Electronic Supplementary Information

A Calixarene Based Metal Organic Material, CalixMOM, That Binds Potassium Cations

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General methods.

Commercially available reagents were purchased as high purity from FisherScientific or Frontier Scientific and used without further purification. L_1 was synthesized by the literature[1-2]. Solvents were purified according to standard methods and stored in the presence of molecular sieve. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA 2950 Hi-Res from 30°C-700°C at the speed of 10°C/min. X-ray powder diffraction (XPRD) data were recorded on a Bruker D8 Advance X-ray diffractometer at 40 kV, 40 mA for Cu_{kR}(λ=1.5418 Å), with a scan speed of 0.5 s/step (6°/min) and a step size of 0.05° in 2θ at room temperature. The simulated XPRD patterns were produced using Powder Cell for WindowsVersion 2.4 (programmed by W. Kraus and G. Nolze, BAM Berlin, 2000). The estimations of the second order nonlinear optical intensity were obtained by comparison of the results obtained from a powdered sample in the form of a pellet (Kurtz powder test), with that obtained for urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate the SHG signal. The Inductively coupled plasma(ICP-MS) was conducted on the Perkin Elmer Elan II DRC. Energy-dispersive X-Ray spectroscopy (EDS) instrument is equipped on a Hitachi S-800 Scanning Electron Microscope (SEM).

Synthesis of calixMOM-1

A mixture of L_1 (10.0mg), $MnCl_2 \cdot 4H_2O$ (10.0mg), and 1.5 mL mixture solvent(DMF:H_2O =20:1) was sealed in a Pyrex tube undervacuum and heated to 100 °C for 24 hours, The resulting pale yellow block crystals were washed with DMF to give pure calixMOM-1 of 7.4mg(yield of 57% based on L_1). Elemental analysis: Calculated: C 47.60%; H 4.24%; N 0.38%; Experimental: C 48.15%; H 4.35%; N 0.40%;

Synthesis of calixMOM-2

A mixture of L_1 (10.0mg), $MnCl_2 \cdot 4H_2O$ (10.0mg), KCl(3.0mg)and 1.5 mL mixture solvent(DMF:H_2O =20:1) was sealed in a Pyrex tube undervacuum and heated to 100 °C for 24 hours, The resulting pale yellow block crystals were washed with DMF to give pure calixMOM-2 of 8.1mg(yield of 62% based on L_1). Elemental analysis: Calculated: C 52.48%; H 4.81%; N 3.52%; Experimental: C 52.66%; H 4.82; N 3.59%;

X-ray Structure Determination

The X-ray intensity data for calixMOM-1 were measured on a Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu Kα INCOATEC Imus micro-focus source (λ = 1.54178 Å). Indexing was performed using APEX2 [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus[2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL97 SHELXL-2012 Beta version contained in OLEX2 [9] and WinGX v1.70.01 [4,5,6,7] programs. All non-H atoms were found in the difference Fourier map and refined anisotropically except the p-tert-butyl groups and free DMF in the channel. All of the methyl carbon atoms on the tert-butyl group were disorder over 3 places and were refined isotropically. Mn atoms were disorder over 3 places and were refined with fractional occupancies of 0.8:0.1:0.1. The free DMF molecules were refined with fractional occupancies. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) =

1.2Ueq(-CH). In the structure of calixMOM-1, the ligand is located on -4 inversion axis and therefore asymmetric unit contains ¼ of the ligand. Additionally the following atoms lie on symmetry elements: site symmetry of (.3.): Mn, Mn1, Mn2, C4, O3, O8; site symmetry of (2. .): O1, O9. Crystal data and refinement conditions are shown in Table S1.

