Supplementary Information

Valence-Dependent Catalytic Activities of Iron Terpyridine Complexes for Pollutant Degradation

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Page: 13

Text: 5

Figure: 8

Table: 1

Text S1. Chemicals. 2,2':6',2''-terpyridine (tpy), phenol, $FeCl_3 \cdot 6H_2O$, $FeCl_2$, 30% H_2O_2 aqueous solution, dimethyl sulfoxide (DMSO) and natural organic matters (NOM) were purchased from Aladdin Co. (Shanghai, China). Methanol (HPLC grade) was purchased from J&K Co., Ltd. (Beijing, China). 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was obtained from Sigma-Aldrich (Shanghai, China). All chemical reagents were used as purchased without further purification. Milli-Q water was used throughout this study. The catalysts $Fe^{III}(tpy)Cl_3$ and $Fe^{II}(tpy)Cl_2$, were prepared according to previous published methods as followed.

Text S2. Preparation of $Fe^{III}(tpy)Cl_3$. The ligand (tpy) (233 mg, 1 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (324 mg, 1.2 mmol) in acetonitrile (20 mL) while stirring at room temperature. After the mixture was stirred for 4 h, the yellow product was collected by rotary evaporation, washed with acetone, and dried in a vacuum at room temperature. The mass-to-charge ratio of 358.9681 determined by using high resolution mass spectrometry can be assigned to $[Fe^{III}(tpy)Cl_2]^+$ (Figure S1). Electrospray ionization source in positive mode was used, and ethanol was used as solvent. The characteristic IR spectra, i.e. ν(C-H) 3081 and 785 cm^{-1}, ν(C=C, C=N) 1596, 1475 and 1446 cm^{-1}, were recorded.

Text S3. Preparation of $Fe^{II}(tpy)Cl_2$. The ligand (tpy) (233 mg, 1 mmol) was added to a solution of $FeCl_2$ (152 mg, 1.2 mmol) in acetonitrile (20 mL) while stirring at room temperature in Ar atmosphere. After the mixture was stirred for 4 h, the purple product was collected by rotary evaporation, washed with acetone, and dried in a vacuum at room temperature. As shown in Figure S2, the complex was characterized by ^1H NMR (400 MHz, DMSO-d_6): δ 9.24 (d, J = 8.1 Hz, 2H), 8.82 (dd, J = 11.5, 8.0 Hz, 3H), 7.98 (t, J = 7.8 Hz, 2H), 7.15 (dt, J = 13.0, 5.8 Hz, 4H). The mass-to-charge ratio of 324.19 determined by using ion trap mass spectrometer was assigned to $[Fe^{II}(tpy)Cl]^+$ (Figure S1). Electrospray ionization source in positive mode was used, and ethanol was used as solvent. The characteristic IR spectra, i.e. ν(C-H) 3061 and 768 cm^{-1}, ν(C=C, C=N)

1603, 1452 and 1396 cm^{-1}, were recorded.

Text S4. Degradation experiments. The degradation experiments were carried out in a 50 mL Schlenk tube containing 5 mg L^{-1} phenol. In a typical experiment, a certain amount of catalysts was added into 20 mL of phenol solution. The reaction was initiated by adding a certain volume of 30% H_2O_2 aqueous solution. At predetermined time intervals, 1 mL of the reaction solution was withdrawn and immediately quenched with 0.1 mL of ascorbic acid (0.1 M). Then, 0.8 ml of hexane was added, and the supernatant was harvested after half an hour of vortex at 1000 rpm to prepare the sample. To evaluate the effect of initial pH of the reaction solution, the initial pH was adjusted by sulfuric acid and sodium hydroxide.

