Supporting Information

for

D–A–D-type orange-light emitting thermally activated delayed fluorescence (TADF) materials based on a fluorenone unit: simulation, photoluminescence and electroluminescence studies

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Experimental and additional information

Contents

Materials: Solvents and reagents were purchased from commercial sources and used as received. Raw materials of 2,7-dibromo-9-fluorenone, 3,6-dibromo-9-fluorenone and 9,9-dimethyl-9,10-dihydroacridine were synthesized according to literature procedures [1,2]. 27DACRFT (**1**) and 36DACRFT (**2**) were further purified by recrystallization and repeated temperature gradient vacuum sublimation.

Synthesis of 27DACRFT (1): 2,7-Dibromo-9-fluorenone (0.676 g, 2 mmol), 9,9-dimethyl-9,10-dihydroacridine (1.046 g, 5 mmol), sodium *tert*-butoxide (0.48 g, 5 mmol) and palladium acetate (45 mg, 0.2 mmol) were dissolved in toluene (180 mL) and stirred under an argon (Ar) flow in a 250 mL three-necked flask for 30 minutes. Then, tris(1,1-dimethylethyl)phosphine (1.0 M solution in toluene, 0.4 mL) was dropped into the mixture, followed by heating under reflux for 72 hours. The formed precipitate was extracted with dichloromethane (DCM) and washed with deionized water after cooling to room temperature. The organic layer was separated and further purified by chromatography on silica gel to afford the title compound as orange powder (0.7 g, 58%) after evaporation of the solvent. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.96 (d, *J* = 7.8 Hz, 1H), 7.46 (dd, *J* = 7.8, 1.6 Hz, 3H), 7.35 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.00 (dddd, *J* = 16.3, 14.9, 7.3, 1.5 Hz, 4H), 6.48 (dd, *J* = 8.1, 1.3 Hz, 2H), 1.66 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 191.52 (s), 148.06 (s), 146.52 (s), 140.18 (s), 133.31 (s), 131.37 (s), 126.74 (s), 126.49 (s), 125.41 (s), 122.56 (s), 121.49 (s), 114.85 (s), 36.16 (s), 30.94 (s). EI-MS (electron ionization mass spectrometry, m/z): calcd for C$_{43}$H$_{34}$N$_2$O 594.76; found 595.7 [M +].

Synthesis of 36DACRFT (2): 36DACRFT (**2**) was synthesized in a similar way as described for 27DACRFT (**1**) starting from 3,6-dibromo-9-fluorenone instead of 2,7-dibromo-9-fluorenone (0.676 g, 2 mmol). The precipitate was extracted with dichloromethane (DCM) and washed with deionized water after cooling to room temperature. The organic layer was separated and further purified by chromatography on silica gel to afford the title compound as orange powder (0.6 g, 50%) after evaporation of the solvent. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.46 (dd, *J* = 7.7, 1.6 Hz, 3H), 7.35 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.99 (dtd, *J* = 25.2, 7.3, 1.4 Hz, 4H), 6.48 (dd, *J* = 8.1, 1.3 Hz, 2H), 1.66 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 148.06 (s), 146.52 (s), 140.18 (s), 133.31 (s), 131.37 (s), 126.73 (s), 126.49 (s), 125.41 (s), 122.56 (s), 121.49 (s), 114.85

(s), 36.16 (s), 30.94 (s). EI-MS (electron ionization mass spectrometry, m/z): calcd for $C_{43}H_{34}N_2O$ 594.76; found 595.6 [M +].
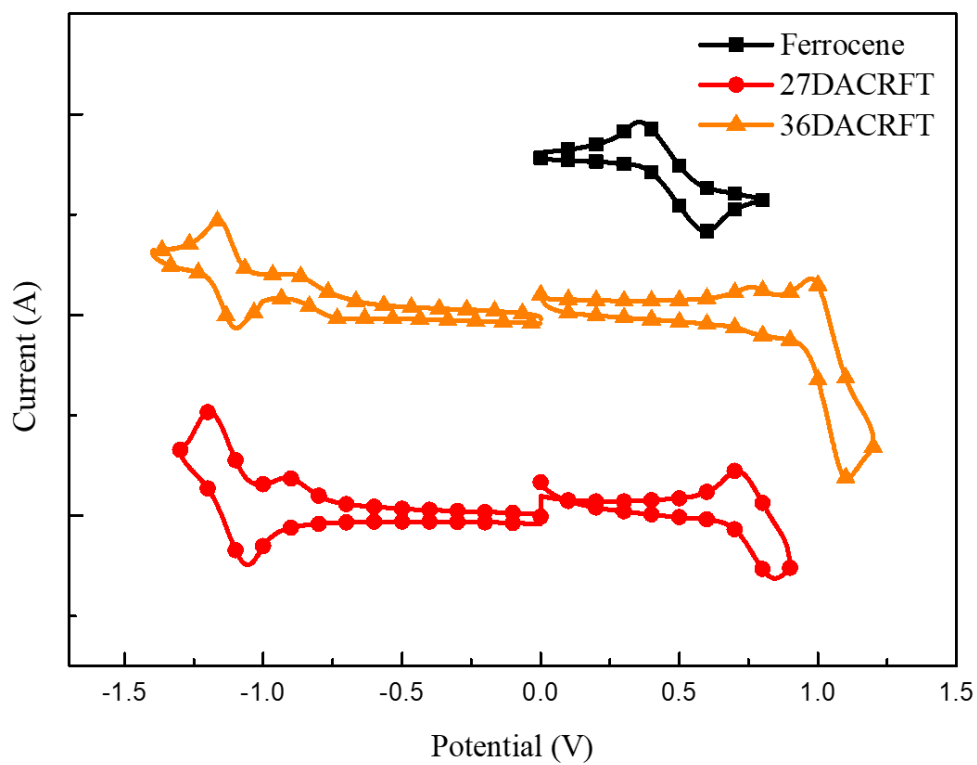

