

ONLINE PUBLICATIONS



Enhancing the fluorescence of a europium complex by co-doping with terbium

Rafeeqe Puthiyottil, Soney Varghese, Unnikrishnan Gopalakrishnapanicker, and James Guthrie

When two rare-earth ions in complexes are added to a polymer matrix, light emission becomes five times brighter due to energy transfer between the metal ions.

Rare-earth metal complexes have gained significant attention due to their unique long-lived, line-like light emission at a variety of wavelengths. These cover the spectral range from the near-UV through the visible and into the near-IR region. The pure complexes, however, have poor physical and mechanical properties. For practical application of their fluorescence, polymeric host materials doped with complex molecules offer better thermal and mechanical properties and easier processing than the complexes alone. Doping can also reduce the concentration quenching of the emission by the complex that could otherwise be caused by the aggregation of the complex molecule. Hence, polymers doped with rare-earth complexes often possess the advantageous features of both the matrix and the dopant. The luminescent properties of selected lanthanide ion complexes dispersed in polymer matrices have been the subject of extensive research in recent years because of their potential applications in various fields. Examples include tunable lasers, amplifiers for optical communications, light-emitting active layers in multilayer organic LEDs, and efficient light-converting molecular devices for fluoroimmunoassays and photovoltaic cells.¹⁻³

In rare-earth complexes, light emissions are due to movement of electrons between f orbitals in the metal ions, commonly referred to as f-f transitions. Claudio Lo Sterzo's group discovered that fluorescent lanthanide ions can accept energy from the ligands, i.e., the molecules that bind to the metal to create a complex, if the excited state of the ligand is greater than that of the acceptor.⁴ Also, Qijin Zhang and colleagues reported that lanthanide ions can accept energy from other complexes that are in close proximity: the energy from one metal ion transfers to the other, increasing the light emission from the latter ion. This phenomenon is termed co-fluorescence or enhanced fluorescence.⁵

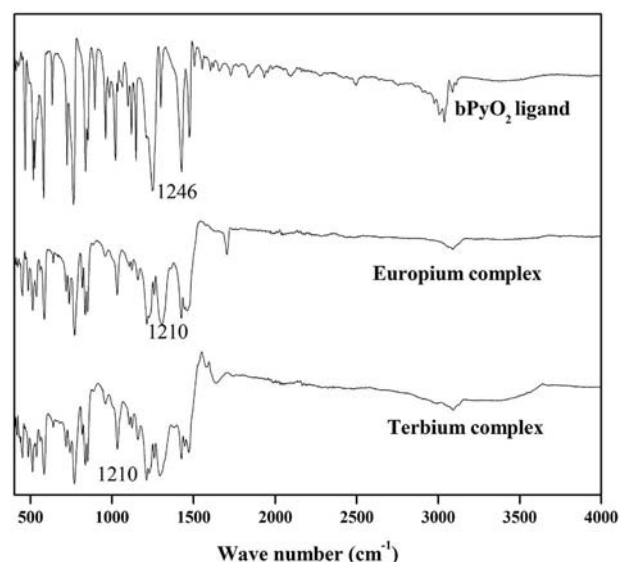


Figure 1. IR spectra of (2,2'-bipyridine-N,N-dioxide) ligand ($bPyO_2$), europium (2,2'-bipyridine-N,N-dioxide)₃ (NO_3)₃, and terbium (2,2'-bipyridine-N,N-dioxide)₃ (NO_3)₃ complexes. The shift in IR absorption lines in the lower two spectra confirms that europium and terbium ions formed complexes with the ligand.

Our present work focuses on the co-fluorescence features of europium (2,2'-bipyridine-N,N-dioxide)₃ (NO_3)₃ and terbium (2,2'-bipyridine-N,N-dioxide)₃ (NO_3)₃-doped poly(methyl methacrylate) (PMMA) films.⁶ Initially, we synthesized and characterized these europium and terbium complexes. They were then successfully dispersed in a PMMA matrix, which provides a uniform, thin-film format that can be relatively easy to handle for future applications.

We first wanted to confirm that the lanthanide ions had formed complexes. We characterized them by elemental analysis and by IR spectroscopy. Elemental analysis showed that for $Eu_{20}H_{16}O_{13}N_7$,

C = 33.45%, H = 2.55%, and N = 13.20%. For $TbC_{20}H_{16}O_{13}N_7$, we found that C = 32.35%, H = 2.65%, and N = 12.70%. The IR spectra of (2,2'-bipyridine-N,N-dioxide) ligand (bPyO₂), europium (2,2'-bipyridine-N,N-dioxide)₃ (NO₃)₃, and terbium (2,2'-bipyridine-N,N-dioxide)₃ (NO₃)₃ complexes are shown in Figure 1. The absorption bands due to N–O stretching and bending vibrations are found at 1246 and 850cm⁻¹, respectively, for the ligand alone. If the metal coordinates with the ligand to form a complex, we would expect these bands to shift to lower frequencies. This can be attributed to the double-bond character of the N–O bonds, which exist in the free ligands due to resonance but decrease in the complex when the metal ion is coordinated through the oxygen atom. In Figure 1, we observe such a shift of the bands in the IR spectra for both lanthanides, confirming the formation of complexes. The elemental analyses also support the formation of the proposed complexes.

