Macromolecules

Finely Tuning the Free Volume Architecture in Iptycene-Containing Polyimides for Highly Selective and Fast Hydrogen Transport

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S Supporting Information

ABSTRACT: Iptycene-based polyimides have attracted extensive attention recently in the membrane gas separation field due to their unique structural hierarchy and chemical characteristics that enable construction of well-defined yet tailorable free volume architecture for fast and selective molecular transport. We report here a new series of iptycene-based polyimides that are exquisitely tuned in the monomer structure to afford preferred microcavity architecture for hydrogen transport. In particular, a triptycene-containing dianhydride (TPDAn) was prepared to react with two iptycene-containing diamines (i.e., TPDAm and PPDAm) or



2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6FAP) to produce entirely or partially iptycene-based polyimides. The incorporation of iptycene units effectively disrupted chain packing, which resulted in ultrafine microporosity in the membranes with a desired bimodal size distribution with maxima at ~3 and ~7 Å, respectively. Depending on the combination of diamine and dianhydride, the microporosity was feasibly tuned and optimized to meet the needs of challenging H₂ separations, especially for H₂/N₂ and H₂/CH₄ gas pairs. Particularly, a H₂ permeability of 27 barrers and H₂/N₂ and H₂/CH₄ selectivities of 142 and 300, respectively, were obtained for TPDAn-6FAP.

1. INTRODUCTION

Precise control over the free volume architecture (size and size distribution) in polymer materials is central to fast and selective molecular transport that concerns many critical separation applications such as membrane gas separations implemented in hydrogen recovery (H_2/CO_2 , H_2/N_2 , H_2/CH_4), air separation (O_2/N_2), natural gas purification (CO_2/CH_4), and carbon capture (CO_2/N_2).^{1–4} However, polymeric membranes are frequently challenged by a trade-off between permeability and selectivity, characterized by the well-known Robeson's upper bounds,^{5,6} and the challenge originates largely from the limited amount of free volume and very broad free volume size distribution.^{1–4} In this regard, high free-volume macromolecules with well-defined yet tailorable free volume architecture are potential materials for high performance polymeric membranes for gas separations.

Polyimides (PIs) are among the most widely used materials for membrane gas separation, owing to their exceptional thermal and chemical stability, excellent mechanical properties, a large family of monomer variants, and good gas selectivities. However, most common polyimides have relatively low fractional free volume (FFV) and thus low gas permeabilities, limiting their practical applications in large-scale gas separations. Recently, high free-volume polyimides, such as polyimides with intrinsic microporosity (PIM-PIs and $(KAUST-PIs)^{7-12}$ and polyimides containing Tröger's base,^{13,14} were reported, some of which demonstrated high separation performance for several gas pairs exceeding the Robeson's upper bounds. However, it has been observed that the significant improvement in permeabilities of these new polyimides was not always accompanied by the improvement of selectivities, and the gas separation properties, especially H₂-related separations, of some of these new polyimides are still challenged by the permeability—selectivity trade-off.

Our recent research^{15–17} as well as the studies reported by other groups^{10,11,18–22} showed that polyimide membranes prepared from iptycene-based monomers have great potential as gas separation membranes. It has been shown that iptycene structures are instrumental in generating large fractional free volume as well as constructing a well-defined free volume architecture that deliver impressive gas separation properties in the resulting polyimide membranes for various separation needs. In particular, we demonstrated that the intrinsic molecular cavities (i.e., internal free volume) defined by the shape of the iptycene molecules, especially the pentiptycene structure, provide great opportunity for architectural tailoring

Received: March 7, 2016 Revised: April 6, 2016 Scheme 1. Synthesis of Triptycene-Containing Dianhydride (TPDAn)



Scheme 2. Synthesis of Iptycene-Based Polyimides Based on TPDAn



through incorporation of different substituent groups that may partially fill the molecular cavities depending on their size. As such, precise control and fine manipulation of molecular sieving properties of the membranes have been achieved. In these studies, the aromatic polyimides containing iptycene structures were prepared via condensation polymerization between commercial 6FDA dianhydride and custom-synthesized iptycene-based diamines that were systematically varied in the structure (i.e., triptycene- or pentiptycene-based, CH₃- or CF₃substituted).^{15,16} We have found that the detailed monomer structure has significant impact on the chain rigidity, fractional free volume, and consequent gas transport properties of the solution-cast polymeric membranes. A study reported by Pinnau et al. on a series of triptycene-based PIM-PIs has also demonstrated the impact of the dianhydride-diamine combination on the properties of polyimide membranes.¹¹

In this study, we extend the efforts to develop a new series of entirely iptycene-based polyimides derived from a triptycenecontaining dianhydride (TPDAn)^{23,24} and our previously reported iptycene-containing diamines as well as a $-C(CF_3)_2$ bridged diamine (i.e., 6FAP, 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane) that mirrors 6FDA dianhydride structure in comparable polyimides. This new series of triptycene-dianhydride based polyimide membranes are discussed in depth regarding their synthesis (both the monomer and polymers) and characterization with a focus on establishing the correlation between the monomer/polymer structure and free volume architecture in the membranes by comparing them with our previously reported iptycenecontaining polyimides. Pure-gas transport properties in terms of permeability and selectivity are tested for H₂, N₂, Ar, CH₄, and CO₂ at 10 atm and 35 °C, which are assessed via comprehensive analyses of diffusivity and solubility coefficients to provide fundamental understanding on their transport properties. As such, combining with the data we reported earlier on iptycene-diamine-based polyimides^{15,16} and 6FDA-

6FAP polyimide,²⁵ this study provides a broad set of dianhydride-diamine combinations to elucidate the respective role of iptycene structure, either as diamine or dianhydride of the imide structure, in tailoring free volume architecture and impacting gas transport properties of the membranes.

