

Novel Ligands Incorporating Phosphin oxide Groups as Particularly Efficient Sensitizers for Lanthanide Emission

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(Received: 15 July 2003; in final form: 19 December 2003)

Key words: 2,2'-bipyridine, cavitands, cyclotriphosphazene, lanthanides, phosphin oxides, photoluminescence, pyridine, quantum yield, 1,3,5-triazine

Abstract

Several novel phosphin oxide ligands have been obtained, based on molecular scaffolds: pyridine, 2,2'-bipyridine, cavitands, cyclotriphosphazene and 1,3,5-triazine. These compounds form highly luminescent complexes with Eu(III) and Tb(III). Particularly good luminescent properties were observed in case of cyclotriphosphazene, pyridine and 2,2'-bipyridine ligands with photoluminescence quantum yields approaching 25%. Cavitand-based phosphin oxides turned out to be rather poor sensitizers for the lanthanide ion emission. Particularly long emission lifetime was observed in case of pyridine P-oxide complexes of Eu(III) and Tb(III), exceeding 3 ms.

Introduction

Lanthanide complexes have attracted ever-growing attention due to their outstanding electronic, magnetic and photophysical features. Lanthanide metals have been used in magnetic alloys, and their luminescent compounds in many other high-tech fields, such as: optoelectronic devices, fiber-optic amplifiers, phosphors for displays, molecular spintronics, DNA intercalators, luminescent labels for medical diagnostics, laser materials, planar waveguides, electroluminescent devices, hybrid organic/inorganic sol-gel and xerogel materials, etc. Still, there is a lot of room for innovative research in the area of high-quantum yield luminescent lanthanide complexes for their numerous practical applications, in particular: as luminescent devices based on Absorption – Energy Transfer – Emission process, e.g., the UV radiation absorbance by lanthanide complexes possessing elaborated π -electronic systems results in light conversion to emitted light in visible region.

There have been numerous luminescent lanthanide complexes published to date, based on 1,3-diketonates, nitrogen-containing heterocycles, heterocyclic N-oxides, and mixed-group ligands. In order to achieve remarkable photostability and good luminescence in aqueous solutions, a number of approaches to molecular architectures has been developed: pendent arm heterocyclic

ligands [1], 1,3-diketonates and related structures [2], azacrown ethers and cryptands [3], heterocyclic nitrogen-containing ligands [4], and ionizable groups such as carboxylates [5] and phosphonates [6] attached to heterocyclic, or polyazamacrocyclic ligands. Despite their satisfactory stabilities in aqueous media, the luminescent properties – in particular their luminescence quantum yields – were still not outstanding, barely exceeding 50% in only few cases. Remarkable progress was achieved with heterocyclic N-oxides, since this class of ligands, as hard bases, were compatible with the properties of lanthanide ions as hard Lewis–Pearson acids, and at the same time much better sensitizers for lanthanide ion emission than their parent heterocycles [3]. However, stabilities of the complexes possessing nitrogen donor atoms as ligating groups depended on the pH of the solution, due to the protonation of the nitrogen atom and release of the Ln^{3+} from the complex. It has been noted that lipophilic phosphin oxides have been recognised as good extracting agents for lanthanide and actinide ions, even in highly acidic media, and this extraction technique has been applied to the enrichment and separation of lanthanide and actinide ions from highly diluted solutions. More recently, several synthetic ligands based on calixarene architecture have been developed as efficient extracting agents for lanthanides and actinides [7]. These ligands contained phosphin oxide groups. Although there have been numerous papers on calixarene-phosphines and

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phosphinoxides [7], none of them had been dedicated to luminescence studies of their lanthanide complexes, to our knowledge. An excellent review on metal complexes, including phosphine and phosphinoxide-bearing calixarenes appeared recently [8]. In some cases acyclic phosphinoxides turned out to be very good, and pH-independent sensitiser for lanthanide ion luminescence [9]. Since phosphinoxides display much better affinity for Ln^{3+} complexation than N-oxides, and excellent sensitising properties, it was fully justified to explore the possibility in designing the novel ligands incorporating P—O groups would lead to remarkable complex stability and outstanding luminescence properties.

We have selected several molecular scaffolds serving as molecular architectures to attach phosphinoxide groups. They are shown in Scheme 1.

Experimental

The starting materials are easily available: cyanuric chloride, hexachlorocyclotriphosphazene, and 2,6-dibromopyridine are commercially available, and tetra-bromocalixresorcinarene can be prepared in large quantities following standard literature methods.

All reagents were of analytical grade from Aldrich. The solvents for spectrofluorimetric studies were of spectrofluorimetric grade from Merck. All novel compounds were analytically characterised, based on NMR, MS and elemental analyses.

