

## Supporting Information

### Self-hydroxylation of perbenzoic acids at a nonheme iron(II) center

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## Experimental Conditions.

All chemicals obtained from Aldrich Chemical Co. were the best available purity and used without further purification unless otherwise indicated. Solvents were dried according to published procedures and distilled under Ar prior to use [1].  $\text{H}_2^{18}\text{O}$  (95%  $^{18}\text{O}$ -enriched) and  $^{18}\text{O}_2$  (95%  $^{18}\text{O}$ -enriched) were purchased from ICON Services Inc. (Summit, NJ, USA). *m*-Chloroperbenzoic acid (*m*-CPBA) purchased from Aldrich was purified by washing with phosphate buffer (pH 7.4) followed by water and then dried under reduced pressure. Peracetic acid ( $\text{CH}_3\text{CO}_3\text{H}$ , 32 wt. % solution containing <6%  $\text{H}_2\text{O}_2$ ) was obtained from Aldrich. Perbenzoic acids and phenylperacetic acid (PPAA) were prepared by literature methods [2]. Iron(II) complexes such as  $\text{Fe}(\text{TPA})(\text{ClO}_4)_2$ ,  $\text{Fe}(\text{BPMEN})(\text{ClO}_4)_2$ ,  $\text{Fe}(\text{N4Py})(\text{ClO}_4)_2$ , and  $\text{Fe}(\text{TMC})(\text{CF}_3\text{SO}_3)_2$  were prepared in a glovebox by literature methods [3-6].

