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# 1D Tubular Chains and 3D Polycatenane Frameworks Constructed with $\text{Cu}_2\text{X}_2$ Dimers ( $\text{X} = \text{Br}^-$ , $\text{I}^-$ , $\text{CN}^-$ ) and Flexible Dipyridyl Spacers

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**ABSTRACT:** Five new coordination polymers based on copper(I) halides or pseudohalide,  $[\text{Cu}_2\text{Br}_2(\text{bpe})_2]$  (**1**),  $[\text{Cu}_2(\text{CN})_2(\text{bpe})]$  (**2**),  $[\text{Cu}_2\text{Br}_2(\text{bpp})_2]$  (**3**),  $[\text{Cu}_2\text{I}_2(\text{bpp})_2] \cdot (\text{toluene})$  (**4**), and  $[\text{Cu}_2\text{I}_2(\text{bpp})_2] \cdot (\text{naphthalene})$  (**5**) ( $\text{bpe} = 1,2\text{-bis(4-pyridyl)ethane}$ ,  $\text{bpp} = 1,3\text{-bis(4-pyridyl)propane}$ ), have been synthesized by solvothermal methods and characterized by X-ray crystallography. All structures can be deconstructed into rhomboid  $\text{Cu}_2\text{X}_2$  ( $\text{X} = \text{Br}$ ,  $\text{I}$ ,  $\text{CN}$ ) dimers and flexible bridged dipyridyl ligands. In **1**, two sets of (4,4) layers adopt the “diagonal–diagonal” 4-fold interpenetration mode, giving high catenation and generating a novel  $2\text{D} \rightarrow 3\text{D}$  interpenetrating framework. **2** is a 3D (3,6)-connected rutile-like net of 2-fold interpenetration. Each 3D rutile-like net consists of 2D flat  $[\text{Cu}_2(\mu_3\text{-CN})(\mu\text{-CN})]$  layers and  $\text{bpe}$  pillars. **3** is a 2D polycatenane formed by interlocking of 1D double-stranded tubular chains. 1D double-stranded tubular chains are also present in **4** and **5**, similar to that found in **3**; however, the presence of toluene or naphthalene guests prevents the 1D double-stranded tubular chains from interpenetration. The photoluminescent properties of **1** and **3** in the solid state have been studied.

## Introduction

Rational design and synthesis of net-based coordination polymers with intriguing structural features and potential useful properties, for example, magnetism, photoluminescence, electric conductivity, adsorption, and heterogeneous catalysis, are of great current interest.<sup>1</sup> Among the different types of net-assembled molecular frameworks, the networks constructed from interlocking and interweaving of individual motifs such as polycatenation, Borromean, polythreading, and polyknotting have received much attention in recent years not only for their intriguing architectures and topologies but also from the perspective of establishing useful relationships between structure and properties.<sup>2</sup>

Copper(I) halides<sup>3</sup> have been employed as inorganic components in the construction of novel coordination polymers with various structural motifs such as a linear  $\text{Cu}_2\text{Cl}$  dimer,<sup>4</sup> square (rhomboid)  $\text{Cu}_2\text{X}_2$  ( $\text{X} = \text{Br}^-$ ,  $\text{I}^-$ ) dimers,<sup>5</sup> cubane or step-cubane  $\text{Cu}_4\text{X}_4$  tetramers,<sup>6</sup> zigzag  $[\text{CuX}]_n$  or  $[\text{Cu}_3\text{I}_4]_n^{n-}$  chains,<sup>5f,h,7</sup>  $[\text{Cu}_2\text{X}_2]_n$  ladders or ribbons,<sup>5f,h,8</sup> and 2D  $[\text{CuX}]_n$  layers.<sup>5h,9</sup> Among those copper halide motifs, the rhombic  $\text{Cu}_2\text{X}_2$  secondary building units (SBUs), formed by two  $\text{X}^-$  atoms linking two neighboring Cu(I) atoms, have been found to be characteristic of excellent planar 4-connecting nodes whose remaining coordination sites of the Cu(I) atoms are bridged by the N,N'-bridging ligands, being facile at constructing multidimensional coordination frameworks.<sup>5</sup> However, most bridging ligands adopted to date to connect the  $\text{Cu}_2\text{X}_2$  building blocks have been rigid, including pyrazine, pyrimidine, 2,7-diazapyrene, 4,7-phenanthroline, 4,4'-bipyridine, 2,4-bis(4-pyridyl)-1,3,5-triazine, 3,5-bis(4-pyridyl)pyridine, and 5-(4-pyridyl)pyrimidine. In contrast, only a few coordination polymers based on  $\text{Cu}_2\text{X}_2$  SBUs with flexible conformations have been documented so far,<sup>5i,10</sup> probably due to the flexibility of the backbones, which makes it more difficult to predict and control the final coordination networks. We have recently investigated the assembly rule of

the coordination polymers with metal clusters as building blocks; several metal cluster units, such as  $\text{Ag}_2(\text{RCO}_2)_2$ ,<sup>11a,b</sup>  $\text{Cu}_2(\text{RCO}_2)_3$ ,<sup>11c</sup>  $\text{M}_2(\text{RCO}_2)_4$ ,<sup>11d</sup>  $\text{Cu}_4\text{I}_4$ ,<sup>6e</sup>  $\text{Zn}_4\text{O}$ ,<sup>11e</sup> and  $\text{M}_x(\text{OH})_y$ ,<sup>11f,g</sup> have been successfully introduced to act as secondary building units for the construction of two- and three-dimensional frameworks. As an extension of our study of the construction of new structural types of cluster-based coordination networks, rhombic  $\text{Cu}_2\text{X}_2$  units were selected for our assembled systems, since they are excellent inorganic functional modules for their planar 4-connectivity as well as their rich photophysical properties.<sup>12</sup> Herein, we report a series of complexes constructed from  $\text{Cu}_2\text{X}_2$  units and flexible N,N'-spacers of 1,2-bis(4-pyridyl)ethane ( $\text{bpe}$ ) or 1,3-bis(4-pyridyl)propane ( $\text{bpp}$ ) under solvothermal conditions in the presence of benzene or naphthalene molecules, in which the bridging ligand or templating molecule plays a vital role in the formation of the structures and topologies.

## Experimental Section

**Materials and Physical Measurements.** The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range  $4000\text{--}400\text{ cm}^{-1}$  on a Bio-Rad FTS-7 spectrometer. X-ray powder diffraction (XRD) intensities for **1** and **3** were measured at 293 K on a Rigaku D/max-III A diffractometer ( $\text{Cu K}\alpha$ ,  $\lambda = 1.54056\text{ \AA}$ ). The crushed single-crystal powder samples were prepared by crushing the crystals and scanned from  $3$  to  $60^\circ$  with a step of  $0.1^\circ/\text{s}$ . Calculated patterns of **1** and **3** were generated with PowderCell. The emission/excitation spectra and the lifetimes were measured on an Edinburgh FLS-920 spectrophotometer equipped with a continuous Xe-900 Xenon lamp, a  $\mu\text{F900}$  nanosecond flash lamp.

