Supporting Information

Photoinduced Catalysis of Redox Reactions. Turnover Numbers, Turnover Frequency and Limiting Processes: Kinetic Analysis and Application to Light-Driven Hydrogen Production.

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1. Derivation of equations

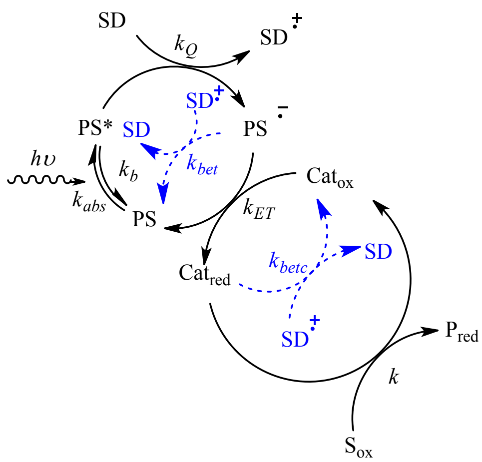
1.1. Ideal system

We consider a simple kinetic scheme for a photocatalytic process with reductive quenching including a photosensitizer (PS), a sacrificial donor (SD), a catalyst (Cat_{ox} and Cat_{red}) and a substrate (S_{ox}) leading the product (P_{red}) (Scheme S1).

We make the following simplification assumptions:

- SD is in excess so that its concentrations remain constant throughout the experiment.
- S_{ox} is in excess so that its concentrations remain constant throughout the experiment.
- No back reaction between the final product and the oxidized sacrificial donor.
- The irradiation is constant so that the excitation of PS can be described as a pseudo-first order process with a rate constant k_{abs}.
- All intermediate are at steady-state which implies that the rate determining step is the quenching process.

Scheme S1



Kinetic equations:

$$\frac{d\left[\mathrm{P_{red}}\right]}{dt} = k\left[\mathrm{S_{ox}}\right]\left[\mathrm{Cat_{red}}\right]$$

and

$$\frac{d\left[\mathrm{Cat_{red}}\right]}{dt} = k_{ET}\left[\mathrm{PS^{\bullet-}}\right]\left[\mathrm{Cat_{ox}}\right] - k\left[\mathrm{S_{ox}}\right]\left[\mathrm{Cat_{red}}\right] - k_{betc}\left[\mathrm{SD^{\bullet+}}\right]\left[\mathrm{Cat_{red}}\right] \approx 0$$

$$\frac{d\left[\mathrm{PS^{\bullet-}}\right]}{dt} = k_Q\left[\mathrm{PS^{*}}\right]\left[\mathrm{SD}\right]_0 - \left(k_{ET}\left[\mathrm{Cat_{ox}}\right] + k_{bet}\left[\mathrm{SD^{\bullet+}}\right]\right)\left[\mathrm{PS^{\bullet-}}\right] \approx 0$$

$$\frac{d\left[\mathrm{PS^{*}}\right]}{dt} = k_{abs}\left[\mathrm{PS}\right] - k_b\left[\mathrm{PS^{*}}\right] - k_Q\left[\mathrm{PS^{*}}\right]\left[\mathrm{SD}\right]_0 \approx 0$$

$$\frac{d\left[\mathrm{SD^{\bullet+}}\right]}{dt} = k_Q\left[\mathrm{PS^{*}}\right]\left[\mathrm{SD}\right]_0 - k_{bet}\left[\mathrm{SD^{\bullet+}}\right]\left[\mathrm{PS^{\bullet-}}\right] - k_{betc}\left[\mathrm{SD^{\bullet+}}\right]\left[\mathrm{Cat_{red}}\right]$$

Resolution

Because $\mathrm{Cat_{red}}$ is at steady state, it does not accumulate and $\left[\mathrm{Cat_{ox}}\right]_0 \approx \left[\mathrm{Cat_{ox}}\right]$ and the steady-state approximations lead to:

$$\left[\mathrm{PS^{*}}\right] = \frac{k_{abs}}{k_b + k_Q\left[\mathrm{SD}\right]_0}\left[\mathrm{PS}\right]$$

and

$$\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)}\left[\mathrm{PS}^*\right]=\left[\mathrm{PS}^{\bullet-}\right]$$

Therefore:

$$\left[\mathrm{PS}^{\bullet-}\right]=\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

with

$$[\mathrm{PS}]_0=[\mathrm{PS}]+\left[\mathrm{PS}^*\right]+\left[\mathrm{PS}^{\bullet-}\right]$$

Thus:

$$[\mathrm{PS}]=\frac{[\mathrm{PS}]_0}{\left(1+\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}+\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}$$

We also have:

$$\left[\mathrm{Cat_{red}}\right]=k_{ET}\left[\mathrm{PS}^{\bullet-}\right]\frac{\left[\mathrm{Cat_{ox}}\right]}{k\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\approx\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$ leading

to:

$$\frac{d\left[\mathrm{P_{red}}\right]}{dt}=\frac{k\left[\mathrm{S_{ox}}\right]}{k\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\frac{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0\frac{k_Q[\mathrm{SD}]_0}{k_b+k_Q[\mathrm{SD}]_0}\right)[\mathrm{PS}]_0}{\left(\frac{1}{k_{abs}}+\frac{1}{k_b+k_Q[\mathrm{SD}]_0}\right)\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)+\frac{k_Q[\mathrm{SD}]_0}{k_b+k_Q[\mathrm{SD}]_0}}$$

Now we need to get $\left[\mathrm{SD}^{\bullet+}\right]_t$

We have:

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=k_Q\left[\mathrm{PS}^*\right][\mathrm{SD}]_0-k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{PS}^{\bullet-}\right]-k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{Cat_{red}}\right]$$

Combined with $\frac{d\left[\mathrm{PS}^{\bullet-}\right]}{dt}=k_Q\left[\mathrm{PS}^*\right][\mathrm{SD}]_0-\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)\left[\mathrm{PS}^{\bullet-}\right]\approx 0$

We obtain:

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=k_{ET}\left[\mathrm{Cat_{ox}}\right]\left[\mathrm{PS}^{\bullet-}\right]-k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{Cat_{red}}\right]$$

Combined with:

$$\frac{d\left[\mathrm{Cat_{red}}\right]}{dt}=k_{ET}\left[\mathrm{PS}^{\bullet-}\right]\left[\mathrm{Cat_{ox}}\right]-k\left[\mathrm{S_{ox}}\right]\left[\mathrm{Cat_{red}}\right]-k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{Cat_{red}}\right]\approx 0$$

We obtain:

$$\frac{d\left[SD^{\bullet+}\right]}{dt} = k\left[S_{ox}\right]\left[Cat_{red}\right]$$

therefore: $\frac{d\left[SD^{\bullet+}\right]}{dt} = \frac{d\left[P_{red}\right]}{dt}$ and hence $\left[SD^{\bullet+}\right]_t = \left[P_{red}\right]_t$ because $\left[SD^{\bullet+}\right]_0 = \left[P_{red}\right]_0 = 0$

thus:

$$\frac{d\left[SD^{\bullet+}\right]}{dt} = \frac{k\left[S_{ox}\right]}{k\left[S_{ox}\right]+k_{betc}\left[SD^{\bullet+}\right]} \frac{\left(\frac{k_{ET}\left[Cat_{ox}\right]_0}{\left(k_{ET}\left[Cat_{ox}\right]_0+k_{bet}\left[SD^{\bullet+}\right]\right)} \frac{k_Q[SD]_0}{k_b+k_Q[SD]_0}\right)[PS]_0}{\left(\frac{1}{k_{abs}}+\frac{1}{k_b+k_Q[SD]_0}+\frac{1}{\left(k_{ET}\left[Cat_{ox}\right]_0+k_{bet}\left[SD^{\bullet+}\right]\right)} \frac{k_Q[SD]_0}{k_b+k_Q[SD]_0}\right)} \text{ thus:}$$

Which can be rearranged to:

$$\left[\begin{array}{l} 1+\left(\frac{k_{betc}}{k\left[S_{ox}\right]}+\frac{\left(1+\frac{k_{abs}}{k_b+k_Q[SD]_0}\right)}{k_{ET}\left[Cat_{ox}\right]_0+k_{abs}\frac{k_{ET}\left[Cat_{ox}\right]_0+k_Q[SD]_0}{k_b+k_Q[SD]_0}} k_{bet}\right)\left[SD^{\bullet+}\right] \\ +\frac{k_{betc}}{k\left[S_{ox}\right]} \frac{\left(1+\frac{k_{abs}}{k_b+k_Q[SD]_0}\right)}{k_{ET}\left[Cat_{ox}\right]_0+k_{abs}\frac{k_{ET}\left[Cat_{ox}\right]_0+k_Q[SD]_0}{k_b+k_Q[SD]_0}} k_{bet}\left[SD^{\bullet+}\right]^2 \end{array}\right] d\left[SD^{\bullet+}\right] = \frac{k_{ET}\left[Cat_{ox}\right]_0 \frac{k_Q[SD]_0}{k_b+k_Q[SD]_0} k_{abs}[PS]_0}{k_{ET}\left[Cat_{ox}\right]_0+k_{abs}\frac{k_{ET}\left[Cat_{ox}\right]_0+k_Q[SD]_0}{k_b+k_Q[SD]_0}} dt$$

which integration gives:

$$\left[SD^{\bullet+}\right]+\left(\frac{k_{betc}}{k\left[S_{ox}\right]}+\frac{\left(1+\frac{k_{abs}}{k_b+k_Q[SD]_0}\right)k_{bet}}{k_{ET}\left[Cat_{ox}\right]_0+k_{abs}\frac{k_{ET}\left[Cat_{ox}\right]_0+k_Q[SD]_0}{k_b+k_Q[SD]_0}}\right)\frac{\left[SD^{\bullet+}\right]^2}{2}$$

$$+\frac{k_{betc}}{k\left[S_{ox}\right]}\left(\frac{\left(1+\frac{k_{abs}}{k_b+k_Q[SD]_0}\right)}{k_{ET}\left[Cat_{ox}\right]_0+k_{abs}\frac{k_{ET}\left[Cat_{ox}\right]_0+k_Q[SD]_0}{k_b+k_Q[SD]_0}} k_{bet}\right)\frac{\left[SD^{\bullet+}\right]^3}{3}$$

$$=\frac{k_{ET}\left[Cat_{ox}\right]_0 \frac{k_Q[SD]_0}{k_b+k_Q[SD]_0} k_{abs}[PS]_0}{k_{ET}\left[Cat_{ox}\right]_0+k_{abs}\frac{k_{ET}\left[Cat_{ox}\right]_0+k_Q[SD]_0}{k_b+k_Q[SD]_0}} \times t$$

