

A Porous Aromatic Framework Functionalized with Nitro Groups and Its Carbon Dioxide Adsorption

Eunyoung Kang, Sang Beom Choi, Nakeun Ko, and Jin Kuk Yang*

Department of Chemistry, Soongsil University, Seoul 156-743, Korea. *E-mail: jinkukyang@ssu.ac.kr
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Linking of rigid organic molecules by coupling and/or condensation reactions can yield extended organic polymer networks usually as amorphous solids except for the COFs (covalent organic frameworks) developed by Yaghi and co-workers.^{1,2} As organic polymer networks are formed through covalent bonds, they are usually stable in water and even in acidic or basic conditions. In addition these are comprised of light elements (*i.e.* C, H, N, O, and B),² some organic polymer networks demonstrate very high Brunauer–Emmett–Teller (BET) surface areas.³ It is believed that high chemical stability and porosity of organic polymer networks allow more opportunity of their industrial applications such as CO₂ capture in humid flue gases emitted by coal-fired power plants.

Connection of the tetrahedral building units by C–C coupling reactions is expected to produce a diamond-like network, although a long-range order is not always guaranteed.^{1,3} For instances, Yamamoto-type Ullmann coupling was applied for linking tetrakis-4-bromophenyl-methane (BPM) monomers to give amorphous PAF-1 (porous aromatic framework-1).⁴ PAF-1 showed a high surface area of 5600 m²/g. Even higher surface area (6461 m²/g for PPN-4 (porous polymer network-4)) was obtained by linking of tetrakis-4-bromophenyl-silanes.⁵ The emergent of organic polymer networks with high-surface areas can provide the opportunity to tune the property of these materials by post-synthetic modification. Indeed, PAF-1 (and PPN-6 having a same chemical composition as PAF-1) was directly able to be sulfonated,⁶ lithiated,⁷ and decorated with various organic amines.⁸ However, there are at least two challenges to be addressed. One is development of simple and inexpensive synthetic route because the crystallinity and porosity of organic porous network are generally poor. Another challenge is improvement of thermal

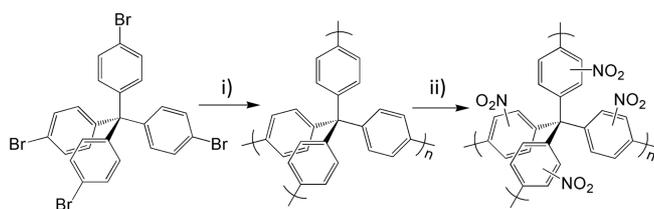
stability. Here we report a new synthetic procedure of PAF-1, and its easy nitration (Scheme 1). The nitro-functionalized PAF-1 shows enhanced CO₂ adsorption properties. Interestingly, in due course we found that a thermolysis product of PAF-1 has very high thermal stability in air.

PAF-1 was prepared by a Yamamoto-type Ullmann coupling reaction conducted at 80 °C according to the published procedure.⁴ However, we were only able to obtain PAF-1 with the surface area of 2100 m²/g even after repeated trials. One of the reasons for the low surface area may be ascribed to the incomplete removal of occluded Ni metal particles. Thermogravimetric analyses imply that crude products contain a significant amount of Ni metal (15 wt %, Fig. 3S). The embedded Ni was not fully removed even after the treatment of crude products with concentrated HCl.

Instead of the homo-coupling reaction, we next prepared PAF-1 by Suzuki–Miyaura reactions^{9,10} between tetrakis(4-phenylboronic acid pinacol ester)methane (PBPM) and BPM in the presence of a Pd(0) catalyst. The product (termed **1S**) is insoluble in most of organic solvents, which is indicative of the formation of extended structure. Progress of the coupling reaction was also confirmed by IR spectra; absorbance for C–Br stretching bands at 512 and 532 cm⁻¹ was almost disappeared (Fig. 6S). To our disappointment, the BET surface area of **1S** was 630 m²/g only. Besides the occluded Pd (*ca.* 10 wt % based on TGA analyses, Fig. 8S), the structural regularity of **1S** may be lower than the PAF-1 obtained by a Yamamoto-type Ullmann reaction. As the Suzuki reaction requires alternative attachments of two units (*i.e.* BPM and more bulky PBPM), uniform growth of ordered polymer network seems to be disturbed during the coupling reaction.

