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Supporting Information

A flexible metal-organic framework with adaptive pores for high column-capacity gas chromatographic separation

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Table of content

Fabrication of Capillary Column for GC Separation

The empty capillary column. The fused silica capillary (l = 12 m, d = 0.53 mm) was washed sequentially by NaOH (2 mol/L) for three times (immersed 3 h at the last time), deionized water (until the pH value of outflow reached 7.0), HCl (1 mol/L) for three times (immersed 1 h at the last time) and deionized water (until the pH value of outflow reached 7.0), and then dried at 120 ^{o}C for 3 h under N_2 atmosphere.

The RTV column. RTV (room temperature vulcanized silicone rubber, 300 mg) was dissolved in cyclohexane (2 mL). After 15 min ultrasonic treatment the solution was pressed into the prepared silica capillary by N_2 flow (inlet pressure: 0.4 MPa) for 1 h to form a well-distributed coating. The fabricated capillary was then aged 3 times using the following program: first the capillary was hold under 60^{o}C for 30 min, then raised to 160^{o}C for 60 min at a rate of 5^{o}C·min^{-1}; at last the temperature was raised to 300^{o}C at 5^{o}C·min^{-1} and hold for 60 min, and then naturally cooled down to room temperature.

The 1&RTV column. Except adding mechanical grinded powders of **1** (40 mg) into the RTV solution, all processes were the same as for the RTV column.

Calculation of selectivity and resolution. The selectivity factors ($\alpha_{A1/A2}$) for analytes A1 and A2 on the capillary column were calculated from gas chromatogram according to the following equations.

$$\alpha_{A1/A2} = \frac{t_{A1} - t_0}{t_{A2} - t_0}$$

where t_{A1}, t_{A2} and t_0 are the retention time of analytes A1, A2, and reference methanol, respectively, under the same operation conditions.

The resolution for analytes A and B on the capillary column were calculated from the gas chromatogram according to

$$R = \frac{t_B - t_A}{1/2(w_B + w_A)}$$

where t_A and t_B are the retention times of analytes A and B, and w_A and w_B are the peak widths of analytes A and B, respectively.

Calculation of thermodynamic parameters. The enthalpy change (ΔH) for the transfer of solutes from the mobile phase to the stationary phase was calculated from the van't Hoff equation.

$$\mathrm{In}\,\mathrm{k}' = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} + \mathrm{In}\Phi$$

k' is the retention factor, R is the gas constant, T is the absolute temperature, and Φ is the phase ratio. Φ was defined as the volume of the stationary phase divided by the volume of the mobile phase. Retention factor k' and Φ was calculated by follow equation.

$$\mathrm{k}' = \frac{t - t_0}{t}$$

$$\Phi = \frac{V_s}{V_0}$$

t is the retention time for the analytes and t_0 is the column void time under constant temperature gas chromatographic separation. V_S is the volume of the stationary phase in the column, and V_0 is the void volume of the column.

Computational Calculations

The computational calculations were performed by using the Material Studio 5.5 package. The grand canonical Monte Carlo (GCMC) simulations were carried out by the Sorption module adopting the Metropolis method and both the host frameworks and the guest molecules were regarded as rigid. The cutoff radius was chosen as 15.5 Å for the Lennard-Jones (LJ) potential, and 5×10^6 equilibration steps were followed with 5×10^6 production steps. To determine the guest adsorption energy of the flexible framework, one guest molecule was first forced into the empty pore of **1** with geometry optimization using molecular mechanics (MM) in the Forcite module. The resulting initial configurations were further performed molecular dynamics (MD) simulations to obtain more accurate lattice parameters and guest-host configurations. All of the MD simulations adopted isothermal–isobaric ensemble with constant pressure/temperature (NPT) using Nose thermostat and random initial velocities. Van der Waals interactions and the electrostatic interactions were evaluated by the Ewald summation method, while all the Buffer widths were set as 0.5 Å. The time step was 1.0 fs and total simulation time was 1000 ps under 473 K. The final energy minimization of the MD result structures was performed by using MM with all the lattice parameters fixed. For MM, the convergence criterions were set as: energy 2×10^{-5} kcal/mol, force 1.0×10^{-3} kcal/mol/Å, displacement 1.0×10^{-5} Å. All the simulations were based on universal forcefield (UFF). The charges of host frameworks and guest molecules employed the QEq partial charges and ESP charges, respectively (O = -0.706 e, H = 0.353 e, e = 1.6022×10^{-19} C). The binding energy was calculated based on the following equations.

