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PAPER

Novel thermally stable and soluble triarylamine functionalized polyimides for gas separation†

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A novel series of solution-processable aromatic polyimide membranes with trimethyl-substituted triphenylamine units for gas separation were prepared from a newly synthesized dianhydride, *N,N*-bis(3,4-dicarboxyphenyl)-2,4,6-trimethylaniline dianhydride (**2**), and various diamines *via* one-step high-temperature solution polymerization. The corresponding polyimides derived from structurally related dianhydrides with different pendant groups such as phenyl, naphthyl, and pyrenyl moieties were also prepared for comparison. All the polyimides were readily soluble in many polar solvents and showed useful levels of thermal stability associated with high glass-transition temperatures (T_g, 324–455 °C) and high char yields (higher than 58% at 800 °C in nitrogen). The noncoplanar triphenylamine-containing polyimides **IV** with pendant trimethyl-phenyl moieties exhibited an effective improvement of gas permeability with a minor decrease in permselectivity.

Introduction

Polymer-based gas separation membranes are anticipated to contribute to a number of significant environmental and energy technologies including gas purification and capture.[1] The requirement of high permeability and good selectivity is therefore considered as a main parameter for the design and preparation of high-performance gas separation membranes.[2] However, there is an inherent trade-off of gas pairs between permeability and selectivity for all the gas separation polymer membranes, which was quantified in 1991 and 2008 by Robeson. The upper bound was identified on plots of double logarithmic plots of selectivity against permeability for a wide range of gas pairs using a comprehensive list of existing polymer permeabilities.[3]

Polyimides (PIs) are well-known super engineering plastics and widely used in membranes for gas separation and fuel cells due to the inherent advantages, such as good gas transport properties, excellent mechanical properties, high thermal stability, and chemical and solvent resistance.[4] Despite the outstanding properties, most of the conventional aromatic PIs possess high melting or glass-transition temperatures (T_g) and

limited solubility in most organic solvents due to the rigid backbones and strong inter-chain interactions thus restricting their applications. One of the simplest modifications for improving processability of PIs is using bis(phthalic anhydride)s with flexible or kinked groups between two fragments of phthalic anhydrides.[5] However, the decrease in thermally dimensional stability is always a consequence of the reduced chain stiffness. Therefore, PIs derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) with the presence of a bulky –C(CF$_3$)$_2$– moiety have been attracting much attention, which effectively hinders intra-segmental mobility and disrupts inter-chain-packing thus stiffening the backbone,[6] and the prepared PIs also exhibit a good combination of solubility, T_g, thermal stability, and mechanical properties.[5f] On the basis of this conception, the incorporation of bulky and propeller-shaped triphenylamine (TPA) or triarylamine units along the polyimide backbone has also been reported recently, and could be regarded as a successful approach to obtain PIs with good film-forming capability, excellent thermal stability, and improved gas separation performance.[7]

In this paper, in order to obtain solution-processable PI membranes with higher T_g and enhanced gas separation properties, we therefore designed and synthesized a novel series of PIs derived from a new Me$_3$TPA-based (Me$_3$TPA; trimethyltriphenylamine) dianhydride monomer, *N,N*-bis(3,4-dicarboxyphenyl)-2,4,6-trimethylaniline dianhydride (**2**), and various diamines. Polycondensation of dianhydride monomers with various diamines allows for an enhancement of the solubility and gas permeability, facilitating both processing and application due to the introduction of highly nonplanar bulky CF$_3$ and tetra-methyl benzene groups that disrupt inter-chain-packing
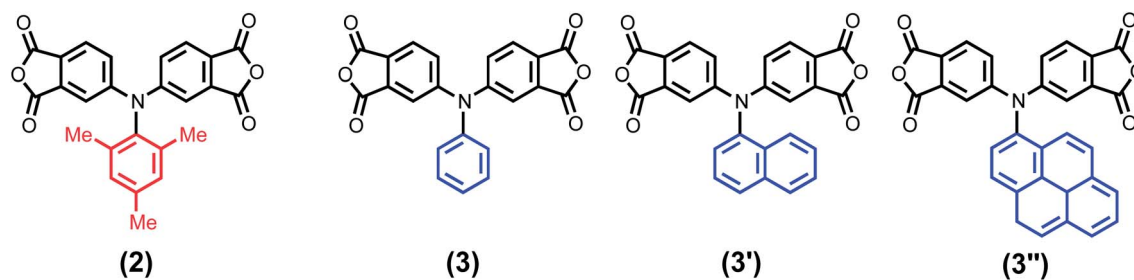
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† Electronic supplementary information (ESI) available: Table: inherent viscosity, solubility behavior, and thermal properties. Figure: NMR spectra of compound **1** and IR spectra of compounds and PIs. See DOI: 10.1039/c4py00449c

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thus stiffening the backbones. The general properties such as solubility, viscosity, and thermal properties are described. For a comparative study, gas separation behaviors of the present PIs were also compared with those of structurally related corresponding PIs derived from *N,N*-bis(3,4-dicarboxyphenyl)aniline dianhydride (**3**), *N,N*-bis(3,4-dicarboxyphenyl)-1-aminonaphthalene dianhydride (**3′**), and *N,N*-bis(3,4-dicarboxyphenyl)-1-aminopyrene dianhydride (**3″**), respectively.[5d,8] Dianhydride **3** with the benzene pendent group was used as a basic structure, while dianhydrides **3′** and **3″** were incorporated and expected to increase the gas permeability due to the large steric hindrance of naphthalene/pyrene groups. Moreover, the π–π interaction of pyrene groups in dianhydride **3″** could also be discussed and considered as a parameter for preparing gas separation membranes.

