

The Effect of the Complexation of *p*-*N*,*N*-Dimethylaminobenzoic Acid and *p*-*N*,*N*-Dimethylaminobenzonitrile with LaCl₃ on Spectral-luminescent Parameters of Fluorophores

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Abstract The LE band fluorescence enhancement of *p*-*N*,*N*-dimethylaminobenzoic acid (DMABA) and *p*-*N*,*N*-dimethylaminobenzonitrile (DMABN) was found in aprotic acetonitrile and butyronitrile at the addition of LaCl₃. The corresponding ICT fluorescence band remains unchanged. This enhancement is explained by the decrease of the internal conversion rate constant in a coordination complex with LaCl₃. The formation of the coordination complex between DMABA and LaCl₃ in ethanol is accompanied by the efficient fluorescence quenching in LE and ICT bands, in parallel with the enhancement of ICT/LE emission ratio. The experimental data are well described by the proposed kinetic schemes.

Keywords Fluorescence quenching · Fluorescence enhancement · DMABA · DMABN · Coordination complex with LaCl₃

Introduction

The process of the excited-state intramolecular charge transfer (ICT) in various organic molecules bearing the different electron donor and electron acceptor groups was studied in detail [1–3]. The crucial effect of a solvent polarity on the formation of ICT states was repeatedly shown by the example of DMABN-related compounds. In some papers the efficiency of the ICT process is changed due to the coordination of a fluorophore with the external

compounds of a various nature (cyclodextrins, zeolites, colloidal solutions, micelles, and others) [4–8].

So, the efficient fluorescence quenching of 4-(*N*,*N*-dimethylamino)pyrimidine (4-DMAP) by Zn²⁺ ions in MeCN or in DMF with a simultaneous increase of the low-energy emission band was explained by the enhanced excited-state intramolecular charge transfer favored by metal ion bonding to the pyrimidine nitrogen atom [4]. The fluorescence spectra of DMABN adsorbed from high vacuum on the polycrystalline silica and alumina show the TICT fluorescence as the main emission component, even at 77 K [5]. The enhanced ICT/LE emission ratio of DMABA in NaY zeolites compared with the homogeneous polar solvent was interpreted by the enhanced hydrogen-bond strength between the carboxylic acid group and the zeolite surface at the excitation [6]. A photoinduced intramolecular charge transfer of DMABA in CdS colloidal solutions is accompanied by the enhanced ICT/LE emission ratio. On the other hand, in TiO₂ colloidal solutions the reduced ICT/LE emission ratio of DMABA was observed. DMABA is adsorbed on CdS surface in the carboxylate form. The formation of the ICT state favors the electron transfer from CdS to DMABA at the DMABA-CdS interface. The electron transfer from S₁ (LE) state of DMABA at the DMABA-TiO₂ interface inhibits the formation of the ICT state of DMABA [7]. In acetonitrile reverse micelle of AOT (dioctylsulfosuccinate, sodium salt) DMABN and DMABA exhibit a strong ICT fluorescence peak along with LE emission; the ICT fluorescence peak of DMABA in aqueous reverse micelle is not observed. The latter was interpreted as the result of the enhanced internal conversion from the hydrogen bonded ICT state due to the hydrogen bond formation between –COOH group of DMABA and aqueous reverse micelle [8].

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It is known that heteroaromatic molecules bearing heteroatoms with lone-pair electrons may form stable coordination complexes with transition metals(II) and lanthanides salts [9,10]. Depending on the position of the heteroatom in the donor-acceptor molecule, these reactions may either favor the formation of the ICT states or inhibit them. In present work we have studied a possibility to control the efficiency of the LE→ICT process in DMABA and DMABN by the complex formation between these fluorophores and LaCl_3 .

