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PII: S0009-2509(16)30052-5
DOI: <http://dx.doi.org/10.1016/j.ces.2016.02.007>
Reference: CES12799

To appear in: *Chemical Engineering Science*

Received date: 29 November 2015

Revised date: 2 February 2016

Accepted date: 4 February 2016

Cite this article as: Swapan K. Das, Xinbo Wang, Mayur M. Ostwal, Yunfeng Zhao, Yu Han and Zhiping Lai, Highly Stable Porous Covalent Triazine-Piperazine Linked Nanoflower as a Feasible Adsorbent for Flue Gas CO₂ Capture, *Chemical Engineering Science*, <http://dx.doi.org/10.1016/j.ces.2016.02.007>

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Highly Stable Porous Covalent Triazine-Piperazine Linked Nanoflower as a Feasible Adsorbent for Flue Gas CO₂ Capture

Swapan K. Das, Xinbo Wang, Mayur M. Ostwal, Yunfeng Zhao, Yu Han and Zhiping Lai*

Advanced Membrane and Porous Materials Center, Division of Physical Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Kingdom of Saudi Arabia.

Tel: +96628082408; E-mail address: Zhiping.lai@kaust.edu.sa

ABSTRACT

Here, we report a porous covalent triazine-piperazine linked polymer (CTPP) featuring 3D nanoflower morphology and enhanced capture/removal of CO₂, CH₄ from air (N₂), essential to control greenhouse gas emission and natural gas upgrading. ¹³C solid-state NMR and FTIR analyses and CHN and X-ray photoelectron spectroscopy (XPS) elemental analyses confirmed the integration of triazine and piperazine components in the network. Scanning electron microscopic (SEM) and transmission electron microscopic (TEM) analyses revealed a relatively uniform particle size of approximately 400 to 500 nm with 3D nanoflower microstructure, which was formed by the self-assembly of interwoven and slight bent nanoflake components. The material exhibited outstanding chemical robustness under acidic and basic medium and high thermal stability up to 773 K. The CTPP possess high surface area (779 m²/g) and single-component gas adsorption study exhibited enhanced CO₂ and CH₄ uptake of 3.48 mmol/g, 1.09 mmol/g, respectively at 273 K, 1 bar; coupled with high sorption selectivities for CO₂/N₂ and CH₄/N₂ of 128 and 17, respectively. The enriched Lewis basicity of the CTPP favors the interaction with CO₂, which results in an enhanced CO₂ adsorption capacity and high CO₂/N₂ selectivity. The binary mixture breakthrough study for the flue gas composition at 298 K showed a high CO₂/N₂ selectivity of 82. CO₂ heats of adsorption for the CTPP (34 kJ mol⁻¹) were

realized at the borderline between strong physisorption and weak chemisorption (Q_{stCO_2} ; 25-50 kJ mol^{-1}) and low Q_{st} value for N_2 (22.09 kJ mol^{-1}), providing the ultimate validation for the high selectivity of CO_2 over N_2 .

Keywords: Covalent triazine-piperazine polymer, 3D Nanoflower, Chemical robustness and thermal stability, Lewis basicity, Flue gas and natural gas, mixture breakthrough study

1. Introduction

The rapid increase in atmospheric CO_2 is a major environmental issue due to its adverse effects on the environment, such as global climate change and ocean acidification.[1] This has, in turn, necessitated technology and materials development for effective and economical CO_2 capture. Flue gas, which contains approximately 10 to 15% CO_2 , is considered one of the main CO_2 emission sources.[2, 3] The commercial aqueous amine scrubbing process is corrosive and energy intensive and thus economically and energetically unfeasible in a large scale capture applications.[4, 5] To date, related to the gas separation/purification various technologies have been developed such as cryogenic distillation, membrane separation, and adsorption/separation.[6] Among of them adsorption/separation by the porous solid adsorbents has been proposed as a feasible alternative.[5, 7, 8] Pivotal research effort has been focused on the development of new adsorbents and processes related to the carbon capture and sequestration (CCS) technology. In principle, physisorption in porous solid adsorbents offers lower-energy penalty than amine scrubbing, but in the present scenario it has not yet been realized in a practical and scalable way in the stationary point sources.[5] The main issues are still related to

the material properties since capture of CO₂ from flue gas requires not only high adsorption capacity, but also high selectivity and high material stability.[5, 9, 10]

