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ARTICLE TYPE

## Tunable white-light emission from a mixed lanthanide ( $\text{Eu}^{3+}$ , $\text{Gd}^{3+}$ , $\text{Tb}^{3+}$ ) coordination polymers derived from 4-(dipyridin-2-yl)amino benzoate

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Herein, we have developed a series of isostructural mixed  $\text{Ln}^{3+}$ -4-(dipyridin-2-yl)amino benzoate coordination polymers [ $\text{Ln}^{3+} = \text{Eu}^{3+}$  (1),  $\text{Tb}^{3+}$  (2), and  $\text{Gd}^{3+}$  (3)], characterized and investigated their photophysical properties. The results demonstrated that by gently tuning the excitation wavelength of these mixed lanthanide complexes, white light emission can be realized with the Commission Internationale de l'Éclairage coordinates (0.32, 0.34). Furthermore, by changing the concentration profiles of lanthanide ions stoichiometrically in mixed-lanthanide complexes and exciting at particular wavelength, various emission colours can also be successfully obtained. The antenna ligand, 4-(dipyridin-2-yl)aminobenzoic acid provides an efficient energy transfer for the sensitization of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  complexes and exhibits red and green emissions, respectively. Most importantly, due to the high energy (32150  $\text{cm}^{-1}$ ) of the  $\text{Gd}^{3+}$  ion lowest-lying emission level, the corresponding  $\text{Gd}^{3+}$  complex displays ligand-centered visible emission in blue light region, and hence it acts as a blue emitter. Therefore,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  complexes in conjunction with  $\text{Gd}^{3+}$  complex is a suitable choice to obtain tunable white-light-emission from  $\text{Ln}^{3+}$  coordination polymers. The morphological analyses of the mixed lanthanide coordination polymers by Transmission Electron Microscopy (TEM) discloses that these compounds exist as unique crystalline nano-rods with an average diameter of 200 nm. The developed mixed lanthanide complexes also exhibit high thermal stability ( $\sim 420$  °C).

### Introduction

White-light emitting materials and devices have recently attracted considerable interest because of their potential applications in solid-state lighting, low-cost back-lighting and full-color displays.<sup>1-3</sup> The lanthanide based molecular materials display unique optical properties such as sharp and intense luminescence, long excited state life times, emissions in the primary color range (red, green and blue) that fully spans in the entire visible spectrum and therefore can be well suitable for designing white-light emitting materials.<sup>4-9</sup> Interestingly,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions emit intense red and green light, respectively. On the other hand,  $\text{Gd}^{3+}$  complex emits in the blue region in view of its high lowest emitting level (32,150  $\text{cm}^{-1}$ ). Consequently, mixed lanthanide complexes ( $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$ ) have potential applications in generating white-light emission.<sup>10,11</sup> The aromatic carboxylate ligands not only play a role as new building blocks for the coordination networks of lanthanides, but also act as efficient sensitizers for  $\text{Ln}^{3+}$  ions via an “antenna effect”.<sup>12</sup> Zhang and co-workers have reported a strong white-light emission based on isostructural mixed-lanthanide metal-organic complexes by varying the stoichiometric ratio of the lanthanide ions.<sup>13</sup> Previously, efforts have been made to generate white-light emission by adjusting the doping concentration of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions in the  $\text{Gd}^{3+}$ -coordination polymer constructed based on benzimidazole-5,6-dicarboxylic acid, and 1,10-phenanthroline.<sup>14</sup> In recent years, metal-organic frameworks (MOFs) with exceptional tenability and structural diversity, represent a new

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class of light-emitting materials, with the possibility of color tuning of the light emission, including the production of white light.<sup>15,16</sup> Single-phase white light emitters based on MOFs have also been reported.<sup>17</sup> However, developing suitable lanthanide coordination compounds capable of generating white light is still a challenging task because the blue and yellow light emitters or blue, green and red light emitters should compensate exactly through the dichromatic and trichromatic approaches, respectively.

