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# Luminescent properties of lanthanide dibenzoylmethide triethylammonium compounds

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## Abstract

Triboluminescence (TL) is defined as the emission of cold light based on mechanical action. In 1999, Sage and Geddes used this property to design a sensor capable of discerning the location of impacts. By coating a structure with various triboluminescent materials, impacts to structures could be monitored with simple light detectors. However, the intensity of most materials is very low. Of the thousands of known triboluminescent materials, only a few can emit enough light to be seen in daylight. One of these materials is europium dibenzoylmethide triethylammonium (EuD<sub>4</sub>TEA). This material shows 206% of the TL yield compared to the more commonly known manganese-doped zinc sulfide. Due to the high TL yield of EuD<sub>4</sub>TEA, exploration of the lanthanide series compounds was attempted for different emission wavelengths. This will help to monitor the locations of impacts on structures. This paper will investigate the TL yields, TL decay times, and the spectra of various lanthanide dibenzoylmethide triethylammonium compounds.

**Keywords:** Triboluminescence, Rare earth luminescence, Lanthanide luminescence, Mechanoluminescence, Europium tetrakis, EuD<sub>4</sub>TEA, Lanthanide tetrakis, Emission, Excitation

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## Background

The generalized process of 'cold light' emission is called luminescence, and it refers to the absorption of energy by a material with the subsequent emission of photons [1]. It is a phenomenon distinct from blackbody radiation, incandescence, or other such effects that cause materials to glow at high temperatures [1-4]. There are various forms of luminescence, usually denoted by the method from which the electrons were excited. For example, electroluminescence happens when an electrostatic field excites the electrons. Photoluminescence is the excitation of electrons due to electromagnetic radiation. Likewise, triboluminescence (TL) is light produced by the fracture of crystals [4,5].

The word triboluminescence comes from the Greek *tribein*, meaning 'to rub,' and the Latin prefix *lumen*, meaning 'light.' TL is a specific form of mechanoluminescence, which is the production of non-thermal light from any type of mechanical action or application of stress [4,5]. The mechanisms of TL light are still not

fully understood, but it is believed that TL is associated with asymmetric crystal structure. Crystal bonds are broken along planes with opposing charge, and when they re-connect, light is emitted as the charges pass through the separations created from the fracture. A classic example of TL light is found in the crystals used for real wintergreen-flavored Lifesavers® [6,7]. The green/blue sparks seen when chewing the candy is TL light being emitted from the crystal breakage in the sucrose [6,7]. TL can also be produced by the peeling of tape in a vacuum [8] and as a result of plate stresses during and just prior to an earthquake [4,9,10].

When a TL crystal is fractured, electrons are torn away from their parent atoms, resulting in a static discharge across the gap of the fracture [11,12]. The light is emitted by several distinct, material-dependent mechanisms. The emission spectrum for sugar indicates that the light comes from the atmospheric nitrogen that fills the gap during fracture. This is the same source of light as that from lightning or touching a doorknob on a winter day. Spectra for other samples show emission characteristic of the material as well as nitrogen lines. Such spectra suggest a secondary energy process [11,12]. Other substances

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exhibit a spectrum characteristic of the material alone. While abrupt charge separation is the same in all cases, emission mechanisms depend on the material [11,12].

In 1999, Sage and Geddes used the property of TL to patent a design for a sensor capable of discerning the locations of impact [13-15]. Their design involved coating a material with a triboluminescent crystal or creating a composite triboluminescent object [13-15]. A sensor would then be embedded within the structure or mounted on its surface [14]. Impacts to the structure would produce light which would be recorded and analyzed to determine the location [14]. In addition, Sage et al. proposed that several different triboluminescent materials could be used and arranged at various locations [13-15]. The advantage is that when an impact takes place, its location could be determined by the wavelength emitted [14]. For example, by placing two different triboluminescent materials at known distances from the detector, it is possible to determine the approximate location of the impact by measuring the emitted wavelength.

However, the triboluminescent emission yield for most materials is small, and the resulting light can be difficult to detect. For the last few years, Fontenot and Hollerman et al. have been working with europium tetrakis dibenzoylmethide triethylammonium ( $\text{EuD}_4\text{TEA}$ ) [16-18]. This material was found to have 206% of the triboluminescent emission yield compared to  $\text{ZnS:Mn}$  when subjected to low-energy impacts [17,19]. Both  $\text{EuD}_4\text{TEA}$  and  $\text{ZnS:Mn}$  emit strong TL when their crystals are crushed, scratched, or struck [20].

The first practical  $\text{EuD}_4\text{TEA}$  material was synthesized by Hurt et al. [18]. In 1987, Sweeting et al. studied the crystal form for  $\text{EuD}_4\text{TEA}$  [21] using the synthesis described by Hurt et al. Purification by recrystallization was accomplished by room temperature evaporation of methanol and dichloromethane [21]. After testing both materials for triboluminescence by grinding each of the crystals with a glass rod or steel spatula, it was discovered that the methanol-based material exhibited TL while the dichloromethane lacked TL [21]. In order to understand the structure of  $\text{EuD}_4\text{TEA}$ , the final products were analyzed using X-ray diffraction. From these results, Sweeting et al. determined that the material made with methanol showed no evidence of solvent incorporation, was monoclinic, and had a centric symmetry belonging to the  $I2/a$  space group [21]. However, in 2001, Cotton et al. showed that  $\text{EuD}_4\text{TEA}$  does not belong to the  $I2/a$  space group, but instead to the non-centric (and polar) space group  $Ia$  [22]. In 2011 and 2012, the synthesis process was modified to optimize the TL of  $\text{EuD}_4\text{TEA}$  [16,17,23,24]. In order to create a sensor as described by Sage and Geddes, another material that emits intense TL of a different color is required.

Lanthanide (Ln) compounds have distinctive optical properties, which include long luminescence lifetimes that range from microseconds to milliseconds and sharp emission bands with a full width half maximum that rarely exceeds 10 nm. These properties make lanthanides useful for organic light-emitting diodes, laser materials, and sensors [25]. In order to increase luminescence excitation, the Ln ion is usually coordinated to the ligands of  $\beta$ -diketone and aromatic amine derivatives. This typically increases the quantum efficiency through 'synergistic effects' and prevents the coordination of solvent molecules that quench the emissions [25].

Besides their outstanding photoluminescent properties, lanthanide  $\beta$ -diketone compounds containing chiral groups have additional properties that include second harmonic generation, ferroelectricity, TL, chirality sensing, circularly polarized luminescence, symmetric catalysis, and enantiomer selective synthesis [25]. In this paper, we investigate the luminescent properties of dibenzoylmethide triethylammonium compounds synthesized using a selection of Ln nitrates.

