ARTICLE

Supplementary Information for

Interfacial structural analysis with X-ray reflectivity for elucidation of alkyl-chain effects on hole-injection in quantum-dot light-emitting diodes

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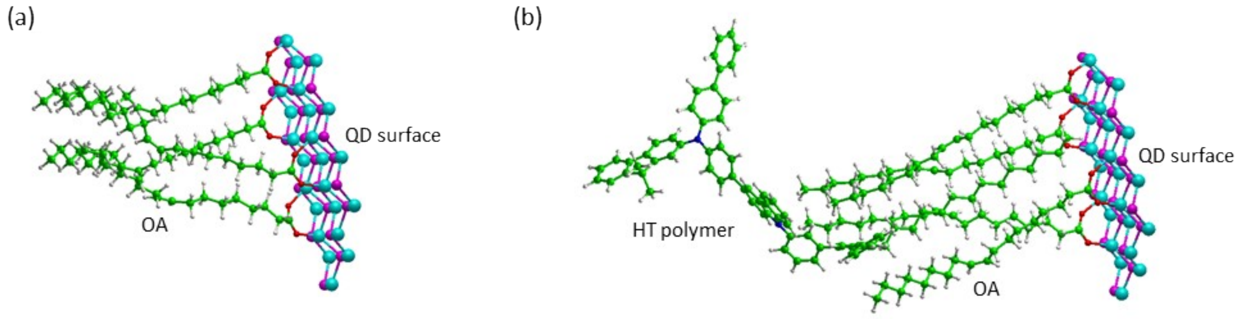

Figure S1 Optimized structure of (a) QD/OA (Cyan: Zn, Magenta: S) and (b) QD/OA+HT-14.

Material Synthesis and Characterization

1. Monomer synthesis

Commonly used chemicals, such as reagent, solvent, catalyst, and base, were purchased from Tokyo-Kasei, Fuji-Film Wako and Sigma-Aldrich and applied to synthesize without further purification. The synthesized monomers were characterized by mass spectroscopy and nuclear magnetic resonance (NMR), and determined its purity by high-performance liquid chromatography (HPLC) peak area%. The impurity contained in the polymer was analysed by inductively coupled plasma mass spectroscopy (ICP-MS), and combustion ion chromatography (IC).

The monomer of HT polymers were synthesized by the following chemical schemes (Figure S2a).

