Facile Synthesis of a Hydroxyl-Functionalized Tröger's Base Diamine: A New Building Block for High-Performance Polyimide Gas Separation Membranes

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Abstract

Two intrinsically microporous polyimides (PIM-PIs) were synthesized by polycondensation reaction of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3,3',3'-tetramethyl-spirobisindane-6,7,6',7'-tetracarboxylic dianhydride (SBI) with a newly designed ortho-hydroxyl-functionalized Tröger's base diamine, 1,7-diamino-6H,12H-5,11-methanodibenzo[1,5]diazocine-2,8-diol (HTB). Both amorphous PIM-PIs were soluble in aprotic solvents and showed excellent thermal stability with onset decomposition temperature of $\sim 380^{\circ}\text{C}$. SBI-HTB displayed higher CO_2 permeability (466 vs. 67 Barrer) than 6FDA-HTB but significantly lower selectivity for CO_2/CH_4 (29 vs 73), H_2/CH_4 (29 vs 181), O_2/N_2 (4.6 vs 6.0) and N_2/CH_4 (1 vs 2.5). 6FDA-HTB displayed the highest gas-pair permselectivity values of all reported OH-functionalized PIM-PIs to date. The high permselectivity of 6FDA-HTB resulted primarily from exceptional diffusion selectivity due to strong size-sieving properties caused by hydrogen bonding between the proton of the hydroxyl group and the nitrogen atoms in the tertiary amine of the Tröger's base ($\text{O-H}\cdots\text{N}$).

INTRODUCTION

Aromatic polyimides are among the most promising membrane materials for large-scale industrial gas separation applications.¹⁻⁴ Early studies demonstrated good performance for CO₂/CH₄ separation of solution-processable polyimides derived from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and pyromellitic dianhydride (PMDA) with various aromatic diamines.⁵⁻⁶ Specifically, 6FDA-based polyimides made from commercially available *hydroxyl-functionalized diamines* demonstrated extraordinarily high CO₂/CH₄ selectivity of up to ~100 with moderate CO₂ permeability of ~5-10 Barrer (1 Barrer = 1 x 10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹).⁷⁻⁹

One strategy to enhance the gas permeability in glassy polymers is to incorporate sterically hindered building blocks in the polymer backbone to disrupt efficient chain packing.¹⁰⁻¹² This concept has been successfully applied to the synthesis of microporous ladder polymers (PIMs) and polyimides of intrinsic microporosity (PIM-PIs).¹³⁻¹⁵ The first PIM-PIs, made by reaction of custom-designed spirobisindane-derived dianhydrides (SBI) and a series of commercially available diamines, were characterized by high Brunauer-Teller-Emmett (BET) surface areas of up to ~ 700 m² g⁻¹ and exhibited high gas permeabilities with moderate gas-pair selectivities with overall performance close to the 2008 permeability/selectivity upper bound.¹⁶⁻¹⁹ PIM-PIs made from ethanoanthracene-, triptycene-, spirobifluorene-, and carbocyclic pseudo Tröger's base-derived *dianhydrides* with conventional diamines also exhibited high permeability and moderate selectivity.²⁰⁻²⁴ To boost selectivity, a series of high-performance PIM-PIs was designed for membrane-based natural gas separation derived from bulky triptycene-based dianhydrides and commercially available hydroxyl-functionalized diamines.²⁵⁻²⁸ For example, PIM-PI synthesized from 9,10-diisopropyl-triptycene-based dianhydride (TPDA) and 4,6-diaminoresorcinol (DAR) displayed excellent performance with CO₂ permeability of 215 Barrer and CO₂/CH₄ selectivity of 46.²⁵ Interestingly, relatively few *OH-functionalized diamines* bearing sterically

restricted contortion sites have been reported. PIM-PIs made from 6FDA and dihydroxyl-based spirobisindane-, spirobifluorene- and triptycene-diamines have shown promising performance for CO₂/CH₄ and H₂S/CH₄ separation.²⁹⁻³³

McKeown and co-workers pioneered the use of Tröger's base (TB) derivatives as versatile new building blocks for the synthesis of PIM ladder polymers and PIM-PIs.³⁴⁻³⁶ Tröger's base is a chiral molecule containing a rigid, V-shaped tertiary amine diazocine bridge.³⁷ Several polyimides made by polycondensation reaction of various dianhydrides with methyl- and bromo-substituted TB diamines demonstrated promising performance for gas separation applications, particularly for CO₂/CH₄ separation.³⁸⁻⁴³ Here, we report PIM-PIs with excellent gas separation properties made from a novel hydroxyl-functionalized Tröger's base diamine (HTB). The synthetic procedures are shown in **Scheme 1**.

