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Optical Properties of Terbium (III) Complex with Benzoylacetanilide Ligand

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Abstract: Preparation and optical properties of terbium (III) complex with benzoylacetanilide ligand were reported in this communication. The synthesis of BAA ligand and its complex was supported by means of ^{1}H-NMR, FT-IR and CHN elemental analysis. The photoluminescence spectroscopy depicted the analysis of optical properties of the complex which showed that ligand act as antenna and transferred the absorbed energy to the metal ion in an effective manner. In this way, the complex possessed excellent luminescent intensity and long decay time (τ). The CIE color coordinates fall under the green region of the chromaticity diagram. Hence, the complex can be used as luminescent material in organic light emitting devices.
Keywords*: Optical properties,decay time, benzoylacetanilide, IR, photoluminescence spectroscopy*

I. INTRODUCTION

The rare earth complexes functionalized with organic ligands have been widely studied due to their attractive photophysical properties. These complexes have sharp as well as narrow emission, large Stoke's shifts, and long lifetime. These properties make them applicable for light emitting devices [1], electroluminescent materials [2], laser materials [3], luminescence probe [4], sensory materials [5] and full color light emitting display devices [6]. Out of three primary colors i.e red, blue and green, which is basic requirement for mechanized application of rare earth complexes, the terbium(III) ion metal complexes provide green color. The emission spectrum of terbium(III) complexes exhibited $^5D_4 \rightarrow {}^7F_j$ characteristic transitions of the terbium(III) ion, here j = 0, 1, 2 and 3, respectively. Upon UV excitation, the central metal ion shows low photoluminescence intensity because transitions are associated with forbidden f-f transitions. Therefore, the central rare earth ion is coordinated with light harvesting organic ligand with high absorption coefficient to increase the luminescence intensity and stability of the complexes. The organic ligand helped in the absorption of the energy and transferred it to the central metal ion through sensitization process [7]. Among the organic ligands, benzoylacetanilide emerged as a good sensitizer for the rare earth complexes. In this report, 2-benzoylacetanilide (BAA) ligand was synthesized and employed it for the synthesis of new terbium(III) complex. The complex was characterized by using different techniques such as CHN elemental analysis, infrared (IR), ^{1}H-NMR, UV-visible, and photoluminescence (PL) spectroscopy. The luminescence decay curves, excitation and emission spectra and CIE color coordinates were analyzed in order to investigate the optical features of terbium(III) complex in detail.

II. EXPERIMENTAL

The BAA ligand and their complex were synthesized by using commercially available analytical grade chemicals and used as such without any purification. The material like rare earth nitrates was purchased from Sigma Aldrich. The carbon, hydrogen and nitrogen elements were analyzed by 2400 CHN Elemental analyzer. The terbium ion present in complexes was estimated with the help of EDTA (ethylenediaminetetraacetate) complexometric titration. The IR spectra were recorded on Nicolet iS50 FT-IR spectrometer in 4000-400 cm^{-1} range using KBr discs. The proton NMR (Nuclear Magnetic Resonance) spectra of ligand and complexes were performed on Bruker Avance II 400 NMR spectrometer using TMS (tetramethylsilane) as a reference. The photoluminescence excitation and emission spectra in UV-visible region were executed on Hitachi F-7000 fluorescence spectrometer equipped with 150 W xenon lamp at room temperature in the wavelength scan mode. The data were collected in the range of 200-800 nm wavelength by keeping excitation and emission slit width 2.5 nm at a scanning speed of 240 nm/min. The luminescence decay curves were obtained in the time scan mode.

