

Surface Modification of Luminescent Lanthanide Phosphate Nanorods with Cationic “Quat-primer” Polymers

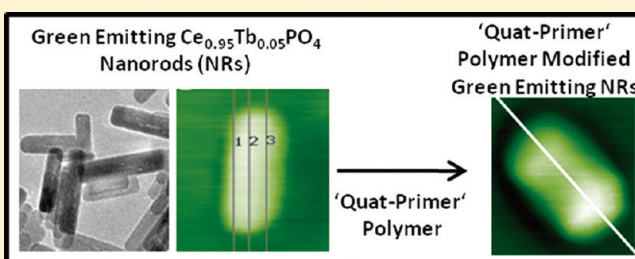
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 Supporting Information

ABSTRACT: “Quat-primer” polymers bearing cationic groups were investigated as a surface modifier for Tb-doped cerium phosphate green-emitting fluorescent nanorods (NRs). The NRs were synthesized by a microwave process without using any complex agents or ligands and were characterized with different analytical tools such as X-ray diffraction, transmission electron microscopy, and fluorescence spectroscopy. Poly(ethyleneimine) partially quarternized with glycidyltrimethylammonium chloride was synthesized separately and characterized in detail. ¹H and ¹³C NMR spectroscopic studies revealed that the quaternary ammonium group was covalently attached to the polymer. UV–vis spectroscopy was used to examine the stability of the colloidal dispersions of the bare NRs as well as the modified NRs. ζ potential, thermogravimetric analysis, and atomic force microscopy studies were carried out to confirm that the positively charged Quat-primer polymer is adsorbed on the negatively charged surface of the NRs, which results in high dispersion stability. Emission spectra of the modified NRs indicated that there was no interference of the Quat-primer polymer with the fluorescence behavior.



INTRODUCTION

Reliable procedures for the surface functionalization of nanoparticles (NPs) present a major prerequisite for their biological application.^{1,2} The attachment of polymers to the particle surface is commonly proposed for this purpose, and polymers with various functional groups have been employed.^{3–6} Among them, polymer-based polyelectrolytes have gained attraction since they impart additional charges on the nanoparticle surface, which can provide dispersion stability in aqueous media as well as a base for biological applications such as immobilizing antibodies or protein biomarkers.^{7–13} Recently, Rege and co-workers showed that polyelectrolytes enhance the short- and long-term stability of gold nanorods dispersed in biologically relevant media.¹⁴ More recently, a direct synthesis of water-soluble nanorods of CdS was demonstrated in the presence of poly(ethyleneimine) (PEI), and it was claimed not only that the amino groups bind to the nanorods, but also that the uncoordinated amino groups can be further modified, such as by coupling to bioactive molecules.¹⁵ Earlier, Quat-primer polymers bearing quaternary ammonium and cyclic carbonate groups covalently linked to the macromolecule were used for carbon fiber reinforcement.¹⁶

In the present study, Quat-primer polymers bearing cationic groups were investigated as surface modifiers for lanthanide phosphate nanorods (LnPO₄ NRs), especially for nanorods of Tb-doped CePO₄, which displays green luminescence upon UV

excitation. The properties of LnPO₄ have been investigated with respect to solid-state proton conductivity,^{17,18} immobilization of radioactive isotopes,¹⁹ and magnetic resonance imaging (MRI).²⁰ Luminescent materials based on lanthanide-doped LnPO₄ nanocrystals are of particular interest since they show high resistance to photobleaching, low toxicity, a high working temperature, narrow emission lines, composition tunable emission from visible to infrared wavelengths, high levels of brightness, and a long emission lifetime. As a consequence, this class of luminescent materials has been proposed for biotechnological and biomedical applications such as biological labels and sensors.^{21–23} Recently, Wiemhoefer and co-workers prepared stable aqueous dispersions of lanthanum phosphate NPs by surface modification of the particles with cyclic phosphazene.²⁴

In the microwave-assisted synthesis of lanthanide phosphate nanoparticles, usually different agents or ionic liquids are used.^{25–27} In the work presented here we prepared well-shaped and almost monodisperse CePO₄:Tb nanorods in a water–ethanol mixture by a simple microwave process in the absence of any complex agent. After the synthesis of the

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green-emitting $\text{CePO}_4\text{:Tb}$ nanorods, PEI partially quarternized with glycidyltrimethylammonium chloride was examined as a surface modifier. For these experiments, PEI polymers having different degrees of quarternization and molecular weight (Quat-primer polymers) were synthesized separately and characterized in depth using different tools. Since the ability of modifiers to stabilize colloidal particles has proved to depend strongly on the specific interactions between the polymer and the particle surface, we first conducted a series of experiments to study the solubility of these Quat-primer polymers in different solvents and performed a few dispersion experiments to identify their most suitable composition. Various analytical studies clearly indicate that positively charged Quat-primer polymers are physically adsorbed on the negatively charged surface of the nanorods. Our detailed literature research reveals that there is no such study reported yet and such organic–inorganic nanocomposites of Quat-primer polymer– LnPO_4 may offer a versatile path toward luminescent functional materials as well as in biological application.

EXPERIMENTAL SECTION

Synthesis of Nanorods of Terbium-Doped Cerium Phosphate. *Materials.* Respective lanthanide chlorides were purchased from Treibacher (99.9%), ethanol was purchased from Stockmeier Chemie GmbH (technical quality), and orthophosphoric acid (H_3PO_4) was purchased from Fluka (99%).

Synthesis. Hexagonal-phase terbium-doped cerium phosphate ($\text{Ce}_{0.95}\text{Tb}_{0.05}\text{PO}_4$) nanorods were prepared by a simple microwave process. For a typical synthesis of $\text{Ce}_{0.95}\text{Tb}_{0.05}\text{PO}_4$, 10 mmol of lanthanide chlorides (1.765 g of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and 0.09 g of $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$) was first dissolved in 20 mL of a 1:1 mixture of ethanol and doubly distilled water. The solution was transferred into a microwave vessel with a capacity of 80 mL, and 10 mmol (0.98 g) of H_3PO_4 dissolved in 20 mL of ethanol/water was added slowly with stirring. Stirring was continued for 5 min, and then the vessel was loaded into a microwave processor (CEM Corp.) and heated for 3 h at 120 °C at a pressure of 14 bar. After the reaction, the suspension obtained was cooled to room temperature by means of the internal cooling system of the microwave processor. The turbid solution was centrifuged, and the precipitate was washed with methanol three times and finally vacuum-dried at 60 °C. X-ray diffraction (XRD) patterns of powder samples were recorded with a PANalytical X'pert Pro system using $\text{Cu K}\alpha$ radiation. Luminescence spectra were measured with a Fluorolog 3 spectrometer (Jobin Yvon, Horiba). Each powder was added to a 1 mm quartz cuvette at a measured right angle using a solid-sample holder (model 1933, Horiba). Transmission electron microscopy (TEM) images were taken with a JEOL JEM 2100 transmission electron microscope using a LaB_6 cathode and an acceleration voltage of 200 kV.