Text S5. Instrumental analysis. Gas chromatography-mass spectrometry (GC-MS, Agilent 7890B-5977A) with a HP-5 MS column (30 m×0.25 mm I.D., coating thickness 0.25 μm) for separation was used to determine the residual phenol and to identify the oxidation products of DMSO. Electron paramagnetic resonance (EPR, Brucker A300 spectrometer) signals of hydroxyl radical were recorded by using DMPO as the trap agent at ambient temperature. UV–vis absorption spectra (Shimadzu, UV-3600) were used to characterize the high-valent iron-oxo intermediates of the catalysts. Quadrupole-Time of Flight mass spectrometry (Q-TOF MS, Agilent 6545), ion trap mass spectrometer (LTQ XL, Thermos), Fourier transform infrared spectroscopy (FTIR, PerkinElmer Frontier) and ^{1}H nuclear magnetic resonance spectra (^{1}H-NMR, Brucker AVANCE III 400 MHz) were used to verify the successful preparation of the catalysts.

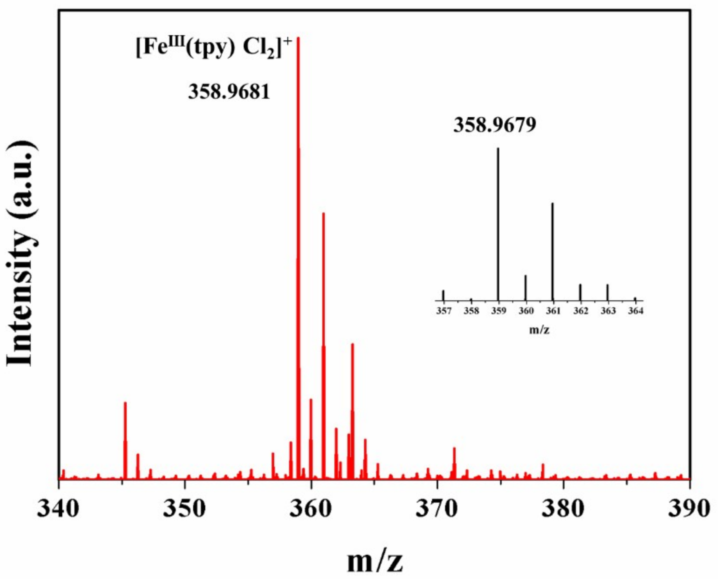

Figure S1. The high resolution mass spectrum of **$[Fe^{III}(tpy)Cl_2]^+$**. The inset was the simulation mass spectrometry of **$[Fe^{III}(tpy)Cl_2]^+$**.

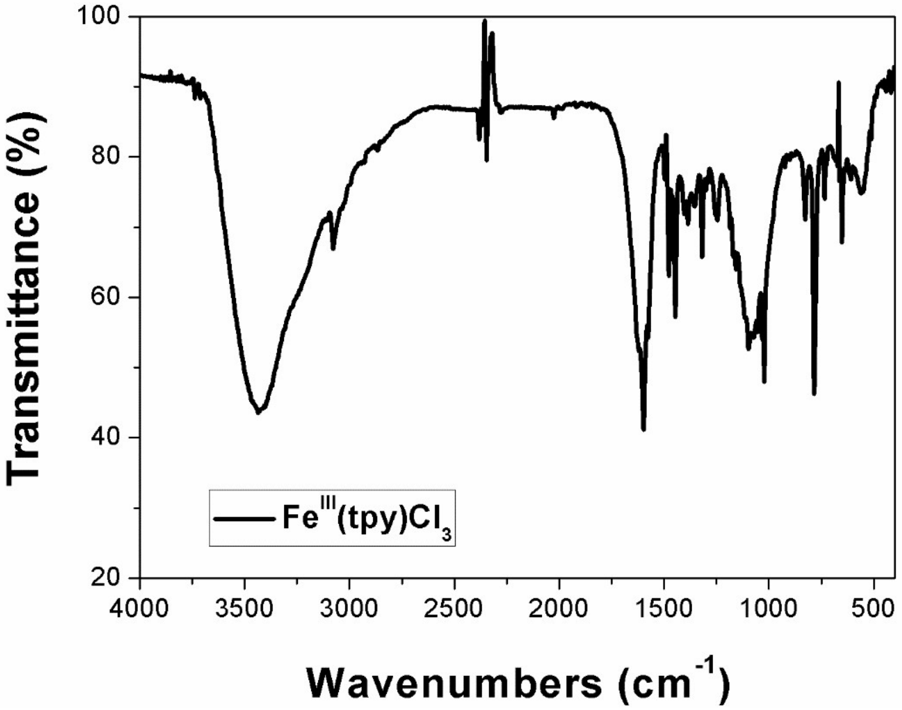

Figure S2. The FTIR spectrum of **Fe^{III}(tpy)Cl$_3$**.

