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**Substituent-Controlled Constructions of M<sub>2</sub>L<sub>4</sub> Cage and 1D Network Structures for Cu(II) Complexes with Bis-benzimidazole Ligands**

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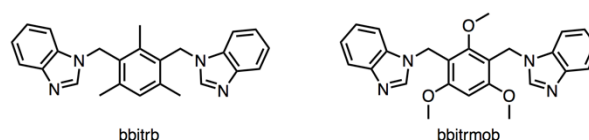
1 Multicopper(II) complexes were synthesized using bis-  
2 benzimidazole ligands expressed as B-CH<sub>2</sub>-C<sub>6</sub>R<sub>4</sub>-CH<sub>2</sub>-  
3 B (B = benzimidazole, R = Me (bbitrb), OMe  
4 (bbitmob)). For the reactions with Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and  
5 CuSO<sub>4</sub>·5H<sub>2</sub>O, bbitrb gave M<sub>2</sub>L<sub>4</sub> cage complexes, while  
6 bbitrmob gave a M<sub>2</sub>L<sub>4</sub> cage complex and a new 1D  
7 coordination polymer. The substituent-controlled  
8 syntheses of the Cu(II) complexes are described.

9  
10 **Keywords:** bis-benzimidazole, M<sub>2</sub>L<sub>4</sub> cage, Coordination  
11 **polymer.**

12 Constructions of multinuclear metal complexes with  
13 cage and network structures have attracted much attention  
14 because of the unique functions of such complexes, such as  
15 separation, and storage of guest molecules or guest ions in  
16 the space created in the frameworks.<sup>1-4</sup> Among the various  
17 bridging ligands that have been used for their syntheses, bis-  
18 benzimidazole ligands expressed as B-CH<sub>2</sub>-C<sub>6</sub>R<sub>4</sub>-CH<sub>2</sub>-B  
19 (B = benzimidazole, R = H, Me, or OMe) have afforded  
20 unique M<sub>2</sub>L<sub>2</sub>,<sup>5</sup> M<sub>2</sub>L<sub>4</sub>,<sup>5-11</sup> and M<sub>2</sub>L<sub>3</sub> cages,<sup>5,6</sup> as well as  
21 network structures.<sup>7,11,12</sup>

22 It has been shown that 1,4-bis((1*H*-imidazol-1-  
23 yl)methyl)benzene (*p*-bix), which is the ligand with R = H,  
24 affords [Cu(*p*-bix)](ClO<sub>4</sub>)<sub>2</sub>,<sup>13</sup> which has a 1D network  
25 structure, by the reaction with Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. We have  
26 reported previously that the tetramethyl derivative, 1,4-  
27 bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (*p*-biteb),  
28 affords a M<sub>2</sub>L<sub>4</sub> cage complex [ClO<sub>4</sub> ⊂ Cu<sub>2</sub>(*p*-  
29 biteb)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>]ClO<sub>4</sub> by the reaction with Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O.<sup>8</sup>  
30 These results indicate that the R groups of B-CH<sub>2</sub>-C<sub>6</sub>R<sub>4</sub>-  
31 CH<sub>2</sub>-B affect the framework motifs of the obtained metal  
32 complexes. Although control of the framework motifs by  
33 the R groups is an attractive subject, it has not been well  
34 explored.

35 In the series of B-CH<sub>2</sub>-C<sub>6</sub>R<sub>4</sub>-CH<sub>2</sub>-B ligands, 1,3-  
36 bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene  
37 (bbitrb) has been widely used for the synthesis of  
38 multinuclear metal complexes.<sup>5,6,14</sup> To study the effects of R  
39 on the structures of the obtained complexes, and which  
40 create the new multinuclear metal complexes, we  
41 synthesized a new bridging ligand 1,3-bis(benzimidazol-1-  
42 ylmethyl)-2,4,6-trimethoxybenzene (bbitmob), the  
43 trimethoxy derivative of bbitrb, and then characterized the  
44 Cu(II) complexes obtained with this ligand. The structures  
45 of bbitrb and bbitrmob are illustrated in Scheme 1.



