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In Situ Doping Strategy for the Preparation of Conjugated Triazine Frameworks Displaying Efficient CO_2 Capture Performance

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Supporting Information

ABSTRACT: An *in situ* doping strategy has been developed for the generation of a novel family of hexaazatriphenylene-based conjugated triazine frameworks (CTFs) for efficient CO_2 capture. The resulting task-specific materials exhibit an exceptionally high CO_2 uptake capacity (up to 4.8 mmol g^{-1} at 297 K and 1 bar). The synergistic effects of ultrananoporosity and rich N/O codoped CO_2-philic sites bestow the framework with the highest CO_2 adsorption capacity among known porous organic polymers (POPs). This innovative approach not only enables superior CO_2 separation performance but also provides tunable control of surface features on POPs, thereby affording control over bulk material properties. We anticipate this novel strategy will facilitate new possibilities for the rational design and synthesis of nanoporous materials for carbon capture.

The interest in curtailing greenhouse gas emissions through removal of CO_2 from flue gas of coal-fired power plants has inspired an extensive search for novel nanoporous materials capable of efficient physical adsorption of CO_2.[1−12] Porous organic polymers (POPs), an advanced class of porous materials, have emerged as a possible solution due to their overall stability and the ability to impart desirable functionalities for task-specific applications. Although much progress has been made in assembling multidentate organic building blocks to yield a wide variety of POP-based CO_2 adsorbents,[13−28] only moderate CO_2-uptake capacities were observed under conditions relevant to industrial carbon capture, where the CO_2 concentration is in the range of 10−15%. This underwhelming performance can largely be attributed the limited CO_2 affinity of POPs reported thus far. Inducing strong electrostatic interactions between the polarizable CO_2 and the material surface is expected to significantly increase the CO_2 capture performance. Unfortunately, conventional postsynthetic incorporation of CO_2-philic sites into the framework often results in a compromise of porosity of the adsorbent,[20] which plays another crucial role on carbon capture. Herein, we report an *in situ* doping strategy to create a novel family of POP-based adsorbents displaying superior adsorption toward CO_2 at low concentrations. The critical development is the preparation of an intrinsic ultrananoporous environment with abundant surface active sites with high affinity for CO_2 binding. Extensive ultrananoporosity imparts inherent molecular sieving capabilities to provide greater accessibility to CO_2-philic sites, therefore cooperatively enhancing the affinity of the materials for CO_2. This innovative approach not only enables us to achieve an exceptionally high CO_2 uptake for POPs but simultaneously provides a means to control the surface features, thereby tuning the properties of the material.

As shown in Scheme 1, we synthesized 3,7,11-trimethoxy-2,6,10-tricyano-1,4,5,8,9,12-hexaazatri-phenylene[29] (**HAT-3CN**) as our scaffold for the construction of task-specific conjugated triazine frameworks (**CTFs**). Among various types of POPs, **CTFs** possess high stability and excellent porosity in addition to intrinsic N-doping and have emerged as promising candidates for carbon capture.[30−33] While displaying adequate CO_2 uptake at higher pressures, these reported materials exhibit rather low CO_2 uptake at 0.15 bar (partial pressure of CO_2 in flue gas) and are not expected to be suitable for carbon capture under realistic conditions. We hypothesized that installation of a methoxy group in the **HAT-3CN** ring would achieve *in situ* incorporation of O-doped CO_2-philic sites on the surface of the material during the $ZnCl_2$-catalyzed high-temperature synthesis.[34,35] In addition to the intrinsic N-doped moieties, we expected these O-dopants would thus significantly enhance the CO_2 affinities of the resultant adsorbents (**HAT-CTFs**, Scheme 1).

We first studied the polymerization of **HAT-3CN** at 400 °C via a well-developed ionothermal technique.[32] As evidenced by the solid state ^{13}C NMR (Figure S1), the trimerization of **HAT-3CN** can be confirmed by the existence of a triazine ring with a peak around 166 ppm.[36] The absence of any signal attributable to a methoxy group indicates complete decomposition of this functionality, putatively achieving *in situ* introduction of O-doped CO_2-philic sites into the final material. However, due to the nature of the synthesis and the modest ordering of the final material, the precise location of these sites in the chemical structure cannot be precisely determined from NMR. Residual nitrile groups (113 ppm) were also observed for **HAT-CTF-400**, suggesting a higher temperature is required to achieve complete trimerization. The N_2 adsorption isotherm of **HAT-CTF-400** at 77 K was subsequently recorded to assess its Brunauer−Emmett−Teller (BET) surface area (Figure S2), which is

