

# Synthesis of pyridine-zinc-based porous organic polymer for cocatalyst-free cycloaddition of epoxides

He Li,<sup>[a]</sup> Chunzhi Li,<sup>[a,b]</sup> Jian Chen,<sup>[a,b]</sup> Lina Liu,<sup>[a,b]</sup> Qihua Yang\*<sup>[a]</sup>

Dedication ((optional))

Abstract: Synthesis of solid catalysts for co-catalyst free CO2 cycloaddition reaction has attracted much research attention. Herein we report a hierarchical porous organic polymer, Py-Zn@MA which could catalyze cycloaddition reaction with epoxides and CO2 without using any additives or co-catalyst to afford turnover frequency (TOF) as high as 250 and 97 h<sup>-1</sup> at 130 °C using pure and diluted CO<sub>2</sub> (a simulating flue gas), respectively. These results are superior to most ever reported heterogeneous co-catalyst free systems. The high activity of Py-Zn@MA is mainly attributed to its bifunctional nature with ZnBr<sub>2</sub> and pyridine activating epoxide in a cooperative way. It is worth mentioning that Py-Zn@MA could be easily prepared in large-scale without using any catalyst and the chemicals are cost-effective. Meanwhile, Py-Zn@MA shows good substrate universality for cycloaddition reactions of epoxides. Our designed POP material Py-Zn@MA has the potential to serve as an efficient catalyst in direct conversion of flue gas with epoxides into value-added cyclic carbonates.

## Introduction

The average global temperature rise is closely related to cumulative emissions of greenhouse gases caused by the utilization of fossil fuels such as coal, oil and nature gas.<sup>[1-3]</sup> Thus carbon capture and storage (CCS) and further usage have attracted worldwide interest and should be a major global task of the twenty-first century.<sup>[4,5]</sup> As an abundant, nontoxic and recyclable carbon source, CO<sub>2</sub> can be used as a C1 building block for synthesizing lots of value-added chemicals such as methanol, formic acid, carbonates, methylamines, carboxylic acids, *etc.*<sup>[6-11]</sup> Among them, synthesis of cyclic carbonates and polycarbonates from epoxides and CO<sub>2</sub> is all-important and has been already industrialized since this reaction is of 100% atom economic and the product is of high economic worth.<sup>[12,13]</sup> Numerous homogeneous and heterogeneous catalysts have been designed for catalyzing CO<sub>2</sub> cycloaddition reaction.<sup>[14-34]</sup> Homogeneous

[a]	H. Li, C. Li, J. Chen, L. Liu, Prof. Q. Yang State Key Laboratory of Catalysis
	Dalian Institute of Chemical Physics
	Chinese Academy of Science
	Dalian 116023, China
	E-mail: yanggh@dicp.ac.cn
[b]	C. Li, J. Chen, L. Liu
	University of Chinese Academy of Sciences
	Beijing 100049, China

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catalysts such as metalloporphyrins and metal-salen complexes exhibit high activity and selectivity for synthesizing cyclic carbonates.<sup>[14-16]</sup> Recently, Ema and co-workers reported a serious of functional zinc-porphyrin complexes which showed high activity (TOF up to 31500 h<sup>-1</sup>) for CO<sub>2</sub> cycloaddition reaction.<sup>[16]</sup> While for most of homogeneous catalysts, the difficulty in catalyst reuse and product purification impedes their wide applications in industry.

Up to now, several types of heterogeneous catalysts have been developed, including metal oxides,[17] functional graphene oxide,<sup>[18]</sup> supported catalysts,<sup>[19]</sup> zeolitic imidazolate frameworks (ZIFs) & metal-organic frameworks (MOFs),<sup>[20-27]</sup> porous organic polymers (POPs),<sup>[28-34]</sup> etc. Recently, porous organic polymers (POPs) have demonstrated potential applications in gas storage and separation,[35-38] energy transfer and conversions,[39,40] sensing,<sup>[41,42]</sup> heterogeneous catalysis<sup>[28-34,43-47]</sup> and so on. POPs are emerging as burgeoning catalysts due to their high surface areas, controllable pore structures, physical and chemical stability. Furthermore, the porosity of POPs enables to overcome diffusion limitation. To date, several research groups have developed POPs for catalyzing CO<sub>2</sub> cycloaddition reactions. Deng's group reported several salen-Co/Zn/Al coordinated POPs which exhibit good activities for catalyzing CO2 cycloaddition reaction at atmospheric pressure and room temperature.<sup>[28,48]</sup> Recently, Liu and co-workers reported that a mesoporous polymer Zn/HAzo-POP shows very high TOF of 2888 h<sup>-1</sup> for cycloaddition of CO<sub>2</sub> and propylene oxide.<sup>[29]</sup> In most cases, co-catalysts are generally needed, which is not beneficial for product purification and practical application. Han and co-workers reported an ionic liquid (IL) based cross-linked polymer for the cycloaddition of CO2 with epoxides without using any co-catalysts at high pressure of CO2 (6 MPa).<sup>[49]</sup> Ding's group reported that porous organic polymers co-functionalized quaternary phosphonium salt and ZnBr<sub>2</sub>-PPh<sub>3</sub> could efficiently catalyse the CO2 cycloaddition reactions without any co-catalyst.<sup>[31]</sup> Recently, we reported the synthesis of polymers functionalized with ILs and hydroxyl group for cocatalyst free cycloaddtion of CO2 and epoxides via a cooperative activation pathway.[50]