46  
47 **Scheme 1.** Structures of bbitrb and bbitrmob.  
48  
49

50 The M<sub>2</sub>L<sub>4</sub> complex [ClO<sub>4</sub> ⊂ Cu<sub>2</sub>(bbitrb)<sub>4</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>)<sub>2</sub>  
51 (**1a**) was characterized by Su et al.<sup>5</sup> as a reaction product of  
52 Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O with bbitrb. Because of the relatively poor  
53 quality of the reported crystal structure of **1a**, we proceeded  
54 to isolate the M<sub>2</sub>L<sub>4</sub> complex from the reaction of bbitrb with  
55 Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, in a mixed solution of THF/Me<sub>2</sub>CO, and  
56 then (in this work) we redetermined the structure of the  
57 complex for structural comparison with other complexes.

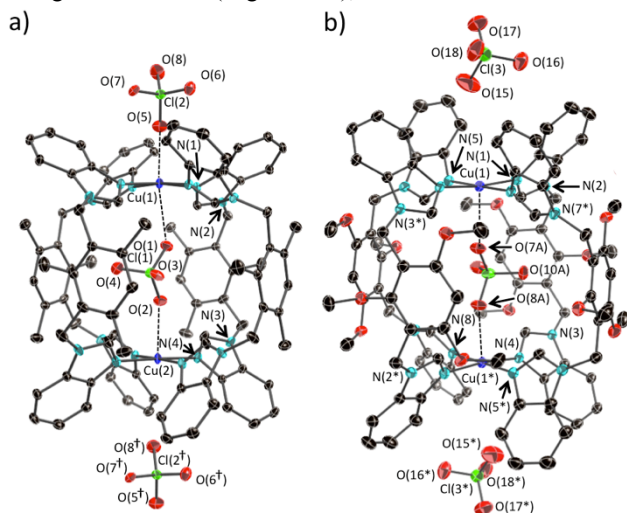
58 We have previously shown that the M<sub>2</sub>L<sub>4</sub> cage  
59 complex [SO<sub>4</sub> ⊂ Cu<sub>2</sub>(bbitrb)<sub>4</sub>](SO<sub>4</sub>) is obtained by the  
60 reaction of CuSO<sub>4</sub>·5H<sub>2</sub>O with bbitrb.<sup>10</sup> In this work, we  
61 found that bbitrmob also gave a M<sub>2</sub>L<sub>4</sub> cage complex [ClO<sub>4</sub>  
62 ⊂ Cu<sub>2</sub>(bbitmob)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub>(MeCN)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> (**2**) by the  
63 reaction with Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. Furthermore, the ligand did  
64 not afford the M<sub>2</sub>L<sub>4</sub> cage complex by the reaction with  
65 CuSO<sub>4</sub>·5H<sub>2</sub>O, but yielded a 1D coordination polymer  
66 [Cu<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(bbitmob)<sub>2</sub>](MeCN)(H<sub>2</sub>O) (**3**). This paper  
67 describes the syntheses and structures of the Cu(II)  
68 complexes with bis-benzimidazole ligands, and the effects  
69 of the methoxy groups (as R) of the ligands on the obtained  
70 structures.

71 The ligand bbitrmob was prepared from 1,3,5-  
72 trimethoxybenzene, following a general procedure.  
73 Treatment of the starting material with 1,3,5-trioxane and  
74 30% HBr in glacial acetic acid afforded 2,4-  
75 bis(bromomethyl)-1,3,5-trimethoxybenzene. Reaction of the  
76 precursor with benzimidazole and KOH then afforded the  
77 target ligand, bbitrmob. The details are shown in the  
78 Supporting Information.