Precaution procedures concerning butyllithium manipulation: extreme care should be undertaken, while

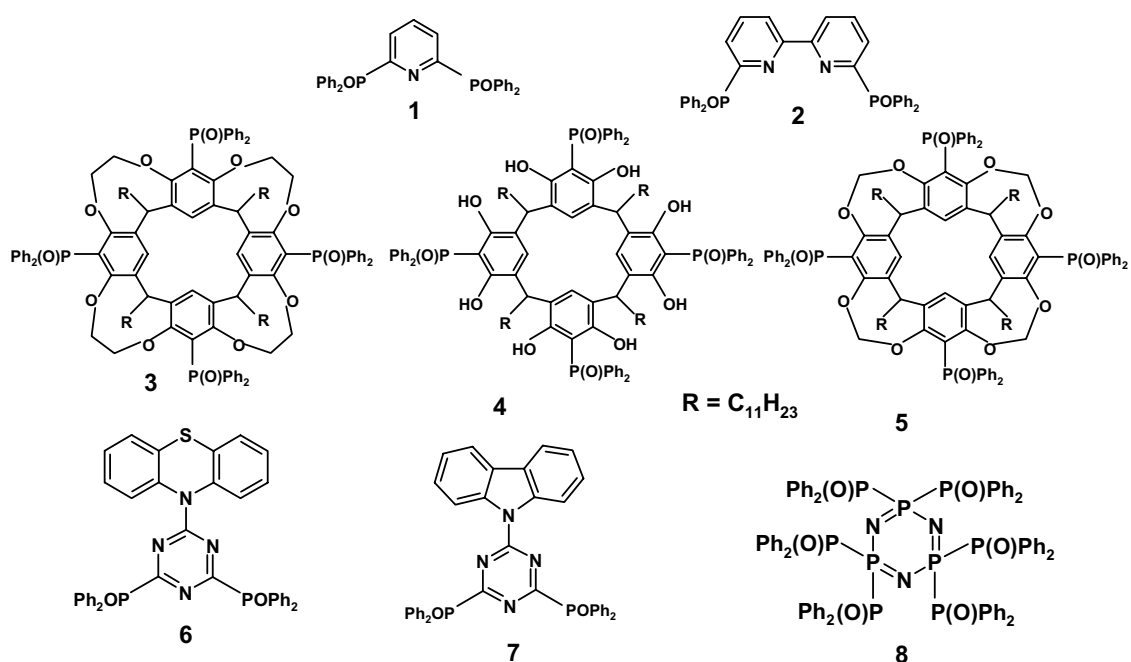
using commercially available butyllithium! Its 2.5 M solutions and more concentrated may ignite spontaneously in contact with air. The glass syringe with stopcock (Aldrich type) should be used to transfer BuLi from SureSeal® bottles to reaction flask *via* septum, under Ar blanket. Once the transfer is completed, the syringe should be washed thoroughly with hexane, ethanol, and water. Protective clothing, gloves and face-protecting mask are necessary. A single person should not work alone, assistance is recommended.

1,3,5-Triazine phosphinoxides

Cyanuric chloride was dissolved in dry THF, cooled to -78°C and one equivalent of carbazole, or phenothiazine lithium salt (nitrogen deprotonation with *n*-butyllithium), was added slowly. The mixture was allowed to warm slowly to room temperature. Evaporation and crystallisation from benzene yielded pure monosubstituted cyanuric chloride, which was subjected to react with diphenylphosphine in the presence of diisopropylethylamine in THF at reflux for 24 h, followed by oxidation with *t*-butyl hydrogenperoxide.

6: $^1\text{H-NMR}$, 200 MHz, ppm, TMS, CDCl_3 : 7.35–7.60 (m, 6H, $\text{C}_{12}\text{H}_8\text{NS}$), 7.65–7.95 (m, 22H, 2CH + 4Ph), MS: 677 (M^+), elemental anal: calcd for: $\text{C}_{39}\text{H}_{28}\text{N}_4\text{O}_2\text{P}_2\text{S}$: C 89.01, H 4.16, N 8.26, found: C 88.96 H 4.13 N 8.19, UV (MeCN, λ , nm): 272, 223.

7: $^1\text{H-NMR}$, 200 MHz, ppm, TMS, CDCl_3 : 7.34–7.50 (m, 4H, $\text{C}_{12}\text{H}_8\text{N}$), 7.54–7.74 (m, 20H, 4Ph), 7.94–8.1 (m, 4H, $\text{C}_{12}\text{H}_8\text{N}$), MS: 646 (M^+), elemental anal: calcd for: $\text{C}_{39}\text{H}_{28}\text{N}_4\text{O}_2\text{P}_2$: C 72.43, H 4.37, N 8.67, found: C 72.36 H 4.31 N 8.49, UV (MeCN, λ , nm): 321, 280, 224.



Scheme 1. Formulas of the ligands studied.

2,6-Bis(diphenylphosphoryloxy)pyridine

2,6-Dibromopyridine was dissolved in dry *N,N*-dimethylimidazolone under argon. 10 Equiv. of potassium carbonate were added and 2 equiv. of diphenylphosphine. The mixture was stirred at 160 °C for 6 h, cooled to r.t., and treated with 2 equiv. of hydrogen peroxide to oxidise selectively phosphine units. The progress of oxidation was followed on TLC (silica). Once the reaction was completed, water was added to dissolve potassium carbonate and precipitation of the product. The product was filtered off, washed with water, and dried in vacuum.

1: ¹H-NMR, 200 MHz, ppm, TMS, CDCl₃: 8.40–8.35, (m, 3H, Py), 7.65–7.20, (m, 20H, 4×Ph), MS: 480 (M⁺), elemental anal: calcd for: C₂₉H₂₃NO₂P₂: C 72.63, H 4.84 N 2.92, found: C 72.57 H 4.77 N 2.89, UV (MeCN, λ, nm): 274, 268, 261, 225.