Next, we examined the emission spectrum of each complex doped into PMMA matrix, and then the spectrum when both are doped into PMMA together, to determine whether we can enhance fluorescence through energy transfer between ions. The europium complex alone doped into PMMA matrix gave an intense emission at 613nm, while terbium gave an intense emission at 546nm (see Figure 2). The emission spectra of the co-doped samples were recorded from 520 to 750nm under excitation at 300nm (see Figure 3). The peak corresponding to 546nm relates to the ⁵D₄ to ⁷F₅ transition of terbium. The other five emission peaks correspond to emissions from europium ions. We experimented with different concentrations of europium and terbium ions in the co-doped samples. The intensity of the emission from the europium

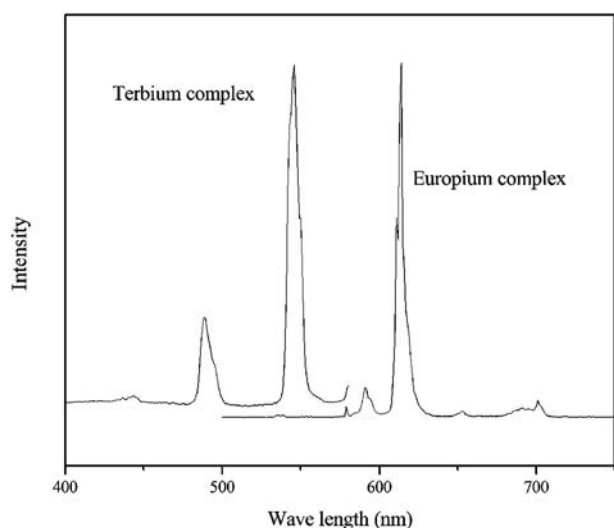


Figure 2. Emission spectra of europium complex and terbium complex, when each, alone, is doped into poly(methyl methacrylate) (PMMA).

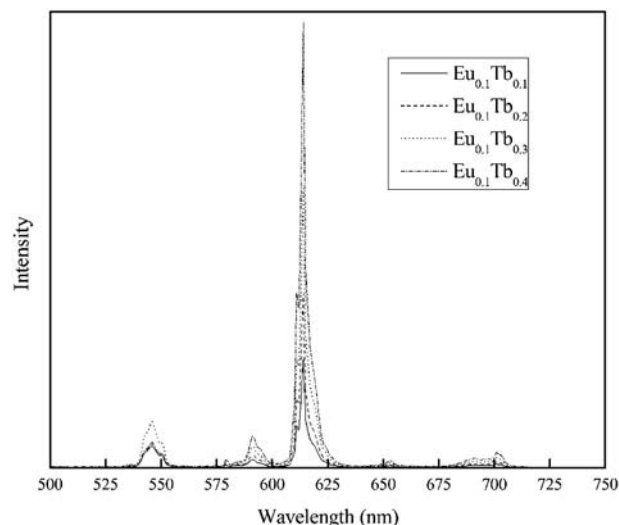


Figure 3. Emission spectra of europium-terbium (Eu-Tb) complexes in co-doped thin films of PMMA show energy transfer from terbium (which emits at 546nm) to enhance the fluorescence of europium at 613nm.

ion increases with increasing loading of terbium ion. The intensity of the peak that is assigned to terbium ions decreased on increasing the terbium ion concentration. This shows that the energy from the terbium ion is transferred to europium ion in close proximity.

We took another look at the energy levels of the ions and ligand to confirm that the transfer is feasible. The suitability of the energy gap between the resonance level of lanthanide ions and the triplet state of the ligand is a critical factor for an efficient energy transfer process to occur. We confirmed that the triplet state energy level of the bPyO₂ ligand is 22,275cm⁻¹ and that of the terbium ion is 20,400cm⁻¹, which meets the criterion.

To study the fluorescence enhancement mechanism, we measured fluorescence decay curves and fluorescence lifetimes. Figure 4 shows the lifetime values of the europium-terbium complex-doped thin films of PMMA, at 613nm. The fluorescence lifetime measurements show almost no change in values. Notably, lifetime values do not depend on the number of terbium ions in the co-doped systems. If the europium and terbium complexes interacted to form a new type of complex, we would observe a change in the lifetime. We see no change, which shows that there is no chemical interaction between the europium and terbium complexes after loading the terbium complex in the polymer matrix. The intermolecular energy transfer occurs between separate europium and terbium complexes.

