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Three thiacalix[4]arene-based Cu(ı) coordination polymers: catalytic activities for azide–alkyne cycloaddition reactions and luminescence properties[†]

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Three new coordination polymers, $[Cu_2(CN)(L)(OCH_3)]\cdot CH_3OH\cdot 3H_2O$ (1), $[Cu_3(Br)_3(L)]$ (2) and [Cu(I) (L)]·1.5H₂O (3), have been solvothermally prepared by reacting L (5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra[(3-pyridylmethyl)oxy]-2,8,14,20-tetrathiacalix[4]arene) with Cu(I) halide. 1 and 2 exhibit layers. 3 displays a chain, a supramolecular layer constructed by hydrogen bonds. The performance of 1–3 was examined as heterogeneous catalysts for azide–alkyne cycloaddition reactions. Most strikingly, 1 and 2 show predominant efficiency with high regioselectivity and excellent recyclability. Remarkably, solids 1–3 all have luminescence characteristics under irradiation with a UV lamp.

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1. Introduction

Recently, Cu(1)-based coordination polymers (CPs) have attracted wide attention because of their good stabilities and fascinating catalytic activities in reactions including the conversion of arylalkanes to ketones,¹ azide-alkyne cycloaddition (AAC) reactions,² sequential alkynylation and cycloaddition reactions³ and carbonyl-olefin photocycloaddition reactions.⁴ AAC reaction is a highly economical method for the synthesis of 1,2,3-triazole derivatives by cycloaddition of alkynes with azides.⁵ This reaction has applications in various fields such as organic synthesis, polymer chemistry, materials science and drug discovery.⁶⁻⁸ Focusing on AAC reactions, a lot of catalytic studies have been carried out. Pioneering research suggests that nickel-, iridium-, silver- and copper-based salts or compounds show fascinating catalytic activities.⁹⁻¹¹ In this regard, copper-catalyzed AACs are the most efficient reactions, and a few Cu(I)-CPs have been studied as catalysts owing to their heterogeneous catalytic features.¹²⁻¹⁵ They can overcome the

disadvantages of homogeneous catalysts such as easy destruction and difficult recycling.^{11,16,17}

Thiacalix[4]arenes have been proved to be versatile building blocks owing to their multidentate coordination sites and cavity structures.¹⁸ The upper *p-tert*-butyl and the lower phenolic hydrogen atoms of the backbone could be replaced by various substituents, and a series of derivatives based on thiacalix[4]arenes have been synthesized.^{19–22} Based on functionalized thiacalix[4]arene ligands, plenty of CPs with intriguing structures and unique properties have been reported.^{23–30} Our group has been engaged in the exploration of CPs based on this type of ligand.³¹ To expand our research, we synthesized a pyridyl-functionalized *p-tert*-butylthiacalix[4]arene ligand 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra[(3-pyridylmethyl)oxy]-2,8,14,20-tetrathiacalix[4]arene (L, Scheme 1). The ligand may be a good backbone for the construction of CPs, because the N



Scheme 1 View of L.



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and the S atoms can provide multiple potential sites to coordinate with metal ions. Also, the pyridyl groups can freely rotate during coordination.

In this work, we first carried out the systematic investigation of the reaction of L with Cu(1) halide and explored three new CPs, $[Cu_2(CN)(L)(OCH_3)]\cdot CH_3OH\cdot 3H_2O$ (1), $[Cu_3(Br)_3(L)]$ (2) and $[Cu(I)(L)]\cdot 1.5H_2O$ (3). Their catalytic properties for AAC reactions and luminescence properties have been discussed. Meaningfully, 1 and 2 are recyclable heterogeneous catalysts and display excellent catalytic capabilities for the AAC reaction.

