

Electronic Supporting Information

Ferrocene-Sensitized Titanium-Oxo Clusters with Effective Visible Light Absorption and Excellent Photoelectrochemical Activity

Chao Wang,^{*a} Shou Juan Wang,^a Fan Gong Kong^a and Ning Chen^a

State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of
Technology, Shandong Academy of Sciences, No. 3501 University Road, Jinan,
250353, China, *E-mail: wangchao@qlu.edu.cn.*

1. Crystallographic details

Table S1. X-ray measurements and structure solution of clusters Ti_8Fcdc_4 and $\text{Ti}_{10}\text{Fcdc}_2$.

Compound	Ti_8Fcdc_4	$\text{Ti}_{10}\text{Fcdc}_2$
Empirical formula	$\text{C}_{48}\text{H}_{71}\text{Fe}_2\text{NO}_{18}\text{Ti}_4$	$\text{C}_{36}\text{H}_{68}\text{FeO}_{19}\text{Ti}_5$
Formula weight	1253.35	1100.25
Crystal system	monoclinic	triclinic
Space group	$\text{P}2_1/\text{n}$	$\text{P}-1$
$a/\text{\AA}$	15.9048(2)	11.7193(5)
$b/\text{\AA}$	20.4727(3)	12.4105(5)
$c/\text{\AA}$	18.7454(2)	19.4298(8)
$\alpha/^\circ$	90	89.007(3)
$\beta/^\circ$	92.8146(13)	72.474(3)
$\gamma/^\circ$	90	68.293(3)
V	6096.41(16)	2489.50(19)
Z	4	2
$\rho_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	1.366	1.468
$\mu_{(\text{MoK}\alpha)}/\text{mm}^{-1}$	8.504	9.364
F(000)	2600.0	1144.0
Data/restraints /parameters	12166/302/789	9201/44/602
R_1/wR_2 ($I > 2\sigma(I)$) ^a	0.0626/0.1816	0.0672/0.1871
R_1/wR_2 (all data) ^a	0.0882/0.2038	0.0804/0.2032
GooF (all data) ^b	1.025	1.001

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

$$^b \text{GooF} = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / (n-p) \}^{1/2}$$

2. Synthetic route of the clusters

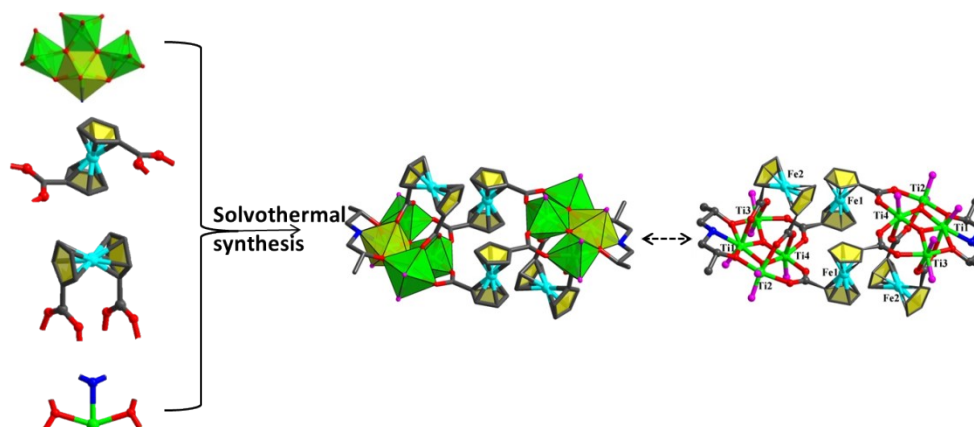


Fig. S1. The assembly of the core structure of the Ti_8Fcdc_4 cluster shows a polyhedron in the metal center.

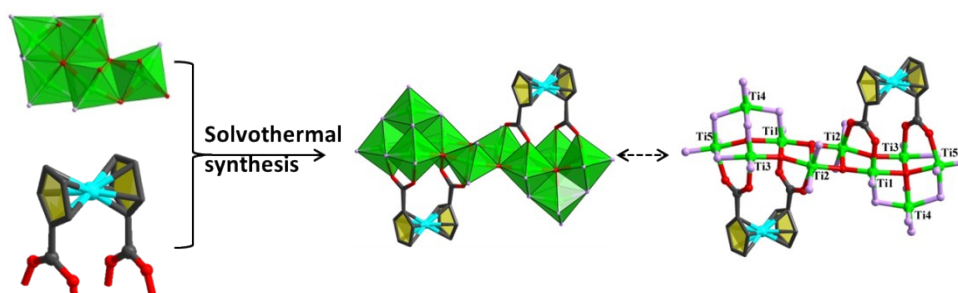


Fig. S2. The assembly of the core structure of the $\text{Ti}_{10}\text{Fcdc}_2$ cluster shows a polyhedron in the metal center.

