Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information for

Titanium-based porous coordination polymer as a catalyst for chemical fixation of CO_2

Ya Du,[a] Haishen Yang,[a, b] Shun Wan,[c] Yinghua Jin[a] and Wei Zhang[a,*]

[a] Department of Chemistry and Biochemistry, University of Colorado Boulder, CO 80309, USA. [b] Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, College of Environmental and Chemical Engineering, Shanghai University of Electric Power, Shanghai 200090, P. R. China. [c] NCO Technologies LLC, Concord, NC 28027, USA

Tel: (+1) 303-492-0652; Fax: (+1) 303-492-5894; E-mail: wei.zhang@colorado.edu

Table of contents

1. Materials and methods

Unless otherwise stated, all commercially available chemicals were used without further purifications. Tetrahydrofuran (THF), dichloromethane and dimethylformamide (DMF) are purified by the MBRAUN solvent purification systems. Macrocycle **1** was synthesized according to the reported procedure.[1] All the reactions were conducted under inert atmosphere (nitrogen or argon).

Flash column chromatography was performed by using a 100-150 times weight excess of flash silica gel 32-63 μm from Dynamic Absorbents Inc. Fractions were analyzed by TLC using TLC silica gel F_{254} 250 μm precoated-plates from SiliCycle Inc.

NMR spectra were taken on Inova 400 and Inova 500 spectrometers. Solid-state cross polarization magic angle spinning (CP/MAS) NMR spectra were recorded on an Inova 400 NMR spectrometer. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA) and used as received.

The FT-IR spectra were obtained in the form of KBr pellets, using a Thermo Nicolet Avatar-370 spectrometer. Elemental analyses were taken at Huffman Laboratories, Inc. Thermogravimetric analysis (TGA) was performed in Pyris 7 TGA (Perkin Elmer) by heating the sample under an atmosphere of nitrogen from 25 ˚C to 800 ˚C at 10 ˚C/min. The Quantachrome Autosorb ASiQ automated gas sorption analyzer was used to measure N_2, adsorption isotherms. The samples were activated by heating at 100 ˚C under the vacuum for at least 22 hours. Ultra-high purity grade (99.999%) N_2, oil-free valves and gas regulators were used for all free space corrections and measurements. For all of the gas adsorption measurements, the temperatures were controlled by using a refrigerated bath of liquid N_2 (77 K) or by ice water (273 K).

Scanning Electron Microscopy images (SEM) were recorded using a JSM-6480LV (LVSEM) at 15 kV.

2. Synthesis of Ti-PCP

To the suspension of macrocycle **1** (96 mg, 0.096 mmol) in DMF (6 mL) was added $Ti(O^iPr)_4$ (58 µL, 0.192 mmol). The mixture was sealed and heated at 120 ˚C for 7 days. The precipitates were collected by centrifugation, washed with anhydrous acetone, and dried under vacuum overnight, to give **Ti-PCP** as a brown solid (100 mg, 98 %): CP-MAS ^{13}C NMR (100 MHz) δ 146.7, 139.8, 130.0, 123.2, 90.5, 65.5, 57.3; Elemental Analysis: calcd. For $(C_{68}H_{40}O_8Ti_2)_n$: C (75.57), H (3.73), Ti (8.86), found C (59.69), H (3.77), Ti (5.63). The inconsistency between the experimental and calculated elemental analysis results is likely due to the surface absorption of small molecules (e.g. H_2O) as well as incomplete combustion of these carbon-rich frameworks.

3. General procedure of cycloaddition of CO_2 to epoxide

To an oven-dried 50 mL flask was added a stir bar, **Ti-PCP** (5.5 mg, 0.01 mmol Ti center, 0.1 mol% Ti-center to epoxide) and tetrabutylammonium bromide (32 mg, 0.1 mmol, 1 mol% to epoxide). The flask was degassed by quickly alternating vacuum evacuation and CO_2 backfill with a balloon. Epoxide (10.0 mmol) was added by syringe. The flask was sealed with a CO_2 balloon and placed in oil bath, and allowed to stir at 100 ^{o}C for 24 hours. The reaction was removed from oil bath and a known amount $CHCl_2CHCl_2$ was added as an internal standard. The yield of carbonate was determined based on the integration of the NMR spectrum of the crude product mixture and $ClCH_2CH_2Cl$.

