Isophthalato-Based 2D Coordination Polymers of Eu(III), Gd(III), and Tb(III): Enhancement of the Terbium-Centered Luminescence through Thiophene Derivatization

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We present here the first examples of lanthanide ion complexes with only isophthalic acid or thiophenylisophthalic acid ligands. The complexes of isophthalic acid with Eu^{3+} (**1**) and Tb^{3+} (**2**) and the moderately soluble complexes of 5-thiophen-3-ylisophthalate with Eu^{3+} (**3**), Gd^{3+} (**4**), and Tb^{3+} (**5**) were isolated as single crystals through gel crystallization. X-ray diffraction studies confirm the cross-linking structure of these complexes, which, in case of the thiophenyl derivatives, results in low solubility in common solvents. The two-dimensional isophthalato complex of Eu^{3+} (**1**) crystallizes in the $C2/c$ space group, with $a = 22.154(4)$, $b = 12.649(3)$, and $c = 15.921(3)$ Å, $\beta = 112.34(3)°$, and $V = 4126.7(14)$ Å^3, while the one-dimensional Tb^{3+} complex of the same ligand, **2**, crystallizes in the space group $P2_1/c$ with $a = 11.921(2)$, $b = 10.838(2)$, and $c = 17.499(4)$ Å, $\beta = 92.44(3)°$, and $V = 2258.9(8)$ Å^3. The thiophenylisophthalato complexes of Eu^{3+} (**3**) and Gd^{3+} (**4**) are two-dimensional and crystallize in the $P2/n$ space group with parameters for **3** of $a = 14.139(3)$, $b = 10.684(2)$, and $c = 15.138(3)$ Å, $\beta = 102.51(3)°$, and $V = 2232.3(8)$ Å^3 and parameters for **4** of $a = 14.1195(13)$, $b = 10.6594(10)$, and $c = 15.1149(14)$ Å, $\beta = 102.529(2)°$, and $V = 2220.7(4)$ Å^3, while the Tb^{3+} complex, **5**, also two-dimensional, crystallizes in the $P\bar{1}$ space group with $a = 11.051(2)$, $b = 14.528(3)$, and $c = 15.041(3)$ Å, $\alpha = 77.63(3)$, $\beta = 87.86(3)$, and $\gamma = 83.51(3)°$, and $V = 2343.48$ Å^3. All complexes of Eu^{3+} and Tb^{3+} luminesce in aqueous solution, and the luminescence lifetimes and quantum yields are 123.8 ± 7.4, 0.14% (**1**), 475.1 ± 14.5, 3.58% (**3**), 129.3 ± 3.5, 0.19% (**4**), and 213.9 ± 2.2 μs, 7.46% (**5**).

Introduction

Lanthanide ions are known for their luminescence properties. These properties make them interesting candidates for luminescent applications such as biochemical sensors and fluoroimmunoassays.[1] Since the emission mechanism is based on f–f transitions with consequent narrow bandwidth and no theoretical cap on the quantum efficiency, they are especially interesting candidates for LED applications. The f–f transitions are spin and parity forbidden, and to exploit the luminescent properties, ligands that function as sensitizers are used. Benzoic acid and its derivatives have been described as efficient sensitizers for lanthanide emission.[2–7] They are also interesting ligands per se, as the carboxylate

functionality can coordinate in several different ways to metal ions. Recently a significant increase in the research of coordination polymers in which metal ion centers are bridged through organic molecules has been observed, due to potential application in optoelectronics, magnetism, and catalysis.[8–15] Most of the described materials are based on

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transition metal ions and have multidimensional structures with geometrically simple repeating units, due to the templating effect of the transition metal ions, which show generally low coordination numbers. Structures have been observed with square tetracoordinated Ni(II) or octahedral hexacoordinated Co(II) ions.[8-12] Fewer examples of coordination polymers which incorporate lanthanide ions are known,[3,4,16-20] along with some examples of polynuclear lanthanide ion complexes.[21-24] However, these large ions achieve high and variable coordination numbers with irregular geometries, leading to potentially highly luminescent coordination polymers with more complicated features. Other recent examples have shown that Eu^{3+} and Tb^{3+} can be successfully incorporated into thiophene-based polymers yielding thin films with Eu(III)- and Tb(III)-based emission.[25-30] In an attempt to optimize lanthanide-centered emission in lanthanide-containing polymers and explore the varied possibilities of lanthanide-based coordination polymers, we are systematically studying the photophysical properties of complexing agents capable of efficiently sensitizing Eu(III) and Tb(III) emission while having a polymerizable moiety, e.g. thiophene. Here, we present the synthesis of ligands containing thiophene and isophthalic acid and the metal ion complexes obtained with these ligands. We have compared the structural and photophysical properties of the metal complexes of isophthalic acid (H_2ipa) with the complexes of thiophene-derivatized isophthalic acid (H_2tipa) to assess the effect of the thiophene moiety on the structure of the coordination polymers and on the emission properties of Eu(III) and Tb(III) in solution and in the solid state.

