This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

www.rsc.org/materialsA
Triptycene based 1,2,3-Triazole linked Network Polymers (TNPs) : Small Gas Storage and Selective CO$_2$ Capture

Snehasish Mondal and Neeladri Das*

Department of Chemistry, Indian Institute of Technology Patna, Patna 800 013, Bihar, India

E-mail: neeladri@iitp.ac.in, neeladri2002@yahoo.co.in; Tel.: +91 9631624708

Abstract
Herein, facile synthesis and characterization of four Triazole linked Network Polymers (TNPs) in high yields is described. These nitrogen rich polymers are derived using “Click” reaction between 2,6,14-triazido triptycene and various di or triethynyl comonomers. The TNPs are microporous and exhibit high surface area (SA$_{BET}$ up to 1348 m$^2$ g$^{-1}$). Due to incorporation of 1,2,3-triazole motif (a CO$_2$philic moiety), the TNPs record moderate to high CO$_2$ uptake (upto 4.45 mmol/g at 273K and 1 bar). The TNPs also show very good CO$_2$/N$_2$ (upto 48) and CO$_2$/CH$_4$ (8 - 9) selectivity. While highest storage capacity has been registered by TNP4 (CO$_2$ 4.45 mmol/g at 273K and 1 bar, CH$_4$ 23.8 mg/g, H$_2$ 1.8 wt%), the highest CO$_2$/N$_2$ and CO$_2$/CH$_4$ selectivity was shown by TNP3 which contains additional nitrogen rich building blocks in the form of heteroaromatic pyrazine rings. These results suggest that TNPs are porous materials with potential practical application in gas storage and separation.

Introduction:
Design and syntheses of porous materials have attracted considerable research attention over the past decade.$^{1-4}$ In recent years, research output in this direction has witnessed considerable growth.$^{5-13}$ Depending on the pore size, porous materials may be classified as ultra-microporous$^{14-16}$ microporous,$^{12,13}$ mesoporous$^{17-19}$ or macroporous.$^{20,21}$ Among these, microporous materials have emerged as potential candidates for applications that include but are not limited to gas storage and separation. Microporous materials, such as zeolites$^{22,23}$ and metal-organic frameworks (MOFs),$^{1,5}$ contain metal atoms. Alternatively, microporous materials can also be designed in the form of metal-free organic polymers that are highly crosslinked. Acronyms such as COFs, CMPs, CTFs, EOFs, HCPs, MOPs, OCFs, PAFs, PIMs, POFs, POPs, PPFs, PPNs, etc have been coined to describe metal-free porous organic polymers.$^{6-13}$ In general, MOFs have limited industrial applications as porous materials because presence of relatively labile coordination bonds that lower their thermal stability.$^{24}$ On the other hand, in microporous organic polymers (MOPs), light weight elements (such as H, C, N, and O) are interlinked via relatively stronger covalent bonds. Therefore these metal-free materials have lesser mass densities and higher stabilities (chemical and thermal). In addition, MOPs can be easily tailored with respect to properties such as guest selectivity and pore properties, due to availability of a plethora of multifunctional organic molecules that can serve as monomers towards the syntheses of MOPs.

In contemporary research dealing with development of microporous materials, design of MOPs for selective CO$_2$ capture and sequestration has received special attention.$^{24-46}$ This has stemmed from environmental and energy concerns related to CO$_2$, which is a major greenhouse gas. It is well known that thermal power plants emitting flue gas (containing approximately 15 % CO$_2$) are a major contributor to anthropogenic CO$_2$. Therefore, in order to contain global climate warming arising out of anthropogenic CO$_2$ emissions, there is a pressing demand to develop novel materials that can efficiently and selectively adsorb large quantities of CO$_2$ emitted from fossil-fuel fired power plants (classified as fixed-point CO$_2$ emission sources). Also it is desirable to separate CO$_2$ (present as an impurity) from natural gas that
contains 80-95 % methane.\textsuperscript{47,48} This explains the growing research interest to design MOPs having practical applications such as selective capture and sequestration of CO\textsubscript{2}.