## Methods

### Synthesizing lanthanide-based dibenzoylmethide triethylammonium compounds

The synthesis of each lanthanide dibenzoylmethide triethylammonium compound was based on the procedures and methods used for  $\text{EuD}_4\text{TEA}$  as shown in [17]. The synthesis began by dissolving 4 mmol of the lanthanide nitrate in a hot solution of 35 mL anhydrous denatured ethyl alcohol. Then, 13 mmol of 1,3-diphenyl-1,3-propanedione also known as dibenzoylmethane (DBM) and 14 mmol of triethylamine (TEA) was added to the hot solution. The solution was then kept aside to cool at ambient temperature. Each Ln compound that formed was filtered and air-dried at room temperature. After formation, the synthesized compounds were shown to be very stable with no degradation due to humidity. Table 1 shows the color of the resulting solution or product at each step of the synthesis process. Table 1 also shows the color of the photoluminescent emission when the synthesized crystallites were exposed to ultraviolet light. The Ho, Ce, and La compounds do not emit fluorescence when excited with ultraviolet irradiation.

All lanthanide elements form trivalent cations whose chemistry is largely determined by the ionic radius, which decreases steadily from lanthanum to lutetium. For this reason, the notation  $\text{LnD}_4\text{TEA}$  can be used to represent a generic lanthanide dibenzoylmethide triethylammonium compound. For individual compounds, Ln will be replaced with the symbol used for the specific lanthanide element. For example,  $\text{TbD}_4\text{TEA}$  is shorthand for the terbium-based dibenzoylmethide triethylammonium compound.

**Table 1 Color of resulting solution and products of the Ln dibenzoylmethide triethylammonium compounds**

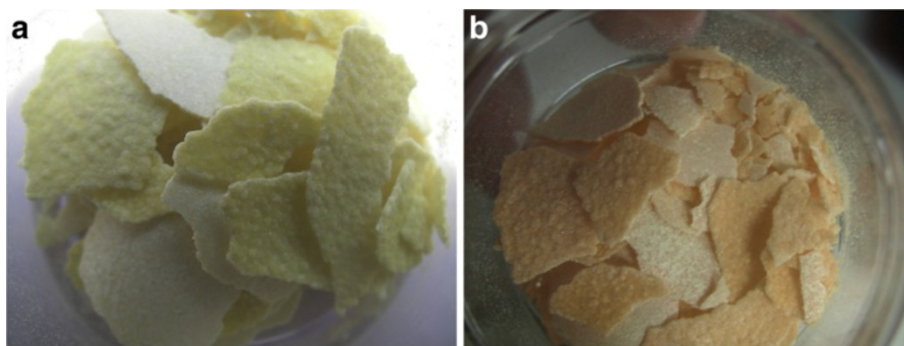
Ln dibenzoylmethide triethylammonium compound	Color of the solution after the material below is added			Color and condition of the finished solid product	Photoluminescence color
	Ln nitrate	DBM	TEA		
Eu	Clear	Dark yellow	Dark yellow	Light yellow sparkly crystalline	Bright red
Ho	Pink	Light orange	Dark orange	Orange or yellow flakes	None
Dy	Clear	Clear yellow	Dark yellow	Crystalline sparkly yellow green	Green
Er	Light pink	Peach	Dark orange	Flaky peach color	Red
Sm	Clear	Clear yellow	Dark yellow	Orange flaky crystalline	Red
Nd	Clear purple	Light clear yellow	Dark orange brown	Pinkish red flaky clumped crystals	Green
Gd	Clear	Clear yellow	Dark yellow	Yellow-orange crystalline	Red
Tb	Clear	Clear yellow	Dark yellow	Yellow crystalline	Green
Pr	Light green	Yellow green	Dark green yellow	Small green flakes	None
Yb	Clear	Light yellow	Dark yellow	Yellow hair-like clumped particles	Green
La	Clear	Clear pale yellow	Dark yellow	Pale yellow crystalline	None
Ce	Clear	Dark yellow	Dark blood red	Black crystalline	None

Notice from Table 1 that  $\text{EuD}_4\text{TEA}$  remained clear when the europium nitrate is added, then turns dark yellow with the addition of DBM and TEA. This synthesis creates a light yellow crystalline structure that sparkles. However, this is not true for all Ln compounds. The holmium nitrate compound turned the ethanol solution pink. When DBM is added to this solution, it turns light orange. When TEA is added, this solution turns dark orange. Figure 1 shows that the holmium compound is flaky and exhibits a color that depends on the nature of ambient light. When viewed under indoor fluorescent light, the holmium compound flakes are light orange in color as shown in Figure 1b. However, when the fluorescent lights are turned off and the sample is exposed to standard daylight, the holmium compound crystallites are light yellow as observed in Figure 1a. The holmium compound crystallites emit no luminescence when excited.

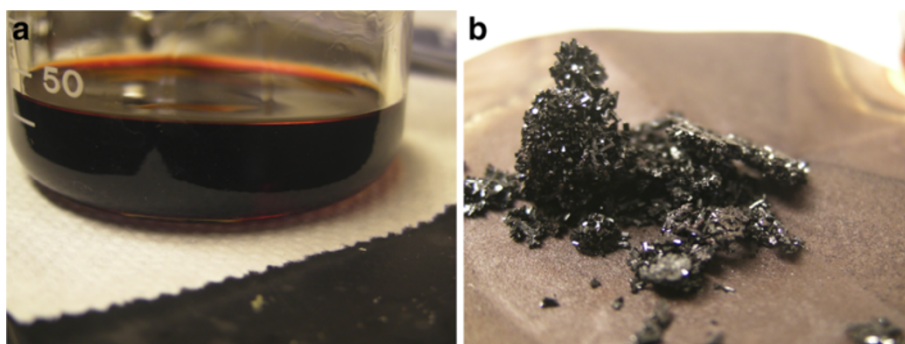
The cerium dibenzoylmethide triethylammonium compound also showed some interesting properties. The cerium nitrate and ethanol solution is completely clear. The addition of DMB turns this solution dark yellow; subsequently, when TEA is added to complete the reaction, the solution becomes blood red as shown in Figure 2a. Figure 2b shows that small black crystallites are produced during synthesis. Due to the limitations of the PTI spectrometer (Photon Technology International, Birmingham, NJ, USA) in measuring the 60-ns decay of cerium compounds, no observed luminescence was observed when excited. As a result, we are unable to say conclusively that  $\text{CeD}_4\text{TEA}$  emits no photoluminescence when excited.

#### Measuring triboluminescence

The relative triboluminescent emission yield from each  $\text{LnD}_4\text{TEA}$  compound was measured using a custom-



**Figure 1** Pictures of the flaky holmium dibenzoylmethide triethylammonium compound when illuminated. (a) By daylight. (b) By fluorescent light.



**Figure 2** Pictures taken during the cerium dibenzoylmethide triethylammonium compound synthesis process showing the resultant. (a) Blood red solution after TEA is added. (b) Black crystalline structure.

