

Covalent Coupling of Luminescent Tris(2-thenoyltrifluoroacetato)lanthanide(III) Complexes on a Merrifield Resin

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Lanthanide(III) β -diketonate complexes (Ln = Nd, Sm, Eu, Gd, Tb, Er, Yb) were immobilized on a 1,10-phenanthroline (phen)-functionalized Merrifield resin (cross-linked chloromethylated polystyrene). 1,10-Phenanthroline was coupled to the polymer beads by nucleophilic displacement of the chlorine with 5-amino-1,10-phenanthroline. Tris(2-thenoyltrifluoroacetato)lanthanide(III) dihydrate complexes were coupled to the resin-bound 1,10-phenanthroline, and the coordinated water molecules were expelled from the first coordination sphere of the lanthanide(III) ion. Depending on the lanthanide ion, the luminescent resin beads emit in the visible region (Ln = Sm, Eu, Tb) or in the near-infrared region (Ln = Sm, Nd, Er, Yb). High-resolution luminescence spectra were recorded, and the radiative lifetimes were measured. It is shown that the spectroscopic behavior of the luminescent material is very comparable with that of the pure $[\text{Ln}(\text{tta})_3(\text{phen})]$ (tta = 2-thenoyltrifluoroacetone) complexes. The gadolinium(III) complex has been used to determine the emission behavior of the resin and ligands.

Introduction

Lanthanide β -diketonate complexes are well-known molecular luminescent materials, which are characterized by characteristic narrow emission bands and long radiative lifetimes of the excited state (resonance level).^{1–11} The emission color depends on the lanthanide ion, for instance, red emission for europium(III) complexes and green emission for terbium(III) complexes. Some trivalent lanthanide compounds emit in the near-infrared region. Examples are neodymium(III), erbium(III), and ytterbium(III) complexes. Most studies of the spectroscopic and photophysical properties of lanthanide β -diketonate complexes were made on pure complexes in the solid state or on solutions of these complexes in organic solvents. However, for practical applications in optical devices, it is advantageous to embed luminescent lanthanide complexes in a matrix. These matrices can be sol–gel glasses,^{7,12–14} inorganic–organic hybrid

materials,^{15–17} polymers,^{18–23} or liquid crystals.^{24,25} Recently, we reported on the coupling of the complexes to sol–gel glasses via covalently bound 1,10-phenanthroline groups.²⁶ Another approach is to embed luminescent lanthanide complexes into a polymer matrix. The two main routes to include lanthanide complexes into polymers are (1) dissolution or dispersion of discrete molecular complexes in the polymer matrix and (2) attachment of the lanthanide complex to the polymer matrix through covalent bonds. The first approach offers the advantage of versatility (both the polymer matrix and the lanthanide complex can be chosen independently), but it is difficult to obtain a uniform distribution of the lanthanide complex in the polymer matrix,^{27,28} and the solubility of the lanthanide complex in the polymer matrix is often low. Because of clustering, concentration quenching

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- (1) Forsberg, J. H. *Gmelin Handbook of Inorganic Chemistry, Sc, Y, La–Lu Rare Earth Elements*; Springer-Verlag: Berlin, 1981; System No. 39, Vol. D3, pp 65–251 and references therein.
- (2) Melby, L. R.; Rose, N. J.; Abramson, E.; Caris, J. C. *J. Am. Chem. Soc.* **1964**, *86*, 5117.
- (3) Bauer, H. J.; Blanc, J.; Ross, D. L. *J. Am. Chem. Soc.* **1964**, *86*, 5125.
- (4) de Sá, G. F.; Malta, O. L.; Donega, C. D.; Simas, A. M.; Longo, R. L.; Santa-Cruz, P. A.; da Silva, E. F. *Coord. Chem. Rev.* **2000**, *196*, 165.
- (5) Batista, H. J.; de Andrade, A. V. M.; Longo, R. L.; Simas, A. M.; de Sá, G. F.; Ito, N. K.; Thompson, L. C. *Inorg. Chem.* **1998**, *37*, 3542.
- (6) Adachi, C.; Balda, M. A.; Forrest, S. R. *J. Appl. Phys.* **2000**, *87*, 8049.
- (7) Streck, W.; Sokolnicki, J.; Legendziewicz, J.; Maruszewski, K.; Reisfeld, R.; Pavich, T. *Opt. Mater.* **1999**, *13*, 41.
- (8) Yang, C. V.; Srdanov, V.; Robinson, M. R.; Bazan, G. C.; Heeger, A. J. *Adv. Mater.* **2002**, *14*, 980.
- (9) McGehee, M. D.; Bergstedt, T.; Zhang, C.; Saab, A. P.; O'Regan, M. B.; Bazan, G. C.; Srdanov, V. I.; Heeger, A. J. *Adv. Mater.* **1999**, *11*, 1349.
- (10) Robinson, M. R.; O'Regan, M. B.; Bazan, G. C. *Chem. Commun.* **2000**, 1645.
- (11) Kido, J.; Okamoto, Y. *Chem. Rev.* **2002**, *102*, 2357.

