Supporting Information

Reversible Visible–Light Photooxidation of an Oxomanganese Water–Oxidation Catalyst Covalently Anchored to TiO₂ Nanoparticles


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**Figure S1.** Powder X–ray diffraction patterns of (a) well–crystallized P25 and (b) near–amorphous D70 TiO$_2$. Diffractions of various anatase (red) and rutile (blue) crystal faces are labeled.

**Figure S2.** Transmission electron micrographs of P25 (left) and D70 TiO$_2$ (right). Scale bars are 100 nm.
**Figure S3.** Spectrum of the visible–light lamp used in this study.

![Plot of spectrum](image)

**Figure S4.** A section of the TiO$_2$ anatase NP model optimized at the DFT level in the PW91/GGA approximation with plane–wave basis ultrasoft Vanderbilt pseudopotentials. Atoms are represented by spheres of different colors and sizes: H (silver, small), O (red), Ti (silver, large).

![Diagram of TiO$_2$ anatase NP](image)
Figure S5. Left: Complex 1 optimized in vacuum; atoms are represented by spheres of different colors: H (silver), O (red), N (blue), C (light green), Mn (purple). Right: A schematic representation of complex 1 deposited on TiO₂ surfaces by substituting one of its water ligand with a TiO₂ NP.

Figure S6. EPR spectra of (a) Mn^{II}–L–P25 and (b) Mn^{II}–L–D70. A broad surface-bound Mn(II) signal centered at $g = 2.0$ is seen in both spectra. A sharp resonance corresponding to organic radicals and a relatively small Ti^{3+} (lattice-trapped electron in TiO₂) signal are labeled in the spectrum of Mn^{II}–L–P25. The 6–line EPR signal characteristic of aqueous Mn^{2+} is also visible in the spectrum of Mn^{II}–L–D70 due to the existence of residual solvated Mn^{3+} ions adsorbed directly on the D70 surface after functionalization. The EPR spectrum of Mn^{II}–L–D70 was scaled down to 1/10 of its original intensity to allow a better comparison. The spectra were collected in dark at 7 K.
Figure S7. EPR spectra of (a) 1–D70 and (b) 1–L–D70 prepared by the KMnO$_4$ method. The same amounts of materials were used in the EPR measurements. The spectra were collected in dark at 7 K.

Figure S8. EPR spectra of functionalized TiO$_2$ NPs obtained by reaction of oxone with (a) Mn$^{II}$–L–P25 and (b) Mn$^{III}$–L–D70. The samples were not washed with water prior to EPR measurements. The 6–line EPR signal characteristic of aqueous Mn$^{2+}$ and a sharp organic radical signal are seen for both samples. A broad surface Mn(II) signal (see Figure S6) is also resolvable in both spectra. The spectra were collected in the dark at 7 K.
Figure S9. Simulated IR spectra of diphenyl amide in *cis* and *trans* configurations. Atoms in the diphenyl amide molecules are represented by spheres of different colors: H (silver), O (red), N (blue), C (light gray).

Figure S10. Light−*minus*−dark EPR spectrum of L−P25. A sharp resonance corresponding to organic radicals and a relatively small Ti$^{3+}$ (lattice−trapped electron in TiO$_2$) signal are labeled. The sample was subject to KMnO$_4$ treatment and was washed with water prior to EPR measurements. The spectrum was collected in the dark at 7 K.
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