**Solvothermal Synthesis. (a)  $[\text{Cu}_2\text{Br}_2(\text{bpe})_2]$  (**1**).** A mixture of  $\text{CuBr}$  (0.5 mmol),  $\text{bpe}$  (0.5 mmol), benzene (2 mL), and MeCN (10 mL) in a 23 mL Teflon reactor was heated to  $160^\circ\text{C}$  for 3 days and then cooled to room temperature at a rate of  $5^\circ\text{C/h}$ . Dark red block crystals were obtained in 24% yield (based on Cu) after washing with MeCN and drying in air. Anal. Calcd for  $\text{C}_{24}\text{H}_{24}\text{Br}_2\text{Cu}_2\text{N}_4$ : C, 43.98; H, 3.69; N, 8.55. Found: C, 42.96; H, 3.60; N, 8.44. IR (KBr,  $\text{cm}^{-1}$ ): 3434

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Table 1. Crystal Data and Structure Refinement Details for 1–5

	1	2	3	4	5
formula	C <sub>24</sub> H <sub>24</sub> Br <sub>2</sub> Cu <sub>2</sub> N <sub>4</sub>	C <sub>28</sub> H <sub>24</sub> Cu <sub>4</sub> N <sub>8</sub>	C <sub>26</sub> H <sub>28</sub> Br <sub>2</sub> Cu <sub>2</sub> N <sub>4</sub>	C <sub>33</sub> H <sub>36</sub> Cu <sub>2</sub> I <sub>2</sub> N <sub>4</sub>	C <sub>36</sub> H <sub>36</sub> Cu <sub>2</sub> I <sub>2</sub> N <sub>4</sub>
formula wt	655.37	726.71	683.42	869.54	905.56
temp/K	293(2)	293(2)	123(2)	293(2)	123(2)
cryst syst	tetragonal	monoclinic	tetragonal	monoclinic	monoclinic
space group	<i>P</i> 4 <sub>3</sub> 2 <sub>1</sub> 2	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 4 <sub>3</sub> 2 <sub>1</sub> 2	<i>C</i> 2/ <i>m</i>	<i>C</i> 2/ <i>m</i>
<i>a</i> /Å	16.622(3)	13.543(1)	12.210(1)	16.072(2)	15.761(2)
<i>b</i> /Å	16.622(3)	6.9515(5)	12.210(1)	13.100(2)	13.149(1)
<i>c</i> /Å	17.733(6)	30.757(2)	35.803(4)	8.475(1)	8.4107(9)
$\beta$ /deg		101.314(1)		94.335(3)	94.423(2)
<i>V</i> /Å <sup>3</sup>	4900(2)	2839.4(4)	5337.5(8)	1779.3(5)	1737.9(3)
<i>Z</i>	8	4	8	2	2
<i>D</i> <sub>c</sub> /g cm <sup>−3</sup>	1.777	1.700	1.701	1.623	1.731
$\mu$ /mm <sup>−1</sup>	5.017	2.988	4.610	2.956	3.031
<i>F</i> (000)	2592	1456	2720	852	888
no. of rflns collected	14 802	15 205	13 707	2691	3082
no. of indep rflns	5595	6102	5162	1554	1678
<i>R</i> <sub>int</sub>	0.0911	0.0342	0.0662	0.0173	0.0197
GOF	0.828	1.014	1.023	1.034	1.095
<i>R</i> 1 <sup>a</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0466	0.0552	0.0641	0.0414	0.0363
w <i>R</i> 2 <sup>a</sup> (all data)	0.0814	0.1646	0.1666	0.1148	0.0928

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

(w), 3035 (w), 2932 (w), 2864 (w), 1606 (s), 1556 (w), 1493 (w), 1451 (w), 1420 (m), 1211 (w), 1072 (w), 1013 (w), 830 (s), 812 (w), 542 (s).

(b) [Cu<sub>2</sub>(CN)<sub>2</sub>(bpe)] (2). A mixture of CuI (0.5 mmol), bpe (0.5 mmol), and MeCN (10 mL) in a 23 mL Teflon reactor was heated to 160 °C for 3 days and then cooled to room temperature at a rate of 5 °C/h. Dark red block crystals were found in very low amount (<2%).

IR (KBr, cm<sup>−1</sup>): 3826 (w), 3450 (s), 2924 (m), 2855 (w), 2071 (s), 1640 (m), 1604 (m), 1463 (w), 1420 (w), 1013 (w), 968 (w), 822 (w), 547 (w).

(c) [Cu<sub>2</sub>Br<sub>2</sub>(bpp)<sub>2</sub>] (3). A mixture of CuBr (1 mmol), bpp (1 mmol), benzene (2 mL), and MeCN (10 mL) in a 23 mL Teflon reactor was heated to 160 °C for 3 days and then cooled to room temperature at a rate of 5 °C/h. Dark red block crystals were obtained in 62% yield