Caution: Perchlorate salts are potentially explosive and should be handled with great care.

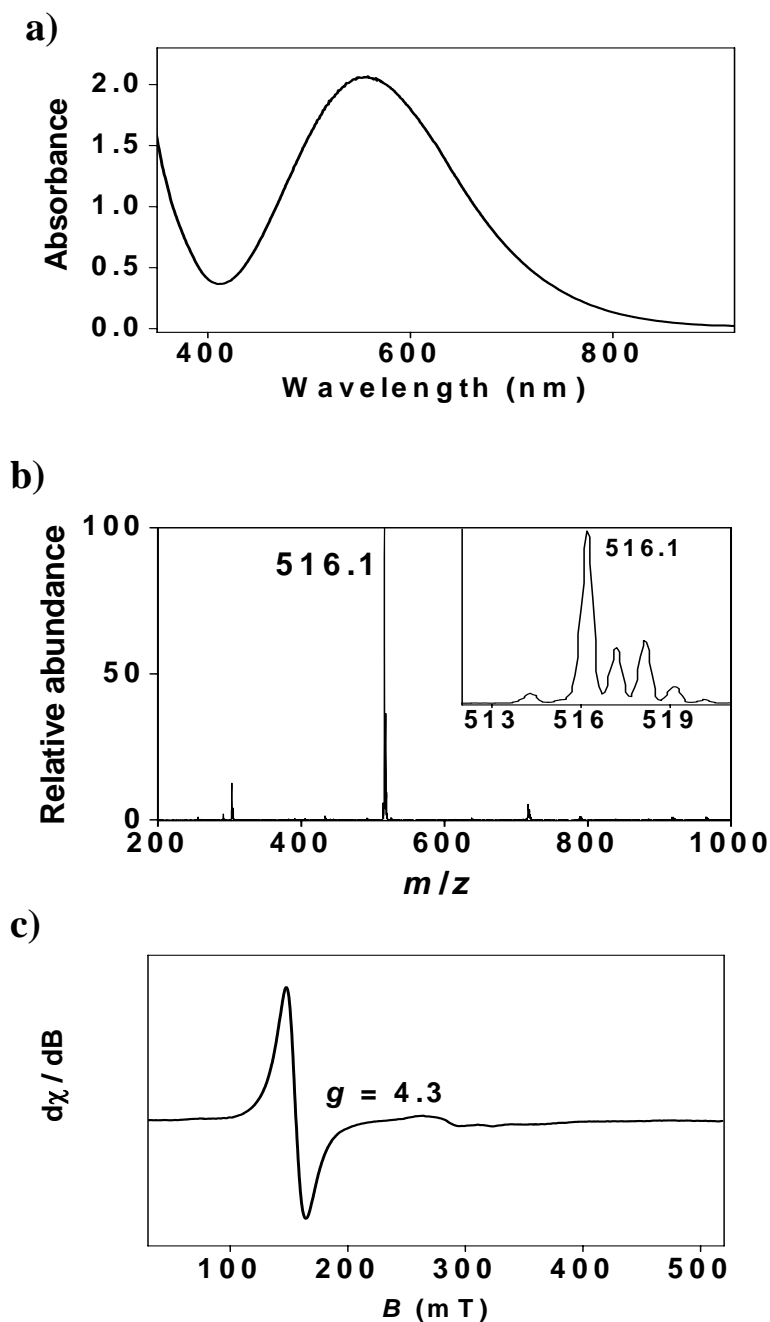
UV-vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer equipped with an Optostat<sup>DN</sup> variable-temperature liquid-nitrogen cryostat (Oxford instruments). Electrospray ionization mass spectra (ESI MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQ<sup>TM</sup> Advantage MAX quadrupole ion trap instrument, by infusing samples directly into the source at 20  $\mu\text{L}/\text{min}$  using a syringe pump. The spray voltage was set at 4 kV and the capillary temperature at 70  $^\circ\text{C}$ . EPR spectra were obtained on a JEOL JES-FA200 spectrometer.  $^1\text{H}$  NMR spectra were recorded on Varian Unity 500 MHz spectrometer. Elemental Analysis was done on a Thermo Finnigan Italia SpA (Flash EA<sup>®</sup> 1112) CHN analyzer. 2,5-Bis(5' *tert*-butyl-2-benzoxazol-2-yl)thiophene (BBOT) was used as a reference standard. Crystallographic analysis was conducted with an SMART APEX CCD equipped with a Mo X-ray tube at the X-ray Crystallographic Laboratory of Ewha Womans University. The structure solution and refinement of the data were handled with the SHELXS-86 and SHELXL-97 programs, respectively [7,8].

