Supplementary Information

Calcium L-Lactate Frameworks as Naturally Degradable Carriers for Pesticides

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Section S1. Synthetic procedures.

Calcium acetate monohydrate ($Ca(OAc)_2 \cdot H_2O$), L-(+)-Lactic acid, anhydrous methanol and ethanol were purchased from commercial source and were used directly without further purification. All synthetic procedures were conducted in air. The MOFs were activated by the following method: As-synthesized MOFs were washed with fresh anhydrous ethanol (MOF-1201) and methanol (MOF-1203) for 1 day, six times per day. The samples were then evacuated to remove guest molecules under vacuum (0.01 Torr) at ambient temperature for 12 hrs. The following measurements were conducted using the activated samples for MOFs unless otherwise noted.

Elemental analysis (EA) of activated MOF-1201 and -1203 were performed using a Perkin Elmer 2400 Series II CHNS elemental analyzer; ^1H NMR spectra on digested solutions of MOFs were acquired on a Bruker AVB-400 NMR spectrometer, with chemical shifts of linkers identified by comparing with spectra for each pure linker. Samples (*ca.* 10 mg for each) were dissolved in D_2O (600 μL) with sonication; Attenuated-total-reflectance Fourier-transform infrared (ATR-FTIR) spectra of neat ZIFs were recorded on a Bruker ALPHA Platinum ATR-FTIR Spectrometer.

MOF-1201, Ca_{14}(L-lactate)$_{20}$(Acetate)$_8$(EtOH)(H_2O). 0.071 g calcium acetate monohydrate ($Ca(OAc)_2 \cdot H_2O$, 0.4 mmol), and 0.072 g L-(+)-Lactic acid (HL, 0.8 mmol) were mixed in 6 mL anhydrous ethanol in a 23 mL Teflon autoclave. The autoclave was then sealed and heated in 120 ^oC isothermal oven for 4 days. After cooling down to room temperature, the crystals were washed with anhydrous ethanol for 1 day. (Yield: 26% based on Ca). EA: Calcd. for $Ca_{14}(C_3H_5O_3)_{20}(C_2H_3O_2)_8(C_2H_6O)(H_2O)$: C, 32.54; H, 4.62. Found: C, 31.67; H, 4.75. ATR-FTIR (4000-400 cm^{-1}): 3250(br), 2979(w), 1563(s), 1422(s), 1314(m), 1267(m), 1122(s), 1089(w), 1044(m), 930(w), 858(m), 773(m), 664(m), 616(m), 550(m), 469(w), 442(w), 423(w).

MOF-1203, Ca_6(L-lactate)$_3$(Acetate)$_9$(H_2O). 0.071 g calcium acetate monohydrate ($Ca(OAc)_2 \cdot H_2O$, 0.4 mmol), and 0.036 g L-(+)-Lactic acid (HL, 0.4 mmol) were mixed in 6 mL anhydrous methanol in a 23 mL Teflon autoclave. The autoclave was then sealed and heated in 100 ^oC isothermal oven for 3 days. After cooling down to room temperature, the crystals were washed with anhydrous methanol for 1 day. (Yield: 25% based on Ca). EA: Calcd. for $Ca_6(C_3H_5O_3)_3(C_2H_3O_2)_9$: C, 30.68; H, 4.20. Found: C, 31.33; H, 4.07. ATR-FTIR (4000-400 cm^{-1}): 3300(br), 2981(w), 1540(s), 1462(s), 1417(s), 1320(w), 1271(m), 1138(m), 1123(m), 1051(w), 1024(m), 956(w), 934(w), 860(m), 774(m), 662(s), 649(m), 617(s), 561(m), 468(m), 419(w).

Section S2. Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction (SCXRD) data was collected for both MOFs using as-synthesized crystals. Data for MOF-1201 and -1203 were collected at beamline 11.3.1 of the ALS at LBNL, equipped with a Bruker Photon 100 CMOS area detector using synchrotron radiation (10-17 KeV), at 0.7749(1) Å. Samples were mounted on MiTeGen® kapton loops and placed in a 100(2) K nitrogen cold stream.

