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# Ionic liquid-decorated COF and its covalently composite aerogel for selective CO<sub>2</sub> adsorption and catalytic conversion

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Atmospheric CO<sub>2</sub> level is closely related to the greenhouse effect. The new practical materials and techniques for highly selective CO<sub>2</sub> adsorption and catalytic conversion are imperative. The covalently composite of covalent organic frameworks (COFs) with polymers (oligomers) might be a promising approach to meeting the multifaceted requirements of CO<sub>2</sub> treatment. Here, a novel COF-chitosan composite aerogel (**COF-IL@chitosan**) is designed and fabricated by chemically crosslinking of the allyl-imidazolium ionic liquid-decorated COF (**COF-IL**) with the thiol-attached chitosan (chitosan-SH) binder via photoinduced thiol-ene reaction. The crystalline structure, highly selective CO<sub>2</sub> adsorption and catalytic conversion features of the **COF-IL** are well maintained in the composite aerogel. The generated covalently coupled COF-chitosan composite material of **COF-IL@chitosan** is robust, uniform and processable even with a remarkably high COF loading (up to 80 wt%). More importantly, the processable **COF-IL@chitosan** aerogel is readily shaped as the simplified fixed-bed reactor model via a facile templated freeze-drying procedure, and the scale-up CO<sub>2</sub> cycloaddition in a recycling way was realized.

#### Introduction

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As is known, atmospheric carbon dioxide concentration is closely related to the greenhouse effect. To reduce the greenhouse effect, CO<sub>2</sub> capture and sequestration (CCS) and its chemical transformation have received much attention recently.<sup>1-5</sup> Among various CO<sub>2</sub> removal technologies, porous materials-based CO<sub>2</sub> adsorption and catalytic transformation are of great significance.<sup>6,7</sup> Thus far, a series of porous solid materials such as zeolites,<sup>8</sup> silica-supported salts,<sup>9</sup> microporous organic polymers,<sup>10,11</sup> and metal-organic frameworks (MOFs)<sup>12</sup> have been reported and some of them exhibited impressive CO<sub>2</sub>-grabbing and/or its catalytic transformation. For example, we and others recently reported ionic liquid (IL)-decorated MOF-based materials, which exhibited excellent selective CO<sub>2</sub> adsorption and catalytic transformation.<sup>13-15</sup> On the one hand, new porous functional materials for CO<sub>2</sub> treatment should be continued to develop; on the other hand, their processability and shaped setups fabrication might be more important for addressing global environmental issues regarding  $CO_2$  in practical applications.

As a promising alternative to MOFs, covalent organic (COFs),<sup>16-18</sup> which showed frameworks also various and storage,<sup>19,20</sup> applications such as gas adsorption sensor.<sup>21,22</sup> separation,<sup>23,24</sup> ionic conductivity,<sup>25,26</sup> and heterogeneous catalysis,27-29 are metal-free and should be more stable to water, polar organic solvents, and even strong acidic or alkaline media due to their organic nature, so their post-synthetic scope could be effectively expanded.

Recently, our group developed an alternative approach to construct the COF-based composite functional materials, in which the COF micro-nanosized particles are covalently composited with organic polymer (oligomer) binder by post-synthesis.<sup>30,31</sup> By this COF-polymer covalently composite approach, not only the compatibility of the micro-nanosized COF crystalline particles with organic polymer was dramatically enhanced, but also their facile processability for different shaped setups were available, consequently, made their practical applications in separation and catalysis possible.

Here, we report, the first of its kind, a novel allyl-imidazolium ionic liquid-decorated and acylhydrazone-connected COF (**COF-IL**), which exhibits a highly selective adsorption for CO<sub>2</sub> over CH<sub>4</sub>, N<sub>2</sub>, and H<sub>2</sub>. In addition, it can be a highly active catalyst for CO<sub>2</sub> transformation by the cycloaddition with epoxides under mild conditions (1 atm and  $\leq 80$  °C) without any co-catalyst assistance. Remarkably, the obtained **COF-IL** could be further moldingly processed via covalently composite approach, in which the crystalline powdered **COF-IL** was

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chemically cross-linked with polymeric chitosan binder via photoinduced thiol-ene reaction and followed by a facile templated freeze-drying step. Besides selective  $CO_2$  separation, the generated **COF-IL@chitosan** aerogel can be a simplified fixed-bed reactor model to highly promote the scale-up  $CO_2$  catalytic cycloaddition in a recycling way.

#### Experimental

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#### Materials and method

The CO<sub>2</sub> cycloaddition reactions were carried out under a prepurified CO<sub>2</sub> atmosphere using vacuum line techniques. All chemicals were obtained from commercial sources and used without further purification. 1,3,5-Triformylphloroglucinol (Tp) was synthesized according to our reported method.<sup>31</sup> The thiol group-modified chitosan (termed as chitosan-SH) was synthesized according to the literature method.<sup>32</sup> The precursors of A, B, and C for IL-ADH were synthesized according to our previous report with slight modification.<sup>14</sup> All the characterization data for the known compounds provided in ESI were well consistent with those reported results. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) data were obtained on Avance-400 HD spectrometer а Bruker with the tetramethylsilane (TMS) as the internal tagging. Fourier transform infrared spectrometry (FT-IR) spectra were performed in the 400-4000 cm<sup>-1</sup> range using a Bruker ALPHA spectrometer. High-resolution mass spectrometry analysis was carried out on a Bruker maXis ultrahigh resolution mass spectrometer. Elemental analyses were performed on a PerkinElmer model 2400 analyser. Inductively coupled plasma (ICP) measurement was performed on an IRIS Intrepid (II) XSP and Nu AttoM. The solid-state <sup>13</sup>C cross-polarization magic angle spinning (CP-MAS) NMR spectra were obtained on Bruker AVANCE III 400 spectrometer. Scanning electron microscopy (SEM) was conducted on a Gemini Zeiss SUPRA scanning electron microscope equipped with an energydispersive X-ray detector. The X-ray diffraction pattern was measured on a D8 Advance X-ray powder diffractometer with the Cu K $\alpha$  radiation ( $\lambda$  = 1.5405 Å). The N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub> adsorption-desorption isotherms were performed on an ASAP 2020/TriStar 3000 (Micromeritics), after exchanged with acetone and ethanol for 48 h, centrifugation and drying thoroughly, about 300 mg sample was loaded in a sample tube and dried under high vacuum at 383 K for 12 h to remove the residual solvent molecules in the channels as previously described.<sup>13</sup> Thermogravimetric analysis (TGA) were performed on a TA Instrument Q5 simultaneous TGA at a heating rate of 10 °C min<sup>-1</sup> from 25 to 650 °C under a 60 mL/min flowing nitrogen. A lyophilizer (CHRIST ALPHA 1-2) was used to dry the sample. The compressive curve of the cylindrical aerogel was determined using an AGS-H 5kN instrument from Shimadzu, Japan.

