

二茂铁功能化的金属有机大环模拟氢化酶光催化硝基还原

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摘要: 使用二茂铁构筑了2个新型金属有机大环: $\mathbf{M}_{Cu}$ 和 $\mathbf{M}_{Fe}$ 。2个大环化合物有效猝灭了有机染料的荧光, 并可触发光致电子转移。较低的还原电位导致 $\mathbf{M}_{Cu}$ 在光催化质子还原和硝基还原2个反应中表现出更好的催化性能。底物的大尺寸导致硝基还原过程的效率降低。用 Michaelis-Menten 机理对光催化体系进行了验证, 揭示了底物与催化剂之间相互作用的重要性。

关键词: 金属有机大环; 二茂铁; 光催化; 超分子; Michaelis-Menten 机理

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Ferrocene-Functionalized Metal-Organic Macrocycles Mimicking Hydrogenase for Photocatalytic Nitro Reduction

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Abstract: Two novel metal-organic macrocycles ($\mathbf{M}_{Fe}$ and $\mathbf{M}_{Cu}$) were constructed using the flexible and redox-active ferrocene ligand. The macrocycles effectively quenched the fluorescence of organic dyes and exhibited the capability to trigger the photoinduced electron transfer. Due to relatively lower reduction potentials, $\mathbf{M}_{Cu}$ exhibited better catalytic features for proton reduction and could better catalyze the reduction of nitro compounds. The large size of the substrates leads to a decreased efficiency in the nitro reduction process. The Michaelis-Menten mechanism was used to verify the photocatalytic system, which revealed the importance of the interaction between substrate and catalyst. CCDC: 2166465, $\mathbf{M}_{Cu}$; 2166466, $\mathbf{M}_{Fe}$.

Keywords: metal-organic macrocycle; ferrocene; photocatalytic; supramolecule; Michaelis-Menten mechanism

0 Introduction

Enzymes in nature utilize their internal microenvironment containing various functional groups to carry out the efficient chemical transformation of various substrates under normal conditions^[1-2]. Supramolecular chemists are committed to simulating the structural characteristics and action mechanism of enzymes using supramolecules with redox-active metal sites and hydrophobic cavities, which can be further functional-

ized and applied in synthetic chemistry^[2-3]. Designed metal-organic supramolecules with specific hydrophobic cavities and functionalized activation sites can act as catalytic hosts^[4]. By recognizing and activating substrate molecules through host-guest interactions, a highly efficient and selective transformation of particular substrates^[5], such as aldehydes^[6], nitro compounds^[7], alkenes, or alkynes^[8], can be achieved. Metal-organic macrocycles are constructed by coordination between functionalized ligands and redox-active transi-

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tion metal centers. In addition, modifying the cavity with functionalized groups to change the cavity structure to adapt to the shape of different substrates or to introduce various properties are attractive routes in the enzyme mimetic process^[9].

Transition metal centers in metal-organic macrocycles can temporarily store energy and electrons by switching between redox states^[10]. After encapsulating dyes, fast electron transfer between the excited dye molecules and metal centers can be achieved through pseudo-intramolecular pathways^[11]. Thereby accelerating and stabilizing the charge separation state generated in the photocatalytic reaction. The host-guest combination supramolecular strategy has broad applications and has been demonstrated in the fields of combining organic dyes to simulate natural photocatalytic systems for specific organic small molecule transformations^[12-14]. It was previously reported that such composite systems can effectively utilize photons and use water as a source of protons to generate hydrogen, and subsequently combine photocatalytic proton reduction with substrate hydrogenation reactions to construct new catalytic platforms^[9,15-16].

Ferrocene has been applied to the peripheral modification of ligands in redox structures, due to its redox activity^[17]. Meanwhile, as a convergence of flexible rotatability and rigidity, it can act as building blocks for metal-organic complexes^[18-19]. In this work, we synthesized a hydrazide primary building block by using the redox-active ferrocene as the foundation and subsequently introduced the triphenylphosphine unit to form the ligand H_2FcP . The triphenylphosphine unit oxidized during the subsequent self-assembly with metal salts in the air, and the final ligand formed two isomorphous supramolecular macrocycles with rhombic cavities with Fe and Cu metal centers (M_{Fe} and M_{Cu}). The macrocycles can encapsulate the classical organic dye fluorescein (**FI**) to form the supramolecule photocatalytic systems, which can catalytic proton reduction and nitro substrates reduction as an enzyme mimetic system with the use of electron sacrificial agent triethylamine. In the photocatalytic hydrogen evolution reaction (HER) and the nitro reduction reaction, M_{Cu} , which carries

both Cu(II) and ferrocene, showed even better catalytic properties. The photocatalytic systems were then validated for the simulation of the enzymic catalytic process by employing the Michaelis-Menten mechanism^[20-21].

