Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.


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

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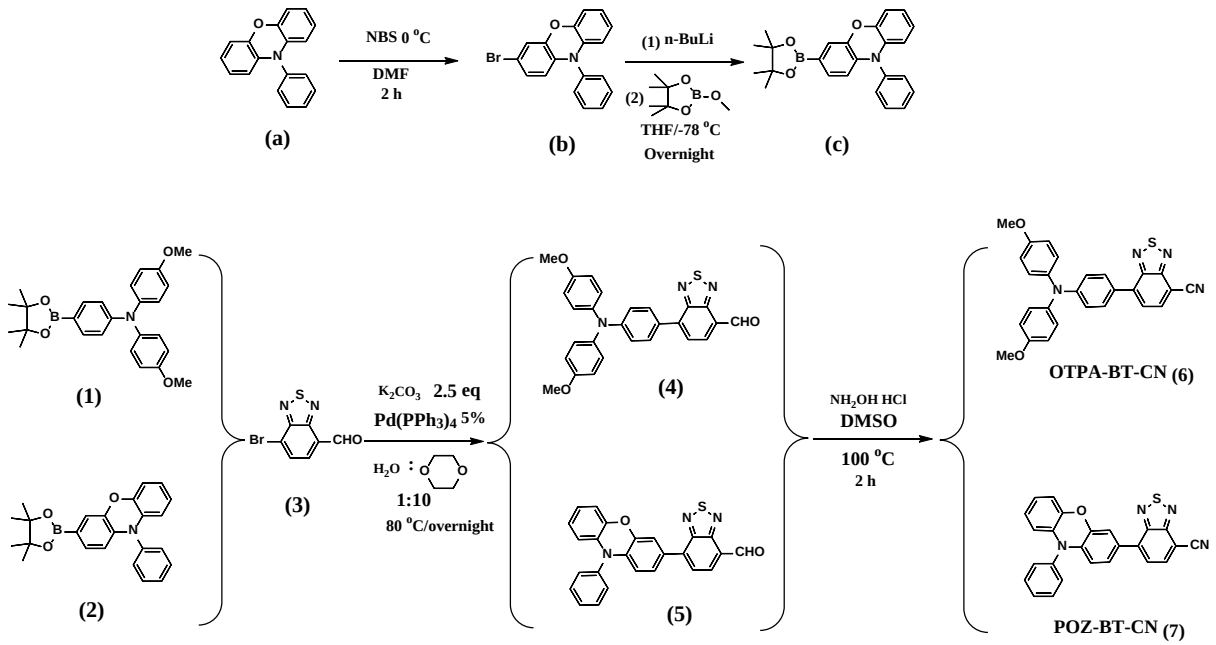
# Synthesis




**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%). $^1$H NMR (600 MHz, $CHCl_3$) 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, 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 $C_{18}H_{12}BrNO$ (%): 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 $^{o}$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 $^{o}$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,$CHCl_3$) 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 $C_{24}H_{24}BNO_3$: 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), $K_2CO_3$ (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 $^{o}$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, $CDCl_3$) δ ( ppm ): δ 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 $C_{27}H_{21}N_3O_3S$(%):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 $^{o}$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, $CDCl_3$): δ ( ppm ): $^{1}$H NMR (600 MHz, $cdcl_3$) δ 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, $CDCl_3$) δ ( ppm ): δ 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 $C_{27}H_{20}N_4O_2S$ (%): 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), $K_2CO_3$ (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 ºC 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, $CDCl_3$) δ (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 $C_{25}H_{15}N_3O_2S$(%): 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 ($NH_2OH$-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 ºC 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, $CDCl_3$): δ ( ppm ): $^1$H NMR (600 MHz, cdcl$_3$) δ 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, $CDCl_3$) δ ( ppm ): δ 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 $C_{25}H_{14}N_4OS$ (%): C 71.75, H 3.37, N 13.39; found: C 71.72, H 3.41, N 13.36.