#### Synthesis of IL-ADH

A mixture of **C** (0.456 g, 1.45 mmol) and hydrazine hydrate (0.425 mL, 8.7 mmol) in methanol (6 mL) was stirred for 14 h at 30 °C. After removal of the solvent in vacuum, the residue

was recrystallized in diethyl ether-methanol mixture (1:1, -//M) to obtain **IL-ADH** as white crystalline solids (0.2238), 490%). FIR (KBr, cm<sup>-1</sup>): 3432 (w), 3311 (w), 3258 (m), 3146 (m), 1661 (s), 1640 (s), 1528 (m), 1491 (m), 1333 (s), 1150 (s), 959 (m), 874 (m), 846 (m), 744 (m), 642 (m). <sup>1</sup>H NMR (400MHz, DMSOd<sub>6</sub>,  $\delta$ ): 4.59 (4H, s, -NHNH<sub>2</sub>), 4.87 (2H, q, -NCH<sub>2</sub>CH-), 5.19-5.37 (2H, d, -CHCH<sub>2</sub>), 5.56 (2H, s, -ArCH<sub>2</sub>N-), 6.01-6.05 (1H, m, -CH<sub>2</sub>CHCH<sub>2</sub>), 7.77 (2H, d, -NCHCHN-), 7.75 (1H, s, -Ar), 7.82-7.90 (2H, d, -Ar), 9.23 (1H, s, -NCHN-), 9.88-9.94 (2H, d, -NHNH<sub>2</sub>). ESI-MS: Calcd for C<sub>15</sub>H<sub>19</sub>N<sub>6</sub>O<sub>2</sub> M<sup>+</sup>, *m/z* 315.16; found, *m/z* 315.15; <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 166.95 (-NHCOAr-), 165.08 (-NHCOAr-), 137.25 (-COAr-), 137.06 (-COAr-), 135.65 (-NCHN-), 133.32 (-ArCH<sub>2</sub>-), 132.19 (-CH<sub>2</sub>CHCH<sub>2</sub>), 129.72 (-Ar), 128.67 (-Ar), 127.8 (-Ar), 123.37 (-NCHCH-), 123.07 (-CHCHN-), 120.7 (-CHCH<sub>2</sub>), 51.39 (-ArCH<sub>2</sub>N-), 50.36 (-NCH<sub>2</sub>CH-).

#### Synthesis and characterization of COF-IL

A mesitylene (5 mL) and 1,4-dioxane (5 mL) mixed solution of IL-ADH (472 mg, 1.5 mmol), Tp (210 mg, 1.0 mmol), and acetic acid (1.0 mL, 6 M) in a pyrex tube was flash frozen in a liquid nitrogen bath and degassed. Upon warming to room temperature, the tightly capped tube was heated at 120 °C for 3 days. The obtained precipitate was collected by centrifugation and completely washed with acetone, THF, and ethanol. The collected solids were dried in vacuum at 80 °C for 12 h to generate the as-synthesized COF-IL crystals as brownish red crystalline solids (556 mg, 82 % yield). Elemental analysis: calcd for (C24H23N6O7Br)n (desolvated) (%): C 49.06, H 4.00, N 14.31, Br, 13.62; found (%): C 49.24, H 4.08, N 14.09, Br, 13.24. FT-IR (KBr, cm<sup>-1</sup>): 3391 (w), 2974 (w), 1628 (s), 1590 (s), 1557 (m), 1454 (s), 1286 (s), 1188 (m), 1155 (m), 1045 (m), 875 (m), 636 (w). Solid-state <sup>13</sup>C CP-MAS NMR (500 MHz, δ): 167.4, 163.3, 147.1, 141.2, 138.1, 134.9, 132.3, 129.7-127.6, 124.34, 123.0, 120.6, 100.4, 53.5, 51.9.

#### Fabrication of COF-IL@chitosan hybrid aerogel

**COF-IL@chitosan** was prepared by mixing crystalline **COF-IL** (1.35 g) and photo-initiator of HMPP (150  $\mu$ L) with acidic chitosan aqueous solution (0.33 g of chitosan-SH, 120  $\mu$ L of HOAc, and 10 mL of deionized water) with ultrasonic shaking. After that, the sticky composite dispersion was immediately transferred into suitable mould, which was allowed to stand at room temperature for several hours until the robust hydrogel formed. After a photo-initiated thiol-ene click reaction (365 nm, 300 W, 0.5 h), the obtained hydrogel was transferred into a cooler for 12 h to generate and fix the ice crystals. After freeze-drying at -50°C for 24 h to remove the ice crystals, a 3D macroporous **COF-IL@chitosan** hybrid aerogel with 80 wt % **COF-IL** content was obtained. For fabrication of the **COF-IL@chitosan** based cuplike reactor, similar procedure was conducted except a split-flask template was used.

#### Catalytic cycloaddition of CO<sub>2</sub> with epoxides

**Reaction conditions.** Epoxide substrate (13.0 mmol) was stirred under  $CO_2$  atmosphere (1 atm) in the presence of **COF-IL** (3.0 mol%) at 80 °C for 48 h (monitored by <sup>1</sup>H NMR). The yield was determined by <sup>1</sup>H NMR data. After reaction, **COF-IL** 

was recovered by centrifugation, then completely rinsed with acetone and dried overnight in vacuum at 80  $^{\circ}\mathrm{C}$  for the next catalytic cycle under the same reaction conditions.