Data were processed with the Bruker APEX2 software package,[1,2] integrated using SAINT v8.34A and corrected for the absorption by SADABS 2014/5 routines (no correction was made for extinction or decay). The structures were solved by intrinsic phasing (SHELXT) and refined by full-matrix least squares on F^2 (SHELXL-2014). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically calculated and refined as riding atoms unless otherwise noted. In both structures, highly disordered guest molecules occupying the cavities of the structure, which could not be modeled and so were accounted for using solvent masking using the Olex2 software package.[3,4] See the CIFs for further details.

MOF-1201. A colorless rod-shaped (100 μm × 20 μm × 20 μm) crystal of as-synthesized MOF-1201 was quickly picked up from the mother liquor, and placed in paratone oil to minimize crystal degradation, and mounted at beamline 11.3.1 at the ALS using radiation at λ = 0.7749(1) Å at 100 K.

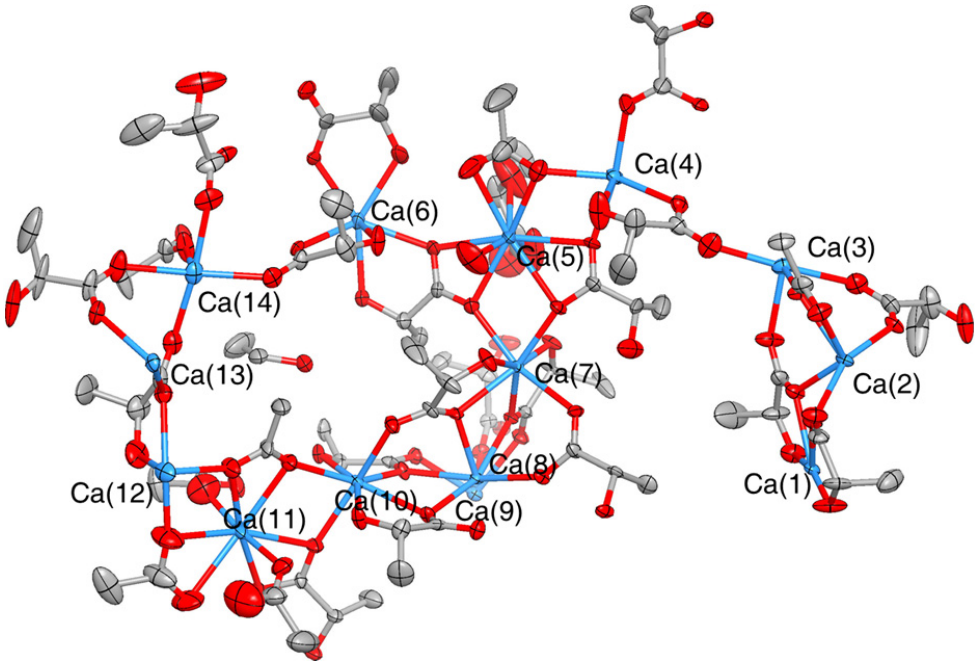

Figure S1. Asymmetric unit of **MOF-1201** (thermal ellipsoids with 30% probability). Hydrogen atoms are omitted for clarity. Color scheme is as follows: C, grey; O, red; Ca, blue.

Table S1. Crystal data and structure determination for MOF-1201

Compound	**MOF-1201**
Chemical formula	$C_{76}H_{127}O_{76}Ca_{14}$
Formula mass	2817.89
Crystal system	monoclinic
Space group	$P2_1$
λ (Å)	0.7749(1)
a (Å)	24.3868(11)
b (Å)	13.2612(6)
c (Å)	24.9710(10)
β (°)	90.327(2)
Z	2
V (Å^3)	8075.4(6)
Temperature (K)	100(2)
Size /mm^3	0.1 × 0.02 × 0.02
Density (g/cm^{-3})	1.159
Measured reflections	119229
Unique reflections	29436
Parameters	1544
Restraints	265
R_{int}	0.0723
θ range (°)	2.10-27.89
R_1, wR_2	0.0621, 0.1772
S (GOF)	1.076
Max/min res. dens. (e/Å^3)	0.60/-0.33
Flack parameter	0.150(10)

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^b wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $^c S = [\Sigma w(F_o^2 - F_c^2)^2/(N_{ref} - N_{par})]^{1/2}$.

