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Electronic Supplementary Information (ESI) for

Cascade Covalent and Coordination Bonds Formation for Ti-Based Cage Assembly: Catalysis and Coordination Bi-functions of $TiCl_4$

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1.Experimental Procedures

1.1. Materials synthesis.

Reagents and Synthesis.

All starting materials are commercially available and used as received without further purification: 4-Aminobenzoic acid (GC, 97%) (Macklin); Acetonitrile (AR); Acetate (AR, 99.5%) (aladdin) and Titanium tetrachloride (99.9% metals basis) (Macklin). $TiCl_4$ (55 μl, 0.5 mmol) was added into a solution of 4-aminobenzoic acid (69 mg, 0.5 mmol) and acetic acid (100 μl) dissolved in dried acetonitrile (3.16 g, 77 mmol). After being stirred for a few minutes, the solution was transferred into a 25 mL Teflon-lined autoclave. The mixture was heated at 80 °C for 3d. Polyhedral yellow crystals were obtained after cooling down to room temperature. Elemental analyses calcd (%) for dried [$C_{36}H_{32}Cl_8N_4O_{14}Ti_4{\cdot}4(H_2O)$]: C%: 35.44, N%: 4.59, H%: 2.63; found C%: 33.44, N%: 4.34, H%: 2.48.

1.2 Characterization methods.

Instrumentation. Elemental analyses of C, H and N were performed on a Vario EL Cube elemental analyser. Ti analyse was measured on an Optima 7300 DV inductively coupled plasma (ICP) spectrometer, Perkin-Elmer. Thermogravimetric analyses was carried on a TGA Q500 integration thermal analyzer from 25 to 800 °C at a heating rate of 10 °C min^{-1} in an air atmosphere. Powder X-ray diffractograms were performed on a Rigaku MiniFlex 600 X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). Fourier transform infrared (FT-IR) spectrums were measured on a SHIMADZU IR Affinity-1 spectrometer with KBr discs in a range from 4000 to 400 cm^{-1}. NMR spectra were performed on a Bruker 400 spectrometer.

1.3 Crystallography.

Single-crystal X-ray diffraction data of Ti-based cage was collected on a Bruker D8 Quest CMOS diffractometer with graphite-monochromatic Mo-Ka radiation (λ=0.71073 Å) at 293 K. Empirical absorption corrections were applied by using the SADABS program (Bruker AXS Inc, Madison, Wisconsin, USA). Structure was solved by direct method and refined by full-matrix least squares based on F^2 using SHELXTL 14XL program package. Hydrogen atoms within the ligand backbones were fixed geometrically at their positions and allowed to ride on the parent atoms. Crystallographic data and details were summarized in Table S1.

Table S1 : Crystallographic data of Ti-based-Cage.

Compound No.	Ti-based cage
Formulae	$C_{36}H_{32}Cl_8N_4O_{14}Ti_4{\cdot}4(H_2O)$
CCDC No.	1544077
Mol. wt.	1291.80
Crystal system	Tetragonal
Space group	I41/amd
Temperature /K	298
Wavelength /Å	0.71073
a /Å	18.0920(19)
b /Å	18.0920(19)
c /Å	17.592(4)
α/°	90.00
β/°	90.00

γ/°	90.00
V/ Å3	5758.2(17)
Z	4
Density/Mgm^{-3}	1.490
Abs. Coeff. /mm^{-1}	0.970
F(000)	2608
Total no. of reflections	1430
Reflections, I > 2σ(I)	891
Max. 2θ/°	25.498
Ranges (h, k, l)	-18 ≤ h ≤ 21 -19 ≤ k ≤ 21 -21 ≤ l ≤ 21
Complete to 2θ (%)	99.3
Data/ Restraints/Parameters	1430/13/123
Goof (F2)	1.005
R indices [I > 2σ(I)]	0.0739
R indices (all data)	0.1243
WR2 [I > 2σ(I)]	0.2008
WR2(all data)	0.2291

2. Results and Discussion

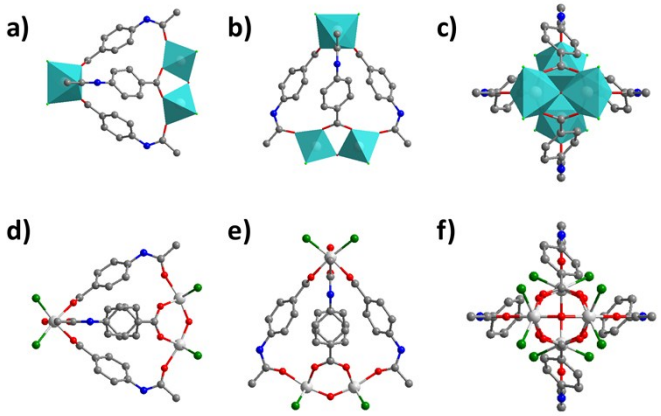

Figure S1. Crystal structure of Ti-based cage of polyhedra and sphere-stick modes viewed along the a,b,c-axis shown in a,d), b,e), c,f), respectively. Hydrogen atoms and guest molecules are omitted for clarity. Ti: silver, C: ray, N: blue, O: red, Cl: green.