For the amplifying catalytic reaction with cuplike reactor, styrene oxide (1.53 mol, 175 mL) was heated at 80 °C under  $CO_2$  atmosphere (1 atm) for 72 h in a split-flask (250 mL) equipped with **COF-IL@chitosan** aerogel (16.8 g, 1.5 mol % **COF-IL** equiv). Once the reaction was finished, the aerogel was washed with acetone and dried overnight in vacuum at 80 °C for the next catalytic cycle under the same reaction conditions. **Leaching test.** The solid catalyst of **COF-IL** was separated from the hot reaction solution right after reaction for 24 h. The reaction was continued with the filtrate in the absence of **COF-IL** for an additional 36 h.

#### Simulated structure of COF-IL

Structural modeling of **COF-IL** was performed by the Materials Studio (version 7.0) for suite of programs for the precise structural information. Molecular geometry optimization was conducted with MS DMol3 module. Finally, Pawley refinement was applied for profile fitting, producing the refined PXRD profile using the space group of *P3* with the lattice parameters of  $a = b = 32.96 (\pm 0.002)$  Å and  $c = 3.62 (\pm 0.002)$  Å. *Rwp* and *Rp* values converged to 3.23% and 4.18%, respectively. PXRD pattern of this unit cell in **COF-IL** well matched with its experimental profile (see ESI<sup>†</sup>).

#### **Results and discussion**

#### Synthesis and characterization of COF-IL



Scheme 1 Synthesis of IL-ADH, COF-IL and its idealized structure.

The building block of **IL-ADH** with the allyl-imidazolium-based IL was synthesized as white crystalline solids via four successive steps (Scheme 1). Its structure was well determined by the NMR, FT-IR, and MS (Fig. S1-S13, ESI†). **COF-IL** was obtained as the brownish red crystalline solids in 82% yield by the reaction of 1,3,5-triformylphloroglucinol (Tp) with **IL-ADH** with the aid of HOAc under solvothermal conditions (mesitylene/1,4-dioxane, 1:1, v/v, 120 °C, 72 h) (Scheme 1). The FT-IR spectrum (Fig. S14, ESI†) of the as-synthesized **COF-IL** showed that the characteristic stretching vibrations at 1639 cm<sup>-1</sup> for C=O in Tp disappeared after the reaction. Meanwhile, the C-N stretching peak at 1286 cm<sup>-1</sup> for the acylhydrazinyl

moiety was observed. Besides, the stretching mode at 3391 cm<sup>-1</sup> was associated with the N-H species in **COF-IL** was also found. Solid-state <sup>13</sup>C CP-MAS NMR (Fig. S15, ESI†) was also used to confirm the formation of **COF-IL**. The existence of the keto,<sup>33</sup> acylhydrazinyl, phenyl, imidazolyl, allyl and methylene species in **COF-IL** was well evidenced by the corresponding resonances at 167.4, 163.3, 141.2, 138.1, 132.3 and 53.5 ppm, respectively.

The obtained **COF-IL** showed good crystallinity, which was revealed by the measured powder X-ray diffraction (PXRD) pattern (Fig. 1a). The structural modeling was thus conducted using the software of Materials Studio (Version 7.0) for more

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precise structural information.<sup>34</sup> Molecular geometry optimization was conducted with the MS DMol3 module (Table S1, ESI†). The most possible structure of **COF-IL** was simulated, analogous to that of **COF-IL** as a 2D eclipsed AA-type stacking structure using the space groups of *P3* with the lattice parameters of a = b = 32.96 Å and c = 3.62 Å. *Rwp* and *Rp* values converged to 3.23 and 4.18 %, respectively. The PXRD pattern of this unit cell well matched with the experimental profiles. As indicated in Fig. 1b, the eclipsed 2D structure contains a hexagonal pore, in which the distances between allyl and opposite and adjacent phenyl groups are ca.

22 Å and 15 Å, respectively (Fig. 1b). The close-packed all layers with an interlayer distance of  $3.6^{\circ}$ Å, indicating that adjacent layers in **COF-IL** are in a weak  $\pi$ - $\pi$  contact (Fig. 1b). As shown in Fig. 1a, the experimental PXRD pattern displayed a strong peak at 3.6° together with some relatively weaker signals at 5.9°, 8.2°, 9.3° and 24.8°, which belong to (100), (110), (200), (210) and (001) reflections, respectively. The slightly broad peak at a higher  $2\vartheta$  (26.4°) might be mainly caused by the defect in  $\pi$ - $\pi$  stacking between the adjacent COF layers.<sup>35</sup>



Fig. 1 (a) The simulated and measured PXRD patterns of COF-IL. (b) Crystal packing pattern viewed down the crystallographic c and b axes based on the PXRD data obtained by using Materials Studio. (c) SEM image of COF-IL. (d) N<sub>2</sub> adsorption isotherms of COF-IL at 77 K, and its pore size distribution based on the DFT method is shown as the inset.

The morphology of **COF-IL** was also examined by scanning electron microscope (SEM). As indicated in Fig. 1c, it was obtained as uniform micro-meter nanofibers (0.8-1.2  $\mu$ m) with diameter of ca. 60 nm, indicating its phase purity. To examine the permanent porosity of **COF-IL**, its N<sub>2</sub> adsorption property at 77 K was performed. As shown in Fig. 1d, the N<sub>2</sub> adsorption-desorption curve of **COF-IL** showed a type-I isotherm microporous structure. The N<sub>2</sub> uptake amount is 197 cm<sup>3</sup>/g, and its Brunauer-Emmett-Teller (BET) specific surface area was 291 m<sup>2</sup>/g. The average pore size distributions were centred as 16.5 and 22.2 Å respectively, which are in good agreement with the proposed crystal model.

