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Electronic Supplementary Information

Target-specific isolation of light-switching metal-organic cage within metal-organic framework for tunable CO_2 adsorption

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Experimental

Chemicals

Copper acetate monohydrate [$Cu(OAc)_2 \cdot H_2O$; Aladdin, 99.99%], aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$; Across, 99%), 2,4,6-tris(4-carboxyphenyl)-1,3,5-triazine (J&K, 97%), *N*,*N*-diethylformamide (DEF, Aladdin, 99%), trifluoroacetic acid (TFA, Adamas, 98%), *N*,*N*-dimethylacetamide (DMA; Sinopharm, 99%), acetone (Sinopharm, >99.9%), and chloroform (Sinopharm, >99.9%) were used directly without any further purification. Deionized water was generated by a Milli-Q integral pure and ultrapure water purification system and used in all experiments.

Synthesis of LMOC

LMOC was prepared according to a similar procedure reported in the literature [1]. Briefly, the ligand of 5-((2,4-dimethylphenyl)diazenyl)isophthalic acid (90 mg, 0.3 mmol) and the metal salt of copper acetate monohydrate (120 mg, 0.6 mmol) were first dissolved in 10 mL and 20 mL of *N*,*N*-dimethylacetamide, respectively. The mixed solution was then sealed and placed in the dark for 48 h. After that, 30 mL of methanol was injected into the solution, resulting in a green precipitate of LMOC. The precipitate sample was throughly washed with methanol for three times to remove the remnant solvent of *N*,*N*-dimethylacetamide. Subsequently, the methanol was removed and the resulting LMOC was dissolved in chloroform before use.

Synthesis of PCN-333

PCN-333 was prepared according to the procedure reported in literature [2]. 2,4,6-tris(4-carboxyphenyl)-1,3,5-triazine (0.05 g, 0.11 mmol) was dissolved in 10 mL of *N*,*N*-diethylformamide by ultrasonication. Then, aluminium chloride hexahydrate (0.2 g, 0.83 mmol) was dissolved and 1 mL trifluoroacetic acid was added with continuned ultrasonic dissolution. The mixture was transferred to a Telfon atuoclave and placed at 135 °C for 48 h. The obtained powder was separated by centrifugation and thoroughly washed with *N*,*N*-diethylformamide and acetone. The final product of PCN-333 was dried in vacuum at 100 °C for 48 h.

Synthesis of LMOC@PCN-333

The composite sample of LMOC@PCN-333 was synthesized as follows. It should be noted that the entire procedure for the synthesis of LMOC@PCN-333 was carried out in dark. The activated PCN-333 (0.1 g) was first dispersed in dry chloroform with vigorous stirring at 0 ºC. Then 0.25 g LMOC in chloroform was added dropwise to the mixture. After stirring for 12 h, the chloroform was removed by evaporation. A green powder was then obtained and washed with chloroform for three times to remove the remaining LMOC on the outer surface. The final solid sample was dried under vacuum, and the obtained powder is denoted as LMOC@PCN-333.

Materials Characterization

Power X-ray diffraction (PXRD) pattern of sample was recorded with an X-ray diffractometer (Japan Rigaku SmartLab 9kW) using Cu Kα radiation. SEM images were collected on a Hitachi S4800 field emission scanning electron microscope. Transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), and corresponding elemental mapping analysis were performed using an FEI Tecnai G2 F30 electron microscope operated at 200 kV. N_2 adsorption-desorption isotherms were performed on ASAP 2020 plus analyzer at 77 K. The Brunauer-Emmett-Teller (BET) surface area was calculated using adsorption data in a relative pressure ranging from 0.001 to 0.03. The total pore volume was determined from the amount adsorbed at a relative pressure of 0.99. The pore diameter was calculated from the adsorption branch by using the non-local density functional theory (NLDFT) methods. Fourier transform infrared (IR) spectra of the sample was carried out on a Thermo Nicolet iS10 spectrometer with KBr wafer. X-ray photoelectron spectroscopy (XPS) was tested through a Thermo Scientific ESCALAB 250Xi spectrometer. UV-vis spectra were collected on SHIMADZU UV-2600 spectrophotometer in the region of 220-850 nm. Thermogravimetry (TGA) and derivative thermogravimetry (DTG) curves were obtained from the use of a thermobalance (STA-499C F3, NETZSCH). The sample was heated from room temperature to 1000 °C with the heating rate 10 $°C\cdot min^{-1}$ under a flow of N_2. As a UV/vis source, a xenon lamp (CEL HXUV300) equipped with a filter was used for *trans*/*cis* isomerization.

