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Formation and decay of a triplet state of dipyrido[3,2-*a*:2′,3′-*c*]phenazine

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S1. Determination of spectral and kinetic parameters of ^{3}dppz* using laser flash photolysis

Molar absorption coefficient of ^{3}dppz* was determined using the method described [S1]. To estimate the molar absorption coefficient of the intermediate, the initial absorption of ^{3}dppz* was plotted as a function of the incident laser pulse energy (Figure S1a). The corresponding dependence is linear at low energies with a trend to saturation at higher energies. This type of dependence is typical for a one-photon process. Following the work [S1], we have fitted the experimental curve by function (S1).

$$\Delta D_0 = a(1 - e^{-bE}) \qquad \text{(S1)}$$

E is laser pulse energy, *a*, *b* are parameters of fitting.

Saturation of the dependence (Figure S2a) could be explained by two factors. First, the intermediate photolysis product could absorb at the wavelength of excitation (355 nm), and the characteristic time of its formation could be small in comparison with the laser pulse duration (5 ns). In this case, the new product should compete for the light quanta with the initial dppz molecules, which should result in saturation of the dependence of intermediate absorption vs. laser pulse energy [S2]. Nevertheless, in our case the intermediate does not absorb significantly in the region of wavelengths shorter that 370 nm (see Figure 2b of the main text), and the corresponding explanation of saturation could be ruled out. Another explanation of saturation is the limited amount of initial substance in comparison with the amount of the incident light quanta. If all the irradiated dppz molecules are converted to products, the further increase in light quanta flux would not result in the intermediate absorption increase. Therefore, fitting parameter *a* in Equation S1 allows us to estimate molar absorption coefficient of ^{3}dppz* (ε_T)

$$a = \varepsilon_T c_0 l \qquad \text{(S2)}$$

where c_0 is the concentration of the initial compound, *l* is the optical path length. For the maximum of ^{3}dppz* absorption (470 nm) we obtain $\varepsilon_T^{470\ \mathrm{nm}} = 2200 \pm 200\ \mathrm{M^{-1}cm^{-1}}$.

Rate constants of the triplet state decay in argon-saturated solutions were determined using method described in work [S3]. Taking into account the possibility of the triplet state decay both in second-order process (T-T annihilation, rate constant $2k_2$) and different first-order processes (total rate constant k_3), the initial parts of the kinetic curves (see Figure 2a of the main text) were fitted by a first order kinetic law. The obtained first order rate constants k_1^{obs} were plotted vs. initial absorption ΔD_0 (Figure S2b). The linear dependence is described by Equation S3:

$$k_1^{obs} = k_3 + \frac{2k_2}{\varepsilon_T l}\Delta D_0 \qquad \text{(S3)}$$

The obtained values of $2k_2$ and k_3 could be found in Table 1 of the main text.

