Supporting Information
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Temperature-Programmed Separation of Hexane Isomers by Porous Calcium Chloranilate Metal-Organic Framework

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Abstract: The full separation of alkane isomers as a function of different degrees of branching through complete molecular exclusion remains a daunting challenge due to its stringent requirement with respect to pore dimensions of the adsorbents. In this work, we report a novel microporous coordination network built on calcium (II) and chloranilate. The compound has a flexible framework and exhibits temperature-dependent adsorption behavior toward hexane isomers. At 30 °C, it accommodates substantial amounts of linear and monobranched hexanes but fully excludes their dibranched isomer, and thus serves as a splitter for linear/monobranched and dibranched alkanes. At elevated temperatures such as 150 °C, monobranched hexane is also prohibited to access the open channel of the compound, hence it also acts as a splitter for linear and branched alkanes at such temperatures. Its capability of efficient discrimination of hexane isomers as a function of branching is verified by experimental breakthrough measurements. *Ab initio* calculations have uncovered the underlying selective size-exclusion separation mechanism. The high performance of the compound renders it a potential candidate for industrial separation of alkane isomers.

DOI: 10.1002/anie.2021XXXXX

Experimental Procedures

Synthesis of HIAM-203: HIAM-203 was prepared via solvothermal reaction. $CaCl_2$ (0.5 g) and chloranilic acid (Alfa Asear, 0.5 g) were dispersed in ethanol (95%, 100 mL) in a 250 mL Teflon bomb (Xi'an Taikang Technology Co., Ltd.). The mixture was stirred for 2 hours at room temperature and was then transferred to an oven preset at 150 ºC and was kept for 2 days. Upon cooling to room temperature, purple strip-shaped crystals were obtained through filtration in 86.4% yield (based on metal salts).

General characterizations: Single-crystal X-ray diffraction data were collected at 190 K on a Bruker APEX-II CCD diffractometer using GaKα radiation tuned to λ = 1.34139 Å. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL package. Powder X-ray diffraction patterns were recorded on a Bruker D8 Advance with Cu Kα radiation (λ= 1.5406 Å). Data were collected at room temperature at 2θ = 5-30°. Thermogravimetric analysis was carried out on a TGA550 (TA Instruments) analyzer. For each run, 3-5 mg of sample was heated from room temperature to 600 °C at a ramp rate of 10 °C/min. Nitrogen adsorption at 77 K and light gas adsorption at ambient temperature were measured on a Micromeritics 3Flex analyzer, and vapor adsorption experiments were conducted on a Belsorp Max II analyzer. ~150 mg of as-synthesized MOF sample was activated under a dynamic vacuum at 150 °C overnight prior to data collection.

Column breakthrough measurements: Column breakthrough measurements were performed with a lab-scale fix-bed reactor. In a typical experiment, 1.0 g of MOF material was packed into a steel column (4.0 mm I.D. × 300 mm) with silane treated glass wool filling the void space. A helium flow (5 mL/ min) was used to purge the adsorbent. The MOF powder was activated at 150 °C overnight and the flow of helium was then turned off while another dry helium flow at a rate of 2 mL/min was bubbled through a mixture of hexane isomers according to the following volumes (the volumes were determined through trial and error and calculated by GC: the experiment was run without any sample and the vapor phase ratios were optimized to an equimolar mixture): 5.84 mL of nHEX, 4.12 mL of 3MP, and 2.57 mL of 22DMB for nHEX/3MP/22DMB ternary mixture. The effluent from the column was monitored using an online GC equipped with HP-PONA column and FID.

***Ab initio* calculations:** To gain a further molecular-level mechanistic understanding of the guest-host interactions, *ab initio* calculations with a plane-wave basis sets were performed using the VASP code. The crucial van der Waals interactions were included by using a non-local vdW-DF functional along with the standard PAW pseudopotentials.[1, 2, 3, 4] The calculations were performed in a $1 \times 1 \times 2$ supercell and only the gamma point was sampled. Our kinetic energy cut-off of 600 eV gave well-converged results. The geometry optimization criteria were kept tight: 10^{-7} eV for the SCF loop and 0.004 eV/Å for forces. For molecular diffusion within the MOF, an *ab initio* transition-state search was carried out using the climbing-image nudged elastic band (cNEB) method; 5 images were simulated between the initial and final geometry configurations. The energy of the loaded MOF was subtracted from the individual empty MOF and the isolated alkanes to get corresponding binding energies:

$$\mathrm{E}_b = E_{MOF} + E_{C6} - E_{loaded}$$

where E_{MOF} and E_{C6} are the energy of the activated MOF and isolated C_6 isomer, respectively. E_{loaded} represents the MOF loaded with C_6 isomers.

