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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.

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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

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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.

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

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, > 99.0%) was purchased from Akron Polymer Systems and dried at 160 °C under vacuum for 12 h 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.

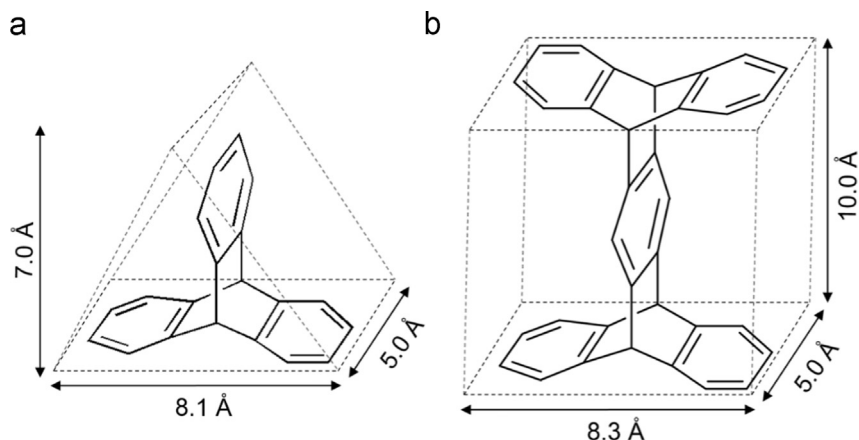


Fig. 1. Three-dimensional structure of (a) triptycene [21] and (b) pentiptycene molecule. (Note: the dimension of pentiptycene was estimated from the centroids of the extreme hydrogen atoms according to the geometry of the molecular configuration at ground energy state.)

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