All reactions were followed by monitoring spectral changes of reaction solutions with a UV-vis spectrophotometer. In general, 3 equiv of perbenzoic acid (3 mM, diluted in 50  $\mu\text{L}$  of  $\text{CH}_3\text{CN}$ ) were added to a reaction solution containing an iron(II) complex (1 mM) in  $\text{CH}_3\text{CN}$  (3 mL) at  $-40\text{ }^\circ\text{C}$ .  $[(\text{TPA})\text{Fe}^{\text{IV}}=\text{O}]^{2+}$  (**2**) was generated by adding 1.2 equiv of

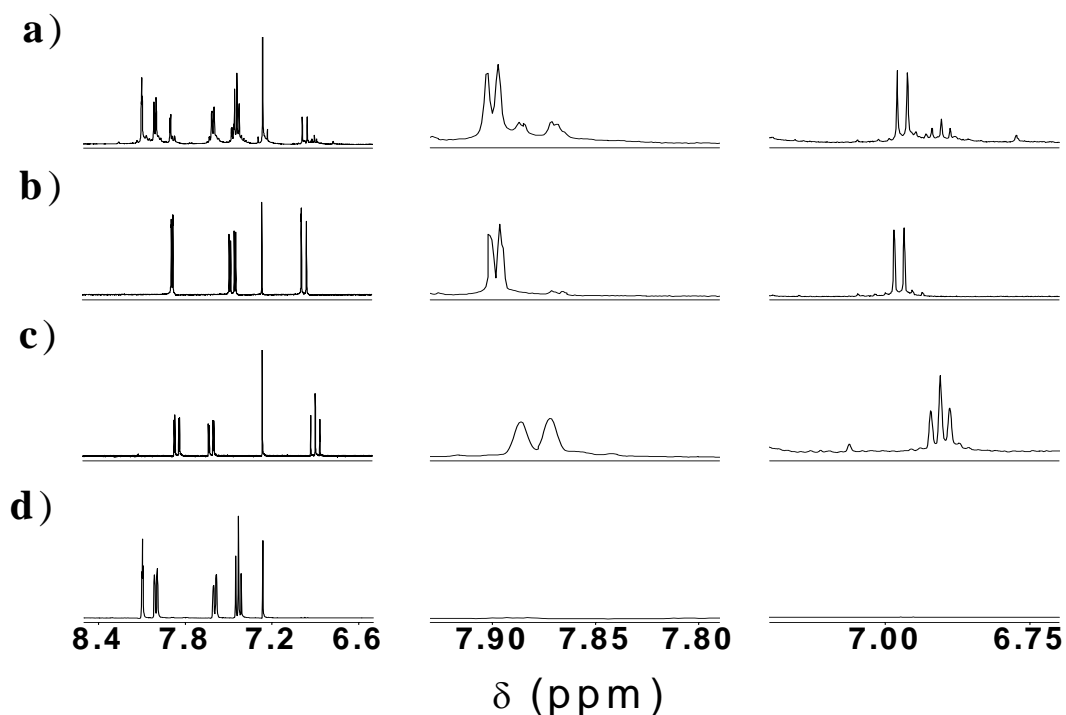
CH<sub>3</sub>CO<sub>3</sub>H (1.2 mM, diluted in 50 µL of CH<sub>3</sub>CN) to a solution of Fe(TPA)(ClO<sub>4</sub>)<sub>2</sub>, (1 mM) in CH<sub>3</sub>CN (3 mL) at -40 °C. [Fe<sup>III</sup>(TPA)(5-Cl-salicylate)(ClO<sub>4</sub>)] was synthesized by reacting equimolar amounts of Fe(TPA)(ClO<sub>4</sub>)<sub>2</sub> and 5-Cl-salicylic acid in CH<sub>3</sub>CN in air. Purple crystals suitable for crystallographic analysis were obtained from CH<sub>3</sub>CN/diethyl ether. Analytical data for [Fe<sup>III</sup>(TPA)(5-Cl-salicylate)(ClO<sub>4</sub>)], C<sub>25</sub>H<sub>21</sub>N<sub>4</sub>FeCl<sub>2</sub>O<sub>7</sub>: Calcd (found) C 48.73 (48.36), H 3.44 (3.77), N 9.09 (9.16).

