3,5-Dihydroxy Benzoic Acid-Capped CaF₂:Tb³⁺ Nanocrystals as Luminescent Probes for the WO₄⁵⁻ Ion in Aqueous Solution

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ABSTRACT: We report a facile and effective luminescence method for the determination of the WO₄²⁻ ion in aqueous medium at initial pH = 6.3. This is achieved using 3,5-dihydroxybenzoic acid-capped CaF₂:Tb³⁺ (5%) nanocrystals (NCs) as a luminescent probe. This is accomplished based on the energy transfer luminescence from the WO₄²⁻ ion to the Tb³⁺ ion in small-size CaF₂:Tb³⁺ NCs. Hydroxyl groups on the surface ligand helps in binding the tungstate ion to the surface of the NCs. With the gradual addition of the WO₄²⁻ ion, the intensity of the Tb³⁺ excitation and emission spectra significantly increased. The linear range of the detection was from 1 to 10 μM for the WO₄²⁻ ion (R² = 0.99). The calculated detection limit was 0.4 μM (by applying the 3σ/K criterion).

1. INTRODUCTION

Tungsten (W) is a metal with unique physical and chemical properties. It has tremendous robustness with the highest melting point and boiling temperature among all elements discovered. The tungsten metal has a high density (19.3 g/cm³). Because of these specific properties of tungsten and its alloys, they have been used in many applications in various fields such as filaments in incandescent bulbs, in X-ray tubes, electronics, solar cells, welding rods, radiation shields, biomedical devices, mining industry, fertilizers, catalysis, and military ammunition. Tungsten is the heaviest metal present in living organisms, and it is present in some biomolecules such as bacteria and single-celled microorganisms. Tungsten occurs naturally in soils, sediments, and water at low concentrations (1.5 mg kg⁻¹). A significant amount of tungsten penetrates into the environment, soils, surface water, and ground water from discharge of tungsten mines, tungsten-utilizing industries, disposal of tungsten-containing products, military activities, coal-based power plants, and using fertilizers. If excess amount of tungsten enters into the soil solution, it will change soil properties such as pH, amount of dissolved oxygen, soil respiration, and toxicity to plants and earthworms. Tungsten has several oxidation states from −2 to +6. In general the +6 oxidation state is the most common and stable oxidation state. After introduction into the environment, tungsten occurs mainly in the form of oxy anions (WO₄²⁻). Depending on the concentration and pH of the medium, WO₄²⁻ undergoes polycondensation reaction and forms poly tungstates. In spite of their extensive use in various fields, the effect of tungsten compounds which strives adverse biological effects on humans and animals has been reported less frequently. The effects of tungsten on environmental systems have not been investigated extensively, and the published data are minimal. This is why it is important to develop innovative, selective, and sensitive methods for the determination of tungsten in aqueous media.

There are various methods to determine the tungstate ion including fluorescence atomic absorption spectroscopy (FAAS), inductively coupled plasma atomic emission spectroscopy (ICPAES), inductively coupled plasma mass spectrometry (ICPMS), X-ray fluorescence (XRF), and neutron activation analysis (NAA). The XRF and NAA methods limited their applications to nuclear reactors and radiochemical laboratories. The FAAS method suffers from poor sensitivity. ICPAES and ICPMS methods have better sensitivity and lower detection limit, but they suffer from high costs of the instrument. On the other hand, fluorescence methods are gaining increasing attention in determination and sensing of metal ions (anions and cations), toxic pollutants, organic molecules, biomolecules, tumors, and so forth. Fluorescence (luminescence) methods have high sensitivity, selectivity, and low detection limits, and they are cheap, mobile, and portable. Using the luminescence method, one can perform the detection studies in both the solution and solid state. However, there are only very few reports on WO₄²⁻
ion sensing using luminescence methods. For example, El-Shahawi et al. reported the determination and chemical speciation of trace concentrations of the WO$_4^{2−}$ ion (LOD = 7.51 μg L$^{−1}$) using the ion pairing reagent (procaine hydrochloride).$^{28}$ Besides, the luminescence detection based on the lanthanide-doped materials is more advantageous than using organic molecules. This is because, the lanthanide ion shows intraconfigurational 4f → 4f transitions resulting in sharp absorption and emission bands over a wide UV–vis–NIR region, large spectral shift of the emission bands versus sharp absorption and emission bands over a wide UV range, large spectral shift of the emission bands versus sharp absorption bands.

