

Spectroscopy of the Excited-State Complex of Zinc(II) with 3,3'-Bis(dipyrrolylmethene)

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Abstract—Spectra of nonstationary transient absorption of metal bis(dipyrrolylmethene) complexes in cyclohexane and ethanol, which exhibit different photophysical and photochemical properties in these solvents, have been measured and the yields of excited triplet states have been evaluated. It has been shown that the yield of triplets is determined by the intramolecular structure and the difference in fluorescence and phototransformation yields is due to intermolecular interaction of the excited molecules with the solvation shell.

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The design of new materials based on linear tetrapyrrole ligands, such as 3,3'-bis(dipyrrolylmethene)s, bears direct relationship to the prospects of wide application of their coordination compounds in specific high-tech devices used as optical probes, markers, sensors, photoresponsive cells, etc. [1, 2]. Targeted synthesis of appropriate structures for a particular application requires that the relation of the molecular structure to the properties of compounds of this class should be studied, as well as the influence on this relation of the medium in which a given compound is placed. Note that there is an increasing interest in the study of coordination compounds formed by oligopyrrole ligands, such as porphyrin and bilirubin, structurally related to chromophore molecules involved in the functioning of living organisms [1, 3]. An integrated approach to investigation of 3,3'-bis(dipyrrolylmethene) complexes of this type with various metals using theoretical calculation data highlights the interest to compounds of this class. Wei et al. [3] interpreted experimental data on light absorption in the IR and visible region by zinc(II) and nickel(II) complexes with one of the 3,3'-bis(dipyrrolylmethene)s with the use of quantum-chemical calculations, including ab initio calculation; however, there is a lack of data on the emission characteristics, which have been studied for some zinc complexes of 3,3'-bis(dipyrrolylmethene)s in [2]. A very important characteristic of an optical material pertaining to interaction with light at various wavelengths is the service life determined by the photochemical stability of compounds under given conditions. The quantitative characteristic of phototransformations can be determined on the basis of a photoinduced change in stationary spectra of absorption from the ground state [2, 4],

whereas it is necessary to study absorption from excited states in order to reveal the mechanism of phototransformations and the ways of controlling it. This absorption in some cases makes it possible to reveal the nature of the excited states and their involvement in the formation of intermediate and final products. In this context, we studied in the present work the spectra of induced transient (6–30 ns) absorption in ethanol and cyclohexane for the complex of zinc(II) with alkylated 3,3'-bis(dipyrrolylmethene), which undergoes substantial changes in photophysical and photochemical properties in different solvents, although its stationary absorption and emission spectra differ insignificantly [2].

MATERIALS AND METHODS

Figure 1 shows the structure of the object of study $[Zn_2L_2]$, the binuclear homoleptic complex of zinc(II) with bis(1,3,7,9-tetramethyl-2-ethyl-dipyrrolylmethen-8-yl)methane (H_2L). In the $[Zn_2L_2]$ molecule, the tetrapyrrole chains of each of the two ligands

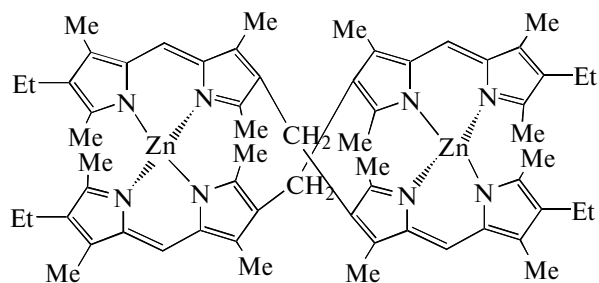


Fig. 1. Structure of the $[Zn_2L_2]$ complex.

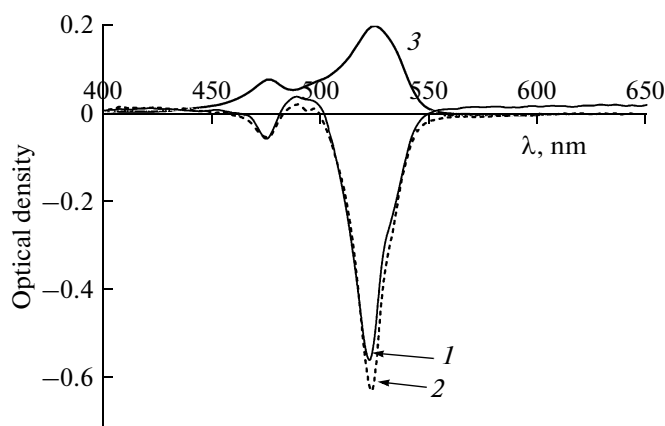


Fig. 2. (1, 2) Nonstationary transient absorption and (3) stationary absorption spectra of $[\text{Zn}_2\text{L}_2]$ in ethanol at $c_0 = 3 \times 10^{-6}$ mol/L (1) during the pulse (without delay) and (2) with a 30-ns delay from the onset of the excitation pulse: $W_{\text{exc}} = 50$ MW/cm². The ordinate of spectrum 3 is multiplied by 0.22.

