

Electronic Supplementary Information

Iron and Zinc Porphyrin Linked MoO(dithiolene) Complexes in Relevance to Electron Transfer between Mo-cofactor and Cytochrome *b*₅ in Sulfite Oxidase.

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1. a) Materials

Solvents like methanol, ethanol, dichloromethane, toluene, diethyl ether, acetonitrile and hexane were purchased from local chemical firm (S. D. Fine Chemicals Ltd.). These were purified and dried before use by standard method. Chemicals like 4-nitrobenzaldehyde, benzaldehyde, DDQ, BF₃.ethariate, sodium bicarbonate, propionic acid, stannous chloride, zinc acetate and various metal salts used were obtained from Spectrochem and pyrrole was purchased from Sigma Aldrich.

1. b) Physical measurements

Electronic absorption spectral measurements (UV-Vis) were performed in Jasco-630 spectrophotometer. Infrared (IR) spectra were recorded on Jasco FT/IR-6800 as pressed KBr disks. Elemental analysis for carbon hydrogen and nitrogen were analyzed with Perkin-Elmer 2400 microanalyser. ¹H NMR and ¹³C NMR spectroscopic measurements in CDCl₃ were recorded with JEOL-500 NMR. Cyclic voltametric measurements were performed with Biologic SP-150 potentiostat. It was recorded for 10⁻³ M solution of compounds with three electrode system, glassy carbon electrode as the working electrode with [Bu₄N][PF₆] as the supporting electrolyte, a platinum counter electrode and Ag/AgCl electrode as reference electrode. All electrochemical experiments were performed under argon atmosphere at 298 K. For the determination of emission properties samples with different analytes were illuminated under UV light (365 nm). The EPR spectral measurements carried out for FeCl₂ at 120K temperature in solid phase (polycrystalline KBr matrix). As the complex could not be grown with diffraction quality crystal for X-ray structure, the alternate K-edge XAS (EXAFS, XANES) experiment was performed at Stanford Synchrotron Radiation Light source (SSRL), Stanford University, to understand the basic structural unit.

2. Synthesis

a) Synthesis of 5-(4-nitrophenyl)-10, 15, 20 triphenyl porphyrin

The compound was synthesized using standard reported procedure.¹ Molecular Weight: 659.75.

b) Synthesis of 5-(4-aminophenyl) 10, 15, 20- triphenyl porphyrin

It was synthesized following the procedure.¹ Molecular Weight: 629.77.

c) Synthesis of H₂L1: 5-(para-N-phenyl-2-propynamide)-10, 15, 20-tris-(4-phenyl)porphyrin

It was synthesized following the procedure.² A 50 mL round bottom flask equipped with a magnetic stir bar was charged with 5-(4-aminophenyl) 10, 15, 20- triphenylporphyrin (151 mg, 0.24 mmol), propiolic acid (18.9 mg, 0.27 mmol), dicyclocarbodiimide (DCC) (54.0 mg, 0.26 mmol), 4-(dimethylamino)pyridine (DMAP) (2.9 mg, 0.02 mmol) and dichloromethane (30 mL). The mixture was stirred for 3 days at room temperature and the reaction was stopped by addition of water. The organic layer was washed three times with water and dried over Na₂SO₄. The solvent was removed under reduce pressure and the resulting purple solid was purified by column chromatography (silica gel, dichloromethane/hexanes 1:1 followed by dichloromethane as eluent) and the second band was collected to provide 122 mg of the title product as a purple solid (60%). The compound was crystallized from DCM and hexane to obtain diffraction quality crystals. Molecular Wt: 681.25; Molecular Formula: C₄₇H₃₁N₅O. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3321 (NH), 2923 (Aryl CH), 2106 (C≡C-), 1650 (-CO-NH-) 1593 and 1515 (aryl C-C); UV-Vis λ_{\max} : 418, 515, 551, 591, 647 nm

d) Synthesis of Fe(III)L1: 5-(para-N-phenyl-2-propynamide)-10, 15, 20-tris-(4-phenyl)porphyrin iron(III) chloride

