

Supporting Information

Photoswitching adsorption selectivity in a diarylethene-azobenzene

MOF

Cong Bin Fan,^{a†} Zhi Qiang Liu,^{c†} Le Le Gong,^{b†} An Min Zheng,^{c*} Le Zhang,^b Chang Sheng Yan,^b Hui Qiong, Wu,^b Xue Feng Feng^b and Feng Luo^{b*}

(1) The synthesis of ECUT-30.

A solvothermal reaction among $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, L and H_2AzDC in a ratio of 1:1:1 in a pure DMF solution (5mL), was heated at 110°C for 2 days, and then cooled to room temperature at 3°C/h. Subsequently, block brick-red crystals were obtained in 86% yield based on Zn. Element analysis (%) for ECUT-30: calc. C (60.11), H (3.04), N(7.94); exp. C (59.82), H (2.76), N(8.14).

(2) Materials and General Methods.

The reagents except that L ligands are synthesized in our lab^{8b} and solvents were commercially available (Alfa) and were used without further purification. X-ray powder diffraction were collected by a Bruker AXS D8 Discover powder diffractometer at 40 kV, 40 mA for Cu $K\alpha$, ($\lambda = 1.5406\text{\AA}$). The simulated powder patterns were calculated by Mercury 1.4. Thermogravimetric analysis (TGA) was performed by a TGA Q500 thermal analysis system and all the experiment were performed under a N_2 atmosphere from 30-800°C at a rate of 5°C/min. Data were analyzed using the TA Universal Analysis software package. UV-Vis was measured by a Hitachi UV-365 spectrophotometer. The gas sorption isotherms were collected on Belsorp-max. The as-synthesized sample (weight of about 80 mg) was degassed in the sample tube and dried for 24 h at 130 °C prior to measurements. Ultrahigh-purity-grade (> 99.999%) N_2 , CO_2 , C_2H_4 and C_2H_2 gases were used in this adsorption measurement. To maintain the experimental temperatures mixed liquid nitrogen and acetone (195K), and temperature-programmed water bath (273 K) were used, respectively. And 293 K was controlled by close air-condition system and traced by thermometer. Moreover, before degassing, the fresh samples were emerged in methanol for three days with changing fresh CH_3OH three times a day. For photo-switching experiments, the UV lamp-house is fixed around the sample tube with the distance more than 40 cm to eliminate possible temperature effect on CO_2 adsorption resulted from UV. And this is confirmed by thermometer. Furthermore, all the photo-switching experiments are tested based on the same samples without any shake under the same conditions of apparatus parameter.

(3) X-ray Crystallography.

Unit cell measurements and intensity data were collected at 296 K on a Bruker-AXS SMART Breeze CCD diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda=0.71073\text{\AA}$). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms. CCDC number is 1483504. The data can be obtained free of charge (http://www.ccdc.cam.ac.uk/data_request/cif).

Compound	ECUT-30
Empirical formula	C ₅₃ H ₃₂ F ₆ N ₆ O ₈ S ₂ Zn ₂
Formula weight	1189.71
Space group	Monoclinic, C2/c
Temperature	296(2)K
a	22.4106(9)Å
b	23.6354(9) Å
c	15.2117(6) Å
β	126.403(2)°
Volume	6485.1(4)Å ³
Z	4
Crystal size	0.2×0.2×0.18 cm
Calculated density	1.219 Mg/m ³
F(000)	2408
Theta range for data collection	2.26°-27.27°
Completeness to theta	100%
Goodness-of-fit	0.966
R indices (all data)	R1=0.0453, wR2=0.1239

(4) Modules and simulation.

