

Enhanced photo-electrochemical responses through photo-responsive ruthenium complexes on ITO nanoparticle surface

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Table S1. TD-DFT data calculated for 1-Cl, 1-H₂O and for the geometric isomers of 2-Cl and 2-H₂O

Compound	State	λ (calcd.) (nm)	λ (exp.) (nm)	$f/a.u.$	MO transition assignment ^a
1-Cl	S ₀ → S ₇	465.22	486.0	0.1000	HOMO-1 → LUMO (19.6%) HOMO → LUMO+1 (15.2%)
1-H ₂ O	S ₀ → S ₃	461.28	479.0	0.0188	HOMO-2 → LUMO (29.9%) HOMO → LUMO+1 (16.0%)
2-Cl ^b	S ₀ → S ₁₃	464.99	488.0 ^c	0.1392	HOMO-2 → LUMO+1 (6.3%) HOMO-3 → LUMO (6.3%)
2-Cl ^c	S ₀ → S ₁₄	464.44	488.0 ^c	0.1199	HOMO-3 → LUMO (13.7%) HOMO-5 → LUMO+4 (8.7%)
2-Cl ^d	S ₀ → S ₁₄	464.48	488.0 ^c	0.1495	HOMO-1 → LUMO+2 (6.6%) HOMO-3 → LUMO (7.7%) HOMO-2 → LUMO+1 (7.6%) HOMO-4 → LUMO+4 (5.4%)
2-H ₂ O ^b	S ₀ → S ₅	461.47	480.0 ^f	0.0259	HOMO-4 → LUMO+1 (26.9%) HOMO → LUMO+3 (13.5%)
2-H ₂ O ^c	S ₀ → S ₆	461.52	480.0 ^f	0.0266	HOMO-5 → LUMO (15.9%) HOMO-4 → LUMO+1 (13.1%) HOMO-1 → LUMO+2 (8.7%)
2-H ₂ O ^d	S ₀ → S ₆	461.54	480.0 ^f	0.0315	HOMO-4 → LUMO+1 (22.4%) HOMO-1 → LUMO+3 (11.6%) HOMO-5 → LUMO (7.5%)

^a Parentheses data are (CI coefficient)² x 100%; ^b *trans-trans* isomer; ^c *trans-cis* isomer; ^d *cis-cis* isomer;

^e the value for the mixture of 2-Cl isomers; ^f the value for the mixture of 2-H₂O isomer

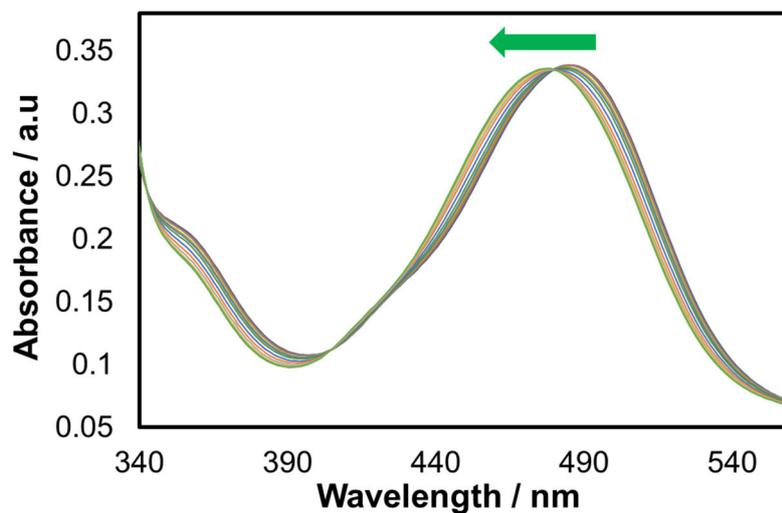


Figure S1. Time-course UV-Vis spectra of 1-Cl during light irradiation (Xenon light 100 mW/cm²) for 120 seconds, showing the change in λ_{\max} from 486 nm (1-Cl) to 479 nm (1-H₂O).