5-(para-N-phenyl-2-propynamide)-10, 15, 20-tris-(4-phenyl) porphyrin (45mg, 0.067 mmol) was dissolved in methanol (25 ml) with anhydrous iron(II) chloride (150 mg, 1.18 mmol) and 2,6-lutidine (0.02ml, 0.17mmol) the solution was warmed to 50°C and stirred for 3 hours. Methanol was then removed by via rotary evaporation, and a 1:1 mixture of ethyl acetate and water added to the flask. After vigorous shaking many insoluble impurities formed which were removed by filtration. The organic phase was collected, reduced by rotary evaporation and eluted through a silica column with 9:1 dichloromethane and methanol. The compound is reduced by rotary evaporation and collected in DCM. The compound was crystallized from DCM/ Hexane the crystals were washed with methanol and isopropanol to remove the green hue. Yield: 55 mg, 98%. Molecular Wt: 770; Molecular Formula: C₄₇H₃₁ClFeN₅O, Elemental analysis calculated (found) in % for C₄₇H₃₁ClFeN₅O; C, 73.21 (73.18); H, 3.79 (3.98); N, 9.08 (8.93) $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3266 (NH), 23054 (Aryl CH), 2105 (C≡C-), 1662 (-CO-NH-) 1590 and 1531(aryl C-C). UV/Vis λ_{\max} : 412, 513, 570, 610 nm.

e) Synthesis of ZnL1: 5-(para-N-phenyl-2-propynamide)-10, 15, 20-tris-(4-phenyl)porphyrin zinc

5-(para-N-phenyl-2-propynamide)-10, 15, 20-tris-(4-phenyl) porphyrin (100 mg, 0.146 mmol) was dissolved in 1:1 DCM/methanol (30ml) with zinc acetate dehydrated (270 mg, 1.46 mmol) stirred overnight. Solvent was then removed by via rotary evaporation; the solid residue was vigorously shaken in water to remove unreacted salt and filtered. The solid residue was dissolved in

DCM and dried over anhydrous MgSO_4 ; the organic phase was collected, reduced by rotary evaporation and eluted through a silica column (60-120) with 9:1 DCM and methanol. The compound was crystallized from DCM/ Hexane the crystals were washed with methanol to remove the green hue. Yield: 55 mg, 98%. Molecular wt: 745.16; Molecular Formula: $\text{C}_{47}\text{H}_{29}\text{N}_5\text{OZn}$, Elemental analysis calculated (found) in % for $\text{C}_{47}\text{H}_{29}\text{N}_5\text{OZn}$; C, 75.76 (75.80); H, 3.92 (4.21), N, 9.40 (9.27) $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3308 (NH), 2923 (Aryl CH), 2106 ($\text{C}\equiv\text{C}$ -), 1644 ($-\text{CO}-\text{NH}-$) 1596 and 1531 (aryl C-C). UV/Vis λ_{max} 417, 544, 587 nm.

f) Synthesis of $[\text{Et}_4\text{N}]_2[\text{MoO}(\text{S}_4)(\text{mnt})]$

It was synthesized following the procedure reported before.³ Molecular weight 865.31 Molecular Formula: $\text{C}_{36}\text{H}_{72}\text{MoN}_4\text{OS}_6$. The complex is stored under 4°C .

g) Synthesis of D1

156 mg of FeClL1 was dissolved in 3 mL of argon purged DMF and to this was added 128 mg $[\text{Et}_4\text{N}]_2[\text{MoO}(\text{S}_4)(\text{mnt})]$ and this was stirred overnight and then the temperature for raised to 80°C , and stirred for 2hrs. This was allowed to cool to precipitate out the sulfur. The solution was filtered and this was added to a solution of toluene to precipitate out the anionic complex and separate out the unreacted FeClL1. The sample was centrifuged as washed with copious amount of methanol and acetonitrile to dissolve the unreacted $[\text{Et}_4\text{N}]_2[\text{MoO}(\text{S}_4)(\text{mnt})]$. The complex was dried under vacuum. Yield: 140 mg, 54%. Molecular wt: 1347.8439; Molecular Formula: $\text{C}_{67}\text{H}_{69}\text{ClFeMoN}_9\text{O}_2\text{S}_4$ Elemental analysis calculated (found) in % for $\text{C}_{67}\text{H}_{69}\text{ClFeMoN}_9\text{O}_2\text{S}_4$; C, 59.71 (59.76); H, 5.16 (5.42); N 9.35 (9.17) $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3052 (Aryl CH), 2189 ($-\text{C}\equiv\text{N}$), 1651($-\text{CO}-\text{NH}-$) 1594 and 1512 (aryl C-C), 910 ($\text{Mo}=\text{O}$). UV/Vis λ_{max} : 411, 513, 570, 611 nm.

