

Supporting Information

Highly efficient deep-red to near-infrared thermally activated delayed fluorescence organic light-emitting diodes using a 2,3-bis(4-cyanophenyl)quinoxaline-6,7-dicarbonitrile acceptor

Shantaram Kothavale¹, Kiun Cheong¹, Seung Chan Kim¹, Seong-Jun Yoon^{2*}, Jun Yeob Lee^{1,3*}

¹*School of Chemical Engineering, Sungkyunkwan University 2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggi, 16419, Republic of Korea*

²*School of Polymer Science and Engineering, Chonnam National University, 77 Yongbong ro, Buk-gu, Gwangju 61186, Republic of Korea*

³*SKKU Institute of Energy Science and Technology, Sungkyunkwan University 2066, Seobu ro, Jangan-gu, Suwon, Gyeonggi, 16419, Republic of Korea*

E-mail: leej17@skku.edu

Experimental section (general information and synthesis).

Figure S1. Natural transition orbitals (NTOs) of *t*BuTPA-Qx4CN TADF emitter in its higher-level singlet and triplet excited states.

Figure S2. Low temperature (at 77 k) fluorescence (LTFL) and photoluminescence (LTPL) spectra of *t*BuTPA-qx4CN TADF emitter in toluene solvent.

Figure S3. Thermogravimetric analysis (TGA) curve of *t*BuTPA-Qx4CN TADF emitter.

Figure S4. Cyclic voltammograms of *t*BuTPA-Qx4CN TADF emitter.

Figure S5. Energy level diagram with chemical structures of the organic materials used in the vacuum-processed OLEDs doped with *4t*BuTPA-QxCN TADF emitter.

Figure S6. Hole and electron only device doped with *4t*BuTPA-QxCN TADF emitter.

Figure S7. ¹H NMR spectrum of **Intermediate 2**.

Figure S8. ¹³C NMR spectrum of **Intermediate 2**.

Figure S9. ¹H NMR spectrum of **Intermediate 3**.

Figure S10. ¹H NMR spectrum of **Intermediate 4**.

Figure S11. ¹H NMR spectrum of *t*BuTPA-Qx4CN.

Figure S12. ^{13}C NMR spectrum of *t*BuTPA-Qx4CN.

Experimental section (General Information)

4,5-diamino-3,6-dibromophthalonitrile, Thionyl chloride (SOCl_2), Triethylamine, tetrakis(triphenylphosphine)palladium, pinacolatodiboron, ($\text{Pd}(\text{dppf})_2\text{Cl}_2$), tetrakis(triphenylphosphine)palladium were purchased from P&H tech. 4,4'-dibromobenzil, Copper cyanide (CuCN), potassium acetate, tri-*tert*-butylphosphine was purchased from Alfa Aesar. Lithium aluminum hydride (LiAlH_4), bis(4-(*tert*-butyl)phenyl)amine, and 1-bromo-4-iodobenzene were purchased from Tokyo Chemical Industry (TCI) Ltd. *N,N* dimethyl formamide (DMF), anhydrous THF, anhydrous toluene, 1,4-dioxane, and acetic acid were obtained from Duksan Sci. Co. All these chemicals were used without further purification. Column chromatography (Silica Gel 60, 230–400 mesh, Merck) and sublimation (10^{-3} Torr at $300\text{ }^\circ\text{C}$) purification processes were used to obtain pure products before applying for OLED devices.

The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in deuterated chloroform (CDCl_3) solution on an Avans 500 MHz spectrometer. Chemical shifts of the ^1H and ^{13}C NMR signals were quoted relative to tetramethylsilane ($\delta = 0.00$). All coupling constants are reported in Hertz. The ultraviolet–visible (UV–vis) spectra were obtained using a UV–vis spectrophotometer (JASCO, Easton, MD; V-730), and the photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (PerkinElmer, Waltham, MA; LS55). CV measurement was carried out in dichloromethane solution with scan rate at 100 mV/s . The glassy carbon, platinum wire and Ag/AgCl were used as working, counter and reference electrodes respectively. Internal standard was ferrocenium/ferrocene couple and supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAClO_4). The mass spectra were recorded using Advion, Expression LCMS spectrometer in APCI mode. Absolute photoluminescence quantum yields (PLQYs) of $1\text{ wt}\%$ doped polystyrene film solid film were measured with a Hamamatsu Quantaurus-QY C11347-11 spectrometer under a nitrogen

atmosphere condition. The transient photoluminescence decay characteristics of solid film samples were recorded using a Quantaaurus-Tau fluorescence lifetime measurement system (C11367-31, Hamamatsu Photonics).

