Cd-MOF: Specific adsorption selectivity for linear alkyne (propyne, 2-butyne and phenylacetylene) molecules

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1. Materials and measurements

All the chemicals were obtained from commercial sources and used without further purification. APPT-Cd-ClO_4^- (**1**) were prepared by our reported methods.[1] Infrared spectroscopy (IR) samples were prepared as KBr pellets, and spectra were obtained in the 4000-400 cm^{-1} range using a Bruler-ALPHA spectrometer. ^1H NMR data were collected using a Bruker Avance-400 spectrometer. The sample solutions for NMR measurements were perfomed by dissolving the guest-loaded single crystals in deuterated solvents. Chemical shifts are reported in δ relative to TMS. Thermogravimetric analyses were carried out using a TA instrument Q5 simultaneous DTA-TGA under flowing nitrogen at a heating rate of 10 °C/min. Powder X-Ray diffraction patterns were collected using a Bruker D8 ADVANCE diffractometer (Cu K_α λ = 1.540598 Å) with an operating power of 40 Kv and fixed divergence slit of 0.76 mm. The data were collected in the range of 2θ = 5-50°.

2. Synthesis and characterization of 2-4

Synthesis and characterization of 2. The single crystals of $[Cd(L)_2(ClO_4)_2]\cdot(H_2O)$ ($H_2O\subset$APPT-Cd-ClO_4^-, **1**) were activated at 403 K for 3 h and then exposed to pure C_3H_4 atmosphere in a sealed vial for 4 h at room temperature to generate $[Cd(L)_2(ClO_4)_2]\cdot2.0(C_3H_4)$ (**2**). ^1H NMR (400 MHz, DMSO-d^6, 25°C, TMS, ppm): 8.71 (d, J = 5.6 Hz, 4H, -C_5H_4N), 8.46 (s, 2H, -C_6H_4), 8.13 (d, J = 8.0 Hz, 2H, -C_6H_4), 8.00 (d, J = 8.0 Hz, 2H, -C_6H_4), 7.84 (d, J = 5.6 Hz, 4H, -C_5H_4N), 7.75 (t, J = 8.0 Hz, 2H, -C_6H_4), 6.50 (s, 2H, -NH_2), 2.62 (q, J = 2.8 Hz, 1.34H, C≡CH), 1.75 (d, J = 2.8 Hz, 4.37H, $C\equiv CCH_3$). IR (KBr pellet cm^{-1}): 3342 (w), 3272(w), 3074(w), 1604 (s), 1480 (m), 1395 (m), 1081 (s), 1010 (m), 795 (s), 689 (m), 612 (s).

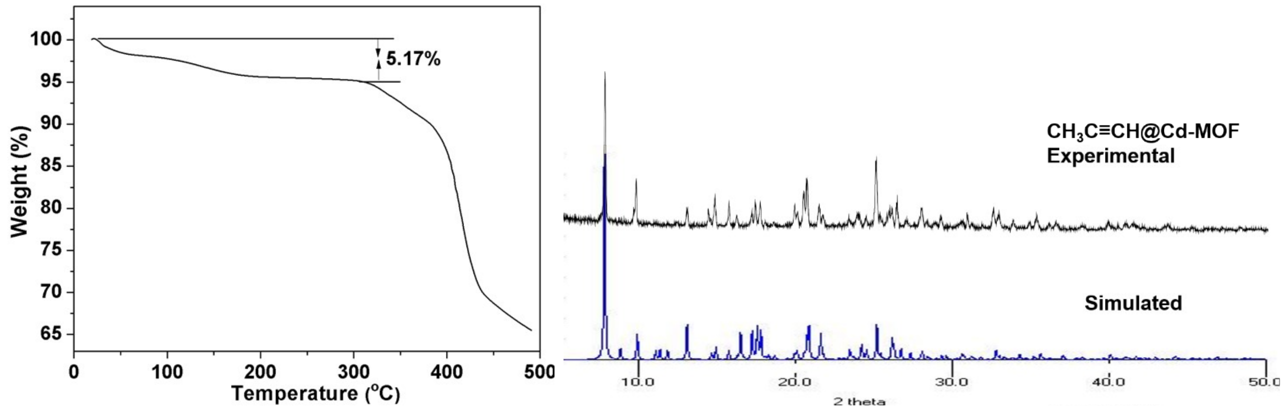

Figure S1. Left: TGA trace of **2**. The measured weight loss is 5.17% (calculated 6.82 %). Right: XRPD pattern of **2**.

