Supporting Information

Photo-Switchable Smart Metal–Organic Frameworks Membranes with Tunable and Enhanced Molecule Sieving Performance

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Experimental details:

Chemicals were used without further purification: Copper nitrate trihydrate (>99%, Aladdin), 4-Nitrobenzoic acid (98%, Energy Chemistry), *trans*-1,2-bis(4-pyridyl)ethylene (BPE, 98%, Energy Chemistry), sodium hydroxide (>99%, Aladdin), glucose (>99%, Aladdin), acetic acid (>99%, Aladdin), *N,N*-dimethylformamide (DMF, 99.8% anhydrous, Aladdin), methanol (MeOH, ≥99.8%, Aladdin), dopamine hydrochloride (DPA, 98%, Aladdin), and tris(hydroxymethyl)aminomethane (Tris, 99%, Aladdin). Porous α-Al_2O_3 disks (Fraunhofer Institute IKTS, former HITK/Inocermic, Hermsdorf, Germany: 18 mm in diameter, 1.0 mm in thickness, 70 nm particles in the top layer) were used as supports.

Synthesis of organic ligand azobenzene-4,4'-dicarboxylic acid (AzDC): Azobenzene-4,4'-dicarboxylic acid (AzDC) was synthesized according to the procedures as shown elsewhere [1]. 4-Nitrobenzoic acid (5.00 g, 29.9 mmol) was added to sodium hydroxide solution (16.8 g, 420 mmol in 50 ml water), and then the solution was heated to 65 °C until dissolved. Glucose solution (30.8 g, 156 mmol in 100 ml water) was added dropwise into the above solution under 80 °C. After the addition of glucose, the solution was stirred at 65 °C overnight form brown precipitate. The precipitate was filtered, dispersed in water and acidified with acetic acid to pH = 4, whereupon an orange precipitate was obtained. The final product was filtered, washed with water until the filtrate was colorless and dried to yield azobenzene-4,4'-dicarboxylic acid (3.04 g, 11.3 mmol, 37.8 %). The successful synthesis of azobenzene-4,4'-dicarboxylic acid (AzDC) was confirmed by electrospray ionization mass spectrometry (ESI-MS).

Synthesis of Cu(AzDC)(4,4′-BPE)$_{0.5}$ crystals: Cu(AzDC)(4,4′-BPE)$_{0.5}$ crystals were synthesized according to the procedures reported previously [2] with minor modification. A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.113 g), ABDC (0.127 g) and BPE (0.045 g) was suspended in DMF (50 mL) and heated in in a Teflon-lined stainless steel autoclave at 100 °C for 24 h. The resulting crystals formed were filtered and washed with fresh DMF for three times and then washed with ethanol

three times. The residual solvents were removed from the pore by heating the samples at 120 °C for 24 h under vacuum.