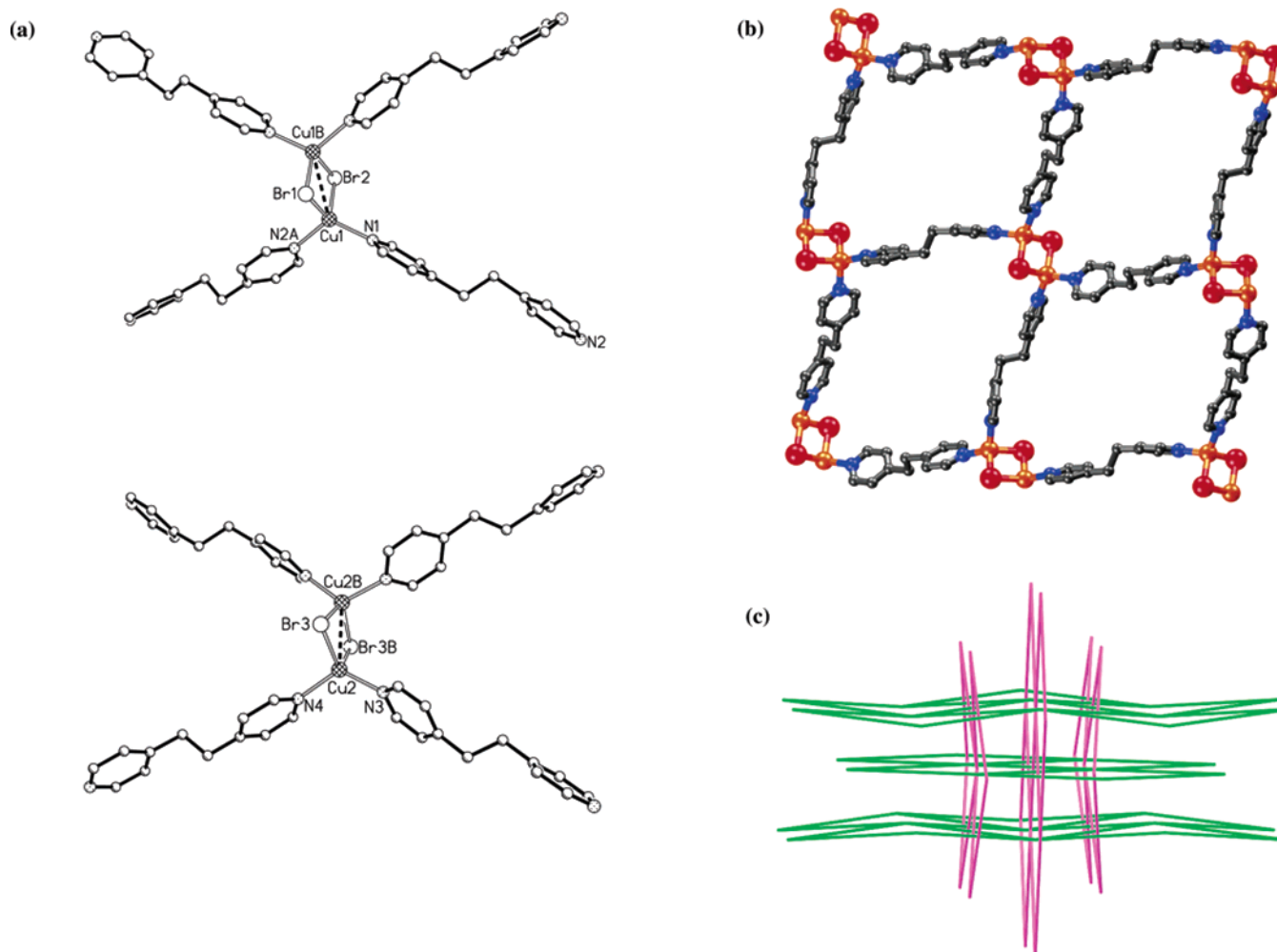


Figure 1. (a) View of the Cu(I) coordination environments found in 1. (b) View of a single (4,4) net in 1. (c) 3D structure constructed by “diagonal–diagonal” interpenetration of 2D layers.

Table 2. Bond Lengths (Å) and Angles (deg) for 1–5

Complex 1			
Cu(1)–N(1)	2.020(5)	Cu(2)–N(3)	2.022(5)
Cu(1)–N(2a)	2.055(4)	Cu(2)–N(4)	2.027(5)
Cu(1)–Br(2)	2.498(1)	Cu(2)–Br(3b)	2.490(1)
Cu(1)–Br(1)	2.510(1)	Cu(2)–Br(3)	2.557(1)
Cu(1)–Cu(1b)	2.870(2)	Cu(2)–Cu(2b)	2.744(2)
C(16)–Br(1c)	3.771(6)	C(22)–Br(2d)	3.790(7)
C(9)–Br(3e)	3.748(6)		
N(1)–Cu(1)–N(2a)	117.0(2)	N(4)–Cu(2)–Br(3b)	108.2(2)
N(1)–Cu(1)–Br(2)	110.7(2)	N(3)–Cu(2)–Br(3)	109.4(2)
N(2a)–Cu(1)–Br(2)	103.0(1)	N(4)–Cu(2)–Br(3)	102.6(2)
N(1)–Cu(1)–Br(1)	109.0(2)	Br(3b)–Cu(2)–Br(3)	113.54(3)
N(2a)–Cu(1)–Br(1)	106.8(2)	Cu(1b)–Br(1)–Cu(1)	69.75(4)
Br(2)–Cu(1)–Br(1)	110.06(4)	Cu(1)–Br(2)–Cu(1b)	70.13(5)
N(3)–Cu(2)–N(4)	117.3(2)	Cu(2b)–Br(3)–Cu(2)	65.85(3)
N(3)–Cu(2)–Br(3b)	106.2(1)	C(16)–H(16)–Br(1c)	158.8
C(22)–H(22)–Br(2d)	152.9	C(9)–H(9)–Br(3e)	164.0
Complex 2			
Cu(1)–C(3)	1.917(6)	Cu(2)–C(2)	2.156(6)
Cu(1)–N(5)	2.085(4)	Cu(3)–C(4)	1.949(6)
Cu(1)–C(2)	2.129(6)	Cu(3)–N(1)	2.020(5)
Cu(1)–C(1)	2.195(6)	Cu(3)–N(8b)	2.041(4)
Cu(1)–Cu(2)	2.4298(9)	Cu(4)–N(2)	2.000(4)
Cu(2)–N(3a)	1.936(6)	Cu(4)–N(4c)	2.034(6)
Cu(2)–N(7)	2.077(4)	Cu(4)–N(6d)	2.038(4)
Cu(2)–C(1)	2.122(6)		
C(3)–Cu(1)–N(5)	112.3(2)	N(7)–Cu(2)–C(2)	103.5(2)
C(3)–Cu(1)–C(2)	115.7(2)	C(1)–Cu(2)–C(2)	112.1(2)
N(5)–Cu(1)–C(2)	102.7(2)	C(4)–Cu(3)–N(1)	132.9(2)
C(3)–Cu(1)–C(1)	112.5(2)	C(4)–Cu(3)–N(8b)	120.6(2)
N(5)–Cu(1)–C(1)	102.2(2)	N(1)–Cu(3)–N(8b)	106.5(2)
C(2)–Cu(1)–C(1)	110.3(2)	N(2)–Cu(4)–N(4c)	133.5(2)
N(3a)–Cu(2)–N(7)	108.6(2)	N(2)–Cu(4)–N(6d)	106.0(2)
N(3a)–Cu(2)–C(1)	115.7(2)	N(4c)–Cu(4)–N(6d)	120.6(2)
N(7)–Cu(2)–C(1)	103.1(2)	Cu(2)–C(1)–Cu(1)	68.5(2)
N(3a)–Cu(2)–C(2)	112.7(2)		
Complex 3			
Cu(1)–N(2a)	2.02(1)	Cu(2)–N(4b)	2.012(8)
Cu(1)–N(1)	2.048(8)	Cu(2)–N(3)	2.036(8)
Cu(1)–Br(2)	2.440(2)	Cu(2)–Br(1)	2.510(2)
Cu(1)–Br(1)	2.535(2)	Cu(2)–Br(2)	2.520(1)
Cu(1)–Cu(2)	2.672(2)	C(6)–Br(1c)	3.938(11)
C(13)–Br(2d)	3.848(18)		
N(2a)–Cu(1)–N(1)	106.7(4)	N(4b)–Cu(2)–Br(1)	108.2(2)
N(2a)–Cu(1)–Br(2)	114.2(3)	N(3)–Cu(2)–Br(1)	108.6(3)
N(1)–Cu(1)–Br(2)	110.2(3)	N(4b)–Cu(2)–Br(2)	110.5(2)
N(2a)–Cu(1)–Br(1)	105.7(3)	N(3)–Cu(2)–Br(2)	101.9(2)
N(1)–Cu(1)–Br(1)	103.4(2)	Br(1)–Cu(2)–Br(2)	113.68(5)
Br(2)–Cu(1)–Br(1)	115.62(6)	Cu(2)–Br(1)–Cu(1)	63.95(5)
N(4b)–Cu(2)–N(3)	113.9(3)	Cu(1)–Br(2)–Cu(2)	65.18(5)
C(6)–H(6A)–Br(1c)	158.0	C(13)–H(13)–Br(2d)	170.7
Complex 4			
I(1)–Cu(1)	2.629(1)	Cu(1)–N(1)	2.048(4)
I(1)–Cu(1a)	2.703(1)	Cu(1)–Cu(1a)	2.685(2)
Cu(1)–I(1)–Cu(1a)	60.46(4)	N(1)–Cu(1)–I(1a)	104.4(1)
N(1)–Cu(1)–N(1b)	112.3(2)	I(1)–Cu(1)–I(1a)	119.54(4)
N(1)–Cu(1)–I(1)	108.2(1)		
Complex 5			
Cu(1)–I(1)	2.6188(9)	Cu(1)–N(1)	2.044(3)
Cu(1)–I(1a)	2.6832(8)	Cu(1)–Cu(1a)	2.689(2)
Cu(1)–I(1)–Cu(1a)	60.95(3)	N(1)–Cu(1)–I(1a)	104.86(9)
N(1)–Cu(1)–N(1b)	112.4(2)	I(1)–Cu(1)–I(1a)	119.05(3)
N(1)–Cu(1)–I(1)	107.9(1)		