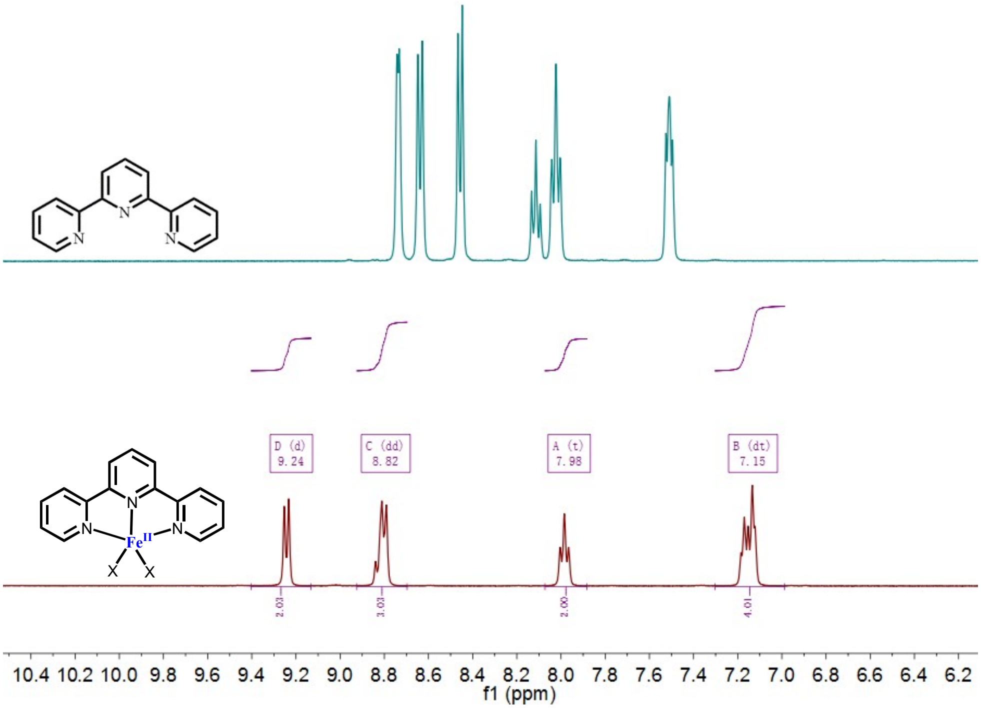

Figure S3. The ^{1}H NMR spectrometry of **tpy** (up) and **Fe^{II}(tpy)Cl$_2$** (bottom).

