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

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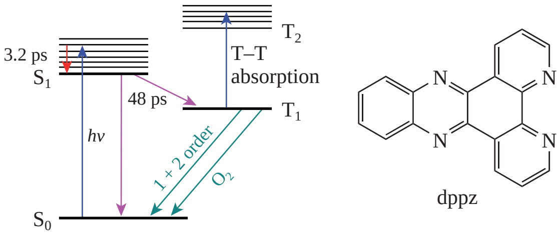
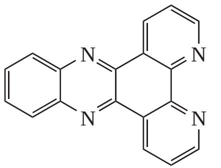
The photophysical and photochemial properties of dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz) in acetonitrile have been investigated by laser flash photolysis and ultrafast pump-probe spectroscopy. The excitation of dppz to the first singlet excited state was followed by vibrational cooling with solvent relaxation for ~3 ps and then intersystem crossing for ~50 ps. Spectral and kinetic characteristics of the triplet excited state have been determined.



Keywords: photophysics, photochemistry, triplet state, dppz, laser flash photolysis, ultrafast pump-probe spectroscopy.

Dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz) is widely used as a ligand in transition metal complexes for different applications. A dppz-containing Cu(I) complex was proposed as a luminescent oxygen-sensing system.[1] Another application area is based on the ability of dppz metal complexes to associate with DNA. Ruthenium(II),[2–4] osmium(II)[5] and rhenium(I)[6] dppz complexes were used as luminescent reporters for binding to double-stranded DNA. Dirhodium complexes with dppz were found promising in photochemotherapy.[7–9] Transition metal complexes containing dppz and its derivatives were used for the synthesis of magnetically bistable compounds[10,11] as well as components of molecular electronics and spintronics.[12–14]



dppz

In spite of these applications, the data on dppz photophysics and photochemistry is scarce. It is known that (*i*) the excitation of dppz in methanol results in the formation of its triplet state ^{3}dppz* and another species, probably a valence isomerization product;[6] (*ii*) the characteristic lifetime of intersystem crossing in acetonitrile is about 50 ps[15] and (*iii*) the irradiation of dppz in ethanol leads to the formation of 9,14-dihydrodipyrido[3,2-*a*:2′,3′-*c*]phenazine through H-atom transfer from the solvent to ^{3}dppz*.[16] The goal of this work was to investigate the formation and decay of the ^{3}dppz* state by stationary photolysis,[†] nanosecond laser flash photolysis[‡] and ultrafast pump-probe spectroscopy.[§]

The prolonged stationary photolysis of dppz[¶] in MeCN resulted in very small absorption change (Figure 1) contrary to the known data for alcohol solutions, where photodegradation is substantial.[6,16] Therefore, acetonitrile is a good solvent for examination of the photophysics of dppz.

Laser flash photolysis of dppz led to the emergence of intermediate absorption. Figure 2 shows typical kinetic curves for air-saturated and deaerated solutions and the intermediate absorption spectra. The dependence of the intermediate absorption

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[†] UV absorption spectra were recorded using a Varian Cary 50 spectrophotometer. Stationary photolysis at 308 nm was performed by an excimer XeCl lamp with half width of light pulse 5 nm, pulse duration 1 µs, frequency 200 kHz and incident light flux 8×10^{15} photon cm^{-2} s^{-1}.[17]

[‡] Laser flash photolysis was performed using a Nd:YAG laser (Lotis TII, Belarus) at 355 nm, with 5 ns pulse duration and up to 10 mJ pulse^{-1} energy.[18] The pulse energy was measured by a SOLO 2 light power meter (Gentec, Canada).

