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Synthesis and luminescent properties of new zirconium(IV) and hafnium(IV) phthalocyanines with various carbonic acids as out-planed ligands

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Abstract

A range of zirconium(IV) and hafnium(IV) phthalocyanines with various carboxylic acids as out-planed ligands has been synthesized by a direct interaction between di(chloro)zirconium(IV)- or hafnium(IV)-phthalocyanines and carboxylic acids. Coordination of two acid fragments is suggested to occur in a *cis*-geometry about the central atom of the macrocycle as evidenced on the basis of ^{1}H NMR, UV–vis and elemental analysis data. Absorption and fluorescence spectroscopic studies have been analyzed in different solvents. These compounds are non-aggregated in the organic solvents. Fluorescence quantum yields (Φ_F) and natural lifetimes (τ) of zirconium phthalocyanine complexes have been calculated in toluene and DMSO.

Keywords: Zirconium and hafnium phthalocyanines; Synthesis; UV–vis spectroscopy; Fluorescence; Quantum yield; Natural lifetime

1. Introduction

Phthalocyanines are pigment dyes that contain π-electron system in the molecular structure which provide them unique spectroscopic and photoelectric properties. They are characterized by significant absorption in the visible region, and large molar extinction coefficient. Phthalocyanines have been investigated for various applications including the production of molecular wires [1], catalysts [2], new optical materials [3–5], and components of molecular-based information storage systems [6]. Moreover, phthalocyanine systems have medical applications and are being used as photosensitizers in photodynamic therapy [7–9].

In our previous papers [10–13] we have studied the spectral, electrochemical and biological properties of zirconium and hafnium phthalocyanines with different out-planed organic ligands. Now our interest in the investigation of fluorescence properties of dyes arises from the application of zirconium and hafnium phthalocyanines in photodynamic therapy. Metallophthalocyanines can aggregate in solution and such aggregation diminishes the photosensitising ability of MPc complexes. Introduction of out-plane ligands to the central metal atom of MPc complexes is known to influence the properties of the metallophthalocyanines to a large degree. Solvents have influence on aggregation in Pc complexes. Aqueous solvents give a high level of complex aggregation; at the same time, organic solvents are known to reduce aggregation process. Solvents also affect the photophysical and photochemical properties of MPc complexes [14].

In this work we present the synthesis and spectral luminescence properties of new axial substituted zirconium and hafnium phthalocyanines with different carbonic acids: octanoic (complexes **I**, **II**), 4-*n*-hexyloxybenzoic (complexes **III**, **IV**) and 11-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)undecanoic acids (complexes **V**, **VI**) (Fig. 1).

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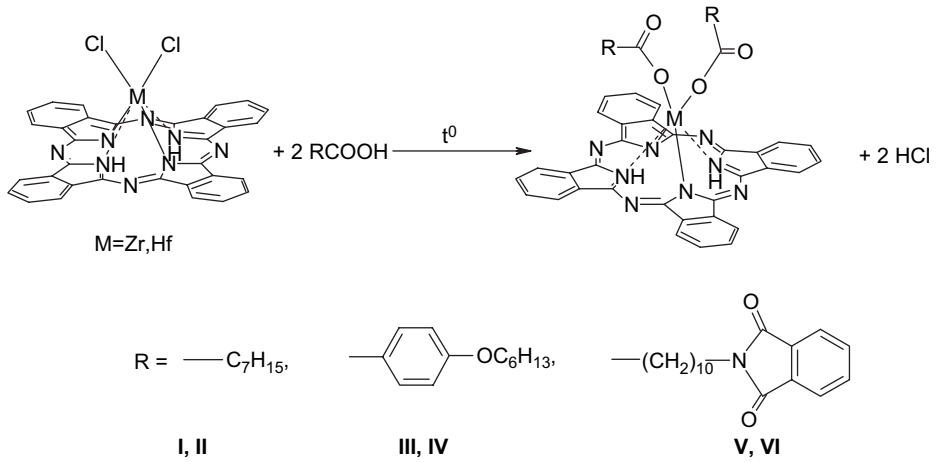

Fig. 1. Synthesis of the axially substituted phthalocyaninato metal complexes with carboxylic acid ligands.

