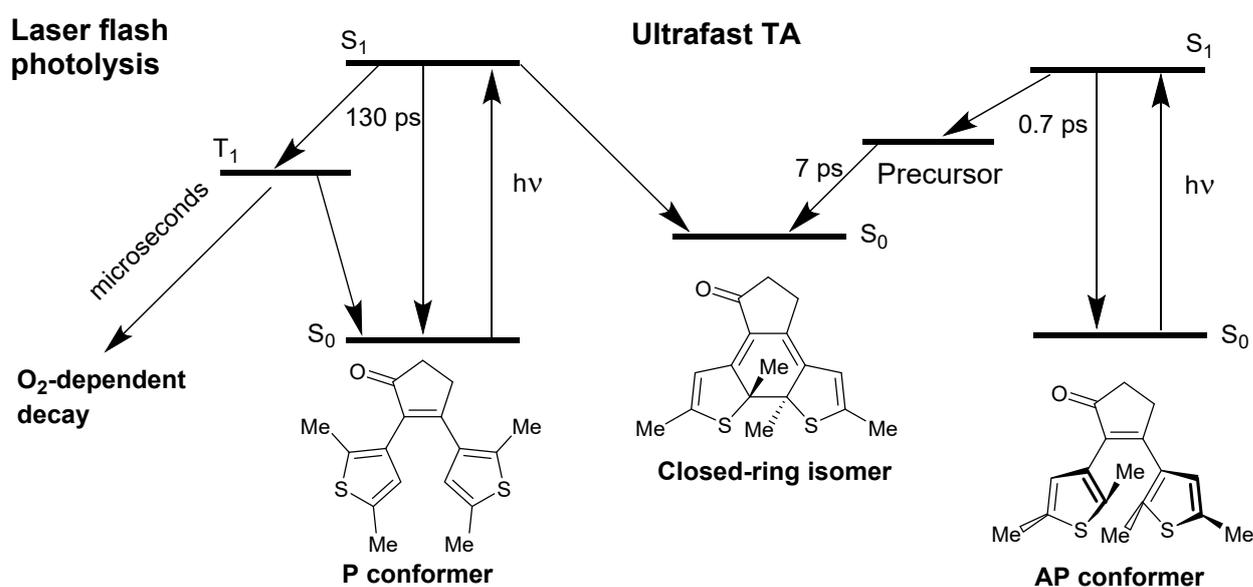


## Electronic Supporting Information to Paper

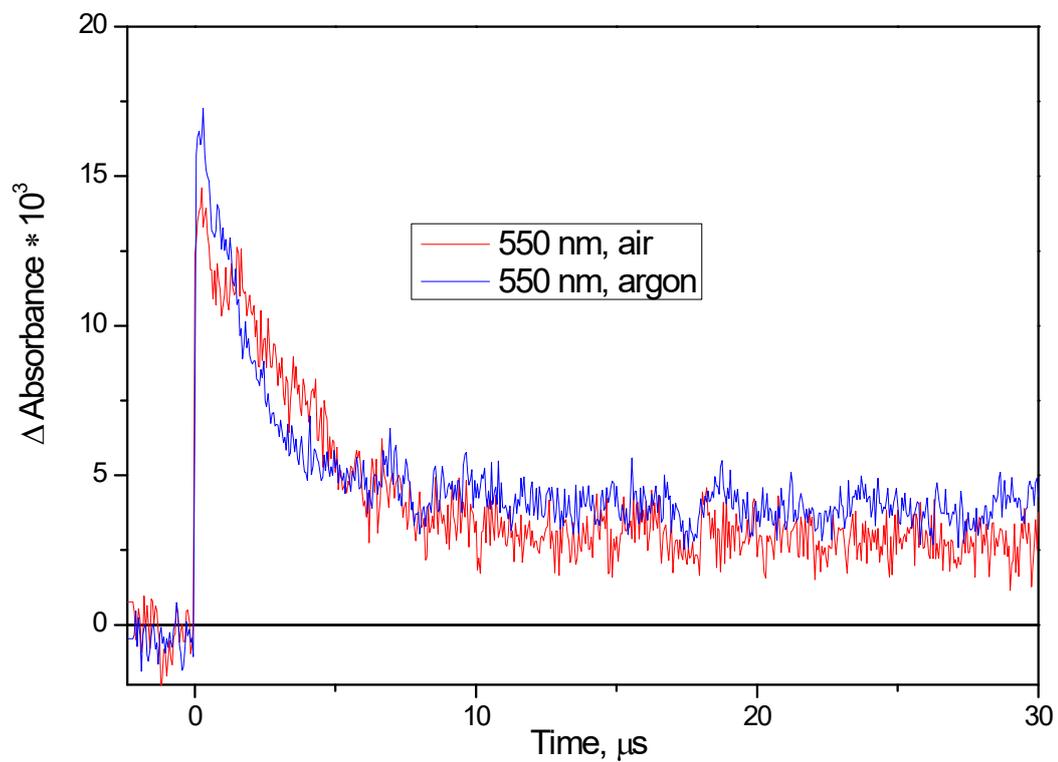
### “Multifunctional fluorescent diarylethene: mechanistic insight into the photoswitching”