Several classes of porous materials are under investigation including metal-organic frameworks (MOFs),[11-14] covalent organic materials (COMs),[9, 15-17] activated carbons,[18-20] and amine-functionalized silicas, etc.[21, 22] Although MOFs material usually exhibited high uptake and sorption selectivity, yet COMs hold potential compared to MOFs, since the covalent bond is, in general robust and stable, whereas metal-ligand bonds (M-L) tend toward instability (oxidation, hydrolysis) owing to the dative nature of the M-L bonds.[9, 11, 23] Recently, a new class of triazine-based covalent framework materials has showed very promising properties such as high thermal and chemical stability and enhanced CO₂ adsorption capacity and selectivity due to enriched Lewis-base sites in the structure. The first structure of its kind was reported by Thomas *et al.* and named as CTF-1.[24] Since then, a series of CTF structures have been developed including CTF-2,[25], CTF-0,[26], PCTF-1 and PCTF-2,[27] and a fully fluorinated framework FCTF-1.[28] However, these CTFs were synthesized under harsh conditions that required high temperatures (> 673 K) in presence of molten ZnCl₂ in sealed tubes and expensive cyanobenzene derivatives as starting materials.

Solvothermal syntheses under mild conditions have also been tried, but often leads to amorphous polymeric structures with low surface area.[29-33] For example, reported COP-1 and PAF-6 has been synthesized using cyanuric chloride and piperazine as the starting components.[29, 30] The obtained materials possessed low surface area around 160 ~ 189 m²/g and low CO₂ uptake (~1.36 mmol/g). Here, we report a new solvothermal synthesis procedure of this system, which is described in scheme 1. In the presence of a proton scavenger, N,N- diisopropylethylamine,

(DIPEA), cyanuric chloride and piperazine was polymerized into a novel porous material, which is named as CTPP. The structure of CTPP is also amorphous, but BET analyses indicated that it is porous with surface area as high as 779 m²/g. Single-component gas adsorption and binary gas mixture breakthrough studies showed the CO₂ uptake and the selectivity of CO₂/N₂ as well as the heat of adsorption were all not only superior than reported CTP framework materials, but also among the best performances that were reported in some excellent COMs that are listed in Table S1 in supplementary information (†ESI).[8, 20, 26, 28, 33-38] The material is highly stable. Moreover, the material possessed an interesting 3D nanoflower-like architecture. Such a hierarchical porous structure can help reduce transport resistance [39, 40] and therefore has been pursued in many porous materials, such as porous silica (KCC-1, HPSNs),[40, 41] zeolite,[42, 43] metal oxide, fluoride and sulphide,[44, 45] layered double hydroxide (LDH),[46, 47] etc. However, to the best of our knowledge, such nanoflower-like architecture has not been explored in COMs.

2. Experimental section

2.1. Materials

Structural monomers including cyanuric chloride (99%), piperazine (Reagent Plus, 99%), and *o*-dichlorobenzene (DCB; anhydrous, 99%), and proton scavenger N,N- diisopropylethylamine (DIPEA) were purchased from Sigma-Aldrich. Solvents such as tetrahydrofuran (THF), 1,4-dioxane, chloroform (CHCl₃), ethanol (EtOH), methanol (MeOH) and acetone were purchased from Sigma-Aldrich. All of these chemicals were used without further purification.

2.2. Solvothermal synthesis

In a typical process, piperazine (142 mg, 1.65 mmol) was first dissolved in 10 mL of DCB (degassed by argon bubbling) through sonication. The solution was then placed in an ice-water bath, and 1.74 mL of DIPEA was added to the mixture using a syringe under vigorous stirring. Cyanuric chloride (184 mg, 1.0 mmol) was dispersed in 5 mL of degassed DCB through sonication and was then added in a dropwise fashion to the piperazine-DCB mixture using a syringe. The solution was kept at ice-cold temperature for 6 h under continuous stirring and then slowly warmed to room temperature (296 K) and stirred for another 6 h. The whole process was carried out under an argon environment. The mixture was then transferred into an autoclave and placed inside an oven at 453 K for 3 days. The resulting mixture was then centrifuged, the white powder was collected and thoroughly washed sequentially with DCB, DMF, EtOH, MeOH, THF and acetone, and the product was finally placed in a drying oven. The yield based on the total starting material is approximately 90%.

2.3. Characterization techniques

Transmission electron microscopy (TEM) images were taken on an FEI Tecnai twin microscope operated at 120 kV. The samples were first ground into a fine powder and dispersed in ethanol. The solvent evaporated, leaving the sample deposited on a 400-mesh copper TEM grid. Scanning electron microscopy (SEM) images were obtained from an FEI Nova Nano630 SEM and a FEI Helios NanoLab™ 600 DualBeam operated at 10 kV. Powder XRD of the samples were recorded on a Bruker AXS D-8 Advance diffractometer operated at 40 kV voltage and 40mA current and calibrated with a standard silicon sample, using Ni-filtered Cu K α ($\lambda = 0.15406$ nm) radiation. The Brunauer-Emmett-Teller (BET) specific surface area was measured on an ASAP 2420 system (Micromeritics) using nitrogen at 77 K. Prior to all gas adsorption measurements,

