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Facile synthesis and gas transport properties of Hünlich’s base-derived intrinsically microporous polyimides

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ABSTRACT

Tröger’s base (TB) has been utilized as an important building block in designing ladder polymers of intrinsic microporosity (PIMs) and microporous polyimides (PIM-PIs) for membrane-based gas separations due to its unique V-shaped bicyclic structure and versatile molecular chemistry. Nearly a century after its discovery, Hünlich’s base (HB) was recently reintroduced as a valuable diamine derivative of TB made by a single-step reaction of 2,4-diaminotoluene and formaldehyde, spurring use in molecular devices such as molecular tweezers and photo-switches. Unlike TB, HB has not been explored as a building block of PIMs and PIM-PIs for membrane-based gas separations. In this study, we synthesized two soluble PIM-PIs for the first time by reaction of HB as diamine and 4,4’-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) or 9,10-diisopropyltriptycene tetracarboxylic dianhydride (TDAi3), respectively. 6FDA-HB exhibited high Brunauer-Teller-Emmett (BET) surface area of 415 m² g⁻¹ and fractional free volume (FFV) of 0.26. The gas separation performance of the 6FDA-HB polymer was similar to other 6FDA-based dimethyl-substituted Tröger’s base polyimide analogues, exhibiting O₂, CO₂ and H₂ permeability of 62, 286, and 391 Barrer with O₂/N₂, CO₂/CH₄ and H₂/CH₄ selectivity of 4.4, 26 and 36, respectively. Compared to 6FDA-HB, the triptycene-containing Hünlich’s base polyimide (TDAi3-HB) displayed a higher BET surface area (501 m² g⁻¹) owing to the presence of the rigid bridged tricyclic triptycene contortion site, resulting in about two-fold increase in O₂ permeability to 188 Barrer coupled with slightly compromised O₂/N₂ selectivity of 4.1. Beside the merit of facile synthesis, the Hünlich’s base-derived polyimides experienced relatively modest effects of physical aging on gas permeation properties.
1. Introduction

2,8-Dimethyl-6H,12H-5,11-methanodibenzo[\textit{h,f}][1,5]diazocine, commonly referred to as Tröger’s base (TB) [1,2], has attracted significant attention as one of the most popular molecular building blocks used for designing polymers of intrinsic microporosity (PIMs) for membrane-based gas separations due to its rigid, bridged bicyclic V-shaped scaffold and supramolecular chemistry [3-7]. Solution-processable ladder PIMs, first reported in 2004, are an emerging class of polymeric membrane materials characterized by high Brunauer-Emmett-Teller (BET) surface area (~200 to 1000 m$^2$ g$^{-1}$), excellent thermal and chemical stability, high gas permeability, and adequate gas-pair selectivity [8-12]. The key design principle to obtain high-performance PIM materials for gas separations is to frustrate efficient polymer chain packing by incorporating rigid, sterically hindered contortion centers that induce large free volume with bimodal pore size distribution in the polymer structure [13,14]. A wide variety of ladder PIM materials were developed using contortion sites such as spirobisindane [8-11,15], ethanoanthracene [3,16,17], tetraphenylethylene [18], triptycene [19-21], Tröger’s base [22-25], etc. Notably, several \textit{ladder PIMs} designed by combing Tröger’s base or 2,3,5,6-tetrafluoroterephthalonitrile building blocks with ethanoanthracene, triptycene or benzotriptycene units are among the best performing polymers for membrane-based gas separations, some of which defined the latest 2015 pure-gas O$_2$/N$_2$, H$_2$/N$_2$, H$_2$/CH$_4$, and 2019 CO$_2$/CH$_4$ and CO$_2$/N$_2$ permeability/selectivity upper bounds [14,26,27].

Alternatively, TB-derived diamines can also be applied for designing polyimides of intrinsic microporosity (\textit{PIM-PIs}) [28-33]. Polyimides made from various aromatic dianhydrides with methyl-substituted TB-diamines have been reported by several research groups for membrane gas separation applications [28-33]. Some examples of TB-based PIM-PI structures based on 4,4’-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and various TB diamines are shown in \textbf{Fig. 1}. In 2014, Jin’s group reported four different TB diamine-based polyimides using two Tröger’s base diamines, 2,8-diamino-4,10-dimethyl-6H,12H-5,11-methanodibenzo[\textit{1,5}]diazocine (TBDA1) and 3,9-diamino-4,10-dimethyl-6H,12H-5,11-methanodibenzo[\textit{1,5}]diazocine (TBDA2), reacted with 6FDA or 3,3’,4,4’-tetracarboxylicdiphenyl ether dianhydride (ODPA) using a one-pot high-temperature polycondensation method in \textit{m}-cresol [28]. It was found that 6FDA-based TB polyimides had higher BET surface area and higher gas permeability than their ODPA-derived analogues. Furthermore, the positions of the methyl groups on the TB diamines
had great impact on their gas separation properties [28]. Location of the methyl groups in ortho position to the imide linkages (TBDA2-6FDA-PI and TBDA2-ODPA-PI) resulted in higher gas permeability with relatively small effect on gas-pair selectivity compared to TBDA1-based polyimides containing meta-positioned methyl groups to the imide linkages (Fig. 1). The best performing polyimide in this series, TBDA2-6FDA-PI, demonstrated microporosity with a BET surface area of 325 m² g⁻¹ and displayed pure-gas CO₂ permeability of 285 Barrer coupled with CO₂/CH₄ selectivity of 36 [28]. Jin’s group also introduced a sterically hindered PIM-type spirobisindane-dianhydride building block to prepare TB diamine-based PIM-PIs with TBDA1 and TBDA2 [29]. The resulting microporous polyimides, TBDA1-SBI-PI and TBDA2-SBI-PI, exhibited enhanced BET surface areas of 560 and 615 m² g⁻¹ with promising gas permeation properties for air separation with O₂ permeability of 190 and 240 Barrer combined with O₂/N₂ selectivity of 5.4 and 4.9, respectively.

