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### ARTICLE

# Static and dynamic coordination behaviours of copper(I) ions in hexa(2-pyridyl)benzene ligand systems

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Two hexaarylbenzenes having six pyridine substituents ( $L_H$  and  $L_M$ ) were prepared and six corresponding coordination complexes with copper(I) chloride were synthesized. The monomeric complexes (**1**, **2a** and **2b**) and 1D coordination polymers (**3**, **4** and **5**) were synthesized *via* the judicious concentration control of copper(I) ions and characterized fully including X-ray crystal analysis. The binding modes of the ligands to copper(I) ions in the coordination polymers were dependent on steric effects and solvents to determine the morphology of the coordination polymers. More interestingly, dynamic behaviours of the monomeric complexes (**1**, **2a** and **2b**) in the solution phase were studied to show potential applications of molecular machines with fluxional motions.

#### Introduction

Multi-metallic systems have been of great interest because of the synergistic effect on various catalytic reactions to lower activation energy. To envision such multi-metallic complexes, a variety of novel ligands have been developed with multiple P, O, N and C donors in the ligand.<sup>2-8</sup> Among them, pyridine based multi-ligand systems have been intensively studied because of the strong and rigid sigma-donor properties that secure the stability of metal complexes.9-12 In particular, polypyridyl ligands with a high symmetry appear to be promising for achieving their intriguing topology and versatile coordination ability.<sup>13,14</sup> Representative examples of polypyridyl ligands that can form unique multi-metallic complexes are described in Figure 1. The ligands A (tppz: 2,3,5,6-tetrakis(2-pyridyl)pyrazine)<sup>15-18</sup> and **B** (tptz: 2,4,6-tris(2pyridyl)-1,3,5-triazine)<sup>19-21</sup> have been extensively studied as multi-metallic systems with various transition metals, showing ligand-assisted energy transfer and fluxional behaviours. The ligand C (hexa(2-pyridyl)[3]radialene) has been studied as coordination complexes with silver(I) salts to form hexapodal prismatic structures and coordination polymers.<sup>22,23</sup> In addition, the ligands ( $D_1^{24,25}$  and  $D_2^{26}$ ) with extended pyridine sites have been utilized as supramolecular building blocks for constructing tetrahedron-, box- and octahedron-shaped coordination cages.

Hexaarylbenzene (HAB) derivatives are of our particular

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interest because they have rotatable peripheral aromatic units to the central benzene ring. Thus, the propeller-shaped and radially  $\pi$  extended HABs are applicable to liquid crystalline materials, building blocks in supramolecular chemistry, molecular receptors and metal sensors.<sup>27-31</sup> We were interested in hexa(2-pyridyl)benzene derivatives ( $L_{H}$  and  $L_{M}$ ) that possess six 2-pyridyl groups attached to a central benzene ring.<sup>32,33</sup> With these ligands, we successfully synthesized various monomeric and polymeric copper(I) coordination complexes by utilizing their diverse coordinating combinations of six pyridine sites in the ligand. In addition, all structural characterization of the coordination complexes was conducted by X-ray single crystal analysis. More importantly, we have also studied the conformation of the ligands and nuclearity of the complexes with different equivalents of copper(I) chloride including the interesting solution behaviours of mono- and dinuclear copper(I) complexes and the luminescence properties of three different 1D coordination polymers with tetranuclear copper(I) chloride cluster.



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Table 1. Selected Crystal Data and Refinement Detail.