the samples were degassed at 453 K for 24 h under high vacuum. The pore size distribution was derived from the adsorption branch using nonlinear density functional theory (NLDFT) and model used as N₂ at 77 K, carbon, slit pores. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99. Single-component CO₂, CH₄ and N₂ adsorption isotherms were measured on an ASAP 2050 sorption analyser (Micromeritics). ¹³C NMR measurements were performed on a Bruker 400M MAS system, and adamantane was used as the internal reference. The rotation frequency was set to 5 kHz. Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet iS10 smart FTIR spectrometer (Thermo Scientific, USA) equipped with a smart OMNI transmission ranging from 4000 cm⁻¹ to 400 cm⁻¹. XPS analysis was conducted on a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α X-ray source (h ν = 1486.6 eV) operated at 150 W with a multi-channel plate and delay line detector under a vacuum of 10⁻⁹ mbar. All spectra were recorded using an aperture slot of 300 μ m x 700 μ m. The survey spectra were collected at a fixed analyser pass energy of 160 eV. CHN elemental analysis was carried out on a Flash 2000 organic elemental analyzer (Thermo Scientific, USA). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on a thermal analyzer TG 209 (Netzsch), under N₂ flow (20 mL/min).

2.4. Breakthrough experiments

Mixture breakthrough experiments were carried out at 298 K with the setup shown in Fig. S7 (Supporting Information, SI). Detailed information of the setup is available elsewhere.[28, 48, 49] In a typical experiment, 0.5 g of CTPP sample was first packed into a solid disc using a hydraulic press under 15 bar. The disc was then broken down by a knife into small pieces of 30 to 40 mesh in size. The resulting pieces were packed into a

quartz column (I.D. 5.8 mm, length 150 mm), and silica wool was used to seal the ends. The sample was activated in the column with a continuous helium flow (5 mL/min) at 453 K for 12 h. After that, the temperature of the column was decreased to 298 K and stabilized. Following this, the feed gas was switched from helium to a dry gas mixture of CO₂ and N₂ (15: 85, v/v) at 5 mL/min. The effluent gas was monitored by a mass spectrometer (Pfeiffer Vacuum, Germany). The absolute adsorption capacity of gas *i* (q_i) is calculated from the breakthrough curve using the following equation,

$$q_i = \frac{F_i \times t_0 - V_{dead} - \int_0^{t_0} F_e dt}{m} \quad (1)$$

where F_i is the influent flow rate of gas *i* (mL/min), t_0 is the total adsorption time (min), V_{dead} is the dead volume of the system (mL), F_e is the effluent flow rate of gas *i* (mL/min) that is calculated from the MS signal, and m is the mass of the sample (g). The selectivity of the breakthrough experiment is defined as,

$$\alpha = (q_1/y_1)(q_2/y_2) \quad (2)$$

where y_i is the molar fraction of gas *i* in the gas mixture. Two CO₂:N₂ (v:v) feed compositions, 10:90 and 15:85, which are associated to the two boundary composition of flue gas were investigated.

2.5. Calculation of isosteric heat of adsorption (Q_{st})

The CO₂ (and N₂; see supplementary information) adsorption isotherms measured at 273 K and 298 K were first fitted to the following Virial equation,

$$\ln p = \ln q + \frac{1}{T} \sum_{i=0}^m a_i q^i + \sum_{i=0}^n b_i q^i \quad (3)$$

where p is the pressure (bar), q is the adsorbed quantity (mmol/g), T is the temperature (K), R is the gas constant, a_i and b_i are Virial coefficients, and m and n represent the number of coefficients used to adequately fit the isotherms (herein, $m = 4$, $n = 3$). The isosteric heat of adsorption was calculated from the following equation,

$$Q_{st} = -R \sum_{i=0}^m a_i q^i \quad (4)$$

2.6. Selectivity calculation based on Henry's law

The CO₂/N₂ Henry selectivity was calculated from Henry's law under low pressure of up to 0.1 bar. The single component of both CO₂ and N₂ adsorption isotherms were fitted linearly up to 0.1 bar. Then, their slope ratio gives the corresponding selectivity of CO₂/N₂.

