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## Polymeric one- and two-dimensional copper(I) iodide complexes showing photoluminescence tunable by azaaromatic ligands

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Four low-dimensional  $[(CuI)_xL]_n$  complexes were structurally characterized [L = 4,6-dimethylpyrimidine (46dmpm; x = 2), 2,5-dimethylpyrazine (x = 2), 2,6-dimethylpyrazine (x = 1), 3,5-dimethylpyridine (x = 1)]. All the compounds exhibited a (CuI)<sub>n</sub> polymeric motif and the azaaromatic ligands were coordinated to each copper(I) ion, thus giving infinite two-dimensional networks for the x = 2 compounds and one-<sup>10</sup> dimensional chain structures for the x = 1 compounds. The photoluminescent properties were investigated

in the solid state at ambient temperature, and blue, green, and orange emissions were observed for the pyridine, pyrimidine, and pyrazine compounds, respectively. The energy level of the  $\pi^*$  orbital of the azaaromatic compounds regulates the emission color, being consistent with the halide-to-ligand charge-transfer mechanism. The photoluminescence quantum yield of 73% was recorded on [(CuI)<sub>2</sub>(46dmpm)]<sub>n</sub>.

#### 15 Introduction

During the last decade of the remarkable progress in electroluminescence science and technology, iridium(III) and platinum(II) complexes have been utilized as promising luminescent materials.<sup>1</sup> However, such metal sources are often <sup>20</sup> claimed to be rare and expensive.<sup>2</sup> To solve this problem, much effort has been paid to copper(I) (3d<sup>10</sup>) complexes as an alternative.<sup>3</sup> Recently, cluster chromophores such as (CuX)<sub>2</sub>, (CuX)<sub>4</sub>, and (CuX)<sub>6</sub> have been intensively studied for electro- and photoluminescent materials.<sup>4</sup>

Polymeric structures are natural expansion from  $(CuI)_x$  (x = 2,4,6) cluster compounds along this strategy. We have studied the structures and magnetic properties of polymeric copper(II) complexes using pyrimidines and pyrazines for two decades.<sup>5</sup> 30 Meanwhile various copper(I) polymer motifs have been well established.<sup>6</sup> Now we focus on polymeric copper(I) complexes with pyrimidine and pyrazine bridges toward development of luminescent materials. The structural characterization of polymeric complexes is considerably difficult, in particular when <sup>35</sup> the ligands used are small and rigid,<sup>7</sup> whereas the ligands having a flexible moiety would afford good crystalline solids.<sup>8</sup> In the present study, we attempted to prepare CuI complexes having rather simple pyrimidines and pyrazines, because the establishment of relationship between the crystal structures and 40 physical properties will be helpful to advance materials chemistry. Eventually, four novel polymeric  $[(CuI)_{x}L]_{n}$ complexes (x = 1, 2; L = azaaromatic compounds) have been prepared and structurally characterized. The photoluminescent

properties were investigated in the solid state at ambient 45 temperature. Discussion will cover the topics on wavelength tuning together with prescription for efficiently emissive (CuI)<sub>n</sub>- based materials.

#### **Results and discussion**

#### Preparation

<sup>50</sup> Single-crystal specimens very slowly grew by means of a vapor diffusion method. An acetonitrile solution containing CuI and another acetonitrile solution containing an azaaromatic ligand were separately located in a sealed vessel at ambient conditions. After the ligand vapor was transferred into the CuI solution, the <sup>55</sup> crystalline solid was formed as yellow prism or plates. The product was separated, washed, dried, and used for crystallographic analysis and physical measurements without further purification. Simply combining two solutions of starting materials only gave powdery products even when rapid mixing <sup>60</sup> was limited.

We utilized 4,6-dimethylpyrimidine (abbreviated as 46dmpm, hereafter), 2,3-, 2,5-, and 2,6-dimethylpyrazines (23dmpz, 25dmpz, and 26dmpz, respectively), and 3,5-dimethylpyridine (35lut). The products were characterized from elemental analysis <sup>65</sup> (C, H, N) and IR spectroscopy. The formulas with the CuI/L ratio of 2/1 were found for L = 46dmpm, 23dmpz, and 25dmpz, while the 1/1 ratio was characterized for L = 26dmpz and 35lut. The CuI/L ratio was found to be related with the dimensionality of the covalent-bond network. The molecular and crystal structures <sup>70</sup> were unequivocally determined by means of single-crystal X-ray diffraction study.

