Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Novel fullerene-based porous materials Constructed by solvent knitting strategy

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Experimental details

Chemicals. The C_{60} (99.9%) was purchased from Suzhou Dade Carbon Nano-tech. Corp. (Suzhou, China), used as received. The reagents 1, 2-bis (bromomethyl) benzene, sodium hydroxymethanesulfinate dihydrate (rongalite), tetrabutylammonium bromide (TBAB) were purchased from Aladdin chemical reagent Corp. (Shanghai, China) and used as received; dichloromethane (DCM), 1, 2-dichloroethane (DCE), DMF and anhydrous aluminum chloride were obtained from Sinopharm chemical reagent Co., Ltd (Shanghai, China) and used as received. In this work, unless otherwise noted, all the reagents were obtained from commercial suppliers and used without any further purification.

Synthesis of monomer $NC_{60}BA$. The synthesis process is based on the literature.[1] Under an argon atmosphere, 1,2-bis (bromomethyl)benzene (1.8024 g, 6.83 mmol) and tetrabutylammonium bromide (TBAB, 0.6600 g, 2.05 mmol) were added to DMF(120 mL), then Sodium hydroxyl-methanesulfinate (rongalite, 3.2224 g, 27.29 mmol) was added into the solution with magnetic stirring. This reaction was kept stirring at 0°C for 4 h. Afterwards, water was added into the solution and the mixture was extracted with CH_2Cl_2. The organic extracts were washed with distilled water several times to remove the residual DMF, and then dried over Na_2SO_4. The solvent was evaporated at 25 °C and a colourless oil, sultine, was obtained.

Next, 217.4 mg of C_{60} powder was dissolved in 250 mL toluene, 152.4 mg sultine was then added into the system. The solution was heated to 80°C under argon atmosphere for 15 h. After cooling down, water was added, the organic extract was obtained by using a separating funnel and dried over Na_2SO_4. After concentrated under reduced pressure with the helping of the rotary evaporation at 40 ^{o}C, a brown powder was obtained. Then the crude product was purified and separated by column chromatography, CH_2Cl_2 and petroleum ether (1:5 volume ratio) were used as eluent， and the monomer N was obtained (**Figure S1** and **S2**).

Synthesis of N-H-1 and N-H-2 by solvent knitting method with different external crosslinkers. Under an Argon atmosphere, in order to synthesize N-H-1, the monomer N (50 mg, 5.39×10^{-2} mmol) was added in DCM (4 mL). Magnetic stirring for 10 minutes until the monomer completely dissolved in the solvent, then the anhydrous Aluminum chloride (0.40 g, 2.99 mmol) was added. The reaction system was kept at room temperature for 12h, then it was heated to 40^{o}C for 12 h, 60^{o}C for 12h, and 80^{o}C for 12h. After cooling to the room temperature, the system was quenched with 10 mL diluted hydrochloric acid (5%). The solid product was filtered and washed with ethanol for three times, further purified by soxhlet extraction with ethanol for 48 h. Finally, the product was dried in a vacuum oven at 60 ^{o}C for 24h. The N-H-1 was obtained as a dark brown powder. Yield: ⩾103%. Following the synthesis conditions of N-H-1, N-H-2 was produced by treating monomer N (50 mg, 5.39×10^{-2} mmol) with $AlCl_3$ (0.40 g, 2.99 mmol) in DCE (4 mL). Yield: ⩾114%.

FT-IR, NMR and Solid-state ^{13}C CP/MAS NMR experiments. The FT-IR spectra were recorded by using Bruker VERTEX 70 FT-IR spectrometer employing the KBr disk method. The ^{1}H and ^{13}C NMR spectra of monomer N, which dissolved in $CDCl_3$, were recorded on a Bruker AV400 spectrometer. Solid-state ^{13}C CP/MAS NMR spectra were obtained on a WB 400 MHz Bruker Avance II spectrometer. The ^{13}C CP/MAS NMR spectra were collected by using the 4 mm double-resonance MAS probe, with a spinning rate of 8 kHz.

FE-SEM, HR-TEM and TGA analysis. The field-emission scanning electron microscopy (FE-SEM) images were recorded employing a Nova Nano SEM 450 field-emission scanning electron microscope (FEI Corp.) (Operated at 10 kV). Before measurement, the samples were dried in a vacuum oven at 60 ^{o}C for at least 24 h and then sputter coated with Pt. The high resolution transmission electron microscopy (HR-TEM) images were recorded on a Tecnai G2 F30 microscope (FEI Corp.) (Operated at 300 kV). Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere, the range from 25 to 800 ^{o}C, employing a Perkin-Elmer Instrument Pyris1 TGA with a heating rate of 10 ^{o}C min^{-1}.