3,3'-Bis(diphenylphosphoryloxy)2,2'-bipyridine

This compound was prepared analogously, as above from 3,3'-dibromo-2,2'-bipyridine.

2: ¹H-NMR, 200 MHz, ppm, TMS, CDCl₃: 8.39, (m, 6H, bipy), 7.96, (m, 10H, 2×Ph), 7.45, (m, 10H, 2×Ph), MS: 557.4 (M⁺), found: elemental anal: calcd for: C₃₄H₂₆N₂O₂P₂: C 73.36 H 4.71 N 5.04, found: C 73.41 H 4.65 N 4.96, UV (MeCN, λ, nm): 225, 282.

Tetra(diphenylphosphinoxy)cavitands – general procedure

The tetrabromocavitands were obtained from tetra-*n*-undecyletrabromoaclix[4]resorcinarene in condensation with bromochloromethane, or 1,2-dibromoethane in the presence of potassium carbonate [10]. The isolated products were subjected to react with potassium diphenylphosphide in dry THF under argon at –78 °C. The resulting phosphine ligands were washed with water, suspended in methanol and oxidised with 30% hydrogen peroxide to give white solids that were crystallised from acetone.

3: ¹H-NMR, 200 MHz, ppm, TMS, CDCl₃: 7.98 and 7.44 (m, 40H, 8×Ph), 7.24 (s, 4H, Ar), 5.26 (t, 4H, 4×Ar–CH–Ar), 4.44 (m, 8H, 4×*in*–O–CH₂CH₂–O), 3.76 (m, 8H, 4×*out*–O–CH₂CH₂–O), 2.03 (m, 8H, Ar–CH–CH₂–C₉H₁₈–), 1.25 (m, 72H, 4×–C₉H₁₈–), 0.88 (t, 12H, 4×CH₃), MS: 2010 (M⁺), elemental anal: calcd for: C₁₂₈H₁₅₆O₁₂P₄: C 76.45, H 7.83, found: C 76.39 H 7.78, UV (MeCN, λ, nm): 295, 225.

4: ¹H-NMR, 200 MHz, ppm, TMS, CDCl₃: 7.98 and 7.44 (m, 40H, 8×Ph), 7.10 (s, 4H, Ar), 4.83 (t, 4H, 4×Ar–CH–Ar), 2.20 (m, 8H, Ar–CH–CH₂–C₉H₁₈–), 1.25 (m, 72H, 4×–C₉H₁₈–), 0.88 (t, 12H, 4×CH₃), MS: 1905 (M⁺), elemental anal: calcd for: C₁₂₀H₁₄₈O₁₂P₄: C 75.59, H 7.83, found: C 75.47 H 7.78, UV (MeCN, λ, nm): 295, 225.

5: ¹H-NMR, 200 MHz, ppm, TMS, CDCl₃: 7.98 and 7.44 (m, 40H, 8×Ph), 7.10 (s, 4H, Ar), 5.96 (t, 4H, 4×*out*–O–CH₂–O), 4.85 (t, 4H, 4×Ar–CH–Ar), 4.44 (t, 4H, 4×*in*–O–CH₂–O), 2.20 (m, 8H, Ar–CH–CH₂–C₉H₁₈–), 1.25 (m, 72H, 4×–C₉H₁₈–), 0.88 (t, 12H, 4×CH₃), MS: 1953 (M⁺), elemental anal: calcd for: C₁₂₄H₁₄₈O₁₂P₄: C 76.19, H 7.64, found: C 76.11 H 7.58, UV (MeCN, λ, nm): 295, 225.

Lanthanide complexes – preparation

The ligands based on 1,3,5-triazine and pyridine were mixed with Eu(III), or Tb(III) trifluoromethanesulfonates in 3:1 ratio, respectively in acetonitrile solution, whereas the ligand **8** [11] (based on cyclotriphosphazene) was mixed with lanthanide salts in 1:1 ratio. Boiling was effected for 30 min. After cooling the precipitates were filtered off and dried in vacuum. ESI MS confirmed the expected stoichiometry. The cavitand-type ligands were mixed with Eu(III), or Tb(III) dibenzoylmethides in 1:1 ratio in boiling acetone. Addition of hexane resulted in precipitation of the complexes that were filtered off and dried in vacuum.

Spectroscopy

The spectral data were recorded on Shimadzu UV-3100 UV–VIS–NIR spectrometer, and fluorescence, luminescence lifetimes and quantum yields (Ru(II)[bipy]₃ as luminescence standard) were recorded in acetonitrile on Edinburgh Analytical Instruments FS 900 spectrofluorimeter. The solutions of lanthanide complexes were not degassed.

1₃ × Eu(CF₃SO₃)₃: MS: 2037 (M⁺), elemental anal: calcd for: C₉₀H₆₉F₉N₃O₁₅S₃P₆Eu: C 53.02, H 3.41, N 2.06, found: C 52.83 H 3.26 N 1.99, UV (MeCN, λ, nm): 274, 268, 261, 225.