In 2014, Zhuang et al. reported a new two-step synthesis method of Tröger’s base-derived polyimides using commercially available starting materials [30]. In the first step, aromatic imide-containing diamines were prepared by high-temperature condensation reaction of 2,5-dimethyl-1,4-phenylenediamine and a dianhydride, 6FDA or 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), with a molar ratio of 3:1. Subsequently, polyimides were formed by TB polymerization of the imide diamines with dimethyoxymethane (DMM) in trifluoroacetic acid. The 6FDA-derived PI-TB-1 (Fig. 1) and BTDA-based PI-TB-2 showed microporous characteristics with BET surface area of 544 and 270 m² g⁻¹, respectively [30]. Three additional TB diamine-based polyimides (PI-TB-3 to PI-TB-5) were reported in 2016 by Zhuang et al. using imide-diamine precursors made by (i) first reacting a monomethyl-substituted phenylene diamine, 2,6-diaminotoluene (DAT), with 6FDA, OPDA and BTDA as dianhydrides, and (ii) subsequent polymerization by applying Tröger’s base formation reaction with DMM [31]. In this series only 6FDA-based PI-TB-3 (Fig. 1) exhibited microporous texture with a BET surface area of 250 m² g⁻¹. Compared to PI-TB-1, the reduced number of methyl groups on the TB unit in PI-TB-3 led to more efficient chain packing and flexibility as indicated by lower BET surface area and higher elongation at break value [31], which resulted in lower gas permeabilities and increased gas-pair selectivities. It is important to note that PI-TB-3 is structurally equivalent to the TBDA2-6FDA-PI reported by Wang et al. [28].
Other intrinsically microporous PIM-PIs include PIM-PI-TB-1 and PIM-PI-TB-2 (Fig. 1) which were prepared from sterically hindered tetramethyl- or dimethyl/dibromine-substituted Tröger's base-derived diamines and 6FDA [32]. Compared to dimethyl-substituted TBDA2-6FDA-PI (or PIM-PI-TB-1 and 6FDA-TBDA), tetramethyl-substituted PIM-PI-TB-2 showed higher surface area and gas permeability but lower gas-pair selectivity due to more restricted rotation around the imide linkages and more twisted structure [32]. Similarly, Lee et al. introduced four new TB diamine-based PIM-PIs using a different tetramethyl-substituted TB diamine (4MTBDA) and a series of dianhydrides including 6FDA (Fig. 1), PMDA, SBIDA, and SBFDA [33]. All tetramethyl-substituted TB-based polyimides demonstrated intrinsic microporosity as indicated by high surface area and high gas permeability with moderate selectivity, with 4MTBDA-PMDA showcasing the best overall gas separation performance [33].

![Fig. 1. Structures of microporous polyimides derived from 6FDA and methyl-substituted Tröger’s base-diamines [28-33].](image)

Nearly a century after its discovery, the structure of Hünlich base (HB), 3,9-diamino-2,8-dimethyl-6H,12H-5,11-methanodibenzo[1,5]diazocine, was recently elucidated and HB was
recognized as a valuable diamine analogue of TB with the advantage of its single-step preparation from reaction of 2,4-diaminotoluene and formaldehyde [34]. The unique V-shaped tetracyclic structure and facile preparation of the HB building block resulted in great interests in employing Hünlich base derivatives in molecular devices such as molecular tweezers and photo-responsive molecular switches [34-37]. Although polymers derived from TB-based diamines have been extensively studied, HB has not been explored as a PIM-PI building block for potential gas separation applications. In this study, we synthesized two novel intrinsically microporous polyimides (6FDA-HB and TDAi3-HB) for the first time using 2,4-diaminotoluene-derived HB and 4,4'-(hexafluoroisopropylidene)dipthalic anhydride (6FDA) and 9,10-diisopropyl-triptycene tetracarboxylic dianhydride (TDAi3), respectively. Their general physical and detailed gas transport properties were studied.

2. Experimental

2.1. Materials

2,4-Diaminotoluene, formaldehyde, trifluoroacetic acid, and isoquinoline were obtained from Aldrich and used as received. 4,4'-((Hexafluoroisopropylidene)dipthalic anhydride (6FDA) was purchased from Aldrich and purified by sublimation at 230 °C under vacuum prior to use. 3,9-Diamo-2,8-dimethyl-6H,12H-5,11-methanodibenzo[1,5]diazocine (Hünlich base) and 9,10-diisopropyl triptycene dianhydride (TDAi3) were prepared according to previously reported procedures [34,38]. m-Cresol was purchased from Aldrich and dried over 4 Å molecular sieves. All other solvents were received from various commercial sources and used as received.

