Electronic Supporting Information

A Family of 2,8-Quinolinediol-Functionalized Titanium-Oxo Clusters with Tunable Photoelectric Properties

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Experimental Procedures

Materials and Instruments

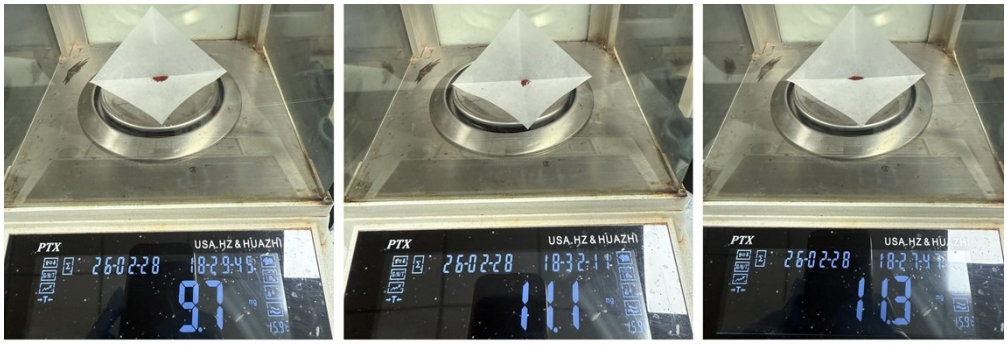
Titanium (IV) tetraisopropanolate ($Ti(^{i}PrO)_{4,}$ 98%, Adamas-beta®), 2,8-quinolinediol (H_2QD, Adamas-beta®), and dimethylglyoxime (DMG, Adamas-beta®) were purchased from Shanghai Titan Scientific Co., Ltd. (China). N, N-dimethylformamide (DMF, 99.7%), methanol (MeOH, 99.7%), n-propanol (99.7%), isopropanol (99.7%), acetonitrile (99.7%), and ethanol (EtOH, 99.7%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). All chemicals and solvents were analytical grade and used without further purification.

Powder X-ray diffraction (PXRD) data were carried out on a microcrystalline powdered sample using a Rigaku SmartLab-9Kw diffractometer using Cu radiation (λ = 1.54184 Å). Thermogravimetry (TG) analysis was performed on a STA449F5/QMS403D instrument (Mettler-Toledo, Schwerzenbach, Switzerland) with a heating rate of 10 °C min^{-1} from 20 to 800 °C in N_2 flow. The solid-state UV/Vis spectra data of the cluster samples were obtained using a Carry 500 UV-VIS spectrophotometer with scanning wavelength range from 200 nm to 800 nm. Fourier transform infrared spectroscopy (FTIR) measurements were obtained using a Nicolet iS50 spectrophotometer. The X-ray photoelectron spectroscopy (XPS) spectra were collected on a Thermo Scientific ESCALAB Xi^{+} instrument. The element mapping of samples were acquired on a Thermo Fisher Scientific FIB-SEM-GX4 scanning electron microscope. Electrochemical measurements were carried out on a CHI 660E electrochemical workstation.

Synthesis

Synthesis of $[Ti_4(\mu_2\text{-}O)_4(QD)_4(DMF)_4]$ (Ti4)

0.2 mmol (32.3 mg) of 2,8-quinolinediol was stirred in 4 mL of N, N-dimethylformamide. 0.33 mmol (0.1 mL) of $Ti(^iPrO)_4$ was then added. The mixture was sealed in a 10 mL glass vial and heated at 80 °C for 7 days. After cooling to room temperature, red crystals were obtained by filtration and washed several times with DMF. The average yields based on three independent experiments are 10.5% for **Ti4**, calculated with respect to $Ti(^iPrO)_4$.

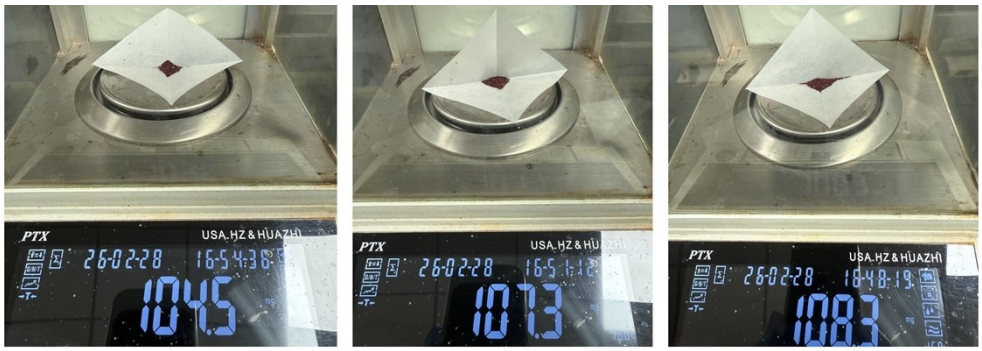


Mass of the first vial | Mass of the second vial | Mass of the third vial

Three completely independent synthesis experiments were performed for **Ti4**, with an average yield of **10.7 mg** per vial. The yield was **10.5%**, calculated based on $Ti(O^iPr)_4$.

Synthesis of $[Ti_5(\mu_3\text{-}O)_2(QD)_4(MeO)_8]$ (Ti5)

1 mmol (160 mg) of 2,8-quinolinediol was stirred in 4 mL of methanol. 1 mmol (0.3 mL) of $Ti(^iPrO)_4$ was then added. The mixture was sealed in a 10 mL glass vial and heated at 80 °C for 3 days. After cooling to room temperature, deep red crystals were obtained by filtration and washed several times with acetonitrile. The average yields based on three independent experiments are 46% for **Ti5**, calculated with respect to $Ti(^iPrO)_4$.

