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Diethyl (Biscyclohexano)BODIPY* Dicarboxylates. Chelation of Alkaline-Earth Metal Ions and Sensor Properties

K. V. Tikhomirova, A. V. Khoroshutin, and A. V. Anisimov

Lomonosov Moscow State University, Moscow, 119991 Russia
e-mail: khorosh@petrol.chem.msu.ru

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Abstract—*meso*-Aryl-substituted (biscyclohexano)bis(ethoxycarbonyl)BODIPY [aryl = phenyl, 3,4-dimethoxyphenyl, and 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl-(*m*-{benzo-15-crown-5}-yl)] were synthesized. The effect of alkaline-earth metals on the absorption and fluorescence spectra of these compounds was investigated. In all compounds along with the mechanism of the photoinduced electron transfer (PET), well-known for the crown-containing BODIPY-based sensors, one more response pattern is observed. The large excess of Ca^{2+} and Ba^{2+} ions in the system leads to the changes both in the UV-Vis and emission spectra. The complex formation results in the decrease of emission intensity and in its red shift. Besides, a new longwave absorption band appears in the UV-Vis spectrum of the BODIPY–metal ion complex. The formation constants of the complexes corresponding to this response pattern is about 100 times less than the formation constant of Ca^{2+}-crown ether complex. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra, the results of quantum-chemical calculations, and their comparison with the literature data of X-ray diffraction study suggest that the binding of Ca^{2+} and Ba^{2+} ions occurs in the cavity formed by the fluorine atoms and the carbonyl oxygen atoms of the ester groups.

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Boron-dipyrrin complexes have been known since the late 1960's [1]. These stable dyes possess a narrow absorption band in the visible region and are capable of fluorescence. The photophysical properties of these substances make it possible to test their applicability, e.g., as laser dyes [2, 3], markers for biochemistry and biomedicine [4, 5], as a signal group in versatile chemical sensors [6–11].

Several signal mechanisms of optical and fluorescent sensors based on BODIPY are described in the literature [6, 9], and the most widely spread among them are intramolecular photoinduced electron transfer (PET) and photoinduced charge transfer (ICT). In particular, large interest is attracted to PET type sensors containing *meso*-aryl-substituted BODIPY where the rotation of the aryl group is hindered either by the substituents in the backbone of the dye, or in the aryl ring.

In the previous article we reported on the synthesis of dicyclohexano-fused diethyl dipyrrindicarboxylates **I** [12], which might exhibit sensor properties due to the presence there of two types of complexing sites: dipyrrin fragment in compounds **Ia–Ic** and crown ether fragment in compound **Ic**. However we found that the dipyrrin fragment existed in two conformations (*cis,syn* and *trans,anti*), which differ significantly in their complexing ability thus impeding the application of these compounds as sensors.

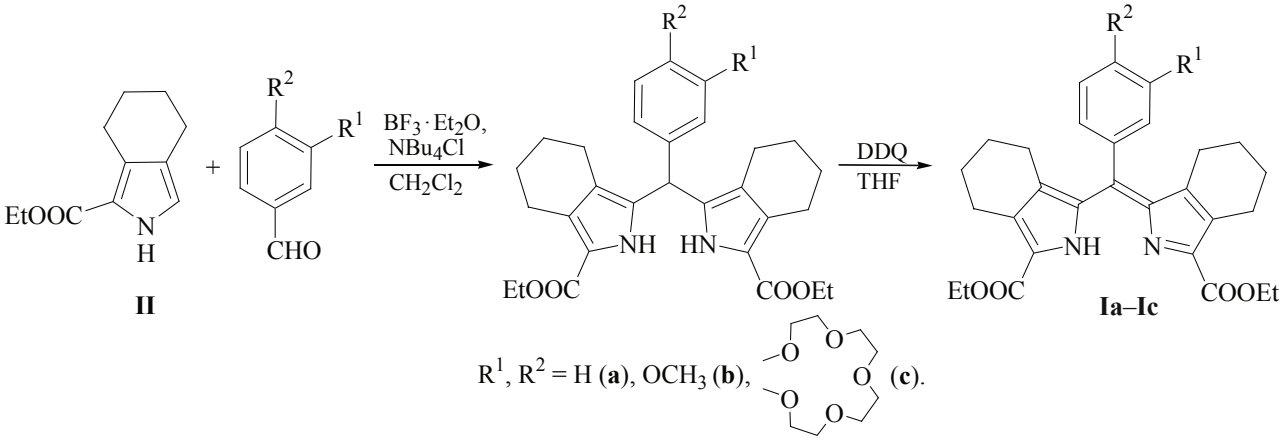
Since this disadvantage is absent in the corresponding BODIPY dyes, the target of this investigation was their synthesis and the study of their sensor characteristics.

BODIPY dyes were obtained from dipyrrins **I**. The latter were prepared by the condensation of substituted benzaldehyde with ethyl 4,5,6,7-tetrahydro-*2H*-isoindolecarboxylate (**II**) [13, 14] followed by the oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Scheme 1).

The most often in the synthesis of BODIPY the addition of boron trifluoride etherate to dipyrrin in the presence of triethylamine or other amines is a standard practice. In the case of the crown derivative **Ic** the yield of its BODIPY-derivative **IIIc** amounted 46% after the

* 4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene.

Scheme 1.



purification of the reaction product by column chromatography on silica gel.

We failed to isolate compounds **IIIa, IIIb** under these conditions. The analysis of the reaction mixtures showed that the addition of $BF_3 \cdot Et_2O$ is reversible, and the excess of the base shifts the equilibrium to the starting dipyrrin. This behavior of substrate may be attributed to the increased basicity of the cyclohexanodipyrrins caused by the out-of-plane deformation of the heterocycle. This effect was already observed in the cyclohexano-fused porphyrins [14].

The optimum conditions consisted in using a stronger base (1,8-diazabicyclo[5.4.0]undec-7-ene, DBU) and toluene as solvent [15, 16] at the reaction time from 30 to 40 min, for at the longer time the reaction products suffered decomposition. All three boron complexes proved to be unstable to the contact with silica gel. The decomposition products were ketones **IVa–IVc**. One of them, **IVc**, was fully characterized. The use of optimized procedure made it possible to obtain compounds **IIIa–IIIc** in the yields of 72, 42, and 68% respectively (Scheme 2).

The absorption and emission spectra of free ligands are well consistent with the published data on BODIPY dyes where the rotation of the *meso*-substituent is hindered (Table 1). The fluorescence of compounds **IIIb, IIIc** is quenched by a mechanism of intramolecular electron transfer. This phenomenon is favored by the polar environment stabilizing the final state with the separated charges. The fluorescence quantum yield (φ_{fl}) in nonpolar solvents is relatively high, and in polar solvents it amounts to ~1%. The quantum yield measured for compound **IIIa** coincided within the limits of experimental error with the published data [17], the values of φ_{fl} for all compounds also correspond to those found for analogs with ester groups or for fused dipyrrins. In the spectra in the visible region a slight solvatochromism was observed.