h) Synthesis of D2

92 mg of ZnL1 was dissolved in 1.25 mL of argon purged DMF and to this was added 85 mg $[\text{Et}_4\text{N}]_2[\text{MoO}(\text{S}_4)(\text{mnt})]$ and then the temperature raised to 80°C , and stirred for 2 hrs. This was allowed to cool to precipitate out the sulfur. The solution was filtered and this was added to 70 mL of toluene to precipitate out the anionic complex and separate out the unreacted ZnL1. The sample was centrifuged as washed with copious amount of methanol to dissolve the unreacted $[\text{Et}_4\text{N}]_2[\text{MoO}(\text{S}_4)(\text{mnt})]$. This was again washed twice with 2 mL toluene. The sample was washed twice with 2 mL of CH_3CN and twice with 3 mL of Et_2O . The complex was dried under vacuum. This was dissolved in CH_2Cl_2 precontaining Bu_4NPF_6 . This solution was filtered again and layered with hexane to obtain crystals at 4°C . The complex is stored under 4°C . Yield: 140 mg, 54%. Molecular

wt: 1321.9289; Molecular Formula: $C_{67}H_{69}MoN_9O_2S_4Zn$ Elemental analysis calculated (found) in % for: $C_{67}H_{69}MoN_9O_2S_4Zn$; C, 60.88 (60.92); H, 5.26 (5.33); N 9.54 (9.48) $\nu_{max}(KBr)/cm^{-1}$ 3102 (NH), 3050, 2929 (Aryl CH), 2192 ($-C\equiv N$), 1626 ($-CO-NH-$) 1596 and 1512 (aryl C-C), 910 (Mo=O). UV/Vis λ_{max} : 418, 544, 588 nm.

3. Infrared Spectroscopy

Table 1. Infrared spectral data (Selected vibrations, cm^{-1}) for the complexes in KBr disks

| | $\nu_{C=O}$ | $\nu_{C\equiv C}$ | $\nu_{Mo=O}$ | $\nu_{C\equiv N}$ |
|---|-------------|-------------------|--------------|-------------------|
| FeClL1 | 1662 | 2105 | - | - |
| ZnL1 | 1644 | 2106 | - | - |
| [Et₄N]₂MoO(mnt)S₄ | - | - | 924 | 2195 |
| D1 | 1651 | - | 910 | 2189 |
| D2 | 1626 | - | 910 | 2192 |

4. Electrospray ionization mass spectrometry

ESI mass spectra of the starting complexes FeClL1 and ZnL1 in positive mode show peaks observed {calculated} for $[FeClL1-Cl]^+$ at 735.1729 {735.1722} and for $[ZnL1+H]^+$ at 744.1740 {744.1742} respectively.

