The Roles of Thermally Activated Delayed Fluorescence Sensitizers for Efficient Red Fluorescent Organic Light-Emitting Diodes with D-A-A Type Emitters

Ya-Kun Wang 1, Chen-Chao Huang 1, Sarvendra Kumar 1, Shen-Fan Wu 1, Yi Yuan 1, Aziz Khan 1, Zuo-Quan Jiang 1* Man-Keung Fung 12 and Liang-Sheng Liao 12*

1Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University
Suzhou 215123, P.R. China

2Institute of Organic Optoelectronics (IOO), JITRI, Wujiang, Suzhou, Jiangsu 215211, P. R. China

E-mail: zqjiang@suda.edu.cn; lsliao@suda.edu.cn.
(Tel) 86-512-65880951/(Fax) 86-512-65882846
Table of Contents

Scheme S1. Synthetic routes of OTPA-BT-CN and POZ-BT-CN.

Figure S1. TGA and DSC (inset figure) curve of OTPA-BT-CN and POZ-BT-CN.

Figure S2. Cyclic voltammetry curves of OTPA-BT-CN and POZ-BT-CN recorded in DCM at room temperature.

Figure S3. Energy level diagram of small molecules in the NIR OLED device.

Figure S4. PL spectra of OTPA-BT-CN and POZ-BT-CN in a film state.

Figure S5. Current Efficiency-Luminance of different concentration of 4CzIPN the sensitizer (a) and corresponding EL spectra (b) with 2.0 wt% OTPA-BT-CN as the NIR emitter.

Figure S6. Transient PL spectra of 4CzIPN (left) and OSTFB (right) doped in mCP host (25 wt%).

Figure S7. CE-Luminescence, J-Voltage-Luminescence and EL spectra of POZ-BT-CN with OSTFB as the sensitizer.

X-Ray crystal structure analysis for OTPA-BT-CN and POZ-BT-CN.

Table S1. Device performances with OSTFB as the sensitizer and POZ-BT-CN as the emitter.
Synthesis

Scheme S1. Synthetic routes of OTPA-BT-CN and POZ-BT-CN

1. Synthesis of 3-bromo-10-phenyl-10H-phenoxazine (b)

A solution of N-bromosuccinimide (NBS) (1.68 g, 10.0 mmol) in DMF (30 mL) was added dropwise to a stirred suspension of a (2.59 g, 10.0 mmol) in DMF (50 mL) at 0 °C and then stirred for 1 h. After that, the reaction solution stirred another 1 h at room temperature. The product (b) was extracted with DCM and further purified by column chromatography through silica gel and utilizing petroleum ether/ dichloromethane (2/8, v/v) as eluent to afford white solids (3.21 g, 95%). ¹H NMR (600 MHz, CHCl₃) δ 7.65 (t, J = 6.0 Hz, 2H), 7.54 (t, J = 6.0 Hz, 1H), 7.40 (d, J = 6.0 Hz, 2H), 6.88 (d, J = 12.0 Hz, 1H), 6.80 (d, J = 12.0 Hz, 1H), 6.75–6.51 (m, 3H), 5.82 (d, J = 6.0 Hz, 1H), 5.75 (d, J = 6.0 Hz, 1H). MS (EI) m/z:338.2[M⁺]. Anal.calcd for C₁₈H₁₂BrNO (%): C 63.93, H 3.58, N 4.14 found: C 63.91, H 3.60, N 4.12.
2. Synthesis of 10-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazine (c)

Compound b (3.38 g, 10 mmol) was dissolved in 100 mL THF in a 200 mL Schlenk tube under argon. After the solution was cooled to -78 °C, n-butyl lithium (4.76 mL, 11 mmol) was added dropwise via a syringe. The resulting mixture was allowed to stir for 1 hour at -78 oC, and then 2-Methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.60 g, 10 mmol) was added slowly over a period of 15 min. After 2 hour reaction at -78 °C, the mixture was gradually allowed to warm up to room temperature overnight. 5 mL water was added to the mixture and THF was evaporated under reduced pressure. The resulting solid was dissolved in 100 mL dichloromethane and washed with water (3 × 50 mL). Then the organic layer was separated, dried over sodium sulfate, filtered and evaporated and further purified by column chromatography through silica gel with eluents of petroleum ether/ dichloromethane (4/6, v/v) to afford white product (c) (3.54 g, 92%) 1H NMR (600 MHz, CHCl₃) δ =7.52 (t, J = 6.0 Hz, 2H), 7.41 (t, J = 6.0 Hz, 1H), 7.25 (d, J = 6.0 Hz, 2H), 7.12 (s, J = 6.0 Hz, 1H), 7.05(d, J = 6.0 Hz, 1H), 7.01 (d, J = 6.0 Hz, 1H), 6.86 (t, J = 6.0 Hz, 1H), 6.80 (d, J = 6.0 Hz, 1H), 6.01 (d, J = 6.0 Hz, 2H), 1.31 (s, 12H). MS (EI) m/z: 385.2[M⁺]. Anal.calcd for C24H24BNO3: C 74.82, H 6.28, N 3.64, found: C 74.80, H 6.30, N 3.63.

