

## Supporting Information

# Investigating light-induced processes in organic covalent dye-catalyst assemblies for hydrogen evolution

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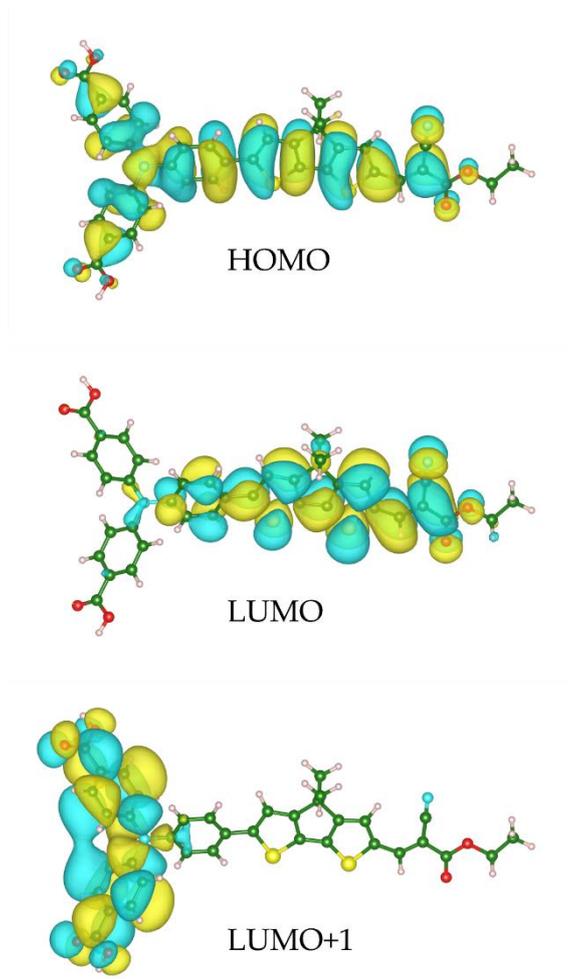
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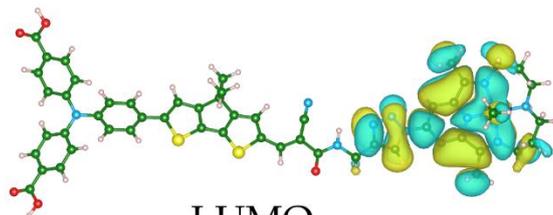


**Figure S1.** Frontier molecular orbitals of T2R obtained by DFT calculations.



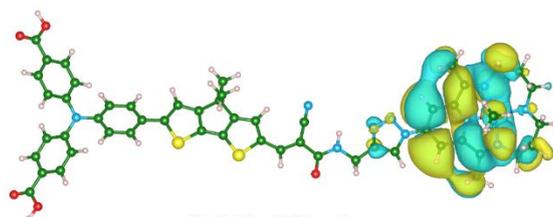
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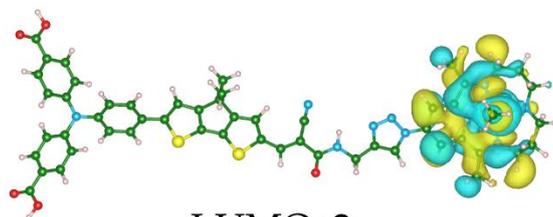
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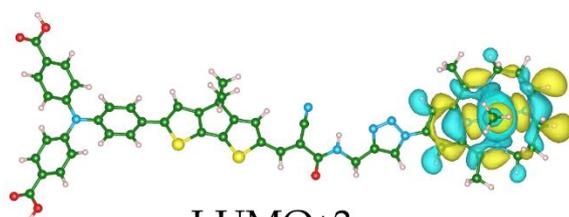
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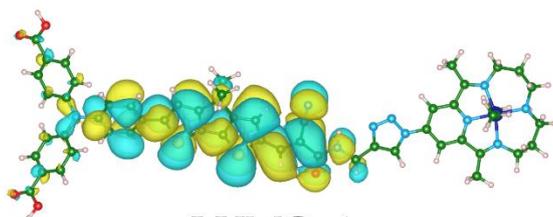
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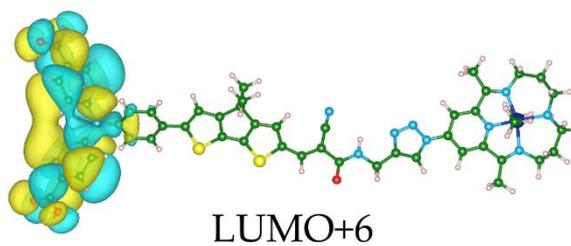
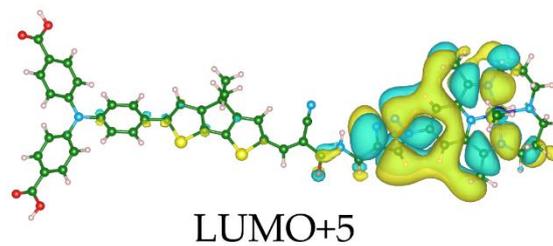