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Results and Discussion

Synthesis of the Metal Complexes. As with several examples of complexes of aromatic and nonaromatic carboxylic acids, the compounds developed here show low solubility in common solvents including water. This fact prevented us from obtaining single crystals of the metal complexes targeted through traditional methods, such as solvent diffusion. To date, for complexes with similar solubility characteristics, the method of choice for the isolation of X-ray-quality single crystals has been solvothermal synthesis.[3,31-36] In fact, the few isophthalato complexes of lanthanides described have been obtained by hydrothermal synthesis.[3,4,16,19,20] In many cases, in addition to the isophthalato ligand which shows several different coordination modes, water and an additional ligand are present, such as phenanthroline or acetate.[4,16,19,20] We have successfully utilized gel crystallization[37,38] as an alternative method to obtaining single crystals of new lanthanide ion complexes with isophthalato (ipa) and thiophenylisophthalato (tipa) as the ligands. Even though water is coordinated to the metal ions, other auxiliary ligands are not present in these molecules. These are therefore the first examples of "homoleptic" europium, gadolinium, and terbium ion complexes of isophthalic acid or thiophenylisophthalic acid without additional organic ligands.

Structure of [$K_2Eu_2(ipa)_4(H_2O)_4 \cdot 8H_2O$] (1). The europium(III) complex of isophthalic acid **1** crystallizes in the monoclinic *C*2/*c* space group. The lanthanide ion is nine coordinate, and it is displayed with a complete coordination sphere in Figure 1. The polyhedron around the Eu(III) ion is distorted, and it is not possible to describe it as one of the usual 9-fold coordination geometries. There are two water molecules completing the coordination sphere of europium ion, and the distances to the two water molecule oxygen atoms are Eu−O(9) 2.483(25) Å and Eu−O(10) 2.487(9) Å. The other oxygen atoms are at distances between 2.337 and 2.641 Å, consistent with similar structures.[4,16,19,20] Two of the isophthalato ligands bind in a bidentate mode through one of the carboxylate groups [O(1), O(2), O(3), and O(4)]. Two other carboxylate groups bridge between two europium ions [O(7), O(8)], and one is coordinated in a monodentate fashion to O(6), while atom O(5) is not coordinated. For charge compensation purposes a potassium ion K(1) is part of the molecule. It is disordered and situated near the Eu-

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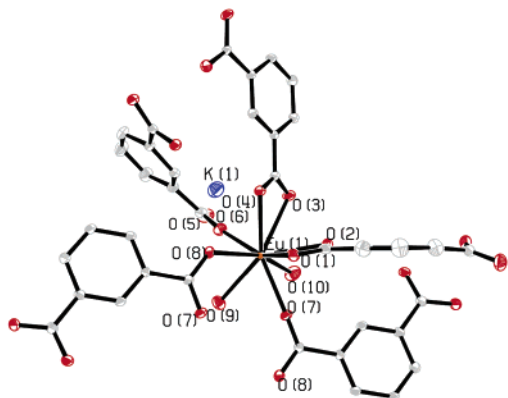
Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are at 50% probability. O(9) and O(10) are coordinated water molecules. Hydrogen atoms, disordered potassium ions, and water molecules of crystallization have been omitted for clarity.

(III) ion. This potassium ion is introduced into the molecule through ions present in the starting material, the potassium salt of the ligand. A total of eight water molecules crystallize in the unit cell.

In Figure 2 a polyhedral representation of this compound is displayed. The orange polyhedra correspond to the europium ions coordinated to nine oxygen atoms. They are connected to each other through the isophthalato ligands. The isophthalato ligands coordinate in chelating bidentate, monodentate bridging, and bidentate bridging modes. This arrangement of five isophthalato ligands around the europium ion leads to a structure of two-dimensional sheets. The metal ions in two adjacent sheets are approximately 11 Å apart. Half of the monodentate isophthalato ligands, which are coordinated to the europium ions through O(6), are pointed toward a neighboring layer and interact through $\pi-\pi$ stacking, as seen in the representation in Figure 2 on the left. The distance between the π-stacked rings is 3.451 Å. This arrangement also leads to channels forming between the two-dimensional layers, shown in the representation on the right. The channels, which run through the crystals along the c axis, have dimensions of approximately 5.5 by 7 Å and are partially occupied by the water molecules of crystallization.

Structure of [Tb(Hipa)(ipa)(H$_2$O)$_4$·3.3H$_2$O] (2). Even though the radius of Tb(III) is only 0.024 Å smaller than that of Eu(III), complex **2** with isophthalic acid crystallizes in a very different manner in the monoclinic space group $P2_1/c$. The metal ion is 9-fold coordinated and surrounded by three isophthalato ligands, as shown in Figure 3. The distances Tb(1)−O are in the range 2.328−2.513 Å and well within the expected values for this type of compound.[4,16,19,20] Four water molecules O(9), O(10), O(11), and O(12) complete the coordination sphere of the terbium ion, at distances between 2.366 and 2.422 Å. In this case, it is also not possible to assign the coordination environment to either tricapped trigonal prismatic or monocapped square antiprismatic geometries. Two of the three coordinating ligands coordinate in a bidentate fashion through O(1), O(2), O(3), and O(4) and serve as a bridge between two ions. The third isophthalato binds monodentate through O(5), while O(6) is

not coordinated and does not coordinate to a second terbium ion. We believe that the second carboxylato moiety on this isophthalato ligand is protonated even though this hydrogen atom could not be found in the difference map of the X-ray diffraction experiment. IR spectroscopy also proved inconclusive, due to the presence of four additional water molecules that complete the coordination sphere of the terbium(III) ion and of the water molecules of crystallization. In Figure 4, a polyhedral representation of this molecule is shown. The presence of bridging isophthalato ligands leads to the formation of a one-dimensional wavelike chain. Adjacent chains interact with each other through π-stacking of the monodentate and nonbridging isophthalato groups. The distance between the π-stacked groups is 3.588 Å.