Recalling that $\left[P_{red}\right]_t = \left[SD^{\bullet+}\right]_t$, we finally obtain the turnover number $TON_{cat} = \frac{\left[P_{red}\right]}{\left[Cat_{ox}\right]_0}$

$$TON_{cat} + \left(\frac{k_{betc}\left[\mathrm{Cat_{ox}}\right]_0}{k\left[\mathrm{S_{ox}}\right]} + \frac{\left(1+\frac{k_{abs}}{k_b + k_Q[\mathrm{SD}]_0}\right) k_{bet}\left[\mathrm{Cat_{ox}}\right]_0}{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0 + k_{abs}\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0 + k_Q[\mathrm{SD}]_0}{k_b + k_Q[\mathrm{SD}]_0}} \right) \frac{(TON_{cat})^2}{2}$$

$$+ \frac{k_{betc}\left[\mathrm{Cat_{ox}}\right]_0}{k\left[\mathrm{S_{ox}}\right]} \left(\frac{\left(1+\frac{k_{abs}}{k_b + k_Q[\mathrm{SD}]_0}\right) k_{bet}\left[\mathrm{Cat_{ox}}\right]_0}{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0 + k_{abs}\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0 + k_Q[\mathrm{SD}]_0}{k_b + k_Q[\mathrm{SD}]_0}} \right) \frac{(TON_{cat})^3}{3}$$

$$= \frac{k_{ET}\frac{k_Q[\mathrm{SD}]_0}{k_b + k_Q[\mathrm{SD}]_0} k_{abs}[\mathrm{PS}]_0}{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0 + k_{abs}\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0 + k_Q[\mathrm{SD}]_0}{k_b + k_Q[\mathrm{SD}]_0}} \times t$$

In most cases $\frac{k_{abs}}{k_b + k_Q[\mathrm{SD}]_0} \ll 1$, thus:

$$TON_{cat} + \left(\frac{k_{betc}\left[\mathrm{Cat_{ox}}\right]_0}{k\left[\mathrm{S_{ox}}\right]} + \frac{k_{bet}\left[\mathrm{Cat_{ox}}\right]_0}{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0} \right) \frac{(TON_{cat})^2}{2} + \frac{k_{betc}\left[\mathrm{Cat_{ox}}\right]_0}{k\left[\mathrm{S_{ox}}\right]} \left(\frac{k_{bet}\left[\mathrm{Cat_{ox}}\right]_0}{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0} \right) \frac{(TON_{cat})^3}{3} = \frac{\frac{k_Q[\mathrm{SD}]_0}{k_b + k_Q[\mathrm{SD}]_0} k_{abs}[\mathrm{PS}]_0}{\left[\mathrm{Cat_{ox}}\right]_0} \times t$$

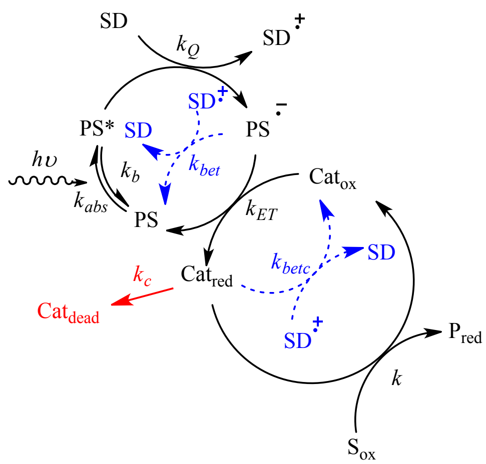
Thus, introducing: $TOF_{cat,0} = \gamma p_Q k_{abs}$ $\gamma = \frac{[\mathrm{PS}]_0}{\left[\mathrm{Cat_{ox}}\right]_0}$, $p_{bet} = \frac{k_{bet}}{k_{ET}}$, $p_{betc} = \frac{k_{betc}[\mathrm{PS}]_0}{k\left[\mathrm{S_{ox}}\right]_0}$ and $p_Q = \frac{k_Q[\mathrm{SD}]}{k_b + k_Q[\mathrm{SD}]}$, we obtain:

$$TON_{cat} + \left(p_{bet} + \frac{p_{betc}}{\gamma} \right) \frac{(TON_{cat})^2}{2} + p_{bet}\frac{p_{betc}}{\gamma}\frac{(TON_{cat})^3}{3} = \gamma p_Q k_{abs} \times t = TOF_{cat,0} \times t$$

1.2. Deactivation of the catalyst

The same system as in section 1.1. is considered (with similar assumptions) excepted that the reduced form of the catalyst can now irreversibly degrades via a first order process (Scheme S2).

Scheme S2



Kinetic equations:

$$\frac{d\left[\mathrm{P_{red}}\right]}{dt}=k\left[\mathrm{S_{ox}}\right]\left[\mathrm{Cat_{red}}\right]$$

and

$$\frac{d\left[\mathrm{Cat_{red}}\right]}{dt}=k_{ET}\left[\mathrm{PS}^{\bullet-}\right]\left[\mathrm{Cat_{ox}}\right]-\left(k\left[\mathrm{S_{ox}}\right]+k_c\right)\left[\mathrm{Cat_{red}}\right]-k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{Cat_{red}}\right]\approx 0$$

$$\frac{d\left[\mathrm{PS}^{\bullet-}\right]}{dt}=k_Q\left[\mathrm{PS}^*\right][\mathrm{SD}]_0-\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)\left[\mathrm{PS}^{\bullet-}\right]\approx 0$$

$$\frac{d\left[\mathrm{PS}^*\right]}{dt}=k_{abs}[\mathrm{PS}]-k_b\left[\mathrm{PS}^*\right]-k_Q\left[\mathrm{PS}^*\right][\mathrm{SD}]_0\approx 0$$

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=k_Q\left[\mathrm{PS}^*\right][\mathrm{SD}]_0-k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{PS}^{\bullet-}\right]-k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{Cat_{red}}\right]$$

$$\frac{d\left[\mathrm{Cat_{dead}}\right]}{dt}=k_c\left[\mathrm{Cat_{red}}\right]$$

Resolution:

The steady-state approximations lead to:

$$\left[\mathrm{PS}^*\right]=\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

and

$$\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)}\left[\mathrm{PS}^*\right]=\left[\mathrm{PS}^{\bullet-}\right]$$

Therefore:

$$\left[\mathrm{PS}^{\bullet-}\right]=\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

with

$$[\mathrm{PS}]_0=[\mathrm{PS}]+\left[\mathrm{PS}^*\right]+\left[\mathrm{PS}^{\bullet-}\right]$$

Thus:

$$[\mathrm{PS}]=\frac{[\mathrm{PS}]_0}{\left(1+\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}+\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}$$

We also have:

$$\left[\mathrm{Cat_{red}}\right]=k_{ET}\left[\mathrm{PS}^{\bullet-}\right]\frac{\left[\mathrm{Cat_{ox}}\right]}{k\left[\mathrm{S_{ox}}\right]+k_c+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\approx\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]}{k\left[\mathrm{S_{ox}}\right]+k_c+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

leading to:

$$\frac{d\left[\mathrm{P_{red}}\right]}{dt}=\frac{k\left[\mathrm{S_{ox}}\right]}{k\left[\mathrm{S_{ox}}\right]+k_c+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\frac{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]\frac{k_Q[\mathrm{SD}]_0}{k_b+k_Q[\mathrm{SD}]_0}\right)[\mathrm{PS}]_0}{\left(\frac{1}{k_{abs}}+\frac{1}{k_b+k_Q[\mathrm{SD}]_0}\right)\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)+\frac{k_Q[\mathrm{SD}]_0}{k_b+k_Q[\mathrm{SD}]_0}}$$

Now we need to get $\left[\mathrm{SD}^{\bullet+}\right]_t$ and $\left[\mathrm{Cat_{ox}}\right]_t$

We have:

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=k_Q\left[\mathrm{PS}^*\right][\mathrm{SD}]_0-k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{PS}^{\bullet-}\right]-k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{Cat_{red}}\right]$$

Combined with $\frac{d\left[\mathrm{PS}^{\bullet-}\right]}{dt}=k_Q\left[\mathrm{PS}^*\right][\mathrm{SD}]_0-\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)\left[\mathrm{PS}^{\bullet-}\right]\approx 0$

We obtain:

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=k_{ET}\left[\mathrm{Cat_{ox}}\right]\left[\mathrm{PS}^{\bullet-}\right]-k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{Cat_{red}}\right]$$