MOF-1203. A colorless needle-shaped (90 μm × 90 μm × 5 μm) crystal of as-synthesized MOF-1203 was quickly picked up from the mother liquor and mounted at beamline 11.3.1 at the ALS using radiation at λ = 0.7749(1) Å.

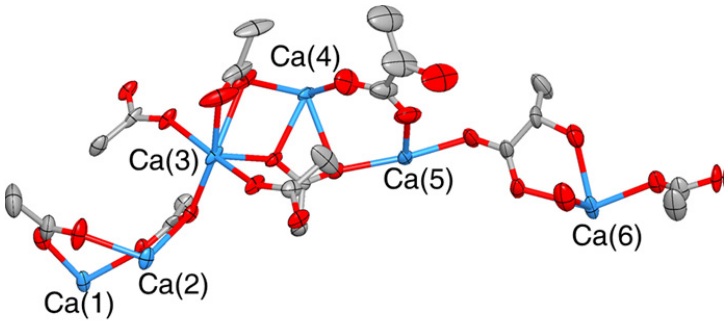

Figure S2. Asymmetric unit of **MOF-1203** (thermal ellipsoids with 30% probability). Hydrogen atoms are omitted for clarity. Color scheme is as follows: C, grey; O, red; Ca, blue.

Table S2. Crystal data and structure determination for MOF-1203

Compound	**MOF-1203**
Chemical formula	$C_{40}H_{59.33}O_{40.67}Ca_9$
Formula mass	1551.64
Crystal system	orthorhombic
Space group	$I2_12_12_1$
λ (Å)	0.7749(1)
a (Å)	10.5046(4)
b (Å)	22.2580(9)
c (Å)	31.2485(13)
Z	4
V (Å^3)	7306.3(5)
Temperature (K)	100(2)
Size /mm^3	0.09 × 0.005 × 0.005
Density (g/cm^{-3})	1.411
Measured reflections	7620
Unique reflections	3865
Parameters	433
Restraints	59
R_{int}	0.1195
θ range (°)	2.23-22.86
R_1, wR_2	0.0524, 0.1406
S (GOF)	1.026
Max/min res. dens. (e/Å^3)	0.60/-0.33
Flack parameter	0.09(3)

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^b wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $^c S = [\Sigma w(F_o^2 - F_c^2)^2/(N_{ref} - N_{par})]^{1/2}$.

Section S3. Powder X-ray diffraction analysis

Powder X-ray diffraction (PXRD) analysis were conducted on a Bruker D8 Advance diffractometer with Cu K_α radiation (λ = 1.54056 Å). Phase purity of the materials is examined by comparing experimental and simulated PXRD patterns.

