

Supporting Information

Dithiolato-Bridged Nickel-Iron Complexes as Models for the Active Site of [NiFe]-Hydrogenases

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Experimental Section

1. General comments

All reactions were performed using standard Schlenk and vacuum-line techniques under an atmosphere of highly purified nitrogen. CO gas should be handled in a well-ventilated hood, since it is highly toxic. Acetone was dried by refluxing with anhydrous K_2CO_3 . CO gas, $NaBF_4$, Me_3NO , $Me_3NO \cdot 2H_2O$ and $HBf_4 \cdot Et_2O$ (50-55% in Et_2O) were available commercially and used as received. $(pnp)NiCl_2$ ($pnp = PhN(CH_2PPh_2)_2$)¹ and $(dppv)Fe(CO)_2(pdt)$ ($dppv = 1,2-C_2H_2(PPh_2)_2$, $pdt = 1,3$ -propanedithiolate)² were prepared according to the published procedures. Electrospray ionization mass spectrometry (ESI-MS) data were obtained by using an Agilent 6520 Q-TOF LC/MS. X-band EPR spectra were measured at 128 K by using a Bruker A300 EPR spectrometer (microwave frequency: 9.426 GHz, microwave power: 5.0 mW). X-ray photoelectron spectroscopy (XPS) experiments were performed on a PHI 5000 Versa Probe XPS system equipped with an Al-K α monochromator X-ray source, and the binding energies were corrected by assuming the C 1s binding energy of the carbon atoms of the ligands in specimens as 284.5 eV.³ IR spectra were recorded on a Bruker Tensor 27 FT-IR infrared spectrophotometer. 1H and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker Avance 400 NMR spectrometer. Elemental analyses were performed on an Elementar Vario EL analyzer. Melting points were determined on a SGW X-4 melting point apparatus with a microscopy and are uncorrected.

2. Preparation of $[(pnp)Ni(pdt)Fe(CO)_2(dppv)](BF_4)_2$ ($[1](BF_4)_2$) and $[(pnp)Ni(pdt)(\mu-Cl)Fe(CO)(dppv)](BF_4)$

A 50 mL three-necked flask fitted with a magnetic stir-bar, two serum caps, and a N_2 inlet tube was charged with $(dppv)(CO)_2Fe(pdt)$ (0.123 g, 0.20 mmol), $(pnp)NiCl_2$ (0.124 g, 0.20 mmol), $NaBF_4$ (0.220 g, 2.00 mmol), and acetone (10 mL). The mixture was stirred at 0 °C for 2 h to give a brown-red solution. Solvent was removed at reduced pressure and then the residue was subjected to column

chromatography (silica gel). Elution with CH₂Cl₂/acetone (v/v = 12:1) developed a small brown band, from which [(pnp)Ni(pdt)Fe(μ -Cl)(CO)(dppv)](BF₄) (0.025 g, 10%) was obtained as a deep brown solid. M.p. 186 °C (dec); Anal. Calcd. for C₆₂H₅₇BClF₄FeNNiOP₄S₂: C 59.24; H, 4.57; N, 1.11. Found: C, 59.35; H, 4.64; N, 1.34. ¹H NMR (400 MHz, CDCl₃): δ 1.66–2.98 (m, 6H, CH₂CH₂CH₂), 3.75, 4.32 (2br.s, 4H, CH₂NCH₂), 6.42–7.67 (m, 47H, 9C₆H₅, CH=CH) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ –3.68 (s, NiP₂), 70.84 (s, FeP₂) ppm. ESI-MS: m/z 1168.0 for (M-BF₄)⁺. IR (KBr disk): $\nu_{C\equiv O}$ 1936 (vs) cm⁻¹. Further elution with CH₂Cl₂/acetone (v/v = 3:1) developed an orange-red band, from which [1](BF₄)₂ (0.222 g, 83%) was obtained as an orange-red solid. M.p. 148 °C (dec); Anal. Calcd. for C₆₃H₅₇B₂F₈FeNNiO₂P₄S₂: C, 56.62; H, 4.30; N, 1.05. Found: C, 56.39; H, 4.60; N, 1.09. ¹H NMR (400 MHz, CD₂Cl₂): δ 2.06–2.10, 2.36–2.43, 2.79–2.82, 3.87–3.98 (4m, 6H, CH₂CH₂CH₂), 4.04–4.12, 4.50–4.56 (2m, 4H, CH₂NCH₂), 6.38–7.96 (m, 45H, 9C₆H₅), 8.35–8.50 (m, 2H, CH=CH) ppm. ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ 0.06 (s, NiP₂), 64.62 (s, FeP₂) ppm. ESI-MS: m/z 580.6 for [1]²⁺. IR (KBr disk): $\nu_{C\equiv O}$ 1991 (vs) cm⁻¹.