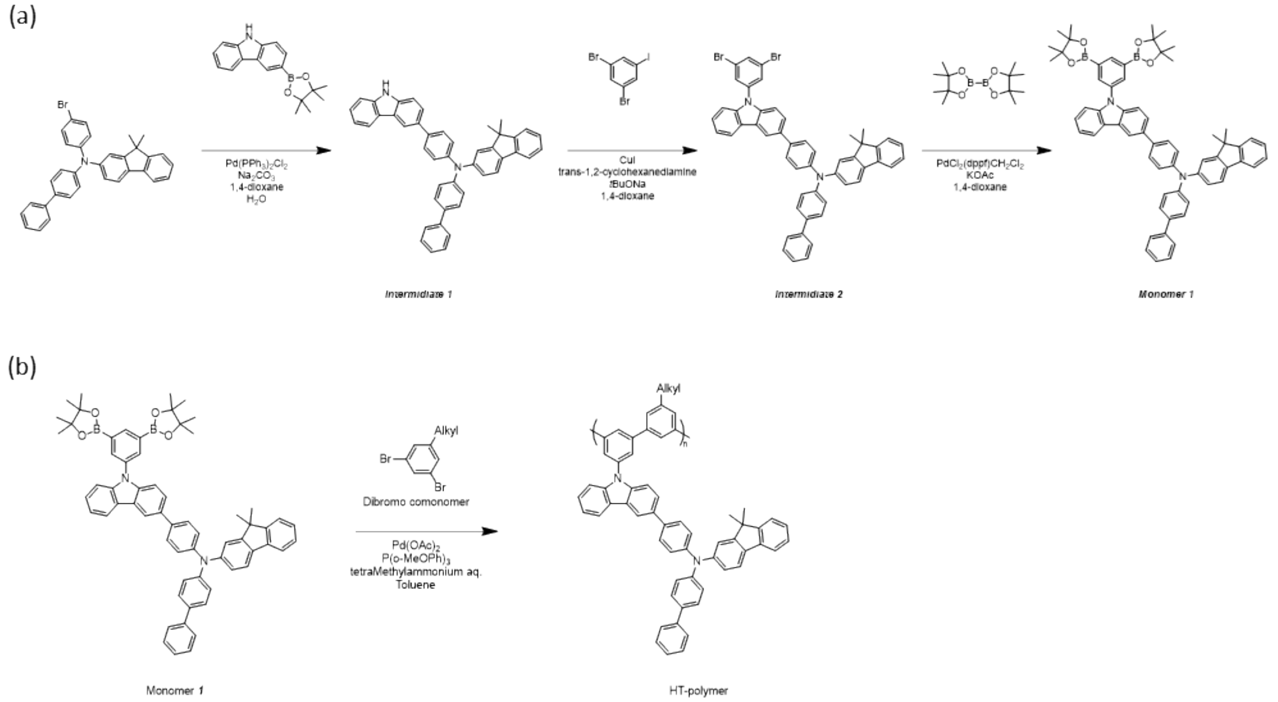

Figure S2 Synthesis schemes of (a) monomer and (b) polymer

Synthesis of Intermediate 1; (N-(4-(9H-carbazol-3-yl)phenyl)-N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-9H-fluoren-2-amine)

In a 1-L three-neck flask 2-Amino-N-[(1,1'-biphenyl)-4-yl]-N-(4-bromophenyl)-9,9-dimethylfluorene (15.0 g, 29.0 mmol) and 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole (7.66 g, 26.1 mmol) were dissolved with 1,4-dioxane (290 mL). A sodium carbonate (7.70 g, 72.6 mmol) aqueous solution (145 mL) was then added to the flask. The mixed solution was deoxygenated by argon bubbling for 15 min. After bubbling Bis(triphenylphosphine)palladium(II), dichloride was added to the flask, and the mixture was refluxed for 4 h under argon atmosphere.

After reaction the mixture was poured into 300 mL of pure water, and the precipitate was filtered and washed with methanol. The precipitate was purified Silica-gel column chromatography using a toluene/hexane mixture as eluent. After removing the solvent by rotary evaporation, the intermediate 1 was obtained as white solid (12.0 g, yield: 69%).

Synthesis of Intermediate 2; N-([1,1'-biphenyl]-4-yl)-N-(4-(9-(3,5-dibromophenyl)-9H-carbazol-3-yl)phenyl)-9,9-dimethyl-9H-fluoren-2-amine

In a 100-mL three-neck flask Intermediate 1 (7.0 g, 11.6 mmol) and 1,3-Dibromo-5-iodobenzene (4.62 g, 12.8 mmol) were dissolved in 1,4-dioxane (35 mL), and sodium tert-butoxide (2.23 g, 23.2 mmol) was added in the flask. Trans-1,2-Cyclohexanediamine was then added to the mixture in argon atmosphere. The mixture was refluxed for 6 h under argon atmosphere.

After the reaction, 50 mL of toluene was added to the mixture, and the mixed solution was filtered with Celite and concentrated by rotary evaporation. The crude was purified by silica-gel column chromatography using the toluene/hexane mixture as eluent. After removing the solvent by rotary evaporation, the intermediate 2 was obtained as white solid (6.8 g, yield: 70%).