Gas adsorption measurements. Gas (N_2, H_2, and CO_2) sorption properties and samples' specific surface area were measured by using a Micromeritics ASAP 2020 surface area and porosity analyzer. The samples were all degassed at 110 °C for 8 h under vacuum condition of 10^{-5} bar before analysis. Pore size distribution was calculated by the N_2 adsorption isotherms employing a nonlocal density functional theory (NLDFT) model assuming slit pore geometry. Total pore volumes (V_{total}) were derived from nitrogen sorption isotherms at relative pressure $P/P_0 = 0.995$.

Isosteric heat (Q_{st}) of CO_2 adsorption. The CO_2 adsorption isotherms of samples were conducted by a Micromeritics ASAP 2020 surface area and pore size analyzer. Commonly, the isosteric heat of CO_2 adsorption (Q_{st}) is calculated based on CO_2 adsorption isotherms at different temperatures (273.15 K and 298.15 K) from 0 to 1.13 bar.

Theoretically, the data were simulated with Virial expression:[2]

$$lnP = lnN + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad \textbf{(1)}$$

Here, in *eq.1*, $\boldsymbol{P}$ is the pressure (Torr), $\boldsymbol{N}$ is the amount of adsorbed CO_2(cm^3 g^{-1}), $\boldsymbol{T}$ is the temperature (K), a_i and b_i are virial coefficients which are independent of temperature, and $\boldsymbol{m}$, $\boldsymbol{n}$ represent the number of coefficients required to adequately describe the isotherms.

In general, a nonlinear curve was obtained, which demonstrating the connection between ***lnP*** and ***N*** (**Figure S7**).

Then, the values of the virial coefficients a_0 through a_m were used to calculate the isosteric heat of adsorption (Q_{st}) using the following expression (*eq.2*):

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i \qquad \textbf{(2)}$$

R is the universal gas constant (8.3145 $\mathbf{J\ mol^{-1}\ K^{-1}}$).[3-6]

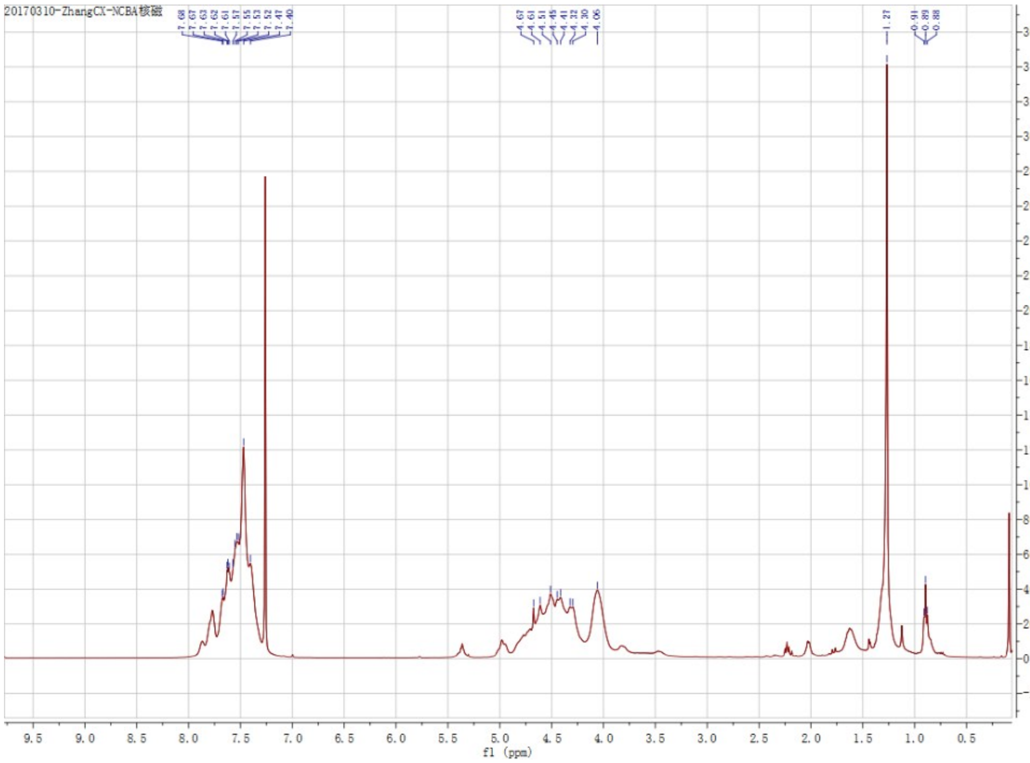

Figure S1. ^{1}H NMR spectrum of monomer N.

