Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A new ZIF molecular-sieving membrane for high-efficiency dye removal

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1. Experimental Section

Preparation of JUC-160 Nanoseeds

In a room temperature synthesis, 0.4 mmol 2-methylimidazole and 0.5 mmol benzimidazole were dissolved in 8 ml DMF, then 8 ml DMF containing 0.45 mmol Zinc nitrate hexahydrate was added drop-wise into the ligand solution. The mixture was kept stirring for 10 hours. After that, the JUC-160 nanoseeds were collected by centrifuging and washed with ethanol for 3 times. Particle size of obtained JUC-160 nanoseeds was ~200nm.

Preparation of Alumina Discs as Membrane Support

Alumina discs (25mm of diameter and 1.5mm of thickness) were home-made. Commercially available high purity α-alumina powders (Aladdin Corp.) with particle size ~200nm were used as received. The powders were compressed under 12 Mpa for 1 min and sintered at 1000°C for 12 h. After cooling down, one side of the α-alumina disc was polished by sand papers (grit #800, #1200), then cleaned in deionized water under sonication for 10 min and dried over night at 60°C.

Preparation of JUC-160 Membranes

JUC-160 membranes supported on alumina discs were prepared through secondary growth. To strengthen the bonding between JUC-160 nanoseeds and the alumina support, we employed polyethylenimine (PEI) as a polymer binder. Well-dispersed seeding solution containing 1wt% JUC-160 nanoseeds and 1% PEI were dip-coated onto alumina support for 3 times to guarantee full coverage of the support surface. After drying, the seeded support was held vertically in a Teflon autoclave. A mixture of 0.3 mmol 2-methylimidazole, 0.375 mmol of benzimidazole and 0.4 mmol of Zinc nitrate hexahydrate in 20 ml DMF was poured into the autoclave. Then the autoclave was sealed and placed in a pre-heated oven under 180°C for 36h. After cooling down, the membrane was washed with ethanol for 3 times and dried at room temperature overnight.JUC-160 powder sediments in the mother solution were also collected by centrifuging and kept in a vial for the following characterization.

2. Characterization

The crystalline structure of JUC-160 membrane was determined by X-ray Diffraction (XRD) measurements using a PANalytical B.V. Empyrean powder diffractometer with Cu Ka radiation (λ = 1.5418 Å). The morphology of JUC-160 nanoseeds and membrane was observed by analytical scanning electron microscope (JEOS JSM-6510A).

3. Dye Removal Performance

Dye removal performance of JUC-160 membrane was conducted using a variety of dyes including Coomassie Brilliant Blue R250 (acid dye, 2.7nm×1.8nm, denoted as CBB), Rhodamine B (basic dye, 1.8nm×1.4nm, denoted as RhB) and Congo Red (direct dye, 2.5nm×0.7nm, denoted as CR). 100 ppm dye solutions were used as feed solutions. UV-vis spectrophotometry was employed to analyze the amount of residual dye contents in collected water.

Flux (J) is volume of permeate (V) collected per unit membrane area (A) per unit time (t), which is calculated as:

$$J = \frac{V}{tA} \tag{1}$$

The Rejection (R) is defined as:

$$R = \left(1 - \frac{C_P}{C_F}\right) \times 100\% \tag{2}$$

where C_P is concentration of dye component in permeate side and C_F is feed concentration.

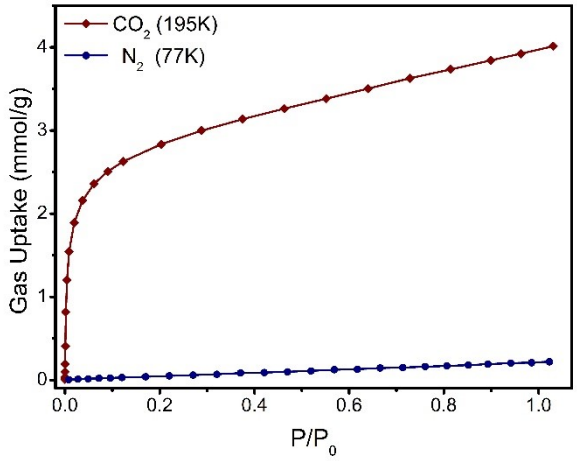

Figure S1. Gas adsorption isotherms of JUC-160. JUC-160 showed significant CO_2 (0.33nm in kinetic diameter, red line) uptake but no N_2 uptake (0.36 in kinetic diameter, blue line), indicating effective aperture size of JUC-160 should be 0.33-0.36 nm.