Thiophenylisophthalic Acid Complexes of Eu(III), Gd(III), and Tb(III) (3−5). Once the isophthalic acid is derivatized with thiophene, a potentially polymerizable group, the coordination environment of the metal ions changes dramatically and the coordination number decreases from 9 to 8 for the complexes of Eu(III) (**3**), Gd(III) (**4**), and Tb(III) (**5**). **3** and **4** are isostructural, monoclinic $P2/n$, while **5** is triclinic $P\bar{1}$. The complexes with complete coordination environments are displayed in Figure 5 for the Gd(III) complex (**4**) and Figure 6 for the Tb(III) complex (**5**). The isostructural europium and gadolinium complexes are coordinated to four thiophenylisophthalato ligands, one in a bidentate fashion through O(1) and O(2) and the other three monodentate coordinated through O(3), O(4), and O(5), respectively. The Ln−O distances are in the range 2.305−2.4318 Å for **3** and 2.295−2.511 Å for **4**, consistent with the values observed for complexes **1** and **2**.

There are three additional water molecules completing the coordination sphere of the gadolinium ions: O(7) at 2.459-(9), O(8) at 2.436(3), and O(9) at 2.409(4) Å (for the europium complex the water molecules are ca. 2.457−2.521 Å). The terbium complex has two terbium ions in the asymmetric unit, as displayed in Figure 6. The two metal ions are bridged through a thiophenylisophthalato, which coordinates bidentate through O(1) and O(2) to Tb(1) and monodentate through O(3) to Tb(2), while O(4) remains uncoordinated. Each terbium ion is further coordinated to three other thiophenylisophthalato ligands. In the case of Tb-(1), all ligands are monodentate, for Tb(2) two are monodentate and one is bidentate. The bidentate ligand is equivalent to the one that bridges Tb(1) and Tb(2) and is responsible for the chain along the binuclear Tb unit. The Tb−O distances vary between 2.289 and 2.455 Å, consistent with the distances found for **1** and **2**. Three additional water molecules/metal ion complete the coordination sphere, at distances ranging from 2.362 to 2.471 Å. Several of the thiophene moieties are disordered in these three structures, due to the free rotation along the C−C bond to the phenyl group, and were successfully modeled by assuming two different orientations rotated 180° from each other, as previously reported.[39,40] All four thiophenylisophthalato

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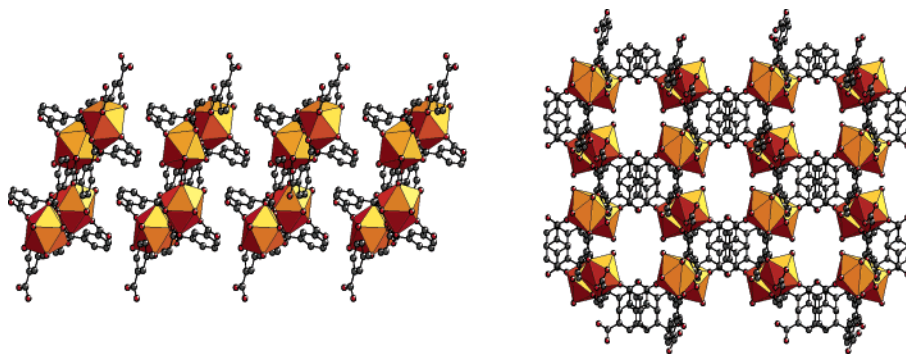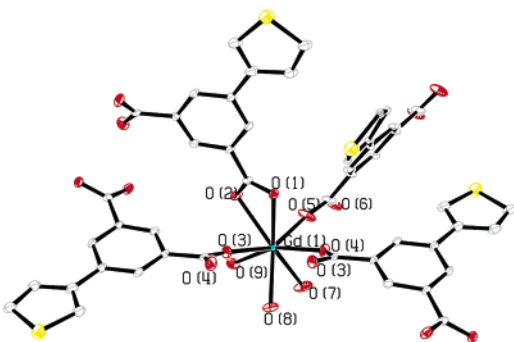
Figure 2. Polyhedral representation of **1** (left, along the *b* axis; right, along the *c* axis). Orange polyhedra are [EuO$_9$] units, which are connected through isophthalato dianions. Hydrogen atoms, disordered potassium ions, and water molecules of crystallization have been omitted for clarity.
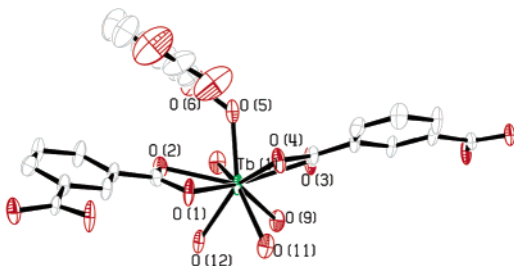
Figure 3. ORTEP drawing of **2**. Thermal ellipsoids are at 50% probability. O(9), O(10), O(11), and O(12) are coordinated water molecules. Hydrogen atoms and water molecules of crystallization have been omitted for clarity.
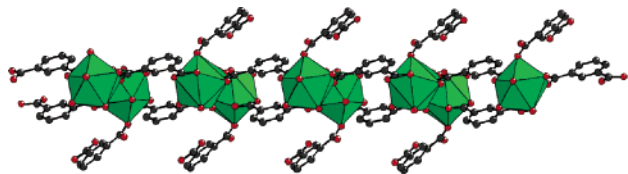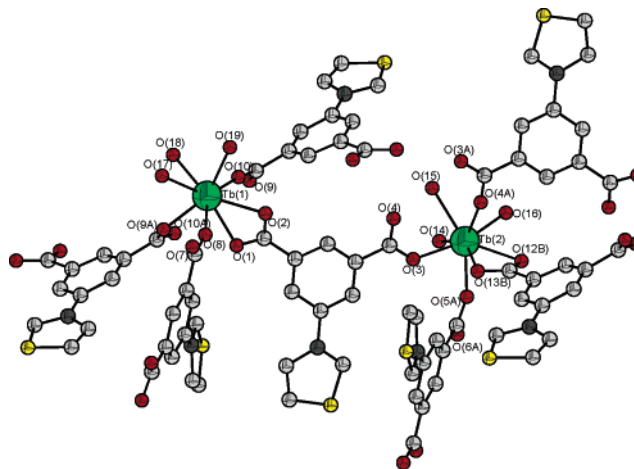