As far as the design of polymers for better CO\textsubscript{2} adsorption and gas selectivity is concerned, it has been reported that incorporation of polar groups in the framework of porous organic polymers not only enhances carbondioxide uptake but also improves its selectivity over methane and nitrogen. This enhancement in CO\textsubscript{2} uptake is attributed to van der Waals interactions (quadrupole-dipole interactions and/or hydrogen bonding) between CO\textsubscript{2} and the polar functional groups that are present in the backbone of MOPs. Additionally, polymeric networks synthesized from electron rich monomers may also exhibit higher CO\textsubscript{2} uptake. This property is attributed to favorable Lewis acid-base interactions between the electron deficient carbon atom in CO\textsubscript{2} and the relatively electron rich polymer.\textsuperscript{49,50}

1,2,3-triazole is a nitrogen rich motif and it can be easily incorporated in the polymer framework by reacting monomers with multiple azide and ethynyl functional groups. Nguyen and co-workers have described synthesis of porous networks by covalently linking tetrahedral monomers using Click Chemistry.\textsuperscript{33} Triazole molecules (1,2,3- and 1,2,4-triazole) may be considered CO\textsubscript{2}–philic, considering the magnitude of their CO\textsubscript{2} binding energies.\textsuperscript{51} It is therefore anticipated that polymers having these nitrogen rich moieties in their backbone may be potential candidates for efficient CO\textsubscript{2} sorption and separation. Triptycene on the other hand, is a robust and structurally rigid motif that has three dimensional orientation of three arene rings fused to a [2.2.2]bicyclooctatriene moiety. Triptycene based porous polymers have often exhibited good gas storage and separation properties.\textsuperscript{52-58} This is often attributed to the “internal molecular free volume (IFV)” that arises from the inefficient packing of rigid three dimensional units of triptycene present in the polymer backbone.\textsuperscript{52,55,57,58}

With these premises in mind, we were interested in designing network polymers that would contain both 1,2,3-triazole motif (as polar groups) and triptycene motif (as a bulky rigid group). It is anticipated that such polymeric networks would be porous and simultaneously exhibit reasonably high uptake of CO\textsubscript{2}, primarily because of CO\textsubscript{2}–philic nature of polar 1,2,3-triazole moiety and the porosity arising from the inefficient packing of the triptycene units in the polymers.

Herein, we report synthesis of a series of new triptycene based and 1,2,3-triazole linked network polymers (TNPs) using 2,6,14-triazidotriptycene and various di- and tri ethynyl substituted comonomer via Cu(I)OAc catalyzed “Click” reaction. Complete structural characterization of these polymers and their performance as materials for gas storage as well as selective gas uptake has been described elaborately. TNPs constructed from monomers with three ethynyl functional groups, have a relatively higher surface area in comparison to TNPs derived from diethynyl comonomers. However, all TNPs exhibit microporosity (pore diameter < 2 nm). Additionally, these microporous TNPs also demonstrated similar or even better carbondioxide storage ability and selectivity than a wide range of the previously reported MOPs.

**Experimental section**

**Materials and methods:** Triptycene, aromatic bromides and Cu(I)OAc were obtained from Sigma Aldrich and were utilized without further purification. 2,6,14-triazidotriptycene was prepared from triptycene using literature reported protocol.\textsuperscript{59} All the aromatic ethynyl compounds were synthesized from corresponding aromatic bromide using Sonogashira cross-coupling reaction.\textsuperscript{60} Chromatographic purifications were performed using silica gel (100-200 mesh). Solid-state $^{13}$C cross-polarization magic angle spinning (CP-MAS) NMR spectra were obtained using BRUKER 300 MHz (H-1 frequency) NMR spectrometer at a mass rate 8 kHz and CP contact time 2 ms with delay time 3 Sec. FTIR analyses were performed using Shimadzu IR Affinity-1 spectrometer. Elemental analyses were performed using vario MICRO cube analyser. P-XRD data were recorded using a Rigaku TTRAX III X-ray diffractometer.
Porosity analyses were performed using Quantachrome autosorb iQ2 analyzer using UHP grade adsorbates. In a typical experiment, TNP (60 ~ 90 mg) was taken in a 9 mm large cell and attached to the degasser unit and degassed at 120 °C for 12-24 hr. The samples were refilled with helium and weighed carefully and then the cells were attached to the analyzer unit. The temperature was maintained using KGW isotherm bath (provided by Quantachrome) filled with liquid N2 (77K), or temperature controlled bath (298K and 273K).

**Synthesis of TNP1:** A typical experiment for the syntheses of TNP, is described using TNP as a representative example. 2,6,14-triazidotriptycene (189 mg, 0.5 mmol), 2,6,14-triethynyltriptycene (163 mg, 0.50 mmol) and Cu(I)OAc (4 mg, 0.03 mmol) were taken in a Schlenk flask under inert atmosphere. Degassed DMF (30 mL) was added to the flask with continuous stirring to dissolve the reactants. The flask (containing reactant) was subsequently heated at 120 °C with vigorous stirring. After a few minutes of stirring, the reaction mixture assumed the form of a light yellow gelatinous precipitate. The reaction mixture was allowed to stir for additional 24 hours with the resultant formation of a large amount of gelatinous precipitate. The reaction mixture was cooled to room temperature and filtered through glass frit followed by washing with DMF, DMSO, acetone, THF and dichloromethane. The product thus obtained was dried under reduced pressure at 100 °C and crushed with a mortar and pestle to yield a brownish yellow powder.