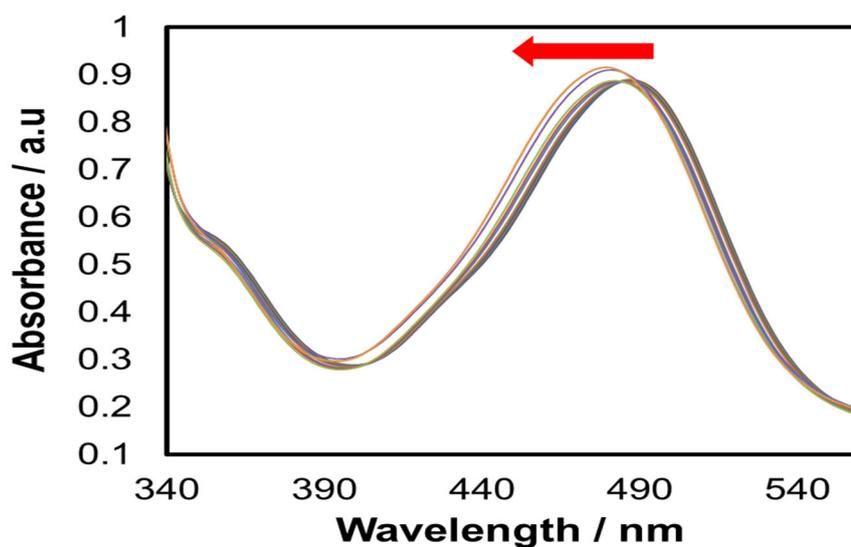


Figure S2. Time-course UV-Vis spectra of 2-Cl during light irradiation (Xenon light 100 mW/cm²) for 120 seconds, showing the change in λ_{\max} from 488 nm (2-Cl) to 480 nm (2-H₂O).

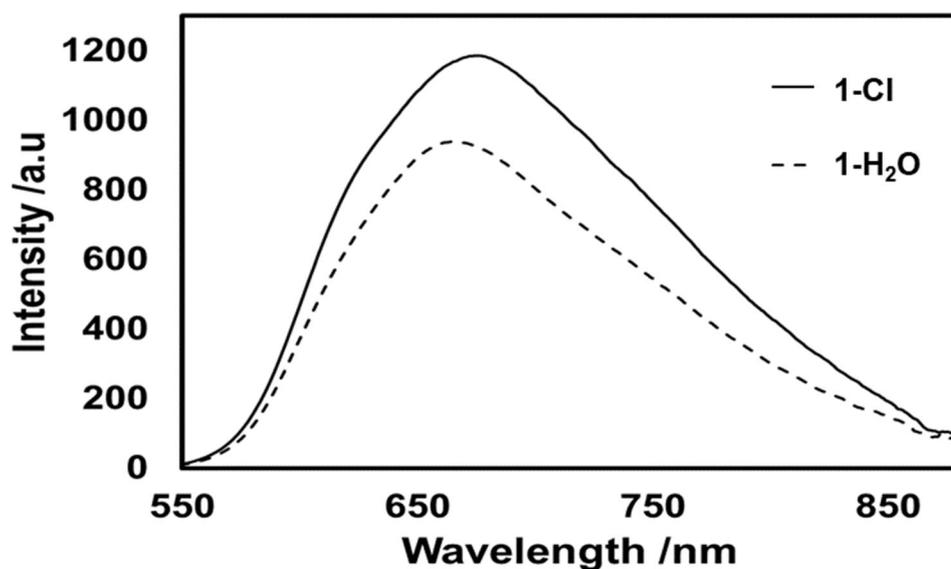


Figure S3. Photoluminescence spectra for 1-Cl (solid line) and for 1-H₂O (dashed line), which was generated *in-situ* by light irradiation (Xenon 160 mW cm⁻²) of 1-Cl for 30 minutes in water. The sample was purged by N₂ to remove the oxygen and kept deaerated throughout.