Scheme 1. Synthetic Routes of the Ortho-Hydroxyl-Functionalized Tröger's Base-Based PIM-PIs (6FDA-HTB and SBI-HTB).

EXPERIMENTAL SECTION

Materials. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, 99%), trifluoroacetic acid, 4-amino-2-nitrophenol and dimethoxymethane, silica gel, dichloromethane, anhydrous *m*-cresol, tetrahydrofuran, isoquinoline, and anhydrous *N,N'*-dimethylformamide were obtained from Sigma-Aldrich and used as received. 3,3,3',3'-Tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetracarboxylic anhydride (SBI) was synthesized according to a previously reported procedure.¹⁷

Characterization and Methods. ¹H NMR and ¹³C NMR spectra of the monomer and polymers were recorded with a Bruker AVANCE-III spectrometer at a frequency of 400 or 500 MHz in deuterated chloroform or deuterated dimethylsulfone with tetramethylsilane as an internal standard; the chemical shifts were recorded in ppm. Proton 2D NOESY spectrum for 6FDA-HTB was performed using a Bruker AVANCE-III 950 MHz NMR instrument; DMSO-*d*₆ was used as solvent. Molecular weight (*M*_n) and molecular weight distribution (PDI) of the polymers were obtained by gel permeation chromatography (GPC, Malvern HT-350 and Agilent GPC 1200) using dimethylformamide (DMF) as solvent and polystyrene as external standard. High-resolution mass spectroscopy (HRMS) of the monomer was conducted on a Thermo LC/MS system with LTQ Orbitrap Velos detectors. Thermal gravimetric analysis (TGA) was carried out with a TGA Q5000 equipped with a thermal analyzer and quadrupole mass spectrometer (Aëolos QMS 403 C) employing helium as the carrier gas. Differential scanning calorimetric analysis (DSC) and melting point of the polymers and intermediates were recorded on a DSC Q2000. Density was obtained using a Mettler-Toledo balance equipped with a density measurement kit based on Archimedes' principle using *iso*-octane as the reference liquid. The BET surface area of the polymers was measured by N₂ adsorption at -196 °C (Micrometrics ASAP 2020); each sample was degassed at 150 °C for 12 h before testing. CO₂ adsorption was also performed on a Micrometrics ASAP 2020 at 0 °C and up to 1 bar. The pore size distributions of the polymers were derived from CO₂ adsorption using the

NLDFT model. CO₂ and CH₄ solubility was determined gravimetrically at 2 bar and 35 °C using an IGA-003 instrument (Hidden Isochema). Single-crystal diffraction of the intermediate 1,7-dinitro-6H,12H-5,11-methanodibenzo[1,5]diazocine-2,8-diol compound was carried out on a Bruker single-crystal diffractometer using Cu (K α) as the X-ray source. Dynamic mechanical stress-strain curves of the polymers were measured using a dynamic mechanical analyzer (DMA, TA Instruments Q800). The samples were kept at 35 °C for one minute and then ramped at 3 N/min to 18 N.

Synthesis of 1,7-dinitro-6H,12H-5,11-methanodibenzo[1,5]diazocine-2,8-diol. 4-Amino-2-nitrophenol (7.70 g, 50.0 mmol) and dimethoxymethane (9.50 g, 2.5 equiv, 125 mmol) were added to a 250 mL three-neck flask and cooled to -20 °C. To it, CF₃COOH (100 mL) was added dropwise over 1 h. The resulting solution was stirred at room temperature for 48 h and then poured into ice water (300 mL). The system was extracted five times (5 $\times$ 100 mL) with dichloromethane. The organic phase was combined and dried with magnesium sulfate, further concentrated by rota-evaporation and then loaded in a column packed with silica gel (200 ~ 300 mesh). A reddish solid (5.00 g, 58.1% yield) was obtained after column chromatography. mp: 266.2 °C. TLC: dichloromethane/ethyl acetate = 8/1, R_f = 0.25. ¹H NMR (400 MHz, CDCl₃): δ 10.68 (s, 2H), 7.43 (d, 2H, *J* = 9.1 Hz), 7.08 (d, 2H, *J* = 9.1 Hz), 4.98 (d, 2H, *J* = 18.2 Hz), 4.48 (d, 2H, *J* = 18.2 Hz), 4.26 (s, 2H).