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|  | 1.2(CH <sub>3</sub> CN)   | 2a                        | 2b · CH <sub>3</sub> CN   | 3                         | 4  | 5   |
|--|---------------------------|---------------------------|---------------------------|---------------------------|--|---|
| Empirical formula                                    | $C_{48}H_{45}CI_1Cu_1N_9$ | $C_{20}H_{15}CI_1Cu_1N_4$ | $C_{25}H_{24}Cl_1Cu_1N_5$ | $C_{18}H_{12}Cl_2Cu_2N_3$ | C <sub>46</sub> H <sub>42</sub> Cl <sub>4</sub> Cu <sub>4</sub> N <sub>8</sub> | C <sub>25</sub> H <sub>26</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>3</sub> O <sub>2</sub> |
| Formula weight                                       | 846.92                    | 410.35                    | 246.74                    | 468.29                    | 1102.83  | 582.47  |
| Temperature/K  | 100                       | 100                       | 100                       | 298                       | 100  | 100   |
| Crystal system                                       | monoclinic                | monoclinic                | Triclinic                 | orthorhombic              | monoclinic   | monoclinic  |
| Space group  | C2/c                      | P2₁/n                     | P-1                       | Pnnm                      | P2₁/c  | P21/c   |
| a / Å  | 23.704(5)                 | 10.933(2)                 | 8.9830(18)                | 10.0389(3)                | 11.435(4)  | 9.4650(19)  |
| b / Å  | 14.101(3)                 | 13.690(3)                 | 12.124(2)                 | 11.3316(3)                | 24.695(9)  | 14.559(3)   |
| c / Å  | 27.437(6)                 | 11.946(2)                 | 12.321(3)                 | 16.6903(4)                | 17.511(6)  | 17.362(4)   |
| α/°  | 90                        | 90                        | 106.64(3)                 | 90                        | 90   | 90  |
| β/°  | 108.20(3)                 | 95.49(3)                  | 94.63(3)                  | 90                        | 108.053(11)  | 95.38(3)  |
| γl°  | 90                        | 90                        | 108.42(3)                 | 90                        | 90   | 90  |
| Volume / Å <sup>3</sup>                              | 8712(3)                   | 1779.8(6)                 | 1198.0(5)                 | 1898.64(9)                | 4701(3)  | 2382.0(8)   |
| Z  | 8                         | 4                         | 2                         | 4                         | 4  | 4   |
| Radiation  | synchrotron               | synchrotron               | ΜοΚα                      | CuKα                      | ΜοΚα   | synchrotron   |
|  | (λ = 0.71073)             | (λ = 0.71073)             | $(\lambda = 0.71073)$     | (λ = 1.54178)             | (λ = 0.71073)  | $(\lambda = 0.700)$   |
| $R_{1}\left[ I \geq 2\delta\left( I \right) \right]$ | 0.0859                    | 0.0492                    | 0.0347                    | 0.0709                    | 0.0505   | 0.0350  |
| $wR_2 [I \ge 2\delta(I)]$                            | 0.2237                    | 0.1011                    | 0.1138                    | 0.1149                    | 0.1359   | 0.1086  |

#### **Experimental Section**

#### Synthesis of hexa(2-pyridyl)benzene (L<sub>H</sub>).

Under N<sub>2</sub> atmosphere, 2-phenylpyridine (0.16 g, 1.0 mmol),  $[(\eta^6-C_6H_6)RuCl_2]_2$  (0.025 g, 0.050 mmol), triphenylphosphine (0.053 g, 0.20 mmol), and potassium carbonate (1.66 g, 12.0 mmol) were added as one pot in a flask that contains 5 mL of N-methyl-2-pyrolidone (NMP). The solution was stirred and heated to 140 °C. At this temperature, 2-bromopyridine (1.58 g, 10.0 mmol) was added dropwise by a syringe pump over 24 hours, and further stirred for 24 hours at the same temperature. The organic portion of the mixture was extracted with chloroform several times after addition of water to the reaction mixture to remove NMP. The extracted solution was dried over anhydrous sodium sulphate and all volatiles of the solution were removed in vacuo. The desired product was purified from the residue by silica gel chromatography (acetone : methanol :  $Et_3N = 20 : 2 : 1$ ). A white solid was recrystallized in THF and dried for further purification. Hexa(2pyridyl)benzene (0.077 g, 14.2% yield). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN): δ 8.06 (ddd, J = 5.0, 1.8, 1.0 Hz, 6H), 7.25 (td, J = 7.8, 1.8 Hz, 6H), 6.94 (d, J = 7.8, 6H), 6.84 (ddd, J = 7.2, 4.8, 1.0 Hz, 6H) ppm.  $^{13}$ C NMR (125 MHz, CD3CN)  $\delta$  158.2, 147.8, 140.2, 134.3, 126.7, 120.7 ppm. HR-MS : [M + H] (m/z) = 541.2139; calcd. value for  $C_{36}H_{25}N_6 = 541.2141$ .