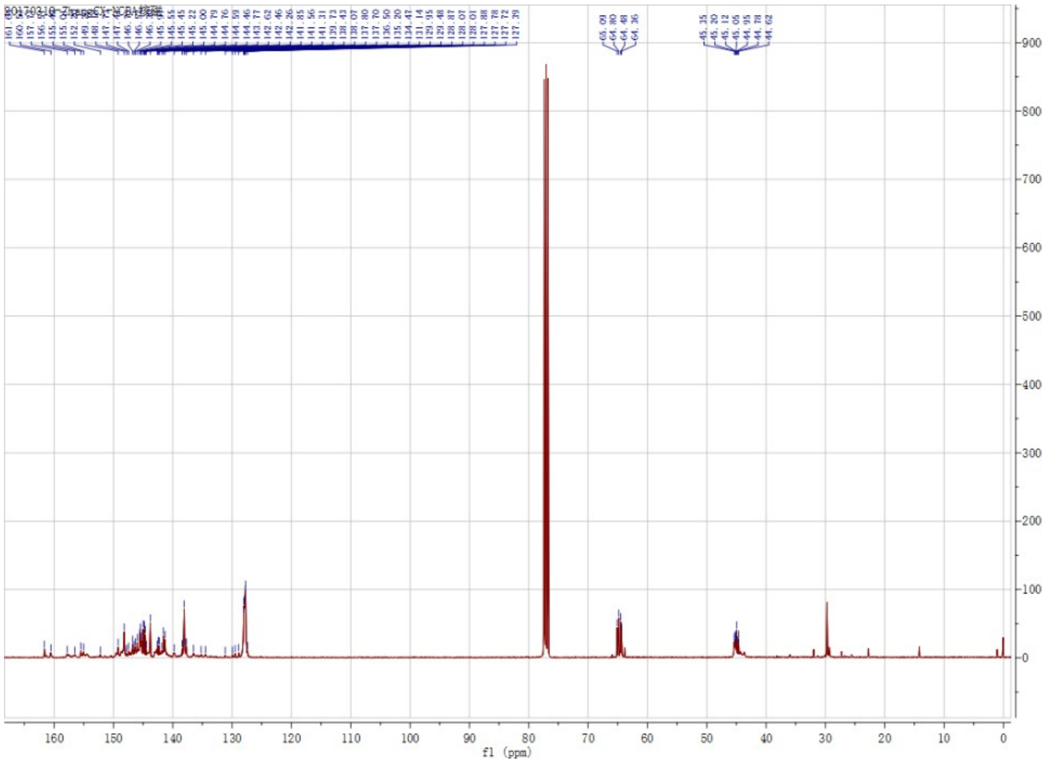

Figure S2. ^{13}C NMR spectrum of monomer N.