Experimental

The absorption and fluorescence spectra of solutions at 293 K were recorded on a Shimadzu UV-3100 spectrophotometer and a Perkin-Elmer LS-55 spectrofluorimeter. The fluorescence and phosphorescence spectra at 77 K were recorded on an Elyumin-2M spectrofluorimeter. The triplet-triplet absorption was recorded on a flash-photolysis apparatus (excitation pulse duration 10 μs). The dissolved oxygen was removed from the solutions by bubbling of argon for 20 min. The ground state equilibrium constants were calculated using program "EQUILI", based on the multivariate nonlinear least-squares method [11]. The *p*-*N*, *N*-dimethylaminobenzoic acid (DMABA), *p*-*N*, *N*-dimethylaminobenzaldehyde (DMABL), and *p*-*N*, *N*-dimethylaminobenzonitrile (DMABN, "Acros Organics") were used as received. The spectroscopically pure ethanol was dehydrated by the distillation with CaH_2 . The spectroscopically pure acetonitrile ("Cryochrom") and butyronitrile ("Merck") were used as received. Lanthanum chloride ("Merck"), samarium chloride, and cerium(IV) sulfate were used as received. The concentrations of DMABN, DMABA, and DMABL used for the measurements in solutions were 10^{-5} M. The extinction coefficients at absorption maxima: DMABN/EtOH, $\epsilon^{292 \text{ nm}}=34400 \text{ M}^{-1} \text{ cm}^{-1}$; DMABA/EtOH, $\epsilon^{290 \text{ nm}}=20150 \text{ M}^{-1} \text{ cm}^{-1}$; DMABL/EtOH, $\epsilon^{339 \text{ nm}}=31100 \text{ M}^{-1} \text{ cm}^{-1}$.

Results and Discussion

The absorption spectra of DMABA in ethanol show a pronounced (~17 nm) red shift, accompanied by the increase of the absorption at the increase of LaCl_3 concentration up to 10^{-3} M. A well resolved isosbestic point is observed (Fig. 1a). The similar behavior is observed for the system DMABN/EtOH/ LaCl_3 at the increase of LaCl_3 concentration up to 10^{-1} M. The isosbestic point is absent. The analogous changes in absorption spectra of DMABA and DMABN in aprotic acetonitrile and butyronitrile are not observed. Also there were no spectral shifts in the systems: DMABL/EtOH/ LaCl_3 , DMABL/MeCN/ LaCl_3 , and DMABA/MeCN/ SmCl_3 .

