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## Synthesis and characterization of a microporous 6FDA-polyimide made from a novel carbocyclic pseudo Tröger's base diamine: Effect of bicyclic bridge on gas transport properties



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## ABSTRACT

A newly designed carbocyclic pseudo Tröger's base diamine (CTB) monomer, 2,8-dimethyl-3,9-diamino-5,6,11,12-tetrahydro-5,11-methanodibenzo[*a*,*e*][8]annulene (CTBDA) and its isomeric analogue 2,8dimethyl-(1,7)(4,10)(3,9)-diamino-5,6,11,12-tetrahydro-5,11-methanodibenzo[*a*,*e*][8]annulene (iCTBDA), were designed for the synthesis of microporous 6FDA-based polyimides (6FDA-CTBDA and 6FDAiCTBDA). Both polyimides were soluble, exhibited excellent thermal stability of ~490 °C, and had high surface areas of 587 m<sup>2</sup> g<sup>-1</sup> (6FDA-CTBDA) and 562 m<sup>2</sup> g<sup>-1</sup> (6FDA-iCTBDA). A 6FDA-based polyimide derived from 4,10-dimethyl-3,9-diamino-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]-diazocine (6FDA-TBDA) was made for comparison to investigate the effects of the basic tertiary nitrogen functionality in the Tröger's base diamine on the polymer properties relative to the carbocyclic 6FDA-CTBDA analogue. 6FDA-TBDA displayed lower gas permeabilities but moderately higher gas-pair permselectivities than 6FDA-CTBDA. The enhanced permselectivity of 6FDA-TBDA resulted exclusively from higher diffusion-based selectivity. Direct gas sorption measurements demonstrated that the basicity in the Tröger's base bridge moiety enhanced the sorption capacity of CO<sub>2</sub> only slightly and had no effect on the CO<sub>2</sub>/CH<sub>4</sub> solubility selectivity in 6FDA-TBDA vs. 6FDA-CTBDA.

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## 1. Introduction

Intrinsically microporous amorphous polymers (PIMs) have emerged as a burgeoning membrane materials class with great potential in highly demanding gas separation applications [1–6]. The unique properties of this new materials class include: (i) high gas permeability and moderate to high selectivity; (ii) high Brunauer-Emmett-Teller (BET) surface area; (iii) narrow pore size distribution with pores < 20 Å; (iv) high thermal stability and (v) solubility in a wide variety of organic solvents for thin-film composite or asymmetric membrane formation [7]. The microporous structure of PIMs results from the presence of highly rigid and contorted molecular building blocks, which severely restrain sufficient chain packing of the polymer matrix leading to high free volume [1,8,9]. The first generation of PIMs were

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based on ladder polymers derived from the reaction of 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane and tetra-fluoroterephtalonitrile (PIM-1) or 5,5',6,6'-tetrachlorophenazyl-spirobisindane (PIM-7) [10,11]. Recently developed ladder PIMs using triptycene [12–14] and Tröger's base [15] building blocks demonstrated enhanced gas separation performance defining the 2015 permeability/selectivity upper bounds for  $O_2/N_2$ ,  $H_2/N_2$  and  $H_2/CH_4$  [5].

The second generation of PIMs for gas separations originated from extensions of earlier developments of low-free-volume polyimides that exhibited high selectivity but only low to moderate permeability [16–20]. McKeown's group reported for the first time the efficient incorporation of kinked spirobisindane contortion sites into intrinsically microporous polyimides (PIM-PIs) [21–23]. PIM-PIs showed significantly higher gas permeability coupled with reduction in gas-pair selectivity compared to conventional polyimides; however, their performance was close to the 2008 upper bounds for various gas pairs. Intensive investigations to tailor the structural design using ethanoanthracene- and 9,10-bridgehead-substituted triptycene moieties resulted in advanced PIM-PIs that



demonstrated significantly enhanced selectivity for several gas pairs, especially  $O_2/N_2$  and  $H_2/CH_4$  while maintaining very high gas permeability [24–28]. Moreover, hydroxyl- and carboxyl-functionalized PIM-PIs have shown excellent performance in removal of  $CO_2$  and  $H_2S$  from methane in natural gas applications [29–35].

Recently, novel ladder PIMs and PIM-PIs using Tröger's basederived building blocks attracted much attention as membrane materials due to their promising gas separation properties and extremely versatile chemistry [15,36–38]. Tröger's base is a chiral organic molecule, in which the chirality results from the presence of two bridgehead stereogenic nitrogen atoms in its structure [39]. The cleft-like shape of Tröger's base conferred by the diazocine bridge has resulted in incorporation of this rigid framework into a variety of polymers with intrinsic microporosity. Tröger's basederived PIM-PIs demonstrated good performance as materials for membrane-based gas separations with high permeabilities and commendable selectivities [15,40–47].

Carbocyclic analogues of Tröger's base biscatecols as new building blocks for ladder PIMs were recently reported by Carta et al. Carbocyclic ladder PIMs made by reaction with tetra-fluoroterephtalonitrile displayed high BET surface area of up to 685 m<sup>2</sup> g<sup>-1</sup> but were either insoluble or had too low molecular weight ( $M_w \sim 10,000 \text{ g mol}^{-1}$ ) to form strong isotropic films for gas permeation testing [48].

