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Tröger's Base-Based Microporous Polyimide Membranes for High-Performance Gas Separation

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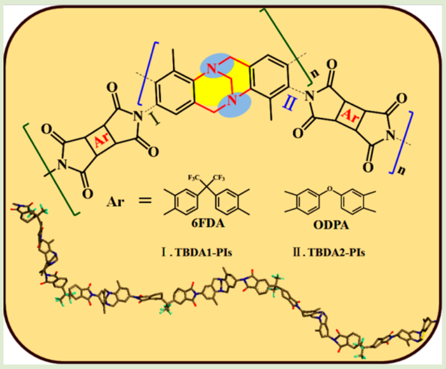
Supporting Information

ABSTRACT: It is a great challenge for polyimide to increase its permeability and at the same time to maintain its high selectivity. In this work, Tröger's Base (TB)-based polyimides through polymerizing Tröger's Base diamines with two kinds of anhydrides were successfully synthesized to enhance the permeability of polyimides for gas separation. The TB-polyimide membranes exhibited greatly improved gas separation performance for H_2/CH_4, H_2/N_2, He/CH_4, and CO_2/CH_4 gas pairs, among which the separation performance of 6-FDA-based TB-polyimides approaches or slightly exceeds the 2008 Robeson upper bound. Our results revealed that the TB unit with rigid and in-built amine structure plays an important role for increasing the permeability of polyimides and simultaneously maintaining high selectivity. In addition, the TB-based polyimide membranes exhibited extremely high solubility selectivity for the CO_2/N_2 gas pair up to 62.7 due to a strong affinity between CO_2 and nitrogen atoms of tertiary amine in TB.



Polymer-dominated membranes have aroused great attention in the field of gas separation owing to their easy processing, great variety, and low cost/environmental effectiveness.[1] In the past decades, abundant polymer membranes have been designed and demonstrated to be potential feasible in gas separation application, such as H_2 recovery from ammonia production or hydrocarbon processing, natural gas purification, N_2 production from air, and CO_2 separation and capture.[2] An ideal gas-separation membrane for industrial application requires both high permeability and high selectivity. However, membranes always suffer from an undesired trade-off between permeability and selectivity as described by the Robeson upper-bound relationship which was also verified in theory by Freeman.[3c] The Robeson upper-bound relationship has been regarded as an empirical criterion to judge the integral performance of membranes. To design a polymer membrane with gas-separation property, surpassing the Robeson upper-bound relationship is becoming the goal of this research field.

Polyimides are an important class of polymers for gas separation and have been widely used in practical application owing to their good thermal and chemical stability, mechanical strength, processability, and structural tenability.[4] The main obstacle for traditional polyimides is low permeability, although they possess high selectivity for most of the gas pairs. Recently, polymers of intrinsic microporosity (PIMs) were discovered and attracted great interest as a novel and rather unusual material for membrane gas separations.[6] The feature of PIMs membranes is their high permeability due to intrinsic micropores. To improve the permeability of polyimides, microporous polyimides were thus widely investigated through designing both dianhydrides and diamines to construct microporous structure. Various microporous polyimides with bulk and kinked structure were thus synthesized, such as dianhydride derived from spirobisindane, triptycene, ethanoanthracene, diamine monomers from spirobifluorene, spirobisindane, fluorene, binaphthalene, triptycene, and so on, and the gas separation performances of these polyimides were evaluated accordingly.[7,8] The introduction of micropores into polyimides indeed enhanced gas permeability, although a decrease in selectivity was often observed. Up to date, only a few polyimides possess the performance that can exceed the Robeson upper bound. It is still a great challenge for polyimide to increase its permeability and at the same time to maintain its selectivity.

According to Freeman's theory, to achieve both high permeability and high selectivity, enhancing the stiffness of the polymer chain backbone is also important besides the introduction of micropores. Recently, the McKeown group developed new polymers based on Tröger's Base (TB) units for gas separation.[9a] The TB-derived polymers exhibited the state-of-the-art performance. Their results revealed that the TB unit with rigid and in-built amine structure plays an important role for enhancing gas separation performance,[9b−e] which was also verified by Guiver et al. and us, recently.[9f,g] The rigidity and kink structure of the TB unit inspires us to construct TB-based polyimide.

