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Efficient white light generation from 2,3-diphenyl-1,2-dihydro-quinoxaline complex

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Abstract In this article, we report two organic materials dispersed in transparent poly (methyl methacrylate) matrix for efficient white light simulation under different optical excitations. A newly synthesized complex of benzoin and *o*-phenyldiamine is observed to be white on illumination with a blue LED. A new concept of white light emitting tube is also demonstrated. A mixture of 2,2″-([1,1′-biphenyl]–4,4′-diyldi-2,1-ethenediyl)-bis-benzenesulfonic acid disodium salt and complex is optimized to emit white light extended in the violet region on 355 nm laser excitation. The optical quality of the emitted white light is adjudged by the CIE coordinate, correlated color temperature and color rendition index in both the cases.

1 Introduction

Considering the ever-increasing demand of electricity consumption for illumination purposes, recently a surge of research has been devoted to the development of efficient and cheaper illuminant materials. Most of conventional illuminant sources (lamp, bulb, tube light etc.) are bulky, expensive and less efficient. Moreover, the use of these sources is based on natural resources (oil and coal) and electricity consumption, which consequently is related with the global warming problem [1]. They are also one of the primary domestic pollutant sources as they contain or emit toxic materials like mercury (Hg), sulphur, carbon dioxide (Co_2), uranium etc.

Light emitting diodes (LED) are the most suitable replacement of the conventional sources [2]. Particularly, in the pursuit of eco-friendly lighting, organic LED has long been touted as an attractive option. LED lighting reduces energy consumption and environmental pollution and saves up to 70–80% of the energy used in lamps. For the household and office purposes white light emitting LEDs are preferably desired. Recently, Reineke et al. have reported an excellent white organic light emitting diode compatible to fluorescent tube light [3]. However, the quest for economical white organic LED is still continuing as about 20% of the electricity consumed worldwide is used for lighting purposes.

The white light can be created in three ways; either by broadband emission or by mixing of primary colors (blue, green and red) or by mixing of complementary colors (yellow/blue). Efforts to simulate the white light emission by controlling the intensities of primary colors have been reported using rare earth ions doped in different lattices [4, 5]. Recently, we have demonstrated the white luminescence through mixing of different upconversion phosphors [6]. As most of the highly fluorescent materials yield poor electroluminescence compared to optical excitation, a concept of hybrid LED coated with yellow organic/inorganic phosphor materials is mostly acceptable [7–9].

Recently, we have synthesized a novel green/yellow emitting organic complex of benzoin and *o*-phenylenediamine using solid-state reaction [10]. In this work we have demonstrated two alternative methods to achieve white light using this complex and also demonstrated a hybrid white light emitting tube for luminescent purpose.

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2 Material and experimental

The starting material *o*-phenylenediamine (S.D. Fine Chemicals, India) was purified by a zone refining technique, while benzoin compound (Sigma Aldrich) was purified by recrystallization from CCl_4 solvent. The complex has been synthesized adopting one of the solid-state reactions by mixing their melts followed by chilling in ice cold water [11]. The process of homogenization and chilling were repeated four times for the completion of reaction. The phase diagram study reveals that 1:1 molar ratio of benzoin and *o*-phenylenediamine forms the complex. The purity of each compound was checked by comparing their melting points. The optimized molecular structure of the complex using density functional theory (6-311G* basis set) on GAUSSIAN 98 program suite is shown in Fig. 1(a).

The quantum efficiency of 2,2″-([1,1′-biphenyl]–4,4′-diyldi-2,1-ethenediyl)-bis-benzenesulfonic acid disodium salt (commonly known as Stilbene 420) (Exciton, USA) has been calculated using a relative fluorescence quantum efficiency method [12] and it is found to be >0.9 and no efficiency loss was observed with Poly (methyl methacrylate) host, while for the complex it is 0.89. The absorption spectra of the parent compounds and their complex were recorded in tetrahydrofuran (THF) solution, using JASCO V-670 double beam spectrophotometer in the range of 200–2300 nm. The fluorescence measurements were carried out using InGaN LED and 355 nm radiation of Nd:YAG laser (Spitlight 600, Innolas, Germany) as an excitation sources. A computer-controlled trix monochromator (iHR320) equipped with grating (blazed at 500 nm) and a photomultiplier tube (model-1424M) to detect the dispersed luminescence. The resolution of the monochromator was ∼0.2 nm. All the measurements were carried out at room temperature (26 ± 2°C).

