Electronic supplementary information

Identifying the best metal–organic frameworks and unravelling different mechanisms for the separation of pentane isomers

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1. Physical properties of C_5 isomers

Table S1 Physical properties of C_5 isomers.[1]

Isomer	Boiling point (°C)	Critical temperature (°C)	Critical pressure (bar)	Kinetic diameter (Å)
n-C_5	36.0	196.6	33.6	4.3
iso-C_5	27.7	187.8	33.8	5.0
neo-C_5	9.5	160.6	31.9	6.2

2. Adsorption energies of single C_5 isomers

Table S2 Adsorption energies of single C_5 isomers in MOFs with very large pores.

MOF	PLD (Å)	LCD (Å)	Δ*E* (kJ/mol)		
			n-C_5	*iso*-C_5	*neo*-C_5
BAZGAM	24.24	42.80	–18.61	–17.66	–15.64
BEDYEQ	31.49	33.06	–32.29	–30.48	–27.81
RAVXIX	56.26	53.58	–36.46	–35.06	–31.43
RAVXOD	71.50	71.64	–36.99	–34.91	–30.25

3. VICDOC

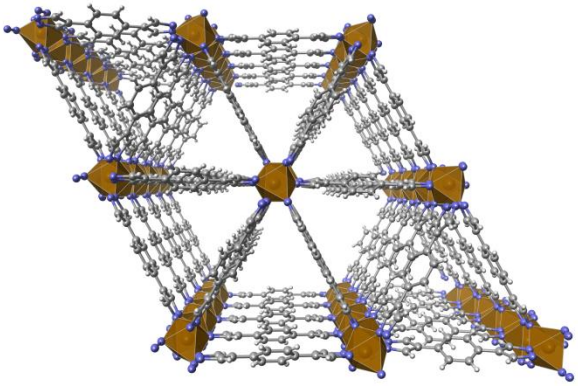


Fig. S1 VICDOC.

Table S3 Adsorption of equimolar C_5 isomer mixture in VICDOC at 373 K and a total pressure of 30 kPa.

N_{C_5} (mol/kg)	2.59
$N_{n\text{-}C_5}$ (mol/kg)	2.48
$N_{iso\text{-}C_5}$ (mol/kg)	0.11
$N_{neo\text{-}C_5}$ (mol/kg)	4.20×10^{-5}
$S_{n\text{-}/iso\text{-}C_5}$	22.97
$S_{n\text{-}/neo\text{-}C_5}$	5.91×10^{4}
$S_{iso\text{-}/neo\text{-}C_5}$	2.57×10^{3}

4. Best MOFs

Table S4 Best MOFs with six separation mechanisms.

