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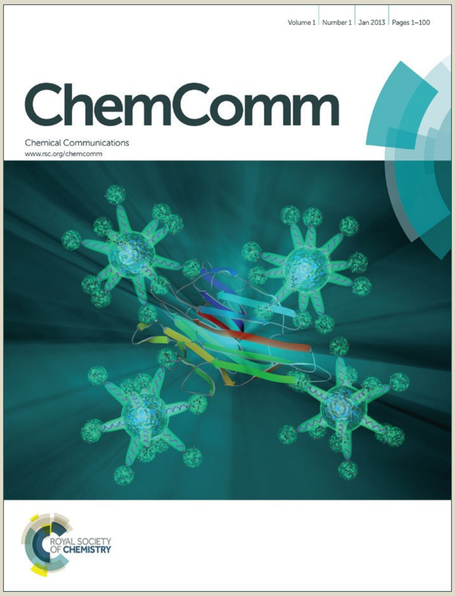

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Immobilization of Ionic Liquids to Covalent Organic Frameworks for Catalyzing Formylation of Amines with CO_2 and Phenylsilane

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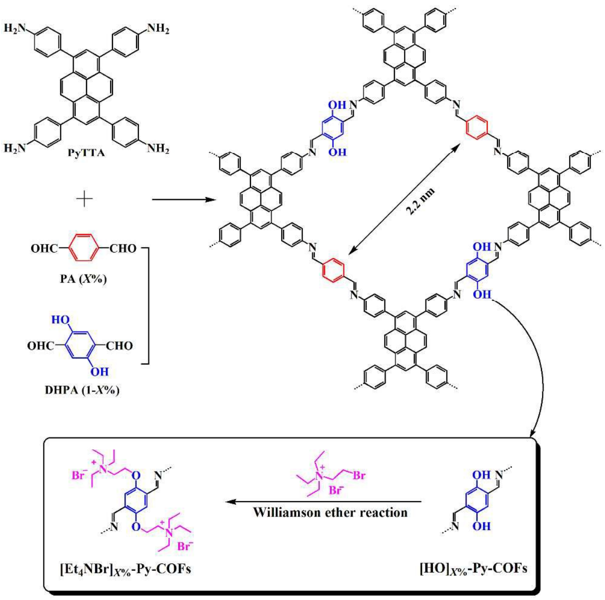
We presented the immobilization of ionic liquids on the channel walls of COFs by post-synthesis strategy. The ionic $[Et_4NBr]_{50\%}$-Py-COF afforded a high CO_2 adsorption capacity of 164.6 mg/g (1 bar, 273 K) and was developed as an effectively heterogeneous catalyst for transformation of CO_2 to value-added formamides under ambient conditions.

As an emerging class of porous and crystalline materials, covalent organic frameworks (COFs) are synthesized based on the principles of reticular chemistry, where organic building blocks with pre-designed geometries and radicals are linked through the formation of covalent bonds to give extended networks.[1–6] These materials exhibit periodic architectures, low densities, and high porosity, rendering them ideal candidates for various applications in catalysis,[7–10] gas storage and separation,[11–18] and optoelectronics.[19–22] The nanosized and charged pores in the ionic architectures exhibit special properties at adsorption and separation towards gas molecules.[23,24] The ionization approach or chemical modification with ionic compounds for the COF materials may afford an opportunity to fine-tune their structures and properties, through which the frameworks are charged either positively or negatively, coupled with counter ions. Due to the restriction of available building blocks, the reports on ionic COFs were limited.[8,25]

CO_2 contributes to global warming but also is a cheap, abundant C1 resource. The chemical fixation of CO_2 is significant since it allows the transformation of waste CO_2 to value-added products.[26–28] Formamides are important chemicals, generally produced through the formylation of amines. Using CO_2 for the formylation of N-H bonds is attractive yet challenging due to the thermodynamic stability of CO_2.[29–33] The reported systems basically suffered from drawbacks such as difficulty in catalyst recovery, requiring metal catalysts, or rigorous reaction conditions. Ordered one-dimensional (1D) open channels found in two-dimensional covalent organic frameworks are beneficial to the diffusion of substances, which facilitates mass transfer with chemical reactions.[7–10] Therefore, the targeted synthesis of two dimensional (2D) COFs can afford recoverable, metal-free catalytic systems for the transformation of CO_2.



