

Supporting Information

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

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1. Synthesis materials

Blue ligand ^1H NMR spectra were acquired on a BrukerAvance400 instrument equipped with a quadruple nucleus probe (QNP). Spectra were generated and analyzed using TopSpin NMR software.

Synthesis of blue fluorescence small molecule (compound 1, PADT): To prepare blue fluorescent molecules with a long alkyl chain were prepared by the following sequence. 9-bromo-10-phenylanthracene (8 g, 24.0 mmol) was first dissolved in anhydrous diethyl ether (300 mL). The solution was cooled to 0°C , and a solution of n-butyllithium (2 M, 18 ml, 36.0 mmol) was then added slowly. After the solution was kept at that temperature over 1 hour, 1,10-dibromodecane (21.6 mL, 96.0 mmol) was added. 30 minutes later, the solution was refluxed for 2 hours. After the end of the reaction, the mixture was cooled down to room temperature, and 80 mL of distilled water was added. The organic layer was collected, and the water layer was extracted 3 times with 40 mL of ether. Water was eliminated by MgSO_4 . Through column chromatography, a yellowish green oil could be retrieved (compound 2) (5.7 g, 50%). This molecule structure was confirmed by NMR with the following peaks: ^1H NMR (CDCl_3 , 400 MHz): 8.32 (2H, d), 7.65 (2H, d), 7.58–7.30 (9H, m), 3.65 (2H, t), 2.52 (2H, t), 1.65-1.63 (2H, m), 1.61-1.59 (4H, m), 1.44–1.33 (10H, m)

The previous product (compound 2) (4 g, 8.4 mmol) and thiourea (1.3 g, 16.9 mmol) were dissolved in anhydrous ethanol (50 mL) and refluxed for 4 hours. NaOH (6 M, 50 mL) was added to the mixture and refluxed for 2 hours. When the reaction ended, extraction by ethyl acetate (30 mL) was executed 3 times after the ethanol was eliminated. The brine solution was washed and the water was removed by MgSO_4 . Greenish powder (compound 1) (1.4 g, 39%) was obtained by

column chromatography. This molecule structure was confirmed by the following NMR peaks(see in Figure S1): ^1H NMR (CDCl_3 , 400 MHz): 8.32 (2H, d), 7.63 (2H, d), 7.59–7.28 (9H, m), 3.92 (2H, t), 3.65 (2H, t), 1.70-1.68 (2H, m), 1.64-1.60 (4H, m), 1.52–1.37 (10H, m)

Synthesis of yellow emitting QD :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.*¹ 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 trioctylphosphine (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 PADT (0.5 mL, 3 mM) in CHCl_3 . After tetramethyl 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.

Synthesis of ZnO nanoparticles: ZnO nanoparticles are used for the electron transport layer. ZnO nanoparticle were prepared modifying the method reported by Qian *et al.*² A mixture of 30 mL of a solution of zinc acetate in dimethyl sulfoxide (DMSO, 0.5 M) and a solution of tetra methyl ammonium hydroxide (TMAH) in ethanol (0.55 M) were stirred for 1 hour in ambient air,

and then washed with a mixture of ethanol and excess acetone by centrifugation. The synthesized ZnO nanoparticles were dispersed in ethanol with a concentration of 30 mg/mL and used as an electron transport layer material for LED device fabrication.

2. General characterization

Optical properties

PL and UV absorption spectroscopy was performed with a FP-6200 spectrofluorometer and a V-630 Bio UV-Vis Spectrophotometer. Fluorescence spectra were acquired on a Cary Eclipse fluorescence spectrophotometer (Varian) using Hellma 100- μ L microcuvettes. The usual excitation wavelength for the QDs was 365 nm, and the sample temperature was 20°C.