#### Selective CO<sub>2</sub> adsorption of COF-IL

Considering the relatively large porosity and the high-density imidazolium-based IL groups in COF-IL, its selective  $CO_2$  adsorption over  $CH_4$  and  $N_2$  was expected.<sup>36</sup>

As illustrated in Fig. 2a and b, **COF-IL** gave a  $CO_2$  uptake amount of 106.04 cm<sup>3</sup>/g at 273 K and 59.37 cm<sup>3</sup>/g at 298 K under 1 atm, respectively. It was different from  $CO_2$ , only a small amount of  $CH_4$  (19.15 cm<sup>3</sup>/g at 273 K, and 11.88 cm<sup>3</sup>/g at

298 K), N<sub>2</sub> (7.29 cm<sup>3</sup>/g at 273 K, and 5.24 cm<sup>3</sup>/g at 298 K), and  $H_2$  (1.36 cm<sup>3</sup>/g at 273 K, and 0.78 cm<sup>3</sup>/g at 298 K) uptake was observed for COF-IL under the same conditions. In addition, the isosteric analysis of CO<sub>2</sub> adsorption isotherms collected at various temperatures allowed an estimation of the coveragedependent isosteric heat of adsorption (Q<sub>st</sub>), where the behaviour of this function was determined by the relative magnitudes of the adsorbent-adsorbate and adsorbateadsorbate interactions. On the basis of CO2 adsorption isotherms at 273 and 298 K, the  $Q_{st}$  of  $CO_2$  was then calculated by the virial method. As shown in Fig. 2c, the  $Q_{st}$  value for  $CO_2$ is 28.8-30.2 kJ/mol, being much higher than those of CH<sub>4</sub>, N<sub>2</sub>, and H<sub>2</sub> (CH<sub>4</sub> 14.8~17.3, N<sub>2</sub> 8.9~12.2, H<sub>2</sub> 8.2~10.5 kJ/mol, Fig. S16, ESI<sup>†</sup>). The higher  $Q_{st}$  of **COF-IL** for CO<sub>2</sub> can be ascribed to the high density of the embedded imidazolium-IL sites on it. To predict the CO<sub>2</sub> selective adsorption over N<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> under ambient conditions, the ideal adsorption selectivity toward 50 : 50 of  $CO_2/CH_4$ ,  $CO_2/N_2$  and  $CO_2/H_2$  binary mixtures was calculated from the ratio of the initial slopes in the lowpressure Henry region of the single-component gas adsorption isotherms. At 273 K, the  $CO_2/N_2$ ,  $CO_2/CH_4$  and  $CO_2/H_2$ 

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selectivity of **COF-IL** was up to 43.38, 15.95, and 235.37 respectively (Fig. S17, ESI<sup>+</sup>). At 298 K, the adsorptive selectivity of **COF-IL** for the equimolar  $CO_2/N_2$ ,  $CO_2/CH_4$ , and  $CO_2/H_2$  mixtures was separately up to 58.96, 13.85, and 216.98 (Fig.

S18, ESI†), which clearly resulted from the imidazolium LL  $GQ_{2\overline{c}}$  philic sites (Table 1). The excellent select  $Wity_10fCOF$  The for  $CO_2$  over N<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub> is comparable to that of UiO-66-based MOF material, which was reported by us recently.<sup>14</sup>



# Synthesis and characterization of COF-IL@chitosan composite aerogel

Eco-friendly and low-cost chitosan is a naturally occurring polymer and its thiol-functionalized derivative has been demonstrated to be an outstanding excipient which can enhance in situ gelling and mucoadhesiveness.<sup>37</sup> Thus, the thiol-attached chitosan (chitosan-SH) was chosen as the polymer binder to construct the COF-polymer composite aerogel.





Fig. 3 (a) Fabrication of COF-IL@chitosan aerogel. (b) COF-IL crystalline solids. (ce) photographs of the generated COF-IL@chitosan aerogel with various shapes based on different moulds (COF-IL, 80 wt %). (f) Pressing test of the column aerogel conducted with a 250 g balance weight.

As shown in Fig. 3a, the covalently cross-linked hybrid aerogel of **COF-IL@chitosan** was prepared by combination of the thioldecorated chitosan<sup>32</sup> and allyl-attached crystalline powdered **COF-IL** (Fig. 3b) in an acidic aqueous medium. After ultrasonic shaking, the obtained sticky composite dispersion was allowed to stand at room temperature for several hours until the robust hydrogel was generated. Once exposed to UV light (365 nm, 300 W) for 0.5 h with 2-hydroxy-2-methylpropiophenone (HMPP), the formed covalently cross-linked hydrogel via thiol-

ene reaction was placed in a cooler for ca. 12 h to afford ice crystals. After freeze-drying at -50 °C for 24 h to remove the template, three-dimensional macroporous ice а COF@chitosan aerogel was eventually generated. As indicated in Fig. 3c-e, the COF-IL@chitosan aerogel can be readily processed and obtained in various desired shapes by simply changing the moulds during hydrogel forming process, although the COF loading in COF-IL@chitosan was up to 80 wt%. In addition, the obtained shaped aerogels were lightweight (density in the range of 0.032 - 0.035 g cm<sup>-3</sup>) and robust. For example, they are able to withstand pressing conducted with a 250 g balance weight, indicating their good mechanical behaviour. In addition, a highest strength of 13.8 MPa could be achieved for the cylindrical aerogel (12 mm in height, 20 mm in diameter) within 0~75 % compressed strain (Fig. S19, ESI†).

In order to confirm the formation of thioether linkage, the obtained aerogel was characterized by FT-IR spectra and solid state <sup>13</sup>C CP-MAS NMR (Fig. S20 and S21, ESI<sup>†</sup>). In FT-IR spectra, the peaks of C=C at 1628 cm<sup>-1</sup> in **COF-IL** and S-H at 2568 cm<sup>-1</sup> in chitosan-SH basically disappeared after the reaction. Meanwhile, the characteristic peak at 1073 cm<sup>-1</sup> associated with C-S-C appeared, indicating the formation of thioether linkage, which was further supported by the new resonance peaks at 36.5 and 23.2 ppm in <sup>13</sup>C CP-MAS NMR corresponding to the carbon atoms on the C-S-C and C-C moieties.