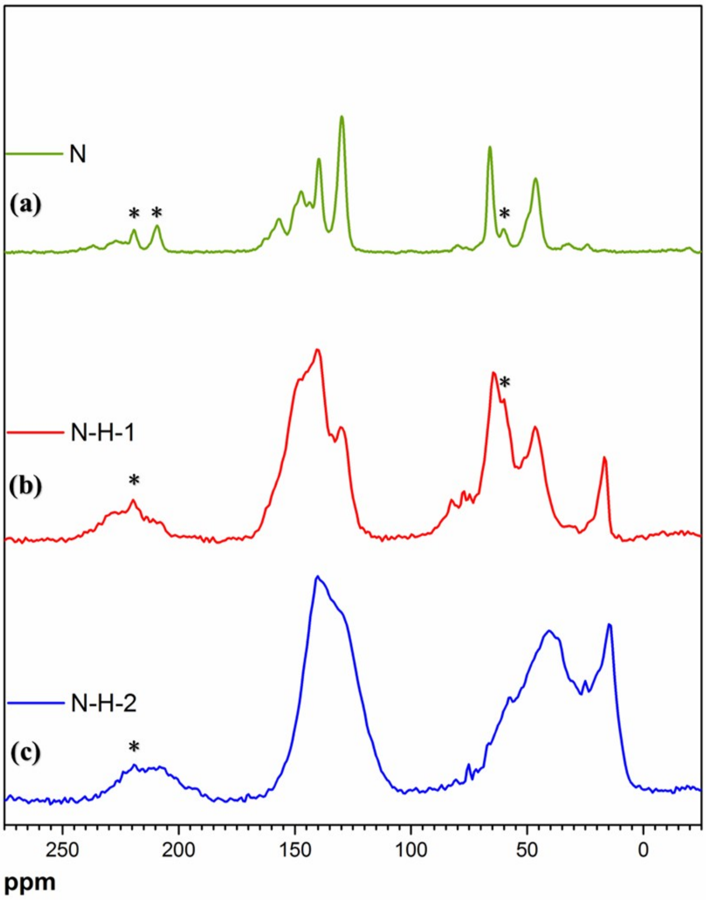

Figure S3. ^{13}C CP/MAS NMR spectra of monomer N (a), N-H-1 (b) and N-H-2 (c). Asterisks denote spinning sidebands.

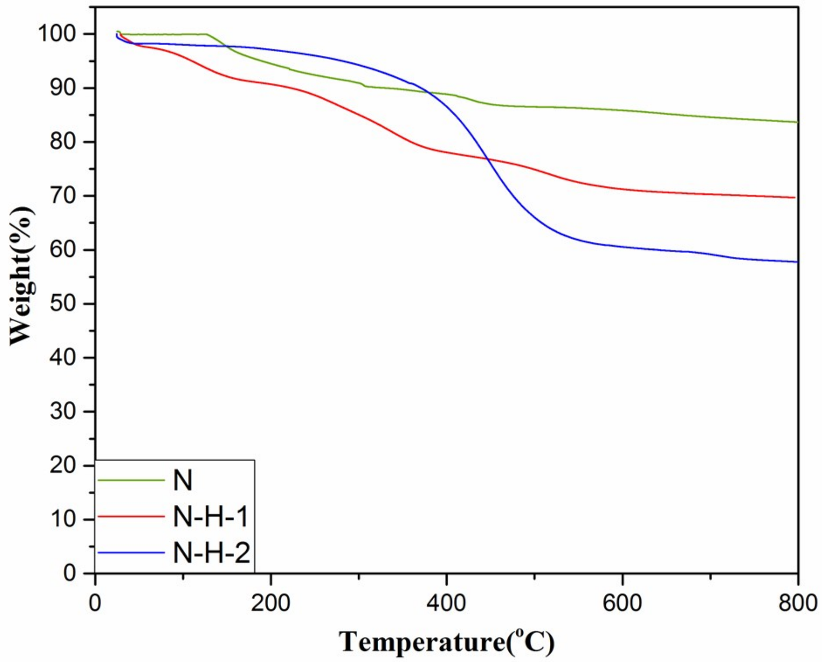

Figure S4. Thermogravimetric analysis (TGA) of N, N-H-1 and N-H-2.

