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Nanoporous triptycene based network polyamides (TBPs) for selective CO_2 uptake

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ABSTRACT

In contemporary research, there has been a surge in the efforts to design novel porous materials as adsorbents for CO_2 capture. Polyamides are a class of robust polymers that are easy to synthesize from readily available starting materials. These have CO_2-philic amide functional groups and hence are being considered as materials for CO_2 adsorption and storage. Herein, we report facile and efficient synthesis as well as characterization of a series of triptycene based polyamide networks (TBPs) that are thermally stable and they exhibit reasonably high surface area (SA_{BET} upto 80 m^2 g^{-1}). The CO_2 uptake and CO_2/N_2 selectivity of these TBPs are noteworthy and these data are comparable to other literature reported polyamides known to demonstrate either highest uptake of carbon dioxide or highest CO_2/N_2 selectivity. In view of the ease of synthesis, thermal stability, porosity/surface area and CO_2 selectivity, **TBPs** reported herein may be considered as promising adsorbent materials for CO_2 contaminated gas purification processes.

1. Introduction

Carbon dioxide (CO_2) is considered as one of the primary greenhouse gases. Over the past few decades, concentration of atmospheric CO_2 has increased considerably. It is therefore a major contributor to climatic changes arising due to global warming by greenhouse gases [1]. As far as the anthropogenic sources of CO_2 are concerned, thermal power plants (emitting flue gas containing approximately 15% CO_2 and 70% N_2) are key “fixed-point” sources of CO_2 emissions [2]. For that reason, there has been a growing interest in the development of novel strategies and materials for efficiently capturing CO_2 that is being emitted from thermal power plants [3]. Monoethanolamine (MEA) is often used industrially to absorb CO_2 and this is a key strategy to capture post-combustion CO_2 [4]. However this technique has several drawbacks such as massive energy expenditure required for MEA regeneration [4]. An alternative to this strategy (for post-combustion CO_2 capture) is to employ solid sorbents (that are highly porous in nature) as smart materials for efficient and selective uptake of CO_2 [5]. Additionally such porous materials may also find application in separation of carbon dioxide from methane in natural gas. Such removal of CO_2 (from natural gas) will ensure increase in energy efficiency of natural gas as a fuel. Additionally, this will reduce corrosion of pipeline (for natural gas) due to the decreased percentage of acidic CO_2.

The main advantage of porous materials over aqueous amine solutions is the ease with which the former can be handled and regenerated. This is attributable to their ability to capture CO_2 using the phenomenon of physisorption instead of chemisorption (in case of MEA and other solvents). Porous materials may either contain metal centers (such as zeolites and MOFs) [5,6] or be free from the presence of any metal atoms in their structure (Covalent organic frameworks -COFs) [7]. The latter class of materials are usually highly crosslinked porous organic polymers containing light weight elements (such as H, C, N, and O) that are chemically connected via strong covalent bonds. From a practical viewpoint, COFs are preferred over MOFs because the former have relatively higher physicochemical stability and low mass density. Moreover, pore properties in COFs can be easily tailored since various functional groups can be incorporated in the polymer backbone by altering the monomers used.

Polyamides are an industrially important class of nonvinyl polymers [8]. The phrase “Aramide” is used to denote a polyamide designed from wholly aromatic monomers. Kevlar® and Nomex® are examples of such polyamides. In general, aramides have excellent thermal stabilities and mechanical properties [9]. Also

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they are known for their chemical resistance. These unique properties are observed due to presence of rigid aromatic motifs in the polymer backbone. The robust nature of aramides is also due to presence of strong interchain (CO···NH) hydrogen bonds which results in its dense packing [10]. Due to the inherent strength of aramides, these polyamides have been used to design products for use in defense and aerospace sectors [11]. Due to presence of amide groups in the polyamide backbone, this class of polymer may also be considered CO_2 philic and hence these may exhibit reasonable CO_2 capture [12]. Despite this fact, development of aramide network as porous materials for gas storage and separation is still in its early stage of research. There are only a handful of reports in literature in this direction [13]. These porous polyamide based COFs have a relatively lower surface area in comparison to other COFs that don't have amide linkage in the backbone of their respective polymeric network [13]. This might be a reason that apparently limited the development of the porous aramide network by reducing gas uptake capacity.

Triptycene is a robust and a structurally rigid motif that has been incorporated in polymeric networks to yield porous COFs with excellent gas storage properties [14]. Triptycene which is the simplest member of iptycene family, has three arene rings that are joined together via a [2.2.2]bicyclic bridge. The paddle wheel orientation of the arene rings in triptycene is responsible for the inefficient packing of these units in the polymeric network leading to appreciable “internal molecular free volume” (IFV) in the resultant material. The IFV in turn attributes to the desirable characteristics such as excellent gas storage capabilities and high surface areas [14a].