Additionally, the inorganic lanthanide-doped nanomaterials are resistant to photodegradation and high-temperature treatment in contrast to the organic fluorophores.$^{28,29}$ Moreover, Ln$^{3+}$ ions can be sensitized with some organic ligands, ions (Ce$^{3+}$ and Yb$^{3+}$), and host lattices.$^{30,31}$ Ln$^{3+}$-doped tungsten materials are used as a host matrix and a sensitizer.$^{33,34}$ Sensitization of lanthanide ion luminescence with WO$_4^{2−}$ ions offers a way to determine the tungstate content in a given solution. Nevertheless, there are very limited reports on the determination of the WO$_4^{2−}$ ion using lanthanide ions. For example, Lee et al. demonstrated the detection and removal of a trace amount of tungstate ion in aqueous solution, thanks to their light-harvesting ability and selective excitation followed by energy transfer to a Tb$^{3+}$ doped layered yttrium hydroxynitrate matrix.$^{35}$ To the best of our knowledge, there are no reports on the detection of tungstate ions in aqueous medium using lanthanide-doped luminescent nanomaterials.

In this study, we report the selective determination of tungstate ions in water via photoluminescence enhancement of the 3,5-dihydroxybenzoic acid (3,5-DHBA)-capped CaF$_2$:Tb$^{3+}$ (5%) nanocrystals (NCs). The 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ (5%) NCs with a smaller size were prepared via the microwave irradiation method (Scheme 1). We choose 3,5-DHBA as a capping ligand by taking into consideration that the carboxylic group on the aromatic ring can act as a passivation agent, the two hydroxyl groups help in dispersion of the NCs in water, and the aromatic ring can act as a sensitizer of the Tb$^{3+}$ ions in CaF$_2$ NCs. We choose the Tb$^{3+}$ ion as a luminescent probe because of its strong emission in the green region. However, CaF$_2$ was used as a host matrix because it has low absorption coefficient, high transmittance in the UV–vis range, and the ionic radii of Ca$^{2+}$ (1) and Tb$^{3+}$ (0.92) are closely similar. This helps in preparing the Ln$^{3+}$-doped NCs with a less amount of crystal defects. Moreover, from our earlier studies, it is realized that Ln$^{3+}$-doped CaF$_2$ NCs can be easily synthesized in small size (10–20 nm), which is very important for the fluorescence resonance energy transfer (FRET) process from the ligand to the Ln$^{3+}$ ion in CaF$_2$ NCs.$^{36,37}$

The synthesized NCs were selectively sensitized with tungstate ions, in the presence of several metal anions in the water system. Our study suggests that this presumably occurs because of energy transfer between tungstate ions and Tb$^{3+}$ ions in the small-sized CaF$_2$:Tb$^{3+}$ (5%) NCs.

2. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) pattern of the synthesized 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ (5%) NCs along with the standard diffraction pattern of the cubic-phase CaF$_2$ crystals are shown in Figure S1. The observed diffraction peaks of the NCs match well with the standard pattern, which confirms the formation of the pure cubic-phase CaF$_2$ NCs doped with Tb$^{3+}$ ions. The NCs have good crystallinity, confirmed by the sharp and intense diffraction peaks in the XRD pattern. The morphology and size of the NCs were analyzed using transmission electron microscopy (TEM). From the TEM image, the formation of the spherical shaped NCs with an average size of ≈19 ± 5 nm was confirmed, which is shown in Figure S2a. The histogram showing the size distribution of the NCs is presented in Figure S2b. The binding of the 3,5-DHBA molecules to the CaF$_2$:Tb$^{3+}$ NCs is confirmed by Fourier transform infrared (FT-IR) analysis. The FT-IR spectra of the 3,5-DHBA-capped CaF$_2$ NCs and pure 3,5-DHBA are shown in Figure S3. For the free 3,5-DHBA molecules, the band at 1684 cm$^{−1}$ is assigned to the C=O stretching vibrations of the −COOH group. In 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ NCs, the 1684 cm$^{−1}$ peak disappears and two new peaks at 1493 and 1418 cm$^{−1}$ corresponding to the asymmetric and symmetric stretching vibrations of the −COO$^{−}$ group were found. This confirms the attachment of 3,5-DHBA molecules to the surface of the NCs, preferably through the carboxylic acid group. The solid-state UV–vis absorption spectra of the pure 3,5-DHBA and 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ NCs are shown in Figure S4. For pure 3,5-DHBA, the broad absorption peak was observed in the range from 210 to 350 nm. In the spectrum of the 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ NCs, the broad peak is split into two peaks centered at 248 and 312 nm, which further confirms the attachment of the 3,5-DHBA ligand to the surface of the NCs.