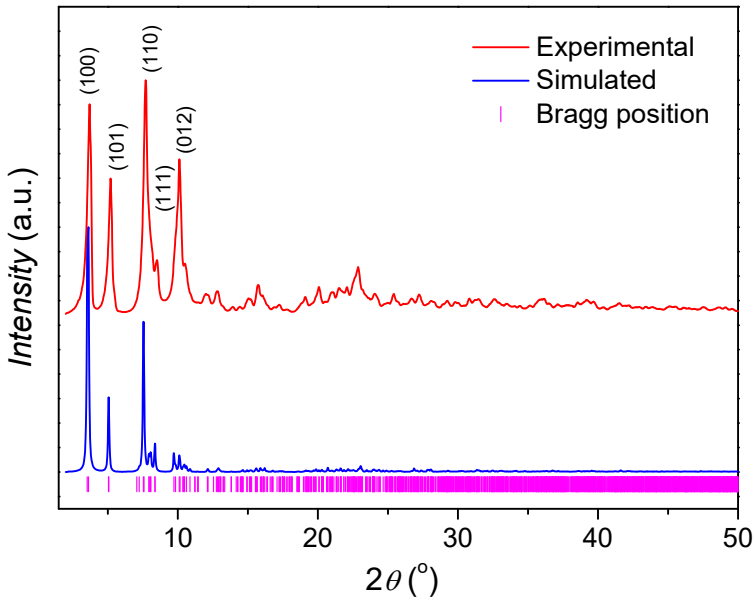

Figure S3. Comparison of the experimental PXRD patterns of **MOF-1201**: activated (red) and simulated pattern (blue) from single crystal X-ray data.

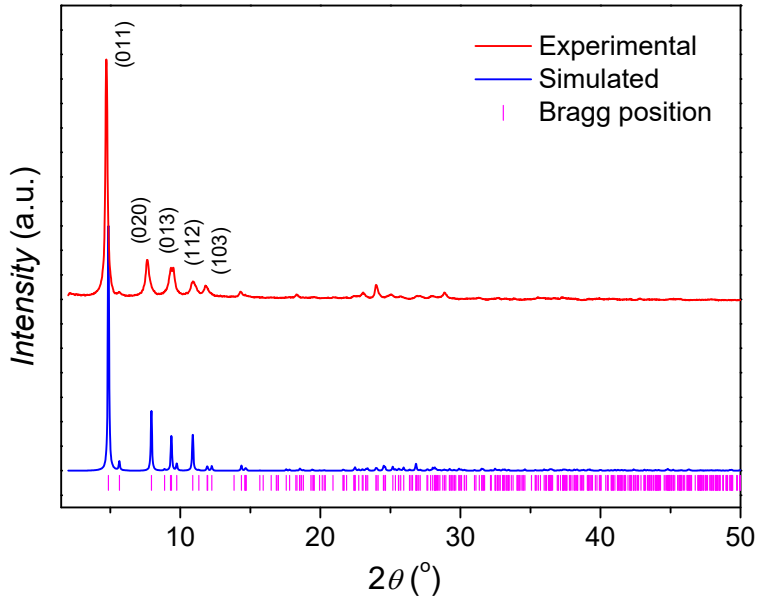

Figure S4. Comparison of the experimental PXRD patterns of **MOF-1203**: activated (red) and simulated pattern (blue) from single crystal X-ray data.

Section S4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) curves were recorded using a TA Q500 thermal analysis system under air flow.

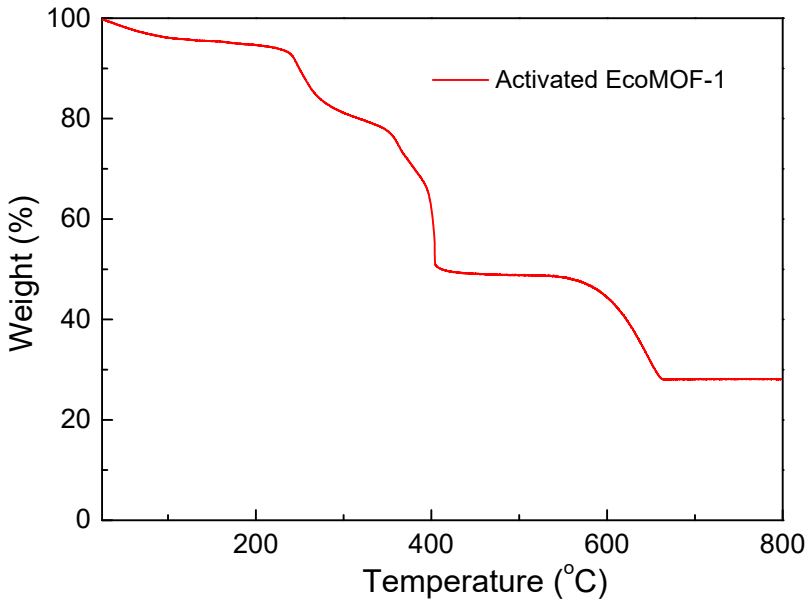

Figure S5. TGA trace for the activated sample of **MOF-1201** in air.

