Luminescent Lanthanide-Based Probes for the Detection of Nitroaromatic Compounds in Water

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Abstract: A new mixed pyridyl-carboxylate ligand with two picolinate chromophores and a flexible linear spacer, potassium 2,2’-(butane-1,4-diylbis((pyridin-2-ylmethyl)-azanediyl))diacetate (K_{2}bpbd), which is obtained in high yield and spectroscopically characterized, has been utilized to make new lanthanide complexes, namely, [Ln(bpbd) (H_{2}O)_{2}(NO_{3})_{x}]·xH_{2}O, where Ln = Tb (1) and x = 6, Ln = Sm (2) and x = 7, and Ln = Dy (3) and x = 7. These complexes have been extensively characterized by various spectroscopic techniques (UV-vis and Fourier transform infrared spectroscopy), elemental analyses, thermogravimetric analysis, field emission scanning electron microscopy, and powder X-ray diffraction. These show very intense characteristic luminescence features that confirm the antenna effect of the ligand on the metal center. These complexes have been utilized for the detection of various nitroaromatic compounds. Among these three complexes, 1 is found to be the best for the selective sensing of 2,4,6-trinitrophenol in water with a detection limit of (0.35 ± 0.05) ppm. Its Stern–Volmer constant, K_{SV} [(5.48 ± 0.1) × 10^{4} M^{-1}], is one of the highest among similar sensors reported so far.

Introduction

In recent years, lanthanide complexes have attracted researchers from various fields for their unique structural features and interesting magnetic, catalytic, and optical properties. Thus, these multifunctional materials have become very important as magnetic probes, nuclear medicine, optical amplifiers, and sensors, where modulation of the structures of lanthanide complexes is found to be the key to their application in such fields. On the basis of the understanding in coordination chemistry, the structures of lanthanide complexes can be controlled by metal ligand interaction, interligand steric constraints, and so forth. The high ionic character of lanthanides favors binding with the atoms, which are hard Lewis bases, requiring a combination of carboxylate and amine as ligands. For ligands with low denticity, the final structure remains difficult to predict in such complexes and often results in coordinated solvent molecules, which are detrimental to certain properties such as luminescence (vide infra). On the other hand, the coordination chemistry of lanthanides with multidentate ligands affords mononuclear, discrete polynuclear, and coordination polymers.

Utilizing such information, most recently, the use of polycarboxylates (two-component systems, where the metal salt is the other component) or a combination of neutral and anionic nitrogen and oxygen-containing ligands (three-component systems) has been initiated for the generation of functional porous frameworks with an expected increased thermal stability. However, the lanthanide chemistry (two-component systems) with mixed ligands, containing both pyridyl and carboxylate groups in the same ligand, has been explored primarily for establishing their physicochemical properties with limited applications. In particular, such neutral species are crucial in the development of new materials with specificity for applications that utilize molecular recognition.

Lanthanide(III) ions show very unique spectroscopic properties because of the shielding of the 4f orbitals by the filled 5s and 5p subshells with very narrow “finger-like” emission bands which emerge from f–f transitions. Each lanthanide ion shows characteristic absorption and emission spectra and can emit in the entire electromagnetic spectrum from near-UV [Gd(III) and Eu(III) (red), Tb(III) (green), Sm(III) (orange), Dy(III) (yellow), Tm(III) (blue)] to near-infrared (NIR) [Yb(III), Nd(III)]. On the basis of the high energy gap between the lowest luminescent energy state and the highest nonluminescent energy state, Sm(III), Eu(III), Tb(III), and Dy(III) ions give strong luminescence in the...
visible range. Their unique luminescence properties include sharp emission, large Stoke shift, insensitivity to oxygen, and a long excited lifetime which ranges from microseconds (for Nd and Yb) to milliseconds (for Tb and Eu). Their luminescence not only decays because of a radiative process but can also be quenched through nonradiative decay of the excited state via coupling of the lanthanide energy level with the vibrational modes in the surrounding of the lanthanide ion. The most efficient quenchers are the O–H oscillators (both in solution and in the solid state). The extent of this quenching is inversely proportional to the energy gap between the emissive state and the ground state of the metal. The other quenchers of luminescence are the harmonics of N–H, C–H, and C=O stretching vibrations, but not as O–H oscillators. Polydentate ligands not only increase the stability of the lanthanide complexes in solution but also allow the metal center to be protected from water molecules. Therefore, the luminescence of the lanthanide-based complexes is controlled by the denticity of the ligand. In the presence of linkers with low denticity, the lanthanides coordinate to solvent molecules, such as water, resulting in the deactivation of the Ln(III) excited states nonradiatively.

