

Review

Synthesis and spectral properties of Zr(IV) and Hf(IV) phthalocyanines with β -diketonates as axial ligands

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Received 21 February 2007; received in revised form 17 July 2007; accepted 2 November 2007

Available online 7 November 2007

Abstract

The series of new zirconium(IV) and hafnium(IV) phthalocyanines with various β -dicarbonyl ligands were prepared via direct interaction between di(chloro)zirconium(IV) or hafnium(IV) phthalocyanines and free β -diketones and also with 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one. The structure of the obtained bis(β -dicarbonylato) zirconium(IV) and hafnium(IV) phthalocyanines was studied by two dimension ¹H NMR spectroscopy (COSY, NOESY, ROESY). Absorption and fluorescence spectroscopic studies have been investigated in various solvents. Analyzed compounds of concentration range below 10^{-5} mol/dm³ do not aggregate in the organic solvents. Fluorescence quantum yields (Φ_F) and natural life times (τ) of zirconium phthalocyanine complexes have been calculated in toluene, DMSO and THF.

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Keywords: Phthalocyanine; Zirconium(IV); Hafnium(IV); β -Diketones; 2D NMR spectroscopy; Electronic absorption and emission spectra; Fluorescence



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1. Introduction

Metallophthalocyanines due to their unique electronic structure display interesting spectroscopic and photoelectric properties, which have been extensively studied for many years, firstly because of their classical use as dyes. Recently, the increasing attention to metallophthalocyanine complexes is result of their applications in modern technology. Their unique properties such as conductivity, electrochromism or variety of catalytic functions, make them ideal compounds for applications as electrochromic materials [1], photoconductors [2], sensors [3] and for the other advanced applications [4]. Although phthalocyanines, with some exceptions, are considered to be toxic, they find application in medicine, as photosensitizers in PDT (photodynamic therapy) [5–8].

Introduction of the substituents to the peripheral position of Pc macrocycle change significantly the physical and chemical properties of the PcM system [9–11]. Moreover, metallophthalocyanine complexes containing metal in valence state higher than two give the possibility to bind directly to the metal one or more additional ligands, usually in so-called out of plane position, perpendicular to the N_8 moiety. The axial ligands can significantly change the spectral, photophysical and other properties of PcM complexes [12–17]. The mixed ligand phthalocyanine compounds are also good substrates for the synthesis even more complicated sandwich-type or trinuclear complexes [18–20].

We report in this work the synthesis of the axially substituted zirconium(IV) and hafnium(IV) phthalocyanines. We also concern on the determination of the structure of obtained mixed ligands bis(β -dicarbonilato)zirconium(IV) and hafnium(IV) phthalocyanine complexes by the 2D 1H

NMR spectroscopy (COSY, NOESY and ROESY). Summarizing all data of 2D 1H NMR spectroscopy we can establish the structure of the synthesized mixed ligand dicarbonilato and phthalocyanine complexes with relatively high precision. Their spectral luminescent properties were also investigated.

2. Experimental

2.1. Materials

Zirconium and hafnium tetrachloride, phthalodinitrile, 2-methylnaphthalene, 2,4-pentandione, 1-phenyl-1,3-butanedione, 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one, 3-chloro-2,4-pentandione were purchased from Aldrich and used as received. 1,2,4-Trichlorobenzene, toluene, hexane, and $CHCl_3$ and all other organic solvents were of reagent grade and were used without further purification.

2.2. Spectral measurements

Measurements of the electronic absorption spectra were carried out at room temperature using a Carl-Zeiss, Jena, Specord M-40 spectrometer. The UV–Vis spectra of the analyzed mixed ligand complexes were recorded in $CHCl_3$ solutions ($c = 10^{-6}$ mol/dm³, $l = 1$ cm). IR spectra were recorded on a Carl-Zeiss, Jena, Specord M-80 spectrometer in KBr (FT-IR grade, Aldrich) disks. Steady-state fluorescence spectra were collected with a spectrofluorimeter Hitachi 1200 in toluene, DMSO and THF ($c = 10^{-6}$ mol/dm³, $l = 1$ cm). A Carl-Zeiss (Jena) refractometer Abbe type was used for the determination the refractive indexes of the phthalocyanine solutions ($c = 10^{-6}$ mol/dm³).

^1H NMR spectra were obtained with a Bruker NMR Avance spectrometer operating in a quadrature mode at 500 MHz (500) NMR spectrometer.

2.3. Synthesis

Synthesis of dichloro(chlorine)- and dichlorophthalocyanines of zirconium(IV) and hafnium(IV) is shown in Scheme 1. The same reaction but without 2-methylnaphthalene, results in chlorination of one benzene ring in the phthalocyanine plane. The presence of 2-methylnaphthalene, avoid the chlorination of the Pc ring inasmuch 2-methylnaphthalene is an easy-chlorinated reagent and “remove” free chlorine radical which usually chlorinate phthalonitrile during tetramerization or formed Pc macrocycle. The products of 2-methylnaphthalene chlorination can be easy removed from reaction mixture. Hanack et al. [21] prepared axially substituted tetrapyrzazinotetraazaporphyrinatotitanoin(IV) oxides. Trying to avoid the complex hydrolysis we applied different condition of the synthesis, as high boiling solvent. In these conditions we do not obtain neither $\text{Pc}(\text{Zr}/\text{Hf})\text{O}$ nor $\text{Pc}(\text{Zr}/\text{Hf})\text{M}(\text{OH})$ [22].

Zirconium and hafnium dichlorophthalocyanines were treated as starting materials for the synthesis of other mixed ligand complexes shown in Schemes 1–3. All reactions were carried out under atmospheric conditions. Details about complex preparation are described below.

2.3.1. Synthesis of dichloro(chlorinephthalocyaninato) zirconium(IV) ($\text{Pc}(\text{Cl})\text{ZrCl}_2$) (I)

Phthalodinitrile (0.1 mol) was dissolved in 15 ml of hot 1,2,4-trichlorobenzene, then 0.025 mol of zirconium tetrachloride was added to the solution. The reaction mixture was heated at 220 °C for 1 h. After completing the reac-

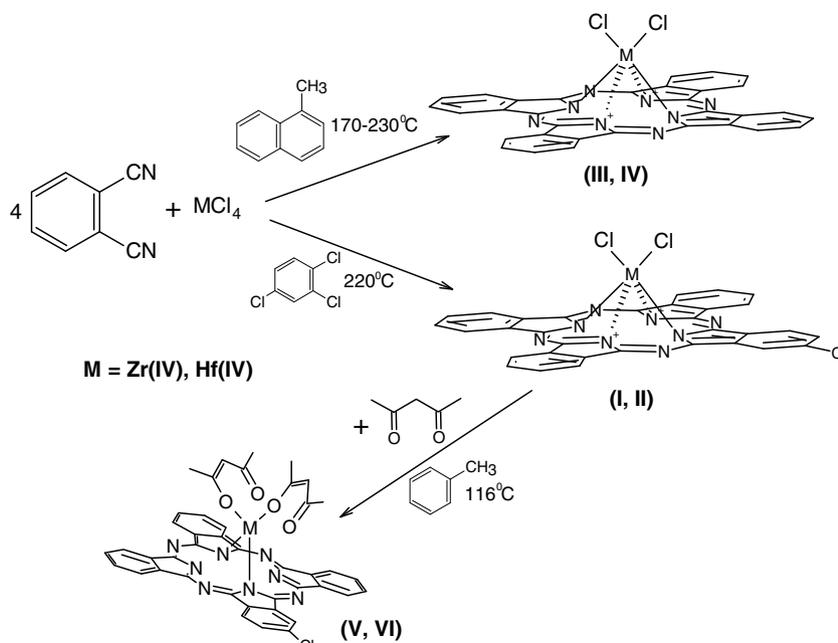
tion, the suspension was cooled to 50 °C and filtered. The precipitate was washed with benzene and methanol until washings were no longer colored and finally air-dried at room temperature. Yield: 71%. *Anal. Calc.* for $\text{C}_{32}\text{H}_{15}\text{Cl}_3\text{N}_8\text{Zr}$: C, 54.20; H, 2.13; N, 15.80; Zr, 12.86. *Found*: C, 54.50; H, 2.50; N, 15.45; Zr, 12.50%. IR (KBr, cm^{-1}): 1685 (w), 1605 (w), 1500 (m), 1465 (w), 1415 (m), 1385 (w), 1330 (s), 1310 (w), 1285 (s), 1155 (m), 1115 (s), 1070 (s), 1050 (s), 1010 (m), 950 (w), 890 (s), 870 (w), 825 (m), 790 (m), 765 (m), 745 (s), 730 (s), 630 (w), 565 (w), 500 (m), 430 (m), 345 (m), [$\nu_{\text{asym}}(\text{Zr}-\text{Cl})$], 315 (s) [$\nu_{\text{sym}}(\text{Zr}-\text{Cl})$].

