Electronic Supplementary Information

Water oxidation by a dye-catalyst diad in natural sunlight: timing and coordination of excitations and reactions across timescales of picoseconds to seconds

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1. **Reaction Scheme**

The reaction steps listed in Table S1 have the stoichiometries of the transformations of the species, written using the mnemonic dye – catalyst(oxidation state)-oxygen form when the dye is in the ground state, and dye-(dye electronic state) – catalyst(oxidation state)-oxygen form when the dye is in an electronically excited singlet state (X*, B* or Y*) or triplet state (TN*). Each step includes a marker species (in italics) which does not influence the chemistry being simulated, but allows the occurrences of that particular step to be counted. This enables a much deeper analysis of the simulation results.

Table S1. Complete reaction scheme used for the simulations.

Process	Process	Kinetic step	Rate coefficient [a]
1st catalytic cycle	Dye photoexcitation	Dye-cat(2)-OH2 => Dye-TN*-cat(2)-OH2 + *excitation-TN1*	18.3 s^{-1}
	Dye photoexcitation	Dye-cat(2)-OH2 => Dye-Y*-cat(2)-OH2 + *excitation-Y1*	4.28 s^{-1}
	Dye photoexcitation	Dye-cat(2)-OH2 => Dye-B*-cat(2)-OH2 + *excitation-B1*	13.2 s^{-1}
	Dye photoexcitation	Dye-cat(2)-OH2 => Dye-X*-cat(2)-OH2 + *excitation-X1*	22.8 s^{-1}
	Dye photoexcitation	Dye-cat(2)-OH2 => Dye-cat(2)-OH2 + *groundstatebleach-TN1*	18.3 s^{-1}
	Dye photoexcitation	Dye-cat(2)-OH2 => Dye-cat(2)-OH2 + *groundstatebleach-Y1*	4.28 s^{-1}
	Dye photoexcitation	Dye-cat(2)-OH2 => Dye-cat(2)-OH2 + *groundstatebleach-B1*	13.2 s^{-1}
	Dye photoexcitation	Dye-cat(2)-OH2 => Dye-cat(2)-OH2 + *groundstatebleach-X1*	22.8 s^{-1}
	Dye photoexcitation	Dye-TN*-cat(2)-OH2 => Dye-cat(2)-OH2 + *emission-TN1*	18.3 s^{-1}
	Dye photoexcitation	Dye-Y*-cat(2)-OH2 => Dye-cat(2)-OH2 + *emission-Y1*	4.28 s^{-1}
	Dye photoexcitation	Dye-B*-cat(2)-OH2 => Dye-cat(2)-OH2 + *emission-B1*	13.2 s^{-1}
	Dye photoexcitation	Dye-X*-cat(2)-OH2 => Dye-cat(2)-OH2 + *emission-X1*	22.8 s^{-1}
	Dye internal conversion	Dye-Y*-cat(2)-OH2 => Dye-B*-cat(2)-OH2 + *IC_B1*	2.4×10^{13} s^{-1}
	Dye internal conversion	Dye-B*-cat(2)-OH2 => Dye-X*-cat(2)-OH2 + *IC_X1*	2.4×10^{13} s^{-1}
	Dye intersystem crossing	Dye-X*-cat(2)-OH2 => Dye-TN*-cat(2)-OH2 + *ISC1*	4×10^{13} s^{-1}
	Dye photoexcitation	Dye-TN*-cat(2)-OH2 => Dye-TN*-cat(2)-OH2 + *esa-TN1*	117 s^{-1}
	Dye photoexcitation	Dye-Y*-cat(2)-OH2 => Dye-Y*-cat(2)-OH2 + *esa-Y1*	117 s^{-1}
	Dye photoexcitation	Dye-B*-cat(2)-OH2 => Dye-B*-cat(2)-OH2 + *esa-B1*	117 s^{-1}