1 Experimental

1.1 Materials and measurements

All the chemicals were of reagent grade quality obtained from commercial sources and used without further purification. All solvents are purified using reported methods before being put into use^[22]. Reaction mixtures were stirred by using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using a Thermostat-controlled silicone oil bath. The elemental analyses of C, H, and N were performed in a Vario EL III elemental analyzer. NMR spectra were measured on a BRUKER 400M spectrometer. Chemical shifts of the NMR spectra were reported relative to DMSO- d_6 (^1H NMR: $\delta=2.50$, ^{13}C NMR: $\delta=39.52$) or CD_3CN (^1H NMR: $\delta=1.94$, ^{13}C NMR: $\delta=1.32$, 118.26). ESI-MS spectra were carried out on an HPLC-Q-TOF MS spectrometer using acetonitrile as the mobile phase.

The fluorescent spectra were measured on an Edinburgh FS920 fluorescence spectrometer. The solution UV-Vis spectra were recorded on a SHIMADZU UV 2600 UV-Vis spectrophotometer. The cuvettes used were WondaQuartz 45 (12.5 mm×12.5 mm) cuvettes from Shimadzu.

The generated H_2 was determined by a GC 7890T instrument analysis using a 5A molecular sieve column (0.6 m×3.0 mm) with a thermal conductivity detector, and argon as carrier gas.

The HPLC analysis was performed on a SHIMADZU LC 2030 Plus analyzer using a ZORBAX SB-C18 reverse phase column (250 mm×4.6 mm ID, $s-5\ \mu\text{m}$) eluting with methanol/water to determine the yields of the catalytic reactions. (Detection: $\lambda=230\ \text{nm}$; Temperature: $25.0\ ^\circ\text{C}$) Methanol and water were used to prepare mobile phase solvents for HPLC.

The cyclic voltammetry (CV) measurements were performed on a CHI 660E electrochemical workstation with a three-electrode system using an Ag/AgCl elec-

trode as the reference electrode, 0.5 mm diameter platinum silk as the counter electrode, and a glassy carbon electrode as the working electrode. The measurements were performed after degassing the solutions with argon to eliminate the effects of oxygen.

1.2 Synthesis of 1,1'-dihydrazideferrocene

1, 1' - dihydrazideferrocene was prepared by the reported procedure^[23]. To a solution of hydrazine hydrate (10 mL) in ethanol (20 mL), dimethyl 1, 1' - ferrocenedicarboxylate (2 g, 6.06 mmol) was added slowly in ethanol. After the mixed solution was stirred and refluxed for 7 h, most of the solvent was evaporated. Then the orange crystal precipitation formed after cooling. The product (1, 1' - dihydrazideferrocene) was collected by filtration and washed with ethanol and diethyl ether. Yield: 70%. ESI - MS: $m/z=303.1$ ($[M+H]^+$). Elemental analysis Calcd. for $C_{12}H_{14}N_4O_2Fe$ (%): C 47.71, H 4.67, N 18.55; Found(%): C 47.67, H 4.70, N 18.51.

1.3 Synthesis of H_2FcP

The mixture of 2-diphenylphosphinobenzaldehyde (1.2 g, 4.2 mmol) and 1,1'-dihydrazideferrocene (604 mg, 2 mmol) was dissolved in 50 mL methanol, then the solution was refluxed overnight at 70 °C. The orange solids were formed and then collected through filtration. Yield: 70%. ESI-MS: $m/z=847.20$ ($[M+H]^+$). 1H NMR (400 MHz, DMSO- d_6): δ 11.88 (s, 2H), 8.62 (s, 2H), 7.82 (dd, $J=15.0$, 8.1 Hz, 2H), 7.72 (dd, $J=8.2$, 6.92 Hz, 2H), 7.61-7.67 (m, 8H), 7.5-7.58 (m, 16H), 5.35 (s, 4H), 4.97 (s, 4H), 4.08 (s, 2H). ^{31}P NMR (162 MHz, DMSO- d_6): δ -15.75.

1.4 Synthesis of macrocycles M_{Cu} and M_{Fe}

Ligand H_2FcP (84.6 mg, 0.1 mmol) was dissolved in 20 mL acetonitrile, then $Cu(OTf)_2$ (35.4mg, 0.1 mmol) was added. The resulting solution was stirred at 60 °C for 24 h. After that, the resulting solution was cooled to room temperature. Then, orange block crystals (M_{Cu}) were obtained after slow diffusion of 100 mL diethyl ether into the solution. Yield: about 70%. Anal. Calcd. for $C_{104}H_{80}N_8O_{20}F_{12}P_4S_4Fe_2Cu_2$ (%): H, 3.25; C, 50.35; N, 4.52. Found(%): H, 3.28; C, 50.36; N, 4.54. 1H NMR (400 MHz, CD_3CN): δ 4.69 (s, 4H), 5.11 (s, 4H), 6.21 (s, 2H), 7.08 (s, 2H), 7.63-7.89 (m, 22H), 8.09 (s, 2H),

8.44 (s, 2H), 10.87 (s, 2H). ^{13}C NMR (101 MHz, CD_3CN): δ 169.86, 150.05, 135.18, 133.62, 132.23, 131.83, 131.53, 130.83, 129.51, 128.56, 128.44, 127.93, 127.57, 72.30. ^{31}P NMR (162 MHz, CD_3CN): δ -3.46. ESI - MS: $m/z=627.742$ 4 ($[Cu_2(FcPO)_2]^{3+}$), 940.607 1 ($[Cu_2(FcPO)_2]^{2+}$).

