

Photophysical Features of Phthalocyanines Metallocomplexes with Out-of-Plane Ligands

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Abstract The objective of this work was synthesizing of Ti-, Zr-, Hf-phthalocyanines, containing chloride ions or dibenzoylmethanate fragments coordinated in out-of-plane positions to macrocycle. Spectroscopic and photophysical parameters of phthalocyanines metallocomplexes with metal atoms Ti(IV), Zr(IV) and Hf(IV) and spectroscopic features of Mg- and Zn-phthalocyanines have been detected and characterized at ambient and liquid nitrogen temperatures. The efficient intersystem crossing observed for Hf-phthalocyanine leads to very weak fluorescence and suppresses the fluorescence lifetimes to less than 1 ns. Changing of nature of central metals from heavy Hf(IV) atom to lighter atoms: Zr(IV), Zn(II), Ti(IV), Mg(II) lead to noticeable increasing of fluorescence lifetimes up to maximum value of 6,6 ns for Mg-phthalocyanine. At the same time the values of fluorescence quantum yield rises from 1 % for Hf-phthalocyanine to 56 % for Mg-phthalocyanine. The heavy atom effect has a substantially greater impact on photophysical parameters metallocomplexes of phthalocyanines than influence of attachment out-of-plane ligands.

Keywords Metallocomplexes of Phthalocyanines, Out-of-Plane Ligands, Spectroscopic and Photophysical Parameters, Heavy Atom effect

1. Introduction

Synthesis, photophysical properties and applications of near infrared absorbing materials based on phthalocyanine (Pc) core complexes become a new, promising and challenging research field [1,2 and Ref. therein]. Phthalocyanines based materials have been developed and applied so far for a variety of applications such as chemosensors [3], therapy [4], NIR OLEDs [5], triplet-triplet annihilation based upconversion [6]. Moreover, NIR

absorption extending beyond the visible region has been considered as a promising property for creation of artificial photosynthetic systems for the conversion of solar energy in infrared region [7]. It's well known, that the absorption spectra of metal complexes of phthalocyanines consist of two main absorption bands: Soret band is located in spectral range about 330-340 nm and essentially more intensive Q-band - near 680-700 nm, and exhibit a lack of absorption in the middle part of the spectrum [1,8]. Seems rather interesting synthesis and developing of new types of phthalocyanine complexes with an electronic absorption expanded to the visible spectral range for more effective light harvesting and conversion. Other parameter of unsubstituted phthalocyanines needs to be improved is low solubility in commonly used polar/unpolar organic solvents. A strategy to tune the spectral and chemical properties through the effect exerted by the substituents to central metal atom was selected. As a first step a series of organic dyes with well-defined spectral properties were sensitized [8]. A second step was preparation of metal complexes of phthalocyanine substituted by out-of-plane ligands for fine-tuning of absorption in a visible spectral region.

In this work a number of dichlorido phthalocyanine metal complexes (PcMCl₂) of IVth group elements (Zr, Hf) as well as out-of-plane bis(dibenzoylmethanato) (Dbm) phthalocyanine complexes (PcZrDbm₂ and PcHfDbm₂) were prepared and investigated. The formation of dye containing out-of-plane complexes a tetravalent central metal atom with the coordination number eight is required. The Ti(IV) coordination number is six and titanium phthalocyanine complex with Dbm dye was not possible. Although, electronic absorption of Dbm molecule is located in near UV region and overlapped with Soret band of phthalocyanine, the ligand was used for preliminary study due to significant improvement of solubility and stability of Dbm-based metal complexes. The photophysical and spectroscopic properties of all compounds were measured at ambient and liquid nitrogen temperatures and compared with data for Mg(II) and Zn(II) phthalocyanines.

2. Experimental

Phthalocyanine complexes of magnesium (PcMg) and zinc (PcZn) were purchased from Sigma-Aldrich Co and used as received. PcMCl_2 ($M=\text{Ti, Zr, Hf}$) were obtained as described in [8], PcZrDbm_2 and PcHfDbm_2 were obtained from PcMCl_2 by [9] and their structures are presented on Fig. 1.