3. Preparation of [(pnp)Ni(pdt)Fe(CO)(*t*-H)(dppv)](BF₄) ([2](BF₄))

To a 30 mL autoclave's inner sleeve (made of PTFE) were added [1](BF₄)₂ (67 mg, 0.05 mmol), Me₃NO (3.75 mg, 0.05 mmol), and acetone (2 mL) under nitrogen. The reaction mixture was stirred at 0 °C for 10 min and then it was frozen by inserting the sleeve into liquid nitrogen. After the autoclave was sealed, the head space of the sleeve was evacuated and refilled with 1.5 MPa of H₂. The frozen reaction mixture was thawed and then the reaction mixture was stirred at room temperature for 4 h. After removal of the solvent at reduced pressure, the residue was subjected to flash column chromatography (silica gel G). Elution with CH₂Cl₂/acetone (v/v = 6:1) developed a brown-red band, from which [2](BF₄) (0.041 g, 67%) was obtained as an air-stable brown solid. M.p. 121 °C (dec); Anal. Calcd. for C₆₂H₅₈BF₄FeNNiOP₄S₂: C, 60.91; H, 4.78; N, 1.15. Found: C, 60.65; H, 5.00; N, 1.25. ¹H NMR (400 MHz, CDCl₃): δ –4.27 (t, *J* = 74.0 Hz, 1H, FeH), 1.40–2.05 (m, 6H, CH₂CH₂CH₂),

4.05–4.20 (m, 4H, CH₂NCH₂), 6.49–7.75 (m, 47H, 9C₆H₅, CH=CH) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 6.11 (s, NiP₂), 91.63 (t, *J* = 7.3 Hz, FeP₂) ppm. ESI-MS: *m/z* 1134.2 for [2]⁺. IR (KBr disk): ν_{C=O} 1911 (vs) cm⁻¹.

4. Preparation of [(pnp)Ni(pdt)(μ-OH)Fe(CO)(dppv)](BF₄) ([3](BF₄))

A 50 mL three-necked flask equipped with two serum caps, a magnetic stir-bar, and a nitrogen inlet tube was charged with [1](BF₄)₂ (0.134 g, 0.10 mmol), Me₃NO·2H₂O (0.011 g, 0.10 mmol), and acetone (6 mL). The reaction mixture was stirred at 0 °C for ca.10 min and then stirred at room temperature for 4 h. After solvent was removed at reduced pressure, the residue was subjected to column chromatography (silica gel). Elution with CH₂Cl₂/acetone (v/v = 8:1) developed a brown-red band, from which [3](BF₄) (0.105 g, 85%) was obtained as a brown-red solid. M.p. 158 °C (dec); Anal. Calcd. for C₆₂H₅₈BF₄FeNNiO₂P₄S₂: C, 60.13; H, 4.72; N, 1.13. Found: C, 59.95; H, 5.01; N, 1.18. ¹H NMR (400 MHz, acetone-d₆): δ -3.66 (s, 1H, OH), 1.46–1.50, 1.90–1.96, 2.47–2.51, 2.81–2.84 (4m, 6H, CH₂CH₂CH₂), 4.35 (s, 4H, CH₂NCH₂), 6.39–8.20 (m, 47H, 9C₆H₅, HC=CH) ppm; ³¹P{¹H} NMR (162 MHz, acetone-d₆): δ -3.14 (s, NiP₂), 76.98 (s, FeP₂) ppm; ESI-MS: *m/z* 1150.2 for [3]⁺. IR (KBr disk): ν_{C=O} 1927 (vs) cm⁻¹.

