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Journal Name

COMMUNICATION

Well-Defined Nitro-Functionalized Aromatic Frameworks (NO₂-PAF-1): A Synthesis by Copper-Mediated Ullmann Homo-Coupling Polymerization on Nitro-Containing Monomer and Its High CO₂ Adsorption

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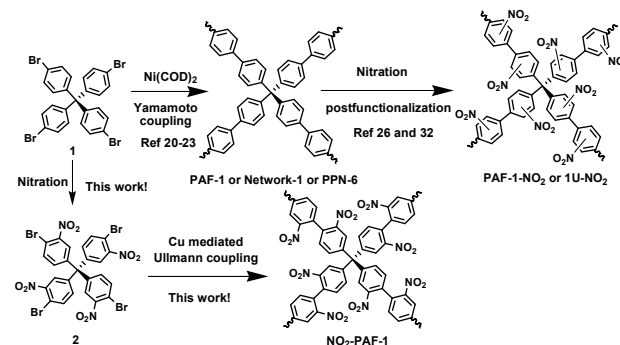
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Ze-Huan Hei,^a Mu-Hua Huang*^a, Yunjun Luo*^a and Yingxiong Wang^b

The well-defined nitro group functionalized porous aromatic frameworks (NO₂-PAF-1) was synthesized via bottom-up strategy using copper-mediated Ullmann reaction. The synthetic route shows cost-efficient and robust for large scale preparation. Brunauer-Emmett-Teller (BET) specific surface area of the obtained NO₂-PAF-1 is up to 610 cm²/g with micro/mesoporosity. Its CO₂ uptake was measured to be higher than that of PAF-1 due to the strong interaction between nitro group and CO₂ molecule, which was proved by the enhanced isosteric heat of CO₂ adsorption (38.4 kJ/mol).

CO₂ capture and utilization of clean energy source such as hydrogen have attracted much attention due to the environmental¹⁻⁴ and energy issues^{5,6}. As a response, lots of contributions have been made to explore suitable materials for CO₂ capture or H₂ uptake^{5,7}. For instance, widely reported candidates as CO₂ adsorbent materials include metal organic frameworks (MOFs)^{3,8-11}, covalent organic frameworks (COFs)^{12,13}, covalent triazine frameworks (CTFs)^{14,15}, polymers of intrinsic microporosity (PIMs)^{16,17}, porous aromatic frameworks (PAFs)¹⁸⁻²⁰ and so on. The introduction of functional groups to porous materials was reported an efficient way to improve their gas adsorption capacity and selectivity^{13,21}, mainly due to the interaction between functional group and gas molecules. PAF-1^{20,22} is an important synthetic polymer for gas absorption and separation, which links tetrahedral rigid building blocks with robust covalent bonds (Scheme 1). It was first launched by Ben *et al.*²⁰ in 2009. Later on, Cooper group²³ and Zhou group²¹ reported network-1 and PPN-6 with the same chemical structure respectively. In the meanwhile, many efforts have been carried out based on the modification of PAF-1²², including pre-modification²⁴, post-synthesis modification^{25,26} and carbonization^{27,28}. PAF-1 was sulfonated²¹, lithiated²⁹ and modified with organic amines²⁵ to improve the gas sorption.

Torrisi *et al.* theoretically predicted an electrostatic interaction between the two oxygens of nitro group and the electron-deficient carbon atom of the CO₂ molecule³⁰. It has been proved by Chang group³¹ in the nitro-functionalized polymers, which exhibited enhanced CO₂ absorption capacity and CO₂/N₂ selectivity. However, only few work has been done (1U-NO₂³² and PAF-1-NO₂²⁶ in Scheme 1) by introduction of nitro group to PAF-1.



Scheme 1 Synthetic scheme for nitro-functionalized PAF-1

As far as synthetic strategy is concerned, both 1U-NO₂ and PAF-1-NO₂ were prepared by a post-modification strategy, i.e., a nitration on PAF-1 (Scheme 1). Those nitrated PAF-1 may have low loading of nitro group and undefined locating position of nitro group. And, PAF-1 was synthesized via Yamamoto type Ullmann coupling²⁰, which is expensive and sensitive to water and air for the large scale preparation. In addition, nitro group is reported to be non-compatible with Yamamoto coupling conditions³³, which limited its application in the synthesis of nitro group functionalized PAF-1 from nitro-containing monomer. Hence, more robust and cost-efficient preparation is in demand to reach porous organic polymers^{34,35}.

