Journal of Atomic, Molecular, Condensed Matter & Nano Physics
Vol. 9, No. 1, pp. 67–74, 2022
ISSN 2582-8215
Published by RGN Publications

http://www.rgnpublications.com

Special Issue:

Nuclear Track Detectors, Luminescence and Their Applications
Guest Editors: P.D. Sahare, Rajesh Kumar, Ashok Kumar

DOI: 10.26713/jamcnp.v9i1.1961

Research Article

Photoluminescence Properties of (Mg^{2+}) Divalent and (Al^{3+}) Trivalent Metal Coumarinolates Doped with Quinoline for PCLED Application

S.M. Sawde*[1], R.R. Patil[2] and S.V. Moharil[1]

[1] *Applied Physics Department, RTM Nagpur University, Nagpur, India*
[2] *Department of Physics, Institute of Forensic Science RT Road, Nagpur, India*
***Corresponding author:** suwarnasawde@gmail.com

Received: October 27, 2021 **Accepted:** May 24, 2022

Communicated by: Tarun Kumar

Abstract. Several Mg-Coumarinolates and Al-Coumarinolates doped with different concentrations of Quinoline were synthesized by simple chemical synthesis method and their PL spectra were studied. Usually, pure coumarin along with the chelates show weak luminescence and the emission is witnessed around 450 nm with excitation around 350 nm. Hence, such chelates do not find any practical applications. Addition of quinoline in lesser amount affects the emission and excitation of Mg-Coumarin and Al-Coumarin considerably. Intense photoluminescence is observed in these Mg based mixed chelates. In all samples, a well-defined emission band at 490 nm is observed with broad excitation in 350 nm to 470 nm range. Hence good overlap of excitation with 420 nm and 440 nm LED emission makes these materials suitable for white LED applications.

Keywords. Di-coumarinolates, Tri-coumarinolates, PCLED application

PACS. 78.55.-m (Photoluminescence, properties and materials), 61.66.Hq (Organic compounds)

1. Introduction

Coumarin chelates have been an object of investigations in recent past. Metal complexes are being used as diagnostic agents and have opened relatively new area of medicinal research and have flourished rapidly from last 4-5 decades. The complexes of metallic salts are more effective than the parent drug.

Several new ionophores derived from crown ethers and iminodiacetic subunits attached to 3-aroylcoumarins have been synthesized and fully characterized. The alkaline-earth complexes of these new ligands were studied from their UV–visible and fluorescence data. Some systems displayed strong bathochromic shifts upon complexation with Mg^{2+} that may make them useful signaling devices [2].

The synthesis and photophysical properties of luminescent lanthanide complexes based on a coumarin derivative for advanced photonic applications such as planar waveguide amplifiers and light-emitting diodes was reported [7].

These chelates also have been prepared and reported for their physiological, photodynamic, anticoagulant and anticancer activity [4, 14]. Mostly the complexes with lanthanides like La, Pr, Sm, Eu, Gd, Tb, Dy, Y[1], Ce[4] and Nd have been studied and showed interesting properties [9, 15]. It was found that the anticoagulant and antifungal activity get enhanced on complexation, particularly with lanthanides [3]. Normally most of the coumarins gives fluorescence and some of them give a low analytical signal [8] and therefore it enhances detection limit using fluorescence. The sensitivity of the fluorimetric determination can be enhanced by the formation of complexes, i.e. using so called sensitized fluorescence. Lanthanide chelates are not the only studied chelates. Several chelates with ions like Co, Cu, Ni, Mn, and Fe were synthesized and evaluated for their efficacy as antibacterial agents. It has been found that some of the coumarins show distinct physiological photodynamic and bacterio-static activities [5]. The complexes of metallic salts are more potent and less toxic in many cases as compared to the parent drug [13]. These metal complexes are found to be interesting due to their biological applications like antifungal, [12] antibacterial [1] and anti tumor [6] activity. Some chalcones derived from coumarin derivatives, possess significant antimicrobial activity [11]. Some 3-acetyl/acetoacetoacetyl-4-hydroxy benzopyran-2-ones have been reported as an anti-HIV agent [10].

