A novel intrinsically microporous ladder polymer and copolymers derived from 1,1',2,2'-tetrahydroxy-tetraphenylethylene for membrane-based gas separation

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Materials. Zinc, TiCl₄, BBr₃, K₂CO₃, 2,3,5,6-tetrafluoroterephthalonitrile, THF, DMAc, dichloromethane toluene and chloroform were obtained from Sigma-Aldrich and were used as received. 3,3,3',3',- tetramethylspirobisindane-5,5',6,6'-tetraol (TTSBI) was obtained from Sigma-Aldrich and recrystallized from methanol/dichloromethane before usage. (3,4-dimethoxyphenyl)(phenyl)methanone was synthesized according to a previous report.¹

Characterization methods NMR spectra of the newly synthesized monomer and polymers were recorded using a Bruker AVANCE-III 400MHz or 500MHz spectrometer in deuterated chloroform with tetramethylsilane as an internal standard. Elemental analysis was carried out using a Perkin-Elmer 2400 CHN elemental analyzer. High-resolution mass spectroscopy (HRMS) was conducted on a Thermo LC/MS system with LTQ Orbitrap Velos detectors. Molecular weights and weight distribution of the polymers were recorded by gel permeation chromatography (Malvan HT-350) using polystyrene as external standard. Thermogravimetric analysis (TGA) was carried out under N₂ atmosphere using TGA Q5000 (TA Instruments); the polymers were heated from room temperature to 800 °C at a heating rate of 3 °C/min. The BET surface areas of the polymers were determined by N₂ sorption at -196 °C (Micrometrics ASAP 2020). The polymer powder was degassed under high vacuum for 12 hours at 120 °C before testing.

Synthesis of TPE-PIM



Scheme S1 McMurrary reaction of (3,4-dimethoxyphenyl)(phenyl)methanone.

Synthesis of the (*E*)-1,2-bis(3,4-dimethoxyphenyl)-1,2-diphenylethene. Zinc (2.60 g, 40.0 mmol) was dispersed in anhydrous THF (40.0 mL) in a 100 mL three-neck flask and cooled in an ice bath. To it, TiCl₄ (2.2 mL) was added dropwise. Thereafter, the ice-bath was removed and the system was refluxed for 2 hours. (3,4-dimethoxyphenyl)(phenyl)methanone (2.42 g, 10.0 mmol) dissolved in anhydrous THF (10 mL) was added dropwise and the solution was then refluxed overnight and cooled to room temperature, poured into water (100 mL) and finally extracted with dichloromethane (3 × 50 mL). The organic phase was combined and dried with MgSO₄. The solvent was removed by rota-evaporation and the residue was loaded in a column. The pure product (0.80 g, yield: 35.4%) was obtained as an off-white powder. TLC: dichloromethane/hexane = 2/1, R_f=0.3; ¹HNMR (400MHz, CDCl₃): δ 7.12-7.21 (m, 10H), 6.68 (d, 2H, *J* = 8.88Hz), 6.58 (d, 2H, *J* = 8.92Hz), 6.57 (s, 2H), 3.86 (s, 6H), 3.51 (s, 6H).



Fig. S1 The ¹H NMR of the Trans (red)/Cis (blue) isomers (left) and their ¹³C NMR (right). The carbon of the dimethyl group and the ethylene double bond were also highlighted in their carbon NMR.



Scheme S2 Synthetic procedure of TPE-PIM homopolymer.

