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EFFECT OF DYE ON CADMIUM COMPLEX FOR ORGANIC LIGHT EMITTING DIODE APPLICATIONS

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Abstract:

A novel complexation method was employed in synthesizing a material of a pure and coumarin assisted cadmium [(2-(2-hydroxyphenyl) benzoxazole) (8-hydoxyquinoline)] Cd (HPB)q nanowires. It was subjected to powder X-ray diffraction, UV-vis-NIR and spectroscopic (PL) analyses. The functional groups present were identified by the FTIR analysis. The SEM microscopy gives a clear picture of the formation of nanorods and nanowires for pure and dye assisted complexes respectively. The particle size was found out to be 68 nm and 87 nm for pure and dye introduced Cd (HPB)q respectively. The narrow PL emission and absorption features suggest the monodispersity and band edge emission. It is clear that the diameters of the rods both at center and tip were well controlled and the shape uniformity has been maintained throughout the process. The time resolved fluorescence spectra shows long lived fluorescence for dye assisted cadmium complex than the pure complex.

Key Words: XRD, SEM, Life Time Fluorescence & OLED

1. Introduction:

Organic light-emitting diodes (OLEDs) emerge as a new flat-panel display technology having excellent display characteristics, such as high luminous efficiency, low driving voltage, low power consumption, fast response time, and wide viewing angle [1-2]. The performance of OLEDs has been enhanced very rapidly to a level adequate for commercial display applications [3]. The doping technique has been widely used for fabricating OLEDs in order to improve device characteristics or change the emission colour. Doping the emissive layer with appropriate fluorescent or phosphorescent dopants can tune the emission colour or enhance the electroluminescence (EL) efficiency and the stability, compared with the undoped materials [4-5]. The EL emission from the dopant is attributed to the exciton energy transfer from the host to the dopant molecules or to the direct recombination of electrons and holes trapped at the dopant molecules [6-8]. One of the key developments in the advancement of organic light-emitting device (OLED) technology for flat panel display applications can be attributed to the discovery of the guest-host doped emitter system [9]. The advantage of the doped emitter system in OLED is the enhancement of its operational stability by transferring the electro-generated exciton to the highly emissive and stable dopant site thus minimizing its possibility for nonradiative decay. Therefore, to enhance the performances of these devices, the electron and hole injection into the emissive layer should be balanced [10-12]. In the present study small amount of a fluorescent dye is doped, which made significant changes in the colour of luminescence. Also from the SEM studies the doping of dye played a major role in morphology which explains its application to OLED material.

2. Experimental Procedure:

A solution of 2-(2-hydroxyphenyl) benzoxaxazole (HPB) with 0.211 g (1 m mol) (Merck, India) was prepared in 20 mL of absolute ethanol in a 100 mL three neck flask and stirred well with a magnetic stirrer for one hour at a constant temperature of 70 °C. Then the solution of cadmium acetate dihydrate 0.267 g (1 m mol) in 3 mL of water and 8-hydroxyquinoline (q) 0.145 g (1 m mol) in 10 mL absolute ethanol was added drop wise in the first solution under stirring. After the addition was completed, the reaction was further carried out for 3 h. The yellow precipitate was collected by filtration by acetone and ethanol wash, and dried overnight. The above preparation procedure was followed in synthesizing the complex by adding dye of coumarin of 5% before the addition of cadmium acetate and 8-hydroxyquinoline in the HPB solution. The reaction scheme for the synthesis of Cd(HPB)q is shown in equation [13].

$$C_{13}H_9NO_2 + C_9H_7NO + Cd(CH_3COO)_2\,2H_2O \xrightarrow[70°C]{dye} C_{22}H_{14}N_20_3Cd \ + \ 2CH_3COOH$$

Reaction Scheme for the Synthesis of [Cd(HPB)q]

3. Results and Discussions:

3.1 Powder X Ray Diffraction Analysis: The crystallographic properties, such as structure, phase purity and size of the as-synthesized Cd(HPB)q were determined using X-ray diffraction study. Figure 1 depicts the XRD patterns of the as-prepared Cd(HPB)q complex and dye influenced one. Intensity versus 2θ values were recorded between 10° to 70°. The X-ray diffraction pattern shows four prominent diffraction peaks with higher intensity, for pure and dye assisted Cd(HPB)q cadmium complex. The particle size was found out to be 68 nm and 87 nm for pure and dye introduced Cd (HPB)q respectively.