The synthesis of macrocycle M_{Fe} was similar to that described for M_{Cu} with the ligand H_2FcP (84.6 mg, 0.1 mmol) and $Fe(OTf)_2$ (35.4 mg, 0.1 mmol). Orange block crystals were obtained after slow diffusion of 100 mL diethyl ether into the solution. Yield: about 60%. Anal. Calcd. for $C_{104}H_{80}N_8O_{20}F_{12}P_4S_4Fe_4$ (%): H, 3.27; C, 50.67; N, 4.55. Found(%): H, 3.32; C, 50.66; N, 4.56. ^{31}P NMR (162 MHz, CD_3CN): δ -4.37. ESI - MS: $m/z=1$ 866.19 ($[H+Fe_2(FcPO)_2]^{+}$), 933.62 ($[Fe_2(FcPO)_2]^{2+}$), 622.75 ($[3H+Fe_2(FcPO)_2]^{3+}$), 467.31 ($[Fe_2(FcPO)_2]^{4+}$).

1.5 X-ray crystallography

The single crystal data were collected on a Bruker SMART APEX CCD diffractometer equipped with graphite monochromated Mo $K\alpha$ ($\lambda=0.071$ 073 nm) ray source using the SMART and SAINT programs collected data^[24-25]. The structure was solved by direct methods and refined on F^2 by full-squares methods with the SHELXTL module in Olex2 software version 1.5^[26-28]. The structure refinement of macrocycles M_{Cu} and M_{Fe} are listed in Table 1.

CCDC: 2166465, M_{Cu} ; 2166466, M_{Fe} .

2 Results and discussion

2.1 Structural description

The ligand H_2FcP respectively reacted with two kinds of transition metal salts in acetonitrile solution to generate two analogical M_2L_2 metal - organic macrocycles. The triphenylphosphine unit oxidized to triphenylphosphine oxide (TPPO) by oxygen in the air during the self - assembly process (Fig. 1a). Therefore, the ligand unit in the self - assembled macrocycle was named H_2FcPO .

The macrocycles' single crystals were obtained by slow diffusion of the diethyl ether vapor into the corresponding acetonitrile solution. Single crystal structure analysis revealed that the crystals of M_{Cu} and M_{Fe} are isomorphic and crystallize in the monoclinic $C2/c$ and

Table 1 Crystal data and structure refinements for M_{Cu} and M_{Fe}

Parameter	M_{Cu}	M_{Fe}
Formula	$C_{106}H_{83}Cu_2F_{12}Fe_2N_9O_{20}P_4S_4$	$C_{112}H_{95}F_6Fe_4N_{13}O_{14}P_4S_2$
Formula weight	2 521.77	2 372.45
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a / nm	3.182 0(2)	1.383 55(8)
b / nm	1.473 28(11)	1.521 81(9)
c / nm	2.733 00(19)	1.527 96(9)
α / ($^\circ$)		94.143 0(10)
β / ($^\circ$)	115.590 9(15)	100.573(2)
γ / ($^\circ$)		114.219 0(10)
V / nm ³	11.555 4(15)	2.844 8(3)
Z	4	1
D_c / (g·cm ⁻³)	1.426	1.313
$F(000)$	5 048.0	1 154.0
Reflection collected	111 144	61 704
Unique reflection (R_{int})	10 173 (0.206 1)	16 648 (0.029 4)
Goodness of fit on F^2	1.036	1.040
Final R indices* [$I > 2\sigma(I)$] R_1, wR_2	0.073 4, 0.169 7	0.044 8, 0.118 7
R indices* (all data) R_1, wR_2	0.127 6, 0.200 9	0.061 1, 0.127 2