2. Experimental

2.1. General

^{1}H NMR spectra were recorded on a Varian (300 MHz) spectrometer ($CDCl_3$/TMS). The MALDI-TOF mass spectra were obtained on a Bruker Daltonics (autoflex II). The UV–vis absorption spectra were obtained on a Specord M-40 in DMSO and toluene ($c = 10^{-6}$ mol/l, $l = 1$ sm). Steady-state fluorescence spectra were collected with a spectrofluorimeter Hitachi 1200.

The fluorescence quantum yields of dyes were determined by the comparative method [15,16] on the ground of the UV–vis and fluorescence spectra, using the following equation:

$$\Phi := \Phi_R \frac{n^2 S A_R}{(n_R)^2 S_R A} \quad (1)$$

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, respectively, n and n_R are refractive indexes for the sample and reference, respectively. Zinc phthalocyanine (PcZn) in DMSO ($\Phi_R = 0.20$) [17] was used as a reference standard. The natural lifetime of the studied phthalocyanine complexes was evaluated from absorption and fluorescence spectra by the known method [15,16], using the following equation:

$$\frac{1}{\tau} := 2.288 \times 10^{-9} n^2 \int \frac{\varepsilon(\lambda)}{\lambda} d\lambda \frac{\int \frac{F(\lambda)}{\lambda^2} d\lambda}{\int F(\lambda)\lambda \, d\lambda} \quad (2)$$

where n is refractive index, and integrals of $F(\lambda)$ and $\varepsilon(\lambda)$ are the areas under the fluorescence and absorption spectra, respectively.

2.2. Materials and synthesis

All reactions were carried out under atmospheric conditions. Dimethyl sulfoxide (DMSO) and ethanol were used without further purification; octanoic, 4-*n*-hexyloxybenzoic and 11-aminoundecanoic acids and phthalodinitrile were purchased from commercial suppliers and used without purification. 11-(1,3-Dioxo-1,3-dihydro-2*H*-isoindol-2-yl)undecanoic acid was synthesized by the literature methods [18]. Initial dichloro(phthalocyaninato)zirconium(IV) ($PcZrCl_2$) and hafnium(IV) ($PcHfCl_2$) were prepared by the reaction of MCl_4 with phthalodinitrile according to the published procedures [19].

2.2.1. Synthesis of bis(octanoato)zirconium(IV) and -hafnium(IV) phthalocyanines (*I*, *II*)

A 0.7 mmol sample of $PcMCl_2$ was suspended in 10 ml of toluene, and 1.7 mmol octanoic acid was added. The reaction mixture was heated at 120 °C for 5–6 h under reflux (evolution in HCl). The hot solution was filtrated for separation from starting materials. The resulting solution was evaporated two times and cooled to room temperature. After that hexane was added to the solution and the formed crystals of the bis(octanoato)-zirconium or hafnium phthalocyanine complexes were isolated and washed abundantly with hexane. The synthesized complexes were first air-dried, and after that dried in vacuum at 60 °C for 8 h. Yield 68%.

Compound ***I***. Anal. Calcd. % for $C_{48}H_{48}N_8O_4Zr$: C 64.62, H 5.42, N 12.56, Zr 10.22; Found C 65.05, H 5.15, N 12.10, Zr 10.60. ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 9.18 (m, Pc, 8H), 8.03 (m, Pc, 8H), 1.04 (q, $2CH_2$, 4H), 0.78 (m, 2(–CH_2CH_3), 10H), 0.55 (q, $2CH_2$, 4H), 0.43 (q, $2CH_2$, 4H), 0.22 (q, $2CH_2$, 4H), 0.02 (q, $2CH_2$, 4H). IR data: ν 2930, 2860 cm^{-1} (C–H, alkyl), 1630, 1530, 1500, 1470, 1420 cm^{-1} (COOZr). MALDI-TOF-MS (toluene) Calcd. 748.98 $PcZr(OOCC_7H_{15})^+$, 605.78 $PcZr^{2+}$; Found 744.96 $PcZr(OOCC_7H_{15})^+$, 607.82 $PcZr^{2+}$.