79 Diffusion of an Me<sub>2</sub>CO solution of bbitrb (prepared  
80 according to a method reported in the literature) into a  
81 MeOH solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O afforded [ClO<sub>4</sub> ⊂  
82 Cu<sub>2</sub>(bbitrb)<sub>4</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>)<sub>2</sub>(Me<sub>2</sub>CO)<sub>4</sub> (**1b**) as purple crystals.  
83 Complex **2** was also isolated as purple crystals after  
84 diffusion of an MeCN solution of bbitrmob into an Me<sub>2</sub>CO  
85 solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. Figure 1 shows the M<sub>2</sub>L<sub>4</sub> cage  
86 structures of **1b** and **2**.<sup>15</sup> For **1b**, there is a crystallographic  
87 C<sub>4</sub> axis, which runs through the two Cu<sup>II</sup> centers. For **2**,  
88 there is a crystallographic inversion center in the M<sub>2</sub>L<sub>4</sub> cage.

89 The Cu-N distances around the Cu<sup>II</sup> centers are 1.9975  
(19) and 1.984 (2) Å (avg. 1.991 Å) for **1b**; for **2** they are in

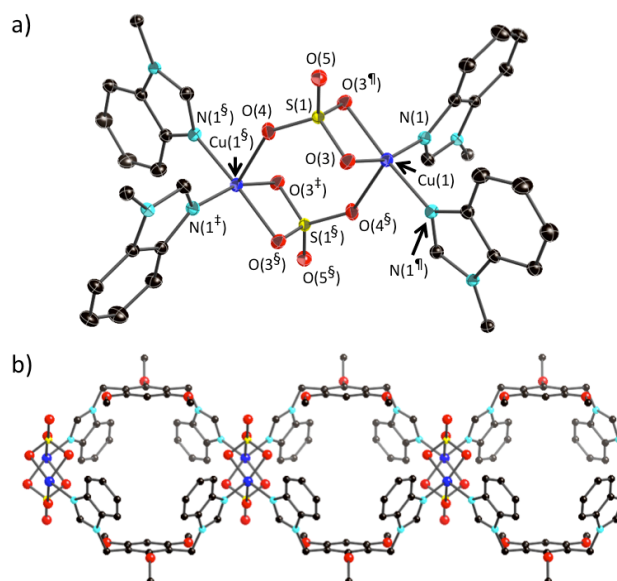
1 the range 1.983–1.996 Å (avg. 1.987 Å). The values are  
 2 referred to in the caption of Figure 1. Both complexes  
 3 include a  $\text{ClO}_4^-$  in the cage and three  $\text{ClO}_4^-$  outside the cage.  
 4 The  $\text{ClO}_4^-$  in **1b**, which is disordered at the four positions  
 5 due to the crystallographic  $C_4$  axis, associates weakly with  
 6 the two  $\text{Cu}^{\text{II}}$  centers ( $\text{Cu}(1)\cdots\text{O}(1) = 2.664$  Å and  $\text{Cu}(2)\cdots$   
 7  $\text{O}(2) = 2.458$  Å, avg. 2.561 Å). These distances are shorter  
 8 than the sum of the van der Waals radii of Cu (1.4 Å) and O  
 9 (1.52 Å). The  $\text{ClO}_4^-$  in the cage of **2**, which is disordered at  
 10 the four positions, also weakly associates with the  $\text{Cu}^{\text{II}}$   
 11 centers (Figure S3). The Cu---O distances, which are in the  
 12 range 2.51–2.61 Å (avg. 2.55 Å), are close to those of **1b**.



