Synthesis of Highly Gas-Permeable Polyimides of Intrinsic Microporosity Derived from 1,3,6,8-Tetramethyl-2,7-diaminotriptycene

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ABSTRACT: A simple synthetic route to a novel sterically hindered triptycene-based diamine, 1,3,6,8-tetramethyl-2,7-diaminotriptycene (TMDAT), and its use in the preparation of high molecular weight polyimides of intrinsic microporosity (PIM-PIs) are reported. The organosoluble TMDAT-derived polyimides displayed high Brunauer–Emmett–Teller surface areas ranging between 610 and 850 m² g⁻¹ and demonstrated excellent thermal stability of up to 510 °C. Introduction of the rigid three-dimensional paddlewheel triptycene framework and the tetramethyl-induced restriction of the imide bond rotation resulted in highly permeable polyimides with moderate gas-pair selectivity. The best performing polyimide made from TMDAT and a triptycene-based dianhydride showed gas transport properties located between the 2008 and 2015 polymer permeability/selectivity trade-off curves with H₂ and O₂ permeabilities of 2858 and 575 barrer combined with H₂/N₂ and O₂/N₂ selectivities of 24 and 4.8, respectively, after 200 days of physical aging.

1. INTRODUCTION

Since their introduction in 2004, a wide variety of ladder polymers of intrinsic microporosity (PIMs) were intensively studied because of their potential commercial applications in catalysis,¹ ‡ sensors for trace substance detection,³ gas storage,⁴–⁶ nanofiltration,⁷ gas permeation,⁸,⁹ pervaporation,¹⁰ and most importantly membrane-based gas separations.¹¹–¹³ The micro-porosity in these unique glassy ladder polymers was induced by design of nonplanar bulky contortion sites and the rigidity of the polymer chains that restricted efficient chain packing and, consequently, introduced high free volume with interconnected micropores (<2 nm).¹²–¹³

Aromatic polyimides are among the most promising materials for advanced gas separation membranes owing to their (i) excellent gas transport properties, (ii) exceptional thermal and chemical stability, (iii) high mechanical strength, (iv) good film-forming properties, and (v) flexible chemistry.³⁰–³³ Recently, polyimides of intrinsic microporosity (PIM-PIs) were developed by introducing sterically hindered diamine- and/or dianhydride building blocks in the polymer backbone, including spiroisindane-, ethanoanthracene-, spirofluorene-,-Tröger's base-, carboxylic pseudo Tröger's base-, and triptycene-derived units.³⁶–³⁸ PIM-PIs showed attractive gas separation properties for several important gas pairs with performance near or above the 2008 permeability/selectivity Robeson upper bounds.³⁷ Specifically, triptycene has been used as an attractive organic building block to construct PIM-PIs because of its unique nonplanar three-dimensional (3D) rigid paddlewheel architecture comprising three benzene groups connected at 120° around a [2,2,2]-tricyclic ring system.⁴⁹ The rigidity and the nonplanar contortion site of the triptycene motif frustrate efficient polymer chain packing and generate high intrinsic internal free volume.⁴⁹,⁵⁰

Previous work showed that the introduction of ortho-substituted methyl groups in diamine monomers restricted the rotation of the imide linkages, thereby enhancing the rigidity, solubility, microporosity, and gas permeability of the corresponding polyimides.³⁷–³⁹,⁴⁶,⁵¹,⁵⁸ In extension to our previous work on triptycene-based PIM-PIs and to combine the potential of using the triptycene moiety and tetra-o-methyl substituents for the construction of new PIM-PI materials, here, we report a facile method for the synthesis of a novel 1,3,6,8-tetramethyl-2,7-diaminotriptycene (TMDAT) monomer. This new protocol has advantages of using a low-cost starting material, m-xylene, and simple synthetic chemistry to prepare solution-processable, high molecular weight triptycene-based PIM-PIs with enhanced porosity and gas permeability. The pure-gas permeation properties of a series of TMDAT-based PIM-PIs are reported for fresh and aged membrane samples.
2. RESULTS AND DISCUSSION

2.1. Synthetic Route to TMDAT. The TMDAT monomer was synthesized by a simple synthetic route in four steps starting from m-xylene, as shown in Scheme 1a. The key intermediate 1,3,6,8-tetramethylanthracene (TMA) was obtained as a major product from the Friedel–Crafts alkylation reaction of m-xylene with dichloromethane (DCM) in the presence of aluminum chloride using the procedure reported by Ellison and Hey. The Diels−Alder reaction of tetramethylanthracene with the diazonium salt of 2-aminobenzoic acid yielded 1,3,6,8-tetramethyltriptycene (TMT). Nitration of TMA using potassium nitrate and trifluoroacetic anhydride followed by palladium-catalyzed hydrazine reduction of the dinitro intermediate [1,3,6,8-tetramethyl-2,7-dinitrotriptycene (TMDNT)] yielded the diamine product TMDAT. The purity and molecular structures of all products were confirmed by standard characterization techniques, such as $^1$H- and $^{13}$C NMR, Fourier transform infrared (FTIR), and high-resolution mass spectroscopic analyses. The molecular structure of TMDNT was also confirmed by single-crystal X-ray crystallography analysis.