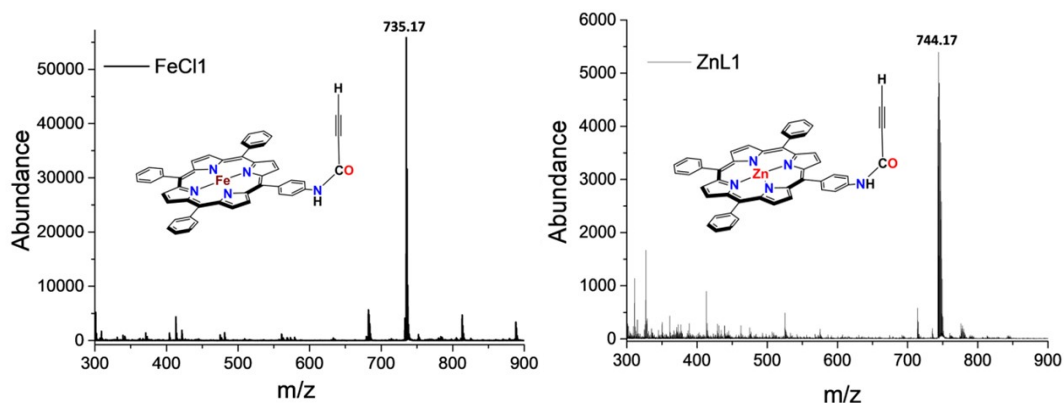


Figure S1 Positive ion ESI mass spectra of FeClL1 and ZnL1 in MeCN.

The formation of the dyad is further corroborated by ESI-MS (m/z) in negative mode; observed {calculated} for D2 shows peak at 1060.9579 {1060.9611}. Mass spectrum of D1 is could not be done due to its insolubility in solvents like acetonitrile and methanol.

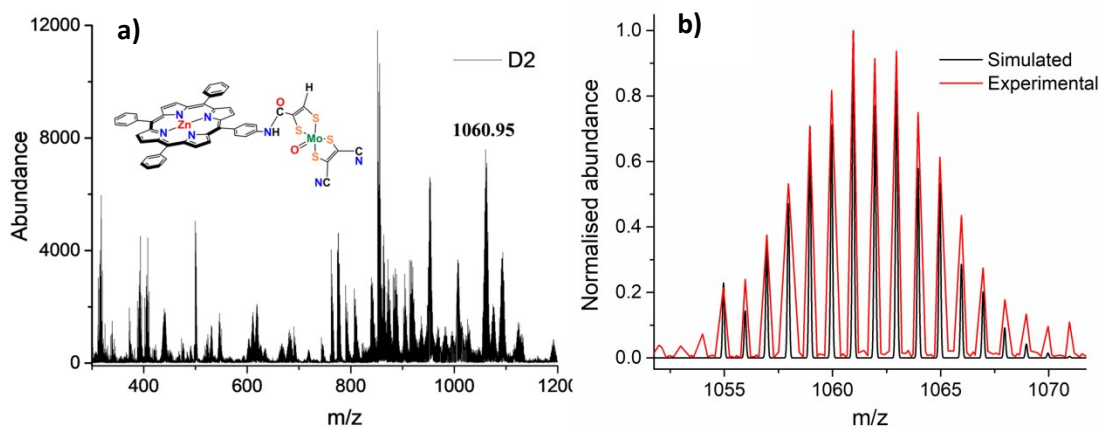


Figure S2 a) Negative ion ESI mass spectrum for D2. b) The simulated and experimental isotope pattern.