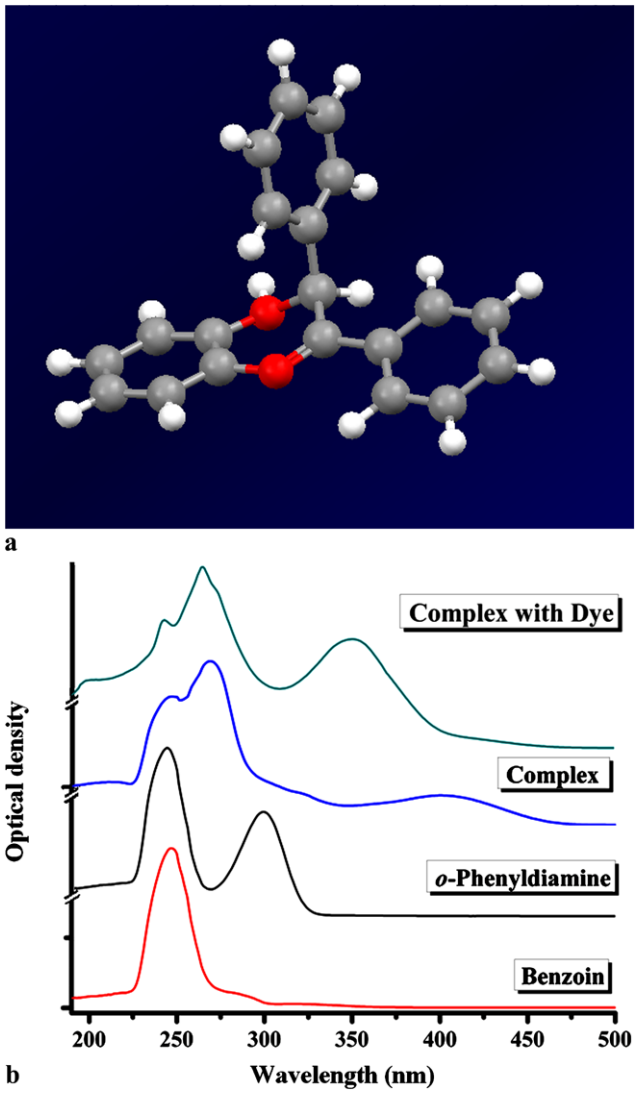

Fig. 1 (**a**) The optimized molecular geometry of the complex of benzoin and *o*-PDA compounds. (**b**) UV-Vis absorption spectra of BN, *o*-PDA, and complex in tetrahydrofuran solution and complex with dye in Poly (methyl methacrylate) polymer matrix

3 Results and discussion

3.1 Absorption spectra

The UV/Vis absorption spectra of benzoin, *o*-phenylenediamine and their complex have been recorded in tetrahydrofuran solution (Fig. 1(b)). The absorption spectrum of benzoin shows peaks at 247 nm and 284 nm, 315 nm ascribed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions due to the presence of the phenyl ketone group (Ar–C=O). The absorption spectra of *o*-phenylenediamine contains two bands at 244 nm and 300 nm, assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [13]. In complex, the band observed at 315 nm becomes intense and broad; it suffers from bathocromic shift with different polar solvents. In the case of charge-transfer transitions, an increase in the polarity of the medium leads to a Stokes shift of the absorption maximum. The study concerned was discussed earlier [10].

3.2 Photoluminescence of complex

3.2.1 Blue LED excitation

The absorption spectrum of the complex contains a broad absorption band centered at 400 nm. This absorption band is extended up to 475 nm. Considering the significant extinction at 457 nm in complex, it is expected that the complex can be excited with the InGaN LEDs which emit a single band at 457 nm which could be an economical alternative excitation source for the complex. The complex was dispersed in Poly (methyl methacrylate) polymer and the thin layer of the mixture was coated over the LED. The luminescence spectra of this hybrid LED was recorded by applying a current of 20 mA (Fig. 2(a)). The broad emission band centered at 550 nm is ascribed to the radiative relaxation of the