$$\Delta E_{\mathrm{fit}} = E_{\mathrm{host+guest}} - E_{\mathrm{apohost}} - E_{\mathrm{guest}}$$

$$\Delta E_{\mathrm{def}} = E_{\mathrm{host}} - E_{\mathrm{apohost}}$$

$$\Delta E_{\mathrm{ads}} = E_{\mathrm{host+guest}} - E_{\mathrm{host}} - E_{\mathrm{guest}}$$

where ΔE_{ads} is the adsorption enthalpy, ΔE_{def} is the energy change of the host framework after adsorption of guest, $\Delta E_{\mathrm{fitting}}$ is the interaction energy between the guest and the final host framework, and $E_{\mathrm{host+guest}}$, E_{guest}, E_{apohost} and E_{host} are the energies of the final host-guest structure, guest, guest-free host framework before adsorption and the transformed host framework after adsorption, respectively.

Supplementary Figures and Tables

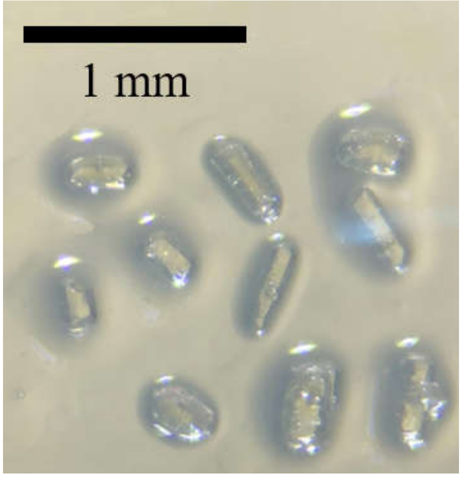

Fig. S1. As-synthesized single crystal of **1**·C_6H_6.

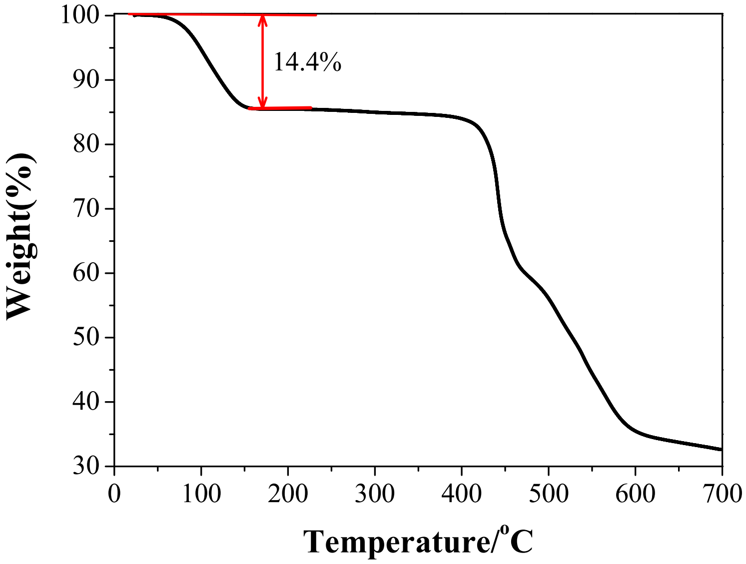

Fig. S2. Thermogravimetric curve of **1**·C_6H_6.

