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Supporting Information

Assembly of Cyclic Ferrocene-Sensitized Titanium-Oxo Clusters with Excellent Photoelectrochemical Activity

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1. Experimental details

Materials, Syntheses and Characterization. All reagents were purchased commercially and not further purified when used. $Ti(O^{i}Pr)_4$, 1,1′-ferrocenedicarboxylic acid, dichloromethane, *n*-propanol, isonicotinic acid, and salicylichydroxamic acid were purchased from Aladdin Ltd. Powder X-ray diffraction (PXRD) data were obtained on a Rigaku SmartLab diffractometer. The diffuse-reflectance spectra for the cluster samples were obtained on a UV-4000 spectrophotometer. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB Xi+ XPS system with Al Kα X-ray radiation. Infrared spectra were recorded on an ALPHA II FT-IR spectrophotometer in the range of 400−4000 cm^{-1}. Thermogravimetric analysis (TGA) patterns were recorded on a TGAQ50 instrument in a N_2 atmosphere.

Photoelectrochemical measurements. All electrochemical measurements were carried out with a CHI660e electrochemical workstation via a conventional three-electrode system in a Na_2SO_4 (0.2 M) aqueous solution. The working electrode was indium-tin oxide (ITO) glass plates coated with a cluster-slurry, the counter electrode was a platinum foil, and the reference electrode was a saturated Ag/AgCl electrode. The Mott-Schottky plots were measured over an alternating current frequency of 1000 Hz. Electrochemical impedance spectra measurements were recorded over a frequency range of 100 kHz–0.1 Hz with alternating current amplitude of 10 mV at 0 V. A 300 W high-pressure xenon lamp with UV cut-off filter was used as a light source. Preparation of the working electrode: 5 mg cluster were dispersed in a solution of ethanol (1 mL) to generate homogeneous slurry. Subsequently, 200 μL of slurry was transferred and coated on ITO glass plates (1 cm^2) then dried at room temperature.

Single-crystal structure determinations. Crystallographic data were collected on a Rigaku XtaLAB Synergy X-ray single crystal diffractometer. The CCDC numbers of clusters **1** and **2** are 2164045 and 2164046, and the specific crystallographic information can be received from the Cambridge Crystallographic Data Centre. The structures are solved by the inherent phase method in the SHELXT program, and refined by the least square method in the SHELXL[1] program. Both programs are used coupling with OLEX2[2]. Crystallographic data for clusters **1** and **2** are summarized in Table S1 and S2.

Computational Details. All calculations were done using the *Gaussian* 09 program.[3] Geometry optimization calculations for these two clusters were performed by using the B3LYP DFT method on the basis of the crystal structures. The basis set used for the C, H, O and N atoms was 6-31G*, and the LANL2DZ pseudopotential basis set was employed for Ti and Fe atoms. Also, in order to save time, the terminal isopropyl groups of two clusters were replaced by methyl groups to simplify the complexity of the calculation.

2. Crystallographic details

Table S1. X-ray measurements and structure solution of clusters **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{144}H_{254}Fe_4O_{52}Ti_{12}\cdot 0.5(CH_2Cl_2)$	$C_{166}H_{278}Fe_2N_6O_{68}Ti_{18}\cdot 2(C_3H_7OH)$
Formula weight	3658.12	4540.01
Crystal system	Orthorhombic	Triclinic
Space group	Pbcn	P-1
a/Å	18.8704(10)	12.8214(4)
b/Å	25.6001(12)	20.1358(6)
c/Å	37.8336(19)	21.7220(5)
α/°	90	95.208(2)
β/°	90	96.328(2)
γ/°	90	96.811(2)
V	18276.8(16)	5503.7(3)
Z	4	1
ρcalc/g·cm^{-3}	1.330	1.370
μ(MoKα)/mm^{-1}	0.365	6.908
F(000)	7700.0	2376.0
Reflections collected/unique	92809/16735	56252/19247
Data/restraints/parameters	16735/240/1104	19247/108/1235
R_1/wR_2 (I>2σ(I))[a]	0.0857/0.2396	0.0585/0.1464
R_1/wR_2 (all data)[a]	0.1027/0.2528	0.0904/0.1620
GooF (all data)[b]	1.035	1.048

[a] $R_1=\Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR_2=\{\Sigma w[(Fo)^2-(Fc)^2]^2/\Sigma w[(Fo)^2]^2\}^{1/2}$

[b] $GooF=\{\Sigma w[(Fo)^2-(Fc)^2]^2/(n-p)\}^{1/2}$

Table S2. Some main bond length and bond angle information.