2. EXPERIMENTAL SECTION

2.1. Materials. Triptycene- and pentiptycene-based diamine monomers (i.e., TPDAm and PPDAm) were prepared according to our previously reported procedures, which were dried at 100 °C under vacuum before use.^{15,16} 2,2'-Bis(3-amino-4-hydroxyphenyl)hexa-fluoropropane (6FAP, >98.5%) was purchased from Akron Polymer Systems and dried at 65 °C under vacuum overnight before use. Anthracene (Alfa Aesar, 97%), *p*-benzoquinone (Sigma-Aldrich, \geq 98%), hydrobromic acid (Sigma-Aldrich, 48 wt %), 4-nitrophthalonitrile (TCI, >98.0%), anhydrous *N*,*N*-dimethylacetamide (DMAc, EMD, 99.8%), acetic anhydride (Sigma-Aldrich, >98.0%), anhydrous pyridine (EMD, 99.8%), anhydrous 1-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich, 99.5%), and 1,2-dichlorobenzene (*a*-DCB, Sigma-Aldrich, 99%) were used as received.

2.2. Synthesis of Triptycene-Containing Dianhydride. Triptycene-based dianhydride monomer (TPDAn) was synthesized following the previously reported procedures with some modifications, shown in Scheme $1.^{23,24}$ In general, the triptycene skeleton containing two phenolic hydroxyl groups at 1,4-positions was first constructed via Diels-Alder cycloaddition of p-benzoquinone to anthracene followed by reduction, which was then substituted with 4-nitrophthalonitrile via nucleophilic aromatic substitution (S_NAr) reaction. The obtained tetranitrile compound was hydrolyzed into tetracarboxylic acid, which was further dehydrated into the final triptycene-based dianhydride. Modifications to the reported procedures were made during the hydrolysis step as follows: triptycene-based tetranitrile compound (5.0 g, 9.3 mmol) and 20 g of potassium hydroxide (KOH, 0.356 mol) were suspended/dissolved in an ethanol/water mixture (50 mL/50 mL), heated, and refluxed for 48 h. The resulting clear solution was acidized to pH = 1.0 with 6 M HCl solution, and white precipitates of tetracarboxylic acid were produced, which were filtered and washed with deionized (DI) water repeatedly. After drying under vacuum at 100 °C overnight, the obtained tetracarboxylic acid compound was refluxed in acetic anhydride (15 mL) for 6 h, followed by filtration and washing with petroleum ether. The final product of triptycenedianhydride (TPDAn, 4.89 g, yield 81%) was obtained as white powder after drying at 120 $^\circ$ C in a vacuum oven overnight; mp (melting point from differential scanning calorimetry at a heating rate of 5 °C min⁻¹): >300 °C. ¹H NMR (500 MHz, DMSO- d_6): δ 5.66 (s, 2H), 6.98-7.01 (m, 4H), 7.05 (s, 2H), 7.27-7.29 (m, 4H), 7.37 (s, 2H), 7.45-7.47 (d, J = 8.35 Hz, 2H), 8.09-8.11 (d, J = 8.40 Hz, 2H).

2.3. Synthesis of Iptycene-Based Polyimides. Iptycene-based polyimides were prepared by condensation polymerization between triptycene-containing dianhydride (TPDAn) and iptycene-containing diamine (i.e., TPDAm and PPDAm) or 6FAP through either chemical imidization or solution thermal imidization (Scheme 2). Specifically, TPDAn-TPDAm was synthesized using the following procedures: TPDAm (1.1731 g, 2 mmol) and anhydrous DMAc (12 mL) were added at room temperature into a flame-dried, three-necked flask equipped with a nitrogen inlet and a mechanical stirrer. After TPDAm was dissolved by stirring the mixture for several minutes, an equimolar amount of TPDAn (1.2259 g, 2 mmol) was added, and the flask was immersed in an oil bath, warmed gradually to 80 °C, and held for 30 min to dissolve TPDAn. The oil bath was then removed, and the solution was cooled down to room temperature and stirred overnight under N₂ purge to form a viscous poly(amic acid) solution. Cyclization of poly(amic acid) into polyimide was done by adding acetic anhydride (1.2 mL) and pyridine (1.2 mL), and the mixture was stirred for another 24 h to allow complete imidization. The resulting polyimide solution was precipitated in excess amount of methanol (500 mL) to give fibrous polyimide product, which was collected, washed with fresh methanol, and then dried at 160 °C under vacuum overnight giving white solid as TPDAn-TPDAm polyimide (2.26 g, yield 94%). ¹H

NMR (500 MHz, CDCl₃): δ 5.56 (s, 2H), 5.59 (s, 2H), 6.66–6.68 (d, J = 8.90 Hz, 2H), 6.84 (s, 2H), 6.87 (s, 2H), 7.01–7.02 (m, 4H), 7.02–7.04 (m, 4H), 7.20–7.22 (m, 4H), 7.24–7.25 (m, 2H), 7.25–7.26 (m, 4H), 7.43–7.45 (m, 2H), 7.50–7.51 (d, J = 2.10 Hz, 2H), 7.90–7.91 (d, J = 2.10 Hz, 2H), 7.94–7.96 (d, J = 8.30 Hz, 2H). ATR-FTIR (membrane, ν , cm⁻¹): 1782 (imide asym C=O str), 1723 (imide sym C=O str), 1374 (imide –C–N), 720 (imide C=O bending). Molecular weight measured by size exclusion chromatog-raphy (SEC) (DMF eluent, polystyrene standards): $M_n = 1.92 \times 10^4$ g mol⁻¹, $M_w = 3.98 \times 10^4$ g mol⁻¹, PDI = 2.08.

TPDAn–PPDAm was synthesized following a similar procedure with TPDAn–TPDAm, and the product was obtained as light-yellow fibrous solid (yield 95%). ¹H NMR (500 MHz, CDCl₃): δ 5.44 (s, 4H), 5.60 (s, 2H), 6.27–6.29 (d, *J* = 8.65 Hz) 6.41–6.43 (d, *J* = 8.95 Hz) (2H), 6.85 (s, 2H), 6.89–6.94 (m, 8H), 6.96–6.97 (m, 4H), 7.04 (s, 4H), 7.25–7.27 (m, 8H), 7.33 (s, 2H), 7.34–7.41 (m, 2H), 7.52 (s, 2H), 7.95–7.97 (d, *J* = 8.20 Hz, 2H), 8.00–8.02 (d, *J* = 10.25 Hz, 2H). ATR-FTIR (membrane, ν , cm⁻¹): 1780 (imide asym C=O str), 1723 (imide sym C=O str), 1374 (imide –C–N), 723 (imide C=O bending). Molecular weight (SEC, DMF eluent, polystyrene standards): $M_n = 2.10 \times 10^4$ g mol⁻¹, $M_w = 5.15 \times 10^4$ g mol⁻¹, PDI = 2.45.