Reference

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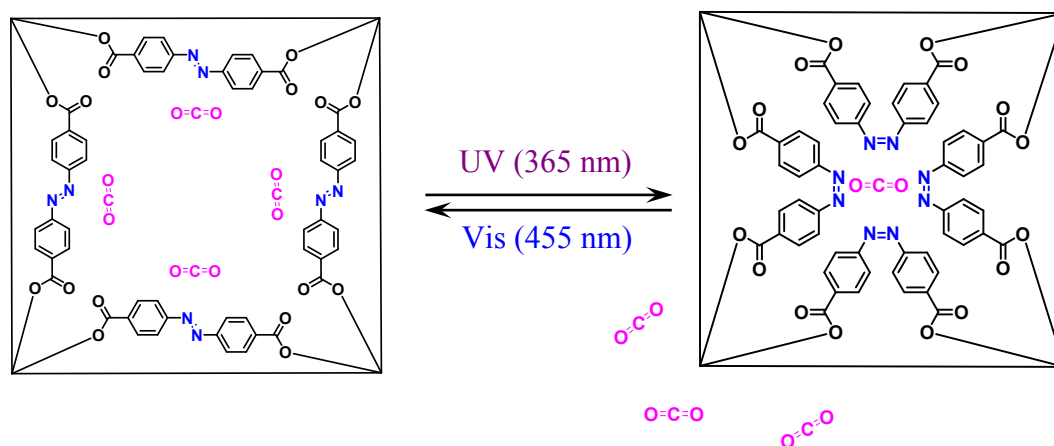
Fig. S1. Scheme of the dynamic photo-switching behaviour of Cu(AzDC)(4,4′-BPE)$_{0.5}$ between 455 nm Vis light (in the trans state) and 365 nm UV light (in the cis state), resulting in reversible CO_2 adsorption. As shown in Figure S1., upon exposure to UV light irradiation, the azobenzene bonds obtain energy and change cis–trans states. Although cis azobenzene group has a dipole moment and should adsorb CO_2 better than trans, but with the azobenzene group's conformational transition reduces the size of the actual aperture which is used to accommodate CO_2 molecules and thus trigger CO_2 release. This is confirmed by the different CO_2 adsorption performance by irradiation with UV light (365 nm) and Vis light (455 nm) of Cu(AzDC)(4,4′-BPE)$_{0.5}$. The double bond of 2-bis(4-pyridyl)ethylene (BPE) has a similar phenomenon.