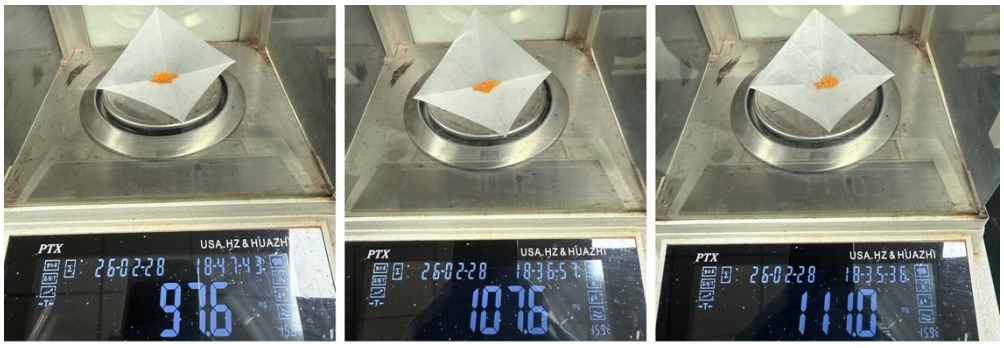


Mass of the first vial Mass of the second vial Mass of the third vial

Three completely independent synthesis experiments were performed for **Ti5**, with an average yield of **106.7 mg** per vial. The yield was **46.0%**, calculated based on $Ti(O^iPr)_4$.

Synthesis of $[Ti_7(\mu_2\text{-}O)(\mu_3\text{-}O)_3(QD)(EtO)_{18}]$ (Ti7)

2,8-Quinolinediol (0.2 mmol, 32.3 mg) and dimethylglyoxime (0.3 mmol, 35.0 mg) were dissolved in 3 mL of ethanol under stirring. Subsequently, $Ti(O^iPr)_4$ (1.69 mmol, 0.5 mL) was added to the solution. The resulting mixture was sealed in a 10 mL glass vial and heated at 80 °C for 7 days. After cooling to room temperature, the vial was kept in a refrigerator (4 °C) for an additional 7 days. The resulting yellow crystals were collected by filtration and washed several times with acetonitrile. The average yields based on three independent experiments are 32.1% for **Ti7**, calculated with respect to $Ti(^iPrO)_4$.



Mass of the first vial Mass of the second vial Mass of the third vial

Three completely independent synthesis experiments were performed for **Ti7**, with an average yield of **105.4 mg** per vial. The yield was **32.1%**, calculated based on $Ti(O^iPr)_4$.

Single-crystal X-ray diffraction

Single crystals of **Ti4**, **Ti5**, and **Ti7** were selected under an optical microscope and quickly coated with high-vacuum grease (Dow Corning Corporation) to prevent decomposition during data collection. SCXRD data for **Ti4** were collected on a Bruker D8 VENTURE diffractometer equipped with an Incoatec IμS 3.0 microfocus Cu Kα radiation source (λ = 1.54184 Å) and a PHOTON III C28 detector at 173 K. Temperature control was achieved using an Oxford Cryosystems CryostreamPlus 800 open-flow N_2 cooling device. SCXRD data for **Ti5** were obtained on a Bruker AXS CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 296 K. SCXRD data for **Ti7** were collected on a Rigaku Oxford X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 298 K. These structures were solved by the inherent phase method in the SHELXT program and refined by full-matrix least squares techniques against F^2 using the SHELXL program through the OLEX2 interface. Hydrogen atoms at carbon were placed in calculated positions and refined isotropically by using a riding model. Appropriate restraints or constraints were applied to the geometry and the atomic displacement parameters of the atoms in the cluster. All structures were examined using the Addsym subroutine of PLATON to ensure that no additional symmetry could be applied to the models. Pertinent crystallographic data collection and refinement parameters are collated in Table S1. Selected bond lengths are collated in Table S2. The crystallographic data for **Ti4, Ti5** and **Ti7** were delivered to the Cambridge Crystallographic Data Centre (CCDC) with *No.* 2527153 for **Ti4**, 2527154 for **Ti5** and 2527155 for **Ti7**. These data can be obtained from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical measurements

Photoelectrochemical measurements

Photoelectrochemical measurements were carried out on CHI 660E electrochemical workstation in a standard three-electrode electrochemical cell with ITO coated with the crystals as the working electrode, a platinum plate as counter electrode and a saturated Ag/AgCl electrode as reference electrode. A sodium sulfate solution (0.2 M) was used as the electrolyte, and a Xe lamp (150 W) was used as the light source. A bias potential of 0.2 V or 0.4 V was maintained. Preparation of the working electrode: 2 mg crystals powder was mixed with 0.99 mL ethanol and 10 μL Nafion D-520 dispersion solutions and sonicated for 30 minutes. Subsequently, 200 μL of slurry was transferred, coated on ITO glass plates (1 cm×2 cm), and then dried at room temperature.

Mott-Schottky plot measurements

The Mott-Schottky plots were carried out on the electrochemical workstation via a conventional three-electrode system with a working electrode, a platinum plate as counter electrode and a saturated Ag/AgCl electrode as reference electrode in a 0.2 M Na_2SO_4 aqueous solution at different frequencies of 1000 Hz, 1500 Hz, and 2000 Hz. The working electrode was prepared same as photoelectrochemical measurements.

Electrochemical impedance spectroscopy

Electrochemical impedance spectra (EIS) measurements were also carried out on CHI 660E electrochemical workstation via a conventional three-electrode system with a working electrode, a platinum plate as counter electrode and a saturated Ag/AgCl electrode as reference electrode in a 0.2 M Na_2SO_4 aqueous solution over a frequency range of 100 kHz-0.01 Hz. The working electrode was prepared same as photoelectrochemical measurements.

Figure S1. The compared PXRD patterns of **Ti4**.