2.7. Selectivity calculation based on the ideal adsorption solution theory (IAST)

The single-component isotherms of CO₂ and N₂ were first fitted with dual site and single-site Langmuir isotherms, respectively, as follows,

$$q_i = q_{i,sat} \frac{b_i p_i}{1 + b_i p_i} \quad (5)$$

where q_i is the amount of adsorption of gas i (mmol/g), p_i is the bulk gas phase pressure (bar), $q_{i,sat}$ is the saturation adsorption capacity (mmol/g), and b_i is the Langmuir parameter (bar⁻¹). IAST assumes that Raoult's law is valid between the gas and the adsorbed phase,

$$p_i = p y_i = p_i^0 x_i \quad (6)$$

$$\sum_{i=1}^n x_i = \sum_{i=1}^n \frac{p_i}{p_i^0} = 1 \quad (7)$$

where p_i is the partial pressure of component i (bar), p is the total pressure (bar), y_i and x_i are the mole fractions of component i in gas and adsorbed phases, and p_i^0 is the equilibrium vapour pressure (bar). p_i^0 is calculated from the following equation,

$$\frac{\pi S}{RT} = \int_0^{p_i^0} \frac{q_i(p_i)}{p_i} dp_i = q_{i,sat} \ln(1 + b_i p_i^0) \quad (8)$$

Where π is the spreading pressure (assumed to be the same for all components), S is the specific surface area of the adsorbent (m^2/g), R is the gas constant, T is the temperature (K), and $q_i(p_i)$ is the amount of adsorption equilibrated with pressure p_i that is obtained from the single-component adsorption isotherm. The third term in equation (8) is the result after the single-site Langmuir isotherm (5) is applied. For binary mixtures, where $n = 2$, there are four unknown parameters S, π, p_1^0 and p_2^0 that can be determined by solving equations (7) and (8). The amount of adsorption in a mixture is found from the following two equations,

$$\frac{1}{q_T} = \sum_{i=1}^n \frac{x_i}{q_i(p_i^0)} = \sum_{i=1}^n \frac{1 + b_i p_i}{b_i p_i^0 q_{i,sat}} \quad (9)$$

$$q_i^{mix} = x_i q_T = \frac{p_i}{p_i^0} q_T \quad (10)$$

where q_T is the total amount of adsorption (mmol/g) and q_i^{mix} is the adsorbed amount of component i (mmol/g). The IAST selectivity S_{ads} is calculated from the following equation,

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \quad (11)$$

The IAST calculation is used to estimate the selectivity for the binary gas mixture containing 15% CO_2 and 85% N_2 , which is typically the flue gas composition.

3. Results and discussion

As illustrated in Scheme 1, CTPP particles were synthesized through polycondensation between the triazine moiety of cyanuric molecules and piperazine. It has been reported that cyanuric chloride and piperazine have a tendency to form a nanofloweric architecture, where the triazine moiety of cyanuric molecules forms the nanofloweric core.[50-52] The use of 1,2-dichlorobenzene as solvent is also advantageous for the synthesis of porous CTPP nanoflowers since it is a non-hygroscopic (i.e., immiscible in water) and polar aprotic solvent (2.27 D) with high density 1.3 g/cc and high boiling point 453.5 K. The unique solvent properties possibly promoted the nucleophilic substitution in all three positions of the cyanuric chloride molecule. The relatively high temperature of solvothermal treatment might also facilitate the extensive polymerization to generate a porous nanostructure with unique nanoflower architecture. While in literature other solvents for example tetrahydrofuran and 1,4-dioxane has been used to prepare microporous materials from the same types of structural linkers but the obtained materials possess much lower surface areas with regular particle morphology.[29, 30]

The SEM and TEM images of the obtained CTPP particles are shown in Fig. 1 and Fig. S1. They indicate that the particles have a relatively uniform size of approximately 400 nm and exhibit the 3D nanoflower structure. Close inspection of the SEM images at high magnification revealed that these fibrous flowers were composed by self-assembly of interweaving and slightly bent nanoflake components with a thickness of 5–10 nm, which allows easy access to its high surface area.[40, 41] Furthermore, in the SEM analysis, no other morphologies were detected, implying a high yield of the flower-like microstructures. The TEM images (Fig. 1c-d) confirmed the nanoflower architecture of the CTPP, and again, this microstructure was generated from the linking of nanoflake components, which agreed with the SEM image analysis (Fig. 1a-b). In the

high-resolution TEM images, low-electron-density spots (pores) were observed throughout the specimen with an average size of approximately 1.3 nm, which was further validated by the NLDFT pore size distribution obtained from the nitrogen sorption isotherm (Inset of Fig. 2).[53] Thus, each nanoflake comprised a microporous structure. The fast reaction rate means that this system is controlled kinetically instead of thermodynamically, which favors a highly porous amorphous structure.[26, 54] However, the exact mechanism for the shape and morphology of the CTPP microstructure remains unclear and is still under investigation.

