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Highly Selective Adsorption of C₂/C₁ Mixtures and Solvent-dependent Thermochromic Properties in Metal-Organic Frameworks Containing Infinite Copper-Halogen Chains

Lihua Wang,[#] Yingxiang Ye,[#] Ziyin Li, Quanjie Lin, Jun Ouyang, Lizhen Liu, Zhangjing Zhang,* and Shengchang Xiang*

Fujian Provincial Key Laboratory of Polymer Materials, College of Material Science and Engineering, Fujian Normal University, 32 Shangsan Road, Fuzhou 350007, P R China

ABSTRACT:

Light hydrocarbon mixtures separation is a very important but challenging industrial separation task. Here, we have synthesized two isostructural cationic metal-organic frameworks {[(Cu(Btz)X]·X·6H₂O·0.25DMSO} (**FJU-53**, Btz =1,4'-Bis(4H-1,2,4-triazol-4-yl)benzene, X = Cl or Br, DMSO = Dimethyl sulfoxide) containing infinite copper-halogen chains and firstly demonstrated that the adsorption selectivity toward C_2/C_1 mixtures in the charged MOFs can be improved by tuning counter-anions. **FJU-53** exhibits the highest selectivity for C_2H_2/CH_4 separation at 296 K and 1 atm, and an exceptional chemical stability in aqueous solutions with pH ranging from 1 to 13. In addition, **FJU-53** also shows the attractive solvent- and halogen-dependent thermochromic behaviors. Its thermochromic mechanism is attributed to the thermally induced vibration of the infinite [(CuX)_n]ⁿ⁺ chains, remarkably different from that for the traditional copper(II) halide materials which thermochromism comes from the coordination geometry transformation or Jahn-Teller distortion.

INTRODUCTION

Natural gas (>80% CH₄) is one of the most promising alternative energy sources and an important chemical raw material for petrochemical industry.¹ Acetylene (C_2H_2) is principally derived from the thermal cracking of natural gas,² during which the separation of acetylene from methane is necessary to meet the requirement of grade A acetylene for organic synthesis. Moreover, the majority chemical industrial processes for oxidative coupling of CH₄ into C₂ hydrocarbons (C_2H_2 , C_2H_4 , and C_2H_6) ultimately need to separate methane from hydrocarbons mixtures owing to the incomplete CH₄ conversion.³ Traditionally, light hydrocarbon separations are carried out by

cryogenic distillation on the basic of different physical properties between CH_4 and C_2 hydrocarbons.⁴ However, this technology is an energy intensive and costly process. Nowadays, zeolites, ⁵ activated carbons, ⁶ porous organic polymer, ^{7 - 9} and metal-organic frameworks $(MOFs)^{2,10-15}$ have shown great advantages in low-energy-consumption C_2/C_1 mixtures separation based on physical adsorption.

By comparison to other solid porous adsorbents, the emerging crystalline porous materials, metal-organic frameworks (MOFs),¹⁶ has received fairly extensive attention, due to structural visualization, fine-tuning of pore surface,¹⁷ and great potential in multifunctional applications.¹⁸⁻⁴³ Additionally, several strategies based upon generating open metal sites,⁴⁴ introducing functional groups,⁴⁵ controlling the pore size/shape,⁴⁶ and forming interpenetrated⁴⁷ and charged⁴⁸⁻⁵⁰ frameworks have been proposed, and demonstrating MOFs are prospective for light hydrocarbon separation and purification. However, there is a big defect for the most of MOFs with low chemical and thermal stability, particularly for those are fabricated through the coordination of divalent metal cations with organocarboxylate bridging ligands.⁵¹ It is well known that compared to the carboxylate-based MOFs, the ones with strong metal-nitrogen (M-N) bonds providing a high chemical and thermal stability.⁵²⁻⁵⁵ Recently, the neutral 4-substitution-1,2,4-triazole derivatives have been proven to be superior ligands exhibiting bi-, tri-, and tetradentate bridging modes when coordinating with metal ions, and it is easy to form the cationic frameworks.⁵⁶⁻⁵⁹ Up to now, enhancing the adsorption selectivity toward light hydrocarbon mixtures in charged MOFs by tuning the counteranions has not been reported.