Figure S1: Cyclic voltammetry curves of 27DACRFT (**1**), 36DACRFT (**2**) and ferrocene. The oxidation potential (E_{ox}) and reduction potential (E_{red}) were determined from the onset of the oxidation and reduction curves.
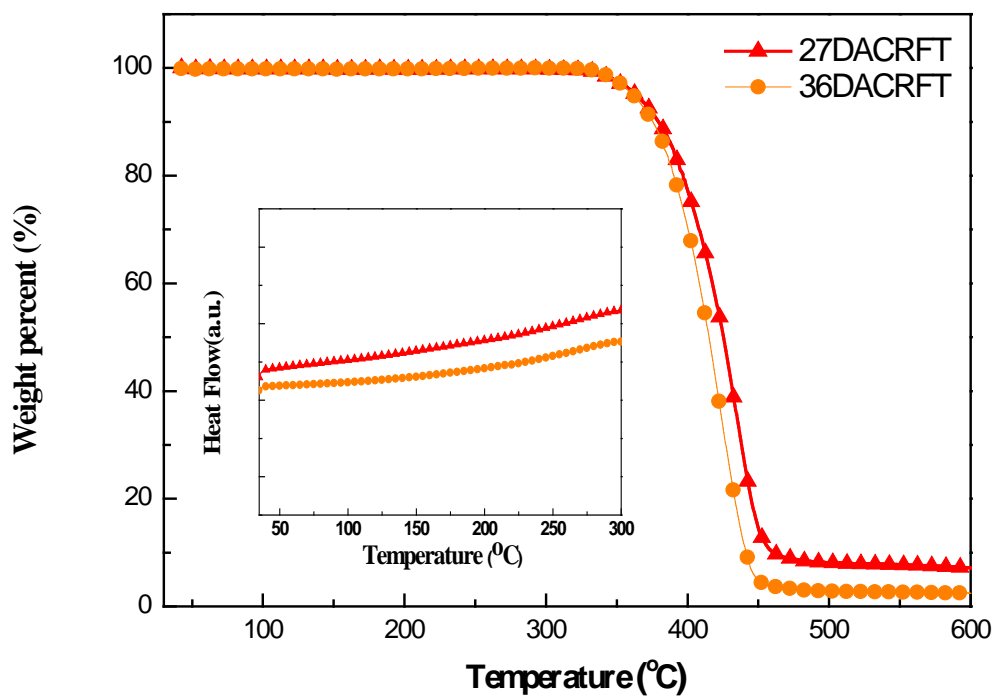
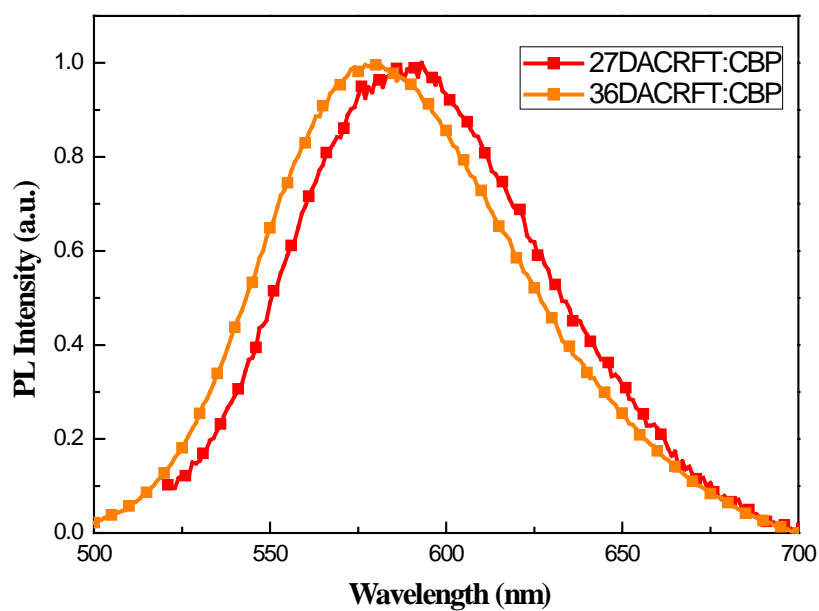**Figure S2:** TGA and DSC (inset) curves of 27DACRFT (**1**) and 36DACRFT (**2**).

Figure S3. Normalized PL spectra of the doped films of 27DACRFT:CBP and 36DACRFT:CBP in a concentration of 6wt%.

References

1. Zhang, Q., Li, B., Huang, S., Nomura, H., Tanaka, H., and Adachi, C., Nat. Photon., 2014. **8**: 326-332.

2. Wu, Z., Xiong, Y., Zou, J., Wang, L., Liu, J., Chen, Q., Yang, W., Peng, J., and Cao, Y., Adv. Mater., 2008. **20**: 2359-2364.