Temperature-Sensitive Luminescent Nanoparticles and Films Based on a Terbium (III) Complex Probe

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The terbium-tris[(2-hydroxy-benzoyl)-2-aminoethyl]amine complex (Tb-THBA) with its high color purity, long luminescence lifetime, and high quantum yield has been found to be a viable indicator for the optical sensing of temperature. Both its luminescence intensity and its lifetime strongly depend on temperature in the range from 15 to 65 °C. When photoexcited at 341 nm, it displays typical Tb^{3+} ion emission bands with the strongest peak at 546 nm and a typical decay time of 1.15 ms at 15 °C. The probe is shown to be excellent for sensing temperature, as demonstrated in two kinds of optical sensor membranes. In the first, it was incorporated into a highly biocompatible polyurethane hydrogel to form a sensing film. In the second, Tb-THBA was converted into nanoparticles with a mean diameter of 10 nm that were then incorporated into a film of poly(vinyl alcohol). The two films display a remarkably high sensitivity toward temperature change, both in luminescence intensity and in luminescence decay time, making them promising for the optical sensing and imaging of temperature in the physiologically relevant temperature range. The mechanism behind the temperature sensing has been investigated using a combination of experimental techniques. For the complex in solution or the polyurethane sensing film, the emission intensity and lifetime decrease with increasing temperature, which is expected and attributed to thermal deactivation of the excited state. For the nanoparticles in solution, however, an interesting and unusual temperature dependence of the emission intensity has been observed. The emission intensity was found to increase with increasing temperature in the range of 20−65 °C, which is possibly due to a shift in equilibrium from a less luminescent species or state to a more luminescent species or state. For the nanoparticle films, this unusual behavior disappeared, likely due to the lack of such an equilibrium shift in the films.

1. Introduction

Temperature is a key physical parameter in numerous fields of science and technology. Possibly as important, the measurement of temperature is almost mandatory in the case of chemical sensors because it affects their response function[1–3] as exemplified, for example, by fiber optic chemical sensors and biosensors.[4,5] Optical sensors have distinct advantages over other sensing schemes, including high sensitivity, contactless operation, and inertness to even strong electrical fields.[6,7] Luminescent optical sensors for temperature are based, for example, on the use of appropriate luminophores, such as rhodamines,[8] but most often certain metal−ligand complexes.[6,9–11] The rhodamines have a moderate slope of the work function (and thus poor resolution), so inorganic phosphors are preferred.[10] Temperature-sensitive probes also were incorporated into nanogels[13] and into sensor films to enable spatially and temporally resolved temperature imaging.[12,13]

Materials doped with ligand complexes of Eu^{3+} and Tb^{3+} ions have been used lately for the optical sensing of temperature.[15–17] These display long lifetimes and sharp emission bands.[18] However, their f electrons are well shielded by the 5s and 5p orbitals from the chemical environment, so the lanthanide complexes are less affected by their (chemical) environment. Obviously, the chemical structures of the ligands play an important role in the design of temperature sensors based on such complexes.[19] Interestingly, probes for temperature based on Tb^{3+} complexes have been reported rather rarely so far, most likely because of being said not to display a highly temperature-dependent luminescence.[19] On the other side, the Tb^{3+} ion complexes predictably exhibit longer decay times than those of the Eu^{3+} ion, which suggests that it would be superior to Eu^{3+} ion for the lifetime-based sensing of temperature.[20,21]

Fluorescence-based sensors are based on the measurement of mainly four parameters, which are (a) fluorescence intensity, (b) its spectral distribution, (c) its temporal distribution (fluorescence lifetime), and (d) its orientation (fluorescence anisotropy).[4] By combining several sources of information, fluorescence-based sensors resolving more than one analyte can be realized, as was demonstrated in different approaches, mostly using a combination of luminescent intensity and lifetime discriminations.[4,5,22–24]

Recently, Wong et al.[25] reported on the efficient upconversion fluorescence from the terbium (III) tris[(2-hydroxybenzoyl)-2-aminoethyl]amine complex (Tb-THBA) under infrared pulsed laser pumping. The potential of such a complex as a temperature indicator was not recognized, however. Herein, we show that Tb-THBA is a most viable temperature probe, whose features

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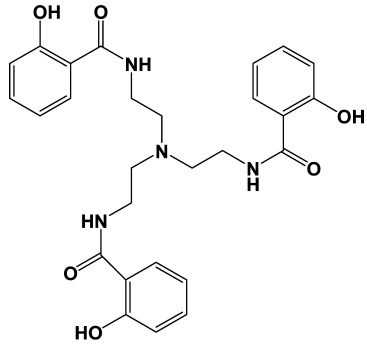
SCHEME 1: Molecular Structure of the Ligand THBA



THBA

include high-temperature sensitivity, unusual brightness, high luminescent quantum yield, high color purity, and a luminescence lifetime in the millisecond range. We also show here that (a) this probe can be used in the form of a film in a polyurethane hydrogel matrix, (b) it can be converted into nanoparticles that also display sensitivity to temperature, and that (c) the nanoparticles can be incorporated into a film poly(vinyl alcohol) to enable the imaging of temperature. The sensitivity to temperature can be seen in the fluorescence intensity and in its decay time. These properties make Tb-THBA a viable probe for the sensing and imaging of temperature in the physiological range.