Combined with:

$$\frac{d\left[\mathrm{Cat_{red}}\right]}{dt}=k_{ET}\left[\mathrm{PS}^{\bullet-}\right]\left[\mathrm{Cat_{ox}}\right]-\left(k\left[\mathrm{S_{ox}}\right]+k_c\right)\left[\mathrm{Cat_{red}}\right]-k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{Cat_{red}}\right]\approx 0$$

We obtain:

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=\left(k\left[\mathrm{S_{ox}}\right]+k_c\right)\left[\mathrm{Cat_{red}}\right]$$

therefore: $\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=\left(\frac{k\left[\mathrm{S_{ox}}\right]+k_c}{k\left[\mathrm{S_{ox}}\right]}\right)\frac{d\left[\mathrm{P_{red}}\right]}{dt}$ and hence $\left[\mathrm{SD}^{\bullet+}\right]_t=\left(\frac{k\left[\mathrm{S_{ox}}\right]+k_c}{k\left[\mathrm{S_{ox}}\right]}\right)\left[\mathrm{P_{red}}\right]_t$ because $\left[\mathrm{SD}^{\bullet+}\right]_0=\left[\mathrm{P_{red}}\right]_0=0$

thus:

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=\frac{k\left[\mathrm{S_{ox}}\right]+k_c}{k\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\frac{\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)}\frac{k_Q[\mathrm{SD}]_0}{k_b+k_Q[\mathrm{SD}]_0}\right)[\mathrm{PS}]_0}{\left(\frac{1}{k_{abs}}+\frac{1}{k_b+k_Q[\mathrm{SD}]_0}+\frac{1}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)}\frac{k_Q[\mathrm{SD}]_0}{k_b+k_Q[\mathrm{SD}]_0}\right)}$$

We also have:

$\left[\mathrm{Cat_{red}}\right]+\left[\mathrm{Cat_{ox}}\right]+\left[\mathrm{Cat_{dead}}\right]=\left[\mathrm{Cat_{ox}}\right]_0$ and $\frac{d\left[\mathrm{Cat_{red}}\right]}{dt}=0$

Hence:

$$\frac{d\left[\mathrm{Cat_{ox}}\right]}{dt}=-\frac{d\left[\mathrm{Cat_{dead}}\right]}{dt}=-k_c\left[\mathrm{Cat_{red}}\right]$$

We end up with:

$$\frac{d\left[\mathrm{Cat_{ox}}\right]}{d\left[\mathrm{SD}^{\bullet+}\right]}=-\frac{k_c}{k\left[\mathrm{S_{ox}}\right]_0+k_c}$$

Thus: $\left[\mathrm{Cat_{ox}}\right]=\left[\mathrm{Cat_{ox}}\right]_0-\dfrac{k_c}{k\left[\mathrm{S_{ox}}\right]_0+k_c}\left[\mathrm{SD}^{\bullet+}\right]$

Hence, we just need to get $\left[\mathrm{SD}^{\bullet+}\right]_t$ via resolution of:

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=k_{abs}\frac{k\left[\mathrm{S_{ox}}\right]+k_c}{k\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\frac{\left\{\left[\mathrm{Cat_{ox}}\right]_0-\dfrac{k_c\left[\mathrm{SD}^{\bullet+}\right]}{k\left[\mathrm{S_{ox}}\right]_0+k_c}\right\}k_{ET}\left[\mathrm{PS}\right]_0\dfrac{k_Q\left[\mathrm{SD}\right]_0}{k_b+k_Q\left[\mathrm{SD}\right]_0}}{\left(\left(1+\dfrac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\right)\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+\left(k_{bet}-k_{ET}\dfrac{k_c}{k\left[\mathrm{S_{ox}}\right]_0+k_c}\right)\left[\mathrm{SD}^{\bullet+}\right]\right)+\dfrac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}k_Q\left[\mathrm{SD}\right]_0\right)}$$

We consider $\dfrac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}<<1$

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=k_{abs}\frac{k\left[\mathrm{S_{ox}}\right]+k_c}{k\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\frac{\left\{\left[\mathrm{Cat_{ox}}\right]_0-\dfrac{k_c\left[\mathrm{SD}^{\bullet+}\right]}{k\left[\mathrm{S_{ox}}\right]_0+k_c}\right\}k_{ET}\left[\mathrm{PS}\right]_0\dfrac{k_Q\left[\mathrm{SD}\right]_0}{k_b+k_Q\left[\mathrm{SD}\right]_0}}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+\left(k_{bet}-k_{ET}\dfrac{k_c}{k\left[\mathrm{S_{ox}}\right]_0+k_c}\right)\left[\mathrm{SD}^{\bullet+}\right]\right)}$$

Rearranged to:

$$\left(\frac{k\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}{k\left[\mathrm{S_{ox}}\right]+k_c}\right)\frac{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+\left(k_{bet}-k_{ET}\dfrac{k_c}{k\left[\mathrm{S_{ox}}\right]_0+k_c}\right)\left[\mathrm{SD}^{\bullet+}\right]\right)}{k_{ET}\left\{\left[\mathrm{Cat_{ox}}\right]_0-\dfrac{k_c\left[\mathrm{SD}^{\bullet+}\right]}{k\left[\mathrm{S_{ox}}\right]_0+k_c}\right\}}d\left[\mathrm{SD}^{\bullet+}\right]=\frac{k_Q\left[\mathrm{SD}\right]_0}{k_b+k_Q\left[\mathrm{SD}\right]_0}k_{abs}\left[\mathrm{PS}\right]_0\,dt$$

We introduce $p_c=\dfrac{k_c}{k\left[\mathrm{S_{ox}}\right]}$ and $\dfrac{\left[\mathrm{SD}^{\bullet+}\right]_t}{\left[\mathrm{Cat_{ox}}\right]_0}=\left(1+p_c\right)TON_{cat}^{c}$, hence:

$$\left(\frac{1+\dfrac{p_{betc}}{\gamma}\left(1+p_c\right)TON_{cat}}{1+p_c}\right)\frac{\left(1+\left(p_{bet}-\dfrac{p_c}{1+p_c}\right)\left(1+p_c\right)TON_{cat}\right)}{\left(1-\dfrac{p_c}{1+p_c}\left(1+p_c\right)TON_{cat}\right)}\left(1+p_c\right)d\left(TON_{cat}\right)=\gamma\,p_Q k_{abs}\times dt$$

Rearranged to:

$$\left(1+\frac{p_{betc}}{\gamma}\left(1+p_c\right)TON_{cat}\right)d\left(TON_{cat}\right)+\left(p_{bet}\left(1+p_c\right)\right)\left(\frac{TON_{cat}}{\left(1-p_cTON_{cat}\right)}\right)d\left(TON_{cat}\right)+\left(p_{bet}\frac{p_{betc}}{\gamma}\left(1+p_c\right)^2\right)\left(\frac{TON_{cat}{}^2}{\left(1-p_cTON_{cat}\right)}\right)d\left(TON_{cat}\right)$$
$$=\gamma\,p_Q k_{abs}\times dt$$

Which integration gives:

$$\left(TON_{cat}+\frac{p_{betc}}{\gamma}\left(1+p_c\right)\frac{TON_{cat}{}^2}{2}\right)+\left(p_{bets}\left(1+p_c\right)\right)\int_0^t \frac{TON_{cat}}{\left(1-p_cTON_{cat}\right)}d\left(TON_{cat}\right)+\left(p_{bet}\frac{p_{betc}}{\gamma}\left(1+p_c\right)^2\right)\int_0^t \frac{TON_{cat}{}^2}{\left(1-p_cTON_{cat}\right)}d\left(TON_{cat}\right)$$
$$=\gamma p_Q k_{abs}\times t$$

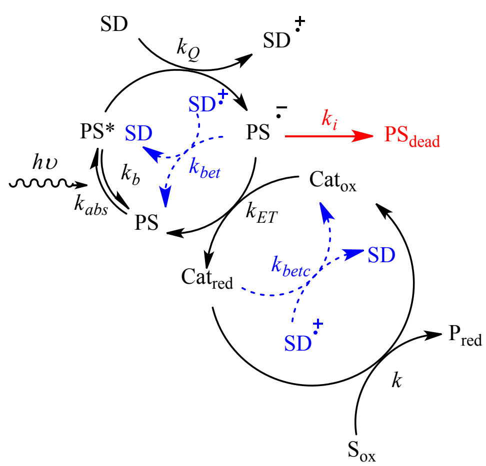
We finally obtain; noting that $TON_{cat} < TON_{cat}^{\lim,c} = \frac{1}{p_c}$:

$$\left(TON_{cat}+\frac{p_{betc}}{\gamma}\left(1+p_c\right)\frac{TON_{cat}{}^2}{2}\right)-\left(p_{bet}\left(1+p_c\right)\right)\left\{\frac{TON_{cat}}{p_c}+\frac{1}{p_c{}^2}\ln\left(1-p_cTON_{cat}\right)\right\}$$
$$-\left(p_{bet}\frac{p_{betc}}{\gamma}\left(1+p_c\right)^2\right)\frac{1}{p_c{}^3}\left\{\frac{\left(1-p_cTON_{cat}\right)^2}{2}-2\left(1-p_cTON_{cat}\right)+\ln\left(1-p_cTON_{cat}\right)+\frac{3}{2}\right\}$$
$$=\gamma p_Q k_{abs}\times t$$

1.3. Deactivation of the photocatalyst

The same system as in section 1.1. is considered (with similar assumptions) excepted that the reduced form of photosensitizer can now irreversibly degrades via a first order process (Scheme S3).

