

## Electronic Supplementary Information

### Optimizing Central Steric Hindrance of Cross-linkable Hole Transport Materials for Achieving Highly Efficient RGB QLEDs

Wenchao Zhao,<sup>†</sup> Liming Xie,<sup>†</sup> Yuan-Qiu-Qiang Yi,<sup>\*</sup> Xiaolian Chen, Jianfeng Hu,<sup>\*</sup> Wenming Su<sup>\*</sup>,  
Zheng Cui

#### EXPERIMENTAL SECTION

##### Materials and Synthesis:

CdSe-ZnS core-shell RGB QDs were provided by Jiaying Nato Optoelectronic Technology Co., Ltd (China). TFB (average molecular weight,  $\sim 25000 \text{ g mol}^{-1}$ ) purchased from Han Feng Chemical Co., Ltd (China).

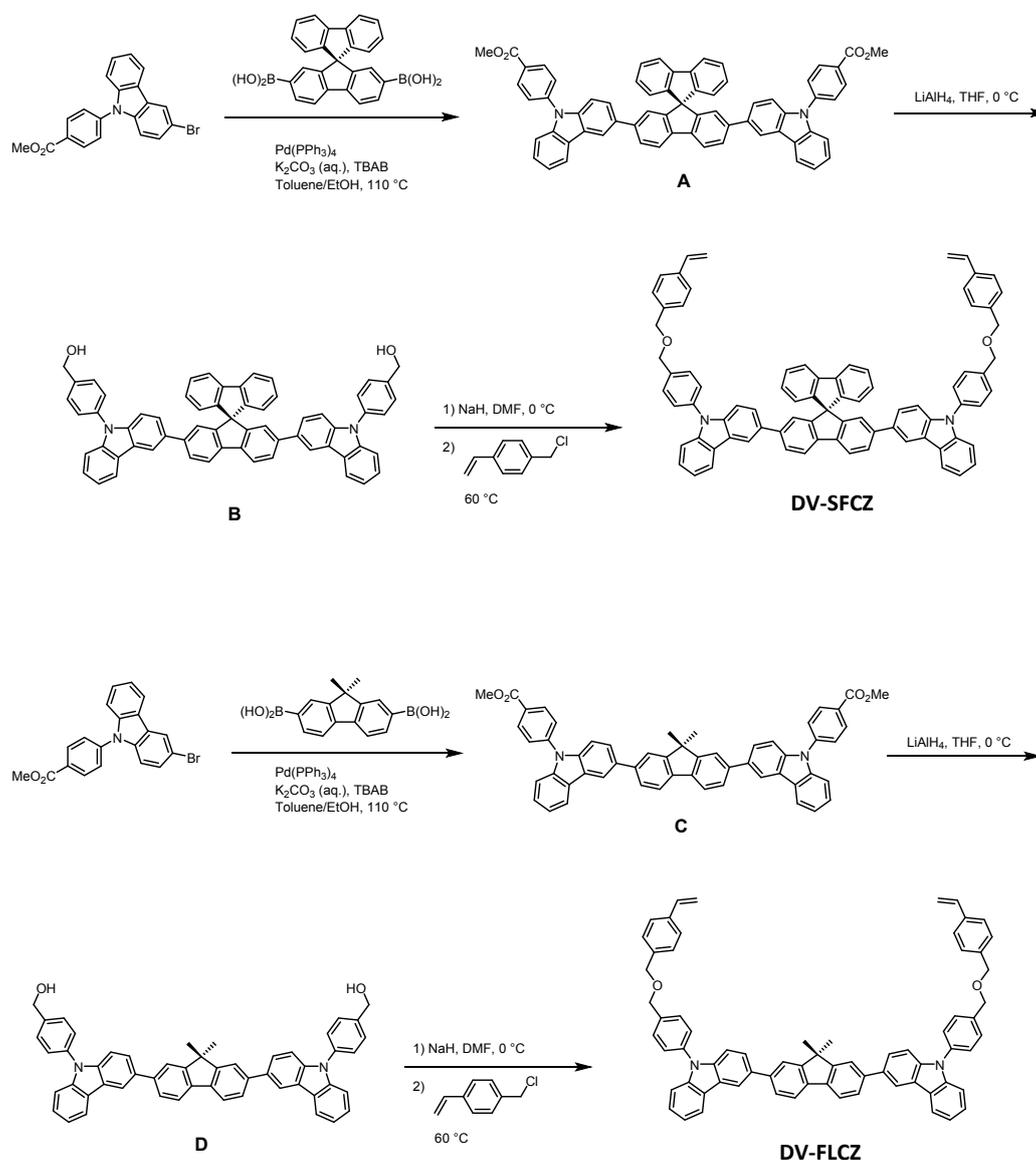


Figure S1. Synthesis routes to DV-SFCZ and DV-FLCZ

**Dimethyl 4,4'-(9,9'-spirobi[fluorene]-2,7-diylbis(9H-carbazole-3,9-diyl)) dibenzoate (A)**

A mixture of methyl 4-(3-bromine-9H-carbazole-9-diyl) methyl benzoate (4.75 g, 12.5 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-spirobifluorene (2.84 g, 5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.40 g, 0.35 mmol), and K<sub>2</sub>CO<sub>3</sub> (2.0 M aqueous solution, 10 mL) were added to a 250 mL three-necked flask. 1,4-dioxane (100 mL) were then added while stirring and heated to 105 °C under nitrogen atmosphere. After heating to reflux for 24 h, the mixture was cooled to room temperature and filtered, then the precipitate was washed with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was washed with water and dried with anhydrous sodium sulfate. After the removal of the solvent by rotary evaporation, the crude product was separated by silica gel column chromatography, and the eluent was CH<sub>2</sub>Cl<sub>2</sub>/n-hexane (1:10 volume ratio). The pure product was obtained 2.49 g with a yield of 