In addition, the structural integrity and uniform dispersion of COF species in the aerogel was demonstrated by SEM and PXRD measurement. As shown in the surface and cross-sectional images (Fig. 4a-c), the **COF-IL** nanofibers are homogeneously blended in the polymer phase and no any detectable interface boundary was observed, demonstrating that the "covalently composite approach" is a very powerful tool to fabricate the highly homogeneous, robust, and shaped COF-based hybrid porous materials. PXRD pattern of the **COF-IL@chitosan** aerogel showed that the **COF-IL** structural integrity and crystallinity were well-maintained in the composite sponge-like aerogel (Fig. 4d).

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Fig. 4 (a-c) SEM images of COF-IL@chitosan aerogel (COF-IL, 80 wt %). (d-f) PXRD patterns, TGA traces and N<sub>2</sub> adsorption isomers (at 77K) of COF-IL@chitosan, COF-IL and chitosan-SH aerogel, respectively.

Moreover, as revealed by the thermogravimetric analysis (TGA), both COF-IL and COF-IL@chitosan showed almost no weight loss up to 230 °C, suggesting their good thermal stability (Fig. 4e). As the ice-templating generated macropores did not significantly contribute to the surface area, so the COF-IL@chitosan showed a decreased N<sub>2</sub> adsorption capacity (162.6 cm<sup>3</sup>/g) and a less BET specific surface area (103.3 m<sup>2</sup>/g) in comparison with the COF-IL crystals. On the other hand, the involved COF crystals significantly enhanced the gas capacity and BET specific surface area of the pure chitosan-SH aerogel (3.05 cm<sup>3</sup>/g and 4.67 m<sup>2</sup>/g) (Fig. 4f). The chemical stability of the COF-IL@chitosan aerogel in different solvent was also examined. It is different from the pure chitosan aerogel, the covalently cross-linked hybrid aerogel was very stable in water and common polar organic solvents such as acetone and ethanol (Fig. S22, ESI<sup>+</sup>), making it possible for COF-IL@chitosan to be practical material.

#### Selective CO2 adsorption of COF-IL@chitosan

Owing to the high **COF-IL** loading (80 wt % **COF-IL**), we inferred that **COF-IL@chitosan** should also display a high affinity for  $CO_2$  other than  $N_2$  and  $CH_4$  (Table 1).

As illustrated in Fig. 5, the CO<sub>2</sub> uptake of COF-IL@chitosan was 38.77 cm<sup>3</sup>/g at 273 K and 25.83 cm<sup>3</sup>/g at 298 K under 1 atm. In contrast, only a small amount of  $CH_4$  (8.27 cm<sup>3</sup>/g at 273 K, and 6.21 cm<sup>3</sup>/g at 298 K),  $N_2$  (3.41 cm<sup>3</sup>/g at 273 K, and 2.02  $cm^3/g$  at 298 K), and H<sub>2</sub> (1.04  $cm^3/g$  at 273 K, and 0.41  $cm^3/g$  at 298 K), loading was detected under the same conditions. For comparison, the gas adsorption behaviour of the pure chitosan-SH aerogel was also measured herein, and its CO<sub>2</sub>, CH<sub>4</sub> and  $N_2$  uptake was found to be only 6.38, 4.80 and 2.80 cm<sup>3</sup>/g at 273 K under 1 atm. At 298 K, even lower CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> uptake as 5.14, 3.20 and 1.71 cm<sup>3</sup>/g was observed (Fig. S23, ESI<sup> $\dagger$ </sup>). After incorporation with **COF-IL**, the high CO<sub>2</sub> selectivity was maintained, and the ideal adsorption selectivity toward 50 : 50 of  $CO_2/N_2$ ,  $CO_2/CH_4$ , and  $CO_2/H_2$  binary mixtures was 93.65, 20.2, and 153.96 at 273K (Fig. S24, ESI<sup>+</sup>), and it was 98.82, 11.73, and 123.94 at 298 K, respectively (Fig. S25, ESI<sup>+</sup>). The isosteric analysis of CO<sub>2</sub> adsorption isotherms collected at various temperatures for COF-IL@chitosan showed a significantly improved Q<sub>st</sub> value (16.3~25.2 kJ/ mol) than that of the pure chitosan-SH aerogel (4.7~8.3 kJ/ mol) for CO2 adsorption. The corresponding data for gas adsorption and selectivity were summarized in Table 1.

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Fig. 5 (a and b) CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> adsorption isotherms of COF-IL@chitosan aerogel at 273 K and 298 K, respectively, (c) the isosteric heat of CO<sub>2</sub> adsorption for chitosan-SH, COF-IL, and COF-IL@chitosan.

able 1 Gas adsorption be	ehavior of <b>C</b>	COF-IL, Chitosan-SH	, and COF-IL@chitos	san		ideal ad			
sample	т (К)	adsorption	adsorption	adsorption	adsorption				Q <sub>st</sub> for CO <sub>2</sub> (kJ/mol)
		(cm³/g)	(cm³/g)	(cm³/g)	(cm³/g)	$CO_2/N_2$	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /H <sub>2</sub>	
COF-IL	273	106.04	19.15	7.29	1.36	43.38	15.95	235.37	28.8~30.2
	298	59.37	11.88	5.24	0.78	58.96	13.85	216.98	
chitosan-SH	273	6.38	4.80	2.80	0.49	11.32	3.09	25.04	4.7~8.3
	298	5.14	3.20	1.71	0.21	15.95	3.52	28.47	
COF-	273	38.77	8.27	3.41	1.04	93.65	20.02	153.96	
IL@chitosan									16.3~25.2
(COF, 80 wt%)	298	25.83	6.21	2.02	0.41	98.82	11.73	123.94	

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#### Catalytic activity of COF-IL and COF-IL@chitosan

With this imidazolium-IL decorated COF, we wondered if **COF-IL** herein could promote CO<sub>2</sub> cycloaddition reactions with epoxides, especially under mild conditions without the aid of co-catalyst such as *n*-Bu<sub>4</sub>–NBr (TBAB). On the other hand, aromatic epoxy such as styrene oxide was considered as the less active substrate for CO<sub>2</sub> cycloaddition based on the previous studies. For example, the reported MOF- and COFcatalysed CO<sub>2</sub>-styrene oxide cycloaddition yields were in a range of 32.7–93.9 % even under more vigorous conditions, including higher CO<sub>2</sub> pressure and temperature, and/or the cocatalyst assistance.<sup>38-41</sup> For above reasons, we initially took the CO<sub>2</sub> cycloaddition with styrene oxide as the model reaction to examine the catalytic activity of **COF-IL** with 1 atm CO<sub>2</sub> in the absence of TBAB as the co-catalyst.