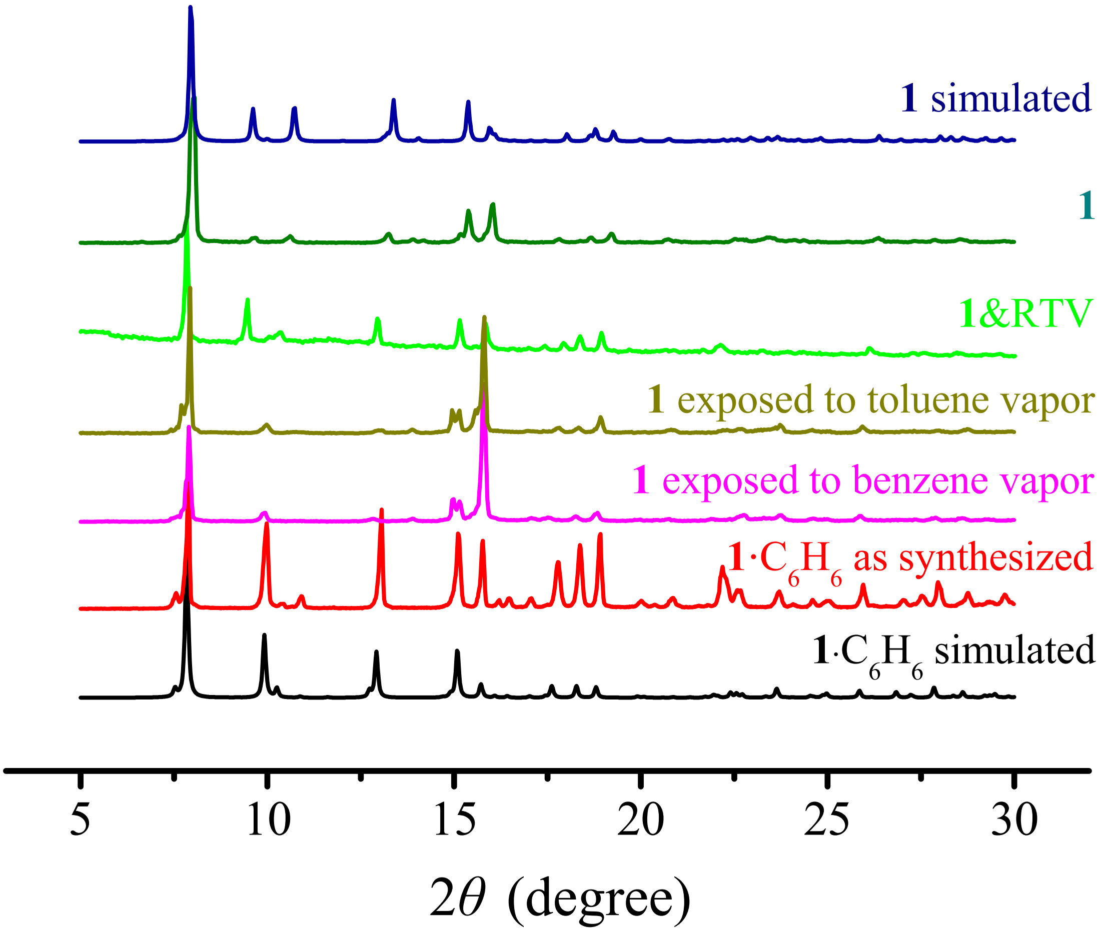

Fig. S3. PXRD patterns.

