Penttiptycene-based Polyimides with Hierarchically Controlled Molecular Cavity Architecture for Efficient Membrane Gas Separation

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ABSTRACT: A series of new penttiptycene-containing diamines with systematically varied substituent groups were designed and synthesized with high purity and high yields. These diamines were used to prepare a series of new polyimides with 4,4'-hexafluoroisopropylidene bisphthalic dianhydride (6FDA) by conventional condensation polymerization. The obtained penttiptycene-containing polyimides possessed high molecule weights, excellent thermal stability, good solubility in a wide range of organic solvents and thus excellent processability for membrane fabrication. Because of the excess amount of internal free volume associated with the molecular cavities in the penttiptycene moieties and the consequently disrupted chain packing, all the polyimides exhibited high fractional free volume (FFV) leading to high gas permeabilities as well as good selectivities that are highly desired for gas separation membranes. In addition, the comparisons between the penttiptycene-containing polyimides bearing various substituent groups indicated that free volume, the vital structural parameter for fast and selective molecular transport, was very sensitive to the size of the substituent groups. Large substituent groups such as CF₃ led to increased FFV, while relatively small substituent groups such as CH₃ resulted in reduced FFV, possibly due to the mechanism of “partial filling” of the molecular cavities of penttiptycene units by the substituent groups. Gas permeability data also supported this unusual trend of the dependence of free volume on the substituent groups. This finding provides a completely new and potentially novel means of molecular-level manipulations to predictably construct preferred free volume

architecture that may maximize the separation performance of polymeric membranes.

Keywords: pentiptycene, polyimides, free volume, gas separation membrane

1. Introduction

Polymeric membrane-mediated gas separation has attracted much attention during the past few decades due to their comparable advantages such as relatively low cost and energy efficiency, and ease of operation in applications like natural gas purification, carbon capture, air separation and hydrogen purification.[1-3] Fast and selective transport combined with scalability and chemical, mechanical, and thermal stability in the process environment are key attributes of an ideal polymer membrane for efficient gas separations. However, polymeric membranes are often challenged by a tradeoff between permeability and selectivity, evidenced as the Robeson's upper bound.[4, 5] This upper bound limit largely originates from the limited amount of free volume and the out-of-the-regime size distribution of the free volume elements in polymer membranes.[3, 6-8] Thus an obvious solution to this challenging problem is to develop novel macromolecular structures featuring high fractional free volume and optimized free volume size distribution to enable fast and selective molecular transport.

Polymers with high fractional free volume are generally highly desired for high gas throughput. The creation of high fractional free volume in polymer membranes generally involves disruption of efficient or dense chain packing. Typically this objective can be achieved via introducing bulky side groups to increase inter-chain spacing, or including certain spiro-centers in the main chain structure to create highly contorted polymer backbone. For example, a novel class of ladder-like polymers known as "polymers of intrinsic microporosity" (PIMs) was developed recently.[9-12] PIMs uniquely contain rigid contorted spiro-units in the main chain structure, which restrict conformational freedom and prevent efficient chain packing leading to high fractional free volume and consequently very high gas permeabilities.[9, 13, 14] However, like other high free volume glassy polymers, the significant improvement in gas permeabilities was not always accompanied by the similar improvement in selectivities. In other words, the ability to tune the transport properties in these polymeric materials through changes in primary and secondary chain architecture still appears to be limited by the upper bound. This is largely due to the lack of control on the size and size distribution of free volume elements in these polymers. Therefore there is an obvious need of the right structural elements and revolutionary molecular manipulation mechanism that can feasibly control the free volume architecture to achieve highly selective and efficient gas separation.

1 Recently we reported a series of new aromatic polyimides containing triptycene units in the main
2 chain structure as gas separation membrane materials, which showed very interesting and promising
3 gas transport properties.[15] Triptycene is a three-dimensional symmetric, bulky and rigid molecule
4 composed of three benzene “blades” in paddlewheel-like configuration (Figure 1a). Because of the
5 disrupted chain packing due to the bulkiness of triptycene units, membranes of triptycene-bearing
6 polyimides show high fractional free volume and decent gas transport properties.[6, 15-18] As
7 demonstrated in our previous paper on triptycene-polyimide membranes,[15] a unique and
8 appealing feature of this simplest triptycene molecule is that the open space between the benzene
9 rings, called “internal free volume”, not only introduces significant amount of “intrinsic” free
10 volume into the polymer for fast transport, but also provides a feasible means to finely tune the size
11 of internal free volume or molecular cavity by varying the substituent groups neighboring the
12 triptycene units. This exciting finding greatly stimulates further studies to explore the potential of
13 these interesting polymers for gas separation membrane applications. As a natural extension of the
14 triptycene-based structure, pentiptycene-containing polyimides are reported here to demonstrate
15 their potential as high performance gas separation membranes. Pentiptycene, another member of the
16 triptycene family, is composed of five arene rings fused together into a rigid, H-shaped scaffold.[19,
17 20] Its three-dimensional structure is shown in Figure 1b. Compared with triptycene, pentiptycene
18 possesses even bulkier structure that can effectively hinder polymer chain packing leading to higher
19 fractional free volume. More importantly, pentiptycene has more open clefts, i.e., more “internal
20 free volume”, and the size of these well-defined molecular cavities is comparable with the kinetic
21 diameters of the common gases (e.g., He, H₂, CO₂, O₂, N₂, CH₄). Such molecular cavities may be
22 (partially) occupied by substituent groups or guest molecules to control the overall free volume size
23 and size distribution of the material, thereby providing an efficient tool for molecular engineering
24 and making pentiptycene a potentially very useful component for the fabrication of gas separation
25 membrane materials.

Fig. 1. Three-dimensional structure of (a) triptycene[21] and (b) pentaptycene molecule. (Note: the dimension of pentaptycene was estimated from the centroids of the extreme hydrogen atoms according to the geometry of the molecular configuration at ground energy state.)

Like triptycene, pentaptycene has found versatile usages in constructing supramolecular structures of both fundamental and practical importance, such as light-driven molecular “brake”, fluorescence and chemical sensors, etc.[22-25] However, incorporation of pentaptycene into polymer backbone structure has been sparsely reported, possibly because the polymerizable pentaptycene monomers are not readily available.[18, 26-28] In this study, we report for the first time the synthesis and characterization of a class of new pentaptycene-containing polyimides derived from a series of newly-designed pentaptycene diamine monomers. The aim of this work was to gain more molecular level understanding of the tunability of free volume architecture induced by iptycene units in the polymer materials to provide useful guidance in developing next generation high performance gas separation membranes. In this research the profound effects of the (partial) occupation of substituent groups in the molecular cavities on the gas transport properties of these new polyimides are demonstrated.

2. Experimental

2.1. Materials

Anhydrous *N,N*-Dimethylacetamide (DMAc, 99.8%), hydrazine monohydrate (98.0%), palladium on carbon (Pd/C, 10 wt.%), acetic anhydride (□98.0%) and anhydrous pyridine (99.8%) were obtained from Sigma-Aldrich (USA) and used as received. 1-Fluoro-4-nitrobenzene (Aldrich, 99.0%), 2-chloro-5-nitrotoluene (TCI, □98.0%) and 2-chloro-5-nitrobenzotrifluoride (Alfa Aesar, 98.0%) were used as received. Potassium carbonate (Alfa Aesar, 99.0%) was dried at 80 °C

overnight prior to use. 4,4'-Hexafluoroisopropylidene bisphthalic dianhydride (6FDA, $\square$ 99.0%) was purchased from Akron Polymer Systems and dried at 160 °C under vacuum for 12 hours before use. All other chemical reagents were obtained from commercial sources and used as received.

2.2. Synthesis of pentiptycene-containing diamine monomers

Pentiptycene-containing diamine monomers (**4a-4c**) were synthesized by a reduction of the intermediate pentiptycene dinitro compounds (**3a-3c**), which were generated via the aromatic nucleophilic substitution (S_NAr) between pentiptycene diol and select halogenated nitro compounds, as shown in Scheme 1. The intermediates, i.e., pentiptycene diquinone (**1**) and pentiptycene diol (**2**) were synthesized according to previous reports.[29, 30] Two different *meta*-substituent groups (i.e., CH₃ and CF₃) were introduced at the position neighboring the pentiptycene units to investigate the tunability of the free volume in the corresponding polymers by probing the molecular cavities defined by the arene planes of the pentiptycene units.

Scheme 1. Synthesis of pentiptycene-containing diamine monomers.

2.2.1. Synthesis of pentiptycene-containing dinitro compounds (**3a-3c**)

Under a nitrogen atmosphere, pentiptycene diol (**2**, 5.0 g, 10.8 mmol) and 1-fluoro-4-nitrobenzene (3.05 g, 21.6 mmol) were dissolved in DMF (30 mL) in a two-necked flask followed by the addition of K₂CO₃ (3.29 g, 23.8 mmol). After stirring at 150 °C under N₂ atmosphere for 8 h, the reaction mixture was poured into a mixture of methanol and water (800 mL, v/v = 1:1) under vigorous stirring. The precipitate was filtered, washed with methanol and deionized (DI) water extensively, and dried at 110 °C in a vacuum oven overnight to obtain a light green powder as the dinitro

compound **3a** (7.02 g, yield 87%). mp (melting point from differential scanning calorimetry at a heating rate of 5 °C·min⁻¹): □ 300 °C. ¹H NMR (500 MHz, CDCl₃): δ 5.37 (s, 4H), 6.87–6.89 (d, *J* = 9.20 Hz, 4H), 6.90–6.92 (m, 8H), 7.06–7.09 (m, 8H), 8.23–8.26 (d, *J* = 9.25 Hz, 4H).

The synthetic procedure of dinitro compound **3b** was similar to that of dinitro **3a**. The resulting mixture was precipitated in the mixture of methanol and water (v/v = 1:1), filtered and washed with methanol and DI water, and then dried under vacuum at 110 °C overnight to yield a white powder as dinitro compound **3b** (yield 90%). mp: 256 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.81 (s, 6H), 5.29 (s, 4H), 6.01–6.03 (d, *J* = 9.00 Hz) 6.10–6.12 (d, *J* = 9.10 Hz) (2H), 6.79–6.87 (m, 8H), 6.95–6.97 (m) 7.30–7.32 (d, *J* = 6.80 Hz) (8H), 7.76–7.78 (m) 7.88–7.90 (d, *J* = 6.95 Hz) (2H), 8.39 (s, 2H).

Dinitro **3c** was synthesized following the similar procedure used for **3a** and **3b**, except that the reaction temperature was lowered to 100 °C. The resulting mixture was poured into the methanol and water (v/v = 1:1), filtered, washed and dried under vacuum at 110 °C overnight giving a white powder as dinitro compound **3c** (yield 90%). mp: 253 °C. ¹H NMR (500 MHz, CDCl₃): δ 5.34 (s, 4H), 6.26–6.28 (d, *J* = 9.10 Hz) 6.40–6.41 (d, *J* = 9.10 Hz (2H), 6.82–6.83 (d, *J* = 7.05 Hz) 6.88–6.90 (m) (8H), 6.97–7.00 (m) 7.29–7.33 (m) (8H), 8.10–8.12 (m) 8.23–8.25 (m) (2H), 8.83–8.85 (m, 2H).

2.2.2. Synthesis of pentiptycene-containing diamine compounds (**4a-4c**)

In a two-necked flask, dinitro **3a** (6.0 g, 8.5 mmol), 10% Pd/C (0.2 g) and ethanol (400 mL) were added under a nitrogen atmosphere. The mixture was heated to reflux, and then hydrazine monohydrate (10 mL, 200 mmol) was added dropwise over 2 h. After stirring under reflux for 48 h, ethanol was evaporated under vacuum and DMF (40 mL) was then added to dissolve the diamine product. The solution was filtered off to remove Pd/C and precipitated in a mixture of methanol and DI water (v/v = 1:1) to obtain a white solid. The solid was washed with methanol and DI water three times and dried under vacuum at 100 °C overnight giving **4a** (5.2 g, yield 85%). mp: □ 300 °C. ¹H NMR (500 MHz, DMSO-*d*₆): δ 4.89 (s, 4H), 5.56 (s, 4H), 6.49□6.51 (m, 4H), 6.52□6.54 (m, 4H), 6.87□6.90 (m, 8H), 7.11□7.14 (m, 8H).

