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Facile synthesis of cost-effective porous aromatic materials with enhanced carbon dioxide uptake

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Porous aromatic frameworks (PAF-32s) derived from tetrahedral monomers as basic building units are successfully synthesized via Friedel-Crafts alkylation reaction in the present of inexpensive catalyst $FeCl_3$. The resulted PAF-32 materials possess high stabilities and high surface areas up to 1679 m^2 g^{-1}. In particular, amino and hydroxyl functional groups are introduced in the networks. The corresponding functionalized PAF materials (PAF-32-NH_2 and PAF-32-OH) display enhanced CO_2 adsorption capacities and higher heat of adsorption (Q_{st}) than the non-functionalized PAF-32.

Introduction

Nowadays, the worsening climatic situation due to global warming has become a widespread public concern, and excessive CO_2 emissions are thought to be one of the major causes. To prevent the continuous environmental degradation, viable CO_2 capture and storage (CCS) technologies are urgently needed. Current methods such as amine scrubbing have been industrially employed in post-combustion process for over 50 years.**Error! Reference source not found.** Despite strong chemical absorbing nature of aqueous amine, large amount of energy consumption for amine regeneration after CO_2 capture inspires people to explore more energy-effective methods. Solid sorbents such as porous materials are promising alternatives as the physical sorption that they rely on could reduce the cost to recycle the capture materials and the readily reversible adsorption/desorption behaviour allows material regeneration without applying heat.**Error! Reference source not found.** Being an important family of porous materials, porous organic frameworks (POFs) derived wholly from light elements have attracted considerable attentions because of their high surface areas and low skeleton densities.**Error! Reference source not found.** Meanwhile, the diversity of synthetic strategies and ease to tailor global properties in POFs skeletons has greatly accelerated POFs development and also expanded their application in gas storage. A significant number of POFs have been synthesized and studied in terms of CO_2 capture in the last decade.**Error! Reference source not found.** As one of the most representative POFs, PAF-1 synthesized via Yamamoto-Ullmann cross-coupling of tetrakis(4-bromophenyl) methane exhibited extraordinarily high surface areas as well as excellent CO_2 sorption ability.**Error! Reference source not found.** After that various POFs derived from tetrahedral monomers were successfully synthesized.**Error! Reference source not found.** They commonly possessed ultrahigh surface areas and also presented excellent gas storage abilities, suggesting that rigid tetrahedral monomers are promising candidates to construct POF materials.**Error! Reference source not found.**

To satisfy the requirements of CCS technologies, low-cost sorbents with high stabilities are preferred due to the large amount of CO_2 involved. However, most POFs were obtained via cross-coupling reactions catalysed by transition metal catalysts or noble metal catalysts**Error! Reference source not found.** which have limited their practical applications. Friedel-Crafts alkylation reaction catalysed by inexpensive $FeCl_3$ or $AlCl_3$ has offered an original opportunity to produce cost-effective POFs.**Error! Reference source not found.** Several hypercrosslinked POFs were prepared using formaldehyde dimethyl acetal (FDA) as external cross-linkers in the presence of $FeCl_3$.**Error! Reference source not found.** Among these materials, microporous binaphthol network derived from alcohol-contained fused aromatics exhibited the highest CO_2 uptake, which might benefit from the hydroxyl group in the network.**Error! Reference source not found.** It has been proved that introducing CO_2-philic functional groups in the skeleton could enhance the CO_2 capability of porous materials.**Error! Reference source not found.** Except for well-developed amine-decorating strategy**Error! Reference source not found.**, the incorporation of heteroatoms (e.g. N, O, S) is also being considered a promising potential route to increase the CO_2 sorption abilities, as the electron-rich functional groups in the networks could result in strong dipole-quadrupole interaction with CO_2 molecule.**Error! Reference source not found.**

Here, with tetraphenylmethane and its derivatives as the rigid building block, we demonstrated the facile synthesis of low-cost PAF materials via Friedel-Crafts alkylation reaction under mild condition. Amino and hydroxyl functional groups were successfully introduced to the frameworks by carefully selecting mono-functionalized tetrahedral monomers as building units. With the incorporation of electron-rich functional groups in the frameworks, PAF-32-NH_2 and PAF-32-OH exhibited higher CO_2 capture abilities than PAF-32.

