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Photo-switchable smart metal-organic framework membranes with tunable and enhanced molecular sieving performance[†]

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Developing a novel MOF membrane material with switchable separation performance is an exciting and challenging research project. In the present work, we report preparation of a new kind of light induced smart MOF membrane, *i.e.*, Cu(AzDC)(4,4'-BPE)_{0.5} membrane, which shows (i) enhanced molecular sieving performance, and (ii) is able to respond quickly to external light stimuli. Two photo-switchable moieties are addressed in the Cu(AzDC)(4,4'-BPE)_{0.5} membrane: azobenzene and bis(4-pyridyl)ethylene. When the Cu(AzDC)(4,4'-BPE)_{0.5} membrane is *in situ* irradiated with Vis and UV light, the separation factor of a H₂/CO₂ mixture can be switched reversibly between 21.3 and 43.7. This switching effect is mainly caused by reduced CO₂ adsorption in the UV-cis state as proven by independent adsorption studies. For a steric reason, adsorption of CO₂ is limited for the UV-cis state. In full agreement with this model, the adsorption of other gases H₂, CH₄ and N₂ as well as their permeation behaviour is not observably influenced by the *trans-cis* switching.

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Introduction

Due to the change of global climate, crisis of energy security, and aggravation of local air pollution, there is a growing demand for a clean and efficient energy in recent years, which is the concept of "hydrogen economy".1 Currently, hydrogen is mainly produced by steam-methane reforming (SMR) followed by the water-gas shift (WGS) reaction.² The resulting gas mixture is mainly composed of H_2 (0.29 nm) and CO_2 (0.33 nm). Before the produced hydrogen gas can be used, it has to be separated and purified from the gas mixtures, which are usually realized by pressure swing adsorption (PSA) or cryogenic distillation. In comparison with traditional H₂ purification methods, membrane-based separation techniques have attracted significant attention due to their lower energy consumption and investment cost.3 Because organic polymer membranes usually suffer from the instability problem at high temperature, inorganic membranes are more attractive under harsh separation conditions.⁴ In recent years, dense Pd-based metal membranes,^{5,6} microporous zeolite membranes,⁷⁻¹¹ silica membranes,¹² and carbon membranes¹³ have been developed for the separation of H₂ from CO₂. Pd-based metal membranes have shown high H₂ selectivity and H₂ permeance at high temperature, but they are easily poisoned by CO or H₂S.⁶ Further, Pd membranes are too expensive to be widely used. Silica membranes have displayed high H₂ selectivity over other small molecular gases, but suffer from instability even in traces of steam. Zeolite membranes usually show relatively low H₂/CO₂ selectivity due to the presence of intercrystalline defects. Therefore, the development of stable molecular sieving membranes with high H₂ permselectivity is still challenging.

Recently, metal-organic framework (MOF) membranes have attracted intense attention for the fabrication of superior molecular sieve membranes due to their highly diversified pore structures and pore sizes as well as specific adsorption affinities. In the past 10 years, a great deal of research effort has been focused on the preparation of MOF or MOF-based membranes with molecular sieving performance.14-25 However, with respect to the fabrication of MOF membranes, not only is the facile growth of a dense polycrystalline layer on porous supports expected, but also the remote control of membrane permeance/ selectivity by external stimuli is highly desired. In this case, mass transfer and interfacial properties of the membranes can be reversibly switched by external stimuli, such as temperature, pH, solution ionic strength, light, electric and magnetic fields, and chemical cues.²⁶⁻³⁰ Among these external stimuli, light is a popular, promising and fascinating candidate because both its irradiation time and wavelength can be precisely controlled



