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Supporting Information

Panchromatic Dirhodium Photocatalysts for Dihydrogen Generation with Red Light

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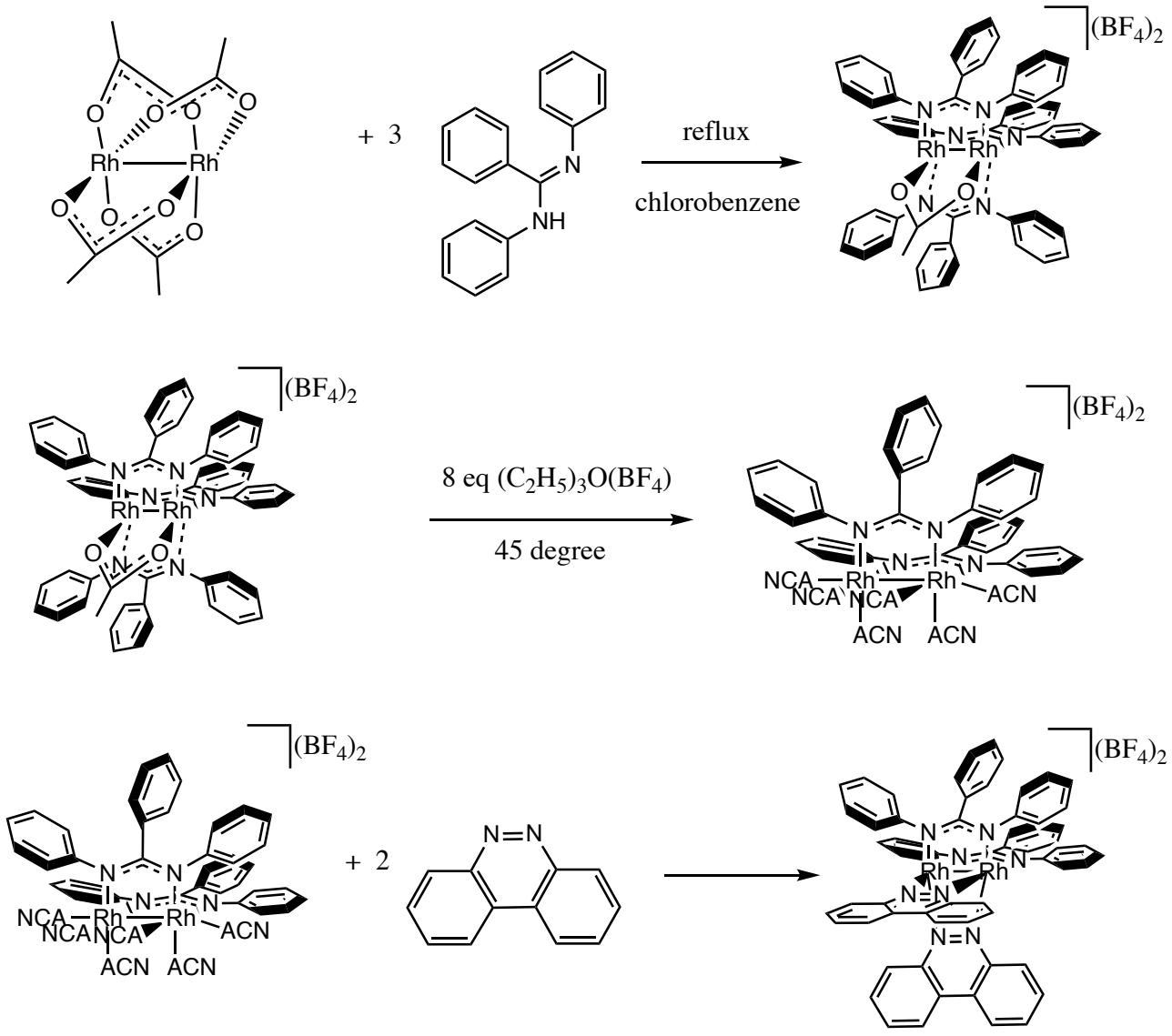
Table S1. Crystal data and structure refinement for **1**.[a]

Empirical formula	$C_{68}H_{55}B_2F_8N_{11}Rh_2$
Molecular formula	$C_{66}H_{52}N_{10}Rh2$, 2(BF_4), C_2H_3N
Formula weight	1405.67
Temperature	150.0 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 14.2611(7) Å α= 90°. b = 37.3119(18) Å β= 115.4260(10)°. c = 14.5988(7) Å γ = 90°.
Volume	7015.7(6) Å
Z	4
Density (calculated)	1.331 Mg/m^3
Absorption coefficient	0.538 mm^{-1}
F(000)	2848
Crystal size	0.243 x 0.228 x 0.069 mm^3
Crystal color, habit	Brown Plate
Theta range for data collection	2.914 to 26.403°.
Index ranges	-17<=h<=17, -46<=k<=46, -18<=l<=18
Reflections collected	135826
Independent reflections	14354 [R(int) = 0.0437, R(sigma) = 0.0227]
Completeness to theta = 25.000°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.0932 and 0.0651
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14354 / 0 / 823
Goodness-of-fit on F^2	1.283
Final R indices [I>2sigma(I)]	R1 = 0.0564, wR2 = 0.1113
R indices (all data)	R1 = 0.0628, wR2 = 0.1135
Extinction coefficient	n/a
Largest diff. peak and hole	0.863 and -1.285 e.$Å^{-3}$

[a]Due to unmodelable solvent disorder, Platon SQUEEZE was used to remove the electron density from the lattice due to the disordered solvent contribution. Solvent appeared to be a mix of Acetonitrile and Diethyl Ether. Six voids were found with approximately 28 electrons in four of the voids and 76 electrons in two of the voids.



Scheme S1. Synthetic scheme for the preparation of complex **1**.

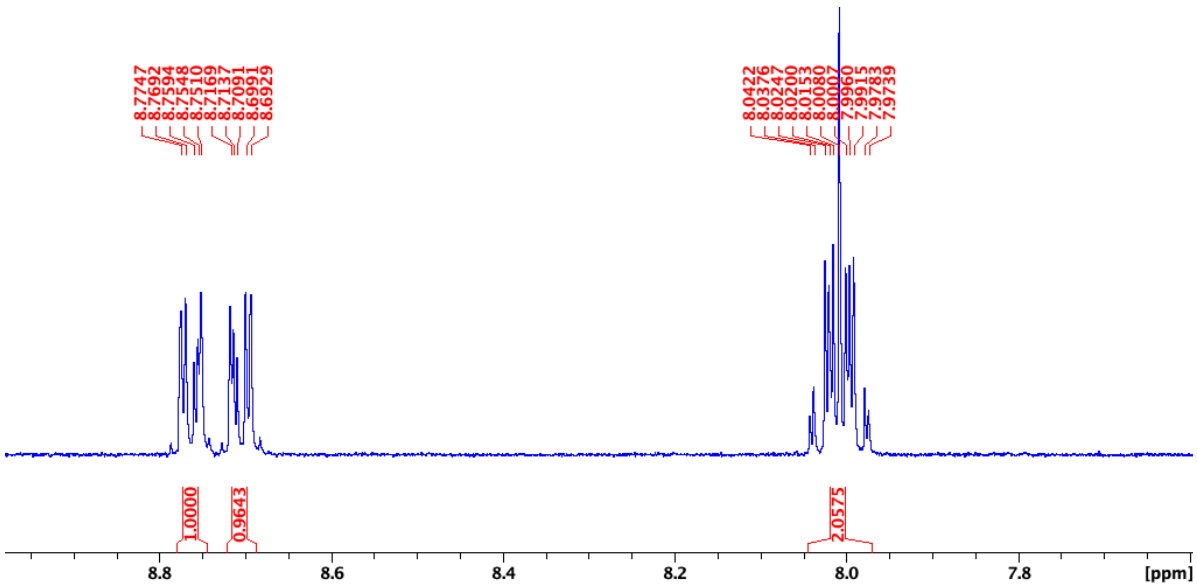


Figure S1. ^{1}H NMR spectrum of free bncn ligand in CD_3CN (400 MHz).