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

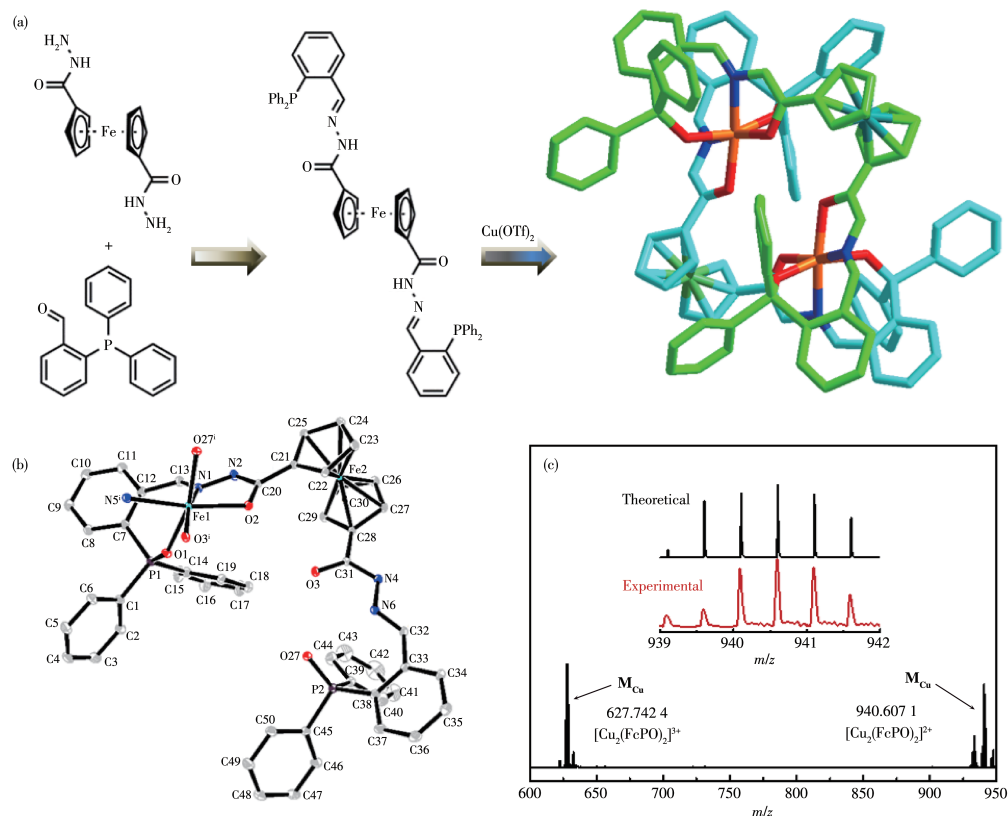


Fig.1 (a) Self-assembly of metal-organic macrocycles M_{Cu} ; (b) Molecular view of macrocycle M_{Fe} with thermal ellipsoids at 30% probability (Symmetry code: $1-x, -y, 1-z$; Fe: cyan, O: red, N: blue, P: purple; H atoms, anions, and solvent molecules are omitted for clarity); (c) Partial ESI-MS spectra of M_{Cu} (0.1 mmol·L⁻¹) in an acetonitrile solution

triclinic $P\bar{1}$ space groups, respectively. The ferrocene units and transition metal cations were located at opposite vertices of the elongated rhombus, respectively. The average distance between two ferrocene units is 0.98 nm, and the distance between the Cu(II)/Fe(II) ions is 0.56 nm in $\mathbf{M}_{\text{Cu}}/\mathbf{M}_{\text{Fe}}$. Thus, there is a 0.56 nm $\times$ 0.98 nm diamond-shaped window in the cross-section of the macrocycles. Then measurements were taken to obtain the torsion angle between the two cyclopentadiene of ferrocene. The result shows the angle is 58° . Each ligand moiety is bound to the metal center using a carbonyl oxygen atom, a hydrazide nitrogen atom, and an oxygen atom of the TPPO unit. Abundant phenyl rings extending from the elongated rhombus may facilitate aromatic stacking interaction with **FI** molecules.

The mass spectra of $\mathbf{M}_{\text{Cu}}$ in homogeneous conditions were obtained by ESI-MS characterization. The ESI-MS spectrum of complex $\mathbf{M}_{\text{Cu}}$ exhibited an intense

peak at $m/z=627.742\ 4$ and $940.607\ 1$, which is respectively allocated to $[\text{Cu}_2(\text{FcPO})_2]^{3+}$ and $[\text{Cu}_2(\text{FcPO})_2]^{2+}$ (Fig. 1c). The macrocycle showed a high positive charge, and the protons at the amide position were desorbed.

2.2 Photocatalytic system characteristics

To construct the subsequent enzyme-mimetic photocatalytic system, the conventional organic molecule **FI** was introduced as the photosensitizer guest for photoinduced electron transfer. This intermolecular interaction between the guest molecule and the macrocycle was captured using the UV-Vis spectrum. Macrocycle $\mathbf{M}_{\text{Fe}}$ ($10.0\ \mu\text{mol}\cdot\text{L}^{-1}$) in a DMF solution exhibited metal-ligand charge transfer bands at 313 nm. Then **FI** solution ($1.0\ \text{mmol}\cdot\text{L}^{-1}$) was added to the cuvette proportionally. With the increasing concentration of **FI**, two sharp isosbestic points appeared at 342 and 439 nm (Fig. 2a). This signal indicates the host-guest interactions between macrocycle $\mathbf{M}_{\text{Fe}}$ and the encapsulated