Compound ***II***. Yield 62%. Anal. Calcd. % for $C_{48}H_{48}N_8O_4Hf$: C 58.86, H 4.94, N 11.44, Hf 18.22; Found C 59.25, H 4.45, N 11.05, Hf 18.50. ^{1}H NMR (300 MHz,

$CDCl_3$) δ, ppm: 9,18 (m, Pc, 8H), 8.02 (m, Pc, 8H), 1.04 (q, $2CH_2$, 4H), 0.78 (m, 2(−CH_2CH_3), 10H), 0.54 (q, $2CH_2$, 4H), 0.39 (q, $2CH_2$, 4H), 0.21 (q, $2CH_2$, 4H), −0.01 (q, $2CH_2$, 4H). IR data: ν 2930, 2860 cm^{-1} (C−H, alkyl), 1610, 1540, 1500, 1470, 1420 cm^{-1} (COOHf). MALDI-TOF-MS (toluene) Calcd. 834.24 $PcHf(OOCC_7H_{15})^+$, 691.03 $PcHf^{2+}$; Found 833.59 PcHf $(OOCC_7H_{15})^+$, 700.74 $PcHf^{2+}$.

Compounds **III**−**IV** were synthesized by the same procedure used for compounds **I** and **II**.

*Compound **III***. It was prepared from $PcZrCl_2$ and 4-*n*-hexyloxybenzoic acid. Yield 55%. Anal. Calcd. % for $C_{58}H_{52}N_8O_6Zr$: C 66.45, H 5.00, N 10.69, Zr 8.70; Found C 66.10, H 5.40, N 10.05, Zr 8.50. ^1H NMR (300 MHz, $CDCl_3$) δ, ppm: 9.49 (m, Pc, 8H), 8.20 (m, Pc, 8H), 6.66 (d, 2Ar, 4H), 6.25 (d, 2Ar, 4H), 3.64 (t, $2CH_2$, 4H), 3.52 (s, CH_2, 2H), 1.55 (q, $2CH_2$, 4H), 1.22 (s, $2CH_3$ and CH_2, 8H), 0.83 (q, $2CH_2$, 4H), 0.03 (q, $2CH_2$, 4H). IR data: ν 2930, 2860 cm^{-1} (C−H, alkyl), 1605, 1520, 1500, 1460, 1425 cm^{-1} (COOZr). MALDI-TOF-MS (toluene) Calcd. 1046.32 $PcZr(OOCC_6H_4OC_6H_{13})_2$, 825.04 $PcZr(OOCC_6H_4OC_6H_{13})^+$, 755.91 $PcZr(OOCC_6H_4)^{\bullet+}$; Found 1045.38 $PcZr(OOCC_6H_4OC_6H_{13})_2$, 824.38 $PcZr(OOCC_6H_4OC_6H_{13})^+$, 755.15 $PcZr(OOCC_6H_4)^{\bullet+}$.

*Compound **IV***. It was prepared from $PcHfCl_2$ and 4-*n*-hexyloxybenzoic acid. Yield 58%. Anal. Calcd. % for $C_{58}H_{52}N_8O_6Hf$: C 61.35, H 4.62, N 9.87, Hf 15.72; Found C 61.50, H 4.10, N 9.25, Zr 15.50. ^1H NMR (300 MHz, $CDCl_3$) δ, ppm: 9.32 (m, Pc, 8H), 8.12 (m, Pc, 8H), 6.59 (d, 2Ar, 4H), 6.21 (d, 2Ar, 4H), 3.60 (t, $2CH_2$, 4H), 3.49 (s, CH_2, 2H), 1.52 (q, $2CH_2$, 4H), 1.19 (s, $2CH_3$ and CH_2, 8H), 0.81 (q, $2CH_2$, 4H), 0.01 (q, $2CH_2$, 4H). IR data: ν 2930, 2860 cm^{-1} (C−H, alkyl), 1585, 1520, 1500, 1460, 1425 cm^{-1} (COOHf). MALDI-TOF-MS (toluene) Calcd. 912.31 $PcHf(OOCC_6H_4OC_6H_{13})^+$, 843.18 $PcHf(OOCC_6H_4)^{\bullet+}$, 723.03 $PcHf(OO)^{2-}$, 691.03 $PcHf^{2+}$; Found 913.58 $PcHf(OOCC_6H_4OC_6H_{13})^+$, 843.78 $PcHf(OOCC_6H_4)^{\bullet+}$, 723.68 $PcHf(OO)^{2-}$, 700.13 $PcHf^{2+}$.