	Dye photoexcitation	Dye-X*-cat(2)-OH2 => Dye-X*-cat(2)-OH2 + *esa-X1*	117 s^{-1}
	Dye radiative relaxation	Dye-TN*-cat(2)-OH2 => Dye-cat(2)-OH2 + *incoherentems-1*	$9.6x10^{4}$ s^{-1}
	Dye non-radiative relaxation	Dye-TN*-cat(2)-OH2 => Dye-cat(2)-OH2 + *nr-ems-1*	$2.6x10^{6}$ s^{-1}
	Dye – substrate injection	Dye-TN*-cat(2)-OH2 => Dye+-cat(2)-OH2 + *electron* + *injection-TN1*	$1.0x10^{12}$ s^{-1}
	Dye – substrate injection	Dye-Y*-cat(2)-OH2 => Dye+-cat(2)-OH2 + *electron* + *injection-Y1*	$1.0x10^{12}$ s^{-1}
	Dye – substrate injection	Dye-B*-cat(2)-OH2 => Dye+-cat(2)-OH2 + *electron* + *injection-B1*	$1.0x10^{12}$ s^{-1}
	Dye – substrate injection	Dye-X*-cat(2)-OH2 => Dye+-cat(2)-OH2 + *electron* + *injection-X1*	$1.0x10^{12}$ s^{-1}
	Dye-catalyst ^{electron} transfer	Dye+-cat(2)-OH2 => Dye-cat(3)-OH2 + *groundstate1*	6.9 x 10^{9} s^{-1} [1]
	Back electron transfer	Dye+-cat(2)-OH2 + electron => Dye-cat(2)-OH2 + *BETox1*	100 s^{-1} [2]
	Back electron transfer	Dye-cat(3)-OH2 + electron => Dye-cat(2)-OH2 + *BETcat1*	100 s^{-1} [2]
2^{nd} catalytic cycle	Dye photoexcitation	Dye-cat(3)-OH2 => Dye-TN*-cat(3)-OH2 + *excitation-TN2*	18.3 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OH2 => Dye-Y*-cat(3)-OH2 + *excitation-Y2*	4.28 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OH2 => Dye-B*-cat(3)-OH2 + *excitation-B2*	13.2 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OH2 => Dye-X*-cat(3)-OH2 + *excitation-X2*	22.8 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OH2 => Dye-cat(3)-OH2 + *groundstatebleach-TN2*	18.3 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OH2 => Dye-cat(3)-OH2 + *groundstatebleach-Y2*	4.28 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OH2 => Dye-cat(3)-OH2 + *groundstatebleach-B2*	13.2 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OH2 => Dye-cat(3)-OH2 + *groundstatebleach-X2*	22.8 s^{-1}
	Dye photoexcitation	Dye-TN*-cat(3)-OH2 => Dye-cat(3)-OH2 + *emission-TN2*	18.3 s^{-1}
	Dye photoexcitation	Dye-Y*-cat(3)-OH2 => Dye-cat(3)-OH2 + *emission-Y2*	4.28 s^{-1}
	Dye photoexcitation	Dye-B*-cat(3)-OH2 => Dye-cat(3)-OH2 + *emission-B2*	13.2 s^{-1}
	Dye photoexcitation	Dye-X*-cat(3)-OH2 => Dye-cat(3)-OH2 + *emission-X2*	22.8 s^{-1}
	Dye internal conversion	Dye-Y*-cat(3)-OH2 => Dye-B*-cat(3)-OH2 + *IC_B2*	$2.4x10^{13}$ s^{-1}
	Dye internal conversion	Dye-B*-cat(3)-OH2 => Dye-X*-cat(3)-OH2 + *IC_X2*	$2.4x10^{13}$ s^{-1}
	Dye intersystem crossing	Dye-X*-cat(3)-OH2 => Dye-TN*-cat(3)-OH2 + *ISC2*	4 x 10^{13} s^{-1}
	Dye photoexcitation	Dye-TN*-cat(3)-OH2 => Dye-TN*-cat(3)-OH2 + *esa-TN2*	117 s^{-1}

