Electronic Supplementary Information (ESI)

Single-Crystal-to-Single-Crystal Desolvation in a Ti_{32} Nano-Ring Cluster

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Contents

Experimental Section

Materials and Characterization. All reagents and solvents were obtained from commercial resources and used without further purification. Powder X-ray diffraction (PXRD) patterns were collected from 3° to 50°, with a step of 0.02°, and the data collection time was 0.5 s, using a Bruker D8 advance X-ray diffractometer with Cu *K*α radiation (λ = 1.54056 Å) equipped with a Lynxeye 1D detector. The elemental analyses (C, H, and N) were carried out with a Vario EL CHNOS elemental analyzer. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449F3 instrument in the range of 30−900 °C under a nitrogen flow with a heating rate of 10 °C/min for the samples of compounds. Scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDS) data and images were collected using an FEI Quanta 200 FEG, with electron energy 30 kV, spectrum acquisition time 100 s. The FTIR spectra over a range 4000-400 cm^{-1} were collected on a Thermo Nicolet 6700 instrument. UV spectroscopy data were recorded from single crystals of two phases using a Craic Technologies microspectrophotometer. Their particle size was determined by a Malvern Zetasize Nano ZS90 armed with a solid-state He-Ne laser (λ =633 nm) at room temperature. A Quantachrome Autosorb Gas Sorption analyzer IQ2 was used to perform gas adsorption measurements.

Synthesis of compound 1 and 1-Dry: A mixture of 4-aminobenzoic acid (192 mg, 1.40 mmol), titanium(IV) isopropoxide (104 µl, 0.35 mmol), isopropanol (3.0 ml) and ethylene glycol (3.0 ml) was placed in a 20 ml glass vial, shaken at RT for 10 mins, and heated to 90 ^{o}C for 72 h. When cooled to room temperature, bright yellow

block crystals of compound **1** was obtained, the crystals were steadily retained in the mother liquor. By washing compound **1** three times with isopropanol and then naturally dry for 24 hours or putting compound **1** in the oven at 50 ^{o}C for 3 hours, new crystal compound **1-Dry** was obtained. Yield: about 67 % (based on Ti). Elemental analysis for compound **1-Dry** Calc: C, 36.615%, H, 4.98%, N, 2.945%; Found: C, 35.55%, H, 5.116%, N, 3.089%. IR (KBr, cm^{-1}): 3343(vw), 3216(vw), 2920(vw), 2854(vw), 1602(w), 1578(w), 1504(s), 1387(s), 1308(s), 1117(w), 1073(m), 1038(m), 896(m), 849(w), 781(m), 739(m), 700(s), 627(s), 587(s), 506(s).

Crystallographic Studies. Crystals of **1** and **1-Dry** were mounted on a loop with paratone and optically aligned on a Bruker D8-Venture single crystal X-ray diffractometer equipped with a digital camera. The diffraction data were collected using a Turbo X-ray Source (Mo–Kα radiation, λ = 0.71073 Å, 45 kV/42 mA power) adopting the direct-drive rotating anode technique and a CMOS detector under 173 K. The structures were solved by the direct method and refined on F^2 by full–matrix least–squares methods using SHELXTL.[1] All the non–hydrogen atoms were refined anisotropically. Contributions of guest molecules filled in nanoring were removed using *SQUEEZE* routine of *PLATON*[2]. The exact formula of **1-Dry** is $Ti_{32}(\mu_2\text{-}O)_8(\mu_3\text{-}O)_8(L)_{16}(gly)_{32}(glyH)_{16}\cdot 12(glyH_2)$, which is consistent with the loss of 9.25 % in the range of 30-300 ^{o}C (calculated 9.78%) and the 511 electrons found in S.A.V. (408 electrons for 12 ethylene glycol molecules and 103 electrons for disordered hydrogens and carbons absent in cif files). The CHN element analysis of **1-Dry** also proves that the mentioned formula is a correct one (Calc: C, 36.615%, H, 4.98%, N, 2.945%;

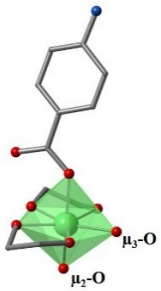
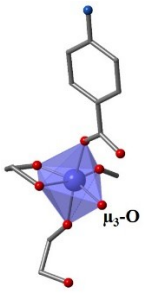
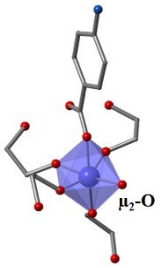
Found: C, 35.55%, H, 5.116%, N, 3.089%). For the compound **1** which is a metastable state, the number and species of solvent molecules are affected by the environment actively, such as room temperature, exposure time, humidity, etc. The properties of isopropanol and ethylene glycol are similar to each other (formula weight is 60.06 and 62.068; the number of electrons for both compounds is 34), the only difference is boiling temperature (82.45 ^{o}C for isopropanol and 197.3 ^{o}C for ethylene glycol). Therefore, the exact formula of **1** can only determine by crystal data and is estimated $Ti_{32}(\mu_2\text{-}O)_8(\mu_3\text{-}O)_8(L)_{16}(gly)_{32}(glyH)_{16}\cdot 12(glyH_2)\cdot 29(IPA)$.

Table S1: Crystal Data and Refinement Details for compound **1** and **1-Dry**.

	1	**1-Dry**
Formula	$C_{319}H_{608}N_{16}O_{197}Ti_{32}$	$C_{232}H_{376}N_{16}O_{168}Ti_{32}$
Formula weight (mol g^{-1})	9352.07	7609.29
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	21.009(10)	21.635(6)
b (Å)	23.513(15)	22.749(6)
c (Å)	44.73(2)	36.225(10)
α (°)	81.041(12)	72.345(6)
β (°)	79.236 (6)	81.085(7)
γ (°)	66.339(11)	65.911(6)
V ($Å^3$)	19802(18)	15500(7)
CCDC number	1851643	1851642
Z	2	2
D_c (g cm^{-3})	1.117	1.427
μ (mm^{-1})	0.675	0.862
F (000)	6796	6800
T (K)	173(2)	173(2)
Reflections collected	426865	251536
Reflections unique	42557	25093
Reflections observed	29793	19729
R_{int}	0.1301	0.0616
GOF on F^2	1.048	1.025
R1,[a] *w*R2[b] ($I > 2\sigma(I)$)	0.0895, 0.2524	0.0600, 0.1640
R1,[a] *w*R2[b] (all data)	0.1187, 0.2795	0.0764, 0.1797

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2: The coordination environment of titanium cations.

