Dyes and Pigments 94 (2012) 187–194

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Novel zirconium (IV) and hafnium (IV) phthalocyanines with dibenzoylmethane as out-of-plane ligand: Synthesis, X-ray structure and fluorescent properties

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ARTICLE INFO

Article history:
Received 5 October 2011
Received in revised form
22 December 2011
Accepted 28 December 2011
Available online 2 January 2012

Keywords:
Zirconium and hafnium phthalocyanines
Synthesis
GALDI mass spectroscopy
UV–vis spectroscopy
Fluorescence
X-ray diffraction

ABSTRACT

Novel phthalocyanine complexes of zirconium (IV) and hafnium (IV) containing dibenzoylmethane groups as out-of-plane ligands were synthesized and characterized by elemental analyses, GALDI mass spectrometry, IR, ^{1}H NMR, UV–vis and fluorescence spectroscopy. The structures of the complexes were determined by single-crystal X-Ray diffraction. The synthesized compounds are isomorphous, with their central atoms exhibiting (ZrN_4O_4 and HfN_4O_4) square-antiprism coordination geometry, which consists of four nitrogen atoms from the phthalocyanine macrocycle and four oxygen atoms from the two bidentate dibenzoylmethane ligands. GALDI mass spectrometry studies have shown that hafnium phthalocyanine forms adducts with masses higher than the mass of the molecular ion, indicating a high ability of this complex to self-associate in the gas phase. The spectral-luminescent properties of the compounds in different solvents were studied. The splitting of the Q-band observed in the absorption spectra is related to the lowering of complexes symmetry due to the incorporation of two rigid ligands to the central metal atom of the macrocycle. Study of the absorption spectra of phthalocyanines over a wide concentration range does not reveal any indications for the formation of aggregates. Fluorescence quantum yield values of the complexes were determined by a comparative method in toluene and DMSO.

1. Introduction

Phthalocyanines today find application in various scientific and technological areas from electronics [1] to medicine [2], thus significant attention is paid to the synthesis of new compounds and their characterization. Particularly, metal phthalocyanine complexes possess unique properties such as chemical and thermal stability, large molar extinction coefficient [3], photoconductivity [4], electrochromism [5] and catalytic activity [6]. Thus the synthesis and studies of novel metal phthalocyanine complexes is a prospective task for the development of new materials for optoelectronics.

The physical and chemical properties of phthalocyanines are determined by their molecular structure, i.e. by the nature of the central metal atom and the presence of axial and peripheral substituents. It should be noted that application of phthalocyanine compounds is strongly limited by their low solubility in organic solvents and water, and by a high aggregation tendency in solutions. The solubility of compounds could be modified by introduction of peripheral or axial substituents. Thus the synthesis of phthalocyanines containing out-of-plane ligands is considered to be one way of obtaining compounds with improved properties.

The di(chloro) zirconium (IV) and hafnium (IV) phthalocyanines can easily be modified at the central metal atom due to its valency, high coordination numbers (up to 8), and high affinity to oxygen. Substitution of two chlorine atoms bound to the central metal atom by the two out-of-plane organic ligands allows modification of the physicochemical properties of the phthalocyanines, particularly spectral characteristics (e.g. fluorescence quantum yield).

Earlier we reported the spectral-luminescent, electrochemical, electrochromic, photocatalytic properties and biological activity of zirconium and hafnium phthalocyanines with different out-of-plane ligands, namely carboxylic acids [7], various β-dicarbonyl compounds [8] and aromatic polyoles [9]. The molecular structure of zirconium and hafnium phthalocyanines with oxygen-containing ligands was described in several papers [10,11]. In the current paper we present the synthesis, crystal structure, spectroscopic and fluorescent properties of new out-of-plane substituted zirconium and hafnium phthalocyanines containing dibenzoylmethane ligands.

2. Experimental

2.1. Materials

Dibenzoylmethane was purchased from Sigma–Aldrich and used without additional purification. Initial di(chloro)zirconium

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doi:10.1016/j.dyepig.2011.12.012

(IV) and hafnium (IV) phthalocyanines were prepared by the reaction of MCl_4 with o-phthalodinitrile according to the published procedures [12]. Dimethyl sulfoxide (DMSO), toluene, hexane were used without further purification.

2.2. Crystallography

The diffraction image frames from the single crystals of zirconium (**1**) and hafnium (**2**) phthalocyanine complexes were measured on Bruker SMART APEX2 (MoKα radiation, graphite monochromator, $\lambda = 0.71073$ Å) in a stream of nitrogen using ω- and φ-scan techniques. The intensities datasets were obtained by integration of diffraction image frames using SAINT program [13]. The intensities were corrected for polarization and Lorentz effects as well as for absorption using a multi-scan technique, implemented in SADABS program [13]. The structures were solved by direct methods and refined by full matrix least square on F^2 in anisotropic approximation for all non-H atoms using SHELXTL program package [14]. All hydrogen atoms were treated geometrically and refined isotropically using "riding model" with $U(H)_{iso} = 1.5U_{iso}(C)$ for CH_3 and $U(H)_{iso} = 1.2U_{iso}(C)$ for all others parent atoms. The extended experimental data are given in Table 1. The CCDC 843780 and CCDC 843781 contain full set of structural information on compounds (**1**) and (**2**) and can be obtained free of charge by request (http://www.ccdc.cam.ac.uk/products/csd/request/).

2.3. ^{1}H NMR, GALDI mass spectroscopy, absorption, IR and fluorescence spectra

^{1}H NMR spectra were recorded on a Varian (300 MHz) spectrometer ($CDCl_3$/TMS). GALDI (graphite-associated laser desorption/ionization) mass spectra were obtained using the Autoflex II, Bruker Daltonics mass spectrometer with nitrogen laser ($\lambda = 337$ nm) in reflectron mode for positive ions. GALDI technique was chosen as alternative to MALDI method in order to avoid possible interaction of synthesized compounds with the matrix and to increase ion intensity. Analysis of the spectra was performed using mMass 3 program [15]. The UV–vis spectra were recorded on a Perkin Elmer UV/VIS Lambda 35. IR spectra (KBr pellets) were recorded on Specord M-80. The fluorescence spectra were recorded on Perkin Elmer LS 55.

