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Supporting Information

Accurate Assembly of Ferrocene-Functionalized $\{Ti_{22}Fc_4\}$ Cluster with Photocatalytic Amines Oxidation Activity

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1. Experimental section

Materials and Characterization. All reagents were purchased commercially and were not further purified before use. Powder X-ray diffraction (PXRD) analysis was performed on a Rigaku Mini Flex II diffractometer at a 2θ range of 5–50° (5° min^{-1}) with CuKα radiation (λ =1.54056 Å). The solid-state UV/Vis spectra of the cluster samples were obtained on UV-4000 spectrophotometer. Fourier transform infrared spectroscopy (FTIR) data (4000-400 cm^{-1}) was collected on a PerkinElmer Spectrum 100 FT-IR Spectrometer. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA 851e analyzer in N_2 at a temperature range of 50~800℃ (10℃ min^{-1}). Crystallographic data for this article were obtained on a Bruker Apex II CCD diffractometer with graphite-mono-chromated Mo/Cu Ka radiation. The structures were solved by direct methods and refined on F^2 by full matrix least-squares using new SHELXL program. All of the non-hydrogen atoms are located from Fourier maps and are refined anisotropically.

Synthesis of cluster $[Ti_5(u_3\text{-}O)_3(O^iPr)_9(Fdc)(Dmg)(Pdc)]$ (Ti_5Fc). $DmgH_2$ (17 mg, 0.147 mmol), $FdcH_2$ (55.2 mg, 0.24 mmol), 2,3-pyrazine dicarboxylic acid (18.6 mg, 0.1 mmol) and 3 mL isopropanol were added into a 25 mL Teflon lined stainless steel autoclave, and then combined with $Ti(O^iPr)_4$ (300 μL, 0.975 mmol). The solution was sonicated for 5 min, then transferred to an oven at 100℃ for 3 days. After cooling to room temperature, yellow block crystals of $\{Ti_5Fc\}$ were obtained and washed with acetonitrile, then dried at room temperature. Yield: about 120 mg.

Synthesis of clusters $[Ti_{11}(u_3\text{-}O)_9\}(O^iPr)_{12}(Fdc)_2(Dmg)_5]$ ($Ti_{11}Fc_2$) and $[Ti_{22}(u_3\text{-}O)_{18}\}(O^iPr)_{30}(Fdc)_4(Dmg)_7]$ $\{Ti_{22}Fc_4\}$. $DmgH_2$ (17 mg, 0.147 mmol), $FdcH_2$ (55.2 mg, 0.24 mmol), and 5 mL isopropanol were added into a 25 mL Teflon lined stainless steel autoclave. Then $Ti(O^iPr)_4$ (300 μL, 0.975 mmol) was added and transferred to an oven at 100 ℃ for 3 days. After cooling to room temperature, yellow needle-like crystals of **$\{Ti_{22}Fc_4\}$** and yellow plate-like crystals of **$\{Ti_{11}Fc_2\}$** were obtained in about 3:1 ratio. The two crystals are very different in color and shape, and can be separated manually. Total yield: about 80 mg.

Individual synthesis of the cluster $\{Ti_{22}Fc_4\}$. $DmgH_2$ (35 mg, 0.3 mmol), $FdcH_2$ (55.2 mg, 0.24 mmol), benzoic acid(29.3 mg, 0.24 mmol) or isonicotinic acid (29.5 mg 0.24 mmol), and 5 mL isopropanol were added into a 25 mL Teflon lined stainless steel autoclave. Then Ti $(O^iPr)_4$ (300 μL, 0.975 mmol) was added and transferred to an oven at 100 ℃ for 3 days. After cooling to room temperature, yellow needle-like crystals of **$\{Ti_{22}Fc_4\}$** were obtained, and only a very small amount of plate-shaped crystals of **$\{Ti_{11}Fc_2\}$** was found in the mother liquor. Total yield: about 75 mg.

Individual synthesis of cluster {$Ti_{11}Fc_2$}. $DmgH_2$ (35 mg, 0.3 mmol), $FdcH_2$ (55.2 mg, 0.24 mmol), and 6 mL isopropanol were added into a 25 mL Teflon lined stainless steel autoclave. Then Ti $(O^iPr)_4$ (500 μL, 1.63 mmol) was added and transferred to an oven at 120 ℃ for 3 days. After cooling to room temperature, a small amount of yellow plate-like crystals of **{$Ti_{11}Fc_2$}** was obtained (Yield: about 30 mg). However, almost no plate-like crystals of **{$Ti_{11}Fc_2$}** were found in the mother liquor.

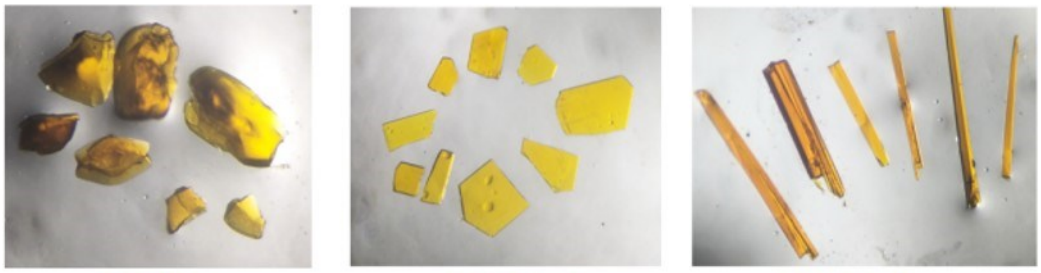

Figure S1. Crystal pictures of the clusters.

Photoelectrochemical measurements were performed on a CHI 660e electrochemical workstation in a standard three-electrode electrochemical cell with a working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode as the reference electrode. These three electrodes were immersed in the 0.2M Na_2SO_4 aqueous solution (pH = 6.6). A 300 W high-pressure xenon lamp with UV cut-off filter was used as a full-wavelength light source, located 20 cm away from the working electrode. The on−off cycling irradiation intervals are 20 s. The working electrode was prepared on fluorinedoped tin oxide (FTO) glass. The colloidal dispersion was obtained by ultrasonic treatment of 5 mg ground crystal sample in 1 ml ethanol for 30 min, and then the dispersion was dropped onto FTO glass (0.75 cm^2 area). After evaporation under an ambient atmosphere for 2 h, the coating film was obtained and used as the working electrode.

Typical procedure for the oxidation of amines. The photocatalytic reactions were carried out under irradiation by a Xe lamp (300 W, PLS-SXE 300, Beijing Trusttech Co.) equipped with a cutoff filter to filter out light below 420 nm and a broad band filter to cutoff light above 750 nm, with magnetic stirring in a 10 mL Pyrex glass bottle. The bottle was sealed with a rubber stopper wrapped in aluminum foil. Benzylamine (1 mmol), catalyst (0.02 mmol), TBHP (300 mL) and solvent (2 mL) were added in a glass bottle. The reaction was stirred at 70℃ under irradiation from the Xe lamp. After reaction, the mixtures were analyzed by GC and ^1H NMR. The catalysts were collected by filtration and washed with CH_3CN, and reused for the subsequent catalytic reactions.

2. Structure of Compounds

Table S1. X-ray measurements and structure solution of compounds.

Compounds	**{Ti_5Fc}**	**{$Ti_{11}Fc_2$}**	**{$Ti_{22}Fc_4$}**
CCDC	2053563	2053564	2053565
Formula	$C_{53}H_{85}N_3O_{22}Ti_5Fe$	$C_{83}H_{137}N_{10}O_{39}Ti_{11}Fe_2$	$C_{166}H_{274}N_{12}O_{80}Ti_{22}Fe_4$
F_w	1411.58	2537.62	4994.27
Crystal system	Triclinic	monoclinic	triclinic
Space group	P-1	$P2_1/c$	P-1
a, Å	13.5246(11)	21.8611(6)	22.0941(6)
b, Å	14.1422(11)	21.3692(5)	22.6404(7)
c, Å	20.7800(15)	25.6759(9)	25.2924(8)
α/°	78.353(3)	90	114.7150(10)
β/°	76.753(2)	110.058(3)	95.4110(10)
γ/°	63.302(2)	90	91.8360(10)
V, $Å^3$	3433.9(5)	11267.1(6)	11405.8(6)
Z	2	4	2
ρ_{calcd}(gcm^{-3})	1.365	1.468	1.447