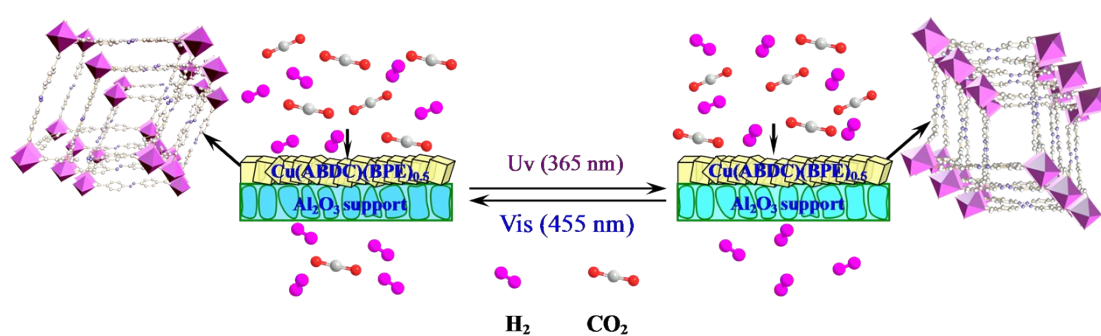
Fig. S2. Scheme of the enhancement of H_2/CO_2 selectivity with the photo-switchable $Cu(AzDC)(4,4'-BPE)_{0.5}$ membrane through controllable irradiation of UV light (365 nm).
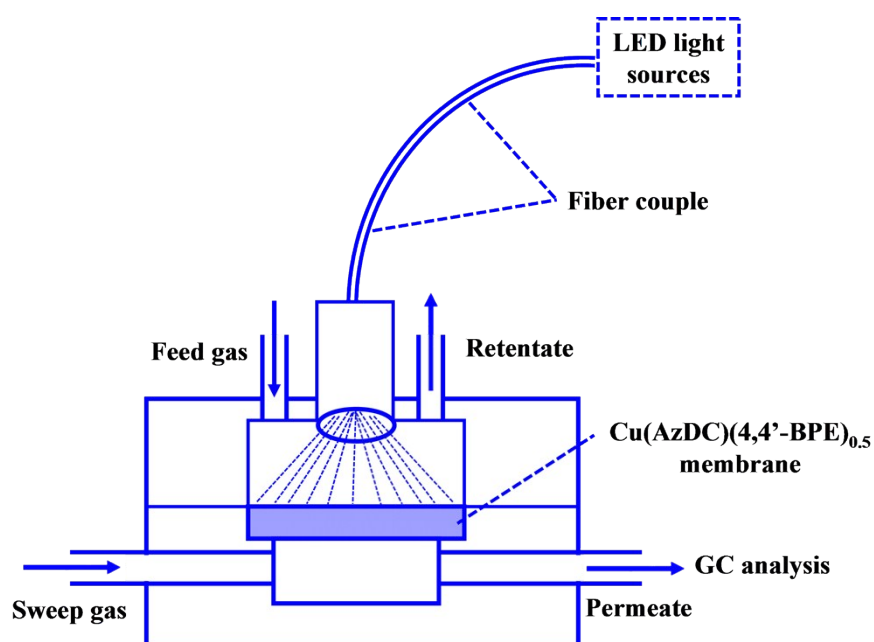
Fig. S3. Schematic diagram of the measurement equipment for gas permeation and separation with UV irradiation. A fiber-coupled LED is used for in-situ irradiation of the Cu(AzDC)(4,4′-BPE)$_{0.5}$ membrane.
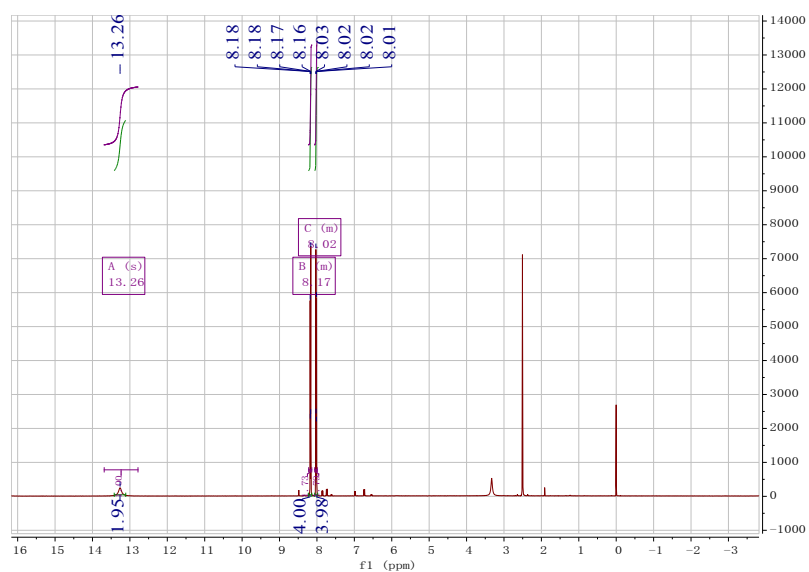
Fig. S4. ^{1}H NMR spectrum for synthesized azobenzene-4, 4'-dicarboxylic acid (500 MHz, DMSO-d6, 298K, TMS): 8.02 ppm, 8.17 ppm (8H, m, ArH), 13.26 ppm (2H, s, -COOH).
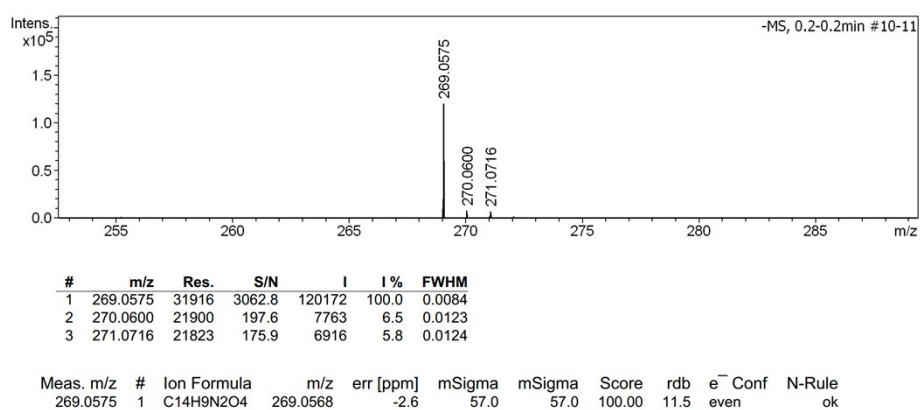
#	m/z	Res.	S/N	I	I %	FWHM
1	269.0575	31916	3062.8	120172	100.0	0.0084
2	270.0600	21900	197.6	7763	6.5	0.0123
3	271.0716	21823	175.9	6916	5.8	0.0124