(Scheme 1). Elemental analysis, FT-IR, and NMR spectroscopic techniques were used to identify structures of the intermediate diimide compound **1** and the target dianhydride monomer **2**. The FT-IR spectra of the synthesized diimide compound and the dianhydride monomer are illustrated in Fig. S1 (ESI†). The carbonyl groups of the diimide compound exhibiting two characteristic bands at around 1770 and 1710 cm^{-1} could be attributed to imide C=O asymmetric and symmetric stretching, respectively. After being hydrolyzed and cyclodehydrated to the dianhydride monomer, the carbonyl groups shifted to around 1843 and 1773 cm^{-1}. Fig. S2† and 1 illustrate the NMR spectra of the diimide compound **1** and dianhydride monomer **2**, respectively, and these spectra agree well with the proposed molecular structures. Thus, the results of all the spectroscopic

and elemental analyses suggest the successful preparation of the target dianhydride monomer **1**.

## Results and discussion

Monomer synthesis

The preparation of diimide compound **1** obtained from double *N*-arylation reactions of 2,4,6-trimethylaniline with *N*-methyl-4-bromophthalimide[8] was carried out in the presence of palladium(II) acetate, *rac*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*rac*-BINAP), and cesium carbonate in toluene. The resulting diimide compound was then hydrolyzed with aqueous potassium hydroxide, giving the corresponding tetracarboxylic acid, which in turn was converted to the new dianhydride monomer **2** by chemical cyclodehydration with acetic anhydride

Polymer synthesis

Four series of PIs, **I–IV**, were prepared by the one-pot, high-temperature solution polymerization of dianhydride monomers with various aromatic diamines in *m*-cresol at 200 °C in the presence of isoquinoline as the catalyst (Scheme 2). The polymerization reactions proceeded homogenously and led to the formation of highly viscous polymer solutions that can be precipitated into tough fiber-like forms when slowly trickling
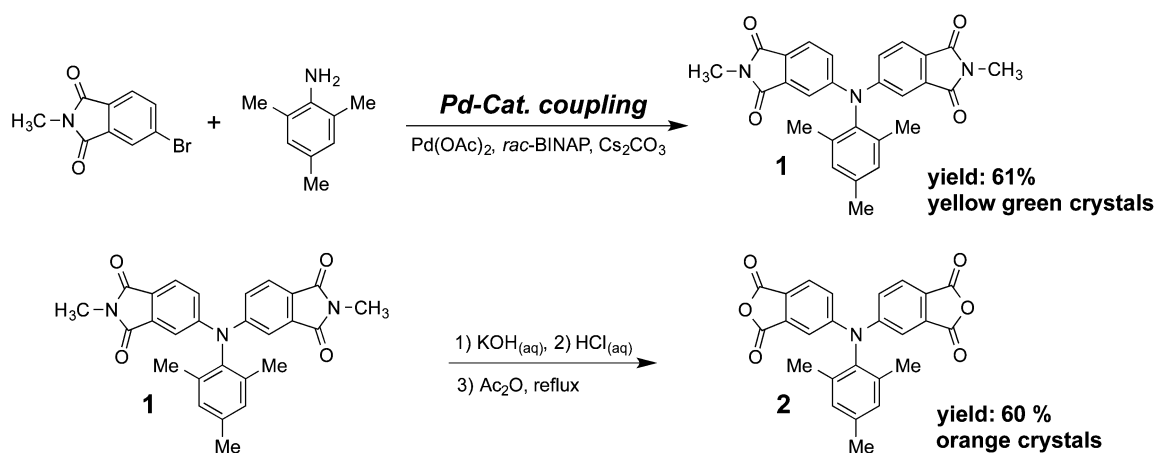
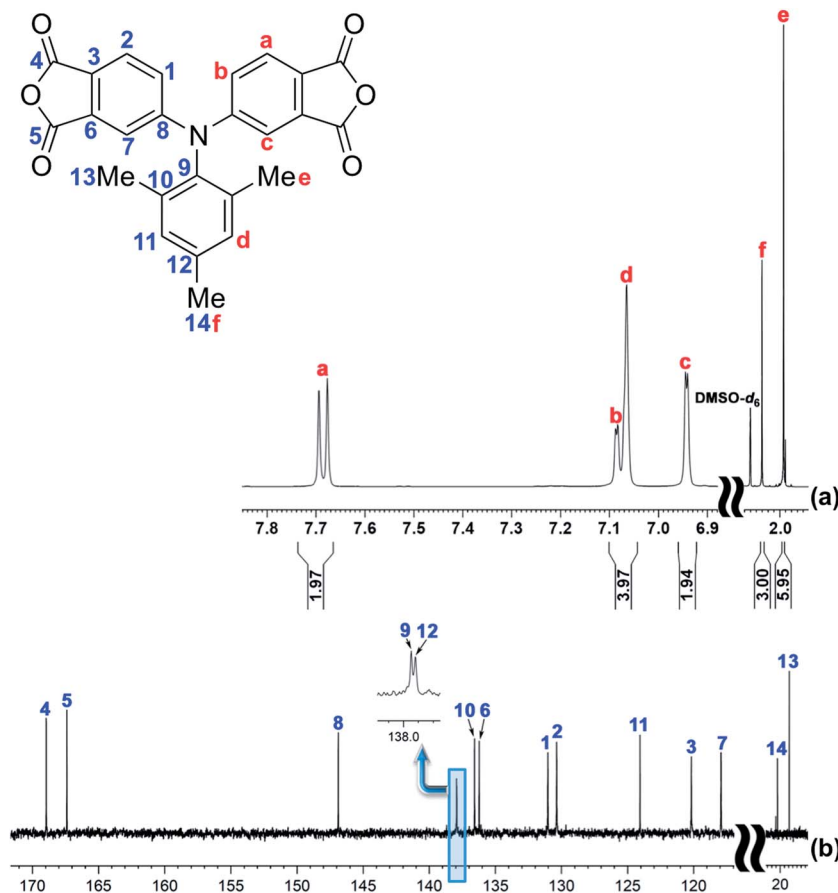Scheme 1 Synthetic route to triarylamine-based dianhydride monomer 2.