As shown in Fig. 6a, the effect of temperature, reaction time, and amount of the catalyst for the model reaction was systematically investigated. The results indicated that the

catalytic performance of COF-IL exhibited a positive correlation with the increase of reaction temperature, catalyst amount, and reaction time. For example, the cycloaddition yield increased from 4 to 97 % within 120 h as the temperature changed from 25 to 80 °C in the presence of 1.5 mol % COF-IL under solvent-free conditions. In addition, when the reaction was carried out with a lower catalyst loading, 1.0 mol% instead of 1.5 mol%, the cycloaddition product was isolated in a lower 89 % yield within 120 h under the same conditions. As in the case of higher catalyst loading at 3.0 mol%, the corresponding cycloaddition product was isolated in 98 % yield but within only 48 h (Fig. S26, ESI<sup>+</sup>). On the basis of these results, the optimal conditions for the model CO<sub>2</sub> cycloaddition could set as solvent free, 1 atm of CO<sub>2</sub>, 1.5 mL (13.0 mmol) of epoxy styrene, 3.0 mol% of COF-IL, 80 °C of temperature, and 48 h of reaction time. Compared to other reported MOF- and COFbased catalysts, COF-IL herein showed the best catalytic performance for the less active styrene oxide without TBAB assistance. As a comparison, the COF of TpTe-1<sup>31</sup> without IL-

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groups showed almost no catalytic performance ( $\leq$ 5.0 % yield) for the CO<sub>2</sub> cycloaddition reaction under the same conditions (80 °C, 48 h, 3.0 mol % of the catalyst, Fig. S27, ESI†). We believe that the mechanism of the catalytic CO<sub>2</sub> cycloaddition with epoxide into cyclic carbonate over **COF-IL** is similar to those of the reported works,<sup>39-41</sup>The process could be subdivided into four detailed ones. That is, firstly, the epoxide ring is activated by the weak interaction between the epoxide O atom and the C-H site of the imidazolium group. Secondly, the activated epoxide ring is attacked by Br<sup>-</sup> at the site of lesshindered C atom in the weakly coordinated epoxide to open the ring and form the anionic intermediate. Thirdly,  $CQ_{2}$  is entry into the formed anionic intermediate associated with electron transfer between O atoms to generate alkylcarbonate anion. Finally, the alkylcarbonate anion was converted into the cyclic carbonate via intramolecular substitution of halide and the ring-closing step, meanwhile, the imidazolium in **COF-IL** is regenerated for the nest catalytic run (Fig. S28, ESI†). Thus, the relatively large pore size and high imidazolium loading of **COF-IL** should be the dominating factor for this highly efficient  $CO_2$  cycloaddition under the given conditions.



Fig. 6 (a) Effect of temperature, reaction time, and catalyst amount on the COF-IL-catalysed CO<sub>2</sub> cycloaddition with styrene oxide. (b) Reaction time examination (black line) and leaching test (red line) for CO<sub>2</sub> cycloaddition with styrene oxide catalysed by COF-IL. Reaction conditions: solvent free, epoxy styrene (13.0 mmol, 1.5 mL), CO<sub>2</sub> (1 atm), 80 °C, COF-IL (232 mg, 3.0 % mol). The solid catalyst of COF-IL was filtered from the reaction solution after 24 h, whereas the filtrate was transferred to a new vial and the reaction was continued for an additional 36 h. (c) Catalytic cycles. (d) Corresponding PXRD patterns for each catalytic cycle.

To gain insight into the heterogeneous nature of **COF-IL**, the hot leaching test was performed. As shown in Fig. 6b, no further reaction occurred without **COF-IL** after ignition of the reaction at 24 h, implying that **COF-IL** herein exhibited a typical heterogeneous catalyst nature. In addition, the recyclability of **COF-IL** was also examined. As shown in Fig. 6c, **COF-IL** still showed an excellent activity and the yield was up to 98 % even after five catalytic cycles. The PXRD data indicated that the crystallinity and structural feature of **COF-IL** were still well maintained (Fig. 6d). The content of Br element after five catalytic runs was determined as 13.21% by ICP, which is in consistent with that of the original **COF-IL** (13.24%). Thus, the porous **COF-IL** herein is an ideal bifunctional porous material for CO<sub>2</sub> selective adsorption and its chemical conversation.

With above results in hand, the scope and generality of the **COF-IL**-catalysed  $CO_2$  cycloaddition was examined. Besides styrene oxide (Table 2, entry 1), **COF-IL** was applicable to other

kinds of epoxides except extremely long hexadecyl-attached epoxide (Table 2, entries 1-7). Under the optimized reaction conditions, epichlorohydrin and epibromohydrin (Table 2, entries 2-3) showed very high activity for the CO<sub>2</sub> cycloaddition, and they gave excellent 98% and ~100% yields within 48 h (Fig. S29 and S30, ESI<sup>+</sup>). For long alkyl chain attached 1,2-epoxyoctane and allyl glycidyl ether (Table 2, entries 4-5), the corresponding cyclic carbonates were obtained in good-to-excellent yields ranging from 89 % to 97 % within 48 h (Fig. S31 and S32, ESI<sup>†</sup>). The reaction of CO<sub>2</sub> with the phenyl-substituted epoxide like glycidyl phenyl ether (Table 2, entry 6), however, gave a moderate 71 % yield (Fig. S33, ESI<sup>†</sup>). Also, we tried the CO<sub>2</sub> cycloaddition with extremely long chain substituted epoxide of 1,2-epoxyoctadecane (Table 2, entry 7), but only 7 % yield was detected (Fig. S34, ESI<sup>+</sup>), which might result from its limited diffusion within the COF framework due to the attached long alkyl chain.

