Electronic Supplementary Material (ESI) for Dalton Transactions

ELECTRONIC SUPPLEMENTARY INFORMATION

CO_2 adsorption properties of a Ca(II)-based organophosphonium coordination material

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1. Experimental Section

1.1 Materials and Measurements

All reagents and solvents were used as received from commercial suppliers without further purification. Powder X-ray diffraction (PXRD) data were collected under both ambient and *in-situ* conditions on dry crystalline solids in borosilicate capillaries using a Rigaku R-Axis Spider diffractometer operating with Cu Kα radiation (1.5418 Å). Thermogravimetric analysis (TGA) was performed under He atmosphere at a scan rate of 2 °C/min using a TA instruments Q50 series.

1.2 Synthesis of the trilithium salt of *tris*(*p*-carboxylated) triphenylphosphine ($ptbcLi_3$)

Our group previously reported[1] a synthetic procedure based on the work reported by Amengual *et al*.[2] to obtain the tris-*p*-carboxylated triphenylphosphine ligand as the trilithium salt, which was dried under vacuum to afford a pale yellow solid, yield 68% based on the tris(*para*-bromo)triphenylphosphine intermediate, ^{1}H NMR (D_2O, 300 MHz) δ = 7.38 (t, 6H); 7.70 (dd, 6H); ^{31}P NMR (D_2O, 162 MHz) δ = -6.66.

1.3 Synthesis of tris(*p*-carboxylate)triphenyl- methyl phosphonium chloride ($[mptbcH_3]Cl$)

Li_3(ptbc) (100 mg, 2.4 mmol) was dissolved into degassed H_2O (5 mL) in a round-bottomed glass reactor tube fitted with magnetic stirred bar and screw cap. A solution of MeI (140 mg, 3.5 mmol) in dry and degassed DCM (5 ml) was added and the mixture was vigorously agitated for 24 h. The resulting mixture was concentrated on a rotary evaporator to remove all DCM and excess MeI. The aqueous phase was then acidified with degassed ice cold HCl solution (1.0 M) at 0 ^{o}C to yield a white precipitate of $mptbcH_3Cl{\cdot}H_2O$, which was isolated by filtration, washed with ether and dried under vacuum, yield 784 mg, 60%. Found: C, 57.4;

H, 4.58 %; $C_{22}H_{20}ClO_7P$ requires: C, 57.1; H, 4.36 %;^{1}H NMR ($CDCl_3$, 300 MHz), δ = 3.15 (d, 3H), 7.85 (dd, 6H), 8.19 (dd, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz), δ = 166.7 (s, $ArCO_2H$), 139.7 (d, Ar), 133.7 (d, Ar), 130.5 (d, Ar), 123.0 (d, Ar), 7.65 (s, PCH_3); ^{31}P NMR (D_2O, 162 MHz) δ = 25.16.

1.4 Synthesis of $[Ca(mptbc)(OH_2)\cdot 2H_2O]_\infty$ PCM-14

The methyl phosphonium ligand $[(H_3C)P(C_6H_4\text{-}p\text{-}CO_2H)_3]I$ (20 mg, 0.037mmol) was dissolved in DMF/H_2O/EtOH (1:1:1, 2.5 cm^3). To this was added a second solution of $Ca(OH)_2$ (8 mg, 0.108 mmol) dissolved in 2.5 cm^3 of the same solvent. NaOH(0.10 cm^3, 1.0 M) was added to the resulting slurry and the solution was sonicated (20 sec). The reaction was heated in a scintillation vial using a graphite thermal bath at 70 ºC for 4-5 days. Yield = 35 mg, 17 %; *ν*max(KBr/cm-1): 1619m, 1617m, 1552 s, 1496 w, 1361 s, 1317 m, 1106, 1016 m, 901 m, 840m, 769 s, 734 s, 691 s.

