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Citation for published version:

Lee, M, Bezzu, CG, Carta, M, Bernardo, P, Clarizia, G, Jansen, JC & McKeown, NB 2016, 'Enhancing the Gas Permeability of Tröger's Base Derived Polyimides of Intrinsic Microporosity', *Macromolecules*, vol. 49, no. 11, pp. 4147-4154. <https://doi.org/10.1021/acs.macromol.6b00351>

Digital Object Identifier (DOI):

[10.1021/acs.macromol.6b00351](https://doi.org/10.1021/acs.macromol.6b00351)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Macromolecules

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Enhancing the gas permeability of Tröger's base derived polyimides of intrinsic microporosity.

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KEYWORDS. Polyimide, Tröger's base, gas separation, microporous polymers, membrane.

ABSTRACT.

A series of four novel Tröger's base (TB) derived Polyimides of Intrinsic Microporosity (PIM-TB-PI) is reported. The TB diamine monomer (4MTBDA) possesses four methyl groups in order to restrict rotation about the C-N imide bonds in the resulting polymers. The polymers possess apparent BET (Brunauer, Emmett and Teller) surface areas between 584 and 739 m² g⁻¹, complete solubility in chloroform, excellent molecular mass, high inherent viscosity and good film-forming properties. Gas permeability measurements demonstrate enhanced performance over previously reported polyimide-based Tröger's base (TB) polymers confirming the benefit of the additional methyl groups within the TB diamine monomer. Notably, a polyimide derived from 4MTBDA and pyromellitic anhydride

(PMDA) demonstrates gas permeability data above the 2008 upper bounds for important gas pairs such as O₂/N₂, H₂/N₂ and H₂/CH₄.

INTRODUCTION

Polymer-based gas separation membranes are of increasing industrial importance. Presently, membranes fabricated from a range of different polymers, including polyimides, are utilized in applications such as O₂ or N₂ enrichment from air, natural gas purification and hydrogen recovery.¹ A desirable polymer for such applications requires both high permeability and high selectivity. However, for each gas pair to be separated (X and Y) there is a well-established inverse relationship between permeability (P_x) and selectivity ($\alpha = P_x/P_y$), which was defined by Robeson,² and then rationalized by Freeman's theoretical analysis.³ Hence there is a challenge to design polymers with permeability behaviour that surpass the current Robeson's upper bounds for important gas pairs, based on the state of the art performance of polymers in 2008, and therefore have potential for membrane materials. Higher gas permeability can be achieved by increasing the inter-chain separation and hence, the polymer's free volume whereas selectivity can be improved by enhancing polymer rigidity.³ In 2004, a new class of materials termed polymers of intrinsic microporosity (PIMs) was introduced.⁴ PIMs possess high free volume due to their contorted and rigid structures and provide not only excellent gas permeability but also moderate selectivities. Recently developed PIMs, in particular polymers fabricated from highly rigid bridged bicyclic units, such as triptycene, have demonstrated a substantial improvement in gas transport performance.^{5,6,7}

Polyimides (PIs) are an important class of polymers for membrane-based gas separations.⁸ Known for their good thermal and chemical stabilities, and excellent mechanical properties,

PIs often demonstrate high gas selectivity but at the cost of low permeability.⁹ However, this obstacle has been overcome by application of the concept of intrinsic microporosity to their structural design to give PIM-PIs with high gas permeabilities.^{10–11} More recently, a PIM-PI (PIM-EA-PI) derived from a dianhydride based on the bridged bicyclic ethanoanthracene demonstrated enhanced gas separation performance.¹² Notable recent work by Pinnau *et al.* has also shown similar performance using a novel spirobifluorene-based dianhydride (SBFDA).¹³ In addition, exceptional performance was demonstrated from polyimides (e.g. KAUST-PI-1) derived from a 9,10-di-*iso*-propyl-triptycene-based dianhydride, with data that lie well above the 2008 Robeson upper bounds for several important gas pairs.^{7a, 14}

PIM-PI development has focused predominantly on the synthesis of suitable dianhydride monomers, whereas the preparation of novel diamines has received less attention. One attractive component for elaboration is the rigid V-shaped bridged bicyclic unit with the formal name of 2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine but more commonly known as Tröger's base (TB). In recent years TB has been incorporated within PIMs to provide enhanced performance.^{5,6,15} Wang *et al.* incorporated the TB structure into the polyimides (e.g. TBAD2-6FDA; Figure 1) using TB-based diamine monomers.¹⁶ It was found that by using a TB component with a single methyl group *ortho* to the imide linking group produced polyimides (e.g. TBDA2-6FDA^{16b}; Figure 1) with significant microporosity and high gas permeability. In an alternative approach to give similar polyimides (e.g. PI-TB-1; Figure 1), Guiver *et al.*¹⁷ used a polymerization reaction involving the formation of the TB unit as the polymerization reaction.

It was anticipated that additional reduction of conformational freedom about the imide linkages, by the introduction of a second methyl substituent adjacent to the two amino groups on the TB monomer, would further enhance gas separation performance. Here we report the

efficient synthesis of the TB monomer (4MTBDA) with the desired methyl substitution and the gas permeability data for a series of PIM-PIs prepared from this novel monomer.

Figure 1. The structures of polyimides TBDA2-6FDA^{16b}, PI-TB-1¹⁷ and 4MTBDA-6FDA.

EXPERIMENTAL SECTION

General methods and equipment. The synthesis of monomer **SBFDA** is given in the SI. Commercially available reagents were used without further purification. Anhydrous dichloromethane was obtained by distillation over calcium hydride under nitrogen atmosphere. Anhydrous *N,N*-dimethylformamide was bought from Aldrich. All reactions using air/moisture sensitive reagents were performed in oven-dried or flame-dried apparatus, under a nitrogen atmosphere. TLC analysis refers to analytical thin layer chromatography, using aluminium-backed plates coated with Merck Kieselgel 60 GF₂₅₄. Product spots were viewed either by the quenching of UV fluorescence, or by staining with a solution of cerium sulfate in aqueous H₂SO₄. Flash chromatography was performed on silica gel 60A (35-70 micron) chromatography grade (Fisher Scientific). Microwaved irradiation synthesis was performed with a CEM Discover microwave reactor. Melting points were recorded using a Gallenkamp Melting Point Apparatus and are uncorrected. ¹H NMR spectra were recorded in the solvent stated using an Avance Bruker DPX 400 (400 MHz) or DPX 500 (500 MHz)