In present isostructural cationic metal-organic frameworks, the study, two $\{(Cu(Btz)X] \cdot X \cdot 6H_2O \cdot 0.25DMSO\}$ (FJU-53, X = Cl or Br, DMSO = Dimethyl sulfoxide), have been synthesized from neutral organic ligands 1,4'-Bis(4H-1,2,4-triazol-4-yl)benzene (Btz) and diverse copper halide salts on the basis of three following considerations: (i) The neutral nitrogen containing ligands (Btz) that can bridge transition-metal ions and are apt to fabricate the cationic frameworks.⁵⁸ (ii) These counter anions (Cl⁻ and Br⁻) with the different radius (0.181 and 0.196 nm) and electronegativity⁶⁰ within the channels not only tune the pore size^{61,62} but also modulate the interactions between counteranions and the trapping gas guests to improve the selective adsorption.⁶³ (iii) Copper(II) halides are a well-known type of thermochromism materials due to

the coordination geometry transformation⁶⁴ or Jahn-Teller distortion,⁶⁵ and will be likely to endow newly synthesized MOFs with thermochromic behaviors. As expected, **FJU-53** exhibits a good chemical stability in aqueous solutions with pH ranging from 1 to 13, and the highest selectivity for C_2H_2/CH_4 by enhanced the host-guest interactions through the counteranions. Additionally, different with the pure inorganic copper(II) halides, the inorganic-organic hybrid MOF **FJU-53** shows attractive solvent- and halogen-dependent thermochromic behaviors owing to the thermally induced vibration of the infinite copper-halogen chains.

EXPERIMENTAL SECTION

Materials and Measurements. All reagents and solvents were used as received from further commercial suppliers without purification. The organic ligands 1,4-Bis(4H-1,2,4-triazol-4-yl)benzene (Btz) were synthesized similar to pervious published procedures.⁶⁶⁻⁶⁸ Powder X-ray diffraction (PXRD) was carried out with a PANalytical X'Pert³ powder diffractometer equipped with a Cu sealed tube ($\lambda = 1.541874$ Å) at 40 kV and 40 mA over the 2θ range of 5-30°. The simulated pattern was produced using the Mercury V1.4 program and single-crystal diffraction data. The Fourier transform infrared (KBr pellets) spectra were recorded in the range of 500~4000 cm⁻¹ on a Thermo Nicolet 5700 FT-IR instruments. Thermal analysis was carried out on a METTLER TGA/SDTA 851 thermal analyzer from 30 to 800 °C at heating rate of 10 °C min⁻¹ under nitrogen atmosphere. TGA-MS was measured using a Rigaku Thermo Mass Photo TG-DTA-PIMS 410/S. Differential scanning calorimetry (DSC) was carried out with a Mettler Toledo DSC 822^e at a heating rate of 5 °C min⁻¹ under N₂ atmosphere. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C analyzer.¹H NMR spectrum was recorded on a Bruker advance III 400 (400 MHz) spectrometer as solutions in DMSO-d₆. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to DMSO (2.50 ppm) as internal standard.

Syntheses. 1,4-Bis(4H-1,2,4-triazol-4-yl)benzene (Btz). Refluxing a mixture of N, N'-dimethylformamide azine dihydrochloride (DMAZ, 2 g, 9.33 mmol) and 1,4-phenylenediamine (0.5 g, 4.67 mmol) in 25 mL o-xylene for 24 h gave light gray solid. The solid was then transferred into a parr Teflon-lined stainless steel vessel (23.0 mL) and heated to 150 °C for 24 h under autogenous pressure, and cooled to room temperature at a rate of 5.0 °C h⁻¹. Brown rod-shaped crystals of Btz suitable for single crystal X-ray analysis were obtained directly, washed with water, and dried in air. Yield: 47% based on 1,4-phenylenediamine. ¹H-NMR (*d*₆-DMSO, 400 MHz): δ 9.21 (S, 4H), 7.95 (S, 4H). The NMR data are consistent with the literature reported.⁶⁶

(Cu(Btz)Cl]·Cl·6H₂O·0.25DMSO (FJU-53-Cl). A mixture of CuCl₂.2H₂O (17.3 mg, 0.1

mmol) and Btz (8.7 mg, 0.04 mmol) were dissolved in 5 mL of DMSO/H₂O (1:4, v/v), and the mixture was transferred to and sealed in a 23 ml Teflon-lined autoclave, which was heated at 120 °C for 2 day. After slow cooling to room temperature, the blue block crystals were separated by decantation, washed with water and dried at room temperature. Yield: 50% based on Btz. Anal. Calc. for $C_{42}H_{86}Cl_8Cu_4N_{24}O_{25}S$ (%): C, 26.59; N, 17.72; H, 4.569. Found: C, 26.93, N, 17.86; H, 4.530. IR (cm⁻¹): 3435(s) 3101(s) 1633(m) 1548(s) 1325(m) 1319(w) 1254(m) 1207(m) 1076(s) 845(s) 640(s) 550(m).