Here, we report the synthesis and gas transport properties of a soluble, high molecular weight intrinsically microporous polyimide made from a novel carbocyclic V-shaped pseudo Tröger basederived diamine (CTBDA) and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) via high-temperature polycondensation reaction. A related 6FDA-based Tröger's base polyimide (6FDA-TBDA) was made to evaluate the effects of the nitrogen-containing bridgehead compared to the carbonsubstituted cleft derivative polyimide (6FDA-CTBDA). The polyimides were fully characterized by <sup>1</sup>H NMR, Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), thermogravimetric analysis (TGA) and gas sorption measurements. Moreover, pure-gas permeation data for fresh and aged samples are reported.

#### 2. Experimental

## 2.1. Materials

The compounds 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) 4-methylbenzyl cyanide, 2-methyl-3-nitroaniline, formaldehyde  $(CH_2O)_n$ , diiodomethane, methanesulfonic acid, potassium hydroxide, lithium aluminum hydride (LiALH<sub>4</sub>), thionyl chloride (SOCl<sub>2</sub>) isoquinoline, diethylether, potassium nitrate, trifluoroacetic anhydride (TFAA), trifluoroacetic acid (TFA), palladium on carbon 5% (Pd/C), and hydrazine monohydrate were used as received. *m*-Cresol was distilled under reduced pressure and stored in the dark over molecular sieves. All other solvents were obtained from various commercial sources and used as received.

#### 2.2. Characterization methods

Flash chromatography was performed on silica gel 60 A (35–70 µm, Fisher Scientific). <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Bruker DRX 400 spectrometer in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub>. Chemical shifts ( $\delta$ ) are reported in ppm. Fourier transform infrared (FT-IR) measurements were performed using a Varian 670-IR FT-IR spectrometer. Thermogravimetric analysis (TGA, TA Q-5000) measurements were carried out

under nitrogen atmosphere with a drying step at 100 °C for 30 min followed by a ramp of 3 °C/min up to 800 °C. Melting point measurements were determined by using differential scanning calorimetry (DSC, Q-2000) (ramping of 3 °C/min to 400 °C). A Micromeritics ASAP 2020 gas sorption analyzer equipped with a micropore upgrade was used to measure the BET surface areas of 6FDA-CTBDA and 6FDA-TBDA. Nitrogen sorption measurements were performed at -196 °C up to 1 bar. Analysis of the pore size distributions was performed using the NLDFT (Non-Local Density Functional Theory) model using N<sub>2</sub> sorption isotherms for carbon slit pore geometry provided by ASAP 2020 version 4.02 software. Powder polymer samples were fully degassed under high vacuum at 120 °C for 24 h prior to analysis. Molecular weights and molecular weight distribution of the polymers were obtained by gel permeation chromatography (Agilent GPC 1200) with polystyrene as external standard. Density was obtained using a Mettler-Toledo balance equipped with a density measurement kit based on Archimedes' principle using iso-octane as the reference liquid. Single-crystal x-ray diffraction was carried out on an Oxford SuperNova single-crystal x-ray diffractometer at liquid nitrogen temperature (-196 °C).

#### 2.3. Monomer synthesis

# 2.3.1. Synthesis of 2,8-dimethyl-5,11-methanodibenzo[a,e][8] annulene-6,12(5H,11H)-dione (III) (Scheme 1a)

2,8-Dimethyl-5,11-methanodibenzo[a,e][8]annulene-

6.12(5H.11H)-dione was prepared as previously reported [49]. 4-Methylbenzyl cyanide (8 g, 61.0 mmol) and KOH (3.41 g, 61 mmol) were dissolved in diiodomethane (8.3 g, 31 mmol) and heated at 165 °C for 2 h. The reaction mixture was cooled down and poured into water (200 mL), extracted with dichloromethane  $(3 \times 50 \text{ mL})$ , washed with brine, dried over MgSO<sub>4</sub>, and the solvent was removed under vacuum to give meso-phenylpentanedinitrile (I) (8 g), which was hydrolyzed by heating for 18 h at 80 °C in a mixture of ethanol (80 mL) and potassium hydroxide solution (160 mL, 40%). Ethanol was removed under vacuum, and the residue was diluted with water and washed with dichloromethane until the organic phase became colorless. The aqueous phase was acidified to pH < 1 by adding conc. HCl (20 mL), extracted with ethyl acetate ( $3 \times 50$  mL) and dried over MgSO<sub>4</sub>. The solvents were removed under vacuum to give crude meso-phenylpentanedioic acid (II) (6 g). The crude acid was heated at 100 °C for 3 h in methanesulfonic acid (CH<sub>3</sub>SO<sub>3</sub>H), poured on ice and extracted with ethyl acetate. The organic layers were combined, washed with KOH solution (5 wt%), dried over MgSO<sub>4</sub>, filtered and evaporated to dryness to give crude (III). Purification by silica gel chromatography using dichloromethane/ethyl acetate: 100/1 afforded pure (III) as a white solid (4 g, yield: 64%); mp = 182.2 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 7.62 (br s, 2H), 7.4–7.43 (dd, 2H, *J* = 8.8 Hz, 1.2 Hz), 7.3 (d, 2H, J = 7.6 Hz), 3.95 (t, 2H, J = 2.8 Hz), 2.92 (t, 2H, J = 2.8 Hz), 2.27 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): 194.7, 138.9, 137.8, 135.7, 129.6, 129.2, 128.6, 127.9, 48.1, 32.0, 21.0.