μ (mm^{-1})	0.829	8.938	1.048
F(000)	1472.0	5124.0	5134.0
Data/restraints/parameter	13385/78/879	20948/88/1351	39999/283/2698
Goof	1.022	1.031	1.073
R_1/wR_2(I> 2σ(I))	0.0474/0.1186	0.0675/0.1689	0.0858/0.2366
R_1/wR_2(all data)	0.0640/0.1335	0.1018/0.1951	0.1631/0.2683

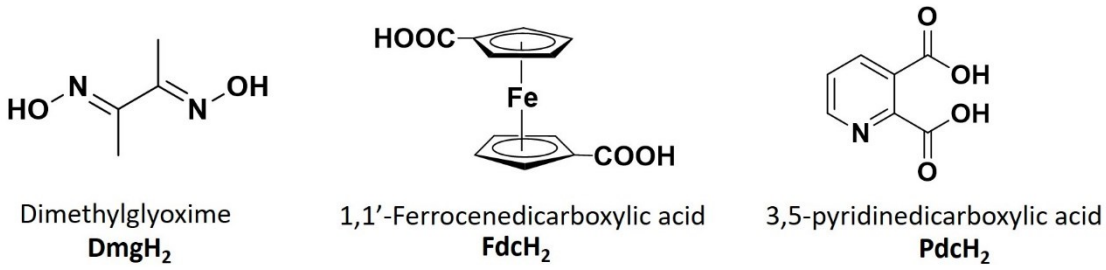

Figure S2. The molecular structures of all three ligands used in this work.

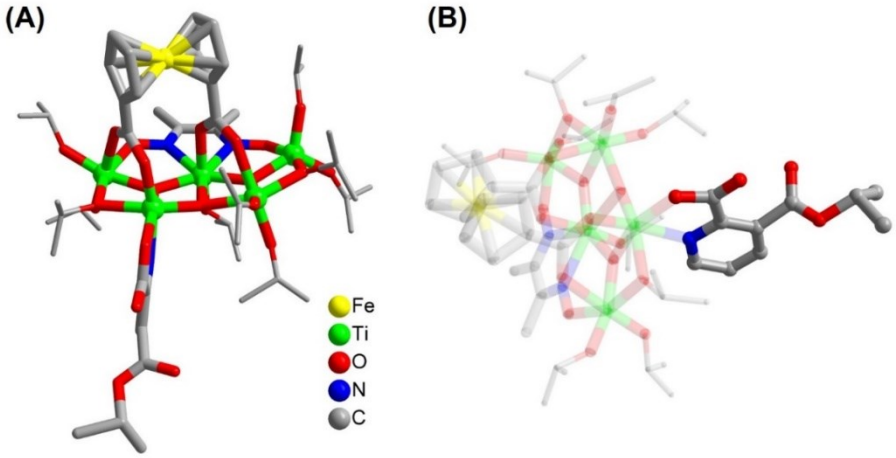

Figure S3. (A) Crystal structure of the cluster {**Ti_5Fc**}. (B) Pdc^{2-} ligand has three coordination groups, which are bonded to the Ti_5 layer through a pyridine N and a carboxylic O. Interestingly, another uncoordinated carboxylic group reacts with the isopropanol molecule in situ to form an ester bond.

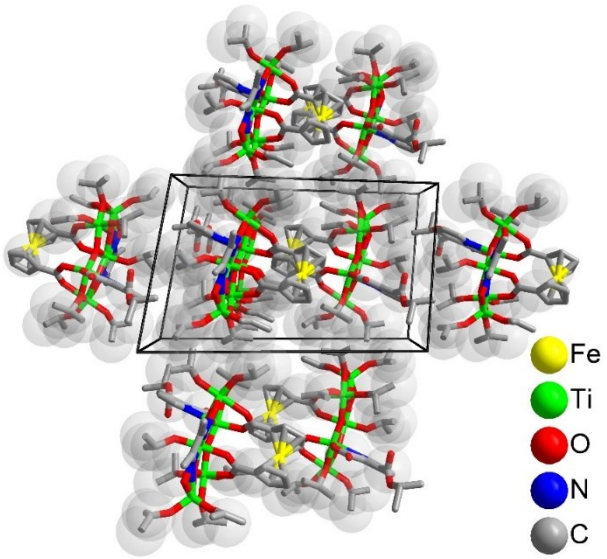

Figure S4. Three-dimensional packing structure of the cluster {**Ti_5Fc**}.

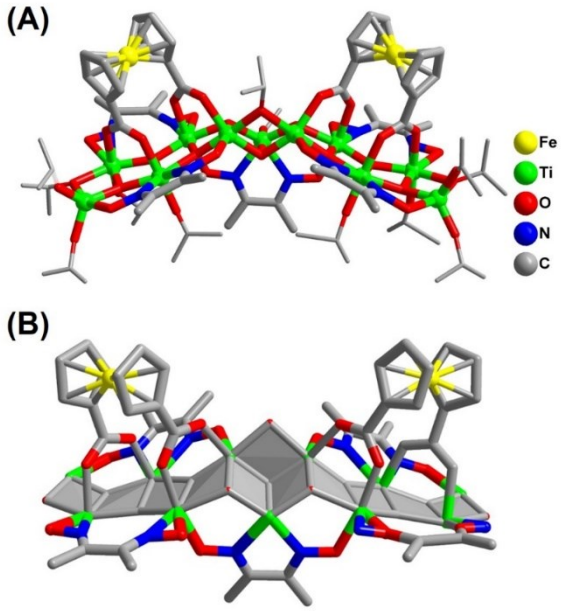

Figure S5. (A) Crystal structure of {**$Ti_{11}Fc_2$**}. (B) The simplified {Dmg_7@Fdc_2@Ti_{11}} unit in {**$Ti_{11}Fc_2$**}.

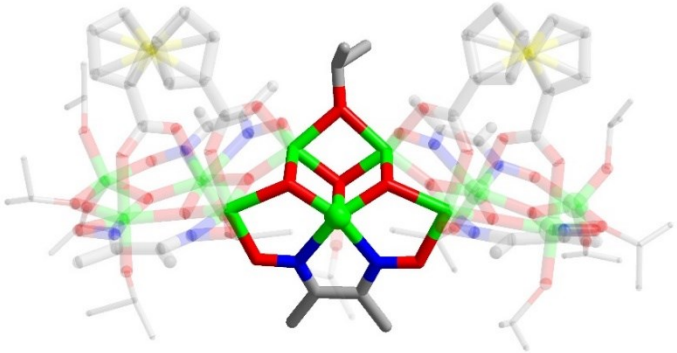

Figure S6. Two {Ti_5Fc} subunits are bridged together by one {Dmg@Ti} unit, three μ_3-O^{2-} atom and one O^iPr^- group.

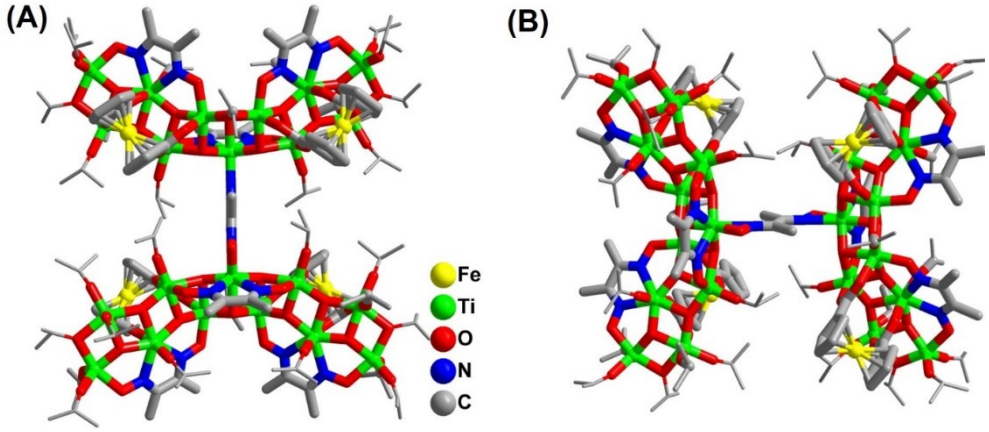

Figure S7. Two different perspectives of the crystal structure of {**$Ti_{22}Fc_4$**}

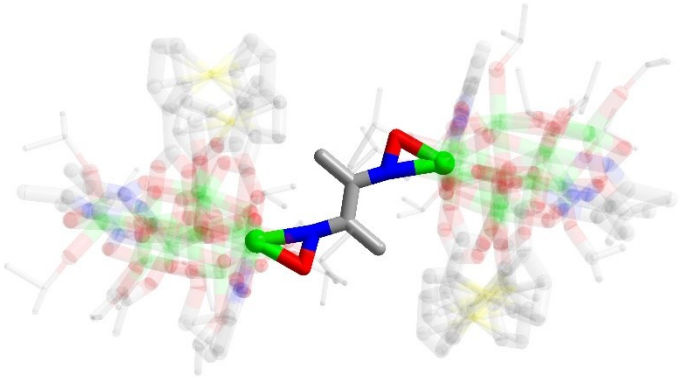

Figure S8. The big {$\mathbf{Ti_{22}Fc_4}$} structure can be viewed as two {Dmg_3@Fdc_2@Ti_{11}} half-clusters linked through a trans-Dmg^{2-} ligand.