The optical properties of the QDs, PADT, and ligand exchanged single compound characterized using UV-visible absorption spectroscopy and photoluminescence (PL) spectroscopy are shown in Figure S2. The yellow solution of CdSe/ZnS core/shell ($h\nu=2.2\text{eV}$) QDs in hexane shows an absorption peak at 540 nm and a PL peak at 565 nm with a narrow bandwidth (and a full width at half maximum (FWHM) of 32 nm (Figure S2 (A)). The blue light-emitting 1 shows four major absorption peaks at 341 nm, 359 nm, 377 nm, and 399 nm in the UV-visible spectrum range and PL peaks shown in Figure S2 (B). The white single compound solution show absorption peaks at approximately the same location as the individual materials themselves (QDs and PADT) (Figure S2 (C)). The photoluminescence quantum yields of the QD and the PADT molecule that were determined with the references of rhodamine 6G (for yellow, QY=95%)^{3,4} and 9,10-diphenylanthracene (for blue, QY=90%)^{5,6} were 63% and 45%, respectively.

Confirmed grafting and weight ratio

FT-IR spectra were recorded on Bruker IFS-66/S equipment in transmittance mode in the spectra range of 500-4000, with 4-cm⁻¹ spectral resolution.

The disappearance of the thiol indicative peak in the FT-IR spectra (Figure S3(A)) of the single compound upon grafting and the presence of anthracene indicative peaks (Figure S3(B)) clearly confirmed the grafting of the PADT on the quantum dot surface.⁷

3. Device fabrication and long alkyl chain effect:

Device fabrication process

I-V-L characteristics were determined using a source unit (2400, Keithley Instruments, Inc., Cleveland, OH, USA) and a luminance meter (CS1000, Konica Minolta Sensing, Inc., Sakai, Osaka, Japan). The measurements were performed under ambient conditions.

QD-LEDs were fabricated(device structure see Figure S4) on indium tin oxide coated glass (ITO/glass) substrates (sheet resistance <10Ω/sq). 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 dioxy-thiophene):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 N₂-filled glove box for spin-coating. Poly(9-vinylcarbazole (PVK, 0.01 g/mL 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) 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: $\sim 1 \times 10^{-6}$ torr) for the deposition of the Al cathode on the top (100-nm thick; deposition rate: 3-5 Å).

Long alkyl chain effect

The current flows were analyzed with a modified electron-tunneling model and showed alkyl chain length dependences. Increasing the applied voltage resulted in a decrease current because of electron-tunneling effect. This observation was mainly explained by EL spectrum ratio at different applied voltage. The I-V curve show before 10V current depend on voltage exponentially and device emitting blue color because long alkyl chain protect electron transfer anthracene to QD.⁸ But during 10V to 12 V dramatically decrease current density at same time device emitting color change blue to white. After 12V almost electron transfer to QD so device emitting yellow color. (See Figure S5)

