Supplementary Information (SI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPORTING INOFRMATION

Photophysics and photochemistry of a prospective light-activated anticancer dirhodium complex

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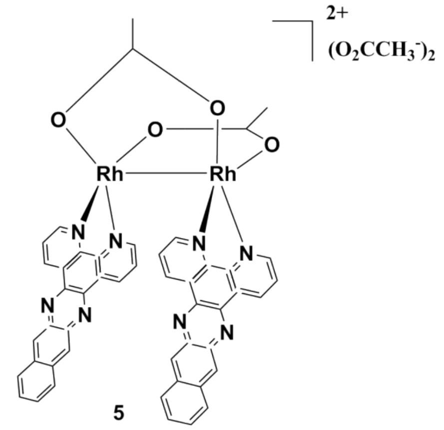
S1. UV spectroscopy of Complex 5



5

$[Rh_2(\mu\text{-}O_2CCH_3)_2(dppn)_2]^{2+}$

Scheme S1. Complex **5.**

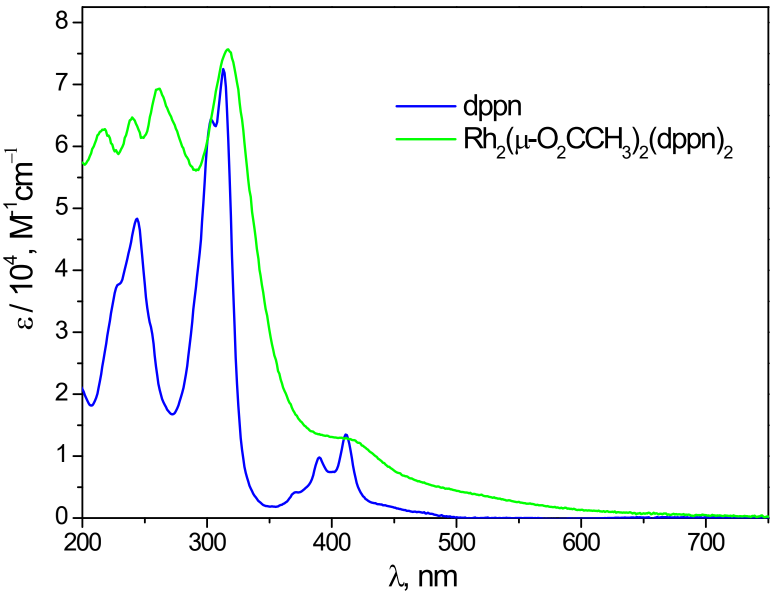


Figure S1. Electronic absorption spectra of dppn in CH_3CN and Complex **5** in H_2O.

S2. Quantum yield of Complex 5 photoaquation

Quantum yield of reaction (S1) was measured with capillary electrophoresis. The dependence of free acetate ions ($O_2CCH_3^-$) released from the first coordination sphere of Rh(II) vs. irradiation time is shown in Fig. S2. The quantum yield was calculated using Eq. SI.