The excitation and emission spectra of the 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ (5%) NCs are shown in Figure 1. All the

![Figure 1. Excitation (left) and emission (right) spectra of the 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ (5%) NCs.](https://dx.doi.org/10.1021/acsomega.9b03956)
photoluminescence studies were performed in aqueous medium. Upon excitation at 255 nm, the strong emission peaks are observed at 488, 544, 583, and 620 nm. These emission bands are assigned to the intraconfigurational $^5D_4 \rightarrow ^7F_j$ ($J = 6 \rightarrow 3$) transition characteristic of Tb$^{3+}$ ions. The presence of a very broad band in the excitation spectrum with maxima at 255 and 307 nm ($\lambda_{nm} = 544$ nm) is plausibly due to the 3,5-DHBA ligand excitation. This clearly suggests the occurrence of energy transfer from 3,5-DHBA to Tb$^{3+}$ ions within the 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ NCs. The other less intense bands observed in the range from about $\approx$320 to 400 nm are associated with the intraconfigurational 4f$\rightarrow$4f transitions, typical of Tb$^{3+}$.

The energy level diagram and the proposed energy transfer mechanism between WO$_4^{2-}$ and Tb$^{3+}$ ions, along with the energy transfer mechanism between the ligand molecule and Tb$^{3+}$, are given in Figure 2.

![Figure 2](image)

**Figure 2.** Schematic energy level diagram and energy transfer mechanism between 3,5-DHBA and Tb$^{3+}$ ions and the WO$_4^{2-}$ ion and Tb$^{3+}$ ion.

Briefly, the 3,5-DHBA ligand is excited from its ground state (highest occupied molecular orbital) to the nearest excited state [lowest unoccupied molecular orbital (LUMO)]. From the LUMO of the ligand, the excitation energy is transferred to the $^5D_1$ level of the Tb$^{3+}$ ion via a nonradiative pathway. Subsequently, the $^5D_1$ energy level (emitting state) is populated via a nonradiative relaxation and further relaxes to the ground state by radiative emission.

In order to investigate the sensing ability of the 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ NCs toward tungstate ions, the aqueous solution of WO$_4^{2-}$ was added to the Tb$^{3+}$-doped NCs dispersion (1 mg/mL) to get the final concentration of WO$_4^{2-}$ ions ranging from 1 to 1000 $\mu$M (the procedure details are given in the previous section).

From Figure 3, it is clear that the Tb$^{3+}$ emission intensity increases gradually with increasing WO$_4^{2-}$ concentration. Nearly, 12-fold enhancement of Tb$^{3+}$ luminescence is observed upon the addition of 1000 $\mu$M WO$_4^{2-}$ ions. This increase is due to energy transfer between the WO$_4^{2-}$ and Tb$^{3+}$ ions in the 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ NCs via the FRET process. The FRET process between Tb$^{3+}$ ions and WO$_4^{2-}$ ions is strongly supported by the emission spectra of WO$_4^{2-}$ ions, in the range from 330 to 450 nm ($\lambda_{nm} = 255$ nm), which strongly overlap with the Tb$^{3+}$ ion absorption region. The emission spectra of different concentrations of WO$_4^{2-}$ ions along with NCs dispersion are given in Figure S5. The occurrence of energy transfer from WO$_4^{2-}$ ions to Tb$^{3+}$ ions is additionally confirmed by observing the excitation spectra presented in to 1000 $\mu$M. This also confirms the influence of WO$_4^{2-}$ ions on the Tb$^{3+}$ luminescence (WO$_4^{2-}$ $\rightarrow$ Tb$^{3+}$ energy transfer).