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without introducing additional chemical species into the systems.³¹⁻³⁴ Therefore, photo-switchable molecules, which can realize reversible photo-isomerization when irradiated with light of a certain wavelength, have drawn intense interest. So far, several photo-responsive molecules have been successfully incorporated into MOF frameworks to modify and control MOF properties such as colour,33 release34,35 and adsorption36-42 of guest molecules. One of the most widely studied photoresponsive molecules in MOFs is azobenzene, which is well known for its reversible trans/cis photoisomerization, with switching its molecular size from 9 to 5.5 Å, and the dipole moment from 0.5 to 3.1 debye.36,37 For the first time, Wang et al. reported a photo-switchable MOF [Cu₂(AzoBPDC)₂(AzoBiPyB)] membrane which offers dynamic control of selectivity by remote signals,⁴⁰ which is realized by assembling linkers containing photoresponsive azobenzene-side-groups. The azobenzene moieties can be switched from the trans to the cis configuration and vice versa by irradiation with ultraviolet or visible light. Therefore, through precise control of the ratio of cis/trans azobenzene by controlled irradiation times or by simultaneous irradiation with ultraviolet or visible light, it is effective to tune continuously the membrane permeability and selectivity of the MOF membrane. Thereafter, Müller et al. prepared a photoswitchable MOF thin film functionalized with o-fluoroazobenzene moieties via layer-by-layer deposition,41 which can reversibly isomerize between the trans and cis configuration with visible light. Very recently, Knebel et al. reported azobenzene-loaded UiO-67 membranes with photo-switchable separation performance for the separation of H₂ and CO₂.⁴² However, the H₂/CO₂ separation factor of the photo-switchable MOF membranes is still relatively low due to their large pore size, *i.e.*, about 8.0 for the Cu₂(AzoBPDC)₂(AzoBiPyB) membrane,40 and about 14.7 for the azobenzene-loaded UiO-67 membrane.42 Therefore, the development of photo-switchable MOF membranes with a small pore size is desired to enhance the H₂/CO₂ selectivity.

Indeed, the tuning of micropores within porous materials is of great importance for their application in the separation of small molecules. Chen et al. prepared a triply interpenetrated porous framework $Zn(AzDC)(4,4'-BPE)_{0.5}$ by using two different photo-isomerizable linkers,43 namely, 4,4'-dicarboxylate (AzDC) and 1,2-bis(4-pyridyl)ethylene (4,4'-BPE). With a small pore size of about 3.4 \times 3.4 Å, Zn(AzDC)(4,4'-BPE)_{0.5} exhibited a highly selective sorption behavior toward H2/N2, H2/CO, and CO2/CH4. Lately, Lyndon et al. reported that Zn(AzDC)(4,4'-BPE)_{0.5} is photosensitive to UV light, triggering the adsorption or release of CO2 under Vis/UV light irradiation, showing promising application in the separation of H₂/CO₂.⁴⁴ In the present work, we report the design and synthesis of a new photo-switchable MOF Cu(AzDC)(4,4'-BPE)_{0.5} membrane. Cu(AzDC)(4,4'-BPE)_{0.5} has the same topological structure as $Zn(AzDC)(4,4'-BPE)_{0.5}$, in which the azobenzene and bis(4-pyridyl)ethylene moieties, as the "backbone" of the linker, are incorporated directly into the framework, forming an interpenetrating network structure with a small pore size of about 3.4×3.4 Å. In particular, under UV irradiation, azobenzene and bis(4-pyridyl)ethylene moieties can be reversibly switched from the *trans* to the *cis* configuration



Fig. 1 The structure of (c) Cu(AzDC)(4,4'-BPE)_{0.5} with the (a) azobenzene and (b) bis(4-pyridyl)ethylene photo-switchable groups. The dynamic photo-switching behavior of Cu(AzDC)(4,4'-BPE)_{0.5} will result in reversible CO₂ adsorption as shown in Fig. S1.†

(Fig. 1a and b), resulting in squeezing out and extrusion of the adsorbed CO_2 in $Zn(AzDC)(4,4'-BPE)_{0.5}$ (Fig. 1c and S1[†]). Therefore, it can be expected that the $Cu(AzDC)(4,4'-BPE)_{0.5}$ membrane will display a switchable selectivity in the separation of H₂ from CO_2 upon irradiation with UV or Vis light (Fig. S2[†]).

