A Fine-Tuned Hollow Porous Metal–Organic Framework in Mixed-Matrix Membranes for Benchmark Performance of CO_2 Separation

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1. Experimental

1.1. Materials

Durene diamine, 6FDA, acetic anhydride (≥99%), TEA (≥99.5%) and pyrazine were purchased from Sigma-Aldrich Company. Copper $CuSiF_6$ and (SDS) were purchased from Oakwood chemical and Merck (Darmastadt, Germany) companies, respectively. Chloroform, methanol and DMAc were supplied from Daejung chemicals and metals company (South Korea). CO_2, N_2 and CH_4 gases were acquired from Saman-Gas company (Arak, Iran). Durene diamine and 6FDA dianhydride monomers were purified using recrystallization method before use.

1.2. Synthesis of 6FDA-Durene polymer

Two-step condensation polymerization method was used for polymer synthesis [1] (Fig. S1). First 1 mmol purified Durene diamine was dissolved in 4.87 g DMAc. Then 1 mmol of purified 6FDA dianhydride was added to the solution. The solution was stirred in an ice bath and under the nitrogen atmosphere for 24 h to produce polyamic acid. Finally, 4 mmol of TEA (basic catalyst) and acetic anhydride (dehydration agent) separately added to imidize

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polyamic acid. The polyimide solution was precipitated in methanol and then after filtration and several time washing with fresh methanol, it was dried in an oven (85 ºC).

