**Tb₂(bpdc)₃ and Eu₂(bpdc)₃ Nanoparticles (bpdc: 2,2′-Bipyridine-4,4′-dicarboxylate) and Their Luminescence**

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Tb₂(bpdc)₃ and Eu₂(bpdc)₃ nanoparticles (bpdc: 2,2′-bipyridine-4,4′-dicarboxylate) have been prepared via straightforward precipitation from aqueous solution. The nanoparticles exhibit mean diameters of 41(5) nm (Tb₂(bpdc)₃) and 56(4) nm (Eu₂(bpdc)₃) and show a very good colloidal stability in aqueous suspension. Particle size and chemical composition have been characterized based on electron microscopy, X-ray diffraction, infrared spectroscopy and thermogravimetry. Photoluminescence validates an efficient excitation of Tb³⁺/Eu³⁺ via the bpdc ligand as an antenna that leads to intense characteristic green and red emissions. The absolute quantum yields of Tb₂(bpdc)₃ and Eu₂(bpdc)₃ have been determined at 28 and 12%, respectively. Although rare-earth metal-based photoluminescence is typically quenched in water due to vibronic loss processes (ν(O–H)), here, the antenna effect and the shielding of the metal centers via the bpdc ligand are very efficient, allowing for an intense green and red emission of the Tb₂(bpdc)₃ and Eu₂(bpdc)₃ nanoparticles even in aqueous suspension.

**Key words:** Terbium, Europium, 2,2′-Bipyridine-4,4′-dicarboxylate, Nanoparticle, Luminescence, Quantum Yield

**Introduction**

2,2′-Bipyridine-4,4′-dicarboxylic acid (H₂bpdc) and its derivatives belong to the most prominent ligands that can be used for achieving the so-called antenna effect [1]. The ligand guarantees for an efficient light absorption, and the absorbed energy is efficiently transferred to a certain cation. On the one hand, this principle is used in dye-sensitized solar cells (so-called Grätzel cells) for efficient light absorption and fast separation of the generated charge carriers [2, 3]. On the other hand, the antenna effect is widely used for energy transfer to a cation showing intense light emission [4]. This strategy is very powerful in order to populate high-energy levels of trivalent rare-earth ions, such as Tb³⁺ or Eu³⁺. For them, a direct excitation into the f manifold via light absorption is spin and/or parity forbidden [5]. As a consequence, the f-lines of the rare-earth ions show only minor absorption strength – and thus, a weak absorption and emission. For molecular complexes of Tb³⁺ or Eu³⁺ with the bpdc ligand the energy transfer is known to be very efficient. Even when dissolved in water, or with water coordinated directly to the rare-earth metal center, the luminescence is not quenched by the O–H vibration [6–8].

While luminescent molecular complexes as well as bulk metalorganic frameworks of rare-earth cations and the bpdc ligand have been widely investigated (bpdc: 2,2′-bipyridine-4,4′-dicarboxylate) [9–12], rare-earth metal 2,2′-bipyridine-4,4′-dicarboxylates as nanoparticles have not been reported till now. The advantage of such nanoparticles is related, on the one hand, to the quasi infinite number of luminescent centers in a single nanoparticle that allows for a much higher emission intensity as compared to the limited number of luminescent centers in a molecular complex. On the other hand, the differentiation between a luminescent nanoparticle and the non-luminescent solvent – thus, the contrast between light and dark – is much higher as compared to a homogeneous solution of luminescent molecular complexes. Both these
aspects are highly relevant for the application of luminescent nanoparticles in terms of labeling, advertising, security markers, or optical imaging [13, 14].

Here, we report on the synthesis of Tb$_2$(bpdc)$_3$ and Eu$_2$(bpdc)$_3$ nanoparticles. These nanoparticles exhibit a very good dispersibility in water and show an efficient excitation of Tb$^{3+}$/Eu$^{3+}$ via the antenna effect of the bpdc ligand, followed by intense green and red light emission. Since the nanoparticles contain molar quantities of the rare-earth cation (thus, it is not a doping) and of the bpdc ligand (thus, it is not a surface capping), the absorption and emission intensity per nanoparticle is very high.

