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#### Introduction

The increasing level of carbon dioxide in the atmosphere is considered as a major contributor to global warming. The non-toxicity and easy availability of carbon dioxide (by-product of chemical and power industries), on the other hand, opens up its potential as a C1 source in the production of compounds such as such as dimethyl carbonate, N,N'-disubstituted ureas, cyclic carbonates, cyclic urethanes, formic acid, *etc.*<sup>1</sup> The cycloaddition of CO<sub>2</sub> with epoxide substrates to yield cyclic carbonates<sup>1*a,b,h,i,2*</sup> is attractive due to the wide application of cyclic carbonates in polar aprotic solvents, electrolytic elements of batteries, intermediates or precursors in fine chemicals, pharmaceuticals, and polymer synthesis.<sup>3</sup> Even though homogeneous catalysts represent the most active catalytic systems, they suffer from unviable catalyst recovery process.<sup>4</sup>

# Aqueous-microwave synthesized carboxyl functional molecular ribbon coordination framework catalyst for the synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>†

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A carboxyl-containing coordination polymer catalyst {Cu(Hip)<sub>2</sub>(Bpy)}<sub>n</sub> (CHB) was synthesized rapidly in an aqueous medium using microwave energy and characterized for its structure, morphology, acid-base sites and heterogeneity using experimental and physicochemical techniques. The microwave route was established as competent with the hydrothermal pathway. Exploration of the coordination modes of metal–organic framework (MOF) ligands, especially carboxyl spacers, in achieving reactive functional groups is herein illustrated as crucial rather than focusing merely on the porosity of MOF catalysts. The work represents the first report of a carboxyl-containing MOF class material employed for synthesizing cyclic carbonates from epoxide and CO<sub>2</sub>. The metal–carboxyl mediated cycloaddition of allyl glycidyl ether and CO<sub>2</sub> by the cooperative influence of Cu<sup>2+</sup> and the COOH of CHB was synergistically enhanced by an ionic liquid co-catalyst to obtain allyl glycidyl carbonate in 89% yield at optimised reaction conditions. The epoxide substrate scope, effect of reaction parameters and catalyst recyclability (up to 5 cycles) were also studied.

Despite their ease of reusability, most heterogeneous catalysts are fraught with insufficient activities, or the requirement for solvent assistance, or harsh conditions. This necessitates the rational design of a recyclable acid-base multifunctional catalyst that works even under mild reaction conditions.<sup>2,5</sup>

Metal-organic frameworks (MOFs) or coordination polymers (CPs), the crystalline compounds constructed from organic linkers that bridge metal atoms or clusters, are an outstanding class of materials with versatile applications.<sup>6</sup> The ability to impart task-oriented properties through the judicious choice of constituent materials and the rigidity of their frameworks make them highly desirable in catalysis.<sup>1h,2,7</sup> A series of multivariate MOF catalysts like IRMOF, MOF-5, MOF-74, MIL etc. based on exo-dentate di-carboxylic acid template ligands were recently employed in cycloaddition.<sup>7a-e</sup> However, reports including ours, showing the promoting role of hydrogenbonding moieties, especially carboxyl groups, at the solid/ liquid interface of various catalysts in the activation of epoxides<sup>1b,8</sup> surmised the catalytic possibility of an MOF that contains reactive carboxyl groups for effectuating cycloaddition. Unfortunately, reactive COOH-containing MOFs have not been reported in cycloaddition reactions to date; the major obstacle being the scarcity of such MOFs, attributable to the preferential binding tendency of linear exo-dentate dicarboxylates towards the metal during a typical MOF assembly.<sup>9a</sup> Angular COOH

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<sup>†</sup> Electronic supplementary information (ESI) available: Experimental details of Knoevenagel condensation and acetalization reactions, experimental and discussion of  $CO_2$ -TPD analysis and results, the GC-MS results of cycloaddition reactants and products, effects of  $CO_2$  pressure with CHB(M)/TBAB system, and the schematic representation of cycloaddition mechanism by CHB(M). CCDC 657329. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3gc41833b



Scheme 1 Binding modes of carboxylic acid in the frameworks of (a) HKUST-1, (b) CHB and (c) ZHB.