<sup>a</sup> Symmetry codes for **1**: (a)  $-y + 1, -x + 2, -z + 1/2$ ; (b)  $y, x, -z$ ; (c)  $x + 1/2, -y + 3/2, z + 1/4$ ; (d)  $x - 1/2, -y + 1/2, z + 1/4$ ; (e)  $y + 1/2, -x + 1/2, z + 1/4$ . Symmetry codes for **2**: (a)  $x, y + 1, z$ ; (b)  $x + 1/2, -y + 1/2, z + 1/2$ ; (c)  $x - 1, y, z$ ; (d)  $x - 1/2, -y + 1/2, z - 1/2$ ; (e)  $x, y - 1, z$ ; (f)  $x + 1, y, z$ . Symmetry codes for **3**: (a)  $x, y - 1, z$ ; (b)  $x, y + 1, z$ ; (c)  $y - 1/2, -x + 3/2, z + 1/4$ ; (d)  $y - 1, x + 1, -z + 2$ . Symmetry codes for **4**: (a)  $-x + 1, -y - 1, -z$ ; (b)  $x, -y - 1, z$ . Symmetry codes for **5**: (a)  $-x + 1, -y + 1, -z$ ; (b)  $x, -y + 1, z$ .

after washing with MeCN and drying in air. Anal. Calcd for  $C_{26}H_{28}Br_2Cu_2N_4$ : C, 45.69; H, 4.13; N, 8.20. Found: C, 45.75; H, 3.673; N, 8.158. IR (KBr,  $cm^{-1}$ ): 3403 (w), 3107 (w), 3069 (w), 3037 (w), 3002 (w), 2922 (w), 1936 (w), 1607 (s), 1553 (w), 1494 (m), 1446 (w), 1421 (s), 1215 (m), 1101 (w), 1067 (w), 1012 (m), 879 (w), 835 (w), 808 (s), 756 (w), 667 (w), 609 (w), 574 (w), 515 (m).

(d) **[Cu<sub>2</sub>I<sub>2</sub>(bpp)<sub>2</sub>](toluene) (4)**. Compound **4** was prepared as for **3** by using CuI in place of CuBr and toluene (1 mmol) in place of benzene. Dark red block crystals were obtained in <3% yield. IR (KBr,  $cm^{-1}$ ): 3425 (w), 3068 (w), 3040 (w), 2923 (w), 2857 (w), 1932 (w), 1841 (w), 1674 (w), 1606 (s), 1495 (w), 1450 (w), 1421 (s), 1214 (m), 1068 (w), 1016 (w), 862 (w), 804 (s), 753 (w), 668 (m), 509 (m).

(e) **[Cu<sub>2</sub>I<sub>2</sub>(bpp)<sub>2</sub>](naphthalene) (5)**. Compound **5** was prepared as for **4** by using naphthalene (1 mmol) in place of toluene. Red crystals were isolated in 10–15% yield. Elemental analysis was impossible, due to loss of naphthalene from the crystal during weighing. IR (KBr,  $cm^{-1}$ ): 3427 (w), 3067 (w), 3043 (w), 3002 (w), 2926 (w), 2857 (w), 1932 (w), 1842 (w), 1675 (w), 1607 (s), 1554 (w), 1496 (m), 1450 (w), 1421 (s), 1352 (w), 1215 (m), 1068 (w), 1015(w), 860 (w), 836 (w), 805 (s), 737 (w), 668 (w), 615 (w), 584 (w), 510 (m).