## 2.3.2. Synthesis of 2,8-dimethyl-5,6,11,12-tetrahydro-5,11methanodibenzo[a,e][8]annulene-6,12-diol (IV) (Scheme 1b)

2,8-Dimethyl-5,11-methanodibenzo[a,e][8]annulene-

6,12(5*H*,11*H*)-dione (III) (2.00 g, 7.24 mmol) was dissolved in THF (100 mL) and then LiAlH<sub>4</sub> (1.1 g, 28.9 mmol) was added in portions. The mixture was stirred at room temperature overnight, then poured on 150 g ice and HCl (6 N) was added. The solution was extracted with dichloromethane ( $3 \times 50$  mL), dried over MgSO<sub>4</sub>, filtered and the solvent was removed by vacuum. The resulting yellowish solid was washed using a *n*-hexane/dichloromethane mixture (1:1) to afford an off-white powder (1.42 g, yield: 71%) as a



Scheme 1. Synthetic route of carbocyclic pseudo Tröger's base (CTB) (VI).

final product; mp = 215.6 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.40 (s, 2H), 7.18 (d, 2H, J = 8 Hz), 7.03 (d, 2H, J = 7.6 Hz), 5.02 (d, 2H, J = 5.6 Hz), 3.3 (m, 2H), 2.4 (t, 2H, J = 3.2 Hz), 2.29 (s, 6H), 1.66 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 139.4, 137.4, 130.9, 129.9, 128.2, 127.8, 72.6, 39.1, 29.5, 21.2.

## 2.3.3. Synthesis of 6,12-dichloro-2,8-dimethyl-5,6,11,12-tetrahydro-5,11-methanodibenzo[a,e][8]annulene (V) (Scheme 1b)

2,8-Dimethyl-5,6,11,12-tetrahydro-5,11-methanodibenzo[*a*,*e*][8] annulene-6,12-diol (v) (2 g, 7.13 mmol) was suspended in SOCl<sub>2</sub> (30 mL) and 0.3 mL DMF were added. The solution was refluxed overnight and SOCl<sub>2</sub> was removed by vacuum. The collected product was dried at 100 °C for 3 h. The resulting product (2.1 g, yield: 93%) was obtained as an off-white solid; mp = 191.0 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 6.19 (d, 2H, *J* = 8 Hz), 7.08 (d, 2H, *J* = 7.6 Hz), 7.02 (s, 2H), 5.05 (d, 2H, *J* = 1.6 Hz), 3.54 (m, 2H), 2.67 (t, 2H, *J* = 2.8 Hz), 2.26 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 137.9, 133.8, 133.6, 131.6, 130, 129.3, 62.2, 40.9, 21.0, 18.7.

## 2.3.4. Synthesis of 2,8-dimethyl-5,6,11,12-tetrahydro-5,11methanodibenzo[a,e][8]annulene (VI) (Scheme 1b)

6,12-Dichloro-2,8-dimethyl-5,6,11,12-tetrahydro-5,11-

methanodibenzo[*a*,*e*][8]annulene (V) (5 g, 15.8 mmol) was dissolved in THF (250 mL) and LiAlH<sub>4</sub> (2.4 g, 63 mmol) was added in portions over 30 min. The reaction was refluxed overnight and the resulting mixture was then poured on ice (200 g) and HCl (6 N, 100 mL) was added. The solution was extracted with dichloromethane three times, dried over MgSO<sub>4</sub>, filtered and then the solvent was removed by rota-evaporation. The resulted light orange powder was washed by *n*-hexane/DCM: 4/1 to afford VI (3 g, yield: 76%) as a white powder product; mp = 109.5 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.11 (d, 2H, *J* = 7.6 Hz), 6.94 (d, 2H, *J* = 7.6 Hz), 6.78 (s, 2H), 3.29 (m, 2H), 3.25 (d, 2H, *J* = 5.2 Hz), 2.81 (d, 2H, *J* = 16 Hz), 2.24 (s, 6H), 2.13 (t, 2H, *J* = 2.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 138.2, 135.4, 134.4, 129.9, 128.7, 126.7, 39.5, 32.56, 29.1, 21.0.

## 2.3.5. Synthesis of 2,8-dimethyl-1,7(4,10)(3,9)-dinitro-5,6,11,12tetrahydro-5,11-methanodibenzo[a,e][8]annulene (VII a) and 2,8dimethyl-3,9-dinitro-5,6,11,12-tetrahydro-5,11-methanodibenzo [a,e][8]annulene (VII b) (Scheme 2)

2,8-Dimethyl-5,6,11,12-tetrahydro-5,11-methanodibenzo[a,e][8] annulene (VI) (1.25 g, 5 mmol) was dissolved in 50 mL acetonitrile (CH<sub>3</sub>CN) followed by the addition of KNO<sub>3</sub> (1.12 g, 11.1 mmol) and then trifluoroacetic anhydride (TFAA) (5.2 mL, 35.7 mmol) was added dropwise. After stirring for 1 h at room temperature the reaction was poured on ice and then extracted with dichloromethane (DCM). The crude product was purified by silica gel column chromatography using DCM/n-hexane: 1/1 as an eluent. The product was obtained as a yellow powder (0.8 g, yield: 47%);

mp = 224.5 °C. <sup>1</sup>H NMR and <sup>13</sup>C NMR showed that the product contained three isomers. Recrystallization was performed to obtain only one isomer as a light yellow powder. The structure of the pure isomer was confirmed by single-crystal XRD (Fig. S1). The crystallographic data for VII b were deposited in the Cambridge Structural Database (CCDC 1545077). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.90 (s, 2H), 6.94 (s, 2H), 3.45 (m, 2H), 3.32 (dd, 2H, J = 12 Hz), 2.91 (d, 2H, J = 17.2 Hz), 2.49 (s, 6H), 2.19 (t, 2H, J = 2.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 147.3, 140.3, 139.4, 133.7, 131.7, 125.2, 39.3, 31.9, 28.2, 20.3.