5. NMR Spectroscopy

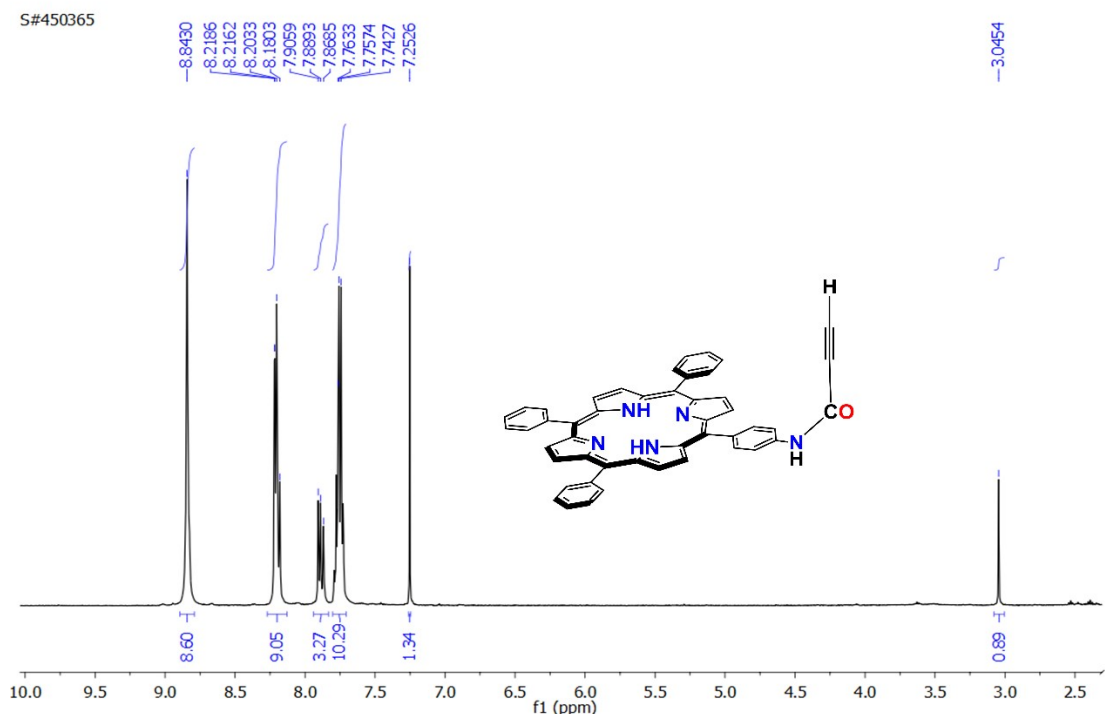


Figure S3 ¹H NMR spectrum of H₂L1 in CDCl₃; { δ 8.84 (s, 8H), 8.20 (dd, 8H), 7.98 – 7.80 (m, 3H), 7.80 – 7.65 (m, 9H), 7.25 (s, 1H), 3.05 (s, 1H) }