Experimental

Synthesis of Cu(AzDC)(4,4'-BPE)_{0.5} membranes

Before synthesis of Cu(AzDC)(4,4'-BPE)_{0.5} membranes on porous α -Al₂O₃ disks, the top surface of the α -Al₂O₃ disks was treated with dopamine (DPA) according to our previous reports.^{20,45} For the synthesis of Cu(AzDC)(4,4'-BPE)_{0.5} membranes, 0.113 g Cu(NO₃)·3H₂O was dissolved in 50 mL DMF by ultrasonic treatment, and then the PDA-modified α-Al₂O₃ disks were placed into the solution and heated to 373 K for 12 h. After the solution was cooled to room temperature, the PDA-modified α-Al₂O₃ disks were taken out, and AzDC (0.127 g) and BPE (0.045 g) were added to the above solution of Cu(NO₃)·3H₂O and DMF. The pre-treated α-Al₂O₃ disks were placed horizontally in a Teflon-lined stainless-steel autoclave which was filled with the synthesis solution and heated at 373 K in an air-circulating oven for 24 h. After the solvothermal synthesis, the $Cu(AzDC)(4,4'-BPE)_{0.5}$ membranes were washed with DMF and methanol several times, and then dried in air at 333 K overnight.

Characterization

The FT-IR spectra were obtained by using a Bruker TENSOR27 impact spectrometer. Raman spectra were obtained by using Renishaw in Via-reflex Raman spectroscopy. All UV/Vis spectra of the samples were recorded in a BaSO₄ matrix in reflection geometry with a PerkinElmer LAMBDA 950. Thermogravimetric analyses (TGA) were carried out using a Mettler Toledo TGA/STDA 851e. Samples (10 mg) which had been solvent exchanged with dry methanol and degassed at 423 K were placed in 70 μ L alumina pans and heated under a N₂ gas flow

(20 mL min⁻¹) from 20 to 1073 K at a heating rate of 5 K min⁻¹. The BET surface area and pore volume of Cu(AzDC)(4,4'-BPE)_{0.5} were investigated using N₂ adsorption–desorption isotherms at 77 K using nitrogen on an automatic volumetric adsorption apparatus (Micrometrics ASAP 2020). Prior to the measurements, the samples were heated at 423 K for 16 h under vacuum. After adsorption, the samples were regenerated by degassing under vacuum at room temperature for a few hours.

The morphology and thickness of the Cu(AzDC)(4,4'-BPE)_{0.5} membranes were characterized by field emission scanning electron microscopy (FESEM). FESEM micrographs were taken on an S-4800 (Hitachi) with a cold field emission gun operating at 4 kV and 10 μ A. The phase purity and crystallinity of the Cu(AzDC)(4,4'-BPE)_{0.5} crystals and membranes were confirmed by powder X-ray diffraction (PXRD). The PXRD patterns were recorded at room temperature under ambient conditions with a Bruker D8 ADVANCE X-ray diffractometer with Cu K α radiation at 40 kV and 40 mA.

Gas adsorption measurements were performed using ultrahigh purity N₂, CO₂ and CH₄. Before gas adsorption measurements at 298 K, the powder samples were activated at 393 K for 6 h under vacuum. Light-responsive gas adsorption was performed under *in situ* UV/Vis light irradiation. For the switching experiments, two different LED light sources from PrizMatix were used. UV irradiation was performed with a 365 nm LED (112 mW). Vis irradiation was performed with a 455 nm LED (135 mW). The distance between the powder sample and the LED was about 5 cm.

Single gas permeation and mixed gas separation

The volumetric flow rates of the single gases H_2 , CO_2 , N_2 , and CH₄ as well as of their equimolar binary mixtures of H₂ with CO₂ through the Cu(AzDC)(4,4'-BPE)_{0.5} membranes were measured at room temperature by using the Wicke-Kallenbach technique.¹⁸⁻²⁰ Before permeation measurements, the Cu(AzDC)(4,4'-BPE)_{0.5} membrane was on-stream activated to remove DMF solvent at 453 K. For single gas and mixture gas permeation, the supported Cu(AzDC)(4,4'-BPE)0.5 membrane was sealed in a permeation module with silicone O-rings. The feed gases were fed to the top side of the membrane, and sweep gas N2 (CH4 was used as a sweep gas when measuring N2 permeation) was fed on the permeate side to keep the concentration of the permeating gas low providing a driving force for permeation. The total pressure on each side of the membrane was atmospheric. In situ irradiation of the Cu(AzDC)(4,4'-BPE)_{0.5} membrane was achieved by a fiber-coupled, monochromatic high power Prizmatix FC-3 LED (Fig. S3[†]). Gas permeation was performed under in situ irradiation alternating with $\lambda = 365$ nm and $\lambda = 455$ nm at room temperature. For both single and mixture gas permeation, the fluxes of feed and sweep gases were determined with mass flow controllers, and a calibrated gas chromatograph (Agilent 7820A) was used to measure the gas concentrations. The separation factor $\alpha_{i,j}$ of binary mixture permeation is defined as the quotient of the molar ratios of the components (i, j) in the permeate, divided by the quotient of the molar ratio of the components (i, j) in the retentate, as shown in eqn (1).