The X-ray intensity data for calixMOM-2 were measured on a Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu Kα INCOATEC Imus micro-focus source (λ = 1.54178 Å). Indexing was performed using APEX2 [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus[2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL97 SHELXL-2012 Beta version contained in OLEX2 [9] and WinGX v1.70.01 [4,5,6,7] programs.All non-H atoms were found in the difference Fourier map and refined anisotropically except the carbon atoms(C10 and C14) of DMF molecules which coordinate to the Mn atoms and free DMF molecules in the channel. DMF molecules coordinating to the Mn atoms were refined with half occupancies. 2 carbon atoms and 1 oxygen atoms of free DMF molecule were also refined with 1/3 occupancies, the rest of carbon atoms, and nitrogen atoms of free DMF molecule were refined with full occupancy. The K atoms were refined with 2/3 occupancies based on the result from ICP-MS and EDS.Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). In the structure of calixMOM-2, the ligand is located on -4 inversion axis and therefore asymmetric unit contains ¼ of the ligand. Additionally the following atoms lie on symmetry elements: site symmetry of (.3.): Mn1, C15; site symmetry of (2. .): K2. Crystal data and refinement conditions are shown in Table S2.

Table S1. Crystal data and structure refinement for calixMOM-1	
Identification code	calixMOM-1
Empirical formula	$C_{49}H_{52}O_{24.3}N_{0.3}S_4Mn_{1.3}$
Formula weight	1235.15
Temperature	120.03K
Wavelength	1.54178
Crystal system, space group	Cubic, I-43d
Unit cell dimensions	a=27.0246(6) alpha=90 b=27.0246 (6) beta=90 c=27.0246 (6) gamma=90
Volume	19736.9(4) A^3
Z, Calculated density	12, 1.247 g cm^{-3}
Absorption coefficient	3.925m/mm
F(000)	7677.0
Crystal size	0.11*0.11*0.11 mm

Theta range for data collection	8.014 to 138.124 deg.
Limiting indices	-25<=h<=26, -28<=k<=26, -20<=l<=32
Completeness to theta =69.06	99.4%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2852 / 42 / 206
Goodness-of-fit on F^2	1.125
Final R indices [I>2sigma(I)]	$R_1 = 0.0973$, wR2 = 0.2794
R indices (all data)	$R_1 = 0.1031$, wR2 = 0.2916
Absolute structure parameter	0.08(2)
Largest diff. peak and hole	0.561 and -0.469 e.A^{-3}

Table S2. Crystal data and structure refinement for calixMOM-2	
Identification code	calixMOM-2
Empirical formula	$C_{58}H_{63.33}O_{16.67}N_{3.33}S_4K_{1.33}Mn_{1.33}$
Formula weight	1327.67
Temperature	119.97K
Wavelength	1.54178
Crystal system, space group	Cubic, I-43d
Unit cell dimensions	a=27.1849(4) alpha=90 b=27.1849(4) beta=90 c=27.1849(4) gamma=90
Volume	20090.2(9) A^3
Z, Calculated density	12, 1.317 g cm^{-3}
Absorption coefficient	4.550m/mm
F(000)	8290.0
Crystal size	0.05*0.05*0.05 mm
Theta range for data collection	3.98 to 66.51 deg.
Limiting indices	-27<=h<=17, -32<=k<=27, -15<=l<=28

Reflections collected / unique	20314 / 2826 [R(int) = 0.0602]
Completeness to theta = 66.51	98.9%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2868 / 26 / 215
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R_1=0.0767 wR_2=0.2000
R indices (all data)	R_1=0.0941 wR_2=0.2195
Absolute structure parameter	0.051(18)
Largest diff. peak and hole	1.335 and -0.592 e.A^{-3}

Gas Adsorption Experiments

Gas adsorption isotherms of calixMOM-1 and calixMOM-2 were collected using the surface areaanalyzer ASAP-2020. Before the measurements, the freshly prepared samples were soaked with ethanol, and calixMOM-2 were degassedat RT for 24h under vacuum, while calixMOM-1 were activated using the supercritical CO_2 in a Tousmimis Samdri PVT-3D critical point dryer. N_2 gas adsorption isotherms were measured at 77 K using a liquid N_2 bath, and CO_2 and CH_4 gas adsorption isotherms were measured at 273 K and 298K using ice-water bathrespectively.