Synthesis of 1,1',2,2'-tetrahydroxy-tetraphenylethylene. 0.50 g of (*E*)-1,2-bis(3,4-dimethoxyphenyl)-1,2-diphenylethene (1.10 mmol) were dissolved in 20 mL DCM and cooled in an ice-bath. To it, BBr₃ (3.3 mL, 1M in DCM) was added dropwise. The solution was stirred at room temperature overnight and then poured into 100 mL water. The DCM was removed by N₂ flow and the remaining solid was filtrated, and dried in a vacuum oven at 70 °C overnight. The final product was obtained as an off-white powder (415 mg, yield: 90.9%). ¹HNMR (400MHz, DMSO-d₆): δ 8.78 (s, 1H), 8.75 (s, 1H), 8.67 (s, 1H), 8.65 (s, 1H), 7.06 -7.17 (m, 6H), 6.93 -6.95 (m, 4H), 6.44 - 6.52 (m, 2H), 6.34 - 6.39 (m, 2H), 6.19 -6.22 (m, 2H). ¹³C NMR (125 MHz, DMSO-d₆): δ 144.8, 144.2, 139.5, 135.3, 135.2, 131.2, 131.0, 128.0, 126.4, 112.8, 112.5, 118.5, 115.3. HRMS for [C₂₆H₂₁O₄]⁺, Calcd. for 397.1434. Found: 397.1434.

Synthesis of Polymers

Synthesis of TPE-PIM. 1,1',2,2'-tetrahydroxy-tetraphenylethylene (250 mg, 0.630 mmol) and 2,3,5,6-tetrafluoroterephthalonitrile (126 mg, 0.650 mmol) were dissolved in 1.5 mL DMAc. The solution was heated to 120 °C under N₂ for 20 seconds before K₂CO₃ (230 mg, 1.45 mmol) was added in one portion. The system was further heated to 150 °C and the resulting mixture became very viscous in 2 to 3 minutes. Toluene (1.00 mL) was added and the resulting solution was stirred further for 3 minutes. The solution was poured into methanol, filtrated and re-precipitated twice in methanol. A yellowish powder (306 mg, yield: 95%) was obtained after drying in a vacuum oven at 120 °C for 24 hrs. ¹H NMR (400MHz, CDCl₃): δ 7.18-7.25 (m, 6H), 7.01-7.08 (m, 4H), 6.68 -6.82 (m, 6H). Anal. Calcd. for C₃₄H₁₆N₂O₄: C, 78.45; H, 3.08; N, 5.38. Found: C, 77.84; H, 2.92; N, 5.03; Molecular weight (GPC in chloroform) M_n = 7.83 × 10⁴ g/mol; PDI = 2.3. T_d = 475 °C; S_{BET} = 550 m²/g.

Synthesis of TTSBI-TFTPN (PIM-1). PIM-1was synthesized according to the method reported by Du et al.³

Synthesis of TPE-TTSBI- TFTPN PIM copolymers. All copolymers were made by the same synthetic method, as described in the example for TPE-25 shown below.



Scheme S3 Synthetic procedure of the Co-PIMs.

Synthesis of TPE-25. 3,3,3',3',-tetramethylspirobisindane-5,5',6,6'-tetraol (255 mg, 0.75 mmol), 1,1',2, 2'-tetrahydroxy-tetraphenylethylene (99 mg, 0.25 mmol), and 2,3,5,6-tetrafluoroterephthalonitrile (200 mg, 1.00 mmol) were added to a Schlenk tube under nitrogen atmosphere. To it, anhydrous DMAc (2.00 mL) was added and the system was heated to 120 °C for 20 seconds to form a clear solution. Thereafter, K_2CO_3 (414 mg, 3.00 mmol) was added in one portion. The reaction system was then put into a preheated (150 °C) oil bath and kept for 3 min before toluene (1.00 mL) was added. The system was further kept at 150 °C for 5 min before being poured into methanol (100 mL). The precipitate was filtrated and dissolved in chloroform (50 mL) and then washed with HCl (2N). The chloroform phase was separated in a separatory funnel and dried with magnesium sulfate. The yellow copolymer (450 mg, yield: 94.1%) was obtained by solvent evaporation. ¹H NMR (400MHz, CDCl₃): δ 7.18-7.25 (m, 3.3H), 6.82 (s, 2H), 6.68 - 6.82 (m, 2H), 6.43 (s, 2H), 2.30 (s, 2H), 2.14 (s, 2H), 1.38 (s, 6H), 1.26 (s, 6H); Anal. Calcd. for $C_{121}H_{80}N_8O_{16}$: C, 76.41; H, 4.24; N, 5.89;. Found: C, 75.09; H, 3.77; N, 5.40; Molecular weight (GPC in chloroform) $M_n = 4.90 \times 10^4$ g/mol, PDI = 2.3; T_d = 440 °C; S_{BET} = 660 m²/g.