4. FT-IR spectra of macrocycle 1 and Ti-PCP

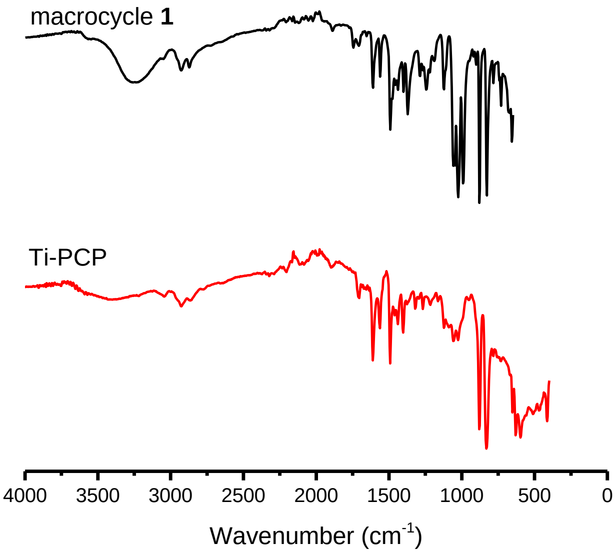

Figure S1. IR spectra of macrocycle **1** and “as synthesized” **Ti-PCP**.

Table S1. Peak assignments for FT-IR spectrum of macrocycle **1**.

Peak (cm^{-1})	Assignment and Notes
3220 (m)	O-H stretch from hydroxyl groups
2925 (w)	C−H stretching
2876 (w)	
2206 (w)	C≡C stretch

1743 (w)	Comb useful for determining substitution patterns in 6-membered aromatic rings
1611 (w)	C=C stretch in typical region for fused aromatics.
1560 (w)	C=C stretch in typical region for fused aromatics.
1490 (m)	δ C–H band of CH_2
1369 (s)	δ C–O–H, characteristic band for alcohol
1123 (w)	C−H in plane bending modes
1078 (m)	
1025 (s)	C−O stretch, characteristic band for alcohol
877 (m)	C−H out of plane bands for *p*-substituted aromatic
828 (m)	
730 (m)	

Table S2. Peak assignments for FT-IR spectrum of **Ti-PCP**.

Peak (cm^{-1})	Assignment and Notes
3398 (w)	O−H stretch from hydroxyl groups
2920 (w)	C−H stretch
2901(w)	
2191 (w)	C≡C stretch
1609(m)	C=C stretch in typical region for fused aromatics
1561 (w)	C=C stretch in typical region for fused aromatics
1490 (m)	δ C–H band of CH_2
1056 (m)	Possible Ti-O bands
1020(m)	
878 (m)	C−H out of plane bands for *p*-substituted aromatic
830 (m)	