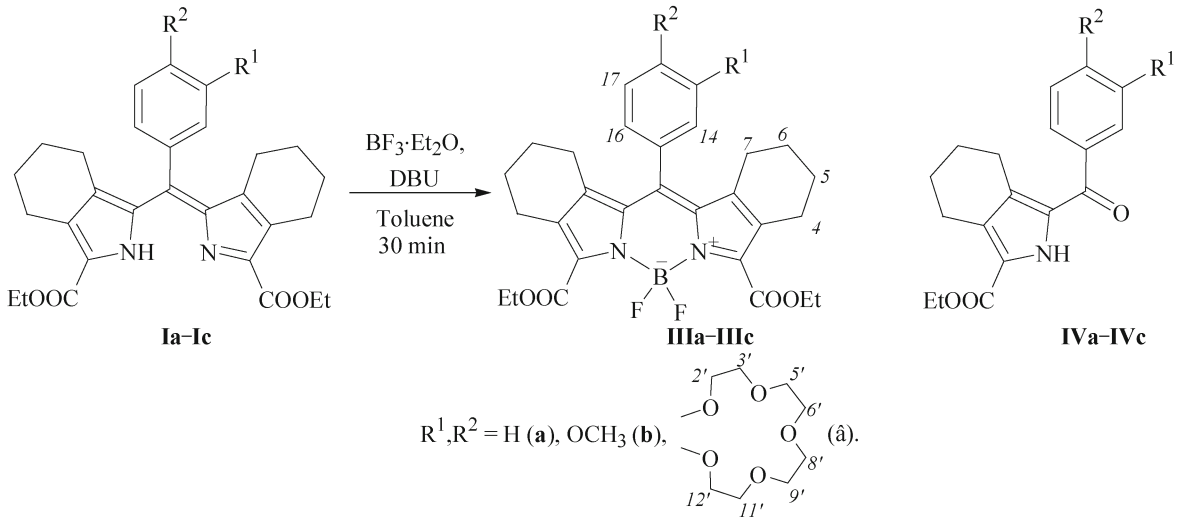
The synthesis and the study of fluorescence of compound **IIIa** and a number of other cyclohexanodipyrrins were recently published [17], but the synthesis of crown derivative **IIIc** as well as its analog **IIIb** possessing similar electronic properties we described for the first time. The interaction of compounds **III** with ions of alkaline-earth metals also has not been studied before.

Optical characteristics of crown-dipyrrin complex **IIIc** in hexane and acetonitrile and also the changes in its

Table 1. Optical properties of compounds **IIIa–IIIc** (excitation wavelength λ_{ex} 480 nm)

Compound no.	Solvent	Absorption, λ_{max}, nm	Emission, λ_{max}, nm	φ_{fl}, %
IIIa	Hexane	259, 429, 541	564	37
	Toluene	284, 430, 542	568	32
	CH_3OH	260, 427, 535	563	27
	CH_3CN	259, 425, 533	560	31
IIIb	Hexane	281, 419, 541	561	26
	Toluene	285, 429, 541	567	34
	CH_3OH	259, 409, 535	560	0.21
	CH_3CN	258, 426, 531	561	0.12
IIIc	Hexane	259, 419, 541	563	37
	Toluene	285, 429, 541	568	38
	CH_3OH	258, 421, 535	566	0.14
	CH_3CN	257, 426, 532	564	0.13

Scheme 2.



absorption and emission spectra in the presence of sodium and potassium cations were previously described in the literature [18–20]. We studied the absorption and emission spectra and also the quantum yields of fluorescence of compounds **IIIa–IIIc** in four different solvents (Table 1).

The data obtained show that electron-donor substituents in the benzene ring in the *meso*-position insignificantly affect the position of the absorption and emission maxima in the spectra of compounds **III**. However the quantum yields of fluorescence considerably differ and strongly depend on the polarity of the solvent. This, as follows from the published data, is caused by the possibility to occur in the presence of electron-donor substituents in the *meso*-position in compounds **IIIb, IIIc** of a photoinduced intramolecular electron transfer (PET) from the HOMO of the substituent to the HOMO of the excited fragment of BODIPY. This process results in significant quenching of the fluorescence in the solvents of high polarity [9].Yet in nonpolar solvents (hexane, toluene) this process is practically absent, therefore the fluorescence quantum yields remain sufficiently high (25–38%). The fluorescence quenching is a function of solvent polarity which favors the stabilization of the charge-separated state, and of the energy difference between the substituent's and the dye's HOMOs [21]. Evidently in the case of unsubstituted BODIPY **IIIa** PET is impossible due to the low HOMO energy of the unsubstituted phenyl group. Similar relations were thoroughly studied for bicyclo[2.2.2]octene-substituted BODIPY containing a crown ether fragment [22].

We investigated the complex formation of all compounds obtained with Mg^{2+}, Ca^{2+}, and Ba^{2+} cations and the effect of this process on the optical properties of the studied substances.

Crown ethers are known to be capable of complexes formation with cations of alkali and alkaline-earth metals [23]. Crown ether substituents attached to the BODIPY molecule yield highly efficient fluorescence sensors of metal cations [9].

In **IIIc** molecule the substituent in the *meso*-position is orthogonal to the dipyrrin plane, therefore it is expectable that the metal cations complexation should weakly affect the absorption spectrum, but it should sharply increase the fluorescence intensity due to suppressing PET. Indeed, in the case of Mg^{2+} we observed the changes in the optical spectra of compound **IIIc** similar to those described in the literature at the formation of complexes with Na^+ [18]: addition of Mg^{2+} excess lead to very small red shift of the absorption band, and the fluorescence intensity sharply increased (Fig. 1, Table 2).

Table 2. Effect of magnesium cation on the optical properties of compounds **IIIa–IIIc**

Complex[a]	Absorption, λ_{max} (nm)	Emission, λ_{max} (nm)	φ_{fl}, %
IIIa + Mg	260, 425, 533	561	29.35
IIIb+ Mg	257, 424, 532	561	0.12
IIIc+ Mg	257, 405, 534	564	29.40

[a] Complexes were obtained *in situ* by adding ~100-fold excess of $Mg(ClO_4)_2$ to a solution of compounds **IIIa–IIIc** in CH_3CN (1×10^{-5} mol L^{-1}), λ_{ex} 480 nm.

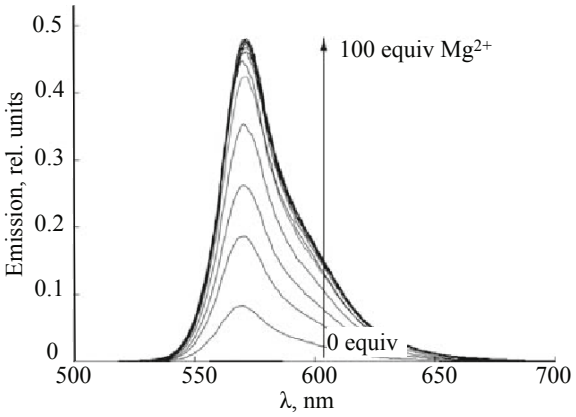


Fig. 1. Variation in the fluorescence spectrum of compound **IIIc** (1×10^{-4} mol l^{-1} in CH_3CN) at the titration with the solution of $Mg(ClO_4)_2$ in CH_3CN. λ_{ex} 480 nm.

The optical properties of compounds **IIIa, IIIb** lacking the crown ether fragment are virtually insensitive to the addition of excess Mg^{2+} (Tables 1,2) confirming the complexing of magnesium cations only with the crown ether fragment of **IIIc** molecule.

