PHOTOPHYSICS
AND MAGNETOCHEMISTRY

The Effect of Chromophore–Chromophore Interaction on the Spectral Luminescent Properties of Oxazine Dye Dimers

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Abstract—Spectral and luminescent properties were studied for chemical dimers and molecular aggregates of Nile Red oxazine dye in solutions. Chemical bonding of two oxazine dye molecules leads to the formation of a dimer whose spectral behavior is in close agreement with the exciton model constructed for "physical" molecular aggregates. Chemical dimers luminesce, whereas dimers formed because of van der Waals interactions do not.

INTRODUCTION

Molecular aggregation is a phenomenon widely spread in condensed media. Aggregates of complex organic molecules are intermediate stable structures between molecules and macroscopic objects and possess a number of unique features. The formation of aggregates can be caused by van der Waals forces and hydrogen bonding [1]. Molecular aggregates can be obtained in various ways, such as simple concentration of solutions, the use of a mixture of polar and nonpolar solvents, etc. [2–4]. In recent years, the Langmuir–Blodgett method has been used to effect controlled changes in the properties of aggregates [5].

Molecular aggregates can also be obtained by chemical bonding of two or more like molecules. The effect of interaction between nonconjugated *bis*-cyanine dye chromophores on their spectral luminescent properties was analyzed in [6, 7]. It was shown [8] that the spectroscopic properties of chemical dimers can correctly be described by the exciton model of molecular aggregates. In this paper, we report data on the spectral and luminescent properties of Nile Red oxazine dye chemical dimers and molecular aggregates in solutions.

EXPERIMENTAL

Structural formulas of mother dye Nile Red (NR) and its chemical dimer (dioxazine, CDND) are

(NR)
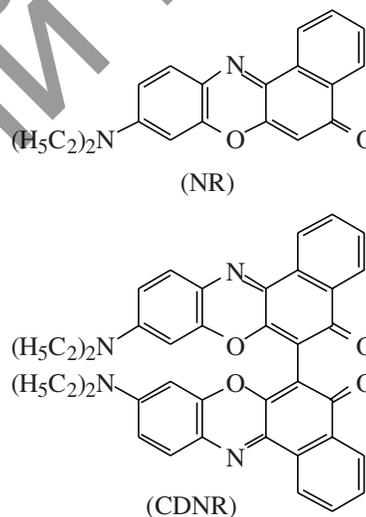
(CDNR)

The synthesis of Nile Red, 9-diethylaminobenzo[a]phenoxazin-5-one, was described in [9]. CDNR dioxazine, 6,6'-*bis*(9-diethylaminobenzo[a]phenoxazin-5-one), was synthesized by the following procedure. Ammonium persulfate (2.04 g, 0.09 mol) dissolved in H_2O (25 ml) was added dropwise to an intensely stirred suspension containing Nile Red (0.67 g, 0.002 mol), acetic acid (2 ml), $AgNO_3$ (0.2 g), acetone (100 ml), and H_2O (40 ml), and the mixture was heated at 75–80°C for 40 min. The precipitate was purified chromatographically on silica gel with chloroform. The yield of dioxazine was 0.3 g (45%). Found, %: C, 75.52; H, 5.52; N, 8.55; $M^+ = 634$; $C_{40}H_{34}N_4O_4$. Calculated, %: C, 75.70; H, 5.36; N, 8.63.

The absorption spectra were recorded on an SF-26 spectrophotometer, and the fluorescence spectra, on a sensitive spectrofluorimeter.

RESULTS AND DISCUSSION

The absorption and fluorescence spectra of the mother dye and chemical dimer in ethanol are presented in Fig. 1. Dye concentrations were 10^{-6} mol/l. These spectra show that the absorption band of the dimer (curve *2*) is much broader than the absorption band ($\lambda_{max} = 547$ nm) of the monomeric dye (curve *1*). The use of the first derivative technique for the more accurate determination of band maxima gives $\lambda_{max} = 530$ nm for the short-wave maximum and $\lambda_{max} = 565$ nm for the long-wave maximum. The fluorescence spectrum of the dimer contains a single band with $\lambda_{max} = 648$ nm which is shifted to longer waves compared with monomeric molecules ($\lambda_{max} = 642$ nm).

Note that, in photoexcitation in the long-wave absorption spectrum part ($\lambda_{ex} = 570$ nm), the intensity of fluorescence is considerably higher compared with excitation in the short-wave absorption spectrum wing ($\lambda_{ex} = 500$ nm).

According to the theory of molecular aggregates [8], the excitonic zone of a physically or chemically bonded dimer consists of two discrete levels, S_1^h and S_1^l (Fig. 2). For such dimers, the probability of electron transition from the ground singlet state S_0 to either S_1^h, or S_1^l excited state is a function of the angle α between the directions of the transition dipole moments of the chromophores constituting the molecule. Because of dipole–dipole interaction, the $S_0 \longrightarrow S_1^h$ transition is allowed at $\alpha = 0°$, whereas the $S_0 \longrightarrow S_1^l$ transition is allowed at $\alpha = 180°$. At intermediate angles, both transitions are partly allowed. When the chromophores make a strictly right angle, the transitions to the S_1^h and S_1^l states are equiprobable, and the absorption spectrum should contain two bands of equal intensities. The excitonic splitting ΔE (the difference between the S_1^h and S_1^l levels) depends on the strength of interaction between the chromophores.