54%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28-8.26 (d, 4H), 8.18 (d, 2H), 8.12 (d, 2H), 7.99 (d, 2H), 7.91 (d, 2H), 7.77 (dd, 2H), 7.67-7.64 (d, 4H), 7.52 (dd, 2H), 7.46-7.38 (m, 8H), 7.33-7.27 (m, 2H), 7.16 (td, 2H), 7.07 (d, 2H), 6.92 (d, 2H), 3.98 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.36, 149.87, 148.92, 141.92, 141.87, 141.35, 140.62, 140.25, 139.58, 133.86, 131.50, 131.46, 131.40, 131.34, 128.65, 127.94, 127.09, 126.25, 125.69, 124.39, 124.20, 123.83, 122.74, 120.60, 120.29, 120.06, 118.80, 109.80, 104.99, 66.24, 46.87, 46.85, 46.80, 46.76.

**((9,9'-Spirobi[fluorene]-2,7-diylbis(9H-carbazole-3,9-diyl))bis(4,1-phenylene))dimethanol (B)**

LiAlH<sub>4</sub> (2.4 M THF solution, 2.4 mL) was added to a 100 mL round bottom flask, then anhydrous THF (50 mL) was added while stirring at 0 °C under nitrogen. After stirring for 30 min, a solution of **A** (1.83 g, 2 mmol) in anhydrous THF (40 mL) was added and the mixture was stirred for 7 h at 0 °C under nitrogen. After warming to room temperature, the reaction was quenched with anhydrous methanol and the mixture was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent: ethyl acetate/n-hexane, 1:1) to afford **B** (1.55 g, 90%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (d, 2H), 8.12 (d, 2H), 7.98 (d, 2H), 7.91 (d, 2H), 7.76 (dd, 2H), 7.59 (d, 4H), 7.55-7.47 (m, 6H), 7.43-7.36 (m, 6H), 7.32 (d, 2H), 7.18-7.13 (m, 2H), 7.06 (d, 2H), 6.92 (d, 2H), 5.34 (s, 2H), 4.83 (s, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.82, 148.99, 141.86, 141.52, 141.24, 140.21, 140.05, 136.95, 133.30, 131.31, 131.27, 131.25, 131.20, 128.41, 127.91, 127.06, 126.03, 125.50, 124.40, 123.77, 123.42, 122.75, 120.47, 120.22, 120.01, 118.71, 109.74, 64.86, 46.25.