3. XPS spectra of {$Ti_{22}Fc_4$}

The XPS spectra of {$\mathbf{Ti_{22}Fc_4}$} shows that the Ti 2p spectra has two peaks with binding energies of 457.6 and 463.6 eV, representing the $2p^{2/3}$ and $2p^{1/2}$ states of Ti(IV) respectively, while the Fe 2p peaks with binding energies of 706.9 and 719.6 eV correspond to electrons in the $2p^{2/3}$ and $2p^{1/2}$ states of Fe(II), respectively.

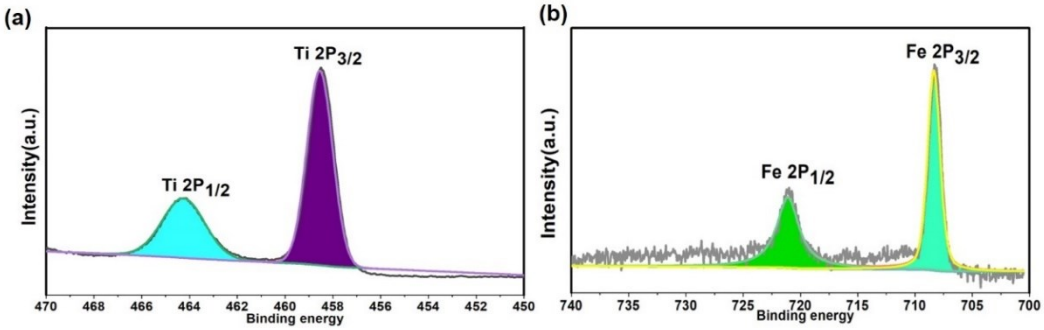

Figure S9. The XPS spectra of {$\mathbf{Ti_{22}Fc_4}$}.

4. . Powder X-ray diffraction

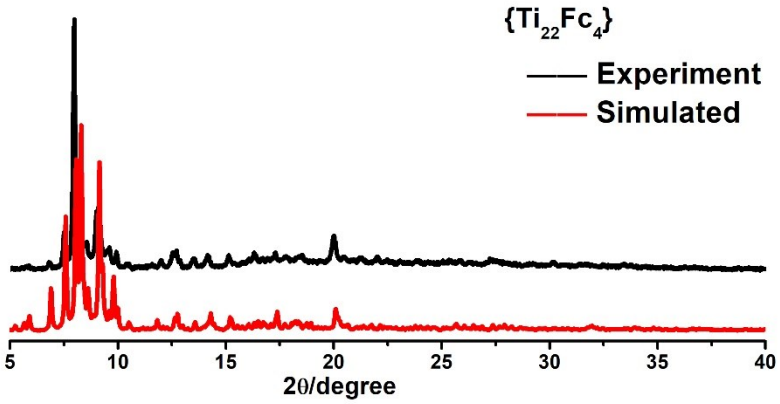

Figure S10. The XRD patterns of {$\mathbf{Ti_{22}Fc_4}$}.

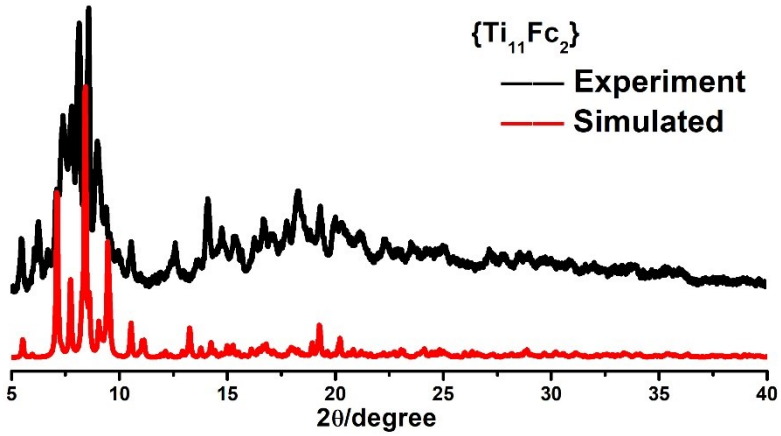

Figure S11. The XRD patterns of $\{Ti_{11}Fc_2\}$.

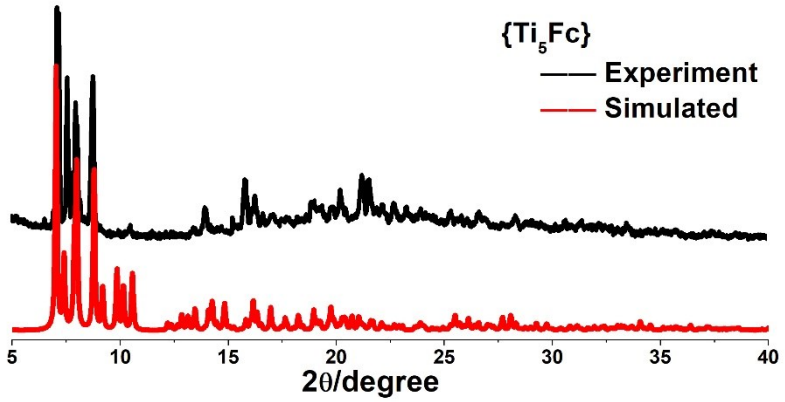

Figure S12. The XRD patterns of $\{Ti_5Fc\}$.

5. EDS patterns

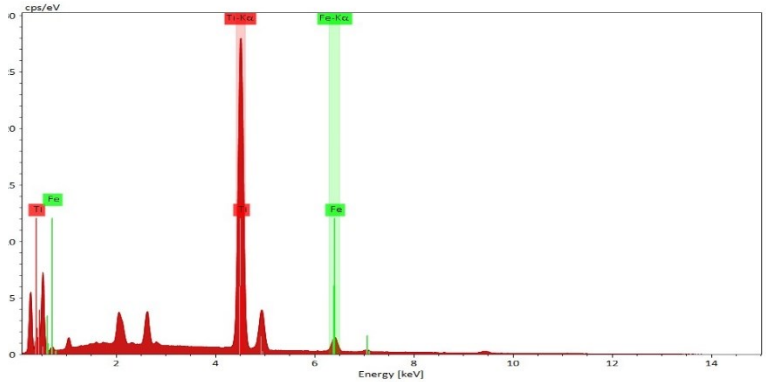

Figure S13. The EDS patterns of $\{\mathbf{Ti_5Fc}\}$.

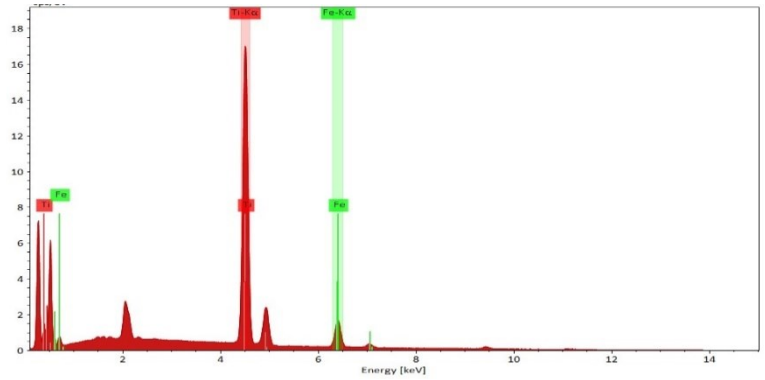

Figure S14. The EDS patterns of {$\mathbf{Ti_{11}Fc_2}$}.