The procedure to prepare diamine **4b** was similar to that used for **4a**. After all the ethanol was evaporated, DMF was added into the flask to dissolve the amine product and facilitate the filtration to remove the catalyst. The solution was precipitated in methanol and water (v/v = 1:1), washed and dried to obtain a white powder as **4b** (yield 88%). mp: □ 300 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ

2.45 (s, 6H), 4.75 (s, 4H), 5.37 (s, 4H), 5.55□5.57 (d, $J = 7.90$, 2H), 6.05□6.07 (d, $J = 7.25$, 2H), 6.66 (s, 2H), 6.85 (br, s, 8H), 7.05 (br, s, 8H).

Diamine **4c** was synthesized according to the same procedure as diamine **4b**. The product was obtained as a white powder (yield 88%). mp: □ 300 °C. ^1H NMR (500 MHz, DMSO- d_6): δ 5.33 (s, 4H), 5.44 (s, 4H), 5.67–5.69 (d, $J = 11.05$ Hz) 5.78–5.80 (d, $J = 10.90$ Hz) (2H), 6.50□6.52 (m) 6.58□6.60 (d, $J = 9.40$ Hz) (2H), 6.87□6.89 (m, 8H), 6.94□6.96 (m) 7.26□7.28 (d, $J = 8.70$ Hz) (8H), 7.16□7.17 (d, $J = 3.15$ Hz, 2H).

Scheme 2. Synthesis of pentiptycene-based polyimides.

2.3. Synthesis of pentiptycene-containing polyimides

Pentiptycene-based polyimides were synthesized by condensation polymerization between pentiptycene-containing diamines (**4a-4c**) and 6FDA via conventional chemical imidization method as shown in Scheme 2.[31] The procedure to prepare 6FDA-PPDA(H) is described below as an example: to a flame-dried, three-necked flask equipped with a nitrogen inlet and a mechanical stirrer were added the diamine monomer **4a** (2.4214 g, 3.7 mmol) and anhydrous DMAc (18 mL). After dissolution, the flask was immersed into ice water, and an equimolar amount of the dianhydride monomer 6FDA (1.6683 g, 3.7 mmol) was added. Under stirring, the resulting mixture was warmed gradually to room temperature and held overnight under nitrogen atmosphere to form viscous poly(amic acid) solution. A mixture of acetic anhydride (2.2 mL) and pyridine (2.2 mL) was then added into the flask to cyclize the poly(amic acid) to the polyimide. After stirring for

another 24 h, fibrous polyimide product was obtained by precipitating the solution into excess amount of methanol (500 mL) as a thin, continuous stream. The resulting solid was filtered, washed with fresh methanol, and then dried at 140 °C under vacuum for 24 h giving fully imidized 6FDA-PPDA(H) (3.89 g, yield 95%). ¹H NMR (500 MHz, CDCl₃): δ 5.46 (s, 4H), 6.88 (s, 8H), 6.91–6.93 (d, *J* = 8.30 Hz, 4H), 7.10 (s, 8H), 7.33–7.35 (d, *J* = 8.35 Hz, 4H), 7.90–7.92 (d, *J* = 7.90 Hz, 2H), 7.97 (s, 2H), 8.06–8.07 (d, *J* = 7.95 Hz, 2H). ATR-FTIR (membrane, ν, cm⁻¹): 1784 (imide asym C=O str), 1723 (imide sym C=O str), 1377 (imide –C–N), 720 (imide C=O bending). Molecular weight, by size exclusion chromatography (SEC), (DMF eluent, polystyrene standards): $M_n = 3.46 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 8.10 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, PDI = 2.34.

Following the above procedure, 6FDA-PPDA(CH₃) was prepared from **4b** diamine and dianhydride 6FDA as a light-yellow fibrous solid (yield 96%). ¹H NMR (500 MHz, CDCl₃): δ 2.78 (s, 6H), 5.36 (s, 4H), 6.08–6.10 (d, *J* = 7.50 Hz) 6.18 (s) (2H), 6.88 (s, 8H), 6.91 (br, s, 2H), 6.95 (s) 7.30 (s) (8H), 7.47 (s, 2H), 7.90–7.92 (d, *J* = 7.55 Hz, 2H), 7.97 (s, 2H), 8.06–8.08 (d, *J* = 7.75 Hz, 2H). ATR-FTIR (membrane, ν, cm⁻¹): 1784 (imide asym C=O str), 1726 (imide sym C=O str), 1374 (imide –C–N), 720 (imide C=O bending). Molecular weight (SEC, DMF eluent, polystyrene standards): $M_n = 4.25 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 9.16 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, PDI = 2.16.

Similarly 6FDA-PPDA(CF₃) polyimide was the same as that used for 6FDA-PPDA(H) and 6FDA-PPDA(CH₃). The polymer was obtained as white fibrous solid with a yield of 97%. ¹H NMR (500 MHz, CDCl₃): δ 5.43 (s, 4H), 6.28–6.30 (d, *J* = 8.85 Hz) 6.41–6.43 (d, *J* = 8.90 Hz) (2H), 6.87–6.90 (m, 8H), 6.95–6.98 (m) 7.32 (s) (8H), 7.25–7.26 (d, *J* = 1.10 Hz, 2H), 7.33 (s) 7.38–7.40 (d, *J* = 8.80 Hz, 2H), 7.95–7.97 (d, *J* = 11.65 Hz, 2H), 8.00 (s, 2H), 8.11–8.13 (d, *J* = 7.50 Hz, 2H). ATR-FTIR (membrane, ν, cm⁻¹): 1787 (imide asym C=O str), 1730 (imide sym C=O str), 1377 (imide –C–N), 720 (imide C=O bending). Molecular weight (SEC, DMF eluent, polystyrene standards): $M_n = 4.63 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 1.02 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$, PDI = 2.20.

2.4. Film casting

Dense films of the pentyptycene-containing polyimides were fabricated by solution casting method. The polymer with predetermined amount was first dissolved in DMAc (~ 7% w/v, g·mL⁻¹) and filtered using a 0.45 μm PTFE syringe filter; the filtered solution was cast on leveled glass plates which was then dried under an infra-red lamp (Staco Energy Products Co., 120 V) overnight to evaporate most of the solvent. The obtained isotropic film (20-40 μm thick) was further dried at

140 °C overnight under vacuum, then soaked in methanol for 24 h, removed from the plates, and dried again at 140 °C in a vacuum oven for 24 h. Complete removal of residual solvent was confirmed by thermo-gravimetric analysis (TGA). Film thickness and effective area for gas permeation measurement were determined by a digital micrometer and scanner, respectively.

2.5. Characterization methods

¹H NMR spectra of all the monomers and polymers were measured on a Bruker 500 spectrometer using either deuterated chloroform or deuterated dimethylsulfone as a solvent. The attenuated total reflection mode Fourier transform infrared (ATR-FTIR) spectra of the polymer membranes were recorded with a Jasco FT/IR-6300 spectrometer with a resolution of 4 cm⁻¹. Molecular weight and molecular weight distribution was measured by size exclusion chromatography (SEC) at 35 °C using polystyrene as standard and DMF as the eluent. Thermo-gravimetric analysis (TGA) was performed using a TGA Q500 instrument (TA Instrument) at a heating rate of 10 °C·min⁻¹ with nitrogen purge. Differential scanning calorimetry (DSC) analyses were performed on a DSC Q2000 (TA Instrument) at a heating rate of 10 °C·min⁻¹ with nitrogen purge.

The densities of polymer films were measured by the buoyancy method using a density kit of an analytical balance (ML204, Mettler Toledo) at room temperature. Water was chosen as the medium because there were negligible water uptakes for all the three films after soaking the films in DI water for 24 h. Density for each film was measured for at least six times and the average value was taken for the fractional free volume estimation.

Fractional free volume (FFV) of each polymer film was determined by the following equation:

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

Where V_0 is the molar volume of the polymer determined by the density measurement, and V_w is the van der Waals volume obtained from Bondi's group contribution method.[32, 33]

Pure gas permeabilities of the polymer membranes were measured at 35 °C using the constant-volume variable-pressure method.[34] Five gases were tested for each film in the following order: H₂, CH₄, N₂, O₂ and CO₂. The membrane was degassed for at least 24 h before measurement. Upstream pressure was maintained at a certain pressure while the downstream pressure increase as a function of time was monitored for each upstream pressure (i.e., 3.0, 6.4, 9.8, 13.0 and 16.6 atm) and used to calculate the pure gas permeability as follows:

$$P = 10^{10} \frac{V_d l}{p_{up} TRA} \frac{dp}{dt} \quad (2)$$

where P (Barrer, 1 Barrer = 10^{-10} cm³(STP)·cm/cm²·s·cmHg) is the gas permeability, V_d is the calibrated downstream volume (cm³), l is the film thickness (cm), p_{up} is the upstream pressure (cmHg), A is the effective area (cm²), dp/dt is the steady-state pressure increment in downstream (cmHg/s), T is the 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 were determined by the ratio of permeability of these two components:

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (3)$$

2.6. Geometric modeling

The ground state geometric structure of pentiptycene molecule was optimized by using density functional theory (DFT) at the B3LYP/6-31+G(d, p) level of Gaussian09 package.[35] The optimized van der Waals isosurface model was calculated by using [DMol3 module](#) of Material Studio 6.0.[36]

3. Results and discussion

3.1. Synthesis of pentiptycene-containing diamines and corresponding polyimides

Pentiptycene-containing diamine monomers were synthesized via a reduction of the intermediate dinitro compounds in high yields (□ 85%) and high purities. The synthetic procedure for the dinitro compounds is similar to that reported recently,[15, 37] in which the halogenated nitrobenzene of three different *meta*-substituent groups, namely, −H, −CH₃ and −CF₃, were used to explore the effect of side groups on the polymer free volume architecture and consequent membrane gas permeation properties. Interestingly, while the peaks in the NMR spectrum of **3a** could be unambiguously assigned according to its chemical structure, two sets of peaks showed in the NMR spectra of **3b** and **3c** suggesting isomeric structures (Figure 2). In both **3b** and **3c**, there are bulky substituent groups (e.g., CH₃ and CF₃) next to the pentiptycene units, which are expected to hinder the free rotation of the C□O bonds mostly due to steric effect. As a result, the two nitrobenzene moieties could be either on the same side of the middle arene plane of pentiptycene, i.e., *cis* conformation, or on different sides, i.e., *trans* conformation (Figure S1 in the Supporting

Information).[38, 39] The ratios of these two conformations were found to be 1.5:1 and 2:1 for **3b** and **3c**, respectively, indicating an effect of the substituent groups on the spatial placement of the nitrobenzene moieties due to the difference in the bulkiness of the substituent groups. Ground state geometric modeling showed that *trans* conformations of both **3b** and **3c** had lower potential energies than *cis* conformations suggesting a more stable state of *trans* conformation. Thus the isomer with higher molar ratio most likely assumes the *trans* conformation. Additionally, the potential energy difference between *cis* and *trans* conformations is smaller for **3b** ($\Delta G = 0.73$ kJ/mol) than that for **3c** ($\Delta G = 1.92$ kJ/mol), which explained the smaller isomeric ratio of 1.5:1 in **3b** as compared with 2:1 in **3c**. This is reasonable because $-\text{CH}_3$ is less bulky than $-\text{CF}_3$ such that less rotational hindrance may be induced leading to a lower isomeric ratio.

Fig. 2. ^1H NMR of pentiptycenen-containing dinitro compounds.

