**Supporting information for**

# Water-soluble Manganese and Iron *meso*-tetrakis(carboxyl)porphyrin: DNA Binding, Oxidative Cleavage, and Cytotoxic Activities

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## 1. Characterization of compounds

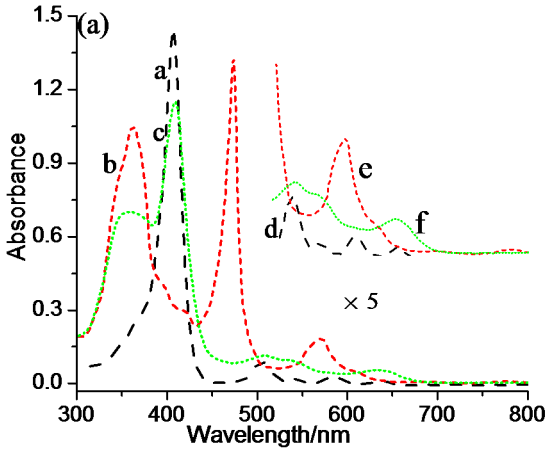



**Figure S1.** UV-Vis absorption spectra of **1**, **1-Mn** and **1-Fe** in dichloromethane.

**a**: **1**-Soret band; **b**: **1-Mn**-Soret band; **c**: **1-Fe**-Soret band; **d**: **1**-Q band; **e**: **1-Mn**-Q band; **f**: **1-Fe**-Q band

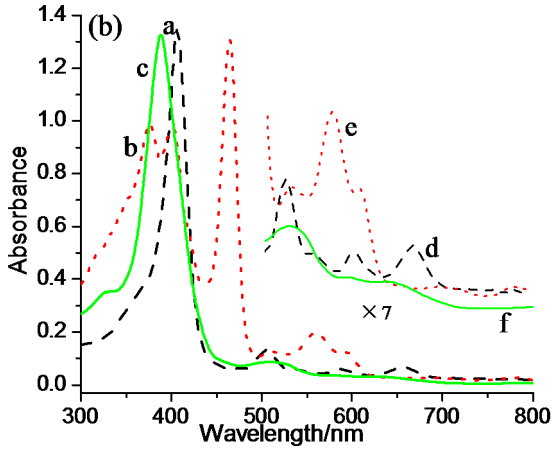



**Figure S2.** UV-Vis absorption spectra of **2**, **2-Mn** and **2-Fe** in 5 mM Tris-HCl/50 mM NaCl buffer.

**a**： **2**-Soret band; **b**: **2-Mn**-Soret band; **c**: **2-Fe**-Soret band; **d**: **2**-Q band; **e**: **2-Mn**-Q band; **f**: **2-Fe**-Q band