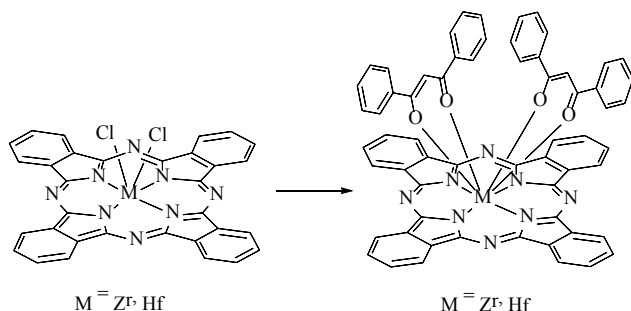


Figure 1. Scheme for synthesis of phthalocyanine metallocomplexes of Zr and Hf with out-of-plane coordinated two Dbm dye molecules.

Steady-state fluorescence and fluorescence excitation spectra were measured at room temperature on a high sensitivity home-built spectrometer [10]. The fluorescence quantum yield (Φ_F) was determined using the comparative method methodological details of which are depicted in [11]. As the standard of fluorescence quantum yield Zn-*meso*-tetraphenylporphyrin [10] ($\Phi_F=3,5\%$) was employed. For several compounds of interest phosphorescence spectra, as well as phosphorescence excitation spectra were recorded by a two-disk phosphoroscope driven by two synchronous motors. The operating spectral region was from 200 nm to 1100 nm, and the exciting light sources were xenon and tungsten lamps or several different photodiodes (Thorlabs, Inc.). The experimental set-up was equipped with a thermocooling system for the photomultiplier (FEU-83 or FEU-100). The systematic errors of measurements of the luminescence

intensity were about 5 %. The accuracy in the estimation of quantum yields was less than 10 %. The apparatus has been described in details elsewhere [10].

Time-resolved fluorescence decays in the nanosecond range were recorded upon using a modular time-correlated single-photon-counting (TCSPC) system of single photons with applying of module TCC900 (Edinburg Instruments) upon excitation of emission by LED pulsed PLS-8-2-130 (457 nm, pulse duration about 713 ps) or LED pulsed PLS-8-2-135 (409 nm, pulse duration about 990 ps) production of PicoQuant GmbH.

Spectroscopy grade dimethylsulfoxide (DMSO) and 2-methyltetrahydrofuran (2-mTHF) (Sigma-Aldrich Co.) were used as solvents.

3. Calculations

The ground state geometries of above-mentioned compounds were optimized using density functional theory with the B3LYP functional and def2SVP basis set in the Gaussian 09 suite of programs [12].

The optimized ground state geometry of $\text{PcZrDbm}_2/\text{PcHfDbm}_2$ corresponds well with the X-ray data [9] and are presented for PcZrCl_2 (1) and PcZrDbm_2 on Fig. 2. The central atoms of Zr/Hf exhibits nearly regular square-antiprism ($\text{Zr/Hf})\text{N}_4\text{O}_4$ coordination geometry. The distances between the central ion (Zr/Hf) and the polyhedron bases defined by four nitrogen and four oxygen atoms, respectively, are 1.237/1.236 Å and 1.198/1.200 Å, and are only slightly higher than values evaluated from crystallographic data (1.211/1.194 Å and 1.184/1.181 Å). Similarly, computed average Zr/Hf-N and Zr/Hf-O bond lengths, 2.329/2.329 Å and 2.199/2.198 Å, respectively are somewhat higher than experimental one, 2.292/2.279 Å and 2.170/2.164 Å. The phthalocyanine macrocycle shows non-planar crown-like distortion in the direction opposite to the central metal ion.