Using the hydrazine-Pd/C reduction system, the final pentiptycene diamines (**4a-4c**) were successfully obtained from **3a-3c** in high yield and high purity. Chemical structures of the pure diamine monomers were verified by ^1H NMR (Figure 3). Interestingly, the isomeric structures disappeared in the CH_3 substituted pentiptycene diamine **4b**, while the CF_3 substituted diamine **4c** still showed the isomeric structure with the same isomeric ratio of 2:1. This seems to suggest that the reduction of NO_2 groups to NH_2 groups reduced the overall bulkiness of the side groups leading to enhanced rotational freedom of the C-O links and the disappearance of isomeric structures in

CH₃ substituted pentiptycene diamine **4b**. Additionally, CF₃ in **4c** is much bulkier compared with CH₃ in **4b**; thus there were still rotational barrier resulting in the same type of isomeric structures in **4c** despite of the reduction of NO₂ to NH₂. As evidenced by the ground state geometric modeling, there was still a significant potential energy difference ($\Delta G = 1.54$ kJ/mol) between *cis* and *trans* conformations in **4c**. However, the in-depth investigations regarding the differentiation between the *cis* and *trans* isomeric structures in the monomers and the corresponding polyimides are beyond the research scope of this paper and will not be further discussed here, but will be addressed in future in a separate publication. In the following discussions, consistent reaction conditions were used in producing the pentiptycene-dinitro intermediates and the corresponding diamines and thus fixed isomeric ratios were expected in all the synthesis batches.

Fig. 3. ¹H NMR of the pentiptycene-containing diamine monomers.

Three polyimides containing pentiptycene, namely, 6FDA-PPDA(H), 6FDA-PPDA(CH₃) and 6FDA-PPDA(CF₃) were obtained by the condensation polymerization between 6FDA and the pentiptycene-containing diamine monomers (Scheme 2). The successful polymerizations producing high molecular weight polyimides suggested good reactivity of the pentiptycene diamines towards polycondensation reactions. The fully imidized structure was verified with ¹H NMR (Figure S2 in the Supporting Information) and ATR-FTIR (Figure 4). Peak assignments in ¹H NMR spectra clearly confirmed the anticipated chemical structure of polyimides and the high purities of

synthesized pentiptycene diamine monomers to ensure successful polycondensation. Again, isomeric structures appeared in 6FDA-PPDA(CH₃) and 6FDA-PPDA(CF₃) polyimides due to the restricted rotational freedom as previously discussed in the corresponding diamines. As shown in FTIR spectra (Figure 4), the characteristic imide adsorption appeared at ~1784 cm⁻¹ for the imide asymmetric carbonyl stretching, ~1726 cm⁻¹ for the imide symmetric carbonyl stretching, ~1374 cm⁻¹ for the imide C-N stretching and ~720 cm⁻¹ for the imide carbonyl bending. Additionally, the absence of peaks in the range of 1620-1680 cm⁻¹, which are characteristic carbonyl stretching of poly(amic acid), confirmed the fully imidized structure. All the obtained polyimides showed sufficiently high molecule weight of more than 34, 000 g·mol⁻¹ for film casting, as shown in Table 2.

Fig. 4. ATR-FTIR spectra of the pentiptycene-based polyimide membranes.

3.2. *Polymers and membranes properties*

Generally, due to the inherent rigidity of aromatic imide rings and the strong inter-molecular interactions, aromatic polyimides exhibit limited solubility in common organic solvents and consequently poor processability, which restrict their scope of practical applications. Typical approaches to improve the solubility of polyimides involve incorporation of bulky side groups to separate polymer chains and disrupt chain packing,[40, 41] introduction of flexible linkages such as ether bonds in polyetherimides to reduce chain stiffness,[42] creating kinked linkages to suppress coplanar structures and lower regularity and molecular ordering,[43, 44] and use of fluorinated diamines and dianhydrides.[45, 46] In this research, the newly designed and synthesized

pentiptycene polyimides contain very bulky pentiptycene units, have flexible ether linkages and were synthesized from a fluorinated dianhydride, 6FDA. Therefore, enhanced solubility is expected for these aromatic polyimides. Solubility of the three pentiptycene-containing polyimides in a wide range of organic solvents was tested at room temperature with a polymer solution concentration of 10 mg·mL⁻¹. As shown in Table 1, all the pentiptycene-containing polyimides exhibited the expected excellent solubility in many common organic solvents such as THF, chloroform, toluene, DMF, DMAc and NMP. It should be noted that these are room temperature measurements suggesting their superior solution processability. As a general observation, introducing bulky side groups of CH₃ and CF₃ further improved the solubility from the non-substituted 6FDA-PPDA(H). Particularly, in the case of 6FDA-PPDA(CF₃), the additional contribution of the substituent CF₃ groups in pentiptycene diamine allowed it to dissolve in all the tested solvents except DMSO, in which it was partially soluble at room temperature. These aromatic polyimides were easily cast in solution to produce transparent and flexible thin films (Figure S3 in the supporting information).

Table 1

Room temperature solubility of pentiptycene-containing polyimides^a.

polymer	Solvent									
	DMF	DMAc	NMP	DMSO	THF	DCM	acetone	CHCl ₃	toluene	xylene
6FDA-PPDA(H)	+	+	+	+	+	+	□	+	+	□
6FDA-PPDA(CH ₃)	+	+	+	+	+	+	□	+	+	+
6FDA-PPDA(CF ₃)	+	+	+	+/-	+	+	+	+	+	+

^a“+”, Soluble at room temperature; “-”, insoluble at room temperature; “+/-”, partially soluble.

Molecular weights and thermal properties of polyimides are shown in Table 2, and the original DSC and TGA curves are presented in Figure S4 in the Supporting Information. Glass transition temperatures (T_g's) for 6FDA-PPDA(H), 6FDA-PPDA(CH₃) and 6FDA-PPDA(CF₃) measured by DSC were 373, 363 and 374 °C, respectively, indicating the high chain rigidity and high molecular weights of the pentiptycene-containing polyimides. Additionally, pentiptycene-containing polyimides exhibited much higher glass transition temperatures (more than 70 °C higher) than those of the triptycene-containing polyimides that we previously reported,[15] indicating an even more

rigid backbone induced by the pentiptycene units compared to the triptycene units. Moreover, no melting or crystallization behavior was detected in the DSC curves up to 450 °C. Thermal stability was measured with TGA, and it was found that the pentiptycene polyimides were thermally stable up to 480 °C under nitrogen atmosphere. Specifically, 5% and 10% weight loss temperatures were observed to be in the range of 492–512 °C and 516–537 °C, respectively, and char yields were all more than 58% at 800 °C. Importantly, no weight loss due to residual casting solvent was observed in TGA thermographs of the polymer films, suggesting that the protocol of high temperature vacuum drying followed by non-solvent extraction was very efficient to produce solvent-free thin films. The solvent-free condition of thin films is critical to obtain accurate density measurements to estimate FFV as well as to obtain reliable gas permeation properties.

Table 2

Molecular weights and thermal properties of pentiptycene-containing polyimides.

polymer	M_n (g·mol ⁻¹)	PDI (M_w/M_n)	T_g (°C)	$T_{d, 5\%}$ (°C) ^a	$T_{d, 10\%}$ (°C) ^b	char yield (%) ^c
6FDA-PPDA(H)	34, 600	2.34	373	512	537	62
6FDA-PPDA(CH ₃)	42, 500	2.16	363	492	517	58
6FDA-PPDA(CF ₃)	46, 300	2.20	374	511	533	60

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

Densities of the pentiptycene-containing thin films were measured with a density kit, which were used to calculate the fractional free volume (FFV) of these polyimide films based on group contribution method. The results are shown in Table 3. As shown, the densities of all pentiptycene polyimides were in the range of 1.268-1.327 g·cm⁻³, which is lower than typical aromatic polyimides. Due to the incorporation of the bulky hourglass-shape pentiptycene units into the polymer backbone, all three films show high FFV values close to 20%, which easily surpass those of commercial polymeric membrane materials such as Matrimid[®] polyimide and polysulfones.[47, 48] Matrimid[®] is a benchmark commercial polyimide that has been frequently used in natural gas purification (i.e., removal of CO₂ from CH₄), and polysulfone is typically used for air separation (O₂/N₂). Compared with 1,4-triptycene-based polyimides previously reported by our group,[15] pentiptycene-containing polyimides still exhibited much higher FFV. For example, for CH₃

substituted series, more than 18% increase in FFV was observed in pentiptycene polyimides than that of a triptycene-containing counterpart (i.e., 6FDA-1,4-trip-CH₃). We believe that there are two molecular origins to account for the higher free volume: the larger internal free volume (molecular cavity) of pentiptycene and the increased inter-chain spacing due to bulkier pentiptycene configuration than triptycene.

Table 3

Densities and fractional free volume (FFV) of pentiptycene-containing polyimides compared with triptycene-containing polyimides[15], Matrimid[®][47] and polysulfones[48]

Samples	Density (g·cm ⁻³)	FFV (%)	Samples	Density (g·cm ⁻³)	FFV (%)
6FDA-PPDA(H)	1.286 ± 0.004	18.3	6FDA-1,4_ para	1.349 ± 0.006	15.6
6FDA-PPDA(CH ₃)	1.268 ± 0.004	17.9	6FDA-1,4-trip-CH ₃	1.323 ± 0.002	15.1
6FDA-PPDA(CF ₃)	1.327 ± 0.002	19.7	6FDA-1,4-trip-CF ₃	1.381 ± 0.002	18.3
Matrimid [®]	1.175	17	Polysulfones	1.15-1.24	0.13-0.17

To test the tunability of the molecular cavity size of pentiptycene, three different substituent groups (□H, □CH₃ and □CF₃) were positioned *meta* to the pentiptycene moieties in the diamine monomers (Scheme 2). It is expected that the overall fractional free volume and the accessible size of the molecular cavities of polyimides can be tuned depending on the size of the substituent groups to possibly meet different gas separation needs. As shown in Table 3, 6FDA-PPDA(CF₃), which contains bulky CF₃ groups neighboring the pentiptycene units, exhibited the anticipated highest FFV among the three polymers, possibly due to the larger inter-chain spacing and the more disrupted chain packing induced by CF₃ groups. However, 6FDA-PPDA(CH₃), which contains less bulky methyl groups, showed the smallest FFV, indicating that the spatial placement of methyl groups in this pentiptycene polyimide is different from what is normally expected for bulky side groups, i.e., increasing the inter-chain spacing and thus increasing the free volume. Due to the free rotation of the ether bond, the relatively smaller methyl groups may partially occupy and reside in the cleft spaces of pentiptycene units, which results in decreased FFV as compared with the 6FDA-PPDA(H) which contains no substituent groups next to the pentiptycene moieties. This so-called “partial filling” mechanism of substituent groups in the molecular cavity was first proposed in the triptycene polymers by our group and was discussed extensively in our recent

paper.[15] The results in this paper further proved the tunability of the molecular cavity size associated with iptycene structures (i.e., triptycene and pentiptycene), which is unique and very useful in constructing interesting and well-defined molecular cavity architectures. It should be mentioned that the “partial filling” of the substituent groups in the molecular cavities of the iptycene units can occur both intra-molecularly and inter-molecularly although the latter is expected to be more likely.

To obtain a quantitative understanding of the molecular configuration effect (i.e., triptycene vs. pentiptycene) on FFV, geometric modeling was conducted to estimate the internal molecular free volume of pentiptycene and the results were compared with the reported triptycene structure.[21] The ground state geometry of pentiptycene molecule was optimized by using density functional theory (DFT) using Gaussian09 package. The optimized van der Waals isosurface model was generated using Material Studio 6.0, which was then used to calculate the occupied volume by the pentiptycene unit. Van der Waals isosurface pentiptycene models are shown in Figure 5, wherein the internal molecule free volume was defined and calculated by the difference between the overall volume generated by the structure geometry and the occupied volume calculated from the van der Waals isosurface model according to a reported method.[21] As shown in Figure 5, the internal molecule free volume of an individual pentiptycene unit is estimated to be about $326 \text{ \AA}^3$, which is more than three times that of the triptycene unit ($93 \text{ \AA}^3$). [15, 21] Thus the significantly large amount of internal free volume intrinsically associated with pentiptycene units is favorable for increasing the overall fractional free volume allowing high gas permeability. Furthermore, because of the more and larger molecular cavities available, naturally there is more tunability at molecular level in the pentiptycene units to obtain desired molecular cavity size by following the similar mechanism of “partial filling” previously reported for the triptycene-containing polymers.[15] In this regard, the studies reported in the paper represent the first attempt in exploring the tunability of molecular cavity size in pentiptycene structure, which may open up doors of more intriguing molecular-level manipulation approaches to produce novel material structures for many advanced applications beyond membrane separations.

