Nitrogen-doped porous aromatic frameworks for enhanced CO₂ adsorption

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Abstract

Recently synthesized porous aromatic frameworks (PAFs) exhibit extremely high surface areas and exceptional thermal and hydrothermal stabilities. Using computer-aided design, we propose new PAFs, designated as NPAFs, by introducing nitrogen-containing groups to the biphenyl unit and predict their CO₂ adsorption capacities with grand canonical Monte Carlo (GCMC) simulations. Among various NPAFs considered, one with imidazole groups shows the highest adsorption capacity for CO₂ (11.5 wt% at 1 bar and 298 K), in comparison with 5 wt% for the parent PAF (PAF-1) at the same condition. At higher pressures (around 10 bar), however, another NPAF with pyridinic N groups performs much better than the rest due to its greater pore volume in addition to the N functionality. This study suggests that adding N functionality to the organic linkers is a promising way to increase CO₂ adsorption capacity of PAFs at ambient condition.

Keyword: CO₂ Capture, Porous Material, Material Design, Nitrogen-Doping, Molecular Simulation

1. Introduction

CO₂ capture and sequestration (CCS) is critically important in addressing the issue of global warming [1]. The U.S. Department of Energy (DOE) launched a carbon sequestration program in 2009 aiming to achieve 90% CO₂ capture at an increase in the cost of electricity of no more than 35% for the post-combustion process by 2020. One promising way to meet the DOE target is by finding proper porous materials that offer easy release of CO₂ compared to the conventional reactive sorbents such as aqueous ammonia and amine functionalized solids. Porous materials with a wide variety of topologies, pore sizes, and functionalities have been explored for CO₂ capture, including porous carbons, zeolites, metal-organic frameworks, and zeolitic-imidazolate frameworks [1-3]. For example, Yaghi et al. reported ultra-high porosity MOF-210 which has a BET surface area (6240 m²/g), one of the highest among all reported MOF materials, and exhibits a CO₂ uptake of 2396 mg/g at 50 bar and 298K [4]. Long et al. reported Mg-MOF-74, which shows high CO₂/CH₄/H₂ selectivity, even surpassing zeolite 13X – a commonly available and used microporous material for pressure swing adsorption [5].

One of the major drawbacks of existing nanoporous MOFs is their limited physicochemical stability. Recently, Ben et al. developed a new class of stable porous materials, porous aromatic frameworks (PAFs), with diamond-like structures held together by strong C-C covalent bonds [6]. Unlike most MOFs, PAF-1 shows exceptional thermal and hydrothermal stabilities. More interestingly, the PAF-1 framework provides a perfect platform for introducing functionalities on its biphenyl units. Zhou et al. synthesized a series of porous polymer networks (PPNs) [7-9], and among them, sulfonate-functionalized PPN-6 (PPN-6 is another name for PAF-1), shows high CO₂

uptake (~13 wt% at 298 K and 1 bar) [10]. Babarao et al. investigated PAFs functionalized with polar organic groups for CO₂ adsorption and separation, and found that the tetrahydrofuran- and ether-functionalized PAF-1 structures have high adsorption capacity for CO₂ at ambient conditions [11]. Their simulation also suggested that imine-linked interpenetrated frameworks with diamondoid structures would have high CO₂ uptake [12]. Cao et al. investigated the CO₂ storage and separation performance of new PAFs with longer phenyl-linked chains, and found that selectivity is closely related to the difference in isosteric heats of adsorption between different gases [13].

N-containing groups, however, have not been systematically investigated as potential functional groups in PAF frameworks for enhancing CO₂ adsorption, even though N-doped carbons have shown great potential for CO₂ capture [14-17]. For instance, newly synthesized microporous N-doped carbon materials exhibit a high CO₂ uptake up to 6.9 mmol/g at 273 K and 1 bar; and up to 4.4 mmol/g [17] and a CO₂/N₂ selectivity of 16 at 298 K and 1 bar [18]. How N-functionalized PAFs will perform against these reported N-doped carbons would be very interesting to find out. To that end, in this work we use PAF-1 as a template to examine systematically the effect of the N-containing functional groups on CO₂ adsorption capabilities of this class of materials.

2. Molecular models and simulation methods

To construct new NPAFs, we propose a large number of organic linkers as shown in Figure 1. All these organic linkers contain a biphenyl framework with different nitrogen functional groups. The NPAF structures were constructed by inserting those target linkers between the C–C covalent bonds in diamond structure as shown in Figure 2.