instruments, with ^{13}C NMR spectra recorded at 100 MHz or 125 MHz respectively. Low-resolution mass spectrometric data were determined using a Fisons VG Platform II quadrupole instrument using electron impact ionization (EI) unless otherwise stated. High-resolution mass spectrometric data were obtained in electron impact ionization (EI) mode unless otherwise reported, on a Waters Q-TOF micromass spectrometer. Low-temperature (77 K) N_2 adsorption/desorption measurements of methanol treated powders were made using a Coulter SA3100. CO_2 sorption measurements (273 K) were made using a Quadrasorb Evo. Samples were degassed for 800 min at 120 °C under high vacuum prior to analysis. The TGA was performed using the device Thermal Analysis SDT Q600 at a heating rate of 10 °C/min from room temperature to 1000 °C. Viscosity measurement were carried out with an Ubbelohde capillary (Nr 532 00/0, Schott Germany) on a SCHOTT Instruments GmbH: AVS 370, maintaining 25 °C, using CHCl_3 as solvent with 0.0013 g cm^{-3} concentration. Gel Permeation Chromatography was carried out using a Viscotek GPC Max1000 system which includes a refractive index detector and two 2 columns (KF-805L Shodex). The analysis used dilute solution of polymer in chloroform (1 mL min^{-1}).

N-(2,6-dimethylphenyl)-4-methylbenzenesulfonamide (**M1**). 2,6-dimethylaniline (12.00 g, 99.0 mmol) and *p*-toluenesulphonyl chloride (20.77 g 108.9 mmol) were dissolved/suspended in pyridine (75 mL) and stirred for 16 h. The reaction mixture was poured whilst stirring into 2 M hydrochloric acid solution (250 mL), filtered and washed thoroughly with water. The resulting solid was triturated in hot *n*-hexane to yield *N*-(2,6-dimethylphenyl)-4-methylbenzenesulfonamide (15.83 g, 58 %) as a white powder; m.p. 131-133 °C (Lit 130 °C)¹⁸; ν_{max} ($\text{CHCl}_3/\text{cm}^{-1}$): 3269, 2925, 1597, 1474, 1379, 1326, 1158, 900, 673; ^1H NMR (500 MHz, CDCl_3) δ 7.64 (d, 2H, $J = 8.1 \text{ Hz}$, TsAr *H*), 7.27 (d, 2H, $J = 8.1 \text{ Hz}$, TsAr *H*), 7.11 (t, 1H, Ar *H*), 7.03 (d, 2H, Ar *H*), 6.55 (br s, 1H, NH), 2.45 (s, 3H, TsCH₃), 2.08 (s, 6H, CH₃);

^{13}C NMR (126 MHz, CDCl_3) δ 143.4, 137.6, 132.4, 129.4, 128.6, 127.6, 127.0, 21.4, 18.6; LRMS (EI, m/z) calculated 275.1 found: 275.1 [M^+].

N-(2,6-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide (**M2**). *N*-(2,6-dimethylphenyl)-4-methylbenzenesulfonamide (3.00 g, 10.9 mmol) was suspended in a 50:50 mixture of acetic acid and water (120 mL) and a catalytic amount of sodium nitrite was added. Concentrated nitric acid (16 mL) was carefully added and the reaction was heated at 140 °C for 3h. The reaction mixture was cooled to room temperature and quenched over ice. The resulting off white solid was filtered and washed repeatedly with water until the washings were neutral. After drying, *N*-(2,6-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide was isolated (2.61 g, 75 %) as a white solid; m.p. 163-166 °C (Lit 165-167 °C)¹⁹; ν_{max} ($\text{CHCl}_3/\text{cm}^{-1}$): 3268, 1512, 1334, 1158, 675; ^1H NMR (500 MHz, CDCl_3) δ 7.88 (s, 2H, Ar *H*), 7.60 (d, 2H, $J = 8.2$ Hz, TsAr *H*), 7.28 (d, 2H, $J = 8.2$ Hz, TsAr *H*), 6.47 (br s, 1H, NH), 2.44 (s, 3H, TsCH₃), 2.15 (s, 6H, CH₃); ^{13}C NMR (126 MHz, CDCl_3) δ 146.3, 144.6, 139.4, 138.8, 137.3, 130.1, 127.2, 123.7, 21.8, 19.3; LRMS (EI, m/z) calculated 320.1 found 320.0 [M^+].

N-(4-amino-2,6-dimethylphenyl)-4-methylbenzenesulfonamide (**M3**). Under a nitrogen atmosphere, *N*-(2,6-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide (7.10 g, 22.2 mmol) was dissolved in dry tetrahydrofuran (150 mL). Raney nickel (~ 40 mg) and hydrazine monohydrate (5.55 g, 110.8 mmol, 5 eq.) was added and the mixture was refluxed for 24 h. The colourless mixture was cooled in ice and filtered under nitrogen. The organic phase was extracted with diethyl ether and the solvent was removed under vacuum at 25 °C to afford the desired product *N*-(4-amino-2,6-dimethylphenyl)-4-methylbenzenesulfonamide as colourless crystals (5.62 g, 87 %); m.p. 201-204 °C; ν_{max} ($\text{CHCl}_3/\text{cm}^{-1}$): 3378, 3269, 2924, 1598, 1323, 1158; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{CO}$) δ 7.64 (br s, 1H, NH), 7.59 (d, 2H, $J = 8.0$ Hz, TsAr *H*), 7.34 (d, 2H, $J = 8.0$ Hz, TsAr *H*), 6.26 (s, 2H, Ar *H*), 4.49 (br s, 2H, NH₂), 2.42 (s, 3H,

TsCH₃), 1.88 (s, 6H, CH₃); ¹³C NMR (126 MHz, (CD₃)₂CO) δ 148.5, 143.9, 140.7, 139.7, 130.4, 128.1, 123.7, 115.1, 21.6, 19.2; HRMS (EI⁺, *m/z*) calculated 290.1089 found 290.1088 [M⁺].