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	mSigma	Score	rdb	e⁻ Conf	N-Rule
269.0575	1	C14H9N2O4	269.0568	-2.6	57.0	57.0	100.00	11.5	even	ok

Fig. S5. ESI-MS of the synthesized azobenzene-4, 4'-dicarboxylic acid.

S4800 4.0kV x5.00k SE(U)   10.0um
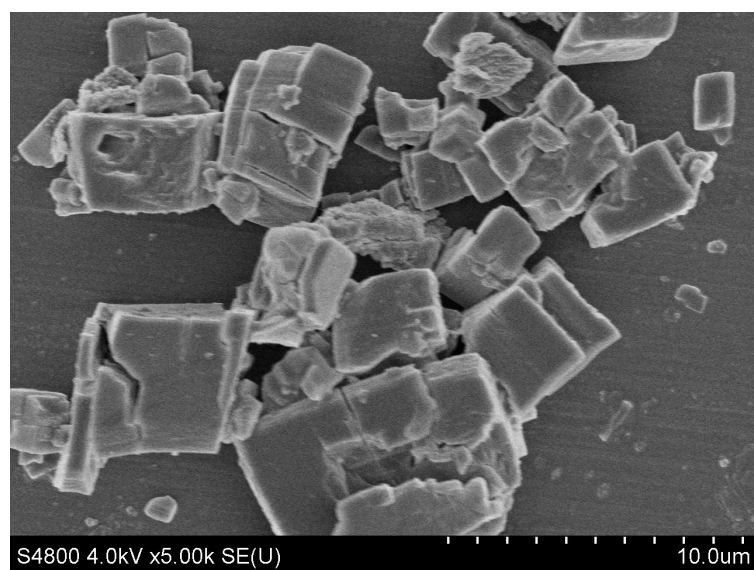
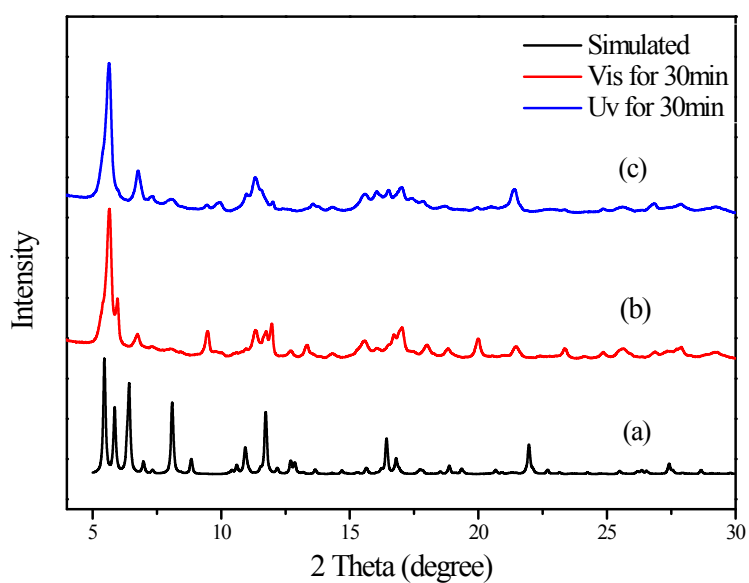**Fig. S6.** Typical FESEM image of the Cu(AzDC)(4,4′-BPE)$_{0.5}$ crystals.

Fig. S7. Typical XRD patterns of the simulated Cu(AzDC)(4,4′-BPE)$_{0.5}$ (a), Cu(ABDC)(BPE)$_{0.5}$ powder before UV irradiation (b) and after UV irradiation. The XRD were taken off-line since the life time of the MOF in the photo-switched state is longer than 1 week (in the dark).
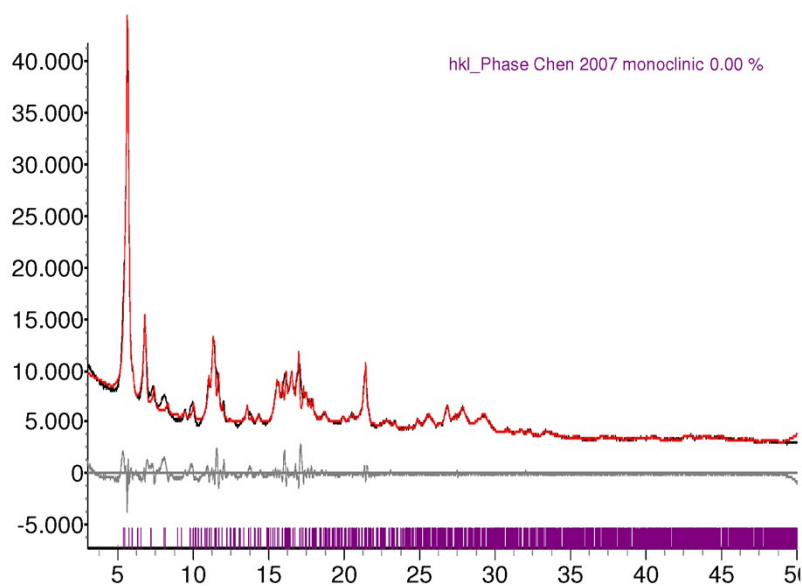
Fig. S8. Pawley analysis of XRD pattern of Cu(AzDC)(4,4′-BPE)$_{0.5}$ under UV irradiation. Black: Experimental XRD. Red: Pawley-simulated XRD pattern. Grey: Difference curve.