TPDAn-6FAP was synthesized via solution thermal imidization instead of chemical imidization to avoid the reactions between hydroxyl groups of 6FAP and acetic anhydride: diamine 6FAP (1.1969 g, 3.3 mmol) and anhydrous NMP (13 mL) were added into a flamedried, three-neck flask equipped with a mechanical stirrer and nitrogen purge at room temperature. After complete dissolution of 6FAP, dianhydride TPDAn (1.8905 g, 3.3 mmol) was added, and the flask was warmed gradually to 80 °C and held for 30 min to dissolve TPDAn. The solution was then cooled down to room temperature and stirred overnight to form viscous poly(amic acid). To conduct solution thermal imidization, a Dean-Stark trap and a reflux condenser were connected to the flask and o-dichlorobenzene (6 mL) was added as an azeotropic reagent. The flask was gradually heated to 190 °C and refluxed for 12 h before the solution was cooled down and precipitated in a mixture of methanol and water (v/v = 1/1, 500 mL). Fibrous, white solid was collected, washed with fresh methanol, and then dried at 180 $^{\circ}\text{C}$ under vacuum overnight (2.96 g, yield 96%). ^{1}H NMR (500 MHz, DMSO-d₆): δ 5.71 (s, 2H), 6.96 (s, 4H), 7.01 (s, 2H), 7.08-7.10 (d, J = 8.75 Hz, 2H), 7.24 (s, 2H), 7.26 (s, 2H), 7.27 (s, 4H), 7.31 (s, 2H), 7.39 (s, 2H), 7.90–7.92 (d, J = 8.20 Hz, 2H), 10.52 (s, 2H). ATR-FTIR (membrane, ν , cm⁻¹): 3394 (broad, –OH), 1782 (imide asym C=O str), 1729 (imide sym C=O str), 1378 (imide -C-N), 724 (imide C=O bending). Molecular weight (SEC, DMF eluent, polystyrene standards): $M_{\rm p} = 3.97 \times 10^4$ g mol⁻¹, $M_{\rm w} = 1.24 \times 10^5$ g mol^{-1} , PDI = 3.12.

2.4. Film Casting. Thin films of the iptycene-based polyimides were prepared by casting polymer NMP solutions (~7% w/v, g mL⁻¹) onto clean, leveled glass plates. Solvent was evaporated slowly under an infrared lamp (Staco Energy Products Co., 120 V) at ~60 °C overnight; the obtained isotropic films were peeled off and soaked in methanol for 24 h for solvent exchange and finally dried at 180 °C under vacuum for 24 h. TPDAn-6FAP film was further thermally treated at 300 °C under nitrogen purge for 2 h to achieve fully imidized structure. All the films prepared are solvent-free using the above drying procedures, which was confirmed by thermogravimetric analysis (TGA). Film thickness (40–80 μ m) was measured with a digital micrometer, and effective area of the films in the gas permeation tests was determined using a digital scanner (LiDE120, Canon) and ImageJ software.

2.5. Characterization Methods. ¹H NMR spectra of both monomers and polymers were recorded on a Bruker 500 spectrometer using either deuterated chloroform or deuterated dimethyl sulfone as a solvent. The attenuated total reflection mode Fourier transform infrared (ATR-FTIR) spectra of the films were acquired on a Jasco FT/IR-6300 spectrometer with a resolution of 4 cm⁻¹ and 64 scans. Molecular weight and molecular weight distribution of the polyimides were measured by size exclusion chromatography (SEC, Waters GPC System) using polystyrene as an external standard and DMF as the eluent. A Waters 515 HPLC pump and three Polymer Standards



Figure 1. ¹H NMR spectra of iptycene-based polyimides (note: $CDCl_3$ was used as the solvent for TPDAn-TPDAm and TPDAn-PPDAm and DMSO- d_6 for TPDAn-6FAP).

Service (PSS) columns (GRAM, 10^4 , 10^3 , and 10^2 Å) were equipped in the DMF SEC at 55 °C with a DMF flow rate of 1 mL min⁻¹, and a Waters 2414 refractive index detector was connected using PSS WinGPC 7.5 software.

Thermogravimetric analysis (TGA) was carried out under a nitrogen atmosphere using a TGA Q500 instrument (TA Instruments) at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) analyses were performed under nitrogen purge (50 mL min⁻¹) on a DSC Q2000 (TA Instruments) at a heating rate of 10 °C min⁻¹ and cooling rate of 20 °C min⁻¹, and the thermal transition temperatures were reported based on the second heating cycle in the temperature range of 150–400 °C. Glass transition temperature (T_g) was determined based on the automatic mode of TA Universal Analysis software. Wide-angle X-ray diffraction (WAXD) patterns were recorded in the reflection mode at 40 mA and 40 kV on a Bruker D8 Advance Davinci diffractometer with Cu K α radiation (wavelength $\lambda = 1.54$ Å), and the scan speed and rate were 5 s per step and 0.02° per step, respectively.

