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SYNTHESIS, SPECTRAL-LUMINESCENT PROPERTIES, AND PHOTOSTABILITY OF Zn(II) COMPLEXES WITH DIPYRRINS MODIFIED BY THE PERIPHERY AND *meso*-SPACER

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A comparative spectral-luminescent characterization was performed for the homoleptic zinc(II) chelates with dipyrrins containing four methyl or aryl substituents in the pyrrole rings and methine group or nitrogen atom as meso-spacer. It was shown that zinc dipyrrinates with substituted pyrrole rings and a methene spacer exhibited an intense fluorescence in nonpolar media. The phenyl-substituted complex had an order of magnitude stronger fluorescence than the methyl-substituted analog. Changing from a methene spacer to a nitrogen atom caused a substantial (up to 64 nm) red shift of the electronic absorption spectrum, and the chelate completely lost its fluorescent properties. The effects of the chelate ligand structure on the photostability of zinc(II) complexes were established.

Keywords: azadipyrrin, complex, dipyrrin, zinc, photostability, spectral-luminescent properties.

Dipyrrins (dipyrrolylmethenes) are the simplest representatives of chromophores with an open-chain oligopyrrole structure. The stable covalent complexes of these compounds with cations of *p*-, *d*-, and *f*-elements are effective visible-light chromophores ($\varepsilon > 10^5$ l·mol^{-1}·cm^{-1}, $\lambda_{max} \geq 450$ nm) [1-5]. The intensity of *d*-element dipyrrinates fluorescence is often comparable to that of boron dipyrrinates (BODIPY), which are the most promising luminophores among those with such ligands. In comparison to BODIPY, the dipyrrin complexes of *d*-elements offer the advantages of easy self-assembly with the complex-forming metal ions under mild conditions both in solutions and in biological systems, and a high sensitivity of the spectral-luminescent properties even to the slightest changes of the chromophore structure and the medium (polarity, viscosity, pH, etc.), which enables the use of these compounds as fluorescent probes.

While the spectral-luminescent properties of BODIPY have been relatively well investigated [6, 7], the effects of dipyrrin metal complex structure on the chromophore characteristics and luminescent properties remain little known and without practical applications. A possible reason for this is the low fluorescence of most dipyrrinates that have been previously synthesized and tested, and which typically

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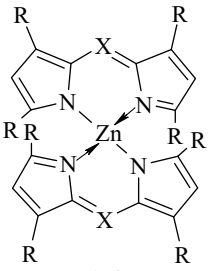
contained a phenyl group in the *meso*-spacer. The rotation of this phenyl group was found to quench fluorescence [8-10]. A subsequent modification of the ligand structure enabled the preparation of the first effective fluorophores among zinc(II) dipyrrinates.

An important current task in this field is the search for methods of influencing the spectral-luminescent properties and photostability of dipyrrinate through the modification of peripheral substituents and the *meso*-spacer structure. Our work was focused on establishing the spectral-luminescent and photostability effects caused by periferal methyl and phenyl substituents, as well as resulting from changing the methene spacer of the dipyrrin ligand to an aza spacer. The investigated zinc(II) complexes [ZnL_2] had the following ligands: 2-[(3,5-dimethyl-2*H*-pyrrol-2-ylidene)methyl]-3,5-dimethyl-1*H*-pyrrole (**1**), 2-[(3,5-diphenyl-2*H*-pyrrol-2-yl-idene)-methyl]-3,5-diphenyl-1*H*-pyrrole (**2**) and *N*-(3,5-diphenyl-2*H*-pyrrol-2-ylidene)-3,5-diphenyl-1*H*-pyrrol-2-amine (**3**).



1–**3**

1 X = CH, R = Me; **2** X = CH, R = Ph; **3** X = N, R = Ph

The electronic absorption spectra (EAS) of the complexes **1**-**3** were quite different from each other, both in the number of bands caused by electronic transitions $S^o \rightarrow S^n$, as well as the absorption wavelengths (Fig. 1, Table 1). The complex **2** with a phenyl-substituted dipyrrin was obtained for the first time, while the electronic absorption spectra of the chelates **1** and **3** were previously described only in one solvent [11, 12], and no detailed testing of luminescent properties was performed. We should note that the value and direction of the auxochromic effect was determined by the wavelength change of the strongest absorption band of dipyrrin and its complex, and it was highly structure-dependent.