5. Treatment of [3](BF₄) with HBF₄·Et₂O under CO to give [1](BF₄)₂

A 50 mL three-necked flask equipped with two serum caps, a magnetic stir-bar, and a nitrogen inlet tube was charged with an acetone (5 mL) solution of [3](BF₄) (0.062 g, 0.05 mmol). To this solution was added HBF₄·Et₂O (7.4 μL, ca. 0.05 mmol) by syringe and then the new solution was stirred and bubbled with CO at room temperature for 0.5 h. Solvent was removed at reduced pressure and the residue was subjected to flash column chromatography (silica gel). Elution with acetone developed an orange-red band, from which [1](BF₄)₂ (0.064 g, 96%) was obtained as an orange-red solid, which was identified by obtaining the same IR, ¹H NMR, and ³¹P{¹H} NMR spectra as those of the authentic material indicated above.

6. X-ray structure determinations of [1](BF₄)₂, [2](BF₄), and [3](BF₄)

Single crystals of [1](BF₄)₂ suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into its CH₂Cl₂ solution at room temperature. A single crystal of [1](BF₄)₂ was mounted on a Rigaku MM-007 (rotating anode) diffractometer equipped with a Saturn 70 CCD. Data were collected at 113 K by using a confocal monochromator with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) in the ω scanning mode. Data collection, reduction, and absorption correction were performed with the CRYSTALCLEAR program. The structure was solved by direct methods using the SHELXS program and refined by full-matrix least-squares techniques (SHELXL) on F^2 . Hydrogen atoms were located by using the geometric method.

Single crystals of [2](BF₄) and [3](BF₄) suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into their acetone solutions at about $-5 \text{ }^\circ\text{C}$. A single crystal of [2](BF₄) or [3](BF₄) was mounted on a Rigaku MM-007 (rotating anode) diffractometer equipped with a Pilatus 200 K. Data were collected at 113 K by using a confocal monochromator with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) in the ω scanning mode. Data collection and reduction were performed with the CRYSTALCLEAR-SM program. Data absorption correction was performed with the REQAB program. The structures were solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares techniques (SHELXL or XL) on F^2 . Hydrogen atoms were located by using the geometric method.