2. Experimental section

2.1. Synthesis of L

Ligand L was synthesized by similar procedures to those reported in the literature.^{32,33}

2.2. Preparation of [Cu₂(CN)(L)(OCH₃)]·CH₃OH·3H₂O (1)

L (11 mg, 0.01 mmol), CuCl₂·2H₂O (8 mg, 0.04 mmol) and NH₄VO₃ (6 mg, 0.06 mmol) in *N*,*N*-dimethylformamide (DMF)/ methanol (MeOH) (2/6 mL) were heated at 110 °C for 72 h in a 15 mL Teflon reactor. After cooling, yellow-green block crystals were obtained. The product ratio is 42% based on L. Anal. calcd (%) for $C_{67}H_{81}Cu_2N_5O_9S_4$: C, 59.35; H, 6.02; and N, 5.17. Found (%): C, 59.38; H, 5.70; and N, 5.23. IR (cm⁻¹): 3053 (w), 2959 (s), 2903 (m), 2866 (m), 2122 (w), 1772 (w), 1677 (w), 1577 (m), 1541 (w), 1477 (m), 1443 (s), 1426 (s), 1375 (m), 1329 (w), 1264 (s), 1232 (m), 1085 (m), 1021 (m), 975 (m), 945 (m), 878 (m), 850 (w), 761 (w), 794 (m), 703 (m), 646 (w), 536 (w) (Fig. S1†).

2.3. Preparation of $[Cu_3(Br)_3(L)](2)$

L (11 mg, 0.01 mmol), $CuBr_2$ (9 mg, 0.04 mmol) and DMF/ EtOH (2/6 mL) were added in a 15 mL Teflon reactor and then heated at 110 °C for three days. Yellow block crystals were obtained, and the yield is 73%. Anal. calcd (%) for

 Table 1
 Crystallographic data and structure refinements for 1–3

$C_{64}H_{68}Cu_3Br_3N_4O_4S_4$: C, 50.71; H, 4.52; and N, 3.70. Found (%):
C, 50.55; H, 4.37; and N, 3.91. IR (cm $^{-1}$): 3446 (m), 3046 (m),
2963 (s), 2867 (s), 1773 (w), 1598 (m), 1578 (m), 1476 (s),
1460 (s), 1441 (s), 1378 (s), 1364 (s), 1322 (m), 1263 (s), 1225 (s),
1124 (w), 1083 (s), 1021 (s), 972 (s), 942 (s), 873 (m), 849 (m),
821 (w), 792 (s), 761 (m), 724 (m), 702 (s), 646 (m), 536 (w).

2.4. Preparation of [Cu(I)(L)]·1.5H₂O (3)

An admixture of L (11 mg, 0.01 mmol), CuI (8 mg), $H_3Mo_{12}O_{40}$ ·x H_2O (18 mg) and DMF/ H_2O (6/2 mL) was transferred to a 15 mL Teflon reactor and then kept at 110 °C for 72 h. The yield of colorless block crystals is 36%. Anal. calcd (%) for $C_{64}H_{71}CuIN_4O_{5.5}S_4$: C, 58.94; H, 5.44; and N, 4.29. Found (%): C, 58.70; H, 5.38; and N, 4.53. IR (cm⁻¹): 2959 (s), 2904 (m), 2867 (m), 1680 (m), 1478 (m), 1445 (s), 1424 (s), 1376 (s), 1264 (s), 1234 (m), 1085 (m), 1016 (m), 794 (m), 707 (m).

Crystallographic data are listed in Table 1.

3. Results and discussion

3.1. Syntheses

For CPs **1** and **2**, we tried the syntheses by using CuCl and CuBr as well, but we only obtained powder forms. Since the structures of **1** and **3** contain only L ligands without polyoxometalates, their crystals could only be obtained by adding NH_4VO_3 and $H_3MO_{12}O_{40}$, respectively. The reason may be that they altered the pH values of the reaction solutions.

3.2. Crystal structure of [Cu₂(CN)(L)(OCH₃)]·CH₃OH·3H₂O (1)

The structure of **1** was refined by using the SQUEEZE program in PLATON and the disordered solvents were determined by electron diffraction density analysis, elemental analysis and TGA. The self-contained unit of **1** consists of one L, two Cu(I) cations, one CN⁻ anion, one CH₃O⁻ anion, one free MeOH and three free H₂O molecules. The CN⁻ anion comes from the

