

Functional conjugated microporous polymers: from 1,3,5-benzene to 1,3,5-triazine†

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Conjugated microporous polymers (CMPs) based on the electron-withdrawing 1,3,5-triazine node (TCMPs) were synthesized by palladium-catalyzed Sonogashira-Hagihara cross-coupling. The porosity in these polymers was found to be comparable to the analogous 1,3,5-connected benzene CMP systems that we reported previously, demonstrating that nodes can be substituted in these amorphous materials in a rational manner, much as for certain crystalline porous metal–organic frameworks. The CO₂ adsorption properties of the TCMPs were measured and compared with the corresponding CMPs, and it was found that the TCMP networks adsorbed more CO₂ than CMP analogues with comparable BET surface areas. Network TNCMP-2 showed the highest surface area (995 m² g⁻¹) and a CO₂ uptake of 1.45 mmol g⁻¹ at 1 bar at 298 K. The band gap in these triazine-based CMPs could also be engineered through copolymerization with other functional monomers.

Introduction

Microporous organic polymers (MOPs) are attracting increasing attention due to their potential applications in areas such as gas adsorption, separation, and heterogeneous catalysis.^{1–4} Compared with their inorganic or hybrid counterparts, such as silica, metal oxides, zeolites, and metal–organic frameworks (MOFs), MOPs have possible advantages in terms of the combining wide synthetic diversity with reasonable chemical and thermal stability.⁵ A variety of MOPs have been developed including polymers of intrinsic microporosity (PIMs),^{6–10} hypercrosslinked polymers (HCPs),^{11–14} porous aromatic frameworks (PAFs),^{15–17} covalent triazine-based frameworks (CTFs),^{18,19} and covalent organic frameworks (COFs).^{20,21} The latter two classes of materials (CTFs and COFs) show a degree of crystalline order, while the other porous networks are amorphous.

In the last few years, there has been significant interest in a new class of materials described as ‘conjugated microporous polymers’ (CMPs).^{22,23} CMPs are usually prepared by well-established transition metal catalyzed coupling chemistry. The distinguishing feature of CMP materials is that they combine microporosity and high surface areas with extended conjugation, suggesting a range of new applications. Various chemical

functionalities have been incorporated into CMPs^{24–30} and we have shown that pore size and surface area in CMPs can be tailored through synthetic control.^{31–33} CMPs are currently being investigated for various applications in areas such as heterogeneous catalysis,^{34–37} light-harvesting networks,³⁸ metal nanoparticle composites,³⁹ supercapacitors,⁴⁰ and metal-doped materials with remarkable H₂ sorption properties.⁴¹

To cater for these various applications, there is a need to further broaden the range of chemical functionalities that can be incorporated into CMPs and particularly to enable applications that can exploit the conjugated nature of the materials. 1,3,5-Triazine containing materials have been widely used in industry because of their high thermal stability, derived from the structural symmetry of 1,3,5-triazine units.^{42–44} Recently, much attention has been paid to 1,3,5-triazine containing π -conjugated systems because of unique properties such as high electron deficiency and spatial coplanarity.^{45–56} Introduction of these stable and electron-withdrawing triazine units into CMP systems could be advantageous for stability and also in terms of electronic state manipulation of the polymers. In this context, we report the synthesis and characterization of a series of 1,3,5-triazine based CMPs (TCMPs), and compare the porosity of these materials with the analogous benzene-linked CMPs that we reported previously.^{25,31}

One important potential application for porous materials is the capture and separation of CO₂, for example from flue gas. Efficient CO₂ adsorption depends not only on the surface area of the material, but also on its chemical functionality^{57,58} – moreover, physical stability would be important in many real-life applications. It is known that the introduction of functional groups such as amines or carboxylic acids can improve CO₂

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adsorption properties in porous polymer networks. Potentially, nitrogen-rich triazine units could be advantageous for CO₂ adsorption in CMPs, and this was also studied here.

Experimental section

Chemicals

4-Bromobenzonitrile, trifluoromethanesulfonic acid, 1,4-diethynylbenzene, tetrakis(triphenylphosphine)palladium, copper(I) iodide and anhydrous *N,N'*-dimethylformamide (DMF) and chloroform were all purchased from Aldrich and used as received. 1,3,5-Triethynylbenzene was purchased from ABCR. 4,4'-Diethynyl-1,1'-biphenyl³³ and tris(4-ethynylphenyl)amine²⁵ were synthesized according to the reported procedures.