Some bond length information of $\mathbf{Ti_{12}Fcdc_4}$									
Ti1—O1	2.007 (4)	Ti5—O25	1.815	O24—C48	1.250 (7)	C31—C35	1.400	C64A—C65A	1.464
Ti1—O2	1.800 (4)	Ti6—O18	1.984	O25—C70	1.28 (2)	C32—C33	1.431	C64A—C66A	1.505
Ti1—O3	1.815 (5)	Ti6—O20	1.838	O25—C70A	1.550 (18)	C33—C34	1.423	C67—C68	1.44
Ti1—O8	1.984 (4)	Ti6—O22	1.789	O26—C64	1.60 (4)	C33—C48^{i}	1.485	C67—C69	1.55
Ti1—O9	2.053 (4)	Ti6—O23	2.050	O26—C64A	1.367 (15)	C34—C35	1.404	C67A—C68A	1.51
Ti1—O13	2.137 (4)	Ti6—O26	1.761	C1—C2	1.452 (13)	C36—C37	1.493	C67A—C69A	1.56
Ti2—O1	2.012 (4)	O1—C1	1.439	C1—C3	1.423 (11)	C37—C38	1.405	C70—C71	1.63
Ti2—O4	1.817 (4)	O2—C4	1.466	C4—C5	1.463 (18)	C37—C41	1.437	C70—C72	1.441
Ti2—O5	1.788 (4)	O3—C7	1.404	C4—C6	1.358 (18)	C38—C39	1.408	Fe1—C26	2.043
Ti2—O6	2.143 (4)	O4—C10	1.423	C7—C8	1.471 (15)	C39—C40	1.385	Fe1—C27	2.025
Ti2—O7	2.025 (4)	O5—C13	1.405	C7—C9	1.488 (13)	C40—C41	1.415	Fe1—C28	2.035
Ti2—O8	2.004 (4)	O6—C25	1.277	C10—C11	1.503 (11)	C42—C43	1.454	Fe1—C29	2.039
Ti3—O7	1.991 (4)	O7—C16	1.472	C10—C12	1.518 (11)	C43—C44	1.411	Fe1—C30	2.028
Ti3—O8	1.853 (4)	O9—C36	1.240	C13—C14	1.459 (12)	C43—C47	1.458	Fe1—C31	2.038
Ti3—O10	2.053 (4)	O10—C36	1.260	C13—C15	1.378 (13)	C44—C45	1.419	Fe1—C32	2.051
Ti3—O11	1.771 (5)	O11—C19	1.369	C16—C17	1.491 (12)	C45—C46	1.417	Fe1—C33	2.044
Ti3—O12	1.789 (5)	O12—C22	1.399	C16—C18	1.467 (13)	C49—C50	1.484	Fe1—C34	2.030
Ti4—O14	1.819 (6)	O13—C25	1.256	C19—C20	1.462 (17)	C49—C51	1.514	Fe1—C35	2.022
Ti4—O15	1.795 (5)	O14—C67	1.50	C19—C21	1.413 (15)	C52—C53	1.496	Fe2—C37	2.026
Ti4—O16	2.016 (5)	O14—C67A	1.366	C22—C23	1.514 (13)	C52—C54	1.485	Fe2—C38	2.039
Ti4—O17	2.141 (5)	O15—C49	1.405	C22—C24	1.426 (13)	C55—C56	1.516	Fe2—C39	2.038
Ti4—O18	2.040 (4)	O16—C52	1.453	C25—C26	1.468 (8)	C55—C57	1.411	Fe2—C40	2.032
Ti4—O20	2.018 (4)	O17—C42	1.277	C26—C27	1.423 (8)	C58—C59	1.450	Fe2—C41	2.032
Ti5—O16	2.010 (5)	O18—C55	1.432	C26—C30	1.453 (9)	C58—C60	1.483	Fe2—C43	2.035
Ti5—O19	1.815 (5)	O19—C61	1.434	C27—C28	1.402 (10)	C61—C62	1.508	Fe2—C44	2.036
Ti5—O20	1.996 (4)	O21—C42	1.271	C28—C29	1.418 (10)	C61—C63	1.409	Fe2—C45	2.043
Ti5—O21	2.109 (6)	O22—C58	1.406	C29—C30	1.419 (9)	C64—C65	1.470	Fe2—C46	2.046
Ti5—O24	2.045 (4)	O23—C48	1.263	C31—C32	1.404 (10)	C64—C66	1.513	Fe2—C47	2.031
Some bond length information of $\mathbf{Ti_{18}Fcdc_2}$									
Ti1—O2	1.798 (3)	Ti7—O7	2.204	O23—C32	1.253 (5)	C19—C45	1.494	C56—C64	1.472
Ti1—O9	1.966 (3)	Ti7—O21	1.777	O24—C64	1.270 (5)	C20—C67	1.472	C57—C59	1.386
Ti1—O15	2.004 (3)	Ti7—O22	2.031	O26—C12	1.454 (6)	C21—C48	1.377	C59—C63	1.401
Ti1—O16	2.049 (3)	Ti7—O26	2.058	O27—C71	1.447 (6)	C22—C70	1.511	C67—C78	1.466
Ti1—O23	2.154 (3)	Ti7—O31	1.878	O28—C38	1.392 (7)	C23—C47	1.414	C71—C73	1.443
Ti1—O33	1.806 (3)	Ti8—O14	1.881	O29—C52	1.411 (7)	C23—C56	1.426	C81—C82	1.422
Ti2—O8	1.757 (4)	Ti8—O25	1.819	O30—C30	1.432 (8)	C24—C25	1.421	C81A—C82A	1.514
Ti2—O9	1.871 (3)	Ti8—O30	1.774	O32—C45	1.457 (5)	C24—C29	1.421	C82—C83	1.414
Ti2—O12	1.778 (3)	Ti8—O31	1.932	O33—C33	1.423 (6)	C25—C41	1.415	C82A—C83A	1.452
Ti2—O13	1.990 (3)	Ti8—N3	2.134	O34—C16	1.262 (5)	C26—C55	1.482	Fe1—C23	2.032
Ti2—O34	2.059 (3)	Ti9—O4	1.773	N1—C48	1.342 (5)	C27—C37	1.416	Fe1—C24	2.020
Ti3—O9	2.016 (3)	Ti9—O6	1.867	N1—C80	1.346 (5)	C27—C56	1.418	Fe1—C25	2.043
Ti3—O13	2.013 (4)	Ti9—O10	1.983	N2—C72	1.302 (6)	C28—C51	1.494	Fe1—C27	2.050
Ti3—O15	2.039 (4)	Ti9—O22	2.008	N3—C31	1.351 (6)	C29—C35	1.399	Fe1—C29	2.020
Ti3—O19	2.180 (3)	Ti9—O26	2.029	C1—C21	1.390 (6)	C30—C68	1.391	Fe1—C35	2.061
Ti3—O28	1.779 (3)	Ti9—N2	2.172	C1—C32	1.491 (6)	C30—C76	1.529	Fe1—C37	2.052
Ti3—O29	1.801 (3)	O2—C51	1.426	C1—C40	1.381 (6)	C31—C57	1.442	Fe1—C41	2.063

Ti4—O1	1.986 (3)	O3—C64	1.264	C2—C36	1.482 (12)	C33—C69	1.487	Fe1—C47	2.041
Ti4—O5	1.775 (3)	O4—C2	1.419	C2—C74	1.499 (12)	C34—C52	1.496	Fe1—C56	2.039
Ti4—O17	1.803 (3)	O6—C49	1.348	C3—C33	1.507 (8)	C35—C41	1.402		
Ti4—O24	2.043 (3)	O7—N2	1.400	C4—C52	1.475 (10)	C37—C47	1.426		
Ti4—O32	1.994 (3)	O8—C82	1.410	C5—C6	1.378 (8)	C38—C62	1.396		
Ti4—N1^{i}	2.322 (3)	O8—C82A	1.43	C5—C57	1.414 (7)	C39—C43	1.376		
Ti5—O1	1.965 (3)	O10—C31	1.292	C6—C42	1.368 (9)	C39—C49	1.393		
Ti5—O3	2.052 (3)	O11—C72	1.307	C7—C55	1.504 (9)	C39—C72	1.465		
Ti5—O20	1.786 (3)	O12—C61	1.424	C8—C13	1.414 (10)	C40—C80	1.375		
Ti5—O25	1.855 (3)	O13—C22	1.461	C9—C75	1.443 (10)	C42—C63	1.367		
Ti5—O27	2.033 (3)	O14—C59	1.334	C10—C38	1.399 (12)	C43—C77	1.382		
Ti5—O31	2.139 (3)	O15—C75	1.449	C11—C13	1.454 (9)	C44—C61	1.492		
Ti6—O1	1.890 (3)	O16—C16	1.248	C12—C58	1.497 (10)	C45—C53	1.522		
Ti6—O7	2.020 (3)	O17—C13	1.388	C12—C66	1.472 (11)	C46—C65	1.367		
Ti6—O11	1.993 (3)	O18—C67	1.418	C14—C61	1.485 (10)	C46—C77	1.352		
Ti6—O18	1.803 (3)	O19—C32	1.255	C15—C22	1.531 (10)	C49—C65	1.412		
Ti6—O27	1.993 (3)	O20—C55	1.387	C16—C24	1.472 (6)	C50—C75	1.510		
Ti6—O32	2.052 (3)	O21—C54	1.426	C17—C54	1.514 (9)	C51—C79	1.483		
Ti7—O5	1.848 (3)	O22—N3	1.379	C18—C71	1.449 (9)	C54—C60	1.481		