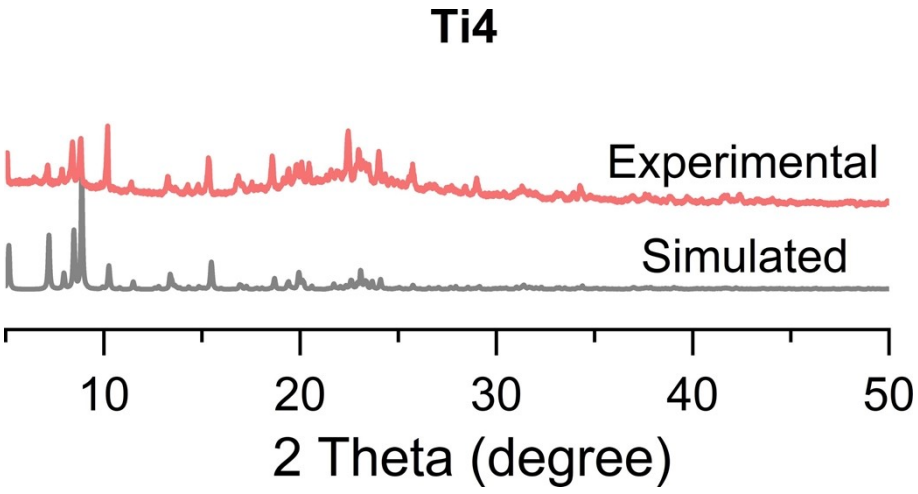


Figure S2. The compared PXRD patterns of **Ti5**.

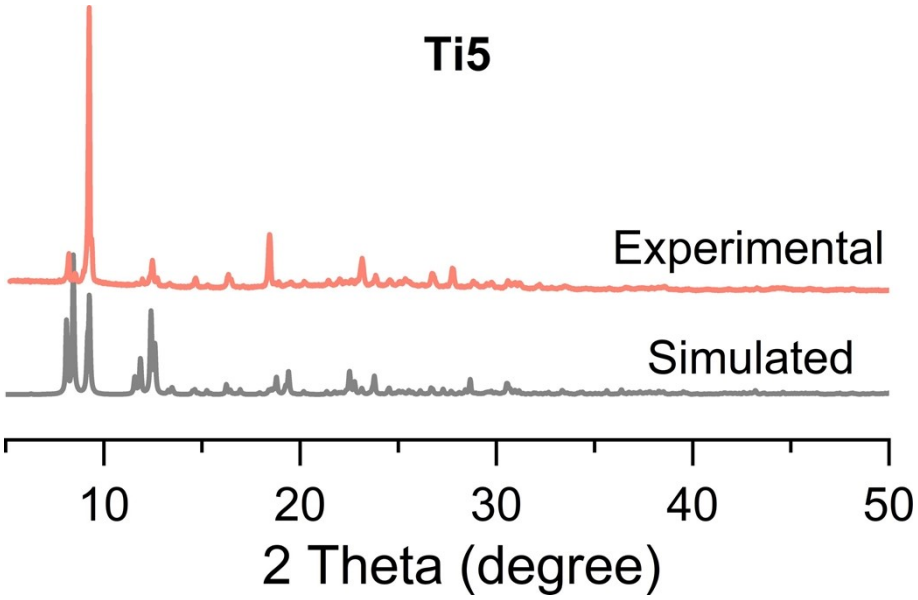


Figure S3. The compared PXRD patterns of **Ti7**.

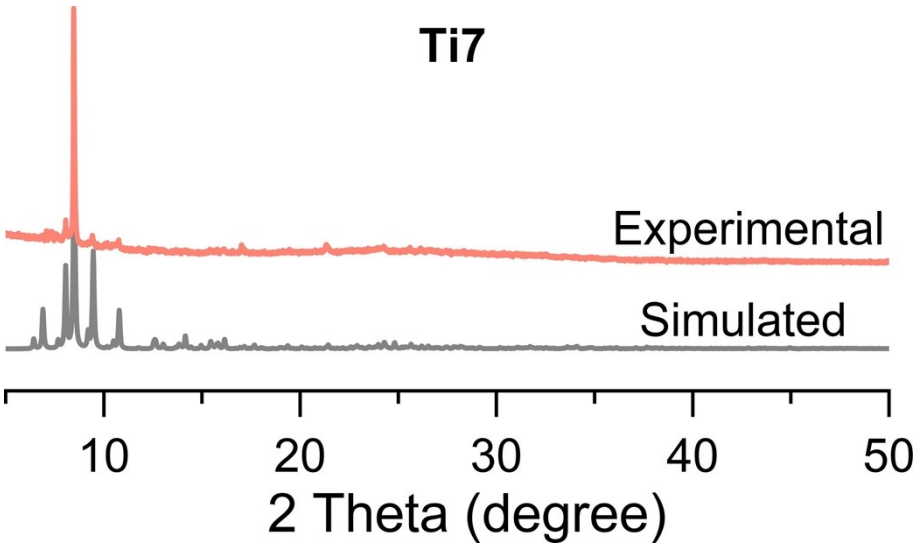


Figure S4. The thermogravimetric analysis (TGA) curves of **Ti4, Ti5** and **Ti7**.

