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Strong and Reversible Binding of Carbon Dioxide in a Green Metal-Organic Framework

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— SUPPLEMENTARY INFORMATION —

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Section S1.0: Materials and General Procedures

All reagents were obtained from commercial sources (Sigma Aldrich, Wacker Chemical, Cambridge Isotopes, Airgas) and were used without further purification.

Section S2.0: Synthetic Procedures

Preparation of CD-MOF-2: γ-Cyclodextrin (1.30 g, 1 mmol) and RbOH (0.82 g, 8 mmol) were dissolved in deionized H_2O (20 mL). The solution was filtered through a 13 mm syringe filter (0.45 μm PTFE membrane) into pre-washed borosilicate culture tubes (16 × 150 mm). MeOH (ca. 50 mL) was allowed to vapor-diffuse into this solution over a period of two weeks. Colorless cubic single crystals (1.25 g, 71 %), suitable for analysis by X-ray crystallography, were isolated, filtered and washed with MeOH (2 x 30 mL) before being left to dry in air.

Activation for Analytical Studies: Activation of CD-MOF-2 was achieved by immersion of the crystals in CH_2Cl_2 for three days. During the solvent exchange process the CH_2Cl_2 was refreshed three times. The solvent was decanted and the wet sample was then evacuated (10^{-3} Torr) at room temperature for 24 h.

Activation with Incorporation of Methyl Red: Activation of CD-MOF-2 and incorporation of methyl red into the pores was achieved by immersion of the crystals in a 1 mM solution of CH_2Cl_2 for two days. The solvent was decanted and the resulting yellow crystals were washed with CH_2Cl_2 (2 x 10 mL). The wet sample was then evacuated (10^{-3} Torr) at room temperature for 24 h.

Preparation of KBenz CD-MOF: γ-Cyclodextrin (1.30 g, 1 mmol) and potassium benzoate (1.28 g, 8 mmol) were dissolved in deionized H_2O (20 mL). The solution was filtered through a 13 mm syringe filter (0.45 μm PTFE membrane) into pre-washed borosilicate culture tubes (16 × 150 mm). EtOH (ca. 50 mL) was allowed to vapor-diffuse into this solution over a period of two weeks. Colorless cubic single crystals, suitable for analysis by X-ray crystallography, were isolated, filtered and washed with MeOH (2 x 30 mL) before being left to dry in air.

Activation for Analytical Studies: Activation of KBenz CD-MOF was achieved by immersion of the crystals in CH_2Cl_2 for three days. During the solvent exchange process the CH_2Cl_2 was

refreshed three times. The solvent was decanted and the wet sample was then evacuated (10^{-3} Torr) at room temperature for 24 h.

Preparation of RbF CD-MOF: γ-Cyclodextrin (1.30 g, 1 mmol) and rubidium fluoride (0.82 g, 8 mmol) were dissolved in deionized H_2O (20 mL). The solution was filtered through a 13 mm syringe filter (0.45 μm PTFE membrane) into pre-washed borosilicate culture tubes (16 × 150 mm). EtOH (ca. 50 mL) was allowed to vapor-diffuse into this solution over a period of six weeks. Colorless cubic single crystals, suitable for analysis by X-ray crystallography, were isolated, filtered and washed with MeOH (2 x 30 mL) before being left to dry in air.

Activation for Analytical Studies: Activation of RbF CD-MOF was achieved by immersion of the crystals in CH_2Cl_2 for three days. During the solvent exchange process the CH_2Cl_2 was refreshed three times. The solvent was decanted and the wet sample was then evacuated (10^{-3} Torr) at room temperature for 24 h.

Activation with Incorporation of Methyl Red: Activation of RbF CD-MOF and incorporation of methyl red into the pores was achieved by immersion of the crystals in a 1 mM solution of CH_2Cl_2 for two days. The solvent was decanted many times and the resulting yellow crystals were washed by Soxhlet extraction for 24 h with CH_2Cl_2 (2 x 10 mL). The wet yellow sample was then evacuated (10^{-3} Torr) at room temperature for 24 h.

Preparation of OD_x-CD-MOF-2: γ-Cyclodextrin (0.65 g, 0.5 mmol) and RbOH (0.41 g, 4 mmol) were dissolved in deionized D_2O (10 mL). The solution was filtered through a 13 mm syringe filter (0.45 μm PTFE membrane) into pre-washed borosilicate culture tubes (13 × 100 mm). CD_3OD (ca. 50 mL) was allowed to vapor-diffuse into this solution over a period of two weeks. Colorless cubic single crystals suitable for analysis by X-ray crystallography were isolated, filtered and washed with CD_3OD (2 x 30 mL). The crystals were stored in anhydrous CD_3OD until activation.

