

# Chelating Coordination Modulation Method for the Synthesis of Ti-MOF Single Crystals

Hui-Zi Li<sup>a,b</sup>, Shangda Li<sup>a</sup>, Fei Wang<sup>a\*</sup> and Jian Zhang<sup>a\*</sup>

<sup>a</sup>State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China;

<sup>b</sup>University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

## Supporting Information

### Content

1. Materials and Characterization .....	2
1.1 Materials .....	2
1.2 Characterization .....	2
2. Synthesis and Characterization of Ti-MOF single crystals .....	2
2.2 X-Ray Crystallography .....	3
2.2.1 Single crystal structure determination .....	3
2.2.2 Powder X-ray diffraction analysis .....	5
3. Other Characterizations .....	6
4. Photocatalytic properties .....	8
5. References .....	9

## 1. Materials and Characterization

### 1.1 Materials

All reagents were purchased commercially and used without further purification. Titanium(IV) isopropoxide ( $\text{Ti}(\text{OiPr})_4$ ), 2,5-dihydroxyterephthalic acid, salicylic acid, thiosalicylic acid, L(+)-ascorbic acid, L(+)-tartaric acid L-tyrosine, D(-)-tartaric acid, 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid), barium sulfate ( $\text{BaSO}_4$ , AR), diethylphosphite, 2,2,6,6-tetramethylpiperidinoxy (TEMP) and N, N-diethylformamide (DEF) were purchased from Adamas-beta. Acetic acid (HOAc), formamide, ethyl acetate (EA), dimethyl sulfoxide (DMSO), methyl alcohol (MeOH), ethanol (EtOH), isopropyl alcohol (IPA), acetone, acetonitrile ( $\text{CH}_3\text{CN}$ ), toluene, cyclohexane, dichloromethane, chloroform and N, N-dimethylformamide (DMF) were purchased from Sinopharm Group Co., Ltd. (China).

### 1.2 Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a MiniFlex2 X-ray diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) with a step size of  $3^\circ/\text{min}$ . The thermogravimetric analyses (TGA) were carried out on a NETSCHZ STA-449C thermoanalyzer with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  from 25 to  $800 \text{ }^\circ\text{C}$  under an  $\text{N}_2$  atmosphere.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE III HD spectrometer (400 MHz and 101 MHz, respectively). The UV-Vis diffuse reflection data were recorded at room temperature using a powder sample with  $\text{BaSO}_4$  as a standard (100 % reflectance) on a Perkin Elmer Lambda-950 UV spectrophotometer and scanned at 300-800 nm. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker BioSpin E500 EPR spectrometer at room temperature.

## 2. Synthesis and Characterization of Ti-MOF single crystals

**Synthesis of  $\text{Ti}(\text{Sal})_3 \cdot \text{H}_2\text{en} \cdot 2\text{H}_2\text{O}$ :** Crystals of  $\text{Ti}(\text{Sal})_3 \cdot \text{H}_2\text{en} \cdot 2\text{H}_2\text{O}$  were synthesized according to the previous report.<sup>1</sup> A mixture of salicylic acid (550 mg, 4 mmol), piperazine (140 mg, 1.62 mmol), tetraisopropoxytitanium (0.6 mL, 2 mmol) and distilled water (4 mL) was sealed in a 25 ml Teflon liner and transferred to a preheated oven at  $120 \text{ }^\circ\text{C}$  for 3 days. After cooled to room temperature, yellow crystals were obtained.

**Synthesis of FIR-117 single crystals:** A mixture of  $\text{Ti}(\text{OiPr})_4$  (0.40 mmol, 120  $\mu\text{L}$ ), 2,5-dihydroxyterephthalic acid (1.60 mmol, 0.317 g), salicylic acid (1.2 mmol, 0.165 g), DEF (1 mL) and HOAc (3 mL) in a 23 mL Teflon-lined stainless-steel autoclave. The mixture was heated at  $160 \text{ }^\circ\text{C}$  for 3 days and then cooled to obtain red flake single crystals. FIR-117 single crystals can also be synthesized by replacing salicylic acid (1.2 mmol, 0.165 g) with 2, 5-dihydroxy-1, 4-benzenedisulfonic acid ( $\text{H}_4\text{DOBSC}$ ), L(+)-ascorbic acid, L(+)-tartaric acid, respectively. The yield of FIR-117 obtained was low and several FIR-119 were mixed together.

**Synthesis of FIR-117 single crystals:** A mixture of  $\text{Ti}(\text{Sal})_3 \cdot \text{H}_2\text{en} \cdot 2\text{H}_2\text{O}$  (250 mg), 2,5-dihydroxyterephthalic acid (2 mmol, 0.396 g), DEF (1 mL) and HOAc (3 mL) in a 23 mL Teflon-lined stainless-steel autoclave. The mixture was heated at  $160 \text{ }^\circ\text{C}$  for 3 days and then cooled to obtain red flake single crystals.

**Synthesis of FIR-118 single crystals:** A mixture of  $\text{Ti}(\text{OiPr})_4$  (0.40 mmol, 120  $\mu\text{L}$ ), 2,5-dihydroxyterephthalic acid (1.60 mmol, 0.317 g), (1.20 mmol, 0.137 g), DEF (2 mL) and HOAc (2 mL) in a 23 mL Teflon-lined stainless-steel autoclave. The mixture was heated at  $160 \text{ }^\circ\text{C}$  for 3 days and then cooled to room temperature. A small amount of red flake single crystals was obtained.