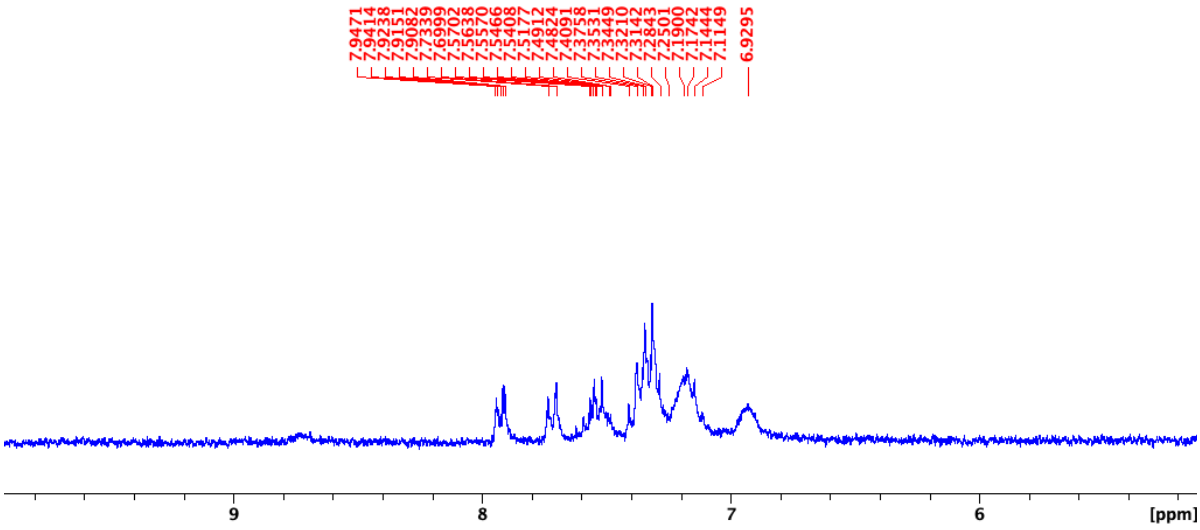


Figure S2. ^{1}H NMR spectrum of free DPhB ligand in CD_3CN (250 MHz).

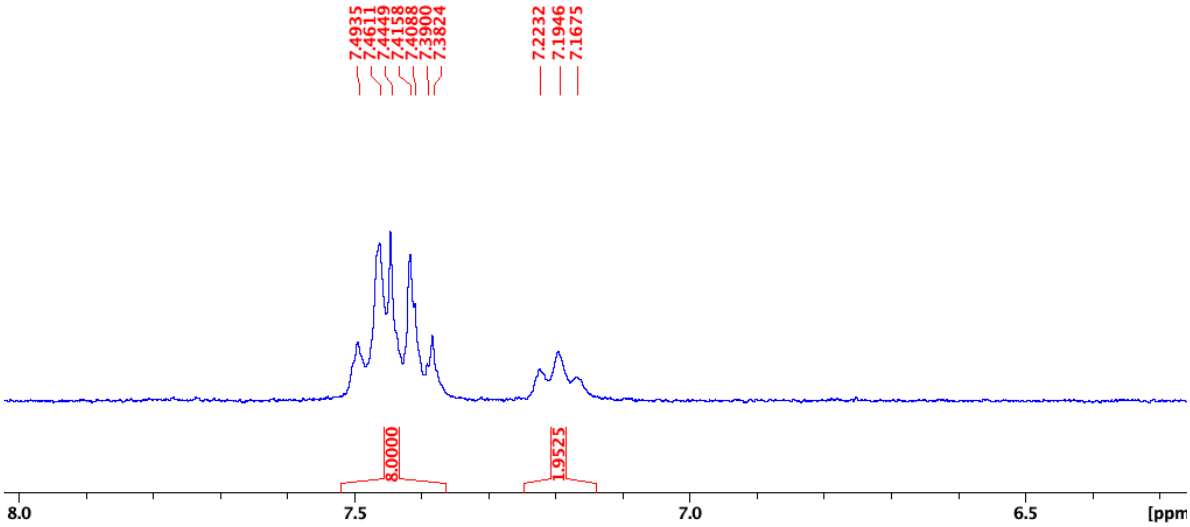


Figure S3. ^{1}H NMR spectrum of free DPhTA ligand in $(CD_3)_2O$ (400 MHz).

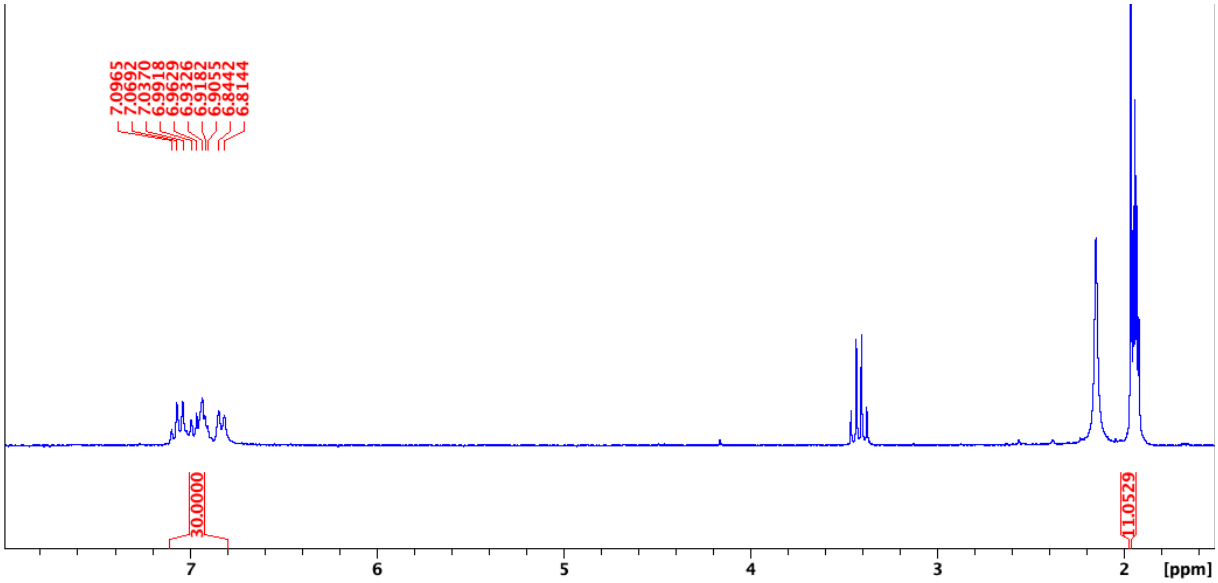


Figure S4. ^{1}H NMR spectrum of *cis*-$[Rh_2(DPhB)_2(CH_3CN)_6][BF_4]_2$ in CD_3CN (400 MHz).

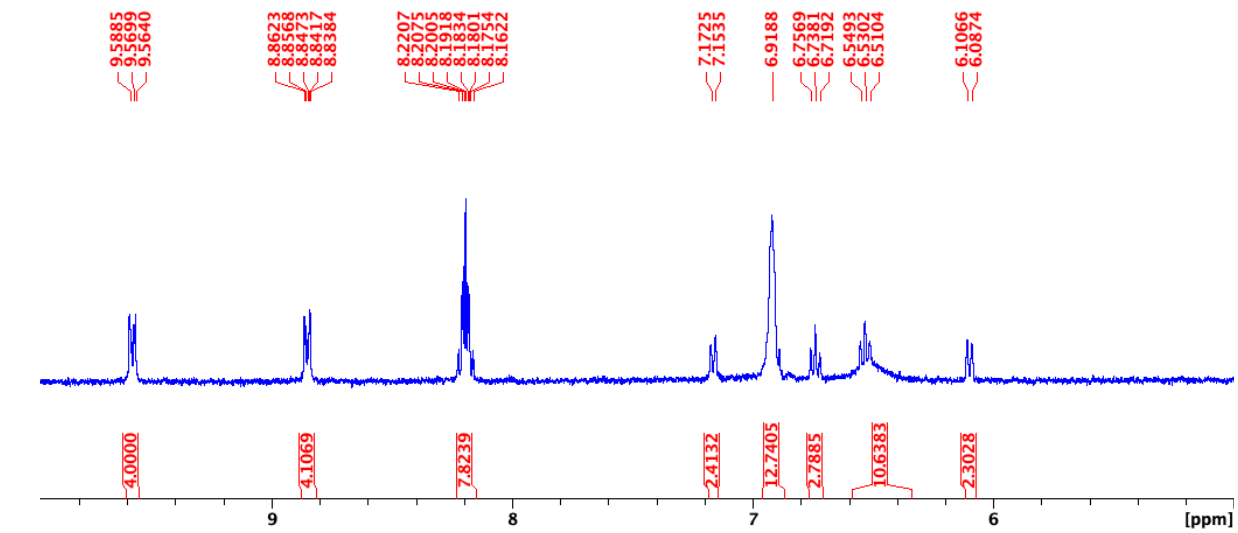


Figure S5. ^{1}H NMR spectrum of complex **1** in CD_3CN (400 MHz).