Activation for Analytical Studies: Activation of CD-MOF-2 was achieved by immersion of the crystals in $CDCl_3$ for three days. During the solvent exchange process the $CDCl_3$ was refreshed three times. The solvent was decanted and the wet sample was then evacuated (10^{-3} Torr) at room temperature for 7 d.

Section S3.0: Colorimetric Detection of CO_2

Color Change Experiments:

The vial was exposed to CO_2 by allowing a gentle stream of carbon dioxide (bone dry) to flow into the vial for 5 min to allow for full color change (from yellow to red) to take place. Full reversion of the color, from red back to the initial yellow, was obtained 5 min after removing the source of CO_2 and allowing the vial to equilibrate ambient air. In order to determine the sensitivity of this procedure to atmospheric moisture, a similar experiment was conducted wherein the CO_2 was sourced from subliming dry ice. In this experiment, the scintillation vial and a 100 mL beaker of dry ice were placed under a second, 2000 mL beaker. Again, after 5 min, a clear color change had occurred. Full reversion of the color was obtained 5 min after removing the 2000 mL beaker and allowing the vial to equilibrate with the ambient atmosphere.

Section S3.1: Colorimetric change of KBenz CD-MOF upon exposure to CO_2

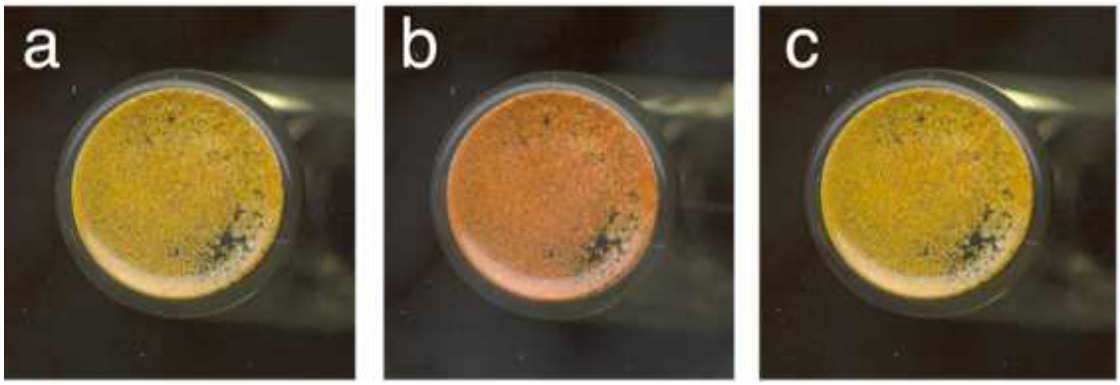

Figure S1: (a-c) Scanned images of CD-MOF synthesized from potassium benzoate, which have methyl red incorporated into their framework. The crystals before CO_2 incorporation are bright yellow (a). After 5 min of exposure to CO_2 vapor at ambient pressure, the crystals turn dark red-orange indicating a protonation of methyl red (b). Removing the source of CO_2 and allowing ambient air to displace the atmosphere of CO_2 causes the crystals to revert to their yellow color over a period of 5 min (c)

Section S4.0 Gas Adsorption Experiments and Calculation of Surface Area by BET Method

Low-Pressure Gas Adsorption Measurements. Low-pressure CO_2, CH_4 and N_2 adsorption measurements (up to 1 bar) were performed on an Autosorb-1 (Quantachrome) volumetric analyzer. The samples were out-gassed to 10^{-6} Torr. Helium was used for the estimation of the dead volume, assuming that it is not adsorbed at any of the temperatures investigated. Ultra-high purity grade CH_4, N_2, He (99.999% purity) and CO_2 gases (99.995% purity) were used throughout the adsorption experiments.

Section S5.0: Structure Resolution from Powder X-Ray Diffraction

pXRD Experiments: Powder X-ray data were collected using a Bruker D8-Discover θ-2θ diffractometer in reflectance Bragg-Brentano geometry employing Ni filtered Cu Kα line focused radiation at 1600 W (40 kV, 40 mA) power and equipped with a Vantec Line detector. Radiation was focused using parallel focusing Gobel mirrors. The system was also outfitted with an anti-scattering shield that prevents incident diffuse radiation from hitting the detector, preventing the normally large background at $2\theta < 3$. Samples were mounted on zero background sample holders by dropping powders from a wide-blade spatula and then leveling the sample with a razor blade. The structure of CD-MOF-2 is a known [S1] and crystalline powders were shown to match simulated powder patterns from single crystal data.