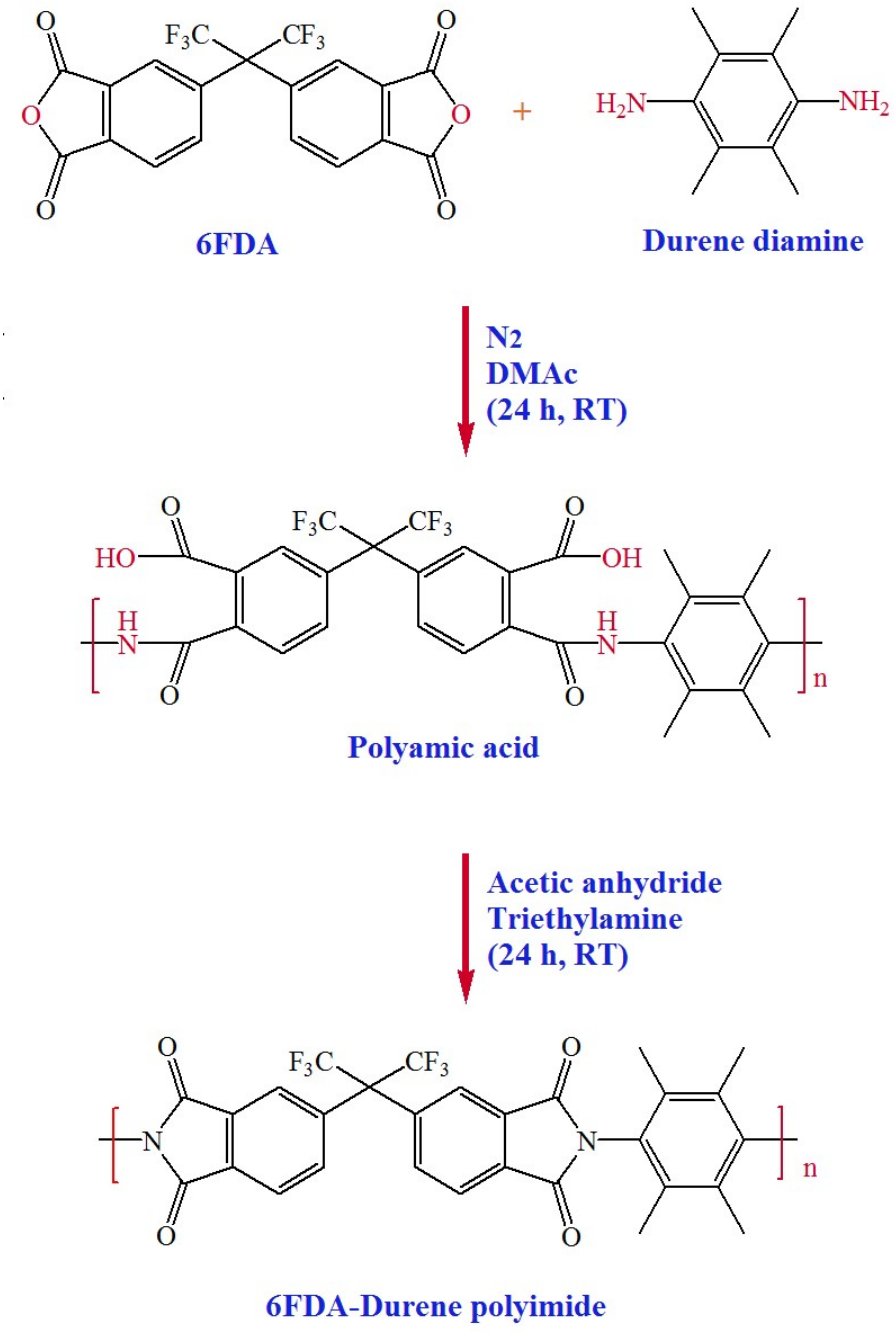

Fig. S1. Schematic representation of the 6FDA-Durene synthesis process.

1.3. Synthesis of S-SIFSIX-3-Cu

First 0.6 g of pyrazine and 0.65 g of $CuSiF_6$ were dissolved separately in 10 ml of methanol. Then, by layering the pyrazine-methanol solution on the $CuSiF_6$-methanol solution, a purple solution was obtained, which was stirred for 24 h. The S-SIFSIX-3-Cu solution was filtered and washed several times with methanol. The obtained powder was activated by acetone and then dried in a vacuum oven for 24 h before use [2].

1.4. Synthesis of H-SIFSIX-3-Cu

Fabrication of hollow nanostructures with appropriate morphology and controlled size and dimensions is one of the important challenges in the synthesis of such structures. Hollow nanoparticles can be prepared by various methods such as template-assisted routes, sol-gel process, and self-assembly techniques [3]. The template-assisted method is the most effective and common route compared to other methods of preparing hollow nanomaterials. Different synthesis methods provide different morphologies and dimensions. In this research, the soft-template method was used because of the easy molding of the soft template and its easy removal. In the soft-template assisted assembly route, the reduction of potential energy at the interface acts as a driving force for the adsorption of structural blocks on this surface [4, 5]. First, 0.126 g of SDS, as a soft-template, was dissolved in 9.39 ml of distilled water. Then 0.65 g of $CuSiF_6$ salt was added to the solution and after stirring for several hours, 0.6 g of pyrazine was also added. After 24 h stirring, the solution was filtered and washed several times with distilled water. Then the resulting powder was activated by acetone and then completely dried in a vacuum oven for 24 h. It should be noted that the spherical micelles can be formed by adjusting the concentration of surfactants in the solution (Fig. S2).

