### **Electronic Supporting Information**

## Highly tunable periodic imidazole-based mesoporous polymers as cooperative catalysts for efficient carbon dioxide fixation

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#### **Experimental Section**

#### Materials and instrumentation

All reagents such as m-bromophenol (97%), Pluronic F-127 (The triblock poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) copolymer), propylene oxide (99.5%), bromoethane (98%), Phenol (99.5%), formaldehyde (38wt %) were purchased from Sigma Aldrich. Chloromethyl Polystyrene Resin cross-linked with 1% DVB (100-200 mesh) (2.0-3.0mmol/g) (PS-C1) was bought from Alfa. Small angle X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE instrument using Cu-K $\alpha$  radiation ( $\lambda = 1.5418$  Å) at 35 kV and 30 mA. Nitrogen adsorption-desorption isotherms were measured on a Quancachrome Autosorb-3B instrument after evacuating the samples at 423 K for 12 h. The specific

surface areas were evaluated via the Brunauer-Emmett-Teller (BET) method by using the adsorption data at P/P<sub>0</sub> of 0.05-0.2; The total pore volume ( $V_{total}$ ) was estimated from the adsorbed amount at  $P/P_0$  of 0.995, and the pore distribution was calculated by the Barrett-Joyner-Halenda (BJH) method deriving from the adsorption branches of isotherms. The TEM images were recorded using a JEOL-JEM-2010 microscope after the specimens were dispersed in ethanol and placed on holey copper grids. The FT-IR spectra were recorded on a Nicolet NEXUS 670 infrared spectrometer. N elemental analyses were performed on an Elementar VarioEL III CHN elemental analyser. The X-ray photoelectron spectroscopy (XPS) measurements were performed with AXIS Ultra DLD spectrometer (Kratos) with monochromatic Al Ka radiation. 1H spectra were acquired on a Bruker DRX500 spectrometer at 400 MHz in CDCl<sub>3</sub> with TMS was as an internal standard. Thermogravimetric analysis (TGA) was performed in an N<sub>2</sub> atmosphere from 30 °C to 800 °C with a heating rate of 3 °C /min by using a METTLER TOLEDO TGA/SDTA851 apparatus. The conversion and selectivity of products were quantified on Agilent's 7890A GC equipped with a flame ionization detector and a DB-WAX column (30 m  $\times$  0.32 mm  $\times$  0.25µm) using biphenyl as an internal standard.

# Procedure for 2-(imidazole-1-yl) phenol (2-IP) and 3-(imidazole-1-yl) phenol (3-IP) preparation

In a typical experimental procedure, the 0.065 mol of imidazole, 0.05 mol of mbromophenol, 0.2 mol of sodium hydroxide, 0.01 mol of cuprous iodide and DMSO (20 ml) was added to a 100 mL three-necked flask under argon flow. Then the mixture was stirred at room temperature for 30 min and heated to reflux for 24 h at 120 °C. After the reaction was finished, the mixture was cooled to room temperature, filtered and washed with deionized water three times to collect filtrate. The hydrochloric acid solution was added to the filtrate and adjusted the pH to about 7, then collected the solid precipitated. The above precipitated was refluxed in a methanolic solution of activated carbon for 2 h, then filtered, rotary steamed and purified by column chromatography to give the target product 3-(imidazole-1-yl) phenol (3-IP). According to the above similar procedure, the 2-IP was synthesized respectively by changing m-bromophenol to 2-Bromophenol.

#### Procedure for 2-IPMPs, 3-IPMPs and 4-IPMPs mesoporous polymers preparation

For a typical synthesis procedure of 3-IPMPs, IP (0.385 g), 2.9 g (38 wt. %) formaldehyde, 1.15 g (10wt. %) NaOH solutions and 1 mL ethanol were mixed and stirred at 40°C for 10 min. Then the mixture was refluxed at 75 °C for 120 min with the addition of 0.9 g of phenol. After cooling, the mixed solution of pH was adjusted to 7 by 2 mol/L HCl solution, and the water in the system was removed by rotating evaporation of 2 h. Then, the obtained co-precursors were dissolved in a 50 ml ethanol solution containing 2 g F127, stirring at room temperature for 30 minutes to obtain a transparent solution. It was spread on a self-made glass plate, evaporating at room temperature for 8 h, and then placed in a 120 °C oven for 24 h with the corresponding

film obtained. The film was then calcined for 3 h at 350 °C under a nitrogen atmosphere to remove the template F127. The solid sample was denoted as 3IPMPs. The 2-IPMPs and 4-IPMPs were synthesized by a similar procedure as 3-IP was replaced by 2-IP and 4-IP, respectively.