However, upon excitation of about 255 nm, the Tb$^{3+}$ ions are excited by three possible mechanisms: (a) d$\rightarrow$f transition (allowed) of the Tb$^{3+}$ ions, (b) surface ligand (3,5-DHBA) to Tb$^{3+}$ ion energy transfer, and (c) WO$_4^{2-}$ to Tb$^{3+}$ ion energy transfer. We assume that, in the system studied, the third (c) mechanism is dominant. This is confirmed by measuring the absolute quantum yield (QY) for the 0.1 wt % of the colloidal NCs with the addition of WO$_4^{2-}$ ions in an aqueous medium, using an integrating sphere. The undoped, citric acid-capped CaF$_2$ aqueous colloidal NCs (0.1 wt %) were used as a reference. The QY was calculated assuming the ratio of the number of emitted photons to the absorbed ones. The calculated QY values are about 8% for the Tb$^{3+}$-doped NCs (without tungstate ions), and they increase to around 45, 49, 53, and 56% after adding 100, 200, 500, and 1000 $\mu$M WO$_4^{2-}$ ions, respectively (see Figure S6). These results confirm that the energy transfer from WO$_4^{2-}$ ions to Tb$^{3+}$ ions is more efficient than that of the other two mechanisms.

The digital image of the colloidal 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ NCs under UV light is given in Figure S7. It shows bright green emission of Tb$^{3+}$ ions from the colloidal NCs, recorded upon gradual addition of WO$_4^{2-}$ ions.

Figure 3. Photoluminescence spectra of the 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ NCs, collected upon gradual addition of WO$_4^{2-}$ ions.

![Figure 3](image)

Figure 4. The excitation maxima are blue-shifted from around $\approx$255 to 245 nm upon gradual addition of WO$_4^{2-}$ ions from 1

![Figure 4](image)

Figure 4. Excitation spectra of the 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ NCs, recorded upon gradual addition of WO$_4^{2-}$ ions.
where $I_0$ and $I$ represent the luminescence intensity of the NCs before and after the addition of $\text{WO}_4^{2-}$ ions, respectively, $[C]$ is the concentration of $\text{WO}_4^{2-}$ ions, and $K_{SV}$ is the quenching constant. As shown in Figure 5, a good linearity was observed between the luminescence intensity of the 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ NCs and $\text{WO}_4^{2-}$ concentration, in the range between 1 and 10 $\mu$M.

It is well known that the D$_2$O oscillators have lower energy of vibrations compared to H$_2$O, so they quench luminescence to a much less extent, and the expected luminescence lifetimes of the systems dissolved/dispersed in the deuterated solvents should be longer. Therefore, to understand the effect of water molecules on the luminescence lifetimes of the NCs, the lifetime experiments were also performed in D$_2$O before and after the addition of $\text{WO}_4^{2-}$ ions. The semilog plot of the decay curve in the figure implies multiexponential decay. The results are shown in Figure S10 and Table S3. The average lifetime value for the Tb$^{3+}$ ions of the NCs in D$_2$O is 7.06 ms, which is shorter than that in H$_2$O. This is due to greater aggregation of the NCs in D$_2$O (hydrodynamic size is 161.8 ± 1.07 nm) than that in H$_2$O, confirmed by DLS measurements (see Figure S9c). After the addition of $\text{WO}_4^{2-}$ ions to the NCs in D$_2$O, the percentage of the short-lived decay component gradually increases with the increase of $\text{WO}_4^{2-}$ ions because of the absence of vibrational quenching from −OH groups of H$_2$O molecules. The long-lived decay components slightly decrease because of the increase in the aggregation of the NCs with the addition of $\text{WO}_4^{2-}$ ions (531.76 ± 7.59 nm for 50 $\mu$M), as shown in Figure S9d. Therefore, the overall average lifetime values decrease to 6.59, 6.36, 5.92, 5.78, 5.7, and 5.6 ms after the addition of 10, 20, 50, 100, 200, and 500 $\mu$M $\text{WO}_4^{2-}$ ions, respectively. It is clear from Tables S2 and S3 that water molecules exert a considerable effect on the lifetime decay components of the Tb$^{3+}$ ion with the addition of the $\text{WO}_4^{2-}$ ion. The short-lived decay component of Tb$^{3+}$ ions decreases with the addition of $\text{WO}_4^{2-}$ ions in an aqueous medium. This is due to the effect of the vibrational relaxation of −OH groups on the excited lifetime (lifetime of the short-lived decay component decreases) of Tb$^{3+}$ ions in aqueous medium. The absence of vibrational relaxation of the −OH groups (high-energy oscillators) increases the lifetime of the short-lived decay component of Tb$^{3+}$ ions in D$_2$O.

