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Early Lanthanides (Porphyrinato)(Crownphthalocyaninates): Efficient Synthesis and NIR Absorption Characteristics

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Series of early lanthanides heteroleptic complexes of double- and triple-decker sandwich-type structure with tetra(15-crown-5)phthalocyanine [(15C5)$_4$PcH$_2$] and tetrakis-meso-(4-methoxyphenyl)porphyrin [An$_4$PH$_2$] ([An$_4$P] Ln[(15C5)$_4$Pc] and [An$_4$P]Ln[(15C5)$_4$Pc]Ln[An$_4$P]) are synthesized. It is found that the whole series of La-Eu acetylacetonates can be applied for a one-step formation of heteroleptic sandwich-type complexes. Triple-decker heteroleptic complexes [An$_4$P]Ln[(15C5)$_4$Pc]Ln[An$_4$P] are formed regioselectively as a single isomer with internal position of crownphthalocyanine deck. Heteroleptic double- and triple-decker complexes are found to be the only products of the reaction. Ligand scrambling is not observed and no homoleptic complexes are detected as side products. All the synthesized complexes are characterized with a set of physical-chemical methods. It was shown that the lanthanide-sensitive bands are present in NIR region of the spectra of all synthesized complexes. The position of NIR absorption is found to be linearly dependent on lanthanide ionic radius. Analysis of electronic absorption spectra of all synthesized complexes allowed to determine the influence of ligand environment on the oxidation state of cerium metal center. The comparison of the mentioned linear correlation and spectral data for cerium complexes allowed determination of the oxidation state in each particular case. It is found that cerium atom may utilize both +3 and +4 oxidation states in double-decker complex [An$_4$P]Ce[(15C5)$_4$Pc]. In contrast, coordination environment of triple-decker complex [An$_4$P]Ce[(15C5)$_4$Pc]Ce[An$_4$P] effectively stabilizes Ce^{III} state and prevents its oxidation to Ce^{IV}. The comparison of behaviour of Eu and Ce double- and triple-decker complexes upon chemical oxidation is performed, that allowed to determine a set of redox forms and their stability.

Keywords: Porphyrins, phthalocyanines, crown ether, lanthanide, heteroleptic complexes, near-IR absorption.

Introduction

Non-linear optics, multibit information storage and molecular recognition are foreground trends of current molecular design. These topics of science require highly stable molecules of variable and tunable structure, allowing to manipulate their physico-chemical properties. Metal complexes with porphyrins and phthalocyanines attract interest as promising starting compounds for development of materials possessing unique properties. Depending on the coordination features of metal center, diverse architectures can be synthesized. Coordination features of lanthanide ions allow formation of sandwich-type homo- and heteroleptic complexes with porphyrins and phthalocyanines. Peripheral part of the macrocyclic ligands can be easily modified before or after formation of complex. Variation of ionic radius of metal centers in sandwich-type complexes allows to tune the interligand distance and thus the efficiency of π−π-interaction between macrocycles. In turn, optical properties and redox potentials of the molecules are dependent on π−π-interaction between ligands.

All mentioned features of lanthanide heteroleptic complexes with cyclic tetrapyrrolic ligands resulted in a series of investigations of these types of molecules in recent years.[1-6] Selective receptors for ions and molecules were constructed on the basis of sandwich-type complexes.[4,5,7-10]

In recent work[11] selective binding at sandwich-type receptor site was utilized as driving force for contraction of "molecular spring". Series of papers of Lindsey's group were devoted to selective synthesis of heteroleptic complexes containing porphyrin and phthalocyanine ligands and their application for development of molecular storage devices.[3,12-16]

The typical synthetic route to preparation of lanthanide (porphyrinato)(phthalocyaninates) consists in stepwise formation of heteroleptic complexes with a target structure and is usually called "raise-by-one-storey" technique. This method is applicable mostly for the synthesis of complexes with late lanthanides. The main problem of this approach is preparation of lanthanide monoporphyrinates and monophthalocyaninates as intermediates, which are unstable in the case of early lanthanides.

Several attempts were performed in order to simplify the procedure and to decrease the number of experimental steps for the preparation of heteroleptic lanthanide complexes. A pseudo-one-step procedure was developed for selective synthesis of double-decker europium (porphyrinato)-(phthalocyaninates).[17] This method consisted in generation of europium monoporphyrinate [Por]Eu(acac) semiproduct in refluxed trichlorobenzene, which was evaporated and the residual monoporphyrinate was further treated with phthalonitrile and DBU in amyl alcohol. This procedure leads to heteroleptic double-decker compound with moderate

yields. Interaction of octa-β-ethylporphyrin (OEPH$_2$) and naphthalonitrile with lanthanide acetylacetonate (Ln(acac)$_3$) in high-boiling alcohol in the presence of strong base leads to the formation of double-decker complexes [OEP]Ln[Nc] for the whole La-Lu series.[18-20] It was shown[18] that in the case of Nd and Eu additional treatment of [OEP]Ln[Nc] complex with Ln(acac)$_3$ and OEPH$_2$ allows to synthesize triple-decker heteroleptic complexes of [OEP]Ln[Nc] Ln[OEP] structure. Mixtures of heteroleptic triple-decker lanthanide (porphyrinato)(phthalocyaninates) containing different number of porphyrin decks can be prepared through interaction of lanthanide monoporphyrinates and Li$_2$Pc.[21,22]

A stepwise procedure was also applied by group of J. Jiang for synthesis of heteroleptic triple-decker europium complexes [TPP]Eu[(15C5)$_4$Pc]Eu[TPP] and [TPP]Eu[(15C5)$_4$Pc]Eu[(15C5)$_4$Pc].[23] The first step was the synthesis of homo- and heteroleptic double-decker complexes. Heteroleptic double-decker compound was synthesized *via* tetramerization of corresponding phthalonitrile at monoporphyrinate as template. The double-deckers were further additionally treated with europium monoporphyrinate that resulted in formation of target molecules. Authors specially mentioned that they performed attempts to synthesize heteroleptic triple-decker complex of symmetrical type [TPP]Eu[(15C5)$_4$Pc]Eu[TPP] in 1-octanol at 200°C through interaction of phthalonitrile and europium monoporphyrinate. This attempt was not successful and resulted in formation of desired triple-decker with low yield and its separation from other sandwich-type side products was complicated.