Experimental

Chemicals

4-Tritylphenylamine, 4-Tritylphenol and formaldehyde dimethyl acetal (FDA) were purchased from Alfa Aeser. Other chemicals and reagents were purchased from commercial suppliers without further purification unless otherwise stated. Methylene dichloride (CH_2Cl_2) was dehydrated with CaH_2. Tetraphenylmethane was prepared according to the previously reported method.**Error! Reference source not found.**

Synthesis of PAF-32, PAF-32-NH$_2$ and PAF-32-OH

As shown in Fig. 1, FDA (0.36mL, 4 mmol) was injected into a mixture of tetrahedral monomers (1 mmol) and $FeCl_3$ (0.65g, 4 mmol) in 10mL anhydrous CH_2Cl_2 in a two-neck flask equipped with condenser. After degassing via three freeze-pump-thaw cycles, the mixtures were heated at 45 °C for 24h under N_2 atmosphere. After cooling to room temperature, the precipitate was collected by filtration. Then the resulted PAF materials were washed thoroughly with methanol to remove the unreacted monomers or catalyst residues, and dried under vacuum at 120 °C to give PAF-32s as brown powders (92~96% yields). The samples for characterizations were activated under vacuum at 150 °C for 10 h before employments.
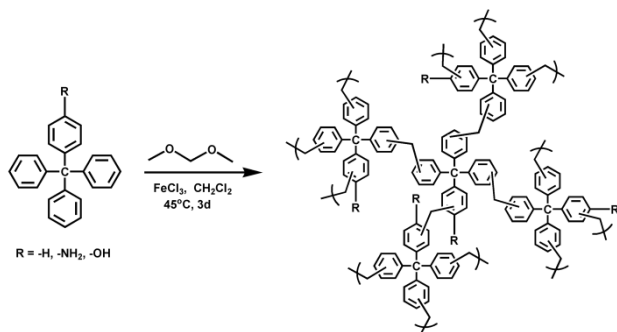

Fig. 1 Schematic depiction of the synthesis of PAF-32 and its functionalized analogues PAF-32-NH$_2$ and PAF-32-OH.

Physical Measurements

The Fourier Transform Infrared Spectroscopy (FTIR) spectra (film) were measured using a IFS 66V/S Fourier transform infrared spectrometer. Solid-state ^{1}H-^{13}C cross polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR) measurements were performed on a Bruker Avance III model 400 MHz NMR spectrometer at a MAS rate of 5 KHz. Scanning electron microscopy (SEM) imaging was performed on a JEOS JSM 6700. Transmission electron microscopy (TEM) was recorded using a JEOL JEM 3010 with an acceleration voltage of 300 kV. The thermogravimetric analysis (TGA) was performed using a Netzch Sta 449c thermal analyzer system at the heating rate of 10 °C/min in air condition. X-ray photoelectron spectroscopy (XPS) was performed using Thermo ESCALAB 250. The powder X-ray diffraction (PXRD) was performed by a Riguku D/MAX2550 diffractometer using CuKα radiation, 40 kV, 200 mA with scanning rate of 4°/min (2θ). The gas adsorption/desorption isotherms were measured on Quantachrome Autosorb-iQ2 analyzer.