#### **Crystal structure analysis**

Figure 1 shows the molecular and crystal structures of  $[(CuI)_2(46dmpm)]_n$  solved in an orthorhombic *Pcca* space group <sup>75</sup> (Table 1). An asymmetric unit contains CuI and a half of 4dmpm. The CuI portion constructs a somewhat distorted (CuI)<sub>4</sub> cubane

with two opposing edges considerably long. The shortest Cu---Cu distance is 2.9862(10) Å as a diagonal of the (CuI)<sub>2</sub> rhombus repeating motif, suggesting the presence of a  $d^{10}$ - $d^{10}$  metallophilic interaction.<sup>9</sup> A four-leg column structure is found along the *c* 

- s axis, which can be regarded also as a face-sharing polycubane. Each iodide works as a  $\mu_3$ -type bridge, and each Cu(I) ion has a tetragonal geometry. The 46dmpm ligand connects the (CuI)<sub>n</sub> columns with the Cu-N bond length of 2.082(4) Å. All of the 46dmpm nitrogen donors and all of the Cu ion acceptors in the
- <sup>10</sup> four-leg column are utilized as inter-column bridges (i.e., fully interlocked), leading to an infinite two-dimensional (2D) sheet parallel to the *ac* plane. The density ( $d_{cald}$ ), 3.154 g cm<sup>-3</sup>, is considerably high.
- Compound  $[(CuI)_2(25dmpz)]_n$  crystallizes in a triclinic *P*-1 15 space group. An asymmetric unit corresponds to CuI and a half of 25dmpz (Figure 2). The CuI portion forms a rhombus, and the rhombuses fuse to construct a ladder (or stair-step). The 25dmpz ligand works as a bridge among the ladders. Similarly to the 46dmpm compound, each iodide works as a  $\mu_3$ -type bridge, and
- <sup>20</sup> each Cu ion has a tetragonal geometry. The ladders are entirely interlocked and form an infinite 2D sheet, affording a relatively high  $d_{cald} = 3.097$  g cm<sup>-3</sup>. The Cu-N bond length is 2.066(6) Å. The shortest Cu---Cu distance is 2.797(3) Å as a diagonal of the (CuI)<sub>2</sub> rhombus. This value is just close to the sum of the van der <sup>25</sup> Waals radii (2.80 Å).<sup>10</sup>



Figure 1. (a) Crystal structure of [(Cul)<sub>2</sub>(46dmpm)]<sub>n</sub> depicting two cubane-like moieties and two bridges. Thermal ellipsoids are drawn at the 40 50% probability. (b) Polymeric 2D structure. Hydrogen atoms are omitted.



**Figure 2.** (a) Crystal structure of  $[(CuI)_2(25dmpz)]_n$  depicting two ladder fragments and a bridge. Thermal ellipsoids are drawn at the 50% probability. (b) Polymeric 2D structure. Hydrogen atoms are omitted.

<sup>60</sup> The 23dmpz derivative  $[(CuI)_2(23dmpz)]_n$  crystallizes in a monoclinic system  $P2_1/n$  space group. We have determined the cell parameters at ambient temperature (see Experimental Section) and found that the present crystal structure was identical to the known one.<sup>11</sup> The fully interlocked 2D structure was <sup>65</sup> confirmed, giving a relatively high  $d_{cald} = 3.157$  g cm<sup>-3</sup> at 293 K (3.180 g cm<sup>-3</sup> at 220 K<sup>11</sup>).