2.3.2. Synthesis of dichloro(chlorinephthalocyaninato) hafnium(IV) ($\text{Pc}(\text{Cl})\text{HfCl}_2$) (II)

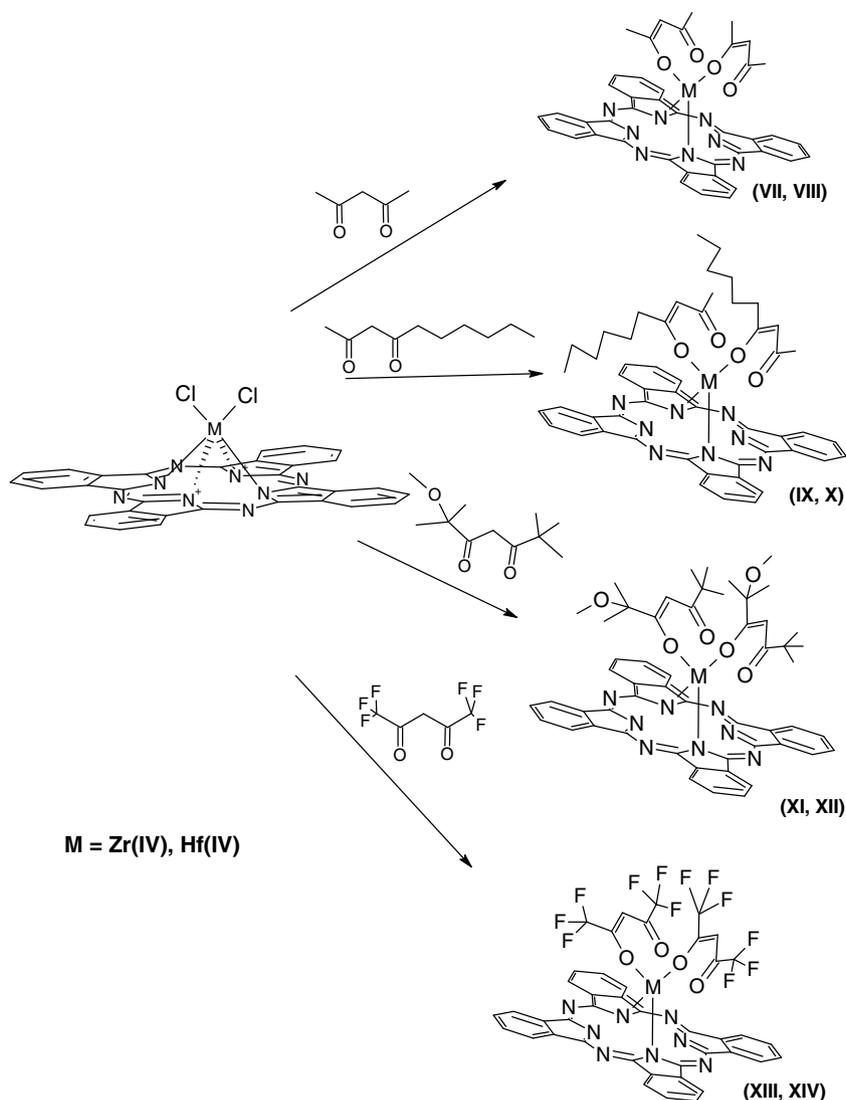
It was prepared from hafnium tetrachloride by the same procedure as (I). Yield: 77%. *Anal. Calc.* for $\text{C}_{32}\text{H}_{15}\text{Cl}_3\text{N}_8\text{Hf}$: C, 48.26; H, 1.90; N, 14.07; Hf, 22.41. *Found*: C, 48.50; H, 2.00; N, 13.90; Hf, 22.50%. IR (KBr, cm^{-1}): 1605 (w), 1500 (m), 1465 (m), 1415 (m), 1385 (w), 1330 (s), 1285 (s), 1155 (m), 1115 (s), 1070 (s), 1050 (s), 1005 (m), 945 (w), 890 (s), 870 (w), 825 (m), 790 (m), 765 (m), 745 (s), 730 (s), 625 (w), 565 (w), 500 (m), 430 (m), 300 (s) [$\nu_{\text{asym}}(\text{Hf}-\text{Cl})$], 285 (m) [$\nu_{\text{sym}}(\text{Hf}-\text{Cl})$].

2.3.3. Synthesis of dichloro(phthalocyaninato) zirconium(IV) (PcZrCl_2) (III)

Phthalodinitrile (0.1 mol) and 2-methylnaphthalene (0.025 mol) were dissolved in 15 ml of hot 1,2,4-trichlorobenzene and 0.025 mol of zirconium tetrachloride was added to solution, then the reaction mixture was heated at 220 °C for 1 h. After completing the reaction, the sus-



Scheme 1.



Scheme 2.

pension was cooled to 50 °C and filtered. The precipitate was washed with benzene and methanol until washings were no longer colored and finally air-dried at room temperature. Yield: 73%. *Anal. Calc.* for $C_{32}H_{16}Cl_2N_8Zr$: C, 56.97; H, 2.39; N, 16.61; Zr, 13.52. Found: C, 56.80; H, 2.50; N, 16.20; Zr, 13.50%. IR (KBr, cm^{-1}): 1685 (w), 1605 (w), 1500 (m), 1465 (w), 1415 (m), 1385 (w), 1330 (s), 1310 (w), 1285 (s), 1155 (m), 1115 (s), 1070 (s), 1050 (s), 950 (w), 890 (s), 870 (w), 825 (m), 790 (m), 765 (m), 745 (s), 730 (s), 630 (w), 565 (w), 500 (m), 430 (m), 345 (m) [$\nu_{asym}(Zr-Cl)$], 315 (s) [$\nu_{sym}(Zr-Cl)$].

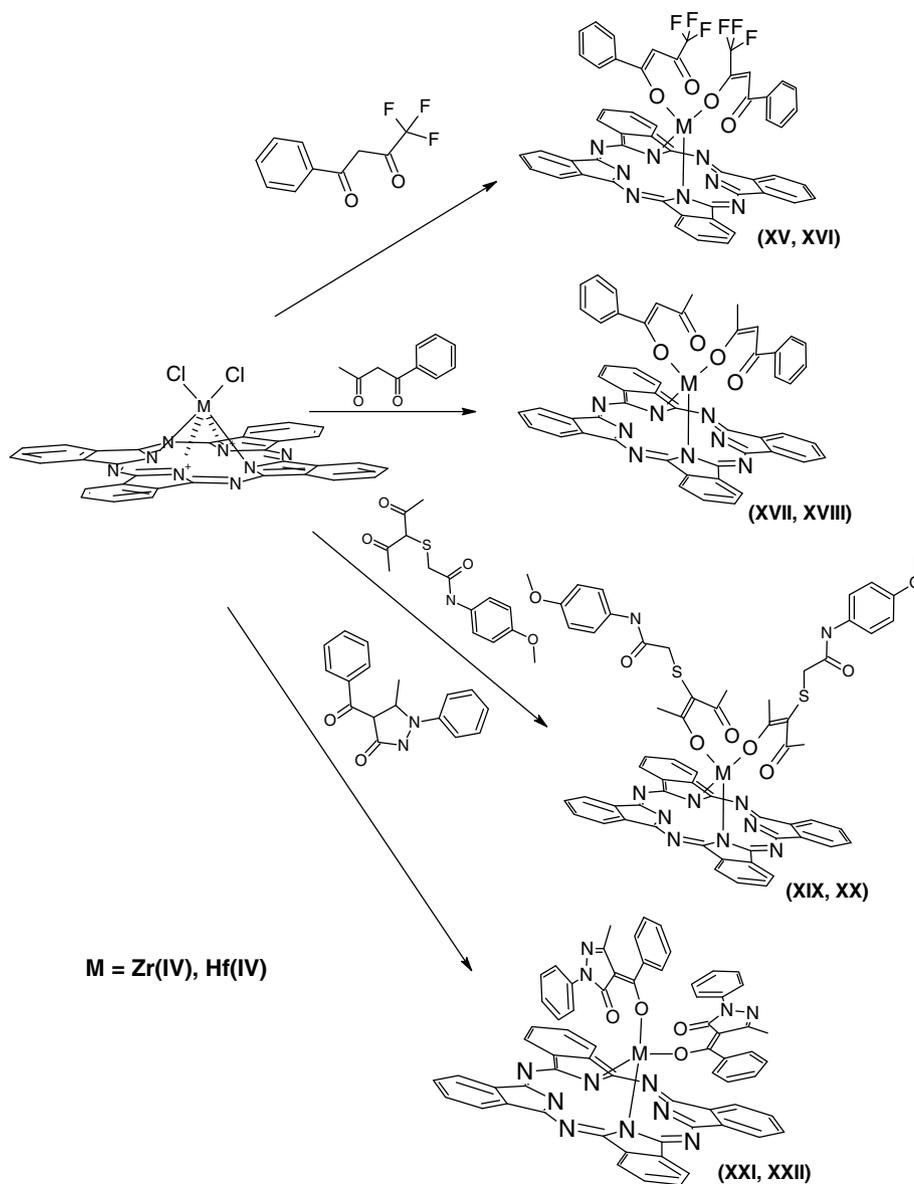
2.3.4. Synthesis of dichloro(phthalocyaninato) hafnium(IV) ($PcHfCl_2$) (IV)

It was prepared from hafnium tetrachloride by the same procedure as (III). Yield: 76%. *Anal. Calc.* for $C_{32}H_{16}Cl_2N_8Hf$: C, 50.44; H, 2.12; N, 14.71; Hf, 23.43. Found: C, 50.50; H 2.00; N, 14.50; Hf, 23.50%. (KBr, cm^{-1}): 1605 (w), 1500 (m), 1465 (m), 1415 (m), 1385 (w), 1330 (s), 1285 (s), 1155 (m), 1115 (s), 1070 (s), 1050 (s),

945 (w), 890 (s), 870 (w), 825 (m), 790 (m), 765 (m), 745 (s), 730 (s), 625 (w), 565 (w), 500 (m), 430 (m), 300 (s) [$\nu_{asym}(Hf-Cl)$], 285 (m) [$\nu_{sym}(Hf-Cl)$].