Film densities were determined with a density kit of an analytical balance (ML204, Mettler Toledo) in deionized (DI) water using the buoyancy method at room temperature. Fractional free volume (FFV) of the polymer films was calculated as follows:

$$FFV = \frac{V_0 - 1.3V_w}{V_0}$$
(1)

where V_0 is the molar volume of the films derived from the density measurement, and V_w is the van der Waals volume estimated from Bondi's group contribution method.^{26,27}

The cavity size and size distribution within polymer membranes were investigated by positron annihilation lifetime spectroscopy (PALS), which was performed under vacuum $(1 \times 10^{-5} \text{ Torr})$ at room temperature using an EG&G Ortec (Oak Ridge, TN) fast–fast coincidence spectrometer. Polymer membranes were cut into ~1 × 1 cm pieces, which were then stacked to a thickness of 2 mm on either side of the positron source $(1.5 \times 10^6 \text{ Bq of } ^{22}\text{NaCl}$ sealed in a Mylar envelope). At least five files were collected for every sample, and each file contained 4.5 × 10⁶ integrated counts. The obtained data were analyzed with LT v9 software²⁸ using a source correction (1.609 ns and 4.002%) and modeled as the sum of four components. The first two components were attributed to the para-positronium self-annihilation (τ_1 , 0.125 ns) and the free annihilation (τ_2 , ~0.4 ns). The last two components were due to ortho-positronium (o-Ps) decay

in the free volume elements of the films. The size of free volume elements was calculated using the Tao–Eldrup equation: 29,30

$$\tau = \frac{1}{2} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right]$$
(2)

where τ is the lifetime, *R* is the radius of the pores, and $R_0 = R + \Delta R$ is the radius of potential well, where ΔR was determined to be 1.66 Å due to the thickness of the electron layer within the potential well. The pore size distributions were calculated using PAScual software.³¹

Pure gas permeabilities of the membranes were measured at 35 °C with five gases (H_2 , N_2 , Ar, CH_4 , and CO_2) using the constant-volume variable-pressure method.³² All membranes were degassed on both sides overnight before permeation tests. Upstream pressure was maintained at a predetermined value (i.e., 3.0, 6.4, 9.8, 13.0, and 16.6 atm), and the downstream pressure increase was recorded as a function of time. Gas permeability was then calculated based on the steady-state rate of pressure increase in the fixed downstream volume as follows:

$$P = 10^{10} \frac{V_{\rm d}l}{p_{\rm up} TRA} \left[\left(\frac{\mathrm{d}p}{\mathrm{d}t} \right)_{\rm ss} - \left(\frac{\mathrm{d}p}{\mathrm{d}t} \right)_{\rm leak} \right]$$
(3)

where *P* (barrer, 1 barrer = 10^{-10} cm³ (STP) cm/(cm² s cmHg)) is the gas permeability, *l* is the film thickness (cm), *V*_d is the calibrated downstream volume (cm³), *p*_{up} is the upstream pressure (cmHg), *A* is the effective film area (cm²), (d*p*/d*t*)_{ss} and (d*p*/d*t*)_{leak} are the steadystate pressure increment in downstream and the leak rate of the system (cmHg/s), respectively; *T* is the test temperature (K), and *R* is the gas constant (0.278 cm³ cmHg/(cm³ (STP) K)). The ideal selectivity ($\alpha_{A/B}$) for two different gases A and B was defined as the ratio of pure gas permeability of the two gases:

$$\alpha_{\rm A/B} \equiv \frac{P_{\rm A}}{P_{\rm B}} \tag{4}$$

The apparent diffusion coefficient $D(\text{cm}^2 \text{ s}^{-1})$ was obtained from the time-lag method using the equation³²

$$D = \frac{l^2}{6\theta} \tag{5}$$

where *l* is the film thickness (cm) and θ is the lag time (s). Solubility coefficient (*S*, cm³ (STP)/(cm³ atm)) was calculated via *S* = *P*/*D*.

3. RESULTS AND DISCUSSION

3.1. Polyimides Synthesis and Characterization. The triptycene-based dianhydride monomer (TPDAn) was prepared via dehydration of the intermediate tetracarboxylic acid compound with high yield (>80%) and high purity. Iptycenebased diamine monomers, i.e., TPDAm and PPDAm, were synthesized according to our previous reports,^{15,16} and a noniptycene diamine monomer (6FAP) was used for comparison. Three iptycene-based polyimides were synthesized via two-step condensation polymerization between TPDAn and an iptycene diamine or 6FAP, in which poly(amic acid) intermediates were prepared first followed by either chemical imidization to obtain TPDAn-TPDAm and TPDAn-PPDAm polyimides or solution thermal imidization to TPDAn-6FAP polyimide. TPDAn-6FAP films were further treated at 300 °C under a nitrogen purge in a furnace to achieve complete imidization. All polyimides have fully imidized structures as confirmed by ¹H NMR and ATR-FTIR spectra. As shown in Figure 1, peak assignments in the ¹H NMR spectra clearly verify the designed chemical structures of the polyimides. Specifically, the characteristic bridgehead protons of iptycene units (peaks 3 and c) are presented in the range of $\delta = 5.3-5.8$ ppm, suggesting successful incorporation of iptycene units in the main chains. The isometric structures of pentiptycene diamine (PPDAm) arising from restricted rotation of the ether bonds are also shown in the NMR spectra, which is in consistent with our previous studies.¹⁶ ATR-FTIR spectra of the polyimides (Figure 2) show the



Figure 2. ATR-FTIR spectra of the iptycene-based polyimide membranes.

characteristic imide bands at ~1784 cm⁻¹ (imide carbonyl, asymmetric stretching), ~1726 cm⁻¹ (imide carbonyl, symmetric stretching), ~1374 cm⁻¹ (imide C–N stretching), and ~720 cm⁻¹ (imide–carbonyl bending). No residual carbonyl

groups of poly(amic acid) intermediates is observed in the spectra, suggesting all polyimides are fully imidized.

