Received: 9 September 2008

(www.interscience.com) DOI 10.1002/jms.1534

A MALDI-TOF MS study of lanthanide(III)-cored poly(phenylenevinylene) dendrimers

Accepted: 29 October 2008

Joaquín C. García-Martínez, Carmen Atienza, Milagros de la Peña, Ana C. Rodrigo, Juan Tejeda and Julián Rodríguez-López*

An extensive study by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (MS) of some first-generation and second-generation lanthanide(III)-cored poly(phenylenevinylene) dendrimers is described. The complexes were obtained by self-assembly of suitably functionalized carboxylate dendrons around the lanthanide ion (La^{3+} , Er^{3+}). Fourier transform infrared (FT-IR) spectroscopy gave reasonable evidence for the proposed structures. However, MS was used to ascertain unequivocally the complex formation. The most reliable results were found in the negative reflector mode, using 2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix. Well-defined and highly resolved base peaks corresponding to negative ions of [Gn₄La]⁻ and [Gn₄Er]⁻ were found in all cases, with an excellent match between the theoretical and observed isotope distributions. However, the 3:1 stoichiometry used in the synthesis guarantees an empirical formula Gn₃Ln for the complexes. Copyright (C 2008 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: dendrimers; poly(phenylenevinylene); lanthanide complexes; MALDI-TOF

Introduction

Luminescent lanthanide complexes have attracted a great deal of attention because of their academic interest and potential utility in a wide variety of photonic applications such as planar waveguide amplifiers, plastic lasers, light-emitting diodes, and luminescent probes.^[1-8] The encapsulation of luminescent lanthanide (III) ions (Ln³⁺) within luminescent dendrimers can lead to systems capable of shielding the Ln³⁺ ion from a non-radiative environment, and efficiently transferring excited energy from the peripheral chromophores to the central Ln³⁺ core. Thus, Fréchet^[9,10] and Kawa^[11] reported the site-isolation and antenna effects of Eu³⁺, Tb³⁺, and Er³⁺-cored dendrimer complexes obtained by selfassembly of suitably functionalized carboxylate aryl ether-type dendrons around the lanthanide ion. Kim and co-workers used dendritic luminescent ligands based on metalloporphyrin,[12-14] naphthalene,^[15,16] and 9,10-diphenylanthracene^[17] units that also bear aryl ether-type dendrons.

However, the characterization of these self-assembled complexes is not easy due to their fragile nature, which results from the weak non-covalent ionic interaction between the Ln³⁺ ion and the dendritic carboxylate sub-units. Experimental evidence for the proposed structures is usually provided by techniques such as Fourier transform infrared (FT-IR) and elemental analysis. Unfortunately, the paramagnetic properties of the lanthanide ion preclude conventional nuclear magnetic resonance (NMR) studies. Laser light scattering allows the estimation of the assembly size,^[9] while size exclusion chromatography (SEC) was found to be inappropriate for these fragile complexes. Similarly, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF), electrospray (ESI), or fast atom bombardment (FAB) mass spectrometry (MS) do not give rise to a signal corresponding to the Ln³⁺-complex in a variety of matrices, with complex spectra including the signal due to the starting dendron obtained instead.^[9,17,18] The structure is too weak to withstand the conditions of the mass analyses.

Thus, the complete elucidation of the structure of these Ln(III)-cored dendrimers is still a challenge, and further work is necessary in order to overcome this issue. Typically, they are depicted in the literature as three dendrons that are probably assembled as carboxylate ligands surrounding the lanthanide core.^[9–11,13–18] Some studies with different poly(benzyl ether) dendrons indicate that the co-ordination structure depends on the type and generation of the dendron as well as the lanthanide ion.^[19]

As part of our research program aimed at the construction of π -conjugated dendritic architectures,^[20] we prepared some first-generation and second-generation lanthanide(III)-cored dendrimers with a poly(phenylenevinylene) backbone (Fig. 1). The ligand-exchange reaction of a lanthanide triacetate with the appropriate acid dendron afforded the desired complexes in good yields (Experimental). FT-IR spectroscopy gave reasonable evidence for the proposed structures. Thus, the carbonyl absorptions associated with the precursor acid dendrons, *ca*. 1690 cm⁻¹, were absent in the spectra of the corresponding Ln³⁺-cored dendrimer complexes. In this paper, we present a MALDI-TOF MS study that provides further evidence for complex formation, confirming the occurrence of dendritic ligand–lanthanide interactions.