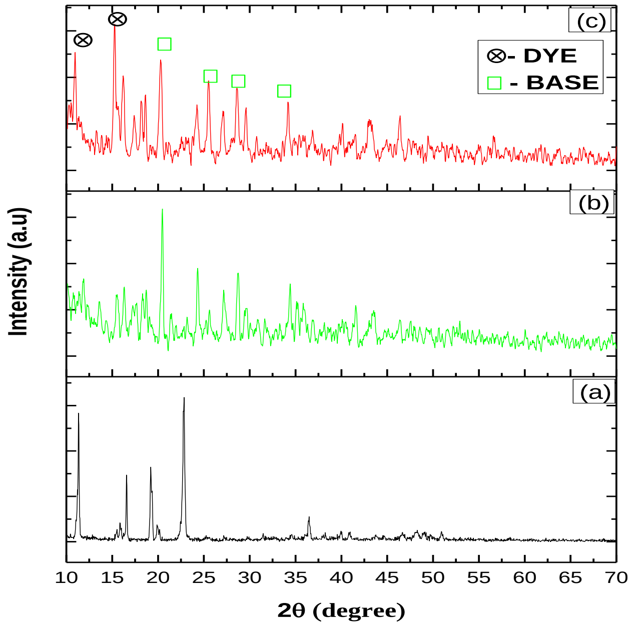
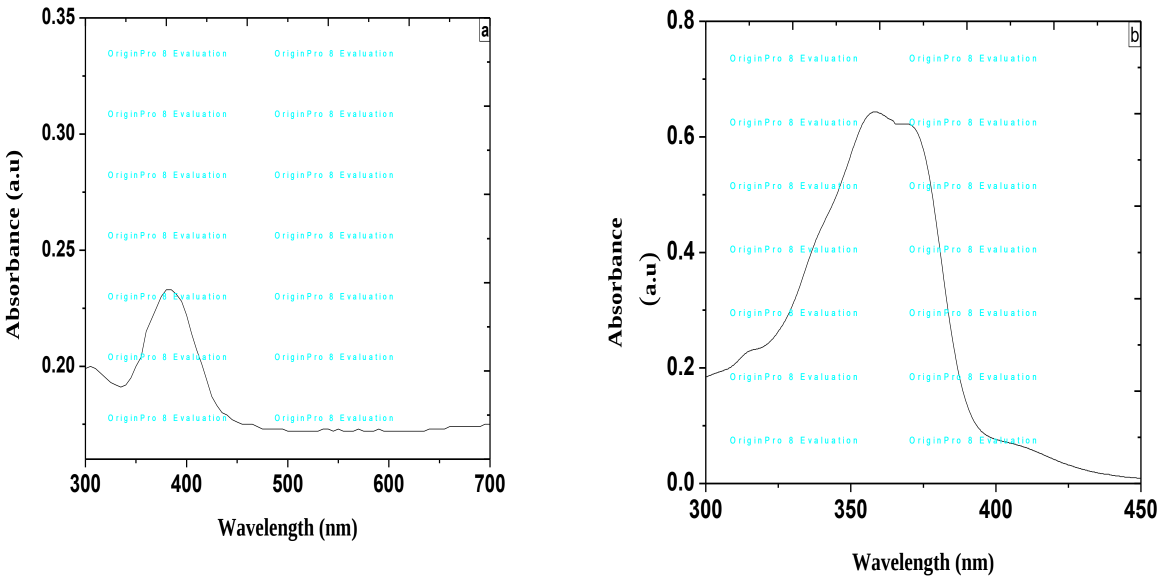


Figure 1: Powder XRD spectra for (a) dye, (b) Cd(HPB)q and (c) dye assisted cadmium complex [Cd(HPB)q]

3.2 UV-vis-NIR Spectral Analysis: The UV-vis-NIR absorption spectra for the synthesized samples are shown in Figure 2(a, b). The the maximum of the UV-vis-NIR absorption peak of Cd(HPB)q, as shown in Figure 2(a), is observed at 380 nm.In the case of dye assisted cadmium complex two absorption maxima at 358 nm and 368 nm are observed. This is due to the coordination of cadmium and organic ligands (HPB and q) and dye. It is clear from the optical absorption study that the dye assisted cadmium complex shows a hypsochromic shift compared to the pure.



