



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.

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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 298 K [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; up to 4.4 mmol/g [17] and a CO₂/N₂ selectivity of 16 at 298 K and 1 bar [18]. How

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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 Fig. 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 Fig. 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].

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:

$$E(r_{ij}) = E_{LJ} + E_{Coul} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

In Equation (1), r_{ij} , σ_{ij} and ϵ_{ij} are the distance, collision diameter and well depth (between sites i and j), respectively; q_i and q_j are

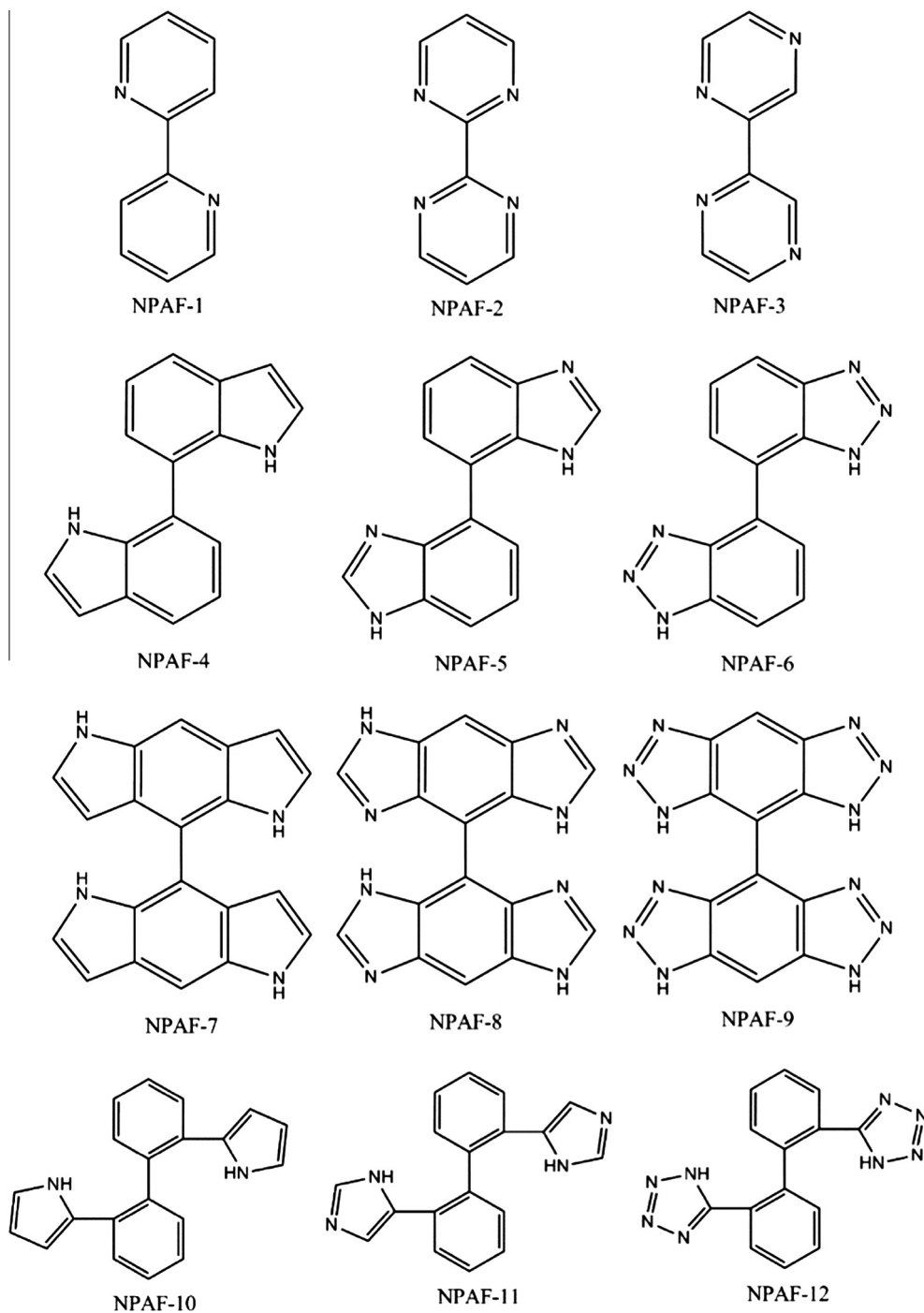


Fig. 1. N-containing organic linkers used to construct NPAFs (Fig. 2).

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