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Thermal Oxidative Degradation of the Functionally Substituted 2,2'-Dipyrrolylmethenes Hydrobromides and Difluoroborates

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Abstract—Thermal oxidative decomposition of samples of crystalline hydrobromide and borofluoride complexes (BODIPY) of a series of 2,2'-dipyrrolylmethenes (HL) was studied by means of thermogravimetry in an atmosphere of air oxygen. An increase in the degree and symmetry of substitution, aromaticity, and the length of the substituents in 4,4'-positions of the pyrrole ligand rings increases stability of the BODIPY-dyes to oxidative degradation. A comparative analysis of the influence of structural factors on the thermolability of hydrobromdes (HL·HBr), *d*-metal (ML_2) and boron(III) complexes with 2,2'-dipyrrolylmethenes was carried out.

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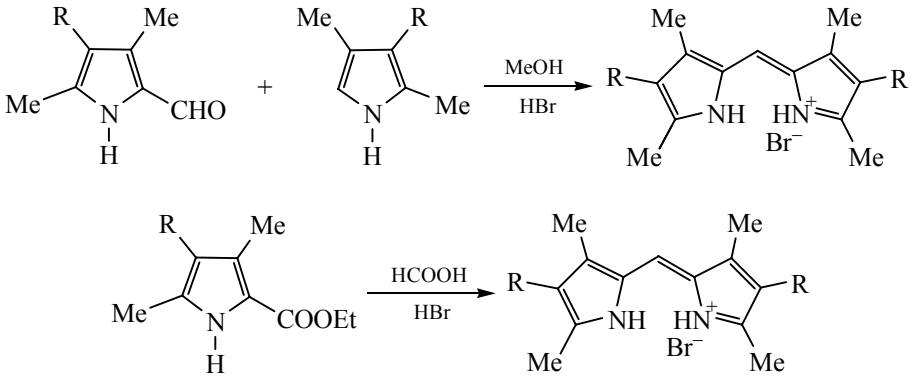
An urgent problems of modern chemistry is the creation and improvement of fluorescent dyes suitable for application in various fields, like medicine, biology, biotechnology and analytical chemistry, laser and other optical instrumentation. To date, a lot of organic dyes have already been created and applied, including fluorescein [1], rhodamine [2], etc., but in recent decades a new class of fluorophores became an object of the scientists attention, the BF_2 complexes of dipyrrolylmethenes (BODIPY) [3, 4]. These compounds are promising for use as fluorescent probes and labels [5], photosensitizers [6, 7], antioxidants [8], limiters of hard laser radiation [9, 10], active components of new nanomaterials [11] etc. The practical application of BODIPY can often occur at elevated temperature and vacuum sublimation. An important indicator of the effectiveness of using such compounds in polythermal conditions is their thermal stability to decomposition, including that in the presence of oxidants like atmospheric oxygen. While quite a large database is accumulated on the thermal stability of *d*-metal dipyrrolylmethenates and their analogs in both oxidizing and inert (argon, nitrogen) atmosphere [12, 13], there is no data in the literature on the thermal analysis of the BODIPY. It is obvious that the main influence on the BODIPY thermolability should have the variations in the structure of the dipyrrolylmethene ligands, the most common of which are the properties of the substituents at the pyrrole rings and the *meso*-spacer [12, 14, 15].

As the objects of investigation of the BODIPY thermal destruction processes, we selected 2,2'-dipyrrolylmethenes (HL) with varied degree and nature of substitution at the pyrrole rings. For a comparative evaluation of the effect of thermal stabilization of the ligand in the BODIPY composition, we obtained the data on thermal oxidative degradation of the ligands as hydrobromide salts.

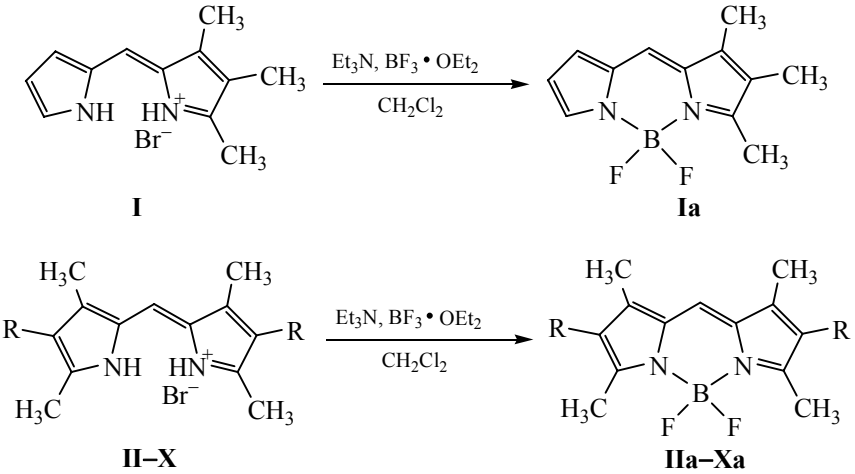
The dipyrrolylmethene hydrobromides were prepared according to the schemes bellow.