(a) (b)

Figure 2: Absorption spectra for pure (a) and (b) dye assisted cadmium complex [Cd(HPB)q]

3.3 PL Analysis: The room temperature photoluminescence spectra of the synthesized samples are shown in Figure 3(a, b). The PL spectra show strong emission peaks at 502 and 492 nm for pure and coumarin dye assisted [Cd(HPB)q] complexes respectively. It is observed that the emission colour varied from the original green to the dopant emission colour. The narrow PL emission and absorption features suggest the monodispersity and band edge emission.

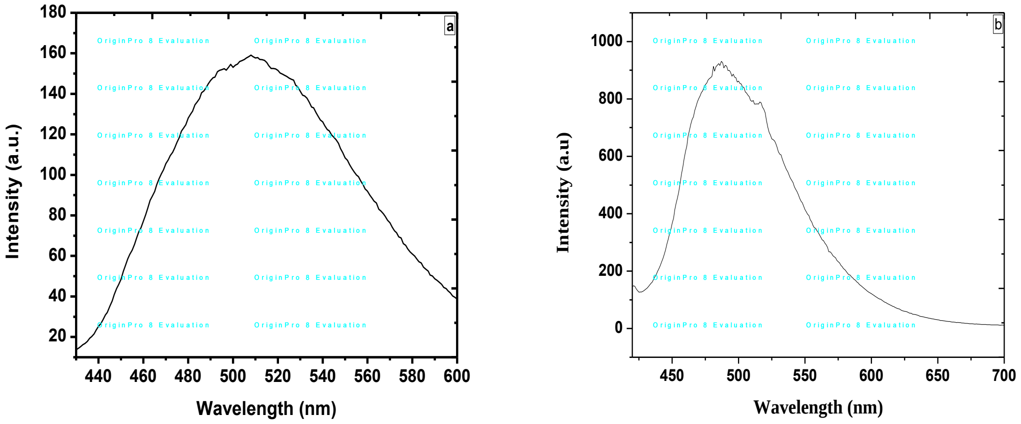


Figure 3: PL spectra for (a) pure and (b) dye assisted cadmium complex

3.4 Time Resolved Fluorescence Decay Analysis:

Time-resolved fluorescence decay spectra for the samples were recorded by a time-correlated single-photon counting (TCSPC) system from IBH (UK). It is a powerful technique to measure energy relaxation and recombination dynamics of the synthesized Cadmium complex. The measured fluorescence decay is the convolutions of true fluorescence decay, excitation function and the instrument response function. The fluorescence kinetic parameters (lifetime, amplitudes etc.) are obtained by deconvoluting the excitation and the instrument response function from the measured fluorescence decay. The excitation wavelength and repetition rate for the sample kept at 375 nm and 1 micro hertz respectively. The instrument response time was 240 ps.

Figure 4 displays the life time decay curve of base and coumarin influenced cadmium complex [14]. The decay curve is fitted by $I = B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2}$, where τ_1 and τ_2 are the life time of the components with amplitude B_1 and B_2 as reported.[15]. The decay curve shows a multi exponential behavior for both the pure and the dye assisted complex. The analysis was carried out by the software provided by IBH (DAS-6) which is based on reconvolution technique using iterative non-linear least square methods. The reconvolution is preceded by the series of iterations until a Chi-square is reduced. The quality of fit is normally identified by the reduced χ^2. The fluorescence decay characteristics of Cadmium complex are presented in table 1. Coumarin is an appropriate fluorophore to serve as the molecular platform to illustrate the strategy owing to its near unit blue fluorescence efficiency in solution, but weak fluorescence in the solid state. It clearly reveals that the nature of emission behavior was not only a charge transfer band but also the p-conjugation bands that play an important role in the excited state. It shows multi-exponential decay kinetics and has also showed the surface related emission in highly luminescent Cadmium complex by using this lifetime decay measurements.

