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Supporting Information

Unprecedented gas separation performance of a difluoro-functionalized triptycene-based ladder PIM membrane at low temperature

*Xiaohua Ma,** [a,b] *Zhiyang Zhu,*[a,b] *Wenxiong Shi,* [a,b] *Wenhui Ji,* [a,b] *Jianxin Li,** [a,b]
Yingge Wang,[c] *and Ingo Pinnau**[c]

[a] State Key Laboratory of Separation Membranes and Membrane Processes, School of Materials Science and Engineering, Tiangong University, Tianjin, 300387, P. R. China

[b] National Center for International Joint Research on Membrane Science and Technology, Tiangong University, Tianjin, 300387, P. R. China

[c] Functional Polymer Membranes Group, Advanced Membranes and Porous Materials Center, Physical Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia

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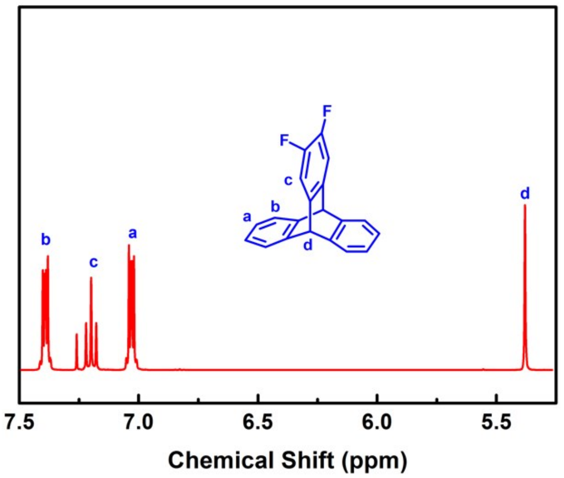

Figure S1. ^{1}H NMR spectrum of DFTrip.

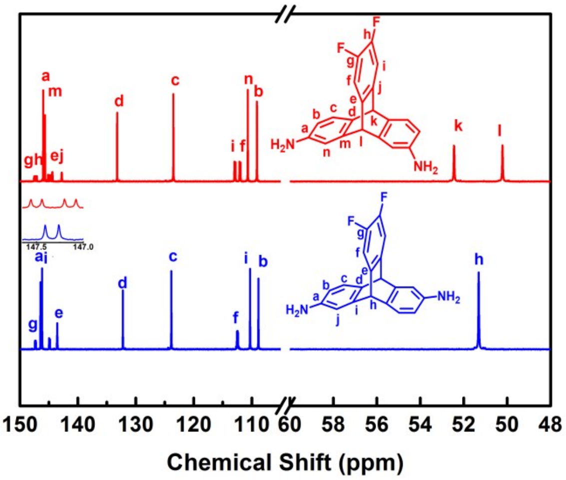

Figure S2. ^{13}C NMR spectra of DFTA regioisomers.

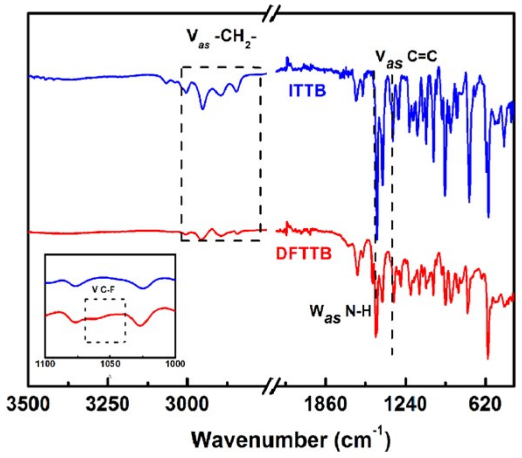

Figure S3. FT-IR spectra of DFTTB (red) and ITTB (blue) ladder polymers.