	Dye photoexcitation	Dye-Y*-cat(3)-OH2 => Dye-Y*-cat(3)-OH2 + *esa-Y2*	117 s^{-1}
	Dye photoexcitation	Dye-B*-cat(3)-OH2 => Dye-B*-cat(3)-OH2 + *esa-B2*	117 s^{-1}
	Dye photoexcitation	Dye-X*-cat(3)-OH2 => Dye-X*-cat(3)-OH2 + *esa-X2*	117 s^{-1}
	Dye radiative relaxation	Dye-TN*-cat(3)-OH2 => Dye-cat(3)-OH2 + *incoherentems-2*	$9.6x10^{4}$ s^{-1}
	Dye non-radiative relaxation	Dye-TN*-cat(3)-OH2 => Dye-cat(3)-OH2 + *nr-ems-2*	$2.6x10^{6}$ s^{-1}
	Dye – substrate injection	Dye-TN*-cat(3)-OH2 => Dye+-cat(3)-OH2 + *electron* + *injection-TN2*	$1.0x10^{12}$ s^{-1}
	Dye – substrate injection	Dye-Y*-cat(3)-OH2 => Dye+-cat(3)-OH2 + *electron* + *injection-Y2*	$1.0x10^{12}$ s^{-1}
	Dye – substrate injection	Dye-B*-cat(3)-OH2 => Dye+-cat(3)-OH2 + *electron* + *injection-B2*	$1.0x10^{12}$ s^{-1}
	Dye – substrate injection	Dye-X*-cat(3)-OH2 => Dye+-cat(3)-OH2 + *electron* + *injection-X2*	$1.0x10^{12}$ s^{-1}
	1 electron 2 proton transfer	Dye+-cat(3)-OH2 => Dye-cat(4)--O + 2 H+ + *protonrelease*	0.036 s^{-1} [3]
	Back electron transfer	Dye+-cat(2)-OH2 + electron => Dye-cat(2)-OH2 + *BETox1*	100 s^{-1} [2]
3rd catalytic cycle	Dye photoexcitation	Dye-cat(4)--O => Dye-TN*- cat(4)--O + *excitation-TN3*	18.3 s^{-1}
	Dye photoexcitation	Dye-cat(4)--O => Dye-Y*- cat(4)--O + *excitation-Y3*	4.28 s^{-1}
	Dye photoexcitation	Dye-cat(4)--O => Dye-B*- cat(4)--O + *excitation-B3*	13.2 s^{-1}
	Dye photoexcitation	Dye-cat(4)--O => Dye-X*- cat(4)--O + *excitation-X3*	22.8 s^{-1}
	Dye photoexcitation	Dye-cat(4)--O => Dye-cat(4)--O + *groundstatebleach-TN3*	18.3 s^{-1}
	Dye photoexcitation	Dye-cat(4)--O => Dye-cat(4)--O + *groundstatebleach-Y3*	4.28 s^{-1}
	Dye photoexcitation	Dye-cat(4)--O => Dye-cat(4)--O + *groundstatebleach-B3*	13.2 s^{-1}
	Dye photoexcitation	Dye-cat(4)--O => Dye-cat(4)--O + *groundstatebleach-X3*	22.8 s^{-1}
	Dye photoexcitation	Dye-TN*- cat(4)--O => Dye-cat(4)--O + *emission-TN3*	18.3 s^{-1}
	Dye photoexcitation	Dye-Y*- cat(4)--O => Dye-cat(4)--O + *emission-Y3*	4.28 s^{-1}
	Dye photoexcitation	Dye-B*- cat(4)--O => Dye-cat(4)--O + *emission-B3*	13.2 s^{-1}
	Dye photoexcitation	Dye-X*- cat(4)--O => Dye-cat(4)--O + *emission-X3*	22.8 s^{-1}
	Dye internal conversion	Dye-Y*- cat(4)--O => Dye-B*- cat(4)--O + *IC_B3*	$2.4x10^{13}$ s^{-1}
	Dye internal conversion	Dye-B*- cat(4)--O => Dye-X*- cat(4)--O + *IC_X3*	$2.4x10^{13}$ s^{-1}
	Dye intersystem crossing	Dye-X*- cat(4)--O => Dye-TN*- cat(4)--O + *ISC3*	$4 x 10^{13}$ s^{-1}