In this work, we report the preparation of a series of mixed lanthanide complexes based on earlier reported three  $\text{Ln}^{3+}$ -4-(dipyridin-2-yl)amino benzoate coordination polymers [ $\text{Ln}^{3+} = \text{Eu}^{3+}$  (1),  $\text{Tb}^{3+}$  (2), and  $\text{Gd}^{3+}$  (3)].<sup>18</sup> In these complexes, 4-(dipyridin-2-yl)aminobenzoate is utilized, not only as an energy absorption antenna for the red  $\text{Eu}^{3+}$  and green  $\text{Tb}^{3+}$  emissions, but also as a blue emission source (Fig. 1). To maximize the blue emission, the composition percentage of  $\text{Gd}^{3+}$  is much higher than the other two components to dilute the other two lanthanide ions in the solid state. With careful adjustment of the relative concentration of the lanthanide ions and excitation wavelength, the color of the luminescence can be modulated, and white light-emission can indeed be achieved. The mechanisms possibly responsible for the observed photophysical properties of these mixed complexes are also discussed.

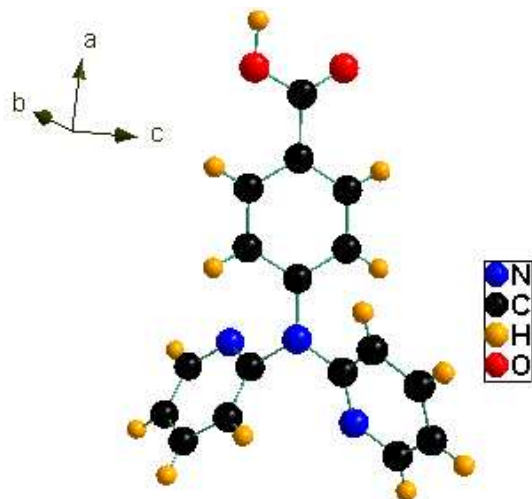


Fig. 1. Structure of the ligand 4-(dipyridin-2-yl)aminobenzoic acid.

## Experimental Section

### Materials

The following chemicals were procured commercially and used without subsequent purification: Europium(III) nitrate hexahydrate (99.9%), terbium(III) nitrate hexahydrate (99.9%), and gadolinium(III) nitrate hexahydrate (99.9%) were procured from Triebacher. Methyl 4-aminobenzoate (98%) and 2-bromopyridine (99.9%) were purchased from Sigma-Aldrich and used without further purification. All the other chemicals used were of analytical reagent grade. The ligand 4-(dipyridin-2-yl)amino)benzoic acid and their corresponding lanthanide complexes (**1-3**) were synthesized in our lab and has been characterized by various spectral techniques as described in our previous publication.<sup>18</sup> The mixed lanthanide complexes **4-11** were synthesized by means of the following general procedure: 1 mmol of the lanthanide nitrate mixture (Ln = Eu<sup>3+</sup>, Tb<sup>3+</sup> and Gd<sup>3+</sup>) in 2 mL of ethanol was added to an ethanolic solution of 3 mmol of ligand and 3 mmol of NaOH in 5 mL of water. Precipitation took place immediately, and the reaction mixture was stirred subsequently for 12 h at room temperature. The product was collected on a filter, washed with ethanol, and dried in vacuo. The resulting complexes were then purified by recrystallization from a dichloromethane/methanol solvent mixture. The molar ratios of Gd<sup>3+</sup>/Eu<sup>3+</sup>/Tb<sup>3+</sup> in the resulting mixed-lanthanide complexes are exclusively confirmed by energy-dispersive spectrometry (EDS) analysis (Table 1 and Fig. S1 in the ESI†). The elemental analysis data of the complexes **4-11** are shown in Table S1 in ESI†.

### Physical measurements

The C, H, and N elemental analyses were performed on a Perkin-Elmer Series 2 Elemental Analyzer 2400. The IR spectra were recorded as KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer operating between 4500 and 400 cm<sup>-1</sup>. Thermogravimetric analyses (TGA) were performed on a TG/DTA-6200 instrument (SHI Nano Technology Inc., Japan) in a nitrogen atmosphere. TEM and SEM were used to determine the morphology and particle size. TEM analyses were done on a JEOL 2100 (300 kV). A pinch of material was suspended in acetone and sonicated for 10 min, then dropped in a carbon-

coated grid and allowed to dry at room temperature. The quantitative microanalysis of the mixed lanthanide complexes were recorded on an energy-dispersive spectrometer (Technai G<sup>2</sup> 30LaB<sub>6</sub>, ST with EDAX). Scanning electron microscopy (SEM) was performed on a ZEISS EVO-18 Cryo-SEM instrument. Powder X-ray diffraction (XRD) patterns were carried out in the 2θ range of 10–70° using Cu Kα radiation (Philips X'pert). PL spectra were measured on a SPEX Fluorolog FL22 spectrofluorometer (HORIBA JobinYvon) equipped with a double-grating 0.22 m SPEX 1680 monochromator and a 450 W xenon lamp as the excitation source operating in the front-face mode.