The monovalent Silver Ag(I) forms good complexes with nitrogen, sculpture and halogen donor ligands. It forms complexes via oxygen in carboxylate ligands. The common coord modes are Linear, Trigonal Planar, Tetrahedral and Octahedral. Unidentate mode is also possible e.g. Silver (I) carboxylates. The divalent Copper (II), Zinc (II) carboxylates form mostly bridged dimers however mononuclear complexes are also reported. Copper Cu (II) Zinc (II) Common coord modes are Tetrahedral, Square Planar, Trigonal, Bipyramidal and Octahedral.

The survey shows, though several coumarin chelates were prepared but its luminescence was not studied. Usually, pure coumarin along with the chelates show weak luminescence and the emission is witnessed around 450 nm with excitation around 350 nm. Hence, such chelates do not find any practical applications. If some other molecule such as quinoline is doped in these chelates then it may enhance the luminescence substantially and will be useful for practical applications. With this idea, Magnesium and Aluminium based coumarinolates doped with quinoline were made and the photoluminescence was studied.

2. Experimental

All the coumarinolate based chelates were prepared by dissolving the corresponding metal salt mostly nitrates in desired amount of double distilled water. The desired amount of pure Coumarine procurred from Loba Chemie India is dissolved in Methanol separately. Both the solutions are mixed and then desired amount of 0.1 molar solution of NaOH is added. The solution of NaOH is needed to maintain basicity in the solution (i.e. pH > 7). As soon as NaOH solution was added precipitate appears in the solution which was then filtered using Whatmann 42 filter paper. This filtrate was washed several times using alcohol and then dried under the drying lamp. The precipitate was then sealed in the bottle for various measurements. Photoluminescence measurements were made on Hitachi 7000 spectrophotometer. LED spectra of the prepared samples were also taken.

PL spectra of Mg Coumarinolates doped with Quinoline

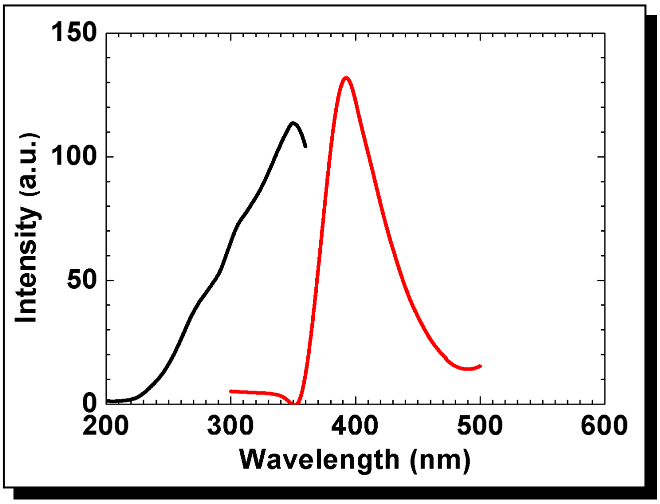

Figure 1. *Excitation*: (a) Coumarin; *Emission*: (b) Coumarin

Figure 1 shows PL spectra for the pure coumarin. The emission is observed around 400 nm (Figure 1b). The excitation to this emission is broad and peaks around 350 nm (Figure 1a). The emission intensity is very weak.

Figure 2 shows the photoluminescence spectra of Magnesium Coumarinolates doped with various amount of Quinoline. Intense photoluminescence is observed for these Mg based mixed chelates. In all samples a well-defined emission band at 490 nm is observed. The intensity of the emission is found to depend on the amount of quinoline doped. For 1% doping the emission is observed around 490 nm (Figure 2d). The emission is shifted by 10 nm compared to the MgCoum (Figure 2b). Thus when quinoline is added, a shift of 10 nm is observed in the emission spectrum. No change in emission intensity is observed. When the amount of quinoline is increased to 5%, the emission intensity increases by 12 times as compared to 1% doped sample (Figure 2f).