Type		Separation*	Benchmark	CSD code	LCD (Å)	N_{C_5} (mol/kg)	$S_{n\text{-}/iso\text{-}C_5}$ [$S_{iso\text{-}/n\text{-}C_5}$]**	$S_{n\text{-}/neo\text{-}C_5}$ [$S_{neo\text{-}/n\text{-}C_5}$]**	$S_{iso\text{-}/neo\text{-}C_5}$ [$S_{neo\text{-}/iso\text{-}C_5}$]**
1		*n*-/*iso*-C_5 *n*-/*neo*-C_5	N_{C_5} > 1 mol/kg $S_{n\text{-}/iso\text{-}C_5}$ > 6000 $S_{n\text{-}/neo\text{-}C_5}$ > 10^4	ADIQEL	4.43	2.75 ± 0.04	(8.18 ± 0.69) × 10^4	> 10^6	
				WUCRUH	4.32	1.13 ± 0.06	(6.08 ± 1.42) × 10^3	> 10^6	
				HEXNII	4.82	1.17 ± 0.02	(1.50 ± 0.77) × 10^4	> 10^6	
				MIMVEJ	4.72	2.32 ± 0.05	(9.18 ± 2.85) × 10^5	> 10^6	
				FUDQIF	4.38	1.32 ± 0.06	> 10^6	> 10^6	
				PARMIG	4.62	2.20 ± 0.11	> 10^6	> 10^6	
2	2i	*n*-/*neo*-C_5 *iso*-/*neo*-C_5	N_{C_5} > 1.9 mol/kg $N_{iso\text{-}C_5}$ > 0.4 mol/kg $S_{n\text{-}/neo\text{-}C_5}$ > 400 $S_{iso\text{-}/neo\text{-}C_5}$ > 400	XUNGOD	5.28	2.31 ± 0.26		(4.88 ± 0.78) × 10^2	(4.22 ± 0.71) × 10^2
				GIFKAH	4.61	1.92 ± 0.33		> 10^6	> 10^6
				AFITEP	4.64	2.63 ± 0.36		> 10^6	> 10^6
	2ii	*n*-/*neo*-C_5 *iso*-/*neo*-C_5	N_{C_5} > 1.9 mol/kg $N_{iso\text{-}C_5}$ > 0.4 mol/kg $S_{n\text{-}/neo\text{-}C_5}$ > 400 $S_{iso\text{-}/neo\text{-}C_5}$ > 400	GOGWAB	4.96	2.82 ± 0.59		(1.06 ± 0.83) × 10^4	(7.52 ± 6.01) × 10^3
				WAZQIZ	5.13	2.15 ± 0.32		(2.10 ± 0.40) × 10^3	(1.15 ± 0.28) × 10^3
3	3i	*iso*-/*n*-C_5 *neo*-/*n*-C_5	N_{C_5} > 0.4 mol/kg $S_{iso\text{-}/n\text{-}C_5}$ > 8 $S_{neo\text{-}/n\text{-}C_5}$ > 10	INAMUG	5.66	0.89 ± 0.22	0.091 ± 0.077 [11.05 ± 9.43]	0.032 ± 0.023 [31.50 ± 23.27]	
				XUVGUQ	5.67	0.43 ± 0.09	0.053 ± 0.017 [18.78 ± 6.05]	0.032 ± 0.008 [31.18 ± 7.65]	
				MAJHUC	5.75	0.91 ± 0.29	0.119 ± 0.058 [8.38 ± 4.09]	0.088 ± 0.021 [11.32 ± 2.72]	
				OVICUS	5.89	1.26 ± 0.22	0.044 ± 0.026 [22.71 ± 13.43]	0.037 ± 0.022 [26.99 ± 15.79]	
				SEMFIB	6.30	1.98 ± 0.37	0.094 ± 0.068 [10.59 ± 7.60]	0.031 ± 0.020 [31.84 ± 20.48]	
				SEMFEX	5.92	2.14 ± 0.27	0.063 ± 0.015 [15.88 ± 3.89]	0.024 ± 0.003 [41.14 ± 5.42]	
	3ii	*iso*-/*n*-C_5 *neo*-/*n*-C_5	N_{C_5} > 0.7 mol/kg $S_{iso\text{-}/n\text{-}C_5}$ > 3 $S_{neo\text{-}/n\text{-}C_5}$ > 4	TACPAP	6.19	0.77 ± 0.23	0.332 ± 0.323 [3.00 ± 2.92]	0.201 ± 0.182 [4.98 ± 4.51]	
4		*neo*-/*n*-C_5 *neo*-/*iso*-C_5	N_{C_5} > 0.9 mol/kg $S_{neo\text{-}/n\text{-}C_5}$ > 15 $S_{neo\text{-}/iso\text{-}C_5}$ > 2	QUPJAN	5.93	0.95 ± 0.12		0.063 ± 0.050 [15.93 ± 12.68]	0.465 ± 0.078 [2.15 ± 0.36]
5		*iso*-/*n*-C_5 *iso*-/*neo*-C_5	N_{C_5} > 0.7 mol/kg $S_{iso\text{-}/n\text{-}C_5}$ > 2 $S_{iso\text{-}/neo\text{-}C_5}$ > 25	DAWBUA	5.53	1.64 ± 0.39	0.28 ± 0.16 [3.57 ± 2.02]		72.38 ± 13.96
				QARCET	5.63	1.21 ± 0.11	0.27 ± 0.04 [3.64 ± 0.58]		29.43 ± 3.79
				HIZQEN	5.11	1.66 ± 0.36	0.47 ± 0.17 [2.12 ± 0.77]		76.67 ± 47.86
				VAPFUP	5.16	0.75 ± 0.18	0.20 ± 0.13 [5.09 ± 3.45]		(7.04 ± 1.78) × 10^3
				ACOLIP	4.91	1.53 ± 0.36	0.39 ± 0.17 [2.53 ± 1.11]		(5.95 ± 5.06) × 10^3
				QULLEP	4.90	0.93 ± 0.21	0.26 ± 0.12 [3.86 ± 1.78]		> 10^6
6		*n*-/*iso*-C_5 *neo*-/*iso*-C_5	N_{C_5} > 1.0 mol/kg $S_{n\text{-}/iso\text{-}C_5}$ > 100 $S_{neo\text{-}/iso\text{-}C_5}$ > 100	ODOXEK	5.23	1.04 ± 0.12	189.27 ± 90.40		0.0029 ± 0.0015 [344.80 ± 173.76]

* *a*/*b*: *a* is preferentially adsorbed. If $S_{a/b}$ > 10^6, the capacity of *b* is vanishingly small. **[…]: inverse-shape selectivity in blue.