Cations Ba^{2+} also are capable of the formation of complexes with benzo-15-crown-5, therefore the changes in the absorption and emission spectra were expectable similar to those observed for Mg^{2+}. It was observed that addition of first portions of $Ba(ClO_4)_2$ solution to the solution of compound **IIIc** resulted in a sharp growth of the fluorescence intensity, as it was in the previous case. However on further addition the emission maximum suffered a red shift by 30 nm with simultaneous decrease in the intensity (Fig. 2a).

Analogous changes in the fluorescence spectrum were also observed on adding Ba^{2+} solutions to the solution of compound **IIIa** (Fig. 2b). In this case a gradual quenching of the fluorescence also occurred with the simultaneous red shift of the emission maximum. The solution of compound **IIIb** in acetonitrile possesses a very weak fluorescence, yet in this case also the red shift of the spectrum is observed (the figure is not shown).

Considerable changes are also observed during the UV-Vis titration of compounds **IIIa–IIIc** with Ba^{2+} solution: For all three compounds the absorption maximum at 532 nm gradually decreases, and a new band with the maximum at 558–561 nm arises (Fig. 3). The red shift is accompanied with the change in the solution color from orange-red to crimson.

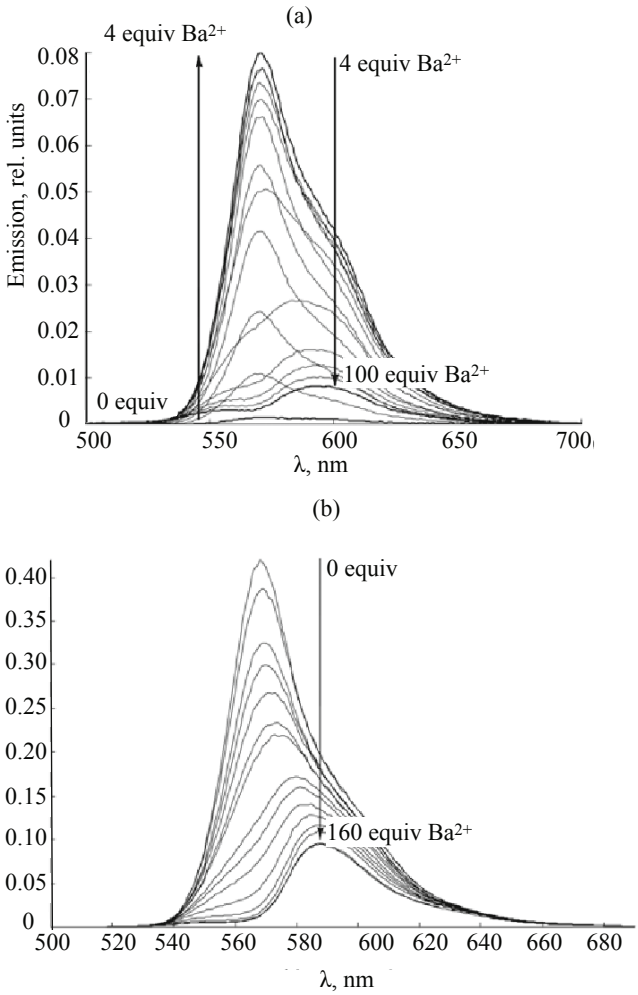


Fig. 2. Variation in the fluorescence spectrum at the titration with the solution of $Ba(ClO_4)_2$ in CH_3CN: (a) of compound **IIIc** (1×10^{-4} mol L^{-1}); (b) of compound **IIIa** (1×10^{-4} mol L^{-1}). λ_{ex} 480 nm.

To account for the observed changes we presumed that Ba^{2+} cations get bound to ester fragments of initial dipyrrins **III**. Similar changes (i.e. a considerable red shift of absorption and emission maxima, partial quenching of fluorescence) were described in the literature for molecules

Table 3. Calculated stability constants (log K) of complexes 1 : 1, 2 : 1

Complex	$\log K_{cation/ligand}$
Mg–**IIIc**	$\log K_{11}$ 5.02 ± 0.05
Ba–**IIIa**	$\log K_{11}$ 2.86 ± 0.07
Ba–**IIIb**	$\log K_{11}$ 2.90 ± 0.02
Ca–**IIIa**	$\log K_{11}$ 2.15 ± 0.10
Ca–**IIIc**	$\log K_{11}$ 4.57 ± 0.22; $\log K_{21}$ 6.04 ± 0.22

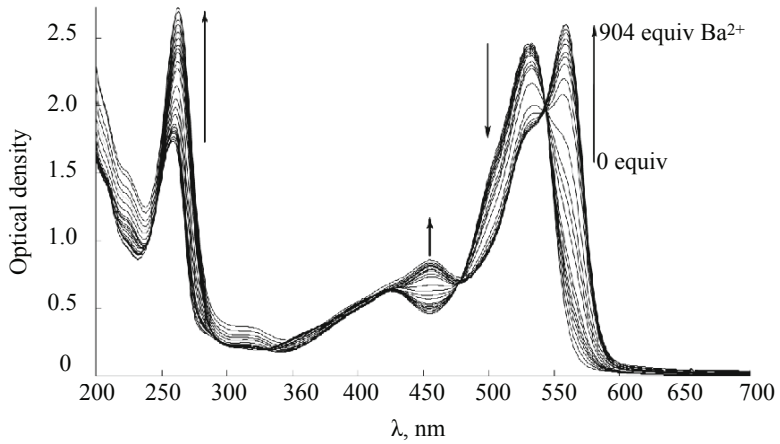


Fig. 3. Variation of EAS of compound **IIIa** (1×10^{-4} mol L^{-1}) at the spectrophotometric titration with solution of $Ba(ClO_4)_2$ in CH_3CN.

of BODIPY and their analogs when in the complex formation the electron-acceptor groups were involved being a part of the the chromophore system [24–26]. However no published examples exist of complexing of Ca^{2+} and Ba^{2+} ions with ester groups of BODIPY, although complexes are known where the barium atom is coordinated to the oxygen atom of the other ester groups [27–29].

The presence of an isosbestic point at 543 nm (Fig. 3) indicates the formation of a single type of a complex. The processing of the data of the UV-Vis titration of **IIIa** with the $Ba(ClO_4)_2$ solution using SPECFIT/32 program showed that one ligand–metal complex was in this case formed, i.e. 1 : 1. Compound **IIIb** is also able to form a complex at the ester fragment, and its stability constant also has been calculated (Table 3). The accurate calculation of the constant of complex formation at ester groups for the crown-containing ligand **IIIc** was impeded by the presence of several colored complexes of various types.

The study of the effect of Ca^{2+} cations on the optical spectra of compounds **IIIa–IIIc** revealed that the Ca^{2+} ions also cause a red shift of the absorption and emission maxima and the quenching of fluorescence (Figs. 4, 5).

However, compared to that Ba^{2+}, the addition of Ca^{2+} solutions leads to more complex shapes of the final spectra in all cases. I.e. a shoulder is clearly seen at 538–540 nm, a broad band in the 430–460 nm region also possesses a dual-band structure, and the main absorption maximum is shifted further to the red region by 33–36 nm. The fluorescence spectra also contain two maxima of emission bands: at 555–560 and 592–599 nm.

