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Microporous covalent triazine polymers: efficient Friedel-Crafts synthesis and adsorption/storage of CO₂ and CH₄

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Abstract

Two kinds of microporous covalent triazine-based organic polymers (MCTPs) were synthesized from inexpensive starting materials *via* a simple and cost effective Friedel-Crafts reaction route, and their CO₂ and CH₄ gas uptake capacities were investigated. The synthesized microporous materials showed high BET surface areas of 1452 (MCTP-1) and 859 m² g⁻¹ (MCTP-2). MCTP-1 exhibited significant CO₂ uptake capacity (204.3 mg g⁻¹, 273 K/1 bar) with moderate CO₂/N₂ selectivity (15.4), whereas MCTP-2 showed a moderate CO₂ uptake capacity (160.6 mg g⁻¹, 273 K/1 bar) but exceptional CO₂/N₂ selectivity (68.6). MCTP-1 also exhibited substantial CO₂ (497.4 mg g⁻¹) and CH₄ (85.4 mg g⁻¹) storage capacities at 300 K and 35 bar.

Introduction

Over the past few decades, global energy and environmental issues have attracted increasing attention and intense research efforts have been devoted to their solution.¹ CO₂ gas emissions from fossil fuel combustion can result in global warming, leading to a range of environmental disorders. CO₂ capture and sequestration (CCS) is an attractive approach to resolve the environmental issues, and the generally adopted industrial practice is predominantly by the chemisorption of CO₂ in various monoethanolamine solutions.² However, the absorption process has problems, such as a large energy requirement for solvent regeneration, equipment corrosion, and the declining adsorbent performance in the presence of oxygen. Consequently, the development of more efficient and environmentally-benign CCS technologies has become a key issue to be addressed by the scientific community.

Compared to liquid amine absorption methods, CO₂ removal *via* adsorption-based processes, normally employing a solid adsorbent, is considered to be more energy-efficient in capturing CO₂ from flue gases. Currently, a wide range of porous materials, such as activated carbons,³ zeolite,⁴ metal-organic frameworks (MOFs),⁵ covalent organic frameworks (COFs),⁶ and amine modified porous silicas,⁷ have been studied extensively as CO₂ adsorbents. The development of an adsorbent with high CO₂ capture capacity and high selectivity against N₂ or CH₄ to meet the requirements for commercial applications remains a challenge.

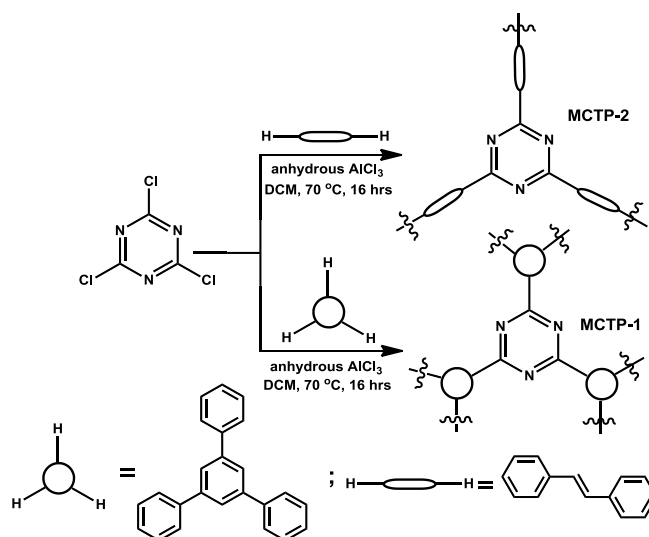
Over the last decade, there has been considerable interest in porous organic polymers (POPs) because of their potential applications in heterogeneous catalysis,⁸ gas storage⁶ and drug release.⁹ POPs have several advantages, such as large surface area, high thermal and chemical stability, and air/moisture stability, which normally exhibit relatively high gas storage capacities.

Most POPs are synthesized by palladium-catalyzed Sonogashira¹⁰ and Suzuki coupling,¹¹ Ni(0)-catalyzed Yamamoto coupling,¹² Co(0)-catalyzed trimerization of alkynes,¹³ methane-sulfonic acid-catalyzed Friedel-Crafts reaction,¹⁴ ZnCl₂-catalyzed trimerization of nitrile under ionothermal conditions,¹⁵ or trifluoromethane sulfonic acid (TFMS)-catalyzed trimerization of nitriles,¹⁶ which requires a high cost catalyst, high reaction temperatures, and hazardous chemicals for the preparation of these materials.