In the case of the zinc(II) complex with 3,3',5,5'-tetramethyl-2,2'-dipyrrolylmethene, similarly to most of the other alkyl-substituted dipyrrolylmethenes [13], the auxochromic effect was manifested in the spectrum of the complex as a bathochromic shift (~20 nm) of the intense absorption band compared to the ligand spectrum. The opposite direction of the auxochromic effect was observed for the complexes formed with the phenyl-substituted dipyrrin and azadipyrrin, which gave a clearly different EAS from those of the alkyl-substituted dipyrrinates. The solutions of all three complexes **1**, **2**, and **3** gave EAS exhibiting one high-intensity band with the maximum (λ_{max}^{abs}) in the range of 485-490, 525-532, and 586-595 nm, as well as a broad low-intensity band at 350-367, 391-414, and 470-500 nm, respectively. Unlike the complex **1**, the phenyl-substituted dipyrrinate **2** and the azadipyrrinate **3** had EAS (Fig. 1, Table 1) with an additional shoulder at the long wavelength side of the intense absorption band (at 572-575 and 650-652 nm, respectively) and distinct intense UV absorption bands at 286-293 and 301-306 nm, respectively.

The examination of spectral changes during the formation of the tetraphenyl-substituted azadipyrrin zinc(II) complex **3** in tetrahydrofuran showed that the characteristic ligand absorption band with the maximum at 596 nm ($\log \varepsilon = 4.66$) underwent a slight hypsochromic shift to 591 nm, while the intensity was doubled to $\log \varepsilon = 4.93$. At the same time, a shoulder appeared on its long wavelength side (λ_{max}^{abs} = 640 nm, $\log \varepsilon = 4.76$), caused by the corresponding transition $S^o \rightarrow S^n$ [12]. A similar spectral change was observed also

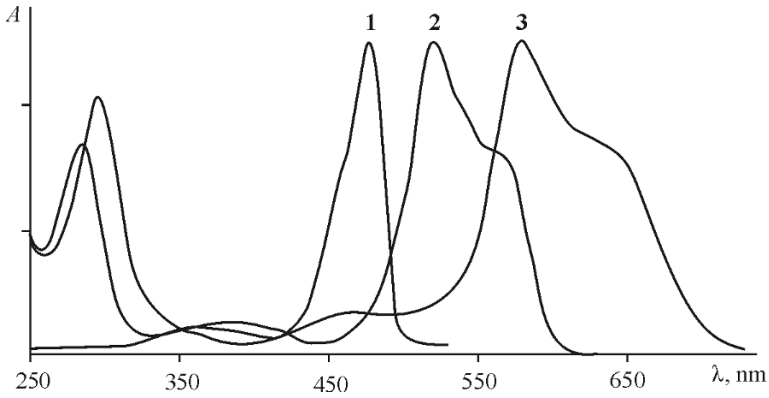


Fig. 1. The electronic absorption spectra of zinc(II) complexes **1**-**3** in cyclohexane, where *A* is absorbance in arbitrary units.

during the formation of the phenyl-substituted dipyrrin analog, the chelate **2**. It must be noted that a change from methyl groups (complex **1**) to phenyl groups (complex **2**) resulted in a considerable red shift in the EAS: depending on the organic solvent type, the maximum of the intense band was shifted by 39-45 nm, while the extinction coefficient was significanty decreased (1.5-2 times) (Fig. 1, Table 1). The dipyrrin having an aza group in the *meso*-spacer exhibited an even greater bathochromic shift of the chelate **3** absorption maximum (by 59-64 nm), compared to the EAS of the complex **2** with a similar peripheral substitution pattern (Fig. 1, Table 1).