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Andrey G. Lvov<sup>\*g,h</sup>, Evgeni M. Glebov<sup>\*a,b</sup>

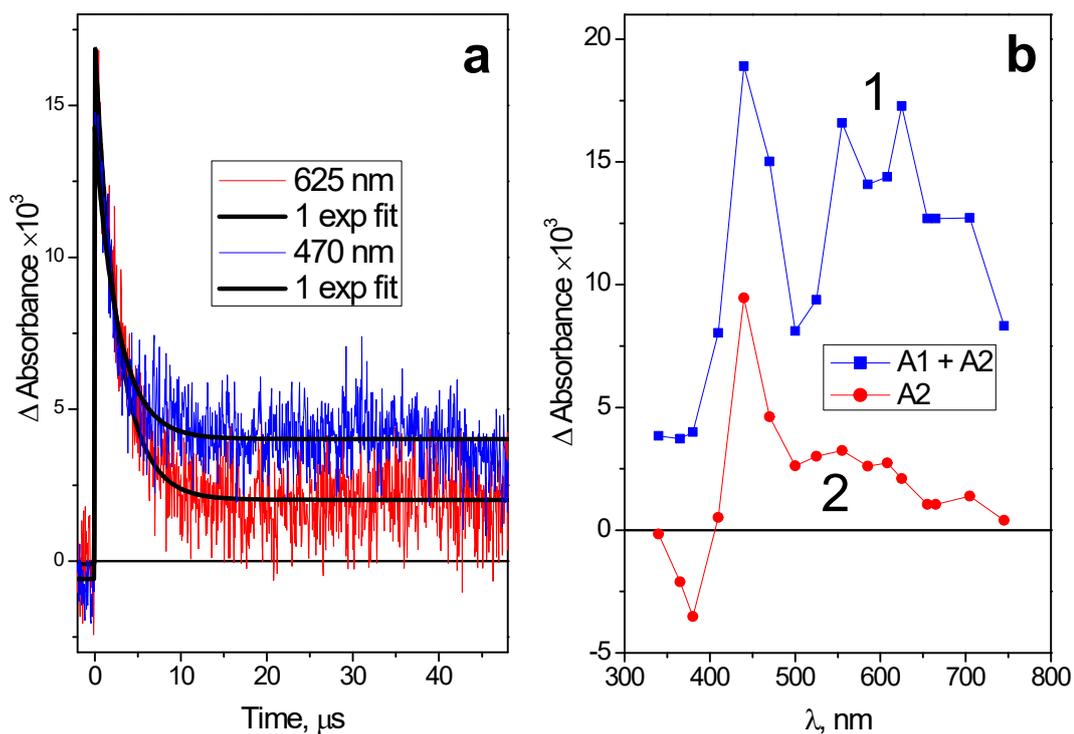


**Scheme S1.** Photophysical and photochemical processes for compound DCP based on the results of works [1, 2].

### S1. Laser flash photolysis of *E*-D1-o in n-hexane

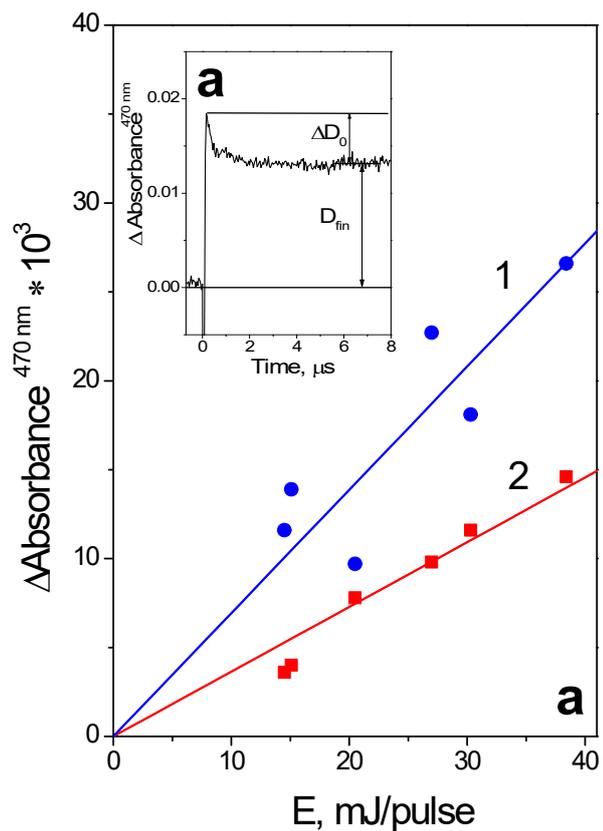


**Figure S1.** Laser flash photolysis (355 nm) of *E*-D1-o in n-hexane ( $2.3 \times 10^{-5}$  M, 1 cm cell). Red and blue curves correspond to air-saturated and argon-saturated solutions.



**Figure S2.** Laser flash photolysis (355 nm) of *E-D1-o* in n-hexane ( $2.3 \times 10^{-5}$  M, 1 cm cell, argon-saturated solutions). Results of 1-exponential global fit using formula S1. **a** – examples of experimental kinetic curves with the fits. **b** – Species Associated Difference