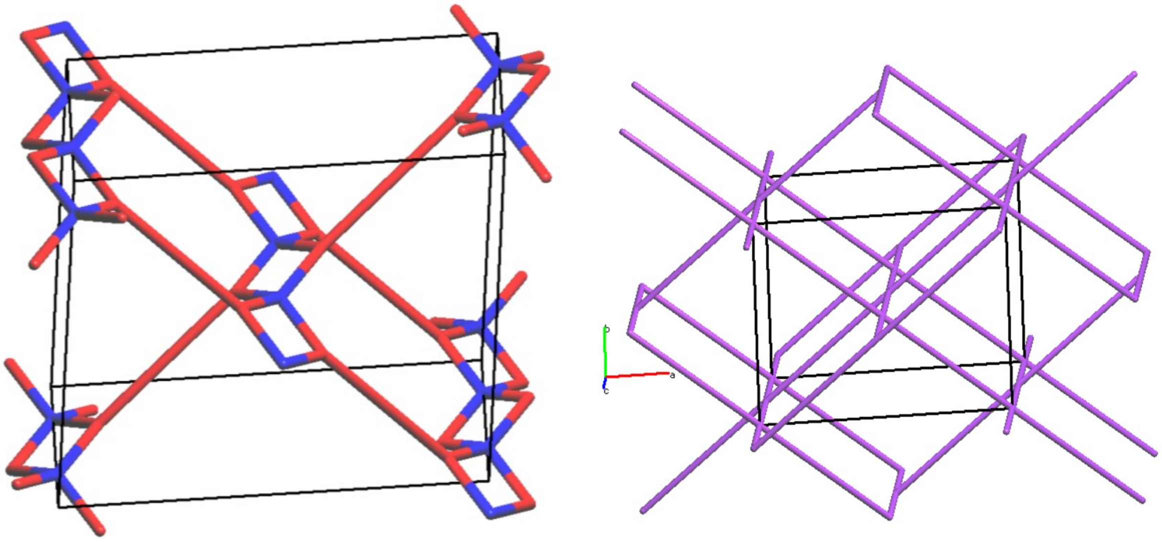

Figure S1. Topology of HIAM-203 described as 3,4-**dmd** (left) and 4-**cds** (right) nets.