From the results of the spectrophotometric titration compound **IIIa** was shown to form a single complex

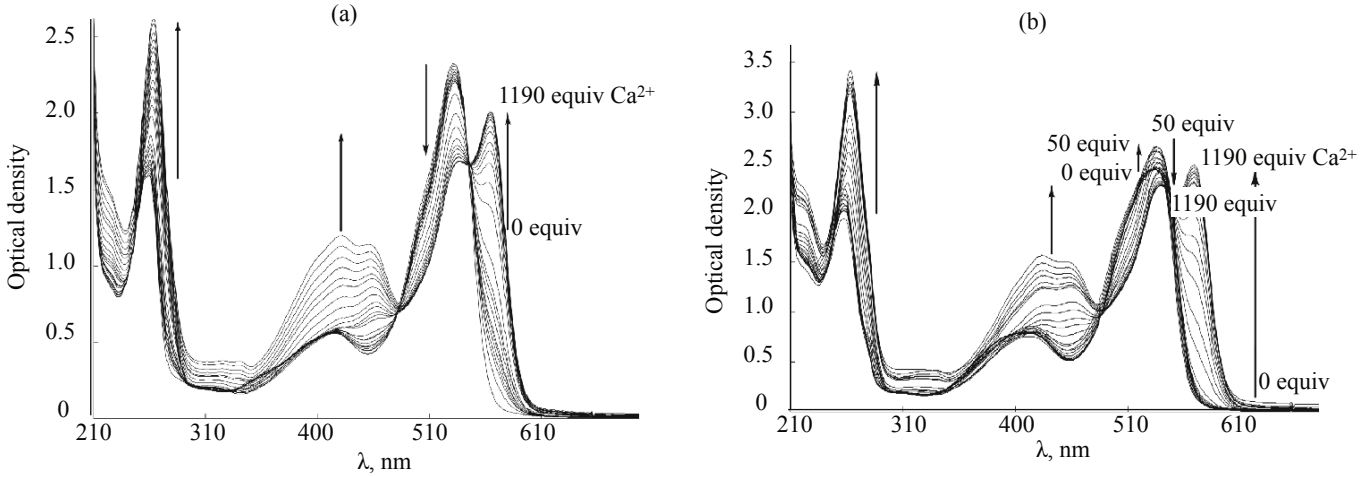


Fig. 4. Variation of EAS at the titration with a solution of $Ca(ClO_4)_2$ in CH_3CN: (a) of compound **IIIa** (1×10^{-4} mol L^{-1}); (b) of compound **IIIc** (1×10^{-4} mol L^{-1}).

1 : 1 like in the case of Ba^{2+}. Compound **IIIc** formed complexes with the calcium cation both at the crown ether and at the ester fragments therefore the spectral changes at the titration are more complicated (Fig. 4b).

UV-Vis titration data were used to calculate the stability constants of the corresponding complexes (Table 3). Similarly using the method of fluorimetric titration we determined the association constant of **IIIc** complex with Mg^{2+} (Table 3)

The formation of Ca^{2+} and Ba^{2+} complexes with the ester fragments of the studied compounds leads to the decrease in the fluorescence quantum yield in contrast to the increased fluorescence intensity in the Mg^{2+}-**IIIc** complex (Tables 1, 2). However it was difficult to estimate quantitatively the changes in the fluorescence quantum yields since the described complexes were obtained in rather concentrated solutions. At the strong dilution used for the precise quantum yield measurement the absorption and emission maxima broadened and suffered a blue shift evidently due to the partial decomposition of the complexes.

To confirm the structure of the obtained complexes we explored the effect of Mg^{2+}, Ca^{2+}, and Ba^{2+} cations on the NMR spectra of **IIIa, IIIc** (Tables 4, 5).

The data obtained are in good agreement with the results of optical spectra measurements and with the assumption of the interaction between calcium and barium cations with the ester groups of the molecules under study.

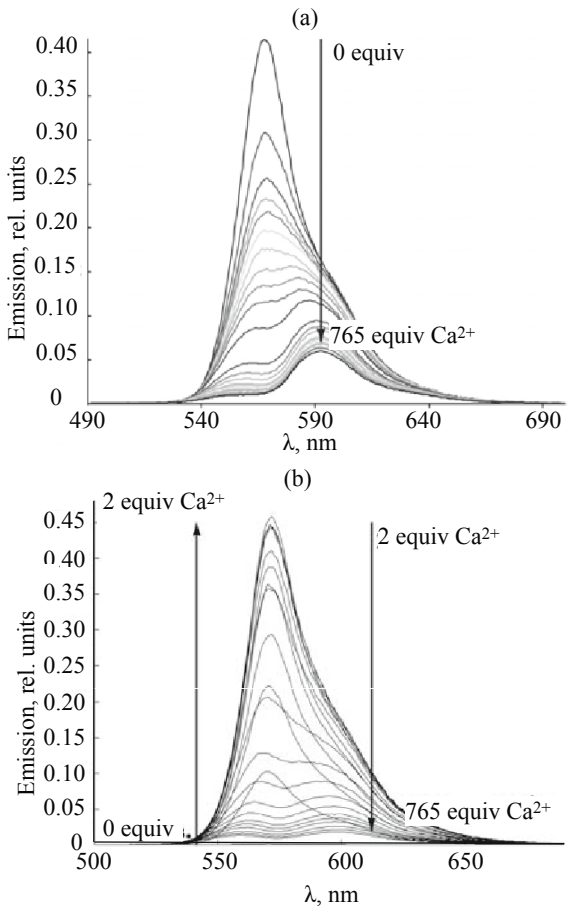


Fig. 5. Variation of fluorescence spectra of compound **IIIa** (1×10^{-4} mol L^{-1}) (a) and **IIIc** (1×10^{-4} mol L^{-1}) (b) at the titration of their solutions with a solution of $Ca(ClO_4)_2$ in CH_3CN. λ_{ex} 480 nm.

Table 4. Chemical shifts of ^1H NMR signals (δ, ppm) in the spectra of compounds **IIIa, IIIc** and their complexes in CD_3CN (25-fold excess of metal perchlorates)

Compound or complex	ArH	H^4	H^5	H^6	H^7	OCH_2CH_3	OCH_2CH_3
IIIa	7.35–7.37, 7.55–7.58	2.53	1.57	1.38	1.64	4.36	1.35
IIIa + Mg^{2+}	7.35–7.37, 7.55–7.58	2.53	1.57	1.38	1.64	4.36	1.35
IIIa + Ca^{2+}	7.36–7.38, 7.58–7.63	2.69	1.59	1.38	1.68	4.49	1.41
IIIa + Ba^{2+}	7.35–7.37, 7.58–7.62	2.70	1.58	1.38	1.65	4.49	1.40

	H^{14}	H^{16}	H^{17}	H^4	H^5	H^6	H^7	OCH_2CH_3	OCH_2CH_3
IIIc	6.91	6.86	7.06	2.54	1.60	1.44	1.80	4.36	1.34
IIIc + Mg^{2+}	7.21	7.16	7.33	2.54	1.60	1.44	1.71	4.36	1.34
IIIc + Ca^{2+}	7.24	7.15	7.38	2.71	1.62	1.44	1.80	4.50	1.42
IIIc + Ba^{2+}	7.12	7.05	7.28	2.72	1.61	1.44	1.82	4.50	1.40

