

## Investigations of organic light emitting diodes with CdSe(ZnS) quantum dots

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### Abstract

In this study, we report results on investigation of bilayer light emitting diodes made of organic capped CdSe(ZnS) core/shell type nanocrystals and poly[2-phenyl-3-(9,9-dihexyl-fluoren-2-yl) phenylene vinylene]-co-[2-methoxy-5-(2'-ethylhexyloxy) phenylene vinylene] (FP-PPV-co-MEH-PPV) electroluminescent co-polymer. Light emitting diodes of structure: indium-tin-oxide (ITO)/polyethylene dioxythiophene: polystyrene sulfonate (PEDOT:PSS)/FP-PPV-co-MEH-PPV/Ca/Al devices have been fabricated and studied. The co-polymer device emits a yellow light with a maximum brightness of 3949 cd/m<sup>2</sup> and a maximum external quantum efficiency of 0.27 cd/A at 10 V. Incorporation of CdSe(ZnS) quantum dots into the active polymer film resulted in an increase in device brightness, which reached 8192 cd/m<sup>2</sup> and in external quantum efficiency, which became 1.27 cd/A at 7 V with a lower turn-on voltage. The results indicate that CdSe(ZnS) quantum dots improved significantly the emission of the devices by modifying the injection and transport of the charge carriers. We suggest a non-uniform dispersion of QDs in the co-polymer layer with carrier blocking process by the particles, which produced a balanced charge distribution inside the co-polymer, and thus increased the emission efficiency.

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### 1. Introduction

Conjugated polymers have been extensively studied for potential applications in electroluminescent displays, solar cells, and thin film transistors. Since the first report of an electroluminescence device based on conjugated polymers by Burroughes et al. [1], many conjugated polymers have been synthesized and investigated in order to fabricate efficient devices for industrial applications [2–6]. The science of polymer and organic devices has greatly progressed since then. The development of new materials and device designs has enabled the fabrication of high performance devices: various colors, low turn-on voltage, long lifetime, low energy consumption, and high brightness.

In parallel, nanotechnology science has emerged and is advancing rapidly. In particular, inorganic particles exhibit interesting physical properties as the size approaches nanoscale

dimensions. Quantum dots (QDs) are nanomaterials having specific and unique optical properties that can be exploited in display technology. Indeed, the luminescent color of nanocrystals differs from that of the bulk material, and changes with the crystal size due to quantum confinement effects. Several semiconductor QDs exhibit a size-dependent color variation, which covers almost the whole visible range [7,8]. Therefore, QDs have been used in electro-optic devices such as light emitting diodes (LEDs), photovoltaics, and lasers. An obvious advantage of the nanomaterial-based devices is their low production price by using mass production techniques.

The combination of both materials (polymers and QDs) and technologies (LEDs and QDs) is expected to lead to devices of good optical and electronic properties. The adjustable and sharp emission characteristics of these materials make them interesting to be used in light emitting diodes by just varying the particle size because of quantum confinement effects [9–12]. However, the first hybrid organic/inorganic LEDs made with poly(phenylene vinylene) (PPV) and cadmium selenide (CdSe) gave a rather limited performance of light emission, with uncontrolled color

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light [9]. Furthermore, CdSe showed poor photoluminescence as compared to some conjugated polymers and its stability is strongly influenced by the photo-processes occurring in the luminescent medium. Therefore, a new approach was developed by adding a shell of zinc sulfide (ZnS) to a CdSe particle in order to strengthen its structure and to enhance its emission. The photoluminescence (PL) quantum efficiency of the CdSe/ZnS core-shell QDs can reach more than 50% [13,14]. Further improvements of performance were achieved by the use of new designs of diodes, modifying the spatial distribution of carriers inside the emitter, and favoring their recombination, thereby improving the emission.

Despite the progress in performance of devices, the physical processes in the hybrid materials, especially the specific role of the QDs, have not been fully understood. In some combinations, these particles emit their characteristic light in addition to that of the polymer, and in others, only light from the polymer was obtained with an improved efficiency. In the Section 2, we shall briefly review the different aspects of devices making use of hybrid organic/QDs as active materials in LEDs.