Synthesis of Monomer 1; N-([1,1'-biphenyl]-4-yl)-N-(4-(9-(3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazol-3-yl)phenyl)-9,9-dimethyl-9H-fluoren-2-amine

In a 200-mL three-neck flask, Intermediate 2 (4.0 g, 4.8 mmol) and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (3.64 g, 14.3 mmol) were dissolved with 1,4-dioxane (48 mL),and potassium acetate (2.82 g, 28.7 mmol) was added to the flask. The mixture was then deoxygenated by argon bubbling for 15 min. After bubbling [1,1'-Bis(diphenylphosphino)ferrocene]-dichloropalladium was added, and the mixture was refluxed for 4 h under argon atmosphere.

After the reaction, the mixture was filtered with Celite and concentrated by rotary evaporation. The residue crude product was dissolved in toluene. Activated carbon (100 wt% for the crude) was added for the crude solution, and the solution was stirred for 30 min at 100ºC. After removing activated carbon by filtering with Celite, the filtration was purified by silica-gel column chromatography using the toluene/hexane mixture as eluent. After removing the solvent by rotary evaporation, the residue solid was purified by recrystallization using toluene/hexane mixture. The residue was dried in vacuum at 40ºC for overnight. Finally, the monomer 1 was obtained as white solid (2.6 g, yield: 58%, the purity was 99.55%, m/z=931.4 (calcd. for $C_{63}H_{60}B_2N_2O_4$: 930.47)). The ^{1}H-NMR (300 MHz, CH_2Cl_2, δ) spectrum was measured using Bruker 300 Ultrashield, as shown in Figure S3a: 8.39 (s, 1H), 8.27 (t, 1H), 8.19-8.22 (d, 1H), 8.04 (d, 1H), 7.55-7.70 (m, 9H), 7.18-7.47 (m, 16H), 1.45 (s, 6H), 1.36 (s, 24H).

2. Polymer synthesis

General Procedure of HT Polymer Synthesis

All polymers in this study were polymerized and purified by the same procedure described below. Their difference was only dibromide comonomer; the comonomer having different length of normal alky substituent was used in the polymerization (Figure S2b).

In a 200-mL four-neck flask, monomer 1 (1.60 g, 1.7 mmol), dibromo comonoer (1.7 mmol), Palladium acetate (3.9 mg, 0.017 mmol), and Tris(2-methoxyphenyl)phosphine (31.7 mg, 0.10 mmol) were dissolved in toluene (46 mL) under argon atmosphere. Tetraethylammonium hydroxide aqueous solution (20 wt%, 8.95 g) was added to the solution and refluxed for 8 h under argon atmosphere. Phenyl boronic acid (21.0 mg, 1.7 mmmol), Bis(triphenylphosphine)palladium dichloride (73.1 mg, 0.10 mmol), and Tetraethylammonium hydroxide aqueous solution (20 wt%, 8.95 g) were then added to the mixture and refluxed for 7 h under argon atmosphere. After polymerization, the water phase was removed from the reaction mixture. Sodium N, N-diethyldithiocarbamate trihydrate aqueous solution (5.4 g dissolved in 50 mL of deionized water) was added to the mixture and refluxed for 2 h under argon atmosphere. After reaction, the water phase was removed from the reaction mixture, then the oil phase was washed with deionized water (50 mL), 3 wt% acetic acid aqueous solution (50 mL), and deionized water (50 mL) sequentially. The washed oil phase was dropwised into excess methanol, and the precipitation was collected by filtration. The crude polymer was purified by silica-gel column chromatography using toluene as eluent, then also purified by reprecipitation (toluene was used as a rich solvent and methanol was used a poor solvent). The obtained polymer was dried in vacuum at 50ºC overnight. Finally, the HT polymers were obtained as pale yellow powder. The ^{1}H-NMR spectra are shown in Figure S3. The synthesis results of HT polymers are summarized in Table S1. The molecular weight of the polymer was determined by size exclusion chromatography by using SHIMADZU prominence composed of SIL-10AF, DGO-20A, CBM-20A, SPD-20A, CTO-20A. The size exclusion chromatography (SEC) measurement condition was the following: column was PL1110-1120 and PL1110-6100 provided by Agilent technology, eluent was THF, flow rate was 1 mL min^{-1}, and oven temperature was 40ºC. Polystyrene standard (Tosoh, PStQuick kit-H) was used to create the calibration curve.