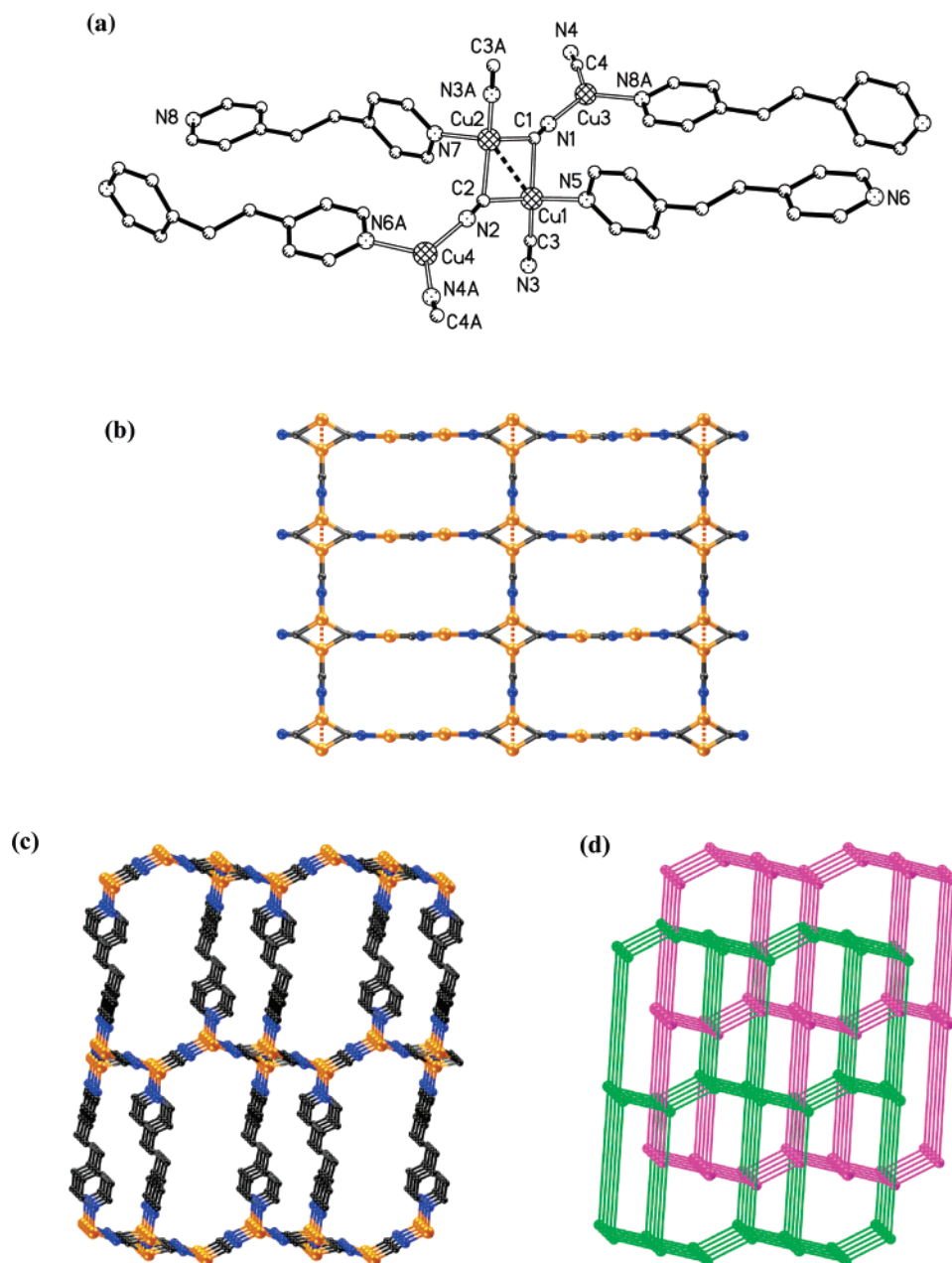
**X-ray Crystallography.** Diffraction intensities of **1–5** were collected on a Bruker Apex CCD area-detector diffractometer (Mo K $\alpha$ ,  $\lambda = 0.71073$  Å). Absorption corrections were applied by using the multiscan program SADABS.<sup>13</sup> The structures were solved with direct methods and refined by a full-matrix least-squares technique with the SHELXTL program package.<sup>14</sup> Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically ( $C_{aryl}-H = 0.93$  Å;  $C_{alkyl}-H = 0.97$  Å); the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Crystal data as well as details of the data collection and refinement for complexes **1–5** are summarized in Table 1. Selected bond distances and bond angles are listed in Table 2.

## Results

**Synthesis.** Previous studies by us<sup>15</sup> and other research groups<sup>16–18</sup> have shown that Cu(I) compounds were easily synthesized via hydrothermal reactions of Cu(II) salts with nitrogen-containing aromatic heterocycles, where the Cu(II) salt underwent a redox process and the resulting Cu(I) tended to form a one-dimensional ribbon-like structural moiety with halogens ( $X = Cl, Br$ ).<sup>16,17</sup> Recently, we observed Cu<sup>2+</sup>-mediated dehydrogenative coupling and hydroxylation of 1,3-bis(4-pyridyl)propane (bpp) and obtained a series of interesting Cu<sup>I</sup> coordination polymers.<sup>4</sup> As an extension of our study on the Cu(I) halide-based compounds, we focused our attention on investigating solvothermal reactions of copper(I) halide with the conformationally flexible ligands. Although the bpp ligand is characteristic of flexible trans-trans, trans-gauche, and gauche-gauche configurations which have led to the generation of many interesting coordination polymers of first-row transition-metal ions, few products incorporating copper(I) halides and bpp as the SBUs were obtained.<sup>19</sup> In our current work, the flexible bpe and bpp ligands are introduced into the solvothermal reaction systems.

The synthetic conditions for **1** and **3–5** are similar, and the possible templates including benzene, toluene, and naphthalene are introduced. Compounds **1** and **2** were prepared by using CuX ( $X = Br, I$ ) and bpe in a 1:1 molar ratio under solvothermal conditions in the presence or absence of benzene. However, the final products are quite different. As expected, **1** is a two-dimensional layer rather than a one-dimensional double-chain structure due to the configuration of bpe. In **2**, however, the CN<sup>−</sup> anion was generated in situ from the C(sp<sup>3</sup>)–C(sp) cleavage of acetonitrile, which led to another interesting structure different from that of **1**. Recent reports have shown that the C–C cleavage of MeCN<sup>20</sup> and S–C cleavage of SCN<sup>−18b,c,21</sup> are two routes to in situ formation of CN<sup>−</sup>.