Synthesis of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (1)

Monomer **1** was synthesized using literature procedures.⁵⁹ ¹H NMR (CDCl₃) δ (ppm): 8.63 (d, 6H), 8.73 (d, 6H). MALDI-TOF MS *m/z*: 542.9 M⁺. Anal. Calcd for C₂₁H₁₂Br₃N₃: C, 46.19; H, 2.22; N, 7.70. Found: C, 45.94; H, 2.03; N, 7.59.

Synthesis of polymer networks by Sonogashira-Hagihara cross-coupling chemistry

All polymerization reactions were carried out with similar monomer concentration and a fixed reaction temperature and reaction time (100 °C/72 h). The molar ratio of ethynyl to bromo functionalities in the monomer feed was set at 1.5 : 1 based on our previous findings for CMP networks.^{23,31} A representative experimental procedure for **TCMP-3** is given as an example.

TCMP-3

1,4-Diethynylbenzene (142 mg, 1.125 mmol), monomer **1** (273 mg, 0.5 mmol), tetrakis(triphenylphosphine)palladium (60 mg), and copper(I) iodide (30 mg) were dissolved in a mixture of anhydrous DMF (5 mL) and Et₃N (5 mL). The reaction mixture was heated to 100 °C and stirred for 72 h under a nitrogen atmosphere. The mixture was cooled to room temperature, and the insoluble precipitated network polymer was filtered and washed four times with chloroform, water, methanol, and acetone (100 mL each) to remove any un-reacted monomers or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with methanol and CHCl₃ successively for 24 h each. The product was then dried under vacuum for 24 h at 60 °C to give brown powder (yield: 226 mg, 92%). FT-IR (KBr, cm⁻¹): 3034, 2207, 1505, 1364, 812. Anal. Calcd for C₃₆H₁₈N₃: C, 87.79; H, 3.68; N, 8.53. Found: C, 77.92; H, 3.77; N, 2.87. The deviation of the elemental analysis results from the theoretical value can be due to remaining end groups and incomplete combustion and is consistent with our previous observations.³¹

TCMP-0

1,3,5-Triethynylbenzene (113 mg, 0.75 mmol), monomer **1** (273 mg, 0.5 mmol), tetrakis(triphenylphosphine)palladium (60 mg), copper(I) iodide (30 mg), DMF (5 mL) and Et₃N (5 mL) were used this polymerization. **TCMP-0** was obtained as brown

power (yield: 214 mg, 94%). FT-IR (KBr, cm⁻¹): 3055, 2205, 1516, 1369, 814. Anal. Calcd for C₃₃H₁₅N₃: C, 87.40; H, 3.33; N, 9.27. Found: C, 77.80; H, 3.46; N, 6.41.

TNCMP-2

Tris(4-ethynylphenyl)amine (238 mg, 0.75 mmol), monomer **1** (273 mg, 0.5 mmol), tetrakis(triphenylphosphine)palladium (60 mg), copper(I) iodide (30 mg), DMF (5 mL) and Et₃N (5 mL) were used this polymerization. **TNCMP-2** was obtained as dark-brown power (yield: 305 mg, 98%). FT-IR (KBr, cm⁻¹): 3036, 2206, 1505, 1368, 816. Anal. Calcd for C₄₅H₂₄N₄: C, 87.08; H, 3.90; N, 9.03. Found: C, 82.24; H, 4.12; N, 7.12.

TCMP-5

4,4'-Diethynyl-1,1'-biphenyl (228 mg, 1.125 mmol), monomer **1** (273 mg, 0.5 mmol), tetrakis(triphenylphosphine)palladium (60 mg), copper(I) iodide (30 mg), DMF (5 mL) and Et₃N (5 mL) were used this polymerization. **TCMP-5** was obtained as brown power (yield: 289 mg, 95%). FT-IR (KBr, cm⁻¹): 3031, 2208, 1508, 1367, 814. Anal. Calcd for C₄₅H₂₄N₃: C, 89.09; H, 3.99; N, 6.93. Found: C, 82.08; H, 4.01; N, 4.78.

Infrared spectroscopy

IR spectra were collected as KBr disks using a Bruker Tensor 27.

Thermogravimetric analysis (TGA)

TGA analysis was carried out using a Q5000IR analyzer (TA Instruments) with an automated vertical overhead thermobalance. The samples were heated at the rate of 20 °C min⁻¹ under a nitrogen atmosphere.

