

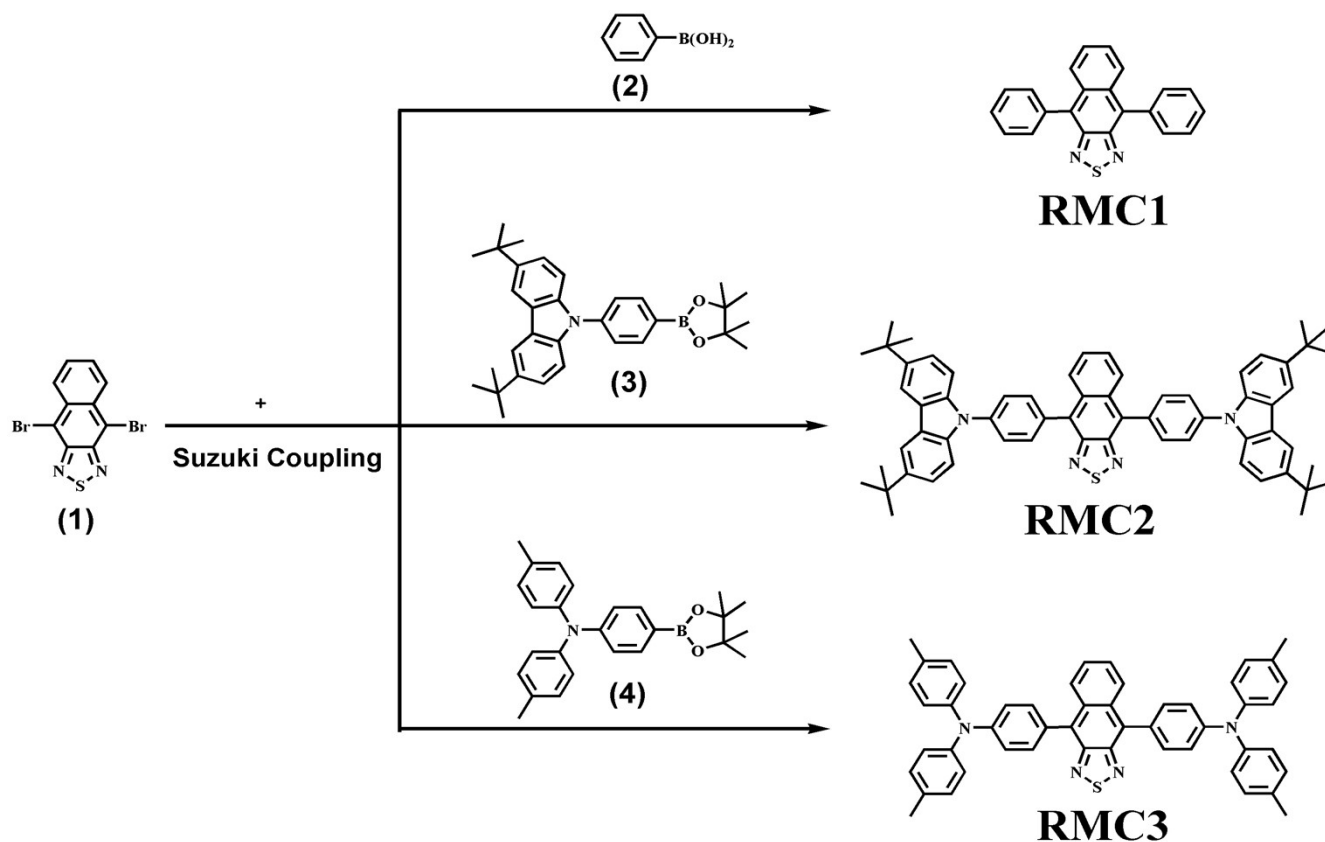
## SUPPORTING INFORMATION

### **Purely Organic and Saturated Red Emitter for Non-doped Electroluminescent Device with An EQE of 6.3% and Low Efficiency Roll-off**

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## 1. Synthesis of three red model compounds (RMCs):

RMC1, RMC2 and RMC3 were synthesized from 4,9-dibromo-naphthothiadiazole (1) with phenylboronic acid (2), 3,6-di-tert-butyl-9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (3) and 4-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl)-di-*p*-tolyl-amine (4) through classic Suzuki coupling reaction. Intermediate (1), (3) and (4) was synthesized as literature from raw material of 2,3-diaminonaphthalene, 3,6-di-tert-butyl-9H-carbazole and Di-*p*-tolyl-amine, respectively.<sup>[S1-S3]</sup> Phenylboronic acid (2) and all the other reagents were purchased from Sigma-Aldrich and used directly without any further purification.