**2,7-Bis(9-(4-(((4-vinylbenzyl)oxy)methyl)phenyl)-9H-carbazol-3-yl)-9,9'-spirobi[fluorene] (DV-SFCZ)**

NaH was added (dispersion in paraffin, min. 60%, 84 mg, 3.52 mmol) to a solution of **B** (0.76 g, 0.88 mmol) in DMF (40 mL) at room temperature under a flow of N<sub>2</sub>. The reaction mixture was stirred for 3 h and then cooled to 0 °C. 4-vinylbenzyl chloride (min. 90%, 2 mmol) was added dropwise. The reaction mixture was stirred at 60 °C overnight under a nitrogen atmosphere and then quenched with methanol (6 mL) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL). Subsequently, the organic layer was washed with water (3×100 mL). The combined organic layers were dried with MgSO<sub>4</sub> and the solvent removed by rotary evaporation. The crude product was purified by chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>/n-hexane, 20:1) to afford DV-SFCZ (0.56 g, 58%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (d, 2H), 8.11 (d, 2H), 7.97 (d, 2H), 7.90 (d, 2H), 7.76 (dd, 2H), 7.60-7.26 (m, 25H), 7.24-7.22 (m, 1H), 7.15 (td, 3H), 7.06 (d, 2H), 6.96-6.83 (m, 3H), 6.73 (dd, 2H), 5.76 (dd, 2H), 5.25 (dd, 2H), 4.65 (d, 8H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.93, 148.91, 148.85, 147.50, 147.08, 146.93, 141.93, 140.47, 140.35, 140.09, 136.57, 136.25, 135.37, 134.85, 131.09, 131.02, 129.43, 129.34, 128.71, 128.02, 127.90, 127.70, 127.17, 126.80, 126.76, 126.54, 124.65, 124.40, 124.27, 124.10, 123.26, 122.83, 122.34, 120.38, 120.17, 113.75, 66.21, 47.33. TOF-MS (MALDI, m/z) [M]: Calcd. for C<sub>81</sub>H<sub>58</sub>N<sub>2</sub>O<sub>2</sub>: 1090.450.

**Dimethyl 4,4'-(9,9'-spirobi[fluorene]-2,7-diylbis(9H-carbazole-3,9-diyl)) dibenzoate (C)**

A mixture of methyl 4-(3-bromine-9H-carbazole-9-diyl) methyl benzoate (7.12 g, 18.7 mmol), (9,9-dimethyl-9H-

fluorene-2,7-diyl)diboronic acid (2.12 g, 7.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.60 g, 0.53 mmol), and K<sub>2</sub>CO<sub>3</sub> (2.0 M aqueous solution, 15 mL) were added to a 250 mL three-necked flask. 1,4-dioxane (100 mL) were then added while stirring and heated to 105 °C under nitrogen atmosphere. After heating to reflux for 24 h, the mixture was cooled to room temperature and filtered, then the precipitate was washed with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was washed with water and dried with anhydrous sodium sulfate. After the removal of the solvent by rotary evaporation, the crude product was separated by silica gel column chromatography, and the eluent was CH<sub>2</sub>Cl<sub>2</sub>/n-hexane (1:10 volume ratio). The pure product was obtained 4.8 g with a yield of 81%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.43 (d, 2H), 8.33-8.31 (d, 4H), 8.25-8.24 (d, 2H), 7.88-7.86 (d, 2H), 7.80 (d, 2H), 7.77-7.72 (m, 8H), 7.58-7.56 (d, 2H), 7.53-7.45 (m, 4H), 7.38-7.34 (t, 2H), 4.01 (s, 6H), 1.68 (s, 6H).

#### **((9,9'-Spirobi[fluorene]-2,7-diylbis(9H-carbazole-3,9-diyl))bis(4,1-phenylene))dimethanol (D)**

LiAlH<sub>4</sub> (2.4 M THF solution, 3.6 mL) was added to a 100 mL round bottom flask, then THF (50 mL) was added while stirring at 0 °C under nitrogen. After stirring for 30 min, a solution of C (2.37 g, 3 mmol) in anhydrous THF (40 mL) was added and the mixture was stirred for 7 h at 0 °C under nitrogen. After warming to room temperature, the reaction was quenched with anhydrous methanol and the mixture was concentrated in vacuo. The crude material was purified by column chromatography on silica gel (eluent: ethyl acetate/n-hexane, 1:1) to afford D (1.98 g, 90%) as a white solid. <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 8.7 (s, 2H), 8.42-8.40 (d, 2H), 8.03 (s, 2H), 7.98-7.96 (d, 2H), 7.87-7.80 (dd, 4H), 7.67-7.61 (dd, 8H), 7.47-7.45 (d, 4H), 7.41-7.39 (d, 2H), 7.35-7.32 (t, 2H), 5.42-5.39 (t, 2H), 4.68-4.67 (d, 4H), 1.66 (s, 6H).