Solid-state NMR

Solid-state NMR spectra were measured on a Bruker Avance 400 DSX spectrometer operating at 100.61 MHz for ¹³C and 400.13 MHz for ¹H. ¹H-¹³C cross-polarization magic angle spinning (CP/MAS) NMR experiments were carried out at an MAS rate of 10.0 kHz using zirconia rotors 4 mm in diameter. The ¹H π/2 pulse was 3.4 μs, and two-pulse phase modulation (TPPM) decoupling⁶⁰ was used during the acquisition. The Hartmann-Hahn condition was set using hexamethylbenzene. The spectra were measured using a contact time of 2.0 ms and a relaxation delay of 10.0 s. Typically 984 scans were accumulated. The ¹³C {¹H} MAS NMR spectra were measured at an MAS rate of 10.0 kHz using TPPM decoupling. The ¹³C π/2 pulse was 2.6 μs. The spectra were measured using a recycle delay of 10.0 s. Typically, 6144 scans were accumulated. The values of the chemical shifts are referred to that of TMS. The analysis of the spectra (deconvolution) was carried out using Bruker TOPSPIN software.

UV-vis spectra

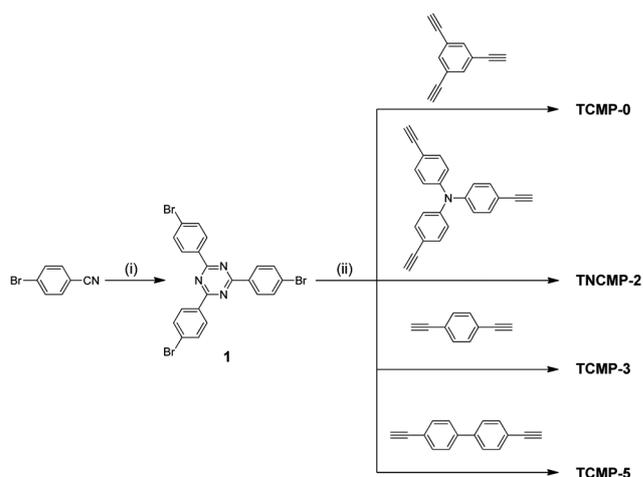
UV-vis Spectra were recorded by a SHIMADZU UV-2550 spectrophotometer using powder samples of the networks.

Gas sorption analysis

Polymer surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using either a Micromeritics ASAP 2420 or ASAP 2020 volumetric sorption analyzer. The surface areas were calculated in the relative pressure (P/P_0) range from 0.01 to 0.05. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the nonlocal density functional theory (NL-DFT) pore model for pillared clay with cylindrical pore geometry. Samples were degassed at 120 °C for 15 h under vacuum (10^{-5} bar) before analysis. CO₂ isotherms were measured at 273 and 298 K on a Micromeritics ASAP 2050. The temperature was controlled using a chiller circulator.