2.2. Synthesis of Hünlich base diamine monomer

Formaldehyde (37%, 6.1 ml) was added dropwise to a solution of 2,4-diaminotoluene (20.27 g) in 550 ml 5% sulfuric acid. After stirring for 2 days, the reaction mixture was basified by the addition of ammonia solution and the resulting precipitate was collected by vacuum filtration and washed with distilled water. Further purification was achieved by recrystallization from THF/petroleum ether using activated charcoal to give white powder. Melting point = 225-227 °C (dec.), literature (225-230 °C) [34]. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 1.90 (s, 6H), 3.78 (d, 2H),
3.82 (d, 2H), 4.03 (s, 2H), 4.36 (d, 2H), 4.57 (s, 4H), 6.23 (s, 2H), 6.41 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 16.8, 57.9, 66.8, 109.2, 115.4, 117.6, 127.5, 145.3, 146.7. FT-IR (powder, ν, cm$^{-1}$): 3237, 3331, 3365, 3406, 3452 (NH$_2$ str.), 3025 (C-H str. aromatic), 2843, 2923 (C-H str. aliphatic), 1571, 1619, 1494 (C=C str.).

2.3. *Synthesis of HB-based polyimides: typical procedure*

The polyimides were prepared by a standard one-pot, high-temperature polycondensation method. Equimolar amounts of the diamine monomer (Hünlich base) and the desired dianhydride monomer were stirred in a dry Schlenk tube containing m-cresol. Isoquinoline was added as catalyst. After stirring for 30 minutes under continuous nitrogen purging, the temperature was gradually raised to 200 °C and kept at this temperature for ~ 2-3 h. The viscous solution was then added into stirred methanol and a fibrous material was obtained and filtered.

2.3.1. *Synthesis of 6FDA-HB polyimide*

Following the above procedure, 6FDA-HB polyimide was prepared from a solution of 6FDA (0.80 mmol) and HB diamine (0.80 mmol) monomer in m-cresol (9% wt/v); three drops of isoquinoline were added to the solution. The polyimide product was obtained after precipitation in methanol as a light yellow powder in 74% yield after reprecipitation from chloroform twice into methanol and drying at 120 °C for 15 h. $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 2.12 (s, 6H), 4.19 (d, 2H), 4.31 (s, 2H), 4.68 (d, 2H), 6.98 (d, 4H), 7.92 (s, 4H), 8.04 (s, 2H). FTIR (ν, cm$^{-1}$): 2922 (C-H str. aliphatic), 3026 (C-H str. aromatic), 1786 (asym C=O, str), 1724 (sym C=O, str). BET surface area = 415 m$^2$ g$^{-1}$, total pore volume = 0.265 cm$^3$ g$^{-1}$ at (p/p$_0$) = 0.98, adsorption. TGA analysis: (Nitrogen), initial weight loss due to thermal degradation commenced at $T_{d,5\%}$ = 452 °C.

2.3.2. *Synthesis of TDAi3-HB polyimide*

Following the above general procedure, TDAi3-HB was prepared under continuous stirring of 9,10-diisopropyl-triptycene tetracarboxylic dianhydride (0.91 mmol) and HB diamine (0.91 mmol) in m-cresol (17% wt/v) and benzoic acid (3.3 mmol). The temperature was slowly raised and isoquinoline was added at 80 °C. At 170 °C, stirring became very slow and the mixture was diluted with additional m-cresol. After reacting the mixture at 200 °C for ~ 2 h and subsequent cooling to room temperature the polymer was precipitated in methanol. The final product was obtained as a
light yellow powder in 89% yield after reprecipitation twice from chloroform into methanol. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 1.69-2.01 (m, 18H), 3.65-4.63 (m, 6H), 6.87-8.39 (m, 12H). FTIR ($\nu$, cm$^{-1}$): 2895-2979 (C-H str. aliphatic and aromatic), 1779, (asym C=O, str), 1717 (sym C=O, str). BET surface area = 501 m$^2$ g$^{-1}$, total pore volume = 0.329 cm$^3$ g$^{-1}$ at (p/p$_0$) = 0.98, adsorption. TGA analysis: (Nitrogen), initial weight loss due to thermal degradation commenced at $T_{d,5\%} = 470$ °C.

2.4. Characterization methods

$^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were performed on a Bruker AVANCE-III spectrometer in CDCl$_3$ or DMSO-$d_6$. Column chromatography was carried out on silica gel 60A using suitable solvents. Fourier transform infrared (FTIR) measurements were recorded on a Varian 670-IR FT-IR spectrometer. Thermogravimetric analysis (TGA, TA Q-5000) measurements were carried out under nitrogen atmosphere. All TGA runs entailed a drying step at 100 °C for 30 min followed by a temperature ramp of 3 °C/min up to 800 °C. The BET surface area of the polymers was determined by N$_2$ sorption at -196 °C using a Micromeritics ASAP-2020 with micropore option. Prior to analysis polymer samples were degassed under high vacuum at 150 °C for at least 24 hours. Molecular weights and polydispersity index (PDI) of the two polymers were measured by gel permeation chromatography (Agilent Technologies 1200 series) using polystyrene as calibration standards. X-ray diffraction (XRD) spectra were collected using a Bruker D8 Advance diffractometer with 2$\theta$ ranging from 5 to 40$^\circ$ at a scanning rate of 0.5$^\circ$ min$^{-1}$. The geometric polymer density was determined by accurately measuring the weight, area and thickness of polyimide film samples. A dynamic mechanical analyzer (DMA, TA Instruments Q800) was used to obtain stress-strain curves by applying a force on the sample by ramping of 3 N min$^{-1}$ up to 18 N.