By using an analogous procedure, nanorods of europium-doped lanthanum phosphate ($\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$) can be synthesized which have the same crystal phase and almost the same size as the $\text{Ce}_{0.95}\text{Tb}_{0.05}\text{PO}_4$ nanorods (corresponding XRD, TEM, and fluorescence data are presented in the Supporting Information, Data S1). For the study with Quat-primer polymers presented here, however, we used only the $\text{Ce}_{0.95}\text{Tb}_{0.05}\text{PO}_4$ nanorods since this material can be very efficiently excited via the allowed $4f-5d$ transition of Ce^{3+} .

The X-ray diffraction patterns of the samples were further analyzed by the Rietveld method using ICSD data sets for bismuth phosphate hydrate (hexagonal structure, space group $P3121$ (No. 152), ICSD 67986) and the FullProf program.^{28,29} In the analysis, bismuth was replaced by the lanthanides, the nanostructures were assumed to be strain-free, and the Thompson–Cox–Hasting function was used as the

profile function. The scale factor and the lattice parameters were refined first followed by background parameters and peak profiles. Subsequently, the parameters corresponding to the texture, size, and shape of the nanoparticles were refined. To account for the anisotropic width of the Bragg peaks, the structure model ISize Model-1 was used in the refinement procedure. In this model the particles are assumed to have a rod shape with the main axis of the rod given by a predefined $[hkl]$ direction. The length and width of the rod determine the average rod thickness in each $[hkl]$ direction. From these thickness values, the widths of the corresponding Bragg peaks are calculated by using a Scherrer-type formula. Thus, the diameter and length of the particles are directly obtained from the Rietveld data. Details can be found in the literature.^{28,29} In our case, the length of the rod-shaped particles corresponds to the dimension along the main axis in the $[003]$ direction and their diameter is given by the width in the $[300]$ direction.

Synthesis of Quarternized Polyethyleneimine (Quat-primer Polymer). *Materials.* The solvents acetone (Stockmeier Chemie GmbH, technical), dimethylformamide (Fluka, >98%), ethanol (AHK Alkoholhandel GmbH & Co. KG, drained 100% and denatured with 1% petroleum ether), ethyl acetate (Aldrich, puriss., $\geq 99.5\%$), methanol (Stockmeier Chemie GmbH, technical), 2-propanol (Sasol Germany GmbH, technical), tetrahydrofuran (Aldrich, $\geq 99.9\%$), and toluene (Fluka, $\geq 99.7\%$), the poly(ethyleneimine)s PEI-423 ($M_n = 423$ g/mol, Aldrich, oligomer mixture), PEI-1.2K ($M_n = 1200$ g/mol, Aldrich, 50 wt % aqueous solution), PEI-10K ($M_n = 10\,000$ g/mol, $M_w = 25\,000$ g/mol, branched, Aldrich), and PEI-60K ($M_n = 60\,000$ g/mol, $M_w = 750\,000$ g/mol, branched, Aldrich, 50 wt % aqueous solution), and glycidyltrimethylammonium chloride (Aldrich, 90% in water) were used as received. Deionized water was distilled twice prior to use. The buffer solutions buffer 1 (Merck, CertiPUR, pH 4.0, citric acid/ NaOH/HCl), buffer 2 (Merck, CertiPUR, pH 7.0, $\text{Na}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$), buffer 3 (Merck, CertiPUR, pH 9.0, $\text{H}_3\text{BO}_3/\text{KCl}/\text{NaOH}$), and buffer 4 (Merck, CertiPUR, pH 11.0, $\text{H}_3\text{BO}_3/\text{KCl}/\text{NaOH}$) were used as received.

Synthesis. Synthesis of a typical Quat-primer polymer, PEI_{10K}^{30Q}(9), was performed by slow addition of 30 mL of a solution of 2.53 g (16.7 mmol) of glycidyltrimethylammonium chloride in water to 20 mL of a well-stirred aqueous solution containing 2.00 g (46.4 mmol of ethyleneimine units) of PEI-10K. This solution was stirred for 24 h at 25 °C. Then the solvent was removed under reduced pressure at 55 °C. The isolated polymer was dried in vacuum at 55 °C for three days, yielding a highly viscous slightly yellow oil. Yield: 4.47 g (98.7% of theoretical yield). ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded on a Bruker TopSpin spectrometer operated at 500 and 125 MHz, respectively. The chemical shifts are given in parts per million. FT-IR spectra were measured by means of a Bruker Vertex 70 spectrometer equipped with a Golden Gate diamond attenuated total reflection (ATR) unit. The samples were placed on the ATR unit and measured in reflection. Elemental analysis of carbon, hydrogen, and nitrogen contents was carried out on an Elementar vario MICRO cube instrument. Differential scanning calorimetry was performed with a Netzsch 204 F1 Phoenix thermal analyzer equipped with a T-sensor and Netzsch intracooler. The differential scanning calorimeter was calibrated against cyclohexane, tin, and indium standards. Samples of 5–15 mg were weighed in 25 μL aluminum pans and sealed. The thermogram was measured between –80 and +140 °C at a heating and cooling rate of 10 °C/min. Data evaluation was done by means of the Netzsch Proteus software, version 5.0. Ultrasound dispersion experiments were performed with a Branson Sonifier 250 equipped with an ultrasound horn probe (5 mm diameter, length 15.5 cm). Dispersion experiments were performed in a 20 mL rosette-shaped glass circulation vessel with 10 mL of the respective mixtures for 15 min at Sonifier output control level four and constant duty cycle. The solubility of Quat-primer polymers was tested by weighing 100 mg of a Quat-primer polymer in a glass vial, adding 10 mL of the respective solvent, closing the lid, and allowing the

Table 1. Reaction Mixture Composition, Reaction Conditions, and Yields in the Synthesis of Quat-primer Polymers 1–15