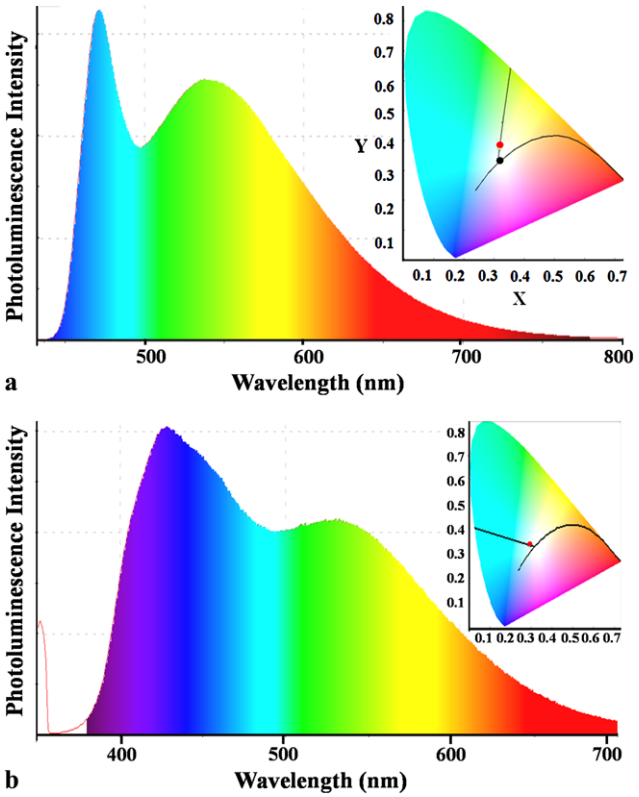

Fig. 2 (**a**) A full range visible spectrum of the complex combined with the emission of blue LED. A CIE diagram of the emitted white light is given in *the inset*. (**b**) The visual spectrum and the CIE diagram of the emitted white light by the complex and dye combination on 355 nm laser excitation

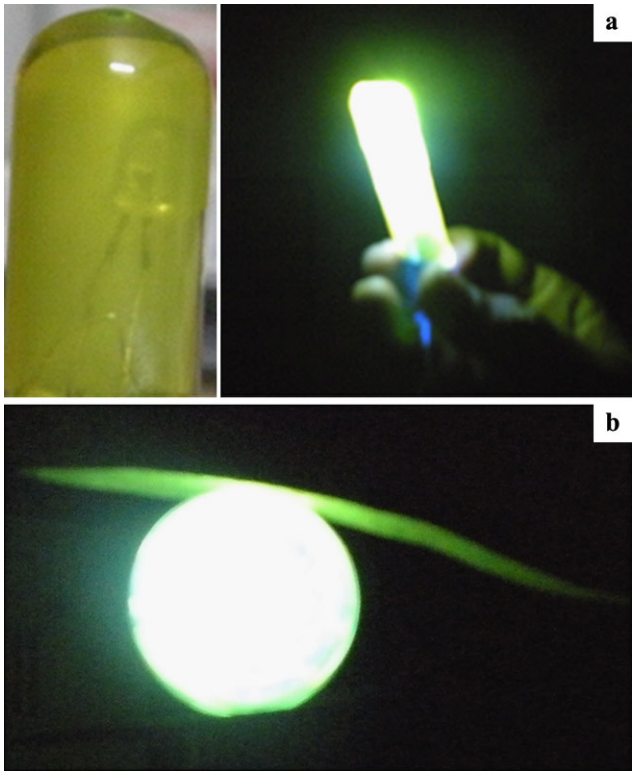

Fig. 3 Demonstration of a tube made of Poly (methyl methacrylate) polymer doped with the synthesized complex, a blue LED (inside the tube) is used as excitation source. The optical combination of complex emission and LED gives a white perception. The reflected blue light of LED is observed in the lower portion of the tube (**a**). A combined visual spectrum of the complex and the dye dispersed in Poly (methyl methacrylate) circular polymer disc on 355 nm laser excitation (**b**)

complex. The resulting white light is due to the combination of the green/yellow emission of the complex and blue band of the LED. Thus through this way the monochromatic LED light (457 nm) can be transformed into a bright rainbow of colors spanning in the blue and red regions; as a result white perception is appearing to the naked eye.

The calculated chromaticity coordinates for this case confirm the same further. The CIE system involves parameters x and y to specify the chromaticity which covers the optical properties, hue and saturation on a two-dimensional chromaticity diagram. The color rendition index (CRI) is a numerical measure of how 'true' colors look when viewed with the light source and can be determined quantitatively using output spectrum of the light source [14]. Luminescent perspective of white perception lies primarily to the color, correlated color temperature (CCT) and color rendition index of the light. Generally illumination applications need the color of temperature equivalent to that of a blackbody source between 3000–6000 K. The high illumination quality sources typically have CRI values greater than 80. In the present case, the CIE chromaticity coordinates were found to be (0.34, 0.37) while CCT and the CRI is ∼5234 K and 83 respectively. The calculated CIE coordinates are close to the day light coordinates (0.33, 0.33) and found to be well within the gamut of white perception (Fig. 2(a)). The deviation observed from the day light coordinate is due to the weak blue color emission.

