

Electronic supplementary information

for

Selective alkane hydroxylation and alkene epoxidation using H₂O₂ and Fe(II) catalysts electrostatically attached on fluorinated surface

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1. **General**
2. **Synthesis**
3. **Measurements**
4. **Supplementary Figures**
5. **Supplementary Tables**

1. General.

NMR measurements were performed on Bruker AVANCE 400 and DPX 400 spectrometers. Gas chromatography-mass (GC-MS) measurements were performed using a Shimadzu GC-2010 Plus equipped with a Shimadzu GCMS-QP2020 and an Agilent DB-Wax UI capillary column (30 meters, ID 0.25 mm, DF 0.25 μ m). ESI-TOF-MS spectra were obtained on a JEOL JMS-T100CS mass spectrometer. UV-vis-NIR reflectance spectra were measured on a Jasco UV-780 spectrophotometer at room temperature with an integrating sphere for solid samples. UV-Vis absorption spectra were measured on a Shimadzu UV-2450 spectrophotometer at room temperature. Nitrogen sorption/desorption studies were performed at liquid nitrogen temperature (77K) using Microtrac BELSORP MINI X. Before the adsorption experiments, the samples were outgassed under reduced pressure for 3 h at 333 K. Inductively coupled plasma mass spectrometry (ICP-MS) was performed on Agilent Technologies 7700 Series ICP-MS. Thermogravimetric analysis was performed on Rigaku Thermo plus EVO. Contact angle measurements were performed on Excimer SImage AUTO 100. Electrospray-ionization time-of-flight mass spectrometry (ESI-TOF-MS) measurements were made on a JEOL JMS-T100CS mass spectrometer. ESR spectroscopy was performed on a Bruker BioSpin EMXPlus 9.5/2.7 spectrometer.

Chemicals and solvents were used as received from Tokyo Chemical Industry (TCI) Co., FUJIFILM Wako Pure Chemical Corp., Nacalai Tesque or Sigma-Aldrich Corp., unless otherwise mentioned. All syntheses were performed under Ar atmosphere.

b

2. Synthesis.

1,3-dihydro-1,3-bis(2-pyridyl)methyl-2H-benzimidazolium bromide (PY₄H₂BIm-H•Br). 1,3-*N,N'*-bis(di-pyridylmethyl)-phenylenediamine (PY₄H₂BDA) was synthesized as a precursor according to the literature procedure.⁵¹ A solution of 1,2-phenylenediamine (200 mg, 1.9 mmol), di-2-pyridylketone (818 mg, 2.4 mmol) and *N,N,N',N'*-tetramethyl-ethylenediamine (2.0 mL, 14 mmol) in toluene (10 mL) was heated at 80 °C for 30 min. TiCl₄ (400 μ L, 3.4 mmol) was then added dropwise over 20 min, during the temperature was raised to 110 °C in an oil bath. After stirring at the temperature for 1 d, the reaction mixture was cooled to R.T. and filtered through a Celite pad to remove insoluble materials. The solids on the Celite pad were washed well with AcOEt (30 mL) and then CH₂Cl₂ (30 mL), and the combined filtrate was evaporated to dryness. NaBH₄ (300 mg, 7.8 mmol) and dry EtOH (20 mL) were added to the residue and the reaction mixture was stirred at R.T. for 18 h in the dark. After addition of distilled water (50 mL) to quench unreacted NaBH₄, the reaction mixture was stirred at R.T. for several hours. Then, CH₂Cl₂ (25 mL) and distilled water (25 mL) were added to the reaction mixture. The organic layer was separated, washed with water (30 mL) three times, dried over Na₂SO₄. By removing the volatile using a rotary evaporator under reduced pressure, crude PY₄H₂BDA was obtained and used for the next reaction without purification. The crude PY₄H₂BDA was dissolved into CH(OMe)₃ (15 mL, 137 mmol), and NH₄PF₆ (0.52 g, 3.19 mmol) in MeOH (5 mL) and a drop of 12 M HCl were added to the solution. The reaction mixture was stirred at 40 °C for 24 h in the dark. After neutralization by adding a saturated aqueous solution of NaHCO₃, CH₂Cl₂ (15 mL) and distilled water (30 mL) were added to the reaction mixture. The organic layer was separated, washed with water (30 mL) three times, dried over Na₂SO₄, and then the volatile was evaporated under reduced pressure. The crude mixture obtained was dissolved into MeCN/AcOEt (1:1, v/v) (5 mL), and the solution of TBABr (1.6 g, 5.0 mmol) in MeCN/AcOEt (1:1, v/v) was added.

After stirring for 1 h, the reaction mixture was filtered through membrane to obtain white-yellow crystals (750 mg, 1.40 mmol) of **PY₄H₂BIm-H•Br** in 73% yield for the three steps. ¹H NMR (dms_o-d₆): δ 7.49 (dd, *J* = 8, 5 Hz, 4H), 7.68–7.74 (m, 2H), 7.72 (d, *J* = 8 Hz, 4H), 7.98 (s, 4H), 8.00 (td, *J* = 8, 1 Hz, 4H), 8.17–8.23 (m, 4H), 8.55 (dd, *J* = 5, 1 Hz, 4H), 10.60 (s, 1H). ESI-TOF-MS: *m/z* = 455.12 (sim for [M – Br]⁺: *m/z* = 455.20).

[Fe^{II}(PY₄H₂BIm)(MeCN)](PF₆)₂ (Fe^{II}-^HNHC•(PF₆)₂). To a suspension of iron(II) acetate (100 mg, 0.57 mmol) in DMSO (3.0 mL), ^HNHC-H•Br (50 mg, 0.093 mmol) was added and the mixture was stirred at 50 °C for 24 h in the dark. After addition of KPF₆ (351 mg, 1.9 mmol) and distilled water (20 mL), the reaction mixture was filtered through membrane to obtain red solid. The crude product was recrystallized from MeCN/Et₂O and pale-red crystals of Fe-^HNHC (50 mg, 0.059 mmol) were obtained in 64% yield. ¹H NMR (CD₃CN): δ 7.35 (dd, *J* = 8, 5 Hz, 4H), 7.50–7.53 (m, 2H), 7.67 (s, 4H), 7.82 (td, *J* = 8, 1 Hz, 4H), 7.89 (d, *J* = 8 Hz, 4H), 8.08–8.14 (m, 4H), 9.44 (dd, *J* = 5, 1 Hz, 4H). UV-Vis: λ_{max} [nm] = 310, 390, 450. ESI-TOF-MS: *m/z* = 275.49 (sim for [M – 2PF₆]²⁺: *m/z* = 275.57). Anal. Calcd. for C₃₁H₂₅N₇Fe•2PF₆•5H₂O: H 3.79, C 39.97, N 10.53; Found: H 3.91, C 39.72, N 10.58.

5,6-dimethyl-1,3-dihydro-1,3-bis(2-pyridyl)methyl-2H-benzimidazolium bromide (PY₄Me₂BIm-H•Br). 1,3-*N,N'*-bis(di-pyridylmethyl)-5,6-dimethylphenylenediamine (PY₄Me₂BDA) was synthesized as a precursor according to the literature procedure.⁵¹ A solution of 5,6-dimethyl-1,2-phenylenediamine (370 mg, 2.7 mmol), di-2-pyridylketone (1.04 g, 5.63 mmol) and *N,N,N',N'*-tetramethyl-ethylenediamine (4.0 mL, 28 mmol) in toluene (20 mL) was heated at 80 °C for 30 min. TiCl₄ (800 μL, 6.8 mmol) was then added dropwise over 20 min, during the temperature was raised to 110 °C in an oil bath. After stirring at the temperature for 1 d, the reaction mixture was cooled to R.T. and filtered through a Celite pad to remove insoluble materials. The solids on the Celite pad were washed well with AcOEt (30 mL) and CH₂Cl₂ (30 mL), and the combined filtrate was concentrated to dryness. NaBH₄ (600 mg, 15 mmol) and dry EtOH (20 mL) were added to the residue and the reaction mixture was stirred at R.T. for 18 h in the dark. After addition of distilled water (50 mL) to quench unreacted NaBH₄, the reaction mixture was stirred at R.T. for several hours. Then, CH₂Cl₂ (25 mL) and distilled water (25 mL) were added to the reaction mixture. The organic layer was separated, washed with water (30 mL) three times, dried over Na₂SO₄. By removing the volatile using a rotary evaporator under reduced pressure, crude PY₄Me₂BDA was obtained and used for the next reaction without purification. The crude PY₄Me₂BDA was dissolved into CH(OMe)₃ (15 mL, 137 mmol), and NH₄PF₆ (0.52 g, 3.19 mmol) in MeOH (5 mL) and a drop of 12 M HCl were added to the solution. The reaction mixture was stirred at 40 °C for 24 h in the dark. After neutralization by adding a saturated aqueous solution of NaHCO₃, CH₂Cl₂ (15 mL) and distilled water (30 mL) were added to the reaction mixture. The organic layer was separated, washed with water (30 mL) three times, dried over Na₂SO₄, and then the volatile was evaporated under reduced pressure. The crude mixture obtained was dissolved into MeCN/AcOEt (1:1, v/v) (5 mL), and the solution of TBABr (1.6 g, 5.0 mmol) in MeCN/AcOEt (1:1, v/v) was added. After stirring for an hour, the reaction mixture was filtered through membrane to obtain white-yellow crystals (820 mg, 1.46 mmol) of **PY₄Me₂BIm-H•Br** in 54% yield for the three steps. ¹H NMR (CD₃CN): δ 2.39 (s, 6H), 7.48 (dd, *J* = 8, 5 Hz, 4H), 7.70 (d, *J* = 8 Hz, 4H), 7.88 (s, 2H), 7.98 (s, 2H), 7.99 (td, *J* = 8, 1 Hz, 4H), 8.62 (dd, *J* = 5, 1 Hz, 4H), 10.44 (s, 1H). ESI-TOF-MS: *m/z* = 483.12 (sim for [M – Br]⁺: *m/z* = 483.23).