2,8-di-(4-methylbenzenesulfonamido)-1,3,7,9-tetramethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine (**M4**). N-(4-amino-2,6-dimethylphenyl)-4-methylbenzenesulfonamide (5.60 g, 19.3 mmol) was dissolved in trifluoroacetic acid (50 mL) and cooled in an ice bath. Dimethoxymethane (3.8 mL, 42.4 mmol, 2.2 eq.) was added dropwise and the reaction was stirred for 16 h. The mixture was poured slowly into an aqueous ammonia solution (200 mL) and stirred thoroughly. The precipitate was extracted with chloroform and the solvent was removed under vacuum. After re-precipitation from chloroform with *n*-hexane, the desired product of 2,8-di-(4-methylbenzenesulfonamido)-1,3,7,9-tetramethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine was obtained (5.81 g, 98 %) as a white solid; m.p. 184-188 °C; $\nu_{\max}$ (CHCl₃/cm⁻¹): 3267, 2923, 1598, 1471, 1321, 1158, 1092; ¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, 4H *J* = 8.2 Hz, TsAr *H*), 7.21 (d, 4H, *J* = 8.0 Hz, TsAr *H*), 6.76 (s, 2H, Ar *H*), 6.21 (s, 2H, NH), 4.41 (d, 2H, *J* = 16.7 Hz, CH₂), 4.15 (s, 2H, CH₂), 3.99 (d, 2H *J* = 16.7 Hz, CH₂), 2.41 (s, 6H, TsCH₃), 1.88 (s, 6H, CH₃), 1.82 (s, 6H, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 147.4, 143.5, 137.7, 136.3, 136.0, 129.5, 128.2, 127.0, 124.6, 124.5, 65.3, 57.4, 21.5, 18.4, 14.0; HRMS (ES⁻, *m/z*) calculated 616.2178 found 615.2108 [M – H⁺].

2,8-diamino-1,3,7,9-tetramethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine (**4MTBDA**). 2,8-di-(4-methylbenzenesulfonamido)-1,3,7,9-tetramethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine (3.0 g, 9.4 mmol) was dissolved in concentrated sulphuric acid (15 mL) and heated at 50 °C for 3 h. The reaction mixture was poured slowly into ice water and ammonia solution was added dropwise until a value of pH 8 was observed. The precipitate was extracted with dichloromethane and the solvent was removed under reduced

pressure. The resulting solid was purified via re-precipitation from dichloromethane with *n*-hexane to yield 2,8-diamino-1,3,7,9-tetramethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine (4MTBDA, 1.13 g, 75 %) as cream coloured crystals; m.p. >235 °C (dec.); $\nu_{\max}$ (CHCl₃/cm⁻¹): 3430, 3356, 2935, 2880, 2844, 1625, 1476, 1421; ¹H NMR (500 MHz, CDCl₃) δ 6.80 (s, 2H, Ar *H*), 4.51 (d, 2H, *J* = 16.4 Hz, CH₂), 4.22 (s, 2H, CH₂), 4.11 (d, 2H, *J* = 16.5 Hz, CH₂), 3.37 (s, 4H, NH₂), 2.14 (s, 6H, CH₃), 1.89 (s, 6H, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 139.2, 124.3, 124.2, 121.7, 118.2, 66.2, 57.9, 17.8, 11.8; HRMS (EI⁺, *m/z*) calculated 308.2001 found 308.2005 [M⁺].

General Procedure A. Polyimide Synthesis (via ester-acid precursor). Under a nitrogen atmosphere, the bis-anhydride was dissolved in ethanol in a two-necked flask equipped with Dean-Stark apparatus and reflux condenser. Triethylamine was injected and the mixture was refluxed for 1 h. The sidearm was opened to remove the solvent under a stream of nitrogen to give a highly viscous solution. The trap was filled with toluene before a solution of the diamine in NMP:toluene (4:1 mixture) was added and the reaction was heated at 80 °C for 1 h. The reaction mixture was gradually heated to 200 °C and maintained at this temperature until the desired viscosity was achieved. The mixture was cooled to room temperature and diluted with chloroform. The mixture was poured into ethanol to precipitate a solid. The solid was collected by filtration, washed with ethanol until the washings were clear. The resulting powder was dissolved in chloroform and methanol was added dropwise until the solution became turbid. The solution was stirred for a further 30 min to precipitate a gel. The re-precipitation from chloroform was repeated twice. The polymer was dissolved in chloroform and added drop-wise to *n*-hexane with vigorous stirring and the precipitated fine powder was filtered. The powder was refluxed in methanol for 24 h, filtered and then dried in a vacuum oven at 120 °C for 9 h to afford the desired polymer.

4MTBDA-6FDA. General procedure **A** was followed using 2,8-diamino-1,3,7,9-tetramethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine (0.5900 g, 1.91 mmol), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (0.8498 g, 1.91 mmol), ethanol (15 mL), triethylamine (0.97 g, 1.33 mL, 9.56 mmol) and NMP:toluene (5 mL) to afford PIM-6FDA-TB-PI (1) (1.17 g, 85 %) as an off-white powder; $\nu_{\max}$ (cm⁻¹): 2955, 2927, 1785, 1727, 1343, 725; ¹H NMR (601 MHz, CDCl₃) δ 8.26 – 7.73 (br m, 6H, Ar *H*), 7.03 (br s, 2H, Ar *H*), 4.77 – 3.99 (br m, 6H, CH₂), 2.13 (br s, 6H, CH₃), 1.94 (br s, 6H, CH₃); ¹³C NMR (151 MHz, CDCl₃) δ 167.0, 166.7, 150.0, 139.6, 136.4, 135.9, 134.8, 133.3, 132.9, 125.6, 124.7, 65.7, 57.7, 18.8, 13.9; GPC (Chloroform): M_n = 18,800, M_w = 54,000; BET surface area = 584 m²/g; total pore volume = 0.72 cm³/g at (P/P_o = 0.98); TGA analysis: Initial weight loss due to thermal degradation commences at ~ 457 °C.