**Scheme S1.** Synthetic routes of the RMCs.

### **4,9-diphenyl-2,1,3-naphthothiadiazole (RMC1)**

A mixture of 4,9-dibromo-2,1,3-naphthothiadiazole (1) (0.43 g, 1.0 mmol), phenylboronic acid (2) (0.37 g, 3.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.06 g, 0.05 mmol), toluene (30 mL), 2 mol L<sup>-1</sup> K<sub>2</sub>CO<sub>3</sub> (10 mL), Aliquat 336 (3 drops) was heated to 100 °C and stirred in the dark for 12 hours. After workup, the mixture was poured to 150 mL dichloromethane, washed with brine three times and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The residue was purified by column chromatography (elute: petrol ether/dichloromethane 5/1) and

then recrystallized from mixed petrol ether/dichloromethane solvent to afford a needle-like red crystal. Yield: 0.27 g (71.2%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.00 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 9.6$  Hz, 2H), 7.69~7.61 (m, 8H), 7.59~7.53 (m, 2H), 7.35 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 9.6$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 151.4, 136.6, 131.9, 131.2, 128.5, 128.3, 127.1, 126.4. Anal. Calcd. for  $\text{C}_{22}\text{H}_{14}\text{N}_2\text{S}$ : C, 78.08; H, 4.17; N, 8.28; Found: C, 79.86; H, 4.26; N, 8.57; MALDI-TOF-MS ( $m/z$ ): 337.8 [ $\text{M}^+$ ].

#### ***4,9-Bis(4-(3,6-di-tertbutyl-carbazol-9-yl)phenyl)-2,1,3-naphthothiadiazole (RMC2)***

RMC2 was synthesized following the same procedure for RMC1 using 3,6-di-tert-butyl-9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (3) instead of phenylboronic acid. The residue was purified by column chromatography (elute: petrol ether/dichloromethane 3/1) and then precipitated from mixed petrol ether/dichloromethane solvent for three times to give an orange-red solid. Yield: 1.14 g (64.0%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.21~8.18 (m, 6H), 7.94 (d,  $J = 12$  Hz, 4H), 7.88 (d,  $J = 12$  Hz, 4H), 7.64 (d,  $J = 12$  Hz, 4H), 7.55 (d,  $J = 2.8$  Hz, 2H), 7.52 (d,  $J = 2.8$  Hz, 2H), 7.49 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 9.6$  Hz, 2H), 1.51 (s, 36H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 151.5, 143.2, 139.1, 138.4, 134.8, 132.8, 132.2, 129.7, 127.1, 126.8, 126.4, 123.7, 116.3, 109.5, 34.8, 31.1. Anal. Calcd. for  $\text{C}_{62}\text{H}_{60}\text{N}_4\text{S}$ : C, 83.37; H, 6.77; N, 6.27; Found: C, 83.71; H, 6.42; N, 6.56; MALDI-TOF-MS ( $m/z$ ): 891.9 [ $\text{M}^+$ ].

#### ***4,9-Bis(4-(N,N-di(4-methylphenyl)amino)phenyl)-2,1,3-naphthothiadiazole (RMC3)***

RMC3 was synthesized following the same procedure for RMC1 using 4-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl)-di-p-tolyl-amine (4) instead of phenylboronic acid. The residue was purified by column chromatography (elute: petrol ether/dichloromethane 2/1) and then recrystallized from mixed petrol ether/dichloromethane solvent to obtain a purple solid. Yield: 0.59 g (80.9%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.13 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 9.6$  Hz, 2H), 7.49 (d,  $J = 12$  Hz, 4H), 7.35 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 9.6$  Hz, 2H), 7.22 (d,  $J = 12$  Hz, 4H), 7.17 (d,  $J = 12$  Hz, 8H), 7.13 (d,  $J_1 = 12$  Hz, 8H), 2.34 (s, 12H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 151.6, 148.1, 145.0, 133.1, 132.2, 132.0, 130.0, 129.8, 126.0, 125.4, 120.9, 20.9. Anal. Calcd. for  $\text{C}_{50}\text{H}_{40}\text{N}_4\text{S}$ : C, 82.38; H, 5.53; N, 7.69; Found: C, 82.23; H, 5.72; N, 7.35; MALDI-TOF-MS ( $m/z$ ): 727.4 [ $\text{M}^+$ ].

