Electronic Supplementary Information

Selective CO_2 Capture by a 3d-4d Coordination Polymer Material with 1D Channel

Sheng-Li Huang, Guo-Xin Jin*

Experimental Section

Materials and physical measurements:

All reagents and solvents employed were commercially available and used as supplied without further purification. Powder XRD patterns were recorded with CuKα radiation by using a PANalytical X'Pert PRO diffractometer. TGA analyses of the complexes were performed on a NETZSCH STA 409 PC Simultaneous Thermal Analyzer under an N_2 atmosphere at a scan rate of 10 ºC min^{-1}. Elemental analysis was performed on an Elementar vario EL III analyzer. IR (KBr) spectra were recorded on the Nicolet FT-IR spectrophotometer. All the gas sorption experiments were measured with an IGA-002 gas adsorption instrument.

Synthesis:

[Pd(2,4-Hpydca)$_2$)] 1. To a MeOH solution (20 mL) of pyridine-2,4-dicarboxylic acid (2.00 mmol, 0.24 g), was added sodium methanol (2.00 mmol, 0.11 g). After stirring in half an hour, a MeOH solution (10 mL) of $PdCl_2(CH_3CN)_2$ (1.00 mmol, 0.26 g) was slowly added. A pale yellow precipitate was formed immediately. The mixture was stirred for a further 2 h to ensure completion of the reaction. The solid was collected by filtration, washed with MeOH and ethyl ether, and dried in vacuo to afford a pale yellow powder. Yield: 94%. Anal. Calcd for $C_{12}H_8N_2O_8Pd$: C, 38.33; H, 1.84; O, 29.18. Found: C, 38.01; H, 2.16; O, 29.71. IR (KBr, cm^{-1}): 3448 (s), 1728 (m), 1676 (s), 1290 (m), 1257 (m), 1167 (w), 684 (w).

[Ni(cyclam)Pd(2,4-pydca)$_2$·4H$_2$O]$_n$ 2. [Pd(2,4-Hpydca)$_2$)] **1** (1.00 mmol, 0.44 g) was added to an aqueous solution of NaOH (2.00 mmol, 0.08 g). After stirring in half an hour, an aqueous solution of [Ni(cyclam)]$(ClO_4)_2$ (1.00 mmol, 0.46 g) was slowly added. A deep yellow precipitate was formed immediately. The mixture was stirred for a further 2 h to ensure completion of the reaction. The solid was collected by filtration, washed with H_2O and THF, and dried in air to afford a pale yellow powder. Yield: 91%. Anal. Calcd for $C_{24}H_{38}N_6NiO_{12}Pd$: C, 37.55; H, 4.99; O, 25.01. Found: C, 37.14; H, 5.23; O, 25.46. IR (KBr, cm^{-1}): 3429 (m), 3212 (m), 1670 (s), 1381 (s), 1315 (s), 1105 (m), 947 (m), 780 (w).

[Ni(cyclam)Pd(2,4-pydca)2]$_n$ 2'. Heating **2** at 100℃ under vacuum for 6 h, **2'** was formed and the colours of solid changed from deep yellow to pale yellow. Yield: 99%. Anal. Calcd for $C_{24}H_{30}N_6NiO_8Pd$: C, 41.44; H, 4.35; O, 18.40. Found: C, 41.17; H, 4.58; O, 18.73. IR (KBr, cm^{-1}): 3416 (m), 1668 (s), 1384 (s), 1317 (s), 1101 (m), 940 (m), 783 (w).

[Ni(cyclam)Pd(2,4-pydca)$_2$·4H$_2$O]$_n$ 2''. **2'** was exposed to atmosphere or water vapor the pale yellow color of the crystal returned to brown over a few hours. Anal. Calcd for

$C_{24}H_{38}N_6NiO_{12}Pd$: C, 37.55; H, 4.99; O, 25.01. Found: C, 36.87; H, 5.56; O, 25.91. IR (KBr, cm^{-1}): 3429 (m), 3212 (m), 1670 (s), 1381 (s), 1315 (s), 1105 (m), 947 (m), 780 (w).

