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Construction of Four Copper Coordination Polymers Derived from a Tetra-Pyridyl-Functionalized Calix[4]arene: Synthesis, Structural Diversity and Catalytic Applications in the A^3 (Aldehyde, Alkyne and Amine) Coupling Reaction

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ABSTRACT: Solvothermal reactions of CuX_2 (X = NO_3, Cl, Br, I) with tetra-pyridyl-functionalized calix[4]arene at 130 °C afforded four novel coordination polymers, $\{[(CuNO_3)_2L]\cdot MeOH\}_n$ (**1**), $[(Cu_2Cl_4)L]_n$ (**2**), $[(Cu_3Br_3)L]_n$ (**3**) and $[(Cu_3I_3)L]_n$ (**4**), where L = 25,26,27,28-tetra[(3-pyridylmethyl)oxy]calix[4]arene. All the products were characterized by infrared spectroscopy, thermogravimetric analysis, single-crystal X-ray diffraction and powder X-ray diffraction. Crystal structure analysis reveals that **1** holds a one-dimensional (1D) double-chain constructed by mononuclear $[Cu(NO_3)]$ units and L linkers, while **2** features a 1D chain and its bowl-shaped L ligands work as linkers to connect the dinuclear $[Cu_2Cl_4]$ units. Compounds **3** and **4** bear similar 2D networks, in which each trinuclear $[Cu_3Br_3]$/$[Cu_3I_3]$ unit works as a three-connecting node to connect its six equivalents by sharing L ligands. These results demonstrated that different anions have significant effect on the final structure formation. Compounds **1–4** were employed as catalysts for the A^3 coupling reaction under microwave irradiation. Notably, **3** showed the best catalytic properties for the synthesis of versatile propargylamines (yield up to 94% in only 10 min) from the A^3 reaction of formaldehyde with a variety of alkynes and amines.

Introduction

Owing to the procedural simplicity and synthetic efficiency, one-pot multicomponent reactions (MCRs) have aroused wide concern in the past decades,[1] which provided a feasible synthetic strategy to access complex structures using rather simple starting materials by a one-pot method, and exhibited high selectivity and atom economy.[2] An increasing number of MCRs have been designed for the synthesis of versatile structures with high yield and simple operation.[3-8] Among various MCRs, considerable attention have been paid to the catalytic coupling reaction of aldehyde, amine and alkyne (so-called A^3 coupling), as the main product propargylamine is the key and versatile intermediate to prepare many biologically active nitrogen-containing compounds.[9-13] Therefore, it is important to explore an efficient catalyst with simple procedure for A^3 coupling reaction.

Over the past several decades, calix[4]arene-based molecules have emerged as a class of molecular hosts due to their bowl-shaped cavity and ability to interact with various guest molecules.[14-20] Recently, the calix[4]arenes and their derivatives have also been utilized as potential molecular units to construct coordination polymers because of the easy modification and functionalization both on the lower and upper rims.[21-27] Moreover, the calix[4]arene core displays inherent advantageous features, such as preorganization,[28] flexibility[29] and bulkiness skeleton,[30] as well as its widely tolerance of functional groups and metals. As a consequence, by tethering particular transition metals on such structure, the as-synthesized coordination polymers would be potential catalysts. The calix[4]arene platform provides peculiar arrangement for the binding/catalytic site in a complementary array to recognize/transform a potential substrate, which would be favorable for the design of versatile catalysts.[31,32] Furthermore, owing to the presence of the well-defined cavity near the catalytic centre, we envisioned that the calix[4]arene-based coordination polymers could give high selectivity for the catalytic reaction.[33,34]

Nowadays, it is widely acknowledged that the microwave irradiation have great advantages over traditional heating because of its shorter reaction time, higher product yield and lower energy consumption.[35-41] Thus, our studies report the microwave-assisted Cu(I/II)-calix[4]arene-based catalysis as an efficient catalytic platform for direct access to propargylamines. Based on the design, the Cu(I/II) ion was chosen as active site to catalyze the A^3 reaction due to its high catalytic activity.[12,42-49] The ligand tetra-pyridyl-functionalized calix[4]arene, 25,26,27,28-tetra -[(3-pyridylmethyl)oxy]calix[4]arene (denoted as L) was employed to assemble with copper salts, as its abundant aromatic rings would facilitate the substrates alkyne to approach the active site of Cu(I/II) ion through π–π interactions between the substrates and the aromatic rings.[18,50,51] Hence, four coordination polymers, $\{[(CuNO_3)_2L]\cdot MeOH\}_n$ (**1**), $[(Cu_2Cl_4)L]_n$ (**2**), $[(Cu_3Br_3)L]_n$ (**3**) and $[(Cu_3I_3)L]_n$ (**4**) were synthesized by the assembly of L with CuX_2 (X = NO_3, Cl, Br, I), giving different structural architectures. Their catalytic activities were assessed by the microwave-assisted A^3 coupling reaction. Interestingly, compound **3** exhibited the best catalytic properties for the synthesis of diverse propargylamines (yield up to 94% in only 10 min) from the A^3 reaction.

Experimental section

Preparation of $\{[(CuNO_3)_2L]\cdot MeOH\}_n$ (1). A solution of $Cu(NO_3)_2\cdot 3H_2O$ (14 mg, 0.06 mmol), L ligand (12 mg, 0.015 mmol), and 4 mL of MeOH/DMF (1:1 V/V, DMF = *N*,*N*-dimethylformamide) was sealed in a 10 mL Pyrex glass tube and heated at 130 °C for 3 days. Subsequent cooling to ambient temperature (5 °C h^{-1}) afforded the colorless blocks of **1**. Yield: 7 mg (44%, based on L). Anal. Calcd. for $C_{53}H_{48}N_6Cu_2O_{11}$: C, 59.38; H, 4.51; N, 7.84. Found: C, 59.71; H, 4.17; N, 7.99. IR (KBr disc): 3065 (w), 2916 (w), 1456 (m), 1430 (s), 1342 (m), 1236 (m), 1186 (s), 1086 (s), 987 (s), 949 (m), 801 (s), 762 (s), 712 (s), 649 (m), 568 (w), 550 (w), 518 (m) cm^{-1}.