Inspired by the previous report that pyridine-zinc complex could efficiently catalyze the cycloaddition of  $CO_2$  with epoxides without using any co-catalysts,<sup>[15]</sup> herein, we report the construction of hierarchical POPs Py-Zn@MA, which was synthesized via a catalyst-free one-pot polycondensation of (4-pyridinecarboxaldehyde)<sub>2</sub>ZnBr<sub>2</sub> and melamine. Py-Zn@MA could efficiently catalyze  $CO_2$  cycloaddition reactions using pure  $CO_2$  or diluted  $CO_2$  (a simulating industrial flue gas: 20%  $CO_2$  and 80% N<sub>2</sub>) without using any additives or co-catalysts.

# **FULL PAPER**

## **Results and Discussion**

Zinc pyridine bromide based polyaminal network Py-Zn@MA, and non-metal coordinated pyridine based polyaminal network Py@MA, were synthesized via heating the corresponding aldehyde with melamine in DMSO at 170 °C for three days. Synthetic routes for these polyaminal networks are depicted in Scheme 1. Using this method, metal can be easily fixed in the skeleton of the polymer in a one-pot polycondensation approach. Generally, constructing of porous organic polymer (POP) based heterogeneous catalysts requires multiple synthesis steps or using costly precious metal catalyst, which may limit their largescale synthesis. The synthesis of POP based catalysts in onestep without using any catalyst has been rarely reported. Py-Zn@MA and Py@MA are insoluble in common organic solvents such as methylene dichloride, hexane, toluene, ethanol and tetrahydrofuran. They are stable in nitrogen atmosphere up to 300 °C, as revealed by thermogravimetric analysis (TGA) (Figure S1).



Scheme 1. Schematic illustration for the synthesis of porous polyaminal network, Py@MA and Py-Zn@MA.

Py@MA and Py-Zn@MA were characterized by Fouriertransform infra-red (FT-IR) spectroscopy and solid-state <sup>13</sup>C-NMR technique (Figure 1). The FT-IR spectrum of Py@MA exhibits two broad peaks at 3410 and 1195 cm<sup>-1</sup>, which can be assigned to the characteristic stretching vibration of the N-H bond of secondary amine. The peaks at 2970 and 2920 cm<sup>-1</sup> are from C-H vibration. The disappearance of C=O stretching vibration of the aldehyde at around 1700 cm<sup>-1</sup> confirmed the complete polymerization of melamine and aldehyde for two polyaminals. In addition, the characteristic vibrations of triazine rings at 1550, 1480 and 1362 cm<sup>-1</sup> for Py@MA are clearly observed. Py-Zn@MA shows almost identical FT-IR spectrum to Py@MA. The slight shifts in wavenumber of N-H and triazine vibration is possibly due to the incorporation of Zn in the polymer network. The solid state <sup>13</sup>C cross-polarization magic-angle spinning (CP-MAS) NMR spectra of Py@MA and Py-Zn@MA are shown in Figure 1B. The strong resonance at about 166 ppm is assigned to the aromatic carbons of the triazine ring. Signals for the carbons in the aminal groups appear in the range of 40-65 ppm. Additionally, two signals at around 123 and 149 ppm could be assigned to the carbons in pyridine units. The results of FT-IR and solid <sup>13</sup>C CP-MAS NMR confirm the successful formation of the aminal linkage for Py@MA and Py-Zn@MA via one-step polycondensation of melamine with the corresponding aldehyde.



Figure 1. (A) FT-IR and (B)  $^{13}\text{C}$  CP-MAS NMR spectra of Py@MA and Py-Zn@MA (\* refers to sideband).

X-ray photoelectron spectroscopy (XPS) studies were conducted to characterize the coordination environment of Zn (Figure S2). The Zn 2p<sub>3/2</sub> peak of (4pyridinecarboxaldehyde)<sub>2</sub>ZnBr<sub>2</sub> (Py-Zn) is located at 1022.7 eV, lower than that of ZnBr<sub>2</sub> (1023.5 eV),<sup>[51]</sup> due to the variation of the electronic enviroment of Zn after coordination with 4pyridinecarboxaldehyde. The Zn 2p<sub>3/2</sub> peak of Py-Zn@MA is about 1022.0 eV, suggesting that the coordination environment of Zn in Py-Zn@MA is similar to that of Py-Zn.