Scheme 1 Synthesis of $[Et_4NBr]_{X\%}$-Py-COFs with the ionization of chanel walls through the Williamson ether reaction of $[HO]_{X\%}$-Py-COFs with (2-bromoethyl)triethylammonium bromide. The $[HO]_{X\%}$-Py-COFs were synthesized by the condensation of PyTTA with DHPA and PA at various molar ratios.

Herein, we described a postsynthetic strategy for the ionization of the channel walls in 2D COFs and presented its effectiveness in CO_2 adsorption and transformation to highly value-added formamides. Mesoporous imine-linked pyrene COFs were utilized as the scaffold, which were initially synthesized by a three-component condensation system (Scheme 1). 4,4′,4′′,4′′′-(Pyrene-1,3,6,8-tetrayl) tetraaniline (PyTTA) was used as the vertices and two linearly shaped dialdehyde monomers, namely 2,5-dihydroxyterephthalaldehyde (DHPA) and 1,4-phthalaldehyde (PA), at various molar ratios were used as edges. The COFs with different phenol contents on their channel walls were fabricated and

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nominated as $[HO]_{X\%}$-Py-COFs (X = 0, 25, 50, 75, 100), where X% represented the molar percentage of DHPA present in the dialdehyde blend. The immobilization of ionic liquids onto COFs was directly accomplished through the Williamson ether reaction between the phenol group in $[HO]_{X\%}$-Py-COFs and (2-bromoethyl)triethylammonium bromide ionic liquid (Scheme 1).[34] The ionization degree on the channel walls was modulated by controlling the content of phenol groups. The resulting ionic COFs were termed as $[Et_4NBr]_{X\%}$-Py-COFs (X = 25, 50). To the best of our knowledge, this is the first example that COFs have been successfully decorated with catalytically-active ionic compounds.

The crystalline nature of all the COFs was confirmed by powder X-ray diffraction (PXRD) measurements. The $[HO]_{0\%}$-Py-COF sample exhibited strong XRD peaks at 3.72, 5.23, 7.47, 8.67, 11.29, 15.17, and 23.69°, which were assignable to (110), (020), (220), (030), (040), (060), and (001) facets, respectively (Fig. 1a), similar to the reported $[HO]_{100\%}$-Py-COF.[35] The identical diffraction patterns were also observed for other $[HO]_{X\%}$-Py-COFs (Fig. S1). The $[Et_4NBr]_{X\%}$-Py-COFs (X = 25, 50) exhibited XRD patterns (Fig. 1b) similar to those of $[HO]_{X\%}$-Py-COFs, indicating that they owned the similar crystal structures. Nevertheless, the $[Et_4NBr]_{X\%}$-Py-PAFs (X = 75, 100) exhibited the amorphous frameworks (Fig. S2), indicating that the crystal structures were retained after modification only when the ionization degree on the channel walls was moderate. The following examinations were focused on the COF materials unless otherwise stated. The use of lattice modeling and Pawley refinement processes led to an eclipsed AA stacking model that could reproduce the PXRD results in the peak position and intensity with R_{wp} of 8.8% and R_p of 6.7% (Fig. S3). The unit cell was created with a $PMMN$ space group of a = 33.7188 Å, b = 32.6690 Å, c = 3.8206 Å, and $\alpha = \beta = \gamma = 90°$. By contrast, an alternatively staggered AB model did not match the observed data.