Synthesis and characterization of 3. The single crystals of $[Cd(L)_2(ClO_4)_2]\cdot(H_2O)$ ($H_2O\subset$APPT-Cd-ClO_4^-, **1**) were activated at 403 K for 3 h and then exposed to the vapor of 2-butyne in a sealed vial for 4 h at room temperature to generate $[Cd(L)_2(ClO_4)_2]\cdot2.0$(2-butyne) (**2**). ^{1}H NMR (400 MHz, DMSO-d^6, 25°C, TMS, ppm): 8.71 (d, J = 5.6 Hz, 4H, -C_5H_4N), 8.46 (s, 2H, -C_6H_4), 8.13 (d, J = 8.0 Hz, 2H, -C_6H_4), 8.00 (d, J = 8.0 Hz, 2H, -C_6H_4), 7.84 (d, J = 5.6 Hz, 4H, -C_5H_4N), 7.75 (t, J = 8.0 Hz, 2H, -C_6H_4), 6.50 (s, 2H, -NH_2), 1.70 (s, 7.24H, $CH_3C\equiv CCH_3$). IR (KBr pellet cm^{-1}): 3345 (w), 3079 (w), 1609 (s), 1481 (m), 1401 (m), 1090 (s), 1014 (m), 795 (s), 688 (m), 618 (s).

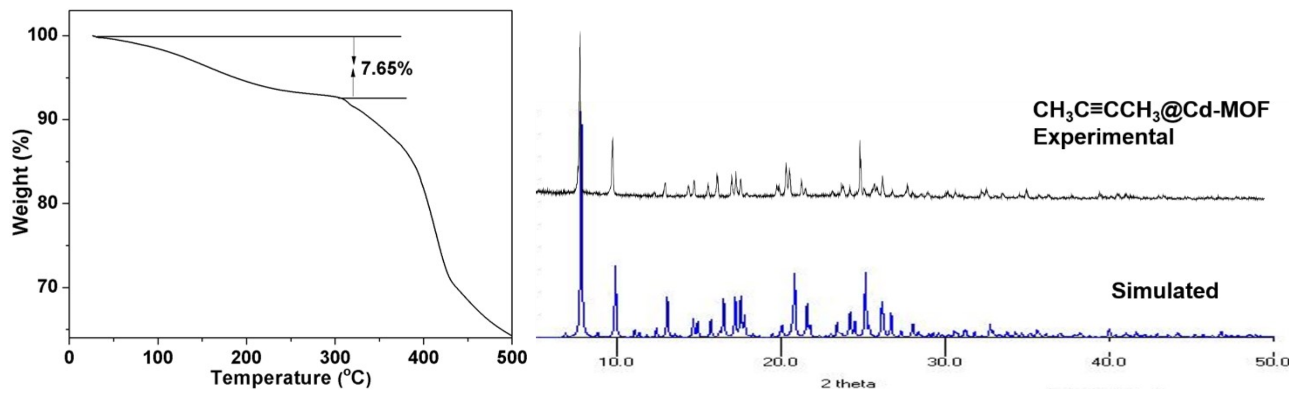

Figure S2. TGA trace of **3**. The measured weight loss is 7.65% (calculated 9.01%). Right: XRPD pattern of **3**.