2.5. Polymer film preparation

Polymer solutions in chloroform (5 wt/vol%) were prepared and filtered through 0.45 $\mu$m PTFE filters onto a flat glass Petri dish. A dense polyimide film was obtained by slow evaporation of each solution at room temperature. Afterwards, the films were dried at 120 °C in a vacuum oven overnight, immersed in methanol for 12 h, and air-dried. Finally, the films were sandwiched between two glass plates and dried at 120 °C under vacuum for 24 h. Prior to gas permeability
measurements, TGA was performed to ensure complete solvent removal. A digital micrometer and scanner were used to determined film thickness and effective areas for gas permeation measurements. The average thicknesses of these polyimide films were \(~70 \pm 5\) µm. For long-term physical aging studies, film samples were removed from the permeation cell after each test cycle and stored under vacuum in a desiccator.

2.6. *Molecular dynamics simulations*

Molecular dynamics simulations were carried out using Materials Studio 8.0 software (the COMPASS force field was assigned to account for charge and force field parameters). The energy-minimized amorphous cells of the HB-based PIM-PIs were constructed employing five chains of five repeat units each; the geometric density of each polymer and the temperature of 298 K were used as simulations constrains. Long-range coulombic interactions were taken into account with the Ewald sum method, and the non-bonded energy was calculated with a cut-off distance of 9.5 Å. A probe radius of 1.65 Å was used to calculate the fractional free volume (FFV) using the following equation: \(\text{FFV} = V_f/(V_f+V_o)\), where \(V_f\) and \(V_o\) are the free and occupied volume of the polymer chains in the amorphous cell, respectively.

2.7. *Pure-gas sorption and permeation measurements*

Gravimetric pure-gas sorption experiments for N\(_2\), O\(_2\), CH\(_4\), and CO\(_2\) were conducted using an Intelligent Gravimetric Analyzer apparatus (IGA, Hiden Isochema, Warrington, UK). Each polymer film sample was fully degassed for at least 24 h before any sorption experiment. Then, each single pure gas (purity > 99.999%) was introduced into the sample chamber at a rate of 0.1 bar min\(^{-1}\) to reach the desired equilibrium pressure at constant temperature of 35 °C. Pure-gas sorption tests were conducted at 2 bar in the sequence of N\(_2\), O\(_2\), CH\(_4\), and CO\(_2\). For CH\(_4\) and CO\(_2\), gas sorption were recorded as a function of pressure ranging from ~0.5 bar to 15 bar. Pure gas was added cumulatively after equilibration at each pressure point before reaching the next desired pressure. After reaching the highest pressure of the sorption system (~ 15 bar), the sample chamber was again fully degassed before introducing the next pure gas.

The pure-gas permeability of the polymers for He, H\(_2\), N\(_2\), O\(_2\), CH\(_4\), and CO\(_2\) was measured at 35 °C and 2 bar using the constant-volume/variable-pressure method by:
\[ P = D \times S = 10^{10} \times \frac{V_d \times l}{p_{feed} \times T \times R \times A} \times \frac{dp}{dt} \]

where \( P \) is the gas permeability (Barrer) \( = 1 \) Barrer \( = 10^{-10} \) cm\(^3\)(STP) cm cm\(^{-2}\) s\(^{-1}\) cmHg\(^{-1}\), \( p_{feed} \) is the upstream pressure (cmHg), \( dp/dt \) is the steady-state permeate pressure increase (cmHg s\(^{-1}\)), \( V_d \) is the calibrated downstream permeate volume (cm\(^3\)), \( l \) is the film thickness (cm), \( A \) is the effective film area (cm\(^2\)), \( T \) is the operating temperature (K), and \( R \) is the gas constant \( (0.278 \) cm\(^3\) cmHg cm\(^{-3}\)(STP) K\(^{-1}\)). The gas-pair selectivity, \( \alpha_{A,B} \), was calculated based on the ratio of the pure-gas permeability of gas A and B. The solubility coefficient \( S \) (cm\(^3\)(STP) cm\(^{-3}\) cmHg\(^{-1}\)) was obtained from pure-gas gravimetric sorption, and the apparent diffusion coefficient \( D \) (cm\(^2\) s\(^{-1}\)) was determined by the relationship \( D = P/S \). The pressure dependence of pure-gas CO\(_2\) and CH\(_4\) permeability was evaluated up to 15 bar.