The dipole moments μ of the $S_0 \longrightarrow S_1^h$ and $S_0 \longrightarrow S_1^l$ transitions can be calculated from the experimental absorption spectrum of the dye using the equation

$$|\mu|^2 = 1.09 \times 10^{-19} \int \varepsilon(\nu) d\nu, \quad (1)$$

where $\varepsilon(\nu)$ is the absorption spectrum of the corresponding band. The oscillator strength f is related to the transition dipole moment μ as

$$f = 8\pi^2 m_e c\nu|\mu|^2/3he^2, \quad (2)$$

where ν is the transition frequency, cm^{-1}, and m_e and e are the mass and charge of the electron.
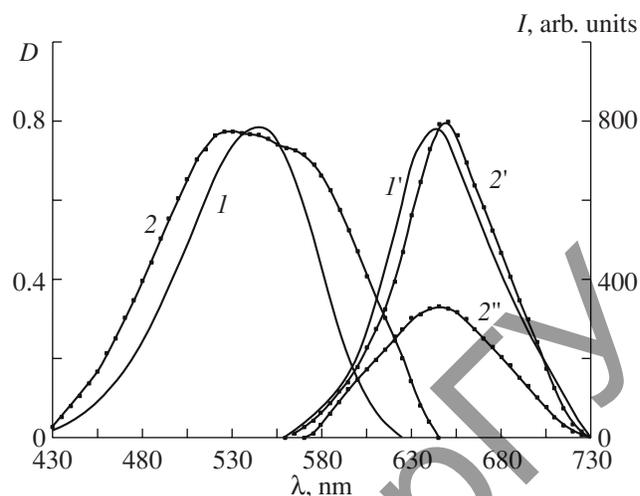
Fig. 1. Absorption and fluorescence spectra of (*1*, *1'*) Nile Red and (*2*, *2'*, *2''*) dioxazine in ethanol; dioxazine fluorescence is excited at (*2'*) $\lambda_{ex} = 500$ and (*2''*) 570 nm.
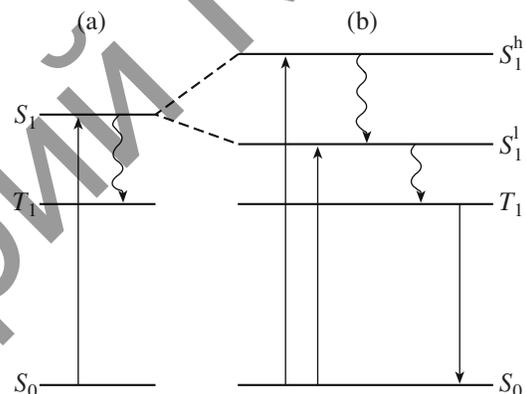

Fig. 2. A scheme of energy levels of molecules with (a) one and (b) two chromophores.

In [10], the ratio between the transition dipole moments of the short- and long-wave absorption spectrum bands was related to the angle α between the chromophores in the dimer,

$$\frac{\mu_{sw}}{\mu_{lw}} = \frac{1 + \cos\alpha}{1 - \cos\alpha}, \quad (3)$$

where μ_{sw} and μ_{lw} are the electron transition dipole moments for the short- and long-wave bands, respectively.

It follows that we can find the angle α between the directions of transition dipole moments from the absorption spectrum of dioxazine by Eq. (3). The table summarizes the spectral and photophysical characteristics of the mother dye and dimer obtained from the experimental data.

An analysis of the absorption spectrum of the dye in ethanol gives $\alpha = 56°$. Pariser–Parr–Pople calculations

Spectral and photophysical characteristics of Nile Red and dioxazine in ethanol

Dye	Absorption		Fluorescence		f	τ, s	μ, D	α_{calc}, deg	ΔE, cm^{-1}
	λ_{max}^{ab}, nm	$\Delta\lambda_{1/2}^{ab}$, nm	λ_{max}^{fl}, nm	$\Delta\lambda_{1/2}^{fl}$, nm					
Nile Red	547	60	642	70	0.47	9.4×10^{-9}	7.41	–	–
Dioxazine	530; 565	126	648	64	0.38; 0.30	–	6.53; 5.96	56	992

Notation: f is the oscillator strength, τ is the excited state lifetime; μ is the transition dipole moment; α is the angle between the directions of transition dipole moments; and ΔE is the excitonic splitting.

including configuration interaction (PPP CI) of the Nile Red molecule show that the transition dipole moment lies in the plane of the chromophore. It follows that the angle between the planes of the chromophores is 56°.

The equilibrium mutual arrangement of chromophores in the dioxazine molecule obtained by the molecular mechanics method with the MM+ force field is shown schematically in Fig. 3. Arrows indicate the directions of the transition dipole moments in the chromophores. The $\alpha = 54°$ value obtained is in close agreement with that calculated from spectroscopic data.

