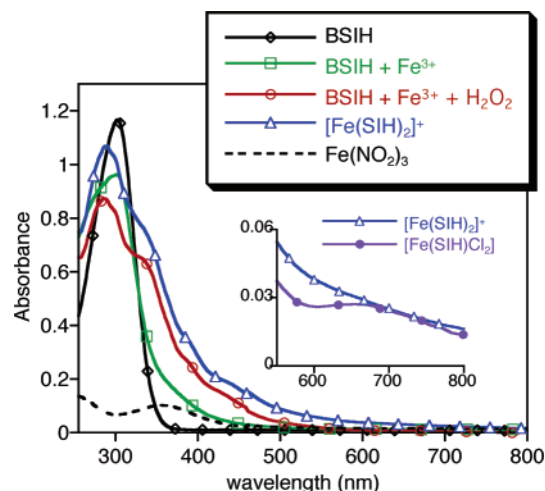
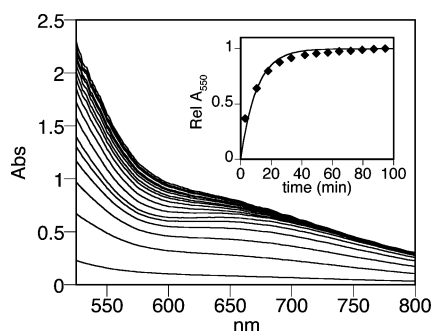


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**Figure 2.** UV-vis spectra of 60  $\mu\text{M}$  **BSIH** in MeOH in the absence and presence of 30  $\mu\text{M}$   $\text{Fe}(\text{NO}_3)_3$ . Addition of 0.6 mM  $\text{H}_2\text{O}_2$  results in a spectrum (open red circles) matching that of  $[\text{Fe}(\text{SIH})_2]^+$  (blue triangles). The expanded view in the inset compares the mono and bis species,  $[\text{Fe}(\text{SIH})\text{Cl}_2(\text{CH}_3\text{OH})]$  and  $[\text{Fe}(\text{SIH})_2]\text{NO}_3$ , respectively, at 60  $\mu\text{M}$ .

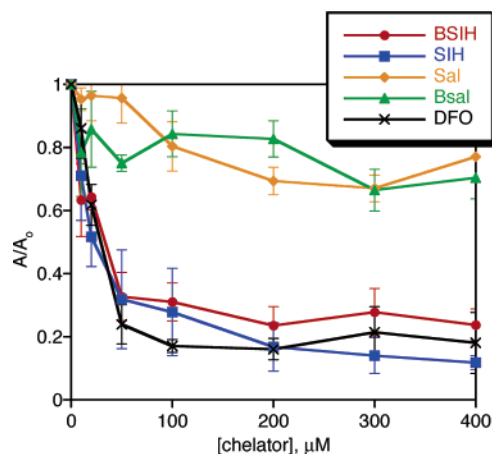


**Figure 3.** UV-vis spectra showing the formation of  $[\text{Fe}(\text{SIH})_2]^{2+}$  and  $[\text{Fe}(\text{SIH})_2]^+$  upon addition of 100 mM  $\text{H}_2\text{O}_2$  to a solution of 1.5 mM  $\text{Fe}(\text{NO}_3)_3$  and 3.0 mM **BSIH** in MeOH.

expression to give  $k_{\text{obs}} = 1.6 \times 10^{-3} \text{ s}^{-1}$ . This value is consistent with preliminary kinetic data for the conversion of **BSIH** to **SIH** in the absence of iron (not shown), indicating that the rate-limiting step for iron sequestration is oxidation of **BSIH** to **SIH**, followed by rapid metal complexation.

To test the effectiveness of **BSIH** for inhibiting  $\text{OH}^\bullet$  formation, we used an in vitro deoxyribose assay in which hydroxyl radicals that are generated via typical Fenton conditions of  $\text{Fe}^{3+}$ , ascorbic acid, and  $\text{H}_2\text{O}_2$  degrade deoxyribose to give products that form a chromophore with thiobarbituric acid (TBA) with  $\lambda_{\text{max}}$  at 532 nm.<sup>18</sup> Figure 4 displays the effect of increasing chelator concentration on the degradation of deoxyribose under these conditions. Values of  $A/A_0$  above 1 indicate that the additive promotes  $\text{OH}^\bullet$  formation, whereas values below 1 indicate that the additive either scavenges  $\text{OH}^\bullet$  more efficiently than deoxyribose, or that it inhibits iron-catalyzed  $\text{OH}^\bullet$  formation via effective iron chelation. EDTA, a ligand known to promote Fenton chemistry, causes a significant increase in  $A/A_0$  (Supporting Information), whereas desferrioxamine (**DFO**) and **SIH**, chelators known to inhibit Fenton chemistry,<sup>19</sup> show a decrease in  $A/A_0$ . As shown in Figure 4, **BSIH** protects against deoxyribose degradation as well as both **DFO** and **SIH**.

To show that the protective effect of **BSIH** is not solely due to consumption of  $\text{H}_2\text{O}_2$ , we tested the boronate-masked salicylaldehyde, **Bsal**, which converts to salicylaldehyde (**Sal**) in the presence of  $\text{H}_2\text{O}_2$ . Neither **Bsal** nor **Sal** has a significant influence on the



**Figure 4.** Effect of chelator concentration on deoxyribose degradation by  $\text{OH}^\bullet$ .  $A$  and  $A_0$  are the absorbance at 532 nm in the presence and absence of chelator, respectively. Values below  $A/A_0 = 1$  indicate protection of deoxyribose. Conditions: 200  $\mu\text{M}$   $\text{H}_2\text{O}_2$ , 10  $\mu\text{M}$   $\text{FeCl}_3$ , 2 mM ascorbic acid, 15 mM deoxyribose in pH 7.4  $\text{NaH}_2\text{PO}_4$  buffer.

deoxyribose assay, as shown by the nearly constant  $A/A_0$  values near unity in Figure 4. Whereas **DFO** and **SIH** protect deoxyribose when  $\text{OH}^\bullet$  are generated in the absence of added  $\text{H}_2\text{O}_2$ , **BSIH** has little effect under these conditions (Supporting Information). Taken together, these data indicate that the protective effect of **BSIH** against deoxyribose degradation derives from its  $\text{H}_2\text{O}_2$ -dependent conversion to **SIH**, which in turn provides the right coordination environment around Fe to prevent iron-promoted  $\text{OH}^\bullet$  generation.

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**Supporting Information Available:** Complete refs 9 and 10, experimental details, and X-ray crystallographic data, including CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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