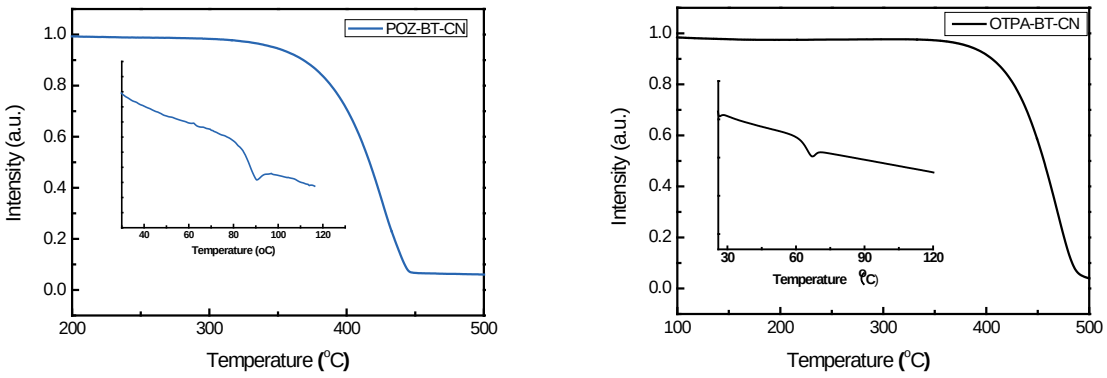



**Figure S1.** TGA and DSC (inset figure) curve of **OTPA-BT-CN** and **POZ-BT-CN**.

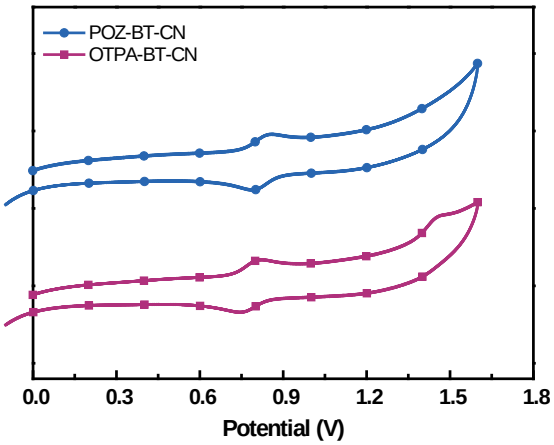



**Figure S2.** Cyclic voltammetry curves of **OTPA-BT-CN** and **POZ-BT-CN** recorded in DCM at room temperature.

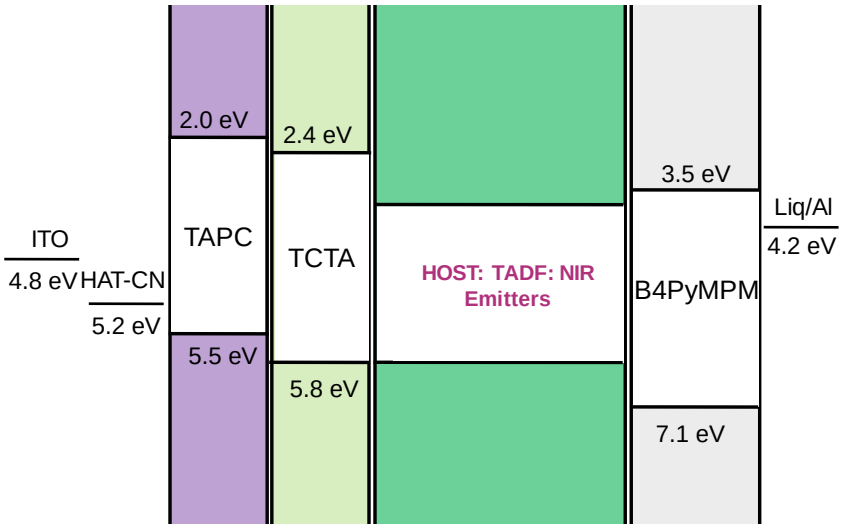



