Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Effects of Organic Ammonium Cations on Isolation of {Ti_4} Cyclic Clusters from Water: An ^{17}O NMR Study

Weiming Liu,[a] Caiyun Liu,[a] Wenli Wu,[b] Guanyun Zhang,[a] Jian Zhang,[c] Chen-Ho Tung[a] and Yifeng Wang[a]*

[a] Key Lab for Colloid and Interface Science of Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

[b] Qilu University of Technology (Shandong Academy of Sciences), Shandong Analysis and Test Center, Keyuan Street No 19, Jinan 250014, China

[c] State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

1. Crystallography

Single crystal X-ray diffraction analysis was performed on a Bruker SMART APEX II diffractometer using Cu-Kα radiation (λ = 1.54178 Å) at 173 K. APEX2, SaintPlus 6.01,[1] SADABS[2] and Olex2[3] were used for indexing, data integration/reduction, absorption correction and refinement. Hydrogen atoms of the organic ammonium cations were added as riding atoms theoretically. The crystallographic data are list in the following table:

Table S1. The crystallographic data

Compound	Ti_4b-CHexDA	Ti_4b-BuDA	Ti_4c-OcDA	Ti_4c-HMTA
Formula unit	$C_{12}H_{48}N_4O_{36}S_6Ti_4$	$C_8H_{44}N_4O_{36}S_6Ti_4$	$C_{36}H_{114.5}Cl_{1.5}N_9O_{45}S_{8.5}Ti_4$	$H_{36}O_{50}S_8Ti_4$
CCDC number	1977579	1977578	1977580	1977581
Moieties	$(C_6H_{16}N_2)_2[Ti_4O_4(OH_2)_8(SO_4)_4](SO_4)_2$	$(C_4H_{14}N_2)_2[Ti_4O_4(OH_2)_8(SO_4)_4](SO_4)_2$	$(C_8H_{22}N_2)_{4.5}[Ti_4O_4(OH_2)_4(SO_4)_8](SO_4)_{0.5}\cdot 1.5HCl\cdot 3H_2O$	$[Ti_4O_4(OH_2)_4(SO_4)_8H_8]\cdot 10H_2O$
Formula weight (g/mol)	1208.4	1156.3	1911.0	1284.2
Crystal system	tetragonal	tetragonal	triclinic	tetragonal
Space group (Nr.)	I4/mcm	I4/mcm	P-1	I-42d
a (Å)	13.7675(2)	13.8316(2)	15.4295(4)	24.0919(2)
b (Å)	13.7675(2)	13.8316(2)	17.3585(5)	24.0919(2)
c (Å)	20.9391(4)	20.2120(4)	18.1126(4)	23.1592(3)
α (°)	90	90	109.769(2)	90
β (°)	90	90	90.193(2)	90
γ (°)	90	90	109.105(2)	90
Volume ($Å^3$)	3968.88(14)	3866.82(14)	4278.1(2)	13442.1(3)
Z	1	4	1	12
$Density_{calc}$ (g/cm^3)	2.022	1.959	1.482	1.892
Abs. Coeff. μ (mm^{-1})	10.700	10.944	6.253	10.586
Temperature (K)	173	173	173	173
Total reflections	5055	5413	42809	17257
Min-max 2θ (°)	9.084 to 152.578	8.75 to 152.536	5.228 to 153.256	5.294 to 144.96
Unique reflections	1094	1080	16946	6388
R_1 [I>=2σ(I)]	0.0858	0.0995	0.1504	0.0439
wR_2 (all data)	0.1897	0.2269	0.4155	0.1175
R_{int}	0.0407	0.0393	0.1331	0.0328
Goodness of fit on F^2	1.228	1.129	1.045	1.082
Parameters	131	149	987	401
Restraints	108	187	303	359
Largest diff. peak/hole (e $Å^{-3}$)	0.78/-0.76	1.34/-077	1.65/-1.26	0.54/-0.46