Casting of TPE- and TPE-TTSBI PIM films

0.3 g of TPE-PIM (or the TPE-TTSBI co-PIMs) was dissolved in CHCl₃ (10 mL). The resulting yellow solution was filtrated into a flat Petri dish using a 1.0 μ m filter cartridge. A yellowish membrane was obtained by slowly evaporating the solvent for 2 days under ambient conditions. Finally, the resulting membrane was soaked in methanol for 4 hours and thereafter heated in a vacuum oven at 120 °C for 24 hrs before testing. Complete solvent removal was confirmed by TGA. The average thickness of the membranes was around 70 - 80 μ m.

Dihedral Angle Calculation

The dihedral angle rotation energy calculation was performed using Materials Studio (8.0) software package (Accelrys Software Inc., CA, US). The calculation method was the same as previously reported.² The dihedral angle selected for calculation of TPE-PIM and PIM-1 are highlighted in Figure 4. Its conformations were calculated using Conformer Modules, and the dihedral angles were selected from - 180° to +180° with 2° steps. All intermediate conformers were optimized by CAMPASS forcefield using smart algorithm to ultra-fine convergence. The energy of each conformer was calculated by its optimized energy (E_{opt}) minus the minimum energy (E_{min}): $E = E_{opt} - E_{min}$. The degree of the rotational freedom was selected from those conformers, where the rotational energy was lower than the activation energy at 35 °C, which is approximately 3RT.

Gas Permeation Testing

The gas permeability of the membranes was determined using the constant-volume/variable-pressure method. The membranes were degassed in the permeation system on both sides under high vacuum at 35 °C for at least 24 h. The increase in permeate pressure with time was measured by a MKS Baratron transducer. The permeability of all gases was measured at 2 bar at 35 °C and was calculated by:

$$P = D \times S = 10^{10} \times \frac{V_d \times l}{p_{up} \times T \times R \times A} \times \frac{dp}{dt}$$

where P is the gas permeability (Barrer) – 1 Barrer = 10^{-10} cm³(STP)·cm/cm²·s·cmHg, p_{up} is the upstream pressure (cmHg), dp/dt is the steady-state permeate-side pressure increase (cmHg/s), V_d is the calibrated permeate volume (cm³), l is the membrane thickness (cm), A is the effective membrane area (cm²), T is the operating temperature (K), and R is the gas constant (0.278 cm³·cmHg/cm³(STP)·K). The apparent diffusion coefficient D (cm²/s) of the polymer membrane at 2 bar was calculated by $D = l^2/6\theta$, where l is the membrane thickness and θ is the time lag of the permeability measurement. The solubility coefficient S (cm³(STP)/cm³·cmHg) was obtained from the relationship S=P/D. The pure-gas selectivity was calculated as: $\alpha_{A/B} = P_A/P_B$.

Polymers	DMF	DMAc	THF	Chloroform	Acetone	Ethanol	Toluene
TPE-PIM	++	++	++	++			+
TPE-25	++	++	++	++			+
TPE-50	++	++	++	++			+
TPE-75	++	++	++	++			+
PIM-1	++	++	++	++			+
++, solubility over 10mg/mL; +, solubility between 1 mg/mL to 10 mg/mL;, not soluble.							

Table S1 Solubility of TPE-PIM and Co-PIMs and PIM-1 in organic solvents.



Fig. S2 Permeability/selectivity trade-off plots of different gas pairs (H_2/N_2 , CO_2/CH_4 , CO_2/N_2 and O_2/N_2) for tetraphenylethylene-based PIMs and PIM-1.

References

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