

Electronic Supplementary Information

Synthesis and crystal structure of the first lanthanide complex of *N*-confused porphyrin with an η^2 agostic C–H interaction

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General Information

Dichloromethane were distilled from calcium hydride. Toluene and THF were distilled under nitrogen in the presence of sodium chips using benzophenone ketyl as an indicator. The freshly distilled solvents were bubbled with nitrogen for at least 10 min to remove the residue oxygen. Pyrrole was freshly distilled from calcium hydride before use. Other starting materials were obtained commercially and used without further purification. Elemental analyses (C, H, N) were performed by the Shangxi University, China. NIR emission was detected by a liquid nitrogen cooled InSb IR detector (EG & G) with a preamplifier and recorded by a lock-in amplifier system. The third harmonics, 355 nm line of a Nd:YAG laser (Quantel Brilliant B) was used as the excitation light source. NMR spectra were recorded on a JEOL EX270 spectrometer. Chemical shifts of ^1H and ^{13}C NMR spectra were referenced to internal deuteriated solvents and then recalculated to SiMe_4 (δ 0.00). Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded on a QSTAR mass spectrometer, the electronic absorption spectra in the UV–vis region on a Hewlett Packard 8453 UV-Visible spectrophotometer, steady-state visible fluorescence and PL excitation spectra on a Photon Technology International (PTI) spectrophotometer. Single crystals of **2** and **3** suitable for structural determination were grown by slow evaporation of a methanol solution of the respective complex in air. X-Ray intensity data were collected at 293 K on a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The collected frames were processed with the software SAINT and an absorption correction was applied (SADABS) to the collected reflections. The structures of all compounds were solved by direct methods (SHELXTL) and refined against F^2 by full matrix least-squares analysis. All non-hydrogen atoms were refined anisotropically for these structures. Hydrogen atoms were generated in their idealized positions and allowed to ride on their respective parent carbon atoms.

Preparations of [Yb(NCTPP)L_{OMe}] (2) and [Er(NCTPP)L_{OMe}] (3)

Yb[N(SiMe₃)₂]₃·[LiCl(THF)]_x (A). HN(SiMe₃)₂ (10.8 mL, 0.050 mol) was dissolved in 20 mL of THF in an ice bath, then *n*-BuLi (1.6 M in hexane) (31.0 mL, 0.050 mol) was added slowly for a period of 30 min. The resulting solution was magnetically stirred for 12 h until a clear pale yellow solution was obtained. Then the solution was transferred slowly to a Schlenk flask with YbCl₃ (4.74 g, 0.017 mol) suspended in 20 mL THF. The resulting mixture was magnetically stirred for 24 h until all of the solid YbCl₃ disappeared. The resulting solution **A** contains Yb[N(Si Me₃)₂]₃·[LiCl(THF)]_x (*x* = 3 ~ 5).

Er[N(Si Me₃)₂]₃·[Li(THF)Cl]_x (B). Er[N(Si Me₃)₂]₃·[LiCl(THF)]_x (*x* = 3 ~ 5) was prepared by the same methods as solution **A** except that HN(SiMe₃)₂ (10.8 mL 0.050 mol), *n*-BuLi (1.6 M in hexane) (31.0 mL, 0.050 mol) and ErCl₃ (4.65 g, 0.017 mol) in THF were used.

[Yb(NCTPP)L_{OMe}] (2). Solution **A** (2.5 mL, 0.52 mmol Yb) prepared above was transferred to a Schlenk flask and the the solvent was removed under vacuum. Then dichloromethane (10 mL) was added for the precipitation of LiCl. The mixture was centrifuged and the clear layer was transferred to another Schlenk flask with dry NCTPP (0.1 g, 0.16 mmol) dissolved in 15 mL toluene. The resulting solution was refluxed until most of the free base was coordinated with the metal ion. Upon cooling the reaction mixture to room temperature, dry NaL_{OMe} (0.1 g, 0.22 mmol) was added and magnetically stirred for another 12 h. After the reaction complete, the solvent was removed in vacuum and the esidue dissolved in chloroform, filtered and chromatographed on silica gel using chloroform/P.E (v/v, 1:1) as the eluent. The title product was obtained in 86% yield. Elemental analysis: C₅₅H₅₁CoN₄O₉P₃Yb: found (calc.) C, 53.28 (53.41), H, 4.33 (4.16), N, 4.36 (4.53). ESI-HRMS (in methanol) *m/z*: positive mode, 1238.1591 (M + 1)⁺, C₅₅H₅₁CoN₄O₉P₃Yb requires 1238.1678.