Because of the parity-forbidden intraconfigurational f–f transitions by the Laporte selection rule, the Ln(III) ions show these transitions with a very low molar extinction coefficient ($\epsilon < 10 \text{ M}^{-1} \text{cm}^{-1}$), limiting the practical applications of the lanthanides. Fortunately, this drawback of lanthanides can be circumvented by using aromatic chromophores, which are directly bound to the Ln(III) center and absorbed in the UV–vis spectral region. Thus, the absorption spectra of lanthanide complexes are dominated by the ligand-centered absorption bands, and the extent of this quenching is inversely proportional to the energy gap between the emissive state and the ground state of the metal.

The aromatic and heteroaromatic carboxylate-based ligands are extensively used for the sensitization of lanthanide emitters. However, exploitation of such compounds has been limited for sensing applications.

Sensing based on luminescence is gaining more attention because of its simplicity, selectivity, and sensitivity. The nitroaromatic compounds (NACs) such as nitrobenzene (NB), dinitrobenzene (DNB), dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), and 2,4,6-trinitrophenol (TNP) (also known as picric acid, PA) are strong oxidizing agents because of the presence of the electron-withdrawing groups. Out of these, TNT and TNP, which are highly explosive and dangerous energy sources, have been frequently used as common ingredients of explosive devices, such as bombs, grenades, and mine fillings. TNP is also used in dyes, fireworks, and leather industries. During its production and use, it is released into the environment, polluting air, underwater, soil, and the biosystem, consequently leading to serious health and environmental issues. Therefore, the detection of NACs has attracted more attention in the last decade for the concerns of national security, civilian safety, and environmental protection.

There are many organic polymers, coordination polymers, and metal–organic frameworks which are used for the detection of NACs. However, the lanthanide systems remain far less explored compared to the frameworks based on the d-block transition-metal elements for the reasons mentioned above.

With an understanding for the choice of ligand and its denticity, in this work, a new mixed pyridyl–carboxylate ligand with two picolinate chromophores and a flexible linear spacer, potassium 2,2’-(butane-1,4-diyl bis((pyridin-2-ylmethyl)-azanediyl))-diacetate (K$_2$bpbd), was synthesized (Scheme 1). The picolinate moiety acts as an antenna, whereas the carboxylate and the C4 spacer direct the dimensionality and the geometry of the self-assembled metal complexes. Using this ligand, three new lanthanide complexes, namely, [Ln(bpbd)-$(\text{H}_2\text{O})_2$(NO$_3$)]$_x$H$_2$O, where Ln = Tb (1) and x = 6, Ln = Sm (2) and x = 7, and Ln = Dy (3) and x = 7, have been prepared and extensively characterized by various spectroscopic techniques [UV–vis and Fourier transform infrared (FTIR) spectroscopy], elemental analyses, thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), and powder X-ray diffraction (PXRD). These complexes show very intense characteristic luminescence features that confirm the antenna effect of the ligand on the metal center. Their luminescence property was exploited to do sensing experiments with various NACs.
complexes, 1 is found to be the best for the selective sensing of TNP in water with a detection limit of (0.35 ± 0.05) ppm.

Results and Discussion

Synthesis. The ligand K2bpbd was obtained in two steps from commercially available 2-pyridinecarboxaldehyde, 2-bromoacetic acid, and 1,4-diaminobutane in an overall yield of 60% (see Scheme 1). In the first step, the condensation of the aldehyde and diamine in a ratio of 2:1 resulted in the formation of a Schiff base which was reduced by sodium borohydride in a single pot to yield the intermediate bpbn in 98% yield. The 1H nuclear magnetic resonance (NMR) spectrum confirmed the formation of bpbn (see Figure S1). In the second step, bpbn was reacted with the potassium salt of 2 equiv of potassium hydroxide to synthesize K2bpbd in high purity (see Figure S2). Its high-resolution mass spectrometry data are consistent with its formula (see Figure S3). It was further characterized by FTIR spectroscopy (see Figure S4). For K2bpbd, a peak at 1592 cm−1 corresponds to the asymmetric stretching frequency of carboxylate, a peak at 1402 cm−1 corresponds to the symmetric stretching of carboxylate, and a peak at 768 cm−1 corresponds to the C−H stretching near the nitrogen of pyridine. Compared to the ethylene−1 or propylene−2, where these were isolated as the perchlorate salt or the acid itself requiring either extra steps or further neutralization of the ligand with a base prior to reacting with metal salts, we prepared it as a potassium salt, K2bpbd. This provides added advantages to isolate it and to separate the by-product KNO3 (which is much more soluble in water than the metal complex) in making the metal complexes.