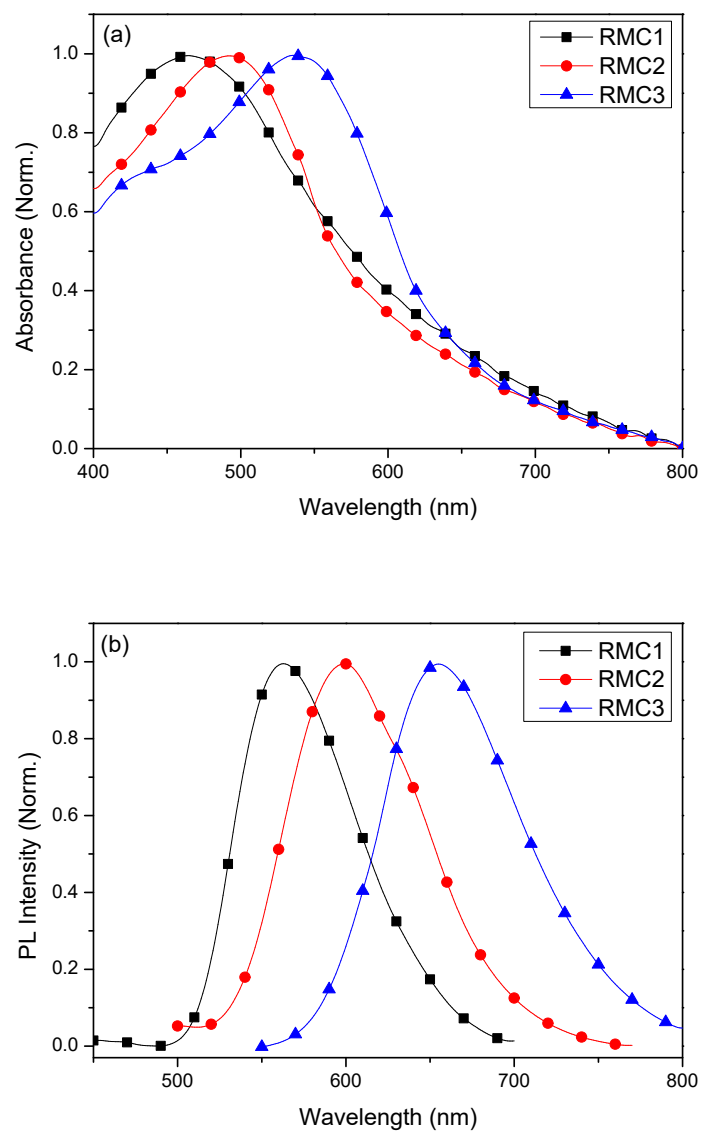
## **2. Measurement and instruments**

$^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were collected on a Bruker DRX spectrometer operating at 400 MHz using chloroform as solvent with tetramethylsilane (TMS) as reference. The

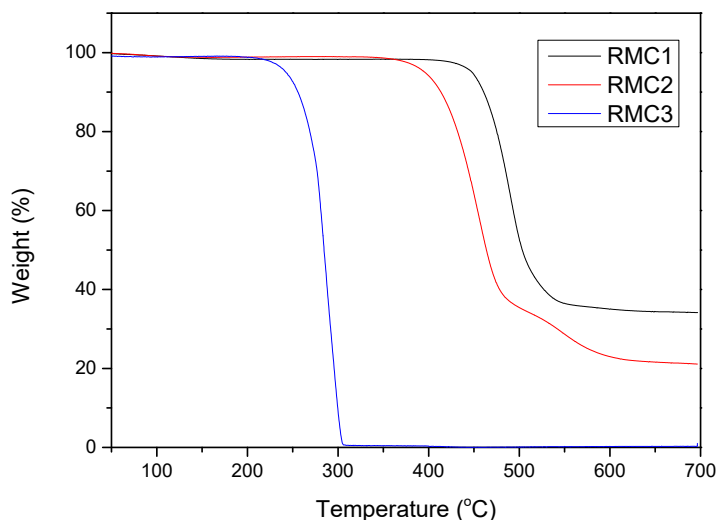
elemental analysis was performed on a Vario EL III CHNS Elemental Analyser (EA). Molecular weight was acquired using an AXIMA Performance Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MOLDI-TOF-MS). UV-visible absorption spectra and emission spectra were recorded on Shimadzu UV-2501 PC UV-Vis Spectrophotometer and Shimadzu RF 5301 spectrofluorometer, respectively. The relative fluorescent quantum yields of RMCs in diluted toluene solution were calculated using the equation of  $\Phi_u = \Phi_s(A_s S_u n_u^2 / A_u S_s n_s^2)$ .<sup>[54]</sup> The standard reference is Nile Red in 1,4-dioxane(0.68) for RMC1 and RMC2, and Nile Red in CH<sub>3</sub>CN (0.78) for RMC3.<sup>[55]</sup> The absolute fluorescent quantum yields of the neat films of RMCs were determined by an integrating sphere using 409 nm excitation of a He-Cd laser. Cyclic voltammetry was carried out on a CHI660A electrochemical workstation at a scan rate of 100 mV s<sup>-1</sup> in a nitrogen-saturated solution of 0.1 M Tetrabutylammonium perchlorate ((C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NClO<sub>4</sub>) in anhydrous methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>), using a glassy carbon electrode as working electrode, a Pt wire as counter electrode, and an Ag/AgCl electrode as reference electrode. Differential scanning calorimetry (DSC) was recorded by TA Instrument of DSC-Q10 under nitrogen with a heating rate of 10 °C min<sup>-1</sup>, the data shown in Figure 2d is the second-round heating curve. Thermal gravimetric analysis (TGA) was carried out on a TA Instrument of TGA-2950 at a heating rate of 10 °C min<sup>-1</sup>.