There is a trend that less-ordered polymer network structures are obtained by a rapid coupling reaction of organic units. In order to improve the crystallinity of polymeric networks, we implemented a Yamamoto-type

Ullmann reaction again at a lower temperature, 25 °C. To evaluate the porosity, N₂ isotherm of the final product (termed **1U**) was recorded. As shown in Figure 1(b), **1U** demonstrated a steep rise of N₂ uptake below $P/P_0 < 0.1$, indicating the presence of microporosity. The BET surface area of **1U** is estimated to be 3270 m²/g. The small hysteresis of the isotherm may reflect the flexible nature of the polymer networks. Indeed, the powder X-ray diffraction pattern



Scheme 1. Preparation of PAF-1, and its functionalization with nitric acid: i) 1,5-cyclooctadiene, bis(1,5-cyclooctadiene)nickel(0), 2,2'-bipyridyl, DMF, 25 °C; ii) 3 M HNO₃, DMF, 50 °C.

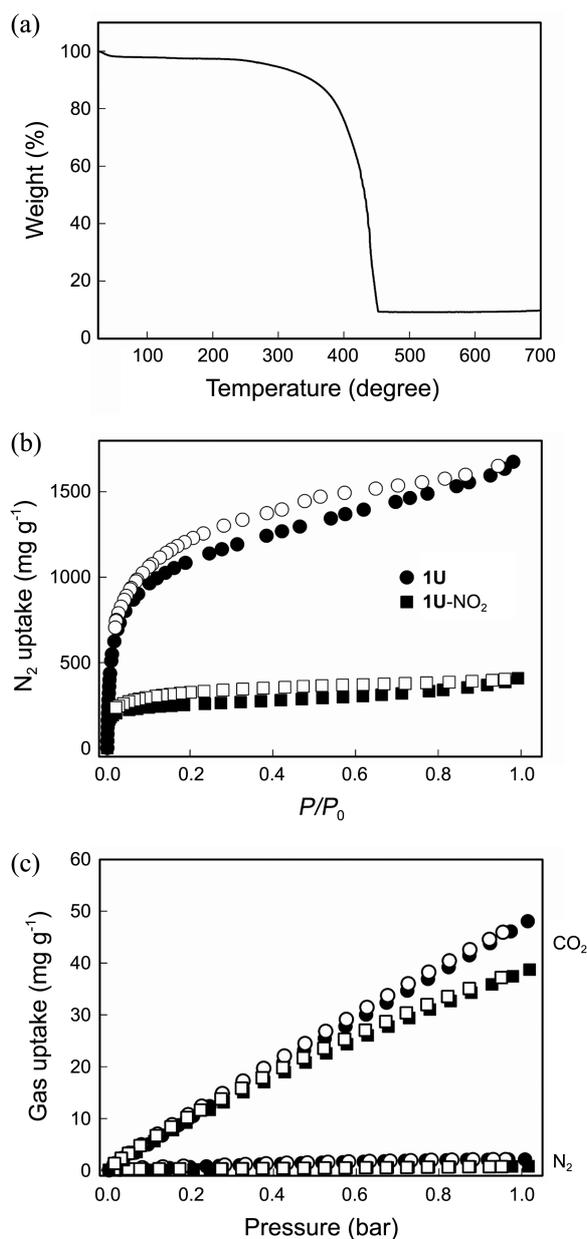


Figure 1. (a) TGA trace of **1U** under air flow. The NiO residue weight (12 wt %) is converted to 9.4 wt % of Ni in **1U**. (b) N_2 isotherms of **1U** (circle) and **1U-NO₂** (square) measured at 77 K. (c) CO_2 and N_2 adsorption isotherms of **1U** (circle) and **1U-NO₂** (square) measured at 298 K. Filled and open symbols represent adsorption and desorption branches, respectively.