2. Additional characterization

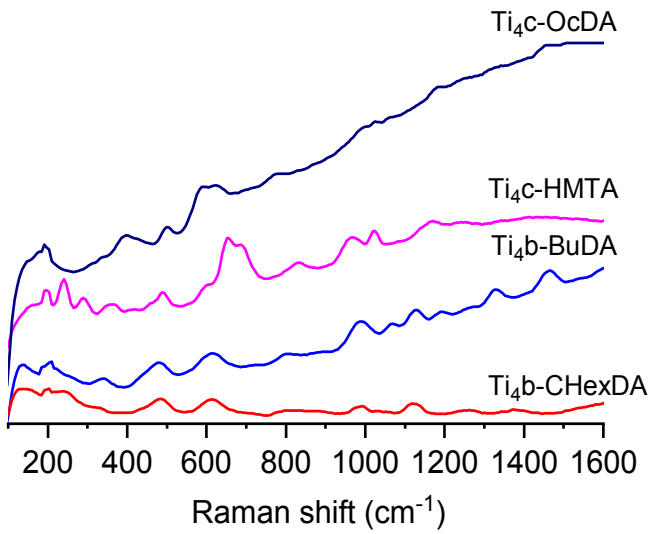
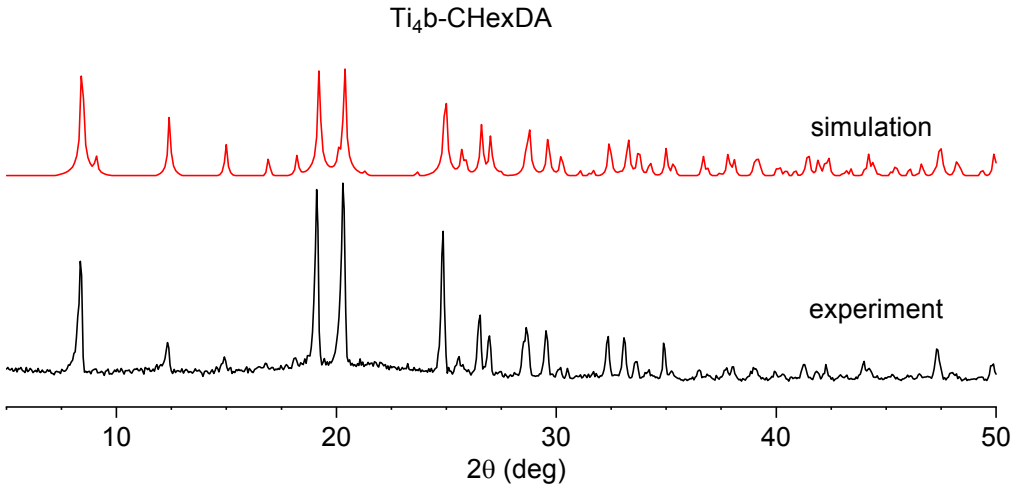


Figure S1. The Raman spectra of the {Ti_4} compounds.