To avoid the involvement of the d−f transition in the excitation of Tb(III), we measured the lifetime decay components of 3,5-DHBA-capped CaF$_2$ NCs at 280 nm excitation in H$_2$O and D$_2$O before and after the addition of $\text{WO}_4^{2-}$ ions. However, the obtained results are similar (slightly shorter lifetime values), and the tendencies are the same, as for the 255 nm excitation. The lifetime results at 280 nm excitation are given in Figure S11 and Table S4 as well as Figure S12 and Table S5 in H$_2$O and D$_2$O, respectively.

The effect of pH on the luminescence properties of the 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ NCs in the presence of $\text{WO}_4^{2-}$ ions was investigated in aqueous dispersion of the NCs. The pH plays a vital role in the nature of the $\text{WO}_4^{2-}$ ions in aqueous medium. This is because the acidic or alkaline nature of the solution greatly affects the polymerization process of tungsten ions (VI). The $\text{WO}_4^{2-}$ ions show polymorphism in different pH ranges of the solution. To analyze the effect of pH on the $\text{WO}_4^{2-}$ ion sensitization, we performed the luminescence studies of the NCs with 50 $\mu$M concentration of the $\text{WO}_4^{2-}$ ions at different pH values. Initially, at pH 6.3, the intense Tb$^{3+}$ emission was observed. Together with the increase or decrease in the pH of the NCs dispersion, the Tb$^{3+}$ emission (in the presence of $\text{WO}_4^{2-}$) decreased, as shown in Figure S13. The pH-dependent changes in the Tb$^{3+}$ emission intensity are probably due to the variations in the polymeric states of the $\text{WO}_4^{2-}$ ions at different pH values of the system.

Figure 5. Stern-Volmer plots of 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ (5%) NCs with the addition of 1000 $\mu$M concentration of $\text{WO}_4^{2-}$ ions in aqueous medium.

The limit of detection (LOD) value was calculated using eq 3 $\sigma/K$, where $\sigma$ is the standard deviation of the NCs blank emission and $K$ is the slope of the linear calibration plot. The calculated LOD value is about 0.41 ± 0.01 $\mu$M. The calculated LOD of $\text{WO}_4^{2-}$ ions using our method is comparable with that of other available methods (see Table S1) reported in the literature.

The emission lifetimes of Tb$^{3+}$ in the 3,5-DHBA-capped CaF$_2$:Tb$^{3+}$ NCs, before and after the addition of different concentrations of $\text{WO}_4^{2-}$ ions, were determined on the basis of the measured luminescence decay curves (see Figure S8, Table S2, and fitting procedure in the Supporting Information data), at $\lambda_{ex} = 255$ nm and $\lambda_{em} = 544$ nm. The semilog plot of the decay curve in the figure implies multiexponential decay. In order to determine the luminescence lifetimes, the recorded decay profiles were fitted to the bi-exponential function: $I = A_1 \exp(-x/\tau_1) + A_2 \exp(-x/\tau_2)$, with $R^2 > 0.99$, where $I$ is the emission intensity at time $x$; $A_1$ and $A_2$ are the amplitudes; $\tau_1$ and $\tau_2$ are the luminescence lifetimes (short-lived and long-lived components, respectively); and $R^2$ is the correlation coefficient. The initial (before the addition of $\text{WO}_4^{2-}$ ions) lifetime of Tb$^{3+}$ is ($\tau$) = 10.15 ms. Upon the addition of $\text{WO}_4^{2-}$ ions, the average lifetime values of Tb$^{3+}$ are shortened to 7.30, 6.39, 5.12, 4.33, 3.94, 3.71, and 3.64 ms for 5, 10, 20, 50, 100, 200, and 500 $\mu$M concentrations of the $\text{WO}_4^{2-}$ ions added, respectively. This shows the shortening effect of Tb$^{3+}$ emission lifetimes along with increasing $\text{WO}_4^{2-}$ concentration, which is opposite to the luminescence enhancement of Tb$^{3+}$ ions with the addition of $\text{WO}_4^{2-}$ ions. This can be explained by two effects: (I) increase in the number of H$_2$O molecules closer to the NCs surface, together with increase in concentration of the $\text{WO}_4^{2-}$ ion—lifetime of the surface Tb$^{3+}$ ions will be shorter because of the vibrational quenching by −OH groups of water molecules—and (II) aggregation of the small-sized NCs. This is confirmed by dynamic light scattering (DLS) measurements. The NC hydrodynamic size (without tungstate ions) is 122.7 ± 0.7 nm, and the size increases to 199.16 ± 7.67 nm after the addition of 50 $\mu$M $\text{WO}_4^{2-}$ ions (see Figure S9a,b).
The 3,5-DHBA-capped CaF₂:Tb³⁺ NCs are efficient materials for WO₄²⁻ ion determination compared to the other ligand-capped CaF₂:Tb³⁺ (5%) NCs. To confirm this, we have performed the luminescence measurements of trisodium citrate-capped CaF₂:Tb³⁺ (5%) NCs in the presence and absence of the WO₄²⁻ ion. We have used this ligand as citrates are commonly used surfactants/capping agents for Ln³⁺-doped NPs. No enhancement in the Tb³⁺ emission and excitation spectra was observed upon the addition of WO₄²⁻ ions, as shown in Figure S14. Indeed, the effective energy transfer occurs from the WO₄²⁻ to Tb³⁺ ions only in the case of the 3,5-DHBA-capped CaF₂:Tb³⁺ NCs, which act as a probe for the determination of WO₄²⁻ ions. The interactions between –OH groups of the 3,5-DHBA ligand and WO₄²⁻ ions keep the WO₄²⁻ ions in a close proximity to the surface of the NCs and helps in effective energy transfer from WO₄²⁻ to Tb³⁺ ions.