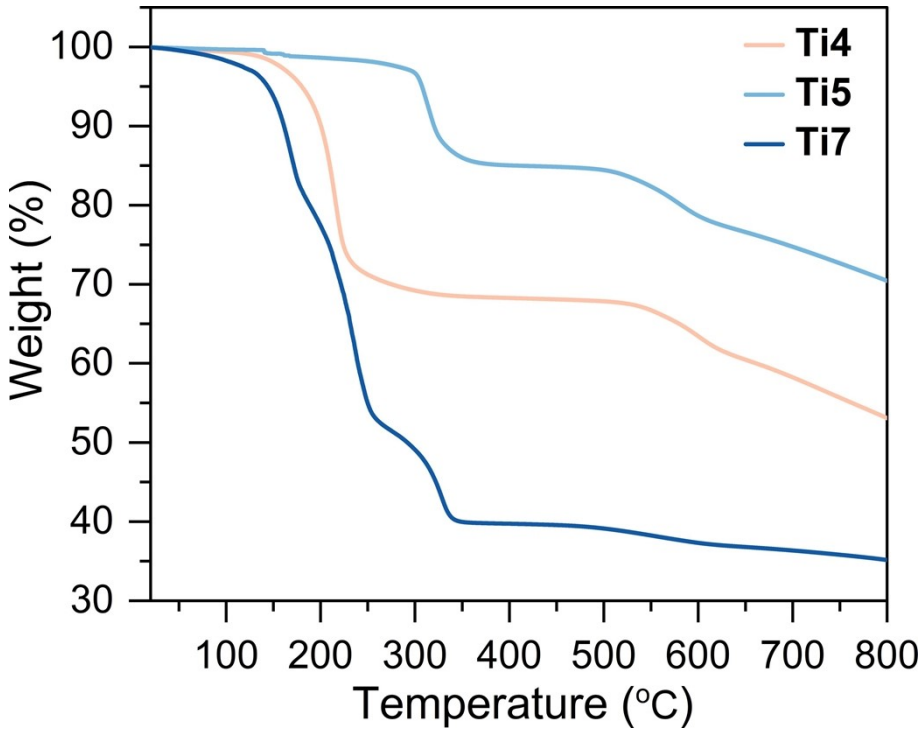


Figure S5. The Fourier transform infrared spectroscopy (FT-IR) of H_2QD, **Ti4, Ti5** and **Ti7**.

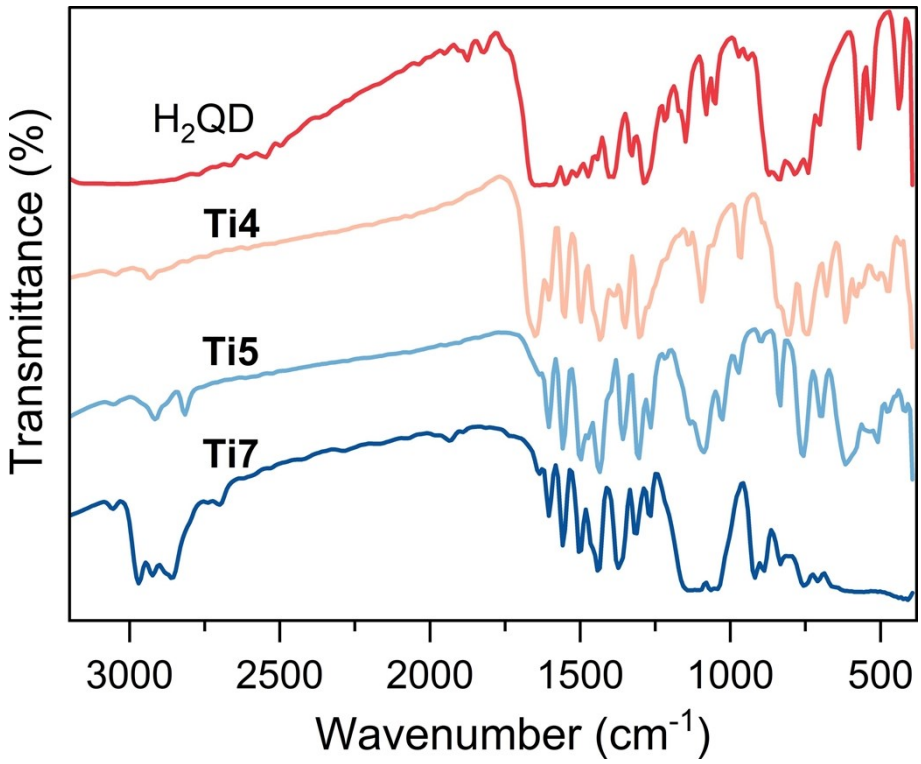


Figure S6. Elemental mapping images of Ti, C and N of selected area for **Ti4**.

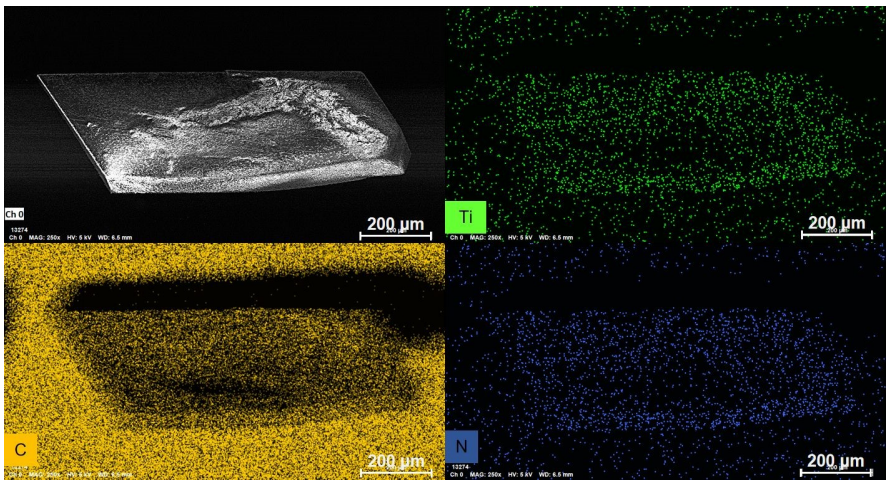


Figure S7. Elemental mapping images of Ti, C and N of selected area for **Ti5**.

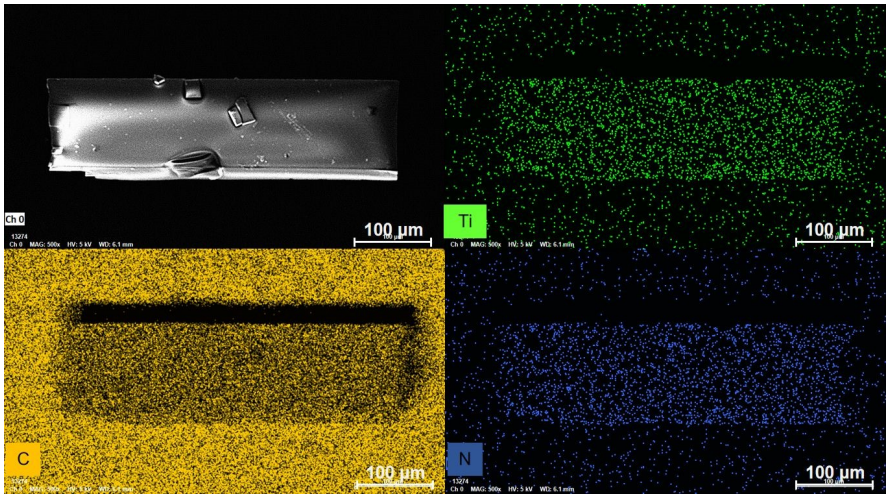


Figure S8. Elemental mapping images of Ti, C and N of selected area for **Ti7**.