Crystallographic Studies:

Diffraction data of **2** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Ka radiation (λ = 0.71073 Å). The data was collected at 296 K temperature and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL),[1] SADABS[2] absorption corrections were applied to the data. There are disordered water molecules in the asymmetric unit which cannot be refined properly. So the SQUEEZE algorithm was run to remove them before the structures were refined to convergence. All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. However, hydrogen atoms of water molecules cannot be found.

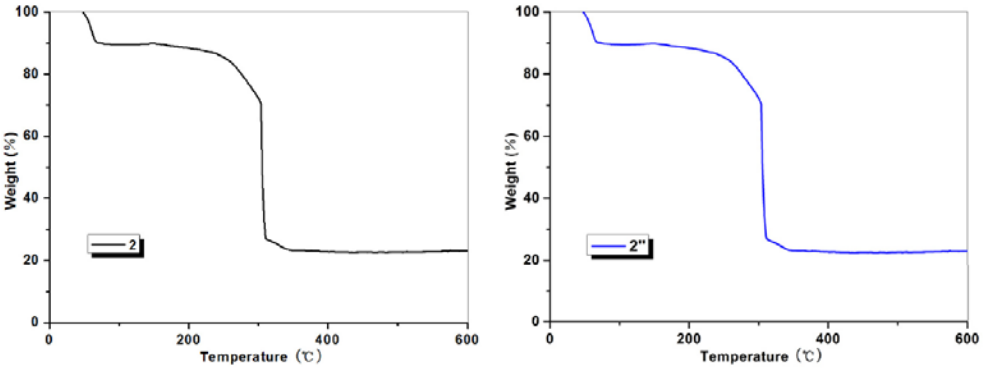

Figure S1. TGA of compound **2** and **2''**

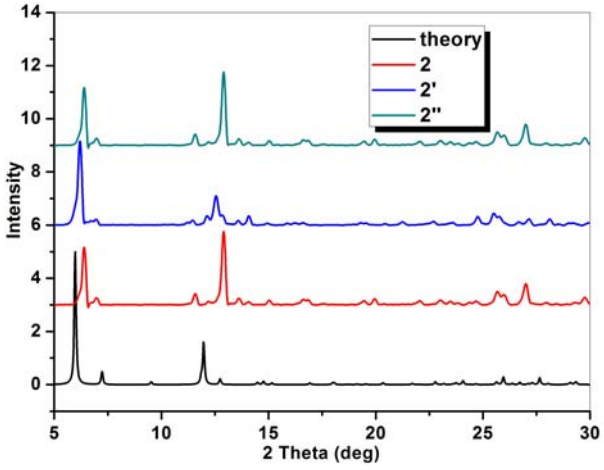

Figure S2. PXRD patterns for different samples

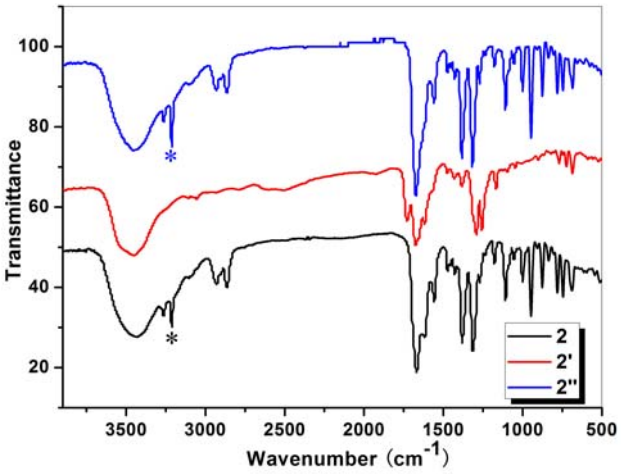

Figure S3. IR spectrum of different samples

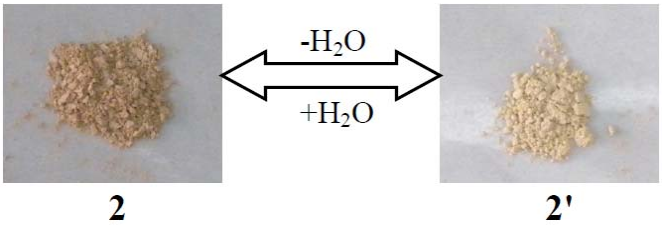

Figure S4. Color change from **2** to **2'**