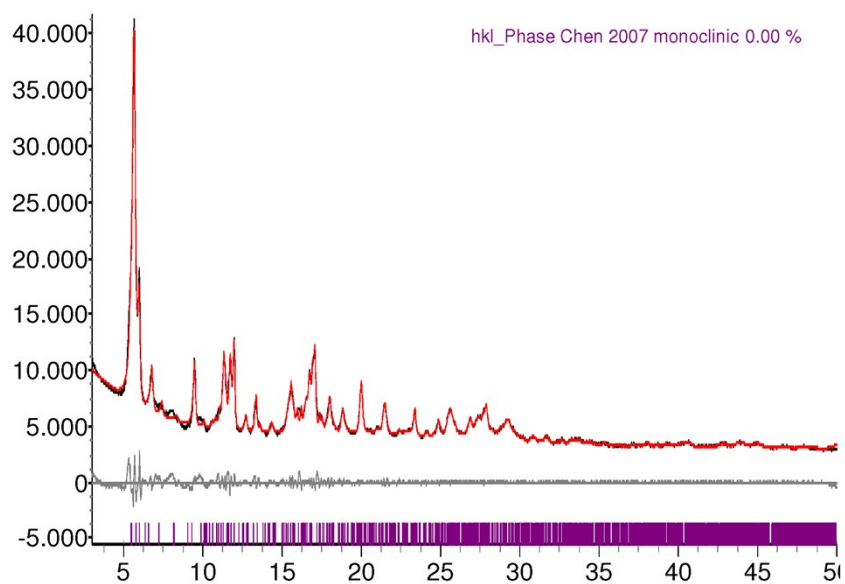**Fig. S9.** Pawley analysis of XRD pattern of Cu(AzDC)(4,4′-BPE)$_{0.5}$ under vis irradiation. Black: Experimental XRD. Red: Pawley-simulated XRD pattern. Grey: Difference curve.
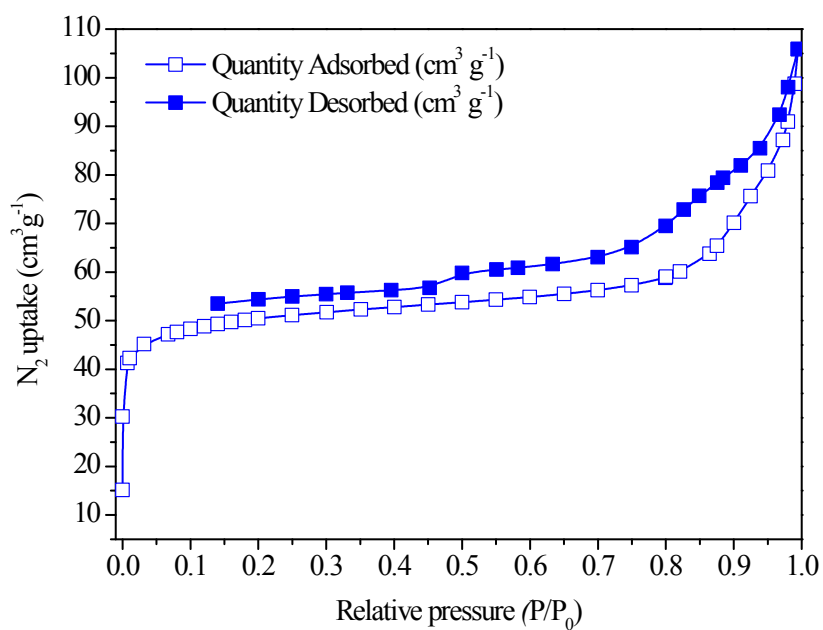
Fig. S10. N_2 adsorption isotherms of the Cu(AzDC)(4,4′-BPE)$_{0.5}$ powder measured at 77 K.

