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Synthesis, structure and multifunctional catalytic properties of Cu(I)-coordination polymer with outer-hanging CuBr₂

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A 1D Cu(I)-coordination polymer ([(CuL1)(CuBr₂), 1] carrying external copper bromide moiety was synthesized. The outer-hanging [CuBr₂]⁻ moiety is attached to 1D Cu(I)-CP backbone via Cu-··Cu bonding interaction, which makes it look like coordination polymer supported CuBr₂ species. 1 exhibits excellent multifunctional catalytic activity for phenol acetylation, A^3 -coupling (aldehyde-alkyne-amine) and styrene oxide methanolysis reactions. Its heterogeneous catalytic nature was confirmed by solution leaching experiment and it can be reusable without significant loss its catalytic activity and selectivity for above reactions.

Introduction

Coordination polymers (CPs) are hybrid polymeric complexes with infinite network structures composed of organic ligands and metal ions. As an attractive class of hybrid solid materials, CPs received considerable attention because of their fascinating physical and chemical properties.¹ Among various CPs, Cu(I) halides-based CPs have been widely explored due to their interesting structural feature and possible applications in luminescence-based sensors, solar system, and biological probes.²

It is well known that noble metals such as Pd, Rh and Ru are valuable species to catalyse C-C, C-O and C-N bond formation, but usually with the assistance of toxic organic phosphorus ligands. It is similar to these soft metal Lewis acids, Cu(I) can easily form adducts with a wide range of organic donors such as amine, N-containing heterocycles, organic nitriles and so on,³ and their Cu(I) complexes have long been employed in organic synthesis as catalysts via metal-complexed intermediates such as π -copper complexes.⁴ On the other hand, copper has been demonstrated to be not eco-friendly and is an important nonpoint source pollutant in aquatic ecosystems worldwide.⁵ So the development of new type of eco-friendly heterogeneous cheaper Cu(I) CPs-based catalysts is a topic of great interest.

Phenol acetylation, styrene oxide methanolysis, and A³coupling (aldehyde-alkyne-amine) reactions are three important types of reactions and frequently used in synthetic chemistry such as multi-step pharmaceutical synthesis and food or cosmetic industries. For example, phenol acetylation is widely used as protecting group in multi-step pharmaceutical synthesis and food or cosmetic industries.⁶ In this procedure, organic phosphine and inorganic metal triflate complexes are often used as the catalysts.⁷ As for A³-coupling (aldehyde-alkyne-amine) reaction, which is a typical one-pot multi-component coupling reaction, the resulted propargylamines are the important intermediates for synthesis of various nitrogen-containing biologically active compounds.⁸ The precious metal complexes, including Au, Ag, Ir and Ru-compounds,9 are often selected to facilitate these multicomponent coupling reactions. In addition, ring-opening of epoxides with nucleophilic regents is an important path to access to compounds with versatile 1, 2 type functional groups, including β -alkoxyalcohols. So far, many molecular metal complexes such as In(III), Sn(II, IV), Cr(II, III), Al(III), Co(III) and Cu(II)-complexes¹⁰ are used as the catalysts to epoxide methanolysis.

As shown above, most of these homogeneous catalyst systems for these three types of reactions cannot be reusable and suffer from the loss of the hazardous or precious catalysts at the end of the reactions. For achieving more eco-friendly catalysts and minimizing environmental pollution, the construction of CPsbased heterogeneous catalysts is highly demanded.

In this contribution, we report a new 1D Cu(I)-CP which is generated from CuBr₂ and the fluorene-bridged imidazolecapped ligand L with methyl side chain under solvothermal reactions. Interestingly, 1 contain $[CuBr_2]^-$ species as the counter ions instead of simple bromide anion. Furthermore, it, as an external counter anion, attached to the chain backbone via Cu···Cu bonding interaction, which is rarely observed in CPs. In addition, 1 can be a highly heterogeneous catalyst to promote phenol acetylation, A³-coupling (aldehyde-alkyne-amine) and styrene oxide methanolysis reactions under mild conditions.