**Figure S3.** Energy level diagram of small molecules in the NIR OLED device.

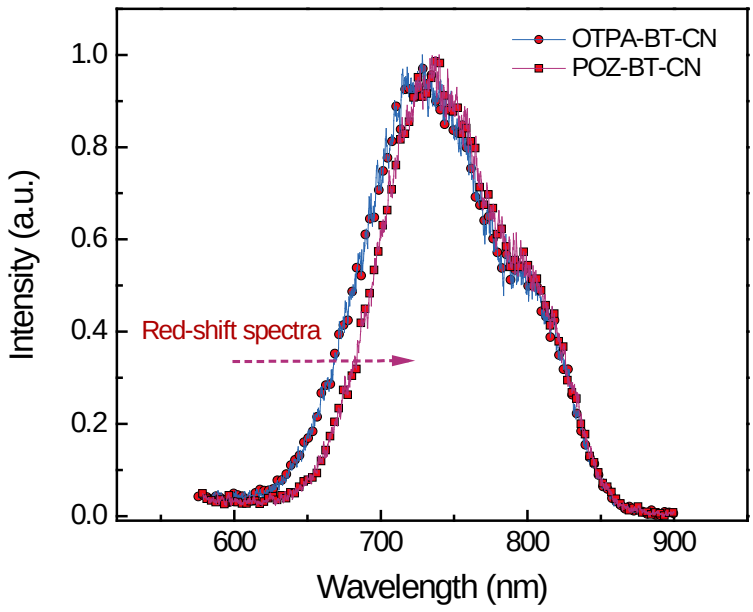



**Figure S4.** PL spectra of **OTPA-BT-CN** and **POZ-BT-CN** in a film state.

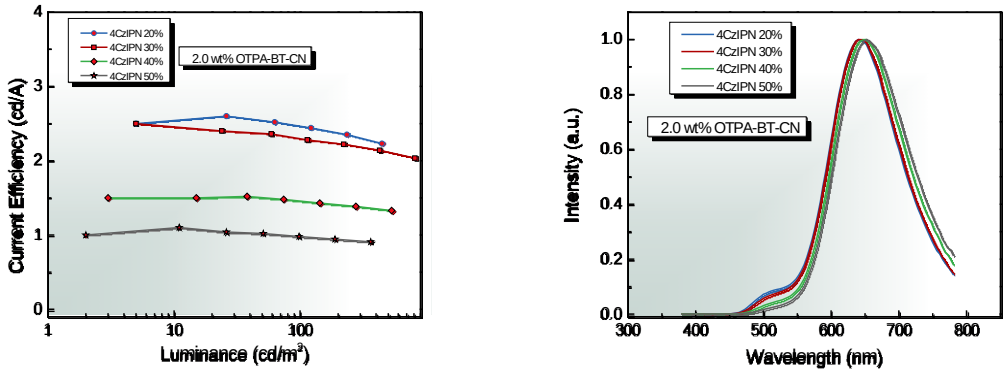



**Figure S5.** Current Efficiency-Luminance of different concentration of 4CzIPN (a) and corresponding EL spectra (b) with 2.0 wt% **OTPA-BT-CN** as NIR emitter.