Recently, several nitrogen containing POPs have been reported to be favorable adsorbents for CO₂ adsorption.¹⁷ Cooper *et al.* synthesized covalent triazine frameworks (CTFs) using a TFMS catalyst that exhibited 136.4 mg g⁻¹ CO₂ uptake with a CO₂/N₂ selectivity of 16.6 measured at 273 K/1 bar.¹⁶ Yavuz *et al.* synthesized melamine-based porous organic amide polymers with 84 m² g⁻¹ surface area that exhibited only 5.7 mg g⁻¹ CO₂ uptake at 273 K/1 bar.¹⁸ Pan *et al.* reported nano POP-3 with an 894 m² g⁻¹ surface area and 110 mg g⁻¹ CO₂ adsorbed with a CO₂/N₂ selectivity of 27.1 at 273 K/1 bar.¹⁴ Han *et al.* synthesized a perfluorinated CTF (FCTF-1), which exhibited a high CO₂ uptake capacity (205.4 mg g⁻¹ at 273 K/1 bar) with a CO₂/N₂ selectivity of 31.0 at 298 K/1bar.¹⁹ Lotsch *et al.* reported a fluorine-based CTF that showed 188.3 mg g⁻¹ CO₂ uptake at 273 K/1 bar with a CO₂/N₂ selectivity of 27.0 at 298 K/1bar.²⁰ Wang *et al.* developed carbazole-modified polytriazine frameworks (NOP-19, NOP-20 and NOP-21) with 106-123 mg g⁻¹ CO₂ uptake and CO₂/N₂ selectivity of 24-71 at 273 K/1 bar.²¹ Recently, a triazine-based [4+6] organic molecular cage was reported to exhibit a high surface area (1181 m² g⁻¹) and CO₂ adsorption of 75.6 mg g⁻¹ at 1.08 bar.²² The cage network selectivity of CO₂ over N₂ reached a maximum of 28.8, and the CO₂/CH₄ selectivity was 4.7-3.9 at 273 K/1 bar. Very recently, Pan *et al.* constructed microporous triazine-based polyimide networks (TPI-1-3@IC) with high BET surface areas (814-1053 m² g⁻¹) with CO₂ uptake (90.6-141.7 mg g⁻¹ at

273 K/1 bar) and a CO₂/N₂ and CO₂/CH₄ selectivity of 32.2-69.6 at 273 K and 2-11 at 298 K, respectively.²³ The design and facile synthesis of MOPs with high CO₂ storage and selectivity still remains difficult.

In this communication, we reports the design and efficient synthesis of microporous covalent triazine-based organic polymers (MCTPs) based on relatively inexpensive starting materials, such as cyanuric chloride with 1,3,5-triphenylbenzene / *trans*-stilbene *via* a simple anhydrous aluminium chloride-catalyzed Friedel-Crafts reaction, as illustrated in Scheme 1. The produced MCTP-1 and MCTP-2 materials were investigated for their adsorption properties for CO₂, N₂ and CH₄ under 273-308 K/1 bar conditions. Their high pressure CO₂ and CH₄ storage capacities were also measured gravimetrically up to 35 bar at 300 K.



Scheme 1. Synthetic routes of the MCTP networks used in this study

Results and discussion

The successful synthesis of MCTP-1 and MCTP-2 were confirmed by Fourier transform infrared (FT-IR) spectroscopy, elemental analysis (EA), powder X-ray diffraction (PXRD),

scanning electron microscopy-energy dispersive X-ray (SEM-EDX), thermogravimetric analysis (TGA), and nitrogen gas adsorption isotherms at 77 K. The previously reported synthesis of networks similar to MCTP-1 employed either harsh reaction conditions or hazardous catalysts in the multi-step synthesis of the starting materials, leading to products with a relatively low surface area.^{15,16} This communication reports, for the first time, a new and straightforward synthesis of triazine and stilbene units containing MCTP-2 network.