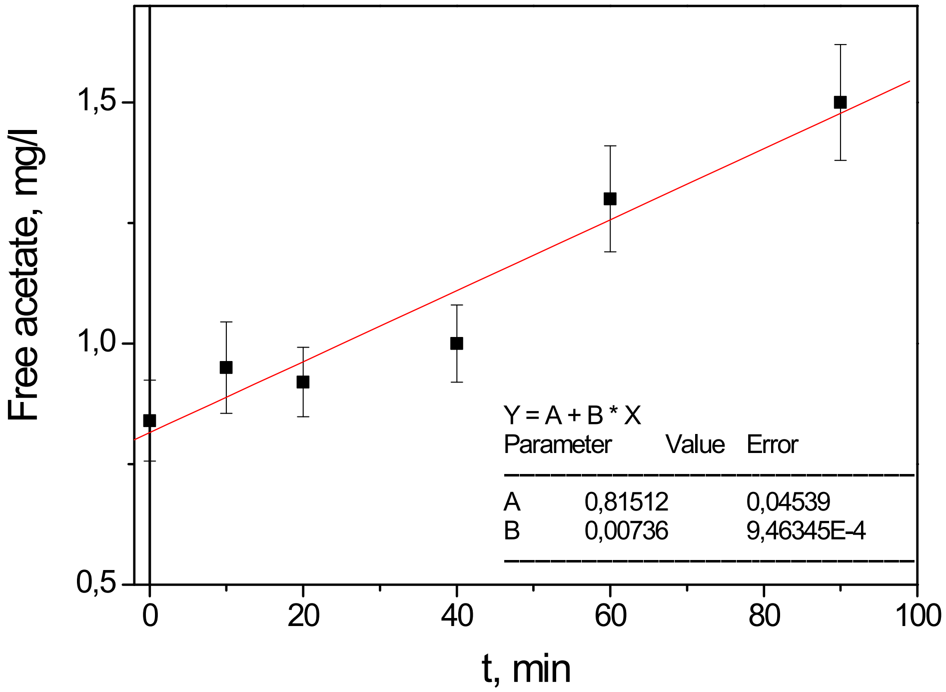


Figure S2. Dependence of acetate ions ($O_2CCH_3^-$) measured by capillary electrophoresis as a function of irradiation time. Irradiation (282 nm) $6{,}87\times10^{-6}$M of Complex 5 in an 1 cm cell, air-saturated aqueous solution.

$$[Rh_2(dppn)_2(\mu\text{-}O_2CCH_3)_2]^{2+} \xrightarrow[2H_2O]{h\nu} [Rh_2(dppn)_2(\mu\text{-}O_2CCH_3)(H_2O)_2]^{3+} + (O_2CCH_3)^- \qquad \text{(S1)}$$

$$\varphi = \frac{dC}{dt}\Big/(I_0 \times (1\text{-}10^{D(282)})) \qquad \text{(SI)}$$

$I_0 = 7.6\times10^{-4}$ moles of quanta per minute — the concentration (moles per liter) of quanta per one minute provided by the 282 nm excilamp in a 2 ml cell. The light is absorbed completely.

The result is $\varphi = 0.026$ (relative error ca. 10%).

S3. Singlet oxygen formation

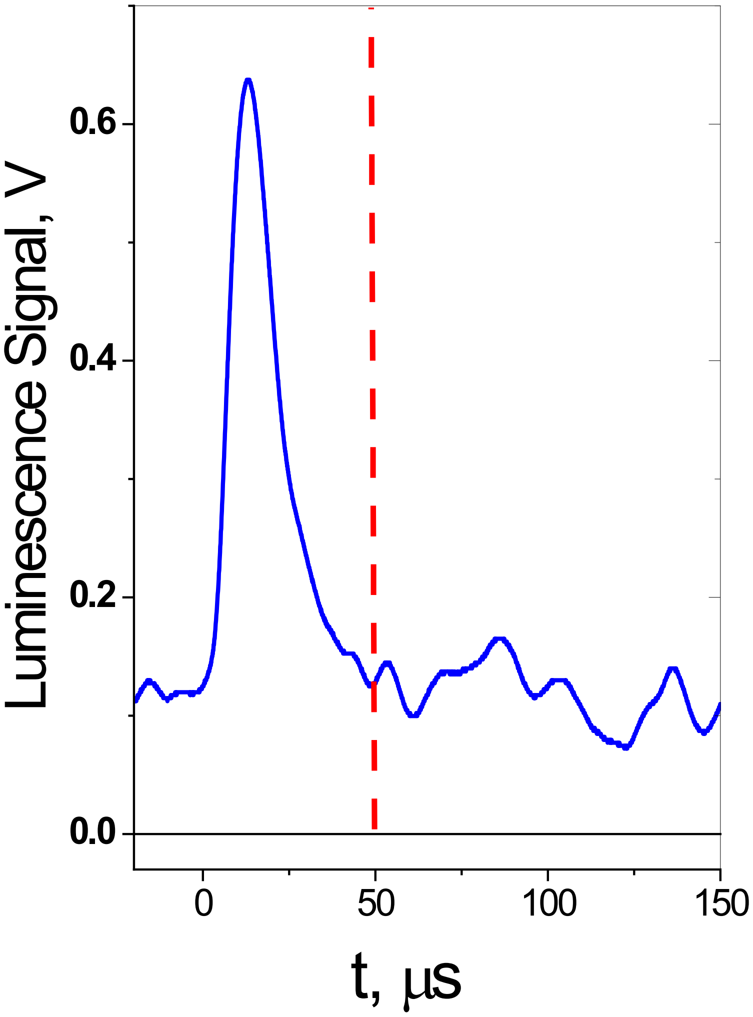


Figure S3. Signal of IR photodetector obtained from the quartz cell filled with deionized water. Excitation at 355 nm, laser energy is 5.7 mJ. Red-dash vertical line indicates the short-time edge of temporal interval used for fitting of singlet oxygen luminescence signal.