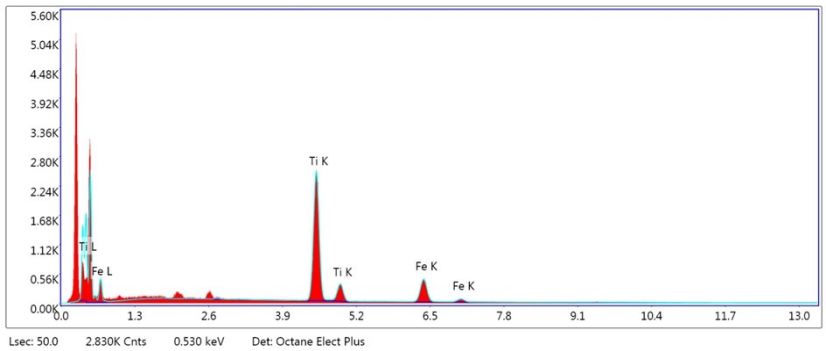

Figure S15. The EDS patterns of {$\mathbf{Ti_{22}Fc_4}$}.

6. IR spectra

Figure S20-22 shows the FTIR spectra of three clusters. The broad band between 3200-3500 cm^{-1} attributable to OH stretching. The strong vibration band at ca. 1620-1650 cm^{-1} can be ascribed to C=O stretching of the Fdc^{2-} ligand. The characteristic bands of Ti-O-C and Ti-O-Ti appears in the ranges of 1000–1200 and 700–800 cm^{-1}, respectively. The characteristic peak of Fe-C vibration of the f Fdc^{2-} ligand appears in the ranges of 500–600 cm^{-1}, respectively.

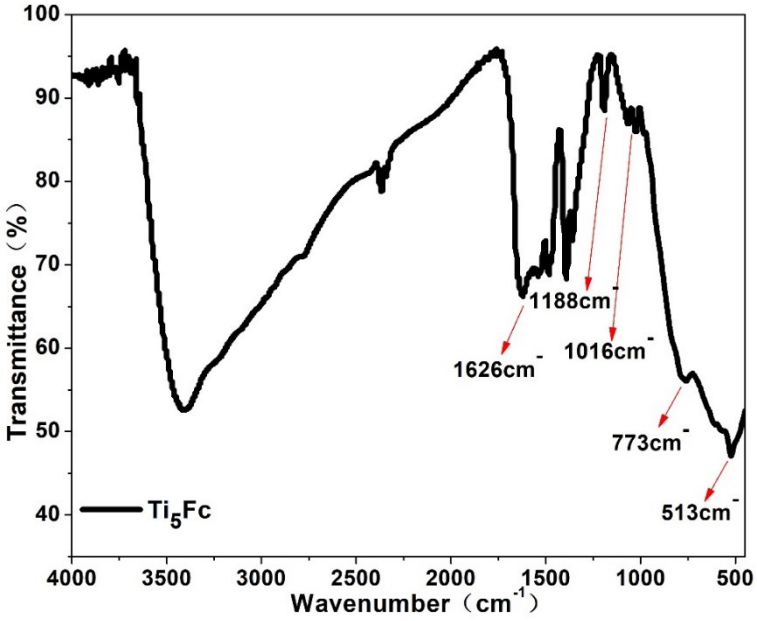

Figure S16. IR spectra of crystal sample of {$\mathbf{Ti_5Fc}$}.

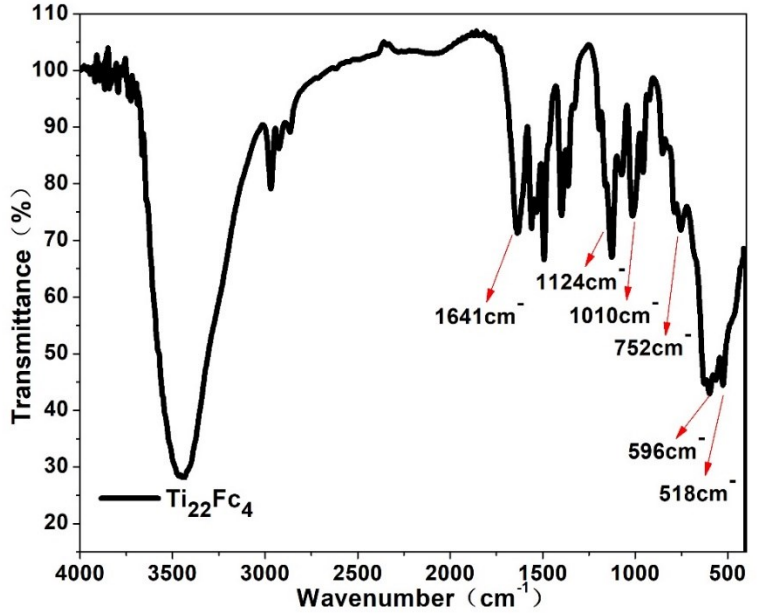

Figure S17. IR spectra of crystal sample of {$\mathbf{Ti_{11}Fc_2}$}.

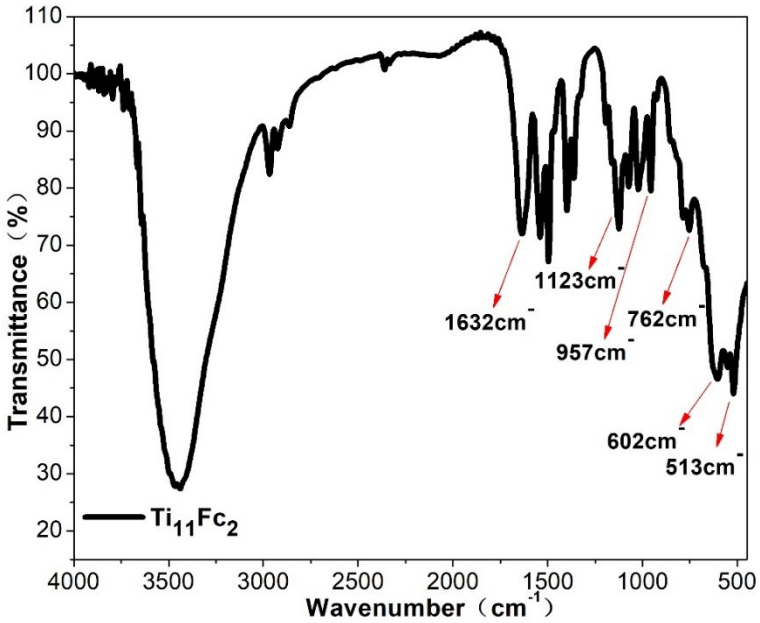

Figure S18. IR spectra of crystal sample of {$\mathbf{Ti_{22}Fc_4}$}.

7. TG-Measurement

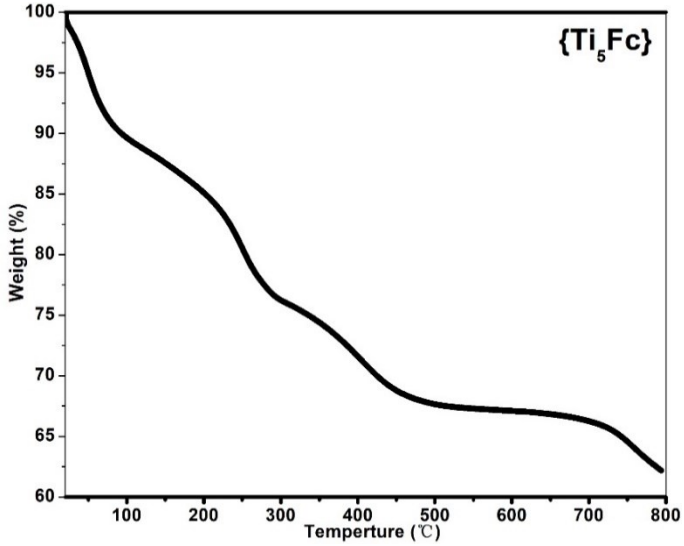

Figure S19. Thermal decomposition curve of {$\mathbf{Ti_5Fc}$}.