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For practical application, together with the advantages of COF@chitosan aerogel, we designed and fabricated a cuplike reactor in situ templated by split-flask as a simplified fixed-bed catalytic model for CO<sub>2</sub> cycloaddition (Fig. 7a-c, Fig. S35, ESI<sup>+</sup>). In this way, the aerogel was easily shaped and fixed within a larger reaction container, therefore, the reaction scale could be dramatically amplified. As shown in Table 2 (entry 8) and Fig. 7d, when 175 mL (1.53 mol) epoxy styrene was used instead of 1.5 mL (13.0 mmol) to perform the reaction in the cuplike reactor (16.8 g aerogel, 1.5 mol % COF-IL equiv) at 80 °C for 72 h, the CO<sub>2</sub> cycloaddition smoothly proceeded and the product was obtained in 91% yield (Fig. S36, ESI<sup>+</sup>). Thus, the catalytic activity of COF-IL was well maintained within the aerogel-based cuplike reactor. After reaction, the productcatalyst separation was easy, and the cuplike reactor could be directly used for the next catalytic cycle by the simply acetone washing and vacuum drying procedures. It was noteworthy that the cuplike COF@chitosan aerogel was very stable and robust, and it could be reused at least five times without loss of its catalytic activity. The CO<sub>2</sub> cycloaddition yield for epoxy styrene in the fifth run was still up to 89 % yield (Fig. 7e and Fig. S37, ESI<sup>†</sup>). Additionally, the PXRD patterns showed that the crystallinity of COF-IL was well kept during the reusable catalytic process (Fig. 7f).

Table 2  $\text{CO}_2$  cycloaddition with substituted epoxides catalysed by COF-IL and COF-IL@chitosan^

entry	substrate	<b>COF-IL</b> (mol%) <sup>b</sup>	т (°С)	t (h)	yield (%) <sup>c</sup>
1		3.0	80	48	98
2	CI	3.0	80	48	98
3	Br	3.0	80	48	~100
4		3.0	80	48	97
5		3.0	80	48	89
6		3.0	80	48	71
7		3.0	80	48	7
8 <i>d</i>	A − A − A − A − A − A − A − A − A − A −	1.5	80	72	91

<sup>a</sup> Reaction conditions: 13.0 mmol of epoxide, 1 atm of CO<sub>2</sub>, solvent-free, COF-IL equiv. Calculated based on the number of active sites on <u>CoF-USP</u> (CoF-USP) (Correct determined by <sup>1</sup>H NMR spectra. <sup>d</sup> Scale-up experiment based on cuplike aerogel reactor: 175 mL (1.53 mol) of epoxy styrene, 1 atm of CO<sub>2</sub>, 16.8 g of COF-IL@chitosan (1.5 mol % COF-IL equiv), solvent-free.



**Fig. 7** (a-c) Top and side photographic views of the cuplike **COF-IL@chitosan** aerogel reactor. (d) Reaction monitoring. Reaction conditions: styrene oxide (1.53 mol, 175 mL), CO<sub>2</sub> (1 atm), aerogel (16.8 g, 1.5 mol % **COF-IL** equiv), 80 °C, solvent free. (e) Catalytic cycles. After each run, the reaction solution was poured out, and the cuplike aerogel was washed with acetone and dried in vacuum. (f) Corresponding PXRD patterns of the cuplike aerogel reactor after each catalytic cycle.

#### Conclusions

In summary, a new allyl-imidazolium-IL decorated COF-IL was successfully designed synthesized, and it exhibited a highly CO2 selective adsorption over N<sub>2</sub> and CH<sub>4</sub> under ambient conditions. Moreover, the obtained COF-IL can be a highly active heterogeneous catalyst to promote CO<sub>2</sub> chemical conversion by the cycloaddition with epoxides under mild conditions without co-catalyst assistance. In addition, we prepared a novel COF-IL@chitosan aerogel based on COF-IL and chitosan-SH polymer binder with a remarkably high COF loading (up to 80 wt%) via covalent composite approach by photoinduced thiol-ene click reaction. The generated chemically cross-linked aerogel was robust, uniform and processable, but with COF-IL crystallinity and functionalities. More importantly, the processable COF-IL@chitosan aerogel could be used to fabricate a highly efficient and reusable aerogel-based cuplike reactor, by which the COF-catalysed CO<sub>2</sub> cycloaddition scale was significantly enlarged. Hopefully, the results reported herein can bridge the crystalline powdered COFs and the COFs-based setups, furthermore, make COFs practical applications available.

#### **Conflicts of interest**

There are no conflicts to declare.

