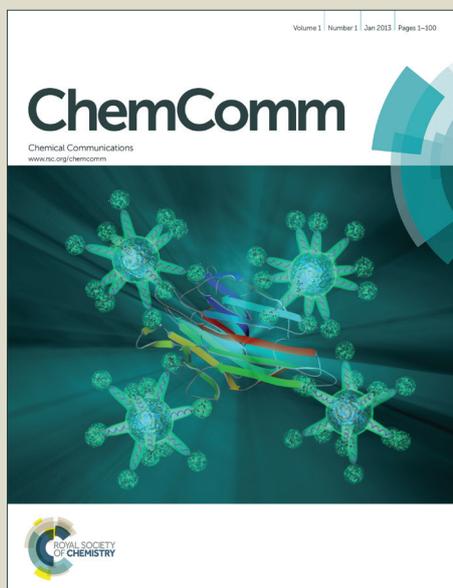


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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Imidazolium salts-modified porous hypercrosslinked polymers for a synergistic CO₂ capture and conversion

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

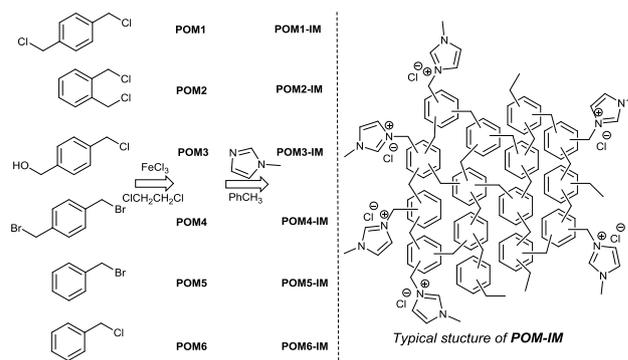
A new type of imidazolium salt-modified porous hypercrosslinked polymer (BET surface area up to 926 m²/g) was reported. These porous materials exhibited good CO₂ capture capacities (14.5 wt%) and catalytic activities for the conversion of CO₂ into various cyclic carbonates under metal-free conditions. The synergistic effect of CO₂ capture and conversion was observed.

Porous materials modified with imidazolium salts have received wide attentions as they have potential applications in the fields of catalysis, gas separation as well as energy related technology.¹ Currently, imidazolium salts are mainly immobilized onto the surface of porous inorganic materials, such as silica or metal oxides.² In comparison, immobilization of imidazolium salts onto porous organic materials has received significantly less attention, due to the difficulties in synthesis.³ Although microporous main-chain imidazolium organic framework^{3a} and vinylimidazolium/divinyl-benzene based hypercrosslinked side-chain imidazolium porous materials^{3b-f} have been reported, these synthetic methods largely depend on the specific pre-functionalized imidazolium groups and/or other starting materials. Hence, developing a practical method for the synthesis of imidazolium-modified porous organic materials from easily available starting materials is highly desirable.

The global climate change and the excessive CO₂ emission have attracted widespread public concern in recent years. The combination of CO₂ capture and conversion is an attractive strategy for reducing CO₂ emissions.⁴ Porous materials can capture and store CO₂ in their pore structure. The CO₂ density in the pore could be tens to hundreds of times higher than gaseous CO₂ under ambient atmosphere. To this end, functionalized porous materials with both porous characteristics and active catalytic sites could provide potential synergistic effect for CO₂ transformation.⁵⁻⁷ Recently, few porous materials with metal catalytic centres have been identified as promising materials to fulfil the requirement.⁸ These include the salen-based organic polymer *via* multi-step synthesis as solid ligand^{8a} and Mg-MOF *via* sonochemical synthesis.^{8b}

Recently, Friedel-Crafts polymerization has provided a new method for preparing hypercrosslinked aromatic porous polymers,⁹ and these polymer materials have received considerable interests due to their ease preparation, high chemical and thermal stability, and low cost. These polymers have demonstrated potentials for CO₂ capture, however, hydrophobic

hypercrosslinked ones show better performance under more realistic “wet” conditions.^{9b} The synthetic approach is based on the one-step Friedel-Crafts alkylation between aromatic monomers and formaldehyde dimethyl acetal. Although this approach has been successfully applied to some simple aromatics, there is still limitation for substrate scope, especially for monomers with specific functionalized group. This becomes the main obstacle for application of porous hypercrosslinked polymers in catalysis.^{9c}



Scheme 1 The synthesis of supported imidazolium salts and the typical structure of POM-IM.