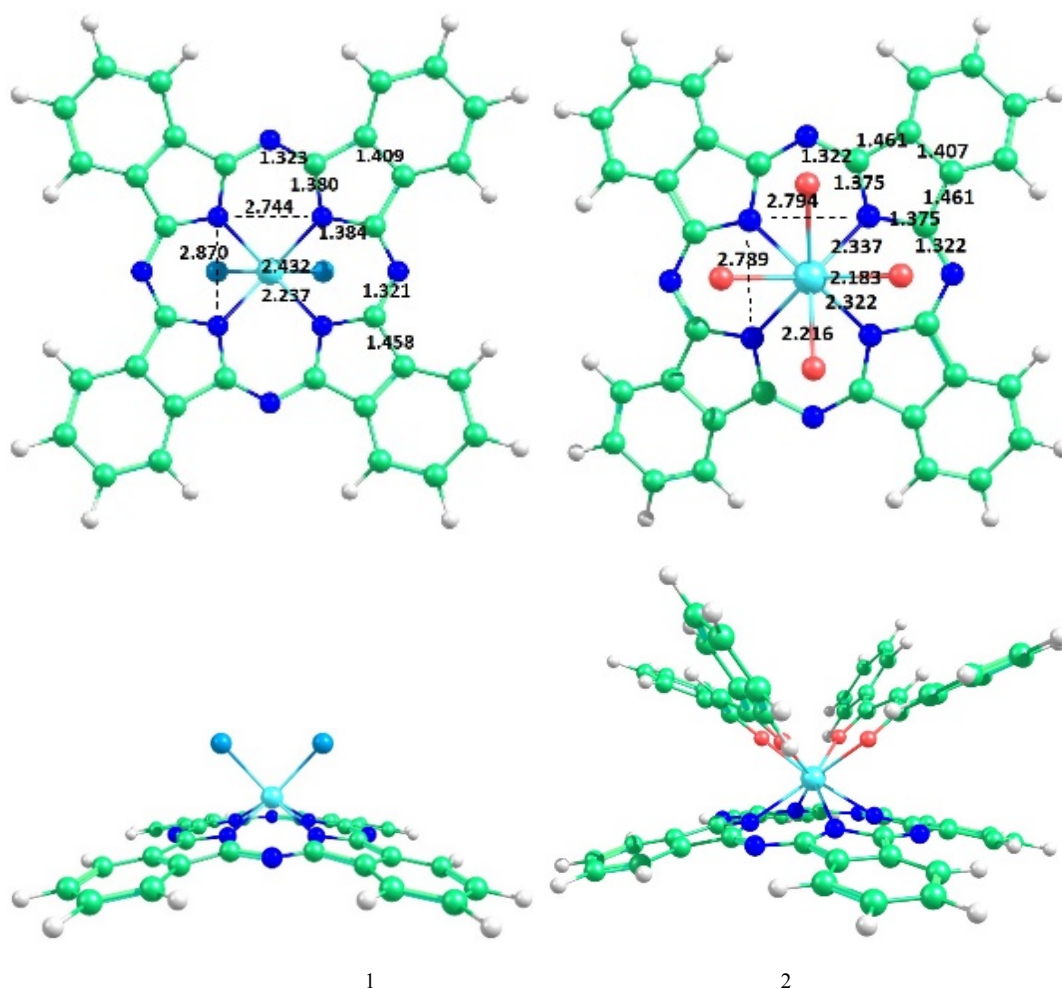


Figure 2. The optimized ground state geometry of PcZrCl_2 (1) and PcZrDbm_2 (2).

The modelled averaged dihedral angle formed by isoindole plane and the plane defined by four nitrogen atoms, $11.38/11.9^\circ$ is very close the crystallographic one, $11.21/11.15^\circ$. Two dibenzylmethane molecules coordinated bidentantly at opposite site of central ion in a symmetrical fashion form dihedral angle of $41.14/40.99^\circ$ with the nitrogen atoms plane. In crystal, non-symmetrical coordination by dibenzylmethane ligands which forms angles of $40.92/40.72^\circ$ and $61.74/61.91^\circ$, respectively, is imposed by crystal packing (dibenzylmethane unit forming higher angle is in close contact with a corresponding unit of a neighboring Pc molecule).

4. Results and Discussion

The fluorescence excitation, fluorescence and absorption spectra of PcHfCl_2 are shown on Fig. 3.

Fig.3 shows absorption and fluorescence spectra of metal complexes of symmetrically substituted phthalocyanines. Compared with the absorption spectrum of the free bases of phthalocyanines (four bands in visible spectral range) the absorption spectrum of phthalocyanine metallocomplexes possesses a more simple structure.