The porous structure of Py@MA and Py-Zn@MA were characterized by sorption analysis using nitrogen as sorbent molecule at 77 K (Figure 2A), and the results are summarized in Table 1. Py@MA and Py-Zn@MA have Brunauer-Emmett-Teller (BET) surface areas of 729 and 207 m<sup>2</sup>/g, respectively. Py@MA and Py-Zn@MA show typical type-I isotherm pattern with a steep increase at low relative pressure, indicating that the microporous structure is dominant of two polymers. Furthermore, significant increases in  $N_2$  uptakes could be found in the P/P<sub>0</sub> range from 0.8 to 1.0, showing the existence of meso/macropores for both polymers. The TEM and SEM images showed that the two polymers are composed of unregularly conglomerated small particles (Figure S3). This suggests that meso/macropores are mainly formed by the inter-particulate void due to the packing of the polymer particles. The pore size distribution of Py@MA and Py-Zn@MA were calculated using nonlocal density functional theory (NLDFT) method (Figure 2B). Both samples have micropores centered at 1.3 to 1.6 nm. Meanwhile Py@MA possesses an additional micropore centered at 0.68 nm, which can explain the reason that Py@MA has larger BET surface area and micropore volume than Py-Zn@MA does.

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Table 1. Textural properties and CO <sub>2</sub> adsorption performance of Py@MA and Py-Zn@MA. <sup>[a]</sup>									
	S <sub>BET</sub> (m²/g) (	N/	V <sub>micro</sub> (cm³/g)	CO <sub>2</sub> adsorption capacity			Sel. CO <sub>2</sub> /N <sub>2</sub>		
Sample		v <sub>total</sub> (cm <sup>3</sup> /g)		273 K	298 K	403 К 🔍	(KJ/mol)	Henry's Law	IAST
Py@MA	729	1.90	0.10	1.94	1.33	0.08	34.7	44	25
Py-Zn@MA	207 (189)	0.84 (0.89)	0.01 (-)	1.32	0.91	0.15	33.2	18	9

[a] Data in parentheses refer to the textural properties of Py-Zn@MA after three catalytic cycles.



Figure 2. (A)  $N_2$  sorption isotherms, (B) NLDFT pore-size distribution curves, (C)  $CO_2$  uptake isotherms measured at 273 K (circle), 298 K (triangle), 403 K (square) and (D) the isosteric heat of adsorption for Py@MA and Py-Zn@MA.

The CO<sub>2</sub> uptake isotherms of two polymers at 273 and 298 K are shown in Figure 2C. No saturation of the uptake could be found with pressure of CO<sub>2</sub> in the range of 0 to 1 bar. Py@MA affords moderate CO<sub>2</sub> uptakes of 1.94 and 1.33 mmol/g at 273 and 298 K, respectively. While Py-Zn@MA gives relatively lower CO<sub>2</sub> uptake capacity than Py@MA, which may be due to its less amount of micropores and lower BET surface area. Meanwhile, the CO<sub>2</sub> uptake isotherms for two samples at high temperature (403 K) were also investigated (Figure 2C). To our surprise, Py-Zn@MA could also afford CO<sub>2</sub> capture capacity of 0.15 mmol/g at such high temperature, higher than that of Py@MA. Interestingly, no nitrogen could be adsorbed under such high temperature. This indicates that Py-Zn@MA has a potential to serve as catalyst using flue gas or diluted CO<sub>2</sub> under high temperature. To determine the strength of the interactions between polymers and

CO2, isosteric heats of adsorbtion (Qst) were calculated based on the Clausius-Clapeyron equation using CO<sub>2</sub> uptake isotherms measured at 273 and 298 K (Figure 2D), and Q<sub>st</sub> value at the initial adsorption stage (low CO<sub>2</sub> loading) are provided in Table 1. Py@MA and Py-Zn@MA have similar Qst (34.7 vs 33.2 kJ/mol), suggesting the physical adsorption nature for CO<sub>2</sub>. For both samples, Q<sub>st</sub> decreases as the CO<sub>2</sub> uptake capacity increases, indicating CO<sub>2</sub> is preferentially adsorbed on the strong binding sites (the polyaminal skeleton) at first, and weak binding sites and the CO<sub>2</sub> molecules aggregation are dominant at higher CO<sub>2</sub> loading. The Qst for Py@MA is lower than that of Py-Zn@MA at  $CO_2$  loading higher than 0.2 mmol/g, showing that the interaction of CO<sub>2</sub> with Py@MA is weaker than that with Py-Zn@MA. This is possibly due to the existence of Zn<sup>2+</sup> in Py-Zn@MA enhances the interaction for CO<sub>2</sub>.<sup>[52,53]</sup> The Q<sub>st</sub> of both polymers is higher than that of most reported POPs, such as azo-COPs (24.8-32.1 kJ/mol),[54,55] carbazole-based conjugated microporous polymers (27.1-30.8 kJ/mol),<sup>[56,57]</sup> hyper-cross linked polymers (21.0-23.5 kJ/mol),[58] etc. The above results indicate that the abundant N atoms in the polyaminal skeleton could produce high surface polarity, leading to enhanced binding affinity for CO<sub>2</sub>.