spectra (SADS) corresponding to initial intermediate (curve 1) and residual (curve 2). The characteristic lifetime is  $2.7 \pm 0.5 \mu\text{s}$ .

$$\Delta D(\lambda, t) = A_1(\lambda) e^{-t/\tau_1} + A_2(\lambda) \quad (\text{S1})$$

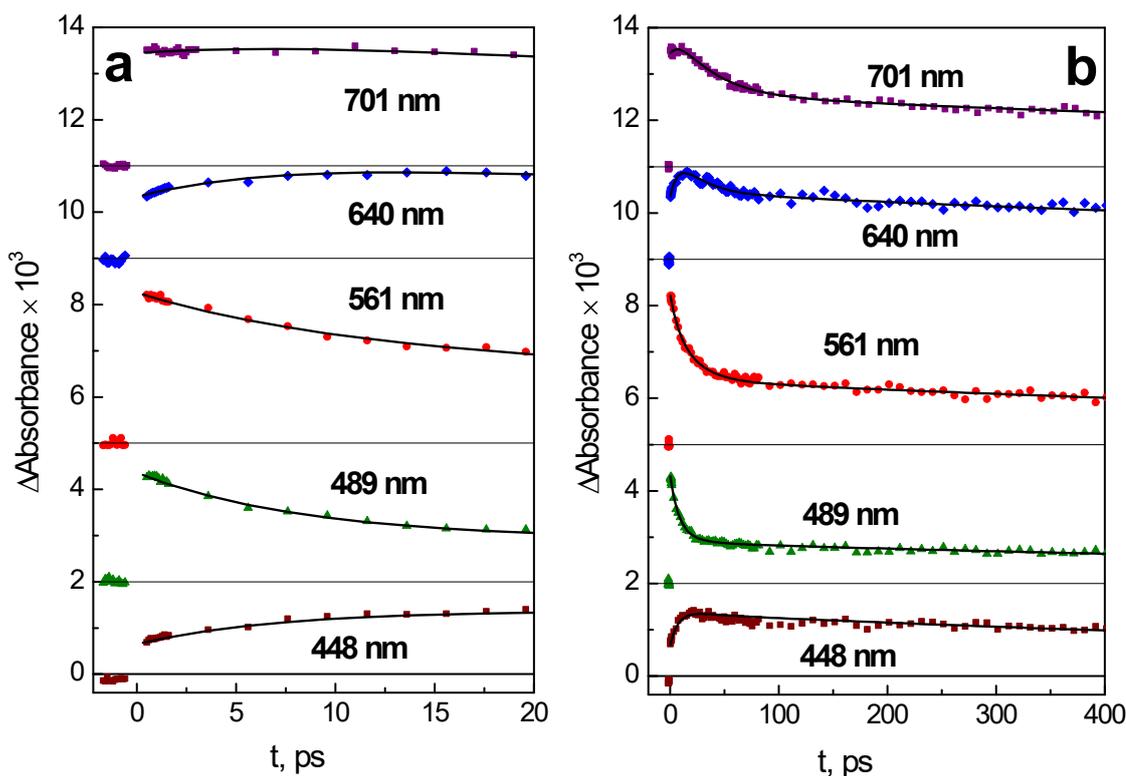


**Figure S3.** Laser flash photolysis (355 nm) of *E-D1-o* in n-hexane ( $5.6 \times 10^{-5}$  M, 1 cm cell, argon-saturated solutions, registration at 470 nm). **a** – example of a kinetic curve and determination of parameters  $D_{\text{fin}}$  and  $\Delta D_0$ . **b** – Dependencies of parameters  $D_{\text{fin}}$  (curve 1) and  $\Delta D_0$  (curve 2) vs. laser pulse energy ( $E$ ). Experimental points and their best fits linear function  $y = \alpha E$  with parameter  $\alpha = 0.69 \pm 0.06$  for  $D_{\text{fin}}$  and  $0.36 \pm 0.02$  for  $\Delta D_0$ .