## References

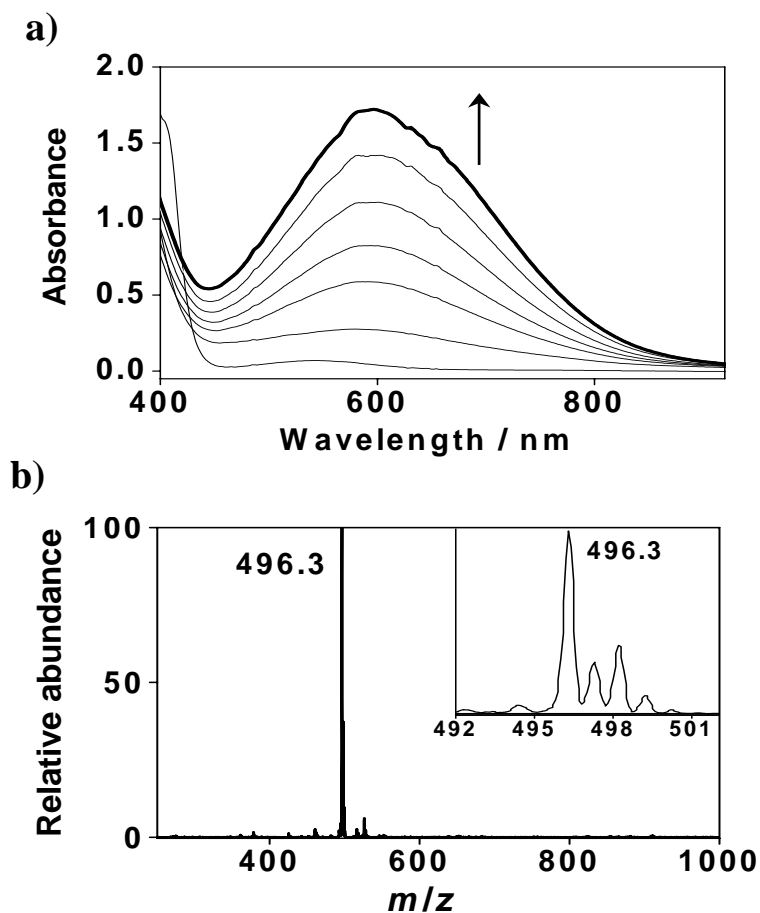
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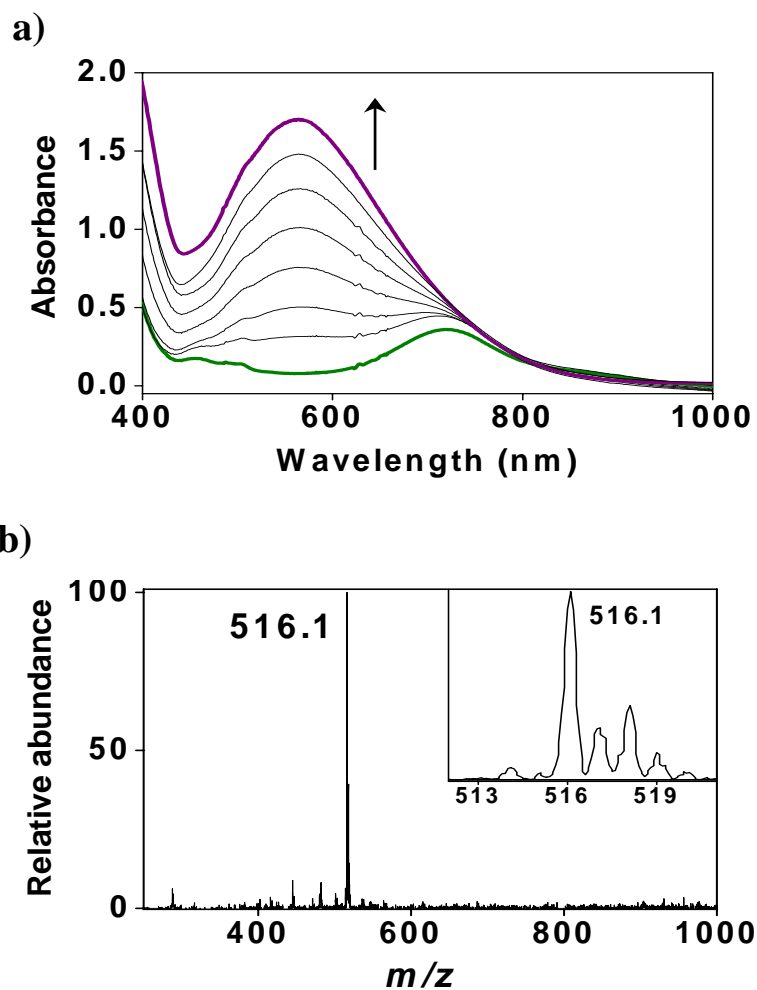
**Figure S1.** (a) UV-vis spectrum of  $[\text{Fe}^{\text{III}}(\text{TPA})(5\text{-Cl-salicylate})](\text{ClO}_4)$  prepared by reacting  $\text{Fe}(\text{TPA})(\text{ClO}_4)_2$  (1 mM) and 5-Cl-salicylic acid (1 mM) in  $\text{CH}_3\text{CN}$  in air. (b) Electrospray ionization mass spectrum of  $[\text{Fe}^{\text{III}}(\text{TPA})(5\text{-Cl-salicylate})]^+$ . Inset shows observed isotope distribution pattern for an ion at  $m/z$  of 516.1. (c) EPR spectrum of  $[\text{Fe}^{\text{III}}(\text{TPA})(5\text{-Cl-salicylate})](\text{ClO}_4)$ . Instrumental parameters: Temperature, 4 K; microwaves, 9.05 GHz at 1 mW; modulation 100 KHz.