	$H^{2'}$	$H^{3'}$	$H^{5',6',8',9'}$	$H^{11'}$	$H^{12'}$
IIIc	4.15	3.83	3.63–3.67	3.77	4.05
IIIc + Mg^{2+}	4.53	4.15	3.92, 3.99	4.10	4.41
IIIc + Ca^{2+}	4.52	4.10	3.97–4.01	4.05	4.44
IIIc + Ba^{2+}	4.43	3.85–3.97	3.85–3.97	3.85–3.97	4.34

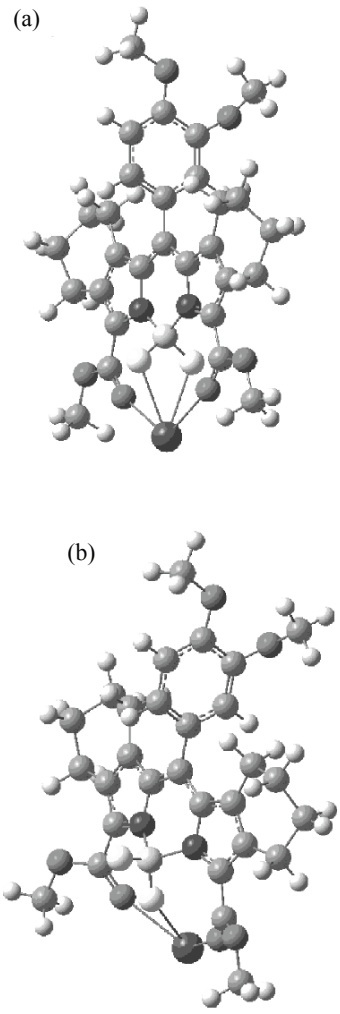


Fig. 6. Spatial arrangement of complexes of model compound analogous to compound **IIIb** according to the data of ab initio calculations: (a) the interaction of Ba^{2+} ion with carbonyl oxygen atom of ester group and two fluorine atoms inside the cavity; (b) Ba^{2+} interacts with carbonyl groups of two COOEt fragments and one fluorine atom, being located outside of cavity.

Table 5. Chemical shifts of ^{11}B and ^{19}F NMR signals in the spectra of compounds **IIIa, IIIc** and their complexes in CD_3CN (25-fold excess of metal perchlorates)

Compound or complex	^{11}B, δ, ppm	^{19}F, δ, ppm
IIIa	0.15	–140.61
IIIa + Mg^{2+}	0.15	–140.52
IIIa + Ca^{2+}	0.70	–138.71
IIIa + Ba^{2+}	0.58	–137.05
IIIc	0.16	–140.45
IIIc + Mg^{2+}	0.15	–140.49
IIIc + Ca^{2+}	0.71	–138.50
IIIc + Ba^{2+}	0.60	–136.82

Table 6. Energy of complexes of model dipyrrin with Ca^{2+} and Ba^{2+} ions (kcal mol^{-1}) of various spatial structures by the data of quantum-chemical calculations

Configuration	Relative energy of complexes, kcal mol^{-1}	
	Ca^{2+}	Ba^{2+}
"Inside cavity" (Fig. 6a)	0	0
"Above cavity" (Fig. 6b)	27.2	25.3
"At the side of cavity" (not shown on the figure, see the text)	124.0	17.4

The addition of Mg^{2+} to a solution of compound **IIIa** has virtually no effect on the position of ^1H signals in agreement with the absence of the optical response. On adding Ca^{2+} or Ba^{2+} the proton signals of the ethyl group of the ester fragment significantly shifted downfield, the greater shift occured in the signals of the methylene protons (0.13–0.14 ppm). The positions of proton peaks of the cyclohexane fragment do not practically change except the signal of H^4 that also suffers a significant downfield shift (0.16–0.18 ppm). These protons are in close proximity to the ester carbonyl and are affected by its anisotropic influence. At the formation of the complex with metal cations apparently changes the spatial position of the COOEt fragment with respect to the boron-dipyrrin fragment. The downfield shift of the adjacent groups evidently indicates that the ester group interacting with the metal ion is situated in the same plane as the dipyrrin fragment. The signals of the phenyl group do not visibly change in the presence of metal cations.

In the ^1H NMR spectrum of compound **IIIc** at adding cations of Mg^{2+}, Ca^{2+}, and Ba^{2+} the proton signals of benzocrown ether fragment suffer a considerable downfield shift (~0.2–0.4 ppm), and the shifts are larger in the case of Mg^{2+} and Ca^{2+}, which are known to form stronger complexes with 15-crown-5. Similar changes in NMR spectra are typical of compounds containing benzocrown ether fragment at complexing with magnesium and barium cations [30, 31]. In the signals of protons from the ester and cyclohexane fragments changes are observed analogous to the above described for the complex with **IIIa** ligand.

We also registered the ^{11}B and ^{19}F NMR spectra of initial compounds and their complexes (Table 5). **IIIa, IIIc** have spectra typical of BODIPY [32–35]. Adding excess Mg^{2+} in both cases does not affect the position of F and B signals. However in the presence of Ca^{2+} and Ba^{2+} both nuclei suffer a downfield shift (0.43–0.55 ppm for boron atoms and 1.90–3.63 ppm for fluorine). Rao

et al. [34, 36] observed a downfield shift in the ^{11}B and ^{19}F NMR spectra at the introduction in positions *3, 5* of the BODIPY molecule of aldehyde or amide groups capable of forming hydrogen bonds with BF_2. Weak (~2–3 ppm) downfield shifts in ^{19}F NMR spectra were described for BODIPY and their analogs at the formation of complexes involving interactions BF---Cs^+ [37, 38]. A large downfield shift is characteristic of 3,5-diaryl-substituted BODIPY as compared with dibromo-substituted [32]. In our case the observed shifts may be due to the formation of a complex, where the metal cation is located in the immediate proximity of BF_2 (Fig. 6).

Ab initio quantum chemical calculations at the HF/LANL2MB approximation confirm our assumptions. For the complex with calcium or barium ions the minima on the potential energy surface (PES) correspond to the structures analogous to that shown in Fig. 6a. Other minima on PES were also found. The configuration shown in Fig. 6b depicts a metal ion located under the dipyrrin plane and coordinated to two ester groups and a single fluorine atom. One more minimum corresponds to the configuration where the cation is coordinated with a single ester group and it is placed at the side of dipyrrin molecule (not shown in the figure).

Both for Ca^{2+} and Ba^{2+} the structures corresponding to Fig. 6a are the most favorable by the energy (Table 6).

Thus we found that the ethoxycarbonyl-substituted borodipyrrin complexes synthesized in this study exhibited moderate sensing properties to ions of alkaline-earth metals, calcium and barium. This may be due to the presence in the studied compounds of a guest cavity formed of the fluorine atoms of BF_2 moiety and the carbonyl oxygen atoms of the ester group. The sensor effect is observed in the spectra in UV and visible region and in the fluorescence spectra. The structure of the complexes was confirmed by the ^1H, ^{19}F NMR spectra and by ab initio quantum-chemical calculations.