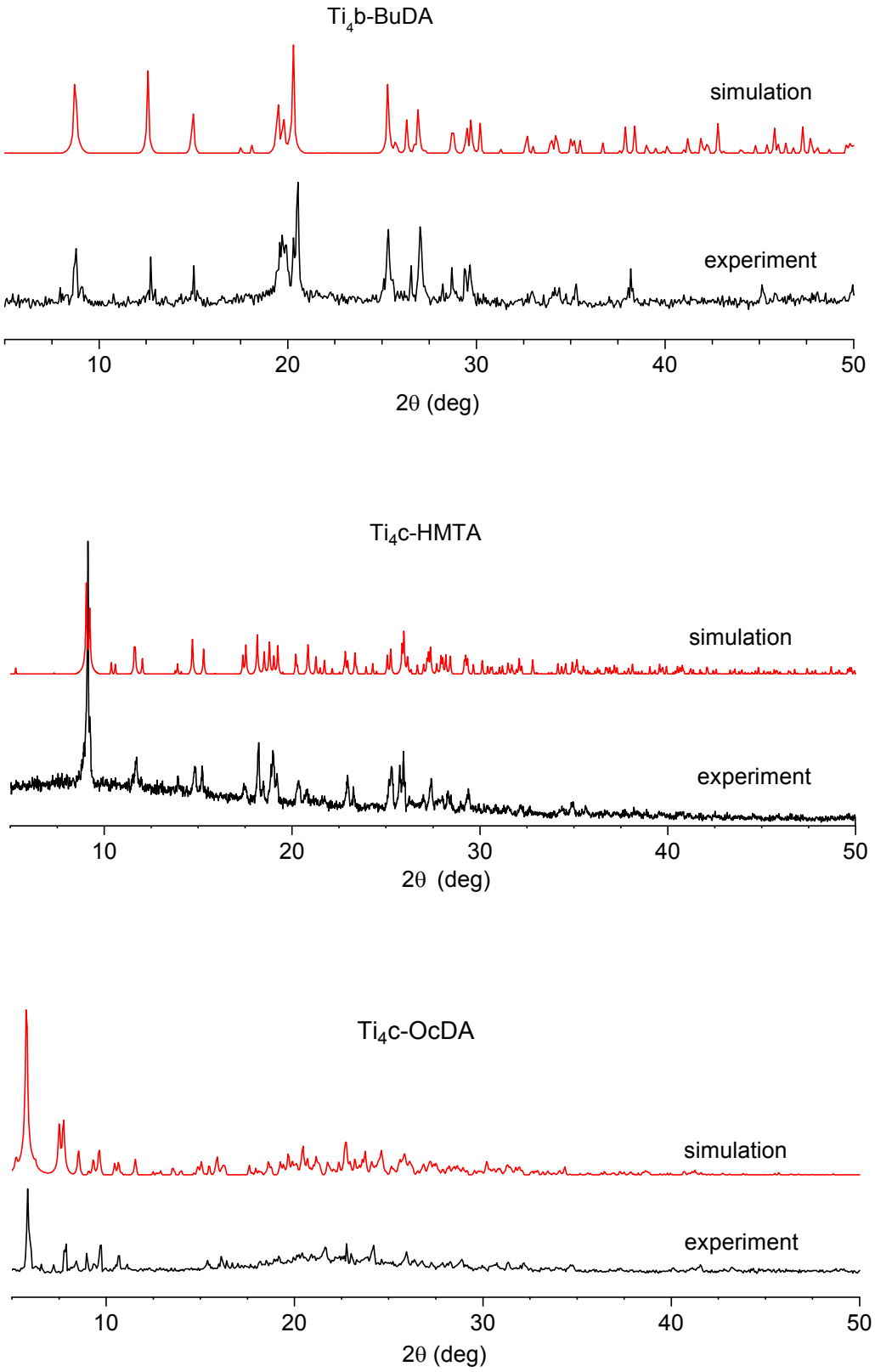


Figure S2. The PXRD spectra of the {Ti_4} compounds.

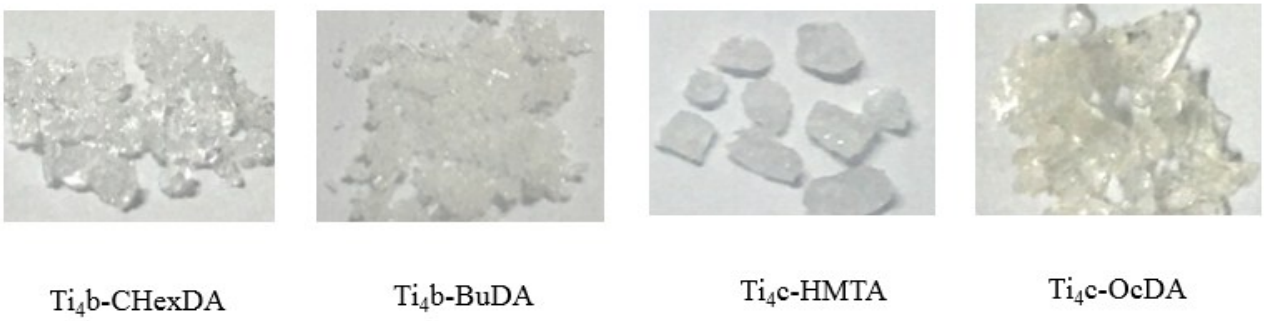


Figure S3. The photos of the crystals.