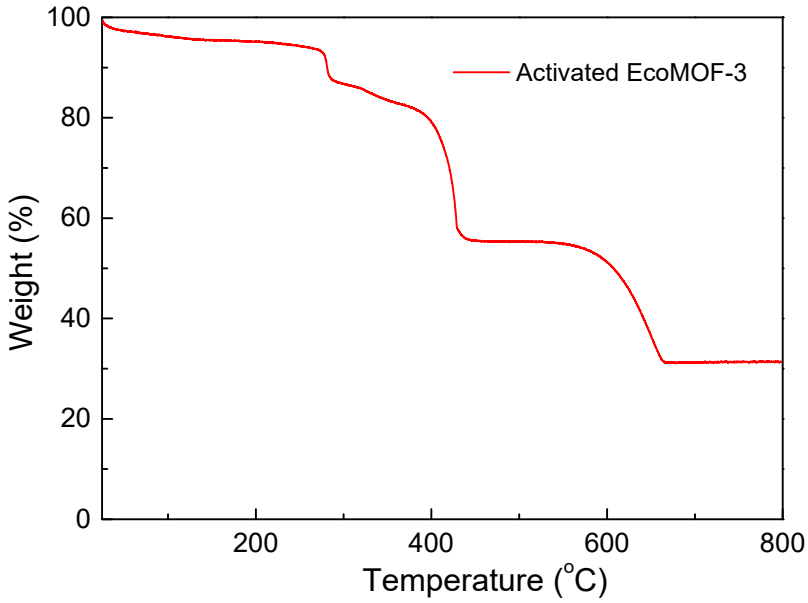

Figure S6. TGA trace for the activated sample of **MOF-1203** in air.

Section S5. ^{1}H NMR spectroscopy

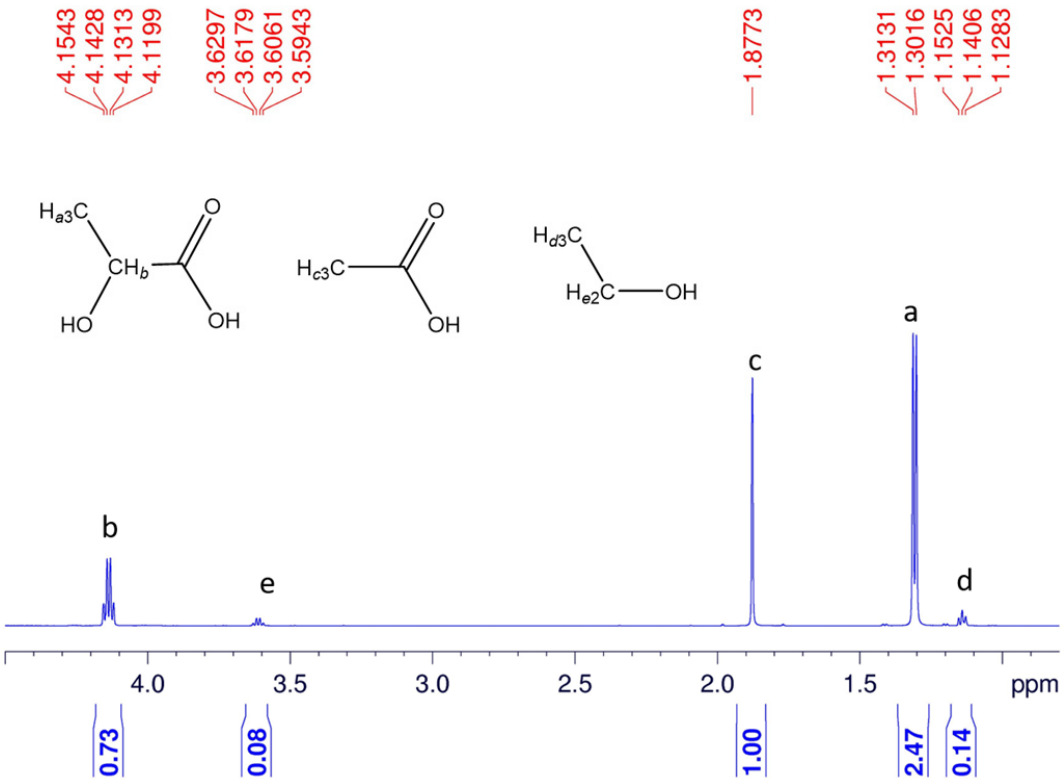

Figure S7. ^{1}H NMR spectrum of solution of **MOF-1201** indicating the presence of lactate and acetate linkers.