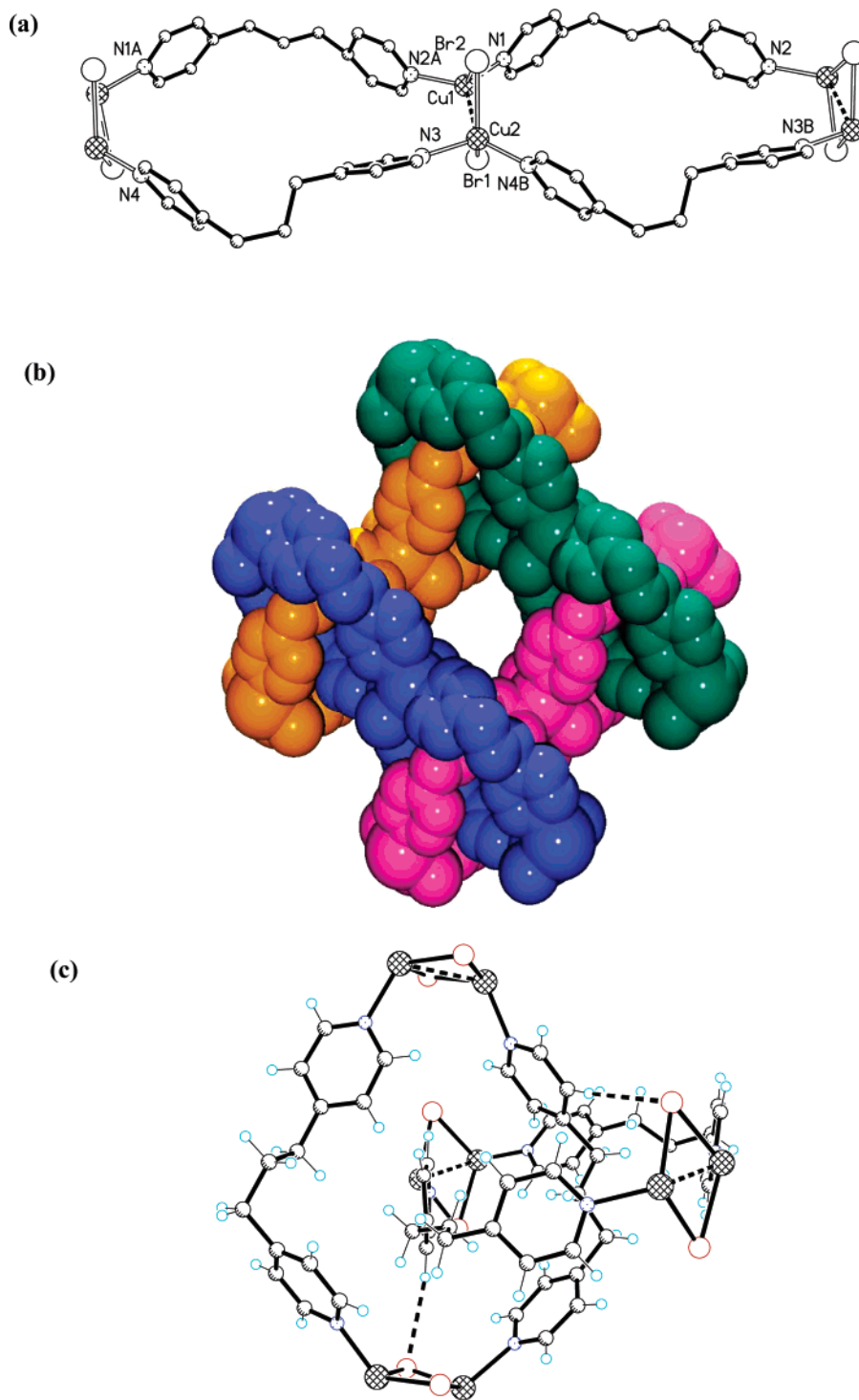
**Figure 2.** (a) Views of the coordination environments of Cu(I) atoms. (b) Top view of the 2D  $\text{Cu}_2(\mu_{1,2}\text{-CN})(\mu_{1,2}\text{-CN})$  net. (c) View of a single 3D bpe-pillared network. (d) View of 2-fold interpenetrating rutile-like topological nets in **2**.

As expected, compound **3** was prepared by CuBr and bpp in a 1:1 molar ratio under solvothermal conditions. When the larger guest molecules of toluene and naphthalene were introduced into the reaction system, compounds **4** and **5** were obtained, showing that the templating of suitable guests significantly affects the formation of final supramolecular architectures.

**Crystal Structures.** (a) **Structure of  $[\text{Cu}_2\text{Br}_2(\text{bpe})_2]$  (**1**).** There are two crystallographically unique Cu atoms per asymmetric unit, both of which have similar coordination environments but belong to two independent sets of infinite 2D square grids based on the (4,4) topology running in almost perpendicular directions. The coordination geometries of Cu1 and Cu2 are shown in Figure 1a. Each Cu(I) atom is tetrahedrally coordinated by two  $\text{Br}^-$  atoms and two bpe ligands with Cu–Br and Cu–N distances of 2.490(1)–2.557(1) and 2.020(5)–2.055(4) Å, respectively. The Cu2···Cu2A distance of 2.744(2) Å is slightly smaller than the Cu1···Cu1A distance of 2.870(2) Å and the sum of the van der Waals radii of copper(I) (2.8 Å).

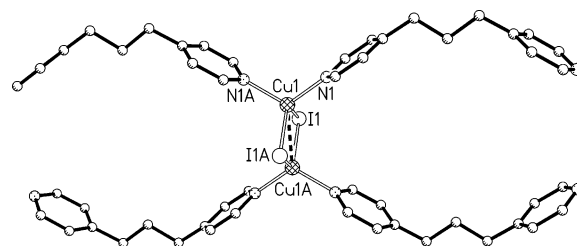
Each  $\text{Cu}_2\text{Br}_2$  SBU is connected by four ditopic bpe ligands in a trans conformation,<sup>22</sup> generating 2D (4,4) layers containing 48-membered metallocycles with dimensions of ca.  $12.5 \times 13.3$  Å<sup>2</sup>. Each layer has enough “empty” space to allow three other layers inclined polythreading into each grid with a high (3/3) degree of catenation in a “diagonal–diagonal” fashion.<sup>2b</sup> The (3/3) catenation finally results in a prototypical 2D → 3D network (Figure 1b,c). The mode of inclined interpenetration is similar to that for other previously identified coordination polymers with (1/1), (2/2), and (3/3) polycatenations, involving (4,4) entangled layers with the diagonal–diagonal fashion.<sup>2j,23</sup> Adjacent (4,4) entangled layers are interlinked by weak nonclassical C–H···Br hydrogen-bonding interactions<sup>24</sup> ( $\text{C}\cdots\text{Br} = 3.748(6)\text{--}3.790(7)$  Å;  $\text{C–H}\cdots\text{Br} = 152.9\text{--}164.0^\circ$ ).

(b) **Structure of  $[\text{Cu}_2(\text{CN})_2(\text{bpe})]$  (**2**).** X-ray crystallography shows that there are four distinct copper environments, two bpe ligands, and four  $\text{CN}^-$  anions of two types (triangular-bridged  $\mu_{1,1,2}$  and linear-bridged  $\mu_{1,2}$ ) in the asymmetric unit of **2** (Figure