(120°) constituted MOFs employed in cycloaddition viz.,  $Cu_3(BTC)_2$ (HKUST-1, benzene tricarboxylicacid, BTC, linker),<sup>9b,c</sup> and ZnHipBpy (ZHB, from 5-hydroxyisophthalic acid, Hip)<sup>7g</sup> were also deprived of reactive COOH groups. Surprisingly, we found that a copper coordination polymer  $\{Cu(Hip)_2(Bpy)\}_n$  (CHB) synthesized from the same organic constituents of ZHB possessed reactive COOH in its framework (Scheme 1).8d CHB consists of the carboxylate end of its mono-deprotonated Hip ligand appended to the Cu-Bpy chain, retaining the second COOH end for intra-molecular H-bonds. Thus CHB offer itself as a potential candidate which contribute reactive carboxyl group. Further, the avoidance of high-boiling organic solvents (DMF, DEF etc.) for material synthesis, and the absence of water molecules in the crystal lattice and coordination sphere of CHB are advantageous in relieving the tedious or prolonged activation and purification steps for typical MOFs.<sup>7e</sup> Other than purification steps, the circumvention of a long material synthesis time is another drawback for many MOFs. Slow evaporation or diffusion methods may require up to several weeks to achieve MOFs despite the crystallinity and phase purity offered. Further, these methods are unfeasible for large-scale applications owing to their scaling-up limitations. A direct mixing method, though, allows an effective scale up but phase purity and crystallinity could be largely affected.<sup>10a</sup> Solvothermal methods also need a considerably long time for MOF synthesis. In contrast to such conventional catalyst synthesis techniques, microwave energy is renowned as a viable alternative for complex thermallymediated synthetic processes. This efficiency of microwave heating as an advantageous alternative to conventional heating in obtaining catalysts with uniform particle morphologies, and excellent phase purities in a rapid and energyefficient manner encouraged us to synthesize CHB using microwave energy.7h,8e,f In addition, microwave chemistry in aqueous media is attractive and efficient due to the popularity of water as a green solvent, the vapour pressure it imparts, and its capability to behave as a pseudo-organic solvent at elevated temperatures.<sup>11</sup> Herein, we report the microwave-assisted synthesis of the carboxyl functional coordination polymer CHB in an aqueous medium for assessing its catalytic activity in the solvent-free synthesis of cyclic carbonate from CO2 and epoxide. The copper center of CHB is expected to operate

synergistically with the hydrogen bonding capable COOH and OH groups in promoting catalysis. Besides, a quaternary ammonium salt was engaged as co-catalyst for the optimisation of reaction conditions.

#### **Results and discussion**

Mixed-linker or multivariate MOFs reported for cycloaddition rely on multi-variant metal clusters and/or template carboxylate spacers with analogous functional groups. Porosity and CO<sub>2</sub> adsorption capacities, the presence of a co-catalyst, or synthetic modifications (PSM) were considered equally important in choosing an efficient MOF catalyst.<sup>1h,7a-c</sup> However, unlike MOF-74 or IRMOFs, multi-variant or iso-structural MOFs are not as simply achievable with every MOF, since the coordination modes of carboxyl group is largely dependent on variety of factors ranging from the nature of metal salt precursor to the reaction conditions employed for synthesis.<sup>9a</sup> HKUST-1, the tri-carboxylic acid derived porous MOF with a BET surface area of 1270  $m^2\ g^{-1}$  and high  $CO_2$  adsorption capabilities, whose Lewis acid sites (framework node) were recently reported to catalyze the cycloaddition of CO2 and epichlorohydrin with a >30% yield of cyclic carbonate.<sup>7i,9c</sup> Even though CHB (the catalyst under study) and HKUST-1 were synthesized from a cupric nitrate precursor and isostructural tripodal ligands, their resultant structures and geometries were totally different. While HKUST-1 had all its carboxylic acids deprotonated and coordinated to Cu, CHB was assembled with a mono-deprotonated mode of Hip ligand, thus retaining a COOH as well as an OH group in the framework. An iso-structural variant of the CHB framework may not be obtained by simply altering the metal atom in the precursor salt. The exact zinc analogue of CHB in its constituents, viz., ZHB (ZnHipBpy) is non-isostructural with CHB, whose both the COOH groups are deprotonatively coordinated with the metal center, thus deficit in reactive COOH groups (Scheme 1).<sup>8d</sup> Therefore, it is also clear that the generation of a reactive carboxyl group in CHB in comparison with HKUST-1 is not merely resultant of the pH or coordinative influence of the Bpy ligand, or even a variation in the geometry of the copper precursor salt (mono versus tri-hydrate). In controlling the geometry for achieving a

Paper

task-specific MOF, a meticulous understanding of the nature of the metal ions, ligands, solvents, pH and reaction conditions are equally important.

The hydrothermal synthesis of the CHB catalyst (herein denoted as CHB(S)) requires two days at 125 °C.<sup>8d</sup> Our own reports of microwave-mediated methods as rapid means of catalyst synthesis with better catalytic activities encouraged us to adopt a microwave-assisted route for CHB synthesis.<sup>8e-g</sup> However, for synthesizing a typical MOF under microwave radiation, the literature suggests temperature programmed synthetic techniques.<sup>7i</sup> Such syntheses however extend even up to an hour for yielding the material, probably owing to the controlled irradiation of microwaves while following the temperature program. Since the CHB synthesis was performed in an aqueous medium, the maximum temperature of the reactant mixture was auto-controlled around 100 °C, and hence a temperature program would not be needed. Thus, the maximum utilization of microwaves within a minimum time frame was achieved by performing a CHB synthesis under sealed conditions and constant microwave power in the aqueous medium. To our delight, a very short reaction time of 6 min with 100 W of microwave power was sufficient to facilitate the synthesis of CHB crystals (denoted as CHB(M)) in exceptional vields (96%).

Yet another shortcoming encountered in the catalysis of conventional MOFs is the evacuation of solvent molecules from the pores of MOFs. DMF or DEF, the most common solvents for MOF synthesis, demand prolonged post synthetic treatment, such as repeated boiling in methanol for purification of the as-synthesized MOFs before activation and catalysis.<sup>7e</sup> However, since CHB was synthesized totally in an aqueous medium, purification was accomplished by sonication in the aqueous medium, and activation by vacuum drying. The absence of any lattice or coordinated water molecules in the crystal of CHB further simplified the activation process.