To verify the selectivity of the 3,5-DHBA-capped CaF₂:Tb³⁺ NCs toward WO₄²⁻ ions, the sensing studies were performed in the presence of the aqueous solutions of other similar anions (analytes). For the selectivity and interference studies, the concentration of other analytes in the solution was 10 times higher (500 μM) in relation to the WO₄²⁻ ions (50 μM). In Figure 6, the presented bar diagram clearly indicates that for other analytes, there is hardly any enhancement in the Tb³⁺ emission, except for MoO₄²⁻ ions. However, please note that the enhancement in the Tb³⁺ luminescence was observed after the addition of 10 times higher concentration of that analyte. The high selectivity of the 3,5-DHBA-capped CaF₂:Tb³⁺ NCs toward tungstate ions was also successfully confirmed by measuring the Tb³⁺ luminescence from the 3,5-DHBA-capped CaF₂:Tb³⁺ NC dispersion, containing both tungstate ions and other analytes (see Figure S15).

Briefly, 100 μL of aqueous solution of each (potentially interfering) analyte was separately added to the 1.8 mL of the NCs dispersion, followed by the addition of 100 μL of aqueous solution of tungstate ions, to get the final concentration of the interfering analyte and tungstate ions equal to 500 and 50 μM, respectively. The bar diagram in Figure S15 shows that except for MoO₄²⁻, the Tb³⁺ emission intensity from the NCs is selectively enhanced only upon the addition of WO₄²⁻ ions. However, there is considerable interference coming from VO₄³⁻, Cr₂O₇²⁻, MnO₄⁻, CN⁻, and Pb²⁺ and some interference from EDTA²⁻ and Cit⁻²⁻.

Evaluation of the WO₄²⁻ ion concentration in environmental samples is important because the WO₄²⁻ ions enter into water, sediments, and soil through fugitive dust generated in the processing from industrial and other sources. Moreover, the real water samples contain various other elements, organic molecules, and microorganisms, which may interfere in the detection and quantification of WO₄²⁻ ions. In order to check the possibility of the determination of WO₄²⁻ ions in real water samples, the luminescence detection experiments were performed in the tap, lake, and river water.

No enhancement in the Tb³⁺ emission was observed upon the addition of the abovementioned water samples to the NCs, confirming the absence of tungstate ions. We have added the desired concentration of WO₄²⁻ ions into the these water samples and observed enhancement in the Tb³⁺ emission from the 3,5-DHBA-capped CaF₂:Tb³⁺ NCs. We have calculated the percentage of recovery for different concentrations of WO₄²⁻ ions in tap, lake, and river water samples. The results are summarized in Table S6. The results suggest that our method can be applied for detection of tungstate ions in real water samples.