Preparation of [(CuCl$_2$)L$_{0.5}$]$_n$ (2). A solution of $CuCl_2 \cdot 2H_2O$ (3.5 mg, 0.02 mmol), L ligand (8 mg, 0.01 mmol) and EtOH (4 mL) was sealed in a 10 mL Pyrex glass tube and heated at 130 °C for 3 days. Subsequent cooling to ambient temperature (5 °C h^{-1}) afforded the red blocks of **2**. Yield: 5 mg (47%, based on L). Anal. Calcd. for $C_{26}H_{22}N_2Cl_2CuO_2$: C, 59.04; H, 4.19; N, 5.30. Found: C, 59.44; H, 3.95; N, 5.69. IR (KBr disc): 3061 (w), 3000 (w), 2910 (w), 1600 (m), 1455 (s), 1425 (m), 1365 (w), 1245 (m), 1185 (s), 1113 (m), 1082 (s), 1041 (m), 986 (s), 944 (m), 842 (m), 818 (m), 794 (m), 752 (s), 692 (s), 656 (m), 638 (m), 590 (m), 511 (w) cm^{-1}.

Preparation of [(Cu$_3$Br$_3$)L]$_n$ (3). Compound **3** (colorless blocks) was synthesized using a same method as that of **2**, except utilizing $CuBr_2$ (4.5 mg, 0.02 mmol) and MeOH/DMF (1:1 V/V) instead of $CuCl_2 \cdot 2H_2O$ and EtOH. Yield: 7 mg (57%, based on L). Anal. Calcd. for $C_{52}H_{44}N_4Cu_3Br_3O_4$: C, 51.22; H, 3.64; N, 4.60. Found: C, 50.95; H, 3.37; N, 4.73. IR (KBr disc): 3059 (w), 2906 (w), 1572 (w), 1471 (m), 1455 (s), 1426 (s), 1397 (m), 1370 (m), 1245 (s), 1190 (s), 1093 (m), 1050 (m), 980 (s), 944 (m), 865 (w), 798 (m), 758 (s), 698 (s), 643 (m), 621 (w), 566 (m), 511 (w) cm^{-1}.

Preparation of [(Cu$_3$I$_3$)L]$_n$ (4). A solution of CuI_2 (6 mg, 0.02 mmol), L ligand (8 mg, 0.01 mmol) and DMF (4 mL) was sealed in a 10 mL Pyrex glass tube and heated at 130 °C for 3 days. Gradual cooling at a rate of 5 °C h^{-1} to ambient temperature afforded the colorless blocks of **4**. Yield: 7 mg (51%, based on L). Anal. Calcd. for $C_{52}H_{44}N_4Cu_3I_3O_4$: C, 45.91; H, 3.26; N, 4.12. Found: C, 45.49; H, 2.98; N, 3.79. IR (KBr disc): 3061 (w), 2905 (w), 1575 (w), 1473 (m), 1456 (s), 1425 (s), 1395 (m), 1371 (m), 1317 (w), 1245 (s), 1191 (s), 1089 (m), 1052 (m), 980 (s), 944 (m), 866 (w), 800 (m), 758 (s), 698 (s), 644 (m), 620 (w), 565 (m), 511 (w) cm^{-1}.

Catalytic studies. The reactions of alkyne (1.0 mmol), amine (1.2 mmol), HCHO (1.2 mmol), catalyst (0.001 mmol) and MeCN (10 mL) were conducted in a closed vessel containing under microwave power (80 W) at 100 °C. After that, the system was cooled to ambient temperature and the MeCN was removed by evaporation in vacuum. By diluting with 8 mL H_2O, the residual mixture was extracted with ethyl acetate (3 × 10.0 mL). The combined organic phases were treated to remove the solvent and further purified by column chromatography using petroleum ether/ethyl acetate as the eluent to give the corresponding products. These products were characterized by ^{1}H NMR, ^{13}C NMR and HRMS.

Results and discussion

Synthetic and spectral aspects. Reactions of L ligand with $Cu(NO_3)_2\cdot 3H_2O$ and CuX_2 (X = Br, I) in different solvents (MeOH/DMF for **1**, MeOH/DMF for **3** and DMF for **4**) at 130 °C for 3 days afforded colorless crystals of **1** (44% yield), **3** (57% yield) and **4** (51% yield), respectively. Interestingly, for compounds **1**, **3** and **4**, Cu(II) were reduced to Cu(I), which may stem from the reduction of Cu(II) was mediated by the DMF decomposition products.[52] Similarly, reactions of $CuCl_2\cdot 2H_2O$ with L ligand in EtOH produced red crystals of **2** (47% yield). To verify the valence of copper in these compounds, XPS investigations were carried out. In Figure S1b, the peak of Cu $2p_{3/2}$ at *ca.* 932.1 eV in **1**, **3** and **4** are attributed to Cu(I).[53] Compared Cu 2p XPS spectrum of **1**, **3** and **4** with that of **2**, the higher binding energy of Cu $2p_{3/2}$ peak at 934.3 eV in **2** is assigned to Cu(II), accompanied by the characteristic Cu(II) shakeup satellite peaks (938−945 eV) at 942.9 and 940.7 eV.[54-56]

Compounds **1**–**4** were stable towards oxygen and moisture. PXRD measurements were carried out to check their phase purity (Figure S2). Single-crystal diffraction analysis further confirmed the identities of **1**–**4** and the corresponding crystallographic information were summarized in Table 1.

(**Table 1** here)

Crystal structures. Compound **1** crystallizes in the orthorhombic space group *Ibca*. Its asymmetric unit contains half of $[(CuNO_3)_2L]$ unit and one MeOH molecule. In Figure 1a, each Cu centre is three-coordinated by one O atom of one NO_3^- anion and two pyridyl N atoms from one L ligand. A flattened cone conformation was formed in calix[4]arene core of **1** (Figure 1a). The mononuclear $[Cu(NO_3)]$ subunit works as a 2-connected node to interconnect the L ligands, resulting in a 1D $[(CuNO_3)_2L]_n$ double-chain (Figure 1b).