[Er(NCTPP)L_{OMe}] (3). The synthesis of **3** followed the same procedures as for **2** except that solution **B** (2.5 mL, 0.52 mmol Er) was used and the clear layer was transferred to a Schlenk flask with dry NCTPP (0.1 g, 0.16 mmol) in toluene. Then NaL_{OMe} (0.1 g, 0.22 mmol) was added after reflux for 12 h. The complex was isolated with a yield of 80% after purification. Elemental analysis: C₅₅H₅₁CoN₄O₉P₃Er: found (calc.) C, 53.45 (53.65), H, 4.29 (4.18), N, 4.38 (4.55). ESI-HRMS (in methanol) *m/z*: positive mode, 1232.1593 (M + 1)⁺, C₅₅H₅₁CoN₄O₉P₃Er

requires 1232.1618.

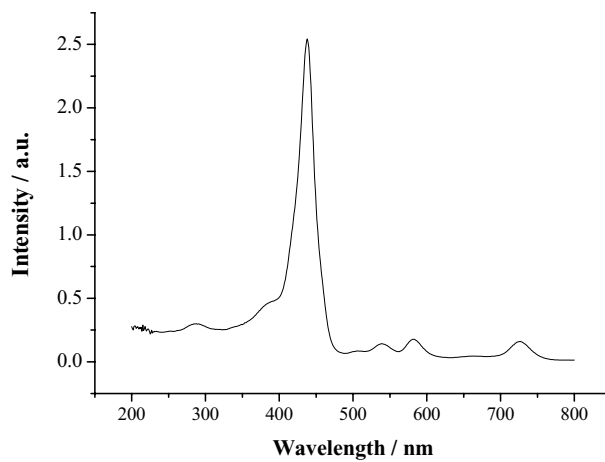


Fig. S1. Absorption of H_2NCTPP in CH_2Cl_2 at room temperature.

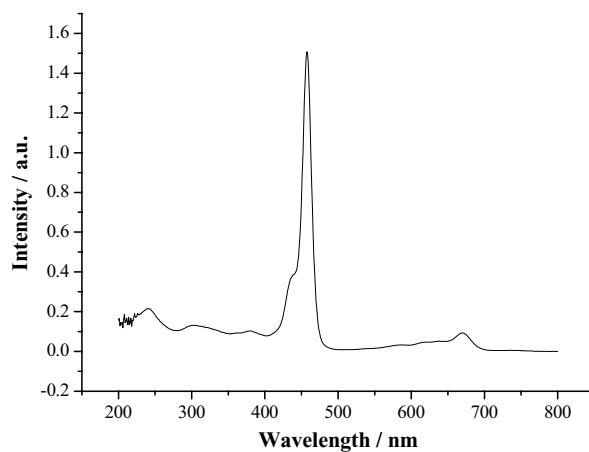


Fig. S2. Absorption of $[\text{Yb}(\text{NCTPP})\text{L}_{\text{OMe}}]$ (**2**) in CH_2Cl_2 at room temperature.

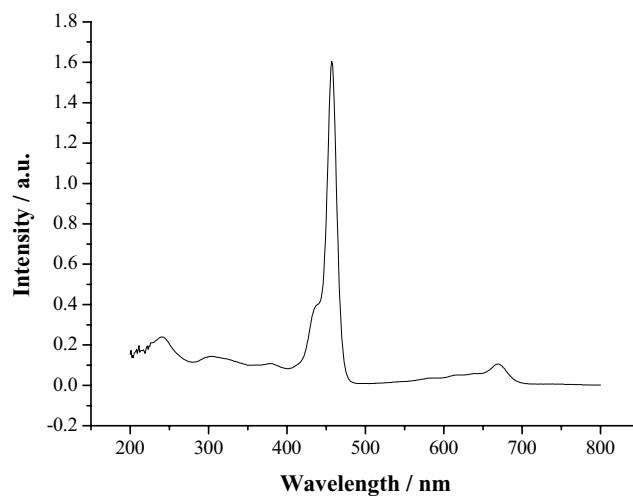


Fig. S3. Absorption of $[\text{Er}(\text{NCTPP})\text{L}_{\text{OMe}}]$ (**3**) in CH_2Cl_2 at room temperature.