In contrast,  $[(CuI)(26dmpz)]_n$  constructs a one-dimensional (1D) array, as shown by the crystal structure solved in a monoclinic  $P2_1/c$  space group (Figure 3). A whole 70 (CuI)(26dmpz) unit is crystallographically independent. The N2 atom does not participate in ligation, probably because of the steric hindrance. Each tetragonal Cu ion is coordinated by a 26dmpz ligand, indicating the CuI/L ratio of 1/1. The ladder structure consisting of  $(CuI)_n$  runs in the *a* axis direction, and the 75 26dmpz ligands are bound as a pendant in a zigzag manner. A very short Cu---Cu distance was found (2.748(2) Å) as a rhombus diagonal. The Cu-N bond length is 2.061(9) Å. The density ( $d_{cald}$ =  $2.289 \text{ g cm}^{-3}$ ) is much smaller than those of the previous CuI/L = 2/1 compounds. There seems to be no contact between ladders. <sup>80</sup> The shortest interatomic distances between ladders are 3.82(1) Å (C4---I1<sup>i</sup>) and 3.84(2) Å (C5---N2<sup>ii</sup>) for non-hydrogen atoms, where the symmetry operation codes for i and ii are (x, y, z+1)and (x, -y+1/2, z+1/2), respectively.



**Figure 3.** (a) Crystal structure of  $[(CuI)(26dmpz)]_n$  as a ladder moiety and a pendant. Thermal ellipsoids are drawn at the 50% probability. (b) Polymeric 1D structure. Hydrogen atoms are omitted.



**Figure 4.** (a) Crystal structure of  $[(CuI)(35lut)]_n$  as a ladder moiety and a pendant. Thermal ellipsoids are drawn at the 50% probability. (b) Polymeric 1D structure. Hydrogen atoms are omitted.

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Table 1. Selected crystallographic data for  $[(Cul)_2(46dmpm)]_{n_3}$   $[(Cul)_2(25dmpz)]_n$ ,  $[(Cul)(26dmpz)]_n$ , and  $[(Cul)(35lut)]_n$ .

	$[(CuI)_2(46dmpm)]_n$	$[(CuI)_2(25dmpz)]_n$	$[(CuI)(26dmpz)]_n$	$[(CuI)(35lut)]_n$
Chemical Formula	$C_6H_8Cu_2I_2N_2$	$C_6H_8Cu_2I_2N_2$	C <sub>6</sub> H <sub>8</sub> CuIN <sub>2</sub>	C7H9CuIN
Formula Weight	489.04	489.04	298.59	297.61
Crystal Habit	yellow prism	yellow platelet	yellow platelet	colorless platelet
Crystal System	orthorhombic	triclinic	monoclinic	monoclinic
Space Group	Pcca	<i>P</i> -1	$P2_{1}/c$	C2/c
<i>a /</i> Å	14.8105(6)	4.2971(12)	4.1718(2)	14.102(5)
<i>b /</i> Å	10.1034(6)	8.220(3)	27.4616(14)	15.392(6)
<i>c</i> / Å	6.8817(3)	8.247(3)	7.6232(6)	8.233(3)
$\alpha$ / °	90.	110.85(3)	90.	90.
eta / °	90.	102.04(3)	97.299(3)	97.833(18)
γ/°	90.	94.82(3)	90.	90.
$V/ \text{\AA}^3$	1029.75(9)	262.23(17)	866.27(10)	1770.3(11)
Ζ	4	1	4	8
$d_{\rm cald}$ /g cm <sup>-3</sup>	3.154	3.097	2.289	2.233
$\mu$ (MoK $\alpha$ ) /mm <sup>-1</sup>	10.077	9.892	6.015	5.883
Unique data	1183	1200	1990	2024
$R^{a}(I \ge 2\sigma(I))$	0.0307	0.0590	0.0263	0.0352
$R_{\rm w}^{\rm b}({\rm all})$	0.0549	0.0786	0.1122	0.0607
GOF	1.052	1.034	1.473	1.034
<i>T</i> / K	293	293	293	293

<sup>a</sup>  $R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|$ . <sup>b</sup>  $R_{w} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}$ .