## S2. Ultrafast pump-probe spectroscopy of *E*-D1-o in n-hexane. Kinetics and Species Associated Difference Spectra (SADS).

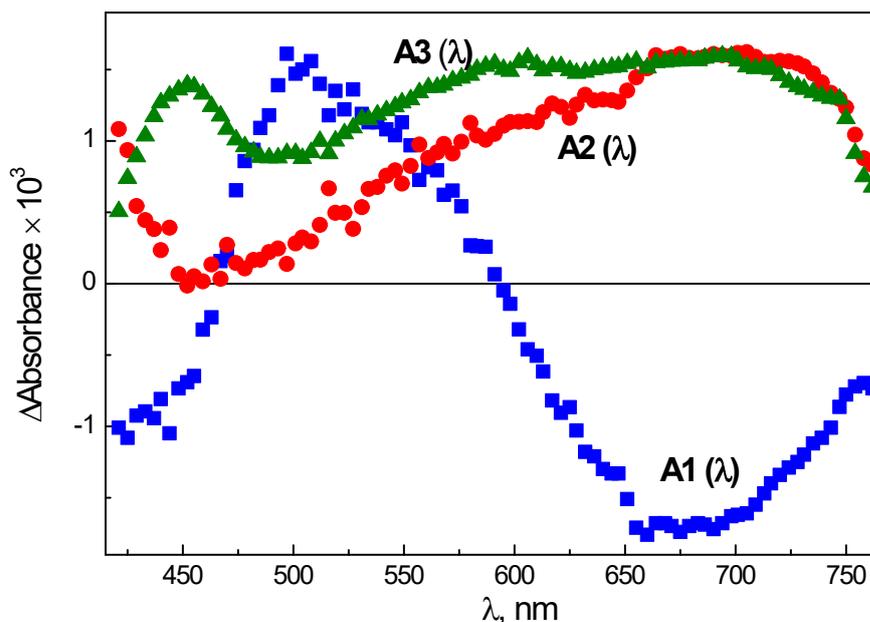
Here we present formulae and figures demonstrating calculation of SADS for *E*-D1-o in n-hexane. Examples of the kinetic curves obtained in ultrafast TA experiment are shown in Fig. S2. The whole set of the kinetic curves was globally fitted using Eq. (S2)

$$\Delta D(\lambda, t) = A_1(\lambda)e^{-t/\tau_1} + A_2(\lambda)e^{-t/\tau_2} + A_3(\lambda)e^{-t/\tau_3}, \text{ where } \tau_3 \rightarrow \infty \quad (\text{S2})$$



**Figure S4.** Examples of kinetic curves obtained by the ultrafast pump-probe spectroscopy (320 nm) of *E*-D1-o ( $3.3 \times 10^{-5}$  M, 1 mm cell) in n-hexane. Panels **a** and **b** demonstrate different time regions. Experimental points in the time region ( $-400 \text{ fs} < t < 300 \text{ ps}$ ) are excluded from the kinetic curves because of coherent artifact [3]. This figure coincides with Fig. 8 of the main text.

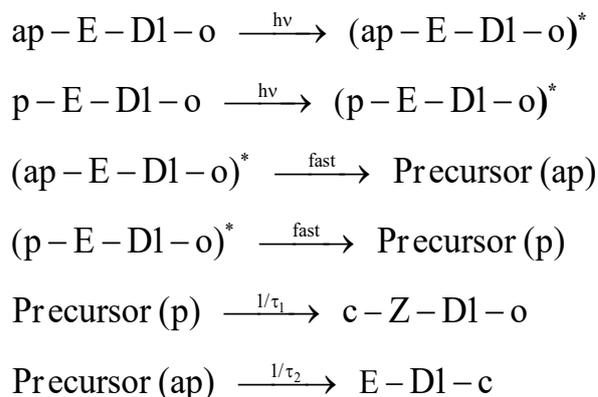
The values of the amplitudes are shown in Fig. S3.



