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Self-assembly of Homochiral Porous Supramolecular Organic Frameworks with Significant CO_2 Capture and CO_2/N_2 Selectivity

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ABSTRACT

A pair of homochiral porous supramolecular organic frameworks (**JLU-SOF1-R** and **JLU-SOF1-S**) has been assembled from brand-new enantiopure blocks via hydrogen-bonding and π-π interactions. The frameworks not only maintain crystallinity well until 250 ^{o}C but also exhibit a steep slope N_2 adsorption isotherm at 77 K with moderately high surface areas, indicating that the new materials own robust structure and permanent porosity. **JLU-SOF1-R** shows excellent adsorption capacity for CO_2 and C_2H_6 at ambient conditions. Remarkably, the material takes up a significant amount of CO_2, up to 213 cm^3 g^{-1} at 195 K under 1 bar. Furthermore, **JLU-SOF1-R** exhibits high selectivity towards CO_2 over N_2 and CH_4 as well as C_2H_6 over CH_4.

INTRODUCTION

Porous materials, from traditional zeolites,[1] mesoporous silicas[2] and carbons[3] to metal-organic frameworks (MOFs),[4,5] porous organic frameworks (POFs),[6-9] with superior properties have been extensive investigated in many fields, such as separation, catalysis, sensing, biomedicine, ferroelectric and others.[10-13] In recent years, MOFs with structural diversity have been largely developed thanks to the majority of linkers, which can coordinate metals in many different ways.[14,15] Compared with MOFs, POFs constructed by light elements (*etc.* C, H, O, N, B) with low framework density have aroused more attention.[7-9,] However, the development and practical applications of covalent-organic frameworks (COFs) have been limited by the reason of expensive catalyst, strict reaction conditions and synthetic complexity. Nevertheless, supramolecular organic frameworks (SOFs) can be easily achieved through simple recrystallization, which avoids cumbersome operations of synthesis.[16-20] Furthermore, the advantage of SOF-based materials is straightforward recycling through dissolution and recrystallization, suggesting that the materials are promising for the applications in industry.

Inspired by the above superiorities of porous SOFs, many kinds of applications, such as adsorption and separation of gases and liquids,[21-30] proton conduction[31,32] and fluorescence probe,[12,33,34] have been exploited by the groups of Chen, Zhong, Mastalerz, Ghosh and Tohnai as well as others. For molecular constituents, owning electron donor-acceptor component on external is the fundamental requirement and in this case, the building units will engender hydrogen-bonding, π-π stacking and van der Waals interactions. These primary driving forces will assemble building blocks to form diverse porous supramolecular aggregates. To date, lots of organic molecular constituents have been selected as building blocks to assemble porous SOFs.[8,35-38] A pioneering example of the ideal hydrogen-bonding motif is the 2,4-diaminotriazine

(DAT) molecule, proposed by Wuest and co-workers.[39-41] Recently, Chen *et al.* designed a series of organic molecules through incorporating DAT moiety on various central backbones to generate robust porous hydrogen-bonded organic frameworks (HOFs).[19,21-23] Besides, other functional groups, notably amide,[20] carboxyl,[24] pyridly,[25] urea[26] or sulphonyl,[31] have been also introduced into a number of molecular constituents to realize the assembly of porous SOFs. Despite all that, most of them are rigid and exhibit high symmetry. Therefore, the design and synthesis of new molecular constituents with special steric configuration to form distinctive porous SOFs, are vitally important.

Herein, we designed and synthesized a pair of novel enantiopure molecules (**R-H_4L** and **S-H_4L**) with flexible and irregular shape, which were comprised of two amide and four carboxyl groups. These functional sites can sever as electron donor-acceptor components to generate multiple hydrogen bonds. The excellent characteristic indicates that the molecular constituents as promising building units are expected to form the stable and distinctive frameworks. As anticipated, the homochiral SOFs, **JLU-SOF1-R** and **JLU-SOF1-S**, were constructed based on the molecular constituents, **R-H_4L** or **S-H_4L** respectively, via hydrogen-bonding and π-π interactions. The frameworks display high thermal stability and permanent porosity. Particularly, **JLU-SOF1-R** exhibit excellent adsorption capacity for CO_2 and C_2H_6 as well as high selectivity towards CO_2/N_2, CO_2/CH_4 and C_2H_6/CH_4.