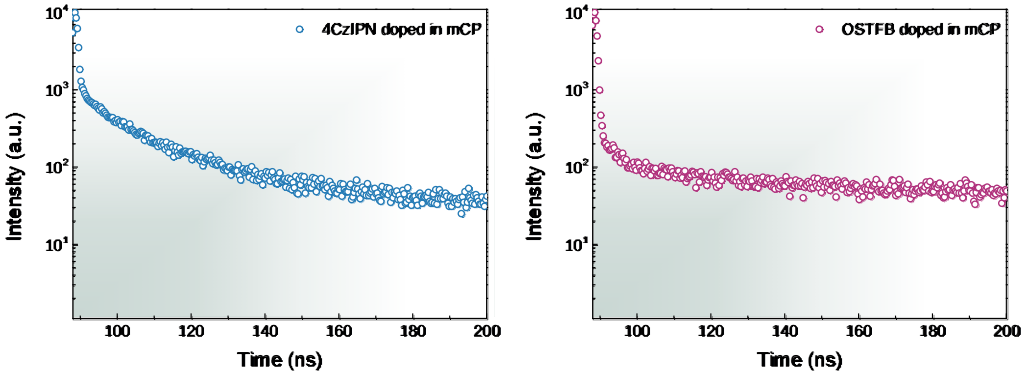



**Figure S6.** Transient PL spectra of 4CzIPN (left) and OSTFB (right) doped in mCP host (25 wt%).

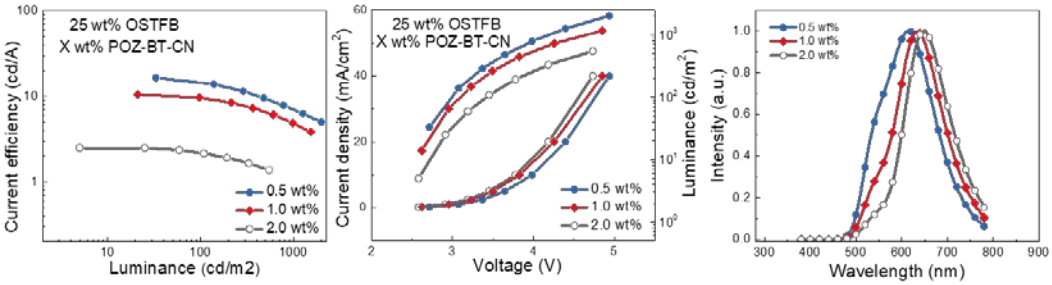



**Figure S7.** CE-Luminescence, J-Voltage-Luminescence and EL spectra of **POZ-BT-CN** with OSTFB as the sensitizer.

## 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/.

## Datablock: OTPA-BT-CN

Bond precision: C-C = 0.0050 A 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

| | Calculated | Reported |
|---|---|---|
| Volume | 4660.7(7) | 4660.7(7) |
| Space group | P -1 | P-1 |
| Hall group | -P 1 | ? |
| Moiety formula | 4(C27 H20 N4 O2 S), C O, O | ? |
| Sum formula | C109 H80 N16 O10 S4 | C109 H80 N16 O10 S4 |
| Mr | 1902.13 | 1902.13 |
| Dx,g cm-3 | 1.355 | 1.355 |
| Z | 2 | 2 |
| Mu (mm-1) | 0.175 | 0.175 |
| F000 | 1980.0 | 1980.0 |
| F000' | 1981.76 | |
| h,k,lmax | 14,24,25 | 14,24,25 |
| Nref | 17360 | 17048 |
| Tmin,Tmax | 0.929,0.949 | |
| Tmin' | 0.924 | |

Correction method= Not given

Data completeness= 0.982 Theta(max)= 25.500

R(reflections)= 0.0648( 10447) wR2(reflections)= 0.1812( 17048)

S = 1.003 Npar= 1252

## Datablock: POZ-BT-CN

Bond precision: C-C = 0.0033 A Wavelength=0.71073

Cell: a=17.804(2) b=9.2170(11) c=12.5258(17)
alpha=90 beta=107.795(4) gamma=90
Temperature: 296 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1957.1(4) | 1957.1(4) |
| Space group | P 21/c | P2(1)/c |
| Hall group | -P 2ybc | ? |
| Moiety formula | C25 H14 N4 O S | ? |
| Sum formula | C25 H14 N4 O S | C25 H14 N4 O S |
| Mr | 418.46 | 418.46 |
| Dx,g cm-3 | 1.420 | 1.420 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.192 | 0.192 |
| F000 | 864.0 | 864.0 |
| F000' | 864.80 | |
| h,k,lmax | 21,11,15 | 20,10,15 |
| Nref | 3636 | 3220 |
| Tmin,Tmax | 0.929,0.948 | |
| Tmin' | 0.917 | |

Correction method= Not given

Data completeness= 0.886 Theta(max)= 25.500

R(reflections)= 0.0410( 2528) wR2(reflections)= 0.1027( 3220)

S = 1.071 Npar= 280

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

| Emitter | Doping Ratio | Assistant Dopant | Voltage @100 cd $m^{-2}$ | Max. CE | Max. EQE | $\lambda_{EL}$,max |
|---|---|---|---|---|---|---|
| | (%) | | (V) | (cd $A^{-1}$) | (%) | (nm) |
| POZ-BT-CN | 0.5 | OSTFB | 3.0 | 16.5 | 10.6 | 618 |
| | 1.0 | OSTFB | 3.1 | 10.5 | 9.6 | 637 |
| | 2.0 | OSTFB | 3.4 | 2.5 | 3.3 | 652 |