To check the role of the uncoordinated nitrogen atom in  $[(CuI)(26dmpz)]_n$  we moved to prepare the complex having 35lut. Interestingly, although the space group of  $[(CuI)(35lut)]_n$  (*C*2/*c*) is different, the supramolecular archetecture is similar; the <sup>5</sup> polymeric structure is 1D. Figure 4 shows the repeating motif and arrangement of the ladders. The CuI polymer runs along the *c* axis, and the 35lut pendants are bound to the Cu ions with the Cu-N bond length of 2.042(4) Å. Two Cu---Cu diagonal distances are 2.8893(12) and 3.051(1) Å. The interatomic distances among the

<sup>10</sup> ladders are 4.059(6) Å (C7---I1<sup>iii</sup>) and 4.078(8) Å (C7---C3<sup>iv</sup>) for non-hydrogen atoms, where the symmetry operation codes for iii and iv are (-x+1/2, -y+1/2, -z+3) and (x, -y+1, z+1/2), respectively. The relatively long distances seem to be related with  $d_{cald} = 2.233$  g cm<sup>-3</sup>, which is smaller than that of 15 [(CuI)(26dmpz)]<sub>n</sub> by 2.4%.

The single-crystal X-ray structure determinations were successful for the present compounds. We suppose that the choice of the dimethylated aromatic ligands would be a key to produce crystalline compounds suitable for crystallographic analysis. The

<sup>20</sup> increase of the molecular mass reduces the vapor pressure in a reaction vessel, and the rate of the crystal growth is significantly slowed down.

To our knowledge, the four-leg column structure from polymeric CuI is unprecedented, although the three-<sup>12</sup> and four-<sup>25</sup> leg ladders<sup>13</sup> and (CuX)<sub>3</sub>-based columns<sup>14</sup> are known. The derivative using unsubstituted pyrimidine,  $[(CuI)_2(pyrimidine)]_n$ , has already been reported, and the 2D polymeric motif belongs to a bridged ladders<sup>15</sup> like  $[(CuI)_2(23dmpz)]_n$  and  $[(CuI)_2(25dmpz)]_n$ . Unfortunately its luminescent property was not described. There

<sup>30</sup> have been several reports on X-ray crystal structures of CuI ladders bridged by methylpyrazine<sup>16</sup> and quinoxaline<sup>17</sup> for an

instance, but the emission characteristics are unknown.

#### Photoluminescent properties

The 1D and 2D coordination polymers seem to be a rigid 35 skeleton, so that it may improve the efficiency of photoluminescence. The emission spectra were recorded (Figure 5), and the quantum yields ( $\mathcal{O}$ 's) were measured (Table 2) on a Hamamatsu Photonics Quantaurus-QY at room temperature. The excitation wavelength was set to the absorption maximum at the 40 solid state unless otherwise stated.

As shown in Figure 5, the emission wavelengths vary from 436 to 572 nm (blue to light orange). Our result on  $[(CuI)_2(23dmpz)]_n$  ( $\lambda_{max}^{em} = 572$  nm) reproduced the reported properties (544 - 581 nm<sup>11</sup>). The color was insensitive to the excitation wavelength in <sup>45</sup> any case. Each spectrum seems to have a shoulder on the longer wavelength side, and actually deconvolution analysis resolved two peaks. The spectrum of  $[(CuI)(35lut)]_n$  showed major and minor peaks at 23,100 and 21,100 cm<sup>-1</sup>, respectively. Similarly, that of  $[(CuI)_2(46dmpm)]_n$  was analyzed to involve a main peak <sup>50</sup> at 19,900 cm<sup>-1</sup> with a small shoulder at 18,500 cm<sup>-1</sup>. A double-peak profile was assumed for the spectrum of  $[(CuI)_2(23dmpz)]_n$ , and the emission energies were determined to be 17,700 (major) and 16,300 cm<sup>-1</sup> (minor).