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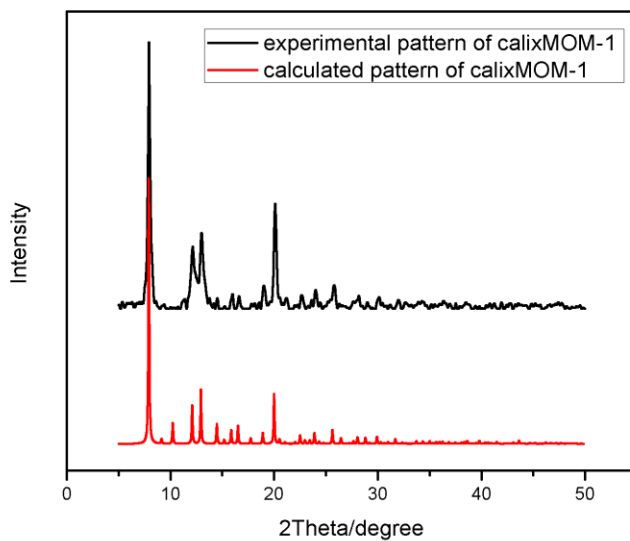
Figure S1 Comparison of experimental and calculated powder x-ray diffraction patterns of calixMOM-1
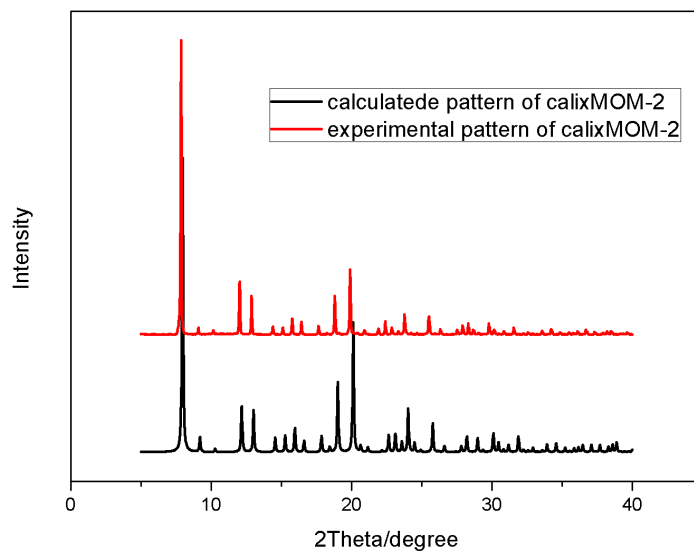
Figure S2 Comparison of experimental and calculated powder x-ray diffraction patterns of calixMOM-2
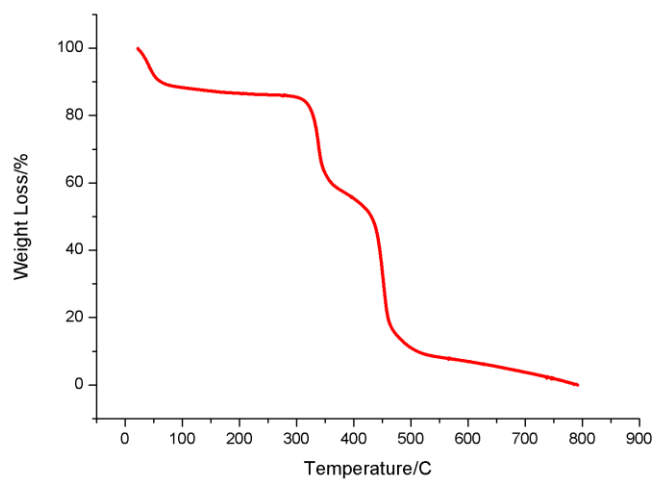
Figure S3 Thermogravimetric analysis of calixMOM-1
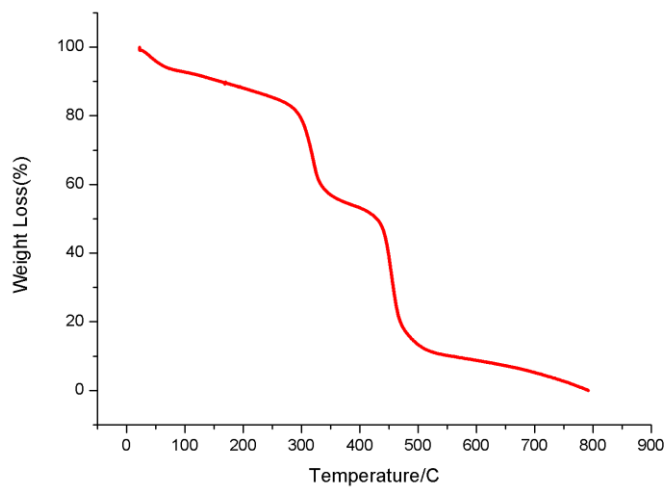
Figure S4 Thermogravimetric analysis of calixMOM-2