**Figure S5.** Results of analysis of the intermediate absorption data obtained by the ultrafast pump-probe spectroscopy (320 nm) of *E-D1-o* ( $3.3 \times 10^{-5}$  M, 1 mm cell) in n-hexane. Amplitudes  $A_1(\lambda)$ ,  $A_2(\lambda)$ ,  $A_3(\lambda)$  extracted from the global fit of the set of kinetic curves using Eq. S2 with the characteristic lifetimes 7.8; 22 and 1250 ps correspondingly. This figure coincides with Fig. 9b of the main text.

To describe the ultrafast experiment and to match it to the stationary and laser flash photolysis data, the following reaction scheme (Mechanism 1) was proposed (see also main text):

#### Mechanism 1



In the framework of Mechanism 1 the description of the kinetic curves in the ultrafast TA experiments is very simple. In fact, we have two parallel reactions, in which four species are involved, namely A = Precursor (p); B = **c-Z-D1-o**; C = Precursor (ap); D = **E-D1-c**. Assuming that both concentrations of parallel and anti-parallel conformations of the closed form in the

initial solutions and quantum yields of precursors formation are equal, we can introduce SADS corresponding to intermediates as  $S_X = \varepsilon_X c_0 l$ , where  $X = A, B, C, D$ ;  $\varepsilon_X$  are the molar absorption coefficients;  $c_0$  is the concentration of A and C after the laser pulse; and  $l$  is the optical path length. Note that the SADS allow one to compare the relative absorbance of the intermediates, but do not give absolute values of the molar absorption coefficients. In the framework of Mechanism 1 and the assumptions made, the TA of the sample after the laser pulse is described by Eq. S3. Comparing Equations S2 and S3, we obtain formulae (S4-S6) for amplitudes. Finally, formulae (S7, S8) allowed one to calculate SADS  $S_A$  and  $S_C$  corresponding to short-lived species.

$$\Delta D(\lambda, t) = (S_A(\lambda) - S_B(\lambda))e^{-t/\tau_1} + (S_C(\lambda) - S_D(\lambda))e^{-t/\tau_2} + (S_B(\lambda) + S_D(\lambda)) \quad (\text{S3})$$

$$A_1(\lambda) = S_A(\lambda) - S_B(\lambda) \quad (\text{S4})$$

$$A_2(\lambda) = S_C(\lambda) - S_D(\lambda) \quad (\text{S5})$$

$$A_3(\lambda) = S_B(\lambda) + S_D(\lambda) \quad (\text{S6})$$

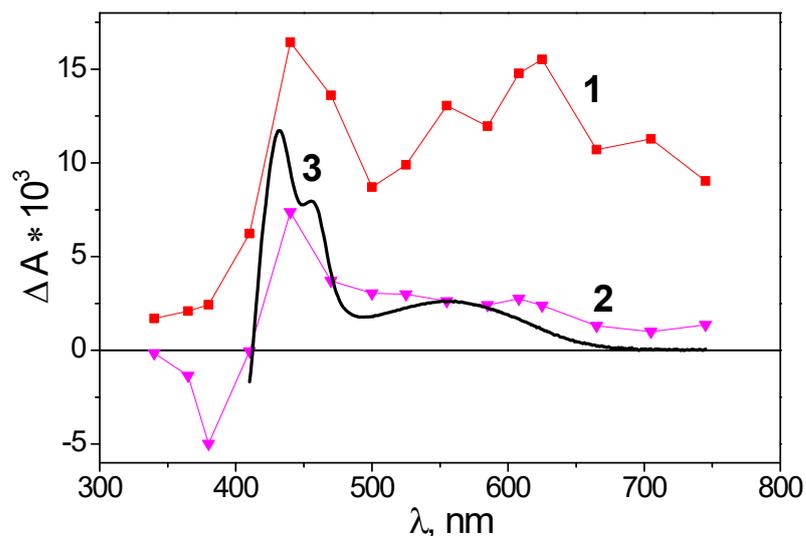
$$A_1(\lambda) + A_3(\lambda) = S_A(\lambda) + S_D(\lambda) \quad (\text{S7})$$