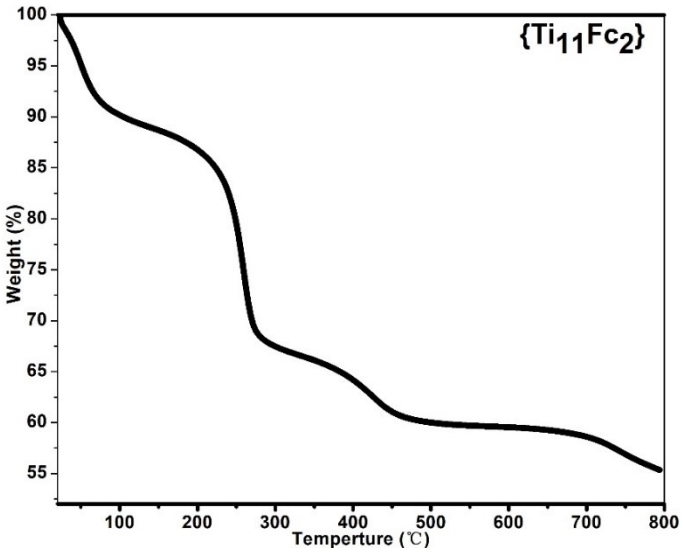

Figure S20. Thermal decomposition curve of {$\mathbf{Ti_{11}Fc_2}$}

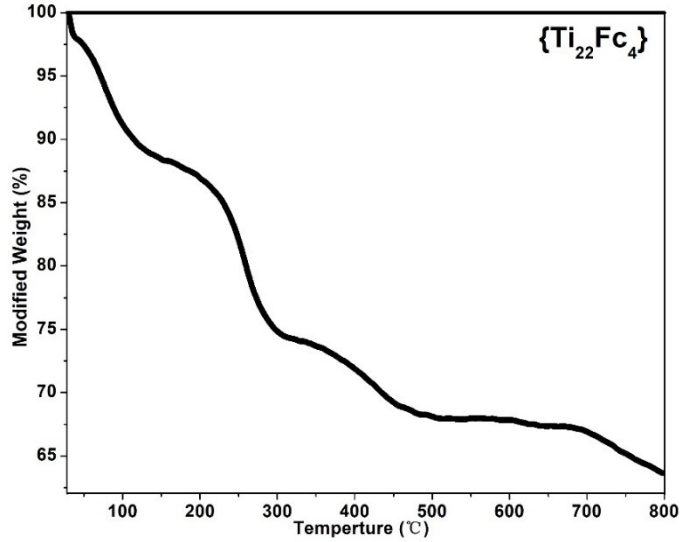

Figure S21. Thermal decomposition curve of {$Ti_{22}Fc_4$}.

8. ESI-MS measurements.

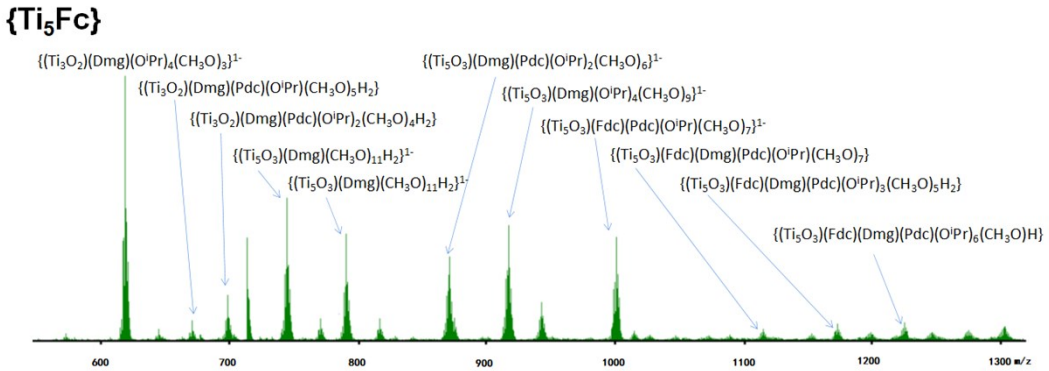

Figure S22. ESI-MS spectrum of the CH_3OH solution of **{$\mathbf{Ti_5Fc}$}**.

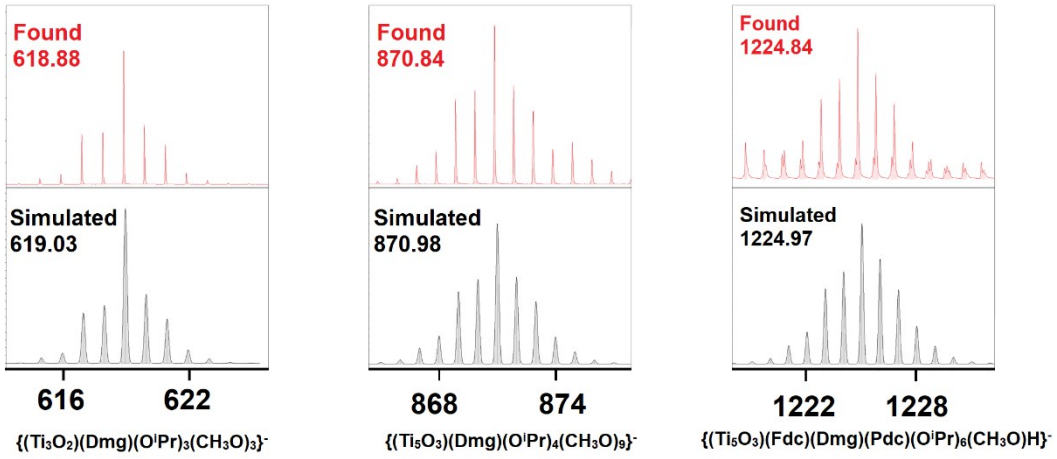

Figure S23. The isotope distributions of main peaks of ESI-MS spectrum of {**Ti5Fc**}.

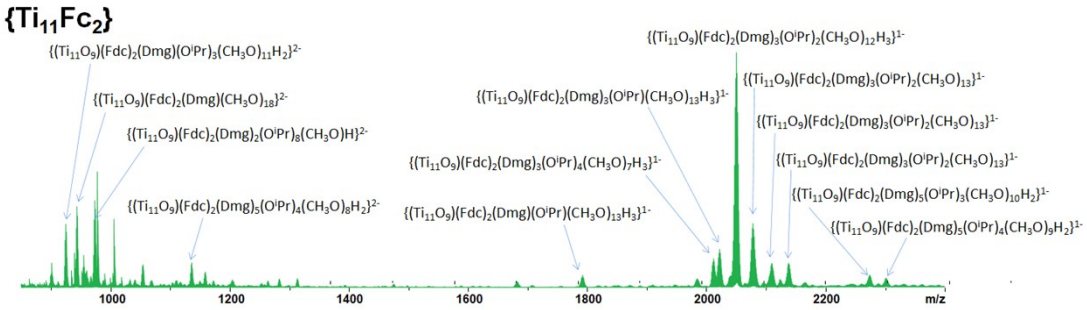

Figure S24. ESI-MS spectrum of the CH_3OH solution of **{$Ti_{11}Fc_2$}**.