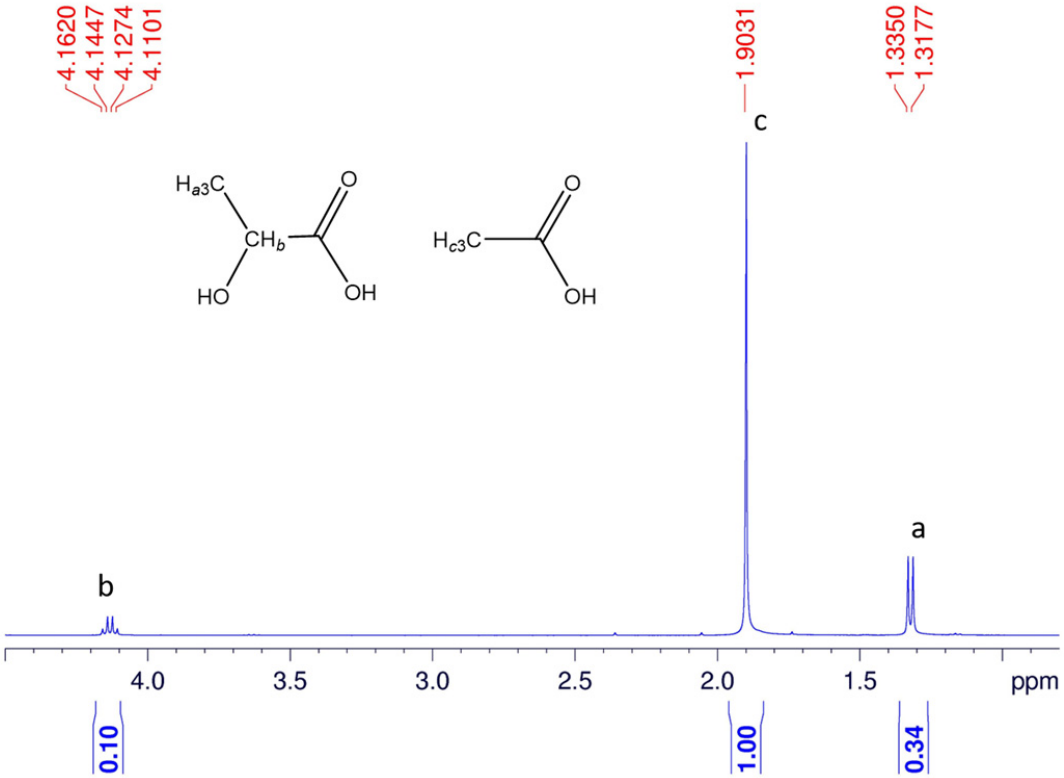

Figure S8. ^{1}H NMR spectrum of solution of **MOF-1203**.