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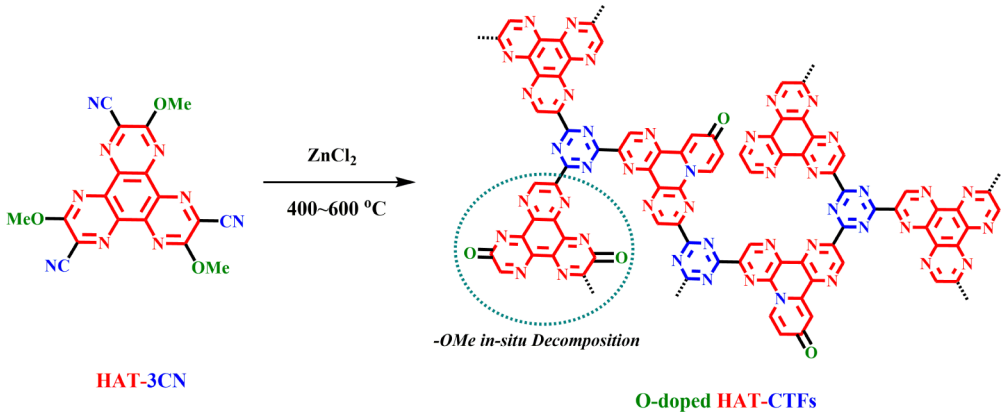
Scheme 1. Synthesis Route of Proposed O-Doped HAT-CTFs



much lower than expected (17 $m^2 g^{-1}$). This may be attributed to the planar structure of the **HAT**-based scaffold. However, to our delight, the CO_2 isotherm measured at 273 K reveals a permanent CO_2 uptake of 2.7 mmol g^{-1} (Figure 1a). Such

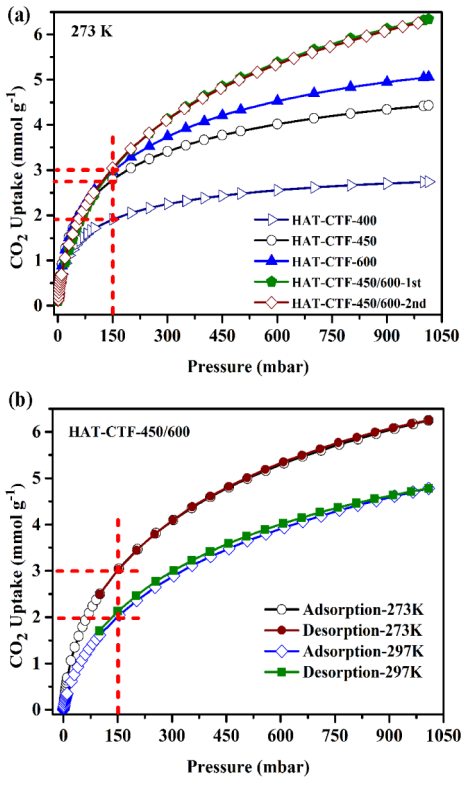


Figure 1. CO_2 uptake of **HAT-CTFs** at 273 K and 1 bar (a) and CO_2 adsorption−desorption of **HAT-CTF-450/600** at both 273 and 297 K. Red lines were used to highlight the uptake at 0.15 bar.

counterintuitive phenomena were also reported by Schröder et al. for a supramolecular organic framework derived CO_2 adsorbent. It was suggested that interactions between N_2 and the channel windows of the framework at 77 K may hinder the diffusion of N_2 into the material, resulting in the modest specific surface area.[37]

Trimerization reactions at higher temperatures were subsequently performed in an effort to enhance the BET surface areas of the resulting **HAT-CTFs**. As the synthesis temperature increased, the corresponding BET surface area was also enhanced (Table 1). We attribute this to the partial carbonization of the material,[29] supported by the solid state ^{13}C NMR spectrum

Table 1. Comparison of Structural Parameters and CO_2 Capture Performance of HAT-CTFs with Other High-Performing Porous Adsorbents

			CO_2 uptake (mmol g^{-1})	
sample	S_{BET} ($m^2 g^{-1}$)	temperature (K)	0.15 bar	1 bar
HAT-CTF-400	17	273	1.9	2.7
HAT-CTF-450	756	273	2.8	4.4
HAT-CTF-600	899	273	3.0	5.1
HAT-CTF-450/600	1090	273	3.0	6.3
		297	2.0	4.8
PPF-1[a]	1740	273		6.1
		295		3.35
bipy-CTF600[b]	2479	273		5.6
SU-MAC-500[c]	941	273		6.03
		298		4.5

[a]Reported in ref 38. [b]Reported in ref 31. [c]Reported in ref 10.

of **HAT-CTF-450/600** (prepared at 450 °C for initial 20 h and another 20 h at 600 °C), where weak and broad signals around ~151 and 137 ppm from aromatic carbons in **HAT** ring were observed. The characteristic peak from the triazine ring disappeared during this process, similar to previously reported **CTFs** prepared at 600 °C.[29] The resulting new materials display Type I adsorption profiles (Figure S2). Notably, the amorphous framework **HAT-CTF-450/600** (Figure S3) also possesses the largest BET surface area of 1090 $m^2 g^{-1}$. The existence of "ultra-nanopores," extensive subnanometer (<0.6 nm) material porosity, was demonstrated by a CO_2 isotherm at 273 K and analyzed by density functional theory modeling (Figure S4). The pore volume estimated from the CO_2 isotherm is 0.263 $cm^3 g^{-1}$ at P/P_0 = 0.99, suggesting vast potential for the application of **HAT-CTF-450/600** in CO_2 capture.