A. Synthesis of 2-benzoylacetanilide (BAA) ligand

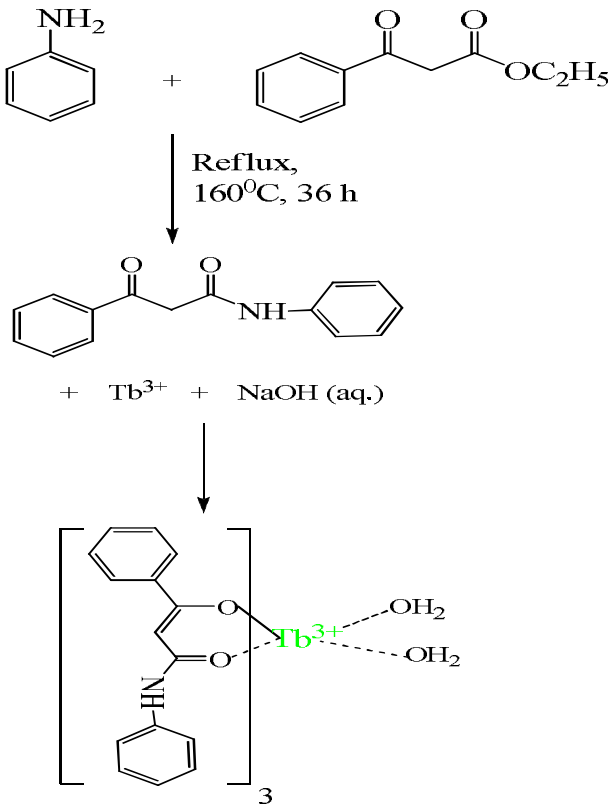
The synthetic route of ligand BAA has been illustrated in scheme 1. In a round bottom flask, 9.1 mL (0.1 mol) of aniline was added to the 17.3 mL (0.1 mol) of ethyl benzoylacetate. Then, the resulting reaction mixture was refluxed on the heating mantle at about 160°C for 35 h. The progress of the reaction was monitored by TLC (thin layer chromatography). After the refluxing, 300 mL hot water was added to the reaction mixture and heated to boiling. Reaction mixture was filtered and cooled. Then, mixture was kept in the ice bath till the white solid was separated. Finally, the obtained solid was dried in hot air oven with 75% yield and 107°C

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melting point [8]-[9]. IR (KBr): cm^{-1} 3301 (s), 3199 (m), 3139 (m), 3088 (m), 1660 (s), 1562 (s), 1500 (s), 1447 (s), 1407 (s), 1341 (s), 1248 (m), 1208 (m), 1168 (m), 1079 (m), 999 (m), 964 (m), 893 (m), 871 (m), 750 (s), 680 (s), 596 (w); ^{1}H-NMR (400 MHz): δ 14.10 (s, 1H, enolic OH), 9.3 (s, 1H, NH), 7.10-8.02 (m, 10H, Ar-H), 5.68 (s, 1H, enol CH), 4.01 (s, 2H, keto $–CH_2$) ppm. Elemental analysis calculated for $C_{15}H_{13}NO_2$: C, 75.31; H, 5.43; N, 5.85; Found C, 75.28; H, 5.32; N, 5.78.

B. Synthesis of terbium(III) complex

The terbium(III) complex was prepared with the help of alcoholic solution of BAA (0.76 g, 3.2 mmol) and an aqueous solution of terbium nitrate (0.43 g, 1.0 mmol). These mixtures were mixed on a magnetic stirrer under constant stirring. The formation of precipitates was started when the pH of solution was adjusted to 6.5-7.0 with 0.05 M aqueous NaOH solution. Then the resulting solution was stirred at about 35-40°C for 2 h. After stirring, the solution allowed to stand for half an hour. The precipitates were filtered, washed with water followed by ethanol and dried in hot air oven [10]. $Tb(BAA)_3(H_2O)_2$: off white powder, 76% yield; IR (KBr): cm^{-1} 3300, 3054, 1620, 1538, 1501, 1476, 1424, 1312, 1236, 1196, 1103, 1072, 1008, 896, 760, 690, 416; ^{1}H-NMR (400 MHz): δ 9.80 (s, 3H, NH), 7.10-8.40 (m, 30H, Ar-H), 3.26 (s, 3H, enol CH) ppm. Elemental analysis calculated for $TbC_{45}H_{40}N_3O_8$: C, 59.40; H, 4.40; N, 4.62; Tb, 17.49; Found C, 59.28; H, 4.32; N, 4.52; Tb, 17.38.



Scheme 1 The synthetic pathway of BAA ligand along with synthetic route of terbium(III) complex.