EXPERIMENTAL SECTION

Materials and Physical Characterizations

All reagents and starting materials were purchased from commercial sources, which were used as received and without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 300 MHz NMR spectrometer. Elemental analyses (C, H and N) were collected on a vario MICRO elemental analyzer. Fourier transform infrared (FT-IR) spectra were carried out with a Bruker IFS-66v/S FTIR spectrometer in the range of 400-4000 cm^{-1} using the KBr pallet. Powder X-ray diffraction (PXRD) measurements were achieved by using a Rigaku D/max-2550 diffractometer with Cu-Kα radiation (λ = 1.5418 Å). Thermal gravimetric analyses (TGA) were performed on a TGA Q500 thermogravimetric analyzer with a heating rate of 10 °C/min in air. The circular dichroism (CD) and UV spectra were recorded on a JASCO J-815 spectropolarimeter using a 1.0-cm cell. Surface areas were measured by N_2 adsorption isotherms using a Micromeritics ASAP 2040 instrument at 77 K. CO_2 adsorption isotherm at 195 K was recorded with a Micrometrics ASAP 2020 instrument. N_2, CO_2, CH_4, and C_2H_6 adsorption isotherms at 273 and 298 K were measured with a Micrometrics ASAP 2020 PLUS HD88 and a Micrometrics 3-Flex instruments. The GC measurements were performed on FULI GC9790-2 gas chromatograph.

The molecules, **R-H_4L** and **S-H_4L**, were successfully synthesized in good yield on a large scale and confirmed by ^{1}H NMR spectra, ^{13}C NMR spectra, elemental analyses and IR spectra (Figure S1-S5). The synthetic route for **R-H_4L** was presented in Scheme 1 and the detailed synthesis information was given as follows:[42]

Synthesis of trimethyl-1, 3, 5-benzenetricarboxylate (M1). Benzene-1, 3, 5-tricarboxylic acid (16.8 g, 80 mmol) was dissolved in dry methanol (300 mL). Then, concentrated sulfuric acid (5 mL) was added to the solution and the mixture was refluxed for 12 h. Excess methanol was removed by rotary evaporation. The residue was slowly added to the saturated sodium bicarbonate solution (600 mL), and stirred at room temperature for a few minutes, then filtered to result in **M1** as a white solid (19.2 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.86 (s, 3H), 3.98 (s, 9H).

Synthesis of 3, 5-bis(methoxycarbonyl)benzoic acid (M2). M1 (12.6 g, 50 mmol) was dissolved in methanol (500 mL), then aqueous sodium hydroxide (50 mL, 45 mmol) was slowly added to the solution and the mixture was stirred vigorously for 15 h under reflux. The solution was removed under reduced pressure and the residue was added to the saturated sodium bicarbonate solution (9.5 g, 90 mmol) with stirring for 1 h at 50 ^{o}C. The suspension was filtered to remove the unreacted starting material (**M1**), then the filtrate was acidified with concentrated hydrochloric acid. The formed precipitate was filtrated and washed with deionized water to give **M2** as a white powder (7.8 g, 73%). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 13.69 (s, 1H), 8.64 (d, J=1.8 Hz, 2H), 8.62 (d, J=1.5 Hz, 1H), 3.93 (s, 6H).