The FTIR spectra of TMDNT and the TMDAT monomer are shown in Figure 1a. TMDAT showed characteristic absorption bands in the range of 3450, 3377, and 2943 cm$^{-1}$ because of N−H stretching vibrations of the amine groups and the C−H stretching frequency of the methyl groups, respectively. The disappearance of the two characteristic absorption bands at 1515 and 1364 cm$^{-1}$ assigned for the symmetric and asymmetric stretching frequency of the nitro groups in TMDNT confirmed the complete reduction to the diamine groups, respectively.

The $^1$H NMR spectra for both TMDAT and TMDNT products confirmed their chemical structures and purity. As shown in Figure 1b, the signals at (2.07, 2.37) and (2.21, 2.44) ppm are assigned for the methyl protons of TMDAT and TMDNT, respectively. The protons of the amino groups appeared as broad singlet at 4.07 ppm. The signals assigned for the bridgehead protons of TMDAT and TMDNT appeared at (5.12, 5.86) and (5.39, 5.90) ppm, respectively. The molecular

![Scheme 1](image1.png)  
Figure 1. (a) FTIR spectra of TMDNT and TMDAT and (b) $^1$H NMR spectra of TMDNT and TMDAT.
structure of TMDNT was further validated by single-crystal X-ray crystallographic analysis (Figures 2 and S2), which confirmed the nonplanarity and 3D architecture of the triptycene moiety and the selective nitration at the 2,7-positions of triptycene.

2.2. Synthesis and Characterization of TMDAT-Based Polyimides. Five polyimides were prepared under nitrogen via a one-step high-temperature solution cycloimidization reaction of equimolar amounts of TMDAT and the aromatic dianhydride monomers in m-cresol containing two drops of isoquinoline, as shown in Scheme 1b. The polymers were characterized by 1H NMR, FTIR, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), and Brunauer–Emmett–Teller (BET) surface area measurements. The 1H NMR spectra for all polymers were consistent with their proposed chemical structures. The 1H NMR spectrum of a representative polyimide, 4,4′-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA)-TMDAT, is shown in Figure 3. The two singlets at 2.08 and 2.30 ppm each integrated for six protons were assigned to the methyl protons. The bridgehead protons appeared at 5.40 and 5.90 ppm, whereas the aromatic protons appeared in the range of 7.03–8.01 ppm. The complete imidization of the polyamic acid precursor was confirmed by the disappearance of the acid or amide signals at 10–12 ppm. The FTIR spectrum of 6FDA-TMDAT (Figure S1) showed two characteristic absorptions bands at 1787 and 1720 cm⁻¹ assigned to asymmetric and symmetric stretching of imide carbonyl groups, respectively. Another band at 1374 cm⁻¹ due to C–N bond stretching further confirmed the formation of imide linkages. No peaks corresponding to polyamic acid were observed, indicating complete imidization. Gel permeation chromatographic measurements showed that the polyimides were prepared in high weight-average molecular weights $M_w$ in the range of 122,000–192,000 g mol⁻¹ and with narrow polydispersity index ($M_w/M_n$) in the range of 1.4–1.6 (Table 1).

![Figure 2. Molecular structure of TMDNT (CCDC 1515556).](image)

![Figure 3. 1H NMR spectrum of 6FDA-TMDAT in CDCl₃.](image)

![Figure 4. Thermal gravimetric analysis of TMDAT-based polyimides under a N₂ atmosphere.](image)

| polymer          | $M_w$ (g mol⁻¹) | PDI (−) | $S_{BET}$ (m² g⁻¹) | $T_d$ (°C) |
|------------------|----------------|---------|---------------------|------------|
| 6FDA-TMDAT       | 122,000        | 1.6     | 620                 | 470        |
| PMDA-TMDAT       | 125,000        | 1.5     | 720                 | 500        |
| TPD-TMDAT        | 192,000        | 1.4     | 850                 | 470        |
| NTDA-TMDAT       | 156,000        | 1.5     | 790                 | 510        |
| BCD-TMDAT        | 183,000        | 1.4     | 610                 | 450        |

Table 1. Basic Properties of TMDAT-Based Polyimides

Aromatic polyimides derived from rigid planar dianhydrides such as pyromellitic dianhydride (PMDA) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) generally show poor solubility in common organic solvents because of π–π stacking of polymer chains, which results in strong interchain interactions. To improve their solubility, polyimides made from PMDA with nonplanar bulky diamines have shown significantly improved solubility. The TMDAT-derived PIM-Pis, including PMDA-TMDAT and NTDA-TMDAT, also displayed very good solubility in low- and high-boiling point organic solvents (Table S1) because of the nonplanarity of the 3D-paddlewheel triptycene architecture and the effect of the sterically restricted tetra-o-methyl substituents on the C–N–imide bond rotation. The thermal properties of the polymers were evaluated by TGA, demonstrating excellent thermal stability with onset decomposition temperatures between 450 and 510 °C in a N₂ atmosphere (Figure 4, Table 1).