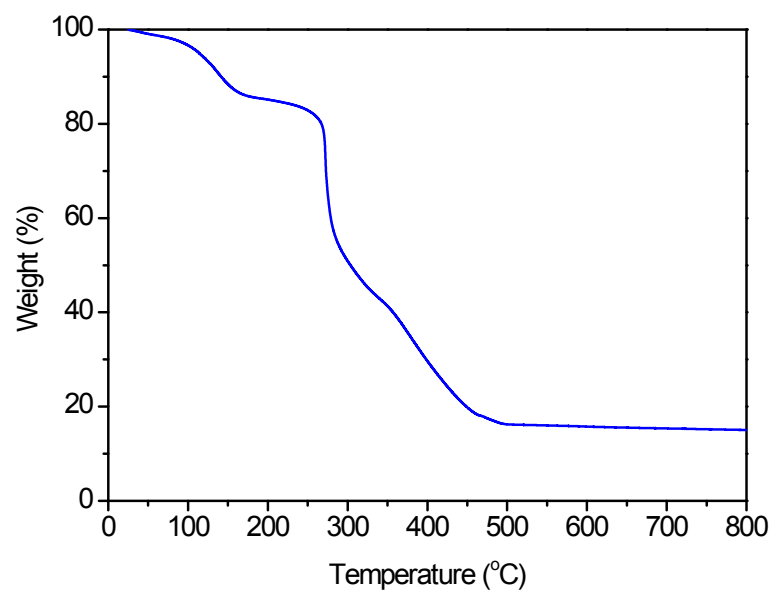**Fig. S11.** TGA analysis of the Cu(AzDC)(4,4′-BPE)$_{0.5}$ powder.
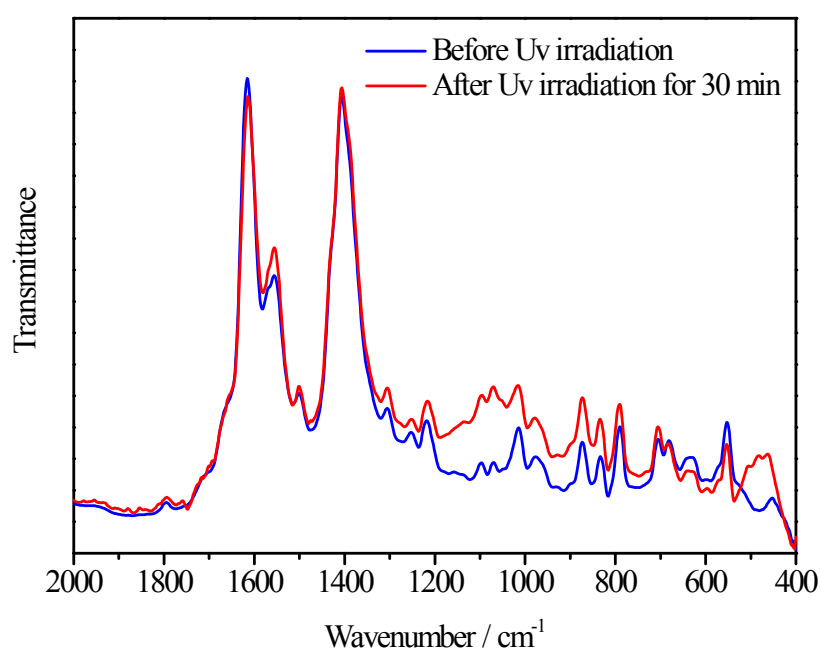
Fig. S12. FT-IR spectroscopy of Cu(AzDC)(4,4′-BPE)$_{0.5}$ before and after UV irradiation in air at room temperature.