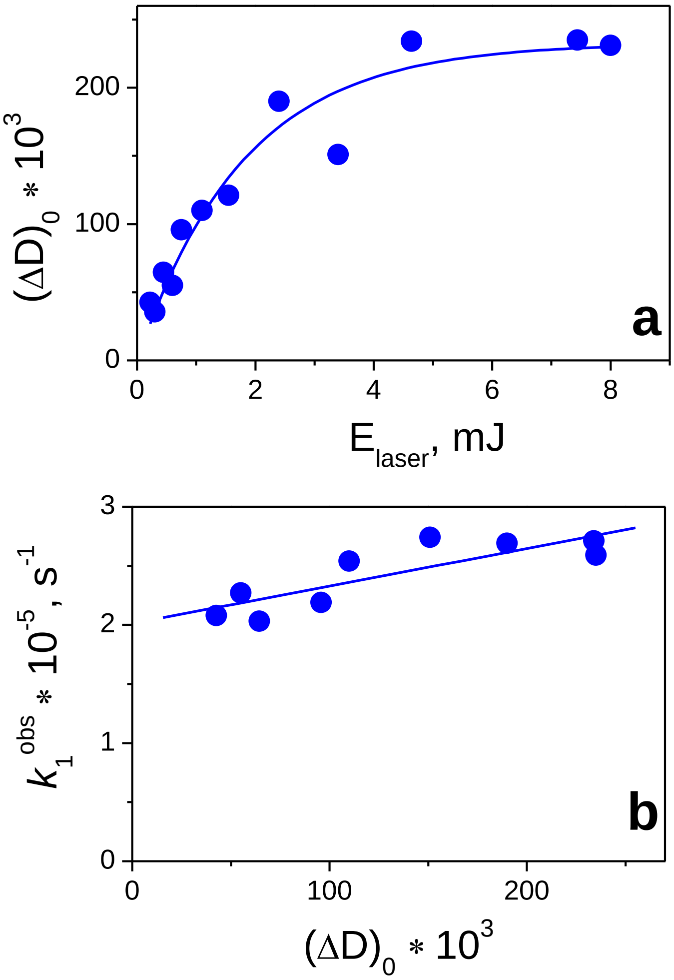
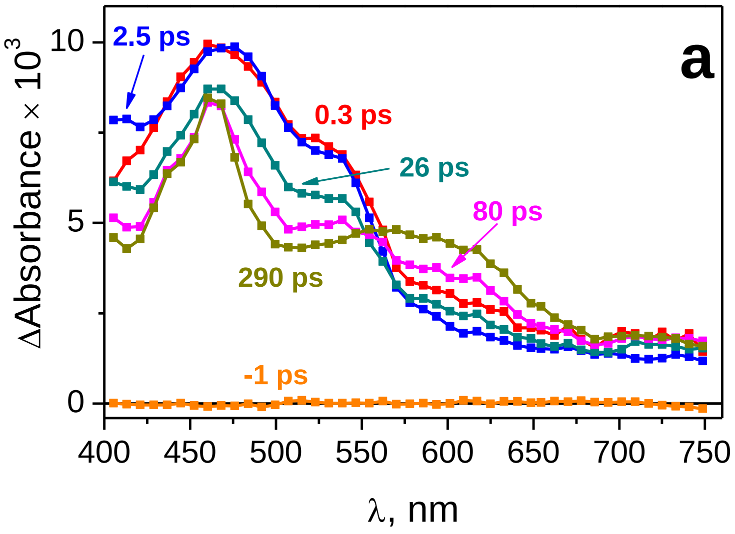


Figure S1 Laser flash photolysis (355 nm) of dppz (5.0×10^{-5} M; absorption at 355 nm is 0.73) in CH_3CN. Data treatment. 1 cm cell, argon-saturated solutions, registration at 470 nm, irradiated sample volume 0.05 cm^3. **a** – dependence of initial intermediate absorption vs. laser pulse energy. Experimental points and their fit by function (S1) with parameters a = 230 ± 20; b = (0.56± 0.09) mJ^{-1}. **b** – dependence of the observed 1st order rate constant vs. initial intermediate absorption. Experimental points and linear fit.

S2. Ultrafast pump-probe spectroscopy of dppz

The examples of raw data obtained by ultrafast kinetic spectroscopy of dppz in CH_3CN (intermediate absorption spectra corresponding to different time delays between pump and probe pulses) are presented in Figure S2a. The examples of kinetic curves and their fit using 2-exponential function with residual (equation 4) are shown in Figure S2b. The amplitudes $A_i(\lambda)$ obtained by global fit are presented in Figure S3.

$$\Delta A(\lambda,t) = A_1(\lambda)e^{-\frac{t}{\tau_1}} + A_2(\lambda)e^{-\frac{t}{\tau_2}} + A_3(\lambda) \qquad \text{(S4)}$$



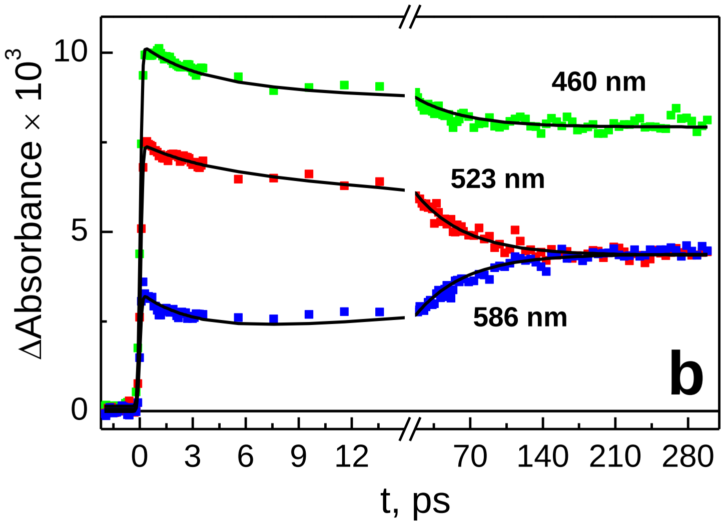


Figure S2 Results of the experiment on the ultrafast pump-probe spectroscopy (320 nm) of dppz (9×10^{-4} M, 1 mm cell) in CH_3CN. **a** – examples of intermediate absorption spectra corresponding to different time delays between pump and probe pulses **b** – examples of the kinetic curves at different wavelengths. Solid lines are the best fit approximations by Equation S4.