3. CONCLUSIONS

In summary, we have synthesized small-sized 3,5-DHBA-capped CaF₂:Tb³⁺ NCs via a microwave irradiation route. The NCs are water-dispersible and show bright green luminescence from Tb³⁺ ions. We have successfully used the obtained NCs for the optical detection of tungstate ions in water samples. With gradual addition of tungstate ions, the Tb³⁺ luminescence intensity significantly enhances (by an order of magnitude) because of energy transfer from WO₄²⁻ to Tb³⁺ ions via the FRET process. Thanks to this, we were able to correlate the luminescence signal intensity with WO₄²⁻ concentration and use it for optical determination of the ions in the solution. Moreover, measurement of the NC QY were carried out for different concentrations of WO₄²⁻ ions. The QY values of the NCs increase with increasing concentration of WO₄²⁻ ions. The study indicates that the developed detection method is highly sensitive and selective, with minimal interference from very few anions (at a very high concentration of the interfering analytes). Applying this method, we were able to detect tungstate ions in aqueous media in a concentration range from 1 to 1000 μM. Moreover, this method was successfully applied for the determination of tungstate ion concentration in real water samples (tap, lake, and river water).

4. EXPERIMENTAL SECTION

4.1. Materials. Tb₄O₇ (99.99%), NH₄F (99%), 3,5-DHBA (97%), Na₂WO₄·2H₂O (99%), NaIO₃ (99%) NH₄VO₃·2H₂O (99%), NaNO₃ (99%), Na₂EDTA (99%), Na₂PO₄ (99%), NaClO₄ (98%), CH₃COONa (99%), Na₂SO₄ (99%), K₂Cr₂O₇ (99%), Na₂MoO₄·2H₂O (99.5%), KSCN (99%), Pb(NO₃)₂ (99%), and D₂O (99.9 atom % D) were purchased from Sigma-Aldrich (www.sigmaaldrich.com). Ca(NO₃)₂ (98.5%), KMnO₄ (99%), NaNO₃ (97.5%), trisodium citrate-2H₂O (99%), Zn(NO₃)₂·6H₂O (99%), Cd(NO₃)₂·4H₂O (97%), Hg(NO₃)₂·H₂O (97%), KCN (97%), HNO₃ (65%), HCl (35–38%), and NaOH (98.8%) were purchased from POCH (Poland) (www.poche.com.pl). Deionized water was used for synthesis and experiments. All chemicals were of analytical grade and used without further purification.

4.2. Synthesis. 3,5-DHBA-capped CaF₂:Tb³⁺ (5 mol %) NCs were prepared via a microwave irradiation route. Briefly, the stoichiometric amount of Tb₄O₇ was converted into the
corresponding nitrate by dissolving it into 1 M nitric acid. Ca(NO₃)₂ and NH₄F were used as received. In a typical procedure, Ca(NO₃)₂·4H₂O (0.95 mmol) and Tb(NO₃)₃ (0.05 mmol) were transferred to a 100 mL beaker and dissolved in to 10 mL of water. 3,5-DHBA (2 mmol) was taken into a 50 mL beaker and mixed with 20 mL of water. The ligand solution was added to the nitrate mixture and stirred vigorously for 1 h. Then, 5 mL of 4 mmol NH₄F aqueous solution was added dropwise into the abovementioned precursor and stirred for 30 min. Subsequently, the colloidal solution was transferred into a 100 mL Teflon vial. The vial was tightly sealed with a Teflon cap and heated to 150 °C for 45 min via the microwave irradiation method (Ertec microwave reactor). After completion of the reaction, the white precipitate was collected by centrifugation and washed multiple times with water and then dried under vacuum. The similar method was applied for the preparation of trisodium citrate-capped CaF₂:Tb³+ (5%) NCs. In the latter case, the 3,5-DHBA ligand was replaced with trisodium citrate as a capping ligand.

4.3. Characterization. Powder diffractograms were recorded on a Bruker AXS D8 ADVANCE diffractometer in the Bragg–Brentano geometry, with Cu Kα1 radiation (0.15406 nm) in a 2θ range from 6 to 60°. TEM analysis was performed with a Hitachi HT7700 transmission electron microscope, at 100 kV accelerating voltage. The FT-IR spectra were recorded for the samples mixed with KBr and pressed into disks using a JASCO FT/IR-4200 spectrometer in the range from 4000 to 400 cm⁻¹. Luminescence measurements were performed with a Hitachi F-7000 spectrophotometer at ambient conditions, and the spectra were corrected for the apparatus response. The optical absorption spectra of all the samples were recorded in a diffuse reflectance mode with a JASCO V770 UV−vis−NIR spectrophotometer equipped with a spherical integrator (150 mm in diameter). DLS measurements were performed using a Malvern Zetasizer Nano ZS Instrument.

