Supporting Information

Modulation of iron spin states in highly distorted iron(III)porphyrin: H-bonding interactions and implications for the hemoproteins

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X-ray Structure Solution and Refinement. Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low-temperature apparatus, and intensity data were collected using graphite monochromated MoKα radiation (λ= 0.71073 Å). The data integration and reduction were processed with SAINT software.[1] An absorption correction was applied.[2] The structure was solved by the direct method using SHELXS-97 and was refined on F2 by the full-matrix least-squares technique using the SHELXL-2018 program package.[3] Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using SHELXL default parameters.

$[Fe^{III}(TPPBr_8)(H_2O)_2]ClO_4$ and $Fe^{II}(TPPBr_8)(1\text{-}MeIm)_2$ contain several severely disordered solvent molecules which could not be modelled properly due to weakly diffracting nature of the crystals and thus, the SQUEEZE routine of PLATON[4] were used to remove such unbound and highly disordered solvent molecules (four THF and eight C_6H_6 molecules per unit cell for $[Fe^{III}(TPPBr_8)(H_2O)_2]ClO_4$ and $Fe^{II}(TPPBr_8)(1\text{-}MeIm)_2$, respectively) but the reported formula includes the solvent molecules.

$Fe^{III}(TPPBr_8)(OCHMe_2)$ [CCDC Number: 2247017]

SADABS (Bruker) was used for absorption correction. R(int) was 0.1191 before and 0.0361 after correction. Ratio of minimum to maximum apparent transmission: 0.247600. Lambda/2 correction factor = 0.0015.

Exposure time, 18 sec

$Fe^{II}(TPPBr_8)(1\text{-}MeIm)_2$ [CCDC Number: 2247018]

SADABS(Bruker) was used for absorption correction. R(int) was 0.1440 before and 0.0485 after correction. Ratio of minimum to maximum apparent transmission: 0.328215. Lambda/2 correction factor = 0.0015.

Exposure time, 18sec

$[Fe^{III}(TPPBr_8)(H_2O)_2]ClO_4$ [CCDC Number: 2247019]

SADABS (Bruker) was used for absorption correction. R(int) was 0.0869 before and 0.0321 after correction. Ratio of minimum to maximum apparent transmission: 0.097427. Lambda/2 correction factor = 0.0015

Exposure time, 28 sec

$[Fe^{III}(TPPBr_8)(MeOH)_2]ClO_4$ [CCDC Number: 2247020]

SADABS (Bruker) was used for absorption correction. R(int) was 0.1071 before and 0.0667 after correction. Ratio of minimum to maximum apparent transmission: 0.735336. Lambda/2 correction factor = 0.0015.