polymer no. (abbreviation)	m_{PEI} g/mol	$M_n(\text{PEI})$, g (mmol)	M_{epoxide} g (mmol)	solvent (vol, mL)	temp, ^a °C	R time, ^b h	yield, g (%)
1 (PEI _{0.423K} ^{05Q})	2.00 (46.4)	423	0.42 (3.1)	H ₂ O (50)	25	24	2.35 (97.1)
2 (PEI _{0.423K} ^{15Q})	4.00 (92.8)	423	2.53 (16.7)	H ₂ O (50)	25	24	6.38 (97.7)
3 (PEI _{0.423K} ^{30Q})	2.00 (46.4)	423	2.53 (16.7)	H ₂ O (50)	25	24	4.43 (97.8)
4 (PEI _{1.2K} ^{05Q})	2.00 (46.4)	1.200	0.42 (3.1)	H ₂ O (50)	25	24	2.46 (101.6)
5 (PEI _{1.2K} ^{15Q})	2.00 (46.4)	1.200	1.26 (8.3)	H ₂ O (50)	25	24	3.23 (99.0)
6 (PEI _{1.2K} ^{30Q})	2.00 (46.4)	1.200	2.53 (16.7)	H ₂ O (50)	25	24	4.38 (96.7)
7 (PEI _{10K} ^{05Q})	2.00 (46.4)	10.000	0.42 (3.1)	H ₂ O (50)	25	24	2.30 (95.0)
8 (PEI _{10K} ^{15Q})	4.00 (92.8)	10.000	2.53 (16.7)	H ₂ O (50)	25	24	6.15 (94.2)
9 (PEI _{10K} ^{30Q})	2.00 (46.4)	10.000	2.53 (16.7)	H ₂ O (50)	25	24	4.47 (98.7)
10 (PEI _{10K} ^{50Q})	2.00 (46.4)	10.000	4.21 (27.8)	H ₂ O (50)	25	24	5.67 (91.3)
11 (PEI _{10K} ^{75Q})	1.00 (23.2)	10.000	3.16 (20.8)	H ₂ O (50)	25	24	3.75 (90.1)
12 (PEI _{10K} ^{100Q})	1.00 (23.2)	10.000	4.21 (27.8)	H ₂ O (50)	25	24	4.69 (90.0)
13 (PEI _{60K} ^{05Q})	2.00 (46.4)	60.000	0.42 (3.1)	H ₂ O (50)	25	24	2.48 (102.4)
14 (PEI _{60K} ^{15Q})	4.00 (92.8)	60.000	2.53 (16.7)	H ₂ O (50)	25	24	6.31 (96.6)
15 (PEI _{60K} ^{30Q})	2.00 (46.4)	60.000	2.53 (16.7)	H ₂ O (50)	25	24	4.60 (101.6)

^a Reaction temperature. ^b Reaction time

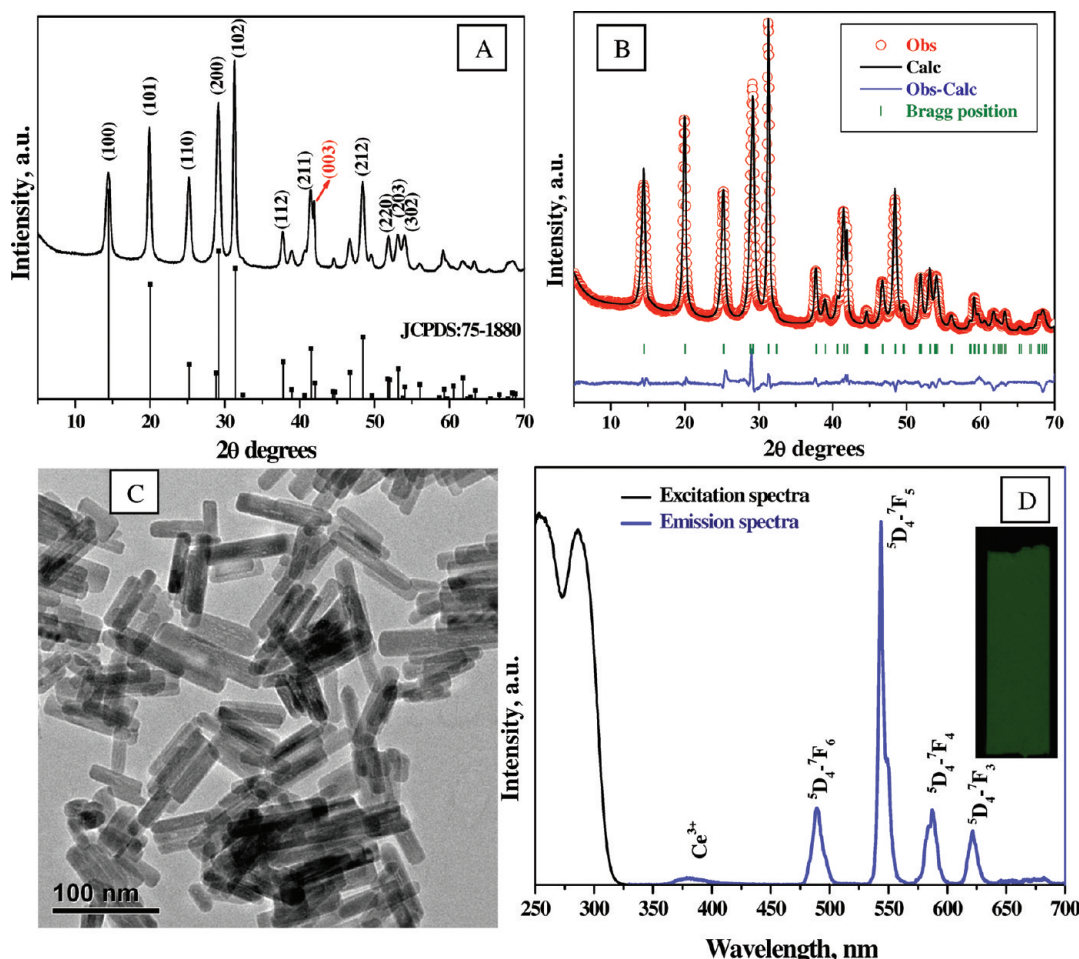


Figure 1. (A) XRD pattern of the NRs. (B) Reitveld refined XRD of (A). (C) TEM of NRs. (D) Excitation and emission spectra of the NRs (the inset photo shows the green luminescence from the sample recorded with a digital camera).

mixture to stand for 12 h at room temperature. The solubility was qualitatively judged by optical inspection, distinguishing (i) complete

dissolution, (ii) partial dissolution with swelling, (iii) swelling of the polymer, and (iv) no visible change.

The synthesis and characterization of Quat-primer polymers 1–8 and 10–15 were performed with the same procedures as described for compound 9 (PEI_{10K}^{30Q}). The composition of the reaction mixtures and reaction conditions used to obtain the polymers are summarized in Table 1, as are the yields. The IR, ¹H NMR, ¹³C NMR, and elemental analysis data of PEIs 1–15 are provided in the Supporting Information, Data S2–S16.

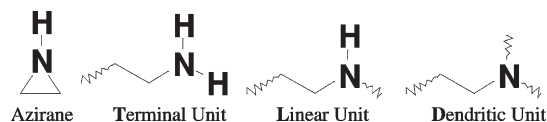
Preparation of Quat-primer Polymer Modified NRs. First, stock solutions containing 1 wt % polymer were prepared by dissolving each of the Quat-primer polymers in doubly distilled water. By combining an appropriate amount of nanorod powder, doubly distilled water, and one of the stock solutions, colloidal suspensions containing 0.1 g of nanorods and 0.1 g of Quat-primer polymers in 10 g of solution were prepared. Each suspension was ultrasonicated for 10 min and subsequently centrifuged at 13 000 rpm. The filtrate was decanted off, and the precipitate was dispersed again by ultrasonication in an equal amount of doubly distilled water. For comparison, colloids containing no polymers were also prepared analogously. The stability of the dispersions was analyzed by recording their apparent absorption (caused by the light scattering of the 50 nm particles) with a UV–vis (Cary 6000i dual-beam) spectrometer at different times after the preparation. The size and the ζ potential of the particles were measured with a Zetasizer (Nano ZS, Red Badge, model ZEN3600, Malvern Instruments). The atomic force microscopy (AFM) analysis (Bruker MultiMode with a Nanoscope V controller) was carried out in tapping mode. Samples were prepared by spin coating 100 μL of dispersion onto freshly cleaved mica surfaces. For thermogravimetric measurements the nanoparticle powders were dried at 60 °C and heated at a rate of 10 °C/min in a Jupiter STA thermobalance (Netzsch) using either an air or a helium atmosphere. For UV–vis, particle size, and ζ potential measurements, the colloids were further diluted by adding 9 g of water to 1 g of colloid, followed by ultrasonication.