[Fe^{II}(PY₄Me₂BIm)(MeCN)](PF₆)₂ (Fe^{II}-^{Me}NHC•(PF₆)₂). To a suspension of iron(II) acetate (100 mg, 0.57 mmol) in DMSO (3.0 mL), ^{Me}NHC-H•Br (50 mg, 0.089 mmol) was added and the mixture was stirred at 50 °C for 24 h in the dark. After addition of KPF₆ (351 mg, 1.9 mmol) and distilled water (20 mL), the reaction mixture was filtered through membrane to obtain red solid. The crude product was recrystallized from MeCN/Et₂O and pale-red crystals of **Fe^HNHC** (50 mg, 0.059 mmol) were obtained in 64% yield. ¹H NMR (CD₃CN): δ 2.50 (s, 6H), 7.34 (dd, *J* = 8, 5 Hz, 4H), 7.58 (s, 2H), 7.81 (td, *J* = 8, 1 Hz, 4H), 7.88 (td, *J* = 8, 1 Hz, 4H), 7.90 (s, 2H), 9.44 (dd, *J* = 5, 1 Hz, 4H). UV-Vis: λ_{max} [nm] = 316, 390, 452. ESI-TOF-MS: *m/z* = 309.49 (sim for [M - 2PF₆]²⁺: *m/z* = 309.54). Anal. Calcd. for C₃₃H₂₉N₇Fe•2PF₆•3H₂O: H 3.82, C 42.92, N 10.62; Found: H 3.91, C 42.62, N 10.58.

Preparation of aluminosilicates

SBA-15 type aluminosilicate (Al-SBA-15). SBA-15 type mesoporous aluminosilicate support, Al-SBA-15, was prepared according to the procedure reported by Krishana and Selvam with some modifications.⁵² In a flask, 3.0 g of the surfactant Pluronic P123 (triblock copolymer EO₂₀PO₇₀EO₂₀ where EO = poly(ethylene oxide) and PO = poly(propylene oxide)) was dissolved in 112.5 mL of aqueous HCl solution (pH 1.5) and the resulting solution was stirred at ambient condition for 3h. In another flask, the ammonium salt of a trinuclear aluminum citrate complex⁵³ ((NH₄)₅[Al₃(C₆H₄O₇)₃(OH)(H₂O)](NO₃)•6H₂O; 0.69 g, 0.74 mmol) was dissolved in 7.5 mL of aqueous HCl solution (pH 1.5) and the resulting solution was stirred for 3 h. This aluminum complex solution was added to the surfactant solution. With a stirring of the mixture, 6.9 mL of Si(OEt)₄ (30.8 mmol) was added. After stirring at 40 °C for 20 h, the resulting mixture was sealed into an autoclave and left to stand at 100 °C for 24 h. Once cooled, the solid product was filtered and washed with water and ethanol. The P123 surfactant was removed by calcination at 550 °C for 5 h. The resulting white solid (1.81 g yield) was identified as the desired SBA-15 type mesoporous aluminosilicate, namely Al-SBA, based on its physicochemical property determined by N₂ isotherm measurement (BET surface area: 1236 m² g⁻¹, Average pore diameter: 4.79 nm, Pore volume: 1.48 cm³ g⁻¹). The content of aluminum determined by ICP-MS was 0.125 mmol g⁻¹.

Hydrophobized SBA-15 type aluminosilicate (H⁺@Al^F). The hydrophobic support was obtained by the reaction of Al-SBA-15 with fluoroalkyl silanol ester. To the suspension of Al-SBA-15 (0.60 g) in non-distilled toluene (30 mL), triethoxy-1*H*,1*H*,2*H*,2*H*-tridecafluoro-*n*-octylsilane ((C₈H₄F₁₃)Si(OEt)₃; 0.28 mL; 0.72 mmol) was added and stirred at 90 °C for 30 min. Filtration and then washing with toluene, methanol, and dichloromethane (each 20 mL) yielded the white powder of **H⁺@Al^F** (1.15 g). The loading amount of the fluoroalkyl group was 0.62 mmol g⁻¹ determined by TG analysis.

Preparation of Fe^{II-R}NHC@Al^F (R = Cl, H, Me)

[Fe^{II}(PY₄Cl₂BIm)(MeCN)]²⁺@Al^F (Fe^{II-Cl}NHC@Al^F). In a 100 mL round neck-flask, 50 mg of Al^F and 7.8 mg of Fe^{II-Cl}NHC•(PF₆)₂ were placed and then 20 mL of CH₃CN was added. The resulting suspension was stirred at 80 °C for 12 hours. The solid product was filtered and washed with CH₃CN, CH₂Cl₂, CH₃OH and toluene. After washing CH₃CN with sonication for 15 min, the resulting pale-yellow solid was filtered and dried under vacuum to obtain 50 mg of **Fe^{II-Cl}NHC@Al^F**.

[Fe^{II}(PY₄H₂BIm)(MeCN)]²⁺@Al^F (Fe^{II}-^HNHC@Al^F). In a 100 mL round neck-flask, 50 mg of Al^F and 6.0 mg of Fe^{II}-^HNHC•(PF₆)₂ were placed and then 20 mL of CH₃CN was added. The resulting suspension was stirred at 80 °C for 12 hours. The solid product was filtered and washed with CH₃CN, CH₂Cl₂, CH₃OH and toluene. After washing CH₃CN with sonication for 15 min, the resulting pale-yellow solid was filtered and dried under vacuum to afford 50 mg of Fe^{II}-^HNHC@Al^F.

[Fe^{II}(PYMeI₂BIm)(MeCN)]²⁺@Al^F (Fe^{II}-^{Me}NHC@Al^F). In a 100 mL round neck-flask, 50 mg of Al^F and 9.4 mg of Fe^{II}-^{Me}NHC•(PF₆)₂ were placed and then 20 mL of CH₃CN was added. The resulting suspension was stirred at 80 °C for 12 hours. The solid product was filtered and washed with CH₃CN, CH₂Cl₂, CH₃OH and toluene. After washing CH₃CN with sonication for 15 min, the resulting pale-yellow solid was filtered and dried under vacuum to obtain 50 mg of Fe^{II}-^{Me}NHC@Al^F.

3. Measurements.

Determination of loading amounts of Fe catalysts on Al^F. The loading amount of Fe catalysts was quantified by ¹H NMR spectroscopy. Fe-^RNHC@Al^F (*ca.* 10 mg) and a pellet of NaOH were dissolved in 1 mL D₂O with heating for several hours.^{S4} Subsequently, a solution of sodium 3-(trimethylsilyl)propanesulfonate (0.2 mmol in 300 mL of D₂O) was added to the reaction mixture (300 mL) as an internal standard. The loading amount of Fe catalysts was calculated by the integration ratio of the 2-H protons of pyridine moieties of the Fe catalysts to trimethyl protons of DSS. Then, the loading amounts of Fe complexes on Al^F for Fe^{II}-^{Cl}NHC@Al^F, Fe^{II}-^HNHC@Al^F and Fe^{II}-^{Me}NHC@Al^F were calculated to be 7.3, 16, 23 nmol mg⁻¹, respectively.