3. Synthesis of 7-(4-(bis(4-methoxyphenyl)amino)phenyl)benzo[c][1,2,5]thiadiazole-4-carbaldehyde (4)

Compound 1 (4.31 g, 10 mmol), compound 3 (2.43 g, 10 mmol), K₂CO₃ (3.45 g, 25 mmol) and Pd(PPh₃)₄ (0.01 g) were dissolved in 200 mL solvents (water:dioxane 1:10) in a 500 mL round-bottom flask under argon. The resulting mixture was allowed to stir at 86 °C for 24 hours. After that, the mixture was gradually cooled to room temperature and then 300 mL ice water was added to the mixture. The organic layer was separated, dried over sodium sulfate, filtered and evaporated. The solid then dissolved in dichloromethane and were made into sol-
gel and was purified by column chromatography through silica gel using petroleum ether/dichloromethane (3/7, v/v) as eluent to afford final product. The final product (4) was a deep-red color powder (4.25 g, 91.1%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ ( ppm ): $\delta$ 10.72 (s, 1H), 8.25 (d, J = 6.0 Hz, 1H) 7.89 (d, J = 6.0 Hz, 2H) 7.81(d, J = 6.0 Hz, 1H), 7.15 (d, J = 6.0 Hz, 4H) 7.03 (d, J = 6.0 Hz, 2H), 6.88(d, J = 6.0 Hz, 4H) 3.81 (s, 6H). MS (EI) m/z: 467.1[M$^+$. Anal.calcd for C$_{27}$H$_{21}$N$_3$O$_3$S(%):C 69.36, H 4.53, N 8.99; found: C 69.33, H 4.59, N 8.97.

4. Synthesis of 7-(4-(bis(4-methoxyphenyl)amino)phenyl)benzo[c][1,2,5]thiadiazole-4-carbonitrile (6)

Compound 4 (2.3 g, 5.0 mmol) and hydroxylamine hydrochloride (NH$_2$OH-HCl) (0.7g, 10.0 mmol) were dissolved in 50 ml DMSO in a 100 mL Schlenk tube under argon. The resulting mixture was allowed to stir at 100 °C for 4 hours. After that, the mixture was gradually cooled to room temperature and poured to 200 ml ice water. Then the mixture was filtered and the deep-red crude product was dissolved in dichloromethane. The organic layer was separated, dried over sodium sulfate, filtered and evaporated. Crude product was purified by column chromatography through silica gel using petroleum ether/dichloromethane (6/4 v/v) as eluent to afford final product. The final product  (6) was a bright and deep-red color powder (2.05 g, 88.3%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ ( ppm ): $^1$H NMR (600 MHz, cdc$_{13}$) $\delta$ 8.05 (d, J = 12 Hz, 1H), 7.85 (d, J = 12 Hz, 2H), 7.68 (d, J = 6 Hz, 1H) 7.15 (d, J = 12 Hz, 4H), 7.02 (d, J = 12 Hz, 2H), 6.88 (d, J = 12 Hz, 4H), 3.81 (s, 6H). $^{13}$C NMR (600 MHz, CDCl$_3$) $\delta$ ( ppm ): $\delta$ 156.65, 154.01, 152.80, 150.31, 139.76, 139.43, 136.13, 130.55, 130.29, 127.48, 126.49, 126.32, 124.74, 118.71, 118.25, 115.90, 114.88, 102.49, 55.49. MS (EI) m/z: 464.5[M$^+$. Anal.calcd for C$_{27}$H$_{20}$N$_4$O$_2$S (%): C 69.81, H 4.34, N 12.06; found: C 69.76, H 4.39, N 12.03.

5. Synthesis of 7-(10-phenyl-10H-phenoxazin-3-yl)benzo[c][1,2,5]thiadiazole-4-carbaldehyde (5)
Compound 2 (3.85 g, 10 mmol), compound 3 (2.43 g, 10 mmol), K$_2$CO$_3$ (3.45 g, 25 mmol) and Pd(PPh$_3$)$_4$ (0.01 g) were dissolved in 200 mL solvents (water:dioxane 1:10) in a 500 mL round-bottom flask under argon. The resulting mixture was allowed to stir at 86 °C for 24 hours. After that, the mixture was gradually cooled to room temperature and then 300 mL ice water was added to the mixture. The organic layer was separated, dried over sodium sulfate, filtered and evaporated. The solid then dissolved in dichloromethane and were made in to silica gel and was purified by column chromatography using petroleum ether/ dichloromethane (3/7, v/v) as eluent to afford final product (5). The final product was a deep-red color powder (3.76 g, 89.3%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 10.71 (s, 1H), 8.23 (d, J = 6.0 Hz, 1H), 7.77 (d, J = 12.0 Hz, 1H), 7.62 (t, J = 12.0 Hz, 2H), 7.51 (t, J = 12.0 Hz, 1H), 7.44 (s, 1H), 7.37 (t, J = 12.0 Hz, 3H), 6.70 (m, 2H), 6.61 (t, J = 12.0 Hz, 1H), 6.06 (d, J = 6.0 Hz, 1H), 5.95 (d, J = 6.0 Hz, 1H). MS (EI) m/z: 421.5[M$^+$. Anal.calcd for C$_{25}$H$_{15}$N$_3$O$_2$S(%): C 71.24, H 3.59, N 9.97; found: C 71.21, H 3.63, N 9.95.

