Electronic Supplementary Information (ESI)

Carboxylate-functionalized polyoxo-titanium clusters for adsorption/solar photocatalytic synergistic tetracycline degradation

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Materials and physical measurements

The crystal structure was measured by single crystal diffractometer (XRD, Bruker D8 Venture) with Mo Kα at 70 kv radiation (λ = 0.71073 Å). The infrared spectrum data was recorded in KBr pallets on Fourier transform infrared spectroscopy (FT-IR, Bruker VERTEX) in the range of 400–4000 cm^{-1}. The purity of the samples were investigated by Powder X-ray diffractometer (PXRD, Bruker D8 Advance) with Cu Kα radiation at room temperature. The thermal stability of the samples were measured by Thermogravimetric analyzer (TGA, Perkin-Elmer 7 thermal analyzer) in flowing N_2 with a slow heating rate of 10 °C min^{-1}. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) was recorded by instrument with an Al Kα micro-focused X-ray source. The ultraviolet-visible diffuse reflectance spectrum of the samples were obtained by an ultraviolet-visible spectrophotometer (DSR, Hitachi UH4150). The photocurrent and impedance of the samples were performed by an electrochemical workstation (CHI 760E). The photoluminescence spectra of the samples were recorded on a fluorescence spectrophotometer (PL, Hitachi f-7000). The Brunauer-Emmett-Teller (BET, Autosorb-2, Quantachrome) surface areas were measured and calculated by nitrogen adsorption-desorption isotherms using an adsorption analyzer.

Adsorption and photocatalytic performance

The compounds (10 mg) were dispersed in TC (50 mg/L, 50 mL) aqueous solution, respectively. Dark adsorption was carried out in the photocatalytic reactor at the speed of 800 rpm. 2 mL of sample was taken out every 20 min, centrifuged at 8000 rpm and filtered with a 0.22 μm PTFE syringe filter. The light absorption of the solution was measured at 357 nm using a UV-vis spectrophotometer.

Adsorption rate(%) $= 100 \times (C_0–C_t)/C_0$, where C_0 and C_t are the initial and retained concentrations of TC, respectively.[1]

The photocatalytic reaction was continued after dark for 3 h when reached adsorption-desorption equilibrium. The light source was a 500 W mercury lamp with a cutoff filter (>420 nm). 2 mL of sample was taken out and measured by UV-vis spectrophotometer.

Degradation efficiency(%) $= 100 \times (C_0–C_t)/C_0$, where C_0 and C_t are the initial and

degradation concentrations of TC, respectively.[1]

Photoelectrical performance of the compounds

A standard three-electrode system was used to test photocurrent in Na_2SO_4 solution (0.2 M) on an electrochemical workstation (CHI 760E). A xenon lamp (300 W) equipped with a cutoff filter (>420 nm) served as the light source. The compound-coated electrode, $Hg/HgCl_2$ electrode and Pt electrode were used as the working, reference and counter electrode, respectively.

Photodegradation mechanism test ESR

The free radicals generated during the photocatalytic reaction were detected by Bruker A300 electron spin resonator with a light source of 500 W mercury lamp (>420 nm). 10 mg of the sample was added to 1 mL methanol solution at room temperature, and 10 μL DMPO was used as the trapping agent for detection $\bullet O_2^-$. 50 μL of TEMPO was dissolved in 5 mL water, and then 10 mg catalyst sample was placed into 1 mL trapping agent solution for h^+ detection. The free radical signal in the reaction was detected at 0, 5 and 10 min respectively.

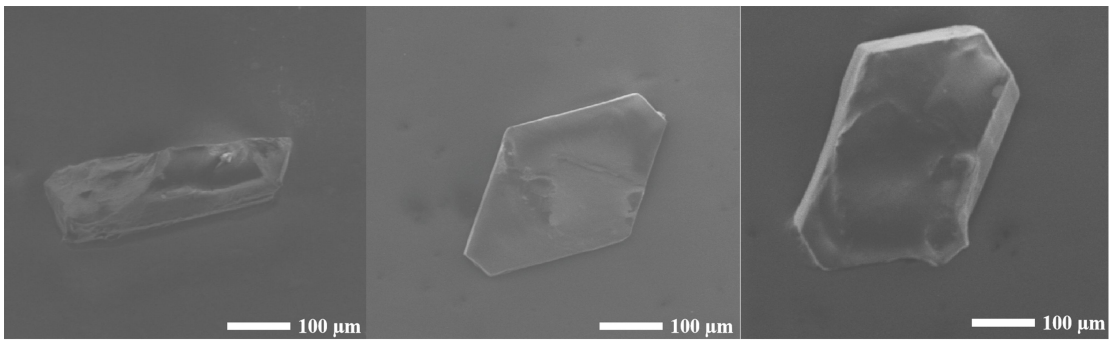

Figure S1. SEM of Ti_6-BIDC, Ti_6-CMBA and Ti_6-MA.

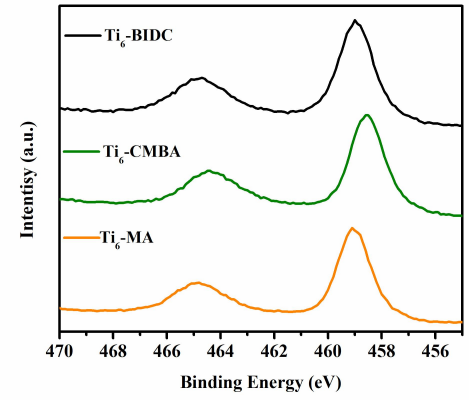

Figure S2. XPS spectra of Ti_6-BIDC, Ti_6-CMBA and Ti_6-MA Ti 2p.