## Procedure for 2-IPMPs-EtX, 3-IPMPs-EtX and 4-IPMPs-EtX (X=Br, I) mesoporous ionic polymers preparation

For a typical synthesis procedure of 3-IPMPs-EtBr, 3-IPMPs (2 g) was added into 20 mL acetonitrile, then bromoethane (EtBr, 0.5 g) was added slowly with vigorous stirring and the mixture was refluxed for 24 h. The solid phase was filtered and washed repeatedly with acetone and then dried overnight at 80 °C. The resulting solid was denoted as 3-IPMPs-EtBr. According to the above similar procedure, the 3-IPMPs-EtI catalysts were synthesized respectively using iodoethane (EtI) instead of bromoethane (EtBr).

#### Procedure for porous poly (DVB-VIM)-EtI preparation

For a typical synthesis procedure of poly (DVB-VIM)-EtI ionic polymer, the comonomers, vinylimidazole (VIM) and divinylbenzene (DVB) were added into the mixture of acetonitrile and toluene. Then, adding 40.0 mg of AIBN as an initiator. The reaction was conducted in a nitrogen atmosphere at 80 °C for 24 hours. The precipitated poly (DVB-VIM) was then filtered and washed with acetonitrile, to remove the unreacted monomers. Next, poly (DVB-VIM) (2 g) was added into 20 mL acetonitrile, then iodoethane (EtI, 0.5 g) was added slowly with vigorous stirring and the mixture was refluxed for 24 h. The solid phase was filtered and washed repeatedly with acetone and then dried overnight at 80 °C. The resulting solid was denoted as poly (DVB-VIM)-EtI.

#### **Preparation of Imidazole/FDU-15**

The FDU-15 mesoporous polymer was prepared following the procedure reported in the previous literature.<sup>1</sup> Next, FDU-15 (5 g) was added to the mixture of AlCl<sub>3</sub> (12 g) . and chloromethyl methyl ether solvent (40 ml) by string for 12 h in an ice water bath.<sup>2</sup> Then, the resulting FDU-Cl (2 g) was mixed with 1 g of imidazole in 50 ml acetonitrile solution at 83 °C for 24 hours. The solid product was filtered and then washed with water and acetone, subsequent drying in a vacuum oven at 80 °C overnight to yield imidazole/FDU-15.

#### **Preparation of Imidazole/SBA-15**

The mesosilica SBA-15 was prepared according to the procedure reported by Zhao et al. <sup>3</sup> Then, 5 g of SBA-15 and 3-chloropropyl triethoxysilane (5 mmol) were added to 50 mL dry toluene and the mixture was refluxed in nitrogen for 24 hours. Next, the solid was filtered and washed with toluene. Followed by drying in a vacuum oven at 80 °C for 12 h. The obtained SBA-Cl (5 g) was further reacted with imidazole (5 mmol) in 50 mL of toluene solvent at 110 °C for 12 h. After that, the suspension was filtered,

washed with water and acetone, and then dried at 80 °C overnight to yield imidazole/SBA-15.