Fig. 2 shows the nitrogen physisorption isotherm and Table 1 shows the corresponding surface area and pore volume. The isotherm displayed a typical type I curve as defined by IUPAC. A steep increase in the gas uptake at low relative pressures (P/P_0) up to 0.14, indicates the presence of a permanent microporosity.[8] Moreover, the gradual increase of uptake combined with the existence of minor hysteresis suggested the presence of mesoporosity. The observed steep increase in nitrogen uptake at a relative pressure from 0.9 to 1.0 is due to the large mesopores.[54] A polymeric framework architecture (i.e., the linking of monomer constituents) generates a framework with micropores, whereas the interweaving and slight bending of nanoflake units in nanospheres, along with the interparticles separation, were responsible for the mesoporous nature of the CTPP material. The isotherm gives a BET surface area of 779 m²/g and a Langmuir surface area of 1012 m²/g as shown in Table 1. The pore size distribution calculated by NLDFT shows that the majority of the pores are micropores with a pore size centred at 1.27 nm, while the mesopores have a broad range of sizes. This is consistent with the microscopic observations that these pores are formed by the gaps between nanoflakes, and their size

increases gradually from the core to the outside layer. Materials synthesized without the proton scavenger provided negligible surface area of approximately $3.5 \text{ m}^2/\text{g}$, indicating that it is a nonporous material.

The observed PXRD pattern of the CTPP showed broad diffraction peaks at approximately 2θ of 6.8° , 13.5° , 19.5° and 40.9° , which suggests that the framework of the CTPP materials has little order and is amorphous (Fig. S2).[32] The small-angle diffraction peaks at 2θ of 6.8° correspond to the characteristic distribution maximum of the nearest-neighbor pore-center-to pore-center distance between the disordered pores and calculated pore size is 1.3 nm,[55] which agreed to the BET analysis (Fig. 2).

The ^{13}C NMR spectrum of the CTPP material is shown in Fig. 3. The spectrum contains two well-defined chemical shift peaks at 42 ppm and 165 ppm. The chemical shift band at 42 ppm is due to the presence of the aliphatic CH_2 group of the piperazine component.[56] This well-resolved band indicated that all four aliphatic CH_2 groups in piperazine are equivalent in the CTPP network, as shown in Fig. 3. The ^{13}C NMR spectral band detected at 165 ppm implies the presence of the CH carbon of the triazine moiety in the cyanuric chloride component, and all three carbons of triazine moiety are equivalent in the CTPP (Fig. 3).[26, 29, 33] The ratio of the aromatic carbon peak to the CH_2 peak is approximately 2, which is consistent with the number of these two types of carbon in a fully polymerized structure. Hence, the NMR spectrum confirmed the incorporation of triazine and piperazine components in the CTPP microstructure. The absence of chemical shifts from 130 to 140 ppm due to carbon of benzene moiety, signified that DCB does not integrate within the CTPP frameworks.[8]

Fig. 4 shows the FTIR spectra for the CTPP, cyanuric chloride and piperazine. There are several strong vibrational bands detected in the region from 1200 to 1600 cm^{-1} , representing typical stretching modes of CN heterocycles.[57, 58] Moreover, the characteristic breathing mode bands of the triazine unit at 797 cm^{-1} was shifted to 809 cm^{-1} in the synthesized CTPP network.[57, 58] The bands at approximately 2930 and 2860 cm^{-1} , signifying the respective asymmetric and symmetric stretching modes of CH_2 group of the piperazine rings, were observed and reconcile the linking of the piperazine moiety in the constructed CTPP networks. The stretching vibrational bands near 850 cm^{-1} were observed in the cyanuric chloride because of the C-Cl bond, whereas this vibrational band disappeared in the porous CTPP network, which implies the complete substitution of the three chloride atoms from the cyanuric chloride molecule.[32, 33]

The CHN elemental contents of a fully polymerized CTPP microstructure should be 41.57 wt%, 50.97 wt% and 5.98 wt% for nitrogen, carbon, and hydrogen, respectively. This is in close agreement with the theoretical elemental composition that is given in Table 2. This elemental analysis signified that the CTPP microstructure is a highly nitrogen-rich (*i.e.*, Lewis base site-enriched) framework. The XPS analysis shows that the microstructure is mainly composed of carbon and nitrogen, which coincides with the CHN results (Fig. S5).

To investigate the thermal stability, thermogravimetric analyses of the CTPP materials were carried out for temperatures up to 1173 K at a ramping rate of 15 K min^{-1} under a

continuous N_2 atmosphere, and the results are presented in Fig. 5. The material synthesized without the proton acceptor, *i.e.*, the bulky material, showed very poor thermal stability, as it started to decompose at 373 K and steadily continued up to 773 K. Whereas the porous CTPP material showed very high thermal stability, *i.e.*, it retained its structural stability up to 773 K before it started to be sharply decomposed, although it was entirely composed of organic moieties.