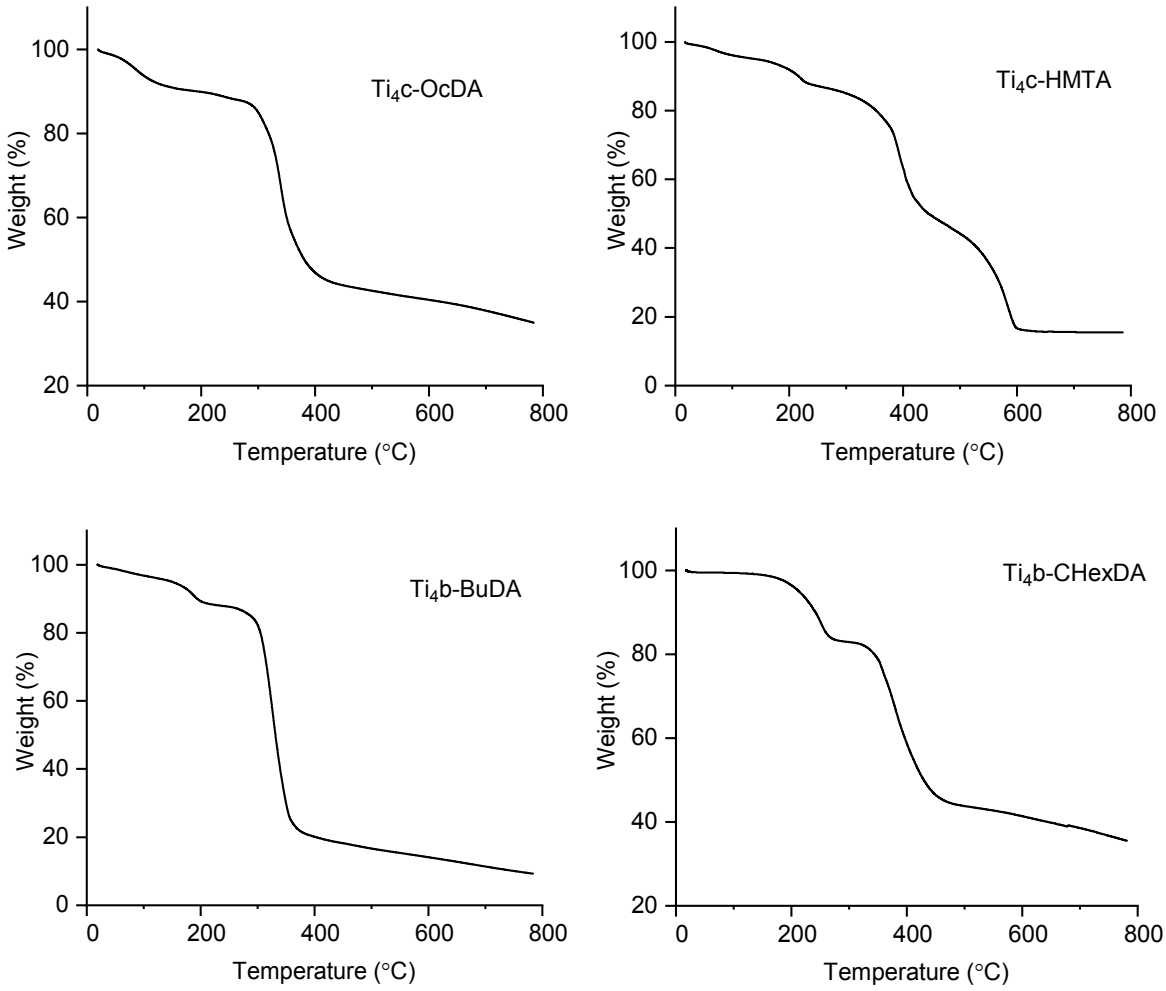


Figure S4. TGA data. The data were recorded on an SDT Q600 instrument from room temperature to ca. 800 °C at a heating rate of 10 °C min^{-1}, under high purity N_2 flow (100 mL min^{-1}).