	1	2	3
Formula	$C_{67}H_{81}Cu_2N_5O_9S_4$	$C_{64}H_{68}Cu_3Br_3N_4O_4S_4$	C ₆₄ H ₇₁ CuIN ₄ O _{5.5} S ₄
$M_{ m r}$	1355.68	1515.81	1302.92
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a(Å)	15.1320(8)	10.9843(7)	15.282(8)
$b(\dot{A})$	15.5740(8)	16.0778(11)	15.561(8)
$c(\dot{A})$	16.9320(8)	19.4622(10)	15.889(9)
α (°)	75.653(4)	108.212(5)	105.876(5)
$\beta(\circ)$	82.818(4)	91.375(4)	111.146(5)
γ (°)	61.305(5)	99.797(Š)	90.496(4)
$V(Å^3)$	3391.0(3)	3206.4(4)	3365.3(3)
Z	2	2	2
$D_{\text{calc}} (\text{g cm}^{-3})$	1.328	1.570	1.286
F(000)	1424	1536.0	1346.0
R _{int}	0.0390	0.0443	0.0339
GOF on F^2	1.138	0.979	1.062
$R_1^a \left[I > 2\sigma(I) \right]$	0.1123	0.0533	0.0514
wR_2^b (all data)	0.2464	0.1255	0.1333

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. {}^{b}wR_{2} = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}] \}^{1/2}.$

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Fig. 1 (a) Coordination spheres of Cu(I) ions in 1. (b) View of the layer.

decomposition of DMF. The two Cu(1) cations show different coordination modes: Cu1 exhibits a distorted tetrahedron and is surrounded by three N atoms of three L ligands and one CN^- anion, while Cu2 is ligated by one N atom, one CN^- anion and one CH_3O^- anion (Fig. 1a). Rather than the cone conformation in other thiacalix[4]arene CPs,^{34,35} L exhibits a 1,3alternate conformation, and all four N atoms participate in the coordination. CN^- anions further linked the Cu(1) ions and L ligands to form a layer (Fig. 1b).

3.3. Crystal structure of 2

The independent unit of 2 incorporates one L, three Cu(1) cations and three Br⁻ anions (Fig. 2a). The three Cu(1) cations have different coordination environments. Each of the Cu₁ and Cu₂ cations are surrounded by two N atoms from L ligands and two Br⁻ anions. Cu3 is coordinated by two Br⁻ anions. Cu1, Cu2 and Cu3 are bridged by three Br⁻ anions to form a [Cu₃(Br)₃] cluster. Cu(2)…Cu(3) and Cu(1)…Cu(3)^{#2} distances are 2.7977(11) and 2.8041(11) Å, respectively (Table S1†). The [Cu₃(Br)₃] clusters are connected by 1,3-alternate L ligands to afford a layer (Fig. 2b).

3.4. Crystal structure of 3

One Cu(1) cation, one L, one I^- anion, and one and a half free $\rm H_2O$ molecules constitute the independent unit of 3. Cu_1 is



Fig. 2 (a) Coordination spheres of Cu(i) ions in 2. (b) View of the $[{\rm Cu}_3({\rm Br})_3]$ cluster and the 2D layer.

surrounded by two N atoms of L ligands and two I⁻ anions (Fig. 3a). Two Cu(1) cations are held together by two I⁻ anions to form a [Cu₂(I)₂] dimer. As revealed in Fig. 3b, the dimers are interconnected by L ligands to form a double chain. Only two N atoms of L participate in the coordination. The chains are further held together by C–H…N bonds among L ligands (Table S2†), forming a supramolecular layer (Fig. 3c).

3.5. Chemical and thermal stability

To examine their chemical stability, CPs 1-3 (15 mg) were immersed in various solvents (including acetone, dichloromethane (DCM), DMF, MeOH, EtOH, acetonitrile and ethyl acetate) and aqueous solutions with various pH values for one day, respectively. As shown in Fig. 4, the PXRD patterns of immersed 2 are consistent with the simulated patterns. This shows that 2 displays excellent stability in both organic solvents and acid/base solutions with a wide range of pH values. This high stability may be because the structure of 2 contains no coordinated or free solvents. The PXRD patterns of immersed 1 in DMF, acetone, and acid/base solutions show minute shifts at $2\theta = 5.3^{\circ}$, 6.7° and 9.6° compared with the simulated patterns (Fig. S2[†]), which may be caused by the changing of coordinated solvents. The PXRD patterns of immersed 3 are not consistent with the simulated patterns, indicating that the framework has changed.

TGA of 1–3 was performed under nitrogen (Fig. S3[†]). For 1, a weight loss was observed in the range of 97–278 °C corresponding to the loss of free CH₃OH, H₂O and coordinated



Fig. 3 (a) Coordination spheres of Cu(i) ions in 3. (b) View of the chain.(c) View of the supramolecular layer (blue dots represent H bonds).