Synthesis of 1,7-diamino-6H,12H-5,11-methanodibenzo[1,5]diazocine-2,8-diol. 1,7-Dinitro-6H,12H-5,11-methanodibenzo[1,5]diazocine-2,8-diol (2.00 g, 5.81 mmol) was added to *N,N*-dimethylformamide (80 mL) in a 250 mL three-neck flask. To it, hydrazine monohydrate (2.0 mL, 70 wt%) and palladium on carbon (10%, 100 mg) were added in sequence under N₂ flow. The system was heated at 130 °C for 2 h and then cooled to room temperature. The solution was filtered through a Celite pad into 200 mL ice-cold dichloromethane. White microcrystals were formed, collected by filtration and dried in a

vacuum oven at 135 °C for 24 h. An off-white powder (1.32 g, yield: 80%) was obtained and used directly for polymerization reactions. mp: 344.2 °C; ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 8.66 (s, 2H), 6.47 (d, 2H, $J = 8.35$ Hz), 6.18 (d, 2H, $J = 8.35$ Hz), 4.17 (m, 6H), 3.94 (s, 2H), 3.82 (d, 2H, $J = 7.7$ Hz). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ 141.2, 139.6, 132.6, 114.2, 113.2, 112.6, 66.3, 56.3. HRMS (APPI) m/z : $[\text{M}+\text{H}]^+$: calcd. for $\text{C}_{15}\text{H}_{17}\text{N}_4\text{O}_2$: 285.1346; Found: 285.1346.

Synthesis of 6FDA-HTB. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (444.4 mg, 1.00 mmol) and 1,7-diamino-6H,12H-5,11-methanodibenzo[1,5]diazocine-2,8-diol (284.1 mg, 1.00 mmol) were added to *m*-cresol (3.6 mL) and flushed with N_2 . The system was stirred at room temperature for 15 min and then at 60 °C for 1 h to form a clear solution. A drop of isoquinoline was added and the solution was heated to 180 °C for 3 h. Thereafter, the viscous solution was precipitated in methanol and the solid was collected by filtration. Traces of remaining *m*-cresol in the polymer were removed by Soxhlet extraction using methanol as solvent. The polyimide 6FDA-HTB was obtained as light yellow filaments (690 mg, yield: 96%) after drying in a vacuum oven at 120 °C for 24 h. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 9.61 (s, 2H), 8.16 (s, 2H), 7.96 (s, 2H), 7.84 (s, 2H), 7.02 (s, 2H), 6.78 (s, 2H), 4.24 (s, 2H), 4.03 (s, 4H). FT-IR (polymer film, ν , cm^{-1}): 2200 ~ 3700 (s, br, -OH), 2931 (s, m, C-H), 1788, 1719 (s, str, imide), 1380 -1600 (m, str, ph), 1251 (m, str, C-F). The onset of polymer degradation ($T_{\text{d, onset}}$) commenced at ~380 °C; $S_{\text{BET}} = 340 \text{ m}^2/\text{g}$.

Synthesis of SBI-HTB. The general synthetic procedure of SBI-HTB was the same as for 6FDA-HTB. The polymer was obtained as light yellow powder with a yield of 96%. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 9.53 (s, 2H), 7.95 (s, 2H), 7.31 (s, 2H), 7.00 (s, 2H), 6.72 (s, 2H), 4.20 (s, 2H), 3.92 (s, 4H), 2.34 (m, 4H), 1.51 (d, 12H, $J = 5.3$ Hz). FT-IR (polymer film, ν , cm^{-1}): 2200 ~ 3700 (s, br, -OH), 2931 (s, m, C-H), 1788, 1719 (s, str, imide), 1380 -1600 (m, str, ph). $T_{\text{d, onset}}$ commenced at ~380 °C; $S_{\text{BET}} = 400 \text{ m}^2/\text{g}$.