Fig. 1 (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **2** in DMSO-d_6.

into methanol. The resulting PIs exhibited inherent viscosities of 0.36–0.93 dL g^{-1} in N-methyl-2-pyrrolidinone (NMP) (Table S1†) and can afford transparent/self-standing films *via* solution casting, indicating they are high molecular weight polymers. The appearance and quality of a representative flexible **IVb** film are shown in Fig. 2. The structures of these PIs were also confirmed by IR and NMR spectroscopic techniques, and the spectra agree well with the proposed molecular structures (Fig. S4† and 3). The IR spectra of PIs exhibit characteristic imide absorption bands at around 1774 (imide asymmetrical C=O), 1717 (imide symmetrical C=O), 1369 (C–N), and 745 cm^{-1} (imide ring deformation). A typical ^{1}H NMR spectrum of PI **IVa** shown in Fig. 3 reveals that all the peaks could be readily assigned to the hydrogen atoms of the recurring unit.
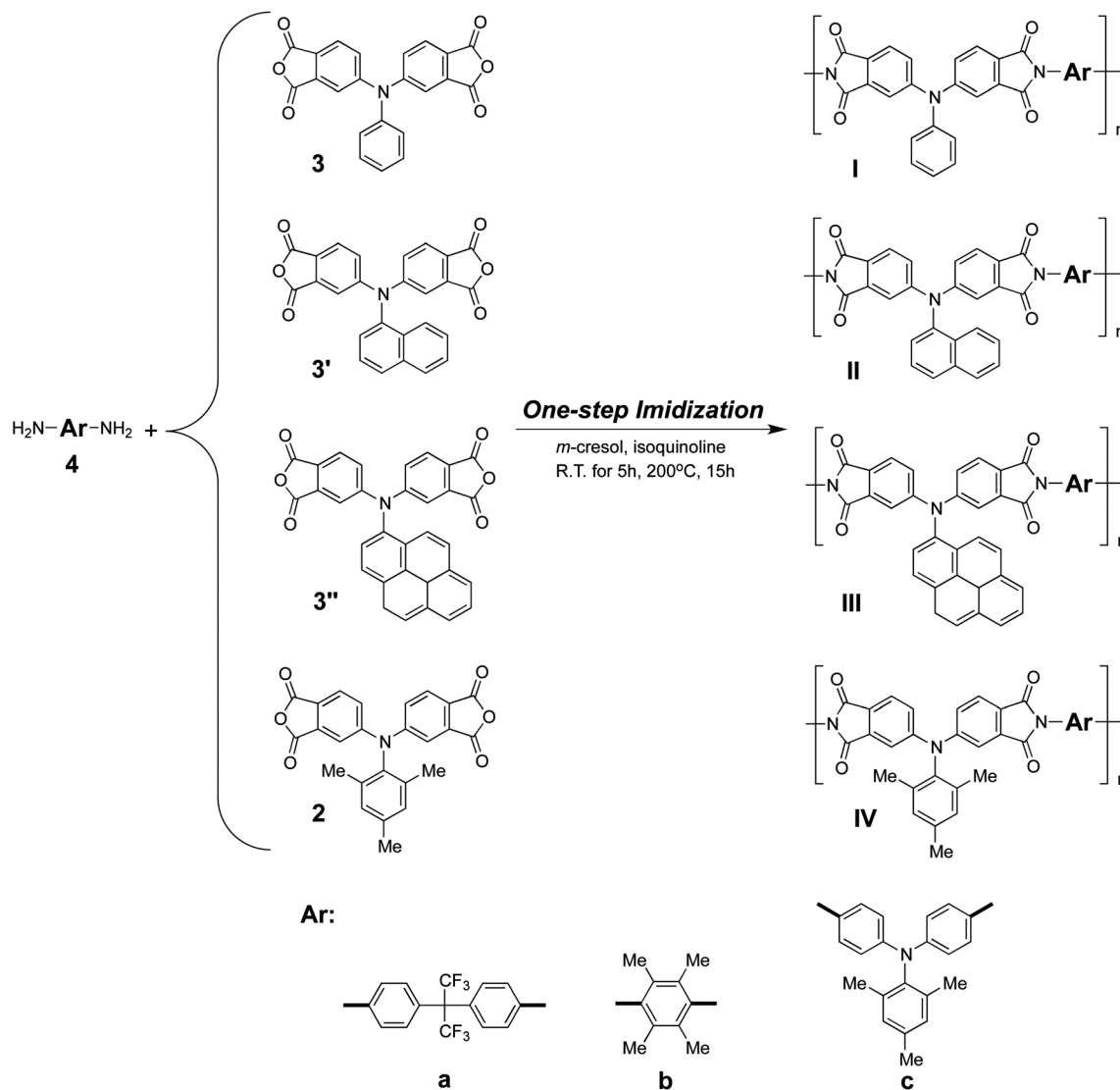
Polymer properties