Synthesis and characterization of 4. The single crystals of $[Cd(L)_2(ClO_4)_2]\cdot(H_2O)$ ($H_2O\subset$APPT-Cd-ClO_4^-, **1**) were activated at 403 K for 3 h and then exposed to the vapor of phenylacetylene in a sealed vial for 4 h at 70 °C to generate $[Cd(L)_2(ClO_4)_2]\cdot0.75$(phenylacetylene) (**2**). ^{1}H NMR (400MHz, DMSO-d^6, 25°C, TMS, ppm): 8.71 (d, J = 5.6 Hz, 4H, -C_5H_4N), 8.46 (s, 2H, -C_6H_4), 8.13 (d, J = 8.0 Hz, 2H, -C_6H_4), 8.00 (d, J = 8.0 Hz, 2H, -C_6H_4), 7.84 (d, J = 5.6 Hz, 4H, -C_5H_4N), 7.75 (t, J = 8.0 Hz, 2H, -C_6H_4), 6.50 (s, 2H, -NH_2), 7.49-7.39 (m, 4.16H, $C_6H_5C\equiv C$), 4.20 (s, 0.82H, $C\equiv CH$). IR (KBr pellet cm^{-1}): 3352 (w), 3283 (w), 3074 (w), 1608 (s), 1482 (s), 1404 (m), 1091 (s), 1011 (m), 798 (s), 690 (m), 622 (s).

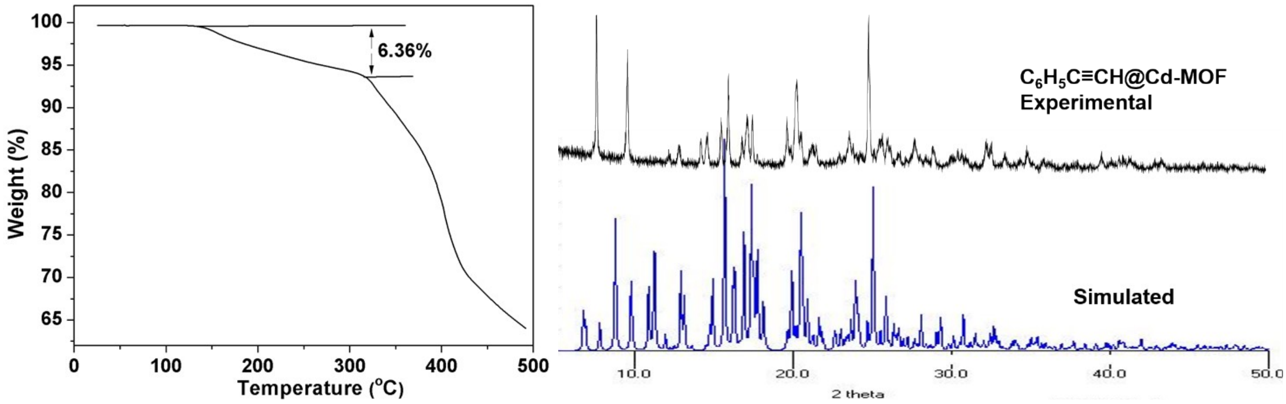

Figure S3. TGA trace of **4**. The measured weight loss is 6.36% (calculated 6.55 %). Right: XRPD pattern of **4**.

3. Crystallographic data

Suitable single crystals of complexes **2-4** were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 150 ~173K on an Agilent SuperNova CCD-based diffractometer (Cu Kα radiation λ = 1.54184 Å). The raw frame data for the complexes were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[2] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[2] None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions with isotropic displacement parameters set to 1.2Ueq of the attached atom.

For compound **2**: the asymmetric unit contains half of a Cd atom, one coordinated $C_{24}H_{18}N_6$ ligand, two parts of disordered ClO_4^- anion and one propyne molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to C atoms were placed in geometrically idealized positions and hydrogen atoms attached to N atoms were located in different map and all H atoms were refined in riding model. The bond-length of O4-Cl2, O5-Cl2, O6-Cl2, O7-Cl2 were restrained to be same with a standard deviation of 0.01 Å. The ADPs of atoms C25, C26 and C27 were restrained to be same with a standard deviation of 0.005 Å^2. The ADPs of atoms O4, O5, O6 and O7 were restrained to be isotropic within a standard deviation of 0.01 Å^2. Total 42 restrains were used to model this structure.

For compound **3**: the asymmetric unit contains half of a Cd atom, one coordinated $C_{24}H_{18}N_6$ ligand, two parts of disordered ClO_4^- anion and one 2-butyne molecule.