5. Adsorption capacity and selectivity *versus* ϕ, LCD and VSA

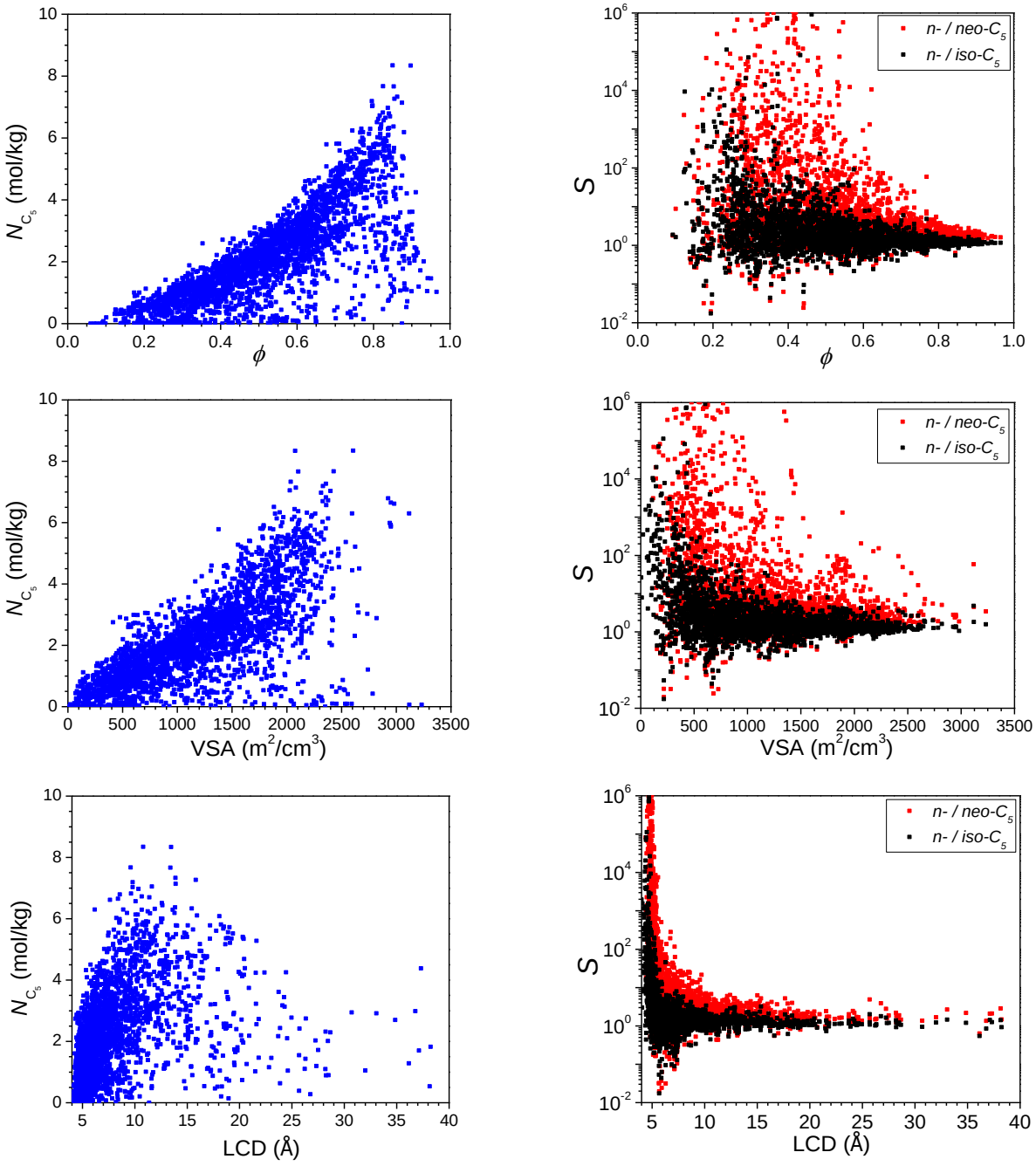


Fig. S2 Adsorption capacity and selectivity *versus* ϕ, VSA and LCD.

6. Pore size distribution between d_1 and d_2

The pore size distribution (PSD) between d_1 and d_2 is defined as[2]

$$\mathrm{PSD}\%_{(d_1 \sim d_2)} = A_{12} / A_{\mathrm{total}} \times 100\%$$

where A_{total} is the area under the entire PSD curve and A_{12} is the area between d_1 and d_2.