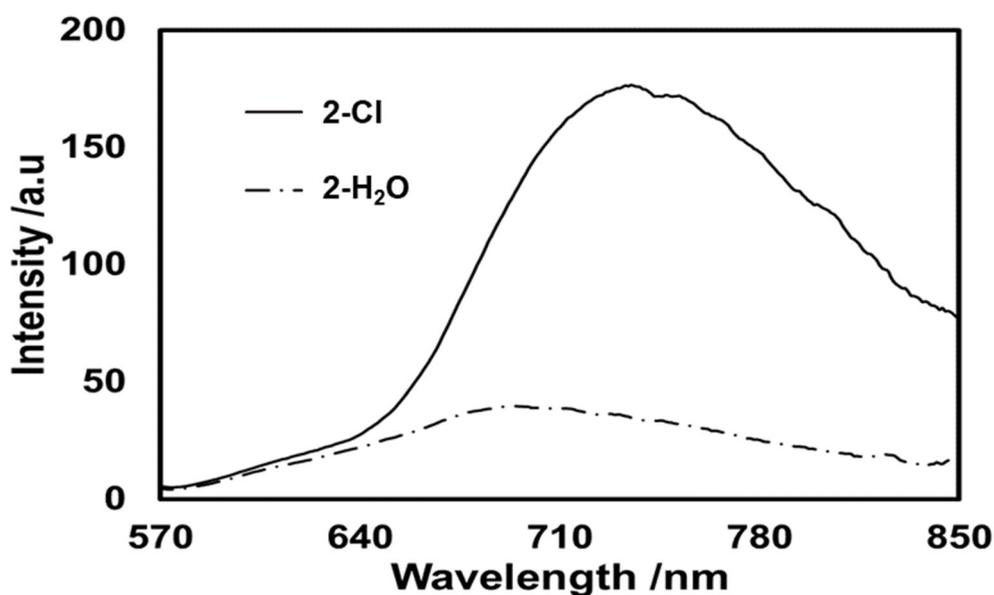


Figure S4. Photoluminescence spectra for 2-Cl (solid line) and for 2-H₂O (dashed line), which was generated *in-situ* by light irradiation (Xenon 160 mW cm⁻²) of 2-Cl for 30 minutes in water. The sample was purged by N₂ to remove the oxygen and kept deaerated throughout.

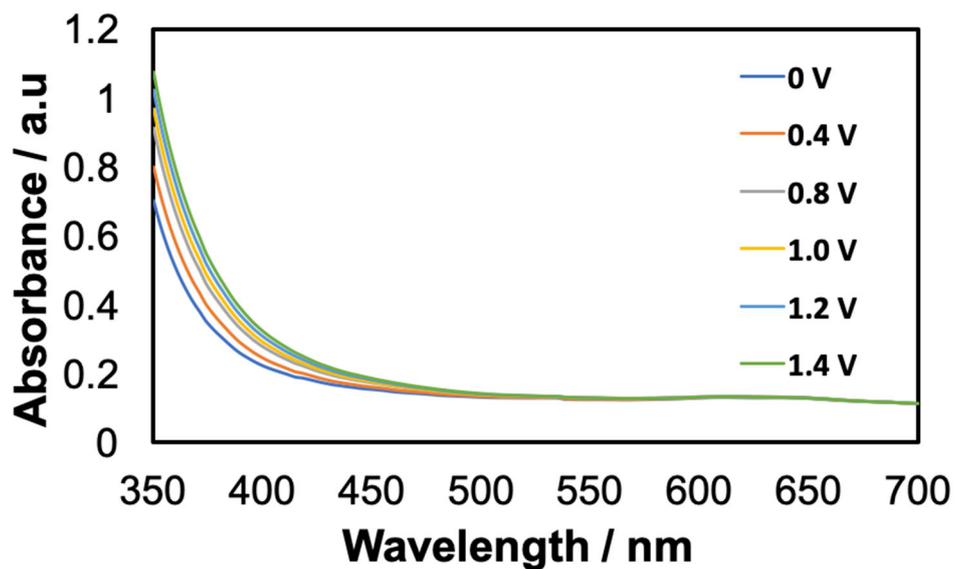


Figure S5. The absorption spectra of *nanoITO* in buffer-only system (phosphate buffer pH 7), showing the red-shift and increase in absorption intensity due to increasing potential.