Catalytic reaction. Typical reaction procedure is as follows: In a 3 mL grass tube, Fe^{II}-^RNHC@Al^F catalyst ([Fe] = 0.01 mM) was suspended in 1 mL of MeCN. Cyclohexene (10 μL, 100 mM), and 30 wt % aqueous H₂O₂ (20 μL, 16 mM) were added to this suspension and the mixture was stirred at 323 K for a certain period of time. All reactions were carried under Ar and the products were analysed by GC-MS measurement after quenching the excess amount of H₂O₂ by addition of PPh₃ or ¹H NMR spectroscopy by using PhCN as internal standard.

4. Supplementary figure

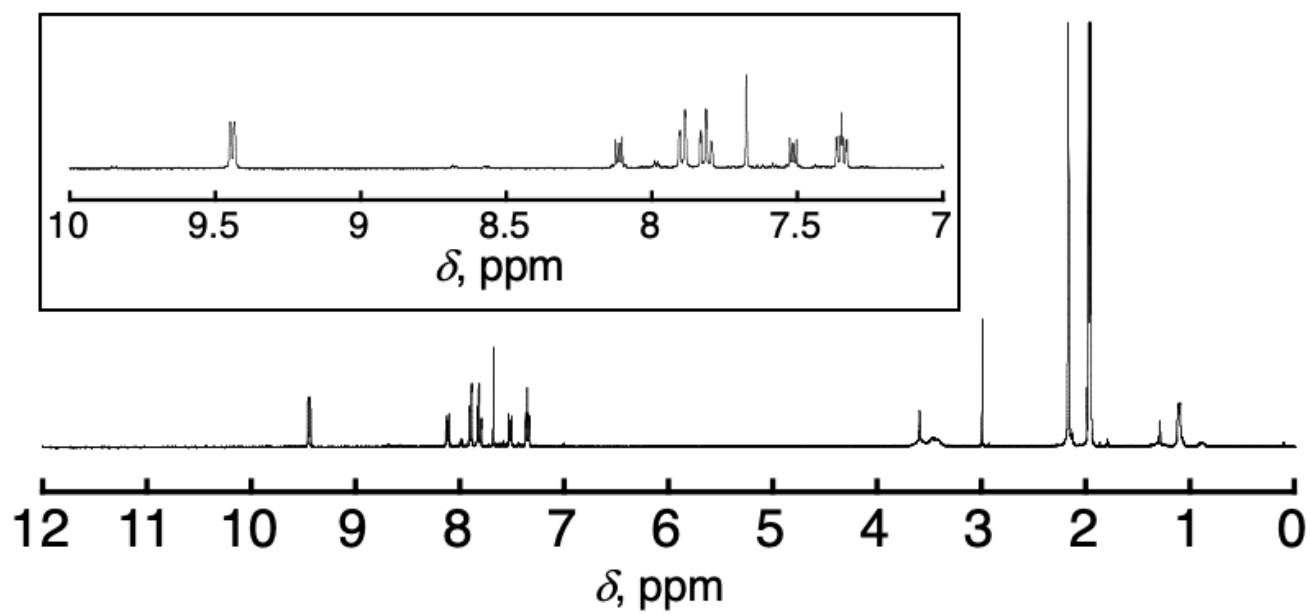


Fig. S1 ^1H NMR spectrum of $\text{Fe}^{\text{II}}\text{-HNHC}\cdot(\text{PF}_6)_2$ in CD_3CN .

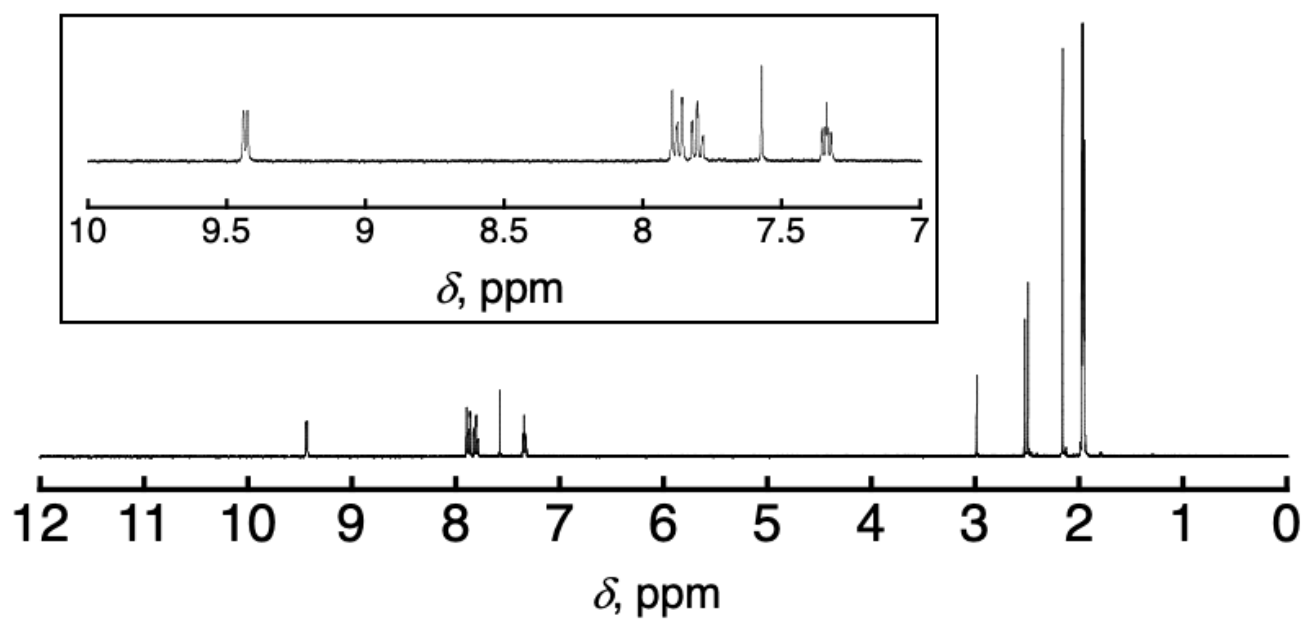


Fig. S2 ^1H NMR spectrum of $\text{Fe-MeNHC}(\text{PF}_6)_2$ in CD_3CN .

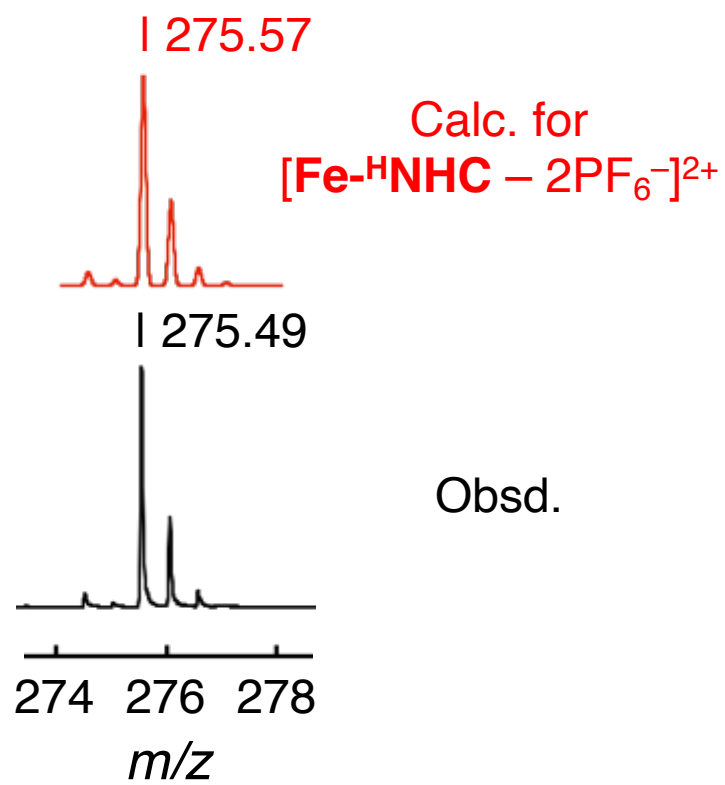


Fig. S3 ESI-TOF-MS spectrum of $\text{Fe}^{\text{II}}\text{-HNHC}(\text{PF}_6)_2$ in CH_3CN .