Some bond angle information of **Ti$_{12}$Fcdc$_4$**

O1—Ti1—O9	162.19	C13—O5—Ti2	163.5 (5)	C31—C35—C34	110.2	C27—Fe1—C34	107.7
O1—Ti1—O13	87.75	C25—O6—Ti2	129.9 (4)	C34—C35—Fe1	70.0 (4)	C28—Fe1—C26	68.5
O2—Ti1—O1	101.1 (2)	Ti3—O7—Ti2	100.13 (16)	O9—C36—O10	126.3	C28—Fe1—C29	40.7
O2—Ti1—O3	97.4 (2)	C16—O7—Ti2	128.5 (4)	O9—C36—C37	118.6	C28—Fe1—C31	157.8
O2—Ti1—O8	167.6 (2)	C16—O7—Ti3	129.8 (4)	O10—C36—C37	115.2	C28—Fe1—C32	123.2
O2—Ti1—O9	94.5 (2)	Ti1—O8—Ti2	103.62 (19)	C36—C37—Fe2	124.0	C28—Fe1—C33	108.5
O2—Ti1—O13	85.0 (2)	Ti3—O8—Ti1	141.9 (2)	C38—C37—Fe2	70.3 (3)	C29—Fe1—C26	69.0
O3—Ti1—O1	93.94	Ti3—O8—Ti2	105.89 (18)	C38—C37—C36	127.3	C29—Fe1—C32	107.5
O3—Ti1—O8	94.86	C36—O9—Ti1	136.2 (4)	C38—C37—C41	108.5	C29—Fe1—C33	123.8
O3—Ti1—O9	92.4 (2)	C36—O10—Ti3	136.3 (4)	C41—C37—Fe2	69.5 (3)	C30—Fe1—C26	41.8
O3—Ti1—O13	176.7 (2)	C19—O11—Ti3	157.8 (7)	C41—C37—C36	124.2	C30—Fe1—C28	68.9
O8—Ti1—O1	76.60	C22—O12—Ti3	140.3 (6)	C37—C38—Fe2	69.3 (3)	C30—Fe1—C29	40.8
O8—Ti1—O9	86.32	C25—O13—Ti1	128.8 (4)	C37—C38—C39	107.6	C30—Fe1—C31	105.6
O8—Ti1—O13	82.74	C67—O14—Ti4	135.2 (12)	C39—C38—Fe2	69.7 (4)	C30—Fe1—C32	121.9
O9—Ti1—O13	85.11	C67A—O14—Ti4	142.6 (11)	C38—C39—Fe2	69.8 (4)	C30—Fe1—C33	159.1
O1—Ti2—O6	83.66	C49—O15—Ti4	149.5 (5)	C40—C39—Fe2	69.9 (4)	C30—Fe1—C34	157.6
O1—Ti2—O7	148.68	Ti5—O16—Ti4	102.40 (19)	C40—C39—C38	108.6	C31—Fe1—C26	122.7
O4—Ti2—O1	98.53	C52—O16—Ti4	123.7 (4)	C39—C40—Fe2	70.3 (4)	C31—Fe1—C29	121.3
O4—Ti2—O6	177.5 (2)	C52—O16—Ti5	129.9 (5)	C39—C40—C41	109.5	C31—Fe1—C32	40.1
O4—Ti2—O7	94.87	C42—O17—Ti4	130.5 (5)	C41—C40—Fe2	69.6 (4)	C31—Fe1—C33	68.5
O4—Ti2—O8	94.75	Ti6—O18—Ti4	100.20 (18)	C37—C41—Fe2	69.0 (3)	C33—Fe1—C32	40.9
O5—Ti2—O1	105.1 (2)	C55—O18—Ti4	125.6 (5)	C40—C41—Fe2	69.6 (4)	C34—Fe1—C26	121.6
O5—Ti2—O4	95.76	C55—O18—Ti6	133.6 (5)	C40—C41—C37	105.8	C34—Fe1—C28	124.3
O5—Ti2—O6	84.84	C61—O19—Ti5	141.8 (6)	O21—C42—C43	117.9	C34—Fe1—C29	160.6
O5—Ti2—O7	101.5 (2)	Ti5—O20—Ti4	102.84 (18)	C42—C43—Fe2	122.8	C34—Fe1—C31	68.8
O5—Ti2—O8	169.12	Ti6—O20—Ti4	106.3 (2)	C42—C43—C47	127.4	C34—Fe1—C32	68.6
O7—Ti2—O6	82.60	Ti6—O20—Ti5	142.8 (2)	C44—C43—Fe2	69.8 (4)	C34—Fe1—C33	40.9
O8—Ti2—O1	76.04	C42—O21—Ti5	128.1 (5)	C44—C43—C42	126.2	C35—Fe1—C26	107.5
O8—Ti2—O6	84.54	C58—O22—Ti6	142.4 (6)	C44—C43—C47	106.3	C35—Fe1—C27	124.3

O8—Ti2—O7	74.74	C48—O23—Ti6	135.6 (4)	C47—C43—Fe2	68.9 (4)	C35—Fe1—C28	160.8
O7—Ti3—O10	164.89	C48—O24—Ti5	136.9 (4)	C43—C44—Fe2	69.7 (4)	C35—Fe1—C29	157.2
O8—Ti3—O7	78.93	C70—O25—Ti5	142.5 (11)	C43—C44—C45	108.2	C35—Fe1—C30	121.4
O8—Ti3—O10	86.69	C70A—O25—Ti5	155.2 (14)	C45—C44—Fe2	69.9 (4)	C35—Fe1—C31	40.3
O11—Ti3—O7	100.1 (2)	C64—O26—Ti6	147.0 (14)	C44—C45—Fe2	69.4 (4)	C35—Fe1—C32	67.3
O11—Ti3—O8	121.0 (2)	C64A—O26—Ti6	160.1 (8)	C46—C45—Fe2	69.8 (4)	C35—Fe1—C33	67.8
O11—Ti3—O10	91.2 (2)	O1—C1—C2	109.2 (7)	C46—C45—C44	108.3	C35—Fe1—C34	40.5
O11—Ti3—O12	114.4 (3)	C3—C1—O1	115.2 (7)	C45—C46—Fe2	69.6 (4)	C37—Fe2—C38	40.4
O12—Ti3—O7	96.0 (2)	C3—C1—C2	113.6 (9)	C47—C46—Fe2	69.7 (4)	C37—Fe2—C39	67.9
O12—Ti3—O8	124.5 (2)	O3—C7—C8	108.9 (10)	C47—C46—C45	108.3	C37—Fe2—C40	68.2
O12—Ti3—O10	88.27	O3—C7—C9	110.2 (8)	C43—C47—Fe2	69.1 (4)	C37—Fe2—C41	41.5
O14—Ti4—O16	96.7 (2)	C8—C7—C9	114.5 (10)	C46—C47—Fe2	70.8 (4)	C37—Fe2—C43	159.1
O14—Ti4—O17	178.1 (2)	O5—C13—C14	112.5 (7)	C46—C47—C43	108.8	C37—Fe2—C44	159.7
O14—Ti4—O18	95.0 (2)	C15—C13—O5	114.7 (8)	O23—C48—C33^{i}	117.2	C37—Fe2—C45	124.6
O14—Ti4—O20	95.8 (2)	C15—C13—C14	112.7 (10)	O24—C48—O23	126.7	C37—Fe2—C46	109.3
O15—Ti4—O14	96.7 (2)	O7—C16—C17	109.3 (7)	O24—C48—C33^{i}	116.1	C37—Fe2—C47	123.3
O15—Ti4—O16	104.6 (2)	C18—C16—O7	111.8 (7)	O15—C49—C50	108.9	C38—Fe2—C45	160.1
O15—Ti4—O17	84.7 (2)	C18—C16—C17	112.6 (8)	O15—C49—C51	108.8	C38—Fe2—C46	123.6
O15—Ti4—O18	102.4 (2)	O11—C19—C20	108.9 (10)	C50—C49—C51	112.6	C39—Fe2—C38	40.4
O15—Ti4—O20	167.1 (2)	O11—C19—C21	114.7 (10)	O16—C52—C53	119.3	C39—Fe2—C45	158.6
O16—Ti4—O17	84.2 (2)	C21—C19—C20	120.2 (14)	O16—C52—C54	107.9	C39—Fe2—C46	158.6
O16—Ti4—O18	148.97	O6—C25—C26	117.1 (5)	C54—C52—C53	110.6	C40—Fe2—C38	67.7
O16—Ti4—O20	76.44	O13—C25—O6	124.9 (6)	O18—C55—C56	109.4	C40—Fe2—C39	39.8
O18—Ti4—O17	83.45	O13—C25—C26	118.0 (5)	C57—C55—O18	113.8	C40—Fe2—C41	40.7
O20—Ti4—O17	82.68	C25—C26—Fe1	123.3 (5)	C57—C55—C56	116.5	C40—Fe2—C43	120.6
O20—Ti4—O18	73.83	C27—C26—Fe1	68.9 (4)	O22—C58—C59	110.9	C40—Fe2—C44	106.8
O16—Ti5—O21	89.8 (2)	C27—C26—C25	127.3 (6)	O22—C58—C60	111.3	C40—Fe2—C45	124.0
O16—Ti5—O24	162.24	C27—C26—C30	107.1 (6)	O19—C61—C62	108.5	C40—Fe2—C46	160.9
O19—Ti5—Ti4	138.24	C30—C26—Fe1	68.5 (4)	C63—C61—O19	112.6	C41—Fe2—C38	69.0
O19—Ti5—O16	103.6 (2)	C30—C26—C25	125.3 (6)	C63—C61—C62	113.9	C41—Fe2—C39	68.3
O19—Ti5—O20	166.2 (3)	C26—C27—Fe1	70.2 (4)	C65—C64—O26	101 (3)	C41—Fe2—C43	156.7
O19—Ti5—O21	84.0 (2)	C28—C27—Fe1	70.2 (4)	C65—C64—C66	114 (3)	C41—Fe2—C44	121.9
O19—Ti5—O24	92.0 (2)	C28—C27—C26	108.6 (6)	C66—C64—O26	101 (3)	C41—Fe2—C45	108.4
O19—Ti5—O25	97.6 (3)	C27—C28—Fe1	69.4 (4)	O26—C64A—C65A	114.8	C41—Fe2—C46	124.7
O20—Ti5—O16	77.09	C27—C28—C29	108.7 (6)	O26—C64A—C66A	105.7	C43—Fe2—C38	122.0
O20—Ti5—O21	82.15	C29—C28—Fe1	69.8 (4)	C65A—C64A—C66A	119.8	C43—Fe2—C39	105.8
O20—Ti5—O24	85.71	C28—C29—Fe1	69.5 (4)	O14—C67—C69	100 (2)	C43—Fe2—C44	40.6
O24—Ti5—O21	83.49	C28—C29—C30	108.3 (6)	C68—C67—O14	106 (2)	C43—Fe2—C45	68.4
O25—Ti5—O16	94.7 (2)	C30—C29—Fe1	69.2 (4)	C68—C67—C69	121 (3)	C43—Fe2—C46	68.8
O25—Ti5—O20	96.1 (2)	C26—C30—Fe1	69.7 (4)	O14—C67A—C68A	116.6	C44—Fe2—C38	157.7
O25—Ti5—O21	174.8 (2)	C29—C30—Fe1	70.0 (4)	O14—C67A—C69A	109.0	C44—Fe2—C39	121.7
O25—Ti5—O24	91.4 (2)	C29—C30—C26	107.2 (6)	C68A—C67A—C69A	111 (2)	C44—Fe2—C45	40.7
O18—Ti6—O23	165.68	C32—C31—Fe1	70.4 (4)	O25—C70—C71	101.6	C44—Fe2—C46	68.6
O20—Ti6—O18	79.15	C35—C31—Fe1	69.2 (4)	O25—C70—C72	128 (2)	C45—Fe2—C46	40.5
O20—Ti6—O23	86.94	C35—C31—C32	107.3 (7)	C72—C70—C71	106 (2)	C47—Fe2—C38	107.8
O22—Ti6—O18	96.6 (2)	C31—C32—Fe1	69.4 (4)	C71A—C70A—O25	119 (3)	C47—Fe2—C39	122.8
O22—Ti6—O20	124.3 (2)	C31—C32—C33	108.3 (7)	C71A—C70A—C72A	106.2	C47—Fe2—C40	158.0
O22—Ti6—O23	88.4 (2)	C33—C32—Fe1	69.3 (4)	C72A—C70A—O25	99.1	C47—Fe2—C41	159.9
O26—Ti6—O18	99.1 (2)	C32—C33—Fe1	69.8 (4)	Cl1—C73—Cl2	114 (2)	C47—Fe2—C43	42.0