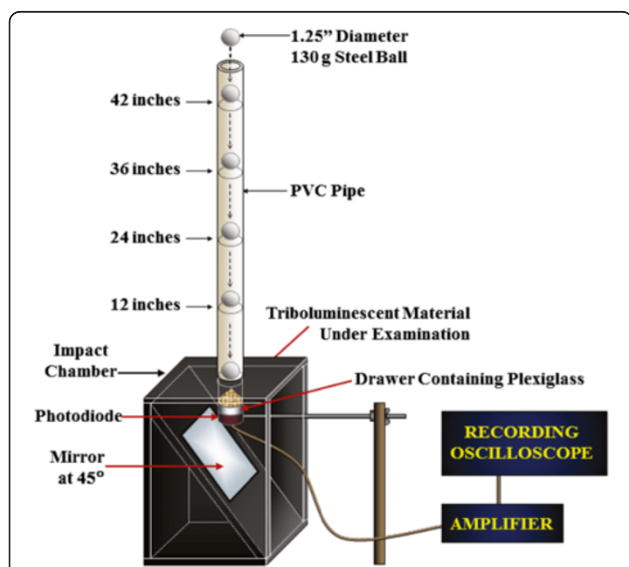
built drop tower as shown in Figure 3 and described in [19]. The visible emission spectrum for a candidate Ln compound can be made using a fiber optic spectrometer connected in place of the photodiode. The test begins by placing a small 0.1-g pile of each sample material on a plexiglass plate. The material is arranged so that it is positioned around the center of the tube with a minimum height. A 130-g steel ball is positioned on a pull pin at a distance of 1.06 m (42 in.) above the pile. The pin is pulled and the ball falls, producing TL at impact with the sample material. After each drop, the tube is removed, the ball is cleaned, and the sample powder is redistributed near the center of the target area [19,23].

To determine the triboluminescent yield for a given sample, a United Detector photodiode (United Detector Technology, Hawthorne, CA, USA) is positioned under the plexiglass plate 2.25 cm below the sample. A Melles

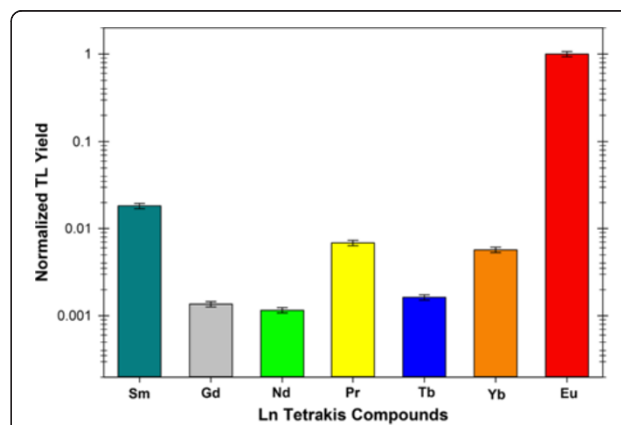
Griot large dynamic range linear amplifier (Melles Griot, Rochester, NY, USA) set to a gain of 200  $\mu$ A increases the signal amplitude. A Tektronix 2024B oscilloscope (Tektronix, Beaverton, OR, USA) records the signal in single sequence mode with a 500- $\mu$ s measurement time. Once the signal is acquired, it is analyzed using custom LabVIEW software that integrates the area under the curve and calculates the decay time for the particular emission [19,23]. In addition, five drops were made on each Ln compound sample so an average TL emission yield could be calculated.

#### Measuring photoluminescent spectra

For most lanthanide compounds, their ligand absorbs energy, undergoes intersystem crossing into a triplet state, and then transfers its energy to the Ln<sup>3+</sup> ion [26]. The excitation and emission phosphorescence from each compound was measured using a PTI QuantaMaster™ 14 spectrofluorometer located at Oak Ridge National Laboratory in Oak Ridge, TN, USA. The QuantaMaster™ was equipped with a Xe pulsed light source that allowed



**Figure 3** Schematic diagrams of the specially designed drop tower used to measure integrated triboluminescent light yield [19].



**Figure 4** Comparison of the average normalized triboluminescent light yield for the synthesized Ln compounds. All the collected results were normalized to the EuD<sub>4</sub>TEA light yield.

**Table 2 Decay time (1/e) results for the Ln dibenzoylmethide triethylammonium compounds**

Ln dibenzoylmethide triethylammonium compound	Average decay time (μs)
Sm	63.8 ± 4.9
Gd	56.8 ± 3.3
Nd	36.3 ± 4.0
Pr	432.0 ± 25.9
Tb	494.4 ± 7.9
Yb	49.5 ± 0.5
Eu	519.2 ± 9.2

for a continuously tunable repetition rate of up to 300 Hz. Each spectra measurement was completed using a step size of 0.25 nm, five samples per average, five shots per wavelength, and a frequency of 100 Hz. In addition, the integration time and delay were varied depending on the decay time of each material. EuD<sub>4</sub>TEA for example had a delay of 40 μs with respect to the flashlamp firing and an integration time of 500 μs.

## Results and discussion

### Triboluminescent light yield results

Results of the TL drop tower measurements for the synthesized lanthanides are shown in Figure 4. Since this is a relative measurement, the resulting emission light yield for each compound was normalized to the previously measured EuD<sub>4</sub>TEA value. In other words, the relative light yield for EuD<sub>4</sub>TEA is equal to one. The error in emission yield was estimated to be 7% which is the total uncertainty for the experiment. It is from combination of the uncertainties from material synthesis and drop tower operation [27]. As shown in Figure 4, it is evident that no tested Ln compound produces as much TL as EuD<sub>4</sub>TEA. The next largest TL yield was emitted by the Sm compound, which is 1.8% of that measured for

**Table 3 The electronic transitions for EuD<sub>4</sub>TEA with the associated wavelengths and energies**

Excitation transition	Wavelength (nm)	Energy (eV)	Emission transition	Wavelength (nm)	Energy (eV)
<sup>7</sup> F <sub>1</sub> → <sup>5</sup> F <sub>2</sub>	312.0	3.97	<sup>7</sup> D <sub>0</sub> → <sup>7</sup> F <sub>1</sub>	591.0	2.10
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> H <sub>3</sub>	326.0	3.80	<sup>7</sup> D <sub>0</sub> → <sup>7</sup> F <sub>2</sub>	611.5	2.03
				614.0	2.02
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>4</sub>	362.4	3.42	<sup>7</sup> D <sub>0</sub> → <sup>7</sup> F <sub>3</sub>	651.8	1.90
<sup>7</sup> F <sub>3</sub> → <sup>5</sup> D <sub>4</sub>	378.4	3.28	<sup>7</sup> D <sub>0</sub> → <sup>7</sup> F <sub>4</sub>	702.1	1.77
<sup>7</sup> F <sub>4</sub> → <sup>5</sup> D <sub>4</sub>	405.1	3.06			
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>3</sub>	410.4	3.02			
<sup>7</sup> F <sub>4</sub> → <sup>5</sup> G <sub>3</sub>	420.7	2.95			
	424.9	2.92			
<sup>7</sup> F <sub>6</sub> → <sup>5</sup> D <sub>4</sub>	433.8	2.86			
<sup>7</sup> F <sub>3</sub> → <sup>5</sup> G <sub>3</sub>	441.5	2.81			
<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>2</sub>	447.6	2.77			
<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>3</sub>	460.4	2.69			
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>2</sub>	465.8	2.66			
<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>2</sub>	484.6	2.56			
<sup>7</sup> F <sub>2</sub> → <sup>5</sup> D <sub>2</sub>	488.0	2.54			
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>1</sub>	526.4	2.36			
<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>1</sub>	536.6	2.31			