Phase homogeneity of the CHB(M) and CHB(S) catalysts was confirmed by comparing their powder X-ray diffraction (PXRD) patterns with the single-crystal-simulated pattern (Fig. 1). XRD analysis also revealed that CHB(M) exhibited 77%



Fig. 1 XRD patterns of CHB(S) and CHB(M) compared to the single crystal simulated pattern.



Fig. 2 FT-IR spectra of CHB(S) and CHB(M).



Fig. 3 Thermal gravimetric analyses (TGA) of CHB(M) and CHB(S).

crystallinity with respect to CHB(S), calculated from the relative intensities of the central reflections, in the  $2\theta$  range 15–30° (assuming 100% crystallinity of the solvothermal catalyst). However, the higher intensity peak of CHB(M) than CHB(S) at 39°  $2\theta$  might be ascribed to some minor amounts of metal oxides.<sup>10</sup>

The FT-IR spectrum of CHB(M) resembled that of CHB(S) displaying their compositional similarity (Fig. 2). The carboxyl and phenol O–H stretching frequencies of Hip (3450 cm<sup>-1</sup>) shifted to lower wavenumbers (3295 cm<sup>-1</sup>) in CHB owing to the extensive H-bonds in CHB. The C=O stretching frequency, characteristic of carboxylic acids, appeared at 1690 cm<sup>-1</sup>. However, two asymmetric (1600 and 1427 cm<sup>-1</sup>) and symmetric (1566 and 1390 cm<sup>-1</sup>) carboxylate stretches were observed. The former carboxylate stretches, existent also in Hip, correspond to COOH, whereas the latter ones having  $\Delta v(v_{asym} - v_{sym}) = 176 \text{ cm}^{-1}$  belong to the chelated bidentate carboxylate. The C–O stretching frequencies at 1300 cm<sup>-1</sup> (reactive carboxyl) and 1237 cm<sup>-1</sup> (coordinated carboxylate) supplemented them further.

The thermal stability of CHB up to 300 °C from the TGA curve points at similarities in the thermal stabilities of CHB(S) and CHB(M) (Fig. 3). However a closer analysis of the degradation curves around 250–300 °C reveals the better stability of CHB(M). The residual mass of ~18% at 600 °C could be correlated to the oxidized inorganic part of the sample, presumably



Fig. 4 FE-SEM images of (a) CHB(S) and (c) CHB(M); and their respective magnified images (b) and (d).

cupric oxide.<sup>10*a*</sup> Further, CHB(M) had 1% higher residual mass than CHB(S). The surface area measurements of CHB(M) and CHB(S) and their respective isotherms are depicted in the ESI (Fig. S2 and S3†). The BET surface areas of CHB(M) and CHB(S) ( $0.4 \text{ m}^2 \text{ g}^{-1}$  and  $1.3 \text{ m}^2 \text{ g}^{-1}$ , respectively) were negligible in comparison with HKUST-1 ( $1270 \text{ m}^2 \text{ g}^{-1}$ ) and most of the other functional MOFs.<sup>9*c*</sup> Examination of the textural features using FE-SEM (Fig. 4) revealed that the CHB(M) catalyst (Fig. 4(a)) exhibits a morphology and particle dimensions comparable to CHB(S) (Fig. 4(b)). Magnified views of the crystals are shown in Fig. 4(b) and (d).

In order to compare the acid-base sites of the catalysts, the initial rate calculation from the Knoevenagel and acetalization reactions is a generally accepted experimental procedure.<sup>13</sup> While comparing two similar catalysts, the higher the initial rate of reaction, the higher the number of active sites. The Knoevenagel condensation reaction is a base catalyzed reaction, while the acetalization reaction is an acid catalyzed reaction. Using CHB(S) or CHB(M) as catalyst, a Knoevenagel condensation was performed between benzaldehyde and malononitrile to yield benzylidenemalononitrile, whereas an acetalization reaction was carried out using benzaldehyde and ethanol as the substrates (ESI<sup>†</sup>). The initial rates ( $r_0$ ) of 43.0 ×  $10^3$  and  $40.0 \times 10^3$  mol min<sup>-1</sup> g<sup>-1</sup> were recorded for CHB(M) and CHB(S), respectively. The slightly higher  $r_0$  value calculated for the Knoevenagel condensation with CHB(M) than CHB(S) implies a slightly higher basicity of CHB(M) (Fig. S4<sup>†</sup>). Ahn et al.15 observed using Temperature Programmed Desorption (TPD) that lone pair electrons in the metal coordinated O- and N atoms of MOFs can act as base sites. Therefore, we performed a CO2-TPD experiment with CHB(S) (representatively) and found that it possess 29.5 mmol  $g^{-1}$  of base sites. Hence, the slight basicity of the metal-carboxylate system was verified. In the acetalization reaction, a higher  $r_0$  value of  $16.5 \times 10^3$  mol min<sup>-1</sup> g<sup>-1</sup> was obtained for CHB(M), than the  $r_0$ value of  $14.0 \times 10^3$  mol min<sup>-1</sup> g<sup>-1</sup> observed for CHB(S). These observations could be attributed to slight amounts of metal oxide in CHB(M).



Scheme 2 Representation of the cycloaddition of allyl glycidyl ether (AGE) and  $CO_2$  to yield allyl glycidyl carbonate (AGC).