When the amount is further increased, the emission intensity decreases (Figure 2h,i) and hence 5% quinoline is the optimum concentration for this mixed chelate. The quinoline doped Mg coumarin chelate excitation is broad compared to the pure Mg coumorin. The excitation in all cases is flat from 350 nm - 420 nm and then intensity falls slowly up to 470 nm (Figure 2a,c,e,g,i). If the excitation is closely observed then there is good overlap of excitation with the emission of the 420 nm and 440 nm LED emission. Thus, these phosphors could be excited by near UV LED emitting around 400 nm and the near blue LED having emission at 440 nm. Thus Mg coumarin doped with quinoline will find applications as a white phosphor in PCLED applications.

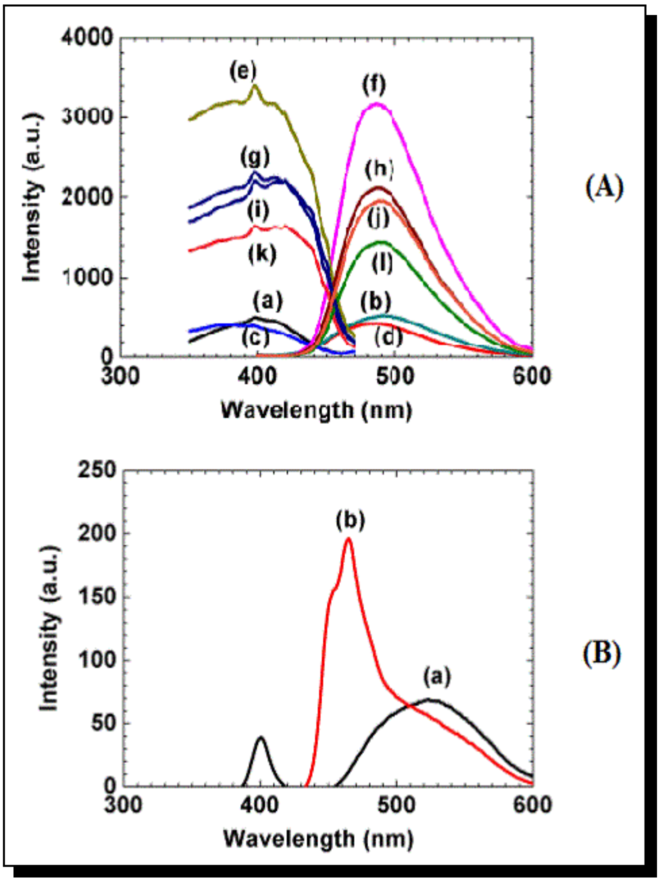

Figure 2. (A) Excitation: (a) MgCoum, (c) MgCoum99Q1, (e) MgCoum95Q5, (g) MgCoum80Q20, (i) MgCoum70Q30, (k) MgCoum60Q40, Emission: (b) MgCoum, (d) MgCoum99Q1, (f) MgCoum95Q5, (h) MgCoum80Q20, (j) MgCoum70Q30, (l) MgCoum60Q40; (B) Excitation: (a) MgCoum95Q5, Emission: (b) MgCoum95Q5

Figure 2B shows the LED spectra of MgCoum95Q5 with near UV LED emitting at 400 nm and GaN blue emitting LED. For 400 LED intense broad emission is observed around 525 nm (Figure 2B.a). The emission is broad and spans the entire blue - yellow region from 450 nm - 600 nm. Thus the emission is near to white light emission with greener component compared to blue and red. The less intense emission peak at 400 nm is due to unconverted 400 nm light by phosphor. The emission of the phosphor with 450 nm LED is shown in Figure 2B.b. Intense emission is observed around 475 nm with the tail extending in green-yellow region of the spectrum. The shoulder around 450 nm is the blue unconverted light from the LED. Thus in the emission all the three components of light are present and hence the emission is very near to true white emission. From the above observations, it can be concluded that MgCoum95Q5 finds application as a white phosphor in PCLED applications.