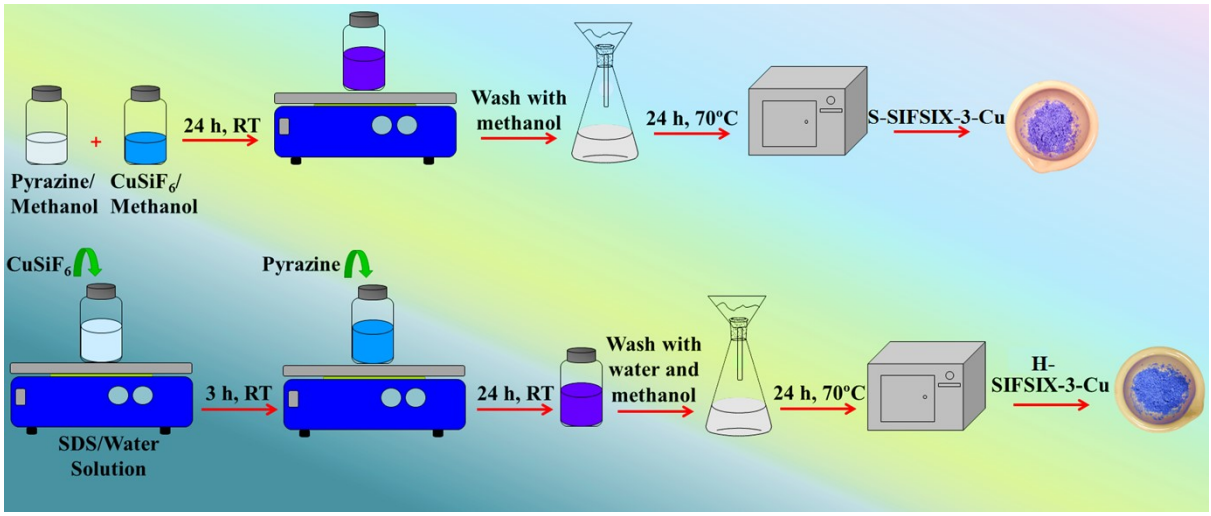

Fig. S2. Schematic representation of the synthesis process of SIFSIX-3-Cu with solid and hollow morphologies.

1.5. Membrane preparation

Pure polyimide membrane was fabricated via solution casting-solvent evaporation method. The synthesized 6FDA-Durene was dissolved in chloroform (5 wt.%) at room temperature for 24 h. Consequently, the polymer solution was cast onto a clean petri dish. The final film was dried at 85 ºC for 24 h. The preparation method of MMMs is similar to the pure membrane. First, chloroform was added to a certain amount of particles in glass bottle and stirred and then sonicated to obtain a homogenous suspension. Then the polymer was added to the suspension in two steps (priming method) and stirred until a uniform solution was obtained. Finally, the solution was casted and after the complete evaporation of the solvent, the polymer film was dried in an oven at 85 ºC for 24 h.

1.6. Characterization

Material characterization was performed to evaluate structural and morphological properties and their effect on membrane performance. In this research, XPS spectra of the synthesized S-SIFSIX-3-Cu was performed using SPECS-UHV (Germany). TEM images of

the synthesized particles were taken by a TEM apparatus (LEO, 906 E) to investigate particles size and their morphology. FTIR and ATR spectroscopies were used by using a spectrometer (BRUKER, ALPHA) in the 400-4000 and 600-4000 cm^{-1} scan ranges respectively to confirm the chemical structure of the synthesized membranes and particles, and any modification thereof in MMMs. XRD patterns of membranes and particles were performed by a diffractometer (PHILIPS-PW1730, Netherland, Cu Kα (λ=0.15406 nm) anode material, 40 kV accelerating voltage, 40 mA tube current, 0.05 º/s step size) to investigate the microstructural properties, such as d-spacing. DLS analysis (Nan optic 90 Plus) was employed to determine the particle size distribution of the synthesized particles. Adsorption-desorption N_2 porosimetry-BET analysis was measured using the Belsorp-mini volumetric adsorption apparatus to evaluated the effective surface area of the particles. The CO_2 isotherms of synthesized particles were investigated using Micromeritics (ASAP 2020) analyzer in the 0-1 bar relative pressure range and temperature of 273 and 298 K. FESEM as well as EDS were performed by using a TESCAN microscope and an EDS instrument (TESCAN, MIRA 3 LMU) respectively, to investigate the morphology of the synthesized membranes (cross-sectional morphology) and particles, as well as the dispersion quality of the dispersed phase in polymer matrices. In this case the membranes were first broken in liquid nitrogen and then coated with gold thin film by a sputter coater (DSR1). The thermal behavior of the pure membrane and MMMs was evaluated through TGA using an instrument (TGA STA 6000). The mechanical properties of the pure membrane and MMMs were evaluated using a tensile testing machine (Hiwa 200, ASTMD638) at 25 ºC and 10 mm/min strain rate. The M_w, number average molecular weight M_n and poly dispersity index PDI of the synthesized polymer were determined by GPC analysis (KNAUER, Germany).