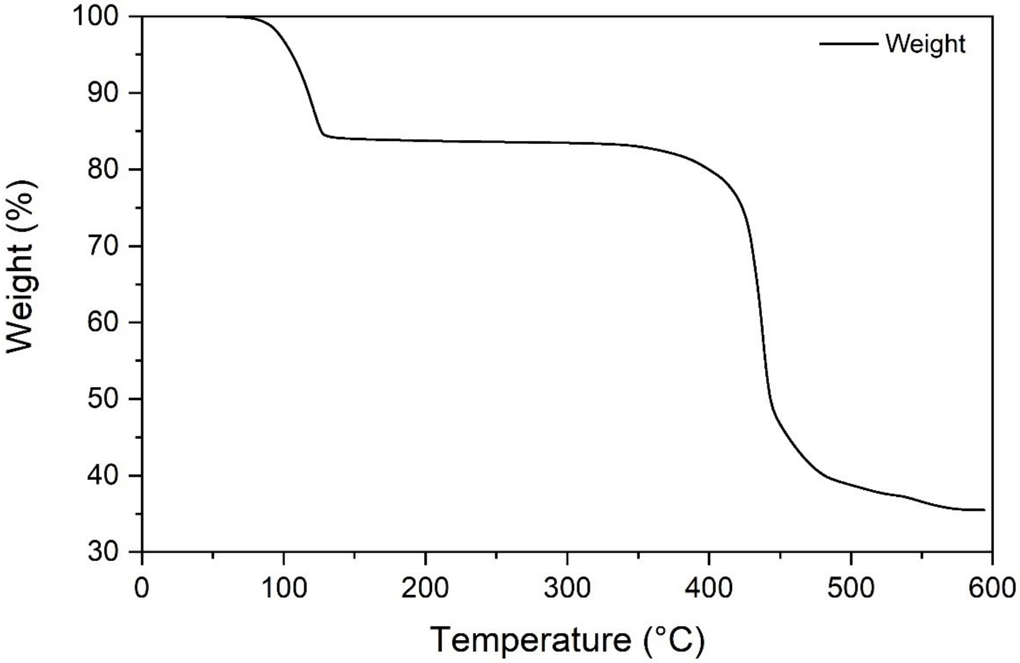

Figure S2. TGA curve of as-synthesized HIAM-203.

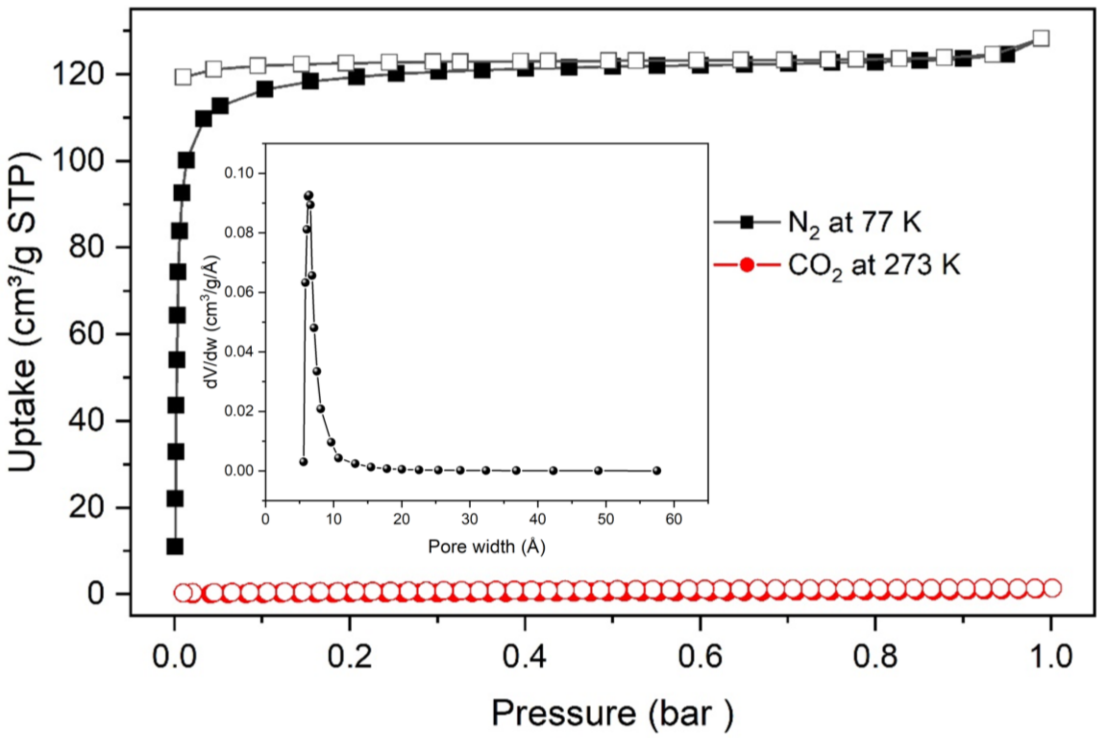

Figure S3. Adsorption-desorption isotherms of N_2 at 77 K and CO_2 at 273 K by HIAM-203. Insert: pore size distribution calculated from N_2 adsorption at 77K.