In[3,13] authors investigated in details and applied the rational routes for preparation of heteroleptic homo- and heterometallic triple-decker (porphyrinato) (phthalocyaninates) with different position of decks. Europium and cerium monoporphyrinates were used as key intermediates for the synthesis. In the case of cerium application of sterically hindered extra-ligands required for stabilization of monoporphyrinic species. The triple-decker complexes were obtained with moderate yields. Different types of heteroleptic triple-decker complexes were synthesized as a statistical mixture resulting in low yields of each particular compound.[12,14,15]

Although one-step and pseudo-one-step routs were found for preparation of heteroleptic double-decker lanthanide (porphyrinato)(phthalocyaninates) the selective procedures for preparation of triple-decker complexes are still limited. The addition of the third deck requires a special synthetic step which is performed at high temperature. In turn it results in formation of complicated mixture of complexes owing to ligand scrambling processes. On the other hand triple-decker complexes of early lanthanides cannot be synthesized in terms of this protocol owing to low stability of corresponding monoporphyrinates. These problems forced us to develop effective one-step procedure for regioselective preparation of triple-decker heteroleptic (porphyrinato)-(phthalocyaninates) of early lanthanides.

Recently we have reported on a procedure allowing to obtain early lanthanides heteroleptic triple-decker complexes of symmetrical [Por]Ln[Pc]Ln[Por] structure in one-step process for La, Ce and Pr.[24] The triple-decker compounds were obtained regioselectively as a single isomer and the

only side products were the corresponding double-decker complexes. Herein we report on applicability and synthetic details of the found synthetic route for regioselective preparation of heteroleptic triple-decker (porphyrinato) (phthalocyaninates) of general structure [An$_4$P]Ln[(15C5)$_4$Pc] Ln[An$_4$P] for the whole early lanthanides series (La-Eu).

As it was shown earlier,[25] the valent state of cerium atom in sandwich-type complexes with tetrapyrrolic ligands is very sensitive to coordination environment. This particular feature allows precise tuning of its oxidation state, resulting in modification of electronic properties, redox-potentials, stability and absorption spectra of the complexes. A comprehensive research to determine the influence of the structure of tetrapyrrolic ligands on the cerium oxidation state was undertaken by the group of J. Jiang for the series of double-decker homo- and heteroleptic complexes.[25] It was shown that electron-donating properties of the ligands stabilize the Ce^{III} state of the metal center. Thus, in the case of cerium bis-phthalocyaninates the Ce^{IV} state was determined. Expansion of π-system of the ligand increases the electron-donating properties of the ligand. As a result, in the case of cerium bis-naphthalocyaninate the intermediate valent state between Ce^{III} and Ce^{IV} was determined. Recently we have investigated the homoleptic double-decker cerium bis[tetra(15-crown-5)phthalocyaninate] Ce[(15C5)$_4$Pc]$_2$ in order to determine the valent state of metal center.[26] We have shown that the presence of eight alkoxy-substituents in the phthalocyanine macrocycle results in partial electron back-donation to metal center, resulting in the intermediate cerium valent state.

The determination of oxidation state of metal center was done through analysis of electron absorption spectra of the series of isostructural lanthanide complexes.[25,26] In the case of all types of compounds lanthanide-sensitive bands were found, which gradually shift with variation of metal center. The determination of the mentioned dependencies is important for development of novel materials. Thus, we have found that in the case of cerium double-decker bis[tetra15-crown-5)phthalocyaninate] the electrochemical switching of cerium valent state is possible in Langmuir-Blodgett films of the compound.[27] The alteration of cerium oxidation state results in contraction and expansion of metal center and the physical dimensions of the molecule itself. The found system can be called the "electronic muscle", which may perform mechanical work under influence of electric field.

Herein we report on the synthesis of series of double- and triple-decker heteroleptic (porphyrinato)-(phthalocyaninato) early lanthanides. The investigation of synthesis of the whole La-Eu subgroup complexes allows to prove the possible application of the developed route. The preparation of a series of the related lanthanide complexes allows to analyze the absorption characteristics of the compounds, particularly the absorptions in NIR region. The analysis of spectral characteristics of the series of complexes allowed determining the influence of ligand environment onto oxidation state of cerium atom.

Experimental

1-Octanol (OctOH, Acros Organics, 98%) was used freshly distilled over Na. Chloroform was dried over CaCl$_2$ and used

freshly distilled over CaH₂. MeOH (99%, Merk), CDCl₃ (99.8%, Aldrich) and hexane (reagent grade) were used as obtained without further purification. Acetylacetonates of La-Eu (99%, Aldrich), hydrazine monohydrate (100%, Acros Organics) and propionic acid (Riedel de Haën, 99%) were also used as obtained. Pyrrole (99%, Acros Organics), 4-methoxybenzaldehyde (99%, Aldrich) and 1,8-diazabicyclo[5.4.0]undec-7-en (DBU, Merck, >97%) were used freshly distilled over CaH₂. Tetrakis-*meso*-(4-methoxyphenyl)porphyrin (An₄PH₂)[28] and 4,5-dicyanobenzo-(15-crown-5) (DCB-15C5) were prepared according to described procedures.[29]

Chromatographic separation and purification of the complexes were performed at cylindrical glass columns filled with neutral alumina (Merck, 0.063-0.2 mm). UV-vis absorption spectra were recorded in 250-900 nm spectral region with Varian Cary-100 spectrophotometer in 1-10 mm rectangular quartz cells. MALDI-TOF mass-spectra were obtained on Bruker Daltonics Ultraflex mass-spectrometer in positive ion mode with nicotinic acid as a matrix. ¹H-NMR spectra were recorded at Bruker Avance-II spectrometer with 300.21 MHz frequency. Samples with concentration *ca.* 10⁻⁵-10⁻⁶M were prepared in CDCl₃. Chemical shifts were measured at T = 298 K relatively to external standard (tetramethylsilane, δ = 0.00 ppm). Acquired spectra were processed with line broadening factor of 1 Hz.

