

## Supporting Information

### Bilateral photocatalytic Mechanism of Dye Degradation by a Target Designed Ferrocene -Functionalized Cluster under Natural Sunlight

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#### 1. Materials and methods

##### 1.1 Material

Hydrogen peroxide, Methylene Blue, methanol, Ag<sub>2</sub>O, Cu<sub>2</sub>O, NH<sub>3</sub>, Fc(COOH)<sub>2</sub> and triphenylphosphine were purchased from Merck or Fluka Co and used as received without further purification. All chemicals used in this study were of analytical grade. All of the solutions used were prepared daily, with deionized water made from the Millipore system.

##### 1.2 Procedures

Both the adsorption and the photodegradation experiments were performed in 250 mL glass vessels. A water bath system was used to keep the temperature in the range of 313-283 ± 1 °C for kinetic studies. The initial solution pH values were recorded and pH values adjusted with 0.1 mol/L HNO<sub>3</sub> and 0.1 mol/L NaOH. The adsorption of MB was investigated by putting the solutions in contact with a 10 mg of clysters until equilibrium; during adsorption experiments, slurry composed of dye solution and catalyst suspension was stirred magnetically and placed in

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the dark for the adsorptive removal of MB. Samples were picked up and detected after filtration. 100 $\mu$ l of H<sub>2</sub>O<sub>2</sub> was added into vessel, to initiate the heterogenous Fenton and Fenton-like catalyzed by the photocatalyst in solution. Samples were withdrawn at predetermined time intervals, and detected immediately. All solutions were thoroughly stirred to make them well-distributed before the addition of the reagents. Degradation reactions were started with the addition of H<sub>2</sub>O<sub>2</sub>. Finally, the reaction solution was filtered to separate the catalyst particles out for analysis. Experiments were carried out at least for time, and all results were expressed as a mean value. The error between replicate runs was maintained to within 4%.

### 1.3 Analysis

The concentrations of remained Methylene Blue in solution were detected by a UV-visible spectrophotometer (Shimadzu, 2450) at 660 nm, corresponding to the maximum absorbance of MB. All samples centrifuged by 14000 Cycle-min and then filtered through a 0.45  $\mu$ m filter film. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm<sup>-1</sup> with a WQF-520A FT-IR spectrometer. The powder X-ray diffraction (PXRD) pattern was recorded with DX-2700 X-ray diffractometer. The solid UV-vis diffuse reflectance spectra were recorded on a Cary-5000 spectrophotometer at room temperature. The TGA curve was recorded on Q50 Thermogravimetric Analyzer (The sample was heated from 20 °C to 800 °C at 10 °C/min) under neutral N<sub>2</sub> atmosphere. The electrochemical measurements were conducted on a CHI-660D electrochemical workstation (CH Instruments, Inc.). Voltammetric experiments were carried out in 0.1 M n-Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> solution / CH<sub>2</sub>Cl<sub>2</sub> and N<sub>2</sub> degassed) at room temperature (25 °C) using a conventional three electrode cell consisting of a Pt (2 mm diameter) working electrode, a platinum wire counter electrode, and a home-made silver/silver chloride (Ag/AgCl) wire pseudoreference electrode. All potentials were reported versus the redox couple of internal

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ferrocene/ferrocenium ( $\text{Fc} / \text{Fc}^+$ ) standard. Among all the methods, voltammetric techniques have become versatile tool as they can overcome the limitation of other methods, and provide better sensitivity, simplicity, less time consuming and low detection limit in the quantitative measurements than other methods.

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Table S1. Crystal data and structure refinement of D<sub>1</sub> and D<sub>2</sub> clusters.

Identification code	D <sub>1</sub>	D <sub>2</sub>
Chemical formula	C <sub>122.5</sub> H <sub>108.5</sub> Cu <sub>2</sub> Fe O <sub>7</sub> P <sub>6</sub>	C <sub>175</sub> H <sub>164</sub> Ag <sub>4</sub> Fe <sub>2</sub> O <sub>15</sub> P <sub>8</sub>
computing_structure_refinement	SHELXL-2014/7	SHELXL-2014/7
Chemical formula weight	2061.34	3297.99
T(K)	150(2)	150(2)
Crystal syst	Orthorhombic	Monoclinic
Space group	P <sub>bca</sub>	P2 <sub>1</sub>
a (°A)	24.582(3)	13.2313(9)
b (°A)	20.281(2)	30.795(2)
c (°A)	40.461(5)	18.5560(12)
$\alpha$ (deg)	90	90
$\beta$ (deg)	90	94.183(2)
$\gamma$ (deg)	90	90
V (Å <sup>3</sup> )	20172(4)	7540.5(9)
Z	8	2
F(000)	8588	3388
R(int)	0.0809	0.0392
Goodness-of-fit on $F^2$	1.063	1.089
wR factor	0.1398	0.0672
CCDC number	1947012	1947011