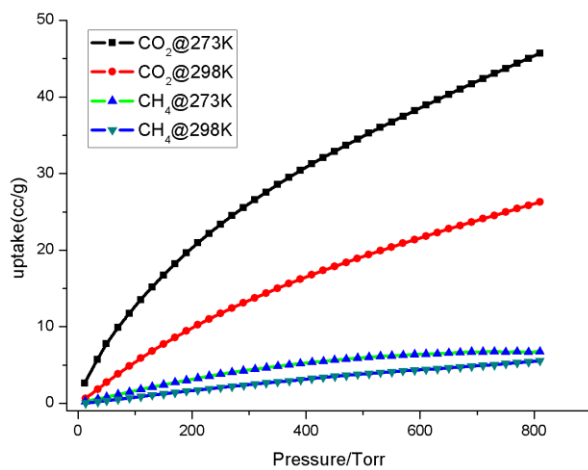
Figure S5 Low pressure CO_2 and CH_4 isotherms of calixMOM-1 at 273K and 298K
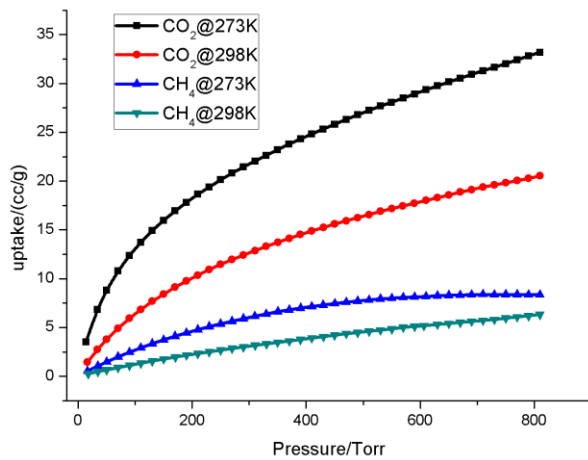
Figure S6 Low pressure CO_2 and CH_4 isotherms of calixMOM-2 at 273K and 298K
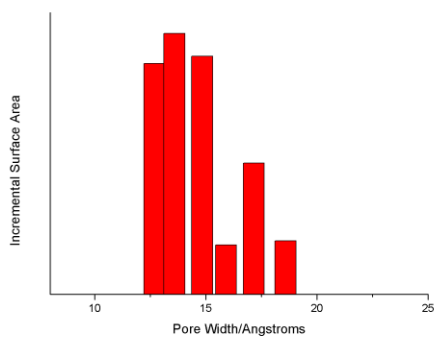
Figure S7. Pore size distribution of calixMOM-2
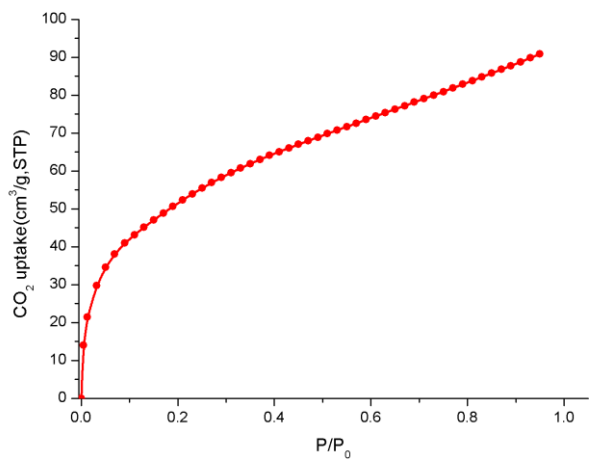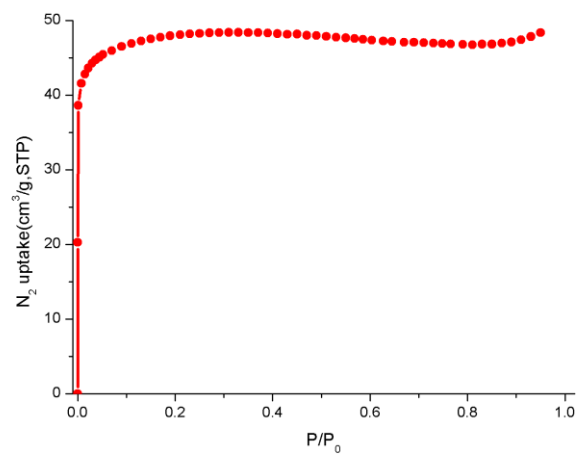
Figure S8. CO$_2$ adsorption isotherm of calixMOM-1 at 195K and N$_2$ adsorption isotherm of calixMOM-2 at 77K