#### Synthesis of hexa(2-(5-methylpyridyl))benzene (L<sub>M</sub>).

Under  $N_2$  atmosphere, 5-methyl-2-phenylpyridine (0.239 g, 1.4 mmol),  $[(\eta^6-C_6H_6)RuCl_2]_2$  (0.100 g, 0.2 mmol), triphenylphosphine (0.210 g, 0.8 mmol), and potassium carbonate (3.32 g, 24.0 mmol) were added as one pot in a flask

that contains 5 mL of N-methyl-2-pyrrolidone (NMP). The solution was stirred and heated to 140 °C. At this temperature, the solution of NMP (3 mL) with 2-bromo-5-methylpyridine (2.38 g, 14 mmol) was added dropwise by a syringe pump over 24 h, and further stirred for 24 h at the same temperature. The organic portion of the mixture was extracted with chloroform several times after addition of water to the mixture to remove NMP. The extracted solution was dried over anhydrous sodium sulfate and all the volatiles of the solution were removed in vacuo. The residue was purified by silica gel chromatography (acetone : methanol :  $Et_3N = 20 : 2 : 1$ ). A white solid was recrystallized in THF and dried for further purification. Hexa(2-(5-methylpyridyl))benzene (0.139 g, 15.8% yield). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN): δ 7.92 (s, 6H), 7.08 (dd, J = 7.8, 1.8 Hz, 6H), 6.82 (d, J = 7.8, 6H) ppm.  $^{13}$ C NMR (125 MHz, CD<sub>3</sub>CN)  $\delta$  156.6, 149.0, 141.1, 135.7, 130.9, 127.0, 18.0 ppm. HR-MS : [M + H] (m/z) = 625.3084; calcd. value for  $C_{42}H_{36}N_6 = 625.3079$ .

#### Synthesis of $[L_MCuCl(CH_3CN)] \cdot 2(CH_3CN) (1 \cdot 2(CH_3CN)).$

Under N<sub>2</sub> atmosphere, hexa(2-(5-methylpyridyl))benzene (10.0 mg, 0.016 mmol, 1.0 equiv) and CuCl (1.6 mg, 0.016 mmol, 1.0 equiv) was dissolved in acetonitrile (1 mL) at room temperature. Bright yellow block formed in a week. After 2 weeks, the yellow solution was decanted and the yellow crystalline solid was washed with THF (2 x 1 mL) and dried. The product was isolated as a bright yellow colored crystalline solid 1 (6.2 mg, 46% yield). The yellow crystals were suitable for single crystal X-ray diffraction (XRD) analysis. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  8.03 (s, 6H), 7.13 (d, *J* = 7.6, 6H), 6.88 (d, *J* = 7.6, 6H), 2.10 (s, 18H) ppm.

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Scheme 1. Synthesis of copper(I) complexes. (a) L<sub>W</sub>, 1 equiv. of CuCl, CH<sub>3</sub>CN, rt, 14 days, 46%, (b) L<sub>H</sub>, 2 equiv. of CuCl, CH<sub>3</sub>CN, rt, 2hrs, 88%, (c) L<sub>M</sub>, 2 equiv. of CuCl, CH<sub>3</sub>CN, rt, 14 days, 40%, (d) L<sub>H</sub>, 10 equiv. of CuCl, CH<sub>3</sub>CN, rt, 2hrs, 95%, (e) L<sub>W</sub>, 10 equiv. of CuCl, CH<sub>3</sub>CN, rt, 14 days, 73%, (f) L<sub>M</sub>, 4equiv. of CuCl, CH<sub>3</sub>CN, rt, 14days, 91%.

 $^{13}$ C NMR (125 MHz, CD<sub>3</sub>CN):  $\delta$  155.8, 149.0, 141.0, 136.3, 131.7, 127.2, 18.0 ppm. Anal. Calcd for C\_{44}H\_{39}Cl\_1Cu\_1N\_7: C, 69.10; H, 5.14; N, 12.82. Found: C, 69.10; H, 5.11; N, 13.02.

#### Synthesis of L<sub>H</sub>Cu<sub>2</sub>Cl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (2a).

Under N<sub>2</sub> atmosphere hexa(2-pyridyl)benzene (30.0 mg, 0.056 mmol, 1.0 equiv) and CuCl (10.8 mg, 0.112 mmol, 2.0 equiv) was dissolved in acetonitrile (1 mL) at room temperature. Bright yellow block crystals were formed immediately. After 2 h, the yellow so-lution was decanted and the crystalline solid was washed with THF (2 x 1 mL) and dried. The product was isolated as a yellow colored crystalline solid 2a (39.8 mg, 88% yield). The yellow crystals were suitable for single crystal XRD analysis. 1H NMR (500 MHz, CD3CN, 323K):  $\delta$  8.26 (s, 6H), 7.36 (t, J = 7.3, 6H), 7.07 (d, J = 7.6, 6H), 6.97 (t, J = 7.6, 6H) ppm. Anal. Calcd for C40H30Cl2Cu2N8: C, 58.54; H, 3.67; N, 13.65. Found: C, 58.41; H, 3.56; N, 13.57.

