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Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201900570

Link to VoR: http://dx.doi.org/10.1002/cssc.201900570



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Imidazolium Salts Functionalized Covalent Organic Frameworks for Highly Efficient Catalysis of CO₂ Conversion

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Abstract: The conversion of CO₂ into valuable chemicals is one of the most ideal pathways for CO₂ utilization in industry, while the development of highly efficient catalysts remains a challenge. Herein, we report the design and synthesis of two novel imidazolium salts functionalized covalent organic frameworks (COFs) for the catalysis of CO₂ conversion. The resultant COFs possess high crystalline structure, show high stability and surface area, and contain dense catalytic active sites on the pore walls. They exhibit outstanding catalytic performance for the reaction of CO₂ with epoxides without any solvent and co-catalyst under mild conditions, and afford a record turnover number of 495000. In addition, the COFs can be served as effective catalysts in the reductive reaction of CO₂ with amines. The results presented here thus give the exceptional potential of the functionalized COFs for challenging various CO₂ transformations.

Introduction

With the large consumption of fossil energy, the emission of greenhouse gas carbon dioxide (CO2) has caused serious environmental problems such as global warming.[1] The conversion of CO2 into valuable chemicals is one of the most ideal pathways to reduce CO2 emission and fully utilize this abundant, cheap, and nontoxic C1 source.^[2,3] As a result, considerable efforts have been devoted to the development of catalytic methodologies for chemical fixation of CO₂ to produce valuable chemicals.^[4-6] In particular, the cycloaddition of epoxides with CO₂ to form cyclic carbonates is an important and atom-economic reaction, and the resultant products are important heterocyclic compounds widely used in organic synthesis.^[7-9] Various catalysts have been investigated for the cycloaddition reaction. Recently, some crystalline porous materials have shown promising applications in gas adsorption and catalysis because of their predictable control over structure. ^[10, 11] For example, metal-organic frameworks (MOFs) have been served as excellent heterogeneous catalysts for this reaction. [12-14]

Covalent organic frameworks (COFs)^[15-17] are another novel

class of crystalline porous materials with wide applications in molecule storage and separation,^[18-20] catalysis,^[21-26] energy storage, and others.^[27-29] These materials are constructed from organic building blocks through reversible covalent bonds.^[30-32] A significant feature is that they possess excellent properties such as inherent porosity, high stability, ordered pore walls, and extremely low density.^[33-36] In recent years, COFs have been employed as heterogeneous catalysts for the cycloaddition of epoxides with CO2. For example, Roeser and Yu groups [37, 38] reported that covalent triazine frameworks composed of high number of basic nitrogen sites efficiently catalyzed the cycloaddition of CO2 with different starting epoxides. Bhanage and Liu groups [39, 40] demonstrated that hydrogen bond donor (HBD) such as -OH decorated COF materials could be used as excellent catalysts for the chemical fixation of CO₂ to cyclic carbonate. Ma and co-workers [41] developed a novel porous heterogeneous catalyst by encapsulating linear ionic polymers and metal Lewis acid catalytic sites on the opened channels of COFs, and then used as catalyst for the reaction of CO₂ with various epoxides. However, it is noted that most of these catalysts exhibit low catalytic efficiency and/or work under assistance of co-catalysts. Therefore, development of novel COF catalysts with highly catalytic capacity remains a challenge in CO₂ transformation.

Numerous studies have confirmed that imidazolium salts are a unique species for activating and subsequently transforming CO2 into valuable chemicals. [42-44] Nevertheless, the catalytic activity of these homogenous catalysts is usually not high, and the separation of them from raw materials and products is often difficult. Herein, we report a novel class of imidazolium salts functionalized COFs synthesized by post-modification strategy. The as-synthesized COFs show high crystalline structure and porosities with the pore size of 2.6 nm and the surface area of up to 2027 m²g⁻¹, which provides the required accessibility to guest molecules for quick diffusion. The materials possess highly dispersed active sites in the pore channels, and exhibit remarkable catalytic performance for the cycloaddition of CO₂ with epoxides with a record turnover number under mild conditions. Moreover, the COFs can also be served as highly active catalysts for the formylation of amines with CO₂.