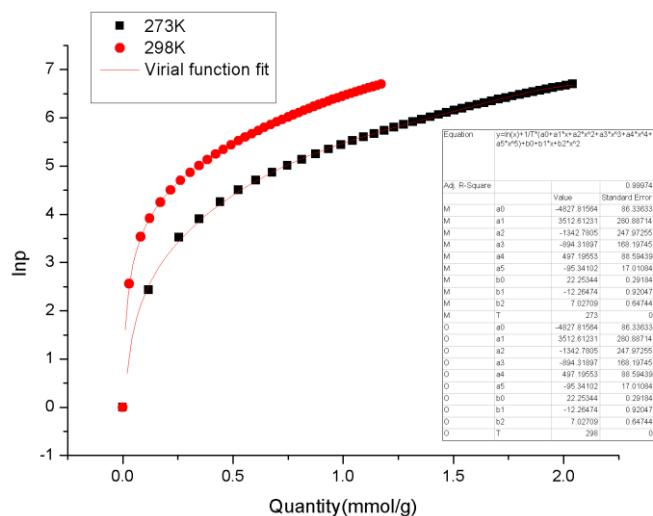
Figure S9. CO_2 adsorption isotherms of calixMOM-1 at 273K and 298K fitted using the virial equation
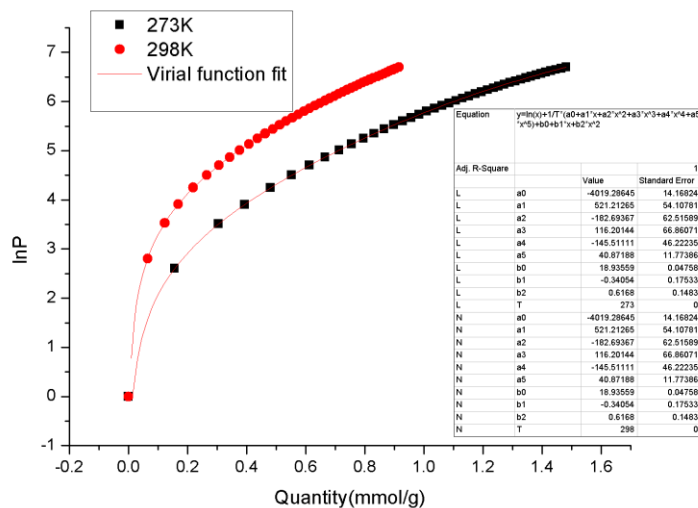
Figure S10. CO_2 adsorption isotherms of calixMOM-2 at 273K and 298K fitted using the virial equation
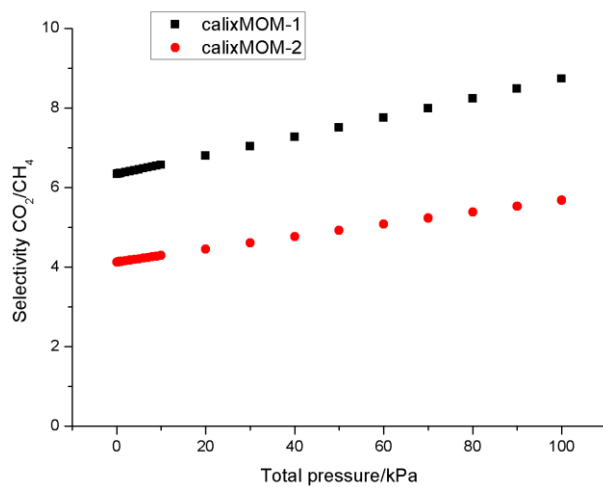
Figure S11. IAST calculated selectivities for adsorption from equimolar gas-phase mixtures based upon the experimentally observed adsorption isotherms of the pure gases
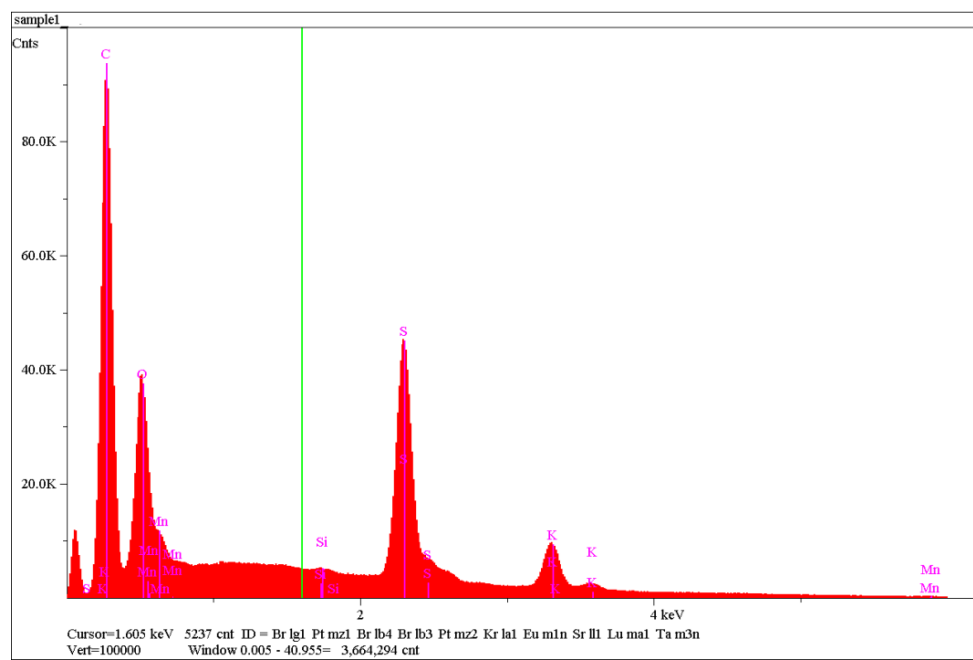