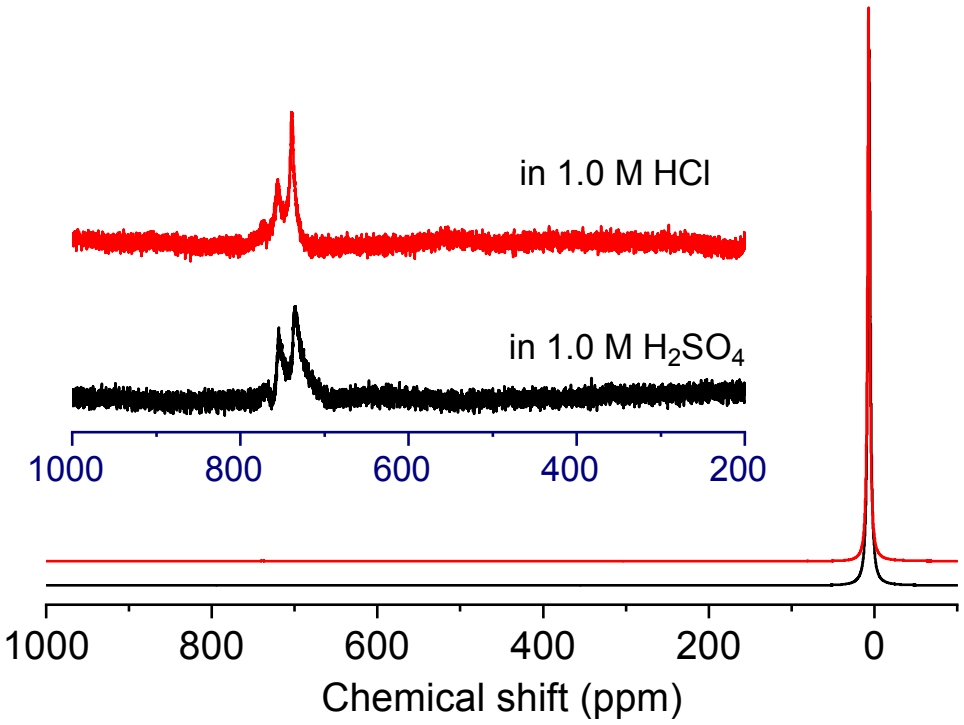


Figure S5. The ^{17}O NMR spectra of Ti_4c-OcDA (ca. 0.10 M) dissolved in 1.0 M HCl or H_2SO_4.

Discussion. For above experiments, ^{17}O-enriched Ti_4c-OcDA was first prepared using an ^{17}O-enriched solution (5%). ^{17}O-enriched Ti_4c-OcDA was then dissolved in 5% ^{17}O-enriched 1.0 M HCl or H_2SO_4. The concentration of Ti_4c-OcDA was ca. 0.10 M. Thus, the concentration of Ti^{4+} was ca. 0.40 M. The three peaks of μ_2-O suggest Ti_4c decomposed in prior to the NMR measurements. Moreover, according to the peak area analysis, the concentrations of μ_2-O are estimated to be 0.11 and 0.10 M in the two solutions, respectively. The much lower concentrations of μ_2-O than that of Ti^{4+} clearly indicate Ti_4c decomposed.