1₃ × Tb(CF₃SO₃)₃: MS: 2045 (M⁺ + 1), elemental anal: calcd for: C₉₀H₆₉F₉N₃O₁₅S₃P₆Tb: C 52.86, H 3.40, N 2.06, found: C 52.77 H 3.17 N 1.87, UV (MeCN, λ, nm): 274, 268, 261, 225.

2₃ × Eu(CF₃SO₃)₃: MS: 2269 (M⁺), elemental anal: calcd for: C₁₀₅H₇₈F₉N₆O₁₅S₃P₆Eu: C 55.55, H 3.47, N 3.70, found: C 55.42 H 3.35 N 3.59, UV (MeCN, λ, nm): 225, 275, 315.

2₃ × Tb (CF₃SO₃)₃: MS: 2275 (M⁺), elemental anal: calcd for: C₁₀₅H₇₈F₉N₆O₁₅S₃P₆Tb: C 55.40, H 3.46, N 3.69, found: C 55.31 H 3.34 N 3.58, UV (MeCN, λ, nm): 225, 275, 315.

6₃ × Eu(CF₃SO₃)₃: MS: 2635 (M⁺), elemental anal: calcd for: C₁₂₀H₈₄F₉N₁₂O₁₅P₆S₆Eu: C 54.67, H 3.21, N 6.38, found: C 54.59 H 3.15 N 6.29, UV (MeCN, λ, nm): 272, 222.

6₃ × Tb(CF₃SO₃)₃: MS: 2641 (M⁺ + 1), elemental anal: calcd for: C₁₂₀H₈₄F₉N₁₂O₁₅P₆S₆Tb: C 54.54, H 3.21, N 6.36, found: C 54.29 H 3.15 N 6.27, UV (MeCN, λ, nm): 271, 223.

$7_3 \times \text{Eu}(\text{CF}_3\text{SO}_3)_3$: MS: 2835 (M^+), elemental anal: calcd for: $\text{C}_{120}\text{H}_{84}\text{F}_9\text{N}_{12}\text{O}_{15}\text{S}_3\text{P}_6\text{Eu}$: C 56.73, H 3.34, N 6.62, found: C 56.67 H 3.27 N 6.53, UV (MeCN, λ , nm): 320, 281, 225.

$7_3 \times \text{Tb}(\text{CF}_3\text{SO}_3)_3$: MS: 2545 ($\text{M}^+ + 1$), elemental anal: calcd for: $\text{C}_{120}\text{H}_{84}\text{F}_9\text{N}_{12}\text{O}_{15}\text{S}_3\text{P}_6\text{Tb}$: C 56.60, H 3.33, N 6.60, found: C 56.41 H 3.22 N 6.51, UV (MeCN, λ , nm): 320, 279, 224.

Results and discussion

There were four classes of compounds regarding the skeleton to construct phosphin oxide ligands. One based on pyridine derivatives, the second – on 1,3,5-triazine, third – on calix[4]resorcinarene, and fourth – on cyclotriphosphazene. Heterocyclic units appended to 1,3,5-triazine phosphin oxides were supposed to reinforce the “antenna effect” in UV radiation harvesting. Also, they were thought to provide “hole transport” unit for potential electroluminescent devices. Four phosphin oxide units in calixarene scaffold were supposed to form a convergent nesting site for lanthanide cations, and at the same time, good antenna effect. The

fluorescence studies revealed several unexpected features that will be discussed systematically.

Pyridine phosphin oxides

The best luminescence results were obtained with pyridine derivatives, **1,2**. The luminescence spectra of Eu(III) and Tb(III) complexes are shown in Figure 1.

The emission spectra show a set of narrow lines characteristic to $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions in case of Eu(III) complex and $^5\text{D}_4 \rightarrow ^7\text{F}_J$ in case of Tb(III) complexes. Particularly long luminescence lifetimes were noted, exceeding 3 ms (see Table 1).

1,3,5-Triazine phosphin oxides

It turned out that attachment of carbazole, or phenothiazine to 1,3,5-triazine changed profoundly their electronic properties, that were evident in the UV spectra. Replacement of chlorine atoms with phosphin oxide groups led to the ligands forming stable complexes with Eu(III) and Tb(III), however, the carbazole ligand **7** and its lanthanide complexes displayed only strong blue luminescence originating from carbazole, which is known to emit visible light very strongly.