Section S6. Low-pressure gas adsorption measurements

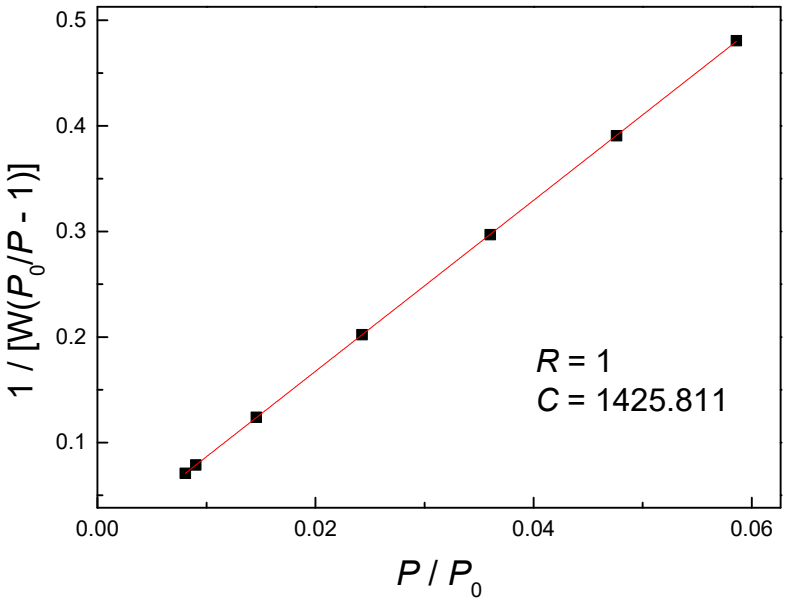

Figure S9. Multiple point BET plot of **MOF-1201** giving a specific surface area of 430 m^2/g.

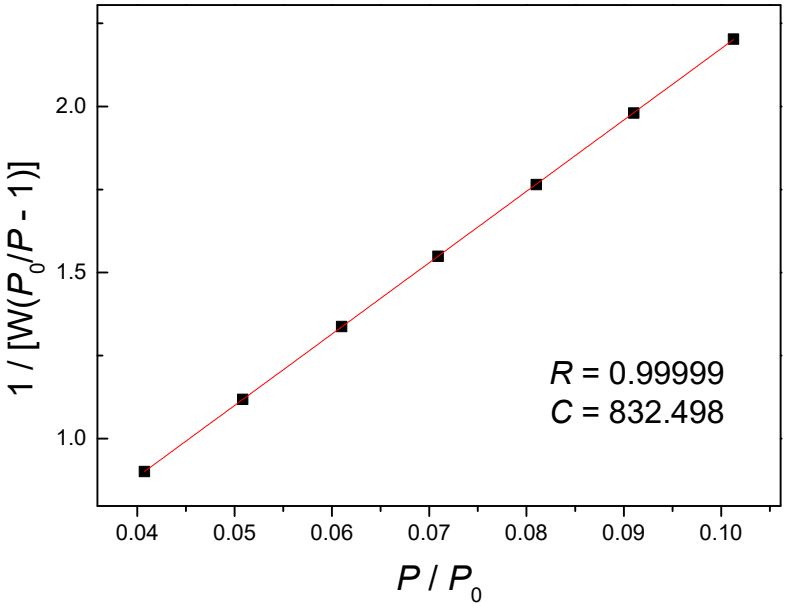

Figure S10. Multiple point BET plot of **MOF-1203** giving a specific surface area of 160 m^2/g.

Section S7. Fumigant adsorption and slow release measurements

cis-1,3-dichloropropene vapor sorption isotherm at 25 ^{o}C were measured in-house on a BEL Japan BELSORP-aqua3. Prior to measurements, the sample was flash frozen in liquid nitrogen and then evacuated under dynamic vacuum at least twice to remove any gases from the reservoir. The measurement temperature was controlled and monitored with a water bath held at 25 ^{o}C. Helium was used to estimate dead space for vapor adsorption measurements.

Slow release experiments were carried out using the TA Q500 thermal analysis system under constant air flow of 1 cm^3 min^{-1}. We carried out the demonstrating experiments in lab to show the capability of slow release by MOF-1201. Systematic studies considering air flow rate, humidity, and in-field studies will be of future work.

References:

(1) Bruker. *APEX2*. (Bruker AXS Inc., Madison, Wisconsin, U.S.A. 2010).

(2) Sheldrick, G. M. *Acta Cryst. A* **2008**, *64*, 112–122.

(3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. *Appl. Cryst.* **2009**, *42*, 339–341.

(4) Rees, B.; Jenner, L. B.; Yusupov, M. *Acta Cryst. D* **2005**, *61*, 1299–1301.