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Preparation and Spectral Properties of Zn(II) Complexes with Aryl-Substituted Dipyrrolylmethene and Azadipyrrolylmethene

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Abstract—The homoleptic complexes of Zn(II) with 3,3',5,5'-tetraphenyl-2,2'-dipyrrolylmethene and 3,3',5,5'-tetraphenyl-*ms*-aza-2,2'-dipyrrolylmethene [ZnL_2] have been prepared, and their spectral and luminescent properties have been studied. The complex with 3,3',5,5'-tetraphenyl-2,2'-dipyrrolylmethene exhibited an intense fluorescence in the nonpolar medium, efficiently quenched in the polar solvents; thus, it can be used as a fluorescent sensor of the medium polarity.

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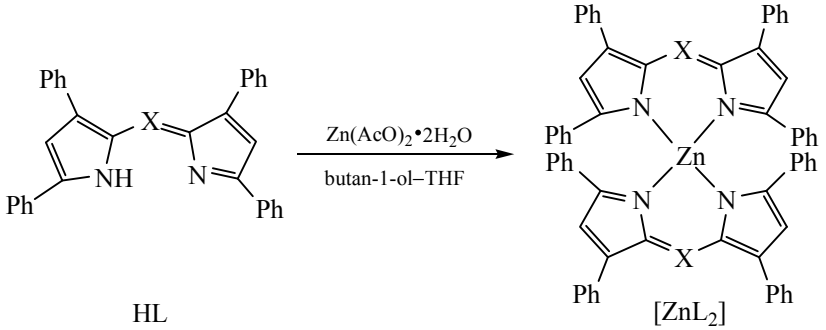
Electron absorption and fluorescence spectra of dipyrrolylmethene complexes are sensitive to their molecular structure, in particular, to the nature of *meso*-spacer and functional substituents in the chromophore ligand [1–3]. The chromophore properties modification in order to shift and enhance the absorption in the range of phototherapy window is of high importance. One of the approached to achieve this is the variation of the *meso*-spacer nature by substitution of methylene bridge with nitrogen atom. The number and position of phenyl substituents in the pyrrole rings as well as the *meso*-spacer nature affect strongly the fluorescence properties of dipyrrolylmethenates; however, these effects are ambiguous. The luminescence properties of aryl-substituted dipyrrolylmethenates have not been systematically studied. The optimal combination of the above-mentioned effects (aryl-substitution and aza-substitution) was illustrated in this work using homoleptic Zn(II) complexes [ZnL_2] [L was 3,3',5,5'-tetraphenyl-2,2'-dipyrrolylmethene (**I**) or 3,3',5,5'-tetraphenyl-*ms*-aza-2,2'-dipyrrolylmethene (**II**)] as examples. The complexes were prepared by exchange reaction of the ligand (**I**, **II**) with zinc(II) acetate in butanol-1 or tetrahydrofuran.



HL [ZnL_2]

X = CH (**I**), N (**II**).

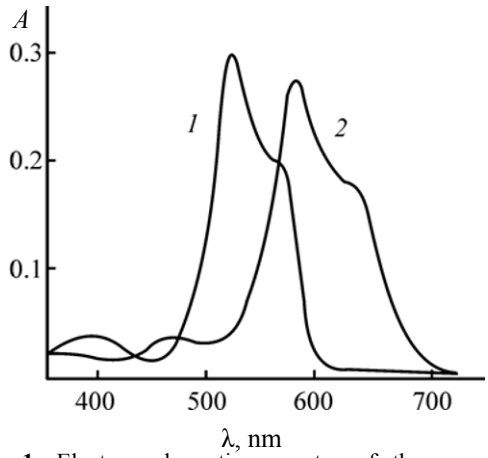


Fig. 1. Electron absorption spectra of the complexes solutions in C_6H_{12}: (*1*) [Zn(**I**)$_2$], $c = 3.4\times10^{-5}$ mol L^{-1} and (*2*) [Zn(**II**)$_2$], $c = 3.9\times10^{-5}$ mol L^{-1}.

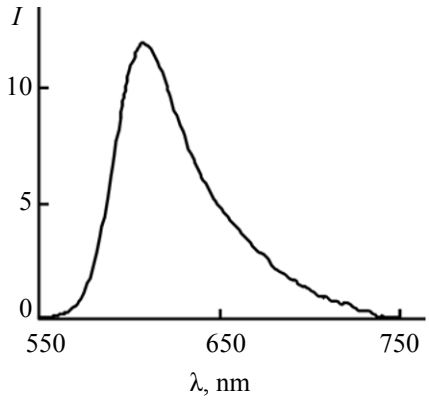


Fig. 2. Fluorescence spectrum of [Zn(**I**)$_2$].

In the electron absorption spectra of [Zn(**I**)$_2$] an intense band (λ_{max} = 524–530 nm, shoulder at 571–576 nm) was observed and a weak band in the 385–410 nm range (Fig. 1). The change of the spacer to nitrogen atom did not change the absorption spectrum qualitatively, however led to significant red shift of the band maxima. Depending on the solvent, the intense band λ_{max} was of 586–595 nm with a shoulder at 650–655 nm, whereas the weak band was located at 470–495 nm. The type of the spectrum was independent of the solvent nature (chloroform, propanol-1, dimethylformamide), the solvatochromic effect being of 1–9 nm.