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In this work, TB-based polyimides through polymerizing TB diamines with two kinds of anhydrides are successfully synthesized. Gas permeation results reveal that the TB-polyimide membranes exhibit greatly improved gas separation performance for H_2/CH_4, H_2/N_2, He/CH_4, and CO_2/CH_4 gas pairs benefiting from the introduction of the TB unit. Among them, the separation performances of 6-FDA-based TB-polyimides approach or slightly exceed the 2008 Robeson upper bound. The permeability of TB polyimide membranes increases with a decrease of gas molecular size (except for He < H_2), indicating a molecular sieve function of the polymers.

Two TB-derived diamine monomers with different position of methyl relative to amine, 2,8-diamino-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzo[1,5]-diazocine (TBDA1) and 3,9-diamino-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzo[1,5]-diazocine (TBDA2), are first designed and synthesized via two steps: the dimerization of substituted aniline and the reduction of nitro groups.[10] Four TB-based polyimides are subsequently prepared via a one-step solvothermal azeotropic cycloimidization reaction between the two diamine monomers and the two anhydride monomers, 4,4′-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) and 4,4′-oxidiphthalic anhydride (ODPA), respectively, as shown in Figure 1a. All the four TB-based polyimides are fully characterized by ^{1}H NMR, ^{13}C NMR, and ATR-FTIR spectra (Figures S1–S3, Supporting Information). These results determine the molecular structures precisely as shown in Figure 1b and indicate the full imidization in the polymers. The molecular weight (M_w) and polydispersity indices (PDI, M_w/M_n) of the four TB-based polyimides are in the range of 52 000–78 000 and 2.3–2.7, respectively, as obtained from gel permeation chromatography (GPC) measurements (Table S1, Supporting Information). The solubility of the four polyimides in various solvents has been investigated in detail (Table S2, Supporting Information). The two TBDA-6FDA-PIs exhibit excellent solubility in most of the common solvents such as $CHCl_3$, $CHCl_2$, THF, DMF, NMP, and DMSO, and the two TBDA-ODPA-PIs can also dissolve in the above solvents except THF. The four polyimide films were obtained by casting the four polyimide polymers in chloroform solution onto a circular Teflon mold. The thickness of the four films is similar around 70–80 μm as confirmed by SEM observation. The photographs of the films are shown in Figure 1c. It can be seen that all the films are homogeneous and transparent with good flexibility and high mechanical strength (Table S1, Supporting Information), suggesting they can be used for gas permeation test. The membranes also show an excellent thermal stability with high decomposition temperature up to around 450 °C. The rigidity of polymer backbones might be responsible for the high thermal stability.

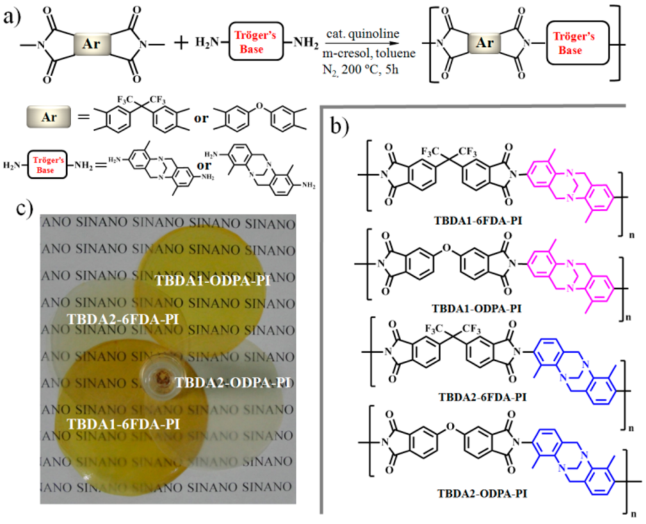

Figure 1. (a) Synthesis route of TB-based polyimides. (b) Chemical structures of four TB-based polyimides. (c) Photographs of four TB-based polyimide membranes.

Figure 2a shows the nitrogen adsorption/desorption curves of the four TB-based polyimides measured at 77 K.