1.5 CO_2, N_2, O_2 and H_2 adsorption isotherms.

CO_2, N_2, O_2 and H_2 isotherms were recorded on an Autosorb-1 system (Quantachrome) at the University of Texas at Austin under ultra high vacuum in a clean system with a diaphragm and turbo pumping system. Ultra-pure grade (99.9995 %) CO_2, N_2, O_2 and H_2 were purchased from PRAXAIR. The surface area was calculated using the BET method based on adsorption data in the partial pressure (P/Po) range 0.05 to 0.30 for CO_2.

2. TGA plot

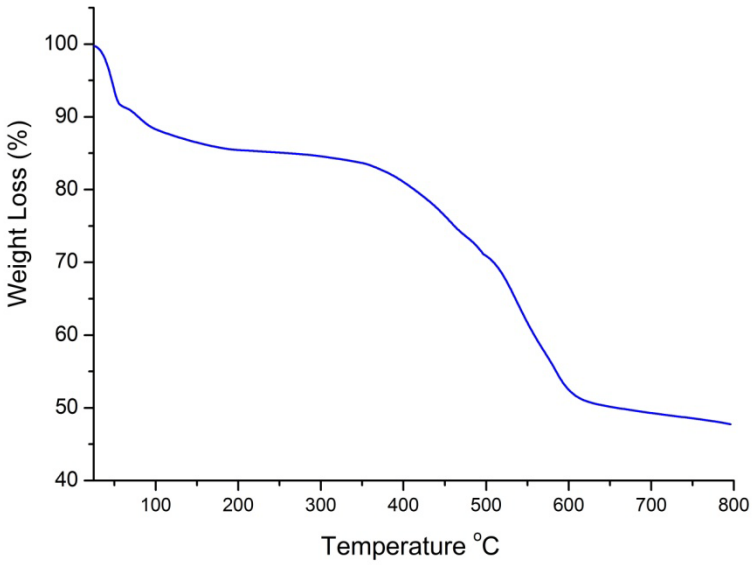

Figure S1: TGA analysis of compound PCM-14 under He carrier flow.

3. PXRD Patterns

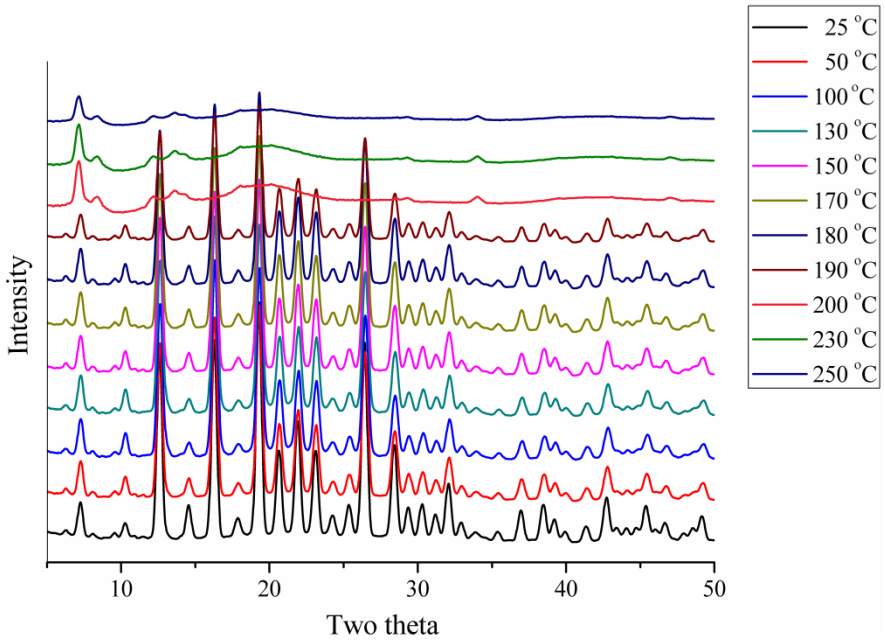

Figure S2: PXRD of samples of PCM-14 after CO_2 gas adsorption activated at different temperatures and $1x10^{-10}$ bar. From 25 to 190 °C the crystallinity of the sample is retained. From 200 to 250 °C the crystallinity of the material is lost, suggesting a partial decomposition of the material.