The lanthanide complexes (1−3) were synthesized by reacting the corresponding lanthanide nitrate salt and the ligand in a 1:1 ratio in water by the conventional one-pot synthesis at room temperature. All the complexes obtained are off-white in color. Our attempts to get suitable single crystals of 1−3 were not successful. This is consistent with the reported fact that the crystallization of such compounds is difficult. Thus, numerous other analytical techniques have been used to fully characterize them.

Spectroscopic Characterization. The FTIR spectra of 1−3 were collected at room temperature in the solid state using KBr pellets from 4000 to 400 cm−1. These spectra (Figures S5) are very similar in nature. To utilize the FTIR data of these metal complexes for their structural characterization, the binding of the carboxylate groups in the bpbd ligand and the nitrate anion was analyzed based on the data listed in Table 1. The asymmetric and symmetric stretching vibrations of the dicarboxylate groups in 1−3 are at ~1584−1594 and ~1407−1410 cm−1, respectively. The difference in the symmetric and asymmetric stretching vibrations (184, 176, and 180 cm−1, respectively, for 1−3) is in the range observed for chelated bidentate carboxylates but below the typical value (>225 cm−1) for the monodentate binding mode. These values are similar to those observed for over 10 lanthanide compounds with the ethylene−1 and propylene−2 analogs of bpbd. This suggests that the carboxylate group is coordinated to the metal center in a bidentate chelated binding mode. Similarly, a peak at 1384 cm−1 in 1−3 corresponds to the nitrate binding in a monodentate fashion to the metal center. For a concrete confirmation of the chelated binding mode of the carboxylate group and the monodentate binding mode of the nitrate group in 1−3, the FTIR data of few similar compounds, which are also characterized by single-crystal X-ray diffraction, are considered. For example, in (Me2NH)3[Eu3(HMFDA)4(NO3)4(DMF)2]·4H2O·2MeCN (where H2HMFDA = 9-methyl-9-hydroxy-fluorene-2,7-dicarboxylic acid), the values for the symmetric and asymmetric stretching frequencies of the chelated carboxylate group were observed at 1589 and 1429 cm−1, respectively, whereas for the monodentate nitrate group, a peak at 1388 cm−1 was observed.

For the lattice and coordinated water molecules, the characteristic broad features at 3423 and ~3247–3256 cm−1, respectively, are observed because of the O−H stretching frequency. Our group has been working with such systems containing mixed carboxylate and pyridyl ligands for a decade and thus has developed a database to supplement the data compiled in Nakamoto book. In one such study, we have unequivocally established the stretching frequencies of the lattice and coordinated water molecules similar to those observed for 1−3 through variable-temperature FTIR and single-crystal-to-single-crystal transformation.

Thermal Properties. For studying the thermal stability as a function of temperature, TGA was conducted for the single-phase polycrystalline samples of 1−3 between 25 and 500 °C under a dinitrogen atmosphere (see Figure 1). From the multistep decomposition process observed for these compounds, it is clearly evident that they show similar thermal stability. Using the differential thermal analysis (DTA) curves (see Figure S6), three steps in their decomposition process are established. In the first step, six lattice water molecules are lost below 100 °C with a good agreement between the calculated and found values (14.4% calc, 12.8% found for 1; 16.6% calc, 16.8% found for 2; and 16.7% calc, 16.5% found for 3). With this initial loss of lattice water molecules, these compounds are stable up to 220 °C. The second step corresponds to the loss of coordinated water molecules and the multistep decomposition process observed for these compounds, it is clearly evident that they show similar thermal stability. Using the differential thermal analysis (DTA) curves (see Figure S6), three steps in their decomposition process are established. In the first step, six lattice water molecules are lost below 100 °C with a good agreement between the calculated and found values (14.4% calc, 12.8% found for 1; 16.6% calc, 16.8% found for 2; and 16.7% calc, 16.5% found for 3). With this initial loss of lattice water molecules, these compounds are stable up to 220 °C. The second step corresponds to the loss of coordinated water molecules and the