Coordination modes	TiO_7	TiO_6		
Metal centers	Ti1, Ti5, Ti9, Ti13, Ti17, Ti21, Ti25, Ti29	Ti2, Ti4, Ti12, Ti23, Ti26, Ti31	Ti3, Ti8, Ti11, Ti16, Ti20, Ti24, Ti28, Ti32	Ti6, Ti7, Ti10, Ti14, Ti15, Ti18, Ti19, Ti22, Ti27, Ti30
Coordination environments				

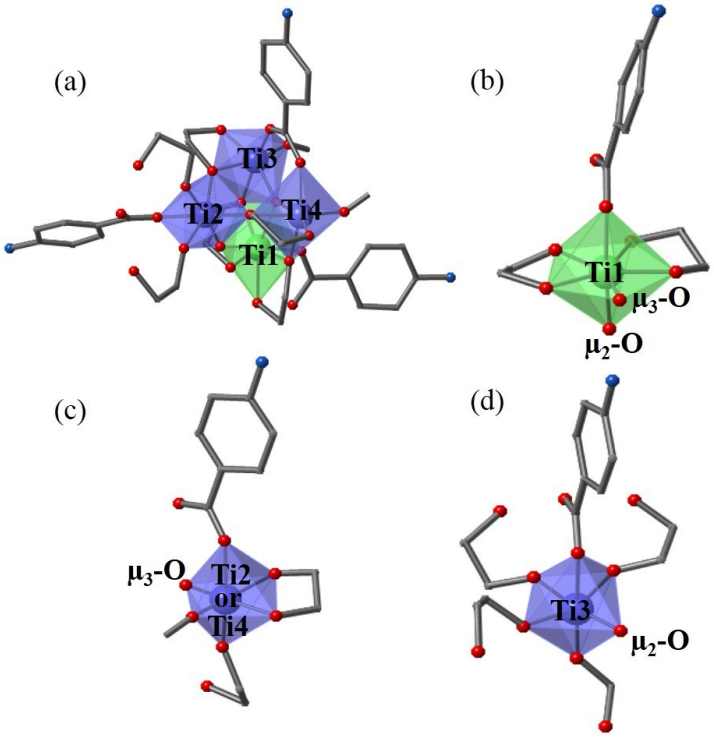


Fig. S1: (a) A typical tetramer (Ti_4) secondary building unit (SBU) including one TiO_7 (Ti1) and three TiO_6 (Ti2, Ti3, Ti4). (b) The coordination environment of Ti1. (c) The coordination environment of Ti2 or Ti4. (d) The coordination environment of Ti3.

In a typical SBU, there are one TiO_7 (Ti1) and three TiO_6 (Ti2, Ti3, Ti4). For Ti1, Ti (IV) cation adopts a pentagonal bipyramid coordination geometry, giving the TiO_7 unit, one oxygen atom is from one 4-aminobenzoate ligand, four oxygen atoms are given by two double deprotonated ethylene glycols, respectively. The leaving oxygen atoms are provided by μ_2-O and μ_3-O. For Ti2, Ti3, Ti4, all Ti (IV) cations adopt a tetragonal bipyramid coordination geometry, giving TiO_6 units. For Ti2, one of the oxygen atoms is from the ligand; one oxygen atom is given by μ_3-O, and three oxygen atoms are given by two double deprotonated ethylene glycols, the remaining one oxygen atom is provided by one mono-deprotonated ethylene glycol. As for Ti3, there is also one oxygen atom from the ligand. Besides, one oxygen atom is provided by μ_2-O, four oxygen atoms come from four double deprotonated ethylene glycols. The coordination environment of Ti4 is the same as Ti2. Furthermore, the ethylene glycol molecules not only play a role in bridging but also acting as terminal ligands. In one SBU, there are three 4-aminobenzoate ligands involved in the coordination, one of which bridge two TiO_6 units from the same tetramer, the rest connect with one TiO_7 and one TiO_6 coming from two neighboring SBUs.

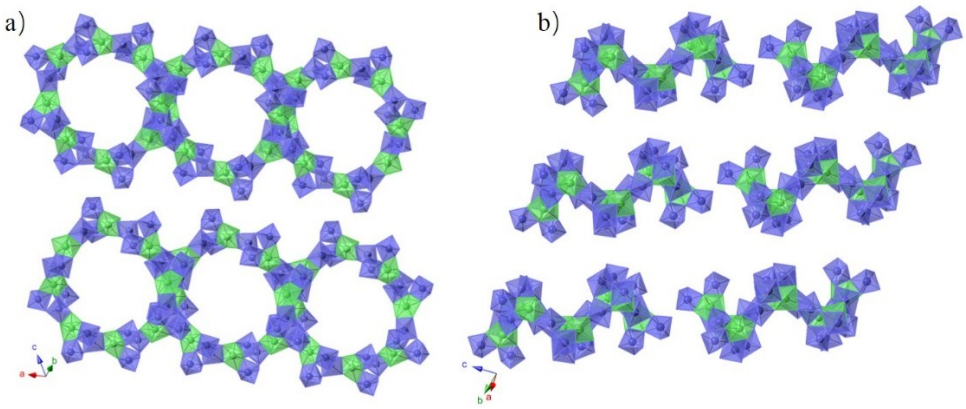


Fig. S2: The polyhedral presentation of compound **1** in different directions.

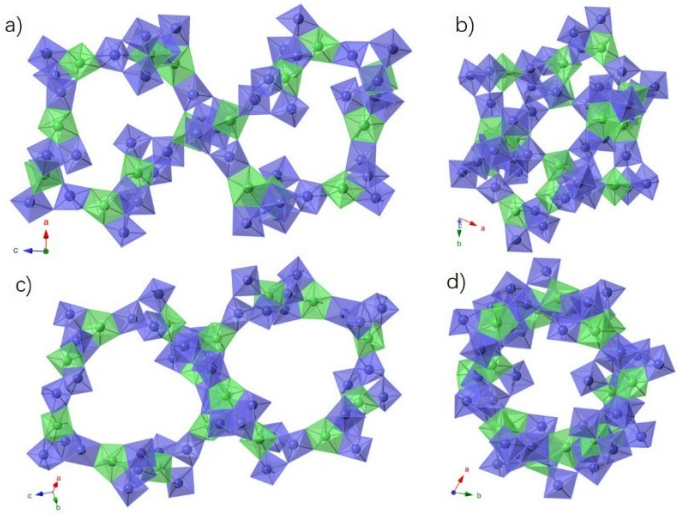


Fig. S3: The polyhedral presentation of compound **1-Dry** in different directions.