2.3.5. Synthesis of bis(2,4-pentanedionato)zirconium(IV) chlorinephthalocyanine (V)

A 0.74 mmol of $Pc(Cl)ZrCl_2$ was suspended in 10 ml of toluene and 1.67 mmol 2,4-pentandione was added to the suspension. The reaction mixture was heated at 116 °C for 4 h under reflux (evolution of HCl was observed). Then the hot reaction mixture was filtered and the obtained solution was cooled to room temperature. The formed crystals of bis(2,4-pentadionato)phthalocyanine complex of zirconium were separated and washed abundantly with hexane. Hexane was added to the remaining solution what caused an additional crystallization of the final product. The resulting precipitates were collected and dried, firstly in the air and finally in a vacuum at 60 °C for 8 h. *Anal. Calc.* for $C_{42}H_{29}ClN_8O_4Zr$: C, 60.31; H, 3.49; N, 13.40; Zr, 10.91. Found: C, 59.90; H, 3.50; N, 13.10; Zr, 10.50%.



Scheme 3.

IR (KBr, cm^{-1}): 2950–2940 (w), 1600 (s), 1575 (s), 1540 (s), 1510 (s), 1468 (m), 1420 (m), 1387 (m), 1360 (m), 1335 (s), 1288 (s), 1164 (m), 1120 (s), 1080 (sh), 1070 (s), 1032 (m), 1008 (m), 898 (m), 830 (m), 825 (sh), 780 (s), 755 (s), 743 (s), 460 (m), 450 (m).

2.3.6. Synthesis of bis(2,4-pentanedionato)hafnium(IV) chlorinephthalocyanine (VI)

It was prepared from $\text{Pc}(\text{Cl})\text{HfCl}_2$ and 2,4-pentandione by the same procedure as (V). Yield: 44%. *Anal.* Calc. for $\text{C}_{42}\text{H}_{29}\text{ClN}_8\text{O}_4\text{Hf}$: C, 54.61; H, 3.16; N, 12.13; Hf, 19.32; Found: C, 54.50; H, 3.00; N, 11.90; Hf, 19.50%. IR (KBr, cm^{-1}): 2960–2920 (w), 1610 (s), 1575 (s), 1540 (s), 1510 (s), 1468 (m), 1420 (m), 1390 (s), 1335 (s), 1288 (s), 1164 (m), 1120 (s), 1080 (sh), 1070 (s), 1030 (m), 1000 (m), 898 (m), 830 (m), 825 (sh), 780 (s), 755 (s), 743 (s), 440 (m), 420 (m).

2.3.7. Synthesis of bis(2,4-pentanedionato)zirconium(IV) phthalocyanine (VII)

It was prepared from PcZrCl_2 and 2,4-pentandione by the same procedure as (V). Yield: 64%. *Anal.* Calc. for $\text{C}_{42}\text{H}_{30}\text{N}_8\text{O}_4\text{Zr}$: C, 62.90; H, 3.77; N, 13.97; Zr, 11.37. Found: C, 62.50; H, 3.75; N, 13.45; Zr, 11.52%. IR (KBr, cm^{-1}): 2950–2940 (w), 1600 (s), 1575 (s), 1540 (s), 1510 (s), 1468 (m), 1420 (m), 1387 (m), 1360 (m), 1335 (s), 1288 (s), 1164 (m), 1120 (s), 1080 (sh), 1070 (s), 1032 (m), 898 (m), 830 (m), 825 (sh), 780 (s), 755 (s), 743 (s), 460 (m), 450 (m). ^1H NMR (δ ppm, CDCl_3): 9.46 (8H, m, H^a); 8.16 (8H, m, H^b); 4.25 (2H, s, 2CH); 1.23 (12H, s, 4 CH_3).

2.3.8. Synthesis of bis(2,4-pentanedionato)hafnium(IV) phthalocyanine (VIII)

It was prepared from PcHfCl_2 and 2,4-pentandione by the same procedure as (V). Yield: 66%. *Anal.* Calc. for

$C_{42}H_{30}N_8O_4Hf$: C, 56.73; H, 3.40; N, 12.60; Hf, 20.07. Found: C, 56.60; H, 3.20; N, 12.10; Hf, 20.10%. IR (KBr, cm^{-1}): 2960–2920 (w), 1610 (s), 1575 (s), 1540 (s), 1510 (s), 1468 (m), 1420 (m), 1390 (s), 1335 (s), 1288 (s), 1164 (m), 1120 (s), 1080 (sh), 1070 (s), 1030 (m), 898 (m), 830 (m), 825 (sh), 780 (s), 755 (s), 743 (s), 440 (m), 420 (m). 1H NMR (δ ppm, $CDCl_3$): 9.17 (8H, m, H^a); 8.10 (8H, m, H^b); 4.60 (2H, s, 2CH); 1.19 (12H, s, 4CH₃).

2.3.9. Synthesis of bis(2,4-decanedionato)zirconium(IV) phthalocyanine (IX)

It was prepared from $PcZrCl_2$ and 2,4-decanedione by the same procedure as (V). Yield: 49%. Anal. Calc. for $C_{52}H_{50}N_8O_4Zr$: C, 66.29; H, 5.35; N, 11.89; Zr, 9.68. Found: C, 66.50; H, 5.10; N, 11.40; Zr, 9.50%. IR (KBr, cm^{-1}): 2960 (m), 2930 (m), 2860 (m), 1602 (s), 1592 (s), 1575 (s), 1567 (sh), 1531 (s), 1505 (s), 1467 (m), 1420 (m), 1400 (m), 1365 (sh), 1335 (s), 1285 (s), 1162 (m), 1120 (s), 1075 (s), 1050 (sh), 900 (m), 825 (m), 780 (m), 770 (m), 750 (s), 740 (s), 1420 (m), 1335 (s), 1285 (s), 1162 (m), 1120 (s), 1075 (s), 1050 (sh), 900 (m), 780 (m), 770 (m), 750 (s), 740 (s), 440 (m), 430 (sh). 1H NMR (δ ppm, $CDCl_3$): 9.43 (8H, m, H^a); 8.12 (8H, m, H^b); 4.19 (2H, d, 2CH); 1.54; 1.28 (4H, m, 2CH₂); 1.20, 1.14 (6H, s, 2CH₃); 1.04, 0.93 (10H, m, 5CH₂); 0.79 (12H, m, 3CH₂, 2CH₃).

2.3.10. Synthesis of bis(2,4-decanedionato)hafnium(IV) phthalocyanine (X)

It was prepared from $PcHfCl_2$ and 2,4-decanedione by the same procedure as (V). Yield: 47%. Anal. Calc. for $C_{52}H_{50}N_8O_4Hf$: C, 60.67; H, 4.90; N, 10.88; Hf, 17.34. Found: C, 60.50; H, 5.00; N, 10.45; Hf, 17.34%. IR (KBr, cm^{-1}): 2930 (m), 2860 (m), 1605 (s), 1593 (s), 1578 (s), 1570 (s), 1530 (s), 1506 (s), 1465 (m), 1418 (m), 1400 (m), 1375 (m), 1362 (sh), 1330 (s), 1285 (s), 1160 (m), 1118 (s), 1080 (sh), 1070 (s), 1050 (m), 900 (m), 825 (m), 775 (m,d), 750 (s), 740 (s), 435 (m), 425 (sh). 1H NMR (δ ppm, $CDCl_3$): 9.43 (8H, m, H^a); 8.14 (8H, m, H^b); 4.14 (2H, d, 2CH); 1.54; 1.27 (4H, m, 2CH₂); 1.18; 1.12 (6H, s, 2CH₃); 1.04; 0.93 (10H, m, 5CH₂); 0.79 (12H, m, 3CH₂, 2CH₃).