Film Preparation. The HTB-based PIM-PIs were dissolved in DMF (3-5 wt/v%) and purified using small 1.0 μm PTFE filter cartridges. The solutions were carefully transferred into a flat glass Petri dish covered by a larger Petri dish to control the evaporation rate under N_2 flow. The solvent was evaporated for at least 2 days and dry polymer films (~ 40 to $60\ \mu\text{m}$) were obtained. Finally, each film was dried in a vacuum oven at $250\ ^\circ\text{C}$ for 24 h. Complete solvent removal was confirmed by TGA analysis.

RESULTS AND DISCUSSION

Synthesis, Structure and Physical Properties of the Polyimides. The synthesis of the ortho-hydroxyl-functionalized Tröger's base-based diamine was performed by the following steps: First, 4-amino-2-nitrophenol was reacted with dimethoxymethane in trifluoroacetic acid acting both as solvent and catalyst to give 1,7-dinitro-6H,12H-5,11-methanodibenzo[1,5]diazocine-2,8-diol as reddish crystals. Single-crystal data (**ESI**) confirmed the cleft-like structure with a C_2 symmetric axis of the dinitrol compound, as shown in **Figure 1**. Surprisingly, no isomers were formed - the Tröger's base formation reaction occurred only at the C3-position (ortho to the NO_2 group). Hence, the two NO_2 groups are positioned orthogonal to the Tröger's base bridge, which gives rise to a sterically hindered and twisted structure.

Figure 1. Single-crystal molecular structure of 1,7-dinitro-6H,12H-5,11-methanodibenzo[1,5]diazocine-2,8-diol. The dihedral angle is highlighted as yellow bond.

The second synthetic step was the reduction of the dinitrol intermediate to the diamine, which was conducted by a standard procedure using hydrazine monohydrate and palladium on activated carbon as catalyst in DMF. After filtration through a Celite pad into a large amount of dichloromethane, the diamine compound was obtained as off-white microcrystals. The monomer was then reacted with 6FDA and SBI in *m*-cresol under catalytic amount of isoquinoline. The resulting hydroxyl-functionalized polyimides, 6FDA-HTB and SBI-HTB, were readily soluble in highly polar aprotic solvents such as DMF, NMP, DMAc and *m*-cresol (Table S1) and had high M_n of $\sim 330 \text{ kg mol}^{-1}$ and narrow polydispersity index (PDI) of ~ 1.2 (Table 1).

Table 1. Physical Properties of the OH-Functionalized Tröger's Base Polyimides.

Polymer	$M_n (\text{g mol}^{-1})^a$	PDI	$S_{\text{BET}} (\text{m}^2 \text{g}^{-1})$	$T_{\text{d, onset}} (^{\circ}\text{C})$	$\rho (\text{g cm}^{-3})$
6FDA-HTB ^a	35.3×10^4	1.19	340	380	1.46
SBI-HTB ^a	33.7×10^4	1.23	400	380	1.26

^a The molecular weight of the polymer was determined by GPC using DMF as solvent.

The proton NMR spectra of the monomer and polymers are shown in **Figure 2**. Similar to previously reported ortho-hydroxyl-functionalized PIM-PIs,^{29, 44} 6FDA-HTB and SBI-HTB showed much broader peaks than those displayed in the OH-functionalized diamine monomer (**Figure 2a**). In addition, a large shift of the hydroxyl group towards lower field from 8.66 ppm of the monomer to 9.60 ppm of the polyimides was observed. This effect resulted from the change in the chemical environmental of the ortho-positioned OH groups from the amine to the imide group. Strong interaction between the proton of the OH group and the protons in the Tröger's base due to hydrogen bonding was confirmed by the 2D NOESY NMR spectrum of 6FDA-HTB, indicating that these protons were in the range below 5 Å even when dissolved in polar DMSO (**Figure 2b**).⁴⁵

Figure 2. a) ^1H NMR of the hydroxyl-functionalized Tröger's base-based diamine monomer (HTB) in comparison with 6FDA-HTB and SBI-HTB polyimides in $\text{DMSO-}d_6$ solution; b) Proton 2D NOESY of 6FDA-HTB in $\text{DMSO-}d_6$ solution.

Figure 3. FT-IR spectra of 6FDA-HTB and PIM-6FDA-OH.