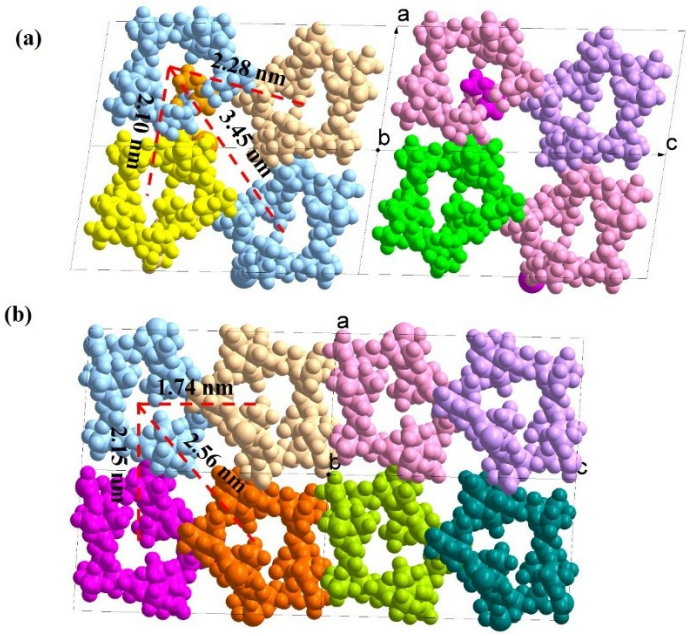


Fig. S4: The stacking arrangements of **1** (a) and **1-Dry** (b) in *b* direction.

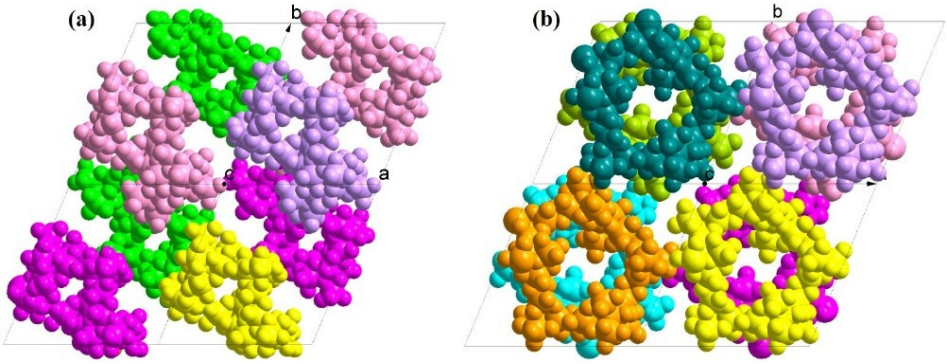


Fig. S5: The stacking arrangements of **1** (a) and **1-Dry** (b) in *c* direction.

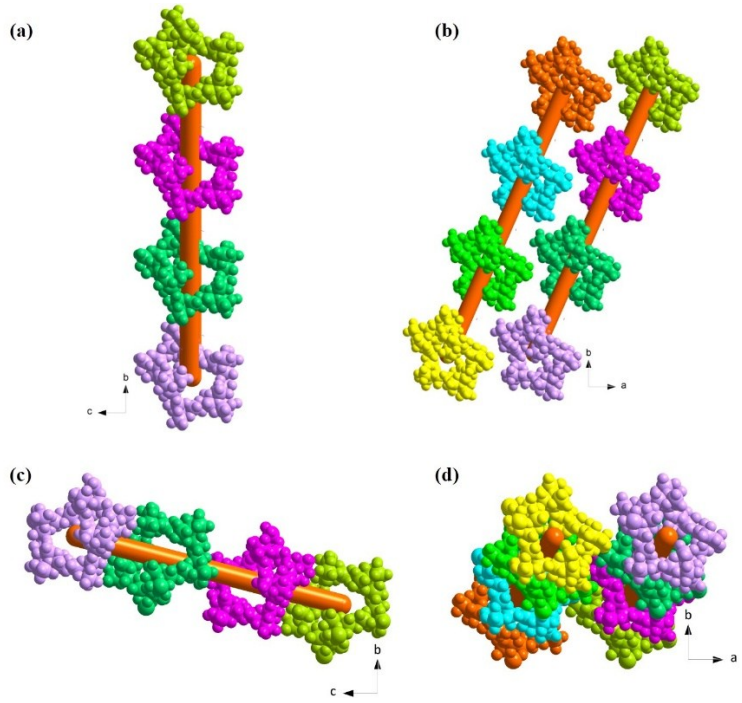


Fig. S6: The stacking arrangements and channels of **1** (a, b) and **1-Dry** (c, d) in different directions.

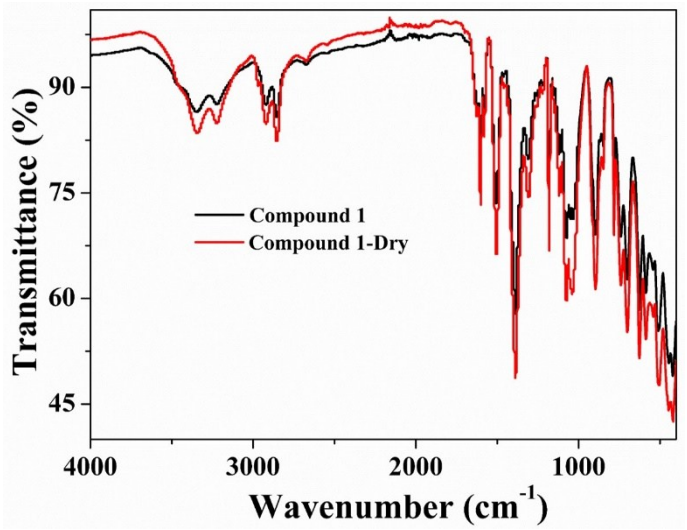


Fig. S7: FT- IR spectra of compound **1** washed with anhydrous ethanol and blown dry immediately, and compound **1-Dry**.