#### **2,7-Bis(9-(4-(((4-vinylbenzyl)oxy)methyl)phenyl)-9H-carbazol-3-yl)-9,9'-spirobi[fluorene] (DV-FLCZ)**

NaH was added (dispersion in paraffin, min. 60%, 168 mg, 7.04 mmol) to a solution of D (1.29 g, 1.76 mmol) in DMF (60 mL) at room temperature under a flow of N<sub>2</sub>. The reaction mixture was stirred for 3 h and then cooled to 0 °C. 4-vinylbenzyl chloride (min. 90%, 4 mmol) was added dropwise. The reaction mixture was stirred at 60 °C overnight under a nitrogen atmosphere and then quenched with methanol (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL). Subsequently, the organic layer was washed with water (3×100 mL). The combined organic layers were dried with MgSO<sub>4</sub> and the solvent removed by rotary evaporation. The crude product was purified by chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>/n-hexane, 20:1) to afford DV-FLCZ (1.23 g, 72%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.44 (s, 2H), 8.26-8.24 (d, 2H), 7.88-7.85 (d, 2H), 7.81 (s, 2H), 7.74-7.71 (m, 4H), 7.65-7.59 (dd, 8H), 7.51-7.40 (m, 14H), 7.35-7.32 (m, 2H), 6.79-6.72 (dd, 2H), 5.81-5.76 (d, 2H), 5.29-5.26 (d, 2H), 4.69 (s, 8H), 1.68 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.61, 141.36, 141.07, 140.32, 137.67, 137.05, 136.52, 133.98, 129.28, 128.10, 126.37, 125.64, 123.96, 123.54, 121.58, 120.09, 118.84, 113.96, 110.04, 109.95, 72.38, 71.65, 47.14, 27.49. HR-MS (MALDI, m/z) [M]: Calcd. for C<sub>81</sub>H<sub>58</sub>N<sub>2</sub>O<sub>2</sub>: 969.2048.

#### **Fabrication of QLED Devices**

Before use, the ITO glass was washed with glass cleaner, deionized water and absolute ethanol, and treated with oxygen plasma for 3 minutes. In the atmosphere, PEDOT:PSS (Heraeus Clevis, AI 4083, filtered through a 0.45 μm N66 filter) was spin-coated on the ITO glass at 4000 rpm for 50 s. Afterwards, the substrate coated with PEDOT:PSS was transferred to a vacuum glove box under nitrogen atmosphere (O<sub>2</sub> <1 ppm, H<sub>2</sub>O <1 ppm) and dried at 130 °C for 20 minutes. DV-SFCZ (dissolved in chlorobenzene, 5 mg/ml), DV-FLCZ (dissolved in chlorobenzene, 8 mg/ml) as HTM were spin coated at 3000 rpm for 30 s, and all samples were annealed at 130 °C for 15 min to remove residual solvent. After that, DV-SFCZ was cured at 250 °C for 1 h for cross-linking, and DV-FLCZ was cured at 175 °C for 20 min for cross-linking. Red-green-blue QDs (in octane, ≈15 mg mL<sup>-1</sup>) were spin-coated at 3000 rpm for 30 s on substrates with DV-SFCZ and DV-FLCZ as HTL, respectively. All

samples were annealed at 100 °C for 15 minutes.  $Zn_{0.95}Mg_{0.05}O$  NP (dissolved in ethanol solution, 30 mg mL<sup>-1</sup>) was spin-coated at 3000 rpm for 30 s, and the resulted films were annealed at 90 °C for 15 minutes. Finally, the metal electrode Al was deposited using vacuum evaporation equipment (100 nm thickness). The devices were packaged with UV-curable resin and glass sheet.

#### **Characterizations and Device Measurement.**

NETZSCH TG 209 F1 (Germany) was used to perform thermogravimetric analysis by heating the sample from 25 to 700 °C at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. Veeco Dimension 3100 was used to characterize the surface morphology of the film in the tapping mode. Differential scanning calorimetry was performed on a Netzsch DSC F3 Maia (Germany) at a heating rate of 10 °C min<sup>-1</sup> from room temperature to 300 °C under nitrogen atmosphere. An unfiltered HeI (21.22 eV) gas discharge lamp was used to analyze the ultraviolet emission spectrum with the VG Scienta R4000 analyzer, and apply a sample bias of -5 V to observe the secondary electron cutoff (SEC). Alpha Step profiler (Veeco, Dektak150) was used to measure the thickness of the solution-treated film. MODEL: SL150L was used to perform contact angle. Spectra Scan PR655 was used to measure electroluminescence spectra. A computer-controlled Keithley 2400 source was used to characterize current-voltage (IV) and brightness-voltage (LV) relationships and PGSTAT302N electrochemical workstation was used for AC impedance analysis. All devices have a light-emitting area of 2×2 mm<sup>2</sup>.