Results and discussion

Via well-developed Friedel-Crafts alkylation reaction in the preparation of hypercrosslinked organic polymers, PAF-32 was synthesized by tetraphenylmethane in the present of FDA and $FeCl_3$ under the similar reaction conditions to those described by Tan and Cooper**Error! Reference source not found.**, in which the solvent was replaced with CH_2Cl_2 and the reaction temperature thus dropped to 45 °C which would bring energy saving and make the resulted materials more practical in gas storage application. It is well known that the incorporation of functional groups with heteroatoms would bring enhanced gas uptake capacities. A series of microporous copolymers with increased gas selectivity were synthesized by Cooper and his co-workers using benzene and aniline as co-monomers via Friedel-Crafts alkylation, and the existence of nitrogen contents in the network was confirmed.**Error! Reference source not found.** However, the values of surface areas decreased sharply when the ration of aniline monomer increased since aniline possessed strong reactivity. With the successful synthesis of PAF-32 and high surface area PAF-32 possessed, we then selected the rigid tetrahedral monomers with mono-functional group as building blocks, and carried out the same crosslinked polymerization. The functionalized networks PAF-32-NH$_2$ and PAF-32-OH were thus obtained. Typically, the tetrahedral building blocks would be connected with methylene groups after reaction, and the functional groups would be retained in the networks.

Structural information of PAF-32, PAF-32-NH$_2$ and PAF-32-OH

Comparisons of the FTIR spectra of PAF-32 materials and their corresponding tetrahedral monomers were firstly performed to confirm the bonding and structural features in the resulted polymeric materials. The weakened C-H vibrations at *ca.* 3000 (stretching) and 1500 (bending) cm^{-1} and the appearance of methylene group stretching vibrations at 2962 and 2872 cm^{-1} in FTIR spectra revealed the networks were linked by methylene groups as desired (Fig. S1). The aromatic C=C bands at *ca.* 1660 and 1600 cm^{-1} showed the presence of phenyl rings in PAF-32s networks which was consistent with the expected networks. Additionally, the FTIR spectra of PAF-32-NH$_2$ and PAF-32-OH clearly indicated the presence of amino (*ca.* 3400 cm^{-1}) and hydroxyl (*ca.* 3500 cm^{-1}) groups in the network indicating the functional groups were well-retained.**Error! Reference source not found.** Nitrogen and oxygen elements were found in corresponding functionalized PAF-32 materials which were confirmed by XPS analysis (Fig. S2). Meanwhile, no iron was detected (the average molar ratio of Fe/C < 0.001) in all the three networks (Fig. S3), indicating that the catalysts were thoroughly removed.

Further investigation on the local structures of PAF-32 materials was performed by solid-state ^{13}C CP/MAS NMR studies. In ^{13}C CP/MAS NMR spectra of the resulted polymeric materials (Fig. S4), three different types of resonance peaks were clearly observed. The strong signals in the range of 140~125 ppm are attributed to the aromatic carbon atoms. The signals at approximately 64 ppm could be assigned to the quaternary carbon atom in the tetrahedral building units. Moreover, the signal near 30 ppm is related to the methylene carbon atoms, thus further

indicating the FDA participated in the reaction. The resonance peaks of these PAF-32 materials showed a little variation (-2~3 ppm) due to the incorporation of functional groups and the difference of polymerized degrees.

In order to certify the long-range structures of these PAF-32 materials, PXRD was carried out. The PXRD patterns show that the resulted polymeric materials are in amorphous phase (Fig. S5), which is common in kinetics controlled irreversible coupling process.**Error! Reference source not found.**