Figure 4. Polyhedral representation of **2** along the *b* axis. Green polyhedra are [TbO$_9$] units, which are connected through isophthalato dianions. Hydrogen atoms and water molecules of crystallization have been omitted for clarity.

Figure 6. Thermal ellipsoid drawing of **5** with thermal ellipsoids at 50% probability. O(14)−O(19) are coordinated water molecules. Hydrogen atoms and water molecules of crystallization have been omitted for clarity.
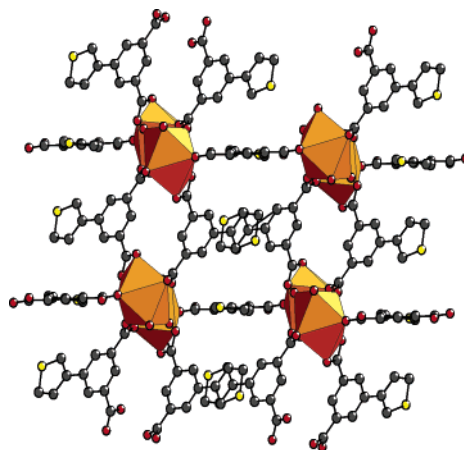

Figure 5. ORTEP drawing of **4**. Thermal ellipsoids are at 50% probability. O(7), O(8), and O(9) are coordinated water molecules. Hydrogen atoms and water molecules of crystallization have been omitted for clarity.

Figure 7. Polyhedral representation of **3** along the *b* axis. Orange polyhedra are [EuO$_8$] units, which are connected through thiophenylisophthalato dianions. Hydrogen atoms and water molecules of crystallization have been omitted for clarity.

ligands of **3**−**5** bridge the metal ions with other metal ions. The packing structures of the three complexes are very similar and are displayed as polyhedral representations in Figures 7−9. Due to the bridging ligands two-dimensional coordination polymers are formed.

Locally, all metal ions are part of a pseudo-three-dimensional coordination polymer environment, due to the

angles between the four ligands being 90° or greater. The metal ions are thus arranged in layers of two sheets each. These layers interact with their neighbors through hydrogen bonding (Figures 8 and 9). The metal ion-coordinated water molecules are within hydrogen-bonding distance of the oxygen atoms of the carboxylate groups at 2.644 for **3**, 2.649 for **4**, and 2.736 Å for **5**. The sheets within the layers are formed through the bridging and bidentate chelation of the

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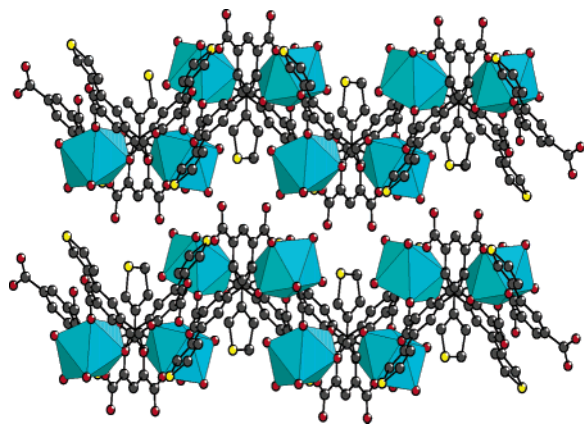
Figure 8. Polyhedral representation of **4** along the *c* axis. Blue polyhedra represent [GdO$_8$] units, which are connected through thiophenylisophthalato dianions. Hydrogen atoms and water molecules of crystallization have been omitted for clarity.
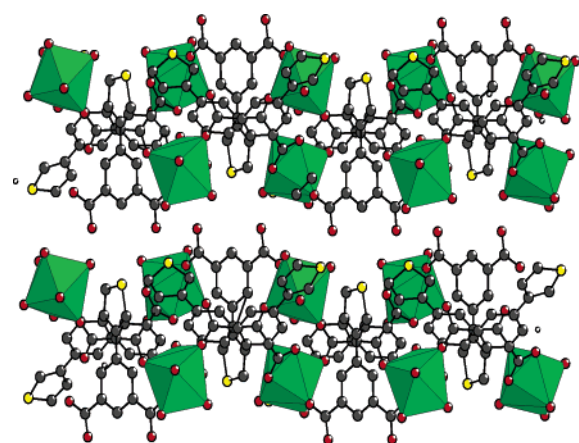
Figure 9. Polyhedral representation of **5** along the *b* axis. Green polyhedra represent [TbO$_8$] units, which are connected through thiophenylisophthalato dianions. Hydrogen atoms and water molecules of crystallization have been omitted for clarity.