[(Cu(Btz)Br]·Br·6H₂O·0.25DMSO (FJU-53-Br). The synthesis method was the same as FJU-53-Cl and except using CuBr₂ (22.5 mg, 0.1 mmol) replace CuCl₂.2H₂O. Blue block crystals of FJU-53-Br were obtained. Yield: 56% based on Btz. Anal. Calc. for C₄₂H₈₆Br₈Cu₄N₂₄O₂₅S (%): C, 22.39; N, 14.92; H, 3.848. Found: C, 23.06, N, 14.25; H, 3.864. IR (cm⁻¹): 3429(s) 3080(s) 1633(s) 1550(s) 1435(m) 1325(s) 1248(s) 1074(s) 1022(m) 843(s) 640(s) 550(m).

Gas Adsorption. After the bulk of the solvent was decanted, the freshly prepared sample of **FJU-53** (~0.15 g) was soaked in methanol for 1 hour, and then the solvent was decanted. Following the procedure of methanol soaking and decanting 10 times, the solvent-exchanged samples were activated by vacuum at room temperature for 24 hours until a pressure of 5 μ m Hg. N₂, CO₂, methane, ethylene, ethane, and acetylene adsorption isotherms were measured on Micromeritics ASAP 2020 HD88 surface area analyzer for the guest-free **FJU-53a**. As the centre-controlled air condition was set up at 23 °C, a water bath of 23 °C was used for adsorption isotherms at 296 K, whereas liquid nitrogen, dry ice-acetone and ice-water bathes were used for the isotherms at 77, 196 and 273 K, respectively.

Virial Equation Analysis. The virial equation can be written⁶⁹ as follows:

$$\ln(n/p) = A_0 + A_1 n + A_2 n^2 + \dots$$
 (1)

where *n* is the amount adsorbed (mol g⁻¹) at pressure *p* (Pa). At a low surface coverage, the A_2 and higher terms can be neglected and the equation becomes

$$\ln(n/p) = A_0 + A_1 n \tag{2}$$

A linear graph of $\ln(n/p)$ versus *n* was obtained at low surface coverage and this is consistent with neglecting the higher terms in eqn (2). A_0 is related to the adsorbate-adsorbent interactions, Whereas A_1 describes the adsorbate-adsorbate interactions. The virial parameters are given in **Table S6**, Supporting Information.

Enthalpies of Adsorption. Zero surface coverage. The isosteric enthalpies of adsorption at

van't Hoff isochore. The isosteric enthalpies of adsorption as a function of surface coverage were calculated from the isotherms using the van't Hoff isochore, which is given by the equation

$$\ln(p) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{3}$$

A graph of $\ln P$ versus 1/T at a constant amount adsorbed (*n*) allows the isosteric enthalpy and entropy of adsorption to be determined. The pressure values for a specific amount adsorbed were calculated from the adsorption isotherms by: (1) assuming a linear relationship between the adjacent isotherm points starting from the first isotherm point; and (2) using the virial equation at low surface coverage. The agreements between the two methods for **FJU-53a** are shown in **Figures S19** and **S20**.

Prediction of the Gas Adsorption Selectivity by IAST. The ideal adsorption solution theory (IAST)⁷⁰ was used to predict the binary mixture adsorption from the experimental pure gas isotherms. To perform the integrations required by IAST, single-component isotherms should be fitted by the correct model. In practice, several methods are available; for this set of data we found that the single-site Langmuir-Freundlich equation was successful in fitting the results.

$$N = N^{\max} \times \frac{bp^{1/n}}{1 + bp^{1/n}}$$
(4)

where *P* is the pressure of the bulk gas in equilibrium with the adsorbed phase (kPa), *N* is the amount adsorbed per mass of adsorbent (mmol g⁻¹), N^{max} is the saturation capacities of site 1 (mmol g⁻¹), *b* is the affinity coefficients of site 1 (1/kPa) and *n* represents the deviations from an ideal homogeneous surface. The fitted parameters were then used to predict multi-component adsorption with IAST. The adsorption selectivities based on IAST for mixed C₂H₂/CH₄, C₂H₄/CH₄, and C₂H₆/CH₄ are defined by the following equation:

$$S_{A/B} = (x_A/y_A)/(x_B/y_B)$$
 (5)

where x_i and y_i are the mole fractions of component i (i = A, B) in the adsorbed and bulk phases, respectively.

Single-Crystal X-ray Diffraction (SCXRD) Studies. Variable-temperature SCXRD

experiments were carried out on an Oxford Diffraction/Agilent SuperNova diffractometer (graphite-monochromated Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å) fitted with an Oxford Cryosystems Cryostream 700 open flow cooling device. The single crystal was supported on top of a glass fiber and mounted in the open nitrogen flow from a nitrogen cryostream (Oxford). Using Olex2,⁷¹ the structure was solved with the Superflip⁷² structure solution program using charge flipping and refined with the ShelXL⁷³ refinement package using least squares minimization. All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on the ligands were placed in idealized positions and refined using a riding model. We employed PLATON⁷⁴ and SQUEEZE⁷⁵ to calculate the diffraction contribution of the solvent molecules and thereby produce a set of solvent-free diffraction intensities. A summary of crystallographic refinement details is given in **Tables S1-S5** for **FJU-53** (CCDC 1518972-1518989).