(Figure 1 here**)**

Compound **2** crystallizes in the monoclinic space group *P*2/*n*. Its asymmetric unit includes half of $[(Cu_2Cl_4)L]$ unit. Each Cu(II) atom is five-coordinated by three Cl^- anions and two pyridyl N atoms from one L ligand, producing a distorted $[CuN_2Cl_3]$ pentagonal pyramid coordination geometry (Figure 2a). Similar to that in **1**, a flattened cone conformation was also formed in the calix[4]arene core of **2**, and parallel or sharply inclined position was observed for the opposed phenyl rings (Figure 2a). Two [CuCl] subunits are connected by two μ_2-Cl anions to form a dinuclear [Cu_2Cl_4] unit (Figure 2b). The Cu1···Cu1A separations are 3.4847(10) Å. These [Cu_2Cl_4] units are also employed as 2-connected nodes to link L ligands through the N atoms of pyridyl arms, producing a 1D [$(Cu_2Cl_4)L]_n$ chain (Figure 2c).

(**Figure 2** here)

Both compounds **3** and **4** crystallize in the monoclinic space group *Cc*. Their asymmetric units include one [$(Cu_3Br_3)L$] and [$(Cu_3I_3)L$] unit, respectively. While the Cu atoms in **3** and **4** adopted different coordination geometries. For **3**, Cu1 and Cu2 atoms adopt the same coordination geometries, which is coordinated by one pyridyl N atom from one L ligand and two μ_2-Br atoms to complete the triangular geometries (Figure 3a). The Cu3 atom is tetrahedrally coordinated by two pyridyl N atoms from L ligands and two μ_2-Br atoms (Figure 3a). For **4**, each Cu center is bonded with μ_2-I or μ_3-I atoms and pyridyl N atoms from L ligands, resulting in the distorted [CuI_3N]/[CuI_2N_2] tetrahedral coordination geometries (Figure 3b). A flattened cone conformation was also formed in the calix[4]arene core of **3** and **4**, and parallel or sharply inclined position was observed for the opposed phenyl rings (Figures 3a-3b). As shown in Figures 3c-3d, the Cu1, Cu2 and Cu3 centers are interconnected by three μ_2-Br atoms or one μ_2-I and two μ_3-I atoms to afford the trinuclear [Cu_3Br_3] and [Cu_3I_3] units, respectively. The Cu···Cu separations are in the range of 2.5604(12)–2.9101(12) Å and 2.4166(8)–2.8415(9) Å for **3** and **4**. Furthermore, each [Cu_3Br_3] or [Cu_3I_3] unit in **3** and **4** connects its three equivalents by sharing L ligands to give 2D networks (Figure 3e and Figure S3).

(**Figure 3** here)

Thermal behavior. To investigate the thermal stability, thermogravimetric (TG) measurements of **1**–**4** were conducted (Figure S4). In **1**, the first weight loss of 2.46 % (calculated 2.99 %) at the temperature range of 35–240 °C is attributed to MeOH solvent molecules. After that, further heating lead to gradual decomposition of the compound. For **2**–**4**, TG analysis indicated that they are stable up to 255 °C (**2**), 295 °C (**3**) and 305 °C (**4**), then they begin to decompose.

Catalytic applications. Copper(I)/(II) complexes are fascinating not only for their interesting structures,[57,58] but also for their catalytic application in many organic transformations.[59-64] In order to assess the catalytic utility of copper compounds **1**–**4** and further determine the best reaction conditions to afford propargylamines with excellent yields, a series of A^3 coupling reactions have been performed under microwave irradiation using formaldehyde, amine and alkyne in the presence of copper catalysts **1**–**4**.

Initially, to optimize the reaction conditions, ethynylbenzene, formaldehyde and morpholine were chosen as the model substrates (Table 2). Various copper catalysts (0.001 equiv) were tested at 100 ^{o}C in MeCN under microwave irradiation (Table 2, entries 1-4), resulting in the desired products with the yields of trace, 62%, 91% and 78%, respectively. To ascertain the role of the structural features in catalysis, the ESI-MS spectra of **1**–**4** were recorded. As shown in Figure S5, the base peak at 1640.0834 in the spectra of **1** is attributed to $[CuL_2]^+$ fragment, in which the catalytic sites Cu(I) are buried in the packing arrangement formed by L ligands that adopt the up and down modes (Figure 1b), making the alkyne molecules difficult to approach the catalytic sites Cu(I). While, for **2**–**4**, the peaks of the spectra at 1812.5001, 1138.8334 and 1232.9167 are attributed to $[(Cu_2Cl_3)L_2]^+$ (**2**), $[(Cu_3Br_2)L]^+$ (**3**) and $[(Cu_3I_2)L]^+$ (**4**) fragments, respectively. In the above fragments, the catalytic sites of Cu(I/II) are exposed, as the L ligands arranged as single layer with the bowl-shaped fashions (Figure 2c and Figures S6-S7), which may facilitate the alkyne molecules to approach the active site Cu(I/II) through the π–π interactions between alkyne and pyridyl rings of L ligands.[18] Furthermore, open active sites were obtained for **2**–**4** by losing halogen anions to effectively interact with substrates alkyne. In comparison with **3** and **4**, the species of copper in **2** are Cu(II), which have a lower catalytic activity than Cu(I) to interact with the ethynylbenzene.[65,66] The active site Cu(I) in **3** and **4** are three-coordinated and four-coordinated by N atoms and Br/I anions, which suggested that the Cu(I) in **3** have more active sites to catalyze the A^3 coupling reaction, giving higher catalytic performance for **3**.

Hence, compound **3** was finally selected as the catalyst for the reaction, considering its excellent yield for expected product (Table 2, entry 3). Our next studies focused on the effect of solvent in the model reaction. Considerably low yields were observed when other solvents such as toluene, DCE, EtOH, and EtOAc were used (Table 2, entries 5-8), which may be due to catalyst **3** was insoluble in these solvents. Lowering the reaction temperature to 60 ^{o}C or 30 ^{o}C, resulted in relatively low yields of 39% or 26% (Table 2, entries 9-10). The amount of catalyst is also an important factor in catalytic reaction. As can be seen in Table 2, by lowering the amount of catalyst, a lower yield was obtained

(Table 2, entry 11) and no reaction occurred when the amount of copper catalyst was reduced to zero (Table 2, entry 12). After sufficient screening, the optimal condition eventually emerged as ethynylbenzene (1.0 mmol), formaldehyde (1.2 mmol), morpholine (1.2 mmol), and MeCN (10.0 mL) at 100 °C under microwave irradiation (Table 2, entry 3).