**Results and Discussion**

The synthesis of Tb$_2$(bpdc)$_3$ and Eu$_2$(bpdc)$_3$ nanoparticles was performed via straightforward precipitation from aqueous solution. To this end, the rare earth chlorides were dissolved in water and injected at 60 °C into an aqueous solution of H$_2$bpdc. The nucleation of the nanoparticles was initiated according to LaMer’s model of particle nucleation and growth established after the hot-injection [15]. In addition to the temperature during the injection, two additional aspects have to be considered to obtain nanoparticles. On the one hand, the acidity of the 2,2′-bipyridine-4,4′-dicarboxylic acid needs to be moderated by addition of Na$_2$CO$_3$ to a slightly basic pH of 8.5. On the other hand, the bpdc ligand has to be added with a significant molar excess (33%). As a consequence, excess bpdc is continuously available for surface adsorption during particle growth. Due to its size as well as its charge, the bpdc capping on the surface guarantees for a sufficient steric as well as electrostatic stabilization of the nanoparticles [16]. As a result, the nanoparticle suspensions have a very high colloidal stability and do not show any precipitation on the timescale of several weeks.

The size and shape of the as-prepared Tb$_2$(bpdc)$_3$ and Eu$_2$(bpdc)$_3$ nanoparticles were investigated in suspension by dynamic light scattering (DLS), and as a powder by scanning electron microscopy (SEM). DLS analysis of Tb$_2$(bpdc)$_3$ in water shows a comparably narrow size distribution with a mean hydrodynamic diameter of 41(5) nm (Fig. 1). The hydrodynamic diameter of the Eu$^{3+}$ particles is somewhat larger and at a mean value of 56(4) nm (Fig. 1). According to SEM, Tb$_2$(bpdc)$_3$ and Eu$_2$(bpdc)$_3$ particles exhibit a spherical shape and a high uniformity. The mean particle diameter was determined based on a statistical evaluation of at least 100 nanoparticles and resulted in 20(5) nm for Tb$_2$(bpdc)$_3$ and 40(5) nm for Eu$_2$(bpdc)$_3$. Thus, the particle diameter as determined from SEM is below the hydrodynamic diameter stemming from DLS. This finding is in accordance with expectation since the non-mobile solvent shell surrounding the nanoparticles is comparably thick for water as a highly polar solvent. Moreover, some agglomeration occurs in aqueous suspension. Considering the fact that the nanoparticles were obtained via simple precipitation from aqueous solution without any specific colloidal stabilizer involved, the particle size and size distribution of the as-prepared Tb$_2$(bpdc)$_3$ and Eu$_2$(bpdc)$_3$ are indicative of a high quality.

To identify the chemical composition of the as-prepared nanoparticles, powder X-ray diffraction (XRD) analysis, Fourier-transform infrared spectroscopy (FT-IR) and thermogravimetry (TG) were conducted. According to XRD, however, the nanoparticles turned out to be completely amorphous and do not show specific Bragg peaks. The FT-IR spectra of the nanoparticles were compared to that of 2,2′-bipyridine-4,4′-dicarboxylic acid as a free ligand (Fig. 2). While the characteristic molecular vibrations are clearly visible ($v$(C–H): 2950–2800 cm$^{-1}$, $v_s$(OCO): 1750–1700 cm$^{-1}$, $v_1$(OCO): 1300–1250 cm$^{-1}$, fingerprint area: 1250–600 cm$^{-1}$), significant differences between the nanoparticles and the free ligand become obvious. While the wavenumber of $v_1$(OCO) is decreased to 1650–1600 cm$^{-1}$, $v_s$(OCO) is increased to 1450–1400 cm$^{-1}$. This finding can be rationalized based on a bpdc ligand that is deprotonated and coordinated as a chelate to a metal center in the nanoparticle. Moreover, the manifold of sharp bands referring to the fingerprint area (1250–600 cm$^{-1}$) is only of minor intensity for the nanoparticles. This is due to the low site symmetry of the ligands in the amorphous, solid nanoparticles. Together, these data provide good evidence that Tb$^{3+}$/Eu$^{3+}$ are coordinated to the carboxylic oxygen atoms of the bpdc ligand, which is also well in accordance with the literature [10]. The broad $v$(O–H) vibration at 3700–3100 cm$^{-1}$, moreover, points to a significant absorption of water on the nanoparticle surface. In sum, FT-IR spectra confirm the presence of bpdc in the
Fig. 1. Particle size and particle size distribution of the as-prepared Tb$_2$(bpdc)$_3$ and Eu$_2$(bpdc)$_3$ nanoparticles according to DLS (aqueous suspensions) and SEM analysis.