General procedure for preparation of heteroleptic complexes [An₄P]Ln[(15C5)₄Pc]Ln[An₄P] was equal to one described earlier.[24] The mixture of Ln(acac)₃ (0.1 mmol), 5,10,15,20-tetrakis (4-methoxyphenyl)porphyrin (An₄PH₂) (37 mg, 0.05 mmol), 4,5-dicyanobenzo-15-crown-5 (127 mg, 0.4 mmol) and DBU (50 μl, 0.33 mmol) was refluxed in 1-octanol (4 ml) for 18 hours under slow stream of dry argon. The reaction mixture was cooled to room temperature and added dropwise into 50 ml of hexane. The dark precipitate was filtered and washed with hexane. Chloroform solution of the residue was applied on chromatographic column filled with neutral alumina. The column was eluted with CHCl₃-MeOH mixture (0-1% v/v MeOH). Brown fraction of triple-decker complex Ln₂[An₄P]₂[(15C5)₄Pc] was collected at 0.5-1% of MeOH in eluent. Green fraction of double-decker complex Ln[An₄P][(15C5)₄Pc] was collected at further elution with 4-5% MeOH in CHCl₃.

La[An₄P][(15C5)₄Pc] (**DD1**). Yield 26%. UV-vis (CHCl₃) λ_max nm: 292, 368, 422, 486, 600, 756. ¹H NMR (CDCl₃) δ ppm (*J*, Hz): 8.56 (s, 8H, H_Pc), 8.13 (s, 8H, H_Pyrr), 8.03 (s, 4H, H_An), 7.36 (s, 4H, H_An), 6.84 (s, 8H, H_An), 4.86 (s, 8H, α-Cr), 4.63 (s, 8H, α'-Cr), 4.24 (s, 16H, β-Cr), 4.00 (s, 32H, γ+δ-Cr), 4.09 (s, 12H, OMe). MALDI-TOF MS (*m/z*): 2145.3, calcd. for C₁₁₂H₁₀₈N₁₂O₂₄La 2145.28.

Ce[An₄P][(15C5)₄Pc] (**DD2**). Yield 20%. UV-vis (CHCl₃) λ_max nm: Ce^IV – 293, 368, 405, 621, 824; Ce^III – 291, 368, 421, 624, 763. ¹H NMR (CDCl₃) δ ppm (*J*, Hz): 8.62 (s, 8H, H_Pc), 8.37 (s, 8H, H_Pyrr), 7.53 (s, 4H, H_An), 7.40 (s, 4H, H_An), 6.75 (s, 4H, H_An), 6.39 (s, 4H, H_An), 4.96 (s, 8H, α-Cr), 4.68 (s, 8H, α'-Cr), 4.25 (s, 16H, β-Cr), 4.00 (s, 32H, γ+δ-Cr), 4.07 (s, 12H, OMe). MALDI-TOF MS (*m/z*): 2146.3, calcd. for C₁₁₂H₁₀₈N₁₂O₂₄Ce 2146.24.

Pr(An₄P)[(15C5)₄Pc] (**DD3**). Yield 18%. UV-vis (CHCl₃) λ_max nm: 292, 368, 421, 485, 599, 777. MALDI-TOF MS (*m/z*): 2147.9, calcd. for C₁₁₂H₁₀₈N₁₂O₂₄Pr 2147.03.

Nd(An₄P)[(15C5)₄Pc] (**DD4**). Yield 15%. UV-vis (CHCl₃) λ_max nm: 291, 370, 420, 487, 601, 783. MALDI-TOF MS (*m/z*): 2150.2, calcd. for C₁₁₂H₁₀₈N₁₂O₂₄Nd 2150.36.

Sm(An₄P)[(15C5)₄Pc] (**DD5**). Yield 16%. UV-vis (CHCl₃) λ_max nm: 289, 368, 417, 485, 600, 795. ¹H NMR (CDCl₃) δ ppm (*J*, Hz): 8.16 (s, 8H, H_Pc), 7.36 (s, 8H, H_Pyrr), 6.77 (s, 8H, H_An), 6.63 (s, 4H, H_An), 6.18 (s, 4H, H_An), 4.60 (s, 8H, α-Cr), 4.43 (s, 8H, α'-Cr), 4.09 (s, 16H, β-Cr), 3.88 (s, 44H, γ+δ-Cr + OMe). MALDI-TOF MS (*m/z*): 2156.4, calcd. for C₁₁₂H₁₀₈N₁₂O₂₄Sm 2156.68.

Eu(An₄P)[(15C5)₄Pc] (**DD6**). Yield 30%. UV-vis (CHCl₃) λ_max nm: 291, 368, 417, 486, 605, 813; ¹H NMR (CDCl₃) δ ppm (*J*,

Hz): 10.93 (s, 4H, H_An), 8.28 (s, 4H, H_An), 6.75 (s, 4H, H_An), 5.98 (s, 4H, H_An), 9.88 (s, 8H, H_Pc), 7.16 (s, 8H, H_Pyrr), 5.64 (s, 8H, α-Cr), 5.02 (s, 8H, α'-Cr), 4.61 (s, 8H, β-Cr), 4.45 (s, 8H, β'-Cr), 4.33 (s, 12H, OMe) 4.16 (s, 32H, γ+δ-Cr); MALDI-TOF MS (*m/z*): 2158.1, calcd. for C₁₁₂H₁₀₈N₁₂O₂₄Eu 2158.09.

La₂[An₄P]₂[(15C5)₄Pc] (**TD1**). Yield 32%. UV-vis (CHCl₃) λ_max nm: 291, 373, 422, 556, 608. ¹H NMR (CDCl₃) δ ppm (*J*, Hz): 9.84 (d, ³*J*=8.7, 8H, H_oi), 8.65 (s, 8H, H_Pc), 7.85 (dd, ³*J*=8.4, ⁴*J*=2.2, 8H, H_mi), 7.40 (s, 8H, H_Pyrr), 6.80 (dd, ³*J*=8.6, ⁴*J*=2.0, 8H, H_mo), 6.75 (dd, ³*J*=8.1, ⁴*J*=1.9, 8H, H_oo), 4.83 (s, 16H, H_α-Cr), 4.38 (s, 16H, H_β-Cr), 4.14 (s, 24H, H_OMe), 4.06 (m, 32H, H_γ+δ-Cr). MALDI-TOF MS (*m/z*): 3016.8, calcd. for C₁₆₀H₁₄₄N₁₆O₂₈La₂ 3016.76.