Furthermore, control catalytic experiments of A^3 coupling reaction were performed under the same condition. When the CuBr and L were employed as catalysts, the corresponding yields were 75% and 0 (Table 2, entries 13-14), respectively. The higher yield obtained for **3** (91%) may originate from the introduction of L into the catalytic system that altered the coordination environment of the Cu(I) ions and the interaction between Cu(I) centers and L in **3**, resulting in the improvement of the catalytic activity of copper centers.[67]

(**Table 2** here)

After our successful efforts, we shifted our attention to the scope of A^3 coupling reaction catalyzed by compound **3**, and Table 3 exhibited the summarized results. Surprisingly, the reaction of morpholine with both electron-donating and electron-withdrawing groups of *p*-substituted phenylacetylene afforded the desired products with high yields of 92% and 94% (**5b**-**5c**). It is noteworthy that the reactions with sterically hindered polycyclic aromatic alkynes, such as 9-ethynylphenanthrene and 1-ethynylpyrene, also proceeded smoothly to give the expected products **5d** and **5e** in high yields. In addition, other representative secondary amines, such as pyrrolidine and *N*-benzylethanamine, were also found to be suitable for this transformation and gave good to excellent yields (**5f**-**5i**). These results indicated that both the electronic effect of substituents and steric effects on the aromatic alkynes had limited influence on this copper-catalyzed three-component coupling reaction. Further to compare the catalyst dosage to the literature methods, it is worth pointing out that good to excellent yields were still obtained in the present protocol within 10 min, involving only 0.1 mol % catalyst loading without any additives.[12,42,68,69]

(**Table 3** here)

A plausible mechanism was proposed based on the experimental results and previous literature.[70,71] As demonstrated in Scheme 1, the catalyst **3** initially reacts with terminal alkyne to activate the C–H bond and form a copper–acetylide **A** (*m*/*z* 995.1152; Figure S8). This is a very favourable step because Cu metal is well known to give high alkynophilicity for terminal alkynes.[72,73] The copper–acetylide **A** further reacts with **B** (*m*/*z* 100.0761; Figure S9), which is generated in situ from morpholine and formaldehyde, affording a coordinatively saturated intermediate **C**. Finally, the newly generated intermediate **C** dissociates to afford the expected product **5a** and regenerates the catalyst. The only theoretical by-product in the reaction is water.

(**Scheme 1** here)

Conclusions

In this paper, four coordination polymers **1–4** have been constructed under the solvothermal reactions between CuX_2 (X = NO_3, Cl, Br, I) and tetra-pyridyl-functionalized calix[4]arene (L). These compounds exhibit different architectures, such as 1D chain, double-chain and 2D networks, which demonstrates that a change in the species of anions played a crucial role in the self-assembly process. These coordination polymers have been employed in the A^3 coupling reaction under microwave irradiation and **3** give the best performance, which could effectively catalyze the A^3 reaction of formaldehyde with various alkynes and amines, producing the corresponding propargylamines with high yields in a short time (yields up to 94% in 10 min). Such good performance can be attributed to its abundant pyridyl rings facilitating the substrates alkyne to approach the active site of Cu(I) through π–π interactions between the substrates and the pyridyl rings. The above observations provide further evidence that copper-based coordination polymers catalysis as an efficient catalytic platform for direct access to the important intermediates of propargylamines, by a sustainable and atom economical approach from easily accessible starting materials under mild conditions. Further studies of the construction and applications of these coordination polymers are in progress.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/ 10.1021/acs.cgd.7b00xxxx.

X-ray data collection and structure determination, XPS spectra, PXRD patterns, TGA curves, ESI-SI spectra, ^{1}H NMR, ^{13}C NMR and HRMS spectra and additional figures (PDF).

Accession Codes

CCDC 1542817-1542820 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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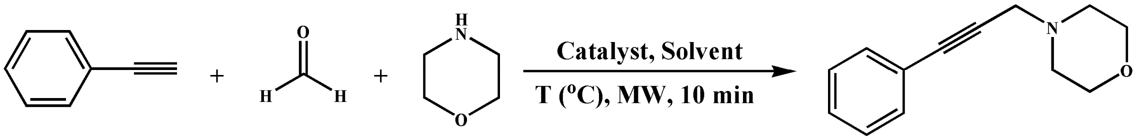
Table 1. Summary of Crystallographic Data for 1−4

Compound	**1**	**2**	**3**	**4**
Empirical Formula	$C_{53}H_{48}Cu_2N_6O_{11}$	$C_{26}H_{22}Cl_2CuN_2O_2$	$C_{52}H_{44}Br_3Cu_3N_4O_4$	$C_{52}H_{44}Cu_3I_3N_4O_4$
Formula Weight	1072.07	528.91	1219.27	1360.27
Crystal System	orthorhombic	monoclinic	monoclinic	monoclinic
Space Group	*Ibca*	*P*2/*n*	*Cc*	*Cc*
a (Å)	15.196(3)	10.289(2)	24.543(5)	24.519(5)
b (Å)	15.650(3)	16.890(3)	14.009(3)	14.249(3)
c (Å)	39.540(8)	13.191(3)	16.521(3)	16.820(3)
α (°)	90	90	90	90
β (°)	90	95.83(3)	125.68(3)	125.76(3)
γ (°)	90	90	90	90
V (Å^3)	9403(3)	2280.5(8)	4614(2)	4769(2)
Z	8	4	4	4
T (K)	100	100	100	100
ρ_{calc} (g/cm^3)	1.526	1.541	1.755	1.895
F (000)	4448	1084	2432	2648
μ (MoKα, mm^{-1})	0.977	1.220	4.020	3.318
Total reflections	72387	19852	15849	16375
Unique reflections (R_{int})	4134 (0.0471)	4031 (0.0720)	7904 (0.0263)	7311 (0.0208)
No. of observations	3241	2987	7310	7158
No. of parameters	349	299	615	595
$R_1{}^a$	0.0423	0.0469	0.0338	0.0204
$wR_2{}^b$	0.1274	0.1284	0.0769	0.0476
GOF^c	1.050	1.031	1.041	1.031

[a] $R_1 = \Sigma||F_o|-|F_c|/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma w(F_o{}^2-F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{1/2}$. [c] GOF = $\{\Sigma w(F_o{}^2-F_c{}^2)^2/(n-p)\}^{1/2}$, where n = number of reflections and p = total numbers of parameters refined.