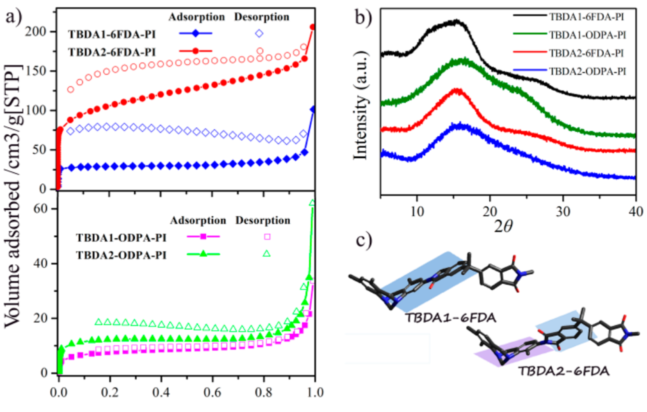

Figure 2. (a) Nitrogen adsorption/desorption isotherms of TBDA1-6FDA-PI, TBDA2-6FDA-PI, TBDA2-ODPA-PI, and TBDA1-ODPA-PI measured at 77 K. (b) WAXD patterns of the four TB-based polyimide membranes. (c) Energy-optimized repeated unit of TB-based polyimides with different position of methyl on diamine.

For TBDA1-6FDA-PI and TBDA2-6FDA-PI, open hysteresis loops formed by irreversible adsorption and desorption curves are observed. This hysteresis loop is the characteristic of intrinsic microporous polymers, which has been often observed by others.[7g,8a] The adsorption isotherms show a high uptake at very low relative pressure, which indicates the presence of micropores in the polymers. The presence of micropores can also be verified by pore width distributions obtained by analysis of N_2 adsorption at 77 K by the Horvath–Kawazoe method (see Figure S7, Supporting Information). It can be seen that the TBDA1-6FDA-PI and TBDA2-6FDA-PI polymers show apparent micropore distribution (<1 nm). The TBDA1-ODPA-PI and TBDA2-ODPA-PI polymers show the tendency of micropore distribution (<1 nm) but with relatively low d*V*/d*W*. This result indicates the microporous properties of the TB-based PIs especially in the case of TBDA1-6FDA-PI and TBDA2-6FDA-PI. It indicates the coexistence of microporous and glassy state property in TBDA1-ODPA-PI and TBDA2-ODPA-PI. The BET surface areas are 89 m^2/g for TBDA1-6FDA-PI, 24 m^2/g for TBDA1-ODPA-PI, 325 m^2/g for TBDA2-6FDA-PI, and 38 m^2/g for TBDA2-ODPA-PI. It shows that TBDA2-contained polyimides have larger BET surface areas than TBDA1-contained polyimides, and 6FDA-contained polyimides have larger BET surface areas than ODPA-contained polyimides. The surface area is related to gas permeability to a certain extent. Our gas permeability test also confirms that higher surface area corresponds to high gas permeability as discussed below. To further investigate the microstructure of the four TB-based polyimides, wide-angle X-ray diffraction (WAXD) is measured. As shown in Figure 2b, a broad peak around 15° is observed in every polyimide

Table 1. Gas Permeability (P) and Ideal Selectivity (α) of TBDA1-6FDA-PI, TBDA1-ODPA-PI, TBDA2-6FDA-PI, TBDA2-ODPA-PI, and Polymers[a]

	permeability (barrer)						selectivity					
polymers	H_2	He	CO_2	O_2	N_2	CH_4	H_2/CH_4	He/CH_4	H_2/N_2	O_2/N_2	CO_2/N_2	CO_2/CH_4
TBDA1- 6FDA-PI	253	199	155	28	6.5	3.3	76.7	60.3	35.1	3.9	23.8	46.9
TBDA1- ODPA-PI	36.4	30.3	13.4	2.5	0.5	0.37	107	89.1	71.4	5.0	26.8	36.2
TBDA2- 6FDA-PI	390	223	285	47	12	8	48.7	27.8	32.5	4.0	23.8	35.6
TBDA2- ODPA-PI	159	119	106	16.2	3.8	2.2	72.3	54.1	41.8	4.3	27.9	48.2

[a] 1 barrer = 10^{-10} [cm^3(STP) cm]/(cm^2 s cm Hg).