Exposure time, 15sec

1 SAINT+, 6.02 ed., Bruker AXS, Madison, WI, 1999.

2 G. M. Sheldrick, SADABS, Bruker AXS Inc., Madison, WI, 2000.

3 G. M. Sheldrick, SHELXL: Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 2018.

4 A. L. J. Spek, *Appl. Crystallogr*., 2003, **36,** 7.

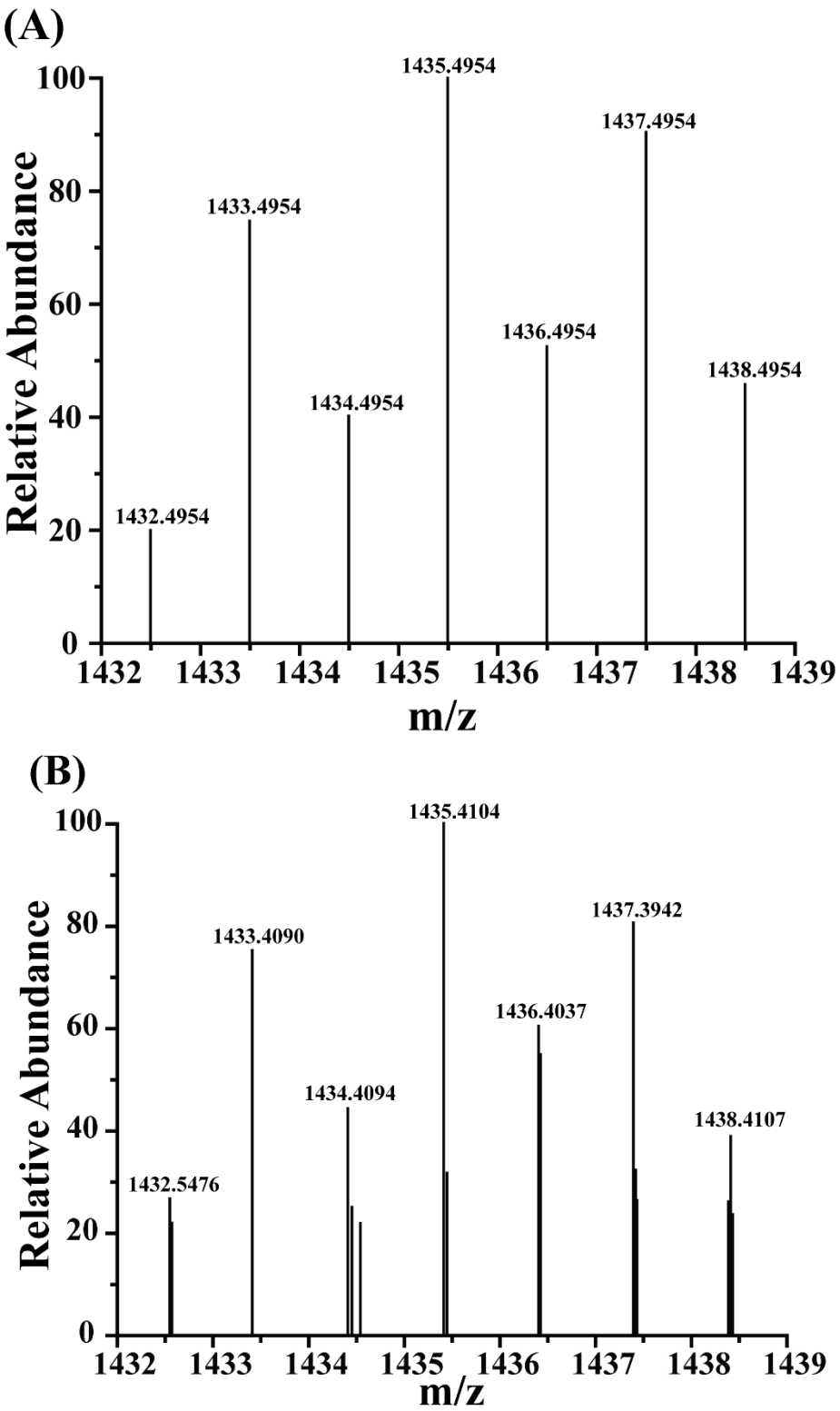

Figure S1. Isotopic distribution pattern of $[Fe^{III}(TPPBr_8)Cl + (CH_3CN)_2 + H_2O + H]^+$, (A) simulated, and (B) experimental ESI mass spectrum displaying m/z peak at 1435.4104 (positive-ion mode).