The first procedure consist in the condensation of the corresponding trialkylpyrrole with formylpyrrole in methanol in the presence of HBr as a catalyst. Another one-step method for the synthesis of symmetrical hexaalkyldipyrrolylmethenes is the self-condensation of 4-alkyl-3,5-dimethylpyrrolecarboxylic acids in a mixture of formic and hydrobromic acids. In this case, the methylene carbon source is formic acid, and the



yield of hydrobromide dipyrrolylmethenes, apparently, is determined by their solubility in the reaction mixture.

Difluoroborate complexes **Ia–Xa** were prepared from the respective ligands hydrobromides at room temperature according to the scheme:



I **Ia**

II–X **IIa–Xa**

R = H (**II, IIa**), CH_3 (**III, IIIa**), C_2H_5 (**IV, IVa**), C_3H_7 (**V, Va**), C_4H_9 (**VI, VIa**), C_5H_{11} (**VII, VIIa**), C_6H_{13} (**VIII, VIIIa**), C_7H_{15} (**IX, IXa**), $CH_2C_6H_5$ (**X, Xa**).

Examples of syntheses are described in the experimental section.

The main difference in the molecular structure of the investigated salts, hydrobromides of dipyrrolylmethenes (HL·HBr, compounds **I–X**) and BF_2-complexes (BODIPY, compounds **Ia–Xa**) consist in the degree of substitution at the pyrrole rings of the ligands: from three (compounds **I, Ia**) or four (**II, IIa**) methyl groups to a fully substituted pyrrole rings in compounds **III–X** and **IIIa–Xa,** length (from two to seven carbon atoms) of alkyl substituents R (**IV–IX, IVa–IXa**) and benzyl substituents (compound **X** and **Xa**) in the 4,4'-positions of the pyrrole rings.

Dipyrrolylmethene hydrobromides I–X. Table 1 lists the results of thermogravimetric analysis of the samples of crystalline dipyrrolylmethene hydrobromides **I–X,** Fig. 1 shows a typical thermogram. Destruction of salts **I–X** proceeds in two separate stages, as was observed previously for other dipyrrolylmethene oligopyrrole hydrobromides [14, 15]. The first stage comprises the process of thermal dissociation of salt through the removal of gaseous HBr from the crystalline sample:

$$\text{HL·HBr(solid)} \xrightarrow{t} \text{HL(solid)} + \text{HBr(gas)}.$$

The process is accompanied by endoeffect on the DTA curve; therewith the sample mass loss (from the curve TG) at this stage is consistent with the theoretical amount of HBr in the initial weighed portion of the salt (Table 1). The most unstable dipyrrolylmethene hydrobromide is that containing the fully

Table 1. The results of thermogravimetric analysis of 2,2'-dipyrrolylmethene hydrobromides (HL·HBr) in atmospheric oxygen[a]

Compound	Thermal dissociation of HL·HBr			Thermal oxidative degradation of HL		
	t_{onset1}	Δ^{theor}	Δ^{exp}	t_{onset2}	$t_{max.\ exo}$	t_{end}
I	127	30.3	30.8	301	382	421
II	200	28.8	29.0	299	370	425
III	255	26.2	25.7	300	389	470
IV	210	23.9	24.0	318	422	496
V	200	22.2	21.6	306	410	465
VI	194	20.6	20.5	300	408	457
VII	193	19.2	20.0	298	395	464
VIII	192	18.0	18.5	295	395	460
IX	189	16.9	17.0	285	405	470
X	226	17.5	17.8	346	391	455

[a] t_{onset1} is the temperature of the beginning of the thermal dissociation of HL·HBr, °C; t_{onset2} is the temperature of the beginning of termal oxidative degradation of HL; $t_{max.\ exo}$ is the temperature of the maximum exo effect, °C; t_{end} is the temperature of the end of thermal decomposition, °C; Δ^{theor} and Δ^{exp} are theoretical and experimental weight loss at the salt decomposition, %.