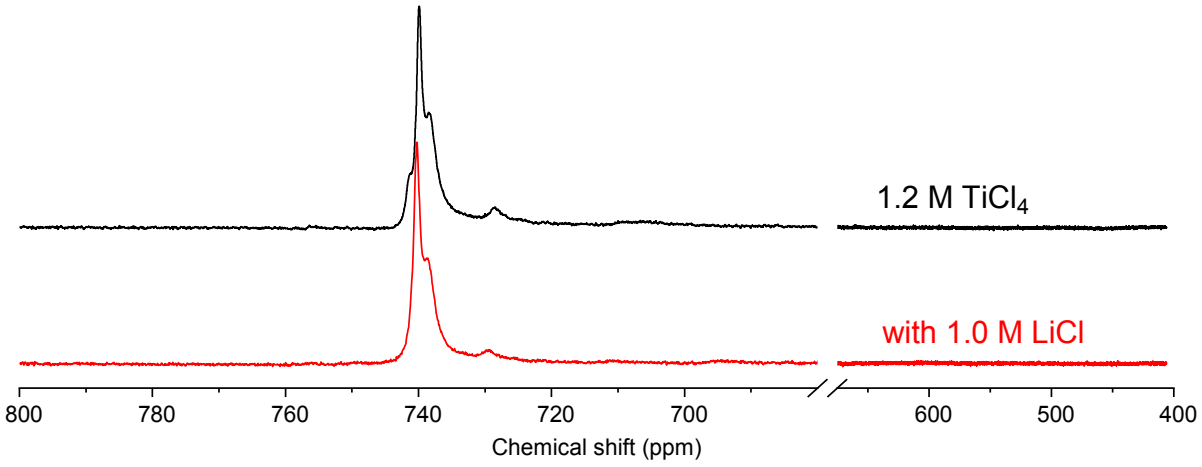


Figure S6. ^{17}O NMR spectra of $TiCl_4$ with and without added LiCl. It can be seen that LiCl leads to little change to the speciation.

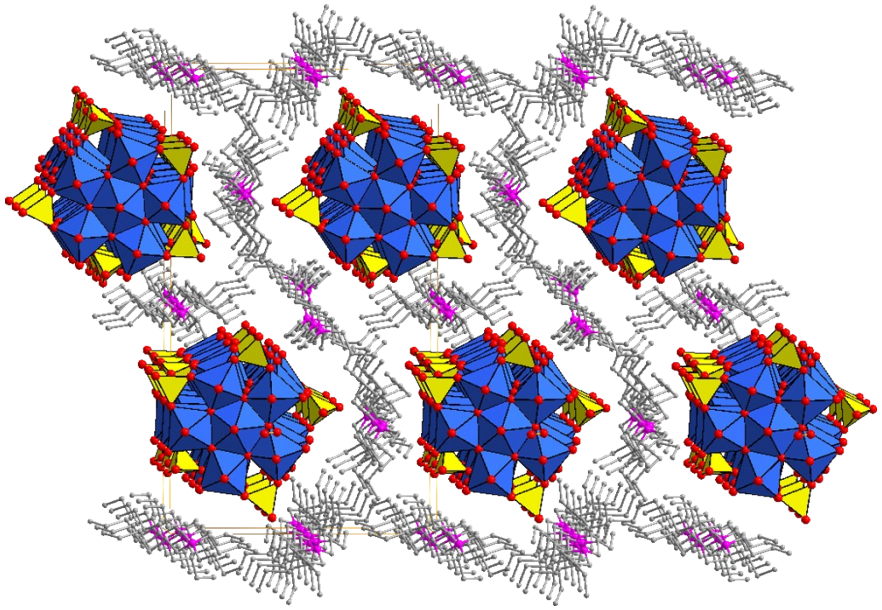


Figure S7. The packing diagram of $\{Ti_{18}O_{27}\}$ clusters in $\{Ti_{18}O_{27}\}$-TBAC.[4] The TBA^+ cations assemble into a "honeycomb" for accommodating the $\{Ti_{18}O_{27}\}$ clusters, Cl^- anions and solvent H_2O.