The microporosity of the TMDAT-based polyimides was evaluated by nitrogen adsorption analysis measured at −196 °C up to 1 bar (Figure 5). As previously demonstrated for other PIM-Pis, the introduction of sterically hindered o-methyl substituents to the imide linkages increased chain rigidity and...
reduced efficient chain packing. All TMDAT-derived polymides exhibited very high BET surface areas ranging from 610 to 850 m$^2$ g$^{-1}$ (Table 1), which rank among the highest values reported for PIM-PIs to date.

The pore size distributions of the TMDAT-based polymides derived by NLDFT from nitrogen adsorption isotherms measured at −196 °C are shown in Figure S3. The estimated pore sizes range between ~5 and 7.5 Å, as typically observed for PIM-PIs. The general trend of the pore size distributions of all polymides is similar, which correlates qualitatively with their similar gas-pair selectivities for fresh film samples, as discussed below.

2.3. Gas Permeation Properties of PIM-PIs. Pure-gas permeabilities and ideal gas-pair selectivities for 1 day old samples of TMDAT-derived PIM-PIs measured at 2 bar and 35 °C are shown in Table 2. It is well known that the gas transport properties of microporous polymers strongly depend on film preparation, film thickness, drying, and aging conditions. In this work, all polyimide films were made by the same methodology including a methanol treatment after an initial drying step to remove any residual casting solvent that has proven useful in obtaining reproducible gas permeation properties for fresh samples. The TMDAT-based polymides showed high gas permeabilities and moderate gas-pair selectivities regardless of the dianhydride type. For example, fresh PIM-PI samples made from TMDAT and conventional dianhydrides, 6FDA-TMDAT and PMDA-TMDAT, displayed $O_2$ permeabilities of 374 and 680 barrer with $O_2/N_2$ selectivities of 3.3 and 3.8, respectively. Notably, the PIM-PI made from the inexpensive PMDA-derived polyamide exhibited higher gas permeability without sacrificing selectivity when compared to 6FDA-TMDAT. This trend has also been demonstrated previously for 6FDA- and PMDA-derived PIM-PIs made from tetramethyl-substituted Tröger’s base diamine. It is interesting to compare the gas permeation properties of 6FDA-TMDAT with those of the previously reported 6FDA-DAT1, which was made from 6FDA and 2,6-diaminotriptycene (DAT1). 6FDA-DAT1 exhibited a much lower BET surface area of 320 m$^2$ g$^{-1}$ than 6FDA-TMDAT (620 m$^2$ g$^{-1}$). Furthermore, 6FDA-DAT-1 displayed a much lower $O_2$ permeability of 25.4 barrer but higher $O_2/N_2$ selectivity of 5.4 compared to 6FDA-TMDAT ($O_2$ permeability = 374 barrer and $O_2/N_2 = 3.3$). Clearly, the enhanced permeability of 6FDA-TMDAT resulted from the tetramethyl-substitution that severely restricted the mobility of the imide linkages, resulting in higher free volume. Unfortunately, the desirable increase in permeability is coupled with a significant loss in selectivity, indicating undesirable effects in the pore size distribution that reduce the size-sieving properties of 6FDA-TMDAT.

Similar to other high surface area PIM-PIs, the gas permeability of fresh aromatic TMDAT-derived polyimide films increased in the following sequence: $PN_2 < PCH_4 < PO_2$. Table 2. Gas Permeability and Selectivity of TMDAT-Derived Polyimides and Related Tetramethyl-Substituted Polyimides ($T = 35 °C; p = 2$ bar)

| polymer          | pure-gas permeability (barrer) | ideal selectivity (α) |
|------------------|-------------------------------|-----------------------|
| 6FDA-TMDAT       |                               |                       |
| 6FDA-TMDAT       |                               |                       |
| PMDA-TMDAT       |                               |                       |
| PMDA-TMDAT       |                               |                       |
| TMDAT-TMDAT      |                               |                       |
| TMDAT-TMDAT      |                               |                       |
| TMDAT-TMDAT      |                               |                       |
| NMDA-TMDAT       |                               |                       |
| NMDA-TMDAT       |                               |                       |
| BCDA-TMDAT       |                               |                       |
| BCDA-TMDAT       |                               |                       |
| BCDA-TMDAT       |                               |                       |
| BCDA-TMDAT       |                               |                       |
| 6FDA-4MTBDA      |                               |                       |
| 6FDA-4MTBDA      |                               |                       |
| 6FDA-4MTBDA      |                               |                       |
| 6FDA-4MTBDA      |                               |                       |
| PMDA-4MTBDA      |                               |                       |
| PMDA-4MTBDA      |                               |                       |
| TPDA-TMDAP       |                               |                       |
| TPDA-TMDAP       |                               |                       |
| TPDA-TMDAP       |                               |                       |
| TPDA-TMDAP       |                               |                       |
| TPDA-TMDAP       |                               |                       |
| TPDA-TMDAP       |                               |                       |
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| TPDA-TMDAP       |                               |                       |
| TPDA-TMDAP       |                               |                       |
| TPDA-TMDAP       |                               |                       |
| TPDA-TMDAP       |                               |                       |
| TPDA-TMDAP       |                               |                       |
| TPDA-TMDAP       |                               |                       |