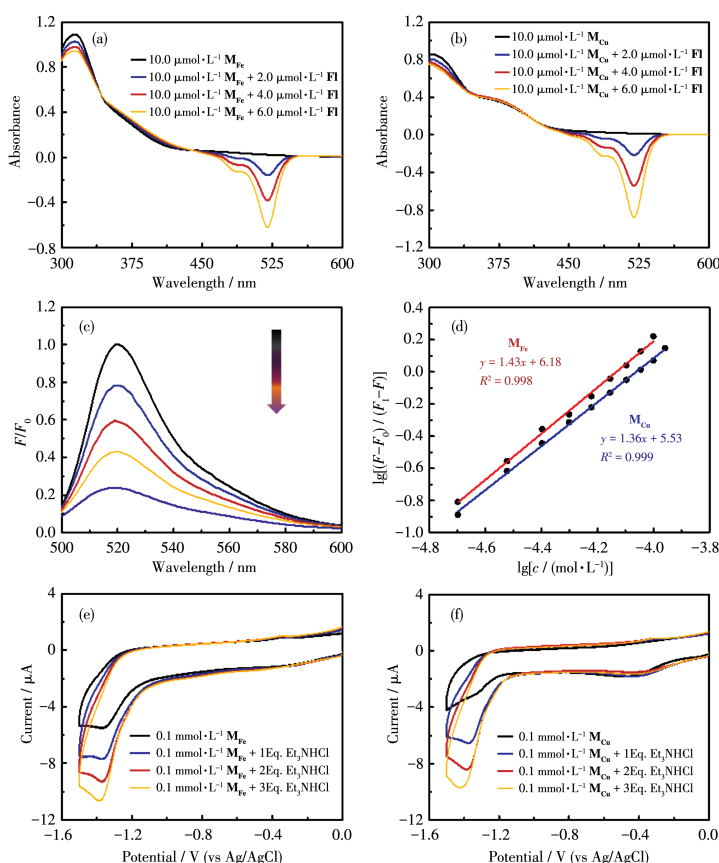


Fig.2 UV-Vis spectra of the DMF solution containing (a) $\mathbf{M}_{\text{Fe}}$ or (b) $\mathbf{M}_{\text{Cu}}$, upon addition of **FI**; (c) Emission spectra of the EtOH/H₂O solution containing **FI** ($10.0\ \mu\text{mol}\cdot\text{L}^{-1}$) (black line) upon addition of $\mathbf{M}_{\text{Fe}}$ (colored lines); (d) Summary of curve Hill-plot fitting results for the addition of $\mathbf{M}_{\text{Fe}}$ or $\mathbf{M}_{\text{Cu}}$ to **FI** solutions (EtOH/H₂O); CV curves of (e) $\mathbf{M}_{\text{Fe}}$ or (f) $\mathbf{M}_{\text{Cu}}$, upon addition of Et₃NHCl (colored lines), Scan rate: $100\ \text{mV}\cdot\text{s}^{-1}$

FI. Unlike $\mathbf{M}_{\text{Fe}}$, the DMF solution of $\mathbf{M}_{\text{Cu}}$ ($10.0 \mu\text{mol} \cdot \text{L}^{-1}$) exhibited absorption peaks at 273 and 316 nm, and after adding **FI** solution ($1.0 \text{ mmol} \cdot \text{L}^{-1}$), isosbestic points of 346 and 430 nm appeared (Fig.2b).

Fluorescence spectroscopy was also used to characterize host-guest molecular interactions, which helps to provide an overview of electron transfer pathways. The macrocycles have also been shown to be effective in quenching **FI** in the excited state. In the process of adding $\mathbf{M}_{\text{Fe}}$ to the EtOH/H₂O (1:1, V/V) solution of **FI** ($10.0 \mu\text{mol} \cdot \text{L}^{-1}$), the fluorescence spectra were characterized and found that the emission intensity of the excited state of **FI** (**FI**^{*}) was continuously quenched (Fig.2c). Hill-plot fitting of fluorescence spectral curve indicated that host-guest clathrate was formed with an association constant as $K_a = 1.5 \times 10^6 \text{ L} \cdot \text{mol}^{-1}$ (Fig. 2d). The constant indicates that $\mathbf{M}_{\text{Fe}}$ binds tightly to **FI**, while the fluorescence curves suggest the quenching process is carried out by electron transfer from **FI**^{*} to $\mathbf{M}_{\text{Fe}}$ in a pseudo - intramolecular pathway. Afterward, $\mathbf{M}_{\text{Fe}}$ was replaced with $\mathbf{M}_{\text{Cu}}$ and the same titration experiment was carried out. After continuous quenching of the solution of **FI**^{*} using the solution of $\mathbf{M}_{\text{Cu}}$ ($10.0 \mu\text{mol} \cdot \text{L}^{-1}$), it was found that $\mathbf{M}_{\text{Cu}}$ strongly quenched **FI**^{*}. The Hill - plot fitting of the titration curve showed that the association constant $K_a = 3.4 \times 10^5 \text{ L} \cdot \text{mol}^{-1}$ (Fig.2d).