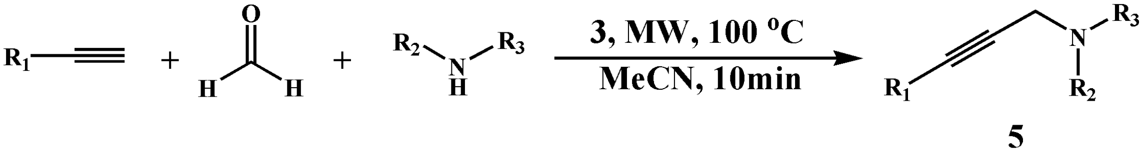
Table 2. Optimization of the reaction conditions[a]

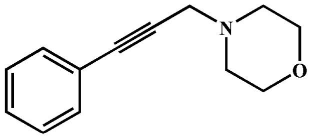


Entry	Catalyst	Solvent	T (°C)	Yield (%)[b]
1	**1**	MeCN	100	trace
2	**2**	MeCN	100	62
3	**3**	MeCN	100	91
4	**4**	MeCN	100	78
5	**3**	toluene	100	16
6	**3**	DCE	100	54
7	**3**	EtOH	100	15
8	**3**	EtOAc	100	49
9	**3**	MeCN	60	39
10	**3**	MeCN	30	26
11[c]	**3**	MeCN	100	32
12	–	MeCN	100	0
13	CuBr	MeCN	100	75
14	L	MeCN	100	0

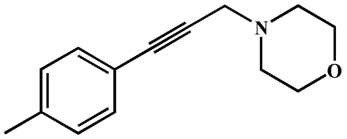
[a] Reaction conditions: ethynylbenzene (1.0 mmol), formaldehyde (1.2 mmol), morpholine (1.2 mmol), Catalyst (0.001 mmol), Solvent (10.0 mL), microwaves, 10 min. [b] Yield of the isolated product. [c] Catalyst (0.0005 mmol).

Table 3. The scope of A^3 coupling reaction catalyzed by 3^{a,b,c}

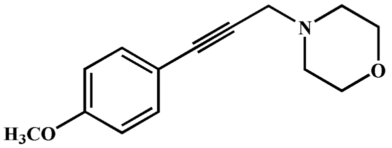




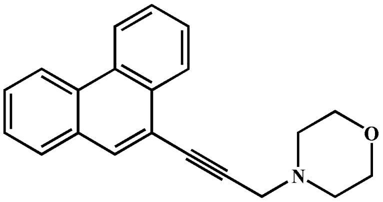
5a, 91%



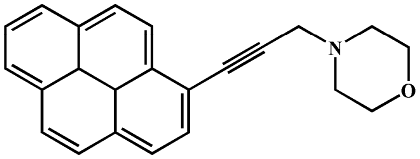
5b, 92%



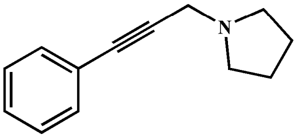
5c, 94%



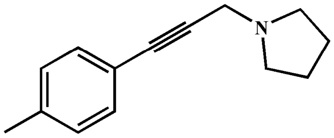
5d, 80%



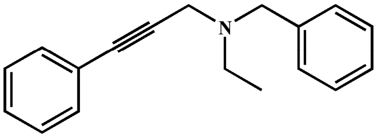
5e, 82%



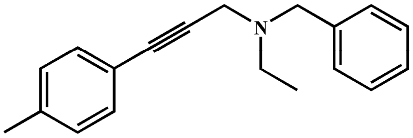
5f, 78%



5g, 80%



5h, 92%



5i, 94%

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[a] Standard reaction conditions: alkyne (1.0 mmol), formaldehyde (1.2 mmol), amine (1.2 mmol), **3** (0.001 mmol), MeCN (10.0 mL), microwaves, 100 °C, 10 min. [b] Yield of the isolated products. [c] The products of corresponding propargylamines were characterized by ^{1}H NMR, ^{13}C NMR and HRMS (Figures S11-S19).

Captions for Schemes & Figures

Scheme 1. Plausible mechanism for the A^3 coupling reaction catalyzed by compound **3**.

Figure 1. (a) View of the coordination environment of Cu centers in **1** with labeling schemes. Symmetry codes: (A) – *x* + 1, – *y* + 1/2, *z*; (B) *x* – 1/2, – *y* + 1/2, – *z* + 2; (C) – *x* + 3/2, *y*, – *z* + 2. (b) View of a 1D $[(CuNO_3)_2L]_n$ chain of **1**. Atom color codes: Cu, cyan; O, red; N, blue; C, gray. All H atoms are omitted for clarity. Selected bond lengths (Å): Cu(1)–N(1) 1.925(2), Cu(1)–N(2B) 1.929(2), Cu(1)–O(3) 2.256(5).

Figure 2. (a) View of the coordination environment of Cu center in **2** with labeling schemes. Symmetry codes: (A) – *x* + 3/2, *y*, − *z* + 1/2; (B) *x*, *y*, *z* + 1; (C) – *x* + 3/2, *y*, − *z* − 1/2. (b) View of a $[Cu_2Cl_4]$ unit of **2**. (c) View of a 1D $[(Cu_2Cl_4)L]_n$ chain in **2** extending along the *c* axis. Atom color codes: Cu, cyan; O, red; N, blue; C, gray; Cl, green. All H atoms are omitted for clarity. Selected bond lengths (Å): Cu(1)–N(1) 1.993(3), Cu(1)–N(2B) 2.189(3), Cu(1)–Cl(3) 2.2597(12), Cu(1)–Cl(2) 2.3236(11), Cu(1)–Cl(1) 2.3834(12).