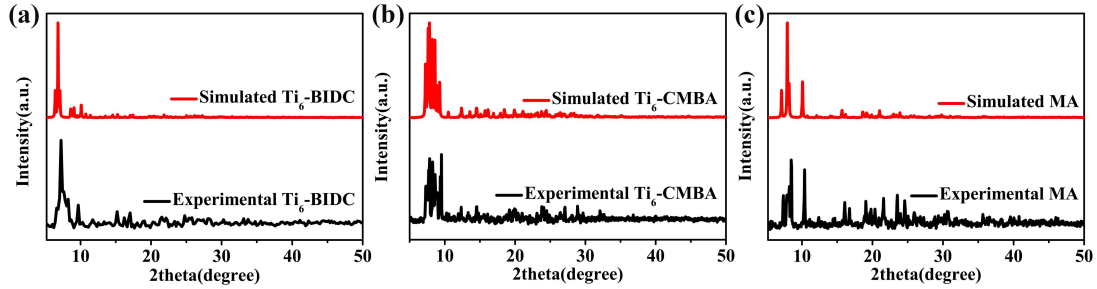

Figure S3. The as-synthesized and simulated PXRD patterns for (a) Ti_6-BIDC, (b) Ti_6-CMBA and (c) Ti_6-MA.

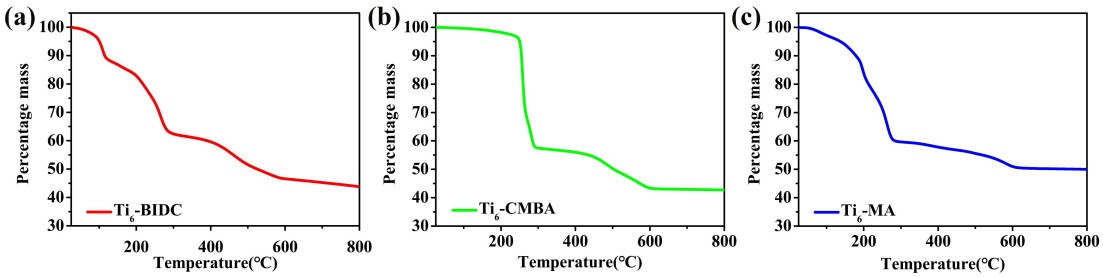

Figure S4. Thermal gravimetrical analysis of (a) Ti_6-BIDC, (b) Ti_6-CMBA and (c) Ti_6-MA.

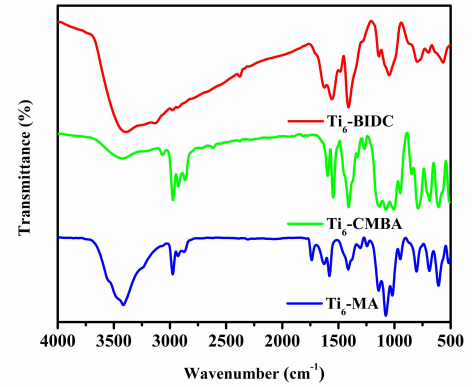

Figure S5. FT-IR spectrum of Ti_6-BIDC, Ti_6-CMBA and Ti_6-MA.

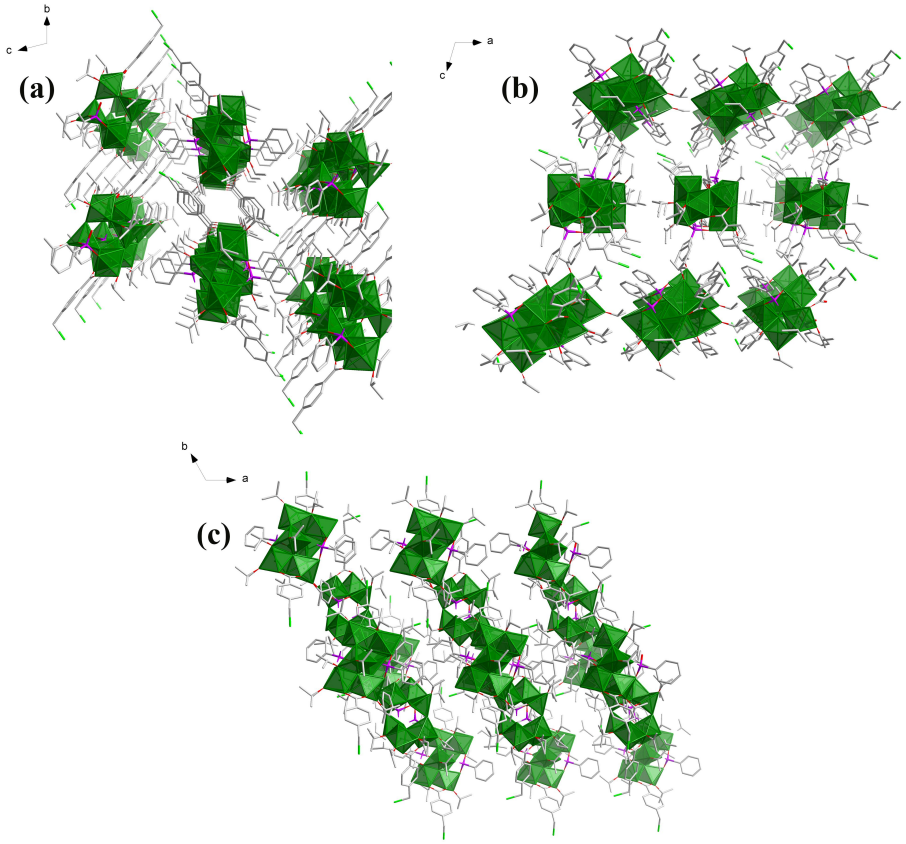

Figure S6. Molecular packing of compounds Ti_6-CMBA.