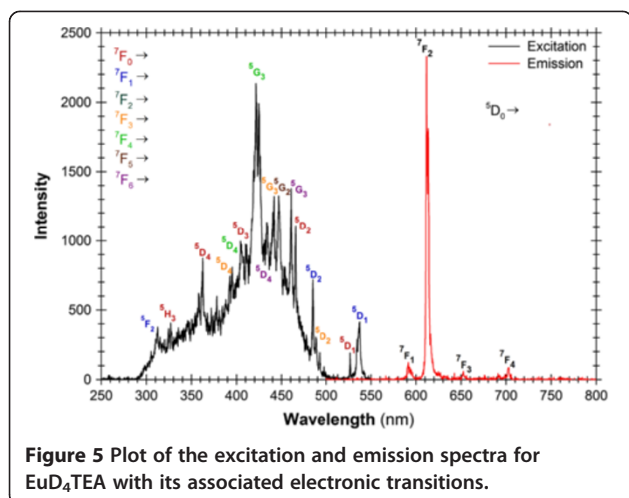
EuD<sub>4</sub>TEA. More research is needed to fully understand these results.

Once the average light yields were determined, the triboluminescent decay times for each compound were determined as shown in Table 2. This was accomplished using the decay time software as described in [19]. It is evident that the triboluminescent decay time is unique for each Ln compound. EuD<sub>4</sub>TEA has the longest decay time, while the Yb compound has the shortest decay time. Interestingly, it appears as though the decay time and triboluminescent emission yield are not correlated. While EuD<sub>4</sub>TEA has the longest decay time and is the brightest material, the Tb compound has the second longest decay time and has one of the smallest TL emission yields. Likewise, the Sm compound has the second highest TL yield, but it has one of the fastest decay times.

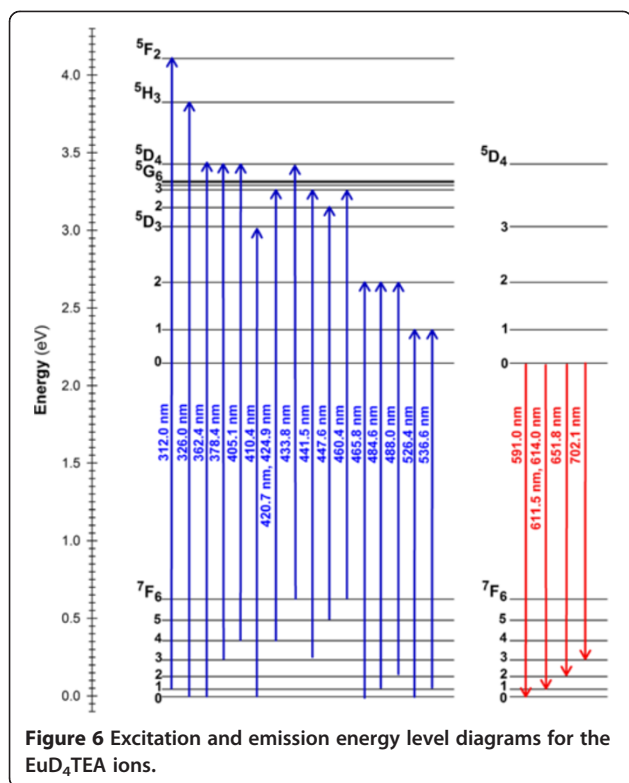
### Photoluminescent spectra

#### Europium dibenzoylmethide triethylammonium

The measured photoluminescent emission and absorption spectra for EuD<sub>4</sub>TEA are shown in Figure 5. The excitation spectrum was measured using the 612-nm (2.03-eV) emission peak, while the emission spectrum was measured using the 412-nm (3.01-eV) excitation wavelength. The spectrum indicates that the luminescence from



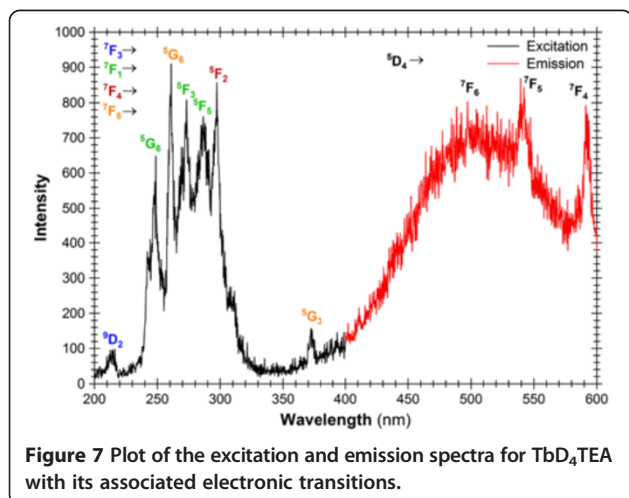
**Figure 5 Plot of the excitation and emission spectra for EuD<sub>4</sub>TEA with its associated electronic transitions.**



**Figure 6** Excitation and emission energy level diagrams for the  $\text{EuD}_4\text{TEA}$  ions.

the europium compound is due to its  $\text{Eu}^{3+}$  ion that produces the excited-state  $\text{Eu}^{3+}$ -centered transitions from the  $^5D_0$  levels to the lower  $^7F_{0-4}$  levels [28,29]. Due to overwhelming numbers, the wavelengths corresponding to each measured transition are shown in Table 3.