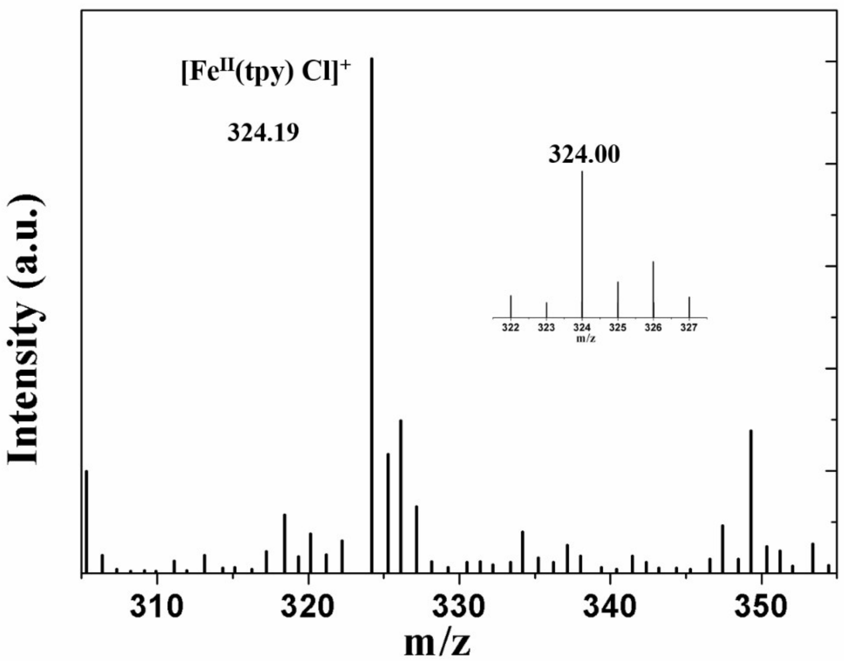

Figure S4. The mass spectrum of **[Fe^{II}(tpy)Cl]$^+$**. The inset was the simulation mass spectrometry of **[Fe^{II}(tpy)Cl]$^+$**

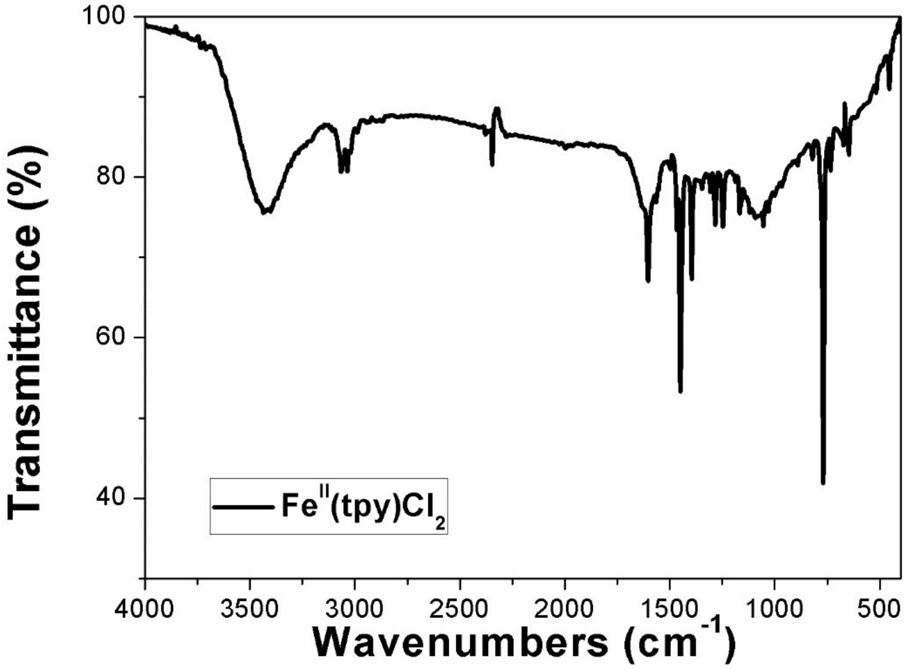

Figure S5. The FTIR spectrum of **Fe^{II}(tpy)Cl$_2$** .