unsubstituted pyrrole rings: its temperature of the onset of salt dissociation (t_{onset1}) is as low as 127ºC (Table 1). The hydrobromides with symmetric incompletely (**II**) and completely (**III–X**) substituted two pyrrole rings are much stabler. The maximum t_{onset1} value is observed in the salt of hexamethylated ligand (**III**, 252ºC), the next is the salt of the ligand with the benzyl substituent (**X**, 226ºC). With increasing length of 4,4'-dialkyl substituents in the series of compounds from **III** to **IX**, the t_{onset1} value decreases monotonically from 255ºC to 189ºC. Thus, there is a tendency of increased resistance to thermal decomposition of the investigated salts HL·HBr with an increase in total +*I*-effect of substituents, which is consistent with results for the previously studied dipyrrolylmethene hydrobromide analogs [14–16], and it is explained by the increased binding of the HBr proton to the pyrrole nitrogen atom.

After removal of gaseous HBr from the solid sample in the temperature range 285–346ºC (Table 1) the second stage begins: the thermal-oxidative degradation of the organic ligand HL. In the thermograms this process is manifested as several stages of mass loss with expressed exothermic peaks on the DTA curve (Fig. 1). The temperature of beginning the thermal oxidative degradation of the ligands (t_{onset2}) weakly depends on the degree of substitution and the length of the substituents. For compounds **I–IX** the t_{onset2} values fall within the range of 285–318ºC, and only for the ligand X with benzyl group the t_{onset2} increases to 346ºC.

The BF_2 complexes of dipyrrolylmethenes Ia–Xa. By the example of compounds **Ia–Xa** we obtained the first data (Table 2, Fig. 2) on the stability of the dipyrrolylmethene BF_2-complex in polythermal conditions in an oxidizing atmosphere of air oxygen. The thermogravimetric analysis showed that the initial stage at heating the crystalline samples of compounds

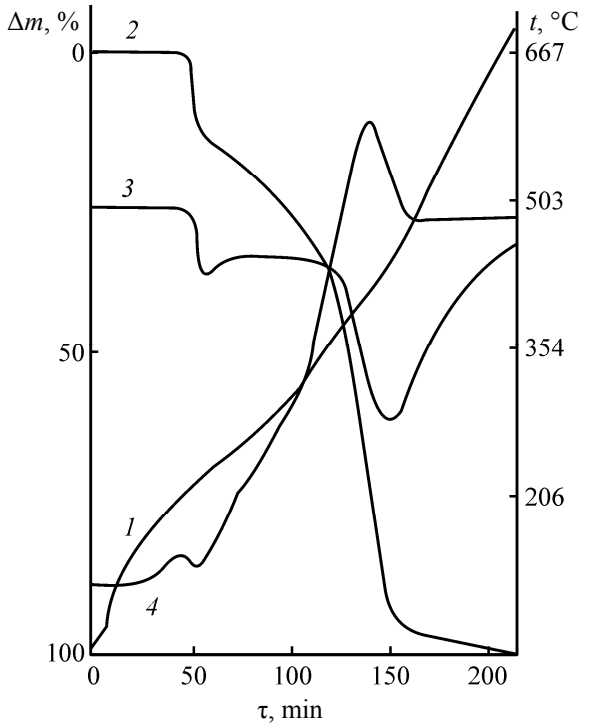


Fig. 1. Derivatogram of compound **X**. (*1*) *T*, (*2*) TG, (*3*) DTG, and (*4*) DTA.

Table 2. The results of thermogravimetric analysis of 2, 2'-dipyrrolylmethenes difluoroborates (BODIPY) in an environment of atmospheric oxygen[a]

Compound	t_{conf}	t_{onset1}	t_{onset3}	t_{onset3}	t_{end}	Residual weight	
						Δ^{theor}	Δ^{exp}
Ia	155	185	287	407	595	29.7	29.2
IIa	152	188	298	442	607	28.1	27.5
IIIa	143	199	255	–	531	25.2	24.8
IVa	141	203	290	476	637	22.9	22.0
Va	139	206	294	441	548	20.9	20.5
VIa	138	212	309	442	539	19.3	18.5
VIIa	130	235	342	447	551	17.9	17.1
VIIIa	129	236	334	473	550	16.7	16.2
IXa	127	245	335	438	559	15.7	15.0
Xa	190	254	459	–	596	16.3	15.8

[a] t_{conf} is the maximum temperature of the conformational transition, °C; t_{onset1}, t_{onset2}, and t_{onset3} are the temperatures of onset of the first and subsequent stages of termal oxidative degradation of BODIPY, °C; t_{end} is the temperature of the end of thermal decomposition, °C; $\Delta^{theor.}$ and Δ^{exp} are theoretical (calculated on B_2O_3) and experimental weight of the solid residue.