III.RESULTS AND DISCUSSION

A. Elemental analysis

The result of CHN elemental analysis showed that there was good agreement between observed values and the calculated values and conformed the complex as $Tb(BAA)_3(H_2O)_2$. The complex was light yellow solid and stable at normal room temperature conditions. The solubility of terbium complex was examined in different solvents. The complex showed the solubility in chloroform, dimethylsulphoxide (DMSO), acetone, dichloromethane and dimethylformamide (DMF) solvents.

B. IR and ^{1}H-NMR spectral analysis

The binding site of BAA ligand was analyzed with the help of infrared spectral study. The IR spectrum of complex exhibited some remarkable changes as compared to IR spectrum of free ligand which is described below. The strong absorption band of >CO stretching vibration appeared at 1660 cm^{-1} in the spectrum of ligand, which was shifted to 1620 cm^{-1} region in the spectrum of the

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complex. This shifting of band indicated that the >CO group was bound to the terbium(III) ion [11]. In the IR spectrum of the ligand, the band at 1562 cm^{-1} ascribed to >C=C stretching vibration, were displaced to the 1501 cm^{-1} region in the spectrum of the complex, indicating the coordination of ligand in the enol form and extended π-conjugation in the complex. The stretching vibrations around 3300 cm^{-1} and bending vibrations around 1500 cm^{-1} of N-H group showed no remarkable changes, which suggested that the N-H group was not involved in the chelation. The chelation of >CO group was also supported by the band at 416 cm^{-1} region which were assigned to the Tb-O stretching vibrations. These IR results confirmed the binding site of BAA showing that the ligand was chelated through oxygen atoms of >CO group to the central terbium(III) ion.In order to get the structural information about the terbium complex, ^{1}H-NMR spectra of BAA ligand and terbium complex were analyzed. In the spectrum of free BAA ligand, the singlets of enolic –OH, NH proton, enolic =CH proton and keto $–CH_2$ protons were displayed at 14.10 ppm, 9.3 ppm, 5.68 ppm and 4.01 ppm, respectively. But, in spectrum of complex, the signal of enolic –OH and keto $–CH_2$ protons diminished which clearly indicated that the enolic form of ligand was involved in coordination. On the other hand, the shifting of enolic =CH proton signal toward upfield was observed in the spectrum of complex as compared to spectrum of free BAA ligand, suggesting the paramagnetic nature of terbium metal ion .

C. UV-visible spectra

The UV-visible absorption spectra of BAA ligand and terbium(III) complex in DMSO solution (10^{-5} mol/L) are depicted in Fig. 1. A broad band in the range 290-370 nm was observed in the spectra of ligand and complex. In the spectrum of ligand, the maximum absorption band centered at 318 nm was assigned to the π-π* transition of the aromatic ring in ligand [12]. The maximum absorption of the complex was red shifted as compared to the free ligand, suggesting the extended π-conjugation in the complexes. The absorption in the complexes was also attributed to the π-π* transition of the ligand, since, the rare earth showed very weak absorption in UV range, indicating the key contribution of ligand in absorption process. This fact is further supported by the similar absorption profile of complex and free ligand although differ in absorption maxima.

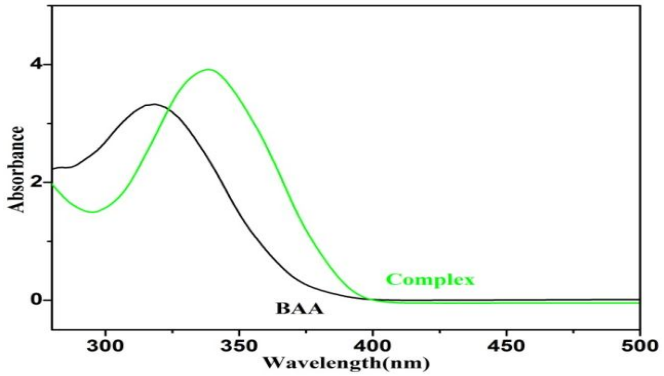


Fig. 1 The UV-visible spectra of BAA ligand and Tb(III) complex.