[§] Ultrafast pump-probe spectroscopy was performed as described.[19,20] The pulse duration was ~100 fs and the exciting pulse energy was 1 µJ at a repetition frequency 1 kHz. A portion of exciting laser beam was focused on a cell with heavy water to generate a probe radiation (continuum). The solutions were placed in an 1 mm rotating optical cell and 45 experimental kinetic curves were globally fitted using the PyGSpec program.[21]

[¶] Dppz was synthesized as described[22] and characterized by elemental analysis and NMR and UV spectroscopy. Solutions were prepared in spectrally pure grade acetonitrile (Cryochrom, Russia) and if necessary deoxidized by bubbling argon for 30 min.

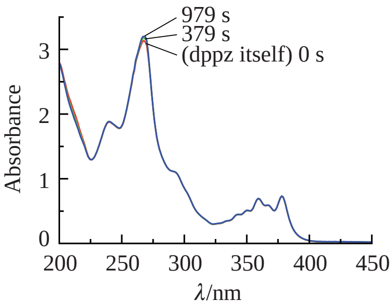

Figure 1 Changes in the electronic absorption spectrum of 3.8×10^{-5} M dppz in MeCN (1 cm cell, air-saturated solution) caused by irradiation at 308 nm.

decay lifetime on the dissolved oxygen concentration is typical of the triplet state. The triplet ^{3}dppz* spectrum with a maximum at ~470 nm and a long tail at 550–750 nm [Figure 2(*b*)] is similar to that reported.[6] Residual absorption with a maximum at ~400 nm [Figure 2(*b*)] probably belongs to a valence isomerization product.[6] The absence of absorption in this region during the prolonged stationary photolysis (Figure 1) reveals, that the lifetime of this isomerization product is 0.1–10 s.

Table 1 summarizes the spectral and kinetic parameters of the dppz triplet state. The rate constant of ^{3}dppz* quenching by dissolved oxygen [reaction (1)] was calculated using the effective rate constant of intermediate absorption decay in air-saturated solutions under pseudo-first-order reaction conditions taking into account the O_2 concentration in air-saturated MeCN equal to 2.4×10^{-3} mol dm^{-3},[23] which was much higher than the concentration of ^{3}dppz*. This rate constant k_1 is an order of magnitude lower than the rate constant of a diffusion-controlled reaction in acetonitrile under normal conditions k_D, which is equal to 1.9×10^{10} dm^3 mol^{-1} s^{-1}.[24] The values of 0.1 k_D are typical of the rate constants for the quenching of triplet states of aromatic molecules by dioxygen.[25]

$$^3\text{dppz}^* + {}^3\text{O}_2 \xrightarrow{k_1} {}^1\text{dppz} + {}^1\text{O}_2 \tag{1}$$

$$^3\text{dppz}^* + {}^3\text{dppz}^* \xrightarrow{2k_2} {}^1\text{dppz} + {}^1\text{dppz}^{**} \tag{2}$$

$$^3\text{dppz}^* \xrightarrow{k_3} {}^1\text{dppz} \tag{3}$$

The molar absorption coefficient of ^{3}dppz* $\varepsilon_{\max}$ at $\lambda_{\max} = 470$ nm and the quantum yield of its formation φ_T after excitation at 355 nm were determined as described[26,27] (see Section S1 in Online Supplementary Materials).

The rate constants of triplet state decay in argon-saturated solutions were determined using the known procedure[28] (see Section S1). The second-order rate constant k_2 [reaction (2)] corresponds to T–T annihilation. Note, that k_2 (see Table 1) is lower by a factor of 30 than the rate constant for the diffusion-controlled reaction, probably, due to the combination of spin-statistical factor for the process triplet + triplet → singlet + singlet as well as steric effects. Typically, the rate constant of T–T annihilation for small cyclic structures like anthracene[29] or benzophenone[30] is lower by a factor of 3–5 times than the rate constant of the diffusion-controlled reaction. For larger molecules, this difference could be an order of magnitude or higher.[31]

The first-order rate constant of the triplet state decay k_3 [reaction (3)] is determined by intersystem crossing as well as from quenching by residual oxygen and possible impurities.

Table 1 Spectral and kinetic parameters of the dppz triplet state.