Solubility and film property. The solubility property of PIs was investigated qualitatively and is summarized in Table S1.† The solubility behavior of these PIs depends on their chain packing and intermolecular interaction that are affected by the rigidity, symmetry, and regularity of the molecular backbone. All the PIs derived from dianhydrides with high steric hindrance and bulky pendent groups were highly soluble not only in polar aprotic organic solvents such as NMP, N,N-dimethylacetamide (DMAc), and m-cresol but also in less polar
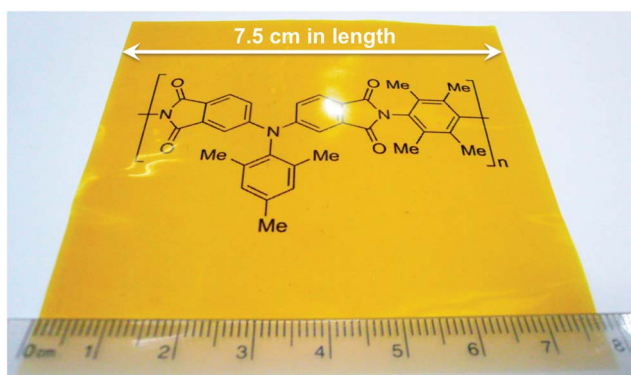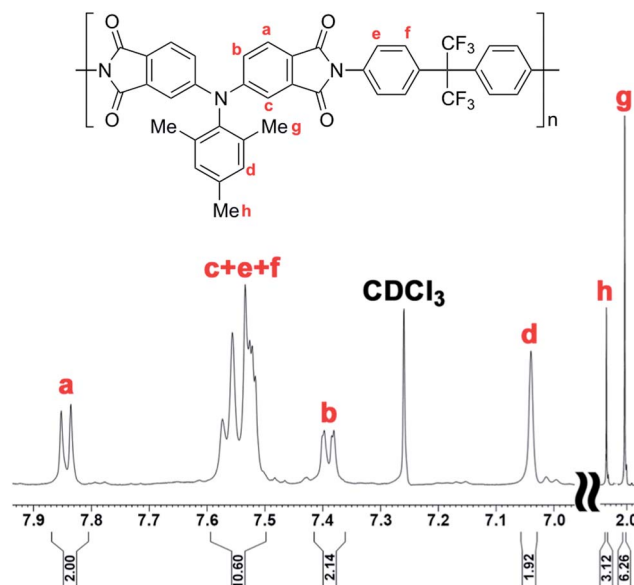
solvents like THF and CHCl$_3$. Their high solubility can be also attributed to the incorporation of the bulky and noncoplanar triarylamine moiety along the polymer backbone. In addition, the PIs obtained from diamine **4a** revealed better solubility than those prepared from other diamines because of the additional contribution of the hexafluoroisopropylidene ($-$C(CF$_3$)$_2$$-$) fragment in the polymer backbone which reduced the intermolecular interactions.

Thermal properties. The thermal properties of PIs were evaluated by TGA and TMA techniques. Typical TMA and TGA curves of PIs **Ib**, **IIb**, **IIIb**, and **IVb** are shown in Fig. 4, and the thermal behavior data of all PIs are summarized in Table S2.† All the prepared PIs exhibit good thermal stability with no remarkable weight loss up to 450 °C in nitrogen or in air. Their decomposition temperatures (T_d (ref. 10)) at a 10% weight-loss in nitrogen and air were recorded at 535–630 and 480–620 °C, respectively. The carbonized residue (char yield) of these PIs in a nitrogen atmosphere is more than 58% at 800 °C, ascribed to their high aromatic content. Judged from the slope difference on the TMA thermograms, the PIs exhibit high glass-transition temperatures (T_g) in the range of 324–455 °C, depending upon the stiffness of the polymer chain, and the higher T_g of PI **III** could be attributed to higher chain stiffness resulting from the strong π–π interaction of pyrene groups. In addition, the highest T_g of PIs derived from diamine **4b** can be attributed to

Scheme 2 Synthesis of triarylamine-based high performance polyimides.

Fig. 2 The photograph of a self-standing and flexible **IVb** film with *ca*. 55 μm thickness (film area is 7.5 cm × 7.5 cm).