3. Results and discussion

3.1. Synthesis and characterization of Hünlich’s base diamine monomer and polyimides

Following the procedure reported by Rigol et al. [34] Hünlich’s base diamine monomer was prepared as white powder by the one-step acid-mediated condensation reaction of 2,4-diaminotoluene with formaldehyde (Scheme 1). Because of steric hindrance of the methyl group in 2,4-diaminotoluene only the amino group para to the methyl group reacted with formaldehyde to form the Hünlich’s base product. This single-step procedure of 2,4-diaminotoluene, which is a readily available commercial compound, together with the use of a cheap acid and the mild reaction conditions are advantages over previously reported procedures for the synthesis of analogous TB diamine monomers. After purification, the molecular structure of the Hünlich’s base diamine monomer was identified by \(^1\)H and \(^{13}\)C NMR, FTIR and melting point measurements.
Scheme 1. Synthesis of Hünlich’s base monomer and its derived polyimides (6FDA-HB and TDAi3-HB).

3.1.1. Synthesis and characterization of HB-based polyimides

Two new intrinsically microporous HB diamine-based polyimides (6FDA-HB and TDAi3-HB) were prepared via one-step high-temperature polycondensation reaction of equimolar amounts of Hünlich’s base diamine monomer and two dianhydride monomers 6FDA and TDAi3 in m-cresol and isoquinoline as catalyst (Scheme 1). The two prepared polyimides were characterized by FT-IR and ^1H NMR spectroscopy. FT-IR spectra (Fig. 2a and 3a) showed two characteristic bands at 1786 and 1724 cm⁻¹ for 6FDA-HB, and 1779 and 1717 cm⁻¹ for TDAi3-HB, confirming the presence of asymmetric and symmetric stretches of imide carbonyl groups, respectively. Aliphatic and aromatic protons stretching frequencies appeared at 2922 and 3026 cm⁻¹, and 2895 and 2979 cm⁻¹ for 6FDA-HB and TDAi3-HB, respectively. ^1H NMR spectra of the two polymers showed excellent agreement with their proposed structures (Fig. 2b and 3b). The Tröger’s base nitrogen bridge moiety in the polyimide backbones was confirmed by the presence of three signals in the range of 3.65 - 4.68 ppm. Furthermore, complete imidization of the polyamic
acid intermediates was confirmed by the absence of any signals above 10 ppm. The two polyimides were further characterized by TGA and BET surface area measurements.

Fig. 2. (a) FTIR spectrum and (b) $^1$H NMR spectrum of 6FDA-HB polyimide using CDCl$_3$ as solvent.

Fig. 3. (a) FTIR spectrum and (b) $^1$H NMR spectrum of TDAi3-HB polyimide using CDCl$_3$ as solvent.
The two polyimides exhibited good solubility in various low- and high-boiling point solvents when tested at room temperature (Table 1). Robust self-standing isotropic membranes suitable for gas permeation measurements were obtained by casting from their chloroform solutions.

Table 1
Solubility of 6FDA-HB and TDAi3-HB polyimides in various organic solvents.

<table>
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<th>Polymer</th>
<th>Acetone</th>
<th>CHCl₃</th>
<th>DCM</th>
<th>THF</th>
<th>DMAc</th>
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<tr>
<td>6FDA-HB</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>TDAi3-HB</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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+: Completely dissolved; -: insoluble. N,N-Dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), chloroform (CHCl₃), dichloromethane (DCM), and tetrahydrofuran (THF).

The molecular weights of the two polymers were determined by GPC from chloroform solutions as shown in Table 2. TDAi3-HB exhibited higher molecular weight (Mn = 42,430 g mol⁻¹) but also higher polydispersity index (PDI = 4.2) compared to 6FDA-HB (Mn = 15,670 g mol⁻¹ and PDI = 2.7).

Table 2
Molecular weights and polydispersity index (PDI) of 6FDA-HB and TDAi3-HB polyimides.

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<th>Mw (g mol⁻¹)</th>
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<td>6FDA-HB</td>
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<td>2.7</td>
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<tr>
<td>TDAi3-HB</td>
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<td>4.2</td>
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Both 6FDA-HB and TDAi3-HB demonstrated excellent thermal stabilities with onset decomposition temperature of greater than 400 °C and T\textsubscript{d,5\%} (5% weight loss) of 452 and 470 °C, respectively (Fig. 4 and Table 3).

**Table 3**

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<tr>
<th>Polymer</th>
<th>T\textsubscript{d,5%} (°C)\textsuperscript{a}</th>
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</tbody>
</table>

\textsuperscript{a} Degradation temperature at 5% weight loss; \textsuperscript{b} BET surface area determined from N\textsubscript{2} adsorption at -196 °C; \textsuperscript{c} measured geometric density using film thickness, area, and weight; \textsuperscript{d} estimated using molecular dynamics simulation.

TDAi3-HB showed higher charcoal remains (65%) compared to 6FDA-HB (57%) at 800 °C as expected due to the higher carbon skeleton content present in the triptycene building block. In addition, both 6FDA-HB and TDAi3-HB exhibited good mechanical properties with tensile strength of 40.5 and 65.5 MPa, respectively. TDAi3-HB displayed lower elongation at break than 6FDA-HB (3.1 vs. 10.5%) and higher Young’s modulus (2.12 vs. 0.72 GPa) in accordance with the added rigidity of the triptycene moiety in TDAi3-HB.
3.1.2. **Intrinsic microporosity of the HB-based polyimides**

Intrinsic microporosity of the two novel HB-based polyimides was demonstrated using N\(_2\) sorption experiments conducted at -196 °C up to 1 bar, as shown in **Fig. 5**. Note the significant N\(_2\) gas uptake observed in the low relative pressure region (p/p\(_0\) < 0.05) for both polymers, indicating a large fraction of intrinsic microporosity resulting from inefficient polymer chain packing. 6FDA-HB had a moderately high BET surface area of 415 m\(^2\) g\(^{-1}\) (**Table 3**), which is comparable to other previously reported dimethyl-substituted intrinsically microporous 6FDA-TB polyimides, such as TBDA2-6FDA-PI (325 m\(^2\) g\(^{-1}\)) [28]. TDAi3-HB showed higher BET surface area of 501 m\(^2\) g\(^{-1}\) due to its bulky and rigid triptycene dianhydride building block.