*Compound **V***. It was prepared from $PcZrCl_2$ and 11-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)undecanoic acid. Yield 42%. Anal. Calcd. %, for $C_{70}H_{66}N_{10}O_8Zr$: C 66.38, H 5.25, N 11.06, Zr 7.20; Found C 66.70, H 5.80, N 10.85, Zr 7.50. ^1H NMR (300 MHz, $CDCl_3$) δ, ppm: 9.45 (m, Pc, 8H), 8.20 (m, Pc, 8H), 7.82 (d, 2Ar, 4H), 7.70 (d, 2Ar, 4H), 3.68 (t, $2CH_2$, 4H), 1.66 (q, $2CH_2$, 4H), 1.25 (m, $5CH_2$, 10H), 1.07 (q, $2CH_2$, 4H), 0.88 (q, $2CH_2$, 4H), 0.58 (q, $3CH_2$, 6H), 0.32 (q, $2CH_2$, 4H), 0.15 (q, $2CH_2$, 4H). IR data: ν 2930, 2860 cm^{-1} (C−H, alkyl), 1770 cm^{-1} (C═O), 1630, 1580, 1400 cm^{-1} (COOZr). MALDI-TOF-MS (toluene) Calcd. 1264.57 $PcZr(OOCC_{10}H_{20}NC_8H_4O_2)_2$, 934.17 $PcZr(OOCC_{10}H_{20}NC_8H_4O_2)^+$, 635.76 $PcZr(OO)^{2-}$; Found 1267.09 $PcZr(OOCC_{10}H_{20}NC_8H_4O_2)_2$, 935.07 $PcZr(OOCC_{10}H_{20}NC_8H_4O_2)^+$, 635.44 $PcZr(OO)^{2-}$.

*Compound **VI***. It was prepared from $PcHfCl_2$ and 11-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)undecanoic acid. Yield 40%. Anal. Calcd. % for $C_{70}H_{66}N_{10}O_8Hf$: C 62.10, H 4.91, N 10.35, Hf 13.18; Found C 62.60, H 5.10, N 10.05, Hf 13.50. ^1H NMR (300 MHz, $CDCl_3$) δ, ppm: 9.40 (m, Pc, 8H), 8.14 (m, Pc, 8H), 7.85 (d, 2Ar, 4H), 7.69 (d, 2Ar, 4H), 3.68 (t, $2CH_2$, 4H), 1.66 (q, $2CH_2$, 4H), 1.26 (m, $4CH_2$, 8H), 1.05 (q, $2CH_2$, 4H), 0.86 (q, $2CH_2$, 4H), 0.59 (q, $2CH_2$, 4H), 0.50 (q, $2CH_2$, 4H), 0.29 (q, $2CH_2$, 4H), 0.09 (q, $2CH_2$, 4H). IR data: ν 2930, 2860 cm^{-1} (C−H, alkyl), 1770 cm^{-1} (C═O), 1605, 1520, 1400 cm^{-1} (COOHf). MALDI-TOF-MS (toluene) Calcd. 1351.84 $PcHf(OOCC_{10}H_{20}NC_8H_4O_2)_2$, 1021.44 $PcHf(OOCC_{10}H_{20}NC_8H_4O_2)^+$, 723.03 $PcHf(OO)^{2-}$; Found 1358.01 $PcZr(OOCC_{10}H_{20}NC_8H_4O_2)_2$, 1025.24 $PcZr(OOCC_{10}H_{20}NC_8H_4O_2)^+$, 726.48 $PcHf(OO)^{2-}$.

3. Results and discussion

3.1. Synthesis

It was earlier shown that $PcZrCl_2$ and $PcHfCl_2$ contain highly mobile halogenide ions that can be easily exchanged for various organic ligands [10–12]. This behaviour gives possibility to obtain axially substituted phthalocyanine complexes with the tailor-made properties. The carbonic acids containing long alkyl chain in different positions about carboxylic groups were selected as axial ligands: octanoic, 4-*n*-hexyloxybenzoic and 11-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)undecanoic acids. The high stability of the starting di(chloro)zirconium and hafnium phthalocyanine complexes allowed us to obtain new compounds by direct interaction of the components (Fig. 1). The HCl generated in the reaction does not influence the reaction or the yield of the products. The isolated mixed-ligand complexes are soluble in most organic solvents (DMSO, toluene, chloroform and other).

The obtained mixed-ligand metallophthalocyanines were characterized on the basis of elemental analysis and spectroscopic measurements. ^1H NMR data and elemental analysis suggest that two organic ligands are coordinated to the central atom of the macrocycle.