13  
 14  
 15 **Figure 1.** Thermal ellipsoids of the molecular structures of  
 16 **1b** (a) and **2** (b) at 30% probabilities. Disordered  $\text{ClO}_4^-$ ,  
 17 guest organic molecules, other  $\text{ClO}_4^-$  located side the cage,  
 18 and hydrogen atoms are omitted for clarity. Color code: blue,  
 19 copper; red, oxygen; green, chlorine; cyan, nitrogen; black,  
 20 carbon. Symmetry operation  $^\dagger X, Y, -1+Z$ ,  $^* -X, -Y, -Z$ .  
 21 Selected bond distances for **1b** are  $\text{Cu}(1)\text{--N}(1) = 1.9975$   
 22 (19);  $\text{Cu}(2)\text{--N}(4) = 1.984$  (2) Å, and for **2** are  $\text{Cu}(1)\text{--N}(1) =$   
 23  $1.983$  (2);  $\text{Cu}(1)\text{--N}(5) = 1.996$  (2);  $\text{Cu}(1)\text{--N}(4^*) = 1.9799$   
 24 (19);  $\text{Cu}(1)\text{--N}(8^*) = 1.987$  (2) Å.

25  
 26 Of the three  $\text{ClO}_4^-$  outside the cage of **1b**, one  $\text{ClO}_4^-$   
 27 associates with the  $\text{Cu}^{\text{II}}$  center ( $\text{Cu}(1)\cdots\text{O}(5) = 2.401$  Å).  
 28 Although this anion locates between the two  $\text{Cu}^{\text{II}}$  centers of  
 29 the two different  $\text{M}_2\text{L}_4$  cages, it does not associate with the  
 30 other  $\text{Cu}^{\text{II}}$  center ( $\text{Cu}(2)\cdots\text{O}(8^\ddagger) = 3.847$  Å). That is, there  
 31 are no coordinating molecules or anions above the Cu(2)  
 32 center. As a result, Cu(1) is based on the elongated  
 33 octahedral, while Cu(2) is based on the distorted square  
 34 pyramidal. In the case of **2**, although  $\text{ClO}_4^-$  outside the cage  
 35 is observed above each  $\text{Cu}^{\text{II}}$  center, the anion does not  
 36 associate with the  $\text{Cu}^{\text{II}}$  center ( $\text{Cu}(1)\cdots\text{O}(15) = 4.22$  Å).  
 37 Furthermore, the two  $\text{Cu}^{\text{II}}$  centers of **2** are based on the  
 38 distorted square pyramidal. For both complexes, the other  
 39  $\text{ClO}_4^-$  are located in the hydrophobic space created among  
 40 the  $\text{M}_2\text{L}_4$  cages.

41



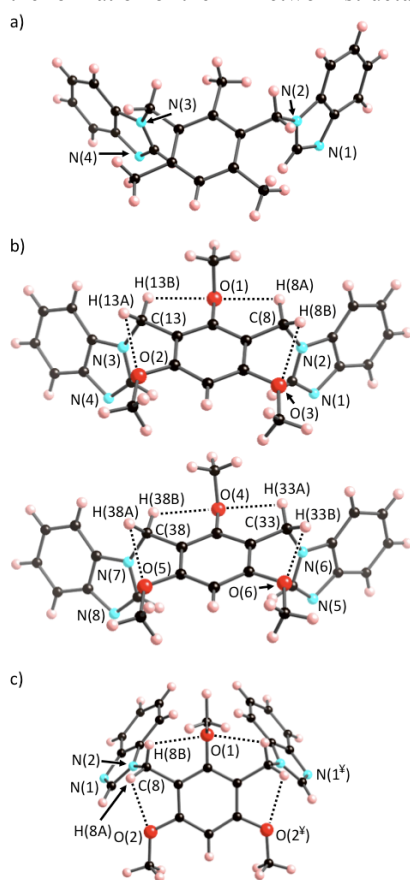
42  
 43 **Figure 2.** Thermal ellipsoids of the coordination  
 44 environments of **2** at 30% probabilities (a) and the 1D  
 45 structure, which is constructed by bridging the  $\text{Cu}_2(\text{SO}_4)_2$   
 46 units with bbitrmob (b). Symmetry operation  $^\ddagger X, -Y, Z$ ,  $^\S 1-$   
 47  $X, Y, 1-Z$ ,  $^\ddagger 1-X, -Y, 1-Z$ .