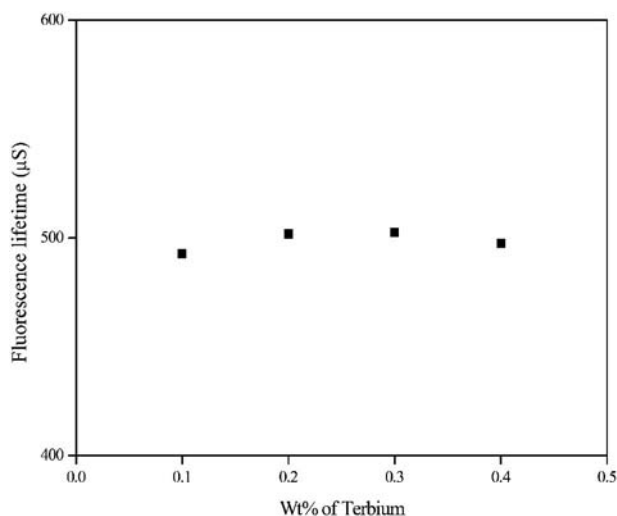


Figure 4. Fluorescence lifetime of co-doped systems. Only a very small variation in the fluorescence lifetime results from changing the loading of terbium ions in co-doped europium-terbium complexes in PMMA.

In conclusion, we observed a fivefold increase in luminescence when 0.4wt% terbium complex is co-doped with 0.1wt% europium complex in PMMA. Thus it seems a promising route to developing a high-performance luminescent polymer material. For commercial applications, however, the materials' thermal stability and weathering characteristics must be optimized. We are currently examining these properties in our laboratory.

The authors acknowledge the Council of Scientific and Industrial Research, India, and the UK-India Education and Research Initiative program for their support.

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Adieu And Back

I had flown over a bridge
a bridge that lead to pearly gates.
While on my way I stumbled, stopped by
a milestone that read 'it's not yet.
Directed me back to land
of seven wonders
Where grave diggers and followers
of Hippocrates lived.
They brought me back and chained
me to life.
Suffocated I feel now in sympathetic air.
Both blown and breathed out of
blood relations care.
Night blankets day and day wakes
night summer, winter autumn and
spring again
Thoughts remain as life remains
when its time, I will fly again.

Hashmina Habeeb

Submitted: Saturday, August 31, 2013

Edited: Tuesday, September 03, 2013

(<http://www.poemhunter.com/poem/adieu-and-back>)

My Priced Possession

I hung in a corner dusty and aloof,
Fecklessly placed near an unwanted roof.
Faded with lifeless cobwebs i lay,
An unwanted piece in my on-looker's way.
Moonlit nights three in a row.
How many more had i to know.
Neither did day or his better half,
Come up with a sigh or a better laugh.
Then one day did the winds chime,
In agreement with the sooth sayer's rhyme.
He locked his eyes in a single glance,
With the picture that lay, in the corner by chance.
An artist in his creative best,
Described her beauty distinct from the rest.
Every touch of his was a colorful stroke,
Painters' envied, their brushes broke.
What more colors do I on you stroke?
The artist in me, on you awoke.

Hashmina Habeeb

Submitted: Saturday, August 24, 2013

Edited: Wednesday, September 04, 2013

(<http://www.poemhunter.com/poem/my-priced-possession>)

Pear

I longed to be eaten
Relished, enjoyed not thrown out half beaten
I waited to be cleansed, groomed and kept
Held in just hands
While Ripe and blush
Summer crawled
And winter crept
Grabbed me by the waist
Squeezed of pulp and taste
Ruined of luster, weak and worn out
I wait for justice
Till time takes its chance
When worms take charge
Of my wasted youth
Cast me away
To my mother's lap
For pests I prefer
To an unjust man

Hashmina Habeeb

Submitted: Saturday, August 24, 2013

Edited: Monday, August 26, 2013

(<http://www.poemhunter.com/poem/pear>)

She

They dig up the ashes
From the depths of her psyche
Unperished remains her fate
Embalmed in the culture of
A forgone civilization
Unscathed they hail
A fate so dear to the taker
Of the procession
A celebration to the mass
And doomed the victim
For a dawn awaits her soul
Tomorrows furl and unfurl in pain
Forever remains "she" in her fate.

Hashmina Habeeb

Submitted: Saturday, August 24, 2013

Edited: Monday, August 26, 2013

(<http://www.poemhunter.com/poem/she-322>)

Of Mothers

How I brood over the forgotten lunch box
while a mother somewhere suckles her wrinkled child
her parched breasts failing even a salty drop
Yet another pinches meat from discarded bones
to add flesh to a frail form.

How I curse the books on my child's back
while a mother somewhere watches hers drag,
a sack filled with his folks' woes.

How I coax the nonchalant ears
to read and write and win some prize
while a mother somewhere fails to sew
some tattered dreams and frayed smiles,
Her trophy is her child's catch!

How I nurse a playful knee
with balmy words and modish bands
while a mother somewhere clings in pain
to a dismembered leg in her hands
Her shrieks: her words, her tears: his aid.

Zeenath Ibrahim

(Zeenath Ibrahim is currently working as Assistant Professor in the Department of English at Farook College, Calicut, India. She loves to read and write poetry. Many of her poems have appeared in national and international anthologies).

(<http://bigriverpoetry.com/1/archives/10-2013/1.html>)