

Supporting information

Distance dependent charge separation and recombination in semiconductor / molecular catalyst systems for water splitting

Anna Reynal,^a Janina Willkomm,^b Nicoleta M. Muresan,^b Fezile Lakadamyali,^b Miquel Planells,^a Erwin Reisner,^b and James. R. Durrant^a

^a Department of Chemistry, Imperial College London, Exhibition Road, London SW7 2AZ, UK.

^b Christian Doppler Laboratory for Sustainable SynGas Chemistry, Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, UK.

Contents	Page
Experimental details	S1
Figures S1-S5	S2
Table S1-S3	S7
Additional references	S7

EXPERIMENTAL DETAILS

Synthesis

Chemicals were purchased from commercial suppliers from the highest purity available and used without further purification.

(Et₃NH)[Co^{III}Cl(dimethylglyoxime)₂(pyridyl-4-hydrophosphonate) (**Co1**), [Co^{III}Br((DO)(DOH)(4-BnPO₃H₂)(2-CH₂py)-pn)]Br (**Co2**) and [Co^{III}Br₂((DO)(DOH)(4-BnPO₃H₂)₂-pn)] (**Co3**), were prepared as described previously.^[S1-S3]

Anatase TiO₂ films were deposited onto microscope or fluorine-doped tin oxide (FTO) coated glass by the Doctor blading technique from their respective colloidal pastes and calcined in a furnace at 450 °C for 30 min. The anatase TiO₂ paste was prepared as described in the literature.^[S4] The films employed herein have an area of 1 cm x 1.5 cm and a thickness of 4 μm, determined by profilometry.

TiO₂ films loaded with a monolayer of catalyst were prepared by dipping the films into a 10⁻⁴ M catalyst aqueous solution for 12 h, at r.t. and in the dark to avoid degradation. The films were rinsed with distilled water to remove the excess of molecules not anchored onto TiO₂ prior to measurement.

Transient absorption spectroscopy measurements

The microsecond-second transient absorption decays were measured using a Nd:YAG laser (Big Sky Laser Technologies Ultra CFR Nd:YAG laser system, 6 ns pulse width). The third harmonic of the laser, corresponding to 355 nm, at a frequency of 1 Hz, was used as excitation pulse. Typical excitation densities of 350 - 500 μJ/cm² were used. A liquid light guide with a diameter of 0.5 cm was used to transmit the laser pulse to the sample. The probe light source was a tungsten lamp (Bentham IL1 tungsten lamp), and the probing wavelength was selected by using a monochromator (OBB-2001 dual grating, Photon Technology International) placed prior to the sample. Transient absorption data was collected with a Si photodiode (Hamamatsu S3071). The information was passed through an amplifier box (Costronics) and recorded using a Tektronics TDS 2012c oscilloscope (microsecond to millisecond timescale) and a National Instruments (NI USB-6211) DAQ card (millisecond to second timescale). The decays observed are the average between 500 and 1000 averages laser pulses. The data was processed using home-built software based on Labview.

Transient absorption experiments were measured while submerging the catalyst-loaded TiO₂ films into N₂-purged aqueous solutions (with or without 0.1 M TEOA buffered at pH 7).

Definition of t_{50%}

t_{50%} is defined as the time required for the signal amplitude (ΔO. D.) to decrease half of its initial value (full width half maximum). A detailed description of the calculation of t_{50%} for the direct electron transfer and the recombination reaction is provided in the figure captions of Figure S2 and S4, respectively.

Density functional theory (DFT) calculations

The molecular structures were optimised in vacuum without any symmetry constrains, using the crystal structure provided as starting point geometry when available. The presence of local minimum was confirmed by the absence of imaginary frequencies. All calculations were carried out using the Gaussian 09 program^[S5] with the Becke three parameter hybrid exchange, Lee Yang-Parr correlation functional (B3LYP). All atoms were described by the 6-311G(d) basis set. All structures were input and processed through the Avogadro software package.^[S6]

Calculation of the amount of catalyst loaded onto TiO₂

The number of catalyst molecules loaded per TiO₂ particle was estimated by UV-visible absorption spectroscopy (Perkin Elmer Lambda 35 UV/Vis spectrophotometre) after desorbing the catalyst from the nanoparticles by dipping a catalyst-loaded TiO₂ film (thickness: 4 μm, area: 1 cm²) into a 0.1 M NaOH solution and comparing the absorption spectra with that of a solution containing a known amount of the cobalt catalysts.