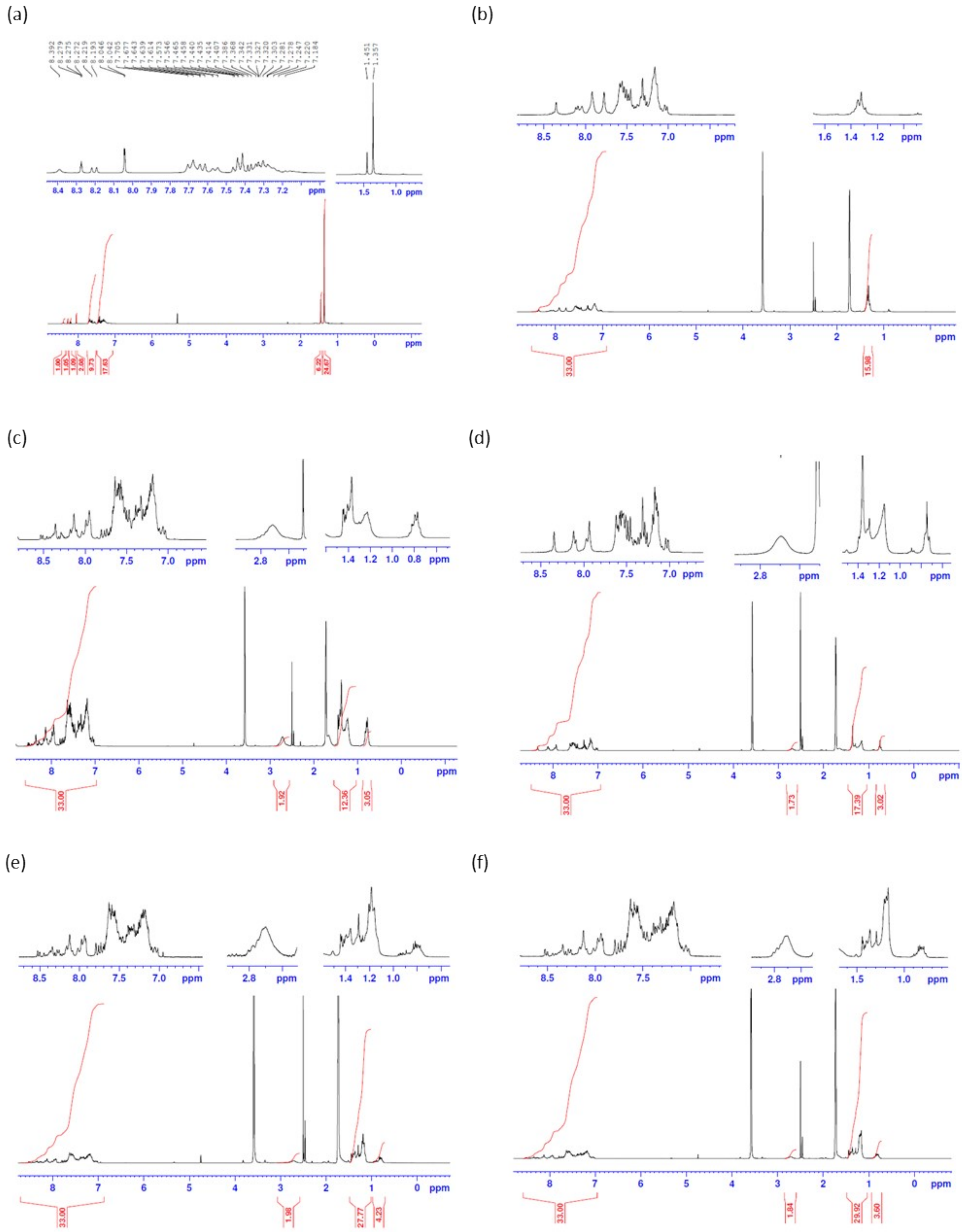

Figure S3 ^{1}H-NMR spectra of (a) monomer, (b) HT-4’, (c) HT-6, (d) HT-8, (e) HT-12, and (f) HT-14