Ce₂[An₄P]₂[(15C5)₄Pc] (**TD2**). Yield 20%. UV-vis (CHCl₃) λ_max nm: 289, 372, 420, 554, 607. ¹H NMR (CDCl₃) δ ppm (*J*, Hz): 10.08 (s, 8H, H_oo), 6.67 (s, 8H, H_mo), 3.15 (s, 16H, H_Pyrr), 2.77 (s, 24H, H_OMe), 2.75 (s, 8H, H_mi), 2.28 (s, 16H, H_δ-Cr), 2.12 (s, 16H, H_γ-Cr), 1.32 (s, 16H, H_β-Cr), -0.35 (s, 16H, H_α-Cr), -2.53 (s, 8H, H_Pc), -2.65 (s, 8H, H_oi). MALDI-TOF MS (*m/z*): 3019.2, calcd. for C₁₆₀H₁₄₄N₁₆O₂₈Ce₂ 3019.18.

Pr₂[An₄P]₂[(15C5)₄Pc] (**TD3**). Yield 24%. UV-vis (CHCl₃) λ_max nm: 287, 372, 420, 555, 607. ¹H NMR (CDCl₃) δ ppm (*J*, Hz): 9.04 (d, 8H, H_oo), 6.74 (dd, ³*J*=8.4, ⁴*J*=2.0, 8H, H_mo), 5.79 (s, 16H, H_Pyrr), 4.33 (d, ³*J*=8.1, 8H, H_mi), 3.19 (s, 24H, H_OMe), 2.83 (t, ³*J*=4.7, 16H, H_δ-Cr), 2.73 (t, ³*J*=4.7, 16H, H_γ-Cr), 2.27 (s, 16H, H_β-Cr), 1.30 (s, 16H, H_α-Cr), 1.12 (d, ³*J*=8.2, 8H, H_oi), 0.88 (s, 8H, H_Pc). MALDI-TOF MS (*m/z*): 3021.7, calcd. for C₁₆₀H₁₄₄N₁₆O₂₈Pr₂ 3020.76.

Nd₂[An₄P]₂[(15C5)₄Pc] (**TD4**). Yield 20%. UV-vis (CHCl₃) λ_max nm: 295, 375, 421, 606. ¹H NMR (CDCl₃) δ ppm (*J*, Hz): 8.16 (d, ³*J*=8.0, 8H, H_oo), 7.45 (s, 16H, H_Pyrr), 6.77 (d, ³*J*=8.2, 8H, H_mo), 5.57 (s, 8H, H_mi), 4.12 (s, 8H, H_oi), 3.55 (s, 8H, H_Pc), 3.52 (s, 24H, H_OMe), 3.25 (m, 16H, H_δ-Cr), 3.20 (m, 16H, H_γ-Cr), 2.99 (s, 16H, H_β-Cr), 2.57 (s, 16H, H_α-Cr). MALDI-TOF MS (*m/z*): 3027.6, calcd. for C₁₆₀H₁₄₄N₁₆O₂₈Nd₂ 3027.43.

Sm₂[An₄P]₂[(15C5)₄Pc] (**TD5**). Yield 35%. UV-vis (CHCl₃) λ_max nm: 293, 375, 420, 608. ¹H NMR (CDCl₃) δ ppm (*J*, Hz): 8.16 (d, ³*J*=8.4, 8H, H_oi), 7.32 (s, 8H, H_Pc), 7.16 (dd, ³*J*=8.0, ³*J*=2.3, 8H, H_oo), 6.94 (dd, ³*J*=8.2, ³*J*=1.8, 8H, H_mi), 6.73 (dd, ³*J*=8.5, ³*J*=2.5, 8H, H_mo), 6.60 (s, 8H, H_Pyrr), 4.22 (s, 16H, H_α-Cr), 4.01 (s, 16H, H_β-Cr), 3.94 (s, 24H, H_OMe), 3.85 (s, 32H, H_γ+δ-Cr). MALDI-TOF MS (*m/z*): 3039.7, calcd. for C₁₆₀H₁₄₄N₁₆O₂₈Sm₂ 3039.67.

Eu₂[An₄P]₂[(15C5)₄Pc] (**TD6**). Yield 12%, UV-vis (CHCl₃) λ_max nm: 290, 376, 419, 606. ¹H NMR (CDCl₃) δ ppm (*J*, Hz): 13.00 (s, 8H, H_oi), 12.01 (s, 8H, H_Pc), 9.01 (s, 8H, H_mi), 6.57 (d, ³*J*=7.8, 8H, H_mo), 6.23 (s, 16H, H_α-Cr), 5.32 (s, 24H, H_β-Cr +H_oo), 4.68 (s, 16H, H_γ-Cr), 4.61 (s, 16H, H_δ-Cr), 4.45 (s, 24H, H_OMe), 4.30 (s, 16H, H_Pyrr). MALDI-TOF MS (*m/z*): 3043.1, calcd. for C₁₆₀H₁₄₄N₁₆O₂₈Eu₂ 3042.87.

It is difficult to obtain satisfactory elemental analysis for the crownphthalocyanine complexes, because the voids of crown ether substituents can contain residual molecules of the solvents,[30] which can distort the results of the analysis.

