.62 and 7.60 (t, 1H, *J* = 8 Hz), 7.31 and 7.29 (d, 1H, *J* = 9 Hz), 5.80 (s, 2H, quinolyl-CH<sub>2</sub>), 2.69, 2.68 and 2.66 (t, 2H, triazole-CH<sub>2</sub>-CH<sub>2</sub>, *J* = 8 Hz), 1.72–1.64 (m, 2H, triazole-CH<sub>2</sub>-CH<sub>2</sub>), 0.98–0.95 (m, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125.8 MHz) δ 156.8, 149.0, 148.5, 138.4, 131.0, 129.8, 128.9, 128.4, 127.8, 123.2, 120.6 and 118.3 (quinolyl and triazole groups), 56.5 (quinolyl-CH<sub>2</sub>-triazole), 28.2, 23.5 and 14.0 (propyl group).

2-[(4-Isobutyl-1*H*-1,2,3-triazol-1-yl)methyl]-quinoline (L4), C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>, 266.35. Yield: 359 mg, 67%. ESI-MS (*m/z*, %): [L4+H]<sup>+</sup> (267, 100). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500.2 MHz) δ 8.18 and 8.16 (d, 1H, *J* = 9 Hz), 8.12 and 8.10 (d, 1H, *J* = 8 Hz), 7.83 and 7.82 (d, 1H, *J* = 8 Hz), 7.78–7.75 (m, 1H), 7.59–7.56 (m, 1H), 7.45 (s, 1H, triazole), 7.27 and 7.25 (d, 1H, *J* = 9 Hz), 5.84 (s, 2H, quinolyl-CH<sub>2</sub>), 2.58 and 2.57 (d, 2H, triazole-CH<sub>2</sub>-CH, *J* = 7 Hz), 1.98–1.92 (m, 1H, triazole-CH<sub>2</sub>-CH), 0.91 (s, 3H, CH<sub>3</sub>) and 0.90 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.8 MHz) δ 154.8, 148.1, 146.9, 138.5, 130.7, 128.7, 127.9, 127.7, 127.5, 122.1 and 119.8 (quinolyl and triazole groups), 55.7 (quinolyl-CH<sub>2</sub>-triazole), 34.9, 28.8 and 22.4 (isobutyl group).

2-(1-((Quinolin-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl) propan-ol (L7), C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>O, 268.32. Yield: 399 mg, 74%. ESI-MS (*m/z*, %): [L7+H]<sup>+</sup> (269, 100). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500.2 MHz) δ 8.21 and 8.19 (d, 1H, *J* = 9 Hz), 8.14 and 8.12 (d, 1H, *J* = 9 Hz), 7.84 and 7.82 (d, 1H, *J* = 8 Hz), 7.79, 7.77 and 7.76 (t, 1H, *J* = 8 Hz), 7.60, 7.59 and 7.57 (t, 1H, *J* = 8 Hz), 7.54 (s, 1H, triazole), 7.33–7.30 (m, 1H), 5.84 (s, 2H, quinolyl-CH<sub>2</sub>), 3.69, 3.68 and 3.67 (t, 2H, CH<sub>2</sub>OH, *J* = 6 Hz), 2.83, 2.81 and 2.80 (t, 2H, triazole-CH<sub>2</sub>CH<sub>2</sub>, *J* = 7 Hz), 2.77 (b, 1H, OH), 1.93–1.88 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>OH). <sup>13</sup>C

NMR (CDCl<sub>3</sub>, 125.8 MHz) δ 154.5, 148.3, 146.7, 138.8, 130.9, 128.5, 127.9, 127.8, 127.6, 121.9 and 120.0 (quinolyl and triazole groups), 61.9 (CH<sub>2</sub>OH), 55.6 (quinolyl-CH<sub>2</sub>-triazole), 32.0 and 22.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH).

#### General procedure for the synthesis of the complexes

The complexes 1–7 were prepared by mixing a CH<sub>3</sub>CN solution (2 mL) of quinolyl-triazole ligand (L1–L7, 0.05 mmol) with a CH<sub>3</sub>CN solution (5 mL) of CuI (0.1 mmol, 19 mg) in a test tube. The tube was sealed and left to stand at room temperature affording the corresponding crystals of Cu(I) complexes 1–7 within two weeks.