The morphology and textural nature of PAF-32 materials were investigated by SEM and TEM. As shown in SEM images (Fig. 2 a, 2b & 2c), PAF-32 and its functionalized analogues PAF-32-NH_2 and PAF-32-OH are agglomerated microgel particles with a size of *ca.* 100 nm. The TEM investigations (Fig. 2d, 2e & 2f) show worm-like porous textures in all three PAF-32 materials but also with uniform pore diameters.
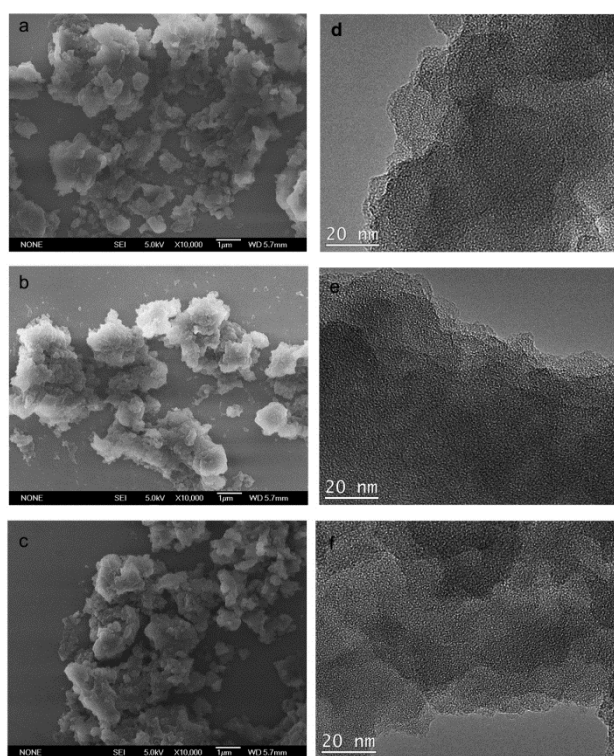

Fig. 2 SEM images (left) and TEM images (right) of PAF-32 (a, d) and its functionalized analogues PAF-32-NH_2 (b, e) and PAF-32-OH (c, f).

Porosity of PAF-32, PAF-32-NH_2 and PAF-32-OH

As the most important feature of porous materials, the pore characters of PAF-32 materials were studied by nitrogen sorption measured at 77K. As shown in the nitrogen adsorption-desorption isotherms (Fig. 3a), PAF-32 and its functionalized analogues PAF-32-NH_2 and PAF-32-OH exhibited sharp uptakes at low relative pressures, indicating the existence of micropores in their networks. And the distinct hysteresis loops in desorption branches were observed which were the featured symbols for the presence of some mesopores. The sorption isotherm of PAF-32-NH_2 increased rapidly at $P/P_0 \approx 1.0$, which might be attributed to the surface adsorption of assembled small particles. The apparent surface areas calculated from the Brunauer-Emmett-Teller (BET) model are 1679 $m^2\,g^{-1}$, 1230 $m^2\,g^{-1}$ and 1608 $m^2\,g^{-1}$ for PAF-32,