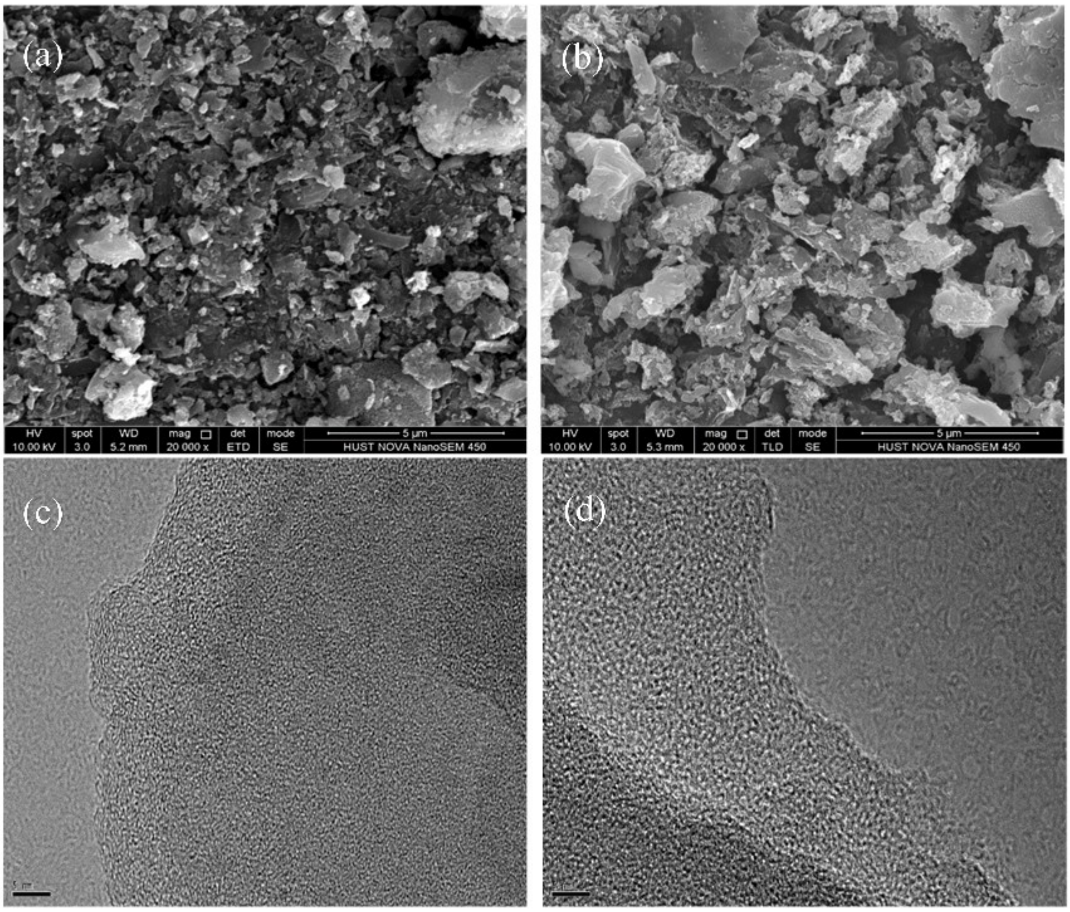

Figure S5. FE-SEM images of N-H-1(a) and N-H-2(b); HR-TEM images of N-H-1(c) and N-H-2(d). (Scale bar: SEM-5 µm, TEM-5 nm)

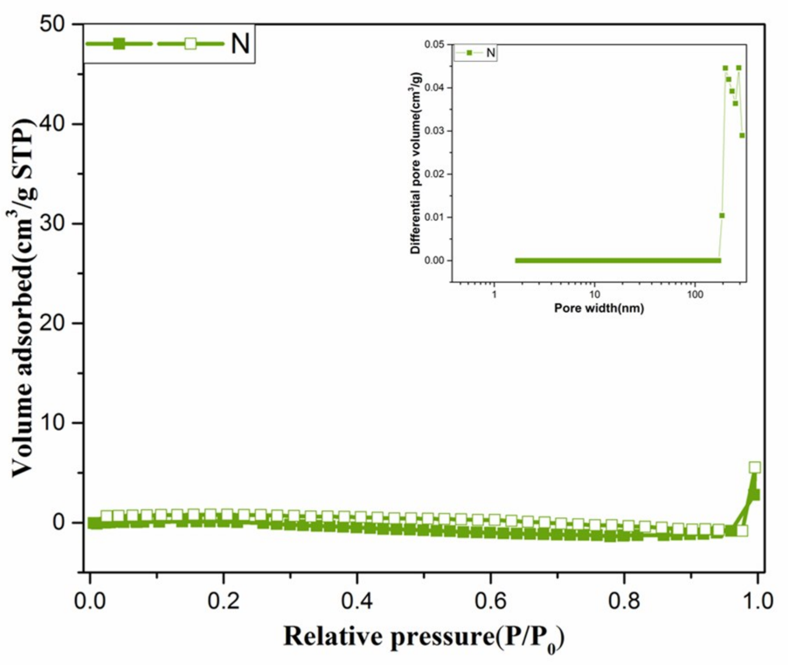

Figure S6. Nitrogen adsorption and desorption isotherms (77.3 K) of monomer N powder.