Fig. 3 ^{1}H NMR spectrum of polyimide **IVa** in CDCl$_3$.

the rigid tetramethylbenzene moieties in the polymer backbone. Compared with the commercially available PIs Ultem 1000 (T_g = 217 °C) and Uplex-R (T_g = 266 °C),[9] it further
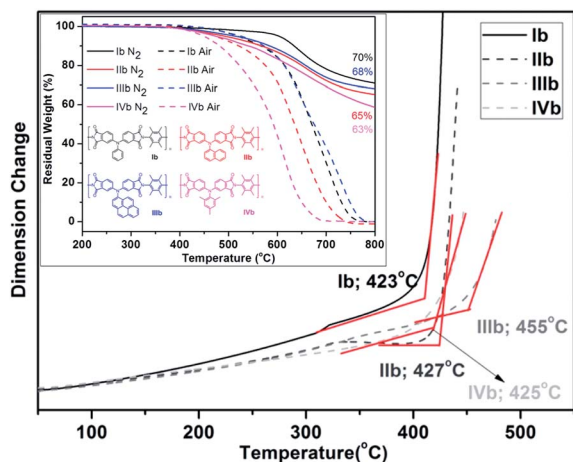
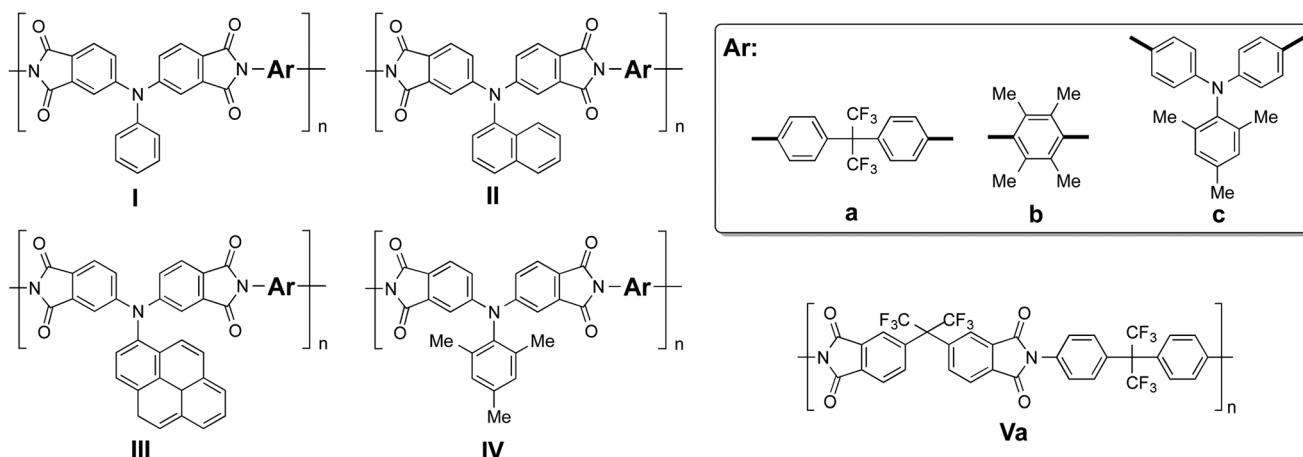Fig. 4   TMA and TGA traces of PIs **Ib**, **IIb**, **IIIb**, and **IVb**.

demonstrates that the incorporation of triarylamine units can effectively enhance the glass transition temperature of the prepared PIs. The combination of excellent solubility, film quality, and thermal stability makes these PIs as potential candidates for high-performance gas-separation membrane applications by solution-casting processes.

Gas separation. Gas permeability measurements were carried out for all the PI dense membranes, which were prepared by casting the polymer solutions with the concentration of 20–25 wt% in NMP on glass. The membranes were dried in a vacuum oven at 75 °C for 6 h, and then 160 °C for 8 h. The obtained films were around 30 μm in thickness for the comparative study. To exclude the effect of solvent, pressure, temperature, and thickness on gas separation properties, all the PI films were prepared and measured under the same conditions, except for **Kapton** which was prepared by two-step thermal polymerization. The gas permeability was calculated by the following equation:

Table 1   Permeability coefficients and ideal separation factors measured at 35 °C

Index	Permeation permeabilities[a] (barrer)				Permselectivities ($\alpha_{A/B}$)			
	P_{O_2}	P_{N_2}	P_{CO_2}	P_{CH_4}	P_{O_2}/P_{N_2}	P_{CO_2}/P_{CH_4}	P_{CO_2}/P_{N_2}	Thickness (μm)
Ia	6.84	1.62	35.34	2.14	4.22	16.51	21.81	39.6
Ib	12.66	4.37	77.37	8.88	2.90	8.71	17.70	27.0
Ic	5.82	1.16	29.44	2.51	5.02	11.73	25.38	24.2
IIa	8.46	1.79	46.24	2.94	4.73	15.73	25.83	32.5
IIb	20.43	10.96	96.73	23.19	1.86	4.17	8.83	27.0
IIc	4.98	1.08	26.25	2.11	4.61	12.44	24.31	34.5
IIIa	7.13	1.66	37.31	2.56	4.30	14.57	22.48	23.7
IIIb	16.59	4.60	88.06	8.46	3.61	10.41	19.14	26.7
IIIc	4.44	1.06	24.03	2.01	4.19	11.96	22.67	23.9
IVa	13.57	2.86	74.84	4.73	4.74	15.82	26.17	30.0
IVb	19.89	5.40	127.08	13.48	3.68	9.43	23.53	20.0
Va	14.96	6.12	64.90	10.55	2.44	6.16	10.60	25.0
Kapton	0.64	0.11	3.51	0.06	5.82	58.50	31.91	31.2

[a] Permeability values are given in units of barrers, where 1 barrer = 10^{-10} cm^3 (STP) cm (cm^{-2} s^{-1} cmHg).

$$P = l/(p_1 - p_2) \times \frac{q/t}{A} \in$$

where P is the gas permeability [$cm^3(STP)$ cm cm^{-2} s^{-1} cmHg], q/t is the volumetric flow rate of the gas permeate [$cm^3(STP)$ s^{-1}], l is the thickness of the free-standing film

(cm), A is the effective area of the free-standing film (cm^2), and p_1 and p_2 are the pressures (cmHg) on the high-pressure and low-pressure sides of the free-standing film, respectively. The gas permeability coefficients and the separation factors (α) of the PI membranes are summarized in Table 1.