The peaks located in the range of 3350-2800 cm^{-1} are mainly assigned to the stretch of N-H and C-H from the organic ligand. The peaks appearing in the range of 1605-1500 cm^{-1} are assigned to the anti-symmetric and symmetric stretch peaks of the

aromatic ring and bending vibration absorption peaks of N-H. The stretching vibration peaks of C-N are observed with the wavenumber of 1185 and 1077 cm^{-1}. The frequencies at 896, 849 and 781 cm^{-1}were assigned to the stretching vibration of Ti-O. Moreover, Ti-O also had vibrational absorption at 400-700 cm^{-1}, which is consistent with the literature[3].

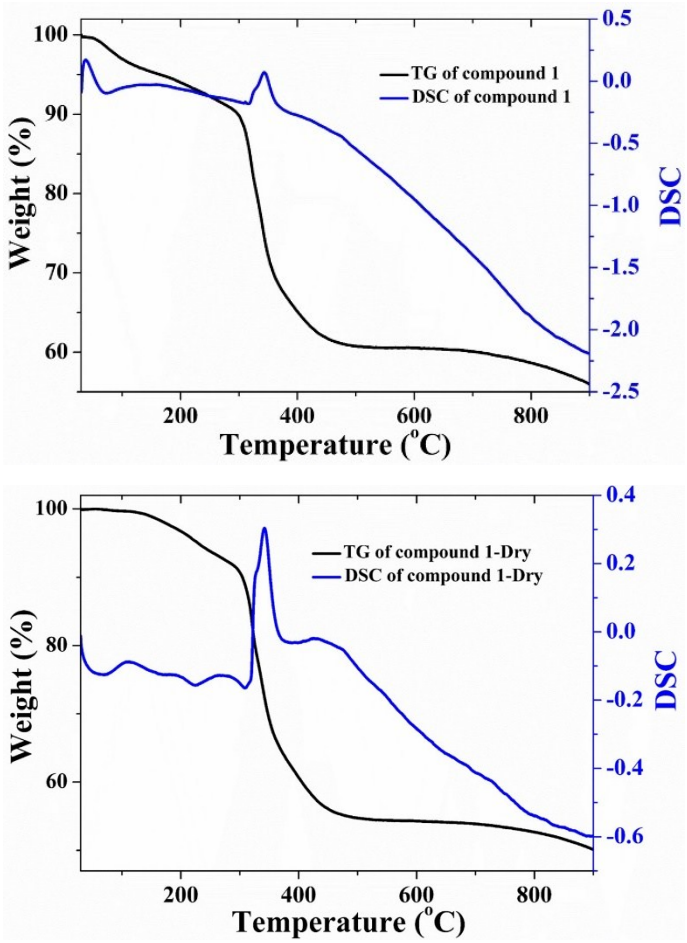


Fig. S8: The TGA (black) and DSC (blue) curves of compound **1** washed with anhydrous ethanol and blown dry immediately, and compound **1-Dry**.

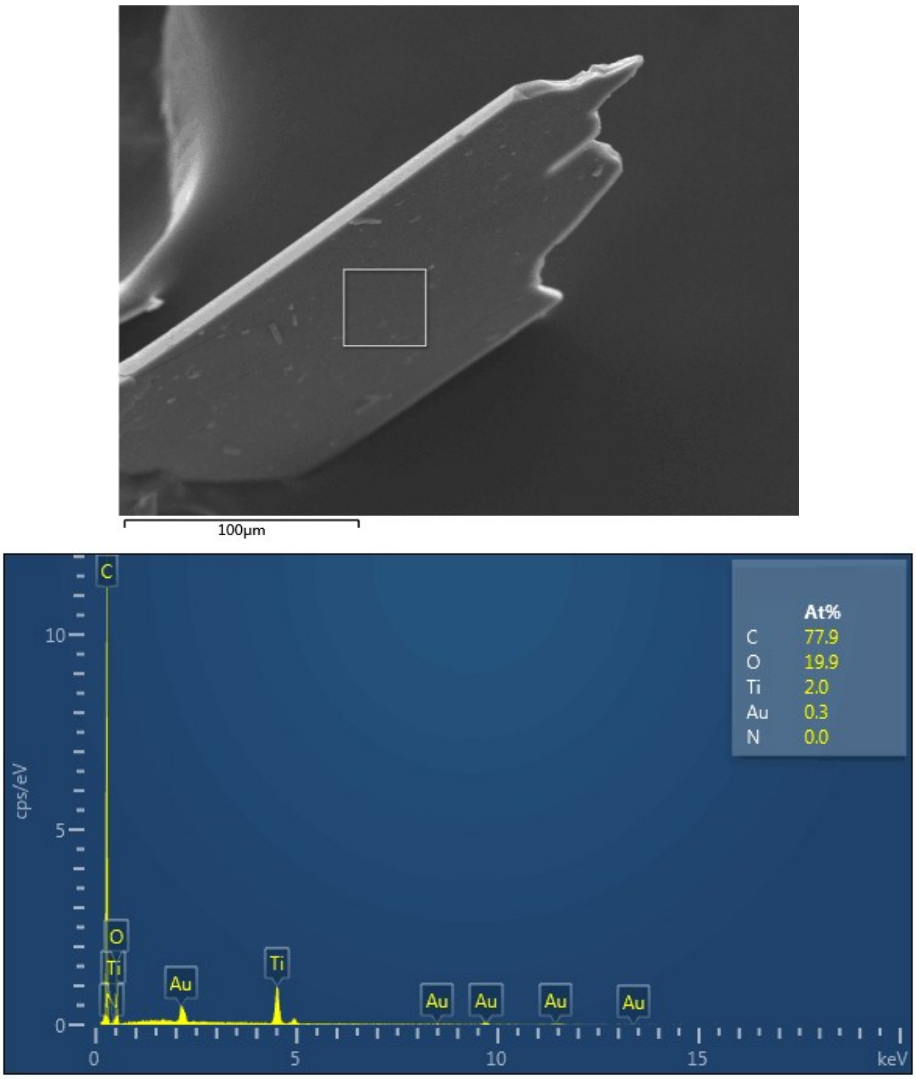


Fig. S9: The SEM images and EDS spectrum of compound **1-Dry**.

Particle Size Distribution measurements. Particle size distribution studies were commanded by taking 1.5 mg compound **1-Dry** into 2 ml DMF (AR) with the concentration about 10^{-4} mol/L, ultrasonic treatment for half hours to be dispersed evenly before testing.