The number of catalyst molecules attached onto a TiO₂ film was found to be 3.3 x 10¹⁶ for Co1, 3.9 x 10¹⁶ for Co2 and 4.0 x 10¹⁶ for Co3.

We have calculated the number of TiO₂ nanoparticles in a film, taking into account their volume.

Volume of 1 nanoparticle: $V_{part} = \frac{4}{3} \cdot \pi \cdot R^3 = \frac{4}{3} \cdot \pi \cdot (10 \times 10^{-9})^3 = 4.2 \times 10^{-24} m^3$, where V_{part} corresponds to the volume of the nanoparticle (m³) and R is the radius of the nanoparticle (m).

Volume of the film: $V_{film} = A_{film} \cdot L_{film} \cdot (1 - P_{film}) = 10^{-4} m^2 \cdot 4 \times 10^{-6} m \cdot (1 - 0.6) = 1.6 \times 10^{-10} m^3$, where A_{film} is the area of the film (m²), L_{film} is the thickness of the film (m) and P_{film} corresponds to the film porosity (60%)^{S7}.

The number of nanoparticles in a film was calculated as: $\#_{part} = \frac{V_{film}}{V_{part}} = \frac{1.6 \times 10^{-10}}{4.2 \times 10^{-24}} = 3.8 \times 10^{13} TiO_2 \text{ nanoparticles/film}$.

Thus, the number of cobalt molecules per TiO₂ particle was found to be approximately 900 for Co1, 1000 for Co2 and 1050 for Co3.