5. Solid state ^{13}C & “as synthesized” Ti-PCP

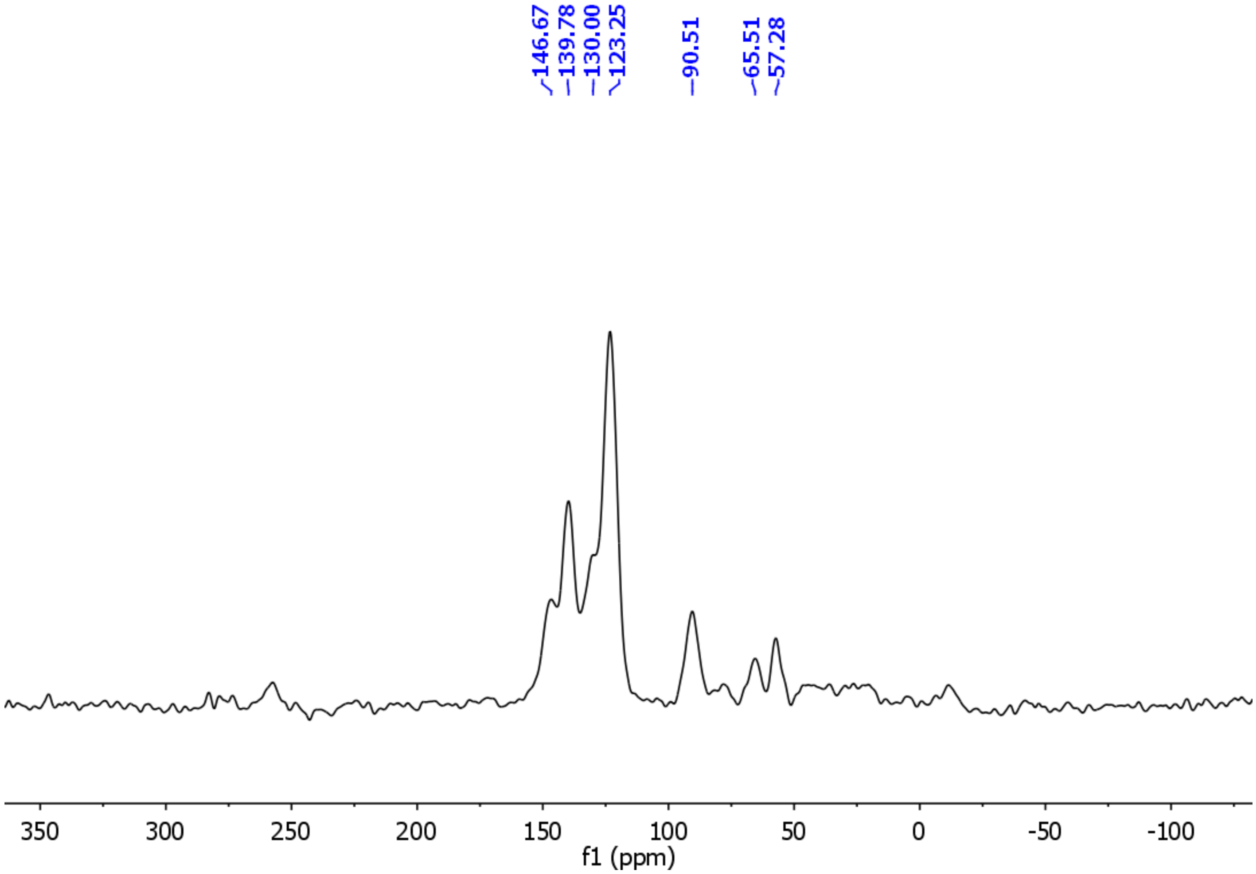

Figure S2. ^{13}C-CPMAS spectrum of “as synthesized” **Ti-PCP**.

6. Thermal gravimetric analysis of Ti-PCP

Sample was run on a TA Instruments Q-500 series thermal gravimetric analyzer with samples held in a platinum pan under nitrogen atmosphere. A 10 K min^{-1} ramp rate was used.

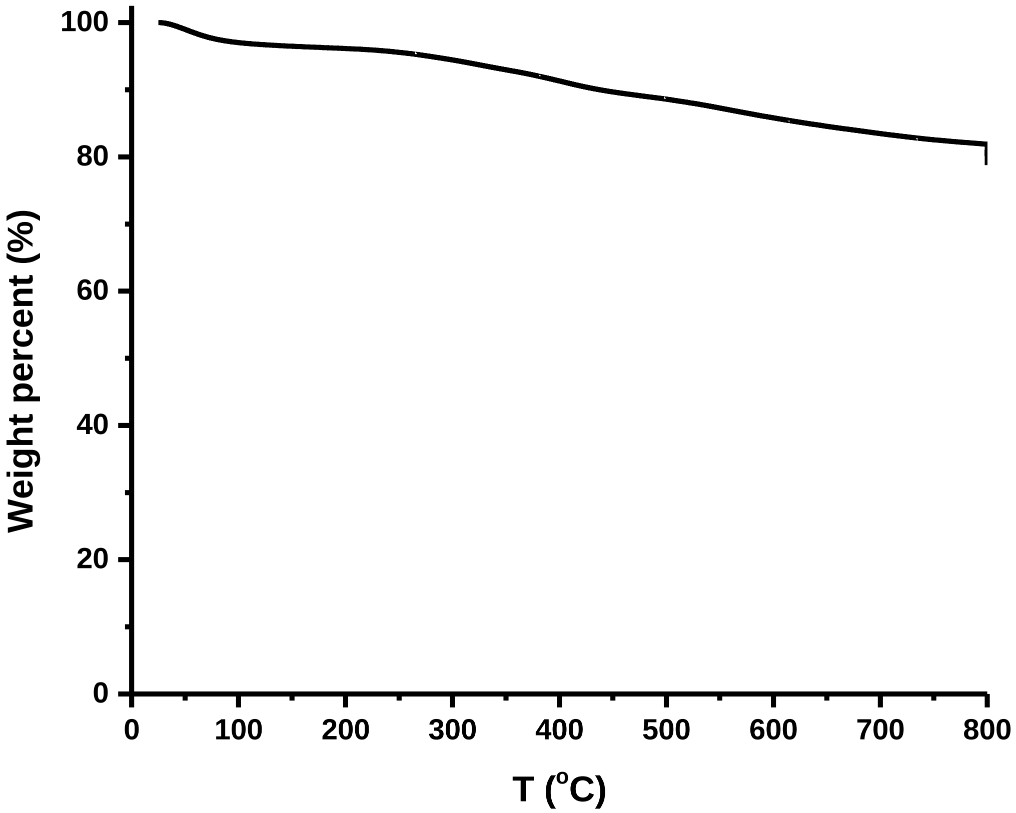

Figure S3. TGA of **Ti-PCP**.