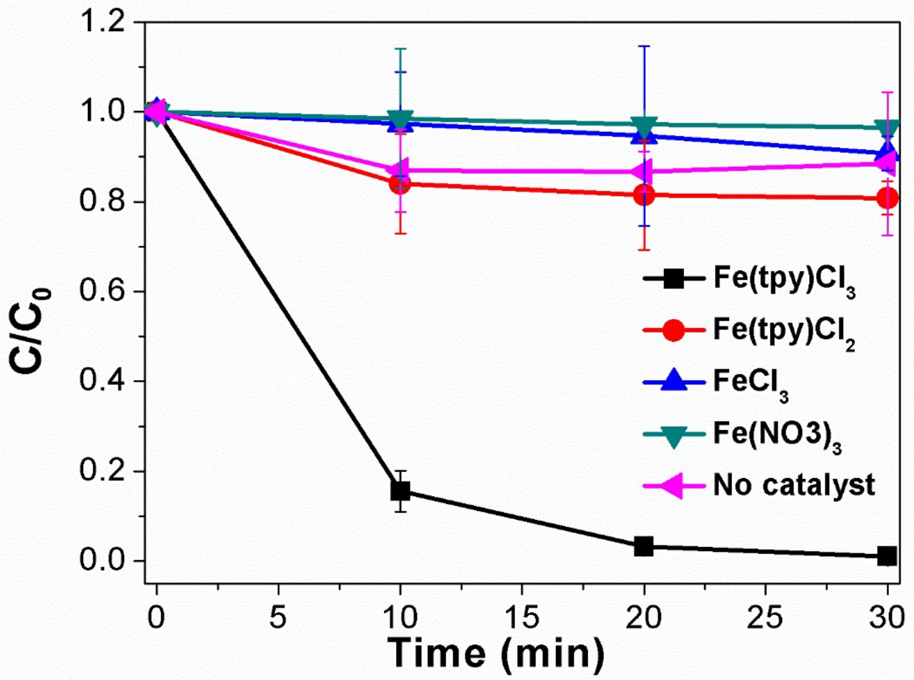

Figure S6. Degradation of phenol in different systems. $[\text{Cat.}]_0 = 10.0\ \mu\text{M}$, $[H_2O_2]_0 = 5.0\ \text{mM}$, $[\text{phenol}]_0 = 50\ \mu\text{M}$ and the initial pH was not adjusted. The subscript “0” indicates the values were recorded before degradation.

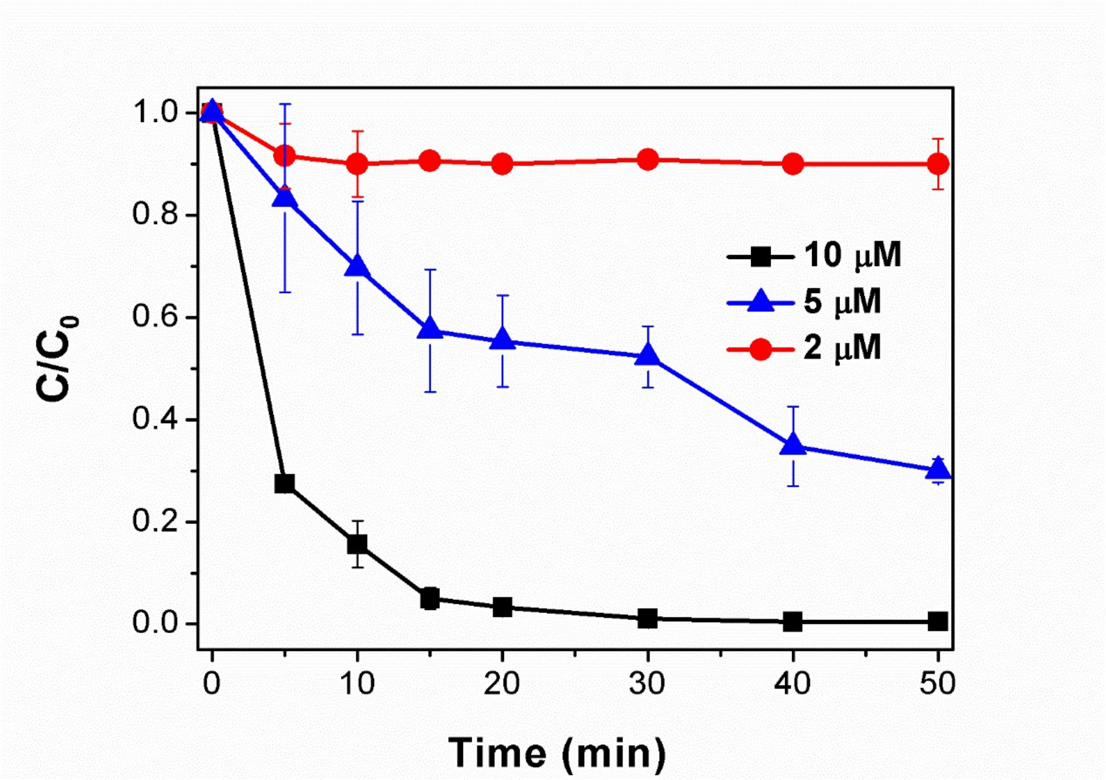

Figure S7. Effects of catalyst dosage on phenol degradation in the $Fe^{III}(tpy)Cl_3/H_2O_2$ system. $[H_2O_2]_0 = 5.0$ mM and $[phenol]_0 = 50$ μM. The subscript "0" indicates the values were recorded before degradation.

