Electronic Supplementary Information

Ti_4(embonate)$_6$ based Cage-Cluster Construction in a Stable Metal-Organic Framework for Gas Sorption and Separation

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EXPERIMENTAL SECTION

All reagents were purchased commercially and used without further purification. All of the synthesis was done in 20 ml vials under autogenous pressure. Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ = 1.54056 Å) with a step size of 0.05°. Thermal stability studies were carried out on a NETZSCH STA-449C thermal analyzer with a heating rate of 10 ℃/min under a nitrogen atmosphere. ICP analysis was conducted by using Inductively Coupled Plasma OES spectrometer (Ultima2, JobinYvon). ESI-MS was carried out on Thermo Scientific Exactive Plus. SEM measurement was performed by using the field-emission scanning electron microscope (FESEM, JSM6700-F). Gas adsorption measurement was performed in the ASAP (Accelerated Surface Area and Porosimetry) 2020 System.

Synthesis of $(NH_4)[Zn_5Ti_4L_6(OH)_3(H_2O)_5]$ *Guests* (PTC-205). PTC-101 (100 mg, 0.027 mmol), $Zn(CH_3COO)_2 \cdot 2H_2O$ (35 mg, 0.16 mmol), 5-ethyl-1H-tetrazole (30 mg, 0.30 mmol) and 3 drops of ammonia were added to 5 mL of H_2O/EtOH (3:2 v/v) and mixed at room temperature. The mixture was heated at 80 ℃ for 3 days. After the reaction mixture was cooled to room temperature, red dodecahedron crystals were obtained. Yield: 72% based on PTC-101.

X-ray Crystallography. Crystallographic data for **PTC-205** (**PTC-205(Δ)** and **PTC-205(Λ)**) were collected on a Supernova single-crystal diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ = 1.54056) at 100 K. Absorption corrections were applied using SADABS. The structures were solved by the direct method and refined by full-matrix least-squares on F^2 using SHELXTL. In these structures, some free solvent molecules and cations were highly disordered and could not be located. The diffuse electron densities resulting from these residual solvent molecules and cations were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated. Crystal data and details of data collection and refinement of **PTC-205** (**PTC-205(Δ)** and **PTC-205(Λ)**) are summarized in Table S1. CCDC 1955567-1955568 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Table S1. Crystallographic Data and Structure Refinement Details for **PTC-205**.

Compound	**PTC-205(Δ)**	**PTC-205(Λ)**
Formula	$C_{138}H_{82}O_{47}Ti_4Zn_5$	$C_{147}H_{93}N_3O_{47}Ti_4Zn_5$
Formula weight	3010.46	3171.72
Crystal system	Cubic	Cubic
Space group	$P2_13$	$P2_13$
a (Å)	25.4719(3)	25.57570(10)
b (Å)	25.4719(3)	25.57570(10)
c (Å)	25.4719(3)	25.57570(10)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å)	16526.6(6)	16729.5(2)
Z	4	4
*D*calcd ($g \cdot cm^{-3}$)	1.231	1.259
μ (Mo K*a*) (mm^{-1})	2.970	2.944
F (000)	6208	6440
Temperature (K)	100	100
Theta min, max (deg)	3.470, 50.393	3.456, 63.664
Tot., uniq. Data	9097, 5272	23471, 8448
Observed data [($I > 2\sigma(I)$]	3760	8064
R_{int}	0.0786	0.0182
Data/restraints/parameters	5272/ 54/ 574	8448/6/614
R1, wR2 [I > 2σ(I)]	0.0898, 0.2396	0.0754, 0.2099
R1, wR2 (all data)	0.1188, 0.2732	0.0781, 0.2159
Goodness-of-fit on F^2	1.053	1.046
$\Delta\rho$min, $\Delta\rho$max ($e \cdot Å^{-3}$)	-0.569, 0.909	-1.409, 1.350

$aR_1 = \Sigma||Fo| - |Fc|/\Sigma|Fo|$, $wR_2 = \{\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$; where $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$ and $P = (Fo^2 + 2Fc^2)/3$