2.3.11. Synthesis of bis(2-methoxy-2,6,6-trimethyl-3,5-heptanedionato)zirconium(IV) phthalocyanine (XI)

It was prepared from $PcZrCl_2$ and 2-methoxy-2,6,6-trimethyl-3,5-heptanedione by the same procedure as (V). Yield: 51%. Anal. Calc. for $C_{54}H_{54}N_8O_6Zr$: C, 64.71; H, 5.43; N, 11.18; Zr, 9.10%. Found: C, 64.50; H, 5.50; N, 10.90; Zr, 9.25%. (KBr, cm^{-1}): 2950 (m), 1615 (sh), 1590 (s), 1570 (s), 1550 (sh), 1510 (s), 1470 (m), 1420 (m), 1409 (m), 1400 (sh), 1365 (m), 1335 (s), 1290 (s), 1235 (m), 1180 (m), 1168 (m), 1120 (s), 1080 (s), 960 (m), 938 (m), 900 (m), 780 (m), 770 (m), 750 (s), 740 (s), 430 (m), 425 (sh). 1H NMR (δ ppm, $CDCl_3$): 9.65 (8H, m, H^a); 8.42 (8H, m, H^b); 5.01 (2H, d, 2CH); 2.83 (6H, q, 2OCH₃); 1.40 (6H, q, 2CH₃); 0.78 [18H, m, 2C(CH₃)₃]; 0.46 (6H, q, 2CH₃).

2.3.12. Synthesis of bis(2-methoxy-2,6,6-trimethyl-3,5-heptanedionato)hafnium(IV) phthalocyanine (XII)

It was prepared from $PcHfCl_2$ and 2-methoxy-2,6,6-trimethyl-3,5-heptanedione by the same procedure as (V). Yield: 49%. Anal. Calc. for $C_{54}H_{54}N_8O_6Hf$: C, 59.53; H, 5.00; N, 10.28; Hf, 16.38. Found: C, 59.20; H 5.15; N, 10.05; Hf, 16.55%. (KBr, cm^{-1}): 2940 (m), 1605 (sh), 1590 (s), 1568 (s), 1550 (sh), 1509 (s), 1499 (sh), 1465m, 1455 (sh), 1420 (m), 1405 (m), 1390 (m), 1360 (m), 1330 (s), 1290 (s), 1230 (m), 1175 (m), 1160 (m), 1118 (s), 1082 (sh), 1070 (s), 1050 (m), 960 (m), 938 (m), 900 (m), 825 (m), 820 (sh), 775 (m), 765 (m), 750 (s), 740 (s), 735 (s), 427 (m), 415 (m). 1H NMR (δ ppm, $CDCl_3$): 9.69 (8H, m, H^a); 8.51 (8H, m, H^b); 5.07 (2H, d, 2CH); 2.90 (6H, q, 2OCH₃); 1.52 (6H, q, 2CH₃); 0.89 [18H, m, 2C(CH₃)₃]; 0.54 (6H, q, 2CH₃).

2.3.13. Synthesis of bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)zirconium(IV) phthalocyanine (XIII)

It was prepared from $PcZrCl_2$ and 1,1,1,5,5,5-hexafluoro-2,4-pentandione by the same procedure as (V). Yield: 43%. Anal. Calc. for $C_{42}H_{18}F_{12}N_8O_4Zr$: C, 49.56; H, 1.78; N, 11.01; Zr, 8.96. Found: C, 49.20; H, 1.50; N, 10.50; Zr, 9.05%. (KBr, cm^{-1}): 1700 (sh), 1685 (s), 1662 (s), 1650 (s), 1612 (s), 1600 (sh), 1560 (w), 1510 (m), 1475 (m), 1425 (m), 1400 (m), 1335 (s), 1290 (s), 1260 (m), 1210 (s), 1165 (s), 1145 (m), 1120 (s), 1078 (s), 1065 (sh), 900 (m), 830 (m), 775 (m), 750 (m), 740 (s), 730 (sh), 430 (m), 425 (sh). 1H NMR (δ ppm, $CDCl_3$): 9.25 (8H, m, H^a); 8.11 (8H, m, H^b); 4.70 (2H, s, 2CH).

2.3.14. Synthesis of bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)hafnium(IV) phthalocyanine (XIV)

It was prepared from $PcHfCl_2$ and 1,1,1,5,5,5-hexafluoro-2,4-pentandione by the same procedure as (V). Yield: 45%. Anal. Calc. for $C_{42}H_{18}F_{12}N_8O_4Hf$: C, 45.65; H, 1.64; N, 10.14; Hf, 16.15. Found: C, 45.40; H, 1.50; N, 10.00; Hf, 16.25%. IR (KBr, cm^{-1}): 1680 (sh), 1663 (s), 1648 (s), 1610 (m), 1555 (w), 1509 (m), 1478 (m), 1420 (m), 1395 (w), 1380 (s), 1295 (s), 1257 (s), 1213 (s), 1160 (s), 1140 (s), 1120 (s), 1080 (s), 1070 (sh), 900 (m), 815 (m), 780 (m), 750 (m), 740 (s), 730 (s), 430 (m), 425 (sh). 1H NMR (δ ppm, $CDCl_3$): 9.17 (8H, m, H^a); 8.10 (8H, m, H^b); 4.60 (2H, s, 2CH).

2.3.15. Synthesis of bis(1-phenyl-4,4,4-trifluoro-1,3-butanedionato)zirconium(IV) phthalocyanine (XV)

It was prepared from $PcZrCl_2$ and 1-phenyl-4,4,4-trifluoro-1,3-butandione by the same procedure as (V). Yield: 57%. Anal. Calc. for $C_{52}H_{28}F_6N_8O_4Zr$: C, 60.40; H, 2.73; N, 10.84; Zr, 8.82. Found: C, 60.05; H, 2.65; N, 10.35; Zr, 8.55%. IR (KBr, cm^{-1}): 3050 (w), 1625 (sh), 1615 (s), 1600 (s), 1578 (s), 1570 (sh), 1543 (m), 1508 (s), 1492 (sh), 1470 (m), 1420 (m), 1335 (s), 1325 (s), 1298 (s), 1290 (sh), 1250 (s), 1200 (s), 1165 (m), 1145 (s), 1120 (s), 1100 (sh), 1075 (s), 1030 (m), 900 (m), 830 (m), 820 (m), 780 (s), 755 (s), 743 (s), 725 (sh), 705 (s), 680 (m), 450 (m), 440

(sh). ^1H NMR (δ ppm, CDCl_3): 9.27 (8H, m, H^α); 8.21 (8H, m, H^β); 7.56 (2H, q, $2\text{C}_6\text{H}_5$); 7.25 (4H, q, $2\text{C}_6\text{H}_5$); 6.96 (4H, t, $2\text{C}_6\text{H}_5$); 5.52 (2H, s, 2CH).

2.3.16. Synthesis of bis(1-phenyl-4,4,4-trifluoro-1,3-butanedionato)hafnium(IV) phthalocyanine (XVI)

It was prepared from PcHfCl_2 and 1-phenyl-4,4,4-trifluoro-1,3-butanedione by the same procedure as (V). Yield: 61%. *Anal.* Calc. for $\text{C}_{52}\text{H}_{28}\text{F}_6\text{N}_8\text{O}_4\text{Hf}$: C, 55.70; H, 2.52; N, 9.99; Hf, 15.92. Found: C, 55.20; H, 2.15; N, 10.15; Hf, 15.85%. (KBr, cm^{-1}): 3060 (w), 1625 (m), 1610 (s), 1599 (s), 1565 (sh), 1542 (m), 1505 (m), 1495 (sh), 1470 (m), 1460 (sh), 1420 (m), 1335 (s), 1325 (s), 1300 (s), 1295 (sh), 1250 (s), 1200 (s), 1188 (sh), 1160 (m), 1148 (s), 1120 (s), 1100 (sh), 1080 (s), 1050 (m), 898 (m), 820 (m), 810 (m), 770 (s), 750 (s), 740 (s), 725 (m), 700 (s), 685 (sh), 440 (m), 430 (sh). ^1H NMR (δ ppm, CDCl_3): 9.37 (8H, m, H^α); 8.02 (8H, m, H^β); 7.39 (2H, q, $2\text{C}_6\text{H}_5$); 7.08 (4H, q, $2\text{C}_6\text{H}_5$); 6.65 (4H, t, $2\text{C}_6\text{H}_5$); 5.06 (2H, s, 2CH).