In this communication, we report a more robust and cheap procedure for the synthesis of well-defined nitro-functionalized PAF-1 (termed NO₂-PAF-1) based on bottom-up strategy, using copper-mediated Ullmann coupling reaction³⁶ (Scheme 1). And the properties of the resulted NO₂-PAF-1 were investigated, including CO₂ adsorption and CO₂/N₂ selectivity.

Tetra(4-bromo-3-nitro)phenylmethane (*abbr.* TBNPM, **2**, Scheme 1) was prepared in 61% yield by the nitration of

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tetra(bromophenyl)methane (**1**) (see ESI), which was synthesized by bromination of commercial available tetraphenylmethane^{37,38}. It's interesting that leaving the nitration reaction mixture at room temperature for 24 h lead to high yield of **2** and easy work-up, and this procedure could be scaled up to tens of grams. One singlet at 8.05 ppm and two doublets at 7.89 ppm and 7.59 ppm in the ¹H-NMR of **2** (see Figure S1 in ESI) confirmed the 1,2,4-trisubstitution fashion of benzene ring. The structure of **2** was further proved by its ¹³C-NMR (Figure 1). The absorption peaks at 1351 cm⁻¹ and 1533 cm⁻¹ in the IR spectra of **2** (Figure S3 in ESI) indicated the existence of nitro group in the molecule. The [M]⁺ peak of 811.7400 (calculated C₂₅H₁₂Br₄N₄O₈⁺, required for 811.7383) in the high-resolution mass spectroscopy (EI) (see Figure S5 in SI) confirmed the right structure of **2** unambiguously. The Ullmann coupling polymerization on **2** was carried out using copper powder in hot and dry N,N-dimethylformaldehyde (DMF) under nitrogen atmosphere. The temperature higher than 150 °C (oil bath) was found necessary for the polymerization reaction. The concentration of the reactants also matters, high concentration gave good results, low concentration gave poor yields. For reaction time, any reaction that was heated less than 12 h resulted no solid product, and a long period of reaction time up to 4 days gives no better result. After polymerization, the desired polymer NO₂-PAF-1 was treated with diluted nitric acid followed by several washes with ethanol and dried with super critical CO₂. The structure of NO₂-PAF-1 was clearly characterized at the molecular level by ¹³C CP/MAS-NMR spectrum and comparison with its monomer **2** (see Figure 1). The assignment of the chemical shifts is shown in Figure 1. The signal peak of 146.9 ppm corresponds to the substituted phenyl carbons binding with -NO₂ and quaternary carbon (meta to -NO₂). The peak at 131.5 ppm is assigned to the substituted carbon linked to phenyl and the two unsubstituted carbons (meta- and para- to -NO₂). The peak at 123.1 ppm is ascribed to unsubstituted carbon ortho- to -NO₂. The quaternary carbon of tetraphenylmethane is located at 64.1 ppm. And the ¹³C CP/MAS-NMR spectrum of our NO₂-PAF-1 is quite similar to reported data of PAF-1²⁰.

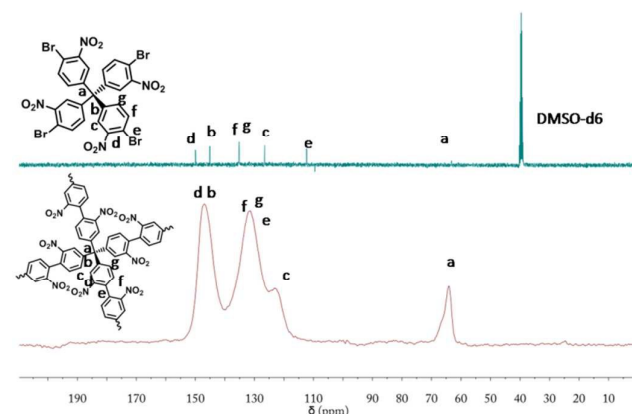


Figure 1 ¹³C-NMR spectrum of TBNPM (up) in DMSO-d₆ and ¹³C CP/MAS-NMR spectrum of NO₂-PAF-1 (down).