In this work, a new type of imidazolium salt-modified porous hypercrosslinked polymers was synthesized by Friedel-Crafts reaction from benzyl halides¹⁰ and subsequently functionalized with *N*-methylimidazole. The benzyl halide monomers provided both a functional handle for direct crosslinkage *via* Friedel-Crafts reaction, as well as opportunities for further modification towards different applications. The new materials have large BET surface area (up to 926 m²/g) and exhibit good CO₂ capture capacity (14.5 wt%, 273 k and 1 bar). Interestingly, when compared with traditional polystyrene resin supported imidazolium salt and homogeneous imidazolium salt,¹¹ these materials showed much higher activities for the conversion of CO₂ into various cyclic carbonates,¹² which may be due to the synergistic effect of porous structure (CO₂ capture) and functionalized imidazolium salt (CO₂ conversion). More importantly, the new multi-functional materials were synthesized using easily available starting materials that may be suitable for large scale application.

The synthetic approach to imidazolium-modified porous hypercrosslinked polymers is shown in Scheme 1. The monomers

were directly self-polymerized *via* Friedel-Crafts reactions. The resultant polymers with remaining benzyl chloride (or benzyl bromide) groups were further reacted with *N*-methylimidazole. All the polymers were produced as insoluble dark brown solids in yields over 90% on a typical scale of 10 g per batch. The materials were characterized by ¹³C NMR (solid-state), FT-IR and elemental analysis (See the ESI†). The resolved resonance around 129 ppm and 134 ppm corresponded to the aromatic carbons of benzene ring and imidazole ring (Fig. S1-S4).^{3g} The signal around 35 ppm was assumed to the methylene carbon formed *via* Friedel-Crafts reaction. In FT-IR spectra, the presence of imidazolium salts was confirmed by strong absorption bands around 1600 cm⁻¹ (Fig. S12-S16 vs S5-S11, ESI†).^{3g} The nitrogen content of porous materials from bis-substituted monomers was determined by elemental analysis to be among 1.8~2.8 wt% (imidazolium loading 0.6~1.0 mmol/g) (Table S1, ESI†). Polymers synthesized from mono-substituted monomers gave much lower nitrogen loading, especially for POM6-IM. Thermal gravimetric analysis (TGA) shows that all porous organic materials (POM1~6 and POM1~6-IM) have excellent thermal stability (Fig. S17-S28, ESI†).

Table 1 Physical properties for porous organic materials^a

Polymers	S _{BET} ^{a/} m ² /g	S _{micro} ^{b/} m ² /g	V _{total} ^b cm ³ /g	V _{micro} ^b cm ³ /g	CO ₂ uptake ^c /wt% (273K)
POM1	1089	390	1.31	0.17	13.8
POM2	1047	486	0.82	0.22	13.0
POM3	1088	563	0.71	0.26	16.4
POM4	752	418	0.54	0.19	12.4
POM5	81	0	0.75	0	3.8
POM6	664	297	0.45	0.13	9.5
POM1-IM	926	373	1.06	0.17	13.9
POM2-IM	653	335	0.51	0.15	14.5
POM3-IM	575	334	0.39	0.15	14.2
POM4-IM	632	375	0.48	0.17	10.6
POM5-IM	50	0	0.12	0	5.7
POM6-IM	659	278	0.45	0.12	5.5
POM3-IM ^d	530	320	0.32	0.12	14.2

^aThe BET surface area was calculated in a relative pressure range P/P₀ = 0.01-0.1. ^bThe micropore surface area S_{micro} and micropore volume V_{micro} were estimated from the *t*-plot method. ^cMeasured at 273 k and 1 bar. ^dAfter six runs.