#### Synthesis of [L<sub>M</sub>Cu<sub>2</sub>Cl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] · (CH<sub>3</sub>CN) (2b · CH<sub>3</sub>CN).

Under N<sub>2</sub> atmosphere, hexa(2-(5-methylpyridyl))benzene (10.0 mg, 0.016 mmol, 1.0 equiv) and CuCl (3.2 mg, 0.032 mmol, 2.0 equiv) was dissolved in acetonitrile (1 mL) at room temperature. Yellow block crystals were formed in a week. After 2 weeks, the yellow solution was decanted and the yellow crystalline solid was washed with THF (2 x 1 mL) and dried. The product was isolated as a yellow colored crystalline solid **2b** (5.9 mg, 40% yield). Obtained yellow crystals were suitable for single crystal XRD analysis. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  8.08 (s, 6H), 7.15 (d, *J* = 7.8, 6H), 6.89 (s, 6H). 2.11 (s, 18H) ppm. <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN):  $\delta$  155.2, 148.9, 140.9, 136.7, 132.3, 127.2, 18.0 ppm. Anal. Calcd for C<sub>48</sub>H<sub>45</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>9</sub>: C, 60.95; H, 4.80; N, 13.33. Found: C, 60.11; H, 4.72; N, 13.36.

Synthesis of [L<sub>H</sub>Cu<sub>4</sub>Cl<sub>4</sub>]<sub>n</sub> (3).

Under N<sub>2</sub> atmosphere, hexa(2-pyridyl)benzene (10.0 mg, 0.018 mmol, 1.0 equiv) was added in the solution of CuCl (18.0 mg, 0.18 mmol, 10.0 equiv) in acetonitrile (1 mL) at room temperature. Yellow rod-shaped crystals were formed in 2 hours. After 2 days, the yellow solution was decanted and the yellow crystalline solid was washed with THF (2 x 1 mL) and dried. The product was isolated as an orange colored crystalline solid **3** (16.4 mg, 95% yield). Obtained yellow crystals were suitable for single crystal XRD analysis. Anal. Calcd for  $C_{18}H_{12}Cl_2Cu_2N_3$ : C, 46.17; H, 2.58; N, 8.97. Found: C, 46.23; H, 2.51; N, 9.26.

#### Synthesis of $[L_MCu_4Cl_4(CH_3CN)]_n \cdot (CH_3CN)_n$ (4).

Under N<sub>2</sub> atmosphere, hexa(2-(5-methylpyridyl))benzene (15.0 mg, 0.024 mmol, 1.0 equiv) and CuCl (24.0 mg, 0.24 mmol, 10.0 equiv) was dissolved in acetonitrile (1 mL) at room temperature. Orange needle crystals were formed in a week. After 2 weeks, the yellow solution was decanted and the orange crystalline solid was washed with THF (2 x 1 mL) and dried. The product was isolated as an orange crystalline solid **4** (19.4 mg, 73.3% yield). Obtained yellow crystals were suitable for single crystal XRD. analysis. Anal. Calcd for  $C_{46}H_{42}Cl_4Cu_4N_8$ : C, 50.10; H, 3.84; N, 10.16. Found: C, 49.70; H, 3.83; N, 10.11.

#### Synthesis of $[L_M Cu_4 Cl_4]_n \cdot (THF)_n$ (5).

Under N<sub>2</sub> atmosphere, hexa(2-(5-methylpyridyl))benzene (10.0 mg, 0.016 mmol, 1.0 equiv) and CuCl (6.4 mg, 0.064 mmol, 4.0 equiv) was dissolved in acetonitrile (1 mL) and in the vapor diffusion of THF into acetonitrile solution at the room temperature. Red block formed in 2 days. After a week, yellow solution was decanted and Red crystalline solid was washed with THF (2 x 1 mL) and dried. The product was isolated as a red crystalline solid **5** (16.9 mg, 90.9% yield). Obtained yellow crystals were suitable for single crystal XRD analysis. Anal. Calcd for  $C_{100}H_{104}Cl_8Cu_8N_{12}O_4$ : C, 51.55; H, 4.50; N, 7.21. Found: C, 51.43; H, 4.41; N, 7.60.