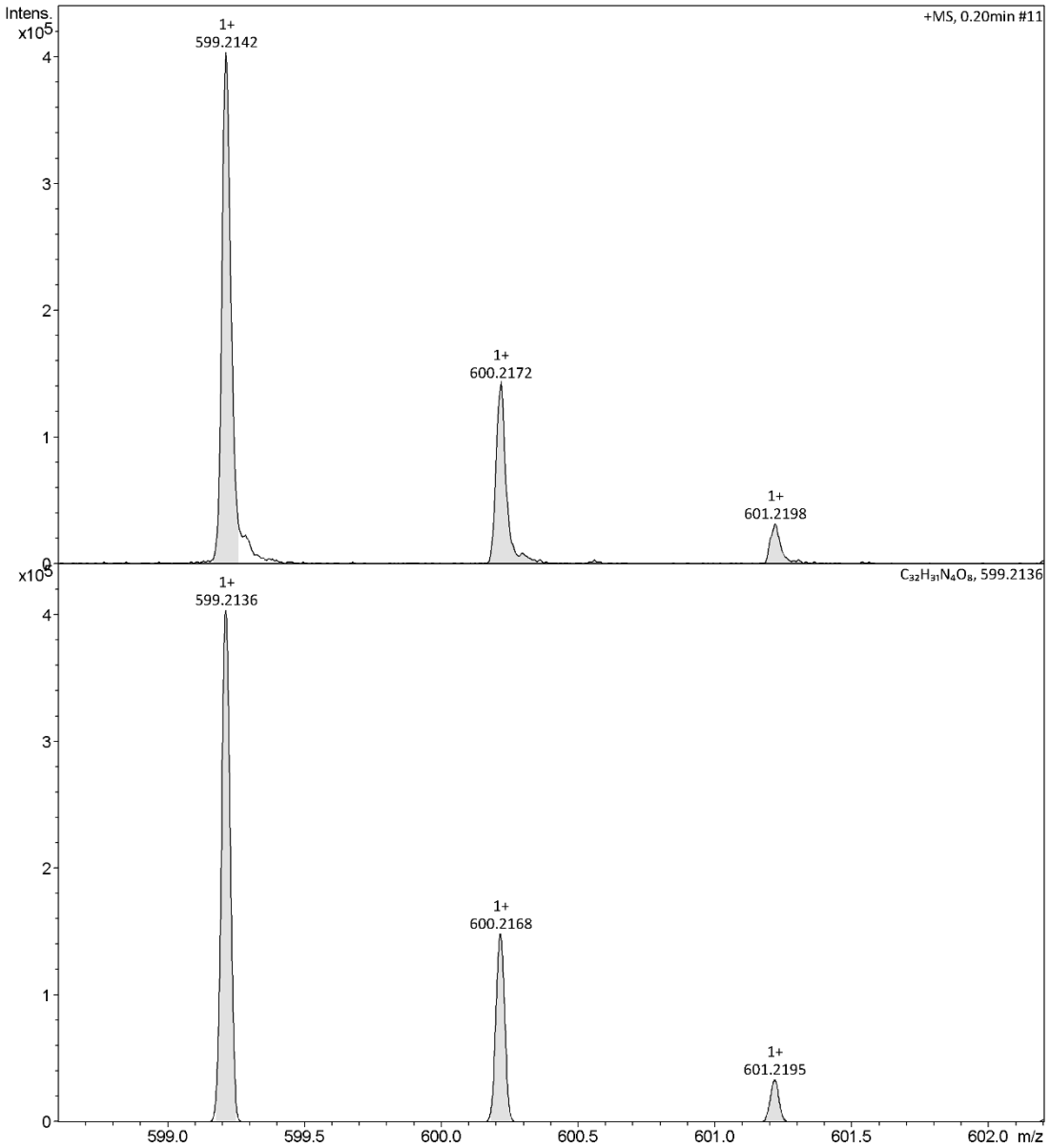



**Figure S3.** HR-MS of 5, 10, 15, 20-tetrakis(ethoxycarbonyl)porphyrin (**1**)

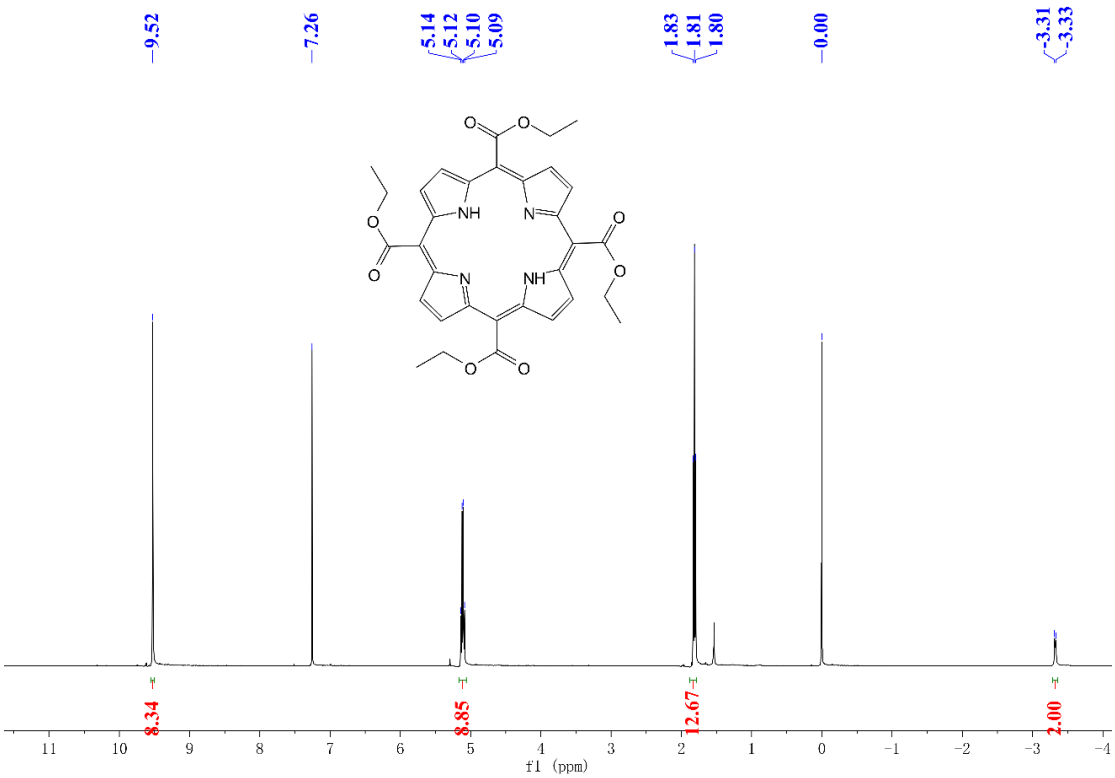



**Figure S4.