48  
 49 Complex **3** was isolated as blue crystals by diffusion of  
 50 an MeCN solution of bbitrmob into a MeOH solution of  
 51  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The 1D framework is constructed by bridging  
 52 the  $\text{Cu}_2(\text{SO}_4)_2$  units with 2 equiv bbitrmob. Figure 2 shows  
 53 the coordination circumstances around the  $\text{Cu}^{\text{II}}$  centers and  
 54 structure of the 1D chain. The two  $\text{Cu}^{\text{II}}$  ions are connected  
 55 by two  $\text{SO}_4^{2-}$ . Each  $\text{SO}_4^{2-}$  binds to two  $\text{Cu}^{\text{II}}$  centers in the  
 56 monodentate and bidentate chelating fashions, respectively.  
 57 Two bbitrmob connect these units, producing a 1D network  
 58 along the  $b$  axis (Figure 2b). There are crystallographic  
 59 mirrors perpendicular to the chains, and the  $C_2$  axis runs  
 60 through the 1D chain. The space created by the two  
 61  $\text{Cu}_2(\text{SO}_4)_2$  units and two bbitrmob in the chain has a size of  
 62 about  $8.5 \times 7.5$  Å<sup>2</sup> at the middle part. **For the bbitrmob, the**  
 63 **plane-plane angle defined by the benzimidazole ring and**  
 64 **phenyl ring with methoxy groups is  $68.7(1)^\circ$ . The size of the**  
 65 **void space, which has volume of about  $225$  Å<sup>3</sup>, in the 1D**  
 66 **chain decreases to about  $6.0 \times 5.0$  Å<sup>2</sup> at the top and bottom**  
 67 **of the space due to capping by the phenyl rings of the**  
 68 **benzimidazole and methoxy groups of the bbitrmob. A  $\text{H}_2\text{O}$**   
 69 **molecule is trapped in the space, with remarkable disorders,**  
 70 **which were solved at O(6A), O(7B), O(8C), and O(9A) with**  
 71 **occupancies of 0.10, 0.10, 0.15, and 0.20, respectively.**

72 As mentioned above, the reaction of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$   
 73 with bbitrmob gave a  $\text{M}_2\text{L}_4$  cage complex, while the  
 74 reaction of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with the ligand gave the 1D  
 75 coordination polymer. The ligands  $\text{B}-\text{CH}_2-\text{C}_6\text{R}_4-\text{CH}_2-\text{B}$   
 76 often give the  $\text{M}_2\text{L}_4$  cage complexes that trap a  $\text{ClO}_4^-$ .<sup>5-9</sup> We  
 77 have shown that this tendency is because the  $\text{ClO}_4^-$   
 78 functions as the template guest for the  $\text{M}_2\text{L}_4$  cage  
 79 constructions due to the hydrophobic surface.<sup>11</sup> In contrast  
 80 to  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$  would not function as the template guest for

1 the  $M_2L_4$  cage constructions due to the hydrophilic surface.  
 2 The formation of the  $M_2L_4$  cage that traps a  $SO_4^{2-}$  would  
 3 result from strong Cu---O bond formations between the Cu<sup>II</sup>  
 4 center and  $SO_4^{2-}$ , as reflected by the shorter Cu---O  
 5 distances. For example, the distances (about 2.1 Å) observed  
 6 in  $[SO_4 \subset Cu_2(\text{bbitrb})_4](SO_4)^{10}$  are remarkably shorter than  
 7 those of **1b** (avg. 2.561 Å) and **2** (avg. 2.55 Å).