Table 2. Diffusion Coefficient (D), Solubility Coefficient (S), Diffusion Selectivity (α_D), and Solubility Selectivity (α_S) for Different Gases (CH_4, N_2, CO_2) of TBDA1-6FDA-PI, TBDA1-ODPA-PI, TBDA2-6FDA-PI, and TBDA2-ODPA-PI

	D (10^{-8} cm^2/s)			S (cm^3/cm^3 cm Hg^{-1})			CO_2/N_2		CO_2/CH_4	
polymers	N_2	CH_4	CO_2	N_2	CH_4	CO_2	α_D	α_S	α_D	α_S
TBDA1- 6FDA-PI	7	0.8	3.35	0.0093	0.041	0.469	0.48	50.4	4.2	11.4
TBDA1- ODPA-PI	0.48	-	0.2	0.0067	-	0.42	0.42	62.7	-	-
TBDA2- 6FDA-PI	13.0	1.1	5.3	0.0092	0.073	0.54	0.41	58.7	4.8	7.40
TBDA2- ODPA-PI	4.1	0.52	2.3	0.0093	0.042	0.46	0.56	49.5	4.4	11.0

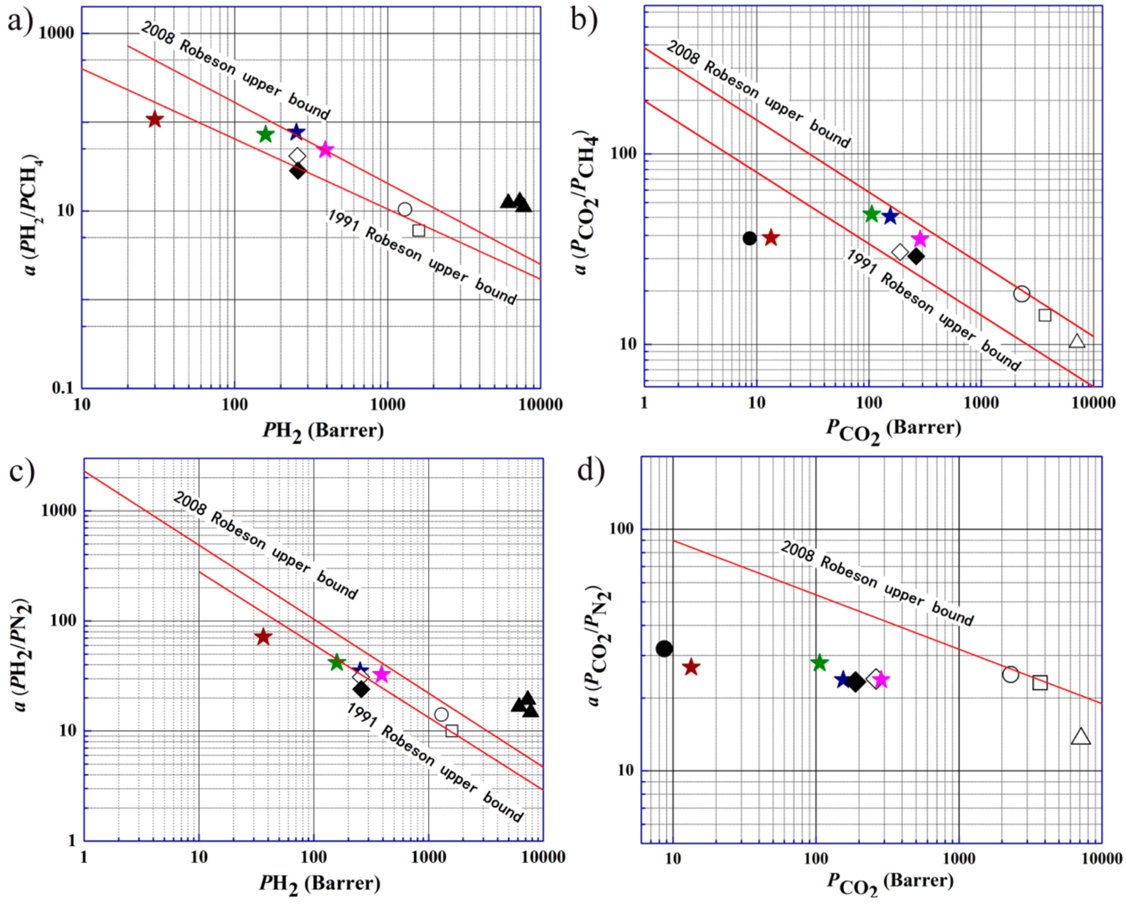

Figure 3. Relationship between gas permeability and gas pair selectivity of TB-based polyimide membranes with the Robeson upper bound (red ★, TBDA1-ODPA-PI, green ★, TBDA2-ODPA-PI, blue ★, TBDA1-6FDA-PI, and pink ★, TBDA2-6FDA-PI). Other data points represent commercial polyimide Matrimid-5218 and other highly permeable polyimides that have been reported since the upper bounds were updated in 2008 (●Matrimid-5218,[5c] ▲PIM-EA-TB,[9a] □PIM−PI-8,[8a] ○PIM-1,[6b] ◆6FDA-TADRI,[7e] ◊6FDA-PIM−OH[7g]).