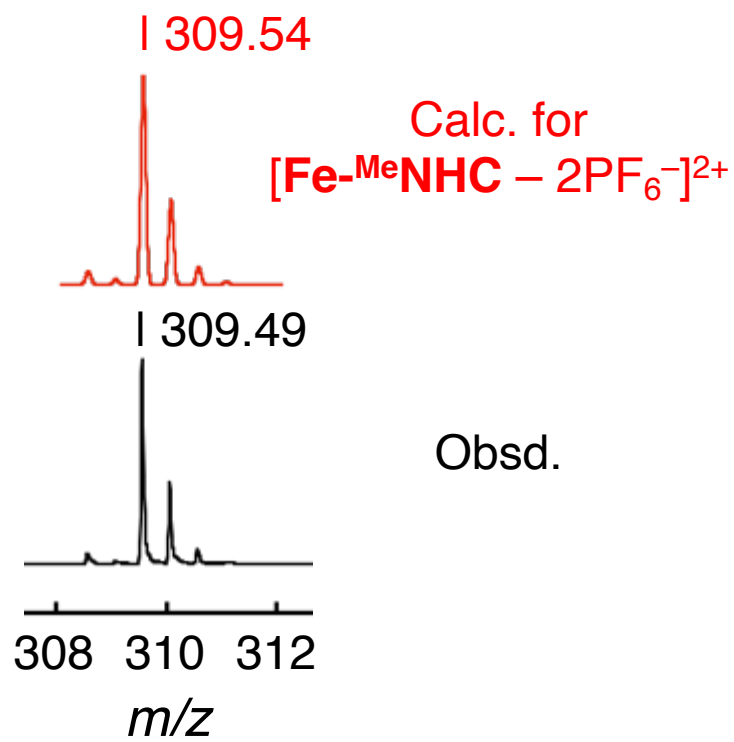


Fig. S4 ESI-TOF-MS spectrum of $\text{Fe}^{\text{II}}\text{-MeNHC}\cdot(\text{PF}_6)_2$ in CH_3CN .

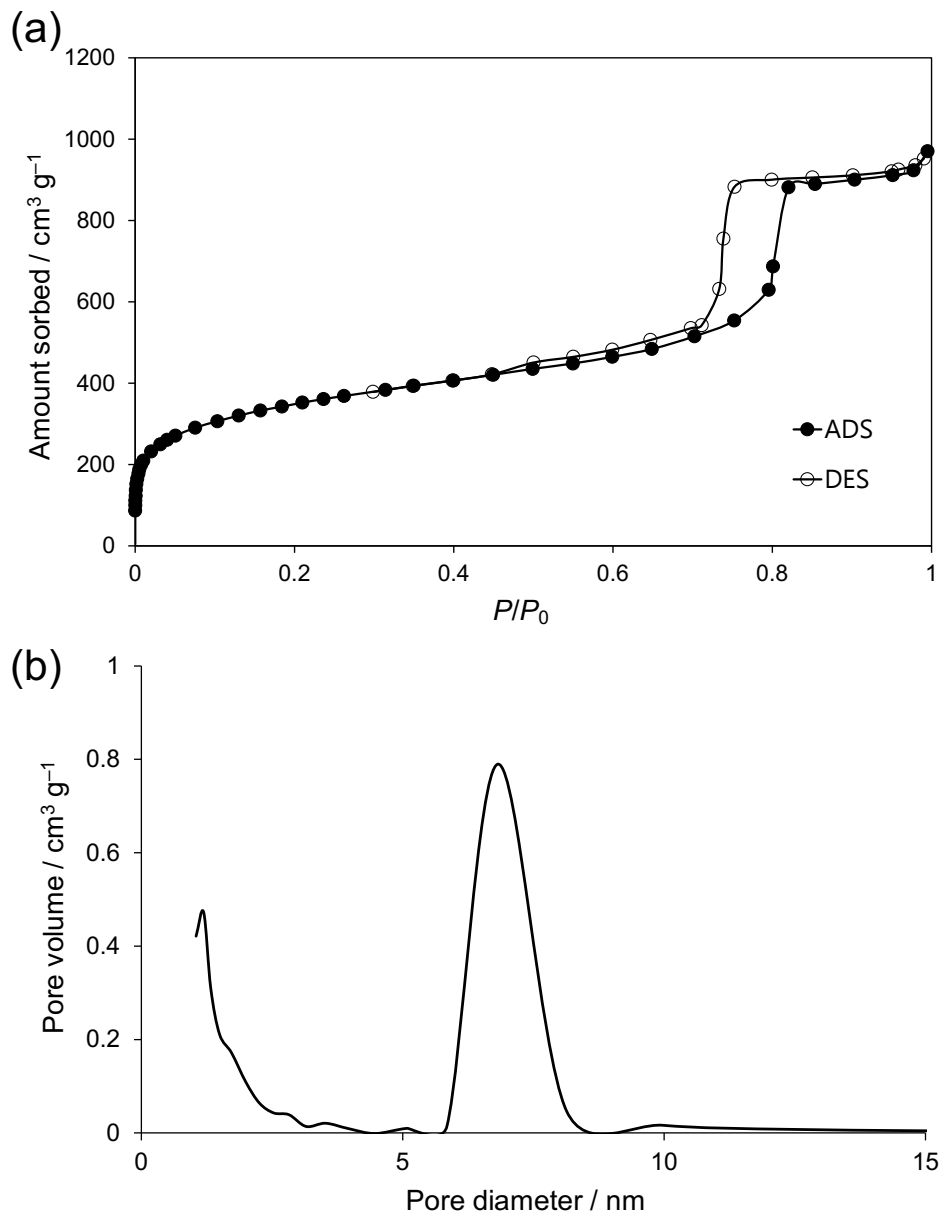


Fig. S5 (a) N_2 adsorption-desorption isotherm of Al-SBA-15 at 77 K. Closed and open symbols indicate the adsorption and desorption branches, respectively. (b) Distribution of the pore diameters of Al-SBA-15.

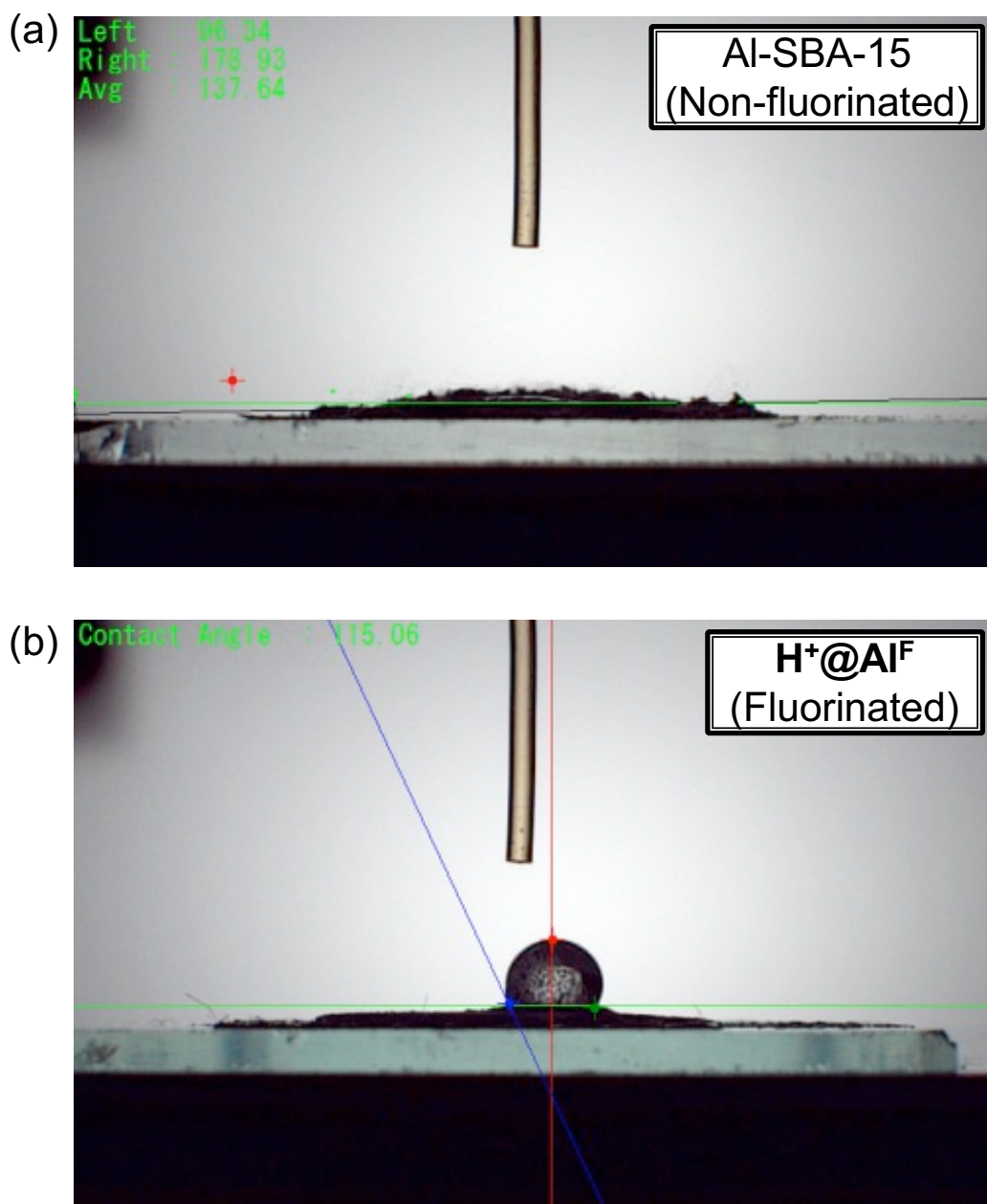


Fig. S6 Contact angles of the supports (a) Al-SBA-15. (b) H⁺@Al^F.

