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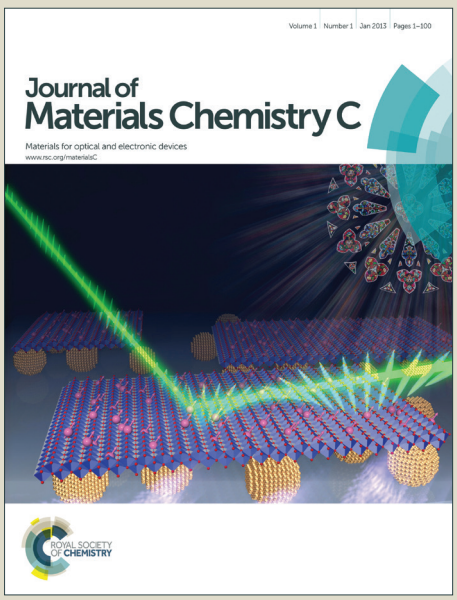

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Color Temperature Control of Quantum Dot White Light Emitting Diodes by Grafting Organic Fluorescent Molecules

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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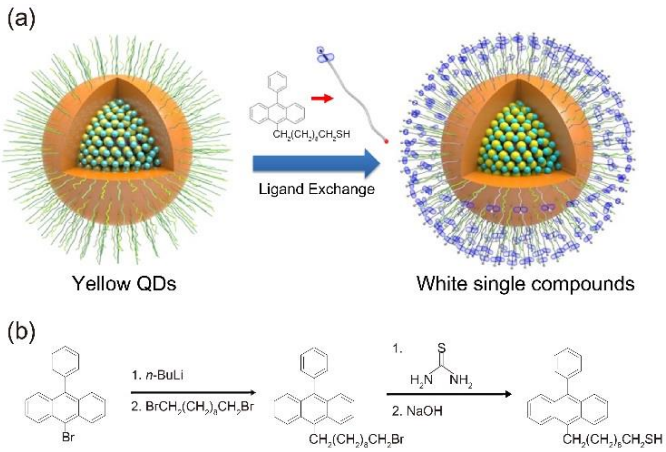
White-light emitting single compounds were synthesized by grafting blue-emission fluorescent molecules onto yellow emitting CdSe/ZnS core/shell quantum dots (QD) and white light emitting diode (WLED) were demonstrated. Facile adjustment of color temperature was also demonstrated by controlling the size of quantum dots and the amount of grafted organic blue-emitting molecules

Solid state lighting devices are replacing conventional incandescent bulbs and fluorescent tubes rapidly due to its high energy efficiency and reliability.[1] Currently white color emission is typically realized by complementary-color light emission. For example, yellow phosphorescent materials are coated on top of GaN-based blue inorganic light emitting diodes (LED) to generate white light emission.[2, 3] Despite its excellent internal quantum efficiency, inorganic LEDs are point light sources and they need light guiding systems or light diffusion films to convert them into planar light sources. Those extra light guiding systems and light diffusion films cause reduction in power conversion efficiency. In recent years, organic light emitting diode (OLED) lighting devices have been developed as perfect planar LED lighting sources.[4-6] OLED lighting are also getting attention due to its light weight and flexibility. However, OLED lightings often show their limitation in lifetime due to unstable organic light emitting materials. Inorganic compound semiconductor quantum dots (QDs) are getting attentions due to their chemical stability and high-quality light emission.[7] for planar and flexible applications.

Various methods are demonstrated for the generation of white light emission with QD-LED by stacking red (R), green (G) and blue (B) light-emission layers,[8] mixing RGB emitting materials[9, 10] and patterning RGB pixels.[11] The methods based on three RGB materials generally requires rather complicated processes of thin film formation and patterning processes possibly with different lifetime of materials. Therefore, it would be highly desirable to have single light emitting materials that emits white light all by itself and the process for lighting devices can be significantly simplified. One possibility is to synthesize a single molecule or compound that is capable of emitting white light via complementary emission of light from constituent component of the molecule and organic white-emitting single molecules were demonstrated. [12-14]



Scheme 1. (a) Schematic illustration of preparation of white-light emitting quantum dot of single compound through ligand exchange and (b) scheme for the synthesis of thiol-containing long alkyl chain anthracene ligands(PADT).