EXPERIMENTAL

^1H, ^{13}C, and ^{11}B NMR spectra were registered on a Bruker Avance 400 spectrometer (400, 100, 128 MHz respectively). Chemical shifts of ^{11}B signals were measured with respect to external H_3BO_3 reference. ^{19}F spectra were recorded on a Bruker AM300 spectrometer at a frequency 282 M Hz, chemical shifts ^{19}F were measured with respect to external $CFCl_3$ reference. Chemical shifts were measured with an accuracy of 0.01 ppm, coupling constants, with an accuracy of 0.1 Hz. In the NMR spectra ^{13}C-APT (Attached Proton Test) the signals of secondary and quaternary carbon atoms are marked with asterisk *.

Mass spectra with laser desorption ionization (LDI-TOF) were recorded on a Bruker Daltonics Autoflex II instrument by nitrogen laser irradiation at 337 nm and 19kV accelerating voltage.

Commercial products and solvents were purchased from Reachim, Aldrich, Acros Organics. The solvents were distilled before use.

UV-Vis spectra were measured on a spectrophotometer Agilent-8453, operating range 190–1100 nm. The spectrophotometer control, the data collection and processing was performed using a UV-Visible Chem.Station program, Rev. A.10.01. Fluorescence spectra were recorded on a spectrofluorimeter Flyuorat-02-Panorama, the instrument being controlled with the program Panorama Lite.

Quantum yields of fluorescence were determined at room temperature in air-saturated acetonitrile solutions with respect to the solution of rhodamine 6G in ethanol used as reference (φ_{fl} 0.94) [39]. The fluorescence quantum yield was calculated by the formula [40]

$$\varphi_{exp} = \frac{(1-10^{-D_{ref}})\ S_{exp}\ n_{exp}^2}{(1-10^{-D_{exp}})\ S_{ref}\ n_{ref}^2}\varphi_{exp},$$

where S is the integral intensity of the fluorescence, D is the optical density at the excitation wavelength, n is the refraction index of the solvent used, φ is the fluorescence quantum yield.

The stability constants of complexes of dipyrromethene ligands with metal cations were determined by spectrophotometric and fluorimetric titrations at room temperature in acetonitrile with appropriate metal perchlorates. The processing spectrophotometric titration results and the calculation of the stability constants of the complexes were carried out using SPECFIT/32 software applying the nonlinear least squares method by the Levenberg–Marquardt algorithm.

Elemental analysis was carried out in the Microanalysis laboratory of the Chemical Department of Lomonosov Moscow State University.

Melting points were measured on an instrument MelTempII and were uncorrected.

TLC analyses were carried out on DC-Alufolien Kieselgel 60 F254 plates (Merck). For column chromatography silica gel Kieselgel 60 0.063–0.200 mm (Merck) was used.

The optimization of the structure of molecules was performed applying the program GAUSSIAN03 [41] using the HF/LANL2MB approximation.

Complexes of bis(ethoxycarbonyl)cyclohexanodipyrrins with BF_2 IIIa–IIIc. General procedures. *a.* Dipyrrin **I** (1 equiv) was dissolved in $CHCl_3$, the reaction flask was flushed with argon at stirring, 20 equiv of triethylamine was added, the mixture was stirred for 30 min, then 30 equiv of freshly distilled $BF_3 \cdot Et_2O$ was added, and the stirring under an argon atmosphere was continued (TLC monitoring). On completing the reaction the reaction mixture was washed in succession with saturated water solution of Na_2CO_3, water, and brine, and dried with Na_2SO_4.

b. The synthesis was carried out similarly to procedure *a*, using instead of triethylamine the corresponding quantity of *N*-ethyl-*N*-diisopropylamine.

c. 1 equiv of dipyrrin **I** was dissolved in toluene, the reaction flask was flushed with argon at stirring, 6 equiv of DBU was added, the stirring continued for 10 min, then 20 equiv of freshly distilled $BF_3 \cdot Et_2O$ was added, and the stirring under an argon atmosphere was continued for 30–40 min. The reaction mixture was washed with 5% water solution of HCl, reaction product was extracted with $CHCl_3$, the combined organic solutions were washed with water and brine, dried with Na_2SO_4.

(Ethyl 1-{[3-(ethoxycarbonyl)-4,5,6,7-tetrahydro-2*H*-isoindol-1-yl-κN](phenyl)methylene}-4,5,6,7-tetrahydro-1*H*-isoindole-3-carboxylato-κN))(difluoro)boron IIIa. All attempts to prepare compound **IIIa** by procedures *a, b* (varying reaction time, amount of used reagents, temperature) failed.

c. From 0.0400 g (0.085 mmol) of dipyrromethene **Ia** in 8 mL of toluene on removing the solvent 0.0483 g of solid was obtained consisting (according to NMR data) of compound **IIIa** with a slight impurity of initial dipyrromethene **Ia**. After addition 6 mL of hexane and boiling the filtered off insoluble residue contained pure compound **IIIa**. Yield 0.0317 g (0.061 mmol, 72%). Red solid, mp 130–132°C. UV-Vis spectrum (CH_3CN), λ_{max}, nm (log ε): 259 (4.24), 425 (3.80), 533 (4.39). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 m (10H, $OCH_2C\underline{H}_3$, H^6, ^3J 7.0 Hz), 1.53–1.59 m (8H, H^5, H^7), 2.56 m (4H, H^4), 4.43 q (4H, $OC\underline{H}_2CH_3$, ^3J 7.0 Hz), 7.21–7.23 m ($2H_{arom}$), 7.49–7.52 m ($3H_{arom}$). ^{13}C APT NMR spectrum ($CDCl_3$), δ, ppm: 14.03, 22.02*, 22.33*, 22.62*, 24.41*, 61.67*, 127.18, 127.30, 129.38, 129.48, 129.66, 132.54*, 132.90*, 134.60*, 143.65*, 143.79*, 147.62*, 161.56*. ^{11}B NMR spectrum (CD_3CN), δ, ppm: 0.15 t (^1J 27.4 Hz). ^{19}F NMR spectrum (CD_3CN), δ, ppm: –140.61 q (^1J 27.6 Hz). Mass spectrum (LDI-TOF, 19 kV), *m/z* (I_{rel}, %): 559.26 (12) $[M + K]^+$, 543.26 $[M + Na]^+$ (100), 521.21 (15) $[M + H]^+$, 501.23 (21) $[M - F]^+$. Found, %: C 66.75; H 6.19; N 5.18. $C_{29}H_{31}BF_2N_2O_4$. Calculated, %: C 66.93; H 6.00; N 5.38. *M* 520.38.