[Cu<sub>4</sub>I<sub>4</sub>(L1)<sub>2</sub>] (1), yield: 18 mg, 60%. Anal. Calcd. for C<sub>24</sub>H<sub>20</sub>Cu<sub>4</sub>I<sub>4</sub>N<sub>8</sub> (1182.24): C, 24.38; H, 1.71; N, 9.48%. Found: C, 24.39; H, 1.71; N, 9.48%. Main IR bands (cm<sup>-1</sup>): 3123(m), 2989(m), 1649(m), 1620(m), 1594(m), 1508(m), 1470(m), 1420(m), 1380(m), 1337(m), 1301(m), 1277(m), 1237(m), 1209(m), 1161(m), 1128(m), 1080(m), 1024(m), 975(m), 906(m), 869(m), 828(m), 792(s), 766(s), 732(m), 630(m), 485(m) and 439(m). ESI-MS (*m/z*, %): [L1+H]<sup>+</sup> (211, 100) and [Cu(L1)<sub>2</sub>]<sup>+</sup> (483, 5).

[Cu<sub>4</sub>I<sub>4</sub>(L2)<sub>2</sub>] (2), yield: 16 mg, 50%. Anal. Calcd. for C<sub>30</sub>H<sub>32</sub>Cu<sub>4</sub>I<sub>4</sub>N<sub>8</sub> (1266.40): C, 28.45; H, 2.55; N, 8.85%. Found: C, 28.33; H, 2.53; N, 8.80%. Main IR bands (cm<sup>-1</sup>): 3132(m), 2954(m), 2929(m), 2867(m), 1594(m), 1538(m), 1507(m), 1460(m), 1412(m), 1377(m), 1314(m), 1213(m), 1140(m), 1051(m), 1023(m), 970(m), 945(m), 899(m), 868(m), 813(m), 778(s), 660(m), 620(m), 490(m) and 424(m). ESI-MS (*m/z*, %): [L2+H]<sup>+</sup> (253, 100), [Cu(L2)<sub>2</sub>]<sup>+</sup> (567, 37) and [Cu<sub>2</sub>I(L2)]<sup>+</sup> (507, 3).

[Cu<sub>4</sub>I<sub>4</sub>(L3)<sub>2</sub>] (3), yield: 18 mg, 55%. Anal. Calcd. for C<sub>32</sub>H<sub>36</sub>Cu<sub>4</sub>I<sub>4</sub>N<sub>8</sub> (1294.44): C, 29.69; H, 2.80; N, 8.66%. Found: C, 29.61; H, 2.73; N, 8.52%. Main IR bands (cm<sup>-1</sup>): 3135(m), 2961(m), 2930(m), 2861(m), 1595(m), 1540(m), 1508(m), 1459(m), 1418(m), 1377(m), 1312(m), 1213(m), 1141(m), 1057(m), 1022(m), 971(m), 945(m), 899(m), 872(m), 826(m), 778(s), 662(m), 621(m) and 491(m). ESI-MS (*m/z*, %): [L3+H]<sup>+</sup> (267, 100), [Cu(L3)<sub>2</sub>]<sup>+</sup> (595, 46) and [Cu<sub>2</sub>I(L3)]<sup>+</sup> (519, 6).

[Cu<sub>4</sub>I<sub>4</sub>(L4)<sub>2</sub>] (4), yield: 19 mg, 58%. Anal. Calcd. for C<sub>32</sub>H<sub>36</sub>Cu<sub>4</sub>I<sub>4</sub>N<sub>8</sub> (1294.44): C, 29.69; H, 2.80; N, 8.66%. Found: C, 29.66; H, 2.76; N, 8.61%. Main IR bands (cm<sup>-1</sup>): 3132(m), 2954(m), 2925(m), 2865(m), 1620(m), 1596(m), 1537(m), 1510(m), 1461(m), 1432(m), 1415(m), 1376(m), 1316(m), 1217(m), 1144(m), 1125(m), 1060(m), 973(m), 945(m), 900(m), 871(m), 829(m), 807(m), 777(s), 730(m), 655(m), 628(m), 491(m) and 427(m). ESI-MS (*m/z*, %): [L4+H]<sup>+</sup> (267, 100) and [Cu(L4)<sub>2</sub>]<sup>+</sup> (595, 18).