Table 1 Molar ratios of multi component Gd<sup>3+</sup>/Eu<sup>3+</sup>/Tb<sup>3+</sup> for complexes **4-11** by EDS analysis

Compounds	Molar ratios of multi-components		
	Gd	Tb	Eu
<b>4</b>	0.208	0.602	0.190
<b>5</b>	0.283	0.555	0.162
<b>6</b>	0.520	0.392	0.088
<b>7</b>	0.570	0.132	0.298
<b>8</b>	0.665	0.245	0.091
<b>9</b>	0.755	0.121	0.124
<b>10</b>	0.828	0.102	0.070
<b>11</b>	0.870	0.068	0.062

The X-ray diffraction data were collected on a Rigaku AFC-12 Saturn 724+ CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å) and a Rigaku XStream low temperature device cooled to 100 K. Corrections were applied for Lorentz and polarization effects. The structure was solved by direct methods and refined by full-matrix least-squares cycles on F2 using the Siemens SHELXTL PLUS 5.0 (PC) software package<sup>19</sup> and PLATON.<sup>20</sup> All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in fixed, calculated positions using a riding model. Selected crystal data and data collection and refinement parameters are listed in Table 2.

Table 2 Crystallographic and refinement data for complex **3**

formula	C <sub>51</sub> H <sub>40</sub> N <sub>6</sub> O <sub>8</sub> Gd	
fw	1064.17	85
cryst sys	Monoclinic	
space group	C2/c	
crystal size	0.30 × 0.20 × 0.20	
Temp/K	300 K	
a/(Å)	30.229 (8)	
b/(Å)	14.919(3)	90
c/(Å)	10.217(3)	
α (°)	90	
β (°)	102.947(3)	
γ (°)	90	
V/Å <sup>3</sup>	4490.5(19)	
Z	4	95
D <sub>calcd</sub> , g cm <sup>-3</sup>	1.574	
μ(Mo, Kα)mm <sup>-1</sup>	1.545	
F(000)	2148.0	
R1 [I > 2σ(I)]	0.0282	
wR2 [I > 2σ(I)]	0.0651	
R1 (all data)	0.0403	
wR2 (all data)	0.0709	
gof	1.020	

## Results and Discussion

### Characterization

The elemental analysis data of the complexes **4-11** revealed that in each case the  $\text{Ln}^{3+}$  ion had reacted with the corresponding benzoate ligand in a metal-to-ligand mole ratio of 1:3 (Table S1 in ESI†). The metal compositions of the designed mixed lanthanide complexes were confirmed by energy-dispersive spectrometry (EDS) analysis and found to be matching with the initial compositions of the metal ions. The FT-IR spectrum of the coordinated benzoate ligand exhibits two intense bands at approximately 1434 and 1699  $\text{cm}^{-1}$ , which are attributable to the symmetric  $\nu_s(\text{C}=\text{O})$  and *anti*-symmetric  $\nu_{as}(\text{C}=\text{O})$  vibration modes, respectively. The coordination of the ligand to the respective lanthanide ion in compound **6** was confirmed by the absence of the  $\nu(\text{COOH})$  absorption bands of the ligand at  $\sim 1699 \text{ cm}^{-1}$ . Moreover, the asymmetric and symmetric stretching vibrational modes of the benzoate ligand in complex **6** further split into two peaks [ $\nu_s(\text{C}=\text{O})$ : 1428, 1407  $\text{cm}^{-1}$ ;  $\nu_{as}(\text{C}=\text{O})$ : 1648, 1595  $\text{cm}^{-1}$ ]. The difference between the asymmetric and symmetric stretching vibration modes ( $\Delta\nu_{(\text{C}=\text{O})} = \nu_{as} - \nu_s$ ) is 220 and 188  $\text{cm}^{-1}$ , which indicates that carboxylate groups are coordinated to  $\text{Ln}^{3+}$  ions in a bidentate bridging and chelating modes.<sup>18</sup> A broad band observed above 3000  $\text{cm}^{-1}$  (maximum at 3400  $\text{cm}^{-1}$ ) in the FT-IR spectrum of the typical complex **6** is attributed to the characteristic  $\nu(\text{OH})$  stretching vibration and is indicative of the presence of water molecules.