 CH_3O^- molecules. The framework of 2 began to collapse at 280 °C. The weight loss of 3 was observed at about 100 °C due to the loss of the solvent molecules.

3.6. Catalytic performance of 1-3 in AAC reactions

Considering the Lewis acidic Cu(1) sites in CPs 1-3, AAC reaction of benzyl azide and phenylacetylene was conducted (Table 2 and Fig. S4[†]). Firstly, a blank experiment was carried out, and only 13% yield was obtained (entry 1). To confirm the active sites in the reactions, the halides of Cu(1) were utilized as homogeneous catalysts, and low conversion yields were achieved (33% and 35% for CuCl and CuI, entries 2 and 3). An optimization experimental study was carried out with 2 because of its high yield during the synthesis. Firstly, to optimize the solvents, the reactions were operated in MeOH, EtOH and dichloromethane (DCM), respectively. A maximum yield of >99% in MeOH and EtOH was obtained (entries 4-6). In order to explore the reaction time, the process was monitored every two hours. The yields were elevated from 66% to 86% and 97% at 2, 4 and 6 h, respectively (entries 7-9). Subsequently, the reaction was done at 50 °C to identify the suitable temperature. Only 67% yield was obtained (entry 10). Under the optimum conditions summarized in the above experiments, the catalytic yields of 1 and 3 were found to be >99% and 34%, respectively (entries 11 and 12).

In order to study the generalities of **1** and **2**, diverse azides and alkynes with different functional groups were studied under the optimized conditions (Fig. S5 and S6†). When 4-CH₃-, 3-CH₃-, 2-F- and 4-NO₂-substituted (azidomethyl) benzene reacts with ethynylbenzene, yields of >99% and 97% were obtained (entries 1–4 in Table 3). This demonstrates that an electron-donating or -withdrawing group substituted (azidomethyl)benzene has no effect on AAC reactions. However, when (azidomethyl)benzene reacts with ethynylbenzene derivatives, the yields are affected. As for the 4-CH₃- and 4-OCH₃-groups, the yields are 96% and 85%, respectively (entries 5 and 6). For 4-Cl- and 4-Br-substituted groups, the yields reduced to 65%, 63% and 60% for both **1** and **2** (entries



Fig. 4 The PXRD patterns of **2** immersed in different organic solvents and solutions with various pH values.

Table 2 Optimization of reaction conditions for AAC reactions



Entry	Catalyst	Time, h	Solvent	Temperature, °C	Yield, %
1	None	8	MeOH	70	13
2	CuCl	8	MeOH	70	33
3	CuI	8	MeOH	70	35
4	2	8	MeOH	70	>99
5	2	8	EtOH	70	>99
6	2	8	DCM	70	90
7	2	2	MeOH	70	66
8	2	4	MeOH	70	86
9	2	6	MeOH	70	97
10	2	8	MeOH	50	67
11	1	8	MeOH	70	>99
12	3	8	MeOH	70	34

Reaction conditions: catalyst (10 mg), benzyl azide (1 mmol), phenylacetylene (2 mmol), solvent (4 mL), 8 h 70 °C and amyl acetate (0.92 mmol).

Table 3	Catalytic reactions	of substrates v	with different	functional groups ^a
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				Yield, %	
Entry	Azides	Alkynes	Product	1	2
1	N ₃	=-{>		>99	>99
2	N ₃	=-{>		>99	>99
3	F N ₃			>99	>99
4	O ₂ N N ₃			>99	97
5	N ₃	≡-∕_}-		96	96
6	N ₃	≡-∕СУ-осн₃		96	85
7	N ₃			65	63
8	N ₃			65	60

^a Reaction conditions: azide (1 mmol), alkyne (2 mmol), amyl acetate (0.92 mmol), catalyst (10 mg) and methanol (4 mL) at 70 °C for 8 h.

7 and 8). This shows that ethynylbenzene with electron-withdrawing groups results in lower yields.³⁶ According to the related literature, during the reaction pathway of substituted 1,2,3-triazoles, an initial Cu(I)–acetylide intermediate is formed by Cu(I)-CPs and alkynes.¹⁰ The alkynes with electron withdrawing groups tend to form dimers,³⁶ which may decrease the formation of Cu(I)–acetylide intermediates. Therefore, the yields obtained using electron-withdrawing group substituted ethynylbenzenes are low. The catalytic effects of **1** were obviously better than those of **2** for several substituted ethynylbenzene reactions, which may be caused by the higher porosity and more open Cu(I) sites of **1** than **2**.¹¹

Recyclability is crucial for catalytic reactions (Fig. S7 and S8†). So we conducted cycle experiments after the catalysts **1** and **2** were removed from AAC reactions. Both catalysts could be easily separated from the reaction systems by filtration.