[Cu<sub>4</sub>I<sub>4</sub>(L5)<sub>2</sub>] (5), yield: 19 mg, 61%. Anal. Calcd. for C<sub>26</sub>H<sub>24</sub>Cu<sub>4</sub>I<sub>4</sub>N<sub>8</sub>O<sub>2</sub> (1242.30): C, 25.14; H, 1.95; N, 9.02%. Found: C, 25.12; H, 1.93; N, 9.15%. Main IR bands (cm<sup>-1</sup>): 3502(b, ν<sub>O-H</sub>), 3114(m), 3051(m), 2984(m), 2933(m), 1642(m), 1618(m), 1593(m), 1537(m), 1509(m), 1461(m), 1427(m), 1384(m), 1354(m), 1335(m), 1300(m), 1219(m), 1183(m), 1142(m), 1123(m), 1072(m), 1048(m), 1023(m), 975(m), 946(m), 906(m), 873(m), 824(m), 800(m), 785(s), 762(m), 728(m), 660(m), 628(m) and 494(m). ESI-MS (*m/z*, %): [L5+H]<sup>+</sup> (241, 100) and [Cu(L5)<sub>2</sub>]<sup>+</sup> (543, 5).

[Cu<sub>2</sub>I<sub>2</sub>(L6)]<sub>*n*</sub> (6), yield: 25 mg, 81%. Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>Cu<sub>2</sub>I<sub>2</sub>N<sub>4</sub>O (635.17): C, 26.47; H, 2.22; N, 8.82%. Found:

C, 26.48; H, 2.21; N, 8.90%. Main IR bands ( $\text{cm}^{-1}$ ): 3446(s),  $\nu_{\text{O-H}}$ , 3129(m), 3064(m), 2985(m), 2903(m), 2874(m), 1618(m), 1592(m), 1544(m), 1508(m), 1478(m), 1452(m), 1424(m), 1378(m), 1360(m), 1300(m), 1243(m), 1219(m), 1139(m), 1123(m), 1066(m), 1043(m), 1018(m), 978(m), 957(m), 898(m), 865(m), 839(m), 799(m), 774(s), 751(m), 730(m), 659(m), 627(m) and 485(m). ESI-MS ( $m/z$ , %):  $[\text{L6+H}]^+$  (255, 100) and  $[\text{Cu(L6)}_2]^+$  (571, 2).

$[\text{Cu}_2\text{I}_2(\text{L7})]_n$  (**7**), yield: 26 mg, 80%. Anal. Calcd. for  $\text{C}_{15}\text{H}_{16}\text{Cu}_2\text{I}_2\text{N}_4\text{O}$  (649.20): C, 27.75; H, 2.48; N, 8.63%. Found: C, 27.80; H, 2.45; N, 8.22%. Main IR bands ( $\text{cm}^{-1}$ ): 3460(s),  $\nu_{\text{O-H}}$ , 3114(m), 3062(m), 2904(m), 2879(m), 1648(m), 1620(m), 1592(m), 1544(m), 1509(m), 1452(m), 1424(m), 1379(m), 1347(m), 1310(m), 1268(m), 1238(m), 1219(m), 1152(m), 1123(m), 1074(m), 1062(m), 1039(m), 979(m), 910(m), 840(m), 804(m), 772(m), 728(m), 660(m), 628(m) and 486(m). ESI-MS ( $m/z$ , %):  $[\text{L7+H}]^+$  (269, 100) and  $[\text{Cu(L7)}_2]^+$  (599, 6).

### X-ray crystallography

**Table 1** Summary of crystallographic data for complexes **1–7**

Experimental reflections were collected with a Bruker AXS APEX II diffractometer equipped with a CCD area-detector using Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). (Table 1) The collecting frames of data, indexing reflection and determination of lattice parameters and polarization effects were performed with the Bruker SMART programs.<sup>34</sup> The integration of intensity of reflections and scaling was carried out using Bruker SAINT.<sup>34</sup> The empirical absorption correction was performed using SADABS.<sup>35</sup> The space group determination, structure solution and least-squares refinements on  $|F|^2$  were carried out with the Bruker SHELXL.<sup>36</sup> The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined isotropically. CCDC reference numbers: 1036540(**1**), 958911(**2**), 958912(**3**), 1036541(**4**), 1036542(**5**), 1036543(**6**) and 1036544(**7**).

## Results and discussion

### Synthesis and characterization

Ligands **L1–L7** were synthesized from one-pot CuAAC reactions. The Cu(I) complexes **1–7** were prepared by the reaction of the corresponding ligand (**L1–L7**) and CuI in  $\text{CH}_3\text{CN}$  solution. Powder samples were collected from filtration under vacuum and washed with  $\text{CH}_3\text{CN}$ , ethanol and diethyl ether. The identity and purity of the crystal and powder samples of complexes **1–7** were confirmed by single-crystal and powder XRD and microanalysis. The infrared spectroscopy of complexes **5–7** display characteristic vibrations for the O–H bond between 3446–3502  $\text{cm}^{-1}$ . All complexes were thermally stable below 200  $^\circ\text{C}$  in air.