	Dye photoexcitation	Dye-TN*- cat(4)--O => Dye-TN*- cat(4)--O + *esa-TN3*	117 s^{-1}
	Dye photoexcitation	Dye-Y*- cat(4)--O => Dye-Y*- cat(4)--O + *esa-Y3*	117 s^{-1}
	Dye photoexcitation	Dye-B*- cat(4)--O => Dye-B*- cat(4)--O + *esa-B3*	117 s^{-1}
	Dye photoexcitation	Dye-X*- cat(4)--O => Dye-X*- cat(4)--O + *esa-X3*	117 s^{-1}
	Dye radiative relaxation	Dye-TN*- cat(4)--O => Dye-cat(4)--O + *incoherentems-3*	9.6x10^{4} s^{-1}
	Dye non-radiative relaxation	Dye-TN*- cat(4)--O => Dye-cat(4)--O + *nr-ems-3*	2.6x10^{6} s^{-1}
	Dye – substrate injection	Dye-TN*- cat(4)--O => Dye+-cat(4)--O + electron + *injection-TN3*	1.0x10^{12} s^{-1}
	Dye – substrate injection	Dye-Y*- cat(4)--O => Dye+-cat(4)--O + electron + *injection-Y3*	1.0x10^{12} s^{-1}
	Dye – substrate injection	Dye-B*- cat(4)--O => Dye+-cat(4)--O + electron + *injection-B3*	1.0x10^{12} s^{-1}
	Dye – substrate injection	Dye-X*- cat(4)--O => Dye+-cat(4)--O + electron + *injection-X3*	1.0x10^{12} s^{-1}
	Dye-catalyst electron transfer	Dye+-cat(4)--O => Dye-cat(5)--O + *groundstate3*	6.9 x 10^{9} s^{-1} [1]
	O-atom proton transfer	Dye-cat(5)--O => Dye-cat(3)-OOH + H+ + *OOformation*	0.0096 s^{-1} [4]
	Back electron transfer	Dye+-cat(4)--O + electron => Dye-cat(4)--O + *BETox3*	100 s^{-1} [2]
	Back electron transfer	Dye-cat(5)--O + electron => Dye-cat(4)--O + *BETcat3*	100 s^{-1} [2]
4th catalytic cycle	Dye photoexcitation	Dye-cat(3)-OOH => Dye-TN*-cat(3)-OOH + *excitation-TN4*	18.3 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OOH => Dye-Y*-cat(3)-OOH + *excitation-Y4*	4.28 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OOH => Dye-B*-cat(3)-OOH + *excitation-B4*	13.2 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OOH => Dye-X*-cat(3)-OOH + *excitation-X4*	22.8 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OOH => Dye-cat(3)-OOH + *groundstatebleach-TN4*	18.3 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OOH => Dye-cat(3)-OOH + *groundstatebleach-Y4*	4.28 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OOH => Dye-cat(3)-OOH + *groundstatebleach-B4*	13.2 s^{-1}
	Dye photoexcitation	Dye-cat(3)-OOH => Dye-cat(3)-OOH + *groundstatebleach-X4*	22.8 s^{-1}
	Dye photoexcitation	Dye-TN*-cat(3)-OOH => Dye-cat(3)-OOH + *emission-TN4*	18.3 s^{-1}
	Dye photoexcitation	Dye-Y*-cat(3)-OOH => Dye-cat(3)-OOH + *emission-Y4*	4.28 s^{-1}
	Dye photoexcitation	Dye-B*-cat(3)-OOH => Dye-cat(3)-OOH + *emission-B4*	13.2 s^{-1}
	Dye photoexcitation	Dye-X*-cat(3)-OOH => Dye-cat(3)-OOH + *emission-X4*	22.8 s^{-1}