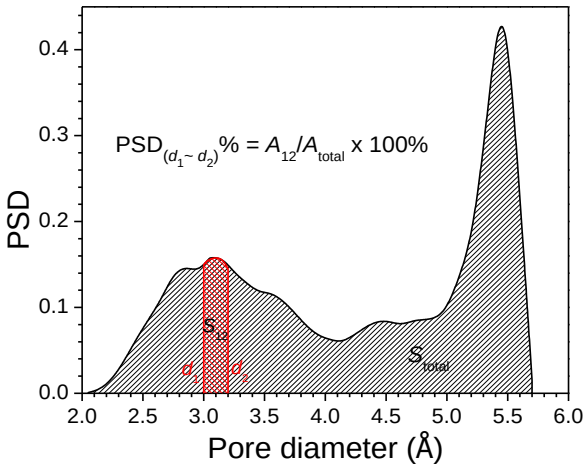
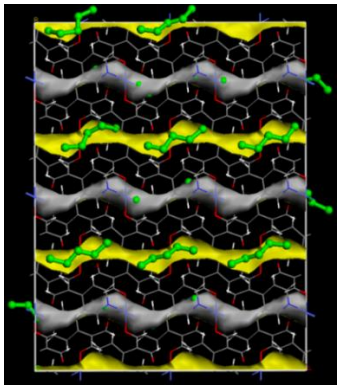


Fig. S3 Pore size distribution between d_1 and d_2.

7. Simulation snapshots for different separation mechanisms



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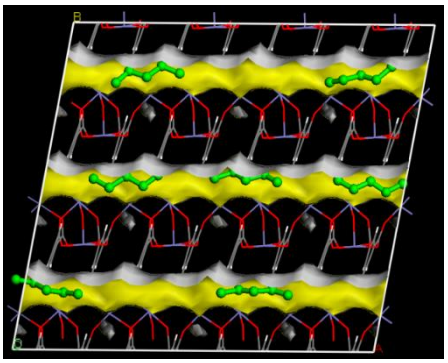

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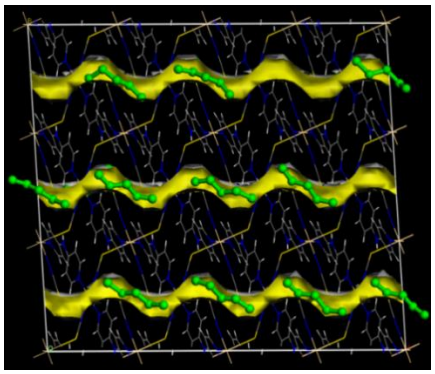

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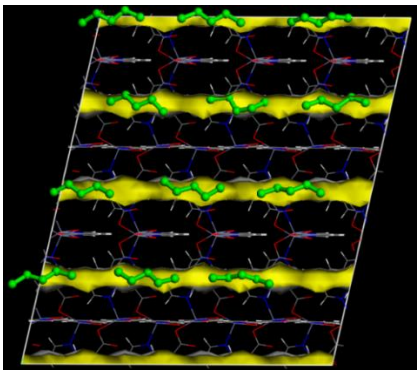

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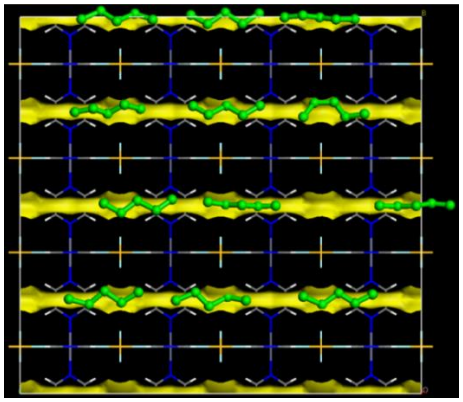

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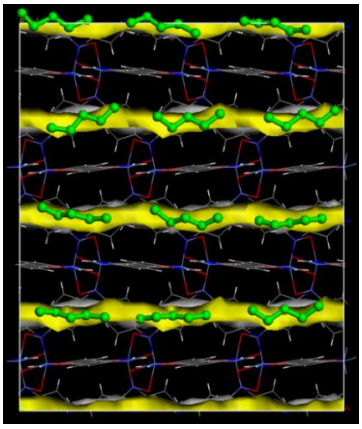
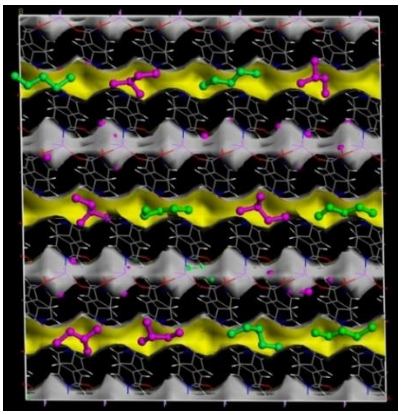
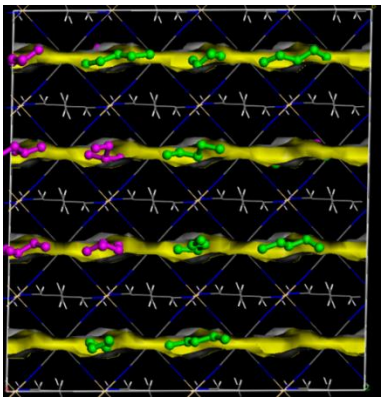