The molecular framework is then structurally pre-optimized by applying the UFF force field [19]. The final structures were obtained by geometry optimization with VASP [20].

Figure 1. N-containing organic linkers used to construct NPAFs (Figure 2).

Figure 2. Schematic of the NPAF-generation strategy: Every C-C bond in the diamond structure (left) is replaced by a N-containing biphenyl-like linker (middle) to obtain the desired NPAF structure (right).

Molecular simulations of gas adsorption in various NPAFs were based on a combination of the pairwise site-site Lennard-Jones (LJ) 12-6 terms and Coulombic potentials for the interactions between gas-adsorbent and gas-gas molecules:

$$E(r_{ij}) = E_{LJ} + E_{Coul} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \quad (1)$$

The Lorentz-Berthelot combination rule was used for constructing parameters for different atom pairs.

In simulations of CO₂ adsorption in NPAF frameworks, we used a 2×2×2 supercell and a rigid model for the solid crystal atoms, since the flexibility of the molecular framework has only a marginal effect on the adsorption of small gas molecules. The Lennard-Jones potential parameters of NPAF frameworks were from the DREIDING

force field [21], which has been shown to be accurate for predicting gas adsorption in MOFs and PAFs [11, 22]. We calculated the atomic partial charges from the fragmental models cleaved from the NPAF crystal structure as shown in Figure S1 in Supporting Information, although we note that periodic DFT calculation based on partial charge derivation methods were also introduced recently [23]. The dangling bonds were saturated by hydrogen atoms. The fragment structure optimization was based on quantum mechanical calculations using Gaussian 09 with the PW91 functional and the 6-31G(d,p) basis set [24]. Meanwhile the atomic charges were derived by fitting to the electrostatic potential using the ChelpG scheme [25], which has been successfully used in the previous simulation [26]. Table S1 in the electronic supplementary material shows all atomic charges of the proposed NPAF frameworks. To describe the interactions between the gases and adsorbents, we used the well-established potentials from a previous work [11]. For both CO₂ and N₂ molecules, 3-site models were used. The C-O bond length in CO₂ is 1.18 Å and the bond angle O-C-O is 180°. The charges on C and O atoms were +0.576e and -0.288e, respectively, while $\epsilon_C/k_B=29.66$ K, $\sigma_C=2.789$ Å, $\epsilon_O/k_B=82.96$ K, and $\sigma_O=3.011$ Å. The model reproduced the isosteric heat and isotherm of CO₂ adsorption in silicate. N-N bond length in N₂ is 1.10 Å, and a -0.482e charge on each N atom while +0.964e charge on the center-of-mass, which were fitted to the experimental bulk properties of N₂; Lennard-Jones parameter is only valid on N atoms, $\epsilon_N/k_B=39.89$ K, $\sigma_N=3.385$ Å.

The gas adsorption in various NPAFs was simulated by the grand canonical Monte Carlo (GCMC) method [27]. The non-bonded interactions were evaluated with a spherical cutoff of 12.9 Å (or half of the simulation box if r_{cut} is less than 12.9 Å), and the

Coulombic interactions were calculated using the Ewald method [28]. 3×10^6 trial moves were used to reach the equilibrium state in a typical GCMC simulation, and subsequent 3×10^6 moves were collected for ensemble averages. Three types of trial moves were attempted in the GCMC simulations: insertion/deletion, displacement, and rotation of gas molecules in the simulation box. Chemical potentials were calculated by the Widom insertion method under isothermal-isobaric (NPT) ensemble. The data of each simulation trajectory were divided into 10 blocks in order to estimate statistical uncertainties. Unless specifically mentioned, the statistical uncertainty was generally smaller than the symbol sizes presented in the figures. All MC simulations were carried out by using the Towhee program v.7.0.4 [29].

3. Results and discussion

We first validated the above simulation procedure by comparing the predicted and experimental CO₂ adsorption data for PAF-1 at 298 K below 10 bar [6]. Figure 3 shows that the simulation data from our charge model reproduce the experimental results almost quantitatively, especially at low pressures (below 4 bar). At high pressures, our model tends to slightly overestimate the amount of CO₂ adsorption. Because a precise measurement of the adsorption isotherm is experimentally challenging and CO₂ capture is usually performed at ambient conditions, our method should be sufficiently accurate to predict the relative performance of different porous materials especially at low pressures.

Figure 3. Comparison of experimental and simulation data (this work) for CO₂ adsorption isotherms at 298K under 10 bar [6].

Figure 4. Comparison of NPAFs CO₂ adsorption isotherms at 298K under 1 bar; the results for PAF-1 and NPAF-1 almost exactly overlap each other.