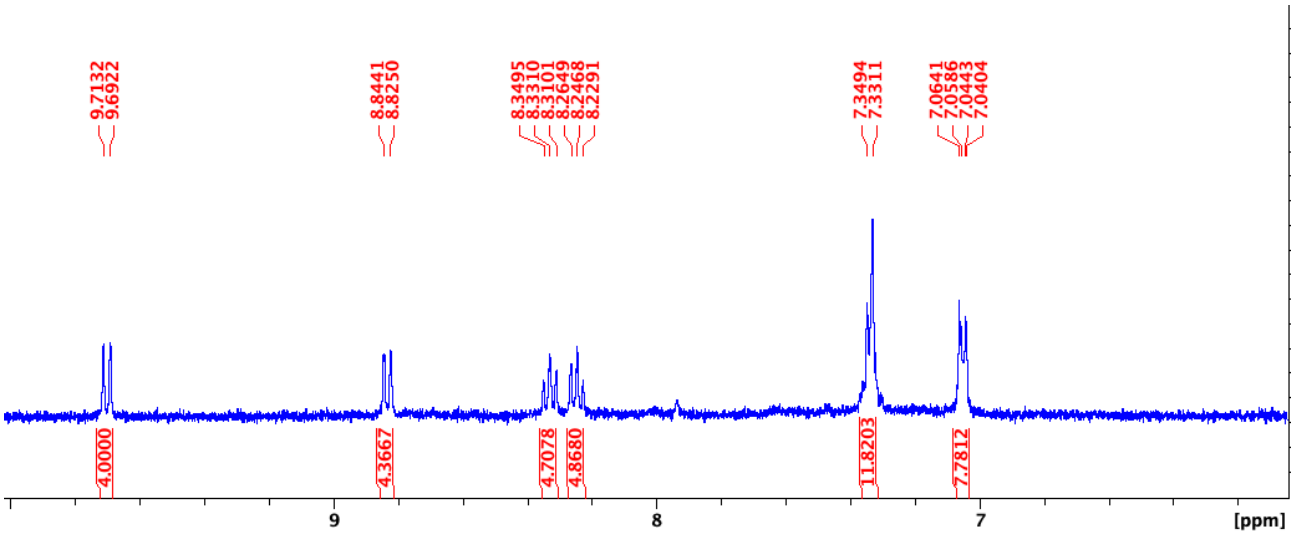


Figure S6. ^{1}H NMR spectrum of complex **2** in CD_3CN (400 MHz).

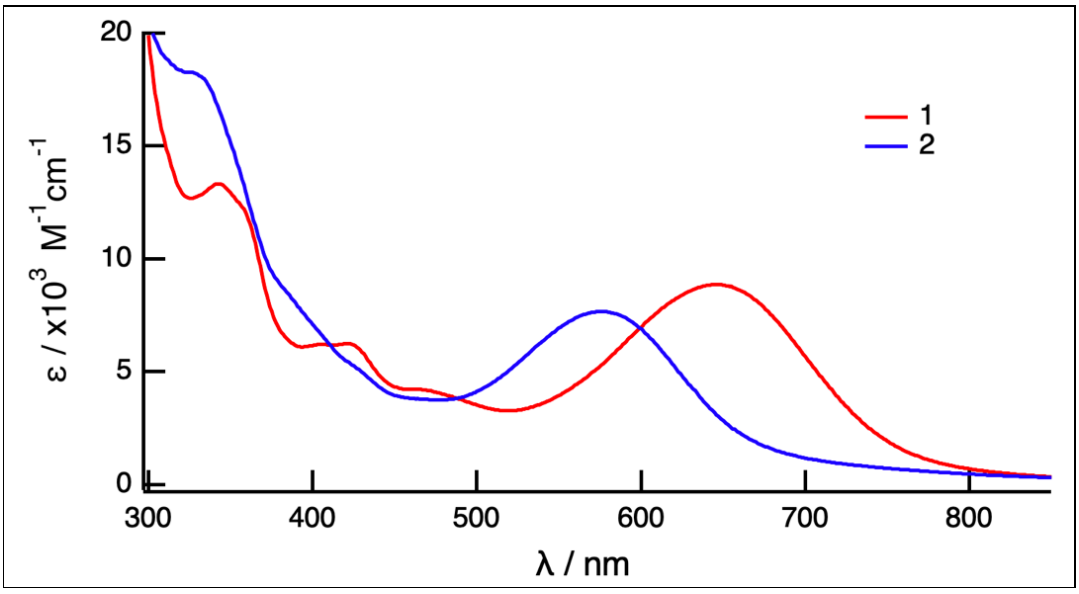


Figure S7. Electronic absorption of **1** and **2** recorded in CH_3CN.

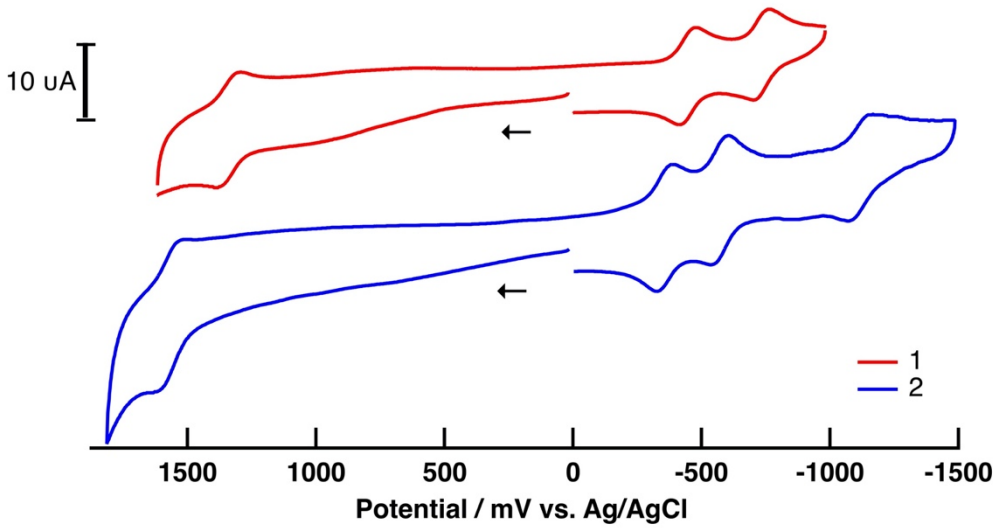


Figure S8. Cyclic Voltammogram of 0.5 mM **1** and **2** in 0.1 M $TBAPF_6$ CH_3CN (0.1 M $TBAPF_6$, scan rate: 200 mV/s).

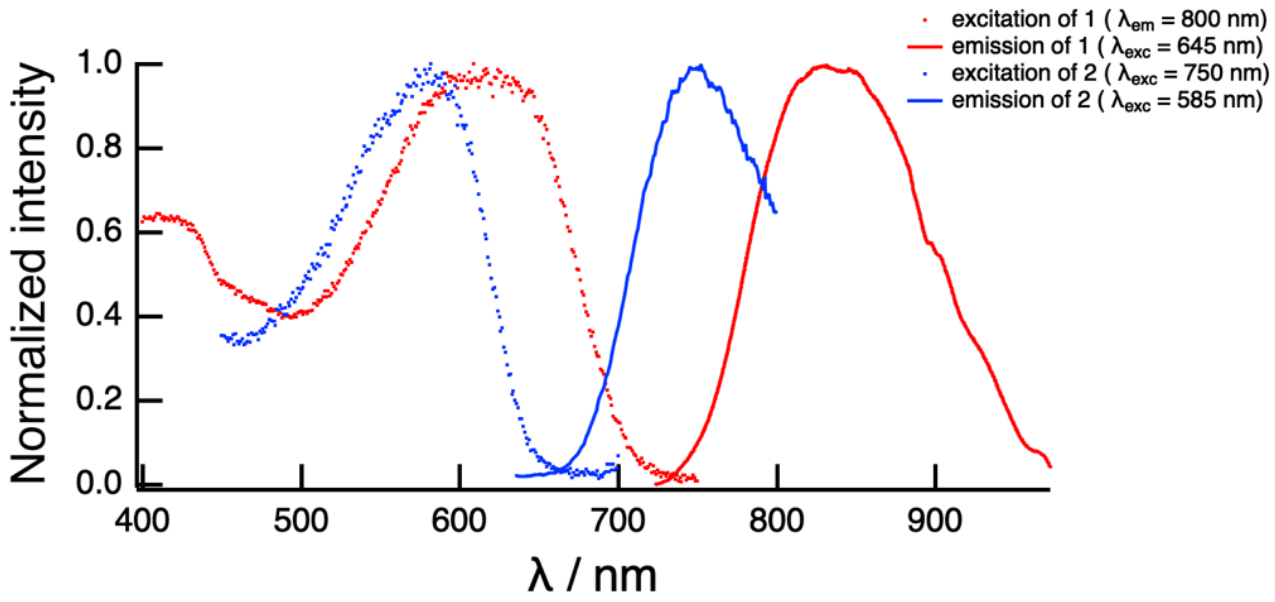


Figure S9. Emission (solid lines) and excitation (dashed lines) spectra of **1** and **2** in CH_3CN at 77 K.