Experimental

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Electronic Supplementary Information (ESI) available: synthesis of ligands, product characterization, additional spectra, bond lengths and angles of **1-2**. CCDC 1454107-1454108. See DOI: 10.1039/x0xx00000x

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Materials and methods

All chemicals and solvents were at least of analytic grade and employed as received without further purification. The Infrared (IR) spectra were recorded from dry KBr pellets in the 400-4000cm⁻¹ range on a PerkinElmer 1600 FTIR spectrometer. The C, H and N elemental analysis were conducted on a PerkinElmer Model 2400 analyzer. Solution phase ¹H NMR and ¹³C spectra were obtained on an AM-300 spectrometer. Chemical shifts are reported in δ units relative to TMS. Powder X-ray diffraction (PXRD) measurements were performed at 293K on a D8 ADVANCE diffractometer (Cu K α , λ = 1.5406Å). GC-MS analysis was performed on a J&K S011525-300 gas chromatographic (Agilent 6890GC-5973MS). XPS spectrum was obtained from THI5300 (PE). ESI-MS spectra were obtained on Thermo LCQ-Fleet machine.

Synthesis of [(CuL1)(CuBr₂)] (1)

L1 (5.2 mg, 0.016 mmol), CuBr₂ (11 mg, 0.05 mmol), water (2 mL) and THF (0.22 mL) was sealed in a glass tube (6 mL). The mixture was heated at 150°C for 72 h and cooled slowly to room temperature over a period of 50 h. Yellow crystals of 1 were obtained. Yield: 61% (based on L1). IR (KBr pellet, cm ¹): 3459(w), 3124(m), 2960(w), 1613(w), 1513(s), 1445(w), 1308(s), 1255(m), 1151(w), 1064(m), 958(w), 831(m), 737(w), 647(w). Anal. Calcd for C₂₁H₁₈BrCuN₄: C 53.68, H 3.86, N 11.92. Found: C 53.96, H 3.79, N 11.41. ESI-MS (DMSO) for $[Cu_2Br_2]^+$: m/z = 284.5 (11), 286.3 (73), 288.5 (100), 290.6 (31), 292.6 (33). ESI-MS (DMSO) for $[Cu_2L1]^+$: m/z = 453.5 (100), 454.3 (16), 455.3 (39), 456.4 (17).

Synthesis of $[(CuL2)_2(Cu_2Br_4)]$ (2)

L2 (5.6 mg, 0.016 mmol), CuBr₂ (11 mg, 0.05 mmol), water (2 mL) and THF (0.22 mL) was sealed in a 6 mL glass tube. The mixture was heated at 150°C for 72 h and cooled slowly to room temperature over a period of 50 h. Yellow crystals of 2 were obtained. Yield: 59% (based on L2). IR (KBr pellet, cm ¹): 3445(w), 3120(w), 2926(w), 1614(w), 1509(s), 1470(w), 1304(w), 1251(w), 1107(w), 1063(m), 811(w), 732(w), 651(w). Anal. Calcd for C₂₃H₂₂BrCuN₄: C 55.48, H 4.45, N 11.25. Found: C 55.26, H 4.71, N 11.53.

X-ray crystallography

Single-crystal X-ray diffraction data of 1 was measured on an Agilent Technologies SuperNova diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and Cu K α radiation ($\lambda = 1.54184$ Å), respectively. Data corrections for incident and diffracted beam absorption effects were done with CrysAlisPro software. Single-crystal X-ray diffraction data of 2 were measured on a Bruker SMART APEX CCD-based diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å). The raw frame data were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.¹¹ Corrections for incident and diffracted beam absorption effects were applied using SADABS.¹¹ None of the crystals showed evidence of crystal decay during the process of data collection. The structures of 1-2 were solved by direct methods with SHELXS program and refined by full matrix least-squares technique on F^2 including all reflections using the SHELXL-97 program package.11 The crystal data and refinement parameters are summarized in Table 1, and selected

Catalytic reaction

Phenol acetylation. Acetic anhydride (4 mmol) was added to a CH₂Cl₂ (1 mL) solution of *p*-bromophenol (173 mg, 1 mmol). After addition of 1 (5 % mol), the mixture was stirred at room temperature for 2 h (monitored by TLC, petroleum/CH₂Cl₂ = 1 : 1). 1 was recovered by centrifugation, washed with MeOH and dried at 80°C.