carboxylate moieties, but extensive π-stacking is also present in each layer. The thiophene- and phenyl-containing planes in the layers are at distances between 3.182 and 3.950 Å for **3**, 3.221 and 4.227 Å for **4**, and 3.461 and 3.552 Å for **5** of each other. Disordered water molecules of crystallization are also present in these structures, and they occupy the voids, which are more easily seen in Figures 8 and 9, spanned by the thiophene rings and the carboxylate oxygen atoms between the pseudo-three-dimensional coordination layers.

Emission Behavior of the Complexes. Despite their low solubility in common solvents, aqueous solutions displaying strong luminescence at micromolar concentrations could be obtained of the europium and terbium complexes. It is perhaps due to solubility limitations that few and mostly qualitative reports have appeared on luminescence properties of isophthalato complexes of Eu(III) and Tb(III).[4,16,20,41−43] Details of the emission spectroscopy measurements are summarized in Table 1. Representative excitation and

emission of all four complexes in the solid state are displayed in Figure 10. In these spectra, we see emission bands at 594, 617, and 696 nm for the $^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 4$) transitions of **1**, 593 and 618 nm for the $^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2$) transitions of **2**, 491, 547, 588, and 619 nm for the $^5D_4 \rightarrow {}^7F_J$ ($J = 6{-}3$) transitions of **3**, and 491, 547, 588, and 620 nm $^5D_4 \rightarrow {}^7F_J$ ($J = 6{-}3$) transitions of **5**. The broad bands below 450 nm correspond to emission from the ligand itself, as ligand fluorescence is not completely quenched by coordination to the lanthanide ion. The luminescence spectra of solutions of the ligands with the metal ion salts are in all aspects similar to the solid-state ones.

Europium-Centered Emission. A solution of Eu^{3+} with dipotassium isophthalate in a 1:1 stoichiometry displays a luminescence lifetime of 123.8 ± 7.4 μs. This value is in agreement with the value of 128 μs determined by Choppin and co-workers.[42] By complementing the lifetime measurements with potentiometric and calorimetric data, Choppin concluded that this lifetime value is consistent with the presence of a species in solution in which the metal ion-to-ligand ratio is 1:1.[44] Despite the fact that a small amount of the 1:2 species forms in solution, its presence is negligible for the solution emission properties if the solution conditions are optimized for the formation of the 1:1 complex.[42] For the solution with the thiophenylisophthalato ligand and Eu^{3+}, the lifetimes determined in this paper are 129.3 ± 3.5 μs in water and 1.70 ± 0.03 ms in D$_2$O. Following the method formalized by Horrocks and co-workers,[45] we conclude that 7.5 water molecules are coordinated to the metal ion in the 1:1 solution with tipa, in comparison to 8.1 for the 1:1 ipa solution. Both hydration numbers are smaller than the value for the aquo complex, which is reported to have 9.6 water molecules in its first coordination sphere.[45] We can then conclude that the thiophenyl-containing species displaces roughly half a water molecule from the inner coordination sphere more than the isophthalato complex. A smaller number of water molecules coordinated to the metal ion is in agreement with the coordination environment seen in the solid state, as the Eu(III) in the thiophenylisophthalato complex displays a coordination number of 8 vs 9 for the isophthalato complex. The quantum yield of luminescence for 1:1 solutions of Eu^{3+} with tipa, determined as described by Bünzli,[46] is slightly greater than the one for the 1:1 solution of Eu^{3+} with ipa. As powders, the complexes display luminescence lifetimes of 422.6 ± 4.1 μs for **1** and 264.7 ± 11.7 ms for **3**, consistent with fewer water molecules coordinated to the metal ion in comparison to the complexes in solution.

Terbium-Centered Emission. Solutions of Tb^{3+} with isophthalato or thiophenylisophthalato are green luminescent. The luminescence lifetime for a 1:1 solution with isophthalato is 475.1 ± 14.5 μs in water, consistent with values previously reported,[43] and 3.24 ± 0.08 ms in D$_2$O. The excited state of

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Table 1. Photophysical Characterization of Aqueous Solutions of the Complexes of Eu(III) and Tb(III)[a]

complex	$[Ln^{3+}]$/M	λ_{ex}/nm	λ_{em}/nm	τ_{H_2O}/μs	τ_{D_2O}/ms	n	Φ_{rel}/%	^{3}T/cm^{-1}
Eu^{3+}ipa (**1**)	4.52×10^{-4}	299	618	123.8 ± 7.4	3.10 ± 0.08	8.1 ± 0.5	0.14	
	solid	273	617	422.6 ± 4.1^b				26 949
Tb^{3+}ipa (**2**)	1.03×10^{-3}	301	548	475.1 ± 14.5	3.24 ± 0.08	7.5 ± 0.5	3.58	
	solid	270	546	905.5 ± 21.0^b				
Eu^{3+}tipa (**3**)	1.7×10^{-4}	327	619	129.3 ± 3.5	1.70 ± 0.03	7.5 ± 0.5	0.19	
	solid	275	617	264.7 ± 11.7^b				21 901
Tb^{3+}tipa (**5**)	1.68×10^{-4}	328	547	213.9 ± 2.2	0.29 ± 0.00	5.2 ± 0.5	7.46	
	solid	270	547	762.7 ± 29.3^b				