**Synthesis of FIR-119 single crystals:** A mixture of  $\text{Ti}(\text{OiPr})_4$  (0.81 mmol, 250  $\mu\text{L}$ ), 2,5-dihydroxyterephthalic acid (0.30 mmol, 0.060 g), thiosalicylic acid (0.39 mmol, 0.060 g), DEF (1 mL) and HOAc (3 mL) in a 23 mL Teflon-lined

stainless-steel autoclave. The mixture was heated at 160 °C for 3 days and then cooled to room temperature. Red polyhedral single crystals were collected and washed by formamide. Similarly, FIR-119 single crystals can also be synthesized by replacing thiosalicylic acid (0.39 mmol, 0.060 g) with L-tyrosine and D-(-)- tartaric acid, respectively.

## 2.2 X-Ray Crystallography

### 2.2.1 Single crystal structure determination

Single-crystal X-ray diffraction data of FIR-117, FIR-118, and FIR-119 were collected on a Rigaku Synergy Custom (Liquid MetalJet D2+) diffractometer with Ga K $\alpha$  radiation ( $\lambda = 1.3405 \text{ \AA}$ ). Absorption corrections were applied by using multi-scan program. The X-ray diffraction crystallographic data and structure refinements are demonstrated in **Table S1**. Crystallographic data reported in this paper have been deposited in the Cambridge Crystallographic Data Centre with CCDC. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1.** Crystal data and structure refinement for FIR-117, FIR-118 and FIR-119.

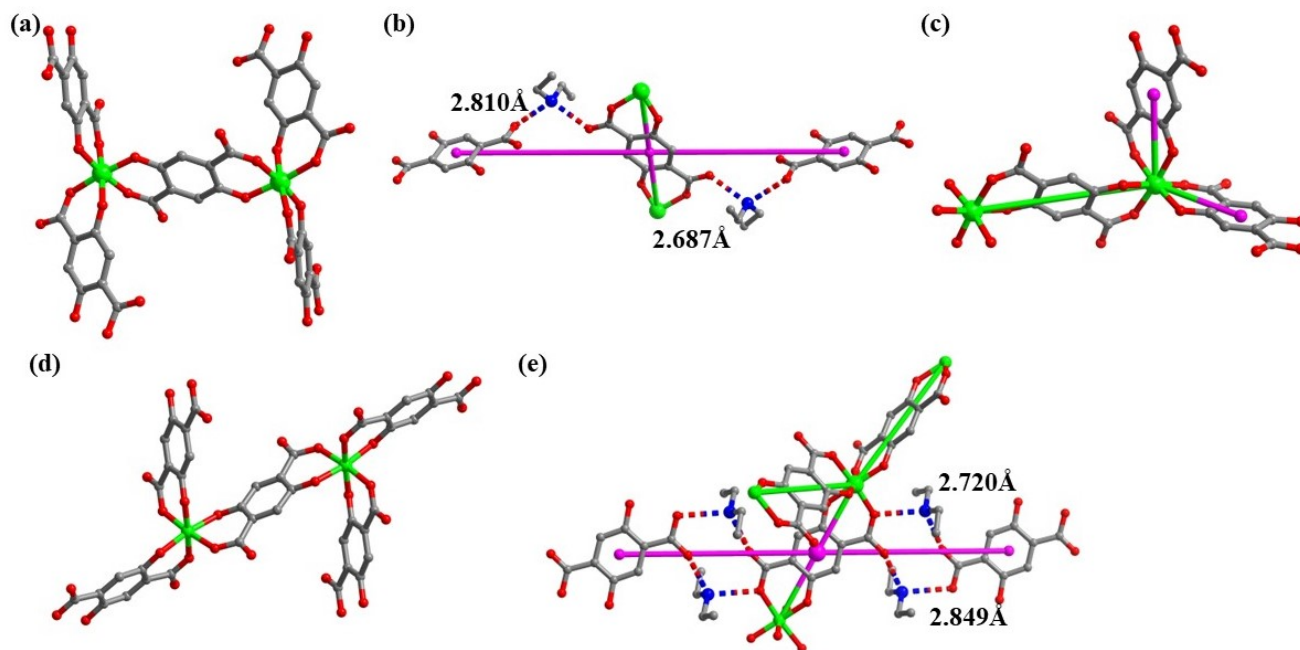
Identification code	FIR-117	FIR-118	FIR-119	MIL-167 <sup>2</sup>
Empirical formula	C <sub>16</sub> H <sub>15</sub> NO <sub>9</sub> Ti	C <sub>16</sub> H <sub>15</sub> NO <sub>9</sub> Ti	C <sub>12</sub> H <sub>3</sub> O <sub>9</sub> Ti	Ti(DOBDC) <sub>1.5</sub> (Et <sub>2</sub> MeNH) <sub>2</sub> ·nH <sub>2</sub> O
Formula weight	413.19	413.19	339.04	
Temperature/K	99.99(10)	293(2)	100.00(10)	
Crystal system	triclinic	triclinic	cubic	cubic
Space group	<i>P</i> -1	<i>P</i> -1	<i>I</i> -43 <i>d</i>	<i>I</i> -43 <i>d</i>
<i>a</i> /Å	10.1764(4)	9.5880(2)	21.8295(8)	22.91180(37)
<i>b</i> /Å	11.4887(4)	10.2373(3)	21.8295(8)	22.91180(37)
<i>c</i> /Å	13.5180(4)	10.7261(3)	21.8295(8)	22.91180(37)
$\alpha$ /°	92.861(3)	103.159(2)	90	90
$\beta$ /°	102.938(3)	94.609(2)	90	90
$\gamma$ /°	110.782(3)	90.904(2)	90	90
Volume/Å <sup>3</sup>	1425.53(9)	1021.23(5)	10402.3(11)	12027.56(59)
Crystal size/mm <sup>3</sup>	0.2 × 0.1 × 0.1	0.1 × 0.1 × 0.05	0.1 × 0.1 × 0.1	
Goodness-of-fit on F <sup>2</sup>	1.062	1.059	0.982	
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0741, wR_2 = 0.2302$	$R_1 = 0.0910, wR_2 = 0.2599$	$R_1 = 0.0798, wR_2 = 0.2334$	
Final R indexes [all data]	$R_1 = 0.0938, wR_2 = 0.2479$	$R_1 = 0.1027, wR_2 = 0.2714$	$R_1 = 0.1609, wR_2 = 0.2863$	
CCDC	2287493	2287494	2287495	