The absorption peaks at 1346 cm⁻¹ and 1532 cm⁻¹ in the IR spectra of NO₂-PAF-1 (Figure S4 in ESI) indicate the presence of nitro group, which is not observed in PAF-1²⁰. The comparison between the IR spectra of **2** and NO₂-PAF-1 (see Figure S4 in ESI) revealed the supersimilarity of them, except the disappearance of 510 cm⁻¹ for C-Br in **2** after polymerization.

The above results were further confirmed by the elemental analysis data, showing 9.70% N, 58.64% C and 2.87% H. It is close to the

corresponding theoretical value (11.29% N, 60.48% C and 2.42% H). Thus, a well-defined NO₂-PAF-1 with high degree of nitro functionalization was obtained via bottom-up strategy. X-ray diffraction measurements support that NO₂-PAF-1 is noncrystalline (Figure S8).

The porous structure of NO₂-PAF-1 was examined by nitrogen sorption measurements at 77 K, which indicated the presence of mesopores as well as a small fraction of micropores (Figure 2a).

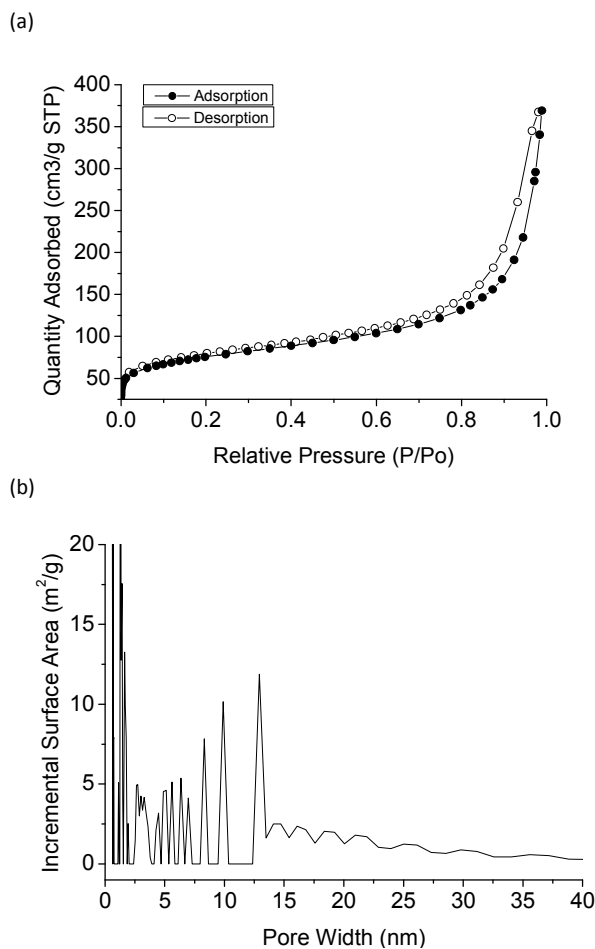


Figure 2 (a) Nitrogen sorption-desorption isotherms of NO₂-PAF-1 and (2) Pore distribution of NO₂-PAF-1 obtained with the non-local density functional theory (NLDFT).