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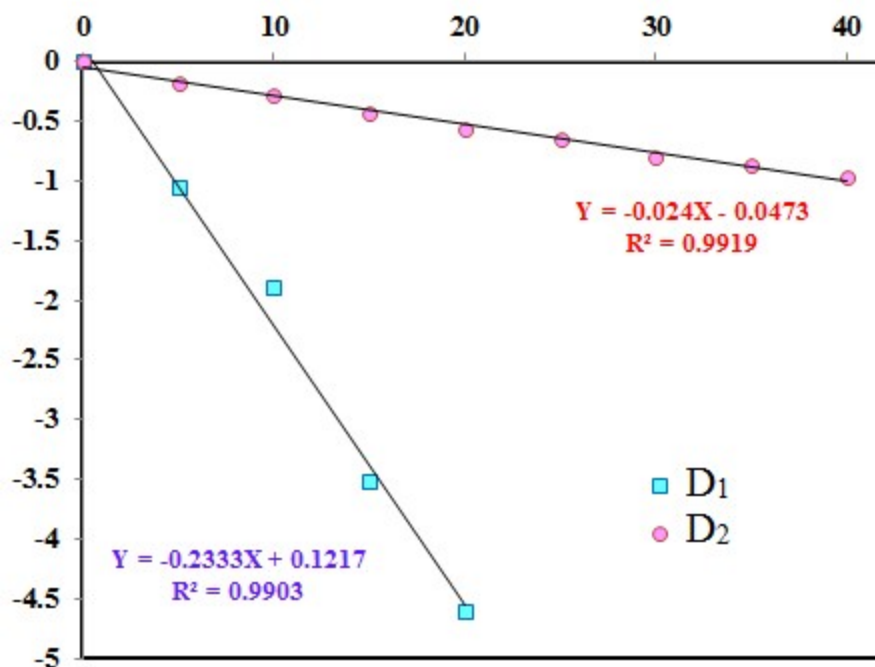
**Table S.2.** Selected bond length and angle for D<sub>1</sub> complex.

<b>Bond</b>	<b>(Å)</b>	<b>Angle</b>	<b>(°)</b>
<b>Cu<sub>1</sub>-P<sub>1</sub></b>	2.337(1)	<b>O<sub>1</sub>-Cu<sub>1</sub>-P<sub>1</sub></b>	114.45(7)
<b>Cu<sub>1</sub>-P<sub>2</sub></b>	2.3214(9)	<b>O<sub>1</sub>-Cu<sub>1</sub>-P<sub>2</sub></b>	106.26(7)
<b>Cu<sub>1</sub>-P<sub>3</sub></b>	2.3468(9)	<b>O<sub>1</sub>-Cu<sub>1</sub>-P<sub>3</sub></b>	87.37(7)
<b>Cu<sub>2</sub>-P<sub>4</sub></b>	2.3646(9)	<b>O<sub>4</sub>-Cu<sub>2</sub>-P<sub>4</sub></b>	90.80(7)
<b>Cu<sub>2</sub>-P<sub>5</sub></b>	2.3285(9)	<b>O<sub>4</sub>-Cu<sub>2</sub>-P<sub>5</sub></b>	1.6.93(7)
<b>Cu<sub>2</sub>-P<sub>6</sub></b>	2.325(1)	<b>O<sub>4</sub>-Cu<sub>2</sub>-P<sub>6</sub></b>	114.49(7)
<b>Cu<sub>1</sub>-O<sub>1</sub></b>	2.081(2)	<b>C<sub>1</sub>-C<sub>12</sub>-O<sub>1</sub></b>	116.4(3)
<b>Cu<sub>1</sub>-O<sub>4</sub></b>	2.072(2)	<b>C<sub>1</sub>-C<sub>12</sub>-O<sub>2</sub></b>	118.2(3)

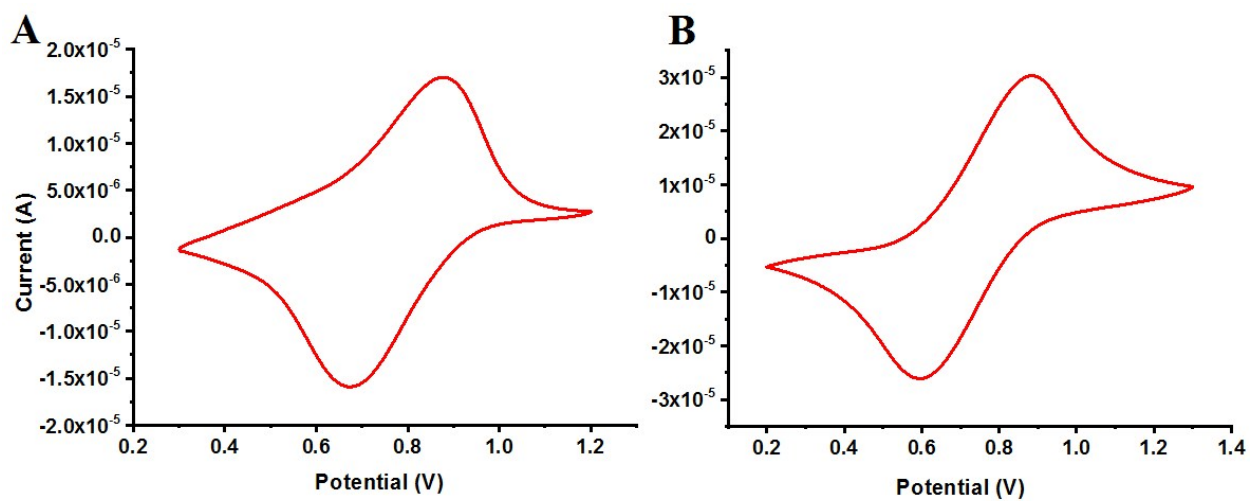
**Table S.3.** Selected bond length and angles for D<sub>2</sub> complex.