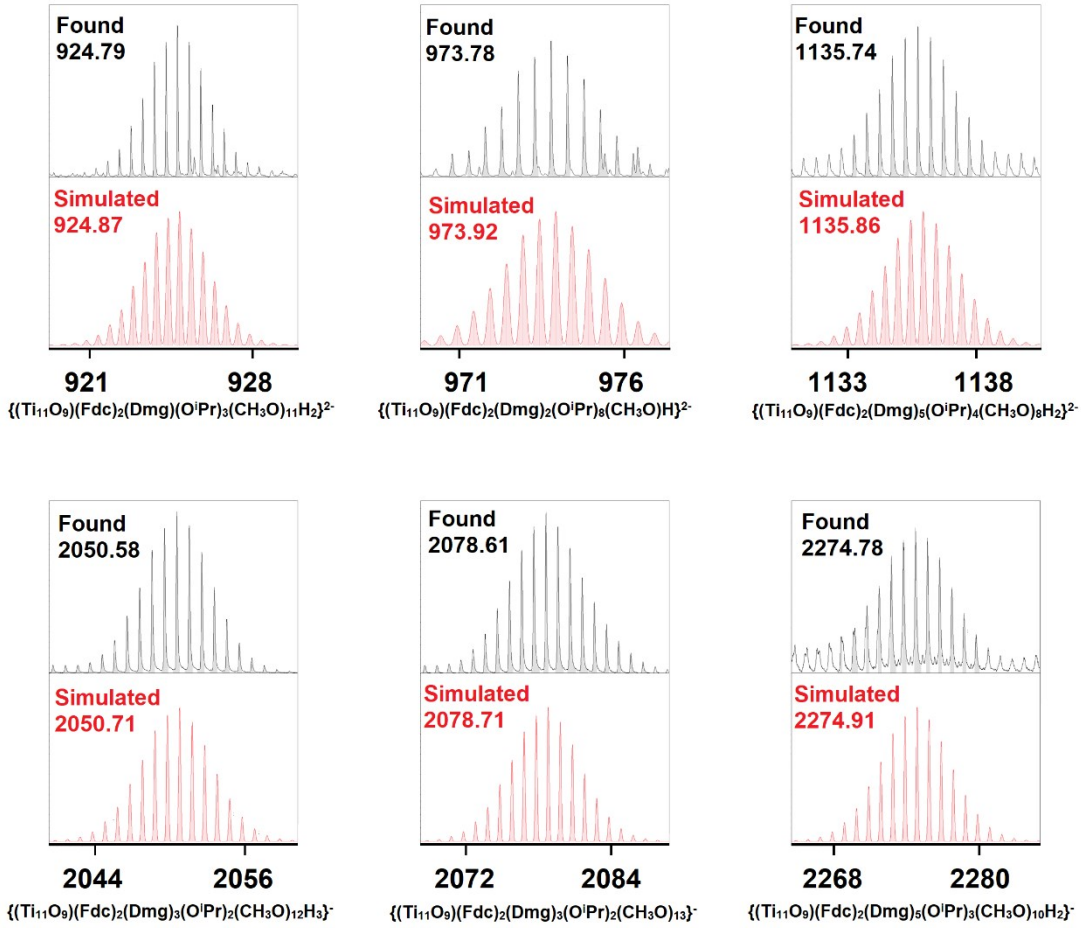

Figure S25. The isotope distributions of main peaks of ESI-MS spectrum of **{$Ti_{11}Fc_2$}**.

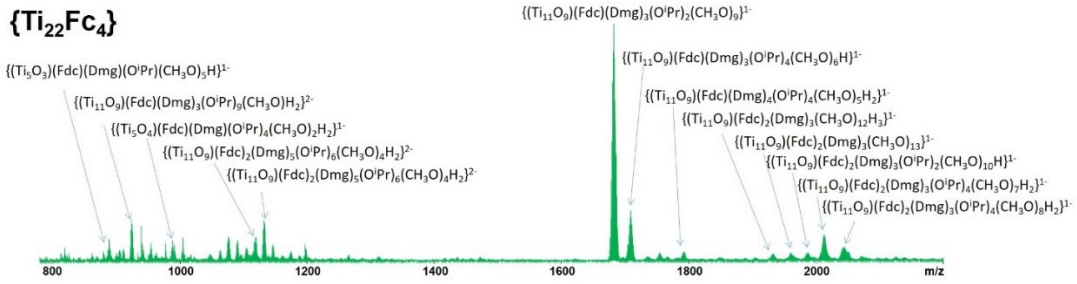

Figure S26. ESI-MS spectrum of the CH_3OH solution of **{$Ti_{22}Fc_4$}**.

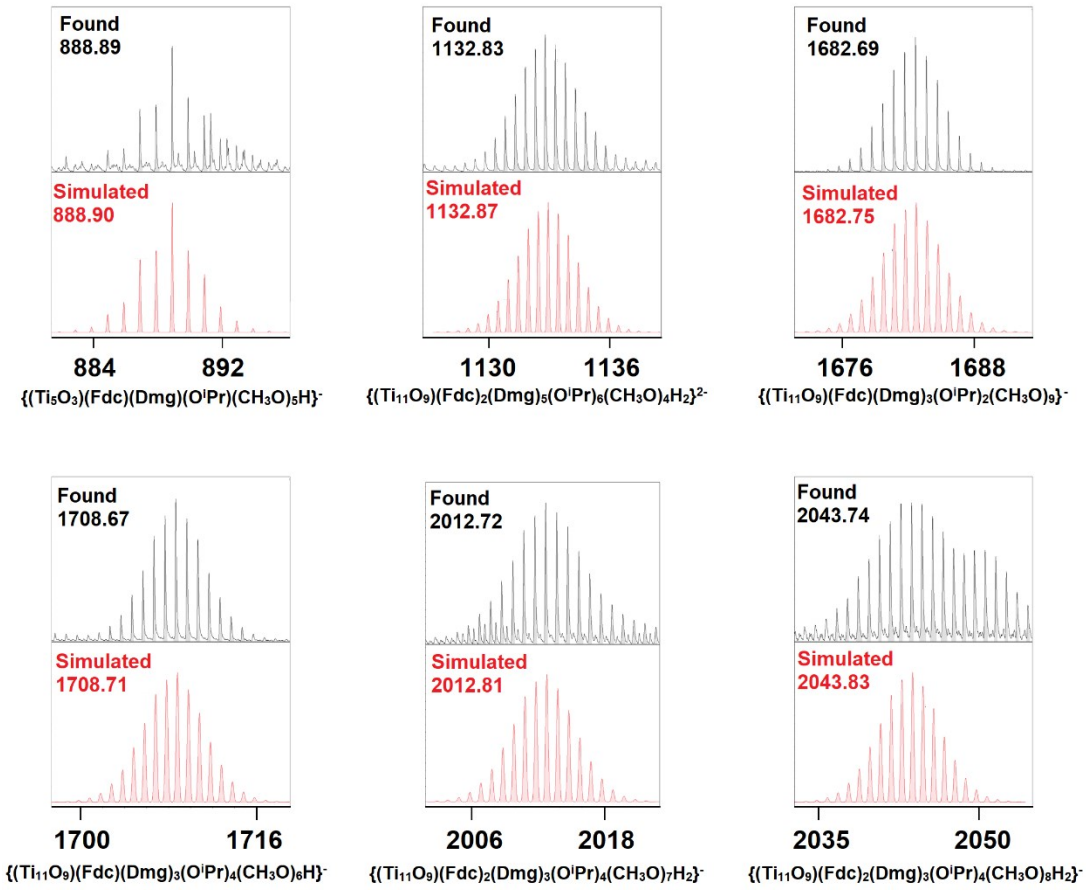

Figure S27. The isotope distributions of main peaks of ESI-MS spectrum of **{$Ti_{22}Fc_4$}**.

10 Photocatalysis

Table S2. The optimization of different reaction conditions of benzylamine to N-benzylidine-1-phenylmethanamine [a]

Entry	Cat.	Sol.	Temp.(℃)	TBHP(μL)	Yield(%) [b]
1	**{Ti_5Fc}**	CH_3CN	70	300	99
2	none	CH_3CN	70	300	12
3	**{Ti_5Fc}**	CH_3CN	70	0	4
4	**{Ti_5Fc}**	CH_3CN	70	(H_2O_2) 300	2
5	**{Ti_5Fc}**	CH_3CN	70	(O_2) 1 atm	3
6	**{Ti_5Fc}**	CH_3CN	70	100	59
7	**{Ti_5Fc}**	CH_3CN	70	200	79
8[c]	**{Ti_5Fc}**	CH_3CN	70	350	92
9	**{Ti_5Fc}**	CH_3CN	45	300	94
10	**{Ti_5Fc}**	CH_3CN	20	300	88
11	**{Ti_5Fc}**	Ethanol	70	300	80
12	**{Ti_5Fc}**	Toluene	70	300	77
13	**{Ti_5Fc}**	1,4-Dioxane	70	300	12
14	**{Ti_5Fc}**	DMF	70	300	65
15	**{Ti_5Fc}**	DMSO	70	300	40
16[d]	**{Ti_5Fc}**	CH_3CN	70	300	27
17	**{$Ti_{11}Fc_2$}**	CH_3CN	70	300	95

18	**{$Ti_{22}Fc_4$}**	CH_3CN	70	300	90

[a] Reaction conditions: substrate, benzylamine (110 μL, 1 mmol); catalyst (0.02 mmol); solvent (2 mL); TBHP=tert-butyl hydroperoxide; 12 h. [b] Determined by GC analysis and ^{1}H NMR, and the selectivity of imine is over 99% unless specifically mentioned. [c] Convention of benzylidine is 99%, selectivity of *N*-benzylidine-1-phenylmethanamine is 95%. [d] Using sunlight replaces Xe lamp.