2.3.6. Synthesis of 2,8-dimethyl-3,9-diamine-5,6,11,12-tetrahydro-5,11-methanodibenzo[a,e][8]annulene (VIII b, CTBDA) (Scheme 2) 2,8-Dimethyl-3,9-dinitro-5,6,11,12-tetrahydro-5,11-

methanodibenzo[*a*,*e*][8]annulene (VII b) (0.4 g, 1.2 mmol) was suspended in 20 mL ethanol followed by the addition of Pd/C (0.2 g) and 2 mL N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O. The mixture was refluxed for 3 h under nitrogen and then cooled down to room temperature, precipitated in water and filtrated. The white solid was dried in the vacuum oven for 24 h at 60 °C (0.26 g, yield: 80%); mp = 192.2 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 6.44 (d, 2H, *J* = 4 Hz), 6.40 (d, 2H, *J* = 3.6 Hz), 4.46 (br s, 4H), 3.1 (d, 2H, *J* = 18 Hz), 3.0 (m, 4H), 2.47 (m, 2H), 1.9 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): 144.6, 139.3, 130.5, 122.4, 120.2, 114.3, 39.0, 32.8, 18.0, 17.4. The same synthetic procedure was applied to the produce the 2,8-dimethyl-(3,9)(1,7)(4,10)-diamine-5,6,11,12-tetrahydro-5,11-methanodibenzo[*a*,*e*] [8]annulene (VIII a, iCTBDA). The NMR spectrum of iCTBDA is shown in Fig. S2.

## 2.3.7. Synthesis of 4,10-dimethyl-3,9-dinitro-6H,12H-5, methanodibenzo[b,f][1,5] diazocine (IX) (Scheme 3)

4,10-Dimethyl-3,9-dinitro-6*H*,12*H*-5,methanodibenzo[*b*,*f*][1,5] diazocine (IX) was synthesized by a previously reported procedure [40]. 2-Methyl-3-nitroaniline (5 g, 32.86 mmol) and paraformaldehyde (2.07 g, 69.01 mmol, 2.1 equiv) were dissolved in trifluoroacetic acid (TFA) (65 mL) to form a black-colored solution. The reaction was stirred for 48 h and then poured into H<sub>2</sub>O (200 mL) to yield an intensely yellow precipitate. Aq. NaOH (6 N) was added to this suspension to afford a basic solution (pH = 9). The precipitate was filtered off and washed with hot acetone. Yellow crystals were obtained with 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 6.56 (d, 2H, *J* = 8.4 Hz), 6.93 (d, 2H, *J* = 8.4 Hz), 4.67 (d, 2H, *J* = 17.6 Hz), 4.32 (s, 2H), 4.01 (d, 2H, *J* = 17.6 Hz), 2.59 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 149.8, 147.3, 132.9, 128.8, 124.9, 119.8, 67.2, 55.4, 13.5.

## 2.3.8. Synthesis of 4,10-dimethyl-3,9-diamino-6H,12H-5,

methanodibenzo[b,f][1,5]-diazocine (X) (TBDA) (Scheme 3)

4,10-Dimethyl-3,9-dinitro-6H,12H-5, methanodibenzo[ $b_f$ ][1,5]-diazocine (IX) (1 g, 2.94 mmol) was suspended in 100 mL ethanol followed by the addition of Fe powder (2.22 g, 39.7 mmol) and



Scheme 2. Synthetic route of iCTBDA (VIII a) and CTBDA (VIII b) monomer.



Scheme 3. Synthetic route of diamino Tröger's base monomer (TBDA).

acetic acid (10 mL). The obtained mixture was refluxed for 12 h under nitrogen, then cooled down to room temperature and precipitated in water. Excess iron was filtered off, and the aqueous layer was extracted using dichloromethane (3 × 50 mL). The organic layer was washed with saturated solution of NaHCO<sub>3</sub> and dried over MgSO<sub>4</sub>; volatiles were removed by rota-evaporation at room temperature to afford a light brown powder as a final product (0.7 g, 85% yield). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 6.46 (d, 2H, J = 8.4 Hz), 6.33 (d, 2H, J = 8.4 Hz), 4.57 (br s, 4H), 4.35 (d, 2H, J = 16 Hz), 4.11 (s, 2H), 3.67 (d, 2H, J = 16 Hz), 2.04 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): 146.4, 145.8, 124.4, 116.4, 115.4, 111.2, 67.7, 55.3, 11.3.

## 2.4. Typical procedure for the synthesis of polyimides (Scheme 4)

To a dry 25 mL reaction tube equipped with a Dean-Stark trap, nitrogen inlet and outlet, and reflux condenser were added the

diamine (VIII a, VIII b or X) (1.0 mmol), equimolar amount of the dianhydride monomer (6FDA) (1.0 mmol) and isoquinoline (0.1 mL). The reaction mixture was stirred at room temperature for 1 h, and the temperature was then raised gradually to 200 °C and kept at that temperature for 4 h under a steady flow of nitrogen. Fibrous polyimide was obtained by the dropwise addition of the polymer solution to an excess of methanol (300 mL). The resulting solid fibers were filtered off and the polymer was purified by reprecipitation from chloroform solution into methanol and dried at 120 °C in a vacuum oven for 24 h.