Fig. 5 The yields of cycle experiments catalyzed by 1 and 2.

After five cycles, the yields of the reactions catalyzed by 1 and 2 did not change significantly and the PXRD patterns of 1 and 2 were nearly consistent with their simulated patterns (Fig. 5 and S9†). This demonstrates that the structural integrities of 1 and 2 are well preserved.

To investigate whether the catalysis is a heterogeneous reaction, the catalysts were separated from the reaction systems by hot filtration after 2 h (Fig. 6). Even after continuing the reactions with filtrates for 6 h, there was no significant increase in yields for both CPs. The results show that **1** and **2** act as heterogeneous catalysts in AAC reactions.

The catalytic performance of the CPs prepared in this work has been compared with the reported CP-catalysts for AAC reaction of benzyl azide and phenylacetylene. As shown in Table 4, 1 and 2 exhibit approximate or higher catalytic efficiencies. The advantage of this work lies in the shorter reaction time.^{37–42} Another advantage of 1 and 2 is that they have excellent recyclabilities.^{37,38,42}

3.7. Luminescence properties

The solid-state luminescence features of **1**–3 and L were evaluated at RT. As illustrated in Fig. 7, the emission of **1** led to red light with a peak value of 633 nm ($\lambda_{ex} = 363$ nm). **2** and **3** show green luminescence with the maximum peaks at 548 nm ($\lambda_{ex} = 389$ nm) and 526 nm ($\lambda_{ex} = 400$ nm), respectively. The greenlight of **2** and **3** may be caused by the short distances of Cu…Cu (2.670–2.804 Å) (Table S1†) and halogen-to-metal charge transfer (XMCT).⁴³ Compared with the L ligand ($\lambda_{em} =$



 Table 4
 Comparison of cycloaddition of benzyl azide and phenylacetylene by various catalysts

Catalyst	Conditions	Yield, %	Ref.
$[Cu_6I_6(L_1)_2]_n$	24 h/MeOH + H ₂ O/50 °C	100	37
$[CuCl_2(L_2)_2]$	15 h/MeOH + H ₂ O/35 °C	99	38
[Cu(dmph) ₂]Cl	12 h/H ₂ O/70 °C	97	39
[Cu(tzol) ₂]	12 h/H ₂ O/70 °C	96	40
CuL ₂	12 h/H ₂ O/70 °C	95	41
Cu(BTC)-MOF	16 h/MeOH/50 °C	81	42
CP 1	8 h/MeOH/70 °C	>99	This work
CP 2	8 h/MeOH/70 °C	>99	This work



Fig. 7 Solid state luminescence spectra of 1-3.



Fig. 6 Hot filtration experiments catalyzed by 1 and 2 after 2 h.

565 nm, yellow light, Fig. S10†), 1 displays an obvious red shift of 68 nm, which could be ascribed to MLCT.^{44,45}

To investigate the effect of temperature on luminescence, different-temperature emissions of 1–3 were studied at 97 K, 197 K and 257 K, respectively. The results show that the emission intensities decreased with increasing temperature (Fig. S11†), which may be caused by the increasing loss of energy *via* nonradiative decay.⁴⁶

4. Conclusions

In conclusion, three new Cu(1)-CPs constituted by $CuCl_2$, $CuBr_2$, CuI and a pyridyl-functionalized *p-tert*-thiacalix[4]arene ligand have been prepared. The study represents the first example of Cu(1)-halide CPs bearing the L ligand. 1 and 2 exhibit layer structures, and 3 displays a double chain. 2 has good chemical and thermal stability. Strikingly, 1 and 2 can efficiently catalyze AAC reactions. They can also be easily separated from their reaction systems. After cycling, the activities of 1 and 2 exhibited no obvious decreases and their integrities were maintained. High stability, easy separation, high catalytic ability and reusability make CPs 1 and 2 excellent heterogeneous catalysts for the AAC reactions. The solid-state lumine-scence spectra indicate that 1–3 exhibit red or green emissions.

Conflicts of interest

There are no conflicts to declare.

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