Results and Discussion

In order to chemically bind imidazolium salts on the pore walls of COFs, we first synthesized the imine-linked COF material containing hydroxyl groups via condensation reaction between 2-hydroxybenzene-1,4-dialdehyde 1 and amine 2 (Figure 1). The hydroxyl groups could remain intact during the COF synthesis, thus facilitating further chemical modifications. The reaction was carried out in a mixture of o-dicholorobenzene and n-butanol under solvothermal conditions at 120 °C for 3 days by using

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Figure 1. Schematic representation for the direct construction of imidazolium salts functionalized COF materials, COF-HNU3 and COF-HNU4, through channelwalls engineering of COF-HNU2.

acetic acid as catalyst (see Experimental section for details). The as-synthesized COF was designated as COF-HNU2, and its FT-IR spectrum was compared with the building blocks (1 and 2), It was found from Figure S1 (see Supporting Information) that the characteristic peak for C=N at 1612 and 1212 cm⁻¹ appeared, while the peaks for aldehydic C-H stretching (at 2889 cm⁻¹) and C=O (at 1663 cm⁻¹) of 1 and the N-H stretching (at 3209, 3354, and 3434 cm⁻¹) of 2 disappeared, which indicate that the condensation was successful. The ¹³C solid state NMR spectrum of COF-HNU2 showed a characteristic signal at 167 ppm originated from the imine linkage carbon atoms (Figure S2). Moreover, thermo gravimetric analysis (TGA) indicates that this COF material was stable up to 430 °C (Figure S3).

The morphology of the COF-HNU2 was characterized using scanning electron microscopy (SEM). The complex aggregates were formed in the material with the size between 0.2 and 1.0 μ m (Figure 2a and Figure S4). The structure of COF-HNU2 was measured by transmission electron microscopy (TEM), and clear lattice fringes with a spacing of 3.5 nm were commonly observed (Figure 2b-c), confirming the formation of long-ordered channels in the structure. In addition, the parallel crystal planes with the interlayer distance of 0.34 nm (Figure 2d) was also observed for COF-HNU2. This was very close to the (100) reflection as seen in the profile, indicating highly ordered alignment for the COF.

The exact crystal structure of COF-HNU2 was determined by powder X-ray diffraction (PXRD) analyses in conjunction with structural simulations. As shown in Figure 3, the as-synthesized COF-HNU2 exhibited strong diffraction peaks at $2\theta = 2.8$, 4.9, 5.7, 7.5, and 9.98° (blue curve), corresponding to the (100), (110), (200), (210), and (220) planes, respectively. The broad peak at $2\theta \sim 25.3^{\circ}$ corresponded to the (001) facet, indicating an interlayer distance of 0.35 nm. Using the optimal monolayer structure, the ecliped orientaion (AA stacking mode) could generate the PXRD pattern (Figure 3, black curve, and Figures S5-6). The simulated PXRD pattern is in good agreement with the experimental data. The refinement results gave the hexagonal unit cell (P_6) with the parameters of a =37.642298, b= 37.642298, c=3.468514, α = β =90° and γ =120° (Table S1). In this model, the Pawley refined pattern (red curve) matched well with the experimental profile (blue curve), and their difference (green curve) was very small. Figure 3 also showed the extended structure of the framework. In contrast, the staggered orientation (AB stacking mode) showed significant deviation from the experimentally observed PXRD profile (Figures S7-S8, Table S2).



Figure 2. SEM image (a) and TEM images (b-d) of COF-HNU2. The red arrows in (c) highlight the straight channels with a diameter of \sim 3.5 nm; The white arrows in (d) highlight the parallel crystal planes with the interlayer distance of 0.34 nm. Scale bars, 500 nm, 100 nm, 50nm, and 5 nm for (a–d), respectively.