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and to a chloride anion outward the arene center. The ligands in complexes **2a** and **2b** have the same conformation, functioning as a bis-bidentate ligand with copper(I) chloride.

#### **Result and Discussions**

#### Synthesis and Characterization.

The synthesis of  $\boldsymbol{L}_{\!H}$  and  $\boldsymbol{L}_{\!M}$  was carried out by one-pot procedure. The dropwise addition of 2-bromopyridine to the mixture of 2-phenylpyridine,  $[(\eta^6-C_6H_6)RuCl_2]_2$ , PPh<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> in NMP solution gives the  ${\bf L}_{\! H}$  in affordable yield. To improve the solubility of the ligand, methyl groups were added in the 5position of pyridines.  $\boldsymbol{L}_{\boldsymbol{M}}$  was synthesized by using 2-bromo-5methylpyridine and 5-methyl-2-phenylpyridine as starting materials. The copper(I) complexes of  $L_H$  (2a and 3) and  $L_M$  (1, 2b, 4 and 5) were prepared by combining the ligand with different equivalents of copper(I) chloride as described in the experimental section. The addition of one equivalent of copper(I) chloride to the acetonitrile solution of  $L_{H}$  affords  $L_{H}$ and 2a crystals. Isolation of the complex with one equivalent of copper(I) chloride (1) was achieved by using  $L_M$ . The addition of two equivalents of copper(I) chloride in the acetonitrile solution of  $\boldsymbol{L}_{\!\boldsymbol{H}}$  and the solution of  $\boldsymbol{L}_{\!\boldsymbol{M}}$  resulted in the formation of yellow crystalline solid 2a and 2b, respectively. The addition of more than 4 equivalents of copper(I) chloride in the acetonitrile solution of  $L_H$  and the solution of  $L_M$  induced the formation of coordination polymers, 3 and 4, respectively. The complex 3 was obtained as a yellow crystalline solid while the complex 4 was obtained as an orange crystal. The coordination polymer 5 was obtained as a red crystalline solid by vapor diffusion of THF into an acetonitrile solution of  $L_M$ with 4 equivalents of copper(I) chloride.

Due to the solubility issue of hexa(2-pyridyl)benzene, the copper(I) complexes containing  $L_H$  were formed immediately while the slow formation of the copper(I) complexes with  $L_M$  was observed (~ a week). The color of the complexes 1, 2a, 2b and 3 turned to green after being exposed to air for one day as a sign of oxidative decomposition in the solid state while the color of the complexes 4 and 5 stayed the same, even after 2 days, which indicates their oxidative stability.

The <sup>1</sup>H NMR data of **1**, **2a** and **2b** in  $CD_3CN$  show the same pattern as the signals from the free ligand, even though the overall chemical shifts of each complex moved downfield compared to the ones of the free ligand. The X-ray structures of **1**, **2a**, and **2b** showed that the six pyridine rings are nonequivalent, but the <sup>1</sup>H NMR data do not distinguish the six pyridine units, presumably because of the fast ligand exchange in the copper(I) ions on the NMR time scale.

The  $^{13}$ C NMR spectra of **2a** cannot be obtained due to low solubility.

#### Solid-State Structures of Copper Complexes of $L_H$ and $L_M$ .

Complex **1** has only one copper(I) ion in the ligand. The two pyridine units in the ligand chelate a single copper(I) ion with a typical bite angle of a distorted tetrahedral geometry ( $\angle N(1)-Cu(1)-N(4) = 87.91 (11)^\circ$ ) to form a rigid mononuclear metallacycle that contains seven members. One acetonitrile molecule binds to the copper ion inward to the central arene



Figure 2. Molecular structures of the  $[L_M \text{CuCl}(\text{CH}_3 \text{CN})]2(\text{CH}_3 \text{CN})$  1·2(CH\_3 CN) (a) and  $[L_M \text{Cu}_2 \text{Cl}_2 (\text{CH}_3 \text{CN})_2]2(\text{CH}_3 \text{CN})$  2b-CH\_3 CN (b). Ellipsoids are shown at the 25% and 50% probability levels for 1·2(CH\_3 \text{CN}) and 2b-CH\_3 \text{CN}, respectively. Hydrogen atoms and acetonitrile molecules in the lattice are omitted for clarity.