Área de Química Orgánica, Facultad de Química, Universidad de Castilla-La Mancha, Avda. Camilo José Cela, 10, 13071-Ciudad Real, Spain

^{*} Correspondence to: Julián Rodríguez-López, Área de Química Orgánica, Facultad de Química, Universidad de Castilla-La Mancha, Avda. Camilo José Cela, 10, 13071-Ciudad Real, Spain. E-mail: julian.rodriguez@uclm.es



Scheme 1. Synthesis of first-generation and second-generation poly(phenylenevinylene) acid dendrons.

Experimental

General

In air-sensitive and moisture-sensitive reactions all glassware was flame dried and cooled under Ar. O-dichlorobenzene (ODCB) was dried over CaH₂, filtered, distilled under reduced pressure, and stored over molecular sieves (4 Å). Infrared (IR) spectra were recorded on a Shimadzu Prestige 21 FT-IR spectrophotometer equipped with an attenuated total reflectance (ATR) sample unit. Mass spectra were measured by an Autoflex II time-of-flight (TOF)/TOF Bruker spectrometer (Bremen, Germany). trans-3-indoleacrylic acid (IAA), α -cyano-4hydroxycinnamic acid (HCCA), 2-mercaptobenzothiazole (MBT), 1,8,9-trihydroxyanthracene (Dithranol), 2,5-dihydroxybenzoic acid (DHB) and 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2enylidene]malononitrile (DCTB) were used as matrix materials. Samples co-crystallized with matrices on the probe were ionized by a nitrogen laser pulse (337 nm) and accelerated under 20 kV with time-delayed extraction before entering the TOF mass spectrometer. Matrix (20 mg/mL) and sample (2 mg/mL) were dissolved in tetrahydrofuran (THF). The ratio of matrix solution to sample was 100:1. For all matrices, 5 µl mixture of matrix and sample was applied to a MALDI-TOF MS probe and air-dried. The laser intensity was attenuated appropriately to obtain the best signal-to-noise ratio and isotopic resolution for the matrix used. External calibration was performed using Peptide Calibration Standard II (covered mass range: 700–3200 Da) and Protein Calibration Standard I (covered mass range: \sim 5000–17500 Da) from Care (Bruker) for both positive and negative mode. Calculated and experimental values are referred to base peaks.

The synthesis of the acid dendrons was performed in a convergent manner following the methodology outlined in Scheme 1, which is based in our previous experience in the synthesis of poly(phenylenevinylene) dendrons.^[20]

Diphosphonates **1** and **2** were obtained by Arbuzov reaction of methyl 3,5-bis(bromomethyl)benzoate and 1,3-bis(bromomethyl)-5-iodobenzene, respectively, with triethyl phosphite following a standard methodology.^[21–23]

(E,E)-3,5-Bis(4-hexyloxystyryl)benzoic acid (3)

To a stirred solution of diphosphonate **1** (1 g, 2.29 mmol) and 4-hexyloxybenzaldehyde (945 mg, 4.58 mmol) in anhydrous THF (20 mL) under argon was added potassium *tert*-butoxide (642 mg, 5.72 mmol) in small portions. The mixture was stirred at room temperature for 3 h. After hydrolysis with 1M KOH (5 mL), the mixture was heated under reflux for an additional 4 h and acidified with concentrated HCl. The precipitated dendron was isolated by filtration and purified by washing with hot ethanol. Yield 75%. Colorless solid. Mp 154–156 °C. ¹H-NMR (CDCl₃, 500 MHz) δ : 0.92 (t, 6H, *J* = 7.0 Hz, 2xCH₃), 1.36 (m, 8H, 4xCH₂), 1.48 (m, 4H, 2xCH₂), 1.80 (m, 4H, 2xCH₂), 3.99 (t, 4H, *J* = 7.0 Hz, 2xOCH₂), 6.91 (A of AB_q,





Figure 1. First-generation and second-generation lanthanide(III)-cored poly(phenylenevinylene) dendrimers.