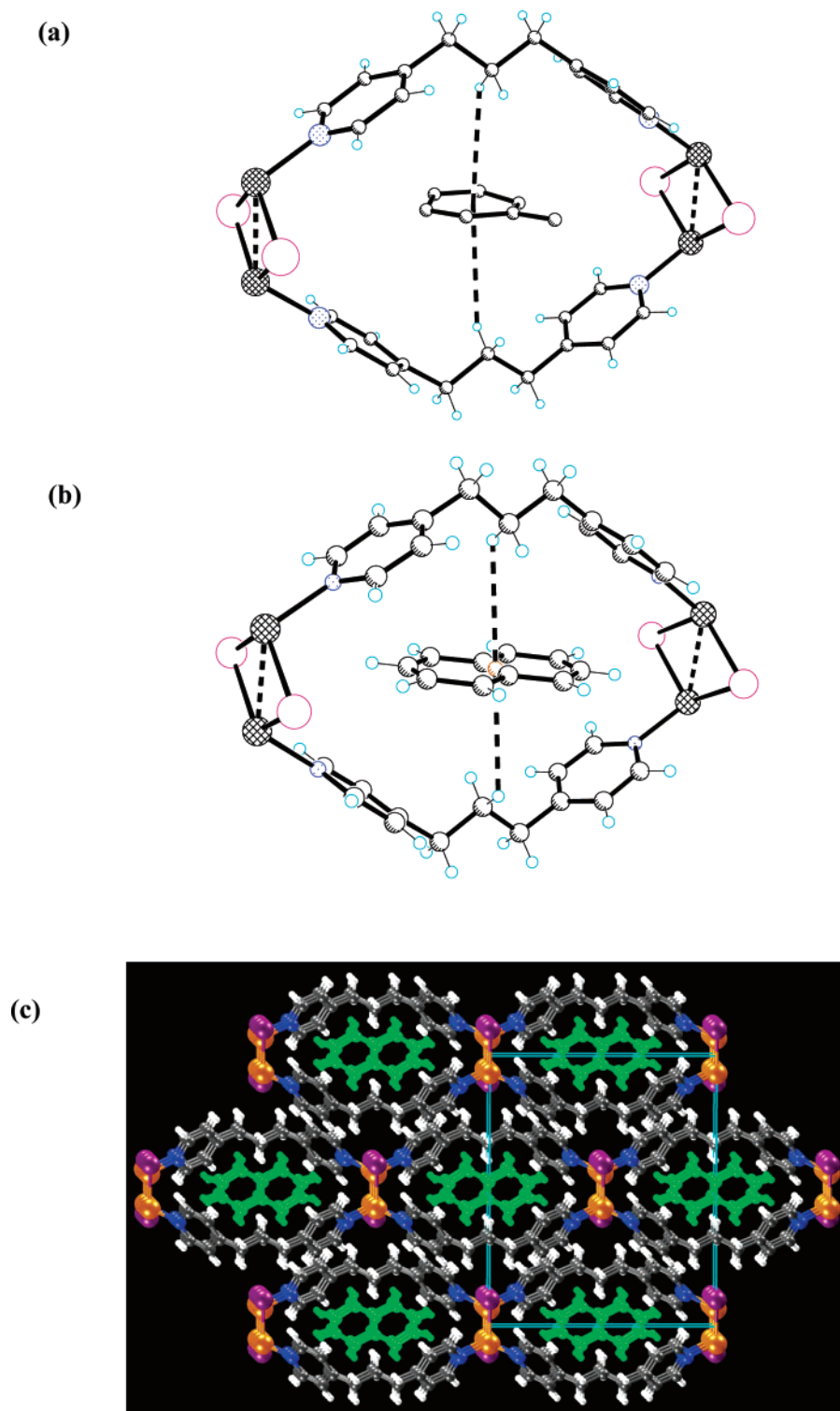


**Figure 3.** (a) View of **3** showing the double-stranded 1D chain and the Cu(I) coordination environments. (b) View of the 2D polycatenated net interlocked by 1D double-stranded chains. (c) View of the interchain interactions.

2a). The Cu1 and Cu2 atoms are both coordinated in tetrahedral geometries to three cyanide groups and one bpe ligand. The Cu1 and Cu2 atoms are linked by a pair of  $\mu_{1,1}$ -CN bridges via the carbon ends to form a dimeric  $\text{Cu}_2(\text{CN})_2$  SBU with Cu—C and Cu $\cdots$ Cu distances of 2.129(6)–2.195(6) and 2.4298(9) Å, respectively. Cu3 and Cu4 are coordinated in similar tetrahedral geometries to two cyanide groups and one bpe ligand. Each  $\text{Cu}_2(\text{CN})_2$  SBU is connected by two linear Cu( $\mu_{1,2}$ -CN)Cu units and two linear  $\mu_{1,2}$ -cyanide groups, generating a 2D (4,8<sup>2</sup>) layer along the *ab* plane (Figure 2b), which is different from the substructures of the copper(I) cyanides in reported coordination polymers ranging from 1D chains, double-stranded ribbons, to



**Figure 4.** View of the Cu(I) coordination environment found in **4** or **5**.



**Figure 5.** Views of the host–guest interactions in **4** (a) and **5** (b) and a crystal packing diagram of **5** (c).

2D sheets and to 3D structures decorated by introducing a series of nitrogen-containing ligands.<sup>25</sup> Adjacent layers are pillared by bpe spacers to generate an interesting 3D coordination polymer of 2-fold interpenetration. The network topology can be simplified by considering the  $\text{Cu}_2(\text{CN})_2$  SBU (represented by a 6-connected node) and trigonal  $\text{Cu}_3$  and  $\text{Cu}_4$  atoms (represented by a 3-connected node); the bidentate bpe ligands and the linear  $\mu_{1,2}$ -cyanide ligands can be represented simply as links between the nodes. The resulting net is shown in Figure 2c and has the rutile topology, which is constructed by 3-connected ( $\text{Cu}_3$  and  $\text{Cu}_4$ ) and 6-connected nodes [ $\text{Cu}_2(\text{CN})_2$ ]

in a ratio of 2:1. Such a (3,6)-connected net can be characterized by the short vertex symbol  $(4.6^2)_2(4.2.6^{10}.8^3)-a$ .<sup>26</sup>

**(c) Structure of  $[\text{Cu}_2\text{Br}_2(\text{bpp})_2]$  (**3**).** Thanks to the greater number of conformations that the flexible bpp ligands display, the bpp ligand is an excellent spacer in the construction of novel coordination polymers. The  $\text{Cu}_2\text{Br}_2$  dimers with a  $\text{Cu}\cdots\text{Cu}$  separation of 2.672(2) Å are linked by bpp ligands in two different conformations (trans-trans and trans-gauche) in a 1:1 ratio to form a 1D double-stranded tubular chain, containing a repeating unit of a 28-membered ring composed of two  $\text{Cu}_2\text{Br}_2$  dimers, one bpp ligand with a trans-trans conformation and one bpp

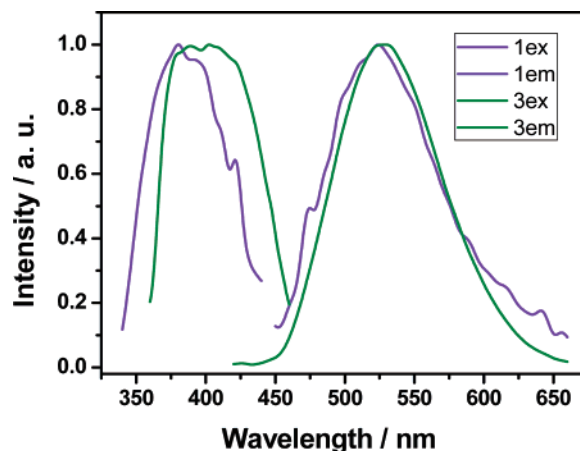
ligand with a *trans-gauche* conformation (Figure 3a). Each metallocyclic ring has cross-section dimensions of approximately  $8.5 \times 12.2$  Å. The intrarhomboid Cu1–Cu2 distance is 2.672(2) Å, slightly smaller than that in **1** and the sum of the van der Waals radii of copper(I) (2.8 Å). A particularly interesting structural feature of **3** is that each chain is interlocked with an infinite number of other independent chains in almost perpendicular directions and generates a graceful 1D  $\rightarrow$  2D polycatenation network (Figure 3b) with (1/1) catenation. This type of infinite 2D arrays of polycatenane is rare, and the first example has only recently been observed in a self-assembled system of cadmium(II) and manganese(II) sulfates with 1-(1-imidazolyl)-4-(imidazol-1-ylmethyl)benzene (IIMB).<sup>27</sup> **3** is isostructural with another recently reported example,<sup>19b</sup> which was obtained from a room-temperature reaction of *bpp* with CuI in a DMF–THF–H<sub>2</sub>O mixture in the presence of excess KI.