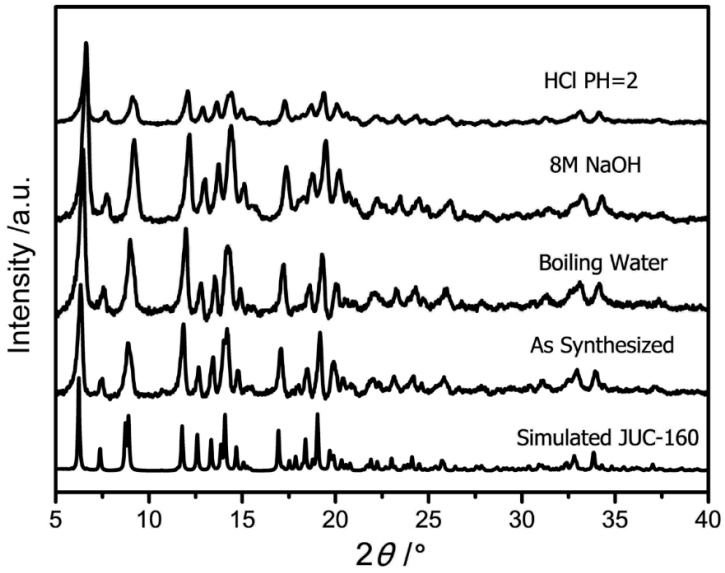

Figure S2. PXRD patterns of JUC-160 after being treated in boiling water, NaOH and HCl. JUC-160 remained integrity of its crystalline structure after being treated in harsh conditions, exhibiting excellent stability.

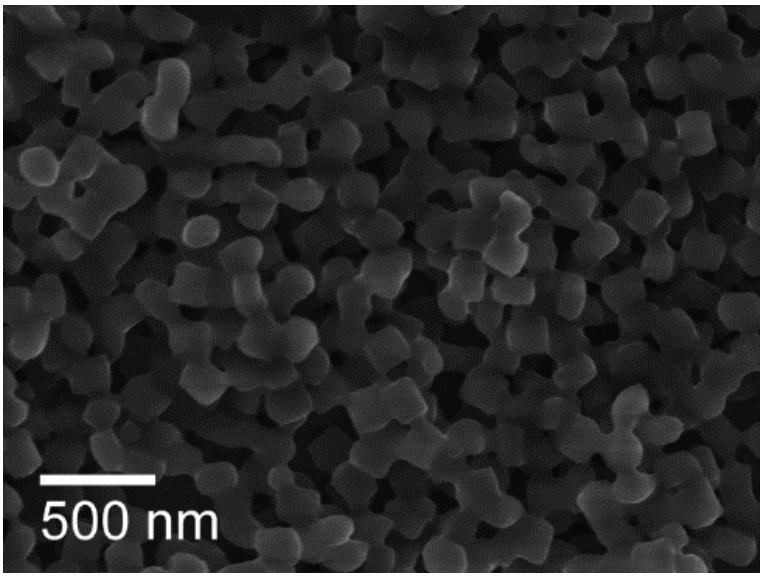

Figure S3. SEM image of as-prepared JUC-160 nanoseeds. Particle size was measured to be around 200 nm.

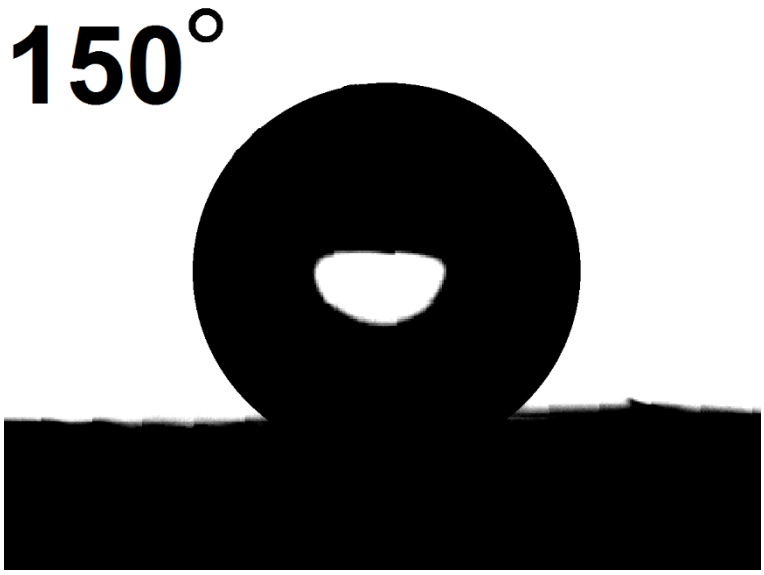

Figure S4. Water contact angle of JUC-160.