A³-coupling (aldehyde-alkyne-amine) reaction. A mixture of phenylacetylene (120 mg, 1.2 mmol), paraformaldehyde (PFA, 30 mg, 1.0 mmol), piperidine (94 mg, 1.1 mmol) and 1 (5 % mol) was stirred at room temperature in nitrogen atmosphere for 6 h (monitored by TLC). After addition of ether, the product was purified by column chromatography on silica gel (hexane/ethyl acetate = 3 : 1). 1 was recovered by centrifugation and washed with ether and MeOH and dried at 80°C.

Styrene oxide methanolysis. A methanol (5 mL) solution of styrene oxide (1 mmol) and catalyst (0.02 mmol, 2 mol %) was stirred at 50°C for 7 hours. The reaction was monitored by TLC. The conversion and selectivity were determined by GC-MS and HPLC. The product was further confirmed by ¹H NMR. After each catalytic run, the catalyst was recovered by centrifugation and washed by fresh methanol. After dried at 70°C for 1 hour, the catalyst was used in the next catalytic run. XRPD patterns of the recovered catalyst indicated the structure integrity of the CPs were maintained.

Leaching test

Solid catalyst of 1 was separated from the reaction solution by filtration during the reaction process. The reaction was continued with the filtrate in the absence of 1. No further increase in either conversion or selectivity of the product was detected, which confirms that the catalytically active sites for phenol acetylation, A³-coupling (aldehyde-alkyne-amine) and styrene oxide methanolysis reactions located on 1.

Results and discussion



Scheme 1. Synthesis of L1 and 1. The photograph of ground 1 is inserted.

Synthesis and structural analysis

As shown in Scheme 1, L was synthesized by heating the DMF solution of imidazole and corresponding 2,7-bromide substituted fluorines (120°C for 8 hours) in the presence of Cs₂CO₃ and CuI in satisfied yields (76 %, ESI). Compound 1 was obtained as yellow crystalline solids by the combination of CuBr2 and L in a mixed-solvent system of MeOH/THF at 150°C for 72 h in moderate yields (61 %).

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The structure of **1** was resolved through X-ray single-crystal diffraction analyses. The pure phase of the obtained yellow crystals was confirmed by XRPD (ESI). It is noteworthy to point out that the copper ions in **1** is univalent (ESI). The in situ reduction of Cu(II) to Cu(I) by *N*-heterocycle containing ligands, especially under hydro/solvothermal conditions, is quite common, with a series of reports having appearing in the literature for Cu(SO₃CF₃)₂,^{12a} Cu(NO₃)₂,^{12b-d} CuSO₄^{12e} and CuCl₂^{12f} salts. Notably, **1** is stable in common organic solvent systems such as toluene, CHCl₃, THF, cyclohexane, CH₃CN and acetone (ESI), which will allow it to be used as heterogeneous catalyst in various organic solvents.



Fig. 1 a) The zigzag chain of 1 was shown. The asymmetric unit was selected in the purple oval. Linear [CuBr₂] were adhered to Cu(I) centre on the chain backbone as balanced ions through weak Cu…Cu interactions. Hydrogen atoms were omitted for clarity. b) Crystal packing of 1. c) Side view of 1. Polymer back bone is shown in space-filling model.

Single crystal X-ray diffraction analysis (Table 1) revealed that 1 crystallizes in the monoclinic P21/c space group. As shown in Fig. 1, there are two kinds of crystallographic independent Cu(I) ions. The Cu(1) atoms on the ionic chain backbone adopt an approximate linear coordination environment which is consisting of two nitrogen atoms from two L1 ($\angle N(1)$ -Cu(1)-N(4) = 169.82(17)°). The Cu(1)-N(1) and Cu(1)-N(4) bond lengths are 1.885(3) and 1.884(3) Å respectively. The other Cu(2) ion, together with two Br, forms the [CuBr₂]⁻ counter ion. The [CuBr₂]⁻ moiety is nearly linear $(\angle Br(1)-Cu(2)-Br(2) = 174.50(4)^{\circ})$ and symmetrical (Cu(2)-Br(1) and Cu(2)–Br(2) bond lengths are 2.2345(8) and 2.2292(8) Å respectively). These distances are slightly longer than average value of 2.216 Å for another twelve examples of linear [CuBr₂]⁻ anions reported in the Cambridge Structural Database.¹³ In the solid state, the Cu(1) nodes are connected to each other by the bidentate bent L1 ligands to generate a zigzag polymer chain extended along the crystallographic [101]

direction. Interestingly, the $[CuBr_2]$ cuprate ions are adhered to the chain backbone by weak Cu…Cu interaction with a Cu(1)…Cu(2) bond length of 2.8717(8) Å.