2. Experimental Section

Materials. $Tb(NO_3)_3$, poly(vinyl alcohol) (PVA, MM ~195 kDa), ethyl salicylate, tris-(2-aminoethyl)amine, quinine hemisulfate monohydrate, and acetonitrile were obtained from Sigma-Aldrich (www.sigma-aldrich.com) and used without further purification. The polyurethane hydrogel polymer (type D4) was obtained from Cardiotech (www.cardiotech-inc.com) and dimethyl sulfoxide from Merck (www.merck.de). Doubly distilled water was used throughout.

Tris[(2-hydroxybenzoyl)-2-aminoethyl]amine (THBA). This compound was synthesized, in essence, according to the literature.[26] Ethyl salicylate (22.5 mmol) was mixed with tris-(2-aminoethyl)amine (5 mmol). The mixture was sealed and heated to 100 °C for 48 h. After cooling, the orange solid gel was purified on a silica column eluted with dichloromethane (CH_2Cl_2) and methanol/CH_2Cl_2 (4/100 in volume). Evaporation of the eluting solvent gave the product as a white gel. Yield: 49%. ^{1}H NMR (300 MHz, chloroform-d, 298 K), δ 2.78 (t, J = 5.49 Hz, 6H, CH_2), 3.57 (q, J = 5.40 Hz, 6H, CH_2), 6.52 (t, J = 7.00 Hz, 3H, ArH), 6.82 (d, J = 7.41 Hz, 3H, ArH), 7.22 (d, J = 7.14 Hz, 3H, ArH), 7.30 (d, J = 8.23 Hz, 3H, ArH), 7.99 (s br, 3H, NH), 11.94 (s br, 3H, ArOH). ^{13}C NMR (DMSO-d_6, 298 K) δ 37.80 (CH_2), 54.18 (CH_2), 114.22 (Ar), 118.15 (Ar), 118.90 (Ar), 125.86 (Ar), 134.12 (Ar), 160.78 (ArCOH), 170.59 (C=O). ES-MS (m/z): $(M - H^+)^-$, 505.2 (100.0%), 506.2 (31.7%), 507.2 (5.4%), 508.2 (1.2%). Anal. Calcd. for $C_{27}H_{30}N_4O_6$: C, 64.02; H, 5.97; N, 11.06. Found: C, 63.58; H, 6.12; N, 11.20%. The molecular structure of the ligand THBA is shown in Scheme 1.

Terbium (III) tris[(2-hydroxybenzoyl)-2-aminoethyl]amine (Tb-THBA). This compound was synthesized according to the literature.[25]

Preparation of a Sensor Film Containing the Tb-THBA Complex in a Polyurethane Hydrogel. The probe Tb-THBA (3.75 mg) was dispersed in 2.71 mL of 99% ethanol and 0.2375 mL of water (9:1, w/w). A 0.125 g portion of the hydrogel D4 was then added and the mixture stirred for 10 h. The resulting "cocktail" was knife-coated onto a glass slide and the resulting layer (referred to as the temperature-sensing film TSF-1) dried in ambient air.

Synthesis of Tb-THBA Nanoparticles. Our previous method of encapsulation−reprecipitation was adopted.[27] In a typical synthesis, Tb-THBA was dissolved in acetonitrile in a concentration of 1000 ppm. A 200 μL quantity of the solution was then rapidly injected, under sonication, into 8 mL of doubly distilled water using a microsyringe. The concentration of the Tb-THBA nanoparticles in the aqueous dispersion was about 20 ppm. The resulting colloid was used in further experiments, including spectral characterization, TEM, AFM, and studies on the effects of temperature.

For preparing the sensor film described below, Tb-THBA in acetonitrile in a concentration of 2000 ppm (rather than 1000 ppm) was used for preparing the dispersion of Tb-THBA nanoparticles. The rest of the procedure was the same.