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left[ \frac{\sum (|F_o|^2 - |F_c|^2)^2}{\sum |F_o|^2} \right]^{1/2}.$$

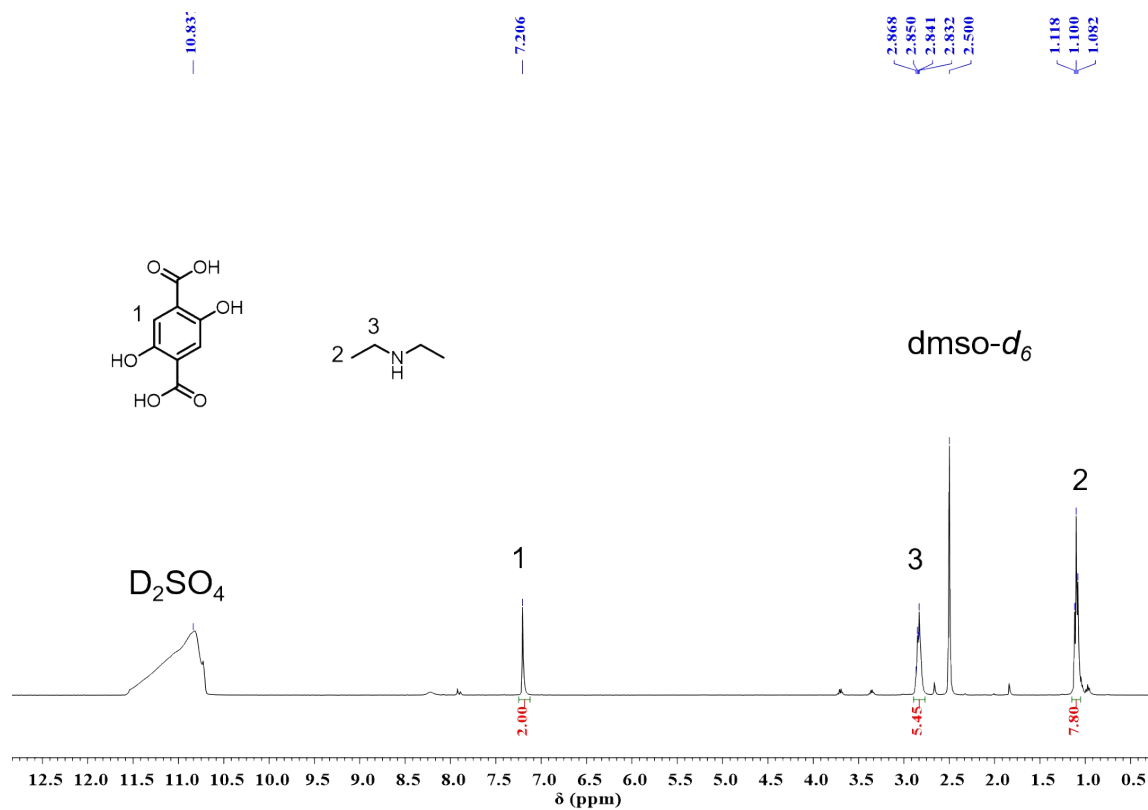
**Table S2.** Bond Lengths for FIR-117, FIR-118, FIR-119 and MIL-167.

FIR-117		FIR-118	
Atom-Atom	Length/Å	Atom-Atom	Length/Å
Ti1-O3	1.866(2)	Ti1-O3	1.877(3)
Ti1-O6	1.880(2)	Ti1-O4	2.013(3)
Ti1-O4	2.010(2)	Ti1-O7	1.962(3)
Ti1-O1	2.000(2)	Ti1-O1	1.969(3)
Ti1-O9	1.874(2)	Ti1-O6	1.873(3)
Ti1-O7	2.011(2)	Ti1-O9	1.932(3)
FIR-119		MIL-167	
Atom-Atom	Length/Å	Atom-Atom	Length/Å
Ti1-O3	1.884(10)	Ti1-O3(Ar)	1.830(55)
Ti1-O1	1.980(9)	Ti1-O2	1.871(55)

Symmetric operation code: <sup>1</sup>1-X, 1-Y, 1-Z; <sup>2</sup>2-X, 2-Y, 1-Z; <sup>3</sup>2-X, 2-Y, 2-Z.