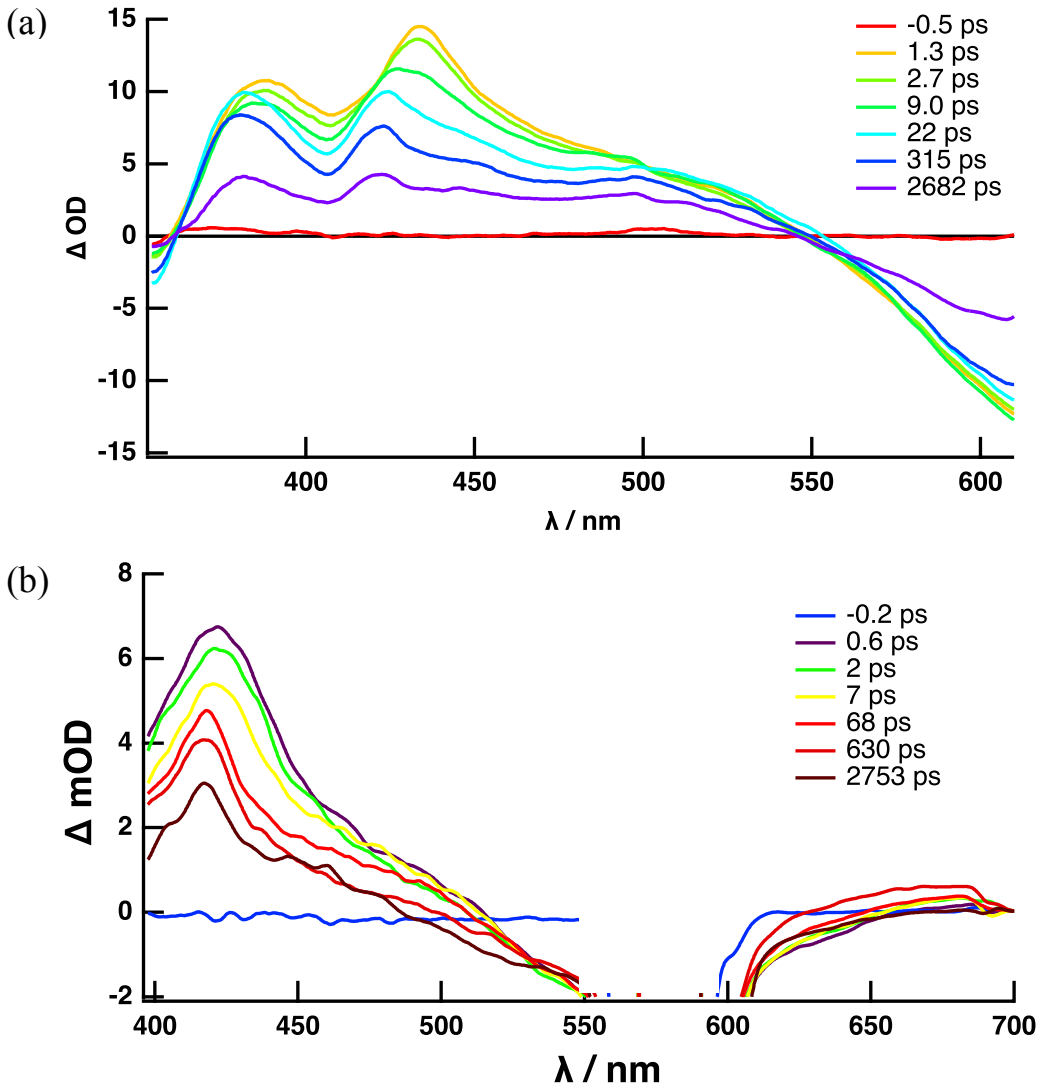


Figure S10. Femtosecond transient absorption spectra of (a) **1** (λ_{exc} = 650 nm, 2.5 μJ) and (b) **2** (λ_{exc} = 580 nm, 2.5 μJ) in CH_3CN.

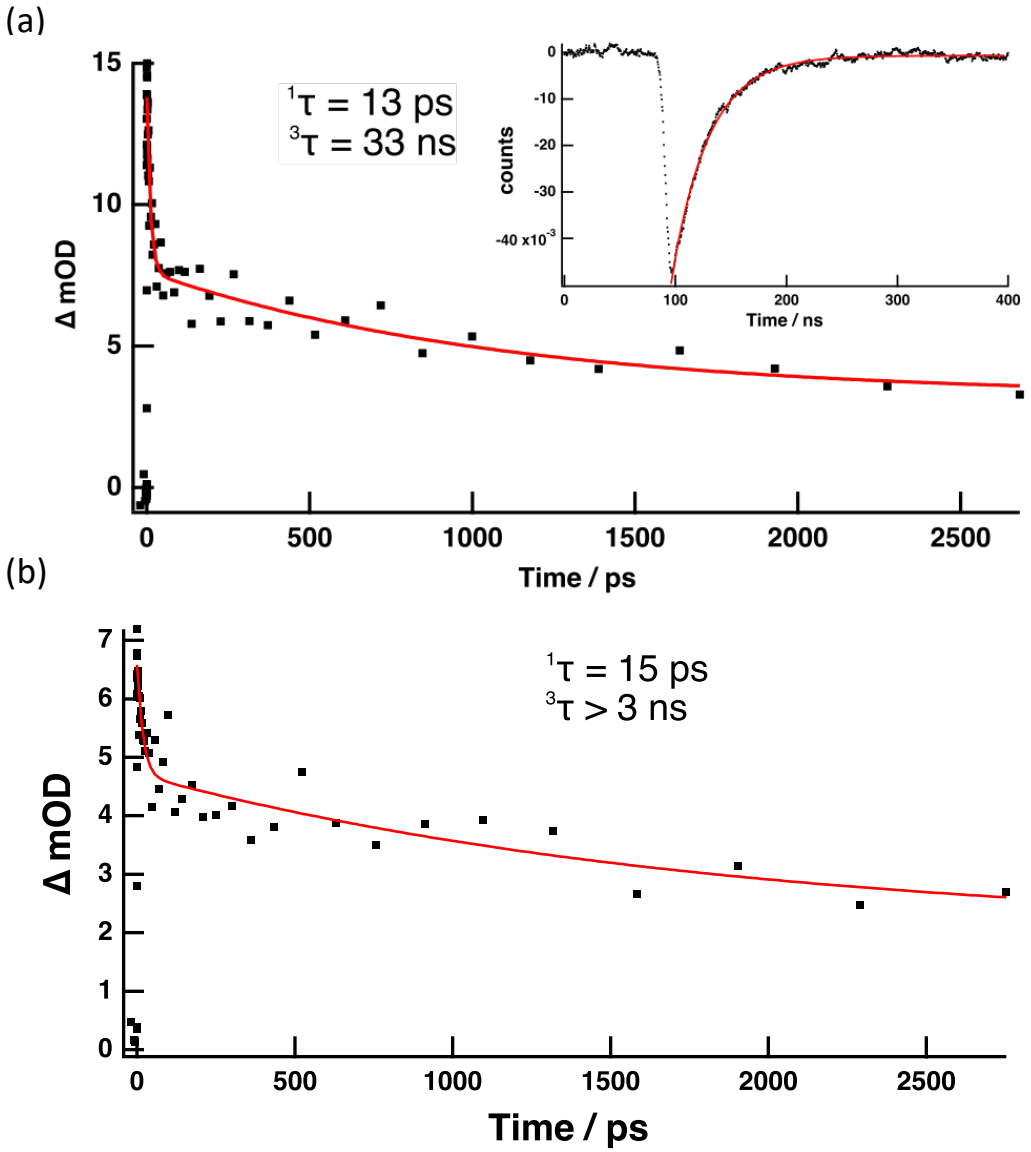


Figure S11. Kinetic traces of transient absorption signals of (a) **1** at 433 nm for the short component and at 640 nm for the long component (inset) and of (b) **2** at 416 nm.