D. Photoluminescence Behavior

The excitation spectrum of terbium(III) complex was measured in solid state at room temperature as shown in Fig. 2. The spectrum was recorded by monitoring the highest green emission of 546 nm ($^5D_4 \rightarrow {}^7F_5$) and gave rise to a broad band in the range 200- 500 nm, having maximum excitation at 380 nm. This maxima was assigned to π-π* transition of the organic ligand and associated with the $^7F_6 \rightarrow {}^5L_{10}$ transition of terbium(III) ion. The spectrum was devoid of intraconfigurational f-f electronic transitions of the metal ion in larger wavelength region.

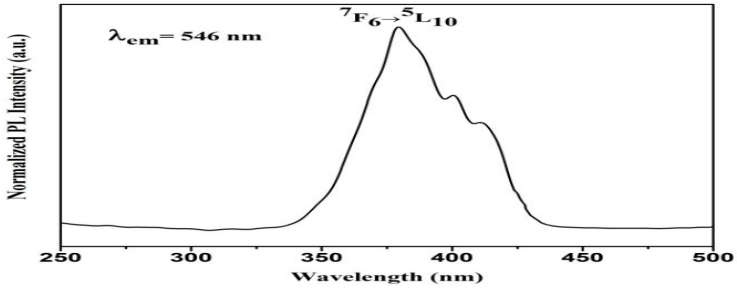


Fig. 2 The excitation spectrum of Tb(III) complex monitored at 546 nm.

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(380 nm) in solid state at room temperature are displayed. The emission spectrum manifests the three main characteristic peaks which originate by the transition between $^5D_4$ resonating levels to $^7F_5$ ground levels of terbium (III) ion. The peaks at 480 nm, 546 nm and 645 nm assigned to $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_3$ transition respectively. Among these peaks, the highest intensity peak at 546 nm is directed by electric dipole $^5D_4 \rightarrow {}^7F_5$ transition which is accountable for green emission color of the complexes .

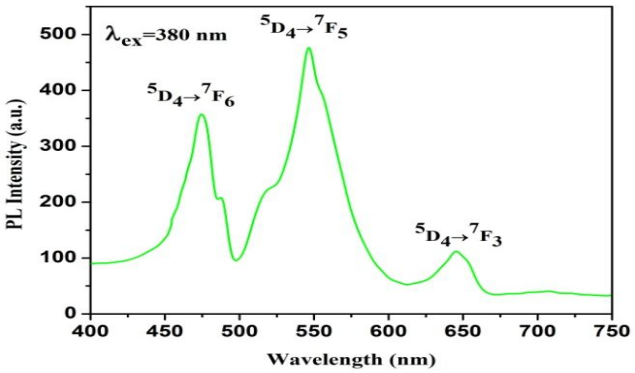


Fig. 3 The emission spectrum of Tb(III) complexes excited at 380 nm.

The CIE (Commission Internationale de Eclairage) chromaticity color coordinates (x and y) further confirm the green emission color of the terbium(III) complex. The color coordinates were calculated from the emission spectrum. The x and y values found to be 0.3126; 0.5342. The CIE coordinates of the complexes fall in the light green region of the chromaticity coordinate diagram as depicted in Fig. 4 and these terbium complexes find application in the display and lighting field.