**Figure S1.** (a) The chiral  $\text{Ti}(\text{DOBDC})_3$  units with  $\Lambda$  and  $\Delta$  configurations in FIR-117; (b) The defined 4-connected node of DOBDC ligand by considering the H-bond interactions; (c) The 3-connected node of Ti atom; (d) The chiral  $\text{Ti}(\text{DOBDC})_3$  units with  $\Lambda$  and  $\Delta$  in FIR-118; (e) The defined 4-connected node of DOBDC ligand by considering the H-bond interactions and 3-connected node of Ti atom. The H-bond interactions were highlighted in dish line.



**Figure S2.**  $^1\text{H}$  NMR spectrum (solvent:  $\text{dms0-d}_6$ ) of FIR-119.

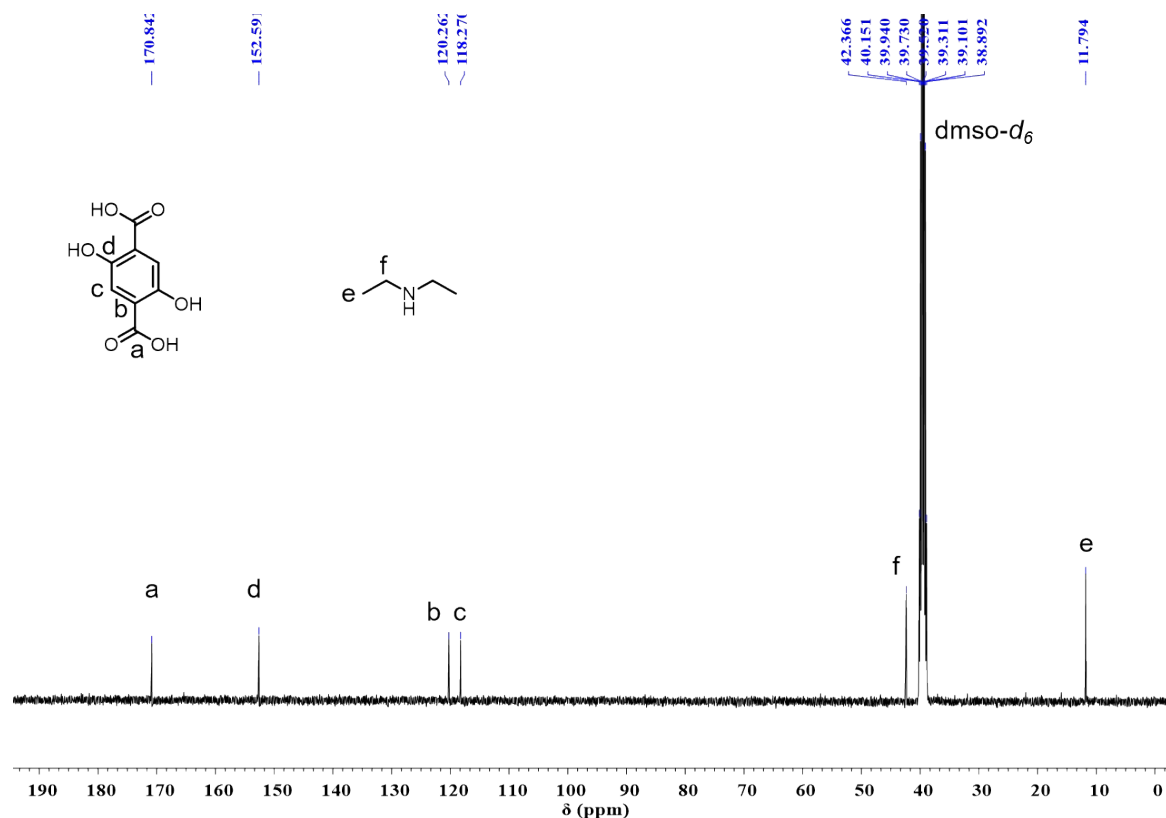


Figure S3.  $^{13}\text{C}$  NMR spectrum (solvent:  $\text{dms0-d}_6$ ) of FIR-119.