Yield: 338 mg, 96%; FTIR (KBr): 3404, 1660, 1464, 1221, 1035 cm\(^{-1}\). Elemental Analysis: Calculated for C\(_{46}\)H\(_{25}\)N\(_9\): C 78.51, H 3.58, N 17.91. Found: C 72.57, H 3.67, N 15.13.

**Synthesis of TNP2:** TNP has been prepared following the similar procedure as described for TNP using 2,6,14-triazidotriptycene (189 mg, 0.5 mmol), 4,4'-diethynyl-biphenyl (152 mg, 0.75 mmol) and Cu(I)OAc (4 mg, 0.03 mmol). Unlike TNP, large amount of yellow precipitate was observed after 24 hours stirring at 120 °C. After drying at reduced pressure at 100 °C, the final product was obtained as a light yellow powder.

Yield: 300 mg, 88%; FTIR (KBr): 3400, 1606, 1477, 1226, 1038 cm\(^{-1}\). Elemental Analysis: Calculated for C\(_{44}\)H\(_{26}\)N\(_9\): C 77.63, H 3.85, N 18.52. Found: C 71.97, H 4.36, N 15.93.

**Synthesis of TNP3:** This polymer was synthesized using 2,6,14-triazidotriptycene (189 mg, 0.5 mmol), 2,6-diethynylpyrazine (96 mg, 0.75 mmol) and Cu(I)OAc (4 mg, 0.03 mmol). Unlike other TNP, formation of light brown fluffy precipitate was observed within a few minutes of stirring at 120 °C. After 24 hours of stirring, formation of considerable amount of fluffy precipitate was observed. After drying at reduced pressure at 120 °C, the final product was obtained as light brown fluffy powder.

Yield: 242 mg, 85%; FTIR (KBr): 1569, 1489, 1238, 1033 cm\(^{-1}\). Elemental Analysis: Calculated for C\(_{32}\)H\(_{17}\)N\(_{12}\): C 67.48, H 3.01, N 29.51. Found: C 62.36, H 3.61, N 25.93.

**Synthesis of TNP4:** This polymer was synthesized using 2,6,14-triazidotriptycene (189 mg, 0.5 mmol), 1,3,5-triethynylbenzene (75 mg, 0.50 mmol) and Cu(I)OAc (4 mg, 0.03 mmol). In this case, large amount of dark yellow gelatinous precipitation was observed after stirring for 24 hours. After drying at reduced pressure at 120 °C, the final product obtained as a dark brown solid. The solid product was then crushed in a mortar to yield the final product as a brownish yellow powder.

Yield: 259 mg, 98%; FT-IR (KBr): 3391, 1614, 1486, 1226, 1046 cm\(^{-1}\). Elemental Analysis: Calculated for C\(_{32}\)H\(_{17}\)N\(_{9}\): C 72.86, H 3.25, N 23.90. Found: C 65.74, H 4.09, N 20.82.

**Result and discussion**

**Synthesis and characterization of TNP.**

The TNP were synthesized utilizing the well known Cu(I) catalyzed Click reaction that is known to regioselectively yield the 1,4-disubstituted 1,2,3-triazole derivative. It is well documented in literature
that “standard” azide-alkyne click reactions, carried out in water or water/DMF mixture, utilize Cu(I) species generated in situ via reduction of CuSO$_4$ with sodium ascorbate. However, in recent years, copper (I) acetate is being used as the source of Cu(I) instead of CuSO$_4$/sodium ascorbate mixture, since the later catalytic system either yields insoluble products or reactions are sluggish in nature.$^{61}$ Chen and Guan reported Click polymerization using CuOAc (source of Cu$^{1}$) in DMF (as a solvent).$^{62}$ Based on this literature report, we have synthesized a series of 1,4-disubstituted 1,2,3-triazole bridged network polymers (TNP$s$) using 2,6,14-triazidotriptycene and various monomers containing multiple ethynyl functional groups as outlined in Scheme 1.