Air-dried film soaked in methanol for 24 h, then dried under vacuum at 120 °C for 24 h, and tested after 1 day. Tested after 200 days. Tested after 30 days. Tested after 60 days. From ref 46, methanol-treated, air-dried, and tested after 1 day, $p = 1$ bar, $T = 25 °C$. From ref 46, tested after 524 days. From ref 46, tested after 333 days. From ref 46, methanol-treated, air-dried, and tested after 15 days. From ref 46, tested after 150 days. From ref 48, no methanol treatment, dried at 200 °C, $p = 10$ bar, $T = 35 °C$.
< PH2 < PHe < PCO2; the only exception in this series was the polyimide based on the cycloaliphatic dianhydride, bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA), where PH2 > PCO2, indicating a more dominating size-sieving behavior.

It is well known that the gas transport properties of microporous glassy polymers typically undergo a physical aging process during which the polymer free volume decreases with time because of chain rearrangement to tighter intra- and interchain packing. Consequently, physical aging leads to reduction in gas permeability as the polymer is slowly approaching its equilibrium chain configuration. Physical aging of 6FDA-TMDAT and PMDA-TMDAT films tested after 200 days resulted in ~25–30% drop in O2 permeability with only small gain in O2/N2 selectivity. Interestingly, the most permeable PIM-PI in this series, TPDA-TMPDA, showed the largest relative decrease in O2 permeability of ~50% from 1153 to 575 barrer after 200 days of aging, but O2/N2 selectivity increased significantly from 3.8 to 4.8. The loss in permeability with concomitant increase in selectivity is believed to be due to a relative increase in the fraction of ultramicropores (<7 Å) relative to larger micropores in TPDA-TMPDA.

The gas permeation properties of PIM-PIs previously made from other tetramethyl-substituted diamine building blocks, 2,8-diamino-1,3,7,9-tetramethyl-6H,12H-5,11-methanodibenzo-[b,f][1,5]diazocine (4MTBDA) and 2,3,5,6-tetramethyl-p-phenylene diamine (TMPD), are also listed in Table 2. It is noteworthy to compare the gas permeation properties of 6FDA- and PMDA-derived polyimides made from 3D tetramethyl-substituted triptycene and Tröger’s base diamines. It appears that polyimides made either from triptycene or Tröger’s base PIM motif diamine building blocks with the same dianhydride had similarly high permeabilities coupled with moderate gas-pair selectivity. The effect of diamine building blocks on gas permeability in PIM-PIs can be further elucidated by comparing 6FDA-TMPD and the two polyimides containing 3D-PIM motifs, 6FDA-TMDAT and 6FDA-4MTBDA. Clearly, the planar 6FDA-TMPD exhibits about 50% lower permeability with similar selectivity values compared to the 3D-type triptycene and Tröger’s base polyimides. The notable exception in this series of tetramethyl-substituted polyimides (KAUST-PI-1) is based on a previously reported triptycene-based dianhydride (TPDA) and planar TMPD, which showed an exceptional combination of gas permeability and gas-pair selectivity because of high intrinsic microporosity and significant fraction of ultramicroporosity.

The performance of the TMDAT-based polyimide series for O2/N2 and H2/N2 separation is summarized and compared to other tetramethyl-substituted polyimides in Figure 6. Clearly, TPDA-TMPD is the most promising candidate membrane material with performance between the 2008 and 2015 O2/N2 and H2/N2 permeability/selectivity trade-off curves. On the other hand, although the TMDAT-based polyimides showed very high CO2 permeability (>1000 barrer), their applicability for viable CO2/CH4 separation in natural gas or biogas treatment is unlikely because of their modest pure-gas CO2/CH4 selectivity of <20.

1 = 6FDA-TMDAT; 2 = PMDA-TMDAT; 3 = TPDA-TMDAT; 4 = NTDA-TMDAT; 5 = BCDA-TMDAT; 6 = 6FDA-4MTBDA; 7 = PMDA-4MTBDA; 8 = TPDA-TMDP (KAUST-PI-1); 9 = 6FDA-TMPD.