Adsorption Experiments

Adsorption isotherm

Adsorption isotherms of CO_2 were conducted on ASAP 2020 plus analyzer. The free space was determined using He (99.999%), assuming that He could not be adsorbed at the investigated temperatures. Before gas adsorption testes, the as-prepared sample was firstly evacuated on a vacuum line for 12 h at room temperature, and subsequently degassed at 373 K on ASAP 2020 plus analyser for 24 h. The UV/Vis adsorption experiments for *trans*/*cis* isomerization were performed on a xenon lamp (CEL HXUV300) as UV/Vis light resource. In UV/vis light resource, the UV light output power is 6.6 W and the visible light output power is 16.6 W. After degas, the samples (in the quartz tube with thickness about 0.5 mm) were irradiated with UV light (wavelength 365 nm) or visible light (wavelength 450 nm) by xenon lamp equipped with a filter, and used for the adsorption measurement. The test sample was exposed to sufficient light irradiation about four hours, and then turned off the light source while conducting the adsorption test at given temperature.

Breakthrough experiment

The breakthrough separation experiments were performed in a home-made breakthrough apparatus under ambient conditions (298 K, 1 atm) using a pure gas of CO_2. The degassed sample was firstly packed into an adsorption column and then purged with helium (He) at 373 K for 120 min. After that, the degassed sample was irradiated with UV light or vis light before conducting the breakthrough experiments. The outlet gas from the adsorption column was monitored using gas chromatography with a thermal conductivity detector (TCD) coupled with a flame ionization detector (FID) continuously.

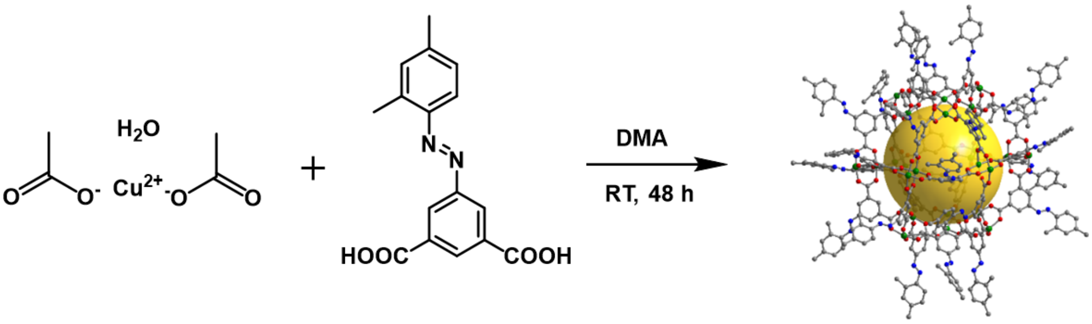

Fig. S1 Schematic illustration of the synthesis procedures of LMOC.

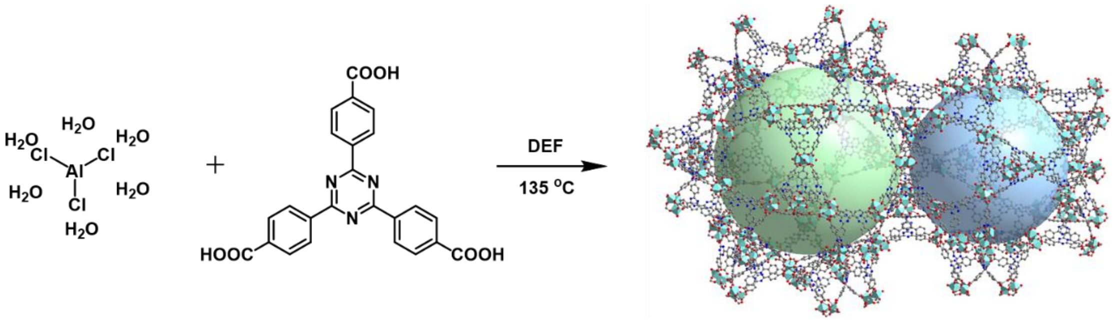

Fig. S2 Schematic illustration of the synthesis procedures of PCN-333.