$$A_2(\lambda) + A_3(\lambda) = S_C(\lambda) + S_B(\lambda) \quad (\text{S8})$$

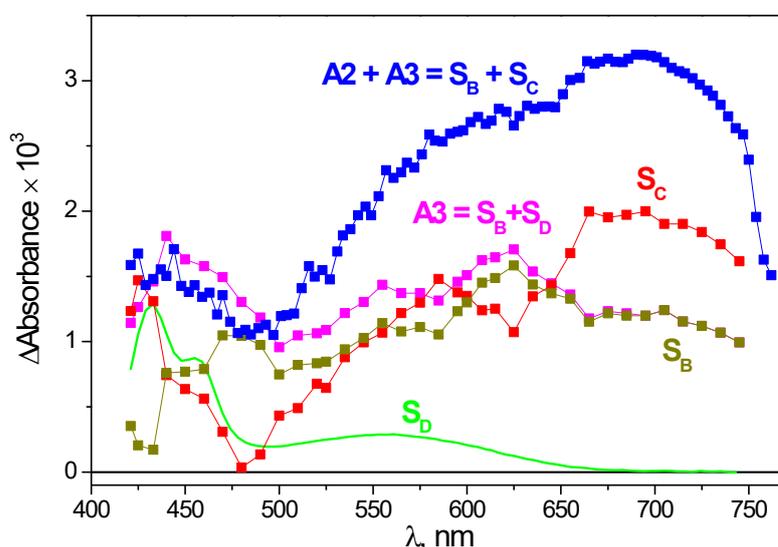
Calculation of SADS needs matching of ultrafast TA, laser flash photolysis and stationary photolysis data. The procedure of calculation is illustrated by Figures S4-S6. Combining the data of laser flash photolysis and stationary photolysis, we obtain the ratio of the values  $S_D$  and  $A_3 = S_B + S_D$  (Fig. S4). Curve 1 in Fig. S4 is the sum of absorbancies of species  $B = \mathbf{c-Z-D1-o}$  and  $D = \mathbf{E-D1-c}$ , which concentrations are proposed to be equal. Therefore, the spectrum represented by curve 1 is proportional to  $A_3 = S_B + S_D$ . Curve 3 in Fig. S4 is the absorbance of species D, which is the stable reaction product. Therefore, the spectrum represented by curve 3 is proportional to  $S_D$ . Therefore, we know the  $S_D / (S_B + S_D)$  ratio.

Fig. S5 illustrates the calculation of SADS  $S_C$ . Values of  $A_3$  and  $A_2 + A_3$  are taken from ultrafast TA data (Fig. S3). SADS  $S_D$  is normalized to  $A_3$  according to Fig. S4. SADS  $S_B$  and  $S_C$  are calculated using formulae S6 and S8.

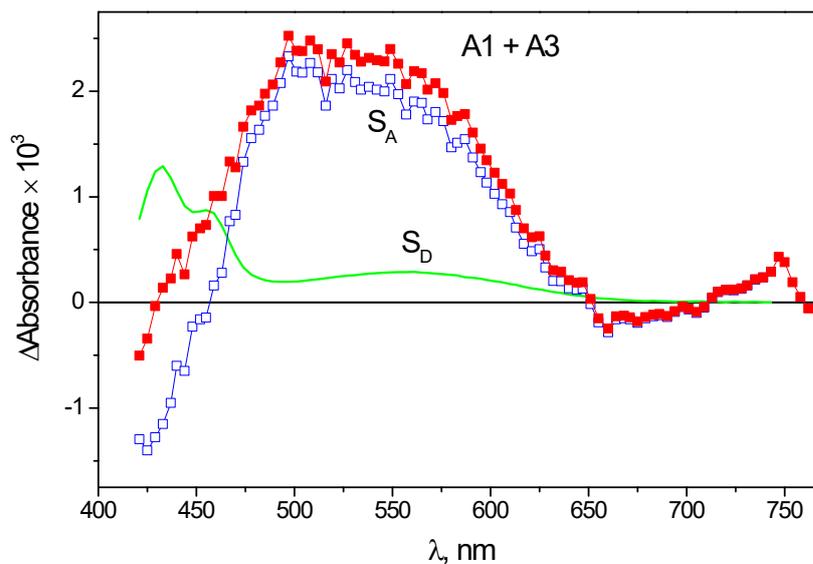
Calculation of SADS  $S_A$  is illustrated by Fig. S6. The values of  $A_1 + A_3$  and  $S_D$  are taken from Figs. S3 and S5 correspondingly.  $S_A$  is calculated by formula S7. Finally, SADS  $S_A$  and  $S_C$  are shown in Fig. S9, which coincides with Fig. 8 of the main text.