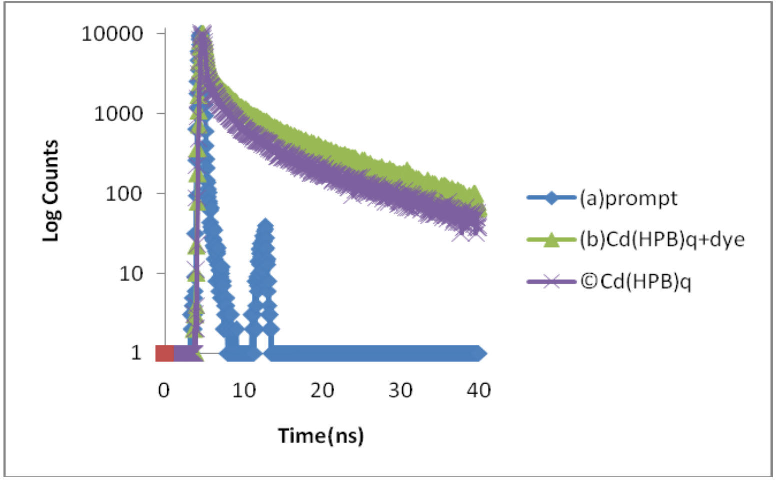


Figure 4: Life time decay curve of (a) prompt (b) Cd(HPB)q+dye and (c) Cd(HPB)q

Table 1: The data of the fluorescence lifetime measurements

S.No	Compound	τ_1(ns)	τ_2(ns)	B_1%	B_2%	χ^2
1	Cd(HPB)q	0.26	2.64	17.63	51.42	1.14
2	Cd(HPB)+dye	2.47	4.81	96.47	3.53	1.35

3.5 FTIR Spectral Analysis: The FT-IR spectra of the as-prepared [Cd(HPB)q] are shown in Figure 5. The bands at 1592 cm^{-1}, 1571 cm^{-1} and 1523 cm^{-1}can be assigned to the asymmetric stretching vibration of O-H, which means that the water molecules remain intact on the surface of the synthesized [Cd(HPB)q] complex. This O-H band shows a shift towards higher wave number with shortened peaks. The absorption bands occur at 1455 cm^{-1}, 1325 cm^{-1} for pure, and the peaks at 1156 cm^{-1}, 1037 cm^{-1} for dye assisted complex represent C-O stretching. The peaks positioned at 1037cm^{-1}, 731cm^{-1} are ascribed to the C=C stretching and bending vibrations of $–CH_2$ respectively. The band observed at 579 cm^{-1} can be attributed to Cd-O stretching vibrations.