**Scheme 1. Synthesis of TNP1-TNP4**

In a typical reaction for the synthesis of TNP$s$, 2,6,14-triazidotriptycene,$^{59}$ the corresponding ethynyl monomer (di or triethynyl) and 6 mole % (with respect to 2,6,14-triazidotriptycene) Cu(I)OAc were dissolved in 30 ml of DMF and refluxed for 24 hours under N$_2$ atmosphere. In case of TNP1 and TNP4 that utilized triethynyl monomers, gelatinous precipitation was observed after completion of the reaction.
In this case, upon drying the precipitate under vacuum, the final product was obtained as brownish yellow solid. FESEM images of the product obtained for TNP1 and TNP4 revealed aggregated sheet like structure. On the other hand, in case of reactions leading to the formation of TNP2 and TNP3 (using diethynyl monomers in conjugation with 2,6,14-triazidotriptycene), the corresponding products precipitated as fluffy solid which were distinctly different from the gelatinous precipitates observed in case of TNP1 and TNP4. As a consequence, for TNP2 and TNP3, the FESEM images revealed presence of aggregated particles in their morphologies which was distinctly different from that observed in case of TNP1 and TNP4 (Figure 1). Wide-angle X-ray diffraction (WAXD) analyses of TNPs suggested that these polymeric materials are amorphous in nature due to the featureless broad nature of the diffraction pattern in each case (Figure 1). This amorphous nature of the TNPs is due to the rapid and irreversible formation of triazole linkage during polymerization.12b

Figure 1. FESEM micrograph of TNP1-TNP4 (Left); WAXD pattern of the TNP1-TNP4 recorded at ambient temperature at a scan rate 3°/min (right)

The TNPs thus obtained were structurally characterized using solid state $^{13}$C (CP-MAS) NMR, and Fourier transform infrared (FTIR) spectroscopy. The $^{13}$C CP-MAS spectrum of TNP4 has been shown as a representative example (Figure 2). The peak centered at 53 ppm corresponds to the bridgehead carbon of triptycene. The appearance of this peak is consistent with that of literature reported triptycene based monomer or polymers54-57,59 thereby confirming the successful incorporation of triptycene motif in the polymer backbone. The peaks due to the phenyl ring carbons of the triptycene appear in the range 120-150 ppm. The resonance signal centered at 168 ppm is assigned to a carbon present in the 1,2,3-triazole motif, thereby confirming the formation of 1,2,3-triazole linkages via Click reaction. The $^{13}$C CP-MAS spectra (Figure S1) of the other TNPs match well with that of TNP4, thereby supporting the formation of the desired polymers as shown in Scheme 1.

Polymerization has also been confirmed by FTIR spectroscopic data analysis (Figure S2). FTIR spectrum of TNP2 is shown as a representative example in Figure 3. The characteristic band of azide functional group present in the triptycene monomer (2096 cm$^{-1}$) is absent in TNP2. Simultaneously, a band due to C–H stretching vibration of terminal alkynes (3280 cm$^{-1}$), observed in the corresponding diethynyl comonomer is missing in the FTIR spectrum of TNP2. This strongly suggests Click polymerization reaction between monomers containing terminal azide and terminal alkyne groups.
Figure 2. $^{13}$C CP-MAS NMR spectrum of TNP4, asterisks represent the spinning sideband.

Figure 3. FT-IR spectrum of 2,6,14-triazidotriptycene (top), TNP2 (middle), and 4,4'-diethynylbiphenyl (bottom).
Porous properties of the TNP s were investigated by subjecting these polymers to N\textsubscript{2} adsorption-desorption measurements at 77K. The isotherms are characterized by steep increase in slope in low relative pressure range ($P/P_0 = 0$–0.1) and this implies uptake of large quantities of N\textsubscript{2} gas. Additionally, the isotherms are reversible in nature. These characteristic features of the obtained adsorption-desorption isotherms (Figure 4) suggest that these are Type-I isotherms and the corresponding TNP polymers reported herein are microporous materials, as per IUPAC classifications. A gradual increase in N\textsubscript{2} uptake in the relatively high pressure range ($P/P_0 = 0.1$–0.9) was also observed in these isotherms. In case of all TNP s, the adsorption and desorption branches of the hysteresis loop remain almost parallel over an appreciable range of $P/P_0$, thereby suggesting that these materials (TNP 1-4) show type H4 adsorption-desorption hysteresis. According to IUPAC, “the Type H4 loop appears to be associated with narrow slit-like pores, but in this case the Type I isotherm character is indicative of microporosity”.

An additional feature observed in the isotherm of TNP2 and TNP3 is their steep rise while relative pressure ($P/P_0$) is greater than 0.9, which is an indication of the presence of larger pores (macropores) and interparticle voids. Thus isotherms of TNP2 and TNP3 are distinctly different from those of TNP1 and TNP4. It may be recalled that in the FESEM micrographs, TNP2 and TNP3 exhibited particle like nature having inter particle porosity, while TNP1 and TNP4 exhibit more aggregated plate like morphologies suggesting that these have insignificant inter particle porosity. Thus conclusions drawn from analysis of FESEM micrographs and adsorption-desorption isotherms substantiate each other.