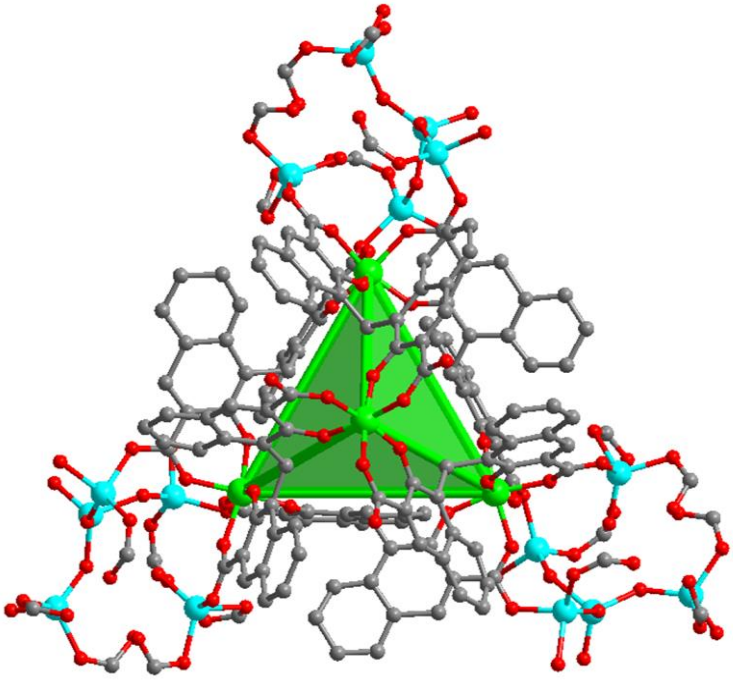

Figure S1. Coordination environment of Ti_4L_6 cage in **PTC-205**.

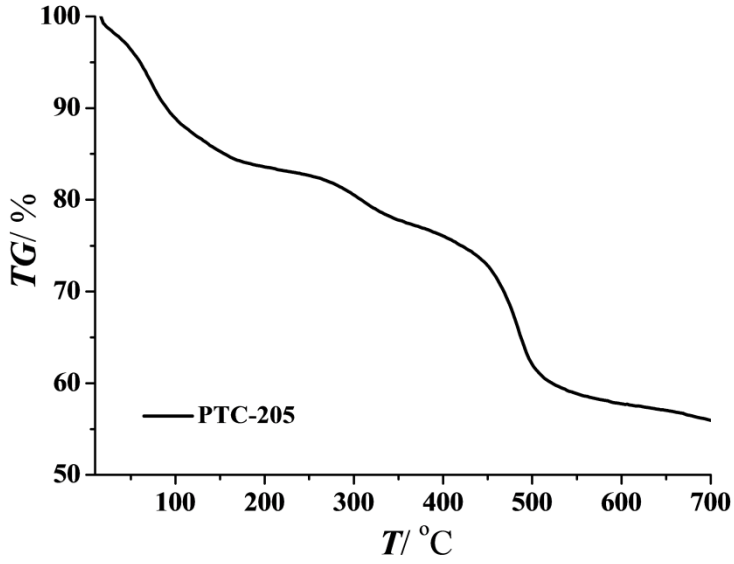

Figure S2. TGA curve of **PTC-205**.