Ia–Xa is associated with conformational transition, which results in a small endo effect on the DTA curve while the weight of the sample remains unchanged (Fig. 2). For BODIPY **Ia–IXa** an increase in the number and length of the substituents leads to a decrease in the maximum of conformational transition temperature (t_{conf}) from 155 to 127ºC. The conformational rearrangements in benzyl-substituted BODIPY **Xa** occur at much higher temperature (t_{conf} = 190ºC). Note that the conformational transitions in the range 130–190ºC with intense endo- or *exo*-effects are typical also for the crystalline samples of d-metal dipyrrolylmethenates [12].

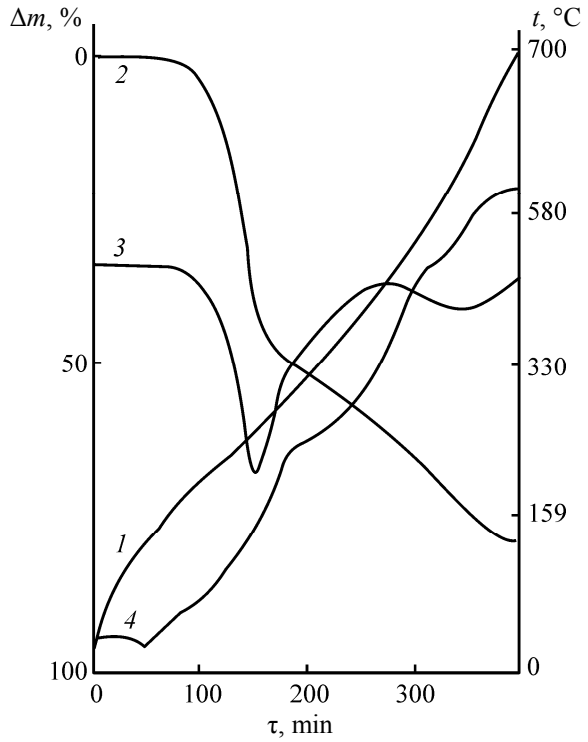


Fig. 2. Derivatogram of compound **Xa**. (*1*) *T*, (*2*) TG, (*3*) DTG, and (*4*) DTA.

The processes of thermal oxidative degradation of crystalline samples of compounds **Ia–Xa** begin in the temperature range of 185–254ºC. Changes in TG, DTG, and DTA curves in the thermograms of all the samples are similar in nature. The process involves three stages of weight loss (TG and DTG curves), which are accompanied by low intensity extended *exo*-effects on the DTA curve.

Comparison of the experimentally observed and calculated values of the weight of a solid residue produced at the decomposition of complexes **Ia–Xa**, as well as the results of its elemental analysis suggest that the main solid product of BODIPY decomposition is B_2O_3. Then the total equation of thermal oxidative degradation process of the dipyrrolylmethene borofluoride complexes can be written as:

$$[BF_2L](solid) + O_2(gas) \xrightarrow{t} B_2O_3(solid) + HF(gas) + CO_2(gas) + H_2O(gas) + N_2(gas).$$

The results of thermogravimetric analysis of the crystalline samples **Ia–Xa** indicate that the thermal stability of the BODIPY with alkylated pyrrole nuclei

significantly increases with the number and length of the substituents in the ligand. The lowest thermal resistance shows compound **Ia** with one unsubstituted pyrrole fragment, its temperature of degradation onset (t_{onset1}) is 185ºC. The introduction of the fourth methyl group into the dipyrrolylmethene ligand slightly (by about 3ºC) increases the stability of compound **IIa** compared to **Ia**, while the complete methylation of the two pyrrole rings increases the t_{onset1} value of compound **IIIa** compared with **Ia** by 14ºC. In the series of compounds **IIIa–IXa** the length of the alkyl substituents in the 4,4'-position varies from one to seven carbon atoms, which causes an increase in t_{onset1} of compound **IXa** by ~46ºC as compared with **Ia**. An even greater (by ~55ºC) growth of the effect of thermal stability is observed in the compound **Xa** with benzyl radicals in the 4,4'-positions.