Synthesis of tetramethyl-5, 5'-(((1R, 2R)-cyclohexane-1, 2-diylbis(azanediyl)) bis(carbonyl))diisophthalate (R-M4). To a solution of **M2** (4.76 g, 20 mmol) in freshly distilled $SOCl_2$ (30 mL) with stirring, a few drops of dimethylformamide (DMF) was added and heated at 90 ^{o}C for 2 h under nitrogen atmosphere. The excess $SOCl_2$ was removed by rotary evaporation to result in dimethyl-5-(chlorocarbonyl)-isophthalate (**M3**) as a white solid. In order to get the target molecule, (1R, 2R)-cyclohexane-1, 2-diamine (1.14 g, 10 mmol) was added to a solution of **M3** in dry CH_2Cl_2 (30 mL) under nitrogen atmosphere and ice-water bath conditions. Then, triethylamine (4.2 mL, 30 mmol) was added dropwise, and the mixture was stirred for 6 h at room temperature. The precipitate was filtered and washed with CH_2Cl_2, then the filtrate was concentrated by rotary evaporation. The resulting residue was purified by column chromatography (SiO_2: EtOAc/CH_2Cl_2, 1:2) to give **R-M4** as a white powder (3.4 g, 61%): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.74 (t, J=3 Hz, 2H), 8.57 (d, J=1.8 Hz, 4H), 7.08 (d, J=7.5 Hz, 2H), 4.08 (m, 2H), 3.93 (s, 12H), 2.24 (m, 2H), 1.87 (m, 2H), 1.46 (m, 4H).

Synthesis of 5, 5'-(((1R, 2R)-cyclohexane-1, 2-diylbis(azanediyl))bis(carbonyl)) diisophthalic acid (R-M5, R-H_4L). Aqueous NaOH solution (2 g, 50 mmol) was added to a solution of **R-M4** (5.54 g, 10 mmol) in MeOH (100 mL). The reaction mixture was stirred and heated under reflux for 12 h. The mixture was concentrated by rotary evaporation to remove MeOH and the residue was diluted into deionized water (200 mL), and then acidified with concentrated hydrochloric acid. The resulting precipitate was collected by filtration, washed with deionized water and dried under vacuum to give the final product (**R-H_4L**) as a white solid (4.2 g, 84%): ^{1}H NMR (300 MHz, DMSO-d_6, 25^{o}C) δ (ppm): 13.39 (s, 4H), 8.74-8.72 (d, *J*=7.5 Hz, 2H), 8.52-8.51 (d, *J*=1.8 Hz, 4H), 8.50-8.49 (t, *J*=3 Hz, 2H), 4.04 (m, 2H), 1.92-1.87 (d, *J*=12.3 Hz, 2H), 1.78-1.75 (d, *J*=8.4 Hz, 2H), 1.59-1.56 (m, *J*=9.6 Hz, 2H), 1.34-1.23 (m, *J*=31.8 Hz, 2H); ^{13}C NMR (300 MHz, DMSO-d_6, 25^{o}C) δ (ppm): 166.20, 164.64, 135.86, 132.03, 131.45, 52.97, 31.59, 24.85; Elemental analysis (%) Calcd for **R-H_4L** $C_{24}H_{22}N_2O_{10}$: C 57.83, H 4.45, N 5.62; found: C 56.26, H 4.56, N 5.40.

Preparation of JLU-SOF1-R and JLU-SOF1-S. R-H_4L/S-H_4L (0.5 g) was dissolved into ethanol solution (60 mL), then vapored dichloromethane to the solution at room temperature for 24 h. The colorless and highly crystalline block single crystals, **JLU-SOF1-R/JLU-SOF1-S**, were collected and dried in air with the yield of 81%.

X-ray Structure Determinations

Crystallographic data of as-synthesized **JLU-SOF1-R** and **JLU-SOF1-S** were collected on a Bruker Apex II CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at room temperature. The structures of the two crystals were solved by direct method and refined by full-matrix least-squares on F^2 (SHELXTL). All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located geometrically with isotropic parameters. The detailed crystal data and structure refinements were presented in Table S1, and the hydrogen bond data for **JLU-SOF1-R** and **JLU-SOF1-S** were given in Table S2 and S3, respectively. The supplementary crystallographic data of the two compounds (CCDC numbers 1548522 and 1548523) can be obtained free of charge from the Cambridge Crystallographic Data Centre upon request at www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Structure Descriptions