Results and discussion

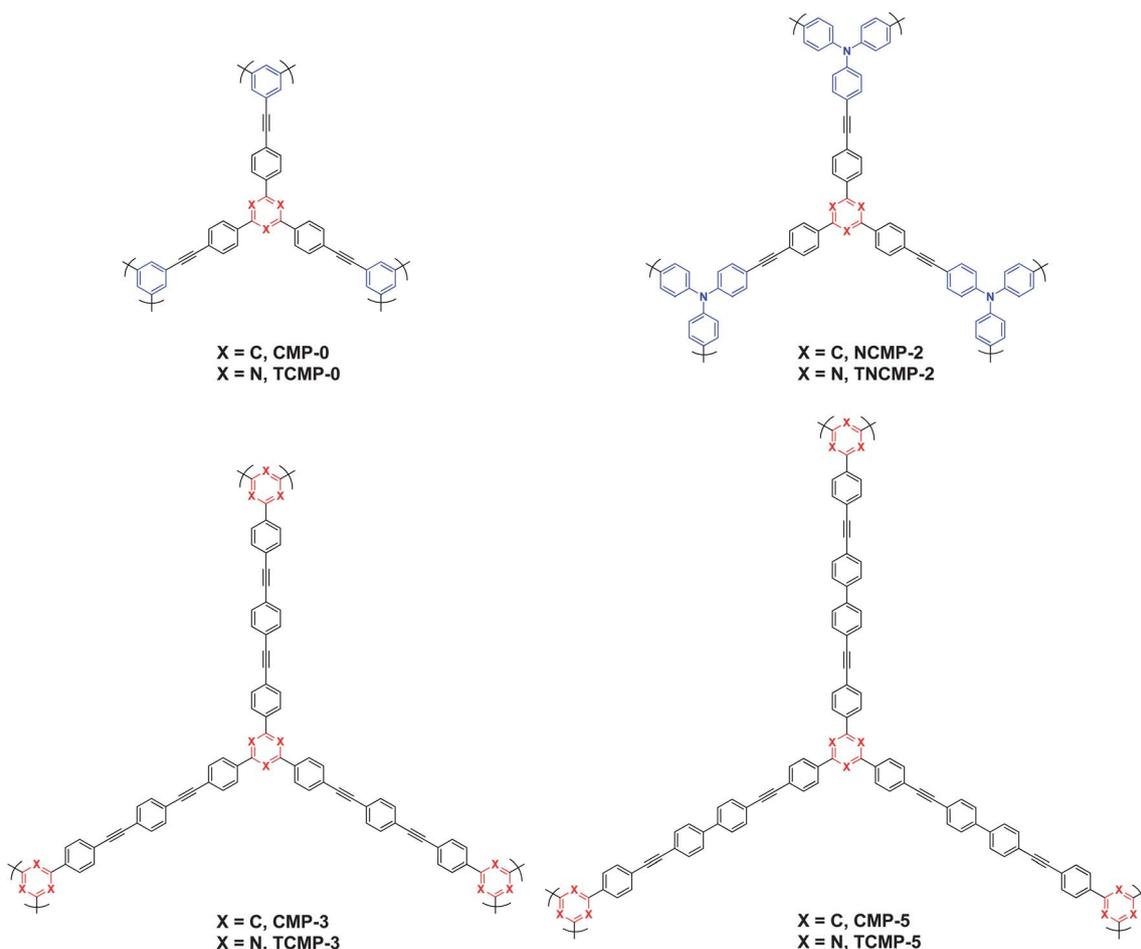
As shown in Scheme 1, the network structures of the triazine based networks **TCMP-0**, **TNCMP-2**, **TCMP-3** and **TCMP-5** are, in principle, isomorphous with respect to our previously reported CMPs, **CMP-0**,³¹ **NCMP-2**,²⁵ **CMP-3**³¹ and **CMP-5**.³¹ In the TCMP materials, the benzene node is replaced by a 1,3,5-triazine unit. Synthetic routs to the triazine containing monomers and polymers are shown in Scheme 2. 1,3,5-Triazine monomer **1** was synthesized by the trimerization reaction of



^a Reagents and conditions: (i) CF₃SO₃H, CHCl₃, r.t., 24 h; (ii) Pd(PPh₃)₄, CuI, DMF/Et₃N, 100 °C, 72 h.

Scheme 2 Synthesis of the triazine monomer and TCMP networks.

4-bromobenzonitrile, catalyzed by trifluoromethanesulfonic acid at room temperature. As for our previous CMP networks,^{25,31} the TCMPs were prepared by using (A₃ + B₂) or (A₃ + B₃) Sonogashira-Hagihara cross-coupling reactions using a 1.5 : 1 molar



Scheme 1 Representative molecular structures for TCMP networks and the corresponding CMPs.

ratio of ethynyl to bromo functionalities, and employing DMF as a solvent. We have shown previously that these conditions give rise to higher surface area materials.^{24,31,61} The polymer networks were recovered as brown powders in yields of greater than 90%. As for the CMP networks,^{25,31} the newly synthesized TCMP networks were insoluble in all solvents tested such as THF, toluene, DMF, and chloroform. They were also found to be chemically stable in various aqueous conditions. Thermogravimetric analysis (TGA) performed under a nitrogen atmosphere showed good thermal stability of these polymers (Figure S1, Electronic Supporting Information), with 5% weight loss temperatures at 458 °C, 612 °C, 345 °C and 478 °C, respectively, for **TCMP-0**, **TNCMP-2**, **TCMP-3** and **TCMP-5**. **TNCMP-2** is therefore one of the most thermally stable polymer networks reported so far in this class. Powder X-ray diffraction measurements (Figure S2) showed that the TCMP networks were amorphous, and no evidence for characteristic reflections from a crystalline phase or layered sheets was observed.