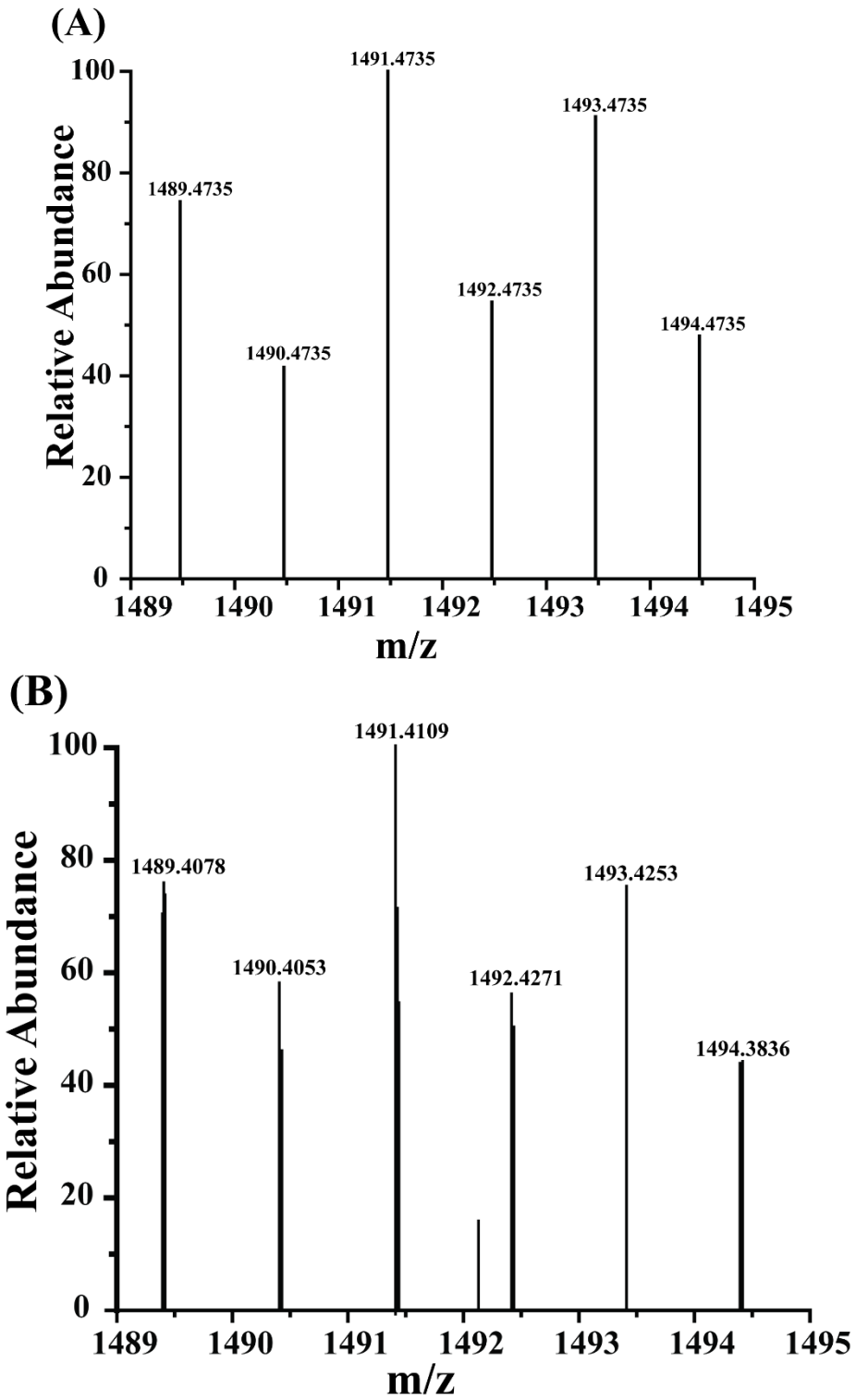

Figure S2. Isotopic distribution pattern of $[Fe^{III}(TPPBr_8)ClO_4 + PhCH_3 + H]^+$, (A) simulated, and (B) experimental ESI mass spectrum displaying m/z peak at 1491.4109 (positive-ion mode).