The oxygen permeability coefficients (P_{O_2}) of PI **IVa** (P_{O_2} = 13.57) or **IVb** (P_{O_2} = 19.89) having Me₃TPA substituents were higher than most of the corresponding PIs with phenyl, naphthyl, or pyrenyl pendant groups. Similar tendencies were observed with CO_2 gas, which can be attributed to the presence of highly nonplanar Me₃TPA units that hinder intrasegmental mobility and disrupt inter-chain-packing, thus stiffening the backbones.[10] Conversely, the lower permeability coefficients for PI **III** would be attributed to the strong π–π interaction of pyrene groups thus decreasing the free volume between the polymer inter-chains.[8] These results are consistent with the solubility behavior, which is highly dependent on the interchain packing density and intermolecular free volume (see Table S1†). In addition, PIs based on diamine **4b** possessing four methyl groups at the *ortho*-position of the imide bond displayed higher gas permeability among the present polymers. PIs prepared from diamine **4a** having two CF₃ groups also showed high gas permeabilities, which were comparable with those of the fluorinated PI **Va** from 6FDA and the same diamine.[11] These results further demonstrate that the incorporation of bulky and propeller-shaped triarylamine units can effectively improve the gas separation performance.

An increase in permeability is generally known to be accompanied by decreased permselectivity, which is consistent with the well-known permeability/selectivity trade off rule common in strongly size-sieving polymers. Robeson[3,12] demonstrated an upper bound in double logarithmic plots of selectivity against permeability for a wide range of polymers. To provide some perspective of the gas separation performance of these PIs, Robeson plots (double logarithmic plots) of selectivity *versus* permeability of all the PIs for O_2/N_2, CO_2/N_2, and CO_2/CH_4 pairs are depicted in Fig. 5. The PIs in this study all fall below the upper bound. Nevertheless, the present PIs showed large improvements in gas-separation performance as proved by their tradeoff points close to the Robeson's upper bound as opposed to the conventional PIs **Va** and **Kapton**.

Conclusions

A novel series of gas permeable aromatic PIs with Me₃TPA units were prepared from a new dianhydride, *N,N*-bis(3,4-dicarboxyphenyl)-2,4,6-trimethylaniline dianhydride (**2**), *via* one-step high-temperature solution polymerization. All the PIs are organosoluble with high T_g and excellent thermal stability. The gas transport properties of the PIs for CO_2, CH_4, O_2, and N_2 have been investigated and the results demonstrate that the introduction of a Me₃TPA moiety into the PI backbone as a dianhydride can effectively improve gas separation properties in terms of increasing permeability with only a minor decrease in
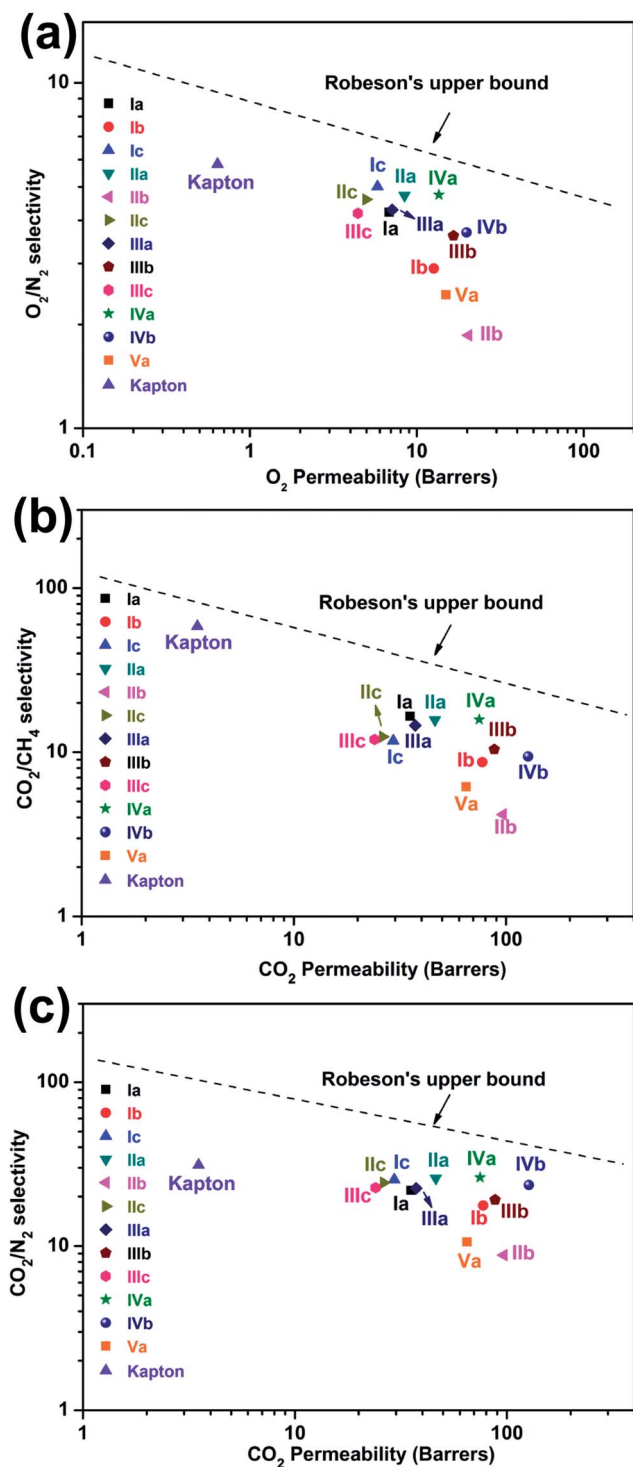