RESULTS AND DISCUSSION

Green-Emitting Ce_{0.95}Tb_{0.05}PO₄ Nanorods. Figure 1A shows the XRD pattern of a Ce_{0.95}Tb_{0.05}PO₄ powder sample dried at 60 °C. The peaks are well-defined and indexed with those of hexagonal-phase CePO₄ (JCPDS no. 75-1880) as shown in the figure. Rietveld fits of the XRD data provided in Figure 1A are depicted in Figure 1B. The deviations between the measured and the calculated pattern are very small, as shown by the residuum (blue line) in the figure and the low values obtained for the R factors ($R_p \approx 2.9$ and $R_{wp} \approx 3.8$). Rietveld fits of high quality were achieved only, however, when a rod model for the particles was used and a preferred growth direction along the [003] axis was assumed. Using this method, the mean length (48.5 nm) of the particles in the direction of the [003] plane and the mean diameter (13.5 nm) in the [100] or [200] direction could be deduced from the refinement. The values are in accord with the mean sizes determined from TEM images of the nanorods as shown in Figure 1C.

Excitation ($\lambda_{em} = 543$ nm) and emission ($\lambda_{exc} = 282$ nm) spectra of the powder sample of Ce_{0.95}Tb_{0.05}PO₄ nanoparticles are presented in Figure 1D. The excitation spectrum consists of two broad peaks with maxima at 282 and 250 nm which are in accordance with the transitions from the ²F_{5/2} ground state of Ce³⁺ to the Ce³⁺ 5d state. After excitation of the Ce³⁺ ions into the 5d state, energy transfer from Ce³⁺ to Tb³⁺ leads to radiative transitions from the terbium ⁵D₄ to the terbium ⁷F_J level. The emission spectrum consist of four main peaks between 450 and 650 nm, which correspond to four ⁵D₄–⁷F_J transitions of Tb³⁺ (⁵D₄–⁷F₆, at ~489 nm; ⁵D₄–⁷F₅, at ~543 nm; ⁵D₄–⁷F₄, at

Scheme 1. Structural Formulas of Azirane (Ethyleneimine) as Well as the Terminal, Linear, and Dendritic Structure Units in Polyethyleimine



Scheme 2. Reaction of Glycidyltrimethylammonium Chloride with (a) Primary and Secondary and (b) Tertiary Amino Groups of Poly(ethyleneimine)

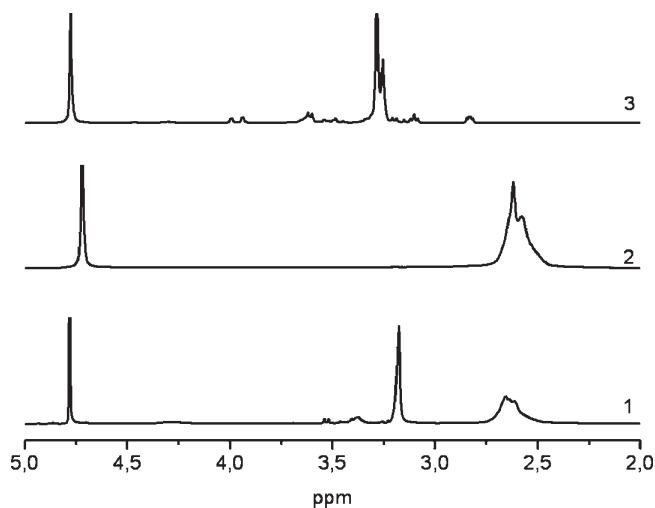
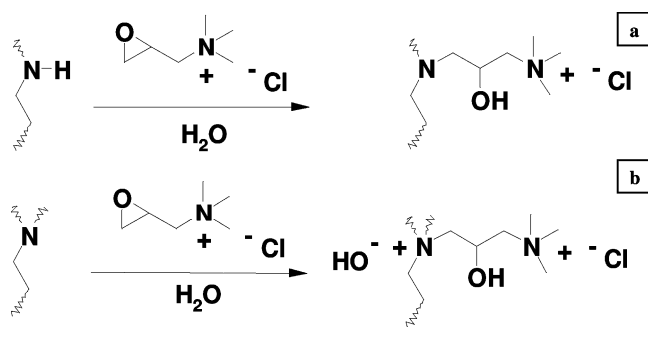


Figure 2. ¹H NMR spectra of (1) PEI_{10K}^{30Q}, (2) nonmodified PEI_{10K}, and (3) glycidyltrimethylammonium chloride (GlyQ).

~586 nm; ⁵D₄–⁷F₃, at ~621 nm). As a result of these transitions, the NR powder sample shows excellent green emission as is clearly visible in the photograph as shown in the inset of the emission spectra. The weak broad emission band between 300 and 400 nm is due to the d–f radiative transition from Ce³⁺.³⁰

Quat-primer Polymer. Technical PEI is prepared by cationic polymerization from azirane (ethyleneimine). Due to frequent transfer reactions to the growing polymer chain during polymerization, a hyperbranched polymer architecture is formed; hence, PEI can formally be described as a P[AB₂]-type polymer. The macromolecule contains three different structural units, namely, terminal units (T), dendritic units (D), and linear units (L).^{31,32}

The terminal units contain a primary amino group, the linear units a secondary amino group, and the dendritic units a tertiary nitrogen atom (Scheme 1).³³

In this study hyperbranched PEI was used to generate Quat-primer polymers by reacting commercial branched PEI with glycidyltrimethylammonium chloride (Quat-reagent) in aqueous solution (Scheme 2). The analysis of the contents of the structural units was not possible by means of ¹H NMR spectroscopy because the $-\text{CH}_2-$ signals of the PEI chains exhibited broad, strongly overlapping resonances between $\delta = 2.2$ ppm and $\delta = 2.8$ ppm³⁴ that did not allow methylene groups bearing different types of amine substituents to be distinguished. Quantitative analysis of the ratio of primary to secondary to tertiary amino moieties of the PEI educts has been determined by inverse gated ¹³C NMR. A T:L:D = 30:40:30 (mol %) ratio was measured. These values are close to the composition of branched PEI previously published in refs 33 and 35.