4.4. Experimental Procedure for WO₄²⁻ Assay. For the luminescence assay of WO₄²⁻ ions, 1.9 mL of 0.1 wt % (1 mg/mL) 3,5-DHBA-capped CaF₂:Tb³⁺ (5%) NC aqueous colloidal was each time mixed with 0.1 mL of Na₂WO₄ aqueous solution of increasing concentration to achieve the final concentrations ranging from 1 to 1000 μM. The stock solution concentration of WO₄²⁻ used was equal to 20 mM. The blank solution was prepared by mixing 1.9 mL of 3,5-DHBA-capped CaF₂:Tb³⁺ NCs (1 mg/mL) with 0.1 mL of water. The as-prepared colloidal solutions were each time incubated for 15 min at room temperature. The luminescence spectra for the obtained solutions were recorded using λₜₐₓ = 255 nm and λₘₜₐₓ = 544 nm, for the emission and excitation spectra, respectively. For lifetime experiments with deuterated solvents, the NC dispersion and WO₄²⁻ ion solution were prepared using deuterium oxide. All the luminescence experiments were conducted at room temperature, and the initial pH of the NCs solution was around 8±3. For the pH-dependent luminescence studies, the pH of the NC aqueous dispersion was adjusted with diluted HCl or NaOH aqueous solutions. To verify the interference of other ions in the detection of WO₄²⁻ the detection studies were performed in the presence of the following ions: IO₃⁻, VO₄³⁻, NO₃⁻, NO₂⁻, EDTA²⁻, PO₄³⁻, ClO₄⁻, ACO⁻, SO₄²⁻, Cit⁻, Cr₂O₇²⁻, MnO₄⁻, MoO₄²⁻, Zn²⁺, Cd²⁺, Hg²⁺, CN⁻, SCN⁻, and Pb²⁺.

4.5. Procedure for Real Water Sample Analysis. In order to obtain proof of concept of this work and show the real application potential of our method, we have used it for the direct determination of WO₄²⁻ ions in tap, lake, and river water samples. Tap water was collected from a water tap, installed in our laboratory, (Poznań, Poland). Lake water was collected from the Malta Lake, Poznań, Poland. River water was collected from the Warta river, Poznań, Poland. All water samples were filtered using a 2 μm Whatman filter paper to eliminate solid impurities. For real water analysis, WO₄²⁻ stock solution was separately mixed with tap, lake, and river water. Real water sample solutions (100 μL) containing different concentrations of WO₄²⁻ ions were separately added to 1.9 mL of NCs solution to get the final concentrations of WO₄²⁻ ions equal to 5, 8, and 10 μM. The experiments were conducted after 15 min of incubation at room temperature. The previously described luminescence detection method was followed to investigate the detection ability of the 3,5-DHBA-capped CaF₂:Tb³⁺ NCs toward WO₄²⁻ ion detection in real water samples.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03956.

XRD of 3,5-DHBA-capped CaF₂:Tb³⁺ NCs; TEM image and particle size histogram; FT-IR spectra of pure 3,5-DHBA and 3,5-DHBA-capped CaF₂:Tb³⁺ NCs; absorption spectra of pure 3,5-DHBA and 3,5-DHBA-capped CaF₂:Tb³⁺ NCs; emission spectra for different concentrations of WO₄²⁻ ions in the presence of NCs dispersion; scattered and emission spectra for QY measurements in the integrating sphere; digital images, table of comparison of the LOD; lifetime spectra of NCs with WO₄²⁻ ions in aqueous medium; table of lifetime decay values of NCs with WO₄²⁻ ions in aqueous medium; lifetime spectra of NCs with WO₄²⁻ ions in D₂O; table of lifetime decay values of NCs with WO₄²⁻ ions in D₂O; DLS measurements in H₂O and D₂O in the absence and presence of WO₄²⁻ ions; effect of pH on the emission intensity in the presence of WO₄²⁻ ions; photoluminescence and excitation spectra of trisodium citrate-capped CaF₂:Tb³⁺ NCs without and after the addition of WO₄²⁻ ions; bar diagram of interference study of NCs containing both WO₄²⁻ ions and other analytes; and table of recovery results of the proposed luminescence method for WO₄²⁻ ions in tap, lake, and river water (PDF).

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