Photophysical properties of novel luminescent dyes: difluoroborate complexes of benz[c,d]indole derivates

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The fluorescence and absorption spectra of new boron-containing dyes have been studied. Using standard techniques, the quantum yield and fluorescence decay characteristics for these substances in liquid solutions were determined. It has been shown that these dyes in solutions are characterized by high quantum yield. The full interpretation of the absorption and fluorescence spectra has been done using quantum-chemical calculations. It is established that superposition of the fluorescence spectra dyes covers almost the entire visible range of wavelengths. The absorption region can be varied by changing the end groups in these dyes. Dyes with these properties can be used for creation of white OLEDs.

Исследованы спектры флюоресценции и поглощения новых борсодержащих красителей, определены квантовые выходы и времена затухання люминесценции в жидких растворах. Установлено, что исследуемые красители в растворах характеризуются высоким квантовым выходом. Дана полная интерпретация спектров поглощения и флюоресценции. Установлено, что спектры флюоресценции красителей охватывают почти весь видимый диапазон длин волн. Показано, что область поглощения красителей можно варьировать путем изменения их конечных групп. Красители с такими свойствами могут быть использованы для создания белых органических светодиодов.

1. Introduction

Up to 19 % of electricity produced in the developed countries is known to be used for illumination purposes [1]. One of the ways out of this situation is LED technology. Special role in the development of LED lighting technology (due to a number of advantages) belongs to organic light emitting diodes (OLED) [2–4]. Also, an OLED with emission spectrum covering the visible region of the spectrum would be promising for creation of a new "white light" source — WOLED. High efficiency of WOLED can be achieved using light emitting centers with high quantum yield of luminescence, high probability of transition in the excited state (high value of extinction coefficient), and total "white radiation" spectral characteristics [5–7]. This paper presents the photophysical properties of new specially synthesized boron-containing cyanine dyes for these purporses.

2. Experimental

The formulae of the investigated molecules are presented in Fig. 1a.

These compounds belong to the typical cyanine dyes. Their chromophors/fluorophors include two cycles with extended π-electron systems connected by π-bridge. Additionally,
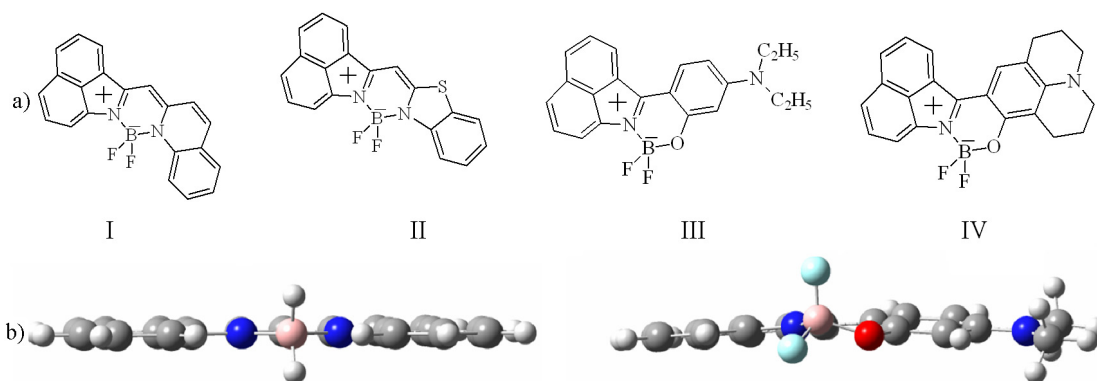
Fig. 1 a) – molecular formulas of days I-IV; b) – optimized molecular geometry of dyes I (left) and III (right) in ground state.

both π-cycles of the chromophor systems are bounded by σ-bridge: BF_2 (I and II) or BF_2O (III and IV). BF_2 groups provide neutrality of the dyes without notable changing of their spectral properties. The neutral dyes are more suitable to create thin films based on them by methods of vacuum deposition.

Spectral properties of these substances were studied in liquid solutions of tetrahydrofurane at room temperature. Optical absorption spectra of solutions were recorded using a Specord UV VIS spectrophotometer. Fluorescence spectra were recorded by Carry Eclipse spectrofluorometer, and time measurements were carried out using the home-made laboratory designed equipment.

For obtaining the equilibrium molecular geometry and electron structure of the dye molecules, the quantum-chemical calculations were performed on the software package Gaussians, version 9. The molecular geometry was optimized by DFT/6-31G(d,p)/B3LYP method, while the characteristics of the electron transitions were calculated using the TD DFT method with the same basis set.