3. Structure of the clusters

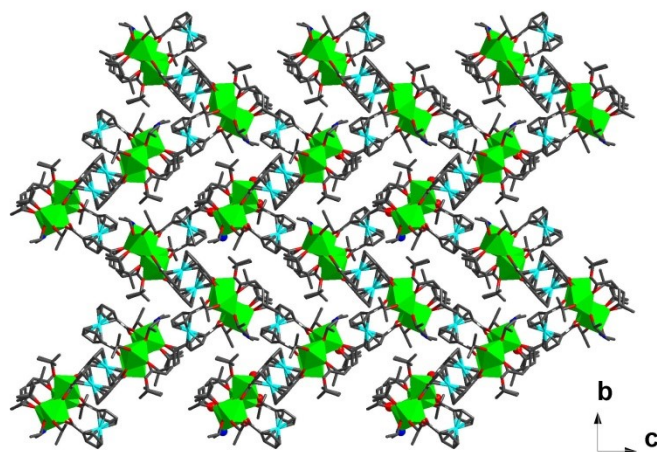


Fig. S3. Three-dimensional supramolecular stacking of Ti_8Fcdc_4 cluster.

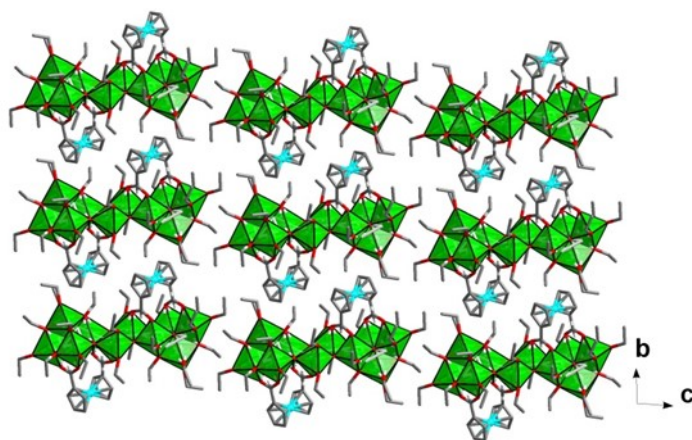


Fig. S4. Three-dimensional supramolecular stacking of $\text{Ti}_{10}\text{Fcdc}_2$ cluster.

4. Powder X-ray diffraction

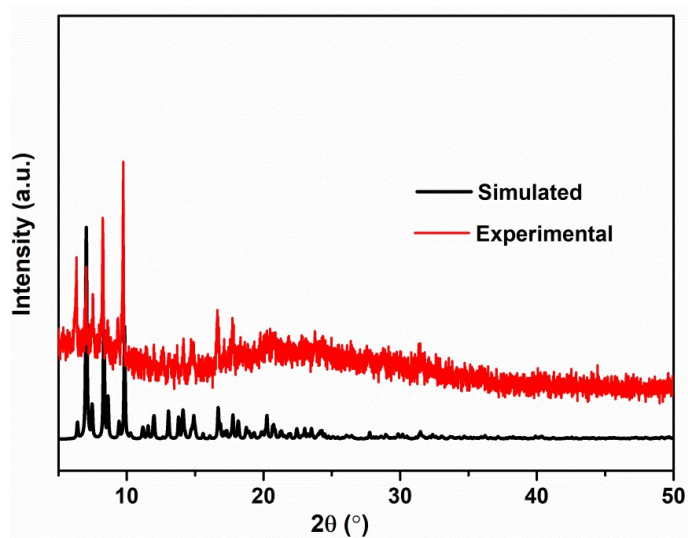


Fig. S5. The XRD patterns of cluster Ti_8Fcdc_4 cluster.