DFT model based analysis results of pore size distributions (PSD) of TNP s (calculated from N\textsubscript{2} adsorption data at 77K) are depicted in Figure 4b. In the case of TNP1 and TNP4 wherein both comonomers are trifunctional, the pores are smaller than 2 nm. For these polymers, a narrow peak is observed in the ultramicroporous region (pore width < 0.7 nm) at 0.59 nm and 0.57 nm respectively, thereby suggesting presence of ultramicropores in these polymers. The PSD profiles of TNP2 and TNP3 also confirm the presence of micropores. Here a major peak is centered at 1.7 nm and 1.6 nm respectively for TNP2 and TNP3. Total pore volume of TNP s (calculated at $P/P_0 = 0.99$) are in the range of 0.53 to 0.66 cm\textsuperscript{2}g\textsuperscript{-1}(Table 1). In general, PSD is relatively narrow in case of polymers (TNP1 and TNP4) that utilized both trifunctional monomers relative to polymers (TNP2 and TNP3) where one of the comonomer is bifunctional. These results clearly show that pore size distribution of TNP s can be controlled by varying the number of reactive sites in the monomers. The microporous nature of TNP s is attributed to presence of rigid three dimensional triptycene motifs in the polymer backbone.

The surface area (SA) of TNP s have been obtained using Brunauer–Emmett–Teller (BET) model within the pressure range $P/P_0 = 0.01$ to 0.1 (Figure S3). The SA\textsubscript{BET} obtained for TNP1, TNP2, TNP3 and TNP4 are 1090 m\textsuperscript{2}g\textsuperscript{-1}, 460 m\textsuperscript{2}g\textsuperscript{-1}, 745 m\textsuperscript{2}g\textsuperscript{-1} and 1348 m\textsuperscript{2}g\textsuperscript{-1} respectively. The corresponding Langmuir surface areas are 1475 m\textsuperscript{2}g\textsuperscript{-1}, 756 m\textsuperscript{2}g\textsuperscript{-1}, 1006 m\textsuperscript{2}g\textsuperscript{-1} and 1723 m\textsuperscript{2}g\textsuperscript{-1} respectively (Table 1 and Figure S4). Polymers TNP1 and TNP4 synthesized from triethynyl comonomer exhibit higher surface area relative to the other two polymers (TNP2 and TNP3) where diethynyl comonomer has been utilized for polymerization. This difference in surface area of network polymers (TNP1 and TNP4) resulting from triethynyl monomers relative to polymers (TNP2 and TNP3) derived from disubstituted monomers is attributed to the higher extent of cross-linking as well as difference in the geometry of the comonomers. Irrespective of the nature of ethynyl monomer used in conjugation with 2,6,14-triazidotriptycene, the resulting TNP s are significantly porous and their corresponding surface areas (SA\textsubscript{BET}) are comparable or better than a wide variety of microporous polymers reported in literature such as mPAF (948-1314 m\textsuperscript{2}g\textsuperscript{-1}),\textsuperscript{27} Benzimidazole-Linked Polymers (BILPs, 599-1306 m\textsuperscript{2}g\textsuperscript{-1}),\textsuperscript{25,65,66} imine-linked PPFs (419-1740 m\textsuperscript{2}g\textsuperscript{-1}),\textsuperscript{24} Nitrogen-Doped Microporous Carbons (263-744 m\textsuperscript{2}g\textsuperscript{-1}),\textsuperscript{29} Imine-Linked POFs (466-1521 m\textsuperscript{2}g\textsuperscript{-1}),\textsuperscript{31} nanoporous azo-linked polymers (ALPs, 862-1235 m\textsuperscript{2}g\textsuperscript{-1}),\textsuperscript{52} “click-based” POPs (1090-1440 m\textsuperscript{2}g\textsuperscript{-1})\textsuperscript{13} and triptycene-based microporous polymers such as benzimidazole network (600 m\textsuperscript{2}g\textsuperscript{-1}),\textsuperscript{56} porous polymer
derived from Tröger's Base (TB-MOP, 694 m²g⁻¹), and microporous polyimides (STPIs, 4-541 m²g⁻¹). The surface area and pore properties are summarized in Table 1.

Table 1. Reaction yield and pore properties of TNP1-TNP4.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>SA_BET (m²g⁻¹)ᵃ</th>
<th>SA_Lang (m²g⁻¹)ᵇ</th>
<th>V_total (cm³g⁻¹)ᶜ</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNP1</td>
<td>1090</td>
<td>1475</td>
<td>0.58</td>
<td>96</td>
</tr>
<tr>
<td>TNP2</td>
<td>460</td>
<td>756</td>
<td>0.53</td>
<td>88</td>
</tr>
<tr>
<td>TNP3</td>
<td>745</td>
<td>1006</td>
<td>0.62</td>
<td>85</td>
</tr>
<tr>
<td>TNP4</td>
<td>1348</td>
<td>1723</td>
<td>0.66</td>
<td>98</td>
</tr>
</tbody>
</table>

ᵃSurface area calculated based on the BET model from the nitrogen adsorption isotherm (P/P₀ = 0.01-0.1).ᵇSurface area calculated based on the Langmuir model from the nitrogen adsorption isotherms (P/P₀ = 0.05-0.35).ᶜThe total pore volume calculated at P/P₀ = 0.99.