- (12) Matthews, L. R.; Kobbe, E. T. *Chem. Mater.* **1993**, *5*, 1697.
- (13) Costa, V. C.; Vasconcelos W. L.; Bray, K. L. *J. Sol-Gel Sci. Technol.* **1998**, *13*, 605.
- (14) Klonkowski, A. M.; Lis, S.; Pietraszkiewicz, M.; Hnatejko, Z.; Czarnobaj, K.; Elbanowski, M. *Chem. Mater.* **2003**, *15*, 656.
- (15) Tanner, P. A.; Yan, B.; Zhang, H. J. *J. Mater. Sci.* **2000**, *35*, 4325.
- (16) Bekiari, V.; Pistolis, G.; Lianos, P. *Chem. Mater.* **1999**, *11*, 3189.
- (17) Li, H.; Inoue, S.; Machida, K.; Adachi, G. *Chem. Mater.* **1999**, *11*, 3171.
- (18) Yang, C. Y.; Srdanov, V.; Robinson, M. R.; Bazan, G. C.; Heeger, A. J. *Adv. Mater.* **2002**, *14*, 980.
- (19) Kuriki, K.; Koike, Y.; Okamoto, Y. *Chem. Rev.* **2002**, *102*, 2347.
- (20) Wolff, N. E.; Pressley, R. J. *Appl. Phys. Lett.* **1963**, *2*, 152.
- (21) Ueba, Y.; Banks, E.; Okamoto, Y. *J. Appl. Polym. Sci.* **1980**, *25*, 2007.
- (22) Gao, R. Y.; Koeppen, C.; Zheng, G. Q.; Garito, A. F. *Appl. Opt.* **1998**, *37*, 7100.
- (23) Lin, S.; Feuerstein, R. J.; Mickelson, A. J. *Appl. Phys.* **1996**, *79*, 2868.
- (24) Binnemans, K.; Görlner-Walrand, C. *Chem. Rev.* **2002**, *102*, 2303.
- (25) Van Deun, R.; Moors, D.; De Fré, B.; Binnemans, K. *J. Mater. Chem.* **2003**, *13*, 1520.
- (26) Binnemans, K.; Lenaerts, P.; Driesen, K.; Görlner-Walrand, C. *J. Mater. Chem.* **2004**, *14*, 191.
- (27) Li, H. R.; Fu, L. S.; Lin, J.; Zhang, H. J. *Thin Solid Films* **2002**, *416*, 197.
- (28) Du, C. X.; Ma, L.; Xu, Y.; Li, W. L. *J. Appl. Polym. Sci.* **1997**, *66*, 1405.

can occur in the matrix.^{29,30} Concentration quenching can be avoided by choosing large ligands, such as dendrimers,³¹ but can also be avoided by the second approach for incorporation of lanthanide complexes in a polymer matrix, namely, covalent attachment.^{32,33} Most of the approaches to bind a lanthanide(III) β -diketonate complex to a polymer backbone make use of a polymerizable ligand. Alternatively, ternary lanthanide complexes can be linked to the polymer via the neutral ligand, such as 1,10-phenanthroline.^{34–36}

In this paper, we discuss how tris(2-thenoyltrifluoroacetato)lanthanide(III) complexes can be linked covalently to a polymer chain by adduct formation with a polymer-bound 1,10-phenanthroline group. The 1,10-phenanthroline-functionalized polymer was obtained by reaction between a Merrifield resin and 5-amino-1,10-phenanthroline. A Merrifield resin is often used as a support for organic synthesis on solid phases.^{37–41} The resin consists of chloromethylated polystyrene that is cross-linked with 1,4-divinylbenzene. The matrix was chosen because of its wide availability and easy derivatization, but the approach is a general one and can be extended to other matrices as well. We want to illustrate the versatility of linking lanthanide β -diketonate complexes to a polymeric matrix through a 1,10-phenanthroline ligand.²⁶ The resulting materials emit either in the visible spectral region or in the near-infrared.

Experimental Section

General Procedures. CHN elemental analyses were performed on a CE Instruments EA-1110 elemental analyzer. ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer. Mass spectra were taken on a Thermo Finnigan LCQ Advantage mass spectrometer. Photoluminescence spectra in the visible region have been recorded on an Edinburgh Instruments FS900 steady-state spectrofluorimeter. This instrument is equipped with a xenon arc lamp, a microsecond flashlamp (pulse length 2 μ s), and a red-sensitive photomultiplier (300–850 nm). The steady-state luminescence spectra and the lifetime measurements in the infrared region were measured on an Edinburgh Instruments FS920P near-infrared spectrometer, with a 450 W xenon lamp as the steady-state excitation source, a double excitation monochromator (1800 lines mm⁻¹), an emission monochromator (600 lines mm⁻¹), and a liquid nitrogen cooled Hamamatsu R5509-72 near-infrared photomultiplier tube. For the lifetime measurements, the setup includes a Nd:YAG laser pumped dye laser, which allows laser excitation of the sample in a wavelength range of 370–850 nm. The repetition rate is 10

Hz, and the pulse width is 3–5 ns. The luminescence lifetime has been determined by measurement of the luminescence decay curve. All photoluminescence spectra were recorded at room temperature, except for the resins with gadolinium(III) and europium(III) complexes. These samples were cooled to 77 K in an Oxford Instruments OptistatDN nitrogen bath cryostat.

The quantum yield of the europium sample was determined using an integrating sphere (150 mm diameter, BaSO₄ coating) from Edinburgh Instruments. The spectra were corrected for variations in the output of the excitation source and for variations in the detector response. The quantum yield can be defined as the integrated intensity of the luminescence signal divided by the integrated intensity of the absorption signal. Only the intense luminescence band of the ⁵D₀ → ⁷F₂ transition around 612 nm was measured by the integrating sphere, but this intensity value was corrected by taking into account the relative intensity of the other transitions (as determined from the steady-state luminescence spectrum). In this way, an intensity value that corresponds to the total luminescence output was obtained. The absorption intensity was calculated by subtracting the integrated intensity of the light source with the sample in the integrating sphere from the integrated intensity of the light source with a blank sample in the integrating sphere. A solution of [Eu(tta)₃(phen)] (tta = 2-thenoyltrifluoroacetone) in DMF was used to validate the measurements with the integrating sphere.

Triethylamine and 2-thenoyltrifluoroacetone were purchased from Acros and the lanthanide(III) salts from Aldrich. The Merrifield resin is chloromethylated polystyrene (~0.7 mmol of Cl/g of resin) cross-linked with 2% divinylbenzene and was obtained from Fluka.