Two distorted tetrahedral copper(I) centers have the same composition as one of the copper center in complex 1 with the bite angles of 89.92 (13)° (2a) and 89.81 (8)° (2b). Two copper centers are located on the opposite sides of the ring and the remaining two pyridine rings are not involved in the coordination of copper ions. In 1, the C=N triple bond in acetonitrile, which binds on the copper atom, is inclined about 11° toward the central arene compared to its original direction  $(\angle Cu(1) - N(5) - C(29) = 168.9 (3)^{\circ})$ . The C=N triple bond also leans to the one side of the ring. This indicates that there is a  $\pi$ - $\pi$  orbital interaction between the C=N bond and the central phenyl ring. On the other hand, the angle of Cu(1)-N(4)-C(9)(Cu(1)-N(3)-C(15)) is 176.6 (2)° (175.6 (8)°) in 2b (2a). The acetonitrile molecules in 2b (2a) placed straight toward the center of the central phenyl ring indicate that there is no interaction between the C=N bond and the phenyl ring (Figure S26 and S27). This difference may originate from the longer

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distance between the central arene and C=N triple bond in **2b** (**2a**) than the distance in **1**, as two C=N triple bonds on the both



 Figure 3. Molecular structure of the [L<sub>H</sub>Cu<sub>4</sub>Cl<sub>4</sub>]<sub>n</sub> 3 ((a) monomeric unit and (d) polymer), [L<sub>M</sub>Cu<sub>4</sub>Cl<sub>4</sub>(CH<sub>3</sub>CN)]<sub>n</sub> (CH<sub>3</sub>CN)<sub>n</sub> 4 ((b) monomeric unit and (e) polymer), and [L<sub>M</sub>Cu<sub>4</sub>Cl<sub>4</sub>]<sub>n</sub> (THF)<sub>n</sub>

 5 ((c) monomeric unit and (f) polymer). Ellipsoids are shown at the 25%, 25%, and 50% probability levels for 3, 4, and 5, respectively. Hydrogen atoms and lattice solvent molecules are

 omitted
 for
 clarity.

sides of the arene ring may disperse the interaction between the arene and the C=N bonds.

# Solid-State Structures of the 1D Copper(I) Coordination Polymers of $L_{H}$ and $L_{M}.$

The structures of the monomeric units and polymeric structures of the complexes 3, 4 and 5 are shown in Figure 3. In the complex  $\mathbf{3}$ , six pyridine binding sites in  $\mathbf{L}_{\mathbf{H}}$  are involved in the coordination of two sets of copper(I) dimers. Two copper(I) dimers are located on the opposite sides of the central phenyl ring and each dimer binds to the three pyridines. The pyridine on the middle of the copper(I) dimer is perpendicular to the attached arene units (Figure 3a). The distance between Cu(1) and N(1) is 2.045 (5) Å while the distance between Cu(1) and N(2) is 2.392(7) Å, which is longer than the typical Cu–N bond distance. Each monomer is linked with tetranuclear copper(I) clusters to form a 1D coordination polymer. The vertical distance between each monomer was measured as 7.910 Å. The  $Cu_4Cl_4$  cluster of **3** is constituted by a planar  $Cu_4Cl_2$  ring (Figure 4a). The bond length of the bimetallic coppers in complex 3 is 2.657 (5) Å (Cu(1)-Cu(1')).

In the complex **4**, the ligand shows almost the same configuration as the one of the ligand in **3**. Each binding site in the  $L_M$  ligand is coordinated by two sets of copper(I) dimers. Two copper(I) dimers are located on the opposite sides of the ring. The distance between Cu(2) and N(3) (2.081 (3) Å) is shorter than the distance between Cu(1) and N(3) (2.832 (5) Å). Likewise, the distances between Cu(4) and N(7) (2.278 (3) Å) is shorter than the distance between Cu(3) and N(7) (2.719

(5) Å). One chloride anion on the copper connects each monomeric complex to expand the unit to the 1D coordination polymer. The vertical distance between each monomer is 6.806 Å. The structure of the  $Cu_4Cl_4$  metal cluster in **4** is shown in **Figure 4b**. The dis-tances between the copper atoms in complex **4** correspond to 2.728 (8) Å (Cu(2)–Cu(1)), 2.905 (5) Å (Cu(2)–Cu(3)), and 2.808 (2) Å (Cu(3)–Cu(4)), indicating that all four copper(I) ions in the cluster stand in a line, as they interact with each other.