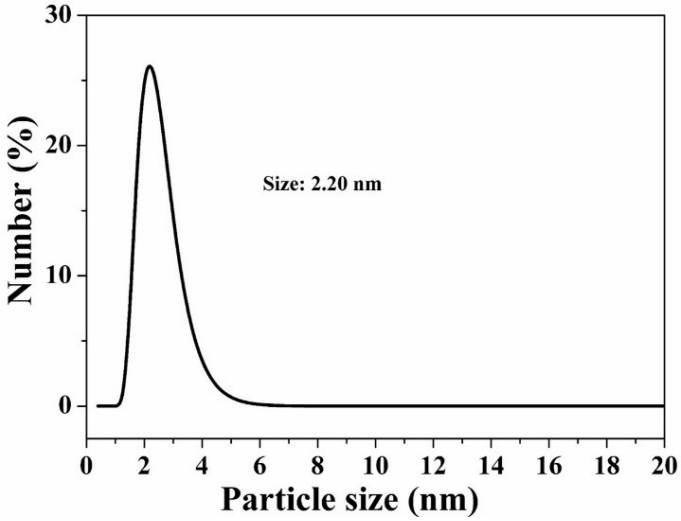


Fig. S10. The hydrodynamic size of compound **1-Dry** dispersed in DMF.

Table S3: Summary of particle size distribution measurements for **1-Dry**.

Times	Particle size (nm)	Number (%)	Average value of particle size(nm)	Average value of number (%)
1	2.01	28.1	2.202	26.86
2	2.33	27.8		
3	2.33	27		
4	2.01	23.9		
5	2.33	27.5		

Solvent Stability. Solvent stability studies were conducted by taking 20 mg compound **1-Dry** into 5ml different solvents respectively, such as 1,4-dioxane, acetone, methanol, water, acetonitrile, isopropanol, then magnetic stirring for 12 hours and centrifugation, finally, vacuum drying for 12 hours at 80 ^{o}C. The powder X-ray diffraction results show that compound **1-Dry** could be stable in different solvents.

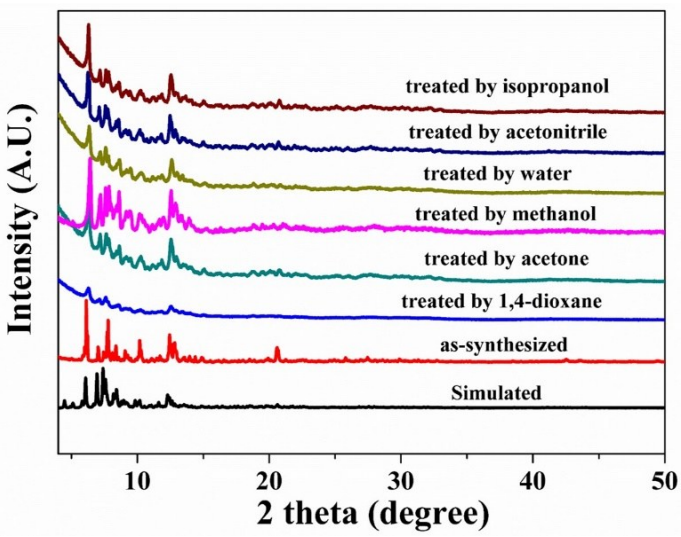


Fig. S11: Powder X-ray diffraction spectra of compound **1-Dry** after stirring in various solvents confirming their solvent stability.

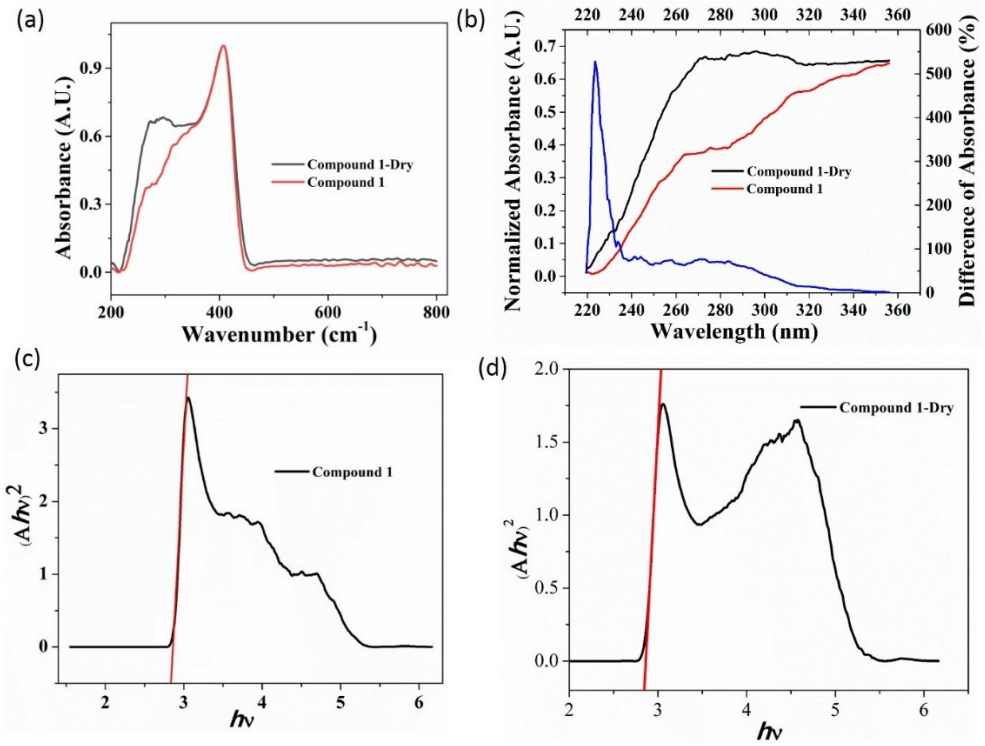


Fig. S12: The normalized UV-Vis spectrum and the bandgap of compound **1** (a,b c) and **1-Dry** (a, b, d) calculated to be about 2.8 eV according to the tauc equation.

Gas absorption measurements. Volumetric gas sorption date for compound **1-Dry** was collected at 77 K with high-purity N_2 gas in a liquid nitrogen bath and the

detecting pressure in the range of 0-760 Torr. CO_2 sorption measurements were performed at 195 K in a bath of acetone and dry ice. The pretreatment of compound **1-Dry** was treated as follows: the samples were soaked into a methanol solution, which was refreshed every 3 h for 10 h. After decanting the methanol solution by centrifugation, the samples were dried under a dynamic vacuum at room temperature for 12 h. Before adsorption measurement, the samples were activated using the "outgas" function of the surface area analyzer for eight hours at 80 °C.