The FT-IR spectrum (Fig. S1, ESI) of MCTP-1 revealed bands at 1381 and 1510 cm^{-1} , indicating the presence of a triazine unit, which is in accordance with previous reports.^{15,16} Similarly, the triazine bands appeared at 1352 and 1510 cm^{-1} in MCTP-2. The C-Cl stretching band at 851 cm^{-1} disappeared, suggesting the virtually complete conversion of cyanuric chloride in the synthesis of both MCTP-1 and MCTP-2. Elemental analysis of MCTP-1 and MCTP-2 showed the C, H and N contents, which were in close agreement with the calculated values for the theoretical fully-condensed networks (Table S1, ESI). The crystallinity of the networks in MCTP-1 and MCTP-2 were determined by PXRD (Fig. S2 and S3, ESI). The observed powder XRD pattern of both MCTP-1 and MCTP-2 showed three broad diffraction peaks at approximately 2θ of 10.1°, 21.5° and 43.2°, which suggests that the framework of the materials has little order and is amorphous.^{17b,21,24} The broad peak at 21.5° 2θ could be assigned to the stacking of triazine linkage in (001) plane.^{15,16} According to SEM analysis of the networks (Fig. S4 (ESI)), both MCTP-1 and MCTP-2 showed morphologies with an elongated spherical shape, 1.0 - 2.5 μm in size. The presence of an irregular particle size appears to be due to aggregation of the particles. The amount of aluminium in MCTP-1 and MCTP-2 was found to be negligible (0.16 and 0.15 wt%, respectively) by the ICP-OES analysis. The thermal stability of the networks was determined by TGA under an argon atmosphere, as shown in Fig. S5 (ESI). The

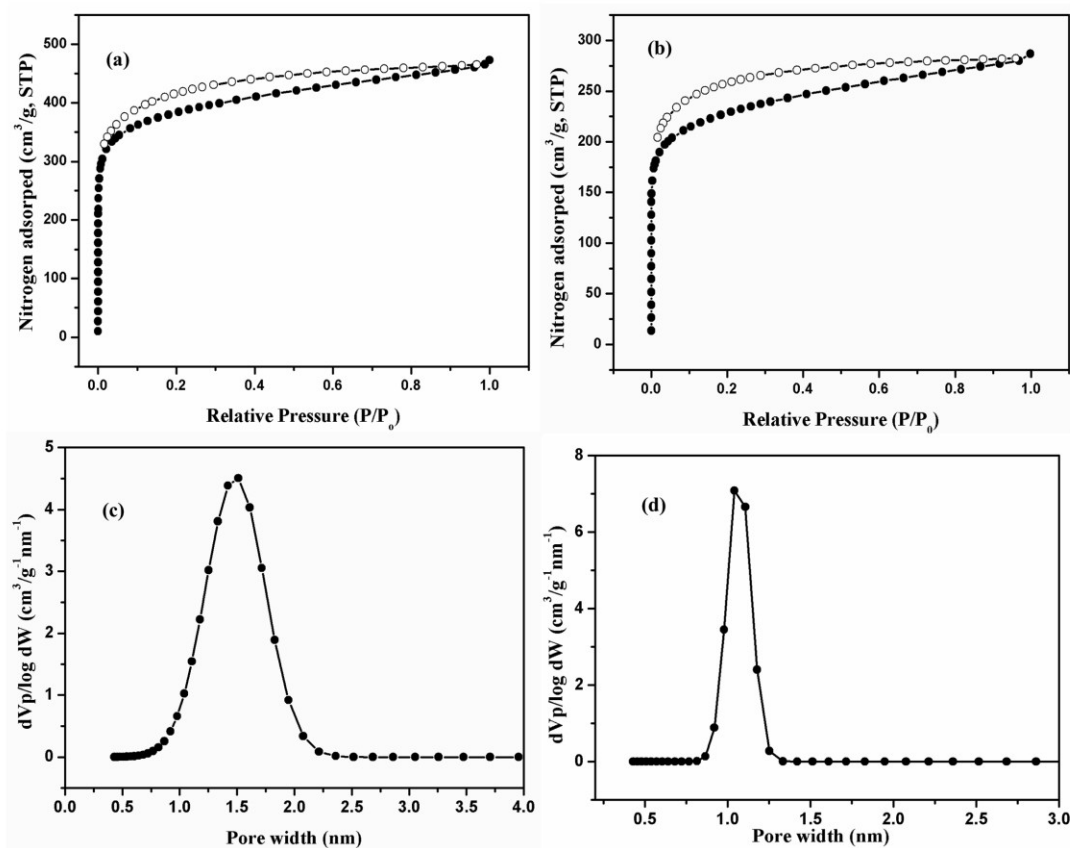
MCTP-1 and MCTP-2 networks were quite stable and sharp decomposition started at 290 and 220 °C, respectively. These networks were also highly stable in water and organic solvents, which is desirable for the potential applications of CCS.