Synthetic Procedures. *Synthesis of 5-Amino-1,10-phenanthroline.* The synthesis of this compound was performed by nitration of 1,10-phenanthroline in a mixture of concentrated sulfuric acid and fuming nitric acid, followed by reduction of the nitro derivative with hydrazine over a 5% Pd/C catalyst. The synthetic procedure has been described in detail elsewhere.^{26,42} Yield: 443 mg (50%). *R*_f = 0.45 (alumina, CHCl₃/CH₃OH, 96/4). Mp: 253–254 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ 6.13 (s, 2H, NH₂), 6.87 (s, 1H), 7.52 (m, 1H), 7.75 (m, 1H), 8.05 (d, 1H), 8.67 (m, 2H), 9.05 (d, 1H). IR (KBr, cm⁻¹): 3414 (asymm stretch, NH₂), 3336 (symm stretch, NH₂), 1638 (bending, NH₂). MS (CI): *m/z* = 196 (MH⁺). Anal. Calcd for C₁₂H₉N₃: C, 73.82; H, 4.64; N, 21.52. Found C, 73.58; H, 4.72; N, 21.54.

*Synthesis of Resin-Bound 1,10-Phenanthroline.*⁴³ A 1 g sample of Merrifield resin (~0.7 mmol of Cl/g of resin) was swelled in anhydrous dioxane for 1 day. After this period a suspension of pure 5-amino-1,10-phenanthroline (220 mg, 1.13 mmol) in dioxane (60 mL) was added with a syringe. After this addition, the mixture was gently stirred and heated to reflux. 5-Amino-1,10-phenanthroline was dissolved in hot dioxane. Triethylamine (0.16 mL, 1.13 mmol) was added after 1 h to the refluxing solution. After 1 day, an additional amount of 0.07 mL of triethylamine (0.5 mmol) was added to the solution. The solution was further refluxed for 40 h. Finally the reaction mixture was filtered. The resin was washed with several portions of absolute ethanol and hot dioxane until the filtrate became colorless. The light brown resin was stirred in dioxane overnight, boiled for 10 min, and then filtered. The light brown product was dried under vacuum. The characterization of the functionalized resin is discussed further in the text.

Synthesis of the Lanthanide(III) Complexes [Ln(tta)₃(H₂O)₂]. [Ln(tta)₃(H₂O)₂] complexes were prepared for Ln = Nd, Sm, Eu, Gd, Tb, Er, and Yb, according to the procedure described by Melby

- (29) Streck, W.; Legendziewicz, J.; Lukowiak, E.; Maruszewski, K.; Sokolnicki, J.; Boiko, A. A.; Borzechowska, M. *Spectrochim. Acta, A* **1998**, *54*, 2215.
(30) Wang, Q. M.; Yan, B. *J. Mater. Chem.* **2004**, *14*, 2450.
(31) Kawa, M.; Frechet, J. M. J. *Chem. Mater.* **1998**, *10*, 286.
(32) Li, H. R.; Lin, J.; Zhang, H. J.; Li, H. C.; Fu, L. S.; Meng, Q. G. *Chem. Commun.* **2001**, *13*, 1212.
(33) Franville, A. C.; Mahiou, R.; Zambon, D.; Cousseins, J. C. *Solid State Sci.* **2001**, *3*, 211.
(34) Petrochenkova, N. V.; Mirochnik, A. G.; Karasev, V. E. *Sov. J. Coord. Chem.* **1991**, *17*, 829; *Koord. Khim.* **1991**, *17*, 1567.
(35) Mirochnik, A. G.; Petrochenkova, N. V.; Karasev, V. E. *Russ. Chem. Bull.* **1997**, *46*, 2135.
(36) Mirochnik, A. G.; Petrochenkova, N. V.; Karasev, V. E. *Polym. Sci., B* **2000**, *42*, 271.
(37) Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149.
(38) Crowley, J. I.; Rapoport, H. *Acc. Chem. Res.* **1976**, *9*, 135.
(39) Leznoff, C. C. *Acc. Chem. Res.* **1978**, *11*, 327.
(40) Dörwald, F. Z. *Organic Synthesis on Solid Phase*; VCH-Wiley: Weinheim, Germany, 2000.
(41) Booth, R. J.; Hodges, J. C. *J. Am. Chem. Soc.* **1997**, *119*, 4882.

- (42) Lecompte, J. P.; Kirsch-De Mesmaeker, A.; Demeunynck, M.; Lhomme, J. J. *Chem. Soc., Faraday Trans.* **1993**, *89*, 3261.
(43) Wang, R. M.; Li, S. B.; Wang, Y. P.; Chang, Y.; He, Y. F.; Lei, Z.-Q.; Feng, H. X. *React. Funct. Polym.* **1999**, *42*, 87.

Table 1. Elemental Analysis of the $[\text{Ln}(\text{tta})_3(\text{phen})]$ Complexes ($\text{Ln} = \text{Nd, Sm, Eu, Gd, Tb, Er, Yb}$)

| compound | empirical formula | calcd (%) | | found (%) | |
|---------------------------------------------------|---------------------------------------------------------------------|-----------|------|-----------|------|
| | | C | H | C | H |
| $[\text{Nd}(\text{tta})_3(\text{H}_2\text{O})_2]$ | $\text{C}_{24}\text{H}_{16}\text{F}_9\text{O}_8\text{S}_3\text{Nd}$ | 34.16 | 1.91 | 33.96 | 2.13 |
| $[\text{Sm}(\text{tta})_3(\text{H}_2\text{O})_2]$ | $\text{C}_{24}\text{H}_{16}\text{F}_9\text{O}_8\text{S}_3\text{Sm}$ | 33.91 | 1.89 | 34.15 | 2.31 |
| $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ | $\text{C}_{24}\text{H}_{16}\text{F}_9\text{O}_8\text{S}_3\text{Eu}$ | 33.85 | 1.89 | 33.90 | 2.25 |
| $[\text{Gd}(\text{tta})_3(\text{H}_2\text{O})_2]$ | $\text{C}_{24}\text{H}_{16}\text{F}_9\text{O}_8\text{S}_3\text{Gd}$ | 33.64 | 1.88 | 33.64 | 2.27 |
| $[\text{Tb}(\text{tta})_3(\text{H}_2\text{O})_2]$ | $\text{C}_{24}\text{H}_{16}\text{F}_9\text{O}_8\text{S}_3\text{Tb}$ | 33.57 | 1.87 | 33.77 | 2.12 |
| $[\text{Er}(\text{tta})_3(\text{H}_2\text{O})_2]$ | $\text{C}_{24}\text{H}_{16}\text{F}_9\text{O}_8\text{S}_3\text{Er}$ | 33.25 | 1.86 | 32.95 | 1.77 |
| $[\text{Yb}(\text{tta})_3(\text{H}_2\text{O})_2]$ | $\text{C}_{24}\text{H}_{16}\text{F}_9\text{O}_8\text{S}_3\text{Yb}$ | 33.03 | 1.84 | 32.95 | 2.12 |