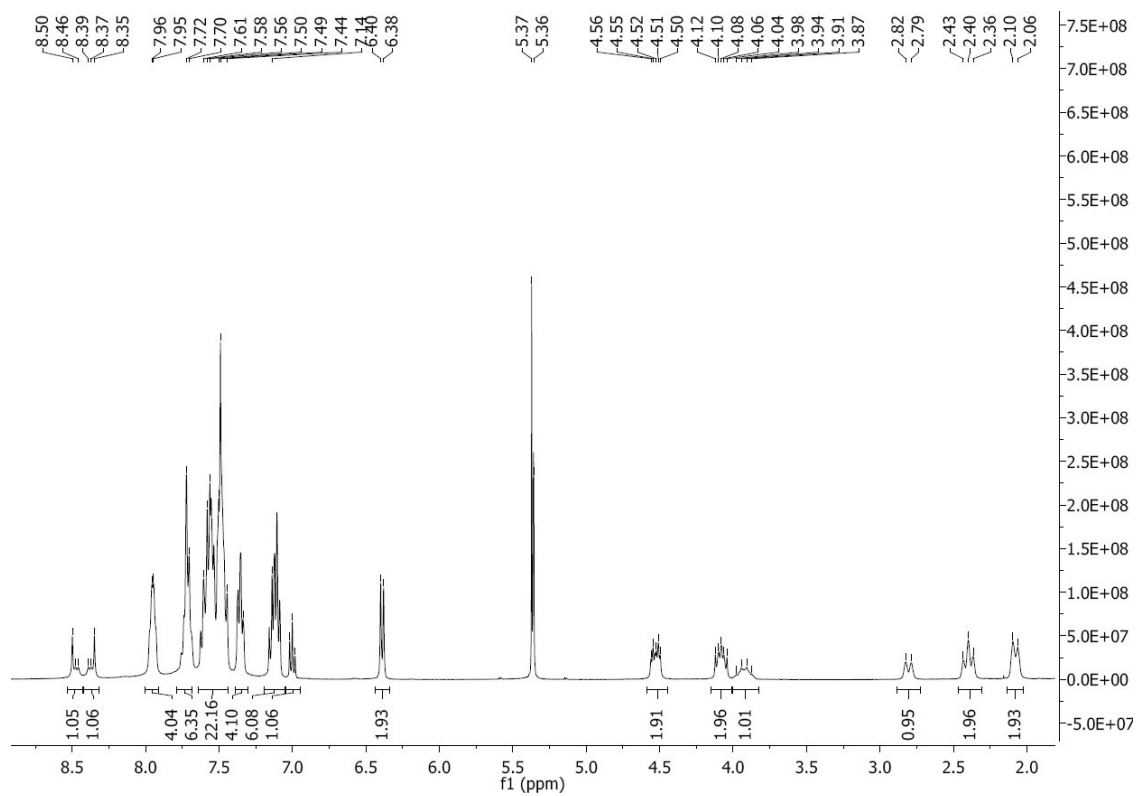


Figure S1. ^1H NMR spectrum of $[\mathbf{1}](\text{BF}_4)_2$

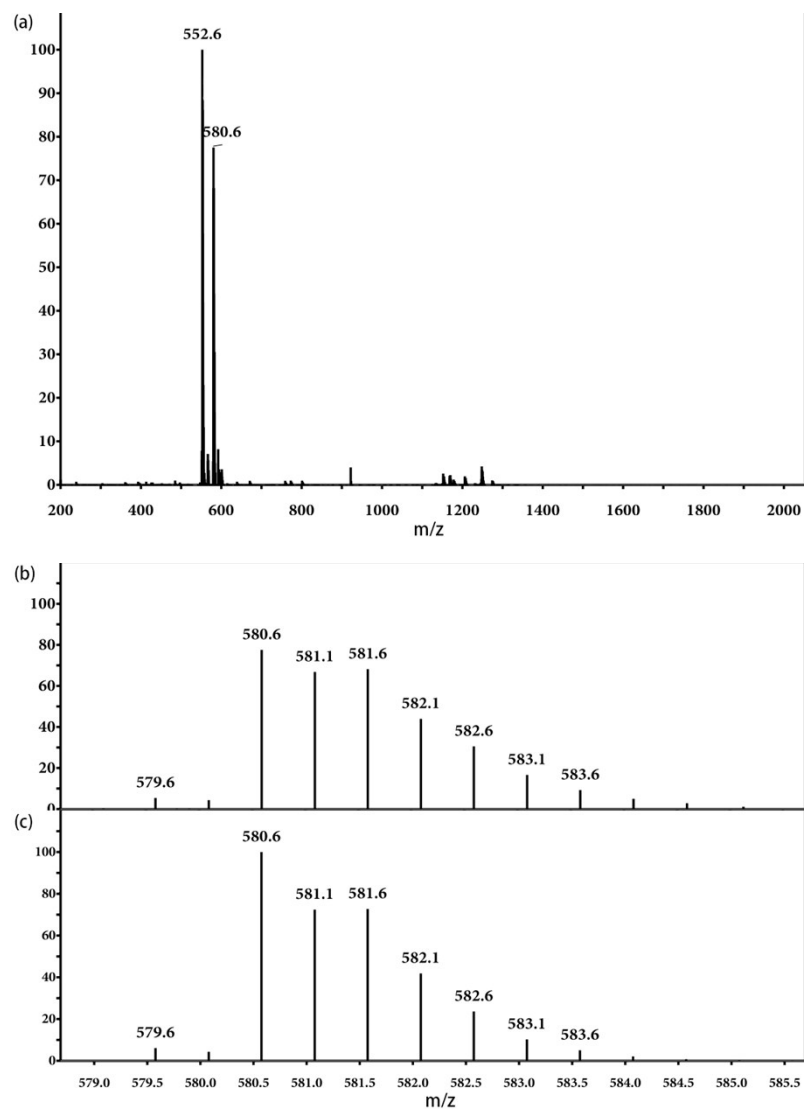


Figure S2. (a) A positive-ion ESI mass spectrum of $[1](BF_4)_2$ in CH_3OH . (b) The signal at m/z 580.6 corresponds to $[1]^{2+}$. (c) Calculated isotopic distribution for $[1]^{2+}$.