In addition to the thermal stability, we further investigated stability of the CTPP material towards humidity or air and/or acid or alkaline media. For example, the CTPP material was immersed in boiling water for a week and in 1 (M) HCl or 1 (M) NaOH for 2 days. We investigated the materials by SEM and TEM image analyses, and it was observed that the materials retain their distinct nanoflower morphology, as shown in Fig. S3 and Fig. S4. Moreover, the CTPP material is completely insoluble in water and many other common organic solvents.

Fig. 6a shows the single-component adsorption isotherms for CO_2 and N_2 at 273 K and 298 K. The detailed adsorption data are listed in Table S4 (for CO_2) and S5 (for N_2). The adsorption data are fitted by a dual Langmuir adsorption model and the fitted Langmuir parameters for CO_2 are listed in Table S2 and for N_2 in Table S3. The CO_2 uptake capacities are approximately 3.48 mmol/g and 2.01 mmol/g at 273 K and 298 K, respectively at 1 bar, whereas the N_2 uptake is 0.14 mmol/g and 0.06 mmol/g at for the same temperatures. For the experimental pressure range, it can be seen from the CO_2 sorption isotherm that the uptake amount increases with pressure and does not reach equilibrium or a saturated state.[36] From the

adsorption isotherms, the CO₂/N₂ selectivity in the low pressure range (up to 0.1 bar, Table 3) was estimated using Henry's law.[37] The linear plots of CO₂ and N₂ at 273 K and 298 K over this pressure range are shown in Fig. S6 (SI). The calculated Henry selectivity for the porous CTPP at 273 K is 88, whereas at 298 K is 82, which is comparable to the reported materials.[8, 59] This decrease in selectivity with temperature in the Henry regime could possibly be because at higher temperatures, the interaction between host and guest molecules is reduced. The IAST model was also utilized to calculate the selectivity of CO₂ over N₂ for a 15/85 CO₂/N₂ feed composition as a function of total feed pressure.[34] The results are presented in Fig 6b, which shows that the selectivity for the porous CTPP increases with the total feed pressure at a given temperature, while it decreases with increasing temperature at a given feed pressure. At a total feed pressure of 1 bar, the estimated selectivity for the CTPP is 128 and 84 at 273 K and 298 K, respectively, as shown in Table 3.

In addition, we investigated the methane sorption behaviour of the CTPP material and obtained the corresponding sorption isotherms, as shown in Fig. 6c. The studied porous CTPP material reversibly adsorbed methane with a maximum uptake capacity of 1.09 mmol/g at 273 K and 1 bar, whereas its uptake capacity was reduced to 0.52 mmol/g at 298 K. The observed high uptake capacity of the CTPP materials for methane is possibly due to the electron-rich nature of the CTPP material.[9] The achieved methane uptake capacity (1.09 mmol/g) of the CTPP material is much higher than the reported methane sorption (0.49 mmol/g) of microporous *tris-o*-phenylenedioxycyclo-triphosphazene van der Waals crystals but is comparable to those of covalent organic cages.[60, 61] However, the latter can only be obtained by expensive synthesis methods, whereas our material can

be produced on a large scale from cheap and commercially available starting materials by using a facile synthetic pathway. The marginal amount of nitrogen uptake and the large methane uptake exhibited by the CTPP material resulted in a high CH_4/N_2 selectivity, which is of paramount importance in natural gas upgrading application. The calculated CH_4/N_2 Henry selectivities of the CTPP material are 17 and 7 at 273 K and 298 K, respectively, as shown in Table 3.

Fig. 6d and 6e show the isosteric heats of adsorption (Q_{st}) for CO_2 and N_2 that were calculated using Virial equations. The Q_{st} value calculated for the low uptake range (i.e., low pressure range) represents the interaction strength between the gas and the CTPP framework, whereas at higher loadings, it represents the interactions between the gas molecules. In the low loading range, the Q_{st} was calculated as 34 kJ mol^{-1} , which is comparable to some other CTF materials reported in the literature, such as CTF-1 (30 kJ mol^{-1}) and fluorinated FCTF-1 (32.9 kJ mol^{-1}). [28] When compared with covalent organic solids reported in literature, e.g., COP-3 (24.5 kJ mol^{-1}) [8], azo-COP-1 to azo-COP-3 ($24.8\text{--}32.1 \text{ kJ mol}^{-1}$), [37] and NOP-19 to NOP-21 ($28\text{--}37 \text{ kJ mol}^{-1}$), [34, 36] and to other classes of materials SIFSIX-2-Cu ($Q_{\text{st}} 22 \text{ kJ mol}^{-1}$), [38] CMP-1-COOH (33 kJ mol^{-1}), [62] and BILPs ($26.7\text{--}28.8 \text{ kJ mol}^{-1}$), [35] the CTPP reported here has higher Q_{st} values. This could be because the triazine-based frameworks, with an enriched Lewis base functionality, intrinsically favor the interaction with CO_2 . In fact, both CO_2 and N_2 are apolar molecules with similar kinetic diameters, typically 0.34 nm and 0.364 nm , respectively. [3, 10, 11] Additionally, the quadrupole moment of CO_2 is 2.85 times, and its polarizability is 1.5 times more than N_2 . [8] All of these differences result in CO_2 interacting more favorably than N_2 with the Lewis base enriched CTPP, [28, 36, 37] which leads to a high CO_2 uptake capacity