However, those organic white light emitting materials are known to be extremely unstable because of their complex structure. In this work we synthesized yellow-emitting CdSe/ZnS QD and anchored blue emitting ligands onto the QD surface to demonstrate a white light emitting single compound.

The schematic diagram of a blue fluorescent molecule-grafted QD is shown in Scheme 1(a). The blue fluorescent molecule of anthracene derivative (10-(10-phenylanthrace-9-yl)decane-1-thiol, PADT) was synthesized according to the procedure shown in Scheme 1(b). The molecular structure was confirmed with nuclear magnetic resonance (NMR) spectroscopy, as shown in Figure S1 in the Supporting Information (SI). Anthracene derivatives are one of common blue fluorescent materials, emitting light of wavelengths below 450 nm with a relatively high quantum yield.[15, 16] In the synthesis, long alkyl chains were attached to the anthracene derivatives to minimize fluorescence resonance energy transfer(FRET) from the blue-emitting to the yellow-emitting band gaps.[17-19] The thiol functional groups were attached as anchoring groups.[20] Grafting of the molecule onto the QDs was confirmed by Fourier transform infrared spectroscopy (FT-IR) as detailed in Supporting Information.

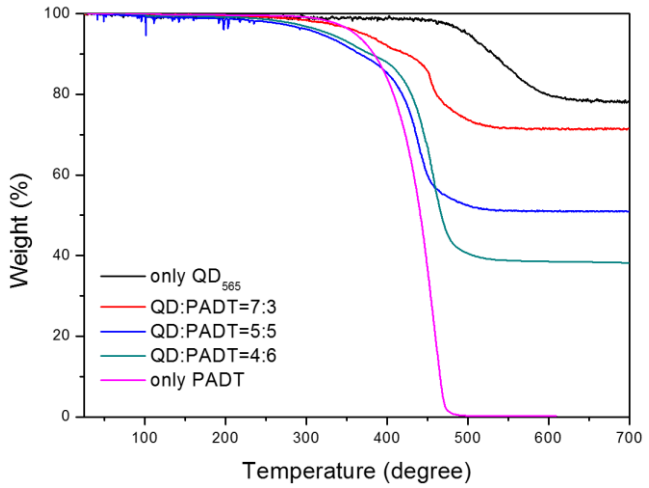


Figure 1. Thermal gravimetric analysis of pristine QDs, PADT, and different weight ratio of single compound.

Thermal gravimetric analysis (TGA) was performed to determine the weight ratio of organic molecules and inorganic compounds in QDs,[21, 22] as shown in Figure 1. The organic materials are burned off as the temperature is increased and the relative weight at the high temperature represents the relative amount of the inorganic materials.

Data were taken at a heating rate of 20 K/min in a nitrogen atmosphere. The degradation temperature is defined as the temperature at which 10 wt% is burned off. The degradation temperature of the without blue fluorescent molecule grafting (PADT only) was determined to be 387°C, and that of oleic-acid-capped QDs was determined to be 506°C. Upon completely burning off the organic species, a weight loss of 22.0 wt% was observed from the oleic-acid-coated QDs. The degradation temperature of single compound was determined to be 383°C, which is similar to the temperature of without blue fluorescent molecule grafting. Upon completely burning off the organic species (composed of a mixture of the PADT and small amount oleic acid) in the white emitting single compound, a weight loss of 30-60% was observed. The increased weight loss in the organic materials attached to the QD surfaces and the reduced degradation temperature indicate that the QD surfaces are covered mainly by the PADT. From the final weight percentage that is representative of the QDs, the average weight ratio between the attached QDs and PADT can be estimated as QD:PADT = 7:3, 5:5, 4:6.