Device Fabrication and Measurements

The device structure was indium tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 60 nm)/4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (TAPC, 20 nm)/ 9,9-Dimethyl-10-(9-phenyl-9H-carbazol-3-yl)-9,10-dihydroacridine (PCZAc) (10 nm)/ 2-phenyl-4,6-bis(12-phenylindolo[2,3-a]carbazole-11-yl) -1,3,5-triazine(PBICT): 4-(3-(triphenylen-2-yl)phenyl)dibenzo[b,d]thiophene (DBTTPI) : *t*BuTPA-CNQx dopant (25 nm: 75 nm: 1, 3 and 5 wt %) /diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 5 nm)/2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) (40 nm)/LiF(1.5 nm)/Al(200 nm). All layers of the device structure were deposited by vacuum thermal evaporation under a high pressure of 3.0×10^{-7} Torr. The material was thermally evaporated and then encapsulated with a glass lid in a nitrogen-filled glove box to protect the device from moisture and oxygen. Electrical characterization of the devices was performed using a Keithley 2400 source meter and optical characterization was carried out using a CS 2000 spectroradiometer.

Experimental (Synthesis)

Synthesis of 4,7-dibromobenzoc[[1,2,5]thiadiazole-5,6-dicarbonitrile (Intermediate 1)

4,5-diamino-3,6-dibromophthalonitrile (3 g, 9.49 mmol) was dissolved in dichloromethane and triethylamine (3.3 mL, 23.73 mmol) was added slowly. Thionyl chloride (SOCl₂) (1.72 mL, 23.73 mmol) was added dropwise at 0 °C and the reaction mixture was refluxed for 12 hrs. After the consumption of all starting material, the reaction mixture was quenched in ice water and extracted with dichloromethane. The organic layer was washed with sodium bicarbonate and dried over anhydrous MgSO₄. The crude product obtained was further purified by column chromatography (30 % DCM in hexane) to obtain white colored solid as pure product. (2.2 g, 67.5 %). MS (FAB) *m/z* 342 [(M + H)⁺].

Synthesis of 4,7-bis(4-(bis(4-(tert-butyl)phenyl)amino)phenyl)benzo[[1,2,5]thiadiazole-5,6-dicarbonitrile (Intermediate 2)

Intermediate 1 (0.5 g, 1.45 mmol) and 4-(tert-butyl)-N-(4-(tert-butyl)phenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (1.75 g, 3.63 mmol) were dissolved in toluene (168 mL), ethanol (70 mL) and aqueous K₂CO₃ (56 mL, 2 M). The reaction mixture

was degassed with argon for half an hour, tetrakis(triphenylphosphine)palladium (0.16 g, 0.14 mmol) was added and the mixture was stirred at 120 °C for 12 h. After cooling to room temperature, the reaction mixture was evaporated on a rotary evaporator, water was added to the residue, and was extracted with ethyl acetate (3 x 150 mL). The organic layer was dried over anhydrous MgSO₄, concentrated on rotary evaporator and purified by column chromatography (40 % dichloromethane in hexane) to afford a pure product (0.68 g, 52.30 %). ¹H NMR (500 MHz, CDCl₃): δ 7.47-7.52 (m, 8 H), 7.42-7.43 (m, 4H), 7.32-7.34 (m, 8H), 7.15-7.18 (m, 12 H). 1.34 (s, 36H). ¹³C NMR (126 MHz,) δ 154.7, 150.8, 147.6, 143.8, 140.5, 131.5, 126.5, 125.8, 123.8, 119.4, 116.4, 111.4, 34.5, 31.5. MS (FAB) m/z 897 [(M + H)⁺].

Synthesis of 5',6'-diamino-4,4''-bis(bis(4-(tert-butyl)phenyl)amino)-[1,1':4',1''-terphenyl]-2',3'-dicarbonitrile (Intermediate 3)

Intermediate 2 (0.6 g, 0.67 mmol) was dissolved in anhydrous ethanol and cooled to 0°C. Sodium borohydride (0.25 g, 6.78 mmol) was added slowly to the reaction mixture and it was stirred at room temperature for 4-5 hrs. After the complete consumption of starting material, the reaction mixture was quenched in ice water and extracted with ethyl acetate. The organic layer was dried over magnesium sulfate and concentrated on a rotary evaporator to obtain a pure product. (0.36 g, 62.06 %). ¹H NMR (500 MHz, CDCl₃): δ 7.65-7.68 (m, 4H), 7.32-7.35 (m, 8H), 7.11-7.17 (m, 12H), 1.33 (s, 36H). MS (FAB) m/z 869 [(M + H)⁺].