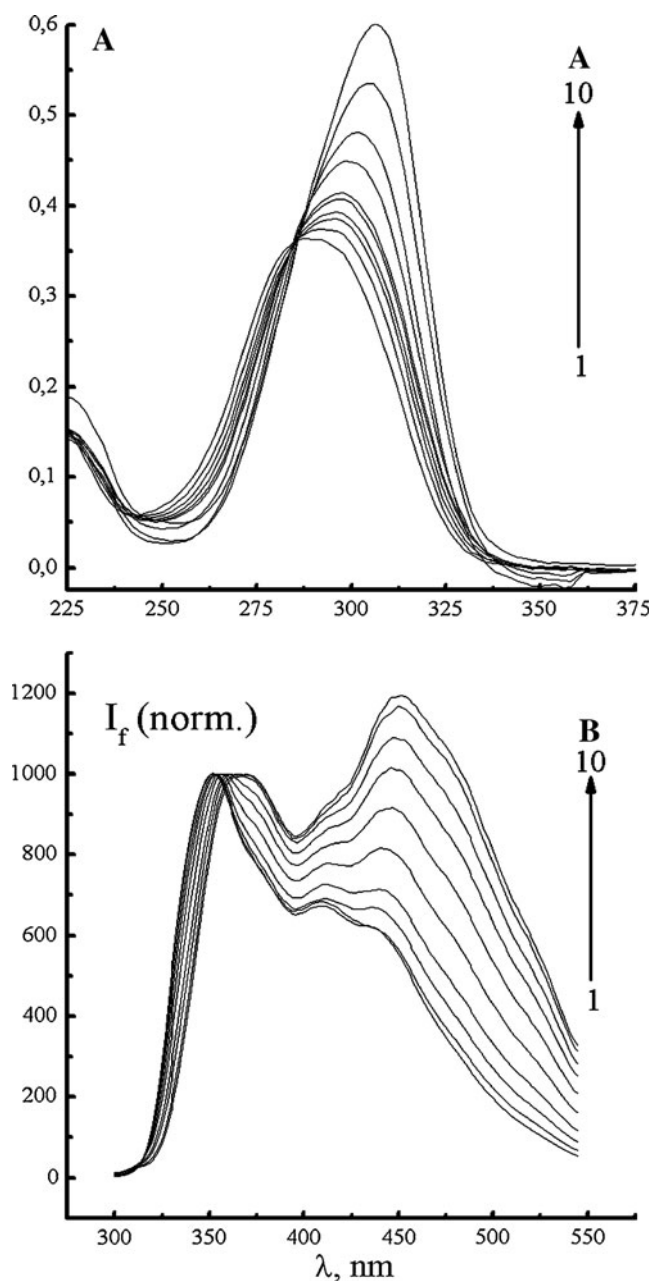


Fig. 1 The absorption (a) and normalized fluorescence spectra of DMABA (b) in ethanol at various concentrations of LaCl_3 : 0 (1), 4.98×10^{-6} (2), 9.90×10^{-6} (3), 1.48×10^{-5} (4), 1.96×10^{-5} (5), 2.44×10^{-5} (6), 4.76×10^{-5} (7), 9.09×10^{-5} (8), 1.67×10^{-4} (9), and 10^{-3} M (10); $\lambda_{\text{exc}}=285 \text{ nm}$ (isosbestic point)

At the increase of LaCl_3 concentration the double-band fluorescence of DMABA in ethanol is subjected to the efficient quenching. In parallel with the quenching, the ICT/LE emission ratio of areas gradually increases (from 2.9 in the absence of LaCl_3 to 5.4 in 10^{-3} M solution of LaCl_3). Then the fluorescence intensity of the ICT band slightly increases, and finally a complete quenching of both bands is observed. The corresponding fluorescence spectra normalized at the LE bands maximum are shown on

Fig. 1b. The fluorescence spectra of the systems: DMABA/MeCN/LaCl₃, DMABA/MeCN/SmCl₃, DMABA/MeCN/Ce(SO₄)₂, DMABA/PrCN/LaCl₃, DMABN/EtOH/LaCl₃, DMABN/MeCN/LaCl₃, and DMABN/PrCN/LaCl₃ show quite another behavior, namely: from a small to a pronounced enhancement of the LE band and the absence of significant changes in the ICT band (Fig. 2). Neither fluorescence quenching, nor fluorescence enhancement were registered in the system DMABL/MeCN/LaCl₃.

In a low temperature glassy matrix of butyronitrile the single (LE) band fluorescence and phosphorescence of DMABA rise at the increase of LaCl₃ concentration. As shown in Fig. 3, the intensities of both bands rise practically to the same extent.

To estimate the effect of the complex formation on the interconversion processes, we have carried out flash-photolytic experiments of two systems: DMABA/MeCN/LaCl₃ and DMABN/MeCN/LaCl₃. In saturated solution of LaCl₃ in acetonitrile ($\sim 2 \times 10^{-2}$ M) the intensity of triplet-triplet absorption of DMABA in relation to the solution without LaCl₃ increases by a factor of 1.5; for DMABN—by a factor of 1.1. The slopes of the corresponding kinetic curves remain practically the same, i. e.: LaCl₃ is not a quencher of the triplet states.