**Fig. 5.** N\(_2\) sorption isotherms of 6FDA-HB and TDAi3-HB measured at -196 °C up to 1 bar.

The geometrically determined density of these two polyimides showed a higher value for 6FDA-HB compared with TDAi3-HB (1.22 vs. 1.07 g cm\(^{-3}\)). In addition, the fractional free volume (FFV) calculated from molecular dynamics simulations using the experimental densities (**Fig. 6**) was lower for 6FDA-HB than TDAi3-HB (0.26 vs. 0.29), which was in good qualitative agreement with the trend of the BET values determined by N\(_2\) sorption at -196 °C.
Fig. 6. Amorphous cell representations of 6FDA-HB and TDAi3-HB using molecular dynamics simulation and the corresponding calculated FFV values. Grey/blue isosurfaces represent the accessible free volume.

As shown in Fig. 7, the broad feature of the x-ray diffraction (XRD) spectra for both 6FDA-HB and TDAi3-HB revealed the typical amorphous nature of these polymers. The XRD spectrum of 6FDA-HB was deconvoluted to one major peak with an average main-chain $d$-spacing of 5.8 Å. In contrast, the XRD spectrum of TDAi3-HB displays a bimodal pattern which was deconvoluted to two main amorphous peaks with average chain $d$-spacings of 5.7 and 8.5 Å, respectively.

Fig. 7. X-ray diffraction spectra of 6FDA-HB and TDAi3-HB.
The tighter chain spacing of 6FDA-HB compared to TDAi3-HB agreed well with the lower BET surface area, lower density and lower FFV calculated from molecular dynamics simulations, as discussed above.

3.1.3. Pure-gas sorption and permeation properties of HB-based polyimides

Pure-gas CO₂ and CH₄ sorption isotherms at 35 °C for both polymers are shown in Fig. 8a and 8b, respectively. Consistent with higher BET surface area and fractional free volume, pure-gas sorption of CO₂ and CH₄ in TDAi3-HB was greater than in 6FDA-HB. However, the difference in gas sorption between the two polymers was more pronounced for CH₄ than CO₂. For example, CO₂ sorption by TDAi3-HB at 2 bar increased by ~30% compared to 6FDA-HB, whereas CH₄ sorption increased by ~70%. As a result, the CO₂/CH₄ pure-gas solubility selectivity of 6FDA-HB (3.95) was higher than TDAi3-HB (2.99).

![Fig. 8. Pure-gas sorption isotherms of 6FDA-HB and TDAi3-HB measured at 35 °C: (a) CO₂ and (b) CH₄.](image)

Pure-gas permeation experiments for both fresh and aged polymer films were carried out under standard conditions at 35 °C and 2 bar pressure for six gases in the order of He, H₂, N₂, O₂, CH₄, and CO₂ using the procedure described in Section 2.7. The gas permeability and selected gas-pair selectivity data are presented in Table 4. The gas permeability of 6FDA-HB followed the trend: CH₄ < N₂ < O₂ < CO₂ < H₂, a common behavior of PIMs with moderate intrinsic microporosity. 6FDA-HB displayed gas permeability and selectivity values comparable to previously reported 6FDA-based dimethyl-substituted TB-derived polyimides with equivalent structure, i.e. TBDA2-
6FDA-PI, PI-TB-3, and 6FDA-TBDA (Fig. 1), as shown in Table 4 [28,31,39]. The 6FDA-HB polyimide had a CO$_2$ permeability of 286 Barrer with CO$_2$/CH$_4$ selectivity of 26. Compared to PI-TB-3, CO$_2$ permeability of 6FDA-HB was 31% higher coupled with 20% lower CO$_2$/CH$_4$ selectivity. The difference in gas permeation properties among these structurally similar polymers was likely a result of differences in the positions of the methyl groups in the Tröger’s base unit, polymer film preparation, drying procedure, and testing conditions.