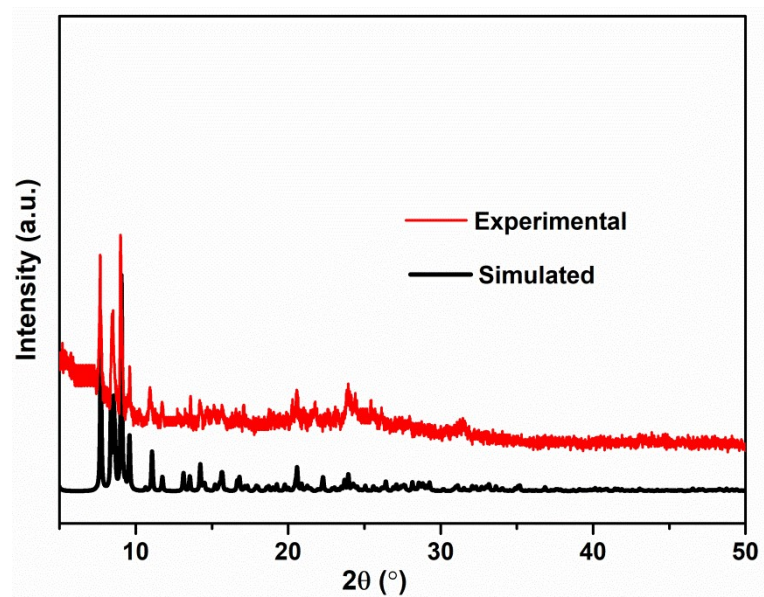


Fig. S6. The XRD patterns of cluster $\text{Ti}_{10}\text{Fcdc}_2$ cluster.

5. TG-Measurement

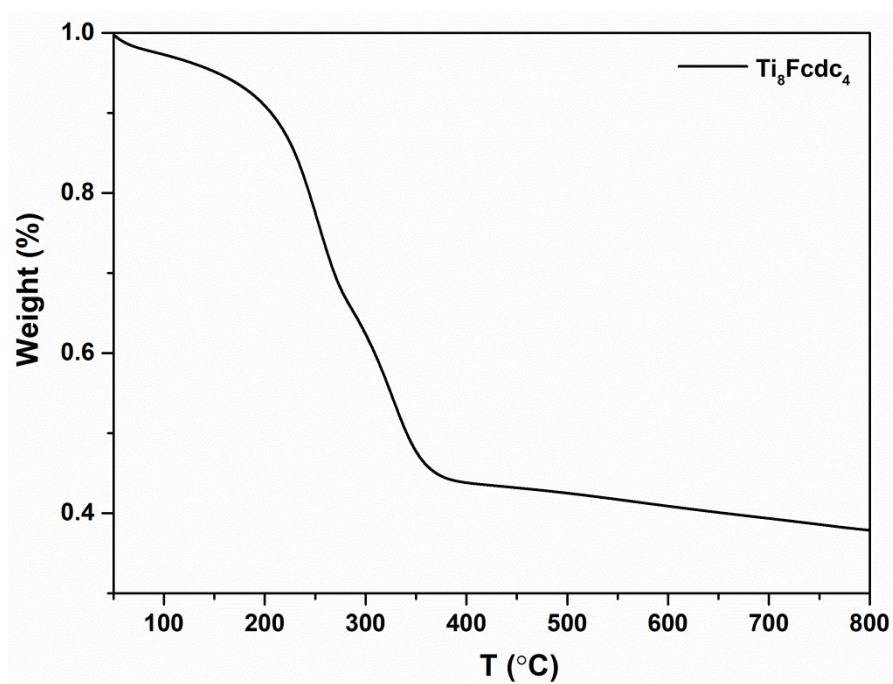


Fig. S7. Thermal decomposition curve of Ti_8Fcdc_4 cluster.