The porosities of the original porous polymers (POM) and imidazolium salt functionalized porous polymers (POM-IM) were evaluated by N₂ adsorption-desorption isotherms (Fig. S29-40, ESI†). The micropore size distributions of these materials are predominantly around 1.4 nm (Fig. S41-52, ESI†). However, there are also meso- and macrostructures (> 2.0 nm) were observed based on related isotherms curves (Fig. S41-52, ESI†). The transmission electron microscopy (TEM) image of POM1-IM also demonstrated the uniform micropore structure (Fig. S53-56, ESI†). The textural properties of the first-step polymers (POM1~6) and imidazolium modified polymers (POM1~6-IM) are shown in the Table 1. The BET surface areas for the imidazolium modified porous polymers are in the range of 99 and 926 m²/g. The total pore volume and the micropore volume are as

high as 1.06 cm³/g and 0.17 cm³/g, respectively. The BET surface area and pore volume of the imidazolium-modified polymers are similar or lower than the respective original polymers (POM1~6-IM vs POM1~6). In addition, the porosity of the materials from bis-substituted precursors (POM 1- 4) is much larger than those from mono-substituted precursors (POM 5-6), as bis-substituted precursors could form more crosslinks during the reaction. As for the choice of halide, benzyl chloride resulted in better porous materials than corresponding benzyl bromide (POM 5 vs 6).

Recently, considerable attentions has been devoted to developing functional materials for CO₂ capture.⁶ Both microporosity and imidazolium functionality have been identified as important characteristics for CO₂ adsorption.^{6, 13} The imidazolium salt-modified porous hypercrosslinked polymers, possessing both micropore and imidazolium salt, were tested as potential candidates for CO₂ capture. As expected, the materials derived from bis-substituted benzenes exhibited good CO₂ capture capacity (10.6~14.5 wt% by BET at 273 K and 1 bar (Fig. S57-68, ESI†) and 4.6~4.8 wt% by TGA at 298 K and 1 bar (Fig. S69-74, ESI†). The CO₂ capture capacity of different polymers is closely correlated with micropore volumes and contents of imidazolium salts.¹³ In general, the introduction of functional groups decreased its porosity of the material (such as BET surface area and pore volume), as well as CO₂ capture capacity.^{8c} For imidazolium-modified polymers (POM1, 2, 4, 5-IM), their porosities are indeed decreased. Unexpectedly, their CO₂ capture capacities were kept in the same range or slightly increased (Table 1). On the contrary, the CO₂ capacities of POM3-IM and POM6-IM were lower than that of POM3 and POM6 possibly because of the significant decrease in BET surface area and pore volume in these two cases. POM3 has highest CO₂ capture capacity due to its high micropore volume and the presence of hydroxyl group.^{9b} Polymers derived from mono-substituted monomers (benzyl chloride and benzyl bromide) have lower CO₂ capture capacities. The heat of absorption for POM1~3-IM is 25.6, 31.1 and 31.5 kJ/mol, respectively (Fig. S75, ESI†). In addition, these materials have fast adsorption rate, over 97% of CO₂ was adsorbed within 8 min (Fig. S69-74, ESI†). The CO₂ and N₂ selectivity of these materials is as high as 13 at the equilibrium conditions (Fig. S76, ESI†). The CO₂ adsorption of these materials is fully reversible (Fig. S77, ESI†). Further study showed that our material is stable in hot water. No polymer degrading was observed and the CO₂ capture capacity of polymer kept the same after hot water treatment (80 °C, 18 h) (Fig. S71, ESI†). Although the CO₂ capture capacity of current materials is not the highest as comparing to other "knitted" polymer,⁹ this imidazolium modified porous polymer provided an excellent opportunity to look for the synergistic effect of CO₂ capture and conversion.