Photoluminescence of Al Coumarin based Chelates

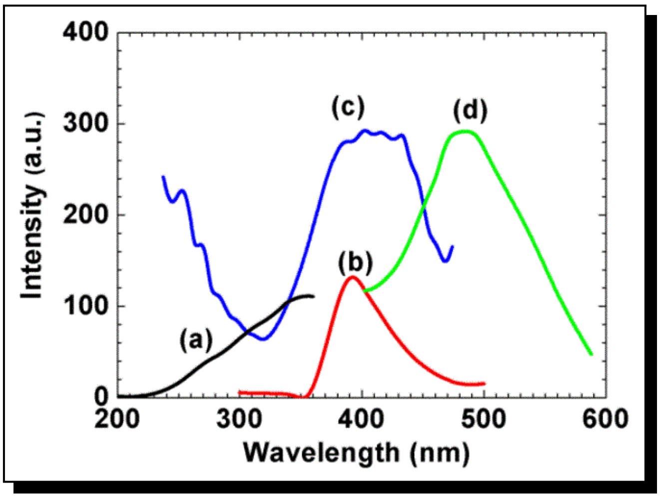

Figure 3. *Excitation*: (a) Pure Coumarin, (c) AlCoum; *Emission*: (b) Pure Coumarin, (d) AlCoum

Figure 3 shows the photoluminescence spectra of the purchased Coumarin. The emission is observed around 400 nm (Figure 3b) with a broad excitation around 350 nm (Figure 3a). The photoluminescence spectra from Al-Coumarinolate is entirely different compared to the pure coumarin. The emission is observed at 500 nm instead of 400 nm (Figure 3d). The excitation is also very broad and centered around 400 nm (Figure 3c). The emission intensity is also 2.7 times more compared to pure coumarin. Thus, luminescence from Al-Coumarinolate not only changes position but a change in emission intensity is also observed.

PL Spectra of Some Al-Coumarinolates Doped with Quinoline

Figure 4A shows the photoluminescence spectra of Al-Coumarinolates doped with various amount of quinoline. When 1% quinoline is added in coumarin moiety, the emission is observed around 490 nm (Figure 4A) with excitation at 380 nm (Figure 4c). Significant rise in emission intensity is observed compared to the pure coumarin. The observed emission is 5 times more than the pure Al coumarin. When the amount of quinoline is increased to 5% the emission intensity further increases and the emission is observed around 505 nm (Figure 4A.f). The excitation also get broadened with peak appearing around 400 nm with tail extending upto 450 nm (Figure 4e). For 20% doping, the emission is observed at the same position however the emission intensity is 1.5 times compared to that for 5% doped quinoline (Figure 4A.h).

The observed excitation is also broad with tail extending upto 470 nm (Figure 4A.g). This excitation has got better overlap with the emission from GaN based blue LED emitting in the 440 - 450 nm wavelength range. For 40% quinoline the emission intensity further increases (Figure 4A.l) with further broadening of excitation (Figure 4A.k) towards the longer wavelength side. This opens the possibility of using these complexes as white phosphors in PCLED applications with near UV LED or blue LED emitting around 440 nm - 450 nm. (Figure 4A.l) shows the AlCoum60Q40 phosphor emission excited by near UV LED emitting at 400 nm and GaN blue emitting LED. When the sample is excited by UV LED at 400 nm broad blue green emission is observed (Figure 4B.a). Similar emission is observed when excited by blue LED emitting at 450 nm (Figure 4B.b). Thus, this phosphor may be developed as a white phosphor for PCLED applications.