The three-component condensation reaction was allowed for the integration of phenol groups in $[HO]_{X\%}$-Py-COFs with a controlled manner (Table S1, Fig. S4,S5).[16,17] After modification, the $[Et_4NBr]_{X\%}$-Py-COFs (X = 25, 50) with controlled ion density were confirmed by several technologies. Fourier transform infrared (FTIR) spectroscopy (Fig. S4) and solid-state ^{13}C cross-polarization/magic-angel spinning (CP/MAS) NMR spectroscopy (Fig. S5) supported the grafted ionic liquids onto $[Et_4NBr]_{X\%}$-Py-COFs (X = 25, 50), implying the validity of this modification strategy. The contents of bromide ions across $[Et_4NBr]_{X\%}$-Py-COFs (X = 25, 50) were determined by ion chromatography (4.6% and 8.9%, respectively). The obtained values were lower than the theoretical values (8.1% and 13.2%, respectively), resulting from the incomplete conversion of the Williamson ether reaction. Thermogravimetric analysis (TGA) revealed that the $[Et_4NBr]_{X\%}$-Py-COFs (X = 25, 50) exhibited high thermal stability with the decomposition temperature over 300 °C (Fig. S6).

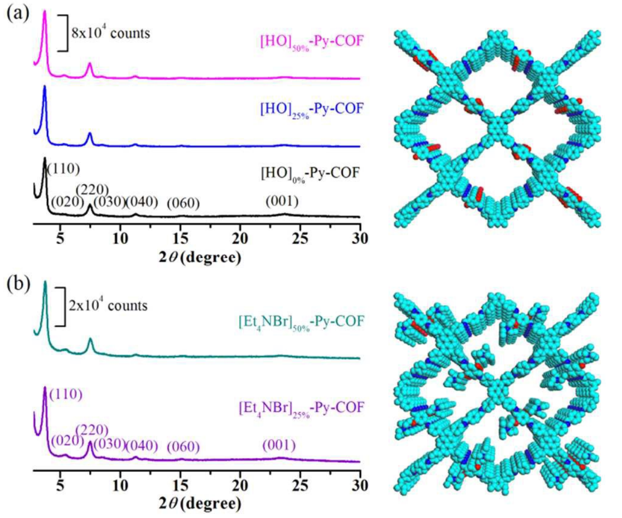

Fig. 1 PXRD patterns of (a) $[HO]_{X\%}$-Py-COFs (X = 0, 25, 50) and (b) $[Et_4NBr]_{X\%}$-Py-COFs (X = 25, 50). Right: Top views of $[HO]_{50\%}$-Py-COF and $[Et_4NBr]_{50\%}$-Py-COF. Carbon, cyan; nitrogen, blue; and hydrogen atoms and counter anions were omitted for clarity.

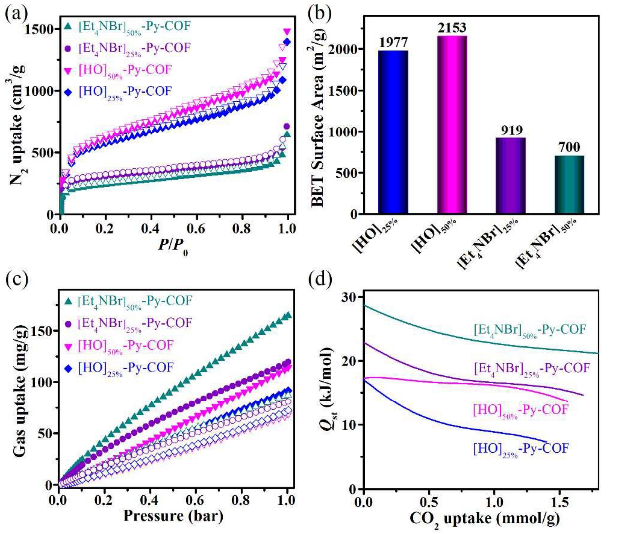

Fig. 2 (a) N_2 sorption isotherms measured at 77 K, (b) BET surface area, (c) CO_2 adsorption isotherms under 273 K (solid symbol) and 298 K (opean symbol), and (d) the respective isosteric heats of adsorption for CO_2 of $[HO]_{X\%}$-Py-COFs and $[Et_4NBr]_{X\%}$-Py-COFs (X = 25, 50).