The structure of **ECUT-30a** was optimized at PW91/DNP theoretical level as implemented in the DMol3 package to obtain the accurate atom position of MOF material. In the structure optimization, the cell parameters of the MOF material were maintained as experimentally observed. The obtained atom coordinates and according atomic charges were used for the further Monte Carlo (MC) simulation. In this work, three kinds of gas molecules, carbon dioxide (CO₂), ethylene (C₂H₄) and acetylene (C₂H₂), were investigated by the MC simulation, and their locations inside the framework will be discussed. In the MC simulation, 2×2×3 MOF super cell was used and the loading number were fixed at 49, 81 and 89 molecules for CO₂, C₂H₄ and C₂H₂, according to the experimental adsorption isotherms at 100 kPa. The MOF structures were considered rigid and fixed at above optimized positions. Periodic boundary conditions were applied in all three dimensions. The charges were added for each atom in the MOF unit cell for the simulations. The TraPPE and TraPPE-UA potential were used to describe CO₂ and C₂H₄, while the potential parameters for C₂H₂ were taken from the work of Fischer et al. It's confirmed that these force fields can well consist of the Van der Waals (vdW) and electrostatic interactions of host-guest and guest-guest in the adsorbed systems. The vdW interactions were described by a Lennard-Jones (LJ) potential truncated and shifted at a cutoff distance of 12.8 Å. The LJ parameters for framework atoms of the MOF were taken from the general DREIDING force field except for Zn metal atoms, which correspond to UFF. All the LJ cross-interaction parameters were determined by the Lorentz-Berthelot mixing rules. The long-range electrostatic interactions were handled using the Ewald summation technique. The MC simulations proceeded for 50000 cycles of equilibration followed by 50000 of production, the structure was printed every 100 cycles after equilibration to analyze the density maps (a powerful analysis tool that could show the preferred positions of the sorbates in the MOF) and radial distribution functions (a useful quantity for representing the local structure of gas molecules adsorbed in MOF framework). The MC simulations were performed by using RASPA2.0 simulation package, and the following density maps were made using VTK software.

(5) Fitting of pure component isotherms.

The pure component isotherm data for C₂H₂, C₂H₄, and CO₂ were fitted with the dual-site Langmuir-Freundlich isotherm model

$$q = q_{A,sat} \frac{b_A p^{v_A}}{1 + b_A p^{v_A}} + q_{B,sat} \frac{b_B p^{v_B}}{1 + b_B p^{v_B}} \quad (1)$$

with T -dependent parameters b_A , and b_B

$$b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right); \quad b_B = b_{B0} \exp\left(\frac{E_B}{RT}\right) \quad (2)$$

(6) Isostatic heat of adsorption.

The binding energy of C₂H₂, C₂H₄, and CO₂ is reflected in the isosteric heat of adsorption, Q_{st} , defined as

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_q \quad (3)$$

(7) IAST calculations of adsorption selectivities.

We consider the separation of binary mixtures. The adsorption selectivity for C₂H₂/CO₂, C₂H₄/CO₂, and C₂H₂/C₂H₄ separation is defined by

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \quad (4)$$

q_1 , and q_2 are the molar loadings in the adsorbed phase in equilibrium with the bulk gas phase with partial pressures p_1 , and p_2 .

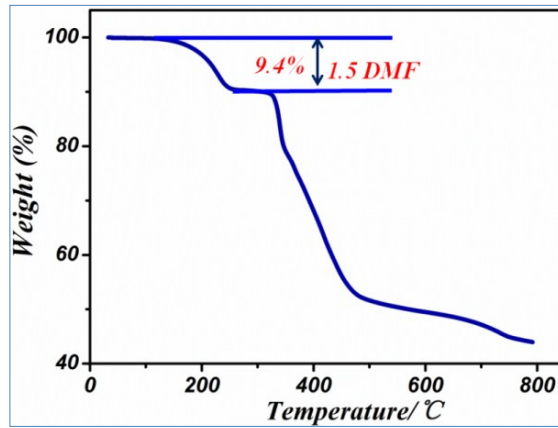


Fig. S1 The TG plot of as-synthesized samples.

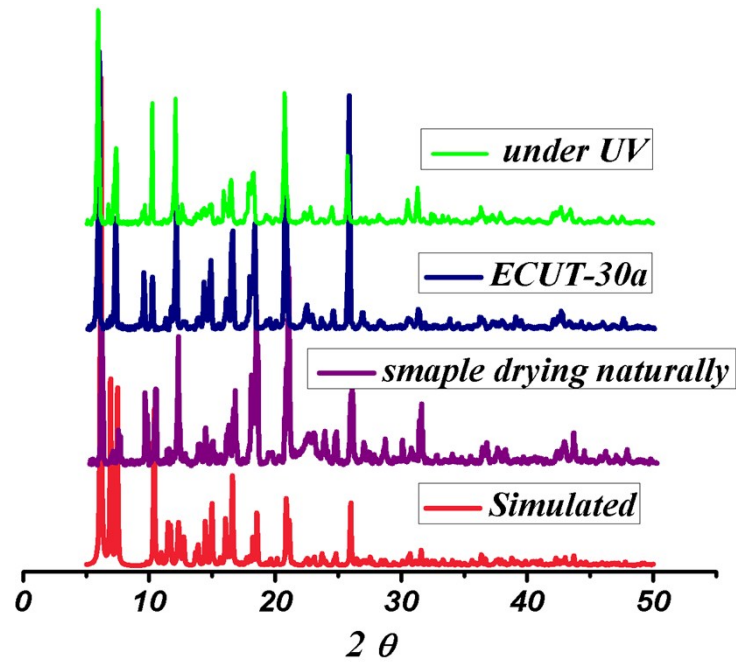


Fig. S2 The PXR D patterns simulated from single crystal data, of the as-synthesized samples after drying naturally, of the as-synthesized samples after activation at 130°C under vacuum, of the activated samples after UV-irradiation about 1min.