The fluorescence quantum yield values of complexes were determined basing on the absorption and fluorescence spectra according to the method described in Ref. [16] using the following equation:

$$\Phi = \Phi_R \cdot \frac{n^2}{(n_R)^2} \frac{SA_R}{S_R A} \quad (1)$$

where Φ_R is the fluorescence quantum yield of the reference, S and S_R are the areas under the fluorescence curves of the sample and reference, respectively, A and A_R are the absorption intensities of the sample and reference at the excitation wavelength, respectively, n and n_R are refractive indexes of the solvents used for the sample and reference, respectively. Zinc phthalocyanine (PcZn) in DMSO ($\Phi_R = 0.20$) [17] was used as a reference standard.

Table 1
Experimental data on X-ray diffraction study of **1** and **2**.

Compound	1	2
Empirical formula	C69 H46 N8 O4 Zr	C69 H46 Hf N8 O4
Crystal size	0.42 × 0.25 × 0.12	0.48 × 0.32 × 0.25
Formula weight	1142.36	1229.63
Temperature, K	173	100
Crystal system, space group	Monoclinic, P2(1)/c	Monoclinic, P2(1)/c
Unit cell dimensions	$a = 13.9444(2)$ Å	$a = 13.9021(2)$ Å
	$b = 30.0298(4)$ Å	$b = 29.9157(5)$ Å
	$c = 13.4931(2)$ Å	$c = 13.4438(2)$ Å
	$\beta = 105.5400(10)$	$\beta = 105.6680(10)$
Volume	5443.65(13)	5383.40(14)
Z, Calculated density, g/cm^3	4, 1.394	4, 1.517
μ, mm^{-1}	0.263	1.999
F(000)	2352	2480
θ range	$1.36 \le \theta \le 26.44$	$1.36 \le \theta \le 30.63$
Limiting indices	$-17 \le h \le 17$	$-19 \le h \le 19$
	$-37 \le k \le 35$	$-42 \le k \le 42$
	$-16 \le l \le 16$	$-19 \le l \le 18$
Reflections collected/ unique	43354/11162 [R(int) = 0.0528]	62100/16398 [R(int) = 0.0337]
Data/restraints/ parameters	11162/0/740	16398/0/740
Goodness-of-fit on F^2	1.021	1.024
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0408$, $wR2 = 0.0902$	$R1 = 0.0275$, $wR2 = 0.0613$
R indices (all data)	$R1 = 0.0699$, $wR2 = 0.1032$	$R1 = 0.0366$, $wR2 = 0.0646$
Largest diff. peak and hole	0.315 and −0.382	1.335 and −0.801

2.4. Synthesis

2.4.1. Bis(dibenzoylmethanato)zirconium(IV) phthalocyanine ($PcZrL_2$, 1)

A 0.5 mmol (337 mg) sample of di(chloro)zirconium (IV) phthalocyanine was suspended in toluene (10 mL), and dibenzoylmethane (268.8 mg, 1.2 mmol) was added. The reaction mixture was heated at 110 °C for 5–6 h under reflux (evolution in HCl). The hot solution was filtered for separation from starting materials. A single crystal was formed by cooling the resulting solution. After the single crystal was extracted the mixture was evaporated up to half of the starting volume and cooled to the room temperature. Then hexane (10 mL) was added to the solution and the formed crystals of the bis(dibenzoylmethanato)zirconium phthalocyanine complexes were isolated and washed thoroughly with hexane. The synthesized complexes were air-dried initially, and after that dried in vacuum at 60 °C for 8 h. Yield 70%. IR (KBr pellets): ν_{max}/cm^{-1} 3060, 1595, 1528, 1480, 1385, 1330, 1290, 1225, 1160, 1120, 1078, 898, 750, 735,690, 640, 545, 315. UV/Vis (toluene, λ_{max}/nm, (log ε)) 340 (5.05), 617 (4.56), 656sh (4.48), 683 (5.31). ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 9.39–9.36 (q, Pc, 4H$^{\alpha}$), 9.14–9.11 (q, Pc, 4H$^{\alpha}$), 8.31–8.29 (q, Pc, 4H$^{\beta}$), 8.05–8.03 (q, Pc, 4H$^{\beta}$), 7.47 (t, *p*-Ar–H, 4H), 7.23 (t, *m*-Ar–H, 8H), 7.04 (d, *o*-Ar–H, 8H), 5.72 (s, CH, 2H). GALDI, *m*/*z*: 824.7 [PcZrL]$^+$, 864.1 [PcZrL + K]$^+$, **1047.6 [PcZrL$_2$]$^+$**. Anal. Calcd., %, for **$C_{62}H_{38}N_8O_4Zr$**:− C 70.91, H 3.65, N 10.67, Zr 8.69; found C 70.75, H 3.48, N 10.30, Zr 8.80.

2.4.2. Bis(dibenzoylmethanato)hafnium(IV)phthalocyanine ($PcHfL_2$, 2)

Compound **2** was synthesized according to the same methodic as **1**. The 0.5 mmol (381 mg) of di(chloro) hafnium (IV) phthalocyanine and 1.2 mmol (268.8 mg) dibenzoylmethane were used for the synthesis. Yield 75%. IR (KBr pellets): ν_{max}/cm^{-1} 3060, 1595, 1530, 1482, 1395, 1335, 1290, 1225, 1163, 1120, 1080, 900, 750, 735, 690, 625, 555, 320. UV/Vis (toluene, λ_{max}/nm, (log ε)) 340 (5.05), 617 (4.54), 655sh (4.48), 683 (5.30). ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 9.38–9.36 (q, Pc, 4H$^{\alpha}$), 9.14–9.12 (q, Pc, 4H$^{\alpha}$), 8.31–8.29 (q, Pc, 4H$^{\beta}$), 8.06–8.04 (q, Pc, 4H$^{\beta}$), 7.47 (t, *p*-Ar–H, 4H), 7.22 (t, *m*-Ar–H, 8H), 7.01 (d, *o*-Ar–H, 8H), 5.67 (s, CH, 2H). GALDI, *m*/*z*: 915.0 [PcHfL]$^+$, 954.5 [PcHfL + K]$^+$, **1138.0 [PcHfL$_2$]$^+$**, 1826.7 [(PcHfL)$_2$]$^+$, 1869.2 [(PcHfL)$_2$ + K]$^+$, 2051.7 [PcHfL + PcHfL$_2$]$^+$. Anal. Calcd., %, for