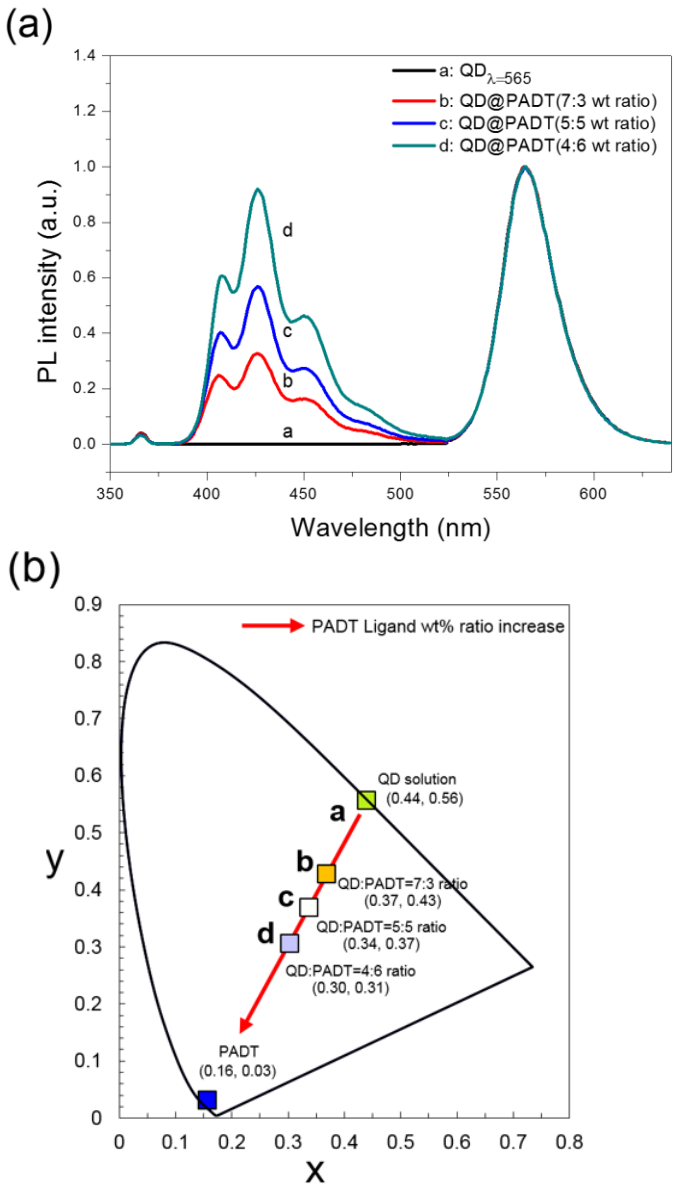


Figure 2. (a) Emission spectra (λ_{ex}=365nm) of CdSe/ZnS QDs with variable weight ratio of QD to PADT (b) CIE 1931 chromaticity diagram. The color square shows the luminescent color coordinates for the corresponding states **a**(0.44, 0.56), **b** (0.37, 0.43), **c** (0.34, 0.37), **d** (0.30, 0.31) and PADT (0.16, 0.03), respectively.

Photoluminescence (PL) spectrum of the single compound was investigated by varying the ratio of the PADT molecule to QD. The ratio was varied by changing the concentration of the molecule in toluene, to which the QDs were introduced for the grafting. The actual amount grafted onto the QDs was estimated as detailed in Supporting Information. The results are shown in Figure 2(a).