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Table 1. Crystal Data and Structural Refinement Parameters for 1 and 2.			
	1	2	
formula	$C_{21}H_{18}Br_2Cu_2N_4$	$C_{23}H_{22}Br_2Cu_2N_4$	
fw	613.29	641.35	
λ/Å	0.71073	0.71073	
crystal system	monoclinic	Triclinic	
space group	P21/c	P-1	
7/К	100.01(10)	298(2)	
a (Å)	12.9017(3)	10.749(3)	
b (Å)	17.3862(5)	10.987(3)	
<i>c</i> (Å)	9.3722(2)	11.774(3)	
α (deg)	90.00	68.908(4)	
<i>6</i> (deg)	100.322(3)	64.794(4)	
γ (deg)	90.00	76.046(4)	
V (Å ³)	2068.27(9)	1167.5(5)	
Ζ	4	2	
$ ho_{cak}/g\cdotcm^{-3}$	1.970	1.824	
μ / mm ⁻¹	5.936	5.262	
F (000)	1200	632	
GOF	1.033	0.783	
Data/restraints/parameters	3874/0/264	4103/36/310	
$R_1[I > 2\sigma(I)]$	0.0383	0.0513	
wR ₂ [all data]	0.0928	0.1014	

The crystal packing (Fig. 1, viewed down the chain direction) shows that the [CuBr₂]⁻ anions are located at both sides of the chains, and the interchain Cu···Cu distances are 7.6 and 7.7 Å, respectively. **1** herein is a rare example of a complex containing an unsupported Cu(I)···Cu(I) interaction, with a short distance similar to that of [CuL]⁺[CuCl₂]⁻ (L = 1, 1'-bis(2-pyridyl)octamethylferrocenene species ($d_{Cu(I)\cdots Cu(I)} = 2.810(2)$ Å).¹⁴ Such close contact may be interpreted in terms of a weak bonding interaction between the two d¹⁰ metal atoms.

As shown above, the structural feature of **1** is interesting. First, the 1D CP chain contains univalent copper nodes which are in low-coordination environment. Second, the $[CuBr_2]^-$ moiety instead of simple halide ion serves as the counter anion, furthermore, attached to the chain backbone via weak Cu-Cu binding interaction. As shown in Fig. 1, **1** herein could be considered as a CPs-supported CuBr₂ composite material. Such material would be good catalyst candidate for those organic transformations usually promoted by Lewis acid type inorganic catalysts.

Catalytic property

Phenol acetylation.



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Fig. 2 1-catalyzed 4-bromophenol acetylation: a) 1 H NMR (300 MHz, CDCl₃) spectrum of the acetylation product. b) Reaction time examination and leaching test. c) Recycling catalytic test.

Phenol acetylation is generally catalysed by inorganic metal salts or substrate-supported inorganic composite materials. To our knowledge, only one phenol acetylation example which is catalysed by CPs (Zn/Cd CPs) was reported.¹⁵ 1 carrying external CuBr₂ herein can be considered as a Cu(I) CP-supported CuBr₂ Lewis acid species, in which the CuBr₂ unit is stabilized by the weak Cu···Cu bonding interaction. Based on the unique structural feature, 1 was expected to be the catalyst for phenol acetylation which us usually catalysed by the Lewis acids.