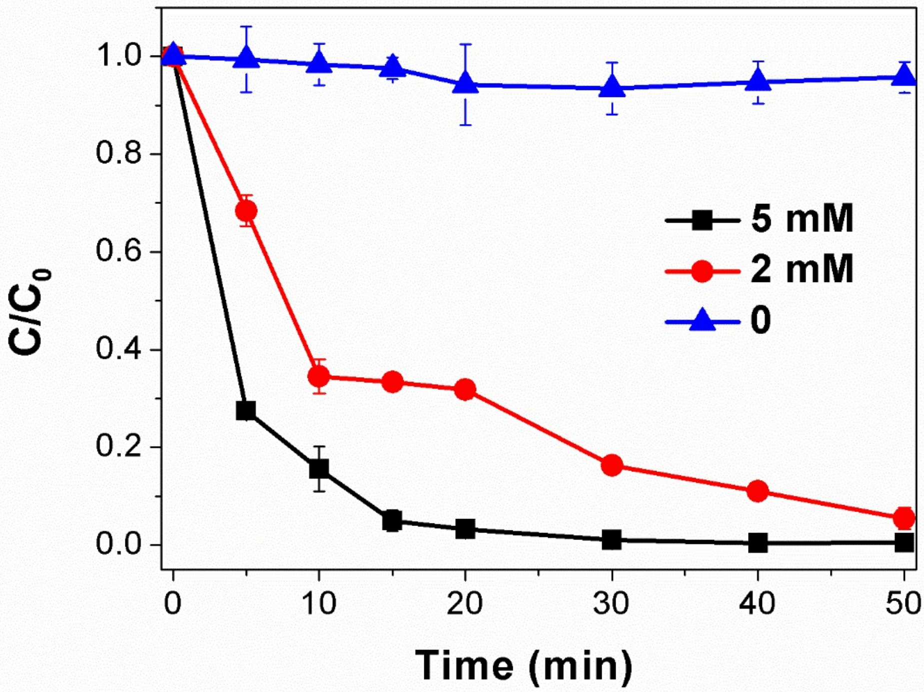

Figure S8. Effects of H_2O_2 dosage on phenol degradation in the $Fe^{III}(tpy)Cl_3/H_2O_2$

Table 1. Comparison of degradation efficiencies of various iron complexes.

Catalyst (Initial valence)	**Organic Pollutant**	**Oxidant**	**Reaction Condition**	**Degradation Efficiency**	**Reference**
Fe(tpy)Cl_3 (III)	Phenol	H_2O_2	[Fe^{III}(tpy)Cl_3]=10 μM, [Phenol]=50 μM, [H_2O_2]=5 mM, pH=4.0–5.87	97% in 30 min	This study
Fe(tpy)Cl_2 (II)	Phenol	H_2O_2	[Fe^{II}(tpy)Cl_2]=10 μM, [Phenol]=50 μM, [H_2O_2]=5 mM, pH=4.0–5.87	19% in 30 min	This study
Fe(PcS) (III)	Rhodamine B	H_2O_2	[Fe(PcS)]=40 μM, [Rhodamine B]=10 μM, [H_2O_2]=1 mM, visible light	96% in 160 min	S1
$FePcCl_{16}$ (II)	Carbamazepine	PMS	[$FePcCl_{16}$]=100μM, [Carbamazepine]=25 μM, [PMS]=0.3 mM, pH=7, sunlight	99% in 90 min	S2
$FeCl_2$(bpmcn) (II)	2,4,6-Trichlorophenol	H_2O_2	[$FeCl_2$(bpmcn)]=100 μM, [2,4,6-Trichlorophenol]=2 mM, [H_2O_2]=8 mM, pH=7	75% in 90 min	S3
Hemin (II)	Reactive Red 195	H_2O_2	[Hemin]=169 μM, [Reactive Red 195]=50 μM, [H_2O_2]=50 mM, pH=6.9	40% in 60 min	S4

Note: PMS peroxymonosulfate.

References

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