^1H NMR spectral data of the all synthesized metal phthalocyanine complexes in $CDCl_3$ at 25 °C are given in Table 1. Proton signals of ^1H NMR spectra can be divided by two parts: signals of phthalocyanine protons ($^{\alpha}H$: 9.40–8.75; $^{\beta}H$: 8.80–8.25 ppm) and signals of out-planed ligand protons. In case of bis(octanoato)zirconium and hafnium phthalocyanines signals of $^{\alpha}H$ and $^{\beta}H$ phthalocyanine protons are in less down-field in comparison to the signals of the same protons in complexes **III**, **IV**, **V** and **VI** (Table 1). The signals of aryl protons of 4-*n*-hexyloxybenzoic and 11-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)undecanoic ligands have different position. In case of complexes **III** and **IV** we observe shifting of signals of aryl protons 4-*n*-hexyloxybenzoic fragments in up-field in comparison to the same signals of free 4-*n*-hexyloxybenzoic acid. At the same time, shifting of aryl protons of 11-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)undecanoic ligands of complexes **V** and **VI** are not observed. It shows that the aryl group in 4-*n*-hexyloxybenzoic ligand is influenced by the π-conjugated system because it is situated near the carboxyl group. The aryl group of 11-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl) undecanoic fragment is at the end of the chain (far from the carboxyl group) of ligand and that is why the aryl protons are not influenced by the phthalocyanine macrocycle (Fig. 2). The alkyl protons of out-planed ligands of all synthesized complexes lie in up-fields and the more the CH_2-group is

Table 1
^{1}H NMR data of synthesized phthalocyanine complexes

Complex	Pc		CH_2	CH_3	Aryl
	$^{\alpha}$H	$^{\beta}$H			
I	9.18 (8H)	8.03 (8H)	1.04 (4H), 0.78 (4H), 0.55 (4H), 0.43 (4H), 0.22 (4H), 0.02 (4H)	0.76 (6H)	
II	9.18 (8H)	8.02 (8H)	1.04 (6H), 0.78 (2H), 0.54 (4H), 0.39 (4H), 0.21(4H), −0.01 (4H)	0.76 (6H)	
III	9.49 (8H)	8.20 (8H)	3.64 (4H), 3.52 (2H), 1.55 (4H), 1.22 (2H), 0.83 (4H), 0.03 (4H)	1.20 (6H)	6.66 (4H) 6.25 (4H)
IV	9.32 (8H)	8.12 (8H)	3.60 (4H), 3.49(2H), 1.52 (4H), 1.19 (2H), 0.81 (4H), 0.01 (4H)	1.19 (6H)	6.59 (4H) 6.21 (4H)
V	9.45 (8H)	8.20 (8H)	3.68 (4H), 1.66 (4H), 1.25 (10H), 1.07 (4H), 0.88 (4H), 0.58 (6H), 0.32 (4H), 0.15 (4H)		7.82 (4H) 7.70 (4H)
VI	9.40 (8H)	8.14 (8H)	3.68 (4H), 1.66 (4H), 1.26 (8H), 1.05 (4H), 0.86 (4H), 0.59 (4H), 0.50 (4H), 0.29 (4H), 0.09 (4H)		7.85 (4H) 7.69 (4H)

nearer to carboxyl group, the more we observe larger shift of its proton signals in up-field. And correspondingly, the more the CH_2-group is farther from carboxyl group, the more little shift is present in up-field.

The IR spectra of synthesized complexes display vibrational bands typical of the phthalocyanine ligand [18,19]. Two moderately strong absorptions in the far-IR region at 350 and 320 cm^{-1} assigned to the symmetric and asymmetric M–Cl modes of the starting $PcMCl_2$ complexes are absent. Characteristic IR absorption bands of symmetric and asymmetric stretching vibrations of the COOM bond of carboxylate group bonded to the central metal ion appear in the range 1640–1400 cm^{-1} (Table 2). Moreover, the absorption assigned to the stretching vibration ν (C=O) at 1720–1700 cm^{-1} is for the complexes **V** and **VI**.