4MTBDA-PMDA. General procedure **A** was followed using 2,8-diamino-1,3,7,9-tetramethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine (0.7000 g, 2.27 mmol), pyromellitic dianhydride (0.4951 g, 2.27 mmol), ethanol (15 mL), triethylamine (1.15 g, 1.58 mL, 11.35 mmol) and NMP:toluene (5 mL) to afford PIM-PMDA-TB-PI (2) (0.855 g, 77 %) as a light yellow powder; $\nu_{\max}$ (cm⁻¹): 1778, 1721, 1373, 733; ¹H NMR (500 MHz, CDCl₃) δ 8.48 (br s, 2H, Ar *H*), 7.03 (br s, 2H, Ar *H*), 4.57 (br s, 2H, CH₂), 4.22 (br s, 4H, CH₂), 2.10 (br s, 6H, CH₃), 1.91 (br s, 6H, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 165.4, 165.1, 149.6, 137.3, 135.3, 134.2, 125.1, 124.9, 119.6, 57.3, 31.9, 29.7, 29.4, 22.7, 18.2, 14.1, 13.3; GPC (Chloroform): M_n = 26,500, M_w = 43,500; BET surface area = 651 m²/g; total pore volume = 0.57 cm³/g at (P/P_o = 0.98); TGA analysis: Initial weight loss due to thermal degradation commences at ~ 461 °C.

4MTBDA-SBIDA. General procedure **A** was followed using 2,8-diamino-1,3,7,9-tetramethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine (0.5925 g, 1.92 mmol), bisanhydride of 3,3,3',3'-tetramethyl-6,6',7,7'-tetracarboxy-1,1'-spirobisindane (0.8000 g,

1.92 mmol), ethanol (15 mL), triethylamine (0.97 g, 1.34 mL, 9.61 mmol) and NMP:toluene (5 mL) to afford PIM-SBIDA-TB-PI (3) (0.95 g, 72 %) as an off-white powder; $\nu_{\max}$ (cm⁻¹): 2958, 2865, 1776, 1717, 1348, 733; ¹H NMR (601 MHz, CDCl₃) δ 7.79 (br s, 2H, Ar *H*), 7.35 (br s, 2H, Ar *H*), 7.00 (br s, 2H, Ar *H*), 5.01 – 3.63 (br m, 6H, CH₂), 2.75 – 2.21 (br m, 4H, CH₂), 2.24 – 1.68 (br m, 12H, CH₃), 1.73 – 1.00 (br m, 12H, CH₃); ¹³C NMR (151 MHz, CDCl₃) δ 168.1, 167.7, 160.1, 157.1, 149.7, 132.4, 126.0, 125.5, 59.2, 58.4, 57.7, 44.8, 32.0, 30.2, 18.8, 18.6, 13.9, 13.7; GPC (Chloroform): M_n = 31,700, M_w = 70,700; BET surface area = 733 m²/g; total pore volume = 0.71 cm³/g at (P/P_o = 0.98); TGA analysis: Initial weight loss due to thermal degradation commences at ~ 488 °C.

4MTBDA-SBFDA. General procedure **A** was followed using 2,8-diamino-1,3,7,9-tetramethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine (0.7500 g, 2.43 mmol), spirobifluorene-based dianhydride (1.1099 g, 2.43 mmol), ethanol (15 mL), triethylamine (1.23 g, 1.70 mL, 12.16 mmol) and NMP:toluene (5 mL) to afford PIM-SBFDA-TB-PI (5) (1.43 g, 81 %) as a light brown powder; $\nu_{\max}$ (cm⁻¹): 2953, 1776, 1719, 1374, 750; ¹H NMR (500 MHz, CDCl₃) δ 8.40 (br s, 2H, Ar *H*), 8.00 (br s, 2H, Ar *H*), 7.53 (br s, 2H, Ar *H*), 7.36 – 7.16 (br m, 4H, Ar *H*), 7.12 – 6.70 (br m, 4H, Ar *H*), 4.99 – 3.66 (br m, 6H, CH₂), 2.08 (br s, 6H, CH₃), 1.88 (br s, 6H, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 168.2, 167.8, 152.7, 149.7, 135.9, 134.8, 130.7, 125.9, 125.3, 117.1, 57.4, 44.6, 35.2, 19.2, 18.5, 13.6; GPC (Chloroform): M_n = 25800, M_w = 57600 BET surface area = 739 m²/g; total pore volume = 0.54 cm³/g at (P/P_o = 0.98); TGA analysis: Initial weight loss due to thermal degradation commences at ~ 486 °C.

Film preparation and gas permeation measurements. Films were prepared by slow evaporation (in ambient conditions, typically over 96 hours) of a 2.5-3% (w/w) solution of the polymer into chloroform. The reported data refer to membranes after a soaking in methanol. This treatment was carried out to cancel the history of the sample and to remove

traces of the solvent used for preparation. Each membrane sample was put in methanol and left there overnight. The successive day it was removed from the alcohol and put between two porous glass disks, left to dry at room conditions overnight. The permeation tests were carried out the subsequent day. Single gas permeation measurements were carried out in a fixed volume/pressure increase apparatus at 25 °C using the time-lag method and at a feed pressure of 1 bar, as described elsewhere.²⁰ The gas diffusivity and solubility data for each polymer was indirectly obtained assuming the solution-diffusion model for the gas permeation (Table 2). Samples were aged under ambient conditions.

RESULTS AND DISCUSSION

Synthesis. The synthetic route used to prepare monomer 4MTBDA, starting from commercially available 2,6-dimethylaniline, is presented in Scheme 1. Overall the route proved efficient with the key TB-forming reaction to produce the tosyl-protected monomer being achieved in near-quantitative yield. Due to its greater stability, it proved convenient to store the monomer in its protected state and perform the removal of the tosyl groups immediately prior to polymerization.

Scheme 1. Synthesis of Tröger's base diamine (**4MTBDA**); i) *p*-toluenesulphonyl chloride, pyridine; ii) KNO₃, NaNO₂, CH₃COOH/H₂O, 140 °C; iii) NH₂NH₂·H₂O, Raney[®]-Ni, THF; iv) DMM, TFA; v) H₂SO₄, 50 °C

Figure 2. Chemical structures of TB-based polyimides and three aromatic diamines commonly used for PIM-PI synthesis.

A series of TB-based PIM-PIs (Figure 2) were prepared *via* the cycloimidization reaction between 4MTBDA and four dianhydride monomers: 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), pyromellitic dianhydride (PMDA), spirobisindane-based dianhydride (SBIDA)¹¹ and spirobifluorene-based dianhydride (SBFDA).¹³

Physical characterization. All four PIs proved readily soluble in chloroform, which enabled characterization by NMR spectroscopy and gel permeation chromatography (GPC), the latter of which indicated molecular weights (M_w) for the four polyimides in the range of $43\text{--}71 \times 10^3 \text{ g mol}^{-1}$. As a result, robust films for each PI were cast from chloroform, which allowed gas permeability measurements to be carried out.