For compound **4**: the asymmetric unit contains one Cd atom, two coordinated $C_{24}H_{18}N_6$ ligands, two disordered ClO_4^- anion and three parts of phenylacetylene molecules. 0.75 phenylacetylene molecules was disordered and refined over three parts in ratio of 0.25:0.25:0.25, and the bond-length of O1-Cl2, O2-Cl2, O3-Cl2 and O4-Cl2 were restrained to be same with a standard deviation of 0.01 Å. The ADPs of atoms O1, O2, O3 and O4 were restrained to be isotropic within a standard deviation of 0.005 Å^2. Total 52 restrains were used to model this structure.

Table S1. Crystal data collection and structure refinement for **2-4**.

	2	**3**	**4**
Chemical formula	$C_{54}H_{44}CdCl_2N_{12}O_8$	$C_{56}H_{48}CdCl_2N_{12}O_8$	$C_{54}H_{40.5}CdCl_2N_{12}O_8$
Formula weight	1172.31	1200.36	1168.78
Temperature	150.00(10) K	173.01(10) K	159(14) K
Wavelength	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system	Tetragonal	Tetragonal	orthorhombic
Space group	$P4_32_12$	$P4_32_12$	$P2_12_12_1$
Unit cell dimensions	a = 15.8548(3) Å	15.8898(3) Å	a = 15.7006(2) Å
	b = 15.8548(3) Å	15.8898(3) Å	b = 16.1755(2) Å
	c = 21.4208(5) Å	21.4310(7) Å	c = 21.6748(3) Å
	α = 90°	α = 90°	α = 90 °
	β = 90 °	β = 90 °	β = 90 °
	γ = 90°	γ = 90°	γ = 90 °
Volume	5384.63(19) Å^3	5411.0(2) Å^3	5504.65(13) Å^3
Z	4	4	4
Density (calculated)	1.446 g cm^{-3}	1.473 g cm^{-3}	1.410 g cm^{-3}
Absorption coefficient	4.708 mm^{-1}	4.698 mm^{-1}	4.605 mm^{-1}
F(000)	2392	2456	2378
Reflections collected/ unique	10200 / 4955 [R(int) = 0.0283]	10897 4833[R(int) = 0.0405]	39470 / 10522[R(int) = 0.0363]
Data/ restraints/ parameter	4955 / 42 / 377	4833 / 0 / 369	10522 / 52 / 693
GOOF	1.004	1.087	1.069
R[I>2sigma(I)]	R1 = 0.0383, wR2 = 0.0967	R1 = 0.1086, wR2 = 0.2725	R_1 = 0.0520, wR_2 = 0.1517
R(all data)	R1 = 0.0446, wR2 = 0.1014	R_1 = 0.1166, wR_2 = 0.2805	R1 = 0.0556, wR2 = 0.1572

Table S2. Selected bonds (Å) and angles (°) for compounds **2-4**.