Infrared spectra for these polymers are shown in Fig. 1. The characteristic terminal C–C triple bond vibration peaks at about 3300 cm⁻¹ have very low intensity while the peaks at around 2200 cm⁻¹, which are characteristic of bis-substituted acetylene, are easily detected. This indicates, qualitatively, a high degree of polymerization. All polymers were further characterised at the molecular level by ¹H-¹³C CP/MAS NMR. The assignment of resonances for these networks were straightforward based upon our previous work,^{23–26} as shown in Fig. 2. The aryleneethynylene units in the struts show peaks at ca. 132 ppm, which correspond to non-protonated C_{Ar}–C_{Ar} groups, and peaks at ca. 124 ppm are observed for protonated C_{Ar}–C_{Ar} groups. Ethynylene C_{Ar}–C≡C–C_{Ar} units are observed at 91–92 ppm. Resonances observed at 147 ppm can be ascribed to the tris(phenylethynylene)amine unit in **TNCMP-2**, which is also consistent with our previous work.²⁵ The triazine functionality displays peaks in the range 170–171 ppm.⁶² To assess the content of end groups, we have previously calculated the quaternary-to-terminal alkyne ratios (C_{Ar}–C≡C–C_{Ar} to C_{Ar}–C≡C–H).²⁶

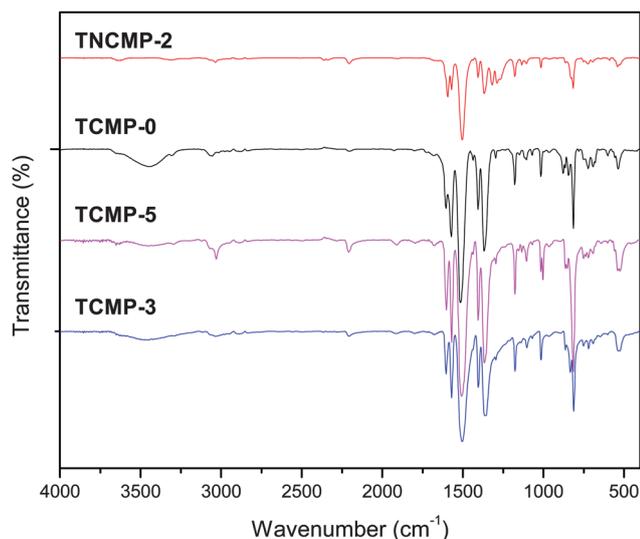


Fig. 1 Infrared spectra of the TCMP networks. The spectra were recorded using KBr pellets.

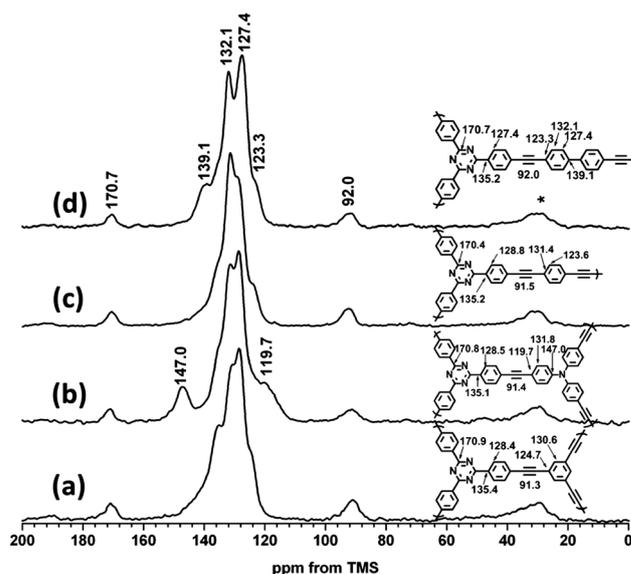


Fig. 2 ¹H-¹³C CP/MAS NMR spectra of triazine containing networks. (a) **TCMP-0**, (b) **TNCMP-2**, (c) **TCMP-3**, and (d) **TCMP-5**. Spectra were collected at an MAS rate of 10 kHz. Asterisks denote spinning sidebands.

However, in the case of TCMPs, all of the networks showed negligible amounts of terminal alkyne. No peaks were visible above the level of noise at 70–80 ppm, suggesting high levels of polycondensation for these networks, in accordance with the IR data.

UV-vis spectra of the TCMP networks were recorded in the solid state and are shown in Fig. 3. All four polymers showed a broad absorption across the wavelength range 200–600 nm, which is consistent with other reported networks.^{23,63} Although the shapes of the spectra were similar, they did show differences in terms of the onset of the absorption, which correlates with the band gap of the conjugated system. The highly branched A₃ + B₃ type polymer, **TCMP-0**, showed an absorption onset at around