4H, J = 8.5 Hz, ArH), 7.01 (A of AB_q, 2H, J = 17.0 Hz, 2xCH=), 7.18 (B of AB_q, 2H, J = 17.0 Hz, 2xCH=), 7.48 (B of AB_q, 4H, J = 8.5 Hz, ArH), 7.78 (br s, 1H, ArH), 8.09 (br s, 2H, ArH). ¹³C-NMR and DEPT (CDCl₃, 125 MHz) δ : 171.2 (COOH), 159.2 (C), 138.5 (C), 129.9 (C), 129.8 (CH), 129.4 (C), 129.0 (CH), 127.9 (CH), 126.3 (CH), 125.1 (CH), 114.8 (CH), 68.1 (OCH₂), 31.6 (CH₂), 29.2 (CH₂), 25.7 (CH₂), 22.6 (CH₂), 14.0 (CH₃). FT-IR (ATR) ν : 2400–3100 (broad), 1693 (C=O), 1508, 1248, 1173 cm⁻¹. MALDI-TOF (dithranol) *m/z* 526.3 (M⁺⁻, 100). Anal. calculated for C₃₅H₄₂O₄: C, 79.81; H, 8.04. Found: C, 79.59; H, 8.02.

(*E*,*E*,*E*,*E*)-3,5-Bis-[3,5-bis(4-hexyloxystyryl)styryl]benzoic acid (6)

This compound was prepared from diphosphonate **1** and firstgeneration dendritic aldehyde **5** following a similar procedure as described above. The product was purified by washing with hot ethyl acetate. Yield 70%. Colourless solid. ¹H-NMR (THF-d₈, 500 MHz) δ : 0.93 (t, 12H, J = 7.0 Hz, 4xCH₃), 1.38 (m, 16H, 8xCH₂), 1.50 (m, 8H, 4xCH₂), 1.80 (m, 8H, 4xCH₂), 3.99 (t, 8H, J = 7.0 Hz, 4xOCH₂), 6.91 (A of AB_q, 8H, J = 8.5 Hz, ArH), 7.10 (A of AB_q, 4H, J = 16.5 Hz, 4xCH=), 7.26 (B of AB_q, 4H, J = 16.5 Hz, 4xCH=), 7.41 (s, 4H, 4xCH=), 7.51 (B of AB_q, 8H, J = 8.5 Hz, ArH), 7.60 (br s, 2H, ArH), 7.68 (br s, 4H, ArH), 8.06 (br s, 1H, ArH), 8.17 (d, 2H, J = 1.5 Hz, ArH), 10.82 (s, 1H, COOH). ¹³C-NMR and DEPT (THF-d₈, 125 MHz) δ : 167.5 (COOH), 160.2 (C), 139.6 (C), 139.3 (C), 138.8 (C), 132.9 (C), 131.0 (C), 130.8 (CH), 129.7 (CH), 128.8 (CH), 128.8 (CH), 128.5 (CH), 127.7 (CH), 126.8 (CH), 124.8 (CH), 124.1 (CH), 115.4 (CH), 68.6 (OCH₂), 32.6 (CH₂), 30.3 (CH₂), 26.7 (CH₂), 23.5 (CH₂), 14.4 (CH₃). FT-IR (ATR) ν : 2400–3100 (broad), 1686 (C=O), 1605, 1584, 1508, 1248, 1173, 955 cm⁻¹. MALDI-TOF (dithranol) *m/z* 1135.3 (M⁺⁻). Anal. calculated for C₇₉H₉₀O₆: C, 83.56; H, 7.99. Found: C, 83.27; H, 7.95.

Preparation of the lanthanide(III)-cored poly(phenylenevinylene) dendrimers

The Ln(III)-cored poly(phenylenevinylene) dendrimers were prepared according to the procedure previously described in the literature.^[9] A stoichiometric mixture of the anhydrous lanthanide triacetate, $Ln(OAc)_3$, and the appropriate acid dendron (1:3 molar ratio) were refluxed in ODCB. The acetic acid generated by the exchange reaction was distilled off with ODCB continuously during the reaction for 3 h followed by final evaporation to dryness under reduced pressure.