membrane, indicating they are amorphous just like the conventional polyimides. The corresponding d-spacing is 5.7 Å for TBDA1-6FDA-PI, 5.4 Å for TBDA1-ODPA-PI, 5.8 Å for TBDA2-6FDA-PI, and 5.6 Å for TBDA2-ODPA-PI. In general, the d-spacing could be considered to represent the distance between the polymer chain segments in the membrane, and it is also related to free volume. The difference in d-spacing was also verified by fractional free volume (FFV) where TBDA2-6FDA-PI > TBDA1-6FDA-PI > TBDA2-ODPA-PI > TBDA1-ODPA-PI.[11] This result is in agreement with WAXD.

The pure-gas permeation experiments of the four TB-based polyimide membranes for H_2, He, N_2, O_2, CH_4, and CO_2 gases were carried out on a fixed-volume pressure increase time-lag apparatus with gas feed at 35 °C. The measured values of permeability (P) and calculated ideal selectivity (α) are given in Table 1. The diffusion coefficient (D) and the solubility coefficient (S) derived from the solution-diffusion model ($S = P/D$) are summarized in Table 2. For all the TB-based polyimides, the order of permeability is $H_2 > He > CO_2 > O_2 > N_2 > CH_4$, which has been also observed in other glassy polymers such as aromatic polyimides and polysulfones.[5,12] The permeability is strongly related to the size of the gas molecule. As can be seen from the plots of permeability versus kinetic diameter of gases (Figure S8, Supporting Information), for most of the gases except for He, permeability decreases with the increase of kinetic diameter of gases, showing the organic molecular sieving properties. For each gas, the sequence of permeability is TBDA2-6FDA-PI > TBDA1-6FDA-PI > TBDA2-ODPA-PI > TBDA1-ODPA-PI, which is consistent with the results of nitrogen sorption studies and FFV analysis as described above. As compared to traditional polyimide membranes, our TB-polyimides exhibit extremely improved permeability. Among them, TBDA2-6FDA-PI achieves the highest permeability for H_2 up to 390 barrer and CO_2 up to 285 barrer. These values far surpass commercial polyimide Matrimid 5218 with PCO_2 of around 8.7 barrer. Besides high permeability, our TB polyimides also exhibit high selectivity for the gas pairs of H_2/CH_4, CO_2/CH_4, and H_2/N_2. Robeson plots of P versus α for gas pairs of H_2/CH_4, CO_2/CH_4, H_2/N_2, and CO_2/N_2 are shown in Figure 3. It can be seen that 6FDA-based TB-polyimides (TBDA2-6FDA-PI and TBDA1-6FDA-PI) surpass the 2008 Robeson plot for the gas pair H_2/CH_4 and approach the 2008 Robeson upper bound for gas pairs CO_2/CH_4 and H_2/N_2. It should be noted that for the gas pair CO_2/CH_4 the solubility effect of CO_2 might cause the plasticization of the membranes when the CO_2 feed pressure goes up to a much higher value.[13] Due to such plasticization the actual separation performance for mixed-gas feed of CO_2/CH_4 would be weakened more or less. It has been acknowledged that 6FDA as one of the best anhydride units is advantageous to construct polyimides with improved permeability and selectivity due to its stiff and bulk structure. The 6FDA-based polyimides could basically represent high-level separation performance of polyimides.[14] As compared to the 6FDA-based polyimides reported so far, our 6FDA-based TB-polyimides exhibit the best performance in consideration of both high selectivity and high permeability. The two ODPA-based TB-polyimides, especially TBDA1-ODPA-PI, present high selectivity but less permeability.