#### 2.4.1. Synthesis of 6FDA-CTBDA and 6FDA-iCTBDA

Following the above general procedure 6FDA-CTBDA and 6FDAiCTBDA were prepared from 6FDA dianhydride and TB diamine VIII a or VIII b, respectively, and obtained as off-white powder (~80–90% yield). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ ): 2.02 (br s, 6H), 2.68 (br m, 2H), 3.25–3.34 (br m, 6H), 6.98 (br s, 2H), 7.24 (br s, 2H),



Scheme 4. Synthesis of 6FDA-based TBDA and CTBDA polyimides.

7.79 (br s, 2H), 7.96 (br s, 2H), 8.15 (br s, 2H). FT-IR (Powder,  $\nu$ , cm<sup>-1</sup>): 1785 (C=O *asym*), 1724 (C=O *sym*, str), 1367 (C–N, str), 722 (imide ring deformation); BET surface area = 587 [562] m<sup>2</sup> g<sup>-1</sup>; GPC (DMF): M<sub>n</sub> = 100,000 [85,000] g mol<sup>-1</sup>, M<sub>w</sub> = 164,000 [155,000] g mol<sup>-1</sup>; PDI = 1.64 [1.82]. TGA: T<sub>d,5%</sub> at ~490 [490] °C. Numbers in brackets refer to 6FDA-iCTBDA.

#### 2.4.2. Synthesis of 6FDA-TBDA

Following the above general procedure 6FDA-TBDA was prepared from the 6FDA dianhydride and diamine X (TBDA) as an off-white powder (95% yield). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 2.32 (s, 6H), 4.04 (d, 2H, *J* = 13.6 Hz), 4.2 (s, 2H), 4.38 (d, 2H, *J* = 13.6 Hz), 7.03 (br s, 2H), 7.18 (br s, 2H), 7.78 (d, 2H, *J* = 10.8 Hz), 7.94 (s, 2H), 8.17 (s, 2H). FT-IR (Powder,  $\nu$ , cm<sup>-1</sup>): 1787 (C=0 *asym*), 1727 (C=0 *sym*, str), 1375 (C–N, str), 725 (imide ring deformation); BET surface area = 403 m<sup>2</sup> g<sup>-1</sup>; GPC (DMF): M<sub>n</sub> = 33,000 g mol<sup>-1</sup>, M<sub>w</sub> = 61,700 g mol<sup>-1</sup>; PDI = 1.86. TGA: T<sub>d,5%</sub> at ~450 °C.

## 2.5. Polymer film preparation

6FDA-CTBDA and 6FDA-TBDA solutions in chloroform (2–3% w/ v, g/mL) were filtered through 0.45  $\mu$ m polypropylene filters and clear isotropic films were obtained by slow evaporation of the solvent at room temperature from a leveled petri dish. The dry films were soaked for 24 h in methanol to remove any residual solvent traces, air-dried and then heated at 120 °C for 24 h in a vacuum oven. TGA was used to confirm complete removal of solvent traces. Films with thickness of ~40  $\mu$ m were used for gas permeability measurements.

#### 2.6. Gas sorption measurements

Carbon dioxide and methane sorption in 6FDA-CTBDA and 6FDA-TBDA was measured at 35 °C up to ~15 bar using a Hiden Intelligent Gravimetric Analyzer (IGA-003, Hiden Isochema, UK). After drying a polymer film (~40–50 mg) under vacuum at 80 °C for 2 days, the sample was mounted in the sorption apparatus and degassed under high vacuum ( $<10^{-7}$  mbar) at 35 °C until constant sample weight readings were obtained before beginning collection of the isotherm data. Then, gas was introduced in the sample chamber by a stepwise pressure ramp of 100 mbar/min until a desired pressure was reached. After equilibrium weight uptake was recorded, the next pressure point was set, and this process was continued until the complete isotherm was determined.

#### 2.7. Gas permeation measurements

The pure-gas permeability of  $H_2$ ,  $N_2$ ,  $O_2$ ,  $CH_4$  and  $CO_2$  was measured at 35 °C and 2 bar via the constant-volume/variable pressure method and calculated by:

$$P = 10^{10} \frac{V_d \cdot l}{P_{up} \cdot ART} \frac{dp}{dt}$$

where *P* is the permeability coefficient in Barrers (1 Barrer =  $10^{-10}$  cm<sup>3</sup> (STP) cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>), *V* is the calibrated volume of the downstream gas reservoir (cm<sup>3</sup>), *l* is the film thickness (cm), *A* is the effective membrane area (cm<sup>2</sup>), *R* is the gas constant (0.278 cm<sup>3</sup> cmHg cm<sup>-3</sup> (STP) K<sup>-1</sup>), *T* is the operating temperature (K),  $p_{up}$  is the upstream pressure (cmHg), and dp/dt is the steady-state permeate-side pressure increase (cmHg s<sup>-1</sup>). Gas permeation in polymers follows a solution/diffusion transport mechanism according to:  $P = D \ge S$ , where *D* is the diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>) and *S* is the solubility coefficient (cm<sup>3</sup> (STP) cm<sup>-3</sup> cmHg<sup>-1</sup>). Gas solubilities of CO<sub>2</sub> and CH<sub>4</sub> were measured gravimetrically at 35 °C up to ~15 bar and then diffusion coefficients were calculated from D = P/S.

The ideal pure-gas selectivity for a gas pair is given by the following relationship:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A}{D_B} x \frac{S_A}{S_B}$$

where  $\alpha_{A/B}$  is the permselectivity of gas A over gas B which can be factored into the diffusion  $(D_A/D_B)$  and solubility  $(S_A/S_B)$  selectivity, respectively.