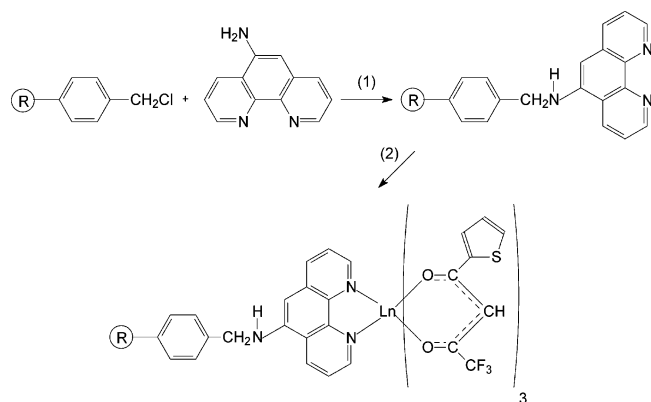
et al.² 2-Thenoyltrifluoroacetone (1.33 g, 6 mmol) was dissolved in 30 mL of ethanol. NaOH (1 N, 6 mL) and a solution of $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ (2 mmol) in 10 mL of water were successively added to the solution of 2-thenoyltrifluoroacetone. Water (200 mL) was added, and the mixture was heated to 60 °C. The complexes precipitated during cooling to room temperature. The precipitate was filtered off, washed with water, and dried in vacuo. All complexes were found to be dihydrates. The purity of the compounds was verified by CHN elemental analysis (Table 1).

Synthesis of the Resin-Bound $[\text{Ln}(\text{tta})_3(\text{phen})]$ Complexes. A batch of 100 mg of the 1,10-phenanthroline-functionalized Merrifield resin (maximum loading 0.07 mmol of 1,10-phenanthroline) was stirred with 100 mg of the $[\text{Ln}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex in ethanol while the solution was heated at reflux. After 24 h, the resin was filtered, and the excess of unbound complex was washed away with ethanol and chloroform. The dried resins thus obtained were pale brown.

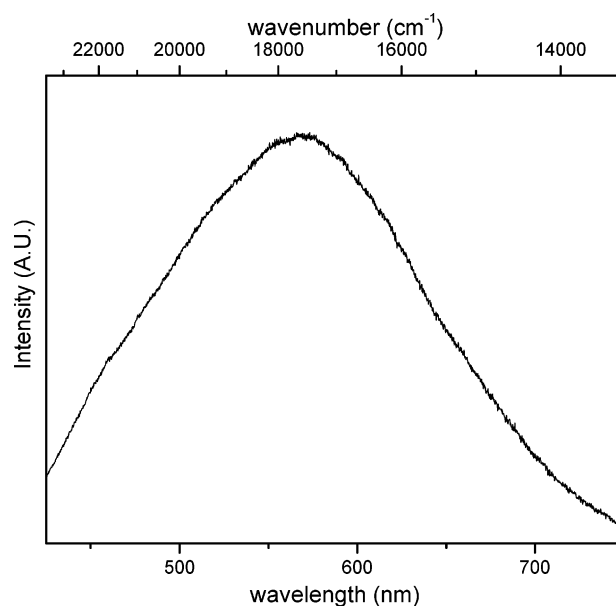
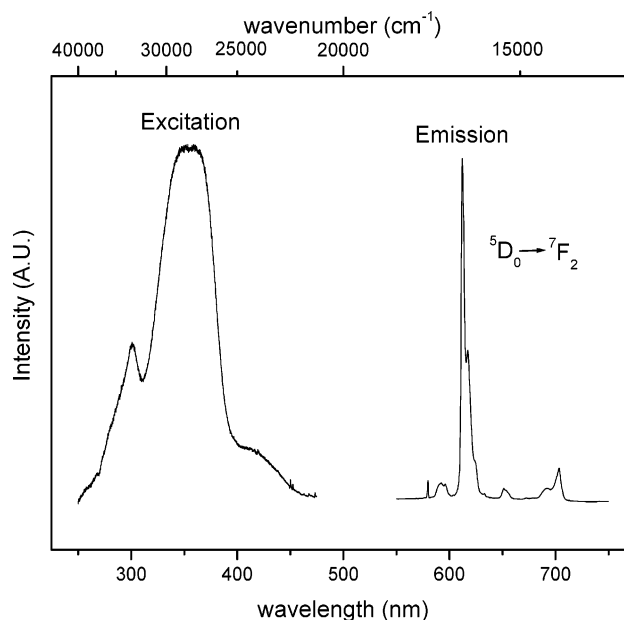
Results and Discussion

By nucleophilic displacement of the chlorine, we succeeded to couple 5-amino-1,10-phenanthroline on the cross-linked chloromethylated polystyrene (Merrifield resin) and to form complexes with $[\text{Ln}(\text{tta})_3(\text{H}_2\text{O})_2]$ ($\text{Ln} = \text{Nd, Sm, Eu, Gd, Tb, Er, Yb}$). The synthesis of this material is outlined in Scheme 1.