Figure 3. (a) View of the coordination environment of Cu centers in **3** with labeling schemes. Symmetry codes: (A) *x*, *y* – 1, *z*; (B) *x*, – *y*, *z* + 1/2. (b) View of the coordination environment of Cu centers in **4** with labeling schemes. Symmetry codes: (A) *x*, *y* + 1, *z*; (B) *x*, – *y* + 2, *z* + 1/2. (c) View of a $[CuBr]_3$ unit of **3**. (d) View of a $[CuI]_3$ unit of **4**. (e) View of a 2D network in **3** extending along the *bc* plane. Atom color codes: Cu, cyan; O, red; N, blue; C, gray; Br, dark yellow; I, pink. All H atoms are omitted for clarity. Selected bond lengths (Å) for **3**: Cu(1)–N(1) 1.943(4), Cu(1)–Br(3) 2.3986(15), Cu(1)–Br(1) 2.5036(11), Cu(2)–N(3A) 2.018(5), Cu(2)–Br(2) 2.3314(11), Cu(2)–Br(1) 2.3895(11), Cu(3)–N(2) 2.029(4), Cu(3)–N(4B) 2.040(4), Cu(3)–Br(3) 2.4859(9), Cu(3)–Br(2) 2.5365(15), Cu(1)–Cu(2) 2.5901(12), Cu(1)–Cu(3) 2.9101(12), Cu(2)–Cu(3) 2.5604(12). Selected bond lengths (Å) for **4**: Cu(1)–N(2) 1.968(3), Cu(1)–I(3) 2.6268(8), Cu(1)–I(1) 2.7392(15), Cu(1)–I(2) 2.9571(9), Cu(2)–N(4A) 1.972(3), Cu(2)–I(3) 2.6064(8), Cu(2)–I(2) 2.7247(9), Cu(2)–I(1) 2.8259(12), Cu(3)–N(1) 2.031(3), Cu(3)–N(3B) 2.041(3), Cu(3)–I(1) 2.6416(7), Cu(3)–I(2) 2.6543(15), Cu(1)–Cu(2) 2.4166(8), Cu(1)–Cu(3) 2.8415(9), Cu(2)–Cu(3) 2.5836(8).

Scheme 1

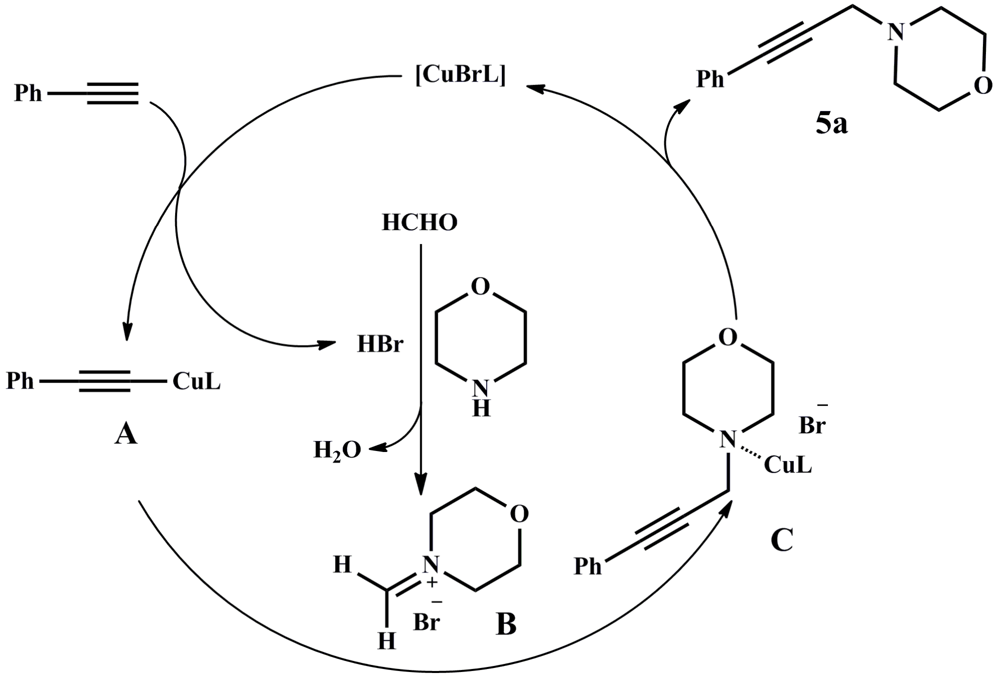
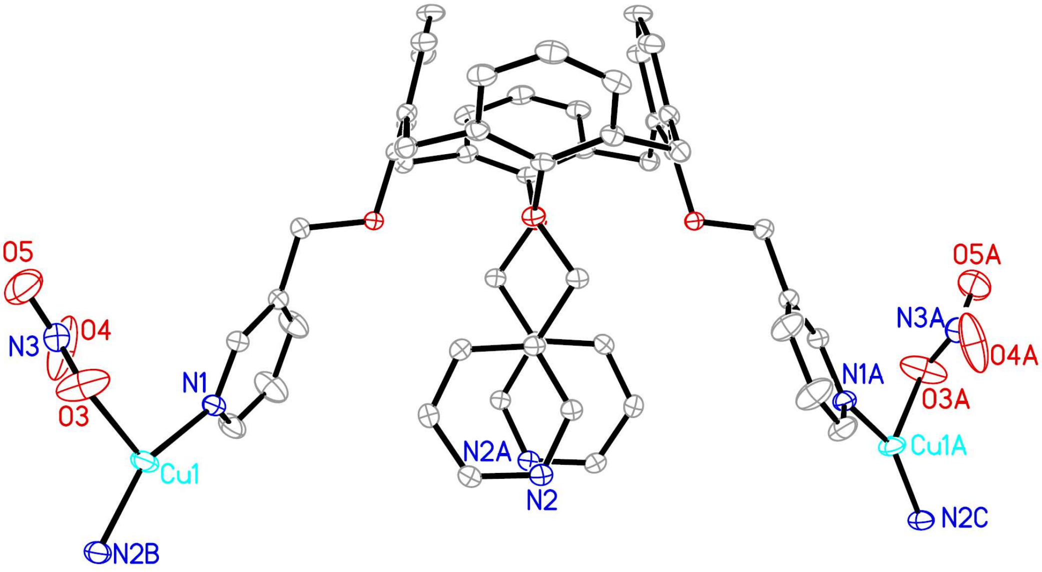


Figure 1

(a)



(b)