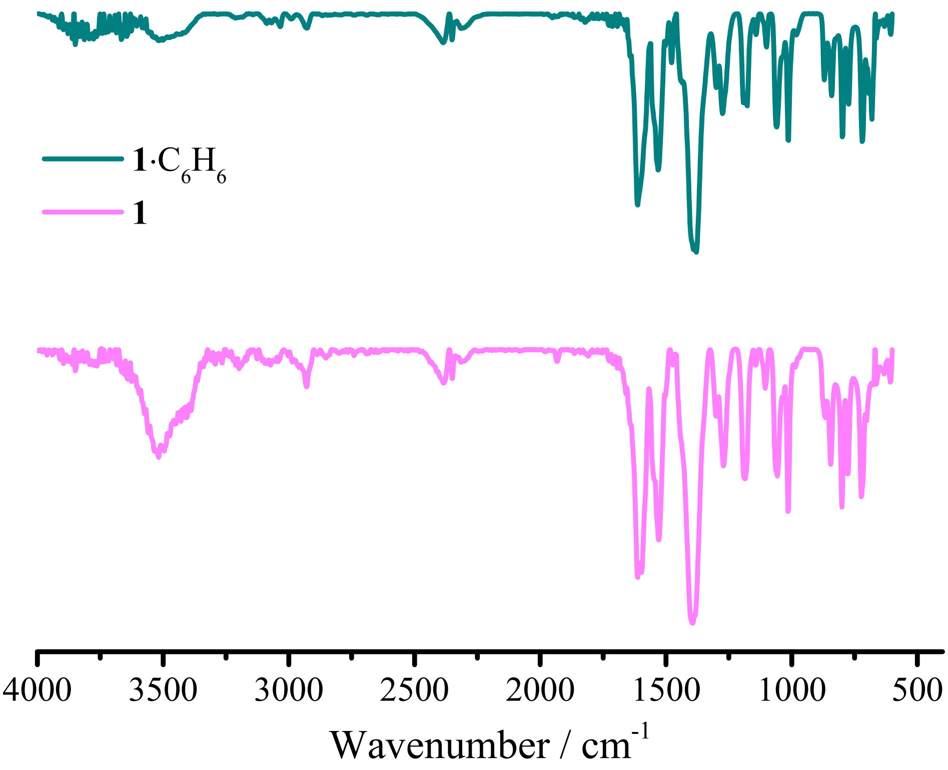

Fig. S4. IR-spectrums.

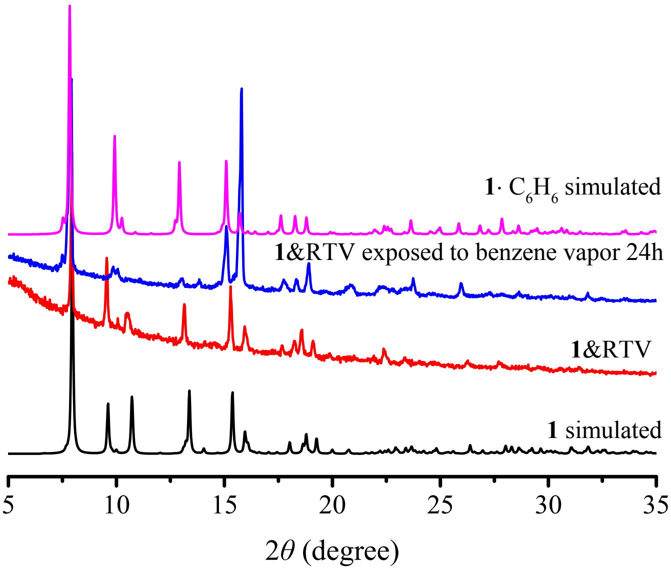

Fig. S5 PXRD patterns of **1**&RTV.