G1₃La : Yield 97%. Brown solid. FT-IR (ATR) ν : 1605, 1508, 1450, 1393, 1244, 1173, 1028, 845, 814 cm⁻¹. MALDI-TOF *m/z* 2241.1 ([G1₄La]⁻). (Although La³⁺ is a diamagnetic ion, the NMR spectra of the La³⁺-complexes described here also showed very broad signals, avoiding their characterization by this technique.)

G1₃Er : Yield 98%. Yellow-brown solid. FT-IR (ATR) ν : 1605, 1524, 1508, 1450, 1404, 1426, 1172, 1028, 959, 845, 814 cm⁻¹. MALDI-TOF *m/z* 2269.1 ([G1₄Er]⁻).

G2₃**La** : Yield: 98%. Pale yellow solid. FT-IR (ATR) ν : 1605, 1584, 1506, 1244, 1171, 1028, 957 cm⁻¹. MALDI-TOF *m/z* 4676.3 ([G2₄La]⁻).

G2₃**Er** : Yield 98%. Pale yellow solid. FT-IR (ATR) ν : 1605, 1584, 1506, 1454, 1393, 1244, 1171, 955 cm⁻¹. MALDI-TOF *m/z* 4703.8 ([G2₄Er]⁻).

Results and Discussion

Selection of the matrix

DCTB produced good quality spectra in positive and negative modes and was chosen for further studies. The relative softness of this aprotic matrix compared to other polar matrices is evidenced by a highly unlikely impossible protonation of the analytes and lower laser power requirements. These advantages make DCTB a suitable matrix for metal complex characterization.^[24] Polar acid matrices, such as IAA and HCCA, are not specifically designed to promote the formation of radical ions but to give protonated ions, and consequently these cause the complex to split during the mass spectrometric measurement. Indeed, the experiments performed with these matrices yielded MALDI spectra that showed, in either positive or negative ion mode, exclusively the peak corresponding to the dendritic free fragment. A similar finding was previously reported by Fréchet et al.^[9] and clearly indicates dissociation of the complex. On the other hand, dithranol, MBT and DHB, which are typically used as matrices for desorptionionization of synthetic polymers and small molecules,^[25] always gave lower quality spectra when compared with DCTB. The main peak again corresponded to the free ligand ion, although other peaks, fragments and matrix-related ions were also observed. The resolution and signal-to-noise ratio of the base peak were lower,



Figure 2. Negative reflector mode spectra of Ln^{3+} -cored first-generation dendrimers **G1₃Ln** with expanded regions comparing the theoretical isotope distribution for the complex anion [G1₄Ln]⁻ (on the left) with the data acquired (on the right).





Figure 3. MALDI-TOF negative reflector mode spectrum of a physical mixture prepared by mixing $G1_3Er$ with the first-generation acid dendron G'1 using DCTB as the matrix.

especially when DHB was used, because greater laser power was needed to acquire the spectra (see Supporting information, Fig. S11-S12). Thus, all figures presented in this paper relate to spectra obtained using DCTB as the matrix.

Positive ion mode

When the Ln³⁺-cored dendritic complexes were analysed in the positive ion extraction mode, peaks corresponding to radical ion $[M]^{\bullet+}$ or protonated $[M + H]^+$ forms were not observed and nor were single alkali metal adducts $[M + Na]^+$ or $[M + Aq]^+$ when a cationization reagent was added. A number of signals above the molecular mass of the compounds were found instead. For instance, the spectrum of the Er³⁺-cored first-generation dendrimer, G1₃Er, showed three main peaks (m/z = 4706.2, 6448.3, 8199.7) and these can be attributed to the species $[G1_8Er_3]^+$ (calculated m/z = 4707.2), $[G1_{11}Er_4]^+$ (calculated m/z = 6451.0) and $[G1_{14}Er_5]^+$ (calculated m/z = 8195.9), respectively (see Supporting information, Figs. S13-S15). The tendency of lanthanide ions towards a high co-ordination environment may explain the formation of adducts during the desorption process. When a cationization reagent such as sodium iodide was added to the matrix/sample mixture, the spectrum only showed peaks corresponding to the substitution of one Er^{3+} atom by three Na⁺ in the form $[G1_2Na_3]^+$ (*m*/*z* = 1120.4), among other combinations. Smaller peaks close to the base peak at higher m/z values were also found and these could be related to an interaction between the matrix and the adducts (Supporting information, Fig. S16). Similar spectra were obtained with the La^{3+} cored first-generation dendrimer G1₃La (Supporting information, Fig. S17).