Comparison of the data in Tables 1 and 2 shows that for BF_2-complex **Ia** with unsubstituted pyrrole ring occurs maximum (by ~58ºC) increase in thermal stability in comparison with the salt **I** of the same ligand. Temperature of the decomposition onset of the complexes **IIa**, **IIIa,** and **IVa** is slightly lower than for the corresponding salts **II, III,** and **IV**. Complexes **Va–Xa** with longer substituents and with benzyl substituents in 4,4'-positions are markedly more stable than the corresponding salt **V–X**. Moreover, with increasing alkyl chain length of 4,4'-substituents in a series of complexes **Va–IXa** the effect of thermal stabilization increases from 6 to 56ºC compared with the corresponding HL·HBr, while for **Xa** with the benzyl radical it grows by ~28ºC only.

It should be noted that the stability of coordination compounds of *d*-metals with 2,2'-dipyrrolylmethenes, in some cases is higher than that of the BODIPY formed by the same ligands [12].

Thus, our results suggest that the increase in the degree and symmetry of the substitution, in the length of the alkyl substituents, as well as the introduction of the benzyl substituent in the 4,4'-positions of the pyrrole rings of the homologs of BODIPY dyes based on 2,2'-dipyrrolylmethene markedly increases the stability of the compounds against the oxidative degradation compared to the not fully substituted analogs.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker NMR 500 instrument (Germany), solvent deuterated chloroform, internal reference TMS.

Thermogravimetric studies were performed on a 1000D derivatograph (MOM, Hungary) in a static air atmosphere in a non-isothermal mode in the temperature range of 15–600°C. For compounds **I–X** the heating rate was 2.5 deg min^{-1}, a sample weight ~18–25 mg; for compounds **Ia–Xa** the heating rate was 1.25°C min^{-1}, sample weight 15–20 mg.

The signals recorded by the instrument (*T* is temperature curve, TG is the curve of sample weight change under the influence of temperature variation in time, DTG is differential curve of the rate of weight change, DTA is the curve of differential thermal analysis of the sample) were processed using the PowerGraph software. The error in measuring temperature did not exceed ±1°C.

Compounds **I**, **III**, and **IV** were synthesized, isolated, and identified according to [16]. Other ligands were prepared as follows.

3,3',5,5'-Tetramethyl-2,2'-dipyrrolylmethene hydrobromide (II). To a solution of 1.2 g (12.6 mmol) of 2,4-dimethylpyrrole and 1.55 g (12.6 mmol) of 2-formyl-3,4-dimethylpyrrole in 20 ml of methanol while stirring at room temperature was added 2 ml of HBr (conc.). The mixture was stirred for 2 h, the precipitate was filtered off, washed with methanol, ether, and dried at room temperature in air. Yield 2.4 g (67.7%). ^{1}H NMR spectrum, δ, ppm: 13.12 br.s (2H, NH); 7.09 s (1H, *meso*-H); 6.19 s (2H, 4,4'-H); 2.71 s (6H , CH_3); 2.37 s (6H, CH_3). Found, %: C 55.25, H 6.05, N 9.89. $C_{13}H_{17}BrN_2$. Calculated, %: C 55.70, H 6.12, N 10.00.

3,3',5,5'-Tetramethyl-4,4'-dipropyl-2,2'-dipyrrolylmethene hydrobromide (V). A mixture of 5.0 g (19.5 mmol) of 2-ethoxycarbonyl-4-propyl-3,5-dimethylpyrrole, 10 ml of HBr (conc.), and 20 ml of 90% formic acid was stirred for 4 h at heating on a boiling water bath. After cooling the mixture, the precipitate was filtered off, washed with methanol and ether, and dried at room temperature in air. Yield 1.3 g (84.8%). ^{1}H NMR spectrum, δ, ppm: 12.94 s (2H, NH); 7.06 s (1H, *meso*-H); 2.67 s (6H, 5,5'-CH_3); 2.40 t (4H, J = 7.4 Hz, 4,4'-CH_2-Pr); 2.27 s (6H, 3,3'-CH_3); 1.50 q (4H, J = 7.4 Hz, CH_2-Pr); 0.94 t (6H, J = 7.4 Hz, CH_3-Pr). Found, %: C 62.11, H 7.91, N 7.49. $C_{19}H_{29}BrN_2$. Calculated, %: C 62.61, H 8.03, N 7.69. Other dipyrrolylmethene hydrobromides were synthesized similarly.