We believe that in the systems studied (excluding DMABL/MeCN/LaCl₃) the coordination occurs between carboxyl fragment of DMABA (nitrile fragment of DMABN) and lanthanum atom of nonionized salt. The composition of the resulting complexes: (DMABA)_nLaCl₃

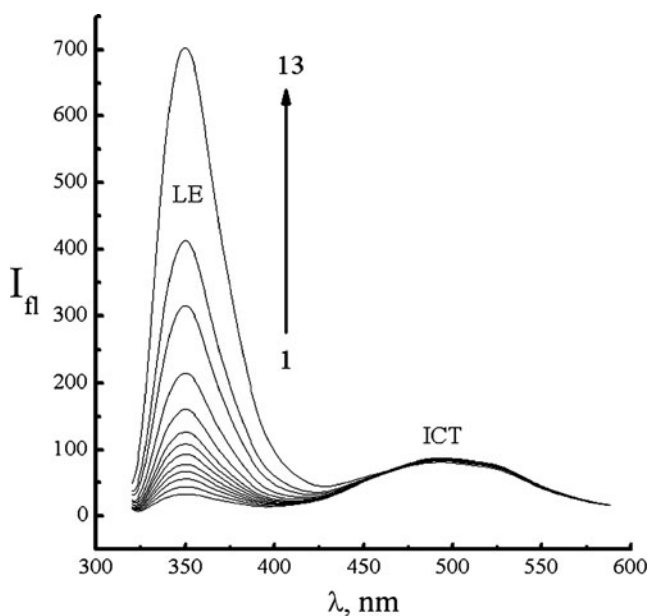


Fig. 2 The fluorescence spectra of DMABA in acetonitrile at various concentrations of LaCl₃: 0 (1), 1.71×10^{-4} (2), 3.40×10^{-4} (3), 5.05×10^{-4} (4), 6.67×10^{-4} (5), 8.27×10^{-4} (6), 1.06×10^{-3} (7), 1.47×10^{-3} (8), 2.23×10^{-3} (9), 3.58×10^{-3} (10), 6.14×10^{-3} (11), 9.33×10^{-3} (12), and 1.88×10^{-2} M (13); $\lambda_{exc}=308$ nm (λ_a^{max} of DMABA in MeCN)

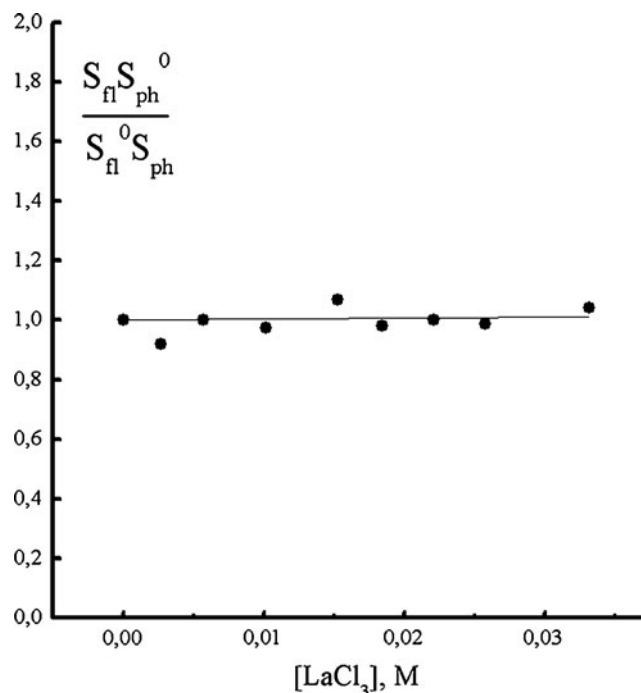
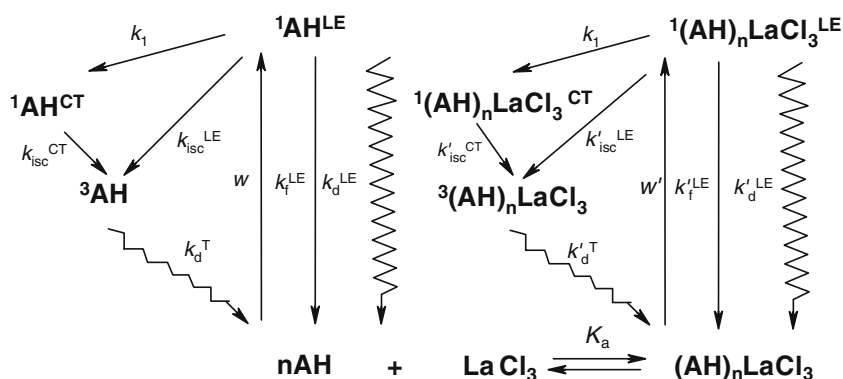