** $^{1}$H NMR of 5, 10, 15, 20-tetrakis(ethoxycarbonyl)porphyrin (**1**).

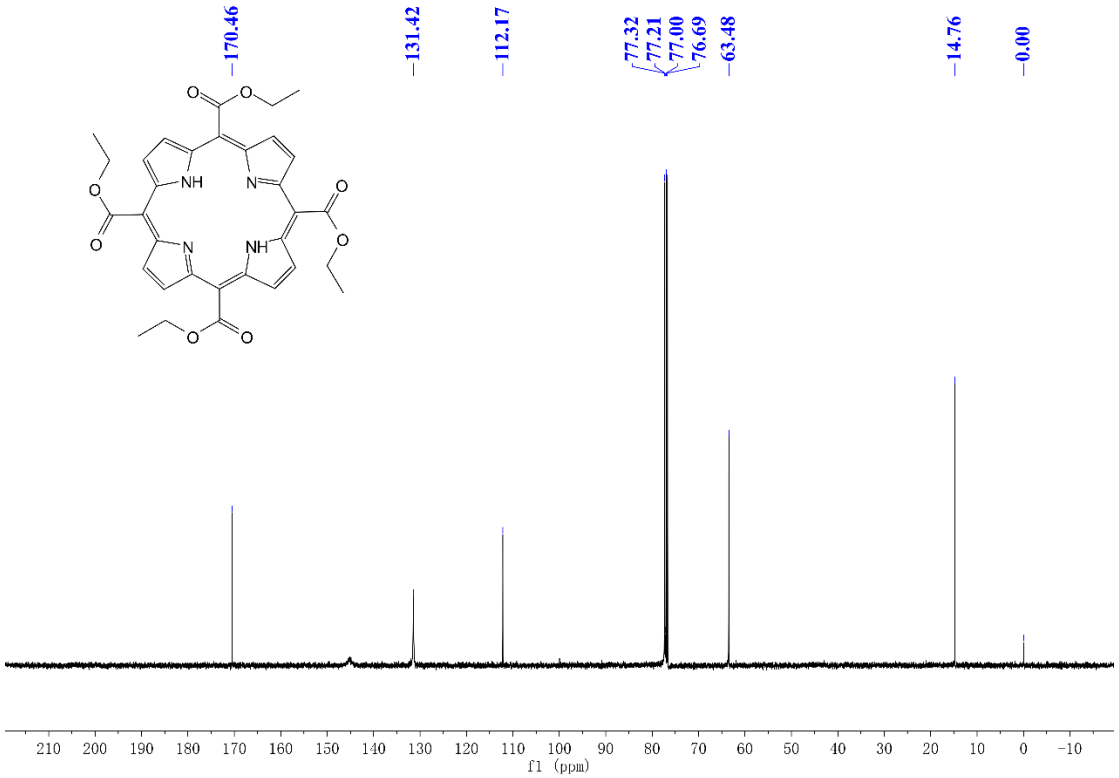



**Figure S5.** $^{13}$C NMR of 5, 10, 15, 20-tetrakis(ethoxycarbonyl)porphyrin (**1**).