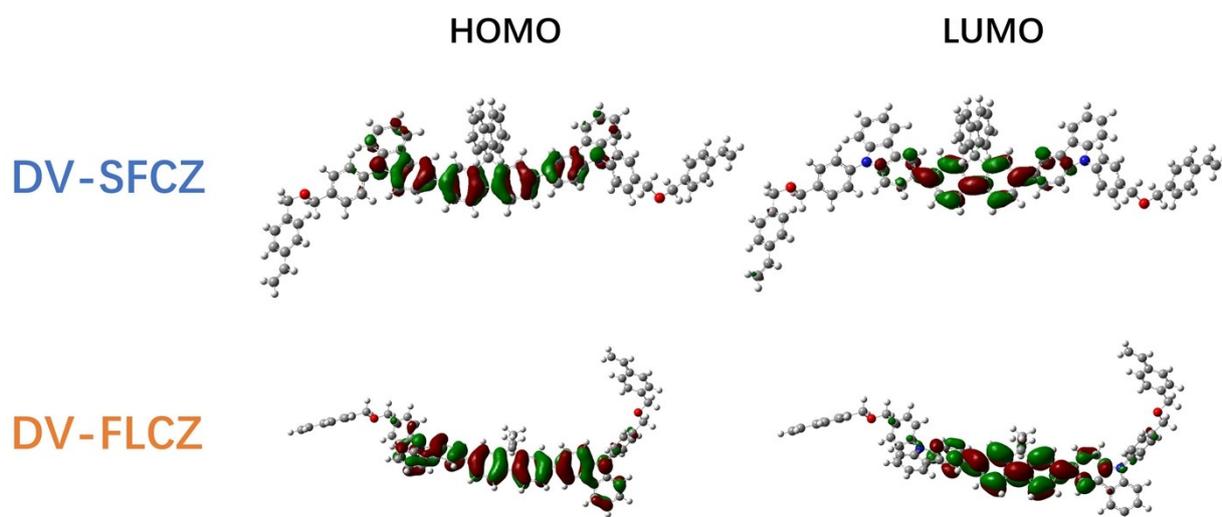


Figure S2. Calculated frontier orbitals and energy levels of the DV-SFCZ and DV-FLCZ