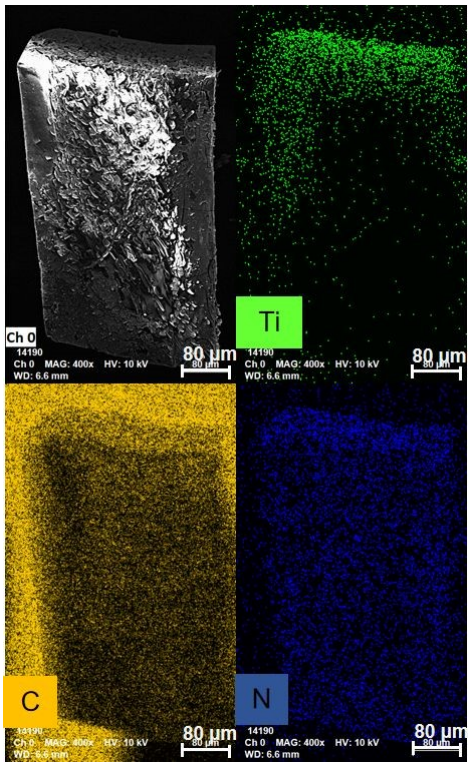


Figure S9. Tauc plots used to estimate the optical band gaps of (a) **Ti4**, (b) **Ti5**, and (c) **Ti7**.

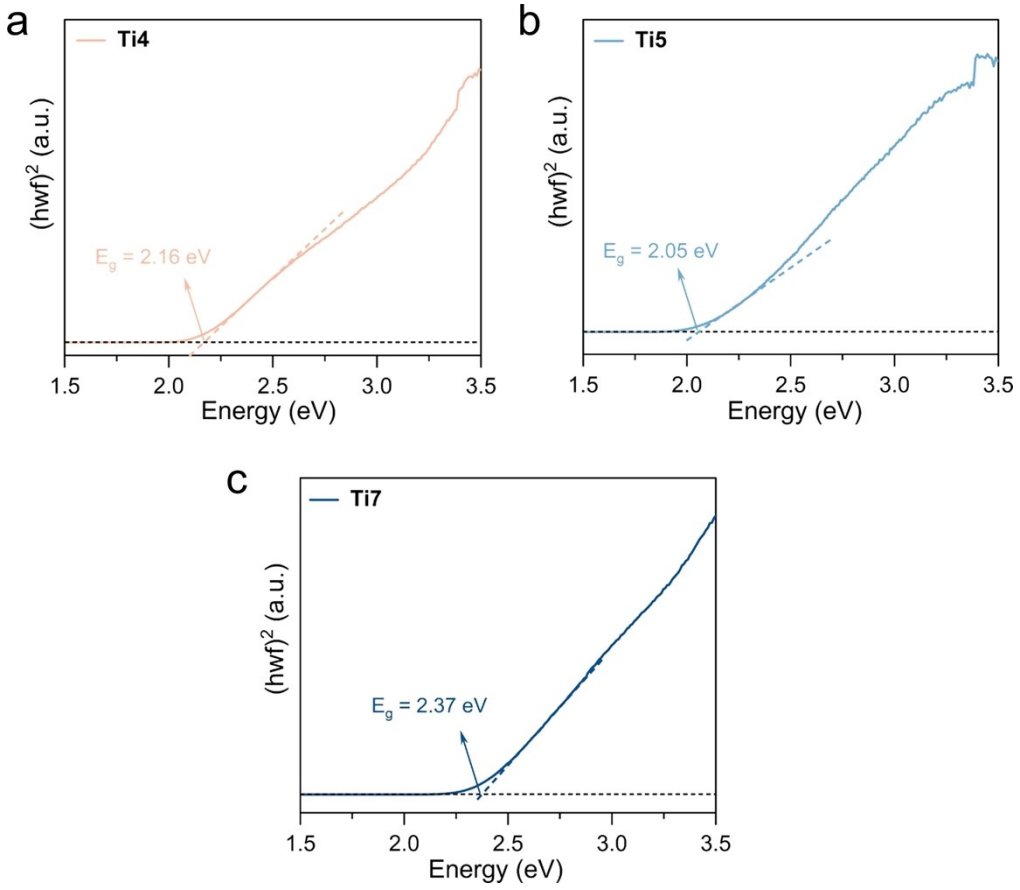


Figure S10. Mott–Schottky plots of (a) **Ti4**, (b) **Ti5**, and (c) **Ti7**.