Molecular weights and molecular weight distributions of the iptycene-based polyimides were measured with SEC, and the results are listed in Table 1. All the synthesized polyimides exhibit molecular weights greater than 19 200 g mol⁻¹ with polydispersity in the range of 2.0-3.1, suggesting sufficient reactivity and reasonably good purity of the triptycenedianhydride monomer synthesized in this work. It is expected that higher molecular weight polyimides can be feasibly obtained by applying more rigorous monomer purification processes and/or refining polycondensation reaction conditions. Thermal properties of these polymers were evaluated with DSC and TGA, and the results are tabulated in Table 1. No melting and crystallization peaks were observed in the DSC curves (Figure S1 in the Supporting Information), suggesting a completely amorphous structure of all three polyimides. Glass transition temperatures of TPDAn-TPDAm, TPDAn-PPDAm, and TPDAn-6FAP were determined to be 284, 350, and 305 °C, respectively, suggesting very high chain rigidity of these polymers. TPDAn-PPDAm polyimide shows the highest T_{α} due to the presence of very bulky pentiptycene units that tend to restrict chain motion. TPDAn-TPDAm shows a lower T_{a} than TPDAn-6FAP, most likely due to the flexible ether bonds of TPDAm monomer that decrease the chain rigidity. Entirely iptycene-based polyimides (e.g., TPDAn-TPDAm and TPDAn-PPDAm) exhibit high thermal stability, as shown in Table 1 and Figure S1. The thermal decomposition temperatures at 5% and 10% weight loss are in the range of 551-553 and 581-586 °C, respectively, and the char yields at 800 °C in nitrogen are all higher than 64%. For TPDAn-6FAP polyimide, a two-step weight loss profile was observed. This is a characteristic feature of o-hydroxyl-containing polyimides that can be thermally rearranged at high temperatures (>400 °C) into polybenzox-azole (PBO) structures.^{25,33-35} Studies of thermal rearrangement (TR) of TPDAn-6FAP polyimide will be reported in a different paper to avoid excessive information in this paper. It should be noted that no weight loss was observed up to 300 °C in all TGA curves, suggesting that all films were solvent-free after vacuum drying and the nonsolvent extraction procedure.

Aromatic polyimides generally have poor solubility in common organic solvents due to the rigid imide ring structure and the strong interchain interactions,³⁶ which frequently results in difficulties in membrane fabrication and processing for practical applications. However, the iptycene-based polyimides prepared in this study exhibit excellent solubility in a wide range of organic solvents such as DMF, chloroform, NMP, and DMSO, shown in Table 2. The good organic solubility of these iptycene-containing polyimides can be attributed primarily to the Y- or H-shaped structures of iptycene units as well as the bulky CF₃ substituent groups, both of which tend to reduce the interchain interactions in the polyimides by disrupting efficient chain packing and increasing

Table 1. Molecular Weights, Thermal Properties, and Fractional Free Volume (FFV) of Iptycene-Based Polyimides

polymer	$M_{\rm n}~({\rm g~mol^{-1}})$	X_n	PDI $(M_{\rm w}/M_{\rm n})$	T_{g} (°C)	$T_{d,5\%}^{a}$ (°C)	$T_{d,10\%}^{b}$ (°C)	char yield ^c (%)	density (g cm ⁻³)	FFV
TPDAn-TPDAm	19, 200	17	2.08	284	551	581	64	1.291	0.175
TPDAn-PPDAm	21, 000	16	2.45	350	553	586	67	1.260	0.187
TPDAn-6FAP	39, 700	44	3.12	305	424	490	60	1.339	0.170

 ${}^{a}T_{d,5\%}$: decomposition temperature at 5% weight loss. ${}^{b}T_{d,10\%}$: decomposition temperature at 10% weight loss. 'Residual weight retention after heated to 800 °C in a nitrogen atmosphere.

Tab	le 2.	Room	Temperature	Organic	Solvent	Solubility	y of I	ptycene	e-Based	Pol	yimides	
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	solvent ^a											
polymer	DMF $(12.1)^{b}$	DMSO (12.0)	NMP (11.2)	DMAc (10.8)	DCM (9.9)	acetone (9.8)	THF (9.5)	CHCl ₃ (9.2)	toluene (8.9)			
TPDAn-TPDAm	+	+	+	+	+	-	+	+	-			
TPDAn-PPDAm	+	+	+	+	+	-	+	+	+/-			
TPDAn-6FAP	+	+	+	+	+	+	+	+	+/-			
aD - 1		10	»11-1+			1.1	"	· / " ·· · · · · · · · · · · · · · · · ·	b _{TL}			

"Polymer solution concentration, 10 mg mL⁻¹; "+", soluble at room temperature; "-", insoluble at room temperature; "+/-", partially soluble. ^bThe numbers in parentheses denote the solubility parameters of testing solvents.³⁷

interchain distance. Particularly, the presence of bulky -C- $(CF_3)_2-$ groups in TPDAn-6FAP polyimide makes it soluble in almost all the solvents tested at room temperature. Additionally, the ether linkages introduced in the backbone structures is also believed to promote organosolubility of these entirely aromatic polyimides. As a result, these aromatic polyimides could be easily solution-casted into dense thin films (Figure S2).

3.2. Polymer Chain Packing and Microporosity. Free volume architecture (i.e., size and size distribution) is considered as a key structural parameter that determines gas transport properties of polymer separation membranes. Multiple characterization techniques were utilized to obtain a clear picture of how polymer chain packing and consequential free volume architecture are affected by incorporating iptycene structures in polymer backbone. Fractional free volume (FFV) values of these membranes were estimated using group contribution method coupled with density measurements, and the results are shown in Table 1. The iptycene-based polyimides easily fall into the family of high FFV polymers with FFV in the range of 0.170-0.187, which are higher than commercial membrane materials such as Matrimid polyimide (0.17) and polysulfones (0.13-0.17).³⁸ Entirely iptycene-based polyimides, i.e., TPDAn-TPDAm and TPDAn-PPDAm, have higher fractional free volume than partially iptycene-based polyimide of TPDAn-6FAP, indicating that the incorporation of iptycene structure into the polymer backbone is an effective approach to disrupt chain packing and introduce large amount of free volume. In particular, TPDAn-PPDAm polyimide containing both triptycene and pentiptycene units shows the highest FFV, which is due to the larger internal free volume of pentiptycene unit as well as bulkier structure of pentiptycene.¹⁶