PARMIG

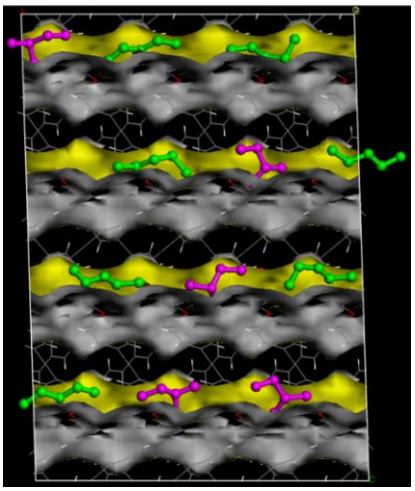
Fig. S4.1 Simulation snapshots for the separation of *n*-/*iso*-C_5, *n*-/*neo*-C_5.



XUNGOD



GIFKAH



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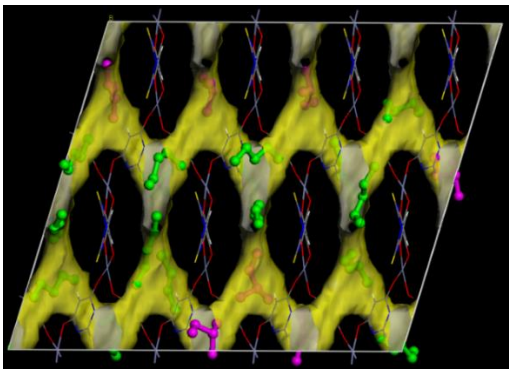
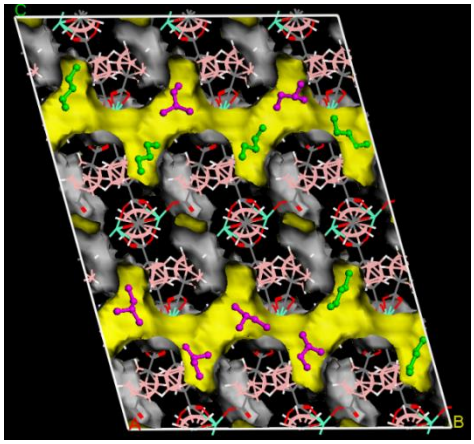


GOGWAB



WAZQIZ

Fig. S4.2 Simulation snapshots for the separation of *n*-/*neo*-C_5, *iso*-/*neo*-C_5.