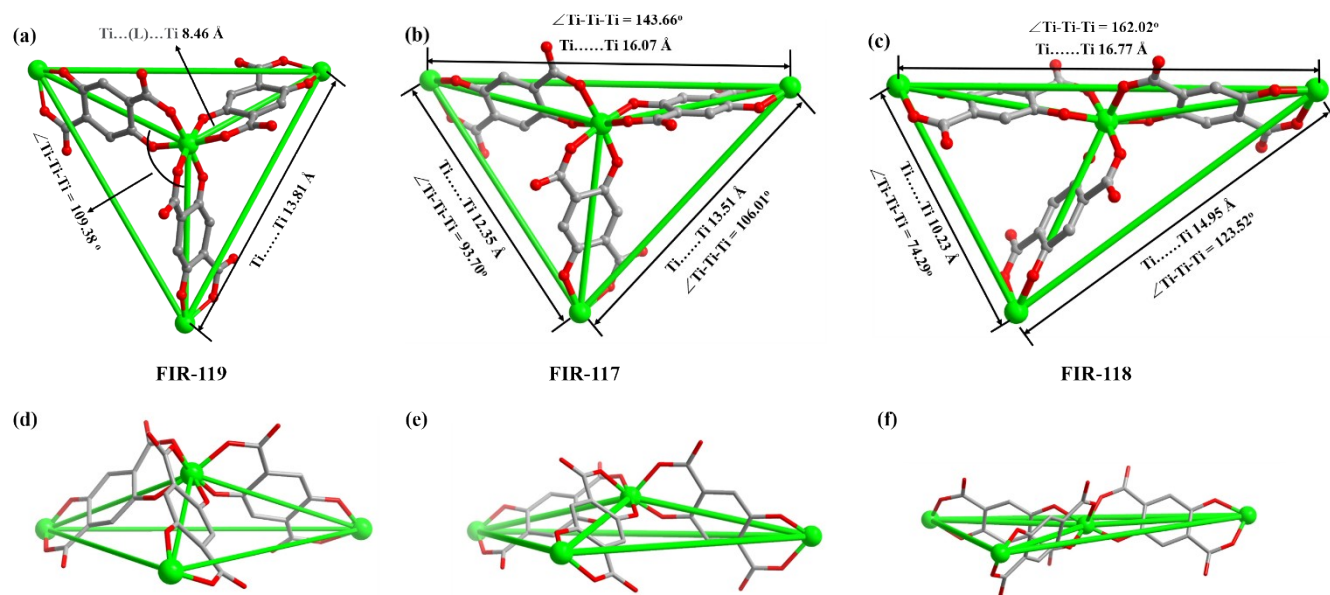


Figure S4. A tetrahedral configuration from: (a)(d) FIR-119; (b)(e) FIR-117; (c)(f) FIR-118 in different directions.

Each titanium atom is connected with three DOBDC ligands to obtain an octahedral configuration. As shown in figure S4, the maximum angle between Ti-Ti atoms increases gradually from FIR-119 to FIR-117 to FIR-118 (109.38, 143.66, and 162.02, respectively). Similarly, the maximum distance between Ti-Ti atoms increases gradually (13.81, 16.07, and 16.77, respectively). The  $\text{Ti(L)}_3$  unit in FIR-119 is close to the intermediate, which exhibits 3D frameworks. In FIR-117 to FIR-118, the  $\text{Ti(L)}_3$  unit showed a distorted geometric configuration and was close to a planar triangle, which is prone to forming a 2D layer.

All these differences are ultimately caused by the differences in chelation coordination modulators. In brief, the impact of various modulators may result in different configurations of the  $Ti(L)_3$  intermediate, ultimately determining their distinct topologies.

### 2.2.2 Powder X-ray diffraction analysis

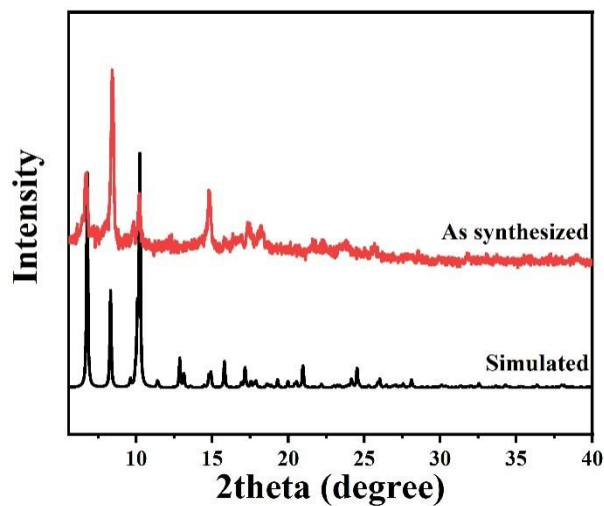


Figure S5. Powder XRD (PXRD) patterns of as synthesized and simulated FIR-117.