The FT-IR spectra of 6FDA-HTB and a previously reported OH-functionalized, spirobisindane-derived PIM-PI (PIM-6FDA-OH) are shown in **Figure 3**. After normalization of the spectra at 1720 cm^{-1} , a much broader and more intensive OH bond was observed in

6FDA-HTB (3700 to 2200 cm^{-1}) than in PIM-6FDA-OH (3700 to 2900 cm^{-1}). This result indicates stronger hydrogen bonding in 6FDA-HTB than in PIM-6FDA-OH according to previous findings.⁴⁶ The effects of hydrogen bonding on the gas transport properties of 6FDA-HTB are discussed in more detail below.

Thermal and Mechanical Properties of the Polymers. 6FDA-HTB and SBI-HTB demonstrated high thermal stability with onset decomposition temperature of ~ 380 °C (**Figure S1a and Table 1**). No glass transition temperature was detected in the OH-functionalized Tröger's base polyimides by DSC scans up to 350 °C (**Figure S1b**). 6FDA-HTB demonstrated excellent mechanical properties with a Young's modulus of 2.44 GPa and elongation at break of 6% (**Table S2; Figure S2**).

Intrinsic Microporosity of the Polyimides. The microporosity of the polyimides was evaluated by N_2 adsorption at -196 °C up to 1 bar. All polyimides demonstrated Type I adsorption isotherms, as shown in **Figure 4a**, with remarkable microporosity as indicated by large gas sorption uptake at very low relative pressure ($p/p_0 < 0.05$). 6FDA-HTB showed high BET surface area of 340 $\text{m}^2 \text{g}^{-1}$, which is the highest value among all 6FDA-based OH-functionalized PIM-PIs, including spirobisindane-based PIM-6FDA-OH (190 $\text{m}^2 \text{g}^{-1}$)²⁹, spirobifluorene-based 6FDA-HSBF (70 $\text{m}^2 \text{g}^{-1}$)³² and triptycene-based 6FDA-DAT1-OH (160 $\text{m}^2 \text{g}^{-1}$).³³ SBI-HTB had a higher surface area of 400 $\text{m}^2 \text{g}^{-1}$ because of introduction of the bulky, sterically more hindered SBI contortion site. CO_2 adsorption of the polymers followed the same sequence as their N_2 -derived BET surface area: SBI-HTB > 6FDA-HTB (**Figure 4b**). The pore size distribution obtained from CO_2 adsorption by NLDT analysis (**Figure S3**) demonstrated ultra-microporosity (< 7 Å) present in the Tröger's base-based 6FDA-HTB polyimide with a large fraction of ultra-micropores of ~ 7 Å.

Figure 4. a) N₂ adsorption isotherms of 6FDA-HTB and SBI-HTB at -196 °C; b) CO₂ adsorption isotherms of 6FDA-HTB and SBI-HTB at 0 °C.

Gas Permeation Properties. The gas permeation properties of the HTB-based polyimides were determined at 2 bar and 35 °C using the constant-volume/variable-pressure method (ESI). The gas permeabilities and gas-pair selectivities of 6FDA-HTB and SBI-HTB are compared with previously reported hydroxyl-functionalized 6FDA-derived PIM-PIs in **Table 2** and some conventional low-free-volume 6FDA-based OH-containing PIs in **Table S3**. The permeabilities of all hydroxyl-based polyimides follow the sequence: PH₂ > PCO₂ > PO₂ > PN₂ > PCH₄. This trend can be ascribed to the size-selective chain packing of the polyimides due to the presence of ultra-micropores (< 7 Å) as determined by gas sorption and NLDFT analysis. The 6FDA-HTB polyimide sample demonstrated significantly higher H₂, CO₂ and O₂ permeabilities of 167, 67 and 13.6 Barrer, respectively, compared to values reported for other 6FDA-based hydroxyl-functionalized polyimides without kinked contortion sites, such as 6FDA-HPI (H₂ = 68 Barrer),⁸ 6FDA-DAP (H₂ = 38 Barrer),⁹ and 6FDA-DAR (H₂ = 34 Barrer)⁹ (**Table S3**). Furthermore, 6FDA-HTB showed the highest gas-pair selectivities of all presently reported OH-functionalized PIM-PIs with O₂/N₂, CO₂/CH₄ and H₂/CH₄ selectivity values of 6.0, 73 and 181, respectively. Physical aging over a period of one month reduced the

gas permeability by about 10 to 20% with a small increase in H₂/CH₄, O₂/N₂ and CO₂/CH₄ selectivity (**Table 2**). Introduction of the bulky spirobisindane-based dianhydride in the OH-functionalized Tröger's based polyimide (SBI-HTB) resulted in higher gas permeabilities for H₂ (467 Barrer) and CO₂ (466 Barrer) coupled with significant reductions in H₂/CH₄ (29), CO₂/CH₄ (29) and O₂/N₂ (4.6) selectivity.