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The permanent porosities were investigated by nitrogen absorption-desorption isotherm. It was found that the COF-HNU2 displayed a typical IV type absorption curve at 77 K (Figure 4a, red curve), indicating the characteristic of mesoporous materials. The Brunauer-Emmett-Teller (BET) surface area was calculated to be 4313 m² g⁻¹, which is the highest value among the reported 2D COFs up to date. The large BET surface area could be attributed to the high crystallinity. The total pore volume was also estimated (at $P/P_0 =$ 0.99) to be $V_p = 2.9 \text{ cm}^3 \text{g}^{-1}$ for COF-HNU2. Calculated by nonlocal density functional theory (NLDFT), COF-HNU2 showed a large pore size of 3.6 nm (Figure S9), which agrees well with the predicted value from the eclipsed structure. In addition, the framework of COF-HNU2 was very stable and retained its crystallinity after soaking for 72 hours in a variety of solvents such as DMF, THF, n-hexane, water, and aqueous acid (0.1 M HCI) and base (3 M NaOH) solutions (Figure S10). The high stability was ascribed to its structural characteristics including intramolecular hydrogen bonding (-O-H...O=C-NH) and high crystallinity. [45, 46]

Encouraged by the high crystallinity, large BET surface area, and excellent stability of COF-HNU2, we developed two novel COF materials (COF-HNU3 and COF-HNU4) by anchoring the imidazolium salts onto the channel walls through nucleophilic substitution reaction between the phenolic hydroxyl groups in COF-HNU2 and 1-(3-bromopropyl)-3-methyl-1H-imid-azol-3-ium bromide or 1-(3-bromopropyl)-4-chlorine-3-methyl-1H-imidazol3-ium bromide in the presence of a base (Figure 1). The detailed synthetic procedures were described in Experimental section. It was found that the PXRD profile of the COF-HNU3 (Figure 3a, orange curve) exhibited a similar XRD pattern shown by COF-HNU2, and no noticeable morphological change was observed as compared with that of COF-HNU2 (Figure S4 and Figure S11). The BET surface area was calculated to be as high as 2027 m² g⁻¹ (Figure 4a, blue curve), the highest reported for an imine-linked COF derived from post-modification strategy. The pore size for the sample decreased from 3.6 nm to 2.6 nm (Figure S12). These findings indicated that the lattice structure maintained intact and the pore was accessible after modification. In addition, COF-HNU3 was also stable in air and common solvents, such as DMF, THF, MeOH, and hot water, and the high crystallinity was retained under these conditions (Figure S13).



Figure 4. Nitrogen absorption curves of COF-HNU2 and COF-HNU3 (a) performed at 77 K; ¹³C CP/MAS solid state NMR spectrum of COF-HNU3 (b). The assignments of 13C chemical shifts of alkyl chain in COF-HNU3 are indicated in the chemical structure. Asterisks indicate spinning side bands.

The atomic-level structure of COF-HNU3 was assessed by Xray photoelectron spectroscopy (XPS) and solid-state NMR spectroscopy. The XPS spectrum revealed a bromine signal at binding energy of 70.2 and 69.2 eV (Figure S14), verifying the successful post modification. The ¹³C NMR spectra showed the signals at 56, 46, 36, and 31 ppm (Figure 4b), respectively, FULL PAPER

which could be assigned to the alkyl-C species of the imidazolium salt moieties. Furthermore, the content of imidazolium salt sites was analyzed by elemental analysis, and the bromine content up to 17.9 wt% was found, which corresponds to 2.2 mmol per gram of the imidazolium salt moieties. This result reveals that more than 90% of the OH groups (2.35 mmol per gram of the COF-HNU2) reacted with the imidazolium bromide salt. The COF-HNU4 was prepared under the similar conditions and detailed characterization of COF-HNU4 was given in Supporting Information (Figures S15-S19).

Table 1. The cycloaddition reactions of (1a) with CO₂ catalyzed by kinds of catalysts^[a]

0 1a	+ CO₂	Catal.	0 0 2a
Entry	Cat.	Yield/% ^[b]	TON
1	COF-HNU3	99	495000
2	COF-HNU4	95	475000
3 ^[c]	COF-JLU7	98	9000
4	N N O	32	-
5		29	- >
7 ^[d]	COF-HNU2	trace	

^[a]Reaction conditions: 1a (10 mmol), 100 °C, 48 h, $CO_2 = 2$ MPa, catalyst (0.002 mol%, based on the imidazolium salt catalytic site). ^[b] Isolated yield. ^[c]Data were obtained from Ref.^[40]. ^[d]COF-HNU2 (5 mg).