3. Results and discussion

In Fig. 2 absorption spectra of dye solutions in tetrahydrofurane at high ($c = 6 \cdot 10^{-4}$ mol/l) and low ($c = 1.5 \cdot 10^{-5}$ mol/l) dye concentrations are shown in comparison with their fluorescence spectra. One can clearly see the similarity in line shapes and spectral positions of the dye absorption bands for high and low concentrations. Accordingly, we can conclude that molecular aggregation does not occur in solutions.

Also in Fig. 2 one can compair of the fluorescence spectrum with absorption spectrum for each dye. Fluorescence spectra of I and II dyes are mirror symmetric to absorption spectra in accordance with Levshyn rule. This means that the same chromophore centers absorb and emit. However, two dyes — III and IV have a certain asymmetry between absorption and fluorescence spectra.

Table. Calculated wavelengths (λ) and oscillator strengths (F) of electron transitions (TD DFT/6-31(d,p)/B3LYP), φ is a quantum yield, τ is a time of luminescence decay

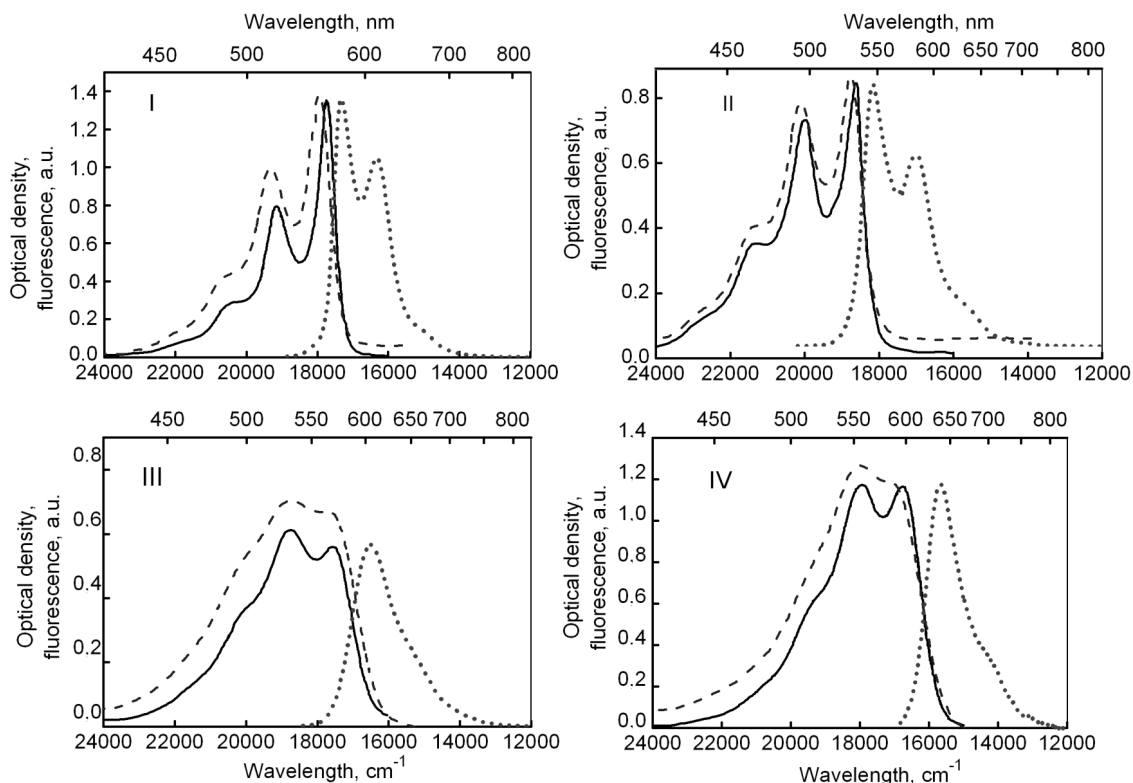| Dye	Transition	λ_{max}^{calc}, nm	F	λ_{max}^{abs}, nm	λ_{max}^{fl}, nm	φ, %	τ, ns
I	$S_0 \rightarrow S_1$	583	0.354	521	574	61	3.4
	$S_0 \rightarrow S_2$	420	0.012	563	612		
II	$S_0 \rightarrow S_1$	559	0.353	500	546	70	3.5
	$S_0 \rightarrow S_2$	347	0.255	536	584		
III	$S_0 \rightarrow S_1$	495	0.514	533	605	25	2.9
	$S_0 \rightarrow S_2$	442	0.006	569			
IV	$S_0 \rightarrow S_1$	512	0.543	555	634	12	2.7
	$S_0 \rightarrow S_2$	476		595			

Fig. 2. Fluorescence (dot lines) and absorption (solid lines) dye spectra at $c = 1.5 \cdot 10^{-5}$ mol/l and absorption (dush lines) at $c = 6 \cdot 10^{-4}$ mol/l dye concentration in tetrahydrofurane solution.