The porous properties of the COFs were determined by nitrogen sorption isotherms measured at 77 K. The $[HO]_{X\%}$-Py-COFs exhibited typical type-IV isotherms characteristic of mesoporous nature (Fig. 2a and Fig. S7), while the $[Et_4NBr]_{X\%}$-Py-COFs (X = 25, 50) exhibited type-I isotherms (Fig. 2b). The Brunauer–Emmett–Teller (BET) surface area, pore volume, and pore size were all decreased, as expected, when $[HO]_{X\%}$-Py-COFs were modified through immobilization of ionic liquids (Fig. S8 and Table S2). These results indicated that the tetraalkylammonium cations together with counter anions occupied the pore space. Note that these COFs basically possessed one main type of pore in the framework as shown in the pore size distribution profiles (Fig. S9), revealing that the tetraalkylammonium cations were randomly integrated onto the pore walls of $[Et_4NBr]_{X\%}$-Py-COFs (X = 25, 50).

The CO_2 adsorption experiments were then performed at pressures up to 1 bar at 273 and 298 K (Fig. 2c). As listed in Table S3, the $[Et_4NBr]_{X\%}$-Py-COFs (X = 25, 50) exhibited elevated CO_2 uptake capacities and higher isosteric heats of adsorption (Q_{st}) (Fig. 2d and Fig. S10) than those of $[HO]_{X\%}$-Py-COFs, supporting the effectiveness of pore-wall functionalization for CO_2 capture. The $[Et_4NBr]_{50\%}$-Py-COF owned the CO_2 uptake capacity of 164.6 mg/g at

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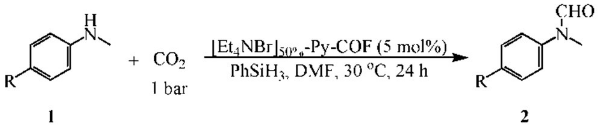
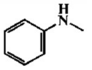
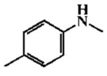
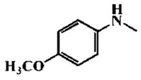
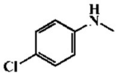
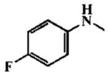
1 bar and 273 K, higher than the most reported COFs (Table S4). The high uptake and Q_{st} for CO_2 of $[Et_4NBr]_{X\%}$-Py-COFs can be mainly ascribed to the following factors: (i) after immobilization of ionic liquids on pore walls, the pore sizes are further reduced to be micropores, which enhances the performance of CO_2 capture and separation since micropores or ultramicropores dominate the low-pressure adsorption via pore-filling process;[36,37] (ii) the high positive charge density of the tetraalkylammonium cations strengthens their interaction with CO_2.[38]

Table 1 The $[Et_4NBr]_{50\%}$-Py-COFs catalyzed formylation of amines **1** with CO_2 and $PhSiH_3$ at room temperature.

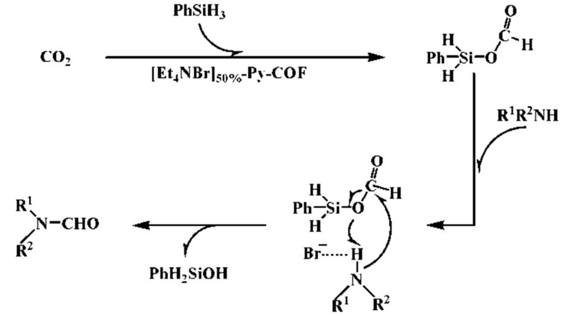


Entry	Amine substrates (**1**)	Product (**2**)	Yield (%)[a]
1	 (**1a**)	**2a**	94
2	 (**1b**)	**2b**	91
3	 (**1c**)	**2c**	92
4	 (**1d**)	**2d**	92
5	 (**1e**)	**2e**	88[b]

[a] Isolated yield. [b] Reaction time (48 h)