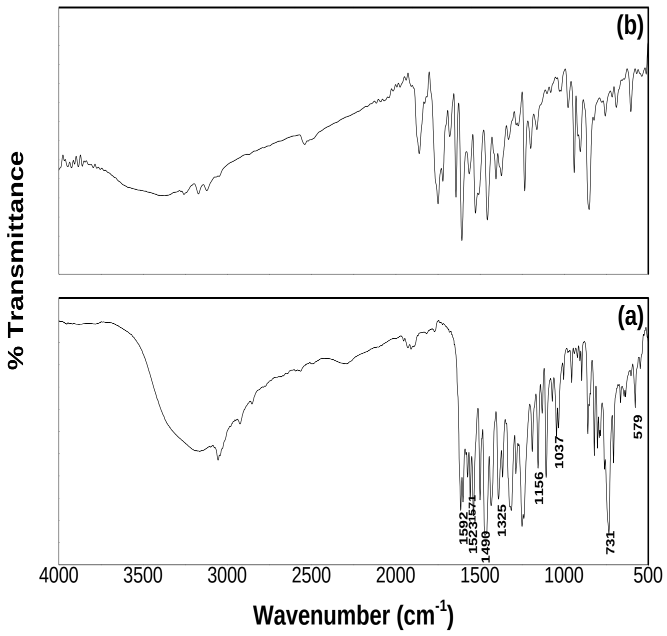
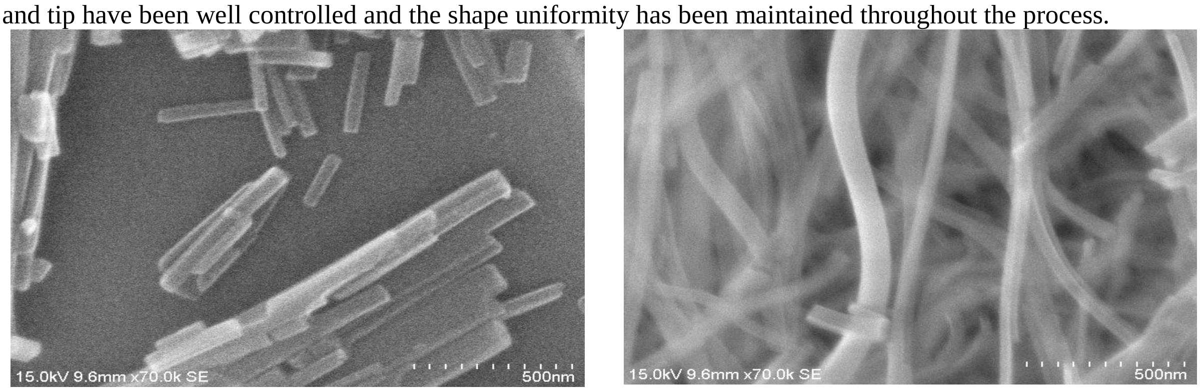


Figure 5: FTIR spectra for (a) pure and (b) dye assisted cadmium complex [Cd(HPB)q]

3.6 SEM Micrograph Analysis: The morphology of the pure and dye influenced [Cd(HPB)q] complex prepared in the present case was studied by scanning electron microscopy. The SEM images of [Cd(HPB)q] nanorods synthesized are shown in Figure 6. The rod shaped [Cd(HPB)q] are observed to have agglomeration throughout the surface. The nanorods of pure complex has transformed to nanowires in the dye assisted complex. This is due to the linkage phenomenon of the complex and also the transformation from nanorods to nano wires introduces a change in aspect ratio. The aspect ratio has increased in the case of dye assisted complex which shows more flexibility of the complex. The average length and diameter of these nanorods and nanowires are found to be 175and 160 nm, respectively. It is clear that the diameters of the rods both at center and tip have been well controlled and the shape uniformity has been maintained throughout the process.



(a) (b)

Figure 6: SEM micrograph for (a) pure and (b) dye assisted cadmium complex [Cd(HPB)q]

4. Conclusions:

In this work, we report the synthesis of a pure and coumarin assisted cadmium [(2-(2-hydroxyphenyl) benzoxazole) (8-hydoxyquinoline)] Cd(HPB)q nanorods and its optical properties (photoluminescence, UV-visible-spectra), structural properties (PXRD), Functional groups (FTIR) and surface analysis (SEM) were analyzed. From the powder X-ray diffraction studies the particle size was found out to be 68 nm, and 87 nm for pure and dye introduced Cd[HPB]q respectively. The absorption spectra of compound exhibited excitonic peaks with an absorption edge at 380 nm and 348 nm for pure and dye assisted complex. The studies on functional group confirms that the water molecules remain intact on the surface of the synthesized [Cd(HPB)q] complex. The narrow PL emission and absorption features suggest the monodispersity and band edge emission. It is clear that the diameters of the rods both at center and tip have been well controlled and the shape uniformity has been maintained throughout the process.The time resolved fluorescence spectra shows long lived fluorescence for the dye assisted cadmium complex than the pure. The flexibility of nanowires form of dye assisted complex is more favorable for the OLED applications.

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