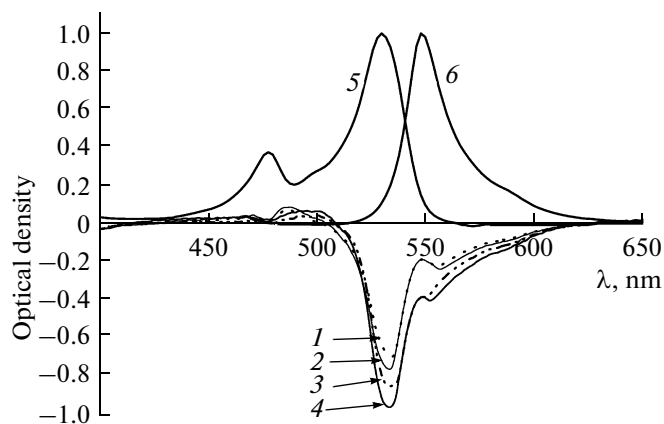


Fig. 3. (1–4) Nonstationary transient absorption spectra and normalized (5) stationary absorption and (6) fluorescence spectra of $[\text{Zn}_2\text{L}_2]$ in cyclohexane as recorded (1, 2) during the excitation pulse or (3, 4) with a delay of 30 ns from the onset of the pulse at $W_{\text{exc}} = (1, 3) 25$ or (2, 4) 50 MW/cm²; $c_0 = 3 \times 10^{-6}$ mol/L. The NTA spectra were measured without allowance for fluorescence.

occur in the ridge-tilde conformation and braid the two metal coordination atoms [3, 5]. In each coordination center, the metal atom coordinates four nitrogen atoms of the dipyrrolylmethene moieties of the two ligands with the coordination unit having a distorted tetrahedron geometry. All these features provide for a three-dimensional architecture of the molecule in the form of double helix. Along with covalent bonds, there are donor–acceptor coordination interactions between the central metal atoms and the tetrapyrrole nitrogen atoms, which are due to partial redistribution of electron density between the metal and the organic ligand, resulting in the appearance of electronic states that affect the absorption and deactivation of excitation energy. The synthesis of this compound is detailed in [5]. The compound is insoluble in water, sparingly soluble (up to $\sim 10^{-3}$ mol/L) in nonpolar solvents (aromatics inclusive), and much poorer soluble in polar organic solvents. Intermolecular interactions play a substantial role in deactivation of excitation energy of $[\text{Zn}_2\text{L}_2]$: almost undetectable fluorescence in ethanol and the fluorescence quantum yield close to unity in cyclohexane with very small shifts of the stationary absorption and emission spectra, which ensure generation of stimulated emission of $[\text{Zn}_2\text{L}_2]$ in cyclohexane upon excitation by Nd-YAG laser second-harmonic radiation [2]. Despite this difference in emission efficiency, we found [2] that the quantum yield of phototransformations in the case of excitation to the long-wavelength band is higher in cyclohexane than in ethanol and the fluorescence intensity in frozen ethanol solution is two orders of magnitude above that at room temperature.

Nonstationary transient absorbance (NTA) of the dye was studied by the pump–probe technique [6] using a unique setup with a fluorescent probe [7]. The

device makes it possible to record nonstationary absorption spectra with nanosecond time resolution in the range of 350–900 nm. Experimentally measured nonstationary absorption was analyzed using the approach developed in [8, 9]. A specific feature of this approach is that at an appropriate wavelength selected for analysis of the results, it is possible to determine the yield of excited triplet states without involving reference standards with a known value of the extinction coefficient of T – T absorption from NTA spectra for compounds that exhibit narrow high-intensity bands in stationary absorption spectra. Note that similar approaches have been reported in the literature, e.g., by Lament et al. [10] who also estimated the quantum yield of excited triplet molecules without a standard on the basis of the rate curve measured for the back transition of molecules to the ground state with the use of picosecond pulse excitation and a similar choice of compounds and spectral regions.