Table 1. Selected FTIR Data for the Coordinated Carboxylate and Nitrate in 1−3

| complex | νasym (CO2−) (cm−1) | νsym (CO2−) (cm−1) | νasym (NO3−) (cm−1) | νsym (NO3−) (cm−1) |
|---------|---------------------|---------------------|---------------------|---------------------|
| 1       | 1594                | 1410                | 1384                | 1384                |
| 2       | 1584                | 1408                | 1384                | 1384                |
| 3       | 1587                | 1407                | 1384                | 1384                |
release of nitrate ion (15.3% calcd, 17.3% found for 1; 14.5% calcd, 14.46% found for 2; and 15.6% calcd, 13.5% found for 3). In the final step, up to 500 °C, it is found that a partial decomposition of the bpbd ligand (carboxylate and pyridyl groups) has occurred (34.99% calcd, 33.22% found for 1; 35.5% calcd, 35.6% calcd for 2; and 38.02% calcd, 36.7% found for 3).

**Crystallinity and Morphology.** The PXRD patterns were recorded for 1–3 at room temperature, as shown in Figure 2. On the basis of these patterns, 1, 2, and 3 are found to be isostructural. It also confirms the phase purity and crystallinity of bulk samples of 1–3.

![Figure 2. PXRD patterns of 1–3.](image)

To comprehend the surface morphology of 1–3, FESEM was performed (see Figure 3). The samples 1, 2, and 3 show polyhedral, flake, and globular type of morphology, respectively.

**Proposed Structure.** As mentioned earlier, our efforts to elucidate the structures of 1–3 by single-crystal XRD were not successful. However, their intensive characterization described in the above sections provides important observations to propose their structures, as shown in Figure 4 for 1 as an example. First of all, their PXRD data suggested the isostructural nature of 1–3. Furthermore, their TGA patterns are very similar in nature, whereas the absorbance in 1–3 is ligand-centered. Second, based on the analysis of FTIR data, the binding modes of the carboxylate groups in the bpbd ligand and the nitrate anion are found to be bidentate (chelated) and monodentate, respectively. Utilizing such detailed and conclusive information, a polymeric chain structure can be proposed. In this structure, the coordination number of the metal center is 11, which is not unusual but observed in many lanthanide complexes. Considering a few crystal structures of lanthanides with similar ligands where the carboxylate groups are attached to the pyridyl groups instead of the alkyl nitrogen (compared to bpbd) as well as other polycarboxylate ligands, this structure is reasonable. This provides an understanding for the interaction of NACs with 1–3 (vide infra), and thus their application as luminescent probes for the detection of NACs can be studied utilizing the antenna effect of the ligand. Furthermore, the stability of these complexes in water is confirmed by the observation of the antenna effect of the ligand (see “Photophysical Properties” section).

**Photophysical Properties.** The emission spectra of 1–3 recorded at room temperature with 1 mg in 2 mL Milli-Q water are displayed in Figures 5–7. As a reference, the emission spectrum of the K2bpbd ligand is shown in Figure S7. The characteristic luminescent behavior of 1–3 suggests that the intramolecular energy transfer from the ligand to Ln(III) is...
observed, with no ligand-centered broad emission. In case of Tb(III), intramolecular energy transfer is much more effective than those for Dy(III) and Sm(III) complexes. Comparing the emission spectra of \( \text{1} \) and \( \text{Tb(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \) in Figure 5, it is clear that the ligand has sensitized the Tb(III) center and thus demonstrates the antenna effect in the lanthanide complexes.

\[ \text{[Tb(bpbd)(H}_2\text{O})_2\text{(NO}_3\text{)}]\cdot6\text{H}_2\text{O (1).} \]

