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Anionic Cu_nI_n Cluster-Based Architectures Induced by In Situ Generated *N*-Alkylated Cationic Triazolium Salts

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ABSTRACT: Five new copper(I) iodide coordination polymers, $(\text{Cu}_{10}\text{I}_{10})(\text{Cu}_6\text{I}_6)[(\text{Cu}(\text{Bta})_2]_3^-\cdot(\text{DMBta})_4^+\cdot(\text{I}^-)\cdot x(\text{I}_2)$ ($x \approx 1.5$) (**1**), $[\text{Cu}_2\text{I}_2(\text{MBta})]$ (**2**), $[\text{Cu}_2\text{I}_2(\text{MTa})]$ (**3**), $(\text{Cu}_5\text{I}_5)[\text{Cu}(\text{Ta})_2]^- \cdot (\text{DETa})^+$ (**4**), and $[\text{Cu}_3\text{I}(\text{Bta})_2]$ (**5**) (Bta = benzotriazole, DMBta = 1,3-*N*-dimethylbenzotriazolium, MBta = 1-*N*-methylbenzotriazole, MTa = 1-*N*-methyltriazole, Ta = 1,2,3-triazole, DETa = 1,3-*N*-diethyltriazolium), have been prepared by the solvo(hydro)thermal reactions of CuI, KI, and benzotriazole (or 1,2,3-triazole) in methanol (or ethanol or water) and structurally characterized. Complex **1** shows a highly unusual two-dimensional (2D) \rightarrow three-dimensional (3D) interpenetrated anionic network containing two new discrete neutral $\text{Cu}_{10}\text{I}_{10}/\text{Cu}_6\text{I}_6$ cluster units, and complex **4** consists of 2D anionic layers with Cu_5I_5 cluster units, both of which involve in situ di-*N*-alkylated cationic triazolium to induce the anionic frameworks. Complexes **2** and **3** both contain neutral in situ mono-*N*-alkylated ligands and exhibit similar one-dimensional (1D) double-stranded stairlike ribbon structures. Complex **5** exhibits a 2D simple sheet structure containing nonalkylated Bta[−] ligands. A mechanism of the solvo(hydro)thermal reaction is proposed. As evidenced by means of electrospray ionization mass spectrometry measurements, a simultaneous redox, *N*-alkylated and self-assembly reaction occurs.

Introduction

Copper(I) halides have been employed and systematically investigated as inorganic components in the construction of inorganic–organic hybrid coordination polymers, which lies at the frontier of crystal engineering.^{1–4} In particular, the structural variation of copper(I) iodide aggregates, ranging from discrete oligomers² to polymeric chains³ and two-dimensional (2D) layers,⁴ is due to the strongly coordinating nature of the iodide anion, which can bridge two or more copper centers, giving various species of the form $[(\text{Cu}_x\text{I}_y)^{x-y}]_n$. Among these copper(I) iodide motifs, discrete neutral Cu_nI_n clusters are facile acting as secondary building units (SBUs) for constructing multidimensional coordination frameworks.^{5–8} Compared with those commonly reported ones such as Cu_2I_2 rhomboid dimers⁶ and Cu_4I_4 cubane tetramers,⁷ coordination architectures constructed by discrete high-nuclear Cu_nI_n clusters ($n > 4$) have rarely been documented previously.⁸

Most of the reported copper(I)-iodide cluster-based frameworks are neither cationic nor anionic but neutral.^{5–8} A rational consideration for constructing charged frameworks is to introduce templates with opposite charges to direct the self-assembly.⁹ For example, the organic cations have been widely utilized as templates of pores or intercalary guests of interlayers in the preparation of zeolites and inorganic materials,¹⁰ where the organic cations not only contribute to enlarge the porous size, but also direct the formation of the anionic frameworks. However, little attention has been drawn to the application of in situ generated organic cations to fabricate charged frameworks.

As our continuous research on the solvothermal syntheses of new copper(I) halides complexes,¹¹ we adopted a synthetic approach by introducing organic cationic triazolium salts to the self-assembly processes and report herein a range of anionic copper(I)-iodide cluster-based coordination polymers. We chose multidentate triazole as a precursor to in situ generate *N*-alkylated cationic triazolium by the solvothermal reaction of triazole and methanol (or ethanol) induced by nucleophilic

haloid ions.¹² As will be seen, the di-*N*-alkylated triazolium organic cations practically induce the formation of multidimensional anionic frameworks as observed in $(\text{Cu}_{10}\text{I}_{10})(\text{Cu}_6\text{I}_6)[(\text{Cu}(\text{Bta})_2]_3^-\cdot(\text{DMBta})_4^+\cdot(\text{I}^-)\cdot x(\text{I}_2)$ ($x \approx 1.5$) (**1**) and $(\text{Cu}_5\text{I}_5)[\text{Cu}(\text{Ta})_2]^- \cdot (\text{DETa})^+$ (**4**). Interestingly, complex **1** exhibits a novel two-dimensional (2D) \rightarrow three-dimensional (3D) interpenetrated network with two new discrete neutral $\text{Cu}_{10}\text{I}_{10}/\text{Cu}_6\text{I}_6$ clusters as SBUs, and complex **4** consists of a 2D layer structure containing Cu_5I_5 cluster units. The reaction of CuI, KI, and benzotriazole in methanol produces not only complex **1** but a minor product $[\text{Cu}_2\text{I}_2(\text{MBta})]$ (**2**), which has a structure similar to $[\text{Cu}_2\text{I}_2(\text{MTa})]$ (**3**) of a one-dimensional (1D) double-stranded stairlike ribbon containing neutral in situ formed mono-*N*-alkylated ligands. In contrast, the reaction with the nonalkylated Bta[−] ligand in water results in a neutral 2D simple sheet structure $[\text{Cu}_3\text{I}(\text{Bta})_2]$ (**5**).