Preparation of a Temperature-Sensing Film Containing the Tb-THBA Nanoparticles in Poly(vinyl alcohol). A 10 wt % aqueous solution of PVA was prepared by dissolving 1.0 g of PVA in 10 mL of water at about 90 °C. The dispersion of the Tb-THBA nanoparticles (by using 2000 ppm Tb-THBA in acetonitrile) was then mixed with the 10% PVA solution in a volume ratio of 1:1, giving a viscous and clear solution with a total PVA concentration of about 5 wt %. The mixture was stirred for 1 h, and then the "cocktail" was knife-coated onto a glass slide and dried in ambient air. After the solvent was removed, a colorless and transparent sensing film (referred to as the temperature-sensing film TSF-2) was obtained.

Characterization of Materials. UV−visible absorption spectra of the ligand and the Tb complex were recorded on a U-3000 spectrophotometer (Hitachi). Steady-state and time-resolved fluorescence spectra were recorded on an Aminco AB 2 luminescence spectrometer (www.thermo.com). Temperatures are accurate to ±0.1 °C. The error in the determination of the fluorescence intensity is ±1%, and that of the lifetime is ±5%. The quantum yield (QY) was determined relative to quinine sulfate in 0.1 M sulfuric acid as the standard (QY = 0.58).[28] Dissolved oxygen was removed by bubbling solutions with pure nitrogen. The concentrations of the solution of quinine sulfate and of Tb-THBA in DMSO were adjusted to have almost the same absorption at 350 nm as that of the solution of Tb-THBA and an absorbance of <0.05. Absorption spectra in context with QY determinations were recorded on a Cary WinUV spectrophotometer (Varian, Victoria, Australia). The corrected integrated area of the emission spectrum was used to calculate the QY of Tb-THBA in dimethylsulfoxide by using the following equation[29]

$$QY_s = \frac{n_s^2 I_s A_{ref}}{n_{ref}^2 A_s I_{ref}} QY_{ref}$$

where n is the refractive index of the solvent, I is the wavelength-integrated area of the corrected emission spectrum, and A the absorbance at the excitation wavelength (350 nm). The molar extinction coefficient at 350 nm is 4319 L/mol·cm. Because the absorption at 350 nm is dominated by the Tb-THBA complex, the possible presence of free ligands has little effect on the luminescence properties measured, including the QY. Atomic force microscopy (AFM) was performed by placing one drop of the nanoparticle dispersion on a freshly cleaned

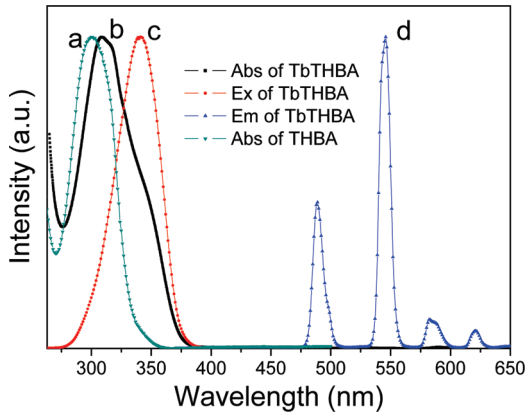


Figure 1. Absorption spectra of the ligand THBA (0.1 mM in acetonitrile) (a) and of the Tb-THBA complex (0.1 mM in DMSO) (b). Excitation spectrum (c) of Tb-THBA in DMSO at an emission wavelength of 546 nm. (d) Emission spectrum following excitation at 341 nm. All spectra were acquired at room temperature and are normalized to a constant intensity at the maximum.

coverslip. After the evaporation of water, the surface was scanned with a Digital Instruments multimode AFM in tapping mode. Transmission electron microscopy images were obtained with an electron microscope (type Leo 912AB, from Zeiss; www.smt.zeiss.com) at an acceleration voltage of 120 kV.

3. Results and Discussion

Tb-THBA Complex As a Probe for Temperature. Lanthanide ions without an organic ligand have rather weak absorption bands, but if bound to certain ligands, they display intriguing features in terms of luminescence.[6,30] We find the terbium (III) complex of the ligand THBA to be particularly attractive. Respective absorption and luminescence spectra are shown in Figure 1. The absorption band of the THBA ligand is dominated by a broad band centered at 300 nm. A red shift of the absorption band can be observed after the formation of the Tb-THBA complex, with a maximum at 309 nm and a shoulder at around 340 nm.

