

Supporting Information

Direct synthesis of ordered imidazolyl-functionalized mesoporous polymers for efficient chemical fixation of CO₂

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Experimental Section

Chemicals

All reagents were commercially available and were directly used without further purification. 4-(imidazole-1-yl) phenol (IMP, 97%), Pluronic F-127 were purchased from Sigma-aldrich. Other reagents, such as propylene oxide (99.5%), bromoethane (98%), Phenol (99.5%), formaldehyde (38wt %) were brought from Acros Reagent Company.

Characterization

Small angle X-ray scattering (SAXS) patterns were collected on Nanostar U small-angle X-ray scattering system (Bruker) using Cu-K α radiation ($\lambda= 1.5418 \text{ \AA}$) at 40 kV and 35 mA. The X-ray photoelectron spectroscopy (XPS) measurements were performed with AXIS Ultra DLD spectrometer (Kratos) with monochromated Al K α radiation. Nitrogen adsorption–desorption isotherms were measured on a Quancachrome Autosorb-3B instrument after evacuating the samples at 423 K for 6 h. The specific surface areas were evaluated using Brunauer–Emmett–Teller (BET) method and the pore distribution was calculated by BJH method. 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. ¹H spectra were acquired on a Bruker DRX500 spectrometer at 400 MHz in CDCl₃ with TMS as an internal standard. Thermogravimetric analysis (TGA) was performed in a N₂ 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 × 0.32 mm × 0.25µm) using biphenyl as an internal standard.

Preparation of imidazolyl-functionalized ordered mesoporous polymer (IM-MPs)

The IM-MPs were prepared by using 4-(imidazole-1-yl)phenol (IMP), phenol and formaldehyde as precursors, amphiphilic triblock copolymer F127 as a structure directing agent via evaporation-induced self-assembly (EISA) method. For a typical synthesis procedure of IM-MPs-20%, IMP (0.77g) and phenol (1.8 g) was dissolved in a mixture 5.8 g (38wt %) formaldehyde aqueous solution and 2.3g (10wt %) NaOH solutions, and a blue solution was obtained after stirring at 40 °C for 30 min, Then the mixture was refluxed at 80 °C for 60 min, After cooling down, the pH value of the reaction mixture was adjusted to 7 by adding 2.0 M HCl solution. Water was removed by rotary evaporation to obtain the imidazolyl-functionalized resol precursor. The imidazolyl-functionalized resol precursor was then dissolved in a transparent solution made up of 4.0g of Pluronic F127 and 100ml ethanol by stirring for 30 min. Then, the solution was poured into dishes to evaporate ethanol at room temperature for 8 h to produce a transparent membrane, followed by thermopolymerization at 100 °C for 24 h. Subsequently, the as-made sample was pyrolyzed under vacuum at 350 °C to remove F127, with a heating rate of 1°C/min up to 350 °C. The resulting solid was denoted as IM-MPs-20%. According to the above similar procedure, the IM-MPs-x (where x = IMP/ (IMP+phenol) 5%, 40% and 60%) were synthesized respectively by regulating the molar ratio of IMP to phenol.

Preparation of IM-MPs-EtBr

For a typical synthesis procedure of IM-MPs-20%-EtBr, IM-MPs-20%-EtBr (5.0 g) was added into 40 mL acetonitrile, then bromoethane (0.8 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 IM-MPs-EtBr-20%.

Typical procedure for the synthesis of cyclic carbonate from epoxide and CO₂

In a typical catalytic cycloaddition, propylene oxide (30 mmol), catalyst (50 mg) and biphenyl (0.1 g, internal standard for GC analysis) were placed in a 25 mL stainless-steel autoclave equipped with a magnetic stirrer. CO₂ was then charged in the autoclave. The reaction was carried out at specified temperature and a constant pressure for a desired period of time. After the reaction, the reactor was cooled in an ice-water bath and slowly depressurized. The catalyst was washed with acetone, dried, and reused

without any further activation. The resulting reaction mixture was analyzed by GC analysis and the products were also identified by ^1H NMR spectra.

Table S1. The textural parameters of the IM-MPs materials

Samples	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	$V_{\text{total}}^{\text{a}}$ (cm ³ /g)	$V_{\text{micro}}^{\text{a}}$ (cm ³ /g)	D_{p}^{a} (nm)	d_{10}^{b} (nm)	a_0^{b} (nm)	Pore wall thickness (nm)
IM-MPs-5%	433	0.55	0.04	5.42	12.1	14.0	8.6
IM-MPs-20%	418	0.57	0.06	6.87	13.8	15.9	9.1
IM-MPs-40%	319	0.74	0.02	11.55	16.1	18.6	7.0
IM-MPs-60%	175	0.61	0.02	14.45	19.2	22.2	7.7

^a Values obtained from N₂ sorption at 77 K: S_{BET} -BET specific surface area; V_{total} -total pore volume; V_{micro} -microporous volume calculated from t-method; D_{p} -pore diameter calculated from BJH method. ^b Values obtained from SAXS studies: d_{10} - the d-spacing values of the (100) diffractions, using the formula $d_{10}=2\pi/q$; a_0 - Unit cell parameter, was calculated using the formula $a_0=2d_{10}/\sqrt{3}$.