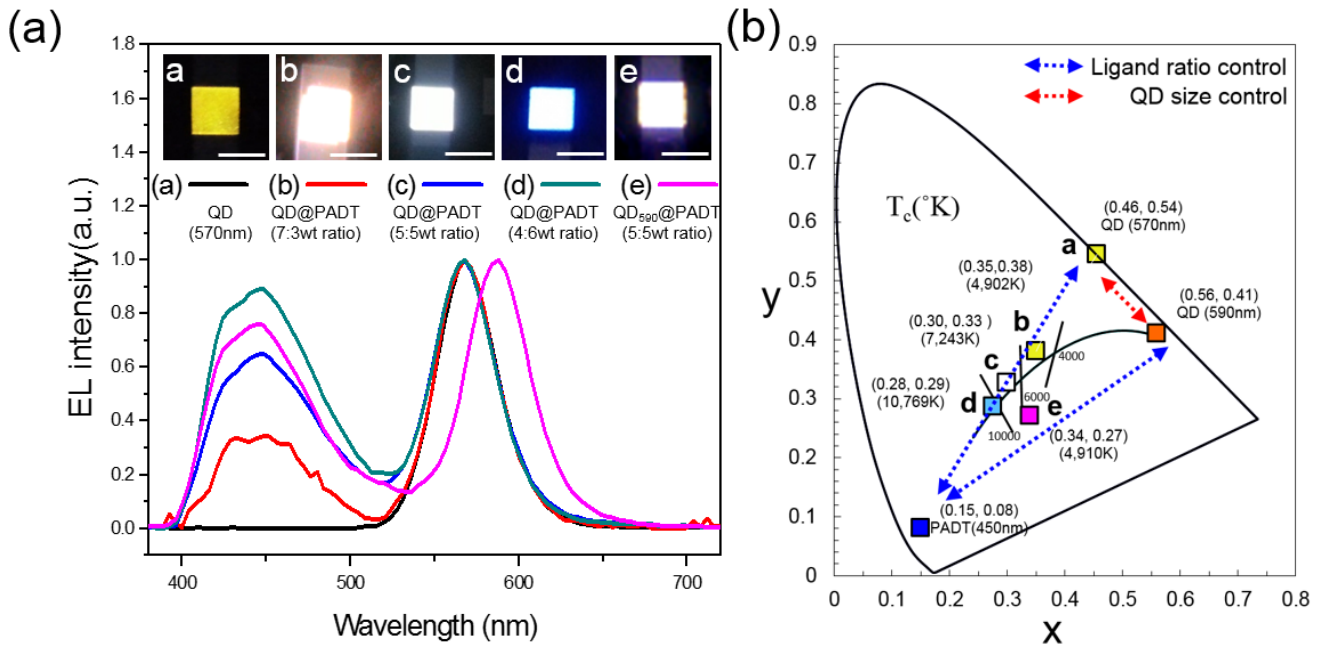


Figure 3. (a) Normalized EL spectra of QD-WLEDs with different ratio of QD to grafted molecule (inset: photographs of the device with different color emission, scale bar = 3mm) (b) CIE color coordinates for the colors in (a) are **a**(0.46, 0.54), **b** (0.35, 0.38), **c** (0.30, 0.33) and **d**(0.28, 0.29), respectively. The CIE color coordinates for control of different QDs sizes(590nm QDs) are QDs(0.56, 0.41), PADT (0.15, 0.08) and single compound with different QD(590nm) **e**(0.34, 0.27), respectively

It is clear from the figure that the PL intensity of blue light increases with increasing ratio of the PADT molecules to QD. The intensity of the blue emission peak around 425 nm increased from 0.325 at a molecule to QD ratio of 3:7 (curve **b**) to 0.919 at a ratio of 6:4 (curve d). The blue emission complements the yellow emission from the QDs, leading to apparent white light emission. The ratio change results in a change in the Commission Internationale de I'Eclairege (CIE) color coordinate, as shown in Figure 2(b). The color coordinate of the QDs themselves (a in Figure 2(b)) was (0.44, 0.56), which corresponds to yellow emission. A continual color change was observed as the amount of the grafted molecule on the QDs was increased. As the ratio was increased from QD:PADT = 7:3 to 5:5 and 4:6 (as estimated with TGA calculations), the CIE color coordinate changed from b (0.37, 0.43), c (0.34, 0.37) and d (0.30, 0.31).