### Crystal structures

Quinolyl-1,2,3-triazole ligands display a common tridentate-bridging mode in all of the complexes **1–7** using the quinolyl

nitrogen( $\text{N}_q$ ), the 2'- and 3'-triazole( $\text{N}_{\text{tri}}$ ) nitrogen atoms. The ligands **L1–L5** support  $[\text{Cu}_4\text{I}_4]$  stair-step aggregate structures in complexes **1–5** (Fig 1). Ligands **L6** and **L7** support six-membered  $[\text{Cu}_3\text{I}_3]$  aggregate-based 1-D structures in **6** and **7** (Figs 2 and 3). There are two crystallographically independent Cu(I) centers in the asymmetric units of the complexes **1–7**. The Cu1 center is coordinated by two bidentate N atoms from the  $\text{N}_q$  and 2'- $\text{N}_{\text{tri}}$  donors, one  $\mu_2$ -I and one  $\mu_3$ -I. The Cu2 center is coordinated by one 3'- $\text{N}_{\text{tri}}$  from the neighbouring ligand, one  $\mu_2$ -I and two  $\mu_3$ -I bridges. Both Cu(I) centers possess tetrahedral geometries with coordination environments of  $\text{Cu}(\text{N}_q\text{-}2'\text{-N}_{\text{tri}})\text{I}_2$  and  $\text{Cu}(3'\text{-N}_{\text{tri}})\text{I}_3$ , respectively.

$[\text{Cu}_4\text{I}_4]$  aggregate complexes **1–5** crystallize in the triclinic crystal system with a space group of  $P\bar{1}$ . Each  $[\text{Cu}_4\text{I}_4]$  stair-stepped core is supported by two tridentate-bridging ligands (**L1–L5**). The Cu1...Cu2 and Cu2...Cu2 distances are 2.65 and 2.86  $\text{\AA}$  in **1**, 2.67 and 2.99  $\text{\AA}$  in **2**, 2.71 and 3.07  $\text{\AA}$  in **3**, 2.60 and 3.00  $\text{\AA}$  in **4** and 2.64 and 2.95  $\text{\AA}$  in **5**. There are intermolecular  $\pi\cdots\pi$  stacking interactions between parallel quinolyl groups from neighbouring aggregates with average centroid-centroid distances of 3.9, 3.6, 3.7, 3.6 and 3.7  $\text{\AA}$  in complexes **1–5** respectively (Fig. 1). The shortest intermolecular Cu...Cu distances are 6.5, 6.1, 6.2, 6.4 and 7.1  $\text{\AA}$  in the lattices of complexes **1–5**, respectively.

<< Fig. 1 Here >>

**Fig. 1** Molecular structures of **1(a)**, **2(b)**, **3(c)**, **4(d)** and **5(e)** indicating intermolecular  $\pi\cdots\pi$  stacking interactions.

<< Fig. 2 Here >>

**Fig. 2** (a) Molecular structure of **6**. (b) Packing structure with H-bonding interactions. (only hydrogens involved in H-bonding are included)

<< Fig. 3 Here >>

**Fig. 3** (a) Molecular structure of **7**. (b) Packing structure with H-bonding interactions. (only hydrogens involved in H-bonding are included)

The six-membered  $[\text{Cu}_3\text{I}_3]$  based 1-D coordination polymers **6** and **7** crystallize in the monoclinic crystal system with space groups of  $P2_1/c$  and  $C2/c$ , respectively. Although their supporting ligands are similar to that of complex **5**, complexes **6** and **7** exhibit quite different structures and crystal systems. The cyclic  $[\text{Cu}_3\text{I}_3]$ -based polymer networks have Cu(I) centers that share corners *via*  $\mu_2$ -I and  $\mu_3$ -I to form extended 1-D chains (Scheme 1, Figs 2 and 3). The six-membered  $[\text{Cu}_3\text{I}_3]$  unit has a chair conformation and ligands sit on only one side of the  $[\text{Cu}_3\text{I}_3]_n$  chain in both **6** and **7**. This is a rare 1-D structural type among the reported copper-iodide networks.<sup>8,9,12</sup> The Cu–I bond lengths in the  $[\text{Cu}_3\text{I}_3]_n$  cycle are in the range 2.55–2.78  $\text{\AA}$  in **6** and 2.55–2.80  $\text{\AA}$  in **7**. The Cu...Cu distances within the six-membered cycles are 3.58, 3.80 and 4.23  $\text{\AA}$  in **6** and 3.60, 3.83 and 4.23  $\text{\AA}$  in **7**. These distances are longer than those (2.29–2.63  $\text{\AA}$  for Cu–Cl; 2.94, 3.30 and 3.84  $\text{\AA}$  for Cu...Cu) in a six-membered  $[\text{Cu}_3\text{Cl}_3]$