Synthesis of 5,8-bis(4-(bis(4-(tert-butyl)phenyl)amino)phenyl)-2,3-bis(4-bromophenyl)quinoxaline-6,7-dicarbonitrile (Intermediate 4)

Intermediate 3 (0.28 g, 0.32 mmol) and 1,2-bis(4-bromophenyl)ethane-1,2-dione (0.12 g, 0.32 mmol) were dissolved in acetic acid (30 mL) and the mixture was heated to reflux for 12 hrs. The reaction mixture was cooled to room temperature and water was added. The solid precipitated out was filtered and dried well as pure product. (0.36 g, 93.02 %). ¹H NMR (500 MHz, CDCl₃): δ 7.47-7.52 (m, 8 H), 7.42-7.43 (m, 4H), 7.32-7.34 (m, 8H), 7.15-7.18 (m, 12 H). 1.34 (s, 36H). MS (FAB) m/z 1199 [(M + H)⁺].

Synthesis of 5,8-bis(4-(bis(4-(tert-butyl)phenyl)amino)phenyl)-2,3-bis(4-cyanophenyl)quinoxaline-6,7-dicarbonitrile (tBuTPA-Qx4CN)

Intermediate 2 (0.33 g, 0.27 mmol) was dissolved in DMF (30 mL), copper cyanide (0.12 g, 1.37 mmol) was added and the reaction mixture was heated at 160 °C for 24 hrs. After completion, the mixture was cooled to room temperature and water was added. Solid precipitated out was filtered and dried well. The crude product was further purified by column chromatography to obtain a pure product (0.21 g, 70 %) (60 % dichloromethane in hexane). ¹H NMR (500 MHz, CDCl₃): δ 7.62-7.66 (m, 8 H), 7.50-7.51 (dd, *J* = 8.5 and 4.5 Hz, 4H), 7.33-7.35 (m, 8H), 7.14-7.17 (m, 12 H). 1.34 (s, 36H). ¹³C NMR (126 MHz,) δ 156.0, 147.6, 141.2, 140.4, 132.5, 132.3, 130.7, 126.5, 125.5, 119.5, 118.0, 114.2, 34.5, 31.5. MS (FAB) m/z 1093 [(M + H)⁺].

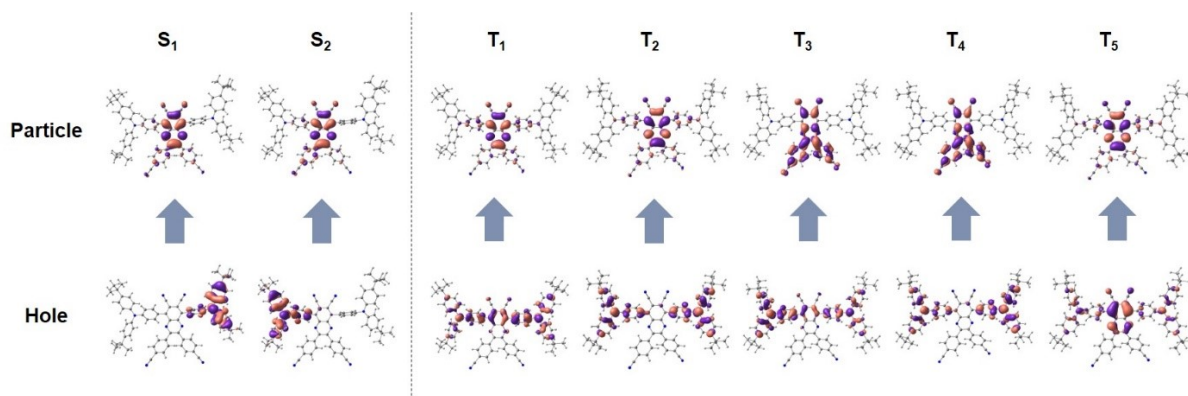


Figure S1. Natural transition orbitals (NTOs) of *t*BuTPA-qx4CN emitter in its higher-level singlet and triplet excited states.