3. CONCLUSIONS

In this study, a series of PIM-PIs was successfully prepared by a conventional one-step high temperature cycloimidization reaction of a novel, sterically highly contorted triptycene-based dianhydride, TMDAT, with five different dianhydrides (6FDA, PMDA, TPDA, NTDA, and BCDA). The polyimides exhibited high molecular weight (Mw > 100,000 g mol⁻¹), excellent solubility in organic solvents, and high thermal stability. Intrinsic microporosity of the polyimides was demonstrated by high BET surface area values (610–850 m² g⁻¹). All polymers showed high gas permeabilities with moderate gas-pair selectivities. Interestingly, the most permeable polyimide in this series, TPDA–TMDAT, also displayed the highest gas-pair selectivities with performance located between the 2008 and 2015 permeability/selectivity trade-off curves for O2/N2 and H2/N2 separations.

4. EXPERIMENTAL SECTION

4.1. Materials. Potassium nitrate, m-xylene, acetonitrile, trifluoroacetic anhydride, hydrazine monohydrate, Pd/C catalyst (10 wt %) isequinosine, anthranilic acid, and isopentyl nitrite were obtained from Aldrich and used as received. PMDA and 6FDA were purchased from Aldrich and purified by sublimation under vacuum prior to use. Sublimed NTDA and BCDA were obtained from TCI (America). 9,10-Diisopropyl-triptycene dianhydride (TPDA) monomer was prepared according to a previously reported procedure. m-Cresol was purchased from Aldrich and dried over 4 Å

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molecular sieves. All other solvents were obtained from various commercial sources and used as received.

4.2. Characterization. 1H NMR and 13C NMR spectra for all monomers and polymers were obtained with a Bruker AVANCE-III spectrometer at a frequency of 400 or 500 MHz in deuterated chloroform (CDCl3) or dimethylsulfoxide (DMSO-d6). FTIR measurements were performed using a Varian 670-IR FTIR spectrometer. Single-crystal X-ray data were collected at 140 K using a Bruker D8 Venture diffractometer equipped with a PHOTON 100 CMOS area detector and a Cu (Kα) source, λ = 2.54 Å. Yellow crystals of TMDNT suitable for X-ray diffraction were obtained by slow evaporation from solution in n-hexane/DCM (3:1) after 2 days. Column chromatography was carried out on silica gel 60A. Molecular weights (Mn and Mw) of the polymers were determined by gel permeation chromatography using chloroform (CHCl3) or N,N-dimethylformamide (DMF) as eluents (GPC, Viscotek and Agilent 1200) and polydisperse polystyrene as the external standard. High-resolution mass spectroscopy (HRMS) was conducted on a Thermo LC/MS system with LTQ Orbitrap Velos detectors. The onset thermal decomposition temperatures of the polymers were determined by TGA (TA Q5000) under nitrogen flow at a heating rate of 3 °C min⁻¹ from room temperature to 700 °C. The BET surface area of the polymers was determined by nitrogen adsorption at −196 °C up to 1 bar using Micromeritics ASAP-2020 equipped with micropore option. Prior to analysis, powder samples were degassed under high vacuum at 150 °C for 24 h.

4.3. Synthesis of TMA. TMA was prepared according to the previously reported procedure by Ellison and Hey.59 To a stirred mixture of anhydrous m-xylene (200 mL) and AlCl3 (60 g, 0.44 mol) was added DCM (37.6 mL) for a period of 1 h. After heating at 60 °C for 1 h, the cooled mixture was filtered to give the desired product in 23% yield. Melting point = 296 °C.

4.4. Synthesis of TMT. To an ice-cooled anthranilic acid (15.00 g, 36.0 mmol) solution in ethanol (150 mL) were added concentrated HCl (12.6 mL) and isopentyl nitrite (31 mL) under stirring. After 15 min, diethyl ether (200 mL) was added and the reaction mixture was stirred for additional 5 min. The resulting diazonium salt was then filtered, washed with ether, and dried in a vacuum aspirator and added in portions to a hot solution of TMA (4.81 g, 17.83 mmol) in dichloroethane (120 mL) and 1,2-epoxypropane (15 mL). The reaction mixture was refluxed under a nitrogen atmosphere for 10 h, and the solvent was then removed under vacuum. After the crude product was subjected to column chromatography (silica gel, n-hexane), the desired product was obtained as white crystals in 50% yield. Melting point = 191–193 °C.

4.5. Synthesis of TMDNT. Trifluoroacetic anhydride (7.06 g, 33.61 mmol) was added dropwise to a mixture of TMT (1.47 g, 4.74 mmol), potassium nitrate (0.99 g, 9.67 mmol), and acetonitrile (55 mL). After stirring at room temperature for 20 h, the reaction mixture was added to 600 mL water. The resulting precipitate was purified by column chromatography on silica gel with n-hexane/DCM 4:1 (eluent) to give the dinitro product as a pale yellow powder (0.95 g, 67% yield). Melting point = 326–328 °C. 1H NMR (400 MHz, CDCl3, δ): 2.21 (s, 6H), 2.44 (s, 6H), 5.39 (s, 1H), 5.90 (s, 1H), 7.06–7.08 (m, 2H), 7.18 (s, 2H), 7.38–7.41 (m, 2H). 13C NMR (100 MHz, CDCl3, δ): 13.9, 17.5, 46.5, 54.3, 124.1, 124.2, 124.5, 126.2, 126.4, 127.0, 142.4, 143.3, 143.8, 146.5, 149.9.