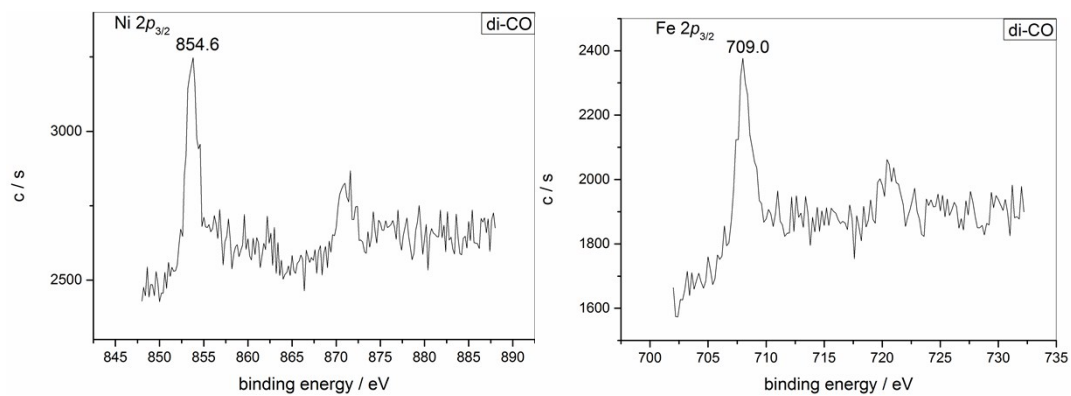


Figure S3. XPS spectra of Ni 2*p* and Fe 2*p* region for [1](BF₄)₂

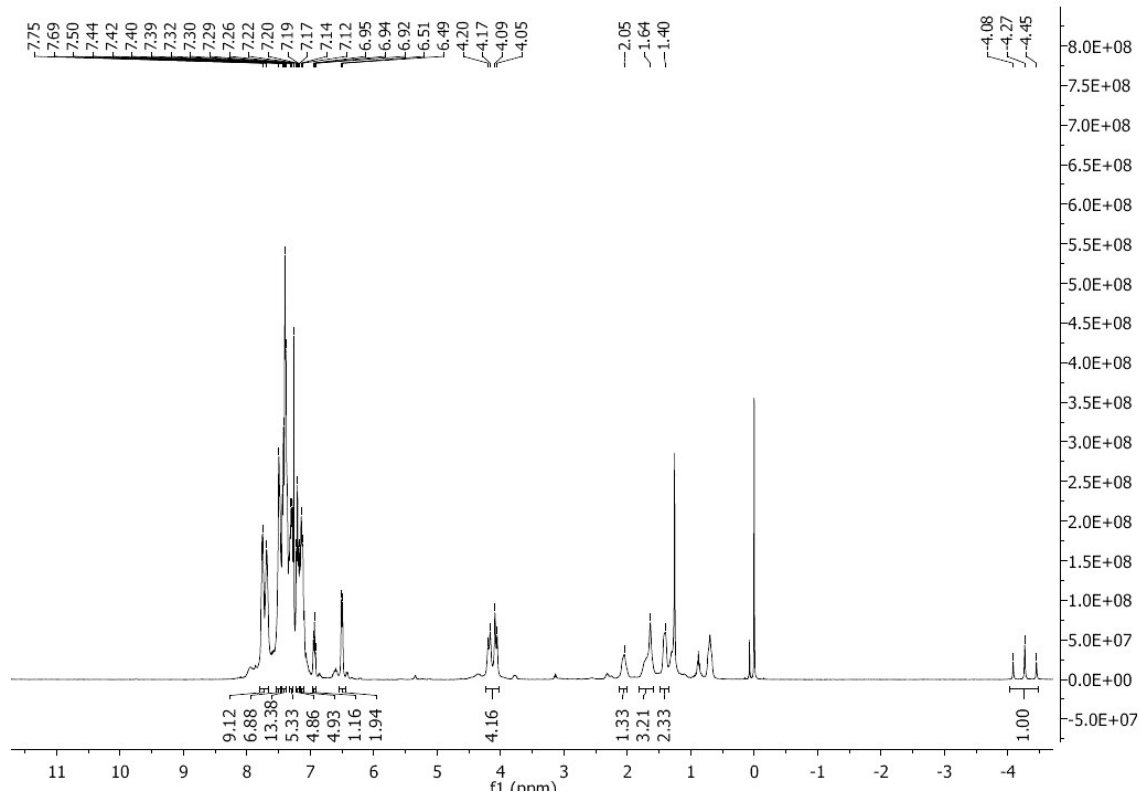


Figure S4. ¹H NMR spectrum of [2](BF₄)