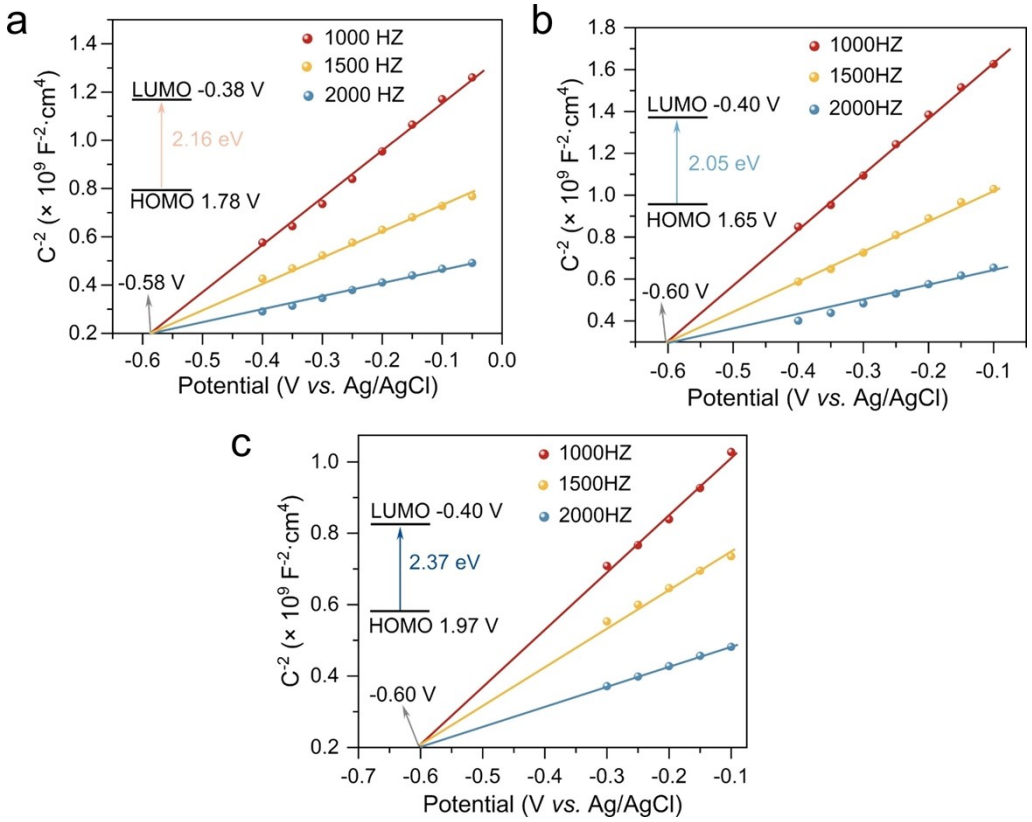


Figure S11. PXRD patterns after soaking in 0.2 mol/L Na_2SO_4 aqueous solution for 24 h, compared with the simulated PXRD patterns derived from their SCXRD data: (a) **Ti4**, (c) **Ti5**, and (e) **Ti7**. IR spectra before and after soaking in 0.2 mol/L Na_2SO_4 aqueous solution for 24 h: (b) **Ti4**, (d) **Ti5**, and (f) **Ti7**.

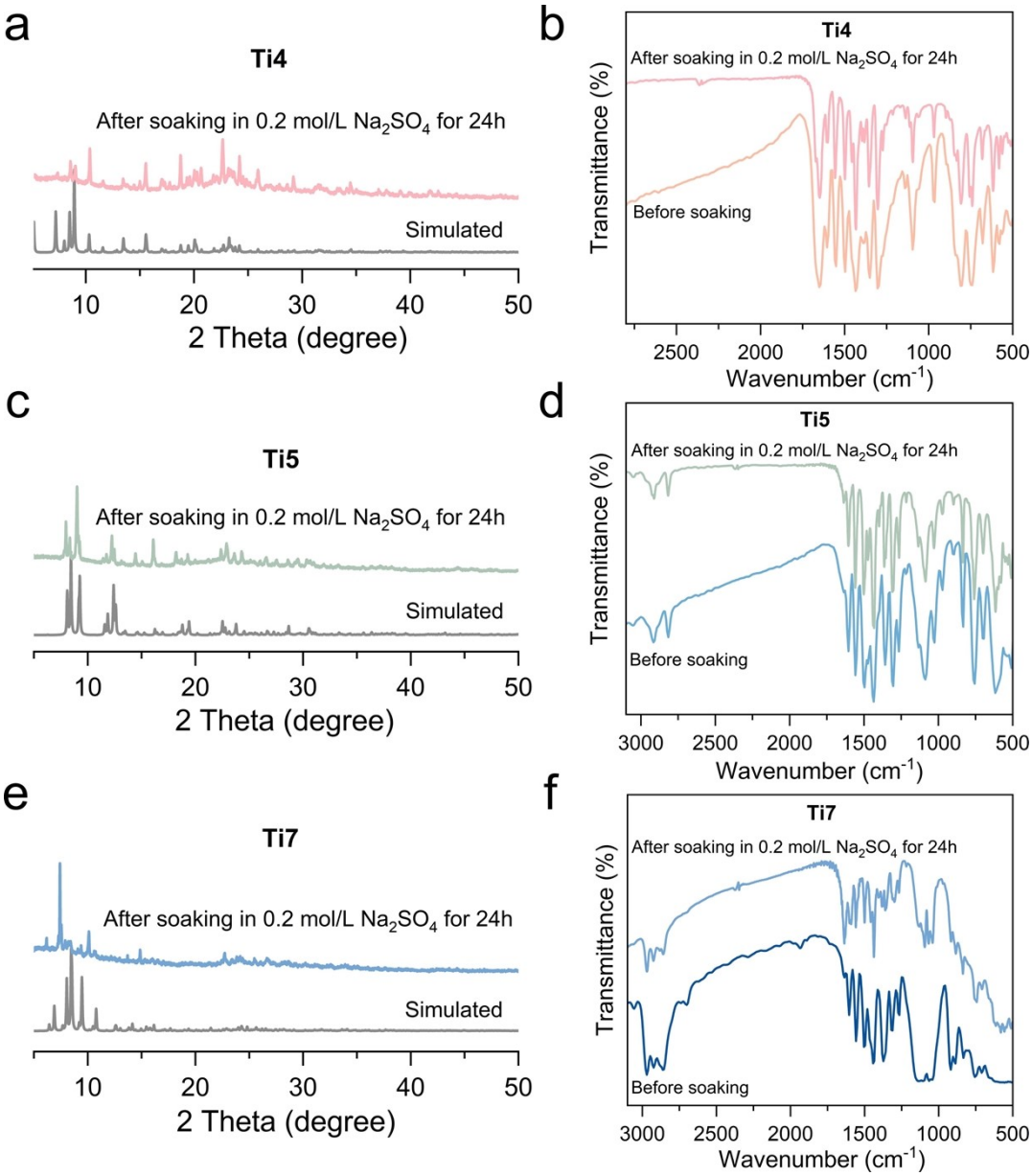


Table S1. Crystal data collection and sructure refinement for **Ti4**, **Ti5**, and **Ti7**.