 $CO_2/N_2$  selectivity is an important parameter for adsorptiondriven separation,<sup>[35]</sup> thus  $CO_2/N_2$  selectivity of Py@MA and Py-Zn@MA were calculated based on Henry' law and ideal adsorption solution theory (IAST) at 298 K (Table 1, Figure S4 and S5). IAST  $CO_2/N_2$  selectivity at 298 K with composition of gas mixture similar to the flue gas ( $CO_2/N_2$ : 0.15/0.85) for Py@MA and Py-Zn@MA is calculated to be 25 and 9, and the values of  $CO_2/N_2$ selectivity calculated using Henry's law are 44 and 18, respectively. The difference in  $CO_2/N_2$  selectivity using Henry's law and IAST theory was believed to be related with the adsorption site heterogeneity as literatures reported previously.<sup>[59]</sup> It is known that  $CO_2/N_2$  selectivity strongly depends on the amount of ultramicropore volume and N species. Thus the  $CO_2/N_2$ selectivity of Py@MA is higher than that of Py-Zn@MA, since Py@MA possesses higher amount of nitrogen and micropores.

To assess the catalytic performance of Py@MA and Py-Zn@MA for  $CO_2$  cycloaddition reaction, we employ propylene oxide (PO) as a model substrate and the results are summarized

in Table 2. Py@MA only showed low conversion of 5.6% conversion after 6 h. Also the selectivity to carbonate was rather low on Py@MA due to the formation of the side product 1,2propanediol. To our delight, zinc intercalated polyaminal polymer Py-Zn@MA could serve as an excellent catalyst for CO<sub>2</sub> cycloaddition reaction with PO with 96% conversion and 99% selectivity. According to the kinetic curves of the cycloaddition reaction between CO2 and PO catalyzed by Py-Zn@MA, the reaction rate was faster in the initial 30 minutes and after that the reaction rate gradually slows down, possibly due to the consumption of CO<sub>2</sub> and PO (Figure 3A). Turnover frequency of Py-Zn@MA was calculated to be 250 h<sup>-1</sup>, which is higher than those of heterogeneous co-catalyst free catalytic systems, such as MOFs, POPs, ZIFs and multi-functional grapheme oxide materials (Table S1). For instance, salen-Zn based conjugated microporous polymer Zn-CMP affords TOF of 51 h<sup>-1</sup> at 120 °C and 3 MPa without using co-catalyst.<sup>[48]</sup> Multi-functional graphene oxide material GO-DMEDA-I could obtain TOF with 46.4 h<sup>-1</sup> under 140 °C and 2 MPa CO<sub>2</sub> pressure.<sup>[18]</sup>

Table 2. The performance of various catalysts for the cycloaddition reaction of PO and  $\text{CO}_{2,}{}^{[a]}$ 

Cat.	CO <sub>2</sub> purity (%)	T (°C)	Conv. (%) <sup>[b]</sup>	Sel. (%)	TOF (h <sup>-1</sup> ) <sup>[c]</sup>
Py@MA	100	130	5.6	75	
Py-Zn@MA	100	130	96	99	250
ZnBr <sub>2</sub>	100	130	9.1	>99	4.8
Py@MA+ ZnBr <sub>2</sub> <sup>[d]</sup>	100	130	95	99	67
Py@MA-Zn <sup>[e]</sup>	100	130	92	99	101
Py-Zn@MA	100	100	63	98	51
Py-Zn@MA	100	120	81	99	112
Py-Zn@MA	100	150	96	99	260
Py-Zn@MA <sup>[f]</sup>	20	130	95	99	97

[a] Reaction conditions: S/C = 360, PO (6.11 mmol), polymer (20 mg), 2 MPa, 6 h. [b] Conversion and selectivity were determined by GC using butyl acetate as the internal standard. [c] TOF was calculated at the conversion below 30%. [d] Reaction conditions: S/C = 360, PO (6.45 mmol), Py@MA (16 mg), ZnBr<sub>2</sub> (4 mg), 2 MPa, 6 h. [e] Reaction conditions: S/C = 360, PO (9.16 mmol), Py@MA-Zn (30 mg), 2 MPa, 6 h. [f] For diluted CO<sub>2</sub> (20% CO<sub>2</sub> and 80% N<sub>2</sub>, a simulating component of flue gas), the initial pressure is 3 MPa.