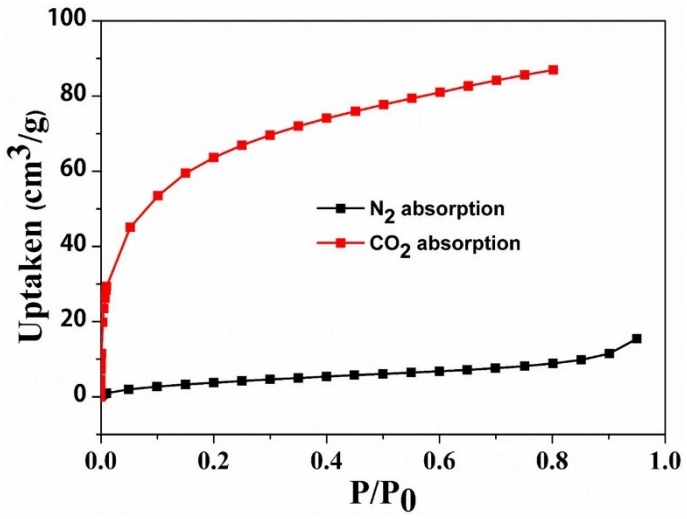


Fig. S13: The gas adsorption isotherm of compound **1-Dry**.

Table S4: **S**elected Bond Distances (Å) and Bond valence sum (BVS)[4] analysis for compound **1** and **1-Dry**.

Compound 1		
Ti1 Ti1-O7 1.861(7) Ti1-O5 2.009(7) Ti1-O3 2.026(7) Ti1-O4 2.047(7) Ti1-O6 2.065(7) Ti1-O2 2.078(7) Ti1-O1 2.082(6) BVS 4.061	Ti2 Ti2-O8 1.792(8) Ti2-O9 1.882(8) Ti2-O5 1.935(7) Ti2-O4 1.977(7) Ti2-O10 2.028(8) Ti2-O11 2.198(7) BVS 4.184	Ti3 Ti3-O7 1.783(7) Ti3-O11 1.933(7) Ti3-O15 1.981(7) Ti3-O14 1.988(7) Ti3-O13 2.055(7) Ti3-O12 2.100(7) BVS 4.068
Ti4 Ti4-O17 1.787(8) Ti4-O16 1.876(8) Ti4-O5 1.928(7) Ti4-O18 2.042(7) Ti4-O15 2.155(7) Ti4-O2 1.961(7) BVS 4.278	Ti5 Ti5-O23 1.859(7) Ti5-O20 1.995(7) Ti5-O13 2.011(7) Ti5-O22 2.035(7) Ti5-O21 2.066(7) Ti5-O19 2.061(7) Ti5-O14 2.083(7) BVS 4.150	Ti6 Ti6-O24 1.779(7) Ti6-O25 1.888(7) Ti6-O20 1.920(6) Ti6-O21 1.984(7) Ti6-O27 2.019(8) Ti6-O26 2.169(7) BVS 4.270
Ti7 Ti7-O28 1.799(8) Ti7-O29 1.856(7)	Ti8 Ti8-O23 1.787(7) Ti8-O30 1.952(7)	Ti9 Ti9-O39 1.854(7) Ti9-O36 2.009(7)

Ti7-O20 1.945(6) Ti7-O19 1.966(7) Ti7-O31 2.019(8) Ti7-O30 2.192(7) BVS 4.245	Ti8-O26 1.971(7) Ti8-O34 2.000(7) Ti8-O32 2.063(7) Ti8-O33 2.069(7) BVS 4.047	Ti9-O33 2.037(7) Ti9-O35 2.064(7) Ti9-O37 2.061(7) Ti9-O38 2.060(7) Ti9-O34 2.088(6) BVS 4.059
Ti10 Ti10-O42 1.771(9) Ti10-O40 1.874(8) Ti10-O36 1.947(7) Ti10-O37 1.968(7) Ti10-O41 2.013(9) Ti10-O43 2.213(7) BVS 4.267	Ti11 Ti11-O39 1.795(7) Ti11-O47 1.932(7) Ti11-O43 1.943(7) Ti11-O45 2.005(7) Ti11-O46 2.049(7) Ti11-O44 2.053(7) BVS 4.147	Ti12 Ti12-O50 1.791(8) Ti12-O48 1.869(8) Ti12-O36 1.918(7) Ti12-O35 1.984(7) Ti12-O49 2.048(8) Ti12-O47 2.191(7) BVS 4.216
Ti13 Ti13-O52 1.892(8) Ti13-O54 2.013(7) Ti13-O53 2.027(6) Ti13-O44 2.049(7) Ti13-O55 2.070(7) Ti13-O45 2.075(7) Ti13-O51 2.081(7) BVS 3.977	Ti14 Ti14-O56 1.798(8) Ti14-O57 1.892(7) Ti14-O54 1.917(7) Ti14-O55 1.987(7) Ti14-O58 2.038(8) Ti14-O59 2.151(7) BVS 4.197	Ti15 Ti15-O60 1.799(8) Ti15-O61 1.847(7) Ti15-O54 1.948(6) Ti15-O53 1.982(7) Ti15-O63 2.035(8) Ti15-O62 2.246(7) BVS 4.160
Ti16	Ti17	Ti18