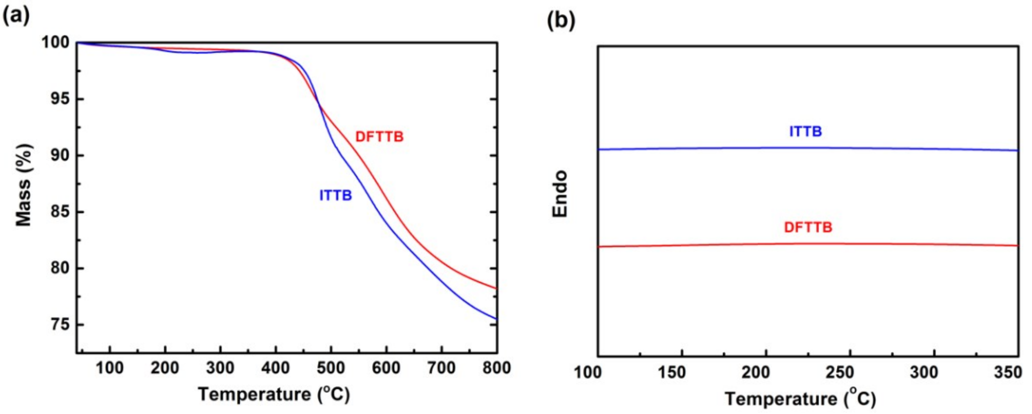

Figure S4. a) TGA curves of DFTTB and ITTB. b) DSC curves of DFTTB and ITTB.

Table S1: Physical properties of DFTTB and ITTB.

Polymers	M_n × 10^4 [a]	PDI	S_{BET} [b]	V_{total} [c]	T_d (°C) [d]	Density (cm^3 g^{-1})[e]	FFV [f]
DFTTB	9.18	4.12	918	0.68	425	0.983	0.364
ITTB [g]	9.02	1.62	900	0.64	445	0.930	0.349

[a] Molecular weight of the polymers was characterized by GPC using chloroform as solvent, unit: g mol^{-1}. [b] The BET surface area was obtained from N_2 adsorption isotherms, unit: m^2 g^{-1}. [c] Total pore volume of the polymers was obtained at a relative pressure (p/p_0) of 0.99, unit: cm^3 g^{-1}. [d] Onset decomposition temperature. [e] Density measured by buoyancy method. [f] Fractional free volume of polymer membranes measured by Bondi's group contribution method.[g] Data from reference 1.

Table S2: Solubility of DFTTB and ITTB.

Polymer	$CHCl_3$	DCE	Toluene	DMSO	DMF	THF	NMP	DMAc
DFTTB	+	+	-	-	+	+	+	+
ITTB	+	+	-	-	+	-	+	+

+: soluble; -: not soluble

Table S3. Mechanical properties of DFTTB and ITTB

Polymer	Young's Modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
DFTTB	0.39	30	24

Table S4. Diffusion and solubility coefficients of fresh and aged DFTTB.

	Permeability (Barrer)				Selectivity (αx/y)			
Polymers	N_2	O_2	CH_4	CO_2	D_{O2}/D_{N2}	S_{O2}/S_{N2}	D_{CO2}/D_{CH4}	S_{CO2}/S_{CH4}
DFTTB	109	650	144	3146				
D [a]	20.7	121	3.74	26.1	5.85		6.98	
S [b]	5.29	5.37	38.4	121		1.02		3.15
Aged 7 days	76	467	93	2102				
D	14.1	84.3	3.61	21.7	5.98		6.01	
S	5.38	5.55	25.8	97		1.03		3.76
Aged 180 days	43	281	49	1005				
D	12.7	76.3	3.51	19.5	6.01		5.56	
S	3.38	3.68	13.9	51.5		1.09		3.71

[a] Data obtained by time-lag method, unit:10^{-8} cm^2 s^{-1}. [b] Data from $S = P/D$, unit: 10^{-2} cm^3(STP) cm^{-3} $cmHg^{-1}$.

Table S5. Activation energy of permeation for H_2, O_2 and N_2 of DFTTB and other PIMs reported in the literature.

Polymer	Activation energy of permeation E_p (Kcal mol^{-1})		
	H_2	O_2	N_2
DFTTB[a]	2.88	3.84	5.17
ITTB[b]	-	1.33	1.68
PIM-TMN-Trip[c]	-0.67	-0.76	1.06
PIM-Btrip[c]	-0.21	1.49	4.34
PIM-1[d]	0.4	0.6	2.8

[a] DFTTB with thickness of 65 μm soaked in MeOH for 12 h and then air-dried for 24 h before testing. [b] Data from reference 1. [c] Data from reference 2. [d] Data from reference 3.