PAF-32-NH_2 and PAF-32-OH, respectively. Compared to PAF-32, a small reduction in the BET surface areas of PAF-32-NH_2 and PAF-32-OH was observed, which might be caused by the existence of amino and hydroxyl groups in the network. However, better than the post-functional treatment of porous materials, which commonly caused sharp surface area decrease,Error! Reference source not found. the simple one-step Friedel-Crafts alkylation reaction has offered a great opportunity to directly introduce functional groups and tailor global properties in the skeleton. The pore size distributions of PAF-32 materials (Fig. 3b) were calculated from nonlocal density functional (NLDFT) theory and give the primary pore size at 8Å, suggesting that the polymeric materials are predominately microporous. Also, the pores around *ca.* 2nm were observed suggesting the presence of a small amount of mesopores. It is worthy-noted that the incorporation of amino and hydroxyl groups in the networks gives negligible change of the pore size distribution within the PAF-32 materials, indicating the functionalised PAF-32 materials possess similar pore properties as PAF-32.
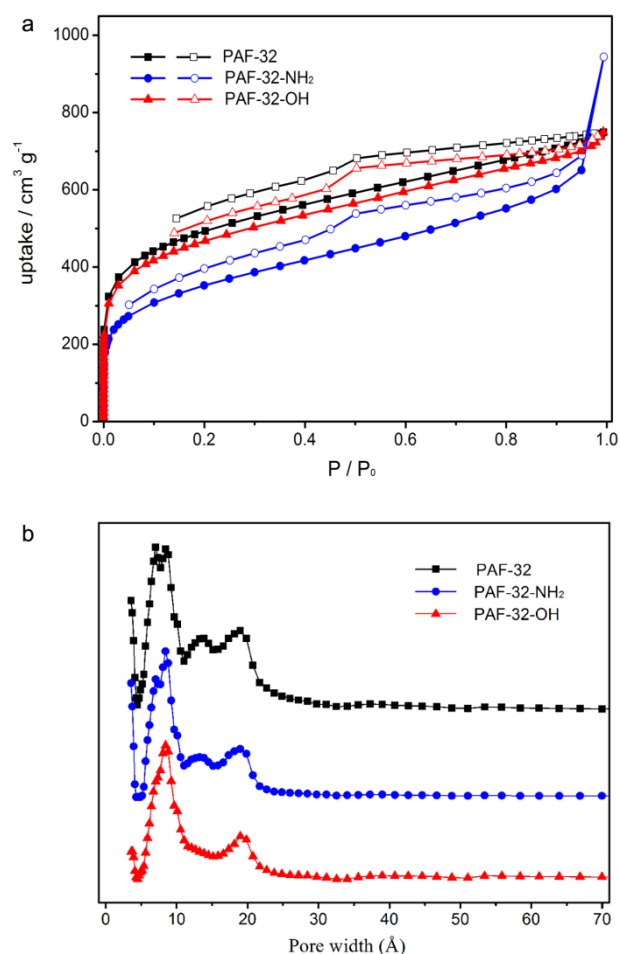

Fig. 3 Nitrogen adsorption (solid symbols) -desorption (open symbols) isotherms (a) measured at 77K and the pore size distributions (b) calculated from NLDFT of PAF-32 and its functionalized analogues PAF-32-NH_2 and PAF-32-OH, respectively.

Stability of PAF-32, PAF-32-NH_2 and PAF-32-OH

The stability of sorbents is a vital factor in CCS technologies. Sorbents with high stability would efficiently increase the

recyclability and thus reduce the energy consumption and cost per cycle. Here, the thermal and chemical stabilities of PAF-32 materials were investigated. TGA displayed the decomposition of PAF-32 materials started above 350 $^{\circ}$C under air condition, suggesting high thermal stabilities they afforded. Compared to PAF-32, the functionalized materials revealed slightly lower thermal stabilities which might be attributed to prior decomposition of the functional groups in the networks. In addition, PAF-32 materials could not be dissolved and decomposed in common organic solvents, such as DMF, CHCl$_3$, THF, etc, indicating their high chemical stability. The high stability ensures these materials could be utilized under rigorous conditions.
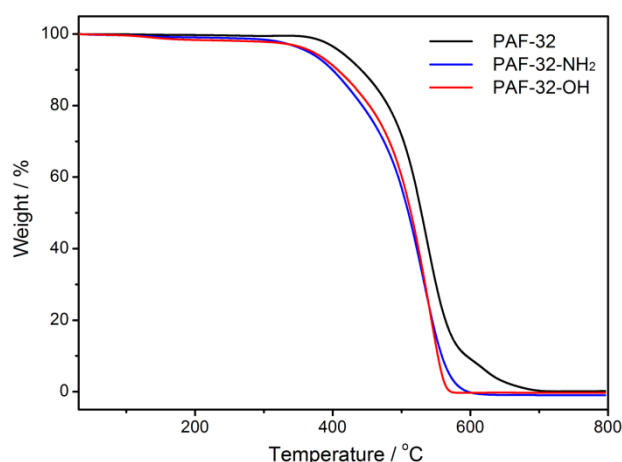

Fig. 4 TGA plots of PAF-32, PAF-32-NH$_2$ and PAF-32-OH, respectively.