Generally, the peaks were broad, isotopically unresolved and with intensities that were highly dependent on the matrix/sample ratio. This fact supports the idea of a recombination of species during the desorption process and makes the experiment very irreproducible and unsuitable for an unequivocal characterization. When the La³⁺- or Er³⁺-cored second-generation dendrimers **G2**₃Ln were analysed, the formation of adducts was very difficult due to steric hindrance and, for instance, peaks associated with the species [G2₈Er₃]⁺ (m/z = 9578.1) and [G2₁₁Er₄]⁺ (m/z = 13149.1) were not found. Although the positive ion extraction

mode shows the formation of complexes between dendrons and Ln^{3+} , the poor quality and low peak resolution rule out the use of this mode as a definitive technique to characterize the compounds.

Negative ion mode

In a similar way to the positive mode, the Ln³⁺-cored dendritic complexes did not show the radical ion [M]. in the negative reflector mode. However, well-defined and highly resolved base peaks were found in all cases. The MALDI-TOF spectrum of the Er³⁺-cored first-generation dendrimer, **G1₃Er**, in DCTB is shown in Fig. 2 (top). The spectrum is easy to interpret with only one peak at m/z = 2269.1. This is the only signal observed – there are no fragmentations or matrix-related ions at lower m/z values or signals corresponding to a sample/matrix adduct at higher m/z values. The lack of other ions also gives an indication of the purity of the sample. This peak corresponds to the negative ion of [G1₄Er]⁻ (calculated m/z = 2269.1). The presence of multi-isotopic elements means the isotope distribution is very distinguishable, almost like a finger print, and this proved to be an excellent match with the theoretical distribution, thus providing strong evidence for the formation of $[G1_4Er]^-$.

A MALDI-TOF MS/MS experiment in negative mode on the base peak was also performed with the intention of confirming the composition of the formed species (see Supporting information, Fig. S18). The MS/MS spectrum showed a few peaks with an isotopic pattern that indicated the presence of an Er atom in the fragments. It is important to highlight that a peak at m/z = 1744.5 corresponding to the species [G1₃Er]^{•-} (calculated m/z = 1743.8) was observed, i.e. loss of a dendron from the complex [G1₄Er]⁻. Moreover, the presence of the dendritic unit on the structure was definitively confirmed by the existence of fragmentation peaks associated with ligand loss: i.e. [G1]⁻ (m/z =525.3), [G1₂]⁻ (m/z = 1051.6) and [G1₃]⁻ (m/z = 1577.7).

The formation of $[G1_4Er]^-$ can again be explained in terms of the tendency of the lanthanide metal ions to have a high co-ordination environment, which during the desorption process incorporate other dendritic ligands to reach a stable co-ordination number of eight. The same peak was observed when dithranol or MBT were used as matrices, but in these cases its intensity was lower. Other peaks related to fragmentations or matrix interactions also appeared in the spectrum, thus complicating the study.

Analogous results were found for the La^{3+} -cored firstgeneration dendrimer **G1₃La**. The MALDI-TOF spectrum showed a base peak corresponding to $[G1_4La]^-$ (m/z = 2241.1, calculated m/z = 2241.1) and an excellent match for the isotope distribution of the complex anion (Fig. 2, bottom). Analysis of the fragments in the MS/MS spectrum revealed the presence of the dendritic ligand coordinated to the metal, also becoming visible a peak at m/z = 1716.6 corresponding to $[G1_3La]^{\bullet-}$ (calculated m/z = 1715.8) (see Supporting information, Fig. S19).