Fig. 5. Van der Waals isosurface pentiptycene models showing (a) three dimensional sizes, (b) molecule width along the pentiptycene axis, and (c) method for the calculation of internal molecular free volume, where A and B are the projected area of cleft spaces. The internal molecular free volume of an individual pentiptycene unit is estimated as: $2 \times (A + B) \times 7.2 \text{ \AA}^3 \approx 326 \text{ \AA}^3$, where 2 indicates two sets of symmetrical molecular cavities.

A detailed FFV comparison between the pentiptycene-containing polymers with their triptycene counterparts is necessary to provide a better molecular level understanding of how the tunability really works via “partial filling” mechanism and to what extent can membrane transport properties be tuned by the “filling efficiency” determined by the size and possibly the nature of the substituent groups. As shown in Table 3, although the change of fractional free volume as a function of substituent groups followed the same trend in these two series of polymers (i.e., $-\text{CF}_3 > -\text{H} > -\text{CH}_3$), there is obviously different “filling efficiency” due to the different sizes of accessible molecular cavities of triptycene and pentiptycene units. Compared with 6FDA-PPDA(H) which contains no substituent group, the FFV of 6FDA-PPDA(CH_3) was decreased by 2.2% due to the introduction of CH_3 groups. However, this value was 3.2% for the corresponding triptycene-based polyimide i.e., 6FDA-1,4-trip- CH_3 . The smaller decrease of FFV for pentiptycene-based polyimides is due to the higher overall internal free volume of pentiptycene units compared with triptycene. As shown in Figure 5, the internal free volume of the middle cleft (denoted as B) of pentiptycene unit is $133 \text{ \AA}^3$, which is about three times larger than that of triptycene (the same as cleft A, $31 \text{ \AA}^3$). When CH_3 groups fill this volume, it results in a smaller FFV decrease for pentiptycene. In the case of CF_3 substitution, the FFV has increased by 7.6% and 17.3% for pentiptycene-based polyimide and triptycene-based polyimide, respectively. The less significant increase in FFV for pentiptycene polyimide again is due to the larger clefts and the more open structure in pentiptycene that is accessible to substituent groups. For triptycene-based polyimide, the bulky CF_3 groups (occupied

volume of 46 Å³) cannot fill in the small clefts (31 Å³), which resulted in a significant increase of the FFV (17.3%) due to the disrupted chain packing and increased inter-chain spacing. While for pentiptycene, the large open space of the middle clefts (clefts B in Figure 5) allows the CF₃ groups to fill in this volume at least in part, which counteracts the effect of chain packing disruption of CF₃ groups leading to a less significant increase of the overall FFV (by 7.6%) for pentiptycene-based polyimide. These effects are schematically illustrated in Figure 6. The observed difference in volume change supports that our previously proposed “partially filling” mechanism which may be readily generalized to other iptycene-containing polymers.[15]

Fig. 6. Dependence of “filling efficiency” on the size of the substituent groups in the clefts of iptycene units

3.3. Pure gas permeation properties

Pure gas permeabilities of five gases (H₂, N₂, O₂, CH₄ and CO₂) for the three pentiptycene-containing polyimides were measured by using the constant-volume variable-pressure method.[34] The feed pressure dependence of permeability is shown in Figure S5 in the Supporting Information. Gas permeabilities had a very weak dependence on the feed pressure, and there was no plasticization pressure point for CO₂ with increasing fugacity up to 17 atm. The pure gas transport properties of all polyimides are reported at 10 atm and 35 °C.

Table 4

Pure gas permeability and ideal selectivity of pentiptycene-containing polyimides and related polyimides in the literature.

	Permeability (Barrer)					Ideal Selectivity (α)			
	H ₂	N ₂	O ₂	CH ₄	CO ₂	H ₂ /N ₂	O ₂ /N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
6FDA-PPDA(H)	131	3.2	17	2.5	73	41	5.3	29	23
6FDA-PPDA(CH ₃)	100	2.4	12	2.0	55	42	5.0	28	23

6FDA-PPDA(CF ₃)	188	7.0	30	5.5	132	27	4.3	24	19
6FDA-1,4-trip_para[15]	49	0.66	4.07	0.37	14.4	74	6.0	39	22
6FDA-1,4-trip_CH ₃ [15]	37	0.41	2.64	0.23	9.0	90	6.4	39	22
6FDA-1,4-trip_CF ₃ [15]	59.4	0.99	5.75	0.53	19.7	60	5.8	37	20
Matrimid®[47]	18	0.32	2.1	0.28	10	56	6.6	36	31
Polysulfone[48]	□	0.18	1.2	0.18	5.6	□	6	22	31

Gas permeability and ideal selectivity of pentiptycene-containing polyimides, along with triptycene-containing polyimides, Matrimid® and polysulfone for comparison, are listed in Table 4. The following trends could be immediately drawn from the results: 1) The permeabilities sequence of all three polyimides is $P(H_2) \square P(CO_2) \square P(O_2) \square P(N_2) \square P(CH_4)$, which follows the order of kinetic diameters of the test gases. It indicates that diffusivity plays an important role in the gas permeation for these glassy polymers, which largely rely on size sieving mechanism to perform separations; 2) The gas permeability of pentiptycene-containing polyimides depends strongly on the substituent groups, which is closely related to the fractional free volume. The sequence in permeability agrees well with the FFV sequence discussed earlier. For example, the CO_2 permeability of 6FDA-PPDA(CF₃) is about 2-fold higher than that of 6FDA-PPDA(CH₃) because of the much higher fractional free volume in 6FDA-PPDA(CF₃); 3) Permeabilities of large size gas molecules (e.g., N₂ and CH₄) seem to be more sensitive to the free volume change compared with small gases like H₂. For example, $P(CH_4)$ was more than doubled from 6FDA-PPDA(H) to 6FDA-PPDA(CF₃) while only less than 50% increase in $P(H_2)$ was observed. This is also evidenced by the comparison between the pentiptycene polyimides and triptycene polyimides. For example, $P(CH_4)$ was increased by more than 10 times from 6FDA-PPDA(CF₃) to its triptycene counterpart (6FDA-1,4-trip_CF₃), while only about 3 times increase in $P(H_2)$ was observed by replacing triptycene with pentiptycene. It seems to suggest that the increase in free volume is most likely due to the creation of more large-size free volume elements upon using pentiptycene or incorporating bulky CF₃ groups, which facilitates the transport of large-size gas molecules; 4) The detailed architecture of the free volume elements, i.e., the shape, size, and size distribution of the molecular cavities may play an important role for gas permeation. For example, given the same FFV (18.3%) for the pentiptycene-based 6FDA-PPDA(H) and the triptycene-based 6FDA-1,4-trip_CF₃, the same,

or at least very similar, gas permeabilities were expected for these two polyimide. However, as shown in Table 4, the gas permeabilities of 6FDA-PPDA(H) are much higher than those of 6FDA-1,4-trip_{CF}₃ for all the gases tested while maintaining comparable selectivities, which seems to suggest that a preferred free volume architecture was generated in the pentiptycene-containing polyimides series leading to much improved overall separation performance. Studies of the fundamental transport properties regarding the respective contribution from diffusivity (D) and solubility (S) factor are undergoing, which will provide insights into the molecular origins for the gas transport in these new membranes. Overall, introduction of pentiptycene units into polymer backbone improved the permeability significantly when compared with both triptycene-polyimides and commercial polymers.[15, 47] For instance, the permeabilities of pentiptycene polyimides for all the five gases tested are about an order of magnitude higher than those of Matrimid[®] polyimide and polysulfone. More importantly, the significant increase in the permeabilities was accompanied with very moderate decrease in the selectivities. This is actually a preferred combination in practical applications since high permeability with reasonable selectivity would mitigate the requirement of high feed pressure and allow smaller membrane area thus enabling good capital and energy efficiency.[1-3, 49]

Fig. 7. Permeability-selectivity upper bound plots of 6FDA-PPDA(H) (red open square), 6FDA-PPDA(CH₃) (red open circle) and 6FDA-PPDA(CF₃) (red open triangle) for (a) CO₂/CH₄ and (b) O₂/N₂ pairs. Other comparative data points are: 1-Matrimid[®];[47] 2-6FDA-1,4-trip_{CF}₃:[15] 3-6FDA-1,4-trip_{para}:[15] 4-6FDA-1,4-trip_{CH}₃:[15] 5-polysulfone.[48]

The permeability-selectivity tradeoff plots for CO₂/CH₄ and O₂/N₂ gas pairs of the

1 pentiptycene-containing polyimides are shown in Figure 7 to evaluate their separation performance
2 against the Robeson's upper bounds. Some reported data points, i.e., triptycene-containing
3 polyimides, Matrimid[®] and polysulfone, were included for comparison. As shown, significant
4 improvement in the permeability-selectivity combinations was readily achieved by the
5 pentiptycene-containing polyimides when compared with the benchmark commercial polymers.
6 Additionally, all three pentiptycene-containing polyimides outperformed the corresponding
7 triptycene-based polyimides, verifying that introduction of pentiptycene into polymer backbone
8 generated more free volume due to more accessible molecular cavities and bulkier structure of
9 pentiptycene. More importantly, preferred free volume architecture was obtained in
10 pentiptycene-based polyimides as clearly evidenced by the trend of moving the separation
11 performance rather laterally approaching the upper bound, instead of following the trade-off slope
12 as conventional glassy polymers generally behave. This finding also suggests the better tunability of
13 pentiptycene-polyimides in terms of optimizing the free volume fraction and architecture to meet
14 different separation requirements.
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30 4. Conclusions

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33 Three new pentiptycene-based diamine monomers containing different substituent groups were
34 synthesized successfully with high purity and high yields. A general methodology was developed to
35 feasibly incorporate pentiptycene units into polyimide structures by a polymerization of the newly
36 designed and synthesized pentiptycene-containing diamines with a dianhydride, 6FDA. The
37 obtained pentiptycene-containing polyimides showed excellent solubility in a wide range of organic
38 solvents and had excellent thermal stability suggesting their excellent processability and durability.
39 In general, all the pentiptycene-containing polyimides exhibited high fractional free volume, which
40 naturally resulted in high gas permeabilities, due to the incorporation of rigid bulky pentiptycene
41 units that contains large size molecular cavities. The fractional free volume and consequently the
42 gas transport properties were found to be very sensitive to the detailed primary structure of the
43 pentiptycene diamines, i.e., the substituent groups neighboring the clefts of the pentiptycene units.
44 Depending on the size of these substituents relative to the molecular cavity, the overall free volume
45 fraction and the size of the free volume elements can be feasibly tuned. In the case of large size
46 group like CF₃, an increased FFV and permeability were obtained; while for relatively small size
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CH₃ group, opposite results were obtained. These observations are consistent with, and again support the mechanism of “partial filling” of molecular cavities by the substituent groups previously proposed for triptycene-polyimides, suggesting a general molecular manipulation mechanism for iptycene-containing polymers. Notably, the significant increased gas permeability was accompanied with a very moderate reduction in selectivity. These results suggest great potential for further tuning of the pentiptycene-polyimide structure to enhance gas separation properties.

ASSOCIATED CONTENT

Supporting Information

¹H NMR spectra for the pentiptycene-containing polyimides, three-dimensional ball-stick model of pentiptycene diamine **4c**, DSC and TGA curves, and the feed pressure dependence of gas permeabilities.

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Notes

The authors declare no competing financial interest.