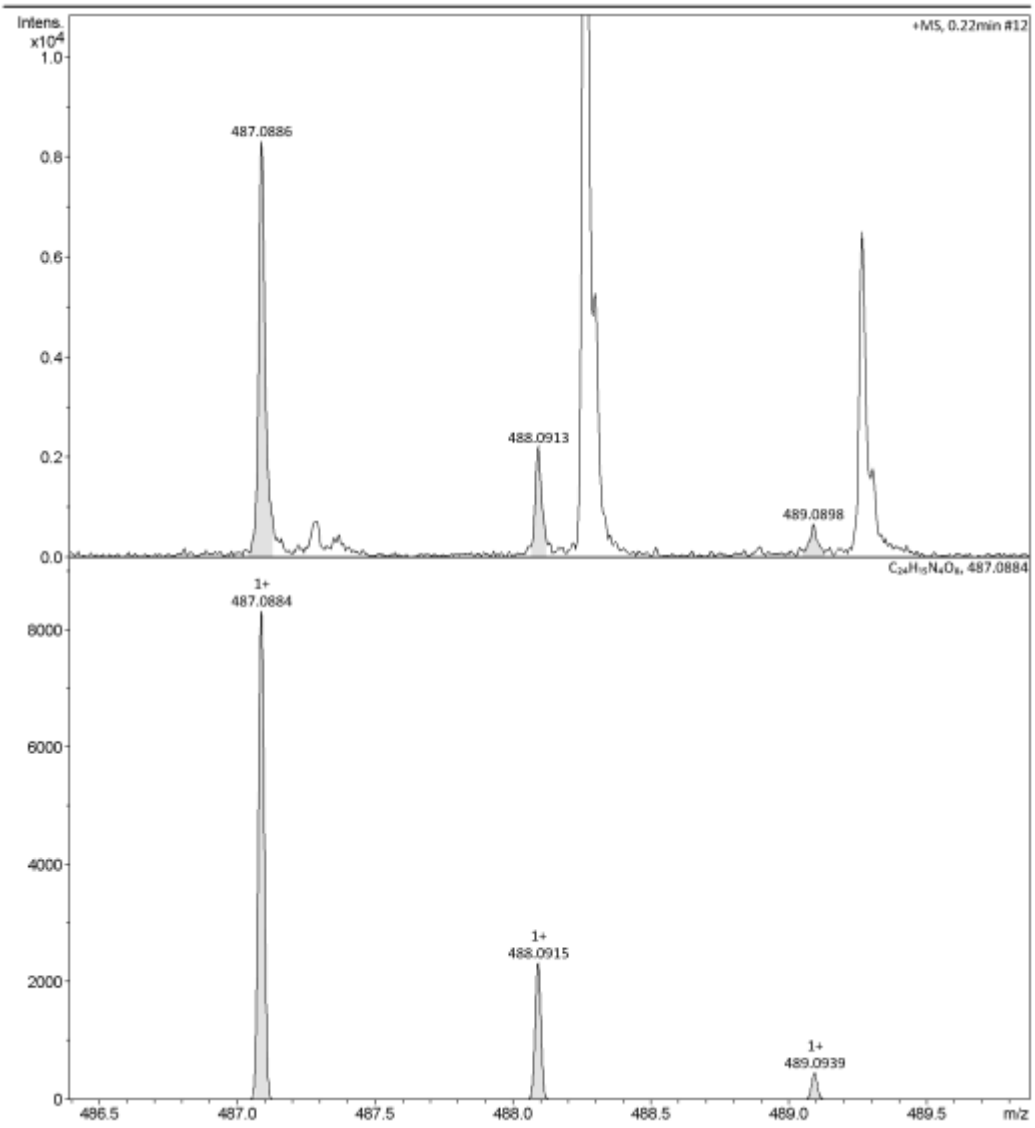



**Figure S6.** HR-MS of 5, 10, 15, 20- tetrakis (carboxyl) porphyrin (**2**)

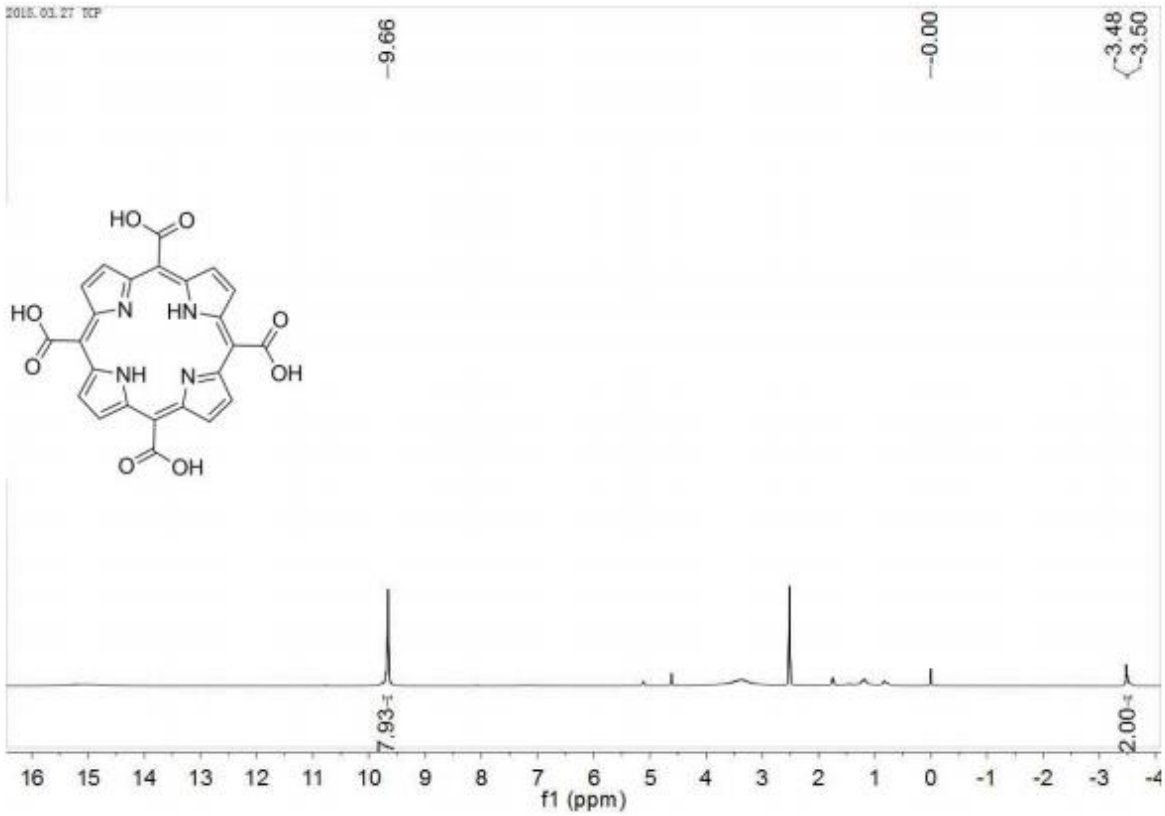



**Figure S7.