The adjacent 2D layers stack in an ABAB fashion. Weak interchain nonclassical C–H $\cdots$ Br hydrogen-bonding interactions<sup>24</sup> (Figure 3c) as well as van der Waals interactions play a vital role in the consolidation of the solid structure (C $\cdots$ Br = 3.848(2) Å; C–H $\cdots$ Br = 170.6(1)°).

**(d) Structures of [Cu<sub>2</sub>I<sub>2</sub>(*bpp*)<sub>2</sub>](toluene) (**4**) and [Cu<sub>2</sub>I<sub>2</sub>(*bpp*)<sub>2</sub>](naphthalene) (**5**).** Similar to the chainlike components of compound **3**, the structures of compounds **4** and **5** can also be described as 1D double-stranded tubular chains running along the *b* axis. Each Cu(I) atom is ligated in a tetrahedral fashion (Figure 4) by two *bpp* ligands and two I atoms (for **4**, Cu–N = 2.048(4) Å, Cu–I = 2.629(1)–2.703(1) Å; for **5**, Cu–N = 2.044(3) Å, Cu–I = 2.6188(9)–2.6832(8) Å). The intrarhomboid Cu $\cdots$ Cu distances are 2.703(1) and 2.689(2) Å for **4** and **5**, respectively. The repeating 28-membered metallacyclic rings have cross-sectional dimensions of approximately  $6.85 \times 13.10$  and  $6.70 \times 13.15$  Å<sup>2</sup> for **4** and **5**, respectively, based on the distances of closest methylenes of two *bpp* ligands and two Cu<sub>2</sub>I<sub>2</sub> dimers (Figure 5a). All *bpp* ligands adopt the *trans-trans* conformation, different from that found in **3**. It is worth noting that the toluene and naphthalene guests play a templating<sup>28</sup> role in the formation of nonentanglement structures of **4** and **5**. Each empty space of the double-stranded 1D chain is large enough to host a toluene or naphthalene guest, preventing the 1D double-strand chains from interpenetration of the 1D chains. A significant C–H $\cdots$  $\pi$  interaction also exists between the methene groups and toluene/naphthalene guests with H(7a) $\cdots$ centroid distances of 3.38–3.51 and 3.42 Å for **4** and **5**, respectively (Figure 5b,c). However, no nonclassical C–H $\cdots$ I hydrogen-bonding interaction is found between the host frameworks and the guests in **4** or **5**, different from those found in **1** and **3**.

## Discussion

Cu<sub>2</sub>X<sub>2</sub> moieties (X = Br, I) acting as the square-planar nodes and the N,N'-donor ligands as connectors usually result in the formation of one-dimensional chains or two-dimensional layers.<sup>5</sup> Taking account of the main difference between **1** and **3**, the flexible conformation of the N-donor ligands is responsible for controlling the overall structures of the interpenetration arrays. In **1**, four Cu<sub>2</sub>Br<sub>2</sub> dimers are bridged by four flexible *bpe* ligands to form a 48-membered metallacyclic ring which is large enough to permit three other layers to thread through. However, owing to the prominent twists of the *bpp* ligands, two different conformations of *bpp* ligands and two Cu<sub>2</sub>X<sub>2</sub> dimers comprise a smaller 28-membered ring in **3**. The small empty space only accommodates another closed loop catenating with it. On the other hand, **3**–**5** are supramolecular pseudo-isomers in which the templating molecules play a decisive role in orienting the



**Figure 6.** Emission and excitation spectra of **1** and **3**.

outcome of the crystallization processes. The resulting nonentanglement structures in **4** and **5** may be due to the steric hindrance of toluene or naphthalene molecules, so that the entanglement of *bpp* ligands is considerably more difficult.

**Photoluminescent Properties.** The photoluminescent properties of compounds **1** and **3** have also been studied. The excitation and emission maxima ( $\lambda_{\text{ex}}^{\text{max}}$  and  $\lambda_{\text{em}}^{\text{max}}$ ) and the lifetimes at room temperature are shown in Figure 6 and Figures S2 and S3 (Supporting Information). Upon excitation at 380 and 389 nm, **1** and **3** in the solid state exhibit strong photoluminescence at room temperature with emission maxima at ca. 529 ( $\tau = 90.5$ –(14) and 10.2(2) ns) and 530 nm ( $\tau = 2.41$ (2)  $\mu$ s), respectively, very similar to that of the dimeric complex Cu<sub>2</sub>I<sub>2</sub>(py)<sub>4</sub> (py = pyridine) with  $\lambda_{\text{em}}^{\text{max}} = 517$  nm at 294 K.<sup>29</sup> The emissions of complexes **1** and **3** may be therefore assigned to both cluster-centered transition and XLCT.<sup>5e,29</sup> It should be noted that the luminescent properties of complexes with the rhombic Cu<sub>2</sub>( $\mu$ -X)<sub>2</sub> units have been reported in only a few cases,<sup>5g</sup> though many Cu<sub>2</sub>( $\mu$ -X)<sub>2</sub>L<sub>2</sub> complexes have been structurally characterized by X-ray diffraction,<sup>5</sup> in contrast to the well-explored photoluminescent [Cu<sub>4</sub>( $\mu$ -X)<sub>4</sub>L<sub>4</sub>] complexes.<sup>30</sup>

## Conclusions

In this study, we successfully synthesized and characterized five new coordination polymers based on the Cu<sub>2</sub>X<sub>2</sub>–*bpe*/*bpp* system under similar solvothermal conditions. Polycatenations of 1D  $\rightarrow$  2D and 2D  $\rightarrow$  3D are observed, and these results indicate that the flexible spacers and the size-selective templating molecules have a significant effect on the entanglements of multiple motifs, implying an effective method for controlling the synthesis of wonderful polycatenanes.

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**Supporting Information Available:** CIF files giving X-ray crystallographic data for **1**–**5** and figures giving a crystal packing diagram of **3**, plots of the luminescence decay of **1** and **3**, and simulated and experimental XRPD data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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