RESULTS AND DISCUSSION

The object of study was $[\text{Zn}_2\text{L}_2]$, a compound that exhibits a narrow intense band of absorption from the ground state in organic solvents (Figs. 2, 3). Solutions in ethanol and cyclohexane have very close spectral characteristics of absorption, which have been studied in detail in [2]: S_0 – S_1 (526 nm, $\epsilon_{\text{max}} = 306250$ M⁻¹cm⁻¹), S_0 – S_2 (476 nm), and S_0 – S_3 (360 nm) in ethanol and 530 ($\epsilon_{\text{max}} = 260000$ M⁻¹cm⁻¹), 478, and 360 nm, respectively, in cyclohexane. The position of the fluorescence maximum also differs slightly: 544 nm in ethanol versus 548 nm in cyclohexane, whereas the quantum yield of this emission varies by two orders of magnitudes from 0.007 in ethanol to 0.5 in cyclohexane

upon UV excitation (355 nm) or 0.9 in the case of excitation to the long-wavelength band [2].

[Zn₂L₂] Complex in Ethanol

The differential nonstationary transient absorption spectra of [Zn₂L₂] in ethanol shown in Fig. 2 were excited by third-harmonic radiation of a LOTIS TII, LS-2132UTF Nd:YAG laser ($\lambda = 355$ nm, $\tau = 6$ ns, $E_{\text{pulse}} = 40$ mJ) with a power density of 25–50 MW/cm². Nonstationary absorption was measured in the range of 370–700 nm either synchronously with excitation of the medium or with a time delay of 30 ns. The differential absorption spectrum was represented in optical density units as the negative logarithm of the intensity ratio of the probe radiation transmitted through the unexcited and the excited test medium at every wavelength. Powerful pulse excitation of the dye leads to reduction in the ground state population, a change that is manifested as “brightening” in differential nonstationary absorption spectra, i.e., negative absorbance (curve below the abscissa) in the region of linear stationary absorption, owing to the departure of molecules from the ground state during a nanosecond pulse. This finding is consistent with the results showing an increase in the transmission of Nd:YAG laser second-harmonic radiation (532 nm) at a power density of 50 mW/cm² by a [Zn₂L₂] solution in ethanol; note that the transmittance was found [2] to decrease in the case of UV radiation (355 nm) with the same power. Upon powerful excitation, all molecules occurring in the excited volume undergo transition to the S_1 state (i.e., $c_0 = c_{S_1}$), since the concentration of molecules is $c_0 = 3 \times 10^{-6}$ mol/L (1.8×10^{15} molecule/cm³) and the light flux density is 50 MW/cm² ($>10^{25}$ photon/(cm² c $>10^{17}$ photon/(cm² pulse)), a conclusion that is consistent with saturation of NTA spectra with an increase in excitation intensity above 25 MW/cm² as revealed in [9]. Part of the molecules return to the ground state via fluorescence or in a nonradiative mode during the pulse, and the other part pass at a rate determined by the intersystem crossing constant to the triplet states, whose lifetime is significantly longer than the duration of the excitation pulse. It is noteworthy that some part of molecules can transfer to excited singlet states as well during the pulse, but they relax to the excited S_1 state within a few femto- or picoseconds hardly have an effect on NTA on the nanosecond time scale. Prolonging the stay of molecules in excited state during the excitation pulse and 30 ns after its end leads to a decrease in the “negative absorption” as compared to the stationary absorption. This difference determines the proportion of molecules remaining in the triplet states. Thus, the concentration of molecules returned to the ground state in the excited volume during the laser pulse, $-c^*$, will be lower than the initial concentration $-c_0$ by the value of concentration of molecules passed to triplets, $-c_t$; consequently, $c_t = c_0 - c^*$. Then the yield of triplet states will be $\phi_T =$

$c_t/c_{S_1} (c_0 - c^*)/c_0 = 1 - c^*/c_0 = 1 - D^*/D_0$, where D^* is the optical density corresponding to the negative absorption (in absolute value) of molecules from the ground state in the excited volume and D_0 is the optical density in the stationary spectrum (at the maximum, of the intense absorption band). The error of evaluation of the yield of triplets in terms of this approach is largely determined by the D^* measurement error, which is due to laser operation instability and makes up $\pm 10\%$. In addition, the wavelength at which D^* and D_0 are measured must be selected in such a way that the extinction coefficient of $T-T$ absorption will be not greater than 10% of the extinction of stationary absorption in this region. As is seen in Fig. 2, this condition is fulfilled at the maximum of the long-wavelength stationary-absorption band, since induced absorption on both sides of the maximum does not exceed 5% of stationary absorption.