Considering the microporous nature of TNP and the presence of nitrogen-rich 1,2,3-triazole moieties present in the polymer framework, we were interested to investigate the potential of TNP as porous materials for gas storage applications. It has been reported in literature that nitrogen enriched microporous organic polymers perform well as materials for storage of small gas molecules in general and particularly CO₂. Therefore to assess the performance of TNP in selective gas storage materials, adsorption isotherms for CH₄, CO₂, and H₂ were collected under different conditions.

The CO₂ sorption isotherms of TNP were collected at 273 and 298 K and pressures upto 1 bar. The corresponding CO₂ isotherms register a steep rise in the initial low pressure region and are completely reversible in the entire region due to the absence of any significant adsorption-desorption hysteresis [Figure 5a (273K) and Figure S5 (298K)]. The reversibility suggests that interactions between TNP and CO₂ are weak to the extent of regeneration of the polymers without application of heat. As observed in case of N₂ sorption analysis, TNP (1 and 4) derived from triethynyl comonomers shows higher uptake of CO₂ relative to TNP (2 and 3) derived from diethynyl comonomers. At 273 K and 1.0 bar, TNP4 demonstrates highest CO₂ uptake of 196 mg/g (4.45 mmol/g), while TNP2 shows lowest value of CO₂ uptake at 70 mg/g (1.59 mmol/g). Importantly, the magnitude of CO₂ uptake by these TNP is comparable or better than various literature reported COFs. For example, the uptake of TNP4 (4.45 mmol/g at 273K/1 bar) exceeds this value for –OH functionalized POFs (4.2 mmol/g), imine linked ILP
(1.97 mmol/g),\textsuperscript{29} BLP1 (4.27 mmol/g),\textsuperscript{65} and tetraphenyladamantane based PAN (3.36-4.0 mmol/g).\textsuperscript{37} In general, the CO\textsubscript{2} uptake values (1.59-4.45 mmol/g at 273K/1bar) of TNPs are comparable with various microporous organic polymers such as triazine based TBILP (2.66-5.18 mmol/g),\textsuperscript{42} microporous covalent triazine polymers (MCTP, 3.65-4.64 mmol/g),\textsuperscript{40} and carbazolic porous organic frameworks (Cz-POFs, 1.75-4.77 mmol/g).\textsuperscript{38} Furthermore, The CO\textsubscript{2} uptake capacities of these TNPs are comparable to MOFs such as Zn\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})(C\textsubscript{2}N\textsubscript{4}H\textsubscript{3})\textsubscript{2}·(H\textsubscript{2}O)\textsubscript{0.5} (4.35 mmol g\textsuperscript{-1})\textsuperscript{58} and amine-functionalized MOFs such as bio-MOF-11 (6.0 mmol g\textsuperscript{-1}).\textsuperscript{69} The observed substantial uptake of CO\textsubscript{2} by these triptycene-based TNPs can be considered as a consequence of high internal molecular free volume (IMFV) due to the triptycene units and high nitrogen content due to the triazole motifs. Recently, theoretical studies have shown that 1,2,3-triazole molecules have large CO\textsubscript{2} binding energy (BE) (20.0 kJ mol\textsuperscript{-1}) possibly due to high affinity of triazole rings for CO\textsubscript{2} via strong electrostatic interactions.\textsuperscript{51}

To further understand the interaction of CO\textsubscript{2} with TNPs, the isosteric heats of adsorption (Q\textsubscript{st}) for CO\textsubscript{2} in TNPs were estimated from the CO\textsubscript{2} adsorption isotherm at 273 and 298 K. The Q\textsubscript{st} values for CO\textsubscript{2} at zero coverage (at the onset of adsorption) are in the range of 34.8-38.5 KJ/mol. Strong interactions between CO\textsubscript{2} and polar 1,2,3-triazole motifs as well as the narrow distribution in the microporous region may be the reason for high Q\textsubscript{st} value observed in low pressure region. The Q\textsubscript{st} values (34.8-38.5 KJ/mol) of TNPs are higher than a variety of previously reported porous organic polymers such as nanoporous azo-linked polymers (ALPs: 27.9-29.6 KJ/mol),\textsuperscript{32} imine-linked porous polymer frameworks (PPFs: 21.8-29.2 KJ/mol),\textsuperscript{24} benzimidazole-linked polymers (BLPs: 26.7-28.0 KJ/mol),\textsuperscript{25,65,66} nitrogen-rich networks (PECONFs: 26-34 KJ/mol),\textsuperscript{64} nitrogen-rich diaminotriazine-based polymers (APOPs, 26.6-33.3 KJ/mol),\textsuperscript{70} and carbazolic porous organic frameworks (Cz-POFs, 24.8-27.8 KJ/mol).\textsuperscript{38} However these values are slightly less than microporous covalent triazine polymers (MCTPs, 30.6-40 KJ/mol).\textsuperscript{40}