Fig. 5 Triple-logarithmic plots of (a) O_2/N_2 selectivity *versus* O_2 permeability, (b) CO_2/CH_4 selectivity *versus* CO_2 permeability, and (c) CO_2/N_2 selectivity *versus* CO_2 permeability for permeable PIs.

permselectivity. The combination of high permeability, good selectivity, excellent processability, and thermal stability demonstrates Me₃TPA-based PI **IV** as a highly promising candidate for gas separation membranes.

Experimental section

Materials

N,N-Bis(3,4-dicarboxyphenyl)aniline dianhydride[5d] (**3**), *N,N*-bis(3,4-dicarboxyphenyl)-1-aminonaphthalene dianhydride[8] (**3′**), *N,N*-bis(3,4-dicarboxyphenyl)-1-aminopyrene dianhydride[8] (**3″**), 4,4′-diamino-2″,4″,6″-trimethyltriphenylamine[7b] (**4c**), and *N*-methyl-4-bromophthalimide[8] were prepared according to the previously reported procedures. Commercially available 2,2-bis(4-aminophenyl)hexafluoropropane (**4a**) and 2,3,5,6-tetramethylbenzene-1,4-diamine (**4b**) were purified by vacuum sublimation. All other reagents were used as received from commercial sources.

Monomer synthesis

N,N-Bis(N′-methyl-4-phthalimide)-2,4,6-trimethylaniline (1). In a 100 ml three-neck round-bottomed flask equipped with a stirring bar under a nitrogen atmosphere, 0.56 g (0.9 mmol) of *rac*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (*rac*-BINAP), 0.13 g (0.6 mmol) of Pd(OAc)₂ and 15.64 g (48.0 mmol) of cesium carbonate were dispersed in 24 ml of anhydrous toluene. After pre-catalyzing for 1 h at 90 °C, 12.48 g (52.0 mmol) of *N*-methyl-4-bromophthalimide and 2.70 g (20.0 mmol) of 2,4,6-trimethylaniline were added to the mixture. After heating under stirring at 110 °C for 6 days, the mixture was concentrated and washed with water and methanol. The precipitated product was collected by filtration and recrystallized by acetic anhydride to give 5.57 g (61% in yield) of yellow green crystals with a mp of 248–250 °C. FT-IR (KBr): 1770 cm⁻¹ (asymmetric C=O), 1710 cm⁻¹ (symmetric C=O) and 1377 cm⁻¹ (C–N stretching). ¹H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.76 (d, 2H, H$_a$), 7.41 (s, 2H, H$_c$), 7.19 (dd, 2H, H$_b$), 7.11 (d, 2H, H$_d$), 2.95 (s, 6H, H$_e$), 2.32 (s, 3H, H$_g$) and 1.94 (s, 6H, H$_f$). ¹³C NMR (125 MHz, DMSO-d_6, δ, ppm): 167.4 (C⁴), 167.1 (C⁵), 149.9 (C⁸), 138.3 (C⁹), 138.1 (C¹²), 136.4 (C¹⁰), 134.0 (C⁶), 130.4 (C¹¹), 124.8 (C²), 124.4 (C¹), 123.9 (C³), 113.3 (C⁷), 23.6 (C¹³), 20.5 (C¹⁵) and 17.8 (C¹⁴). Anal. calcd (%) for C₂₇H₂₃N₃O₄ (453.49): C, 71.51; H, 5.11; N, 9.27. Found: C, 71.31; H, 5.19; N, 9.24.

N,N-Bis(3,4-dicarboxyphenyl)-2,4,6-trimethylaniline dianhydride (2).
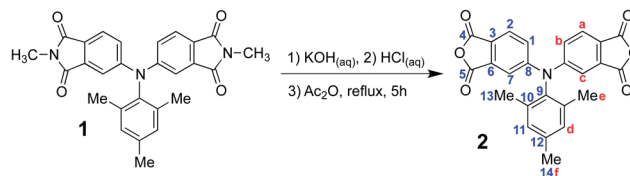