Spectral parameters	Kinetics parameters
$\lambda_{\max} = 470$ nm	$k_1 = (1.0\pm0.1)\times10^9$ dm^3 mol^{-1} s^{-1}
$\varepsilon_{\max} = 4500\pm400$ dm^3 mol^{-1} cm^{-1}	$2k_2 = (1.4\pm0.4)\times10^9$ dm^3 mol^{-1} s^{-1}
$\varphi_T = 0.6\pm0.1$ at 355 nm	$k_3 = (2.1\pm0.2)\times10^5$ s^{-1}

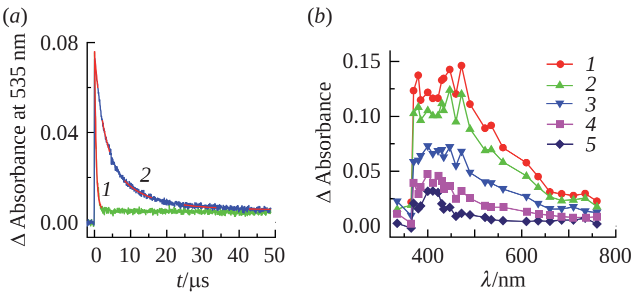

Figure 2 Laser flash photolysis at 355 nm of 5.0×10^{-5} M dppz (1 cm cell) in MeCN. (*a*) Kinetic curves at 535 nm of (*1*) air-saturated solution (experiment as green line, single-exponential fit as red line) and (*2*) argon-saturated solution (experiment as blue line, double-exponential fit as red line). (*b*) Intermediate absorption spectra at time delays between exciting and probing pulses *t*/μs: (*1*) 0.4, (*2*) 1.2, (*3*) 4, (*4*) 10 and (*5*) 42.

The formation of ^{3}dppz* was examined by ultrafast pump-probe spectroscopy with excitation at 320 nm, pulse duration of ~100 fs and detection at 400–750 nm. The experimental intermediate absorption spectra corresponding to different time delays between pump and probe pulses as well as kinetic curves are shown in Figure S2(*a*) (see Online Supplementary Materials). The experimental kinetic curves [Figure S2(*b*)] were globally fitted using double-exponential function with residual [equation (1)]. The spectra of the amplitudes $A_i(\lambda)$ are shown in Figure S3, Online Supplementary Materials. The characteristic lifetimes extracted from the global fit were $\tau_1 = 3.2\pm1.5$ and $\tau_2 = 48\pm8$ ps.

$$\Delta A(\lambda,t) = A_1(\lambda)\exp(-t/\tau_1) + A_2(\lambda)\exp(-t/\tau_2) + A_3(\lambda) \tag{1}$$

Treatment of the kinetic curves by function (1) 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), see Online Supplementary Materials.[32] For a large difference in lifetimes, as in our case, the SADS represent simply the sums of the corresponding components [Equations (2)–(4)]. The extracted SADS are shown in Figure 3.

$$S_A(\lambda) = A_1(\lambda) + A_2(\lambda) + A_3(\lambda) \tag{2}$$

$$S_B(\lambda) = A_2(\lambda) + A_3(\lambda) \tag{3}$$

$$S_C(\lambda) = A_3(\lambda) \tag{4}$$

The initial intermediate SADS S_A (Figure 3, curve *1*) has an absorption band at 470 nm and a shoulder at 515–540 nm. The spectrum of the second intermediate SADS S_B (Figure 3, curve *2*) does not differ significantly from the first one, in fact, a spectral signature of the first process represents narrowing of the absorption band. This is typical of relaxation processes. Finally, the shape of the residual spectrum SADS S_C (Figure 3, curve *3*) resembles that of the dppz triplet state obtained in a laser flash photolysis experiment as the difference of spectra corresponding to 1.2 and 42 μs delays in Figure 2(*b*).