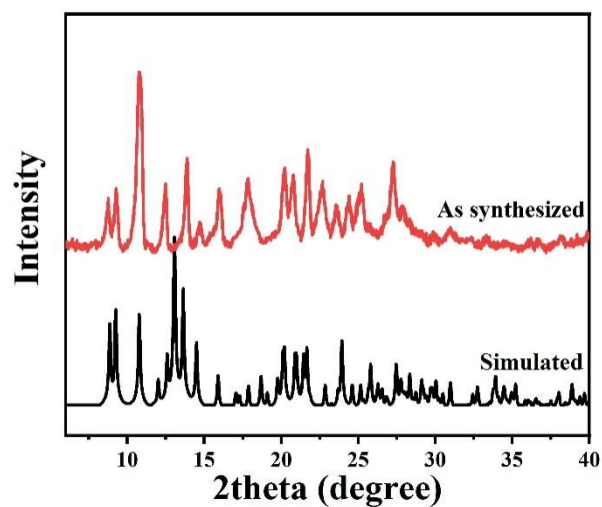
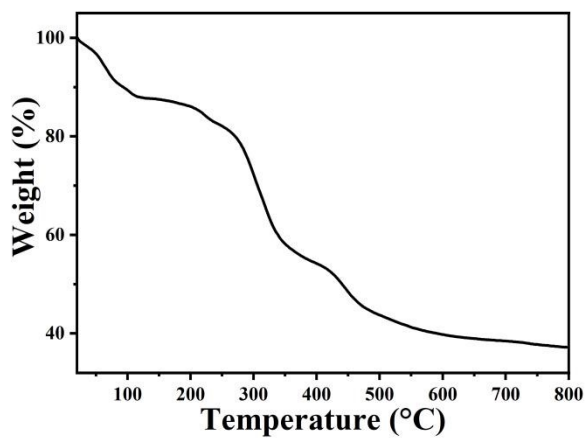
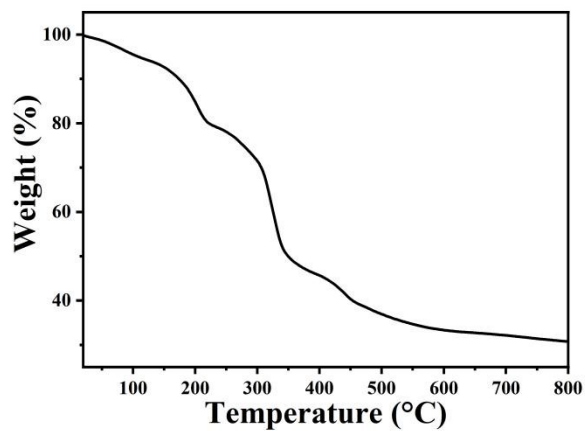


Figure S6. PXRD patterns of as synthesized and simulated FIR-118.

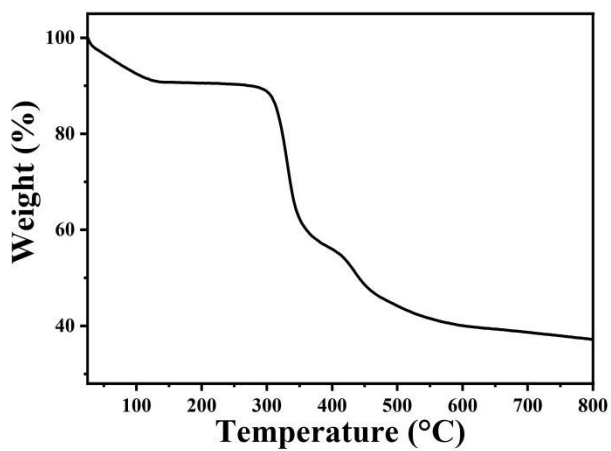
### 3. Other Characterizations



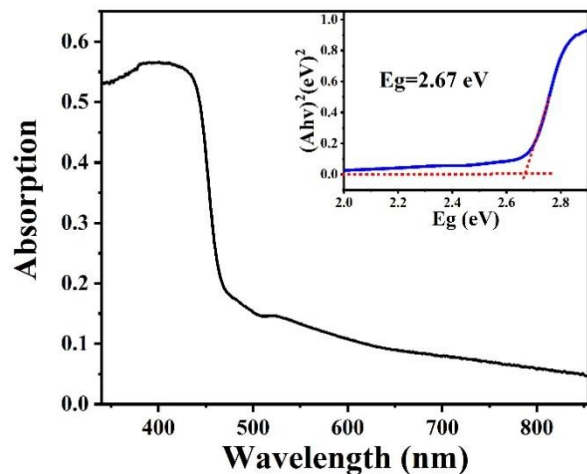
**Figure S7.** Thermogravimetric (TG) curve of as synthesized FIR-117.



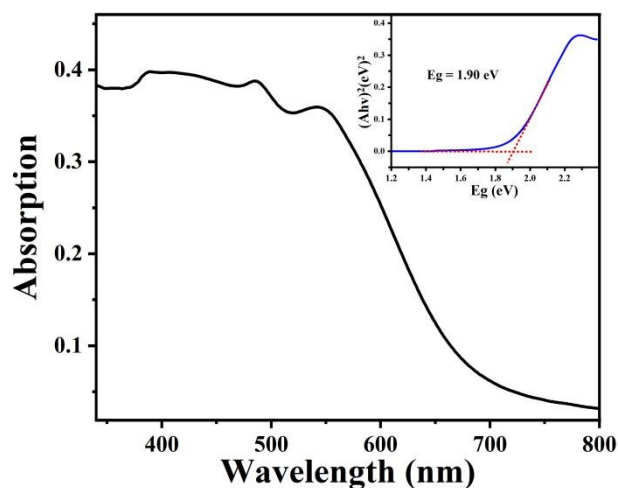
**Figure S8.** Thermogravimetric (TG) curve of as synthesized FIR-118.