The thermal stability of the typical mixed lanthanide complex **6** was examined by means of thermogravimetric analysis (TGA) in the temperature range 30–1000 °C and the corresponding thermogram is depicted in Fig. S2 in the ESI†. The onset of weight loss occurs between 100 and 260 °C (Found: 4.65%) for compound **6**. This weight loss corresponds to the release of lattice and coordinated water molecules (Calcd: 4.99%). The second weight loss, between 420 and 830 °C for complex **6** (found: 77.35%; calcd: 80.67%), is attributed to the thermal decomposition of three ligand molecules. The final residue for each complex corresponds to the formation of the respective lanthanide oxide. The mixed lanthanide complex is found to be thermally stable up to  $\sim 420$  °C.

The SEM and TEM micrographs of Gd complex **3** and mixed lanthanide complex **6** are displayed in Figs. 2 and 3, respectively. It is interesting to note that both the complexes exhibit a rod-like morphology with an average diameter of 200 nm. Thus, this observation suggests that the flexible coordination mode of the 4-(dipyridin-2-yl)aminobenzoic acid ligand in combination with the high coordination number of the  $\text{Ln}^{3+}$  ions favours the formation of a 1D rod-like structure.

Analysis of the single-crystal X-ray diffraction data for Gd compound **3** reveals that it exists as infinite one-dimensional (1-D) coordination polymer of the formula  $[\text{Gd}(\text{L})_3(\text{H}_2\text{O})_2]_n$ , which is isostructural as compared to previously reported Eu (**1**) and Tb (**2**) compounds.<sup>18</sup>

The compound **3** crystallizes in the monoclinic space group  $C2/c$ . The Gd1 center of **3** is coordinated to four carboxylate oxygen atoms of the bridging 4-(dipyridin-2-yl-amino)benzoate ligands, two carboxylate oxygen atoms of the chelating benzoate ligand, and two water molecules (Fig. 4). The coordination geometry around the Gd1 center can be described as a bicapped trigonal prism, with O–Gd1–O bond angles ranging from 52.14(8)° to 162.99(9)°. The longest Gd1–O bonds involve the oxygen atoms of the bidentate chelating ligand [Gd1–O33, 2.502(17) Å], and the shortest bonds are associated with bridging carboxylate ligand [Gd1–O31, 2.318(18) Å; Gd1–O27, 2.294(19) Å]. These trends

in the distances are found to be same as those observed in lanthanide carboxylate complexes featuring bidentate chelating and bridging modes.

The powder XRD pattern of typical mixed complex **6** was found to be similar to that of complexes **1-3**, thus implying that all these complexes are isostructural (Fig. S3, ESI†).

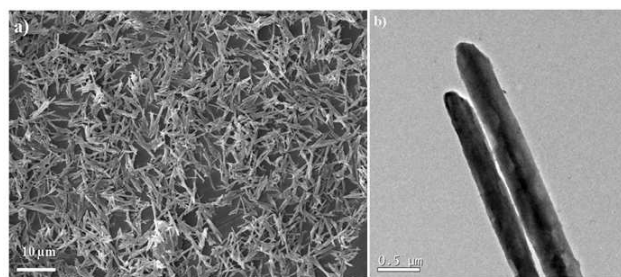


Fig. 2 a) SEM and b) TEM micrographs of complex **3**.

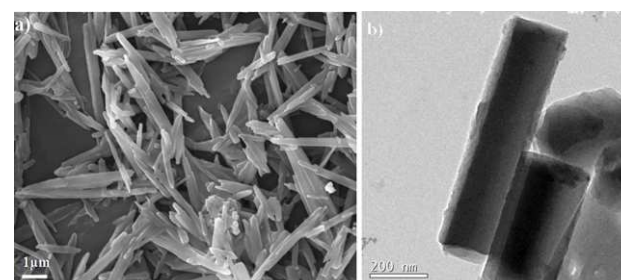


Fig. 3 a) SEM and b) TEM micrographs of complex **6**.