** $^{1}$H NMR of 5, 10, 15, 20- tetrakis (carboxyl) porphyrin (**2**)

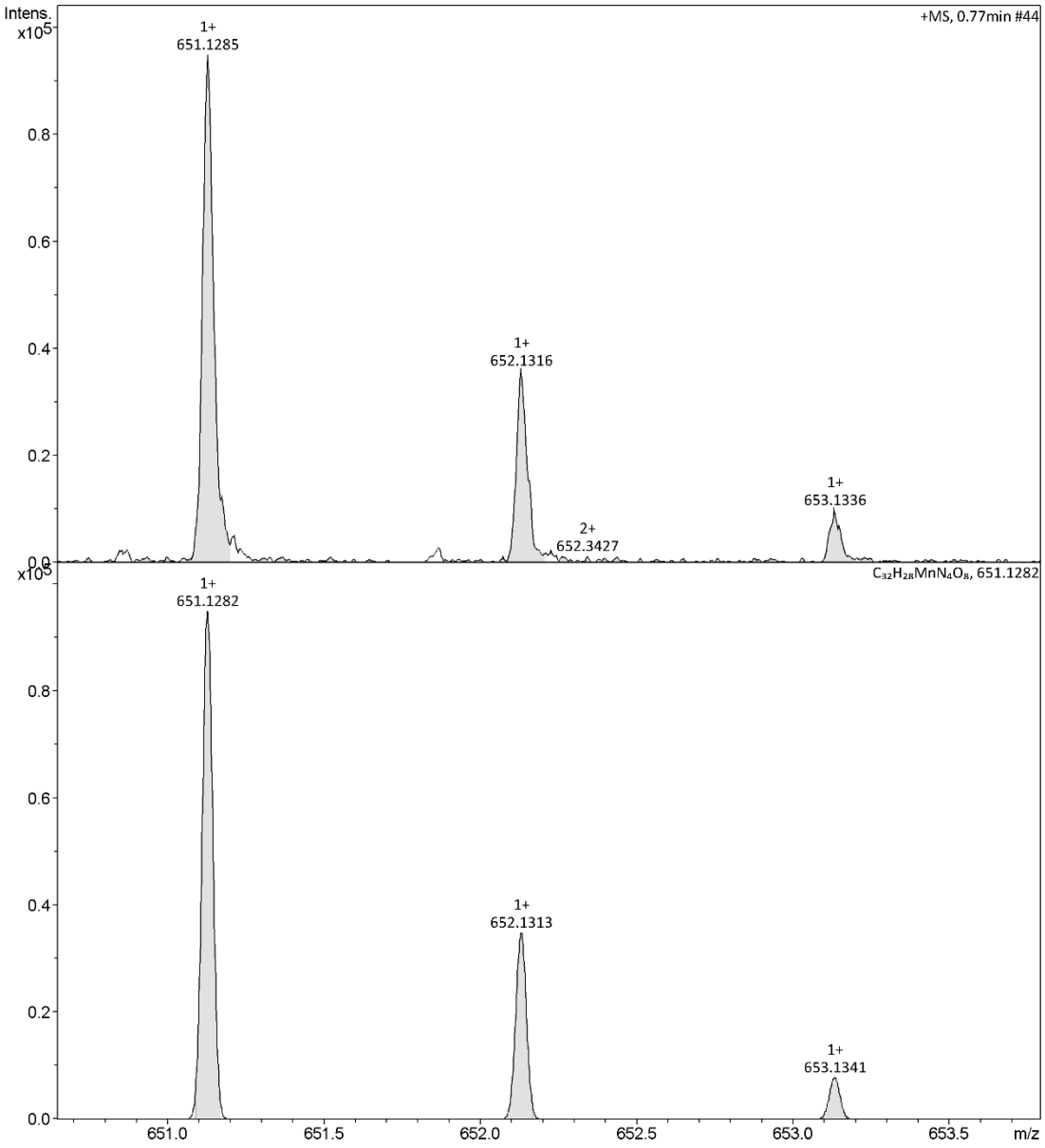



**Figure S8.** HR-MS of 5, 10, 15, 20-tetrakis(ethoxycarbonyl)porphyrin manganese (III) (**1-Mn**)