Nitrogen adsorption isotherms for the TB-based polyimides were obtained at 77 K and each showed significant uptake at low relative pressures ($p/p_0 < 0.05$) indicative of intrinsic microporosity (SI). Apparent BET surface areas calculated from these data were in the range 584-739 m² g⁻¹.

Table 1. Physical characterization of PIM-PI-TBs.

PIM-PI	BET Surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹) at P/P ₀ = 0.98	CO ₂ (cc/g) at 273 K/ 1 bar	$M_w \times 10^{-3}$ (g mol ⁻¹)	PDI	Inherent Viscosity (cm ³ g ⁻¹)	TGA Decomposition Temperature (°C)
4MTBDA-6FDA	584	0.72	49	59	2.25	87	457
4MTBDA-PMDA	650	0.57	61	43	1.79	53	461
4MTBDA-SBIDA	733	0.71	65	71	2.25	86	488
4MTBDA-SBFDA	739	0.54	59	58	2.23	64	486

The polymers also display excellent thermal stability with decomposition temperatures up to around 490 °C measured by thermogravimetric analysis (TGA). A summary of the physical properties of these PIM-PIs is shown in Table 1. Nitrogen adsorption isotherms and Gel Permeation Chromatography (GPC) traces are presented in Figure S2. An enhancement of microporosity is indicated by an apparent BET surface area of 584 m² g⁻¹ for 4MTBDA-6FDA as compared to 544 m² g⁻¹ for PI-TB-1¹⁷ and 325 m² g⁻¹ for TBDA2-6FDA^{16b} (Figure 1), demonstrating the effect due to the two methyl groups adjacent to the C-N bond of the imide linking group restricting rotation.

Figure 3. a) CO₂ Adsorption isotherms for 4MTBDA-based polyimides measured at 273 K. b) Estimated pore size distribution obtained from CO₂ isotherms using the Horváth-Kawazoe (HK) method assuming carbon slit-pore geometry

CO₂ adsorption at 273 K was also performed on the polymers, both to test the gas uptake (Figure 3a) and to perform evaluation of micropore size distribution (PSD). All polyimides demonstrate significant uptake of CO₂ (2-3 mmol g⁻¹), in the order 4MTBDA-SBIDA ~ 4MTBDA-PMDA > 4MTBDA-SBFDA > 4MTBDA-6FDA, showing the presence of ultramicropores (<0.7 nm). Horváth-Kawazoe analysis (Figure 3b) indicates that 4MTBDA-PMDA has a particularly narrow and well-defined micropore structure, which is desirable for gas separation (see below).

Gas permeability. Films suitable for gas permeation measurements were successfully prepared for all polyimides. It is of interest to assess the relative gas permeability performance of 4MTBPA-6FDA versus that of the isomeric TB monomer-based PIs PI-TB-1¹⁷ and similar TBDA2-6FDA^{16b} (Figure 1). In addition, very few diamines have been used as monomers for the synthesis of PIM-PIs or high free volume PIs with the commercially available 3,3'-dimethylnaphthidine (DMN), 2,3,5,6-tetramethyl-1,4-phenyldiamine (4MPDA) and 2,3,6-trimethyl-1,3-diamine being employed most often (Figure 2). Therefore,

it is of value to compare the performance of the four novel PIs derived from diamine 4MTBDA related to previously reported PIs based on the same bisanhydride monomers but made using these three commercial diamines (e.g. DMN-SBFDA; 4MPDA-6FDA; 3MPDA-PMDA; 4MPDA-SBIDA (PIM-PIM-9) and DMN-SBIDA (PIM-PI-10)). Direct comparisons of polymer gas permeabilities are made difficult due to the differences in film history prior to measurement. For example, those films freshly treated with methanol demonstrate higher permeabilities but lower selectivities than films made from the same polymer that have been annealed in vacuum to remove casting solvent. Therefore, to assess the relative potential performance of polymers in the separation of a given gas pair, it is best to compare the distance of their data points relative to the relevant 2008 Robeson upper bound (Figure 4). For example, to evaluate the molecular sieving properties of a polymer (i.e. diffusivity selectivity), its position relative to the upper bound for O_2/N_2 is particularly informative due to the similar solubility of these gases in polymers and the small difference in size and mass. For 4MTBDA-6FDA, its much higher values of gas permeability relative to other 6FDA-containing polymers (i.e. 4MPDA-6FDA, TBAD2-6FDA-PI and PI-TB-1) are likely due to being obtained from a freshly methanol treated film, nevertheless, the position of its data point just below the 1991 upper bound in the O_2/N_2 Robeson plot is consistent with those from the other 6FDA based polymers. The relatively low permeability of 4MTBDA-6FDA relative to the other polyimides in this study is consistent with its lower BET surface area and uptake of CO_2 (Table 1 and Figure 3).

All O_2/N_2 data for the SBIDA-based PIs (i.e. 4MTBDA-SBIDA, 4MPDA-SBIDA (PIM-PIM-9) and DMN-SBIDA (PIM-PI-10)) were obtained from methanol treated films. The data points from each of these polymers lie between the 1991 and 2008 upper bounds but 4MTBDA-SBIDA lies closest to the 2008 upper bound, thus indicating a slightly enhanced performance for 4MTBDA as a component diamine as compared to 4MPDA or DMN.

Similarly, the O₂/N₂ data point for 4MTBDA-SBFDA lies closer to the upper bound relative to that from the recently reported methanol treated film of DMN-SBFDA, which also suggests that 4MTBDA provides enhanced performance over DMN. Similar trends are observed for the H₂ containing gas pairs (i.e. H₂/N₂ and H₂/CH₄, Figure 4) both of which are important gas commercial gas separation application.