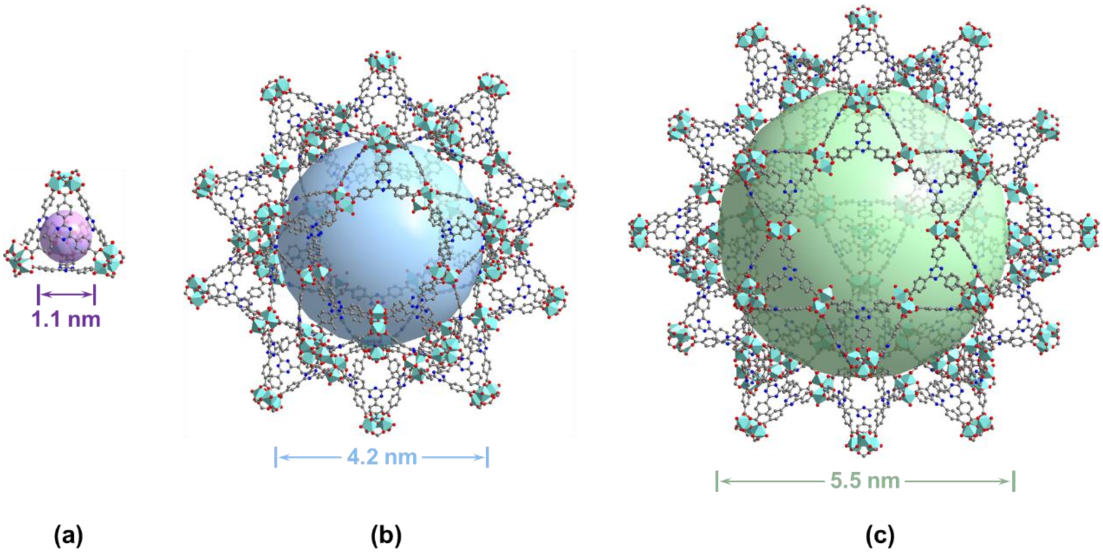

Fig. S3 Schematic illustrations of the structures of PCN-333 with different windows and cavities.

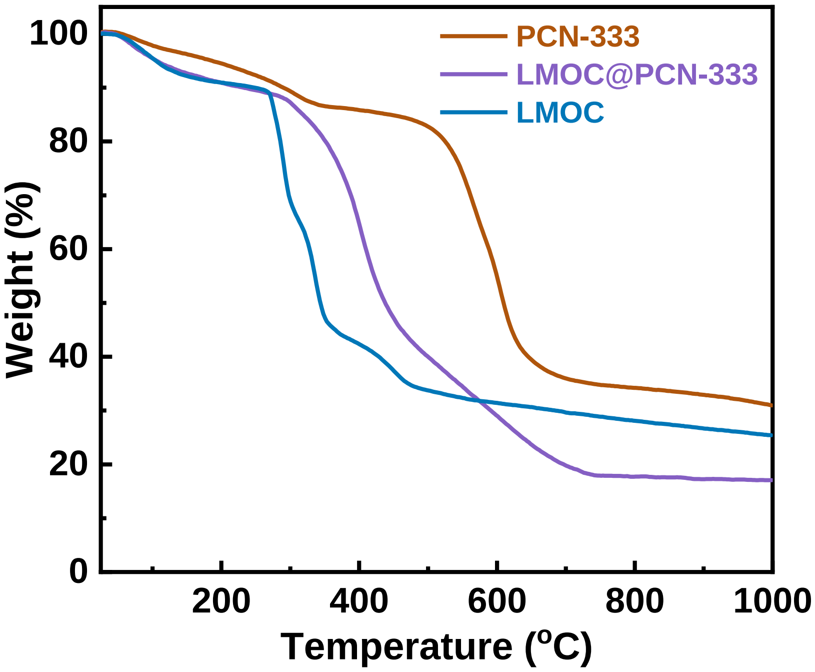

Fig. S4 TGA curves of different samples.