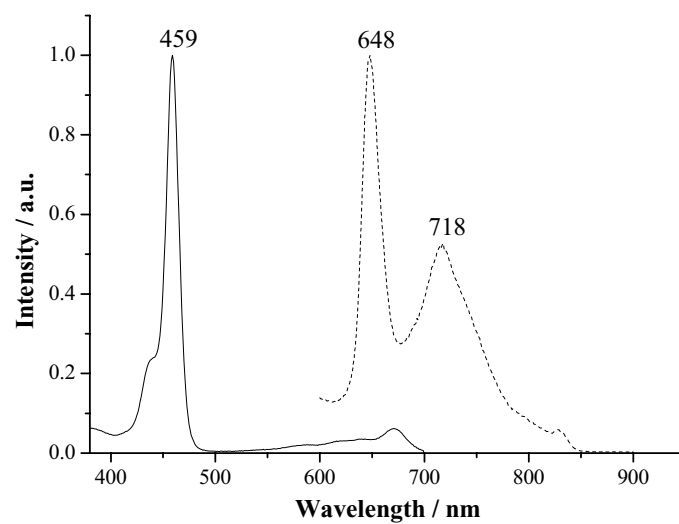


Fig. S4. Absorption (————) and emission (-----) spectra of [Yb(NCTPP)L_{OMe}] (**2**) in CH₂Cl₂ at room temperature.