The functionalized Merrifield has only very few 1,10-phenanthroline groups attached, for different reasons. First, we use a resin with only 0.7 mmol of Cl/g. Second, the yield of reaction between the Merrifield polymer and the 5-amino-1,10-phenanthroline is rather low because of the low reactivity of the aromatic amine. By gravimetric analysis, it was determined that 7.3 mg of $[\text{Er}(\text{tta})_3(\text{H}_2\text{O})_2]$ was coupled to

Scheme 1. Synthesis of the Phenanthroline-Functionalized and Luminescent Merrifield Resin^a

^a Reagents and experimental conditions: (1) dioxane, triethylamine, 115 °C; (2) ethanol, $[\text{Ln}(\text{tta})_3(\text{H}_2\text{O})_2]$ ($\text{Ln} = \text{Nd, Sm, Eu, Gd, Tb, Er, Yb}$), 85 °C, 24 h.

**Figure 1.** Photoluminescence spectrum of the Merrifield-phen resin at room temperature. The excitation wavelength was 349 nm.**Figure 2.** Excitation and photoluminescence spectra of the $[\text{Eu}(\text{tta})_3(\text{phen})]$ -functionalized Merrifield resin at room temperature. The excitation spectrum was monitored at 612 nm. The excitation wavelength in the photoluminescence spectrum was 349 nm. All the transitions in the photoluminescence spectrum start from the $^5\text{D}_0$ state and end at the $^7\text{F}_J$ levels ($J = 0-4$ for this spectrum).

100 mg of the 1,10-phenanthroline-functionalized Merrifield polymer. This corresponds to 0.084 mmol of $[\text{Ln}(\text{tta})_3(\text{H}_2\text{O})_2]$ for 1 g of the substituted resin. The yield of the reaction between 5-amino-1,10-phenanthroline and the Merrifield resin (0.7 mmol of Cl/g) was calculated to be 12%. This corresponds with earlier published results, where a yield of 11% was obtained for the reaction between 5-amino-1,10-phenanthroline and a Merrifield polymer with a higher loading of 4.75 mmol of Cl/g.⁴³ This partial functionalization is no problem, since we only need a very low concentration of the complex in the polymer to have a good luminescence. In addition, problems with concentration quenching will arise

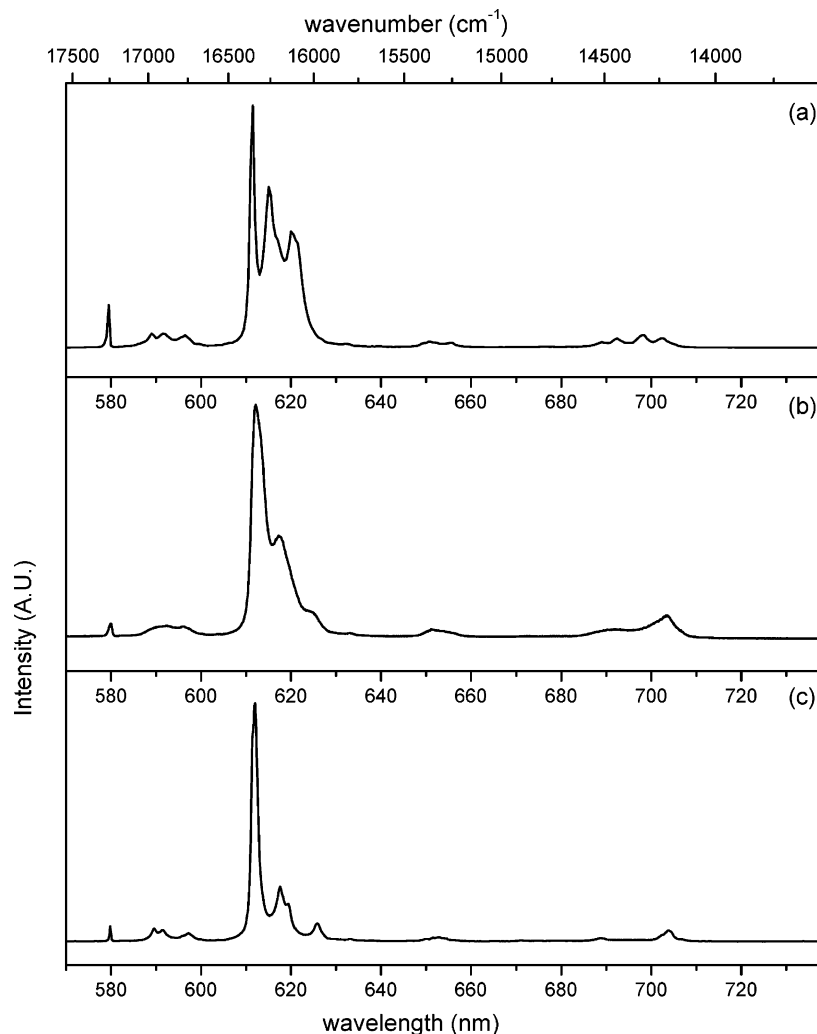


Figure 3. Photoluminescence spectrum of (a) the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex, (b) the $[\text{Eu}(\text{tta})_3(\text{phen})]$ -functionalized Merrifield resin, and (c) the $[\text{Eu}(\text{tta})_3(\text{phen})]$ complex at room temperature. The excitation wavelength was 349 nm. All the transitions start from the $^5\text{D}_0$ state and end at the $^7\text{F}_J$ levels ($J = 0-4$ for this spectrum).

when the concentration of the complex on the polymer is too high. So this material is optimal for our purpose.

The amount of 1,10-phenanthroline groups on the polymer was too low to detect the N–H bond in an FTIR spectrum or to determine the amount of nitrogen by CHN analysis. Nevertheless, we succeeded to show the presence of chemically bound 1,10-phenanthroline on the resin by indirect methods. After coupling of the 1,10-phenanthroline groups on the resin, the functionalized resin was checked for residues of 5-amino-1,10-phenanthroline that did not chemically bind to the resin. Therefore, the last portion of ethanol that was used to wash the resin was evaporated, and the residue was checked by ^1H NMR. No peaks of 5-amino-1,10-phenanthroline could be detected in this way. Next, a more sensitive method was used, namely, measurement of the mass spectrum of the Merrifield–1,10-phenanthroline resin. The resin itself does not dissolve in the solvent, but residues of 5-amino-1,10-phenanthroline do. Again no signal of 5-amino-1,10-phenanthroline ($m/z = 196$ (MH^+)) was detected.