In order to clarify if the species $[G1_4Ln]^-$ are really formed during the mass analysis, we registered the MALDI-TOF spectrum of a physical mixture prepared by mixing **G1_3Er** with a different, although structurally related, acid dendron G'1. Together with the signal associated to $[G1_4Er]^-$, several peaks corresponding to crossover species $[G1_3G'1Er]^-$, $[G1_2G'1_2Er]^-$ and $[G1G'1_3Er]^$ were also observed (Fig. 3). Interestingly, the signal intensities of the crossover species became more noteworthy as the amount of G'1 increased in the mixture.

Alternatively, mass analyses in negative linear mode were also performed for G1₃Ln complexes. In a comparable manner



Figure 4. Negative reflector mode spectra of Ln^{3+} -cored second-generation dendrimers **G2**₃**Ln** with expanded regions comparing the theoretical isotope distribution for the complex anion [G2₄Ln]⁻ (on the left) with the data acquired (on the right).

to the positive mode, the spectra showed peaks at higher m/z values, which can be attributed to higher co-ordination polynuclear species, containing 7, 10 and even 13 monodendrons: i.e. $[G1_7Ln_2]^-$, $[G1_{10}Ln_3]^-$ and $[G1_{13}Ln_4]^-$, respectively (see Supporting information, Fig. S20-S21). These peaks appeared much more intense in the analysis of a physical mixture prepared by mixing **G1_3Ln** with the corresponding acid dendron G1. All these results strongly support the formation of the higher co-ordination species during the mass analysis.

When a mixture of the lanthanide triacetate $Ln(OAc)_3$ and the first-generation acid dendron **3** in a 1 : 4 molar ratio was refluxed in ODCB under the same experimental conditions described above, the analysis of the final product showed unreacted free acid. The same result was obtained in the treatment of **G1₃Ln** with an equimolar amount of the acid dendron **3**. These two experiments guarantee an empirical formula of **G1₃Ln** for the complexes, i.e. a fourth ligand is not incorporated under the reaction conditions.

MALDI-TOF MS in negative reflector mode was also useful to study the second-generation complexes. The spectra of the Ln^{3+} -cored dendrimer **G2**₃Ln are shown in Fig. 4. Comparable outcomes were obtained under the same experimental conditions. Base peaks corresponding to $[G2_4Er]^-$ (m/z = 4703.8) and $[G2_4La]^-$ (m/z = 4676.3) were found along with a few others less significant (calculated values are $[G2_4Er]^-$ m/z = 4704.6 and $[G2_4La]^-$ m/z = 4676.6). Once again, the excellent agreement between the theoretical and observed isotope distribution confirms the formation of a complex between the dendrons and the lanthanide metal ion.

Conclusions

Regrettably, the structure elucidation of Ln³⁺-cored dendrimer complexes obtained by self-assembly of suitably functionalized carboxylate dendrons around lanthanide ions is quite elusive because of their fragile nature. The strong paramagnetism of lanthanides impedes the use of NMR techniques and, on the other hand, the gathering of good single crystals for X-ray diffraction is seldom possible. However, in this paper MALDI-TOF MS was used to ascertain the formation of first-generation and second-generation lanthanide(III)-cored poly(phenylenevinylene) dendrimer complexes, confirming the occurrence of dendritic ligand-lanthanide interactions. The most reliable results were found in the negative reflector mode, using DCTB as matrix. Welldefined and highly resolved base peaks attributed to the adducts [Gn₄Ln]⁻ were found in all cases due to their high stability, with an excellent match between the experimental and theoretical isotope distributions. The observed species in the mass analysis do indicate that dendritic complexes have been formed (FT-IR results are also an evidence), but not that they comprise three dendrons. However, the 3:1 stoichiometry used for their synthesis guarantees an empirical formula of **Gn₃Ln**. Identification of this type of structure can be standardized and a specially tuned spectrometer is not required. Identical results were obtained with an Applied Biosystems 4700 Proteomics Analyzer.