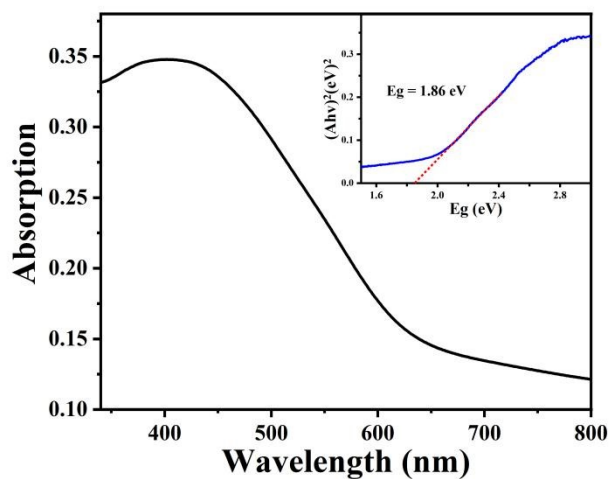
**Figure S9.** Thermogravimetric (TG) curve of as synthesized FIR-119.



**Figure S10.** UV-Vis diffuse reflectance spectra of DOBDC ligand (Tauc plot of DOBDC derived from UV-Vis diffuse reflectance spectra).



**Figure S11.** UV-Vis diffuse reflectance spectra of FIR-117 (Tauc plot of FIR-117 derived from UV-Vis diffuse reflectance spectra).



**Figure S12.** UV-Vis diffuse reflectance spectra of FIR-118 (Tauc plot of FIR-118 derived from UV-Vis diffuse reflectance spectra).



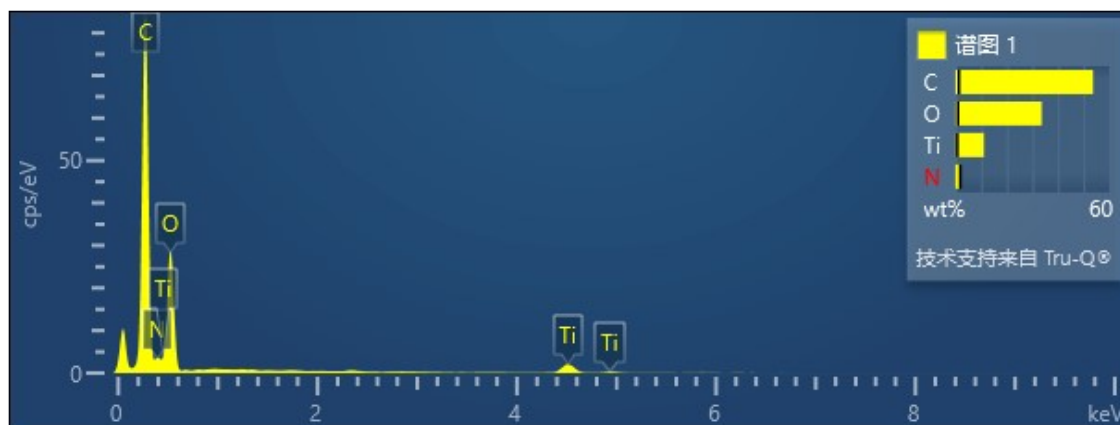


Figure S13. The EDS spectrum of compound FIR-119.

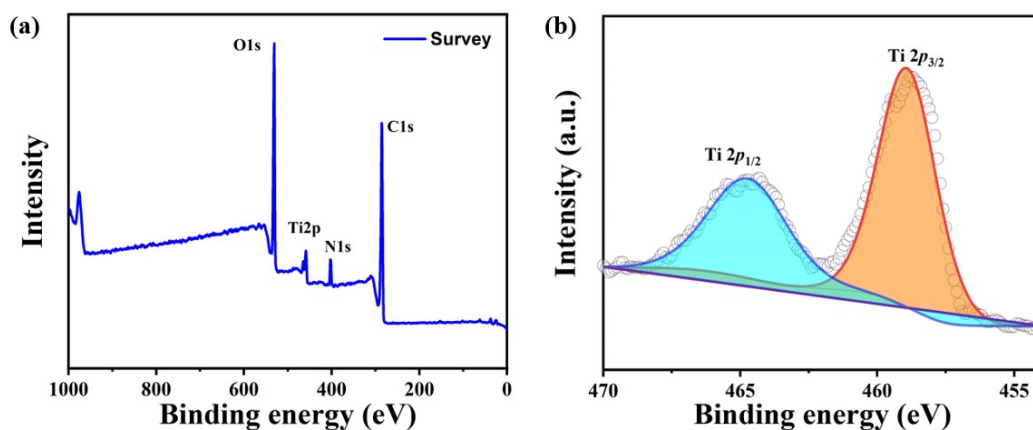
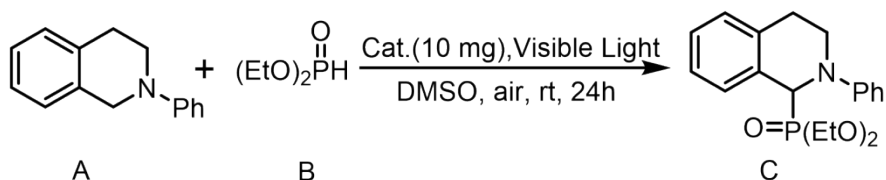
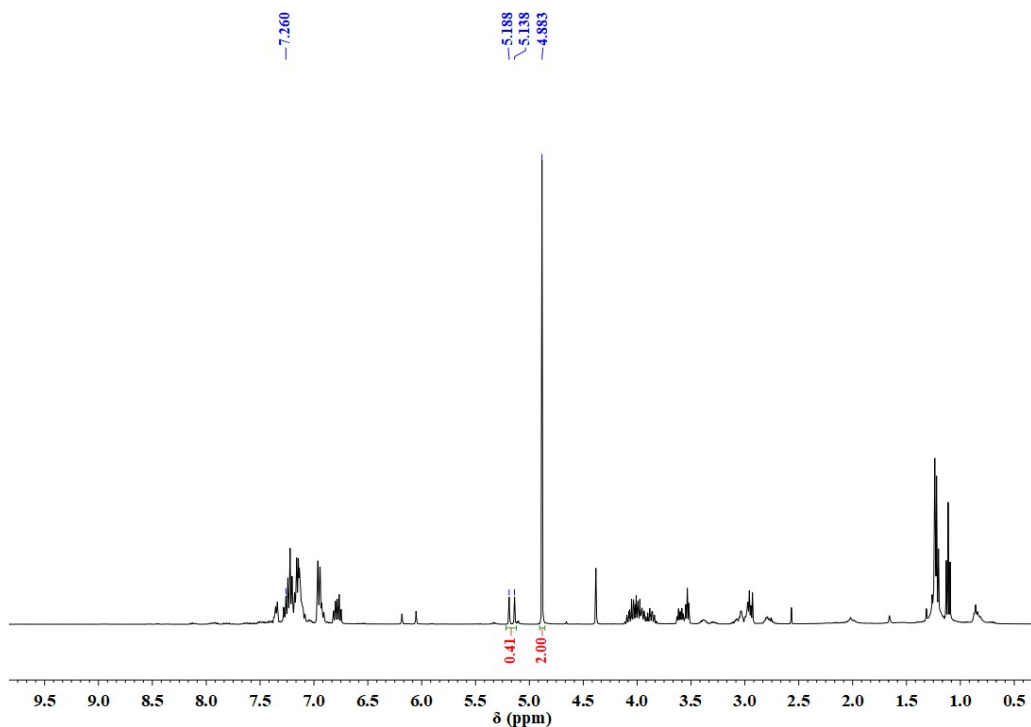