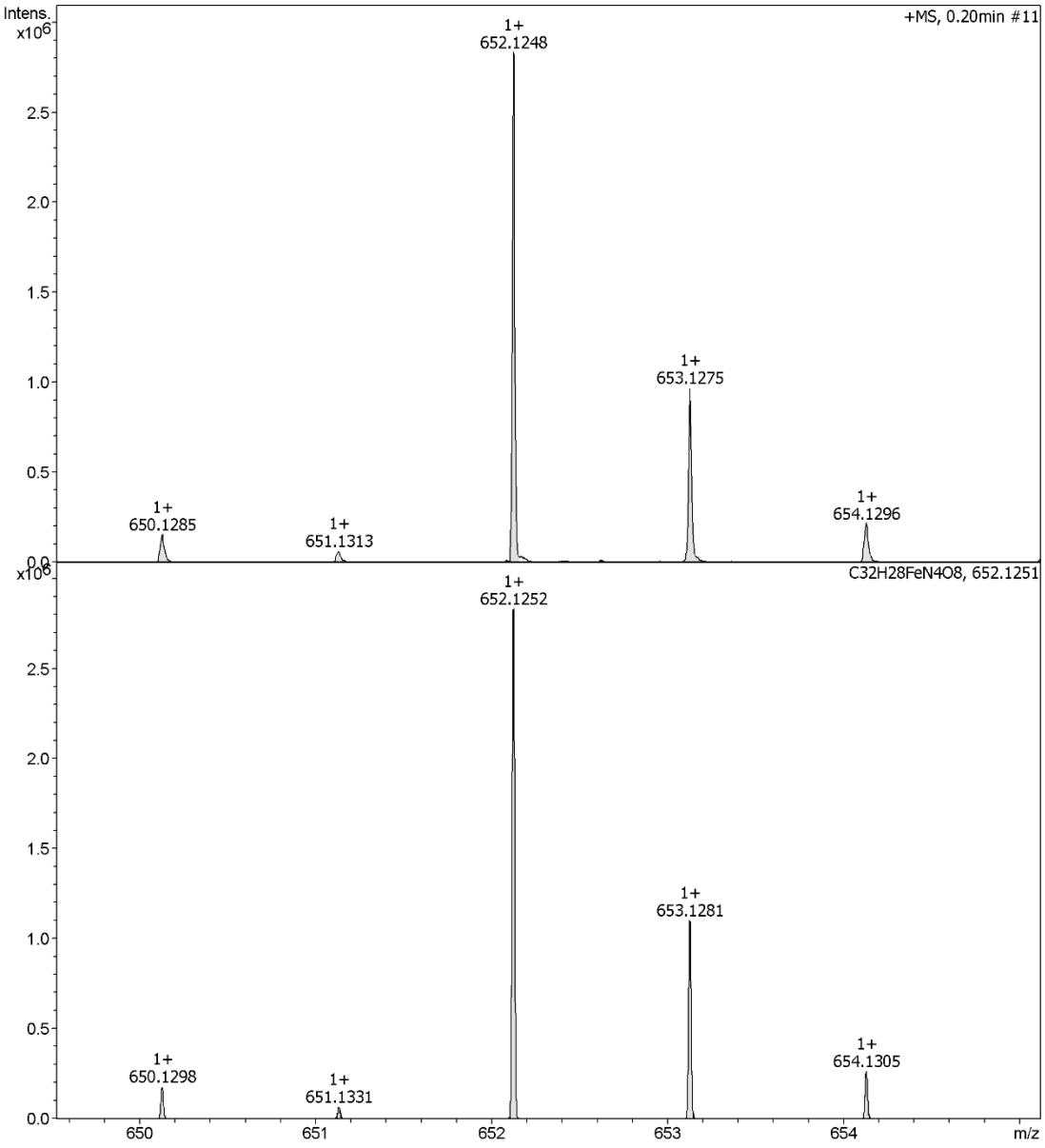



**Figure S9.** HR-MS of 5, 10, 15, 20-tetrakis(ethoxycarbonyl)porphyrin iron (III) (**1-Fe**)

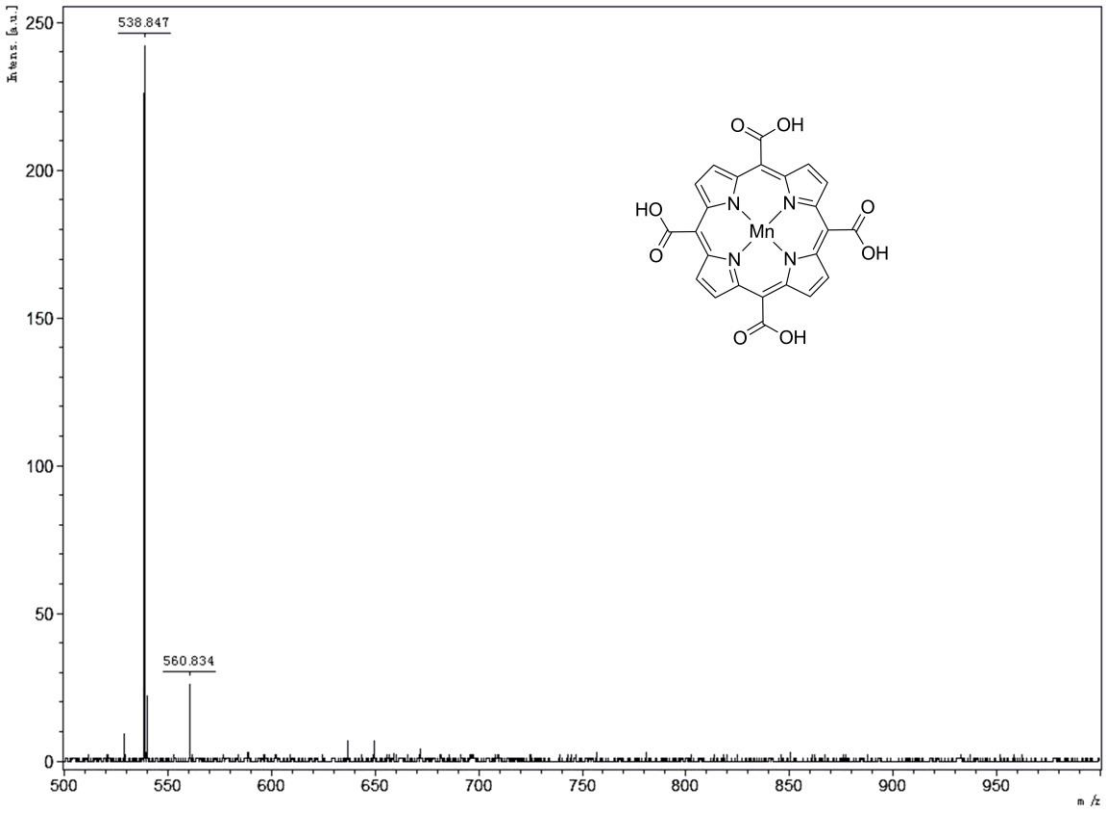