Independently of the excitation wavelength and the medium nature, [Zn(**II**)$_2$] complex did not show any fluorescence; [Zn(**I**)$_2$] complex was an efficient phosphor. In the studied solvents, the fluorescence spectrum of [Zn(**I**)$_2$] was almost a regular reflection of the absorption spectrum and had the only emission band with a maximum at 608–610 nm (Fig. 2). In cyclohexane, the fluorescence quantum yield (Φ) of [Zn(**I**)$_2$] reached 0.331. In polar solvents, the fluorescence was quenched: almost completely in dimethylformamide (Φ = 0.003) and almost by an order of magnitude in chloroform (Φ = 0.043). The observed trend should allow using [Zn(**I**)$_2$] as a fluorescent sensor of the medium polarity. Similar fluorescence quenching in the polar, electron-donor solvents was previously found in the case of Zn(II) complexes with bis(dipyrrolylmethenes) [4]. For a set of Zn(II) bis(dipyrrolylmethenates) it was demonstrated that the increase of probability of radiationless processes in the excited states were connected with supramolecular complexes formation due to the additional coordination of electron-donor solvent molecules to the complex-forming atom.

EXPERIMENTAL

^{1}H NMR spectra were registered on a Bruker 500 spectrometer in $CDCl_3$ solutions. Electron absorption and fluorescence spectra were registered on a SF-103 spectrometer (Akvilon) and SM 2203 spectrofluorimeter (SOLAR). Zinc(II) acetate, chemically pure grade, was recrystallized from glacial acetic acid with subsequent dehydration; the hydrates composition was determined gravimetrically. The organic solvents, chemically pure grade, were purified as described in [5, 6]. Residual water content according to the Fischer titration was below 0.02%.

Zinc(II) complex with 3,5-diphenyl-2-[(3,5-diphenyl-2*H*-pyrrol-2-ylidene)methyl]-1*H*-pyrrole (3,3',5,5'-tetraphenyl-2,2'-dipyrrolylmethene) [Zn(I)$_2$] (*M* 960.50). A mixture of 0.144 g (0.321 mmol) of **I** and 0.06 g (0.273 mmol) of $Zn(AcO)_2\cdot2H_2O$ dissolved in 6 mL of butanol-1 was heated and refluxed during 1 h. The mixture was cooled; the precipitate was filtered off, washed with hot water, and dried in air. Then the product was dissolved in methylene chloride and purified by chromatography on silica gel. The eluate was evaporated, and the complex was precipitated with methanol at effective cooling. Yield 0.150 g (95%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.45 s (4H, $CH_{pyrrole}$), 7.10 s (2H, –CH=$_{meso}$), 7.46–7.50 m (40H, Ph). UV spectrum, λ_{max}, nm (log ε): 576 (4.74), 528 (4.94), 394–410 (C_6H_{12}); 576 (4.73), 529

(4.91), 396–410 ($C_6H_5CH_3$); 576 (4.70), 530 (4.88), 391–409 ($CHCl_3$); 571, 524, 388–410 (PrOH-1); 576 (4.73), 529 (4.91), 385–408 (DMF). Found, %: C 81.95; H 4.23; N 5.57. $C_{66}H_{46}N_4Zn$. Calculated, %: C 82.53; H 4.83; N 5.83.

Zinc(II) complex with 3,5-diphenyl-*N*-(3,5-diphenyl-2*H*-pyrrol-2-ylidene)-1*H*-pyrrole-2-amine (*ms*-aza-3,3',5,5'-tetraphenyl-2,2'-dipyrrolylmethene) [Zn(II)$_2$] (*M* 962.47). Solution of 0.1 g (0.46 mmol) of $Zn(AcO)_2 \cdot 2H_2O$ in 10 mL of THF was added to a solution of 0.3 g (0.667 mmol) of **II** in 10 mL of THF, and the mixture was stirred during 24 h at room temperature. The solvent was evaporated, the residue was dissolved in methylene chloride and purified by chromatography on silica gel. The eluate was evaporated, and the complex was precipitated with methanol. Yield 0.234 g (73%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.73 s (4H, $CH_{pyrrole}$), 7.51–7.52 m (20H, Ph), 7.87–7.89 m (20H, Ph). UV spectrum, λ_{max}, nm (log ε): 655 (4.66), 586 (4.90), 470–495 (C_6H_{12}); 652 (4.71), 590 (4.91), 478–494 ($C_6H_5CH_3$); 652 (4.71), 590 (4.91), 480–495 ($CHCl_3$); 651, 588, 475–495 (PrOH-1); 650 (4.74), 595 (4.91), 480–494 (DMF). Found, %: C 78.44; H 4.23; N 8.50. $C_{64}H_{44}N_6Zn$. Calculated, %: C 79.87; H 4.61; N 8.73.

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