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SUPPORTING INFORMATION

Figure SM1. Reactions of Fd and its cysteine mutants with tiron. Holo Fd (50 μM, 1 mL 100 mM Tris-HCl, pH 7.4) was mixed with tiron at 25 C, with a final ligand concentration of 10 mM. (Top) The reaction of Sp Fd with tiron was monitored by the change in absorbance over a period of 20 min. (Bottom) The reaction of Sp Fd and cysteine mutants with tiron were monitored at 480 nm. In all cases the time-dependent profiles were fit to equation (1).
Figure SM2. Reactions of the Fe-S proteins *Hs* ISU and D37A *Hs* ISU with tiron and bipy. Holo proteins (50 μM in 1 mL 100 Mm Tris-HCl, pH 7.4) were added to tiron (dotted line) or bipy (solid line) with a final ligand concentration of 10 mM.
Figure SM3.  (Top) Dependence of reaction rate on [Fd] for the reaction of Hs Fd with bipy (10 mM).  The slope yielded a \( k_2 \sim 4.6 \times 10^{-3} \) min\(^{-1}\).  (Bottom) Reaction of Hs Fd (50 \( \mu \)M) with bipy (5 or 10 mM, as indicated) in the presence of urea (none or 3 M, as indicated).  The plots were fit to equation (1) and yielded apparent rate constants as noted in the main paper.