Fig. 2. FT-IR spectra of the as-prepared Tb$_2$(bpdc)$_3$ nanoparticles and 2,2'-bipyridine-4,4'-dicarboxylic acid (H$_2$bpdc) shown for comparison.

In order to confirm the chemical composition of Tb$_2$(bpdc)$_3$ and Eu$_2$(bpdc)$_3$ as well as a cation-to-anion ratio of 2 : 3, TG analysis was performed in air (Fig. 3). In order to remove water adsorbed on the particle surface, both materials were first dried in vacuum for 6 h at 50 °C. Thereafter, the powder samples were subjected to TG analysis in air. During heating, both nanoparticle compounds first show a slow weight loss (Tb$_2$(bpdc)$_3$: 10 wt-% up to 350 °C; Eu$_2$(bpdc)$_3$: 13 wt-% up to 250 °C) that can be ascribed to a decarboxylation of one of the two carboxylate groups per bpdc molecule (calcd. 12 wt-%). In comparison to bulk materials of similar composition [11], this decarboxylation occurs at reduced temperature, which can be ascribed to the generally higher reactivity of Tb$_2$(bpdc)$_3$ and Eu$_2$(bpdc)$_3$ nanoparticles and indicate its coordination to the metal cation.
Fig. 3. TGA analysis of the as-prepared Tb\(_2\)(bpdc)\(_3\) and Eu\(_2\)(bpdc)\(_3\) nanoparticles (total weight of 10 mg per sample in air).

the nanoparticles. Very strong weight losses of 50 wt-
% (Tb\(_2\)(bpdc)\(_3\)) and 53 wt-
% (Eu\(_2\)(bpdc)\(_3\)) are ob-
served at 400 – 500 °C (Tb\(_2\)(bpdc)\(_3\)) and 350 – 450 °C
(Eu\(_2\)(bpdc)\(_3\)) that are related to a complete oxidative
decomposition of the bpdc ligand. The thermal rem-
nants were observed with 40 wt-
% (Tb\(_2\)(bpdc)\(_3\)) and
34 wt-
% (Eu\(_2\)(bpdc)\(_3\)) and can be identified
via XRD
as Tb\(_4\)O\(_7\) and Eu\(_2\)O\(_3\). These data can be explained
based on the following decomposition processes and
calculated weight losses:

\[(1)\] 2Tb\(_2\)(C\(_{12}\)H\(_8\)N\(_2\)O\(_4\))\(_3\) + 72.5O\(_2\) →
72CO\(_2\) + 18H\(_2\)O + 6N\(_2\) + Tb\(_4\)O\(_7\)
(calcd. 64\%) (calcd. 36\%)

\[(2)\] Eu\(_2\)(C\(_{12}\)H\(_8\)N\(_2\)O\(_4\))\(_3\) + 36O\(_2\) →
36CO\(_2\) + 9H\(_2\)O + 3N\(_2\) + Eu\(_2\)O\(_3\)
(calcd. 66\%) (calcd. 34\%)

Altogether, a total weight loss of 60 wt-
% (Tb\(_2\)(bpdc)\(_3\)) and
66 wt-
% (Eu\(_2\)(bpdc)\(_3\)) due to the gaseous oxida-
tion products CO\(_2\), H\(_2\)O and N\(_2\), as well as the weight
of the solid remnant (40 wt-
% of Tb\(_4\)O\(_7\), 34 wt-
% of Eu\(_2\)O\(_3\)) match well with the calculated data. Thus,
a cation-to-anion ratio of 2 : 3 and an overall com-
position Tb\(_2\)(bpdc)\(_3\) and Eu\(_2\)(bpdc)\(_3\) is validated and
matches with the bulk composition of already known
metalorganic frameworks [9 – 11].