2			
N1–Cd1^1	2.374(3)	Cd1–N6^5	2.430(3)
Cd1–N1^2	2.375(3)	Cd1–N6^6	2.430(3)
Cd1–N1^3	2.375(3)	Cd1–N2	2.320(3)

Cd1–N2^{4}	2.320(3)		
N1^{2}–Cd1–N1^{3}	106.55(16)	N1^{2}–Cd1–N6^{4}	87.32(13)
N1^{2}–Cd1–N6^{5}	78.38(12)	N1^{3}–Cd1–N6^{5}	87.32(12)
N1^{3}–Cd1–N6^{4}	78.38(12)	N2^{6}–Cd1–N1^{3}	159.39(12)
N2–Cd1–N1^{3}	87.88(11)	N2–Cd1–N1^{2}	159.39(12)
N2^{6}–Cd1–N1^{2}	87.88(11)	N2–Cd1–N2^{6}	82.50(17)
N2–Cd1–N6^{4}	110.38(12)	N6^{5}–Cd1–N6^{4}	156.04(16)
N2–Cd1–N6^{5}	87.92(12)	N2^{6}–Cd1–N6^{4}	87.93(12)
3			
Cd1–N1^{1}	2.382(9)	Cd1–N6^{4}	2.417(11)
Cd1–N1^{2}	2.382(9)	N1–Cd1^{6}	2.382(9)
Cd1–N3	2.319(10)	N6–Cd1^{7}	2.417(11)
N1^{1}–Cd1–N1^{2}	105.4(5)	N3–Cd1–N1^{2}	160.3(3)
N1^{2}–Cd1–N6^{3}	78.7(4)	N3^{5}–Cd1–N1^{2}	87.9(3)
N1^{1}–Cd1–N6^{3}	86.5(4)	N3–Cd1–N1^{1}	87.9(3)
N1^{2}–Cd1–N6^{4}	86.5(4)	N3^{5}–Cd1–N3	83.5(5)
N3–Cd1–N6^{3}	87.9(4)	N3–Cd1–N6^{4}	110.7(3)
N6^{3}–Cd1–N6^{4}	155.5(5)		
4			
Cd1–N1^{1}	2.378(5)	Cd1–N2	2.341(4)
Cd1–N6^{2}	2.448(5)	Cd1–N7^{3}	2.380(5)
Cd1–N8	2.309(5)	Cd1–N12^{4}	2.428(5)
N1–Cd1^{5}	2.378(5)	N6–Cd1^{6}	2.448(5)
N7–Cd1^{7}	2.380(5)	N12–Cd1^{8}	2.428(5)
N1^{1}–Cd1 N6^{2}	78.13(16)	N1^{1}–Cd1–N7^{3}	105.15(16)
N1^{1}–Cd1–N12^{4}	88.55(17)	N2–Cd1–N1^{1}	87.95(16)
N2–Cd1–N6^{2}	111.50(16)	N2–Cd1–N7^{3}	159.11(16)
N2–Cd1–N12^{4}	86.30(15)	N7^{3}–Cd1–N6^{2}	87.45(17)
N7^{3}–Cd1–N12^{4}	77.99(17)	N8–Cd1–N1^{1}	158.41(16)
N8–Cd1–N2	82.66(16)	N8–Cd1–N6^{2}	87.27(16)
N8–Cd1–N7^{3}	89.82(16)	N8–Cd1–N12^{4}	110.07(16)
N12^{4}–Cd1–N6^{2}	157.04(15)		

Compound **2**: ^{1}-1/2+Y, 3/2-X, 1/4+Z; ^{2}3/2-Y, 1/2+X, -1/4+Z; ^{3}1/2+X, 3/2-Y, 5/4-Z; ^{4}+Y, +X, 1-Z; ^{5}1/2-Y, 1/2+X, -1/4+Z; ^{6}1/2+X, 1/2-Y, 5/4-Z; ^{7}1-Y, 1-X, 3/2-Z; ^{8}-1/2+Y, 1/2-X, 1/4+Z.

Compound **3**: ^{1}-1/2-Y, -1/2+X, -1/4+Z; ^{2}-1/2+X, -1/2-Y, 1/4-Z; ^{3}+Y, +X, -Z; ^{4}1/2-Y, -1/2+X, -1/4+Z; ^{5}-1/2+X, 1/2-Y, 1/4-Z; ^{6}1/2+Y, -1/2-X, 1/4+Z; ^{7}1/2+Y, 1/2-X, 1/4+Z.

Compound **4**: ^{1}2-X, 1/2+Y, 1/2-Z; ^{2}1-X, 1/2+Y, 1/2-Z; ^{3}1/2+X, 3/2-Y, 1-Z; ^{4}1/2+X, 1/2-Y, 1-Z; ^{5}2-X, -1/2+Y, 1/2-Z; ^{6}1-X, -1/2+Y, 1/2-Z; ^{7}-1/2+X, 3/2-Y, 1-Z; ^{8}-1/2+X, 1/2-Y, 1-Z; ^{9}1/2-X, 1-Y, 1/2+Z.