through the dipole and quadrupole interactions of CO₂ molecules. When the CO₂ and N₂ uptakes, the CO₂/N₂ selectivity and the isosteric heat of adsorption for the CTPP are compared to those of various porous materials reported in the high CO₂ uptake capacity and high CO₂/N₂ selectivity.

To demonstrate the effectiveness of the CTPPs material in real applications, we performed breakthrough experiments at ambient pressure and temperature (1 bar; 298 K) under kinetic flow conditions with a CO₂ and N₂ gas mixture for a range of compositions, as shown in Fig. 7. Fig. 7a shows a typical plot for the breakthrough experiment with a CO₂/N₂ (10:90 v/v) mixture. The estimated adsorption capacities for CO₂ and N₂ are 0.243 mmol/g and 0.002 mmol/g, respectively, which translates to a high CO₂/N₂ selectivity of 107, calculated using Eq. 2. When the CO₂/N₂ composition of 15:85 v/v was used, the adsorption capacity for CO₂ and N₂ increased to 0.339 mmol/g and 0.0024 mmol/g with a corresponding selectivity of 82, which is comparable to the IAST selectivity calculated (see Table 3 above) from the single-gas-component adsorption isotherm (equilibrium study). Thus, it observed from the breakthrough results that under flue gas conditions, the CTPP material showed high affinity to capture CO₂ from the flow stream (high selectivity). The framework is enriched by Lewis base functionalities that facilitate the selective capture of CO₂, with its strong quadrupole moment, over N₂.

The obtained breakthrough curves can be split into three phases based on their adsorption characteristics.[63] In phase I (0–1 min), the unsaturated CTPP adsorbent captured both CO₂ and N₂ from the mixed gas feed stream. In phase II (1–8 min), the CTPP continuously captured CO₂; however, no more N₂ was captured, as the adsorbent had been saturated with N₂ in phase I. Moreover, in this phase the CTPP adsorbent may

competitively and/or preferentially uptake CO_2 while a portion of the N_2 from phase I desorbs into the gas flow. This is the reason why extra N_2 molecules are present in the release stream. This observation suggested that CTPP materials can selectively capture CO_2 over N_2 from the mixed gases feed stream. In phase III (> 8 min), the flow rate and composition of the release stream are the same as the feed steam because the CTPP was saturated with both from prior phases. As a basis for comparison, the following are comparable technologies for CO_2 and N_2 separation: conventional activated carbon and metal integrated activated carbon (KNC-A-K) have CO_2/N_2 selectivities of 4.5 and 44, respectively,[48] as calculated from the breakthrough experiments with a 10:90 v/v feed composition of CO_2/N_2 at 298 K and 1 bar; at porous covalent triazine-based materials CTF-1 and fluorinated FCTF-1 exhibited breakthrough selectivities of 18 and 77 respectively;[28] and MOFs such as SIFSIX-2-Cu-I, exhibited an IAST selectivity of 140 and a breakthrough selectivity of 72.[38] In view of the above systems, it can be seen that the CTPP material exhibited comparable or higher selectivity than those excellent porous materials reported in literature. The regeneration characteristics of the CTPP material in the breakthrough experiments were also tested by regenerating the material under relatively mild conditions with helium purging (5 mL/min, 353 K for 0.5 h). The regenerated material exhibited adsorption capacities similar to the CO_2/N_2 selectivity observed in the repeated breakthrough experiments.

4. Conclusions

We demonstrated porous covalent triazine-piperazine-based structures with a 3D-nanoflower architecture fashioned by the self-assembly of interwoven and slightly bent nanoflake components. The triazine-piperazine-linked frameworks displayed a permanent porosity and a high surface area with outstanding chemical robustness and thermal stability. The covalent

linking of the monomers generated the framework and the microporosity, whereas the spatial arrangement of nanoflakes formed the 3D nanoflower architecture and contributed to the mesoporosity. We anticipated that the presence of nitrogen-rich compounds would not only increase structural diversity but also expand the scope of functions currently associated with this highly stable class of covalent organic materials. The availability of Lewis base sites enhances the CO₂ uptake capacity and CO₂/N₂ selectivity from flue gas streams as revealed in the single gas adsorption study and the column breakthrough experiments. The observed CO₂ uptake and CO₂/N₂ selectivity could be due to a quadrupole-dipole interaction between the CO₂ molecules and the Lewis base sites (lone pair of electrons on electronegative nitrogen functionality). Thus, the CTPP material, with its unique nanostructure and competitive properties (stability, CO₂ uptake capacity and selectivity), is a promising candidate for use as an adsorbent for environmental remediation. In addition, the ample presence of nitrogen functionalities in these materials can serve to coordinate transition metals and nanocatalysts, while the combination of bimodal pores may benefit the diffusion of reactant molecules for heterogeneous catalysis.