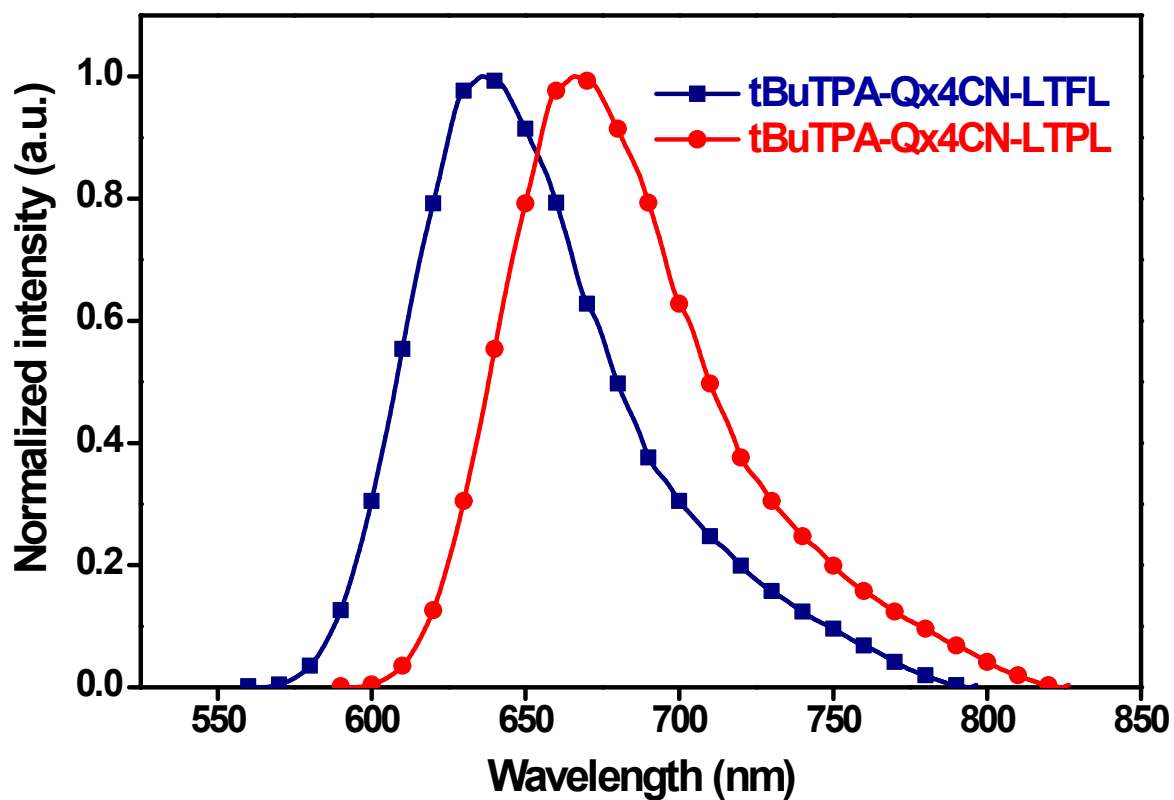


Figure S2. Low temperature (at 77 k) fluorescence (LTFL) and photoluminescence (LTPL) spectra of *t*BuTPA-qx4CN TADF emitter in toluene solvent.

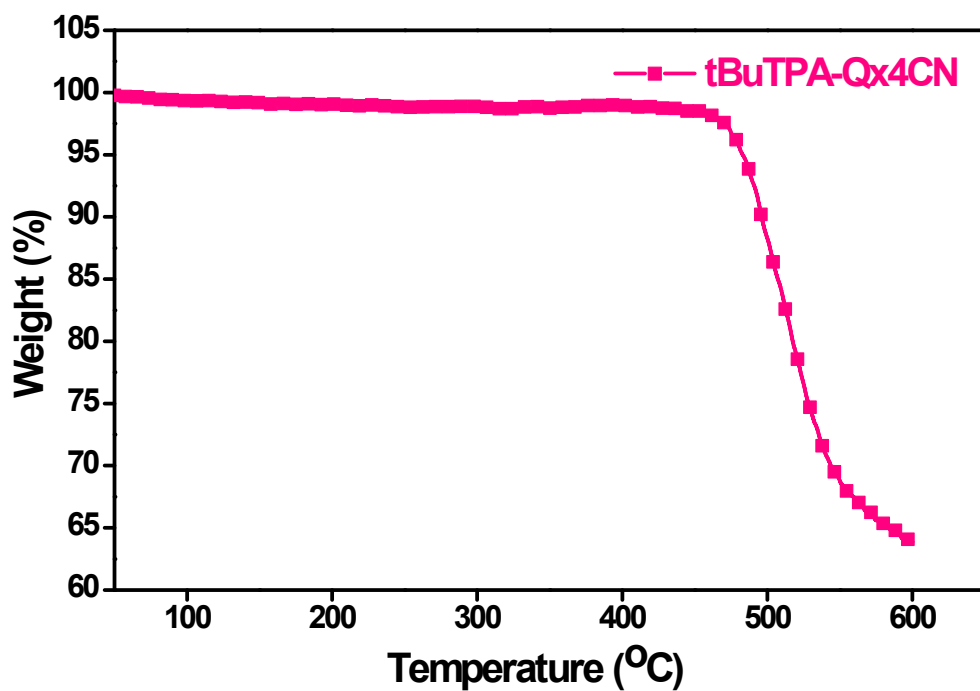


Figure S3. Thermogravimetric analysis (TGA) curve of *t*BuTPA-Qx4CN TADF emitter.