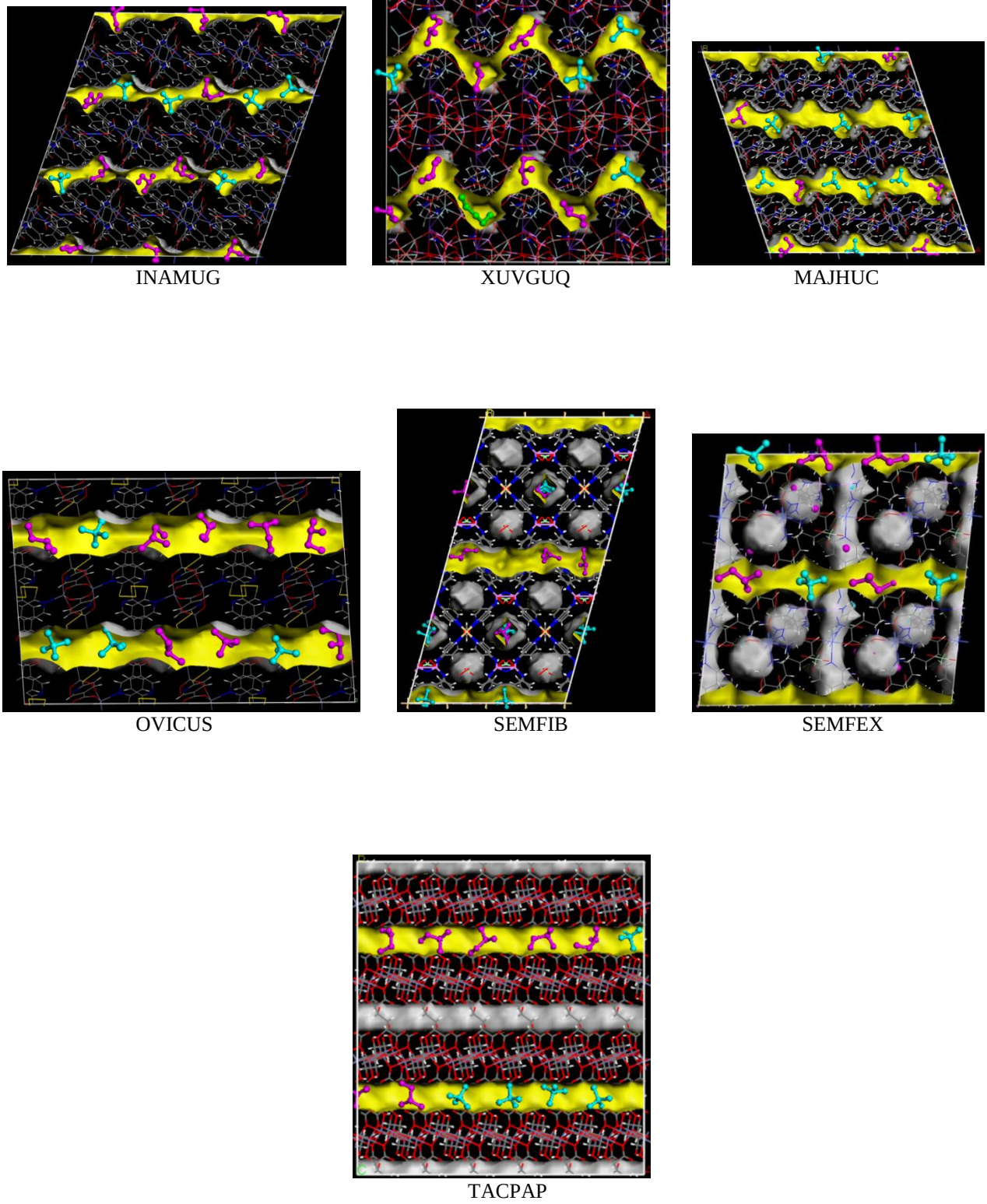
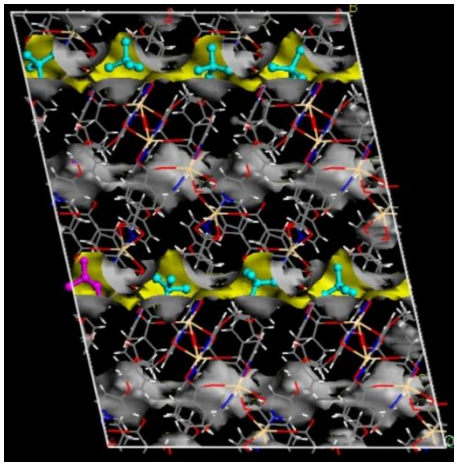
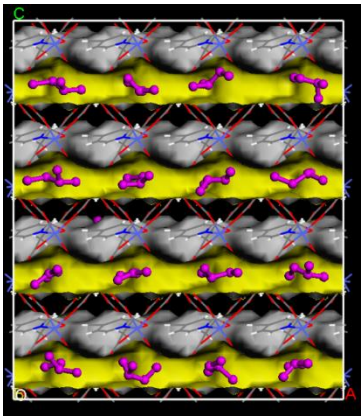


Fig. S4.3 Simulation snapshots for the separation of *iso*-/*n*-C_5, *neo*-/*n*-C_5.



QUPJAN

Fig. S4.4 Simulation snapshot for the separation of *neo*-/*n*-C_5, *neo*-/*iso*-C_5.



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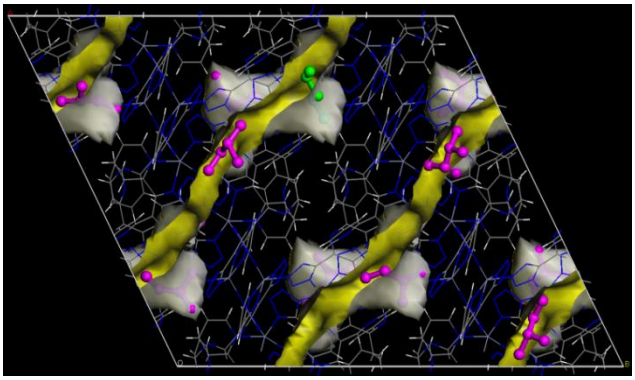

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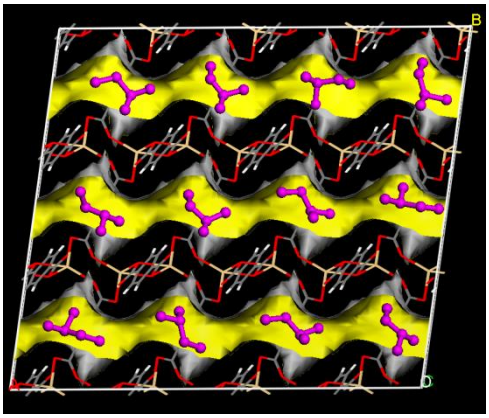