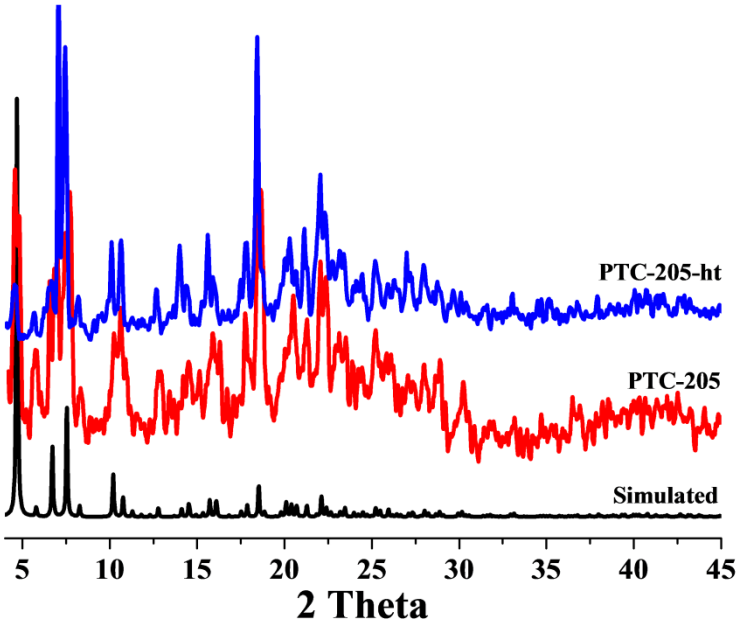

Figure S3. PXRD patterns of simulated from the single-crystal data of **PTC-205** (black); as-synthesized **PTC-205** (red) and activated **PTC-205-ht** (blue).

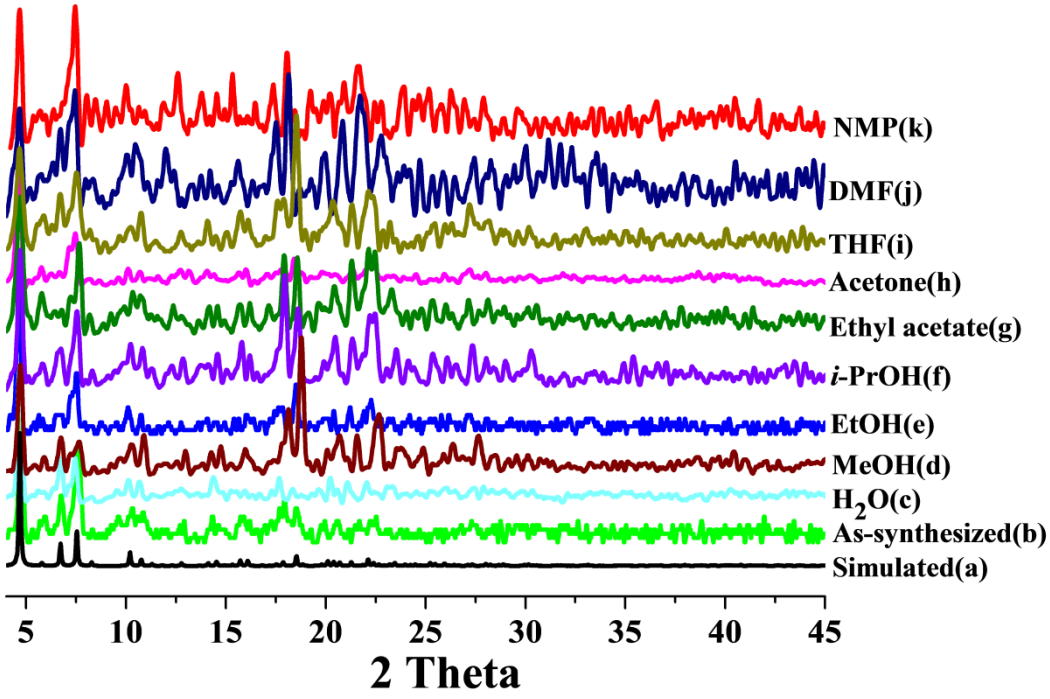

Figure S4. PXRD patterns of simulated **PTC-205** (a), as-synthesized **PTC-205** (b), and crystals of **PTC-205** immersed in H_2O (c), MeOH (d), EtOH (e), *i*-PrOH (f), ethyl acetate (g), acetone (h), THF (i), DMF (j) and n-methyl pyrrolidone (k) for 1 day.