$$\alpha_{i/j} = \frac{y_{i,\text{Perm}}/y_{j,\text{Perm}}}{y_{i,\text{Ret}}/y_{j,\text{Ret}}}$$
(1)

The details of chemicals used for the synthesis of $Cu(AzDC)(4,4'-BPE)_{0.5}$ crystals and membranes, the protocol of the synthesis of organic ligand azobenzene-4,4'-dicarboxylic acid (AzDC) (Fig S4 and 5†), and the synthesis of Cu(AzDC)(4,4'-BPE)_{0.5} crystals are shown in the ESI.†

Results and discussion

 $Cu(AzDC)(4,4'-BPE)_{0.5}$ crystals were prepared by the solvothermal reaction of copper(II) nitrate trihydrate, AzDC, and BPE in DMF according to ref. 43 with minor modification (for details see ESI[†]). As shown in Fig. S6,[†] well-shaped crystals with a block morphology of about 5-10 µm are formed by heating at 373 K for 24 h. As deduced from the PXRD pattern (Fig. S7b⁺), all peaks of $Cu(AzDC)(4,4'-BPE)_{0.5}$ match well with those of the simulated ones (Fig. S7a[†]), indicating that a phase-pure $Cu(AzDC)(4,4'-BPE)_{0.5}$ with high crystallinity has been formed. With UV irradiation, slight changes were observed in the XRD pattern (Fig. S7c[†]). We assumed that the crystal structure of Cu(AzDC)(4,4'-BPE)_{0.5} will change after irradiation with UV (365 nm), and this change should be reflected in the XRD characterization. However, there are no obvious changes in the crystal structure which was confirmed by using TOPAS software to refine the two XRD diffraction pattern data (Fig. S8 and S9, and Table S1[†]), suggesting that the crystalline structure of $Cu(AzDC)(4,4'-BPE)_{0.5}$ is not affected by irradiation with UV, *i.e.*, by photoisomerization of the azobenzene groups, which is in good agreement with previous reports.40-42 The BET surface area and pore volume of the Cu(AzDC)(4,4'-BPE)_{0.5} were investigated by N2 adsorption-desorption isotherms at 77 K. As shown in Fig. S10,[†] the N₂ isotherms of the Cu(AzDC)(4,4'-BPE)_{0.5} show a typical hysteresis behaviour,43,44 indicating the permanent porosity of the Cu(AzDC)(4,4'-BPE)_{0.5} crystals. The calculated BET surface area of the Cu(AzDC)(4,4'-BPE)_{0.5} is about 227.9 m² g⁻¹, which is similar to the previous report.⁴⁴ TGA indicates that the initial weight loss of $Cu(AzDC)(4,4'-BPE)_{0.5}$ is found between 298 and 453 K due to the evaporation of adsorbed DMF, and the activated $Cu(AzDC)(4,4'-BPE)_{0.5}$ is thermally stable up to about 573 K (Fig. S11[†]).