3.2. Spectro luminescent properties

UV–vis data provide information on the possibility of the absorption transition between the ground and excited states

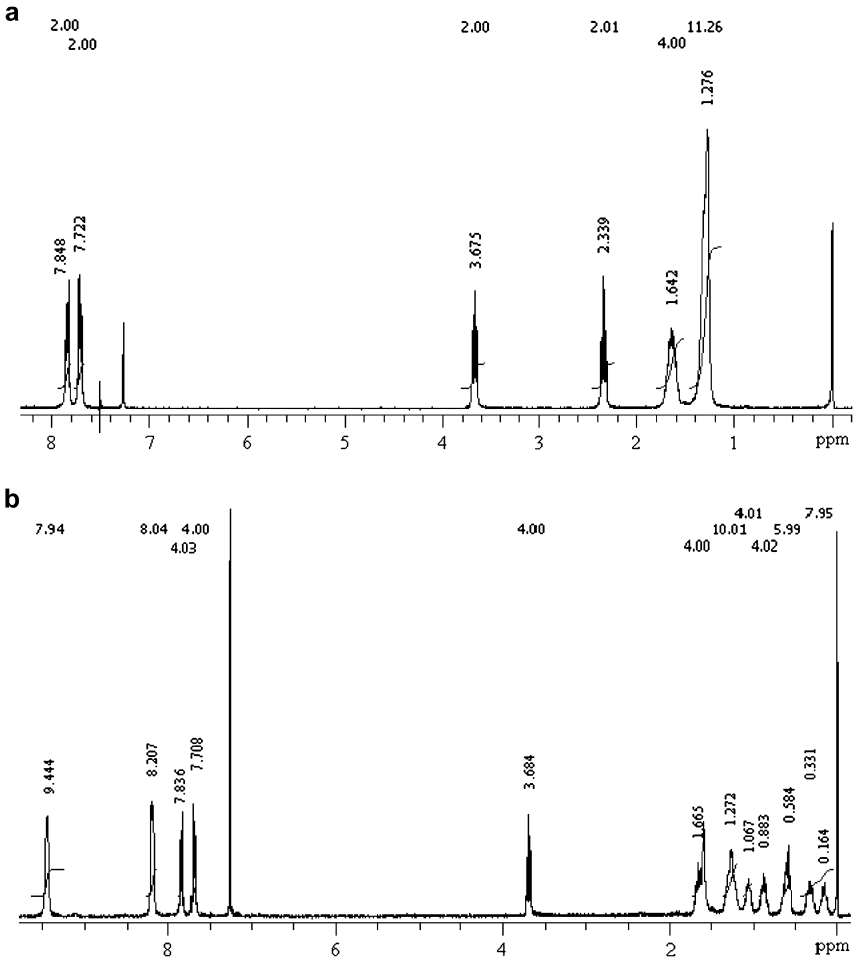

Fig. 2. ^{1}H NMR spectra of 11-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)undecanoic acids (a) and complex **V** (b) in $CDCl_3$.

Table 2
IR data of synthesized phthalocyanine complexes

Compound	ν, cm^{-1}			
	CH_2 (asym, sym)	R_{alk}–COOM (asym, sym)	C=O	M–Cl
$PcZrCl_2$	–			345, 315
$PcHfCl_2$	–			300, 290
I	2930, 2860	1630, 1530, 1500, 1470, 1420		–
II	2930, 2860	1610, 1540, 1500, 1470, 1420		–
III	2930, 2860	1605, 1520, 1500, 1460, 1425		–
IV	2930, 2860	1585, 1520, 1500, 1460, 1425		–
V	2930, 2860	1630, 1580, 1400	1770	–
VI	2930, 2860	1630, 1580, 1400	1770	–

of dye molecule. All synthesized phthalocyanine complexes have two major absorption bands, namely the intense Q-band at 680–690 nm and the B-band or Soret at 320–360 nm (Table 3). Fig. 3 exhibits the example of the UV–vis spectrum for complex **I** in DMSO. Delocalization of π-electrons in the conjugated molecular system and presence free d-electron orbitals in the central metal atom have influence on the HOMO–LUMO transitions and, as result, the bathochromic shift of the Q-absorption band is observed in spectra. Introducing of the elongated chains (alkyl/alkyloxy) [15,20] in the periphery of the macrocycle leads to increasing of the molar absorption coefficient of the Q-absorption band. Replacement of two out-planed Cl atoms for two carbonic acid fragments containing the long alkyl or alkyloxy chain leads to increase in the molar absorption coefficient of the Q-absorption band too (Table 3). For these reasons, metal-containing and out-planed substituted phthalocyanine systems, which absorb intensively in the visible light region, could be used as photoconverters which should absorb light energy suitable for the energetic gap of the semiconductors. Nature of solvents does not have considerable influence