In a typical experiment, 4-bromophenol was treated with acetic anhydride (4 equiv) in the presence of finely ground 1 (5 mol %) in CH₂Cl₂ (1 mL) at room temperature for 2 h (monitored by TLC, petroleum ether/ $CH_2Cl_2 = 1 : 1$), the acetylation product was isolated as white solid in quantitative yield (>99.00 %) and its structure was confirmed by the ${}^{1}H$ NMR spectrum (Fig. 2) The catalyst of 1 can be recovered by centrifugalization. After washed with anhydrous MeOH and dried at 80°C for 2 h, it was reused in the next catalytic cycle. The catalyst amount used herein for this acetylation was determined by a series of parallel experiments. With the successive increase in the amount of 1, (1, 2, 3, 4 and 5 mol %, respectively), the reaction time for the complete 4-bromophenol acetylation significantly decreased (11, 7, 4.5, 3 and 2 h, respectively). 1 performed as a heterogeneous catalyst in the phenol acetylation, which was confirmed by the leaching test. As shown in Fig. 2, no further reaction occurred in the absence of 1 after ignition of the acetylation at 1 h. In addition, Fig. 2 shows that 1 can be reused and the quantitative yield for 4bromophenyl acetate was obtained within the five recycling runs. The corresponding reaction catalysed by reported Zn/Cd CPs afforded 99 % yield under room temperature for 20/40 h using CH₂Cl₂ as solvent.¹⁵

Table 2. Acetylation of the phenols with different substituted groups catalysed by 1.^a

Entry	substrate	T (h)	Conversion (%) ^b	Selectivity (%) ^b
1	Br-OH	2	>99.00	>99.00
2	І-ОН	6	>99.00	>99.00
3	Н ₃ С-ОН	12	>99.00	>99.00
4	O ₂ N-OH	3	>99.00	>99.00
5	н ₃ со-Он	7	>99.00	>99.00
6	OH	15	>99.00	>99.00

^a Reaction conditions: r.t., **1** (5 mol %), CH₂Cl₂, 2-15 h. ^b isolated yields.

Then, we converted a variety of substituted phenol substrates into corresponding aryl acetates to further explore the scope of this 1-catalysed procedure, as summarized in Table 2. Electronwithdrawing groups attached substituted phenols (entries 1, 2 and 4) were converted to the corresponding aryl acetates in yields. On the other hand, acetylated yields of the electrondonating groups containing substrates (entries 3 and 5) are also quantitative, but they took much longer time. In addition, the acetylation of bulky 2-naphthol was also performed, it was found to be acetylated even slower than those electron rich groups, which might be resulted from the sterically blocking effect. The XRPD patterns of 1 and that after being used for five catalytic runs showed that the structural integrity of 1 was well-preserved (ESI).

A³-coupling (aldehyde-alkyne-amine) reaction.

In addition, inorganic copper complexes are known to be good catalysts for A^3 -coupling (aldehyde-alkyne-amine) reaction.¹⁶ Inspired by this, **1** was also used to test its catalytic activity for A^3 -coupling reaction.

For eco-friendly synthesis requirement, the A³-coupling reaction was carried out under solvent-free condition. A mixture of phenylacetylene (120 mg, 1.2 mmol), paraformaldehyde (30 mg, 1.0 mmol) and piperidine (94 mg, 1.1 mmol) in the presence of finely ground **1** (30.6 mg, 5 mol %) was stirred at room temperature for 6 h (monitored by TLC) to afford crude product. The product was purified by column on silica gel (n-hexane/ethyl acetate = 3 : 1). The catalyst of **1** was recovered by the centrifugation. After washed with ether and dried at 80°C for 2 h, **1** was reused for next run.

The reaction was investigated at room temperature for a different period of time. No improved yield was observed by extending the reaction time from 6 h (93.8 %) to 12 h (94.1 %). In addition, when using a smaller amount of 1, for example, 1, 2, 3 and 4 % mol, the three-component coupling yield reduced to 56.4, 67.9, 78.3, 81.6 %, respectively. Thus, the optimized reaction conditions for A³-coupling are 1 (5 mol %) in the absence of an organic solvent at room temperature (Fig. 3). It is similar to phenol acetylation, 1 is stable during the recycling reaction (ESI) and can be reused for five times without loss of its catalytic activity, and the yields lie in a range of 91.4-93.8 % (Fig. 3).

a) 8 1.01 57 3.0 8.0 7.0 6.0 5.0 4.0 20 ppm b) c) no filtration atalyst filtration Conversion (%) (%) 60 ield 20 Cycle Number Time (min)

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Fig. 3 1-catalyzed A³-coupling (phenylacetylene-piperidine-paraformaldehyde): a) ¹H NMR (300 MHz, DMSO-*d*⁹) spectrum of the coupling product. b) Reaction time examination and leaching test. c) Recycling catalytic test.