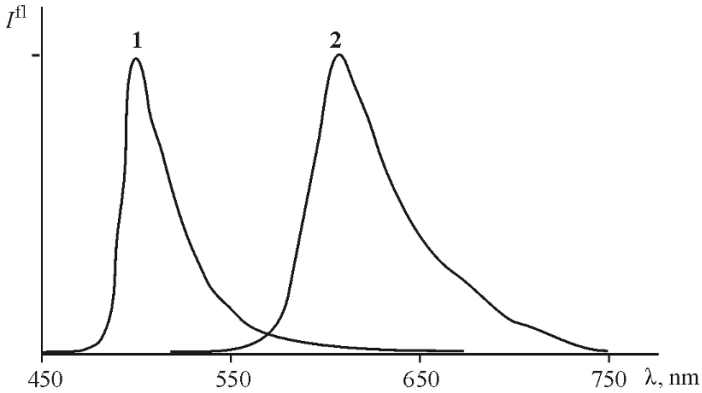


Fig. 2. Fluorescence spectra of zinc(II) complexes **1**, **2** in cyclohexane, where *I* is fluorescence intensity in arbitrary units.

The EAS of the complexes **1** and **3** exhibited significant solvatochromic effects upon changing from polar to nonpolar solvents. While the general character of the spectrum did not change (Table 1), in nonpolar media the absorption maximum in the spectrum of the complex **1** was redshifted by up to 4 nm, but that of the complex **3** was blueshifted by up to 8 nm. There was no solvatochromic effect found for the complex **2** with the solvents used in the study.

The complexes **1** and **2**, when dissolved in organic solvents, each exhibited one fluorescence band with the maximum at 497-503 nm or 607-614 nm, respectively (Fig. 2, Table 2), which mirrored the most intense absorption bands of these compounds.

TABLE 1. The EAS of Zinc(II) Complexes **1**-**3** in Organic Solvents

Solvent	λ_{max}^{abs}, nm (log ε)		
	1	**2**	**3**
C_6H_{12}	488 (5.18), 465 (4.90) sh, 352–358 (3.97)	574 (4.74) sh, 528 (4.94), 394-410 (3.93), 289 (4.77)	652 (4.66) sh, 587 (4.90), 470-495 (4.01), 302 (4.81)
C_6H_{14}	487 (5.05), 464 (4.78) sh, 353–361 (3.95)	573 sh, 526, 398-410, 288	—
PhH	490 (5.11), 465 (4.82) sh, 351–367 (3.88)	575 (4.71) sh, 532 (4.88), 396-410 (3.83), 293 (4.67)	652 (4.76) sh, 591 (4.95), 486-500 (4.11), 305 (4.82)
PhMe	490 (5.09), 465 (4.78) sh, 358–365 (3.90)	575 (4.73) sh, 532 (4.91), 394-410 (3.90), 293 (4.72)	651 (4.71) sh, 590 (4.92), 478-494 (4.04), 306 (4.79)
$CHCl_3$	488 (5.08), 464 (4.80) sh, 354–367 (3.81)	574 (4.70) sh, 529 (4.88), 391-409 (3.79), 293 (4.66)	650 (4.71) sh, 590 (4.91), 480-495 (4.02), 306 (4.81)
1-PrOH	487 (5.05), 464 (4.77) sh, 355–365 (3.92)	573 sh, 526, 388-410, 288	651 sh, 588, 475-495, 302
EtOH	485, 464 sh, 350–367	572 sh, 525, 398-414, 286	651 sh, 586, 480-498, 301
DMF	486 (5.05), 464 (4.77) sh, 354-366 (3.84)	574 (4.73) sh, 531 (4.91), 385-408 (3.94), 291 (4.73)	652 (4.74) sh, 595 (4.91), 480-494 (3.81), 303 (4.80)

TABLE 2. The Fluorescence Characteristics of Zinc(II) Complexes **1**, **2** in Organic Solvents*