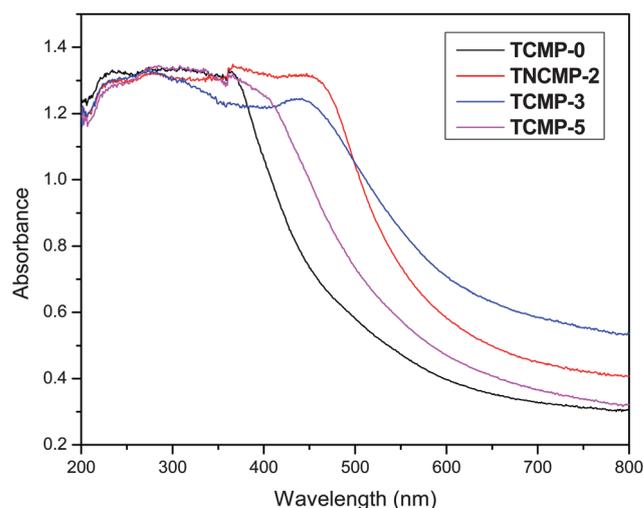


Fig. 3 UV-vis spectra of the TCMP networks. The spectra were recorded using powder samples of the polymers.

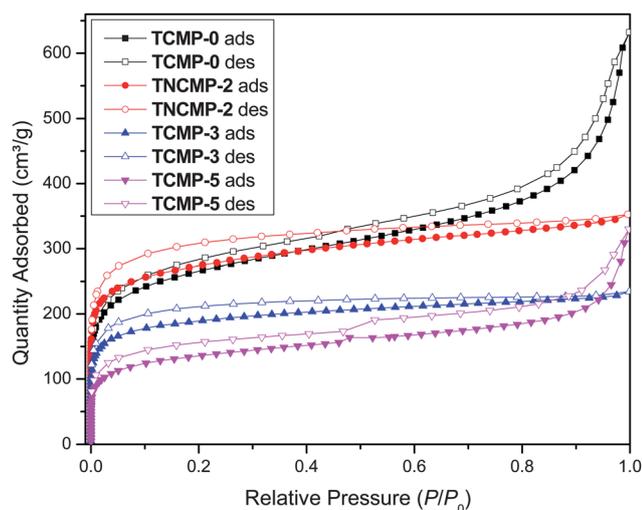


Fig. 4 Nitrogen adsorption and desorption isotherms measured at 77 K (the adsorption and desorption branches are labelled with filled and empty symbols, respectively).

540 nm, while the two less branched $A_3 + B_2$ polymers, **TCMP-3** and **TCMP-5**, showed absorption onsets at 625 nm and 590 nm, respectively. Compared with **TCMP-0**, the other $A_3 + B_3$ network, **TNCMP-2**, synthesized from both an electron-donating unit (triphenylamine) and an electron-withdrawing unit (1,3,5-triazine), showed a significantly red-shifted absorption onset at 625 nm. These results indicate clearly that the electronic states of the CMP systems can be adjusted and tuned by judicious choice of monomers. The results suggest that both lower levels of branching and donor–acceptor approaches can achieve narrower band gaps.

The porosity in the TCMP networks was investigated by nitrogen adsorption/desorption experiments (Fig. 4), from which the Brunauer-Emmett-Teller (BET) surface areas of the polymers were calculated. Detailed porosity data for the TCMPs in this study and the analogous CMPs are compiled in Table 1. As shown in Fig. 4, networks **TNCMP-2** and **TCMP-3** gave rise to typical Type I physisorption isotherms according to IUPAC classifications,⁶⁴ indicating a predominantly microporous

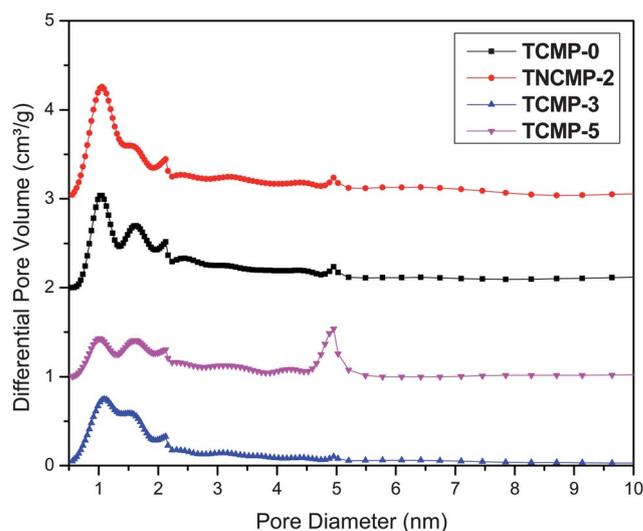


Fig. 5 Pore size distribution curves of the TCMP networks (for clarity, the curves of **TCMP-5**, **TCMP-0** and **TNCMP-2** are shifted vertically by 1, 2 and 3 $\text{cm}^3 \text{g}^{-1}$, respectively).

structure. While still mainly showing Type I isotherms, networks **TCMP-0** and **TCMP-5** gave some H3 hysteresis loop character, indicative of the existence of mesopores and/or small macropores. Pore size distribution curves for the four TCMPs are shown in Fig. 5, as calculated using nonlocal density functional theory (NL-DFT). All the polymer networks exhibit a micropore diameter centering around 1.1 nm with a shoulder peak at about 1.6 nm, similar to the corresponding CMPs.^{25,31} An apparent peak at about 5 nm for **TCMP-5** shows there are some mesopores in the network, in agreement with the shape of the N_2 isotherms (Fig. 4).