Encouraged with the photoluminescence results, we fabricated QD-WLEDs with the layer of white- light emitting QDs as the emission layer (EML) in the following device structure (See Figure S4 in SI): indium tin oxide (ITO) glass / poly(ethylenedioxythiophene) : polystyrene sulfonate (PEDOT:PSS) (40 nm) / poly(9-vinylcarbazole) (PVK) (45 nm) / EML / ZnO nanoparticles (25 nm) / Al (100 nm). All layers were sequentially solution-processed onto ITO glass substrate via spin coating, except for the Al cathode layer (for more details, see the Supporting information). The emission layer for the QD-WLEDs was prepared with the same QD solutions as in the PL experiments.

Normalized electroluminescence (EL) spectra of a single compound QD-WLED at an operating voltage of 5.0 V are shown in Figure 3(a). As in the PL results, the blue EL emission increases as the amount of grafted molecule increases. One difference in the EL, compared with the PL emission data, is that there exists only one broad blue emission peak (450 nm), which is slightly red-shifted. The photographs in the inset of the graph show the light emission from the EL devices fabricated on an 1-in^2 substrate with an emission pixel size of 9 mm^2, which correspond to different molecule to QD ratios indicated by the cases of a through d in Figure 3(a). Shown in Figure 3(b) are the CIE diagrams for all the devices. The color coordinates and color rendering index(CRI) for these four different ratios are as follows: a (0.46, 0.54), warm white b (0.35, 0.38; CRI=23), to natural white c (0.30, 0.33; CRI=42) to cool white d (0.28, 0.29; CRI=48). These changes in the color coordinates are also expressed in terms of color temperature according to McCamy's formula, and the color temperature changed from 4,902 K(b), 7,243 K(c) to 10,769 K(d).[23] With the ratio at 5:5 (sample c), light emission close to the standard white was achieved (CIE coordinate: (0.33, 0.33)). Color of the emitted light can also be controlled by changing the size of quantum dots, owing to quantum confinement effect. As the size of the QDs is increased, the QD color showed a red shift, as shown in Figure 3(b). Therefore, the emission color can be controlled either by changing the QD size or by changing the molecule to QD ratio. In general it would be quite challenging to control the color temperature with organic light emitting molecules in which new molecule synthesis is required. This relatively easy control of color temperature is a key advantage of the molecule grafted QD approach that can make QD-WLED fabrication process quite simple.

The performance of the single compound QD-WLED device is shown in Figure 4. Given in Figure 4(a) are the luminance-