Such double-peak emission spectra often observed in CuIss based complexes have been explained in terms of coexistence of the CC (cluster centered) and XLCT (halide-to-ligand charge transfer) mechanisms.<sup>18</sup> They have been plausibly applied to  $[(CuI)_4py_4]$  and relevant compounds<sup>19,20</sup> (py stands for pyridine). The color variation of the emission of  $[(CuI)_xL]_n$  affords a clue to the mechanism of the emission. The energy level of the  $\pi^*$  orbital of the azaaromatic compounds largely depend on the electronic effect. Methyl groups play a role of an electron donor, and all the present ligands possess two methyl groups in common. Thus, the number and position of the nitrogen atom(s) are crucial. The electron affinities of unsubstituted pyridine, pyrimidine, and s pyrazine in a gas phase were determined to be -0.62, 0.0, and

- 0.40 eV, respectively (a positive value indicates that energy is released).<sup>21</sup> The half-wave reduction potentials in acetonitrile were reported to be -2.66, -2.337, -2.158 V vs SCE, respectively.<sup>22</sup> Theoretical calculations support these trends.<sup>23</sup>
- <sup>10</sup> The order of the lowest unoccupied molecular orbitals (LUMOS) of the aromatic ligands used here is practically the same as above (Figure 6). The highest luminescence energy (436 nm) for [(CuI)<sub>2</sub>(35lut)]<sub>n</sub>, the second highest (512 nm) for [(CuI)<sub>2</sub>(46dmpm)]<sub>n</sub>, and the low energies (533 572 nm) for the <sup>15</sup> dmpz compounds indicate that the luminescence is regulated with the LUMO level of the aromatic rings. Therefore, the major emission band should be assigned to the XLCT emission.
- Furthermore, this logic may allow us to tune the light-emitter wavelength by choosing azaaromatic rings, namely pyridine, di, <sup>20</sup> tri, tetrazines, and their isomers.



**Figure 5.** (a) Photos of (left to right)  $[(Cul)(35lut)]_n$ ,  $[(Cul)_2(46dmpm)]_n$ ,  $[(Cul)(26dmpz)]_n$ ,  $[(Cul)_2(25dmpz)]_n$ , and  $[(Cul)_2(23dmpz)]_n$  under irradiation at 375 nm. (b) Normalized emission spectra in the solid state at ambient temperature. For the excitation conditions, see Table 2.

<sup>45</sup> <b>Table 2</b> . Results of photoluminescence measurem	ents. <sup>a)</sup>
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Ligand (L)	46dmpm	23dmpz	25dmpz	26dmpz	35lut
CuI/L ratio	2/1	2/1	2/1	1/1	1/1
$\frac{\lambda^{ex} / nm}{\lambda_{max}^{em} / nm} \frac{\delta}{\Phi} \frac{\delta}{6}$	370	500	480	460 <sup>b)</sup>	370
	512	572	570	533	436
	73	29	28	34	19

a) Measured in the solid state at ambient temperature.

b) The excitation at 500 nm gave  $\lambda_{max}^{em} = 538$  nm. The excitation

ss wavelength was shifted to 460 nm for the  $\Phi$  measurement, because of the overlap with the emission band.



#### <sup>70</sup> Figure 6. Schematic representation of energy levels of $[(CuI)_x(L)]_n$ .

Copper(I) iodide has polymorphs and is known as a p-type semiconductor with a wide band gap (3.1 eV for the  $\gamma$ -phase).<sup>24</sup> It is likely that the LUMOs of the ligands are located within a CuI band gap (Figure 6). This picture has originally proposed for <sup>75</sup> Cu<sub>2</sub>X<sub>2</sub>-based compounds<sup>4a</sup> and modified to polymeric CuI compounds. We have also to pay attention to the chromophore core dependence; for example [(CuI)py]<sub>n</sub>, [(CuI)<sub>2</sub>py<sub>4</sub>], and [(CuI)<sub>4</sub>py<sub>4</sub>] show blue, green, and orange emissions, respectively.<sup>20</sup> The aromatic ring dependence of the emission wavelength found here seems to hold for those which involve polymeric (CuI)<sub>n</sub> skeletons. A prototype of co-deposit complexes from CuI and 3,5-bis(carbazol-9-yl)pyridine for organic lightemitting diodes was reported.<sup>25</sup> The electroluminescence wavelength was 530 nm, but we cannot directly compare with the DI wavelength of [(CuI)<sub>2</sub>Sh(t)]