Compound	**Ti4**	**Ti5**	**Ti7**
Empirical formula	$C_{48}H_{48}N_8O_{16}Ti_4$	$C_{44}H_{44}N_4O_{18}Ti_5$	$C_{45}H_{95}NO_{24}Ti_7$
Formula weight	1184.54	1156.33	1369.51
Temperature [K]	173	296	298
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	12.1789 (9)	12.2092 (18)	11.8028 (6)
b [Å]	34.017 (2)	14.930 (2)	14.1791 (9)
c [Å]	13.7034 (9)	14.963 (2)	21.4908 (15)
α [°]	90	88.874 (3)	101.187 (6)
β [°]	106.976 (3)	70.367 (3)	99.125 (5)
γ [°]	90	72.202 (3)	97.103 (5)
Volume [Å^3]	5429.8 (6)	2435.5 (6)	3439.0 (4)
Z	4	2	2
ρ_{calc} [gcm^{-3}]	1.449	1.577	1.323
μ [mm^{-1}]	5.466	0.862	0.837
F(000)	2432	1180	1436
Radiation	CuK_α (λ=1.54178 Å)	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2θ range [°]	5.20 to 133.15 (0.84 Å)	2.88 to 50.05 (0.84 Å)	6.65 to 49.43 (0.85 Å)
Index ranges	−13 ≤ h ≤ 14 −39 ≤ k ≤ 40 −16 ≤ l ≤ 16	−14 ≤ h ≤ 14 −13 ≤ k ≤ 17 −17 ≤ l ≤ 15	−13 ≤ h ≤ 13 −16 ≤ k ≤ 16 −25 ≤ l ≤ 25
Reflections collected	34521	13769	29918
Independent reflections	9508 R_{int} = 0.1094 R_{sigma} = 0.1016	8504 R_{int} = 0.0358 R_{sigma} = 0.0726	11703 R_{int} = 0.0739 R_{sigma} = 0.1078
Completeness to θ = 66.779°	99.0%	98.8%	99.7%
Data/Restraints/Parameters	9508/0/693	8504/1/648	11703/1157/928
Goodness-of-fit on F^2	1.026	1.066	1.104
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0587 wR_2 = 0.1533	*R_1 = 0.0719* *wR_2 = 0.1953*	*R_1 = 0.0896* *wR_2 = 0.2370*
Final *R* indexes [all data]	R_1 = 0.0811 wR_2 = 0.1703	*R_1 = 0.1225* *wR_2 = 0.2958*	*R_1 = 0.1519* *wR_2 = 0.2827*
Largest peak/hole [eÅ^{-3}]	0.53/-0.41		1.13/-1.17

Table S2. Selected bond lengths (Å) for for **Ti4**, **Ti5**, and **Ti7**.

Ti4			
Atom-Atom	**Length / Å**	**Atom-Atom**	**Length / Å**
Ti1–O4	1.942(3)	Ti3–O1	1.968(3)
Ti1–O6	1.942(3)	Ti3–O7	1.937(3)
Ti1–O12	2.194(3)	Ti3–O10	2.202(3)
Ti1–O13	1.753(3)	Ti3–O15	1.763(3)
Ti1–O14	1.900(3)	Ti3–O16	1.867(3)
Ti1–N2	2.265(3)	Ti3–N1	2.228(3)
Ti2–O2	1.937(3)	Ti4–O3	1.939(3)
Ti2–O5	1.934(3)	Ti4–O8	1.988(3)
Ti2–O11	2.201(3)	Ti4–O9	2.199(3)
Ti2–O13	1.899(3)	Ti4–O14	1.757(3)
Ti2–O16	1.753(3)	Ti4–O15	1.886(3)
Ti2–N3	2.253(3)	Ti4–N4	2.239(3)

Ti5			
Atom-Atom	**Length / Å**	**Atom-Atom**	**Length / Å**
Ti1–O2	2.052(5)	Ti4–O9	2.098(5)
Ti1–O3	1.937(5)	Ti4–O11	1.943(5)
Ti1–O10	1.920(6)	Ti4–O12	1.767(5)
Ti1–O13	1.754(6)	Ti4–O14	1.965(4)
Ti1–O14	2.020(5)	Ti4–O16	1.939(5)
Ti1–N3	2.231(6)	Ti4–N4	2.219(6)
Ti2–O2	2.076(5)	Ti5–O1	1.976(5)
Ti2–O4	1.984(5)	Ti5–O6	1.915(5)
Ti2–O5	1.935(5)	Ti5–O7	2.004(5)
Ti2–O14	1.920(5)	Ti5–O15	1.978(5)
Ti2–O15	1.815(5)	Ti5–O17	1.789(5)
Ti2–N1	2.191(5)	Ti5–N2	2.254(6)
Ti3–O7	2.023(5)		
Ti3–O8	1.756(5)		
Ti3–O9	1.960(5)		
Ti3–O15	2.236(4)		
Ti3–O16	2.108(5)		
Ti3–O18	1.770(5)		