Scheme S3



Kinetic equations:

$$\frac{d\left[\mathrm{P_{red}}\right]}{dt}=k\left[\mathrm{S_{ox}}\right]\left[\mathrm{Cat_{red}}\right]$$

and

$$\frac{d\left[\mathrm{Cat_{red}}\right]}{dt}=k_{ET}\left[\mathrm{PS}^{\bullet-}\right]\left[\mathrm{Cat_{ox}}\right]-k\left[\mathrm{S_{ox}}\right]\left[\mathrm{Cat_{red}}\right]-k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{Cat_{red}}\right]\approx 0$$

$$\frac{d\left[\mathrm{PS}^{\bullet-}\right]}{dt}=k_Q\left[\mathrm{PS}^*\right]\left[\mathrm{SD}\right]_0-\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_i\right)\left[\mathrm{PS}^{\bullet-}\right]\approx 0$$

$$\frac{d\left[\mathrm{PS}^*\right]}{dt}=k_{abs}\left[\mathrm{PS}\right]-k_b\left[\mathrm{PS}^*\right]-k_Q\left[\mathrm{PS}^*\right]\left[\mathrm{SD}\right]_0\approx 0$$

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=k_Q\left[\mathrm{PS}^*\right][\mathrm{SD}]_0-k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{PS}^{\bullet-}\right]-k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{Cat_{red}}\right]$$

$$\frac{d\left[\mathrm{PS_{dead}}\right]}{dt}=k_i\left[\mathrm{PS}^{\bullet-}\right]$$

Resolution

Because $\mathrm{Cat_{red}}$ is at steady state, it does not accumulate and $\left[\mathrm{Cat_{ox}}\right]_0 ; \left[\mathrm{Cat_{ox}}\right]$

The steady-state approximations lead to:

$$\left[\mathrm{PS}^*\right]=\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

and

$$\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_i\right)}\left[\mathrm{PS}^*\right]=\left[\mathrm{PS}^{\bullet-}\right]$$

Therefore:

$$\left[\mathrm{PS}^{\bullet-}\right]=\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_i\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

$$\left[\mathrm{Cat_{red}}\right]=\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\left[\mathrm{PS}^{\bullet-}\right]$$

Then:

$$\frac{d\left[\mathrm{P_{red}}\right]}{dt}=k\left[\mathrm{S_{ox}}\right]\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_i\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

with

$$[\mathrm{PS}]_0=[\mathrm{PS}]+\left[\mathrm{PS}^*\right]+\left[\mathrm{PS}^{\bullet-}\right]+\left[\mathrm{PS_{dead}}\right]$$

Hence:

$$\frac{d[\mathrm{PS}]}{dt}=-\frac{d\left[\mathrm{PS_{dead}}\right]}{dt}=-k_i\left[\mathrm{PS}^{\bullet-}\right]=-k_i\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_i\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

We need $\left[\mathrm{SD}^{\bullet+}\right]_t$. Combination of the kinetic equations leads to:

$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=\frac{d\left[\mathrm{P_{red}}\right]}{dt}+k_i\left[\mathrm{PS}^{\bullet-}\right]$ thus we can make the approximation $\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}\approx\frac{d\left[\mathrm{P_{red}}\right]}{dt}$ and therefore $\left[\mathrm{SD}^{\bullet+}\right]\approx\left[\mathrm{P_{red}}\right]$

We have:

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=-\left(1+\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}\frac{k\left[\mathrm{S_{ox}}\right]}{k\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\right)\frac{d[\mathrm{PS}]}{dt}$$

Leading to:

$$\left(\frac{k\left[\mathrm{S_{ox}}\right]}{k_{betc}\left[\mathrm{SD}^{\bullet+}\right]+k\left[\mathrm{S_{ox}}\right]\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}+1\right)}+\frac{k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}{k_{betc}\left[\mathrm{SD}^{\bullet+}\right]+k\left[\mathrm{S_{ox}}\right]\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}+1\right)}\right)d\left[\mathrm{SD}^{\bullet+}\right]=-d\left[\mathrm{PS}\right]$$ which integration

gives (considering $\left[\mathrm{SD}^{\bullet+}\right]_0=0$):

$$\left[\mathrm{SD}^{\bullet+}\right]-\frac{k\left[\mathrm{S_{ox}}\right]}{k_{betc}}\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}\right)\ln\left(1+\frac{\left[\mathrm{SD}^{\bullet+}\right]}{\frac{k\left[\mathrm{S_{ox}}\right]}{k_{betc}}\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}+1\right)}\right)=\left[\mathrm{PS}\right]_0-\left[\mathrm{PS}\right]$$

Leading to:

$$\frac{d\left[\mathrm{P_{red}}\right]}{dt}\approx\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=\left(k\left[\mathrm{S_{ox}}\right]\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}+k_i\right)\frac{k_Q\left[\mathrm{SD}\right]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)}\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}$$
$$\times\left\{\left[\mathrm{PS}\right]_0-\left[\mathrm{SD}^{\bullet+}\right]+\frac{k\left[\mathrm{S_{ox}}\right]}{k_{betc}}\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}\right)\ln\left(1+\frac{\left[\mathrm{SD}^{\bullet+}\right]}{\frac{k\left[\mathrm{S_{ox}}\right]}{k_{betc}}\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}+1\right)}\right)\right\}$$

Therefore, introducing $p_i=\frac{k_i}{k_{ET}\left[\mathrm{PS}\right]_0}$, we obtain:

$$\frac{dTON_{cat}}{dt}=\left(\frac{1}{1+\frac{p_{betc}}{\gamma}TON_{cat}}+p_i\gamma\right)\frac{\gamma\, p_Q k_{abs}}{\left(1+p_{bet}TON_{cat}\right)}\times\left\{1-\frac{TON_{cat}}{\gamma}+\frac{1}{p_{betc}}\frac{1}{p_i\gamma}\ln\left(1+\frac{TON_{cat}}{\frac{\gamma}{p_{betc}}\left(\frac{1}{p_i\gamma}+1\right)}\right)\right\}$$

Maximal turnover number: $TON_{cat}^{\lim,i}$

We have: $\left[\mathrm{SD}^{\bullet+}\right]-\frac{k\left[\mathrm{S_{ox}}\right]}{k_{betc}}\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}\right)\ln\left(1+\frac{\left[\mathrm{SD}^{\bullet+}\right]}{\frac{k\left[\mathrm{S_{ox}}\right]}{k_{betc}}\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}+1\right)}\right)=\left[\mathrm{PS}\right]_0-\left[\mathrm{PS}\right]$ with $\left[\mathrm{SD}^{\bullet+}\right]\approx\left[\mathrm{P_{red}}\right]$

Hence the reaction stops when $\left[\mathrm{PS}\right]=0$, i.e.

$$\left[\mathrm{P_{red}}\right]_{\max}-\frac{k\left[\mathrm{S_{ox}}\right]}{k_{betc}}\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}\right)\ln\left(1+\frac{\left[\mathrm{P_{red}}\right]_{\max}}{\frac{k\left[\mathrm{S_{ox}}\right]}{k_{betc}}\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}+1\right)}\right)=\left[\mathrm{PS}\right]_0$$

For small values of k_i, this simplifies to:

$$\left[\mathrm{P_{red}}\right]_{max} + \frac{\dfrac{k\left[\mathrm{S_{ox}}\right]}{k_{betc}}\left(\dfrac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}\right)}{\left(\dfrac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}+1\right)}\frac{1}{2}\left(\frac{\left[\mathrm{P_{red}}\right]_{max}}{\dfrac{k\left[\mathrm{S_{ox}}\right]}{k_{betc}}}\right)^2 = [\mathrm{PS}]_0\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}+1\right) \approx [\mathrm{PS}]_0\left(\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}\right)$$

Thus: $TON_{cat}^{\lim,i} + \dfrac{k_{betc}\left[\mathrm{Cat_{ox}}\right]_0}{k\left[\mathrm{S_{ox}}\right]}\dfrac{1}{2}\left(TON_{cat}^{\lim,i}\right)^2 = \dfrac{k_{ET}[\mathrm{PS}]_0}{k_i}$ leading to:

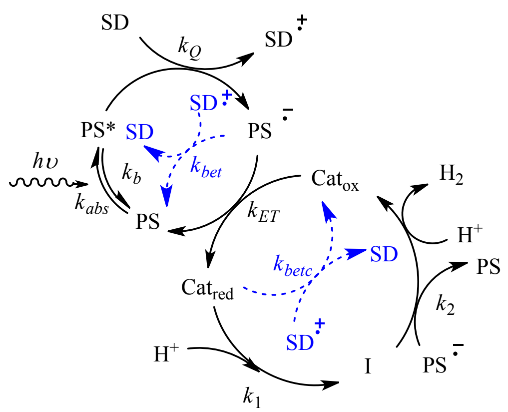
$$TON_{cat}^{\lim,i} = \frac{\gamma}{p_{betc}}\left(-1+\sqrt{1+2\frac{p_{betc}}{\gamma p_i}}\right)$$

1.4. Ideal two electron system for H_2 production

We consider a kinetic scheme for a photocatalytic process with reductive quenching involving a two electron process to form the product H_2 (Scheme S4).

The same assumptions as in the previous sections are made. We also assume that the intermediate species I is at steady-state.