Owing to the excellent porosity and high density of the active sites of imidazolium salts within the nanoscopic channels, the materials were examined for catalyzing the cycloaddition reaction of epoxides with CO2. It was found that all the imidazolium salts functionalized COFs showed excellent catalytic performance for the cyclization reactions under solventfree and co-catalyst-free conditions. In these functionalized COFs, turnover number (TON) of COF-HNU3 was as high as 495000 (Table 1, Entry 1), probably ascribing to its high surface area. In comparison with the COF-JLU7 catalyst that is the best transition-metal-free COF catalyst reported for this reaction, [40] COF-HNU3 and COF-HNU4 displayed about 50-fold higher TON value under similar conditions (Table 1, Entries 1-3). Nevertheless, COF-HNU2 without catalytic sites showed a very low catalytic activity under the same reaction conditions (entry 7). It has been reported that hydrogen bond can active the epoxide. ^[47, 48] The as-prepared COF-HNU3 and COF-HNU4 have large amount of imidazolium cations and Br anions that can form

hydrogen bonding with the epoxide, thus promoting the reaction of epoxides with CO₂. Moreover, it was worth noting that the catalytic system developed here was applicable to the synthesis of cyclic carbonates with excellent yields (94-96%) for the cycloaddition of various epoxides with CO₂ (Table 2). As far as we know, COF-HNU3 exhibited the highest TON value under similar conditions among the very few COF-based heterogeneous catalysts that could catalyze the cycloaddition of epoxides with CO₂. ^[37-41, 49] Especially, the amount of catalyst used was very low, which was usually not the case for metal-free catalysts.

Table 2. Cycloaddition reactions of epoxides with CO_2 to cyclic carbonates catalyzed by COF-HNU3 ^[a]





^[a]Reaction conditions: epoxide (5 mmol), CO₂ (2 MPa), 100 °C, and COF-HNU3 (0.002 mol%, based on the imidazolium salt catalytic site). ^[b] Yields were determined by ¹H NMR spectroscopy.

In general, homogeneous catalysts have superior activity and/or selectivity compared to heterogeneous catalysts.^[50] However, as shown in Table 1, the catalytic activity of the imidazolium salts functionalized COFs reported in this work was remarkably higher than the homogeneous molecular catalysts of the imidazolium salts (entries 1 and 2, entries 4 and 5). It is

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known that the porosity and dispersion of active sites of the catalytic materials are among the most important influential factors for heterogeneous porous catalysis. COF-HNU3 and COF-HNU4 have mesoporous framework, high BET surface areas, and dense imidazolium and Br⁻ active sites. Their mesoporosity and ordered open channels contribute to the exposure of active sites and favors the fast transportation of the substrates. The combination of imidazolium salts endows a high CO_2 absorption capacity (Figure S20) and high enrichment of CO_2 near the active sites, thus promoting the rapid conversion of the reactants. Therefore, the enhanced catalytic efficiency is attributed to the highly dispersed active sites of the imidazolium salts within framework of COFs.

Table 3. Formylation of various amines with CO_2 and phenylsilane using COF-HNU3 as catalyst^{[a]}

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R1 1	H N. _{R2} + F	PhSiH ₃ + CO ₂ equiv 1bar	Cs ₂ CO ₃ (0.5mol ⁹ Cat . (0.5mol%	(6), DMF), 30 °C R ₁ 2	.N. _{R2} +R ₁	3 N.R2
Entry	R_1	R_2	Time/h	Yield/% ^[b]	Y ₂ /Y ₃	TOF/h ⁻¹
1	н	CH_3	1	96	99:1	192
2	н	i-Pr	1	94	98:2	188
3	CH ₃	CH_3	1	95	96:4	190
4	н	CH_3CH_2	1	96	97:3	192
5	Û	5	5	91	97:3	91
6	CI	н	6	90	95:5	90
7 ^[c]	н	CH_3	12	90	98:2	15
8 ^[d]	н	CH ₃	24	99		0.82