Fig. 3 The dependence of the ratio of areas for DMABA fluorescence and phosphorescence spectra in a low-temperature glassy matrix of butyronitrile from the concentration of LaCl₃; $\lambda_{exc}=308$ nm

and (DMABN)_nLaCl₃. So, the similar interaction was found between unsaturated cationic binuclear Tb(III) complex and DMABA (binding of carboxylate anions to the Tb(III) centers via the displacement of the metal bound water molecules) [12]. Considering a high electron affinity of chlorine atoms (ligands), the coordination of electron-deficient lanthanide to carboxyl group, bearing two oxygen atoms with unpaired electrons, may enhance the electron-accepting ability of this group. The enhanced contribution of the ICT band fluorescence to the total emission of DMABA shown in Fig. 1b at the increase of LaCl₃ concentration strictly confirms this assumption.

On the other hand, the fluorescence enhancement of LE bands of the fluorophores at the addition of lanthanide salts is the result of varying spectral-luminescent parameters of complexes in aprotic solvents. The double-band emission character remains, which points to a similarity of fast LE→ICT processes in initial molecules and complexes (DMABA in MeCN: $k_1 = 1.4 \times 10^{11}$ s⁻¹ [7]; DMABN in MeCN: $k_1 = 2.4 \times 10^{11}$ s⁻¹ [13]). The second deactivation channel found in the systems studied is the interconversion to the triplet state (DMABA in MeCN: $\phi_{isc}=0.24$; DMABN in MeCN: $\phi_{isc}=0.60$, [14]). The inhibition of these rather slow processes (¹LE→³T and ¹ICT→³T) during complex formation seems unlikely. The presence of a heavy lanthanide atom in the molecule should, conversely, favor the increase of the triplet state yield, due to the increased spin-orbital interaction. The triplet-triplet

Scheme 1 The kinetic scheme of the interaction of fluorophores with LaCl_3



absorption data confirm this assumption. Thus, it may be concluded, that in the coordination complex between DMABA (DMABN) and LaCl_3 the deactivation efficiency through internal conversion pathway is drastically diminished. The low-temperature experiments point to the equal decrease of k_{ic} in both the ${}^1\text{LE} \rightarrow \text{S}_0$ and ${}^3\text{T} \rightarrow \text{S}_0$ channels.

At first glance, the drastic decrease of k_{ic} in the complexes contradicts the insensibility of the ICT band intensity to the increase of LaCl_3 concentration. However, a possible reason of such stability may consist in a prohibited emissive nature of the ICT state (DMABN in MeCN at 298 K: $k_f(\text{LE}) = 6.5 \times 10^7 \text{ s}^{-1}$, $k_f(\text{ICT}) = 7.9 \times 10^6 \text{ s}^{-1}$, [13]) and a proximity of the ${}^1\text{ICT}$ and ${}^3\text{T}$ levels. We believe that blocking the internal conversion in the ${}^1\text{ICT} \rightarrow \text{S}_0$

channel results in the increase not $k_f(\text{ICT})$, but k_{isc} in the ${}^1\text{ICT} \rightarrow {}^3\text{T}$ deactivation channel.