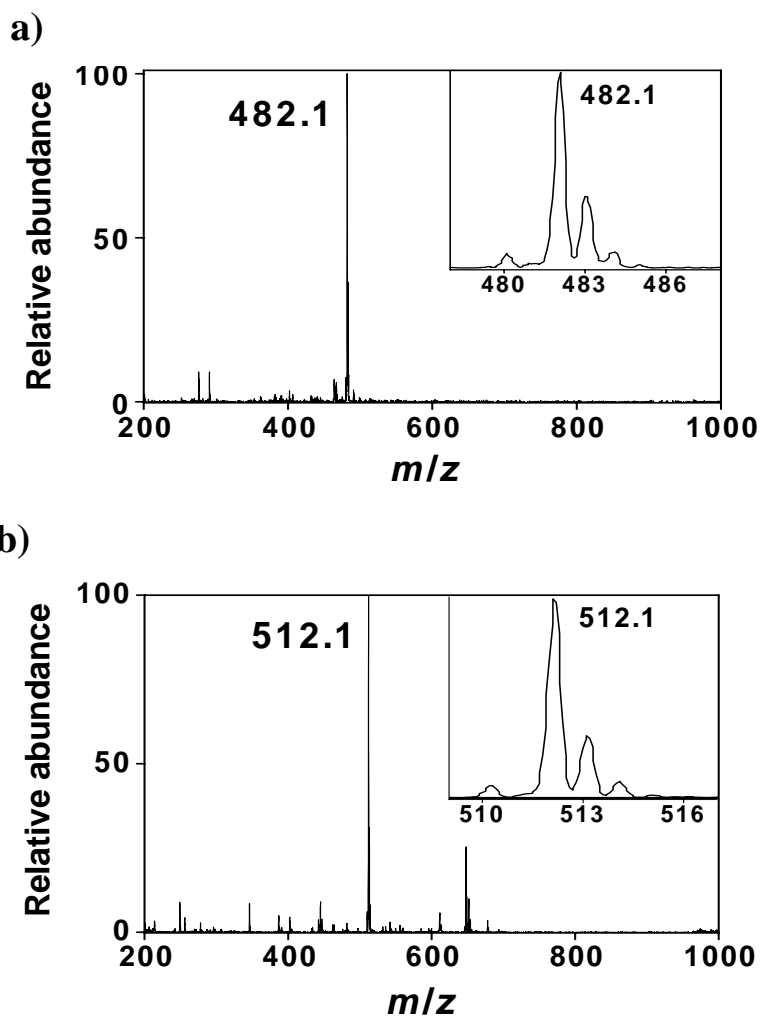
**Figure S2.**  $^1\text{H}$  NMR spectra of (a) the free ligand of **3**; (b) 5-Cl-salicylic acid; (c) 3-Cl-salicylic acid; (d) *m*-CBA. The free ligand of **3** was prepared as follows: **3** was prepared by reacting **1** (4 mM) with *m*-CPBA (12 mM) in  $\text{CH}_3\text{CN}$  at  $-20^\circ\text{C}$ . Then, concentrated HCl was added to the solution of **3** at room temperature. The solution was extracted with ether (2 x 5 mL), and the extracts were washed with water and dried under vacuum. The white residue was taken up into  $\text{CDCl}_3$  and analyzed with  $^1\text{H}$  NMR spectroscopy.



**Figure S3.** (a) UV-vis spectrum and (b) ESI MS of  $[\text{Fe}^{\text{III}}(\text{BPMEN})(\text{Cl-salicylate})]^+$  (calculated  $m/z$  of 496.1). Reaction Conditions:  $\text{Fe}(\text{BPMEN})(\text{ClO}_4)_2$ , (1 mM) was reacted with *m*-CPBA (3 mM) in  $\text{CH}_3\text{CN}$  (3 mL) at  $-20\text{ }^\circ\text{C}$ . The reaction was completed within 10 min.

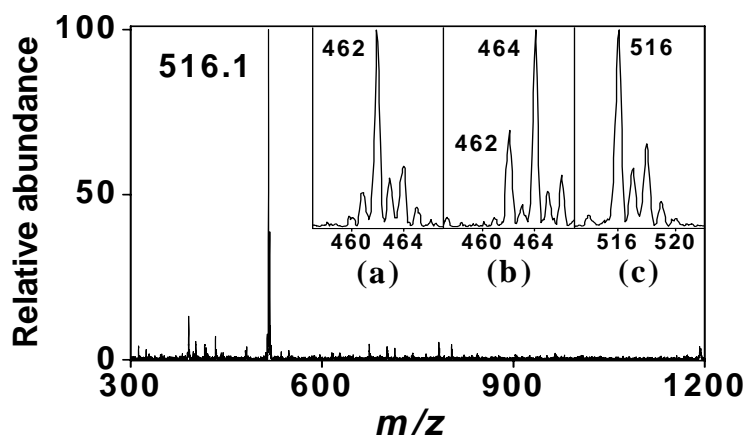


**Figure S4.** (a) UV-vis spectral changes of **2** (green-colored bold line) to **3** (purple-colored bold line) upon addition of 3 equiv of *m*-CPBA to a solution of **2** (1 mM) in CH<sub>3</sub>CN at –20 °C. The conversion from **2** to **3** was completed within 1 h at –20 °C. (b) ESI MS of **3** generated in the reaction of **2** (1 mM) and *m*-CPBA (3 mM). Inset shows observed isotope distribution pattern for an ion at *m/z* of 516.1.



