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Porous polyimides from polycyclic aromatic linkers: Selective CO_2 capture and hydrogen storage

K. Venkata Rao [a,1], Ritesh Haldar [b], Tapas Kumar Maji [b,**], Subi J. George [a,*]

[a] Supramolecular Chemistry Laboratory, New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur, Bangalore 560064, India
[b] Molecular Materials Laboratory, Chemistry and Physics of Materials, Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India

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ABSTRACT

Porous polyimides are important class of macromolecules owing to their excellent redox behaviour, efficient capture of CO_2 and H_2 gases, interesting photocatalytic properties and superior thermal and chemical stabilities. Here we describe in detail, the synthesis and gas storage properties of a series of porous polyimides (**Tr-NPI**, **Tr-PPI**, **Tr-CPI**, **Td-PPI** and **Td-CPI**) with various network topologies derived from polycyclic aromatic hydrocarbon linkers. These polyimides are synthesized in a single step by the condensation of corresponding polycyclic aromatic dianhydrides (**NDA**, **PDA** and **CDA**) with structure directing amine (**TAPA** and **TAPM**) monomers, having trigonal and tetrahedral geometry. The structure of all the polymers was fully characterized by various techniques. The present work also introduces for the first time porous polyimides containing rigid polycyclic aromatic compounds such as coronene. All the polyimides presented here exhibit high thermal stability and show selectivity towards CO_2 uptake at room temperature (293 K), due to the presence of aromatic clouds and CO_2 phillic oxygen and nitrogen functionalities on their pore surface. Moreover these polymers also showed significant uptake of H_2 gas (77 K). The present work has significant implications on the design of robust porous organic solids from small molecules for efficient capture of CO_2 and H_2 gases.

1. Introduction

Low density micro and mesoporous solids are important class of materials due to their great potential in various technological applications [1,2]. In recent years these materials are extensively investigated for gas storage [3–5], separation [6–8] and catalysis [9,10]. In view of environmental pollution control and purification of natural gas fuels, significant attention has been devoted for the development of porous materials that can selectively capture CO_2 over other competing gases such as N_2 and CH_4. Porous materials with polar pore surfaces can exhibit efficient uptake for CO_2 due to its large quadruple moment (-1.4×10^{-39} C m^2). This has been efficiently achieved in metal organic frameworks (MOFs) via open metal sites or by introducing CO_2 phillic groups through pre or post synthetic modifications [6,11–13]. However, presence of moisture and other harsh components in the flue gas can lead to the degradation of most of the MOFs via hydrolysis of coordinate bonds, although exceptional cases like zeolitic imidazolate derived frameworks (ZIFs) are reported [13]. On the other hand, activated carbons are widely used for gas storage applications owing to their high surface areas and cost-effective large scale production [2]. However, they show variable gas adsorption properties due to different textural features and exhibit poor CO_2 adsorption capacities at low pressures due to lower enthalpy of adsorption. Though covalent organic frameworks (COFs) [14,15] resembles as perfect crystalline organic analogues to the MOFs, yet they suffer from chemical and hydrothermal instability, and only specially designed monomers can enhance their stability [16]. In this regard, porous organic polymers (POPs) synthesized from pure organic linkers holds great promise owing to their high chemical and hydrothermal stability and ease of synthesis [17,18]. Taking advantage of diverse organic reactions, several POPs such as polymers with intrinsic microporosity (PIMs) [19,20], conjugated microporous polymers (CMPs) [21–26] and hyper-crosslinked polymers (HCPs)

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* Corresponding author. Fax: +91 80 2208 2627.
** Corresponding author.
E-mail addresses: tmaji@jncasr.ac.in (T.K. Maji), george@jncasr.ac.in (S.J. George).
[1] Fax: +91 80 2208 2627.

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[27–29], have been synthesized in recent years. It has been realized that, POPs containing heteroatoms (nitrogen, oxygen or sulphur) are essential for the efficient and selective uptake of polar gases such as CO_2 over N_2 and CH_4 [30–34]. Following this strategy, Dai et al. have synthesized nitrogen rich polymeric membranes [35,36] and Tan et al. [37] utilized microporous polymers derived from heterocyclic monomers for selective sorption of CO_2 over N_2. Recently we have achieved selective CO_2 adsorption in microporous poly(phenylenes)s over N_2 and Ar by taking advantage of electron rich aromatic π-clouds [38].