Notice that in Figure 5, the excitation energy is always from the ground  $^7F_1$  levels to the higher excited states. In order to save space and make the graph more readable, each energy transition was color coded. Thus, the 3.01-eV (312-nm) energy transition would be the blue  $^7F_1 \rightarrow ^5F_2$ . Also, notice that the majority of the excitation

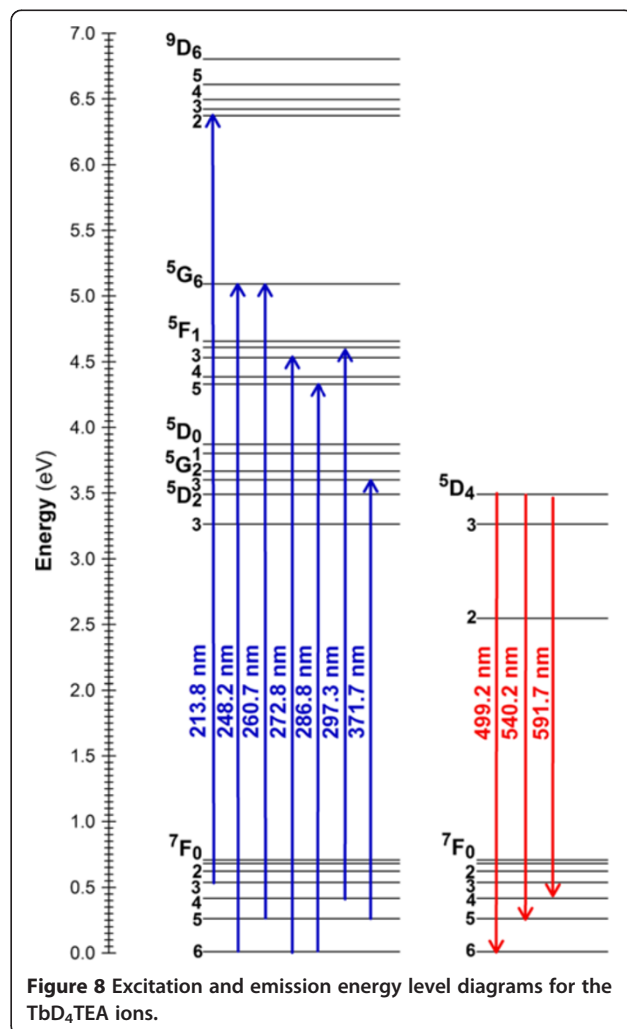


**Figure 7** Plot of the excitation and emission spectra for  $\text{TbD}_4\text{TEA}$  with its associated electronic transitions.

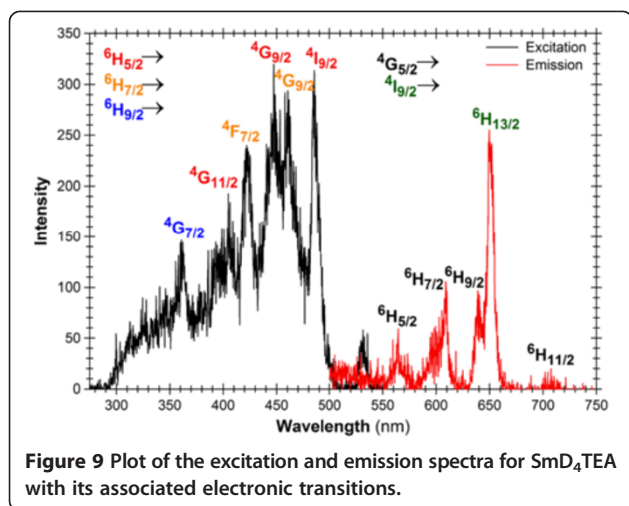
**Table 4** The electronic transitions for  $\text{TbD}_4\text{TEA}$  with the associated wavelengths and energies

Excitation transition	Wavelength (nm)	Energy (eV)	Emission transition	Wavelength (nm)	Energy (eV)
$^7F_3 \rightarrow ^9D_2$	213.8	5.80	$^5D_4 \rightarrow ^7F_6$	499.2	2.48
$^7F_6 \rightarrow ^5G_6$	248.2	5.00	$^5D_4 \rightarrow ^7F_5$	540.2	2.30
$^7F_5 \rightarrow ^5G_6$	260.7	4.76	$^5D_4 \rightarrow ^7F_4$	591.7	2.10
$^7F_6 \rightarrow ^5F_3$	272.8	4.54			
$^7F_6 \rightarrow ^5F_5$	286.8	4.32			
$^7F_4 \rightarrow ^5F_2$	297.3	4.17			
$^7F_5 \rightarrow ^5G_3$	371.7	3.34			

electronic transitions are from the  $^7F_1 \rightarrow ^5D_1$  and  $^5G_1$  levels. The most probable excitation transition is the 3.97-eV  $^7F_4 \rightarrow ^5G_3$  transition, while the most favorable emission transition is the 2.03-eV  $^5D_0 \rightarrow ^5F_2$  transition. This indicates that the europium compound can only be excited by ultraviolet to blue light, which yields a red luminescence. The energy level diagrams corresponding to



**Figure 8** Excitation and emission energy level diagrams for the  $\text{TbD}_4\text{TEA}$  ions.



the Figure 5 transitions that are listed in Table 3 are shown in Figure 6. The energy levels were determined from the measured values in Figure 5 and from the data shown in [28].

#### *Terbium dibenzoylmethide triethylammonium*

The measured photoluminescent emission and absorption spectra for TbD<sub>4</sub>TEA are shown in Figure 7. The excitation spectrum was measured using the 540-nm (2.30-eV) emission peak, while the emission spectrum was measured using the 297-nm (4.17-eV) excitation wavelength. The spectrum indicates that the luminescence from the terbium compound is due to its Tb<sup>3+</sup> ion that produces the excited-state Tb<sup>3+</sup>-centered transitions from the <sup>5</sup>D<sub>4</sub> levels to the lower <sup>7</sup>F<sub>6-4</sub> levels [29,30]. Due to the large number of measured transitions, the corresponding wavelengths are shown in Table 4.

Notice in Figure 8 that the excitation energy is always from the ground <sup>7</sup>F<sub>7</sub> levels to the excited states. Similar to Figure 5, the transitions were color coded in order to make Figure 7 more readable. Notice that a majority of the excitation transitions are from the <sup>7</sup>F<sub>6</sub> ground level. The most probable excitation transition for Tb<sup>3+</sup> is the 4.76-eV <sup>7</sup>F<sub>6</sub>→<sup>5</sup>G<sub>6</sub> transition, while the most favorable emission transition is the 2.30-eV <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub>. This