LUMO+3

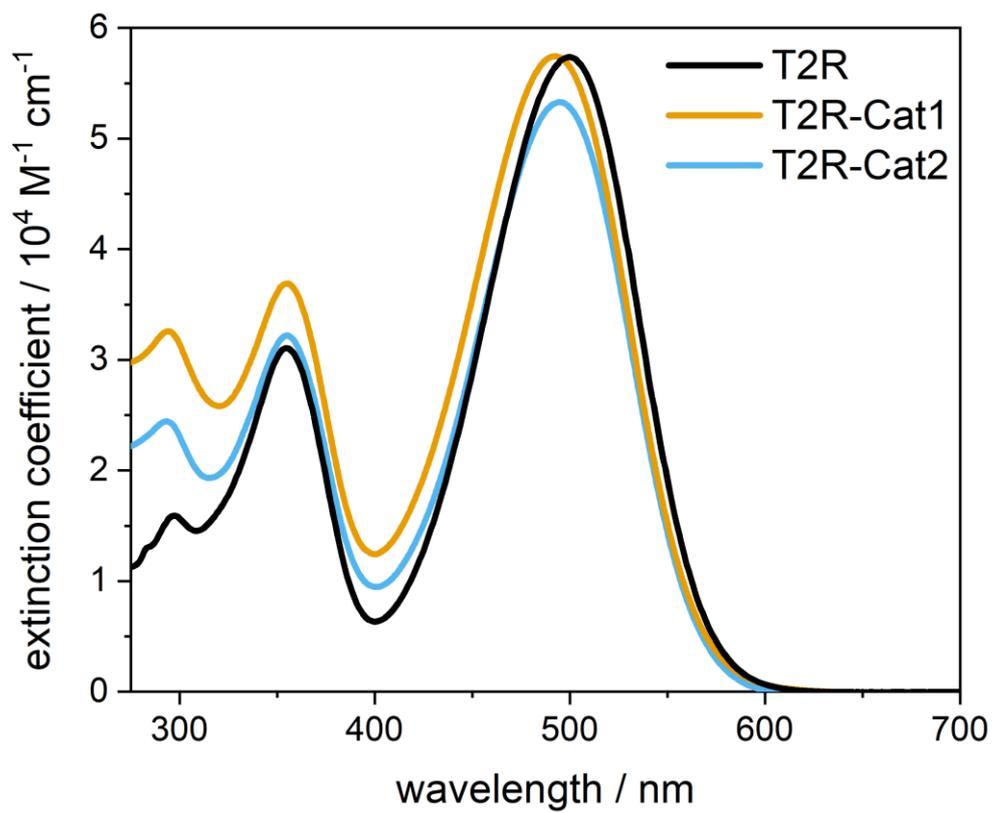
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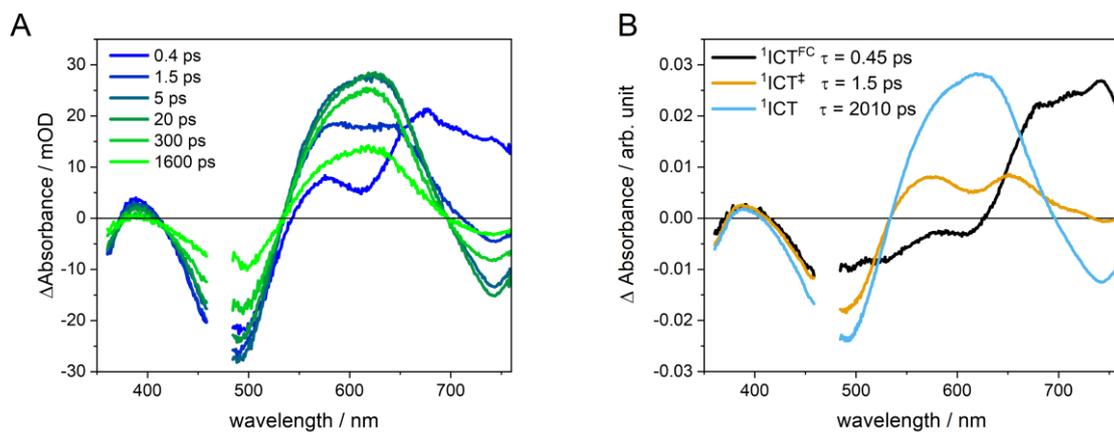
LUMO+4