Imidazolium salts as organocatalyst for the conversion of CO₂ into cyclic carbonate has attracted significant interest.¹⁴ Organic polymer supported imidazolium salts as the stable and recyclable heterogeneous catalysts are especially highlighted.¹¹ However, very few reports refer to porous polymer-supported imidazolium salts, and little is known about the effect of porous structure on catalytic activity.³ In addition, polymers are more hydrophilic after modified by imidazolium salts, which is also beneficial for CO₂ conversion. Thus, the catalytic activities of the synthesized

porous hypercrosslinked polymer-supported imidazolium salts were investigated for the conversion of CO₂ and propylene oxide (PO) into propylene carbonate (PC). Interestingly, these materials (POM-IM) demonstrated much higher activities than the conventional PS supported one under the same reaction conditions (entry 1 vs 7, Table 2). The catalytic activities of POM1-IM and POM3-IM were even higher than the homogeneous imidazolium catalyst (entry 1 vs 8). This is attributed to the synergistic effect of the micropore structure and the catalytic centres which located in the pore structure. The polymers could capture and concentrate CO₂, which results in a higher CO₂ concentration near catalytic centres and makes the catalytic reaction more efficient.^{8a,15} To prove this, reactions under low CO₂ pressure (0.2 MPa *vis* 1 MPa) were carried out. As shown in Table 2, POM3-IM retained more than half of its original catalytic activity at low CO₂ pressure (42% yield *vis* 78% yield), while PS-IM and homogeneous BMIC almost lost all their catalytic activities (entries 9-11). 42% yield of POM3-IM catalyst at 0.2 MPa is higher than PS-IM (30%) and close to BMIC catalysts (49%) under 1 MPa. The total pore volume of POM3-IM is 0.39 cm³. It can capture more than 0.5 wt% (5 mg/g) of CO₂ at 120 °C (SI, Fig S71) under 0.1 MPa. 5 mg of CO₂ will occupy more than 3 cm³ volume (*vis* 0.39 cm³ total pore volume) at 120 °C under 0.1 MPa. This could explain the high activity of POM3-IM as the high capillary pressure driven the reaction and further confirmed that the micropore structure does play an important role in imidazolium salt catalysed CO₂ transformation. In addition, the catalytic activity of polymers was generally corresponded to their BET surface area and halide loading. No activity was observed for POM6-IM due to the low contents of imidazolium salts (entry 6).

Table 2 The activities of supported imidazolium salts for the conversion of CO₂ with propylene oxide into propylene carbonate^a

Entry	Cat.	PO conv. ^b (%)	PC yield ^b (%)
1	POM1-IM	59	58
2	POM2-IM	46	46
3	POM3-IM	78	78
4	POM4-IM	40	40
5	POM5-IM	38	38
6	POM6-IM	Trace	Trace
7 ^c	PS-IM	30	30
8 ^d	BMIC	49	49
9 ^e	POM3-IM	42	42
10 ^e	BMIC	6	6
11 ^e	PS-IM	5	5

^aReaction conditions: PO (1.43 mmol), catalyst (5 mmol% based on the imidazolium salt), ethanol (2 ml), CO₂ pressure (1 MPa), 120 °C, 4 h. ^bYield and conversion were determined by GC using biphenyl as the internal standard. ^c PS = polystyrene resin. ^d BMIC = 1-benzyl-3-methylimidazolium chloride. ^e CO₂ pressure (0.2MPa).

Interestingly, POM3-IM, which has hydroxyl functionality in its framework, demonstrated the highest activity among them for the conversion of CO₂ with PO to propylene carbonate (entry 4 vs 1 and 2). It is believed that the high activity of this material is due to the hydrogen bond interactions between hydroxyl groups and

reactants.¹⁶ Recycling experiments indicated that the POM-IM materials have excellent stability and recyclability. It was reused for six runs and no obvious loss in activity was observed (Fig. S78, ESI†). FT-IR spectra of POM3-IM catalyst before and after the reaction did not show any notable difference which further supported the stability of the porous POM-IM materials (Fig. S79, ESI†). The stability of reused polymeric catalyst is further verified by N₂ adsorption and elemental analysis, the surface area changed slightly from 575 to 530 cm²/g (Table 1), and the contents of nitrogen has no obvious decrease (Table S1).