Complex	Solvent	λ_{max}^{fl}, nm	$\Delta\lambda_{st}$, nm	$\Delta\nu_{st}$, cm^{-1}	γ^{fl} (λ^{ex}, nm)	$k_{rad} \cdot 10^{-8}$, s^{-1}	τ, ns
1	C_6H_{12}	501	13	532	0.024 (475)	2.47	0.097
	C_6H_{14}	501	14	574	0.018 (475)	2.00	0.090
	PhH	503	13	527	0.028 (475)	2.10	0.134
	PhMe	503	13	527	0.031 (475)	1.97	0.157
	$CHCl_3$	501	13	532	0.001 (475)	2.18	0.005
	1-PrOH	499	12	494	0.001 (475)	2.29	0.004
	EtOH	497	12	498	0.001 (475)	—	—
	DMF	—	—	—	—	—	—
2	C_6H_{12}	608	34	975	0.331 (510)	1.64	2.025
	C_6H_{14}	607	34	977	0.115 (505)	—	—
	PhH	615	40	1131	0.157 (510)	1.50	1.047
	PhMe	614	39	1104	0.138 (510)	1.60	0.864
	$CHCl_3$	610	36	1029	0.043 (510)	1.49	0.289
	1-PrOH	607	34	977	0.011 (505)	—	—
	EtOH	607	35	1008	0.007 (510)	—	—
	DMF	610	36	1029	0.003 (510)	1.52	0.020

* λ_{max}^{fl} – the wavelength of the maximum in the fluorescence spectra; $\Delta\lambda_{st}$ and $\Delta\nu_{st}$ – Stokes shift; λ_{ex} – excitation wavelength; k_{rad} – radiative rate constant (the rate constant of the radiative process).

The Stokes shift value ($\Delta\lambda_{st}$) in the solvents used was found to be 12-14 nm for the complex **1** and nearly 3 times higher ($\Delta\lambda_{st}$ = 34-40 nm) for the phenyl-substituted dipyrrinate **2**, which had a higher fluorescence intensity than the complexes **1** and **3**. The highest fluorescence quantum yield for the dipyrrinate **2** (γ^{fl} = 0.33) was observed in cyclohexane. The γ^{fl} value was 14 times lower in the same medium for the methyl-substituted complex **1**. The azadipyrrinate **3** completely lacked fluorescence regardless of the nature of the solvent. The fluorescent excited state half-life (τ) depended on the solvent, and in the case of the complexes **1** and **2** it was in

the range of 0.004-0.157 and 0.020-2.025 ns, respectively (Table 2). In general, the fluorescent properties, Stokes shift values, quantum yields, and excited state half-lives increased in the series **3 < 1 < 2**.

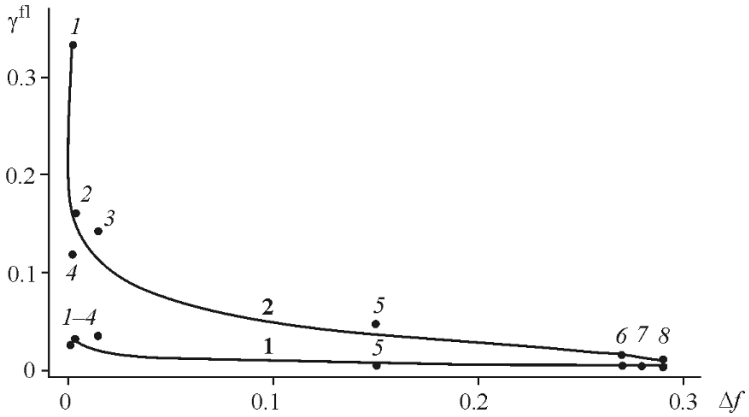


Fig. 3. The dependence of fluorescence quantum yield (γ^{fl}) of the complexes **1** and **2** on the function of the universal intermolecular interactions (Δf). Solvents: *1* – cyclohexane, *2* – benzene, *3* – toluene, *4* – hexane, *5* – chloroform, *6* – 1-propanol, *7* – ethanol, *8* – DMF.

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A comparative analysis of the fluorescence data for the chelates **1** and **2** in various solvents showed that a higher polarity of the medium resulted in significantly lower values of γ^{fl} (Fig. 3, Table 2).

In the case of the methyl-substituted dipyrrinate **1**, the highest values of γ^{fl} = 0.018–0.031 were obtained in nonpolar saturated or aromatic solvents, while in polar or even weakly polar solvents (e.g., chloroform) the fluorescence was almost completely quenched (γ^{fl} = 0–0.001). The complex **2** produced a better correlation of the γ^{fl} values with function of the universal intermolecular interactions (Δf). The weak fluorescence in polar electron- or proton-donating media was caused by the high probability of non-radiative deactivation of the excited state, due to specific interactions in the solvation shell. The specific nature of these interactions was confirmed by the non-linear dependence of the Stokes shift values on the function of the universal intermolecular interactions as the solvent polarizability parameter (Fig. 4) [14, p. 211].