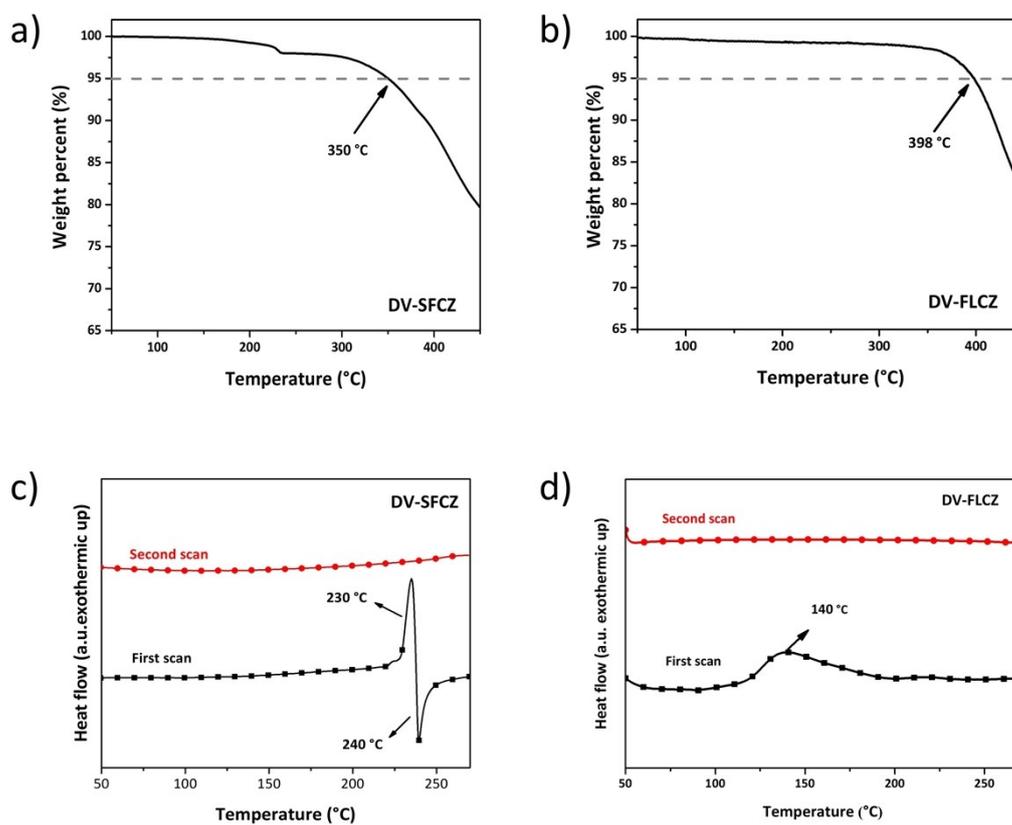
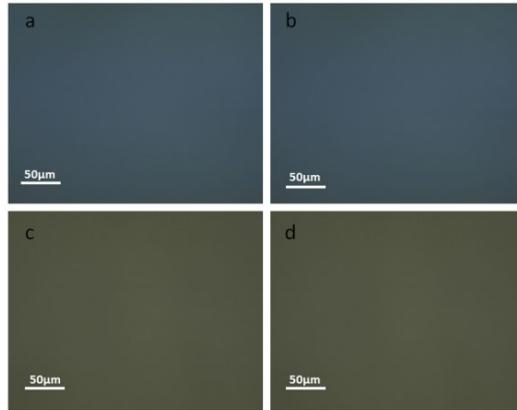
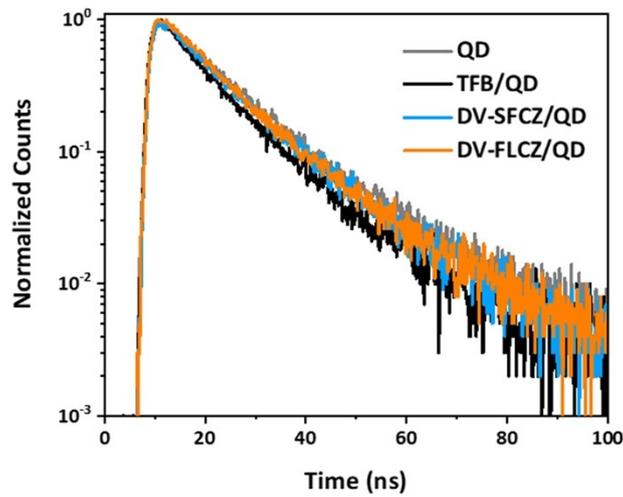


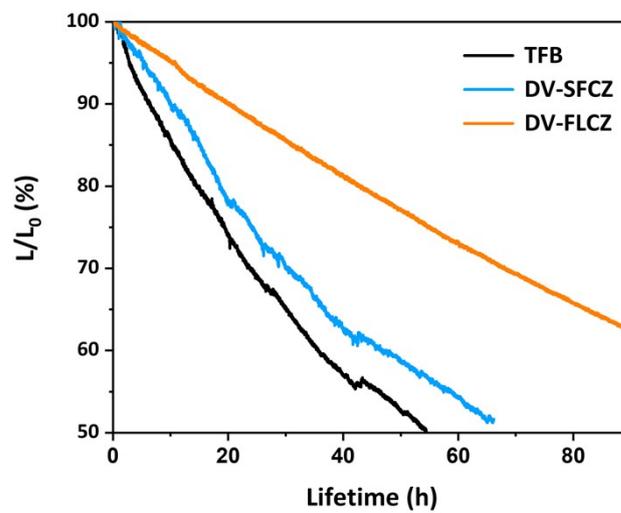
Figure S3. TGA and DSC curves of compounds with a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere



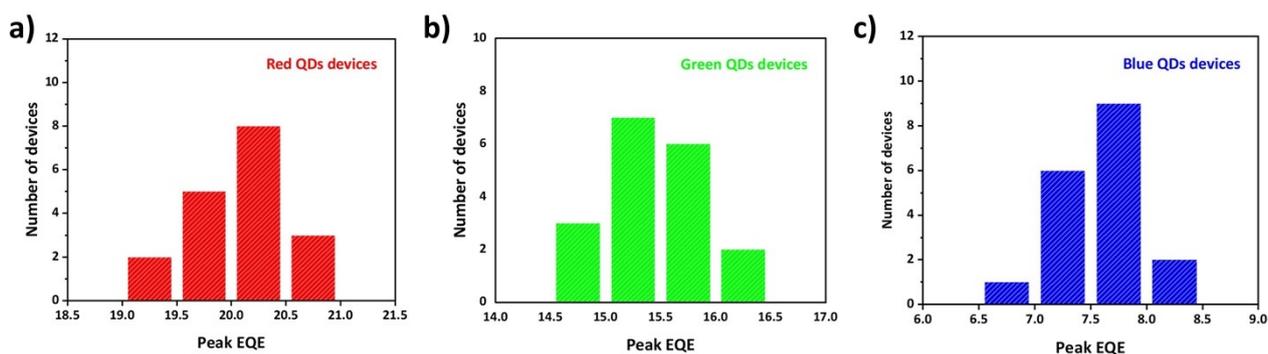
**Figure S4.** Optical microscopic images of a) and b) DV-SFCZ film before and after rinsing with chlorobenzene, c) and d) DV-FLCZ film before and after rinsing with chlorobenzene



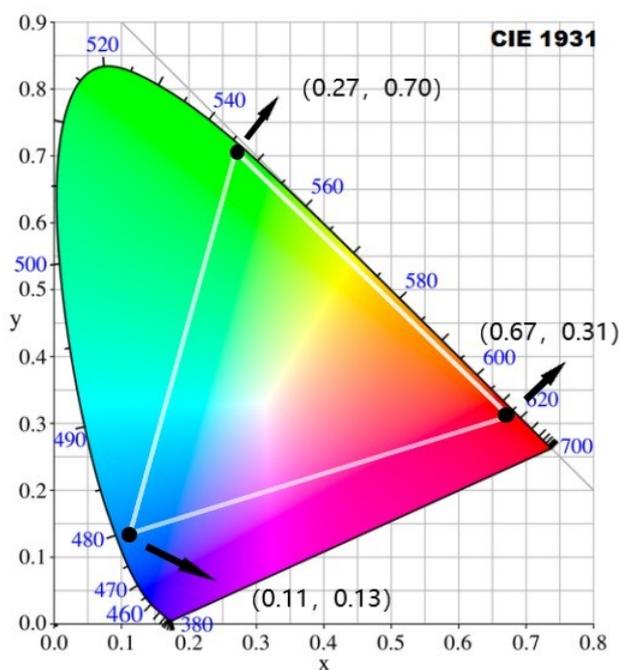
**Figure S5.** TRPL of the QD-only film and QD films on different HTLs



**Figure S6.** Lifetime of the different HTL devices



**Figure S7.** Histograms of peak EQEs from a) 18 red QLEDs, b) 18 green QLEDs and c) 18 blue QLEDs.



**Figure S8.** CIE coordinates of red, green and blue QLEDs.

**Table S1. Thermal and photophysical properties of cross-linked DV-SFCZ and DV-FLCZ**

| Compound | $T_g$ <sup>[a]</sup><br>[°C] | $T_{CL}$ <sup>[a]</sup><br>[°C] | $T_d$ <sup>[b]</sup><br>[°C] | $\lambda_{abs}$ <sup>[c]</sup><br>[nm] | $E_g$ <sup>[d]</sup><br>[eV] | HOMO <sup>[e]</sup><br>[eV] | LUMO <sup>[f]</sup><br>[eV] | HOMO <sup>[g]</sup><br>[eV] | LUMO <sup>[g]</sup><br>[eV] |
|----------|------------------------------|---------------------------------|------------------------------|--|------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| DV-SFCZ  | -                            | 240                             | 350                          | 354                                    | 2.9                          | -5.7                        | -2.8                        | -4.94                       | -1.03                       |
| DV-FLCZ  | -                            | 140                             | 398                          | 354                                    | 2.9                          | -5.7                        | -2.8                        | -4.93                       | -1.03                       |

[a] Obtained from DSC measurement, [b] Obtained from TGA measurement, [c] Measured in thin films by spin-coating from chlorobenzene solution, [d] Calculated from the edge of the UV-vis absorption ( $E_g=1240/\lambda$ ), [e] Calculated from  $21.2-E_k$  from UPS, [f] Calculated from HOMO- $E_g$ , [g] Calculated from DFT.