8 The Cu—N distances (avg. 1.986 Å) of **2** are slightly  
 9 shorter than those (avg. 1.991 Å) of **1b**. It is well known that  
 10 a methoxy group has stronger electron-donating properties  
 11 than a methyl group. The stronger electron-donating  
 12 property of bbitrmob would form stronger Cu—N bonds,  
 13 and then decreases the acidity at the Cu<sup>II</sup> center. This effect  
 14 would weaken the Cu---O bonds between the Cu<sup>II</sup> center  
 15 and  $SO_4^{2-}$  in the  $M_2L_4$  cage with bbitrmob. As a result, the  
 16  $[SO_4 \subset Cu_2(\text{bbitrmob})_4]^{2+}$  structure becomes unstable,  
 17 leading to the formation of the 1D network structure.



18 **Figure 3.** Structures of bbitrmob in **1b** (a), **2** (b), and **3** (c).  
 19 Symmetry operation  $\bar{Y}X, 1-Y, Z$ .

22 Figure 3 shows X-ray structures of the ligands in **1b**, **2**,  
 23 and **3**. Complex **2** has two crystallographically independent  
 24 bbitrmob ligands with similar structures. It is evident that  
 25 conformations of the ligands in the  $M_2L_4$  cages, i.e., bbitrb  
 26 in **1b** and bbitrmob in **2**, are similar, and quite different from  
 27 that of bbitrmob in **3**. The conformation of B—CH<sub>2</sub>—C<sub>6</sub>R<sub>4</sub>—  
 28 CH<sub>2</sub>—B would be fixed sterically in the  $M_2L_4$  cage structures.

29 One of the unique features of the bbitrmob ligand is the  
 30 formation of the intraligand C—H...O interactions. The C—  
 31 H...O interaction is a type of hydrogen bond. When the  
 32 interactions are formed, in most cases, the C---O distance is  
 33 shorter than 3.0 Å, and the C—H...O angle is in the range  
 34 90–180°. Figure 3b and 3c illustrates the plausible C—H...O  
 35 interactions with dotted lines. Table 1 summarizes the C—  
 36 H...O angles and C---O and O...H distances estimated from  
 37 the crystal structures. It was found that all methoxy groups  
 38 of bbitrmob form C—H...O interactions with hydrogen  
 39 atoms of methylene groups in **2** and **3**, although the C(38)—  
 40 H(38A)...O(5) interaction in **2** is significantly weak, as  
 41 estimated by the significantly small C—H...O angle (85.90°)  
 42 and long O...H distance (2.64 Å). Their bond formations  
 43 would stabilize the structures of the obtained complexes.  
 44 These interactions would be useful for the construction of  
 45 new multinuclear structures for metal complexes. Studies  
 46 are in progress.

48 **Table 1.** The C—H...O angles  $\alpha$  (°) and the estimated C...O  
 49 ( $d_1$ ) and O...H distances  $d_2$  (Å) in bbitrmob of **2** and **3**.

C—H...O interactions	$\alpha$	$d_1$	$d_2$
Complex 2			
C(8)—H(8A)...O(1)	104.65	2.84	2.42
C(8)—H(8B)...O(3)	91.86	2.73	2.51
C(13)—H(13A)...O(2)	89.39	2.70	2.52
C(13)—H(13B)...O(1)	106.06	2.87	2.44
C(33)—H(33A)...O(4)	100.74	2.84	2.46
C(33)—H(33B)...O(6)	97.59	2.76	2.44
C(38)—H(38A)...O(5)	85.90	2.75	2.64
C(38)—H(38B)...O(4)	108.10	2.84	2.38
Complex 3			
C(8)—H(8A)...O(2)	92.21	2.71	2.49
C(8)—H(8B)...O(1)	105.75	2.86	2.43

63 In summary, we have designed a new bis-  
 64 benzimidazole ligand, bbitrmob. Reactions of the ligand  
 65 with  $Cu(ClO_4)_2 \cdot 6H_2O$  and  $CuSO_4 \cdot 5H_2O$  gave a  $M_2L_4$  cage  
 66 complex and 1D coordination polymer. The formation of  
 67 Cu<sup>II</sup> complexes with different structures is in contrast to  
 68 products obtained with the ligand bbitrb, which gave  $M_2L_4$   
 69 cage complexes after similar treatment. The structure  
 70 formation obtained when using bbitrmob would be the result  
 71 of a decrease in the acidity at the Cu<sup>II</sup> center due to the  
 72 strong electron-donating effects of the three methoxy groups.  
 73 These results imply that the structures of the complexes  
 74 obtained are conveniently controlled by the R groups in the  
 75 ligands.