The luminescence excitation spectrum of the Tb-THBA complex was obtained by monitoring the emission wavelength of the Tb^{3+} ion at 546 nm. As shown in Figure 1, the excitation spectrum exhibits a broad excitation band between 275 and 390 nm, which can be assigned to the $\pi-\pi^*$ electron transition of the ligand (THBA).[31] Upon exciting the ligand at 341 nm, the emissions at 488, 546, 584, and 619 nm are assigned to the transitions from the $^5D_4$ level to ^7F_J ($J = 6, 5, 4, 3$) levels, of which the $^5D_4 \rightarrow {}^7F_5$ emission is most prominent. No emission from the ligand (expected at 360−400 nm and of the typical width of an organic fluorophore) was detected, suggesting that the energy transfer process from the ligand to the Tb^{3+} ion is very efficient. In addition, the full width at half-maximum (fwhm) of the strongest band is less than 10 nm, which indicates that the Tb-THBA complex exhibits a high color purity.[32] The narrow emission bands facilitate the separation of signals in the case of multiple sensors where two or even three signals are to be processed at the same time.[33,34]

A closer examination of the UV−vis and luminescence excitation spectra in Figure 1 indicates the possibility that the 309 nm peak for spectrum b is due to free ligands, whereas the apparent shoulder near 340 nm is due to the Tb-THBA complex. This interpretation would be consistent with the 341 nm peak observed in the luminescence excitation spectrum monitored with a 546 nm emission from the Tb^{3+} ion. The free ligand is not expected to lead to a 546 nm emission. It should be pointed out that the possible presence of free ligands does not affect the key luminescence results and their interpretations because they were obtained with an excitation near 340 nm where the Tb-THBA complex of primary interest dominates the absorption and thereby the luminescence.

The QY_s of Tb-THBA in DMSO ($n_s = 1.479$) is found to be 0.22. Compared with the QY of other Tb complexes,[35–37] this is rather high and likely to be due to efficient sensitization of the Tb^{3+} ion by THBA.

Figure 2a shows the temperature dependence of the emission intensity of Tb-THBA (50 μM in acetonitrile) at 546 nm in the range from 15 to 65 °C. As the temperature increases, the emission intensity decreases rapidly. It is generally observed that the emission intensity of fluorphores decreases with increasing temperature due to thermal deactivation. In the case of the Tb^{3+} ion, the emission intensity also decreases with increasing temperature due to thermal activation from the emissive $^5D_4$ level of the Tb^{3+} ion to a nonradiative triplet level.[10,38,39] In addition, energy transfer from the THBA ligand to the Tb^{3+} ion is also likely to be influenced by temperature.

It is known that intensity-based measurements may suffer from variation of probe concentration and drifts of the optoelectronic components, including lamps and detectors. Decay-time-based methods, in contrast, are not compromised by these drawbacks and, therefore, are more accurate.[40] The measurement of the decay time also is not affected by variations in the thickness of the sensor film, which has a strong effect on the

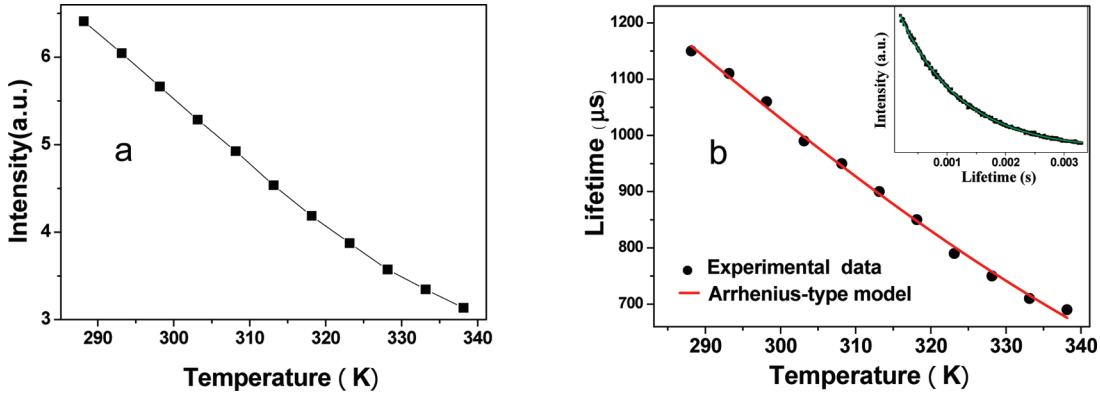


Figure 2. Temperature sensitivity of the Tb-THBA complex between 15 and 65 °C. (a) Luminescence intensity at 546 nm ($\lambda_{ex} = 334$ nm). (b) Luminescence lifetime ($\lambda_{ex} = 334$ nm, $\lambda_{em} = 545$ nm). The inset is the decay profile of the luminescence of a solution at 25 °C, which corresponds to a single-exponential function.