The solid-state reflectance spectra of \( \text{K}_2\text{bpbd} \) and \( \text{1} \) (Figure S8) were recorded to determine the excitation wavelength for \( \text{1} \) at 340 nm. This is in the range of the excitation wavelength (325–340 nm) used for other Tb compounds in the literature. Upon excitation at 340 nm, the emission spectrum was collected in the range 470–650 nm at room temperature. It displays characteristic emission bands at 489, 545, 586, and 621 nm and the typical emission spectrum dominated by the hypersensitive \( ^5\text{D}_4 \rightarrow ^7\text{F}_5 \) transition. The emission band at 545 nm is the most intense, which corresponds to green luminescence, as shown in Figure 5.

\[ \text{[Sm(bpbd)(H}_2\text{O})_2\text{(NO}_3\text{)}]\cdot7\text{H}_2\text{O (2).} \]

The emission spectrum of \( \text{2} \) recorded from 555 to 750 nm at room temperature, which correspond to yellow luminescence, result from the \( ^4\text{F}_9/2 \rightarrow ^6\text{H}_{15/2} \) and \( ^4\text{F}_9/2 \rightarrow ^6\text{H}_{13/2} \) transitions, respectively, whereas a very weak signal at 664 nm is attributed to the \( ^4\text{F}_9/2 \rightarrow ^6\text{H}_{11/2} \) transition. However, the intensity of bands at 484 and 576 nm is 4 times less than that observed for the most intense peak for \( \text{1} \).

\[ \text{[Dy(bpbd)(H}_2\text{O})_2\text{(NO}_3\text{)}]\cdot7\text{H}_2\text{O (3).} \]

The emission spectrum of \( \text{3} \) was recorded at room temperature. The excitation at 270 nm resulted in second-order interference, and thus to avoid this the emission spectrum was recorded in two segments. As shown in Figure 7, the observed metal-centered emission bands at 484 and 576 nm, which correspond to orange luminescence, are attributed to the \( ^4\text{F}_9/2 \rightarrow ^6\text{H}_{11/2} \) transition. However, the intensity of bands at 484 and 576 nm is 4 times less than that observed for the most intense peak for \( \text{1} \).

**Sensing of NACs.** On the basis of the photophysical properties of \( \text{1} \sim \text{3} \), luminescence sensing was carried out with various NACs (TNP, TNT, 2,4-DNP, 2,4-DNT, 2,6-DNT, 1,3-DNB, 4-NP, 2-NP, and NB) in water. The quenching efficiency (%) of different NACs by \( \text{1} \), calculated using the equation \( \left( I_0 - I \right)/I_0 \times 100\% \), is plotted in Figure 8. The luminescence intensity at 545 nm is monitored which decreases with a gradual addition of 10 \( \mu \text{L} \) of NAC (2 mM in water) for a total of 120 \( \mu \text{L} \). It is observed that other NACs exhibit negligible to moderate quenching effect in comparison...
to TNP, thereby showing better selectivity for TNP. The quenching efficiency for 1 for the NACs in water shows the following order: TNP \( \gg \) 2,4-DNP > 4-NP > 2-NP > NB > 1,3-DNB > 2,6-DNT > TNT \( \gg \) 2,4-DNT. The decrease in quenching efficiency with the reduction in the acidity of phenolic NACs can also be ascribed to the presence of Lewis basic moieties like oxygen of the nitrate anion, where these oxygen atoms can form H-bonding interactions with the phenolic protons of the nitrophenol derivatives, which are absent in the other NAC analytes. Focusing on TNP, an incremental addition of TNP to 1 produced an inconceivable and significant luminescence quenching of \( (92 \pm 0.16)\% \) (Figure 9).

The three-dimensional (3D) Stern–Volmer (S–V) plot of all analytes for 1 is shown in Figure 10. In Figure S9, all nitrophenols are compared. The S–V plot of TNP for 1 shows linearity at lower concentrations and deviates from linearity at higher concentrations (Figure S10). This was further elaborated by using the S–V equation

\[
I_0/I = K_{SV}[A] + 1
\]