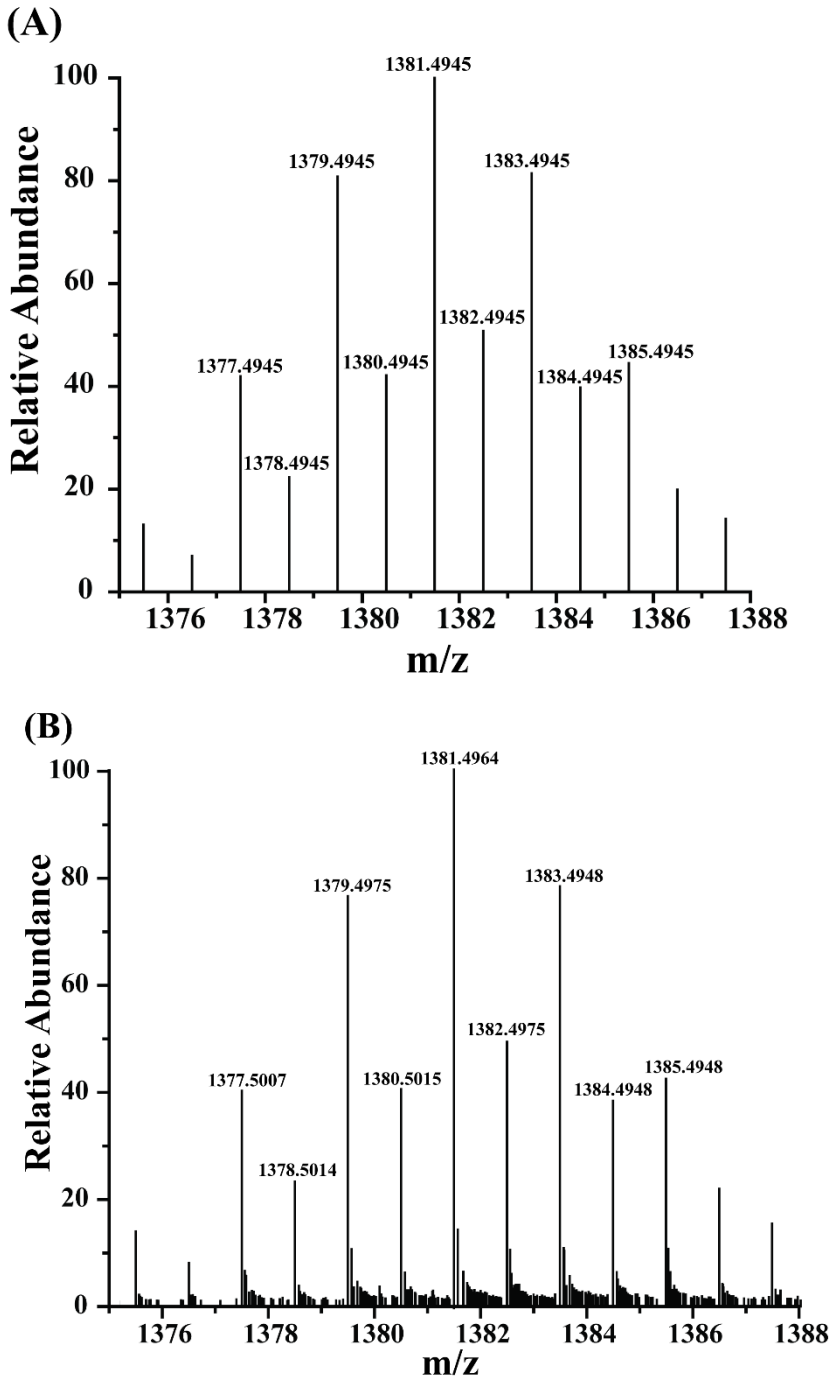

Figure S3. Isotopic distribution pattern of $[Fe^{III}(TPPBr_8)(OCHMe_2) + Na]^+$, (A) simulated, and (B) experimental ESI mass spectrum displaying m/z peak at 1381.4964 (positive-ion mode).