The detail variable-temperature SCXRD experiments are as follows: (1) a full set of diffraction data on one same **FJU-53** crystal were collected over the temperature range from 100 to 300 K with 50 K intervals after equilibration for a period of 30 minutes at each temperature, defined as first run. (2) Then, the test temperature rapidly drops to 100 K, and the single crystal always in the nitrogen atmosphere. After that, the variable-temperature diffraction data were collected over the temperature range from 100 to 350 K with 50 K intervals after equilibration for a period of 30 minutes at each temperature for a period of 30 minutes at each temperature collected over the temperature range from 100 to 350 K with 50 K intervals after equilibration for a period of 30 minutes at each temperature, defined as second run. Complete details can be found in the accompanying cif file.

RESULTS AND DISCUSSION

Description of the Crystal Structure

Blue block crystals of **FJU-53** were solvothermally synthesized by the reaction of various copper (II) salts and Btz in DMSO/H₂O solution for 2 days. Single crystal X-ray crystallography reveals that **FJU-53-Cl** and **FJU-53-Br** are isostructural with different halogen anions in the orthorhombic *Imma* space group. Here, **FJU-53-Cl** is selected to discuss the structure in detail. As shown in **Figure 1a**, one crystallographically independent Cu²⁺ ion is six-coordinated with four N atoms from four individual Btz ligands and two μ_2 -Cl⁻ anions, forming a distorted octahedral geometry, in which four N atoms locate the equatorial plane and two Cl⁻ ions occupy the axial positions. The Cu-Cl distance (2.6722(8) Å) is longer than Cu-N distance (2.0187(17) Å),

indicating an elongated octahedron around Cu1. Meanwhile, the Cu-Br and Cu-N distances in **FJU-53-Br** are 2.8197(10) Å and 2.023(5) Å, respectively. The Btz ligand, employing a symmetrical coordination mode, bonds to four Cu1 through four terminal N atoms of two triazole rings. Through the bridging of μ_2 -Cl⁻ anions, a 1D inorganic zigzag chain of $[(CuCl)_n]^{n+}$ is formed (**Figure 1b**), with the nearest d_{Cu-Cu} distance and $\theta_{Cu-Cl-Cu}$ angle are of 3.608 Å and 84.93°, respectively. The 1D zigzag chains are connected to four neighbouring chains by the Btz ligands to assemble a 3D open frameworks. The resulting framework possesses 1D rhomboidal channel with dimensions of 21.24×15.25 Å (measured distance between diagonal Cu atoms, and 21.53×14.68 Å in **FJU-53-Br**) along the *b*-axis (**Figures 1c** and **S1**). To further understand the structural topology, when we took the {CuN₄Cl₂} unit as a 6-connected node and the Btz ligand as a 4-connected node, respectively, the framework of **FJU-53** could be simplified as a novel (4,6)-connected net with the point symbol { $3^2.6^2.7^2$ } { $3^4.4^2.6^4.7^5$ } (**Figure S2**).⁷⁶ After elimination of guest solvent molecules, the total accessible volume in **FJU-53-CI** and **FJU-53-Br** are 45% and 43%, respectively, by using the PLATON software.⁷⁴



Figure 1. The structures of **FJU-53-Cl** showing: (a) the coordination environment of Cu1 and the symmetric bridging mode of Btz. Symmetry codes: A, x, -y, 1-z; B, 1-x, -y, 1-z; C, 1-x, y, z; D, x, 0.5-y, z; E, 1-x, 0.5-y, z; F, 0.5-x, -y, 0.5+z; G, -0.5+x, 0.5+y, 0.5+z. (b) The μ_2 -Cl⁻ bridged 1D zigzag inorganic chain. (c) The 3D open framework with 1D rhombic channels and containing 1D inorganic chain viewed along the **b** axis. All hydrogen atoms and guest molecules are omitted for clarity.



Figure 2. Powder X-ray diffraction (PXRD) patterns for **FJU-53-Cl** (a) and **FJU-53-Br** (b); PXRD profiles for **FJU-53-Cl** (c) and **FJU-53-Br** (d) soaked in the aqueous solutions with pH values of 1 to 13 for 12 h.