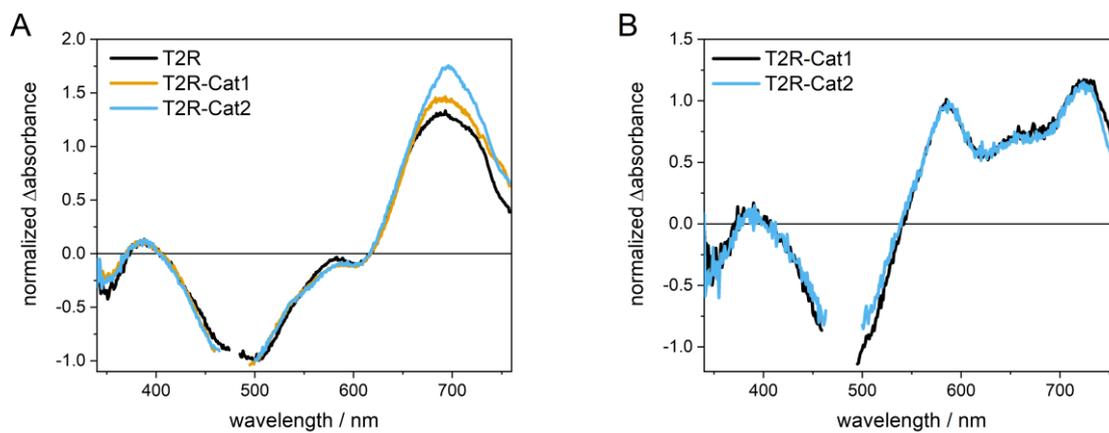
**Figure S2.** Frontier molecular orbitals of T2R-Cat1 obtained by DFT calculations.



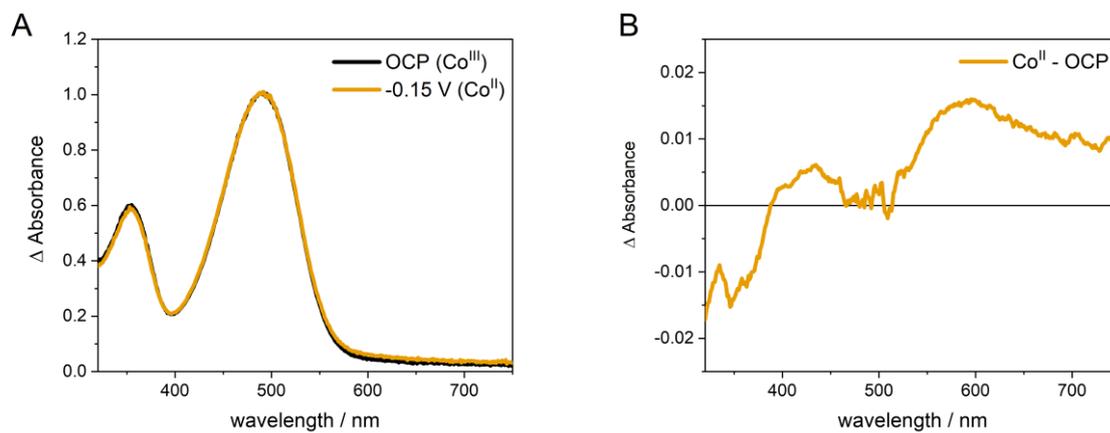
**Figure S3.** UV-Vis absorption spectra of T2R, T2R-Cat1 and T2R-Cat2 in MeOH.