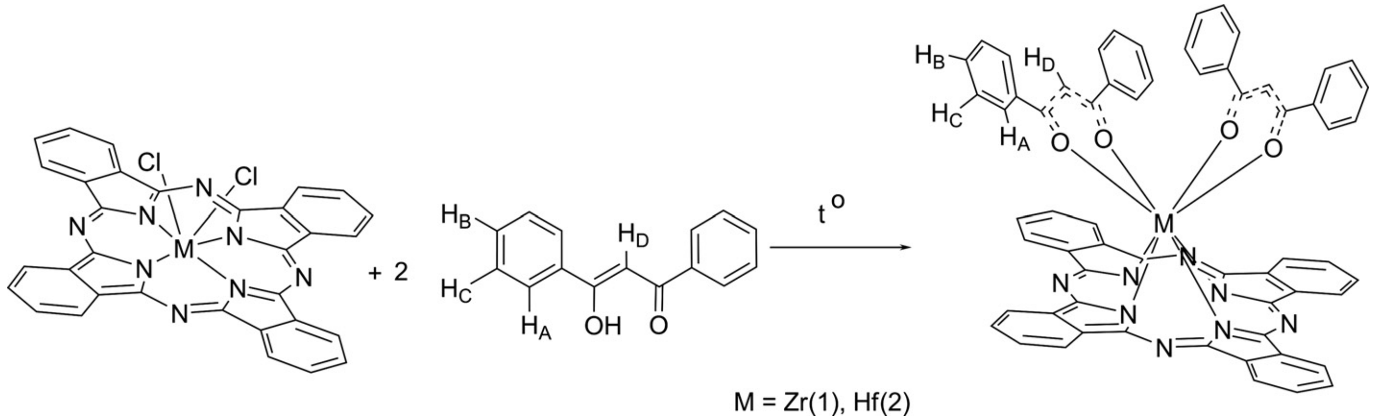

Fig. 1. Synthesis of the bis(dibenzoylmethanato)zirconium(IV) (**1**) and hafnium(IV) (**2**) phthalocyanines.

$C_{62}H_{38}N_8O_4Hf$:— C 65.47, H 3.37, N 9.85, Hf 15.69; found C 65.60, H 3.57, N 9.45, Hf 15.47.

3. Results and discussion

3.1. Synthesis

The method of modification of di(chloro)zirconium and hafnium phthalocyanines, which allows access to the phthalocyanine complexes of zirconium (IV) and hafnium (IV) with coordinated out-of-plane of macrocycle β-dicarbonyl and other chelating ligands was reported earlier in Refs. [7,8,18].

The synthesis of bis(dibenzoylmethanato)zirconium(IV) and hafnium(IV) phthalocyanines was carried out in toluene under reflux and yields were 70% and 75% for **1** and **2,** respectively (Fig. 1).

The composition and structure of the studied complexes were determined by elemental analysis and spectroscopic methods (IR, ^{1}H NMR). The IR spectra of synthesized complexes display vibrational peaks, which are assigned to phthalocyanines macrocycle vibrations [12].

The coordination of two dibenzoylmethane ligands to the central atom of the macrocycle was shown by the ^{1}H NMR spectra. ^{1}H NMR spectra for the compounds **1** and **2** recorded in $CDCl_3$ are very similar. Proton signals in ^{1}H NMR spectra (Fig. 2) can be divided into two groups: signals of phthalocyanine protons ($^{\alpha}$H – 9.40–9.10; $^{\beta}$H – 8.30–8.05 ppm) and signals of out-of-plane ligand protons (Ar–H –7.50–7.05 ppm; CH–5.72 ppm). The position and morphology of the signals of phenyl protons of the phthalocyanine macrocycle are consistent with the literature data [19]. The signals of the out-of-plane ligands undergo significant changes, as compared with the signals of the free dibenzoylmethane.