Scheme S4



Kinetic equations:

We consider and ECEC mechanism where the second reduction (rate constant k_2) is slower than the second chemical step leading to H_2 formation.

$$\frac{d\left[\mathrm{H_2}\right]}{dt} = k_2[\mathrm{I}]\left[\mathrm{PS^{•-}}\right]$$

and

$$\frac{d\left[\mathrm{Cat_{red}}\right]}{dt} = k_{ET}\left[\mathrm{PS^{•-}}\right]\left[\mathrm{Cat_{ox}}\right] - k_1\left[\mathrm{S_{ox}}\right]\left[\mathrm{Cat_{red}}\right] - k_{betc}\left[\mathrm{SD^{•+}}\right]\left[\mathrm{Cat_{red}}\right] \approx 0$$

$$\frac{d\left[\mathrm{PS^{•-}}\right]}{dt} = k_Q\left[\mathrm{PS^*}\right][\mathrm{SD}]_0 - \left(k_{ET}\left[\mathrm{Cat_{ox}}\right] + k_{bet}\left[\mathrm{SD^{•+}}\right] + k_2[\mathrm{I}]\right)\left[\mathrm{PS^{•-}}\right] \approx 0$$

$$\frac{d\left[\mathrm{PS^*}\right]}{dt} = k_{abs}[\mathrm{PS}] - k_b\left[\mathrm{PS^*}\right] - k_Q\left[\mathrm{PS^*}\right][\mathrm{SD}]_0 \approx 0$$

$$\frac{d\left[\mathrm{SD^{•+}}\right]}{dt} = k_Q\left[\mathrm{PS^*}\right][\mathrm{SD}]_0 - k_{bet}\left[\mathrm{SD^{•+}}\right]\left[\mathrm{PS^{•-}}\right] - k_{betc}\left[\mathrm{SD^{•+}}\right]\left[\mathrm{Cat_{red}}\right]$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{S_{ox}}][\mathrm{Cat_{red}}] - k_2[\mathrm{I}]\left[\mathrm{PS}^{\bullet-}\right] \approx 0$$

Thus:

$$\frac{d[\mathrm{H_2}]}{dt} = k_1[\mathrm{S_{ox}}][\mathrm{Cat_{red}}]$$

Resolution:

Because $\mathrm{Cat_{red}}$ is at steady state, it does not accumulate and $[\mathrm{Cat_{ox}}]_0$; $[\mathrm{Cat_{ox}}]$ and the steady-state approximations lead to:

$$\left[\mathrm{PS}^*\right] = \frac{k_{abs}}{k_b + k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

and

$$\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}[\mathrm{Cat_{ox}}]_0 + k_{bet}\left[\mathrm{SD}^{\bullet+}\right] + k_2[\mathrm{I}]\right)}\left[\mathrm{PS}^*\right] = \left[\mathrm{PS}^{\bullet-}\right]$$

Therefore:

$$\left[\mathrm{PS}^{\bullet-}\right] = \frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}[\mathrm{Cat_{ox}}]_0 + k_{bet}\left[\mathrm{SD}^{\bullet+}\right] + k_2[\mathrm{I}]\right)} \frac{k_{abs}}{k_b + k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

With $k_1[\mathrm{S_{ox}}]\dfrac{[\mathrm{Cat_{red}}]}{\left[\mathrm{PS}^{\bullet-}\right]} = k_2[\mathrm{I}]$

Thus $\left[\mathrm{PS}^{\bullet-}\right] = \dfrac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}[\mathrm{Cat_{ox}}]_0 + k_{bet}\left[\mathrm{SD}^{\bullet+}\right] + k_1[\mathrm{S_{ox}}]\dfrac{[\mathrm{Cat_{red}}]}{\left[\mathrm{PS}^{\bullet-}\right]}\right)} \dfrac{k_{abs}}{k_b + k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$

And $\dfrac{k_{ET}[\mathrm{Cat_{ox}}]_0}{k_1[\mathrm{S_{ox}}] + k_{betc}\left[\mathrm{SD}^{\bullet+}\right]} = \dfrac{[\mathrm{Cat_{red}}]}{\left[\mathrm{PS}^{\bullet-}\right]}$

Hence: $\left[\mathrm{PS}^{\bullet-}\right] = \dfrac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}[\mathrm{Cat_{ox}}]_0\left(1 + \dfrac{k_1[\mathrm{S_{ox}}]}{k_1[\mathrm{S_{ox}}] + k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\right) + k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)} \dfrac{k_{abs}}{k_b + k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$

with

$$[\mathrm{PS}]_0 = [\mathrm{PS}] + \left[\mathrm{PS}^*\right] + \left[\mathrm{PS}^{\bullet-}\right]$$

Thus:

$$[\mathrm{PS}] = \frac{[\mathrm{PS}]_0}{\left(1 + \dfrac{k_{abs}}{k_b + k_Q[\mathrm{SD}]_0} + \dfrac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}[\mathrm{Cat_{ox}}]_0\left(1 + \dfrac{k_1[\mathrm{S_{ox}}]}{k_1[\mathrm{S_{ox}}] + k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\right) + k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\right)} \dfrac{k_{abs}}{k_b + k_Q[\mathrm{SD}]_0}\right)}$$

And

$$\left[\mathrm{Cat_{red}}\right]=\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD^{\bullet+}}\right]}\left[\mathrm{PS^{\bullet-}}\right]=\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD^{\bullet+}}\right]}\frac{k_Q\left[\mathrm{SD}\right]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0\left(1+\frac{k_1\left[\mathrm{S_{ox}}\right]}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD^{\bullet+}}\right]}\right)+k_{bet}\left[\mathrm{SD^{\bullet+}}\right]\right)}$$

$$\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\frac{\left[\mathrm{PS}\right]_0}{\left(1+\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}+\frac{k_Q\left[\mathrm{SD}\right]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0\left(1+\frac{k_1\left[\mathrm{S_{ox}}\right]}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD^{\bullet+}}\right]}\right)+k_{bet}\left[\mathrm{SD^{\bullet+}}\right]\right)}\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\right)}$$

leading to:

$$\frac{d\left[\mathrm{H_2}\right]}{dt}=k_1\left[\mathrm{S_{ox}}\right]\left[\mathrm{Cat_{red}}\right]$$

$$\frac{d\left[\mathrm{H_2}\right]}{dt}=\frac{k_1\left[\mathrm{S_{ox}}\right]\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD^{\bullet+}}\right]}k_Q\left[\mathrm{SD}\right]_0\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\left[\mathrm{PS}\right]_0}{\left(\left(1+\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\right)\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0\left(1+\frac{k_1\left[\mathrm{S_{ox}}\right]}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD^{\bullet+}}\right]}\right)+k_{bet}\left[\mathrm{SD^{\bullet+}}\right]\right)+k_Q\left[\mathrm{SD}\right]_0\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\right)}$$

Now we need to get $\left[\mathrm{SD^{\bullet+}}\right]_t$

Combination of kinetic equations gives:

$$\frac{d\left[\mathrm{SD^{\bullet+}}\right]}{dt}=2k_1\left[\mathrm{S_{ox}}\right]\left[\mathrm{Cat_{red}}\right]$$

therefore: $\frac{d\left[\mathrm{SD^{\bullet+}}\right]}{dt}=2\frac{d\left[\mathrm{H_2}\right]}{dt}$ and hence $\left[\mathrm{SD^{\bullet+}}\right]_t=2\left[\mathrm{H_2}\right]_t$

thus:

$$\frac{d\left[\mathrm{SD^{\bullet+}}\right]}{dt}=\frac{2k_1\left[\mathrm{S_{ox}}\right]\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD^{\bullet+}}\right]}k_Q\left[\mathrm{SD}\right]_0\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\left[\mathrm{PS}\right]_0}{\left(\left(1+\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\right)\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0\left(1+\frac{k_1\left[\mathrm{S_{ox}}\right]}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD^{\bullet+}}\right]}\right)+k_{bet}\left[\mathrm{SD^{\bullet+}}\right]\right)+k_Q\left[\mathrm{SD}\right]_0\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\right)}$$

rearranged to:

$$\frac{d\left[\mathrm{SD^{\bullet+}}\right]}{dt}=\frac{2k_1\left[\mathrm{S_{ox}}\right]k_{ET}\left[\mathrm{Cat_{ox}}\right]\frac{k_Q\left[\mathrm{SD}\right]_0}{k_b+k_Q\left[\mathrm{SD}\right]_0}k_{abs}\left[\mathrm{PS}\right]_0}{\left(1+\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\right)\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0\left(k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD^{\bullet+}}\right]+k_1\left[\mathrm{S_{ox}}\right]\right)+k_{bet}\left[\mathrm{SD^{\bullet+}}\right]\left(k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD^{\bullet+}}\right]\right)\right)+\left(k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD^{\bullet+}}\right]\right)}$$

Simplification: $\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}<<1$

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=\frac{2k_1\left[\mathrm{S_{ox}}\right]k_{ET}\left[\mathrm{Cat_{ox}}\right]\frac{k_Q[\mathrm{SD}]_0}{k_b+k_Q[\mathrm{SD}]_0}k_{abs}[\mathrm{PS}]_0}{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0\left(k_{betc}\left[\mathrm{SD}^{\bullet+}\right]+2k_1\left[\mathrm{S_{ox}}\right]\right)+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\left(k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\right)+\left(k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\right)k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}}$$

$$\left[1+\frac{\left(k_{betc}k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}k_1\left[\mathrm{S_{ox}}\right]+k_{betc}k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}{\left(2k_1\left[\mathrm{S_{ox}}\right]k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_1\left[\mathrm{S_{ox}}\right]k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}\left[\mathrm{SD}^{\bullet+}\right]+\frac{k_{bet}k_{betc}}{\left(2k_1\left[\mathrm{S_{ox}}\right]k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_1\left[\mathrm{S_{ox}}\right]k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}\left(\left[\mathrm{SD}^{\bullet+}\right]^2\right)\right]\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=\frac{2k_{ET}\left[\mathrm{Cat_{ox}}\right]\frac{k_Q[\mathrm{SD}]_0}{k_b+k_Q[\mathrm{SD}]_0}k_{abs}[\mathrm{PS}]_0}{\left(2k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}$$