where \( I_0 \) and \( I \) are the luminescence intensities of the probes, before and after the addition of NACs, \( K_{SV} \) is the S–V constant \( (M^{-1}) \), and \([A]\) is the molar concentration of the analyte. Using the linear region of the S–V plot, a \( K_{SV} \) value of \( (5.48 \pm 0.1) \times 10^4 M^{-1} \) is obtained for 1 (Figure S11). Thus, the limit of detection of TNP is found to be as low as \( 0.35 \pm 0.05 \) ppm based on the value of \( 3\sigma/m \) (Figure S12). These results vividly depict that 1 has a high selectivity for TNP over other potentially interfering NACs. The \( K_{SV} \) value of 1 is one of the highest among similar sensors. 5,15,26 Only two Tb(III) compounds containing di- and tricarboxylates have been reported for TNP sensing prior to this study. The \( K_{SV} \) values for these compounds are \( 7.47 \times 10^4 M^{-1} \) ([Tb(L)_1(H_2O)_4]·3H_2O), \( 3H_2L = 2-(2-hydroxy-propionyl amino)terephthalic acid) 5c and \( 3.42 \times 10^4 M^{-1} \) ([Tb(1,3,5-BTC)]_n, 1,3,5-BTC = 1,3,5-benzenetricarboxylate). 5b Similarly, the \( K_{SV} \) value for \{La(TPT)(dimethyl sulfoxide)_2\}(H_2O)_0.5 (H_2TPT = p-terphenyl-3,4',5-tricarboxylic acid) 5b is \( 9.89 \times 10^4 M^{-1} \). Further comparison with any organic or metal–organic probes \( (K_{SV} \) values), such as fluorescein-based F1 \( (3.94 \times 10^4 M^{-1}) \), \{Cd(TPT)_2(DMF)_2\}_0.5(H_2O)_0.5 \( (6.56 \times 10^4 M^{-1}) \), \{Cd-(NDC)_0.5(PCA)\}_0.5 \( (3.5 \times 10^4 M^{-1}) \), and UiO-67-dcppy \( (2.9 \times 10^4 M^{-1}) \), indicates that the selective sensing of TNP by 1 is outstanding. 26 Out of the last three probes, the detection limit \( (0.13 \) ppm) was reported only for F1.

For further elaboration, the strong supramolecular interactions between TNP and 1 can be considered. The acidic hydrogen from TNP can bind with the oxygen of the nitrate anion through hydrogen bonding. On the other hand, the electron transfer from the electron-rich picolinate moiety of 1 to electron-deficient TNP is possible through \( \pi-\pi \) interactions (see Scheme S1). In case of other analytes, electrostatic interaction is the chief and sole principle leading to the quenching of 1, and thus the quenching constants are much lower compared to the hydroxy-containing counterparts. Moreover, there is no deviation from linearity in their S–V plots (Figure S9). Therefore, the luminescence quenching of 1 by TNP can be described as a result of the competitive processes of energy absorption by TNP and the electronic interactions between TNP and the ligands coordinated to the Tb(III) center. On the basis of the absorption spectra of the NACs (Figure S13) and the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy diagrams of the NACs (Figure S14), upon excitation of 1 at 340 nm, TNP absorbs a lot more of excitation energy than the other nonphenolic analytes, leaving less energy source for the bpbd ligand. This reduces the probability of energy transfer from the ligand to the metal center which is the source of the antenna effect on the luminescence intensity of the Tb(III) center in 1. In addition to the primary competitive processes mentioned above, inner filter effect (IFE) can also exist to some extent and contribute to the quenching process with a varying effect. In the past, the correction factor for IFE
is described for solution systems. The IFE has also been utilized as one of the sensing tools where the absorbance changes of the absorber translate exponentially into luminescence intensity changes but with less selectivity. However, the IFE has to be a minor component for the selective sensing of TNP by 1 because of the fact that its concentration used in this study is very low (1 mg in 2 mL water). Interestingly, its concentration is the lowest among all similar probes (e.g., 10 mg in 1.5 mL water), but this variation does not result in much different $K_{SV}$ values and detection limits (vide supra). This effect is further reduced as the instrument used in this study has horizontal slits. For a control experiment to evaluate the contribution of the IFE, a species has to be chosen which will have the same absorption at the excitation wavelength for TNP but will not interact with 1. Unfortunately, it is not easy to find a nonaromatic species, which will not interact with the electron-rich picolinate moiety of the ligand attached to the Tb center in 1 and yet absorb at the desired wavelength. Furthermore, for solid probes dispersed in a solvent (for recyclability purpose), it is not so practical to do measurements for the quantification of the minor contribution of IFE. Thus, no attempt was made for any IFE correction in this case.