After it became clear that both macrocycles could indeed transfer electrons with photosensitizers, the next experiment verified the ability of macrocycles to act as catalysts for reduction reactions. CV experiments were carried out to verify whether both macrocycles can reduce protons in solution and the response of $\mathbf{M}_{\text{Fe}}/\mathbf{M}_{\text{Cu}}$ upon increasing proton concentration. CV characterization of $\mathbf{M}_{\text{Fe}}$ ($10.0 \mu\text{mol} \cdot \text{L}^{-1}$) in a DMF solution under an argon atmosphere displayed the reduction process of $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$ at -1.36 V . The potential fell within the range of aqueous phase proton reduction^[29]. The addition of Et₃NHCl to corresponding DMF solutions led to new catalytic waves which increased with a gradual increase increment of proton concentration (Fig.2e). The newly generated waves indicate that $\mathbf{M}_{\text{Fe}}$, as a catalyst, is capable to reduce proton under electro-

catalytic conditions. The identical experimental approach was used for $\mathbf{M}_{\text{Cu}}$. The host $\mathbf{M}_{\text{Cu}}$ showed redox waves of -1.34 and -0.42 V in the CV test. After the addition of Et₃NHCl, a new catalytic wave was generated, and the wave continued to strengthen as the proton concentration continued to increase, which was similar to $\mathbf{M}_{\text{Fe}}$ (Fig.2f).

2.3 Catalytic behavior of photocatalytic HER

The above characterization results indicate that the macrocyclic - based system has the capability of modeling photocatalytic enzymes and further experiments will verify the homogeneous catalytic reduction capacities of the constructed system. Subsequent photocatalytic HER was carried out under the following conditions: irradiation of the EtOH/H₂O (4.5 mL, 1:1, V/V) solution containing **FI** ($1.0 \text{ mmol} \cdot \text{L}^{-1}$), $\mathbf{M}_{\text{Fe}}$ ($10.0 \mu\text{mol} \cdot \text{L}^{-1}$), Et₃N (0.5 mL) under a 300 W xenon lamp. Greater efficiency of HER was achieved at pH=11.0 (Fig. 3a). The total amount of hydrogen released by catalyst $\mathbf{M}_{\text{Cu}}$ and $\mathbf{M}_{\text{Fe}}$ at the same reaction time was compared at pH =11.0 (Fig.3b). The experiments indicate that the catalysis occurs inside the complex formed by the macrocycle and **FI**. In addition, no hydrogen was released in the shortage of the $\mathbf{M}_{\text{Fe}}$ and $\mathbf{M}_{\text{Cu}}$ catalyst, or the absence of irradiation. Subsequent kinetic experiments showed that the amount of hydrogen released exhibited a linear relationship with the concentration of either catalyst of $\mathbf{M}_{\text{Cu}}$ and $\mathbf{M}_{\text{Fe}}$ (Fig.3c and 3d).

2.4 Photocatalytic nitro reduction and kinetic experiment

Having elucidated that macrocyclic compounds are sufficient to activate protons, we envisage whether the activated protons could be used as hydrogen donors for the reductive hydrogenation of small molecules, directly hydrogenating the encapsulated substrate molecules. To prove this assumption, we combined the hydrogenation of nitro compounds with the photocatalytic system. Under the optimized experimental conditions, nitrobenzene (0.05 mmol) was added to the ethanol/H₂O (1:1, V/V) solution containing macrocycles ($0.1 \text{ mmol} \cdot \text{L}^{-1}$), Et₃N ($\varphi=10\%$), and **FI** ($1.0 \text{ mmol} \cdot \text{L}^{-1}$) at pH =11.0. The product, aniline, was produced directly with a yield up to 99% in 6 h in the $\mathbf{M}_{\text{Cu}}$ system, and a

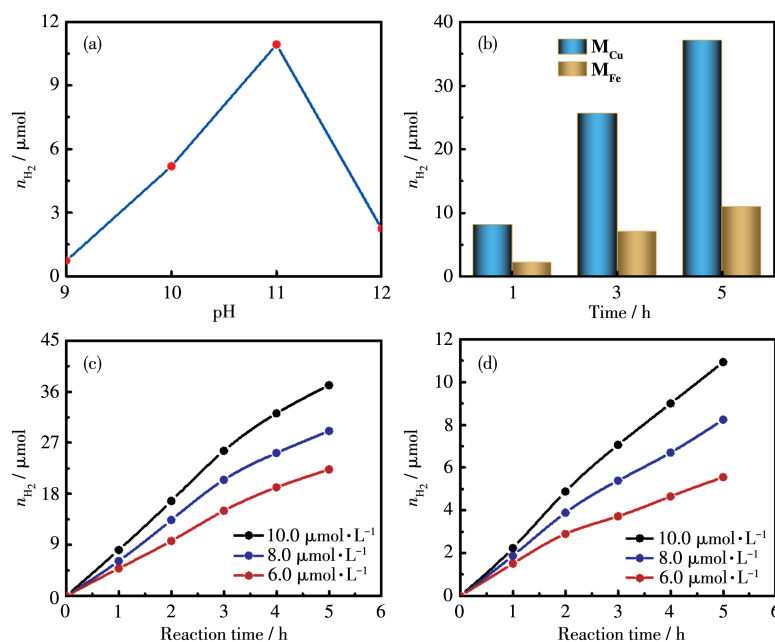


Fig.3 (a) Photocatalytic hydrogen evolution in ethanol/water (1:1, V/V) solution containing M_{Fe} ($10.0 \mu\text{mol}\cdot\text{L}^{-1}$) and Et_3N ($\varphi=10\%$) at different pH values; (b) Graphical representation of the hydrogen production of the above catalytic systems for different reaction times, with M_{Fe} and M_{Cu} catalysts respectively; Kinetic experiment of the photocatalytic hydrogen evolution in ethanol/water (1:1, V/V) solution containing Et_3N ($\varphi=10\%$) at pH=11.0 with different concentrations of (c) M_{Fe} or (d) M_{Cu}