The CO_2 adsorption performance of **HAT-CTFs** were assessed by CO_2 isotherms performed at several different temperatures and 1 bar, revealing CO_2 uptake to be correlated with BET surface area. For example, **HAT-CTF-600** (S_{BET} = 899 $m^2 g^{-1}$) exhibits a better CO_2 adsorption (5.1 mmol g^{-1}) than that of **HAT-CTF-450** (S_{BET} = 756 $m^2 g^{-1}$, CO_2 uptake = 4.4 mmol g^{-1}). Despite **HAT-CTF-450/600** displaying a specific BET surface area lower than that of many previously reported **CTFs** (determined through N_2 adsorption isotherms),[31] an

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exceptionally high CO_2 uptake of 6.3 mmol g^{-1} was achieved (Figure 1a). This represents the highest CO_2 capacity for all POP-based adsorbents reported in the literature, as summarized in Table 1 and Table S1.[31,38] For example, Zhang et al. reported a porous polymer framework (PPF-1, S_{BET} = 1740 m^2 g^{-1}) with a CO_2 capacity at 1 bar of 6.07 mmol g^{-1} at 273 K and 3.35 mmol g^{-1} at 295 K,[38] while the best CTF-based adsorbent (bipy-CTF600, S_{BET} = 2479 m^2 g^{-1}) was previously reported by Lotsch et al. and adsorbs 5.58 mmol g^{-1} CO_2 at 273 K and 1 bar.[31] Therefore, to the best of our knowledge, **HAT-CTF-450/600** is the best POP-based adsorbent reported for carbon capture to date. More importantly, at 0.15 bar/273 K, **HAT-CTF-450/600** adsorbs 3.0 mmol g^{-1} CO_2, while at 297 K, this capacity decreases only modestly to 2.0 mmol g^{-1}, remaining significantly higher than that of a promising perfluorinated **CTF**-based adsorbent.[30] It should be noted that the adsorption of CO_2 at ~0.15 bar is more relevant to realistic carbon capture since flue gas contains approximately 15% CO_2 at total pressures of around 1 bar.[20] This CO_2 uptake achieved at 297 K and 1 bar (4.8 mmol g^{-1}, Figure 1b) also surpasses that of the polyamine-tethered porous polymer networks (4.3 mmol g^{-1}, 295 K, and 1 bar), which were previously the best POP-based adsorbents in the open literature.[19] On account of the partial carbonization within the framework **HAT-CTF-450/600**, we also compared the CO_2 storage performance with N-doped carbonaceous adsorbents, which often exhibit better CO_2 uptake than that of POP-based materials. Very recently, Bao et al. reported a N-doped carbon adsorbent (SU-MAC-500, S_{BET} = 941 m^2 g^{-1}) with an impressive CO_2 uptake of 6.03 mmol g^{-1} at 273 K and 1 bar, which is among the best of physisorptive micro- and mesoporous carbons.[10] The CO_2 capture capacities of **HAT-CTF-450/600** at either low or moderate pressure are superior to those of SU-MAC-500.

We propose that the synergistic effects of ultrananoporosity and abundant CO_2-philic surface sites play crucial roles in achieving this superior CO_2 capture performance. However, to provide a better understanding of the CO_2 adsorption in **HAT-CTF-450/600**, we have also calculated the isosteric heats of adsorption (Q_{st}) by fitting the CO_2 adsorption isotherms at 273 and 297 K and applying a variant of the Clausius−Clapeyron equation.[39] Q_{st} at low adsorption values was calculated to be 27.1 kJ mol^{-1} (Figure S5), suggesting a strong dipole−quadrupole interaction between the polarizable CO_2 molecules and framework **HAT-CTF-450/600**.[36] Pragmatically, this means the CO_2 sorption isotherms of **HAT-CTF-450/600** are effectively reversible (Figure 1b), affording a lower regeneration cost compared with conventional amine solutions.[19] Excellent reuse of **HAT-CTF-450/600** was demonstrated over five cycles of CO_2 adsorption at ~0.15 bar, confirming the electrostatic interaction partially responsible for CO_2 uptake is sufficiently weak to allow a facile regeneration of adsorbent (Figure S6).