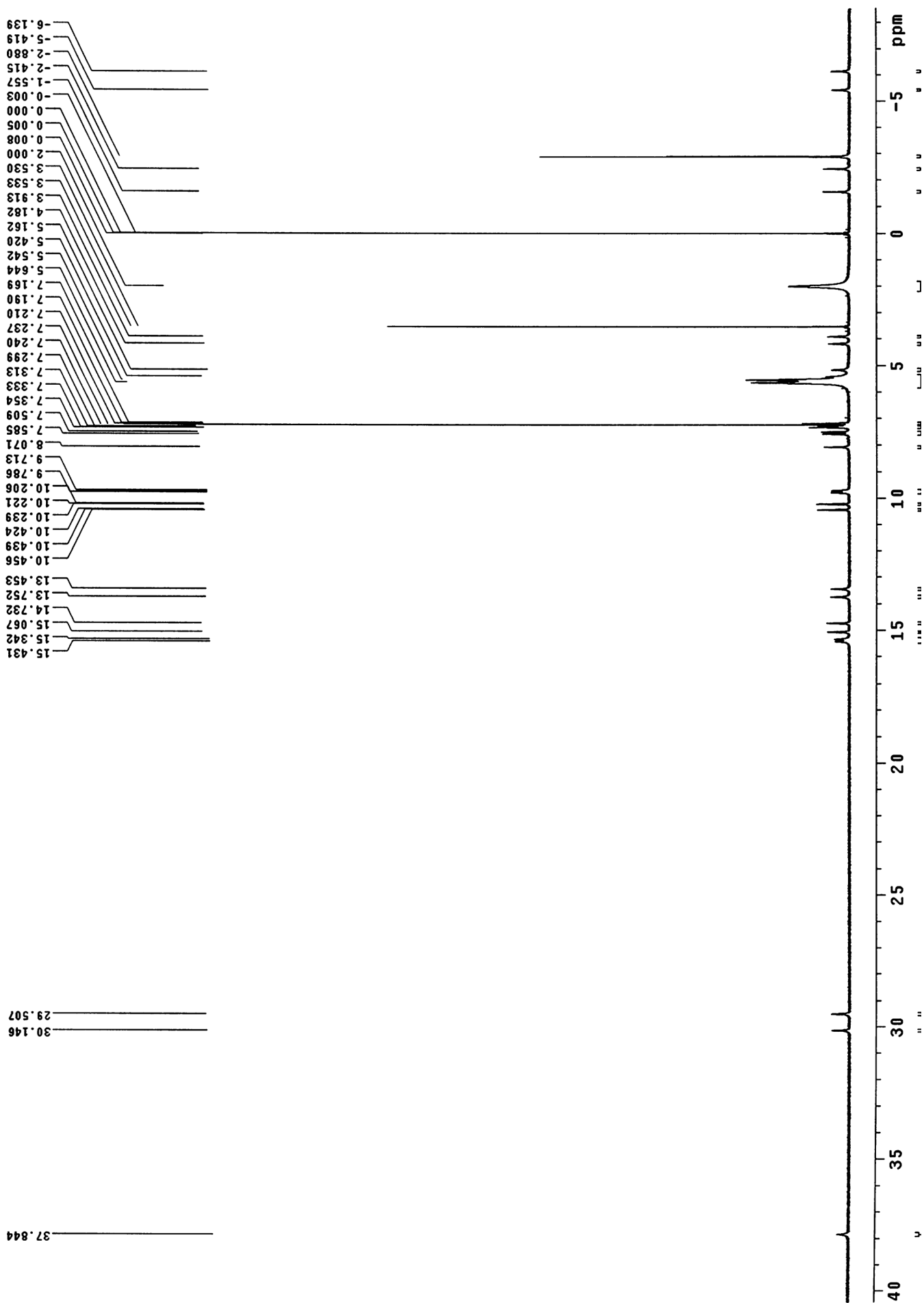


Fig. S5. ^1H NMR of $[\text{Yb}(\text{NCTPP})\text{LOMe}]$ (**2**) in CDCl_3