Only two bands are manifested in the visible part of the spectrum: the long-wavelength band (about 685 nm) corresponds to an electronic transition between doubly degenerated ground electronic states and the lowest excited electronic state. The next band about 620 nm is assigned with transitions between doubly degenerated ground electronic states and vibronic sublevels of the lowest excited electronic state. In the fluorescence spectrum the band around 690 nm corresponds to 0-0 transitions from the excited electronic state to the pure electronic ground state, and next band – transitions to vibronic sublevels of this state.

The positions of absorption bands, values of fluorescence quantum yields (Φ_{Fl}) and fluorescence lifetimes (τ_{Fl}) at ambient temperature of PcMg , PcZn , PcTiCl_2 , PcZrCl_2 , PcHfCl_2 , PcZrDbm_2 , and PcHfDbm_2 are presented in the Tab. 1.

The maximum values of fluorescence quantum yield and lifetime were observed for Mg(II) complex of phthalocyanine. The observation stays in good accordance with calculated plane structure of PcMg and smallest atomic weight of the Mg(II) ion. With increasing of atomic number of central ions, PcZn and PcTiCl_2 complexes, the values of

quantum yields and fluorescence lifetimes undergo two times decreasing compare to PcMg complex. The general tendency that upon increasing of metal ions weight the values of fluorescence quantum yields are systematically reduced from several dozens for metal complexes with Mg(II), Zn(II), Ti(IV), and Zr(IV) ions of to less than 1% for Hf(IV) ion (Tab. 1).

The values of fluorescence lifetimes are decreasing almost synchronously to the values of fluorescence quantum yields. The observed behavior suggests strong increasing of

intersystem crossing rate constant due to a heavy atom effect (spin-orbital coupling) [13,14]. Depending on type of metal ions in the center of phthalocyanine macrocycle (e.g. the exchanging of IVth group elements from Ti to Hf) the values of fluorescence lifetime and quantum yield decreased more than 30 times. Meanwhile exchange of two chlorine ions on two dibenzoylmethanate molecules does not leads to significant changes (about 10 %) of photophysical parameters (Tab. 1).

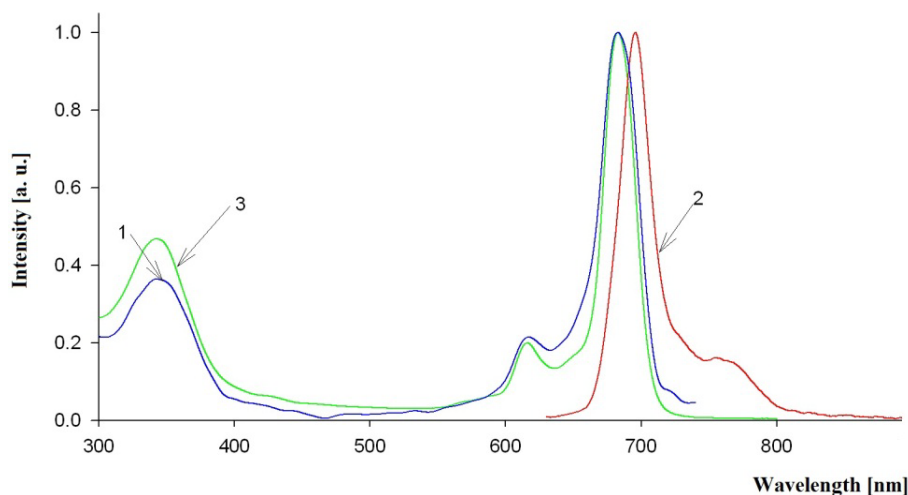


Figure 3. Fluorescence excitation (1), fluorescence (2) and absorption (3) spectra of PcHfCl₂ in DMSO at 293 K

Table 1. Photophysical and spectral characteristics of phthalocyanines metal complexes in DMSO at 293 K

Compound	Absorption	Absorption	Fluorescence	Φ_{FL}	τ_{FL}
	λ_{max} , nm	λ_{max} , nm	λ_{max} , nm	%	ns
PcMg	365	673,5	681	54	6,6
PcZn	355	672,5	680,5	26	3,8
PcTiCl ₂	360	689	700	28	3,5
PcZrCl ₂	343	689	700,5	11	1,02
PcHfCl ₂	343	683	696	1,4	<0,1
PcZrDbm ₂	342	690	701,5	10	0,9
PcHfDbm ₂	338	686	696,5	0,9	<0,1