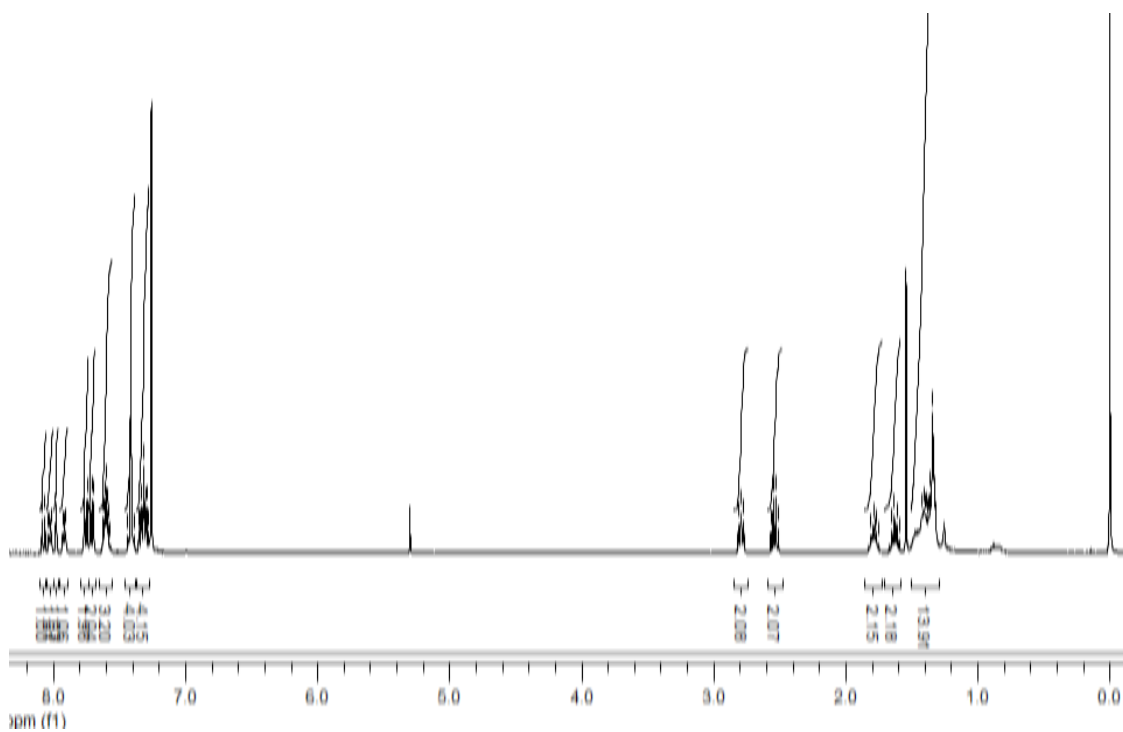
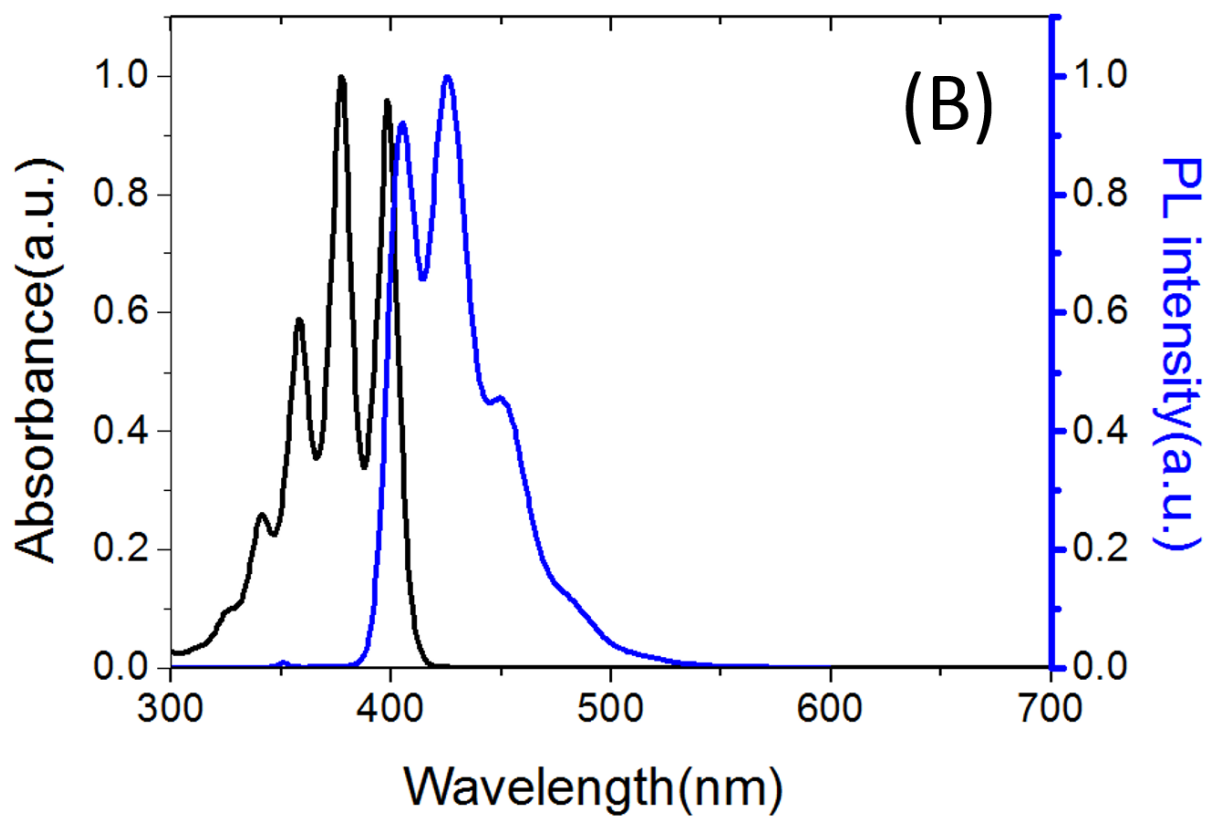