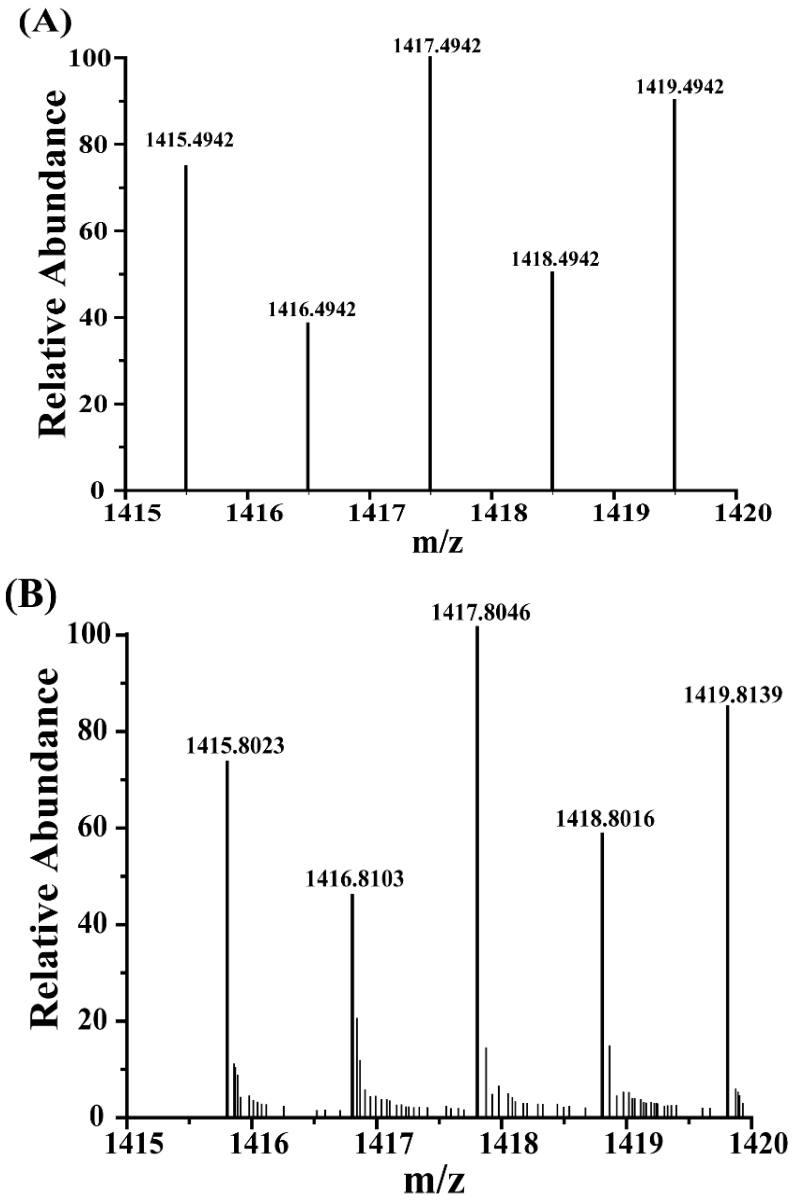

Figure S4. Isotopic distribution pattern of $[Fe^{III}(TPPBr_8)(MeOH)_2 + (H_2O)_3]^+$, (A) simulated, and (B) experimental ESI mass spectrum displaying m/z peak at 1417.8046 (positive-ion mode).