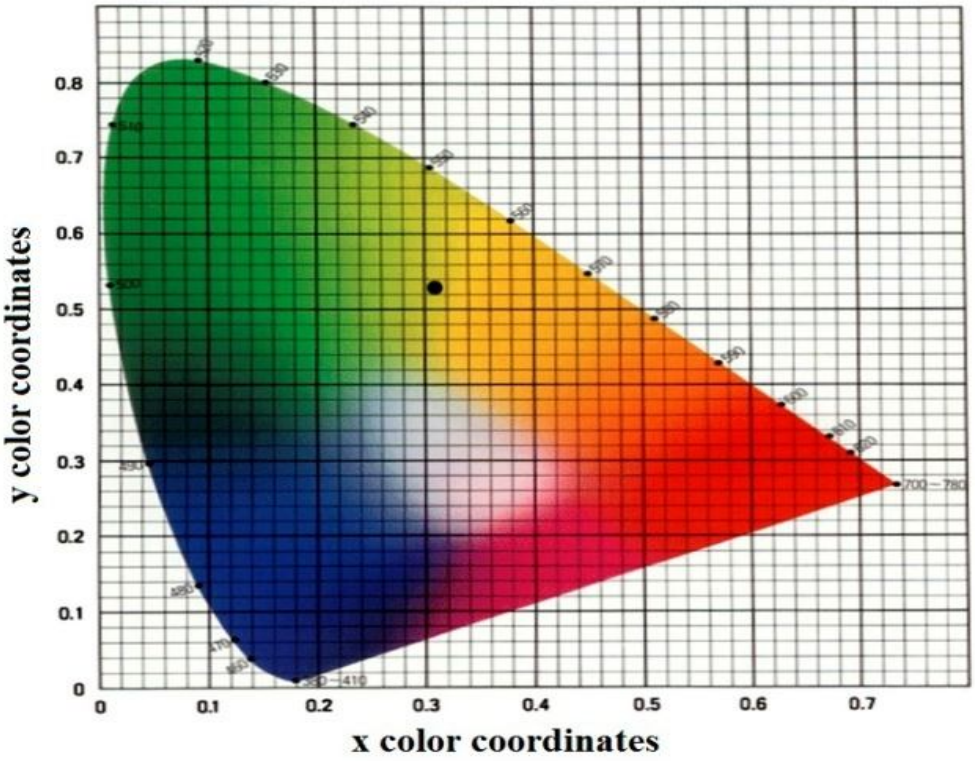


Fig. 4 The CIE coordinates of terbium(III) complex in the chromaticity diagram.

estimate the value of luminescence decay time in terbium(III) complex, the luminescence decay curve was plotted as shown in Fig. 5. The curve was fitted into single exponential function, suggesting the existence of one luminescent centre in the chemical environment of the complexes. By using $I = I_0 \exp^{(t/\tau)}$, where, I and I_0 denote the luminescence intensities at time t and 0, whereas τ represents the radiative decay time, the luminescence decay time of $^5D_4 \rightarrow {}^7F_5$ transition was calculated.

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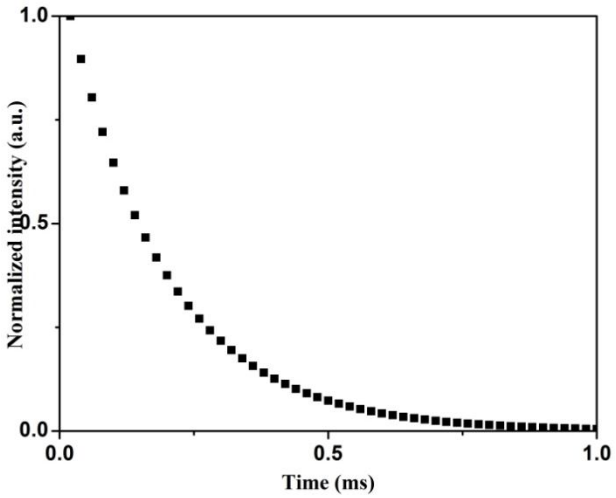


Fig. 5 The luminescence decay curve of the terbium(III) complex.

IV. CONCLUSIONS

In this report, the BAA ligand was synthesized and a terbium(III) complex was prepared by employing it. The green light emitting complexes were characterized by various techniques. The experimental values of elemental analysis were found in good agreement with the calculated values, confirming the successful synthesis of BAA ligand and its terbium complex. The results of IR and NMR revealed the coordination sites of BAA in the complex. In the emission spectra of terbium complexes showed emission peaks at 480 nm ($^5D_4 \rightarrow {}^7F_6$), 546 nm ($^5D_4 \rightarrow {}^7F_5$) and 645 nm ($^5D_4 \rightarrow {}^7F_3$) on excitation at 380 nm. The maximum intensity of electric dipole transition ($^5D_4 \rightarrow {}^7F_5$) indicated that the highly polarizable chemical environment present around the central metal ion which controlled the green luminescent color of the complex. The chromaticity coordinates of terbium complexes located in the green regime of the CIE diagram. As green component, the complex found potential application in the light emitting devices.