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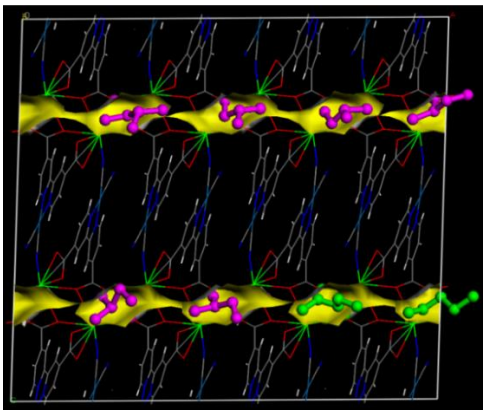
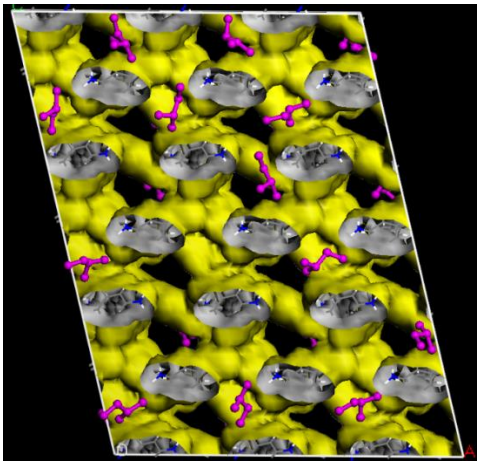


VAPFUP



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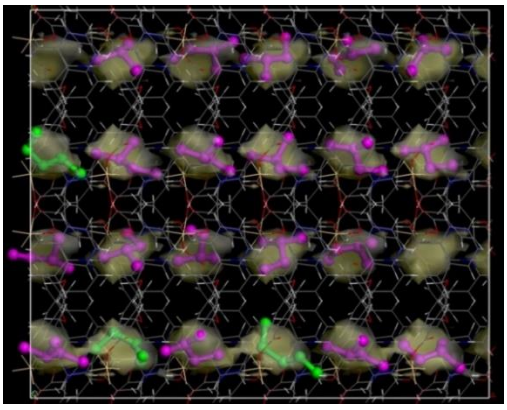
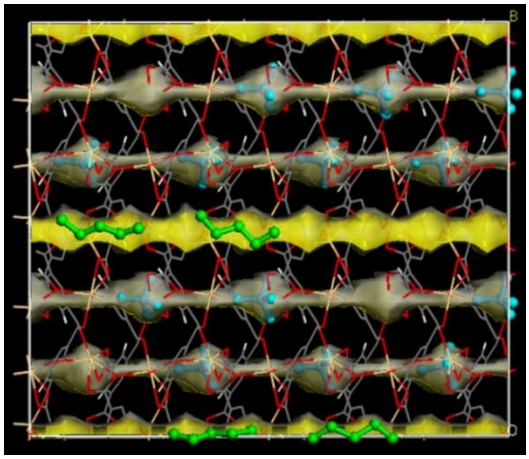


QULLEP

Fig. S4.5 Simulation snapshots for the separation of *iso*-/*n*-C_5, *iso*-/*neo*-C_5.



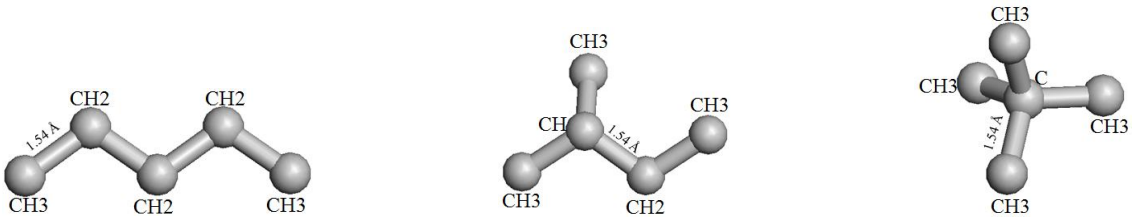
ODOXEK

Fig. S4.6 Simulation snapshot for the separation of *n*-/*iso*-C_5, *neo*-/*iso*-C_5.

8. Molecular models

Table S5 Lennard-Jones parameters of CoRE-MOFs.[3]