S#94613

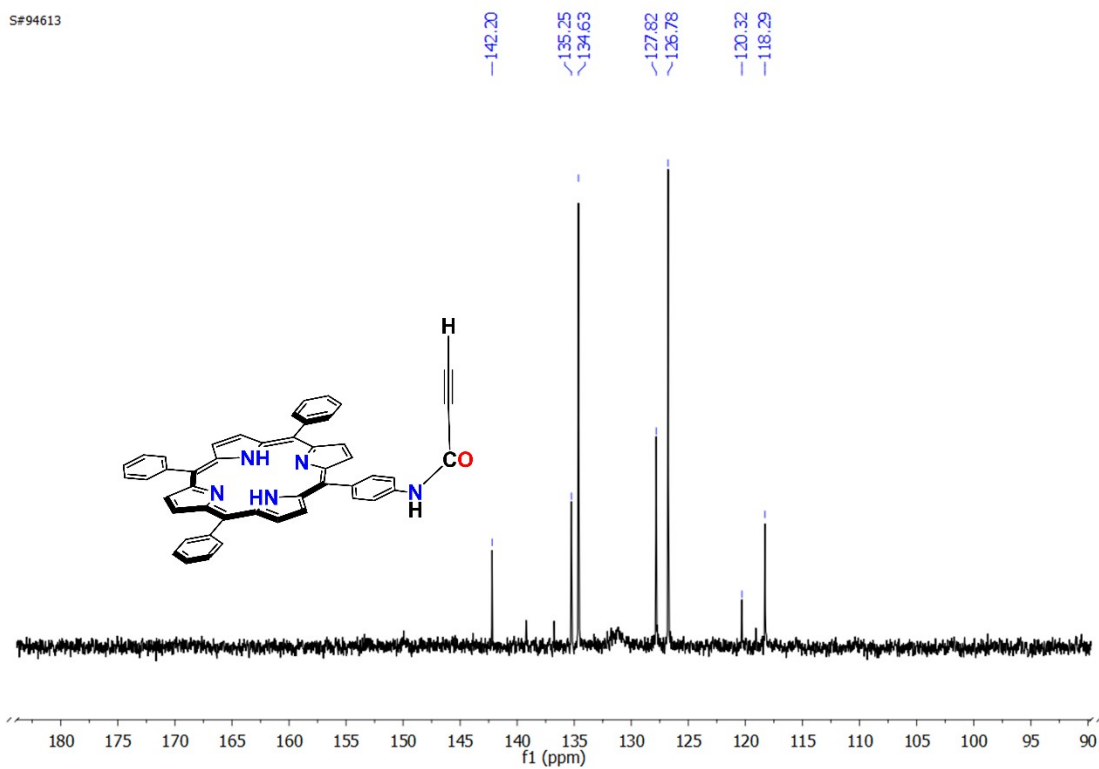


Figure S4 ¹³CNMR spectrum of H₂L1 in CDCl₃

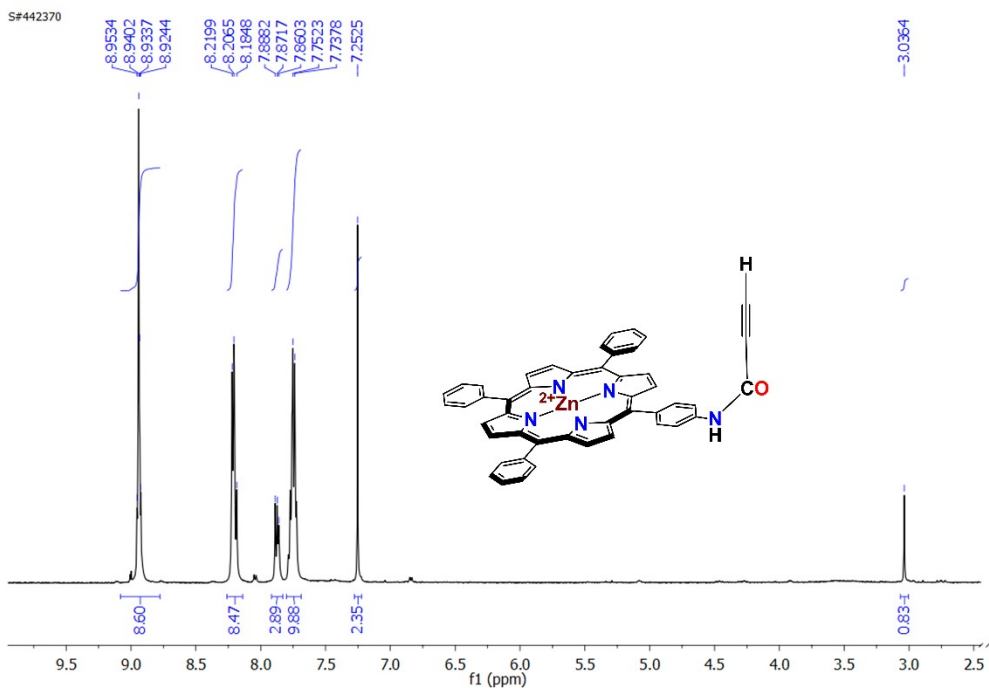


Figure S5 ¹HNMR spectrum of ZnL1 in CDCl₃; { δ 9.08 – 8.78 (m, 8H), 8.20 (t, 8H), 7.92 – 7.83 (m, 3H), 7.75 (d, 9H), 7.25 (s, 2H), 3.04 (s, 1H). }