Single-crystal X-ray diffraction (SCXRD) analyses of **JLU-SOF1-R** and **JLU-SOF1-S** reveal that they are enantiomers and crystallize in orthorhombic system with chiral space group $C222_1$. Herein, we describe the structure of **JLU-SOF1-R** in detail. As depicted in Figure 1a, each molecular constituent, **R-H$_4$L**, is connected with four adjacent ones via six pairs of strong intermolecular hydrogen bonds. There are two types of hydrogen bonds existing in the crystal structure (Figure S6). One is formed by carboxyl and amide group, the other one is formed between two carboxyl groups. Moreover, the distances of O-H···O are 2.580(3), 2.589(3), 2.660(3) and 2.690(3) Å as well as the distances of N-H···O are 2.726(7), 2.913(7) and 2.941(7) Å, indicating that the strong hydrogen bonds exist in the framework (Table S2 and S6). Additionally, the distance of the π-π stacking was measured to be 3.84 Å based on center-to-center distance among the adjacent aromatic rings, which further enhances the stability of the framework (Figure 1b and Table S6).[18] Upon hydrogen-bonding and π-π interactions, a robust three-dimensional supramolecular framework was generated with one-dimensional apertures of 5.1 Å and 4.5 Å in diameter along [001] and [100] directions, respectively (Figure 1c-1f, taking into account the van der Waals radius). Topologically, if one considers the amide group as a 4-connected node and each isophthalic acid group as a 3-connected node (Figure S7a).

Consequently, the framework of **JLU-SOF1-R** can be rationalized as a novel (3, 3, 4)-connected supramolecular network (Figure S7b). Meanwhile, the existence of infinite right-handed helical chains running along the x-axis is another protruding feature for **JLU-SOF1-R** (Figure S8a). The total solvent-accessible volume was estimated to be 30.5% of the cell volume by PLATON, indicating that **JLU-SOF1-R** possesses high porosity and potentials for gas adsorption.

The crystalline phase purities of **JLU-SOF1-R** and **JLU-SOF1-S** were confirmed by obvious similarity between experimental PXRD pattern and the simulated one based on SCXRD data (Figure S9a and S10a). For the as-synthesized **JLU-SOF1-R** and **JLU-SOF1-S**, TGA were performed to assess their thermal stability (Figure S11). The results indicate that the materials can be stable up to 350 ^{o}C, after that the curves exhibit a rapid decline corresponding to the decomposition of the frameworks. To further understand the stability of the structures for **JLU-SOF1-R** and **JLU-SOF1-S**, variable-temperature PXRD were executed thoroughly from room temperature to 250 ^{o}C in the air atmosphere. As shown in Figure S9b and S10b, no obvious change was observed in the patterns with temperature increasing, which proves that the frameworks maintained crystallinity well. Above all, **JLU-SOF1-R** and **JLU-SOF1-S** exhibit high thermal stability, comparable to the famous MOFs and COFs materials, which is due to the collaborative strong hydrogen-bonding and consecutive π-π stacking interactions. The CD and UV spectra of **JLU-SOF1-R** and **JLU-SOF1-S** were recorded and are shown in Figure S12. For **JLU-SOF1-R**, the CD spectrum showed positive signal at 236 nm and negative signal at 206 nm, while, a mirror image was observed from the spectrum of **JLU-SOF1-S**, confirming that they are enantiomers.

Adsorption and Separation Behaviors

To probe the permanent porosity of **JLU-SOF1-R** and **JLU-SOF1-S**, reversible N_2 sorption measurements were confirmed at 77 K. The isotherms show a steep slope uptake at low P/P_0 values, which are the characteristic of microporous materials with typical type-I isotherms (Figure 2a). The Brunauer-Emmett-Teller (BET) surface areas of **JLU-SOF1-R** and **JLU-SOF1-S** were calculated to be 460 and 426 m^2 g^{-1}, respectively. The values exceed that of the homochiral HOF-2a[22] and are similar to that of SOF-1a.[29] The experimental pore volumes of **JLU-SOF1- R** and **JLU-SOF1-S** are 0.21 and 0.22 cm^3 g^{-1}, which are close to the theoretical values, 0.28 and 0.29 cm^3 g^{-1}, deduced from crystal structures, respectively. Based on the high stability and porosity, the adsorption performances on **JLU-SOF1-R** towards small molecules were investigated.