6. **Synthesis of 7-(10-phenyl-10H-phenoxazin-3-yl)benzo[c][1,2,5]thiadiazole-4-carbonitrile (7)**

Compound 5 (2.1 g, 5.0 mmol) and hydroxylamine hydrochloride (NH$_2$OH-HCl) (0.7g, 10.0 mmol) were dissolved in 50 ml DMSO in a 100 mL Schlenk tube under argon. The resulting mixture was allowed to stir at 100 °C for 4 hours. After that, the mixture was gradually cooled to room temperature and poured to 200 ml ice water. Then the mixture was filtered and the deep-red crude product was dissolved in dichloromethane. The organic layer was separated, dried over sodium sulfate, filtered and evaporated. Crude product was purified by column chromatography through silica gel using petroleum ether/ dichloromethane (6/4 v/v) as eluent to afford final product (7). The final product was a bright and deep-red color powder (1.86 g, 89.1%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ ( ppm ): $^1$H NMR (600 MHz, cdcl$_3$) $\delta$ 8.04 (d, J = 12.0 Hz, 1H), 7.63 (m, 3H), 7.51 (t, J = 12.0 Hz, 1H), 7.40 (s, 1H), 7.37 (d, J = 12.0 Hz, 2H), 7.34 (d, J = 12.0 Hz, 1H), 6.70 (m, 2H), 6.62 (t, J = 12.0 Hz, 1H), 6.05 (d, J = 6.0 Hz, 1H),
5.95 (d, J = 6.0 Hz, 1H). $^{13}$C NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): $\delta$ 153.92, 152.59, 144.13, 143.71, 138.42, 138.13, 136.02, 133.43, 131.20, 130.48, 128.90, 128.53, 125.10, 124.67, 123.48, 122.08, 116.08, 115.75, 115.56, 113.64, 113.25, 103.05. MS (EI) m/z: 418.5[M$^+$]. Anal.calcd for C$_{25}$H$_{14}$N$_4$OS (%): C 71.75, H 3.37, N 13.39; found: C 71.72, H 3.41, N 13.36.
Figure S1. TGA and DSC (inset figure) curve of OTA-BT-CN and POZ-BT-CN.

Figure S2. Cyclic voltammetry curves of OTA-BT-CN and POZ-BT-CN recorded in DCM at room temperature.
Figure S3. Energy level diagram of small molecules in the NIR OLED device.

Figure S4. PL spectra of OTPA-BT-CN and POZ-BT-CN in a film state.
**Figure S5.** Current Efficiency-Luminance of different concentration of 4CzIPN (a) and corresponding EL spectra (b) with 2.0 wt% OTPA-BT-CN as NIR emitter.

**Figure S6.** Transient PL spectra of 4CzIPN (left) and OSTFB (right) doped in mCP host (25 wt%).
Figure S7. CE-Luminescence, J-Voltage-Luminescence and EL spectra of **POZ-BT-CN** with OSTFB as the sensitizer.

**X-Ray Crystal Structure Analysis**
Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1828817 (**POZ-BT-CN** (needle)), CCDC-1828818 (**OTPA-BT-CN** (needle)). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [https://www.ccdc.cam.ac.uk/structures-beta/](https://www.ccdc.cam.ac.uk/structures-beta/).
Datablock: OTPA-BT-CN

Bond precision:  \( C-C = 0.0050 \ \text{\AA} \)  
Wavelength=0.71073

Cell:  
\( a=11.8289(11) \)  
\( b=20.0485(17) \)  
\( c=21.3871(18) \)  
\( \alpha=105.379(3) \)  
\( \beta=102.037(4) \)  
\( \gamma=99.001(4) \)

Temperature: 296 K

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\( 4660.7(7) \)

Space group  
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Hall group  
-\( P1 \)

Moléty formula  
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Sum formula  
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\( \text{C109 H80 N16 O10 S4} \)

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Correction method- Not given

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Datablock: POZ-BT-CN

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Correction method: Not given

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Table S1. Device performances with OSTFB as the sensitizer and POZ-BT-CN as the emitter.

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