Results and Discussion

Synthesis

All the peculiarities of the synthesis of heteroleptic (porphyrinato)(phthalocyaninato) lanthanides, mentioned above, forced us to investigate the possible application of the single step regioselective synthetic route. The synthetic procedure applied in current work for preparation of Nd, Sm and Eu complexes was described previously for synthesis of La, Ce and Pr compounds.[24] Variation of lanthanides allows to investigate the possible application of
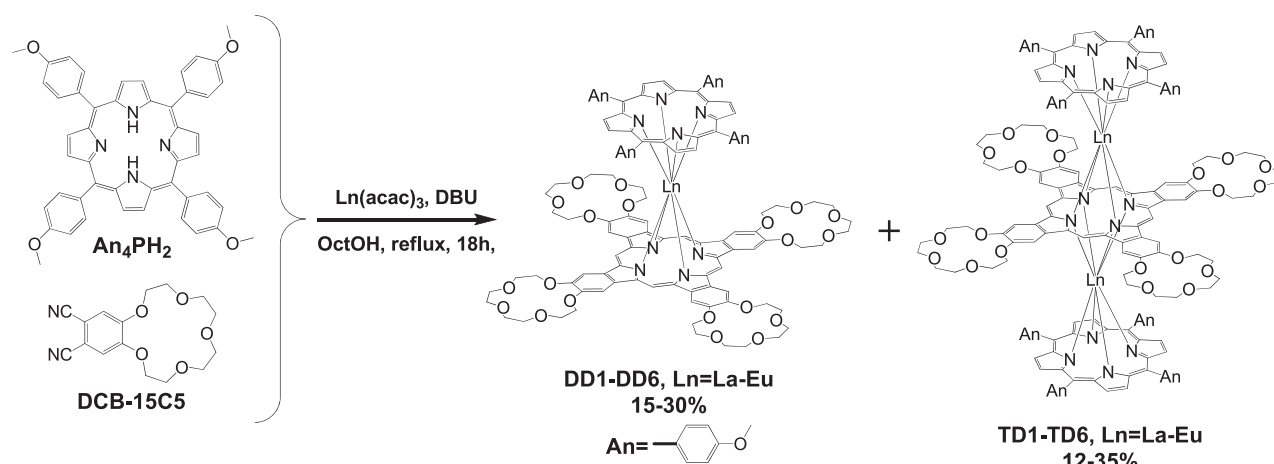
Scheme 1. Synthetic pathway for preparation of double- and triple-decker (porphyrinato)(phthalocyaninato) early lanthanides.

the procedure for preparation of double- and triple-decker (porphyrinato)(phthalocyaninato) complexes. Synthetic details and designation of the complexes are summarized at Scheme 1.

We have shown that the resulting reaction mixture contains only two compounds in all cases: the heteroleptic double-decker $Ln[An_4P][(15C5)_4Pc]$ and triple-decker $Ln_2[An_4P]_2[(15C5)_4Pc]$ complexes. The yields of double- and triple-decker complexes are similar and overall conversion may exceed 50%. Only traces of porphyrin were recovered from reaction mixtures, that can be explained by thermal decomposition of the compounds during reaction process. The yields and ratio of double- and triple-decker compounds are highly dependent on maintenance of inert atmosphere during the reaction. In our research freshly distilled from sodium 1-octanol was used. The presence of trace amounts of water in the solvent significantly suppresses the formation of triple-decker complex. Application of wet solvent may also result in decrease of yield of double-decker complex. Since the interaction occurs during 18 hours the presence of trace amounts of oxygen leads to decomposition of complexes.

The process is presumed to be stepwise. The first stage is *in situ* generation of monoporphyrinic species $Ln[An_4P]$ (acac), which further acts as template for crown-phthalonitrile tetramerization. This stage gives rise to heteroleptic double-decker compounds $[An_4P]Ln[(15C5)_4Pc]$. The formed

double-decker complex may again interact with lanthanide monoporphyrinate which is present in the reaction mixture. This interaction occurs regiospecifically leading to formation of triple-decker compound as a single isomer with internal position of phthalocyanine deck.

The observed selectivity of the process was discussed in details in [24]. The calculations of localization of HOMO in double-decker complex showed dissymmetry of the orbital depending on the nature of substituents in phthalocyanine ligand. In the presence of electron-donating alkoxy-groups the coefficients of HOMO achieve *ca*. 40% and 60% at porphyrin and phthalocyanine ligands, respectively. Polarization of the molecule results in selective interaction of monoporphyrinate at phthalocyanine site of the double-decker complex.

The products in the reaction mixture are easily separated by column chromatography owing to difference in chromatographic affinities of double- and triple-decker compounds. Neutral alumina was used for purification of the complexes with $CHCl_3$-MeOH eluent. Electroneutral symmetrical triple-decker complex is eluted first with 0.5-1% of MeOH in eluent. Double-decker complex is eluted as anionic form $[An_4P^{2-}]Ln[(15C5)_4Pc^{2-}]$ at higher concentrations of methanol as a result of polarisation of the unsymmetrical molecule. The yields of the obtained complexes and their MALDI-TOF MS data are summarized in Table 1.

Table 1. Yields and MALDI TOF MS data of synthesized double- and triple-decker complexes.

Ln	Yield		MALDI TOF MS			
	$Ln[An_4P][(15C5)_4Pc]$	$Ln_2[An_4P]_2[(15C5)_4Pc]$	$Ln[An_4P][(15C5)_4Pc]$		$Ln_2[An_4P]_2[(15C5)_4Pc]$	
			Calculated for $C_{112}H_{108}N_{12}O_{24}Ln$	Found	Calculated for $C_{160}H_{144}N_{16}O_{28}Ln_2$	Found
La	**DD1**, 26%	**TD1**, 32%	2145.28	2145.3	3016.76	3016.8
Ce	**DD2**, 20%	**TD2**, 20%	2146.24	2146.3	3019.18	3019.2
Pr	**DD3**, 18%	**TD3**, 24%	2147.03	2147.9	3020.76	3021.7
Nd	**DD4**, 15%	**TD4**, 20%	2150.36	2150.2	3027.43	3027.6
Sm	**DD5**, 16%	**TD5**, 35%	2156.68	2156.4	3039.67	3039.7
Eu	**DD6**, 30%	**TD6**, 12%	2158.09	2158.1	3042.87	3043.1

Spectral Investigation of the Complexes

All the synthesized compounds were characterized by MALDI-TOF MS and UV-vis spectroscopy. Triple-decker complexes were also investigated by NMR spectroscopy. Application of various correlation techniques allowed the unambiguous assignment of ^{1}H-NMR spectra and determination of lanthanide-induced paramagnetic shifts for each type of protons in the molecule. Precise analysis of lanthanide-induced shifts allowed us to develop a general approach for structural characterization of lanthanide triple-decker heteroleptic complexes.[31,32]

The polarization of the molecule of double-decker complex results in highly effective concentration-dependent aggregation of the compound. Dilution of double-decker complex solution up to 10^{-6} M level does not lead to complete suppression of aggregation, that is determined by UV-vis spectroscopy. NMR spectra of compounds at this concentration are significantly broadened that testifies the formation of different types of unordered aggregates. We succeeded to register ^{1}H NMR spectra at low concentrations for all synthesized double-decker complexes except Nd and Pr. These two lanthanides demonstrate large upfield shift of signals and effective relaxation enhancement. In the case of partial aggregation of compounds and fast exchange within aggregates the signals of the compounds are extremely broadened.