Table 1	Cycloaddition	of	allyl	glycidyl	ether	and	$\rm CO_2$	using	various
catalysts									

ield of GC <sup>a</sup> %)	Selectivity AGC $^{a}$ (%)	Conversion <sup>a</sup> (%)	Surface area (BET, $m^2 g^{-1}$ )	Catalyst	Entry
0	0	0	_	None	1
1.1	66.1	1.7	_	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	2
_	_	Trace		Hip	3
4.5	84.6	29.0	_	Bpy	4
1.7	84.4	84.9	1.3	CHB(S)	5
7.4	90.3	85.7	0.4	CHB(M)	6
0.7	63.5	64.1	2.7	ZnHipBpy (ZHB)	7
5.3	56.2	11.3	$1270^{b}$	HKUST-1	8
7.4	95.7	91.3	0.4	$CHB(M)^{c}$	9
) 1.1 - 4.5 1.7 7.4 0.7 6.3 7.4	0 66.1 	0 1.7 Trace 29.0 84.9 85.7 64.1 11.3 91.3	$ \begin{array}{c} - \\ - \\ - \\ 1.3 \\ 0.4 \\ 2.7 \\ 1270^{b} \\ 0.4 \\ \end{array} $	None Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O Hip Bpy CHB(S) CHB(M) ZnHipBpy (ZHB) HKUST-1 CHB(M) <sup>c</sup>	1 2 3 4 5 6 7 8 9

Reaction conditions: Allyl glycidyl ether (AGE) = 18.6 mmol (2.2 mL), 0.3 mmol catalyst, catalyst to substrate ratio = 1.6 mol%, batch reaction (except entry 9), 1.2 MPa CO<sub>2</sub>, 120 °C, 6 h, 600 rpm. <sup>*a*</sup> Determined by GC. <sup>*b*</sup> Ref. 9*b*,*c*. <sup>*c*</sup> Semi-batch reaction. AGC = allyl glycidyl carbonate. Side product = 3-allyloxy-1,2-propanediol.

The catalytic abilities of CHB were investigated in the cycloaddition reaction of CO<sub>2</sub> using allyl glycidyl ether (AGE) as the epoxide substrate (Scheme 2). In the absence of a catalyst, the cycloaddition reaction (batch reaction) did not afford any product even after 6 h of reaction using 18.6 mmol of AGE and 1.2 MPa of CO<sub>2</sub> at 120 °C (Table 1, entry 1). Under similar conditions, 1.6 mol% of the catalyst precursors viz., cupric acetate monohydrate and 5-hydroxyisophthalic acid (Hip) yielded almost no AGC (Table 1, entries 2 and 3). However, 29% conversion of AGE with 84.6% AGC selectivity was observed with the third precursor of CHB, viz., Bpy, probably due to its Lewis basic pyridyl-nitrogens and homogeneity of reaction due to its solubility in AGE (Table 1, entry 4). The heterogeneous catalysts CHB(S) and CHB(M) provided a manifold increase of AGC yield in comparison with any of its precursor materials (Table 1, entries 5 and 6). Furthermore, among the CHB catalysts in the batch conditions, the microwave-synthesized catalyst CHB(M) was slightly superior in AGC yield than the solvothermally synthesized CHB(S), probably owing to the metal oxide impurities, as evident from the slightly higher residual mass of CHB(M) observed in the TGA (Fig. 3).<sup>12</sup> Thus, microwave energy facilitates a more rapid catalyst synthesis route than solvothermal, while maintaining the essential catalytic activity.

For experimental evidence of the promoting role of the COOH group in cycloaddition, we compared CHB to the catalytic activity of ZHB, a similar catalyst reported by our group which is devoid of any COOH groups.<sup>7g</sup> ZHB, under similar



Fig. 5 Effect of catalyst CHB(M) amount on the reactivity of AGE and CO<sub>2</sub> at 120 °C, 6 h, 600 rpm and  $P_{CO_2}$  = 1.2 MPa.

reaction conditions to CHB, exhibited only 64.1% AGE conversion and 63.5% selectivity of AGC (Table 1, entry 7). In addition, a copper containing catalyst HKUST-1, which also lacked COOH groups,<sup>14</sup> was employed for the same reaction under the same conditions. Despite its high porosity and  $CO_2$ adsorption capacities, HKUST-1 exhibited an AGE conversion of only 11.3%, with 56.2% selectivity for AGC (Table 1, entry 8), which could be attributed to the absence of reactive COOH groups. Hence the positive influence of the COOH group in the cycloaddition reaction of AGE and  $CO_2$  is established. The importance of the awareness of the coordination geometries, ionization states and functional groups of a MOF rather than merely relying on porosity, surface area or gas adsorption is therefore signified.