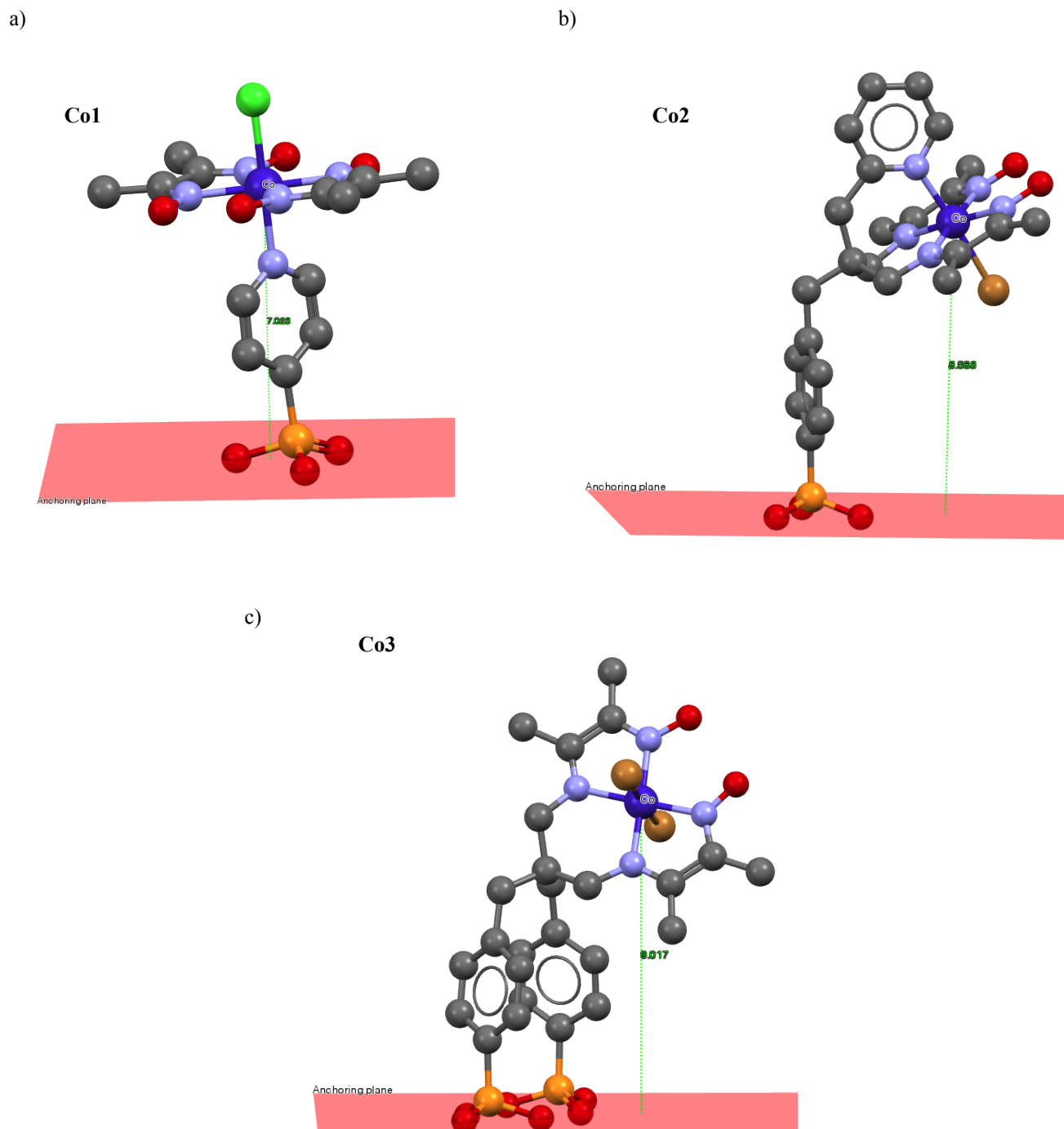


Figure S1. Graphical representation optimised geometries obtained by DFT means at B3LYP/6-311G(d) level of theory of (a) **Co1**, (b) **Co2** and (c) **Co3**. Distances were calculated from the cobalt metal centre to the anchoring plane formed by the three oxygen atoms in the phosphonic acid group using Mercury software package.

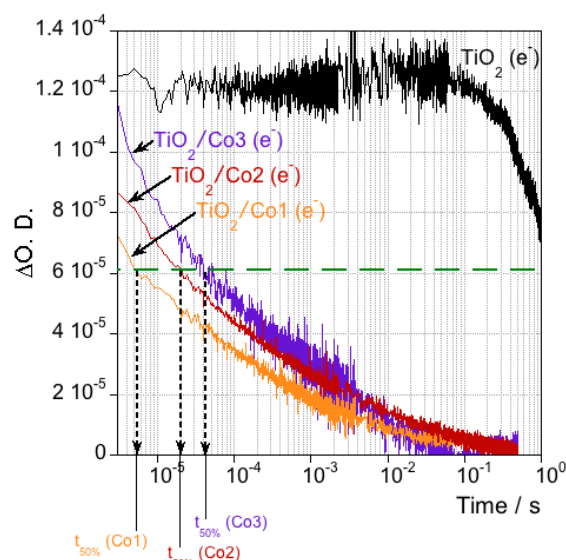


Figure S2. Transient absorption decays corresponding to photoexcited electrons in the TiO_2 for bare films (black trace), and when functionalised with **Co1** (orange trace), **Co2** (red trace) and **Co3** (purple trace), measured in the presence of TEOA (0.1 M, buffered at pH 7) as hole scavenger. **Calculation of $t_{50\%}$ for the direct electron transfer:** $t_{50\%}$ in TiO_2 films functionalised with the cobalt catalyst has been calculated by taking time values when $\Delta\text{O. D.}$ is half of that observed in TiO_2 films in the presence of TEOA as hole scavenger (green slashed line), by considering that the maximum electron density in TiO_2 is achieved when no catalyst is attached onto the surface. Note that light scatter limitations prevented data collection for time delays $< 5 \mu\text{s}$, half times were determined using the unfunctionalised TiO_2 as reference.