Table S6. CH_4 and CO_2 permeability and CO_2/CH_4 ideal selectivity of DFTTB at different upstream pressure

Pressure (bar)	2	5	10	12.5	15
P_{CH4} (Barrer)	120	116	117	121	126
P_{CO2} (Barrer)	2907	2797	3001	3256	3569
Ideal P_{CO2}/P_{CH4}	24.2	24.1	25.6	26.9	28.3

Table S7. Gas separation properties of DFTTB and PIM-PI-1 at 30 and -30 °C

Polymers	Temperature (°C)	Permeability (Barrer)			Selectivity ($\alpha_{x/y}$)	
		H_2	N_2	O_2	P_{H2}/P_{N2}	P_{O2}/P_{N2}
DFTTB	30	5244	119	715	44	6.00
	-30	1532	13.5	137	112	10.14
PIM-PI-1 [a]	30	607	1360	110	12.4	3.64
	-30	395	796	13	61.2	7.92

[a] The synthetic procedure was obtained from reference 4.

Table S8. CO_2/N_2 mixed-gas separation properties of DFTTB

Time (h)	CO_2 (%) [a]	P_{CO2} [b] (Barrer)	P_{N2} (Barrer)	P_{CO2}/P_{N2}
0	86.34	2875	89	32.2
3	86.17	2664	89	30.1
9	86.44	2821	86	32.7
12	86.29	2707	87	31.1
24	86.22	2781	87	31.9
27	86.35	2658	86	31.0
30	86.13	2610	87	30.1
33	86.12	2681	88	30.5
36	86.18	2766	89	31.0
48	86.17	2589	86	30.1

[a] CO_2 percent obtained by GC in the mixed-gas collected in downstream volume.

[b] Permeability of CO_2 back calculated from the CO_2 concentration result and the time-lag method.

Table S9. CO_2/CH_4 mixed-gas separation properties of DFTTB

Pressure	CO_2 (%) [a]	P_{CO2} [b] (Barrer)	P_{CH4} (Barrer)	P_{CO2}/P_{CH4}
2	97.25	2304	82	28.1
5	97.16	2241	84	26.7
10	97.07	2233	87	25.7
12.5	96.65	2257	101	22.3
15	96.56	2254	104	21.7
20	96.10	2253	119	18.9

[a] CO_2 percent obtained by GC in the mixed-gas collected in downstream volume.

[b] Permeability of CO_2 back calculated from the CO_2 concentration result and the time-lag method.

Detailed Molecular Simulation Procedure

Energy minimum of DFTTB and ITTB dimers were performed with a DFT simulation method (B3LYP) using 6-31g++ basis functions in Gaussian 09 code.[5] The atomic charge and related parameters for each dimer was obtained from the Gromos96 force field and Prorg.[6]. The optimized DFTTB dimer was gradually loaded into a preset simulation box with size of 8 × 8 × 8 nm^3. The system energy was minimized using a molecular dynamics method, and during the optimization, a three-dimensional periodic boundary condition (PBC) was applied. After NPT treatment of the simulation box at 200 ns, the density of the box was 0.983g cm^{-3} (which was the same as the measured density). The geometric file of 200 ns is intercepted, and annealed for 10 ns by varying the temperature from 300 to 675 K to build the homogeneous DFTTB membrane cell. A 4 × 4 × 4 nm^3 optimized cell was selected for pore size distribution and fluorine atom distribution analyses, using Zeo++ program and fluorine index in GROMACS (version 4.6.7), respectively.[7] The same methodology was applied for ITTB which gave an estimated density of 0.930 g cm^{-3}.

Mixed-gas separation testing

The mixed-gas separation of DFTTB was also tested using the constant-volume/ variable-pressure method. The set-up was modified according to the pure-gas system, and its schematic diagram was shown in the following **Figure 5**.