A study of the reaction parameters with the CHB(M) catalyst in batch conditions were conducted for understanding the optimal conditions for AGC yield. A study of the effects of catalyst amount (Fig. 5) was conducted in the range of 0.1-0.5 mmol of CHB(M) with 18.6 mmol of AGE (catalyst mol% 0.5-2.68%) at 120 °C and 1.2 MPa CO<sub>2</sub> pressure for 6 h. A steady incremental increase in the yield of AGE was observed from 0.53 to 1.6 catalyst mol% (0.1 to 0.3 mmol of catalyst). No significant increase in the conversion was observed with higher catalyst amounts of 0.4 and 0.5 mmol (catalyst mol% 2.15 and 2.68, respectively), probably because of the hindrance in mass transfer through the H-bonded layers between the active site and reagent, caused by the lesser dispersion of the excess catalyst in the reaction mixture,<sup>1g</sup> or because of the attainment of reaction equilibrium. 0.3 mmol (1.6% catalyst to substrate ratio) was therefore identified as the optimal catalyst amount under the aforementioned conditions (85.7% AGE conversion and 90.3% AGC selectivity).

The effect of reaction time on the CHB(M) catalyzed cycloaddition is depicted in Fig. 6. The conversion increased with respect to reaction time and the highest conversion was obtained at 6 h. Thereafter, the reaction did not proceed promisingly, indicating that the optimum reaction time was 6 h for which 85.7% AGE conversion and 90.3% AGC selectivity was obtained. The catalytic activity increased progressively from 60 to 120 °C, reaching the highest AGC yield (77.3%) at 120 °C



**Fig. 6** Effect of reaction time on the reactivity of AGE and CO<sub>2</sub> using 1.6 mol% CHB(M) at 120 °C and 1.2 MPa  $P_{CO_2}$ .



Fig. 7 Effect of reaction temperature on the reactivity of AGE and  $CO_2$  using 1.6 mol% CHB(M) at 1.2 MPa  $P_{CO_2}$  for 6 h.



Fig. 8 Effect of  $CO_2$  pressure on the reactivity of AGE and  $CO_2$  using 1.6 mol% CHB(M) at 120 °C for 6 h.

(Fig. 7), thereafter no noticeable increase in activity was found. The effect of  $CO_2$  pressure on the yield of AGE is depicted in Fig. 8. AGE conversion increased with an increase in  $CO_2$  pressure from 0.4 MPa to 1.2 MPa. This could be attributed to an increased solubility of  $CO_2$  in the reaction mixture at higher pressures and the subsequently improved  $CO_2$  concentration which shifts the reaction equilibrium favoring an accelerated formation of AGC. CHB(M) exhibited its highest catalytic

Table 2Cycloaddition of  $CO_2$  with various epoxides using the CHB(M)catalyst

Entry	Epoxide	Cyclic carbonate	Conv [Sel] (%)	Yield (%)
1	ڴ	<u>ب</u> ل	75.2 [83.3]	62
2	ci	a Jul	80.7 [89.5]	72
3	$\sim\sim$ å		65.6 [86.3]	56
4	<i>~</i> <sup>∧</sup> <sup>∆</sup>		85.9 [84.4]	73
5			85.1 [83.5]	71
6	$\mathbf{r}^{\mathbf{A}}$		69.8 [80.6]	56
7	$\bigcirc$	$\bigcup =$	19.7 [52.4]	10

Reaction conditions: 0.3 mmol CHB(M), 18.6 mmol epoxide,  $P_{CO_2}$  = 1.2 MPa; 120 °C, 6 h, 600 rpm. Conv. = Conversion, Sel = Selectivity, Yield = Isolated yield.

activity under 1.2 MPa of  $CO_2$  pressure and it decreased slightly at 1.4 MPa. It must be inferred that too high a  $CO_2$ pressure may retard the interaction between AGE and the catalyst by a dilution effect, resulting in a lower conversion.<sup>1g</sup> Thus, the optimum conditions for obtaining maximum yields using the CHB catalyst were identified as 6 h, 120 °C, and 1.2 MPa  $CO_2$ , contributing to an AGE conversion of 85.7% and a selectivity of 90.3% for AGC under batch conditions. Cycloaddition at the same conditions in a semi-batch operation is desirable for an understanding of the AGC yield with  $CO_2$  pressure maintained throughout. Interestingly, an AGC yield of 87.4% was obtained in 6 h at 120 °C and 1.2 MPa  $CO_2$  in semi-batch condition (Table 1, entry 9).

The scope of CHB(M) in catalyzing epoxide– $CO_2$  cycloadditions was explored by extending the catalysis to a variety of epoxides; the results are summarized in Table 2. The internal epoxide cyclohexene oxide gave only comparatively low conversions, which could be ascribed to the hindrance in anionic attack posed by the steric crowding of the cyclohexene ring (entry 7). The comparatively lower conversion of styrene oxide is attributable to the low reactivity at its  $\beta$ -carbon center (entry 6). AGE and phenyl glycidyl ether (PGE), in contrast, gave comparatively better conversions (entries 4 and 5). Recently our group, using experimental and DFT calculations, explained that the enhanced activity of AGE with COOHcontaining catalysts is due to the H-bonding interactions between the side chain ether oxygen of AGE and the COOH group of the catalyst.<sup>8c,g</sup>

Table 3 Influence of TBAB in the cycloaddition of AGE and CO<sub>2</sub>

Entry	Catalyst	% Conversion	% Selectivity	
1	None	0	0	
2	$CHB(M)^{a}$	Trace	_	
3	$TBAB^{a}$	2.4	99.9	
4	$TBAB/CHB(M)^{a}$	24.3	99.9	
5	$CHB(M)^{b}$	24.1	68.2	
6	$TBAB/CHB(M)^{b}$	89.2	99.9	
7	$TBAC/CHB(M)^{b}$	36.9	91.3	
8	TBAI/CHB $(M)^{b}$	88.5	99.9	

Reaction conditions: 18.6 mmol AGE, 1.2 MPa  $P_{CO_2}$ , 6 h, semi-batch. <sup>*a*</sup> At 27 °C, 0.3/0.3 mmol CHB(M)/TBAB. <sup>*b*</sup> 80 °C, 1.6 mol% catalyst, TBAB = 1.6 mol%, wherever used.