**Figure S10.** MALDI-TOF MS of 5, 10, 15, 20-tetrakis(carboxyl)porphyrin manganese (III) (**2-Mn**)

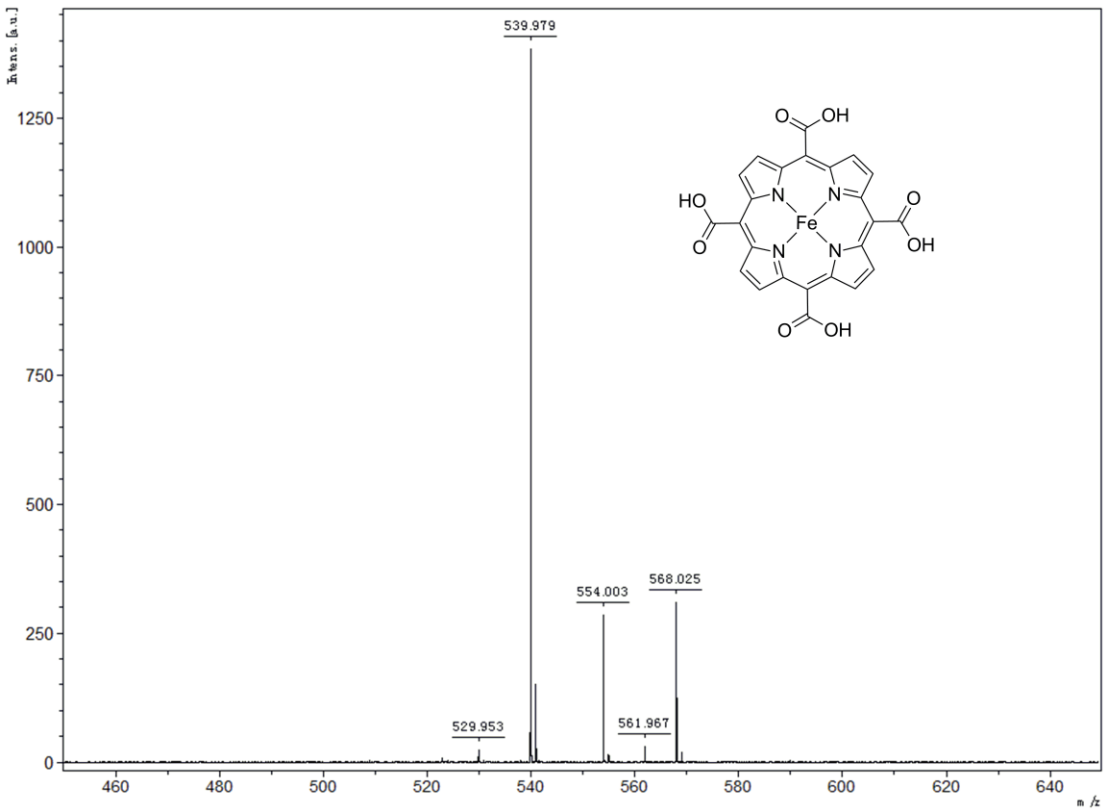
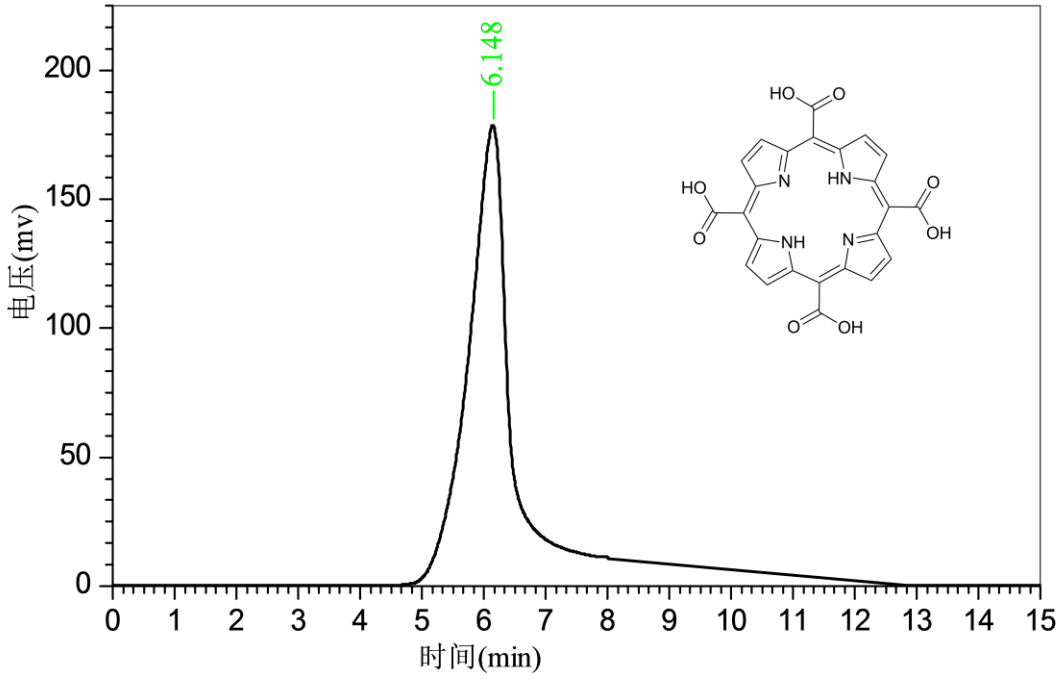
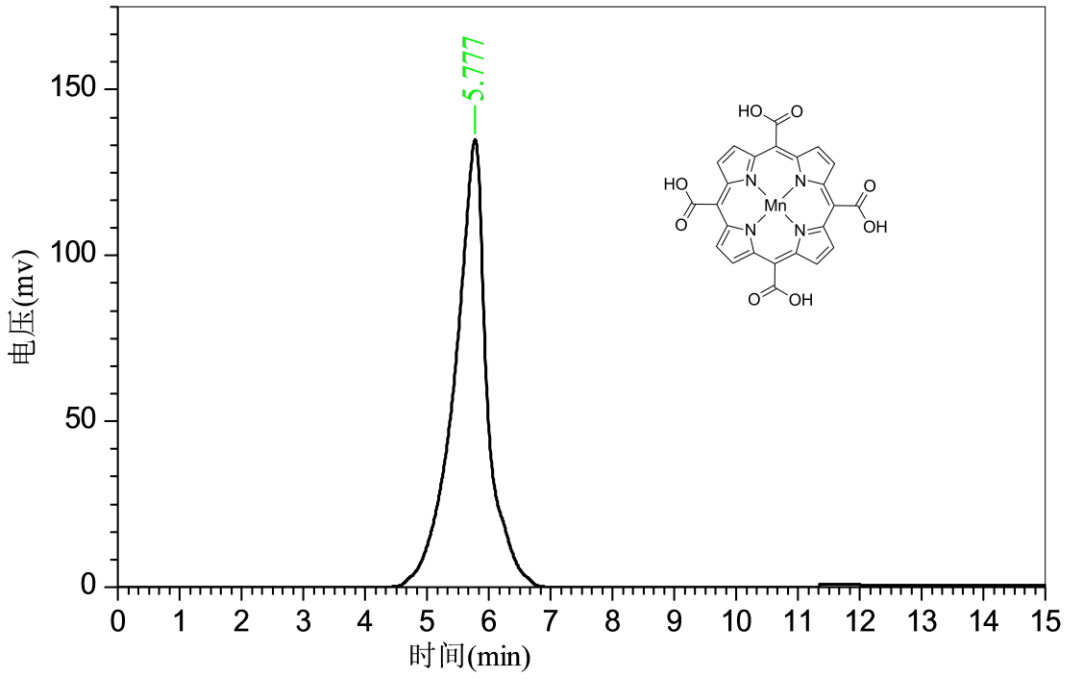