Quantum yield was calculated with Eq. SII. where dA/dE and dA_{st}/dE are the slopes for the target compound and the standard correspondingly, D(355) and D(355)$_{st}$ are the absorbancies at the excitation wavelength (355 nm), and φ_{st} is the quantum yield of the singlet oxygen formation for the reference sensitizer phenalenon.

$$\varphi = \varphi_{st} \frac{dA/dE}{dA_{st}/dE} \frac{1-10^{-D(355)_{st}}}{1-10^{-D(355)}}. \qquad \text{(SII)}$$

Equation (SII) is satisfied for small values of absorbancies, which didn't overcome 0.3 in our experiments. The slopes dA/dE and dA_{st}/dE for pulse energy dependence of the $^1O_2$

luminescence amplitude were measured at the fixed absorbance of investigated substances. The example of the determined slope dA/dE is presented in Fig.4b of Manuscript.

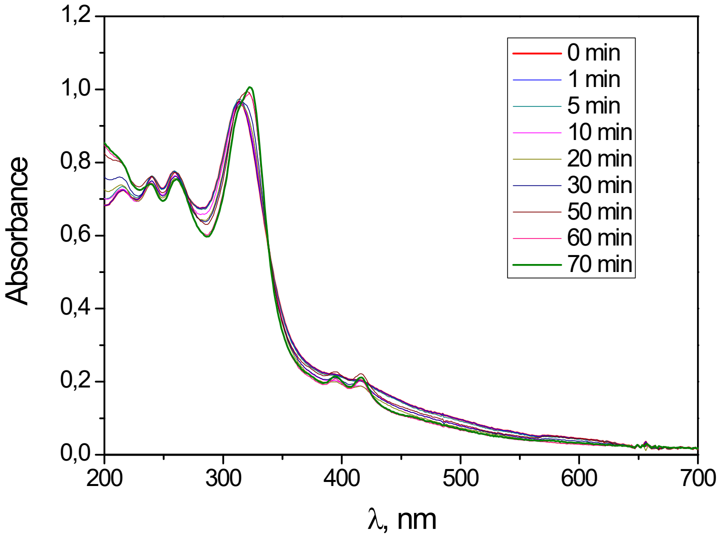


Figure S4. Changes of the UV absorption spectra of $Rh_2(\mu\text{-}O_2CCH_3)_2(dppn)_2$ in CH_3CN air-saturated solution during stationary photolysis (λ = 305 nm). 1 cm cell, concentration 1.35×10-5 M, irradiation time is indicated in the figure**.**

S4. Laser flash photolysis.