Which integration gives:

$$\left[\left[\mathrm{SD}^{\bullet+}\right]+\frac{\left(k_{betc}k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}k_1\left[\mathrm{S_{ox}}\right]+k_{betc}k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}{\left(2k_1\left[\mathrm{S_{ox}}\right]k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_1\left[\mathrm{S_{ox}}\right]k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}\frac{\left[\mathrm{SD}^{\bullet+}\right]^2}{2}+\frac{k_{bet}k_{betc}}{\left(2k_1\left[\mathrm{S_{ox}}\right]k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_1\left[\mathrm{S_{ox}}\right]k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}\left(\frac{\left[\mathrm{SD}^{\bullet+}\right]^3}{3}\right)\right]=\frac{2k_{ET}\left[\mathrm{Cat_{ox}}\right]\frac{k_Q[\mathrm{SD}]_0}{k_b+k_Q[\mathrm{SD}]_0}k_{abs}[\mathrm{PS}]_0}{\left(2k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}\times t$$

Then, taking into account: $\left[\mathrm{H_2}\right]_t=\frac{1}{2}\left[\mathrm{SD}^{\bullet+}\right]_t$ and $TON_{cat}=\frac{\left[\mathrm{H_2}\right]}{\left[\mathrm{Cat_{ox}}\right]_0}$, thus $2TON_{cat}=\frac{\left[\mathrm{SD}^{\bullet+}\right]_t}{\left[\mathrm{Cat_{ox}}\right]_0}$ we have:

$$\left[\frac{\left[\mathrm{SD}^{\bullet+}\right]}{\left[\mathrm{Cat_{ox}}\right]_0}+\frac{\left(k_{betc}k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}k_1\left[\mathrm{S_{ox}}\right]+k_{betc}k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}{\left(2k_1\left[\mathrm{S_{ox}}\right]k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_1\left[\mathrm{S_{ox}}\right]k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}\left[\mathrm{Cat_{ox}}\right]_0\frac{\left(\frac{\left[\mathrm{SD}^{\bullet+}\right]}{\left[\mathrm{Cat_{ox}}\right]_0}\right)^2}{2}+\frac{k_{bet}k_{betc}\left[\mathrm{Cat_{ox}}\right]_0^{\,2}}{\left(2k_1\left[\mathrm{S_{ox}}\right]k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_1\left[\mathrm{S_{ox}}\right]k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}\left(\frac{\left(\frac{\left[\mathrm{SD}^{\bullet+}\right]}{\left[\mathrm{Cat_{ox}}\right]_0}\right)^3}{3}\right)\right]=\frac{2k_{ET}\frac{k_Q[\mathrm{SD}]_0}{k_b+k_Q[\mathrm{SD}]_0}k_{abs}[\mathrm{PS}]_0}{\left(2k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_Q[\mathrm{SD}]_0\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}\right)}$$

$$2TON_{cat}+\frac{\left(k_{betc}k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}k_1\left[\mathrm{S_{ox}}\right]+k_{betc}k_Q\left[\mathrm{SD}\right]_0\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\right)}{\left(2k_1\left[\mathrm{S_{ox}}\right]k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_1\left[\mathrm{S_{ox}}\right]k_Q\left[\mathrm{SD}\right]_0\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\right)}\left[\mathrm{Cat_{ox}}\right]_0\frac{4\left(TON_{cat}\right)^2}{2}$$

$$+\frac{k_{bet}k_{betc}\left[\mathrm{Cat_{ox}}\right]_0^2}{\left(2k_1\left[\mathrm{S_{ox}}\right]k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_1\left[\mathrm{S_{ox}}\right]k_Q\left[\mathrm{SD}\right]_0\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\right)}\frac{8\left(TON_{cat}\right)^3}{3}$$

$$=\frac{2k_{ET}\left[\mathrm{Cat_{ox}}\right]\frac{k_Q\left[\mathrm{SD}\right]_0}{k_b+k_Q\left[\mathrm{SD}\right]_0}k_{abs}\left[\mathrm{PS}\right]_0}{\left(2k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_Q\left[\mathrm{SD}\right]_0\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\right)}\times t$$

In most cases $\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}$ <<1, thus:

$$2TON_{cat}+\frac{\left(k_{betc}k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}k_1\left[\mathrm{S_{ox}}\right]\right)}{\left(2k_1\left[\mathrm{S_{ox}}\right]k_{ET}\left[\mathrm{Cat_{ox}}\right]_0\right)}\left[\mathrm{Cat_{ox}}\right]_0\frac{4\left(TON_{cat}\right)^2}{2}+\frac{k_{bet}k_{betc}\left[\mathrm{Cat_{ox}}\right]_0^2}{\left(2k_1\left[\mathrm{S_{ox}}\right]k_{ET}\left[\mathrm{Cat_{ox}}\right]_0\right)}\frac{8\left(TON_{cat}\right)^3}{3}$$

$$=\frac{2k_{ET}\frac{k_Q\left[\mathrm{SD}\right]_0}{k_b+k_Q\left[\mathrm{SD}\right]_0}k_{abs}\left[\mathrm{PS}\right]_0}{\left(2k_{ET}\left[\mathrm{Cat_{ox}}\right]_0\right)}\times t$$

Thus:

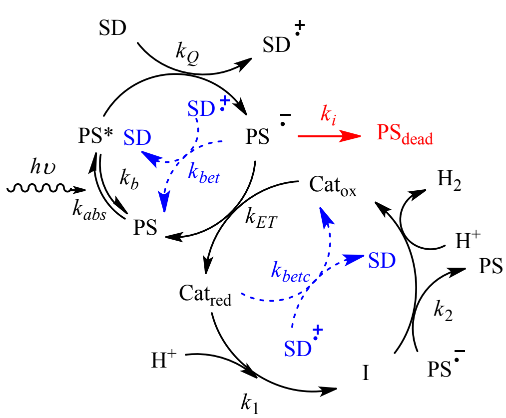
$$TON_{cat}+\left(\frac{p_{betc,2}}{\gamma}+\frac{p_{bet}}{2}\right)\left(TON_{cat}\right)^2+\frac{4}{3}p_{bet}\frac{p_{betc,2}}{\gamma}\left(TON_{cat}\right)^3=\frac{p_Q k_{abs}\gamma}{2}\times t$$

with parameters $\gamma=\frac{\left[\mathrm{PS}\right]_0}{\left[\mathrm{Cat_{ox}}\right]_0}$, $p_{bet}=\frac{k_{bet}}{k_{ET}}$, $p_{betc,2}=\frac{k_{betc}\left[\mathrm{PS}\right]_0}{2k_1\left[\mathrm{S_{ox}}\right]_0}$ and $p_Q=\frac{k_Q\left[\mathrm{SD}\right]}{k_b+k_Q\left[\mathrm{SD}\right]}$

1.5. Two electron system for H_2 production with degradation of the photosensitizer

The same system as in section 1.4. is considered (with similar assumptions) excepted that the reduced form of photosensitizer can now irreversibly degrades via a first order process (Scheme S5).

Scheme S5



Kinetic equations:

$$\frac{d\left[\mathrm{H_2}\right]}{dt}=k_2\left[\mathrm{I}\right]\left[\mathrm{PS}^{\bullet-}\right]$$

and

$$\frac{d\left[\mathrm{Cat_{red}}\right]}{dt}=k_{ET}\left[\mathrm{PS}^{\bullet-}\right]\left[\mathrm{Cat_{ox}}\right]-k_1\left[\mathrm{S_{ox}}\right]\left[\mathrm{Cat_{red}}\right]-k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{Cat_{red}}\right]\approx 0$$

$$\frac{d\left[\mathrm{I}\right]}{dt}=k_1\left[\mathrm{S_{ox}}\right]\left[\mathrm{Cat_{red}}\right]-k_2\left[\mathrm{I}\right]\left[\mathrm{PS}^{\bullet-}\right]\approx 0$$

Thus:

$$\frac{d\left[\mathrm{H_2}\right]}{dt}=k_1\left[\mathrm{S_{ox}}\right]\left[\mathrm{Cat_{red}}\right]$$

And

$$\frac{d\left[\mathrm{PS}^{\bullet-}\right]}{dt}=k_Q\left[\mathrm{PS}^{*}\right]\left[\mathrm{SD}\right]_0-\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_2\left[\mathrm{I}\right]+k_i\right)\left[\mathrm{PS}^{\bullet-}\right]\approx 0$$

$$\frac{d\left[\mathrm{PS}^{*}\right]}{dt}=k_{abs}\left[\mathrm{PS}\right]-k_b\left[\mathrm{PS}^{*}\right]-k_Q\left[\mathrm{PS}^{*}\right]\left[\mathrm{SD}\right]_0\approx 0$$

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=k_Q\left[\mathrm{PS}^{*}\right]\left[\mathrm{SD}\right]_0-k_{bet}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{PS}^{\bullet-}\right]-k_{betc}\left[\mathrm{SD}^{\bullet+}\right]\left[\mathrm{Cat_{red}}\right]$$

$$\frac{d\left[\mathrm{PS_{dead}}\right]}{dt}=k_i\left[\mathrm{PS}^{\bullet-}\right]$$

Resolution

Because $\mathrm{Cat_{red}}$ is at steady state, it does not accumulate and $\left[\mathrm{Cat_{ox}}\right]_0$; $\left[\mathrm{Cat_{ox}}\right]$

The steady-state approximations lead to:

$$\left[\mathrm{PS}^{*}\right]=\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\left[\mathrm{PS}\right]$$

and

$$\frac{k_Q\left[\mathrm{SD}\right]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_2\left[\mathrm{I}\right]+k_i\right)}\left[\mathrm{PS}^{*}\right]=\left[\mathrm{PS}^{\bullet-}\right]$$