[a] All solutions prepared in aqueous 0.1 M KCl. [b] Solid.
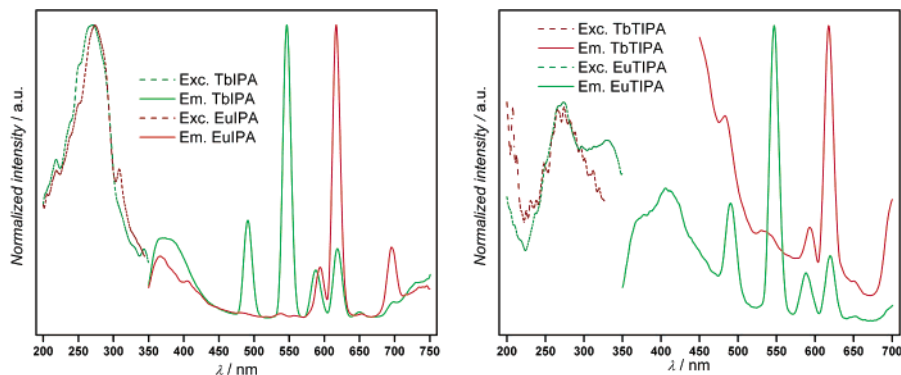
Figure 10. Solid-state excitation (dotted line) and emission (solid line) spectra of **1** and **2** (left) and **3** and **5** (right).

Tb^{3+} in the thiophenylisophthalato-containing solution shows a lifetime of 213.9 ± 2.2 μs in water and 0.29 ms in D$_2$O, respectively. This corresponds to a decrease in the number of coordinated water molecules in going from 7.5 in the ipa to 5.2 in the tipa solution. For comparison, the aquo complex of Tb^{3+} is reported to have 9 water molecules in the first coordination sphere.[45] The decrease in the number of coordinated water molecules is very dramatic in the case of the Tb(III) when compared to the Eu(III) solution complexes and does not reflect the trend observed in the solution lifetimes (which decrease in going from the ipa to the tipa derivative). We believe that the process utilized in preparing proton-free deuterated solutions leads to formation of small oxo and hydroxo aggregates in solution,[47] which we have not attempted to isolate due to the low initial concentration of material and which lead to shorter than expected τ_{D_2O} values. Attempts to prepare the deuterated solutions in other ways did not lead to meaningful results. At the same time that the Tb^{3+} τ_{H_2O} decreases, the quantum yield of luminescence increases by a factor of 2, from 3.58 to 7.46% when going from the isophthalato to the thiophenylisophthalato in solution. This might at first seem contradictory, but is most likely a result of opposing effects of the thiophene derivatization on the overall spectroscopic properties of the complex. The excitation of the lanthanide ion complex is achieved by absorption of energy through the ligand into a singlet excited state. Intersystem crossing populates the ligand's triplet excited state. Energy transfer from this level leads to population of the f* state. It has been reported that the energy transfer is more efficient when the triplet excited state and the lanthanide emissive state have an energy difference around 2000 cm^{-1},[48] and in our case, for the

thiophenyl ligand, this gap is 1401 cm^{-1}, compared to 6449 cm^{-1} for the isophthalato ligand, as detailed in the next section. The triplet state energy of the thiophenylisophthalato ligand is a superior match to the emissive excited state of Tb^{3+}, which lies at 20 500 cm^{-1}, leading to a more efficient energy transfer from the triplet state to the $^5D_4$ level and thus to an increase in the quantum yield of luminescence.

Triplet State Energies of the Ligands. We present here the previously unreported triplet state energy of isophthalato and of the new ligand thiophenylisophthalato. The triplet state energies of the ligands were determined as proposed by Crosby from solutions of the Gd(III) complexes at 77 K.[49] The triplet state energy of the isophthalato ligand is 26 949 cm^{-1}. Its *meta*-derivatization with thiophene leads to a decrease of 5048 cm^{-1} in the energy of the triplet excited state to 21901 cm^{-1}. Latva and co-workers had previously observed that thiophene derivatization of dipicolinic acid leads to a decrease in the triplet state energy of 7250 cm^{-1}.[50] However, in this work the thiophene is derivatized at the 3-position, while Latva and co-workers derivatized thiophene at the 2-position, which corresponds to a more nucleophilic carbon. We are currently in the process of studying the effect of derivatizing thiophene at the 3-position with different aromatic acids on the triplet state energies.