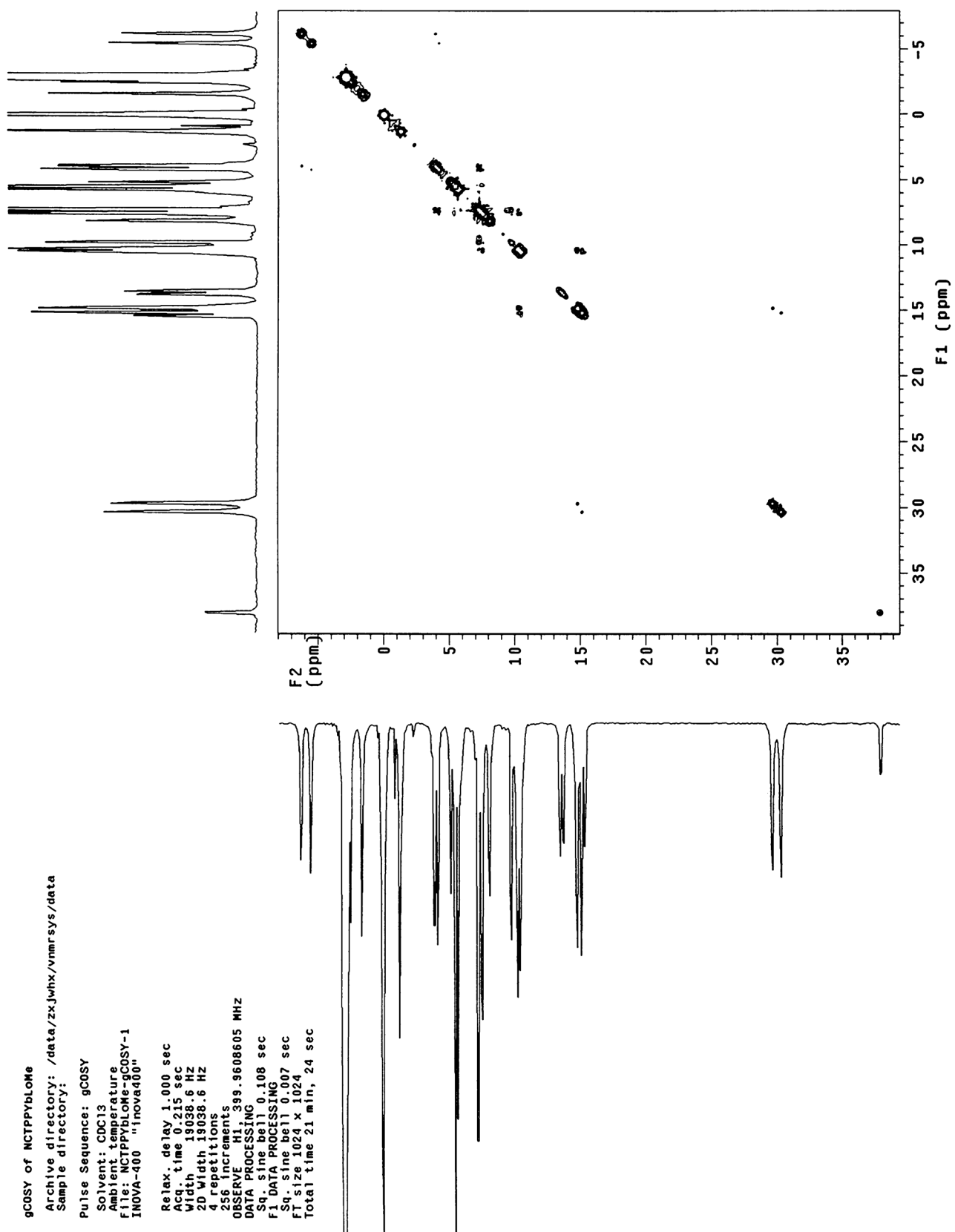


Fig. S6. COSY Spectrum of [Yb(NCTPP)₂LOMe] (2)

Fig. S7. ESI-HRMS of [Yb(NCTPP)L_{OMe}] (2)