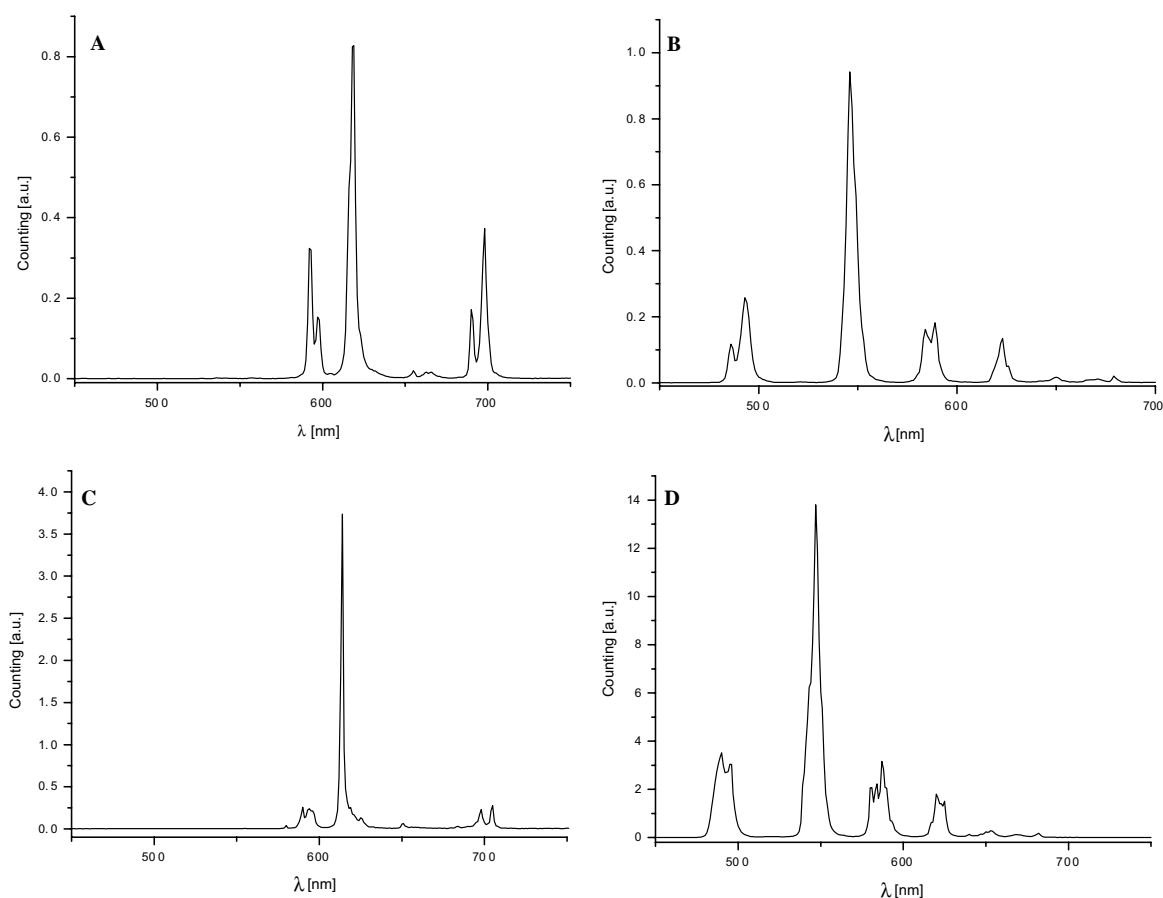


Figure 1. Luminescence spectra in acetonitrile at room temperature: A – **1**: $[\text{Eu}(\text{CF}_3\text{SO}_3)_3]_3$, B – **1**: $[\text{Tb}(\text{CF}_3\text{SO}_3)_3]_3$, C – **2**: $[\text{Eu}(\text{CF}_3\text{SO}_3)_3]_3$, D – **2**: $[\text{Tb}(\text{CF}_3\text{SO}_3)_3]_3$.

Table 1. Luminescence quantum yields (Φ) and lifetimes (τ) of the complexes in acetonitrile solution

Complex	Φ	λ_{exc} (nm)	τ (ms)
1: [Eu(CF ₃ SO ₃) ₃] ₃	0.154	267	3.71
1: [Tb(CF ₃ SO ₃) ₃] ₃	0.124	267	3.21
2: [Eu(CF ₃ SO ₃) ₃] ₃	0.23	308	1.0
2: [Tb(CF ₃ SO ₃) ₃] ₃	0.25	308	0.666
3: Eu(CF ₃ SO ₃) ₃	–	365	–
3: Tb(CF ₃ SO ₃) ₃	0.043	273	–
4: Eu(DBM) ₃	0.074	365	–
4: Tb(DBM) ₃	–	348	–
5: Eu(DBM) ₃	0.056	348	–
5: Tb(DBM) ₃	0.017	290	–
6: [Eu(CF ₃ SO ₃) ₃] ₃	0.035	271	1.94
6: [Tb(CF ₃ SO ₃) ₃] ₃	0.026	271	1.66
7: [Eu(CF ₃ SO ₃) ₃] ₃	–	279	–
7: [Tb(CF ₃ SO ₃) ₃] ₃	–	279	–
8: [Eu(CF ₃ SO ₃) ₃] ₃	–	278	–
8: [Tb(CF ₃ SO ₃) ₃] ₃	–	278	–

In contrary to that, the phenothiazine-appended Eu(III) and Tb(III) complexes of **6** displayed remarkable luminescent properties originating from ligand-to-metal transitions, typical for lanthanide sensitised emission. The luminescence features are shown in Figure 2.

Cavitand phosphinoxides

Cavitand phosphinoxides **3**, **4**, **5** absorb UV radiation distinctly in two different regions, characteristic to short-wavelength absorbance of diphenylphosphin oxide, and longer wavelength characteristic for resorcinol unit. Intriguing enough, these heavily-loaded with phosphin oxide receptors displayed very weak luminescence of their Eu(III) and Tb(III) complexes. It seems that the UV radiation energy was dissipated within this elaborated π -electronic system, and the emissive levels of lanthanide ions were inactive. To tackle the problem, the complexation was effected with

Eu(III) and Tb(III) dibenzoylmethides instead of trifluoromethanesulfonates. In this case several fluorescence spectra were recorded, indicating relatively modest luminescence, when compared to the former results. The representative spectra are shown in Figure 3.