Table 3 Substrate scope^a

Entry	Epoxide	Product	Time/h	Conv./% ^b	Yield/% ^b
1			8	94	92
2			8	96	90
3			12	90	89
4			12	91	91
5			12	76	73
6			12	70	68
7			30	98	93
8			30	86	85

^a Reaction condition: Epoxide (1.43 mmol), POM3-IM (5 mmol% based on the imidazolium salt), ethanol (2 ml), CO₂ pressure (1 MPa), Temperature (120 °C), every experiment was conducted in triplicate. ^bYield and conversion were determined by NMR.

Quantum calculations were also carried out to investigate the reaction mechanism with 1-benzyl-3-methylimidazolium chloride as the model catalyst (Fig. S80, ESI†). The calculation was conducted by use of the B3PW91 functional with the 6-311++G (d, p) basis set as implemented in Gaussian 09 program package. All of the intermediates and transition states are shown in Fig. S81 (see ESI†). The catalytic cycle was presumed to occur in three steps (Fig. S82, ESI†). The first step is ring-opening through the attack of the nucleophile (Cl⁻ from imidazolium salt) on epoxide, which was considered to be the most difficult step with the largest activation energy ($\Delta E = 21.25$ kcal/mol). The second step was the insertion of CO₂. The last step was the formation of cyclic carbonate with activation energy of 19.3 kcal/mol. This catalytic cycle involving C(2)-H of imidazolium salt activation process is exothermic with low activation barrier,^{16e} which allows the reaction to be performed under mild condition. The reaction mechanism of POM3-IM with hydroxyl group was also studied using 1-benzyl-3-methylimidazolium

chloride and benzyl alcohol as the model system (Fig. S83). A double activation process with both C(2)-H of the imidazolium salt and hydroxyl group of benzyl alcohol was proposed (Fig. S84). This double activation process further decreased the activation energy, especially for the ring-opening step (18.35 vs 21.25 kcal/mol) (Fig. S85).^{16a-c}

The epoxide substrate scope was then screened using POM3-IM as the catalyst. As shown in Table 3, the catalytic system was found to be effective for a variety of terminal epoxides (entries 1-8). Furthermore, epoxides functionalized with alkene or long hydrophobic chain were also suitable substrates for this catalytic system (entries 5-8). Compared with other reported functionalized porous organic polymers (Table S3),^{3a, 3h} the POM-IM is indeed very promising as a heterogeneous organocatalyst for two respects: the catalysts were synthesized in a simple and easily controllable way, and the reactions proceeded well under relatively mild condition.

Conclusions

Novel imidazolium salt-modified porous organic polymers were developed. The materials were synthesized in a simple and easily controllable way. These porous materials displayed high BET surface areas and excellent CO₂ capture capacities. Furthermore, the supported imidazolium salts displayed much higher catalytic activities than homogeneous and traditional PS supported imidazolium salts for the conversion of CO₂ and epoxides to cyclic carbonates. Moreover, a synergistic effect of microporosity of porous materials and functionality of imidazolium salts for CO₂ capture and catalytic conversion was observed. In addition, imidazolium-modified porous materials demonstrated high stability and reusability for both CO₂ capture and conversion.

Acknowledgements

We are grateful to the Institute of Bioengineering and Nanotechnology (Biomedical Research Council, Agency for Science, Technology and Research (A*STAR), Singapore) for generous support of this project, and the A*STAR Computational Resource Centre through the use of its high-performance computing facilities. The authors acknowledge Dr. Su Seong Lee for solid state NMR experiments.

Notes and References

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† Electronic Supplementary Information (ESI) available: general experimental and DFT computational methods, synthesis of PS-supported imidazolium salt, characterization of cyclic carbonates, supporting figures, supporting tables and also cartesian coordinates for the optimized geometries of all intermediates and transition states. See DOI: 10.1039/b000000x/

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