3,3',5,5'-Tetramethyl-4,4'-dibutyl-2,2'-dipyrrolylmethene hydrobromide (VI) was obtained from 2-ethoxycarbonyl-4-butyl-3,5-dimethylpyrrole. Yield

75.2%. ^{1}H NMR spectrum, δ, ppm: 12.92 s (2H, NH); 7.04 s (1H, *meso*-H); 2.67 s (6H, 5,5'-CH_3); 2.41 t (4H, *J* = 7.5 Hz, 4,4'-CH_2-Bu); 2.27 s (6H, *J* = 7.5 Hz, 3,3'-CH_3); 1.43 q (4H, *J* = 7.5 Hz, CH_2-Bu); 1.35 q (4H, *J* = 7.5 Hz, CH_2-Bu); 0.94 t (6H, *J* = 7.5 Hz, CH_3-Bu). Found, %: C 64.55, H 8.12, N 7.01. $C_{21}H_{33}BrN_2$. Calculated, %: C 64.26, H 8.48, N 7.14.

3,3',5,5'-Tetramethyl-4,4'-dipentyl-2,2'-dipyrrolylmethene hydrobromide (VII) was obtained from 2-ethoxycarbonyl-4-pentyl-l-3,5-dimethylpyrrole. Yield 60.7%. ^{1}H NMR spectrum, δ, ppm: 12.91 s (2H, NH); 7,04 s (1H, *meso*-H); 2.67 s (6H, 5,5'-CH_3); 2.40 t (4H, *J* = 7.5 Hz, Hz, 4,4'-CH_2-pentyl); 2.27 s (6H, 3,3'-CH_3); 1.44 q (4H, *J* = 7.5 Hz, CH_2-pentyl); 1.34 q (4H, *J* = 7.5 Hz, CH_2-pentyl); 1.29 m (4H, CH_2-pentyl); 0.91 t (6H, *J* = 7.5 Hz, CH_3-pentyl). Found, %: C 65.21, H 8.39, N 6.32. $C_{23}H_{37}BrN_2$. Calculated, %: C 65.68, H 8.87, N 6.66.

3,3',5,5'-Tetramethyl-4,4'-dihexyl-2,2'-dipyrrolylmethene hydrobromide (VIII) was obtained from 2-ethoxycarbonyl-4-hexyl-3,5-dimethylpyrrole. Yield 79.5%. ^{1}H NMR spectrum, δ, ppm: 12.92 s (2H, NH); 7.04 s (1H, *meso*-H); 2.67 s (6H, 5,5'-CH_3); 2.40 t (4H , *J* = 7.5 Hz, 4,4'-CH_2-pentyl); 2.27 s (6H, 3,3'-CH_3); 1.44 q (4H, *J* = 7.5 Hz, CH_2-pentyl); 1.34 q (12H, *J* = 7.5 Hz, CH_2-pentyl); 1.29 m (4H, CH_2-pentyl), 0.90 t (6H, *J* = 7.5 Hz, CH_3-pentyl). Found, %: C 66.11, H 8.99, N 6.03. $C_{25}H_{41}BrN_2$. Calculated, %: C 66.93, H 9.22, N 6.25.

3,3',5,5'-Tetramethyl-4,4'-diheptyl-2,2'-dipyrrolylmethene hydrobromide (IX) was obtained from 2-ethoxycarbonyl-4-heptyl-3,5-dimethylpyrrole. Yield 69.1%. ^{1}H NMR spectrum, δ, ppm: 12.91 s (2H, NH); 7.03 s (1H, *meso*-H); 2.67 s (6H, 5,5'-CH_3); 2,40 t (4H, *J* = 7.4 Hz, 4,4'-CH_2-heptyl); 2.27 s (6H, 3,3'-CH_3); 1.43 m (4H, CH_2-heptyl); 1.30 m (16H, CH_2-heptyl); 0.90 t (6H, *J* = 7.4 Hz, CH_3-heptyl). Found, %: C 67.91, H 9.06, N 5.62. $C_{27}H_{45}BrN_2$. Calculated, %: C 68.03, H 9.52, N 5.88.