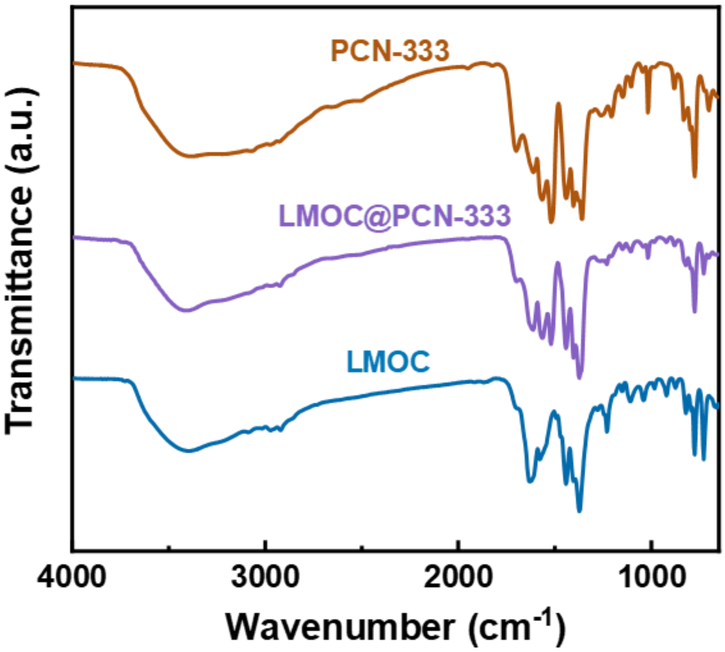

Fig. S5 IR spectra of different samples.

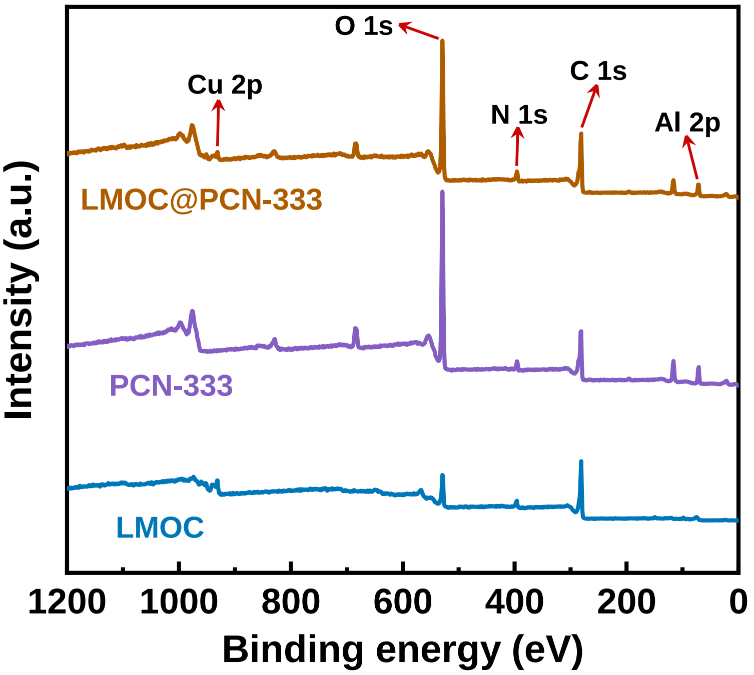

Fig. S6 XPS survey curves of different samples.