Cyclotriphosphazene phosphinoxides

These Eu(III) and Tb(III) are particularly poorly soluble in all solvents. MM+ modelling indicated very tight packing of phenyl rings in the ligand **8** that three oxygen atoms form the binding site on one side of P₃N₃ ring, three other – on the opposite side. This creates the situation for the formation of linear, pseudo-one-dimensional polymeric coordination array that is insoluble in all solvents. The luminescence measurements were performed at very low concentration in water (10⁻⁷ M), but even in these diluted solutions still strong luminescence was observed. Since we were not sure,

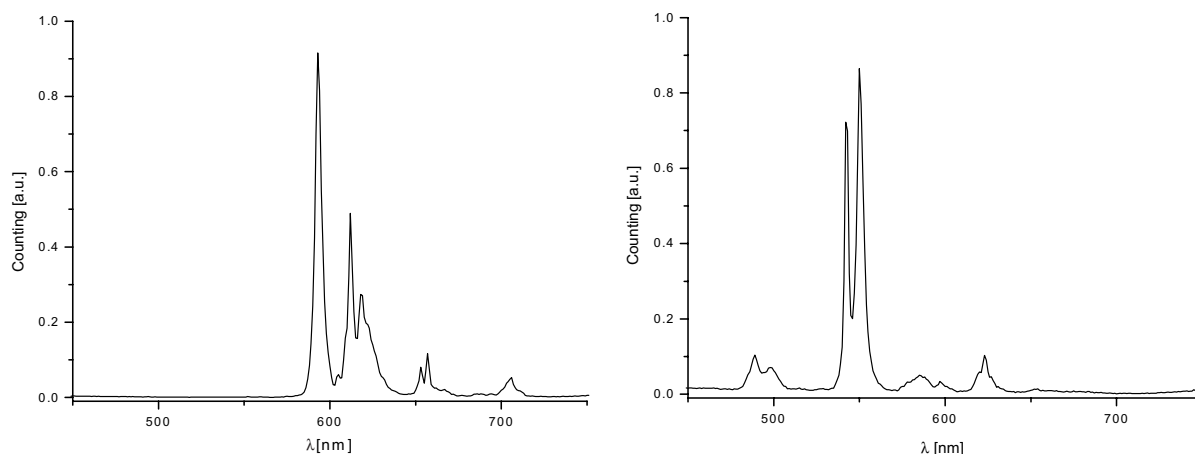


Figure 2. Luminescence spectra in acetonitrile at room temperature: A – **6**: [Eu(CF₃SO₃)₃]₃, B – **6**: [Tb(CF₃SO₃)₃]₃.