**Figure S5.** ESI MS of (a) [Fe(TPA)(salicylate)]<sup>+</sup> (**4**) (calculated  $m/z$  of 482.1) and (b) [Fe(TPA)(CH<sub>3</sub>O-salicylate)]<sup>+</sup> (**5**) (calculated  $m/z$  of 512.1). Insets show observed isotope distribution patterns for ions at  $m/z$  of 482.1 (a) and 512.1 (b). Reaction conditions: Fe(TPA)(ClO<sub>4</sub>)<sub>2</sub> (1 mM) was reacted with perbenzoic acid (3 equiv) for **4** and with *m*-methoxyperbenzoic acid (3 equiv) for **5** in CH<sub>3</sub>CN (3 mL) at −20 °C.





**Figure S6.** ESI MS of (a)  $2\text{-}^{16}\text{O}$ , (b)  $2\text{-}^{18}\text{O}$ , and (c)  $3\text{-}^{16}\text{O}$ . Reaction conditions: All reactions were followed by monitoring spectral changes of reaction solutions with a UV-vis spectrophotometer and by taking ESI MS of the reaction solutions. Complex  $2\text{-}^{18}\text{O}$  was prepared by carrying out the reaction of **1** (1 mM) and 1.2 equiv peracetic acid in  $\text{CH}_3\text{CN}$  containing butyl ether as a co-solvent (5:1 v/v) at  $-40\text{ }^\circ\text{C}$  (unpublished results) in order to facilitate the oxygen-atom exchange between **2** and  $\text{H}_2^{18}\text{O}$ . The formation of **2** was confirmed by a UV-vis spectrophotometer, showing a typical absorption band at 720 nm. The ESI MS of **2** was recorded by infusing the sample directly into the source by keeping reaction solutions at  $-40\text{ }^\circ\text{C}$ . The mass peak at  $m/z$  462 corresponds to  $[\text{Fe}(\text{III})(\text{TPA})(\text{OH})(\text{ClO}_4)]^+$  (calculated  $m/z$  of 462) (see inset a). We have confirmed that when butyl ether is used as a co-solvent, **2** exhibits a mass peak at  $m/z$  462 corresponding to  $[\text{Fe}(\text{III})(\text{TPA})(\text{OH})(\text{ClO}_4)]^+$ , not a mass peak at  $m/z$  461 corresponding to  $[\text{Fe}(\text{IV})(\text{TPA})(\text{O})(\text{ClO}_4)]^+$ . This is probably due to the occurrence of a H-atom abstraction by  $[\text{Fe}(\text{IV})(\text{TPA})(\text{O})(\text{ClO}_4)]^+$  at the spray nozzle. Then,  $\text{H}_2^{18}\text{O}$  (10  $\mu\text{L}$ , diluted in 50  $\mu\text{L}$  of  $\text{CH}_3\text{CN}$ ) was added to the reaction solution to prepare  $2\text{-}^{18}\text{O}$ . After 1 min incubation, ESI MS of the resulting mixture was taken, showing a major peak at  $m/z$  464 which corresponds to  $[\text{Fe}(\text{III})(\text{TPA})(^{18}\text{OH})(\text{ClO}_4)]^+$  (calculated  $m/z$  of 464) (see inset b). By analyzing the relative abundances of 462 and 464 for  $^{16}\text{O}$  and  $^{18}\text{O}$ , respectively, we found that **2** contained 56 %  $^{18}\text{O}$ . **3** was then generated by adding 3 equiv of *m*-CPBA (diluted in 50  $\mu\text{L}$  of  $\text{CH}_3\text{CN}$ ) to the reaction mixture. The ESI MS of **3** exhibits a mass peak at  $m/z$  516 which corresponds to  $[\text{Fe}(\text{III})(\text{TPA})(\text{Cl-salicylate})]^+$  (see inset c),

indicating that the source of oxygen incorporated into the salicylate ligand is not the iron oxo of **2** but *m*-CPBA.