7. SEM image of Ti-PCP

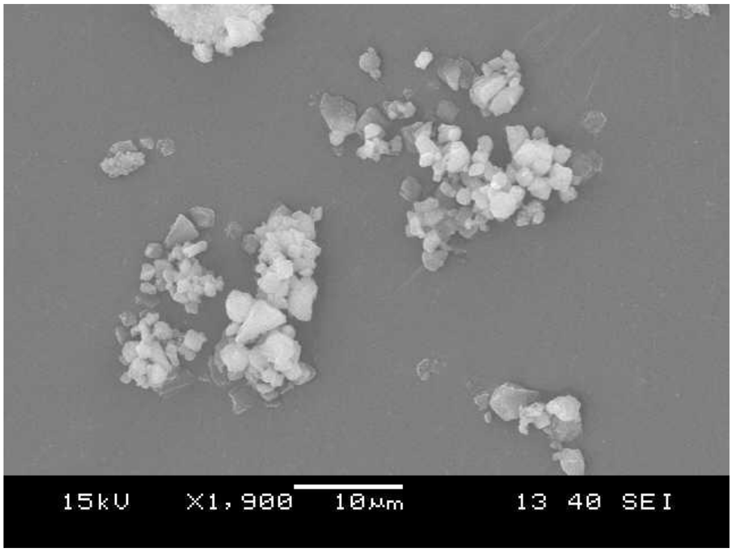

Figure S4. SEM image of **Ti-PCP**.

8. PXRD analysis of Ti-PCP

The PXRD characterization of **Ti-PCP** shows multiple peaks in the 2Θ range of 2–35° indicating certain structure orderliness in the framework. In order to elucidate the structure configuration of **Ti-PCP**, the tetragon model based on 4-coordinated Titanium was modeled after the geometry optimization. The simulated PXRD pattern of the model well reproduced the observed XRD pattern in peak positions and relative intensities. In addition, the predicted pore structures of the proposed model matches with the pore size distribution obtained from N_2 adsorption isotherm. However, due to the complex diffraction patterns and the limited quality and resolution of the PXRD data, we cannot rule out other possibilities. The proposed 2D structural representation of **Ti-PCP** is shown in Figure S5b.

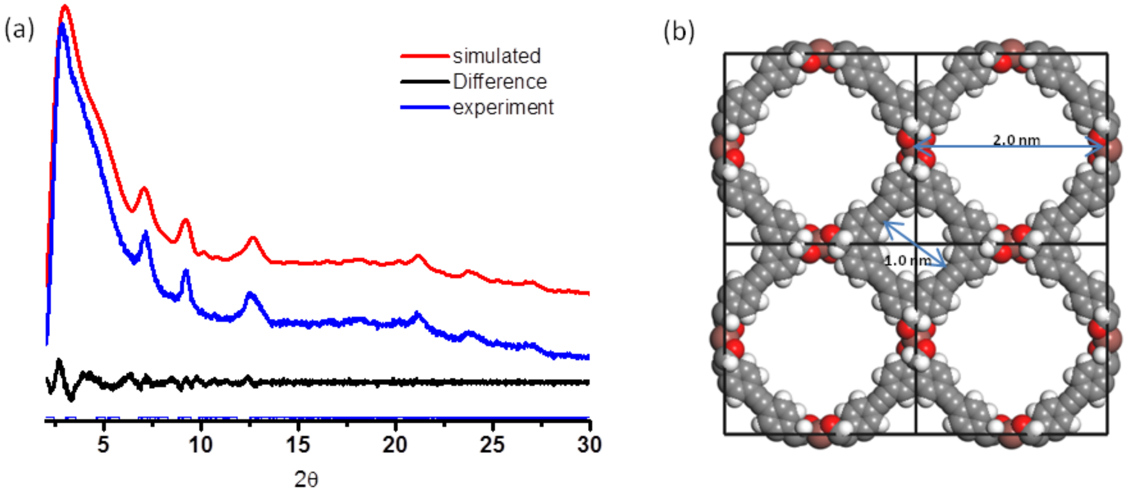

Figure S5. PXRD patterns (a) and energy-minimized model (b) of **Ti-PCP**.