Experimental Section

Materials and Physical Measurements. All reagents were of analytical grade and used as obtained from commercial sources without further purification. Infrared spectra were obtained in KBr pellets in the range of 4000–400 cm^{-1} on a Nicolet Avatar 360 FT-IR spectrometer. Thermogravimetric analysis (TGA) was carried out under argon atmosphere with the heating rate of 10 $^\circ\text{C}/\text{min}$ from room temperature to 800 $^\circ\text{C}$ on a Seiko Extar 6000 TG/DTA equipment. Electrospray ionization mass spectrometry (ESI-MS) analyses were carried out using a Thermo LCQ DECA XP liquid chromatography–mass spectrometry. X-ray photoemission spectroscopy (XPS) measurements were performed at a base pressure of 10^{-8} Torr under Mg K α (1253.6 eV) primary radiation (14 kV, 15 mA) on a Kratos XSAM 800 instrument.

Syntheses. $(\text{Cu}_{10}\text{I}_{10})(\text{Cu}_6\text{I}_6)[(\text{Cu}(\text{Bta})_2]_3^-\cdot(\text{DMBta})_4^+\cdot(\text{I}^-)\cdot x(\text{I}_2)$ ($x \approx 1.5$) (**1**) and $[\text{Cu}_2\text{I}_2(\text{MBta})]$ (**2**). A mixture of CuI (0.190 g, 1.0 mmol), KI (0.166 g, 1.0 mmol), benzotriazole (0.132 g, 1.0 mmol), and methanol (8.0 mL) was stirred for 2 min in air, then transferred and sealed in a 25 mL Teflon-lined reactor. The reactor was heated in an oven to 140 $^\circ\text{C}$ for 72 h and then cooled to room temperature at a rate of 5 $^\circ\text{C}/\text{h}$. Yellow-green columnar crystals of **1** were obtained as major products (0.064 g, 24.3% based on CuI), accompanied by orange crystals of minor product **2**. IR data (KBr, cm^{-1}): **1** $\nu(\text{C}–\text{N})$ 1326 s; **2** $\nu(\text{C}–\text{N})$ 1322 s. The formula of complex **1** was further conformed by XPS and TGA.

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Table 1. Crystallographic and Structure Refinement Parameter for 1, 3–5

	1	3	4	5
empirical formula	C ₆₈ H ₆₄ N ₃₀ Cu ₁₉ I ₂₀	C ₃ H ₅ N ₃ Cu ₂ I ₂	C ₁₀ H ₁₆ N ₉ Cu ₆ I ₅	C ₁₂ H ₈ Cu ₃ N ₆ I
formula weight	5046.75	463.98	1278.06	553.76
crystal system	tetragonal	triclinic	monoclinic	orthorhombic
space group	<i>P</i> 42/ <i>ncm</i>	<i>P</i> 1	<i>P</i> 21/ <i>c</i>	<i>Pnma</i>
<i>a</i> /Å	28.4132(7)	7.9605(5)	10.6931(10)	11.6390(7)
<i>b</i> /Å	28.4132(7)	8.2819(6)	14.4122(15)	29.7697(19)
<i>c</i> /Å	14.0586(7)	8.3378(6)	17.5869(17)	4.1222(3)
α /°	90	116.3220(10)	90	90
β /°	90	99.5430(10)	102.795(2)	90
γ /°	90	104.1530(10)	90	90
<i>V</i> /Å ³	11349.6(7)	453.34(5)	2643.0(4)	1428.30(16)
<i>Z</i>	4	2	4	4
<i>d</i> _{calcd} /g·cm ³	2.954	3.399	3.212	2.575
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)
μ /mm ^{−1}	8.967	11.433	10.599	6.590
reflection collected	69177	3120	12091	11114
unique data	6951	1561	5843	1722
<i>R</i> (int)	0.0434	0.0306	0.0400	0.0287
GOF	1.097	1.107	0.972	1.177
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0559, 0.1596	0.0380, 0.1023	0.0617, 0.1478	0.0486, 0.1283
<i>R</i> 1, <i>wR</i> 2 (all data) ^a	0.0704, 0.1698	0.0395, 0.1038	0.1121, 0.1778	0.0615, 0.1434

^a *R*1 = $[\Sigma(F_o - |F_c|)/\Sigma F_o]$, *wR*2 = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, *w* = $1/[\sigma^2(F_o^2) + (0.0876P)^2 + 103.9405P]$ for **1**, *w* = $1/[\sigma^2(F_o^2) + 0.0662P]^2 + 0.4282P]$ for **3**, *w* = $1/[\sigma^2(F_o^2) + (0.0941P)^2 + 0.0000P]$ for **4**, *w* = $1/[\sigma^2(F_o^2) + (0.0860P)^2 + 1.6555P]$ for **5**, where *P* = $(F_o^2 + 2F_c^2)/3$.

[Cu₂I₂(MTa)] (3). The preparation is analogous to **1** except substituting benzotriazole with 1,2,3-triazole. Grey platelet crystals were obtained (0.087 g, 18.9% based on HTa). IR data (KBr, cm^{−1}): ν (C–N) 1300 s.

(Cu₅I₅)[Cu(Ta)₂][−]·(DETa)⁺ (4). The preparation is analogous to **3** except substituting methanol with ethanol. Pale-yellow crystals were obtained (0.065 g, 10.3% based on HTa). IR data (KBr, cm^{−1}): ν (C–N) 1302 s.

[Cu₃I(Bta)₂] (5). The preparation is analogous to **1** except substituting methanol with water (10 mL). Pale-yellow prismatic crystals were obtained (0.058 g, 21.3% based on HBta). IR data (KBr, cm^{−1}): 1460 vs, 1382 s, 1204 s, 1013 s, 882 m, 743 s.