Conclusions

Five new complexes of Eu(III), Gd(III), and Tb(III) with isophthalato or thiophenylisophthalato ligands have been

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isolated and characterized. These are the first reported structures of complexes in which only one type of ligand other than water is present in the coordination sphere of the metal ions. All but one of these complexes form two-dimensional coordination polymers, in which two-dimensional layers interact with their neighbors through π-stacking and hydrogen-bonding interactions. In the case of the thiophenylisophthalato complexes, the metal ions are in pseudo-three-dimensional coordination environments. These coordination polymers of Eu(III) and Tb(III) complexes are highly luminescent both in the solid state, as well as in aqueous solution. The europium ion solutions display red luminescence at around 618 nm with lifetimes in the order of 123.8 and 129.3 μs, for the isophthalato and thiophenyl-isophthalato ligands, respectively, which is consistent with reported values for similar systems, and quantum yields of 0.14 and 0.19%. The terbium ion solutions are green luminescent, with the characteristic emission at around 547 nm. The lifetimes are 475.1 for the isophthalic acid complex, comparable to previously reported values, and 213.9 μs for the thiophenyl derivative. The decrease in lifetime for the thiophenylisophthalato ligand is considerable, especially since it accompanies a 2-fold increase in quantum yield, from 3.58 to 7.46%. This discrepancy can be explained with the determined values of triplet state energies for these ligands. The triplet state energy of the isophthalato ligand, which we report here for the first time, lies at 26 949 cm^{-1}. This is much higher than the determined 21 901 cm^{-1} for the thiophenylisophthalato ligand. The latter is a better match for the emissive $^5D_4$ state of Tb^{3+} at 20 500 cm^{-1} and therefore leads to a more efficient energy transfer. It could thus be demonstrated that the presence of the polymerizable unit thiophene in the ligand is not detrimental to the emission behavior of lanthanide ion complexes. In fact, in the case of the terbium complex, it does lead to a significant increase in quantum yield of emission.

Experimental Section

NMR spectra were recorded on a Bruker Avance DPX 300 spectrometer. UV spectra were obtained on a Perkin-Elmer Lambda 35 and fluorescence spectra on a Perkin-Elmer LS-55 spectrometer. All chemicals were used as received. Solvents were dried by standard methods.

Synthesis of the Dipotassium Salt of 5-Thiophen-3-ylisophthalic Acid. 5-Thiophen-3-ylisophthalic Acid Diethyl Ester. 5-Bromoisophthalic acid diethylester (2.0 g, 6.6 mmol), tributyl-(3-thiophenyl)stannane (2.48 g, 6.6 mmol), and tetrakis(tri-phenylphosphine)palladium(0) (0.12 g, 0.1 mmol) were added to 5 mL of dry DMF. The reaction mixture was heated to 100 °C under nitrogen overnight. The DMF was removed under reduced pressure, and the crude product was purified by flash chromatography with 9:1 hexanes/ethyl acetate as the eluent: yield 91.4%; mp 97−100 °C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS internal standard) δ 8.60 [1H, t, ^3J = 1.5 Hz], 8.45 [2H, d, ^3J = 1.5], 7.63 [1H, dd, ^3J = 3.0, 1.5], 7.49 [1H, dd, ^3J = 5.1, 1.5], 7.45 [1H, dd, ^3J = 5.1, 3.0], 4.45 [4H, q, ^3J = 7.2], 1.45 ppm [6H, t, ^3J = 7.2]; ^{13}C NMR δ 14.37, 61.47, 121.79, 126.16, 128.87, 128.96, 131.37, 131.48, 136.46, 140.35, 165.82 ppm. Anal. Found (calcd for C$_{16}$H$_{16}$O$_4$S, MM = 304.36): C, 62.98 (63.14); H, 5.02 (5.30); S, 10.28 (10.54). λ = 229.1, 266.8, 210.7 nm.

Table 2. Crystallographic Details for Compounds 1−5

complex	K$_2$Eu$_2$(tipa)$_4$(H$_2$O)$_4$·8H$_2$O (1)	Tb(Hipa)(ipa)(H$_2$O)$_4$·3.3H$_2$O (2)	Eu$_2$(tipa)$_3$(H$_2$O)$_4$·8H$_2$O (3)	Gd$_2$(tipa)$_3$(H$_2$O)$_4$·8H$_2$O (4)	Tb$_2$(tipa)$_3$(H$_2$O)$_6$·8H$_2$O (5)
CCDC no.	244488	244490	244489	244492	244491
formula	C$_{32}$H$_{40}$Eu$_2$K$_2$O$_{28}$	C$_{16}$H$_{23.6}$O$_{15.3}$Tb	C$_{36}$H$_{42}$Eu$_2$O$_{24}$S$_3$	C$_{36}$H$_{42}$Gd$_2$O$_{24}$S$_3$	C$_{36}$H$_{46}$O$_{26}$S$_3$Tb$_2$
M_r	1254.76	619.67	1258.80	1269.38	1308.75
cryst system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	C2/c	P2$_1$/c	P2/n	P2/n	P$\bar{1}$
a/Å	22.154(4)	11.818(2)	14.139(3)	14.1195(13)	11.051(2)
b/Å	12.649(3)	10.761(2)	10.684(2)	10.6594(10)	14.528(3)
c/Å	15.921(3)	17.408(4)	15.138(3)	15.1149(14)	15.041(3)
α/deg	90	90	90	90	77.63(3)
β/deg	112.34(3)	91.79(3)	102.51(3)	102.529(2)	87.86(3)
γ/deg	90	90	90	90	83.51(3)
V/Å^3	4126.7(14)	2212.9(8)	2232.3(8)	2220.7(4)	2343.4(8)
T/K	90(2)	293(2)	95(2)	95(2)	95(2)
Z	4	4	2	2	2
D_c/g cm^{-3}	2.020	2.432	1.873	1.898	1.855
μ(Mo Kα)/mm^{-1}	3.315	6.412	3.012	3.190	3.216
indpndt reflcns, R$_{int}$ [$F_o \geq 4\sigma(F_o)$]	4758, 0.0377	4284, 0.0913	7130, 0.0361	7393, 0.0563	25382, 0
reflcns collcd	30 355	16 227	29 710	29 092	31 086
R$_1$, wR$_2$ (all data)	0.0288, 0.0671	0.101, 0.2395	0.0442, 0.0939	0.07, 0.111	0.0922, 0.2125