For the systems showing the LE band fluorescence enhancement and stability of the ICT fluorescence band the following kinetic scheme will be actual. Let us introduce the following assumptions: 1) the $\text{LE} \rightarrow \text{ICT}$ process in the excited initial molecule and complex occurs with equal efficiency ($k_1 = k'_1$), the reverse $\text{ICT} \rightarrow \text{LE}$ reaction is negligible; 2) the interconversion from the LE and ICT states results in a single triplet state [15]; 3) the reaction in the ground state gives the complexes of one composition only (Scheme 1, where AH, ${}^1\text{AH}^{\text{LE}}$, and ${}^1\text{AH}^{\text{CT}}$ are the initial fluorophore in the ground, excited LE and CT states, respectively; ${}^3\text{AH}$ is the initial fluorophore in the triplet state. The analogous description is valid for the complex $(\text{AH})_n\text{LaCl}_3$). The quantum yield ratio of LE bands observed in the presence and in the absence of LaCl_3 is described by Eq. 1:

$$\frac{\varphi^{\text{LE}}}{\varphi_0^{\text{LE}}} = \frac{k_f^{\text{LE}}[{}^1\text{AH}^{\text{LE}}] + k_f^{\text{LE}'}[{}^1(\text{AH})_n\text{LaCl}_3^{\text{LE}}]}{k_{f,0}^{\text{LE}}[{}^1\text{AH}_0^{\text{LE}}]} \quad (1)$$

From this dependence it is easy to obtain Eq. 2:

$$\frac{\varphi^{\text{LE}}}{\varphi_0^{\text{LE}}} = \frac{1 + \frac{k_f^{\text{LE}'}\tau_0^{\text{LE}'}}{k_f^{\text{LE}}\tau_0^{\text{LE}}} K_a^{1:1}[\text{LaCl}_3]}{1 + nK_a^{1:1}[\text{LaCl}_3]} \quad (2)$$

where k_f^{LE} , $k_f^{\text{LE}'}$ are the radiative emission rate constants of LE states of the initial fluorophore and complex, respectively; τ_0^{LE} , $\tau_0^{\text{LE}'}$ are their fluorescence lifetimes; $K_a^{1:1}$ is the ground state equilibrium constant for the conventional complex 1:1; n is the number of fluorophore molecules in the real complex. Fitting to Eq. 2 was performed using the areas under complete fluorescence LE bands, described as Gaussians (S_i). The experimental data are well fitted by Eq. 2 (Fig. 4); the resulted products of constants are shown in Table 1.

Let us consider the kinetic scheme, actual for the system, showing the efficient LE and ICT bands fluorescence quenching (DMABA/EtOH/ LaCl_3). In Scheme 2, LE and

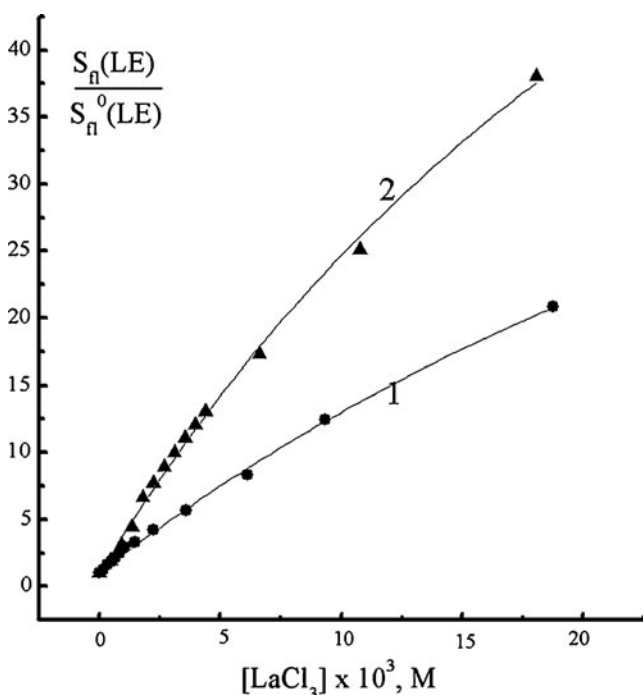


Fig. 4 The dependence of the ratio of areas for DMABA LE bands of fluorescence and the complex in acetonitrile (1); DMABN and the complex in ethanol (2) on the concentration of LaCl_3