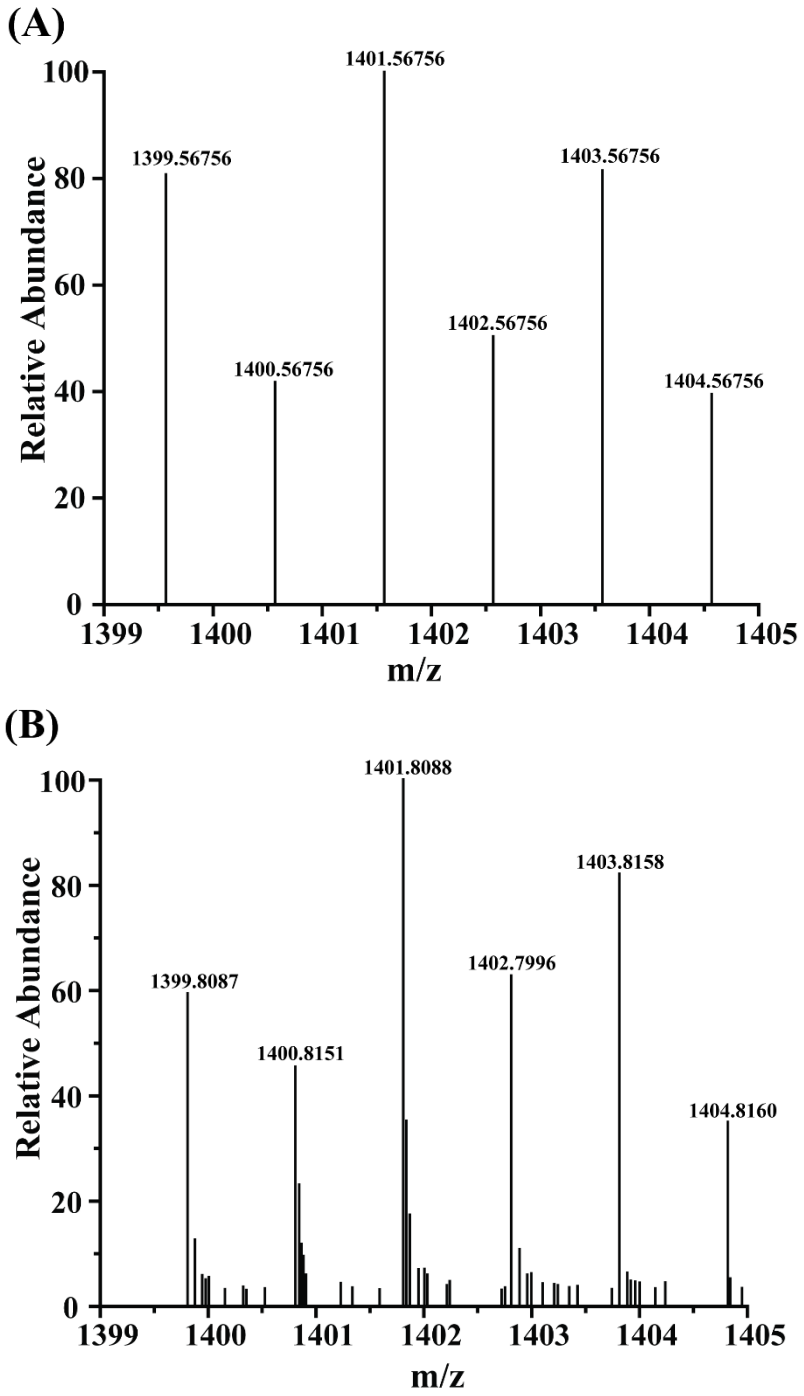

Figure S5. Isotopic distribution pattern of $[Fe^{III}(TPPBr_8)(OH_2)_2 + (MeOH)_2 + H]^+$, (A) simulated, and (B) experimental ESI mass spectrum displaying m/z peak at 1401.8088 (positive-ion mode).

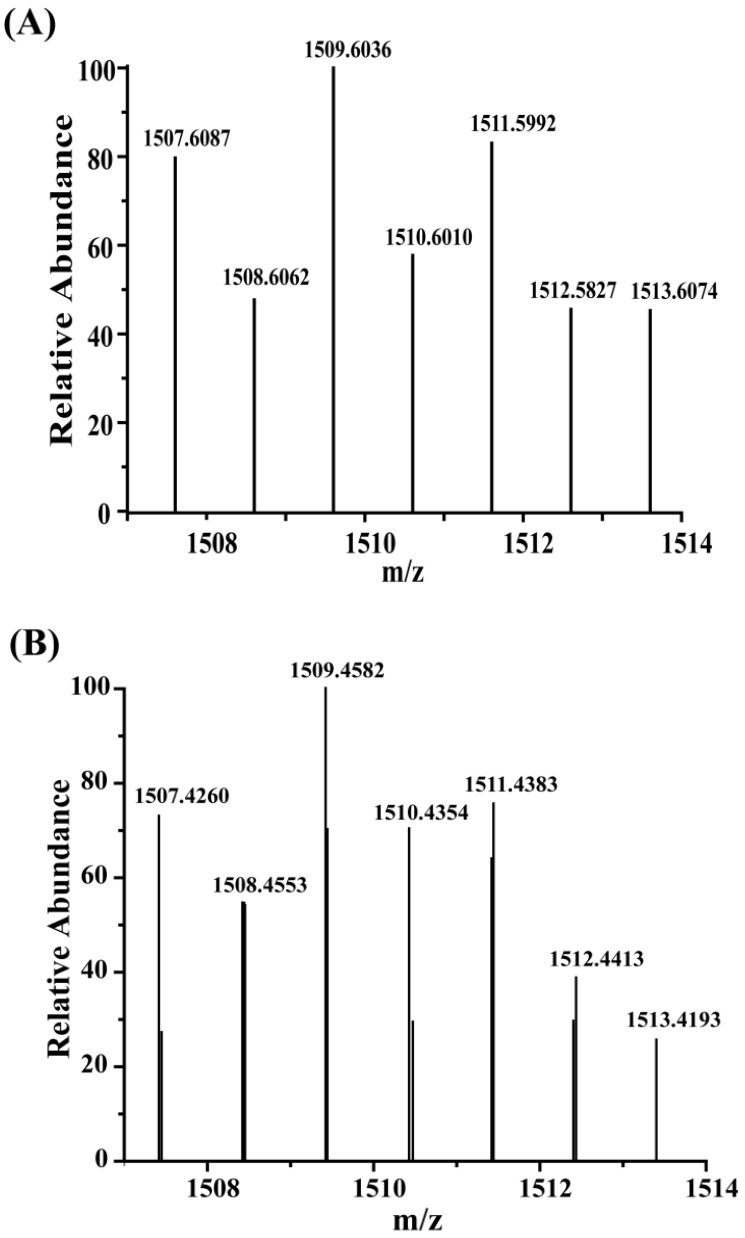

Figure S6. Isotopic distribution pattern of $[Fe^{II}(TPPBr_8)(1\text{-MeIm})_2 + C_2H_5OH]^+$, (A) simulated, and (B) experimental ESI mass spectrum displaying m/z peak at 1509.4582 (positive-ion mode).