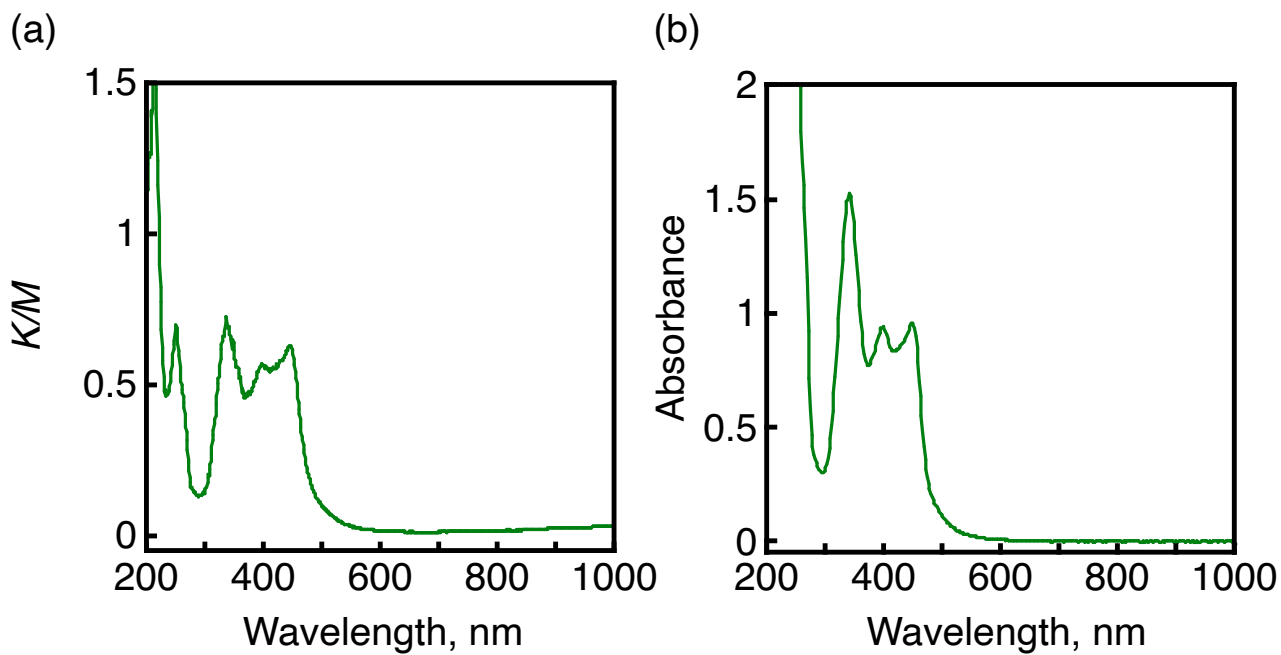


Fig. S7 (a) UV-vis-NIR reflectance spectrum of $\text{Fe}^{\text{II}}\text{-ClNHC@Al}^{\text{F}}$. (b) UV-vis-NIR spectrum of $\text{Fe-ClNHC}\cdot(\text{PF}_6)_2$ in CH_3CN .

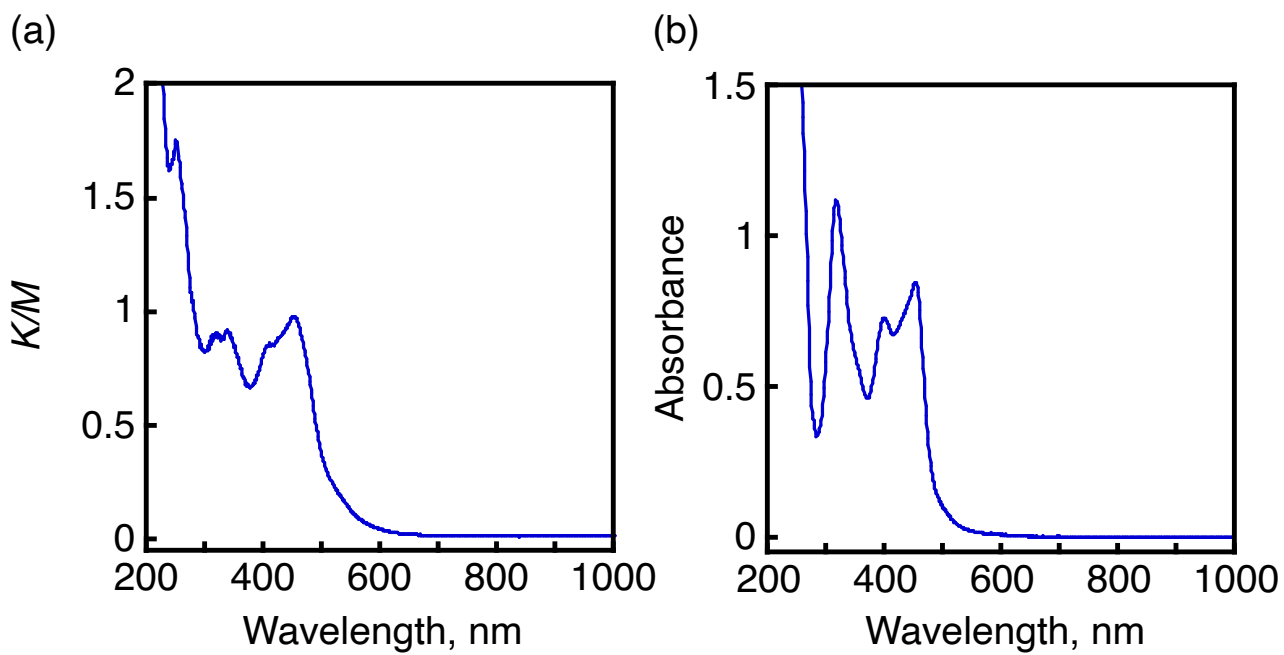


Fig. S8 (a) UV-vis-NIR reflectance spectrum of $\text{Fe}^{\text{II}}\text{-HNHC@AlF}$. (b) UV-vis-NIR spectrum of $\text{Fe-HNHC}\cdot(\text{PF}_6)_2$ in CH_3CN .

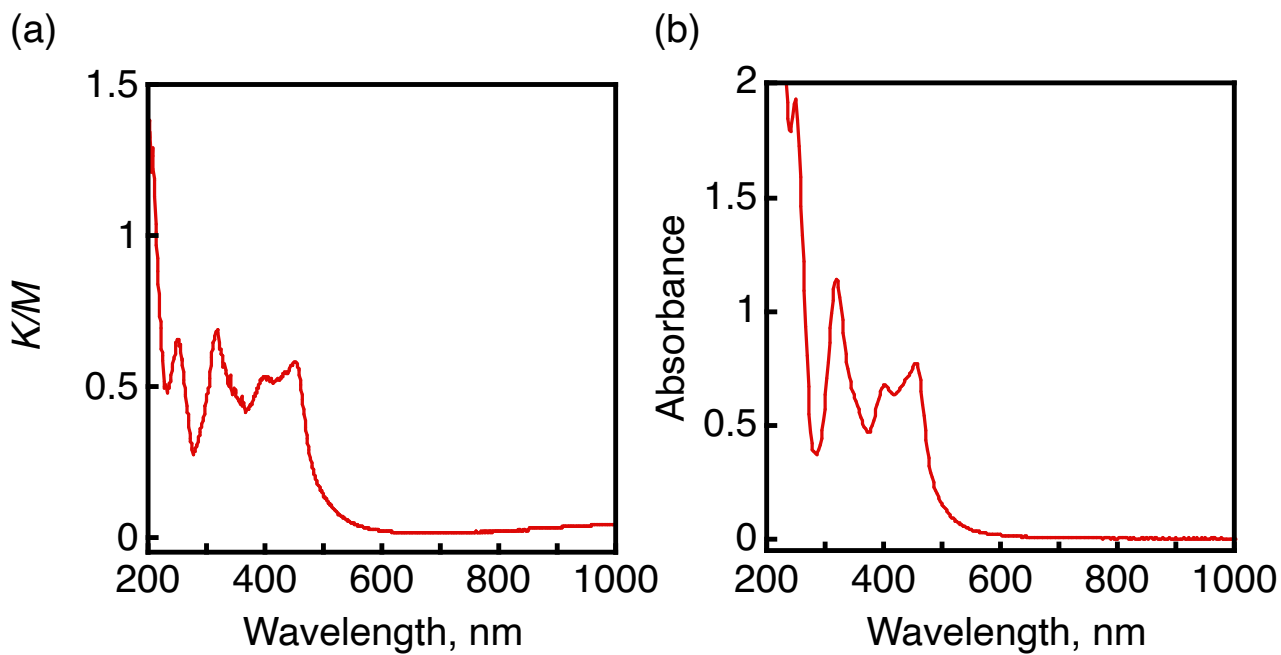


Fig. S9 (a) UV-vis-NIR reflectance spectrum of $\text{Fe}^{\text{II}}\text{-MeNHC@AlF}$. (b) UV-vis-NIR spectrum of $\text{Fe}^{\text{-MeNHC}}\cdot(\text{PF}_6)_2$ in CH_3CN .