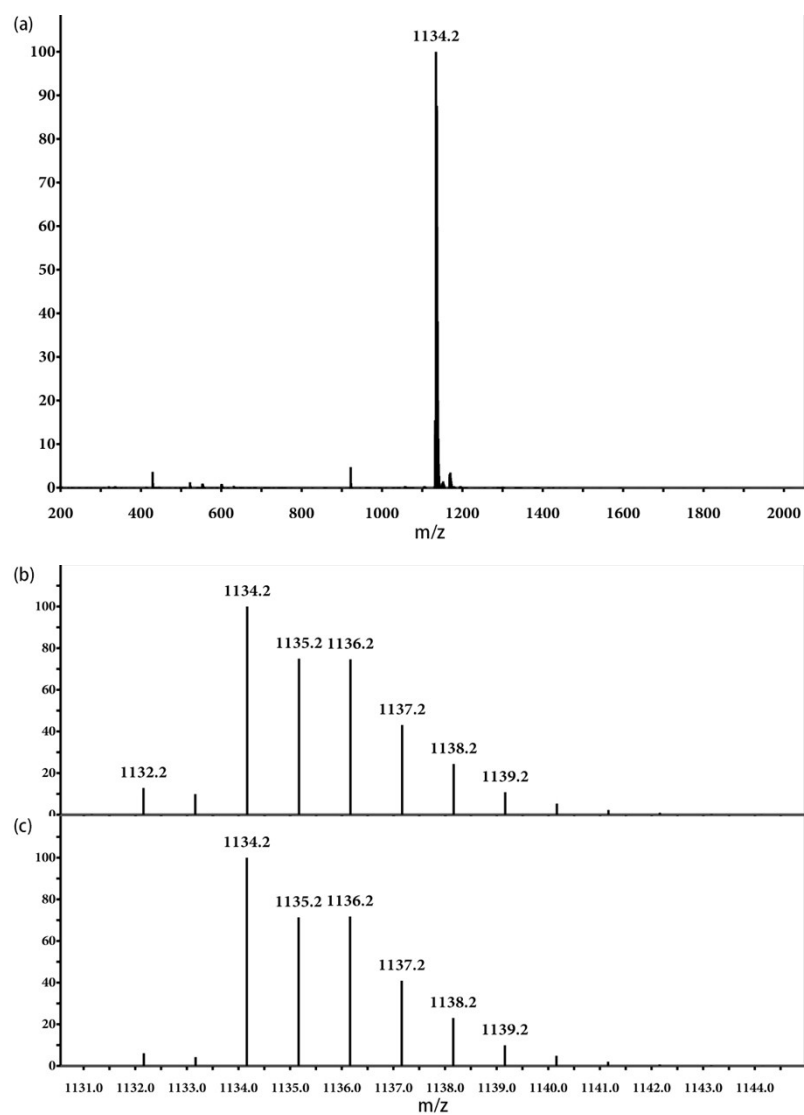


Figure S5. (a) A positive-ion ESI mass spectrum of [2](BF₄) in CH₃OH. (b) The signal at *m/z* 1134.2 corresponds to [2]⁺. (c) Calculated isotopic distribution for [2]⁺.