3,3',5,5'-Tetramethyl-4,4'-dibenzyl-2,2'-dipyrrolylmethene hydrobromide (X) was obtained from 2-ethoxycarbonyl-4-benzyl-3,5-dimethylpyrrole. Yield 84.8%. ^{1}H NMR spectrum, δ, ppm: 12.91 s (2H, NH); 7.28 t (4H, *J* = 7.2 Hz, 3",5"-H-Ph); 7.22 t (2H, *J* = 7.2 Hz, 4"-H-Ph) ; 7.13 s (1H, *meso*-H); 7.09 d (4H, *J* = 7.2 Hz, 2",6"-H-Ph); 3.83 s (4H, CH_2-Bz); 2.64 s (6H, 5,5'-CH_3); 2.27 s (6H, 3,3'-CH_3). Found, %: C 70.11, H 6.18, N 5.23. $C_{27}H_{29}BrN_2$. Calculated, %: C 70.41, H 6.35, N 6.09.

Substituted pyrroles required for the synthesis of dipyrrolylmethene hydrobromides were prepared according to methods described in [17].

3,4,5-Trimethyl-2,2'-dipyrrolylmethene difluoroborate (Ia). To a solution of 0.25 g (0.94 mmol) of 3,4,5-trimethyl-2,2'-dipyrrolylmethene hydrobromide in 40 ml of methylene chloride at room temperature at stirring was added 1.32 ml (9.4 mmol) of triethylamine then immediately was also added 1.19 ml (9.4 mmol) of boron trifluoride etherate. The mixture was stirred for 3 h, then washed 3 times with water, the organic layer was separated and evaporated to dryness on a rotary evaporator at a reduced pressure. The solid residue was dissolved in methylene chloride and chromatographed on silica gel. The eluate was evaporated, the complex was precipitated with methanol, filtered, and dried in air at room temperature. Yield 0.23 g (92.9%). ^{1}H NMR spectrum, δ, ppm: 7.60 s, 7.14 s, 6.87 d (3H, *J* = 2.4 Hz, CH-pyrole); 6.41 s (1H, *meso*-H); 2.57 s, 2.19 s, 1.98s (9H, CH_3). Found, %: C 61.28, H 5.45, N 11.57. $C_{12}H_{13}BF_2N_2$. Calculated, %: C 61.58, H 5.60, N 11.97.

Dipyrrolylmethene difluoroborates **IIa–Xa** were synthesized similarly.

3,3',5,5'-Tetramethyl-2,2'-dipyrrolylmethene difluoroborate (IIa). Yield 65.9%. ^{1}H NMR spectrum, δ, ppm: 7.07 s (1H, *meso*-H); 6.07 s (2H, 4,4'-H); 2.55 s (6H, CH_3); 2.27 s (6H, CH_3). Found, %: C 62.83, H 6.0, N 11.18. $C_{13}H_{15}BF_2N_2$. Calculated, %: C 62.94, H 6.09, N 11.29.

3,3',4,4',5,5'-Hexamethyl-2,2'-dipyrrolylmethene difluoroborate (IIIa). Yield 96%. ^{1}H NMR spectrum, δ, ppm: 6.96 s (1H, *meso*-CH); 2.49 s (6H, 5,5'-CH_3); 2.16 s (6H, 3,3'-CH_3); 1.94 s (6H, 4,4'-CH_3). Found, %: C 65.18, H 6.85, N 10.04. $C_{15}H_{19}BF_2N_2$. Calculated, %: C 65.25, H 6.94, N 10.14.

3,3',5,5'-Tetramethyl-4,4'-diethyl-2,2'-dipyrrolylmethenea-2,2'-difluoroborate (IVa). Yield 91.1%. ^{1}H NMR spectrum, δ, ppm: 6.97 s (1H, *meso*-CH); 2.52 s (6H, 5,5'-CH_3); 2.40 q (4H, *J* = 7.6 Hz, 4,4'-CH_2-Et); 2.19 s (6H, 3,3'-CH_3); 1.09 t (6H, *J* = 7.6 Hz, CH_3-Et). Found, %: C 67.03, H 7.51, N 9.16. $C_{17}H_{23}BF_2N_2$. Calculated, %: C 67.12, H 7.62, N 9.21.

3,3',5,5'-Tetramethyl-4,4'-dipropyl-2,2'-dipyrrolylmethene difluoroborate (Va). Yield 72.2%. ^{1}H NMR spectrum, δ, ppm: 6.97 s (1H, *meso*-H); 2.51 s (6H, 5,5'-CH_3); 2.35 t (4H, *J* = 7.4 Hz, 4,4'-CH_2-Pr); 2.17 s (6H, 3,3'-CH_3); 1.49 q (4H, *J* = 7.4 Hz, CH_2-Pr); 0.95 t

(6H, J = 7.4 Hz, CH_3-Pr). Found, %: C 68.29, H 8.03, N 8.13. $C_{19}H_{27}BF_2N_2$. Calculated, %: C 68.69, H 8.19, N 8.43.