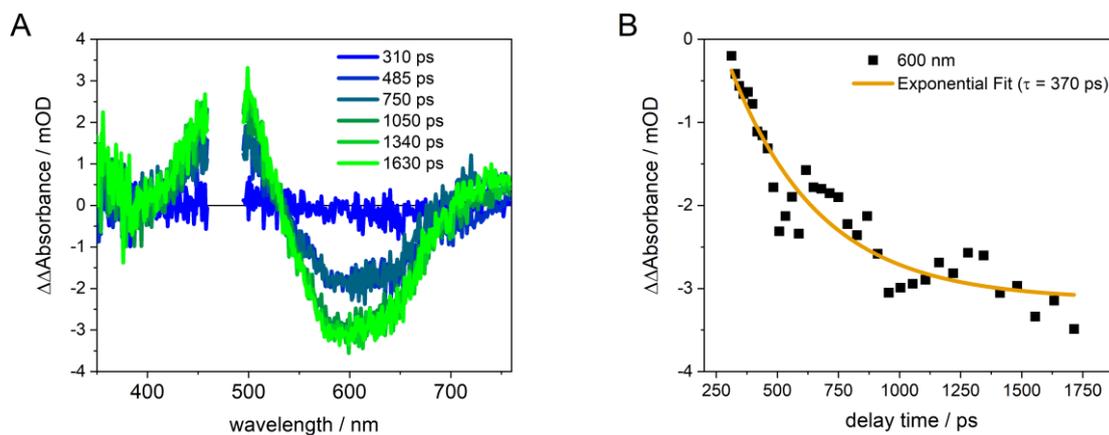
**Figure S4.** a) Transient absorption spectra of T2R in ACN, b) species-associated spectra obtained with a sequential three-component exponential fit; with the lifetimes of the species.



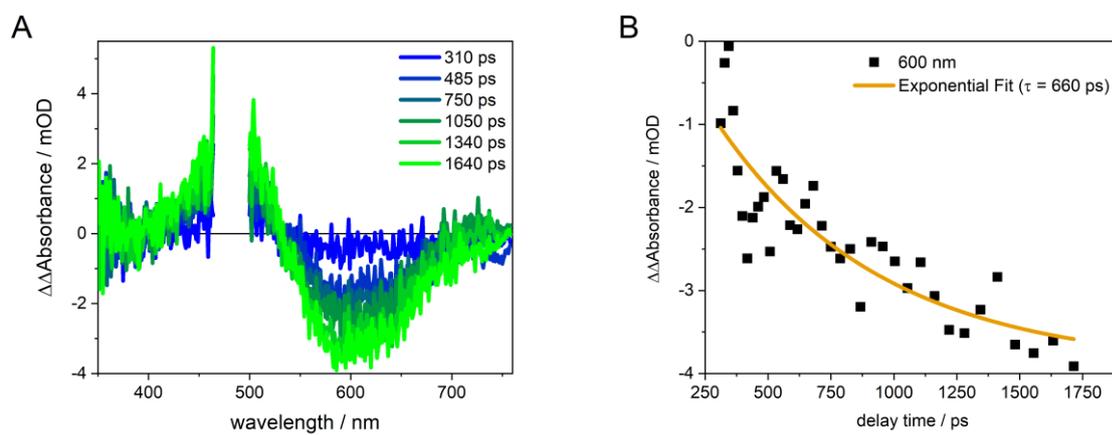
**Figure S5.** Transient absorption spectra at a) 0.4 ps and b) 1600 ps time delay in MeOH. The spectra at 0.4 ps were normalized at 500 nm and the spectra at 1600 ps were normalized at the maximum at 587 nm.



**Figure S6.** a) UV-Vis absorption spectra of T2R-Cat1 at open-circuit potential ( $\text{Co}^{\text{III}}$  state) and at  $-0.15\text{ V}$  vs. Ag wire applied potential (reduction of the cobalt complex to the  $\text{Co}^{\text{II}}$  state). b) Differential spectrum obtained by subtracting the OCP spectrum from the spectrum at  $-0.15\text{ V}$ .



**Figure S7.** a) Differential TA spectra of T2R-Cat1 in MeOH obtained by subtracting the spectrum recorded at 300 ps time delay and b) monoexponential fit of the data thus obtained at the maximum at 600 nm. The spectrum is the inverse spectrum of the T2R  $^1$ ICT state, confirming that the observed signal decay is caused by a return to the ground state from the thermalized singlet excited state of the dye T2R.



**Figure S8.** a) Differential TA spectra of T2R-Cat2 in MeOH obtained by subtracting the spectrum recorded at 300 ps time delay and b) monoexponential fit of the data thus obtained at the maximum at 600 nm. The spectrum is the inverse spectrum of the T2R  $^1$ ICT state, confirming that the observed signal decay is caused by a return to the ground state from the thermalized singlet excited state of the dye T2R.