From comparing **3** and **4**, it is evident that six methyl groups on the ligand provide a steric effect that causes a dramatic change in the formation of copper(I) chloride clusters on each polymer. In **3**, each coordination polymer is closely packed while **4** does not show close packing due to the steric hindrance of methyl groups (**Figure S29** and **S30**). Thus, in **4**, the solvent molecules were diffused into the crystal lattice as well as the metal ion centers during the complexation and crystallization processes since methyl groups interrupt the close packing of the 1D coordination polymers in **4** and create a void volume in the crystal lattice.

Despite having the same component with the same stoichiometry as the complex **4**, complex **5** has an entirely different copper chloride cluster and connectivity. The ligand binds with four copper atoms. Two copper atoms (Cu(1) and Cu(2')) on the same side of the ligand are bridged by a chloride anion located 3.369 Å away from each other, which does not support copper-copper interactions.<sup>34</sup> On each side, one copper ion (Cu(1)) coordinates with two pyridines while the other copper ion (Cu(2') coordinates with the remaining pyridine. The copper-nitrogen bond distances range from

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2.024 (3) (Cu(2)–N(3)) to 2.102 (1) Å (Cu(1)–N(1)), which are in accordance within the range of the common copper-nitrogen bond distance. Each monomer is linked with the stair-step  $Cu_4Cl_4$  cluster<sup>35</sup> to form a coordination polymer. In addition, the distance between the



copper atoms in complex **5** is 2.781 (1) Å (Cu(1) and Cu(2)) for bimetallic coppers in the cluster. The vertical distance between each monomer is 7.914 Å.

The two coordination polymers of  $L_M$  described above, 4 and 5, show the solvent effect in the formation of the copper(I) complex. Crystals of 4 were grown from a solution containing acetonitrile predominantly. In the crystal structure, acetonitrile was found to have occupied the one site of the copper(I) chloride cluster and free acetonitriles were included uniformly in the void of the polymer (Figure S30). Meanwhile, the crystal structure of 5 revealed that no solvent molecules are coordinated with the copper(I) centers and only THF molecules were found in the lattice of the crystals. This difference between 4 and 5 implies that some amount of THF in the acetonitrile solution carried out a key role in controlling the moiety of the coordination polymers (Figure S31).

#### Solution Behaviours of 1, 2a and 2b.

In the <sup>1</sup>H NMR spectra, complexes **1**, **2a** and **2b** show the temperature dependence that indicates dynamic exchange processes occurring in the solutions of **1**, **2a** and **2b**. To study this behaviour of complex **2a**, <sup>1</sup>H variable temperature (VT) NMR studies in d<sub>3</sub>-acetonitrile were conducted (for analysis of the <sup>1</sup>H NMR spectra of **1** and **2b**, see **Figure S16**, **S17**, and **S18**). **Figure 5** shows the <sup>1</sup>H VT-NMR spectra at the range of 323K to 223K. At 323K, <sup>1</sup>H NMR spectra showed only four sets of peaks at 8.27, 7.36, 7.07, and 6.97 ppm, respectively, indicating only

one set of 2-pyridyl chemical shift. This suggests that all six pyridines in the ligand attribute equally to the dynamic motions of copper(I) ligand complexes. As the temperature decreases, the signals became broad due to the comparable rate of the dynamic motions on the NMR time scale. The coalescence of the signal was observed at 273K. A decrease in temperature led to the separation of the signals from each proton due to the slower exchange process. At 223K, all proton signals become narrow and split to each peak.