Table 3
Spectral parameters of investigated phthalocyanine dyes

Complex	Solvent	λ_A, nm	$\varepsilon \times 10^5$ M^{-1} cm^{-1}	λ_F, nm	Φ_F	τ, ns
PcZn	DMSO	673	1.5332	686	0.2	7.56
$PcZrCl_2$	DMSO	688	1.1646	697	0.006	14.17
	Toluene	688	0.8276	–	–	–
$PcHfCl_2$	DMSO	684	1.3831	–	–	–
	Toluene	688	1.1624	–	–	–
I	DMSO	688	1.9971	703	0.013	8.463
	Toluene	684	1.5430	697	0.009	9.083
II	DMSO	684	1.6773	–	–	–
	Toluene	684	1.4624	–	–	–
III	DMSO	684	2.4915	693	0.016	6.841
	Toluene	684	1.9861	693	0.009	6.917
IV	DMSO	684	1.7687	–	–	–
	Toluene	684	1.5637	–	–	–
V	DMSO	686	2.0252	697	0.016	8.101
	Toluene	684	1.7151	699	0.009	8.213
VI	DMSO	684	1.7241	–	–	–
	Toluene	684	1.5008	–	–	–

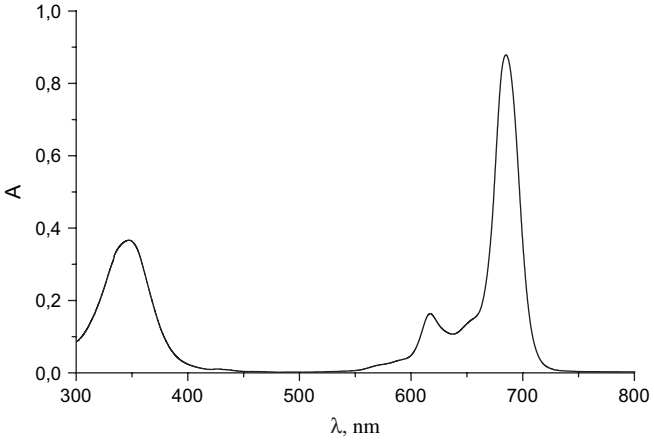

Fig. 3. UV–vis spectra of complex **I**.

on the shape of the UV–vis spectra and the position of Q-band of the investigated complexes. At the same time, negligible decrease in value of the molar absorption coefficient takes place.

The complexes **I**, **III**, **V** ($PcZrL_2$) and $PcZrCl_2$ show weak fluorescence ($\Phi_F < 0.020$), at the same conditions the complexes **II**, **IV**, **VI** ($PcHfL_2$) and $PcHfCl_2$ do not exhibit any fluorescence. The natural lifetimes were calculated (Eq. (1)) and fluorescence quantum yields were determined (Eq. (2)) on the basis of the absorption and fluorescence data. The natural lifetimes of studying phthalocyanines are of the order of nanoseconds. It means that the electron transfer should be approachable for about 10^{-9} s before the excited molecule turns spontaneously to its ground state. The substitution of two out-planed Cl atoms for two carbonic fragments containing the elongated chain leads to increase of the fluorescence quantum yield and decrease of the natural lifetimes (Table 3). It should be noted that decreasing of fluorescence quantum yields and increasing of fluorescence natural lifetimes are observed in non-polar aprotic solvent – toluene, in comparison on bipolar aprotic solvent – DMSO. The Stokes shift between the absorption Q-band and the fluorescence maximum is very small (9–15 nm) for all investigated $PcZrL_2$. This behaviour of investigated phthalocyanine complexes indicates significant participation of other deactivated processes of the excited state of the molecule.

4. Conclusion

New out-planed substituted zirconium(IV) and hafnium(IV) phthalocyanines have been synthesized successfully. The direct introduction of carboxylic acid ligands with lengthy chain to the central atom leads to increase in solubility of Zr(IV) and Hf(IV) phthalocyanine complexes in organic solvents. These compounds are non-aggregated in organic solutions and have very high molar absorption coefficients. Fluorescence study exhibits small magnitudes of the fluorescence quantum yields for the zirconium-containing phthalocyanines and absence of fluorescence quantum yield for the hafnium-containing phthalocyanines.

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