Ti16-O52 1.770(8) Ti16-O62 1.935(7) Ti16-O59 1.976(7) Ti16-O65 1.989(6) Ti16-O64 2.047(7) Ti16-O66 2.079(7) BVS 4.148	Ti17-O71 1.847(6) Ti17-O68 2.016(7) Ti17-O66 2.023(6) Ti17-O69 2.059(7) Ti17-O65 2.071(7) Ti17-O70 2.086(7) Ti17-O67 2.086(7) BVS 4.047	Ti18-O74 1.764(7) Ti18-O73 1.892(7) Ti18-O68 1.933(7) Ti18-O69 1.984(7) Ti18-O72 2.037(7) Ti18-O75 2.201(7) BVS 4.221
Ti19 Ti19-O76 1.782(8) Ti19-O77 1.890(8) Ti19-O68 1.929(7) Ti19-O67 1.978(7) Ti19-O78 2.049(8) Ti19-O79 2.199(7) BVS 4.174	Ti20 Ti20-O71 1.791(7) Ti20-O79 1.940(7) Ti20-O75 1.963(6) Ti20-O82 1.981(6) Ti20-O81 2.059(7) Ti20-O80 2.072(7) BVS 4.106	Ti21 Ti21-O86 1.860(6) Ti21-O84 2.002(6) Ti21-O81 2.022(6) Ti21-O85 2.058(7) Ti21-O87 2.058(7) Ti21-O83 2.072(7) Ti21-O82 2.084(6) BVS 4.080
Ti22 Ti22-O88 1.817(8) Ti22-O89 1.841(7) Ti22-O84 1.944(7) Ti22-O85 1.970(7) Ti22-O90 2.023(7)	Ti23 Ti23-O94 1.813(7) Ti23-O93 1.865(7) Ti23-O84 1.934(7) Ti23-O83 1.974(6) Ti23-O92 2.020(7)	Ti24 Ti24-O86 1.785(6) Ti24-O91 1.962(6) Ti24-O95 1.967(6) Ti24-O97 1.998(6) Ti24-O98 2.069(6)

Ti22-O91 2.229(7) BVS 4.187	Ti23-O95 2.153(6) BVS 4.230	Ti24-O96 2.096(7) BVS 4.001
Ti25 Ti25-O103 1.870(7) Ti25-O100 2.007(6) Ti25-O98 2.020(6) Ti25-O101 2.062(6) Ti25-O102 2.070(6) Ti25-O99 2.083(6) Ti25-O97 2.080(6) BVS 4.020	Ti26 Ti26-O106 1.782(8) Ti26-O104 1.884(7) Ti26-O100 1.949(6) Ti26-O101 1.987(6) Ti26-O105 2.006(7) Ti26-O107 2.212(7) BVS 4.186	Ti27 Ti27-O108 1.790(8) Ti27-O111 1.883(7) Ti27-O100 1.908(7) Ti27-O99 1.981(6) Ti27-O109 2.048(7) Ti27-O110 2.207(7) BVS 4.198
Ti28 Ti28-O103 1.788(7) Ti28-O110 1.929(7) Ti28-O107 1.954(7) Ti28-O113 2.015(6) Ti28-O112 2.053(7) Ti28-O114 2.072(7) BVS 4.105	Ti29 Ti29-O119 1.857(6) Ti29-O116 1.998(7) Ti29-O112 2.038(7) Ti29-O117 2.057(7) Ti29-O113 2.058(6) Ti29-O118 2.067(7) Ti29-O115 2.076(7) BVS 4.088	Ti30 Ti30-O122 1.778(8) Ti30-O121 1.856(7) Ti30-O116 1.950(7) Ti30-O115 1.982(7) Ti30-O120 2.066(7) Ti30-O123 2.191(7) BVS 4.201
Ti31 Ti31-O126 1.778(8) Ti31-O124 1.890(8)	Ti32 Ti32-O119 1.790(6) Ti32-O127 1.937(7)	

Ti31-O116 1.923(7) Ti31-O117 1.963(7) Ti31-O125 2.024(8) Ti31-O127 2.245(7) BVS 4.220	Ti32-O123 1.937(7) Ti32-O128 2.078(7) Ti32-O1 1.975(7) Ti32-O3 2.085(7) BVS 4.130	

Compound 1-Dry		
Ti1 Ti1-O7 1.857(6) Ti1-O5 1.989(6) Ti1-O3 2.008(6) Ti1-O6 2.010(6) Ti1-O2 2.058(5) Ti1-O4 2.055(6) Ti1-O1 2.071(5) BVS 4.243	Ti2 Ti2-O8 1.776(6) Ti2-O9 1.850(6) Ti2-O5 1.921(6) Ti2-O4 1.945(6) Ti2-O10 2.016(6) Ti2-O11 2.168(6) BVS 4.442	Ti3 Ti3-O7 1.769(6) Ti3-O11 1.938(6) Ti3-O15 1.947(6) Ti3-O14 1.987(6) Ti3-O12 2.052(6) Ti3-O13 2.078(5) BVS 4.196
Ti4 Ti4-O17 1.771(6) Ti4-O16 1.858(6) Ti4-O5 1.913(6) Ti4-O2 1.954(6) Ti4-O18 2.025(6)	Ti5 Ti5-O23 1.856(6) Ti5-O13 2.005(6) Ti5-O20 1.995(6) Ti5-O21 2.042(6) Ti5-O22 2.052(6)	Ti6 Ti6-O24 1.763(7) Ti6-O25 1.862(7) Ti6-O20 1.926(6) Ti6-O19 1.958(6) Ti6-O27 2.024(7)

Ti4-O15 2.174(6) BVS 4.417	Ti5-O14 2.059(5) Ti5-O19 2.057(6) BVS 4.214	Ti6-O26 2.193(6) BVS 4.380
Ti7 Ti7-O28 1.781(7) Ti7-O29 1.867(6) Ti7-O20 1.921(6) Ti7-O21 1.966(6) Ti7-O31 2.003(7) Ti7-O30 2.175(6) BVS 4.361	Ti8 Ti8-O23 1.776(6) Ti8-O26 1.935(6) Ti8-O30 1.944(6) Ti8-O34 1.971(6) Ti8-O33 2.052(6) Ti8-O32 2.100(6) BVS 4.186	Ti9 Ti9-O39 1.839(6) Ti9-O36 1.979(6) Ti9-O38 2.037(6) Ti9-O33 2.024(6) Ti9-O35 2.050(5) Ti9-O37 2.054(6) Ti9-O34 2.084(6) BVS 4.234
Ti10 Ti10-O42 1.764(6) Ti10-O40 1.859(6) Ti10-O36 1.920(6) Ti10-O37 1.969(6) Ti10-O41 2.035(6) Ti10-O43 2.220(6) BVS 4.335	Ti11 Ti11-O39 1.788(6) Ti11-O43 1.924(6) Ti11-O47 1.939(6) Ti11-O45 1.983(6) Ti11-O44 2.053(6) Ti11-O46 2.058(6) BVS 4.215	Ti12 Ti12-O50 1.779(6) Ti12-O48 1.867(6) Ti12-O36 1.925(5) Ti12-O35 1.960(6) Ti12-O49 1.985(6) Ti12-O47 2.190(6) BVS 4.384
Ti13 Ti13-O52 1.853(5)	Ti14 Ti14-O56 1.778(7)	Ti15 Ti15-O60 1.776(7)