**Table S2. Fitting parameters for the time-resolved dynamic PL decay process of QD films**

| Structure  | A <sub>1</sub> | τ <sub>1</sub> (ns) | A <sub>2</sub> | τ <sub>2</sub> (ns) | τ <sub>ave</sub> (ns) |
|------------|----------------|---------------------|----------------|---------------------|-----------------------|
| QD         | 0.81           | 11.78               | 0.19           | 34.15               | 20.83                 |
| TFB/QD     | 0.53           | 8.06                | 0.47           | 15.79               | 13.00                 |
| DV-SFCZ/QD | 0.45           | 8.82                | 0.55           | 16.77               | 14.40                 |
| DV-FLCZ/QD | 0.81           | 10.60               | 0.19           | 27.76               | 17.16                 |

The fitting for decay curves is carried out based on a double-exponential function:

$$I = A_1 \cdot \exp[-(\tau_1 - t_0)/t] + A_2 \cdot \exp[-(\tau_2 - t_0)/t] + I_0$$

Where τ<sub>1</sub> and τ<sub>2</sub> represent the decay time constants, and A<sub>1</sub> and A<sub>2</sub> represent the normalized amplitudes of each component; A<sub>1</sub> + A<sub>2</sub> = 1. Therefore, the average lifetime of the decay is calculated by:

$$\tau_{ave} = \frac{A_1 \cdot \tau_1^2 + A_2 \cdot \tau_2^2}{A_1 \cdot \tau_1 + A_2 \cdot \tau_2}$$

**Table S3. Fitting parameters of the Nyquist plots for red QLEDs at 4V**

| HTL     | R <sub>s</sub><br>(Ω/cm <sup>2</sup> ) | R <sub>tr</sub><br>(Ω/cm <sup>2</sup> ) | CPE <sub>1</sub><br>(S·Sec <sup>n</sup> /cm <sup>2</sup> ) | R <sub>rec</sub><br>(Ω/cm <sup>2</sup> ) | CPE <sub>2</sub><br>(S·Sec <sup>n</sup> /cm <sup>2</sup> ) |
|---------|--|---|--|--|--|
| TFB     | 62.36                                  | 301.9                                   | 4.08E-08   | 669.5                                    | 2.21E-08   |
| DV-SFCZ | 61.25                                  | 3316.0                                  | 5.76E-08   | 255.1                                    | 3.51E-08   |
| DV-FLCZ | 69.69                                  | 386.8                                   | 3.04E-08   | 103.2                                    | 1.68E-08   |

**Table S4. Summarized performances of the red QLEDs with different HTLs at different thickness**

| Device | HTL     | V <sub>T</sub><br>[V] | CE <sub>max</sub><br>[cd A <sup>-1</sup> ] | PE <sub>max</sub><br>[lm W <sup>-1</sup> ] | EQE <sub>max</sub><br>[%] | ELλ <sub>max</sub><br>[nm] | FWHM<br>[nm] | CIE(x,y)    |
|--------|---------|-----------------------|--|--|---------------------------|----------------------------|--------------|-------------|
| Green  | TFB     | 2.4                   | 49.0                                       | 43.1                                       | 10.6                      | 540                        | 28           | (0.27,0.70) |
|        | DV-SFCZ | 3.1                   | 56.4                                       | 44.6                                       | 12.2                      | 540                        | 28           | (0.27,0.70) |
|        | DV-FLCZ | 2.1                   | 76.8                                       | 78.0                                       | 16.6                      | 540                        | 28           | (0.27,0.70) |
| Blue   | TFB     | 3.0                   | 4.6  | 3.8  | 5.1                       | 475                        | 27           | (0.11,0.13) |
|        | DV-SFCZ | 3.2                   | 5.4  | 4.0  | 5.8                       | 475                        | 27           | (0.11,0.13) |
|        | DV-FLCZ | 2.8                   | 7.9  | 7.3  | 8.5                       | 475                        | 27           | (0.11,0.13) |

**Table S5. Summary of the energy levels of RGB QDs**

| Energy level         | Red  | Green | Blue |
|----------------------|------|-------|------|
| Valence band (eV)    | -6.5 | -6.7  | -7.0 |
| Conduction band (eV) | -3.6 | -3.7  | -3.4 |