Electronic absorption spectra are quite informative for macrocyclic tetrapyrrolic compounds and their metal complexes. The origin of electronic transitions for double- and triple-decker (porphyrinato)(phthalocyaninates) are discussed in details in [21,33,34]. UV-vis spectra of the synthesized lanthanum double- and triple-decker complexes are shown at Figure 1 as examples. The positions and relative intensities of absorption bands in the spectra allow to distinguish double- and triple-decker complexes. Despite the fact that the most absorption bands are not lanthanide-sensitive some of them in spectrum may be express and reliable marker of composition of complexes. The sets of bands in the spectrum are generally similar and are determined by electronic transitions of each particular ligand. In contrast, relative intensities of bands are determined by ratio of ligands of different nature. As a result, the comparison of intensities of bands, originating from porphyrin and phthalocyanine electron transitions shows that phthalocyanine absorptions
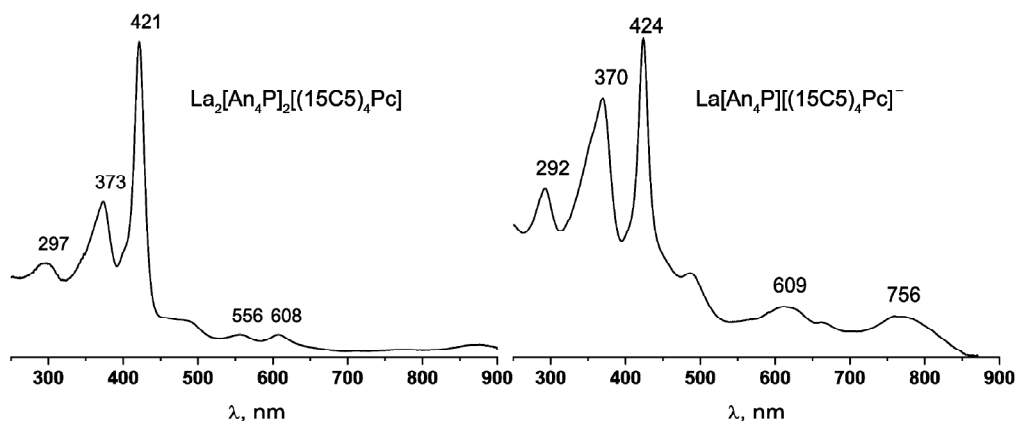
are diminished in the case of triple-deckers. Similarly, in [34] the spectra of heteroleptic triple-decker (porphyrinato)-(phthalocyaninates) with different number of porphyrin and phthalocyanine ligands were considered as superposition of spectra of the corresponding double-decker complexes.

In the spectra of the both types of complexes lanthanide-sensitive bands are present in the NIR region. In the case of the synthesized double-deckers lanthanide-sensitive band occupies position in 750-850 nm range. In the spectra of triple-deckers this band is red-shifted up to 860-950 nm region. We have found that the positions of lanthanide-sensitive bands in NIR region are linearly dependent on lanthanide ionic radius and thus on interligand distance in the complex (Figures 2, 3).
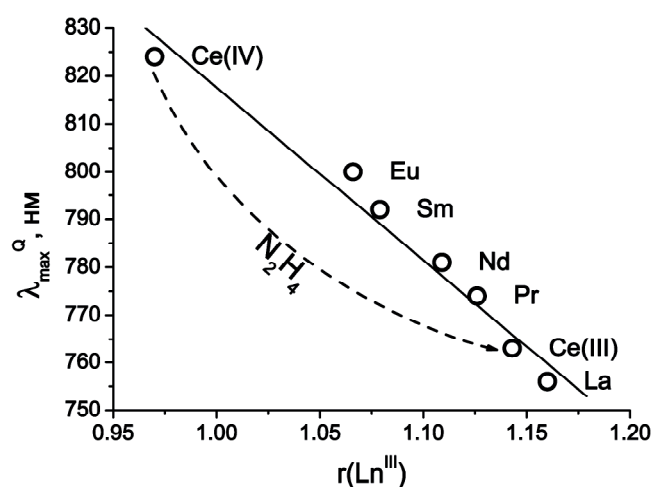
Figure 2. Plot of λ_{max}^Q absorption maxima positions *vs* lanthanide ionic radii in heteroleptic double-decker complexes Ln[An$_4$P][(15C5)$_4$Pc]$^-$ (**DD1-DD6**).

Analysis of the spectra of the synthesized herein double- and triple-decker complexes allowed us to determine the oxidation state of cerium in given coordination environment. Figure 3 shows the linear correlation between ionic radii of metal centers of the double-decker complexes and position of NIR absorption band in the UV-vis spectra. Data for ionic radii of octacoordinated lanthanide ions are taken from the literature.[35] The discussed absorption is mentioned as λ_{max}^Q since it originates from the similar transition as phthalo-

