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SUPPORTING INFORMATION

PARAMETERS AFFECTING ELECTRON TRANSFER DYNAMICS FROM SEMICONDUCTORS TO MOLECULAR CATALYSTS FOR THE PHOTOCHEMICAL REDUCTION OF PROTONS

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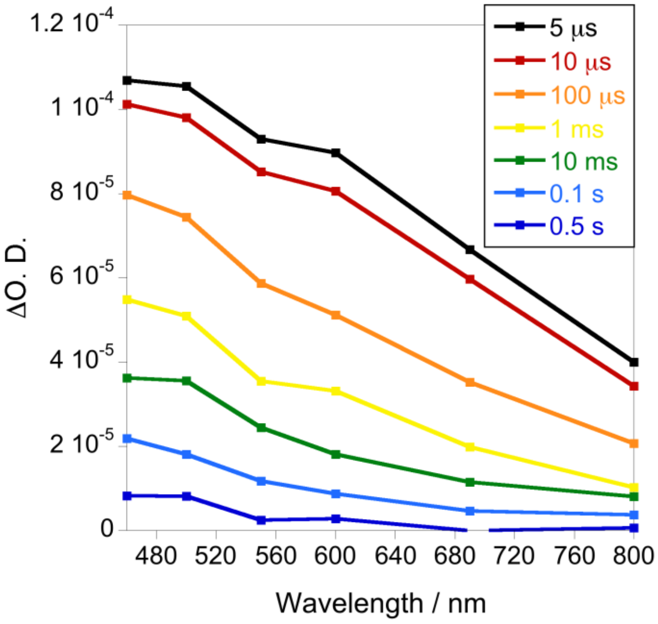

Fig. S1 Transient absorption spectra of **CoP**/TiO_2 films measured in water under N_2. The data was collected with a time delay of 5 µs - 0.5 s, after band gap excitation (λ_{ex} = 355 nm, 350 µJ/cm²). The maximum signal amplitude at 460 nm of **CoP**/TiO_2 films is assigned to the absorption of photoholes in TiO_2.

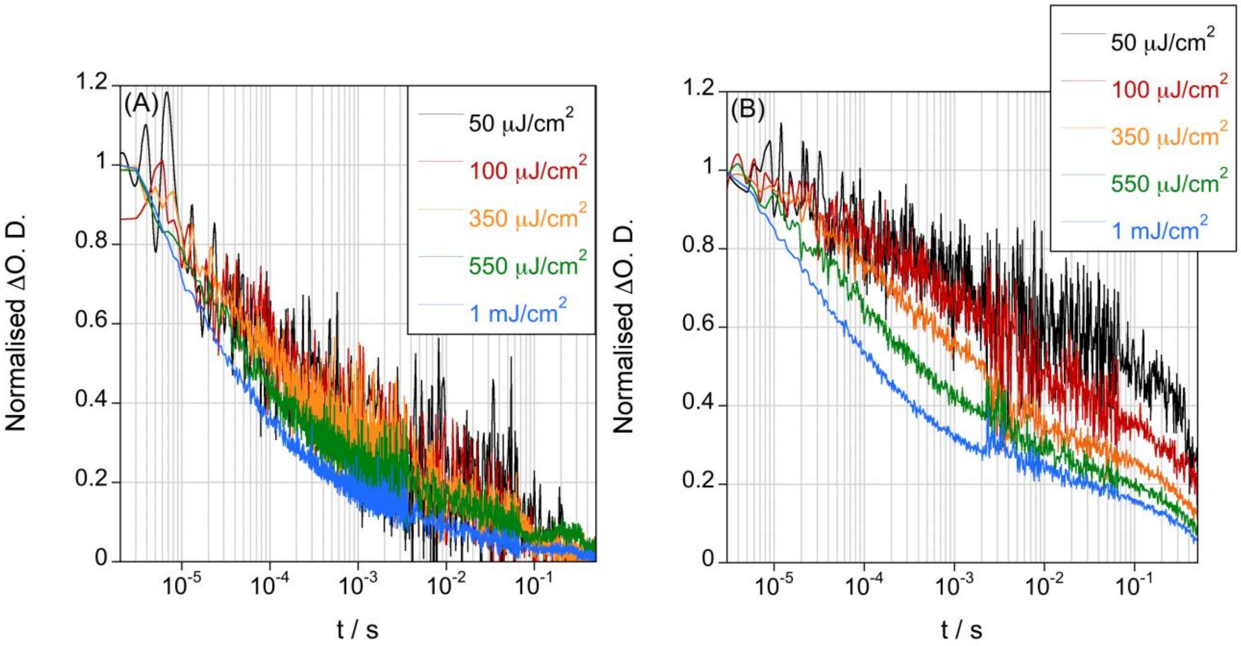

Fig. S2 Normalised transient absorption decays of photoexcited electrons (A) and holes (B) of a **CoP**/TiO_2 film in water under N_2 after band gap excitation (λ_{ex} = 355 nm) with different laser pulse intensities, ranging from 50 µJ/cm² to 1 mJ/cm².