1.7. Gas permeation measurements

The pure gases (CO_2, N_2 and CH_4) permeability was measured using constant volume-variable pressure method (time-lag method) in the 2-10 bar pressure range and at 25 ºC. This permeability was calculated by [6]:

$$P = \frac{273.15 \times 10^{10} Vl}{AT(p_0 \times 76)}\left(\frac{dp}{dt}\right) \quad (1)$$

where P is the pure gas permeability (Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm/(cm^2 cmHg s))) ; V is the downstream chamber constant volume (cm^3); l is the membrane thickness (cm); A is the effective membrane area (cm^2); T is the absolute temperature (K); p_0 is the feed flow pressure (atm); and dp/dt is the pressure rate increment at steady state condition in the downstream side (atm/s).

The ideal selectivity was obtained by [6]:

$$\alpha_{AB} = \frac{P_A}{P_B} \quad (2)$$

where P_A and P_B are A and B pure gases permeability, which are measured at the same conditions.

The diffusivity and solubility coefficients were calculated by the following equations [1]:

$$D = \frac{l^2}{6\theta} \quad (3)$$

$$P = S \times D \quad (4)$$

where D, θ and S are diffusivity coefficient (cm^2/s), time lag (s) and solubility coefficient (cm^3 (STP)/cm^3.cmHg), respectively. θ is obtained from the intersection of the linear part (steady state region) of the pressure-time curve with time axis.

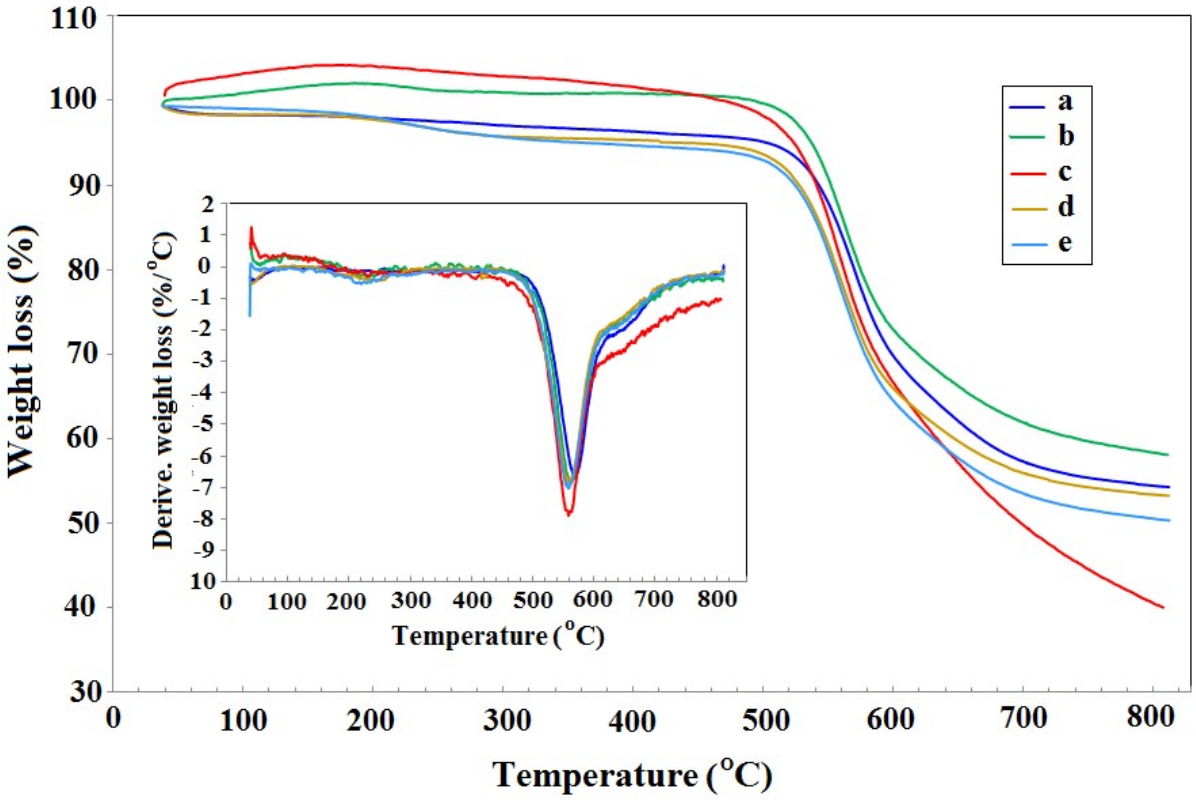

Fig. S3. TGA and DTG plots of 6FDA-Durene (a), 6FDA-Durene/S-SIFSIX-3-Cu (7 wt.%) (b), 6FDA-Durene/S-SIFSIX-3-Cu (8 wt.%) (c), 6FDA-Durene/H-SIFSIX-3-Cu (7 wt.%) (d), and 6FDA-Durene/H-SIFSIX-3-Cu (8 wt.%) (e).