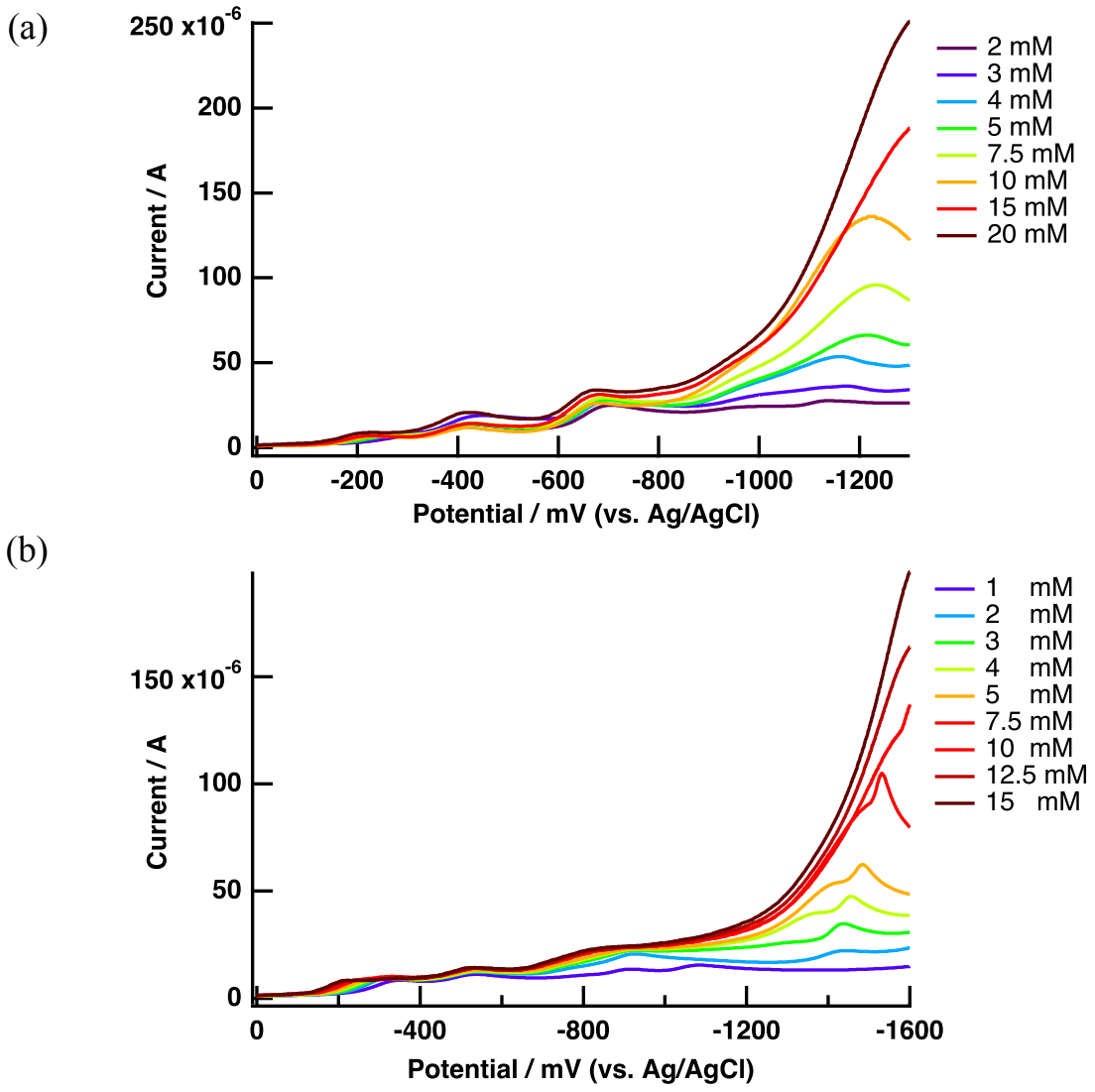


Figure S12. Linear sweep voltammetry of (a) **1** and (b) **2** with the addition of increasing amounts of TsOH in DMF (scan rate: 200 mV/s).

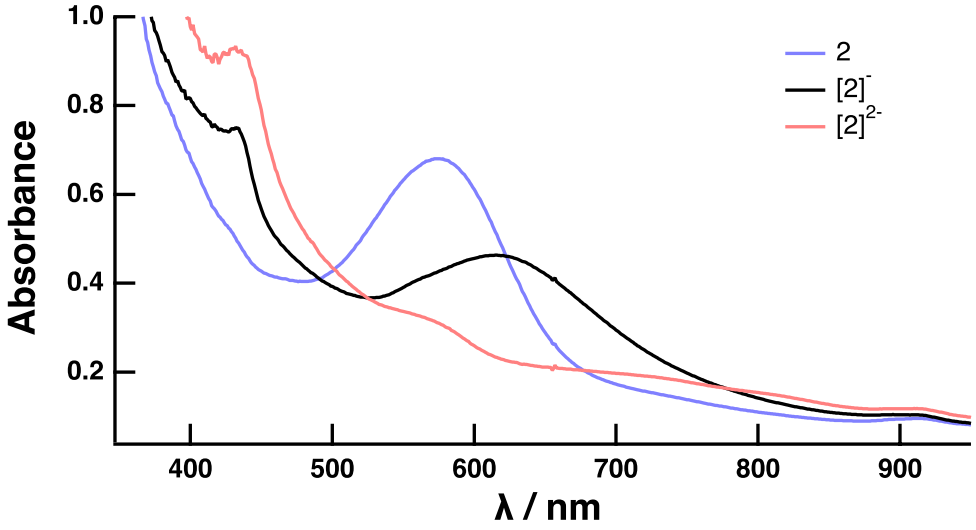


Figure S13. Absorption spectra of the one- and two-electron reduced species generated through chemical reduction of **2** with one or two equivalents of cobaltocene, respectively, in DMF.

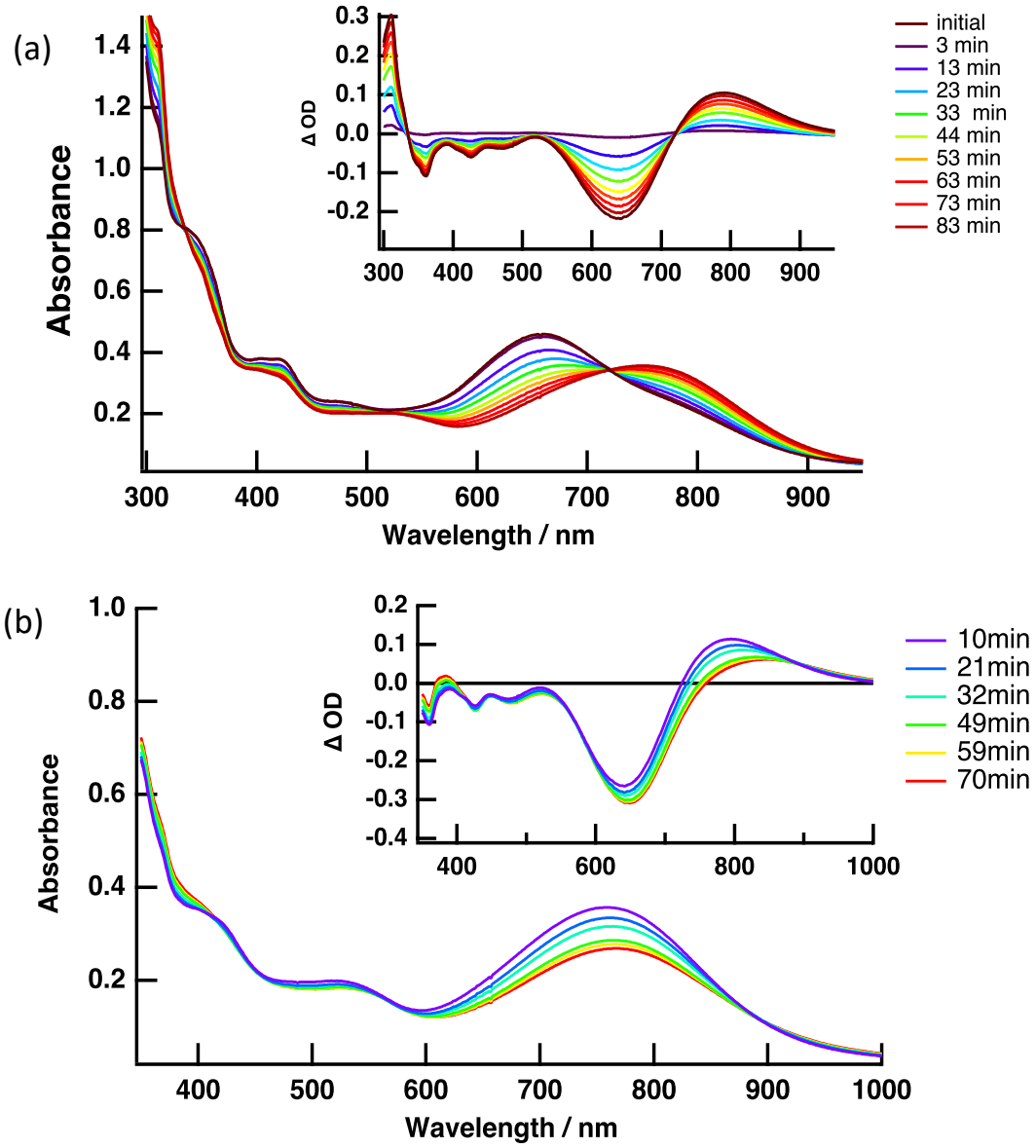


Figure S14. Absorption spectra of **1** collected under applied potential of (a) –0.5 V and (b) –0.9 V *vs* Ag/AgCl in DMF (0.1 $TBABF_4$). Inset: difference spectra.