Figure 4 shows the GCMC results for CO₂ adsorption isotherms in various NPAFs at 298K. At low pressures, the total amount of gas adsorption is mainly determined by the guest-framework interaction energy. As a result, N-containing functional groups with more polarizable electron-density distributions are expected to provide stronger interaction with CO₂, in agreement with a recent quantum mechanical study [30]. This is why all NPAFs show enhanced or better CO₂ adsorption capacity than the parent PAF (PAF-1). To explain the trend in Figure 4, we explore the correlation between NPAFs' structures and their CO₂ adsorption in Table 1. NPAF-11 displays the best adsorption capacity at 1 bar (11.5 wt% compared to 5.1 wt% of PAF-1). This is closely related to the largest heat of adsorption (22.1 kJ/mol). Figure 5 shows that there is a strong correlation between CO₂ adsorption capacity and the heat of adsorption at 1 bar. One can see that NPAF-5, 11, 12 take the largest amount of CO₂, suggesting that the imidazole and tetrazole groups can greatly enhance the CO₂ adsorption capacity. This conclusion is also supported by previous quantum mechanical calculations for the interaction between CO₂ and N-containing heterocycles [31]. It is also known that adding tetrazole groups helps increase CO₂ adsorption capacity of polymers with intrinsic micropores [32]. Moreover, Zhu et al. synthesized a nitrogen-doped porous material called triazole-functionalized triazine framework and obtained an experimental CO₂ adsorption capacity of 6.0 wt% at 298 K and 1 bar [15]. The proposed structure for this triazine framework looks similar to our NPAF-2.

Table 1. NPAFs' structural properties and CO₂ heat of adsorption and adsorption capacity at 298K and different pressures: a) Density in g/cm³; b) Void fraction in percentage; c) Pore limiting diameter (PLD) in Å; d) Maximum pore diameter (MPD) in Å; e) Heat of adsorption (Q_{st}) in kJ/mol; f) Adsorption amount in wt% (Γ). Void, PLD, and MPD are determined by using He as probe [33].

Name	Density	Void	PLD	MPD	Q _{st1bar}	Γ _{1bar}	Q _{st10bar}	Γ _{10bar}
PAF-1	0.312	0.866	10.1	12.9	14.04	5.08	15.88	76.68
NPAF-1	0.332	0.864	10.1	12.8	13.94	5.12	19.42	81.29
NPAF-2	0.354	0.861	10.7	12.5	14.60	6.01	21.70	125.77
NPAF-3	0.354	0.856	10.2	12.3	14.32	5.34	20.05	92.12
NPAF-4	0.454	0.789	7.9	10.5	19.15	7.07	24.38	89.83
NPAF-5	0.447	0.800	8.2	10.9	21.46	10.25	23.98	94.09
NPAF-6	0.450	0.812	9.1	11.8	17.55	7.67	23.56	104.67
NPAF-7	0.589	0.695	7.2	9.2	20.80	7.01	25.92	63.53
NPAF-8	0.596	0.708	7.5	9.3	20.95	7.70	24.32	66.24
NPAF-9	0.589	0.742	8.6	10.4	19.16	8.77	24.82	86.99
NPAF-10	0.568	0.653	5.9	9.4	21.81	8.88	29.21	64.35
NPAF-11	0.572	0.662	5.9	9.6	22.12	11.54	29.87	78.59
NPAF-12	0.580	0.684	6.7	10.2	20.80	10.43	27.44	77.79

Figure 5. Correlation between CO₂ adsorption capacity at 298K/1bar and heat of adsorption.

When the pressure increases, the total amount of gas adsorption depends on both the guest-framework interaction energy and the free volume (or void space). The latter becomes a dominant factor at high pressure. Figure 6 shows the isotherms up to 10 bar. One can see that the adsorption behaviors can be divided into two types: (a) steadily increasing with the pressure (PAF-1, and NPAF-1 to NPAF-6); (b) reaching a plateau (NPAF-7 to NPAF-12). This is closely related to the free volume or void space in the framework (Table 1): the steadily increasing ones have greater free volume than the plateauing ones. For example, NPAF-11 provides the highest absolute adsorption amount up to 6 bar due to strong guest-framework interactions. But as the pressure further increases, most of the favorable binding sites are saturated. On the other hand, NPAF-2

shows the best performance at higher pressures (126 wt% at 10 bar), because it has one of the largest void fraction (86.1%) and the N polar functional groups provide it with a much larger heat of adsorption (21.7 kJ/mol) compared to PAF-1 (15.9 kJ/mol) and NPAF-1 (19.4 kJ/mol), which increases the interaction strength with CO₂.