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Figure 3. Kinetic curves for PO cycloaddition reactions using (A) pure  $CO_2$  catalyzed by Py-Zn@MA and physical mixture of ZnBr<sub>2</sub> and Py@MA; (B) diluted  $CO_2$  (20%  $CO_2$  and 80% N<sub>2</sub>) catalyzed by Py-Zn@MA.

With zinc bromide as catalyst, the conversion was only 9.1%. The physical mixture of ZnBr<sub>2</sub> and Py@MA polymer affords much higher conversion of 95%. This suggests that the active site could be generated smoothly by mixing the ZnBr2 and Py@MA, and Py@MA could serve as a cocatalyst. Thus, Py-Zn@MA should be a bifunctional catalyst with ZnBr2 and pyridine interacted in the network acting as active site and co-catalyst, respectively. Based on the previous work reported by Kim and co-workers,[15,60] we proposed the mechanism of cycloaddition reaction of PO catalyzed by Py-Zn@MA (Scheme 2). First, PO was reacted with Py-Zn@MA to form a dimer, and then CO2 was inserted to form a carbonate-bridged intermediate. After that, the coordination of an additional PO causes a nucleophilic attack of the carbonate followed by cyclization to afford a cyclic carbonate and the catalyst is regenerated. TOF of the mixture of ZnBr<sub>2</sub> and Py@MA is much lower than that of Py-Zn@MA. The higher activity of Py-Zn@MA is attributed to its close contact between Zn and pyridine, which could make the formation of intermediate more easily. Meanwhile, Py-Zn@MA could adsorb more CO<sub>2</sub> than Py@MA does under reaction conditions (0.15 vs 0.08 mmol/g), which also contributed to its higher activity by facilitating the formation of intermediate. A controlled sample Py@MA-Zn synthesized from post-synthetic metalation of Py@MA with ZnBr<sub>2</sub> was prepared. Though high conversion of 92% could be achieved, Py@MA-Zn affords much lower TOF than Py-Zn@MA (101 vs 250 h<sup>-1</sup>). This result revealed the superiority of Py-Zn@MA synthesized via a one-pot incorporation.



Scheme 2. Proposed reaction mechanism for the cycloaddition reaction of  $CO_2$  with PO over bifunctionalized Py-Zn@MA.

The effect of reaction temperature on the catalytic performance of Py-Zn@MA was investigated (Table 2, Figure 4A). As temperature increases from 100 to 130 °C, PO conversion increases monotonously from 63 to 96%, while selectivity maintains at a high level of about 99%. TOF also increased from 51 to 230 h<sup>-1</sup>, indicating that temperature has a big influence on the catalytic activity of Py-Zn@MA. Further increasing temperature to 150 °C, TOF increases slightly to 260 h<sup>-1</sup> and high conversion and selectivity could be maintained, indicating the good stability of Py-Zn@MA at high temperature. The pressure of CO<sub>2</sub> also has a big influence on the catalytic activity of Py-Zn@MA as shown in Figure 4B. In the pressure range from 0.5 to 2 MPa, both of the PO convertion and PC selectivity increase with the increase in CO<sub>2</sub> pressure. At PO pressure less than 2 MPa, only a few CO<sub>2</sub> could be dissolved in PO solution which could limit the reaction equilibrium. Thus, the activity is low. At the same time, PO could be hydrolysed to 1,2-propanediol. Although the formed 1.2-propanediol has the possibility to be convert to the same carbonate product, the efficiency is lower than one-step direct cycloaddition. Thus, the selectivity at low CO<sub>2</sub> pressure is relatively low. If further increasing CO<sub>2</sub> pressure to 3 MPa, both of the PO convertion and PC selectivity decrease slightly, possibly due to the low concentration of PO in the vicinity of active sites of Py-Zn@MA at high CO<sub>2</sub> pressure.<sup>[32]</sup>



Figure 4. Influnce of (A) reaction temperature and (B) CO<sub>2</sub> pressure on the catalytic performance of Py-Zn@MA.

Owing to the great increase in CO<sub>2</sub> emission by the power plant, many systems have been developed for CO<sub>2</sub> capture from flue gas.<sup>[61]</sup> However, CO<sub>2</sub> capture processes still face the drawbacks such as high energy consumption, large cost, equipment corrosion, etc. Thus direct conversion of flue gas to value-added product is more attractive. Inspired of the good activity of Py-Zn@MA in the cycloaddition reaction, we further investigated its catalytic performance in cycloaddition reaction with diluted CO<sub>2</sub> (20% CO<sub>2</sub> and 80% N<sub>2</sub>, a simulating component of flue gas). As shown in Figure 3B, Py-Zn@MA could also efficiently catalyze cycloaddition reaction of PO to obtain 95% conversion with the selectivity of 99% under 3 Mpa diltuted CO<sub>2</sub> at 130 °C. The reaction time was prolonged to 8 h to achieve high conversion. Due to the low CO<sub>2</sub> concentration in simulated flue gas, the reaction was performed under 3 MPa. If the pressure is declined to 2 MPa only 70% PO conversion could be obtained after 12 h. These results further confirm that the carbonation reaction is a pressure-dependent reaction. Whatever, Py-Zn@MA shows excellent activity for catalyzing cycloaddition reaction of PO without using any co-catalyst. To the best of our knowledge, there are few of POPs or MOFs could serve as a catalyst in co-catalyst free system using flue gas or diluted CO<sub>2</sub> as a feedstock.