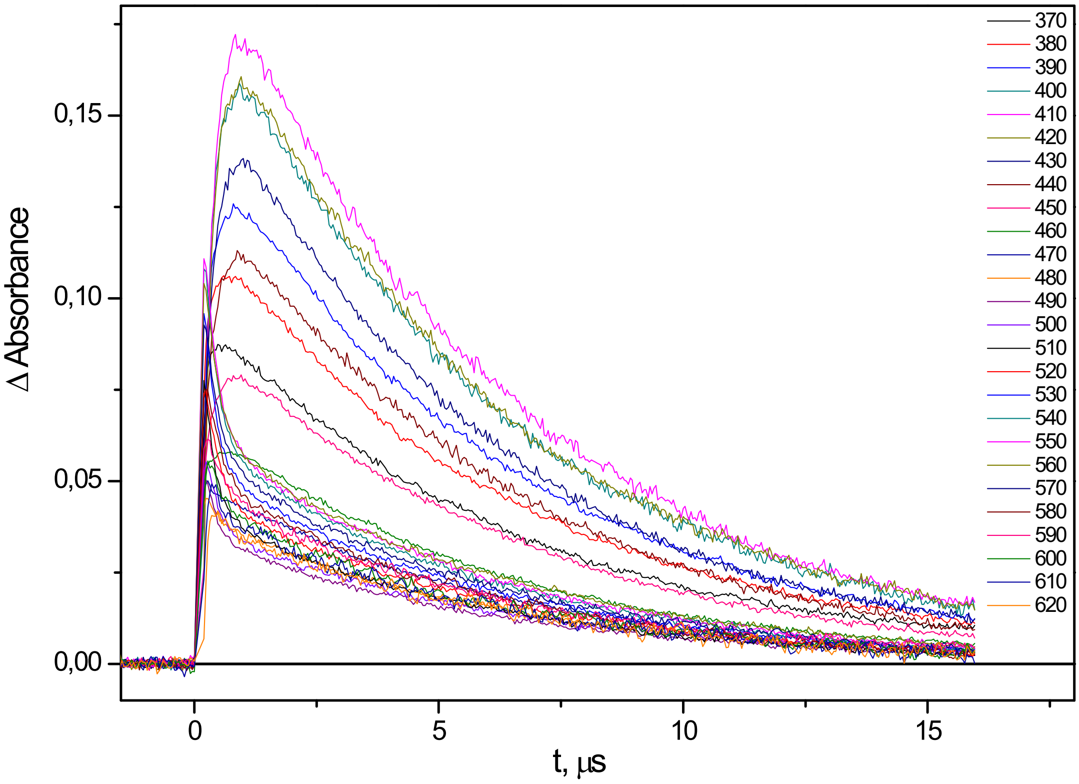


Figure S5. Kinetic curves obtained in the course of laser flash photolysis (355 nm) of Complex 5 (3.1×10^{-4} M in deaerated H_2O). Wavelengths are depicted.

$$\Delta D(\lambda,t) = A_1(\lambda)\exp(-\frac{t}{\tau_1}) + A_2(\lambda)\exp(-\frac{t}{\tau_2}) \qquad \text{(SIII)}$$

Exact formulae for calculation of Species Associated Difference Spectra (SADS) from the amplitudes of Eq. SIII for the case of sequential transitions of intermediates A → B → (Ground State) [S1]:

$$S_A(\lambda) = A_1(\lambda) + A_2(\lambda) \qquad \text{(SIV)}$$

$$S_B(\lambda) = (1-\frac{\tau_1}{\tau_2})A_2(\lambda) \qquad \text{(SV)}$$

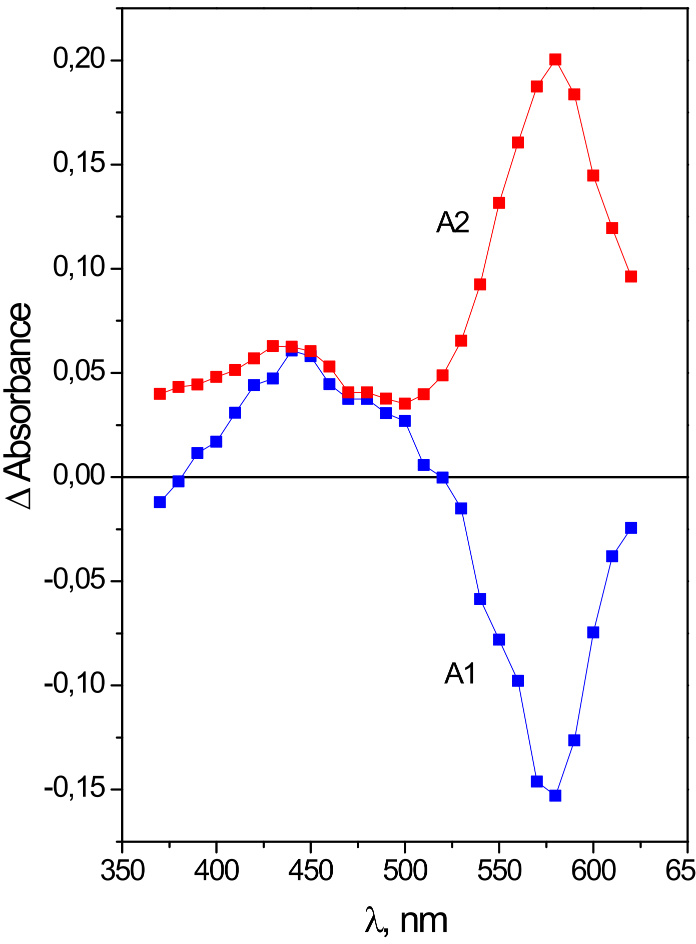


Figure S6. Results of biexponential global fit (Eq. SII) of the kinetic curves (Fig. S5) obtained in the course of laser flash photolysis (355 nm) of Complex **5** (3.1×10^{-4} M in deaerated H_2O). Spectra of amplitudes.