Fig. S13. Raman spectrum of the Cu(AzDC)(4,4′-BPE)$_{0.5}$ without irradiation after removing the solvent DMF, the *trans* –N=N– vibration of Cu(AzDC)(4,4′-BPE)$_{0.5}$ is shown at 1441 cm^{-1}.
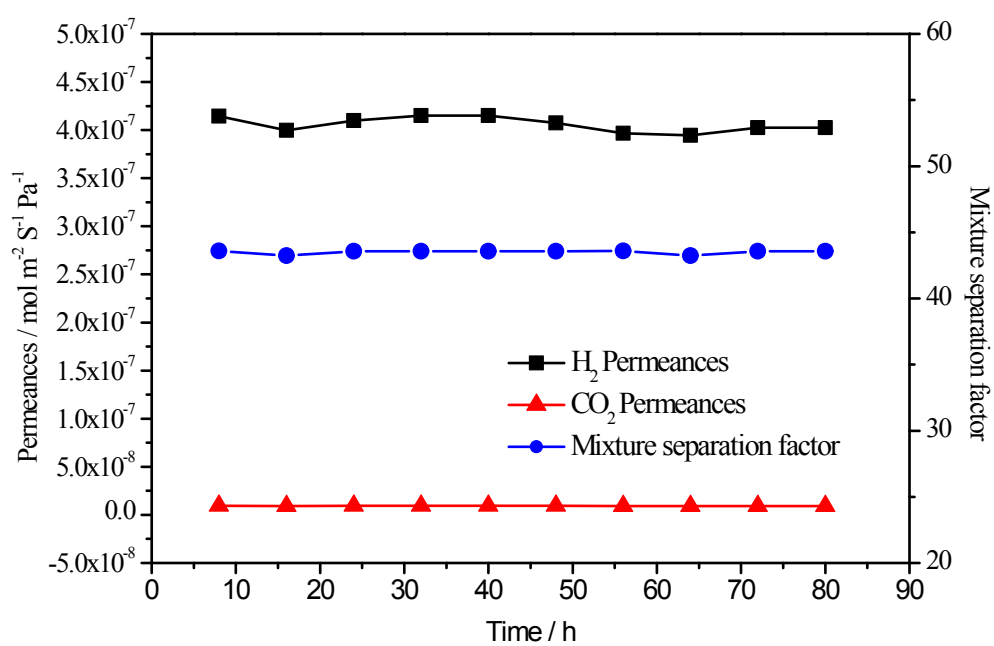
Fig. S14. Stability evaluation of the Cu(AzDC)(4,4′-BPE)$_{0.5}$ membrane for the separation of an equimolar H_2/CO_2 mixture at 298K and 1 bar under UV irradiation.

Table S1. Results of Pawley fits to monoclinic unit cell (space group C2/c, no. 15).

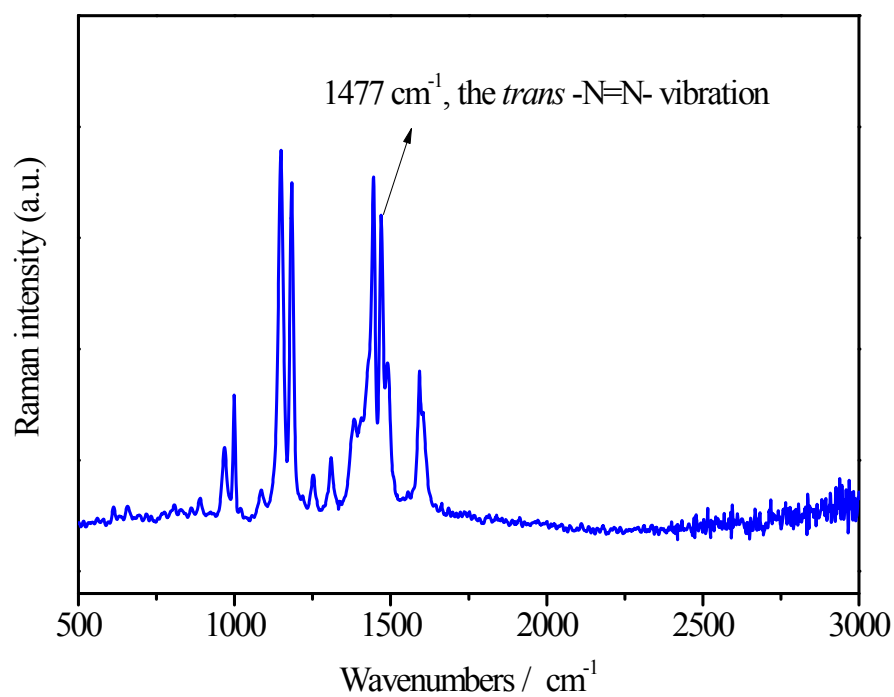| Cu(AzDC)(4,4′-BPE)$_{0.5}$ specimen	Lattice parameter				Cell volume [Å^3]	Good-ness of Fit (GOF)
	a [Å]	b [Å]	c [Å]	β [°]		
Under UV(365 nm) irradiation	19.9361062	29.7430318	32.8315371	98.57906	19249.97	7.68
Under Vis (455 nm) irradiation	19.7462516	29.5520140	32.5983748	98.42498	18817.22	5.25