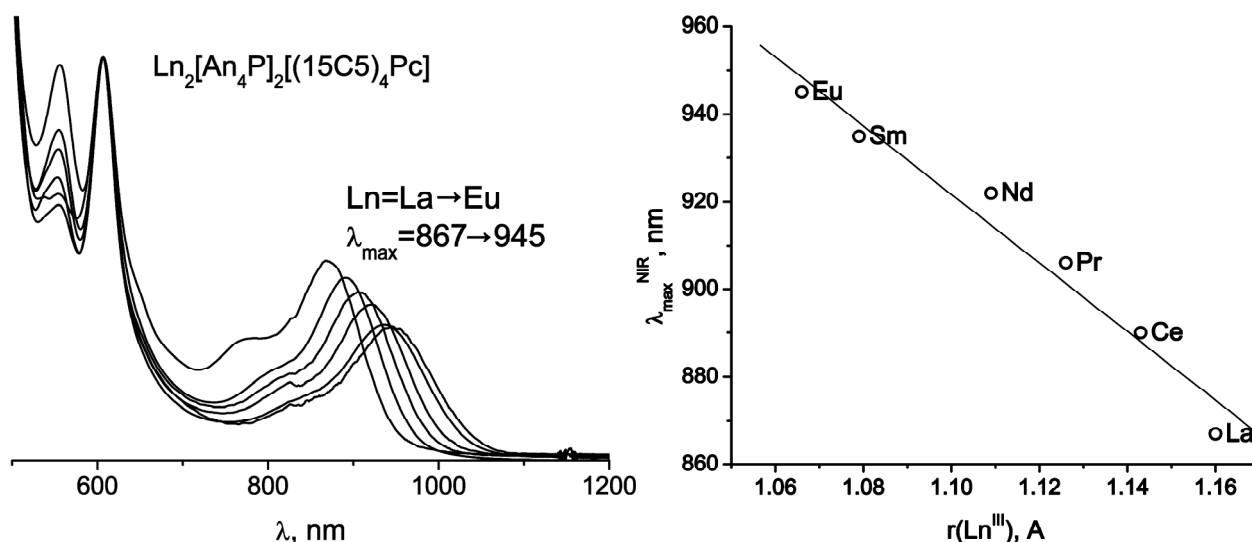**Figure 1.** UV-vis spectra of lanthanum double- and triple-decker (porphyrinato)(phthalocyaninates).

Figure 3. Plot of λ_{max}^{NIR} absorption maxima positions *vs* lanthanide ionic radii in heteroleptic triple-decker complexes Ln$_2$[An$_4$P]$_2$[(15C5)$_4$Pc] (**TD1-TD6**). The spectra are normalized at 606 nm absorption.

cyanine *Q* band. The absorption maxima are gradually shifted to the longer wavelength region in La→Eu series. The behavior of cerium complex differs from the other synthesized complexes of trivalent lanthanides. The position of the discussed band in the spectrum of chromatographically pure complex is 824 nm, while for Ce^{III} complex this band is expected in 756-774 nm range, between positions of absorptions of lanthanum and praseodymium complexes, respectively. Taking into account the general tendency of bathochromic shift of band with decrease of lanthanide ionic radius this position of absorption can be attributed to Ce^{IV} valent state. This data point complies with general linear correlation in the case of Ce^{IV} ionic radius.

An assumption of the tetravalent state of cerium in heteroleptic double-decker complex is also proved by behavior of NIR absorption band upon treatment of the complex with reducing agents. Titration of cerium complex solution with N$_2$H$_4$ in the presence of DBU results in gradual hypsochromic shift of band up to 763 nm. According to the found correlation this process can be attributed to the reduction of cerium center Ce^{IV}→Ce^{III}.

In the case of triple-decker heteroleptic complexes similar correlation was determined. The characteristic lanthanide-sensitive absorption band (λ_{max}^{NIR}) is also gradually shifted with decrease of lanthanide(III) ionic radius. Figure 3 shows a series of spectra of the synthesized triple-deckers in NIR region and the obtained linear correlation.

NIR absorption maximum of cerium triple-decker complex satisfy the trend formed by other lanthanides with Ce^{III} ionic radius. The shape of the band is also gradually changed in La→Eu series. In the case of lanthanum complex a slight splitting of this band is observed. With decrease of the lanthanide ion size the band becomes broader and the splitting disappears.

Since the observed range of absorption maxima of NIR bands is *ca.* 100 nm both in the case of double- and triple-decker complexes this band can be considered as a sensitive marker of metal center in the complexes of discussed types. Synthesized series of complexes allow to cover almost 200 nm range of wavelengths in NIR region that is promising

for development of non-linear optics devices, similarly to [36]. The possibility of cerium to facilitate both +3 and +4 oxidation states in double-decker heteroleptic complex allowed to develop molecular switching devices with optical response on the basis of cerium bis[tetra(15-crown-5) phthalocyaninate].[27]

The behavior of the complexes upon chemical oxidation differs depending on the metal center and structure of the complex. We have compared the oxidation processes for cerium and europium double- and triple-decker complexes as representatives of the series. Chemical oxidation was performed in CHCl$_3$ with N-bromosuccinimide (NBS), containing trace amounts of bromine. First, we have compared the redox behavior of cerium and europium heteroleptic double-decker complexes Ln[An$_4$P][(15C5)$_4$Pc]. Europium double-decker complex is able to form two stable redox forms. The anionic form can be oxidized with loss of one electron to free radical electroneutral form. Upon oxidation with traces of bromine the absorption band at 807 nm disappears and two bands in NIR region appear at 996 and 1336 nm (Figure 4). These bands correspond to the
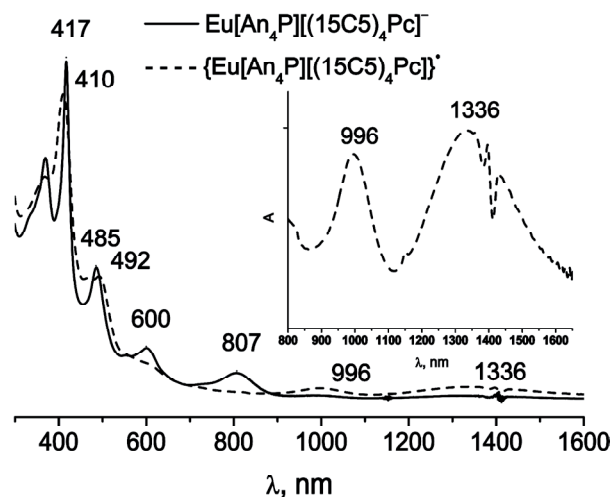

Figure 4. Titration of europium double-decker complex Eu^{3+}[An$_4$P^{2-}][(15C5)$_4$Pc^{2-}] with NBS solution in CHCl$_3$.

transitions of one-electron oxidized phthalocyanine ligands.[37] The observation of porphyrin ligand absorption bands without major changes confirms the preferential localization of unpaired electron at phthalocyanine ligand.