S5. Ultrafast TA spectroscopy

The results of ultrafast TA experiments were globally fitted by 2- or 3-exponential functions with residuals (SVI, SVII). Assuming the successive transitions of the intermediates A → B → C, the SADS could be calculated form amplitudes using formulae (SVI, SVIII-SX) [S1]. For the case of big difference in characteristic lifetimes τ_1 and τ_2 these formulae could be simplified to the sums of amplitudes (SVIII, SXI, SX).

$$\Delta D(\lambda,t) = A_1(\lambda)\exp(-\frac{t}{\tau_1}) + A_2(\lambda)\exp(-\frac{t}{\tau_2}) + A_3(\lambda) \tag{SVI}$$

$$\Delta D(\lambda,t) = A_1(\lambda)\exp(-\frac{t}{\tau_1}) + A_2(\lambda)\exp(-\frac{t}{\tau_2}) + A_3(\lambda)\exp(-\frac{t}{\tau_3}) + A_4(\lambda) \tag{SVII}$$

$$S_A(\lambda) = A_1(\lambda) + A_2(\lambda) + A_3(\lambda) \tag{SVIII}$$

$$S_B(\lambda) = (1-\frac{\tau_1}{\tau_2})A_2(\lambda) + A_3(\lambda) \tag{SIX}$$

$$S_C(\lambda) = A_3(\lambda) \tag{SX}$$

$$S_B(\lambda) = A_2(\lambda) + A_3(\lambda) \tag{SXI}$$

The results of 2-exponential approximation with the residual for the case of Complex **5** ultrafast irradiation at 400 nm are shown in Figs. S7, S8. The characteristic lifetimes are $\tau_1 = 1.8 \pm 0.7$ ps and $\tau_2 = 120 \pm 50$ ps.

Assuming the successive transitions of the intermediates A → B → C → D, the SADS could be calculated form amplitudes using formulae (SVII, SXII-SXV) [S1]. For the case of big difference in characteristic lifetimes τ_1 and, these formulae could be simplified to the sums of amplitudes (SXII, SXVI,-SXVII, SXV).

$$S_A(\lambda) = A_1(\lambda) + A_2(\lambda) + A_3(\lambda) + A_4(\lambda) \tag{SXII}$$

$$S_B(\lambda) = A_2(\lambda)\frac{\tau_2-\tau_1}{\tau_2} + A_3(\lambda)\frac{\tau_3-\tau_1}{\tau_3} + A_4(\lambda) \tag{SXIII}$$

$$S_C(\lambda) = A_3(\lambda)\frac{(\tau_3-\tau_1)(\tau_3-\tau_2)}{\tau_3^2} + A_4(\lambda) \tag{SXIV}$$

