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Novel fullerene-based porous materials constructed by solvent knitting strategy†

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Here we choose a dihydronaphthyl-functionalized C_{60} fullerene as building block and utilize a novel solvent knitting strategy based on *Friedel-Crafts* alkylation reaction to construct two kinds of novel porous materials by using dichloromethane(DCM) and 1,2-dichloroethane(DCE) as solvents and external crosslinkers. The resulting porous materials show relatively high apparent BET surface areas and gas uptake abilities.

Microporous organic polymers (MOPs) have attracted wide attentions in many fields like gas storage and separation,[1-3] catalysis,[4, 5] chemical sensing,[6] energy storage and conversion,[7] *etc*. Compared with traditional inorganic porous materials, such as zeolites and activated carbon, MOPs which consist purely of organic components have many advantages such as low skeletal density, abundant pore structure and easier functionalization,[8,9] which further expands the scope of applications of MOPs. Until now, many different kinds of MOPs, which were classified by the structure and synthetic strategy, have been reported, such as conjugated microporous polymers (CMPs),[10,11] polymers of intrinsic microporosity (PIMs),[12] covalent organic frameworks(COFs),[13,14] hyper-crosslinked polymers (HCPs),[15,16] porous aromatic frameworks (PAFs).[17] With a variety of synthetic strategies and synthetic routes, a large number of molecules with special functions can be synthesized and designed as building blocks to construct novel porous materials with various specific functions and applications. [9,18]

As a novel kind of three-dimensional aromatic compound with unique cage structure, fullerene, which was first reported by Kroto *et al*,[19] shows a variety of applications in many fields including those in solar cells,[20] semiconducting materials,[21] electrochemical systems,[22] catalysis,[23] and biological medicine,[24] and have thus attracted increased worldwide attention. Considering these unique properties and potential applications, many reports about C_{60} and its derivatives have been published on fullerene-functionalized materials.[25] Recently, some porous polymers have been reported in combination with fullerenes, which are usually synthesized by two strategies: introducing fullerene into the porous frameworks by post functionalization, or focused on building fullerene-derivatives based porous materials. For example, Jiang *et al*. reported a novel electron donor-acceptor COFs, of which 2D-skeletons were built from electron-donating monomers and introduced the typical electron acceptor, fullerene, within the open channels of frameworks *via* Click chemistry.[26] In 2016, Zhu *et al*. firstly reported a series of C_{60}-based PAFs materials combining both symmetrical conjugated structure of C_{60} and the porous properties of PAFs using external crosslinker knitting method, which showed relatively high surface area of 1094 m^2g^{-1} and a comparable adsorption capacity for H_2 and CO_2.[27]

It is well established that the pure fullerene C_{60} powder only possess a certain solubility in several aromaticity solvents like toluene, but its derivatives show decent solubility in common solvents like DCM and DCE. Chemical functionalization of the fullerene cage has easily been achieved to make fullerene derivatives and promote their involvement in organic reactions. Recently, our group developed a novel solvent knitting strategy employing $AlCl_3$ as Lewis acid catalyst, chloralkane as solvents and external crosslinkers to knit HCPs materials.[28,29] This simple, versatile and flexible method is very useful for "knitting" aromatic compounds to construct HCPs materials with abundant porosity and without any other additional effects on the structure of building block compounds.

Herein, we employed a dihydronaphthyl-functionalized fullerene $NC_{60}BA$ (N for abbreviation)[30] , with excellent solubility, as the building block to construct microporous C_{60}-based polymers which are named N-H-1 and N-H-2 by using DCM and DCE as solvent and external crosslinking agent, respectively. The resulting porous materials show high surface area, favourable gas adsorption capacity and thermal stability, and they have been thoroughly characterized to understand their structure and properties.