	Dye internal conversion	Dye-Y*-cat(3)-OOH => Dye-B*-cat(3)-OOH + *IC_B4*	$2.4x10^{13}$ s^{-1}
	Dye internal conversion	Dye-B*-cat(3)-OOH => Dye-X*-cat(3)-OOH + *IC_X4*	$2.4x10^{13}$ s^{-1}
	Dye intersystem crossing	Dye-X*-cat(3)-OOH => Dye-TN*-cat(3)-OOH + *ISC4*	4 x 10^{13} s^{-1}
	Dye photoexcitation	Dye-TN*-cat(3)-OOH => Dye-TN*-cat(3)-OOH + *esa-TN4*	117 s^{-1}
	Dye photoexcitation	Dye-Y*-cat(3)-OOH => Dye-Y*-cat(3)-OOH + *esa-Y4*	117 s^{-1}
	Dye photoexcitation	Dye-B*-cat(3)-OOH => Dye-B*-cat(3)-OOH + *esa-B4*	117 s^{-1}
	Dye photoexcitation	Dye-X*-cat(3)-OOH => Dye-X*-cat(3)-OOH + *esa-X4*	117 s^{-1}
	Dye radiative relaxation	Dye-TN*-cat(3)-OOH => Dye-cat(3)-OOH + *incoherentems-4*	$9.6x10^{4}$ s^{-1}
	Dye non-radiative relaxation	Dye-TN*-cat(3)-OOH => Dye-cat(3)-OOH + *nr-ems-4*	$2.6x10^{6}$ s^{-1}
	Dye – substrate injection	Dye-TN*-cat(3)-OOH => Dye+-cat(3)-OOH + electron + *injection-TN4*	$1.0x10^{12}$ s^{-1}
	Dye – substrate injection	Dye-Y*-cat(3)-OOH => Dye+-cat(3)-OOH + electron + *injection-Y4*	$1.0x10^{12}$ s^{-1}
	Dye – substrate injection	Dye-B*-cat(3)-OOH => Dye+-cat(3)-OOH + electron + *injection-B4*	$1.0x10^{12}$ s^{-1}
	Dye – substrate injection	Dye-X*-cat(3)-OOH => Dye+-cat(3)-OOH + electron + *injection-X4*	$1.0x10^{12}$ s^{-1}
	Dye-catalyst electron transfer	Dye+-cat(3)-OOH => Dye-cat(4)-OO + H+ + *groundstate4*	6.9 x 10^{9} s^{-1} [1]
	Oxygen release	Dye-cat(4)-OO => Dye-cat(2)-OH2 + O2 + *watersplitting*	7.5 x 10^{-4} s^{-1} [4]
	Back electron transfer	Dye+-cat(3)-OOH + electron => Dye-cat(3)-OOH + *BETox4*	100 s^{-1} [2]
	Back electron transfer	Dye-cat(4)-OO + electron => Dye-cat(3)-OOH + *BETcat4*	100 s^{-1} [2]

[a] Rate coefficients for dye excitations calculated assuming dye-catalyst complexes are adsorbed inside a nanoparticulate TiO_2 matrix, including optical scattering. All optical transitions are pseudo-first order in absorbed photon flux. All dye photophysical and charge injection rate coefficients are from Ref [5].

2. Additional figures

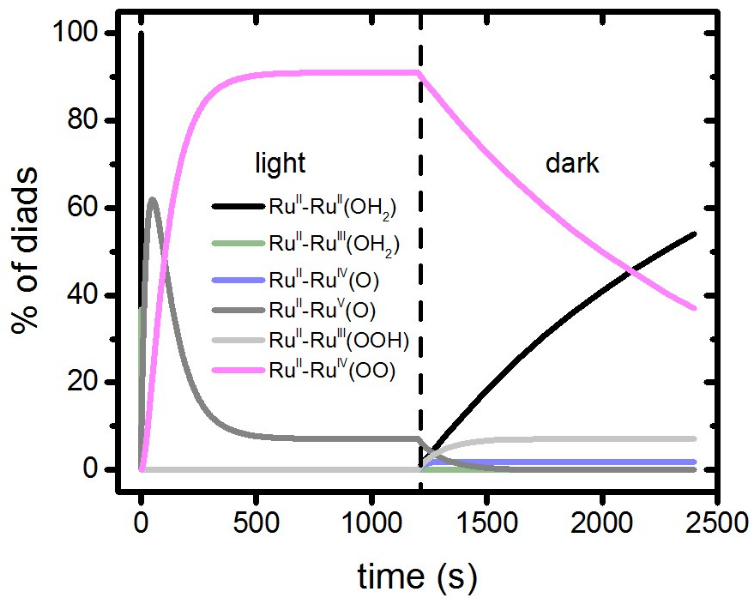

Figure S1. Linear y axis version of Figure 2c, main manuscript. Predictions by simulations in a 1200s light – 1200s dark sequence, diads present with dye in the Ru^{II} state. The colors correspond to the species present in each catalytic stage, Figure 1, main manuscript.

3. References

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