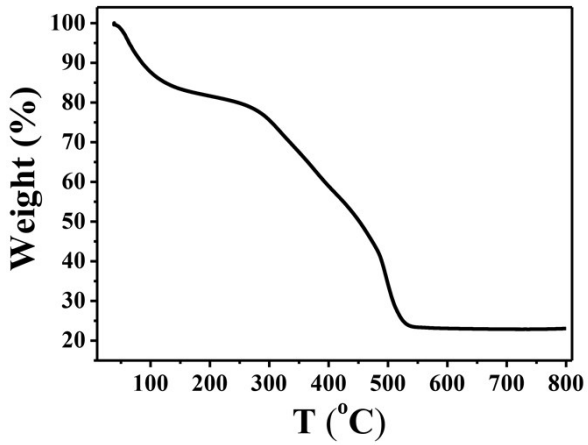

Figure S2. TG curve of Ti-based-cage measured in air atmosphere at 50 ml min^{-1}, revealing that guest water molecules can be removed at around 100 °C. A sharp weight loss around 300 °C indicated the cluster remains intact before 300°C. Above 530 °C, Ti-based-cage collapses completely.

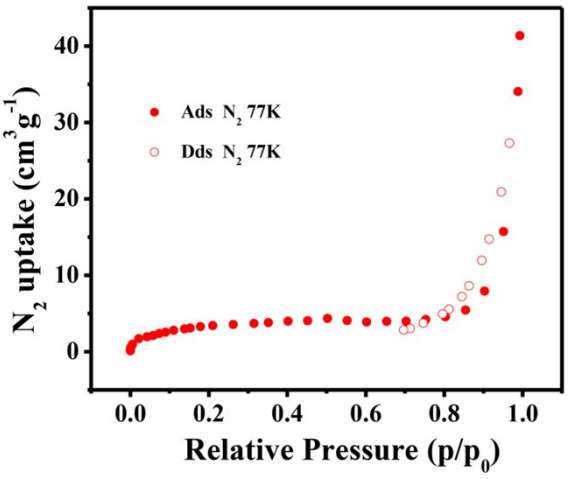

Figure S3. Gas sorption isotherms of N_2 (77 K) of Ti-based cage, which is activated at 100 °C under vacuum.

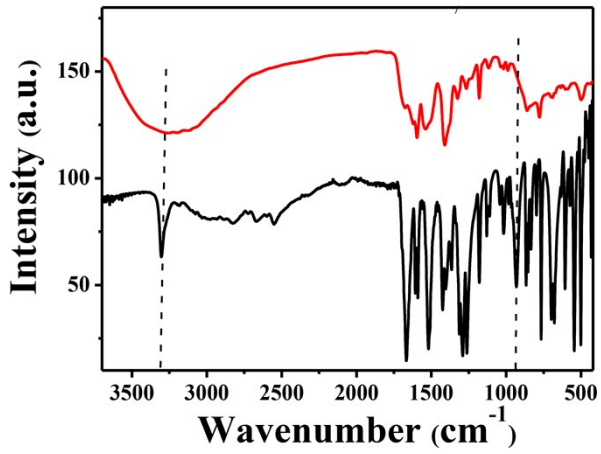

Figure S4. The IR spectrum of Ti-based cage (red) and 4-acetamidobenzoic acid (black). The peak of 4-

acetamidobenzoic acid at 3305 cm^{-1} and 931 cm^{-1} is corresponding to -OH group of the -COOH and completely disappeared in the IR spectrum.

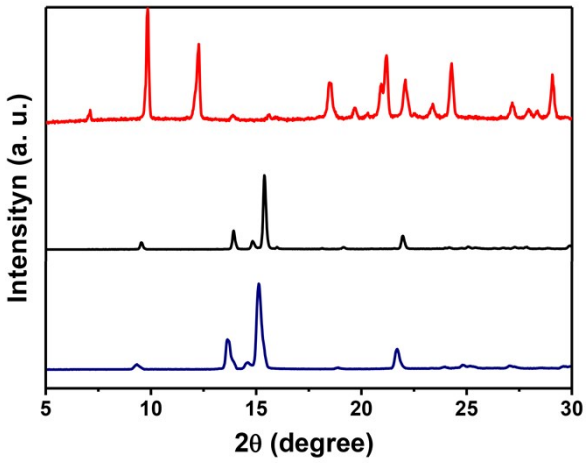

Figure S5. XRD patterns of (black) reaction product of 4-aminobenzoic acid and aceticacid for 100 °C for 3d, (red) Ti-based-Cage, (blue) 4-aminobenzoic acid.