The Cu(AzDC)(4,4'-BPE)_{0.5} powder was measured in reflection geometry by UV-Vis and time-resolved FT-IR spectroscopy to study the light induced conformational *trans-cis* transformation of Cu(AzDC)(4,4'-BPE)_{0.5}. From the UV-Vis spectra (Fig. 2), it can be seen that both azobenzene and bis(4-pyridyl) ethylene groups in the MOF can be reversibly switched by irradiation with UV light (365 nm) from *trans* to *cis* and back with Vis light (455 nm). The time-resolved FT-IR spectra show significant changes in peak intensity in the region of 500– 800 cm⁻¹ under UV irradiation (Fig. S12†). Under UV irradiation, the AzDC ligands in the Cu(AzDC)(4,4'-BPE)_{0.5} frameworks show *cis-trans* isomerization since the C-C-C and C-C-N vibrations at 550 cm⁻¹ increase. The BPE ligands are less clear in the FT-IR spectra due to the overlapping of their bands with



Fig. 2 UV/Vis spectra of the Cu(AzDC)(4,4'-BPE)_{0.5} before irradiation and after irradiation with UV light (365 nm) and Vis light (455 nm) different times.

azobenzene groups. Further, the existence of abundant photoresponsive groups in Cu(AzDC)(4,4'-BPE)_{0.5} frameworks was also tested using the Raman spectrum, which shows a strong *trans* -N=N- vibration intensity at 1441 cm⁻¹ (Fig. S13†).

The photo-responsive properties of Cu(AzDC)(4,4'-BPE)_{0.5} were also confirmed with gas adsorption. As shown in Fig. 3, Cu(AzDC)(4,4'-BPE)_{0.5} displays obviously dynamic switching CO₂ adsorption by irradiation with UV light (365 nm) and Vis light (455 nm). With irradiation with UV light (365 nm), the efficiency of the static CO₂ adsorption of Cu(AzDC)(4,4'-BPE)_{0.5} decreases by about 7.8% in comparison with irradiation with Vis light (455 nm), which is less than the previous report with 42% variations of static CO₂ adsorption.⁴⁴ The azobenzene groups in the pristine Cu(AzDC)(4,4'-BPE)_{0.5} are in a predominantly *trans* conformation, a relatively stable form. After UV irradiation, the azobenzene groups obtain energy and trigger the *trans-cis* transformation, which will reduce the size of the actual aperture to accommodate CO₂ molecules. Just like

wringing out a sponge, the framework structure with lightresponsive groups will be distorted when irradiated with UV light, leading to significant decreases in CO₂ adsorption and consequently promising potential in low energy CO₂ release.⁴² However, N₂ and CH₄ adsorption show lower reduction after UV irradiation due to their lower interaction with Cu(AzDC)(4,4'-BPE)_{0.5}, suggesting that Cu(AzDC)(4,4'-BPE)_{0.5} is promising for dynamitic capture and release of greenhouse gas CO₂. Considering the photo-switchable properties of CO₂ adsorption as well as a small pore size (3.4 × 3.4 Å), Cu(AzDC)(4,4'-BPE)_{0.5} is an ideal candidate to prepare smart molecular sieving membranes for remote-control of membrane permeation and separation.

Due to the poor heterogeneous nucleation of Cu(AzDC)(4,4'-BPE)_{0.5} crystals on the surface of the α -Al₂O₃ support, it is extremely difficult to form directly a continuous Cu(AzDC)(4,4'-BPE)_{0.5} layer on the α -Al₂O₃ support. As shown in our previous reports,²⁰ pre-modification of the support surface with polydopamine (PDA) is very helpful and effective to promote the nucleation and growth of MOF and zeolite membranes on the support surface through the formation of strong covalent bonds with the MOF or zeolite crystals. Therefore, we prepare Cu(AzDC)(4,4'-BPE)_{0.5} membranes on the PDA-modified α -Al₂O₃ disks (for details see ESI[†]). After solvothermal reaction for 24 h at 100 °C, the surface of the PDA-modified a-Al2O3 supports has been completely covered with continuous block-shaped Cu(AzDC)(4,4'-BPE)_{0.5} crystals (Fig. 4a). Additional Cu(AzDC)(4,4'-BPE)_{0.5} crystals are loosely packed on the top of the membranes due to sedimentation, but from the cross-sectional view shown in Fig. 4b, the Cu(AzDC)(4,4'-BPE)_{0.5} membrane is continuous with a thickness of about $\sim 10 \ \mu\text{m}$. The XRD pattern of the Cu(AzDC)(4,4'-BPE)_{0.5} membrane shows a high degree of crystallinity, and all of the peaks match well with those of Cu(AzDC)(4,4'-BPE)_{0.5} besides α - Al_2O_3 signals from the support (Fig. 4c).