As demonstrated before, the thermal analysis of stable solvates of dipyrrin zinc(II) complexes indicated that the specific solvation in electron-donating solvents (DMF, pyridine, etc.) was caused by zinc coordination with additional solvent molecules, involving a change in the coordination geometry from a deformed tetrahedron to a deformed octahedron [15]. The additional coordination in alcohols could be mediated by donor-acceptor interactions between the hydroxyl oxygen and metal, as well as the hydroxyl hydrogen and nitrogen. The fluorescence in chloroform may have been quenched through interactions between the solvent hydrogen atoms and the nitrogen atoms of the ligand pyrrole rings. Besides, the fluorescence of the phenyl-substituted complex **2** was quenched by more than a half in aromatic solvents: in benzene γ^{fl} = 0.157 and in toluene γ^{fl} = 0.138, compared to a saturated hydrocarbon solvent, cyclohexane (Table 2), due to the enhanced π–π stacking interactions with the aromatic rings in the excited chromophore.

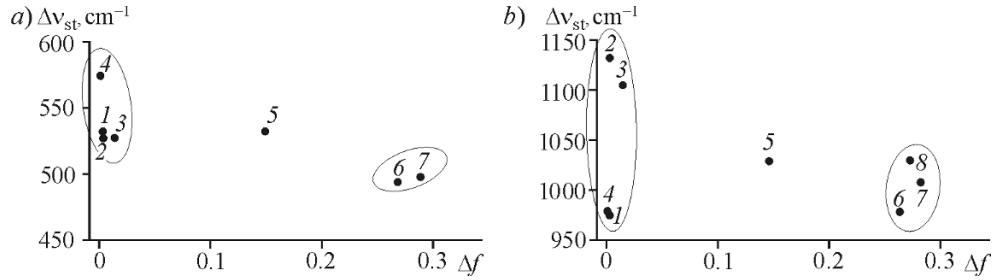

Fig. 4. The dependence of the Stokes shift ($\Delta\nu_{st}$) on the function of the universal intermolecular interactions (Δf) for the complexes *a*) **1** and *b*) **2**. Solvents: *1* – cyclohexane, *2* – benzene, *3* – toluene, *4* – hexane, *5* – chloroform, *6* – 1-propanol, *7* – ethanol, *8* – DMF.

Photostability is one of the most important properties of chromophores. The effects of UV irradiation on the EAS of the phenyl-substituted dipyrrinate **2** in cyclohexane are presented in Fig. 5.

The photodegradation of the complexes **1**-**3** was accompanied by a decreased absorption at the characteristic visible and near-UV ranges (230-720 nm), and an increased absorption at the shorter UV wavelengths (210-230 nm), characteristic of the photodegradation products – oligopyrroles and their phenyl-substituted photoproducts: aromatic pyrrole derivatives, dipyrrolylmethane, and benzene [16]. The photodegradation half-life, as calculated by the loss of optical density at the characteristic EAS band maximum, significantly increased in the series of complexes **3**, **1**, and **2** ($\tau_{1/2}$ = 6, 76, and 475 min, respectively), i.e., the photostability of the zinc (II) complex with tetraphenyl-substituted dipyrrinate (compound **2**) was more than 6 times higher than the photostability of its methyl-substituted analog **1,** and 80 times higher than the photostability of the aza analog **3**.

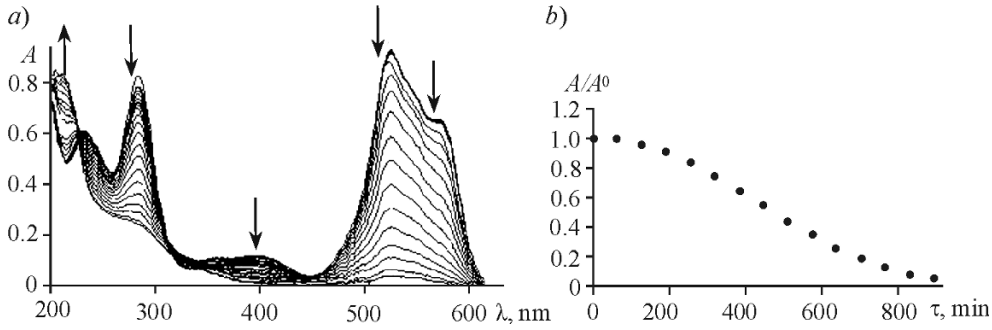

Fig. 5. The changes in *a*) electronic spectra and *b*) relative absorbance of the complex **2** ($c = 1 \cdot 10^{-5}$ mol/l) in cyclohexane under UV irradiation.