In addition to CO\textsubscript{2}, TNPs were also investigated as materials for the sorption of other gases such as H\textsubscript{2} and CH\textsubscript{4} (Table 2). CH\textsubscript{4} gas isotherms of TNPs were collected at 273K (Figure 5c) and 298 K (Figure S5) up to 1 bar pressure. At 273 K, TNP\textsubscript{4} registers highest methane uptake (23.8 mg/g) while TNP\textsubscript{2} records lowest (10.0 mg/g). Irrespective of extent methane sorption, all the isotherms are completely reversible. We have also calculated the isosteric heat of adsorption (Q\textsubscript{st}) for methane in TNPs and values at zero coverage are found to be in the range of 13.2-20.0 KJ/mol. These magnitudes of Q\textsubscript{st} are comparable with the various hetero functionalized porous organic polymer.\textsuperscript{24,25,27,32}
Similarly, H₂ adsorption isotherms were collected at 77K for TNP's (Figure 6). The uptake capacity of H₂ increases in the order of TNP2 < TNP3 < TNP1 < TNP4 which is consistent with the increasing order of surface area (SA_BET). The H₂ uptakes of TNP's are in the range of 0.8-1.8 wt% at 77K and 1bar, which is comparable with various organic porous polymers such as, nanoporous azo-linked polymers (ALPs, 1.39-2.19 wt%), and benzimidazole-linked polymers (BILP1, 1.9%)

Figure 5. CO₂ uptake isotherm of TNP1-TNP4 at 273K (a), Isosteric heat of adsorption {Q_{st}} of TNP's for CO₂ (b), Methane uptake isotherm of TNP1-TNP4 at 273K (c) and Q_{st} of TNP's for CH₄ (d). Adsorption (filled) and desorption (empty)
After evaluation of the porosity and gas-uptake capacities of these TNP s, we were interested to study their ability to selectively capture CO\textsubscript{2} over CH\textsubscript{4} and N\textsubscript{2}. It is well known that in order to reduce environmental pollution due to CO\textsubscript{2} (a green house gas) present in flue gas (N\textsubscript{2}/CO\textsubscript{2}: 85:15), it is necessary to selectively capture CO\textsubscript{2} over N\textsubscript{2}. Also it is well accepted that CO\textsubscript{2} is a contaminant in natural gas (CH\textsubscript{4}/CO\textsubscript{2}: 95:5) and it is necessary to selectively capture CO\textsubscript{2} over methane in order to improve the quality of natural gas as a fuel and also control corrosion in pipeline due to CO\textsubscript{2}.

In order to access the performance of TNP s in CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} gas selectivities, it is required to record the single component adsorption isotherms of these gases at 273K (Figure 7) and 298K (Figure S6) up to 1 bar pressure. For a given TNP, an initial steeper rise in the CO\textsubscript{2} adsorption isotherm in comparison to that in case of corresponding N\textsubscript{2} or CH\textsubscript{4} isotherm was anticipated, considering the higher Q\textsubscript{st} values of TNP s for CO\textsubscript{2} in zero surface coverage (Table 2) due to favorable interactions between CO\textsubscript{2} and N\textsubscript{2} centers present in the 1,2,3-triazole moieties. It must be mentioned here that in flue gas, CO\textsubscript{2} partial pressure is typically 0.15 bar at 273 K.\textsuperscript{25} Thus for a given porous material, it is worth considering its relative uptake of gases (CO\textsubscript{2} vs N\textsubscript{2} or CH\textsubscript{4}) at 0.15 bar while evaluating its performance in selective capture.
gas adsorption. In case of TNPs, at 0.15 bar the adsorption isotherms indicate significantly higher CO$_2$ uptake relative to N$_2$ or CH$_4$. Considering this fact, these TNPs can be considered as useful materials for selective CO$_2$ gas adsorption applications under these conditions.