chair-ring based coordination polymer.<sup>37</sup> The angles of I–Cu–I are 107.8, 108.1, 108.3 and 116.1° in **6** and 107.0, 107.8, 108.6 and 115.2° in **7**. There are intermolecular O–H...I H-bonding interactions between the OH group and coordinated I ligands from neighboring chains in both the lattices of **6** (Fig 2b) and **7** (Fig 3b) (O...I and H...I distances 3.51, 2.70 Å and ∠OHI angle 163° for **6** and 3.54, 2.77 Å and 154° for **7**).

#### Powder XRD, TGA and photoluminescence

<< Fig. 4 Here >>

**Fig. 4** Powder XRD patterns of **1–7**. (T = theoretical profile referenced to the experimentally determined single-crystal XRD pattern; E = experimental data)

<< Fig. 5 Here >>

**Fig. 5** TGA curves of **1–7**.

The experimental powder X-ray diffraction patterns for complexes **1–7** show good agreement with their simulated patterns determined from single-crystal XRD experiments, supporting their phase purity (Fig. 4). Thermogravimetric analysis (TGA) curves from room temperature to 650°C are given in Fig. 5. Complexes **1–7** are stable in air to ~220°C (for **1** and **5**) and 200°C (for **2–4**, **6** and **7**), followed by steady declines until reaching residual weights at ~550, 590, 570, 530, 540, 540 and 510°C for complexes **1–7**, respectively.

The excitation spectra of ligands L1–L7 (Fig. 6) indicate main absorption peaks between 327–434 nm with maxima at ~343, 357, 388, 347, 347, 348 and 347 nm, respectively. These ligands display broad emission spectra between 360–550 nm with maxima at ~397, 455, 464, 398, 427, 419 and 424 nm which most likely originate from intramolecular  $\pi$ – $\pi^*$  transitions.

<< Fig. 6 Here >>

**Fig. 6** Solution excitation (dotted line) and emission (solid line) spectra of ligands L1–L7.

<< Fig. 7 Here >>

**Fig. 7** Solid state excitation (dotted line) and emission (solid line) spectra of complexes **1–7**.

The excitation spectra of complexes **1–7** (Fig. 7) display multiple absorption peaks between 315–420 nm with maxima at ~395 nm. They exhibit broad emissions between 500–700 nm with maxima at ~573, 543, 555, 571, 584, 570 and 592 nm for complexes **1–7**, respectively. These emission wavelengths are different from the quinoline-based copper(I) iodide complexes that have [Cu<sub>4</sub>I<sub>4</sub>] aggregate and [Cu<sub>2</sub>I<sub>2</sub>] rhombohedron structures. The latter exhibit emission maxima at 620 (Cu...Cu 3.36 Å) and 625 nm (Cu...Cu 2.55–3.33 Å), respectively.<sup>38</sup> A [Cu<sub>6</sub>I<sub>6</sub>] aggregate-based MOF based on quinolyl-arylsilane ligand exhibits an emission maxima at 535 nm.<sup>39</sup> The emission spectra of the five [Cu<sub>4</sub>I<sub>4</sub>] aggregate complexes **1–5** are narrower and show stronger intensities than

the [Cu<sub>3</sub>I<sub>3</sub>] cycle-based 1-D polymeric complexes **6** and **7**. The emissions for complexes **1–5** can be attributed to the triplet metal-to-ligand charge transfer (<sup>3</sup>MLCT), iodide-to-ligand charge transfer (<sup>3</sup>XLCT) and/or cluster-centered (<sup>3</sup>CC) transitions.<sup>9,40</sup> The Cu...Cu distances in **6** and **7** exceed 2.80 Å and thus <sup>3</sup>XLCT/<sup>3</sup>MLCT transitions seem more probable.