X-ray Crystallography. Intensity data were collected on a Bruker Smart Apex CCD diffractometer by graphite-monochromated Mo K α (λ = 0.71073 Å) radiation using the ω –2 θ scan method at room temperature. The structures were solved with the direct method and refined on *F*² by full-matrix least-squares technique using the SHELXTL program package.¹³ Anisotropic thermal parameters were applied to all nonhydrogen atoms. The hydrogen atoms were generated geometrically (C–H = 0.960 Å). The crystallographic calculations were conducted using the SHELXL-97 program package. Crystallographic data are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

Results and Discussion

Syntheses. As shown in Scheme 1, the reaction of benzotriazole with CuI, KI in a molar ratio of 1:1:1 in methanol yielded yellow-green columnar crystals [Cu₁₀I₁₀](Cu₆I₆)·[(Cu(Bta)₂)₃][−]·(DMBta)₄⁺·(I[−])·*x*(I₂) (*x* ≈ 1.5) (**1**), as a major product, and orange prismatic crystals [Cu₂I₂(MBta)] (**2**), as a minor product. Mono-*N*-methylated and di-*N*-methylated products were found in the complexes and residual solution (Figure S1a, Supporting Information). Unfortunately, the reaction of benzotriazole and ethanol formed a mixed colloid residue that was difficult to characterize, and no single crystal was obtained. However, ESI-MS analysis confirmed that alkylated compounds EBta and DEBta did exist in the reaction filtrate (Figure S1b, Supporting Information). In contrast, the substitution of methanol with water in the same conditions yielded complex [Cu₃I(Bta)₂] (**5**). When benzotriazole was replaced by 1,2,3-triazole, we also obtained two other coordination polymers [Cu₂I₂(MTa)] (**3**) and (Cu₅I₅)[Cu(Ta)₂][−]·(DETa)⁺ (**4**) in methanol and ethanol, respectively. Although only **3** contained coordinated alkylated compounds, mono- and di-*N*-alkylated heterocycles (MTa and DMTa; ETa and DETa) were identified

in both reaction filtrates (Figure S1d,e, Supporting Information). ESI-MS analyses also confirmed that various corresponding mono- and dialkylated heterocycles existed in the reaction filtrates of other azole compounds such as benzimidazole and 1,2,4-triazole with bromide salt (Figure S1f–j, Supporting Information). Some comparative experiments had been attempted by changing the molar ratio of the starting materials and the reaction temperatures, and unfortunately, no suitable single crystals were obtained.

Interestingly, the addition of a small amount of amylum solution to the reaction filtrates of **1–4** resulted in a color change from orange or brown to dark blue, implying the presence of iodine in the filtrates. However, no iodine was found in the reaction without CuI despite the formation of *N*-alkylated compounds identified by ESI-MS (Figure S1c, Supporting Information). These findings indicated that the self-assemblies of **1–4** involved the oxidation of iodide to iodine. Although the reactions in sealed reactors were complicated, either of the two possible processes should exist: (i) Cu^{II} intermediate (**X**) was formed by the reaction of CuI and oxygen and then oxidized iodide to iodine; (ii) Cu^I intermediate (**X**) was formed directly by the reaction of CuI and oxygen generating Cu^I and iodine. On the basis of the above ESI-MS evidence and hypothesis, the mechanism of these solvothermal reactions is tentatively suggested as follows (Scheme 2): RI (R = −CH₃ or −C₂H₅), formed by the reversible nucleophilic substitution reaction of ROH and iodide ions under high temperature and autogenous pressure, reacts with benzotriazole or triazole to simultaneously produce mono- and di-*N*-alkylated heterocycles. The reactants and in situ *N*-alkylated ligands self-assemble to produce different coordination polymers by the effects of kinetic and thermodynamic stabilities. The solvothermal reactions are simultaneous redox, *N*-alkylated and self-assembly processes, resembling the situation previously reported by Yao et al.^{12b}

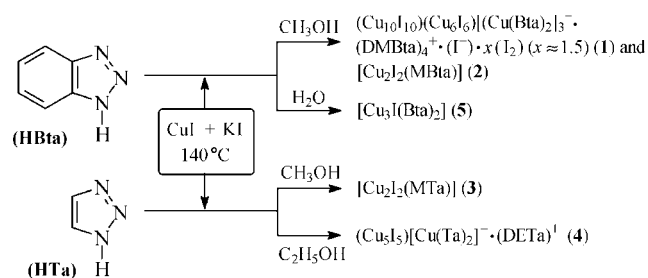
Structures. Single-crystal X-ray crystallography shows that complexes **1–4** all contain mono- or di-*N*-alkylated triazolium [N–C 1.44062(1)–1.46245(4) Å].¹⁴ The FT-IR spectra of complexes **1–4** in the solid state also confirm the formation of in situ *N*-alkylated ligands by the observation of strong absorption at 1330–1300 cm^{−1} for the ν (Ar)N–C(R) stretching vibration.