Table 2. Gas Permeability and Permselectivity of 6FDA-HTB, SBI-HTB and Related OH-Functionalized 6FDA-derived PIM-PIs.

Polymer	Permeability (Barrer)					Selectivity			
	H ₂	N ₂	O ₂	CH ₄	CO ₂	H ₂ / CH ₄	N ₂ / CH ₄	O ₂ / N ₂	CO ₂ / CH ₄
6FDA-HTB ^a	167	2.26	13.6	0.92	67	181	2.5	6.0	73
6FDA-HTB ^b	150	1.80	11.6	0.72	55	208	2.5	6.4	76
SBI-HTB ^a	467	16.6	75.7	16.3	466	29	1.0	4.6	29
PIM-6FDA-OH ^c	181	5.5	23.8	3.4	119	53	1.6	4.3	35
6FDA-HSBF ^d	162	3.8	19.3	2.4	100	68	1.6	5.1	42
6FDA-DAT1-OH ^e	127	2.7	14.0	1.4	70	91	1.9	5.4	50

^a) Fresh film was annealed at 250 °C under vacuum oven for 24 h before testing; ^b) Film aged for 1 month; ^c) Data from reference 47; ^d) Data from reference 32; ^e) Data from reference 33.

CO₂ and CH₄ solubility coefficients (*S*) were determined by gravimetric sorption at 2 bar pressure and 35 °C (**Table 3**). The diffusion coefficients (*D*) were then calculated from the relationship $D = P/S$. 6FDA-HTB and SBI-HTB showed higher CO₂ and CH₄ solubility coefficients than PIM-6FDA-OH and 6FDA-HSBF, which can be ascribed to the higher BET surface area of HTB-based PIM-PIs. The CO₂/CH₄ solubility selectivities of the PIM-PIs varied only over a narrow range of 3.1-3.7. Similar results were obtained by direct gravimetric sorption of a Tröger's base PIM-PI derivative without OH-functionalization, 6FDA-TBDA, which showed a CO₂/CH₄ solubility selectivity of 3.4 at 35 °C and 2 bar.⁴⁸ Hence, no

enhancement in solubility selectivity of CO₂/CH₄ was observed by introducing the tertiary amine-containing Tröger's base building block into the polymer main chain. Clearly, the remarkably high CO₂/CH₄ permselectivity of 6FDA-HTB resulted *exclusively* from its higher CO₂/CH₄ diffusion selectivity (22.3) relative to other OH-functionalized PIM-PIs, such as SBI-HTB (9.2), PIM-6FDA-OH (9.5) and 6FDA-HSBF (11.8).

Table 3. CO₂ and CH₄ Diffusion Coefficients and Solubility Coefficients for 6FDA-HTB, SBI-HTB and Related OH-Functionalized PIM-PIs (T = 35 °C, p = 2 bar).

Polymer	Diffusion coefficient ^a (10 ⁻⁸ cm ² s ⁻¹)		Solubility coefficient ^b (10 ⁻² cm ³ (STP) cm ⁻³ cmHg ⁻¹)	
	CO ₂	CH ₄	CO ₂	CH ₄
6FDA-HTB	2.47	0.11	27.2	8.3
SBI-HTB	14.5	1.55	32.7	11.5
PIM-6FDA-OH	5.48	0.58	21.7	5.9
6FDA-HSBF	4.65	0.39	21.4	6.0

^a Determined from D = P/S (S measured directly by gravimetric method); 2 bar, 35 °C;

^b measured gravimetrically at 2 bar and 35 °C.

Table 4. CO₂/CH₄ Diffusion Selectivity and Solubility Selectivity for 6FDA-HTB, SBI-HTB and Related OH-Functionalized PIM-PIs (T = 35 °C, p = 2 bar).

Polymer	Diffusion selectivity ^a (α) _D	Solubility selectivity ^b (α) _S
	CO ₂ /CH ₄	CO ₂ /CH ₄
6FDA-HTB	22.3	3.3
SBI-HTB	9.2	3.1
PIM-6FDA-OH	9.5	3.7
6FDA-HSBF	11.8	3.5

^a Determined from D = P/S (S measured directly by gravimetric method); 2 bar, 35 °C.