Figure 6. Comparison of NPAFs CO₂ adsorption isotherms at 298K and up to 10 bar.

Figure 3 indicates that above 4 bar a deviation develops between the simulated adsorption capacity and the experimental benchmark; at 10 bar we estimate the deviation or overestimate of simulation over experiment is about 10-15 wt%. In Figure 6, the difference between the highest capacity (from NPAF-2) and that of PAF-1 is about ~100 wt%, so we think that our simulation does provide meaningful predictions of the adsorption capacity for high pressures (such as 10 bar) that are beyond the error level in our simulation.

For post-combustion CO₂ capture purpose (that is, CO₂/N₂ separation), we also studied the pure-gas CO₂/N₂ adsorption selectivity at 298K in the low-pressure range of 1 to 4 bar. Here the selectivity is simply defined as the ratio of adsorption capacity of CO₂/N₂ at a specific pressure. As discussed earlier, the key factor in this pressure range is the heat of adsorption. One can see that all NPAFs display stable CO₂/N₂ selectivity from 1 bar to 4 bar, so we focus our discussion on the 1-bar data. PAF-1 has a CO₂/N₂ selectivity of about 5, while NPAFs with various N functionalities increase the CO₂/N₂ selectivity up to ~ 15 with NPAF-11. This selectivity is comparable to CO₂/N₂ selectivity displayed by organic frameworks (for example, between 14.5 and 20 in porous polymer frameworks [15] and ~16 for N-doped carbon [18] at 298 K and 1 bar).

Figure 7. Comparison of NPAFs pure gas component adsorption selectivity $S(i/j)$ at 298K under 5 bar.

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8 Since the ambient conditions (298 K and 1 bar) are most relevant to post-
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10 combustion carbon capture, our simulation suggests that the best NPAFs can offer CO₂
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12 adsorption capacities of about 10-11 wt% at such conditions. How does this performance
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14 of NPAFs compare with recently reported N-doped porous materials for carbon capture?
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16 Here we choose some experimental N-doped carbons for comparison because their N
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18 content is close to what we are simulating here. Sevilla et al. prepared N-doped
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20 polypyrrole-based porous carbons and found that the 600°C-activated sample has a N
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22 content of 10 wt% and CO₂ uptake of 15 wt% at 298 K and 1 bar [34]. Zhu et al.
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24 synthesized N-doped porous carbonaceous membranes (N-PCM) from trimerization
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26 reactions of acetyl compounds and found that their 550°C-activated material has a N
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28 content of 3.4 at% (atomic percentage) and a CO₂ uptake of 7.5 wt% at 298 K and 1 bar
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30 [15]. El-Kaderi and coworkers have synthesized porous benzimidazole-linked polymers
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32 (BILP) [35]. Their BILP-4 material is also based on a tetrahedral model structure for 3D
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34 linking, similar to the NPAFs in this study. BILP-4 displays an impressive CO₂ uptake of
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36 16 wt% at 1 bar and 298 K [35]. We found that our predicted CO₂ capacities for NPAFs
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38 are in line with these experimental CO₂ uptakes of various N-containing porous materials,
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40 confirming the role of N in enhancing CO₂ uptake.
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50 Looking into the future, it would be very interesting to simulate CO₂ adsorption
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52 capacities of BILP-4 and other PAFs such as sulfonate-functionalized ones and compare
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54 them with those of NPAFs. In addition, in-depth understanding of the relationship
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56 between CO₂ adsorption capacities and the structure/property of various functional
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58 groups is also warranted.
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4. Conclusion

We proposed a series of new porous aromatic frameworks (NPAFs) with N-doped heterocyclic functional groups for enhancing CO₂ adsorption at ambient conditions. A reasonably good agreement was obtained between the simulation and experimental data for CO₂ adsorption in crystalline PAF-1. Among those new hypothetical functional NPAFs, NPAF-11 with imidazolic groups shows the highest adsorption capacity for CO₂ (11.6 wt%) at 1 bar and 298 K, about 130% increase upon that of the parent PAF-1. This study reveals that adding N-doped heterocyclic groups such as imidazole and tetrazoles to a porous framework such as PAF-1 greatly enhances its CO₂ uptake.

Supporting Information. Molecular fragments and their corresponding atomic charges for all NPAFs simulated in the present work. This material is available free of charge via the Internet at <http://www.sciencedirect.com>.

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