Now, we can tentatively describe the processes occurring after excitation of dppz. Irradiation at 320 nm results in transformation to the singlet excited state ^{1}dppz*. The SADS S_A corresponds to this state, which is vibrationally hot, and the solvent structure is still corresponding to the ground state. The first observed time (3.2 ps) corresponds to vibrational cooling and solvent relaxation, whose characteristic times are close to each other. It fits well to the known diffusion solvent relaxation time for acetonitrile, equal to 3.4 ps.[33,34] The vibrational cooling times for organic molecules lie in a range from one to several tens of picoseconds.[34] Therefore, the second intermediate represented by SADS S_B is the relaxed ^{1}dppz* state. The second observed process is the intersystem crossing. Its time constant, equal to 48 ± 8 ps, corresponds to that reported.[15]

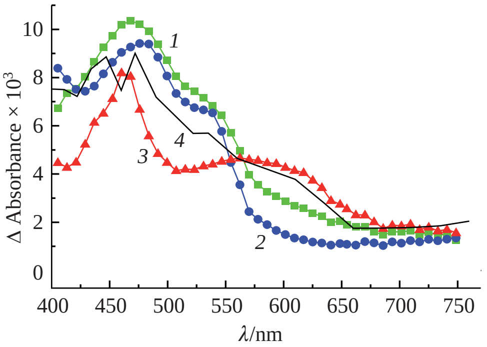

Figure 3 Ultrafast kinetic spectroscopy with excitation at 320 nm of 9×10^{-4} M dppz (1 mm cell) in MeCN. Curves (*1*)–(*3*) correspond to the SADS of intermediates A, B and a final product C. Curve (*4*) is the ^{3}dppz* spectrum obtained by laser flash photolysis matched with product C at 560 nm (see the text).

In summary, we have obtained quantitative data on the photonconversions of dppz, which is promising for further understanding the photochemistry of light-activated anticancer dppz-containing rhodium complexes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.021.