Figure S14. (a) XPS survey plots for FIR-119. (b) XPS Ti 2p region of FIR-119.

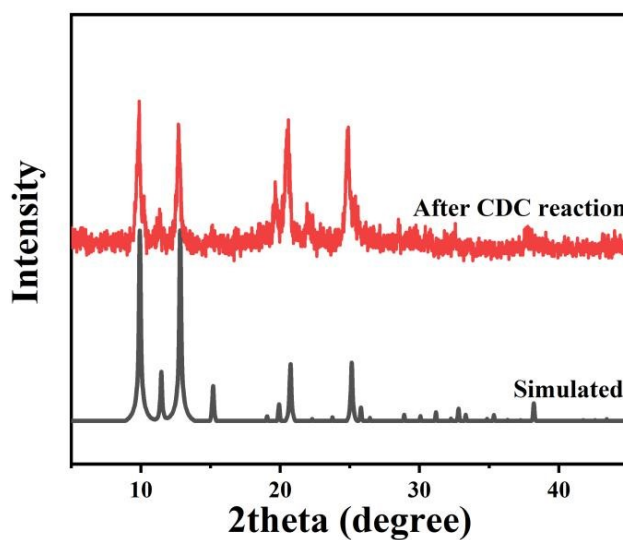
#### 4. Photocatalytic properties



**CDC reaction:** Catalyst (10 mg), substrate **A** (N-phenyltetrahydroisoquinoline, 0.2 mmol), **B** (diethyl phosphite, 0.24 mmol) and DMSO (2 mL) were added to a Pyrex side irradiation reaction vessel connected to an open gas system and dispersed sufficiently to form a uniform suspension. The reaction mixture was stirred gently (100 rpm) and irradiated by visible light generated by a 300 W Xe light-source (PerfectLight, PLS-SXE300/300UV) with a 420 nm cut-off filter at room temperature for 24 h. After the reaction is completed, H<sub>2</sub>O (15 mL) is added to the reaction system and extracted three times with organic phase EA (10 mL\*3). Subsequently, the collected organic phase was collected and the remaining H<sub>2</sub>O was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. Finally, the final product **C** is obtained through rotary drying. The yield of the obtained product was determined by <sup>1</sup>H NMR, with CH<sub>2</sub>Br<sub>2</sub> as the internal standard for quantitative analysis.



**Figure S15.** <sup>1</sup>H NMR (solvent: *d*-CDCl<sub>3</sub>) of product C by **Entry 3**.



**Figure S16.** Powder XRD patterns of FIR-119 after CDC reaction.

## 5. References

1. Dong, G.-L.; Wang, L.; Fang, W.-H.; Zhang, L., Hydrothermal synthesis, structures and visible light harvest of three titanium complexes. *Inorg. Chem. Commun.* **2018**, *93*, 61-64.
2. Assi, H.; Pardo Perez, L. C.; Mouchaham, G.; Ragon, F.; Nasalevich, M.; Guillou, N.; Martineau, C.; Chevreau, H.; Kapteijn, F.; Gascon, J.; Fertey, P.; Elkaim, E.; Serre, C.; Devic, T., Investigating the Case of Titanium(IV) Carboxyphenolate Photoactive Coordination Polymers. *Inorg. Chem.* **2016**, *55* (15), 7192-9.