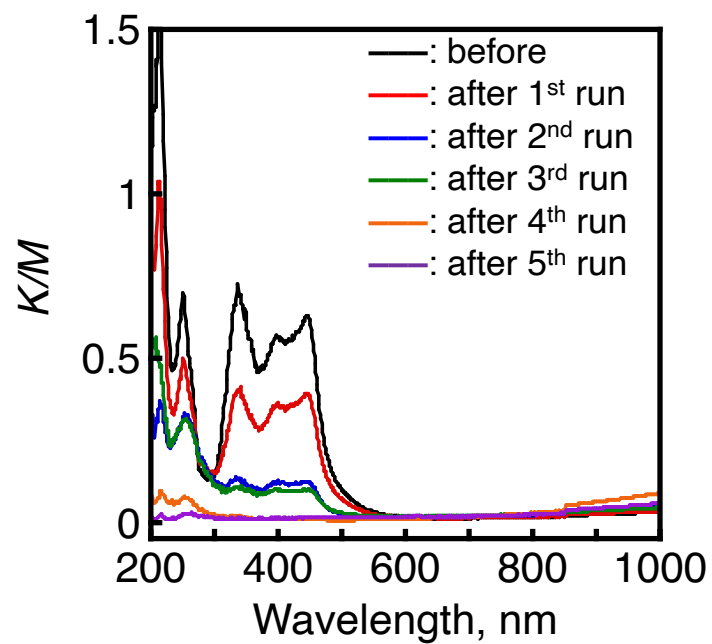


Fig. S10 UV-vis-NIR reflectance spectra after each catalytic run using Fe^{II}-ClNHC@AlF. The summary of Fe contents calculated based on K/M ratio was depicted in Table S5.

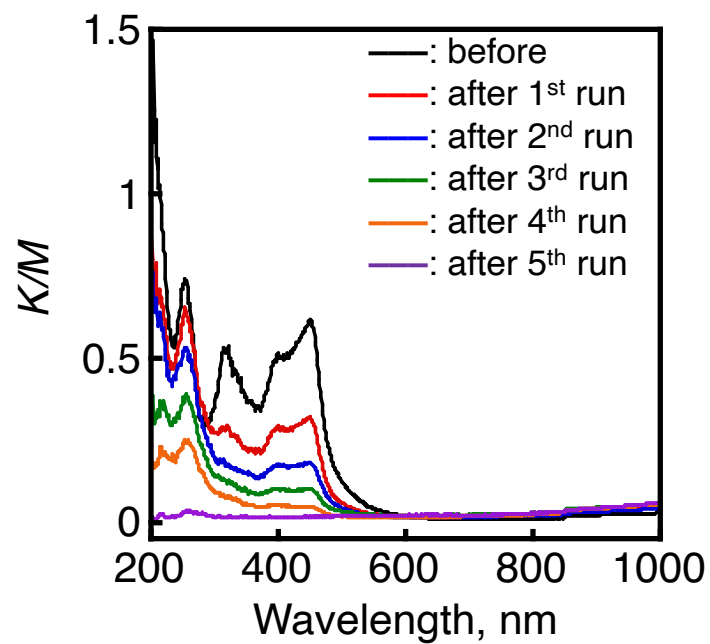


Fig. S11 UV-vis-NIR reflectance spectra after each catalytic run using Fe^{II}-HNHC@Al^F. The summary of Fe contents calculated based on K/M ratio was depicted in Table S6.

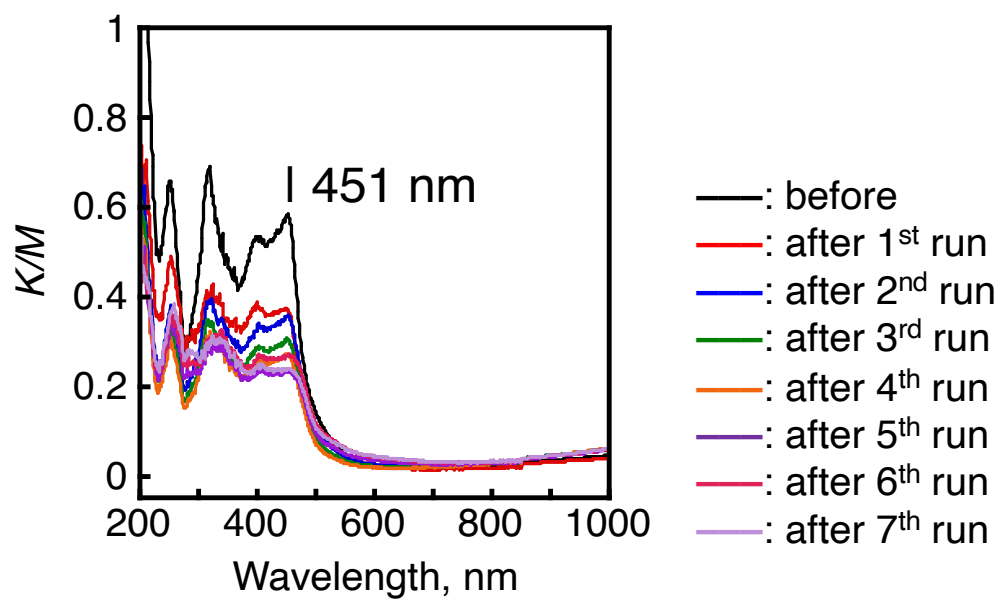


Fig. S12 UV-vis-NIR reflectance spectra after each catalytic run using $\text{Fe}^{\text{II}}\text{-MeNHC@AlF}$. The summary of Fe contents calculated based on K/M ratio was depicted in Table S7.