**Figure S11.** MALDI-TOF MS of 5, 10, 15, 20-tetrakis(carboxyl)porphyriniron (III) (**2-Fe**)

**. HPLC trace of porphyrins 2, 2-Mn and 2-Fe**

Reversed-phase HPLC analysis: The samples were analyzed on AT. ChromC$^{18}$ column (4.6×250mm).



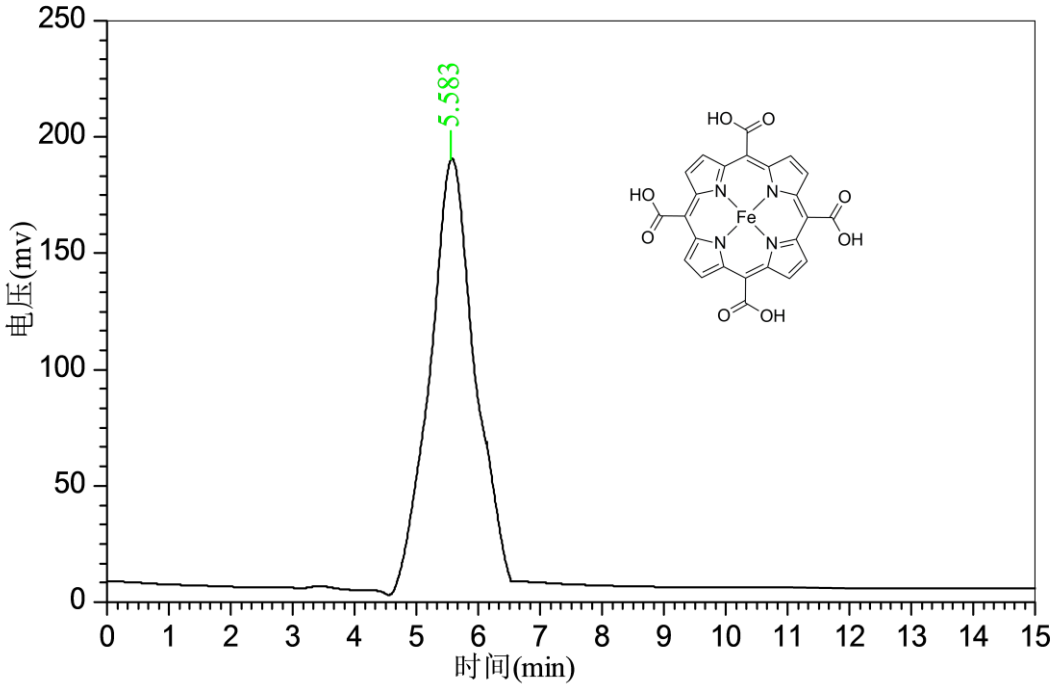



**Figure S12.** Porphyrin **2**, **2-Mn**, **2-Fe**, detection at 400 nm, $CH_3OH$ : $H_2O$ 95 : 5, 0.3 mL/min, retention time is 6.148, 5.777, 5.583min, respectively.

**3. The UV-Vis spectra changes of 2-Mn (a) and 2-Fe (b) upon the addition $H_2O_2$**

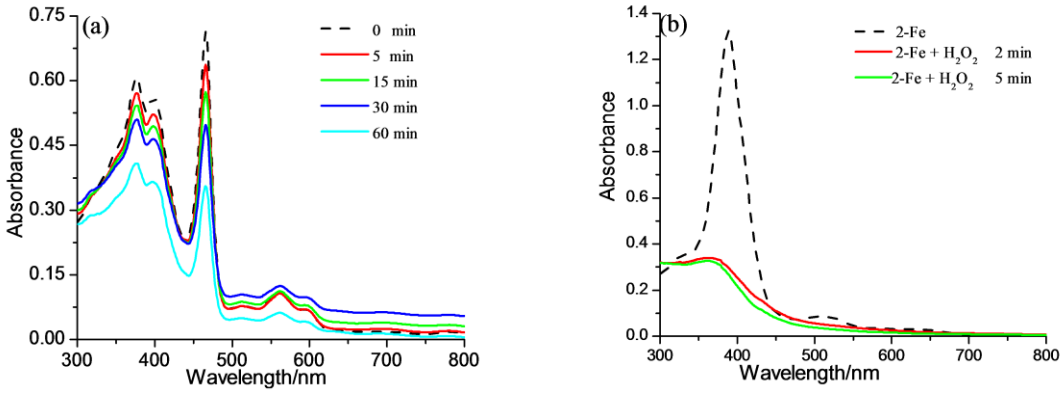



**Figure S13.** The UV-Vis spectra changes of **2-Mn** (**a**) and **2-Fe** (**b**) upon the addition $H_2O_2$ at different time. The arrow shows the absorbance along with the change of time. [**2-Mn**] = [**2-Fe**] = 30 μM, [$H_2O_2$] = 20 mM.