^[a] Reaction conditions: aryl amine (1.0 mmol), COF-HNU3 (0.5 mol% based on the imidazolium salt active site), Cs₂CO₃ (0.5 mmol), PhSiH₃ (1.0 mmol), 2 ml of DMF, 30 °C. ^[b] Yields were determined by ¹H NMR spectroscopy. ^[c] 0.2 mol% of COF-HNU3 was used. ^[d] Result from literature ^[51] (5 mol% IPr was used).

To examine the universality of the imidazolium salts functionalized COFs as useful catalysts for CO₂ transformation, COF-HNU3 which can generate carbene active sites in the presence of base, was used as an effective catalyst in the reductive functionalization of amines with CO₂. Firstly, the reaction conditions were optimized and the results were given in Table S3, where Cs₂CO₃ was chosen as the base, DMF was used as the solvent, and the reaction time was set at 1h. Then, we explored the substrate scope for the reaction under the optimum conditions, and the results were summarized in Table 3. It is clearly indicated that the substituted aryl secondary amines with various substitute groups could afford the target products in excellent yields (up to 96%) and high selectivity (up to 99:1), and the turnover frequency (TOF) of up to 192 h⁻¹ (entry 1) was achieved which is the highest number for metal-free catalysts reported to date for N-formylation of amines with carbon dioxide (Table S4). Interestingly, N-H bonds of p-chlorine PhNH₂ were proved to be reactive and mainly resulted in the monoformylaniline product with a high yield and selectivity (entry 6). Furthermore, when catalyst dosage was reduced from 0.5 to 0.2 mol%, the reaction also worked well, but only with the TOF value of 15 h⁻¹ (entry 7). All these results clearly indicate that the functionalized COFs possess remarkable catalytic activity for this reaction. Compared with the reported homogeneous carbene catalysts, ^[51] the TOF value in our functionalized COF heterogeneous catalysis was 234 times that in homogeneous carbene molecular catalysis (Table S4). Thus, the catalyst loading and reaction time were significantly reduced by using COF-HNU3 catalyst in the present work.



Figure 5. Recycle tests of the COF-HNU3. Reaction conditions: propylene oxide (20 mmol), CO_2 (2 MPa), COF-HNU3 catalyst (0.002 mol%, based on the imidazolium salt catalytic site), 100 °C, and 48 h.

The separation and recyclability of the catalyst is one of the most important advantages for heterogeneous reactions in practical applications. ^[52-54] We investigated the recyclability of COF-HNU3 in the cycloaddition reaction of propylene oxide with CO₂. After each cycle, the catalyst could be simply regenerated by centrifugal separation. As shown in Figure 5, the catalyst could be reused for at least ten times without significant loss of catalytic activity. In addition, high crystallinity and porosity of COF-HNU3 were almost remained after the recycling (Figures S21-22).

Conclusions

In conclusion, we designed and synthesized a novel class of imidazolium salts functionalized COFs, which have high crystalline networks and BET surface area. The dense imidazolium cation and Br anion in the nanoscopic channels could be served as efficient active catalytic centers toward

cycloaddition of epoxides with CO₂. It was shown that COF-HNU3 and COF-HNU4 could effectively catalyze the reactions for CO₂ fixation with excellent yields, and the TON value could reach up to 495000, which is about 50 times that of the best transition-metal-free COF catalyst reported for this reaction. The remarkably high catalytic activity could be contributed to the highly dispersed active catalytic sites within the pore of COFs. In addition, COF-HNU3 also showed remarkable selectivity and catalytic performance in the reductive N-formylation of amines with CO₂. This work reveals the great potential of the imidazolium salts functionalized COFs as a novel class of efficient catalysts in CO₂ conversion.