Our TB-based polyimides show a much lower selectivity for gas pair CO_2/N_2 as compared to the gas pairs of H_2/CH_4, CO_2/CH_4, and H_2/N_2. According to the solution-diffusion separation mechanism, selectivity can be expressed by $\alpha = \alpha_D\alpha_S$, where $\alpha_{\text{(ideal selectivity)}} = Px/Py$, $\alpha_{D\text{(diffusion selectivity)}} = Dx/Dy$, and $\alpha_{S\text{(solubility selectivity)}} = Sx/Sy$. Therefore, the selectivity is basically determined by diffusion selectivity and solubility selectivity. As shown in Table 2, our TB-based polyimides show extremely high solubility selectivity (α_S) for the gas pair CO_2/N_2, 50.4 for TBDA1-6FDA-PI, 62.7 for TBDA1-ODPA-PI, 58.7 for TBDA2-6FDA-PI, and 49.5 for TBDA2-ODPA-PI. These α_S values are much higher than previously reported polyimides.[7] In contrast, the diffusion selectivity (α_D) of 0.48 for TBDA1-6FDA-PI, 0.42 for TBDA1-ODPA-PI, 0.41 for TBDA2-6FDA-PI, and 0.56 for TBDA2-ODPA-PI is a common value among previous reported polyimides. Obviously, the high solubility selectivity does not give rise to a high ideal selectivity. This result is ascribed to the solubility effect of the TB unit on CO_2. The nitrogen atoms of the tertiary amine in the TB structure could strongly interact with CO_2 driven by Lewis acid–base interaction and/or affinity between polymer and CO_2 molecules arising from the quadrupole moment of the C=O bond and thus could quickly adsorb CO_2.[15] The strong adsorption interaction makes the desorption of CO_2 from polymer difficult, which gives rise to a low diffusion. In fact, the solubility effect of the TB unit on CO_2 behaves differently for the polymers with different free volume. Our results show that TBDA1-ODPA-PI and TBDA2-6FDA-PI have similar $\alpha_s(CO_2/N_2)$ and $\alpha(CO_2/N_2)$. However, they exhibit different permeability (PCO_2 = 13.4 barrer for TBDA1-ODPA-PI and PCO_2 = 285 barrer for TBDA2-6FDA-PI) due to their different α_D originated from free volume (FFV = 0.18 for TBDA1-ODPA-PI and FFV = 0.23 for TBDA2-6FDA-PI). This indicates that CO_2 solubility originated from TB units has a positive effect on the polymer with large free volume and thus enhances permeability and has a negative effect on the polymer with small free volume, thus decreasing permeability.

Our results demonstrate that the introduction of the TB unit makes great contributions to the high separation performance of TB-polyimides. The high rigidity of the TB unit brings polyimide a stiff backbone, thus enhancing the segment mobility selectivity dramatically. In addition, the TB unit has a ladder-type bridged bicyclic amine structure with dihedral angles of 112°, and this type of structure makes the polyimide chains more loose packing and results in the formation of micropores. Such kinked structure promotes the increase of gas permeability. It is worthy to note that the TB structure needs to be combined with the building block with high free volume rather than low free volume to better play the function of TB. This has been confirmed by the contrastive results of ODPA-PI and 6FDA-PI where 6FDA-PI with large free volume has much larger permeability than ODPA-PI with small free volume. It is also found that the position of methyl on the TB derivative diamine (TBDA) has a great effect on gas permeability. The *o*-methyl TBDA-PI shows much higher permeability than *p*-methyl TBDA-PI. The CO_2 permeability of TBDA1-6FDA-PI (285 barrer) is almost 2 times that of TBDA1-6FDA-PI (155 barrer). This phenomenon is ascribed to the different effect of the methyl position on the rotation around the imide bond.[16] The *o*-methyl could hinder the rotation around the imide bond due to steric hindrance, which will cause the polymer chain packing to be less efficient and therefore increase the free volume of the polymer. This can be clarified by the energy optimized molecular model as shown in Figure 2c.

In conclusion, a series of polyimides based on Tröger's Base diamine unit has been designed to improve the permeability of polyimide polymers. The gas separation experiments demonstrate that the TB-based polyimide membranes possess superior separation performance with high permeability and simultaneously high selectivity for H_2/CH_4, H_2/N_2, He/CH_4, and CO_2/CH_4 gas pairs benefiting from the introduction of the TB unit. The performance of the 6FDA-based TB-polyimide even exceeds the 2008 Robeson upper bound for the H_2/CH_4 gas pair. Moreover, the TB-based polyimides show good solubility in common solvents, high molecular weight, and high thermal stability. The superior separation performance accompanied by its good film-processing ability as compared to most of the conventional polyimides makes them highly potential to be applied for gas separation.

■ ASSOCIATED CONTENT

S Supporting Information

Experimental procedures including monomer and polymer synthesis, ^{1}H NMR and FTIR spectra, TG, DSC and DMA assays, and physical properties of TB-based polyimides. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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