Photoluminescence spectroscopy was used to elu-
cidate the luminescence properties of the as-prepared
Tb\(_2\)(bpdc)\(_3\) and Eu\(_2\)(bpdc)\(_3\) nanoparticles (Figs. 4 and 5). Both compounds show a broad and intense
absorption at 250 to 350 nm indicating the excitation
of the bpdc ligand [17]. Notably, excitations via the
f-states of Tb\(^{3+}\) and Eu\(^{3+}\) are only visible as very
weak lines. Emission spectra show an opposite situa-
tion as compared to excitation (Figs. 4 and 5). Here, the
as-prepared Tb\(_2\)(bpdc)\(_3\), and Eu\(_2\)(bpdc)\(_3\) nanoparticles
show the characteristic f → f emission lines of Tb\(^{3+}\)
and Eu\(^{3+}\) with high intensity [17, 18]. \(^5\)D\(_4\) → \(^7\)F\(_j\) with
\(j = 5\) at 544 nm is observed as the dominating emis-
sion line for Tb\(_2\)(bpdc)\(_3\), and \(^5\)D\(_0\) → \(^7\)F\(_j\) with \(j = 2\) at
614 nm for Eu\(_2\)(bpdc)\(_3\). An emission of the bpdc lig-
and is, however, not observed. Thus, bpdc serves as
an efficient antenna with all the absorbed energy be-
ing transferred to the rare-earth centers. The absolute
quantum yields of Tb\(_2\)(bpdc)\(_3\) and Eu\(_2\)(bpdc)\(_3\) were
determined for powder samples by photon counting in
an integrating sphere (Ulbricht sphere) and are at mean
levels of 28% for Tb\(_2\)(bpdc)\(_3\) and 12% for Eu\(_2\)(bpdc)\(_3\).

Considering the fact that rare-earth metal-based photo-
luminescence is typically quenched under humid con-
ditions due to \(\nu\!(O–H)\)-driven vibronic losses [16, 17],
the intense emission of the Tb\(_2\)(bpdc)\(_3\) and Eu\(_2\)(bpdc)\(_3\)
nanoparticles even in aqueous suspension is surprising
and can be very interesting for future applications of
such nanomaterials.

Conclusions

Tb\(_2\)(bpdc)\(_3\) and Eu\(_2\)(bpdc)\(_3\) (bpdc: 2,2'-bipyridine-
4,4'-dicarboxylate) are prepared as nanoparticles \textit{via}
controlled precipitation from aqueous solution. These
suspensions show a high colloidal stability and
mean diameters of 41(5) nm for Tb$_2$(bpdc)$_3$ and of 56(4) nm for Eu$_2$(bpdc)$_3$. The nanoparticles are non-crystalline, and their chemical composition has been validated based on FT-IR spectroscopy and fluorescence spectroscopy. Thermogravimetry shows the thermal decomposition of the bpdc ligand and formation of Tb$_4$O$_7$/Eu$_2$O$_3$ as the solid remnants. By quantifying this decomposition, the composition Tb$_2$(bpdc)$_3$/Eu$_2$(bpdc)$_3$ and the cation-to-anion ratio of 2 : 3 have been confirmed. Luminescence spectra provide evidence for an efficient excitation of Tb$^{3+}$/Eu$^{3+}$ via the antenna effect of the bpdc ligand as well as an intense characteristic green and red emission. Since the nanoparticles contain the rare earth cation and the bpdc ligand in molar quantities, the number of luminescent centers per nanoparticle, and thus the absorption and emission intensity, are very high. Although rare-earth metal-based photoluminescence is typically quenched in water due to relaxation via the O–H vibration, the antenna effect and shielding of the metal centers via the bpdc ligand is very efficient, allowing for an intense green and red emission of the Tb$_2$(bpdc)$_3$ and Eu$_2$(bpdc)$_3$ nanoparticles with quantum yields of 28 and 12%, respectively. Be-
ing based on a straightforward synthesis and showing an intense green and red emission in water-based suspensions. Tb$_2$(bpdc)$_3$ and Eu$_2$(bpdc)$_3$ nanoparticles can become relevant for applications, such as labeling, advertising, security marking, or optical imaging.