2.3.17. Synthesis of bis(1-phenyl-1,3-butanedionato)zirconium(IV) phthalocyanine (XVII)

It was prepared from PcZrCl_2 and 1-phenyl-1,3-butanedione by the same procedure as (V). Yield: 53%. *Anal.* Calc. for $\text{C}_{52}\text{H}_{34}\text{N}_8\text{O}_4\text{Zr}$: C, 67.44; H, 3.70; N, 12.10; Zr, 9.85. Found: C, 67.50; H, 3.50; N, 11.85; Zr, 10.00%. IR (KBr, cm^{-1}): 3060 (w), 1605 (sh), 1592 (s), 1552 (s), 1530 (sh), 1522 (s), 1510 (sh), 1490 (m), 1465 (m), 1420 (m), 1375 (m), 1365 (sh), 1335 (s), 1310 (m), 1285 (m), 1160 (m), 1115 (s), 1075 (s), 1030 (m), 895 (m), 840 (m), 820 (m), 770 (s), 750 (s), 735 (s), 710 (s), 685 (m), 430 (m), 425 (sh). ^1H NMR (δ ppm, CDCl_3): 9.66–9.02 (8H, m, H^α); 8.28–7.96 (8H, m, H^β); 7.41 (2H, q, $-\text{C}_6\text{H}_5$); 7.16 (4H, q, $-\text{C}_6\text{H}_5$); 6.87 (4H, t, $-\text{C}_6\text{H}_5$); 4.97 (2H, s, 2CH); 1.40 (6H, s, $-\text{CH}_3$).

2.3.18. Synthesis of bis(1-phenyl-1,3-butanedionato)hafnium(IV) phthalocyanine (XVIII)

It was prepared from PcHfCl_2 and 1-phenyl-1,3-butanedione by the same procedure as (V). Yield: 56%. *Anal.* Calc. for $\text{C}_{52}\text{H}_{34}\text{N}_8\text{O}_4\text{Hf}$: C, 61.63; H, 3.38; N, 11.06; Hf, 17.61. Found: C, 61.50; H, 3.25; N, 10.85; Hf, 17.50%. IR (KBr, cm^{-1}): 3070 (w), 1600 (sh), 1592 (s), 1555 (s), 1535 (sh), 1525 (s), 1510 (sh), 1490 (m), 1470 (m), 1420 (m), 1380 (m), 1365 (sh), 1335 (s), 1312 (m), 1286 (m), 1160 (m), 1117 (s), 1077 (s), 1030 (m); 900 (s), 854 (m), 820 (m), 770 (s), 750 (s), 737 (s), 710 (s), 685 (m), 435 (m), 425 (sh). ^1H NMR (δ ppm, CDCl_3): 9.61–9.04 (8H, m, H^α); 8.28–7.99 (8H, m, H^β); 7.40 (2H, q, C_6H_5); 7.13 (4H, q, $-\text{C}_6\text{H}_5$); 6.85 (4H, t, $-\text{C}_6\text{H}_5$); 4.92 (2H, s, 2CH); 1.36 (6H, s, $-\text{CH}_3$).

2.3.19. Synthesis of N1-(4-methoxyphenyl)-2-(1-acetyl-2-oxopropylsulfanyl)acetamide

10 mmol of N1-(4-methoxyphenyl)-2-sulfanylacetamide was dissolved in 5 ml of 2N KOH in isopropanol. Then

10 mmol of 3-chloro-2,4-pentanedione was added to the solution. The mixture was heated under reflux for 10–15 min. After completion of the reaction a small amount of water was added to the solution which was cooled down to start the crystallization. The formed precipitate was filtrated, washed with cool isopropyl alcohol and air-dried, finally dried in vacuum at 60 °C. Yield = 87%.

2.3.20. Synthesis of bis(N1-(4-methoxyphenyl)-2-(1-acetyl-2-oxopropylsulfanyl)acetamido) zirconium(IV) phthalocyanine (XIX)

1.00 mmol of PcZrCl_2 was suspended in 10 ml xylene and then 2.20 mmol of N1-(4-methoxyphenyl)-2-(1-acetyl-2-oxopropylsulfanyl)acetamide was added to the suspension. The reaction mixture was heated under reflux for 4 h after which the hot mixture was filtrated. The solvent volume was reduced by 50% using vacuum evaporation and the final product was precipitated by hexane. Blue-green crystals were formed slowly while the solution was cooling down. The product was filtered, abundantly washed by hexane, air-dried and eventually dried under vacuum at 100 °C. Yield: 67%. *Anal.* Calc. for $\text{C}_{60}\text{H}_{48}\text{N}_{10}\text{O}_8\text{S}_2\text{Zr}$: C, 60.44; H, 4.06; N, 11.75; Zr, 7.65. Found: C, 60.15; H, 3.85; N, 11.25; Zr, 7.50%. IR (KBr, cm^{-1}): 3050 (w), 1615 (m), 1580 (s), 1565 (sh), 1525 (s), 1505 (s), 1465 (m), 1420 (m), 1390 (m), 1370 (m), 1360 (m), 1330 (s), 1285 (s), 1210 (w), 1185 (w), 1160 (s), 1115 (s), 1075 (s), 1030 (m), 1000 (m), 980 (sh), 950 (w), 935 (w), 895 (s), 870 (m), 810 (m), 780 (s), 750 (s), 740 (s), 725 (w), 670 (w), 640 (m), 580 (m), 530 (w), 510 (m), 495 (w), 460 (m), 280 (m). ^1H NMR (δ ppm, CDCl_3): 9.47 (4H, q, H^α); 9.33 (4H, q, H^α); 8.20 (4H, q, H^β); 8.10 (4H, q, H^β); 7.27 (4H, d., $2\text{C}_6\text{H}_4$); 7.18 (2H, s, 2NH); 6.83 (4H, d., $2\text{C}_6\text{H}_4$); 3.78 (6H, s, 2OCH_3); 2.19 (4H, s, 2CH_2); 1.51 (12H, s, 4CH_3).

2.3.21. Synthesis of bis(N1-(4-methoxyphenyl)-2-(1-acetyl-2-oxopropylsulfanyl)acetamido) hafnium(IV) phthalocyanine (XX)

It was prepared from PcHfCl_2 and N1-(4-methoxyphenyl)-2-(1-acetyl-2-oxopropylsulfanyl)acetamide by the same procedure as XIX. Yield: 66%. *Anal.* Calc. for $\text{C}_{60}\text{H}_{48}\text{N}_{10}\text{O}_8\text{S}_2\text{Hf}$: C, 56.31; H, 3.78; N, 10.95; Hf, 13.95. Found: C, 56.35; H, 3.75; N, 10.25; Hf, 13.50%. IR (KBr, cm^{-1}): 3060 (w), 1610 (m), 1580 (s), 1570 (sh), 1525 (s), 1505 (s), 1465 (m), 1420 (m), 1390 (m), 1370 (m), 1360 (m), 1330 (s), 1285 (s), 1210 (w), 1185 (w), 1160 (s), 1115 (s), 1075 (s), 1030 (m), 1000 (m), 980 (sh), 950 (w), 935 (w), 895 (s), 870 (m), 810 (m), 780 (s), 750 (s), 740 (s), 725 (w), 670 (w), 640 (m), 580 (m), 530 (w), 500 (m), 490 (w), 440 (m), 280 (m). ^1H NMR (δ ppm, CDCl_3): 9.42 (4H, q, H^α); 9.28 (4H, q, H^α); 8.25 (4H, q, H^β); 8.07 (4H, q, H^β); 7.29 (4H, d., $2\text{C}_6\text{H}_4$); 7.16 (2H, s, 2NH); 6.81 (4H, d., $2\text{C}_6\text{H}_4$); 3.77 (6H, s, 2OCH_3); 2.15 (4H, s, 2CH_2); 1.45 (12H, s, 4CH_3).

2.3.22. Synthesis of bis(4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-onato)zirconium(IV) phthalocyanine (XXI)

It was prepared from PcZrCl_2 and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one by the same procedure as XIX. Yield: 71%. Anal. Calc. for $\text{C}_{66}\text{H}_{42}\text{N}_{12}\text{O}_4\text{Zr}$: C, 68.44; H, 3.65; N, 14.51; Zr, 7.87. Found: C, 68.05; H, 3.15; N, 14.10; Zr, 7.50%. IR (KBr, cm^{-1}): 3070 (m), 2930 (w), 2870 (w), 2650 (w), 2610 (w), 2560 (m), 1620 (s), 1605 (s), 1570 (s), 1530 (m), 1505 (s), 1485 (s), 1470 (m), 1445 (m), 1425 (m), 1390 (m), 1365 (w), 1336 (s), 1290 (s), 1255 (w), 1215 (w), 1166 (s), 1120 (s), 1080 (s), 1030 (m), 1005 (w), 960 (m), 900 (s), 880 (w), 850 (m), 830 (m), 800 (w), 785 (w), 760 (m), 755 (s), 740 (s), 705 (m), 695 (m), 670 (w), 630 (m), 560 (w), 510 (m), 455 (w), 435 (w), 355 (w), 300 (m). ^1H NMR (δ ppm, CDCl_3): 9.45 (2H, d, H^α); 9.25 (4H, d, H^α); 8.81 (2H, d, H^α); 8.22 (2H, t, H^β); 8.04 (6H, m, H^β); 7.44 (2H, q, $4\text{C}_6\text{H}_5$); 7.35 (4H, q, $4\text{C}_6\text{H}_5$); 7.18 (4H, t, $4\text{C}_6\text{H}_5$); 7.05 (6H, q, $4\text{C}_6\text{H}_5$); 6.88 (4H, q, $4\text{C}_6\text{H}_5$); 1.34 (3H, s, CH_3); 1.25 (3H, s, CH_3).

