Supplementary Figure Captions:

Supplementary Figure 1: UV-Vis absorbance spectrum (left) and derivative with fit (right) of MetHb in PBS buffered, aqueous solutions, pH 7.4, used to determined total protein concentration.

Supplementary Figure 2: EPR spectra and fits of MetHb with sodium nitrite in equal molar and 5-, 10-, and 20-fold excess over heme, as labeled. Spectra were collected at 20 K with the following parameters: 0.5 s time constant, 5 G modulation amplitude, 16.67 G/s sweep rate, 5 mW microwave power, and 9.24 GHz microwave frequency.

Supplementary Figure 3: Simulated EPR basis spectra used in the fitting of the experimental spectra shown in supplementary figure 2.