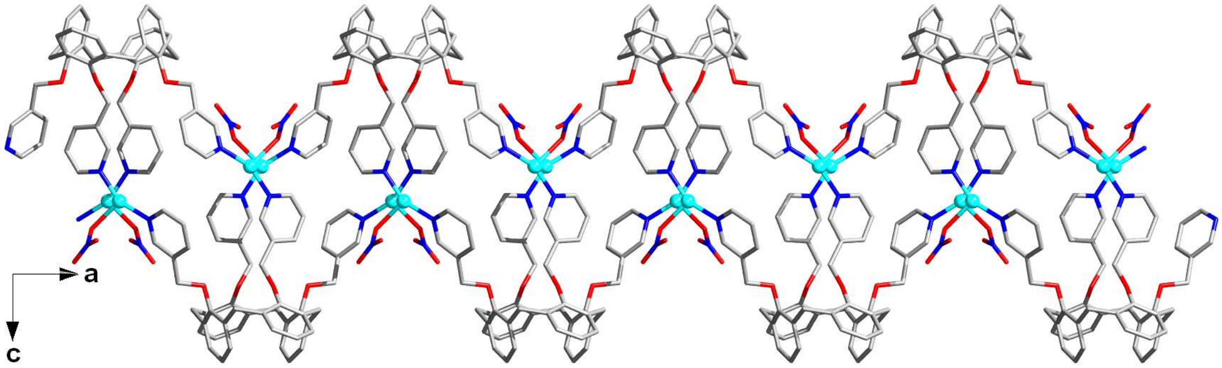
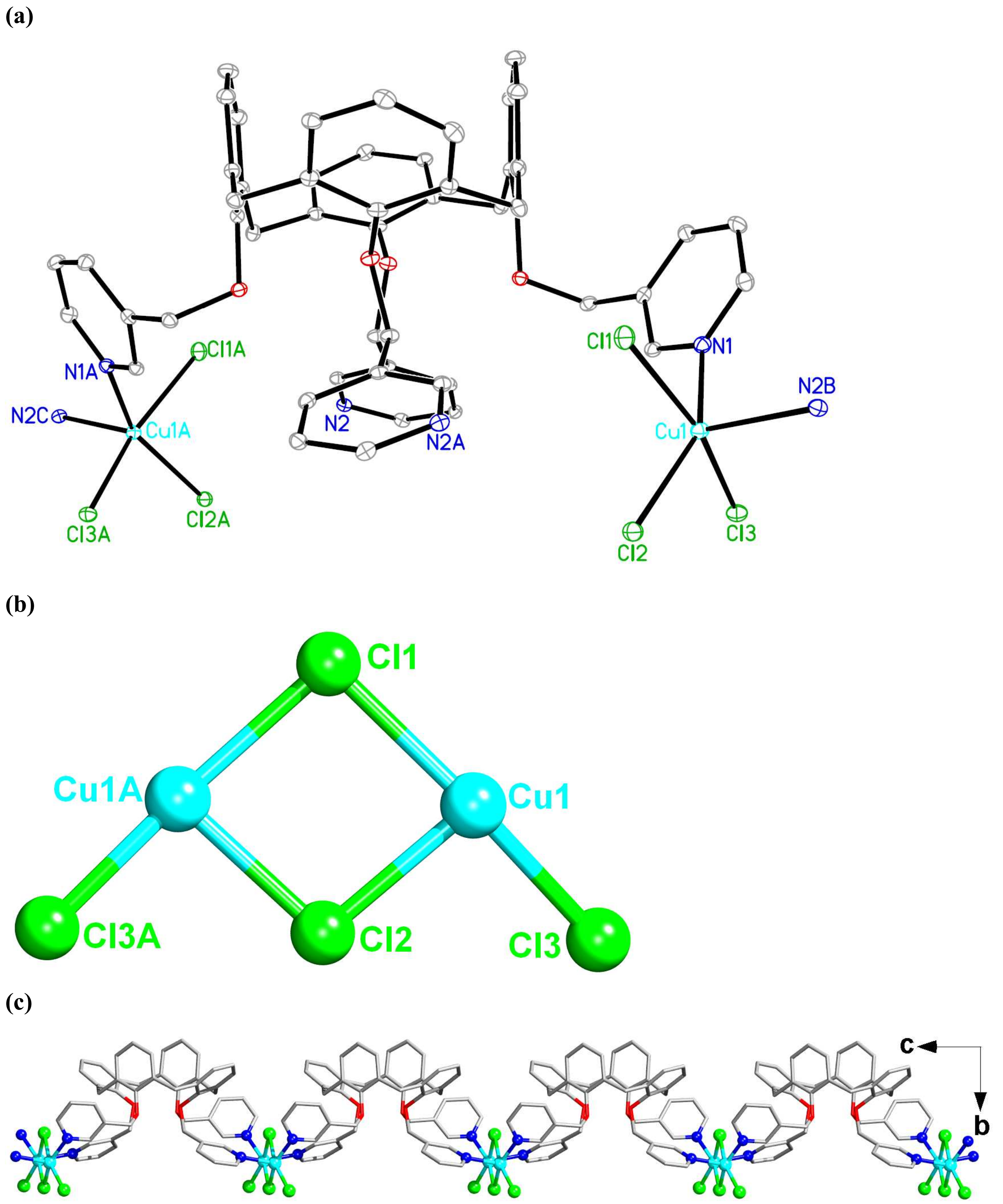


Figure 2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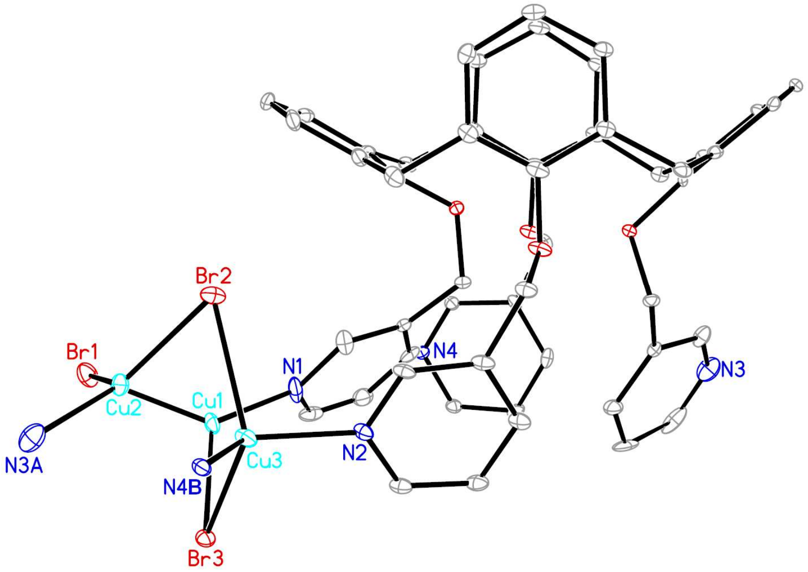
N2C
Cu1A
Cl3A
Cl2A
N2
N2A
Cl1
N1
N2B
Cu1
Cl2
Cl3
(b)
Cl1
Cu1A
Cu1
Cl3A
Cl2
Cl3
(c)
c
b