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Penttiptycene-based Polyimides with Hierarchically Controlled Molecular Cavity Architecture for Efficient Membrane Gas Separation

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ABSTRACT: A series of new penttiptycene-containing diamines with systematically varied substituent groups were designed and synthesized with high purity and high yields. These diamines were used to prepare a series of new polyimides with 4,4'-hexafluoroisopropylidene bisphthalic dianhydride (6FDA) by conventional condensation polymerization. The obtained penttiptycene-containing polyimides possessed high molecule weights, excellent thermal stability, good solubility in a wide range of organic solvents and thus excellent processability for membrane fabrication. Because of the excess amount of internal free volume associated with the molecular cavities in the penttiptycene moieties and the consequently disrupted chain packing, all the polyimides exhibited high fractional free volume (FFV) leading to high gas permeabilities as well as good selectivities that are highly desired for gas separation membranes. In addition, the comparisons between the penttiptycene-containing polyimides bearing various substituent groups indicated that free volume, the vital structural parameter for fast and selective molecular transport, was very sensitive to the size of the substituent groups. Large substituent groups such as CF₃ led to increased FFV, while relatively small substituent groups such as CH₃ resulted in reduced FFV, possibly due to the mechanism of “partial filling” of the molecular cavities of penttiptycene units by the substituent groups. Gas permeability data also supported this unusual trend of the dependence of free volume on the substituent groups. This finding provides a completely new and potentially novel means of molecular-level manipulations to predictably construct preferred free volume

architecture that may maximize the separation performance of polymeric membranes.

Keywords: pentiptycene, polyimides, free volume, gas separation membrane

1. Introduction

Polymeric membrane-mediated gas separation has attracted much attention during the past few decades due to their comparable advantages such as relatively low cost and energy efficiency, and ease of operation in applications like natural gas purification, carbon capture, air separation and hydrogen purification.[1-3] Fast and selective transport combined with scalability and chemical, mechanical, and thermal stability in the process environment are key attributes of an ideal polymer membrane for efficient gas separations. However, polymeric membranes are often challenged by a tradeoff between permeability and selectivity, evidenced as the Robeson's upper bound.[4, 5] This upper bound limit largely originates from the limited amount of free volume and the out-of-the-regime size distribution of the free volume elements in polymer membranes.[3, 6-8] Thus an obvious solution to this challenging problem is to develop novel macromolecular structures featuring high fractional free volume and optimized free volume size distribution to enable fast and selective molecular transport.

Polymers with high fractional free volume are generally highly desired for high gas throughput. The creation of high fractional free volume in polymer membranes generally involves disruption of efficient or dense chain packing. Typically this objective can be achieved via introducing bulky side groups to increase inter-chain spacing, or including certain spiro-centers in the main chain structure to create highly contorted polymer backbone. For example, a novel class of ladder-like polymers known as "polymers of intrinsic microporosity" (PIMs) was developed recently.[9-12] PIMs uniquely contain rigid contorted spiro-units in the main chain structure, which restrict conformational freedom and prevent efficient chain packing leading to high fractional free volume and consequently very high gas permeabilities.[9, 13, 14] However, like other high free volume glassy polymers, the significant improvement in gas permeabilities was not always accompanied by the similar improvement in selectivities. In other words, the ability to tune the transport properties in these polymeric materials through changes in primary and secondary chain architecture still appears to be limited by the upper bound. This is largely due to the lack of control on the size and size distribution of free volume elements in these polymers. Therefore there is an obvious need of the right structural elements and revolutionary molecular manipulation mechanism that can feasibly control the free volume architecture to achieve highly selective and efficient gas separation.

1 Recently we reported a series of new aromatic polyimides containing triptycene units in the main
2 chain structure as gas separation membrane materials, which showed very interesting and promising
3 gas transport properties.[15] Triptycene is a three-dimensional symmetric, bulky and rigid molecule
4 composed of three benzene “blades” in paddlewheel-like configuration (Figure 1a). Because of the
5 disrupted chain packing due to the bulkiness of triptycene units, membranes of triptycene-bearing
6 polyimides show high fractional free volume and decent gas transport properties.[6, 15-18] As
7 demonstrated in our previous paper on triptycene-polyimide membranes,[15] a unique and
8 appealing feature of this simplest triptycene molecule is that the open space between the benzene
9 rings, called “internal free volume”, not only introduces significant amount of “intrinsic” free
10 volume into the polymer for fast transport, but also provides a feasible means to finely tune the size
11 of internal free volume or molecular cavity by varying the substituent groups neighboring the
12 triptycene units. This exciting finding greatly stimulates further studies to explore the potential of
13 these interesting polymers for gas separation membrane applications. As a natural extension of the
14 triptycene-based structure, pentiptycene-containing polyimides are reported here to demonstrate
15 their potential as high performance gas separation membranes. Pentiptycene, another member of the
16 triptycene family, is composed of five arene rings fused together into a rigid, H-shaped scaffold.[19,
17 20] Its three-dimensional structure is shown in Figure 1b. Compared with triptycene, pentiptycene
18 possesses even bulkier structure that can effectively hinder polymer chain packing leading to higher
19 fractional free volume. More importantly, pentiptycene has more open clefts, i.e., more “internal
20 free volume”, and the size of these well-defined molecular cavities is comparable with the kinetic
21 diameters of the common gases (e.g., He, H₂, CO₂, O₂, N₂, CH₄). Such molecular cavities may be
22 (partially) occupied by substituent groups or guest molecules to control the overall free volume size
23 and size distribution of the material, thereby providing an efficient tool for molecular engineering
24 and making pentiptycene a potentially very useful component for the fabrication of gas separation
25 membrane materials.

Fig. 1. Three-dimensional structure of (a) triptycene[21] and (b) pentiptycene molecule. (Note: the dimension of pentiptycene was estimated from the centroids of the extreme hydrogen atoms according to the geometry of the molecular configuration at ground energy state.)

Like triptycene, pentiptycene has found versatile usages in constructing supramolecular structures of both fundamental and practical importance, such as light-driven molecular “brake”, fluorescence and chemical sensors, etc.[22-25] However, incorporation of pentiptycene into polymer backbone structure has been sparsely reported, possibly because the polymerizable pentiptycene monomers are not readily available.[18, 26-28] In this study, we report for the first time the synthesis and characterization of a class of new pentiptycene-containing polyimides derived from a series of newly-designed pentiptycene diamine monomers. The aim of this work was to gain more molecular level understanding of the tunability of free volume architecture induced by iptycene units in the polymer materials to provide useful guidance in developing next generation high performance gas separation membranes. In this research the profound effects of the (partial) occupation of substituent groups in the molecular cavities on the gas transport properties of these new polyimides are demonstrated.

2. Experimental

2.1. Materials

Anhydrous *N,N*-Dimethylacetamide (DMAc, 99.8%), hydrazine monohydrate (98.0%), palladium on carbon (Pd/C, 10 wt.%), acetic anhydride (□98.0%) and anhydrous pyridine (99.8%) were obtained from Sigma-Aldrich (USA) and used as received. 1-Fluoro-4-nitrobenzene (Aldrich, 99.0%), 2-chloro-5-nitrotoluene (TCI, □98.0%) and 2-chloro-5-nitrobenzotrifluoride (Alfa Aesar, 98.0%) were used as received. Potassium carbonate (Alfa Aesar, 99.0%) was dried at 80 °C

overnight prior to use. 4,4'-Hexafluoroisopropylidene bisphthalic dianhydride (6FDA, $\square$ 99.0%) was purchased from Akron Polymer Systems and dried at 160 °C under vacuum for 12 hours before use. All other chemical reagents were obtained from commercial sources and used as received.

2.2. Synthesis of pentiptycene-containing diamine monomers

Pentiptycene-containing diamine monomers (**4a-4c**) were synthesized by a reduction of the intermediate pentiptycene dinitro compounds (**3a-3c**), which were generated via the aromatic nucleophilic substitution (S_NAr) between pentiptycene diol and select halogenated nitro compounds, as shown in Scheme 1. The intermediates, i.e., pentiptycene diquinone (**1**) and pentiptycene diol (**2**) were synthesized according to previous reports.[29, 30] Two different *meta*-substituent groups (i.e., CH₃ and CF₃) were introduced at the position neighboring the pentiptycene units to investigate the tunability of the free volume in the corresponding polymers by probing the molecular cavities defined by the arene planes of the pentiptycene units.

Scheme 1. Synthesis of pentiptycene-containing diamine monomers.

2.2.1. Synthesis of pentiptycene-containing dinitro compounds (**3a-3c**)

Under a nitrogen atmosphere, pentiptycene diol (**2**, 5.0 g, 10.8 mmol) and 1-fluoro-4-nitrobenzene (3.05 g, 21.6 mmol) were dissolved in DMF (30 mL) in a two-necked flask followed by the addition of K₂CO₃ (3.29 g, 23.8 mmol). After stirring at 150 °C under N₂ atmosphere for 8 h, the reaction mixture was poured into a mixture of methanol and water (800 mL, v/v = 1:1) under vigorous stirring. The precipitate was filtered, washed with methanol and deionized (DI) water extensively, and dried at 110 °C in a vacuum oven overnight to obtain a light green powder as the dinitro

compound **3a** (7.02 g, yield 87%). mp (melting point from differential scanning calorimetry at a heating rate of 5 °C·min⁻¹): □ 300 °C. ¹H NMR (500 MHz, CDCl₃): δ 5.37 (s, 4H), 6.87–6.89 (d, *J* = 9.20 Hz, 4H), 6.90–6.92 (m, 8H), 7.06–7.09 (m, 8H), 8.23–8.26 (d, *J* = 9.25 Hz, 4H).

The synthetic procedure of dinitro compound **3b** was similar to that of dinitro **3a**. The resulting mixture was precipitated in the mixture of methanol and water (v/v = 1:1), filtered and washed with methanol and DI water, and then dried under vacuum at 110 °C overnight to yield a white powder as dinitro compound **3b** (yield 90%). mp: 256 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.81 (s, 6H), 5.29 (s, 4H), 6.01–6.03 (d, *J* = 9.00 Hz) 6.10–6.12 (d, *J* = 9.10 Hz) (2H), 6.79–6.87 (m, 8H), 6.95–6.97 (m) 7.30–7.32 (d, *J* = 6.80 Hz) (8H), 7.76–7.78 (m) 7.88–7.90 (d, *J* = 6.95 Hz) (2H), 8.39 (s, 2H).

Dinitro **3c** was synthesized following the similar procedure used for **3a** and **3b**, except that the reaction temperature was lowered to 100 °C. The resulting mixture was poured into the methanol and water (v/v = 1:1), filtered, washed and dried under vacuum at 110 °C overnight giving a white powder as dinitro compound **3c** (yield 90%). mp: 253 °C. ¹H NMR (500 MHz, CDCl₃): δ 5.34 (s, 4H), 6.26–6.28 (d, *J* = 9.10 Hz) 6.40–6.41 (d, *J* = 9.10 Hz (2H), 6.82–6.83 (d, *J* = 7.05 Hz) 6.88–6.90 (m) (8H), 6.97–7.00 (m) 7.29–7.33 (m) (8H), 8.10–8.12 (m) 8.23–8.25 (m) (2H), 8.83–8.85 (m, 2H).

2.2.2. Synthesis of pentiptycene-containing diamine compounds (**4a-4c**)

In a two-necked flask, dinitro **3a** (6.0 g, 8.5 mmol), 10% Pd/C (0.2 g) and ethanol (400 mL) were added under a nitrogen atmosphere. The mixture was heated to reflux, and then hydrazine monohydrate (10 mL, 200 mmol) was added dropwise over 2 h. After stirring under reflux for 48 h, ethanol was evaporated under vacuum and DMF (40 mL) was then added to dissolve the diamine product. The solution was filtered off to remove Pd/C and precipitated in a mixture of methanol and DI water (v/v = 1:1) to obtain a white solid. The solid was washed with methanol and DI water three times and dried under vacuum at 100 °C overnight giving **4a** (5.2 g, yield 85%). mp: □ 300 °C. ¹H NMR (500 MHz, DMSO-*d*₆): δ 4.89 (s, 4H), 5.56 (s, 4H), 6.49□6.51 (m, 4H), 6.52□6.54 (m, 4H), 6.87□6.90 (m, 8H), 7.11□7.14 (m, 8H).