#### Structure-property relationship

The quinoline functionalized 1,2,3-triazole ligands described herein demonstrate stable tridentate-bridging to Cu(I) centers in complexes **1–7**. The variation of substituent groups from H, propyl, butyl, isobutyl to –CH<sub>2</sub>OH give rise to small differences in the [Cu<sub>4</sub>I<sub>4</sub>] stair-step structures and intermolecular  $\pi$ ... $\pi$  stacking interactions of complexes **1–5**. More dramatic is the change from [Cu<sub>4</sub>I<sub>4</sub>] aggregate **5** to cyclic [Cu<sub>3</sub>I<sub>3</sub>] based 1-D coordination polymers **6** and **7** with the increasing length of the substituent alcohol from methanol in L5 to ethanol and propanol in L6 and L7. The intermolecular O–H...I H-bonding interactions in **6** and **7** probably play the key tuning roles in aligning the ligands in 1-D propagation. Moreover, the [Cu<sub>3</sub>I<sub>3</sub>]<sub>n</sub> structures in **6** and **7** are unique motifs among 1-D polymeric [Cu]<sub>n</sub> networks. Complex **1–7** are all yellow emissive compounds with aggregate compounds **1–5** emitting at higher intensities than their polymeric counterparts **6** and **7**.

#### Conclusions

The one-pot preparation of quinolyl-1,2,3-triazoles (L1–L7) with different substituent groups under mild conditions further exemplifies the scope and tolerance of the CuAAC reactions and its usefulness in coordination chemistry. These ligands have been successfully applied to the construction of two kinds of copper(I) iodide architectures, viz stair-step [Cu<sub>4</sub>I<sub>4</sub>] aggregates and a rare form of polymeric cyclic [Cu<sub>3</sub>I<sub>3</sub>] assembly. Formation of two different structural motifs arising from a minor change of ligand substituent suggested that the hybrid ligand could potentially support a range other polynuclear and polymeric assemblies. We are currently studying the use of similar ligand systems to drive the formation of emissive molecular materials through self-assemblies.

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#### Notes and references

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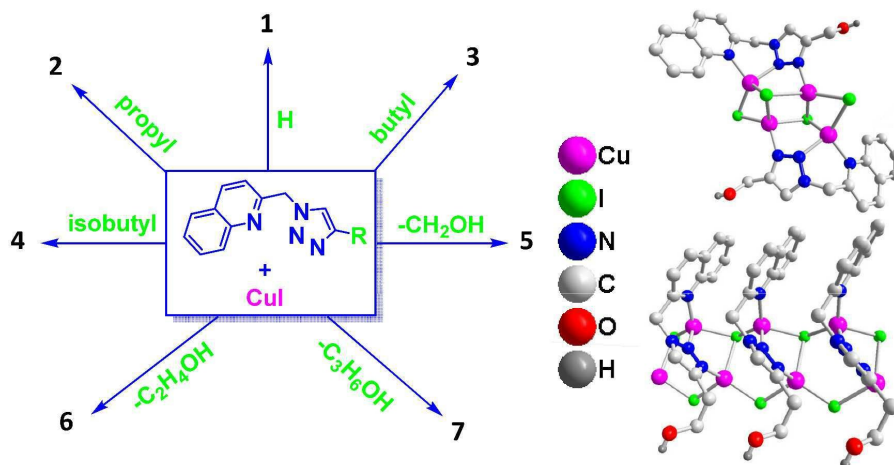
1. O. S. Wenger, *Chem. Rev.*, 2013, **113**, 3686.