<b>Bond</b>	<b>(Å)</b>	<b>Angle</b>	<b>(°)</b>
<b>Ag<sub>1</sub>-P<sub>1</sub></b>	2.420(1)	<b>O<sub>1</sub>-Ag<sub>1</sub>-O<sub>2</sub></b>	52.5(1)
<b>Ag<sub>1</sub>-P<sub>2</sub></b>	2.435(1)	<b>O<sub>1</sub>-Ag<sub>1</sub>-P<sub>1</sub></b>	113.1(1)
<b>Ag<sub>2</sub>-P<sub>3</sub></b>	2.434(1)	<b>O<sub>1</sub>-Ag<sub>1</sub>-P<sub>2</sub></b>	110.9(1)
<b>Ag<sub>2</sub>-P<sub>4</sub></b>	2.445(1)	<b>O<sub>2</sub>-Ag<sub>1</sub>-P<sub>1</sub></b>	113.1(1)
<b>Ag<sub>1</sub>-O<sub>1</sub></b>	2.392(4)	<b>P<sub>1</sub>-Ag<sub>1</sub>-P<sub>2</sub></b>	126.56(5)
<b>Ag<sub>1</sub>-O<sub>2</sub></b>	2.585(4)	<b>O<sub>3</sub>-Ag<sub>2</sub>-O<sub>4</sub></b>	51.7(1)
<b>Ag<sub>2</sub>-O<sub>3</sub></b>	2.350(4)	<b>O<sub>3</sub>-Ag<sub>2</sub>-P<sub>3</sub></b>	115.0(1)

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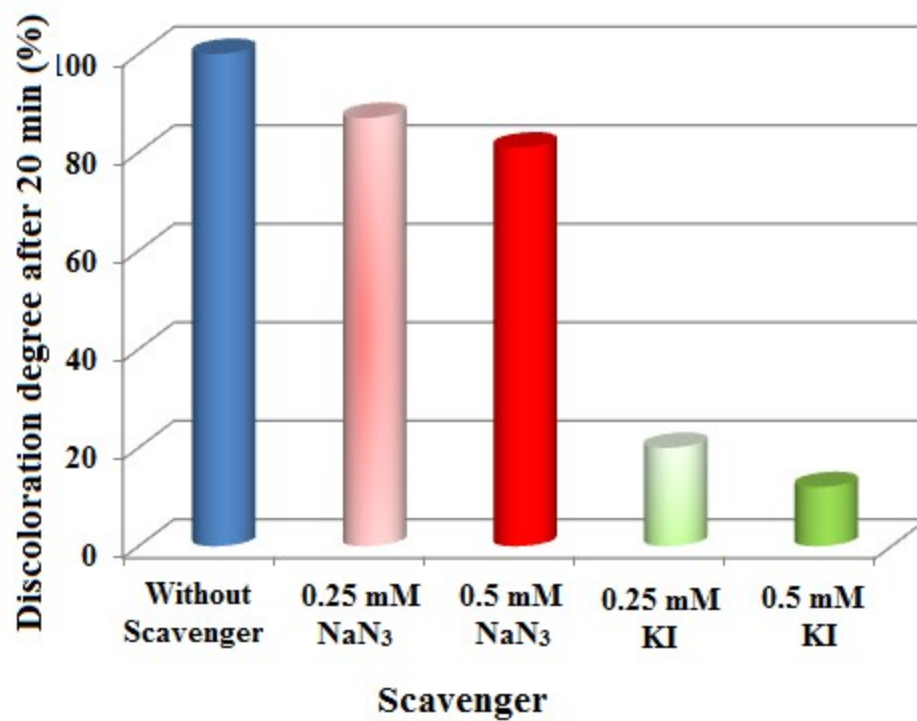


**Figure S1.** Photodegradation rate of the MB solutions with D<sub>1</sub> and D<sub>2</sub> under sunlight illumination.



**Figure S2.** The CV curves of D<sub>1</sub>(A) and D<sub>2</sub>(B).

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**Figure S3.** Effect of different amount of scavengers on photocatalytic performance of D<sub>1</sub>.