The procedure to prepare diamine **4b** was similar to that used for **4a**. After all the ethanol was evaporated, DMF was added into the flask to dissolve the amine product and facilitate the filtration to remove the catalyst. The solution was precipitated in methanol and water (v/v = 1:1), washed and dried to obtain a white powder as **4b** (yield 88%). mp: □ 300 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ

2.45 (s, 6H), 4.75 (s, 4H), 5.37 (s, 4H), 5.55–5.57 (d, $J = 7.90$, 2H), 6.05–6.07 (d, $J = 7.25$, 2H), 6.66 (s, 2H), 6.85 (br, s, 8H), 7.05 (br, s, 8H).

Diamine **4c** was synthesized according to the same procedure as diamine **4b**. The product was obtained as a white powder (yield 88%). mp: ≤ 300 °C. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 5.33 (s, 4H), 5.44 (s, 4H), 5.67–5.69 (d, $J = 11.05$ Hz) 5.78–5.80 (d, $J = 10.90$ Hz) (2H), 6.50–6.52 (m) 6.58–6.60 (d, $J = 9.40$ Hz) (2H), 6.87–6.89 (m, 8H), 6.94–6.96 (m) 7.26–7.28 (d, $J = 8.70$ Hz) (8H), 7.16–7.17 (d, $J = 3.15$ Hz, 2H).

Scheme 2. Synthesis of pentiptycene-based polyimides.

2.3. Synthesis of pentiptycene-containing polyimides

Pentiptycene-based polyimides were synthesized by condensation polymerization between pentiptycene-containing diamines (**4a-4c**) and 6FDA via conventional chemical imidization method as shown in Scheme 2.[31] The procedure to prepare 6FDA-PPDA(H) is described below as an example: to a flame-dried, three-necked flask equipped with a nitrogen inlet and a mechanical stirrer were added the diamine monomer **4a** (2.4214 g, 3.7 mmol) and anhydrous DMAc (18 mL). After dissolution, the flask was immersed into ice water, and an equimolar amount of the dianhydride monomer 6FDA (1.6683 g, 3.7 mmol) was added. Under stirring, the resulting mixture was warmed gradually to room temperature and held overnight under nitrogen atmosphere to form viscous poly(amic acid) solution. A mixture of acetic anhydride (2.2 mL) and pyridine (2.2 mL) was then added into the flask to cyclize the poly(amic acid) to the polyimide. After stirring for

another 24 h, fibrous polyimide product was obtained by precipitating the solution into excess amount of methanol (500 mL) as a thin, continuous stream. The resulting solid was filtered, washed with fresh methanol, and then dried at 140 °C under vacuum for 24 h giving fully imidized 6FDA-PPDA(H) (3.89 g, yield 95%). ¹H NMR (500 MHz, CDCl₃): δ 5.46 (s, 4H), 6.88 (s, 8H), 6.91–6.93 (d, *J* = 8.30 Hz, 4H), 7.10 (s, 8H), 7.33–7.35 (d, *J* = 8.35 Hz, 4H), 7.90–7.92 (d, *J* = 7.90 Hz, 2H), 7.97 (s, 2H), 8.06–8.07 (d, *J* = 7.95 Hz, 2H). ATR-FTIR (membrane, ν, cm⁻¹): 1784 (imide asym C=O str), 1723 (imide sym C=O str), 1377 (imide –C–N), 720 (imide C=O bending). Molecular weight, by size exclusion chromatography (SEC), (DMF eluent, polystyrene standards): $M_n = 3.46 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 8.10 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, PDI = 2.34.

Following the above procedure, 6FDA-PPDA(CH₃) was prepared from **4b** diamine and dianhydride 6FDA as a light-yellow fibrous solid (yield 96%). ¹H NMR (500 MHz, CDCl₃): δ 2.78 (s, 6H), 5.36 (s, 4H), 6.08–6.10 (d, *J* = 7.50 Hz) 6.18 (s) (2H), 6.88 (s, 8H), 6.91 (br, s, 2H), 6.95 (s) 7.30 (s) (8H), 7.47 (s, 2H), 7.90–7.92 (d, *J* = 7.55 Hz, 2H), 7.97 (s, 2H), 8.06–8.08 (d, *J* = 7.75 Hz, 2H). ATR-FTIR (membrane, ν, cm⁻¹): 1784 (imide asym C=O str), 1726 (imide sym C=O str), 1374 (imide –C–N), 720 (imide C=O bending). Molecular weight (SEC, DMF eluent, polystyrene standards): $M_n = 4.25 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 9.16 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, PDI = 2.16.

Similarly 6FDA-PPDA(CF₃) polyimide was the same as that used for 6FDA-PPDA(H) and 6FDA-PPDA(CH₃). The polymer was obtained as white fibrous solid with a yield of 97%. ¹H NMR (500 MHz, CDCl₃): δ 5.43 (s, 4H), 6.28–6.30 (d, *J* = 8.85 Hz) 6.41–6.43 (d, *J* = 8.90 Hz) (2H), 6.87–6.90 (m, 8H), 6.95–6.98 (m) 7.32 (s) (8H), 7.25–7.26 (d, *J* = 1.10 Hz, 2H), 7.33 (s) 7.38–7.40 (d, *J* = 8.80 Hz, 2H), 7.95–7.97 (d, *J* = 11.65 Hz, 2H), 8.00 (s, 2H), 8.11–8.13 (d, *J* = 7.50 Hz, 2H). ATR-FTIR (membrane, ν, cm⁻¹): 1787 (imide asym C=O str), 1730 (imide sym C=O str), 1377 (imide –C–N), 720 (imide C=O bending). Molecular weight (SEC, DMF eluent, polystyrene standards): $M_n = 4.63 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 1.02 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$, PDI = 2.20.

2.4. Film casting

Dense films of the pentiptycene-containing polyimides were fabricated by solution casting method. The polymer with predetermined amount was first dissolved in DMAc (~ 7% w/v, g·mL⁻¹) and filtered using a 0.45 μm PTFE syringe filter; the filtered solution was cast on leveled glass plates which was then dried under an infra-red lamp (Staco Energy Products Co., 120 V) overnight to evaporate most of the solvent. The obtained isotropic film (20-40 μm thick) was further dried at

140 °C overnight under vacuum, then soaked in methanol for 24 h, removed from the plates, and dried again at 140 °C in a vacuum oven for 24 h. Complete removal of residual solvent was confirmed by thermo-gravimetric analysis (TGA). Film thickness and effective area for gas permeation measurement were determined by a digital micrometer and scanner, respectively.

2.5. Characterization methods

¹H NMR spectra of all the monomers and polymers were measured on a Bruker 500 spectrometer using either deuterated chloroform or deuterated dimethylsulfone as a solvent. The attenuated total reflection mode Fourier transform infrared (ATR-FTIR) spectra of the polymer membranes were recorded with a Jasco FT/IR-6300 spectrometer with a resolution of 4 cm⁻¹. Molecular weight and molecular weight distribution was measured by size exclusion chromatography (SEC) at 35 °C using polystyrene as standard and DMF as the eluent. Thermo-gravimetric analysis (TGA) was performed using a TGA Q500 instrument (TA Instrument) at a heating rate of 10 °C·min⁻¹ with nitrogen purge. Differential scanning calorimetry (DSC) analyses were performed on a DSC Q2000 (TA Instrument) at a heating rate of 10 °C·min⁻¹ with nitrogen purge.

The densities of polymer films were measured by the buoyancy method using a density kit of an analytical balance (ML204, Mettler Toledo) at room temperature. Water was chosen as the medium because there were negligible water uptakes for all the three films after soaking the films in DI water for 24 h. Density for each film was measured for at least six times and the average value was taken for the fractional free volume estimation.

Fractional free volume (FFV) of each polymer film was determined by the following equation:

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

Where V_0 is the molar volume of the polymer determined by the density measurement, and V_w is the van der Waals volume obtained from Bondi's group contribution method.[32, 33]

Pure gas permeabilities of the polymer membranes were measured at 35 °C using the constant-volume variable-pressure method.[34] Five gases were tested for each film in the following order: H₂, CH₄, N₂, O₂ and CO₂. The membrane was degassed for at least 24 h before measurement. Upstream pressure was maintained at a certain pressure while the downstream pressure increase as a function of time was monitored for each upstream pressure (i.e., 3.0, 6.4, 9.8, 13.0 and 16.6 atm) and used to calculate the pure gas permeability as follows:

$$P = 10^{10} \frac{V_d l}{p_{up} TRA} \frac{dp}{dt} \quad (2)$$

where P (Barrer, 1 Barrer = 10^{-10} cm³(STP)·cm/cm²·s·cmHg) is the gas permeability, V_d is the calibrated downstream volume (cm³), l is the film thickness (cm), p_{up} is the upstream pressure (cmHg), A is the effective area (cm²), dp/dt is the steady-state pressure increment in downstream (cmHg/s), T is the 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 were determined by the ratio of permeability of these two components:

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (3)$$

2.6. Geometric modeling

The ground state geometric structure of pentiptycene molecule was optimized by using density functional theory (DFT) at the B3LYP/6-31+G(d, p) level of Gaussian09 package.[35] The optimized van der Waals isosurface model was calculated by using DMol3 module of Material Studio 6.0.[36]

3. Results and discussion

3.1. Synthesis of pentiptycene-containing diamines and corresponding polyimides

Pentiptycene-containing diamine monomers were synthesized via a reduction of the intermediate dinitro compounds in high yields (□ 85%) and high purities. The synthetic procedure for the dinitro compounds is similar to that reported recently,[15, 37] in which the halogenated nitrobenzene of three different *meta*-substituent groups, namely, −H, −CH₃ and −CF₃, were used to explore the effect of side groups on the polymer free volume architecture and consequent membrane gas permeation properties. Interestingly, while the peaks in the NMR spectrum of **3a** could be unambiguously assigned according to its chemical structure, two sets of peaks showed in the NMR spectra of **3b** and **3c** suggesting isomeric structures (Figure 2). In both **3b** and **3c**, there are bulky substituent groups (e.g., CH₃ and CF₃) next to the pentiptycene units, which are expected to hinder the free rotation of the C□O bonds mostly due to steric effect. As a result, the two nitrobenzene moieties could be either on the same side of the middle arene plane of pentiptycene, i.e., *cis* conformation, or on different sides, i.e., *trans* conformation (Figure S1 in the Supporting

Information).[38, 39] The ratios of these two conformations were found to be 1.5:1 and 2:1 for **3b** and **3c**, respectively, indicating an effect of the substituent groups on the spatial placement of the nitrobenzene moieties due to the difference in the bulkiness of the substituent groups. Ground state geometric modeling showed that *trans* conformations of both **3b** and **3c** had lower potential energies than *cis* conformations suggesting a more stable state of *trans* conformation. Thus the isomer with higher molar ratio most likely assumes the *trans* conformation. Additionally, the potential energy difference between *cis* and *trans* conformations is smaller for **3b** ($\Delta G = 0.73$ kJ/mol) than that for **3c** ($\Delta G = 1.92$ kJ/mol), which explained the smaller isomeric ratio of 1.5:1 in **3b** as compared with 2:1 in **3c**. This is reasonable because $-\text{CH}_3$ is less bulky than $-\text{CF}_3$ such that less rotational hindrance may be induced leading to a lower isomeric ratio.

Fig. 2. ^1H NMR of pentiptycenen-containing dinitro compounds.