Table S1. Synthesis results of developed HT polymers

Polymer	Dibromo comonomer	Amount (g)	Yield (%)	Molecular weight
HT-4’	1,3-dibromo-5-tert-butyl-benzene	0.40	22	20,000
HT-6	1,3-dibromo-5-hexylbenzene	0.40	22	30,000
HT-8	1,3-dibromo-5-octylbenzebe	0.45	25	38,000
HT-12	1.3-dibromo-5-dodecylbenzene	0.98	54	14,000
HT-14	1,3-dibromo-5-tetradecylbenzene	0.95	53	11,000

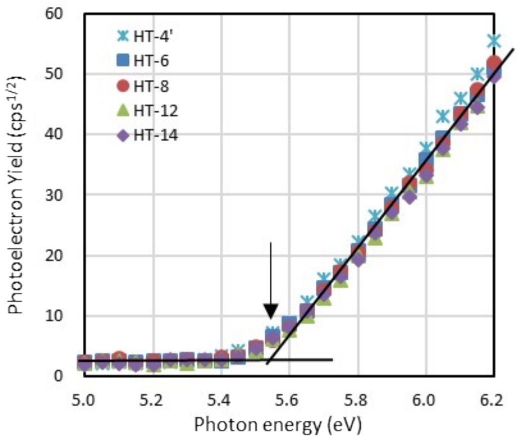

Figure S4 Photoelectron yield spectra of developed HT polymers

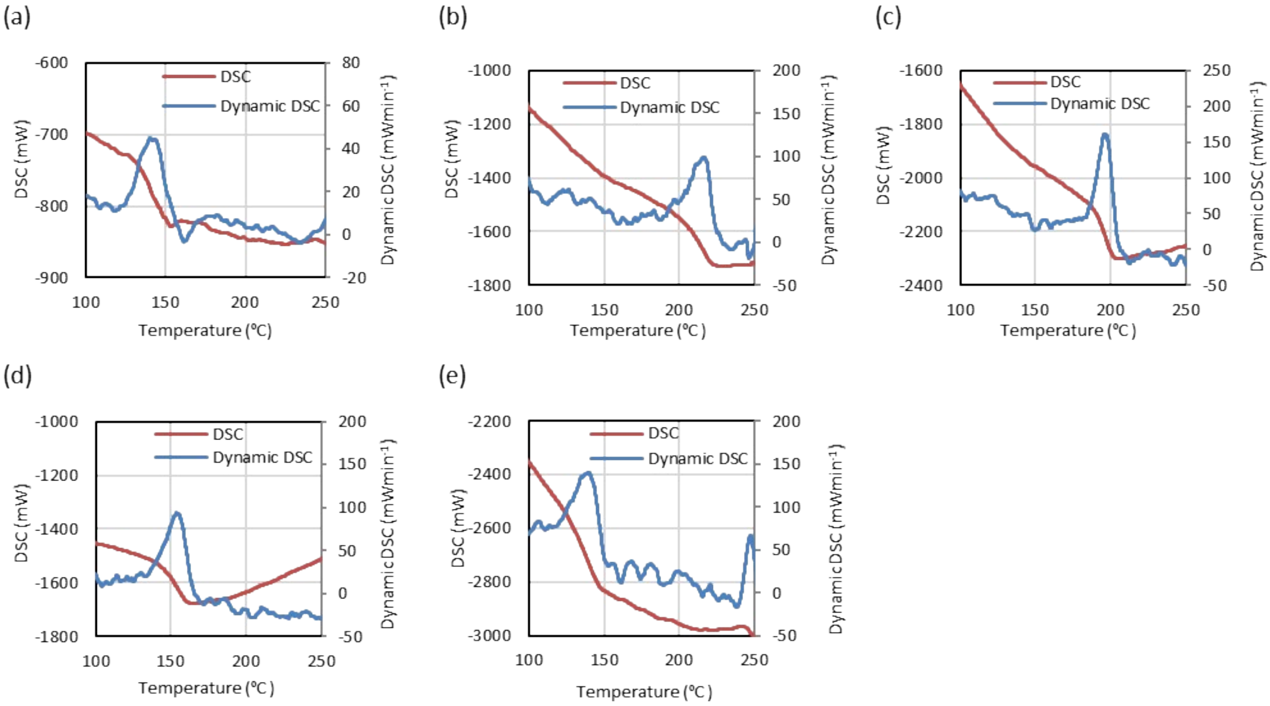