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- Notes and references
- 1 C. Martín, G. Fiorani, A.W. Kleij, *ACS Catal.*, 2015, **5**, 1353–1370.
- A. Dibenedetto, A. Angelini, P. Stufano, J. Chem. Technol. Biotechnol., 2014, 89, 334–353.
- 3 N. Kielland, C. J. Whiteoak, A. W. Kleij, *Adv. Synth. Catal.*, 2013, **355**, 2115–2138.
- 4 M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kuhn, *Angew. Chem., Int. Ed.,* 2011, **50**, 8510–8537.
- 5 S. Klaus, M. W. Lehenmeier, C. E. Anderson, B. Rieger, *Chem. Rev.*, 2011, **255**, 1460–1479.
- 6 A. Decortes, A. M. Castilla, A. W. Kleij, Angew.Chem., Int. Ed., 2010, 49, 9822–9837.
- 7 G. Fiorani, W. S. Guo, A. W. Kleij, *Green Chem.*, 2015, **17**, 1375–1389.
- 8 W. Jeong, J. Kim, J. Phys. Chem. C, 2016, 120, 23500-23510.
- 9 S. Ravi, D. H. Kang, R. Roshan, J. Tharun, A. CKathalikkattil, D. W. Park, *Catal. Sci. Technol.*, 2015, **5**, 1580–1587.
- 10 R. S. Patil, D. Banerjee, C. Zhang, P. K. Thallapally, J. L. Atwood, *Angew. Chem.*, 2016, **128**, 4599–4602.
- 11 J. Li, D. G. Jia, Z. G. Guo, Y. Q. Liu, Y. Lyu, Y. Zhou, J. Wang, Green Chem., 2017, 19, 2675–2686.
- 12 J. M. Yu, L. H. Xie, J. R. Li, J. R. Ma, Y. G. Ma, J. M. Seminario, P. B. Balbuena, *Chem. Rev.*, 2017, **117**, 9674–9754.
- 13 L. G. Ding, B. J. Yao, W. L. Jiang, J. T. Li, Q. J. Fu, Y. A. Li, Z. H. Liu, J. P. Ma, Y. B. Dong, *Inorg. Chem.*, 2017, **56**, 2337–2344.
- 14 B. J. Yao, L. G. Ding, F, Li, J. T. Li, Q. J. Fu, Y. J. Ban, A. Guo, Y. B. Dong, ACS Appl. Mater. Interfaces, 2017, 9, 38919–38930.
   15 M. L. Ding, H. L. Bing, ACS Control. 2019, 9, 2404, 2204.
- M. L. Ding, H. L. Jiang, ACS Catal., 2018, 8, 3194–3201.
   S. Y. Ding, W. Wang, Chem. Soc. Rev., 2013, 42, 548–568.
- 17 C. S. Diercks, O. M. Yaghi, *Science*, 2017, **355**, No. eaal1585.
- 18 X. Feng, X. S. Ding, D. L. Jiang, Chem. Soc. Rev., 2012, 41, 6010–6022.
- 19 H. Furukawa, O. M. Yaghi, J. Am. Chem. Soc., 2009, 131, 8875–8883.
- 20 S. Dalapati, S. B. Jin, J. Gao, Y. H. Xu, A. Nagai, D. L. Jiang, J. Am. Chem. Soc., 2013, 135, 17310–17313.
- 21 S. Y. Ding, M. Dong, Y. W. Wang, Y. T. Chen, H. Z. Wang, C. Y. Su, W. Wang, J. Am. Chem. Soc., 2016, **138**, 3031–3037.
- 22 L. Chen, L. W. He, F. Y. Ma, W. Liu, Y. X. Wang, M. A. Silver, L. H. Chen, L. Zhu, D. X. Gui, J. Diwu, Z. F. Chai, S. Wang, ACS Appl. Mater. Interfaces, 2018, **10**, 15364–15368.
- 23 J. R. Fu, S. Das, G. L. Xing, T. Ben, V. Valtchev, S. L. Qiu, J. Am. Chem. Soc., 2016, 138, 7673–7680.
- 24 W. Ji, L. L., Y. H. Ling, C. Ching, M. Matsumoto, R. P. Bisbey, D. E. Helbling, W. R. Dichtel, J. Am. Chem. Soc., 2018, 140, 12677–12681.
- 25 D. A. Vazquez-Molina, G. S. Mohammad-Pour, C. Lee, M. W. Logan, X. F. Duan, J. K. Harper, F. J. Uribe-Romo, J. Am. Chem. Soc., 2016, **138**, 9767–9770.
- 26 S. Chandra, T. Kundu, T. Kandambeth, R. BabaRao, Y. Marathe, S. M. Kunjir, R. Banerjee, *J. Am. Chem. Soc.*, 2014, 136, 6570–6573.
- 27 S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. G. Song, C. Y. Su, W. Wang, J. Am. Chem. Soc., 2011, 133, 19816–19822.
- 28 J. Zhang, X. Han, X. W. Wu, Y. Liu, Y. Cui, J. Am. Chem. Soc., 2017, 139, 8277–8285.
- 29 H.-C. Ma, J.-L. Kan, G.-J. Chen, C.-X. Chen, Y.-B. Dong, Chem. Mater., 2017, 29, 6518–6524.
- 30 B.-J. Yao, J.-T. Li, N. Huang, J.-L. Kan, L. Qiao, L.-G. Ding, F. Li, Y.-B. Dong, ACS Appl. Mater. Interfaces, 2018, 10, 20448–20457.

- 31 F. Li, L.-G. Ding, B.-J. Yao, N. Huang, J.-T. Li, Q.-J. Fu, Y.-B. Dong, J. Mater. Chem. A, 2018, 6, 11140-114.4639/C8TA12046C
- C. Müller, D. Rahmat, F. Sarti, K. A. Leithner, B. Schnürch, J. Mater. Chem. A, 2012, 22, 3899–3908.
- S. Kandambeth, A. Mallick, B. Lukose, M. V. Mane, T. Heine, T. Banerjee, J. Am. Chem. Soc., 2012, 134, 19524–19527.
- 34 Materials studio release notes ver. 7.0 (Accelrys Software),
- San Diego, 2008.
  B. P. Biswal, S. Chanda, S. Kandambeth, B. Lukose, T. Heine, R. Banerjee, *J. Am. Chem. Soc.*, 2013, **135**, 5328–5331.
- 36 S. J. Zeng, X. P. Zhang, L. Bai, X. C. Zhang, H. Wang, J. J. Wang, D., M. D. Li, X. Y. Liu, S. J. Zhang, *Chem. Rev.*, 2017, **117**, 9625–9673.
- 37 R. Mo, T. Y. Jiang, J. Di, W. Y. Tai, Z. Gu, Chem. Soc. Rev., 2014, 43, 3595–3629.
- 38 L. Liu, S. M. Wang, Z. B. Han, M. L. Ding, D. Q. Yuan, H. L. Jiang, *Inorg. Chem.*, 2016, **55**, 3558–3565.
- 39 Y. F. Zhi, P. P. Shao, X. Feng, H. Xia, Y. M. Zhang, Z. Shi, Y. Mu, X. M. Liu, J. Mater. Chem. A., 2018, 6, 374–382.
- 40 K. K. Xu, Y. H. Dai, B. F. Ye, H. M. Wang, *Dalton Trans.*, 2017, 46, 10780–10785.
- 41 J. Liang, R. P. Chen, X. Y. Wang, T. T. Liu, X. S. Wang, Y. B. Huang, R. Cao, *Chem. Sci.*, 2017, **8**, 1570–1575.

10 | J. Name., 2012, 00, 1-3

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Herein an allyl-imidazolium ionic liquid decorated COF and its covalent composite COF@chitosan aerogel, which can be the excellent selective  $CO_2$  adsorbents and chemical conversion catalysts, are reported.