Supporting Information

Allen et al. 10.1073/pnas.1115364109

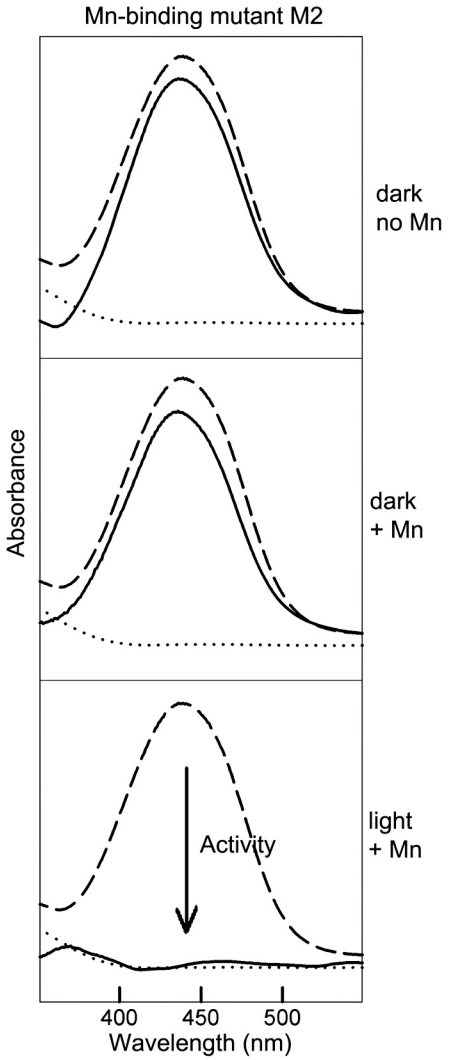

Fig. S1. Assay showing the ability of the Mn-binding mutant M2 to react with superoxide. Activity is observed for the Mn-binding mutant M2 (solid spectra) only in the presence of light and manganese. In this assay, superoxide is generated by the reaction of xanthine with xanthine oxidase. The superoxide converts an indicator reagent (see *Materials and Methods*) into a formazan dye that has an absorption maximum at approximately 440 nm. The maximum absorption under each condition is shown (dashed spectra). If superoxide dismutase activity is present, the dye is not formed and a low absorption is observed (dotted spectra). Spectra for control mutant reaction centers, the Mn-binding mutant M8, and wild-type reaction centers are shown in Fig. 1.

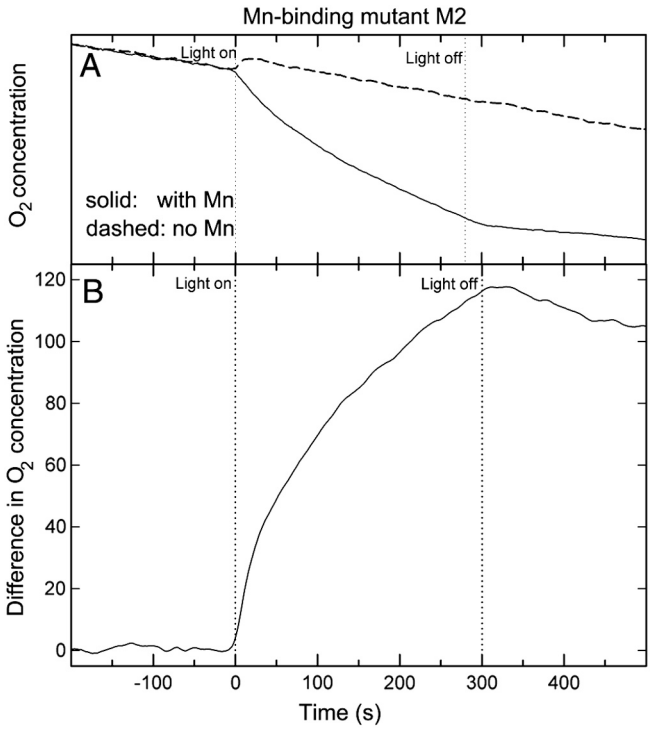

Fig. S2. Assay showing the production of oxygen from the Mn-binding mutant M2. (*A*) At −200 s (i.e., 200 s before illumination), xanthine oxidase is introduced into the solution, initiating the production of superoxide from molecular oxygen and resulting in a steady decrease in the oxygen concentration. From 0 to +300 s, the samples are illuminated. The Mn-binding mutant M2 shows a measurable increase in oxygen with Mn present compared to the absence of Mn. (*B*) The difference in the O_2 concentration for the Mn-binding mutant M2 with and without Mn. When Mn is bound to the Mn-binding reaction centers, $P^{+\cdot}$ is rapidly reduced by the bound metal forming Mn^{3+} that subsequently can react with superoxide to form O_2. Data for other mutants and control conditions are shown in Fig. 2.

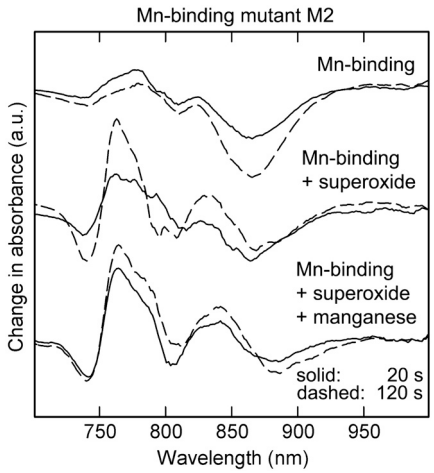

Fig. S3. Stability of the Mn-binding mutant M2 under illumination. The ability of the reaction center to perform charge separation after different times of illumination was determination by measurement of the light-induced absorption changes. Shown are the light-minus-dark spectra after illuminations of 20 s (solid) and 2 min (dotted). The spectra show a light-induced pigment loss of the Mn-binding mutant that is increased in the presence of superoxide. However, when manganese was present, the M2 mutant showed a relatively stable spectrum characteristic of the P $Q_A^{-\cdot}$ state, with $P^{+\cdot}$ being reduced by the manganese. Data for other mutants and wild type are shown in Fig. 4.