Table S2. Mixed gases permeance and separation factors of the Cu(AzDC)(4,4′-BPE)$_{0.5}$ membrane prepared on PDA-modified Al$_2$O$_3$ disk at 298 K and 1 bar.

Gas (i/j)	Knudsen constant	Performance of Cu(AzDC)(4,4′-BPE)$_{0.5}$ membrane					
		Vis (455 nm)			UV (365 nm)		
		Permeances (i) (mol/m^2·s^{-1} Pa·$^{-1}$)	Permeances (j) (mol/m^2·s^{-1} Pa·$^{-1}$)	SF	Permeances (i) (mol/m^2·s^{-1} Pa·$^{-1}$)	Permeances (j) (mol/m^2·s^{-1} Pa·$^{-1}$)	SF
H$_2$/CO$_2$	4.7	4.20 x 10^{-7}	1.98 x 10^{-8}	21.3	4.03 x 10^{-7}	9.22 x 10^{-9}	43.7
H$_2$/N$_2$	3.7	4.25 x 10^{-7}	2.28 x 10^{-8}	18.6	4.16 x 10^{-7}	2.32 x 10^{-8}	17.9
H$_2$/CH$_4$	2.8	4.23 x 10^{-7}	3.06 x 10^{-8}	13.8	4.06 x 10^{-7}	2.96 x 10^{-8}	13.7

SF: separation factor

Table S3. Comparation of H_2/CO_2 selectivity versus H_2 permeability of the $Cu(AzDC)(4,4'\text{-BPE})_{0.5}$ membrane with literature data of other MOF membranes.

Membrane	Thickness (μm)	H_2 permeance ($mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)	H_2 Permeability* (Barrers)	Selectivity (H2/CO2)	References
$Zn_2(bim)_4$ nanosheet	0.1	7.74×10^{-6}	2311.82	230	1
JUC-150	20	1.83×10^{-7}	10931.89	38.7	2
CuBTC/MIL-100	20	1.05×10^{-8}	627.24	89	3
ZIF-90	20	2.83×10^{-7}	16905.61	21	4
MOF-74 (Mg)	10	8.20×10^{-8}	2449.22	28	5
MAMS-1	0.04	1.88×10^{-6}	224.61	235	6
NH2-MIL-53	19.9	1.99×10^{-6}	118282.55	30.9	7
ZIF-95	30	2.46×10^{-6}	220430.10	34.9	8
ZIF-100	50	5.80×10^{-6}	8661.88	72	9
$Cu(AzDC)(4,4'\text{-BPE})_{0.5}$	10	4.00×10^{-6}	11947.43	43.6	This work

* Permeability is calculated as the membrane permeance multiplied by the membrane thickness. 1 Barrer = 3.348×10^{-16} mol m/ (m^2 s Pa).

Reference:

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6. X. Wang, C. Chi, K. Zhang, Y. Qian, K. M. Gupta, Z. Kang, J. Jiang and D. Zhao, *Nat. Commun.*, 2017, **8**, 14460.
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Table S4. Separation performances of three independent Cu(AzDC)(4,4′-BPE)$_{0.5}$ membranes for the separation of H$_2$/CO$_2$ mixtures at 298 K and 1 bar under UV (365 nm) irradiation.

Membrane	H$_2$ permeance (mol·m^{-2}·s^{-1}·Pa^{-1})	CO$_2$ permeance (mol·m^{-2}·s^{-1}·Pa^{-1})	H$_2$/CO$_2$ selectivity	Average selectivity	Standard deviation of selectivity
M1	3.97 x 10^{-7}	9.19 x 10^{-9}	43.2		
M2	4.09 x 10^{-7}	9.25 x 10^{-9}	44.3	43.53	0.54
M3	3.96 x 10^{-7}	9.21 x 10^{-9}	43.1		