Table S1. Mechanical properties of the synthesized membranes.

Membrane	Young's modulus [GPa]	Elongation (Tensile Strength) [%]	Tensile strength [MPa]
6FDA-Durene	2.26	60.23	77.04
6FDA-Durene/S-SIFSIX-3-Cu (7 wt.%)	0.08	76.55	22.19
6FDA-Durene/S-SIFSIX-3-Cu (8 wt.%)	0.03	82.30	22.34
6FDA-Durene/H-SIFSIX-3-Cu (7 wt.%)	0.18	95.22	97.40
6FDA-Durene/H-SIFSIX-3-Cu (8 wt.%)	0.17	108.78	75.81

Table S2. Measured permeability, Diffusivity and Solubility coefficient and pure gas selectivity of the synthesized membrane at 2 bar.

Membrane	Gas	[a]P	[b]D	[c]S	CO_2/N_2			CO_2/CH_4		
					[d]α_p	[e]α_D	[f]α_S	α_p	α_D	α_S
6FDA-Durene	CO_2	529.45	32.46	16.31	23.08	2.34	9.88	26.33	3.10	8.49
	N_2	22.94	13.87	1.65						
	CH_4	20.11	10.47	1.92						
6FDA-Durene/S-SIFSIX-3-Cu (5 wt.%)	CO_2	700.11	33.42	20.95	39.31	3.98	9.88	39.58	4.19	9.44
	N_2	17.81	8.39	2.12						
	CH_4	17.69	7.97	2.22						
6FDA-Durene/H-SIFSIX-3-Cu (5 wt.%)	CO_2	1514.8	54.84	27.62	40.40	4.07	9.90	41.05	4.26	9.62
	N_2	37.50	13.46	2.79						
	CH_4	36.89	12.86	2.87						
6FDA-Durene/S-SIFSIX-3-Cu (7 wt.%)	CO_2	1348.06	52.56	25.65	35.13	4.16	8.41	42.27	5.07	8.35
	N_2	38.57	12.63	3.05						
	CH_4	31.89	10.37	3.07						
6FDA-Durene/H-SIFSIX-3-Cu (7 wt.%)	CO_2	1808.20	61.35	29.47	41.61	4.49	9.27	45.09	5.39	8.37
	N_2	43.46	13.66	3.18						
	CH_4	40.10	11.39	3.52						
6FDA-Durene/S-SIFSIX-3-Cu (8 wt.%)	CO_2	981.79	33.83	29.02	50.69	3.85	13.19	55.07	4.17	13.19
	N_2	19.37	8.78	2.20						
	CH_4	17.83	8.11	2.20						
6FDA-Durene/H-SIFSIX-3-Cu (8 wt.%)	CO_2	1484.25	44.89	33.06	53.38	3.97	13.44	57.94	4.28	13.60
	N_2	27.80	11.31	2.46						
	CH_4	25.61	10.52	2.43						
6FDA-Durene/S-SIFSIX-3-Cu (10 wt.%)	CO_2	503.69	17.74	28.39	49.10	3.37	14.56	54.57	3.78	14.41
	N_2	10.26	5.26	1.95						
	CH_4	9.23	4.69	1.97						
6FDA-Durene/H-SIFSIX-3-Cu (10 wt.%)	CO_2	1018.94	30.37	33.55	51.52	3.52	14.65	57.85	4.07	14.21
	N_2	19.78	8.62	2.29						
	CH_4	17.61	7.46	2.36						

[a] Permeability [cm^3(STP) cm/cm^2.s.cmHg)]*10^{-10}
[b] Diffusivity coefficient [cm^2/s]*10^{-8}
[c] Solubility coefficient [cm^3(STP)/(cm^3.cmHg)]*10^{-2}
[d] Permeability selectivity
[e] Diffusivity selectivity
[f] Solubility selectivity

Table S3. Summary of the best performance of benchmark PI- and 6FDA-based MMMs under different operating conditions.