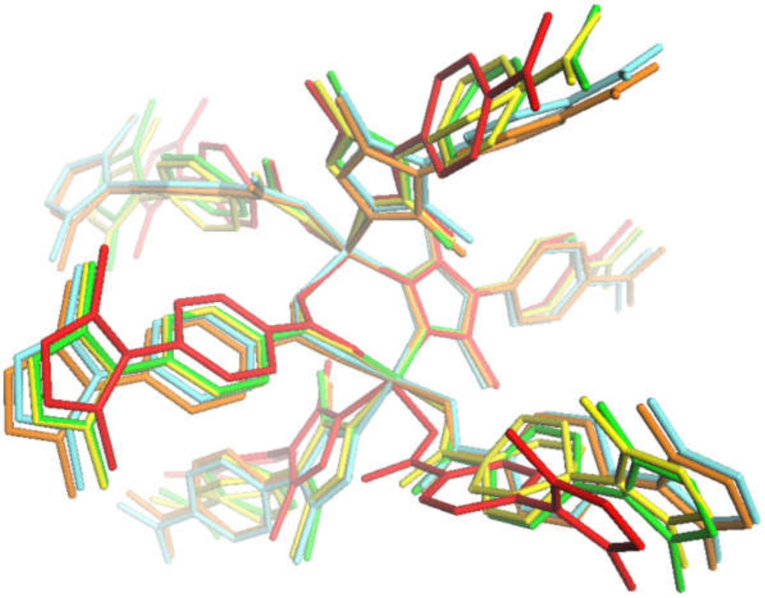

Fig. S6. Overlap of the binuclear Zinc SBUs of **1**·C_6H_6 (green), **1** (red), **1**·C_7H_8 (yellow), **1**·C_6H_{12} (orange), and **1**·MeOH (light blue). Note: the benzene rings of the $Hmpba^{-}$ ligands in **1**·C_7H_8 are in two-fold disordered.

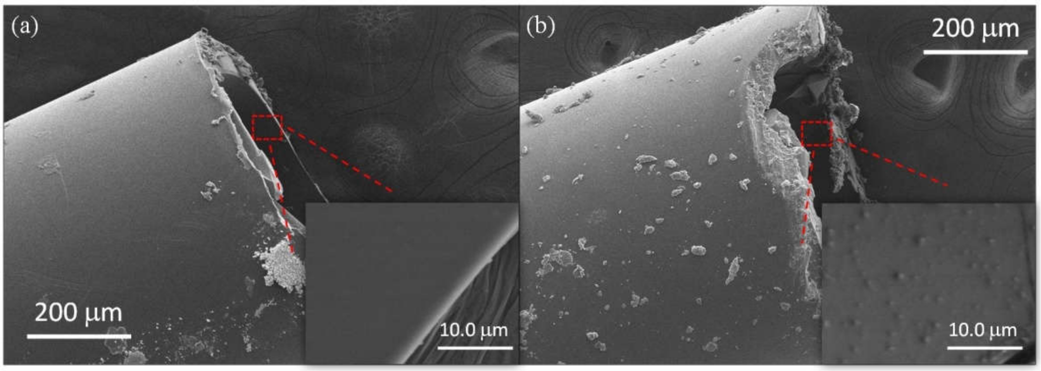

Fig. S7. SEM images of the capillary columns coated with (a) RTV and (b) **1**&RTV.

Table S1 Crystallographic data and structure refinement details

Complex	**1**·C_6H_6	**1**	**1**·C_7H_8	**1**·C_6H_{12}	**1**·MeOH
Formula	$C_{48}H_{44}N_6O_6Zn_2$	$C_{36}H_{32}N_6O_6Zn_2$	$C_{46.5}H_{44}N_6O_6Zn_2$	$C_{48}H_{56}N_6O_6Zn_2$	$C_{40}H_{48}N_6O_{10}Zn_2$
Formula weight	931.63	775.46	913.61	941.75	887.45
Temperature (K)	153(2)	153(2)	153(2)	153(2)	153(2)
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	*Ibca*	*C*2/*c*	*Ibca*	*C*2/*c*	*C*2/*c*
a/Å	17.2385(11)	29.4270(19)	16.6880(17)	28.90(2)	28.3668(17)
b/Å	22.5360(14)	16.4600(10)	22.617(2)	16.978(14)	16.5004(10)
c/Å	23.4694(15)	22.5860(14)	23.535(2)	22.451(18)	22.5401(13)
β/°	90	128.4880(10)	90	127.455(10)	126.7490(10)
V/Å^3	9117.6(10)	8563.1(9)	8882.9(15)	8745.0(12)	8453.5(9)
Z	8	8	8	8	8
D_c/g cm^{-3}	1.357	1.203	1.366	1.335	1.365
reflns coll.	17687	21930	25507	24081	21239
unique reflns	4469	8378	4350	7530	8234
R_1 $[I > 2\sigma(I)]$[a]	0.0570	0.0560	0.0687	0.0911	0.0506
wR_2 $[I > 2\sigma(I)]$[b]	0.1411	0.1193	0.1719	0.2521	0.1323
R_1 (all data)	0.0765	0.0848	0.0903	0.1285	0.0624
wR_2 (all data)	0.1539	0.1341	0.1828	0.2899	0.1397
GOF	1.059	1.055	1.139	1.032	1.070

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bwR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2 Representative bond distances, bond angles and ligand conformations (dihedral angle between the two aromatic rings) in the crystal structures.