3,3',5,5'-Tetramethyl-4,4'-dibutyl-2,2'-dipyrrolylmethene difluoroborate (VIa). Yield 56.8%. ^{1}H NMR spectrum, δ, ppm: 6.96 s (1H, *meso*-H); 2.51 s (6H, 5,5'-CH_3); 2.37 t (4H, J = 7.3 Hz, 4,4'-CH_2-Bu); 2.18 s (6H, 3,3'-CH_3); 1.43 q (4H, J = 7.3 Hz, CH_2-Bu); 1.37 q (4H, J = 7.3 Hz, CH_2-Bu); 0.95 t (6H, CH_3-Bu). Found, %: C 69.93, H 8.56, N 7.69. $C_{21}H_{31}BF_2N_2$. Calculated, %: C 70.01, H 8.67, N 7.78.

3,3',5,5'-Tetramethyl-4,4'-dipentyl-2,2'-dipyrrolylmethene difluoroborate (VIIa). Yield 86.7%. ^{1}H NMR spectrum, δ, ppm: 6.96 s (1H, *meso*-H); 2.50 s (6H, 5,5'-CH_3); 2.36 t (4H, J = 7.3 Hz, 4,4'-CH_2-pentyl); 2.18 s (6H, 3,3'-CH_3); 1.45 q (4H, J = 7.3 Hz, CH_2-pentyl); 1.33 q (8H, J = 7.3 Hz, CH_2-pentyl); 0.92 t (6H, CH_3-pentyl). Found, %: C 71.01, H 8.95, N 7.14. $C_{23}H_{35}BF_2N_2$. Calculated, %: C 71.13, H 9.08, N 7.21.

3,3',5,5'-Tetramethyl-4,4'-dihexyl-2,2'-dipyrrolylmethene difluoroborate (VIIIa). Yield 58.5%. ^{1}H NMR spectrum, δ, ppm: 6.96 s (1H, *meso*-H); 2.50 s (6H, 5,5'-CH_3); 2.36 t (4H, J = 7.3 Hz, 4,4'-CH_2-hexyl); 2.17 s (6H, 3,3'-CH_3); 1.44 q (4H, J = 7.3 Hz, CH_2-hexyl); 1.32 m (12H, CH_2-hexyl); 0.91 t (6H, CH_3-hexyl). Found, %: C 72.01, H 9.32, N 6.59. $C_{25}H_{39}BF_2N_2$. Calculated, %: C 72.11, H 9.44, N 6.73.

3,3',5,5'-Tetramethyl-4,4'-diheptyl-2,2'-dipyrrolylmethene difluoroborate (IXa). Yield 97.2%. ^{1}H NMR spectrum, δ, ppm: 6.96 s (1H, *meso*-H); 2.50 s (6H, 5,5'-CH_3); 2.36 t (4H, J = 7.5 Hz, 4,4'-CH_2-heptyl); 2.17 s (6H, 3,3'-CH_3); 1.44 q (4H, J = 7.5 Hz, CH_2-heptyl); 1.32 m (16H, CH_2-heptyl); 0.91 t (6H, J = 7.5 Hz, CH_3-heptyl). Found, %: C 72.85, H 9.63, N 6.21. $C_{27}H_{43}BF_2N_2$. Calculated, %: C 72.96, H 9.75, N 6.30.

3,3',5,5'-Tetramethyl-4,4'-dibenzyl-2,2'-dipyrrolylmethene difluoroborate (Xa). Yield 81.2%. ^{1}H NMR spectrum, δ, ppm: 7.29 t (4H, J = 7.3 Hz, 3",5"-H-Ph); 7.21 t (2H, J = 7.3 Hz, 4"-H-Ph); 7.15 d (4H, J = 7.3 Hz, 2",6"-H-Ph); 7.07 s (1H, *meso*-H); 3.80 s (4H, CH_2-Bz); 2.47 s (6H, 5,5'-CH_3); 2.18 s (6H , 3,3'-CH_3). Found, %: C 75.67, H 6.29, N 6.42. $C_{27}H_{27}BF_2N_2$. Calculated, %: C 75.71, H 6.35, N 6.54.

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