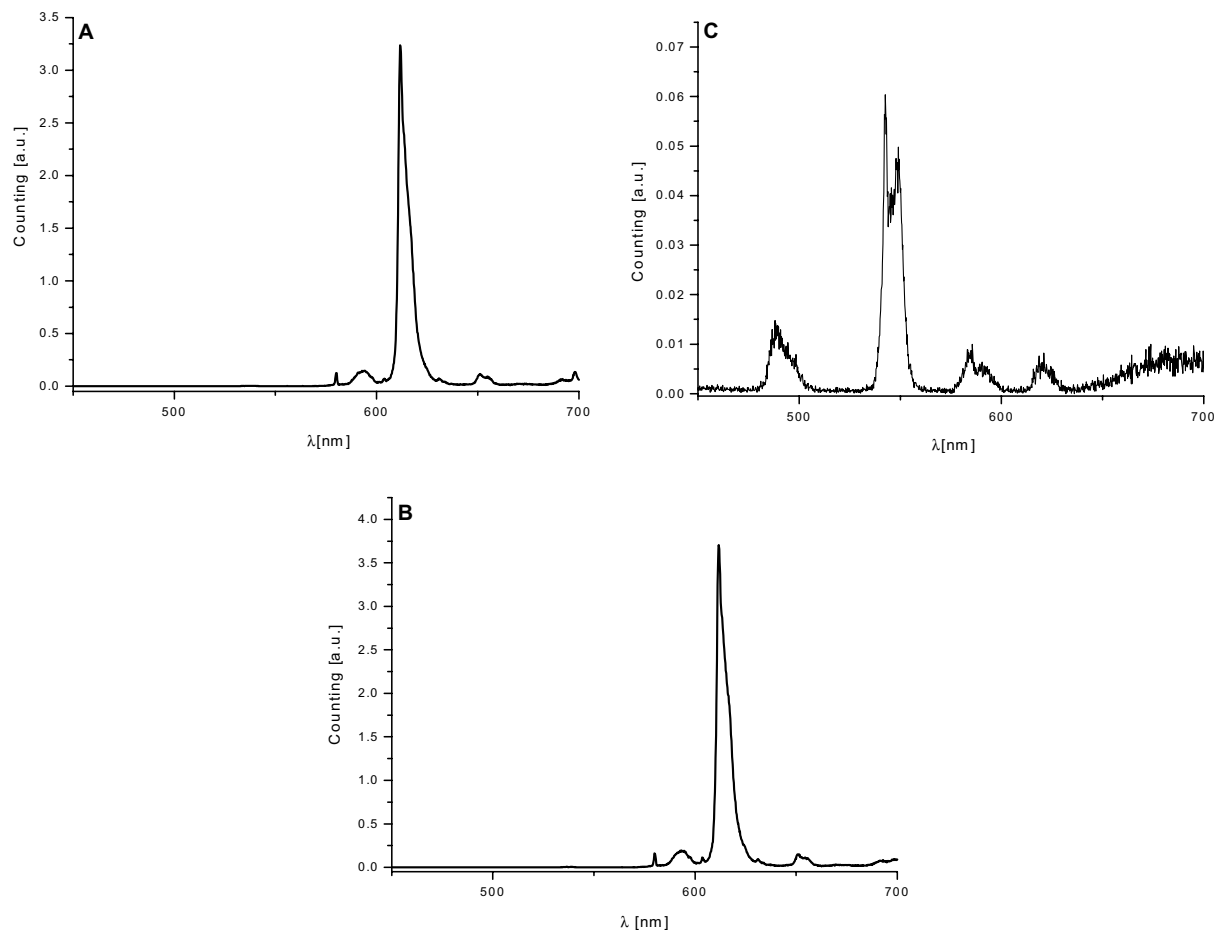


Figure 3. Luminescence spectra in acetonitrile at room temperature: A – 5: $\text{Eu}(\text{DBM})_3$, B – 3: $\text{Tb}(\text{CF}_3\text{SO}_3)_3$, C – 4: $\text{Eu}(\text{DBM})_3$.

whether at this concentration we deal with the proper solution of the complexes, or some colloids are still present, we have not decided to perform quantum yield and luminescence lifetimes measurements Figure 4.

The luminescence data, including lifetimes and the quantum yields of emission are collected for all complexes studied in Table 1.

Very interesting feature was found with 2,6-pyridine phosphinoxide complexes. The luminescence lifetimes of their lanthanide complexes were particularly long, the longest in these series. There is actually no rational explanation for this phenomenon. Even in the case of similar 2,2'-bipyridine derivatives, their luminescence lifetimes were distinctly shorter.

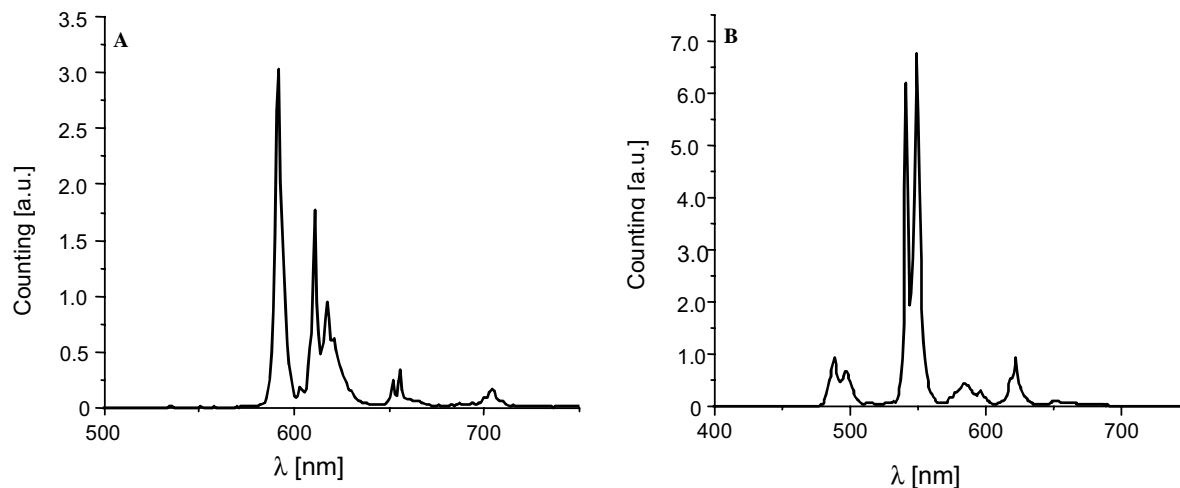


Figure 4. Luminescence spectra in acetonitrile at room temperature: A – 8: $[\text{Eu}(\text{CF}_3\text{SO}_3)_3]$, B – 8: $[\text{Tb}(\text{CF}_3\text{SO}_3)_3]$.

Conclusions

We found the best luminescent properties for Eu(III) and Tb(III) complexes were observed with pyridine and 1,3,5-triazine derivatives, whereas expected convergence of four phosphinoyl groups in calix[4]resorcinarene (“antenna effect”) was not observed. The introduction of carbazole group did not improve the luminescence of the complexes, due to high fluorescence of carbazole itself. It was intriguing that in case of pyridine derivatives long luminescence life times, exceeding 3 ms, were noted.