References

1 W. Yang, W. Yang, W. Liu and W. Qin, *Spectrochim. Acta, Part A*, 2013, **104**, 56.
2 A. E. Friedman, J. C. Chambron, J. P. Sauvage, N. J. Turro and J. K. Barton, *J. Am. Chem. Soc.*, 1990, **112**, 4960.
3 R. M. Hartshorn and J. K. Barton, *J. Am. Chem. Soc.*, 1992, **114**, 5919.
4 Y. Jenkins, A. E. Friedman, N. J. Turro and J. K. Barton, *Biochemistry*, 1992, **31**, 10809.
5 R. E. Holmlin and J. K. Barton, *Inorg. Chem.*, 1995, **34**, 7.
6 H. D. Stoeffler, N. B. Thornton, S. L. Temkin and K. S. Schanze, *J. Am. Chem. Soc.*, 1995, **117**, 7119.
7 P. M. Bradley, A. M. Angeles-Boza, K. R. Dunbar and C. Turro, *Inorg. Chem.*, 2004, **43**, 2450.
8 A. M. Angeles-Boza, P. M. Bradley, P. K.-L. Fu, S. E. Wicke, J. Bacsa, K. R. Dunbar and C. Turro, *Inorg. Chem.*, 2004, **43**, 8510.
9 A. M. Angeles-Boza, P. M. Bradley, P. K.-L. Fu, M. Shatruk, M. G. Hilfiger, K. R. Dunbar and C. Turro, *Inorg. Chem.*, 2005, **44**, 7262.
10 N. Dupont, Y.-F. Ran, S.-X. Liu, J. Grilj, E. Vauthey, S. Decurtins and A. Hauser, *Inorg. Chem.*, 2013, **52**, 306.
11 R. Kulmaczewski, H. J. Shepherd, O. Cespedes and M. A. Halcrow, *Inorg. Chem.*, 2014, **53**, 9809.
12 A. Dei, D. Gatteschi, C. Sangregorio and L. Sorace, *Acc. Chem. Res.*, 2004, **37**, 827.
13 K. S. Kumar and M. Ruben, *Coord. Chem. Rev.*, 2017, **346**, 176.
14 A. A. Starikova and V. I. Minkin, *Russ. Chem. Rev.*, 2018, **87**, 1049.
15 C. Creely, J. Kelly, A. M. Selmi, D. A. McGovern, W. J. Blau, P. Matousek, M. Towrie and A. W. Parker, *Proc. SPIE*, 2003, **4991**, 482.
16 D. A. McGovern, A. Selmi, J. E. O'Brien, J. M. Kelly and C. Long, *Chem. Commun.*, 2005, 1402.
17 E. A. Sosnin, T. Oppenländer and V. F. Tarasenko, *J. Photochem. Photobiol., C*, 2006, **7**, 145.
18 I. P. Pozdnyakov, V. F. Plyusnin, V. P. Grivin, D. Y. Vorobyev, N. M. Bazhin and E. Vauthey, *J. Photochem. Photobiol., A*, 2006, **181**, 37.
19 S. V. Chekalin, *Phys.-Usp.*, 2006, **49**, 634 (*Usp. Fiz. Nauk*, 2006, **176**, 657).
20 E. M. Glebov, I. P. Pozdnyakov, V. P. Chernetsov, V. P. Grivin, A. B. Venediktov, A. A. Melnikov, S. V. Chekalin and V. F. Plyusnin, *Russ. Chem. Bull., Int. Ed.*, 2017, **66**, 418 (*Izv. Akad. Nauk, Ser. Khim.*, 2017, 418).
21 N. V. Tkachenko, *PyG Tools for Spectroscopy Data Analysis. User's Guide*, 2009, http://butler.cc.tut.fi/~tkatchen/prog/users_guide.pdf.
22 J. E. Dickeson and L. A. Summers, *Aust. J. Chem.*, 1970, **23**, 1023.
23 C. Franco and J. Olmsted, III, *Talanta*, 1990, **37**, 905.
24 A. G. Matveeva, E. M. Glebov, V. P. Grivin, V. V. Korolev, V. F. Plyusnin and V. A. Reznikov, *Russ. Chem. Bull., Int. Ed.*, 2010, **59**, 771 (*Izv. Akad. Nauk, Ser. Khim.*, 2010, 755).
25 A. A. Abdel-Shafi and D. R. Worrall, *J. Photochem. Photobiol., A*, 2005, **172**, 170.
26 U. Lachish, A. Shafferman and G. Stein, *J. Chem. Phys.*, 1976, **64**, 4205.
27 S. G. Matveeva, I. P. Pozdnyakov, V. P. Grivin, V. F. Plyusnin, A. S. Mereshchenko, A. A. Melnikov, S. V. Chekalin and E. M. Glebov, *J. Photochem. Photobiol., A*, 2016, **325**, 13.
28 E. M. Glebov, N. V. Ruban, I. P. Pozdnyakov, V. P. Grivin, V. F. Plyusnin, A. G. Lvov, A. V. Zakharov and V. Z. Shirinian, *J. Phys. Chem. A*, 2018, **122**, 7107.
29 F. Tfibel and L. Lindqvist, *Chem. Phys.*, 1975, **10**, 471.
30 Y. M. A. Naguib, C. Steel, S. G. Cohen and M. A. Young, *J. Phys. Chem.*, 1987, **91**, 3033.
31 V. V. Sapunov, *High Energy Chem.*, 2000, **34**, 159 (*Khim. Vys. Energ.*, 2000, **34**, 196).
32 A. S. Rury and R. J. Sension, *Chem. Phys.*, 2013, **422**, 220.
33 M. L. Horng, J. A. Gardecki, A. Papazyan and M. Maroncelli, *J. Phys. Chem.*, 1995, **99**, 17311.
34 T. Kumpulainen, B. Lang, A. Rosspeintner and E. Vauthey, *Chem. Rev.*, 2017, **117**, 10826.

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