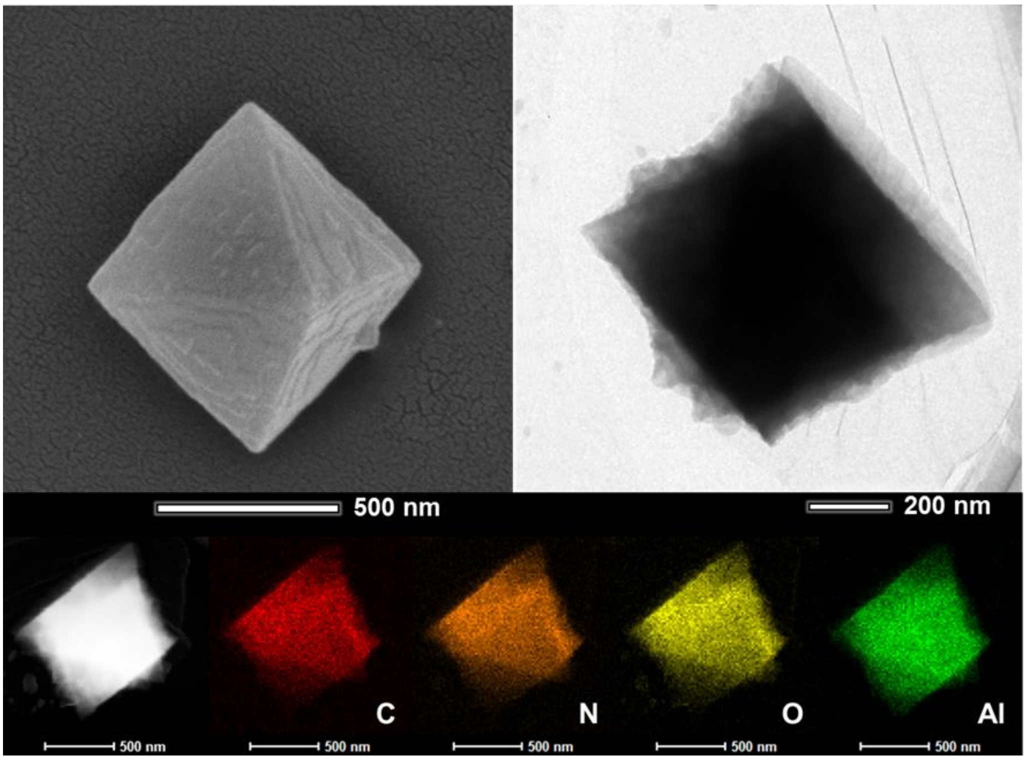

Fig. S7 SEM, TEM, and elemental mapping images of PCN-333.

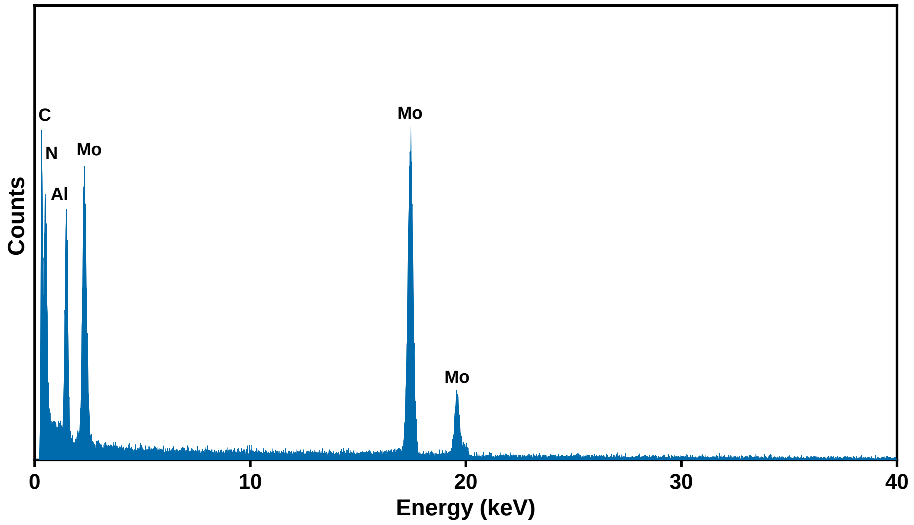

Fig. S8 EDS spectrum of PCN-333.