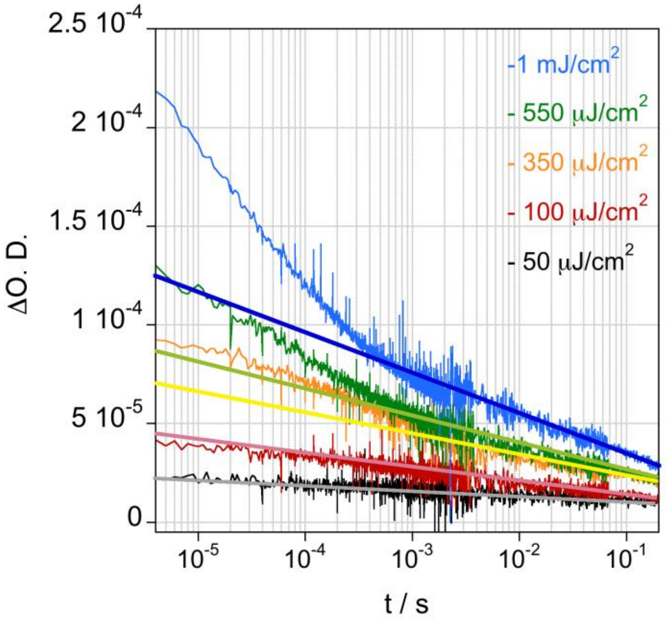

Fig. S3 Transient absorption signal amplitude of TiO_2 h^+ that remain in the conduction band and the estimated signal amplitude of h^+ recombining with e^- in TiO_2/**CoP** films, measured at different laser intensities (50 μJ/cm^2 – 1 mJ/cm^2). The TAS signal corresponding to charge recombination in the semiconductor was estimated as the difference between the signal amplitude of holes at 5 μs and the extrapolation the slow phase signal of photoholes. The films were measured in water under N_2 after band gap excitation (λ_{ex} = 350 nm, λ_{probe} = 460 nm).

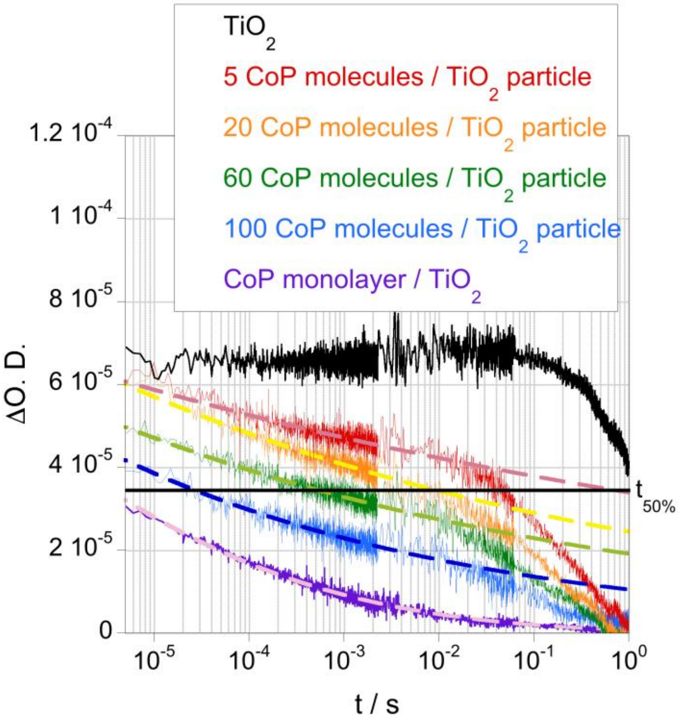

Fig. S4 Transient absorption decays corresponding to TiO_2 photoexcited electrons in bare TiO_2 and TiO_2-functionalized films with different quantities of **CoP** under N_2 and in the presence of a 0.1 M TEOA aqueous solution at pH 7 as sacrificial electron donor (λ_{ex} = 355 nm, λ_{probe} = 900 nm, E_{ex} = 350 μJ/cm^2). The fast phase of the decays was extrapolated to calculate the half lifetime of the electron transfer reaction. $t_{50\%}$ was calculated considering that the maximum electron density in TiO_2 was achieved when no **CoP** was anchored onto the surface.