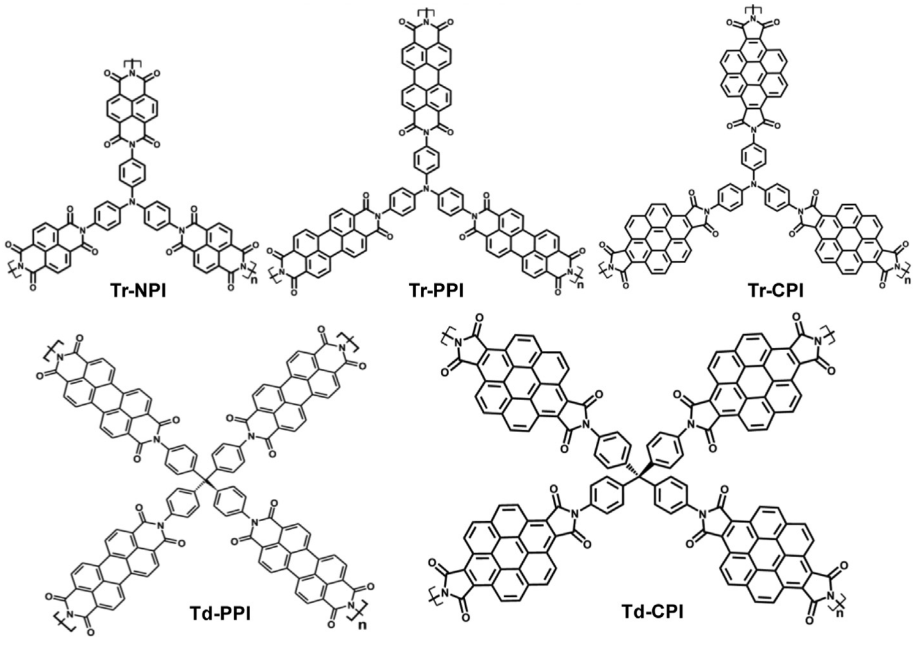
In recent years, porous polyimides have emerged as an important class of POPs for CO_2 capture owing to the presence of large number of CO_2-phillic oxygen and nitrogen functionalities in their backbone [39,40]. Moreover, polyimides derived from polyaromatic anhydrides are shown to have excellent redox behaviour [41–43] and photocatalytic activity [44,45] combined with superior chemical and thermal stability compared to the other porous polymers. Mirkin et al. have shown selective uptake of CO_2 over CH_4 in polyimides containing naphthalene diimide as the network building unit [46,47]. Furthermore, porous polyimides derived from pyromellitic dianhydrides are shown to have excellent H_2 storage property [48]. Recently we have achieved very high surface area and thermal stability in polyimides by employing polyaromatic perylene diimide core [49]. Motivated by their promising selective CO_2 capture [50–53], catalytic behaviour [54] and ease of accessibility, we have investigated in detail various polyimides containing polycyclic aromatic cores.

Here, we describe in detail, the synthesis and gas storage properties of five porous polyimides derived from polyaromatic dianhydrides such as naphthalene (**Tr-NPI**), perylene **(Tr-PPI** and **Td-PPI)** and coronene **(Tr-CPI** and **Td-CPI)** (Scheme 1). For the first time we have used coronene, a large polycyclic aromatic hydrocarbon, in the synthesis of POPs. Porosity has been introduced to the polyimides via the use of either trigonal (**TAPA**) or tetrahedral (**TAPM**) structure directing monomers. All the polyimides reported here showed high thermal stability (>500 °C) and displayed efficient CO_2 uptake due to the presence of polar functional groups in their backbone. Among the series, coronene based polyimides have high thermal stability, **Tr-NPI** showed highest CO_2 uptake (50 wt% at 195 K) and **Td-PPI** showed higher selectivity (25 times) towards CO_2 over N_2 at room temperature (298 K). In addition, all these polyimides showed good H_2 storage capacity and the highest uptake (1.6 wt% at 77 K) was observed for **Td-PPI**.

2. Experimental

2.1. General methods

Scanning Electron Microscopy (SEM) measurements were performed on a Lica-S440I by keeping the samples on copper substrate followed by heating at 150 °C under vaccum and measurements were done with an accelerating voltage of 10 kV. Thermo Gravimetric Analysis (TGA) was carried out usingMetler Toledo analyser in nitrogen atmosphere (flow rate 50 mL min^{-1}) in the temperature range 30–700 °C (heating rate 5 °C/min). Elemental (CHNS) analyses were carried out using Thermo Scientific Flash 2000 Elemental Analyzer. Powder Xray Diffraction (PXRD) pattern of the compounds were recorded in Bruker D8 Discover (40 kV, 30 Ma) instrument using Cu Kα radiation ($2\theta = 0.8$–$60°$). Solid state ^{13}C NMR CPTOSS measurements were performed on a Bruker Avance 400 (400 MHz) spectrometer with a MAS rate of 5 kHz. N_2, H_2 and CO_2 gas adsorption were carried out on degassed polyimides at 200 °C for a period of 18 h under high vacuum (10^{-1} Pa) using QUANTACHROME QUADRASORB-*SI* analyzer at 77 K (for N_2 and H_2) and at 298 K, 293 K and 195 K (for CO_2). The degassed adsorbents were charged into the sample tube, and then the change of the pressure was monitored. The degree of adsorption was determined by the decrease of the pressure at the equilibrium state. All operations were computer-controlled and automatic. High-pressure H_2 and CO_2 sorption measurements at 77 K and 293 K were carried out on a fully computer controlled volumetric BELSORP-HP, BEL JAPAN high pressure instrument. The H_2 and CO_2 gases used for the high pressure measurements are scientific/research grade with 99.999% purity. Dead volume of the sample cell was measured with helium gas of 99.999% purity. Non-ideal correction for H_2 and CO_2 gases



Scheme 1. Structure of polyimide frameworks of various polycyclic aromatics with trigonal/tetrahedral centres.