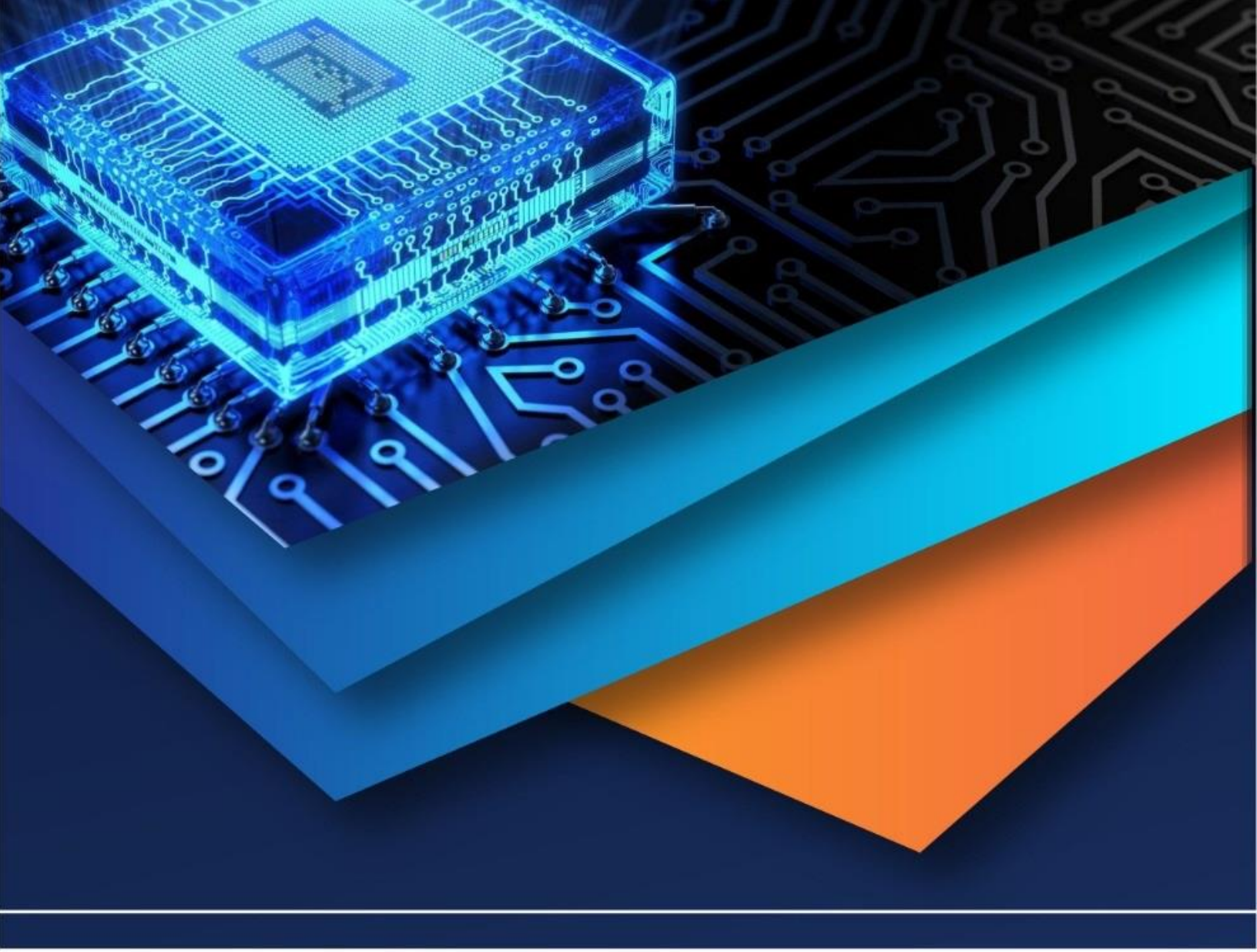
V. ACKNOWLEDGMENT

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