Section S6.0: Data from Dry Grinding CD-MOF-2

Dry Grinding Procedure: CD-MOF-2 (1 g) was placed in a mortar and pestle and subjected to continuous mechanical grinding for 7 min. After grinding, samples were analyzed by pXRD and gas sorption measurements were performed. In both cases, samples had clearly lost crystallinity (Fig. S2) and porosity (Fig. S3).

Color Change Procedure: A sample of CD-MOF-2, which had methyl red indicator incorporated (1 g), was placed into a mortar and pestle and subjected to mechanical grinding for 10 min. After grinding, the sample was placed into a round bottom flask, fitted with a magnetic stirbar. CO_2, sourced from either (a) subliming solid dry ice or (b) a tank of bone-dry grade gaseous CO_2, was introduced as a continuous stream to maintain an atmosphere of CO_2. Stirring was initiated to aerosolize the particulate material in order to facilitate exposure of the solid to the atmosphere. Neither case (a) nor (b) resulted in a color change.

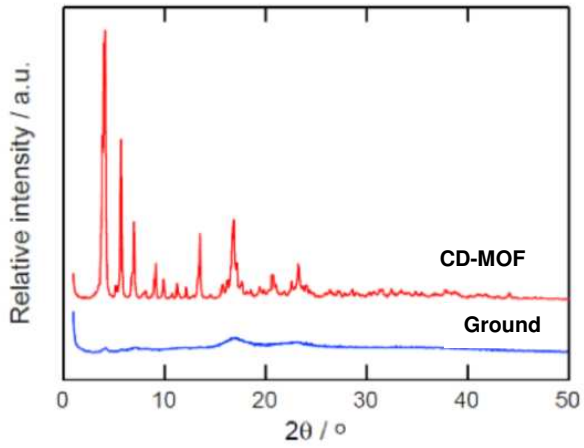

Figure S2: PXRD Patterns for CD-MOF-2 before (red) and after grinding (blue).

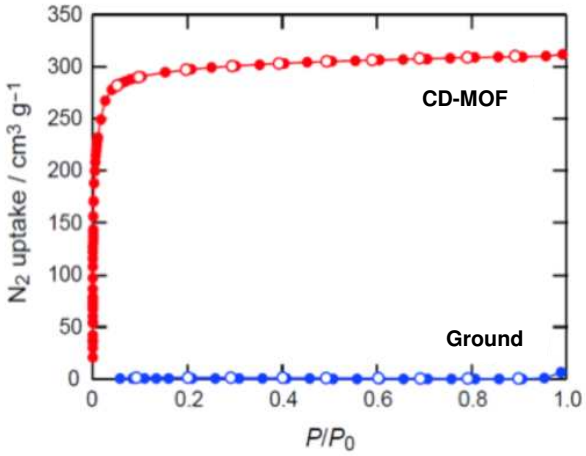

Figure S3: N_2 Isotherms for CD-MOF-2 before (red) and after grinding (blue).

Section S7: Solid State ^{13}C CP/MAS and HETCOR Nuclear Magnetic Resonance Spectroscopy:

High resolution solid-state ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at ambient pressure and room temperature on a Varian VNMRS 400 MHz spectrometer using a standard 5 mm and a 3.2 mm T3 PENCIL probe with 5 mm or 3.2 mm (outside diameter) zirconia rotors, respectively.

The ^{13}C frequency was tuned in the third channel (Y) on the probe and data collection was performed through the second channel by using a kilowatt amplifier to enable a short 90 degree pulse width within 4 μs (5mm probe) and 2.5 μs (3.2mm probe). The cross-polarization pulse sequence called 'tancpx' was used with normal proton decoupling. A typical spectrum parameter set is as follows: spectrum frequency 100.544 MHz, spectral width 50 KHz, pulse width 4 us (5mm) or 2.5 us (3.2mm) for both proton and carbon 90 degree, delay time 5 s, contact time 5 ms, acquisition time 20.5 ms, with the scan number varying from 1024 to 10k. The HETCOR pulse sequence called 'hetcortancp2d' was also used with proton decoupling also. A typical parameter set is: spectral width 50 KHz, pulse width 2.5 us for both proton and carbon 90 degree, delay time 5 s, contact time 5 ms, acquisition time 20.5 ms, scan number 16 and increments 128. All the spectra were referenced to the external adamantine peak at 38.3 ppm which was converted to tetramethylsilane at 0.0 ppm. All the data collected and processed were using software VnmrJ 2.1B.