## 2. Semiconductor quantum dots/polymer hybrid materials

Because of their small size, QDs increase the band gap of a semiconductor as compared to the bulk material according to basic equations of energy in quantum mechanics. In addition, spatial confinement of electrons or holes favors their recombination, and increases the light emission of the material. Techniques for obtaining size controlled QDs have been well known and described [15,16]. In these techniques, factors such as the concentrations of precursor solution, temperature, and reaction duration can be adjusted to provide the desired particle diameter. For CdSe, the size of QDs can vary from 2 to 6 nm, and the emitted colors cover a wide range from blue to red. This particular property has enabled incorporation of QDs in functional polymers to fabricate composites, which are used as an emitter in OLEDs. In earlier work, CdSe QDs were used as chromophores in a polymer matrix [9]. Such diodes could emit light from either the active polymer or the nanoparticles depending on the value of the applied voltage. However, the efficiency of these diodes is low, and they presented little practical interest. A new design of OLED structure using a single layer of QDs, which was sandwiched between two organic layers, gave an external quantum efficiency exceeding 0.4% [10]. In these diodes, the QDs were mixed with an organic material in solution and were deposited by spin coating. After drying, phase segregation occurred, giving a single and self-assembled QD layer, which was formed on the top of the organic film. In this configuration, the QDs act as chromophores, generating excitons either from direct charge injection or by exciton energy transfer from organic molecules (Förster energy transfer). It is expected that QDs act as trapping centers for electrons [10], and capture the injected carriers from the cathode. Subsequently, holes coming from the anode to the vicinity of the particles combine with trapped electrons to form excitons, which decay radiatively. Similar structures have been realized with different sizes of nanoparticles to make white light

emitting devices [17,18]. Another approach used a single QD layer deposited by spin coating of the aqueous solution forming trilayer-emitting diodes [19]. The efficiency is improved as compared to diodes without QDs, and the devices emitted light from both QDs and the organic materials. In order to obtain the light emission directly from the organic material with enhanced performance by QDs, it was suggested to uniformly disperse the particles in the polymer matrix [20,21]. This dispersion can be obtained by using core-shell QDs such as CdSe(ZnS) added to polymer to favor the charge transport in the active layer. A large number of carriers will pass from an electrode to the other without encountering a QD, and excitons will be formed inside the polymer matrix, giving light from the polymer. The role of QDs in carrier transport process in devices has not been clearly established, however. Some results lead to the conclusion that the dots are not involved in transport in hybrid materials, since the current-voltage characteristics are similar for devices containing QDs or not [16]. In devices with a QD monolayer formed on the top of the polymer film, the current density is lower than that measured in similar diodes without QDs [10], suggesting a trapping of charge carriers by the particles. In devices containing well-dispersed dots, the current density is higher as compared to pristine polymer, with improved emission performance.

In this work, we have investigated a hybrid material obtained by mixing a co-polymer of PPV derivatives with QDs. We used CdSe(ZnS) core/shell dots in order to obtain well dispersed nanoparticles in the polymer matrix. By determining the electro-optical characteristics of OLEDs using the material as an active layer, we discuss the role of QDs in the transport and emission processes.

## 3. Experimental

CdSe/ZnS core-shell type quantum dots (QDs) passivated with trioctylphosphineoxide (TOPO) caps were prepared following the technique already described [22]. The size of the dots used in this work was 3.8 nm as determined from transmission electron microscopy (TEM). The co-polymer was obtained from two monomers: 1,4-bis(chloromethyl)-2-phenyl-3-(9,9-dihexylfluorene-2-yl)benzene (M1) and 1,4-bis(bromomethyl)-2-methoxy-5-(2'ethylhexoxy)benzene (M2) whose synthesis was previously described in the literature [23,24]. After preparation of a solution having the defined ratio M1/M2 in the THF, a solution of potassium *tert*-butoxide (*tert*-BuOK) in THF was added. The resulting mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. A solution of 2,6-di-*tert*-butylphenol as end-capping agent in THF was then added and stirred for 6 h. The polymer was obtained by pouring the mixture into methanol and filtering. It was purified by dissolving in THF and reprecipitated from methanol twice. After drying under vacuum for 24 h, the polymer was obtained in a yellow-green powder form. QDs and the polymer were dissolved in CHCl<sub>3</sub> then mixed together in different volume ratios. The 1/2.5 volume ratio of QDs to polymer was chosen for fabrication of hybrid emitting films.

For the fabrication of devices, ITO-coated glass substrates were cleaned sequentially in ultrasonic baths of detergent,

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