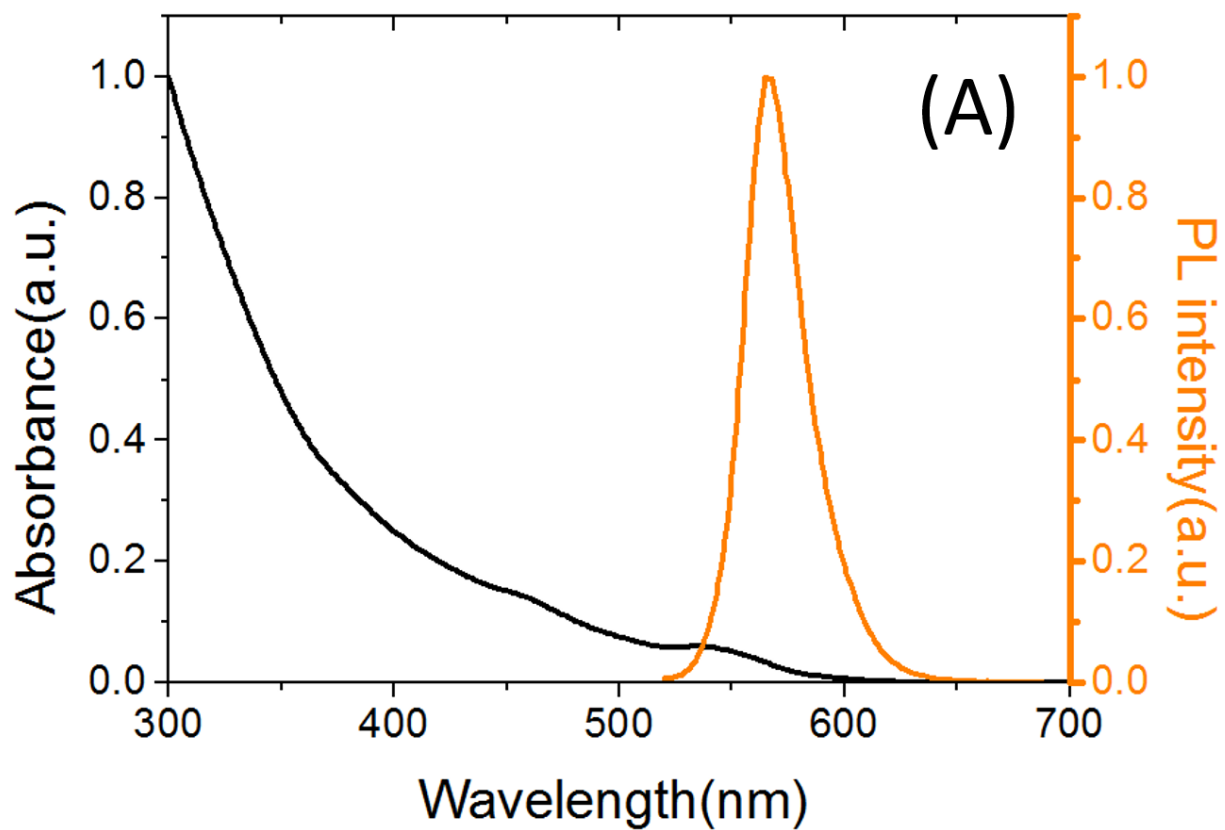