Entry	Alkyne	Aldehyde	Amine	Yield (%) ^a
1		(CH ₂ O) _n	HN	94
2		CHO	HN	86
3		С-сно	HN	90
4	 	(CH ₂ O) _n	HN N-	93
5	\sim	(CH ₂ O) _n	HNO	89
6	H ₃ C-	(CH ₂ O) _n	HN	91
7	Н ₃ СО-	(CH ₂ O) _n	HN	88
8		(CH ₂ O) _n	HN	93

Table 3. A3-coupling (aldehyde-alkyne-amine) reaction catalysed by 1.ª

^a reaction conditions: r. t., **1** (5 mol %), solvent-free, 6 h.

To test the scope of this 1 catalysed A³-coupling reaction, we extended the studies to different combinations of alkynes, aldehydes and amines under the optimal reaction conditions. The results are summarized in Table 3. Compared to phenylacetylene/piperidine/isobutyraldehyde (entry 2), the combination of phenylacetylene, piperidine with paraformaldehyde (entry 1) or cyclohexanecarboxaldehyde (entry 3) gave the better isolated yields. For the aza- (entry 4) and oxa-piperidine (entry 5) with phenylacetylene/paraformaldehyde, the isolated yields are still high, 89-93 %. On the other hand, aromatic alkynes with both electron-donating (entries 6 and 7) and electron-withdrawing groups (entry 8) for this three-component coupling afforded the corresponding propargylamines in good to excellent yields.

So far, there are three examples related to phenylacetylenepiperidine-paraformaldehyde A^3 -coupling reaction catalysed by CPs. Cu(2-pymo)₂ (2-pymo = 2-hydroxypyrimidinolate),^{16a} View Article Online DOI: 10.1039/C6RA20767G ARTICLE

Cu/PMA-MIL-101(Cr)^{17a} and Cu(II)-MOF^{17b} are able to promote this three-component coupling in 99 (21 h, 40°C, 1,4dioxane), 60 (17 h, 40°C, 1,4-dioxane) and 95 % (12 h, 45°C, CH₂Cl₂) yields, respectively. Compared to the reported CPscatalysts, **1** (r.t., solvent-free, 94 %) herein can be a valuable complement for the CPs to heterogeneous A³-coupling catalysts. **Styrene oxide methanolysis**

In organic synthesis, epoxides are invaluable building blocks for introduction of diverse functionalities in a hydrocarbon backbone in a 1, 2-fashion. To get high regioselectivity of the epoxide ringopening reaction toward the expected product, mild conditions, effective and eco-friendly catalysts have to be used. The past few years have witnessed a rapid increase in the number of reports on the use of CPs in organic synthesis, including epoxide ringopening reaction, due to their heterogeneous nature. As indicated in Table 4, a series of CPs have been chosen for alcoholysis of epoxides. The results indicate that these metal-organic polymeric coordination materials exhibit the similar catalytic activity to those inorganic complexes such as metal halides and metal carboxylates.

Table 4. Ring opening of styrene oxide with methanol catalysed by CPs.				
MeOH, 2 mol% 1				
Entry	Cat.	Cond.	Conv. (%) ^a	Ref.
1	Cu(bpy)(H ₂ O) ₂ (BF ₄) ₂ (bpy)	3 h, r.t.	99	18
2	[Fe (BTC)]	1 h, 40°C	93	19
3	MIL-101-SO ₃ H	0.1 h, r. t.	99	20
4	Cu(II)-CPs	3 days, r.t.	99	21
5	Co(II)-BTT	9 h, 50°C	67	22
6	Cu ₃ (BTC) ₂	2.5 h, 40°C	90	23
7	$[La_2(H_3bmt)_2(H_2O)_2].H_2O$	24 h, 55°C	80	24
8	La(H ₄ bmt)(H ₅ bmt)(H ₂ O) ₂	1 h, 55°C	100	25
9	[Eu(Hpmd)(H₂O)]	48 h, 55°C	100	26
10	[La ₂ (H ₃ nmp) ₂ (H ₂ O) ₄] _{4.5} H ₂ O	2 h, 35°C	100	27
11	TMU-18, TMU-19	110 h, 60°C	100	28
12	Cu(II)-CPs	12 h, r.t.	100	29
13	MIL-100(Fe)	24 h, 40°C	62	30
14	[La(H₃nmp)]-MOF	1 h, 40°C	100	31
15	Cu(II)-MOF	2 h, r.t.	93	32
16	Ln(III)-MOF	29 h, 55°C	80	33
17	1	7 h, 50°C	97	This work