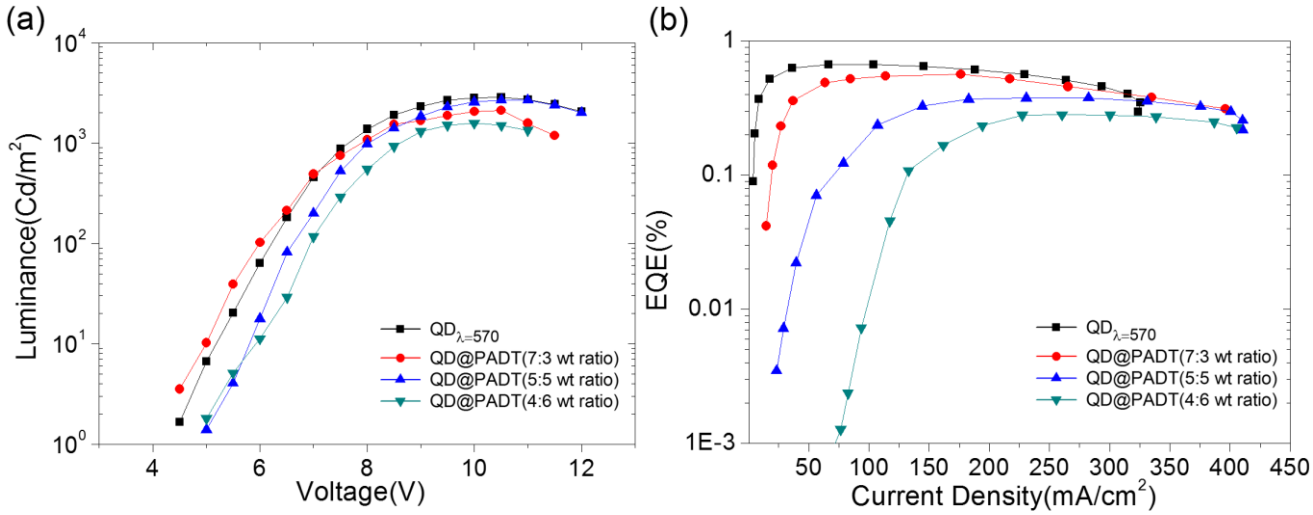


Figure 4. (a)Luminance-voltage (L-V) curves for the QD-WLED devices (b) External quantum efficiency-current density (EQE-J) curves for the devices.

Table 1. Summary of device performance for different ratios of QD_{568} to PADT

Sample QD : PADT weight ratio	V_{on} (V)	Max. Luminescence (cd/m^2)	Max. CE (cd/A)	Max. EQE (%)	CIE (x, y)	CRI
Original QDs (570nm)	4.5	2,847	1.33	0.67	0.46, 0.54	0
7:3	4.5	2,105	0.88	0.57	0.35, 0.38	23
5:5	5.0	2,693	0.81	0.38	0.30, 0.33	42
4:6	5.0	1,582	0.58	0.28	0.28, 029	48

[a] Abbreviations: V_{on}(turn-on voltage), CE(current efficiency), EQE(external quantum efficiency), CIE(Commission Internationale de l'Eclairege), CRI(Color rendering index), (The turn-on voltage is defined as the applied voltage when the luminance is detected by the luminance meter)

-voltage (L-V) characteristics of the device made with different weight ratio of molecule to QD (samples b to d). The maximum luminance for the devices corresponding to the cases of b, c, and d was measured to be 2105, 2693, and 1582 cd/m^2, respectively. These values are sufficient for white lighting, and even for use as a WLED backlight. They all show similar turn-on voltage around 5.0 V. Shown in Figure 4(b) is the external quantum efficiency (EQE) as a function of the current density of the devices. The EQEs of the (b), (c), and (d) devices were 0.56%, 0.38%, and 0.28%, respectively. The efficiency and luminance are believed to be the highest value as compared with other QD-based WLEDs.[7-9, 24] Table 1 summarizes the performance of the QD-WLEDs fabricated with different weight ratios of molecule to QD in detail.

Conclusions

In conclusion, white light emitting quantum dots were synthesized by grafting organic blue-emitting light emitting materials onto yellow emitting CdSe/ZnS quantum dots. White light emitting diodes were demonstrated with the organic molecule grafted quantum dot materials and maximum luminance of 2690 cd/m^2 and a turn-on voltage of 5.0 volts were achieved. Controllability of color temperature was also demonstrated from warm white (4,902K) to cold white (10,769K) by adjusting the weight ratio of QD to grafted molecules and QD size. The white emitting single compound can potentially make the fabrication process simple and cost effective.

Experimental detail

Synthesis of CdSe/ZnS QDs.