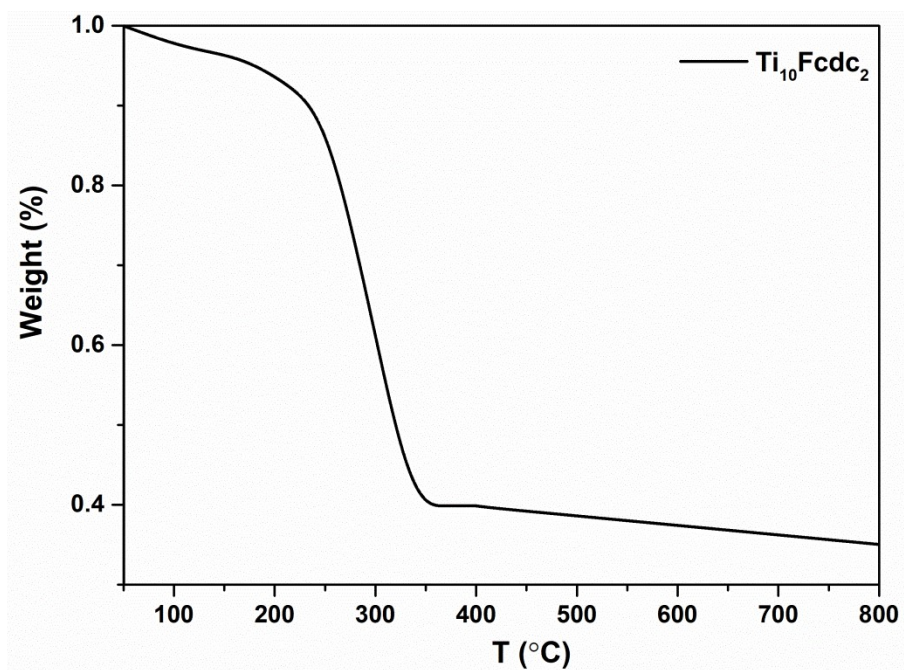


Fig. S8. Thermal decomposition curve of $\text{Ti}_{10}\text{Fcdc}_2$ cluster.

6. FT-IR spectra

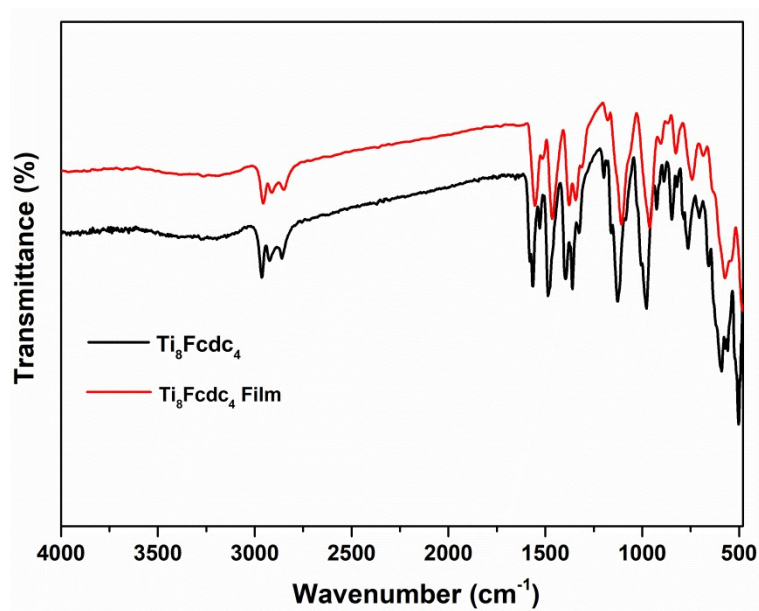


Fig. S9. IR spectra of Ti_8Fcdc_4 cluster and the sample after photoelectrochemical experiment.

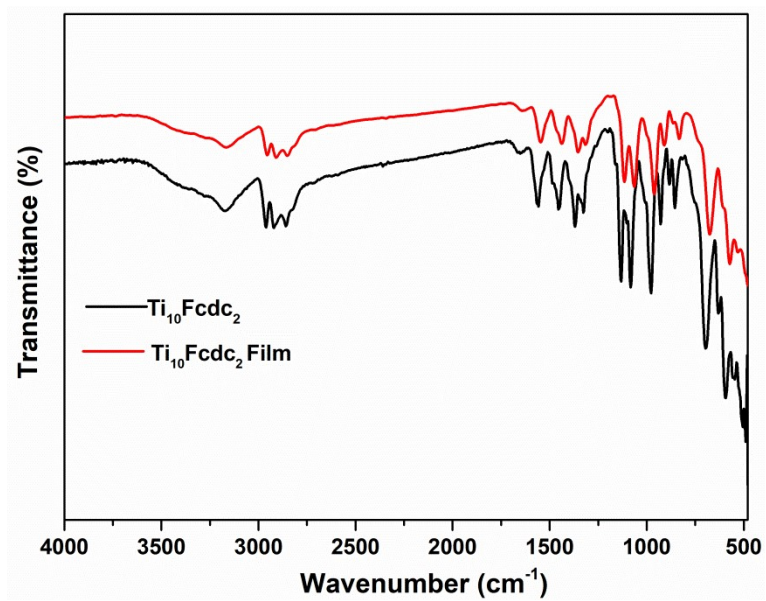


Fig. S10. IR spectra of **Ti₁₀Fcdc₂** cluster and the sample after photoelectrochemical experiment.