N₂ adsorption-desorption measurements at 77K were examined to measure the surface area and textural properties of the resulting networks (Table 1, Fig. 1). Before the analysis, the materials were de-gassed at 130 °C for 6 h in a high vacuum. As shown in Fig. 1a and 1b, both MCTP-1 and MCTP-2 exhibited a pattern closely related to the Type I adsorption isotherm, according to the IUPAC classification, and showed steep N₂ gas uptake at the low relative pressure region ($P/P_0 = 0.001$), which shows the microporous nature of the networks. The Brunauer-Emmett-Teller (BET) surface areas of MCTP-1 and MCTP-2, which were evaluated from the region ($0.01 < P/P_0 < 0.05$) of the adsorption curve, were 1452 m² g⁻¹ and 859 m² g⁻¹ respectively, which are significantly higher than the previous reports of a similar net.^{15,16} The microporosity in the materials was evaluated from the ratio of the micropore volume to the total pore volume ($V_{0.1}/V_{tot}$).^{15,16,25} The $V_{0.1}/V_{tot}$ value of MCTP-1 and MCTP-2 were 0.77 and 0.75 respectively, which shows that the networks are mostly microporous in nature. The pore size of both MCTP-1 and MCTP-2, which were calculated by nonlocal density functional theory (NL-DFT) model with slit pore geometry (Fig. 1c and 1d), were 1.51 and 1.04 nm, respectively, which is in good agreement with previous reports of similar networks.^{15,16} The hysteresis in the isotherms in Fig.1 has also been observed before by others,^{15,16} but no clear explanation was given so far. It could be because of the pore geometry of the amorphous organic polymer material with soft pore walls, which may lead to desorption in irreversible manner.

Table 1. Textural data for the MCTP-1 and MCTP-2 networks from N₂ isotherms at 77 K.

Networks	SA _{BET} (m ² g ⁻¹) ^a	V _{0.1} (cm ³ g ⁻¹) ^b	V _{tot} (cm ³ g ⁻¹) ^c	V _{0.1} /V _{tot}	Pore size (nm) ^d
MCTP-1	1452	0.56	0.73	0.77	1.51
MCTP-2	859	0.33	0.44	0.75	1.04

^aBET surface area at 77 K; ^bV_{0.1}, pore volume at P/P₀ = 0.1 at 77 K; ^cV_{tot}, total pore volume at P/P₀ = 0.995 at 77 K; ^dPore size distribution calculated by nonlocal density functional theory (NL-DFT) model with slit pore geometry.

**Fig. 1.** (a) and (b) Nitrogen adsorption (filled circle) and desorption (open circle) isotherm of MCTP-1 and MCTP-2 at 77K; (c) and (d) pore size distribution of MCTP-1 and MCTP-2.

As the synthesised MCTP-1 and MCTP-2 are highly porous, and have good hydrothermal stability as well as a large number of nitrogen atoms from triazine in the network, it was decided to examine their adsorption properties for CO₂ and other gases. Fig. 2 presents the temperature-dependent adsorption isotherms up to 1 bar of both networks studied at 273, 293, 298, 303, and 308 K, and Table 2 lists the corresponding adsorption capacity. The nitrogen atoms of the

MCTPs play a significant role in the CO₂ adsorption in the low pressure region, where the adsorption capacity is dependent mainly on the CO₂-networks interactions and surface area.¹⁹ As shown in Fig. 2a, the CO₂ isotherm of MCTP-1 at 273 K exhibited ca. 204.3 mg g⁻¹ gas uptake at 1 bar, whereas for the MCTP-2 network, the CO₂ uptakes (Fig. 2b) decreased to 160.6 mg g⁻¹ at 273 K/1 bar, which was attributed to the decrease in surface area of the latter. The CO₂ uptakes of MCTP-1 in this work were substantially higher than those of other reported triazine-based polymers, such as CTF-P2-P6 (83-149 mg g⁻¹),¹⁶ CTF-P1M-P6M (41-185 mg g⁻¹),¹⁶ MCTF-300-500 (100-130 mg g⁻¹),²⁶ *fl*-CTF-300-600 (56-188 mg g⁻¹),²⁰ PCTF-1-7 (47-87 mg g⁻¹),²⁷ supramolecular PCTF-1-2 (81-141 mg g⁻¹)²⁸, and TPI-1-7 (30-55 mg g⁻¹),²⁹ and closely matched the capacity of FCTF-1 (205.4 mg g⁻¹).¹⁹ Furthermore, this value is higher than those using the other previously reported POPs networks in the literature (Table S2, ESI). The CO₂ uptake depends on the surface area, pore size and the strong quadrupole interaction of CO₂ molecules with the heteroatom of the pore walls for the networks at low pressures.³⁰