^b Measured gravimetrically at 2 bar and 35 °C.

Previous studies of polyimides demonstrated that hydroxyl-functionalization in the polymer backbone leads to strong charge-transfer complex (CTC) formation that results in

tighter interchain packing leading to enhanced gas-pair selectivity compared to unfunctionalized PIs.^{9,25} Here, we propose that the enhanced size-sieving properties of the 6FDA-HTB polyimide originated from strong hydrogen bonding. Three potential types of hydrogen bonding that may occur in OH-functionalized polyimides are schematically illustrated for PIM-6FDA-OH and 6FDA-HTB in **Figure 5**. Intrachain- (Type I) and interchain (Type II) O-H $\cdots$ O hydrogen bonding can occur in both types of PIM-PIs. In addition, strong interchain (Type III) O-H $\cdots$ N hydrogen bonding between the N atoms of the Tröger's base and OH group can be present in 6FDA-HTB (**Figure 2b**).

Figure 5. Potential hydrogen bonding types in PIM-6FDA-OH and 6FDA-HTB. Type I and II (O-H $\cdots$ O) can occur in both polyimides; Type III (O-H $\cdots$ N) can only be present in 6FDA-HTB.

The performance of the HTB-derived PIM-PIs for O₂/N₂, H₂/CH₄, H₂/N₂ and CO₂/CH₄ separations is illustrated in **Figure 6** relative to the 2008 and 2015 permeability/selectivity upper bounds.^{19, 49} 6FDA-HTB exhibited the highest gas-pair selectivities of all OH-based PIM-PIs with performance on or above the 2008 trade-off line for H₂/N₂, H₂/CH₄, and CO₂/CH₄ but below the more recently reported 2015 upper bound line. Introduction of the OH-containing Tröger's base in 6FDA-HTB resulted in enhanced gas permeability without significant drop in gas-pair selectivity compared to low-free-volume PIs, such as 6FDA-DAP

and 6FDA-HPI (**Table S3**). 6FDA-HTB showed 2-fold higher CO₂/CH₄ selectivity (73 vs 33) and 10-fold higher CO₂ permeability (67 vs 6.6 Barrer) than the standard industry membrane material, cellulose triacetate (CTA), making it a promising candidate material for membrane-based CO₂/CH₄ separation in natural gas and biogas applications.

Figure 6. a) O₂/N₂, b) H₂/N₂, c) H₂/CH₄ and d) CO₂/CH₄ permeability/selectivity performance upper bound plots for PIM-PIs (6FDA-HTB, SBI-HTB, PIM-6FDA-OH, 6FDA-HSBF, 6FDA-DAT1-OH, colored symbols) and low-free-volume OH-functionalized polyimides (6FDA-HPI, 6FDA-DAP, 6FDA-DAR, black symbols). CTA data are from reference 50.

CONCLUSIONS

A novel hydroxyl-functionalized Tröger's base diamine, 1,7-diamino-6H,12H-5,11-methanodibenzo[1,5]diazocine-2,8-diol (HTB), was synthesized by a facile two-step method. Two intrinsically microporous OH-functionalized polyimides, 6FDA-HTB and SBI-HTB, demonstrated good solubility in polar solvents and exhibited high thermal stability of ~ 380 °C. 6FDA-HTB displayed the highest gas-pair selectivities to date of all currently reported OH-based PIM-PIs combined with commendable gas permeabilities. Specifically, 6FDA-HTB showed promising performance for membrane-based natural gas and biogas treatment with CO₂ permeability of 67 Barrer and CO₂/CH₄ selectivity of 73. The enhanced CO₂/CH₄ permselectivity originated from a very high diffusion selectivity of 22.3, whereas the solubility selectivity of 3.3 was a typical value for polyimides. It is suggested that the highly size-selective chain packing of 6FDA-HTB was caused by strong O-H···N interchain hydrogen bonding between the OH group and the nitrogen of tertiary amine in the Tröger's base unit.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Gas permeation testing procedure, solubility properties, mechanical properties, TGA and TGA-MS, DSC, pore size distributions, gas transport properties. Crystallographic data of 1,7-dinitro-6H,12H-5,11-methanodibenzo[1,5] diazocine-2,8-diol (CCDC 1545701). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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Table of Contents

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