Polymer chain packing of the polyimide membranes was investigated with wide-angle X-ray diffraction (WAXD); diffraction patterns are shown in Figure 3, and the peak positions and calculated *d*-spacing values are tabulated in Table 3. Broad halos instead of sharp peaks were observed in all WAXD patterns, suggesting a generally amorphous structure of the iptycene-based polyimides. This result is consistent with DSC results, in which no melting or crystallization peaks were observed. Depending on the monomer structure (i.e., triptycene or pentiptycene, entirely or partially iptycenebased), quite different diffraction patterns were observed for these polyimide membranes signifying different chain packing structures induced by iptycene moieties. TPDAn-PPDAm membrane that contains alternating triptycene and pentiptycene units along the polymer backbone shows three diffraction peaks (i.e., A, B, and C) located at $2\theta = 9.7^{\circ}$, 16.7°, and 23.3°, which correspond to d-spacing values of 9.1, 5.3, and 3.8 Å, respectively. These *d*-spacing values are likely associated with the main interchain distance disrupted by the rigid pentiptycene units (peak A), the average interchain distance of the imide backbone (peak B), and $\pi - \pi$ stacking of arene



Figure 3. WAXD patterns of iptycene-based polyimides (A, B, and C designate diffraction peak maxima).

Table 3. WAXD Diffraction Peak Positions (2θ) and Calculated *d*-Spacing Values of Iptycene-Based Polyimides and Some Literature Data for Comparison

		$2\theta~(\mathrm{deg})$		d-sj	d-spacing (Å)			
polymer	А	В	С	Α	В	С		
TPDAn-PPDAm	9.7	16.7	23.3	9.1	5.3	3.8		
TPDAn-TPDAm	11.6	20.9		7.6	4.3			
TPDAn-6FAP	13.7	18.4		6.5	4.8			
6FDA-mTMPD ¹⁸	14.4			6.15				
PIM-6FDA-OH ³⁹	13.8			6.4	6.4			
6FDA-DADBSBF ⁴⁰	17.0			5.2				

rings of iptycene moieties (peak C). For the entirely triptycenebased TPDAn-TPDAm membrane, two broad peaks were observed, which represent the main interchain distance disrupted by triptycene units and the average interchain distance of imide backbone, while one dominant broad amorphous halo was detected for TPDAn-6FAP, a partially triptycene-based polyimide. The main interchain distance (peak A) follows the expected trend of TPDAn-PPDAm > TPDAn-TPDAm > TPDAn-6FAP, which is consistent with the trend of FFV results determined by density measurements (Table 1). In particular, the entirely iptycene-based polyimides have much higher main interchain distance values than most of reported noniptycene-containing polyimides (Table 3),^{18,39,40} confirming the disruption of tight chain packing by iptycene units.

Positron annihilation lifetime spectroscopy (PALS) measurements were conducted on TPDAn-TPDAm and TPDAn-PPDAm membranes to quantitatively analyze the cavity size and size distribution. Two *o*-Ps components, i.e., τ_3 and τ_4 , which have annihilation lifetime of ~0.9 and ~3.0 ns,

polymer	τ_3 (ns)	I ₃ (%)	cavity diam d_3 (Å)	τ_4 (ns)	I_4 (%)	cavity diam d_4 (Å)
TPDAn-TPDAm	0.87 ± 0.10	8.8 ± 1.6	2.87 ± 0.38	2.70 ± 0.03	17.0 ± 0.4	6.84 ± 0.04
TPDAn-PPDAm	0.94 ± 0.09	8.2 ± 1.1	3.10 ± 0.33	3.07 ± 0.03	16.9 ± 0.3	7.36 ± 0.04
PTMSP ⁴¹	1.7	7.4	5.1	8.8	34	12.4
aPBO ⁴²	1.06 ± 0.09	7.1 ± 0.7	3.51 ± 0.28	3.90 ± 0.04	12.7 ± 0.7	8.37 ± 0.04
PIM-1 ⁴¹	2.06	6.15	5.8	6.28	18.6	10.6

Table 4. Cavity Size Characterization of Iptycene-Based Polyimides Measured by PALS Compared with Some High FFV Polymers Reported Previously

respectively, were observed, indicating two populations of micropores, or bimodal size distribution of free volume elements, in the membranes. Based on eq 2, the average cavity size was calculated, and the results are shown in Table 4 and compared with a few reported high-free-volume polymers. Two kinds of microcavities can be defined: ultrafine micropores with an average diameter of $d_3 \sim 3$ Å ($\tau_3 \sim 0.9$ ns) and micropores with an average diameter of $d_4 \sim 7$ Å ($\tau_4 \sim 3.0$ ns). As expected, TPDAn-PPDAm polyimide containing alternating triptycene and pentiptycene units shows larger pore sizes (7.36 and 3.10 Å) than those of fully triptycene-based TPDAn-TPDAm membrane (6.84 and 2.87 Å). On the other hand, almost the same annihilation intensities (I_4) were observed for these two membranes, indicating the same concentration of micropores. The results are consistent with FFV data determined from density measurements as well as the interchain spacing results by WAXD. It is evident that iptycene structure, especially bulky pentiptycene structure, is very effective in disrupting chain packing and generating large micropores enabling fast gas transport.^{10,11,18–22}

Conventional polyimides generally show only one *o*-Ps component, which typically suggests a very broad free volume size distribution.^{33,42} In this study, two *o*-Ps components were observed in both entirely iptycene-based polyimide membranes, suggesting a bimodal microcavity size distribution (Figure 4).



Figure 4. Microcavity size distribution of TPDAn-TPDAm and TPDAn-PPDAm from positron annihilation lifetime spectroscopy (PALS) measurements.