Thermal and Chemical Stability

FJU-53 can be readily synthesized in high yield and with good crystal quality, and the phase purity of bulk samples were confirmed by powder X-ray diffraction (PXRD) technique (**Figure 2**). The experimental PXRD patterns correspond well with the results simulated from the single crystal data, indicating the pure phase of **FJU-53**. The thermogravimetric analysis (TGA) measurements were performed to study the thermal stability of the as-synthesized samples. TGA for **FJU-53-CI** reveals a weight loss of 27.7% from 30 to 222 °C, corresponding to the removal of six lattice water and quarter DMSO molecules (calcd: 26.9%), and for **FJU-53-Br**, a weight loss of 23.4% from 30 to 190 °C is found, indicating it also release six water and quarter DMSO molecules (calcd: 22.6%) (**Figure S5**). The types of guest solvents released were also confirmed by the TGA-MS technology (**Figures S6-7**). Then the two compounds begin to decompose upon further heating. It should be noted that **FJU-53** shows extraordinary chemical stability. When exposed to the acid and alkali aqueous solutions with pH values in the range of 1-13 over 12 hours, the frameworks of **FJU-53** still retain which can be proved by the PXRD technique (**Figures 2c-d**). Although some reported MOFs present water tolerance or chemical stability in acidic or basic media, very few MOFs were found to be resistant to both strong acid and base.⁷⁷ The excellent stable behavior of **FJU-53** is of

extreme importance for their practical applications.



Figure 3. 196 K CO₂ and 77 K N₂ adsorption isotherms for **FJU-53-Cl-a** (a) and **FJU-53-Br-a** (d). Adsorption isotherms of C_2H_2 , C_2H_4 , C_2H_6 , and CH_4 for **FJU-53-Cl-a** (b) and **FJU-53-Br-a** (e) at 296 K. Selectivity predicted by IAST of **FJU-53-Cl-a** (c) and **FJU-53-Br-a** (f) at 296 K.

Gas Sorption Properties

The activated samples were prepared by exchanging the solvent in the as-synthesized FJU-53 with CH₃OH and then pumped under high vacuum at room temperature overnight, thus to form guest-free phases FJU-53a. The XRPD patterns of the activated samples show that the broadened peaks keep the positions, indicating the maintenance of the frameworks (Figures 2a-b). N₂ adsorption on the activated FJU-53a at 77 K was very slow because of the activated diffusion effects.⁷⁸ Therefore, CO₂ adsorption at 196 K was used for their pore characterization. As shown in Figures 3a and 3d, both FJU-53-Cl-a and FJU-53-Br-a exhibit typical Type-I isotherm characteristic. The CO₂ adsorption capacity was increased to 60 and 40 cm³ g⁻¹, respectively, by a sharp gas uptake at a low-pressure region ($P/P_0 < 0.1$) and the uptake increased as the pressure increased, which is typically observed for microporous materials.⁷⁹ The Langmuir (BET) surface areas calculated from the first step adsorption isotherms are 527.7 (341.2) and 450.5 (256.7) m² g⁻¹ for FJU-53-Cl-a and FJU-53-Br-a, respectively, within the pressure range of 0.05 < $P/P_0 < 0.3$ (Figures S8-9).

Establishment of the permanent porosity of the two MOFs encouraged us to explore its potential application in light hydrocarbon adsorption and separation. **FJU-53-Cl-a** can adsorb 54.4, 35.4, 32.0 and 8.6 cm³ g⁻¹ of C₂H₂, C₂H₄, C₂H₆ and CH₄, respectively, at 296 K and 1 bar (**Figure**)

3b). The adsorption isotherms for C₂ hydrocarbons and CH₄ on **FJU-53-Br-a** are very similar to those for **FJU-53-Cl-a** and the adsorption capacity follows the same sequence: $C_2H_2 > C_2H_4 > C_2H_6 > CH_4$ (**Figure 3e**). This phenomenon is attributed to the similar pore surface structure resulting from the analogous metal node and ligand connection mode.⁸⁰ However, the lower BET surface areas and weak electronegativity of Br⁻ anion for **FJU-53-Br-a** makes its various gas uptakes lower than the corresponding values in **FJU-53-Cl-a**.