Supporting Information

Copies of FT-IR, ¹H-NMR, ¹³C-NMR and additional MALDI-TOF spectra for the described compounds may be found in the online version of this article.

Acknowledgements

This work was funded by the Spanish Ministerio de Educación y Ciencia (projects NAN2004-08843-C05-02 and CTQ2006-08871) and the Junta de Comunidades de Castilla-La Mancha (projects PCI08-0033 and PAI07-0007-1001). A.C.R. and J.C.G.-M. also thank the Spanish MEC for a predoctoral fellowship and financial support through the Ramon y Cajal program, respectively.

References

- [1] H. K. Kim, S. G. Roh, K.-S. Hong, J.-W. Ka, N. S. Baek, J. B. Oh, M. K. Nah, Y. H. Cha, J. Ko. Novel lanthanide-cored supramolecular systems with highly efficient light-harvesting dendritic arrays towards tomorrow's information technology. *Macromolecular Research* 2003, *11*, 133.
- [2] H. K. Kim, J. B. Oh, N. S. Baek, S.-G. Roh, M. K. Nah, Y. H. Kim. Recent progress in luminescent lanthanide complexes for advanced photonics applications. *Bulletin of the Korean Chemical Society* 2005, 26, 201.
- [3] E. Desurvire. *Erbium-Doped Fiber Amplifiers: Principles and Applications*. Wiley: New York, **1994**.
- [4] K. Kuriki, Y. Koike, Y. Okamoto. Plastic optical fiber lasers and amplifiers containing lanthanide complexes. *Chemical Reviews* 2002, 102, 2347, DOI: 10.1021/cr010309g.
- [5] L. H. Slooff, A. van Blaaderen, A. Polman, G. A. Hebbink, S. I. Klink, F. C. J. M. van Veggel, D. N. Reinhoudt, J. W. Hofstraat. Rare-earth doped polymers for planar optical amplifiers. *Journal of Applied Physics* **2002**, *91*, 3955, DOI:10.1063/1.1454190.
- [6] T. Oyamada, Y. Kawamura, T. Koyama, H. Sasabe, C. Adachi. Formation of europium chelate complexes by vacuum codeposition and their application in organic light-emitting diodes. *Advanced Materials* **2004**, *16*, 1082, DOI: 10.1002/adma.200400090.
- [7] T.-S. Kang, B. S. Harrison, M. Bouguettaya, T. J. Foley, J. M. Boncella, K. S. Schanze, J. R. Reynolds. Near-infrared light-emitting diodes (LEDs) based on poly(phenylene)/Yb-tris(β-diketonate) complexes. *Advanced Functional Materials* **2003**, *13*, 205, DOI: 10.1002/adfm.200390031.
- [8] T.-S. Kang, B. S. Harrison, T. J. Foley, A. S. Knefely, J. M. Boncella, J. R. Reynolds, K. S. Schanze. Near-infrared electroluminescence from lanthanide tetraphenylporphyrin:polystyrene blends. *Advanced Materials* 2003, *15*, 1093, DOI: 10.1002/adma.200304692.
- [9] M. Kawa, J. M. J. Fréchet. Self-assembled lanthanide-cored dendrimer complexes: enhancement of the luminescence properties of lanthanide ions through site-isolation and antenna effects. *Chemistry of Materials* **1998**, *10*, 286, DOI: 10.1021/cm970441q.
- [10] M. Kawa, J. M. J. Fréchet. Enhanced luminescence of lanthanide within lanthanide-cored dendrimer complexes. *Thin Solid Films* **1998**, 331, 259, DOI: 10.1016/S0040-6090(98)00928-6.
- [11] M. Kawa, T. Takahagi. Improved antenna effect of terbium(III)-cored dendrimer complex and green-luminescent hydrogel by radical copolymerization. *Chemistry of Materials* **2004**, *16*, 2282, DOI: 10.1021/cm034873e.
- [12] J.-W. Ka, H. K. Kim. One-pot synthesis of new functionalized azacryptands from resorcinol derivatives for advanced photonic materials. *Tetrahedron Letters* **2004**, *45*, 4519, DOI:10.1016/j.tetlet.2004.04.051.
- [13] J. B. Oh, Y. H. Kim, M. K. Nah, H. K. Kim. Inert and stable erbium(III)cored complexes based on metalloporphyrins bearing arylether dendron for optical amplification: synthesis and emission enhancement. *Journal of Luminescence* **2005**, *111*, 255, DOI:10.1016/j.jlumin.2004.10.006.
- [14] J. B. Oh, M.-K. Nah, Y. H. Kim, M. S. Kang, J.-W. Ka, H. K. Kim. Er(III)cored complexes based on dendritic Pt(II)-porphyrin ligands: synthesis, near-IR emission enhancement, and photophysical studies. Advanced Functional Materials 2007, 17, 413, DOI: 10.1002/adfm.200600451.
- [15] N. S. Baek, M. K. Nah, Y. H. Kim, S.-G. Roh, H. K. Kim. Efficient energy transfer pathways for the sensitization of lanthanide ions by luminescent ligands in luminescent lanthanide complexes. *Bulletin* of the Korean Chemical Society **2004**, 25, 443.