#### **Preparation of Imidazole/PS**

The Imidazole/PS was prepared following the previous procedures. 1 g of PS-Cl was mixed with the imidazole (5 mmol) in acetonitrile (50 mL) reflux at 83 °C for 12 h in a 100 mL round-bottomed flask. After the reaction was completed, the solid residue was filtered and washed with acetonitrile, distilled water, and 0.2 mol/L HCl. Then, the solid was dried under vacuum at 80 °C for 12 h to obtain PS-IM.<sup>4</sup>

#### Catalytic testing for the synthesis of cyclic carbonate from epoxide and CO<sub>2</sub>

In a typical catalytic process of epoxide and  $CO_2$ , the 150 mg catalyst, 100 mg cocatalyst of KI, 100 mg biphenyl (internal standard) and 1.74 g (30 mmol) propylene oxide was added to 25 mL stainless-steel high-pressure reactor with a magnetic stirrer. The reactor was controlled under certain pressure for a certain period of time and then cooled in an ice bath to release excess  $CO_2$  slowly. After taking the reactor, a small amount of reaction solution was diluted with DMF solution and then analyzed by gas chromatography. The catalyst was filtered, washed with water and acetone for several times, and then dried at 80 °C in vacuum for the next cycle.

#### **Density Functional Theory (DFT) Calculations**

DFT calculation was performed using the CP2K software package, <sup>5</sup> uses the combined Gaussian and plane-wave (GPW) method for the calculation of forces and energies.<sup>6</sup> The BLYP functional was used for the exchange-correlation.<sup>7</sup> The valence orbitals were described by DZVP-GTH Gaussian basis set, All calculations were carried out using the PBE density functional augmented with the Grimme D3 dispersion correction. The plane wave kinetic energy cut-off was set to 400 eV. We used the DIMER method to identify the transition states.<sup>[8]</sup> The adsorption energies were defined as  $\Delta E = E_{total} - E_{IP} - E_{CO2} - E_{PO}$ , where  $E_{CO2}$ ,  $E_{PO}$ ,  $E_{IP}$  and  $E_{total}$  refer to the energies of the free CO<sub>2</sub>, propylene oxide (PO), 2-/3-/4-IP and complex system, respectively.

Entry	Sample	$S_{BET}(m^2\!/g)^a$	V <sub>total</sub> (cm <sup>3</sup> /g)	D <sub>p</sub> (nm) <sup>b</sup>	N (wt. %) °
1	2-IPMPs	253	0.56	23	3.05
2	3-IPMPs	446	0.67	8.5	3.11
3	4-IPMPs	440	0.59	11.3	3.29
4	Imidazole/FDU15	391	0.51	6.8	3.54
5	Imidazole/ SBA-15	623	0.79	6.7	2.67
6	Poly(DVB-VIM)	612	0.21	3.4	4.21
7	Poly(DVB-VIM)-EtI	596	0.19	3.2	3.01

Table S1 Textura	l properties of	the samples.
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<sup>a</sup> Calculated (based on N<sub>2</sub> sorption at 77 K). <sup>b</sup> Calculated from BJH method. <sup>c</sup> Based on CHN element analysis



Fig. S1 Representative TEM image of (a) 2-IPMPs and (b) 4-IPMPs mesopolymer.



**Fig. S2** <sup>13</sup>C MAS NMR spectra of (a) F127, (b) pure mesoporous polymer (MPs) without the addition of 3-IP, (c) 3-IPMPs.

As shown in Fig. S2, the template F127 has characteristic peaks at 18 ppm, 75.3 ppm and 73.6 ppm, which can be attributed to the corresponding methyl carbon atoms and methylene carbon atoms in F127. The F127 characteristic peaks disappeared in 3-IPMPs-X, indicating that the template was successfully removed. The 36.2 ppm and 14.7 ppm peaks in the polymer material 3-IP-MPs-X attributed to the methylene carbon of the material; and the characteristic peaks at 127.7 ppm and 150.7 ppm can be assigned to the benzene ring. Clearly, 3-IPMPs show a band centered at 128.3 ppm, which belongs to the C2 atom of the imidazole moiety, in comparison to pure MPs.

**Table S2** Nitrogen element analysis of 3-IPMPs-5, 3-IPMPs-10, 3-IPMPs-20 and 3-IP-MPs-40.<sup>a</sup>

N (%)	3-IPMPs-5	3-IPMPs-10	3-IPMPs-20	3-IPMPs-40
Actual value <sup>[a]</sup>	0.84	1.84	3.11	6.18
Theoretical value	0.9	1.8	3.36	6.19

<sup>a</sup>Based on CHN element analysis.