40 20 2 3 4 Time (h) 5 6 ź 3 4 5 Cycle Number Fig. 4 1-catalyzed styrene oxide methanolysis: a) ¹H NMR (300 MHz, CDCl₃) spectrum of the coupling product. b) Reaction time examination and leaching test. c) Recycling catalytic test. In a typical catalytic experiment, the reaction was performed with 1 mmol of styrene oxide in the presence of 2 mol % of finely ground 1. The reaction was performed at 50°C in methanol (5 mL). The reaction was monitored by TLC and the reaction was finished in 7 h. The obtained product is β -alkoxy substituted alcohol (yield of 97 % with >99 % selectivity), which was further confirmed by ¹H NMR spectrum (Fig. 4). In order to gain insight into heterogeneous nature of 1, leaching test was carried out. As indicated in Fig. 4, no further reaction took place without 1 after initiation of the alcoholysis reaction

c)

at 1.5 h. This finding suggests that the reaction likely proceeded on the heterogeneous surface. As a heterogeneous catalyst, 1 can be reused. After each catalytic cycle, 1 could be easily recovered by centrifugation and filtration, and then washed by fresh methanol. After dried at 80°C for 2 h, the catalyst was directly used in the next run.

As indicated in Fig. 4, after seven consecutive catalytic runs, 1 was demonstrated to be highly crystalline based on XRPD patterns and the XRPD patterns of recovered catalyst indicated the structure integrity of 1 was well maintained (ESI). Fig. 4 shows that the catalytic activity of 1 can be used up to seven catalytic runs without significant activity loss, and the high selectivity toward 2-methoxy-2-phenylethanol product is well maintained. As shown in Table 4, the reported conversion of CPs-catalysed styrene oxide methanolysis lies in a range of 62 -100 %, and the reaction temperature and time are in the range of r.t. - 60°C and 0.1 h - 3 days, respectively. 1 (7 h, 50°C, 97 %) is a competitive new member in the catalyst CPs family for styrene oxide methanolysis.

When the substrates extended from styrene oxide to substituted styrene oxide and 1, 2-cyclohexene oxide (Table 5), the conversions are reduced to 67-82 % (entries 2-5), moreover, took much longer time. For example, only ca. 20 and 50 % conversions for the extended epoxide substrates were observed when these reactions proceeded at 7 and 15 h.

Table 5. Methanolysis of styrene oxide and extended substrates catalysed by 1.^a

Entry	Substrate	T (h)	Conv. (%) ^b	Select. (%) ^b
1	⊘→∽	7	97	>99
2	c⊢∕∕o	24	77	>99
3	F-⟨ ◯ }-⟨⁰	24	80	>99
4	⊘–o~ <o< td=""><td>24</td><td>82</td><td>>99</td></o<>	24	82	>99
5	 0	24	67	>99

^a Reaction conditions: **1** (2 mol %), MeOH, 50°C, 7-24 h. ^b determined by GC.

To further confirm 1 is a typical heterogeneous catalyst for above phenol acetylation, styrene oxide methanolysis and aldehyde-alkyne-amine three component coupling reaction, the XPS and ICP measurements (ESI) were performed on 1 after the catalytic reactions, respectively. The results strongly evidenced that no valence state change occurred for Cu and Br after catalysis and basically no copper and bromine species leaching was observed after the catalytic reactions, which further support 1 is an ideal heterogeneous catalyst herein.

We assume that the exposed CuBr₂ moiety in 1 serves as the main active catalytic sites. For confirming this, we synthesized a Cu(I)-CP (2), which contains the embedded type of CuBr moiety, based on fluorene-bridged imidazole-capped ligand L2 with ethyl side chain under the same solvothermal conditions as that of 1 (Fig. 5).