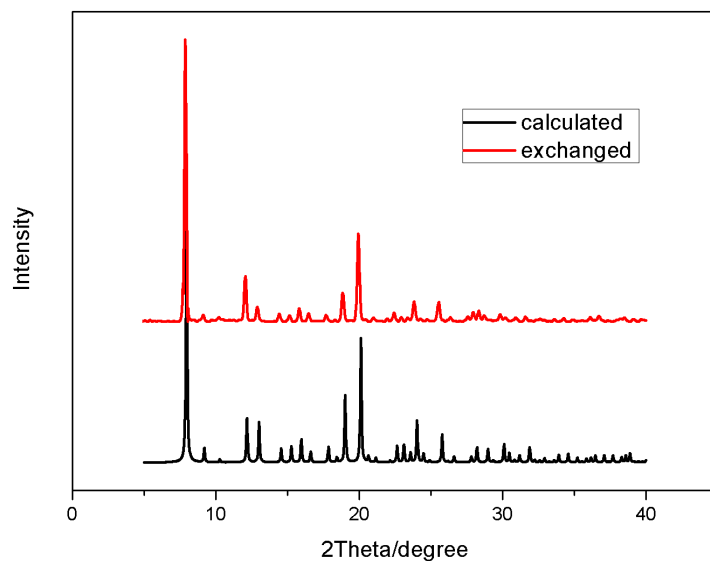Figure S12. EDS plot measured scanning the crystal of as-synthesized calixMOM-2.