S#64696

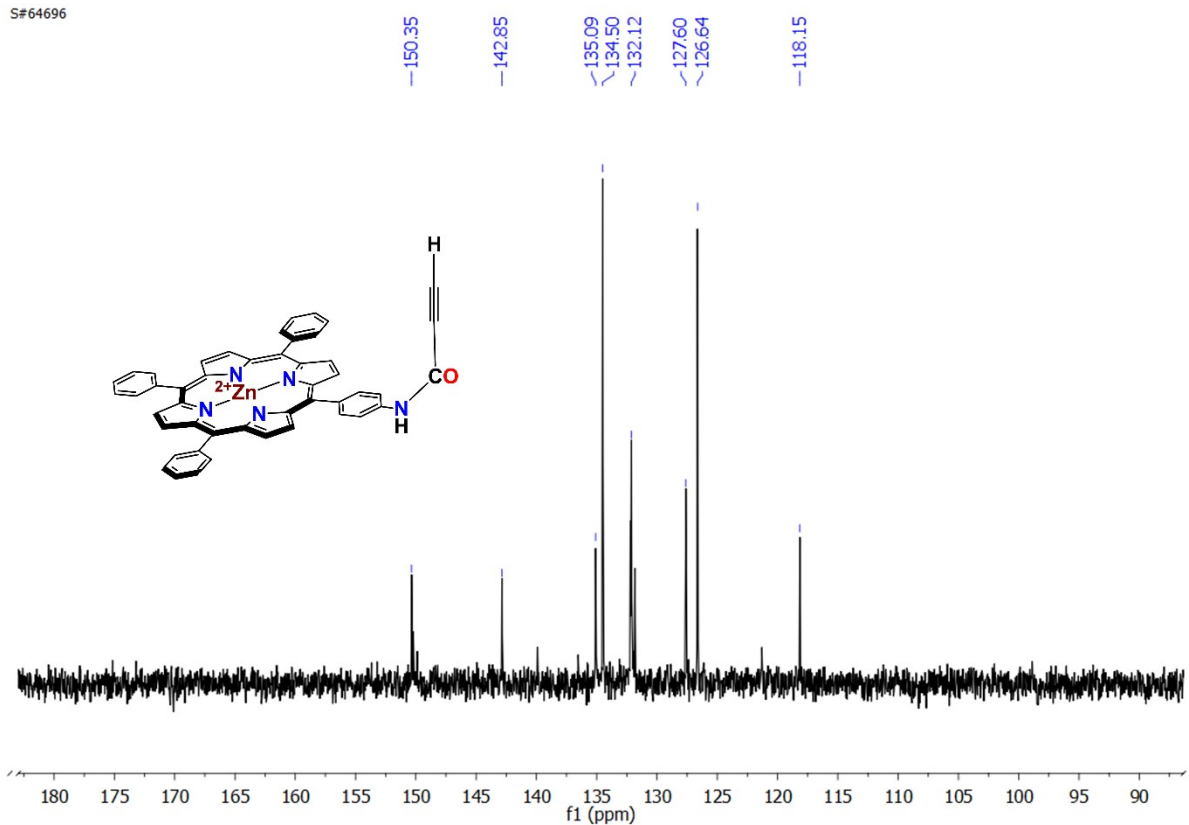


Figure S6 ^{13}C NMR spectrum of ZnL1 in CDCl_3

6. EPR spectroscopy

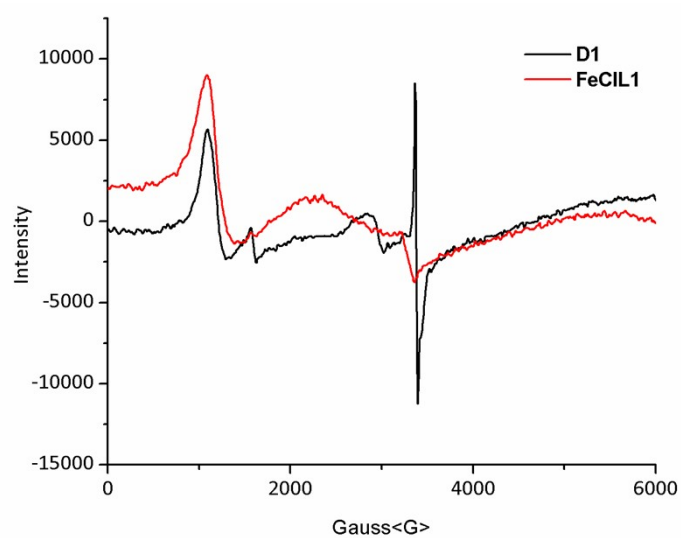


Figure S7 X-band EPR spectra of FeCIL1 and D1 at 120K in polycrystalline KBr matrix.

7. References:

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