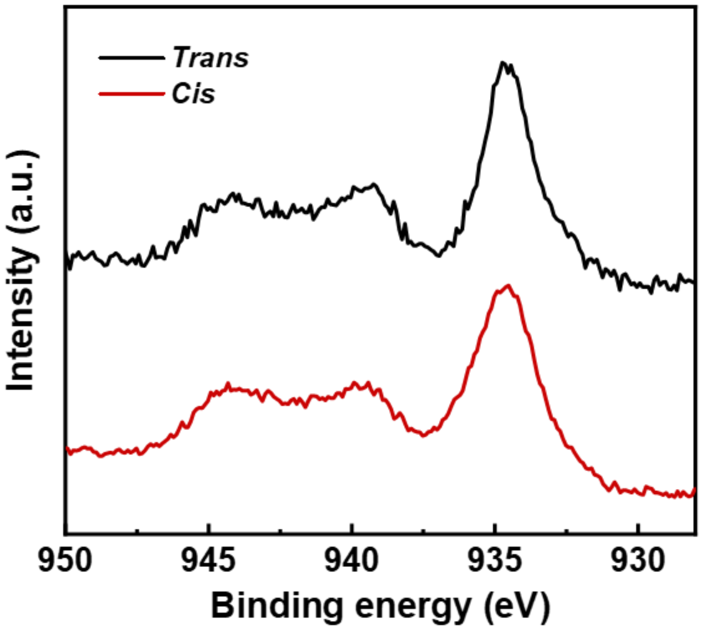

Fig. S9 XPS spectrum of Cu element of LMOC@PCN-333.

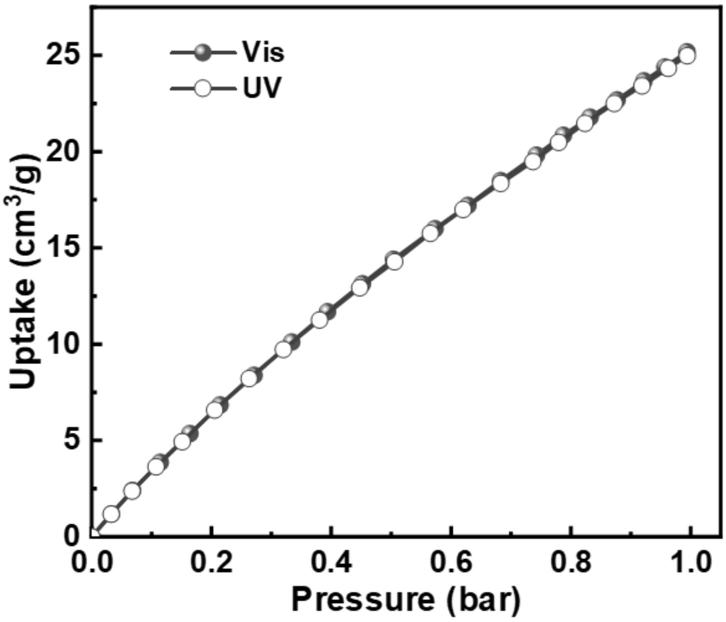

Fig. S10 Adsorption isotherms for CO_2 on the sample of PCN-333 upon *trans*/*cis* isomerization.