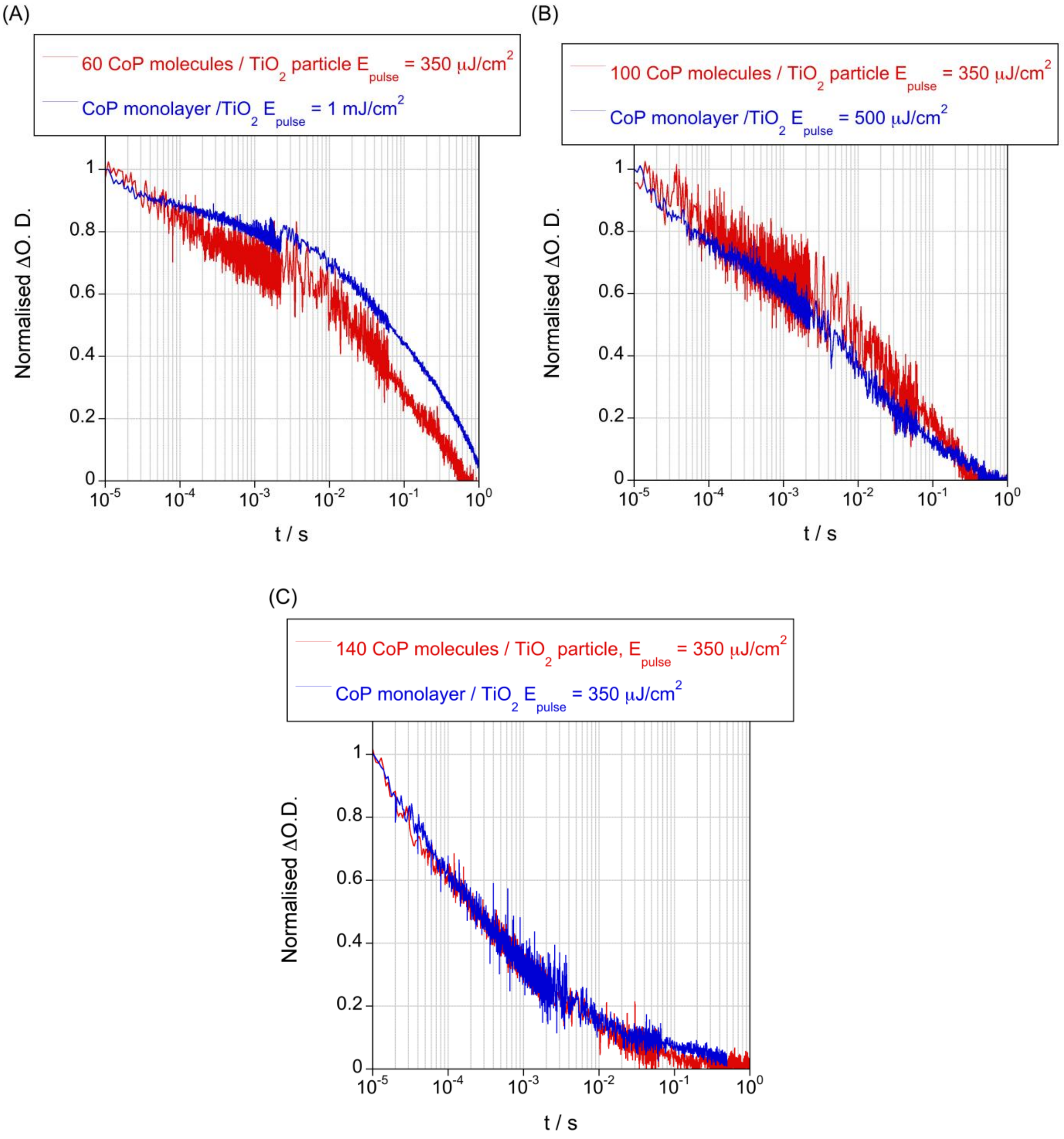

Fig. S5 Normalised transient absorption decays corresponding to photoexcited electrons TiO_2 films functionalized with different quantities of **CoP** and using different excitation densities, measured under the same electron/**CoP** ratio per TiO_2 particle (A: 0.1 e$^-$/**CoP** molecule, B: 0.05 e$^-$/**CoP** molecule, C: 0.035 e$^-$/**CoP** molecule). The blue traces were measured with TiO_2/**CoP** films containing a monolayer of catalyst and varying the excitation laser intensity (1 mJ/cm^2 (A), 500 μJ/cm^2 (B) and 350 μJ/cm^2 (C)), while the red traces were measured at the same laser intensity (350 μJ/cm^2) and modifying the **CoP** coverage (60 **CoP** molecules /TiO_2 particle (A), 100 **CoP** molecules/TiO_2 particle (B) and 140 **CoP** molecules/TiO_2 particle (C)). The films were measured under N_2 and in the presence of a 0.1 M TEOA aqueous solution buffered at pH 7 as sacrificial electron donor (λ_{ex} = 355 nm, λ_{probe} = 900 nm).

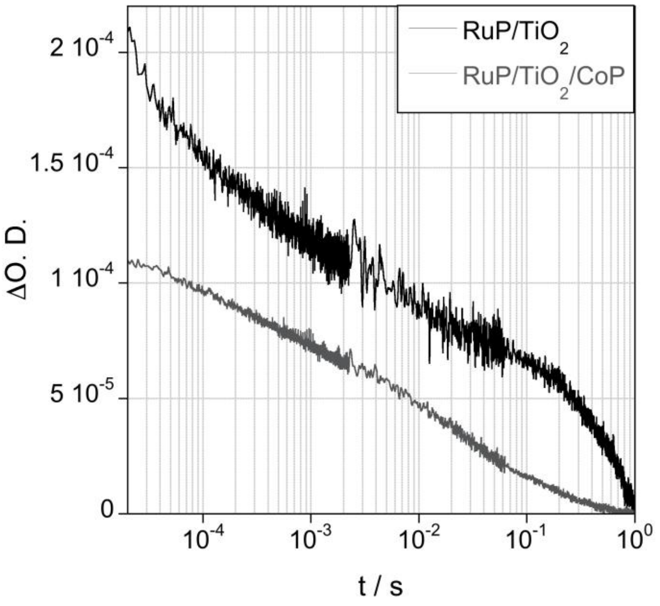

Fig. S6 Transient absorption decays of TiO_2 films functionalized with **RuP** with/without **CoP**, in the presence of a 0.1 M TEOA aqueous solution buffered at pH 7 (λ_{ex} = 450 nm, λ_{probe} = 700 nm).

Calculations using Marcus Theory:

The electron transfer kinetics between TiO_2 and a molecular catalyst are expected to be strongly influenced by their thermodynamic properties. Markus theory predicts the electron transfer rate between a donor and an acceptor using the following equation:

$$k_{et} = \frac{H_{AB}^2}{\sqrt{4\pi k_{BT}}} e^{\left(-\frac{(\Delta G^0-\lambda)^2}{4\lambda}\right)} \qquad (1)$$

where $H_{AB}{}^2$ is the electronic coupling between the donor and acceptor states, k_{BT} is the Boltzmann constant, ΔG^0 is the free energy of the reaction and λ is the reorganization energy. The calculation of the ΔG^0 and λ parameters have already been employed in the field of dye sensitized solar cells to improve the molecular structure of the photosensitizers, in order to reduce the recombination reaction between photo-injected electrons into the TiO_2 and the oxidized dye.[1,2] Since the reduction potential of the molecular catalysts anchored onto TiO_2 affect at the driving force (ΔG^0) of the electron transfer reaction, we propose that the Marcus theory can also be used to optimize the molecular design of the catalysts.

For the conditions used in our experiments, the TiO_2 conduction band -0.56 eV vs NHE,[2,3] and the reduction potentials of **CoP** are -0.15 eV and -0.55 eV vs NHE for the first and second electron reduction, respectively. Thus, results in a free energy value ($-\Delta G^0$) of 0.41 eV for the first electron transfer to the molecular catalyst, and 0.01 eV for the second electron transfer. Assuming a λ of 1.0 eV.[4] The two electron transfers from the semiconductor to **CoP** takes place in the Marcus normal region ($\lambda > -\Delta G^0$), with the second reduction reaction being 5 orders of magnitude slower than the first electron transfer.

Additional references:

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