With the ionic liquids grafted on the channel walls, the ionic COFs were explored to act as the heterogeneous catalyst for the *N*-formylation reactions of different amines. In the initial experiments, the formylation of *N*-methylaniline (**1a**) with CO_2 and phenylsilane ($PhSiH_3$) was used as a model reaction. With the amount of 5 mol% $[Et_4NBr]_{50\%}$-Py-COF, the formylation of **1a** can occur at 1 bar CO_2 and 30 °C with DMF as the solvent. The solely formylated product **2a** was obtained with an isolated yield of 94% (Table 1, entry 1). Nevertheless, the $[HO]_{50\%}$-Py-COF showed a very low catalytic activity with the isolated yield of 32% under the same reaction conditions. Using the $[Et_4NBr]_{50\%}$-Py-COF as the catalyst, *N*-methylanilines with electron-donating (methyl methoxyl) or electron-withdrawing groups (4-choloro- and 4-fluoro-) were well tolerated, producing the formamides in excellent isolated yields (Table 1).

To gain insight into the role of the $[Et_4NBr]_{50\%}$-Py-COF, the ^1H NMR analysis was performed. From the ^1H NMR spectra of $PhSiH_3$ and its mixture with $[Et_4NBr]_{50\%}$-Py-COF in DMF (Fig. S11), the signal assigning to Si-H of $PhSiH_3$ was shifted from 4.16 to 4.12 ppm, suggesting the interaction between $PhSiH_3$ and $[Et_4NBr]_{50\%}$-Py-COF. In other words, the Si-H bond of $PhSiH_3$ was activated by $[Et_4NBr]_{50\%}$-Py-COF, which favored the insertion of CO_2. To confirm this, the mixture of $PhSiH_3$ and $[Et_4NBr]_{50\%}$-Py-COF in DMF was prepared at 30 °C and 1 bar CO_2, which was examined by ^1H NMR analysis after being stirred for 10 h and CO_2 release (Fig. S12). A new signal at 8.24 ppm was attributed to formoxysilane, demonstrating that the reaction of $PhSiH_3$ with CO_2 catalyzed by $[Et_4NBr]_{50\%}$-Py-COF. In addition, the chemical shift of N-H in amine was observed in the ^1H NMR spectra of *N*-methylaniline with $[Et_4NBr]_{50\%}$-Py-COF (Fig. S13), probably caused by the hydrogen bond between the amine and bromide ion of $[Et_4NBr]_{50\%}$-Py-COF. All these results suggested that the $[Et_4NBr]_{50\%}$-Py-COF behaved as a bifunctional catalyst, which activated $PhSiH_3$ to react with CO_2 yielding formoxysilane, and activated the amine through the hydrogen bond (Scheme 2). It can be assumed that the ordered open channels and high CO_2 uptake capacity of $[Et_4NBr]_{50\%}$-Py-COF allows formylation reactions to be conducted under mild conditions. As a heterogeneous catalyst, the $[Et_4NBr]_{50\%}$-Py-COF can be easily recovered from the reaction mixture by a simple filtration and reused for four times (Fig. S14). As evidenced by the decrease in the BET surface area and in the crystallization of the $[Et_4NBr]_{50\%}$-Py-COF after the fourth cycle (Fig. S15,S16), the slightly decreased activity was due to the pore channels blocked after repetitive recycling.



Scheme 2 Possible reaction mechanism of the $[Et_4NBr]_{50\%}$-Py-COF catalyzed formylation of amines using CO_2 and $PhSiH_3$ at room temperature.

In summary, we developed a postsynthetic approach to the immobilization of ionic liquids on the channel walls of COFs and demonstrated a metal-free method for the formylation of amine with CO_2 and $PhSiH_3$ catalyzed by the as-synthesized ionic COF. Different types of formamides were produced in excellent yields under 1 bar CO_2 and room temperature. The ordered open channels and high CO_2 uptake capacity of the ionic COF allows formylation reactions to be conducted under mild conditions. As a heterogeneous catalyst, the ionic COF can be reused at least four times without evident activity loss. We expect the ionic COFs would be modified through other charged guest molecules by means of ion exchange, making them a promising platform for various applications.

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