5-Thiophen-3-ylisophthalic Acid Dipotassium Salt. The diester was saponified with KOH in ethanol (0.1 M) under reflux for 2 h. After cooling, the precipitate was collected by filtration and washed with cold ethanol. Yield: 98%.

Isophthalic Acid Dipotassium Salt. This salt was obtained in the same way as the tipa salt. Yield: 97%.

Metal Complexes. The metal complexes were obtained as single crystals by dissolving either the metal chloride or the dipotassium salt of the ligand in 2 M nitric acid and by adding a solution of sodium metasilicate in water (0.81 g cm^{-3}) until the pH is between 3 and 4 to make the gelling solution. After setting overnight, the gel was layered with a 0.1 M aqueous solution of the lanthanide chloride (or alternatively with a solution of the dipotassium salt of the ligand in water or ethanol). X-ray-quality crystals formed within a few days.

Crystal Structure Determinations. Crystal data, data collection, and refinement details for all the compounds are given in Table 2. Selected bond lengths are given in Tables 1–4 in the Supporting Information. Suitable crystals were mounted on a glass fiber and placed in the low-temperature nitrogen stream. Data were collected on a Bruker SMART CCD area detector diffractometer equipped with a low-temperature device,[51] using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Data were measured using ω scans of 0.3°/frame, and a full sphere of data was collected, for a total of 1850 frames. The first 50 frames were recollected at the end of data collection to monitor for decay. Multiscan absorption corrections were applied. Cell parameters were retrieved using SMART[52] software and refined using SAINTPlus[53] on all observed reflections. Data reduction and correction for *Lp* and decay were performed using the SAINTPlus[53] software. Absorption corrections were applied using SADABS,[54] unless otherwise indicated. The structures were solved by direct methods and refined by least-squares methods on F^2 using the SHELXTL[55] program package. All atoms were refined anisotropically. **5** crystallized as a rotational twin, and refinement was performed with CELL_NOW and TWINABS.[56] Absorption correction was performed with XABS on structure **2**.[57] The majority of the hydrogen atoms were added geometrically and their parameters constrained to the parent site. For all complexes the water hydrogen atoms could not be located on the difference map, could not be added geometrically, and have been omitted, although the formulas are correct. X-ray crystallographic information files can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk). CCDC 244488 contains the supplementary crystallographic data for **1**, CCDC 244489 for **2**, CCDC 244490 for **3**, CCDC 244491 for **4**, and CCDC 244492 for **5** in this paper. Powder data was collected on a Bruker D8 Advance (Cu Kα radiation, 5–60°, 0.01° step, 0.5° s/step).

UV/Vis and Luminescence Measurements. Solutions for spectroscopic studies were prepared by mixing the ligands as the dipotassium salt with the lanthanide chloride in water and used directly or dried and redissolved in deuterium oxide in 1:1 stoichiometry at constant ionic strength (0.1 M KCl). The formed solutions were diluted to an approximate final concentration of 10^{-4} M, and the final metal ion concentration was determined by either titration with EDTA with xylenol orange as the indicator[58] or ICP-MS (Center of Environmental Systems Engineering, Syracuse University, Syracuse, NY 13244). The final pH values of the solutions were 5.14, 5.12, 5.78, and 5.80 for the ipa solutions of Eu(III) and Tb(III) and the tipa solutions of Eu(III) and Tb(III), respectively. The triplet state energies were determined as described by Crosby.[49] Absorption spectra were measured on a Perkin-Elmer Lambda35 spectrometer, and emission spectra on a Perkin-Elmer LS-55 fluorescence spectrometer. Slid widths were 5 and/or 10 nm and scan rates of 125 and 250 nm/s were used. The relative quantum yields of emission were determined as described by Bünzli against Eu(terpy)$_3$(ClO$_4$)$_3$[59] ($\Phi = 1.3\%$)[46] and Tb(terpy)$_3$(ClO$_4$)$_3$[59] ($\Phi = 4.7\%$)[60] as 1×10^{-3} M degassed and dry acetonitrile solutions.[46]

Solid samples for the emission measurements were prepared by mixing aqueous solutions of the ligand as the potassium salt and lanthanide chloride in 3:1 stoichiometry. These solutions were refluxed for 2 h and then cooled to room temperature overnight. The white microcrystalline solids were collected by filtration, washed with ice cold water and ethanol, and dried at room temperature over several days until constant weight was obtained. The identity and purity of the samples was confirmed by comparing the powder with the calculated X-ray diffraction pattern.

Supporting Information Available: Complementary X-ray structural data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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