Materials	Functional sites	IAST Selectivity ^a			$Q_{st} (kJ/mol)^{f}$				D. C
		C_2H_2/CH_4	C_2H_4/CH_4	C ₂ H ₆ /CH ₄	C_2H_2	C_2H_4	C_2H_6	CH ₄	Ket.
FJU-53-Cl-a	Charged skeleton,	1306	34.1	21.5	38.1	25.6	25.0	17.3	This
	Cl ⁻ counterions	322.5 ^b	25.0^{b}	16.3 ^b					work
FJU-53-Br-a	Charged skeleton,	534	25	15.7	20.0	19.9	18.9	12.8	This
	Br ⁻ counterions	200.9^{b}	19.1 ^{<i>b</i>}	12.5 ^b					work
PMOF-3a	C≡C triple bonds,								
	Narrow pore,	156.5	NA ^c	NA	21.9	NA	NA	15.1	81
	OMS^d								
Cu-TDPAT	OMS, LBS^{e}	82	45	16	42.5	49.5	30.2	20.7	87
		127.1 ^b	85.0^{b}	12.1^{b}					02
Cu-TDPAH	OMS, LBS	82	54	24	23.5	45.0	33.0	13.8	83
		80.9^{b}	40.6^{b}	12.5^{b}					0.5
FJU-12a	Narrow pore,	79.7	26.4	30.3	29.2	22.7	21.0	14.7	81
	LBS	31.9 ^b	16.0^{b}	20.7^{b}					04
ZJU-61a	OMS, Narrow	74 4^{b}	49 5^{b}	$11 0^{b}$	23 98	27 60	15 17	12 13	85
	pore	,	.,	11.0			10.11	12.10	
UTSA-15a	Functional OH	55 6^{b}	NA	NA	39.5	NA	NA	136	45
	Groups								
FJI-C4	Narrow pore,								
	Charged skeleton,	51.0	22.1	39.7	27.0 ^g	33.1 ^g	32.7 ^g	20.8 ^g	49
	Cationic								
	counterions,								
M'MOF-20a	Narrow pore,	34.9 ^b	NA	NA	33.7	NA	NA	24.8	86
	OMS								
BUT-52	Charged skeleton	23.5 ^b	14.4 ^b	13.7 ^b	35.5	27.3	31.8	19.0	50

Table 1. Comparison of the selectivity of representative MOFs with that of FJU-53a.

^{*a*}The IAST selectivity value for equimolar C₂s/CH₄ mixture is predicted at 296 K and 100 kPa. ^{*b*}The Henry's law selectivity for gas component *i* over CH₄ is calculated based on the equation $S_i/_{CH4} = K_H(i)/K_H(CH_4)$. ^{*c*}NA = Not Available. ^{*d*}OMS= Open Metal Sites. ^{*e*}LBS= Lewis Basic Sites. ^{*f*}Obtained by the Virial fitting method. ^{*g*}Obtained by the Clausius-Clapeyron equation.

Furthermore, it is worth noting that the C₂ hydrocarbons adsorption isotherms for FJU-53-Cl-a

and **FJU-53-Br-a** both show a rapid uptake at low pressure especially for acetylene, whereas methane uptake are much lower at this pressure, suggesting that **FJU-53-CI-a** and **FJU-53-Br-a** are promising materials for selective separation toward C_2/C_1 mixtures. The Henry's law selectivities in **FJU-53-CI-a** for C_{2} s over CH₄ at 296 K, calculated on the basis of the equation $S_{i/CH4} = K_{\rm H}(i)/K_{\rm H}(\rm CH_4)$,⁷⁸ are 322.5, 25.0 and 16.3, respectively, higher than the corresponding values (200.9, 19.1 and 12.5) in **FJU-53-Br-a** (**Table 1**). The well-defined ideal adsorbed solution theory (IAST) is also employed to evaluate the C_2/C_1 separation selectivity at different pressures.⁷⁰ As shown in **Figure 3c**, the selectivity of C_2H_2 , C_2H_4 , and C_2H_6 with respect to CH₄ in **FJU-53-CI-a** are 1306, 34.1, and 21.5, respectively, at 296 K under 1 atm, which are systematically higher than those calculated in **FJU-53-Br-a**. To the best of our knowledge, the Henry's law and IAST selectivities of 322.5 and 1036 for C_2H_2/CH_4 are both the highest value reported to date (**Table 1**). Such high selectivities further imply that **FJU-53a** is a promising material for C_2/C_1 mixtures purification.