### 3. Results and discussion

## 3.1. Synthesis of carbocyclic pseudo Tröger's base-containing diamine (CTBDA)

The carbocyclic pseudo Tröger's base (VI) was synthesized via a six-step synthetic route (Scheme 1). The intermediate (I) was synthesized through a reaction between 2-phenylacetonitrile and diiodomethane in the presence of KOH at 160 °C. Compound (II) was afforded by hydrolyzing cyano groups (-CN) to carboxylic acid groups (-COOH) using KOH and an ethanol/water mixture (1/1) at 100 °C. The desired product (III) was then prepared by mixing (II) with methanesulfonic acid at 80 °C. The reduction of the diketo groups of the CTB was achieved via a three-step synthetic route, starting by converting the carbonyl-to hydroxyl groups (IV) using lithium aluminum hydride (LiAlH<sub>4</sub>) at room temperature, followed by overnight refluxing with thionylchloride (SOCl<sub>2</sub>) to replace the hydroxyl groups (-OH) by chloro groups (-Cl) (V), and finally by replacing the chlorine groups by hydrogens using LiAlH<sub>4</sub> at 80 °C for 12 h to yield compound (VI). The molecular structures of all products were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR.

The CTB diamine was prepared via a reaction between the CTB precursor (VI) and potassium nitrate (KNO<sub>3</sub>) in trifluoroacetic anhydride (TFAA) solution to afford the dinitro compounds. The molecular structure of 2,8-dimethyl-3,9-dinitro-5,6,11,12-tetrahydro-5,11-methanodibenzo[*a*,*e*][8]annulene (VII b) was confirmed by single-crystal x-ray crystallography (Fig. S1). The dinitro compound was reduced using hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O) and palladium on carbon (Pd/C) to afford the corresponding diamine. The structures of all products were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR.

# 3.2. Synthesis and characterization of CTBDA- and TBDA-based 6FDA polyimides

The polyimides were synthesized via one-step high-temperature cycloimidization reaction between equimolar amounts of the diamine and dianhydride in *m*-cresol, as outlined in Section 2.4. This study revealed that structural isomerism had only small effects on the physical properties of 6FDA-CTBDA (mono) and 6FDAiCTBDA (multi) as indicated by FT-IR spectra, TGA, BET surface area and gas transport data, as discussed below. The molecular structures of the polymers were confirmed by <sup>1</sup>H NMR and FT-IR spectroscopy. The characteristic absorption bands of the imide group were obtained at about 1785 and 1724 cm<sup>-1</sup> (imide asymmetric and symmetric C=O stretching) and 1367 cm<sup>-1</sup> (C–N, stretching frequency), as shown in Fig. 1. Complete imidization was confirmed by the absence of <sup>1</sup>H NMR signals above 10 ppm and lack of FTIR peaks around 3200 - 3500 cm<sup>-1</sup>.

The polyimides were further characterized by GPC, TGA, and BET surface area (Table 1). The CTBDA-based polyimides showed high average molecular weights ( $M_w \sim 155,000-164,000 \text{ g mol}^{-1}$ ) and narrow polydispersity index of ~1.6–1.8. The 6FDA-TBDA polyimide displayed lower  $M_w$  of ~62,000 g mol<sup>-1</sup> which was similar to a



Fig. 1. FT-IR spectra of 6FDA-CTBDA, 6FDA-iCTBDA and 6FDA-TBDA polyimides.

previously reported value for the same TB polyimide [40].

The three polyimides showed excellent solubility in common organic solvents, such as CHCl<sub>3</sub>, THF, DMF, DMAc, NMP, and DMSO. The 6FDA-CTBDA and 6FDA-TBDA polyimides exhibited high thermal stability with  $T_{d,5\%}$  of ~490 and 450 °C, respectively, as determined by TGA in nitrogen atmosphere (Fig. 2).

Nitrogen adsorption isotherms of 6FDA-CTBDA, 6FDA-iCTBDA and 6FDA-TBDA measured at -196 °C up to 1 bar are shown in Fig. 3a. High nitrogen uptake was evident at low relative pressure, indicating the presence of intrinsic microporosity in the polyimides. The BET surface areas of 6FDA-CTBDA (587 m<sup>2</sup> g<sup>-1</sup>) and 6FDA-iCTBDA (562 m<sup>2</sup> g<sup>-1</sup>) were practically identical within experimental error. The 6FDA-TBDA polyimide showed a BET surface area of 403 m<sup>2</sup> g<sup>-1</sup>, which was ~15% higher than the previously reported value of 349 m<sup>2</sup> g<sup>-1</sup> by Wang et al. [40].

The NLDFT-derived pore size distributions for 6FDA-CTBDA, 6FDA-iCTBDA and 6FDA-TBDA calculated based on their N<sub>2</sub> adsorption isotherms are shown in Fig. 3b. All polyimides displayed pore size distributions with pores in the ultra-microporous range (<7 Å) and a large fraction of micropores in the range of 10–20 Å. The shift towards smaller ultra-micropores for 6FDA-TBDA was an indication to yield better size-sieving properties with correspondingly higher gas-pair selectivity compared to 6FDA-CTBDA and 6FDA-iCTBDA, as previously demonstrated for other PIM-PIs [26,50].

