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 TiO₂. 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.



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).



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 TiO_2 surfaces by substituting one of its water ligand with a TiO_2 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 Ti³⁺ (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^{2+} 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 KMnO₄ 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) $\text{Mn}^{II}-\text{L}-\text{P25}$ and (b) $\text{Mn}^{II}-\text{L}-\text{D70}$. 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 KMnO₄ treatment and was washed with water prior to EPR measurements. The spectrum was collected in the dark at 7 K.

Complete Reference 53:

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