(Ethyl 1-{[3-(ethoxycarbonyl)-4,5,6,7-tetrahydro-2*H*-isoindol-1-yl-κ*N*](3,4-dimethoxyphenyl)-methylene}-4,5,6,7-tetrahydro-1*H*-isoindole-3-carboxylato-κ*N*)(difluoro)boron (IIIb). All attempts to prepare compound **IIIb** by procedures *a, b* (varying reaction time, amount of used reagents, temperature) failed.

c. From 0.0384 g (0.072 mmol) of dipyrromethene **Ib** in 10 mL of toluene on removing the solvent 0.0399 g of red solid was obtained consisting (according to NMR data) of compound **IIIb** with a slight impurity of initial dipyrromethene **Ib.** After adding 10 mL of hexane and boiling the filtered off insoluble residue contained pure compound **IIIb**. Yield 0.0176 g (0.030 mmol, 42%), mp 136–137°C. UV spectrum (CH_3CN), λ_{max}, nm (log ε): 258 (4.32), 426 (3.91), 531 (4.39). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 m (10, $OCH_2C\underline{H}_3$ + H^6, ^3J 7.0 Hz), 1.55–1.61 m (4H, H^5), 1.68–1.73 m (4H, H^7), 2.57 m (4H, H^4), 3.85 s (3H, $OC\underline{H}_3$), 3.96 s (3H, OCH_3), 4.42 q (4H, $OC\underline{H}_2CH_3$, ^3J 7.0 Hz), 6.71 d (1H, H^{14}, $^4J_{14,16}$ 1.9 Hz), 6.77 d.d (1H, H^{16}, $^4J_{14,16}$ 1.9, $^3J_{16,17}$ 8.2 Hz), 6.98 d (1H, H^{17}, $^3J_{16,17}$ 8.2 Hz). ^{13}C APT NMR spectrum ($CDCl_3$), δ, ppm: 14.04, 22.09*, 22.36*, 22.70*, 24.58*, 55.93, 56.17, 61.66*, 110.29, 111.75, 119.89, 126.73*, 132.50*, 133.23*, 143.58*, 143.77*, 147.57*, 150.00*, 150.05*, 161.60*. ^{11}B NMR spectrum (CD_3CN), δ, ppm: 0.52 t (^1J 27.4 Hz). Mass spectrum (LDI-TOF, 19 kV), *m/z* (I_{rel}, %): 619.22 (32) $[M + K]^+$, 603.36 (100) $[M + Na]^+$, 561.32 (18) $[M - F]^+$. Found, %: C 63.96; H 5.88; N 4.64. $C_{31}H_{35}BF_2N_2O_6$. Calculated, %: C 64.15; H 6.08; N 4.83. *M* 580.43.

Ethyl 1-{[3-(ethoxycarbonyl)-4,5,6,7-tetrahydro-2*H*-isoindol-1-yl-κN](2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)methylene}-4,5,6,7-tetrahydro-1*H*-isoindole-3-carboxylato-κN)(difluoro)boron (IIIc) and **ethyl 3-[(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13benzopentaoxacyclopentadecin-15-yl)carbonyl]-4,5,6,7-tetrahydro-2*H*-isoindole-1-carboxylate (IVc).** *a.* The substance obtained from 0.0334 g (0.0504 mmol) of dipyrromethene **Ic** in 5 mL of $CHCl_3$ within 20 h was purified by column chromatography (silica gel, $CHCl_3$–

EtOH, 30 : 1, later 20 : 1, 10 : 1). Red fractions not containing impurities (TLC) were combined. Yield 0.0163 g (0.023 mmol, 46%).

b. From 0.0856 g (0.129 mmol) of dipyrromethene **Ic** in 25 mL of $CHCl_3$ on removing the solvent we obtained 0.0825 g of red amorphous substance that was subjected to chromatography (silica gel, $CHCl_3$–EtOH, 50 : 1, later 20 : 1, 10 : 1). First red fractions not containing impurities (TLC) were combined. We obtained 0.0133 g (0.0187 mmol, 14%) of red solid. Fractions containing another individual compound were combined and from the sum of spectral data it was identified as the decomposition product of initial dipyrrin, compound **IVc**. Yield 0.0178 g (0.0365 mmol, 28%).

c. From 0.0802 g (0.121 mmol) of dipyrromethene **Ic** in 20 mL toluene after purification by column chromatography (silica gel, CH_2Cl_2–EtOH, 70 : 1, later 60 : 1, 50 : 1) 0.0582 g (0.082 mmol, 68%) of compound **IIIc** was isolated. Red solid, mp 137–138°C (138°C [18]). UV spectrum (CH_3CN), λ_{max}, nm (log ε): 257 (4.35), 426 (3.93), 532 (4.38). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 m (10H, $OCH_2C\underline{H}_3$, H^6, ^3J 7.0 Hz), 1.57 m (4H, H^5), 1.70 m (4H, H^7), 2.56 m (4H, H^4), 3.78–3.79 m (8H, H$^{5'}$, H$^{6'}$, H$^{8'}$, H$^{9'}$), 3.91 m (2H, H$^{11'}$), 3.96 m (2H, H$^{3'}$), 4.08 m (2H, H$^{12'}$), 4.19 m (2H, H$^{2'}$), 4.42 q (4H, $OC\underline{H}_2CH_3$, ^3J 7.0 Hz), 6.69 d (1H, H^{14}, $^4J_{14,16}$ 1.9 Hz), 6.74 d.d (1H, H^{16}, $^4J_{14,16}$ 1.9, $^3J_{16,17}$ 8.2 Hz), 6.94 d (1H, H^{17}, $^3J_{16,17}$ 8.2 Hz). ^{13}C APT NMR spectrum ($CDCl_3$), δ, ppm: 14.03, 22.08*, 22.38*, 22.66*, 24.65*, 61.65*, 68.24*, 68.67*, 69.09*, 69.14*, 70.00*, 70.89*, 112.21, 113.49, 120.17, 126.94*, 132.51*, 133.21*, 143.49*, 143.87*, 147.53*, 149.81*, 150.00*, 161.58*. ^{11}B NMR spectrum (CD_3CN), δ, ppm: 0.16 t (^1J 27.4 Hz). ^{19}F NMR spectrum (CD_3CN), δ, ppm: –140.45 m. Mass spectrum (LDI-TOF, 19 kV), *m/z* (I_{rel}, %): 749.11 (63) $[M + K]^+$, 733.15 (100) $[M + Na]^+$, 691.18 (42) $[M - F]^+$. Found, %: C 62.33; H 6.59; N 3.65. $C_{37}H_{45}BF_2N_2O_9$. Calculated, %: C 62.54; H 6.38; N 3.94. *M* 710.57.

Compound IVc. Yellow-orange solid. UV spectrum ($CHCl_3$), λ_{max}, nm: 330. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 m (3H, $OCH_2C\underline{H}_3$, *J* 7.2 Hz), 1.60–1.66 (2H, H^6), 1.72–1.77 m (2H, H^5), 2.49 m (2H, H^7), 2.81 t (2H, H^4, *J* 6.3 Hz), 3.76 m (8H, H$^{5'}$, H$^{6'}$, H$^{8'}$, H$^{9'}$), 3.89–3.94 m (4H, H$^{3'}$, H$^{11'}$), 4.15–4.19 m (4H, H$^{2'}$, H$^{12'}$), 4.34 q (2H, $OC\underline{H}_2CH_3$, *J* 7.2 Hz), 6.88 d (1H, H^{17}, $^3J_{16,17}$ 8.2 Hz), 7.25 d (1H, H^{14}, $^4J_{14,16}$ 1.9 Hz), 7.33 d.d (1H, H^{16}, $^3J_{16,17}$ 8.2, $^4J_{14,16}$ 1.9 Hz), 9.44 br.s (1H, NH). ^{13}C APT NMR spectrum ($CDCl_3$), δ, ppm: 14.42, 22.70*, 22.92*, 22.98*, 24.37*, 60.59*, 68.58*, 68.85*, 69.12*, 69.20*, 70.15*, 70.21*, 70.98*, 112.10, 113.65, 121.83*, 123.31, 128.88*, 129.04*, 131.72*, 148.77*, 152.58*, 161.04*, 185.71*. Mass spectrum (LDI-TOF, 19 kV), *m/z* (I_{rel}, %): 525.87 (93) $[M + K]^+$, 509.92 (100) $[M + Na]^+$, 487.96 (84) $[M]^+$. *M* 487.54.