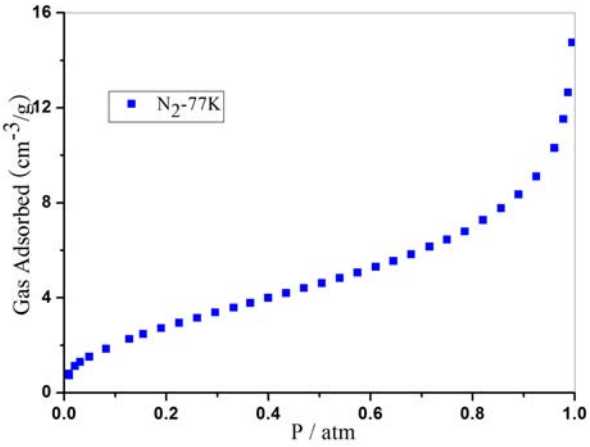

Figure S5. N_2 sorption curves (77 K) of **2'**

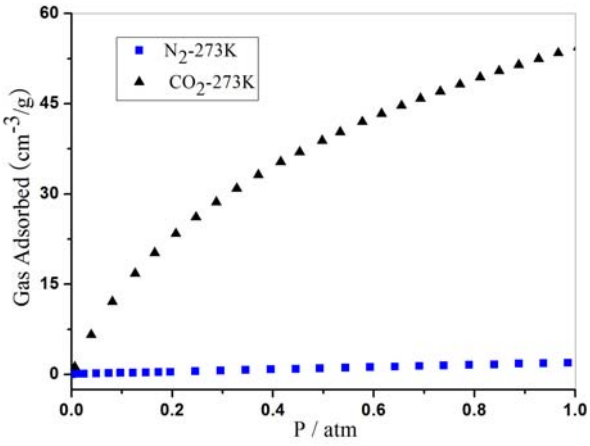

Figure S6. Gas sorption curves (273 K) of **2'**

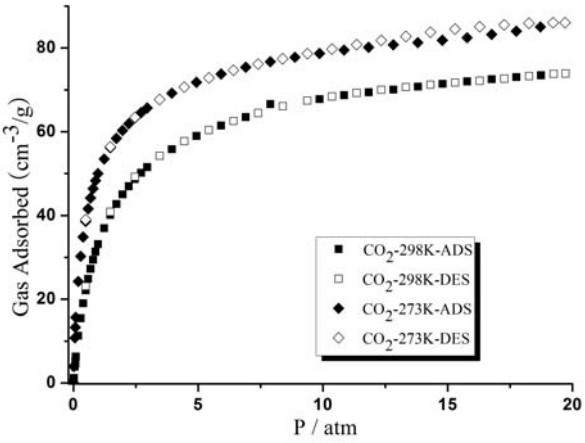

Figure S7. CO_2 sorption curves (298 K) of **2'**

Table S1. Hydrogen bond distances (Å) and angles (º) for compound **2**

D-H···A	D-H	H···A	D···A	<D-H···A
N(2)-H(2') ···O(2)#3	0.87(2)	2.19(4)	2.991(8)	152(8)
N(3)-H(3) ···O(4)	0.89(2)	2.13(4)	2.978(7)	161(8)
O(5)-H(5A) ···O(4)#4	0.86(2)	2.03(3)	2.888(10)	175(12)
O(5)-H(5B) ···O(4)	0.86(2)	2.12(4)	2.956(10)	164(12)

Symmetry transformations used to generate equivalent atoms:#1 -x,-y,-z+1; #2 -x+1/2,-y+1/2,-z; #3 -x+1/2,y+1/2,-z+1/2; #4 x,-y,z+1/2.

Reference:

(1) G. M. Sheldrick. SHELXL-97, *Program for the Refinement of Crystal Structures*, Universität Gtötingen: Germany, **1997**.

(2) G. M. Sheldrick. SADABS (2.01), *Bruker/Siemens Area Detector Absorption Correction Program*; Bruker AXS: Madison, WI, **1998**.