Figure S1. ¹H NMR spectra of 10-(10-phenylanthracene-9-yl)decane-1-thiol (compound 1, PADT)



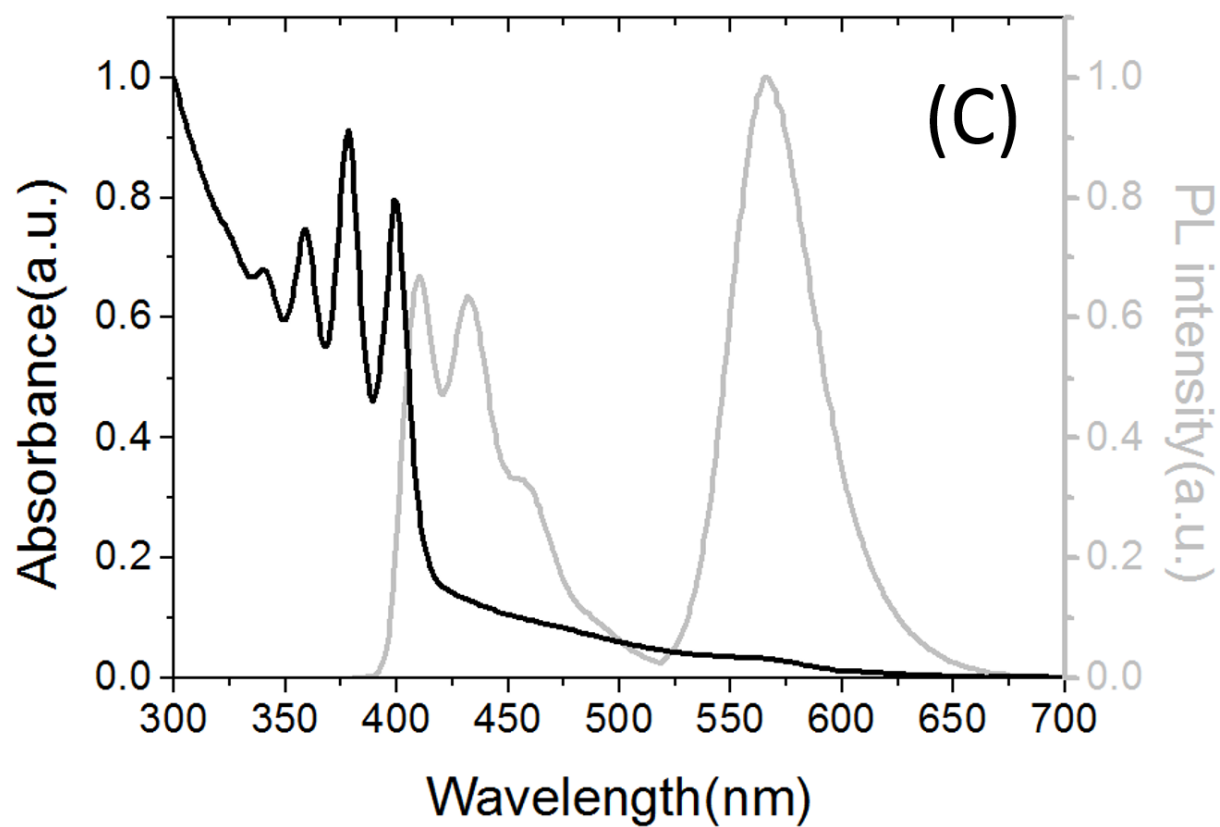


Figure S2. Optical analysis by UV-visible absorption and PL emission spectra of (A) QDs, (B) PADT, (C) white emitting single compound