Compared with TPDAn-TPDAm, both peaks of TPDAn– PPDAm shifted toward larger cavity sizes, which is consistent with FFV and WAXD interchain spacing data, indicating both larger ultrafine cavities and larger microcavities induced by the pentiptycene units. Bimodal free volume size distribution, which has been observed in high performance gas separation membranes such as PIM, is considered to be beneficial for gas separation membranes in that such free volume architecture resembles the shape of an "hourglass", whereby the large openings allow fast adsorption/desorption at the surface while the narrow necking enables size discrimination, leading to both high permeability and high selectivity.^{10,11,33,41,42} In this study, the small \sim 3 Å cavities are likely associated with the (partially filled) internal free volume between the "blades" of iptycene units,^{15,16} which might provide interconnections between the large \sim 7 Å cavities, resulting in improved gas permeabilities.³³ Additionally, these small cavities have an average diameter of \sim 3 Å, which is slightly larger than the kinetic diameter of H₂ (2.89 Å) but smaller than those of other test gases in this study (i.e., CO₂ 3.35 Å, Ar 3.40 Å, N₂ 3.64 Å, and CH₄ 3.80 Å). As will be discussed later, this microstructural feature is responsible for the excellent separation performance of these iptycene dianhydride-based polyimides in hydrogen-related gas separation.

3.3. Gas Permeation Properties. Pure gas permeation tests of iptycene-based polyimides for five gases (H_2 , N_2 , Ar, CH_4 , and CO_2) were conducted at 35 °C with a wide range of feed pressure of 3–17 atm. As shown in Figure S3, all gas permeabilities exhibited very weak dependence on feed pressure. In the case of CO_2 permeation, this observation indicates that the films are resistant to plasticization up to 17 atm feed pressure. Table 5 summarizes the gas transport properties measured at 10 atm and 35 °C along with the calculated diffusivity and solubility coefficients. The data of several commercial membranes are listed for comparison.

For all three iptycene-based polyimides, gas permeabilities follow the order of $P(H_2) > P(CO_2) > P(Ar) > P(N_2) >$ $P(CH_4)$, which is consistent with the kinetic diameters of the testing gases. The same trend is also observed in diffusivity coefficient, suggesting the size sieving mechanism in these separation membranes and the dominant role of gas diffusivity. It is evident that the variation in monomer structure significantly influenced the gas transport properties of the resulting iptycene-based polyimides. Compared with TPDAn-6FAP, TPDAn-TPDAm exhibits higher gas permeabilities for all gases. For example, CO₂ permeability of TPDAn-TPDAm is 2 times that of TPDAn-6FAP (Table 5). This is because TPDAm diamine has very bulky triptycene unit and CF₃ substituent groups that are more effective in disrupting chain packing than 6FAP diamine, leading to a higher free volume fraction. Additionally, the hydroxyl groups in 6FAP diamine induced strong interchain hydrogen bonds, which tend to decrease the interchain distance (Figure 3) and thus diffusivity (Table 5). On the other hand, TPDAn-TPDAm and TPDAn-6FAP polyimides showed very similar solubility coefficients (S), indicating that the separation mechanism is kinetically dominant in these membranes. As expected, replacing triptycene unit with bulkier pentiptycene unit in the diamine structure further increased the gas permeabilities, and TPDAn-PPDAm shows the highest gas permeabilities for all gases among the three polyimides. Although the solubility coefficients

Table 5. Pure Gas Permeability (P), Diffusivity Coefficient (D), Solubility Coefficient (S), and Ideal Selectivity of Iptycene-Based Polyimides Compared with Commercial Membranes

				test gas			ideal selectivity (α)			
polymers		H ₂	CO ₂	Ar	N ₂	CH ₄	H_2/N_2	H_2/CO_2	H_2/CH_4	CO ₂ /CH ₄
TPDAn-PPDAm	Pa	96	39	3.9	1.8	1.5	53	2.5	64	26
	D	1112	39	35	24	11	46	29	98	3.4
	S	0.66	7.7	0.85	0.57	1.0	1.2	0.09	0.66	7.7
TPDAn-TPDAm	Р	36	9.7	0.95	0.44	0.31	82	3.7	116	31
	D	820	14	12	8.6	2.7	95	59	304	5.2
	S	0.33	5.3	0.63	0.39	0.87	0.85	0.06	0.38	6.1
TPDAn-6FAP	Р	27	4.7	0.38	0.19	0.09	142	5.7	300	52
	D	628	7.2	5.3	3.7	1.3	170	87	483	5.5
	S	0.33	5.0	0.55	0.39	0.51	0.85	0.07	0.65	9.8
polysulfone ⁴³	Р	14	5.6		0.25	0.25	56	2.5	56	22
CA-2.45 ^b 44	Р	12	4.8		0.15	0.15	80	2.5	80	32
matrimid ⁴⁵⁻⁴⁷	Р	18	10		0.32	0.28	56	1.8	64	36
aramid ⁴⁸	Р	24.5				0.1			245	

^{*a*}Units: *P*, 10^{-10} cm³ (STP) cm/(cm² s cmHg); *D*, 10^{-9} cm²/s; *S*, cm³ (STP)/(cm³ atm). ^{*b*}CA-2.45: cellulose acetate with degree of acetylation of 2.45.



Figure 5. Effect of the diamine and dianhydride structure on (a) H_2 permeability and (b) H_2/N_2 selectivity for iptycene-based polyimides (note: the triptycene diamine of 1,4-trip_CF₃¹⁵ and pentiptycene diamine of PPDA(CF₃)¹⁶ were renamed from the published ones as TPDAm and PPDAm, respectively, in this paper to keep consistency).

(S) of TPDAn-PPDAm are slightly higher than those of TPDAn-TPDAm and TPDAn-6FAP membranes, it is the significant increases in the diffusivity coefficients (D) of TPDAn-PPDAm membrane that are responsible for the dramatic increase of gas permeabilities, signifying the dominant role of diffusivity in these size-sieving membranes. The permeability results are consistent with FFV analysis, the interchain packing results from WAXD, and the cavity size and size distribution analysis from PALS, as discussed previously. The ideal selectivities generally showed a decreasing trend with increasing gas permeabilities. However, the ideal selectivities decreased at a slower rate than what has been typically observed for glassy membranes, leading to improved overall separation performance.