CO$_2$ sorption for PAF-32, PAF-32-NH$_2$ and PAF-32-OH

It is well known that the incorporation of electron-rich functional groups in the frameworks may provide polar adsorption sites, which could result in strong dipole-quadrupole interaction with CO$_2$ molecule, thus effectively improve CO$_2$ sorption capability in materials.**Error! Reference source not found.** The high surface areas and thermal stabilities PAF-32 materials possessed and successful incorporation of amino and hydroxyl groups in the networks encouraged us to explore their CO$_2$ sorption abilities which is highly attractive due to environmental and economic reasons. CO$_2$ sorption isotherms of PAF-32 and its functionalized analogues were collected at 273K and 298K, respectively. At 273K and 1bar, the CO$_2$ uptakes were 1.66 mmol g^{-1} for PAF-32 (Fig. 5a), 1.62 mmol g^{-1} and 2.27 mmol g^{-1} for PAF-32-NH$_2$ and PAF-32-OH respectively (Fig. 5b & c). These values are comparable with the functionalized CMPs (1.6-1.8 mmol g^{-1})**Error! Reference source not found.**, COFs (1.21-3.84 mmol g^{-1})**Error! Reference source not found.**, and other hyper-crosslinked polymers (1.11-3.96 mmol g^{-1}).**Error! Reference source not found.** Compared to PAF-32, PAF-32-NH$_2$ with lower surface area exhibited comparable CO$_2$ sorption ability, and PAF-32-OH with similar surface area showed higher CO$_2$ uptake with an increase up to 40%. In order to better understand the CO$_2$ capability of functionalized PAF-32 materials without the effect of surface area, CO$_2$ uptakes per surface area at 273K and 298K were calculated for all three networks respectively, in which the CO$_2$ uptake was defined as the ratio of CO$_2$ sorption amounts and surface area of the corresponding PAF-32 materials. As shown in Fig. 5d & e, at 273K and 298K, both PAF-32-NH$_2$ and PAF-32-OH displayed higher CO$_2$ uptakes than PAF-32 at any degree of CO$_2$ loading when setting aside the surface area. The CO$_2$ adsorption values are 9.89 mmol cm^{-2}, 13.2 mmol cm^{-2} and 14.1 mmol cm^{-2} for PAF-32, PAF-32-NH$_2$ and PAF-32-OH respectively at 273K, 1bar. This suggests that the functionalized PAF-32 materials have stronger interaction with CO$_2$ molecule because of the electron-rich functional groups in their networks.
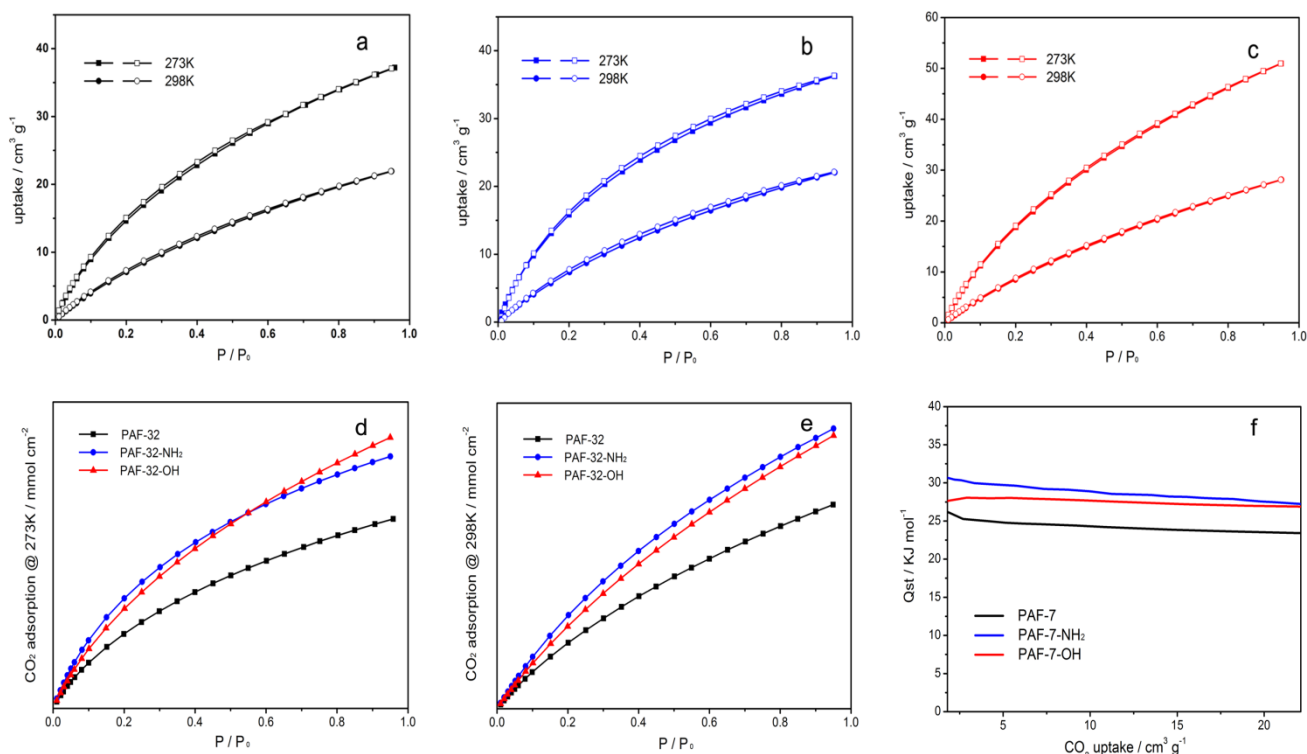
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Fig.5 Above: CO_2 adsorption (solid symbols) -desorption (open symbols) isotherms measured at 273K and 298K, 1bar for PAF-32 (a), PAF-32-NH$_2$ (b) and PAF-32-OH (c), respectively. Below: CO_2 adsorption amounts per surface area of PAF-32 materials at 273K (d) and 298K (e), respectively; (f) the heat of adsorption of the three PAF-32 materials.