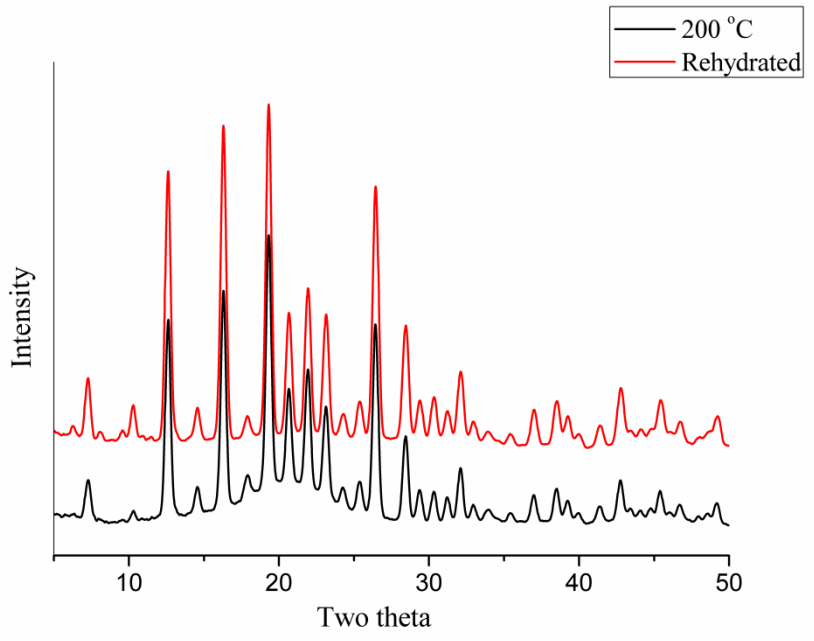

Figure S3: PXRD of samples of PCM-14 heated at 200 °C (black) and then rehydrated (red). At 200 °C and after the rehydration process the crystallinity is retained.

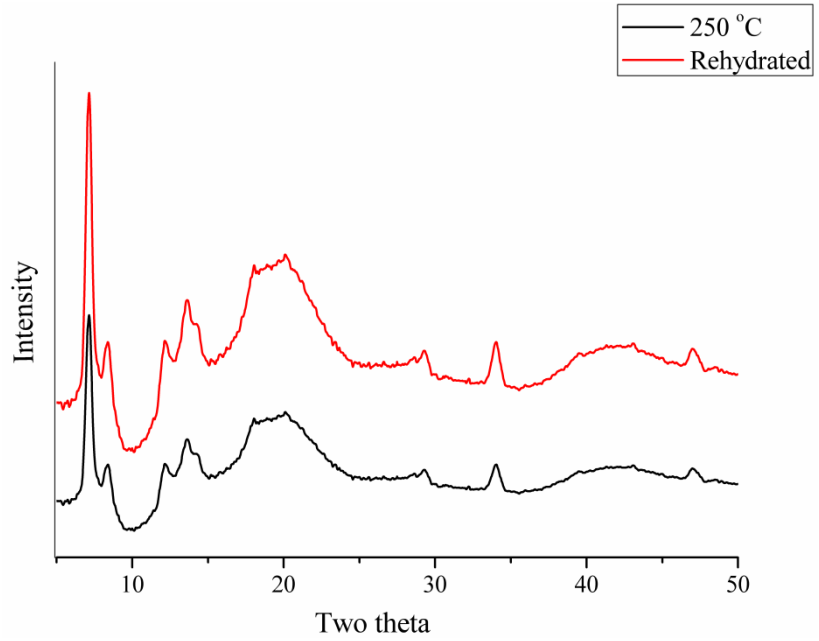

Figure S4: PXRD of samples of PCM-14 heated at 250 °C (black) and then rehydrated (red). At 250 °C the loss of bulk crystallinity is maintained after the rehydration of the sample.

References:

1 S. M. Humphrey, P. K. Allan, S. E. Oungoulian, M. S. Ironside and E. R. Wise, *Dalton Trans.*, 2009, 2298.

2 R. Amengual, F. Genin, V. Michelet, M. Savignac and J.-P. Genê, *Adv. Synth. Catal.*, 2002, **344**, 393.