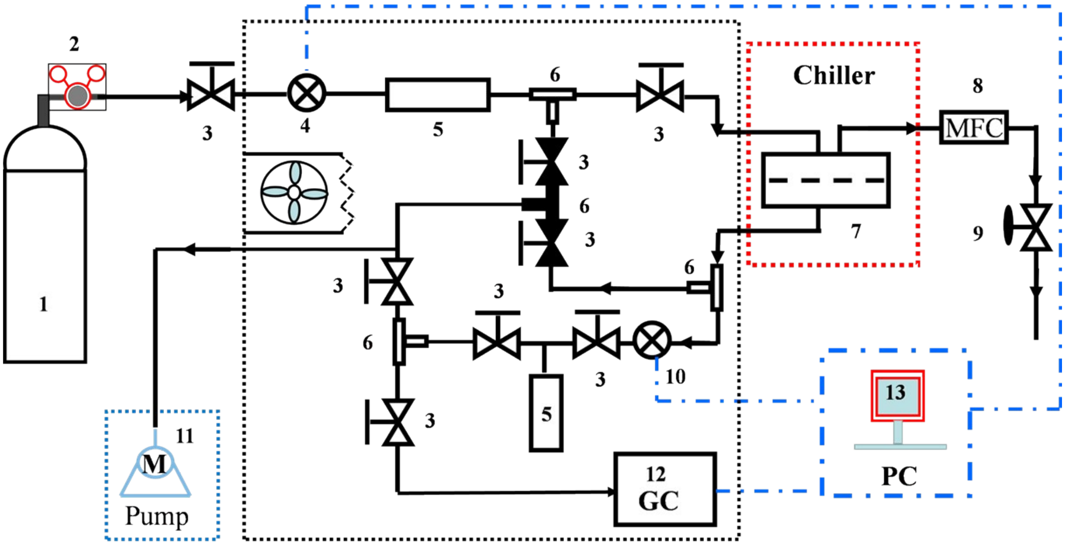

Figure S5. Schematic set-up of mixed-gas permeation testing system, 1: Mixed-gas cylinder, 2: Regulator, 3: Bellows sealed valve, 4: Upstream transducer, 5: Upstream gas storage tank, 6: Tee pipeline with welding, 7: Membrane cell, 8: Mass flow meter, 9: Needle valve, 10: Downstream transducer, 11: Vacuum pump, 12: Gas chromatography, 13: Computer.

For CO_2/N_2 testing, synthesized compressed flue gas with CO_2/N_2 ratio of 15/85 was used as feed gas at a constant upstream pressure of 2 bar. The retention flow was controlled by a mass flow meter (MFC) with the stage cut of 0.01 to keep the component ratio of the feeding mixed gas to be constant. The testing time lasted for 48 h.

As for CO_2/CH_4 separation testing, which is targeted for natural gas and biogas upgrading, the testing was performed at upstream pressure of 2, 5, 10, 12.5, 15 and 20 bar, respectively, using a 50/50 CO_2/CH_4 mixture.

The permeated gas was cumulated in the downstream volume (100 mL) up to ~7 torr, which was pulled into a constant volume loop (1 mL) pre-installed in the six-way valve of the GC (EWAI GC-4100). Then, the gas was sent to the column of GC and analyzed by a thermal conductivity detector (TCD). The gas concentration of each component was analyzed by their GC areas and corrected by a calibration factor (the area ratio of same amount of gasses). Their permeabilities were calculated according to the following equation:

$$P_A = 10^{10} \times \frac{\mathrm{y}_A \times V \times l}{x_A \times f_{up\,A} \times T \times R \times A} \times \frac{dp}{dt}$$

$$P_B = 10^{10} \times \frac{\mathrm{y}_B \times V_d \times l}{x_B \times f_{\mathrm{up}\,B} \times T \times R \times A} \times \frac{dp}{dt}$$

Where x_A is the feed component concentration of CO_2 and x_B is that of N_2 or CH_4, respectively; y_A is the permeate gas concentration of CO_2 and y_B is that of N_2 or CH_4, respectively. f is the fugacity of the upstream partial pressure. The selectivity of gas A/B can be calculated as follows:

$$\alpha_{A/B} = \frac{\mathrm{y}_A / y_B}{x_A / x_B}$$

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