Considering the unique and remarkable structural feature of triptycene, we were curious to study the porous properties of aramide polymers derived from triptycene monomers. Herein, we report design of two series of triptycene based polyamide network (**TBP**s) using either 2,6,14-triaminotriptycene (unsymmetrical) or 2,7,14-triaminotriptycene (symmetrical) and various di- or triacyl chloride monomer via polycondensation reaction in presence of triethylamine (TEA) as an organic base. To the best of our knowledge, this is a unique report describing synthesis, characterization, and gas sorption properties (including CO_2/N_2 selectivity) of a set of triptycene based aramide networks. In this research, the objective was to combine the CO_2 philic nature of amide functional group with tendency of triptycene motifs to generate high IFV. The resulting **TBP**s are anticipated to display rather higher gas sorption and carbon dioxide selectivity in comparison to porous polyamides that have been reported in the literature. Our results indeed indicate that **TBP**s reported in this manuscript perform better as materials for gas storage as well as selective gas uptake, in comparison to most of the other porous polyamides reported in literature till date.

2. Result and discussion

2.1. Synthesis and characterization of polymer

2,6,14- and 2,7,14-triaminotriptycene were synthesized using literature reported protocol as described by Chen and coworkers. The structures of 2,6,14- and 2,7,14-triaminotriptycene were confirmed from the ^1H and ^{13}C NMR spectroscopy (supporting information, Fig. S1) [15]. In presence of a suitable organic base, reaction between an amine and acyl-chloride is a convenient way to yield amide linkage. Herein, we have synthesized two series of triptycene based polyamide network (**TBP**s) using either 2,6,14-triaminotriptycene (Scheme 1) or 2,7,14-triaminotriptycene (Scheme 2) and various monomers containing multiple acyl-chloride groups. In a typical polycondensation reaction towards synthesis of **TBP**s, solution of acyl-chloride (in anhydrous THF) was added to a solution of triaminotriptycene (2,6,14- or 2,7,14 derivative in dry THF) in presence of anhydrous TEA (triethylamine, used as a base) with continuous stirring. During the addition of acyl-chloride, fluffy precipitation was observed. The HCl thus produced in the reaction was quenched by triethylamine. During the addition of acyl-chloride solution, the reaction mixture was maintained at 0 °C (ice cold condition). After complete addition of acyl-chloride, stirring the reaction mixture was continued at ambient temperature for 24 h. During this period, a considerable amount of precipitation was observed. The product thus obtained as precipitate was collected by filtration, washed and dried under reduced pressure at 120 °C for 24 h to yield the **TBP**s in high yield.

The wide-angle X-ray diffraction (WAXD) patterns of the **TBP**s are shown in Fig. 1. The broad feature of the WAXD pattern suggested amorphous nature of these polyamides. The presence of bulky and rigid triptycene units in the backbone of these **TBP**s inhibits close packing and the consequence is loss of crystallinity in case of these **TBP**s.

After synthesis of the triptycene based polyamides (**TBP 1**–**6**), these were structurally characterized by solid state ^{13}C (CP-MAS) NMR, and Fourier transform infrared (FTIR) spectroscopy. Representative ^{13}C CP-MAS spectrum of **TBP3** is shown in Fig. 2. The two peaks around 50 ppm are assigned to the bridgehead carbon of a triptycene unit. The appearance of these peaks is in agreement with previously reported polymers derived from triptycene based monomers [14f,g]. These two peaks are characteristic of triptycene motif and therefore its successful incorporation in the product is confirmed. Peaks due to aromatic carbons from both monomers appear in the range of 105–160 ppm. The band centered at 168 ppm is assigned to the carbonyl carbon corresponding to amide linkages and this confirms presence of amide functional groups in the product that are formed due to reaction between triaminotriptycene and acyl chlorides. Similarly, in case of other **TBP**s, the signals due to bridgehead carbon (triptycene motif), aromatic carbons (due to both triptycene and various acyl chloride monomers) and the carbonyl carbon were appropriately assigned (Supporting information, Fig. S2). Thus formation of desired **TBP**s, as depicted in Schemes 1 and 2, was confirmed by ^{13}C NMR spectroscopy.

FTIR spectroscopic data also confirmed the formation of polyamides due to reaction between triaminotriptycenes and various acyl chlorides. The FTIR spectrum of **TBP3** is depicted as a representative example in Fig. 3. In the FTIR spectrum of **TBP3**, the strong band that appears at 1664 cm^{-1} is assigned to $\nu_{C=O}$ stretching (amide I) while the broad band at 3281 cm^{-1} is due to the ν_{N-H} symmetrical stretching. Moreover, the absence of symmetrical stretching band in the range 3400–3500 cm^{-1} (observed in primary amines) also confirms the successful polycondensation reaction between the triptycene based primary amines and corresponding acid chloride (Scheme 1). FTIR spectra of other polyamides (**TBP1, TBP2,** and **TBP4-TBP6**) also exhibit a strong band (for $\nu_{C=O}$ stretching) and a broad band (for ν_{N-H} symmetrical stretching) in the range of 1644–1664 cm^{-1} and 3194-3284 cm^{-1} respectively (Supporting information, Fig. S3).

2.2. Thermal properties

To check the thermal stability of the **TBP**s reported herein, these polymers were subjected to thermogravimetric analysis (TGA). These experiments were performed by heating the samples in nitrogen atmosphere. The flow rate of N_2 gas was 100 mL/min and the rate of temperature increment was 10 °C/min. In general, a small weight loss of 4–7% was observed at around 80 °C (Fig. 4) for all TBPs. This may be due to the evaporation of the entrapped solvents as well as moisture. Thermal degradation temperature (T_d = 10%