yield up respectively to 99% in 7.5 h in the M_{Fe} system (Table 2). Likewise, the photocatalytic efficiency of M_{Cu} for proton reduction was higher compared to M_{Fe} , and similar catalytic properties were observed in the nitro reduction reaction. At the same time, no hydrogen was produced in the photocatalytic nitroreduction reaction, which has great selectivity.

With a fixed concentration of Et_3N and nitrobenzene, the loading of the macrocycle varied from 0.05 to

$0.2 \text{ mmol}\cdot\text{L}^{-1}$, and the initial reaction rate of nitrobenzene varied linearly with the catalyst concentration (Fig. 4a and 4b). Under the optimized conditions for both systems, the size of aromatic nitro substrates increased from nitrobenzene (S1) to *N,N*-dimethyl-4-nitroaniline (S2), 1-nitronaphthalene (S3), and 1-nitropyrene (S4). All substrates could be completely converted to amino products for different reaction times. For the substrate with the same size, M_{Cu} consistently

Table 2 Photocatalytic nitroreduction reaction of nitro compounds by M_{Fe} or M_{Cu} *

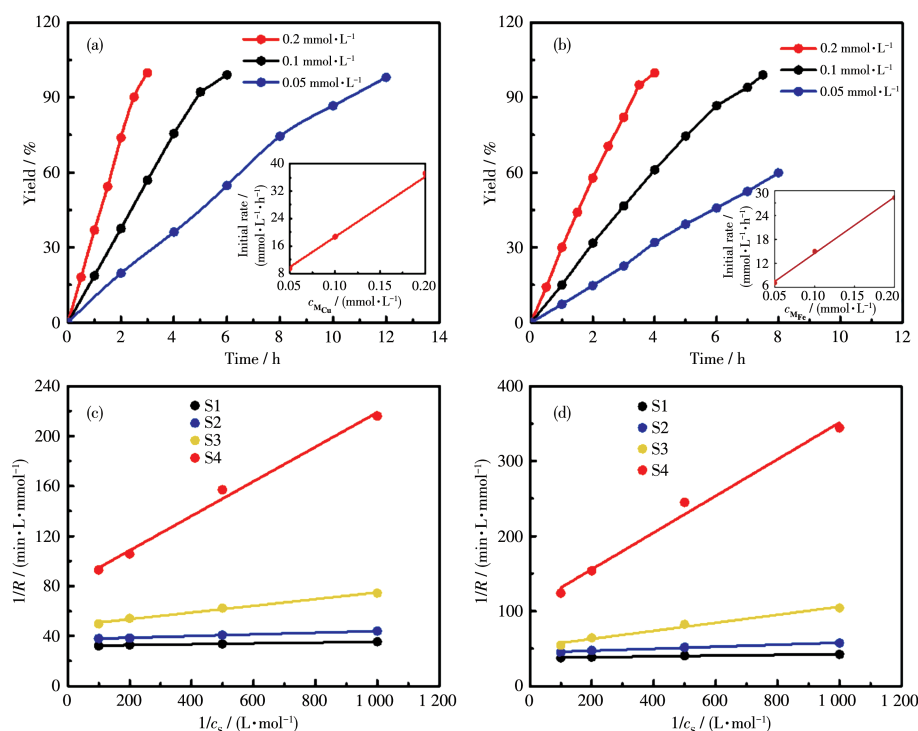
$\text{R}-\text{C}_6\text{H}_4-\text{NO}_2 \xrightarrow[\text{Catalyst (0.1 mmol}\cdot\text{L}^{-1}), \text{FI (1.0 mmol}\cdot\text{L}^{-1})]{\text{Et}_3\text{N } (\varphi = 10\%), 300 \text{ W xenon lamp}} \text{R}-\text{C}_6\text{H}_4-\text{NH}_2$				
	Yield / %			
Catalyst				
M_{Cu}	99 (6 h)	99 (8 h)	99 (9 h)	99 (18 h)
M_{Fe}	99 (7.5 h)	99 (9 h)	99 (10 h)	99 (24 h)

* The reaction was carried out using the following conditions: catalyst (M_{Fe} or M_{Cu}): $0.1 \text{ mmol}\cdot\text{L}^{-1}$, FI: $1.0 \text{ mmol}\cdot\text{L}^{-1}$, substrate: 0.05 mmol , Et_3N : $\varphi=10\%$, 300 W xenon lamp; the amino products were characterized using HPLC and the yields were calculated using the internal standard method.

exhibited better catalytic performance compared to $\mathbf{M}_{\text{Fe}}$. The law of linearity indicates that the reaction follows a first-order kinetic model, which also means that the reaction occurs in the cavity of macrocycles. The interaction of the substrate with the macrocycles can be viewed as the binding of the enzyme to the substrate, and the macrocycles are nitroreductase-like species.