Experimental Section

Instrumentation

FT-IR spectra were collected on a Spectrum 400 spectrometer (Perkin-Elmer). PXRD data were recorded from $2\theta = 2^{\circ}$ to 40° in 0.1° increment on a Bruker D8 Advance diffractometer. The thermal properties of the materials were evaluated using a thermogravimetric analysis (TGA) instrument (STA449C) over the temperature range from 25 to 800 °C under N2 atmosphere. The Brunauer-Emmett-Teller (BET) surface areas were performed on a Quantachrome Instruments ASIQM 00002200-7 system. SEM observations were performed on a Hitachi SU8010 microscope operated at an accelerating voltage of 10.0 kV. TEM images were characterized by a JEM-2010 transmission electron microscope operated at 200 kV. XPS data were collected with an ESCALab220Xi Thermo Scientific electron spectrometer.

Synthesis of COF-HNU2

A solution of o-dicholorobenzene / n-butanol / 6 M acetic acid (1 mL/1 mL/0.2 mL) was put into a 10 mL Pyrex tube, then 2-hydroxybenzene-1,4-dialdehyde (0.12 mmol, 18.0 mg) and 1,3,5-tris(4-aminophenyl) benzene (0.08 mmol, 28.1 mg) were added. The mixture was degassed and stirred at 120°C for 3 days in a sealed tube. The obtained solid was collected and washed with ethanol and tetrahydrofuran for three times, respectively. The product was dried at 120 °C for 12 h to get the corresponding COF-HNU2 in 90% isolated yield.

Synthesis of COF-HNU3 and COF-HNU4

 K_2CO_3 (30 mg), 1-(3-bromopropyl)-3-methyl-1H-imid-azol-3-ium bromide (60 mg) or 1-(3-bromopropyl)-4-chlorine-3-methyl-1H-imidazol-3-ium bromide (67 mg) were dissolved in 5 mL of dry DMF under N_2 atmosphere, and then COF-HNU2 (30 mg) was added. Then, the mixture was heated at 120 °C and stirred for 36 h. The product was isolated and washed with methanol, and then dried at 100 °C under vacuum for 12 h to give the COF-HNU3 and COF-HNU4, respectively.

General procedures for the cycloaddition reactions of epoxides with $\ensuremath{\text{CO}_2}$

In a typical experiment, the mixture of propylene oxide (10 mmol) and COF-HNU3 catalyst (0.002 mol%, based on the imidazolium salt catalytic site) were added in a 15 mL stainless-steel autoclave reactor. The autoclave reactor was sealed with the pressure of CO_2 to 2 MPa, and the mixture was stirred at 100 °C for 48 h. After the reaction was completed, the reaction mixture was centrifuged, filtered, and analyzed by ¹HNMR. The catalyst was collected and washed with methanol for 3 times, and then dried at 100 °C for 12 h. The recovered catalyst was used without further purification.

General procedures for the reductive functionalization of CO_2 with amines

Briefly, COF-HNU3 (0.5% mol based on imidazolium salt), Cs_2CO_3 (0.5% mol) and dry DMF (2 mL) were loaded in a Schlenk tube (25 mL), then the mixture was stirred for 4 h under N₂ condition, then connected to a CO_2 balloon with three CO_2 purge cycles. Amine (1.0 mmol) and PhSiH₃ (1.0 mmol) were introduced into the tube, and stirred for 1 h at 30 °C. The product yield was determined by ¹H NMR (CDCl₃, 600 MHz) spectroscopy.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No.U1704251, 21733011, 21773058), the National Key Research and Development Program of China (2017YFA0403 101), and the 111 project (No.D17007).

Keywords: Covalent organic frameworks • carbon dioxide • imidazolium salts • heterogeneous catalysis • carbonates

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A novel class of imidazolium Salts functionalized covalent organic frameworks with highly crystalline and surface area was designed and synthesized, and found to have a remarkable catalytic activity in CO₂ conversion with a record turnover number.



TON: 495000 Imidazolium Salts Functionalized COFs TOF: 192 h⁻¹

Jikuan Qiu[‡], Yuling Zhao[‡], Zhiyong Li, Huiyong Wang*, Yunlei Shi and Jianji Wang*

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Imidazolium Salts Functionalized Covalent Organic Frameworks for Highly Efficient Catalysis of CO₂ Conversion

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