Ti7			
Atom-Atom	**Length / Å**	**Atom-Atom**	**Length / Å**
Ti1–O2	1.934(5)	Ti5–O12	1.788(6)
Ti1–O3	1.774(5)	Ti5–O13	2.024(6)
Ti1–O4	1.954(5)	Ti5–O21	1.960(4)
Ti1–O18	2.009(5)	Ti5–O23	1.868(5)
Ti1–O20	1.969(4)	Ti5–O24	1.809(5)
Ti1–N1	2.195(6)	Ti6–O13	1.995(6)
Ti2–O1	2.000(5)	Ti6–O14	1.764(6)
Ti2–O4	2.160(4)	Ti6–O15	1.793(6)
Ti2–O5	1.957(5)	Ti6–O16	1.963(4)
Ti2–O6	2.020(4)	Ti6–O21	2.199(5)
Ti2–O20	1.820(4)	Ti6–O22	2.074(5)
Ti2–O21	1.846(4)	Ti7–O16	2.084(5)
Ti3–O5	2.103(5)	Ti7–O17	1.791(6)
Ti3–O6	2.003(5)	Ti7–O18	2.035(4)
Ti3–O7	1.806(6)	Ti7–O19	1.755(7)
Ti3–O8	1.773(6)	Ti7–O20	2.086(5)
Ti3–O9	1.999(5)	Ti7–O22	1.971(5)
Ti3–O23	2.031(5)		
Ti4–O9	2.013(6)		
Ti4–O10	1.772(9)		
Ti4–O11	1.761(8)		
Ti4–O23	1.976(5)		
Ti4–O24	1.859(7)		

Table S3. Bond valence sum (BVS) calculations[a] for **Ti4**, **Ti5**, and **Ti7**.

Ti4								
Ti1 4.134			**Ti2 4.167**			**Ti3 4.170**		
Ti1–O4	1.942	0.709	Ti2–O2	1.937	0.719	Ti3–O1	1.968	0.661
Ti1–O6	1.942	0.709	Ti2–O5	1.934	0.725	Ti3–O7	1.937	0.719
Ti1–O12	2.194	0.359	Ti2–O11	2.201	0.352	Ti3–O10	2.202	0.351
Ti1–O13	1.753	1.182	Ti2–O13	1.899	0.797	Ti3–O15	1.763	1.151
Ti1–O14	1.900	0.795	Ti2–O16	1.753	1.182	Ti3–O16	1.867	0.869
Ti1–N2	2.265	0.379	Ti2–N3	2.253	0.391	Ti3–N1	2.228	0.419
Ti4 4.098								
Ti4–O3	1.939	0.715						
Ti4–O8	1.988	0.627						
Ti4–O9	2.199	0.354						
Ti4–O14	1.757	1.170						
Ti4–O15	1.886	0.825						
Ti4–N4	2.239	0.407						

Ti5								
Ti1 4.168			**Ti2 4.066**			**Ti3 4.321**		
Ti1–O2	2.052	0.527	Ti2–O2	2.076	0.494	Ti3–O7	2.023	0.570
Ti1–O3	1.937	0.719	Ti2–O4	1.984	0.633	Ti3–O8	1.756	1.173
Ti1–O10	1.920	0.753	Ti2–O5	1.935	0.723	Ti3–O9	1.960	0.676
Ti1–O13	1.754	1.179	Ti2–O14	1.920	0.753	Ti3–O15	2.236	0.321
Ti1–O14	2.020	0.575	Ti2–O15	1.815	1.000	Ti3–O16	2.108	0.453
Ti1–N3	2.231	0.415	Ti2–N1	2.191	0.463	Ti3–O18	1.770	1.129
Ti4 4.123			**Ti5 4.117**					
Ti4–O9	2.098	0.465	Ti5–O1	1.976	0.647			
Ti4–O11	1.943	0.708	Ti5–O6	1.915	0.763			
Ti4–O12	1.767	1.139	Ti5–O7	2.004	0.600			
Ti4–O14	1.965	0.667	Ti5–O15	1.978	0.644			
Ti4–O16	1.939	0.715	Ti5–O17	1.789	1.073			
Ti4–N4	2.219	0.429	Ti5–N2	2.254	0.390			

Ti7								
Ti1 4.238			**Ti2 4.162**			**Ti3 4.372**		
Ti1–O2	1.934	0.725	Ti2–O4	2.160	0.394	Ti3–O5	2.103	0.459
Ti1–O3	1.774	1.117	Ti2–O5	1.957	0.681	Ti3–O6	2.003	0.602
Ti1–O4	1.954	0.687	Ti2–O6	2.020	0.575	Ti3–O7	1.806	1.025
Ti1–O18	2.009	0.592	Ti2–O20	1.820	0.987	Ti3–O8	1.773	1.120
Ti1–O20	1.969	0.660	Ti2–O21	1.846	0.920	Ti3–O9	1.999	0.608
Ti1–N1	2.195	0.458	Ti2–O1	2.000	0.607	Ti3–O23	2.031	0.558
Ti4 4.401			**Ti5 4.203**			**Ti6 4.345**		
Ti4–O9	2.013	0.586	Ti5–O12	1.788	1.076	Ti6–O13	1.995	0.615
Ti4–O10	1.772	1.123	Ti5–O13	2.024	0.568	Ti6–O14	1.764	1.148
Ti4–O11	1.761	1.157	Ti5–O21	1.960	0.676	Ti6–O15	1.793	1.061
Ti4–O23	1.976	0.647	Ti5–O23	1.868	0.867	Ti6–O16	1.963	0.670
Ti4–O24	1.859	0.888	Ti5–O24	1.809	1.016	Ti6–O21	2.199	0.354
						Ti6–O22	2.074	0.497
Ti7 4.415								
Ti7–O16	2.084	0.483						
Ti7–O17	1.791	1.067						
Ti7–O18	2.035	0.552						
Ti7–O19	1.755	1.176						
Ti7–O20	2.086	0.481						
Ti7–O22	1.971	0.656						

[a] $V_i = \Sigma S_{ij} = \Sigma \exp[(r_1 - r_{ij})/B]$, where r_{ij} is the bond length between atoms i and j (with r_1 = 1.815 for Ti^{iv}-O, 1.906 for Ti^{iv}-N). The constant B is referred to as the "universal parameter" and is approximately equal to 0.37 Å. S_{ij} is the valence of a bond between atoms i and j, and V_i is the sum of all bond valences of the bonds formed by a given atom.