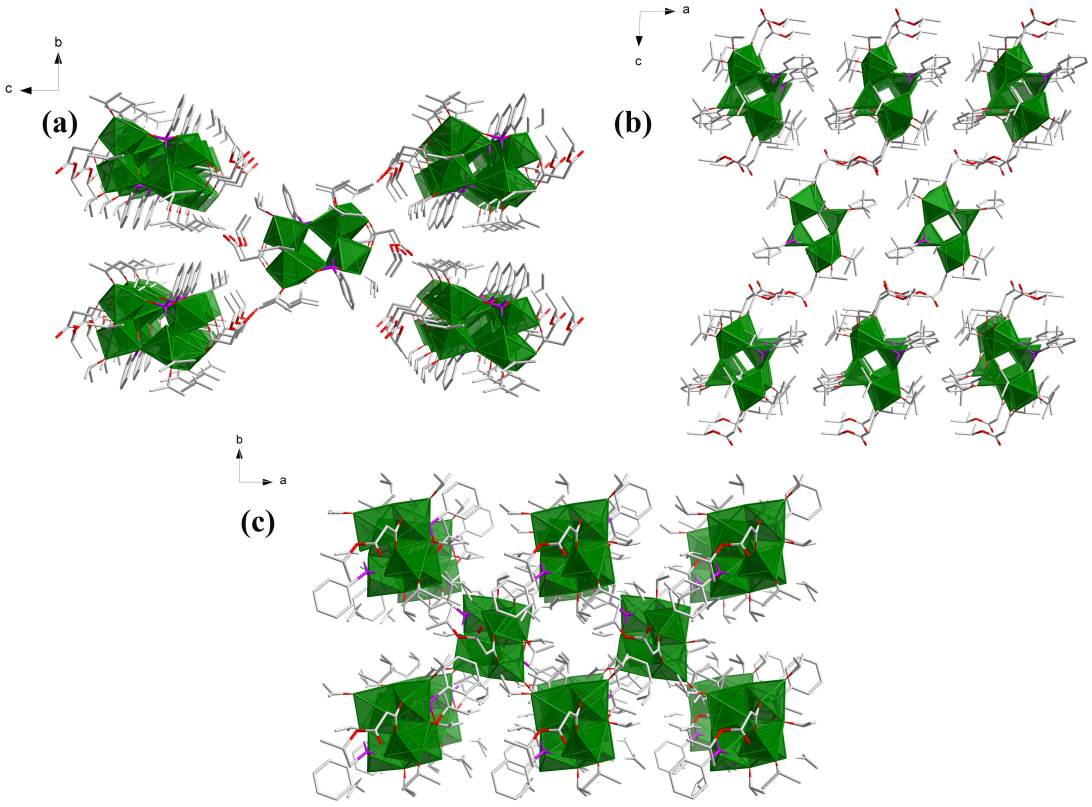

Figure S7. Molecular packing of compounds Ti_6-MA.

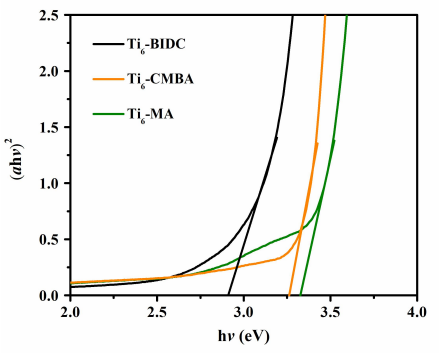

Figure S8. Curve $[F(R)hv]^{1/2}$ versus photon energy of Ti_6-BIDC, Ti_6-CMBA and Ti_6-MA.

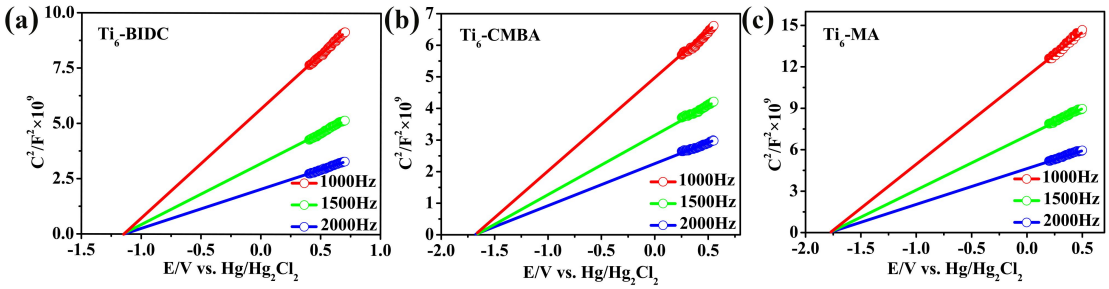

Figure S9. Mott–Schottky of (a) Ti_6-BIDC, (b) Ti_6-CMBA and (c) Ti_6-MA .

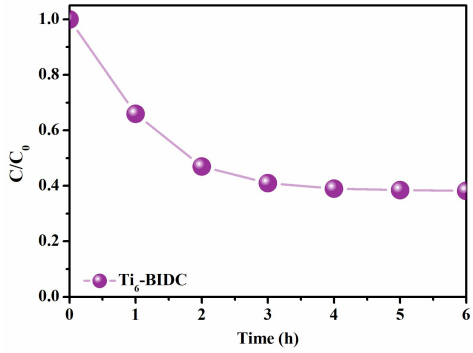

Figure S10. Adsorption equilibrium curve of Ti_6-BIDC.

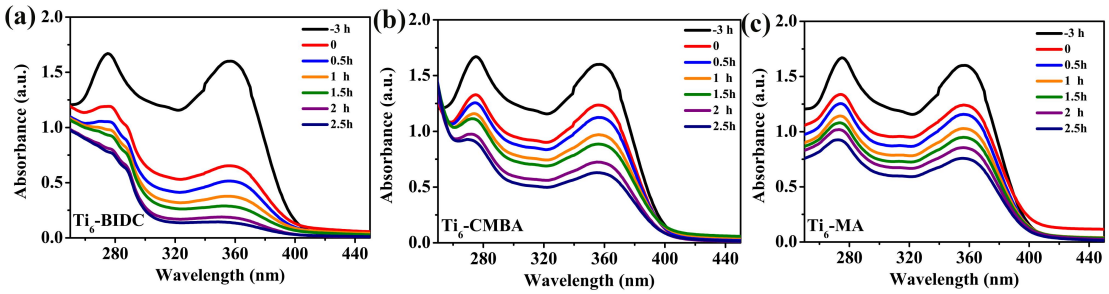

Figure S11. UV-vis spectrum of (a) Ti_6-BIDC, (b) Ti_6-CMBA and (c) Ti_6-MA.