Figure S13. Comparison of powder x-ray diffraction patterns of calixMOM-2 prepared by vigorously stirring calixMOM-1 in KCl methanol solution.
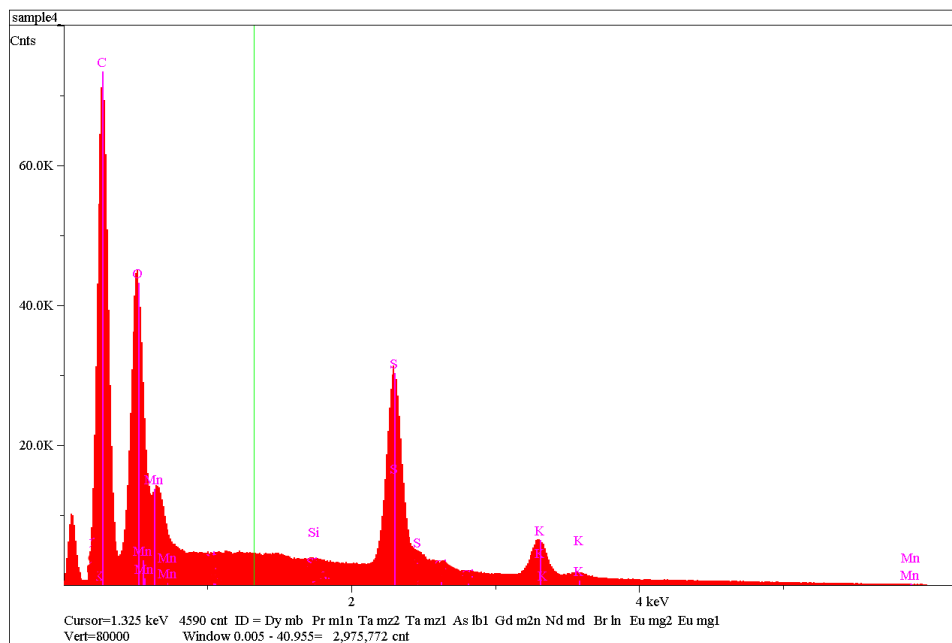