Table 2. Selected Bond Lengths (Å) and Angles (°) for 1,^a 3,^b 4,^c and 5^d

complex 1				complex 4			
I(1)–Cu(1)	2.6676(15)	N(3)–Cu(1)–I(3)	121.9(2)	C(9)–N(9)	1.444(17)	N(1)–Cu(1)–I(2)	116.3(3)
I(1)–Cu(3)	2.8469(16)	N(3)–Cu(1)–I(1)	106.3(2)	I(1)–Cu(2)	2.6211(19)	N(1)–Cu(1)–I(1)	103.9(3)
I(2)–Cu(2)	2.6570(15)	I(3)–Cu(1)–I(1)	115.61(5)	I(1)–Cu(1)	2.6888(19)	I(2)–Cu(1)–I(1)	113.80(7)
I(2)–Cu(2)#2	2.6570(15)	N(3)–Cu(1)–I(2)	105.5(2)	I(1)–Cu(6)	2.726(2)	N(1)–Cu(1)–I(5)	98.6(3)
I(2)–Cu(1)#1	2.8055(17)	I(3)–Cu(1)–I(2)	105.23(5)	I(1)–Cu(5)	2.881(3)	I(1)–Cu(1)–I(5)	111.59(7)
I(2)–Cu(1)	2.8055(17)	I(1)–Cu(1)–I(2)	99.40(5)	I(5)–Cu(6)#1	2.725(2)	I(3)–Cu(2)–Cu(4)#2	61.95(7)
I(3)–Cu(1)	2.5776(14)	I(3)–Cu(2)–I(3)#5	105.98(8)	I(5)–Cu(4)	2.737(2)	I(3)–Cu(2)–I(5)	112.66(6)
I(3)–Cu(3)#1	2.6044(15)	I(3)–Cu(2)–I(2)	107.75(2)	I(5)–Cu(1)	2.778(2)	I(1)–Cu(2)–I(5)	110.79(6)
I(3)–Cu(2)	2.6411(15)	I(3)#5–Cu(2)–I(2)	113.99(2)	I(5)–Cu(3)	2.825(2)	I(4)–Cu(2)–I(5)	92.99(6)
I(4)–Cu(9)#3	2.613(5)	I(3)–Cu(2)–I(2)#2	113.99(2)	I(5)–Cu(2)	2.869(2)	N(6)–Cu(3)–I(2)	118.1(3)
I(4)–Cu(5)	2.6254(14)	I(3)#5–Cu(2)–I(2)#2	107.75(2)	I(3)–Cu(2)	2.617(2)	N(6)–Cu(3)–I(3)	103.6(3)
I(4)–Cu(8)#3	2.644(5)	I(2)–Cu(2)–I(2)#2	107.55(8)	I(3)–Cu(3)	2.6949(19)	I(2)–Cu(3)–I(3)	113.90(7)
I(5)–Cu(8)#3	2.529(2)	N(7)–Cu(3)–I(3)#1	112.2(2)	I(4)–Cu(6)	2.583(2)	N(6)–Cu(3)–I(5)	98.4(3)
I(5)–Cu(8)	2.529(2)	N(7)–Cu(3)–I(7)	110.0(2)	I(4)–Cu(2)	2.692(2)	N(2)–Cu(4)–I(4)#1	118.9(3)
I(5)–Cu(5)#1	2.7356(16)	I(3)#1–Cu(3)–I(7)	118.71(6)	I(2)–Cu(1)	2.584(2)	N(2)–Cu(4)–I(5)	98.1(3)
I(5)–Cu(5)	2.7356(16)	N(7)–Cu(3)–I(1)	97.7(2)	I(2)–Cu(3)	2.584(2)	I(4)#1–Cu(4)–I(5)	14.71(8)
I(6)–Cu(9)	2.508(3)	I(3)#1–Cu(3)–I(1)	108.95(5)	Cu(1)–N(1)	2.014(10)	N(2)–Cu(4)–I(3)#1	102.8(3)
I(6)–Cu(9)#3	2.508(3)	I(7)–Cu(3)–I(1)	107.06(5)	Cu(3)–N(6)	2.014(10)	I(4)#1–Cu(4)–I(3)#1	111.47(8)
I(6)–Cu(5)	2.7099(16)	N(2)#1–Cu(4)–N(2)	177.4(5)	Cu(4)–N(2)	1.975(10)	I(5)–Cu(4)–I(3)#1	109.51(9)
I(6)–Cu(5)#1	2.7099(16)	N(1)–Cu(5)–I(4)	118.9(2)	Cu(4)–I(4)#1	2.573(2)	N(4)#4–Cu(5)–N(4)#2	137.7(5)
I(7)–Cu(3)#1	2.6056(16)	N(1)–Cu(5)–I(6)	107.6(2)	Cu(4)–Cu(6)#1	2.668(3)	N(3)#4–Cu(5)–I(1)	106.7(3)
I(7)–Cu(3)	2.6056(16)	I(4)–Cu(5)–I(6)	111.66(5)	Cu(4)–Cu(2)#1	2.722(3)	I(1)–Cu(5)–I(3)#5	97.01(9)
Cu(5)–N(1)	1.992(7)	N(1)–Cu(5)–I(5)	103.7(2)	Cu(4)–I(3)#1	2.749(3)	N(5)#2–Cu(6)–I(4)	118.8(3)
Cu(5)–Cu(9)#3	2.676(4)	I(4)–Cu(5)–I(5)	112.28(5)	Cu(5)–N(3)#4	1.915(10)	N(5)#2–Cu(6)–I(1)	102.4(3)
Cu(5)–Cu(8)#3	2.678(3)	I(6)–Cu(5)–I(5)	101.01(5)	Cu(5)–N(4)#2	1.924(10)	I(4)–Cu(6)–I(1)	110.38(7)
Cu(1)–N(3)	2.006(7)	N(8)–Cu(6)–N(8)#6	180.000(1)				
Cu(1)–Cu(3)#1	2.976(2)	I(5)#3–Cu(8)–I(5)	122.29(18)				
Cu(4)–N(2)#1	1.878(7)	I(5)#3–Cu(8)–I(4)#3	118.77(9)				
Cu(4)–N(2)	1.878(7)	I(5)–Cu(8)–I(4)#3	118.77(9)				
Cu(2)–I(3)#5	2.6411(15)	I(6)–Cu(9)–I(4)#3	119.09(10)				
Cu(2)–I(2)#2	2.6570(15)	I(6)#3–Cu(9)–I(4)#3	119.09(1)				
complex 3				complex 5			
I(1)–Cu(2)	2.6883(10)	N(2)–Cu(1)–I(2)	128.45(16)	I(1)–Cu(1)#1	2.7620(8)	Cu(1)#1–I(1)–Cu(1)	85.20(3)
I(1)–Cu(1)	2.7063(11)	N(2)–Cu(1)–I(1)#1	98.50(16)	I(1)–Cu(1)	2.7620(8)	Cu(1)#1–I(1)–Cu(1)#2	179.10(2)
I(2)–Cu(1)	2.6024(9)	I(2)–Cu(1)–I(1)#1	106.62(4)	I(1)–Cu(1)#2	2.8036(8)	Cu(1)–I(1)–Cu(1)#2	95.57(3)
I(2)–Cu(2)	2.6318(10)	N(2)–Cu(1)–I(1)	96.34(17)	I(1)–Cu(1)#3	2.8036(8)	Cu(1)–I(1)–Cu(1)#3	179.10(2)
I(2)–Cu(2)#2	2.6760(10)	I(2)–Cu(1)–I(1)	107.04(3)	Cu(2)–N(2)	1.906(4)	Cu(1)#2–I(1)–Cu(1)#3	83.65(3)
Cu(1)–N(2)	2.052(5)	I(1)#1–Cu(1)–I(1)	121.37(3)	Cu(2)–N(2)#1	1.906(4)	N(2)–Cu(2)–N(2)#1	159.2(2)
Cu(1)–Cu(1)#1	2.6430(18)	N(3)#1–Cu(2)–I(2)	119.00(17)	Cu(1)–N(1)	1.943(3)	N(1)–Cu(1)–N(3)#4	137.49(18)
Cu(1)–I(1)#1	2.6915(10)	N(3)#1–Cu(2)–I(2)#2	103.24(15)	Cu(1)–N(3)#4	1.944(4)	N(1)–Cu(1)–I(1)	102.92(12)
Cu(1)–Cu(2)	2.8762(12)	I(2)–Cu(2)–I(2)#2	118.41(3)	Cu(1)–I(1)#5	2.8036(8)	N(3)#4–Cu(1)–I(1)	107.17(11)
Cu(2)–N(3)#1	2.053(6)	N(3)#1–Cu(2)–I(1)	100.19(15)	N(3)–Cu(1)#6	1.944(4)	N(1)–Cu(1)–I(1)#5	105.24(12)
Cu(2)–I(2)#2	2.6760(10)	I(2)–Cu(2)–I(1)	106.72(3)				
N(1)–C(3)	1.453(10)	I(2)#2–Cu(2)–I(1)	107.37(4)				