Such a method works well if fluorescence in this spectral region is absent or has a low efficiency ($<1-3\%$). This condition is met for [Zn₂L₂] solution in ethanol (Fig. 2), in which the quantum yield of fluorescence with a maximum at 544 nm is 0.007 upon excitation at 350 nm [2]. The quantum yield of conversion into triplets as defined above is $\phi_T = 1 - 0.54/0.915 = 0.41 \pm 10\%$. Since fluorescence in ethanol is not effective, it follows that the major portion of excitation energy in the ethanol solution of [Zn₂L₂] is driven away in the radiationless mode not only via intersystem crossing but also as a result of intermolecular S_1-S_0 relaxation via interaction with the solvent in the excited S_1 state. This conclusion agrees with the published data [2], which show that the fluorescence efficiency in frozen ethanol is a few orders of magnitude higher than in the liquid solvent because the solvation shell experiences rearrangement to a lesser extent in the excited state responsible for relaxation of excitation. The general pattern of the NTA spectrum recorded during the pulse and with the 30-ns lag remains unchanged. An insignificant ($<10\%$) increase in negative absorption with a simultaneous (also insignificant) decrease in induced absorption in NTA spectra obtained with a recording delay (Fig. 2) is within the range of error of the method and is due to laser operation instability.

Note that the restriction of powerful pulse radiation (i.e., a decrease in transmittance with an increase in intensity of incident light) detected for an ethanol solution of [Zn₂L₂] in [2] at 355 nm will be observed not only at this wavelength as shown in Fig. 2. Nonlinear absorption from excited states to decrease the transmission of pulsed radiation is observed in the regions of 355–450, 480–500, and 560–650 nm, of which the 480–500-nm range is the most effective.

[Zn₂L₂] Complex in Cyclohexane

Unlike the case of ethanol solutions, the [Zn₂L₂] complex effectively fluoresces in cyclohexane (fluor-

rescence quantum yield is 0.5 for excitation at 350 nm) with a small Stokes shift (Fig. 3); therefore, the spectrum of nonstationary transient absorption is distorted by additional intense fluorescence of the excited medium in the region of 510–620 nm with a maximum at 548 nm. The fluorescence emission is summed with the probe radiation signal, decreasing the total optical density in this region, so that the “negative absorption” maximum in NTA spectra with (w/d) or without (wo/d) delay $D_{w/d}^* = -0.75$ or $D_{wo/d}^* = -0.95$, respectively, is greater in absolute value than the maximum in the stationary absorption spectrum of a 3×10^{-6} M solution, $D_0 = 0.65$ (Fig. 3). Therefore, for a well-emitting cyclohexane solution of $[Zn_2L_2]$, its fluorescence was assessed by subtraction. Similar approaches employing different $[Zn_2L_2]$ fluorescence evaluation procedures are described in [10, 11]. Figure 4 depicts nonstationary absorption spectra in which the effect of fluorescence is taken into account. It is seen that the “negative absorption” decreases and becomes smaller in absolute value than in the case of stationary absorption. The yield to triplets estimated for $[Zn_2L_2]$ in cyclohexane on the basis of these spectra is $1 - 0.4/0.65 = 0.39 \pm 10\%$, which within the limits of error does not differ from the value determined for the ethanol solutions. This means that the yield of triplets due to intersystem crossing in this compound is determined by the intramolecular structure and intermolecular interactions with ethanol enhance the radiationless internal conversion from the S_1 state, decreasing the fluorescence lifetime as shown in [2]. We believe that the yield to triplets for $[Zn_2L_2]$ must decrease in the case of excitation to the S_0-S_1 and S_0-S_2 bands, since the quantum yield of fluorescence increases to 0.9 in this case [2]. This agrees with the experimental data on the fluorescence excitation spectra reported for this compound in [2].

Figure 4 shows that there is coincidence of the “negative absorption” in the NTA spectra recorded during the pulse and 30 ns after its onset; i.e., there is no additional depopulation of triplets to return to the ground state during this period of time. However, absorption from the excited states of $[Zn_2L_2]$ in cyclohexane at 470–510 nm qualitatively changes during this time: the maximum shifts to longer wavelengths, unlike the case of ethanol solutions (cf. Figs. 2–4). The NTA maximum at 485 nm is observed during the pulse in both ethanol and cyclohexane and, as such, can be attributed to $T-T$ absorption of $[Zn_2L_2]$. This absorption in ethanol begins to decay in 30 ns, with the molecules returning to the S_0 state, whereas against the background of its decrease in cyclohexane, absorption at 500–510 nm increases (Figs. 3, 4). We believe that this absorption is due to photoproducts formed from excited triplet molecules; it seems that cyclohexane is a stabilizing solvent for such products. The data on photostability reported in [2] show that the quantum yield of phototransformations in cyclohexane is approximately five times that in ethanol and the sta-