Functionalized five-membered alkylene carbonates are attractive in a variety of applications.<sup>[62]</sup> Apart from PO, we also investigated substrate scope of epoxides and was summarized in Scheme 3. The result showed that Py-Zn@MA was active for all the substrates employed. The TOF increases in the order of cyclohexene oxide < butyl glycidyl ether < styrene oxide < 1,2epoxybutane < epichlorohydrin < propylene oxide. The activity of epoxides decreased as the alkyl length increased. 1,2-Epoxybutane and butyl glycidyl ether with long alkyl length could be smoothly converted to the corresponding cyclic carbonates with high conversion. Styrene oxide with large molecular size could also be efficiently converted to corresponding cyclic carbonate with high conversion of 97% and TOF of 42 h<sup>-1</sup>. The above results show that Py-Zn@MA with hierarchical pore structure could accommodate large molecules and efficiently convert them to carbonates. However, when the internal epoxide, cyclohexene oxide (CHO) was used, the activity was lower presumably due to its high steric hindrance leading to the difficulty in diffusion of CHO to the active sites located in micropores of Pv-Zn@MA.<sup>[32]</sup> From the discussion above we can conclude that the steric effect plays an important role in the cycloaddition reaction of epoxides and CO<sub>2</sub>. Furthermore, substrate scope was also investigated using diluted CO<sub>2</sub>. To our delight, all of the epoxides could be converted to the corresponding cyclic carbonates using diluted CO<sub>2</sub>, though TOFs were lower than those using pure CO<sub>2</sub>. This result further confirms that Py-Zn@MA has the capacity of conversion of flue gas to carbonates.

				Δ.		0
		$\Delta$		$\sim$ $\sim$ $\sim$ $\sim$ $\sim$	~0_1	
Pure CO <sub>2</sub>	Time (h):	6	12	12	12	12
	Conv. (%):	96	96	32	99	97
	TOF (h <sup>-1</sup> ) :	125	61	8.8	34	42
Diluted CO <sub>2</sub>	Time (h):	8	12	12	12	12
	Conv. (%):	98	96	21	98	90
	TOF (h <sup>-1</sup> ):	90	38	5.8	29	30

Scheme 3. Cycloaddition reactions of different types of epoxides with pure or diluted  $CO_2$  catalyzed by Py-Zn@MA.

The recycling stability of Py-Zn@MA was investigated (Figure 5). Herein, we choose PO conversion less than 50% to evaluate the stability of Py-Zn@MA due to the fact that it gives more appropriate results than those obtained at high PO conversion. The PO conversion slightly decreases from 43.5% to 37% after three cycles. Meanwhile, PO conversion decreased from 38% to 23% after two cycles when using Py@MA-Zn as catalyst, suggesting the instability of Py@MA-Zn prepared via the post-synthetic metalation method. For understanding the deactivation of Py-Zn@MA, the zinc content was analyzed for the reused catalyst. Zinc content of Py-Zn@MA after 2<sup>nd</sup> and 3<sup>rd</sup> cycle

# **FULL PAPER**

analyzed by ICP was 5.5 wt% and 5.3 wt%, respectively. Comparing to the zinc content of the fresh sample (5.6 wt%), the leaching of zinc is negligible. Meanwhile, the morphology of Py-Zn@MA could be well maintained as proved by SEM image (Figure S6). The BET surface area and pore structure of the Py-Zn@MA after three cycles was analyzed by N<sub>2</sub> sorption isotherm (Figure S7). Comparing to fresh Py-Zn@MA, the resued sample has only slightly lower BET surface area (189 m<sup>2</sup>/g vs 207 m<sup>2</sup>/g). These results indicate that both leaching of zinc and porous structure are not responsible to the decrease of the activity. Thus, the chemical composition of reused Py-Zn@MA was characterized with FT-IR. The characteristic peaks of Py-Zn@MA in FT-IR spectrum of the reused sample were identical to the fresh one (Figure 1A). However, an extra peak near 1640 cm<sup>-1</sup> could be observed in the FT-IR spectrum of reused Py-Zn@MA. This peak may be assigned to the carbonyl of PC. TG analysis data shows the weight loss of reused Py-Zn@MA is larger than that of fresh one, suggesting that some product or solvent were trapped in the reused catalyst (Figure S1). We washed and dried the catalyst efficiently during the recycling process, however there still remains some PC in the reused catalyst. We speculated the C=O of PC is likely to have some interaction with pyridine N and is more difficult to be removed during the recycle process. As a result, the co-catalyst cannot be regenerated. Thus, tetrabutylammonium bromide (TBAB) was added for the 4<sup>th</sup> cycle. The activity was increased to 55%. Under similar conditions, TBAB only affords 5.8% PO conversion. This confirms that the interaction of PC with Py-Zn@MA may be the main reason for the catalyst deactivation. The PO conversion could be maintained at 55% for the following cycles with the addition of TBAB. This indicates the zinc intercalated in the polymer network is very stable.