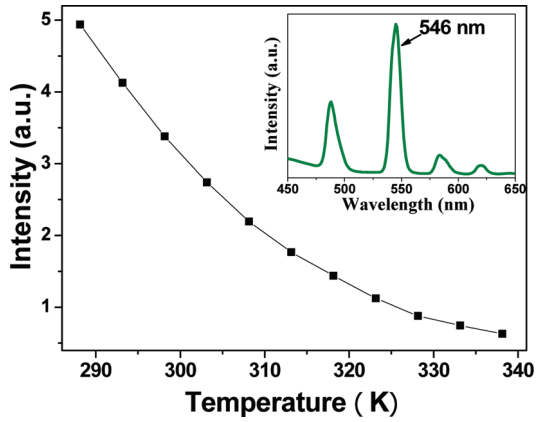


Figure 3. Temperature-dependent luminescence at 546 nm of the sensor film TSF-1 between 15 and 65 °C (excitation at 337 nm). The inset shows the emission spectrum at 15 °C.

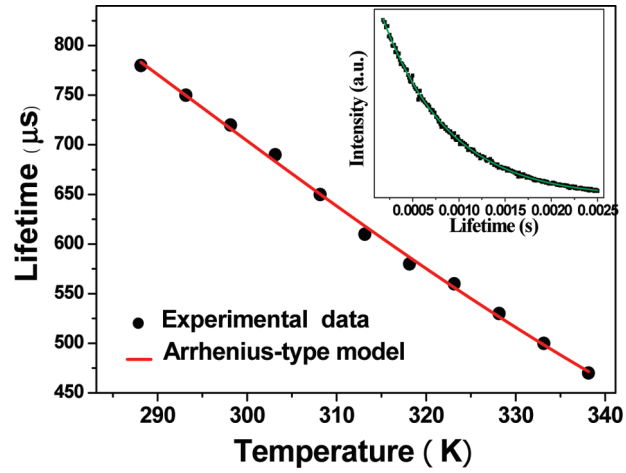


Figure 4. Effect of temperature on the luminescence lifetime of the temperature-sensing film TSF-1 (λ_{exc} = 337 nm, λ_{em} = 546 nm). The inset gives the luminescence decay at 25 °C to demonstrate single exponentiality.

intensity, and by variations in the distance between the light source and the sensor film because the intensity depends on the square of the distance (which holds for both exciting and emitted light).[12] Figure 2b shows the lifetime of the emission of Tb-THBA in acetonitrile solution as a function of temperature. All decay profiles correspond to a single-exponential function, as illustrated by the representative pattern in the inset. The lifetime of Tb-THBA in acetonitrile is 1.15 ms at 15 °C and exhibits a strong temperature dependency, which decreases by a substantial 40% on going from 15 to 65 °C. The decrease in the lifetime with increasing temperature can be described by an Arrhenius-type of equation

$$\tau = \left[k_0 + k_1 \exp\left(-\frac{\Delta E}{RT}\right)\right]^{-1} \quad (1)$$

where τ is the lifetime, k_0 the temperature-independent decay rate for the deactivation of the excited state, k_1 the pre-exponential factor, ΔE the energy gap between the emitting level and the upper deactivating excited state (determined from the fit), R the gas constant, and T the absolute temperature. The temperature dependence of the decay time of the luminescence of Tb-THBA can be well fit with the following parameters: $k_0 = 533\ s^{-1}$, $k_1 = 4.11 \times 10^5\ s^{-1}$, and $\Delta E = 1.71 \times 10^4$ kJ mol^{-1} (with a correlation coefficient r^2 of >0.997).

Temperature-Sensing Properties of the Polyurethane Sensing Film (TSF-1). Sensing temperature over a larger area is often required in medicine (for example, in dermatology) and for continuous sensing of temperature in flowing samples, such as blood. We, therefore, have designed a sensor film for use in continuous sensing that is composed of the temperature indicator Tb-THBA and a polyurethane hydrogel to host the indicator. The polyurethane matrix is highly biocompatible and well soluble in a mixture of ethanol and water but not in water alone.[41] The indicator does not interact with the solvent and gives a very homogeneous solution (a "paint"[6]) in the polymer/ethanol mixture. A colorless and fully transparent sensing film is obtained following the removal of ethanol.

The sensitivity of the resulting sensor film TSF-1 toward temperature was studied in terms of both emission intensity and lifetime. Figure 3 shows the temperature dependency of the emission intensity of the TSF-1 film with the intensity of the 546 nm band decreasing by almost 87% on raising the temperature from 15 to 65 °C. This result is similar to that obtained with Tb-THBA in solution. The average sensitivity of emission intensity to temperature (the change in intensity per °C,[12] defined as $\Delta I/(I_{ref}\Delta T)$) is −1.75% per °C between 15 and 65 °C, but −2.87%/°C in the range from 25 to 45 °C (the physiologically more significant range).