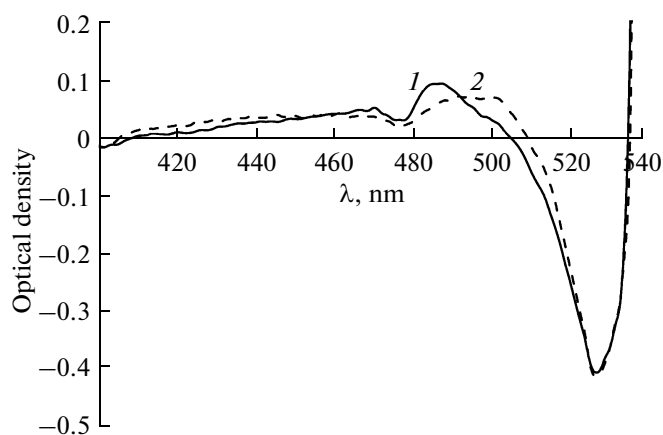


Fig. 4. Nonstationary transient absorption spectra of $[Zn_2L_2]$ in cyclohexane as recorded (1) during the excitation pulse and (2) with a delay of 30 ns from the onset of the pulse at $W_{exc} = 50 \text{ MW/cm}^2$ and $c_0 = 3 \times 10^{-6} \text{ mol/L}$. The spectra were measured with allowance for fluorescence at the stationary absorption band.

tionary spectrum of the final photoproduct has a maximum at 500–510 nm (Fig. 5). According to published data [2, 5, 13], the ligands produced from the complex as a result of its “demetalation” in the excited triplet state can absorb in this region. Substantiation of this assumption requires further investigation.

CONCLUSIONS

The results presented in this paper show that in some cases it is possible to estimate (with uncertainty of 10%) the quantum yield of excited triplet molecules from nonstationary transient absorption spectra excited with a nanosecond pulse without the use of a reference standard and the extinction coefficient of $T-T$ absorption. The wavelength at which the quantities necessary for implementation of the above-described procedure should be selected in such a manner that the extinction of induced $T-T$ absorption will not exceed 10% of the extinction of stationary absorption in this region. A procedure has been proposed for measuring NTA in the presence of intense luminescence in the spectral region of interest.

It has been found that the yield of triplets due to intersystem crossing in $[Zn_2L_2]$ is determined by the intramolecular structure alone. A decrease in fluorescence quantum yield in polar solvents (alcohols, acetonitrile, etc.) is due to intermolecular interactions in the excited S_1 state, which increase the probability of internal radiationless processes reducing the lifetime of this state.

The change in the nonstationary absorption spectra of $[Zn_2L_2]$ in cyclohexane during the time interval of 0–30 ns is due to the formation of photoproducts from the excited triplet states of these complexes.

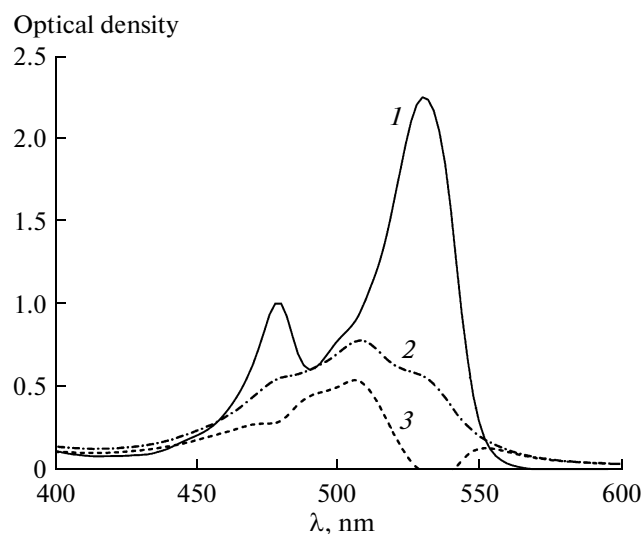


Fig. 5. Stationary absorption spectra of $[Zn_2L_2]$ in cyclohexane (1) before and (2) after irradiation and (3) the spectrum of stationary photoproducts a delay of 30 ns from the onset of the pulse at $W_{exc} = 50 \text{ MW/cm}^2$ and $c_0 = 3 \times 10^{-6} \text{ mol/L}$. The spectra were measured with allowance for fluorescence at the stationary absorption band.

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