Figure 5. The recycle stability of Py-Zn@MA for the CO<sub>2</sub> cycloaddition reaction (5 mg of TBAB was added for the 4<sup>th</sup> to 7<sup>th</sup> runs).

## Conclusions

In summary, we synthesized two polyaminal porous organic polymers, Py-Zn@MA and Py@MA via a one-pot polycondensation approach. Both polymers show good CO<sub>2</sub> uptake capacity and high isosteric heats of adsorbtion due to the abundant N atoms in the polymers. Even at high temperature (130 °C), Py-Zn@MA could also afford CO<sub>2</sub> uptake capacity of 0.15

mmol/g, and no nitrogen could be adsorbed under similar conditions. As a result, Py-Zn@MA shows good catalytic activity for cycloaddition reactions of epoxides with pure CO<sub>2</sub> (TOF: 250 h<sup>-1</sup>) or diluted CO<sub>2</sub> (TOF: 97 h<sup>-1</sup>) at 130 °C without using any additives or co-catalyst. The high efficiency of Py-Zn@MA is mainly attributed to ZnBr<sub>2</sub> and pyridine interacted in polymer network acting as active site and co-catalyst, respectively. Moreover, Py-Zn@MA with hierarchical structure could convert different types of epoxides to carbonates, including butyl glycidyl ether and styrene oxide. Py-Zn@MA could be easily prepared in large-scale without using any catalyst and the chemicals are cost-effective. Using similar method, numerous polymers could be prepared and utilized in various research areas. Further studies are now in progress in our laboratory.

## **Experimental Section**

#### Chemicals and reagents

All chemicals were used as received without any further purification. 4-Pyridinecarboxaldehyde, zinc bromide (ZnBr<sub>2</sub>) and melamine (MA) were obtained from Aladdin Co. (China). Dimethyl sulphoxide (DMSO) was purchased from Sigma-Aldrich Company, Ltd. (USA). Other reagents were bought from Shanghai Chemical Reagent, Inc. of the Chinese Medicine Group. (4-Pyridinecarboxaldehyde)<sub>2</sub>ZnBr<sub>2</sub> (Py-Zn) was synthesized according to literature method.<sup>[63]</sup>

#### Characterization

performed C. Η, Ν elemental analysis was on an Oxygen/Nitrogen/Hydrogen Analyzer (EMGA-930, HORIBA, Japan) and a Carbon/Sulfur Analyzer (EMIA-8100, HORIBA, Japan). FT-IR spectra in the range of 400-4000 cm<sup>-1</sup> were collected with a Nicolet Nexus 470 IR spectrometer using KBr pellets. Solid-state NMR spectra were performed on a Bruker 500 MHz spectrometer equipped with a magic-angle spin probe using a 4-mm ZrO<sub>2</sub> rotor. <sup>13</sup>C signals were referenced to Glycine (C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>). The experimental parameters are as follows: 8 kHz spin rate, 5 s pulse delay, and 2500 scans. The thermo gravimetric analysis (TGA) was performed from 25 to 900 °C under nitrogen atmosphere with a heating rate of 5 °C/min using a NETZSCH STA 449F3 analyzer. Scanning electron microscopy (SEM) was undertaken using a FEI Quanta 200F scanning electron microscope operating at an acceleration voltage of 2-30 kV. Transmission electron microscopy (TEM) was performed on a HITACHI 7700 at an acceleration voltage of 100 kV. Before measurement, the samples were fully dispersed in ethanol and then deposited on a holey carbon film on a Cu grid. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi (Thermo Scientific) with monochromated AIKa radiation (photon energy, 1486.6 eV). The nitrogen sorption isotherms were performed on a Micromeritics ASAP 2020 system volumetric adsorption analyzer at -196 °C. All samples were degassed at 100 °C for 6 h prior to the sorption measurements. The BET surface area was calculated from the adsorption data at a relative pressure P/P0 in the range of 0.05-0.25. Pore size distributions were determined from the adsorption branches using nonlocal density functional theory (NLDFT) method. CO2 and N2 sorption experiments were carried out on a Micromeritics ASAP 2050 system volumetric adsorption analyzer. Zinc content of the materials was determined using a PLASAM-SPEC-II inductively coupled plasma atomic emission spectrometry (ICP) by digesting the polymer in HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (1:1, v/v).