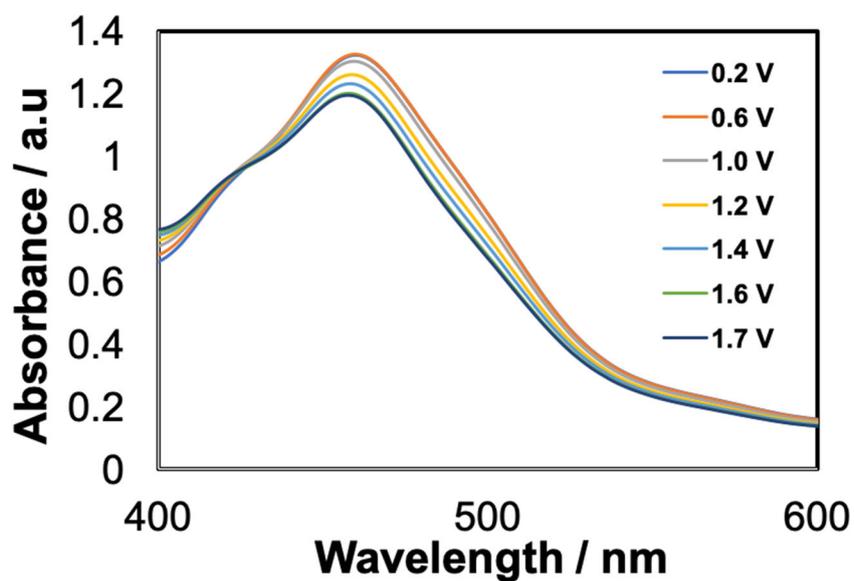


Figure S6. The absorption spectra of 1- H_2O in phosphate buffer pH 7 on the surface of *nanoITO* electrode, showing the change in the MLCT intensity due to increasing potential.

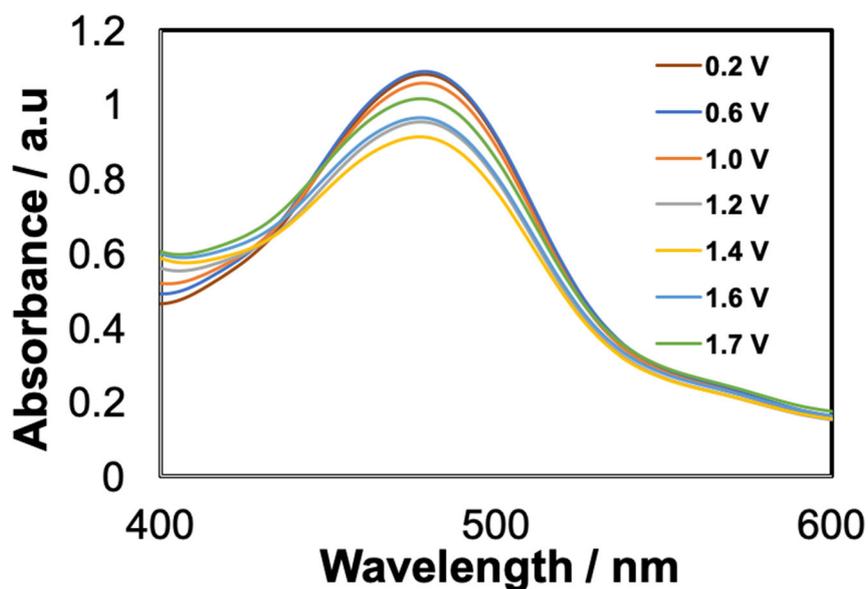


Figure S7. The absorption spectra of 2-H₂O in phosphate buffer pH 7 on the surface of *nano*ITO electrode, showing the change in the MLCT intensity due to increasing potential.

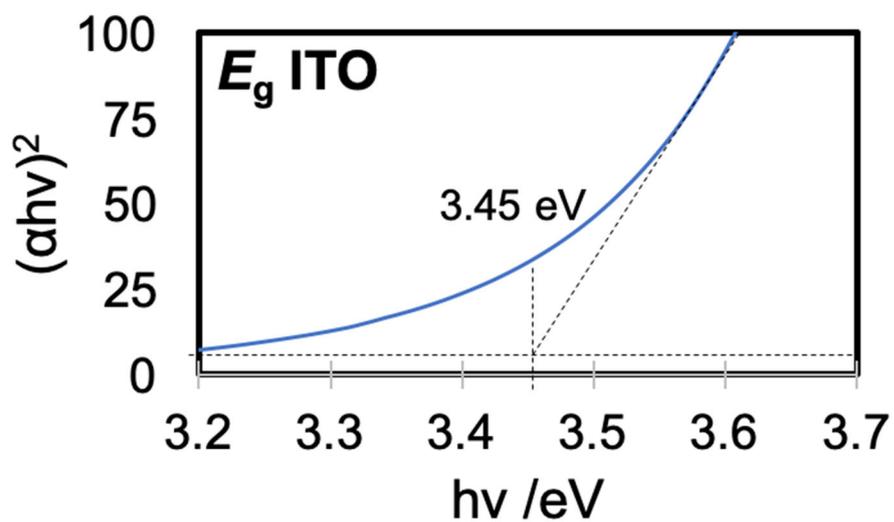


Figure S8. Tauc plot for *nano*ITO at 1.0 V derived from the data in Figure S5 for the determination of the band gap (E_g) energy.