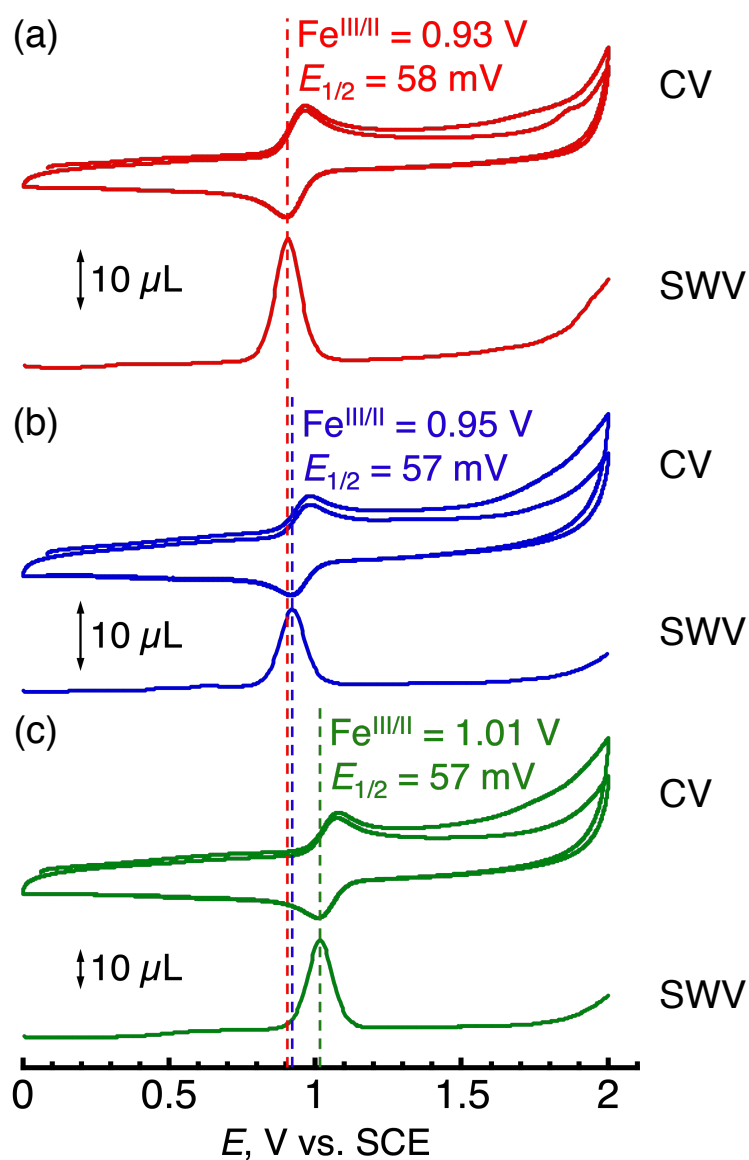


Fig. S13 Cyclic voltammograms (CVs) and square-wave voltammograms (SWVs) of $\text{Fe}^{\text{II-MeNHC}}$ (a), $\text{Fe}^{\text{II-HNHC}}$ (b), and $\text{Fe}^{\text{II-ClNHC}}$ (c) in CH_3CN at room temperature. Conditions: [complex] = 0.1 mM, 0.1 M of $[(n\text{-butyl})_4\text{N}]\text{PF}_6$ as an electrolyte; working electrode, glassy carbon; reference electrode, Ag/AgCl; counter electrode, Pt wire. Redox potentials are referenced to SCE as 0 V by subtracting 0.045 V from the potentials measured.

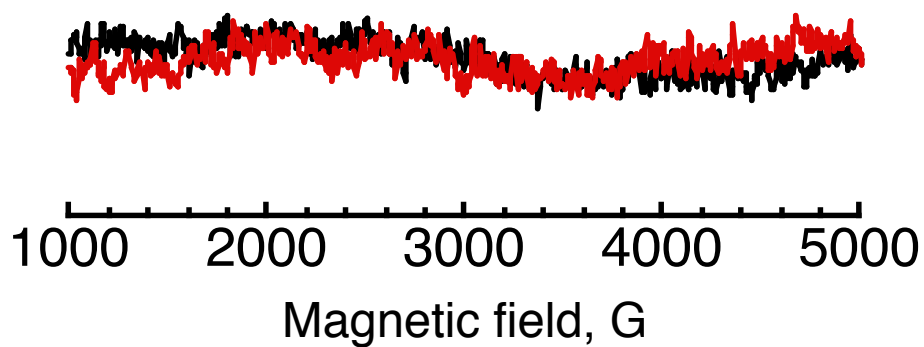


Fig. S14 X-band The ESR spectra of Fe^{II}-ClNHC in acetonitrile before (black line) and after (red line) addition of 10 equiv. of H₂O₂. [Fe^{II}-ClNHC] = 1 mM, [H₂O₂] = 10 mM. EPR spectra were measured at 100 K. Microwave frequency: 9.572 GHz, microwave power: 1.0 mW, modulation frequency: 100.00 kHz, modulation amplitude: 6.00 G.

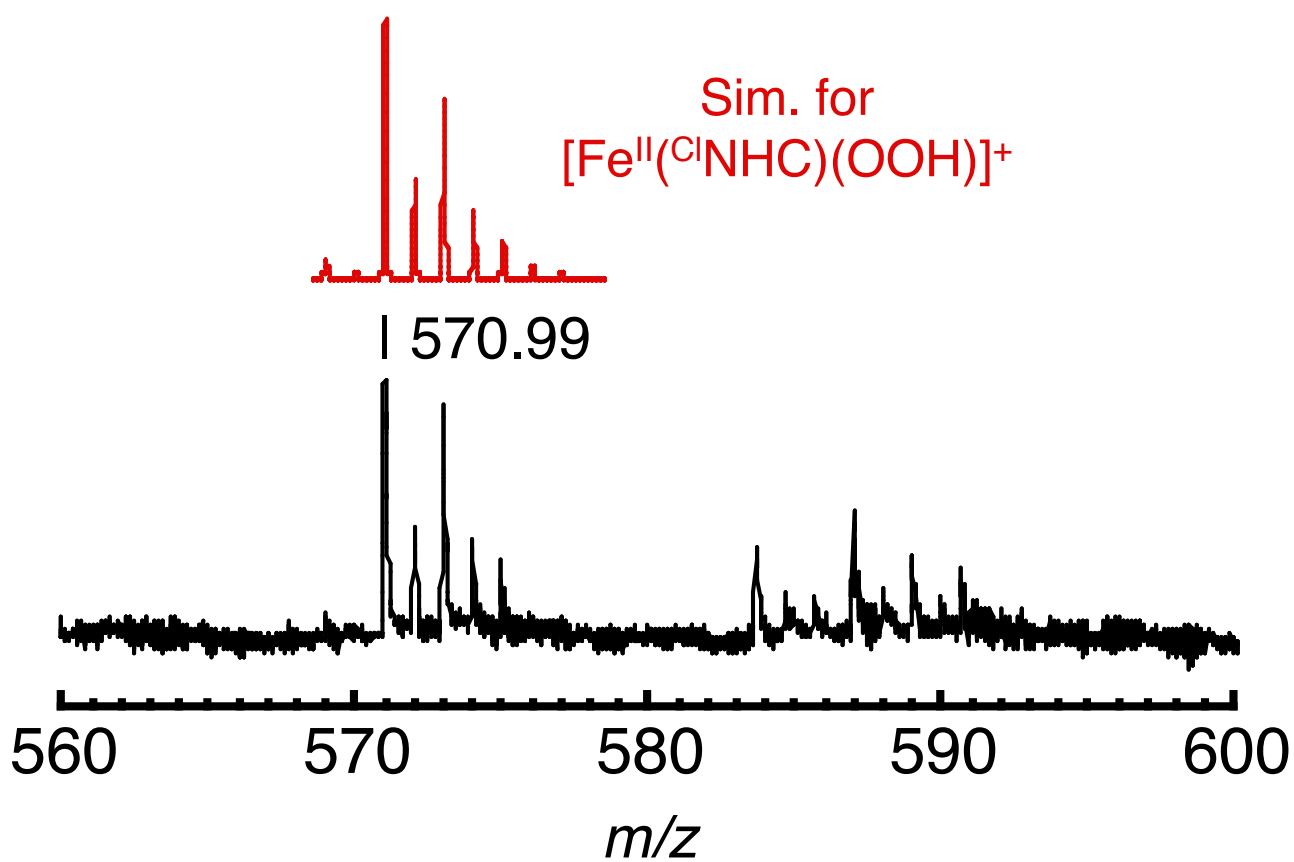


Fig. S15 ESI-MS spectrum of a reaction mixture containing $\text{Fe}^{\text{II}}\text{-ClNHC}$ and 10 equiv. of H_2O_2 in CH_3CN : black trace, observed; red trace, simulated for $[\text{Fe}^{\text{II}}(\text{OOH})(\text{ClNHC})]^+$.

5. Supplementary table

Table S1. Catalytic cyclohexane oxidation using H₂O₂ as an oxidant and Fe^{II}-Cl⁻NHC@Al^F as a catalyst in acetonitrile or trifluoroethanol.

Solvent	Product	TONs ^a
Acetonitrile	Cy-OH	705
	Cy=O	39
Trifluoroethanol	Cy-OH	N.D.
	Cy=O	N.D.

^a TONs = [Product]/[catalyst]. Conditions: Fe^{II}-Cl⁻NHC@Al^F: 10 nmol, [H₂O₂] = 16 mM, [Substrate] = 100 mM, T = 313 K, and reaction time = 3 h. TONs were determined by ¹H NMR and GC-MS analysis. N.D.: Not detected.

Table S2. Control experiments for the cyclohexane oxidation.

Catalyst	Product	TONs ^a	Alcohol/Ketone
Fe^{II}-^{Cl}NHC•(PF₆)₂	Cy-OH	6	1.1
	Cy=O	5	
Fe^{II}-^HNHC•(PF₆)₂	Cy-OH	6	1.5
	Cy=O	4	
Fe^{II}-^{Me}NHC•(PF₆)₂	Cy-OH	5	1.8
	Cy=O	3	
H⁺@Al^F (1.0 mg)	Cy-OH	N.D.	–
	Cy=O	N.D.	

^a TONs = [Product]/[catalyst]. Conditions: **[Fe^{II}-^RNHC•(PF₆)₂] = 0.01 mM**, [H₂O₂] = 16 mM, [Substrate] = 100 mM, *T* = 313 K, and reaction time = 3 h. TONs were determined by GC-MS analysis. Any byproducts other than compounds listed in the table were not observed. N.D.: Not detected.