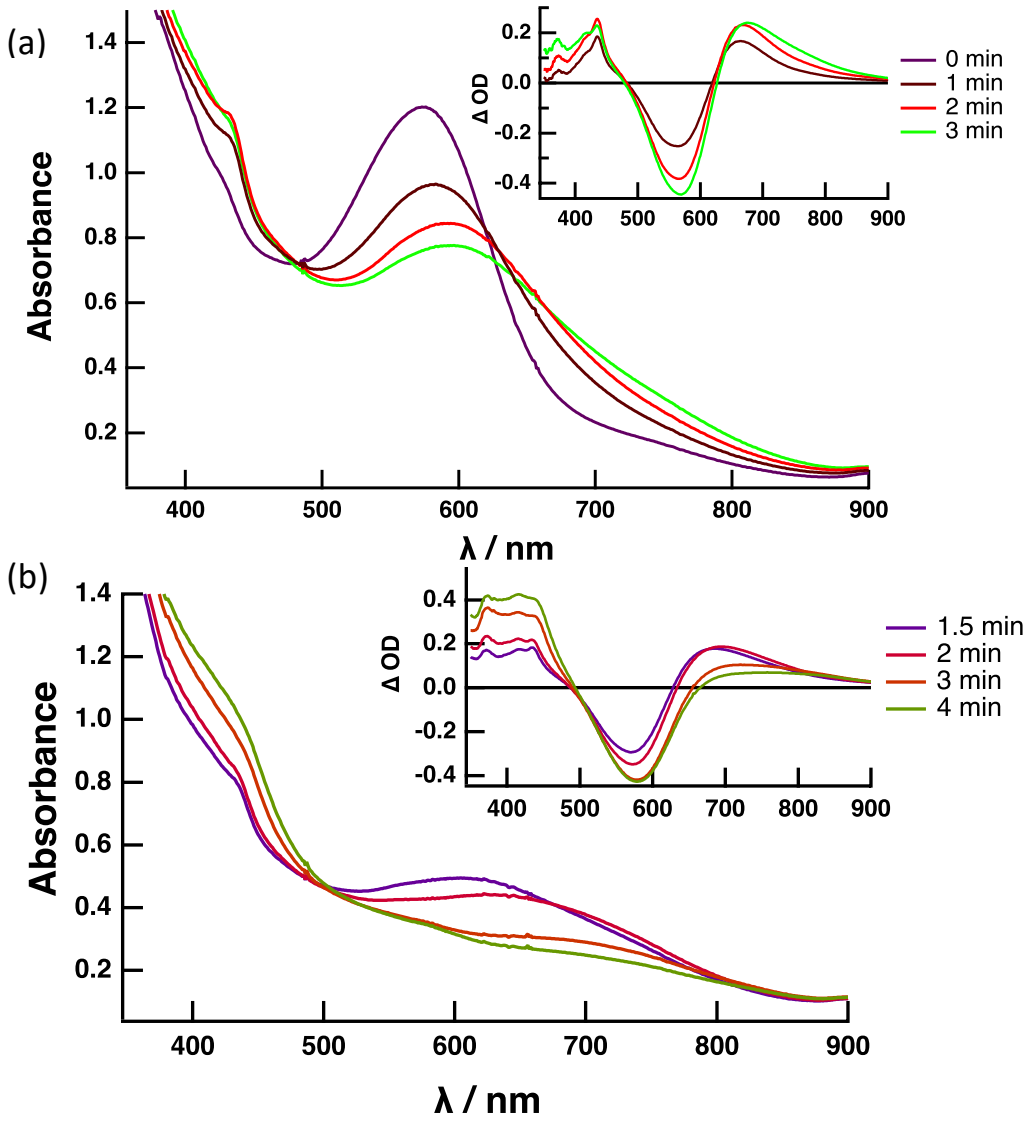


Figure S15. Absorption spectra of **2** collected under applied potentials of (a) –0.42 V and (b) –0.80 V *vs* Ag/AgCl in DMF (0.1 $TBABF_4$). Inset: difference spectra.

Table S2. control experiments on photocatalytic H_2 evolution with **1** and **2** for 4 h in DMF.

No.	sensitizer	Donor	light	acid	Turnover number
1	1 (64 uM)	30 mM BNAH	655nm	0.1 M TsOH	70
2	1	30 mM BNAH	—	0.1 M TsOH	—
3	1	—	655nm	0.1 M TsOH	—
4	1	30 mM BNAH	655nm	—	—
5	2 (200 uM)	30 mM BNAH	655nm	0.1 M TsOH	15
6	2	30 mM BNAH	—	0.1 M TsOH	—
7	2	—	655nm	0.1 M TsOH	—
8	2	30 mM BNAH	655nm	—	—

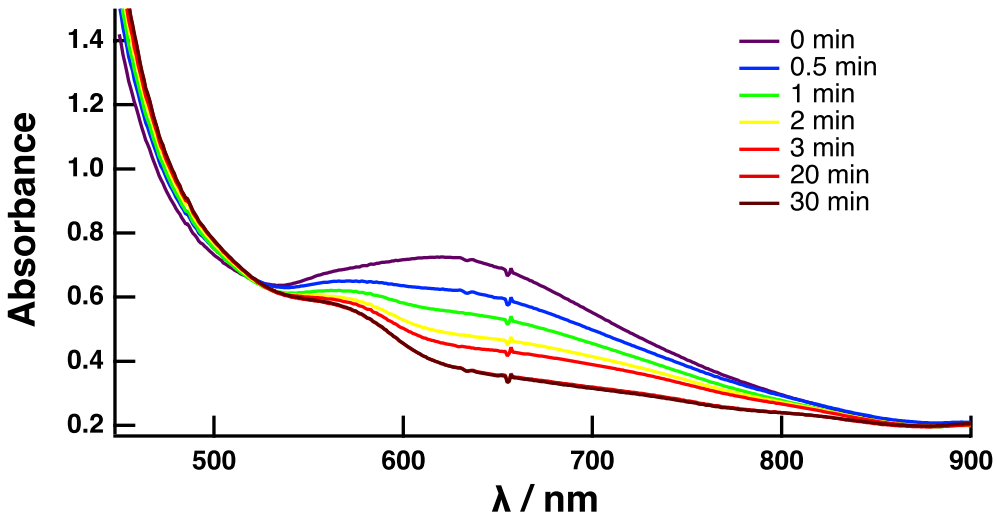


Figure S16. Changes in absorption spectra of **[2]**$^{-}$ as a function of irradiation time (λ_{irr} = 655 nm) in DMF in the presence of 30 mM BNAH.