To further explore the interaction between PAF-32 materials and CO_2 molecule, the heat of adsorption (Q_{st}) for CO_2 was calculated from the adsorption data of PAF-32 materials collected at 273 and 298 K using the Clausius–Clapeyron equation.**Error! Reference source not found.** Unsurprisingly, PAF-32-NH$_2$ and PAF-32-OH exhibited higher Q_{st} (Fig. 5f), indicating stronger interactions between CO_2 molecule and frameworks with polar functionalities than nonfunctionalized PAF-32. At zero coverage, the Q_{st} of PAF-32, PAF-32-NH$_2$ and PAF-32-OH are 26 kJ mol^{-1}, 31 kJ mol^{-1} and 28 kJ mol^{-1}, respectively, which is comparable with other reported POF materials.**Error! Reference source not found.**

Conclusions

In summary, three PAF materials (PAF-32s) based on tetrahedral building blocks were successfully synthesized by simple one-step Friedel-Crafts alkylation reaction in the presence of inexpensive catalyst FeCl$_3$. Amino and hydroxyl functional groups were successfully incorporated in PAF-32 networks, and this fact was confirmed by various spectroscopic methods. PAF-32 and its functionalized analogues possessed high thermal and chemical stabilities as well as high surface areas which satisfied the basic requirements for a good candidate in gas storage application. As

we expected, PAF-32 materials showed comparable CO_2 sorption capacity to other POFs. And the functionalized PAF-32 exhibited enhanced effect for CO_2 capture because of the presence of amino and hydroxyl groups in the frameworks. This is also be proved by the Q_{st} of PAF-32-NH$_2$ and PAF-32-OH, which are both higher than PAF-32. Friedel-Crafts alkylation reaction has provided a simple and efficient synthetic mean to produce cost-effective functionalized porous materials which would be promising solid sorbents for practical use in CCS technologies.

Acknowledge

Notes and references

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