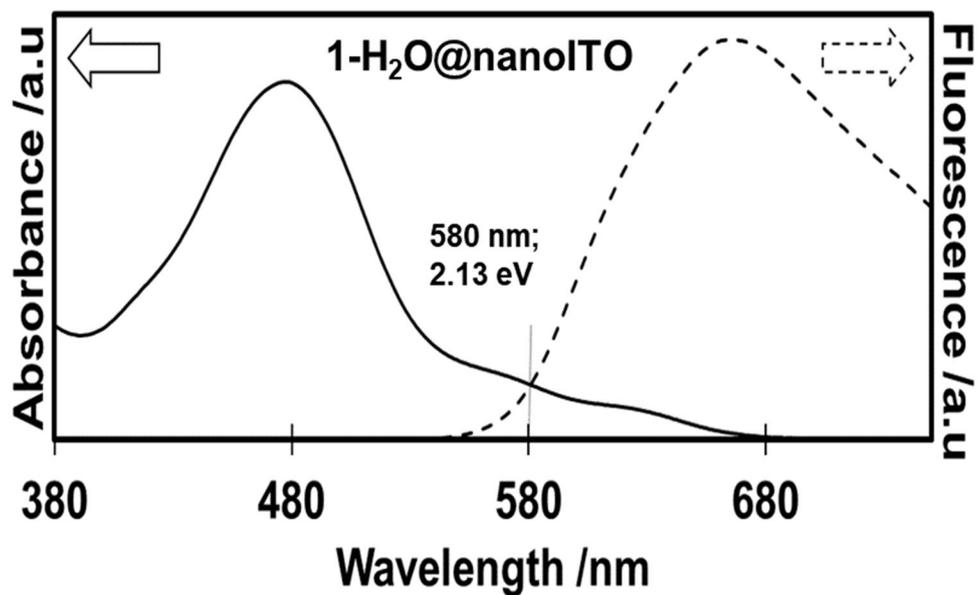


Figure S9. E_{0-0} value for 1-H₂O (2.13 eV) determined from the intersection between absorption and emission.

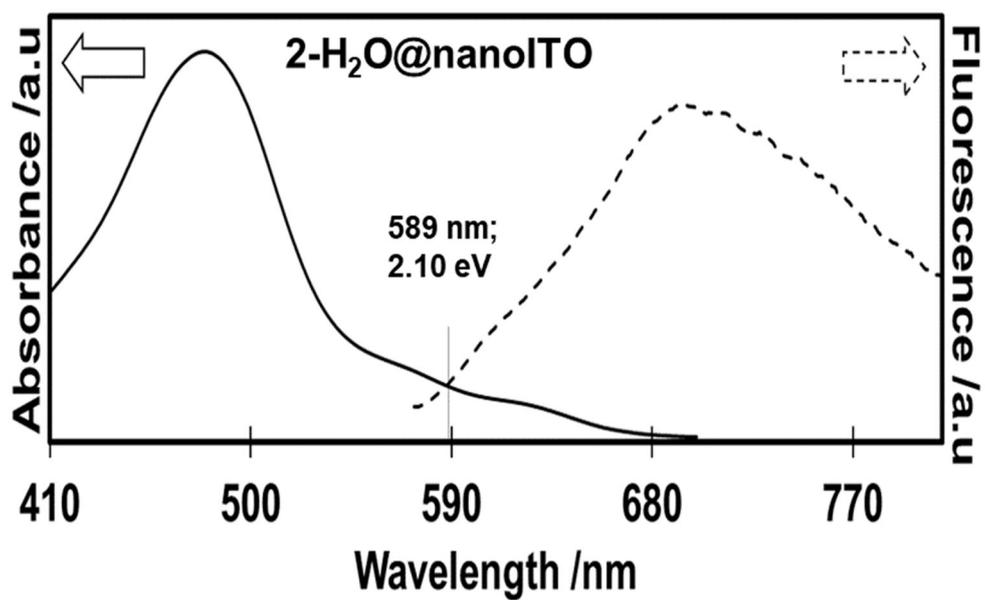


Figure S10. E_{0-0} value for 2-H₂O (2.10 eV) determined from the intersection between absorption and emission.