The quenching efficiency (%) of different NACs by 2 is plotted in Figure S15a. The luminescence intensity at 604 nm is monitored, which decreases with a gradual addition of 10 μL of NAC for a total of 120 μL. Unlike 1, all NACs exhibit moderate but similar quenching effect for 2. The 3D $S-V$ plot of all analytes for 2 is shown in Figure S16. The $S-V$ plot of TNP for 2 shows linearity at a lower concentration (Figure S17), providing a $K_{SV}$ value of $(6.96 \pm 0.1) \times 10^9$ M$^{-1}$. An incremental addition of TNP to 2 (Figure S15b) provides a limit of detection of 14 ppm based on the value of $\sigma/m$ (Figure S18).

The quenching efficiency (%) of different NACs by 3 is plotted in Figure S19a. The luminescence intensity at 484 nm is monitored, which decreases with a gradual addition of 10 μL of NACs for a total of 120 μL. Unlike 1, all NACs exhibit a moderate but similar quenching effect for 3. In case of 3, the 3D plot of all analytes is shown in Figure S20. The $S-V$ plot of TNP for 3 shows linearity at a lower concentration (Figure S21), providing a $K_{SV}$ value of $(1.05 \pm 0.01) \times 10^8$ M$^{-1}$. An incremental addition of TNP to 3 (Figure S19b) provides a limit of detection of 0.9 ppm based on the value of $3\sigma/m$ (Figure S22).

## CONCLUSIONS

Using a new pyridine-carboxylic acid ligand, complexes of Tb(III), Sm(III), and Dy(III) have been synthesized in good yields. Their purity, physicochemical, and luminescent properties were established by various analytical techniques. The FTIR spectroscopy data conclusively confirmed the chelating bidentate binding mode of the carboxylate and the monodentate binding mode of the nitrate. These complexes were found to be stable in the solid state up to 220 °C. On the basis of the PXRD and TGA data, compounds 1, 2, and 3 were found to be isomorphous. All these complexes showed their characteristic visible and NIR luminescence through intramolecular energy transfer from the ligand to the lanthanide center because of the antenna effect. The Tb(III) complex (1) showed selective sensing of TNP over other NACs with the best detection limit of $(0.35 \pm 0.05)$ ppm. This work encourages us to put further efforts to improve the sensitivity and efficacy of the sensors, and thus numerous derivatives are designed for future studies. Furthermore, sensing of other neutral molecules, anions, and cations is being carried out with such compounds.

## EXPERIMENTAL SECTION

### Materials and Methods.

The compounds 2-Pyridinecarboxaldehyde, 2-bromoacetic acid, 1,4-diaminobutane, samarium nitrate, dysprosium nitrate, and terbium nitrate were obtained from Sigma-Aldrich. Anhydrous sodium sulfate was obtained from Merck. The solvents used were of reagent grade and without purification. D$_2$O was obtained from Sigma-Aldrich and CDCl$_3$ was obtained from Merck. Each FTIR spectrum was recorded with 16 scans (resolution: 4 cm$^{-1}$) on a PerkinElmer spectrum RX 1 FT-IR spectrometer using KBr pellets in the range from 4000 to 400 cm$^{-1}$. The $^1$H NMR spectra were recorded at 400 MHz using a Bruker ARX 400 spectrometer, with tetramethylsilane (Si(CH$_3$)$_4$) as an internal standard. SpinWork software was used to analyze the data. TGA–DTA data collection was carried out in a Shimadzu DTG-60H analyzer with a heating rate of 10 °C/min under a flow atmosphere of nitrogen from 25 to 500 °C by using an aluminum pan. UV–vis absorption spectra were obtained on a Cary 5000 UV–vis–NIR spectrophotometer in the range 200–800 nm. C, H, and N analyses were performed on a Leco TruSpec Micro CHNS analyzer; the typical mass of a sample was 2 mg. PXRD patterns were collected in the 2θ = 3–50° range with a scanning speed of 5° per min with a 0.02° interval on a Rigaku Ultima IV diffractometer using CuKα geometry, a sample rotation (120 rpm) attachment, and a Dtex Ultra detector. The luminescence spectra for the solid samples were recorded by a Cary 5000 UV–vis–NIR spectrophotometer in the range 200–800 nm. C, H, and N analyses were performed on a Leco TruSpec Micro CHNS analyzer; the typical mass of a sample was well-dispersed in MeOH, drop-casted on a silicon wafer, dried, and coated with gold using a working distance of 4.5–15 mm and voltage 10–15 kV.