Cerium double-decker complex was reduced with N_2H_4/DBU before investigation. In this case the starting redox form of the compound was the anionic one with metal center in +3 oxidation state. Oxidation processes in the case of cerium double-decker complex differ from ones of europium analogue. Two steps of oxidation were detected giving 2 stable oxidized forms. The first oxidation occurs at metal center and results in formation of electroneutral form of Ce^{IV} complex. This process is detected by bathochromic shift of NIR absorption band 763→824 nm, corresponding to contraction of lanthanide atom. The next oxidation step affects the π-system of the ligand. The changes in absorption spectrum are similar to ones in the case of oxidized europium complex. The band at 824 nm is shifted to 978 nm and new band at 1165 nm appears, originating from intermolecular electron transition between ligands (Figure 5). Soret bands of porphyrin ligands in the oxidized complexes are hypsochromically shifted at each oxidation step. This can be explained by increasing π−π−interaction between ligands in oxidized forms of the compounds. The interaction is
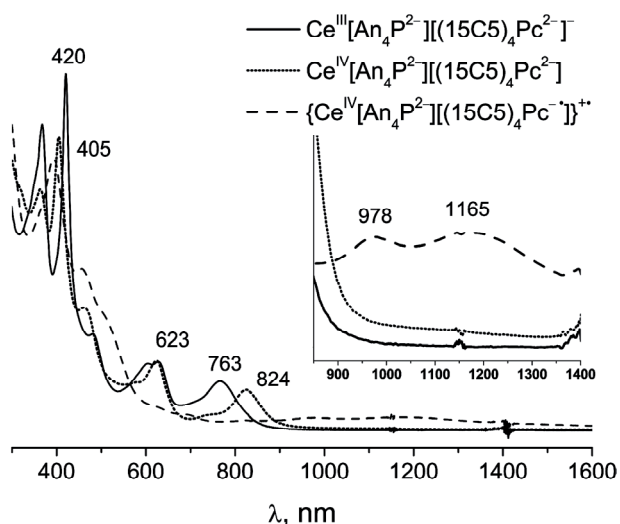
additionally enhanced by contraction of cerium metal center upon oxidation. Since the absorption spectrum is determined by electronic states of ligands and their electron transitions the general charge of the molecule doesn't influence the number and origin of the absorption bands. Nevertheless the size of metal center regulates the interligand distance in the molecule and thus efficiency of π−π−interaction and position of bands arising in NIR region.

Surprisingly, the redox behavior of triple-decker cerium and europium complexes were found to be equal. Only one chemical oxidation process is determined for these compounds affecting π−system of ligands in the investigated conditions. This process results in the formation of one electron oxidized species both in the case of europium and cerium compounds. The bands at 891 nm (Ce complex) and 945 nm (Eu complex) disappear upon oxidation (Figure 6). The further treatment with NBS does not reveal any more processes affecting Ce^{III} metal center.

Comparison of oxidation processes of double- and triple-decker heteroleptic complexes allows to determine the peculiarities of ligand environment and their influence on the oxidation state of cerium atom. Oxidation processes of double-decker complex may involve both metal center (in the case of cerium) and π−system of ligands. Oxidation of triple-decker compound may occur only at ligand system of the molecule. This behavior testifies that coordination environment of triple-decker compound effectively stabilizes trivalent state of cerium atom. Oxidation of metal center to Ce^{IV} state in the case of triple-decker compound should lead to decomposition of molecule giving electroneutral double-decker complex. Formation of double-decker Ce^{IV} complex could be easily detected by electronic absorption spectrum. Nevertheless the decomposition of compound upon oxidation was not observed. The observed set of redox transformations of the complexes and stability of the compounds upon oxidation prove their possible application as starting materials for development of multibit information storage devices, sensing and electrochromic systems.

Conclusions

Summarizing, we have developed a regioselective synthetic approach allowing to prepare triple-decker

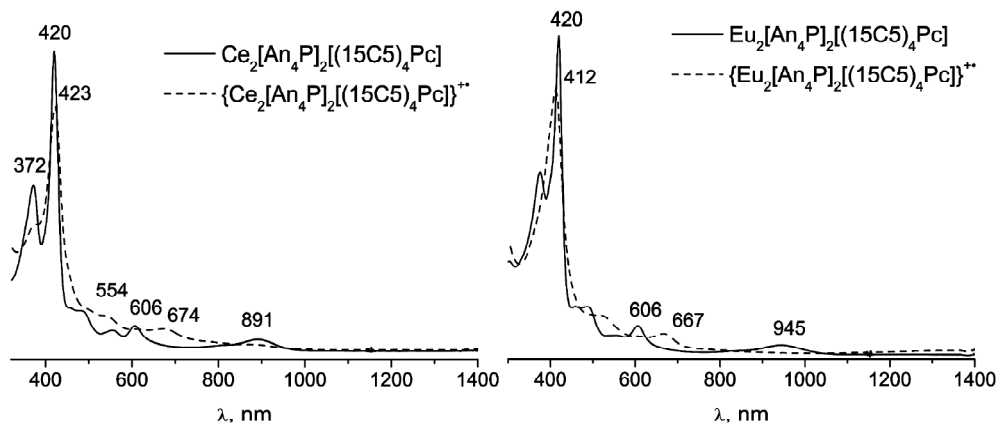**Figure 5**. Titration of cerium double-decker complex Ce[An$_4$P] [(15C5)$_4$Pc] with NBS solution in CHCl$_3$.

Figure 6. Titration of cerium and europium triple-decker complexes Ln$_2$[An$_4$P]$_2$[(15C5)$_4$Pc] with NBS solution in CHCl$_3$.

(porphyrinato)(phthalocyaninates) of early lanthanides in one-step procedure. The triple-decker complexes are formed as a single isomer of symmetrical structure [An₄P]Ln[(15C5)₄Pc]Ln[An₄P]. The double-decker co-product can be easily separated that also simplifies the synthetic procedure.

The NIR absorption of the discussed types of complexes can be tuned finely through variation of metal center. The variation of metal center in the synthesized series of complexes within La-Eu subgroup allows to cover *ca.* 200 nm range of NIR absorption. Presence of NIR-absorption in the spectra of compounds makes them promising starting materials for nonlinear optics.

A set of macroaromatic ligands in the complexes determines the variety of redox transitions of the compounds. Chemical oxidation of both double- and triple-decker complexes is reversible and oxidized compounds do not show any decomposition. The observed set of redox transformations and stability of compounds upon oxidation demonstrate their possible application for development of multibit information storage devices, sensing and electrochromic systems.

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