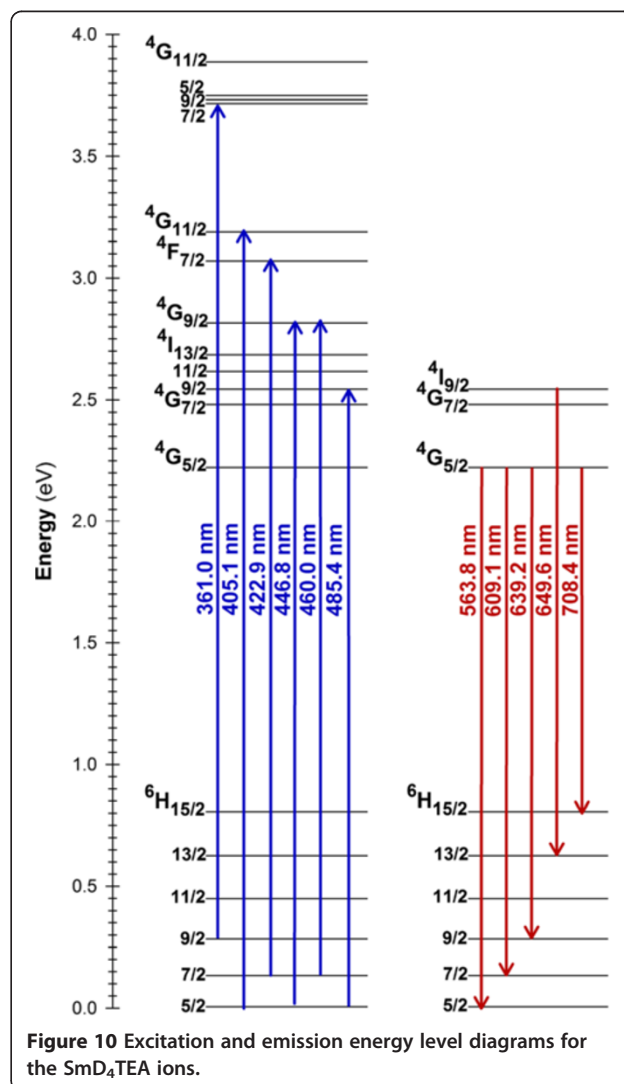
**Table 5** The electronic transitions for SmD<sub>4</sub>TEA with the associated wavelengths and energies

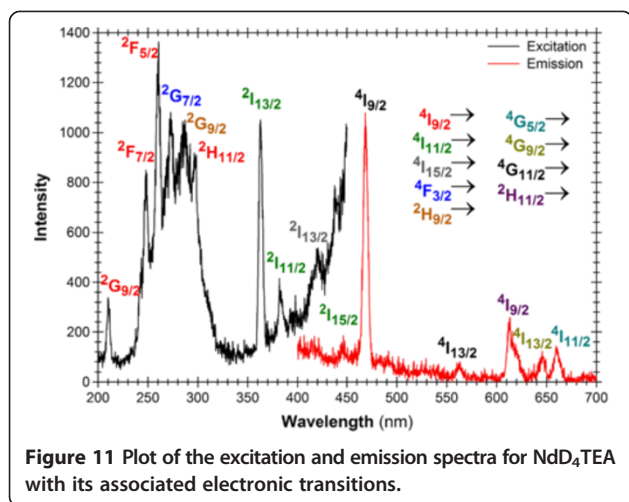
Excitation transition	Wavelength (nm)	Energy (eV)	Emission transition	Wavelength (nm)	Energy (eV)
<sup>6</sup> H <sub>9/2</sub> → <sup>4</sup> G <sub>7/2</sub>	361.0	3.43	<sup>4</sup> G <sub>5/2</sub> → <sup>6</sup> H <sub>5/2</sub>	563.8	2.20
<sup>6</sup> H <sub>5/2</sub> → <sup>4</sup> G <sub>11/2</sub>	405.1	3.06	<sup>4</sup> G <sub>5/2</sub> → <sup>6</sup> H <sub>7/2</sub>	609.1	2.04
<sup>6</sup> H <sub>7/2</sub> → <sup>4</sup> F <sub>7/2</sub>	422.9	2.93	<sup>4</sup> G <sub>5/2</sub> → <sup>6</sup> H <sub>9/2</sub>	639.2	1.93
<sup>6</sup> H <sub>5/2</sub> → <sup>4</sup> G <sub>9/2</sub>	446.8	2.77	<sup>4</sup> I <sub>9/2</sub> → <sup>6</sup> H <sub>13/2</sub>	649.6	1.91
<sup>6</sup> H <sub>7/2</sub> → <sup>4</sup> G <sub>9/2</sub>	460.0	2.70	<sup>4</sup> G <sub>5/2</sub> → <sup>6</sup> H <sub>11/2</sub>	708.4	1.75
<sup>6</sup> H <sub>5/2</sub> → <sup>4</sup> I <sub>9/2</sub>	485.4	2.55			

indicates that TbD<sub>4</sub>TEA can only be excited by middle ultraviolet (MUV) irradiation and will yield a green luminescence. The energy level diagrams corresponding to the Figure 7 transitions that are listed in Table 4 are shown in Figure 8. The energy levels were determined from the measured values in Figure 7 and from the data shown in [29,30].

#### *Samarium dibenzoylmethide triethylammonium*

The measured photoluminescent spectrum for SmD<sub>4</sub>TEA is shown in Figure 9. The excitation spectrum was measured using the 650-nm (1.91-eV) emission peak, while the emission spectrum was measured using the 485-nm (2.56-eV) excitation wavelength. The spectrum indicates that the luminescence from samarium compounds is due to their Sm<sup>3+</sup> ion that produces the excited-state Sm<sup>3+</sup>-centered transitions from the <sup>4</sup>G<sub>5/2</sub> levels to the lower <sup>6</sup>H<sub>5/2-11/2</sub> and <sup>4</sup>I<sub>9/2</sub> to <sup>6</sup>H<sub>13/2</sub> levels [29,31]. Due to the





**Figure 11** Plot of the excitation and emission spectra for NdD<sub>4</sub>TEA with its associated electronic transitions.

large number of measured transitions, the corresponding wavelengths are shown in Table 5.

Notice in Figure 9 that the excitation energy is always from the ground <sup>6</sup>H<sub>j</sub> levels to the excited states. Notice that a majority of the excitation transitions are from the <sup>6</sup>H<sub>5/2</sub> and <sup>6</sup>H<sub>7/2</sub> ground level. The most probable excitation transition for Sm<sup>3+</sup> is the 2.77-eV <sup>6</sup>H<sub>5/2</sub>→<sup>4</sup>G<sub>9/2</sub> and 2.55-eV <sup>6</sup>H<sub>5/2</sub>→<sup>4</sup>I<sub>9/2</sub> transitions, while the most favorable emission transition is 1.91-eV <sup>4</sup>I<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub>. This indicates that the Sm compound has a broad excitation energy ranging from UV to short wavelength green light. The energy level diagrams corresponding to the Figure 9 transitions that are listed in Table 5 are shown in Figure 10. The energy levels were determined from the measured values in Figure 9 and from the data shown in [29,31].