Encouraged by the practical application for the reduction in greenhouse gas emissions, developing safe and effective materials to capture CO_2 has become a hot research theme. The storage capacity of CO_2 was studied on **JLU-SOF1-R** at ambient conditions. As anticipated, the adsorption amounts of CO_2 for **JLU-SOF1-R** are 76 and 53 cm^3 g^{-1} at 273 and 298 K under 1 bar, respectively (Figure 2c). The values are higher among crystalline SOF-based materials, such as SOF-7a,[20] HOF-3a[23] and so on[43-45] (Table S4). Of special note, the significant amount of CO_2 uptake for **JLU-SOF1-R** is 213 cm^3 g^{-1} at 195 K under 1 bar, which extremely exceeds the value of most of materials in this field (Figure 2b and Table S4). The outstanding adsorption capacity may be attributed to the strong host-guest interactions between CO_2 molecules and host cavities. To acquire further insight into the affinity behavior, the isosteric CO_2 adsorption enthalpy (Q_{st}) of **JLU-SOF1-R** was calculated at zero coverage. Expectedly, the Q_{st} value of CO_2 is as high as 34.3 kJ mol^{-1}, which is much higher than those of vast majority of porous materials (Figure S14b and Table S5). Moreover, the special quadrupole moment of CO_2 will enhance the storage capacity of **JLU-SOF1-R**. Single-component gas sorption isotherms of C_2H_6, CH_4 and N_2 were executed on **JLU-SOF1-R** at 273 and 298 K under 1 bar, respectively. **JLU-SOF1-R** exhibits notable adsorption values of C_2H_6, up to 70 and 57 $cm^3\ g^{-1}$, which are dramatically higher than those of HOF-4a (Figure 2d).[27] In contrast, the adsorption amounts of CH_4 (37 and 22 $cm^3\ g^{-1}$) and N_2 (10.9 and 4.2 $cm^3\ g^{-1}$) are much lower than the values of CO_2 and C_2H_6 on **JLU-SOF1-R** under the same conditions (Figure 2e and 2f). Such a large difference between their adsorption amounts indicates that **JLU-SOF1-R** can serve as gas separator in practical applications.

As is well-known, the selective separation of CO_2 over N_2 is a tough issue in chemistry, environmental science and industry due to the analogous kinetic diameters of CO_2 (3.3 Å) and N_2 (3.64 Å). Therefore, developing efficient materials to solve the issue is crucially important. Herein, **JLU-SOF1-R** was used to detect the selectivity of binary mixtures of CO_2 with N_2. The separation ability was calculated by ideal solution adsorbed theory (IAST) model as a general method to predict binary mixture adsorption based on experimental single-component isotherms. Meanwhile, the dual-site Langmuir-Freundlish (DSLF) equation was adopted to fit the data at 298 K. As shown in Figure 3a and 3b, the selectivity of CO_2/N_2 (50% and 50%, 15% and 85%, 10% and 90%) for **JLU-SOF1-R** has been calculated to be 55.3, 31.2 and 29.3, respectively. It is noteworthy that the separation ability of CO_2/N_2 is higher than those of HOF-5a,[19] HOF-9a[28] and some MOF-based materials[46,47] under the same conditions. In addition, the obtained values of the selectivity of CO_2 over CH_4 (50% and 50%, 5% and 95%) are 3.9 and 3.7, respectively (Figure3c and 3d). The results suggest that the new porous SOFs may be a candidate material for post-combustion of greenhouse gas and purification of natural gas. Furthermore, the selectivity of equimolar C_2H_6/CH_4 binary mixture for **JLU-SOF1-R** is 18.7 (Figure S13). To the best of our knowledge, no other SOF materials were used to separate the two components, and the selectivity of **JLU-SOF1-R** even exceeds those of common MOFs under the same condition.[48,49] The delightful selectivity of C_2H_6/CH_4 for **JLU-SOF1-R** confirms that the material will become an important candidate to separate light hydrocarbons. In order to probe the high selectivity of C_2H_6/CH_4 on **JLU-SOF1-R**, the resulting Q_{st} of C_2H_6 and CH_4 were calculated according to the sorption isotherms at 273 and 298 K. At zero loading, the Q_{st} values of C_2H_6 and CH_4 are 32.3 and 18.9 kJ mol^{-1}, respectively (Figure S14d and S14f). Hence, the high selectivity may be ascribed to the discrepant gas affinity and host-guest interactions.