It can be seen in Figure 4 that the lifetime of Tb-THBA in TSF-1 rapidly drops with increasing temperature, a behavior that parallels the behavior of the complex in solution (Figure 2b). The average sensitivity of the lifetime of TSF-1 to temperature (the change in lifetime per °C, defined as $\Delta\tau/(\tau_{ref}\Delta T)$) is −0.8% per °C over the temperature range from 15 to 65 °C. The plot (Figure 4) can be well fit ($r^2 = 0.998$) by an Arrhenius equation (eq 1) and using the following parameters: $k_0 = 860\ s^{-1}$, $k_1 = 7.45 \times 10^5\ s^{-1}$, and $\Delta E = 1.79 \times 10^4$ kJ mol^{-1}. All the decay profiles are single-exponential (Figure 4, inset), thus suggesting that the chemical environment of the Tb^{3+} ion is uniform in the film at different temperatures. The signal changes are fully reversible, and no hysteresis is observed.

Characterization and Temperature-Sensitive Properties of the Tb-THBA Nanoparticles. To date, the Eu^{3+} ion chelates, rather than the Tb^{3+} ion chelates, have been designed and used for temperature sensing, including sensor paints[6] and in the form of microbeads[35] with a diameter of 3−10 μm. The microbead-based sensors work in the macro-realm, which is acceptable for the uses intended in the respective applications, but have limitations when measuring temperature inside cells or in sensor films due to a slow response because of their large size. Recent advances enable the miniaturization of temperature sensors down to the nanoscale.[42,43]

The Tb-THBA nanoparticles (NPs) were characterized by transmission electron microscopy (TEM) and found to have sizes mainly ranging from 10 to 20 nm (Figure 5). Aggregation of NPs was also observed but may be due to the slow evaporation of water during the preparation onto the grid used in TEM.[44] The diverse morphology presented in the image is likely to be due to the strong irradiation used in TEM, which may even crack particles with their substantial fraction of organic components.

The NPs were further characterized by using atomic force microscopy (AFM), which is a powerful tool for the characterization of organic nanostructures. Figure 6 displays a representative AFM image of NPs, which indicates an average particle size of ~10 nm, which is close to the results obtained with TEM.

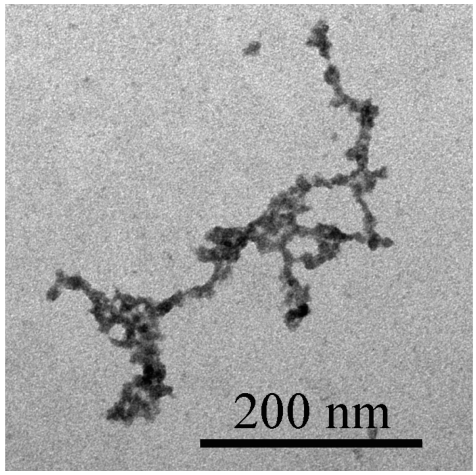


Figure 5. Transmission electron microscopy images of the Tb-THBA nanoparticles.

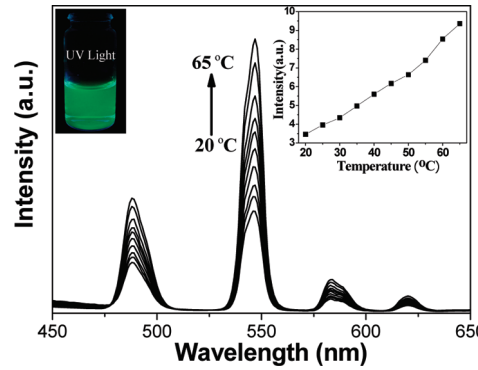


Figure 7. Luminescence spectra of Tb-THBA nanoparticles in an aqueous dispersion as a function of temperature. The inset on the left is a photograph of the aqueous dispersion of the nanoparticles under UV light excitation at room temperature. The inset on the right is a plot of luminescence intensity at 546 nm vs temperature.

The luminescence excitation spectrum (monitored at 546 nm) of the NPs is similar to that of the Tb complex in solution, except for an 11 nm blue shift (see the Supporting Information, Figure S1). Upon illumination with UV light, an aqueous dispersion of the NPs displays a green fluorescence emission peaked at 546 nm that can be easily detected by the naked eye (see the left inset in Figure 7).

The effect of temperature on the emission spectra also is shown in Figure 7. The right inset shows the corresponding emission intensity at 546 nm as a function of temperature profile. The average temperature sensitivity is 3.8% per °C over the full temperature range tested (20−65 °C) but 2.8% per °C in the physiological range (25−45 °C). This behavior is quite different from that of the Tb-THBA complex in solution and the sensor film TSF-1. In the latter two systems, the emission intensity decreased with increasing temperature as expected. On the basis of previous studies,[14,45] there is a nonemitting state that is slightly higher in energy than the S1 emitting state. A temperature increase could populate the nonradiative state, thus causing a decrease of the luminescence intensity.