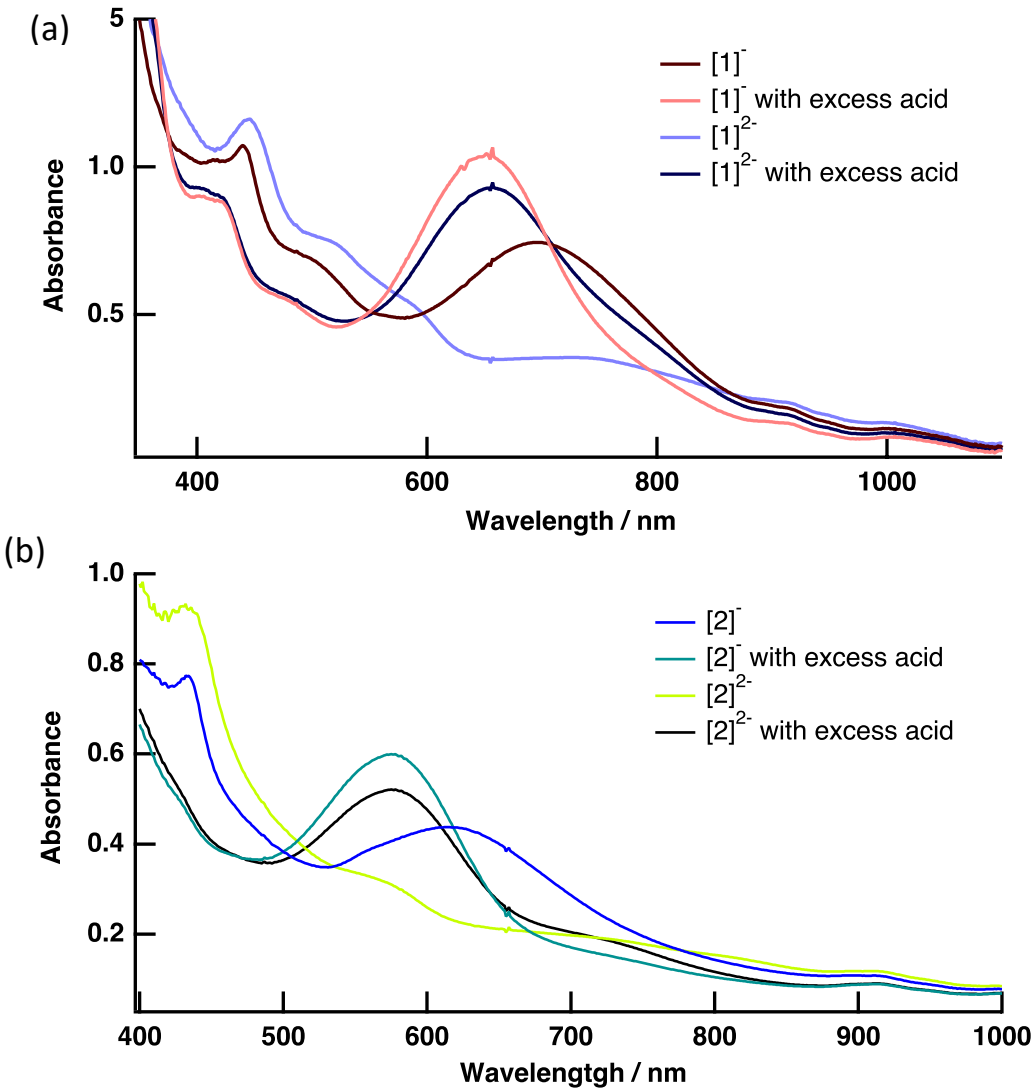


Figure S17. Changes to the absorption spectra of the one- and two-electron reduced (a) **1** and (b) **2** generated through the addition of 1 eq and 2 eq of cobaltocene in DMF, respectively upon the addition of excess TsOH.

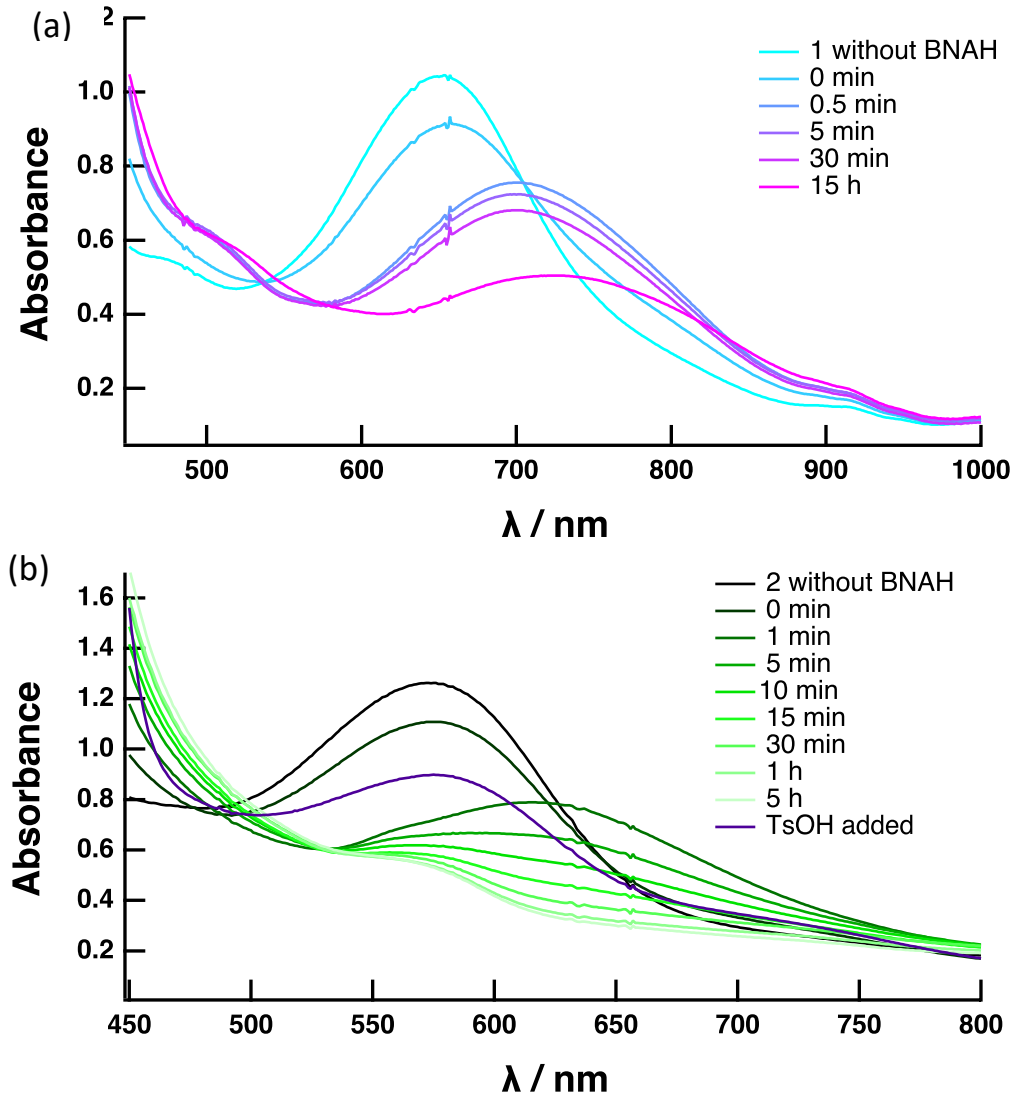


Figure S18. Changes of the absorption spectra of (a) **1** and (b) **2** upon irradiation (λ_{irr} = 655 nm) in DMF solution containing 30 mM BNAH, followed by the addition of excess 0.1 M of TsOH after 24 h irradiation.