O26—Ti6—O20	121.5 (3)	C32—C33—C48^{i}	125.4 (6)	C26—Fe1—C32	158.9	C47—Fe2—C44	68.8
O26—Ti6—O22	114.1 (3)	C34—C33—Fe1	69.0 (4)	C26—Fe1—C33	158.2	C47—Fe2—C45	67.5
O26—Ti6—O23	91.0 (2)	C34—C33—C32	107.5 (6)	C27—Fe1—C26	40.9 (2)	C47—Fe2—C46	39.5
Ti1—O1—Ti2	102.50	C34—C33—C48^{i}	127.0 (7)	C27—Fe1—C28	40.4 (3)		
C1—O1—Ti1	120.7 (4)	C48^{i}—C33—Fe1	123.7 (5)	C27—Fe1—C29	68.6 (3)		
C1—O1—Ti2	134.1 (4)	C33—C34—Fe1	70.1 (4)	C27—Fe1—C30	69.6 (3)		
C4—O2—Ti1	139.7 (6)	C35—C34—Fe1	69.4 (5)	C27—Fe1—C31	159.8		
C7—O3—Ti1	139.3 (5)	C35—C34—C33	106.8 (8)	C27—Fe1—C32	158.9		
C10—O4—Ti2	139.0 (4)	C31—C35—Fe1	70.5 (5)	C27—Fe1—C33	122.8		
Some bond angle information of **$Ti_{18}Fcdc_2$**							
O2—Ti1—O9	97.81	O21—Ti7—O5	99.29 (15)	C45—O32—Ti6	124.5	C23—C56—Fe1	69.2
O2—Ti1—O15	97.23	O21—Ti7—O7	176.99 (14)	C33—O33—Ti1	144.6	C23—C56—C64	125.2
O2—Ti1—O16	93.44	O21—Ti7—O22	97.65 (15)	C16—O34—Ti2	136.2	C27—C56—Fe1	70.1
O2—Ti1—O23	176.63	O21—Ti7—O26	98.45 (16)	C48—N1—Ti4^{i}	118.9	C27—C56—C23	108.2
O2—Ti1—O33	97.38	O21—Ti7—O31	97.53 (15)	C48—N1—C80	117.4	C27—C56—C64	126.5
O9—Ti1—O15	77.71	O22—Ti7—O7	79.51 (12)	C80—N1—Ti4^{i}	123.7	C64—C56—Fe1	126.0
O9—Ti1—O16	86.49	O22—Ti7—O26	69.33 (13)	O7—N2—Ti9	115.4	C5—C57—C31	118.6
O9—Ti1—O23	81.67	O26—Ti7—O7	81.56 (12)	C72—N2—Ti9	134.1	C59—C57—C5	119.2
O15—Ti1—O16	161.97	O31—Ti7—O7	81.24 (12)	C72—N2—O7	110.4	C59—C57—C31	122.1
O15—Ti1—O23	85.93	O31—Ti7—O22	84.71 (13)	O22—N3—Ti8	117.0	O14—C59—C57	121.9
O16—Ti1—O23	83.21	O31—Ti7—O26	151.03 (14)	C31—N3—Ti8	132.6	O14—C59—C63	118.6
O33—Ti1—O9	164.80	O14—Ti8—O31	149.67 (15)	C31—N3—O22	109.0	C57—C59—C63	119.4
O33—Ti1—O15	100.84	O14—Ti8—N3	79.05 (16)	C21—C1—C32	120.2	O12—C61—C14	110.3
O33—Ti1—O16	92.12	O25—Ti8—O14	96.41 (16)	C40—C1—C21	117.8	O12—C61—C44	109.3
O33—Ti1—O23	83.14	O25—Ti8—O31	82.88 (14)	C40—C1—C32	122.0	C14—C61—C44	112.0
O8—Ti2—O9	125.80	O25—Ti8—N3	136.04 (16)	O4—C2—C36	106.7	C42—C63—C59	120.4
O8—Ti2—O12	113.0 (2)	O30—Ti8—O14	103.81 (18)	O4—C2—C74	110.4	O3—C64—O24	124.8
O8—Ti2—O13	98.77	O30—Ti8—O25	110.80 (19)	C36—C2—C74	116.8	O3—C64—C56	118.2
O8—Ti2—O34	89.09	O30—Ti8—O31	104.73 (17)	C6—C5—C57	119.8	O24—C64—C56	117.0
O9—Ti2—O13	78.22	O30—Ti8—N3	112.73 (19)	C42—C6—C5	120.4	C46—C65—C49	119.4
O9—Ti2—O34	86.09	O31—Ti8—N3	80.68 (14)	O26—C12—C58	109.2	O18—C67—C20	110.5
O12—Ti2—O9	120.95	O4—Ti9—O6	97.03 (18)	O26—C12—C66	111.0	O18—C67—C78	110.6
O12—Ti2—O13	98.84	O4—Ti9—O10	99.63 (18)	C66—C12—C58	113.2	C78—C67—C20	109.2
O12—Ti2—O34	90.50	O4—Ti9—O22	102.68 (17)	O17—C13—C8	115.3	O27—C71—C18	109.8
O13—Ti2—O34	164.24	O4—Ti9—O26	95.09 (17)	O17—C13—C11	113.0	C73—C71—O27	113.0
O9—Ti3—O15	75.80	O4—Ti9—N2	168.90 (18)	C29—C24—C16	125.2	C73—C71—C18	115.9
O9—Ti3—O19	82.41	O6—Ti9—O10	95.29 (16)	C24—C25—Fe1	68.7 (2)	O11—C72—C39	120.5
O13—Ti3—O9	74.46	O6—Ti9—O22	158.83 (15)	C41—C25—Fe1	70.6 (3)	N2—C72—O11	118.9
O13—Ti3—O15	148.17	O6—Ti9—O26	115.75 (16)	C41—C25—C24	107.4	N2—C72—C39	120.5
O13—Ti3—O19	83.67	O6—Ti9—N2	78.60 (14)	C37—C27—Fe1	69.9 (3)	O15—C75—C50	110.1
O15—Ti3—O19	81.43	O10—Ti9—O22	74.01 (14)	C37—C27—C56	107.9	C9—C75—O15	110.8
O28—Ti3—O9	96.83	O10—Ti9—O26	143.62 (14)	C56—C27—Fe1	69.3 (2)	C9—C75—C50	117.1
O28—Ti3—O13	97.92	O10—Ti9—N2	90.97 (14)	C24—C29—Fe1	69.4 (2)	C46—C77—C43	119.4
O28—Ti3—O15	96.60	O22—Ti9—O26	70.36 (13)	C35—C29—Fe1	71.5 (3)	N1—C80—C40	122.7
O28—Ti3—O19	178.01	O22—Ti9—N2	83.30 (13)	C35—C29—C24	109.1	O8—C82—C81	117.8
O28—Ti3—O29	97.47	O26—Ti9—N2	77.97 (13)	O30—C30—C76	108.1	O8—C82—C83	114.0
O29—Ti3—O9	165.25	Ti5—O1—Ti4	138.22 (15)	C68—C30—O30	113.2	C83—C82—C81	127.8
O29—Ti3—O13	99.99	Ti6—O1—Ti4	106.77 (13)	C68—C30—C76	113.8	O8—C82A—C81A	100
O29—Ti3—O15	106.00	Ti6—O1—Ti5	106.91 (13)	O10—C31—N3	117.4	O8—C82A—C83A	111.9