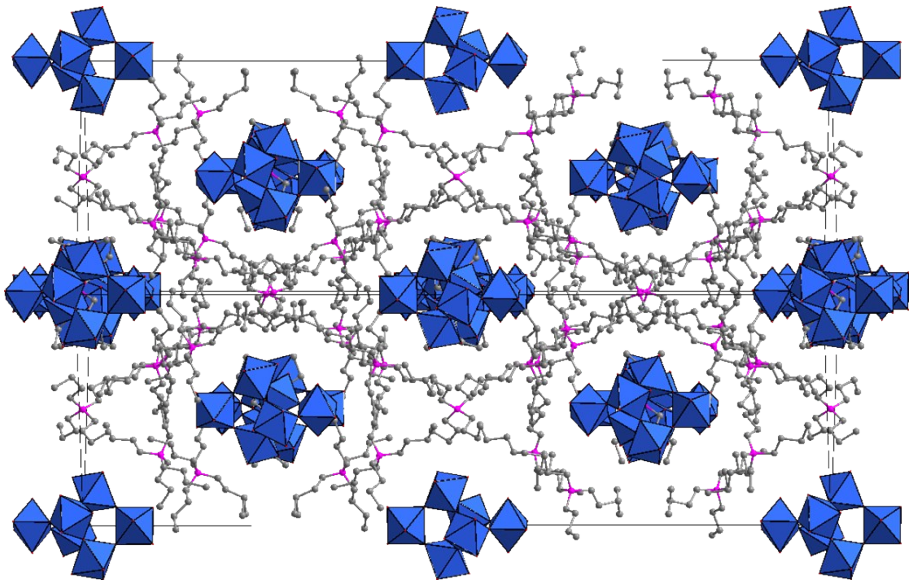


Figure S8. The packing diagram of $\{Ti_6O_8\}$ cluster in Ti_6-TBAC.[5] The TBA^+ cations are organized into hydrophobic shells and inside the shells are located the $\{Ti_6O_8\}$ cluster, $Cl^-$and solvent H_2O.

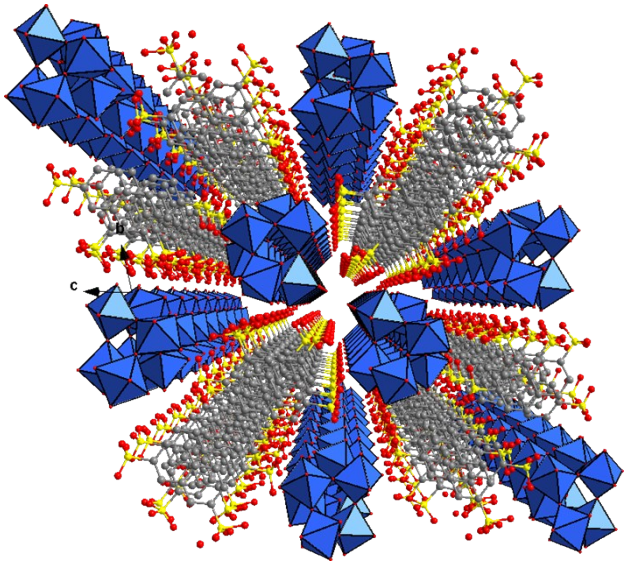


Figure S9. The packing diagram of $\{Ti_6O_8\}$ clusters in $\{Ti_6O_8\}$-NDS. The $\{Ti_6O_8\}$ clusters are separated by many one-dimensional chain-like fabrics of the assembled 2,7-naphthalenedisulfonate.

3. References

(1) SaintPlus: Data Reduction and Correction Program, version 6.22; Bruker AXS: Madison, WI, **2001**.

(2) Sheldrick, G. M. SADABS, A Program for Empirical Absorption Correction; University of Göttingen: Göttingen, Germany, **1998**.

(3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. Olex2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339-341.

(4) Zhang, G.; Liu, C.; Long, D.-L.; Cronin, L.; Tung, C.-H.; Wang, Y. Water-Soluble Pentagonal-Prismatic Titanium-Oxo Clusters. *J. Am. Chem. Soc.* **2016**, *138*, 11097-11100.

(5) Zhang, G.; Hou, J.; Li, M.; Tung, C.-H.; Wang, Y. Counteranion-Stabilized Titanium(IV) Isopolyoxocationic Clusters Isolated from Water. *Inorg. Chem.* **2016**, *55*, 4704-4709.