Table 2 Summary of the CO₂ and CH₄ gas uptakes by MCTP-1 and MCTP-2

Network	CO ₂ uptakes (mg/g)						CH ₄ uptakes (mg/g)			CO ₂ /N ₂ selectivity ^a	CO ₂ /CH ₄ selectivity ^a	Q _{st} ^b for CO ₂
	273K 1 bar	293K 1 bar	298K 1 bar	303K 1 bar	308K 1bar	300K 35 bar	273K 1 bar	298K 1 bar	300K 35 bar			
MCTP-1	204.3	135.7	118.7	96.4	80.4	497.4	39.6	17.1	85.4	15.4	8.2	40.0-32.0
MCTP-2	160.6	118.1	108.2	96.3	-	333.3	14.3	9.0	50.3	68.6	20.1	30.6-25.3

^aThese data were estimated from the ratio of initial slopes of CO₂ and N₂ or CH₄ adsorption isotherms at 298 K unless stated otherwise; ^bHeat of adsorption calculated using the Clausius-Clapeyron equation.

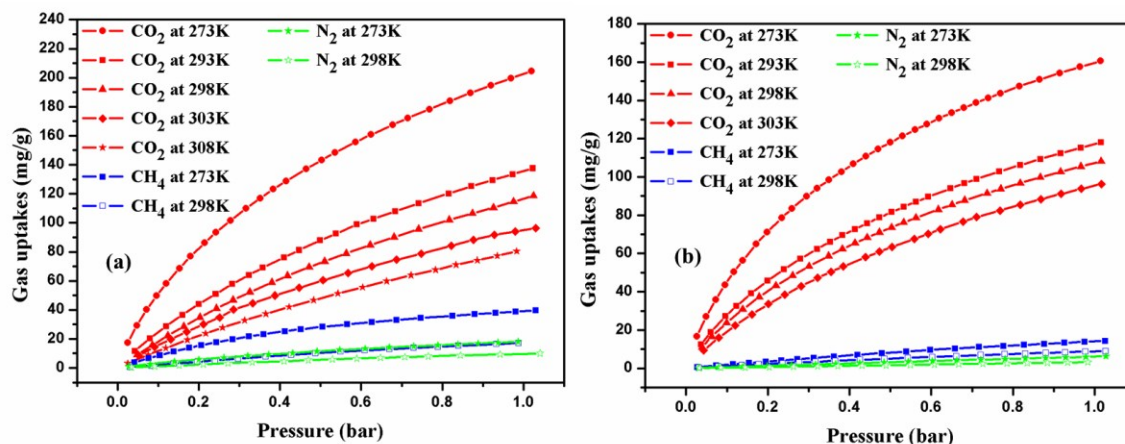


Fig. 2. CO₂, CH₄ and N₂ gas uptakes isotherm for MCTP-1 (a) and MCTP-2 (b) at 1 bar

Fig. 3 shows the isosteric heat of adsorption (Q_{st}) of the MCTP-1 and MCTP-2 networks estimated using the Clausius-Clapeyron equation (Fig. S6, ESI), which were calculated using the four adsorption isotherms at 273 to 303 K. MCTP-1 exhibited a higher heat of adsorption (40.0–32.0 kJ mol⁻¹) than MCTP-2 (30.6–25.3 kJ mol⁻¹) throughout the entire CO₂ loading levels, which are still significantly lower than those by the previously reported POPs, such as the TPis network (46.1–49.3 kJ mol⁻¹),²³ polyindole nanofibers (42.7–24.1 kJ mol⁻¹),³¹ polyamine-tethered porous polymer networks (PPN-6-CH₂-TETA, 63.0–32.0 kJ mol⁻¹; PPN-6-CH₂-DETA, 65.0–38.0 kJ mol⁻¹; and PPN-6-CH₂-EDA, 55.0–36.0, kJ mol⁻¹),³² MTF-Mg (45.2–20.0 kJ mol⁻¹)³³, and some MOFs.³⁴ The reproducibility of the MCTP-1 and MCTP-2 networks for CO₂ adsorption was investigated by the adsorption-desorption cycles carried out at 300 K (Fig. S7 and S8, ESI). Even after 10 cycles, CO₂ could be desorbed quickly after the gas was switched from CO₂ to Ar, which confirmed the stability of the network. In addition, the adsorption-desorption isotherm of MCTP-1 and MCTP-2 for CO₂ at 298 K/1 bar is given in Fig. S9. As shown in Fig. S9, both MCTP-1 and MCTP-2 showed a small hysteresis, but complete desorption of CO₂ at low pressure was achieved.