- [16] N. S. Baek, Y. H. Kim, H. K. Kim. Recent progress in erbium(III)-cored complexes based on dendritic ligands for advanced photonics applications. *Journal of Nonlinear Optical Physics and Materials* **2006**, *15*, 369, DOI: 10.1142/S0218863506003360.
- [17] N. S. Baek, Y. H. Kim, S.-G. Roh, B. K. Kwak, H. K. Kim. The first inert and photostable encapsulated lanthanide(III) complexes based on dendritic 9,10-diphenylanthracene ligands: synthesis, strong near-infrared emission enhancement, and photophysical studies. Advanced Functional Materials 2006, 16, 1873, DOI: 10.1002/adfm.200500835.
- [18] D. L. Stone, G. M. Dykes, D. K. Smith. Dendritic lanthanide complexes and the effect of Lewis-acid encapsulation. *Dalton Transactions* **2003**, 3902, DOI: 10.1039/b309643b.
- [19] T. Seto, M. Kawa, K. Sugiyama, M. Nomura. XAFS studies of Tb or Eu cored dendrimer complexes with various properties of luminescence. *Journal of Synchrotron Radiation* **2001**, *8*, 710, DOI: 10.1107/S0909049500015910.
- [20] J. C. García-Martínez, E. Díez-Barra, J. Rodríguez-López. Conjugated dendrimers with poly(phenylenevinylene) and poly(phenyleneethynylene) scaffolds. *Current Organic Synthesis* **2008**, *5*, 267, DOI: 10.2174/157 017 908 785 133 438.

- [21] E. Díez-Barra, J. C. García-Martínez, J. Rodríguez-López. Synthesis of novel cross-conjugated dendritic fluorophores containing both phenylenevinylene and phenyleneethynylene moieties. *The Journal* of Organic Chemistry **2003**, 68, 832, DOI: 10.1021/jo026019x.
- [22] K. H. Duchêne, F. Vögtle. Ein kohlenwasserstoff-gerüst mit zwölf identischen funktionellen gruppen: synthese einer dodecawirtverbindung. Synthesis **1986**, 659, DOI: 10.1055/s-1986-31738.
- [23] E. Díez-Barra, J. C. García-Martínez, J. Guerra, V. Hornillos, S. Merino, R. del Rey, R. I. Rodríguez-Curiel, J. Rodríguez-López, P. Sánchez-Verdú, J. Tejeda, J. Tolosa. On the synthesis of heterocyclic dendrons. *Arkivoc* 2002, V, 17.
- [24] M. F. Wyatt, B. K. Stein, A. G. Brenton. Characterization of various analytes using matrix-assisted laser desorption/ionization timeof-flight mass spectrometry and 2-[(2E)-3-(4-tert-butylphenyl)-2methylprop-2-enylidene]malononitrile matrix. *Analytical Chemistry* 2006, 78, 199, DOI: 10.1021/ac050732f.
- [25] F. Hillenkamp, J. Peter-Katalinić (eds). In MALDI MS: A Practical Guide to Instrumentation, Method and Applications. Wiley-VCH: Weinheim, 2007.