Electronic Supporting Information

Phase-Transition Ionic Liquid Endows COF-Based Mixed Matrix Membranes with Efficient CO₂ Separation

Shuyu Guo^a, Jingrao He^a, Hailong Han^a, Rui Han^a, Junxi Shou^a, Chenxiang Ai^a, Ruiren Tang^a, Shuai Gu^{ab}*, Juntao Tang^a*, Guipeng Yu^a*

^aHunan Key Laboratory of Micro & Nano Materials Interface Science, College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China. E-mail: shaigu@csu.edu.cn.

^bKey Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China

1. Materials

N,*N*-dimethylacetamide (99.9 %), anhydrous *N*,*N*-dimethylformamide (DMF, 99.9 %), 2,6-diaminoanthraquinone (AR), and 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobiindane (97 %) were purchased from Sun Chemical Technology (Shanghai) Co., Ltd. 1-ethyl-3-methylimidazole hexafluorophosphate (AR), and dichloromethane (CH₂Cl₂, AR) were obtained from Shanghai Titan Technology Co., Ltd. Methanol (AR) was bought from Tianjin Jinfeng Chemical Co., Ltd. Chloroform (99 %) was obtained from Chengdu Cologne Chemical Co., Ltd. Acetic acid (99 %) and trifluoroacetic (99 %) acid were bought from Shanghai Aladdin Biochemical Technology Co., Ltd. Dioxane (99.9 %) was purchased from J&K Scientific. Tetrafluoroterephthalonitrile (98 %) was obtained from Zhengzhou JACS Chem Product Co., Ltd. Anhydrous potassium carbonate (99 %) was bought from Shanghai Macklin Biochemical Technology Co., Ltd.

2. Testing Instruments and Characterization Methods

The monomers of PIM-1 and TFP were characterized using a Bruker Advance III 400 MHz NMR spectrometer (¹H NMR). The crystal structures of DAAQ-COF and MMMs were determined using a Bruker AXS D-8 Advanced SAXS/WAXS diffractometer. Elemental analysis was performed using an Elementar Vario Micro Cube elemental analyzer. The characteristic functional groups of DAAQ-COF, IL@DAAQ-COF, PIM-1, and MMMs were identified via FT-IR spectroscopy (ATR-FTIR, Nicolet iS50, USA) over the range of 4000-500 cm⁻¹. The thermal transitions of IL@DAAQ-COF and [Emim][PF₆] were analyzed by differential scanning calorimetry (DSC, PerkinElmer DSC 8500, USA) under a nitrogen (N₂) atmosphere. Thermogravimetric analysis (TGA, Mettler Toledo TGA/DSC 1, Switzerland) was subsequently performed on all samples under identical N₂ purge conditions to evaluate their thermal stability. The surface and cross-sectional morphologies of DAAQ-COF, IL@DAAQ-COF, and MMMs were examined using a scanning electron microscope (SEM, FEI SIRION 200, USA). The N₂ adsorption isotherms of DAAQ-COF and

IL@DAAQ-COF at 77 K were measured using a gas adsorption analyzer (ASAP 2020, Micromeritics Instrument Corporation). Specific surface areas and pore size distributions were calculated using the Brunauer-Emmett-Teller (BET) method and non-local density functional theory (NLDFT), respectively. The adsorption capacities of DAAQ-COF and IL@DAAQ-COF for CO_2 and N_2 at 273 K and 298 K were evaluated. Gas separation performance of the membrane was assessed using the Wicke-Kallenbach technique on a custom-built gas separation apparatus, and gas permeability and selectivity were measured using the constant-pressure variable-volume method.

3.Synthesis

3.1 Synthesis of Triformylphloroglucinol



Figure S1 Synthesis of TFP.

Under nitrogen protection, hexamethylenetetramine (HMT) (15.1 g, 108 mmol) and phloroglucinol (6.0 g, 49 mmol) were added sequentially to a three-necked flask, followed by the dropwise addition of 90 mL of trifluoroacetic acid under magnetic stirring. The mixture was gradually heated to 100 °C and maintained at this temperature for 2.5 hours. Subsequently, 150 mL of 3 M hydrochloric acid (HCl) was added dropwise, and the reaction was continued at 100 °C for an additional hour. The filtrate was then extracted three times with dichloromethane (50 mL \times 3). The organic layer obtained was dried over magnesium sulfate and filtered. The filtrate exhibited a yellow color. The solution was concentrated under reduced pressure to afford a yellow powder, which was further purified via sublimation at 150 °C to yield a white solid powder.

The structure of triformylphloroglucinol (TFP) was confirmed by NMR spectra, which was in good agreement with the data in the literature^[1].