Therefore:

$$\left[\mathrm{PS}^{\bullet-}\right]=\frac{k_Q\left[\mathrm{SD}\right]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_1\left[\mathrm{S_{ox}}\right]\frac{\left[\mathrm{Cat_{red}}\right]}{\left[\mathrm{PS}^{\bullet-}\right]}+k_i\right)}\frac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}\left[\mathrm{PS}\right]$$

And $\dfrac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}=\dfrac{\left[\mathrm{Cat_{red}}\right]}{\left[\mathrm{PS}^{\bullet-}\right]}$

Hence:

$$\left[\mathrm{PS}^{\bullet-}\right]=\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_1\left[\mathrm{S_{ox}}\right]\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}+k_i\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

Then:

$$\frac{d\left[\mathrm{H_2}\right]}{dt}=k_1\left[\mathrm{S_{ox}}\right]\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_1\left[\mathrm{S_{ox}}\right]\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}+k_i\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

with

$$[\mathrm{PS}]_0=[\mathrm{PS}]+\left[\mathrm{PS}^*\right]+\left[\mathrm{PS}^{\bullet-}\right]+\left[\mathrm{PS_{dead}}\right]$$

Hence:

$$\frac{d[\mathrm{PS}]}{dt}=-\frac{d\left[\mathrm{PS_{dead}}\right]}{dt}=-k_i\left[\mathrm{PS}^{\bullet-}\right]=-k_i\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_1\left[\mathrm{S_{ox}}\right]\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}+k_i\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

We now need $\left[\mathrm{SD}^{\bullet+}\right]_t$:

Combination of the kinetic equations gives:

$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=2\frac{d\left[\mathrm{H_2}\right]}{dt}+k_i\left[\mathrm{PS}^{\bullet-}\right]$ thus we can make the approximation $\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}\approx 2\frac{d\left[\mathrm{H_2}\right]}{dt}$ and therefore $\left[\mathrm{SD}^{\bullet+}\right]\approx 2\left[\mathrm{H_2}\right]$

We thus have:

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=2k_1\left[\mathrm{S_{ox}}\right]\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}\frac{k_Q[\mathrm{SD}]_0}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_1\left[\mathrm{S_{ox}}\right]\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}+k_i\right)}\frac{k_{abs}}{k_b+k_Q[\mathrm{SD}]_0}[\mathrm{PS}]$$

therefore:

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=-\frac{2k_1\left[\mathrm{S_{ox}}\right]\frac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}}{k_i}\frac{d[\mathrm{PS}]}{dt}$$

which integration gives (taking into account $\left[\mathrm{SD}^{\bullet+}\right]_0=0$):

$$\left(1+\frac{k_{betc}}{k_1\left[\mathrm{S_{ox}}\right]}\left[\mathrm{SD}^{\bullet+}\right]\right)\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=-\frac{2k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}\frac{d[\mathrm{PS}]}{dt}$$

$$\left(\left[\mathrm{SD}^{\bullet+}\right]+\frac{k_{betc}}{k_1\left[\mathrm{S_{ox}}\right]}\frac{\left[\mathrm{SD}^{\bullet+}\right]^2}{2}\right)=\frac{2k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}\left([\mathrm{PS}]_0-[\mathrm{PS}]\right)$$

Leading to:

$$\frac{d\left[\mathrm{SD}^{\bullet+}\right]}{dt}=\frac{2k_1\left[\mathrm{S_{ox}}\right]\dfrac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}k_Q\left[\mathrm{SD}\right]_0\dfrac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+k_{bet}\left[\mathrm{SD}^{\bullet+}\right]+k_1\left[\mathrm{S_{ox}}\right]\dfrac{k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]+k_{betc}\left[\mathrm{SD}^{\bullet+}\right]}+k_i\right)}\left\{\left[\mathrm{PS}\right]_0-\frac{\left(\left[\mathrm{SD}^{\bullet+}\right]+\dfrac{k_{betc}}{k_1\left[\mathrm{S_{ox}}\right]}\dfrac{\left[\mathrm{SD}^{\bullet+}\right]^2}{2}\right)}{\dfrac{2k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}}\right\}$$

And thus, taking into account $\dfrac{\left[\mathrm{SD}^{\bullet+}\right]}{\left[\mathrm{Cat_{ox}}\right]_0}\approx 2\dfrac{\left[\mathrm{H_2}\right]}{\left[\mathrm{Cat_{ox}}\right]_0}=2TON_{cat}$

$$\frac{dTON_{cat}}{dt}=\frac{k_1\left[\mathrm{S_{ox}}\right]\dfrac{k_{ET}}{k_1\dfrac{\left[\mathrm{S_{ox}}\right]}{\left[\mathrm{Cat_{ox}}\right]_0}+2k_{betc}TON_{cat}}k_Q\left[\mathrm{SD}\right]_0\dfrac{k_{abs}}{k_b+k_Q\left[\mathrm{SD}\right]_0}}{\left(k_{ET}\left[\mathrm{Cat_{ox}}\right]_0+2k_{bet}\left[\mathrm{Cat_{ox}}\right]_0TON_{cat}+k_1\left[\mathrm{S_{ox}}\right]\dfrac{k_{ET}}{k_1\dfrac{\left[\mathrm{S_{ox}}\right]}{\left[\mathrm{Cat_{ox}}\right]_0}+2k_{betc}TON_{cat}}+k_i\right)}\left\{\frac{\left[\mathrm{PS}\right]_0}{\left[\mathrm{Cat_{ox}}\right]_0}-\frac{\left(2TON_{cat}+\dfrac{k_{betc}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]}\dfrac{4TON_{cat}^{\,2}}{2}\right)}{\dfrac{2k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}}\right\}$$

Hence, introducing the dimensionless parameters already defined ($\gamma=\dfrac{\left[\mathrm{PS}\right]_0}{\left[\mathrm{Cat_{ox}}\right]_0}$, $p_{bet}=\dfrac{k_{bet}}{k_{ET}}$, $p_{betc}=\dfrac{k_{betc}\left[\mathrm{PS}\right]_0}{2k_1\left[\mathrm{S_{ox}}\right]_0}$, $p_Q=\dfrac{k_Q\left[\mathrm{HA}^-\right]}{k_b+k_Q\left[\mathrm{HA}^-\right]}$, $p_i=\dfrac{k_i}{k_{ET}\left[\mathrm{PS}\right]_0}$) we obtain:

$$\frac{dTON_{cat}}{dt}=k_{abs}p_Q\gamma\frac{1-p_i\left(TON_{cat}+2\dfrac{p_{betc,2}}{\gamma}TON_{cat}^{\,2}\right)}{\left(1+2p_{bet}TON_{cat}+p_i\gamma\right)\left(1+4\dfrac{p_{betc,2}}{\gamma}TON_{cat}\right)+1}$$

Maximal turnover number: $TON_{cat}^{\lim,i}$

We have: $\left(\left[\mathrm{SD}^{\bullet+}\right]+\dfrac{k_{betc}}{k_1\left[\mathrm{S_{ox}}\right]}\dfrac{\left[\mathrm{SD}^{\bullet+}\right]^2}{2}\right)=\dfrac{2k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}\left(\left[\mathrm{PS}\right]_0-\left[\mathrm{PS}\right]\right)$

Hence the reaction stops when $\left[\mathrm{PS}\right]=0$, i.e.

$$\left(\left[\mathrm{SD}^{\bullet+}\right]_{\max}+\frac{k_{betc}}{k_1\left[\mathrm{S_{ox}}\right]}\frac{\left[\mathrm{SD}^{\bullet+}\right]_{\max}^2}{2}\right)=\frac{2k_{ET}\left[\mathrm{Cat_{ox}}\right]_0}{k_i}\left[\mathrm{PS}\right]_0$$

thus:

$$\left(\frac{\left[\mathrm{SD}^{\bullet+}\right]_{\max}}{\left[\mathrm{Cat_{ox}}\right]_0}+\frac{k_{betc}\left[\mathrm{Cat_{ox}}\right]_0}{k_1\left[\mathrm{S_{ox}}\right]}\frac{\left[\mathrm{SD}^{\bullet+}\right]_{\max}^2}{2\left[\mathrm{Cat_{ox}}\right]_0^2}\right)=\frac{2k_{ET}}{k_i}\left[\mathrm{PS}\right]_0$$

i.e.

$$2TON_{cat}^{\lim,i} + \frac{k_{betc}\left[\text{Cat}_{\text{ox}}\right]_0}{k_1\left[\text{S}_{\text{ox}}\right]} 2\left(TON_{cat}^{\lim,i}\right)^2 = \left(\frac{2k_{ET}\left[\text{PS}\right]_0}{k_i}\right)$$

$$TON_{cat}^{\lim,i} + 2\frac{p_{betc,2}}{\gamma}\left(TON_{cat}^{\lim,i}\right)^2 - \left(\frac{1}{p_i}\right) = 0$$

Leading to:

$$TON_{cat}^{\lim,i} = \frac{-1 + \sqrt{1 + 8\dfrac{p_{betc,2}}{\gamma\, p_i}}}{4\dfrac{p_{betc,2}}{\gamma}}$$