In the case of NPs, an increase of the emission intensity with increasing temperature was observed, which is in contrast to the situation of the complex in solution. The increase with temperature is rather strong (Figure 7) over the range tested. This effect may be interpreted in terms of aggregation, which is stronger at lower temperatures in a water dispersion and results in increased concentration quenching of the luminescence. With the temperature increasing, the degree of aggregation of the nanoparticles is lessened and the diffusion of the nanoparticles will increase. Thus, the concentration quenching would be decreased, ultimately resulting in the increase of the luminescence intensity. It is also possible that more luminescent monomeric Tb-THBA complexes were generated with increasing temperature and resulted in the increase of luminescence. A similar observation of the increase of emission intensity with increasing temperature has been reported for a luminescent nickel (II) thermometer[14] and for ZnS:Mn nanoparticles.[46] In the case of ZnS:Mn NPs, the activation of nonluminescent surface trap states at higher temperatures was suggested as the possible reason for the increased luminescence at elevated temperatures. This is not likely to be the reason for the nanoparticles presented here because they are composed primarily of molecular complexes. Further research is needed to better understand the origin of this unusual temperature dependence of luminescence.

Next, the emission lifetimes of the Tb-THBA NPs as a function of temperature were determined in an aqueous dispersion. The decrease in decay time with increasing temperature is shown in Figure 8. The signal changes are fully reversible, and no hysteresis is observed. All decays are purely monoexponential, as can be seen in the inset. The average sensitivity of lifetime to temperature is −0.94% per °C over the temperature range from 15 to 65 °C. An Arrhenius fit with a correlation coefficient r^2 of 0.998 is obtained (see Figure 8) with the following parameters: $k_0 = 758\ s^{-1}$, $k_1 = 6.43 \times 10^5\ s^{-1}$, and $\Delta E = 1.56 \times 10^4\ kJ\ mol^{-1}$.

A decrease in lifetime with increasing temperature is quite common and indicates that thermally activated decay processes of the emitting state of the Tb^{3+} ion (via short-lived, upper-

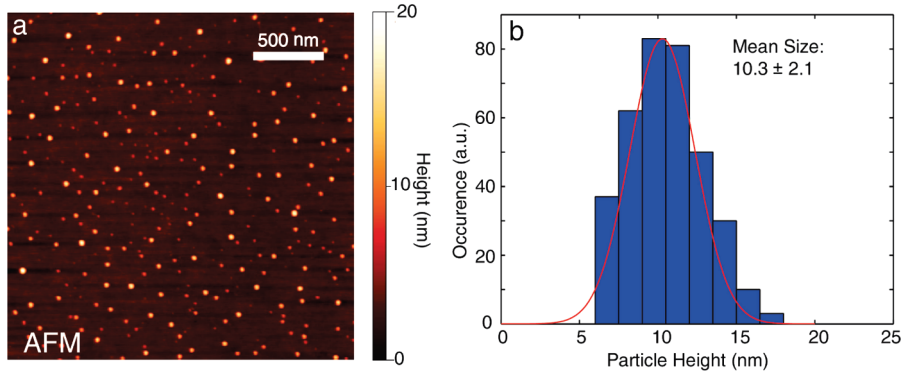


Figure 6. (a) A typical AFM image of the Tb-THBA nanoparticles. (b) Histogram of the height distribution of the nanoparticles; the red line is the Gaussian fit of the histogram and results in a mean size of 10.3 ± 2.1 nm of the particles.

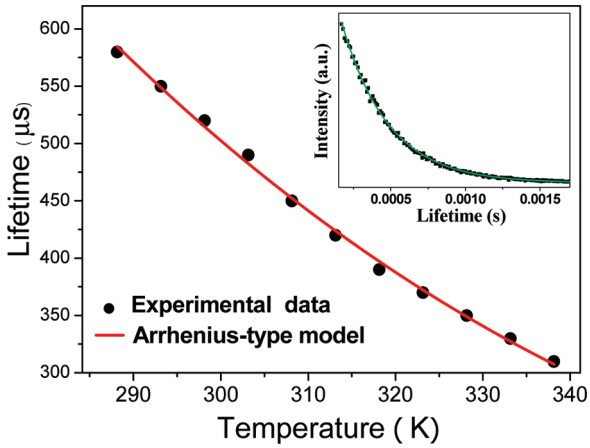


Figure 8. Luminescence lifetime of Tb-THBA nanoparticles in an aqueous dispersion as a function of temperature (excitation at 330 nm, emission at 546 nm). The inset shows the luminescence decay at 65 °C to demonstrate the single exponentiality of the decay.