Figure 2 comparatively depicts the ¹H NMR spectra of nonmodified PEI and of glycidyltrimethylammonium chloride, as well as the spectrum of compound **9**, being the Quat-primer polymer with a nominal degree of quarternization of 30 mol % (PEI_{10K}^{30Q}). The signal of the trimethylammonium group appears at $\delta = 3.17$ ppm ($=A_{\text{NMe}_3}$ in Figure 2), while the peaks at $\delta = 2.20$ – 2.85 ppm have been assigned to the methylene protons of the polymeric backbone A_{NCH_2} .³⁵ The degree of quarternization Q was defined as the ratio of modified repeating units and the degree of polymerization. The parameter has been calculated by means of eq 1

$$Q = \frac{4 A_{\text{NMe}_3}}{9 A_{\text{NCH}_2}} \quad (1)$$

using the relative signal intensities of the ammonium methyl signals and the backbone signals. In eq 1, Q = degree of quarternization, A_{NMe_3} = integrated ¹H NMR signal intensity from 3.1 to 3.2 ppm, and A_{NCH_2} = integrated ¹H NMR signal intensity from 2.2 to 2.9 ppm. The results of the NMR analysis on compounds **1**–**15** are summarized in a table provided in the Supporting Information (Table S1), indicating that the Quat-reagent almost quantitatively reacted with the amino groups of the target poly(ethyleneimine) as indicated by the agreement between the reaction mixture stoichiometry and the NMR data. The high degree of conversion was confirmed by the ¹H NMR spectra due to the absence of the signal of the methylene group ($\delta = 3.85$ – 3.95 ppm) characteristic of the epoxide ring, the absence of the signal of the methylene group between the ammonium group and the epoxide ring ($\delta = 2.75$ – 2.80 ppm), and the absence of the proton signal of the epoxide methine group ($\delta = 2.95$ – 3.05 ppm); cf. Figure 2.

Attaching (2-hydroxypropyl)trimethylammonium chloride moieties to PEI considerably increases the molecular weight of the compounds. A modification of 30 mol % monomer units almost doubles the number average molecular weight of the respective polymer (Table S1, Supporting Information). Due to the strong hydrophilicity of the quarternized products, the compounds could not be obtained free of water after vacuum drying at 55 °C for 72 h. Drying at elevated temperatures resulted in insoluble, partially cross-linked products. For this reason the elemental composition of compounds **1**–**15** considerably deviates from the values calculated for compositions $[\text{C}_2\text{H}_5\text{N}]_{1-x}[\text{C}_8\text{H}_{19}\text{ClN}_2\text{O}]_x$ (cf. Experimental Section). However, since the water content does not affect the carbon:nitrogen

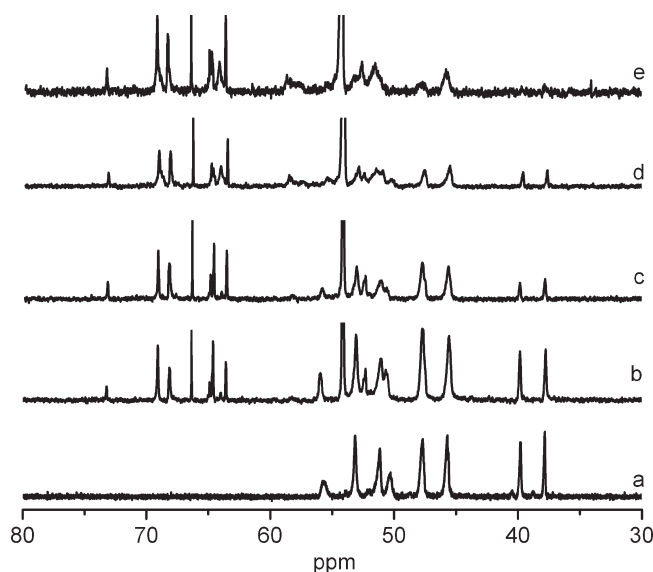


Figure 3. ¹³C NMR spectra of Quat-primer polymers with different degrees of functionalization: a, PEI_{10K}; b, PEI_{10K}^{15Q}; c, PEI_{10K}^{30Q}; d, PEI_{10K}^{50Q}; e, PEI_{10K}^{75Q}.

ratio of the compounds, the degree of quarternization can be obtained from the elemental analysis data by means of eq 2.

$$Q = \frac{A_{\text{N}p_{\text{C}}} - 2A_{\text{C}p_{\text{N}}}}{6A_{\text{C}p_{\text{N}}} - p_{\text{C}}A_{\text{N}}} \quad (2)$$

In eq 2, Q = degree of quarternization, p_{C} = weight percentage of carbon, p_{N} = weight percentage of nitrogen in the compound, A_{C} = atomic weight of carbon, and A_{N} = atomic weight of nitrogen. The obtained degree of quarternization well matched the results of the NMR analysis as shown in Table S1. Since thin layer chromatography and ¹H NMR ruled out the presence of impurities other than water above the 3–5% level, the agreement of NMR and elemental compositional analysis implies a high purity of the modified polymer.

Epoxides easily react with primary and secondary amino groups, while the attack on tertiary amino groups is slower. Methyl oxirane was found to react with ethylamine, diethylamine, and triethylamine in the molar ratio 1:1.75:0.32.³⁶ Assuming similar reactivities between the amino groups of PEI and the Quat-reagent, the resulting partially quarternized Quat-primer polymers should contain ~ 32 mol % Quat-groups attached to primary amines and ~ 57 mol % Quat-groups fixed at the secondary amino moieties, and about 10 mol % would form bicationic bisammonium units as indicated in Scheme 2b. Due to the strong overlap of the broad signals in the ¹H NMR spectra of the Quat-primer polymer, it was, however, not possible to derive these compositional data directly from the prepared macromolecular compounds.

The ¹³C NMR spectrum of branched PEI has already been reported to consist of eight signals arising from the structural units D-CH₂-CH₂-NH₂ (39.99 ppm), L-CH₂-CH₂-NH₂ (41.84 ppm), D-CH₂-CH₂-L (47.66 ppm), L-CH₂-CH₂-L (49.58 ppm), L-CH₂-CH₂-NH₂ (52.62 ppm), D-CH₂-CH₂-D (53.33 ppm), D-CH₂-CH₂-L (54.79 ppm), and D-CH₂-CH₂-NH₂ (57.79 ppm).^{33,37} The ¹³C NMR spectra of a nonmodified PEI (PEI_{10K}) and PEIs quarternized by different degrees are shown in Figure 3, depicting the spectral