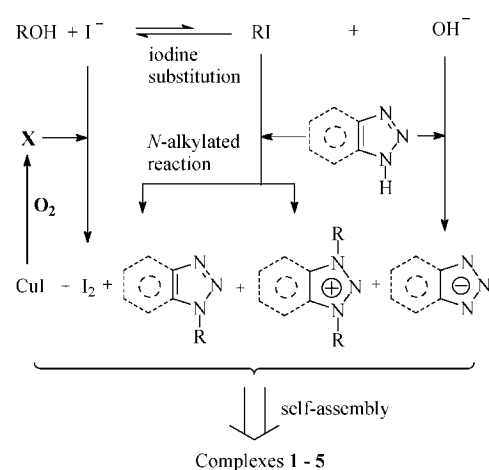
^a Symmetry code: #1 y, x, z ; #2 $-x + 1, -y + 1, -z$; #3 $-x + 3/2, -y + 3/2, z$; #4 $-y + 3/2, -x + 3/2, z$; #5 $-y + 1, -x + 1, -z$; #6 $-x + 1, -y + 1, -z + 1$. ^b Symmetry code: #1 $-x + 2, -y + 2, -z + 2$; #2 $-x + 1, -y + 2, -z + 2$. ^c Symmetry code: #1 $-x + 2, y + 1/2, -z + 1/2$; #2 $-x + 2, y - 1/2, -z + 1/2$; #3 $x, -y + 1/2, z + 1/2$; #4 $-x + 2, -y + 1, -z$; #5 $x, -y + 1/2, z - 1/2$. ^d Symmetry code: #1 $x, -y + 1/2, z$; #2 $x, y, z + 1$; #3 $x, -y + 1/2, z + 1$; #4 $x + 1/2, y, -z - 1/2$; #5 $x, y, z - 1$; #6 $x - 1/2, y, -z - 1/2$.

Scheme 1. Syntheses of Complexes 1–5



$(\text{Cu}_{10}\text{I}_{10})(\text{Cu}_6\text{I}_6)[(\text{Cu}(\text{Bta})_2)_3] \cdot (\text{DMBta})_4^+ \cdot (\text{I}^-) \cdot x(\text{I}_2)$ ($x \approx 1.5$) (1). Complex 1 is a 3D coordination polymer constructed by three types of copper(I) SBUs (SBU-I, SBU-II, SBU-III). In SBU-I (Figure 1a), copper(I) atom is coordinated in a nearly linear fashion $[\text{N}-\text{Cu}-\text{N} 177.536(5)^\circ, \text{Cu}-\text{N} 1.87895(6) \text{ Å}]$ by two 2-nitrogen atoms from two different Bta[−] ligands with a dihedral angle of $13.4512(4)^\circ$. SBU-II (Figure 1b) consists of 10 copper(I) atoms and 10 iodine atoms, fashioning a “S-shaped double-bowl” arrangement with an inverse center by 13 coedge

Scheme 2. Suggested Mechanism of the Solvothermal Reaction



Cu_2I_2 rhomboids $[\text{Cu}-\text{I} 2.60104(8) - 2.84822(9) \text{ Å}, \text{Cu} \cdots \text{Cu} 2.97524(9) - 3.2178(1) \text{ Å}]$. The distorted tetrahedral geometry

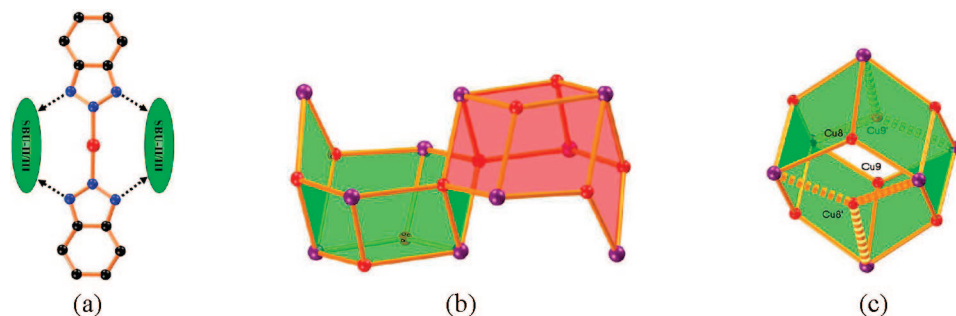


Figure 1. Complex 1: (a) SBU-I: $[\text{Cu}(\text{Bta})_2]^-$, (b) SBU-II: $\text{Cu}_{10}\text{I}_{10}$ cluster, (c) SBU-III: Cu_6I_6 cluster, Cu(8) and Cu(9) locate at two disorder positions (purple, I; red, Cu; blue, N).