- <sup>85</sup> PL wavelength of  $[(CuI)_2(35lut)]_n$ , because the molecular structure of the 3,5-bis(carbazol-9-yl)pyridine complex was assumed to be dinuclear.<sup>25</sup> The structure of  $[(CuI)_2(35lut)]_n$  is infinitely polynuclear. The advantage of our study resides in the well-defined molecular and crystal structures.
- <sup>90</sup> The present  $\Phi$  values are good on the whole. The highest yield (73%) obtained from  $[(CuI)_2(46dmpm)]_n$  is notable, and this compound is the only one that has a four-leg column CuI polymer. The increase of heavy atoms reduces vibration excitation and accordingly suppresses nonradiative deactivation.
- <sup>95</sup> The presence of the bridge also contributes such suppression, as indicated by the good quantum yields obtained from the 2D complexes. In each 1D or 2D series, the specimens having higher density seem to show more efficient luminescence.

We make a comment on the comparison between <sup>100</sup> [(CuI)(26dmpz)]<sub>n</sub> and [(CuI)(35lut)]<sub>n</sub>. Both possess a similar 1D structure, but the former has tighter molecular packing, as indicated by  $d_{cald}$ . The former exhibited higher  $\Phi$ , because the presence of a void space induces vibrational excitation. The presence of the additional nitrogen atom in pyrazine is helpful for <sup>105</sup> dense molecular solids due to intermolecular interaction like dipolar interaction, although the nitrogen atom is apparently free from coordination. Thus, suppression of vibrational deactivation is confirmed to be preferable for the luminescence efficiency.

#### Conclusion

<sup>110</sup> Five low-dimensional  $[(CuI)_xL]_n$  complexes have been prepared and structurally characterized. The PL quantum yield of 73% was recorded on  $[(CuI)_2(46 \text{dmpm})]_n$ . Suppression of vibrational deactivation is confirmed to be preferable for the efficiency. The emission wavelength is dominantly regulated by the types of azaaromatic ligands rather than the dimensionality of the network or detailed coordination geometry. As an application system in future, the light-emitter wavelength can be regulated by the <sup>5</sup> number and position of nitrogen atoms introduced in the bridge

and pendant azaaromatic rings. The introduction of substituents on the aromatic ring also seems to be available for fine-tuning of the emission color.

#### **Experimental Section**

#### 10 Preparation

An acetonitrile solution of copper(I) iodide (c = 0.01 mol/L) was prepared and a 2 mL portion was placed in a 5-mL vial. Another acetonitrile solution containing an azaaromatic ligand (c = 0.1 mol/L) was prepared, and a 4 mL portion was poured into a 50-

- <sup>15</sup> mL reaction vessel. The 5-mL vial was unlidded and quietly kept in the 50-mL vessel, and the whole vessel was sealed. It was allowed to stand at room temperature, until the ligand vapor was transferred and polycrystalline solids were formed in the 5-mL vial. A few milligrams of the product were separated, washed,
- <sup>20</sup> and dried. The products were characterized by means of elemental analysis and IR spectroscopy. The elemental analysis (C, H, N) was performed on a Perkin Elmer 2400 series II CHNS/O analyzer by a usual combustion method. IR spectra were recorded by means of an attenuated total reflection (ATR) <sup>25</sup> method on a Nicolet FT-IR 6700 spectrometer.
- $$\label{eq:cull} \begin{split} & [(Cul)_2(46dmpm)]_n: \ Anal. \ Calc. \ for \ C_6H_8Cu_2I_2N_2: \ C, \ 14.74\%, \\ & H, \ 1.65\%, \ N, \ 5.73\%. \ Found: \ C, \ 14.89\%, \ H, \ 1.63\%, \ N, \ 5.96\%. \ IR \\ & (neat, \ ATR) \ 432, \ 455, \ 567, \ 734, \ 869, \ 941, \ 1062, \ 1429, \ 1610, \\ & 2913 \ cm^{-1}. \ [(Cul)_2(23dmpz)]_n: \ Anal. \ Calc. \ for \ C_6H_8Cu_2I_2N_2: \ C, \end{split}$$
- <sup>30</sup> 14.74%, H, 1.65%, N, 5.73%. Found: C, 14.77%, H, 1.35%, N, 5.89%. IR (neat, ATR) 450, 486, 846, 965, 1086, 1161, 1392, 1417, 3064 cm<sup>-1</sup>. [(CuI)<sub>2</sub>(25dmpz)]<sub>n</sub>: Anal. Calc. for C<sub>6</sub>H<sub>8</sub>Cu<sub>2</sub>I<sub>2</sub>N<sub>2</sub>: C, 14.74%, H, 1.65%, N, 5.73%. Found: C, 14.67%, H, 1.19%, N, 5.77%. IR (neat, ATR) 432, 521, 885,
- <sup>35</sup> 1039, 1150, 1330, 1428, 1447, 1488, 3021 cm<sup>-1</sup>. [(Cul)(26dmpz)]<sub>n</sub>: Anal. Calc. for C<sub>6</sub>H<sub>8</sub>CulN<sub>2</sub>: C, 24.13%, H, 2.70%, N, 9.38%. Found: C, 24.32%, H, 2.47%, N, 9.51%. IR (neat, ATR) 425, 465, 735, 868, 1018, 1159, 1251, 1377, 1415, 1526, 2915 cm<sup>-1</sup>. [(Cul)(35lut)]<sub>n</sub>: Anal. Calc. for C<sub>7</sub>H<sub>9</sub>CulN: C, 40 28.25%, H, 3.05%, N, 4.71%. Found: C, 28.48%, H, 2.80%, N,
- <sup>40</sup> 28.25%, H, 5.05%, N, 4.71%. Found: C, 28.48%, H, 2.80%, N, 4.87%. IR (neat, ATR) 699, 752, 860, 1145, 1171, 1382, 1428, 1594, 2911 cm<sup>-1</sup>.