Acknowledgements

We gratefully acknowledge financial support from the King Abdullah University of Science and Technology (KAUST), competitive research grant URF/1/1378 and baseline fund BAS/1/1375.

Notes and References

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Captions for the Figures

- Scheme 1** Schematic representation of the formation of porous covalent triazine-piperazine linked fibrous nanoflowers.
- Fig.1** FE-SEM images at low magnification (a) and at high magnification (b) of the porous CTPP nanoflower material, TEM image (c) and HRTEM image (d) of the porous CTPP nanoflower material.
- Fig. 2** N₂ sorption isotherms of the porous CTPP nanoflower measured at 77 K (Adsorption: filled circles and desorption: empty circles). The corresponding pore size distribution using NLDFT is shown in the inset.
- Fig. 3** Schematic representation of structural bonding in the CTPP network. (b) ¹³C Solid-State MAS NMR spectra of the porous CTPP material.
- Fig. 4** FT IR spectroscopy of the porous CTPP nanoflower material (a), cyanuric chloride (b) and piperazine (c).
- Fig. 5** TGA analysis of the porous CTPP nanoflower material (a), and the dense CTPP material synthesized without the proton scavenger (b).
- Fig. 6** CO₂ and N₂ sorption isotherms for the CTPP at 273 K and 298 K at 1 bar; (b) CO₂/N₂ selectivity of the CTPP using IAST method with flue gas composition 15:85; CO₂: N₂ (S1) at 273 K and (S2) 298 K; (c) CH₄ and N₂ sorption isotherms for the CTPP at 273 K and 298 K at 1 bar; Isosteric heats of adsorption plot of the CTPP for CO₂ (d) and N₂ (e) [N.B.: The isosteric heats of adsorption is negative].
- Fig. 7** Column breakthrough experimental results for CO₂ and N₂ gas mixture at different feed gas compositions (a) CO₂: N₂ (10: 90 v/v) and (b) 15: 85 measured at 298 K and 1 bar pressure after activation by continuous He flow at 473 K for 12 h of CTPP material.

Table 1: Physico-chemical properties of the porous CTPP material

Sample	S_{BET} (m^2/g)	S_{Lang} (m^2/g)	S_{Micro} (m^2/g)	S_{Ext} (m^2/g)	Pore size (nm)	Pore Volume (cm^3/g)
CTPP ^a	779	1012	343	436	1.27/2.96	0.77
CTPP ^b	3	4.5	-	-	-	0.017

^a: synthesized with proton scavenger; ^b: synthesized without proton scavenger.

Table 2: CHN elemental analysis of the porous CTPP material

Sample	Nitrogen (N)	Carbon (C)	Hydrogen (H)	Total
CTPP	41.57	50.97	5.98	98.53
Theoretical	41.17	52.94	5.88	100

Table 3: CO₂, CH₄ and N₂ uptake capacities and CO₂/N₂ and CH₄/N₂ selectivities of the porous CTPP material

Entry	Tempr (K)	CO ₂ uptake (mmol/g)	CH ₄ uptake (mmol/g)	N ₂ uptake (mmol/g)	Selectivity		
					(CH ₄ /N ₂)	(CO ₂ /N ₂)	
					Henry	Henry	IAST
1	273	3.48	1.09	0.14	17	88	128
2	298	2.01	0.52	0.064	7	82	84

Scheme 1

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

GRAPHICAL ABSTRACT

HIGHLIGHTS

- ❖ Developed porous covalent triazine-piperazine linked polymer with 3D nanoflower microstructure.
- ❖ The nanoflower microstructure was fashioned by the self-assembly of interwoven and slight bent nanoflake components.
- ❖ Material having Lewis base enrich-sites and exhibited outstanding chemical robustness and thermal stability.
- ❖ Materials acts as an adsorbents and showed enhance CO₂ and CH₄ uptake and high CO₂/N₂ and CH₄/N₂ sorption selectivity.
- ❖ Single-component gas adsorption study and binary gas mixture breakthrough experiment validated the material as a promising adsorbent for environmental remediation.