ESI1 The initial rate of CAL bleaching versus \([\text{Mn}^{II}]\). All conditions as for Fig. 4.

ESI2 The initial rate of CAL bleaching versus \([\text{Tiron}]\). All conditions as for Fig. 5.

ESI3 The UV/VIS spectrum of an aqueous solution of 1.50 mM Tiron at pH 8.00 (20 mM, \(N\)-2-hydroxyethylpiperazine-\(N'\)-3-propanesulfonic acid, EPPS, buffer) and at 23±1°C with EPPS (20 mM, pH 8.00) as baseline.

ESI4 Overlap UV/VIS scan (198 – 1,000 nm) of the reaction solution at various times during CAL bleaching at 23±1°C using added hydrogen peroxide with EPPS (20 mM, pH 8.00) as baseline. \([\text{MnCl}_2\cdot4\text{H}_2\text{O}]\) was 50.0 μM. Initial [CAL], \([\text{H}_2\text{O}_2]\) and [Tiron] were 0.100 mM, 50 mM and 1.50 mM respectively. The pH was 8.00 (20 mM, \(N\)-2-hydroxyethylpiperazine-\(N'\)-3-propanesulfonic acid, EPPS, buffer).

ESI5 The change in [CAL] with time monitored at 544 nm and at 23±1°C using in situ generated hydrogen peroxide with initial [CAL] at 0.800 mM. \([\text{MnCl}_2\cdot4\text{H}_2\text{O}]\) was 50.0 μM. Initial [Tiron] and \([\text{NH}_3\text{OH}^+\text{Cl}^-]\) were 1.50 mM and 100 mM respectively. The pH was 8.0 (20 mM, \(N\)-2-hydroxyethylpiperazine-\(N'\)-3-propanesulfonic acid, EPPS, buffer) with \(\text{O}_2\) flow rate 0.6 L min\(^{-1}\).

ESI6 The change in the absorbance at 436 nm with time for an aqueous mixture of 0.10 mM Mn\(^{II}\), 0.10 mM CAL and Tiron at 0, 1.50, 3.00 and 4.50 mM at pH 8.00 (20 mM, \(N\)-2-hydroxyethylpiperazine-\(N'\)-3-propanesulfonic acid, EPPS, buffer) and at 23±1°C.

ESI7 The change in [O II] monitored at 484 nm and [EBT] monitored at 558 nm with time using in situ generated hydrogen peroxide and at 23±1°C. \([\text{MnCl}_2\cdot4\text{H}_2\text{O}]\) was 50.0 μM. Initial [Tiron] and \([\text{NH}_3\text{OH}^+\text{Cl}^-]\) were 1.50 mM and 100 mM respectively. The pH was 8.0 (20 mM, \(N\)-2-hydroxyethylpiperazine-\(N'\)-3-propanesulfonic acid, EPPS, buffer) with \(\text{O}_2\) flow rate 0.6 L min\(^{-1}\).

ESI8 The change in [Me-CAL] with time monitored at 525 nm using in situ generated hydrogen peroxide and at 23±1°C. \([\text{MnCl}_2\cdot4\text{H}_2\text{O}]\) was 50.0 μM. Initial [CAL], [Tiron] and \([\text{NH}_3\text{OH}^+\text{Cl}^-]\) were 0.100 mM, 1.50 mM and 100 mM respectively. The pH was 8.00 (20 mM, \(N\)-2-hydroxyethylpiperazine-\(N'\)-3-propanesulfonic acid, EPPS, buffer) with \(\text{O}_2\) flow rate 0.6 L min\(^{-1}\). **Secondary y-axis**: The formation of \(\text{H}_2\text{O}_2\) (●) with Me-CAL; all conditions as above.
ESI9 ESI-MS chromatograms of the reaction solution near the start of the bleaching of CAL. Initial [CAL], [Tiron] and [NH$_3$OH$^+$Cl$^-$] were 0.100 mM, 1.50 mM and 10 mM respectively with (a) [MnCl$_2$-4H$_2$O] 50.0 µM (b) Na$_5$[Mn$^{III}$(T)$_2$]-10H$_2$O 50.0 µM or (c) no added Mn. The pH was 8.00 (2 mM, N-2-hydroxyethylpiperazine-$N'$-3-propanesulfonic acid, EPPS, buffer) with O$_2$ flow rate 0.6 L min$^{-1}$. 