O29—Ti3—O19	83.40	C51—O2—Ti1	138.6 (3)	O10—C31—C57	123.4	C23—Fe1—C25	151.96
O1—Ti4—O24	87.15	C64—O3—Ti5	138.3 (3)	N3—C31—C57	119.1	C23—Fe1—C27	68.73
O1—Ti4—O32	73.86	C2—O4—Ti9	153.4 (5)	O19—C32—C1	116.0	C23—Fe1—C35	126.3
O1—Ti4—N1^{i}	83.13	Ti4—O5—Ti7	137.26 (17)	O23—C32—O19	127.2	C23—Fe1—C37	68.49
O5—Ti4—O1	94.23	C49—O6—Ti9	142.2 (3)	O23—C32—C1	116.8	C23—Fe1—C41	164.6
O5—Ti4—O17	99.95	Ti6—O7—Ti7	128.74 (14)	O33—C33—C3	108.9	C23—Fe1—C47	40.64
O5—Ti4—O24	91.61	N2—O7—Ti6	117.6 (2)	O33—C33—C69	110.0	C23—Fe1—C56	41.01
O5—Ti4—O32	99.27	N2—O7—Ti7	112.8 (2)	C69—C33—C3	111.9	C24—Fe1—C23	116.60
O5—Ti4—N1^{i}	170.99	C82—O8—Ti2	149.1 (7)	C29—C35—Fe1	68.4 (3)	C24—Fe1—C25	40.92
O17—Ti4—O1	165.53	C82A—O8—Ti2	160.2 (10)	C29—C35—C41	107.5	C24—Fe1—C27	162.49
O17—Ti4—O24	95.28	Ti1—O9—Ti3	104.17 (13)	C41—C35—Fe1	70.2 (3)	C24—Fe1—C29	41.18
O17—Ti4—O32	100.79	Ti2—O9—Ti1	141.56 (16)	C27—C37—Fe1	69.7 (3)	C24—Fe1—C35	68.52
O17—Ti4—N1^{i}	83.27	Ti2—O9—Ti3	105.08 (14)	C27—C37—C47	108.1	C24—Fe1—C37	123.87
O24—Ti4—N1^{i}	79.68	C31—O10—Ti9	119.4 (3)	C47—C37—Fe1	69.2 (3)	C24—Fe1—C41	68.09
O32—Ti4—O24	158.67	C72—O11—Ti6	118.2 (3)	O28—C38—C10	114.1	C24—Fe1—C47	104.07
O1—Ti5—O3	87.60	C61—O12—Ti2	146.2 (3)	O28—C38—C62	117.5	C24—Fe1—C56	153.16
O1—Ti5—O27	74.70	Ti2—O13—Ti3	100.90 (14)	C62—C38—C10	125.1	C25—Fe1—C27	127.31
O1—Ti5—O31	85.82	C22—O13—Ti2	130.7 (4)	C43—C39—C49	119.1	C25—Fe1—C35	67.9
O3—Ti5—O31	82.75	C22—O13—Ti3	128.2 (3)	C43—C39—C72	120.1	C25—Fe1—C37	107.6
O20—Ti5—O1	99.00	C59—O14—Ti8	142.1 (3)	C49—C39—C72	120.6	C25—Fe1—C41	40.32
O20—Ti5—O3	88.35	Ti1—O15—Ti3	101.96 (13)	C80—C40—C1	119.8	C27—Fe1—C35	123.21
O20—Ti5—O25	100.59	C75—O15—Ti1	125.1 (4)	C25—C41—Fe1	69.1 (3)	C27—Fe1—C37	40.39
O20—Ti5—O27	98.33	C75—O15—Ti3	132.5 (3)	C35—C41—Fe1	70.0 (3)	C27—Fe1—C41	111.52
O20—Ti5—O31	169.71	C16—O16—Ti1	137.1 (3)	C35—C41—C25	109.0	C29—Fe1—C23	106.02
O25—Ti5—O1	157.93	C13—O17—Ti4	157.1 (4)	C63—C42—C6	120.7	C29—Fe1—C25	68.4
O25—Ti5—O3	102.97	C67—O18—Ti6	148.0 (3)	C39—C43—C77	121.3	C29—Fe1—C27	156.06
O25—Ti5—O27	92.45	C32—O19—Ti3	129.0 (3)	O32—C45—C19	109.4	C29—Fe1—C35	40.08
O25—Ti5—O31	76.54	C55—O20—Ti5	145.9 (3)	O32—C45—C53	109.4	C29—Fe1—C37	161.34
O27—Ti5—O3	161.82	C54—O21—Ti7	142.4 (4)	C19—C45—C53	113.2	C29—Fe1—C41	67.2
O27—Ti5—O31	91.69	Ti9—O22—Ti7	106.50 (15)	C77—C46—C65	121.6	C29—Fe1—C47	123.64
O1—Ti6—O7	88.51	N3—O22—Ti7	119.9 (2)	C23—C47—Fe1	69.3 (3)	C29—Fe1—C56	120.24
O1—Ti6—O11	160.22	N3—O22—Ti9	119.1 (3)	C23—C47—C37	108.0	C35—Fe1—C41	39.7
O1—Ti6—O27	77.27	C32—O23—Ti1	127.4 (3)	C37—C47—Fe1	70.0 (3)	C37—Fe1—C35	157.0
O1—Ti6—O32	74.55	C64—O24—Ti4	137.5 (3)	N1—C48—C21	123.0	C37—Fe1—C41	122.4
O7—Ti6—O32	90.47	Ti8—O25—Ti5	106.86 (17)	O6—C49—C39	122.4	C47—Fe1—C25	118.1
O11—Ti6—O7	74.52	Ti9—O26—Ti7	104.75 (15)	O6—C49—C65	118.5	C47—Fe1—C27	68.45
O11—Ti6—O27	110.81	C12—O26—Ti7	123.2 (3)	C39—C49—C65	119.1	C47—Fe1—C35	161.8
O11—Ti6—O32	95.10	C12—O26—Ti9	130.5 (4)	O2—C51—C28	109.7	C47—Fe1—C37	40.8
O18—Ti6—O1	109.96	Ti6—O27—Ti5	100.58 (12)	O2—C51—C79	109.2	C47—Fe1—C41	154.7
O18—Ti6—O7	161.51	C71—O27—Ti5	126.3 (3)	C79—C51—C28	112.7	C56—Fe1—C25	165.44
O18—Ti6—O11	87.42	C71—O27—Ti6	133.2 (3)	O29—C52—C4	107.7	C56—Fe1—C27	40.57
O18—Ti6—O27	97.23	C38—O28—Ti3	151.1 (5)	O29—C52—C34	111.7	C56—Fe1—C35	110.22
O18—Ti6—O32	95.14	C52—O29—Ti3	149.2 (4)	C4—C52—C34	112.8	C56—Fe1—C37	68.10
O27—Ti6—O7	85.78	C30—O30—Ti8	148.8 (6)	O21—C54—C17	107.6	C56—Fe1—C41	129.17
O27—Ti6—O32	151.65	Ti7—O31—Ti5	134.10 (15)	O21—C54—C60	109.6	C56—Fe1—C47	68.44
O5—Ti7—O7	83.69	Ti7—O31—Ti8	129.23 (16)	C60—C54—C17	115.1		
O5—Ti7—O22	159.52	Ti8—O31—Ti5	92.79 (13)	O20—C55—C7	108.9		
O5—Ti7—O26	96.76	Ti4—O32—Ti6	100.55 (12)	O20—C55—C26	109.6		
O5—Ti7—O31	104.30	C45—O32—Ti4	133.6 (3)	C26—C55—C7	114.2		