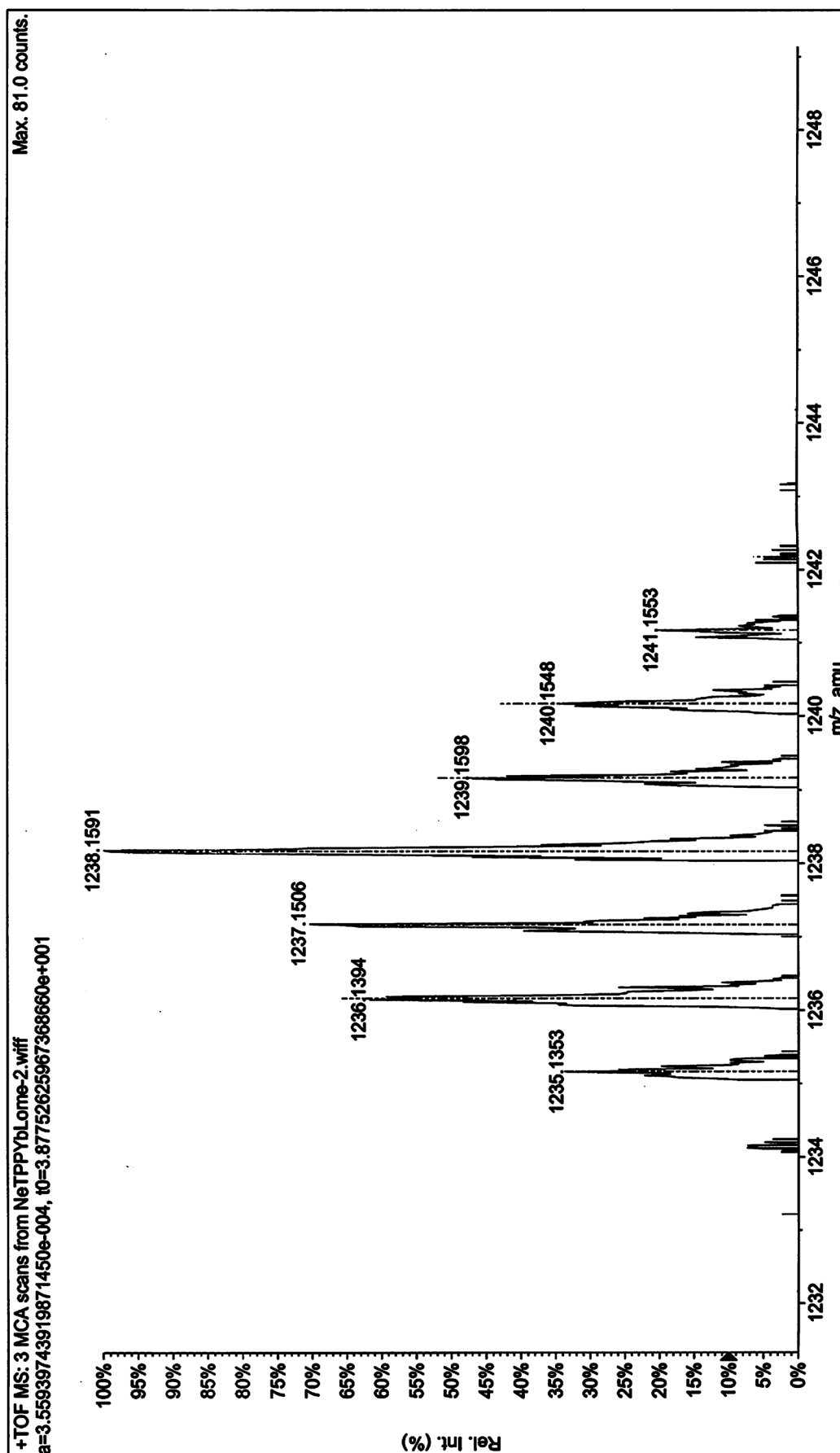
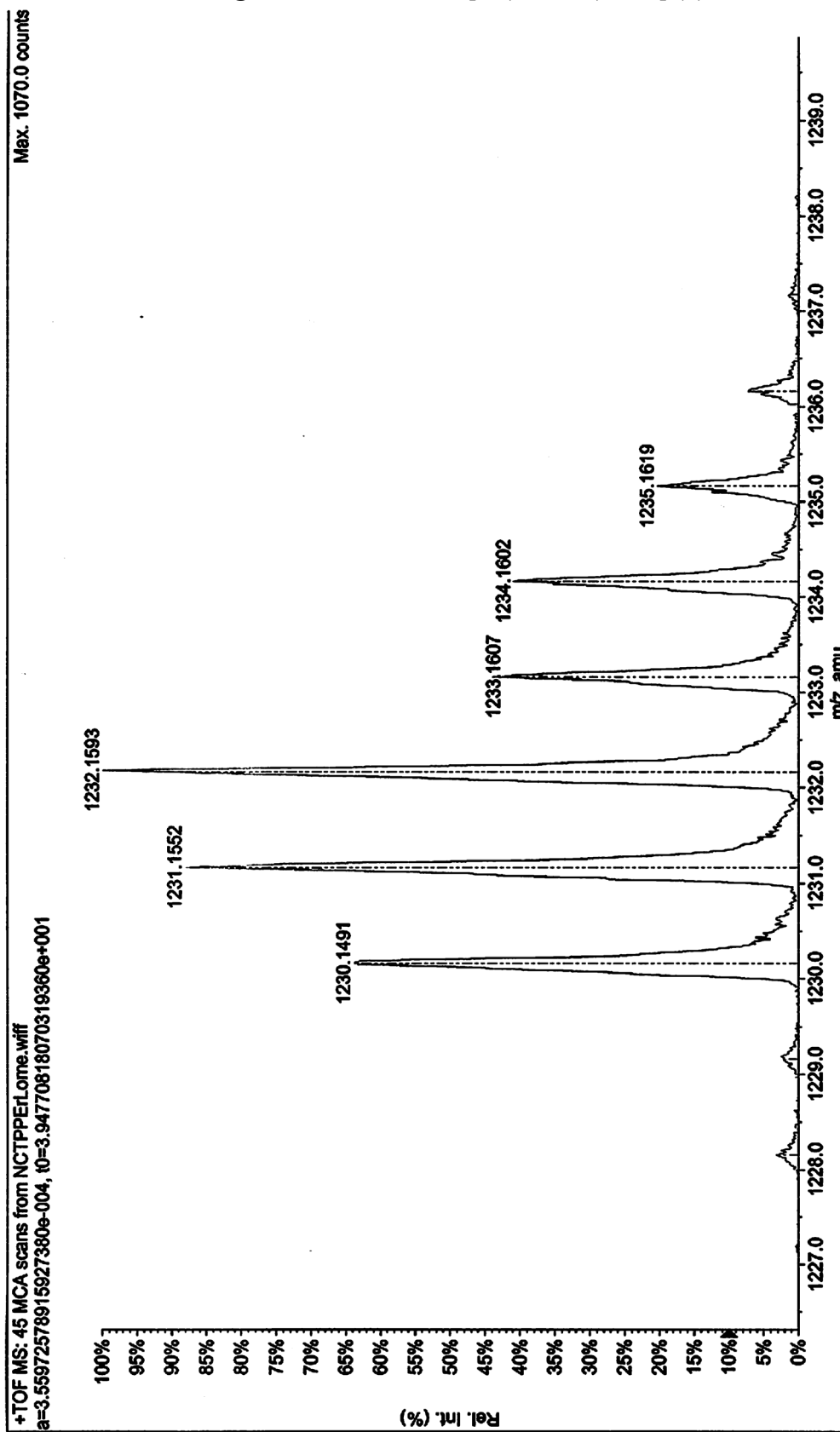