Ti13-O54 1.989(6) Ti13-O44 2.027(6) Ti13-O45 2.048(6) Ti13-O55 2.057(6) Ti13-O53 2.048(6) Ti13-O51 2.052(6) BVS 4.203	Ti14-O57 1.881(6) Ti14-O54 1.928(6) Ti14-O55 1.972(6) Ti14-O58 2.020(7) Ti14-O59 2.169(6) BVS 4.292	Ti15-O61 1.833(7) Ti15-O54 1.922(6) Ti15-O53 1.970(6) Ti15-O63 2.025(7) Ti15-O62 2.185(6) BVS 4.405
Ti16 Ti16-O52 1.775(6) Ti16-O62 1.934(6) Ti16-O59 1.946(6) Ti16-O65 1.983(6) Ti16-O64 2.064(6) Ti16-O66 2.043(5) BVS 4.226	Ti17 Ti17-O71 1.849(6) Ti17-O68 1.987(5) Ti17-O66 2.019(5) Ti17-O70 2.032(6) Ti17-O67 2.055(6) Ti17-O69 2.058(6) Ti17-O65 2.071(5) BVS 4.215	Ti18 Ti18-O74 1.770(6) Ti18-O73 1.881(6) Ti18-O68 1.934(6) Ti18-O69 1.959(6) Ti18-O72 1.983(6) Ti18-O75 2.160(6) BVS 4.397
Ti19 Ti19-O76 1.802(6) Ti19-O77 1.836(6) Ti19-O68 1.923(6) Ti19-O67 1.967(6) Ti19-O78 2.014(6)	Ti20 Ti20-O71 1.776(6) Ti20-O75 1.932(6) Ti20-O79 1.943(6) Ti20-O82 1.980(6) Ti20-O81 2.051(5)	Ti21 Ti21-O86 1.846(6) Ti21-O84 1.999(6) Ti21-O81 2.013(6) Ti21-O83 2.039(6) Ti21-O82 2.065(5)

Ti19-O79 2.211(6) BVS 4.317	Ti20-O80 2.054(6) BVS 4.240	Ti21-O87 2.064(6) Ti21-O85 2.077(6) BVS 4.171
Ti22 Ti22-O88 1.790(7) Ti22-O89 1.869(6) Ti22-O84 1.916(6) Ti22-O85 1.953(6) Ti22-O90 2.016(7) Ti22-O91 2.187(6) BVS 4.330	Ti23 Ti23-O94 1.770(7) Ti23-O93 1.856(6) Ti23-O84 1.919(6) Ti23-O83 1.980(6) Ti23-O92 2.015(7) Ti23-O95 2.167(6) BVS 4.388	Ti24 Ti24-O86 1.789(6) Ti24-O91 1.932(6) Ti24-O95 1.945(6) Ti24-O97 1.984(6) Ti24-O98 2.031(6) Ti24-O96 2.070(7) BVS 4.199
Ti25 Ti25-O103 1.846(6) Ti25-O100 1.997(6) Ti25-O98 2.022(6) Ti25-O99 2.028(6) Ti25-O102 2.044(6) Ti25-O101 2.059(6) Ti25-O97 2.072(6) BVS 4.220	Ti26 Ti26-O106 1.756(7) Ti26-O104 1.875(7) Ti26-O100 1.913(6) Ti26-O101 1.965(6) Ti26-O105 2.036(7) Ti26-O107 2.164(6) BVS 4.397	Ti27 Ti27-O108 1.782(7) Ti27-O111 1.831(6) Ti27-O100 1.930(6) Ti27-O99 1.966(6) Ti27-O109 2.026(7) Ti27-O110 2.287(6) BVS 4.293
Ti28 Ti28-O103 1.790(6)	Ti29 Ti29-O119 1.857(6)	Ti30 Ti30-O122 1.763(6)

Ti28-O110 1.916(6) Ti28-O107 1.953(6) Ti28-O113 1.980(6) Ti28-O112 2.055(6) Ti28-O114 2.069(6) BVS 4.186	Ti29-O116 2.000(6) Ti29-O112 2.019(6) Ti29-O118 2.038(6) Ti29-O117 2.042(6) Ti29-O113 2.065(6) Ti29-O115 2.067(6) BVS 4.179	Ti30-O121 1.871(6) Ti30-O116 1.934(6) Ti30-O115 1.959(6) Ti30-O120 2.032(6) Ti30-O123 2.163(6) BVS 4.360
Ti31 Ti31-O126 1.732(7) Ti31-O116 1.908(6) Ti31-O117 1.967(6) Ti31-O124 1.944(7) Ti31-O125 2.008(7) Ti31-O127 2.259(6) BVS 4.293	Ti32 Ti32-O119 1.775(6) Ti32-O127 1.914(6) Ti32-O123 1.956(6) Ti32-O1 1.996(6) Ti32-O3 2.047(6) Ti32-O128 2.081(6) BVS 4.197	

Table S5: The variation of Bond valence sum between compound **1** and **1-Dry**.

ΔTi1	ΔTi2	ΔTi3	ΔTi4	ΔTi5	ΔTi6	ΔTi7	ΔTi8
0.182	**0.258**	**0.128**	**0.139**	**0.064**	**0.110**	**0.116**	**0.139**
ΔTi9	ΔTi10	ΔTi11	ΔTi12	ΔTi13	ΔTi14	ΔTi15	ΔTi16
0.175	**0.068**	**0.068**	**0.168**	**0.226**	**0.095**	**0.245**	**0.078**
ΔTi17	ΔTi18	ΔTi19	ΔTi20	ΔTi21	ΔTi22	ΔTi23	ΔTi24
0.168	**0.176**	**0.143**	**0.134**	**0.091**	**0.143**	**0.158**	**0.198**
ΔTi25	ΔTi26	ΔTi27	ΔTi28	ΔTi29	ΔTi30	ΔTi31	ΔTi32
0.200	**0.211**	**0.095**	**0.081**	**0.091**	**0.159**	**0.073**	**0.067**

[$\Delta Ti_n(BVS) = Ti_n(BVS)_{\mathbf{1\text{-}Dry}} - Ti_n(BVS)_{\mathbf{1}}$, n=1, 2, 3,……32]

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