The obtained results provided a preliminary roadmap to the design of zinc(II) dipyrrinates with the spectral-luminescent properties required of chromophore and luminophore tags, laser dyes, sensors, etc. Thus, changing the pyrrole ring substituents in the dipyrrin ligand from alkyl groups to aryl groups resulted in a substantial (6-fold) increase of photostability, a significant red shift (by up to 45 nm) of the electronic absorption and emission spectra, 10-40-fold improvement of quantum yields, 5-10 times longer half-life and sensitivity of chelate fluorescence to the nature of solvating environment. Switching from the tetraphenyl-substituted dipyrrin structure to the analogous azadipyrrin structure gave a substantial (up to 64 nm) red shift of EAS towards the spectral window suitable for phototherapy, but completely quenched the fluorescence and sharply decreased the photostability of zinc(II) azadipyrrinate.

EXPERIMENTAL

Electronic absorption and fluorescence spectra for solutions of the complexes **1**-**3** were recorded on an Akvilon SF 103 spectrophotometer (Russia) and a SOLAR SM 2203 spectrofluorimeter (Belarus) in the UV-Vis range of 200-750 nm. Quartz cuvettes with the absorbing layer optical path length (l) of 1 and 10 mm were used with ~10^{-7}-10^{-5} mol/l concentrations of the investigated complexes in organic solvents. The standard for determination of γ^{fl} was an ethanol solution of Rhodamine 6G (γ^{fl} 0.94) [17]. The fluorescence spectra were all recorded under the same conditions when the optical density at the excitation wavelength did not exceed 0.1 [14, p. 143]. The fluorescence half-life (τ) was estimated, based on the spectral and luminescence characteristics [18, 19]. According to $\gamma = k_{rad}/(k_{rad} + k_d)$ and $\tau = 1/(k_{rad} + k_d)$, the fluorescence half-life (τ) was determined as $\tau = \gamma / k_{rad}$, where k_d – the rate of non-radiative processes, k_{rad} – radiative rate constant (the rate of radiative processes), which was estimated according to [14, p. 19; 18] from the characteristics of EAS by the formula $k_{rad} = 2.9 \cdot 10^{-9} [(9n_D^2)/(n_D^2+2)^2] \cdot \nu_{max}^2 \cdot \varepsilon_{max} \cdot \Delta\nu_{1/2}$, where n_D – the solvent refractive index, ν – wavenumber (cm^{-1}), $\Delta\nu_{1/2}$ – half-width of the absorption band (cm^{-1}), ε – extinction coefficient at the absorption band. The value of τ was determined with a 10-15% accuracy.

The Stokes shift was determined as the difference between the wavelengths of maxima in the fluorescence and absorption spectra:

$$\Delta\lambda\ (nm) = \lambda_{max}^{fl} - \lambda_{max}^{abs} \text{ and } \Delta\nu_{st}\ (cm^{-1}) = \nu_{max}^{fl} - \nu_{max}^{abs}.$$

The function of the universal intermolecular interactions (Δf) was calculated according to the Lippert–Mataga equation [14, p. 211]:

$$\Delta f = \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) - \frac{n_D^2 - 1}{2n_D^2 + 1},$$

where ε – dielectric permittivity and n_D – refractive index of the medium.

The photostability of the complexes was investigated by irradiation with an OUFK-01 quartz UV lamp (230-400 nm wavelength). The ~$1 \cdot 10^{-5}$ mol/l cyclohexane solutions of the complexes **1**-**3** were irradiated in 10 mm quartz cuvettes at a 3 cm distance from the UV source with the power density of 1.0 W/m^2.