2 crystallizes in the triclinic *P-1* space group (Table 1). As shown in Fig. 5, there are two kinds of crystallographic independent Cu(I) centres in 2. The Cu(1) centre on the chain lies in a triangular coordination environment, a typical



Fig. 5 a) Synthesis of 2. The photograph of ground 2 is inserted. b) The ladder chain in 2 is shown. The asymmetric unit is depicted in the purple oval. Hydrogen atoms were omitted for clarity.

coordination fashion for Cu(I) ion, composed of two N_{imidazol} atoms and one Br-. The Cu(1)-N(1), Cu(1)-N(4) and Cu(1)-Br(1) bond lengths are 1.89(3), 1.93(2) and 2.7581(14) Å,

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respectively. The sum of three angles around Cu(1) centre are 357.64°(\angle N(1)–Cu(1)–N(4) = 157.7(10)°, \angle N(1)–Cu(1)–Br(1) = 98.64(17)°, \angle N(4)–Cu(1)–Br(1) = 101.3(9)°) indicating three coordinating atoms are basically coplanar. It is different from **1**, **2** features 1D double zigzag chain motif and the [Cu₂Br₄]²⁻ counter ions are located between chains and bridge two neighbouring single chains via Cu(1)-Br(1) linkage (2.7581(14) Å). The [Cu₂Br₄]²⁻ cluster core is a planar divalent anion. The bridging Cu-Br distances ($d_{Cu(2)-Br(2)} = 2.4171(14)$ and $d_{Cu(2)-Br(2)\#1} = 2.4034(16)$ Å) are longer than for the terminal Cu-Br bond length ($d_{Cu(2)-Br(1)} = 2.3258(15)$ Å). In addition, the acute Cu-Br-Cu angle in the moiety (\angle Cu(2)#1-Br(2)-Cu(2) = 68.37(5)°) results in a short Cu-··Cu distance of 2.709 (15) Å. These bond lengths and angles are constituent with those found in other reported [Cu₂Br₄]²⁻ anions.³⁴

The 2-catalysed styrene oxide alcoholysis was carried out under the same conditions (2 mol %, MeOH, 50°C, 7 h), but the conversion is only up to 22% (selectivity >99 %). In addition, the catalytic activity of 2 for p-bromophenol acylation and phenylacetylene-paraformaldehyde-piperidine A^3 coupling reactions were also examined under the reaction conditions. The corresponding yields for acetylated product (5 mol % of 2, 2h) and three-component coupling product (5 mol % of 2, 6 h) are only 41 and 38 %, respectively. Considering that 1 and 2 possess the same 1D chain backbones, the distinct catalytic abilities should be mainly resulted from the different Cu(I)containing anions of [CuBr₂]⁻ and [Cu₂Br₄]²⁻. According to the reported mechanism,35 the CPs catalyst might initially coordinate with styrene oxide by way of an acid-base interaction to produce an increase in the electrophilic nature of the more substituted carbon of the substrate (polarization of the C-O bond); secondly, this partially positive charged carbon atom is attacked by the methanol to generate the 2-methoxy-2-phenylethanol product. Compared to 2 with the embedded $[Cu_2Br_4]^{2}$ balanced anions, the [CuBr₂]⁻ outer-hanging type counter ions, are more exposed, which would facilitate the formation of the acid-base pair between styrene oxide and 1, consequently, the generation of the methanolysis product. In addition, the previous works have well demonstrated that the catalyst "electrophilic activation" plays a central role in phenol acetylation³⁶ and A³-coupling reaction.³⁷ So the more exposed CuBr₂-Lewis acid centre in 1 is sterically less hindered for the nucleophilic substrates accesses, which would logically facilitate the reactions. Therefore, the CuBr₂ moiety should be mainly responsible for the catalytic activity.

Conclusions

In summary, we report a CuBr₂ anion balanced 1D coordination polymer based on a fluorene-based ligand. The CuBr₂ moiety attaches to 1D Cu(I)-CP backbone via weak Cu···Cu binding interaction as an outer-hanging species to generate a CPsupported type material. Furthermore, this material serves as a highly effective multifunctional heterogeneous catalyst to promote phenol acetylation, styrene oxide methanolysis, and A³-coupling (aldehyde-alkyne-amine) reactions under mild reaction conditions.

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A CuBr₂ species attached 1D Cu(I) coordination polymer can be a highly effective multifunctional heterogeneous catalyst to promote phenol acetylation, A^3 -coupling (aldehyde-alkyne-amine) and styrene oxide methanolysis reactions, respectively.