	Zn-N (Å)	Zn-O (Å)	Dihedral angle (^{o})	N-Zn-N (^{o})	O-Zn-O (^{o})
1·C_6H_6	1.966(7)	1.919(7)	51.7(4)*	111.8(3)	100.6(3)
	1.998(7)	1.966(7)	66.3(4)		
1	1.961 (3)	1.921(4)	50.1 (3)	111.3(1)	98.8(1)
	1.966(2)	1.941(4)	53.5(3)*		
	2.002(4)	1.956(3)	61.4 (4)	111.8(2)	102.4(1)
	2.012(5)	1.974(2)			
1·C_7H_8	1.971(4)	1.927(4)	49.5(2)	113.2(2)	101.1(2)
	1.999(5)	1.971(4)	77.8(6)*		
1·C_6H_{12}	1.965(5)	1.926(8)	50.5(6)*	111.5(3)	98.2(2)
	1.967(5)	1.957(6)	51.2(7)		
	1.997(8)	1.957(7)	61.0(8)	111.3(3)	103.0(3)
	2.009(9)	1.965(4)			
1·MeOH	1.957(3)	1.920(4)	49.7(4)	110.5(1)	97.3(1)
	1.970(2)	1.940(3)	50.7(3)*		
	1.991(4)	1.960(2)	57.9(3)	111.1(1)	100.5(1)
	2.011(5)	1.984(2)			

* Fully deprotonated

Table S3 Thermodynamic parameters of benzene derivative adsorption.

Analytes	Experimental adsorption enthalpy derived from GC (kcal·mol^{-1})	Simulated adsorption enthalpy (kcal·mol-1)	Simulated host-guest fitting energy (kcal·mol^{-1})	Simulated framework deformation energy (kcal·mol^{-1})	Simulated framework deformation ratio on unit-cell volume (%)
CH	-13.3	-10.3	-30.1	19.8	2.62
B	-16.7	-13.4	-28.4	15.0	1.67
EB	-17.0	-20.2	-39.5	19.3	2.88
ST	-18.5	-23.0	-38	15.0	0.57
PB	-15.4	-21.9	-44	22.1	2.98
IPB	-14.9	-17.1	-38.8	21.7	2.21
MST	-18.9	-20.4	-38.1	17.7	1.68
135T	-9.11	-8.0	-38.1	30.1	2.01
124T	-18.5	-22.9	-39.4	16.5	2.81

Table S4 Guest boiling points and the selectivity factors in RTV and **1**&RTV coated columns.

Analytes	Boiling point (^oC)	Selectivity factor $\alpha_{A1/A2}$*	
		RTV	**1**&RTV
B/CH	80.1/80.7	1.00	2.85
ST/EB	145.2/136.2	1.16	1.47
MST/IPB	165.4/152.4	1.29	3.70
PB/IPB	159.2/152.4	1.12	1.31
PB/EB	159.2/136.2	1.56	1.23
PB/135T	159.2/165	1.00	2.23
EB/135T	136.2/165	0.64	1.81
124T/135T	169.4/165	1.11	1.48

* when $\alpha = 1$, there is no separation; the poorer selectivity the closer α value to 1.

Table S5 Calculated and measured surface areas.

Complex	**1**·C_6H_6	**1**	**1**·C_7H_8	**1**·C_6H_{12}	**1**·MeOH
Calculated Surface Area*/ $m^2 g^{-1}$	957	705	728	786	588
Measured Langmuir surface area / $m^2 g^{-1}$	879				

* The geometrical surface area was calculated by using Material Studio 5.0 with grind interval of 0.1 Å and solvent radius at 1.2 Å.