The activation of epoxide at mild reaction conditions is widely regarded as an attractive research goal.<sup>7e</sup> Therefore, the possibility of a synergistic enhancement in catalytic activity of CHB(M) by a co-catalyst containing a strong nucleophilic anion for a better cyclic carbonate yield was estimated worthwhile.<sup>15</sup> Accordingly, quaternary ammonium salts were engaged as a cocatalyst with CHB(M) under semi-batch conditions (Table 3). At room temperature, a ten-fold increase in yield of AGC was observed with the CHB(M)/TBAB system, in comparison to the summated AGC yields with individual CHB(M) and TBAB catalysts (entries 2 and 3). This clearly demonstrates the synergistic catalysis by the CHB(M)/TBAB system. Yet another surprising result was the more superior AGC yield (in terms of conversion and selectivity) with the CHB(M)/TBAB system at room temperature than CHB(M) alone at 80 °C (entries 4 and 5). Above all, the high AGC yield of 89.2% (99.9% selectivity) at 80 °C with the CHB(M)/TBAB system clearly demonstrates its high catalytic activity under optimised reaction conditions (entry 6).

In an attempt to study the effect of anions in this cycloaddition, the reactions were performed with tetrabutyl ammonium chloride (TBAC) and tetrabutylammonium iodide (TBAI) co-catalysts. While the effect of nucleophilicity is expected to exhibit activities in the order of I > Br > Cl, steric factors may reverse the order to Cl > Br > I.<sup>16</sup> However in a typical MOF, say for example MOF-5, the combined effect equilibrates to the order Br > I > Cl; explained by the diffusion of the large iodide being hampered by the restriction of the pore size of the MOF.<sup>7b</sup> In the present system also, TBAC exhibited a conversion of 36.9% (91.3% selectivity for AGC), which is much less than that with the bromide anion (entry 7). Surprisingly, the reaction with the iodide containing cocatalyst (TBAI, entry 8) exhibited an AGC yield similar to that with the bromide anion (of TBAB). This sheds light on the open active sites of the CHB catalyst that offer the bromide species easy access in comparison to the difficultly of iodide in its diffusion into the pores of higher dimensional MOFs. However, the expected superior catalytic activity of iodide over bromide might have been nullified by the steric hindrance experienced by iodide around the active sites.<sup>16</sup>

In order to get a clearer understanding of the CHB(M)/TBAB catalysis, the yield of AGC at various temperatures in different time intervals was studied (Fig. 9). The reaction



**Fig. 9** Time variant yield of AGC at various temperatures (room temperature, 50 °C and 80 °C) with 18.6 mmol AGE, 1.2 MPa  $P_{CO_2}$ , and 1.6 mol% CHB(M)/TBAB semi-batch operation.



Scheme 3 Proposed mechanism for the cycloaddition of AGE and  $CO_2$  using CHB/tetrabutylammonium halide. (Bu<sub>4</sub>NX = tetrabutylammonium halide, where X = Cl/Br/I).

proceeds considerably even at room temperature. However, at 80 °C, where the AGC yield was quite high, 6 hours was the optimal time for reaction. Supplemented with the  $CO_2$  pressure study (Fig. S5, ESI†), it could be concluded that with 1.6 mol% TBAB and CHB(M), the optimum conditions were 80 °C, 1.2 MPa  $CO_2$  pressure and 6 h, yielding 89.1% AGC.

A plausible mechanism of the cycloaddition reaction of AGE in the presence of CHB(M), co-catalyzed by TBAB, is illustrated in Scheme 3. The Mercury diagram of CHB (Fig. 10) generated from the crystallographic information file (CIF) of the Cambridge Crystallographic Data Center (CCDC deposit number 657329), depicts the reactive functional groups and Cu in CHB (depicted using a ball-and-stick model). Initially, the epoxide oxygen of AGE is activated by the Cu(II) center of CHB(M). This attack takes place with substitution, breaking the =O-Cu bond, maintaining the octahedral geometry. The AGE-CHB interaction is further strengthened by the





**Fig. 10** Mercury diagram of the molecular ribbon in CHB. O atoms of carboxyl and hydroxyl groups, and Cu atom represented as ball model (H-atoms omitted for clarity).

interaction between the COOH group of CHB and the ether oxygen of AGE (H-bonding), thereby holding AGE more strongly to the proximity of the reactive site (Scheme S1, ESI†).<sup>8c,g</sup> Concomitantly, the Br<sup>-</sup> of TBAB attacks the least hindered carbon atom, thereby resulting in epoxide ring opening. Following this, the O<sup>-</sup> of the ring-opened intermediate attacks the carbon atom of CO<sub>2</sub>, forming the carbonate complex. In the succeeding step, ring closure occurs by intra-molecular carbonate O<sup>-</sup> attack at the C-Br carbon whereby AGC is generated, together with the liberation of TBAB and the regeneration of the original structure and geometry of CHB(M).