### 3. Device fabrication and characterizations

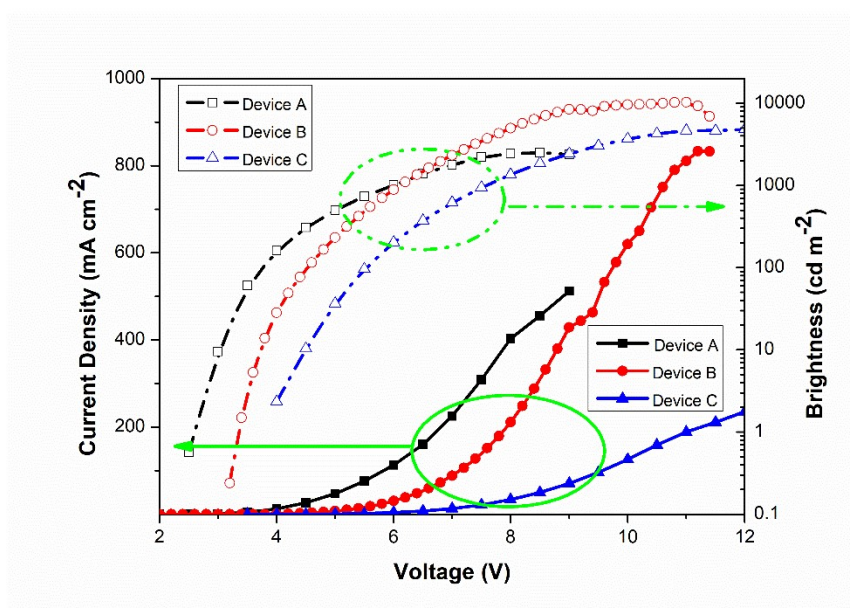
Patterned ITO-coated glass (sheet resistance 10 Ω per square) was cleaned sequentially with detergent, de-ionized water, acetone and isopropanol, each for 20 min in an ultrasonic bath. Then the ITO substrates were treated by O<sub>2</sub> plasma for 10 min. Subsequently, the substrates were transferred into a thermal evaporator, where the organic, inorganic and metal functional layers were grown layer by layer at a base pressure lower than 4×10<sup>-4</sup> Pa. For organic semiconductors, MoO<sub>3</sub> and LiF, the typical evaporation rates were about 0.1 nm s<sup>-1</sup>. For aluminium electrode, the evaporation rate was about 0.5~1.0 nm s<sup>-1</sup>. The active area of the device is 3 mm × 3 mm. *J-V* and *L-V* data were collected using a source meter (Yokogawa GS610) and a luminance meter (Konica Minolta LS-110) with a customized Labview program. Electroluminescent spectra were recorded with a spectrometer (Photo Research PR705).



**Figure S1.** The absorption (a) and PL spectra of RMCs doped in PS film.



**Figure S2.** The TGA curves of RMC1, RMC2 and RMC3.



**Figure S3.** The Voltage- Current density- Brightness curves of neat RMC2-based devices.

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