After it was shown that no uncoupled 5-amino-1,10-phenanthroline was present on the resin, the presence of coupled 1,10-phenanthroline could be proved in several ways. First, the presence of the 1,10-phenanthroline on the resin was demonstrated by the characteristic luminescence of the Merri-

field–phenanthroline resin itself. The broad peak in the spectrum (Figure 1) has its maximum value around 570 nm. Second, a reference sample of unsubstituted Merrifield resin was treated in the same way as the substituted one. Both samples were stirred in refluxing ethanol with the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex in an effort to bind the complex to the resin. After filtration, both products were washed with ethanol and chloroform. When the unsubstituted Merrifield resin was analyzed, no europium(III)-centered luminescence could be observed. In contrast, the Merrifield resin with the bound 1,10-phenanthroline showed a red photoluminescence upon irradiation with ultraviolet light. The excitation and luminescence spectra of the europium sample are shown in Figure 2.

The excitation spectrum of the europium(III)-containing resin was monitored at 612 nm. No f–f transitions could be observed in the excitation spectrum since these are too weak. The observed transitions are due to light absorption by the β -diketonate and the 1,10-phenanthroline ligands. The luminescence spectra were measured with 349 nm as the excitation wavelength. The narrow peaks observed in the luminescence spectrum are transitions from the $^5\text{D}_0$ excited state to the different J levels of the ground term ^7F ($^7\text{F}_J$, $J = 0-6$). The $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition (580 nm) consists of a single peak only (at 77 K), which indicates that all the Eu^{3+} ions occupy a

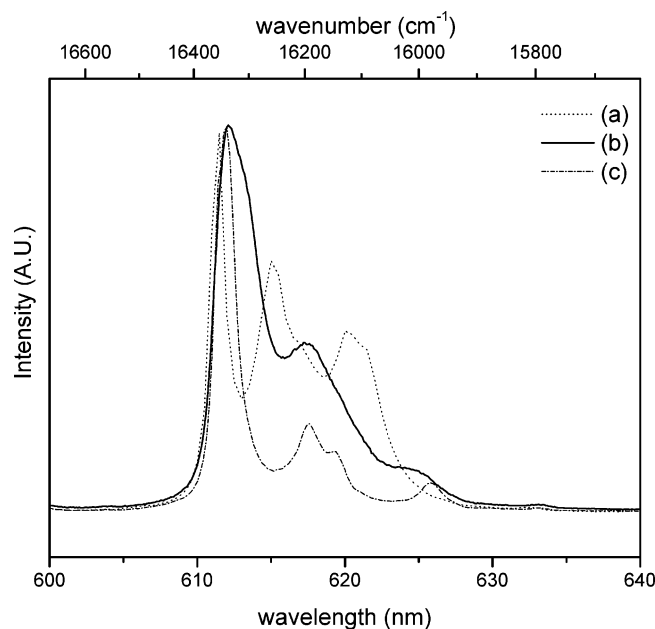


Figure 4. Photoluminescence spectrum of the $^5D_0 \rightarrow ^7F_2$ transition of (a) $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$, (b) the $[\text{Eu}(\text{tta})_3(\text{phen})]$ -functionalized Merrifield resin, and (c) $[\text{Eu}(\text{tta})_3(\text{phen})]$ at room temperature. The excitation wavelength was 349 nm.

site of the same symmetry and experience the same crystal-field perturbation. The fact that only the functionalized resin shows luminescence indicates that the β -diketonate complex must be bound to the 1,10-phenanthroline to be held on the resin.

Moreover, the formation of the $[\text{Eu}(\text{tta})_3(\text{phen})]$ complex bound to the resin was evidenced by analysis of the high-resolution luminescence spectra, in which crystal-field fine structure could be observed. The $^5D_0 \rightarrow ^7F_2$ transition is the most intense induced electric dipole transition in the luminescence spectrum, and the peak positions of this transition are sensitive to the environment of the europium ion. When this spectrum was compared with the spectra of the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ and $[\text{Eu}(\text{tta})_3(\text{phen})]$ complexes (diluted in KBr pellets), it was evident that the spectrum of the complex bound to the Merrifield resin is very comparable to that of the pure $[\text{Eu}(\text{tta})_3(\text{phen})]$ complex. Not only are the peak positions and fine structure for the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex different (Figures 3 and 4), but also the radiative lifetime of Eu^{3+} in $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ (190 μs) is much shorter than that of the europium complex immobilized on the Merrifield resin (500 μs). All these experimental data support the hypothesis that $[\text{Eu}(\text{tta})_3(\text{phen})]$ complexes are covalently linked to the Merrifield resin. The luminescence quantum yield of the europium(III) complex on the polymer matrix was determined by an integrating sphere at room temperature and was found to be $22 \pm 5\%$.

The europium(III) ion can be replaced in this system by other lanthanide ions that show luminescence in the visible ($\text{Ln} = \text{Sm}, \text{Tb}$) or near-infrared ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Er}, \text{Yb}$) regions. The signal of the europium complex is intense because the organic ligands act as an efficient antenna for this lanthanide ion. The ligands absorb the incident light and transfer it to the europium(III) ion. The energy transfer from the organic ligands to the lanthanide ion is less efficient for the terbium(III) and samarium(III) ions. This is evident from