In order to establish why FJU-53a exhibits such a highly selective separation for C₂s/CH₄, its coverage dependent adsorption enthalpies were calculated on the basis of the virial method and the van't Hoff isochore. The virial graphs for adsorption of these gases on two MOFs at 273 and 296 K are shown in Figures S11-18. The comparison of the results from the two methods, the linear extrapolation and the virial equation, shows a very good agreement (Figures S19-20). The $Q_{st,n=0}$ for C₂H₂, C₂H₄, C₂H₆, and CH₄ adsorption on **FJU-53-Cl-a** were 38.1, 25.6, 25.0, and 17.3 kJ mol⁻¹, respectively, over the temperature range from 273 to 296 K. The enthalpies for the four gases (20.0 kJ mol⁻¹ for C_2H_2 , 19.9 kJ mol⁻¹ for C_2H_4 , 18.9 kJ mol⁻¹ for C_2H_6 and 12.8 kJ mol⁻¹ for CH_4) on FJU-53-Br-a are systematically lower than those found in FJU-53-Cl-a, which may be attributed to the weaker electrostatic interactions between the trapping gas molecules and Br anion on the pore surface in FJU-53-Br-a. The adsorption enthalpy for C₂H₂ of 38.1 kJ/mol in FJU-53-Cl-a is comparable with that of Cu-TDPAT (42.5 kJ/mol) and even higher than those of Cu-TDPAH (23.5 kJ/mol), PMOF-3a (21.9 kJ/mol) and ZJU-61a (23.98 kJ/mol) with high density of open Cu²⁺ sites, indicating that the charged skeleton and Cl⁻ counterions play the important roles for the stronger interactions between C2H2 and pore surfaces on FJU-53-Cl-a. Therefore, the high adsorption selectivity of C₂s/CH₄ in FJU-53a could be attributed to three factors: (1) the narrow pore size originates from the flexible framework of FJU-53a matches with the kinetic diameters of C2 hydrocarbons resulting in their high C_{28}/CH_4 sieving effects; (2) the charged skeleton and X⁻ counterions can enhance framework- C_{2s} interactions through charge-induced forces due to the large polarizability of C_{28} in comparison to CH_4 ;^{87,88} and (3) π - π interactions of benzene and triazole rings in **FJU-53a** toward acetylene and ethene may improve their adsorption capacities.⁴⁹



Figure 4. Photomicrographs of a single crystal of (a) FJU-53-Cl and (b) FJU-53-Br mounted on glass fiber, were recorded in the temperature range 100 K \rightarrow 300 K (first run) and 100 K \rightarrow 350 K (second run) at 50 K intervals.

Solvent-dependent Thermochromic Behavior

Taking into consideration the copper(II) halide is a well-known thermochromism materials,⁶⁴ the thermochromic behaviors of **FJU-53** was investigated by the variable-temperature single-crystal X-ray diffraction experiment. The diffraction data on one same **FJU-53** crystal were recorded over the temperature range from 100 to 300 K during the first run and again from 100 to 350 K during the second run with 50 K intervals. As shown in **Figure 4a**, for **FJU-53-CI**, the color keeps blue when the temperature increases from 100 K to 250 K. Then, the crystal color changes from blue to yellow green when the temperature reaching 300 K, which may be owing to the removal of solvent molecules. At 250 K and 300 K, the single crystal diffraction quality was not well enough to refine the crystal structure. After keeping at 300 K for 2.5 hours, the test temperature rapidly drops to 100 K, the crystal shows good diffraction data accompanying with the color change to light green.

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During the second run, **FJU-53-Cl** shows good diffraction data and obvious thermochromic behavior with the color gradually shifting from light green, yellow green to golden with the temperature increasing from 100 to 350 K. Once the crystal **FJU-53-Cl** is exposed to air for 0.5 h after the above experiments are completed, its color turns back to the original blue.

By contrast, the color of **FJU-53-Br** changes from light blue (100 K) to turquoise (250 K), and further changes to olive at 300 K during the first run. The diffraction data of **FJU-53-Br** at 250 K and 300 K were also not well enough to refine the crystal structure. After staying at 300 K for 2.5 h, the test environment again drops to 100 K, **FJU-53-Br** shows good diffraction data accompanying with the color change to ivory. During the second run, the clearly thermochromic behavior was observed in **FJU-53-Br**, and the color gradually change from ivory (100 K), fern green, and finally to grey olive (350 K) upon raising the temperature. The remarkably different behavior of the color change between **FJU-53-Cl** and **FJU-53-Br** indicates that the X⁻ ion plays an important role for the thermochromism in **FJU-53**.



Figure 5. The variation of unit cell parameter *b* as a function of temperature for (a) **FJU-53-Cl** and (b) **FJU-53-Br**. (c) The $d_{Cu \cdots Cu}$ distances (Å) and (d) $\theta_{Cu-X-Cu}$ angles (°) as a function of temperature for **FJU-53**.

In order to elucidate the origin of thermochromic behavior, we obtained single-crystal X-ray structures for **FJU-53** at various temperatures, and all structures were still in the orthorhombic space group *Imma*. During the first run, the single-crystal structures of **FJU-53-Cl** containing the solvents in the channel reveal that upon heating from 100 K to 200 K, its unit cell parameters *a*