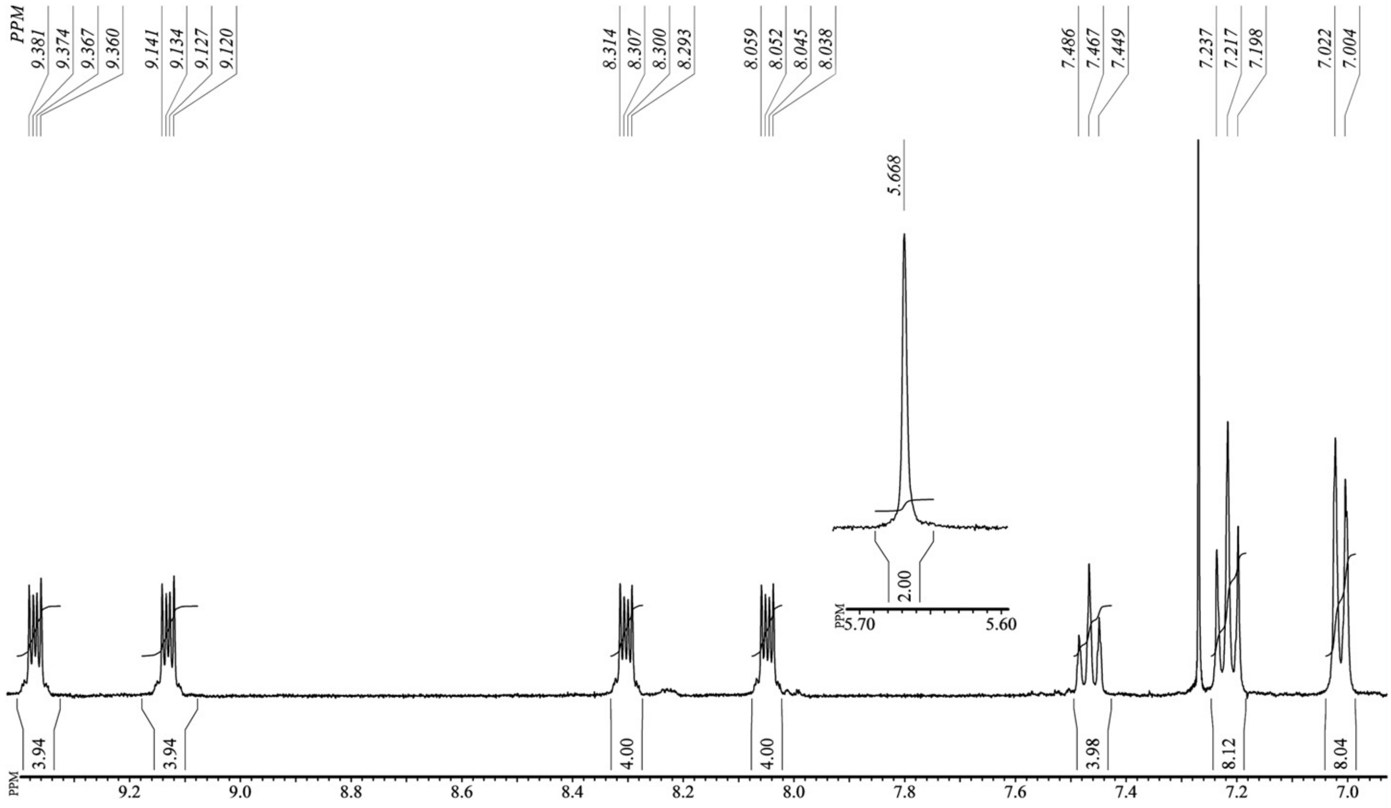

Fig. 2. ^{1}H NMR spectra of **2** complex in $CDCl_3$.

Table 2
Selected bond parameters for **1** and **2**.

Zr(1)–O(1)	2.1610(16)	Hf(1)–O(4)	2.1577(14)
Zr(1)–O(4)	2.1658(16)	Hf(1)–O(2)	2.1591(14)
Zr(1)–O(3)	2.1730(17)	Hf(1)–O(1)	2.1658(14)
Zr(1)–O(2)	2.1807(16)	Hf(1)–O(3)	2.1719(14)
Zr(1)–N(1)	2.282(2)	Hf(1)–N(5)	2.2641(17)
Zr(1)–N(5)	2.289(2)	Hf(1)–N(3)	2.2780(16)
Zr(1)–N(7)	2.2940(19)	Hf(1)–N(1)	2.2800(16)
Zr(1)–N(3)	2.303(2)	Hf(1)–N(7)	2.2919(16)

^{1}H NMR spectrum of the initial dibenzoylmethane in the aromatic part consists of four groups of signals: a singlet of methine proton (D) at 6.88 ppm (1H), a multiplet of *o*-phenyl protons (A) at 8.00 ppm (4H), a multiplet of *p*-phenyl protons (B) at 7.56 ppm (2H) and a multiplet of *m*-phenyl protons (C) at 7.51 (4H) (designations of the atoms are shown in Fig. 1). In the ^{1}H NMR spectra of the complexes **1** and **2** the shift of the methine proton singlet (D) to upfield 5.67 ppm (2H) and the morphology changes of the phenyl proton signals of out-of-plane ligands are observed. *o*-Phenyl proton multiplet (A) for initial dibenzoylmethane is manifested as a doublet, while in the spectra of the complexes **1** and **2** its position shifts to 7.00 ppm (8H); *p*-phenyl proton multiplet (B) is observed as a triplet and its position shifts to 7.47 ppm (4H); *m*-phenyl protons multiplet (C) is observed as a triplet and its position shifts to 7.22 ppm (8H). Thus, the ligands signals in the spectra of complexes exhibit greater splitting and are shifted up field compared with those of the free dibenzoylmethane signals. Cone anisotropy shifts the signal of methine proton (D) on 1.2 ppm, and signals of *o*-, *m*- and *p*-phenyl protons on 1.0, 0.3 and 0.1 ppm, respectively. Related changes in the ^{1}H NMR spectra of out-of-plane ligands were reported previously in Refs. [7,8].

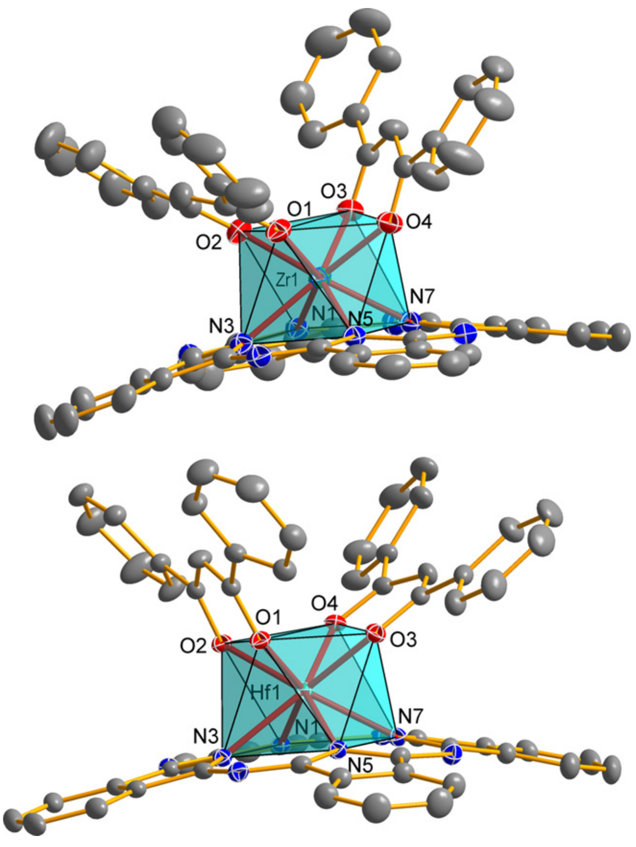

Fig. 3. Ortep III diagrams of the compounds **1** (up) and **2** (down). Thermal ellipses are shown at 50% probability. Hydrogen atoms and solvent toluene molecule are omitted for clarity.