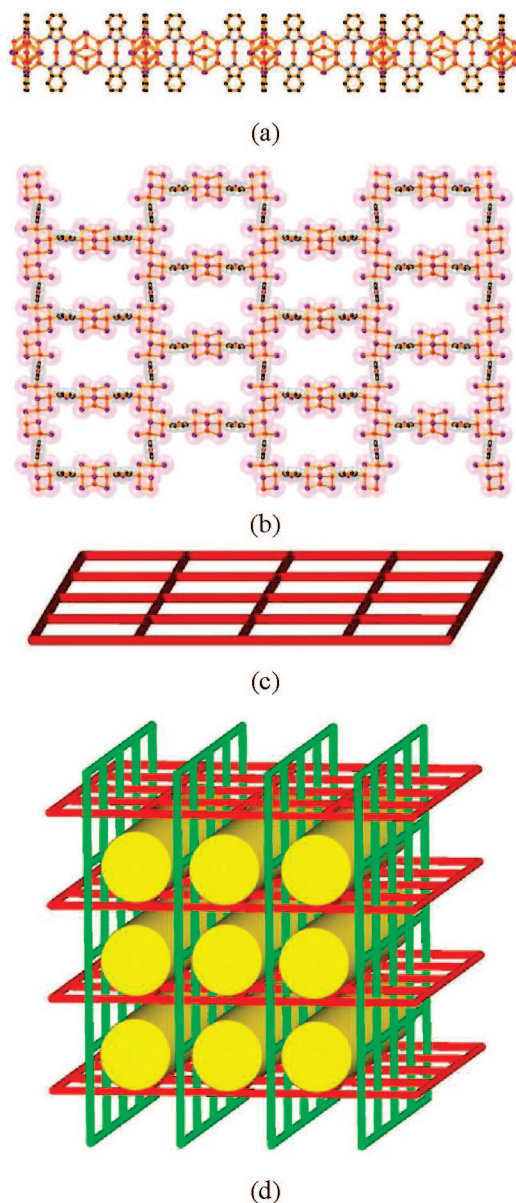


Figure 2. Complex 1: (a) 2D layer viewed along the c -direction, (b) 2D layer viewed along $(1, \bar{1}, 0)$ direction, (c) schematic view of the rationalized $(4, 4)$ topological net, (d) schematic view of the $2\text{D} \rightarrow 3\text{D}$ interpenetrated network containing 1D channel (yellow).

in each copper(I) atom is completed by four iodine atoms or three iodine atoms and one nitrogen atom from Bta^- ligand. Each iodine atom adopts either a μ_2 - or μ_3 - or μ_4 -bridging mode. Four pairs of copper(I) atoms in each SBU-II are square-planar

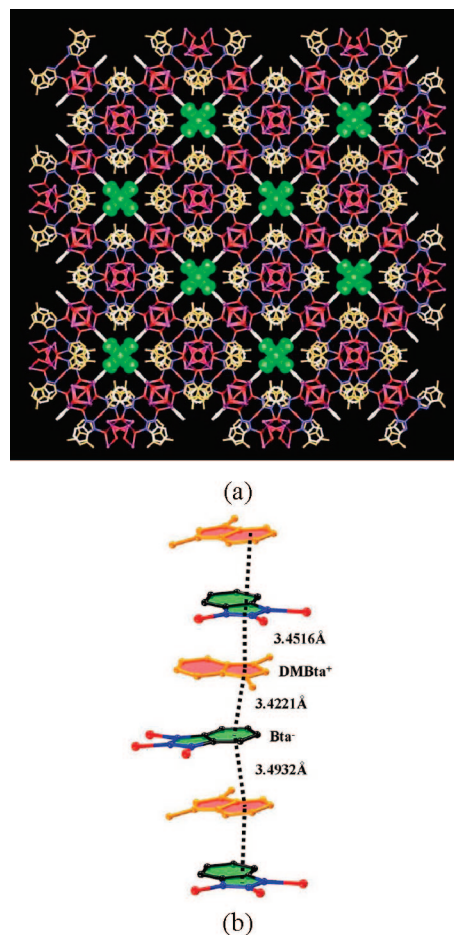


Figure 3. Complex 1: (a) 1D nanochannel filled with iodine atoms (green) along the c -direction, (b) $\pi \cdots \pi$ interaction between DMBta^+ guest cations (orange) and Bta^- ligand (green).

linked to four SBUs-I by four pairs of $\text{Cu}-\text{N}$ coordinated bonds [$\text{Cu}-\text{N}$ 2.0090(6) Å]. In SBU-III (Figure 1c), six copper(I) atoms are linked to six μ_3 -bridged iodide atoms to form a D6R ribbon-shaped ring [$\text{Cu}-\text{I}$ 2.51028(8)–2.73667(9) Å, $\text{Cu} \cdots \text{Cu}$ 2.67677(8)–2.68044(8) Å]. Each SBU-III is linearly linked to two SBUs-I by two pairs of $\text{Cu}-\text{N}$ bonds, satisfying a tetrahedral coordination environment of each copper(I) atom. To be noted, both Cu8 and Cu9 are located in two disordered positions with half occupancy and are coordinated by three iodine atoms, adopting a planar-trigonal geometry. SBU-III is different from the reported Cu_6Br_6 and Cu_6I_6 clusters,⁸ in which all copper(I) atoms have tetrahedral coordinated geometry.