The apparent BET surface areas for these networks range from $494 \text{ m}^2 \text{g}^{-1}$ (**TCMP-5**) to $995 \text{ m}^2 \text{g}^{-1}$ (**TNCMP-2**), as shown in Table 1. Interestingly, the BET surface areas of the TCMPs correlate well with those of the analogous CMPs (to within less than 10%), showing that the replacement of benzene for a triazine unit does not greatly affect the porous character in the systems. In line with our previous work,^{25,31} networks formed by $A_3 + B_3$ copolymerization (**TCMP-0** and **TNCMP-2**) have

Table 1 Porosity and CO_2 and N_2 uptake data of the TCMP networks and corresponding CMPs

Polymer	S_{ABET} ($\text{m}^2 \text{g}^{-1}$) ^a	$V_{0.1}$ ($\text{cm}^3 \text{g}^{-1}$) ^b	V_{tot} ($\text{cm}^3 \text{g}^{-1}$) ^c	$V_{0.1}/V_{\text{tot}}$	CO_2 uptake (mmol g^{-1}) ^d		N_2 uptake (mmol g^{-1}) ^e	CO_2/N_2 ^f
					273 K	298 K		
TCMP-0	963	0.38	0.98	0.39	2.38	1.34	0.14	9.6
CMP-0 ^g	1018	0.38	0.56	0.68	2.10	1.21	0.08	15.1
TNCMP-2	995	0.40	0.55	0.73	2.62	1.45	0.19	7.6
NCMP-2 ^h	900	0.32	0.55	0.58	2.10	1.15	0.11	10.5
TCMP-3	691	0.28	0.36	0.78	2.25	1.26	0.05	25.2
CMP-3 ^g	522	0.18	0.26	0.69	2.18	0.81	0.06	13.5
TCMP-5	494	0.19	0.51	0.37	1.22	0.68	0.04	17.0
CMP-5 ^g	512	0.16	0.47	0.34	1.11	0.63	0.07	9.0

^a BET surface area calculated over the pressure range 0.01–0.05 P/P_0 . ^b $V_{0.1}$ = pore volume at $P/P_0 = 0.1$. ^c V_{tot} , total pore volume calculated at $P/P_0 = 0.99$. ^d CO_2 uptake measured at 1 bar. ^e N_2 uptake measured at 1 bar at 298 K. ^f Selectivity of CO_2 and N_2 uptake at 1 bar at 298 K. ^g Data from ref. 31. ^h Data from ref. 25.

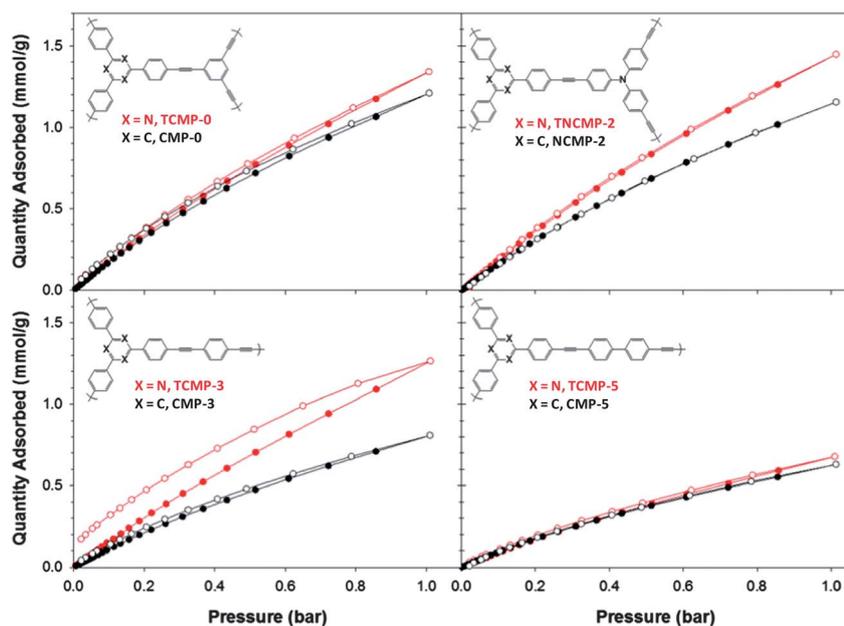


Fig. 6 CO₂ adsorption and desorption isotherms of TCMP networks (red) and the corresponding CMPs (black) measured at 1 bar at 298 K (the adsorption and desorption branches are labelled with filled and empty symbols, respectively).