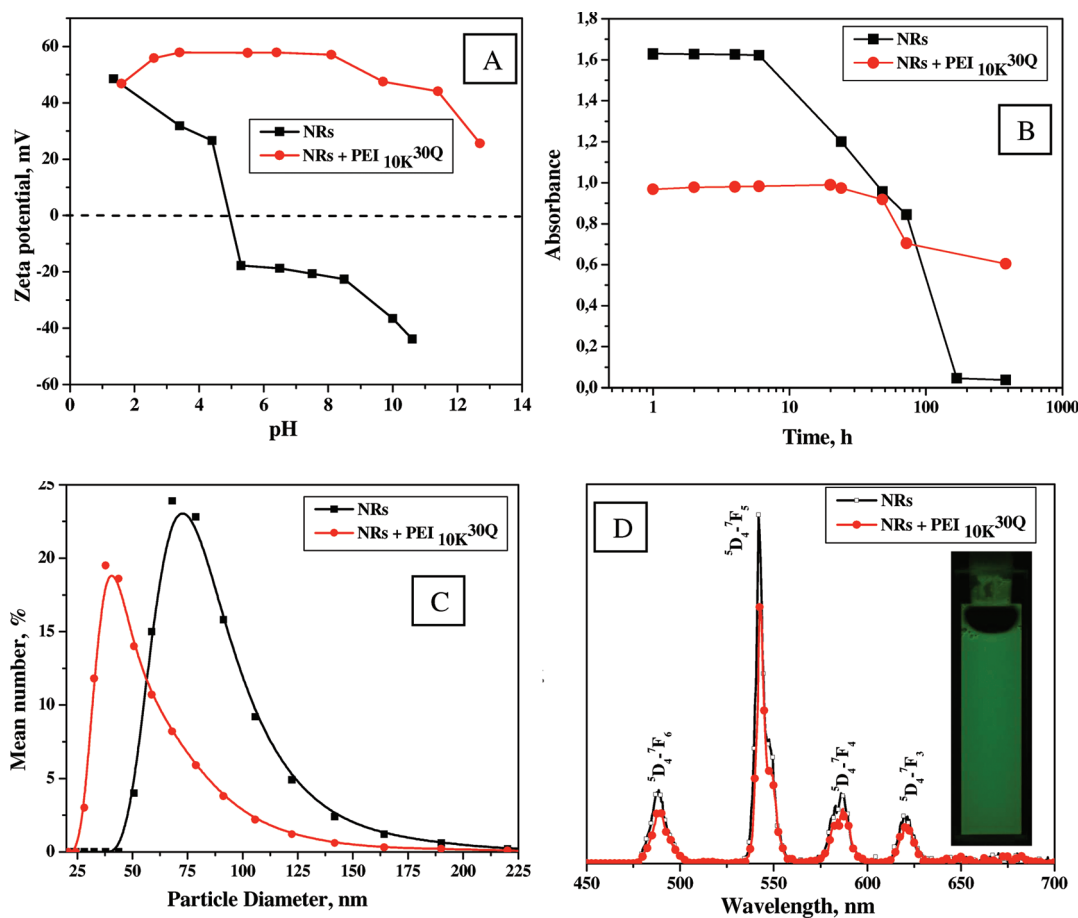


Figure 4. (A) ζ potential measurement. (B) Absorbance versus time at a wavelength of 700 nm. (C) Particle size distributions. (D) Emission spectra at an excitation wavelength of 282 nm. Black squares correspond to bare NRs and the red circles to modified NRs.

changes due to an increasing degree of quarternization. The spectra are dominated by the intensive signal at 54 ppm caused by the ammonium methyl groups. The intensities of signals arising from the carbon atoms connected either adjacently or to the vicinity of primary and secondary amines decrease with increasing degree of quarternization. The analysis of the ¹³C NMR spectra of compounds 1–15 confirmed the covalent connection of (2-hydroxypropyl)trimethylammonium units to the polymer; however, no considerable selectivity of the Quat-reagent toward primary or secondary amino groups was observed. In particular, the formation of biscationic moieties by reaction of the epoxide with tertiary amino groups did not occur in the present case.

Infrared spectroscopy also confirmed the modification of the polymers due to decreasing intensity of the NH stretching and amine deformation vibrations (1600 cm⁻¹) as well as the simultaneous increase of the O–H stretching band (3600 and 3100 cm⁻¹) with growing degree of functionalization. The latter is partially caused by the 2-hydroxypropyl groups and partially by the water content of the samples. Other pieces of spectral evidence are the bands at ~3020 cm⁻¹ (C–H stretching from the >CH(OH) unit) and at 1600 cm⁻¹ (secondary amino groups). The spectral data of compounds 1–15 are provided in the Supporting Information, Data S2–S16.

Differential scanning calorimetry was used to investigate the thermal behavior of unmodified PEI and the PEI Quat-primer

polymers PEI_{nK}^{xQ} in the temperature range –80 to +140 °C (see the Supporting Information, Data S17). All polymers were found to be amorphous, noncrystalline materials exhibiting a single glass transition. PEI exhibited the lowest glass transition temperature of –52 °C, while the glass transition temperature increased to +25 °C for PEI_{10K}^{75Q}. The grafting of positively charged moieties on poly(ethyleneimine) has a significant influence on the thermal properties of the polymer. This result was to be expected since the introduction of charged moieties on PEI will reduce the flexibility of the polymer chain due to electrostatic interactions.³⁹

Poly(ethyleneimine) is soluble in (i) polar protic solvents such as water, methanol, and ethanol, (ii) polar aprotic solvents such as *N,N*-dimethylformamide and dimethyl sulfoxide, and (iii) several halogenated solvents such as dichloromethane and trichloromethane.³⁸ The solubility of the Quat-primer polymers was tested with a 1 wt % concentration of the respective polymer in a series of 10 nonhalogenated solvents (cf. Table S2 in the Supporting Information). Clear solutions (1 wt %) of all prepared Quat-primer polymers could be obtained in water, methanol, ethanol, and 2-propanol, while none of the polymers dissolved in ethyl acetate, toluene, and *n*-hexane. In DMF only the low molecular weight, weakly modified compound 2 dissolved, while the moderately quarternized, medium molecular weight Quat-primer polymers (compounds such as 3, 5, 6, 8, and 9) were swollen by this solvent. Highly