Adjacent SBU-II extends along the c -direction by SBU-I and extends along the $[110]$ direction by SBU-I-III-I to form a 2D

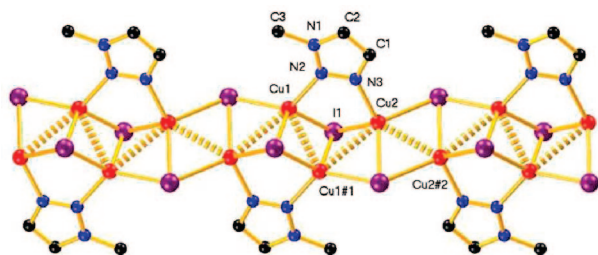


Figure 4. Complex 3: 1D chain containing corrugated double-stranded stairlike $[\text{CuI}]_n$ chain. Symmetry code: #1 $-x + 2, -y + 2, -z + 2$, #2 $-x + 1, -y + 2, -z + 2$.

brick-wall plane with rectangular windows [dimensions $14.0586(4) \times 19.9371(6)$ Å], which can be rationalized to a (4, 4) topological net by treating SBU-II as a square-planar node and SBU-I/III as a linker (Figure 2c). A very fascinating and peculiar structure feature of **1** is that all 2D sheets parallel to the $(\bar{1}10)$ plane are perpendicular to the ones parallel to the (001) plane, resulting in a $2\text{D} \rightarrow 3\text{D}$ interpenetrated topological network (Figure 2d). The interpenetration of two perpendicular 2D sheets

constructs 1D nanochannels along the c -direction with a void space of 1179.7 Å^3 (10.4%) in a unit cell,¹⁵ which are occupied by $(\text{DMBta})^+$ guest cations and I^- ions (Figure 3a). A careful examination indicates that all benzene rings of Bta^- locate in the perpendicular direction of the channel with the edge of $13.8729(4)$ Å, and there exist strong infinite $\pi \cdots \pi$ stacking interactions ($3.4221\text{--}3.4932$ Å) among $(\text{DMBta})^+$ guest cations and Bta^- ligands from the anionic host framework (Figure 3b). The structural solution of **1** reveals that disordered iodide atoms exist in the asymmetric unit of **1**. As suggested in the formula of **1**, we defined one of the iodide atoms as iodide ion and others as iodide molecules due to the charge balance of the whole framework, which is further confirmed by the result of XPS and TGA (Figures S2 and S3, Supporting Information).

[Cu₂I₂(MBta)] (2). Although the single-crystal structure of complex **2** could not be refined properly due to poor reflection data, an preliminary structural solution gives a framework of $[\text{Cu}_2\text{I}_2(\text{MBta})]$. It also contains monoalkylated ligands, similar to the structure of complex **3**.

[Cu₂I₂(MTa)] (3). Complex **3** is a polymeric double-stranded stairlike ribbon with the asymmetric unit containing two

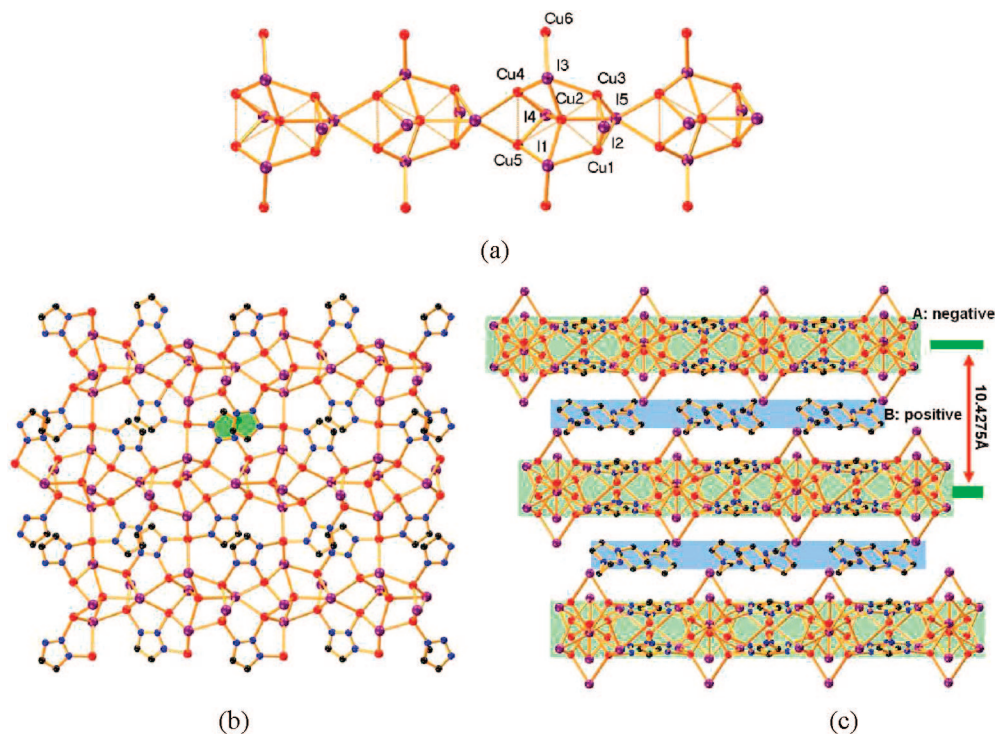


Figure 5. Complex 4: (a) 1D $[\text{Cu}_6\text{I}_5]^+$ chain along the a -axis, (b) 2D anionic layer with intralayer $\pi \cdots \pi$ interaction along the (010) direction, (c) 3D packing diagram, showing the alternate arrangement of anionic layers (green) and cationic layers (blue).