Although fullerenes have attracted much more attention due to vari-

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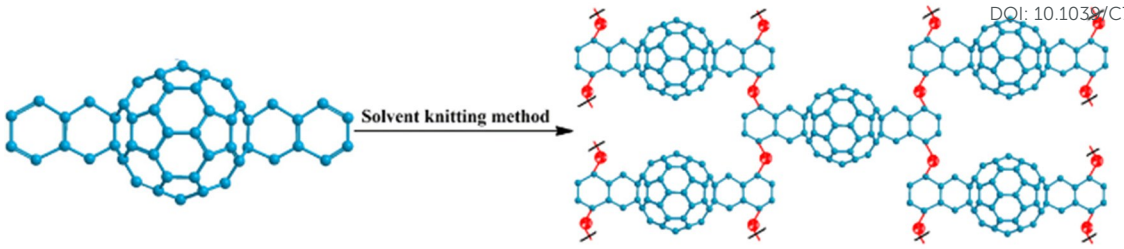

Scheme 1. The synthetic routes of the polymer networks (Red dots represent -CH_2- or -CH_2-CH_2-)

ous applications, but, until now, there is not much focus on the synthesis of C_{60} fullerene-based porous materials and their potential applications. As shown in Scheme 1, we have prepared two novel C_{60} based porous materials using monomer N as building block by a simple *Friedel–Crafts* reaction with two different external crosslinkers (Experimental details, ESI†). At the end of reaction, the solid insoluble products were obtained which were precipitated. In order to determine the structural features of the polymers, FT-IR and solid state ^{13}C CP/MAS NMR were used for chemical characterization. The C–H stretching vibration bands of methylene linkage (ν -CH_2-) near 2960–2800 cm^{-1} are evidently observed. Compared with monomer N, the weak signals of C-H stretching vibrations of the aromatic ring (ν Ar-H) at 3100-3000 cm^{-1} disappeared after the crosslinking reactions for N-H-1 and N-H-2 , as shown in Fig.1. The intensity of out-of-plane bending vibration peaks (γ Ar-H) at 910-665 cm^{-1} also reduced (Fig.1(b)) or even nearly vanished (Fig.1(c)), which suggests that most of the hydrogen atoms in benzene rings have been replaced by methylene groups. The peak near 1425 cm^{-1} clearly shows the original structure of fullerene is completely preserved.[27] We further investigated the chemical structure of the resulting materials by ^{13}C CP/MAS NMR spectra (Fig.S3, ESI†). Two peaks are clearly observed near 140 ppm and 130 ppm for monomer, which are attributed to the substituted aromatic carbons and unsubstituted aromatic carbons in the benzene rings respectively,[28] and a narrow peak around 60 ppm belongs to the sp^3 fullerene carbons for monomer (Fig. S3, ESI†).[31,32] Compared with monomer, the intensity of substituted aromatic carbon (140 ppm) and alkyl carbon peaks (40 ppm) of HCPs increased, which was ascribed to much more alkyl linkers connected with monomer(Fig. S3 (b) (c), ESI†).[33] These data confirmed that the solvent knitting strategy has been successfully employed for the construction of the HCPs materials.

The thermal stability of monomer N, N-H-1 and N-H-2 was recorded by thermogravimetric analysis (TGA). As shown in Fig. S4 (ESI†), the weight of N-H-1 and monomer N lost slowly and continuously, and there was no significant loss of weight until 400 °C for N-H-2, which may be due to the difference in their chemical nature. Moreover, the introduction of alkyl leads to lower residual variability for N-H-1 and N-H-2.

The morphologies and porous textures of the two networks were investigated by field-emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM) (Fig. S5, ESI†). The FE-SEM images revealed that the N-H-1 and N-H-2 showed an amorphous morphologies, and their structures are very similar. The HR-TEM images showed that there were abundant pore structure in both N-H-1 and N-H-2, which could be

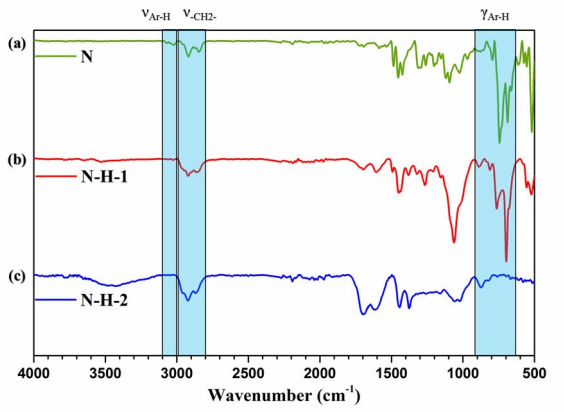

Fig. 1 The Fourier transform infrared (FT-IR) spectra of monomer N (a), N-H-1(b) and N-H-2(c).