$$S_D(\lambda) = A_4(\lambda) \tag{SXV}$$

$$S_A(\lambda) = A_2(\lambda) + A_3(\lambda) + A_4(\lambda) \tag{SXVI}$$

$$S_A(\lambda) = A_3(\lambda) + A_4(\lambda) \tag{SXVII}$$

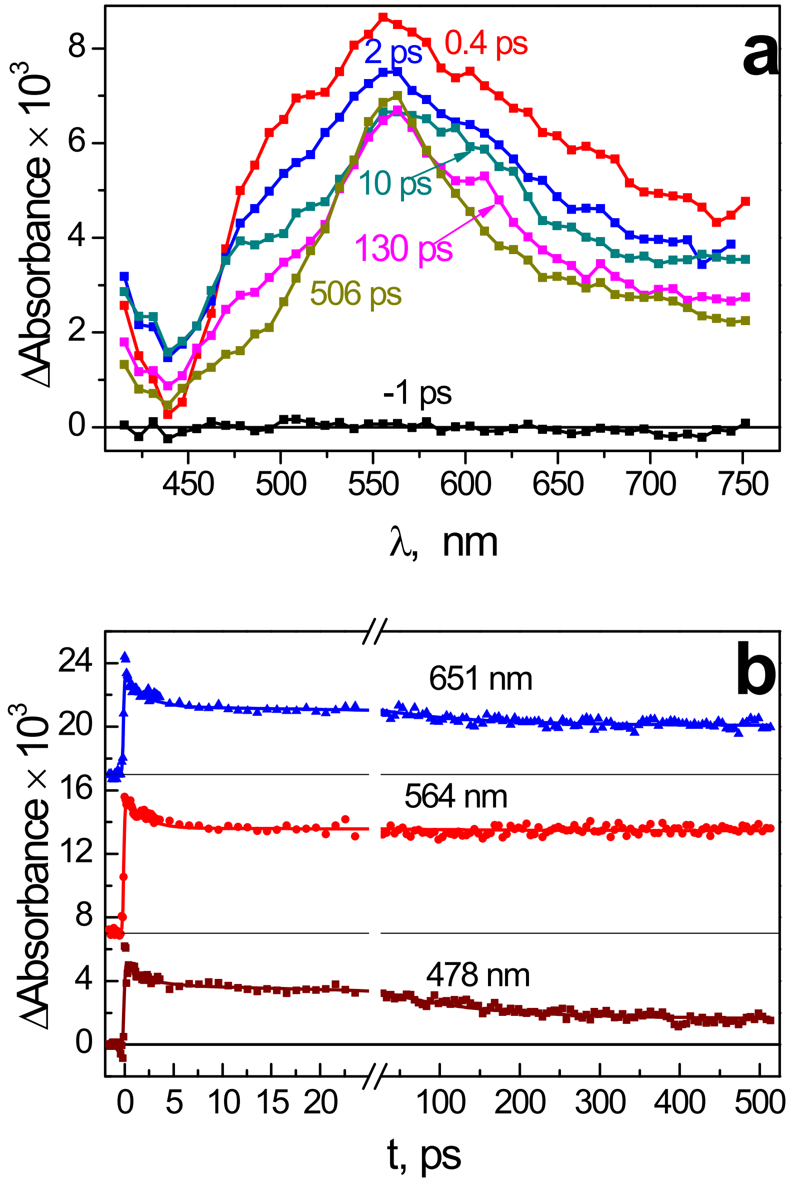


Figure S7. **a** - TA spectra obtained in ultrafast pump-probe experiment with Complex **5** in H_2O (1.2×10^{-4} M, `1 mm cell). Excitation at 400 nm. Curves 1-6 correspond to time delays between exciting and probing pulses equal to -1; 0.4; 2; 10; 130; 506 ps. **b** - examples of kinetic curves obtained by processing TA spectra and their 2-exponential global fit by function (SVI).