In the absence of TBAB, the mechanism proceeds *via* a CHB(M)–AGE interaction that undergoes a ring-opening by the O<sup>-</sup> atom of the polarized CO<sub>2</sub> molecule (polarized either by base sites of CHB or epoxide substrate) at the  $\beta$ -carbon of the epoxide (Scheme S2, ESI†). The higher activity of CHB in comparison with the MOF precursor materials in isolation is justified by the aforesaid CHB(M)–AGE interaction (Table 1, entries 2 and 3). The CHB(M) catalyzed cycloaddition that demands elevated temperatures may be ascribed to the barrier in crossing the transition state for activation of CO<sub>2</sub> either by the carbonyl group of CHB or AGE.

In several MOFs, like  $Cu_2(BTC)_3/HKUST-1$  and ZIF-8, recyclability issues were documented for the cycloaddition of epoxide and  $CO_2$ ,<sup>2,7*i*</sup> resulting from local structural disorders and/or active site/pore blocking by residual carbonaceous deposits. Despite such observations for CHB(M) at 120 °C, it is worthwhile to note that recycling was successful with the CHB(M)/TBAB system at 80 °C and 1.2 MPa  $CO_2$  pressure. Powder XRD patterns of the recycled catalyst were similar to the fresh CHB(M), with 97% retention of crystallinity, implying stability of CHB(M) under the aforementioned conditions (Fig. 11).

Interestingly, an increase in BET surface area (to 7.5 m<sup>2</sup> g<sup>-1</sup>) was observed for CHB(M) after the cycloaddition (ESI, Fig. S6†). This may be ascribed to the partial denaturing of intra-molecular H-bonds between 1-D chains of CHB upon cycloaddition, an imperfect elasticity of hydrogen bonds during substrate diffusion/effusion between the H-bonded layers,<sup>17</sup> or catalyst milling arising from stirring during the course of the reaction. Nonetheless, the covalent or coordinate bonds of CHB were unaffected throughout the cycloaddition, as is evident from PXRD.



Fig. 11 Powder XRD patterns of fresh CHB(M) and recycled CHB(M).

A hot filtration test by Sheldon et al. was conducted to test the heterogeneous nature of the catalyst in the cycloaddition reaction (section 4, ESI†).<sup>18</sup> The cycloaddition was carried out with 1.6 mol% CHB(M), AGE and CO2 at 1.2 MPa CO2 and 100 °C until a 49.6% conversion of AGE was achieved (at 5 h). The contents were filtered while hot; 0.2 µL of the filtrate was used for GC analysis (in CH<sub>2</sub>Cl<sub>2</sub>) and the remaining filtrate was fed back to the same conditions of temperature, CO<sub>2</sub> and stirring. Sampling was performed every 1 hour thereafter. No increase in conversion was observed in the filtered content, implying the absence of any catalytically active homogeneous species in the filtrate (Fig. S7, ESI<sup>+</sup>). Since there is no conversion in the filtered sample compared to the conversion observed in the original sample, there are no homogeneous species catalyzing the reaction in solution. The hot filtration test is regarded as more of a test for homogeneous catalytic contributions to the rate than a test for catalyst leaching. In order to have an accurate determination of catalyst leaching, the filtrate after reaction was therefore analyzed using ICP-OES, which showed only small traces of Cu, counting as less as 0.5 ppm in comparison to 30-50 ppm metal detected with other MOFs such as MILs.<sup>7e</sup>

The recycled CHB(M) catalyst from the CHB(M)/TBAB reaction (Table 3, entry 6) was further employed for successive runs with freshly added co-catalyst. A slight rise in AGC yield was observed after the first run. This could be attributed to the enhanced AGE access as a consequence of intra-molecular Hbonding rupture. This is supplemented by the increased surface area of the recycled CHB with respect to fresh CHB(M). The selectivity and yield of AGE were not significantly affected in further cycles (until the 4<sup>th</sup> reuse, Fig. 12). The chemical stability of CHB(M) after each cycle was confirmed by FT-IR spectroscopy (Fig. 13).

### Conclusions

The aqueous microwave-assisted synthesized coordination polymer  $\{Cu(Hip)_2(Bpy)\}_n$  was employed to demonstrate the



Fig. 12 Catalyst recycling at 80 °C, 1.2 MPa<sub>CO<sub>2</sub></sub>, 6 h; 1.6 mol% CHB(M)/ TBAB in AGE (99% selectivity maintained).