(PXRD) of **1U** showed only a few broad peaks, which is reminiscent of reported materials (Fig. 10S).^{4,5} It should be noted that the amount of Ni residue was smaller than the sample prepared at 80 °C (Figs. 1S, 1(a)).

To introduce nitro-functionalities within its interior, **1U** was heated at 50 °C for 4 h in concentrated nitric acid. The collected solid, **1U-NO₂**, showed a weight increase by 60% and new IR bands at 1350 and 1534 cm^{-1} attributed to nitro groups (not shown). These results indicate that two carbon atoms in one aromatic ring, that is 8 nitro groups per BPM, have been functionalized with $-NO_2$ groups. It was not

possible to propose the formula based on elemental analyses due to the exceptional thermal stability of **1U** even in air (*vide infra*). As expected, the increased framework weight and reduction in the pore space together resulted in a decreased surface area, 1500 m^2/g (Fig. 1(b)).

Low-pressure CO_2 adsorption isotherms for **1U** and **1U-NO₂** were measured at 298 K to see if NO_2 functionalities improve the interaction with CO_2 (Fig. 1(c)). The CO_2 uptake in **1U-NO₂** at 1 bar (0.88 mmol/g) was slightly smaller than that in **1U** (1.09 mmol/g), although **1U-NO₂** has a much smaller surface area. Indeed, CO_2 uptake per surface area for **1U-NO₂** is 1.76 times greater than that for **1U**. The significant increase in the CO_2 affinity of **1U-NO₂** should be due to the nitro functionality with larger electron-withdrawing nature (*i.e.* larger quadrupole moment).

It is reported that PPN-6- SO_3H and PPN-6- SO_3Li have large CO_2/N_2 selectivity which was simply calculated by using the adsorbed amount of N_2 and CO_2 at 0.85 and 0.15 bar, respectively; this is close to the composition of flue gas. The calculated selectivity for PPN-6- SO_3H and PPN-6- SO_3Li was 15 and 17, respectively.⁶ Interestingly, the selectivity of **1U-NO₂** obtained by the same method is 39, while **1U** shows 14 (Supporting Information). This increased selectivity should be related to higher affinity of NO_2 functionalities with CO_2 . This is confirmed by the enhanced isosteric

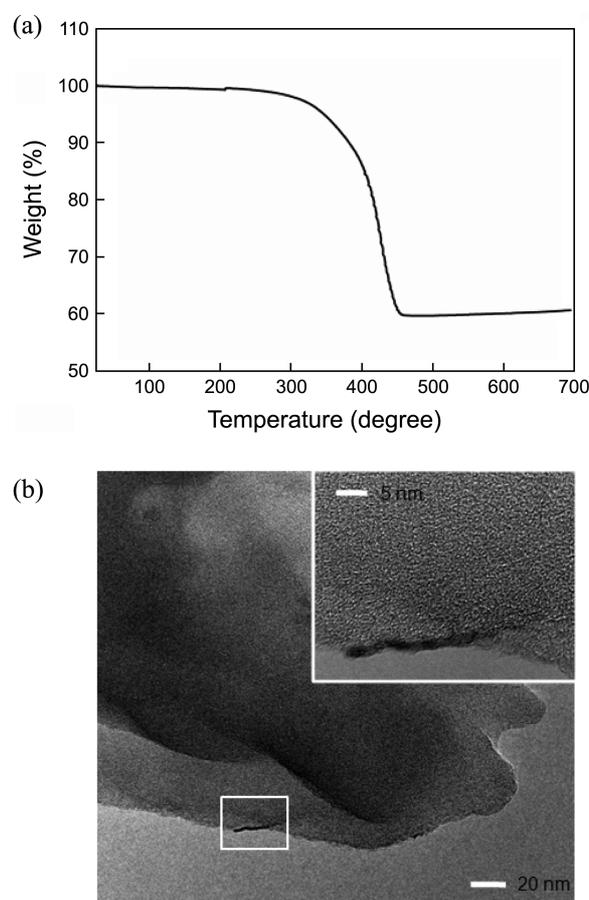


Figure 2. (a) TGA thermogram of **1U-NO₂**, and (b) a TEM image of its thermolysis product. The black line in the inset is NiO.

heat of CO₂ adsorption of **1U**-NO₂ (23 kJ/mol) compared to that of **1U**, 17 kJ/mol.