**Table S1.** Photophysical and redox properties of Cat1, Cat2, T2R, T2R-Cat1 and T2R-Cat2.

		$\lambda_{\text{Abs}} \text{ (TPA)}$	$\epsilon \text{ (TPA)} / \text{M}^{-1}\cdot\text{cm}^{-1}$	$\lambda_{\text{Abs}} \text{ (ICT)}$	$\epsilon \text{ (ICT)} / \text{M}^{-1}\cdot\text{cm}^{-1}$	$\lambda_{\text{Em}}$	$\Phi^{520}$	$E_{\text{ox1}}^{\text{a)}} \text{ (Dye}^{+/0})$	$E_{\text{ox2}}^{\text{a)}} \text{ (Dye}^{2+/+})$	$E_{\text{red1}}^{\text{a)}} \text{ (Co}^{\text{III/II}})$	$E_{\text{red2}}^{\text{a)}} \text{ (Co}^{\text{II/I}})$	$E_{\text{red3}}^{\text{a)}} \text{ (Dye}^{0/-})$	$E_{0-0}^{\text{b)}}$	$\Delta G_1^{\text{c)}}$	$\Delta G_2^{\text{d)}}$
<b>Cat1</b>										-0.01	-0.51				
<b>Cat2</b>										-0.04 <sup>e)</sup>	-0.58 <sup>e)</sup>				
<b>T2R</b>	ACN	355	30570	498	60560										
	MeOH	355	31060	498	57374	674	0.25	1.05	1.23			-1.00	2.15		
<b>T2R-Cat1</b>	ACN	355	32580	493	55830										
	MeOH	355	36900	493	57435	660	0.02	1.00	1.15	0.03	-0.40	-1.08	2.17	-1.18	-0.75
<b>T2R-Cat2</b>	ACN	353	32750	490	57940										
	MeOH	355	32196	495	53287	663	0.08	1.02	1.19	0.04	-0.45	-1.10	2.17	-1.19	-0.70

- a) In V vs NHE.  $\frac{1}{2}(E_{\text{pc}^+} + E_{\text{pa}})$  for  $E_{\text{red1}}$  and  $E_{\text{red2}}$ ;  $E_{\text{pc}}$  for  $E_{\text{red3}}$ . The redox potentials were converted from  $\text{Fc}^{+/0}$  to NHE, obtained from the reduction potential considering  $E^\circ(\text{Fc}^{+/0}) = 0.53 \text{ V vs. NHE}$  in ACN,  $E^\circ(\text{Fc}^{+/0}) = 0.57 \text{ V vs. NHE}$  in DMF. Unless otherwise indicated, the data was recorded in DMF.
- b) 0–0 transition energy,  $E_{0-0}$ , in eV, estimated from the intercept of the normalized absorption and emission spectra.
- c) The Gibbs free energy in eV for the electron transfer from the excited dye to the Co(III) catalyst was calculated according to  $\Delta G_1 = e[E(\text{Dye}^{+/*}) - E(\text{Co}^{\text{III/II}})]$ , with  $E(\text{Dye}^{+/*}) = E(\text{Dye}^{+/0}) - E(0-0)$ .
- d) The Gibbs free energy in eV for the electron transfer from the reduced dye to the Co(II) catalyst was calculated according to  $\Delta G_2 = e[E(\text{Dye}^{+/*}) - E(\text{Co}^{\text{II/I}})]$ , with  $E(\text{Dye}^{+/*}) = E(\text{Dye}^{+/0}) - E(0-0)$ .
- e) In ACN

**Table S2.** Rates and characteristic time constants of samples excited at 480 nm.

	Kinetic rates / s <sup>-1</sup>					Time constants <sup>1</sup> / ps				
	k <sub>1</sub>	k <sub>2</sub>	k <sub>3</sub>	k <sub>4</sub>	k <sub>5</sub>	τ <sub>1</sub>	τ <sub>2</sub>	τ <sub>3</sub>	τ <sub>4</sub>	τ <sub>5</sub>
T2R	7.6 × 10 <sup>11</sup>	8.9 × 10 <sup>10</sup>	7.6 × 10 <sup>8</sup>			1.3	11	1320		
T2R-Cat1	1.3 × 10 <sup>12</sup>	1.5 × 10 <sup>11</sup>	1.4 × 10 <sup>9</sup>	6.5 × 10 <sup>9</sup>	<< 5 × 10 <sup>8</sup>	0.8	7	370	150	>> 2 ns
T2R-Cat2	1.1 × 10 <sup>12</sup>	1.5 × 10 <sup>11</sup>	1.5 × 10 <sup>9</sup>	5.8 × 10 <sup>9</sup>	<< 5 × 10 <sup>8</sup>	0.9	7	660	170	>> 2 ns

<sup>1</sup>: τ<sub>n</sub> = 1/k<sub>n</sub>