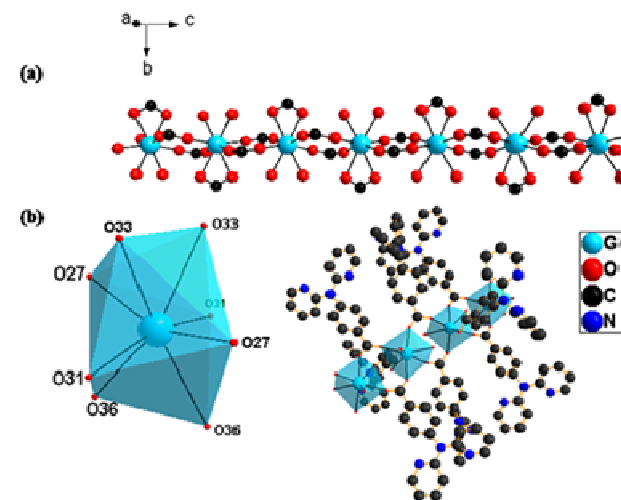


Fig. 4 a) 1D coordination polymer chain of complex **3**. b) Coordination environment of complex **3**. All hydrogen atoms are omitted for clarity.



## Photophysical properties

The solid-state excitation and emission spectra of Tb<sup>3+</sup>, Eu<sup>3+</sup> and Gd<sup>3+</sup> coordination polymers (**1-3**) recorded at room-temperature are displayed in Fig. 5. The red emission of the pure Eu<sup>3+</sup> compound (**1**) is due to the most intense peak at 614 nm for a <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition, and the green colour of the pure Tb<sup>3+</sup> compound (**2**) is due to the most intense peak at 545 nm for a <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> transition. Compound **1** exhibits emission peaks at 582, 590, 614, 655, and 701 nm related to <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>J</sub> transitions of Eu<sup>3+</sup>, where J = 1–4, respectively when excited at λ<sub>ex</sub> = 355 nm.<sup>21,22</sup> On the other hand, the compound **2** displays typical emission bands at 490, 545, 585, and 620 nm, corresponding to transitions from <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>J</sub> (where J = 6–3, respectively) of Tb<sup>3+</sup> (λ<sub>ex</sub> = 355 nm).<sup>23,24</sup> The Gd<sup>3+</sup> compound shows a broad violet-blue emission band between 380 to 430 nm. As the lowest excited states of the Gd<sup>3+</sup> <sup>6</sup>P<sub>7/2</sub> are too high to accept energy from the ligand, its characteristic 4F–4f transition at 311 nm is not visible and hence the broad violet-blue emission noted can be assigned to the ligand emission. Furthermore, the absence of ligand-centered emission bands in the emission spectra of **1** and **2**, indicating the efficient ligand-to-Ln<sup>3+</sup> ion energy transfer in these complexes.

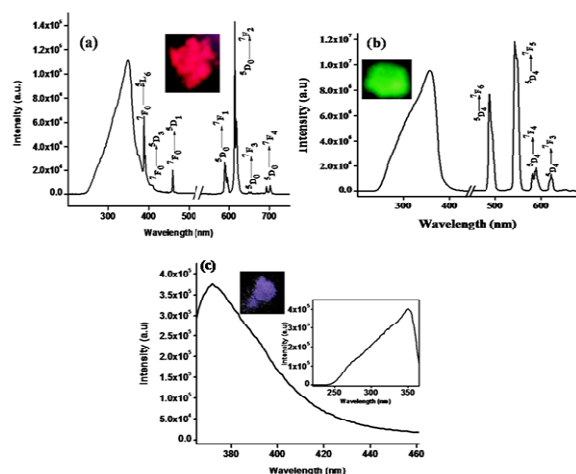


Fig. 5 Room-temperature excitation and emission profiles of compounds **1-3** [(c) Room-temperature excitation (inset)].