**Fig. S3** Thermogravimetric curves of (a) F127; (b) as-made 3-IPMPs and (c) 3-IPMPs.

As shown in Fig. S3, the F127 template could be decomposed and removed at 300 °C. The weight loss of as-made 3-IPMPs begins at 350 °C, indicating that our rigid polymer framework can prevent the template from decomposition (not starting from 300 °C). Additionally, the weight-loss curve of as-made 3-IPMPs agrees well with the F127 template, which suggests that the template of as-made 3-IPMPs was totally removed at 400 °C. For comparison, 3-IPMPs shows no significant weight loss at 420 °C. This results confirmed that imidazole groups were completely integrated into the mesoporous polymer frameworks, and the 3-IMMPs have an ultra-thermal-stable structure, preventing the decomposition of imidazole groups during the process of template removal.

Entry	Temp. (°C)	CO <sub>2</sub> pressure (MPa)	Time (h)	Yield (%) <sup>b</sup>	Selectivity (%) <sup>b</sup>
1	90	1	1	77	99
2	90	1	2	93	99
3	90	1	3	97	99
4	90	1	4	99	99
5	110	1	3	99	98
6	70	1	3	71	99
7	90	0.5	3	75	99
8°	90	1	1	62	99

**Table S3** Influence of reaction parameters on the cycloaddition reaction of  $CO_2$  with propylene oxide over 3-IPMPs <sup>a</sup>

<sup>a</sup> Reaction conditions: propylene oxide 30 mmol, catalyst amount 0.5 mol% (150mg), KI 0.6 mmol (100 mg) <sup>b</sup> Determined by GC using biphenyl as an internal standard. <sup>c</sup> catalyst amount 0.25 mol% (75mg).



**Fig. S4** The Nitrogen adsorption-desorption isotherms of 3-IPMPs with different imidazole loading. The inset shows the corresponding BJH pore size distribution of IPMPs materials.

Entry	Sample	Nitrogen loading (wt.%) <sup>a</sup>	$S_{BET}(m^2/g)^{b}$	$V_{total} (cm^3/g)$	D <sub>p</sub> (nm) <sup>c</sup>
1	3-IPMPs-5	0.84	372	0.5	6.6
2	3-IPMPs-10	1.84	445	0.59	8.4
3	3-IPMPs-20	3.11	446	0.67	8.5
4	3-IPMPs-40	6.18	395	0.62	11.3

Table S4 the textural parameters of 3-IPMPs with different imidazole loading.

 $^a$  Based on CHN element analysis.  $^b$  Given by  $N_2$  sorption at 77 K.  $^c$  By BJH analysis.



Fig. S5 Small-angle XRD patterns of 3-IPMPs-EtI-20 mesoplolymers after used 5

times.

#### **Characterization of Cyclic Carbonates**







#### References

- 1 Y. Meng, D. Gu, F. Zhang, Y. Shi, H. Yang, Z. Li, C. Yu, B. Tu and D. Zhao, *Angew. Chem. Int. Ed.*, 2005, **44**, 7053.
- 2 R. Xing, H. Wu, X. Li, Z. Zhao, Y. Liu, L. Chen and P. Wu, J. Mater. Chem., 2009, 19, 4004.
- W.-L. Dai, L. Chen, S.-F. Yin, S.-L. Luo and C.-T. Au, *Catal. Lett.*, 2010, 135, 295.
- 4 J. Sun, W. Cheng, W. Fan, Y. Wang, Z. Meng and S. Zhang, *Catal. Today*, 2009, 148, 361.
- 5 J. Hutter, M. Iannuzzi, F. Schiffmann and J. VandeVondele, Wiley Interdiscip. *Rev. Comput. Mol. Sci.*, 2014, 4, 15.
- 6 J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, *Comput. Phys. Commun.*, 2005, 167, 103.
- 7 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.
- 8 G. Henkelman and H. Jónsson, J. Chem. Phys., 1999, 111, 7010.