To better confirm that the constructed photocatalytic system can simulate the process of enzyme activation and substrate reduction, the method of changing the substrate concentration was subsequently adopted, and kinetic experiments were carried out. It was found that after the substrate concentration reached satura-

tion, the reciprocal of the reaction rate and the inverse of the substrate concentration had a linear relationship, and this result is in line with the Michaelis-Menten kinetic equation, confirming that the constructed photocatalytic system can be used as a model for enzyme catalysis. The results of the Lineweaver-Burk plot were fitted to obtain Michaelis constant K_m , and further calculations yielded k_{cat} . For the $\mathbf{M}_{\text{Cu}}$ -catalyzed nitrobenzene reduction reaction, the fitted K_m was $1.04 \times 10^{-4} \text{ mmol} \cdot \text{L}^{-1}$ and the k_{cat} was 0.312 min^{-1} . As the substrate size increased, the K_m value gradually increased to $1.73 \times 10^{-3} \text{ mmol} \cdot \text{L}^{-1}$ and the k_{cat} decreased to 0.012 min^{-1} (Table 3).



Insert: the interrelation between the initial rate and the concentration of the catalyst

Fig.4 Variation in the yield of photocatalytic nitrobenzene reduction under standard reaction conditions by varying the loading of (a) $\mathbf{M}_{\text{Cu}}$ or (b) $\mathbf{M}_{\text{Fe}}$; Double reciprocal plot obtained by varying the substrate concentration under standard experimental conditions for the (c) $\mathbf{M}_{\text{Cu}}$ or (d) $\mathbf{M}_{\text{Fe}}$ system

Table 3 Determined values of K_m and k_{cat} of different substrates with different catalysts ($\mathbf{M}_{\text{Cu}}$ and $\mathbf{M}_{\text{Fe}}$) under optimized photocatalytic reduction reaction conditions

Substrate	$\mathbf{M}_{\text{Cu}}$		$\mathbf{M}_{\text{Fe}}$	
	$K_m / (\text{mmol} \cdot \text{L}^{-1})$	$k_{\text{cat}} / \text{min}^{-1}$	$K_m / (\text{mmol} \cdot \text{L}^{-1})$	$k_{\text{cat}} / \text{min}^{-1}$
S1	1.04×10^{-4}	0.312	1.38×10^{-4}	0.266
S2	1.80×10^{-4}	0.268	3.02×10^{-4}	0.255
S3	5.56×10^{-4}	0.208	1.03×10^{-3}	0.192
S4	1.73×10^{-3}	0.012 3	2.29×10^{-3}	0.093 7

After using $\mathbf{M}_{\text{Fe}}$ instead of $\mathbf{M}_{\text{Cu}}$, similar catalytic results and characteristics were obtained. The conversion of the other substrates also showed a corresponding decrease for the same reaction time and conditions. The conclusion was also obtained by comparing the K_{m} and k_{cat} of $\mathbf{M}_{\text{Fe}}$ and $\mathbf{M}_{\text{Cu}}$. Both constants were relatively similar, but $\mathbf{M}_{\text{Fe}}$ performed less well overall than $\mathbf{M}_{\text{Cu}}$. As shown in Table 3, for the same size substrate, $\mathbf{M}_{\text{Cu}}$ exhibited a smaller K_{m} value and larger k_{cat} value (except for S4). This comparison proves that the $\mathbf{M}_{\text{Cu}}$ system has better catalytic activity in nitroreduction reactions.

3 Conclusions

Two isomorphous metal-organic macrocycles ($\mathbf{M}_{\text{Fe}}$ and $\mathbf{M}_{\text{Cu}}$) were constructed using ferrocene-based ligands, which were paired with organic photosensitizers to form a photocatalytic system to pattern the hydrogenation of natural enzymes, such as water splitting reactions and the hydrogenation of nitro compounds. For $\mathbf{M}_{\text{Fe}}$, its loading of fluorescein was followed by a successful hydrogen evolution reaction for the photolysis of water to hydrogen in the presence of triethylamine as an electron sacrificial agent, and it also showed good activity in the subsequent reductive hydrogenation of aromatic nitro compounds. In contrast, $\mathbf{M}_{\text{Cu}}$, which replaces the transition metal in the coordination center with Cu, shows more intense activity in the HER reaction and also performs better in the nitroreduction reaction. Afterward, the Michaelis-Menten mechanism was verified by making changes in the concentration of these two photocatalytic mimetic enzyme systems, and the change in the rate of mimetic enzyme reaction in relation to substrate concentration during this process. The results of the catalytic mechanism validation reveal the affinity of different sizes of substrates to the enzyme, simulate the substrate selective process of natural enzymes, and make an extension to the path of artificially constructing enzyme-mimetic catalytic systems.

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