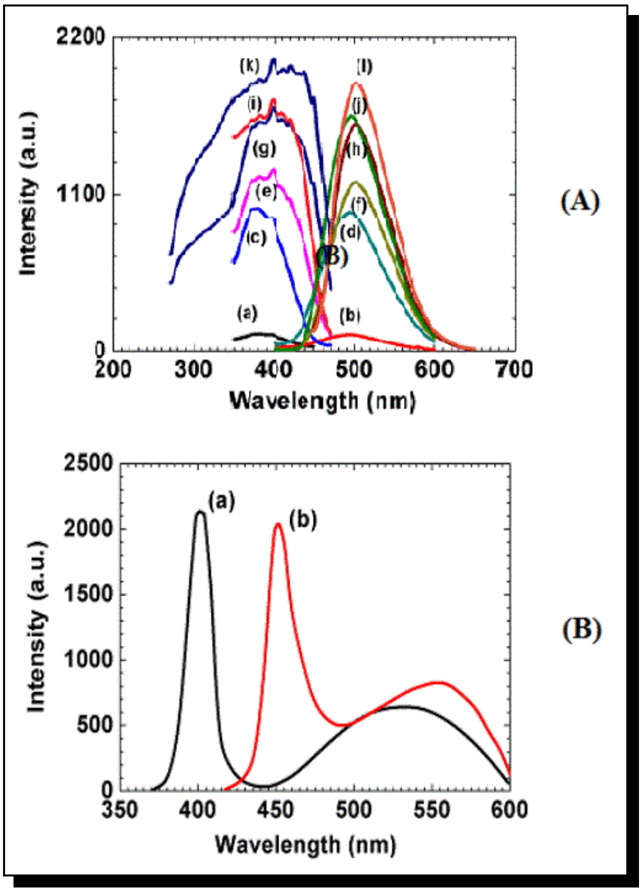

Figure 4. (A) *Excitation*: (a) AlCoum, (c) AlCoum99Q1, (e) AlCoum95Q5, (g) AlCoum80Q20, (i) AlCoum70Q30, (k) AlCoum60Q40; *Emission*: (b) AlCoum, (d) AlCoum99Q1, (f) AlCoum95Q5, (h) AlCoum80Q20, (i) AlCoum70Q30, (l) AlCoum60Q40; (B) *Excitation*: (a) AlCoum60Q40, *Emission*: (b) AlCoum60Q40

3. Conclusions

- Doping quinoline in Mg-Coumarinolate not only affects the position of emission and excitation in PL spectra but also the intensity. Broad emission is observed around 490 nm with a broad excitation peaking at 400 - 420 nm with tail extending beyond 450 nm. Of the several samples, sample doped with 5% quinoline shows the most intense emission. Intense emission along with good overlap of excitation with the near UV to blue emission of GaN based LED; this phosphor will find application as white phosphor in PCLED applications.

- The Al-Coumarinolate shows intense luminescence compared to pure coumarin. The emission and excitation were found to be red shifted compared to pure coumarin and is observed at 500 nm and 400 nm, respectively. This is similar to what is observed for Mg coumarin which suggests that valency of the metal ions is not playing any role in emission and excitation.
- Adding quinoline in small amount affects the emission and excitation of Al-Coumarin significantly. In most of these coumarinolates the emission is observed in blue green region with the excitation shifted in blue region. Of the several samples, sample doped with 40% quinoline shows the most intense emission. Intense emission along with good overlap of excitation with the near UV to blue emission of GaN based LED; this phosphor will find application as white phosphor in PCLED applications.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

References

[1] Z.H. Abd El-Wahab, M.M. Mashaly, A.A. Salman, B.A. El-Shetary and A.A. Faheim, Co(II), Ce(III) and UO_2(VI) bis-salicylatothiosemicarbazide complexes: Binary and ternary complexes, thermal studies and antimicrobial activity, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **60**(12) (2004), 2861 – 2873, DOI: 10.1016/j.saa.2004.01.021.

[2] M.-T. Alonso, E. Brunet, O. Juanes and J.-C. Rodrıguez-Ubis, Synthesis and photochemical properties of new coumarin-derived ionophores and their alkaline-earth and lantanide complexes, *Journal of Photochemistry and Photobiology A: Chemistry* **147**(2) (2002), 113 – 125, DOI: 10.1016/S1010-6030(01)00628-1.

[3] V. Aravindan, J. Gnanaraj, S. Madhavi and H.-K. Liu, Lithium-ion conducting electrolyte salts for lithium batteries, *Chemistry – A European Journal* **17**(51) (2011), 14326 – 14346, DOI: 10.1002/chem.201101486.