Pyromellitic dianhydride (PMDA), despite its low cost, is rarely used as a monomer for the preparation of PIs of interest for polymer membranes. This is presumably due to the insolubility of the PIs arising from the highly linear macromolecular structures obtained when combined with diamines commonly used to make high free volume PIs (e.g. DMN and 4MPDA).²¹ However Tanaka *et al.*²² reported the modest gas permeabilities of 3MPDA-PMDA from a thermally annealed film (Figure 4 and Table 2, entry **1**). In contrast, the data from a methanol treated film of 4MTBDA-PMDA showed high permeability, particularly for the smallest hydrogen molecules and is consistent with the narrow pore size distribution centered at 0.5 nm obtained from CO₂ adsorption data (Figure 3b). The high permeability and good selectivity of 4MTBDA-PMDA places its data points over the 2008 upper bound for O₂/N₂, H₂/N₂ and H₂/CH₄, joining a select few PIs to achieve this feat (Figure 4 and Table 2, entry **9** and **11**).^{7a, 14, 12} This result illustrates the value of 4MTBDA as a component diamine for PIs with potential for gas separation but also confirms the recent suggestion²³ that PMDA is also a useful precursor if its diamine co-monomer possesses a suitably non-linear structure to induce solubility. PMDA provides rigidity, which is the key factor for enhancing selectivity in gas separations.³ The combination of the rigid bridged bicyclic monomer 4MTBDA and PMDA gives a PI of excellent potential as a membrane material.

The gas permeabilities of all polymer films were measured after ageing for a period of at least 330 days (Table 2 and Fig. 4). As is typical for glassy polymers, permeabilities were

reduced but selectivities enhanced. so that the data for the aged and freshly methanol treated films lie at a similar distance from the Robson upper bounds.

CONCLUSIONS

A series of four polyimides based on a novel Tröger's base diamine monomer (4MTBDA) has been prepared. All TB-based polyimides exhibited good solubility, excellent thermal stability and intrinsic microporosity, with apparent BET surface areas in the range 584-739 m² g⁻¹. Their good film-forming properties enable the preparation of films suitable for gas permeability measurements, which indicate that separation performance is correlated with the rigidity of the dianhydride comonomer (i.e. PMDA > SBFDA > SBIDA > 6FDA). Thus 4MTBDA, combined with PMDA, demonstrates an excellent combination of high gas permeability and good selectivity for O₂/N₂, H₂/N₂ and H₂/CH₄ pairs with data that lie above the 2008 Robeson upper bounds. The suitability of cheap and readily available PMDA as a monomer for making highly rigid PIM-PIs with enhanced gas selectivity is notable and is likely to be of general use so long as the diamine selected as co-monomer imparts sufficient solubility on the resulting polymer to allow for solution processability.

Figure 4. Robeson plots for different gas pairs showing the data for methanol treated PIM-TB-PIs. Colour code: Red = polymers prepared with 6FDA; blue = SBIDA; light brown = PMDA; purple = SBFDA. Points with no fill but same colour code refer to aged data (> 330 days). Numbers correspond to previously reported polymers whose data are shown in Table 2.

Table 2. Gas permeabilities P_x , diffusivity D_x , solubility coefficient S_x and ideal selectivities $\alpha (P_x/P_y)$ for a methanol treated film of PIM-polyimides.

Sample	Transport parameters	Selectivity									
		N ₂	O ₂	CO ₂	CH ₄	H ₂	H ₂ /N ₂	H ₂ /CH ₄	CO ₂ /CH ₄	O ₂ /N ₂	
4MTBDA-6FDA (83 micron)	P _x [Barrer]	133 (62)	408 (229)	1672 (1008)	116 (60)	1446 (964)	10.37 (15.55)	12.47 (16.07)	14.41 (16.80)	3.07 (3.69)	
	D _x [10 ⁻¹² m ² /s]	35	100	26	8.6	2250					
	D _x /D _{N2} [-]	-	2.85	0.73	0.24	63.9					
	S _x [cm ³ cm ⁻³ bar ⁻¹]	2.83	3.06	48.5	10.1	0.48					
	S _x /S _{N2} [-]	-	1.08	17.13	3.58	0.17					
4MTBDA-PMDA (102 micron)	P _x [Barrer]	290 (99)	1080 (394)	4460 (1689)	390 (114)	3300 (1531)	11.38 (15.46)	8.46 (13.43)	11.44 (14.82)	3.72 (3.98)	
	D _x [10 ⁻¹² m ² /s]	48.8	195	41.4	15.5	3939					
	D _x /D _{N2} [-]	-	3.99	0.85	0.32	81					
	S _x [cm ³ cm ⁻³ bar ⁻¹]	4.46	4.17	84.4	18.8	0.63					
	S _x /S _{N2} [-]	-	0.93	18.9	4.21	0.14					
4MTBDA-SBIDA ^c (120 micron)	P _x [Barrer]	373 (152)	1132 (575)	5140 (2476)	591 (-)	3200 (-)	8.58 (-)	5.41 (-)	8.70 (-)	3.03 (3.78)	
	D _x [10 ⁻¹² m ² /s]	68	210	66.5	27.0	3723					
	D _x /D _{N2} [-]	-	3.10	0.98	0.40	55.1					
	S _x [cm ³ cm ⁻³ bar ⁻¹]	4.14	4.05	58.1	16.5	0.65					
	S _x /S _{N2} [-]	-	0.98	14.1	3.98	0.16					
4MTBDA-SBFDA (124 micron)	P _x [Barrer]	264 (106)	941 (386)	4476 (1621)	371 (125)	2901 (1200)	10.99 (11.32)	7.82 (9.60)	12.06 (12.97)	3.56 (3.64)	
	D _x [10 ⁻¹² m ² /s]	55	187.5	58	17.8	3870					
	D _x /D _{N2} [-]	-	3.39	1.05	0.32	70					
	S _x [cm ³ cm ⁻³ bar ⁻¹]	3.57	3.77	58	15.7	0.56					
	S _x /S _{N2} [-]	-	1.05	16.2	4.4	0.16					
1 ^a	6FDA-TMPD ²²	P _x [Barrer]	36	122	440	28	549	15.25	19.61	15.71	3.39
2	SBFDA-DMN ¹³	P _x [Barrer]	369	1193	6674	581	3342	9.06	5.75	11.49	3.23
3	PIM-PI-9 ¹¹	P _x [Barrer]	420	1150	5700	610	2990	7.12	4.90	9.34	2.74
4	PIM-PI-10 ¹¹	P _x [Barrer]	340	1010	5910	550	2560	7.53	4.65	10.75	2.97
5	PI 1 ²⁴	P _x [Barrer]	61	213	1.4	72	812	13.31	11.28	0.02	3.49
6	PMDA-3MPDA ²⁵	P _x [Barrer]	8.4	36	n.a	n.a	235	28	n.a	n.a	4.30
7	PI-TB-1 ¹⁷	Px [Barrer]	31	119	457	27	607	19.58	22.48	16.93	3.84
8	TBAD2-6FDA-PI ^{16b}	P _x [Barrer]	12	47	285	8	390	32.50	48.75	35.63	3.95
9	Kaust-PI 1 ^{7a}	Px [Barrer]	107	627	2389	105	3983	37.22	37.93	22.75	5.86
10	TPIM-1 ^{14a}	P _x [Barrer]	54	368	1549	50	2666	49.37	53.32	30.98	6.81
11	PIM-PI-12 ¹²	P _x [Barrer]	369	1380	7340	457	4230	11.46	9.26	16.06	3.74
12	EA-TB(Me) ⁵	P _x [Barrer]	525	2150	7140	699	7760	14.78	11.10	10.21	4.10