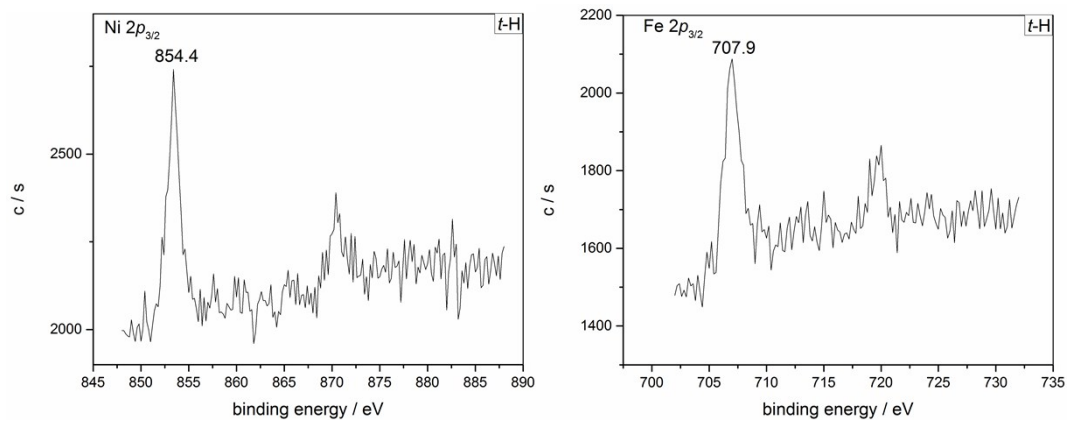


Figure S6. XPS spectra of Ni 2p and Fe 2p region for [2](BF₄)