To obtain better understanding of the respective role of diamine and dianhydride structure in affecting chain packing and consequent transport behavior in the iptycene-based membranes, gas transport properties of the new membranes in this study are compared with our previously reported iptycene-based polyimides as shown in Figure 5. The previously reported polyimides, i.e., 6FDA-1,4-trip CF_3^{15} and 6FDA-

 $PPDA(CF_3)$,¹⁶ differ from the ones in this study in that a noniptycene 6FDA dianhydride was used. Given the same diamine monomers (i.e., TPDAm or PPDAm), TPDAn-TPDAm and TPDAn-PPDAm polyimides in this study exhibit relatively lower gas permeabilities compared with their 6FDAbased counterparts, despite that TPDAn has a very bulky triptycene unit. It has been demonstrated that the hexafluoro substituted carbon (i.e., $-C(CF_3)_2-$) of 6FDA dianhydride increases the stiffness of the polymer chain and frustrates chain packing due to the steric hindrance from the CF₃ groups, leading to large fractional free volume in the corresponding polyimides.^{3,49} On the other hand, the flexible ether bonds in TPDAn structure likely promote tight interchain packing, resulting in lower overall fractional free volume despite of the bulkiness of triptycene structure. However, gas selectivities of TPDAn-based polyimides are higher than those of 6FDA-based polyimides, especially for hydrogen-related gas separations (Figure 5b). For example, H_2/N_2 selectivity of TPDAn-PPDAm is almost 2 times that of 6FDA-PPDAm given the same diamine. A similar trend of improved H2-related selectivity is observed for other gas pairs such as H₂/CO₂



Figure 6. Permeability-selectivity upper bound plots of TPDAn-PPDAm (\blacksquare), 6FDA-PPDAm¹⁶ (\square), TPDAn-TPDAm (\blacklozenge), 6FDA-TPDAm¹⁵ (O), TPDAn-6FAP (\blacktriangle), and 6FDA-6FAP²⁵ (\triangle) for (a) H₂/N₂ and (b) H₂/CH₄ gas pairs. Data points of commercial materials are included for comparison: 1, Matrimid;⁴⁵⁻⁴⁷ 2, polysulfone;⁴³ 3, CA-2.45.⁴⁴

and H_2/CH_4 as shown in Figure S4. This observation suggests that iptycene units are particularly useful in constructing ultrafine micropores for selective hydrogen transport, which is in agreement with the bimodal pore size distribution analysis by PALS discussed earlier.

Comparisons between TPDAn-6FAP and our previously reported 6FDA-6FAP²⁵ further demonstrated that iptycenebased structure is instrumental to boost both H₂ permeability and selectivities. For instance, TPDAn-6FAP not only exhibits the highest H₂/N₂ selectivity of 142 and H₂/CH₄ selectivity of 300 but also outperforms 6FDA-6FAP in terms of H₂ permeability. All above observations suggest that the bimodal size distribution of free volume elements created/induced by iptycene structure in the membranes holds the key to the fast and ultraselective transport of H₂ molecules. Compared with commercially relevant polymer membranes that are typically used for hydrogen recovery,¹ such as polysulfone,⁴³ CA-2.45,⁴ and aramid,⁴⁸ iptycene-based polyimides in this study show much higher H₂ permeability and, more importantly, they show equal or even higher selectivities than these commercial membranes. For example, given the same FFV, TPDAn-6FAP exhibits a 1.5 times H_2 permeability and around 3 times H_2/N_2 selectivity when compared to Matrimid (Table 5). These gas permeation results reveal the synergetic effect of iptycene units on the improvements of both permeability and selectivity for hydrogen separation.

Gas transport data of iptycene-based polyimides were plotted against the Robeson's upper bounds for H_2/N_2 and H_2/CH_4 gas pairs to evaluate their gas separation performance,^{5,6} shown in Figure 6. Commercial membranes, i.e., Matrimid, polysulfone, and CA-2.45, are included for comparison. Generally, iptycene-based polyimides membranes exhibit significantly improved performance in terms of the permeability/selectivity trade-off when compared with commercial polymers, and some of the membranes display separation performance beyond the 1991 upper bound. The permeability/selectivity trade-off of TPDAn-PPDAm outperforms that of TPDAn-TPDAm, suggesting preferred cavity architecture was obtained in TPDAn-PPDAm due to the incorporation of pentiptycene units. Compared with 6FDA-based polyimides, TPDAn-6FAP and TPDAn-PPDAm show better hydrogen-related gas separation performance, and TPDAn-6FAP shows the best hydrogen separation performance among the three polyimides

with a hydrogen permeability of 27 barrers and H_2/N_2 and H_2/CH_4 selectivities of 142 and 300, respectively.

4. CONCLUSIONS

A general methodology was reported for the synthesis of iptycene-based polyimides using a triptycene-based dianhydride (TPDAn) with select iptycene-based diamine (TPDAm or PPDAm) or noniptycene 6FAP. All polyimides exhibited good solubility in common organic solvents and excellent thermal stability. Owing to the incorporation of iptycene units, they all showed high FFV, amorphous chain packing structures, and bimodal microcavity size distribution with two maxima at ~ 3 and \sim 7 Å, respectively. The entirely iptycene-based polyimides, i.e., TPDAn-TPDAm and TPDAn-PPDAm, exhibited higher FFV and higher interchain distances than those of a partially iptycene-based TPDAn-6FAP polyimide, and pentiptycenecontaining TPDAn-PPDAm polyimide showed the highest FFV and main interchain distance indicating the effectiveness of bulkier pentiptycene in disrupting tight chain packing. In comparison with previous reports on 6FDA-based polyimides, TPDAn-based polyimides showed much higher H₂ selectivity, most likely due to the bimodal size distribution of microcavities that features a population of ultrafine microcavities. In general, incorporation of iptycene units resulted in both higher permeabilities and higher selectivities when compared with commercial membrane materials for hydrogen separation. Particularly, H₂ permeability of 27 and H₂/N₂ and H₂/CH₄ selectivities of 142 and 300 was obtained for TPDAn-6FAP, suggesting its great potential for hydrogen purification.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.6b00485.

DSC and TGA curves for the iptycene-based polyimides, pictures of thin films of the polyimides, the feed pressure dependence of gas permeabilities, and effect of diamine and dianhydride structures on gas selectivities (PDF)

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Notes

The authors declare no competing financial interest.

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