3.2. *X-ray diffraction study*

The green-blue prism of Zr (**1**) and Hf (**2**) phthalocyanine complexes crystallize in the monoclinic crystal system (space group P2$_1$/c) with similar cell parameters (Table 2) thus suggesting them to be isomorphic. The asymmetric units of both compounds contain one molecule of complex (Fig. 3) and one toluene molecule. The central atoms of Zr1 (**1**) and Hf1 (**2**) exhibit nearly regular square-antiprism ZrN$_4$O$_4$ and HfN$_4$O$_4$ coordination geometries respectively (Fig. 4). The Zr–O and Hf–O bond lengths are in the close range between 2.1577(14) and 2.1807(16) Å. At the same time, the Zr–N and Hf–N bonds are slightly longer having the values in the range 2.2641(17)–2.303(2) Å. The adjacent O–Zr–O, N–Zr–N, O–Hf–O and N–Hf–N angles in the polyhedron are in the range 70.99(5)–74.91(6)°; the opposite O–Zr–N and O–Hf–N angles have a values from 139.69(6)° to 143.96(5)°. The phthalocyanine macrocycle in the both complexes has a non-planar structure with crown-like distortion in the direction, opposite to the central metal ions. The nitrogen atoms N1, N3, N5 and N7 lie in the plane, which match to one of the coordination polyhedron's base. The distances between the central ion and the polyhedron base are 1.2105(2) Å for (**1**) and 1.1840(1) Å for (**2**) (Fig. 4). Two dibenzoylmethane molecules coordinated bidentantly at opposite site of phthalocyanine macrocycle forming two metallarings with an envelope conformation with different degree of distortion. One of the metallarings in each complex exhibits smaller distortion and forms dihedral angles of 12.31(12)° (Zr1/O1/C33/C34/C35/O2) and 13.21(10)° (Hf1/O3/C48/C49/C50/O4). The interplanar angles in another metallaring have approximately two times larger values: 25.43(10)° for Zr1/O3/C48/C49/C50/O4 and 26.23(9)° for Hf1/O1/C33/C34/C35/O2. The oxygen atoms O1, O2, O3 and O4 form regular plane forming another base of coordination polyhedron for both complexes. The distances from the central ion to mentioned plane are 1.1838(2) Å for Zr complex and 1.1809(1) Å for Hf complex. Two coordinated dibenzoylmethane molecules in both cases (Zr and Hf) have a near planar structure and form dihedral angles of 77.35(6)° in the case of Zr complex and 77.37(4)° in the case of Hf one.

As expected, due to the similarities in molecular structure and cell parameters, the crystal structures of Zr and Hf complexes are similar. The packing diagrams of the Zr and Hf complexes are shown in Fig. 5. In the crystal structures of the both compounds, the molecules interact via numerous weak C–H…π, π…π and Van der Waals interactions. The geometrical parameters of strong interactions with Cg…Cg distances less than 4.5 Å are given in Tables 3 and 4.

3.3. *GALDI-MS studies*

Studied complexes have similar GALDI spectra (Fig. 6) in the mass range lower than [M$^+$]. They contain easily identified intensive peaks of [PcML]$^+$ and peaks of [PcML + K]$^+$ (L – dibenzoylmethane) adducts with low-intensity. The ratio between intensities of the peaks is 4:1 for zirconium-containing and 24:1 for hafnium-containing fragments. This points that ionization of [PcHfL]$^+$ does not occur in presence of potassium ion. Peaks of molecular ions [PcML$_2$]$^+$ are relatively low-intensity, and bands corresponding to potassium adducts of molecular ions are not observed. A comparison of theoretically calculated and experimental isotopic distribution models for the molecular ions of both complexes is carried out (Fig. 6). It should be noted that both the molecular ions and fragments of the [PcML]$^+$ are very stable under the GALDI experiment conditions.

However, significant differences are observed in the spectra of these compounds in the mass range higher than molecular ion mass. In the spectrum of compound **1** no peaks detected in this region. At the same time for **2** the bands corresponding to ions of $[(\mathrm{PcHfL})_2]^+$, $[(\mathrm{PcHfL})_2 + \mathrm{K}]^+$, and also $[\mathrm{PcHfL} + \mathrm{PcHfL}_2]^+$ are present in the spectra. This indicates high ability of hafnium-containing fragments to associate in the gas phase. For both complexes only fragments, containing one dibenzoylmethane ligand are able to form the potassium adducts.

3.4. Absorption and fluorescence studies

Absorption and emission spectra and their characteristics of **1** and **2** are presented on Figs. 7 and 8 and in Table 5. In UV–vis spectra of **1** and **2** two pronounced absorption bands, namely the intense Q-band in visible region and the B band in UV region were