The antenna ligand, 4-(dipyridin-2-yl)aminobenzoic acid has a high efficiency of light absorption (λ = 305 nm, ε = 1.2 × 10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup>) and the energy of its triplet excited state (23697 cm<sup>-1</sup>) is higher than the lowest emitting level of the Eu<sup>3+</sup> (17 250 cm<sup>-1</sup>) and Tb<sup>3+</sup> (20 500 cm<sup>-1</sup>). However, it is lower than that of Gd<sup>3+</sup> (32,150 cm<sup>-1</sup>). Thus the terbium compound **2** exhibits higher quantum yield (Φ<sub>overall</sub> = 64%) and lifetime values (938 ± 7 μs) because of the superior match of the triplet state of the 4-(dipyridin-2-yl)aminobenzoic acid ligand to that of the Tb<sup>3+</sup> emitting level (<sup>5</sup>D<sub>4</sub>) as compared to compound **1**. The Eu<sup>3+</sup> compound displays a moderate quantum yield (Φ<sub>overall</sub> = 7%) and life time (428 ± 2 μs) values because of the poor match of the triplet energy level of the ligand with that of <sup>5</sup>D<sub>0</sub> excited state level.<sup>18</sup>

The emission profiles of mixed lanthanide compounds **4-11** excited at 355 nm are shown in Fig. 6. The mixed lanthanide compounds consists of multiple luminescent dopants display mixed emission patterns with different relative peak intensities

depending on the ratios of the Tb<sup>3+</sup>, Eu<sup>3+</sup> and Gd<sup>3+</sup> ions, resulting in a fluent change of their visible photoluminescence emission colours between green, blue and red. Multiple colours from green, greenish yellow, yellow, yellowish orange, orange yellow, pink to red were thus realized by varying the intensity ratio of RGB emissions. The emission colours for **4-11** are illustrated in the CIE chromaticity diagram (Fig. 7), while their CIE colour coordinates are listed in Table 3.

The emission behaviour of mixed lanthanide compound **6** has been investigated by varying the excitation wavelength between 355 to 375 nm and resulting emission profiles are displayed in Fig. 8. As shown in Fig. 8, when excited at 355 nm, light yellow emission with CIE coordinate of (0.36, 0.46) is obtained.

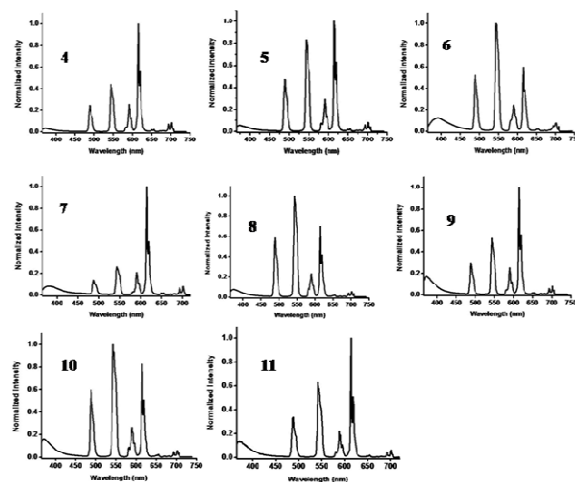


Fig. 6 Emission spectra for compounds **4-11**, excited at 355 nm.

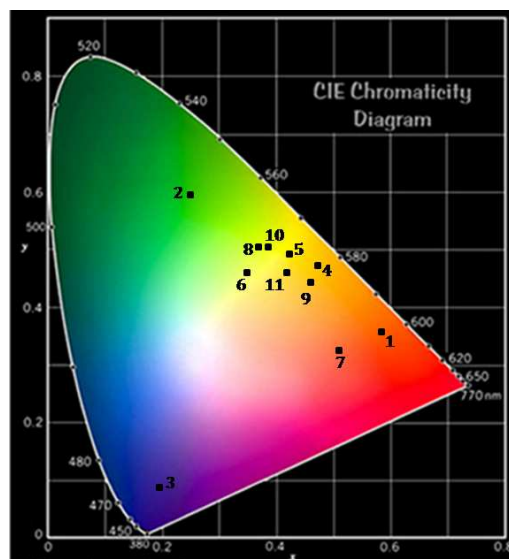


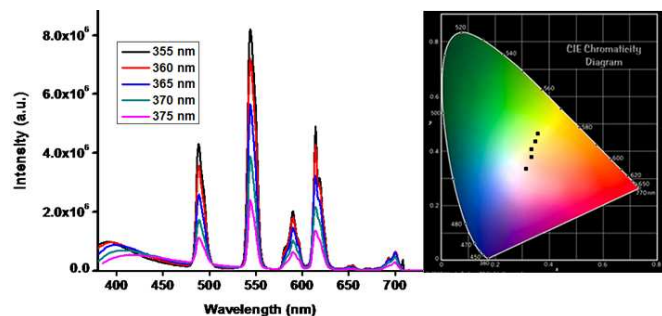
Fig. 7 CIE chromaticity diagram showing the location of the multi-coloured lanthanide mixed complexes (excited at 355 nm).