decreases from 22.1266 to 21.6580 Å, c increases from 13.8663 to 14.700 Å, and only subtle change observes for b. After the solvents release out of the channels and the temperature drops to 100 K again, FJU-53-Cl turns to light green and the obvious structural change features with the remarkable shrinkage of the parameter **b** and the nearest $d_{Cu\cdots Cu}$ distance. The **b** of 7.1180 Å is 0.1386 Å shorter than the one in the first run at 100 K, while the $d_{Cu\cdots Cu}$ distance is shortened 0.0693 Å (Figure 5c). During the second run, upon increasing the temperature to 300 K, there were no obvious change of the parameters a and c, while the crystallographic b axis has a notable increase, the $d_{\text{Cu-Cu}}$ distance increases from 3.559 Å to 3.589 Å and the $\theta_{\text{Cu-Cl-Cu}}$ angle raises from 84.44° to 85.07°. But there is no obvious change of the Cu-Cl and Cu-N bond lengths (Table S7). Thus the solvent-dependent thermochromic behavior for FJU-53-Cl is attributed to the thermally induced vibration of the infinite copper-chlorine chains. During the first run of heating, the solvents occupying the channels may restrict the expansion of the infinite Cu-X chains and simultaneously adsorb the energy so that the FJU-53-Cl framework expands along the c direction, resulting in no obvious thermochromic behavior observed. Once the solvents released, the frameworks may absorb the energy, which induce the vibration of the copper halide chain upon heating, thus FJU-53-Cl shows clear thermochromic behavior during the second run.

Similar to those in **FJU-53-CI**, the feature of structural change in **FJU-53-Br** during the second run of thermochromic process is the $d_{Cu \cdots Cu}$ distance and $\theta_{Cu-Br-Cu}$ angle rises from 3.622 Å to 3.657 Å and from 80.06° to 80.86°, respectively, upon increasing temperature from 100 K to 350 K. The striking difference for the two MOFs is their structural change during the first run before the solvents release. With increasing the temperature from 100 K to 200 K, the $d_{Cu \cdots Cu}$ distance in **FJU-53-Br** increases from 3.674 to 3.684 Å and the $\theta_{Cu-Br-Cu}$ angle rises from 81.39° to 81.46° (**Figures 5c-d**), whereas no obvious change for these two parameters is observed in **FJU-53-CI**. The larger Br⁻ ion with more dispersive electron cloud than Cl⁻ results in the more easily thermochromic behavior for **FJU-53-Br** even containing the solvents. Thus, our two MOFs **FJU-53** show the attractive solvent- and halogen-dependent thermochromic behaviors due to the thermally induced vibration of the infinite copper-halogen chains. Its thermochromic mechanism obviously distinguishes from those for the purely inorganic copper halides.^{64,65}

CONCLUSIONS

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In summary, we have successfully synthesized two isostructural cationic microporous metal-organic frameworks (FJU-53) containing infinite zigzag copper-halogen chains and first demonstrated that the adsorption selectivity toward C_2/C_1 mixtures in the charged MOFs can be improved by modulating the interactions between counterions and the trapping gas molecules. Crucially, FJU-53 shows the highest adsorption selectivity for C_2H_2/CH_4 purification, and ultrahigh chemical stability in the aqueous solutions with pH ranging from 1 to 13. Meanwhile, FJU-53 also shows solvent- and halogen-dependent thermochromic behaviors owing to the thermally induced vibration of the $[(CuX)_n]^{n+}$ chains. Its thermochromic mechanism obviously distinguishes from those for the purely inorganic copper halides. Our research not only provides a new route for the charged MOFs toward the highly selective adsorption of C_2/C_1 mixtures, but also develops CuX_2 -based MOF as a new platform for multifunctional materials.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, table for selected bond lengths and bond angles, additional structural figures, ¹H NMR spectrum, FT-IR spectra, TGA curves, DSC profiles and gas absorption isotherms. This information is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*zzhang@fjnu.edu.cn

*scxiang@fjnu.edu.cn

ORCID

Shengchang Xiang: 0000-0001-6016-2587

Zhangjing Zhang: 0000-0003-1264-7648

Yingxiang Ye: 0000-0003-3962-8463

Author Contributions

[#]Lihua Wang and Yingxiang Ye contributed equally to this work.

Notes

The authors declare no competing financial interest.

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Highly Selective Adsorption of C₂/C₁ Mixtures and Solvent-dependent Thermochromic Properties in Metal-Organic Frameworks Containing Infinite Copper-Halogen Chains

Lihua Wang,[#] Yingxiang Ye,[#] Ziyin Li, Quanjie Lin, Jun Ouyang, Lizhen Liu, Zhangjing Zhang,* and Shengchang Xiang*



We have synthesized two isostructural cationic MOFs containing infinite copper-halogen chains and firstly demonstrated that the adsorption selectivity toward C_2/C_1 mixtures in the charged MOFs can be improved by tuning counter-anions. **FJU-53** shows the highest selectivity for C_2H_2/CH_4 separation, ultrahigh chemical stability, and solvent- and halogen-dependent thermochromic behaviors owing to the thermally induced vibration of the copper-halogen chains.