Fig. 5 shows the single gas permeance of H_2 , CO_2 , N_2 and CH_4 through the Cu(AzDC)(4,4'-BPE)_{0.5} membrane under Vis or UV irradiation at 298 K and 1 bar as a function of the kinetic diameter of the gas molecules. As shown in Fig. 5, the H_2



Fig. 3 Effect of reversible *in situ trans-cis* photo-switching on the adsorption isotherms of CO₂, N₂, and CH₄ on the Cu(AzDC)(4,4'-BPE)_{0.5} powder at 298 K. Irradiation time was 60 min.



Fig. 4 Top view (a) and cross-section (b) FESEM images of the Cu(ABDC)(BPE)_{0.5} membranes prepared on the PDA-modified Al₂O₃ disk. (c) XRD patterns of the simulated Cu(AzDC)(4,4'-BPE)_{0.5}, Cu(AzDC)(4,4'-BPE)_{0.5} powder and Cu(AzDC)(4,4'-BPE)_{0.5} membranes prepared on the PDA-modified Al₂O₃ disk. (\blacklozenge): Al₂O₃ support, (not marked): Cu(AzDC)(4,4'-BPE)_{0.5}.



Fig. 5 Single gas permeance of the Cu(AzDC)(4,4'-BPE)_{0.5} membranes irradiated *in situ* with Vis light (455 nm) and UV light (365 nm) as a function of the kinetic diameter at 298 K and 1 bar. Irradiation time was 60 min. The inset shows the influence of the *trans-cis* switching on the mixture separation factor of the Cu(AzDC)(4,4'-BPE)_{0.5} membrane for H₂ over other gases as determined by gas chromatography.

permeance of about 4.3×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ is much higher than those of the other gases due to its smallest pore size of 0.29 nm. The ideal separation factors of H₂ from CO₂, N₂ and CH₄ are 23.9, 15.4, and 13.9, which by far exceed the corresponding Knudsen coefficients (4.7, 3.7 and 2.8), suggesting that the Cu(AzDC)(4,4'-BPE)_{0.5} membrane is expected to display H₂-selectivity. As reported above, Cu(AzDC)(4,4'-BPE)_{0.5} shows strong adsorption for CO₂ because of the strong quadrupolar interactions of carbon with nitrogen atoms of the organic linkers. Therefore, the diffusion of CO₂ molecules will be restricted much more than that of N₂ and CH₄, leading to a low CO₂ permeance. With UV irradiation, the H₂ permeance only shows slight reduction, while the CO₂ permeance decreases remarkably, thus resulting in an outstanding enhancement of the ideal separation factor of H₂/CO₂ from 23.9 to 48.2.

The molecular sieving performance of the Cu(AzDC)(4,4'-BPE)_{0.5} membrane was confirmed by the separation of equimolar mixtures at 298 K and 1 bar. As shown in Table S2,† comparing the single gas permeance with the mixed gas permeance, the H₂ permeance in the H₂/CO₂, H₂/N₂, and H₂/CH₄ mixtures shows only slight reduction with a H₂ permeance of about 4.2×10^{-7} mol m⁻² s⁻¹ Pa⁻¹, indicating that the larger molecules (CO₂, N₂, and CH₄) only slightly hinder the permeation of the highly mobile H₂. As shown in the inset of Fig. 5, for the 1 : 1 binary mixtures, the mixture separation factors of $H_2/$ CO₂, H₂/N₂, and H₂/CH₄ are 21.3, 18.6, and 13.8, respectively, which also by far exceed the corresponding Knudsen coefficients. Similarly, for the separation of the $1 : 1 H_2/CO_2$ mixture, the H₂ permeance only shows slight reduction with UV irradiation, while the CO₂ permeance decreases remarkably, thus leading to a notable increase of the mixture separation factor of H_2/CO_2 from 21.3 to 43.7 due to different interactions of the H_2 and CO2 multipole moments with the cis- or trans-Cu(AzDC)(4,4'-BPE)_{0.5}.⁴² Compared with literature data of the