Fig. 13 FT-IR spectra of the recycled CHB(M) catalyst.

synergistic role of reactive hydrogen-bonding functional groups such as the carboxyl group with metal centers in enhancing the cycloaddition of epoxide and CO2 under solvent-free conditions. A thorough observation of the topologies and coordination modes of the coordination polymers was demonstrated as a successful strategy for accomplishing an assigned task, instead of functionalizing a higher dimensional, porous, MOF template. The role of the reactive COOH group in a MOF for the successful cycloaddition of epoxides and CO<sub>2</sub> was proposed and demonstrated for the first time. Microwave irradiation, used for accomplishing rapid catalyst synthesis, instigated a better catalytic activity than the hydrothermally synthesized catalyst in the synthesis of AGC from CO2 and AGE. Furthermore, excellent selectivities of AGC were obtained even under ambient reaction temperatures in the presence of the quaternary ammonium salt co-catalyst TBAB. Substantial yields of AGC were obtained at 80 °C and 1.2 MPa CO<sub>2</sub> pressure in 6 h, with 99.9% selectivity. The catalyst was successfully recycled up to four times without the degradation of any covalent/coordinate linkages of the catalyst framework. The high catalytic activity exhibited by CHB in comparison with a typical MOF with high porosity, surface area and gas adsorption property points at the significance of a careful

watch of coordination geometries and ionization in MOFs. A meticulous design or judicious selection of MOFs that could aptly accommodate active sites and functional groups will serve a prospective role in attaining excellent catalytic properties, underlining the so-called versatility of coordination polymers and MOFs in task-oriented catalytic applications. Employing water in association with microwave energy may serve as a green substitute for organic solvents in MOF syntheses.

## **Experimental section**

#### Materials

Copper(II) acetate monohydrate (Cu(OAc)<sub>2</sub>·H<sub>2</sub>O; >98%), and 4,4'-dipyridyl (Bpy; 98%) were purchased from Aldrich, Korea and used as received. 5-Hydroxyisophthalic acid (Hip; 99%, Acros Organics) was purchased from Fisher Scientific. Doubly distilled water was used for catalyst synthesis. Allyl glycidyl ether (AGE) and all other epoxides were procured from Aldrich. CO<sub>2</sub> of 99.999% purity was used. Chemicals for the Knoevenagel condensation and acetalization *viz*. benzaldehyde (>99.5%), malononitrile (>99%), ethanol (>99.5%) were purchased from Aldrich, whereas 1,4-dioxane was purchased from Junsei Chemical Co. Ltd.

#### Synthesis of catalyst

Solvothermal synthesis: CHB(S). Cu(Hip)2(Bpy) was hydrothermally synthesized by a procedure similar to that reported by Feller and Cheetham.<sup>8d</sup> To an aqueous solution of Cu-(OAc)<sub>2</sub>·H<sub>2</sub>O (9 mmol) in water (30 mL, doubly distilled) were added 5-hydroxyisophthalic acid (18 mmol) and 4,4'-bipyridine (9 mmol); the resultant mixture was stirred for 30 min in room temperature (600 rpm). The contents were then transferred to a 100 mL Teflon-lined autoclave, sealed and heated at 125 °C for 48 h in a convection oven. The contents were then regressively cooled to room temperature at a rate of 0.1 °C min<sup>-1</sup>. Deep purple crystals of CHB, denoted as CHB(S), were obtained in a 90% yield from the product mixture by washing with water under sonication. The catalyst was activated to remove any physically adsorbed water molecules by vacuum drying at 100 °C for 4 h (heating rate 5 °C min<sup>-1</sup>). The crystals were ground to a fine powder for catalytic reaction.

**Microwave synthesis: CHB(M).** A rapid synthesis of CHB was accomplished by microwave irradiation of the reaction mixture in a 40 mL Pyrex glass reactor tube. The multimode microwave reactor (KMIC-2 KW), having a continuously adjustable power source (range 0–2 kW) with a 3-stub tuner, operates at a frequency of 2.450 GHz.  $Cu(OAc)_2 \cdot H_2O$  (0.3 mmol) was completely dissolved in water (10 mL, doubly distilled), followed by the addition of 4,4'-bipyridine (0.3 mmol) and 5-hydroxyisophthalic acid (0.6 mmol) in water (5 mL). The contents were transferred to the Pyrex glass tube, sealed and irradiated with a microwave power of 100 W for 6 min. The reaction mixture then remained in the reactor for cooling down spontaneously to room temperature, and purple crystals of CHB, denoted as

#### Cycloaddition of epoxide and CO<sub>2</sub>

All syntheses were carried out in a 25 mL stainless steel reactor equipped with a magnetic stirrer. Procedure for the synthesis of allyl glycidyl carbonate (AGC) from allyl glycidyl carbonate (AGE) is as follows. An appropriate amount of activated, finely ground catalyst was added to the reactor containing AGE (18.6 mmol). The reactor was pressurized with  $CO_2$  to the required pressure at room temperature, brought to the desired temperature, and stirred at 600 rpm. After reaction completion, the reactor was cooled and excess CO<sub>2</sub> was carefully vented off. Dichloromethane (2 mL) was added to the product mixture and filtered. The filtrate was subsequently analyzed using gas chromatography (GC, HP 6890, Agilent Technologies) to determine conversion, selectivity, and yield. The product AGC was further confirmed by <sup>1</sup>H NMR and <sup>13</sup>C NMR experiments. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 5.23–5.14 (2H), 5.86 (1H), 4.82-4.76 (1H), 4.49-4.45 (2H), 4.5 (2H), 4.82–4.9 (2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 61.7, 71.8, 72, 75.1, 115.4, 131.7, 154.2; GC-MS: m/z calcd for C<sub>7</sub>H<sub>10</sub>O<sub>4</sub>: 158.06. Found: *m*/*z* 157.9 (ESI, Fig. S1<sup>†</sup>). The ring-opened side product, 3-allyloxy-1,2-propanediol, was also identified using GC-MS (ESI, Fig. S1<sup>†</sup>).

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