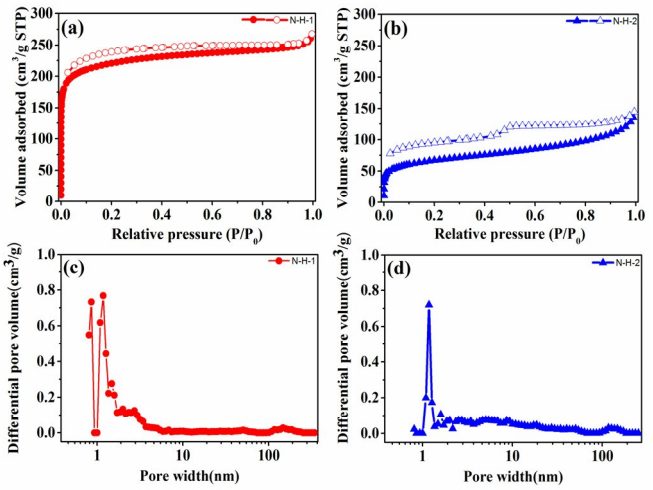

Fig. 2 (a) (b)Nitrogen adsorption and desorption isotherms (77.3 K) and (c) (d)pore size distribution calculated using DFT methods (slit pore models, differential pore volumes) of N-H-1 (red) and N-H-2 (blue).

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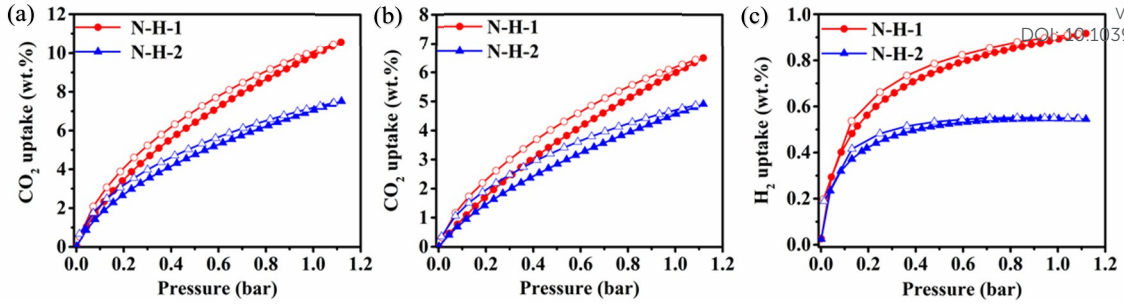

Fig. 3 The Volumetric CO_2 adsorption and desorption isotherms up to 1.13 bar at 273.15 K (a), 298.15 K (b) and volumetric H_2 adsorption isotherms and desorption isotherms up to 1.13 bar at 77.3 K (c) of N-H-1 and N-H-2.

Table 1 Porosity properties and gas uptake capacities of N-H-1 and N-H-2

No.	S_{BET}[a] ($m^2\ g^{-1}$)	S_L[b] ($m^2\ g^{-1}$)	PV[c] ($cm^3\ g^{-1}$)	MPV[d] ($cm^3\ g^{-1}$)	H_2 uptake[e] (wt %)	CO_2 uptake[f] (wt %)	CO_2 uptake[g] (wt %)
N-H-1	753	997	0.41	0.25	0.92	10.59	6.50
N-H-2	235	317	0.22	0.05	0.55	7.51	4.91

[a] Surface area calculated from nitrogen adsorption isotherm at 77.3 K using BET equation. [b] Surface area calculated from nitrogen adsorption isotherm at 77.3 K using Langmuir equation. [c] Pore volume calculated from nitrogen isotherm at P/P_0=0.995, 77.3 K. [d] Micropore volume calculated from the nitrogen isotherm at P/P_0=0.050. [e]H_2 uptake determined volumetrically using a Micromeritics ASAP 2020 M analyzer at 1.13 bar and 77.3 K.[f] CO_2 uptake determined volumetrically using a Micromeritics ASAP 2020 M analyzer at 1.13 bar and 273.15 K. [g] CO_2 uptake determined volumetrically using a Micromeritics ASAP 2020 M analyzer at 1.13 bar and 298.15K.

observed clearly.