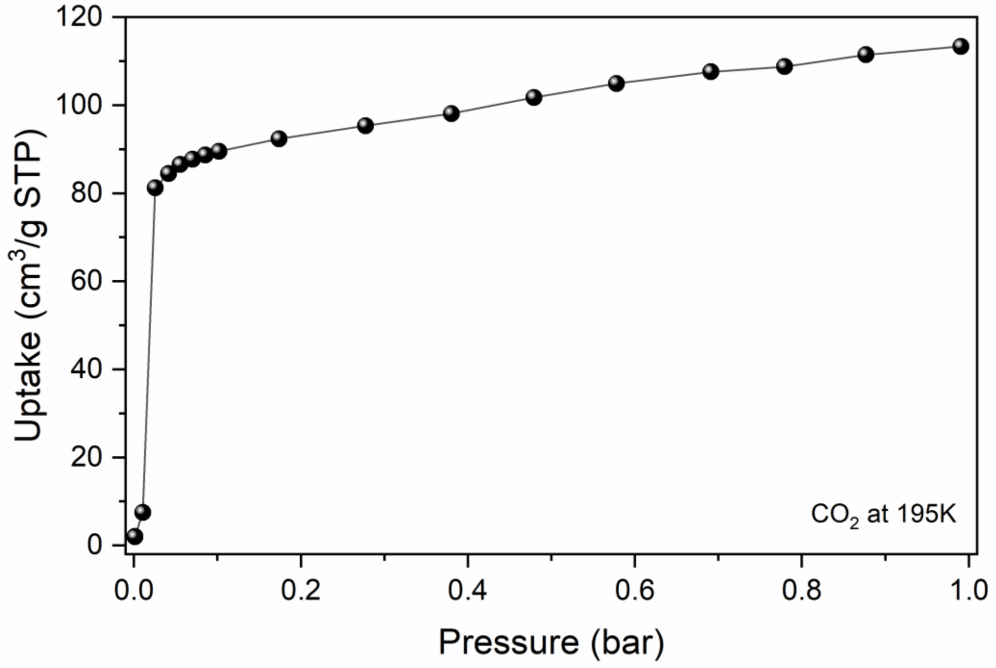

Figure S4. Adsorption isotherms of CO_2 at 195 K by HIAM-203.

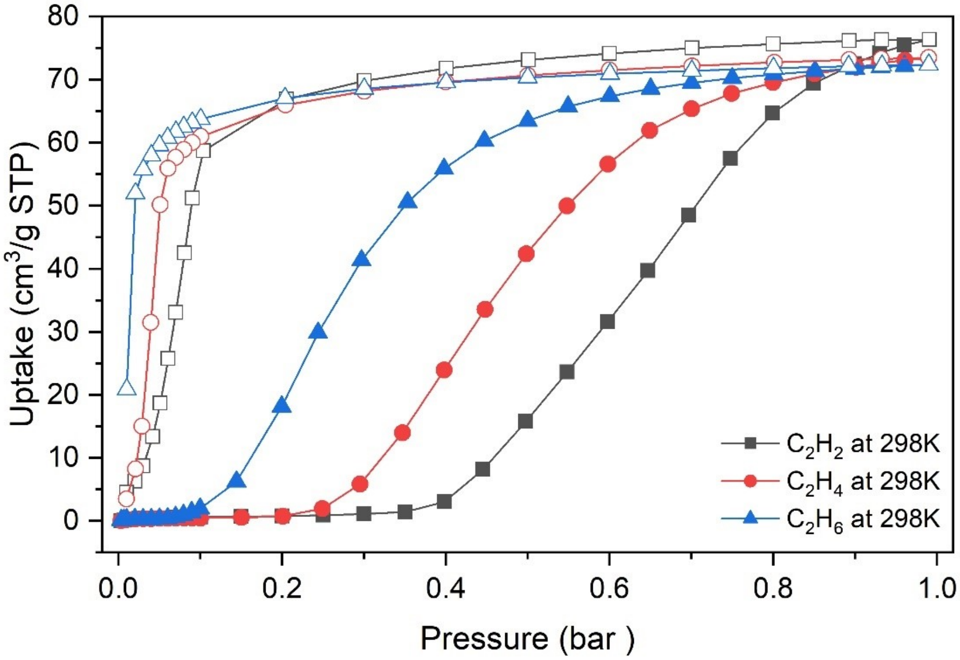

Figure S5. Adsorption-desorption isotherms of C_2H_2, C_2H_4, and C_2H_6 at 298 K by HIAM-203.