Figure S2 ¹H NMR spectra of triformylphloroglucinol (TFP).

3.2 Synthesis of DAAQ-COF

DAAQ-COF was synthesized following the procedures described in the literature. Specifically, 2,6-diaminanthraquinone (DAAQ, 34 mg, 0.142 mmol) and 1,3,5-triformylphloroglucinol (TFP, 20 mg, 0.096 mmol) were individually added to 5 mL ampoules. Subsequently, 1 mL of *N*,*N*-dimethylformamide (DMF) was introduced into the ampoules, and the resulting mixture was sonicated at room temperature for 2 minutes. Next, 50 μ L of 6 M acetic acid was added, and the sonication was continued for an additional 5 minutes under a nitrogen atmosphere. To ensure an anhydrous and oxygen-free environment, the system was subjected to three freeze-vacuum-thaw cycles using liquid nitrogen. The mixture was then heated at 90 °C for 48 hours. Upon completion of the reaction, the solid product was sequentially washed with distilled water (20 mL × 3), acetone (20 mL × 3), and ethanol (20 mL × 3). The crude product was further purified by soaking in DMF for 3 days, followed by drying in a vacuum oven at 90 °C for 12 hours, yielding a reddish-brown powder with a purity of 85 %.



Figure S3 Synthesis of DAAQ-COF

3.3 Synthesis of IL@DAAQ-COF

1,3,5-triformylphloroglucinol (TFP, 20 mg, 0.096 mmol), 2,6-diaminanthraquinone (DAAQ, 34 mg, 0.142 mmol), and 1-ethyl-3-methylimidazolium hexafluorophosphate ([Emim][PF6], 38.4 mg, 0.15 mmol) were individually added to 5 mL ampoules. The ampoules were then filled with 1 mL of *N*,*N*-dimethylformamide (DMF), and the resulting mixture was sonicated for 2 minutes. Subsequently, 50 μ L of 6 M acetic acid was added, and the system was sonicated for an additional 1 minute under a nitrogen atmosphere. To ensure an anhydrous and anaerobic environment, the system underwent three freeze-vacuum-thaw cycles using liquid nitrogen. The reaction mixture was then heated at 120 °C for 3 days. After the reaction was completed and the system had cooled to room temperature, the reaction products in the ampoule were filtered, and the solid powder was sequentially washed with distilled water (30 mL × 3), acetone (30 mL × 3), and ethanol (30 mL × 3). The crude product was soaked in DMF for 3 days to remove any unmodified IL from the COF channels. Finally, the product was dried in a vacuum oven at 60 °C for 12 hours, yielding a reddish-brown powder with a purity of 80 %, and the synthetic steps are shown in Figure 1.

3.4 Synthesis of Polymer PIM-1

The polymer PIM-1 was synthesized according to the known literature^[2]. At room temperature, anhydrous potassium carbonate (7.32 g, 52.88 mmol), 5,5',6,6'tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobiindane (6.00 17.63 mmol), g, tetrafluoroterephthalonitrile (3.53 g, 17.63 mmol), and anhydrous N,Ndimethylformamide (120 mL) were introduced and purged with N2 to create an anhydrous and oxygen-free reaction environment. The reaction was then carried out at 65 °C for a period of 3 days. Upon completion of the reaction, the entire reaction system was cooled to room temperature, and a yellowish precipitate was observed at the bottom of the flask. Subsequently, the product in the flask was poured into 300 mL of pure water, and the crude product was collected by vacuum filtration using a pump. The crude product was dissolved in 30 mL of chloroform and then slowly added dropwise to 1200 mL of methanol to induce precipitation. This dissolution-precipitation process was repeated three times. The product obtained after vacuum filtration was dried in a vacuum oven at 60 °C for 12 hours. The final product yield was determined to be 98 %, and the synthetic steps are shown in Figure S7.

3.5 Synthesis of DAAQ-COF/PIM-1 MMMs

DAAQ-COF/PIM-1 MMMs was prepared by solution casting method, as shown in Figure S8 and S9. Firstly, 200 mg of dried PIM-1 powder was added to a 3 mL chloroform solution and stirred for 1 hour until it was completely dissolved. Subsequently, different masses of DAAQ-COF were weighed and separately added into 3 mL of chloroform. These were then stirred and sonicated for 24 hours until they were fully dispersed. The DAAQ-COF dispersion was subsequently incorporated into the PIM-1 solution that had been filtered through a filter tip, and the mixture was stirred for 12 hours until a homogeneous DAAQ-COF/PIM-1 casting film solution was formed. The obtained casting solution was poured onto a flat petri dish, and the lid of the petri dish was then placed on top. The solvent was allowed to volatilize at room temperature, yielding mixed matrix membranes with different filler ratios. A series of DAAQ-COF/PIM-1 MMMs were obtained by removing the residual solvents in a 45 °C vacuum oven for 12 hours.