2.3.23. Synthesis of bis(4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-onato)hafnium(IV) phthalocyanine (XXII)

It was prepared from PcHfCl_2 and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one by the same procedure as XIX. Yield: 69%. Anal. Calc. for $\text{C}_{66}\text{H}_{42}\text{N}_{12}\text{O}_4\text{Hf}$: C, 63.64; H, 3.40; N, 13.49; Hf, 14.33. Found: C, 63.10; H, 3.00; N, 13.05; Hf, 14.50%. IR (KBr, cm^{-1}): 3070 (m), 2930 (w), 2870 (w), 2650 (w), 2610 (w), 2560 (m), 1625 (s), 1615 (s), 1610 (s), 1575 (s), 1530 (m), 1505 (s), 1485 (s), 1470 (m), 1445 (m), 1425 (m), 1390 (m), 1365 (w), 1336 (s), 1290 (s), 1255 (w), 1210 (w), 1166 (s), 1120 (s), 1080 (s), 1030 (m), 1005 (w), 960 (m), 900 (s), 880 (w), 850 (m), 830 (m), 800 (w), 785 (w), 760 (m), 755 (s), 740 (s), 705 (m), 695 (m), 670 (w), 630 (m), 560 (w), 510 (m), 455 (w), 435 (w), 355 (w), 275 (m). ^1H NMR (δ ppm, CDCl_3): 9.44 (2H, d, H^α); 9.25 (4H, d, H^α); 8.81 (2H, d, H^α); 8.22 (2H, t, H^β); 8.04 (6H, m, H^β); 7.44 (2H, q, $4\text{C}_6\text{H}_5$); 7.28 (4H, q, $4\text{C}_6\text{H}_5$); 7.16 (4H, t, $4\text{C}_6\text{H}_5$); 7.03 (6H, q, $4\text{C}_6\text{H}_5$); 6.86 (4H, q, $4\text{C}_6\text{H}_5$); 1.34 (3H, s, CH_3); 1.23 (3H, s, CH_3).

3. Results and discussion

Two chlorine atoms bound to the central metal atom of dichloro(phthalocyaninato) zirconium(IV) or hafnium(IV) are highly mobile and can be easily exchanged for various organic ligands [23–26]. This ability makes possible synthesis the “out-of-plane” directly to the metal substituted phthalocyanine complexes with the tailor-made properties. Phthalocyanine ring is the π -conjugated macrocycle that has interesting spectral, electrochemical and optical properties. Introduction of two β -dicarbonyl fragments leads to the expansion of π -conjugated system and due to one's turn changes spectral luminescent behaviour. It must be emphasised that we mean not only π -conjugated Pc ring but the whole system where metal play role of connector between Pc ring and two β -dicarbonyl ligands.

The results obtained from IR, ^1H NMR spectroscopy and elemental analysis suggest that substitution of two Cl atoms for two β -dicarbonyl ligands takes place as the result of the reaction between PcZrCl_2 or PcHfCl_2 and free β -dicarbonyl compounds. The isolated complexes with additional axial ligands are soluble in most organic solvents (DMSO, toluene, chloroform and other). However, determination of the complexes structure by X-ray methods is difficult because of obstacle to grow monocrystal of optimal size. Instead of X-ray diffraction the methods of two dimension NMR spectroscopy (COSY, NOESY, ROESY) have been used for studying the structure of the synthesized out-planed substitution phthalocyanine complexes of zirconium(IV) and hafnium(IV).

2D ^1H NMR COSY and NOESY spectra of bis(2,4-pentanedionato)hafnium(IV) chlorinephthalocyanine (V) shown in Fig. 1 reveal that the interaction protons (out of diagonal signals) are related to the compounds of different structure. Analogous effect can be observed for the zirconium complex (VI). It allows asserting that analyzed complexes consist of the mixture of structural monochlorinated phthalocyanine isomers. For all the investigated mixed ligand complexes 2D ^1H NMR spectra, COSY exhibit only correlation between $^\alpha\text{H}$ – $^\beta\text{H}$ protons in phthalocyanine N_8 ring and protons from out-plane ligands. The interactions between ring and ligands protons have not been found. At the same time in the 2D ^1H NMR spectra NOESY for complex XVII shown in Fig. 2, besides diagonal crossing signals also can be observed the signals which arise from the space interaction between phthalocyanine ring protons and protons of the out planed ligands. For example, it can be seen for methyl and $^\alpha\text{H}$ protons or phenyl and $^\beta\text{H}$. It proves that the angle between the β -dicarbonilate ligand plane and the phthalocyanine ring plane is very sharp and the coordination junction has *cis*-configuration. The analogous data have been obtained for the other mixed ligands β -(dicarbonilato)zirconium and hafnium phthalocyanines. The 2D NOESY experiment for complexes XIX (Fig. 3) and XX nicely illustrates the NOE cross peaks between $^\beta\text{H}$ (Pc) and CH_2 , NH, *p*- C_6H_4 (Ar) protons of the out planed ligands; $^\alpha\text{H}$ (Pc) and CH_3 . To determine the structure of complexes XXI and XXII, NOESY and ROESY correlations between protons of phenyl groups of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one and $^\alpha\text{H}$ – $^\beta\text{H}$ protons of Pc macrocycle have been analyzed (Figs. 4a and b). Besides diagonal crossing signals also ROE correlations for $^\alpha\text{H}$ (Pc)– CH_3 and $^\beta\text{H}$ (Pc)–H (Ph) have been observed. In addition, two signals coming from the methyl groups of DMF could be observed. Inasmuch signals of DMF methyl groups are present on all the spectra shown in Figs. 2–4 and also interaction between these DMF protons and protons from both phthalocyanine ring and out-planed ligands are present, we can conclude that molecule of DMF is solvated in a cavity between the “out of plane” dicarbonilato ligand and the N_8 macrocycle.

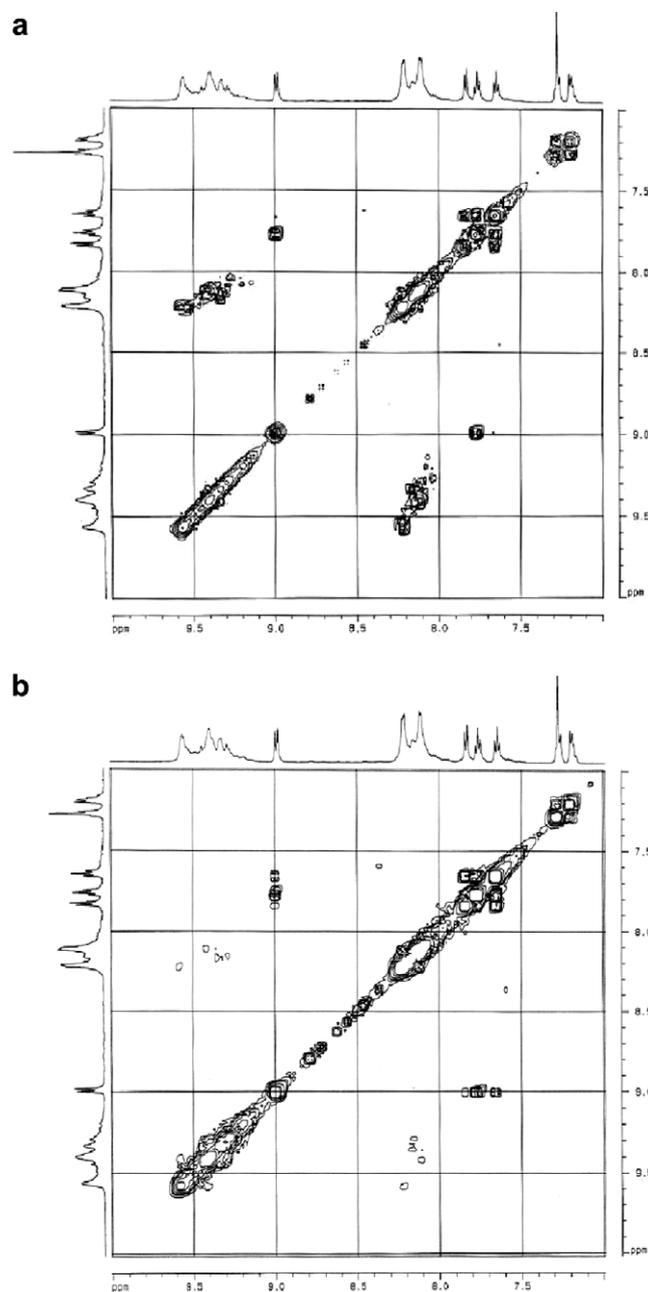


Fig. 1. 2D NMR spectra of complex VI (CDCl_3): COSY (a) and NOESY (b).