Table 4

Pure-gas permeation properties of fresh and aged 6FDA-HB and TDA/3-HB polyimides (35 °C at 2 bar). Data of previously reported 6FDA-based methyl-substituted Tröger’s base polyimides and a commercial membrane material (cellulose triacetate) are included for comparison.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Pure-gas Permeability (Barrer)</th>
<th>Ideal Selectivity (α)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
<td>H$_2$</td>
</tr>
<tr>
<td>6FDA-HB$^a$</td>
<td>271</td>
<td>391</td>
</tr>
<tr>
<td>(90 d aging)</td>
<td>(256)</td>
<td>(359)</td>
</tr>
<tr>
<td>(200 d aging)</td>
<td>(246)</td>
<td>(343)</td>
</tr>
<tr>
<td>TDA/3-HB$^b$</td>
<td>449</td>
<td>982</td>
</tr>
<tr>
<td>(60 d aging)</td>
<td>(430)</td>
<td>(945)</td>
</tr>
<tr>
<td>(330 d aging)</td>
<td>(403)</td>
<td>(866)</td>
</tr>
<tr>
<td>TBDA2-6FDA-PI$^c$</td>
<td>223</td>
<td>390</td>
</tr>
<tr>
<td>(60 d aging)</td>
<td>-</td>
<td>262</td>
</tr>
<tr>
<td>PI-TB-3$^d$</td>
<td>221</td>
<td>299</td>
</tr>
<tr>
<td>6FDA-TBDA$^e$</td>
<td>-</td>
<td>241</td>
</tr>
<tr>
<td>(524 d aging)</td>
<td>-</td>
<td>(964)</td>
</tr>
<tr>
<td>CTA (2.84 D.S.$^f$)</td>
<td>19.6</td>
<td>15.5</td>
</tr>
</tbody>
</table>

$^a$ Film thickness 68 µm, first dried at room temperature and then at 120 °C under vacuum overnight, immersed in methanol for 12 h and air-dried; finally dried at 120 °C under vacuum for 24 h.

$^b$ Film thickness 73 µm, first dried at room temperature and then at 120 °C under vacuum overnight, immersed in methanol for 12 h and air-dried; finally dried at 120 °C under vacuum for 24 h.

$^c$ Film thickness 70-80 µm, dried in vacuum oven at 120 °C for 24 h, then methanol treated, dried again under vacuum at 120 °C for 24 h; tested at 35 °C, 1 bar; Wang et al. 2014 [28].
Films were treated in methanol, dried at 120 °C for 2 h; tested at 35 °C and 1 bar; Zhuang et al. 2016 [31].

Film thickness 40 µm, dried in vacuum oven at 120 °C for 12 hours; tested at T =35 °C, 2 bar; Abdulhamid et al. 2017 [39].

Film thickness 83 µm, methanol treated and air dried; tested at 25 °C, 1 bar; Lee et al. 2016 [33].

CTA = cellulose triacetate; Puleo et al. [40].

It is well known that intrinsically microporous polymers typically show significant loss of gas permeability by physical aging toward their equilibrium chain conformation [41-43]. Unlike many other PIM materials, the permeability of six gases tested for 6FDA-HB after aging over 90 and 200 days did not show significant changes – CO₂ permeability dropped only approximately 7 and 11% with a marginal increase of 3% in CO₂/CH₄ selectivity after 90 and 200 days of physical aging, respectively. A similar aging trend was previously observed by our group for the 6FDA-TBDA analogue polyimide (Table 4) that showed only about 10% loss in permeability with essentially no changes in gas-pair selectivity over a period of 60 days [39]. The relatively moderate effect of physical aging on gas permeation properties of 6FDA-derived dimethyl-substituted TBs or HB-based polyimide compared to the higher free volume and more aging susceptible tetramethyl-substituted analogues (e.g., 4MTBDA-6FDA, Table 4) most likely resulted from (i) smaller absolute free volume (as indicated by BET surface area) and average pore size and (ii) narrower pore size distribution.

Compared to 6FDA-HB, TDAi3-HB displayed much higher permeability for all six gases but also moderately reduced gas-pair selectivity following the well-known permeability/selectivity trade-off relationship [44,45]. For instance, fresh TDAi3-HB showed 203% increase in pure-gas O₂ permeability from 62 to 188 Barrer with 7% decrease in O₂/N₂ selectivity from 4.4 to 4.1. Similarly, CO₂ permeability was boosted by 249% from 286 to 998 Barrer coupled with a modest 23% decrease in CO₂/CH₄ selectivity from 26 to 20. After 60 and 330 days of physical aging, CO₂ permeability of TDAi3-HB dropped only by 9 and 21%, respectively, with negligible effect on CO₂/CH₄ and O₂/N₂ selectivity. Thus, physical aging effects were less pronounced as compared with other high-free-volume triptycene-containing polyimides reported in the literature. For example, 6FDA-TMDAT and TPDA-TMDAT experienced 33 and 54% loss in CO₂ permeability after 200 days of physical aging, respectively [43]. However, it should be noted that variations in aging behavior and their effects on gas permeation properties are not only dependent on the material-specific polymer structure but also film thickness and sample history (casting solvent, drying conditions, storage procedure) [41,42,46,47].
Table 5
Diffusion coefficients of N\textsubscript{2}, O\textsubscript{2}, CH\textsubscript{4}, and CO\textsubscript{2} for 6FDA-HB and TDAi3-HB polyimides and their corresponding O\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} diffusion and solubility selectivity values (35 °C and 2 bar).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>D (×10\textsuperscript{8} cm\textsuperscript{2} s\textsuperscript{-1})</th>
<th>(\alpha) (O\textsubscript{2}/N\textsubscript{2})</th>
<th>(\alpha) (CO\textsubscript{2}/CH\textsubscript{4})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N\textsubscript{2}</td>
<td>O\textsubscript{2}</td>
<td>CH\textsubscript{4}</td>
</tr>
<tr>
<td>6FDA-HB</td>
<td>6.72</td>
<td>26.55</td>
<td>1.9</td>
</tr>
<tr>
<td>TDAi3-HB</td>
<td>14.50</td>
<td>53.53</td>
<td>5.1</td>
</tr>
</tbody>
</table>

\(^a\) Diffusion selectivity. \(^b\) Solubility selectivity directly determined by gravimetric sorption experiments.