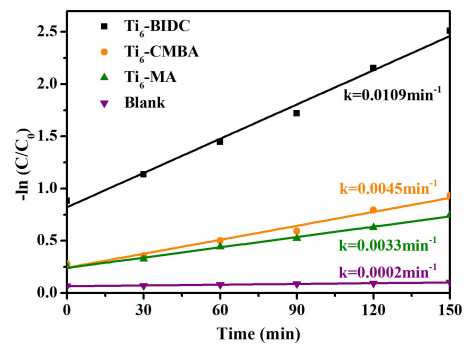

Figure S12. The kinetics plots of photocatalytic TC over Ti_6-BIDC, Ti_6-CMBA and Ti_6-MA towards TC (50 mg/L).

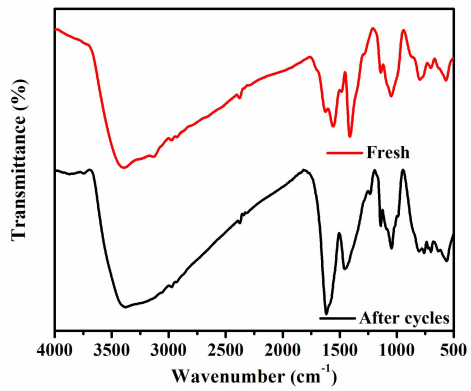

Figure S13. IR spectrum of Ti_6-BIDC clusters before cycles and after cycles.

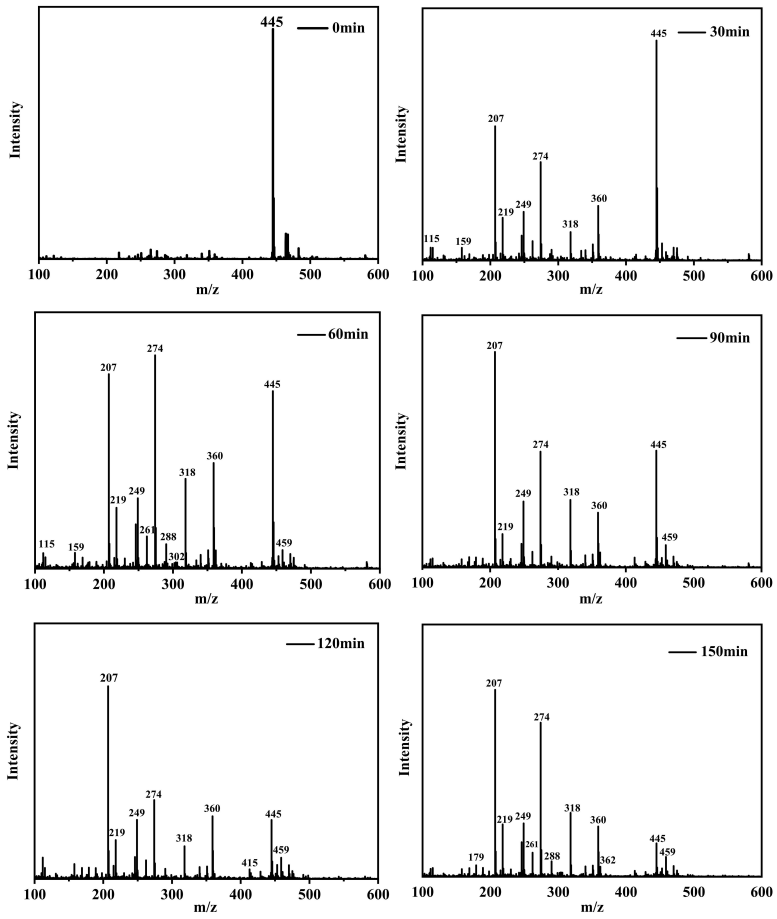

Figure S14. LC-MS mass spectra of TC photodegradation after 0, 30, 60, 90, 120 and 150 min, respectively.

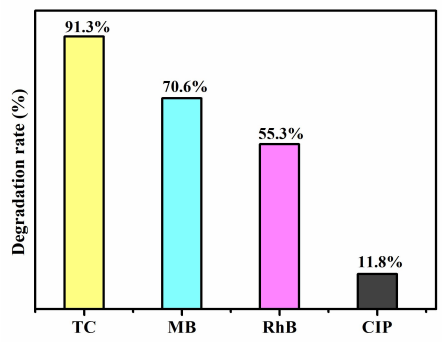

Figure S15. Photocatalytic degradation of MB, RhB, CIP pollutants.

Table S1 Crystallographic Data and Structure Refinements for Ti_6-BIDC, Ti_6-CMBA and Ti_6-MA.

	1	2	3
Formula	$C_{75}H_{128}N_4O_{33}P_2Ti_6$	$C_{59.5}H_{96}O_{24.5}P_2Cl_2Ti_6$	$C_{54}H_{98}O_{28}P_2Ti_6$
Formula weight($g \cdot mol^{-1}$)	1963.15	1623.6	1544.66

Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a(Å)	13.346(3)	13.5725(4)	12.3094(11)
b(Å)	13.772(4)	14.3640(4)	12.5953(8)
c(Å)	14.419(4)	23.7811(7)	25.115(2)
α(deg)	85.210(8)	97.3311(9)	90
β(deg)	80.905(8)	100.9082(9)	93.121(3)
g(deg)	76.396(8)	117.1734(9)	90
V(Å^3)	2540.7(11)	3926.6(2)	3888.0(5)
Z	1	2	2
*D*c(g·cm^{-3})	1.283	1.373	1.319
μ(mm^{-1})	0.554	0.758	0.698
F(000)	1032	1690	1616
GOF on F^2	1.055	1.090	1.018
R_1, wR_2 ($I >= 2\sigma(I)$)	0.0957, 0.1992,	0.0707, 0.1688	0.0624, 0.1625
R_1, wR_2 (all data)	0.1522, 0.2188	0.1024, 0.1925	0.1268, 0.1933

Table S2 Some main Bond length information.