3. The synthesis of clusters

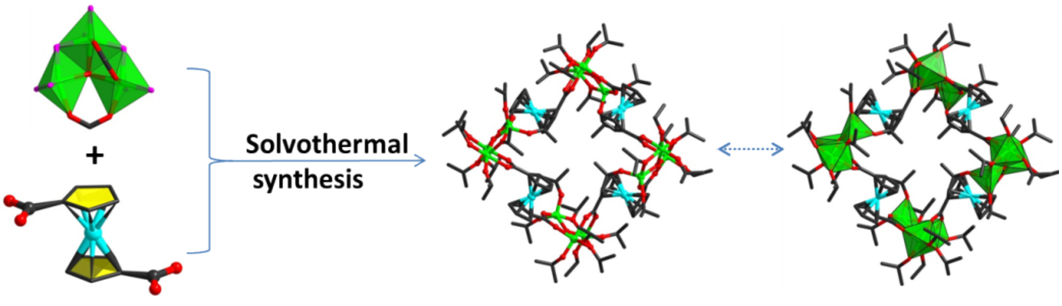

Figure S1. The assembly of the cluster $\mathbf{Ti_{12}Fcdc_4}$.

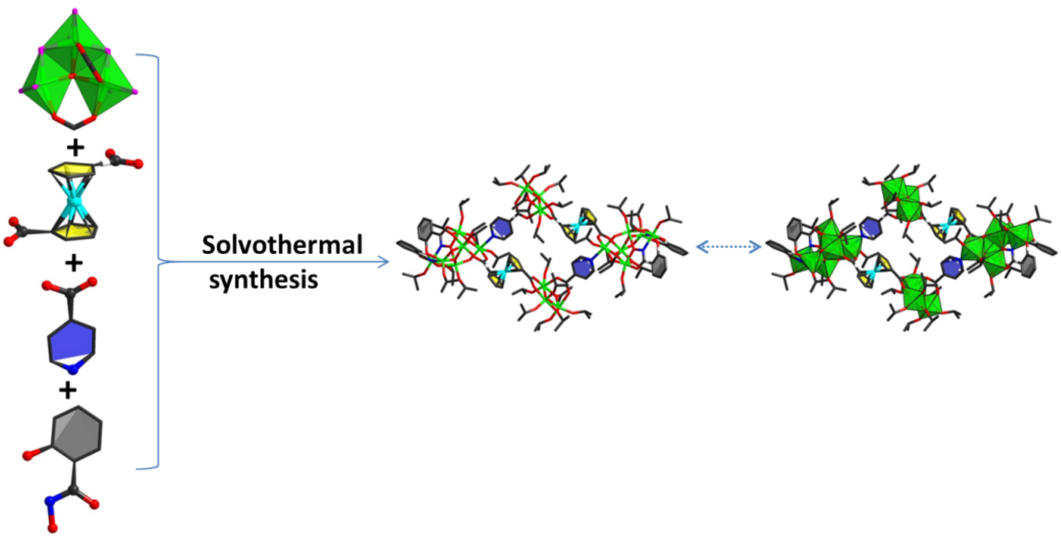

Figure S2. The assembly of the cluster $\mathbf{Ti_{18}Fcdc_2}$.

4. The structure of clusters

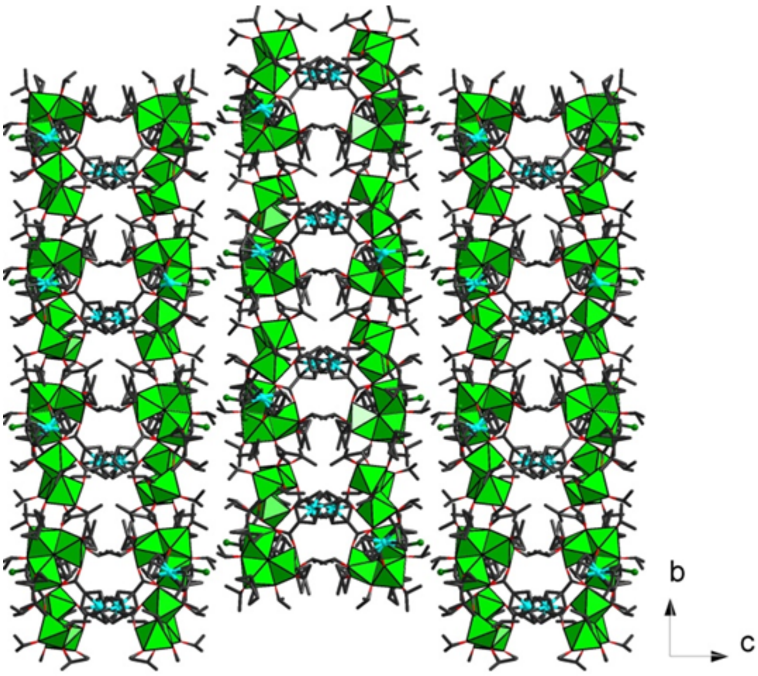

Figure S3. Packing structure of cluster **$Ti_{12}Fcdc_4$** along *a*-axis.