Figure 3

(a)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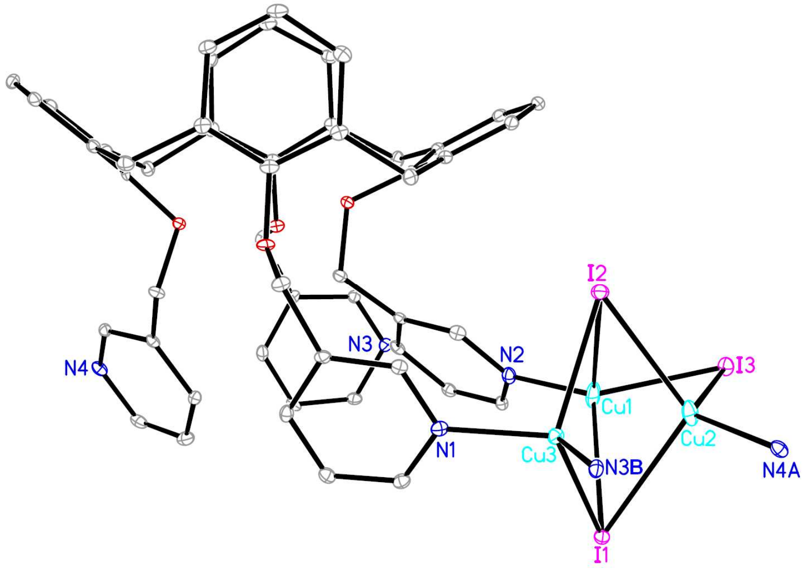
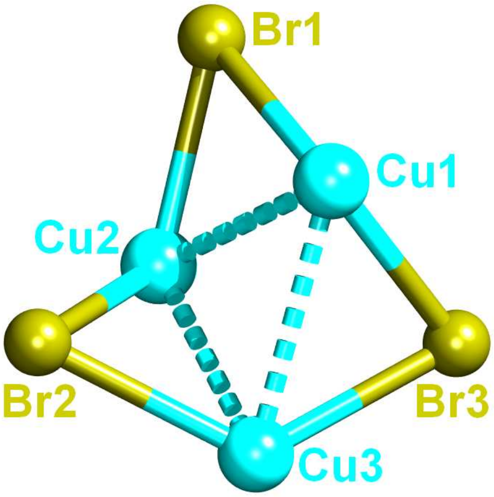
Br1
Cu2
N3A
Cu1
N1
N4
N3
Cu3
N2
N4B
Br3

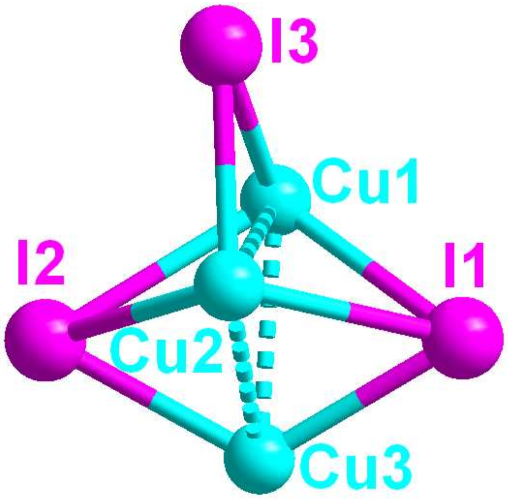
(b)


I2
N3
N2
I3
N4
Cu1
Cu2
N1
Cu3
N3B
N4A
I1

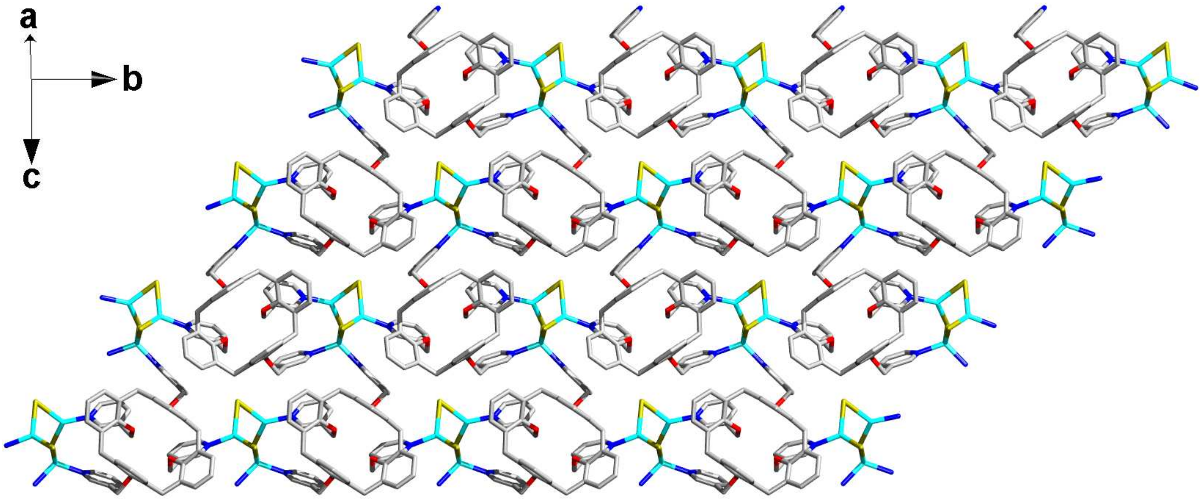
(c)



(d)



(e)



For Table of Contents Use Only

Short Text for TOC

Solvothermal reactions of CuX_2 (X = NO_3, Cl, Br, I) with tetra-pyridyl-functionalized calix[4]arene afforded four novel coordination polymers. Complexes **1**-**4** are characterized by infrared spectroscopy, thermogravimetric analysis, single-crystal X-ray diffraction and powder X-ray diffraction. Complex **3** showed the best catalytic properties for the synthesis of versatile propargylamines from the A^3 reaction of formaldehyde with a variety of alkynes and amines.

Figure for TOC