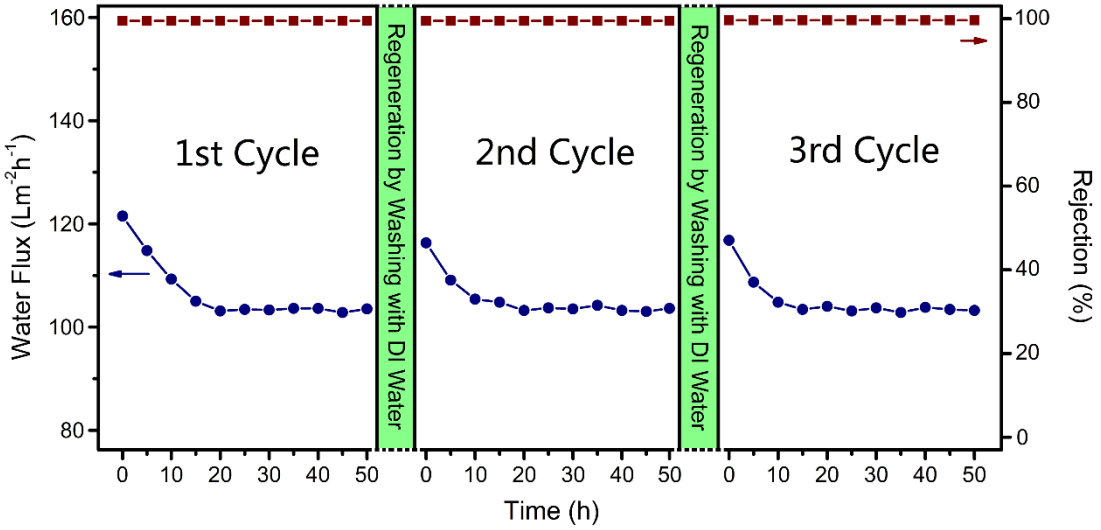

Figure S5. Long-term durability and recyclability test results of JUC-160 membrane. During the entire test, JUC-160 membrane remained thoroughly rejection to dye molecules along with considerable water flux, indicating exceptional long-term durability. After used for 50 hours, membrane showed decreased water flux due to accumulated deposition of dye molecules on the surface of membrane. Water flux can be recovered by after regeneration, proving high recyclability of JUC-160 membrane.

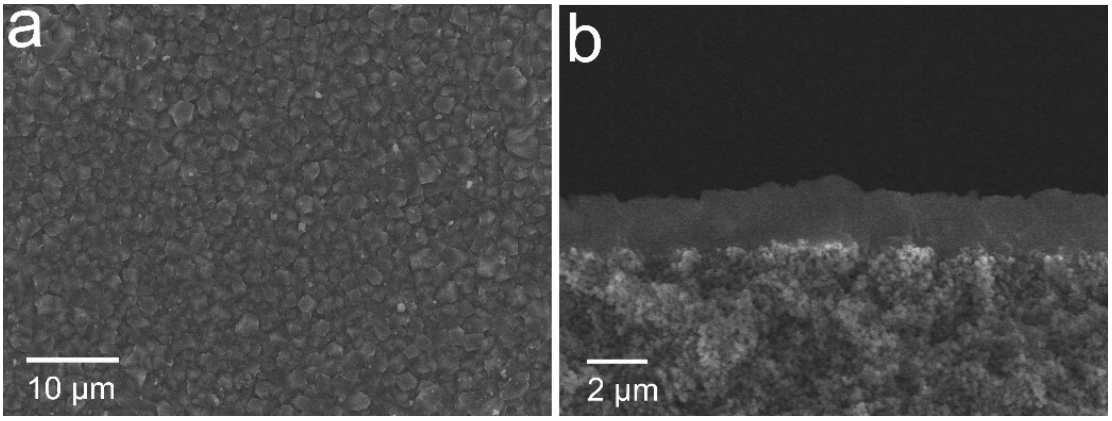

Figure S6. Morphology of JUC-160 membrane after 150 hours dye removal test. The membrane remained high quality after 150 hours test (top view, a) and no loss in membrane thickness was observed (cross-sectional view, b). Some deposited dyes can be observed, which could explain the decrease in water flux at the initial stage of dye removal process.

Table S1. Gas permeation test of JUC-160 membrane before and after dye removal process.

	Before		After		Knudsen Factor
	H_2 Permeance (10^{-7}mol m^{-2} s^{-1} Pa^{-1})	Separation Factor	H_2 Permeance (10^{-7}mol m^{-2} s^{-1} Pa^{-1})	Separation Factor	
H_2/N_2	2.72	6.98	2.64	7.17	3.76
H_2/CH_4	2.81	8.02	2.77	8.31	2.84
H_2/CO_2	2.59	13.49	2.45	14.99	4.89

Table S2. Dye removal performance of JUC-160 membrane.

Dye	Type	Size	Water Flux (L m^{-2} h^{-1})	Rejection (%)
Congo Red	direct dye	2.5nm×0.7nm	102.3	99.8
Coomassie Brilliant Blue R250	acid dye	2.7nm×1.8nm	98.6	99.8
Rhodamine B	basic dye	1.8nm×1.4nm	103.1	99.8