Table 1 Parameters of the system fluorophore/Solvent/LaCl₃, calculated using Eq. 2

Compound	Solvent	Process	$nK_a^{1:1}$ (M ⁻¹)	$\frac{k_f^{eff} \tau_0^{eff}}{k_f^{eff} \tau_0^{eff}} K_a^{1:1}$ (M ⁻¹)
DMABA	MeCN	Pronounced enhancement of LE band	19±3	1450±50
DMABN	EtOH	Pronounced enhancement of LE band	27±3	3000±80

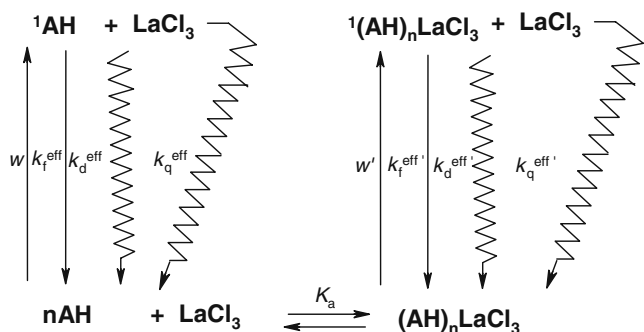
CT states of the fluorophore and the complex are indistinguishable and therefore only averaged values of the corresponding deactivation and quenching rate constants may be obtained. Besides that, condition 3 of Scheme 1 was accepted. The fluorescence quantum yield ratio in the absence and in the presence of a quencher is described by Eq. 3:

$$\frac{\varphi_0}{\varphi} = \frac{k_f^{eff} [^1AH_0]}{k_f^{eff} [^1AH] + k_f^{eff} [^1(AH)_nLaCl_3]} \tag{3}$$

where k_f^{eff} and $k_f^{eff'}$ are the averaged radiative deactivation rate constants of the fluorophore and the complex, respectively. From this dependence we obtain a quenching equation (Scheme 2):

$$\frac{\varphi_0}{\varphi} = \frac{(1 + nK_a^{1:1}[Q])(1 + k_q^{eff} \tau_0^{eff} [Q])}{1 + K_a^{1:1}[Q] \frac{k_f^{eff} \tau_0^{eff} (1 + k_q^{eff} \tau_0^{eff} [Q])}{k_f^{eff} \tau_0^{eff} (1 + k_q^{eff} \tau_0^{eff} [Q])}} \tag{4}$$

where $K_a^{1:1}$ is the ground state equilibrium constant for the conventional complex 1:1, n is the number of fluorophore molecules in the actual complex; k_f^{eff} , k_q^{eff} are the averaged quenching rate constants for the initial fluorophore and the complex; τ_0^{eff} , $\tau_0^{eff'}$ are their averaged fluorescence lifetimes; [Q] is the concentration of a quencher. Analogously to Scheme 1, fitting to Eq. 4 was performed using the areas under complete fluorescence spectra. Using $K_a^{1:1} = 3.55 \times 10^4 \pm 3 \times 10^2$ M⁻¹, calculated by the program “EQUILI”, the experimental data are well described by Eq. 4 (Fig. 5). The minimal values of constants obtained at $n=3$ ($k_q^{eff} \tau_0^{eff} = 80$ M⁻¹, $k_q^{eff'} \tau_0^{eff'} = 260$ M⁻¹, $k_f^{eff'} \tau_0^{eff'} / k_f^{eff} \tau_0^{eff} = 0.41$) allow to suppose the composition of the complex in ethanol: (DMABA)₃LaCl₃. The resulting values of the ground state