Atom	ε/k_B [K]	σ [Å]	Atom	ε/k_B [K]	σ [Å]	Atom	ε/k_B [K]	σ [Å]
Ac	16.60	3.10	Ge	190.69	3.81	Po	163.52	4.20
Ag	18.11	2.80	Gd	4.53	3.00	Pr	5.03	3.21
Al	254.09	4.01	H	22.14	2.57	Pt	40.25	2.45
Am	7.04	3.01	Hf	36.23	2.80	Pu	8.05	3.05
Ar	93.08	3.45	Hg	193.71	2.41	Ra	203.27	3.28
As	155.47	3.77	Ho	3.52	3.04	Rb	20.13	3.67
At	142.89	4.23	I	170.57	4.01	Re	33.21	2.63
Au	19.62	2.93	In	301.39	3.98	Rh	26.67	2.61
B	90.57	3.64	Ir	36.73	2.53	Rn	124.78	4.25
Ba	183.15	3.30	K	17.61	3.40	Ru	28.18	2.64
Be	42.77	2.45	Kr	110.69	3.69	S	137.86	3.59
Bi	260.63	3.89	La	8.55	3.14	Sb	225.91	3.94
Bk	6.54	2.97	Li	12.58	2.18	Sc	9.56	2.94
Br	126.29	3.73	Lu	20.63	3.24	Se	146.42	3.75
C	52.83	3.43	Lr	5.53	2.88	Si	202.27	3.83
Ca	119.75	3.03	Md	5.53	2.92	Sm	4.03	3.14
Cd	114.72	2.54	Mg	55.85	2.69	Sn	285.28	3.91
Ce	6.54	3.17	Mn	6.54	2.64	Sr	118.24	3.24
Cf	6.54	2.95	Mo	28.18	2.72	Ta	40.75	2.82
Cl	114.21	3.52	N	34.72	3.26	Tb	3.52	3.07
Cm	6.54	2.96	Na	15.09	2.66	Tc	24.15	2.67
Co	7.04	2.56	Ne	21.13	2.66	Te	200.25	3.98
Cr	7.55	2.69	Nb	29.69	2.82	Th	13.08	3.03
Cu	2.52	3.11	Nd	5.03	3.18	Ti	8.55	2.83
Cs	22.64	4.02	No	5.53	2.89	TI	342.14	3.87
Dy	3.52	3.05	Ni	7.55	2.52	Tm	3.02	3.01
Eu	4.03	3.11	Np	9.56	3.05	U	11.07	3.02
Er	3.52	3.02	O	30.19	3.12	V	8.05	2.80
Es	6.04	2.94	Os	18.62	2.78	W	33.71	2.73
F	25.16	3.00	P	153.46	3.69	Xe	167.04	3.92
Fe	6.54	2.59	Pa	11.07	3.05	Y	36.23	2.98
Fm	6.04	2.93	Pb	333.59	3.83	Yb	114.72	2.99
Fr	25.16	4.37	Pd	24.15	2.58	Zn	62.39	2.46
Ga	208.81	3.90	Pm	4.53	3.16	Zr	34.72	2.78



n-C_5 *iso*-C_5 *neo*-C_5

Fig. S5 United-atom model of C_5 isomers.

C_5 isomers (*n*-C_5, *iso*-C_5 and *neo*-C_5) were represented by a united-atom model with CH_x (x = 3, 2, 1 and 0) as a single interaction site (**Fig. S5**). In addition to the nonbonded Lennard-Jones potential, there exist bond bending and torsional potentials,

$$u_{\text{bending}}(\theta) = 0.5k_\theta(\theta - \theta^\circ)^2$$

$$u_{\text{torsion}}(\varphi) = c_0 + c_1[1+\cos\varphi] + c_2[1-\cos(2\varphi)] + c_3[1+\cos(3\varphi)]$$

where θ and φ are the bending and torsional angles, respectively; k_θ and c_i are the force constants. These parameters (**Table S6**) were adopted from the transferable potentials for phase equilibria (TraPPE) force field.[4] The cross interaction parameters between MOFs and C_5 isomers were estimated by the Lorentz-Berthelot combining rules.

Table S6 Lennard-Jones, bond bending and torsional potential parameters.

Atom	ε/k_B (K)	σ (Å)
CH_3	98.0	3.75
CH_2	46.0	3.95
CH	10.0	4.68
C	0.5	6.40

n-C_5			*iso*-C_5			*neo*-C_5		
	θ^o	k_θ/k_B (K/rad^2)		θ^o	k_θ/k_B (K/rad^2)		θ^o	k_θ/k_B (K/rad^2)
CH_3–CH_2–CH_2	114.0°	62500	CH_3–CH_2–CH	114.0°	62500	CH_3–C–CH_3	109.5°	62500
			CH_3–CH–CH_3	112.0°	62500			
			CH_3–CH–CH_3	112.0°	62500			

n-C_5				
	c_0/k_B (K)	c_1/k_B (K)	c_2/k_B (K)	c_3/k_B (K)
CH_3–CH_2–CH_2–CH_2	0.00	355.03	-68.19	791.32
iso-C_5				
	c_0/k_B (K)	c_1/k_B (K)	c_2/k_B (K)	c_3/k_B (K)
CH_3–CH–CH_2–CH_3	−251.06	428.73	−111.85	441.27

Table S7 Adsorption of equimolar C_5 isomer mixture in VICDOC at 433 K and a total pressure of 30 kPa.

	This study	Krishna and van Baten[5]
$N_{n\text{-}C_5}$ (mol/kg)	1.84	1.81
$N_{iso\text{-}C_5}$ (mol/kg)	9.5×10^{-2}	6.0×10^{-2}
$N_{neo\text{-}C_5}$ (mol/kg)	2.5×10^{-4}	4.4×10^{-4}

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