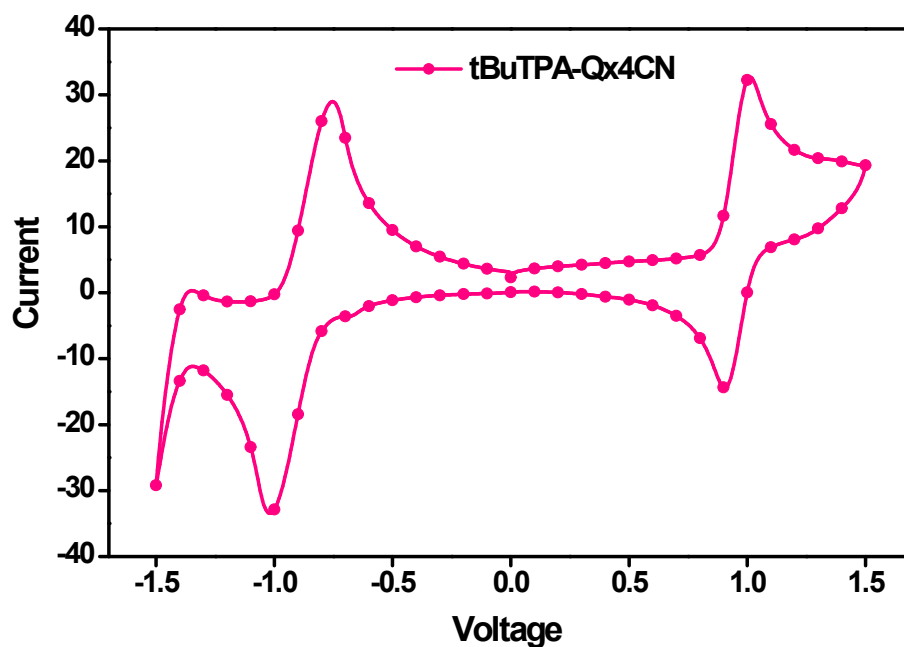


Figure S4. Cyclic voltammograms of *t*BuTPA-Qx4CN TADF emitter.

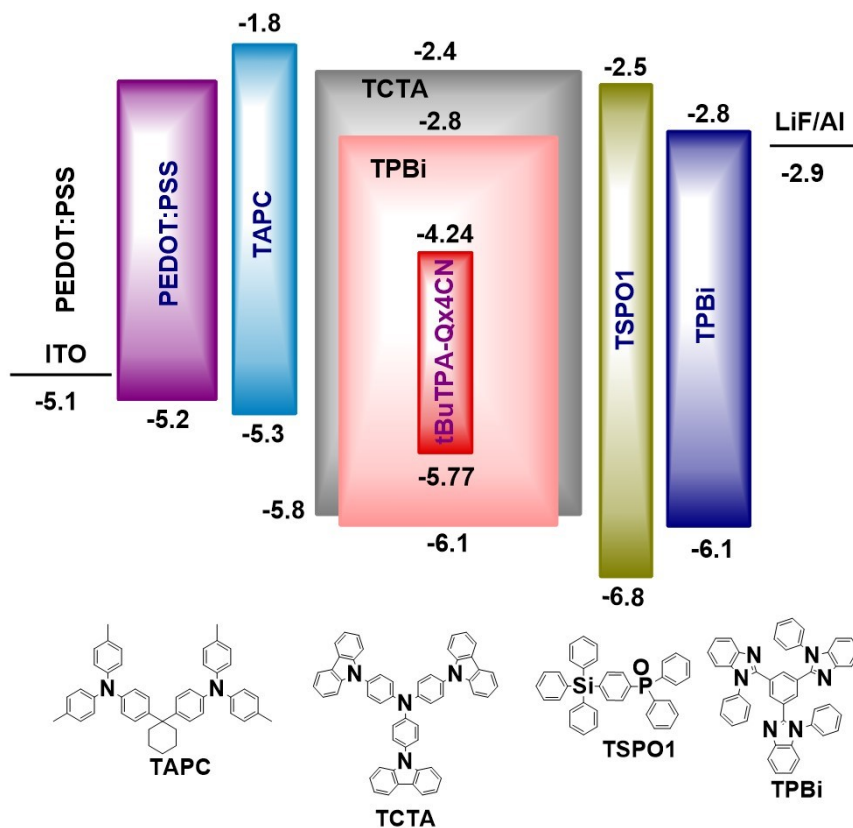
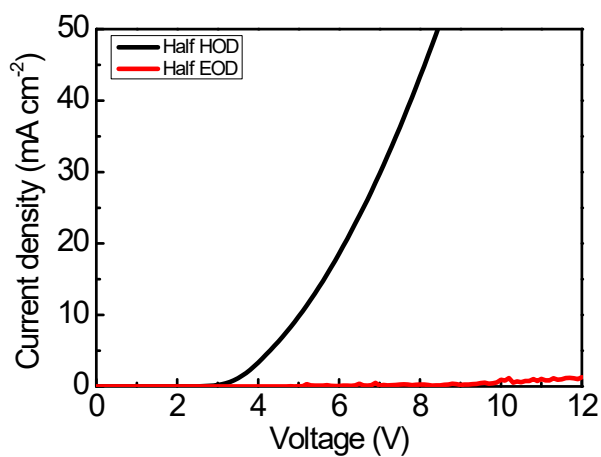