3.6 Synthesis of IL@DAAQ-COF/PIM-1 MMMs

IL@DAAQ-COF/PIM-1 MMMs were prepared through solution casting method. To investigate the influence of filler content on the structure and properties of the mixed matrix membranes, four types of mixed matrix membranes with distinct filler ratios, namely 0 wt%, 2 wt%, 4 wt%, and 8 wt%, were fabricated. 200 mg of dried PIM-1 powder was added into a 3 mL chloroform solution and magnetically stirred for 1 hour until it was completely dissolved. Different masses of IL@DAAQ-COF were blended in 3 mL of chloroform and ultrasonicated for 24 hours until evenly dispersed. The

IL@DAAQ-COF dispersion was then poured into the PIM-1 solution that had been filtered through a filter tip, and stirred for 12 hours until a homogeneous IL@DAAQ-COF/PIM-1 mixture was achieved. The obtained casting solution was poured onto a flat petri dish, and then the lid of the flat petri dish was covered. The solvent was volatilized at room temperature, and mixed matrix membranes with different filler ratios were obtained. Subsequently, it was dried in a 45 °C vacuum oven for 12 hours to eliminate the residual solvents from the membrane.

3.7 Thermal treatment of IL@DAAQ-COF/PIM -1 MMMs

IL@DAAQ-COF/PIM-1 mixed matrix membranes with different filler loading were dried at 80 °C in a vacuum oven for 12 hours. The DSC curve of IL@DAAQ-COF (Figure S16) exhibited a broad peak centered at 77.3 °C, indicating the IL in IL@DAAQ-COF underwent a melting process at 80 °C during the thermal treatment. Higher temperatures may cause membrane shrinkage or cracking.³ To ensure complete transformation of the IL from the solid to the molten state and minimize the impact of temperature on factors other than the IL, the thermal treatment temperature was set at 80 °C. Additionally, considering the potential industrial application for preparing high-performance gas separation MMMs, a lower thermal treatment temperature is cost-effective and energy-efficient. Therefore, based on these considerations, 80 °C was ultimately selected as the optimal thermal treatment temperature.



Figure S4 The SEM mapping images of the IL@DAAQ-COF.



Figure S5 CO_2 and N_2 adsorption isotherms of DAAQ-COF at 273 K and 298 K



Figure S6 CO₂ and N₂ adsorption isotherms of IL@DAAQ-COF at 273 K and 298 K.



Figure S7 DFT calculations on differential charge density maps and the interaction energy changes between DAAQ-COF and CO₂ after introducing IL.



Figure S8 Synthesis of Polymer PIM-1.



Figure S9 Casting solution of DAAQ-COF/PIM-1.



Figure S10 Preparation processes of DAAQ-COF/PIM-1.



Figure S11 CO2 adsorption-desorption isotherms of the IL@DAAQ-COF MMMs at

273 K.



Figure S12 Pore size distribution of the IL@DAAQ-COF MMMs.



Figure S13 CO₂ and N₂ permeability (a) and CO₂/N₂ selectivity (b) of IL@DAAQ-





Figure S14 The long-term stability test of IL@TD-COF/PIM-1-4 wt% MMM.



Figure S15 DSC curves of IL.





Figure S16 DSC curves of IL@DAAQ-COF.



Figure S17 TGA curves of pristine PIM-1 membrane and IL@DAAQ-COF/PIM-1

MMMs.



Figure S18 TGA curves of pristine PIM-1 membrane and DAAQ-COF/PIM-1

MMMs.

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Element analysis (%)								
Sample	Element type							
	С	Н	Ν	Ο	F			
DAAQ-COF	78.12	3.50	14.10	4.27	0.00			
IL@DAAQ-COF	75.27	3.40	9.19	4.01	8.58			

Table S1 Element content analysis of DAAQ-COF and IL@DAAQ-COF

Table S2 The pore structural parameters of DAAQ-COF and IL@DAAQ-COF

	S _{bet}	V _{micro}	V _{tot}	Pore	V _{micro} / V _{tot}
Sample					
	m^2g^{-1}	cm ⁻³ g ⁻¹	cm ⁻³ g ⁻¹	nm	%
DAAQ-COF	405	0.16	0.87	1.83	17.88
IL@DAAQ-COF	413	0.13	0.45	1.06	29.40

References

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