Yellow light-emitting (565 nm)CdSe/ZnS core/shell QDs with chemical-composition gradients were prepared according to the method reported by Bae *et al.*[25] For a typical synthesis, 0.8 mmol of cadmium oxide (CdO, 99.99%), 4 mmol of zinc acetate (99.9%, powder), and 5.58 mL of oleic acid (OA) were placed in a 100-mL 3-neck flask and heated to 150 °C in high-purity N_2 for 30 min. Then, 20 mL of 1-octadecene (ODE) was added to the flask, and the temperature was increased to 310 °C. A stock solution containing 3.0 mL of trioctyl-phosphine (TOP), 1.2 mmol of selenium (Se), and 3 mmol of sulfur (S) was quickly injected into the flask. The reaction temperature was maintained at 310 °C for 10 min. and then cooled to room temperature. QDs were purified by adding 20 mL of chloroform and an excess amount of acetone (at least 3 times). They were then redispersed in chloroform or hexane at a concentration of 5.0 mg/mL.

Ligand exchange.

A QD solution in hexane (5 mg/mL) was added to the solution of anthracene derivative (synthesis method see

Supporting Information) (0.5 mL, 2.5mM, 5mM, 10mM) in $CHCl_3$. After tetra methyl ammonium hydroxide (5 - 10 drops, 10% in MeOH) was added to this solution, the solution was stirred vigorously overnight, and the precipitate was isolated by centrifugation (10,000 rpm, 10 min) and washed with acetone until no UV absorption could be detected from the solution.

Fabrication and characterization of QD-WLED.

QD-WLEDs were fabricated on indium tin oxide coated glass (ITO/glass) substrates (sheet resistance <10Ω/square). ITO glasses were pre-cleaned with acetone and isopropyl alcohol using sonication, and treated with argon/oxygen plasma for 1 min before use to allow for a hydrophilic surface. The poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron P AI 4083) was diluted with isopropyl alcohol, with a volume ratio of 9:1, and then spin-coated at 4,000 rpm for 30s. The PEDOT:PSS-coated ITO glass was annealed using a hot plate at 120°C for 10 min in air. The coated substrates were then transferred to an N_2-filled glove box for spin-coating. Poly(9-vinylcarbazole (PVK) with N,N`-diphenyl-N,N`-bis(3-methylphenyl)-1,1`-diphenyl-4,4`-diamine, 4,4`,4``-tris(N-carbazolyl) -triphenyl-amine(TCTA), (0.008+0.002) g/mL[26] in chlorobenzene was then spin-coated at 3,000 rpm for 30 sec as the hole-transport layer, followed by annealing of the substrate at 180 °C for 30 min. The emitting layer was then spin-coated with different kinds of emitting materials such as yellow QDs and ligand-exchanged white emitting single compound with different weight ratio at 2,000 rpm for 20 sec. Next, the ZnO nanoparticle layer (30 mg/mL, synthesis method in SI) was spin coated at 4,000 rpm for 30 sec, and the substrate was annealed at 150°C for 30 min. Finally, these multilayer samples were loaded into a custom high-vacuum deposition chamber (background pressure: ~1 × 10^{-6}torr) for the deposition of the Al cathode on the top (100-nm thick; deposition rate: 3-5 Å).

Acknowledgment

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Education, Science and Technology (2011-0006268). This research was also supported by the MKE (The Ministry of Knowledge Economy), Korea, under the ITRC (Information Technology Research Centre)) support program (NIPA-2012-H0301-12-4013) supervised by the NIPA (National IT Industry Promotion Agency).

Notes and references

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†Electronic Supplementary Information (ESI) available: Synthetic method and characteristics of QDs (UV−vis and PL spectra), ZnO Nanoparticle and anthracene derivative (1H NMR, UV − vis and PL spectra), confirm grafting single molecule (FT-IR), the device fabrication and characterization methods. See DOI: 10.1039/c000000x/

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Keyword: Color temperature control, Quantum dot, ligand exchange, Grafting fluorescent, white LED

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Color Temperature Control of Quantum Dot White Light Emitting Diodes by Grafting Organic Fluorescent Molecules

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