Figure S5. Energy level diagram with chemical structures of the organic materials used in the vacuum-processed OLEDs doped with **4tBuTPA-Qx4CN** TADF emitter.



Half HOD: PEDOT(60)/TAPC(20)/TCTA(10)/TCTA:TPBi:Shan-69(25:50%:1%)/TAPC(15)/Al(200). Half EOD : DBFTrz(15)/TCTA:TPBi:Shan-69(25:50%:1%)/TSPO1(5)/TPBi(40)/LiF(1.5)/Al(200)

Figure S6. Hole and electron only device doped with **4tBuTPA-Qx4CN** TADF emitter and respective device structures.

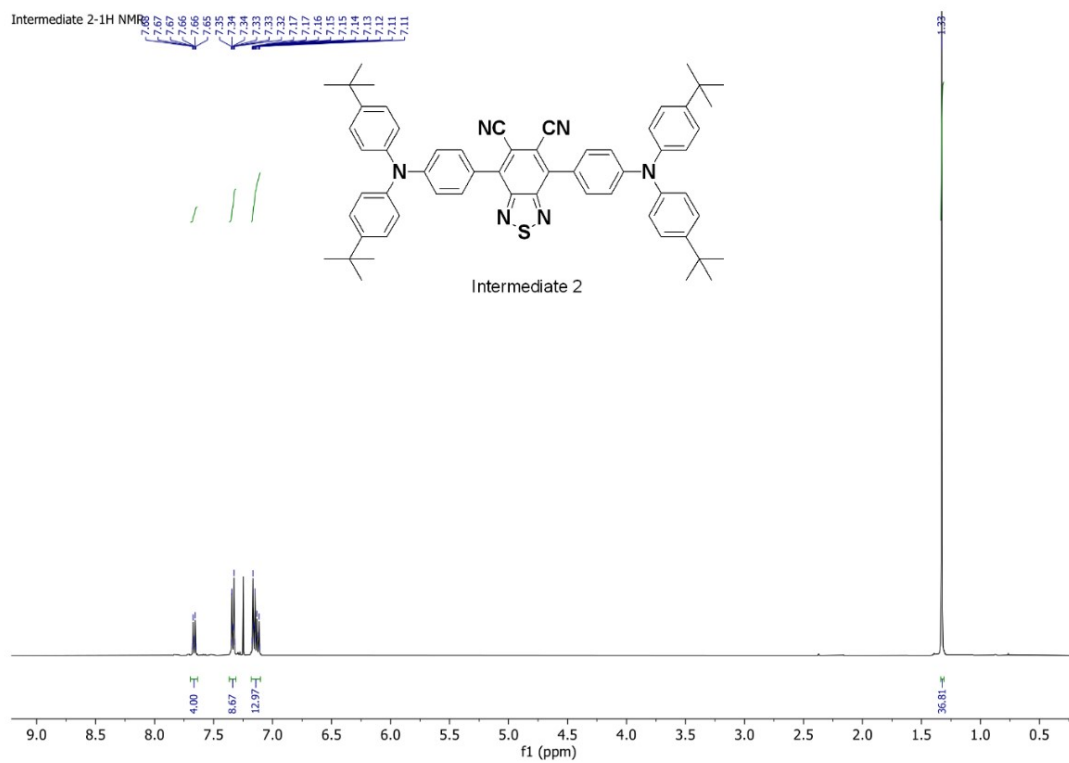


Figure S7. ^1H NMR spectrum of **Intermediate 2**.