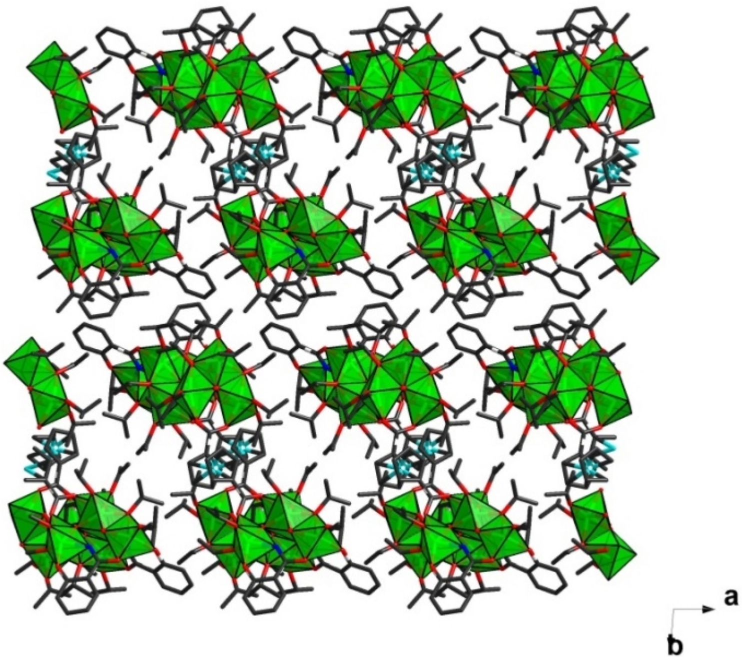

Figure S4. Packing structure of cluster **$Ti_{18}Fcdc_2$** along *c*-axis.

5. Powder X-ray diffraction (PXRD)

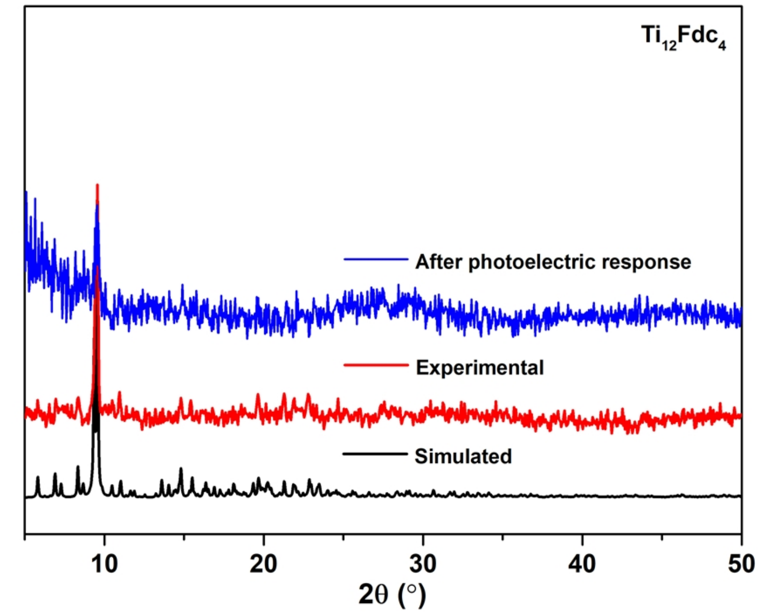

Figure S5. The XRD patterns of cluster **$Ti_{12}Fcdc_4$.**

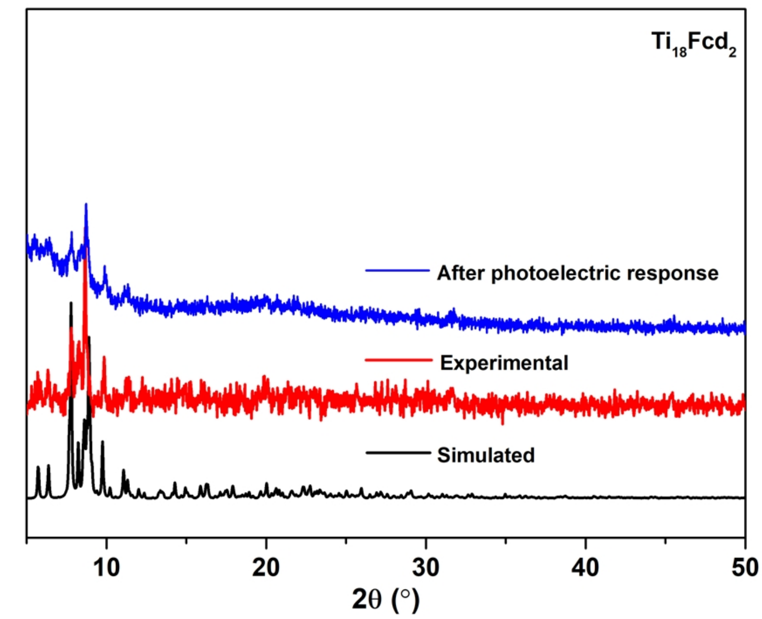

Figure S6. The XRD patterns of cluster **$Ti_{18}Fcdc_2$.**

6. Thermogravimetric analysis (TGA)

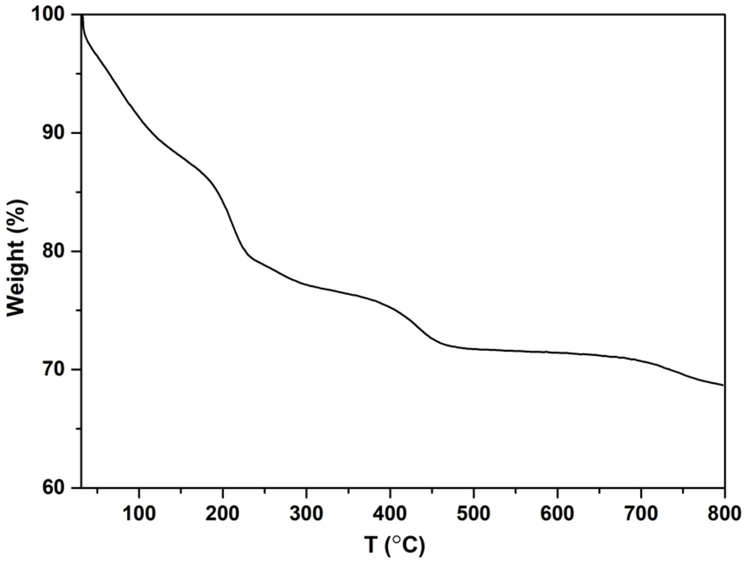

Figure S7. Thermal decomposition curve of cluster $\mathbf{Ti_{12}Fcdc_4}$.

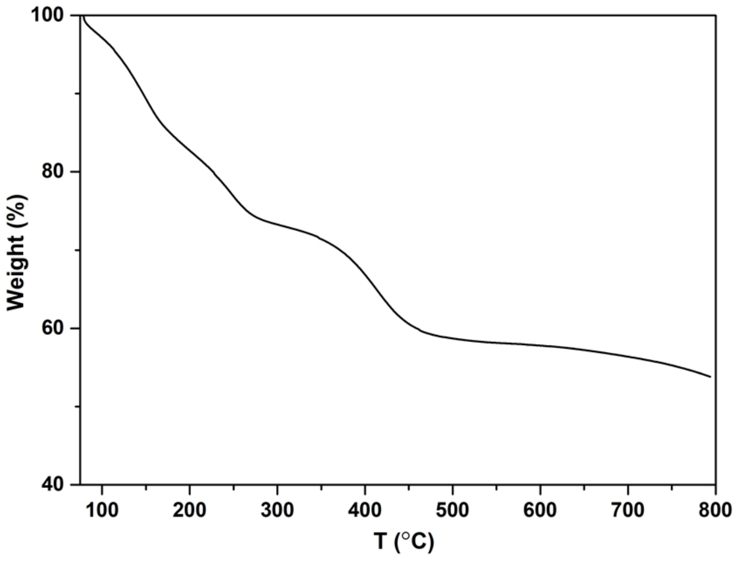

Figure S8. Thermal decomposition curve of cluster $\mathbf{Ti_{18}Fcdc_2}$.