We performed X-ray photoelectron spectroscopy (XPS) to study the active CO_2-philic sites on the surface of **HAT-CTF-450/600** in an effort to gain deeper insight into the interaction between the framework and CO_2 (Figure 2). Previous work has shown that the surface functionalities of the adsorbents have a profound effect on the low-pressure adsorption, where the uptake depends less on the BET surface area than on adsorbent−CO_2 interactions.[30] This is clearly evident when comparing **HAT-CTF-450/600** to the bipy-CTF600 reported by Lotsch et al.[31] Despite possessing a significantly larger BET surface area than that of **HAT-CTF-450/600** (2479 vs 1090 m^2 g^{-1}), better CO_2 uptake was obtained for our framework (5.6 vs 6.3 mmol g^{-1} of CO_2 at 273 K and 1 bar). We reasoned that N/O codoping

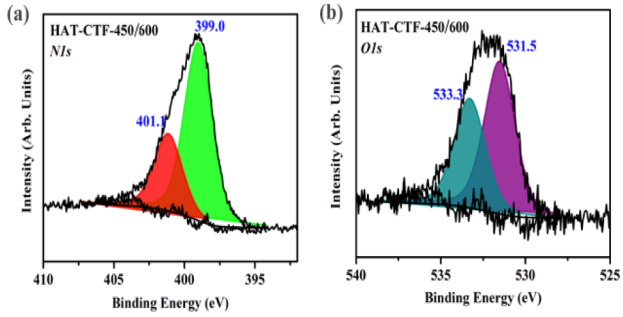

Figure 2. N 1s (a) and O 1s (b) XPS spectra of **HAT-CTF-450/600**.

could play an important role in carbon capture, and as anticipated, exceptionally high N-doping (32.8 at %) was achieved as a result of the N-rich **HAT** precursor. Pyridinic (399.0 eV, 68.9%) and pyrrolic nitrogen (401.1 eV, 31.1%) were the two different nitrogen species identified by XPS. These may serve as the binding sites for CO_2 uptake through electrostatic interaction,[31] as the incorporation of more N-containing sites in POPs has previously been demonstrated to improve CO_2 adsorption capacities. Additionally, we also successfully obtained a high O-doping content of 9.4 at. %. The binding energy of O 1s at 531.5 eV was assigned to O═C (58.2%) and at 533.3 eV to O−C (41.8%), with further support from analysis of the C 1s orbital (Figure S7). We believe these rich O-doped sites help to enhance the affinity of the material surface for CO_2 and facilitate **HAT-CTF-450/600**-CO_2 uptake.

The *in situ* incorporation of additional O-doped sites on the surface of **HAT-CTF-450/600** not only affected enhanced CO_2 uptake capacity but also afforded more preferential adsorption of CO_2 over N_2, i.e., higher CO_2/N_2 selectivity, another key factor for realistic carbon capture. The CO_2/N_2 selectivity for **HAT-CTF-450/600** was calculated to be 160 at 273 K by the ratio of the initial slopes of CO_2 and N_2 adsorption isotherms (Figures S8 and S9). A value of 126 was achieved at 297 K, ranking **HAT-CTF-450/600** among the most selective POP-based adsorbents (Table S1). CO_2/N_2 selectivity was also predicted using the ideal adsorption solution theory (IAST).[39,40] Under simulated flue gas streams (typically 15% CO_2 and 85% N_2), **HAT-CTF-450/600** exhibits high CO_2/N_2 selectivities at 1 bar (183 at 273 K and 110 at 297 K, Figure S10), which match well with those obtained from the initial slope method. This promising CO_2/N_2 selectivity further highlights the synergistic effects of ultrananoporosity and rich N/O codoped CO_2-philic sites within the polymeric architecture. As such, given the exceptionally high CO_2 uptake capacity and the intrinsic high thermal stability, this material may have potential for practical application in a postcombustion CO_2 capture.

In summary, an *in situ* doping strategy has been developed for the generation of a novel family of porous **HAT-CTF**-based adsorbents for efficient CO_2 capture. Significantly, at 297 K, **HAT-CTF-450/600** can adsorb 4.8 mmol g^{-1} of CO_2 at 1 bar (2.0 mmol g^{-1} at 0.15 bar) due to the synergistic effects of ultrananopores and abundant N/O codoped CO_2-philic sites. This impressive result bestows **HAT-CTF-450/600** with the highest CO_2 uptake capacity among known POPs. This innovative approach not only enables us to achieve an exceptionally high CO_2 uptake but also provides a means to control surface features of POPs and may open up new possibilities for the rational design and synthesis of new nanoporous materials for carbon capture.

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■ ASSOCIATED CONTENT

Supporting Information

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Experimental section, Figures S1−12, and Table S1 (PDF)

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Notes

The authors declare no competing financial interest.

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