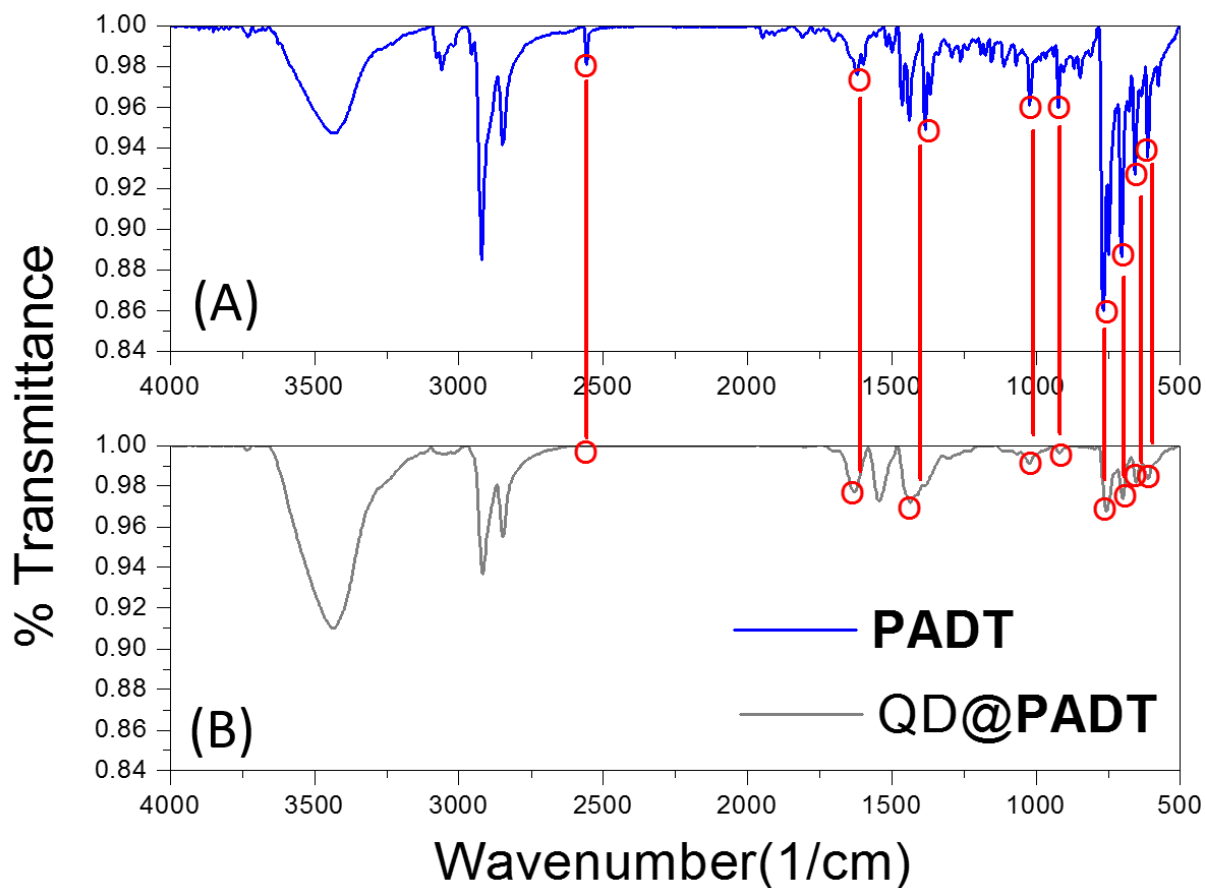


Figure S3. FT-IR spectra of (A) PADT and (B) white emitting single compound. Some labeled peaks in the spectrum below graph show slight shifts compared to those in the spectrum of PADT, indicating PADT was successfully functionalized onto the QD surface.