Some main bond length information of Ti_6-BIDC					
Bond	Length	Bond	Length	Bond	Length
P1- O1	1.5249(43)	Ti1- O14	2.0474(50)	Ti2- O11	2.1183(52)
P1- O3	1.5300(47)	Ti1- O4	2.1493(49)	Ti3- O13	1.7511(49)
P1- O2	1.5315(41)	Ti2- O9	1.7597(43)	Ti3- O3	1.9328(45)
P1- C1	1.7820(73)	Ti2- O8	1.8284(45)	Ti3- O12	1.9733(45)
Ti1- O10	1.7715(50)	Ti2- O2	1.9455(41)	Ti3- O14	1.9812(42)
Ti1- O9	1.8671(48)	Ti2- O12	2.0366(42)	Ti3- O8	2.0221(43)
Ti1- O1	1.9735(45)	Ti2- O6	2.0639(53)	Ti3- O5	2.0468(55)
Ti1- O8	2.0113(40)				
Some main bond length information of Ti_6-CMBA					
Ti1- O8	1.7947(46)	Ti3- O7	1.8971(29)	Ti6- O24	1.7920(68)
Ti1- O6	1.8576(35)	Ti3- O2	1.9541(48)	Ti6- O18	1.8725(32)

Ti1- O1	1.9622(35)	Ti3- O11	2.0213(41)	Ti6- O14	1.9404(42)
Ti1- O7	1.9869(38)	Ti4- O18	1.7660(47)	Ti6- O19	1.9795(49)
Ti1- O9	2.0073(41)	Ti4- O20	1.7931(40)	Ti6- O23	2.0274(44)
Ti1- O4	2.1514(40)	Ti4- O19	1.9161(45)	Ti6- O17	2.1434(33)
Ti2- O10	1.7552(38)	Ti4- O13	1.9632(43)	P1- O2	1.5203(47)
Ti2- O3	1.9474(45)	Ti4- O21	2.0325(49)	P1- O3	1.5215(40)
Ti2- O11	1.9605(34)	Ti5- O22	1.7696(55)	P1- O1	1.5239(30)
Ti2- O9	1.9867(45)	Ti5- O15	1.9438(40)	P1- C1	1.7855(62)
Ti2- O7	1.9968(39)	Ti5- O21	1.9622(55)	P2- O13	1.5164(43)
Ti2- O5	2.0771(47)	Ti5- O23	1.9664(59)	P2- O15	1.5213(40)
Ti3- O6	1.7692(30)	Ti5- O19	1.9798(40)	P2- O14	1.5247(49)
Ti3- O12	1.7985(41)	Ti5- O16	2.0836(40)	P2- C30	1.7873(58)
Some main bond length information of Ti_6-MA					
P1- O3	1.5126(26)	Ti1- O14	1.9792(28)	Ti2- O14	1.9800(28)
P1- O1	1.5264(35)	Ti1- O9	2.0282(34)	Ti2- O5	2.0776(28)
P1- O2	1.5270(29)	Ti1- O4	2.1564(30)	Ti3- O13	1.7443(25)
P1- C1	1.7837(52)	Ti2- O10	1.7528(38)	Ti3- O12	1.7828(42)
Ti1- O8	1.7735(29)	Ti2- O3	1.9368(28)	Ti3- O14	1.9044(27)
Ti1- O13	1.8644(29)	Ti2- O11	1.9648(35)	Ti3- O2	1.9795(31)
Ti1- O1	1.9568(36)	Ti2- O9	1.9750(31)	Ti3- O11	2.0369(32)

Table S3 Some main bond Angle information.

Some main bond angle of Ti_6-BIDC					
O1- P1- O3	111.2(3)	O8- Ti2- O2	92.49(19)	O14- Ti3- O8	75.26(18)
O1- P1- O2	113.0(3)	O9- Ti2- O12	96.4(2)	O13- Ti3- O5	87.2(2)
O3- P1- O2	110.7(3)	O8- Ti2- O12	78.41(18)	O3- Ti3- O5	177.4(2)
O1- P1- C1	109.6(3)	O2- Ti2- O12	167.3(2)	O12- Ti3- O5	87.3(2)
O3- P1- C1	106.3(3)	O9- Ti2- O6	166.8(2)	O14- Ti3- O5	87.7(2)
O2- P1- C1	105.6(3)	O8- Ti2- O6	88.9(2)	O8- Ti3- O5	85.75(19)
O10- Ti1- O9	97.2(2)	O2- Ti2- O6	84.62(19)	O13- Ti3- Ti2	143.81(18)
O10- Ti1- O1	100.1(2)	O12- Ti2- O6	86.39(19)	O3- Ti3- Ti2	92.76(15)
O9- Ti1- O1	94.52(19)	O9- Ti2- O11	90.2(2)	O12- Ti3- Ti2	40.64(12)
O10- Ti1- O8	164.2(2)	O8- Ti2- O11	163.8(2)	O14- Ti3- Ti2	110.04(14)