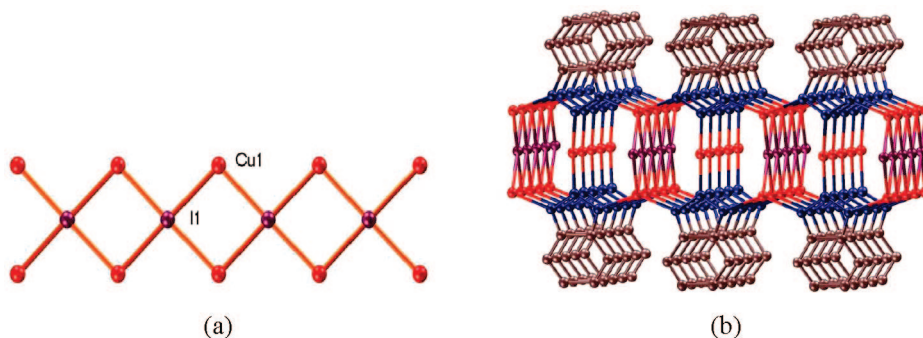


Figure 6. Complex 5: (a) 1D $[\text{Cu}_2\text{I}]^+$ chain with square-planar bridging $\mu_4\text{-I}$ atoms, (b) 2D sheet (grey, C; blue, N; red, Cu; purple, I).

crystallographically independent copper(I) centers, two iodine ions, and one MTa ligand (Figure 4). All copper(I) atoms adopt distorted tetrahedral coordinated geometry comprised of three iodine atoms and one nitrogen atom from the MTa ligand [Cu–I 2.6024(9)–2.7063(11) Å, Cu–N 2.052(5) Å]. There exist three different Cu···Cu diagonal distances [Cu(1)–Cu(1#1) 2.6430(18) Å, Cu(1#1)–Cu(2) 2.8762(12) Å, Cu(2)–Cu(2#2) 2.7178(16) Å]. Cu1 and Cu2 centers are simultaneously bridged by 2- and 3-N of MTa ligand and I1 anions to form zigzag [CuI]_n chains oriented in the *a* direction, and the two [CuI]_n chains are linked by Cu–I bonds to form corrugated double-stranded stairlike structure.

(Cu₅I₅)[Cu(Ta)₂][−]·(DETa)⁺ (4). Complex 4 consists of alternate arranging anionic 2D layers (A) of {(Cu₅I₅)[Cu(Ta)₂]}[−] and cationic (DETa)⁺ layers (B). Layer A contains pentamer Cu₅I₅ cores, in which each of four copper(I) atoms (Cu1, Cu3, Cu4, Cu5) coordinate three iodine atoms and one nitrogen atom from ligand Ta[−], and only Cu2 atom is tetrahedrally connected to four iodine atoms [Cu–I 2.573(2)–2.869(2) Å]. The five copper(I) atoms build two opposite slightly distorted triangles by Cu···Cu weak interactions with the edges of 2.668(3)–2.760(3) Å. Adjacent Cu₅I₅ cores are bridged by sharing I5 to form 1D chain along the *b* direction (Figure 5a). [Cu(Ta)₂][−] subunits connect adjacent 1D chains by a Cu–I bond [Cu–I 2.88044(3)–2.93485(3) Å] along the *c* direction to construct a 2D layer (A) (Figure 5b). In [Cu(Ta)₂][−], Cu6 is tetrahedrally coordinated to two iodide ions and two 1-N atoms from two Ta[−] ligands, whose 2- and 3-N atoms coordinate to two copper(I) atoms located in adjacent 1D [Cu₅I₅][−] chains [Cu–N 1.91557(2)–2.01496(2) Å]. The 2D layers (A) locate alternately parallel to *c* direction, separated by bulky (DETa)⁺ guest cation layers (B), and the distance of the interlayer is 10.4275 Å (Figure 5c). An interesting feature of 4 is that the μ₂-I2, μ₃-I1/I4, μ₄-I3, μ₅-I5 modes coexist in the compound. According to recent version CSD, only one example of a μ₅-I compound is reported,¹⁶ and this is the first example bearing four different bridging-mode iodides.

[Cu₃I(Bta)₂] (5). Complex 5 consists of 2D simple sheets with the asymmetric unit containing one crystallographically unique Bta[−] ligand, half an iodide atom, and one and half copper(I) atoms. The 2D sheet can be regarded as a bilayer structure constructed by a [(Cu₂I)⁺]_n chains and [Cu(Bta)₂][−] subunits. In the 1D [(Cu₂I)⁺]_n chain, I1 adopts square-planar bridging mode to connect four copper(I) atoms [Cu–I 2.7619(1)–2.8039(1) Å], and Cu1 is tetrahedrally joined to two iodide atoms and two nitrogen atoms from two Bta[−] ligand (Figure 6a). The completely planar μ₄-bridging mode in 5 is different from other reported distorted μ₄-bridge examples.¹⁷ In the [Cu(Bta)₂][−] subunit, analogue to SBU-I in 1, Cu2 linearly coordinates two 2-N atoms from two Bta[−] ligands, whose 1- and 3-N atoms link two adjacent [(Cu₂I)⁺]_n chains by Cu–N bonds [Cu–N 1.90645(8)–1.94390(9) Å, N–Cu–N 159.219(7)°] to form a 2D sheet (Figure 6b).

Conclusions

In summary, we have successfully synthesized and characterized five new copper(I) iodide inorganic–organic hybrid coordination polymers based on CuI and in situ *N*-alkylated triazolium ligands. The new simultaneous in situ *N*-alkylated and self-assembly reaction affords a highly unusual 2D → 3D interpenetrated porous framework containing two novel neutral discrete Cu₁₀I₁₀/Cu₆I₆ clusters, which enrich the structure variation of high-nuclear Cu_nI_n cluster-based architectures. The import of the in situ generated *N*-alkylated organic cations is

possibly an effective way to examine the influence of organic cationic templates on the construction of anionic coordination frameworks.

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Supporting Information Available: Crystallographic files in CIF format; figures illustrating ESI-MS analysis spectra of different filtrates, XPS and TGA of complex 1 in PDF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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