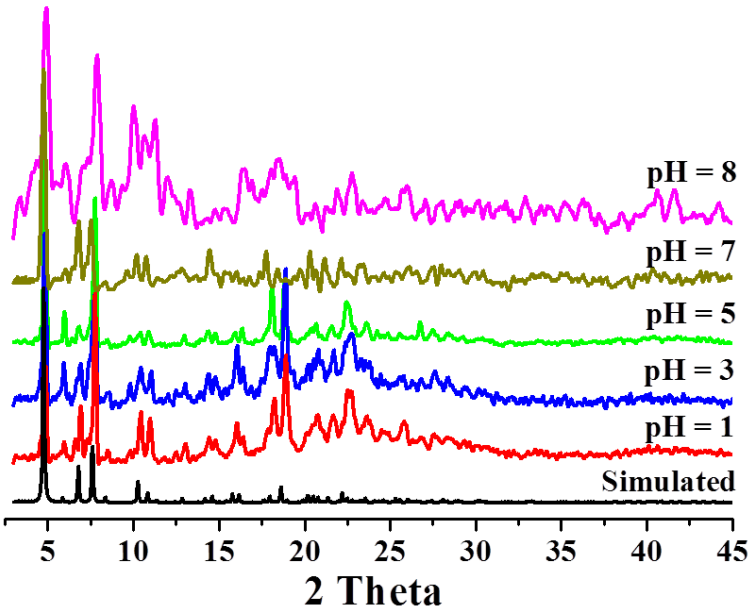

Figure S5. PXRD patterns of simulated **PTC-205** and the crystals of **PTC-205** immersed in HCl or NaOH aqueous solution with different pH values.

Table S2. The ICP-AES original data for **PTC-205**.

ICP-AES		
Weight percent	Ti: 4.61%	Zn:7.32%

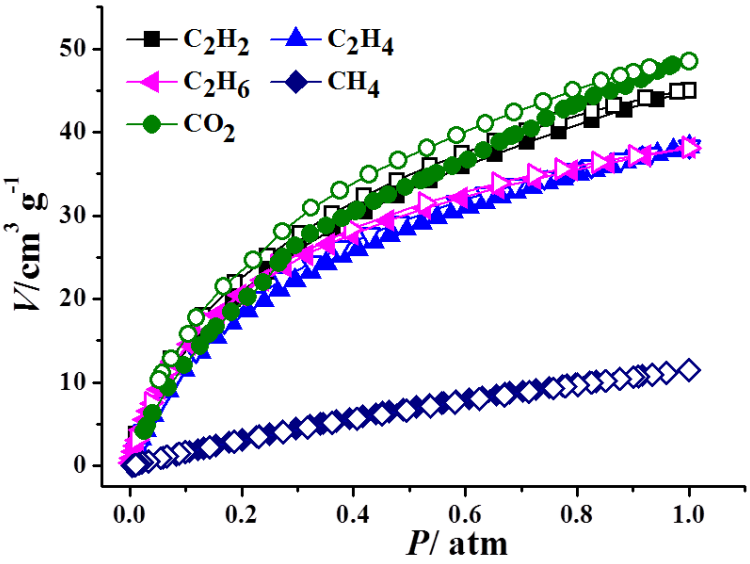

Figure S6. The sorption isotherms of CO_2, CH_4 and C_2 hydrocarbons for **PTC-205-ht** at 298 K.

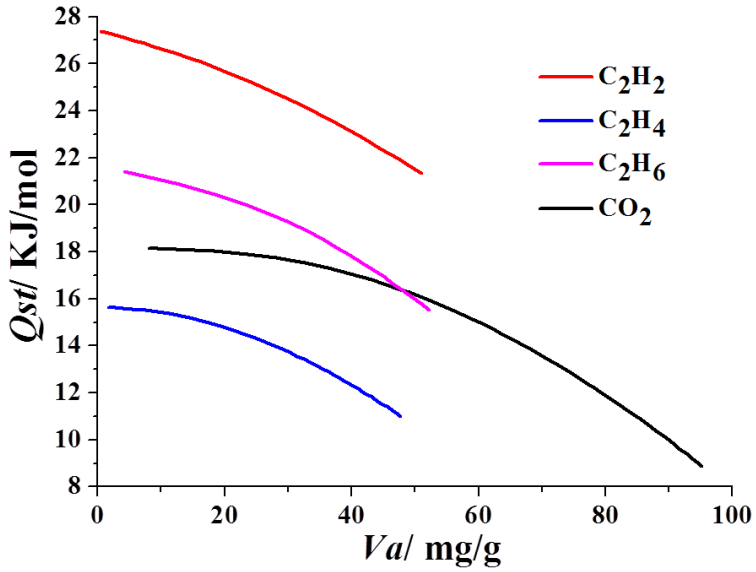

Figure S7. The isosteric heat of adsorption for C_2H_6, C_2H_4, C_2H_2 and CO_2 in **PTC-205-ht**.