O9- Ti1- O8	96.49(19)	O2- Ti2- O11	93.39(19)	O8- Ti3- Ti2	34.87(12)
O1- Ti1- O8	86.62(18)	O12- Ti2- O11	93.22(19)	O5- Ti3- Ti2	84.80(14)
O10- Ti1- O14	97.6(2)	O6- Ti2- O11	76.7(2)	O13- Ti3- Ti1	140.44(19)
O9- Ti1- O14	92.1(2)	O9- Ti2- Ti3	104.24(16)	O3- Ti3- Ti1	101.28(14)
O1- Ti1- O14	160.13(18)	O8- Ti2- Ti3	39.21(13)	O12- Ti3- Ti1	112.12(13)
O8- Ti1- O14	74.01(17)	O2- Ti2- Ti3	130.94(14)	O14- Ti3- Ti1	38.60(13)
O10- Ti1- O4	84.9(2)	O12- Ti2- Ti3	39.20(13)	O8- Ti3- Ti1	37.81(12)
O9- Ti1- O4	177.68(18)	O6- Ti2- Ti3	86.13(14)	O5- Ti3- Ti1	78.72(13)
O1- Ti1- O4	86.06(19)	O11- Ti2- Ti3	130.71(15)	Ti2- Ti3- Ti1	71.87(4)
O8- Ti1- O4	81.30(18)	O13- Ti3- O3	94.3(2)	P1- O1- Ti1	136.2(3)
O14- Ti1- O4	86.62(19)	O13- Ti3- O12	103.8(2)	P1- O2- Ti2	133.7(3)
O10- Ti1- Ti3	130.26(17)	O3- Ti3- O12	90.3(2)	P1- O3- Ti3	150.1(3)
O9- Ti1- Ti3	102.33(14)	O13- Ti3- O14	104.8(2)	Ti2- O8- Ti1	146.1(2)
O1- Ti1- Ti3	123.04(13)	O3- Ti3- O14	93.8(2)	Ti2- O8- Ti3	105.9(2)
O8- Ti1- Ti3	38.04(12)	O12- Ti3- O14	150.63(19)	Ti1- O8- Ti3	104.15(19)
O14- Ti1- Ti3	37.10(13)	O13- Ti3- O8	172.9(2)	Ti2- O9- Ti1	148.3(3)
O4- Ti1- Ti3	75.50(12)	O3- Ti3- O8	92.70(19)	Ti3- O12- Ti2	100.15(18)
O9- Ti2- O8	104.3(2)	O12- Ti3- O8	75.50(17)	Ti3- O14- Ti1	104.3(2)
O9- Ti2- O2	94.3(2)				
Some main Bond Angles of Ti_6-CMBA					
O8- Ti1- O6	97.21(15)	O7- Ti3- O11	76.22(14)	O14- Ti6- O23	162.85(17)
O8- Ti1- O1	94.40(15)	O2- Ti3- O11	158.54(14)	O19- Ti6- O23	75.47(15)
O6- Ti1- O1	94.04(14)	O6- Ti3- Ti2	111.95(11)	O24- Ti6- O17	82.65(19)
O8- Ti1- O7	163.70(14)	O12- Ti3- Ti2	116.29(15)	O18- Ti6- O17	176.88(17)
O6- Ti1- O7	98.67(13)	O7- Ti3- Ti2	38.25(9)	O14- Ti6- O17	88.82(16)
O1- Ti1- O7	88.13(13)	O2- Ti3- Ti2	124.64(10)	O19- Ti6- O17	80.99(16)
O8- Ti1- O9	100.22(15)	O11- Ti3- Ti2	38.05(10)	O23- Ti6- O17	84.65(16)
O6- Ti1- O9	91.65(14)	O6- Ti3- Ti1	21.19(10)	O24- Ti6- Ti5	133.28(15)
O1- Ti1- O9	163.51(14)	O12- Ti3- Ti1	132.69(15)	O18- Ti6- Ti5	101.05(12)
O7- Ti1- O9	75.71(14)	O7- Ti3- Ti1	90.69(9)	O14- Ti6- Ti5	124.98(12)
O8- Ti1- O4	82.96(14)	O2- Ti3- Ti1	95.33(10)	O19- Ti6- Ti5	37.98(10)
O6- Ti1- O4	178.37(15)	O11- Ti3- Ti1	99.88(10)	O23- Ti6- Ti5	37.95(12)

O1- Ti1- O4	87.55(14)	Ti2- Ti3- Ti1	98.58(3)	O17- Ti6- Ti5	76.39(12)
O7- Ti1- O4	81.06(12)	O18- Ti4- O20	108.5(2)	O2- P1- O3	111.29(19)
O9- Ti1- O4	86.72(14)	O18- Ti4- O19	110.77(17)	O2- P1- O1	111.78(19)
O8- Ti1- Ti2	133.53(12)	O20- Ti4- O19	140.2(2)	O3- P1- O1	112.82(19)
O6- Ti1- Ti2	102.16(10)	O18- Ti4- O13	99.84(18)	O2- P1- C1	106.5(2)
O1- Ti1- Ti2	125.38(10)	O20- Ti4- O13	91.1(2)	O3- P1- C1	107.1(2)
O7- Ti1- Ti2	38.29(9)	O19- Ti4- O13	88.48(16)	O1- P1- C1	106.9(2)
O9- Ti1- Ti2	38.13(10)	O18- Ti4- O21	100.53(17)	O13- P2- O15	111.5(2)
O4- Ti1- Ti2	76.62(9)	O20- Ti4- O21	91.0(2)	O13- P2- O14	111.7(2)
O8- Ti1- Ti3	116.34(11)	O19- Ti4- O21	75.87(16)	O15- P2- O14	112.6(3)
O6- Ti1- Ti3	20.14(10)	O13- Ti4- O21	157.70(17)	O13- P2- C30	107.5(3)
O1- Ti1- Ti3	86.30(9)	O18- Ti4- Ti5	112.21(13)	O15- P2- C30	107.1(3)
O7- Ti1- Ti3	79.86(9)	O20- Ti4- Ti5	118.3(2)	O14- P2- C30	106.0(2)
O9- Ti1- Ti3	93.93(10)	O19- Ti4- Ti5	37.82(11)	P1- O1- Ti1	137.42(19)
O4- Ti1- Ti3	160.12(10)	O13- Ti4- Ti5	123.76(12)	P1- O2- Ti3	135.8(2)
Ti2- Ti1- Ti3	91.66(3)	O21- Ti4- Ti5	38.17(13)	P1- O3- Ti2	147.0(2)
O10- Ti2- O3	92.77(16)	O22- Ti5- O15	92.3(2)	C7- O4- Ti1	129.1(3)
O10- Ti2- O11	105.62(18)	O22- Ti5- O21	103.4(2)	C7- O5- Ti2	128.8(3)
O3- Ti2- O11	91.80(14)	O15- Ti5- O21	92.52(19)	Ti3- O6- Ti1	138.67(19)
O10- Ti2- O9	102.27(18)	O22- Ti5- O23	103.0(2)	Ti3- O7- Ti1	146.25(17)
O3- Ti2- O9	94.49(14)	O15- Ti5- O23	93.99(19)	Ti3- O7- Ti2	105.72(14)
O11- Ti2- O9	151.04(14)	O21- Ti5- O23	152.50(16)	Ti1- O7- Ti2	103.64(15)
O10- Ti2- O7	173.06(15)	O22- Ti5- O19	174.7(2)	C16- O8- Ti1	141.2(3)
O3- Ti2- O7	94.05(13)	O15- Ti5- O19	92.98(16)	C19- O9- Ti2	134.7(4)
O11- Ti2- O7	75.43(13)	O21- Ti5- O19	76.11(16)	C19- O9- Ti1	121.8(4)
O9- Ti2- O7	75.94(13)	O23- Ti5- O19	76.88(15)	Ti2- O9- Ti1	103.27(15)
O10- Ti2- O5	87.93(15)	O22- Ti5- O16	88.99(19)	C22- O10- Ti2	170.9(5)
O3- Ti2- O5	178.58(16)	O15- Ti5- O16	178.67(17)	C25- O11- Ti2	134.7(4)
O11- Ti2- O5	86.83(15)	O21- Ti5- O16	87.32(18)	C25- O11- Ti3	122.8(4)
O9- Ti2- O5	86.56(14)	O23- Ti5- O16	85.56(17)	Ti2- O11- Ti3	102.48(14)
O7- Ti2- O5	85.27(13)	O19- Ti5- O16	85.70(15)	C28- O12- Ti3	146.3(5)
O10- Ti2- Ti3	144.17(15)	O22- Ti5- Ti4	142.5(2)	P2- O13- Ti4	133.8(2)