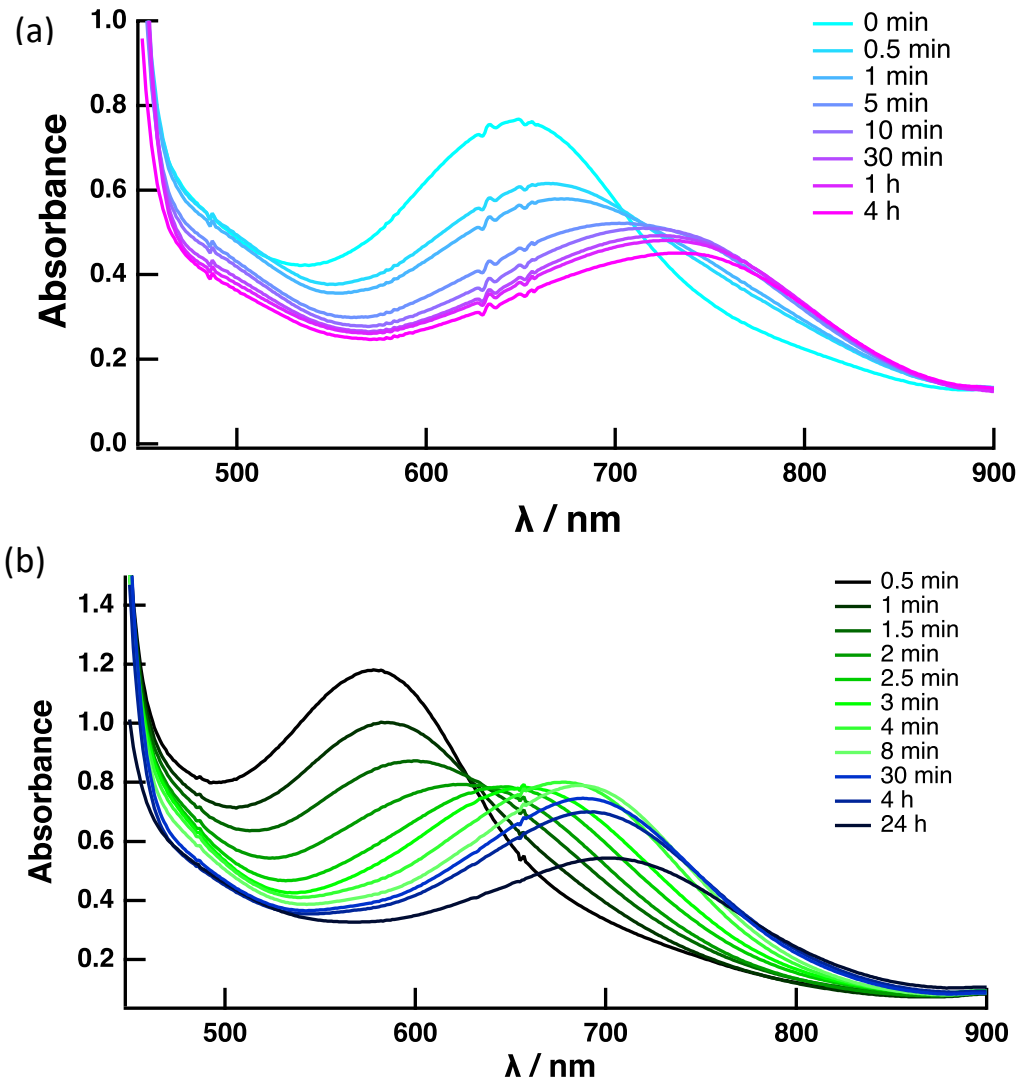


Figure S19. Changes in absorption spectra of the photocatalytic systems (30 mM BMAH, 0.1 M TsOH in 3 mL DMF) of (a) **1** and (b) **2** upon irradiation (λ_{irr} = 655 nm).

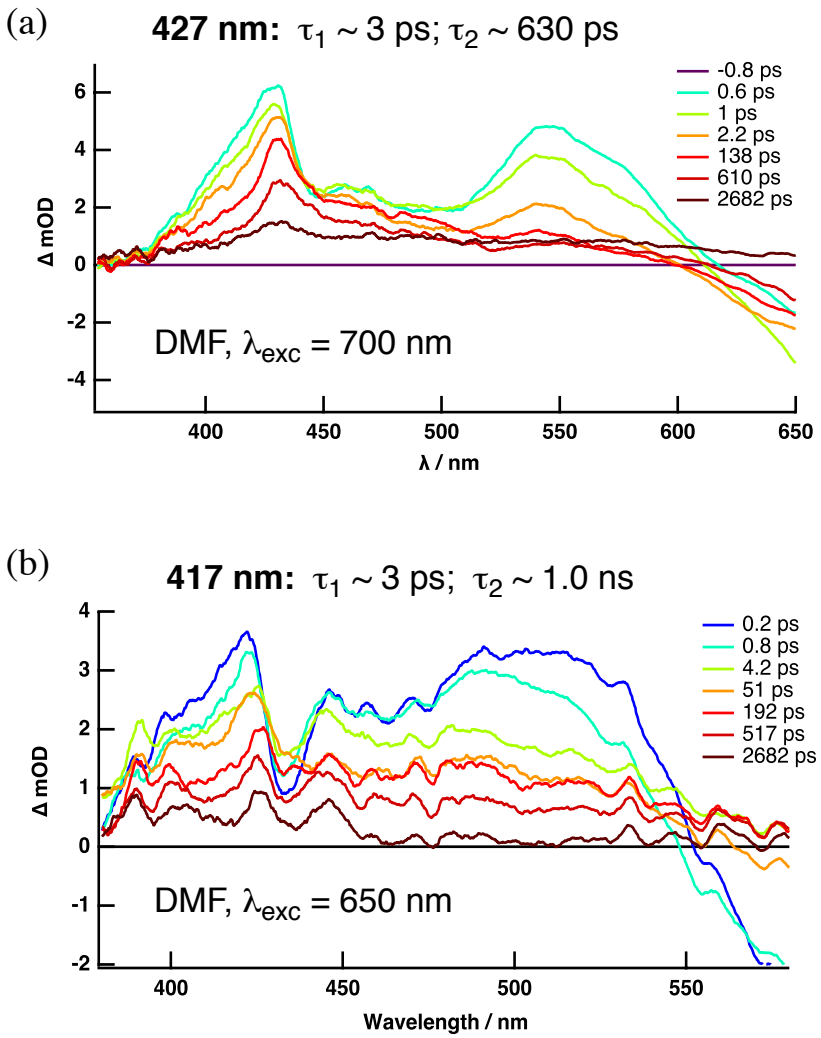


Figure S20. Ultrafast transient absorption spectra the one-electron reduced complexes (a) [**1**]$^{-}$ and (b) [**2**]$^{-}$ in DMF obtained by the treatment with 1 eq of cobaltocene (IRF ~ 85 fs).

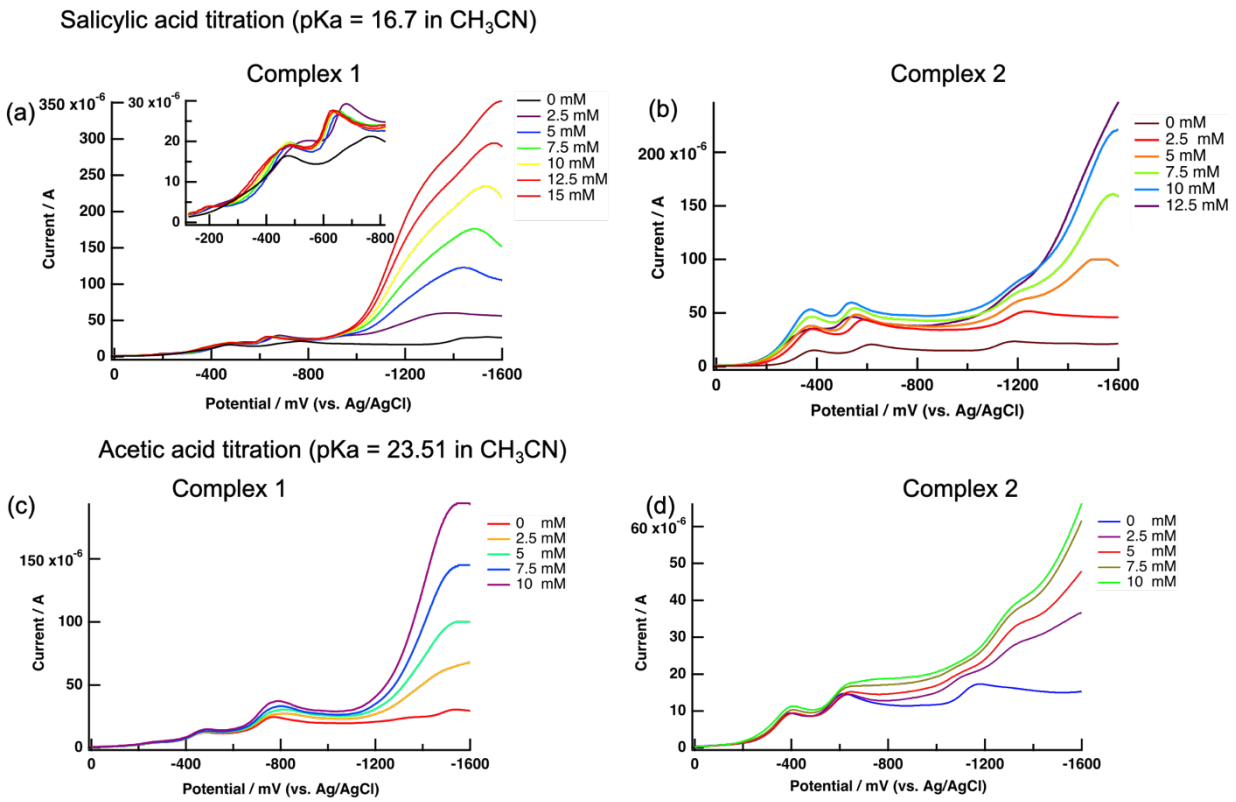


Figure S21. Linear sweep voltammetry of **1** and **2** with the addition of increasing amounts of (a) and (b) salicylic acid and (c) and (d) acetic acid in MeCN (scan rate = 200 mV/s).