Table S3. Catalytic substrate oxidation by H₂O₂ and Fe^{II}-Cl⁻NHC@Al^F in acetonitrile.

Substrate	BDE, kcal/mol ^a	Product	TONs ^b	A/K
Cumene	83.5	Cumene-OH	1430	–
Toluene	88.5	benzylalcohol	1100	20
		benzaldehyde	55	
Cyclooctane	95.7	cyclooctanol	820	23
		cyclooctanone	35	
<i>cis</i> -1,2-dimethylcyclohexane	97.4	<i>cis</i> -1,2-dimethylcyclohexane	420	–

^a ref. S5. ^b TONs = [Product]/[catalyst]. Conditions: Fe^{II}-Cl⁻NHC•(PF₆)₂: 10 nmol, [H₂O₂] = 16 mM, [Substrate] = 100 mM, T = 313 K, and reaction time = 3 h. TONs were determined by ¹H NMR spectroscopy by using PhCN as internal standard. Any byproducts other than compounds listed in the table were not observed.

Table S4. Catalytic activity in oxidation of other substrates using H₂O₂ and Fe^{II}-ClNHC@Al^F in acetonitrile.

Substrate	BDE, kcal/mol ^a	Product	TONs ^b
Cyclohexanol (100 mM)	92.4	Cyclohexanone	30
Cyclooctane, cyclohexanol (50 mM each)	95.7, 92.4	Cyclooctanol	752
		Cyclooctenone	28
		Cyclohexanone	20

^a ref. S5. ^b TONs = [Product]/[catalyst]. Conditions: Fe^{II}-ClNHC•(PF₆)₂: 10 nmol, [H₂O₂] = 16 mM, T = 313 K, and reaction time = 3 h. TONs were determined by ¹H NMR spectroscopy by using PhCN as internal standard. Any byproducts other than compounds listed in the table were not observed.

Table S5. Summary of Fe contents calculated and total TONs in catalytic cyclohexane oxidation in acetonitrile by H₂O₂ and Fe^{II}-Cl⁻NHC@Al^F

	Fe contents, % ^a	Fe contents, nmol mg ⁻¹	Total TON ^b
Before run	100	7.3	–
After 1 st run	61	4.5	744
After 2 nd run	20	1.5	467
After 3 rd run	16	1.2	297
After 4 th run	2	0.15	85
After 5 th run	0	0	N.D.

^a Fe contents, % = $(K/M)_X / (K/M)_0 \times 100$ (X = number of catalytic runs). $(K/M)_X$: The K/M value at 451 nm determined by UV-vis-NIR reflectance measurement of the catalyst after the X-th catalytic run. $(K/M)_0$: The K/M value at 451 nm determined by UV-vis-NIR reflectance measurement of catalyst before reaction. ^b Total TON = [All products]/[catalyst]. Conditions: [H₂O₂] = 16 mM, [Substrate] = 100 mM, T = 313 K, and reaction time = 3 h. N.D.: not detected.

Table S6. Summary of Fe contents calculated and total TONs in catalytic cyclohexane oxidation in acetonitrile by H₂O₂ and Fe^{II}-^HNHC@Al^F

	Fe contents, % ^a	Fe contents, nmol mg ⁻¹	Total TON ^b
Before run	0	16	–
After 1 st run	51	8.2	511
After 2 nd run	30	4.8	326
After 3 rd run	17	2.7	209
After 4 th run	8	1.3	103
After 5 th run	0	0	N.D.

^a Fe contents, % = $(K/M)_X / (K/M)_0 \times 100$ (X = number of catalytic runs). $(K/M)_X$: The K/M value at 451 nm determined by UV-vis-NIR reflectance measurement of the catalyst after the X-th catalytic run. $(K/M)_0$: The K/M value at 451 nm determined by UV-vis-NIR reflectance measurement of catalyst before reaction. ^b Total TON = [All products]/[catalyst]. Conditions: [H₂O₂] = 16 mM, [substrate] = 100 mM, $T = 313$ K, and reaction time = 3 h. N.D.: not detected.

Table S7. Summary of Fe contents calculated and total TONs in catalytic cyclohexane oxidation in acetonitrile by H₂O₂ and Fe^{II}-MeNHC@Al^F

	Fe contents, % ^a	Fe contents, nmol mg ⁻¹	Total TON ^b
Before run	100	23	–
After 1 st run	64	15	379
After 2 nd run	61	14	337
After 3 rd run	52	12	422
After 4 th run	46	11	366
After 5 th run	43	9.9	314
After 6 th run	46	10	316
After 7 th run	41	9.4	352
After 8 th run	25	5.8	237
After 9 th run	21	4.8	151
After 10 th run	0	0	N.D.

^a Fe contents, % = $(K/M)_X / (K/M)_0 \times 100$ (X = number of catalytic runs). $(K/M)_X$: The K/M value at 451 nm determined by UV-vis-NIR reflectance measurement of the catalyst after the X-th catalytic run. $(K/M)_0$: The K/M value at 451 nm determined by UV-vis-NIR reflectance measurement of catalyst before reaction. ^b Total TON = [All products]/[catalyst]. Conditions: [H₂O₂] = 16 mM, [substrate] = 100 mM, $T = 313$ K, and reaction time = 3 h. N.D.: not detected.

Table S8. Control experiments for cyclohexene oxidation.

Catalyst	Product	TONs ^a	Cyen-oxide/ (Cyen-OH + Cyen=O)
Fe^{II}-ClNHC•(PF₆)₂	Cyen-OH	9	1.1
	Cyen=O	6	
	Cyen-oxide	15	
Fe^{II}-^HNHC•(PF₆)₂	Cyen-OH	8	0.86
	Cyen=O	6	
	Cyen-oxide	12	
Fe^{II}-^{Me}NHC•(PF₆)₂	Cyen-OH	8	0.67
	Cyen=O	7	
	Cyen-oxide	10	
H⁺@Al^F (1.0 mg)	Cyen-OH	N.D.	–
	Cyen=O	N.D.	
	Cyen-oxide	N.D.	

^a TONs = [Product]/[catalyst]. Conditions: catalyst: 10 nmol, [H₂O₂] = 16 mM, [Substrate] = 100 mM, *T* = 313 K, and reaction time = 3 h. TONs were determined by GC-MS analysis. Any byproducts other than compounds listed in the table were not observed. N.D.: Not detected.

Table S9. Comparison of cyclohexane hydroxylation and cyclohexene epoxidation with H₂O₂ as an oxidant among selected literature.

Catalyst	Substrate	TON (time)	A/K	Epoxide yield, %	Ref.
Fe^{II}-Cl⁻NHC@Al^F	CyH	744 (3 hours)	18	–	This work
[Fe ^{II} (TPA)(CH ₃ CN) ₂] ²⁺	CyH	3.0 (15 min)	4.3	–	S6
[Fe ^{II} (BPMEN)(CH ₃ CN) ₂] ²⁺	CyH	6.3 (30 min)	8.0	–	S7
[Fe ^{II} (BPQA)(OTf) ₂]	CyH	5.8 (30 min)	10	–	S7
[Fe ^{II} (BQPA)(H ₂ O)(ClO ₄) ⁺	CyH	1.7 (30 min)	2	–	S7
Fe ^{II} (Me ₂ PyTACN)(CF ₃ SO ₃) ₂	CyH	6.0 (30 min)	12	–	S8
Fe^{II}-Cl⁻NHC@Al^F	Cyene	908 (3 hours)	–	90	This work
Fe ^{II} (cyclam)(CF ₃ SO ₃) ₂	Cyene	20 (20 min)	–	40	S9
[Fe(PYBP)(CH ₃ CN) ₂] ²⁺	Cyene	490 (5–10 min)	–	94	S10
[Fe ^{II} (NCCN ^{Me})(MeCN) ₂] ²⁺	Cyene	45 (5 min)	–	90	S11
[Fe ^{III} (calix[4]imidazolyl)(CH ₃ CN) ₂] ³⁺	Cyene	341 (30 min)	–	>99	S12

TPA: tris(2-pyridylmethyl)amine, BPMN: *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-1,2-diaminoethane, BPQA: bis(2-pyridylmethyl)(2-quinolylmethyl)amine, BQPA: bis(2-quinolylmethyl)(2-pyridylmethyl)amine, Me₂PyTACN: 1-(2-pyridylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane, cyclam: 1,4,8,11-tetraazacyclotetradecane, PYBP: 1,1'-bis-(pyridine-2-ylmethyl)-2,2'-bipiperidine NCCN^{Me}: di(*o*-imidazol-2-ylidenepyridine)methane.

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