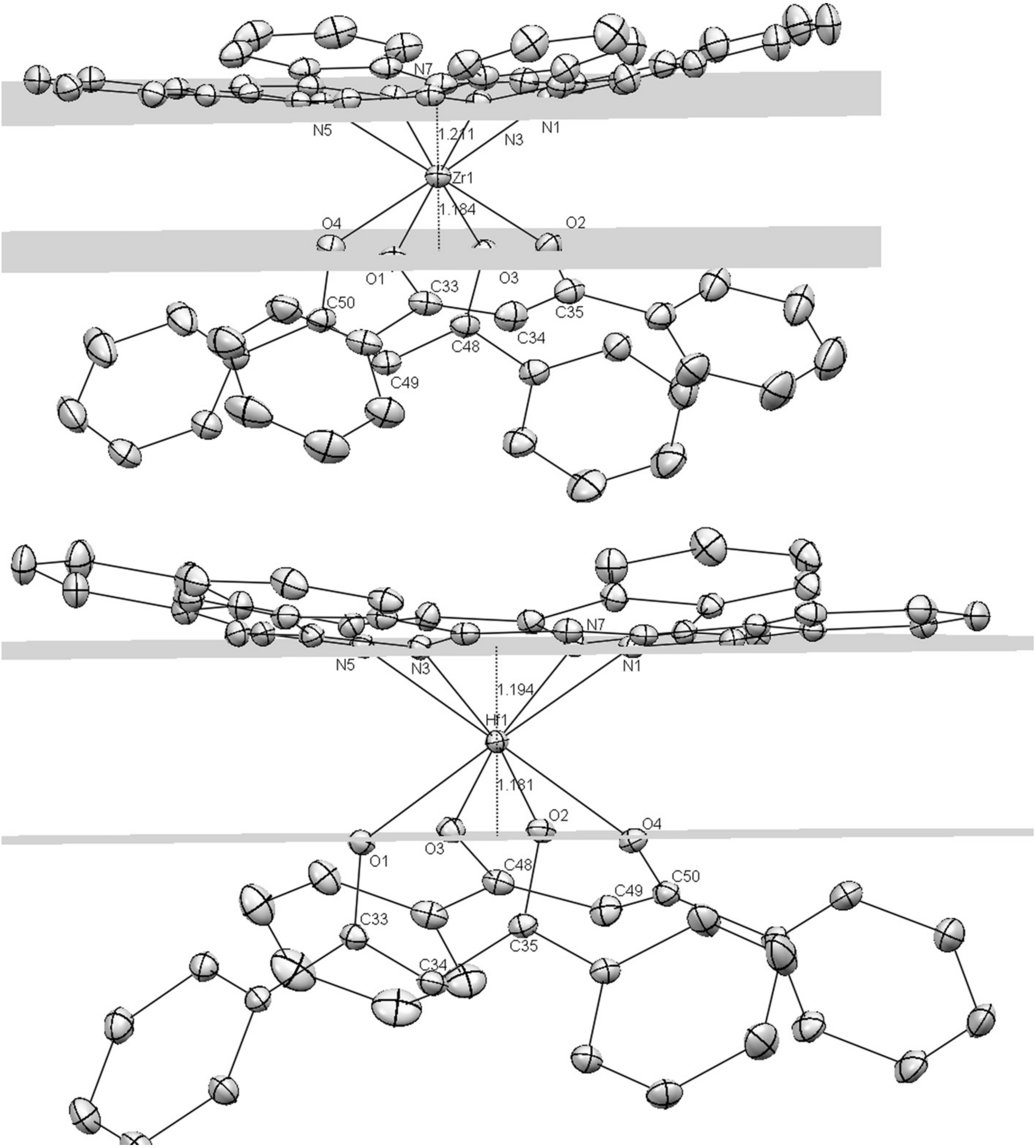

Fig. 4. Molecular structure of compounds **1** and **2** with labeling scheme for coordination environment of central atoms and metallarings. The planes representing the bases of coordination polyhedron are shown. Thermal ellipses are shown at 30% probability. Hydrogen atoms and solvent toluene molecule are omitted for clarity.

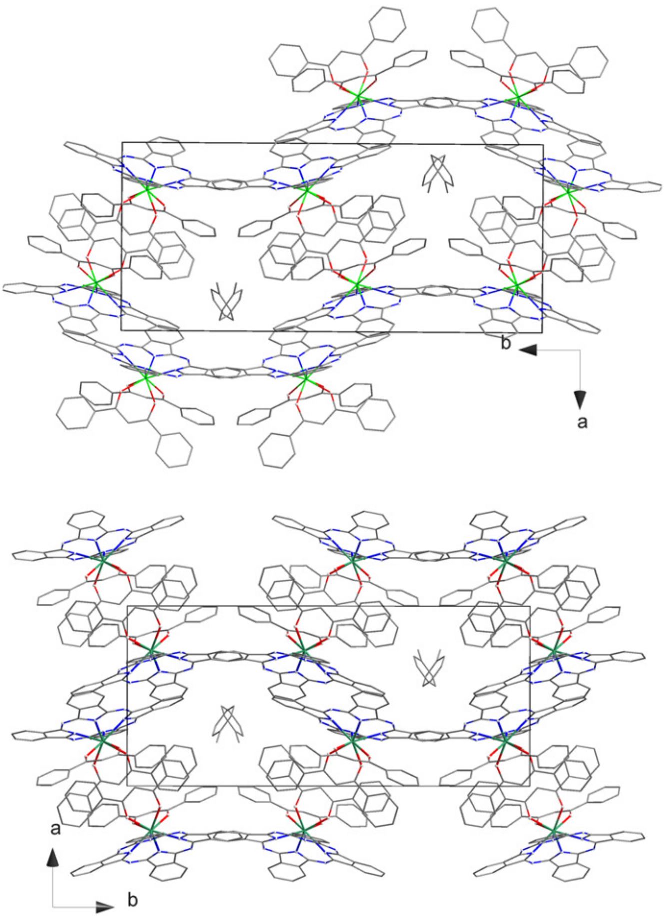

Fig. 5. Packing wires/sticks diagrams of compounds **1** (up) and **2** (down) along *c* direction.

observed (Table 5). The absorption positions of Q-band at 680–690 nm, shoulder at 615 nm and B band at 340 nm for **1** and **2** are typical for metal phthalocyanines [3], and have been ascribed to the deeper p/p* levels of LUMO transitions.

Beer–Lambert linearity is kept in the concentrations range $1 \cdot 10^{-6}$–$5 \cdot 10^{-5}$ M for solutions of studied compounds in toluene and DMSO. This points to the absence of aggregation processes in the foregoing concentration range. The nature of solvents slightly influences on the shape of the UV–vis spectra and the position of Q-band of the complexes. However, in spectra of compounds in toluene the splitting of the Q-band (Fig. 7) is observed, whereas in DMSO solutions, only widening of the bands is detected. Such changes in Q-band could not be explained in the terms of aggregation processes.

Table 3
Selected C–H…π, π…π interactions for compound **1**.