9. Structural modeling and X-ray diffraction analyses.

All the models, including cell parameters and atomic positions were generated using the *Materials Studio* software package, employing the *Materials Visualizer* module. The **Ti-PCP** model was constructed in the tetragonal system, with the layers lying on the ***ab*** plane. The P1 space group was selected at the first place. An energy minimization was performed to optimize the geometry of the building units, employing the *universal force field* implemented in the *Forcite* module of *Materials Studio*. Then, the structure was examined using the *Add sym* subroutine of PLATON software package,[2] which indicated the presence of higher symmetry and suggested *P*422 (No. 89). An energy minimization was performed, and the unit cell parameters for the model were also optimized during the process. Finally, full profile pattern (Pawley) refinement was performed against the experimental powder patterns obtaining the refined unit cell parameters. In **Table S3**, the values of the optimized unit cell parameters, the space group for the constructed model, the refined cell parameters and the fractional atomic coordinates of the final models were summarized.

Table S3. Refined unit cell parameters and fractional atomic coordinates for **Ti-PCP**.

Name	**Ti-PCP**		
Space group	*P422*		
a **(Å)**	24.46		
c **(Å)**	6.13		
Atom name	***x***	***y***	***z***
C1	1.162	0.803	0.508
C2	1.122	0.760	0.524
H3	1.052	0.813	0.494
H4	1.184	0.696	0.553

C5	1.066	0.772	0.512
C6	1.140	0.705	0.544
C7	1.029	0.728	0.513
C8	1.103	0.662	0.545
H9	1.117	0.620	0.553
C10	1.047	0.674	0.527
C11	1.000	0.635	0.500
C12	1.008	0.600	0.289
H13	0.968	0.586	0.223
H14	1.026	0.627	0.160
O15	1.043	0.556	0.320
Ti16	1.000	0.500	0.500

10. High resolution TEM

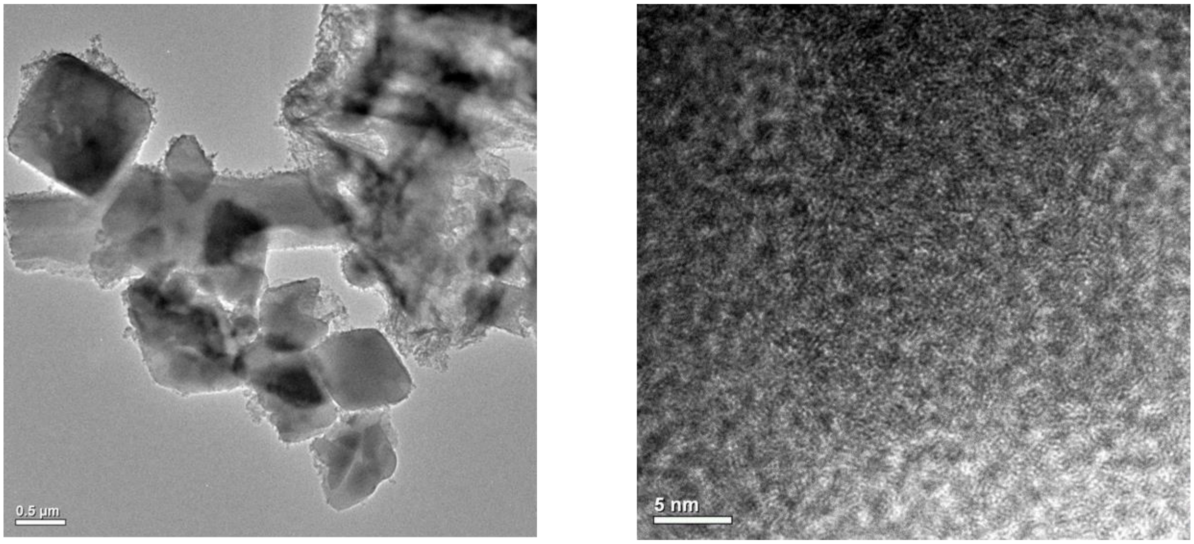

Figure S6. TEM image of **Ti-PCP**.

11. References

(1) Y. Du, H. Yang, J. M. Whiteley, S. Wan, Y. Jin, S.-H. Lee, W. Zhang, *Angew. Chem., Int. Ed.* 2016, *55*, 1737.

(2) Spek, A.L. Acta Cryst. 2009, D65, 148-155.