7. Infrared spectroscopy (IR)

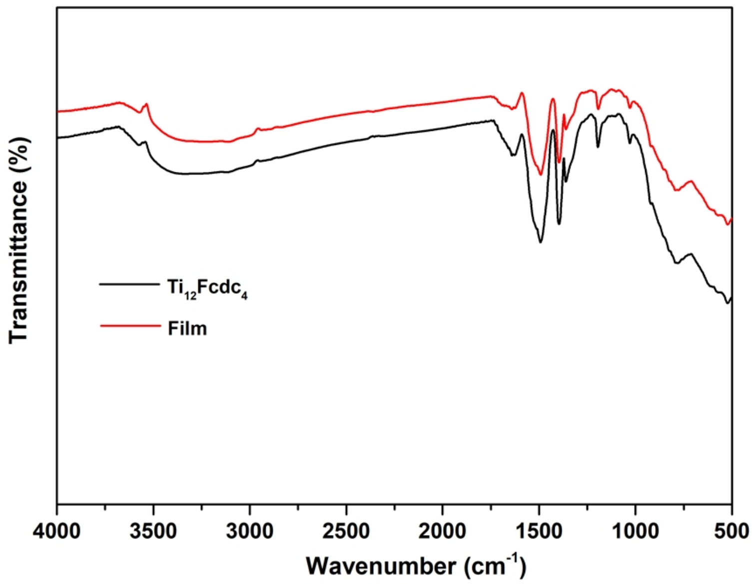

Figure S9. IR spectra of cluster **$Ti_{12}Fcdc_4$**.

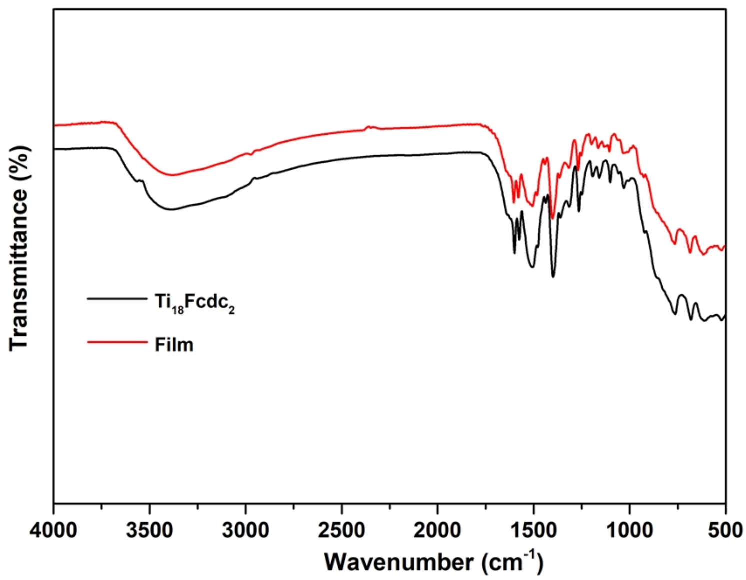

Figure S10. IR spectra of cluster **$Ti_{18}Fcdc_2$**.

8. X-ray photoelectron spectroscopy (XPS)

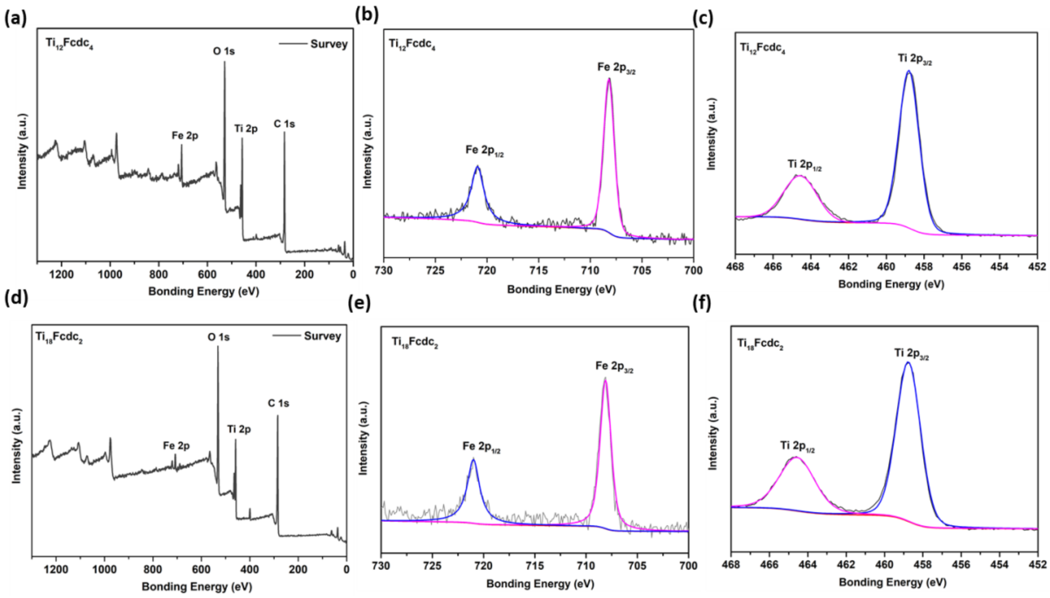

Figure S11. The full-scan and high-resolution XPS spectra of $\mathbf{Ti_{12}Fcdc_4}$ (a, b, c) and $\mathbf{Ti_{18}Fcdc_2}$ (d, e, f) crystals.

9. Electrochemical impedance spectroscopy (EIS)

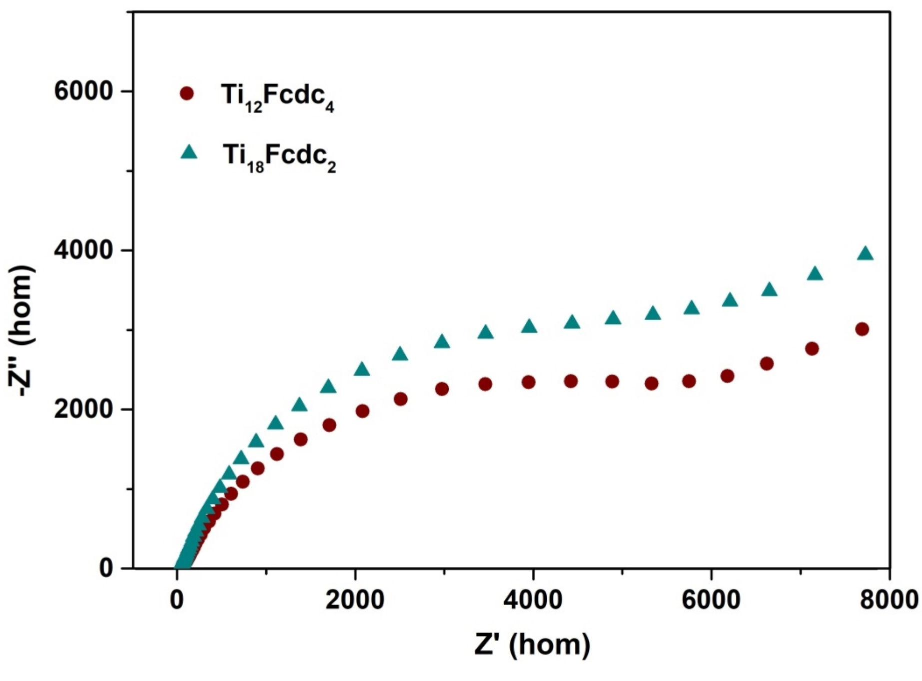

Figure S12. The Nyquist plots of clusters $\mathbf{Ti_{12}Fcdc_4}$ and $\mathbf{Ti_{18}Fcdc_2}$.

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