	Cg…Cg, Å	H…Cg, Å	X–H…Cg, deg	X…Cg, Å
Cg(1)…Cg(2)#1	4.3551(16)			
Cg(3)…Cg(3)#1	3.8293(15)			
Cg(3)…Cg(4)#1	4.2489(16)			
Cg(4)…Cg(7)#1	3.6449(16)			
Cg(6)…Cg(5)#2	4.412(2)			
Cg(7)…Cg(8)#3	3.8100(18)			
C(54)–H(54A)…Cg(9)#4	–	2.85	156	3.737(4)

Symmetry operations: #1 = 2 − *X*, −*Y*, 2 − *Z*; #2 = *X*, 1/2 − *Y*, −1/2 + *Z*; #3 = 1 − *X*, −*Y*, 2 − *Z*; #4 = *X*, 1/2 − *Y*, 1/2 + *Z*.
Centers of gravity of the rings: Cg1 = N(1)/C(1)/C(2)/C(3)/C(4); Cg2 = C(18)/C(19)/C(24)/C(23)/C(22)/C(21); Cg3 = N(5)/C(17)/C(18)/C(19)/C(20); Cg4 = N(7)/C(25)/C(26)/C(27)/C(28); Cg5 = C(2)/C(3)/C(8)/C(7)/C(6)/C(5); Cg6 = C(42)/C(43)/C(44)/C(45)/C(46)/C(47); Cg7 = C(51)/C(52)/C(53)/C(54)/C(55)/C(56); Cg8 = C(57)/C(58)/C(59)/C(60)/C(61)/C(62); Cg9 = C(63)/C(64)/C(65)/C(66)/C(67)/C(68).

Table 4
Selected C–H…π, π…π interactions for compound **2**.

	Cg…Cg, Å	H…Cg, Å	X–H…Cg, deg	X…Cg, Å
Cg(1)…Cg(1)#1	3.8193(12)			
Cg(1)…Cg(2) #1	4.2370(13)			
Cg(2)…Cg(4) #1	3.6576(13)			
Cg(3)…Cg(4) #1	4.3029(13)			
Cg(5)…Cg(6)#2	4.3829(15)			
Cg(7)…Cg(8)#3	3.8091(15)			
C(45)–H(45)…Cg(26)#4	–	2.80	158	3.700(3)

Symmetry operations: #1 = 1 − *X*, 1 − *Y*, 2 − *Z*; #2 = *X*, 3/2 − *Y*, 1/2 + *Z*; #3 = −*X*, 1 − *Y*, 2 − *Z*; #4 = −*X*, 1/2 + *Y*, 3/2 − *Z*.
Centers of gravity of the rings: Cg1 = N(1)/C(1)/C(2)/C(3)/C(4); Cg2 = N(3)/C(9)/C(10)/C(11)/C(12); Cg3 = N(5)/C(17)/C(18)/C(19)/C(20); Cg4 = C(2)/C(3)/C(8)/C(7)/C(6)/C(5); Cg5 = C(18)/C(19)/C(24)/C(23)/C(22)/C(21); Cg6 = C(57)/C(58)/C(59)/C(60)/C(61)/C(62); Cg7 = C(36)/C(37)/C(38)/C(39)/C(40)/C(41); Cg8 = C(42)/C(43)/C(44)/C(45)/C(46)/C(47); Cg9 = C(63)/C(64)/C(65)/C(66)/C(67)/C(68).

The values of the second derivative of the Q-band (Table 5) show that the splitting value for both complexes is approximately 11 nm. Similar splitting or broadening is observed in the electronic spectra of the phthalocyanine complexes of zirconium and hafnium with different β-dicarbonyl ligands [8,11]. In the case of complexes with asymmetric β-dicarbonyl ligands the broadening of the band is usually detected. In some papers [20] such broadening or splitting

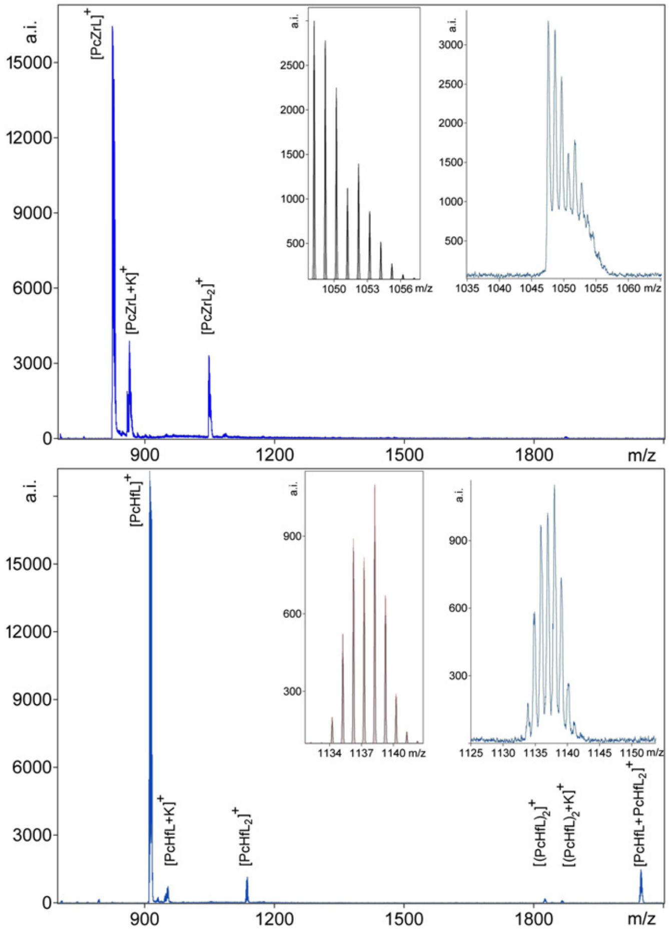

Fig. 6. Positive ion in reflectron mode GALDI-MS spectra of **1** (top) and **2** (bottom) obtained in graphite matrix using nitrogen laser accumulating 10 laser shots. Inset spectra shows calculated and expanded molecular mass region molecular ion of the complexes.