2. Numerical calculations

Numerical resolution of the differential equations:

$$\frac{dTON_{cat}}{dt}=\left(\frac{1}{1+\frac{p_{betc}}{\gamma}TON_{cat}}+p_i\gamma\right)\frac{TOF_{cat,0}}{\left(1+p_{bet}TON_{cat}\right)}\times\left\{1-\frac{TON_{cat}}{\gamma}+\frac{1}{p_{betc}}\frac{1}{p_i\gamma}\ln\left(1+\frac{TON_{cat}}{\frac{\gamma}{p_{betc}}\left(\frac{1}{p_i\gamma}+1\right)}\right)\right\}$$

and

$$\frac{dTON_{cat}}{dt}=\frac{2TOF_{cat,0,2}\left[1-p_i\left(TON_{cat}+2\frac{p_{betc,2}}{\gamma}TON_{cat}{}^2\right)\right]}{\left(1+2p_{bet}TON_{cat}+p_i\gamma\right)\left(1+4\frac{p_{betc,2}}{\gamma}TON_{cat}\right)+1}$$

is simply obtained by discretization of the time t ($t_j = j\times dt$ with dt being a small time interval) and with consideration that $\left(TON_{cat}\right)_{j=0}=0$:

$$\left(TON_{cat}\right)_j=\left(TON_{cat}\right)_{j-1}+\left(\frac{1}{1+\frac{p_{betc}}{\gamma}\left(TON_{cat}\right)_{j-1}}+p_i\gamma\right)\frac{TOF_{cat,0}}{\left(1+p_{bet}\left(TON_{cat}\right)_{j-1}\right)}\left\{1-\frac{\left(TON_{cat}\right)_{j-1}}{\gamma}+\frac{1}{p_{betc}}\frac{1}{p_i\gamma}\ln\left(1+\frac{\left(TON_{cat}\right)_{j-1}}{\frac{\gamma}{p_{betc}}\left(\frac{1}{p_i\gamma}+1\right)}\right)\right\}dt$$

and

$$\left(TON_{cat}\right)_j=\left(TON_{cat}\right)_{j-1}+\frac{2TOF_{cat,0,2}\left[1-p_i\left(\left(TON_{cat}\right)_{j-1}+2\frac{p_{betc,2}}{\gamma}\left\{\left(TON_{cat}\right)_{j-1}\right\}^2\right)\right]}{\left(1+2p_{bet}\left(TON_{cat}\right)_{j-1}+p_i\gamma\right)\left(1+4\frac{p_{betc,2}}{\gamma}\left(TON_{cat}\right)_{j-1}\right)+1}dt$$

3. Details on experimental data [S1]

Photosensitizer TATA⁺

The lifetime of $TATA^{+*}$ in water, at pH 4.5, was measured to be 14 ns,[S1] thus corresponding to $k_b = 7.14\ 10^7\ s^{-1}$.

The luminescence of $TATA^{+*}$ is quenched by the sacrificial donor HA^- with a rate constant $k_Q = 3.6\ 10^9\ M^{-1}s^{-1}$ as measured by a Stern-Volmer plot (reference S1, figure S19).

Using nanosecond transient absorption spectroscopy, it was shown that in the presence of sacrificial donor HA^- but in the absence of catalyst, the regeneration of $TATA^+$ can be fitted according to a second-order kinetics with a rate constant $k_{bet} = 3.26\ 10^9\ M^{-1}s^{-1}$ (figures S20 and S21 in reference S1).

In the presence of catalyst ($[Co^{II}(CR14)(OH_2)_2]^{2+}$, 200 µM), the decay of $TATA^\bullet$ could be fitted with a monoexponential function (figure S21 in reference S1), and taking into account the catalyst concentration, the electron transfer bimolecular rate constant was evaluated to $k_{ET} = 7.35\ 10^8\ M^{-1}s^{-1}$.

Nanosecond transient absorption spectroscopy also revealed the appearance and decay of the absorbance at 680 nm of the reduced Co(I) form (Cat_{red}). The decay of Co(I) with a rate constant of $k_{cat} = k_1\left[S_{ox}\right]_0 = 7.1\ 10^3\ s^{-1}$ (figure S22 in reference S1) was attributed to the catalyst protonation leading to the intermediate hydride (I) which does not accumulate.

As shown in reference S2, the decay of Co(I) actually exhibits a biexponential decay. The first component is attributed to formation of the hydride (see above) whereas the second slower component can be attributed to the back electron transfer from the oxidized sacrificial donor. The corresponding time constant is $\tau_2 = 3.9$ ms. We evaluate that the concentration of $SD^{\bullet+}$ in transient absorption spectroscopy is 10 µM. Hence, estimate: $k_{betc} = \frac{10^5}{\tau_2} = 2.6\ 10^7\ M^{-1}s^{-1}$

Photosensitizer Ru(bpy)₃²⁺

The lifetime of $Ru(bpy)_3^{2+*}$ was measured in water in the absence of sacrificial donor as 607 ns, [S2] thus corresponding to $k_b = 1.65\ 10^6\ s^{-1}$.

The luminescence of $Ru(bpy)_3^{2+*}$ is quenched by the sacrificial donor HA^- with a rate constant $k_Q = 2.5\ 10^7\ M^{-1}s^{-1}$ as given in reference S2.

The back electron transfer rate constant was evaluated as $3.5\ 10^9\ M^{-1}s^{-1}$ in reference S2.

The bimolecular electron transfer rate constant between $[Co^{II}(CR14)(OH_2)_2]^{2+}$ and $Ru(bpy)_3{}^+$ was evaluated in reference S**Error! Bookmark not defined.** to be $k_{ET} = 1.4\ 10^9\ M^{-1}s^{-1}$.

The catalytic rate is the same whatever the catalyst, hence $k_{cat} = k_1\left[S_{ox}\right]_0 = 7.1\ 10^3\ s^{-1}$.

Table S1. Rate constants

Photosensitizer	$TATA^+$	$Ru(bpy)_3^{2+}$
k_b (s^{-1})	$7.14\ 10^7$	$1.65\ 10^6$
k_Q ($M^{-1}s^{-1}$)	$3.6\ 10^9$	$2.5\ 10^7$
k_{bet} ($M^{-1}s^{-1}$)	$3.26\ 10^9$	$3.5\ 10^9$
k_{betc} ($M^{-1}s^{-1}$)	$2.6\ 10^7$	$2.6\ 10^7$
k_{ET} ($M^{-1}s^{-1}$)	$7.35\ 10^8$	$1.4\ 10^9$
$k_{cat} = k_1\left[S_{ox}\right]_0$ (s^{-1})	$7.1\ 10^3$	$7.1\ 10^3$
k_{abs} (s^{-1})	$3.16\ 10^3$	$1.3\ 10^3$

4. Simulations with Gepasi software (http://www.gepasi.org/)

Simulations have been performed with the free of charged kinetic simulator Gepasi software considering the same mechanism as the one corresponding to scheme S4 and the rate constants given in table S1. k_2 was chosen as very large (10^{10} s^{-1}) so that $k_2 \gg k_{cat} = k_1\left[S_{ox}\right]_0$ with $\left[S_{ox}\right]_0$ = 1 M. Initial concentrations are those indicated in caption of figure S1 with $[SD]_0 = [HA]+[A^-]$ = 0.1 M.

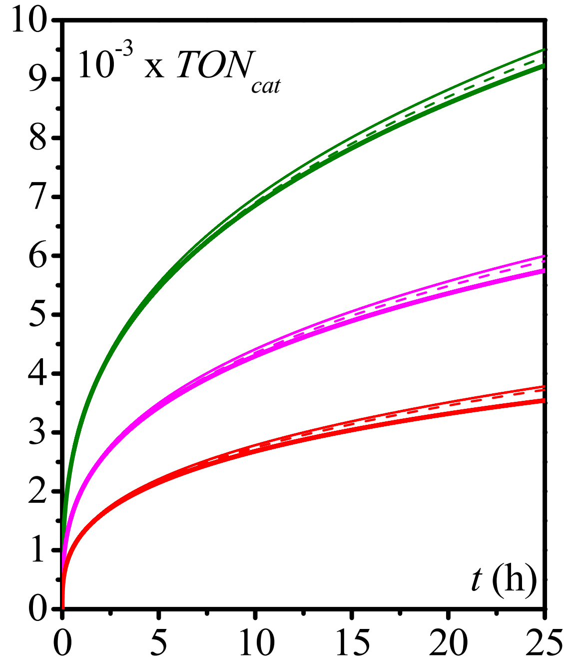


Figure S1. Photocatalytic hydrogen production (TON_{cat}) as a function of time from a deaerated 1 M acetate buffer (5 mL) at pH 4.5 under visible-light irradiation in the presence of $TATA^+$ (0.5 mM), NaHA/H_2A (0.1 M) and various concentration of the catalyst $[Co^{III}(CR14)Cl_2]^+$: 2.5 µM (green), 5 µM (magenta) and 10 µM (red). Dashed lines: simulations according to the analytical model (same as in figure 4 in the text). Full lines: simulations with Gepasi software with constant (thin lines) and non-constant concentration (thick lines) of the sacrificial donor.

5. References

S1. Gueret, R. ; Poulard, L. ; Oshinowo, M. ; Chauvin, J. ; Dahmane, M. ; Dupeyre, G. ; Lainé, P. P. ; Fortage, J. ; Collomb, M-N. Challenging the $[Ru(bpy)_3]^{2+}$ Photosensitizer with a Triazatriangulenium Robust Organic Dye for Visible-Light-Driven Hydrogen Production in Water. *ACS Catal.* **2018**, *8*, 3792-302.

S2. Gueret, R.; Castillo, C. E.; Rebarz, M.; Thomas, F.; Hargrove, A.-A.; Pécaut, J.; Sliwa, M.; Fortage, J.; Collomb, M.-N. Cobalt(III) Tetraaza-Macrocyclic Complexes as Efficient Catalyst for Photoinduced Hydrogen Production in Water: Theoretical Investigation of the Electronic Structure of the Reduced Species and Mechanistic Insight. *J. Photochem. Photobiol., B* **2015**, *152*, 82−94.