^1H NMR spectra were acquired on a Bruker 500 instrument (500 MHz) in $CDCl_3$ solutions, and TMS was used as internal standard. Elemental analysis was performed on a Flash EA 1112 apparatus. The organic solvents (benzene, toluene, hexane, chloroform, ethanol, DMF) were purified to the "chemically pure" grade according to standard methods. The water content in these solvents was determined by Karl Fischer titration and did not exceed 0.02%. Cyclohexane (Panreac) and 1-propanol (UV-IR-HPLC-HPLC preparative, PAI) were used without additional purification.

The 2-[(3,5-dimethyl-2*H*-pyrrol-2-ylidene)methyl]-3,5-dimethyl-1*H*-pyrrole hydrobromide was prepared by an updated method [20].

Zinc(II) Complex with 2-[(3,5-Dimethyl-2*H*-pyrrol-2-ylidene)methyl]-3,5-dimethyl-1*H*-pyrrole (1). 2-[(3,5-Dimethyl-2*H*-pyrrol-2-ylidene)methyl]-3,5-dimethyl-1*H*-pyrrole hydrobromide (0.115 g, 0.407 mmol) was dissolved in methanol (5 ml) with heating and stirring. Triethylamine (0.041 g, 0.405 mmol) was added, followed by a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.178 g, 0.814 mmol) in methanol (3 ml). The solution was refluxed for 1 h. Then the mixture was cooled, the precipitated complex was filtered off, washed with hot water, methanol, ether, and air-dried. Yield 0.090 g (69%). ^1H NMR spectrum, δ, ppm: 1.96 (12H, s, $4CH_3$); 2.34 (12H, s, $4CH_3$); 6.01 (4H, s, pyrrole CH); 7.04 (2H, s, –CH=). Found, %: C 67.05; H 6.48; N 12.02. $C_{26}H_{30}N_4Zn$. Calculated, %: C 67.32; H 6.52; N 12.08.

Zinc(II) Complex with 2-[(3,5-Diphenyl-2*H*-pyrrol-2-ylidene)methyl]-3,5-diphenyl-1*H*-pyrrole (2). 2-[(3,5-Diphenyl-2*H*-pyrrol-2-ylidene)methyl]-3,5-diphenyl-1*H*-pyrrole (0.144 g, 0.321 mmol) was dissolved in 1-butanol (10 ml) and mixed with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.06 g, 0.273 mmol) in 1-butanol (6 ml), and the mixture was refluxed for 1 hour. The mixture was then cooled, the precipitate was filtered off, washed with hot water, and air-dried. The crude product was dissolved in dichloromethane and purified by silica gel chromatography with CH_2Cl_2 as the eluent. The eluate was concentrated by evaporation, and the product was

precipitated with methanol at low temperature. Yield 0.150 g (95%). ^{1}H NMR spectrum, δ, ppm : 6.45 (4H, s, pyrrole CH); 7.10 (2H, s, –CH=); 7.46-7.50 (40H, m, H Ph). Found, %: C 82.17; H 4.48; N 5.65. $C_{66}H_{46}N_4Zn$. Calculated, %: C 82.53; H 4.83; N 5.83.

Zinc(II) Complex with *N*-(3,5-Diphenyl-2*H*-pyrrol-2-ylidene)-3,5-diphenyl-1*H*-pyrrol-2-amine (3). A solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.1 g, 0.460 mmol) in THF (10 ml) was added to a solution of *N*-(3,5-di-phenyl-2*H*-pyrrol-2-ylidene)-3,5-diphenyl-1*H*-pyrrol-2-amine (0.3 g, 0.667 mmol) in THF (10 ml) and stirred for 24 h at room temperature. The solvent was evaporated to dryness, the residue was dissolved in dichloromethane and purified by silica gel chromatography, with CH_2Cl_2 as the eluent. The eluate was concentrated by evaporation, and the product was precipitated with methanol. Yield 0.234 g (73%). ^{1}H NMR spectrum, δ, ppm : 6.73 (4H, s, pyrrole CH); 7.51-7.52 (20H, m, H Ph); 7.87-7.89 (20H, m, H Ph). Found, %: C 79.54; H 4.27; N 8.53. $C_{64}H_{44}N_6Zn$. Calculated, %: C 79.87; H 4.61; N 8.73.

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