Table S2. CHN analysis, XPS analysis and theoretical parameters of the IM-MPs materials.

Samples	Theoretical value	CHN analysis			XPS analysis		
	N (wt. %)	N (wt. %)	C (wt. %)	C/N	N (wt. %)	C (wt. %)	C/N
IM-MPs-5%	0.90	0.77	75.59	98.6	0.91	82.96	91.2
IM-MPs-20%	3.36	3.39	72.46	21.4	3.29	75.65	23.0
IM-MPs-40%	6.19	6.11	68.66	11.2	6.18	76.82	12.4
IM-MPs-60%	8.68	8.38	65.2	7.8	9.17	76.50	8.3

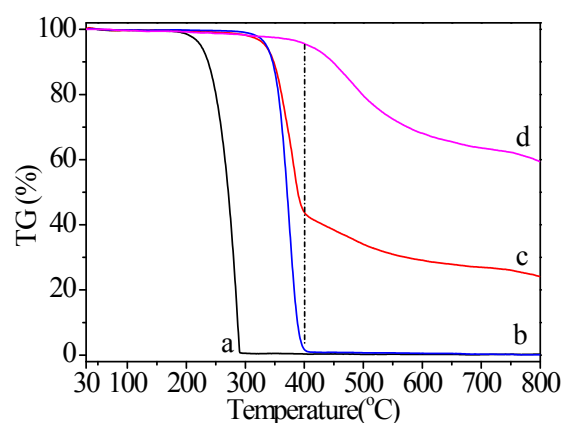


Fig. S1 Thermogravimetric curves of (a) Pure IMP, (b) F127, (c) as-made IM-MPs-20% and (d) IM-MPs-20% calcined under vacuum at 350 °C.

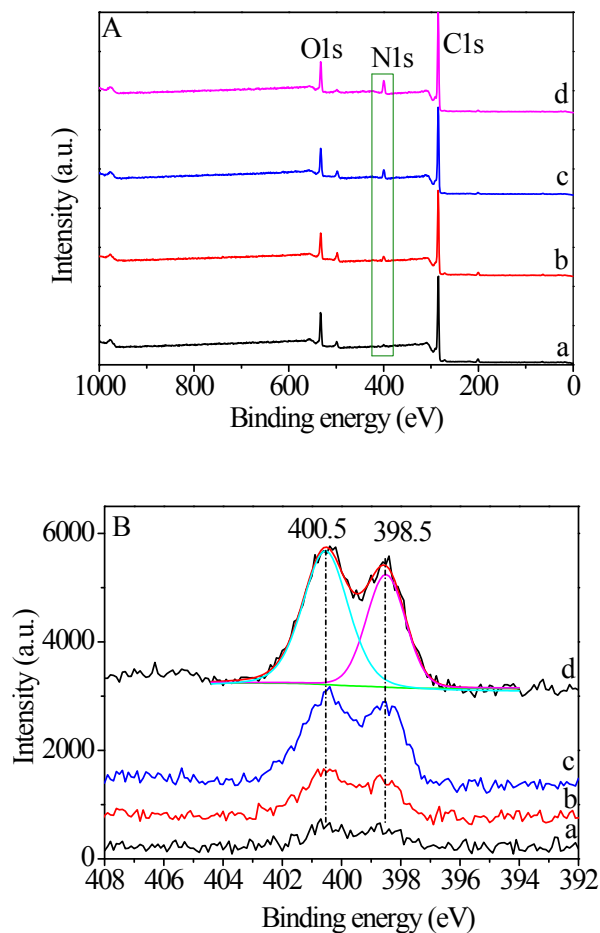


Fig. S2 XPS spectra of the IM-MPs: The full survey spectrum (A) and high resolution N_{1s} spectrum (B). (a) IM-MPs-5%, (b) IM-MPs-20%, (c) IM-MPs-40%, and (d) IM-MPs-60%.

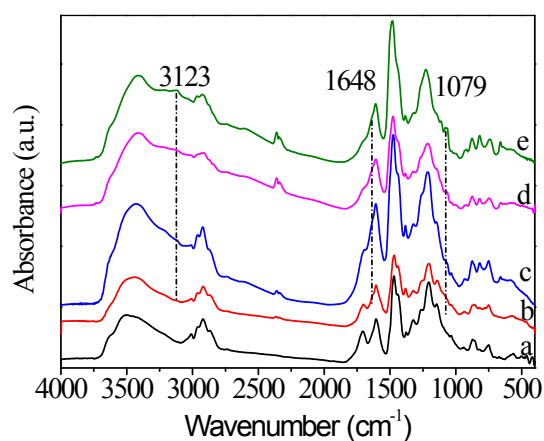


Fig. S3 FT-IR spectra of (a) IM-MPs-0% (FDU-15), (b) IM-MPs-5%, (c) IM-MPs-20%, (d) IM-MPs-40% and (e) IM-MPs-60%. In comparison with IM-MPs-0% (FDU-15, Fig.S2a), the new band at 3123 cm⁻¹, which is assigned to aromatic C–H stretching vibration of imidazole,¹ the bands appeared at 1648 cm⁻¹ and 1079 cm⁻¹, which are assigned to the imidazole ring skeleton stretching vibrations (Fig.S2 b-d).² The FT-IR spectra confirmed the successful incorporation of imidazole moiety into mesoporous frameworks.