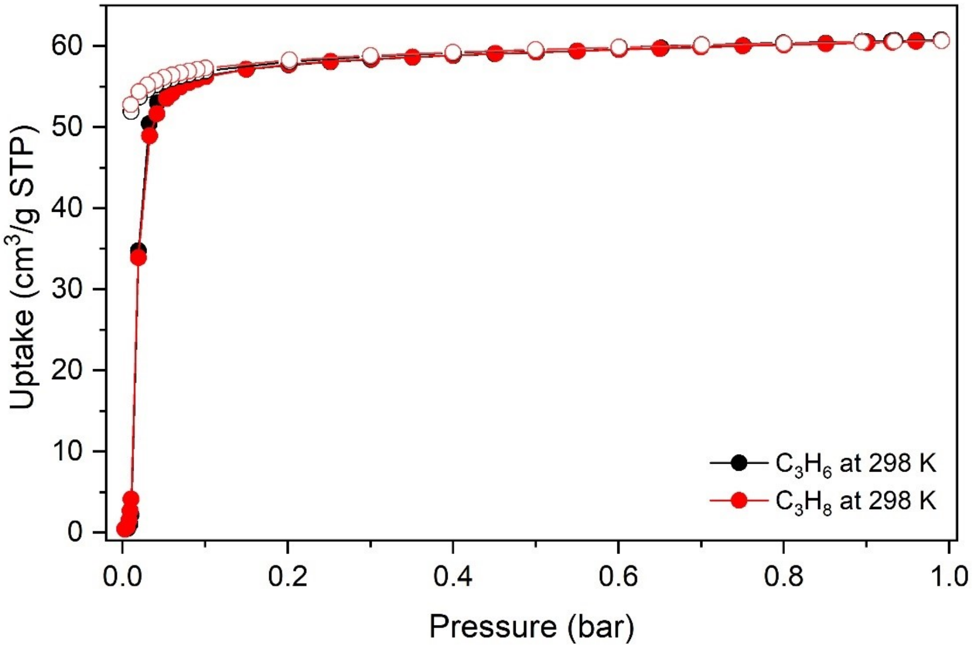

Figure S6. Adsorption-desorption isotherms of C_3H_6 and C_3H_8 at 298 K by HIAM-203.

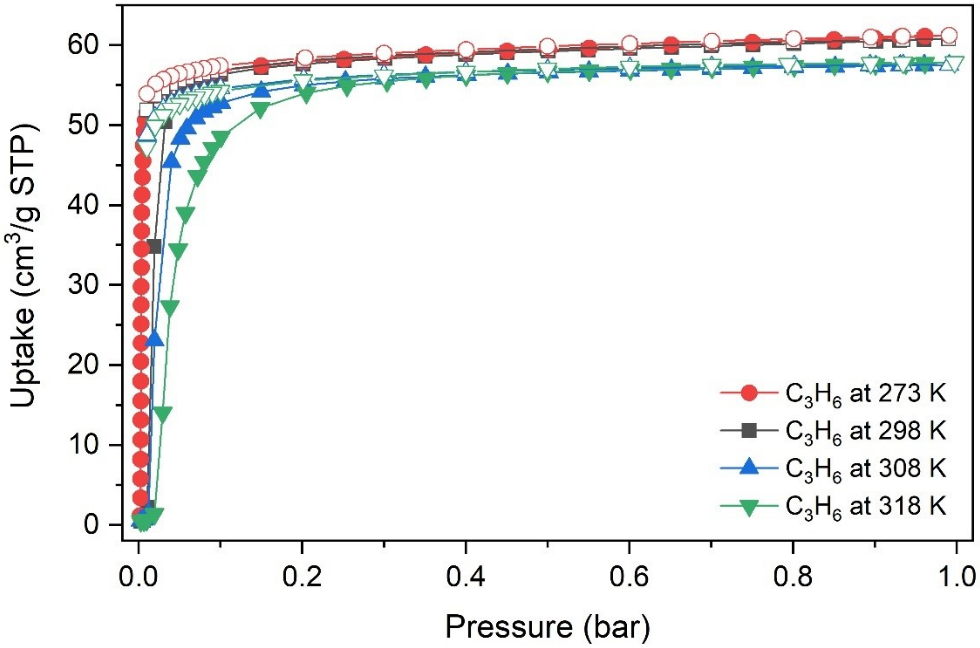

Figure S7. Adsorption-desorption isotherms of C_3H_6 at various temperatures by HIAM-203.