Using the hydrazine-Pd/C reduction system, the final pentiptycene diamines (**4a-4c**) were successfully obtained from **3a-3c** in high yield and high purity. Chemical structures of the pure diamine monomers were verified by ^1H NMR (Figure 3). Interestingly, the isomeric structures disappeared in the CH_3 substituted pentiptycene diamine **4b**, while the CF_3 substituted diamine **4c** still showed the isomeric structure with the same isomeric ratio of 2:1. This seems to suggest that the reduction of NO_2 groups to NH_2 groups reduced the overall bulkiness of the side groups leading to enhanced rotational freedom of the C-O links and the disappearance of isomeric structures in

CH₃ substituted pentiptycene diamine **4b**. Additionally, CF₃ in **4c** is much bulkier compared with CH₃ in **4b**; thus there were still rotational barrier resulting in the same type of isomeric structures in **4c** despite of the reduction of NO₂ to NH₂. As evidenced by the ground state geometric modeling, there was still a significant potential energy difference ($\Delta G = 1.54$ kJ/mol) between *cis* and *trans* conformations in **4c**. However, the in-depth investigations regarding the differentiation between the *cis* and *trans* isomeric structures in the monomers and the corresponding polyimides are beyond the research scope of this paper and will not be further discussed here, but will be addressed in future in a separate publication. In the following discussions, consistent reaction conditions were used in producing the pentiptycene-dinitro intermediates and the corresponding diamines and thus fixed isomeric ratios were expected in all the synthesis batches.

Fig. 3. ¹H NMR of the pentiptycene-containing diamine monomers.

Three polyimides containing pentiptycene, namely, 6FDA-PPDA(H), 6FDA-PPDA(CH₃) and 6FDA-PPDA(CF₃) were obtained by the condensation polymerization between 6FDA and the pentiptycene-containing diamine monomers (Scheme 2). The successful polymerizations producing high molecular weight polyimides suggested good reactivity of the pentiptycene diamines towards polycondensation reactions. The fully imidized structure was verified with ¹H NMR (Figure S2 in the Supporting Information) and ATR-FTIR (Figure 4). Peak assignments in ¹H NMR spectra clearly confirmed the anticipated chemical structure of polyimides and the high purities of

synthesized pentiptycene diamine monomers to ensure successful polycondensation. Again, isomeric structures appeared in 6FDA-PPDA(CH₃) and 6FDA-PPDA(CF₃) polyimides due to the restricted rotational freedom as previously discussed in the corresponding diamines. As shown in FTIR spectra (Figure 4), the characteristic imide adsorption appeared at ~1784 cm⁻¹ for the imide asymmetric carbonyl stretching, ~1726 cm⁻¹ for the imide symmetric carbonyl stretching, ~1374 cm⁻¹ for the imide C-N stretching and ~720 cm⁻¹ for the imide carbonyl bending. Additionally, the absence of peaks in the range of 1620-1680 cm⁻¹, which are characteristic carbonyl stretching of poly(amic acid), confirmed the fully imidized structure. All the obtained polyimides showed sufficiently high molecule weight of more than 34, 000 g·mol⁻¹ for film casting, as shown in Table 2.

Fig. 4. ATR-FTIR spectra of the pentiptycene-based polyimide membranes.

3.2. *Polymers and membranes properties*

Generally, due to the inherent rigidity of aromatic imide rings and the strong inter-molecular interactions, aromatic polyimides exhibit limited solubility in common organic solvents and consequently poor processability, which restrict their scope of practical applications. Typical approaches to improve the solubility of polyimides involve incorporation of bulky side groups to separate polymer chains and disrupt chain packing,[40, 41] introduction of flexible linkages such as ether bonds in polyetherimides to reduce chain stiffness,[42] creating kinked linkages to suppress coplanar structures and lower regularity and molecular ordering,[43, 44] and use of fluorinated diamines and dianhydrides.[45, 46] In this research, the newly designed and synthesized

pentiptycene polyimides contain very bulky pentiptycene units, have flexible ether linkages and were synthesized from a fluorinated dianhydride, 6FDA. Therefore, enhanced solubility is expected for these aromatic polyimides. Solubility of the three pentiptycene-containing polyimides in a wide range of organic solvents was tested at room temperature with a polymer solution concentration of 10 mg·mL⁻¹. As shown in Table 1, all the pentiptycene-containing polyimides exhibited the expected excellent solubility in many common organic solvents such as THF, chloroform, toluene, DMF, DMAc and NMP. It should be noted that these are room temperature measurements suggesting their superior solution processability. As a general observation, introducing bulky side groups of CH₃ and CF₃ further improved the solubility from the non-substituted 6FDA-PPDA(H). Particularly, in the case of 6FDA-PPDA(CF₃), the additional contribution of the substituent CF₃ groups in pentiptycene diamine allowed it to dissolve in all the tested solvents except DMSO, in which it was partially soluble at room temperature. These aromatic polyimides were easily cast in solution to produce transparent and flexible thin films (Figure S3 in the supporting information).

Table 1

Room temperature solubility of pentiptycene-containing polyimides^a.

polymer	Solvent									
	DMF	DMAc	NMP	DMSO	THF	DCM	acetone	CHCl ₃	toluene	xylene
6FDA-PPDA(H)	+	+	+	+	+	+	□	+	+	□
6FDA-PPDA(CH ₃)	+	+	+	+	+	+	□	+	+	+
6FDA-PPDA(CF ₃)	+	+	+	+/-	+	+	+	+	+	+

^a“+”, Soluble at room temperature; “-”, insoluble at room temperature; “+/-”, partially soluble.

Molecular weights and thermal properties of polyimides are shown in Table 2, and the original DSC and TGA curves are presented in Figure S4 in the Supporting Information. Glass transition temperatures (T_g's) for 6FDA-PPDA(H), 6FDA-PPDA(CH₃) and 6FDA-PPDA(CF₃) measured by DSC were 373, 363 and 374 °C, respectively, indicating the high chain rigidity and high molecular weights of the pentiptycene-containing polyimides. Additionally, pentiptycene-containing polyimides exhibited much higher glass transition temperatures (more than 70 °C higher) than those of the triptycene-containing polyimides that we previously reported,[15] indicating an even more

rigid backbone induced by the pentiptycene units compared to the triptycene units. Moreover, no melting or crystallization behavior was detected in the DSC curves up to 450 °C. Thermal stability was measured with TGA, and it was found that the pentiptycene polyimides were thermally stable up to 480 °C under nitrogen atmosphere. Specifically, 5% and 10% weight loss temperatures were observed to be in the range of 492–512 °C and 516–537 °C, respectively, and char yields were all more than 58% at 800 °C. Importantly, no weight loss due to residual casting solvent was observed in TGA thermographs of the polymer films, suggesting that the protocol of high temperature vacuum drying followed by non-solvent extraction was very efficient to produce solvent-free thin films. The solvent-free condition of thin films is critical to obtain accurate density measurements to estimate FFV as well as to obtain reliable gas permeation properties.

Table 2

Molecular weights and thermal properties of pentiptycene-containing polyimides.

polymer	M_n (g·mol ⁻¹)	PDI (M_w/M_n)	T_g (°C)	$T_{d, 5\%}$ (°C) ^a	$T_{d, 10\%}$ (°C) ^b	char yield (%) ^c
6FDA-PPDA(H)	34, 600	2.34	373	512	537	62
6FDA-PPDA(CH ₃)	42, 500	2.16	363	492	517	58
6FDA-PPDA(CF ₃)	46, 300	2.20	374	511	533	60

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

Densities of the pentiptycene-containing thin films were measured with a density kit, which were used to calculate the fractional free volume (FFV) of these polyimide films based on group contribution method. The results are shown in Table 3. As shown, the densities of all pentiptycene polyimides were in the range of 1.268-1.327 g·cm⁻³, which is lower than typical aromatic polyimides. Due to the incorporation of the bulky hourglass-shape pentiptycene units into the polymer backbone, all three films show high FFV values close to 20%, which easily surpass those of commercial polymeric membrane materials such as Matrimid[®] polyimide and polysulfones.[47, 48] Matrimid[®] is a benchmark commercial polyimide that has been frequently used in natural gas purification (i.e., removal of CO₂ from CH₄), and polysulfone is typically used for air separation (O₂/N₂). Compared with 1,4-triptycene-based polyimides previously reported by our group,[15] pentiptycene-containing polyimides still exhibited much higher FFV. For example, for CH₃

substituted series, more than 18% increase in FFV was observed in pentiptycene polyimides than that of a triptycene-containing counterpart (i.e., 6FDA-1,4-trip-CH₃). We believe that there are two molecular origins to account for the higher free volume: the larger internal free volume (molecular cavity) of pentiptycene and the increased inter-chain spacing due to bulkier pentiptycene configuration than triptycene.

Table 3

Densities and fractional free volume (FFV) of pentiptycene-containing polyimides compared with triptycene-containing polyimides[15], Matrimid[®][47] and polysulfones[48]

Samples	Density (g·cm ⁻³)	FFV (%)	Samples	Density (g·cm ⁻³)	FFV (%)
6FDA-PPDA(H)	1.286 ± 0.004	18.3	6FDA-1,4- <i>para</i>	1.349 ± 0.006	15.6
6FDA-PPDA(CH ₃)	1.268 ± 0.004	17.9	6FDA-1,4-trip-CH ₃	1.323 ± 0.002	15.1
6FDA-PPDA(CF ₃)	1.327 ± 0.002	19.7	6FDA-1,4-trip-CF ₃	1.381 ± 0.002	18.3
Matrimid [®]	1.175	17	Polysulfones	1.15-1.24	0.13-0.17

To test the tunability of the molecular cavity size of pentiptycene, three different substituent groups (□H, □CH₃ and □CF₃) were positioned *meta* to the pentiptycene moieties in the diamine monomers (Scheme 2). It is expected that the overall fractional free volume and the accessible size of the molecular cavities of polyimides can be tuned depending on the size of the substituent groups to possibly meet different gas separation needs. As shown in Table 3, 6FDA-PPDA(CF₃), which contains bulky CF₃ groups neighboring the pentiptycene units, exhibited the anticipated highest FFV among the three polymers, possibly due to the larger inter-chain spacing and the more disrupted chain packing induced by CF₃ groups. However, 6FDA-PPDA(CH₃), which contains less bulky methyl groups, showed the smallest FFV, indicating that the spatial placement of methyl groups in this pentiptycene polyimide is different from what is normally expected for bulky side groups, i.e., increasing the inter-chain spacing and thus increasing the free volume. Due to the free rotation of the ether bond, the relatively smaller methyl groups may partially occupy and reside in the cleft spaces of pentiptycene units, which results in decreased FFV as compared with the 6FDA-PPDA(H) which contains no substituent groups next to the pentiptycene moieties. This so-called “partial filling” mechanism of substituent groups in the molecular cavity was first proposed in the triptycene polymers by our group and was discussed extensively in our recent

paper.[15] The results in this paper further proved the tunability of the molecular cavity size associated with iptycene structures (i.e., triptycene and pentiptycene), which is unique and very useful in constructing interesting and well-defined molecular cavity architectures. It should be mentioned that the “partial filling” of the substituent groups in the molecular cavities of the iptycene units can occur both intra-molecularly and inter-molecularly although the latter is expected to be more likely.

To obtain a quantitative understanding of the molecular configuration effect (i.e., triptycene vs. pentiptycene) on FFV, geometric modeling was conducted to estimate the internal molecular free volume of pentiptycene and the results were compared with the reported triptycene structure.[21] The ground state geometry of pentiptycene molecule was optimized by using density functional theory (DFT) using Gaussian09 package. The optimized van der Waals isosurface model was generated using Material Studio 6.0, which was then used to calculate the occupied volume by the pentiptycene unit. Van der Waals isosurface pentiptycene models are shown in Figure 5, wherein the internal molecule free volume was defined and calculated by the difference between the overall volume generated by the structure geometry and the occupied volume calculated from the van der Waals isosurface model according to a reported method.[21] As shown in Figure 5, the internal molecule free volume of an individual pentiptycene unit is estimated to be about $326 \text{ \AA}^3$, which is more than three times that of the triptycene unit ($93 \text{ \AA}^3$). [15, 21] Thus the significantly large amount of internal free volume intrinsically associated with pentiptycene units is favorable for increasing the overall fractional free volume allowing high gas permeability. Furthermore, because of the more and larger molecular cavities available, naturally there is more tunability at molecular level in the pentiptycene units to obtain desired molecular cavity size by following the similar mechanism of “partial filling” previously reported for the triptycene-containing polymers.[15] In this regard, the studies reported in the paper represent the first attempt in exploring the tunability of molecular cavity size in pentiptycene structure, which may open up doors of more intriguing molecular-level manipulation approaches to produce novel material structures for many advanced applications beyond membrane separations.