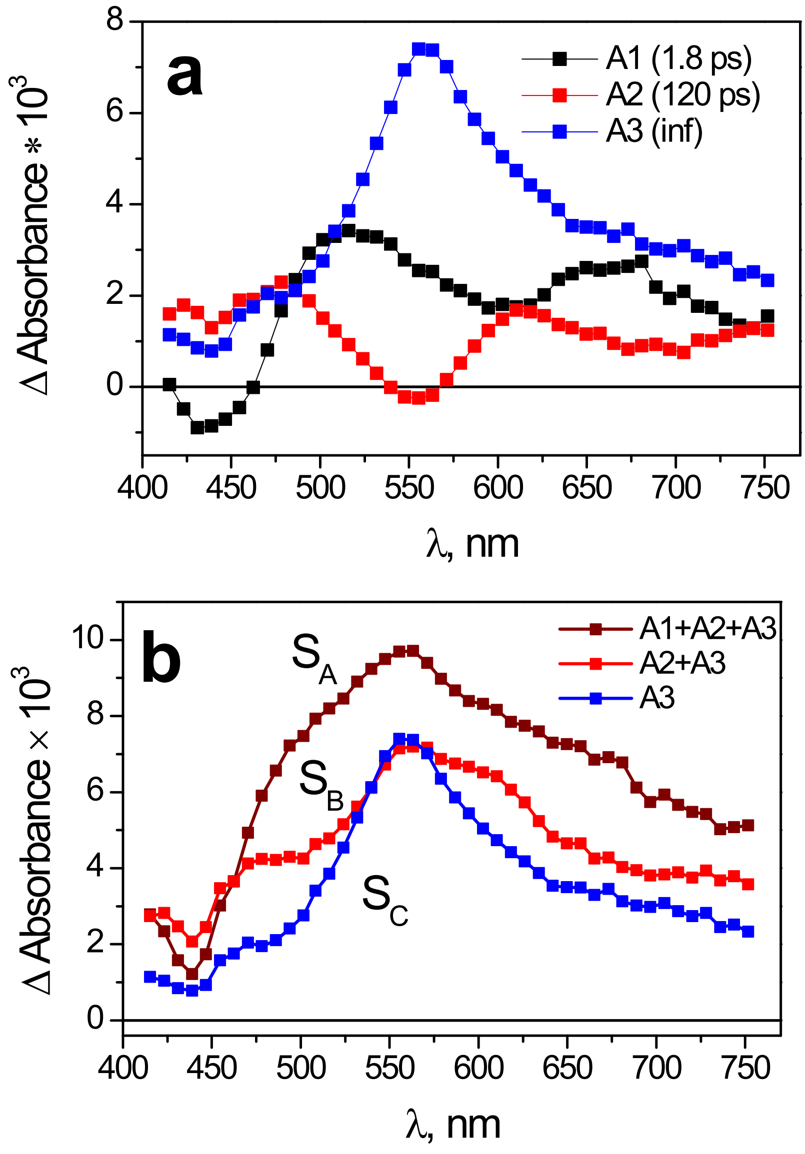


Figure S8. Results of processing of the TA spectra obtained in ultrafast pump-probe experiment with Complex **5** in H_2O (1.2×10^{-4} M, `1 mm cell, excitation at 400 nm) by formulae (SVI, SVIII, SXI, SX). **a** – amplitudes $A_i(\lambda)$, **b** – SADS. The characteristic lifetimes are $\tau_1 = 1.8 \pm 0.7$ ps; $\tau_2 = 120 \pm 50$ ps.

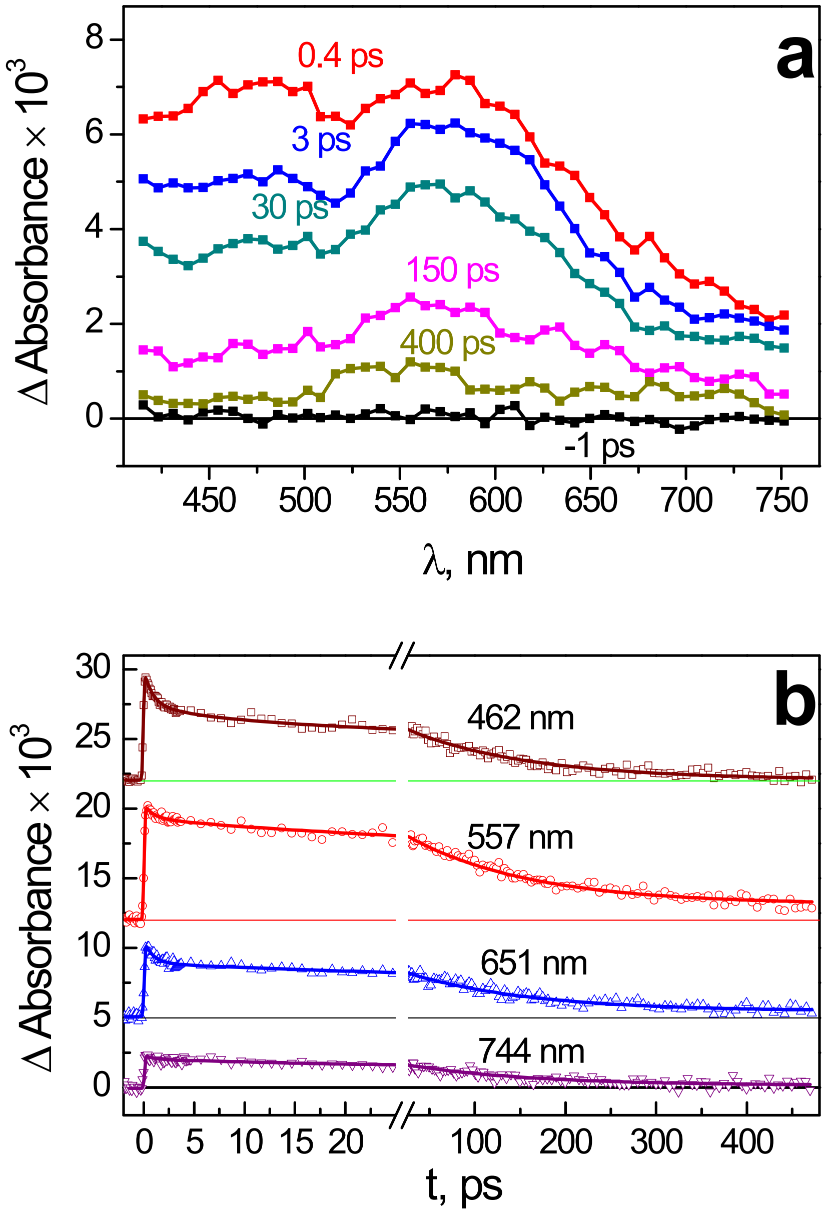


Figure S9. **a** - TA spectra obtained in ultrafast pump-probe experiment with Complex **5** in H_2O (1.28×10^{-4} M, `1 mm cell). Excitation at 320 nm. Curves 1-6 correspond to time delays between exciting and probing pulses equal to -1; 0.4; 2; 10; 130; 506 ps. **b** - examples of kinetic curves obtained by processing TA spectra and their 3-exponential global fit by function (SVII).