To better understand the pore characteristics, the porous nature of polymers was further investigated by N_2 sorption analysis at 77.3 K. As shown in Fig.S6, the BET surface of monomer N was nearly 0 m^2g^{-1}, and there were almost no existence of micropores and mesopores (Fig.S6, ESI†). However, the adsorption isotherms of N-H-1 and N-H-2 exhibit a type I character with a high nitrogen gas uptake at low relative pressure ($P/P_0 < 0.001$), thus indicating the abundant microporous structure,[34,35] which are consistent with HR-TEM results. Moreover, the nitrogen adsorption and desorption isotherms provide a strong evidence that the solvent knitting methods have been successful to construct porous structures.

The BET surface area of N-H-1 and N-H-2 is up to 753 m^2g^{-1} and 235 m^2g^{-1} respectively. The pore size distribution of N-H-1 showed hierarchical pores, in which the abundant micropores (0.8 nm) and continuous mesopores (less than 10 nm) are observed clearly. From Table 1, the total pore volumes of N-H-1 and N-H-2 are 0.41 cm^3g^{-1} and 0.22 cm^3g^{-1}, respectively. It is obvious that the microporosity of N-H-1 (61%) is much higher than that of N-H-2 (23%), which may be due to the difference in the length of carbon chain (from DCM and DCE). DCM with shorter carbon chain, made the monomers connected closely and formed a much more stable and tightly packed dense structure. The compact linking structure helps in constructing micropores and increasing the surface area and pore volume. Based on the above analysis, the solvent knitting method using DCM and DCE as the external crosslinker can effectively link monomer N to obtain fullerene-based porous materials. Abundant porous structure make such porous materials excellent gas absorbents for CO_2 and H_2, and therefore, we also set out to investigate CO_2 and H_2 absorptive capacities of N-H-1 and N-H-2. As shown in Fig. 3a, the CO_2 isotherms of N-H-1 and N-H-2 are fairly consistent. Table 1 shows the values of CO_2 capture at different temperatures. The CO_2 uptake of N-H-1 and N-H-2 was found to be 10.59 wt% (2.41 mmol g^{-1}) and 7.51 wt% (1.48 mmol g^{-1}) at 273 K and 1.13 bar, respectively, which is comparable to that of CTF-FUMs and CTF-DCNs (2.12-3.49 mmol g^{-1}),[36] Cu(II)- and Ni(II)-PCPs (2.49-2.80 mmol g-1),[37] HPPs (1.15-1.69 mmol g^{-1}),[38] POPSs (1.84-2.21 mmol g^{-1}),[39] SHCPs (1.23-1.84 mmol g^{-1}).[40] Moreover, these values are higher than some materials with high surface areas such as COF-102 (3620 $m^2\ g^{-1}$,1.52 mmol g^{-1} at 273K and 1 bar),[41] and PAF-1 (5640 $m^2\ g^{-1}$, 2.07 mmol g^{-1} at 273K and 1 bar).[17] Furthermore, the CO_2 uptake of N-H-1 outperforms the commercially available BPL carbon (2.09 mmol g^{-1}).[42] Moreover, N-H-1 exhibits not only the highest gas uptake capacity of these two porous networks, but also with a higher isosteric heat (Q_{st}) of 25.49-21.28 KJ mol^{-1} (Fig. S8, ESI†). Based on the hydrogen sorption isotherms, we found that all isotherms were fully reversible and unsaturated at low pressures, and the hydrogen uptake capacities reached up to 0.92 wt% and 0.55 wt% for N-H-1 and N-H-2, respectively (Fig. 3(c)).

In summary, we report a new kind of fullerene-based porous materials with abundant pore structure and good gas adsorption properties, which employs the fullerene derivatives as building blocks to construct two different porous networks (N-H-1 and N-H-2) by using a novel and relatively low-cost strategy. The pore characteristics of these porous networks were calculated by surface area and porosity analyzer. The resulting products show good absorption properties for CO_2 and H_2, thus making them promising candidates for applications

in gas adsorption. By using the novel synthetic strategy, fullerene-based HCPs materials can be constructed using relatively mild conditions, which makes the synthetic simple and more robust.

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Conflicts of interest

There are no conflicts to declare.

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