With the increase in excitation wavelength, the relative intensity of green and red emissions gradually decreases and at the same time the blue emission increases and as a result white emission with CIE coordinate (0.32, 0.34) emerges upon excitation at 375

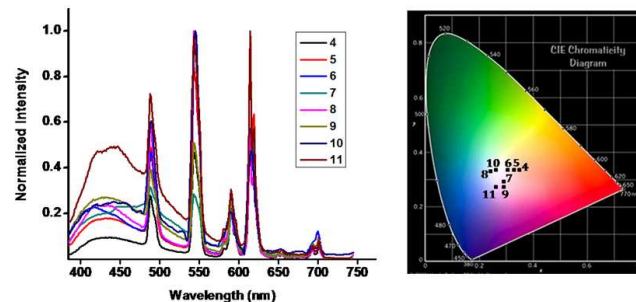
nm. The current concept of excitation dependent photoluminescence tuning in the blue, yellow and white region is controlled by different energy transfer processes. In the case of higher energy absorption, the usual “antenna effect” dominates, which generates a yellow light emission. On the other hand, when the absorbed energy is too low to allow intersystem crossing to occur, the ligand fluorescence in the blue region dominates. Thus, a white light emission can be realized through a combination of usual triplet pathway and a ligand fluorescence process, when an intermediate energy is absorbed. The white light emission thus can be obtained by precisely controlling the concentration profiles of Gd/Eu/Tb and excitation wavelengths. The CIE chromaticity coordinates of **6** are found to be (0.32, 0.34), which is very close to that for pure white light (0.33, 0.33) according to the 1931 CIE coordinate diagram. Furthermore near white-light is generated by all the mixed-lanthanide complexes (irrespective of their composition), when excited them at 375 nm (Fig 9). The present investigation highlights that development of full-colour photo-luminescent materials based on mixed-lanthanide metal-organic complexes would be a promising strategy in the design of RGB-photo luminescent materials for use in the display devices.

Table 3. Colour coordinates of **1–11** according to CIE 1931 at 355 nm excitation wavelength with the approximate colour regions

Complexes	CIE coordinates	Approximate colour regions
1	(0.60, 0.33)	Red
2	(0.30, 0.58)	Green
3	(0.17, 0.08)	Bluish violet
4	(0.48, 0.45)	Orange yellow
5	(0.42, 0.48)	Yellow
6	(0.36, 0.46)	Light yellow
7	(0.50, 0.29)	Pink
8	(0.37, 0.50)	Greenish Yellow
9	(0.46, 0.43)	Yellowish orange
10	(0.38, 0.50)	Greenish Yellow
11	(0.41, 0.45)	Yellow



**Fig. 8** Emission spectra for compound **6** at 355-375 nm excitation wavelengths and variation of colour coordinate value [355 nm: (0.36, 0.46), 360 nm: (0.36, 0.44), 365 nm: (0.35, 0.40), 370 nm: (0.36, 0.38), 375 nm: (0.32, 0.34)]



**Fig. 9** Emission spectra for compounds **4–11**, excited at 375 nm [**4**: (0.36, 0.34), **5**: (0.33, 0.34), **6**: (0.32, 0.34), **7**: (0.29, 0.28), **8**: (0.27, 0.33), **9**: (0.29, 0.27), **10**: (0.27, 0.34), **11**: (0.26, 0.27)]

## Conclusions

A new series of mixed lanthanide metal-organic complexes [Eu<sup>3+</sup>/Tb<sup>3+</sup>/ Gd<sup>3+</sup>] were synthesized based on novel a aromatic carboxylate ligand, namely, 4-(dipyridin-2-yl)aminobenzoic acid. All lanthanide metal-organic complexes are isostructural based upon the analyses of single crystal and powder X-ray diffractions. Notably, the designed mixed lanthanide metal-organic complexes are thermally stable and exhibit unique nano-rod like morphology. Most importantly, by varying concentration profiles of Ln<sup>3+</sup> in mixed lanthanide metal-organic complexes and also varying the excitation wavelengths, white-light emission was achieved. In particular, precisely tuning the white-light emission of RGB-color systems will lead to promising applications in color displays, sensing and labelling.