1U-NO₂ has an interesting thermal property. When **1U**-NO₂ was heated *in air*, a large amount of residue (60%) was remained (Fig. 2(a)). This result is in sharp contrast to the un-functionalized **1U** which is completely decomposed *in air* (Fig. 1(a)) to give only 12% as a NiO residue. A separate TGA analysis on the residue of **1U**-NO₂ did not show any weight loss up to 800 °C (not shown). In addition, the residue has an off-white colour which does not match with the appearance of graphitic carbon materials. The TEM image of the off-white solid shows sheet-like morphology with no graphitic structure, and a magnified image shows that NiO is present at the edge of the solid (Fig. 2(b)). These results may suggest formation of amorphous carbon nitride. However, we could not observe in Raman spectra any significant signals corresponding to carbon nitride or graphitic carbon. A further investigation on the nature of the solid will be performed in our laboratory.

In summary, we prepared PAF-1 by a Yamamoto-type Ullmann reaction at 25 °C. Its BET surface area was of 3270 m²/g. By a nitric acid treatment of **1U**, thermally stable nitrated PAF-1 (**1U**-NO₂) was obtained. Enhanced affinity for CO₂ with larger CO₂/N₂ selectivity (CO₂/N₂ = 39) clearly demonstrated that a simple treatment of PAF in nitric acid can provide effective CO₂-capturing sorbents.

Experimental

Synthesis of 1S. BPM (127 mg, 0.2 mmol) and PBPM (246 mg, 0.15 mmol), which were prepared following literature methods (*Supporting Information*),^{13,14} were dissolved in anhydrous DMF (10 mL) under an argon atmosphere. Cesium carbonate (326 mg, 1.0 mmol), tetrakis(triphenylphosphine)palladium(0) (23.0 mg, 0.02 mmol), water (2.0 mL), and ethanol (2.0 mL) were added to the solution subsequently. The resulting mixture was heated to 110 °C for 48 h. The reaction mixture was cooled to room temperature and the formed precipitate was filtered off and washed with DMF (3 × 20 mL), water (3 × 20 mL), and chloroform (3 × 20 mL). The product was dried under reduced pressure overnight (59.5 mg, 0.19 mmol, 98%).

Synthesis of 1U. BPM (250 mg, 0.39 mmol) was added to a mixture of 2,2'-bipyridyl (320 mg, 2.07 mmol), bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)₂, 562.5 mg, 2.07 mmol), and 1,5-cyclooctadiene (COD, 0.25 mL, 2.08 mmol) in anhydrous DMF/THF (20 mL/10 mL). The mixture was stirred at room temperature under argon atmosphere for 48 h. Then, 15 mL of concentrated HCl (12 M) was added dropwise to the deep purple mixture, the mixture was stirred for another 20 h. The solid was collected by filtration, washed with chloroform (3 × 20 mL), water (3 × 20 mL), and THF (3 × 20 mL), and dried *in vacuo* to give **1U** as an off-white powder (115 mg, 0.37 mmol, 97%).

Synthesis of 1U-NO₂. To a two necked round-bottomed

flask containing **1U** (40.0 mg, 0.131 mmol), 5 M HNO₃ (10 mL) was added in small portions under vigorous stirring at room temperature. After the addition was completed, the resulting solution was heated to 50 °C for 6 h. Then, the reaction mixture was cooled to room temperature and the precipitate was filtered off and washed with water (100 mL). After drying in vacuum, **1U**-NO₂ was obtained as a yellow solid (92.0 mg).

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Supporting Information. FT-IR spectra and PXRD patterns for PAF-1 (80 °C), **1S**, and **1U**. Preparation of PBPM. TGA thermograms of PAF-1 (80 °C) and **1S**. Gas selectivity calculations.

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