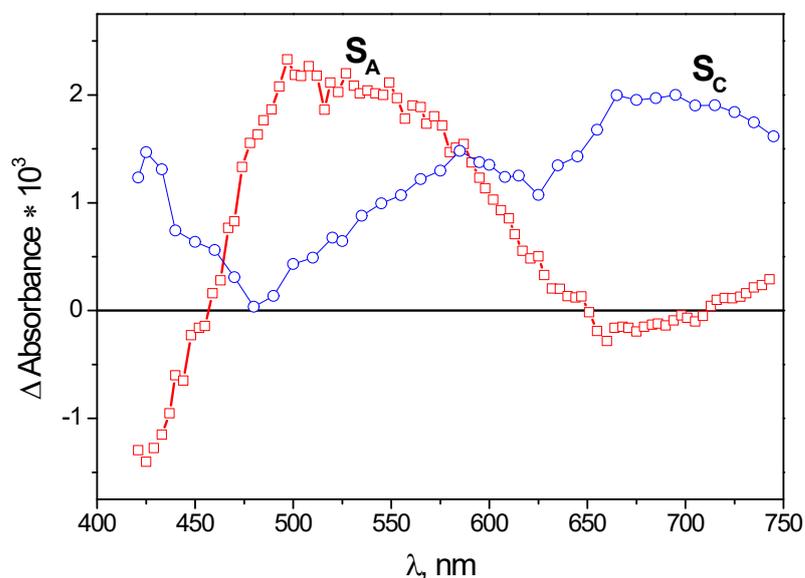
**Figure S6.** Laser flash photolysis (355 nm) of *E-D1-o* in n-hexane ( $2.3 \times 10^{-5}$  M, 1 cm cell, air-saturated solutions). Intermediate absorption spectra. Curves 1 and 2 correspond to time delays 0.4 and 38  $\mu$ s after the laser pulse. Black curve – difference in the spectra of irradiated (370 nm) and initial samples obtained in stationary photolysis experiments matched to curve 2 at 560 nm. Part of Fig. 4b of the main text.



**Figure S7.** Results of analysis of the intermediate absorption data obtained by the ultrafast pump-probe spectroscopy (320 nm) of *E-D1-o* ( $3.3 \times 10^{-5}$  M, 1 mm cell) in n-hexane. Calculation of SADS  $S_C = \text{Precursor (AP)}$ .  $A_2 + A_3$  – sum of amplitudes taken from Fig. S3.  $S_D$  – normalized final absorption obtained in stationary photolysis experiment (Fig. S4).  $S_C = (A_2 + A_3) - S_B$ .

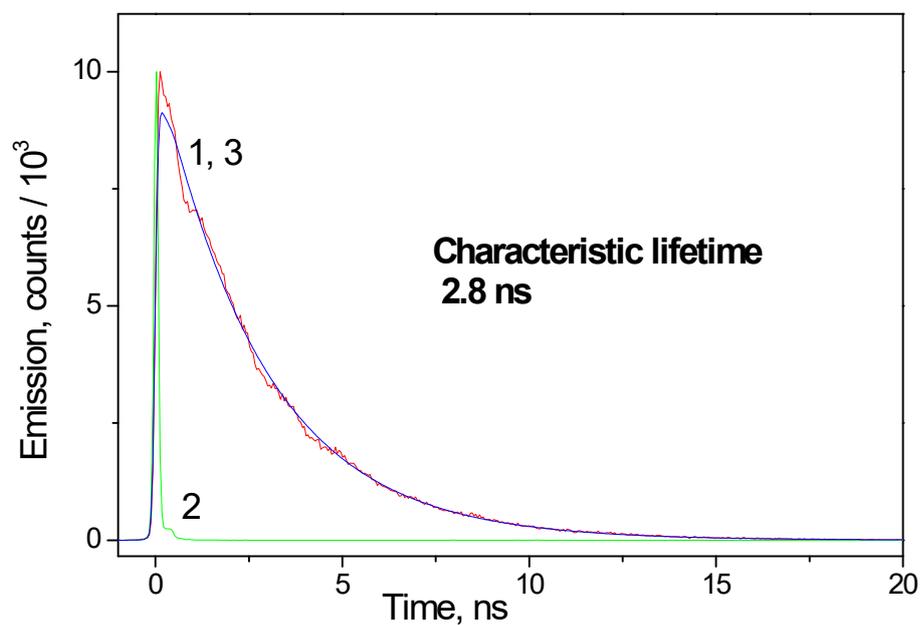


**Figure S8.** Results of analysis of the intermediate absorption data obtained by the ultrafast pump-probe spectroscopy (320 nm) of *E-D1-o* ( $3.3 \times 10^{-5}$  M, 1 mm cell) in n-hexane. Calculation of SADS  $S_A = \text{Precursor (P)}$ .  $A_1 + A_3$  – sum of amplitudes taken from Fig. S3.  $S_D$  – normalized final absorption obtained from stationary photolysis experiment.  $S_A = (A_1 + A_3) - S_D$ .