A mixture of 5.55 g (98.9 mmol) of potassium hydroxide and 2.99 g (6.6 mmol) of **1** in 50 mL of distilled water was stirred at reflux for 24 h. After cooling to room temperature, the solution was filtered and adjusted to pH = 1.0 with 6 N HCl, and then the precipitated intermediate was collected by filtration. The resulting tetracarboxylic acid was dissolved in 29 mL of acetic anhydride refluxed for 4 h. The product was filtered after the solution was cooled to room temperature, and then dried *in vacuo* at 140 °C to give 1.69 g (60% in yield) of orange crystals with a mp of 283–287 °C. FT-IR (KBr): 1843 cm⁻¹ (asymmetric C=O) and 1773 cm⁻¹ (symmetric C=O). ¹H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.69 (d, 2H, H$_a$), 7.09 (dd, 2H, H$_b$), 7.07 (s, 2H, H$_d$), 6.94 (d, 2H, H$_c$), 2.30 (s, 3H, H$_f$) and 1.94 (s, 6H, H$_e$). ¹³C NMR (125 MHz, DMSO-d_6, δ, ppm): 169.0 (C⁴), 167.4 (C⁵), 146.9 (C⁸), 138.0 (C⁹), 137.9 (C¹²), 136.6 (C¹⁰), 136.2 (C⁶), 131.0 (C¹), 130.4 (C²), 124.1 (C¹¹), 120.2 (C³), 117.9 (C⁷), 20.6 (C¹⁴) and 17.9 (C¹³). Anal. calcd (%) for C₂₅H₁₇NO₆ (427.41): C, 70.25; H, 4.01; N, 3.28. Found: C, 69.73; H, 4.17; N, 3.19.

Synthesis of polyimides by a one-step method. The synthesis of PI **IVa** is used as an example to illustrate the general synthetic route used to produce PIs, **I–IV**. Into a 50 mL round-bottom flask were added 0.33 g (1.00 mmol) of diamine (**4a**), 0.43 g (1.00 mmol) of dianhydride (**2**), 0.24 ml isoquinoline and 6 ml *m*-cresol. The reaction mixture was stirred at room temperature in a nitrogen atmosphere for 5 h. Then, the reaction temperature was increased to 200 °C for 15 h. After the imidization reaction, the mixture was cooled to room temperature and the viscous polymer solution was then poured slowly into 300 ml of stirred methanol giving rise to a yellowish fibrous precipitate that was collected by filtration, washed thoroughly with methanol, and dried at 70 °C for 15 h. Re-precipitates of the polymer by DMAc–methanol were carried out twice for further purification. The inherent viscosity of obtained PI **IVa** is 0.36 dL g⁻¹ (measured at a concentration of 0.5 g dL⁻¹ in NMP at 30 °C). The FT-IR spectrum of **IVa** (film) exhibited characteristic imide absorption bands at around 1774 (asymmetrical C=O), 1717
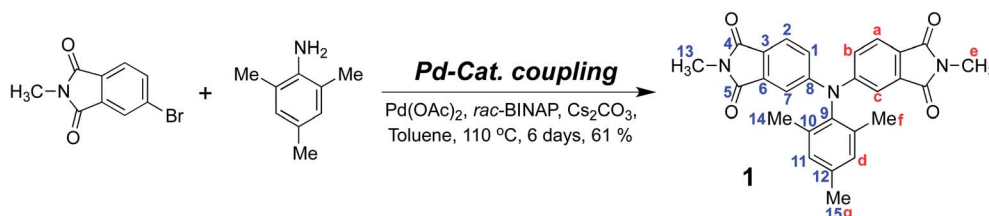
(symmetrical C=O), 1369 (C–N), and 745 cm^{-1} (imide ring deformation). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.84 (d, 2H, H$_a$), 7.51–7.58 (m, 10H, H$_c$ + H$_e$ + H$_f$), 7.39 (dd, 2H, H$_b$), 7.04 (s, 2H, H$_d$), 2.32 (s, 3H, H$_h$) and 1.94 (s, 6H, H$_g$).
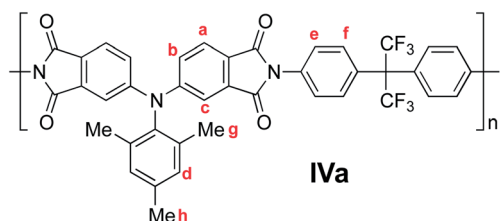
Preparation of the polyimide films. A solution of the polymer was prepared by dissolving about 0.4 g of the PI sample in 2 mL of NMP. The homogeneous solution was casted onto a glass substrate and heated in an oven at 75 °C for 6 h to remove most of the solvent; then the semi-dried film was further dried *in vacuo* at 160 °C for 10 h. The obtained films were around 30 μm thick and were used for solubility tests and thermal analyses.

Measurements. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer. Elemental analyses were carried out in a Heraeus VarioEL-III CHNS elemental analyzer.^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-500 FT-NMR using tetramethylsilane as the internal standard, and peak multiplicity was reported as follows: s, singlet; d, doublet; m, multiplet. The inherent viscosities were determined at 0.5 g dL^{-1} concentration using a Tamson TV-2000 viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6–8 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm^3 min^{-1}) at a heating rate of 20 °C min^{-1}. Thermal Mechanical Analysis (TMA) was conducted with a TA instrument TMA Q400. The TMA experiments were conducted from 40 to 400 °C at a scan rate of 10 °C min^{-1} with a film/fiber probe under an applied constant load of 5 mN. The gas permeability of the polymer membranes with thickness around 30 μm was measured with a model GTR-10 gas permeability analyzer (Yanagimoto, Kyoto, Japan), which consists of upstream and downstream parts separated by a membrane. The gases measured include O$_2$, N$_2$, CO$_2$, and CH$_4$. The pressure on one face of the free-standing film (or called membrane) was kept at 98 kPa, and the other face was at zero pressure initially to allow the gas to permeate through the free-standing film. The rate of transmission of gas was obtained by gas chromatography, from which the gas permeability was calculated by averaging five scans.

Acknowledgements

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