3.1. Luminescence properties

UV–Vis absorption spectra provide information about the possibility of the absorption transition between the ground and excited states of dye molecule. Two absorption bands, the intense Q band at 680–695 nm and less intensive Soret band at 320–360 nm are present in the spectra of bis(β -dicarbonylato)zirconium(IV) and hafnium(IV) phthalocyanine complexes (Table 1). Examples of the UV–Vis absorption spectra for compounds VII, XIX, and XXI in DMSO solutions are shown in Fig. 5. Addition of two β -dicarbonyl ligands leads to the expansion of π -conjugated system as β -dicarbonyl forms together with metal atom

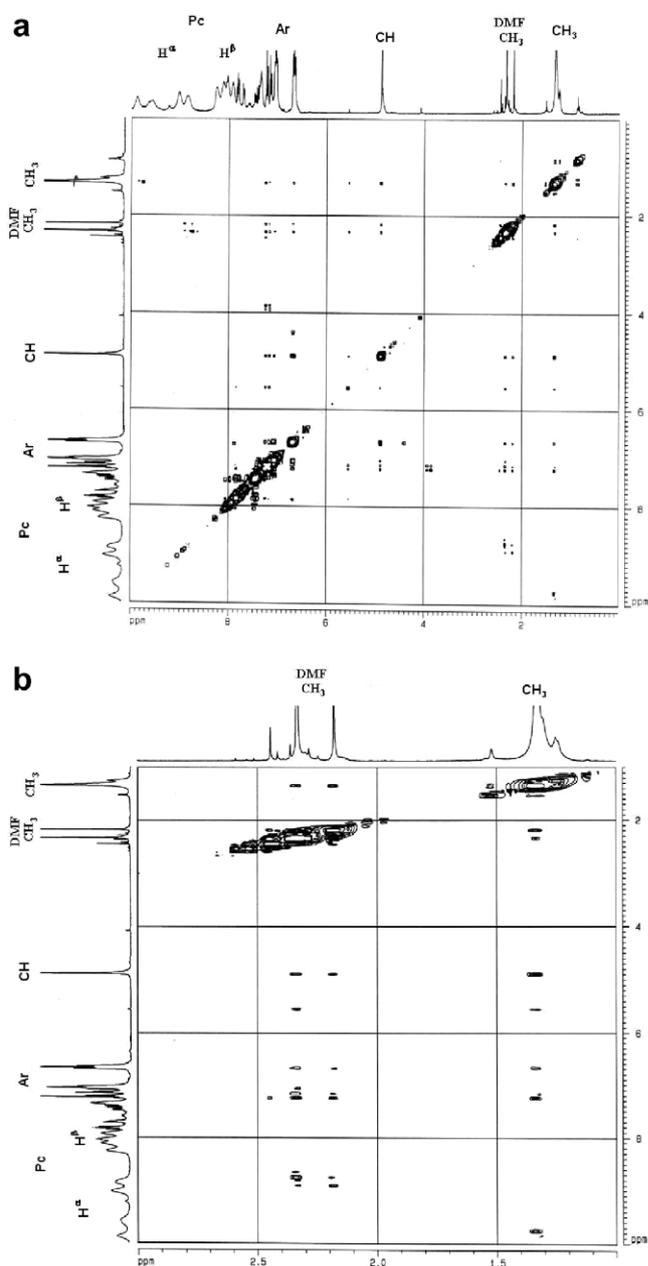


Fig. 2. 2D NMR spectra of complex XVII (CDCl_3): NOESY (a, b).

quasi aromatic cyclic system. Delocalization of π electrons in the conjugated system and presence of free d-electron orbitals of the central metal atom have important influence on the HOMO–LUMO transitions and, as a result, the bathochromic shift of the Q-absorption band is observed in the spectra. For these reasons, metal-containing and out of plane substituted phthalocyanines which absorb intensively in the visible light region, could be used as photoconverters. Photoconverters have to absorb light energy suitable for the energy gap of the semiconductors. The shape of the UV–Vis spectra does not change dramatically in various solvents and only a small shift of the Q-band position is observed. At the same time, insignificant change of the molar absorption coefficient value takes

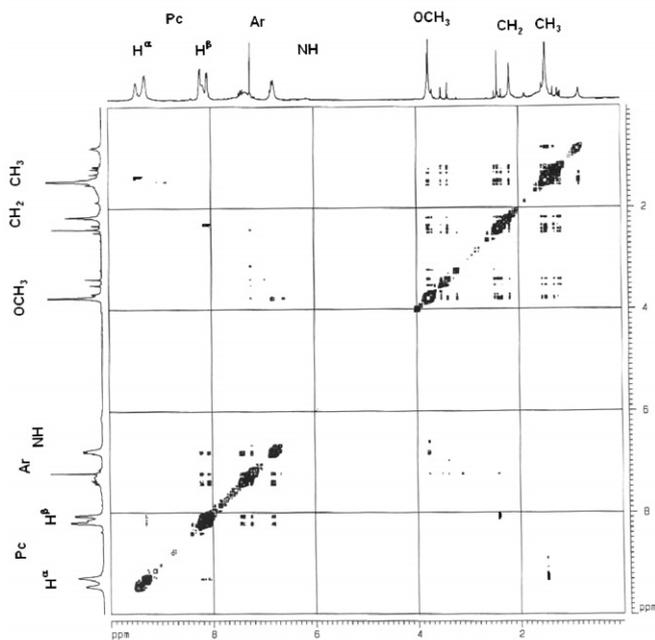


Fig. 3. 2D NMR spectra NOESY of complex XIX (CDCl_3).

place (Table 1, Fig. 6). For all the investigated complexes, except VII and IX, the increasing of the molar absorption coefficient occurs in the series DMSO–THF–toluene. This sequence is in good agreement with Reichardt's solvents polarity parameters [27]. The lowest value of the molar absorption coefficient is observed in DMSO (polarity parameter 0.444), higher for THF (0.207) and the highest for toluene (0.099). Process of phthalocyanine dimerization is easier in the more polar solvents.

The fluorescent properties of the investigated complexes III, VII, IX, XI, XIII, XV, XIX and XXI were studied in the same solvents: toluene, DMSO and THF. All studied zirconium phthalocyanine complexes show weaker fluorescence than zinc phthalocyanine (Table 1). The complex XV gives fluorescent activity only in DMSO solution (Fig. 7). At the same conditions PcHfCl_2 and other synthesized hafnium phthalocyanine complexes do not exhibit any fluorescence. This phenomenon is known and explained by the effect of the “heavy” atom.

The fluorescence quantum yields of dyes were determined by the comparative method [11,28] on the ground of the UV–Vis and fluorescence spectra, using the following equation:

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

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 solution ($\Phi_R = 0.20$) [29] was used

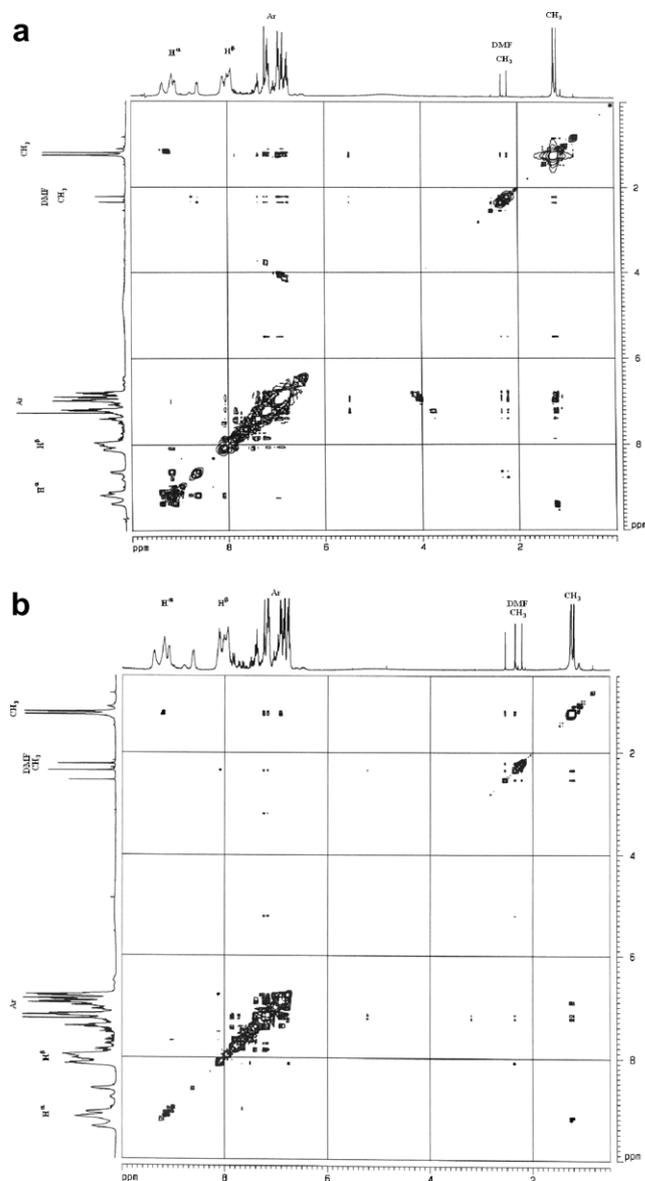


Fig. 4. 2D NMR spectra of complex XXI (CDCl_3): NOESY (a) and ROESY (b).