Table S3. The time conversion for benzylamine to N-benzylidine-1-phenylmethanamine under the optimization condition [a]

Entry	Cat.	Oxidant	Time	Addition	Yield [b]
1	**{Ti_5Fc}**	TBHP	3	None	50%
2	**{Ti_5Fc}**	TBHP	5	None	81%
3	**{Ti_5Fc}**	TBHP	8	None	95%
4	**{Ti_5Fc}**	TBHP	10	None	98%
5	**{Ti_5Fc}**	TBHP	12	None	99%
6	**{$Ti_{11}Fc_2$}**	TBHP	3	None	52%
7	**{$Ti_{11}Fc_2$}**	TBHP	5	None	76%
8	**{$Ti_{11}Fc_2$}**	TBHP	8	None	88%
9	**{$Ti_{11}Fc_2$}**	TBHP	10	None	93%
10	**{$Ti_{11}Fc_2$}**	TBHP	12	None	95%
11	**{$Ti_{22}Fc_4$}**	TBHP	3	None	50%
12	**{$Ti_{22}Fc_4$}**	TBHP	5	None	76%
13	**{$Ti_{22}Fc_4$}**	TBHP	8	None	85%
14	**{$Ti_{22}Fc_4$}**	TBHP	10	None	89%
15	**{$Ti_{22}Fc_4$}**	TBHP	12	None	90%

[a] Reaction conditions: substrate, benzylamine (110 μL, 1 mmol), catalyst (0.02 mmol), TBHP (300 μL), solvent (2 mL), Xe lamp. [b] Determined by GC analysis and ^{1}H NMR.

Table S4. The optimization of different reaction conditions of benzylamine to *N*-benzylidine-1-phenylmethanamine [a]

Entry	Cat.	Oxidant	Time	Addition	Yield [b]
1	**{Ti_5Fc}**	TBHP	12	benzoquinone	42%
2	**{Ti_5Fc}**	TBHP	12	EDTA-2Na	56%
3	**{Ti_5Fc}**	TBHP	12	$Mn(CH_3COO)_2$	47%
4	Fc	TBHP	70	300	12
5	TiO_2	TBHP	70	300	18
6	Fc+TiO_2[c]	TBHP	12	None	40%

[a] Reaction conditions: substrate, benzylamine (110 μL, 1 mmol), catalyst (0.02 mmol), TBHP (300 μL), solvent (2 mL), Xe lamp. [b] Determined by GC analysis and ^{1}H NMR. [c] The mixture were obtained by griding of Fc and TiO_2 with the molar ratio of 1:1.

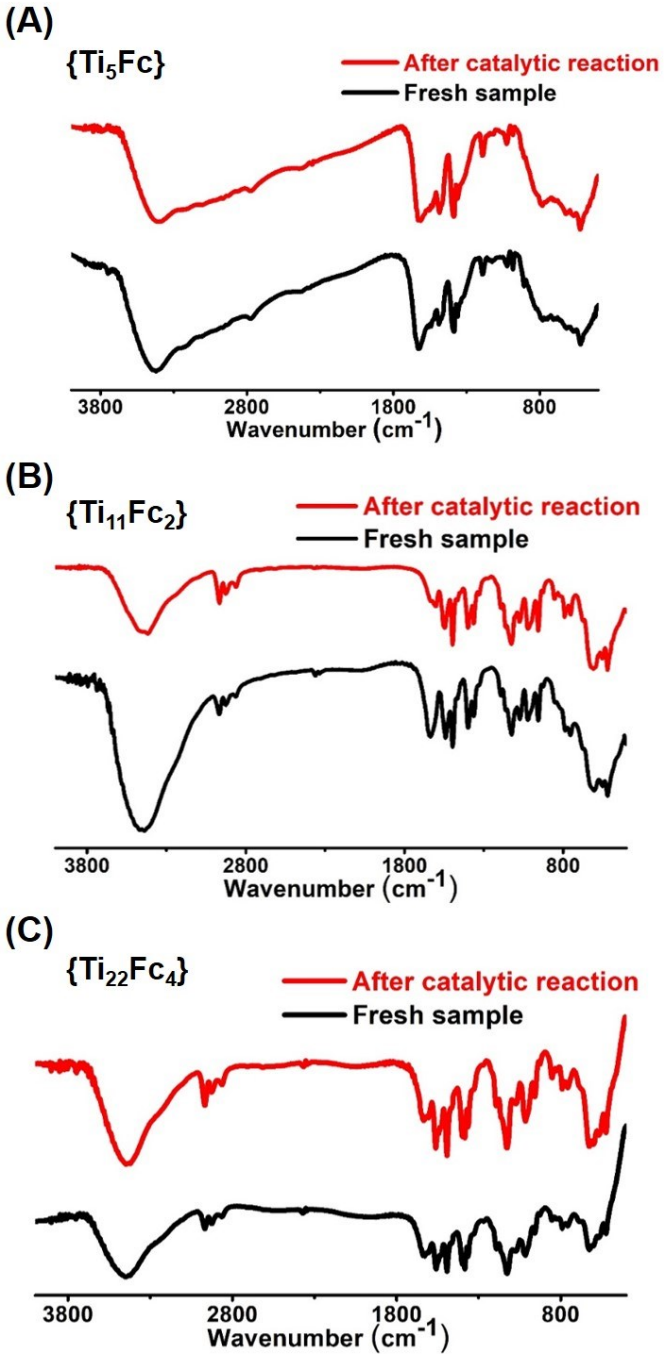

Figure S28. The IR spectrum of **{Ti_xFc_y}** before and after reaction.

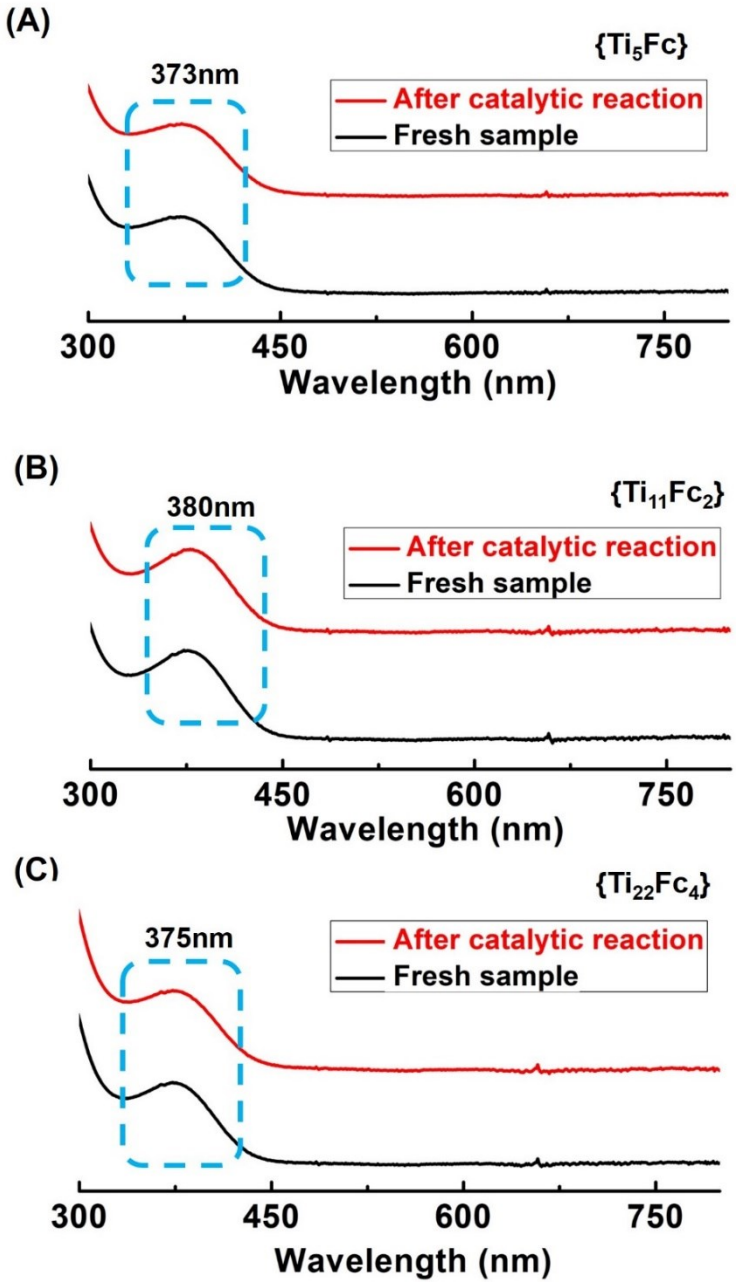

Figure S29. The solution-state UV-Vis spectra of three clusters before and after reaction.