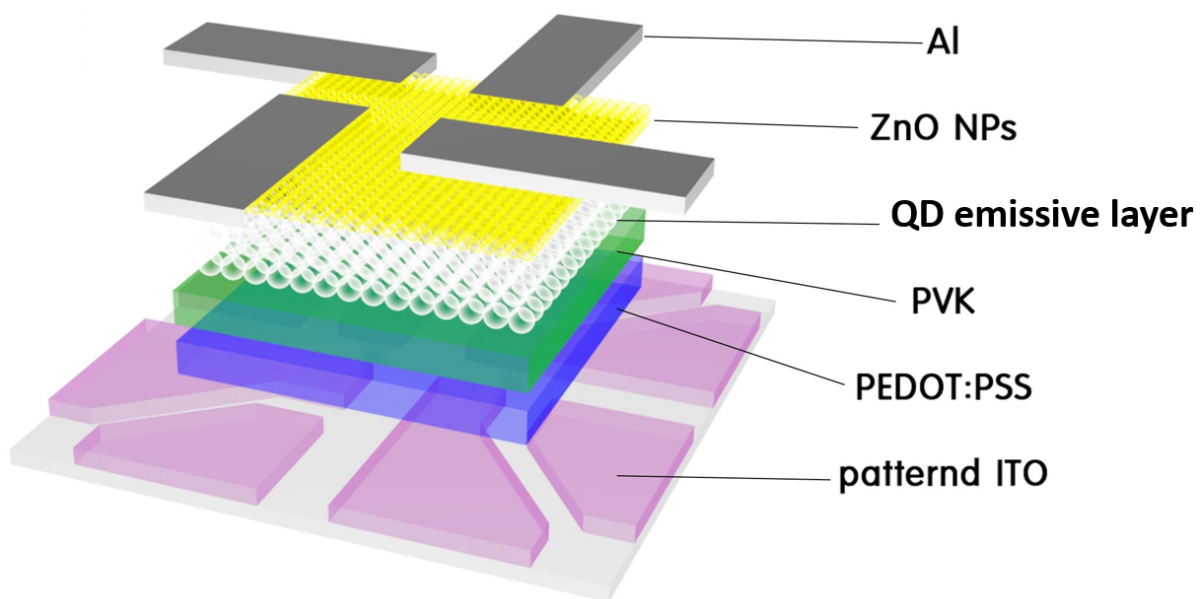


Figure S4. Schematic of layers in the device structure

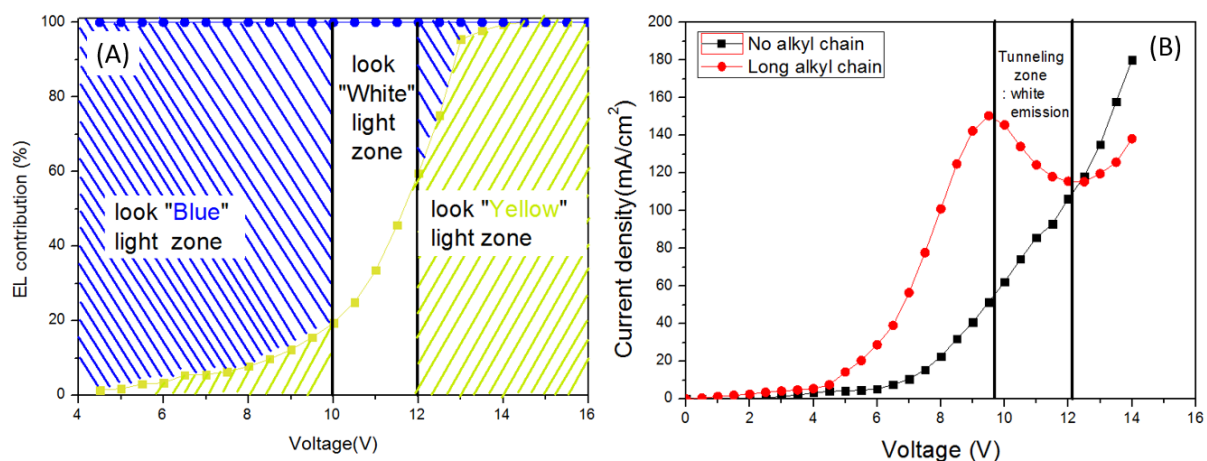


Figure S5. EL contribution ratio and I-V characteristic with long alkyl chain ligand

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