#### Synthesis of Py-Zn@MA and Py@MA

Syntheis of Py-Zn@MA: A dried 25 mL round flask equipped with a stirrer and a condenser was degassed using three evacuation-nitrogen-backfill cycles. Under nitrogen flow, (4-pyridinecarboxaldehyde)<sub>2</sub>ZnBr<sub>2</sub> (Py-Zn) (660 mg, 1.5 mmol), melamine (250 mg, 2.0 mmol) and DMSO (5 mL) were added and heated at 170 °C for 72 h. Finally, the system was cooled to room temperature, the yellow-brown powder was isolated and washed successively with dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), tetrahydrofuran (THF), N,N-dimethylformamide (DMF) until the filtrate was colorless. Then the resultant product was extracted with THF in a Soxhlet apparatus for 24 h, and then dried at 100 °C under vacuum for 24 h. Finally, 0.6 g Py-Zn@MA was obtained as a yellow-brown powder, the yield was about 74%. Elemental analysis: C 28.3, H 3.0, N 30.0%. ICP result of Zinc: 5.6 wt%.

A control sample Py@MA was prepared using similar method to Py-Zn@MA with the exception that 4-pyridinecarboxaldehyde was used instead of (4-pyridinecarboxaldehyde)<sub>2</sub>ZnBr<sub>2</sub>, and the mole ratio of 4-pyridinecarboxaldehyde vs MA is 1.8:1. Py@MA was obtained as a yellow-brown powder, the yield was about 58%. Elemental analysis: C 36.6, H 5.0, N 45.8%.

#### Synthesis of Py@MA-Zn via a post-synthetic metalation method

To a 25 mL round flask equipped with a stirrer and a condenser, 480 mg Py@MA, ZnBr<sub>2</sub> (115 mg, 0.5 mmol) and ethanol (8 mL) were added and refluxed for 24 h. Finally, the system was cooled to room temperature, the yellow-brown powder was isolated and dried at 100 °C under vacuum for 24 h. The resulted yellow-brown powder was named as Py@MA-Zn.

#### General procedure for the coupling reactions of CO2 and epoxides

The coupling of CO<sub>2</sub> and epoxides was performed in a high-pressure stainless steel autoclave (15 mL) equipped with a magnetic stirrer. Typically, Py-Zn@MA (20 mg, 17.1 µmol) and propylene oxide (355 mg, 6.1 mmol) were put into the autoclave. After purging the autoclave with CO<sub>2</sub> for three times, the reactor was pressurized with 2 MPa pure CO<sub>2</sub> or 3 MPa CO<sub>2</sub>/N<sub>2</sub> (20%/80% mixture). Then the temperature of the autoclave was increased and maintained at 130 °C with a stirring speed of 550 rpm for a certain time. After reaction, the autoclave was released slowly, the reaction mixture was added with 10 mL ethyl acetate (EA) for dilution followed by the addition of butyl acetate as internal standard. After that, the catalyst was separated by centrifugation. The supernatant of the reaction was analysed by gas chromatography (GC).

For other substrates, similar procedure were utilized with the exception that epichlorohydrin, 1,2-epoxybutane, butyl glycidyl ether, styrene oxide or cyclohexane oxide was used instead of propylene oxide.

For catalyst recycling, the solid obtained by centrifugation was washed using EA (3 × 10 mL), dried under vacuum at 100 °C for 12 h and then reused directly for the next catalytic cycle. The recycle experiment of Py-Zn@MA for CO<sub>2</sub> cycloaddition reaction with propylene oxide was performed at 100 °C and 2 MPa CO<sub>2</sub> (reaction time, 4 h; propylene oxide, 535 mg; Py-Zn@MA, 30 mg), 5 mg of TBAB was added for the 4<sup>th</sup> to 7<sup>th</sup> runs.

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**Keywords:** porous organic polymers • pyridine-zinc catalyst • CO<sub>2</sub> cycloaddition reaction• cocatalyst-free • cyclic carbonates

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# **FULL PAPER**

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# **FULL PAPER**

# Entry for the Table of Contents (Please choose one layout)

Layout 1:

# FULL PAPER

A bifunctionalized pyridine-zinc-based porous organic polymer, Py-Zn@MA was synthesized and used for cocatalyst-free cycloaddition of epoxides with CO<sub>2</sub>. The high activity of Py-Zn@MA is attributed to its bifunctional nature with ZnBr<sub>2</sub> and pyridine activating epoxide in a cooperative way. The catalyst could be easily prepared in large-scale and shows good substrate universality for cycloaddition reactions of epoxides.



Hierarchical porous organic polymer

He Li, Chunzhi Li, Jian Chen, Lina Liu, Qihua Yang\*

Page No. – Page No.

Synthesis of pyridine-zinc-based porous organic polymer for cocatalyst-free cycloaddition of epoxides