The diffusion coefficients of N\textsubscript{2}, O\textsubscript{2}, CH\textsubscript{4}, and CO\textsubscript{2}, and O\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} diffusion and solubility selectivity values for fresh 6FDA-HB and TDAi3-HB polymers were calculated based on the fresh sample permeabilities from Table 4 and the solubility values measured in pure-gas sorption experiments, and are listed in Table 5. The higher diffusion coefficients of TDAi3-HB for all four gases clearly resulted in higher permeability values compared to 6FDA-HB, in qualitative agreement with the BET surface areas and FFV values of the two polymers.

Besides physical aging, pure-gas pressure dependence of CO\textsubscript{2}/CH\textsubscript{4} separation performance was also investigated for 6FDA-HB and TDAi3-HB. As displayed in Fig. 9a, both CO\textsubscript{2} and CH\textsubscript{4} permeability decreased when the pressure was increased from 2 bar to 15 bar as a result of decreased gas solubility due to increased filling of Langmuir’s sorption sites within the polymer free volume, as previously demonstrated for a Tröger’s base ladder polymer [48]. However, the decrease in CO\textsubscript{2} permeability was more significant compared to that of CH\textsubscript{4} for both polymers; hence, a drop in CO\textsubscript{2}/CH\textsubscript{4} selectivity was observed and decreased with increasing pressure. However, no obvious CO\textsubscript{2}-induced polymer plasticization effects were observed for both polymers as the permeability isotherms did not exhibit an upward trend up to 15 bar (Fig. 9b). At a typical natural gas well-head CO\textsubscript{2} partial pressure of 10 bar, 6FDA-HB and TDAi3-HB showed CO\textsubscript{2} permeability of 198 and 543 Barrer with CO\textsubscript{2}/CH\textsubscript{4} selectivity of 22.5 and 16.6, respectively.
Fig. 9. CO$_2$/CH$_4$ pure-gas pressure-dependence permeation results for 6FDA-HB and TDAi3-HB polyimides: (a) CO$_2$ and CH$_4$ permeability; (b) CO$_2$/CH$_4$ selectivity.

In summary, the overall performance of both 6FDA-HB and TDAi3-HB for O$_2$/N$_2$, H$_2$/CH$_4$ and CO$_2$/CH$_4$ separation was comparable to other di-methyl-substituted Tröger’s base derived 6FDA polyimides but inferior compared to the best ladder PIMs and PIM-PIs recently published [14,26,27]. The performance of 6FDA-HB and TDAi3-HB for H$_2$/CH$_4$ and CO$_2$/CH$_4$ separation is shown in permeability/selectivity trade-off relationships in Fig. 10a and 10b. Clearly, both polyimides displayed significantly higher gas permeability for H$_2$ and CO$_2$ than commercial membrane materials but at the cost of lower gas-pair selectivity. For example, aged 6FDA-HB had about forty-fold higher CO$_2$ permeability (254 vs. 6.6 Barrer) while maintaining moderate CO$_2$/CH$_4$ selectivity (27 vs. 33) compared to commercial cellulose triacetate [40] used in natural gas and biogas applications.
Fig. 10. Permeability/selectivity trade-off relationship for fresh (blue symbols) and aged (red symbols) Hünlich’s base derived polyimides (6FDA-HB and TDA3-HB) for (a) H₂/CH₄ and (b) CO₂/CH₄ separation. Previously reported data for 6FDA-based methyl-substituted Tröger’s base polyimides shown in Table 4 (grey symbols) and commercial gas separation membranes materials (green symbols) are included.

4. Conclusions

We introduced Hünlich’s base (HB) as a Tröger’s base diamine analogue for efficient synthesis of intrinsically microporous polyimides. HB monomer synthesis was carried out by a facile single-step acid-mediated condensation reaction of 2,4-diaminotoluene with formaldehyde using cheap and commercially available starting materials. Two dianhydrides, 6FDA and TDA3, were used for polymerization with HB by a one-pot high-temperature reaction in m-cresol for synthesis of two new polyimides (6FDA-HB and TDA3-HB). Both polymers exhibited high molecular weight, good mechanical properties, excellent thermal stability (Tₘ,5% >400 °C), organic solvent solubility, and intrinsic microporosity as indicated by high BET surface area (~400 to 500 m² g⁻¹). Compared to current commercial gas separation membrane materials, both HB-based polyimides exhibited higher gas permeability with moderate, but lower gas-pair selectivity. Relatively moderate effects of physical aging on gas permeabilities and gas-pair selectivities were observed.
Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement
Yingge Wang: Conceptualization, Methodology, Investigation, Writing - original draft. Bader S. Ghanem: Conceptualization, Investigation, Data curation. Yu Han: Writing: review & editing, funding acquisition. Ingo Pinnau: Conceptualization, Supervision, Funding acquisition, Writing - review & editing.

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