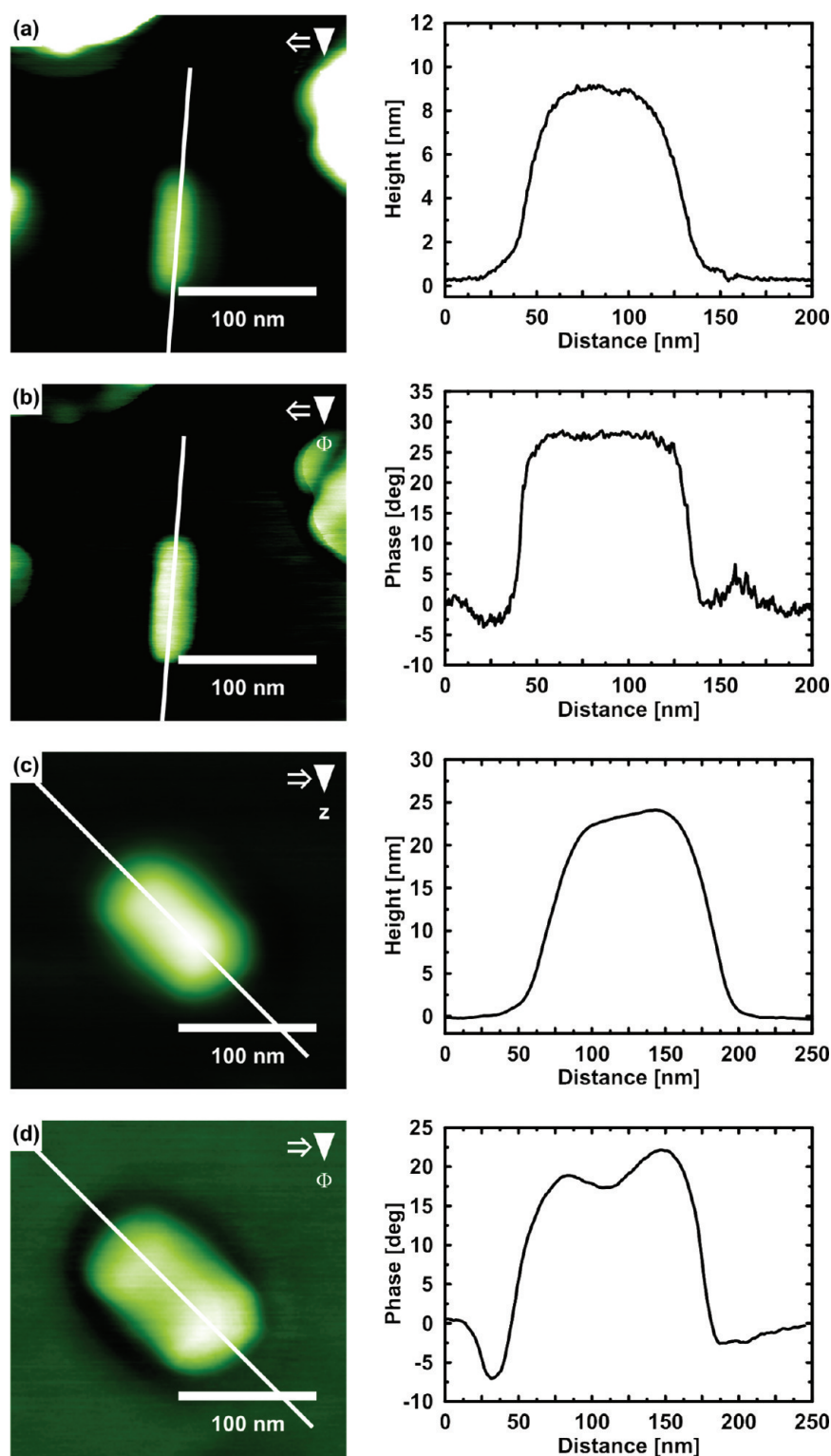


Figure 5. AFM analysis of bare and PEI modified NRs: (a) AFM topographic and (b) phase images of bare NRs along with corresponding height profiles (right); (c) AFM topographic and (d) phase images of modified NRs along with corresponding height profiles (right).

quaternized and high molecular weight products (compounds such as **10**, **11**, **12**, **14**, and **15**) were insoluble in DMF. In a similar way, THF was only able to swell compounds **2**, **3**, **5**, and **8**. These observations are in agreement with the expectations for the solubility behavior of branched polyelectrolytes.³⁴

Quat-primer PEI Modified Fluorescent Ce_{0.95}Tb_{0.05}PO₄ Nanorods. The prepared Quat-primer polymers have been tested as stabilizers to form dispersions of the Ce-doped TbPO₄ NRs in water. The positively charged polymers were expected to adsorb on the negatively charged surfaces of the nanoparticles,

hence forming thin polymer layers that may protect the particles from agglomeration means of electrostatic stabilization. The dispersion properties of the Quat-primer polymers are expected to depend on (i) their molecular weight, (ii) their degree of quarternization, (iii) the polymer concentration used, and (iv) the pH of the dispersion medium. A first series of dispersion screening experiments has been performed with mixtures consisting of 10 mL of a 1 wt % aqueous solution of the respective Quat-primer polymer and 100 mg of NRs (polymer:particle = 1:1, w/w). The pH value of the solution was adjusted with buffers to pH 4 (buffer 1), 7 (buffer 2), 9 (buffer 3), and 11 (buffer 4). The mixtures were treated with an ultrasound horn of a nominal sound power of 250 W in a glass rosette circulation vessel for 15 min, subsequently transferred to glass vials, and allowed to stand for 30 min prior to visual inspection. Without added Quat-primer polymers, no dispersion was obtained. The nanoparticles rapidly settled within a few minutes subsequent to the sonication step. The effect of added polymer depended on the pH of the solution (see the Supporting Information, Table S3). At pH 11 no dispersions were formed, while at pH 9 the initially formed turbid suspension slowly precipitated. At pH 7 the dispersions were stable, except for the mixture containing PEI_{60K}^{5Q}, and at pH 4 dispersions were obtained only in the presence of Quat-primer polymers 9 (PEI_{10K}^{30Q}) and 10 (PEI_{10K}^{50Q}). Since short-time-stable dispersions were found preferably under neutral conditions, the dependence of the long-time stability on the structure and concentration of the used macromolecules was investigated in buffer-free aqueous solutions.

Table S4 in the Supporting Information summarizes the results of the dispersion formation experiments which test the effect of the polymer concentration on the dispersion stability one day after ultrasound treatment of the H₂O/polymer/nanoparticle mixtures at pH ≈ 10. Again, without Quat-primer polymer, no nanoparticle dispersion was obtained, but with addition of as little as 0.001 wt % polymer PEI_{10K}^{15Q}, a dispersion was formed that was stable over the investigated time. At a concentration of 0.01 wt %, stable dispersions were found with virtually all investigated Quat-primer polymers. The high molecular weight forms an exception, highly charged PEI_{60K}^{30Q}, where the particles slowly precipitated from the dispersion within one day. As a general trend, it was found that the dispersion stability decreased with increasing polymer concentration, and at 1 wt % polymer content, no stable dispersion was obtained. It is well-known that, depending on their molecular weights, molecular charges, and concentrations, linear polyelectrolytes can act either as dispersing agents or as flocculants.³⁹ The respective relations are not well investigated for charged hyperbranched polymers, and the results of the screening tests may initiate such studies in future work.

On the basis of these experiments, the Quat-primer polymer PEI_{10K}^{30Q} (i.e., number average molecular weight 10 kDa, 30% degree of quarternization) was chosen for the further experiments. In these experiments the stability of the dispersions containing bare and surface modified nanorods was examined by ζ potential and UV–vis spectroscopic measurements. The results of the ζ potential measurements are shown in Figure 4A. ζ potentials were measured at different pH values which were adjusted with NaOH or HCl. The bare nanorods display an isoelectric point (pI) at 4.5 and strong negative potentials at basic pH, indicating the presence of negative charges on the surface of the NRs. In contrast, nanorods which had been treated with the Quat-primer polymer (PEI_{10K}^{30Q}) exhibit high positive values

for the ζ potential even at basic pH values. Obviously, the polymer imparts strong positive charge on the surface of the NRs in a wide pH range. The higher surface charge is accompanied by a higher colloidal stability of the nanorods. This is shown in Figure 4B displaying the light scattering of the colloid versus time. The scattering, which is measured as apparent absorbance at 700 nm, decreases when sedimentation of the 50 nm long nanorods occurs. The bare particles display a first decrease of the scattering intensity already after 6 h, whereas the Quat-primer polymer modified nanorods are stable for 48 h, followed by a slow decrease of the scattering intensity thereafter. The whole set of measurements, i.e., absorbance measured at different time intervals in the wavelength range of 200–800 nm, are shown in the Supporting Information (Data S18 and S19).