Figure S5 Differential scanning calorimetry (DSC) charts of (a) HT-4’, (b) HT-6, (c) HT-8, (d) HT-12, and (e) HT-14

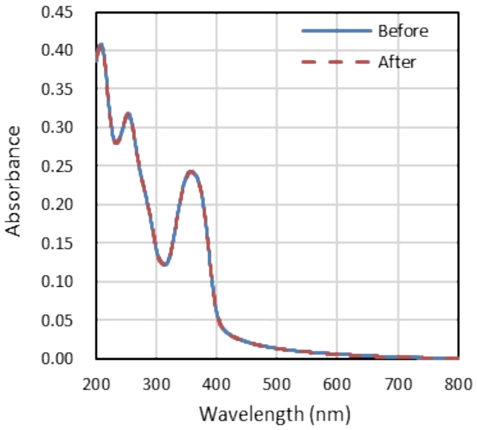

Figure S6 Absorption spectra of HT-14 thin film before and after octane immersion.

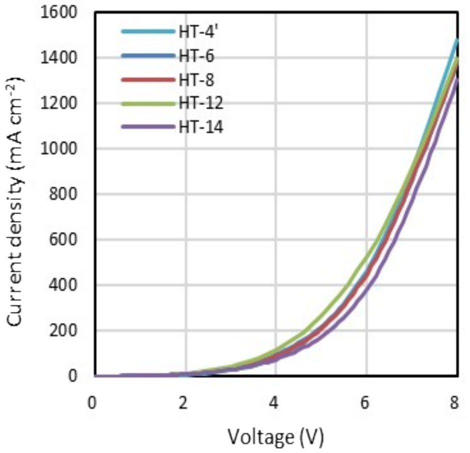

Figure S7 Current density-voltage characteristics of HODs without QDs

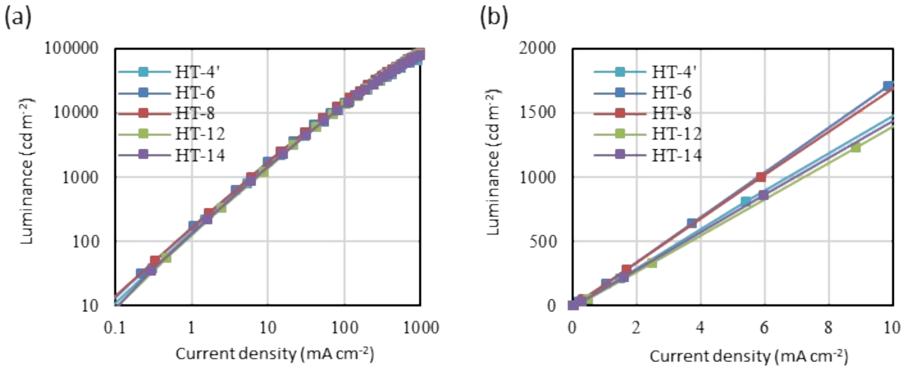

Figure S8 Luminance-current density characteristics of QD-LEDs: (a) whole region by logarithmic scale and (b) around EQE-max region by linear scale.