(Inside: pore size distribution)

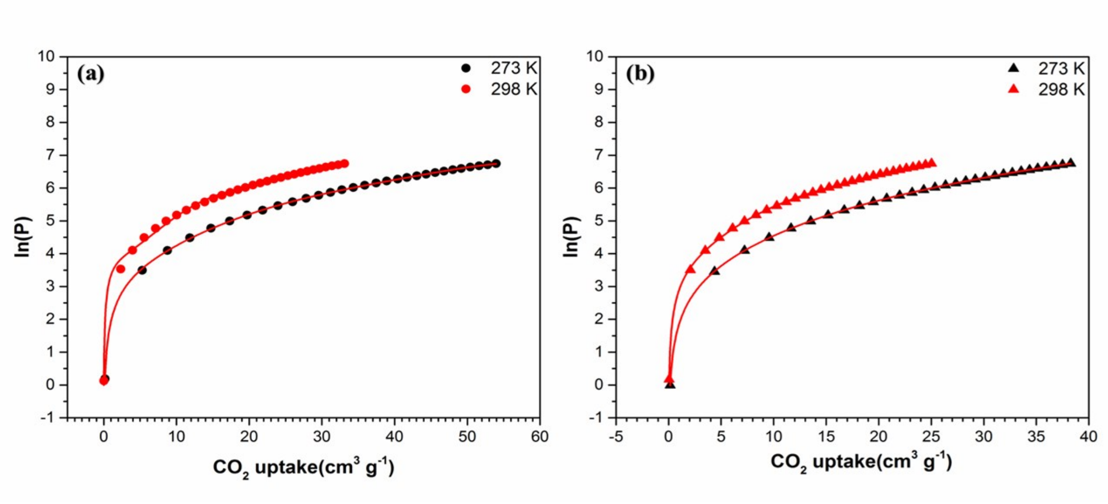

Figure S7. Nonlinear curve of N-H-1(a) and N-H-2(b) at different temperatures.

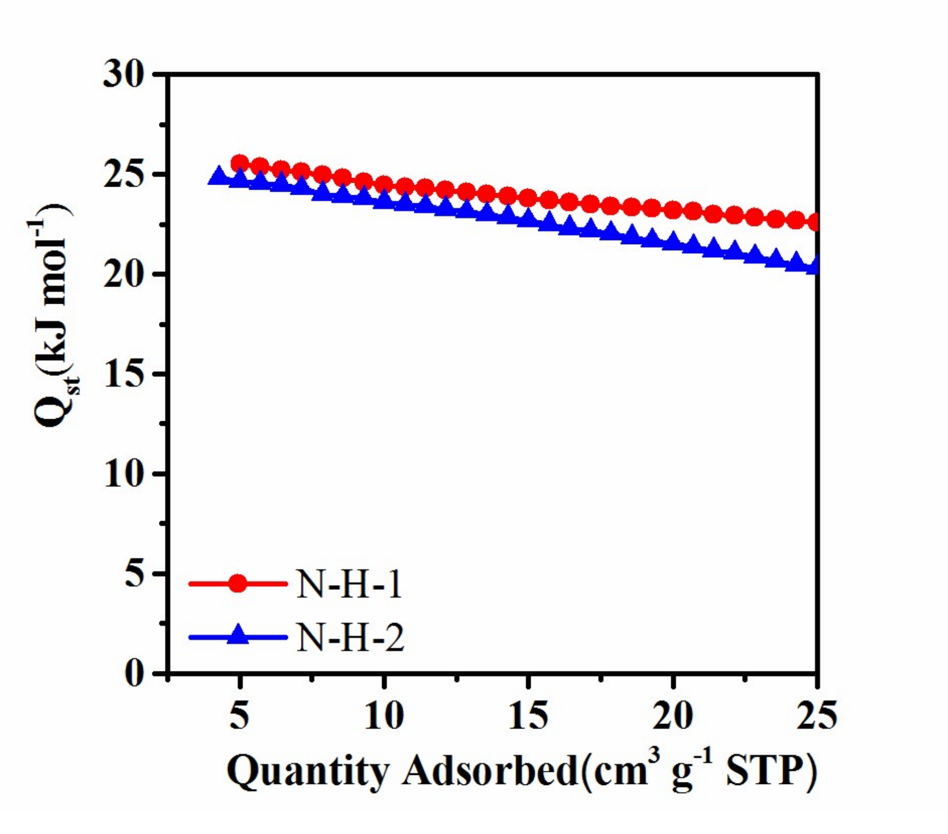

Figure S8. Isosteric heat of adsorption for CO$_2$ at different CO$_2$ loadings.

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