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## Notes and references

<sup>a</sup>CSIR - Network of Institutes for Solar Energy, National Institute for Interdisciplinary Science and Technology (NIIST), Council of Scientific and Industrial Research (CSIR), Thiruvananthapuram-695 019, India. Tel: 91 0471-2515260; E-mail: [mlpreddy55@gmail.com](mailto:mlpreddy55@gmail.com)

<sup>†</sup> Electronic Supplementary Information (ESI) available: EDS spectrum for mixed complex **6**, XRD patterns, thermogravimetric data, elemental analysis for all the mixed complexes and CIF files for the ligand (CCDC, 980347) and complex **3** (CCDC, 975130).

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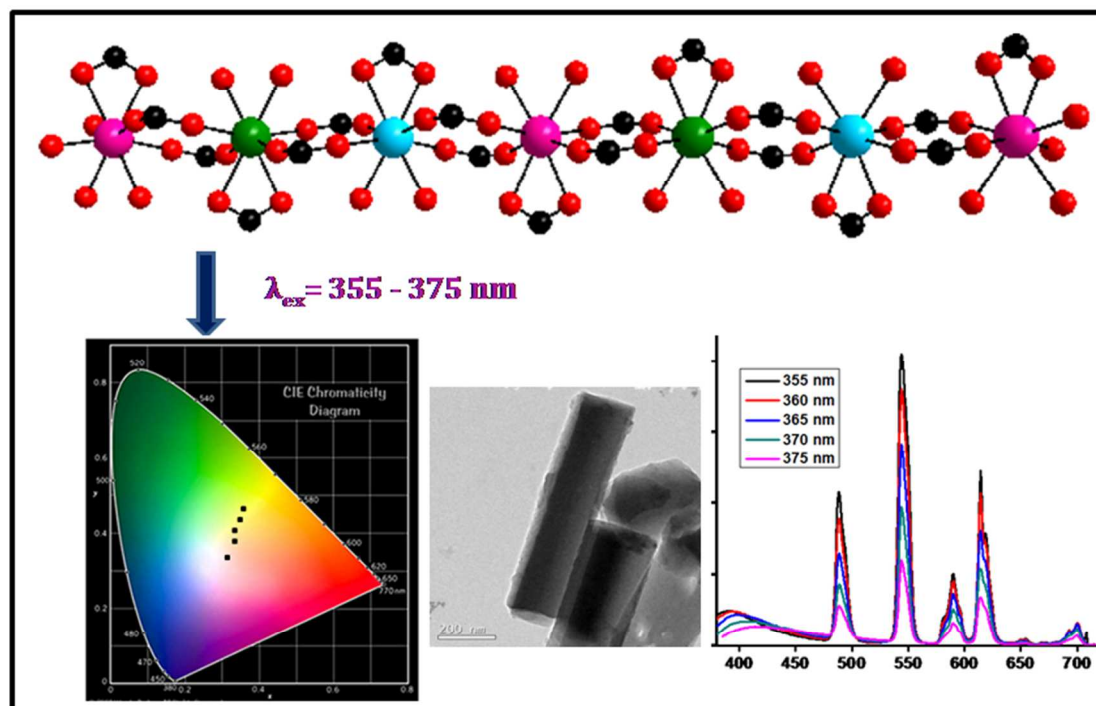
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# Tunable white-light emission from a mixed lanthanide ( $\text{Eu}^{3+}$ , $\text{Gd}^{3+}$ , $\text{Tb}^{3+}$ ) coordination polymers derived from 4-(dipyridin-2-yl)amino benzoate

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A novel approach was developed for the generation of white-light emission from isostructural mixed  $\text{Ln}^{3+}$ -4-(dipyridin-2-yl)aminobenzoate coordination polymers [ $\text{Ln}^{3+} = \text{Eu}^{3+}$  (**1**),  $\text{Tb}^{3+}$  (**2**), and  $\text{Gd}^{3+}$  (**3**)] by tuning the excitation wavelength.