^a The numbers next to entries 1-12 refer to the data points showed in Figure 3, for comparison with the novel 4MTBDA based polyimides. ^b The numbers in brackets refer to the aged data (4MTBDA-6FDA = 524 days; 4MTBDA-PMDA = 333 days; 4MTBDA-SBIDA = 509 days; 4MTBA-SBFDA = 405 days). ^cUnfortunately for 4MTBDA-SBIDA the measurement of the aged data for H₂ and CH₄ was not possible due to film breakage.

Acknowledgements.

We thank the EPSRC Industrial CASE award Scheme and Defense Science and Technology Laboratory (Dstl), UK, for funding (ML) and Dr. Corinne Stone and Martin Smith for useful discussions.

Associated content Supporting Information (SI).

Full experimental details for the synthesis of precursors and polymers. “This material is available free of charge via the Internet at <http://pubs.acs.org>.”

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

References

1. (a) Adewole, J. K.; Ahmad, A. L.; Ismail, S.; Leo, C. P., Current challenges in membrane separation of CO₂ from natural gas: A review. *Int. J. Greenhouse Gas Control* **2013**, *17*, 46-65; (b) Baker, R. W.; Lokhandwala, K., Natural Gas Processing with

Membranes: An Overview. *Ind. Eng. Chem. Res.* **2008**, *47* (7), 2109-2121; (c) Bernardo, P.; Drioli, E.; Golemme, G., Membrane Gas Separation: A Review/State of the Art. *Ind. Eng. Chem. Res.* **2009**, *48* (10), 4638-4663; (d) Murali, R. S.; Sankarshana, T.; Sridhar, S., Air Separation by Polymer-based Membrane Technology. *Sep. Purif. Rev.* **2013**, *42* (2), 130-186; (e) Scholes, C. A.; Stevens, G. W.; Kentish, S. E., Membrane gas separation applications in natural gas processing. *Fuel* **2012**, *96*, 15-28; (f) Yampolskii, Y., Polymeric Gas Separation Membranes. *Macromolecules* **2012**, *45* (8), 3298-3311.

2. (a) Robeson, L. M., Correlation of separation factor versus permeability for polymeric membranes. *J. Membr. Sci.* **1991**, *62* (2), 165-85; (b) Robeson, L. M., The upper bound revisited. *J. Membr. Sci.* **2008**, *320* (1+2), 390-400.

3. Freeman, B. D., Basis of Permeability/Selectivity Tradeoff Relations in Polymeric Gas Separation Membranes. *Macromolecules* **1999**, *32* (2), 375-380.

4. (a) Budd, P. M.; Elabas, E. S.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E.; Wang, D., Solution-processed, organophilic membrane derived from a polymer of intrinsic microporosity. *Adv. Mater.* **2004**, *16* (5), 456-459; (b) Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E., Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials. *Chem. Commun.* **2004**, (2), 230-231.

5. Carta, M.; Malpass-Evans, R.; Croad, M.; Rogan, Y.; Jansen, J. C.; Bernardo, P.; Bazzarelli, F.; McKeown, N. B., An efficient polymer molecular sieve for membrane gas separations. *Science* **2013**, *339* (6117), 303-7.

6. Carta, M.; Croad, M.; Malpass-Evans, R.; Jansen, J. C.; Bernardo, P.; Clarizia, G.; Friess, K.; Lanc, M.; McKeown, N. B., Triptycene Induced Enhancement of Membrane Gas Selectivity for Microporous Troeger's Base Polymers. *Adv. Mater.* **2014**, *26* (21), 3526-3531.

7. (a) Ghanem, B. S.; Swaidan, R.; Litwiller, E.; Pinnau, I., Ultra-Microporous Triptycene-based Polyimide Membranes for High-Performance Gas Separation. *Adv. Mater.* **2014**, *26* (22), 3688-3692; (b) Zhuang, Y.; Seong, J. G.; Do, Y. S.; Lee, W. H.; Lee, M. J.; Guiver, M. D.; Lee, Y. M., High-strength, soluble polyimide membranes incorporating Tröger's Base for gas separation. *J. Membr. Sci.* **2016**, *504*, 55-65; (c) Zhuang, Y.; Seong, J. G.; Do, Y. S.; Lee, W. H.; Lee, M. J.; Cui, Z.; Lozano, A. E.; Guiver, M. D.; Lee, Y. M., Soluble, microporous, Troger's Base copolyimides with tunable membrane performance for gas separation. *Chem. Commun.* **2016**, *52* (19), 3817-3820; (d) Swaidan, R.; Ghanem, B.; Litwiller, E.; Pinnau, I., Physical Aging, Plasticization and Their Effects on Gas Permeation