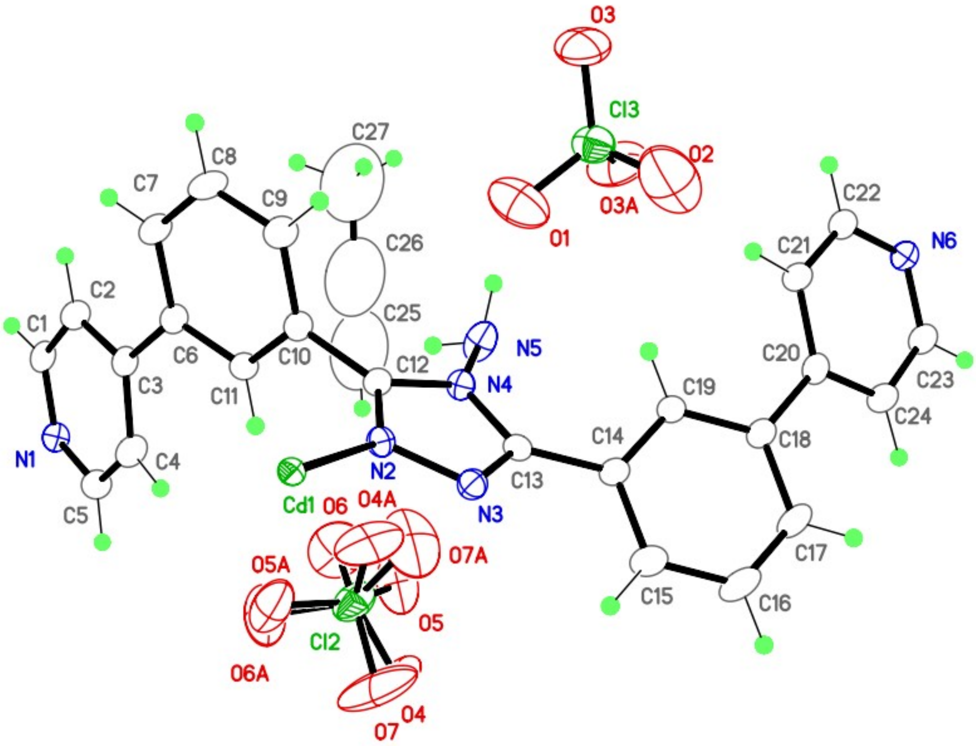

Figure S4. ORTEP figure for compound **2**. Displacement ellipsoids are drawn at the 30% probability level.

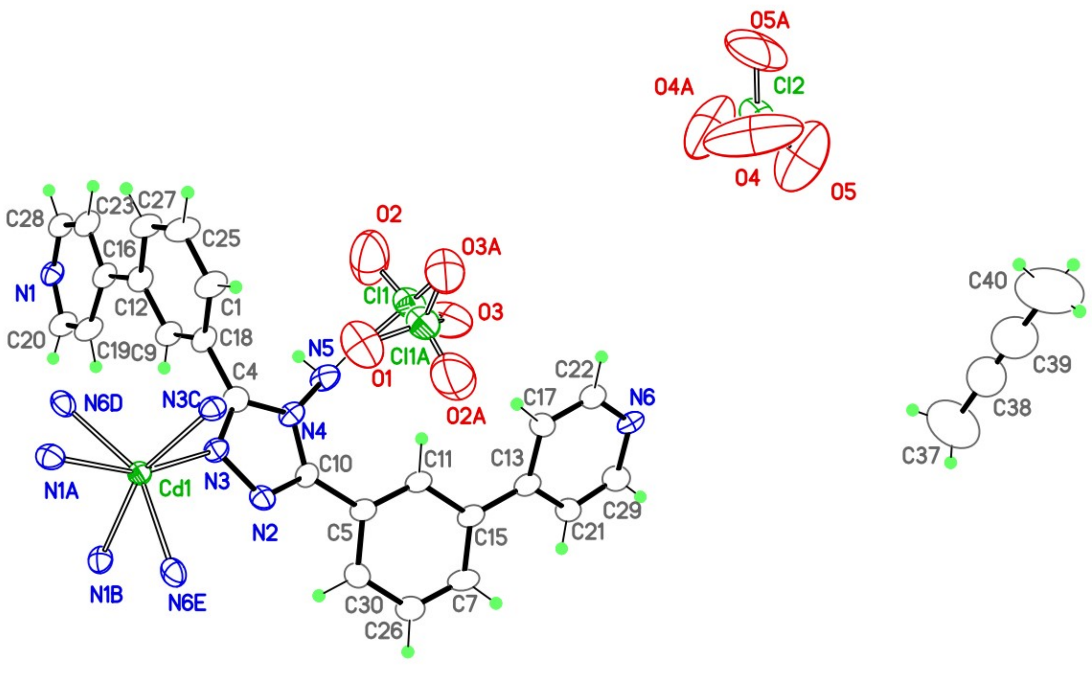

Figure S5. ORTEP figure for compound **3**. Displacement ellipsoids are drawn at the 30% probability level.