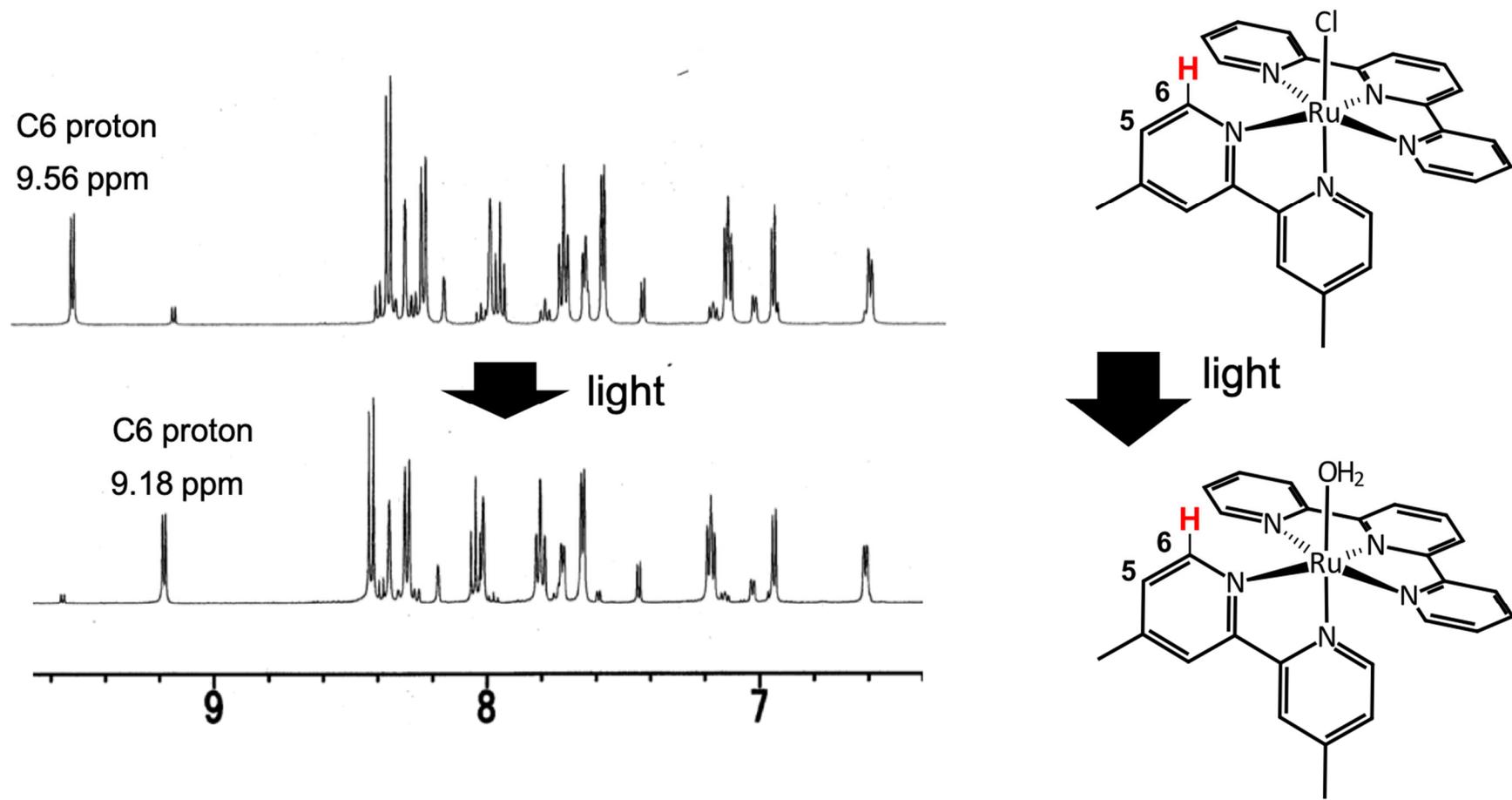


Figure S11. ^1H NMR spectrum of 1-Cl and 1- H_2O in D_2O , showing the shift of the C6 proton after light irradiation