The homochiral porous nature of **JLU-SOF1-R** and **JLU-SOF1-S** motivates us to explore the application of enantioselective separation. Unfortunately, the frameworks exhibit limited enantioselectivity of racemic methyl lactate, which is possibly attributed to the steric hindrance and directional effect (Figure S15).

CONCLUSION

In summary, a pair of robust homochiral porous SOFs, **JLU-SOF1-R** and **JLU-SOF1-S**, was assembled from novel enantiopure constituents through hydrogen-bonding and π-π interactions. The two materials exhibit high thermal stability and permanent porosity. Notably, the materials not only show superior adsorption capacity for CO_2 and C_2H_6, but also display extremely selective separation of CO_2 over N_2 and CH_4 as well as C_2H_6 over CH_4 according to the different gas affinity. The advantages, that is, suitable pore sizes, easily synthesized and reused by simple recrystallization, make the porous SOF-based materials as prospective candidates for industrial applications in the near future.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format for **JLU-SOF1-R** and **JLU-SOF1-S**, CCDC: 1548522 and 1548523. Crystal data and structure refinement for **JLU-SOF1-R** and **JLU-SOF1-S**. These materials are available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interests.

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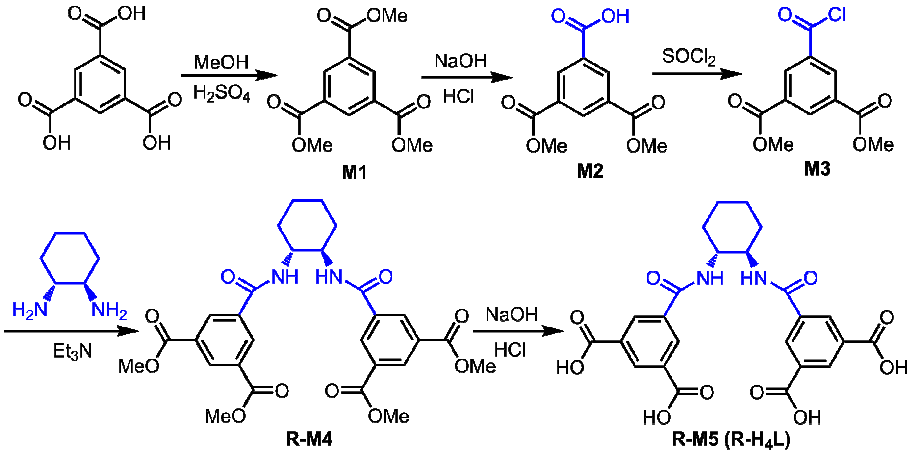
Figure Captions

Scheme 1 Synthetic route for **R-H$_4$L**.

Figure 1 Crystal structure of **JLU-SOF1-R** showing a) hydrogen-bonding and b) π-π stacking interactions among adjacent molecules; c) and d) ball-and-stick models as well as e) and f) CPK models along [001] and [100] directions.

Figure 2 a) N_2 sorption isotherms for **JLU-SOF1-R** and **JLU-SOF1-S** at 77K; b) CO_2 adsorption isotherm for **JLU-SOF1-R** at 195 K; c) CO_2, d) C_2H_6, e) CH_4 and f) N_2 adsorption isotherms for **JLU-SOF1-R** at 273 and 298 K under 1 bar.