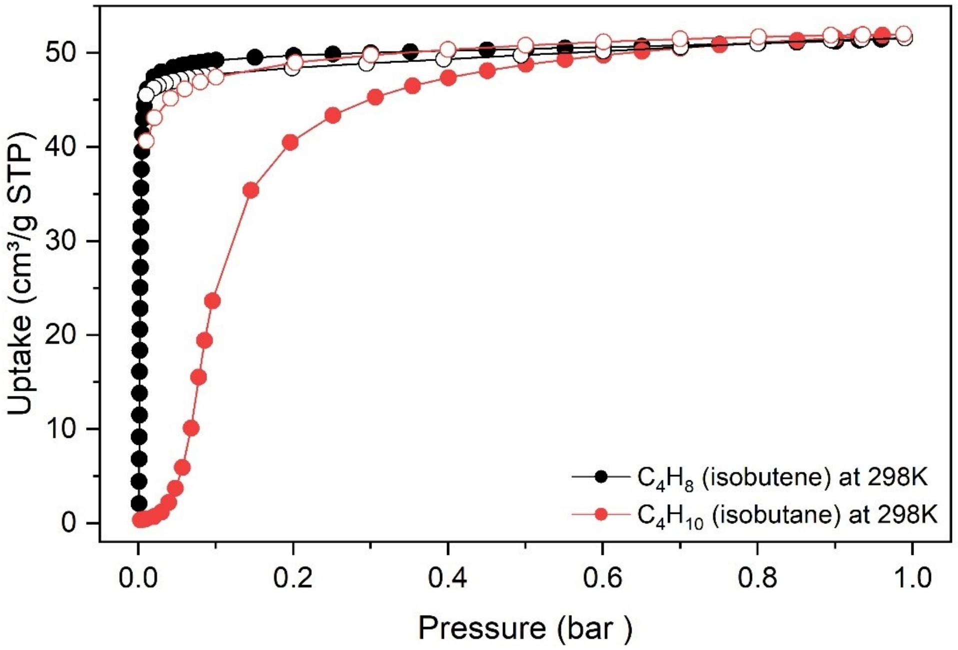

Figure S8. Adsorption-desorption isotherms of C_4H_8 and C_4H_{10} at 298 K by HIAM-203.

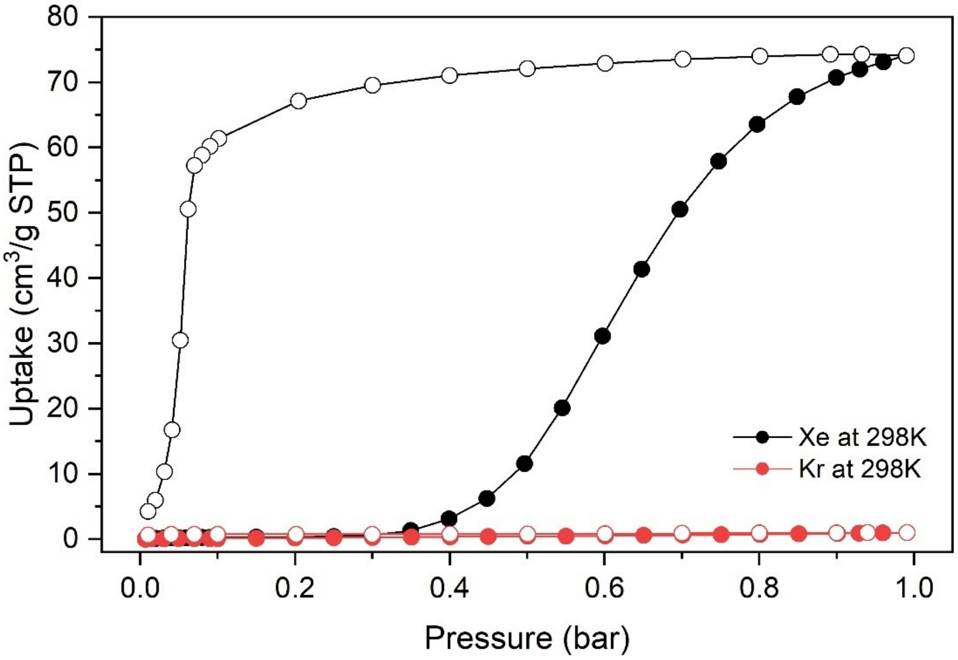

Figure S9. Adsorption-desorption isotherms of Xe and Kr at 298 K by HIAM-203.