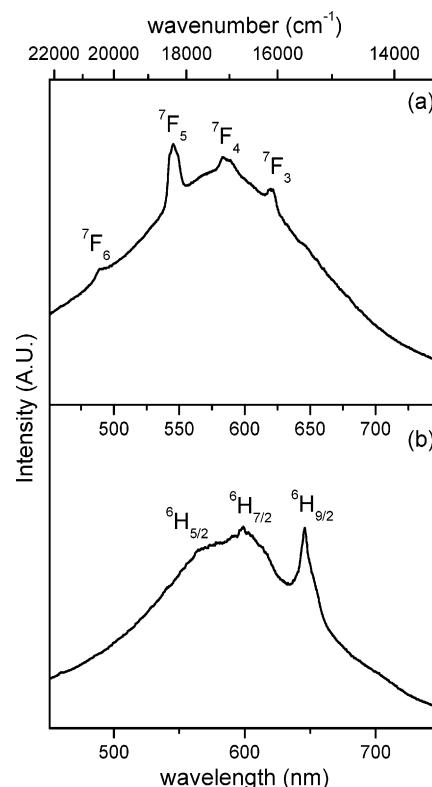


Figure 5. Photoluminescence spectrum of the (a) $[\text{Tb}(\text{tta})_3(\text{phen})]$ - and (b) $[\text{Sm}(\text{tta})_3(\text{phen})]$ -functionalized Merrifield resin. Transitions of terbium start from the 5D_4 level, and those of samarium from the $^4G_{5/2}$ level. The excitation wavelength was 349 nm.

less intense signals of f–f transitions in the luminescence spectra (Figure 5) and from the presence of a broad emission band around 580 nm. The luminescence peaks of these two lanthanide(III) ions are superimposed on this underlying band, which originates from emission of the aromatic groups of the resin.

We measured the luminescence behavior of the resin and ligands by measuring the emission spectra of the gadolinium(III) complex. The excited $4f^7$ levels of Gd^{3+} are at much higher energies than that of the triplet states of the ligands and the resin. Therefore, the ligand-to-metal energy-transfer process cannot take place. The phosphorescence of the ligand triplet level and the resin could be determined by measuring the photoluminescence spectra at low temperature (77 K). The intensity maximum of the phosphorescence band was located at 580 nm, and this corresponds to the underlying band in the spectra of the terbium(III) and samarium(III) complexes. Probably this emission takes place from the Merrifield resin with the bound 1,10-phenanthroline, rather than the 2-thenoyltrifluoroacetate ligands, since the triplet level of the β -diketonate ligand is at 490 nm ($20\,400\text{ cm}^{-1}$).⁴⁴

We also prepared resin beads that contain near-infrared-emitting lanthanide ions ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Er}, \text{Yb}$). In the near-infrared region, there is no interference from the emission of the resin matrix or the ligands. This makes the material useful as a near-infrared emitter. The luminescence spectra of the different near-infrared-emitting lanthanide complexes on the Merrifield resin are shown in Figures 6–9. Ytter-

(44) Zhang, R. J.; Yang, K. Z.; Yu, A. C.; Zhao, X. S. *Thin Solid Films* **2000**, 363, 275.

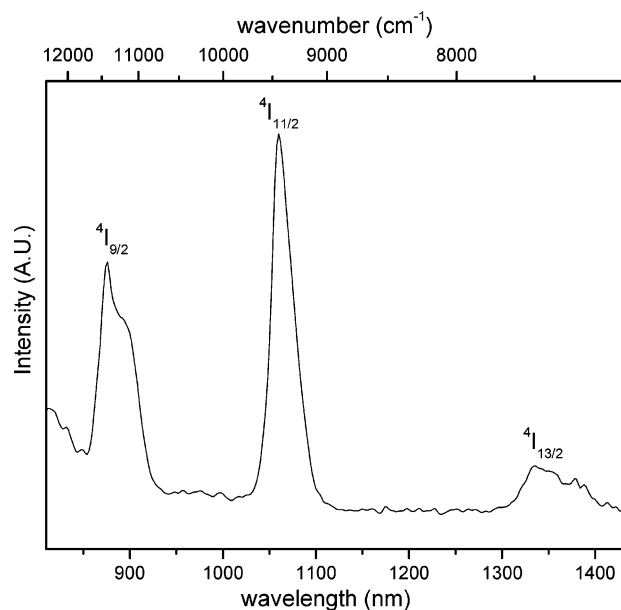


Figure 6. Photoluminescence spectrum of the [Nd(tta)₃(phen)]-functionalized Merrifield resin. Transitions start from the ⁴F_{3/2} level. The excitation wavelength was 349 nm.

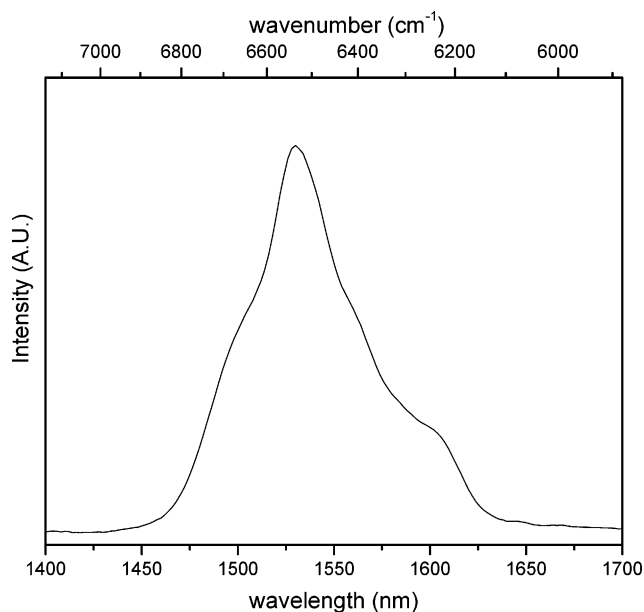


Figure 8. Photoluminescence spectrum of the ⁴I_{13/2} → ⁴I_{15/2} transition of the [Er(tta)₃(phen)]-functionalized Merrifield resin. The excitation wavelength was 349 nm.