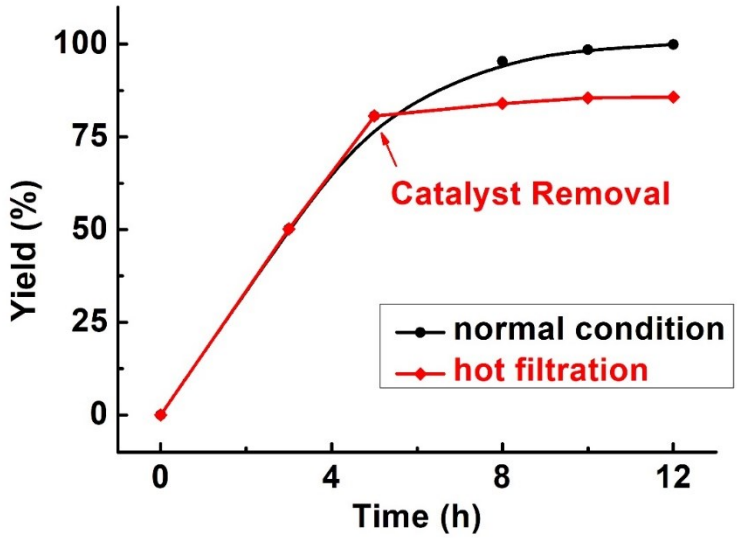

Figure S30. Hot-filtration test of benzylamine oxidation reaction catalytic by **{Ti_5Fc}** at optimal condition.

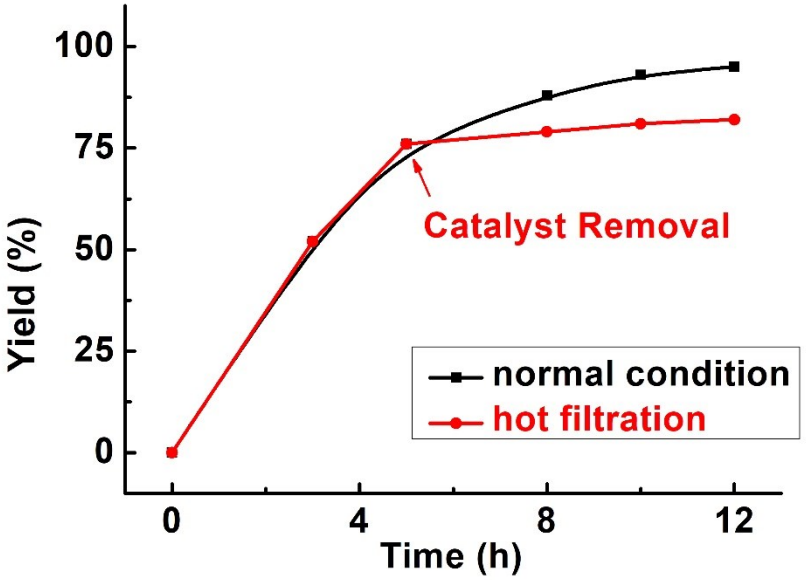

Figure S31. Hot-filtration test of benzylamine oxidation reaction catalytic by **{$Ti_{11}Fc_2$}** at optimal condition.

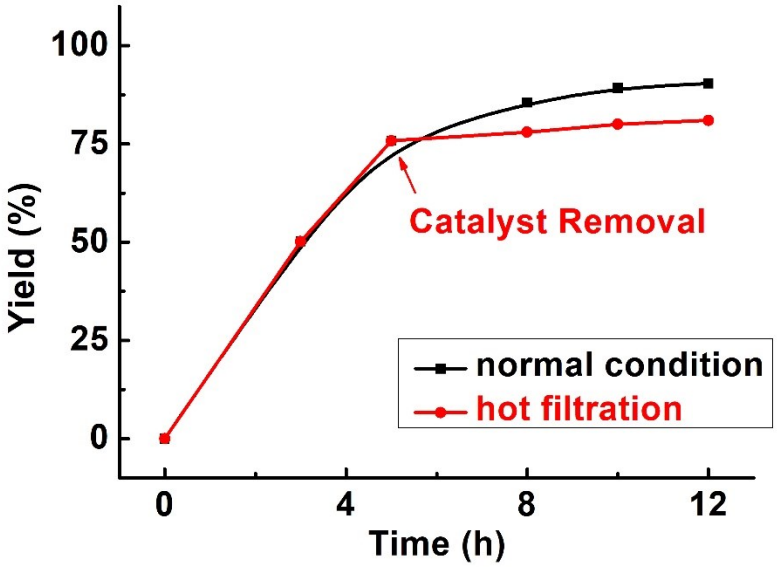

Figure S32. Hot-filtration test of benzylamine oxidation reaction catalytic by **{$Ti_{22}Fc_4$}** at optimal condition.

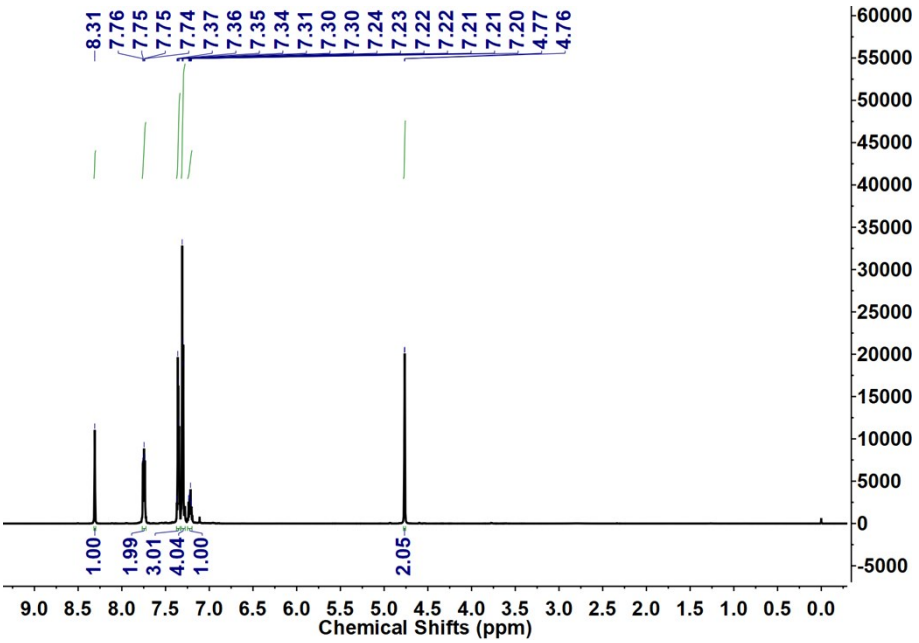

Figure S33. The ^{1}H NMR spectra of N-benzylidine-1-phenylmethanamine.

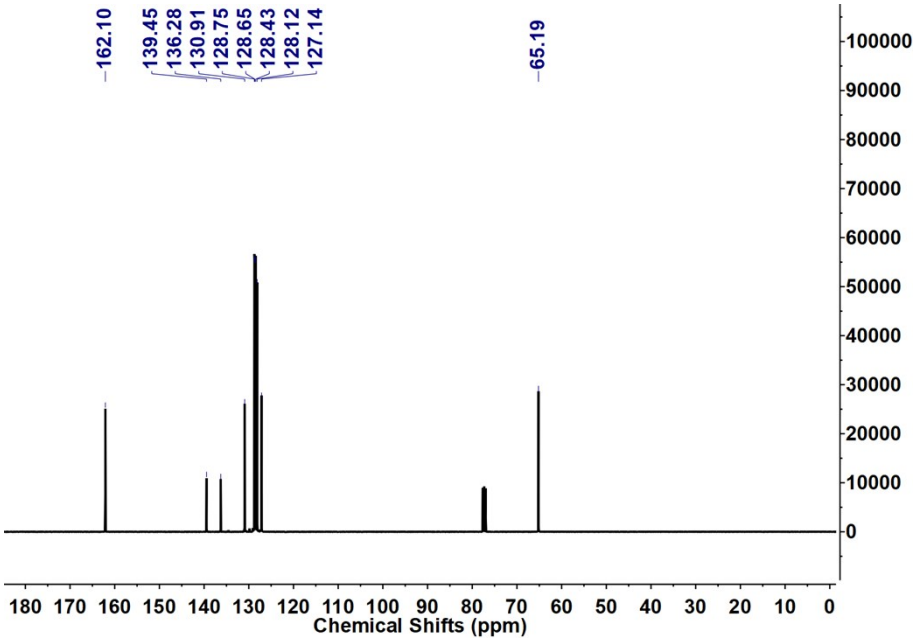

Figure S34. The ^{13}C NMR spectra of *N*-benzylidine-1-phenylmethanamine.