Three characteristic peaks are observed in the absorption region, but in the fluorescence spectrum only two peaks are noticed. This behavior of absorption and fluorescence spectra for dyes III and IV may be associated with the fact that the spatial structure of these molecules in the ground and excited electronic states are not identical.

The calculations have shown that the dye molecules with BF_2 bridge are almost ideally planar in the ground and excited states, as one can see from Fig. 1b for the dye I (the optimized geometry of the dye II is practically identical). Unlike this, the two molecules with the BF_2O bridge are shown in the Fig. 1b for the dye III to be slightly non-planar. So, both cycles of the chromophor are twisted by 9°; while the torsion angle N–B–O–C is 32° (the optimized geometry of the dye IV is also similar). This non-planarity should lead to the change in the equilibrium geometry upon excitation in the corresponding dyes: III and IV. To the contrary, the equilibrium geometry of the dyes I and II remains practically unchanged upon excitation.

The calculated and experimental wavelengths of the first electron transition are collected in Table. One can see that these data are quite close. It follows from Table 1
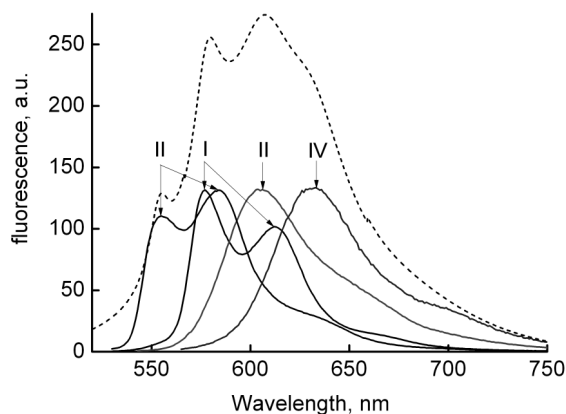

Fig. 3. Fluorescence spectra for investigated set of dyes (solid lines) and total superposition of dyes fluorescence curves (dash line).

that the second electron transition should be appreciably shifted towards the short-wave region. The distinct fluorescence maxima of I (574 nm and 612 nm) and II (545 nm and 584 nm) dyes are related to the vibronic structure. Fig. 2 illustrates that the well-defined vibronic structure is retained in the fluorescence spectra of the dyes with the rigid BF_2 bridge (I and II). An the same time, the vibronic structure disap-

pears in the dyes with the flexible BF_2O bridge (III and IV).

Using standard methods [8, 9], we have determined the decay time and the quantum yield of luminescence dyes in solutions. As a reference substance, the solvent of Rhodamin 6G was used. The obtained values of the quantum yield and the life time of luminescence dyes are given in the Table. It should be noted that two dyes (I and II) have high quantum yield of luminescence (more than 50 percent), the other two (III and IV) have much lower quantum yield, which lies in the range of 10−20 percent.

It should also be noted that the luminescence spectra of this set of dyes with blue matrix cover the almost entire range of visible radiation (Fig. 3).

One of the WOLED fabrication methods [5] proposes to use multiple high fluorescence impurities in the light emitting layer. Therefore, if a set of the present dyes is used as additives in suitable matrices emitting in the violet-blue range, the possibility to fabricate a highly efficient WOLED appears.

4. Conclusions

New Boron-containing dyes have been studied by spectroscopic methods for the first time. I and II dyes have high quantum yield and can be used for manufacturing effective lighting OLED layer.

The quantum-chemical calculations were performed in terms to obtain the equilibrium molecular geometry and electron structure of the dye molecules under study.

The calculations have shown that the dye molecules with BF_2 bridge (I and II) are practically ideal planar in the ground and excited states; two molecules with the BF_2O bridge for the dyes III and IV are slightly non-planar in excited states. This non-planarity can be the possible reason the weakening of the vibronic structure.

It is shown that superposition of the dye fluorescence spectra covers the almost entire visible range of wavelengths, which makes them promising to be additive components in combination with a blue emitting matrix in the manufacturing of white OLED.

References

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Фотофізичні властивості нових люмінесцентних барвників: борфторидні комплекси похідних бензо[c,d]індолу

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Вивчено спектри флюоресценції і поглинання нових бормістких барвників. Використовуючи стандартні методики, знайдено їх квантові виходи і часи затухання флюоресценції в рідких розчинах. Встановлено, що значення квантових виходів цих барвників у розчинах є високими. Зроблено повну інтерпретацію спектрів поглинання і флюоресценції за допомогою квантово-хімічних розрахунків. Встановлено, що спектри флюоресценції барвників охоплють майже весь видимий діапазон довжин хвиль. Область поглинання барвників можна варіювати шляхом зміни їх кінцевих груп. Барвники з такими властивостями можуть бути використані для створення білих органічних світлодіодів.