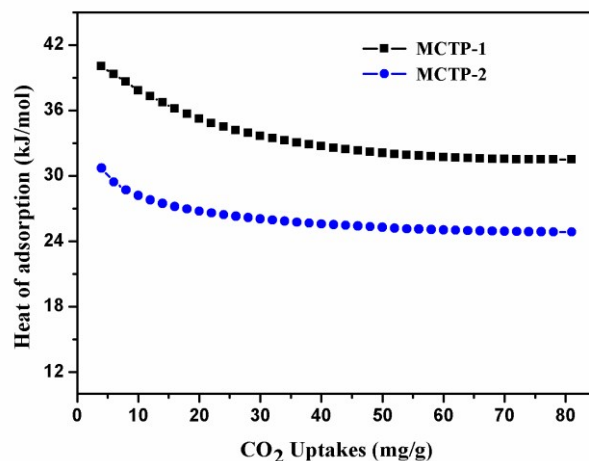


Fig. 3 Heat of adsorption (Q_{st}) of CO_2 for MCTP-1 and MCTP-2 networks

The CH_4 and N_2 uptake properties of MCTP-1 and MCTP-2 were also investigated at 273 and 298 K. The CH_4 uptake capacities of MCTP-1 at 273 and 298 K were 39.6 and 17.1 mg g^{-1} , respectively, whereas for MCTP-2, they were 14.3 and 9.0 mg g^{-1} at 273 and 298 K, respectively. As expected, the N_2 uptake capacities at 273K (18.0 mg g^{-1} for MCTP-1 and 6.2 mg g^{-1} MCTP-2) were significantly lower than those of CO_2 and CH_4 due to the nitrogen content of the pore wall for the networks as well as the high polarizability of CO_2 ($26.3 \times 10^{-25} \text{ cm}^3$), CH_4 ($26 \times 10^{-25} \text{ cm}^3$) compared to that of N_2 ($17.6 \times 10^{-25} \text{ cm}^3$).^{17d,29b,35} The CO_2 over N_2 or CH_4 adsorption selectivity is very important for CCS applications. These values were estimated at 298 K/1 bar based on the initial slope calculation (Fig. S10 and S11, ESI) in the range of 0 to 0.30 bar, and the calculated adsorption selectivities for CO_2/N_2 were 15.4 (MCTP-1) and 68.6 (MCTP-2), and 8.2 (MCTP-1) and 20.1 (MCTP-2) for CO_2/CH_4 , respectively. The MCTP-2 network showed very high CO_2/N_2 selectivity and the CO_2/CH_4 selectivity was also significantly higher than that of other reported materials, such as P-1 (4.0),^{17c} triazine-based cage networks (4.7-3.9),²² TPI-1-3@IC (2.0-11.0),²³ ZIF-68,69,70,78,79,81,82 (~5.0-10.0),³⁶ 2-D MOF (~13.0),³⁷ and TEPD-1-3 (12.6-15.5).³⁸ The excellent performance of MCTP-2 might be due to the higher concentration of

Lewis base nitrogen atoms as well as the smaller micropore size in MCTP-2 compared to the MCTP-1 network.