Complex 2a has four coordinating pyridine rings and two free pyridine rings in the ligand so that the proton peaks should be split to a ratio of 2:1 if there is no accidental degeneracy of each proton peak. Indeed, integration values obtained from all signals at 223K were measured at a 2:1:2:1:2:1:2:1 ratio in accordance with the structure attained by X-ray crystal analysis (Figure 2). In <sup>1</sup>H two-dimensional exchange spectroscopy (2D EXSY) spectra of 2a at 233K, the interconversions between the proton signals of a free pyridine and a bound pyridine to copper were detected (Figure S14). The signals of the phenyl resonance region in <sup>1</sup>H 2D EXSY showed cross peaks between the hydrogen pairs of the coordinating pyridines and the free pyridines in 2a. These cross peaks strongly indicated an exchange process between the non-coordinating pyridines and the pyridines coordinating with copper(I) ion in 2a, either via an intra- or intermolecular pathway. In addition, <sup>1</sup>H NMR spectra of **2a** solution at 223K showed other signals at a range of 8.3 to 8.4 ppm. In 2D EXSY spectra of 2a solution, there are other cross peaks between this signals and the signals of 2a. This cross peak shows that there are intermediates involved in the dynamic process of 2a. The other signals from the intermediates cannot be distinguished due to an intensive overlap. The activation parameters,  $\Delta H^{*} = 16.47 \pm 0.02$  kcal/mol,  $\Delta S^{*} = 13.40 \pm 0.16$ e.u..





**Figure 6.** Photoluminescence emission spectra of **3**. **4**, and **5** in the solid state at  $\lambda_{exc}$  = 380 nm.

 $\Delta G^{\dagger}$  = 13.36 ± 0.11 kcal/mol, and E<sub>a</sub> = 16.9 kcal/mol for the exchange process of 2a were derived from the Eyring plot (Figure S19). The positive  $\Delta S^{\dagger}$  value indicates a dissociative mechanism which is viable for a d<sup>10</sup> electronic configuration with no ligand field stabilization. The addition of copper(I) chloride to the solution of 2a produces a similar signals of 2a in the <sup>1</sup>H NMR spectra at 233K while the solution with one equivalent of copper(I) chloride shows different signals compared with the signals of 2a (Figure S18). This indicates

that, although there are more than 2 equivalents of copper(I) chloride in the solution the ligand binds with only two equivalents of copper(I) ion in the solution. The 1D and 2D  $^{1}$ H NMR spectra of 2a indicated that complex 2a mainly exists in the solution with a substoichiometric amount of the other unknown species as an intermediate of the dynamic process.

#### Luminescent Properties of 3, 4, and 5.

In the solid state at room temperature, 3, 4, and 5 exhibited yellow-red luminescence upon the exposure of ultraviolet excitation ( $\lambda_{exc}$  = 380 nm). The emission maximum ( $\lambda_{max}$ ) of **3** was 577 nm while the emission maximum of 4 (612 nm) and 5 (624 nm) were redshifted relative to that of 3 (Figure S19). All complexes contained at least one Cu-Cu bond shorter than the van der Waals radii (2.80 Å), and thus implies cuprophilic interaction (Figure S28). The luminescent behaviours of 3, 4, and 5 were attributed to the cluster centered excited states along with a chloride to copper charge transfer and coppercentered transition (d  $\rightarrow$  s).<sup>36</sup> The photoluminescence intensity of 4 was five times higher than that of 3 and 50 times higher than that of 5. Variations in the intensity and emission maxima of 3, 4, and 5 result from their respective differences in the structure of Cu<sub>4</sub>Cl<sub>4</sub> clusters and the supramolecular environments.

#### Conclusion

Six copper(I) complexes of hexa(2-pyridyl)benzene derivatives,  $L_{H}$  and  $L_{M}$ , were newly prepared and characterized by single crystal X-ray diffraction. Compounds 1 and 2 (2a and 2b) contained 1 and 2 equivalents of copper(I) chloride, respectively. Interesting solution behaviour of 1, 2a and 2b were studied by <sup>1</sup>H VT-NMR and 2D EXSY, indicating a dynamic motion occurring in the acetonitrile solutions of 1, 2a and 2b. The addition of four equivalents of copper(I) chloride to the ligand in different conditions affords three different coordination polymers. In the 1-D coordination polymers, 3, 4, and 5, every binding sites in the ligand are involved in coordination with four copper(I) atoms. The addition of six methyl groups on the ligand and changes of the solvent caused a dramatic effect on the structure of copper(I) chloride clusters. Due to different structures of the copper cluster, each coordination polymer exhibited different luminescence behaviour. We believe that the understanding on these coordination behaviours of hexa(2-pyridyl)benzene systems provide a new choice of the building block for the potential application on supramolecular chemistry and molecular machines.

#### **Conflicts of interest**

There are no conflicts to declare

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