Fully reversible isotherm shows a rapid uptake at low pressure (0-0.1 bar) indicating a microporous nature. The increase in the nitrogen sorption at a high relative pressure above 0.8, as well as a hysteresis loop at the high relative pressures (0.6 < P/P₀ < 1.0) may arise in part from interparticulate porosity associated with the mesostructures of the samples and interparticulate void. The specific surface areas calculated in the relative pressure range from 0.005 to 0.2 according to the previous reports³⁹ show that the BET specific surface area of NO₂-PAF-1 is 610 cm²/g (806 cm²/g for Langmuir surface area). It was much lower than the BET surface area for PAF-1 (5600 cm²/g). This could contribute to the non-crystalline nature of NO₂-PAF-1 and high loading of nitro groups in the backbone of PAF-1. To characterize the porosity of NO₂-PAF-1, the pore size distribution (PSD) analysis³⁵ based on the non-local density

functional theory (NLDFT) approach has been used. PSD of the polymer calculated from the absorption branch of the isotherms with the NLDFT approach indicate that, NO₂-PAF-1 has a wide pore distribution from micropore to mesopores (Figure 2b) in the range of 1-40 nm. The micropore volume of NO₂-PAF-1 was estimated to be 0.10 cm³/g based on the t-plot method, which was 11% of the total volume (0.93 cm³/g). It was much lower than the BET surface area for PAF-1 (5600 cm²/g), implying the high loading of nitro groups in the backbone of PAF-1.

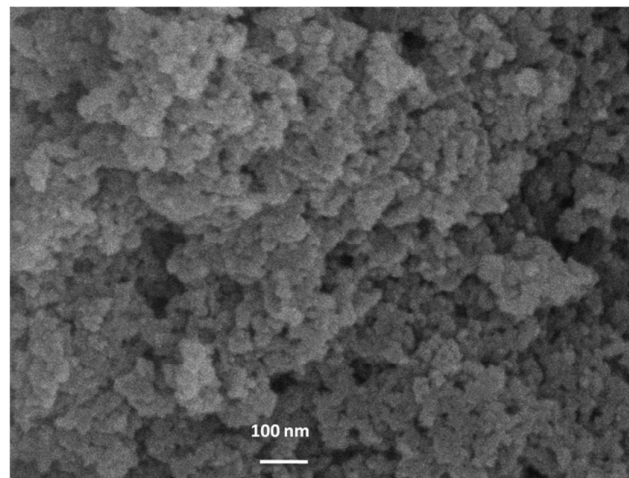


Figure 3 SEM image of NO₂-PAF-1

Scanning electron microscopy (SEM) characterization (Figure 3) of NO₂-PAF-1 displays the distinctive morphology of the micro-/mesoporosity. Particles of 10–50 nm in size were observed as a secondary structure motif. These nanoparticles are believed to be the nitro-functionalized PAF-1 framework built up through Copper promoted Ullmann coupling reaction, and of course they must be porous in themselves.

However, the synthesis using traditional heating required long reaction time, which is the problem in the research of porous materials. Recently, the microwave synthesis strategy has demonstrated significant advantage over traditional heating methods in the preparation of COF⁴⁰⁻⁴² and covalent triazine-based framework (CTF)⁴³. To our delight, the synthesis of NO₂-PAF-1 was achieved in half an hour in 90% yield (See SI).

It was also found that the BET surface area of the as-synthesized NO₂-PAF-1 is sensitive to the way of removing solvent from the material (see Table S1 and Figure S9-11). Super critical drying method produces sample with highest surface area (610 cm²/g). The sample of NO₂-PAF-1 was dried under vacuo at 200 °C for 24 h to give a BET surface area of 468 cm²/g. The try to dry NO₂-PAF-1 at a lower temperature of 150 °C afforded NO₂-PAF-1 with a higher BET surface area of 593 cm²/g. This implied that keeping the sample at high temperature would probably destroy the porosity of the material, especially for non-micropores. Further effort to use acetone as washing solvent resulted in decreased BET surface area of 480 cm²/g. It is interesting that micropore volumes for all the samples are in the range of 0.10-0.15 cm³/g, which may come from the micropores build up via covalent bond formation.