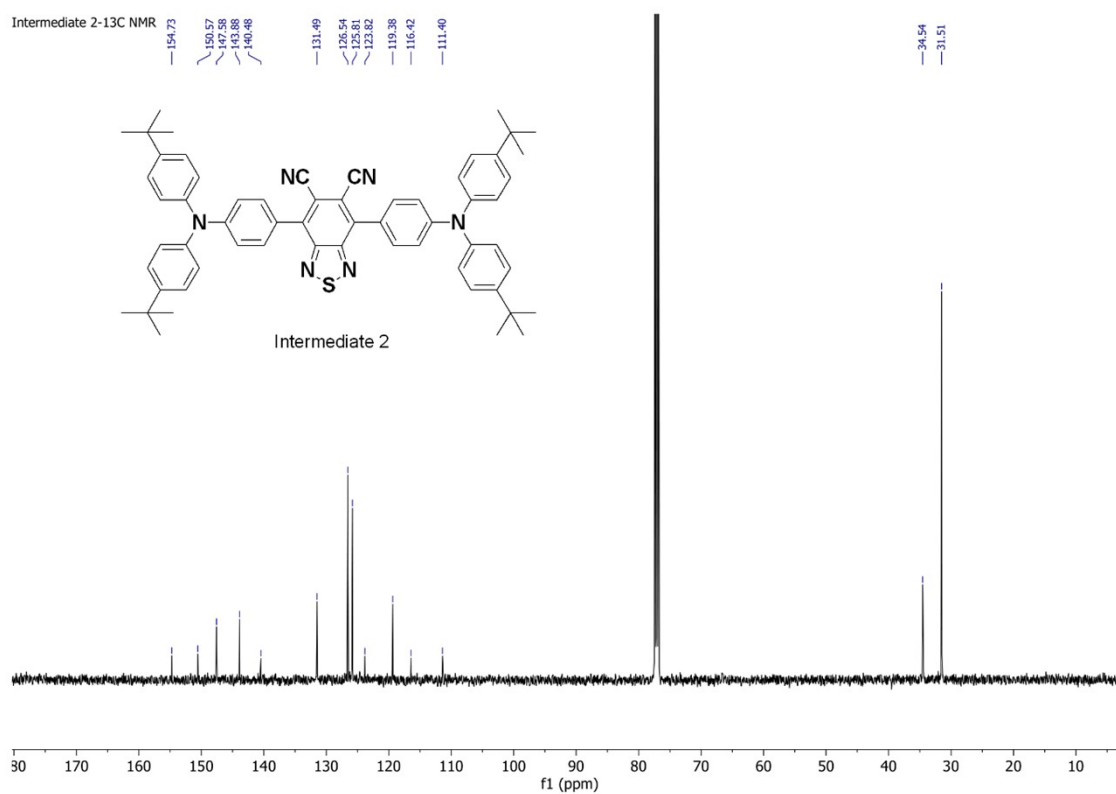


Figure S8. ^{13}C NMR spectrum of **Intermediate 2**.