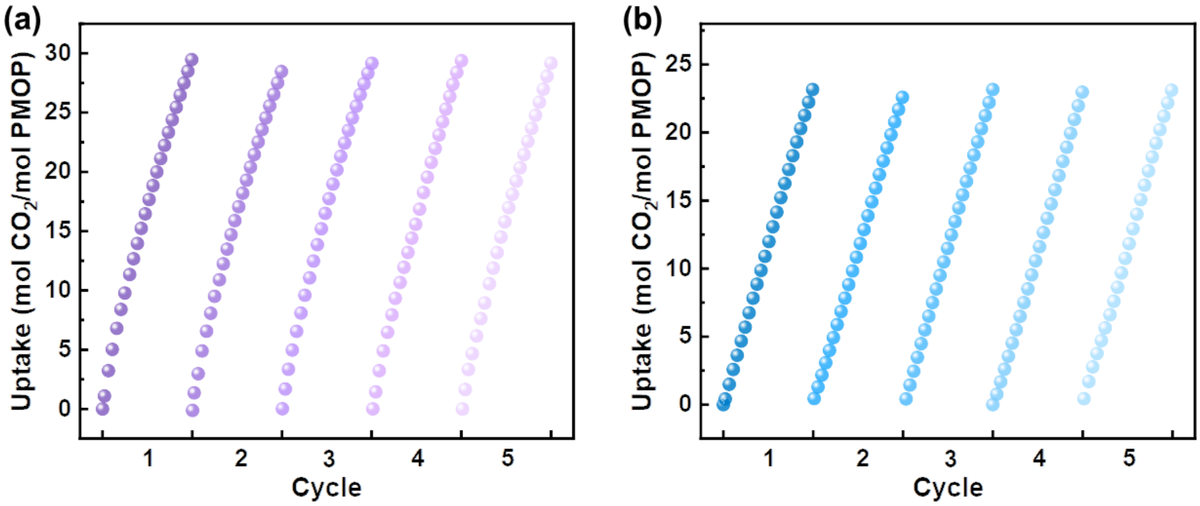

Fig. S11 Adsorption cycles of CO_2 on the sample of LMCO@PCN-333 upon (a) *trans* and (b) *cis* isomerization at 298 K.

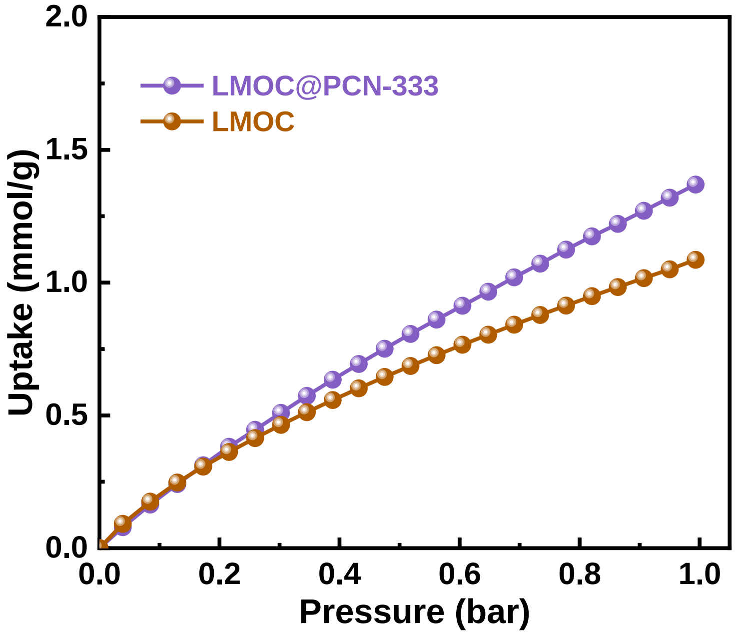

Fig. S12 Adsorption isotherms for CO_2 on the samples of LMOC and LMOC@PCN-333 at 298 K.

Table S1 Physicochemical parameters of different samples

Sample	LMOC content (wt%)	S_{BET} (m^2·g^{-1})[c]	V_p (cm^3·g^{-1})[d]
PCN-333	0	3347	3.24
LMOC@PCN-333	10.3[a]/9.7[b]	2020	2.21
LMOC	100	83	0.22

LMOC content was calculated from the [a] weight loss of TGA and [b] ICP-MS; [c] Specific surface area (S_{BET}) was calculated in the p/p_0 range of 0.01-0.3; [d] Total volume (V_p) was calculated by taking the data at p/p_0 0.99.

References

[1] Park, J.; Sun, L. B.; Chen, Y. P.; Perry, Z.; Zhou, H. C. Azobenzene-functionalized metal-organic polyhedra for the optically responsive capture and release of guest molecules. *Angew. Chem., Int. Ed.* **2014**, *53*, 5842-5846.

[2] Feng, D.; Liu, T.-F.; Su, J.; Bosch, M.; Wei, Z.; Wan, W.; Yuan, D.; Chen, Y.-P.; Wang, X.; Wang, K. Stable metal-organic frameworks containing single-molecule traps for enzyme encapsulation. *Nat. Commun.* **2015**, *6*, 5979.