**Caution!** Bromoacetic acid is a very reactive, toxic, and strong alkylating agent that should be handled wearing nitrile gloves in a chemical hood.

### Synthesis of K$_2$bpbd.

**Step I:** To a solution of 2-pyridinecarboxaldehyde (3.8 mL, 40 mmol) in 5 mL of methanol, 1,4-diaminobutane (2 mL, 20 mmol) was added dropwise at 0 °C with continuous stirring. The reaction mixture was stirred for 4 h at room temperature followed by the addition of a slight excess of sodium borohydride at 0 °C. After stirring for another 12 h, the solvent was evaporated under reduced pressure to obtain a brown residue. The residue was extracted with dichloromethane and washed with water (3 × 2 mL), followed by drying the organic phase with anhydrous sodium sulfate. The evaporation of the dichloromethane layer under reduced pressure afforded a yellow oily product (bpbn). Yield: 4.4 g (98%).

$^1$H NMR (CDCl$_3$): δ: 8.53 (d, 2H), 7.62 (t, 2H), 7.30 (m, 2H), 7.13 (d, 2H), 3.97 (s, 4H), 2.66 (s, 4H), 2.59 (t, 2H), 1.59 (t, 4H). 3D S–V plot of all analytes is shown in Figure S20. The $S-V$ plot of TNP for 3 shows linearity at a lower concentration (Figure S21), providing a $K_{SV}$ value of $(1.05 \pm 0.01) \times 10^8$ M$^{-1}$. An incremental addition of TNP to 3 (Figure S19b) provides a limit of detection of 0.9 ppm based on the value of $3\sigma/m$ (Figure S22).

**Step II:** To a clear solution of bromoacetic acid (830 mg, 6 mmol) in 5 mL water, a solution of potassium hydroxide (349 mg, 6 mmol) in 5 mL water was added in a dropwise fashion over a period of 15 min with constant stirring which was continued for further 30 min. This resultant solution was added dropwise to a solution of bpbn (830 mg 3 mmol) in 5 mL of water kept at 0 °C for 30 min with vigorous stirring. After half an hour, a solution of KOH (354 mg, 6 mmol) in 5 mL of water was added to the above reaction mixture at 0 °C, and the resulting reaction mixture was further stirred for 96 h.
Upon removal of the solvent under reduced pressure, a solid was obtained. To the crude product, dry methanol was added to separate out the by-product potassium bromide via filtration; the filtrate was evaporated to dryness under reduced pressure, and the solid was redissolved in 5 mL of dry methanol and filtered to remove potassium bromide; this step was repeated one more time. The filtrate was evaporated under reduced pressure, yielding a semisolid to which 5 mL of acetonitrile was added and left undisturbed for 12 h. The desired product, an off-white solid, was isolated by decanting the solvent and vacuum-dried. Yield: 800 mg (60%).

**Synthesis of [Dy(bpbd)(H2O)2(NO3)]·6H2O (1).** In a 10 mL round-bottom flask, Tb(NO3)3·6H2O (20 mg, 0.046 mmol) was added to a 2 mL aqueous solution of K2bpbd (21 mg, 0.046 mmol). The reaction mixture was stirred for 1 day at ambient conditions. A white solid product was obtained via filtration, which was washed with cold water and air-dried. Yield: 24 mg (69%). Anal. Calcd (%) for 

\[\text{C}_2\text{H}_9\text{NO}_4\text{O}_5\text{Nb} \]

1H NMR of bpbd and K2bpbd; FTIR spectra of K2bpbd, I, 2, and 3; TGA–DTA scans of I, 2, and 3; emission spectrum of K2bpbd; solid-state reflectance spectra of K2bpbd and I; determination of detection limits; absorbance spectra and HOMO and LUMO energy diagrams of NACs; luminescence quenching % of different NACs; S–V plots of various analytes for I, 2, and 3; calculation of standard deviation; and possible prominent noncovalent interactions (PDF)
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