Polymer	Particle	PCO_2 (Barrer)	CO_2/CH_4	CO_2/N_2	Ref.
at 2 bar and 25-35 °C					
Matrimid®	ZIF-8	24.6	124	-	[7]
Matrimid 5218	SBMA@CNT	4.1	97	-	[8]
Matrimid®	MIL-53-as	40	90.1	-	[9]
Matrimid®	CNTs/GO	38.07	84.6	-	[10]
6FDA-ODA	UiO-66	43.3	57	-	[11]
Matrimid®	MIL-53-ht	51	47	-	[9]
6FDA-Durene	Q-ZrFum	1307.81	44.05	-	[12]
6FDA-DAM:DABA (3:1)	GO/ZIF-8	1600	39.5	-	[13]
6FDA-DAM	UiO-66	1912	31	-	[14]
6FDA-Durene	ZIF-8	2185	17.1	-	[15]
Matrimid®	CNTs/GO	38.07	-	81	[10]
6FDA-Durene	$[Cu(6L)]^{2+}$@13X	1034.1	-	38.28	[16]
6FDA-Durene	Fe^{2+}CTF	1288.3	-	34.08	[17]
6FDA-Durene	H-SIFSIX-3-Cu (7 wt.%)	1808.2	45.09	41.61	**This work**
6FDA-Durene	H-SIFSIX-3-Cu (8 wt.%)	1484.25	57.94	53.38	**This work**
at 10 bar and 25-35 °C					
PEI	Aminated-GO	1.57	142.7	-	[18]
Matrimid	IL@NH_2-MIL-101	19	112	-	[19]
6FDA-ODA	IPA-3ET	40.9	80.2	-	[20]
6FDA-Durene	Q-ZrFum	1137.98	42.93	25.25	[12]
Matrimid5218	Silica (TEOS)	12.1	-	57.6	[21]
6FDA-Durene	$[Cu(6L)]^{2+}$@13X	971.19	-	37.6	[16]
6FDA-Durene	Fe^{2+}CTF	1121.13	-	32.87	[17]
6FDA-Durene	H-SIFSIX-3-Cu (7 wt.%)	1021.28	33.94	28.7	**This work**
6FDA-Durene	H-SIFSIX-3-Cu (8 wt.%)	957.4	50.98	44.06	**This work**

Abbreviation	Full name
MMM	**Mixed matrix membrane**
H-F-MOF	**Hollow fluorinated metal-organic framework**
H-SIFSIX-3-Cu	**Hollow SIFSIX-3-Cu**
6FDA	**4, 4'-(Hexafluoroisopropylidene) diphthalic anhydride**
Durene	**1, 2, 4, 5-tetramethylbenzene**
PI	**6FDA-Durene polyimide**
MOFs	**Metal-organic frameworks**
3D	**Three-dimensional**
2D	**Two-dimensional**
CTCs	**Charge transfer complexes**
C-F bond	**Carbon-fluorine bond**
S-SIFSIX-3-Cu	**Solid (non-hollow) fluorinated MOFs**
Q_{st}	**Isosteric heats of sorption**
Mw	**Weight average molecular weight**
Mn	**Number average molecular weight**
PDI	**Polydispersity index**
FFVs	**Fractional free volumes**
T_d	**Decomposition temperature**
TEA	**Trimethylamine**
$CuSiF_6$	**Hexafluorosilicate hydrate**
SDS	**Sodium dodecyl sulfate**
DMAc	**N,N-dimethylacetamide**
XPS	**X-ray photoelectron spectroscopy**

TEM	**Transmission electron microscopy**
FTIR	**Fourier transform infrared**
ATR	**Attenuated total reflection**
XRD	**X-ray diffraction**
DLS	**Dynamic light scattering**
FESEM	**Field emission scanning electron microscopy**
EDS	**Energy dispersive X-ray spectroscopy**
TGA	**Thermogravimetric analysis**
GPC	**Gel permeation chromatography**

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