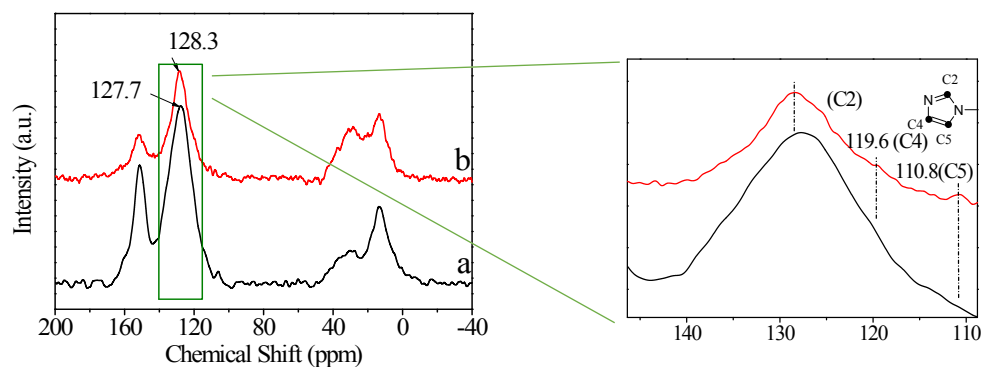


Fig.S4 ^{13}C MAS NMR spectra of (a) IM-MPs-0% (FDU-15), (b) IM-MPs-20%. The IM-MPs-20% sample displayed a distinct band centered at 128.3 ppm, shifted slightly to higher chemical shift compared to that observed in IM-MPs-0% (FDU-15, Fig.S3a), which was attributed to the C2 atom of the imidazole moiety, new bands appeared at 119.6 and 110.8 ppm, which are corresponding to the cis-carbons (C4 and C5 atom) of the imidazole ring.³

Table S3. Textural properties of IM-MPs-x%-EtBr.

Catalyst	CHN analysis			N_2 sorption ^a		
	N	C	H	S_{BET} (m^2g^{-1})	V_{total} (cm^3g^{-1})	D_p (nm)
IM-MPs-5%-EtBr	0.98	72.54	5.23	403	0.54	5.43
IM-MPs-20%-EtBr	3.00	66.23	5.02	300	0.45	6.33
IM-MPs-40%-EtBr	5.18	61.03	4.94	247	0.55	11.53

^a Values obtained from N_2 sorption at 77 K: S_{BET} -BET specific surface area; V_{total} -total pore volume; D_p -pore diameter calculated from BJH method.

Table S4. Catalytic activity of analogous heterogeneous catalyst systems for cycloaddition of CO_2 to propylene oxide.

Entry	Reference	Catalyst	Reaction conditions	PC Yield (%) ^b	TON
1	Zhang et al. 2014 ^{2b}	FDU-15 supported 1-(2-hydroxyethyl)-imidazolium bromide (FDU-HEIMBr)	PO (30 mmol), catalyst (0.5 mol%), CO_2 (1.0 MPa), 110 °C, 3 h	99	198
2	Yang et al. 2014 ⁴	Fluoro-functionalized polymeric ionic liquids with imidazolium bromide (F-PIL-Br)	PO (10 mmol), catalyst (1.0 mol%), CO_2 (1.0 MPa), 120 °C, 9 h	94	94
3	Roshan et al. 2013 ⁵	Microwave synthesized methyl iodide-quaternized cellulose (mQC-1.1)	PO (42.8 mmol), catalyst (0.4 mol%), CO_2 (1.2 MPa), 120 °C, 3 h	97	242

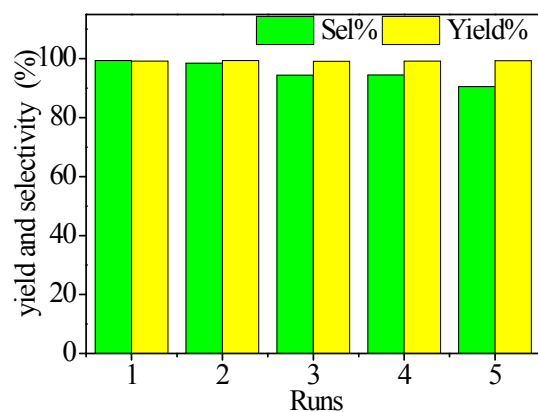


Fig.S5 Reuse of catalyst IM-MPs-20%-EtBr. Reaction condition: PO (30 mmol), Catalyst (150 mg), CO₂ pressure (1.0 MPa), temperature (110 °C), reaction time (3h).

References

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