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REFERENCES

1. Treibs, A. and Kreuzer, F.-H., *Lieb. Ann.,* 1968, vol. 718, p. 208.
2. Garcia-Moreno, I., Amat-Guerri, F., Liras, M., Costela, A., Infantes, L., Sastre, R., Arbeloa, F.L., Prieto, J.B., Arbeloa, I.L., *Adv. Funct. Mater.,* 2007, vol. 17, 3088.
3. Arbeloa, F.L., Banuelos, J., Martinez, V., Arbeloa, T., Arbeloa, I.L. *Int. Rev. Phys. Chem.,* 2004, vol. 24, p. 339.
4. Haughland, R.P. and Kang, H.C., US Patent 4774339, 1988.
5. Monsma, F.J., Barton, A.C., Kang, H.C., Brassard, D.L., Haughland, R.P., and Sibley, D.R., *J. Neurochem.,* 1989, vol. 52, p. 1641.
6. Loudet, A. and Burgess, K., *Chem. Rev.,* 2007, vol. 107, p. 4891.
7. Ando, Y., Hiruta, Y., Citterio, D., and Suzuki, K., *Analyst.,* 2009, vol. 134, p. 2314.
8. Kim, H.J., Kim, S.H., Kim, J.H., Lee, E.-H., Kim, K.-W., and Kim, J.S., *Bull. Korean Chem. Soc.,* 2008, vol. 29, p. 1831.
9. Boens, N., Leen, V., and Dehaen, W., *Chem. Soc. Rev.,* 2012, vol. 41, p. 1130.
10. Fan, J., Guo, K., Peng, X., Du, J., Wang, J., Sun, S., and Li, H., *Sensors and Actuators, B,* 2009, vol. 142, p. 191.
11. Ziessel, R., Ulrich, G., and Harriman, A., *New J. Chem.,* 2007, vol. 31, p. 496.
12. Tikhomirova, K.V., Anisimov, A.V., and Khoroshutin, A.V., *Eur. J. Org. Chem.,* 2012, p. 2201.
13. Finikova, O.S., Cheprakov, A.V., Carroll, P.J., and Vinogradov, S.A., *J. Org. Chem.,* 2003, vol. 68, p. 7517.
14. Lebedev, A.Y., Filatov, M.A., Cheprakov, A.V., and Vinogradov, S.A., *J. Phys. Chem. A.,* 2008, vol. 112, p. 7723.
15. Peters, C., Billich, A., Ghobrial, M., Hogenauer, K., Ullrich, T., and Nussbaumer, P., *J. Org. Chem.,* 2007, vol. 72, p. 1842.
16. Vos, de, Wael, E., Pardoen, J.A., van Koeveringe, J.A., and Lutgenburg, J., *J. Recl. Trav. Chim. Pays-Bas.,* 1977, vol. 96, p. 306.
17. Uppal, T., Hu, X., Fronczek, F.R., Maschek, S., Bobadova-

Parvanova, P., and Vicente1, P.M.G.H., *Chem. Eur. J.,* 2012, vol. 18, p. 3893.
18. Xu, H.-Y., Shen, Z., Okujima, T., and Ono, N., *Chin. J. Inorg. Chem.,* 2006, vol. 22, p. 801.
19. Xu, H., Ma, H., Xu, M., and Zhao, W., *Jiangxi Shifan Daxue Xuebao Ziran Kexueban,* 2007, vol. 31, p. 560.
20. Xu, H., Fang, Y., Xu, M., and Ma, H., *Henan Huagong.,* 2008, vol. 25, p. 16.
21. Sunahara, H., Urano, Y., Kojima, H., and Nagano, T., *J. Am. Chem. Soc.,* 2007, vol. 129, p. 5597.
22. Shen, Z., Rohr, H., Rurack, K., Uno, H., Spieles, M., Schulz, B., Reck, G., and Ono, N., *Chem. Eur. J.,* 2004, vol. 10, p. 4853.
23. Izatt, R.M., Pawlak, K., Bradshaw, J.S., and Bruening, R.L., *Chem. Rev.,* 1995, vol. 95, p. 2529.
24. Coskun, A., Yilmaz, M.D., and Akkaya, E.U., *Org. Lett.,* 2007, vol. 9, p. 607.
25. Ekmekci, Z., Yilmaz, M.D., and Akkaya, E.U., *Org. Lett.,* 2008, vol. 10, p. 461.
26. Komatsu, T., Urano, Y., Fujikawa, Y., Kobayashi, T., Kojima, H., Terai, T., Hanaoka, K., and Nagano, T., *Chem. Commun.,* 2009, p. 7015.
27. Bae, B.-J., Park, J.T., and Suh, I.-H., *J. Organometal. Chem.,* 2002, vol. 648, p. 214.
28. Hill, M.R., Russel, J.J., Roberts, N.K., and Lamb, R.N., *Polyhedron,* 2007, vol. 26, p. 493.
29. Neumayer, D.A., Studebaker, D.B., Hinds, B.J., Stern, C.L., and Marks, T.J., *Chem. Mater.,* 1994, vol. 6, p. 878.
30. Panchenko, P.A., Fedorov, Y.V., Perevalov, V.P., Jonusauskas, G., and Fedorova, O.A., *J. Phys. Chem. A,* 2010, vol. 114, p. 4118.
31. Tulyakova, E., Delbarie, S., Fedorov, Y.V., Jonusauskas, G., Moiseeva, A., and Fedorova, O.A., *Chem. Eur. J.,* 2011, vol. 17, p. 10752.
32. Lakshmi, V. and Ravikanth, M., *J. Org. Chem.,* 2011, vol. 76, p. 8466.
33. Rao, M.R., Bolligarla, R., Butcher, R.J., and Ravikanth, M., *Inorg. Chem.,* 2010, vol. 49, p. 10606.
34. Madhu, S., Rao, M.R., Shaikh, M.S., and Ravikanth, M., *Inorg. Chem.,* 2011, vol. 50, p. 4392.
35. Benniston, A.C., Harriman, A., Whittle, V.L., and Zelzer, M., *Eur. J. Org. Chem.,* 2010, p. 523.
36. Jacobsen, J.A., Stork, J.R., Magde, D., and Cohen, S.M., *Dalton Trans.,* 2010, vol. 39, p. 957.
37. Sakamoto, N., Ikeda, C., and Nabeshima, T., *Chem. Commun.,* 2010, vol. 46, p. 6732.
38. Sakamoto, N., Ikeda, C., Yamamura, M., and Nabeshima, T., *Chem. Commun.,* 2012, vol. 48, p. 4818.
39. Fischer, M. and Georges, J., *Chem. Phys. Lett.,* 1996, vol. 260, p. 115.
40. Lakovich, D., *Osnovy fluorestsentnoi spektroskopii* (Principles of Fluorescence Spectroscopy). Moscow: Mir, 1986.
41. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, Jr. J.A., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., Pople, J.A., *Gaussian 03,* Revision E.01, Gaussian, Inc., Wallingford, CT, 2004.