as a reference standard. The natural lifetimes of the studied phthalocyanine complexes were evaluated from absorption and fluorescence spectra by the known method described in references [11,28], using the following equation:

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

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

The fluorescence quantum yields were determined by formula (1) and natural lifetimes were calculated on the basis of the absorption and fluorescence data (Eq. (2)). For the investigated complexes containing the alkyl fragments in the out of plane ligands, the highest values of

Table 1
Spectral and photophysical measurements

Complex	Solvent	Abs. λ_{\max} (nm)	$\epsilon \times 10^5$	Fluoresc. λ_{\max} (nm)	n^{20}	Φ_F	$\Delta\lambda$ (nm)	τ (ns)
PcZn	Toluene	670	3.4209	676	1.496	0.07	6	2.41
	DMSO	673	1.5900	686	1.478	0.2	13	6.76
	THF	666	2.3305	678	1.408	0.23	12	5.36
III	DMSO	688	1.1646	697	1.479	0.006	11	14.17
VII	Toluene	688	0.8276	703	1.497	0.024	15	1.66
	DMSO	684	1.3140	702	1.479	0.073	18	6.33
	THF	684	1.6225	697	1.407	0.032	13	5.34
IX	Toluene	688	1.9971	701	1.498	0.042	13	1.66
	DMSO	686	1.489	703	1.478	0.072	17	5.42
	THF	682	2.1950	696	1.407	0.069	12	4.09
XI	Toluene	682	7.246	695	1.496	0.004	13	1.27
	DMSO	685	1.610	697	1.480	0.069	12	5.72
	THF	683	2.356	690	1.407	0.029	7	4.59
XIII	Toluene	686	2.871	702	1.497	0.063	16	2.58
	DMSO	682	0.8995	700	1.480	0.075	18	8.87
	THF	680	1.1300	692	1.408	0.117	12	7.78
XV	Toluene	686	4.942		1.496			
	DMSO	686	1.2360	693	1.479	0.066		6.20
	THF	686	1.7725		1.408			
XIX	Toluene	686	3.083	703	1.497	0.029	17	2.55
	DMSO	692	1.1005	702	1.478	0.067	10	6.99
	THF	688	1.7750	691	1.407	0.038	3	4.94
XXI	Toluene	691	4.323	708	1.496	0.073	17	1.99
	DMSO	694	1.4995	709	1.478	0.063	15	5.79
	THF	690	2.3065	701	1.406	0.061	11	4.12

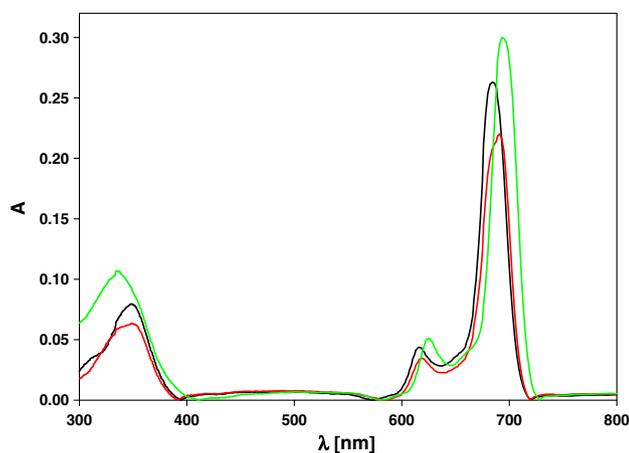


Fig. 5. Electronic absorption spectra of Zr(IV) axially substituted phthalocyanines **VII** (dash-dotted), **XIX** (dashed), **XXI** (solid line) 2×10^{-6} mol/dm³ solutions in DMSO.

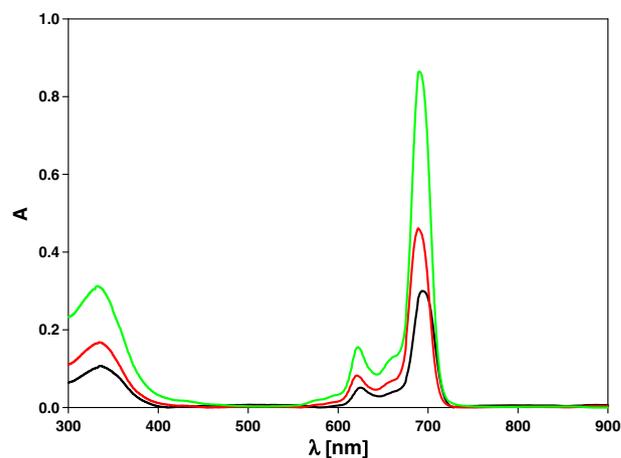


Fig. 6. Electronic absorption spectra of Zr(IV) axially substituted phthalocyanine **XXI** 2×10^{-6} mol/dm³ solutions in DMSO (solid), THF (dotted) and toluene (dashed line).

fluorescence quantum yields are observed in DMSO. For these complexes, some increasing of fluorescence quantum yields is observed in the sequence: toluene–THF–DMSO, analogous with the same effect in the absorption spectra. It can be explained by the increasing viscosity of the solvents. Increasing of solvent viscosity leads to braking of the free rotation alkyl fragments in out of plane ligands

that makes molecule more rigid and in consequence leads to increasing of fluorescence quantum yield. This regularity does not take place for complexes **XIII** and **XXI**. Complex **XIII** in THF has the highest values of fluorescence quantum yield ($\Phi_F = 11.7\%$). It can be explained by the structure of complex **XIII**, which contains 1,1,1,5,5,5-hexafluoro-2,4-pentanedione ligand. In other words, the introduction of electronegative fluorine atoms

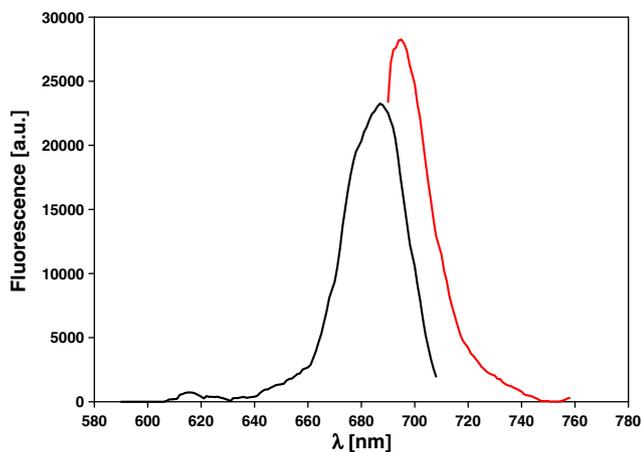


Fig. 7. Excitation ($\lambda_{\text{det}} = 696$ nm) (solid) and fluorescence ($\lambda_{\text{exc}} = 686$ nm) (dashed line) spectra of Zr(IV) axially substituted phthalocyanine (XV) 2×10^{-6} mol/dm³ in DMSO solution.

leads to shift of electronic density in ligand and, respectively, via metal atom in Pc macrocycle, what have significant influence on the HOMO–LUMO transitions. Two π -conjugated pyrazolone ligands are introduced in complex XXI. In result this compound must be considered as rigid π -conjugated system.

The natural lifetimes of studied phthalocyanines are in the range of nanoseconds. It means that the energy transfer should be reachable 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 β -dicarbonyl fragments leads to increasing of fluorescence quantum yield and decreasing of the natural lifetimes (Table 1). The maximum values of the natural lifetimes for studied complexes are in DMSO. The Stokes shifts between the absorption Q-band and the fluorescence maximum are very small (3–18 nm) for all investigated PcZrL_2 .

4. Conclusions

The series of zirconium(IV) and hafnium(IV) phthalocyanines with various β -dicarbonyl ligands has been synthesized. The structure of the obtained bis(β -dicarbonylato) zirconium(IV) and hafnium(IV) phthalocyanines was studied by two dimension ¹H NMR spectroscopy (COSY, NOESY, ROESY). The interaction between phthalocyanine and out of plane ligand protons allows determining the structure of macromolecule by NOESY and ROESY techniques. It was concluded that additionally the molecule of DMF is solvated in a cavity between the “out of plane” dicarbonylato ligand and the N_8 macrocycle.

Absorption and fluorescence spectroscopic properties were studied in three solvents with different polarity. In the concentration range of 10^{-6} M/dm³, there is rather

no tendency to the aggregation; however, absorbance slightly decreases with higher solvent polarity. Fluorescence quantum yields and natural life times of zirconium phthalocyanine complexes have been calculated in toluene, DMSO and THF. Correlation between the structure of phthalocyanine mixed ligand complexes and the properties of the solvents from one side and spectral luminescent properties from the other was found.

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