[4] K.B. Gudasi, R.V. Shenoy, R.S. Vadavi, M.S. Patil and S.A. Patil, Synthesis, characterisation and biological evaluation of lanthanide (III) complexes with 3-Acetylcoumarin-*o*-aminobenzoylhydrazone (ACAB), *Chemical and Pharmaceutical Bulletin* **53**(9) (2005), 1077 – 1082, DOI: 10.1248/cpb.53.1077.

[5] M.V. Hathi, K.B. Vyas, K.S. Nimavat and G.R. Jani, Synthesis, characterization and pH metric study of some novel metal complexes, *International Journal of Chemical Sciences* **7**(3) (2009), 2103 – 2107, URL: https://www.tsijournals.com/articles/synthesis-characterization-and-ph-metric-study-of-some-novel-metal-complexes.pdf.

[6] S. Jayasree and K.K. Arvindakshan, Structural and antitumour studies of metal complexes with thiosemicarbazones of β-diketoesters, *Polyhedron* **12**(10) (1993), 1187 – 1192, DOI: 10.1016/S0277-5387(00)88210-8.

[7] H.-K. Kim, J.-B. Oh, N.-S. Baek, S.-G. Roh, M.-K. Nah and Y.-H. Kim, Recent progress in luminescent lanthanide complexes for advanced photonics applications, *Bulletin of the Korean Chemical Society* **26**(2) (2005), 201 – 214, DOI: 10.5012/bkcs.2005.26.2.201.

[8] I.P. Kostova, I. Manolov and M.K. Radulova, Stability of the complexes of some lanthanides with coumarin derivatives. II. Neodymium(III)-acenocoumarol, *Acta Pharmaceutica* **54**(2) (2004), 119 – 131, URL: https://hrcak.srce.hr/16819

[9] I.P. Kostova, I.I. Manolov and M.K. Radulova, Stability of the complexes of some lanthanides with coumarin derivatives. I. Cerium(III)-4-methyl-7-hydroxycoumarin, *Acta Pharmaceutica* **54**(1) (2004), 37 – 47, URL: https://hrcak.srce.hr/clanak/25406.

[10] D.C. Manvar, D. Karia and A. Shah, Synthesis and anti-HIV activity of some 3-acetyl/aceto acetyl-4-hydroxy benzopyran-2-ones: An invitro evaluation, *Indian Journal of Organic Chemistry* **3** (2007), 170, URL: https://www.tsijournals.com/abstract/synthesis-and-antihiv-activity-of-some-3acetylacetoacetyl4hydroxy-benzopyran2ones-an-in-vitro-evaluation-3776.html.

[11] V.V. Mulwad and R.D. Bhagat, Synthesis of some pyranobenzopyrans and 3-styryl 4H(1) benzopyran[3,4-d] isoxazoles I, *Indian Journal of Heterocyclic Chemistry* **9** (1999), 15.

[12] R.C. Sharma and R.K. Parashar, Synthesis and microbicidal activity of N-(2-substituted) phenyl ureas and their metal complexes, *Journal of Inorganic Biochemistry* **32**(3) (1988), 163 – 169, DOI: 10.1016/0162-0134(88)80024-2.

[13] A. Singh and P. Singh, Synthesis, characterization and antiinflammatory effects of Cr(III), Mn(II), Fe(III) and Zn(II) complexes with diclofe nac sodium, *Indian Journal of Chemistry* **39** A (2000), 874, URL: http://nopr.niscair.res.in/handle/123456789/15479.

[14] B. Thati, A. Noble, B.S. Creaven, M. Walsh, M. McCann, M. Devereux, K. Kavanagh and D.A. Egan, Role of cell cycle events and apoptosis in mediating the anti-cancer activity of a silver(I) complex of 4-hydroxy-3-nitro-coumarin-bis(phenanthroline) in human malignant cancer cells, *European Journal of Pharmacology* **602**(2-3) (2009), 203 – 214, DOI: 10.1016/j.ejphar.2008.11.020.

[15] L. Wu, X. Wang, W. Xu, F. Farzaneh and R. Xu, The structure and pharmacological functions of coumarins and their derivatives, *Current Medicinal Chemistry* **16**(32) (2009), 4236 – 4260, DOI: 10.2174/092986709789578187.