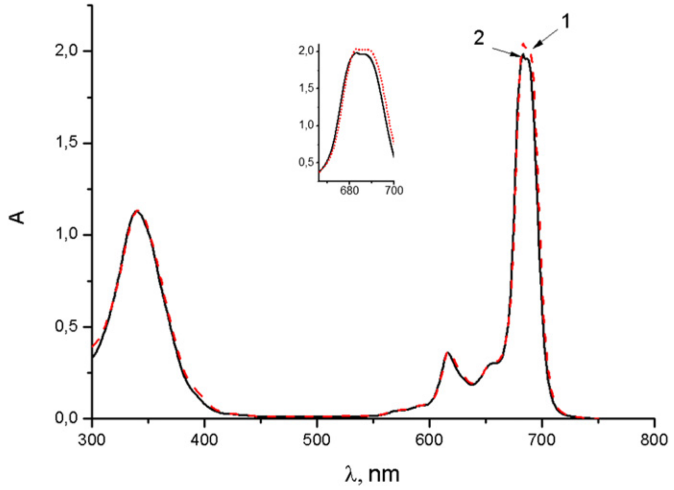

Fig. 7. UV–vis spectra of complex **1** (dash) and **2** (solid) in toluene ($C = 1 \cdot 10^{-5}$ mol/l). Inset spectra shows expanded Q-band region.

is explained by due to exciton coupling between the macrocycle and the out-of-plane ligand. In opposite to typically flat phthalocyanine macrocycles, studied compounds have dome shaped macrocycles that causes an additional lowering of the molecule symmetry. In our opinion, the splitting or broadening of the Q-band is related not only with a domed structure of the macrocycle but also with the presence of two rigid out-of-plane ligands bound to the central metal atom. For example, according to the X-ray diffraction of titanyl phthalocyanine [21] and titanium phthalocyanine dichloride [22], the macrocycle has a domed structure but the splitting of the Q-band in the electronic spectra is not observed [12].

Complexes **1** and **2** have similar electronic absorption and fluorescence excitation spectra. The fluorescence spectra are red-shifted with respect to the absorption spectra (Fig. 8). The Stokes shift between the absorption Q-band and the fluorescence spectra maximum is very small (6–10 nm) (Table 5).

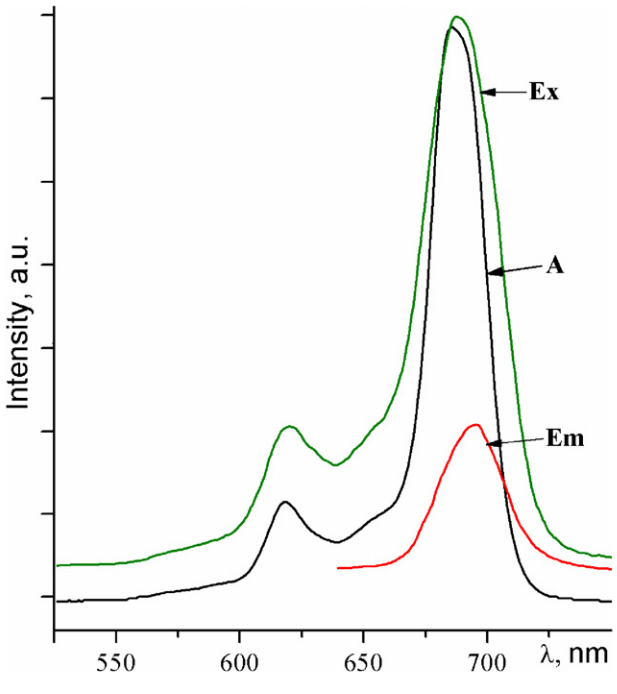

Fig. 8. Absorption (A), excitation (Ex) and emission (Em) spectra of **1** in DMSO ($C = 2.10^{-6}$ mol/l, excitation wavelength – 620 nm).

Table 5
Spectral parameters of investigated complexes.

Complex	Solvent	Q-band λ_{abs}, nm, (log ε)	Q-band 2nd derivative λ_{abs}, nm	Excitation λ_{ex}, nm	Emission λ_{em}, nm	Stokes shift Δ_{Stokes}, nm	Φ_F
PcZn	DMSO	671 (5.29)	–	674	679	8	0.2
1	DMSO	687 (5.22)	683, 694	687	695	8	0.02
	Toluene	683 (5.31)	681, 693	689	693	10	0.01
2	DMSO	687 (5.23)	683, 694	690	693	6	0.0019
	Toluene	683 (5.30)	680, 691	691	693	10	0.0011

The fluorescence quantum yield (Φ_F) values for the obtained complexes are low (Table 5) which is typical for phthalocyanine complexes zirconium and hafnium [7]. It should be noted that fluorescence quantum yield is noticeably higher for the Zr complex (0.02) than that for the Hf complex (0.0019). The solvent also affects the fluorescence quantum yield, particularly in toluene the values of quantum yield are lower than in DMSO (Table 5). This fact is in accord with previously published data and could be explained by the heavy atom effect, i.e. the enhancement of intersystem crossing of the excitation from the singlet state to the triplet one, thereby reducing the fluorescence quantum yield [23].

4. Conclusion

In summary, the synthesis of two novel out-of-plane substituted zirconium (IV) and hafnium (IV) phthalocyanine complexes is reported. The compounds were characterized by elemental analysis, GALDI mass spectroscopy, IR- and ^{1}H NMR spectroscopy and single-crystal X-ray diffraction. The synthesized compounds possess the similar molecular and crystal structure as well as spectral properties due to the similarity of the central atom properties (electronic configuration, ionic radius, valency, oxidation state, coordination geometry). A noticeable difference was observed in the fluorescence spectra and GALDI mass spectra of these complexes. Splitting of the Q-band was found in the electronic spectra. It is considered to be related to a lowering of symmetry of complexes due to the presence of two rigid ligands at the central metal atom of the macrocycle. Fluorescence quantum yield values of synthesized complexes were determined in toluene and DMSO by a comparative method. The fluorescence quantum yield value of the hafnium complex is significantly lower than that for zirconium complex and is explained by the heavy atom effect.

Acknowledgment

This work was supported by a STCU-NASU grant № 5508.

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