DLS measurements of the size distribution of bare and modified NRs in aqueous suspension are plotted in Figure 4C. The influence of the polymer is clearly visible in the size distribution pattern where the average particle size of the modified particles ranges from ~78 nm for the bare nanorods to ~50 nm for the modified particles. This indicates that the polymer increases the colloidal stability by deagglomeration of the particles as a mean size of 50 nm is also deduced from the TEM images as well as from the Rietveld analysis of the XRD data. Another important advantage of the Quat-primer polymer is that it does not negatively affect the emission properties of the nanorods (Figure 4D). In contrast to organic modifiers with aromatic groups, the Quat-primer polymer does not decrease the absorption of UV light by the nanorods. Therefore, the Tb³⁺ luminescence of the modified nanocrystals is still efficiently excited by UV radiation and is easily detected.

Bare and modified NRs were analyzed by thermogravimetric analysis (TGA) in air and helium atmospheres, and the corresponding thermograms are presented in the Supporting Information, Data S20 and S21, respectively. Only the bare particles display a weight loss between approximately 5% and 6%, which occurs due to the removal of absorbed water and also the crystallization water existing in the rhabdophane hexagonal phase. In the case of the Quat-primer polymer modified particles, an additional weight loss is observed in both atmospheres, indicating the removal of Quat-primer polymer from the surface. In the presence of air, this additional weight loss is observed between 260 and 420 °C, a typical temperature range for the oxidation of organic material. When the sample is heated in an inert helium atmosphere, however, higher temperatures of up to 670 °C are required to decompose and volatilize the polymer.

Parts a and b of Figure 5 show the topography and phase images of an unmodified NR along with the corresponding height profiles. Both topography and phase images reveal a homogeneous shape of the NR, indicating that there is no chemical heterogeneity along the NR. This is in contrast to what was found for the Quat-primer polymer modified NRs. AFM topography and phase images of Quat-primer polymer modified NRs are reproduced in Figure 5c,d. The corresponding height profiles are shown on the right. While the topography image of the Quat-primer polymer NR does not differ significantly from the topography image of the bare NR, the phase image reveals a clear difference. As can be seen in Figure 5d, the shape of the phase image exhibits maxima at both ends and a depression in the inner region of the PEI modified NR. This structure within the phase image indicates that the chemical composition changes along the NR surface.

CONCLUSIONS

Quat-primer polymer based on hyperbranched PEI partially quarternized with glycidyltrimethylammonium chloride has proved a good surface modifier for green-emitting $\text{Ce}_{0.95}\text{Tb}_{0.05}\text{PO}_4$ NRs. ζ potential, TGA, and AFM studies reveal the successful surface modification. Particle size and UV–vis spectroscopic analyses show that the modifier imparts deagglomeration of the particles and their colloidal stability. It was also proved that there is no significant difference in the fluorescence behavior before and after the treatment. The positively charged Quat-primer polymer may be physically adsorbed on the negatively charged surface of the nanorods. Since the Quat-primer polymers employed still contain reactive amino groups, further modification of the macromolecules with, e.g., nonpolar moieties may enable dispersion formation of inorganic solvents, of liquid monomers, or even in polymer melts. Hence, Quat-primer lanthanide phosphate composites may offer a versatile path toward luminescent functional materials.

ASSOCIATED CONTENT

Supporting Information. (Data S1a) Reitveld refined XRD pattern of the $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ nanorods, (Data S1b) TEM pictures of the $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ nanorods, (Data S1c) emission ($\lambda_{\text{ex}} = 393$ nm) and excitation ($\lambda_{\text{em}} = 588$ nm) spectra of the $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ nanorods, (Data S2–S16) IR, ^1H NMR, ^{13}C NMR, and elemental analysis results of Quat-primer polymers (Data S2) $\text{PEI}_{0.423\text{K}}^{5\text{Q}}$ (1), (Data S3) $\text{PEI}_{0.423\text{K}}^{15\text{Q}}$ (2), (Data S4) $\text{PEI}_{0.423\text{K}}^{30\text{Q}}$ (3), (Data S5) $\text{PEI}_{1.2\text{K}}^{5\text{Q}}$ (4), (Data S6) $\text{PEI}_{1.2\text{K}}^{15\text{Q}}$ (5), (Data S7) $\text{PEI}_{1.2\text{K}}^{30\text{Q}}$ (6), (Data S8) $\text{PEI}_{10\text{K}}^{5\text{Q}}$ (7), (Data S9) $\text{PEI}_{10\text{K}}^{15\text{Q}}$ (8), (Data S10) $\text{PEI}_{10\text{K}}^{30\text{Q}}$ (9), (Data S11) $\text{PEI}_{10\text{K}}^{50\text{Q}}$ (10), (Data S12) $\text{PEI}_{10\text{K}}^{75\text{Q}}$ (11), (Data S13) $\text{PEI}_{10\text{K}}^{100\text{Q}}$ (12), (Data S14) $\text{PEI}_{60\text{K}}^{5\text{Q}}$ (13), (Data S15) $\text{PEI}_{60\text{K}}^{15\text{Q}}$ (14), and (Data S16) $\text{PEI}_{60\text{K}}^{30\text{Q}}$ (15), (Table S1) composition of the prepared Quat-primer polymers 1–15, (Data S17) differential scanning calorimetry of poly(ethyleneimine) $\text{PEI}_{10\text{K}}$ and Quat-primer polymers $\text{PEI}_{10\text{K}}^{x\text{Q}}$, with $x = 5, 15, 30, 50,$ and 75 ($dT/dt = 10$ K/min), (Table S2) solubility of Quat-primer polymers in different solvents, (Table S3) dispersion experiments of different Quat-primer polymers $\text{PEI}_{n\text{K}}^{x\text{Q}}$ in several buffer solutions (the dispersion stability was observed for 15–30 min), (Table S4) results of dispersion screening experiments with 1.0 wt % NRs in the presence of PEI Quat-primer polymers $\text{PEI}_{n\text{K}}^{x\text{Q}}$ one day after preparation, (Data S18) UV–vis spectra of bare NRs measured at different intervals, (Data S19) UV–vis spectra of modified NRs (NRs + $\text{PEI}_{10\text{K}}^{30\text{Q}}$) measured at different intervals, and (Data S20 and S21) TGA analysis in air and helium, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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