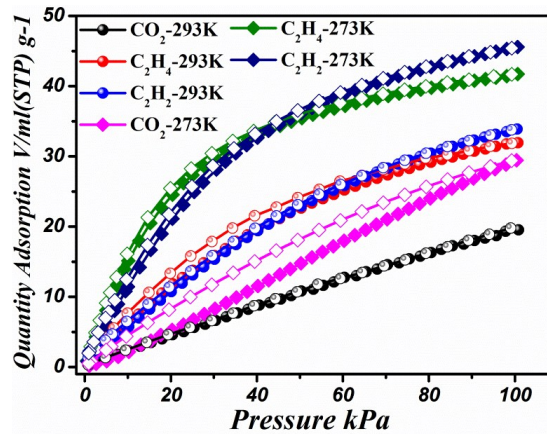
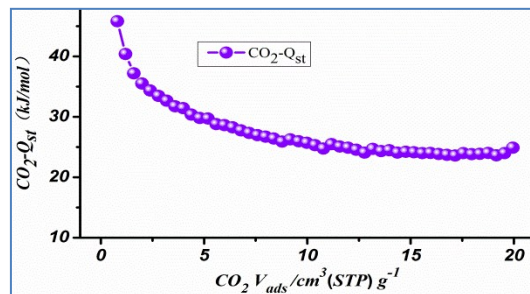


Fig. S3 $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{CO}_2$ adsorption isotherms of ECUT-30a at 293K/273K, respectively: adsorption (solid symbols) and desorption (open symbols).



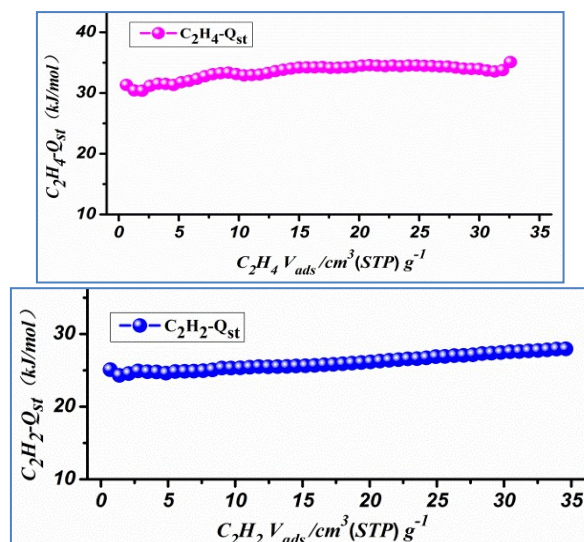


Fig. S4 The isosteric heats of adsorption of CO_2 , C_2H_4 and C_2H_2 , respectively.

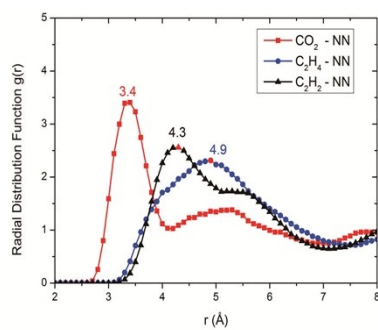


Fig. S5 Radial distribution functions for CO_2 , C_2H_4 and C_2H_2 in MOF material.

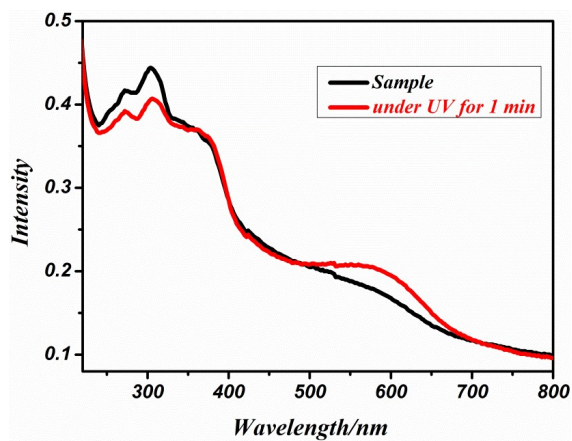


Fig. S6 UV-Vis spectrum for ECUT-30a under UV/red or ambient/black.