Figure S14. EDS plot measured scanning the crystal of calixMOM-2 prepared by vigorously stirring calixMOM-1 in KCl methanol solution.
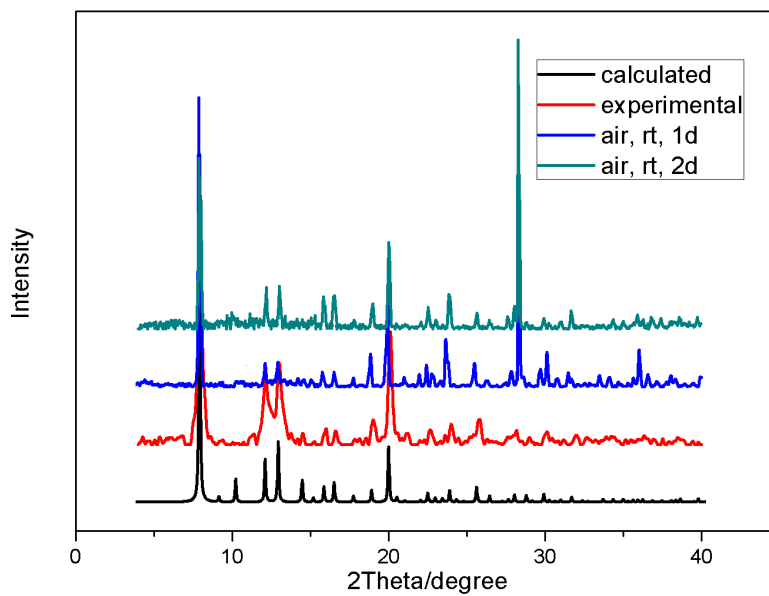
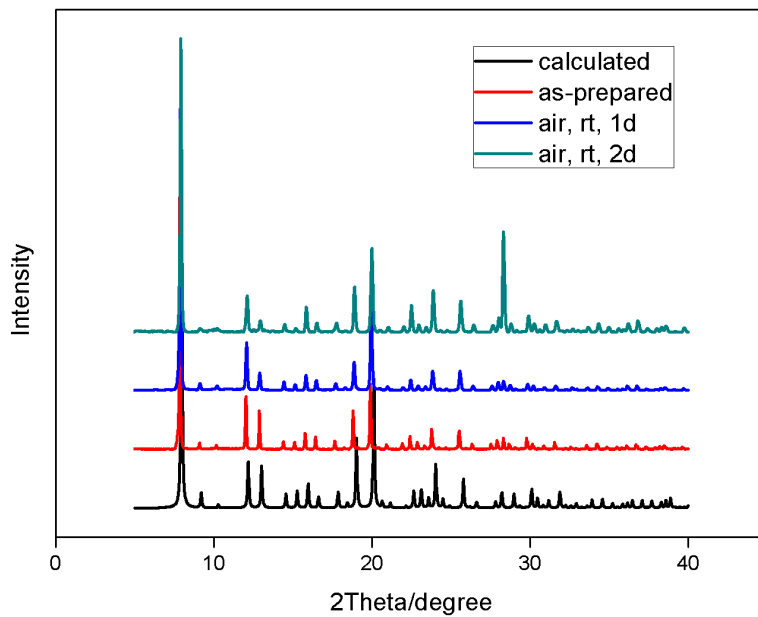Figure S15. Air stability of calixMOM-1 monitored by PXRD.

Figure S16. Air stability of calixMOM-2 monitored by PXRD.

Ideal Adsorbed Solution Theory

The ideal adsorbed solution theory (IAST)[1] was used to predict the equimolar binary mixture adsorption of CO_2 and CH_4 from the experimental pure-gas isotherms. The single-component isotherms were fit to a Langmuir-Freundlich equation:

$$q = q_m \cdot \frac{b \cdot P}{1 + b \cdot P} \quad \text{(S1)}$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mol/kg), q_m is the saturation capacity of adsorption (mol/kg), b is the affinity coefficient (1/kPa).

[1] Myers, A. L.; Prausnitz, *J. M. AIChE J.***1965**, *11*, 121.

[2] Bae, Y. S.; Mulfort K. L.; Frost, H.; Ryan, P.; Punnathanam, S.; Broadbelt, L. J.; Hupp, J. T.; Snurr, R. Q. *Langmuir***2008**, *24*, 8592.

[3] Lu, W.; Yuan, D.; Sculley, J.; Zhao, D.; Krishna, R.; Zhou, H.-C. *J. Am. Chem. Soc.***2011**, *133*, 18126.