Scheme 2 The kinetic scheme of the quenching of fluorophores with LaCl₃

equilibrium constant and fluorescence quenching rate constants are similar to those obtained for the complex formation between 4-DMAP and Zn²⁺ in acetonitrile and dimethylformamide [4]. The absence of any shifts in absorption spectra of DMABL at the addition of LaCl₃ up to 0.2 M points to a lack of the coordination between lanthanum atom and oxygen atom in aldehyde. Therefore, we may suggest that the coordination between lanthanum atom and DMABA occurs primary at oxygen atom of hydroxyl group. The tentative structure of the complex in a diluted solution is shown in Scheme 3.

Thus, the LE bands fluorescence intensity enhancement is observed at the complex formation in the following systems: DMABA/MeCN/LaCl₃, DMABA/MeCN/SmCl₃, DMABA/MeCN/Ce(SO₄)₂, DMABA/PrCN/LaCl₃, DMABN/EtOH/LaCl₃, DMABN/MeCN/LaCl₃, and DMABN/PrCN/LaCl₃. The corresponding ICT bands fluorescence intensities are not changed significantly. This enhancement is explained by the decrease of the internal conversion rate constant in the corresponding coordination complexes. The formation of the coordination complex between DMABA and LaCl₃ in ethanol results in the efficient fluorescence quenching accompanied by the increase of the ICT/LE emission ratio.

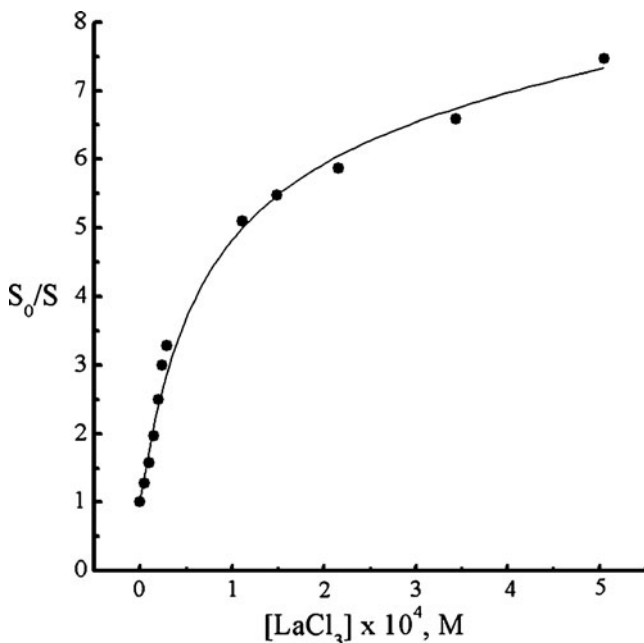
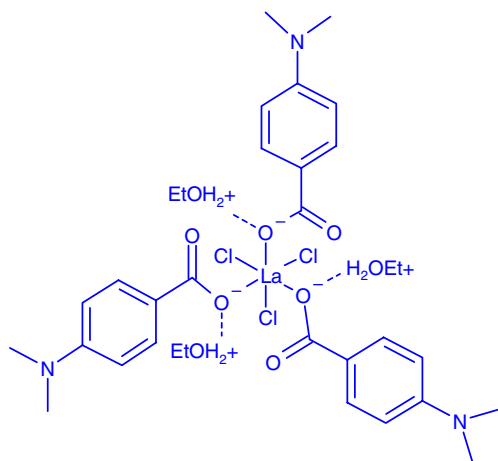


Fig. 5 The dependence of the ratio of areas for DMABA fluorescence spectra in ethanol on the concentration of a quencher



Scheme 3 The tentative structure of the coordination complex of DMABA and LaCl_3 in ethanol

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