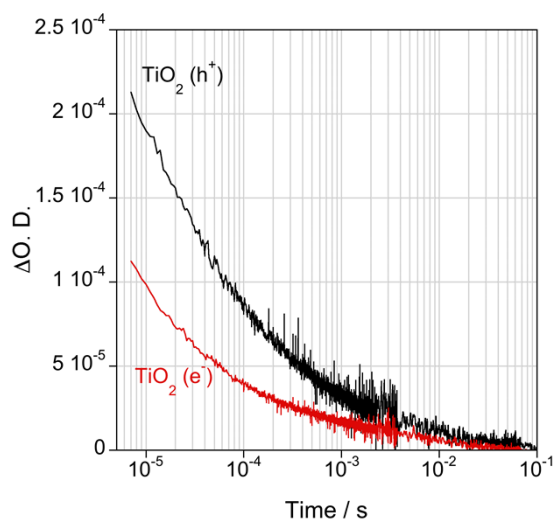


Figure S3. Transient absorption decays corresponding to photoexcited electrons (red trace) and holes (black trace) in a bare TiO_2 film, measured under N_2 purged water in the absence of hole scavenger. The excitation wavelength was 355 nm ($350 \mu\text{J cm}^{-2}$, 1Hz) and the probing wavelengths were 900 nm for electrons and 460 nm for holes.