Although the ligands were designed to provide convergent phosphinoyl binding sites, only in the case of pyridine derivatives remarkable luminescence quantum yields were obtained. Probably, the π -electronic systems of pyridine and diphenylphosphinoyl are compatible and there is no absorbed energy loss via internal conversion between these systems. The systems that absorb at distinctly different wavelengths are not advantageous to promote good emissive properties. The greatest expectations to achieve outstanding luminescent properties are actually with ligands based on 1,3,5-triazine and cyclotriphosphazene, where the possibilities of the formation of more elaborate molecular architectures are challenging.

Acknowledgements

This work was supported by the Polish State Committee for Scientific Research (KBN) grant No. 7T09A 106 20, and the Institute of Physical Chemistry, Polish Academy of Sciences.

References

1. C. Li and W.T. Wong: *J. Chem. Soc., Chem. Commun.* 2034 (2002); C. Galaup, J. Azema, P. Tisnes, C. Picard, P. Ramos, O. Juanes, E. Brunet, and J.C. Rodriguez-Ubis: *Helv. Chim. Acta* **85**, 1613 (2002); V.M. Mukkala, P. Litti, I. Hemmilla, H. Takalo, C. Matachescu, and J. Kankare: *Helv. Chim. Acta* **79**, 295 (1996); C. Piguet, J.C.-G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, and O. Schaad: *J. Am. Chem. Soc.* **118**, 6681 (1996).
2. C. Molina, K. Dahmouche, Y. Messaddeq, S.J.L. Ribeiro, M.A.P. Silva, V.D. Bermudez, and L.D. Carlos: *J. Lumin.* **104**, 93 (2003); L.D. Carlos, C.D. Donega, R.Q. Albuquerque, S. Alves, J.F.S. Menezes, and O.L. Malta: *Mol. Phys.* **101**, 1037 (2003); X.Z. Jiang, A.K.Y. Jen, G.D. Phelan, D.Y. Huang, T.M. Londergan, L.R. Dalton, and R.A Register: *Thin Solid Films* **416**, 212 (2002).
3. M. Kanesato, H. Houjou, Y. Nagawa, and K. Hiratani: *Inorg. Chem. Commun.* **5**, 984 (2002); A. Galembek, M.S. Amorim, H. Bazin, G. Mathis, C.D. Donega, G.F. De Sa, and S. Alves: *Mol. Cryst. Liquid Cryst.* **374**, 267 (2002); J.-M. Lehn, M. Pietraszkiewicz, and J. Karpiuk: *Helv. Chim. Acta* **73**, 106 (1990); B. Alpha, J.-M. Lehn, and G. Mathis: *Angew. Chem. Int. Ed. Engl.* **26**, 266 (1987).
4. A. Dadabhoy, S. Faulkner, and P.G. Sammes: *J. Chem. Soc., Perkin Trans.* 348 (2002); H. Takalo, I. Hemmilla, T. Sutela, and M. Latva: *Helv. Chim. Acta* **79**, 789 (1996); C. Piguet, J.C.-G. Bünzli, G. Bernardinelli, C.G. Bochet, and P. Froidevaux: *J. Chem. Soc., Dalton Trans.* 83 (1995).
5. G.W. Lu, Y. Li, W.H. Lu, Y.Z.Z. Xu, and W.M. Du: *Spectrosc. Spectral Anal.* **23**, 307 (2003); S. Lis, Z. Hnatejko, S. But, A. Szczykowski, and M. Elbanowski: *Mol. Phys.* **101**, 977 (2003); B.L. An, P.Y. Liu, J.X. Shi, M.L. Gong, and Y.S. Yang, N.S. Xu: *J. Mater. Sci. - Mater. Electron.* **14**, 125 (2003).
6. L. Prodi, M. Montalti, N. Zaccaroni, G. Pickaert, L. Charbonniere, and R. Ziessel: *New J. Chem.* **27**, 134 (2003); D. Parker, P.K. Senanayake, and J.A.G. Williams: *J. Chem. Soc., Perkin Trans.* **2**, 2129 (1998).
7. A. Arduini, V. Boehmer, L. Delmau, J.F. Desreux, J.F. Dozol, M.A. Garcia Carrera, B. Lambert, C. Musigmann, A. Pochini, A. Shivaniuk, and F. Ugozzoli: *Chem. - Eur. J.* **6**, 2135 (2000); L.H. Delmau, N. Simon, and M.J. Schwing-Weill: *Sep. Sci. Technol.* **34**, 863 (1999); S. Barbosa, A.G. Carrera, and S.E. Matthews: *J. Chem. Soc., Perkin Trans.* **2**, 719 (1999); F. Arnaud-Neu, J.K. Browne, and D. Byrne: *Chem.-Eur. J.* **5**, 175 (1999).
8. C. Wieser, C.B. Dieleman, and D. Matt: *Coord. Chem. Rev.* **165**, 93 (1997).
9. V. Christou, O.V. Salata, T.Q. Ly, S. Capecchi, N.J. Bailey, A. Cowley, and A.M. Chippindale: *Synth. Metals* **111**, 7 (2000).
10. D.J. Cram, S. Karbach, H.E. Kim, C.B. Knobler, E.F. Maverick, J.L. Ericson, and R.C. Helgeson: *J. Am. Chem. Soc.* **110**, 2229 (1988).
21. M. Pietraszkiewicz, J. Karpiuk, and K. Staniszewski: *J. Alloys Comp.*, **341**, 267 (2002).