O3- Ti2- Ti3	95.61(11)	O15- Ti5- Ti4	95.81(13)	P2- O14- Ti6	138.3(2)
O11- Ti2- Ti3	39.48(10)	O21- Ti5- Ti4	39.80(12)	P2- O15vTi5	149.3(3)
O9- Ti2- Ti3	111.67(10)	O23- Ti5- Ti4	112.86(11)	C36- O16- Ti5	128.0(4)
O7- Ti2- Ti3	36.03(9)	O19- Ti5- Ti4	36.43(11)	C36- O17- Ti6	130.0(4)
O5- Ti2- Ti3	83.11(11)	O16- Ti5- Ti4	83.23(12)	Ti4- O18- Ti6	139.8(2)
O10- Ti2- Ti1	138.76(15)	O22- Ti5- Ti6	140.89(19)	Ti4- O19- Ti5	105.75(18)
O3- Ti2- Ti1	101.11(10)	O15- Ti5- Ti6	99.08(14)	Ti4- O19- Ti6	145.97(19)
O11- Ti2- Ti1	112.45(10)	O21- Ti5- Ti6	113.19(12)	Ti5- O19- Ti6	104.01(16)
O9- Ti2- Ti1	38.59(10)	O23- Ti5- Ti6	39.35(10)	C45- O20- Ti4	131.2(8)
O7- Ti2- Ti1	38.07(9)	O19- Ti5- Ti6	38.01(11)	C48- O21- Ti5	133.2(5)
O5- Ti2- Ti1	79.12(10)	O16- Ti5- Ti6	79.78(12)	C48- O21- Ti4	124.7(5)
Ti3- Ti2Ti1	73.17(3)	Ti4- Ti5- Ti6	73.52(3)	Ti5- O21- Ti4	102.03(18)
O6- Ti3- O12	111.63(18)	O24- Ti6- O18	98.03(19)	C51- O22- Ti5	177.3(7)
O6- Ti3- O7	111.44(14)	O24- Ti6- O14	95.35(18)	C54- O23- Ti5	121.1(9)
O12- Ti3- O7	136.48(17)	O18- Ti6- O14	94.14(17)	C54- O23- Ti6	136.0(9)
O6- Ti3- O2	99.54(15)	O24- Ti6- O19	163.26(19)	Ti5- O23- Ti6	102.70(16)
O12- Ti3- O2	90.25(16)	O18- Ti6- O19	98.12(16)	Ti6- O24- C57	136.6(11)
O7- Ti3- O2	88.61(13)	O14- Ti6- O19	87.86(15)	C6- C1- P1	120.4(4)
O6- Ti3- O11	100.10(14)	O24- Ti6- O23	99.50(18)	C2- C1- P1	120.8(4)
O12- Ti3- O11	90.48(17)	O18- Ti6- O23	92.23(16)		
Some main Bond Angles of Ti_6-MA					
O3- P1- O2	111.32(19)	O10- Ti2- O9	103.69(15)	O14- Ti3- O2	87.67(13)
O3- P1- O1	112.2(2)	O3- Ti2- O9	93.71(14)	O13- Ti3- O11	100.48(14)
O2- P1- O1	112.24(18)	O11- Ti2- O9	153.05(13)	O12- Ti3- O11	91.38(15)
O3- P1- C1	105.7(2)	O10- Ti2- O14	172.84(16)	O14- Ti3- O11	76.21(12)
O2- P1- C1	108.0(2)	O3- Ti2- O14	93.85(13)	O2- Ti3- O11	157.27(14)
O1- P1- C1	107.0(2)	O11- Ti2- O14	76.12(12)	O13- Ti3- Ti2	108.77(11)
O8- Ti1- O13	97.81(15)	O9- Ti2- O14	77.09(12)	O12- Ti3- Ti2	119.90(14)
O8- Ti1- O1	96.16(14)	O10- Ti2- O5	88.55(15)	O14- Ti3- Ti2	37.86(9)
O13- Ti1- O1	95.33(14)	O3- Ti2- O5	178.24(13)	O2- Ti3- Ti2	123.98(10)
O8- Ti1- O14	164.29(15)	O11- Ti2- O5	88.66(14)	O11- Ti3- Ti2	38.35(9)
O13- Ti1- O14	97.06(13)	O9- Ti2- O5	85.86(14)	P1- O1- Ti1	135.67(18)