The best feature of the organic complex dispersed in polymer is that it can be given any shapes, which opens a tremendous scope for commercial applications. One of its applications is demonstrated where a white light emitting tube is accompanied with a blue LED as an excitation source. At first the complex was dispersed in Poly (methyl methacrylate) polymer and formed into the tube shape. Then the blue LED is kept inside the tube and is connected with a 9.0 V battery (Fig. 3). The tube thus prepared was observed to emit white perception. Such white light emitting tube is efficient, economical and of low weight.

3.2.2 355 nm laser excitation of complex with dye

The photoluminescence spectra of *o*-phenylenediamine and benzoin dispersed in PMMA polymer contain weak bands at 519 nm and 493 nm, respectively. However, it was enhanced up to ten manifolds in complex and shows a red

shift. When an electron donating group (amino group) and an electron accepting group (carbonyl group) combine with each other directly or through a bridge of conjugated double bonds, the electrons migrate from the former to the later, resulting in a new absorption band and it is referred to as an intra-molecular charge-transfer band [15, 16]. The enhancement is expected due to the formation of charge-transfer band, which improves extinction corresponding to 355 nm, consequently enhancing fluorescence intensity.

The commercial use of the synthesized complex, as supercontinuum source, is limited due to the blue and red color deficiency. Actually, most of the commercial supercontinuum sources show potential in industries and biomedical applications; they all have a common deficiency in the blue region (<450 nm), which is extremely important for many fluorescence imaging applications, particularly in the biomedical field. The blue deficiency could be overcome by introducing the additional blue emitting compound in the complex. Considering the photo-stability against structural changes with environment temperature, solvent, concentration etc., Stilbene 420 dye (2,2″-([1,1′-biphenyl]–4,4′-diyldi-2,1-ethenediyl)-bis-benzenesulfonic acid disodium salt) is used for this purpose [17]. A significant extinction of the dye appeared at 355 nm due to the $S_1 \leftarrow S_0$ transition (Fig. 1(b)).

As the solubility of the dye is limited in tetrahydrofuran solvent, it was dissolved in dehydrated EtOH and then added dropwise in tetrahydrofuran solution of the complex. The higher fluorescence quantum yield of the dye in Poly (methyl methacrylate) polymer matrix compared to that of the EtOH solution is expected due to the hindrance of dye molecule rotation, which appears to reduce the non-radiative relaxation processes that compete with the fluorescence process [18]. As the dye was added (dye:complex, 3:1) to the complex in solution phase, an intense bluish white light appears under 355 nm laser excitation. Furthermore, an improvement observed in blue color alters the CIE coordinate of the white light (0.31, 0.33) compared to (0.34, 0.37) when only the complex is present (Fig. 2(b)). Color temperature on the blackbody locus is 6642 K and CRI $\sim$ 94 are calculated from the spectrum. It was noted that the CIE coordinates, CCT and CRI, are a function of individual concentrations of the dye and the complex. A large variation is observed in CIE coordinates when dye and complex ratio changes from 3:1 $\rightarrow$ 1:3 the CIE coordinates changes (0.31, 0.33) $\rightarrow$ (0.34, 0.52). This variation indicates that the white light can be fairly tuned by adjusting a relative amount of the complex and the dye. The beauty of the experiment lies in its higher temperature and the concentration sensitive emission, which facilitate the wide range of required color selection and are highly desirable for white light based devices.

A combination of the complex and the dye (dye:complex, 3:1) is dispersed into the liquid Poly (methyl methacrylate) polymer and is allowed to form a circular disc. A bright bluish white light is clearly visible on excitation with 355 nm laser radiation (Fig. 3(b)).

4 Conclusion

Two materials, i.e. newly synthesized complex and a mixture of this complex with stilbene 420 dye, were proposed for efficient white light simulation on excitation with blue LED (InGaAs) and 355 nm laser. A white light emitting organic tube has been demonstrated based on this material. A combination of stilbene 420 dye and the complex was optimized to yield white light, extended in violet region on 355 nm laser excitation. The optical qualities of the emitted white light were adjudged by the Commission Internationale de l' Eclairage (CIE) coordinates, CCT and CRI, in both the cases.

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