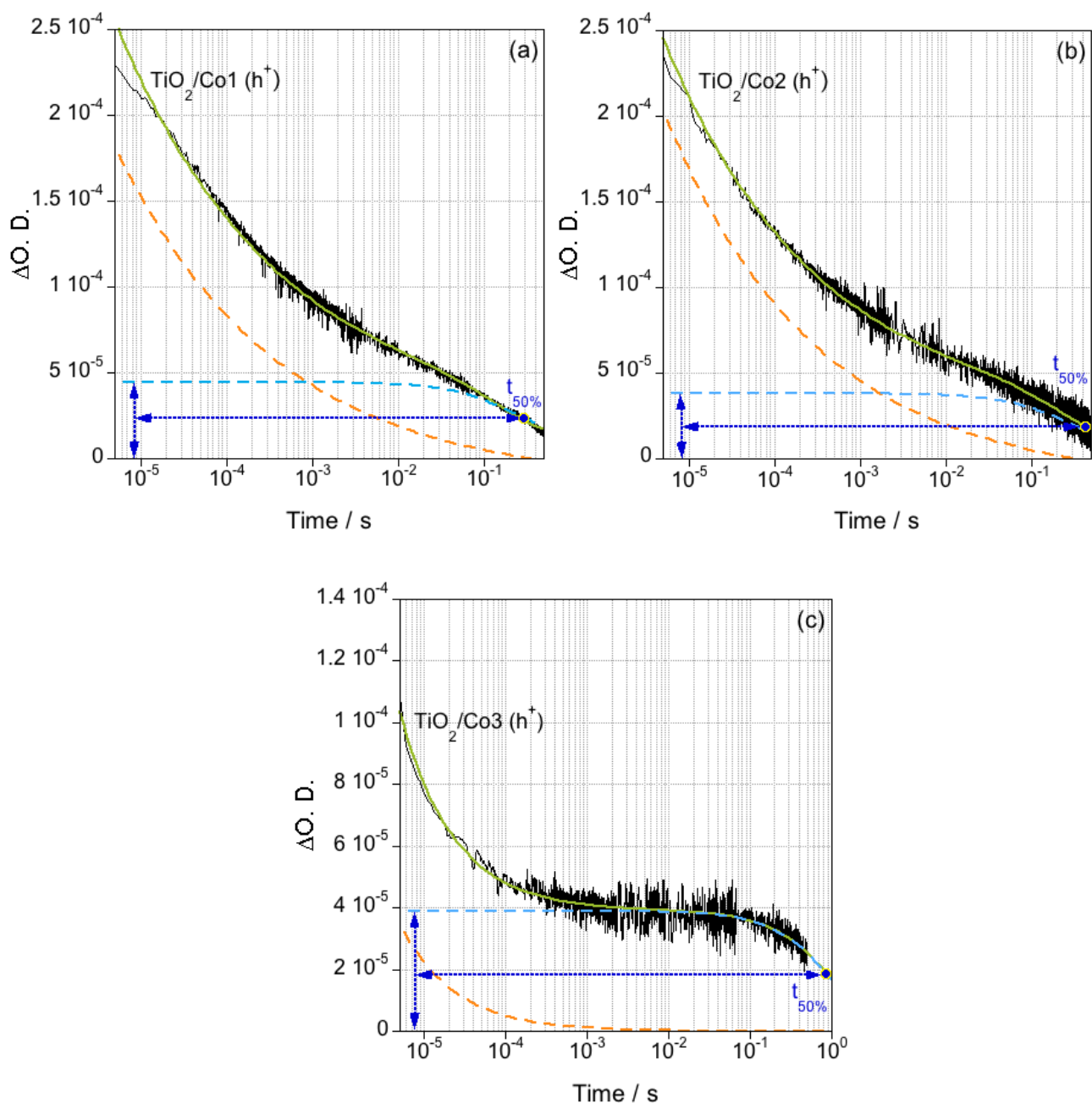


Figure S4. Transient absorption decays of TiO_2 functionalised with (a) Co1, (b) Co2 and (c) Co3, measured in N_2 purged water. The red traces correspond to phototexcited electrons ($\lambda_{\text{probe}} = 900 \text{ nm}$), while the black traces are assigned to holes ($\lambda_{\text{probe}} = 460 \text{ nm}$). The samples were excited at 355 nm with a laser intensity of $500 \mu\text{J}/\text{cm}^2$. The decay of photoexcited holes was fitted by a combination of a power law equation ($\Delta\text{O.D.} \propto t^{-\alpha}$, $\alpha(\text{Co1}) \approx 0.23$, $\alpha(\text{Co2}) \approx 0.24$, $\alpha(\text{Co3}) \approx 0.6$; orange slashed line) and a mono exponential equation (blue slashed trace). **Calculation of $t_{50\%}$ for the electron recombination:** $t_{50\%}$ of the recombination reaction was calculated by taking time values when $\Delta\text{O.D.}$ is half of that of the initial amplitude of the mono exponential fitting, assigned to the recombination of long-lived holes in the semiconductor with electrons transferred to the catalyst.