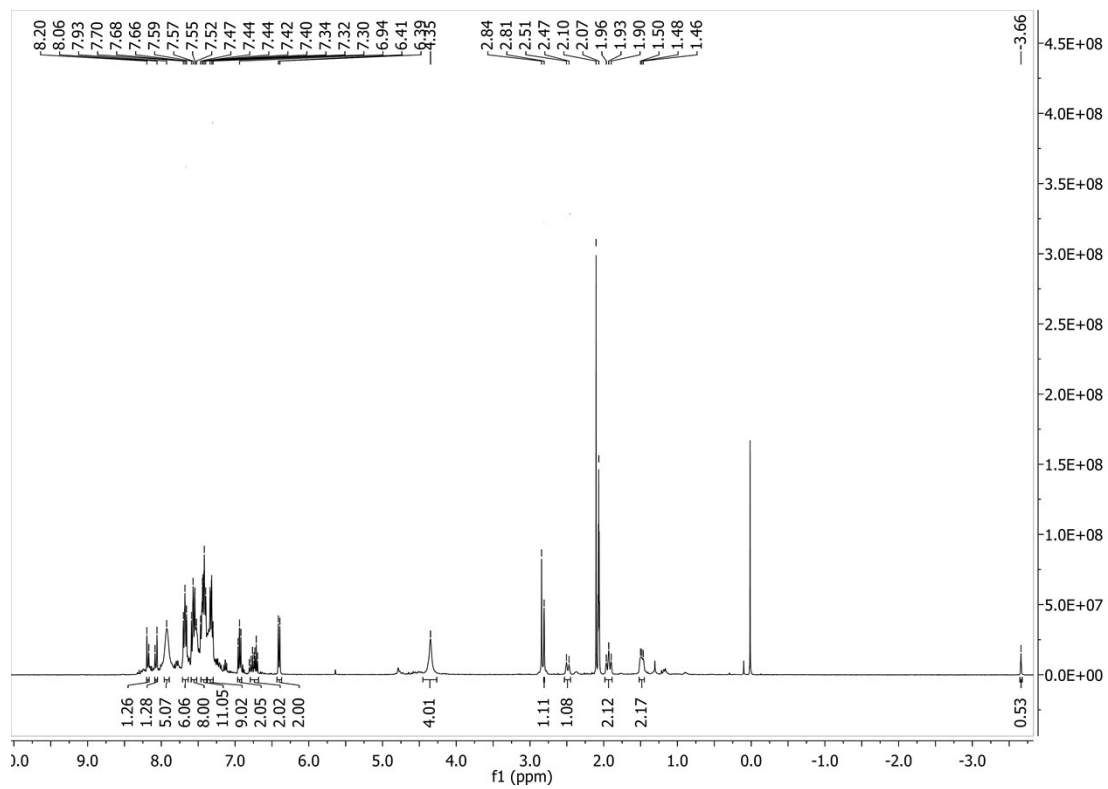


Figure S7. ^1H NMR spectrum of $[\mathbf{3}](\text{BF}_4)$

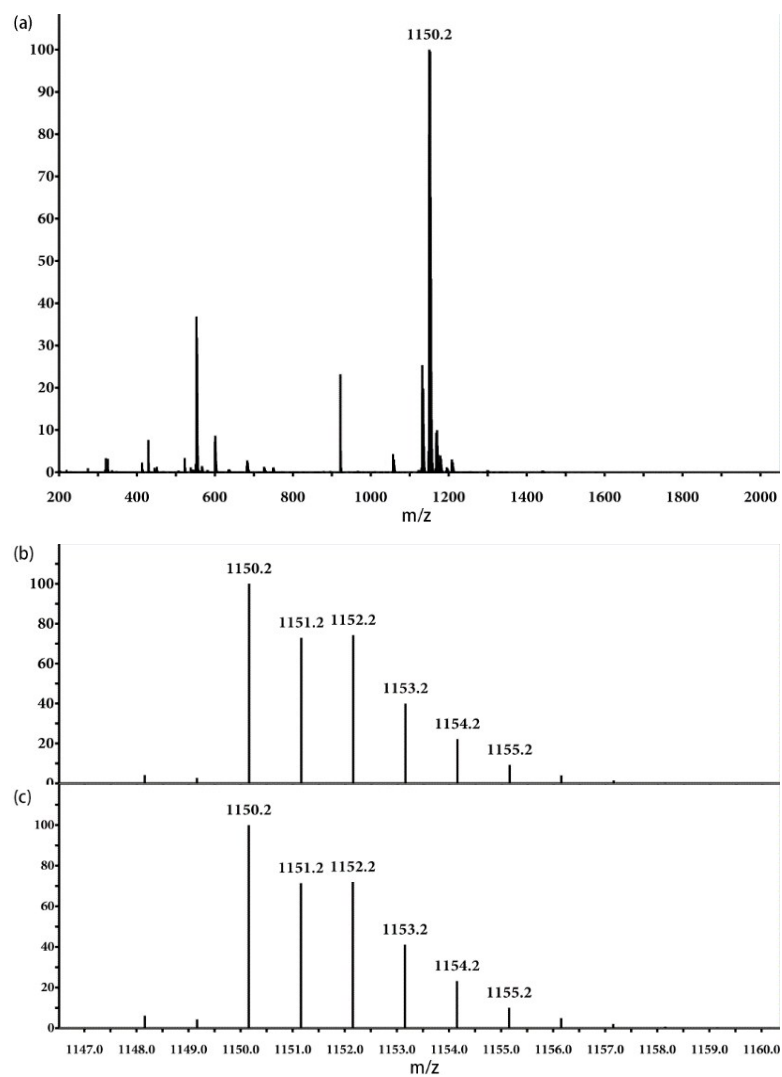


Figure S8. (a) A positive-ion ESI mass spectrum of [3](BF₄) in CH₃OH. (b) The signal at m/z 1150.2 corresponds to [3]⁺. (c) Calculated isotopic distribution for [3]⁺.

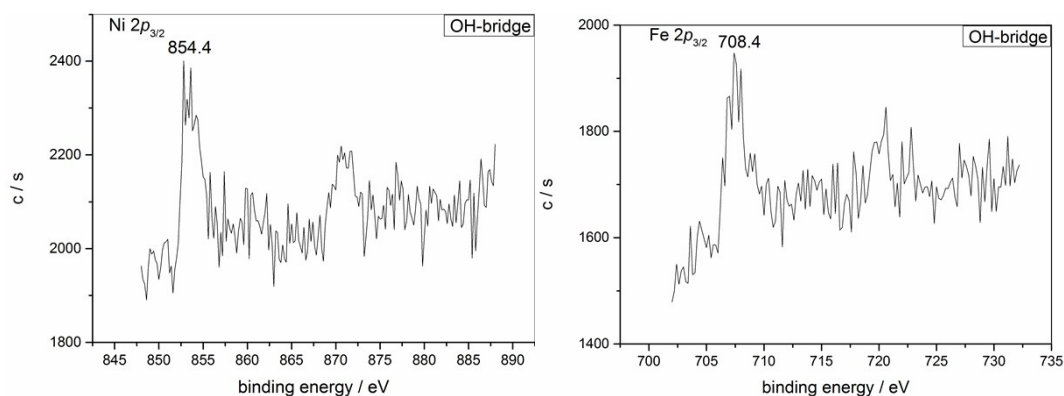


Figure S9. XPS spectra of Ni $2p$ and Fe $2p$ region for $[3](BF_4)$

References

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