## 3.3. Gas transport properties

Pure-gas permeation experiments were performed at 2 bar and 35 °C on fresh and 60-day aged samples of 6FDA-CTBDA, 6FDAiCTBDA and 6FDA-TBDA. Both CTBDA-derived polyimides exhibited high permeabilities and moderate selectivities, as shown in Table 2. The gas permeabilities of the polyimides followed the order:  $H_2>CO_2>O_2>N_2>CH_4$ , a trend that is typically observed for



Fig. 2. Thermal gravimetric analysis (TGA) of 6FDA-CTBDA, 6FDA-iCTBDA and 6FDA-TBDA polyimides.

moderately microporous PIM-PIs. The gas permeabilities of the two CTBDA-based polyimides were similar; for example the CO<sub>2</sub> permeabilities of fresh 6FDA-CTBDA and 6FDA-iCTBDA films were 291 and 230 Barrer, respectively, with identical CO<sub>2</sub>/CH<sub>4</sub> selectivity of 25. This result indicates that isomerism in the CTB moiety of the 6FDA-based polyimides had only a small effect on their gas permeation properties. Physical aging of the 6FDA-CTBDA film over 60 days resulted in ~30-40% decrease in permeabilities with small increase in selectivities. The performance of 6FDA-CTBDA and 6FDA-iCTBDA is shown for CO<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>/CH<sub>4</sub> separation on a 2008 Robeson trade-off curve in Fig. S-6. Compared to commercial membrane materials for CO<sub>2</sub>/CH<sub>4</sub> separation, such as cellulose triacetate (CTA), aged 6FDA-CTBDA showed commendable performance with ~30-fold higher CO<sub>2</sub> permeability of 201 Barrer (vs. 6.6 Barrer for CTA) and similar CO<sub>2</sub>/CH<sub>4</sub> selectivity of 28 (vs. 32 for CTA) [51].

The gas permeation properties of a structurally related 6FDA Tröger's base-derived polyimide containing a methyl group in ortho position to the imide linkages (6FDA-TBDA) are shown in Table 2 for comparison. In qualitative agreement with its lower BET surface area (Fig. 3a), the gas permeabilities of a fresh 6FDA-TBDA film were 40–60% lower than those of the carbocyclic analogue 6FDA-CTBDA polyimide. Concurrently, the gas-pair selectivities of the 6FDA-TBDA polyimide were higher than those of the carbocyclic pseudo Tröger's base analogue. This trend follows the qualitative shift in pore size distribution towards smaller ultra-micropores in the 6FDA-TBDA relative to 6FDA-CTBDA, as shown in Fig. 3b.

6FDA-TBDA showed good stability against physical aging as gaspair selectivities remained constant and gas permeabilities decreased by only 10% over 60 days (Table 2). Previously, Wang et al. [40] reported gas permeation properties for 6FDA-TBDA with ~40–60% higher gas permeabilities than those of the fresh 6FDA-TBDA film reported here; permselectivity values were similar, as

#### Table 1

Physical properties of 6FDA-CTBDA, 6FDA-iCTBDA and 6FDA-TBDA polyimides.

Polymer	M <sub>w</sub> (g mol <sup>-1</sup> )	$M_n$ (g mol <sup>-1</sup> )	PDI <sup>a</sup> (-)	T <sub>d,5%</sub> <sup>b</sup> (°C)	Density (g cm <sup>-3</sup> )	BET surface area $(m^2 g^{-1})$
6FDA-CTBDA	164,000	100,000	1.64	490	1.26	587
6FDA-iCTBDA	155,000	85,000	1.82	490	1.30	562
6FDA-TBDA	61,700	33,000	1.87	450	1.30	403
6FDA-TBDA [40]	52,000	23,000	2.30	450	1.28	349

 $^{a}$  PDI = polydispersity index.

 $^{b}\ T_{d,5\%}=$  temperature at which 5% weight loss was recorded by TGA.



Fig. 3. a) Nitrogen adsorption isotherms measured at -196 °C up to 1 bar and b) NLDFT-derived pore size distributions of 6FDA-CTBDA, 6FDA-iCTBDA and 6FDA-TBDA.

Table 2
Pure-gas permeabilities and selectivities for 6FDA-CTBDA, 6FDA-iCTBDA and 6FDA-
TBDA (2 bar; 35 °C; film thickness ~40 μm).

Polymer	Permeability (Barrer)				Ideal selectivity			
	H <sub>2</sub>	CO <sub>2</sub>	02	$N_2$	$CH_4$	H <sub>2</sub> /CH <sub>4</sub>	$\rm CO_2/CH_4$	$O_2/N_2$
6FDA-CTBDA	375	291	56	14.8	11.6	32	25	3.8
6FDA-CTBDA <sup>a</sup>	286	201	43	10.3	7.2	40	28	4.2
6FDA-iCTBDA	313	230	49	12.2	8.9	35	25	3.9
6FDA-TBDA	262	174	35	7.6	5.2	50	33	4.6
6FDA-TBDA <sup>a</sup>	241	157	33	7.3	4.8	50	33	4.5
6FDA-TBDA <sup>b</sup> [40]	390	285	47	12.0	8.0	49	36	4.0

<sup>a</sup> 60 days aged sample.

<sup>b</sup> Data from Ref. [40]; film thickness 70–80  $\mu$ m; T = 35 °C; p = 1 bar.

shown in Table 2. The differences in gas permeabilities could have stemmed from a variety of reasons including different film formation protocols, storage conditions and film thickness.