2. H. Xiang, J. Cheng, X. Ma, X. Zhou and J. J. Chruma, *Chem. Soc. Rev.*, 2013, **42**, 6128.
3. Q. Zhao, C. Huang and F. Li, *Chem. Soc. Rev.*, 2011, **40**, 2508.
4. Y. Chen, Z.-O. Wang, Z.-G. Ren, H.-X. Li, D.-X. Li, D. Liu, Y. Zhang and J.-P. Lang, *Cryst. Growth Des.*, 2009, **9**, 4963.
5. H.-X. Li, W. Zhao, H.-Y. Li, Z.-L. Xu, W.-X. Wang and J.-P. Lang, *Chem. Commun.*, 2013, **49**, 4259.
6. Y. Chen, Z. Yang, X.-Y. Wu, C.-Y. Ni, Z.-G. Ren and J.-P. Lang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 10781.
- 10 7. V. W.-W. Yam and K. K.-W. Lo, *Chem. Soc. Rev.*, 1999, **28**, 323.
8. A. J. Blake, N. R. Brooks, N. R. Champness, L. R. Hanton, P. Hubberstey and M. Schröder, *Pure Appl. Chem.*, 1998, **70**, 2351.
9. M. Vitale and P. C. Ford, *Coord. Chem. Rev.*, 2001, **219–221**, 3.
10. Y. Chen, H.-X. Li, D. Liu, L.-L. Liu, N.-Y. Li, H.-Y. Ye, Y. Zhang and J.-P. Lang, *Cryst. Growth Des.*, 2008, **8**, 3810.
11. L.-L. Li, H.-X. Li, Z.-G. Ren, D. Liu, Y. Chen, Y. Zhang and J.-P. Lang, *Dalton Trans.*, 2009, 8567.
12. R. Peng, M. Li and D. Li, *Coord. Chem. Rev.*, 2010, **254**, 1.
13. X.-J. Yang, H.-X. Li, Z.-L. Xu, H.-Y. Li, Z.-G. Ren and J.-P. Lang, *CrystEngComm*, 2012, **14**, 1641.
- 20 14. C. H. Arnby, S. Jagner and I. Dance, *CrystEngComm*, 2004, **6**, 257.
15. W.-P. Leung, C.-W. So, K.-H. Chong, K.-W. Kan, H.-S. Chan and T. C. W. Mak, *Organometallics*, 2006, **25**, 2851.
16. R. Visbal and M. C. Gimeno, *Chem. Soc. Rev.*, 2014, **43**, 3551.
- 25 17. V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596.
18. C. W. Tornøe, C. Christensen and M. Meldal, *J. Org. Chem.*, 2002, **67**, 3057.
19. M. Meldal and C. W. Tornøe, *Chem. Rev.*, 2008, **108**, 2952.
- 30 20. J. E. Hein and V. V. Fokin, *Chem. Soc. Rev.*, 2010, **39**, 1302.
21. K. K. Kumar, S. P. Seenivasan, V. Kumar and T. M. Das, *Carbohydr. Res.*, 2011, **346**, 2084.
22. W. S. Brotherton, H. A. Michaels, J. T. Simmons, R. J. Clark, N. S. Dalal and L. Zhu, *Org. Lett.*, 2009, **11**, 4954.
- 35 23. J. D. Crowley and P. H. Bandeen, *Dalton Trans.*, 2010, **39**, 612.
24. J. D. Crowley and D. A. McMorran, *Top. Heterocycl. Chem.*, 2012, **28**, 31.
25. D. Schweinfurth, N. Deibel, F. Weisser and B. Sarkar, *Nachr. Chem.*, 2011, **59**, 937.
- 40 26. H. Struthers, T. L. Mindt and R. Schibli, *Dalton Trans.*, 2010, **39**, 675.
27. B. Schulze and U. S. Schubert, *Chem. Soc. Rev.*, 2014, **43**, 2522.
28. S.-Q. Bai, S. Leelasubcharoen, X. Chen, L. L. Koh, J.-L. Zuo and T. S. A. Hor, *Cryst. Growth Des.*, 2010, **10**, 1715.
29. S.-Q. Bai, J. Y. Kwang, L. L. Koh, D. J. Young and T. S. A. Hor, *Dalton Trans.*, 2010, **39**, 2631.
- 45 30. S.-Q. Bai, A. M. Yong, J. J. Hu, D. J. Young, X. Zhang, Y. Zong, J. Xu, J.-L. Zuo and T. S. A. Hor, *CrystEngComm*, 2012, **14**, 961.
31. S.-Q. Bai, L. Jiang, J.-L. Zuo and T. S. A. Hor, *Dalton Trans.*, 2013, **42**, 11319.
- 50 32. L. Jiang, Z. Wang, S.-Q. Bai and T. S. A. Hor, *CrystEngComm*, 2013, **15**, 10451.
33. L. Jiang, Z. Wang, S.-Q. Bai and T. S. A. Hor, *Dalton Trans.*, 2013, **42**, 9437.
34. *SMART & SAINT Software Reference Manuals*, Bruker AXS GmbH, Karlsruhe, Germany, 2000.
- 55 35. (a) G. M. Sheldrick, *SADABS: a Software for Empirical Absorption Correction*, University of Göttingen, Göttingen, Germany, 2001; (b) L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Cryst.*, 2015, **48**, 3.
- 60 36. (a) G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structures Refinement*, University of Göttingen, Göttingen, Germany, 1997; (c) G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.
- 65 37. J. Y. Lu, B. R. Cabrera, R.-J. Wang and J. Li, *Inorg. Chem.* 1998, **37**, 4480.
38. N. P. Rath, E. M. Holt and K. Tanimura, *J. Chem. Soc. Dalton Trans.*, 1986, 2303.
39. M. S. Deshmukh, A. Yadav, R. Pant and R. Boomishankar, *Inorg. Chem.*, 2015, DOI: 10.1021/ic502207f.
- 70 40. G. F. Manbeck, W. W. Brennessel, C. M. Evans and R. Eisenberg, *Inorg. Chem.*, 2010, **49**, 2834.