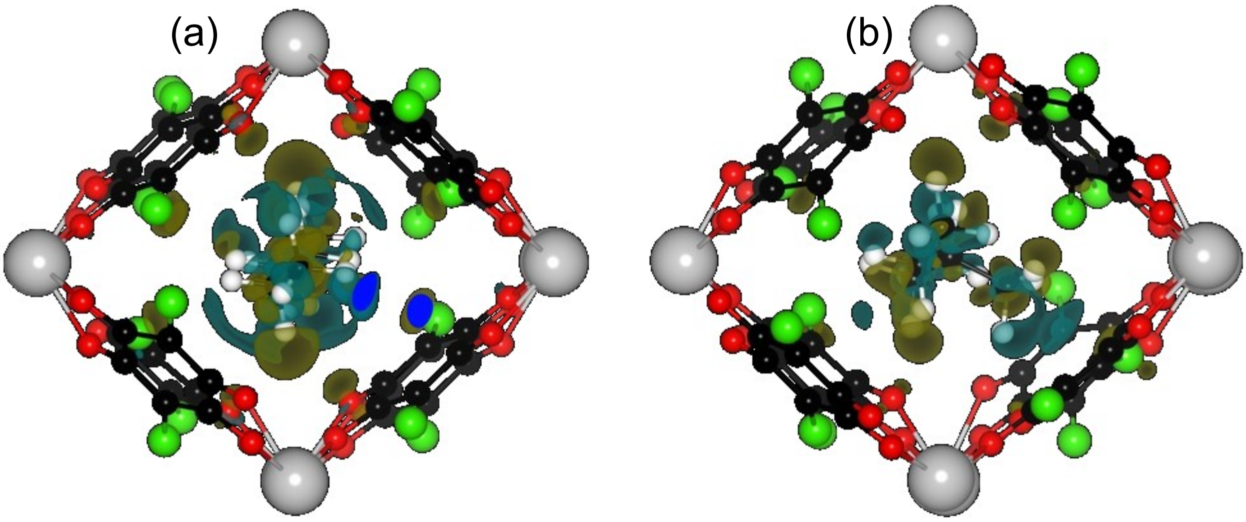

Figure S10. Induced charge density plots of (a) nHEX and (b) 3MP loaded MOF. Yellow and blue lubes show charge accumulation and depletion upon bond formation, respectively, at an iso-value of 0.0003 e.Å^{-3}.

Table S1. Crystal data and structure refinement for HIAM-203.

Identification code	HIAM-203	
Empirical formula	C8 H6 Ca Cl2 O5	
Formula weight	293.11	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 12.6576(6) Å	= 90°.
	b = 10.4995(6) Å	= 101.113(2)°.
	c = 7.7566(4) Å	= 90°.
Volume	1011.51(9) $Å^3$	
Z	4	
Density (calculated)	1.925 Mg/m^3	
Absorption coefficient	1.148 mm^{-1}	
F(000)	592	
Crystal size	0.140 x 0.110 x 0.090 mm^3	
Theta range for data collection	2.540 to 25.009°.	
Index ranges	-15<=h<=15, -12<=k<=9, -9<=l<=8	
Reflections collected	3665	
Independent reflections	899 [R(int) = 0.0338]	
Completeness to theta = 25.009°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	899 / 0 / 87	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0528, wR2 = 0.1082	
R indices (all data)	R1 = 0.0587, wR2 = 0.1125	
Largest diff. peak and hole	0.855 and -1.474 e.$Å^{-3}$	

References

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Author Contributions

Y. Lin: methodology, investigation, resources; L. Yu: investigation; S. Ullah: Validation, formal analysis; X. Li: formal analysis; H. Wang: conceptualization, investigation, supervision, funding acquisition, writing - original draft; Q. Xia: supervision; T. Thonhauser: Formal analysis, supervision; J. Li: conceptualization, supervision, writing – review & editing. All authors have given approval to the final version of the manuscript.