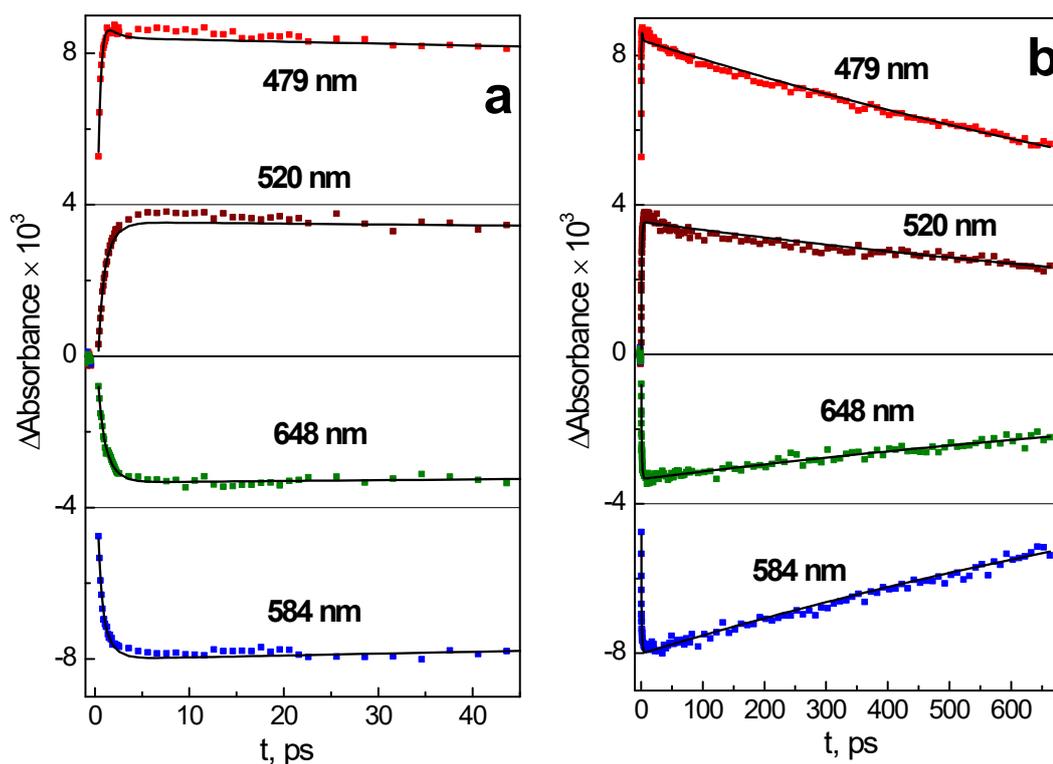
**Figure S9.** Species Associated Absorbance Spectra (SADS) spectra extracted from ultrafast pump-probe spectroscopy experiment (320 nm) for *E-D1-o* in n-hexane. SADS  $S_A$  and  $S_C$  correspond to Precursor (P) and Precursor (AP). The figure coincides with Fig. 10 of the main text.

### S3. Kinetics of *E-D1-o* luminescence in acetonitrile



**Figure S10.** Examples of the kinetic curves of the *E-D1-o* luminescence decay in CH<sub>3</sub>CN, excitation at 375 nm emission at 555 nm. Curve 1 – experiment; curve 2 – instrument response functions (IRF); curve 3 – 1-exponential fit with lifetime 2.8 ns.

#### S4. Ultrafast pump-probe spectroscopy of *E*-D1-o in acetonitrile.



**Figure S11.** Results of the experiment on the ultrafast TA spectroscopy (320 nm) of *E*-D1-o ( $1.2 \times 10^{-4}$  M, 1 mm cell) in  $\text{CH}_3\text{CN}$ . Examples of kinetic curves with 3-exponential fit (Eq. S2) with the lifetimes  $\tau_1 = 0.31 \pm 0.13$  ps,  $\tau_2 = 1.03 \pm 0.39$  ps,  $\tau_3 = 1590 \pm 80$  ps. Panels **a**, **b** correspond to different time regions. The 3-exponential fit gives much worse results in comparison with the 4-exponential fit (see Fig. 11 of the main text).

#### References

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- [2] E. M. Glebov, I. P. Pozdnyakov, V. V Semionova, D. V Lonshakov, A. G. Lvov, V. Z. Shirinian, A. A. Melnikov and S. V Chekalin, *Mendeleev Commun.*, 2020, **30**, 61–63.
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