## Graphical Abstract

# Luminescent $[\text{Cu}_4\text{I}_4]$ Aggregates and $[\text{Cu}_3\text{I}_3]$ -Cyclic Coordination Polymers Supported by Quinoly-Triazoles

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A series of quinoly-1,2,3-triazoles support luminescent  $[\text{Cu}_4\text{I}_4]$  aggregates and six-membered  $[\text{Cu}_3\text{I}_3]$ -cyclic coordination polymers.

**Table 1** Summary of crystallographic data for complexes 1–7

Complex	1	2	3	4	5	6	7
Formula	C <sub>24</sub> H <sub>20</sub> Cu <sub>4</sub> I <sub>4</sub> N <sub>8</sub>	C <sub>30</sub> H <sub>32</sub> Cu <sub>4</sub> I <sub>4</sub> N <sub>8</sub>	C <sub>32</sub> H <sub>36</sub> Cu <sub>4</sub> I <sub>4</sub> N <sub>8</sub>	C <sub>32</sub> H <sub>36</sub> Cu <sub>4</sub> I <sub>4</sub> N <sub>8</sub>	C <sub>26</sub> H <sub>24</sub> Cu <sub>4</sub> I <sub>4</sub> N <sub>8</sub> O <sub>2</sub>	C <sub>14</sub> H <sub>14</sub> Cu <sub>2</sub> I <sub>2</sub> N <sub>4</sub> O	C <sub>15</sub> H <sub>16</sub> Cu <sub>2</sub> I <sub>2</sub> N <sub>4</sub> O
<i>M<sub>w</sub></i>	1182.24	1266.40	1294.44	1294.44	1242.30	635.17	649.20
<i>T</i> / K	100(2)	298(2)	298(2)	110(2)	100(2)	100(2)	110(2)
Crystal size / mm <sup>3</sup>	0.34 × 0.17 × 0.07	0.15 × 0.13 × 0.06	0.30 × 0.14 × 0.04	0.18 × 0.12 × 0.04	0.23 × 0.08 × 0.03	0.42 × 0.16 × 0.14	0.23 × 0.18 × 0.05
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> −1	<i>P</i> −1	<i>P</i> −1	<i>P</i> −1	<i>P</i> −1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> / Å	8.2321(4)	8.9647(4)	9.0803(4)	8.9132(4)	7.8794(7)	21.4131(8)	44.129(1)
<i>b</i> / Å	8.4671(4)	9.4112(4)	9.5611(4)	9.2024(5)	8.6744(7)	4.2319(2)	4.2321(1)
<i>c</i> / Å	11.9898(5)	11.6831(5)	11.9245(5)	12.2475(6)	13.023(1)	19.1375(7)	19.1234(6)
$\alpha$ / °	94.026(1)	100.174(1)	101.565(1)	97.962(1)	78.570(2)	90	90
$\beta$ / °	95.045(1)	92.619(1)	91.688(1)	96.167(1)	76.751(2)	105.302(1)	99.077(1)
$\gamma$ / °	115.853(1)	109.137(1)	110.357(1)	105.429(1)	67.049(2)	90	90
<i>V</i> / Å <sup>3</sup>	743.64(6)	910.87(7)	945.33(7)	948.02(8)	791.9(1)	1672.7(1)	3526.7(2)
<i>Z</i>	1	1	1	1	1	4	8
<i>D</i> <sub>calc</sub> / g cm <sup>−3</sup>	2.640	2.309	2.274	2.267	2.605	2.522	2.445
$\mu$ / mm <sup>−1</sup>	7.004	5.727	5.521	5.505	6.589	6.241	5.924
$\theta$ range / °	1.72–30.59	1.78–29.25	1.75–28.32	1.70–33.29	1.62–28.33	1.97–36.35	1.87–30.53
Reflections collected	31822	36971	32549	51585	27766	61124	40833
Independent reflections [ <i>R</i> <sub>int</sub> ]	4533 [0.0250]	4932 [0.0248]	4680 [0.0233]	7269 [0.0364]	3949[0.0230]	8082[0.0248]	5350[0.0337]
Parameters	181	208	217	217	199	208	217
GOF	1.195	1.051	1.045	1.042	1.071	1.187	1.070
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0188	0.0211	0.0199	0.0237	0.0159	0.0249	0.0221
<i>wR</i> <sub>2</sub> (all data)	0.0443	0.0477	0.0479	0.0588	0.0385	0.0544	0.0474