separation of H₂/CO₂ mixtures on other MOF membranes (Table S3[†]), the Cu(AzDC)(4,4'-BPE)_{0.5} membrane in the present work also shows high separation selectivity and comparable permeance. The Cu(AzDC)(4,4'-BPE)_{0.5} membrane has been tested for longer than 80 h at 298 K, and its separation performance is found to remain unchanged (Fig. S14[†]), indicating that the Cu(AzDC)(4,4'-BPE)_{0.5} membrane has high stability against UV irradiation. Further, since the preparation of the Cu(AzDC)(4,4'-BPE)_{0.5} membrane is controllable with PDA modification of the support surface, the reproducibility of the membrane preparation is high. For three independent membrane preparations and tests, the Cu(AzDC)(4,4'-BPE)_{0.5} membranes show similar separation performances (Table S4[†]), with an average H₂/CO₂ selectivity of 43.53 ± 0.54 (standard deviation).

A reversible switching of the molecular sieving performance of the Cu(AzDC)(4,4'-BPE)_{0.5} membrane is tested for the separation of the equimolar H_2/CO_2 mixture. As shown in Fig. 6, although the CO₂ permeance significantly decreases in the case of trans-to-cis isomerization, the H₂ permeance is kept almost unchanged, resulting in an observable enhancement of the H₂/ CO_2 separation factor from about 20.9 to 43.6 when switching from the trans to the cis state. Further, after irradiation with Vis light (455 nm), the initial gas permeance and the H_2/CO_2 separation factor of 20.9 are found again because the azobenzene groups are switched back to the original trans state. The complete reversible switching of the membrane permeance and selectivity are confirmed by three continuous cycles of irradiation with UV (365 nm) and Vis light (455 nm), showing there is no sign of degradation, which is in good agreement with previous reports of the photo-switchable MOF membranes.37,38 As reported previously, for a photo-switchable MOF membrane, the separation factors (between membranes with minimum and maximum cis ratios) can be facilely controlled by fine-tuning the



Fig. 6 Mixed gas permeances and H_2/CO_2 mixed gas separation factor of the Cu(AzDC)(4,4'-BPE)_{0.5} membrane measured at 298 K and 1 bar. The Cu(AzDC)(4,4'-BPE)_{0.5} membrane is irradiated with Vis light (455 nm) and UV light (365 nm) for 30 min each for each data point in an *in situ* irradiation device as shown in Fig. S3.†

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ratios of *trans/cis* azobenzene. Therefore, the H₂/CO₂ separation factor is expected to switch not only between the minimum and maximum values, but also each value in between realized by choosing appropriate irradiation times, offering a potential and promising road for remote control of membrane permeance/ selectivity by external stimuli.

Conclusions

In conclusion, we have designed and prepared a novel smart $Cu(AzDC)(4,4'-BPE)_{0.5}$ membrane. In the $Cu(AzDC)(4,4'-BPE)_{0.5}$ framework, the azobenzene and bis(4-pyridyl)ethylene moieties as the "backbone" of the linker are incorporated directly into the framework, forming an interpenetrating network structure with a small pore size of about 3.4 \times 3.4 Å. In particular, under irradiation with UV light, azobenzene and bis(4-pyridyl)ethylene moieties can be switched from the trans to cis configuration, resulting in squeezing out of the adsorbed CO₂. Due to different interactions of the H2 and CO2 multipole moments with cis- or trans-Cu(AzDC)(4,4'-BPE)_{0.5}, the H₂ permeance only shows slight reduction with UV irradiation, while the CO2 permeance decreases remarkably, thus leading to a notable enhancement of the mixture separation factor of H₂/CO₂ from 21.3 to 43.7. Further, the molecular sieving performance of the Cu(AzDC)(4,4'-BPE)0.5 membrane can be facilely controlled by fine-tuning the ratios of trans/cis azobenzene, offering a potential and promising road for remote control of membrane permeance and selectivity by external stimuli.

Conflicts of interest

There are no conflicts to declare.

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