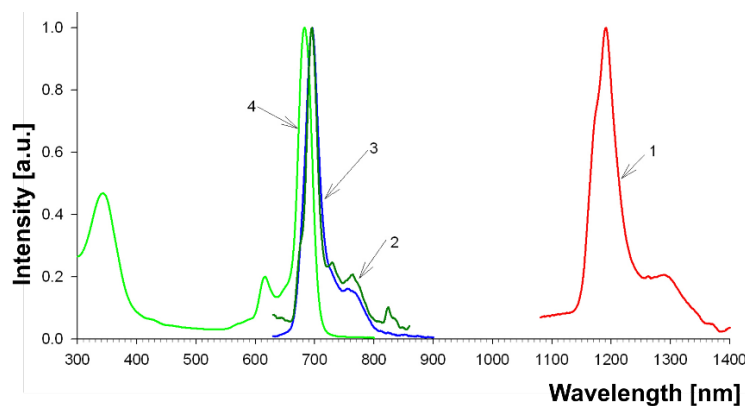


Figure 4. Phosphorescence (1), fluorescence (2) spectra of HfCl₂Pc in DMSO at 77K

Table 2. Spectral characteristics of phthalocyanines metal complexes at 77 K

Compound	Absorption	Fluorescence	Phosphorescence
	λ_{max} , nm	λ_{max} , nm	λ_{max} , nm
PcMg	669,5	673	1103
PcZn	671	673	1096
PcTiCl ₂	693,5	697	-
PcZrCl ₂	688,5	703	-
PcHfCl ₂	686	695,5	1191
PcZrDbm ₂	687,5	701,5	-
PcHfDbm ₂	686,5	695	-

Recently, the splitting effect of long-wavelength bands in absorption and fluorescence excitation spectra of Zr(IV) and Hf(IV) metal complexes of phthalocyanines have been recorded at low temperatures [15]. The comparison of the experimental data with results of quantum-chemical calculation and X-ray data has pointed that the splitting of absorption bands is caused by the type of metal ion in the center of phthalocyanine macrocycle, the distortion of metal phthalocyanines macrocycle upon coordination of the out-of-plane ligand groups and, consequently, by the loss by the macrocycle the high symmetry.

Based on Tab. 1 data, photophysical characteristics of all investigated compounds are more sensitive to the heavy atom effect than the effect of out-of-plane ligands substitution. In contrast, the spectral manifestation of out-of-plane ligands substitution in electronic spectra is very essential. The coordination of ligands provide to nonplanar “*dome*” [16] conformation, the loss of 4-fold symmetry of macrocycle and, consequently, to the splitting of long-wavelength bands in absorption spectra.

In the cases of PcMg, PcZn and PcHfCl₂ phosphorescence spectra were recorded at 77K (Fig. 4 and Tabl.2). Main phosphorescence bands are localized at 1084, 1096 and 1191 nm for PcMg, PcZn and PcHfCl₂, respectively. The spectroscopic features obtained for PcMg and PcZn molecules are well correlated with well-known published data [17].

5. Conclusions

1. Fluorescence, phosphorescence and fluorescence excitation data have been used for photophysical and spectral characterization of the series of phthalocyanines with Mg (II), Zn(II), Ti(IV), Zr(IV) and Hf(IV) ions at ambient and low temperatures. All investigated compounds demonstrated high stability and the reproducibility of experimental data.

2. The increasing heavy atom effect has been observed for metal complexes with Mg(II), Zn(II), Ti(IV), Zr(IV) and Hf(IV) central metal atoms. The effect provide to increasing of intersystem crossing rate constant and, consequently, to fluorescence quenching and shortening of fluorescence

lifetimes.

3. The effect of out-of-plane ligands (Dbm molecule or chlorine atoms) on photophysical parameters of metal phthalocyanines is essentially weaker than observed heavy atom effect.

4. Based on the detected spectral features, results of X-ray data for PcZrDbm₂ and PcHfDbm₂, calculations has been proposed that the electronic absorption bands splitting is caused by the distortion of metal phthalocyanines macrocycle upon coordination of the out-of-plane ligands to the central metal ion that leads to nonplanar “*dome*” conformation and additional loss of 4-fold symmetry by phthalocyanine macrocycle.

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