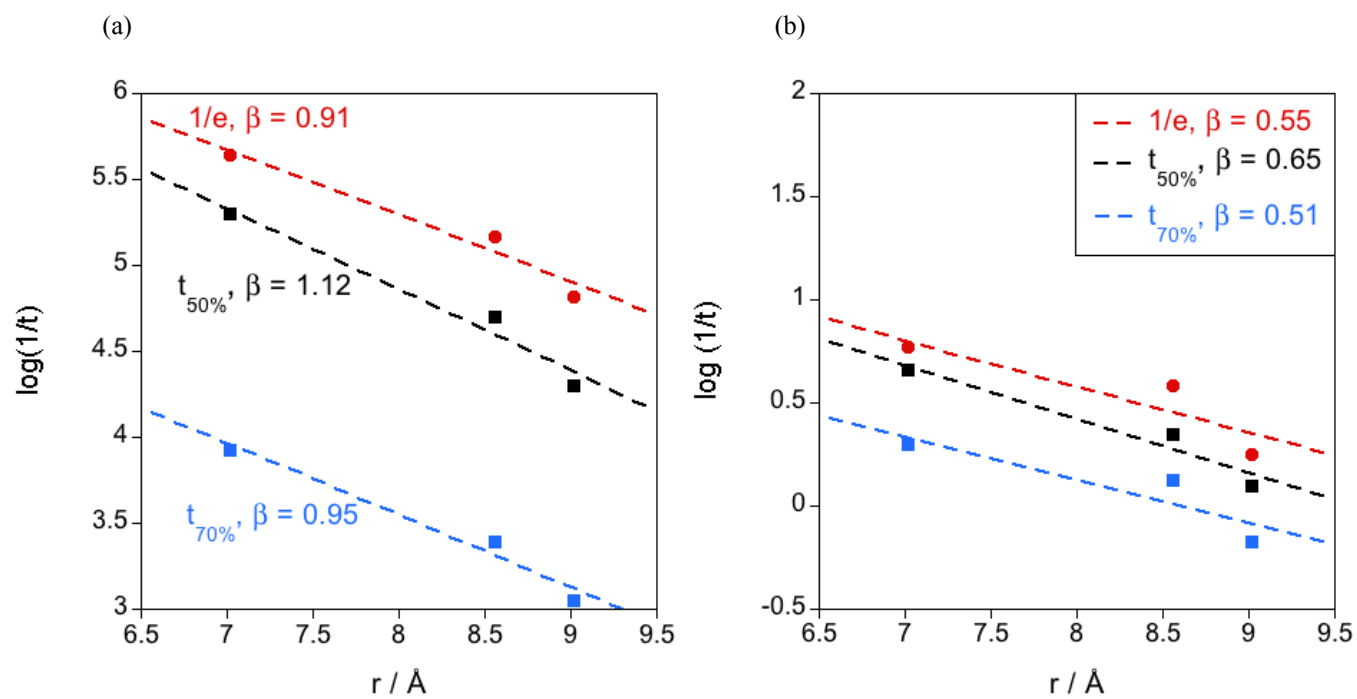


Figure S5. Comparison of the electron transfer kinetics when employing $1/e$ (red trace), $t_{50\%}$ (black trace) and $t_{70\%}$ (blue trace) of (a) the direct electron transfer, and (b) the recombination reaction between the singly reduced molecular catalyst and the TiO_2 .

Table S1: Comparison of the electron transfer kinetics from TiO₂ to the molecular catalysts by using 1/e, t_{50%} and t_{70%}.

	Co1	Co2	Co3	β_{direct}
1/e	2.3 x 10 ⁻⁶ s	6.8 x 10 ⁻⁶ s	1.5 x 10 ⁻⁵ s	0.91
t _{50%}	5.0 x 10 ⁻⁶ s	2.1 x 10 ⁻⁵ s	4.7x10 ⁻⁵ s	1.12
t _{70%}	1.2 x 10 ⁻⁴ s	4.0 x 10 ⁻⁴ s	8.9 x 10 ⁻⁴ s	0.95

Table S2: Comparison of the kinetics of the recombination reaction between the singly reduced molecular catalysts and the holes accumulated at the valence band of TiO₂ by using 1/e, t_{50%} and t_{70%}.

	Co1	Co2	Co3	$\beta_{\text{recombination}}$
1/e	0.17	0.26	0.56	0.55
t _{50%}	0.22	0.45	0.8	0.65
t _{70%}	0.5	0.75	1.5	0.51

Table S3. Reduction potentials for the molecular catalysts and free Gibbs energy for the direct electron transfer from the semiconductor to the molecular catalyst, and the recombination reaction between the reduced catalyst and the semiconductor, represented in V vs NHE.

	Co1	Co2	Co3
E _{p/2} (Co ^{III/II}) / V vs NHE ^a	0.00	0.04	0.22
E _{p/2} (Co ^{II/I}) / V vs NHE ^a	-0.56	-0.49	-0.52
ΔG^0 (direct electron transfer) / eV ^b	0.6	0.64	0.82
ΔG^0 (recombination) / eV ^c	2.6	2.56	2.38

^aValues were determined from cyclic voltammograms recorded in TEOA/NaSO₄ electrolyte (0.1 M each, pH 7) using a glassy carbon working electrode at 100 mV s⁻¹ and 25 °C. ^bDifference in energy between the conduction band of TiO₂ and the first reduction potential of the catalyst (Co^{III}/Co^{II}), assuming a TiO₂ conduction band at pH 7 of -0.6 V vs NHE.^[S8, S9] ^cDifference in energy between the first reduction potential of the catalyst (Co^{III}/Co^{II}) and the valence band of the semiconductor (TiO₂ valence band being at 2.6 V vs NHE).

Additional references

- [S1] F. Lakadamyali, E. Reisner, *Chem. Commun.* **2011**, 47, 1695.
- [S2] N. M. Muresan, J. Willkomm, D. Mersch, Y. Vaynzof, E. Reisner, *Angew. Chem. Int. Ed.* **2012**, 51, 12749.
- [S3] J. Willkomm, E. Reisner, *in preparation*.
- [S4] S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin, M. Gratzel, *Thin Solid Films*, **2008**, 5156, 4613.
- [S5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision B.01*; Gaussian Inc, Wallingford CT. **2009**.
- [S6] M. D. Hanwell *et al.* *J. Cheminform.* **2012**, 4, 17.
- [S7] M. Grätzel, *J. Photochem. Photobiol. C*, **2003**, 4, 145.
- [S8] G. Rothenberger, D. Fitzmaurice, M. Gratzel, *J. Phys. Chem.* **1992**, 96, 5983.
- [S9] B. Enright, G. Redmont, D. Fitzmaurice, *J. Phys. Chem.* **1994**, 98, 6195.