Samples of activated CD-MOF were placed into a glass Schlenk line and evacuated for several hours and backfilled with CO_2. Bone dry grade CO_2 with atmospheric isotopic abundance of ^{13}C were used for CD-MOF-2 and RbF CD-MOF (Figure S4) and bone dry grade enriched ^{13}C CO_2 was used to obtain a larger signal to differentiate from carbonate peaks of the benzoate in the KBenz CD-MOF (Figure S5). The samples were exposed to CO_2 for 30 min after two fill and evacuation cycles and were transferred in the open air to a 3.2 mm zirconium NMR rotor and capped with a gas tight Teflon plug.

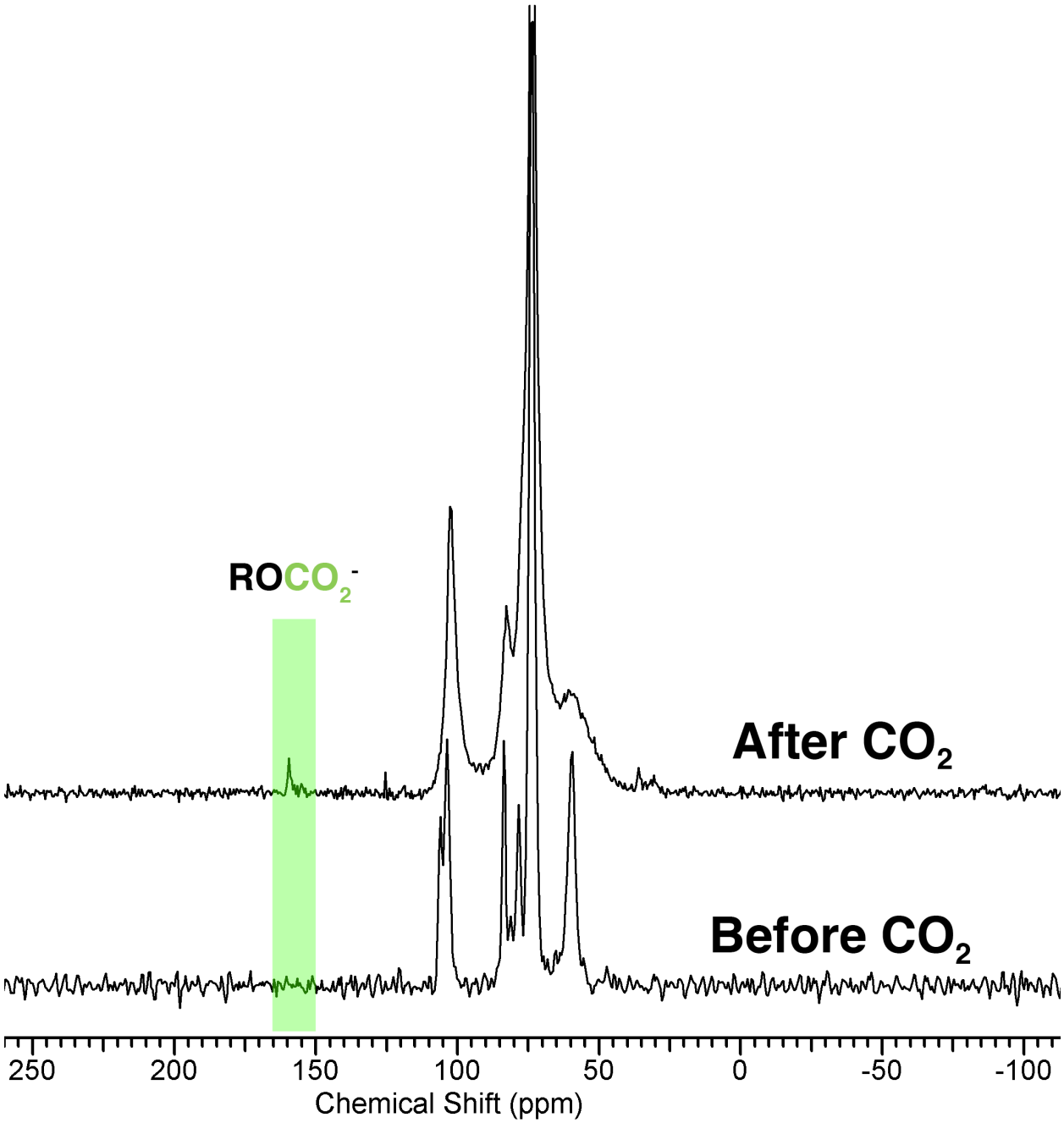

Figure S4: Solid-state CPMAS ^{13}C NMR of RbF CD-MOF (bottom) before exposure to CO_2 and (top) after exposure to CO_2. The carbonate peak resulting from the reaction of CO_2 with the hydroxyl groups on the RbF CD-MOF structure is visible at 159 ppm, consistent with the results obtained from CD-MOF-2.