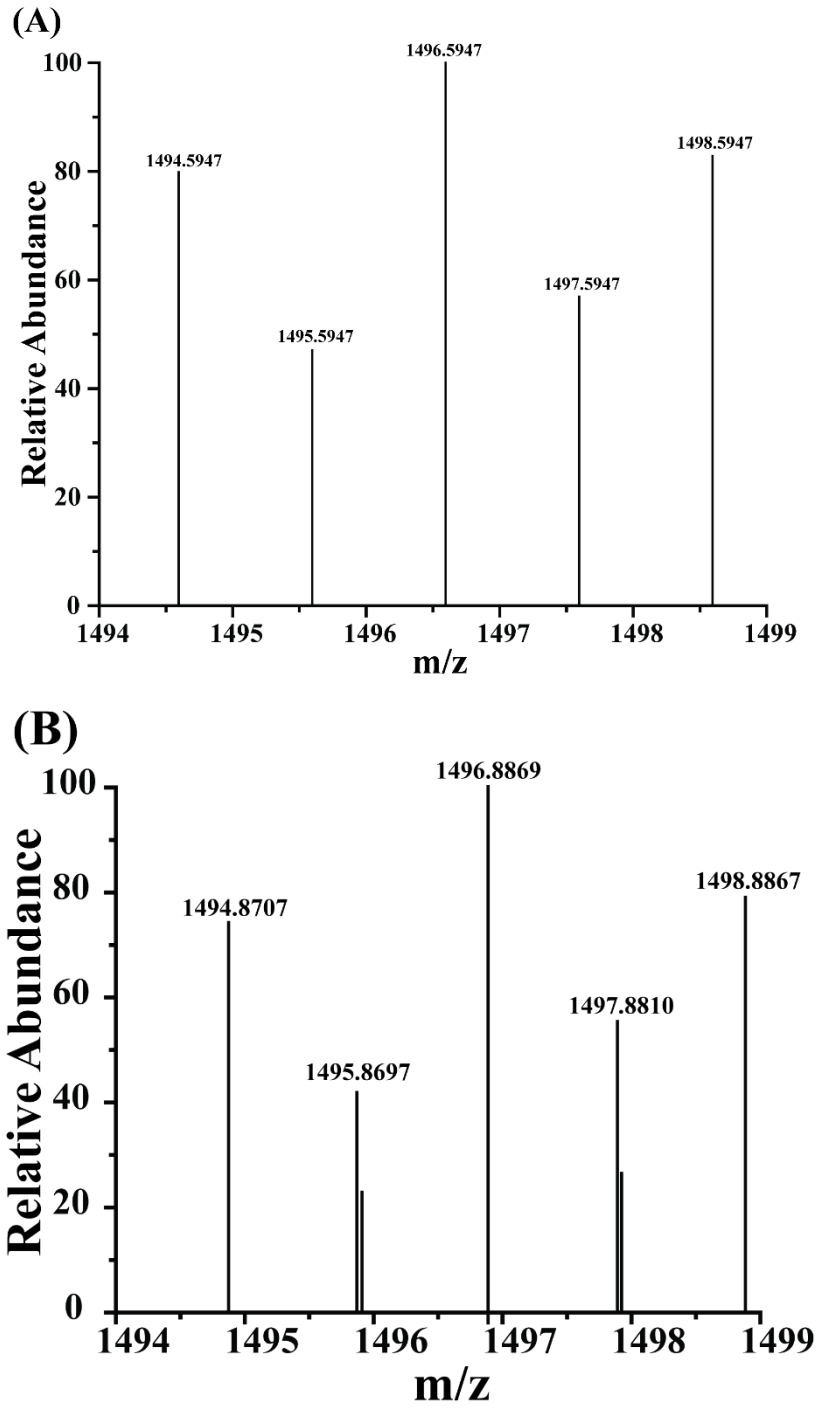

Figure S7. Isotopic distribution pattern of $[Fe^{II}(TPPBr_8)(4\text{-MeIm})_2 + MeOH + H]^+$, (A) simulated and (B) experimental ESI mass spectrum displaying m/z peak at 1496.8869 (positive-ion mode).