Figure 3 CO_2, N_2 and CH_4 adsorption isotherms at 298 K along with the DSLF fits (a and c); gas mixture adsorption selectivity are predicted by IAST at 298 K under 1 bar for **JLU-SOF1-R** (b and d).



Scheme 1

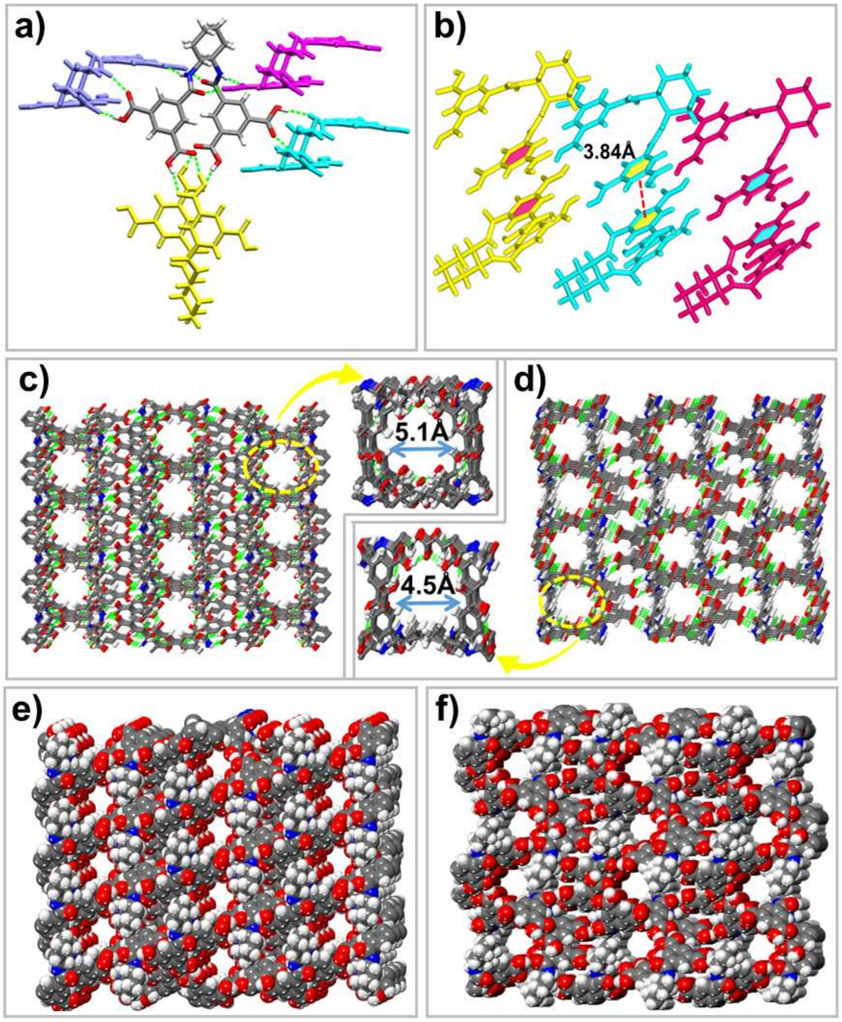


Figure 1

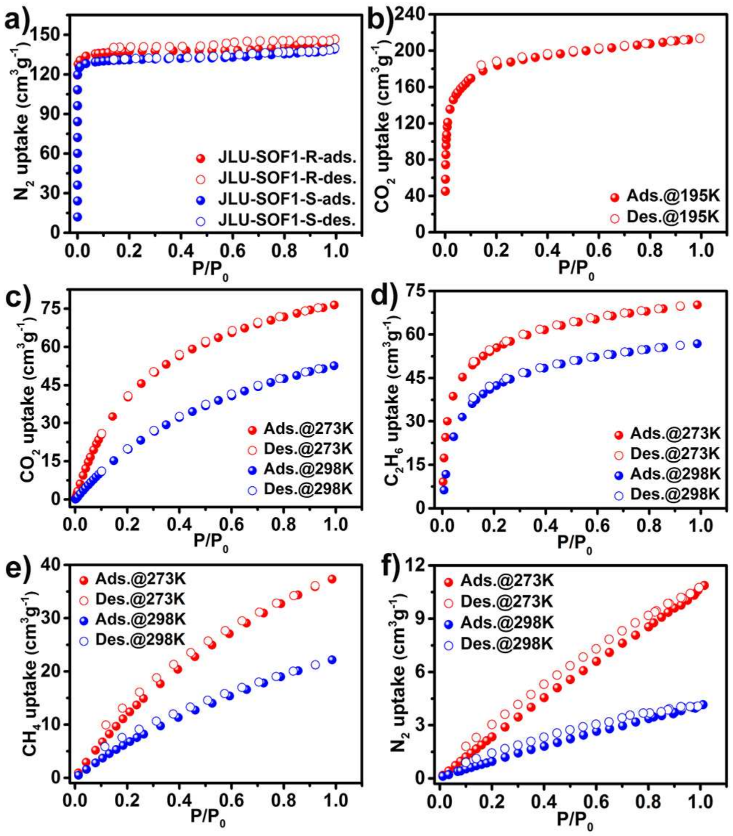


Figure 2

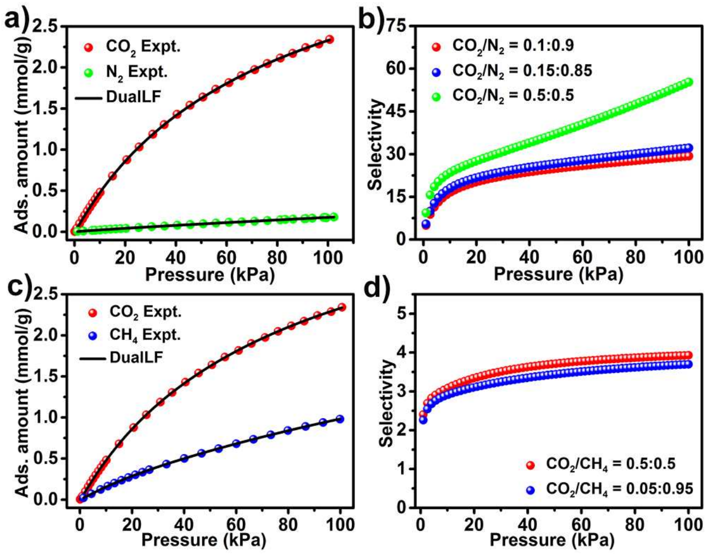
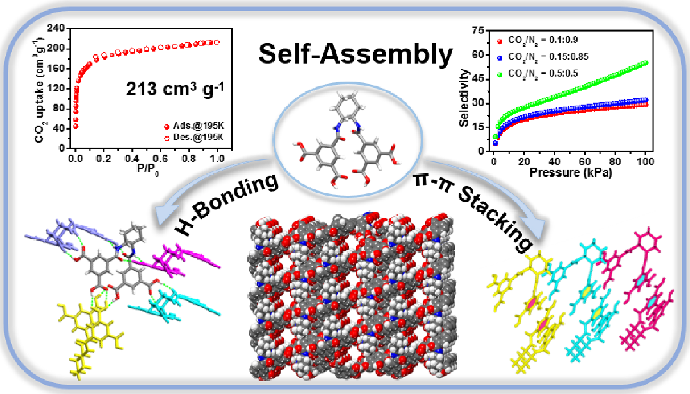


Figure 3

Table of Contents

Self-assembly of Homochiral Porous Supramolecular Organic Frameworks with Significant CO_2 Capture and CO_2/N_2 Selectivity

Yue Zhou, Bing Liu, Xiaodong Sun, Jiantang Li, Guanghua Li, Qisheng Huo and Yunling Liu*



Homochiral porous supramolecular organic frameworks, **JLU-SOF1-R** and **JLU-SOF1-S**, were assembled by brand-new enantiopure blocks via hydrogen-bonding and π-π interactions. The materials exhibit significant CO_2 capture and high separation ability towards CO_2 over N_2 and CH_4.