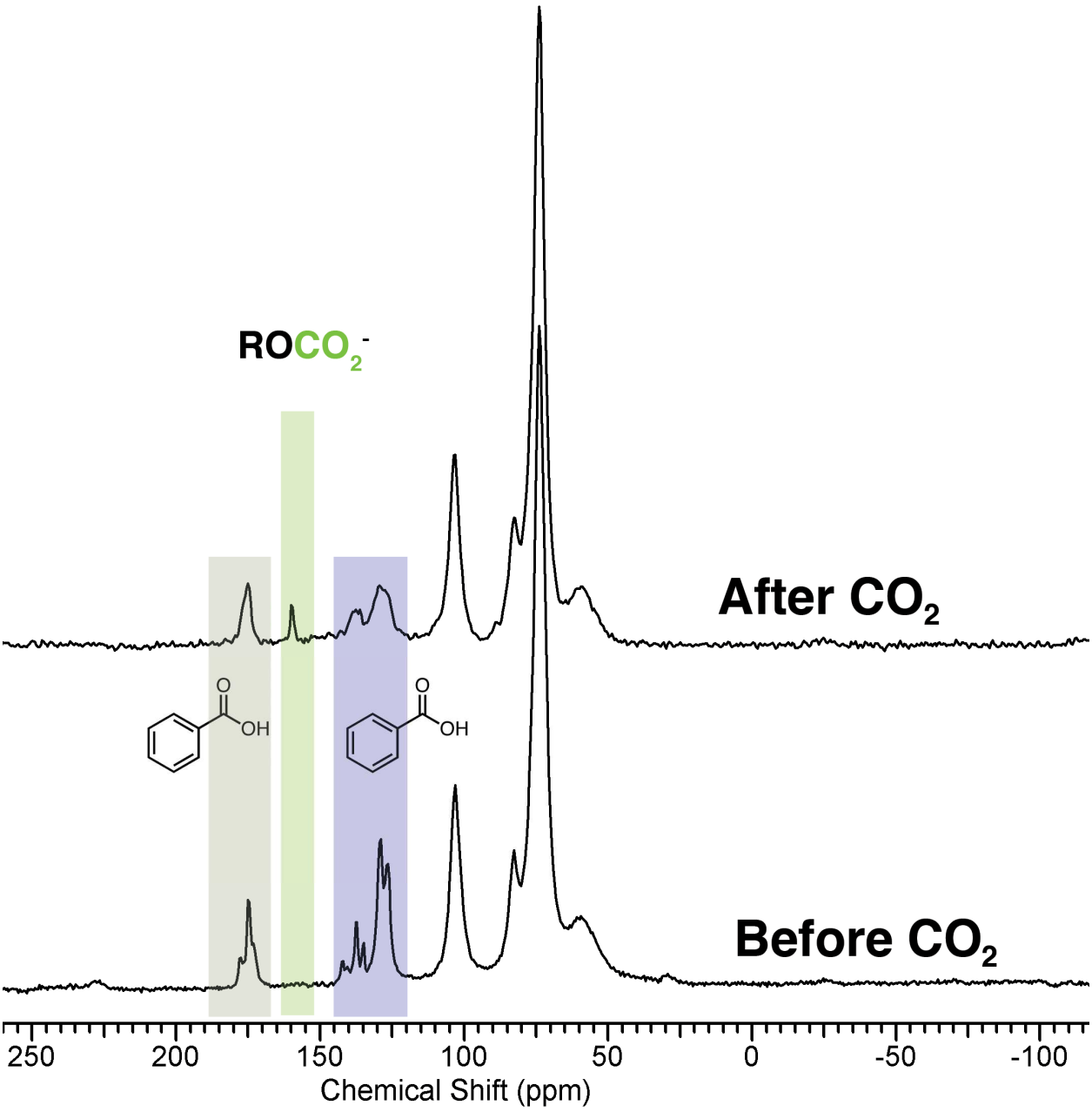

Figure S5: Solid-state CPMAS ^{13}C NMR of KBenz CD-MOF, containing potassium benzoate, (bottom) before exposure to CO_2 and (top) after exposure to CO_2. Notable peak broadening occurs to the benzoate peaks upon addition of CO_2 as a consequence of protonation and more rapid diffusion within the framework as free benzoic acid. The carbonate peak resulting from the reaction of CO_2 with the hydroxyl groups on the KBenz CD-MOF structure is visible at 159 ppm, consistent with the results obtained from CD-MOF-2.

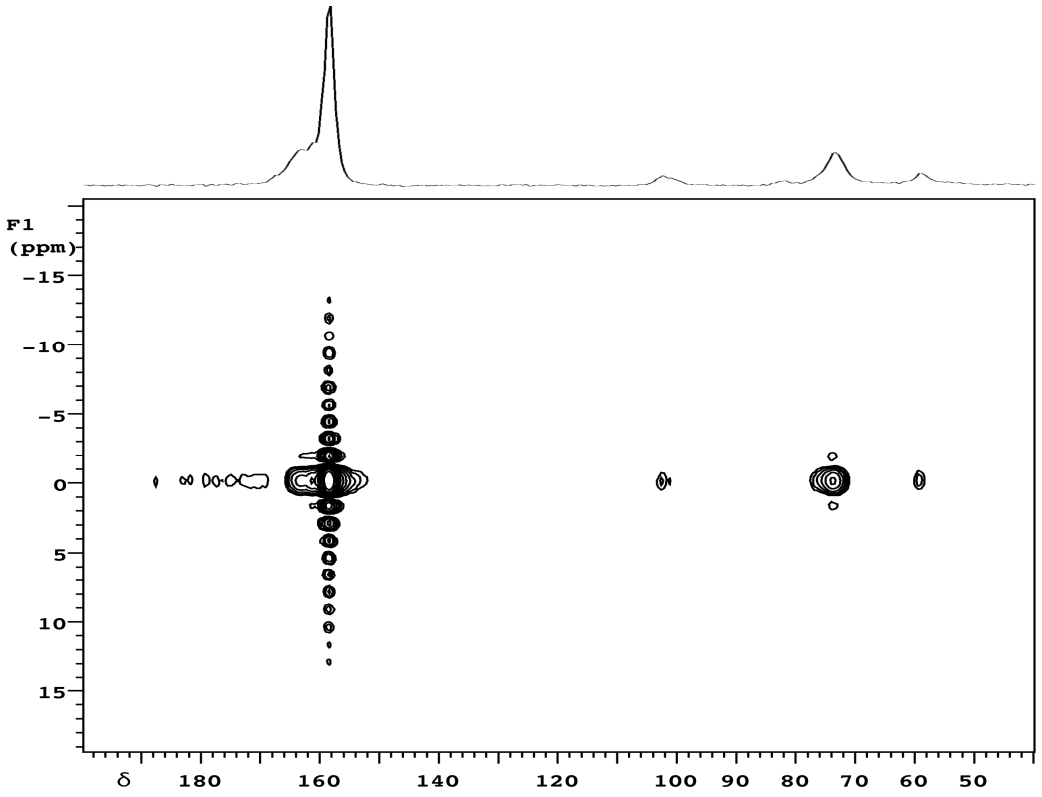

Figure S6: Solid-state CPMAS ^{13}C NMR hetcortancp2d spectra of OD_x-CD-MOF-2 after exposure to ^{13}C enriched CO_2. Data were collected on VNMRS 400 using a 3.2 mm probe at a spin rate of 10 k RPM. ^{13}C (top x-axis). Note that mobile CO_2 resonance at 126 ppm does not appear when cross-polarization is applied. C-H proton peaks were not calibrated on account of the low spectral resolution.

References

S1. Smaldone, R. A.; Forgan, R. S.; Furukawa, H.; Gassensmith, J. J.; Slawin, A. M. Z.; Yaghi, O. M.; Stoddart, J. F. *Angew. Chem. Int. Ed.*, **2010**, *49*, 8630