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81 Supporting Information is available on  
 82 <http://dx.doi.org/xx.xxxx>



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- 97 15 Data collections were carried out on a Rigaku VariMax  
98 diffractometer using multi-layer mirror monochromated Mo-K $\alpha$   
99 radiation (1.2-kW rotating anode) and a PILATUS 200K detector.  
100 Crystallographic data for **1b**: C<sub>112</sub>H<sub>120</sub>Cu<sub>4</sub>Cu<sub>2</sub>N<sub>16</sub>O<sub>20</sub> (MW:  
101 2279.11), tetragonal, space group *I4* (No. 79), *a* = 18.5297(2), *c*  
102 = 15.9530(3) Å, *V* = 5477.46 (16) Å<sup>3</sup>, *Z* = 2,  $\rho(\text{caclcd})$  = 1.382 g  
103 cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha)$  = 0.562 mm<sup>-1</sup>, *T* = 173 K,  $\lambda$  = 0.71073 Å,  $\omega$   
104 scan, reflections collected/unique reflections/ parameters refined:  
105 7257/6545/416, *R*<sub>int</sub> = 0.0518, final *R*1 = 0.0378 (*I* > 2 $\sigma$ (*I*)),  
106 *wR*2 = 0.1001 (all data), GOF = 1.040. CCDC 1988632.  
107 Crystallographic data for **2**: C<sub>104</sub>H<sub>106</sub>Cl<sub>4</sub>Cu<sub>2</sub>N<sub>18</sub>O<sub>30</sub> (MW:  
108 2356.99), triclinic, space group *P*-1 (No. 2), *a* = 14.1410 (11), *b*  
109 = 14.3853 (18), *c* = 15.646 (2) Å,  $\alpha$  = 117.163(4),  $\beta$  = 92.640(3),  
110  $\gamma$  = 91.279(2)°, *V* = 2825.4 (6) Å<sup>3</sup>, *Z* = 1,  $\rho(\text{caclcd})$  = 1.385 g cm<sup>-3</sup>,  
111  $\mu(\text{Mo K}\alpha)$  = 0.554 mm<sup>-1</sup>, *T* = 173 K,  $\lambda$  = 0.71075 Å,  $\omega$  scan,  
112 reflections collected/unique reflections/ parameters refined:  
113 38608/12754/854, *R*<sub>int</sub> = 0.0563, final *R*1 = 0.0592 (*I* > 2 $\sigma$ (*I*)),  
114 *wR*2 = 0.1690 (all data), GOF = 0.856. CCDC 1988630.  
115 Crystallographic data for **3**: C<sub>27</sub>H<sub>29</sub>CuN<sub>5</sub>O<sub>8</sub>S (MW: 647.16),  
116 monoclinic, space group *C2/m* (No. 12), *a* = 18.2894 (10), *b* =  
117 11.8659 (5), *c* = 16.1202 (8) Å,  $\beta$  = 117.9210 (14)°, *V* = 3091.2  
118 (3) Å<sup>3</sup>, *Z* = 4,  $\rho(\text{caclcd})$  = 1.390 g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha)$  = 0.828 mm<sup>-1</sup>,  
119 *T* = 173 K,  $\lambda$  = 0.71075 Å,  $\omega$  scan, reflections collected/unique  
120 reflections/ parameters refined: 24329/3693/244, *R*<sub>int</sub> = 0.0197,  
121 final *R*1 = 0.0472 (*I* > 2 $\sigma$ (*I*)), *wR*2 = 0.1414 (all data), GOF =  
122 1.100. CCDC 1988631.