**Neodymium dibenzoylmethide triethylammonium**

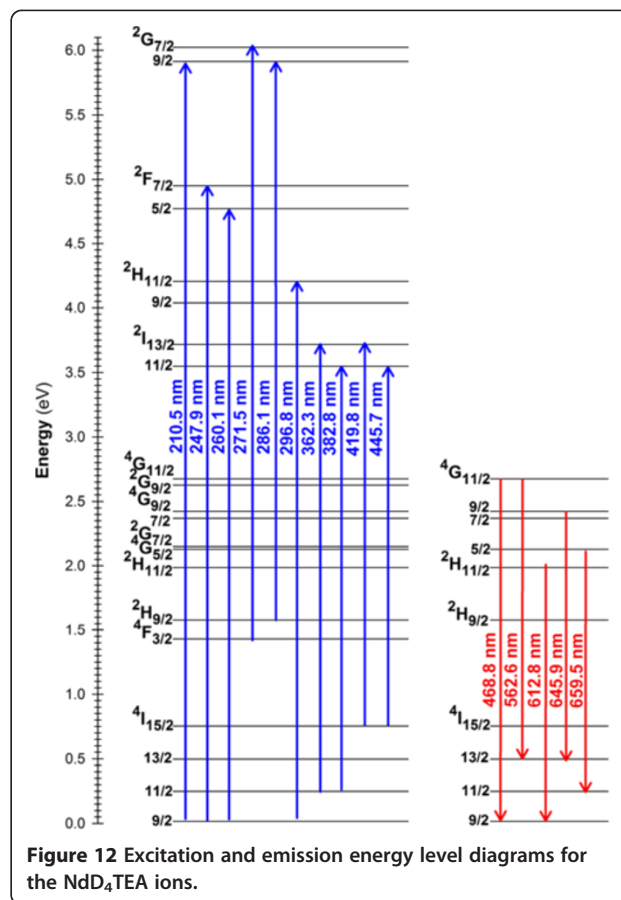
The measured photoluminescent spectrum for NdD<sub>4</sub>TEA is shown in Figure 11. The excitation spectrum was

**Table 6** The electronic transitions for NdD<sub>4</sub>TEA with the associated wavelengths and energies

Excitation transition	Wavelength (nm)	Energy (eV)	Emission transition	Wavelength (nm)	Energy (eV)
<sup>4</sup> I <sub>9/2</sub> → <sup>2</sup> G <sub>9/2</sub>	210.5	5.89	<sup>4</sup> G <sub>11/2</sub> → <sup>4</sup> I <sub>9/2</sub>	468.8	2.64
<sup>4</sup> I <sub>9/2</sub> → <sup>2</sup> F <sub>7/2</sub>	247.9	5.00	<sup>4</sup> G <sub>11/2</sub> → <sup>4</sup> I <sub>13/2</sub>	562.6	2.20
<sup>4</sup> I <sub>9/2</sub> → <sup>2</sup> F <sub>5/2</sub>	260.1	4.77	<sup>2</sup> H <sub>11/2</sub> → <sup>4</sup> I <sub>9/2</sub>	612.8	2.02
<sup>4</sup> F <sub>3/2</sub> → <sup>2</sup> G <sub>7/2</sub>	271.5	4.57	<sup>4</sup> G <sub>9/2</sub> → <sup>4</sup> I <sub>13/2</sub>	645.9	1.92
<sup>2</sup> H <sub>9/2</sub> → <sup>2</sup> G <sub>9/2</sub>	286.1	4.33	<sup>4</sup> G <sub>5/2</sub> → <sup>4</sup> I <sub>11/2</sub>	659.5	1.88
<sup>4</sup> I <sub>9/2</sub> → <sup>2</sup> H <sub>11/2</sub>	296.8	4.18			
<sup>4</sup> I <sub>11/2</sub> → <sup>2</sup> H <sub>13/2</sub>	362.3	3.42			
<sup>4</sup> I <sub>11/2</sub> → <sup>2</sup> I <sub>11/2</sub>	382.8	3.24			
<sup>4</sup> I <sub>15/2</sub> → <sup>2</sup> I <sub>13/2</sub>	419.8	2.95			
<sup>4</sup> I <sub>15/2</sub> → <sup>2</sup> H <sub>11/2</sub>	445.7	2.78			

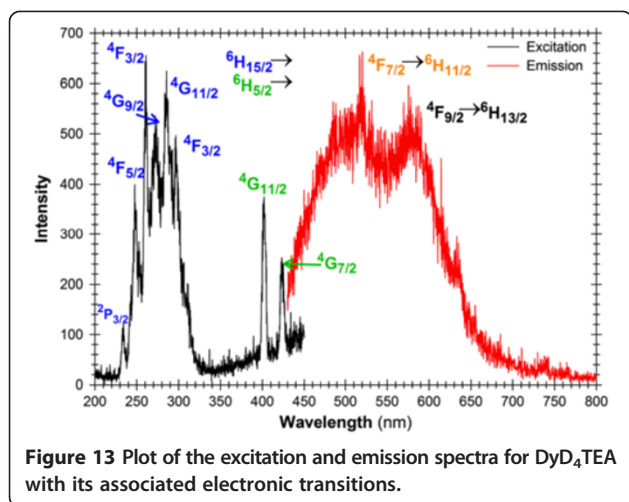
measured using the 469-nm (2.64-eV) emission peak, while the emission spectrum was measured using the 363-nm (3.42-eV) excitation wavelength. The spectrum indicates that the luminescence from the neodymium compound is due to its Nd<sup>3+</sup> ion that produces the excited-state Nd<sup>3+</sup>-centered transitions from the <sup>4</sup>G<sub>j</sub> levels to the lower <sup>4</sup>I<sub>j</sub> and <sup>4</sup>H<sub>11/2</sub> to <sup>4</sup>I<sub>9/2</sub> levels [29,31]. Due to the large number of measured transitions, the corresponding wavelengths are shown in Table 6.

Notice in Figure 11 that the majority of the excitation energy is from the ground <sup>4</sup>I<sub>j</sub> levels to the excited states. However, unlike the Eu<sup>3+</sup> and Sm<sup>3+</sup> excitation transitions, Nd<sup>3+</sup> has transitions from two different excited states. These transitions include <sup>4</sup>F<sub>3/2</sub> to <sup>2</sup>G<sub>7/2</sub> and <sup>2</sup>H<sub>9/2</sub> to <sup>2</sup>G<sub>9/2</sub>. The most probable excitation transition for Nd<sup>3+</sup> is the 4.77-eV <sup>4</sup>I<sub>9/2</sub>→<sup>2</sup>F<sub>5/2</sub> transition, while the most favorable emission transition is 1.91-eV <sup>4</sup>G<sub>11/2</sub>→<sup>4</sup>I<sub>9/2</sub>. This indicates that the Nd compound has broad excitation energy in the MUV area with sharp bands in the 350- to 450-nm range. In addition, when the neodymium compound is excited, it produces a blue light. The energy level diagrams corresponding to the Figure 11 transitions that are listed in Table 6 are shown in Figure 12. The energy levels were determined from the measured values in Figure 11 and from the data shown in [29,31].



**Figure 12** Excitation and emission energy level diagrams for the NdD<sub>4</sub>TEA ions.





**Figure 13** Plot of the excitation and emission spectra for DyD<sub>4</sub>TEA with its associated electronic transitions.