As noted above, the excitation of dioxazine in both short- and long-wave absorption band wings causes the appearance of only one fluorescence band shifted bathochromically with respect to the monomer spectrum. This band corresponds to the $S_1^l \longrightarrow S_0$ long-wave electronic transition. This is evidence of fast nonradiative relaxation form the higher S_1^h to lower S_1^l sublevel of the split excited state of the dimer.

Let us consider the spectral luminescent properties of 2-nonyloxy-9-dimethylamino[a]phenoxazin-5-one (AmAnNR) in a water–ethanol mixture. This dye is an amphiphilic analogue of Nile Red and its synthesis is described in [11]. Only the chromophore part of this molecule is partially soluble in water, while its hydrophobic tale is repelled from water. In ethanol, this dye is solved fully. It was assumed that an increase in the volume fraction of water molecules should increase the

local concentration of dye molecules in "alcohol regions" and the formation of molecular aggregates. The presence of hydrophobic tails should facilitate the aggregation of molecules.

The absorption and fluorescence spectra of AmAnNR in water–alcohol solutions are shown in Fig. 4. The dye concentration was 10^{-5} mol/l. In alcohol, only the absorption band of monomer molecules with a maximum at 547 nm is observed. An increase in the volume fraction of water up to 20% decreases absorption at the maximum of the absorption band of monomeric molecules ($\lambda_{max} = 547$ nm) and shifts the maximum (curve 2) to longer waves, $\lambda_{max} = 560$ nm. At a 40 : 60 water : ethanol ratio (curve 3), the maximum is shifted to $\lambda_{max} = 572$ nm. Simultaneously, an increase in optical density is observed. A further increase in the concentration of water leads to a decrease in optical density over the range 550–600 nm and the appearance of a new maximum at 510 nm. This maximum increases as the fraction of water in solution grows (curves 4, 5).

The fluorescence spectrum of monomeric molecules has a maximum at $\lambda_{max} = 640$ nm (curve 6). An increase in the concentration of water in solution leads to monomer luminescence quenching (curves 7, 8). No additional bands then appear.

The behavior of the absorption spectra is evidence of molecular aggregation caused by the addition of water to the solution of the dye in alcohol. At low water concentrations (20–40%), dimers with a linear arrange-
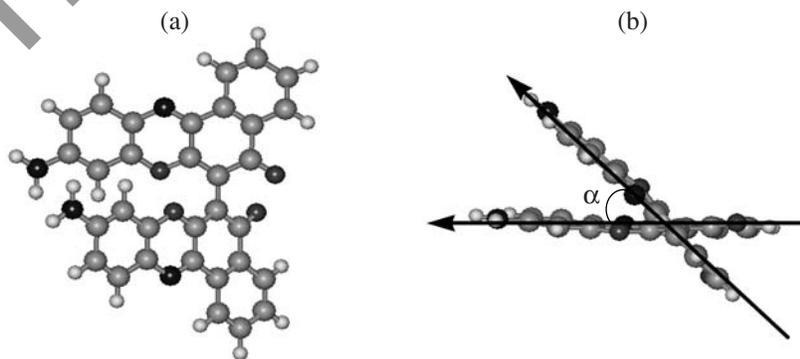
(a)

(b)

Fig. 3. Scheme of the arrangement of chromophores; (a) top view and (b) side view.

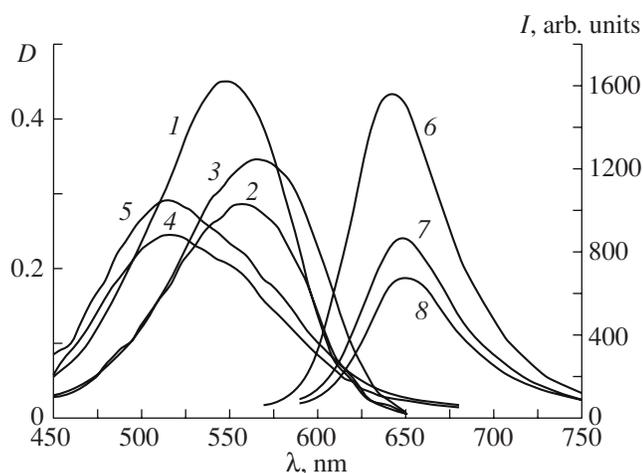noticeable fluorescence ability. This can be caused by effective internal conversion.

Fig. 4. (*1–5*) Absorption and (*6–8*) fluorescence spectra of an amphiphilic analogue of Nile Red in alcohol–water mixtures at alcohol concentrations of (*1*, *6*) 100, (*2*, *7*) 80, (*3*, *8*) 60, (*4*) 20, and (*5*) 10%.

ment of transition dipole moments ($\alpha \longrightarrow 180°$) are largely formed. When water occupies the major fraction of cell volume, dye molecules are displaced into alcohol regions. In this situation, the optimum arrangement of molecules likely corresponds to a parallel arrangement of chromophore planes. This facilitates the formation of dimers with $\alpha \longrightarrow 0°$. As follows from the luminescence spectra obtained, dye dimers have no

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