Subsequently, CO$_2$/N$_2$ and CO$_2$/CH$_4$ gas selectivity of these TNPs was estimated from the initial slope ratios using Henry’s law constants for single-component adsorption isotherms (Figure S7 and Figure S8). This method has been routinely used to study gas selectivity properties of a wide variety of organic and inorganic hybrid materials.

Therefore, the N$_2$/CO$_2$ selectivity of TNPs has been calculated from the isotherms recorded at 273K and 298K in the pressure range below 0.15 bar, and the results are summarized in table 2. Overall, the selectivity at 273K (31-48) is higher than the selectivity at 298K (23-31) for all TNPs. Amongst these four network polymers, TNP3 shows highest selectivity for CO$_2$ over N$_2$ (48 at 273K). This may be attributed to the presence of additional pyrazine motifs in TNP3 that are absent in the other three TNPs. This polymer (TNP3) offers more nitrogen sites for interaction with CO$_2$ in comparison to the other TNPs. The data also suggests a considerable trade-off between gas storage capacity and gas selectivity amongst the four TNPs reported herein. For example, TNP4 having highest surface area (SA$_{\text{BET}}$ = 1348 m$^2$/g), exhibits less selectivity for CO$_2$ over N$_2$ (31 at 273K) in comparison to TNP1 (SA$_{\text{BET}}$ = 1090 m$^2$/g, CO$_2$/N$_2$ = 36 at 273K) and TNP2 (SA$_{\text{BET}}$ = 460 m$^2$/g, CO$_2$/N$_2$ = 40 at 273K). In general, the TNP with a relatively higher surface area exhibited relatively lower CO$_2$/N$_2$ selectivity. TNP3 is an exception since it has higher nitrogen content in comparison to the other TNPs. Thus our results corroborate with the general perception that higher porosity level accompanies with a compromise in CO$_2$/N$_2$ selectivity. Nevertheless, the CO$_2$/N$_2$ selectivity of these 1,2,3-triazole linked network polymers (TNPs) are better than a wide range of microporous materials reported in literature.

Additionally, the CO$_2$/CH$_4$ selectivity of TNPs was also investigated to ascertain their applicability in the purification on natural gas (CH$_4$/CO$_2$: 95:5) by capture of CO$_2$. Methane adsorption isotherms were collected at 273K and 298K and selectivity was determined using the initial slope calculation, and the results obtained are depicted in table 2. CO$_2$/CH$_4$ selectivities at 273K and 1bar are in the range of 8-9. At a higher temperature (298K), the CO$_2$/CH$_4$ selectivity was found to decrease to 5-6. In general, the TNPs exhibit significantly lower CO$_2$/CH$_4$ selectivity relative to CO$_2$/N$_2$ selectivity. It is reported that due to higher polarizability of methane relative to N$_2$, adsorption potential of methane is much higher than that of N$_2$ and this may be the explanation for the observed lower CO$_2$/CH$_4$ selectivities in comparison to CO$_2$/N$_2$ selectivities.
Conclusion:

In conclusion, facile synthesis and characterization of a series of triptycene based and 1,2,3-triazole laced alternating copolymers has been described. The resulting 1,2,3-Triazole linked Network Polymers (TNP$s$) are microporous materials exhibiting BET surface area up to $1348 \text{ m}^2\text{g}^{-1}$. We have also shown that incorporation of nitrogen-rich pyrazine moieties results in enhancement of CO$_2$/N$_2$ gas selectivity relative to TNP$s$ that do not possess this hetero-aromatic structural motif in the polymer backbone. In general, we have shown that integration of triptycene and 1,2,3-triazole motifs in the backbone of organic network polymer results in the yield of materials that demonstrate excellent performance in storage of small gases at low pressure. Considering the microporosity, large gas uptake and high selectivities of CO$_2$ over N$_2$ and CH$_4$, TNP$s$ are potential candidates for practical applications such as CO$_2$ capture as well as purification of flue and natural gas. Currently, we are extending our research in the direction of facile synthesis of novel microporous organic polymers with applications in clean energy sector by utilizing new multifunctional monomers for tailoring the gas sorption properties.

Figure 7. Gas uptake capacities for TNP1-TNP4 at 273 K. CO$_2$ (green square), CH$_4$ (blue star), and N$_2$ (red circle).
Acknowledgements

N.D. thanks the CSIR, Govt. of India, New Delhi [CSIR No. 02(0126)/13/EMR-II] for financial support. S.M. thanks UGC, New Delhi for a Research Fellowship. Authors acknowledge Indian Institute of Technology Patna for providing infrastructure required for this research. The authors also acknowledge Central NMR Facility, CSIR-NCL for acquiring $^{13}$C CP-MAS data.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://..............

References

64. P. Mohanty, L. D. Kull and K. Landskron, Nat. Commun. 2011, DOI: 10.1038/ncomms1405.