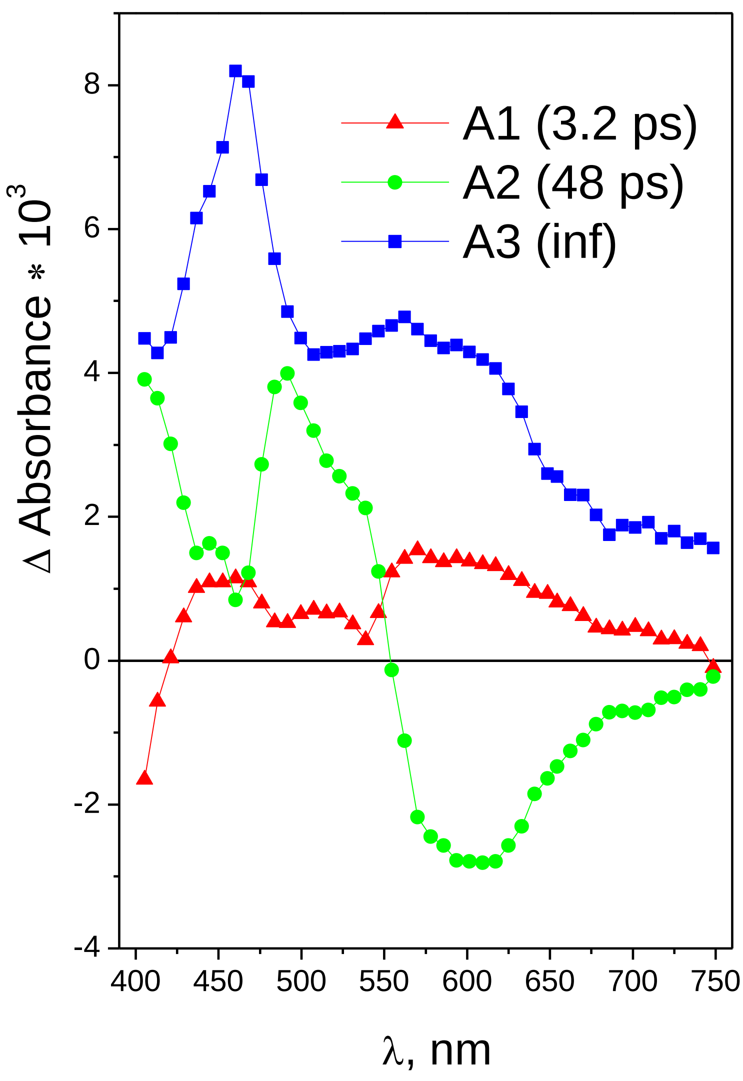


Figure S3 Results of the experiment on the ultrafast kinetic spectroscopy (320 nm) of dppz (9×10^{-4} M, 1 mm cell) in CH_3CN. Amplitudes of the 2-exponential global fit with the residual (Equation S4).

Approximation of the kinetic curves by means of function (4) assumes the sequential decay of the transient absorption A → B → C (C = ground state + products). The species associated difference spectra (SADS) of the individual components could be calculated using formulae (S5-S7) [S4]. For the case of big difference in lifetimes (as it happens in our case) the SADS are simply the sums of the corresponding components (S8-S10). The extracted SADS are shown in Figure 3 of the main text.

$$S_A(\lambda) = A_1(\lambda) + A_2(\lambda) + A_3(\lambda) \tag{S5}$$

$$S_B(\lambda) = A_2(\lambda)\frac{\tau_2 - \tau_1}{\tau_2} + A_3(\lambda) \tag{S6}$$

$$S_C(\lambda) = A_3(\lambda) \quad \text{(S7)}$$

For $\tau_1 >> \tau_1$ we obtain:

$$S_A(\lambda) = A_1(\lambda) + A_2(\lambda) + A_3(\lambda) \quad \text{(S8)}$$

$$S_B(\lambda) = A_2(\lambda) + A_3(\lambda) \quad \text{(S9)}$$

$$S_C(\lambda) = A_3(\lambda) \quad \text{(S10)}$$

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