4.6. Synthesis of TMDAT. Hydrazine hydrate (5.4 mL, 171.9 mmol) was added to a stirred mixture of TMDNT (1.52 g, 2.07 mmol) and palladium/carbon (0.45 g, 10%) in absolute ethanol (120 mL). After refluxing for 6 h, the cooled mixture was filtered into stirred water (700 mL). The resulting white solid was dried under vacuum at 110 °C for 20 h to give the diamine monomer in 87% yield. Melting point = 256–258 °C. 1H NMR (400 MHz, CDCl3, δ): 2.07 (s, 6H), 2.37 (s, 6H), 4.07 (br s, 4H), 5.12 (s, 1H), 5.86 (s, 1H), 6.89–6.98 (m, 4H), 7.24–7.31 (m, 2H). 13C NMR (100 MHz, CDCl3, δ): 13.0, 17.9, 47.3, 53.6, 117.2, 117.6, 122.9, 123.1, 123.6, 124.6, 125.3, 136.7, 139.7, 142.4, 145.7, 147.6. HRMS (ESI) (m/z): calcd for C23H22N4O4: 400.1423; found: 340.1418.

4.7. Typical Procedure for the Synthesis of the Polymides. In a dry 10 mL reaction tube, a mixture of the diamine monomer (1.0 mmol) and dianhydride monomer (1.0 mmol) was stirred in dry m-cresol (4 mL) under a nitrogen atmosphere for 15 min. After heating to 80 °C, two drops of isoquinoline were added, and the reaction temperature was raised gradually to 200 °C and maintained at that temperature for 2 h under steady flow of nitrogen. During this period, water formed by the imidization reaction was removed by a stream of nitrogen. After cooling, the clear and viscous polycrude solution was added dropwise into stirred methanol, and the resulting fibrous polymer was collected by filtration, purified by reprecipitation twice from an appropriate solvent into methanol, and then dried under vacuum at 120 °C for 20 h.

4.8. Synthesis of 6FDA-TMDAT. Following the above typical procedure, 6FDA-TMDAT was prepared from 6FDA and TMDAT as white powder in 78% yield after reprecipitation from chloroform into methanol. 1H NMR (400 MHz, CDCl3, δ (ppm)): 2.08 (s, 6H), 2.30 (s, 6H), 5.40 (s, 1H), 5.90 (s, 1H), 7.03 (m, 2H), 7.26 (s, 2H), 7.39 (d, 2H), 7.89–8.01 (m, 6H). FT-IR (Membrane, ν cm⁻¹): 1787 (asymmetric C=O stretching), 1720 (symmetric C=O stretching), 3450, 3377 (N–H stretching), 3006 (aromatic C–H stretching), 2943 (aliphatic C–H stretching), 1621 (C=C ring stretching).

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4.9. Synthesis of PMDA-TMDAT. Following the above procedure of 6FDA-TMDAT, a polymer was prepared from PMDA and TMDAT in 91% yield after precipitation from chloroform into methanol. The NMR spectra of the polymer were recorded using a Bruker Avance III 400 MHz NMR spectrometer. The NMR spectra were recorded in DMSO-<i>d</i><sub>6</sub> at room temperature. The chemical shifts (ppm) were measured relative to Me<sub>4</sub>N<sup>+</sup> as internal standard. The signals were assigned based on their integration and the known chemical shifts of the monomers. The molecular weight and polydispersity were determined by gel permeation chromatography (GPC) using polystyrene standards. The pure-gas permeabilities of He, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> were measured at 35 °C and 2 bar.

4.10. Synthesis of TPDA-TMDAT. Following the above procedure, TPDA-TMDAT was prepared from TPDA and TMDAT as yellow powder in 92% yield after precipitation from chloroform into methanol. FTIR spectra of 6FDA-TMDAT; NLDFT-derived pore size distribution; and crystallographic data of TMDNT (CCDC 1515556). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (PDF).

4.11. Synthesis of NTDA-TMDAT. Following the above typical procedure, NTDA-TMDAT was prepared from 1,4,5,8-NTDA and TMDAT in 99% yield after precipitation from chloroform into methanol. FTIR spectra of 6FDA-TMDAT; NLDFT-derived pore size distribution; and crystallographic data of TMDNT (CCDC 1515556). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (PDF).

4.12. Synthesis of BCDA-TMDAT. Following the above procedure, BCDA-TMDAT was prepared from BCDA and TMDAT in 91% yield after precipitation from chloroform into methanol. FTIR spectra of 6FDA-TMDAT; NLDFT-derived pore size distribution; and crystallographic data of TMDNT (CCDC 1515556). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (PDF).