#### X-ray crystallographic analysis

X-Ray diffraction data were collected on a Saturn70 CCD and R-45 axis RAPID imaging plate diffractometers with graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were directly solved by a heavy-atom method and expanded using Fourier techniques in the CRYSTALSTRUCTURE 4.0.<sup>26</sup> Numerical absorption correction was used. The hydrogen atoms

- so were located at calculated positions and the parameters were refined as a riding model. The thermal displacement parameters of non-hydrogen atoms were refined anisotropically. Selected crystallographic data are listed in Table 1. The cell parameters of  $[(CuI)_2(23dmpz)]_n$  are determined as follows: monoclinic  $P2_1/n$ , *a* so = 4.3306(11), *b* = 18.014(7), *c* = 13.203(7) Å,  $\beta$  = 92.63(4)°, *V* =
- 1028.9(7) Å<sup>3</sup>, and Z = 4 at T = 293 K.

#### Photoluminescence measurements

The emission spectra and the absolute quantum yields were measured on a Hamamatsu Photonics Quantaurus-QY C11347 <sup>60</sup> absolute PL quantum yields measurement system at room temperature. The absorption spectra were recorded by scanning with a 10 nm interval from 300 to 600 nm. The excitation wavelength is set to the absorption maximum at the solid state. The data were acquired three times and averaged with the sample

<sup>65</sup> holder rotated. The holder blank data were separately measured and subtracted from the raw sample data.

#### Notes and references

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† Electronic Supplementary Information (ESI) available: CCDC 1003197, 1003198, 1003199, and 1003200 contain the supplementary crystallographic data in CIF format for [(CuI)<sub>2</sub>(46dmpm)]<sub>n</sub>, [(CuI)<sub>2</sub>(25dmpz)]<sub>n</sub>, [(CuI)(26dmpz)]<sub>n</sub>, and [(CuI)(35lut)]<sub>n</sub>, respectively. 75 See DOI: 10.1039/b000000x/

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#### CrystEngComm

Polymeric one- and two-dimensional copper(I) iodide complexes showing photoluminescence tunable by azaaromatic ligands

Nobuo Kitada and Takayuki Ishida

Table of contents



#### Synopsis

The photoluminescent properties of five low-dimensional  $[(CuI)_xL]_n$  complexes were investigated in the solid state at ambient temperature, and blue, green, and orange emissions were observed for the pyridine, pyrimidine, and pyrazine compounds, respectively, with a maximum photoluminescence quantum yield of 73%.