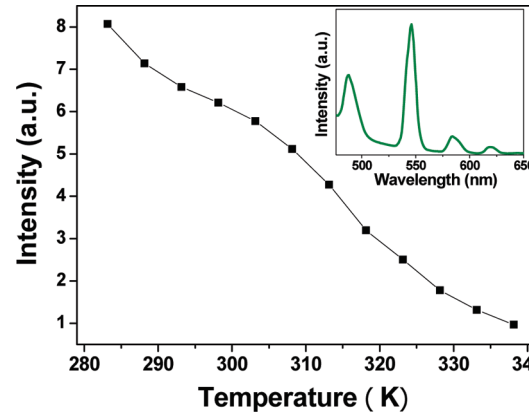


Figure 9. Temperature-dependent luminescence intensity (at 546 nm) of the PVA film containing Tb-THBA nanoparticles. The inset gives the emission spectrum at 10 °C.

lying excited states)[10] are quite efficient. The fact that the lifetime of the emitting state becomes shorter with increasing temperature while the luminescence intensity becomes stronger with increasing temperature is less common, however. It indicates that other electronic states (most likely of a nonemissive nature) are involved. Otherwise, the shortened lifetime is expected to correlate with decreased luminescence intensity. Such correlation may not happen if other states are involved in addition to the initial and final electronic states of luminescence. This is not too surprising because NPs usually possess a manifold of electronic states, including trap states,[46,47] that are more complex than molecules in solution.

Temperature-Sensing Film Containing Tb-THBA Nanoparticles in Poly(vinyl alcohol) (TSF-2). It was obvious to incorporate the nanoparticles (NPs) into a polymer, as described before, in order to obtain the respective sensor film. Unfortunately, attempts to incorporate the Tb-THBA NPs into the hydrogel polymer were not successful. We found, however, poly(vinyl alcohol) (PVA) to represent a viable matrix material. A "cocktail" containing dissolved PVA and the NPs (about 20 ppm of the NPs in the "cocktail") was spread onto a glass surface and dried in ambient air to give sensor film TFS-2. Its luminescence spectra were acquired at temperatures between 10 and 65 °C. Because of the low concentration of the NPs and because of strong background luminescence (see the Supporting Information, Figure S2), we were unable to measure the decay time. As shown in Figure 9, the intensity of emission strongly decreases with increasing temperature, which is different with Tb-THBA nanoparticles in an aqueous dispersion, and this is likely due to changes in the nonemission states, for example, surface trap states, caused by the PVA. All signal changes are fully reversible, and no hysteresis is observed.

4. Conclusions

The terbium complex introduced here is a promising luminescent indicator for the measurement of temperature. It exhibits very sharp emission lines (with an fwhm of less than 10 nm for the green emission) and displays a high quantum yield and a long decay time. Such features are ideal for multicolor (dual) sensing, for example, of temperature in combination with a second parameter. It enables both the emission intensity and the lifetime-based determination of temperature over the range from 15 to 65 °C and possibly even outside this range with further optimization. It can be used in solution (of fluid solvents and in a polymer) and in the form of nanoparticles (as a colloid in solution or in a polymer). Temperature affects both the emission intensities and the lifetimes. In addition, its decay times (between 400 and 800 μs) are well suited for time-resolved measurements, which are an excellent tool in terms of eliminating short-lived fluorescent background that is often observed in the case of biological studies. For the mechanism behind the temperature sensing, we have investigated by using a combination of experimental techniques and further research is clearly needed for a better understanding.

We recently[48] have presented the Eu(III) complex of dinaphthoylmethane-bis(trioctylphosphine oxide) as another lanthanide-based intriguing probe for sensing temperature. This probe is rather hydrophobic and was used in the form of NPs with a shell of an organosilane. It has the advantage of longer wavelengths of excitation (up to >400 nm) but is rather hydrophobic. The terbium complex presented here is much more hydrophilic, and stable NPs are immediately obtained by injecting an acetonitrile solution of Tb-THBA into water. As expected, such hydrophilic materials can be easily incorporated into hydrogels, which is almost mandatory in the case of temperature-sensitive paints or sprays for use in medicine.

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Supporting Information Available: The excitation spectra of Tb nanoparticles in an aqueous dispersion and the TbTHBA complex, the emission spectra of pure PVA film and PVA sensor film containing TbTHBA nanoparticles, and preparation of the pure (undoped) PVA film. This material is available free of charge via the Internet at http://pubs.acs.org.

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