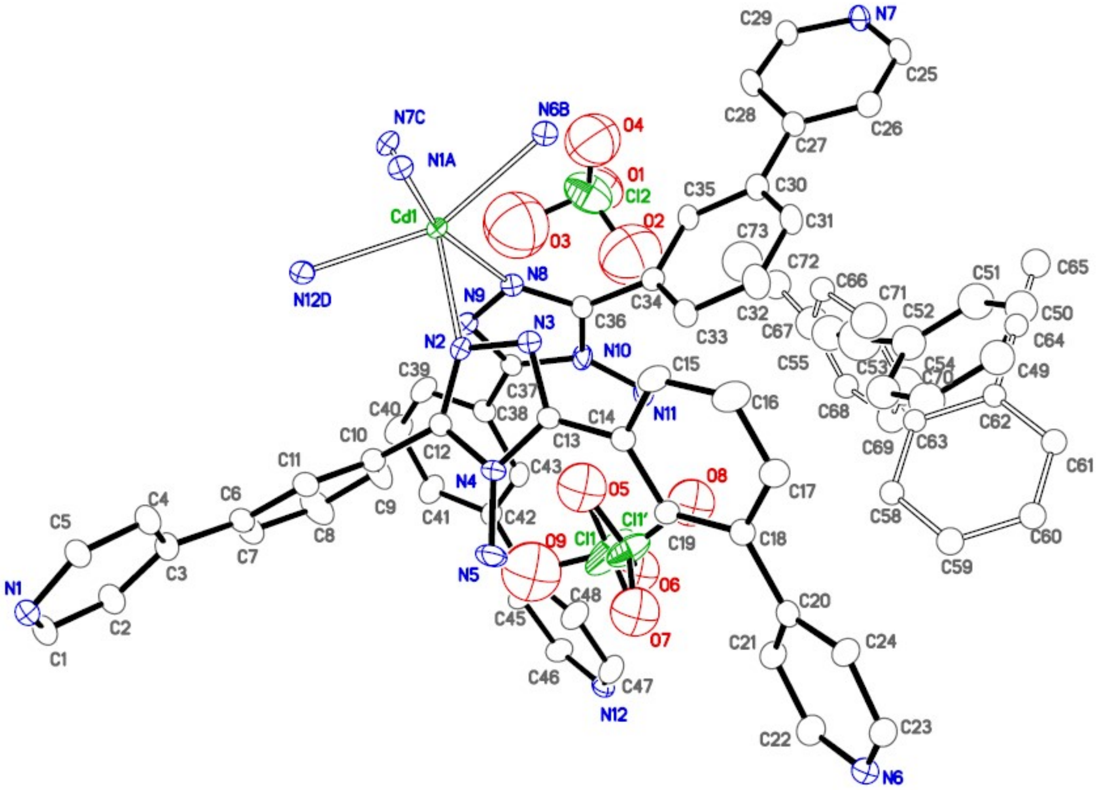

Figure S6. ORTEP figure for compound **4**. Displacement ellipsoids are drawn at the 30% probability level.

4. Adsorption measurements

Gas adsorption experiments were carried out with a MicrotracBel BELSORP-max volumetric gas sorption instrument. Prior to the measurement, the sample was activated under high vacuum at 403 K for 1 h to remove the water molecules in the channel. About 145 mg of the sample was used for the entire adsorption measurement. For selective adsorption evaluation, the gas sorption isotherms of C_3H_4 and C_3H_6 were collected at 273 K in an ice−water bath, and at 298 K in a temperature controlled circular bath, respectively.