- in “Rigid” Polymers of Intrinsic Microporosity. *Macromolecules* **2015**, *48* (18), 6553-6561;
- (e) Rose, I.; Carta, M.; Malpass-Evans, R.; Ferrari, M.-C.; Bernardo, P.; Clarizia, G.; Jansen, J. C.; McKeown, N. B., Highly Permeable Benzotriptycene-Based Polymer of Intrinsic Microporosity. *ACS Macro Letters* **2015**, *4* (9), 912-915.
8. Liaw, D.-J.; Wang, K.-L.; Huang, Y.-C.; Lee, K.-R.; Lai, J.-Y.; Ha, C.-S., Advanced polyimide materials: Syntheses, physical properties and applications. *Prog. Polym. Sci.* **2012**, *37* (7), 907-974.
9. Cecopieri-Gomez, M. L.; Palacios-Alquisira, J.; Dominguez, J. M., On the limits of gas separation in CO₂/CH₄, N₂/CH₄ and CO₂/N₂ binary mixtures using polyimide membranes. *J. Membr. Sci.* **2007**, *293* (1+2), 53-65.
10. (a) Ghanem, B. S.; McKeown, N. B.; Budd, P. M.; Al-Harbi, N. M.; Fritsch, D.; Heinrich, K.; Starannikova, L.; Tokarev, A.; Yampolskii, Y., Synthesis, Characterization, and Gas Permeation Properties of a Novel Group of Polymers with Intrinsic Microporosity: PIM-Polyimides. *Macromolecules* **2009**, *42* (20), 7881-7888; (b) Ghanem, B. S.; McKeown, N. B.; Budd, P. M.; Selbie, J. D.; Fritsch, D., High-performance membranes from polyimides with intrinsic microporosity. *Adv. Mater.* **2008**, *20* (14), 2766-2771.
11. Rogan, Y.; Starannikova, L.; Ryzhikh, V.; Yampolskii, Y.; Bernardo, P.; Bazzarelli, F.; Jansen, J. C.; McKeown, N. B., Synthesis and gas permeation properties of novel spirobisindane-based polyimides of intrinsic microporosity. *Polym. Chem.* **2013**, *4* (13), 3813-3820.
12. Rogan, Y.; Malpass-Evans, R.; Carta, M.; Lee, M.; Jansen, J. C.; Bernardo, P.; Clarizia, G.; Tocci, E.; Friess, K.; Lanc, M.; McKeown, N. B., A highly permeable polyimide with enhanced selectivity for membrane gas separations. *J. Mater. Chem. A* **2014**, *2* (14), 4874-4877.
13. Ma, X.; Ghanem, B.; Salines, O.; Litwiller, E.; Pinnau, I., Synthesis and Effect of Physical Aging on Gas Transport Properties of a Microporous Polyimide Derived from a Novel Spirobifluorene-Based Dianhydride. *ACS Macro Lett.* **2015**, *4* (2), 231-235.
14. (a) Ghanem, B. S.; Swaidan, R.; Ma, X.; Litwiller, E.; Pinnau, I., Energy-Efficient Hydrogen Separation by AB-Type Ladder-Polymer Molecular Sieves. *Adv. Mater.* **2014**, *26* (39), 6696-6700; (b) Swaidan, R.; Al-Saeedi, M.; Ghanem, B.; Litwiller, E.; Pinnau, I., Rational Design of Intrinsically Ultramicroporous Polyimides Containing Bridgehead-Substituted Triptycene for Highly Selective and Permeable Gas Separation Membranes. *Macromolecules* **2014**, *47* (15), 5104-5114.

15. Carta, M.; Malpass-Evans, R.; Croad, M.; Rogan, Y.; Lee, M.; Rose, I.; McKeown, N. B., The synthesis of microporous polymers using Troger's base formation. *Polym. Chem.* **2014**, *5* (18), 5267-5272.
16. (a) Wang, Z.; Wang, D.; Jin, J., Microporous Polyimides with Rationally Designed Chain Structure Achieving High Performance for Gas Separation. *Macromolecules* **2014**, *47* (21), 7477-7483; (b) Wang, Z.; Wang, D.; Zhang, F.; Jin, J., Troger's Base-Based Microporous Polyimide Membranes for High-Performance Gas Separation. *ACS Macro Lett.* **2014**, *3* (7), 597-601.
17. Zhuang, Y.; Seong, J. G.; Do, Y. S.; Jo, H. J.; Cui, Z.; Lee, J.; Lee, Y. M.; Guiver, M. D., Intrinsically Microporous Soluble Polyimides Incorporating Troger's Base for Membrane Gas Separation. *Macromolecules* **2014**, *47* (10), 3254-3262.
18. Moorthy, J. N.; Saha, S., Highly diastereo- and enantioselective aldol reactions in common organic solvents using N-arylprolinamides as organocatalysts with enhanced acidity. *Eur. J. Org. Chem.* **2009**, (5), 739-748.
19. Cockroft, S. L.; Perkins, J.; Zonta, C.; Adams, H.; Spey, S. E.; Low, C. M. R.; Vinter, J. G.; Lawson, K. R.; Urch, C. J.; Hunter, C. A., Substituent effects on aromatic stacking interactions. *Org. Biomol. Chem.* **2007**, *5* (7), 1062-1080.
20. Mason, C. R.; Maynard-Atem, L.; Al-Harbi, N. M.; Budd, P. M.; Bernardo, P.; Bazzarelli, F.; Clarizia, G.; Jansen, J. C., Polymer of Intrinsic Microporosity Incorporating Thioamide Functionality: Preparation and Gas Transport Properties. *Macromolecules* **2011**, *44* (16), 6471-6479.
21. Grubb, T. L.; Ulery, V. L.; Smith, T. J.; Tullos, G. L.; Yagci, H.; Mathias, L. J.; Langsam, M., Highly soluble polyimides from sterically hindered diamines. *Polymer* **1999**, *40* (15), 4279-4288.
22. Tanaka, K.; Okano, M.; Toshino, H.; Kita, H.; Okamoto, K., Effect of methyl substituents on permeability and permselectivity of gases in polyimides prepared from methyl-substituted phenylenediamines. *J. Polym. Sci., Part B Polym. Phys.* **1992**, *30* (8), 907-14.
23. Alvarez, C.; Lozano, A. E.; de la Campa, J. G., High-productivity gas separation membranes derived from pyromellitic dianhydride and nonlinear diamines. *J. Membr. Sci.* **2016**, *501*, 191-198.

24. Hofman, D.; Ulbrich, J.; Fritsch, D.; Paul, D., Molecular modeling simulation of gas transport in amorphous polyimide and poly(amide imide) membrane materials. *Polymer* **1996**, *37* (21), 4773-4785.
25. Liu, Y.; Pan, C.; Ding, M.; Xu, J., Gas permeability and permselectivity of polyimides prepared from phenylenediamines with methyl substitution at the ortho position. *Polym. Int.* **1999**, *48* (9), 832-836.

Enhancing gas permeability of polyimides of intrinsic microporosity containing Tröger's base.

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