The strong interaction between CO₂ and the adsorbent materials is important for gas separation at high temperature and low pressure, and high selectivity at low pressures is important for the efficient

separation of CO₂ in post-combustion gas. The selectivity of NO₂-PAF-1 over N₂ was investigated by collecting pure component physisorption isotherm at 273 K (Figure 4). The CO₂ uptake shows a nearly linear increase with the pressure, while that of N₂ has no apparent increase trend. CO₂ uptake of NO₂-PAF-1 at 1 bar is 50.0 cm³/g, which is even higher than that of PAF-1 (46 cm³/g)²⁸. Considering NO₂-PAF-1 has much lower BET surface area comparing with PAF-1 (610 vs. 5600 cm²/g)²⁰ as well as the low percentage of micropores, it strongly supported that the strong interaction between nitro group and CO₂ molecules³⁰ in low pressure. This is confirmed by its enhanced isosteric heat of CO₂ adsorption (38.4 kJ/mol) by fitting the adsorption isotherms measured at 273 and 298 K (see Table S2 and Figure S12 in SI). NO₂-PAF-1 has better CO₂ adsorption ability than 1U-NO₂³², which showed CO₂ uptake of 0.88 mmol/g (ca. 19.7 cm³/g) at 1 bar and 298 K as well as lower heat of CO₂ adsorption (23 kJ/mol)³². In comparison, the N₂ uptake of NO₂-PAF-1 at 1 bar and 273 K is 3.56 cm³/g, and heat of N₂ adsorption is 12.3 kJ/mol. The selectivity of CO₂ over nitrogen³⁵ for NO₂-PAF-1 is calculated to be 22.1 at 1 bar and 273 K.

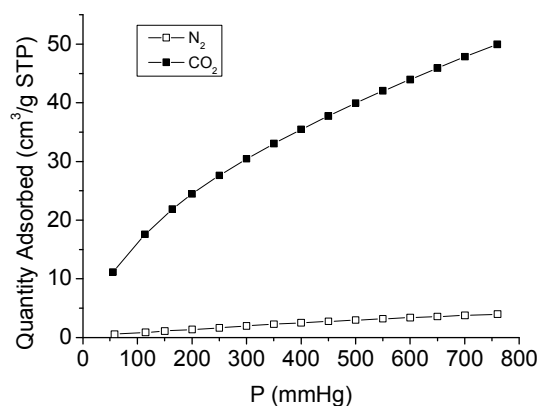


Figure 4 CO₂ and N₂ adsorption isotherms of NO₂-PAF-1 at 273K

The thermal stability is an important parameter for the application as gas absorbent, thus thermo gravity analyses (TGA) were run on NO₂-PAF-1. It is found that NO₂-PAF-1 had a lower decomposition temperature (5 % mass loss at 327 °C) (Figure S12) and maximum decomposition temperature (375 °C) (Figure S7) than PAF-1, mainly due to the decomposition of nitro group. The residual weight mass of 60% was observed for NO₂-PAF-1, which was consistent with the reported data³². It is interesting that of the monomer TBNPM (2) is more thermal stable than NO₂-PAF-1, showing 5 % mass loss at 395 °C and maximum decomposition temperature at 428 °C (Figure S7). While 30% mass residual for the monomer TBNPM was observed. It is rarely reported that polymer is more stable than its corresponding monomer. The unusual thermal decomposition behaviour of NO₂-PAF-1 may be caused by the steric hindrance of nitro group *ortho*- to biphenyl backbone, as well as catalysis of nitrogen oxide intermediate absorbed inner the porous material on the decomposition and cross-linking of the polymer network. The detailed mechanism of the thermal decomposition and its potential new application is undergoing in our lab, the relevant results will be reported in due course.

Conclusions

In summary, well-defined nitro-functionalized PAF (NO₂-PAF-1) was successfully constructed via bottom-up strategy by using copper-promoted Ullmann coupling reaction on the nitrophenyl monomer. The Synthesized NO₂-PAF-1 gave BET specific surface area of 610 cm³/g and wide distribution of micropores and mesopores. The CO₂ uptake of 50.2 cm³/g and CO₂/N₂ selectivity of 22.1 for NO₂-PAF-1 were observed at 273 K and 1 bar, which is even higher than that of PAF-1.

Acknowledgements

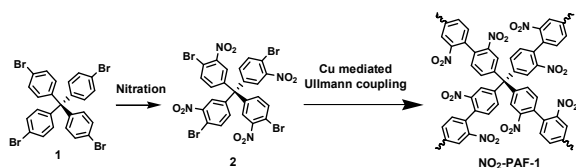
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