It has been proposed that the tertiary amine groups in the Tröger's base building block in PIMs and PIM-PIs may significantly enhance the affinity towards  $CO_2$  due to Lewis acid—base interactions [40–42]. Moreover, it was suggested that the strong

adsorption interaction may hinder CO<sub>2</sub> diffusion [40–42]. This was supported by data for 6FDA-TBDA generated by gas diffusion coefficients deduced from time lag measurements ( $D = l^2/6\theta$  where lis the film thickness and  $\theta$  is the time lag) and *calculated* solubility coefficients from the relationship S = P/D. Using this methodology, very high CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> solubility selectivities were obtained and attributed to the nitrogen functionality of the tertiary amine groups in the bridgehead of the Tröger's base moiety [40–42]. Hence, differences in the gas sorption properties of the nitrogencontaining Tröger's base 6FDA-TBDA polyimide and carbocyclic pseudo Tröger's "base" 6FDA-CTBDA polyimide were expected.

In this work,  $CO_2$  and  $CH_4$  sorption isotherms of 6FDA-TBDA and its carbocyclic analogue 6FDA-CTBDA were measured *directly* by gravimetric gas sorption at 35 °C up to ~15 bar (Fig. 4). Only small differences in both  $CO_2$  and  $CH_4$  sorption uptake for 6FDA-CTBDA and 6FDA-TBDA were evident from the isotherms. The  $CO_2$  and  $CH_4$ solubility coefficients measured at 2 bar are shown in Table 3. The Tröger's base-derived 6FDA-TBDA polyimide exhibited only ~15% higher  $CO_2$  solubility than measured for 6FDA-CTBDA polyimide demonstrating only small sorption enhancement due to  $CO_2$ -selective interactions with the tertiary amine groups in the Tröger's



Fig. 4. CO2 and CH4 sorption isotherms measured gravimetrically at 35 °C. a) 6FDA-CTBDA and b) 6FDA-TBDA.

#### Table 3

CO<sub>2</sub> and CH<sub>4</sub> diffusion coefficients and solubility coefficients for 6FDA-CTBDA and 6FDA-TBDA (T =  $35 \circ C$ , p = 2 bar).

Polymer	Diffusion coefficient <sup>a</sup> $(10^{-8} \text{ cm}^2/\text{s})$		Solubility of (10 <sup>-2</sup> cm <sup>3</sup> )	Solubility coefficient <sup>b</sup> (10 <sup>-2</sup> cm <sup>3</sup> (STP)/cm <sup>3</sup> cmHg)		
	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>		
6FDA-CTBDA	13.3	1.87	21.8	6.2		
6FDA-TBDA	6.8	0.7	25.5	7.4		
6FDA-TBDA <sup>c</sup>	5.3	1.1	54	7.3		

Determined from D = P/S (S measured directly by gravimetric method); 2 bar, 35 °C.

Measured gravimetrically at 2 bar and 35 °C.

Data from Ref. [40]. D determined by time lag method; S calculated from S = P/D(1 bar. 35 °C).

#### Table 4

CO<sub>2</sub>/CH<sub>4</sub> diffusion selectivity and solubility selectivity for 6FDA-CTBDA and 6FDA-TBDA (T = 35 °C, p = 2 bar).

Polymer	Diffusion selectivity <sup>a</sup> ( $\alpha$ ) <sub>D</sub>	Solubility selectivity <sup>b</sup> (α)S		
	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /CH <sub>4</sub>		
6FDA-CTBDA 6FDA-TBDA 6FDA-TBDA <sup>c</sup>	7.1 9.7 4.8	3.5 3.4 7.4		

Determined from D = P/S (S measured directly by gravimetric method); 2 bar, а 35 °C. <sup>b</sup> Measured gravimetrically at 2 bar and 35 °C.

<sup>c</sup> Data from Ref. [40]. D determined by time lag method; S determined indirectly from S = P/D. (1 bar, 35 °C).

base derived polyimide. Moreover, CH<sub>4</sub> sorption uptake in 6FDA-TBDA also increased by ~15%; therefore, both polyimides exhibited  $CO_2/CH_4$  solubility selectivity of 4.1 at 1 bar (Tables S-1) and ~3.5 at 2 bar (Table 4). Hence, our study clearly demonstrated that the basicity of the Tröger's base moiety in 6FDA-TBDA had only a marginal effect on the gas sorption properties. However, it appears that the tertiary amine groups in the 6FDA-TBDA polyimide affected the chain packing due to enhanced chain interactions, which resulted in a tighter polymer structure. This hypothesis is supported by lower BET surface area, reduced diffusion coefficients and higher diffusion selectivity (Table 4), as compared to the carbocyclic 6FDA-CTBDA.

#### 4. Conclusions

A novel carbocyclic pseudo Tröger's base-containing diamine (CTBDA) and its isomeric analogue (iCTBDA) were designed and used to prepare two intrinsically microporous CTB-based polyimides by high-temperature polycondensation reaction with commercially available 6FDA. The polyimides exhibited high thermal stability, high molecular weight, excellent solubility and high BET surface area of ~560-590 m<sup>2</sup> g<sup>-1</sup>. In comparison to a Tröger's base polyimide analogue, 6FDA-TBDA, the carbocyclic polyimide displayed higher BET surface area and higher gas permeability with slightly lower gas-pair selectivity. Physical aging over a period of 60 days reduced the gas permeabilities in 6FDA-CTBDA by 30-40% with small increase in gas-pair selectivity. Direct gravimetric gas sorption measurements indicated that the tertiary amine groups in the Tröger's base polyimide increased the CO<sub>2</sub> sorption uptake only slightly and had no effect on CO<sub>2</sub>/CH<sub>4</sub> solubility selectivity relative to the carbocyclic pseudo Tröger's "base" polyimide.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.polymer.2017.10.017.

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