Calculations of C_2H_2/C_2H_4 selectivities based on IAST [3]-[5]

The experimental isotherm data on pure component for C_3H_4 and C_3H_6 in **1** was measured at temperatures of 273 and 298 K, which were fitted by dual-Langmuir–Freundlich model:

$$q = \frac{q_{A,\ sat} b_A P^{1/n_1}}{1 + b_A P^{1/n_1}} + \frac{q_{B,sat} b_B p^{1/n_2}}{1 + b_B p^{1/n_2}}$$

Here, P is the pressure in kPa, q is the adsorbed amount in mmol/g, $q_{A,sat}$ and $q_{B,sat}$ are the saturation capacities of sites A and B. $\boldsymbol{b_A}$ and $\boldsymbol{b_B}$ are the affinity coefficients of sites A and B in kPa^{-1}, and n_1 and

n_2 represent the deviations from an ideal homogeneous surface. The fitted parameters were used to predict multi-component adsorption with IAST.

The selectivity S_{ads} in a binary mixture of components is defined as:

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

In which, q_i represents the amount of i adsorbed and p_i represents the partial pressure of i in the mixture.

Isosteric heat of adsorption (Q_{st}) calculations [5]-[6]

The virial-type equation was used to calculate the enthalpies of adsorption for C_3H_4 and C_3H_6 at 273 K and 298 K for **1**. At two temperatures, the data were fitted using the equation:

$$lnp = lnN + 1/T\sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j$$

Here, p is the pressure in mmHg, N is the amount adsorbed in mg/g, T is temperature in K, and a_i and b_j are virial coefficients which are temperature independent empirical parameters. Based on the virial coefficients obtained from the fitted isotherms, the isosteric heat of adsorption (Q_{st}) was calculated using the following equation:

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i$$

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

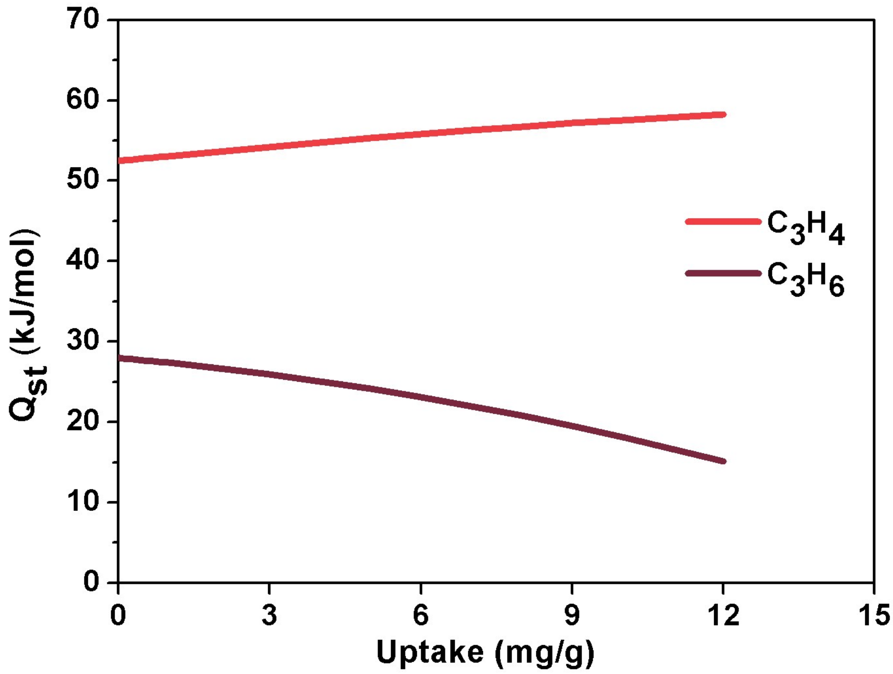

Figure S7. Isosteric heats (Q_{st}) for C_3H_4 and C_3H_6 adsorption on **1**.

5. Breakthrough experiments

The breakthrough curves were measured on a BSD MAB. The instrument is equipped with an internal thermal conductivity detector for the investigation of binary gas mixtures. The sample dry mass for this experiment is 1.9 g. The pre-dried sample was pretreated in Helium flux at 180 °C for 2 hours. Because of technical limitations regarding the demo unit, instead of 1:99, a ratio of 50:50 had to be selected. The results of the breakthrough of 11 % C_3H_4 (propyne) and 11 % C_3H_6 (propylene) in Helium at 25 °C are shown in Figure 3. Corresponding flow rates: 10 ml/min C_3H_4 + 10 ml/min C_3H_6 + 70 ml/min He.

6. Reference

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