O1- Ti1- O14	87.49(12)	O14- Ti2- O5	84.39(13)	P1- O2- Ti3	132.0(2)
O8- Ti1- O9	98.96(14)	O10- Ti2- Ti3	142.14(13)	P1- O3- Ti2	156.3(2)
O13- Ti1- O9	90.10(14)	O3- Ti2- Ti3	92.69(10)	C7- O4- Ti1	128.9(3)
O1- Ti1- O9	163.08(13)	O11- Ti2- Ti3	39.99(9)	C7- O5- Ti2	128.2(3)
O14- Ti1- O9	75.93(12)	O9- Ti2- Ti3	113.19(9)	C14- O8- Ti1	151.5(4)
O8- Ti1- O4	83.75(15)	O14- Ti2- Ti3	36.13(8)	C17- O9- Ti2	130.8(4)
O13- Ti1- O4	174.06(14)	O5- Ti2- Ti3	85.9(1)	C17- O9- Ti1	126.7(4)
O1- Ti1- O4	90.19(14)	O10- Ti2- Ti1	141.46(12)	Ti2- O9- Ti1	102.39(14)
O14- Ti1- O4	80.95(12)	O3- Ti2- Ti1	98.85(9)	C20- O10- Ti2	178.0(5)
O9- Ti1- O4	83.99(13)	O11- Ti2- Ti1	113.64(9)	C23- O11- Ti2	125.5(3)
O8- Ti1- Ti2	133.69(12)	O9- Ti2- Ti1	39.40(9)	C23- O11- Ti3	132.4(3)
O13- Ti1- Ti2	98.46(10)	O14- Ti2- Ti1	38.03(8)	Ti2- O11- Ti3	101.65(13)
O1- Ti1- Ti2	124.93(9)	O5- Ti2- Ti1	79.74(9)	C26- O12- Ti3	146.8(5)
O14- Ti1- Ti2	38.07(9)	Ti3- Ti2- Ti1	73.91(3)	Ti3- O13- Ti1	148.04(19)
O9- Ti1- Ti2	38.21(9)	O13- Ti3- O12	111.63(18)	Ti3- O14- Ti1	148.87(17)
O4- Ti1- Ti2	76.50(9)	O13- Ti3- O14	109.56(14)	Ti3- O14- Ti2	106.01(13)
O10- Ti2- O3	93.21(15)	O12- Ti3- O14	138.49(17)	Ti1- O14- Ti2	103.90(14)
O10- Ti2- O11	102.53(15)	O13- Ti3- O2	99.96(14)	C6- C1- P1	120.4(4)
O3- Ti2- O11	90.95(14)	O12- Ti3- O2	90.25(15)	C2- C1- P1	121.7(4)

Table S4. Bond valence sum (BVS) analysis for Ti_6-BIDC, Ti_6-CMBA and Ti_6-MA.

Ti_6-BIDC	Atoms	Ti1	Ti2	Ti3	P1				
	BVS	4.171	4.328	4.311	5.014				
	assigned O.S.	+4	+4	+4	+5				
Ti_6-CMBA	Atoms	Ti1	Ti2	Ti3	Ti4	Ti5	Ti6	P1	P2
	BVS	4.245	4.282	4.237	4.188	4.296	4.248	5.071	5.076
	assigned O.S.	+4	+4	+4	+4	+4	+4	+5	+5
	Atoms	Ti1	Ti2	Ti3	P1				

Ti_6-MA	BVS	4.276	4.35	4.277	5.078				
	assigned O.S.	+4	+4	+4	+5				

Table S5. The photocatalytic degradation of TC by different photocatalysts reported in literatures.

Photocatalysts	Pollutant	Light source	Time (min)	Initial concentration of TC (mg/L)	Quantity of Photocatalyst (mg)	Removal efficiency (%)	References
$\{(L1')_{1.5}[CeMo_8O_{27}H_2] \cdot (H_2O)_3\}$	TC	300 W Xe	120	20	10	90.5	[2]
10-NBM_2/Cds	TC	300 W Xe	150	20	20	90.9	[3]
π-COF	TC	300 W Xe	90	20	20	94.8	[4]
SP^2C-COF	TC	300 W Xe	90	20	20	73.5	[5]
V_0-rich BWO	TC	300 W Xe	60	20	30	95.1	[6]
N-CQDs/TiO_2	TC	300 W Xe	120	10	20	97.7	[7]
ZnO/Cu_2O	TC	300 W Xe	120	20	10	95.3	[8]
Ti_6-BIDC	TC	Sunlight	150	50	10	92.4	This work

References

1 Y. Zhou, T. Cai, S. Liu, Y. Liu, H. Chen, Z. Li, J. Du, Z. Lei and H. Peng, *Chem. Eng. J.*, 2021, **411**, 128615.

2 C. Ren, X. Zhang, C. Chen and Y. Niu, J. M. Struct., 2024, **1316**, 139062.

3 R. Zhang, K. Jia, Z. Xue, Z. Hu and N. Yuan, J. Alloys compd., 2024, **992**, 174462.

4 Z. Hu, Y. Wang, L. Wang, Q. Wang, Q. Zhang, F. Cui and G. Jiang, Chem. Eng. J., 2024, **479**, 147534.

5 Z. Hu, Y. Luo, L. Wang, Y. Wang, Q. Wang, G. Jiang, Q. Zhang and F. Cui, ACS Appl. Polym. Mater., 2023, **5**, 9263- 9273.

6 W. Gao, G. Li, Q. Wang, L. Zhang, K. Wang, S. Pang, G. Zhang, L. Lv, X. Liu, W. Gao, L.

Sun, Y. Xia, Z. Ren and P. Wang, Chem. Eng. J., 2023, **464**, 142694.
7 M. Karaca, Z. Eroğ lu, Ö . Aç ış lı, Ö . Metin and S. Karaca, ACS Omega, 2023, **8**, 26597- 26609.
8 J. Cui, L. Ye, X. Chen, J. Li, B. Yang, M. Yang, Q. Yang, D. Yun and S. Sun, Appl. Surf. Sci., 2023, **638**, 158046.