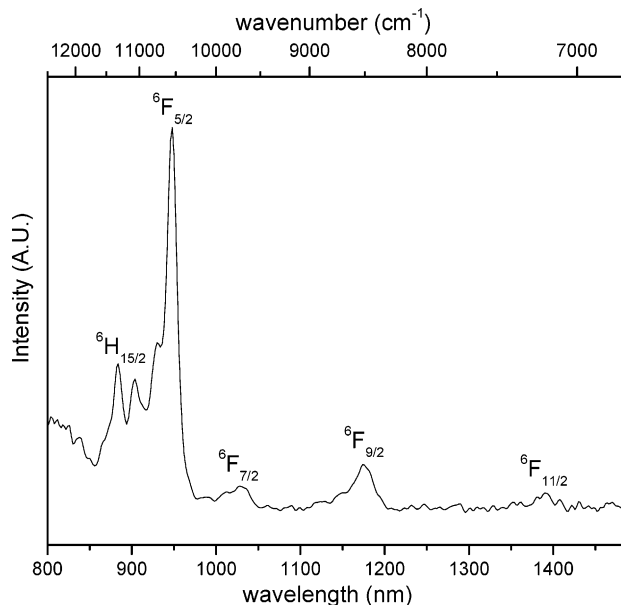


Figure 7. Photoluminescence spectrum of the [Sm(tta)₃(phen)]-functionalized Merrifield resin. Transitions start from the ⁴G_{5/2} level. The excitation wavelength was 349 nm.

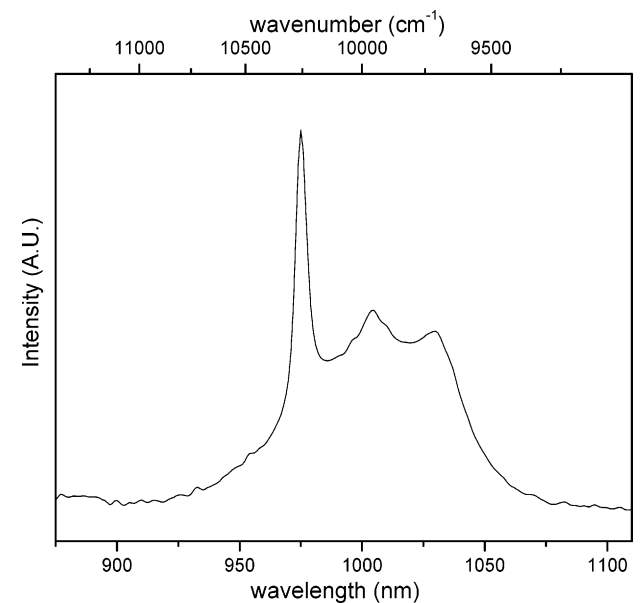


Figure 9. Photoluminescence spectrum of the ²F_{5/2} → ²F_{7/2} transition of the [Yb(tta)₃(phen)]-functionalized Merrifield resin. The excitation wavelength was 349 nm.

bium(III) is a special case of a near-infrared-emitting lanthanide ion, because an excitation mechanism different from the antenna effect is possible. The reason for proposing an alternative excitation mechanism is the fact that an intense luminescence can be observed for ytterbium(III) complexes, although there is a large energy gap between the ligand triplet level and the position of the excited-state ²F_{5/2} of ytterbium(III). Horrocks and co-workers considered an electron-transfer mechanism involving the Yb³⁺/Yb²⁺ redox couple.⁴⁵ Ytterbium(III) has a low reduction potential, −1.05 V versus the normal hydrogen electrode, compared to an average of −3 V for most other trivalent lanthanide ions. If there is

ligand-to-metal charge transfer (LMCT), the charge recombination (ligand*—Yb(II) to ligand—Yb(III)*) leaves ytterbium(III) in an excited state. An alternative approach was presented by Reinhard and Güdel.⁴⁶ These authors do not consider the energy transfer from the ligand to the excited state of the lanthanide ion, but the lanthanide ion with its ligands is described as one chromophore, and the emitting level is populated by nonradiative relaxation processes from highly excited states of the chromophore.

The radiative lifetimes of the different lanthanide complexes bound on the Merrifield resin were measured, and the values are given in Table 2. For the determination of the radiative lifetimes, the most intense transition in the spectral

(45) Horrocks, W.; Bolender, J.; Smith, W.; Supkowsky, R. *J. Am. Chem. Soc.* **1997**, *119*, 5972.

(46) Reinhard, C.; Güdel, H. U. *Inorg. Chem.* **2002**, *41*, 1048.

Table 2. Luminescence Decay Times (τ) of Selected Transitions of the Different [Ln(tta)₃(phen)] Complexes (Ln = Nd, Sm, Eu, Tb, Er, Yb) Attached to the Merrifield Resin^a

| Ln | transition | wavelength (nm) | τ (μ s) |
|----|-------------------------------------|-----------------|-------------------|
| Nd | $^4F_{3/2} \rightarrow ^4I_{11/2}$ | 1059 | 0.4 |
| Sm | $^4G_{5/2} \rightarrow ^6H_{9/2}$ | 645 | 75 |
| Sm | $^4G_{5/2} \rightarrow ^6F_{5/2}$ | 947 | 65 |
| Eu | $^5D_0 \rightarrow ^7F_2$ | 612 | 500 |
| Tb | $^5D_4 \rightarrow ^7F_5$ | 545 | 800 |
| Er | $^4I_{13/2} \rightarrow ^4I_{15/2}$ | 1530 | 1.4 |
| Yb | $^2F_{5/2} \rightarrow ^2F_{7/2}$ | 975 | 10 |

^a All the radiative lifetimes were measured at room temperature.

region of interest was selected. The luminescence decay curves were all single exponential.

Conclusions

In conclusion, new luminescent materials were prepared by coupling lanthanide β -diketonate complexes (Ln = Nd, Sm, Eu, Gd, Tb, Er, Yb) to a Merrifield resin through a functionalized 1,10-phenanthroline ligand. The resulting materials show luminescence in the visible and near-infrared

regions. It should be emphasized that the lanthanide ion should be well shielded from its environment by organic ligands to obtain a good luminescent material. In this case this is done by β -diketonates and the 1,10-phenanthroline ligand. Moreover, these organic ligands can act as an antenna to absorb the incident light and to transfer it to the lanthanide ion. The modified Merrifield resin is an interesting matrix for photophysical applications.

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