4.14. Gas Permeation Measurements. Pure-gas permeation measurements were conducted with a custom-designed permeation system using the constant-volume-variable-pressure method. The pure-gas permeabilities of He, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> were measured at 35 °C and 2 bar.
(9) Fritsch, D.; Merten, P.; Heinrich, K.; Lazar, M.; Priske, M. High Performance Organic Solvent Nanofiltration Membranes: Development and Thorough Testing of Thin Film Composite Membranes Made of Polymers of Intrinsic Microporosity (PIMs). J. Membr. Sci. 2012, 401–402, 222−231.

(10) Tsarok, S.; Khotimskiy, V.; Budd, P. M.; Volkov, V.; Kukushkina, J.; Volkov, A. Solvent Nanofiltration Through High Permeability Glassy Polymers: Effect of Polymer and Solute Nature. J. Membr. Sci. 2012, 423–424, 65−72.

(11) Wu, X. M.; Zhang, Q. G.; Soyekwo, F.; Liu, Q. L.; Zhu, A. M. Pervaporation Removal of Volatile Organic Compounds from Aqueous Solutions Using the Highly Permeable PIM-1 Membrane. AIChE J. 2016, 62, 842−851.

(12) Gao, L.; Alberto, M.; Gorojo, P.; Szekely, G.; Budd, P. M. High-Flux PIM-1/PVDF Thin film Composite Membranes for 1-Butanol/Water Pervaporation. J. Membr. Sci. 2017, 529, 207−214.

(13) Budd, P.; Msayib, K.; Tattershally, C.; Ghanem, B.; Reynolds, M.; McKeown, N.; Fritsch, D. Gas Separation Membranes from Polymers of Intrinsic Microporosity. J. Membr. Sci. 2008, 251, 263−269.

(14) Budd, P.; McKeown, N.; Ghanem, B.; Msayib, K.; Fritsch, D.; Starannikova, L.; Belov, N.; Sanfirova, O.; Yampolskiy, V.; Shantarovich, V. Gas Permeation Parameters and Other Physicochemical Properties of a Polymer of Intrinsic Microporosity: Polybenzoxazidine PIM-1. J. Membr. Sci. 2008, 325, 851−860.

(15) Song, J.; Du, N.; Dai, Y.; Robertson, G. P.; Guiver, M. D.; Thomas, S.; Pinnau, I. Linear High Molecular Weight Ladder Polymers by Optimized Polycondensation of Tetrahydroxytetramethylsiloxanes and 1,4-Dicyanotetrafluoroethene. Macromolecules 2008, 41, 7411−7417.

(16) Du, N.; Robertson, G. P.; Song, J.; Pinnau, I.; Thomas, S.; Guiver, M. D. Polymers of Intrinsic Microporosity Containing Trifluoromethyl and Phenylsulfone Groups as Materials for Membrane Gas Separation. Macromolecules 2008, 41, 9656−9662.

(17) Thomas, S.; Pinnau, I.; Du, N.; Guiver, M. D. Pure- and Mixed-Gas Permeation Properties of a Microporous Spirobisindane-Based Ladder Polymer (PIM-1). J. Membr. Sci. 2009, 333, 125−131.

(18) Bezzu, C. G.; Carta, M.; Tonkins, A.; Jansen, J. C.; Bernardo, P.; Bazzarelli, F.; McKeown, N. B. A Spirobisindane-Based Polymer of Intrinsic Microporosity with Improved Performance for Gas Separation. Adv. Mater. 2012, 24, 5930−5933.

(19) Li, P.; Zhuang, T. S.; Paul, D. R. Gas Sorption and Permeation in PIM-1. J. Membr. Sci. 2013, 432, 50−57.

(20) Carta, M.; Malpass-Evans, R.; Croad, M.; Rognan, Y.; Jansen, J. C.; Bernardo, P.; Bazzarelli, F.; McKeown, N. B. An Efficient Polymer Membrane for Membrane Gas Separations. Science 2013, 339, 303−307.

(21) Carta, M.; Croad, M.; Malpass-Evans, R.; Jansen, J. C.; Bernardo, P.; Clarizia, G.; Fries, K.; Lanč, M.; McKeown, N. B. Triptycine Induced Enhancement of Membrane Gas Selectivity for Microporous Tröger’s Base Polymers. Adv. Mater. 2014, 26, 3526−3531.

(22) Ghanem, B. S.; Swaydan, R.; Ma, X.; Litwiller, E.; Pinnau, I. Energy-Efficient Hydrogen Separation by AB-Type Ladder-Polymer Molecular Sieves. Adv. Mater. 2014, 26, 6696−6700.

(23) Carta, M.; Bernardo, P.; Clarizia, G.; Jansen, J. C.; McKeown, N. B. Gas Permeability of Hexaphenylbenzene Based Polymers of Intrinsic Microporosity. Macromolecules 2014, 47, 8320−8327.