**Experimental Section**

**Materials and synthesis**

All chemicals were used as received from the supplier: terbium chloride hexahydrate (Aldrich, 99.9%), europium chloride hexahydrate (Aldrich, 99.9%), 2,2′-bipyridine-4,4′-dicarboxylic acid (H$_2$bpdc) (ABCR, 98%), sodium carbonate (Fluka, 99.9%). All preparative work could be performed in air. Inert conditions are not necessary which facilitates the synthesis significantly.

The synthesis of the Tb$_2$(bpdc)$_3$ and Eu$_2$(bpdc)$_3$ nanoparticles was performed by precipitation from aqueous solution. To this end, 10 mg (0.04 mmol) of H$_2$bpdc was dissolved in 20 mL degassed demineralized water. By addition of Na$_2$CO$_3$, the pH of the acidic solution was increased to about pH = 8.5. The colorless solution was heated to 60 °C. Thereafter, an aqueous solution of 10 mg of the respective rare earth chloride (0.03 mmol) in 2 mL of water was added via hot-injection. Particle nucleation started instantaneously and resulted in a colorless suspension. Afterwards, the suspension was heated for 1 h at 60 °C. The resulting nanoparticles were separated by centrifugation and purified by sequential resuspension/centrifugation in/from water. Finally, the nanoparticles were washed once with ethanol. For analytical characterization, the as-prepared colorless Tb$_2$(bpdc)$_3$ and Eu$_2$(bpdc)$_3$ nanoparticles were used as aqueous suspensions or as powders.

**Analytical techniques**

*Scanning electron microscopy (SEM)* was conducted on a Zeiss Supra 40 VP, using an acceleration voltage of 10 kV and a working distance of 2 mm. As-prepared samples were redispersed in water or ethanol and deposited on silicon wafers as sample holders for SEM investigation.

*Dynamic light scattering (DLS)* was performed with a Nanosizer ZS from Malvern Instruments. For DLS analysis as-prepared particles were redispersed in water. The nanoparticle diameter was measured in aqueous suspension applying polystyrene cuvettes.

*Powder X-ray diffraction (XRD)* was conducted with a Stoe STADI-P operating with Ge-monochromatized CuK$_\alpha$ radiation.

*Infrared spectra (FT-IR)* were measured with a Bruker Vertex 70 FT-IR instrument. The samples were measured in KBr pellets with a resolution of 4 cm$^{-1}$.

*Thermogravimetry (TG)* was performed with a Netsch STA 409C analyzer. The samples were heated in air to a maximum temperature of 800 °C with a heating rate of 1 K min$^{-1}$.

*Photoluminescence (PL)* was recorded for the powder samples with a Jobin Yvon Spex Fluorolog 3.2 equipped with a 450 W Xe lamp, an integrating sphere as well as double grating excitation and emission monochromators. The absolute quantum yield was determined for powder samples according to Friend [19]. Thus, the diffuse reflection of the sample was first determined at a certain excitation wavelength. Next, the emission was measured under excitation at the same wavelength. Integration over the reflected and emitted photons by use of the Ulbricht sphere resulted in the absolute quantum yield. Corrections were made taking into account the spectral power of the excitation source, the reflection behavior of the Ulbricht sphere, and the sensitivity of the detector.

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