Fig. 5. Van der Waals isosurface pentiptycene models showing (a) three dimensional sizes, (b) molecule width along the pentiptycene axis, and (c) method for the calculation of internal molecular free volume, where A and B are the projected area of cleft spaces. The internal molecular free volume of an individual pentiptycene unit is estimated as: $2 \times (A + B) \times 7.2 \text{ \AA}^3 \approx 326 \text{ \AA}^3$, where 2 indicates two sets of symmetrical molecular cavities.

A detailed FFV comparison between the pentiptycene-containing polymers with their triptycene counterparts is necessary to provide a better molecular level understanding of how the tunability really works via “partial filling” mechanism and to what extent can membrane transport properties be tuned by the “filling efficiency” determined by the size and possibly the nature of the substituent groups. As shown in Table 3, although the change of fractional free volume as a function of substituent groups followed the same trend in these two series of polymers (i.e., $-\text{CF}_3 > -\text{H} > -\text{CH}_3$), there is obviously different “filling efficiency” due to the different sizes of accessible molecular cavities of triptycene and pentiptycene units. Compared with 6FDA-PPDA(H) which contains no substituent group, the FFV of 6FDA-PPDA(CH_3) was decreased by 2.2% due to the introduction of CH_3 groups. However, this value was 3.2% for the corresponding triptycene-based polyimide i.e., 6FDA-1,4-trip- CH_3 . The smaller decrease of FFV for pentiptycene-based polyimides is due to the higher overall internal free volume of pentiptycene units compared with triptycene. As shown in Figure 5, the internal free volume of the middle cleft (denoted as B) of pentiptycene unit is $133 \text{ \AA}^3$, which is about three times larger than that of triptycene (the same as cleft A, $31 \text{ \AA}^3$). When CH_3 groups fill this volume, it results in a smaller FFV decrease for pentiptycene. In the case of CF_3 substitution, the FFV has increased by 7.6% and 17.3% for pentiptycene-based polyimide and triptycene-based polyimide, respectively. The less significant increase in FFV for pentiptycene polyimide again is due to the larger clefts and the more open structure in pentiptycene that is accessible to substituent groups. For triptycene-based polyimide, the bulky CF_3 groups (occupied

volume of 46 Å³) cannot fill in the small clefts (31 Å³), which resulted in a significant increase of the FFV (17.3%) due to the disrupted chain packing and increased inter-chain spacing. While for pentiptycene, the large open space of the middle clefts (clefts B in Figure 5) allows the CF₃ groups to fill in this volume at least in part, which counteracts the effect of chain packing disruption of CF₃ groups leading to a less significant increase of the overall FFV (by 7.6%) for pentiptycene-based polyimide. These effects are schematically illustrated in Figure 6. The observed difference in volume change supports that our previously proposed “partially filling” mechanism which may be readily generalized to other iptycene-containing polymers.[15]

Fig. 6. Dependence of “filling efficiency” on the size of the substituent groups in the clefts of iptycene units

3.3. Pure gas permeation properties

Pure gas permeabilities of five gases (H₂, N₂, O₂, CH₄ and CO₂) for the three pentiptycene-containing polyimides were measured by using the constant-volume variable-pressure method.[34] The feed pressure dependence of permeability is shown in Figure S5 in the Supporting Information. Gas permeabilities had a very weak dependence on the feed pressure, and there was no plasticization pressure point for CO₂ with increasing fugacity up to 17 atm. The pure gas transport properties of all polyimides are reported at 10 atm and 35 °C.

Table 4

Pure gas permeability and ideal selectivity of pentiptycene-containing polyimides and related polyimides in the literature.

	Permeability (Barrer)					Ideal Selectivity (α)			
	H ₂	N ₂	O ₂	CH ₄	CO ₂	H ₂ /N ₂	O ₂ /N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
6FDA-PPDA(H)	131	3.2	17	2.5	73	41	5.3	29	23
6FDA-PPDA(CH ₃)	100	2.4	12	2.0	55	42	5.0	28	23

6FDA-PPDA(CF ₃)	188	7.0	30	5.5	132	27	4.3	24	19
6FDA-1,4-trip_para[15]	49	0.66	4.07	0.37	14.4	74	6.0	39	22
6FDA-1,4-trip_CH ₃ [15]	37	0.41	2.64	0.23	9.0	90	6.4	39	22
6FDA-1,4-trip_CF ₃ [15]	59.4	0.99	5.75	0.53	19.7	60	5.8	37	20
Matrimid®[47]	18	0.32	2.1	0.28	10	56	6.6	36	31
Polysulfone[48]	□	0.18	1.2	0.18	5.6	□	6	22	31

Gas permeability and ideal selectivity of pentiptycene-containing polyimides, along with triptycene-containing polyimides, Matrimid® and polysulfone for comparison, are listed in Table 4. The following trends could be immediately drawn from the results: 1) The permeabilities sequence of all three polyimides is $P(H_2) \square P(CO_2) \square P(O_2) \square P(N_2) \square P(CH_4)$, which follows the order of kinetic diameters of the test gases. It indicates that diffusivity plays an important role in the gas permeation for these glassy polymers, which largely rely on size sieving mechanism to perform separations; 2) The gas permeability of pentiptycene-containing polyimides depends strongly on the substituent groups, which is closely related to the fractional free volume. The sequence in permeability agrees well with the FFV sequence discussed earlier. For example, the CO_2 permeability of 6FDA-PPDA(CF₃) is about 2-fold higher than that of 6FDA-PPDA(CH₃) because of the much higher fractional free volume in 6FDA-PPDA(CF₃); 3) Permeabilities of large size gas molecules (e.g., N_2 and CH_4) seem to be more sensitive to the free volume change compared with small gases like H_2 . For example, $P(CH_4)$ was more than doubled from 6FDA-PPDA(H) to 6FDA-PPDA(CF₃) while only less than 50% increase in $P(H_2)$ was observed. This is also evidenced by the comparison between the pentiptycene polyimides and triptycene polyimides. For example, $P(CH_4)$ was increased by more than 10 times from 6FDA-PPDA(CF₃) to its triptycene counterpart (6FDA-1,4-trip_CF₃), while only about 3 times increase in $P(H_2)$ was observed by replacing triptycene with pentiptycene. It seems to suggest that the increase in free volume is most likely due to the creation of more large-size free volume elements upon using pentiptycene or incorporating bulky CF₃ groups, which facilitates the transport of large-size gas molecules; 4) The detailed architecture of the free volume elements, i.e., the shape, size, and size distribution of the molecular cavities may play an important role for gas permeation. For example, given the same FFV (18.3%) for the pentiptycene-based 6FDA-PPDA(H) and the triptycene-based 6FDA-1,4-trip_CF₃, the same,

or at least very similar, gas permeabilities were expected for these two polyimide. However, as shown in Table 4, the gas permeabilities of 6FDA-PPDA(H) are much higher than those of 6FDA-1,4-trip_{CF}₃ for all the gases tested while maintaining comparable selectivities, which seems to suggest that a preferred free volume architecture was generated in the pentiptycene-containing polyimides series leading to much improved overall separation performance. Studies of the fundamental transport properties regarding the respective contribution from diffusivity (D) and solubility (S) factor are undergoing, which will provide insights into the molecular origins for the gas transport in these new membranes. Overall, introduction of pentiptycene units into polymer backbone improved the permeability significantly when compared with both triptycene-polyimides and commercial polymers.[15, 47] For instance, the permeabilities of pentiptycene polyimides for all the five gases tested are about an order of magnitude higher than those of Matrimid[®] polyimide and polysulfone. More importantly, the significant increase in the permeabilities was accompanied with very moderate decrease in the selectivities. This is actually a preferred combination in practical applications since high permeability with reasonable selectivity would mitigate the requirement of high feed pressure and allow smaller membrane area thus enabling good capital and energy efficiency.[1-3, 49]

Fig. 7. Permeability-selectivity upper bound plots of 6FDA-PPDA(H) (red open square), 6FDA-PPDA(CH₃) (red open circle) and 6FDA-PPDA(CF₃) (red open triangle) for (a) CO₂/CH₄ and (b) O₂/N₂ pairs. Other comparative data points are: 1-Matrimid[®];[47] 2-6FDA-1,4-trip_{CF}₃:[15] 3-6FDA-1,4-trip_{para}:[15] 4-6FDA-1,4-trip_{CH}₃:[15] 5-polysulfone.[48]

The permeability-selectivity tradeoff plots for CO₂/CH₄ and O₂/N₂ gas pairs of the

1 pentiptycene-containing polyimides are shown in Figure 7 to evaluate their separation performance
2 against the Robeson's upper bounds. Some reported data points, i.e., triptycene-containing
3 polyimides, Matrimid[®] and polysulfone, were included for comparison. As shown, significant
4 improvement in the permeability-selectivity combinations was readily achieved by the
5 pentiptycene-containing polyimides when compared with the benchmark commercial polymers.
6 Additionally, all three pentiptycene-containing polyimides outperformed the corresponding
7 triptycene-based polyimides, verifying that introduction of pentiptycene into polymer backbone
8 generated more free volume due to more accessible molecular cavities and bulkier structure of
9 pentiptycene. More importantly, preferred free volume architecture was obtained in
10 pentiptycene-based polyimides as clearly evidenced by the trend of moving the separation
11 performance rather laterally approaching the upper bound, instead of following the trade-off slope
12 as conventional glassy polymers generally behave. This finding also suggests the better tunability of
13 pentiptycene-polyimides in terms of optimizing the free volume fraction and architecture to meet
14 different separation requirements.
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30 4. Conclusions

31
32 Three new pentiptycene-based diamine monomers containing different substituent groups were
33 synthesized successfully with high purity and high yields. A general methodology was developed to
34 feasibly incorporate pentiptycene units into polyimide structures by a polymerization of the newly
35 designed and synthesized pentiptycene-containing diamines with a dianhydride, 6FDA. The
36 obtained pentiptycene-containing polyimides showed excellent solubility in a wide range of organic
37 solvents and had excellent thermal stability suggesting their excellent processability and durability.
38 In general, all the pentiptycene-containing polyimides exhibited high fractional free volume, which
39 naturally resulted in high gas permeabilities, due to the incorporation of rigid bulky pentiptycene
40 units that contains large size molecular cavities. The fractional free volume and consequently the
41 gas transport properties were found to be very sensitive to the detailed primary structure of the
42 pentiptycene diamines, i.e., the substituent groups neighboring the clefts of the pentiptycene units.
43 Depending on the size of these substituents relative to the molecular cavity, the overall free volume
44 fraction and the size of the free volume elements can be feasibly tuned. In the case of large size
45 group like CF₃, an increased FFV and permeability were obtained; while for relatively small size
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CH₃ group, opposite results were obtained. These observations are consistent with, and again support the mechanism of “partial filling” of molecular cavities by the substituent groups previously proposed for triptycene-polyimides, suggesting a general molecular manipulation mechanism for iptycene-containing polymers. Notably, the significant increased gas permeability was accompanied with a very moderate reduction in selectivity. These results suggest great potential for further tuning of the pentiptycene-polyimide structure to enhance gas separation properties.

ASSOCIATED CONTENT

Supporting Information

¹H NMR spectra for the pentiptycene-containing polyimides, three-dimensional ball-stick model of pentiptycene diamine **4c**, DSC and TGA curves, and the feed pressure dependence of gas permeabilities.

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Notes

The authors declare no competing financial interest.

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