### Dysprosium dibenzoylmethide triethylammonium

The measured photoluminescent spectrum for DyD<sub>4</sub>TEA is shown in Figure 13. The excitation spectrum was measured using the 519-nm (2.39-eV) emission peak, while the emission spectrum was measured using the 285-nm (3.35-eV) excitation wavelength. The spectrum indicates that the luminescence from the dysprosium compound is due to its Dy<sup>3+</sup> ion that produces the excited-state Dy<sup>3+</sup>-centered transitions from the <sup>4</sup>F<sub>7/2,9/2</sub> to <sup>6</sup>H<sub>11/2,13/2</sub> levels [29,31]. Due to the large number of measured transitions, the corresponding wavelengths are shown in Table 7.

Notice in Figure 13 that the majority of excitation energy is from the ground <sup>4</sup>H<sub>15/2</sub> levels to the excited states. Interestingly, it seems that the <sup>4</sup>F<sub>3/2</sub> splits into two different levels as shown in [31]. This splitting causes two different excitation energies as shown in Table 7. The most probable excitation transition for Dy<sup>3+</sup> is the 4.76-eV <sup>6</sup>H<sub>15/2</sub>→<sup>4</sup>F<sub>3/2</sub> transition, while the most favorable emission transition is 2.39-eV <sup>4</sup>F<sub>7/2</sub>→<sup>6</sup>H<sub>11/2</sub>. Figure 13 indicates that the Dy compound has broad excitation energy in the MUV region with sharp bands in the 390- to 430-nm range. Using these excitation energies will cause the dysprosium compound to produce a green light. The energy

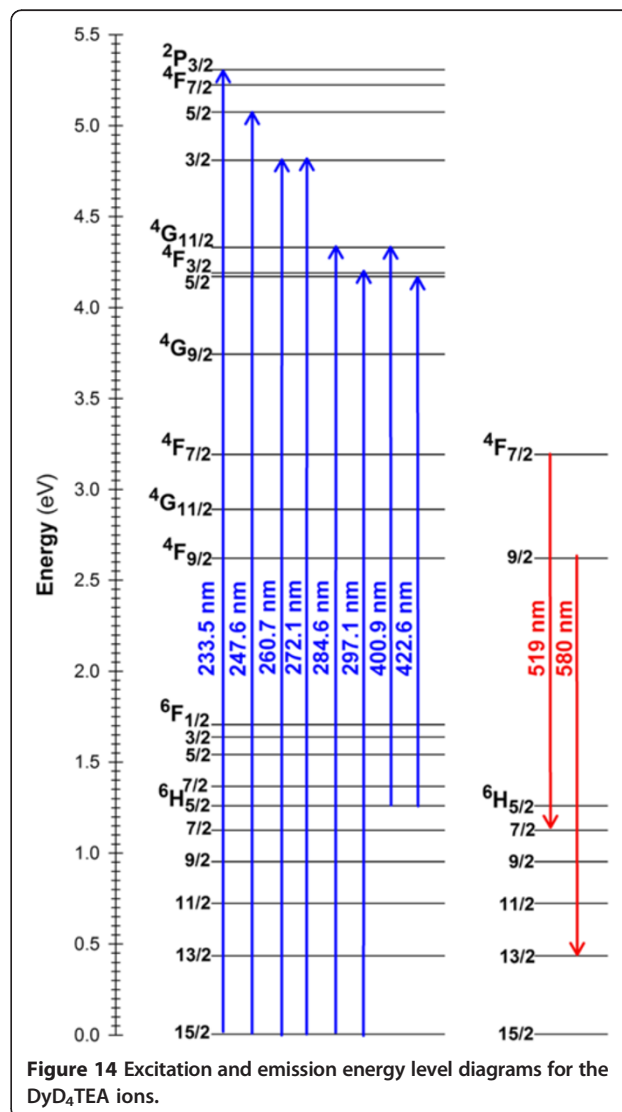
**Table 7** The electronic transitions for DyD<sub>4</sub>TEA with the associated wavelengths and energies

Excitation transition	Wavelength (nm)	Energy (eV)	Emission transition	Wavelength (nm)	Energy (eV)
<sup>6</sup> H <sub>15/2</sub> → <sup>2</sup> P <sub>3/2</sub>	233.5	5.31	<sup>4</sup> F <sub>7/2</sub> → <sup>6</sup> H <sub>11/2</sub>	519	2.39
<sup>6</sup> H <sub>15/2</sub> → <sup>4</sup> F <sub>5/2</sub>	247.6	5.01	<sup>4</sup> F <sub>9/2</sub> → <sup>6</sup> H <sub>13/2</sub>	580	2.14
<sup>6</sup> H <sub>15/2</sub> → <sup>4</sup> F <sub>3/2</sub>	260.7	4.76			
<sup>6</sup> H <sub>15/2</sub> → <sup>4</sup> G <sub>9/2</sub>	272.1	4.56			
<sup>6</sup> H <sub>15/2</sub> → <sup>4</sup> G <sub>11/2</sub>	284.6	4.36			
<sup>6</sup> H <sub>15/2</sub> → <sup>4</sup> F <sub>3/2</sub>	297.1	4.17			
<sup>6</sup> H <sub>5/2</sub> → <sup>4</sup> G <sub>11/2</sub>	400.9	3.09			
<sup>6</sup> H <sub>5/2</sub> → <sup>4</sup> D <sub>7/2</sub>	422.6	2.93			

level diagrams corresponding to the Figure 13 transitions that are listed in Table 7 are shown in Figure 14. The energy levels were determined from the measured values in Figure 13 and from the data shown in [29,31].

### Conclusions

Previous research has shown that EuD<sub>4</sub>TEA can easily be synthesized with 206% of the triboluminescent emission yield compared to ZnS:Mn. The research completed here shows that lanthanide-based dibenzoylmethide triethylammonium compounds other than EuD<sub>4</sub>TEA can also be successfully synthesized and characterized. However, none of the other synthesized lanthanide-based compounds has an emission yield near the values achieved by EuD<sub>4</sub>TEA. In fact, SmD<sub>4</sub>TEA had the next largest triboluminescent emission yield over all the tested lanthanide compounds. However, the SmD<sub>4</sub>TEA emission yield was only 1.8% of what was measured for EuD<sub>4</sub>TEA.



**Figure 14** Excitation and emission energy level diagrams for the DyD<sub>4</sub>TEA ions.

### Competing interests

The authors declare that they have no competing interests.

### Authors' contributions

RSF, WAH, KNB, SWA, and MDA contributed equally to this work. All authors read and approved the final manuscript.

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RSF received his applied physics Ph.D. in May 2013 from Alabama A&M University. WAH holds the position of Dr. and Mrs. Sammie W. Cosper/BORSF endowed associate professor of physics at the University of Louisiana at Lafayette. KNB holds the position of associate professor of chemistry at Alabama A&M University. SWA holds the position of chief scientist at Emerging Measurements Co. (EMCO). MDA holds the position of professor of physics and chairman of the Department of Physics, Chemistry, and Mathematics at Alabama A&M University.

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