(24) Rose, I.; Carta, M.; Malpass-Evans, R.; Ferrari, M.-C.; Bernardo, P.; Clarizia, G.; Jansen, J. C.; McKeown, N. B. Highly Permeable Benzotriptycine-Based Polymer of Intrinsic Microporosity. ACS Macro Lett. 2015, 4, 912−915.

(25) Zhang, J.; Jin, J.; Cooney, R.; Zhang, S. Synthesis of Polymers of Intrinsic Microporosity Using an AB-Type Monomer. Polymer 2015, 57, 45−50.

(26) Ma, X.; Pinnau, I. A Novel Intrinsicly Microporous Ladder Polymer and Copolymers Derived from 1,1′,2,2′-Tetrahydroxytetraphenyllcylethane for Membrane-Based Gas Separation. Polym. Chem. 2016, 7, 1244−1248.
Diamines: Synthesis and Gas Permeation Properties. Polymer 2016, 96, 13–19.

(46) Lee, M.; Bezzu, C. G.; Carta, M.; Bernardo, P.; Clarizia, G.; Jansen, J. C.; McKeown, N. B. Enhancing the Gas Permeability of Tröger’s Base Derived Polymides of Intrinsic Microporosity. Macromolecules 2016, 49, 4147–4154.

(47) Abdulhamid, M. A.; Ma, X.; Xiao, X.; Pinnau, I. Synthesis and Characterization of a Microporous 6FDA-Polyimide Made from a Novel Carboxyclic Pseudo Tröger’s Base Diamine: Effect of Bicyclic Bridge on Gas Transport Properties. Polymer 2017, 130, 182–190.

(48) Ma, X.; Abdulhamid, M. A.; Pinnau, I. Synthesis and Characterization of a Microporous 6FDA-Polyimide Made from a Novel Carbocyclic Pseudo Tröger’s Base Diamine: Effect of Bicyclic Bridge on Gas Transport Properties. Macromolecules 2017, 50, 5880–5887.

(49) Sydlik, S. A.; Chen, Z.; Swager, T. M. Triptycene Polyimides: Soluble Polymers with High Thermal Stability and Low Refractive Indices. Macromolecules 2011, 44, 976–980.

(50) Cho, Y. J.; Park, H. B. High Performance Polyimide with High Internal Free Volume Elements. Macromol. Rapid Commun. 2011, 32, 579–586.

(51) Ghanem, B. S.; Swaidan, R.; Litwiller, E.; Pinnau, I. Ultra-Microporous Triptycene-Based Polyimide Membranes for High-Performance Gas Separation. Adv. Mater. 2014, 26, 3688–3692.

(52) 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, 5104–5114.

(53) Wiegand, J. R.; Smith, Z. P.; Liu, Q.; Patterson, C. T.; Freeman, B. D.; Guo, R. Synthesis and Characterization of Triptycene-Based Polyimides with Tunable High Fractional Free Volume for Gas Separation Membranes. J. Mater. Chem. A 2014, 2, 13309–13320.

(54) Alghunaimi, F.; Ghanem, B.; Alaslai, N.; Swaidan, R.; Litwiller, E.; Pinnau, I. Gas Permeation and Physical Aging Properties of Iptycene Diamine-Based Microporous Polyimides. J. Membr. Sci. 2015, 490, 321–327.

(55) Weidman, J. R.; Guo, R. The Use of Iptycenes in Rational Macromolecular Design for Gas Separation Membrane Applications. Ind. Eng. Chem. Res. 2017, 56, 4220–4236.

(56) Alaslai, N.; Ma, X.; Ghanem, B.; Wang, Y.; Alghunaimi, F.; Pinnau, I. Synthesis and Characterization of a Novel Microporous Dihydroxyl-Functionalized Triptycene-Diamine-Based Polyimide for Natural Gas Membrane Separation. Macromol. Rapid Commun. 2017, 38, 1700303.

(57) Robeson, L. M. The Upper Bound Revisited. J. Membr. Sci. 2008, 320, 390–400.

(58) Tanaka, K.; Okano, M.; Toshino, H.; Kita, H.; Okamoto, K.-I. 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, 907–914.

(59) Ellison, H.; Hey, D. H. 345. The Action of Benzaldehyde on o-, m-, and p-Xylene in the Presence of Aluminium Chloride. J. Chem. Soc. 1938, 1847–1853.

(60) 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.

(61) 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, 6553–6561.

(62) Low, Z.-X.; Budd, P. M.; McKeown, N. B.; Patterson, D. A. Gas Permeation Properties, Physical Aging, and Its Mitigation in High Free Volume Glassy Polymers. Chem. Rev. 2018, 118, 5871–5911.

(63) Swaidan, R.; Ghanem, B.; Pinnau, I. Fine-Tuned Intrinsically Ultramicroporous Polymers Redefine the Permeability/Selectivity Upper Bounds of Membrane-Based Air and Hydrogen Separations. ACS Macro Lett. 2015, 4, 947–951.