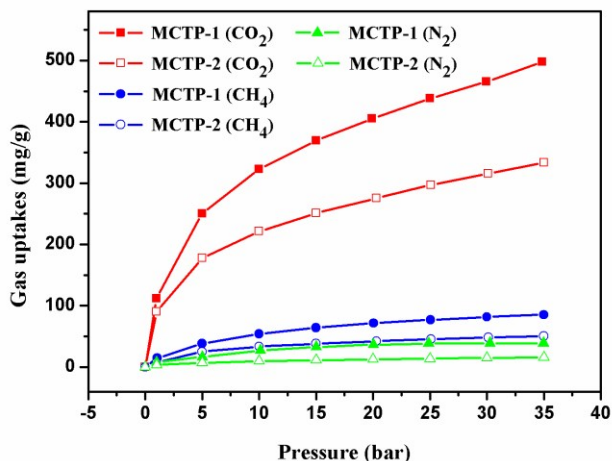


Fig. 4 High pressure gas uptakes of the MCTP-1 and MCTP-2 at 300 K

High pressure gas storage CO₂ and CH₄ using porous polymers is important for natural gas purification processes or for preparing adsorbed natural gas (ANG) for future small-sized vehicles.^{12, 39} To evaluate the gas storage capacity, the high-pressure adsorption of CO₂, CH₄, and N₂ over MCTP-1 and MCTP-2 were measured gravimetrically using a magnetic suspension balance (Rubotherm, Germany; Scheme S1, ESI) with an in situ density measurement in a closed system at 300 K. As shown in Fig. 4, the CO₂ uptakes of MCTP-1 and MCTP-2 were 497.4 and 333.3 mg g⁻¹ at 35 bar, respectively. These adsorption values are comparable to those reported for the best porous MOFs (Table S3, ESI). Similarly, the CH₄ uptake at 35 bar of MCTP-1 and MCTP-2 were 85.4 and 50.3 mg g⁻¹ respectively, which compares well with values reported for porous materials, such as BILP-10 (~56.0 mg g⁻¹, 298 K/40 bar),^{39a} HCP-3 (68.6 mg g⁻¹, 298 K/35 bar),⁴⁰ COF-1 and COF-6 (40.0 and 65.6 mg g⁻¹, 298 K/35 bar)⁴¹, and others listed in Table S3 (ESI).

Conclusions

An efficient and economic synthesis scheme was developed for the preparation of MCTPs with high surface area and high stability through the Friedel-Crafts reaction. The resulting MCTP-1 network exhibited significantly high CO₂ uptakes (204.3 mg g⁻¹, 273 K/1 bar) with moderate selectivity, whereas MCTP-2 exhibited exceptional CO₂/N₂ selectivity (68.6) and CO₂/CH₄ selectivity (20.1) at 298 K/1 bar but with moderate adsorption capacity. Both MCTP-1 and MCTP-2 showed lower heats of adsorption than other comparable organic network materials, and resulted in easy CO₂ desorption so that 10 repeated adsorption-desorption cycles could be conducted rapidly at 300 K by employing an Ar purge only. The proposed synthesis is expected to enable the large scale synthesis of materials that are tunable between high CO₂ uptake and high CO₂/N₂ selectivity.

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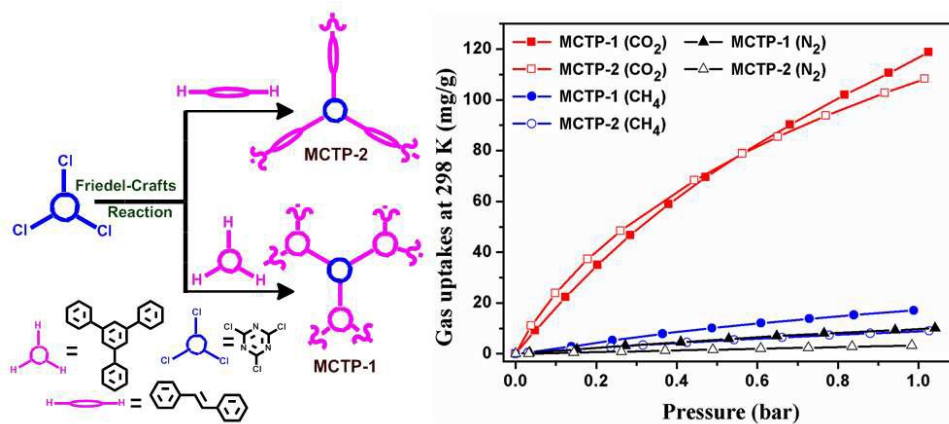
Graphical Abstract

Microporous covalent triazine polymers: efficient Friedel-Crafts synthesis and adsorption/storage of CO₂ and CH₄

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The microporous covalent triazine polymers were synthesized from inexpensive starting materials and their CO₂ and CH₄ gas uptakes were investigated.