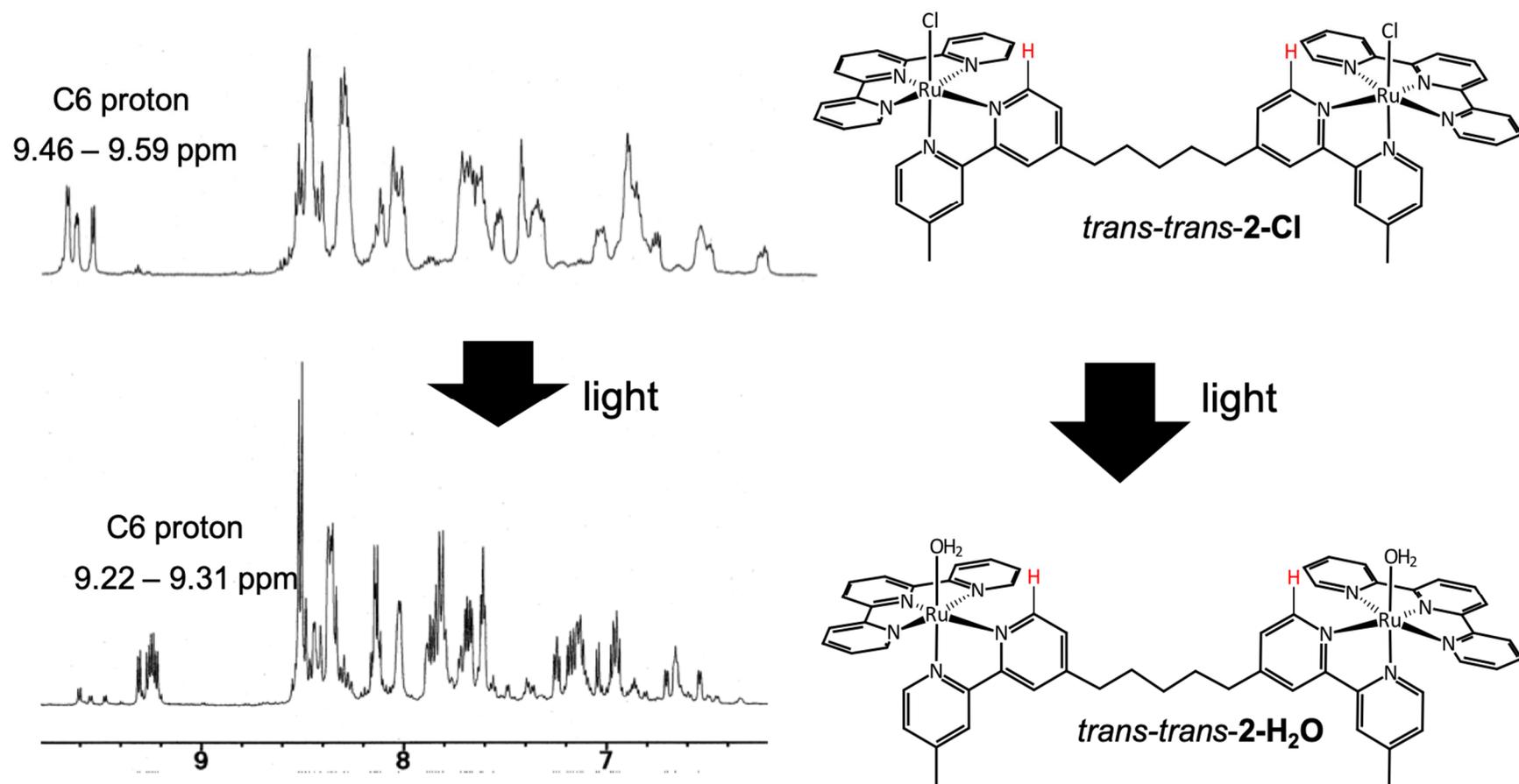


Figure S12. ^1H NMR spectrum of 2-Cl and 2- H_2O in D_2O , showing the shift of the C6 proton after light irradiation