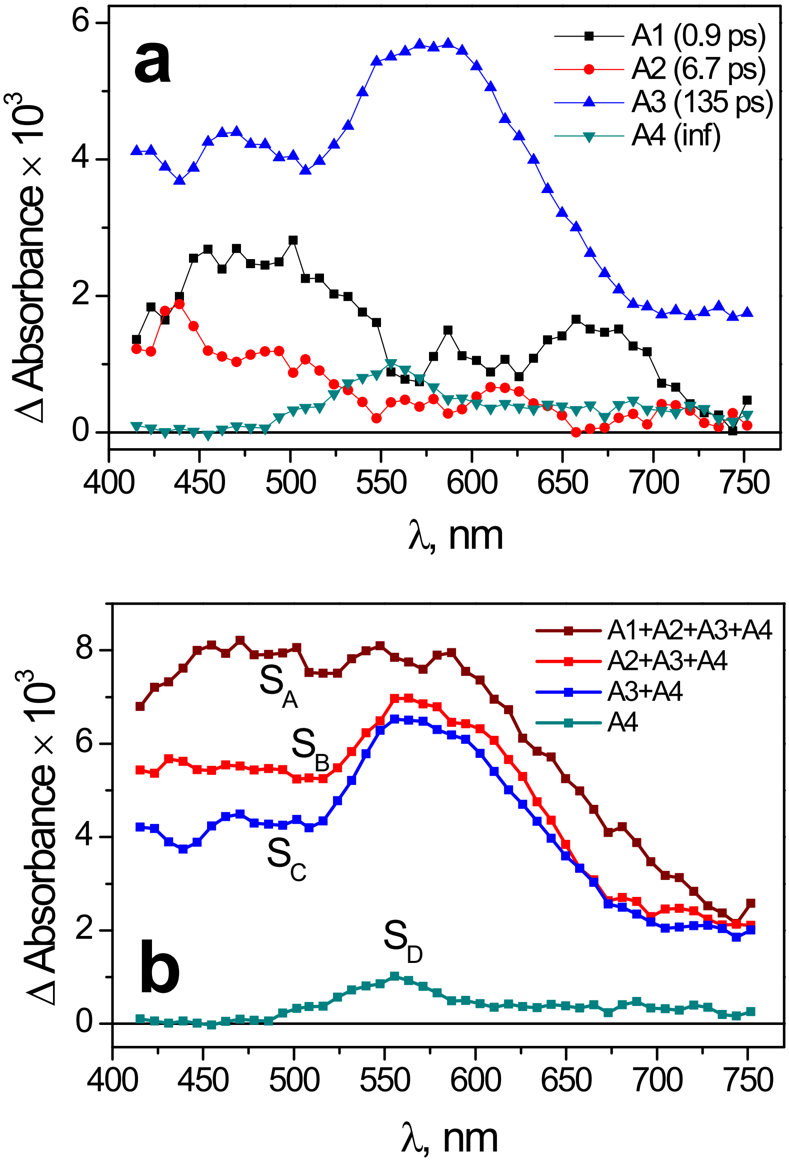


Figure S10. Results of processing of the TA spectra obtained in ultrafast pump-probe experiment with Complex **5** in H_2O (1.28×10^{-4} M, `1 mm cell, excitation at 320 nm) by formulae (SXII, SXVI, SXVII, SXV). **a** – amplitudes $A_i(\lambda)$, **b** – SADS. The characteristic lifetimes are $\tau_1 = 0.9 \pm 0.4$ ps, $\tau_2 = 6.7 \pm 4.6$ ps and $\tau_3 = 135 \pm 18$ ps.

References

[S1] A.S. Rury and R.J. Sension, *Chem. Phys.*, 2013, **422**, 220-228. https://doi.org/10.1016/j.chemphys.2013.01.025