higher surface areas than those obtained from A₃ + B₂ reactions (TCMP-3 and TNCMP-5); we believe this is due to polymers made by the A₃ + B₃ methods having shorter rigid connecting struts between branching nodes, as depicted in Scheme 1. The pore volume in the materials was also calculated from the nitrogen isotherms. The total pore volume at $P/P_0 = 0.1$ gives a good approximation of the micropore volume ($V_{0.1}$), as described previously.²⁶ The micropore volume divided by the total pore volume ($V_{0.1}/V_{\text{tot}}$) gives an indication of the percentage microporosity in the material. In this study, TCMPs have comparable micropore volumes to the corresponding CMPs. The $V_{0.1}/V_{\text{tot}}$ values of TNCMP-2 and TCMP-3 were both greater than 0.70, which means that micropores are dominant in the networks, while the $V_{0.1}/V_{\text{tot}}$ values of TCMP-0 and TCMP-5 were less than 0.40, indicating the coexistence of mesopores or interparticulate porosity.

The CO₂ gas sorption for the four TCMP networks was measured at 273 K and 298 K, and compared with that of the corresponding benzene-centred CMPs (Fig. 6, Table 1 and Figure S5–S12). Among these networks, TNCMP-2, which was synthesized from the triazine and triphenylamine monomers, showed the highest volumetric CO₂ uptake at both 273 K (2.62 mmol g⁻¹) and 298 K (1.45 mmol g⁻¹). These values are comparable or better than those reported for other polymer networks with similar surface areas synthesized by Sonogashira-Hagihara coupling reactions.⁵⁷ As far as the TCMP polymers are concerned, networks with larger surface areas lead to higher CO₂ uptakes; however, the correlations between CO₂ uptake and the surface area or pore volume are not proportional, suggesting that chemical functionality, and perhaps pore size, also plays a role. For example, TCMP-0 and TCMP-3 show comparable CO₂ sorption properties although there are apparent differences in their levels of porosity.

In general, the triazine networks adsorbed more CO₂ at 298 K than the corresponding benzene analogues despite having similar

surface areas (Fig. 6). For example, at 1 bar, TCMP-3 shows 50% higher CO₂ uptake (1.26 mmol g⁻¹) than the corresponding polymer CMP-3 (0.81 mmol g⁻¹). Similar findings were made at lower sorption temperatures (Figure S5–S12). This again indicates that not only the surface area and pore volume are important for the CO₂ adsorption, but also the chemical functionalities in the porous materials.^{57,58} CO₂/N₂ absorption selectivity is another important index for the practical application of the gas adsorbents. The ideal CO₂/N₂ absorption selectivity for these TCMPs and the analogous CMPs were calculated directly from their individual uptakes at 1 bar at room temperature. As listed in Table 1, networks with lower surface areas showed better CO₂/N₂ selectivity. Network TCMP-3 showed the highest CO₂/N₂ selectivity of 25.2 : 1.

Conclusions

A series of 1,3,5-triazine based CMP networks was prepared using Sonogashira-Hagihara cross-coupling chemistry. These TCMP networks are structurally analogous with benzene-linked CMPs we reported previously, and their porous properties can be well fine-tuned using the strategies previously developed in our group. UV-vis spectra measurements showed that the band gap of the networks could be engineered by judicious choice of monomers. Although the TCMPs have surface areas that are similar to the corresponding CMPs, they show better CO₂ absorption capacities. Of the TCMP networks, TNCMP-2 is particularly noteworthy. This network is very thermally stable, highly microporous, and is efficient in terms of CO₂ adsorption. Also, TNCMP-2 is a polymer constructed with both an electron acceptor (1,3,5-triazine) and an electron donor (triphenylamine), and is hence potentially able to afford interesting optoelectronic properties. CMPs comprising such monomer combinations could be useful in applications such as photovoltaics or photocatalysis. Research on this subject and development of new

methods to synthesize 1,3,5-triazine containing porous networks are ongoing.

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