Fig. S8. ESI-HRMS of [Er(NCTPP)LO_{Me}] (3)



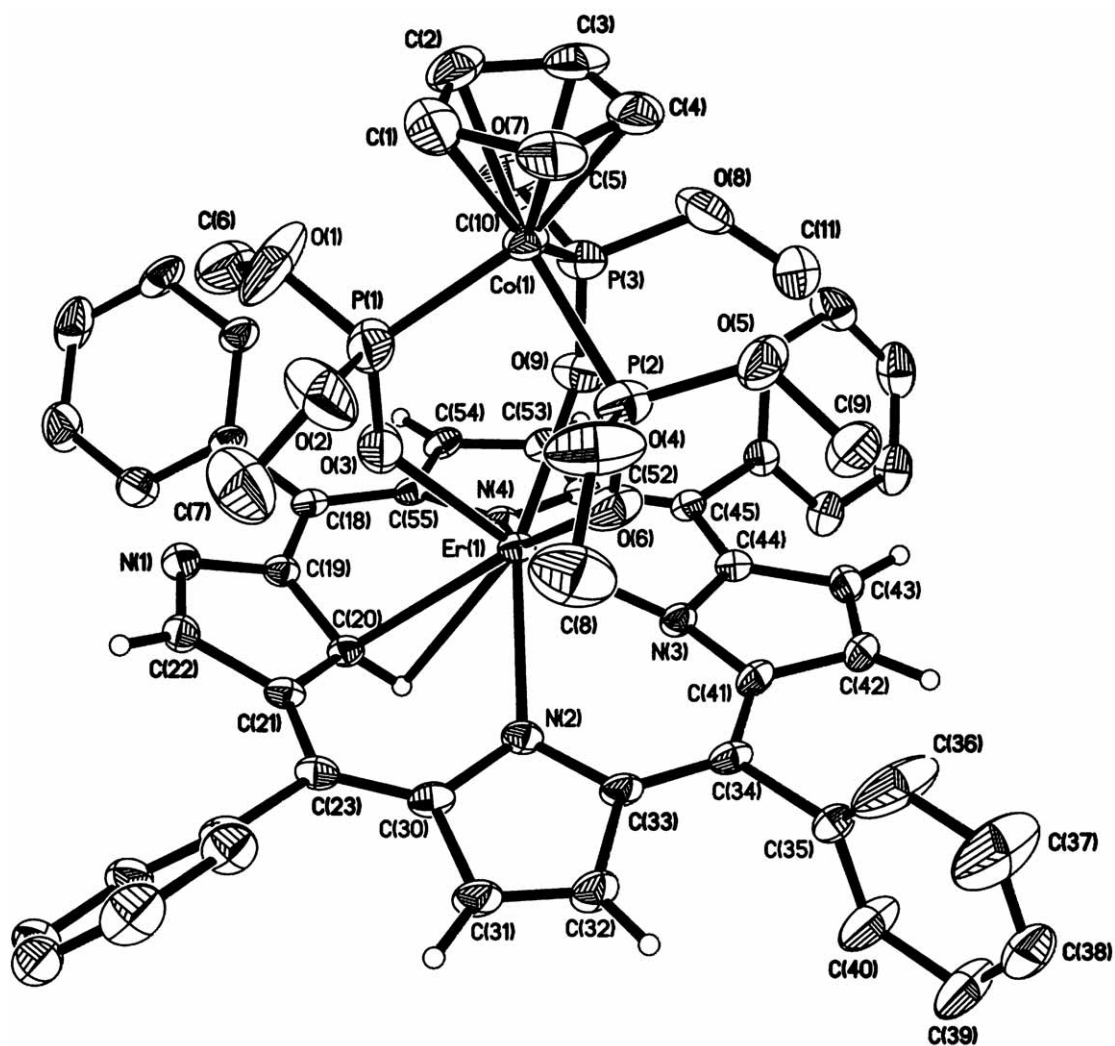


Fig. S9. X-ray structure of [Er(NCTPP)LOMe] (3).