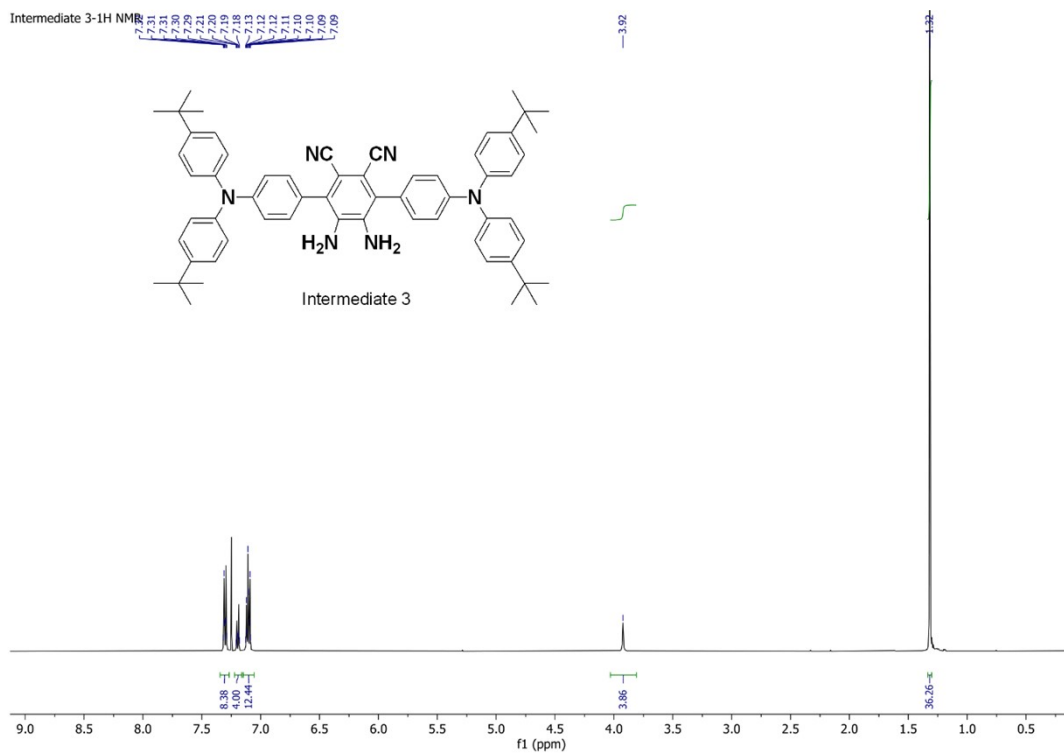


Figure S9. ¹H NMR spectrum of **Intermediate 3**.

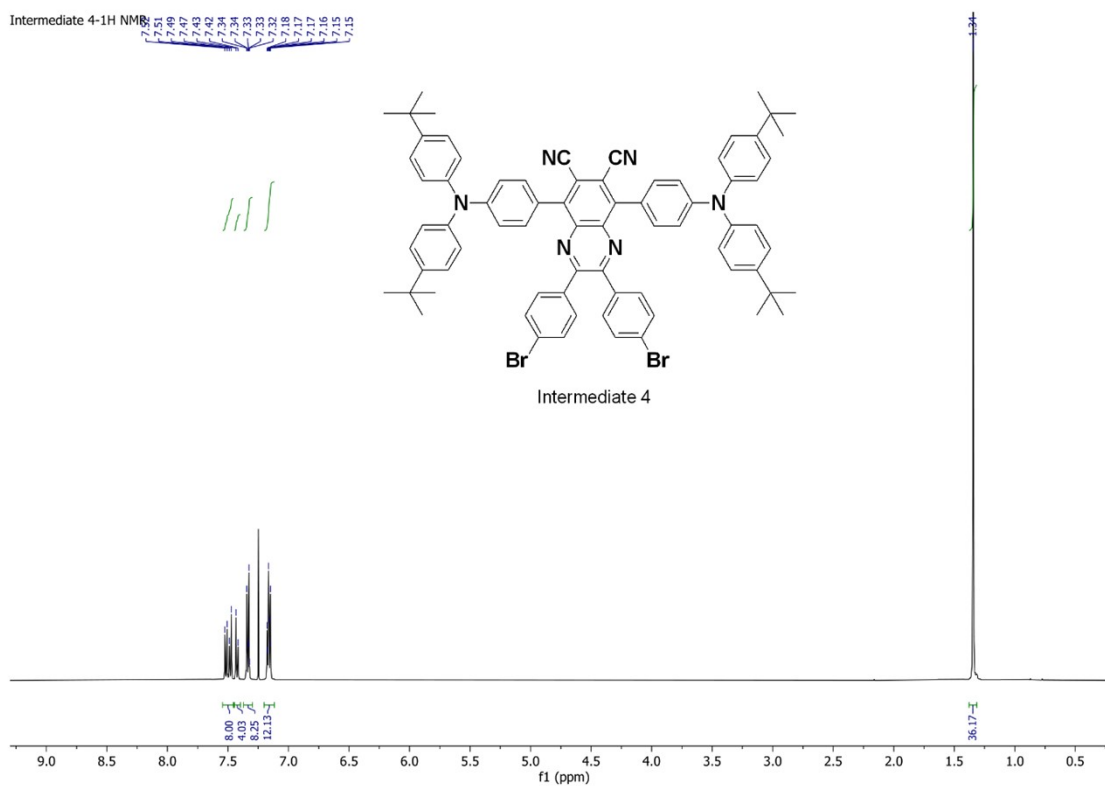


Figure S10. ¹H NMR spectrum of **Intermediate 4**.

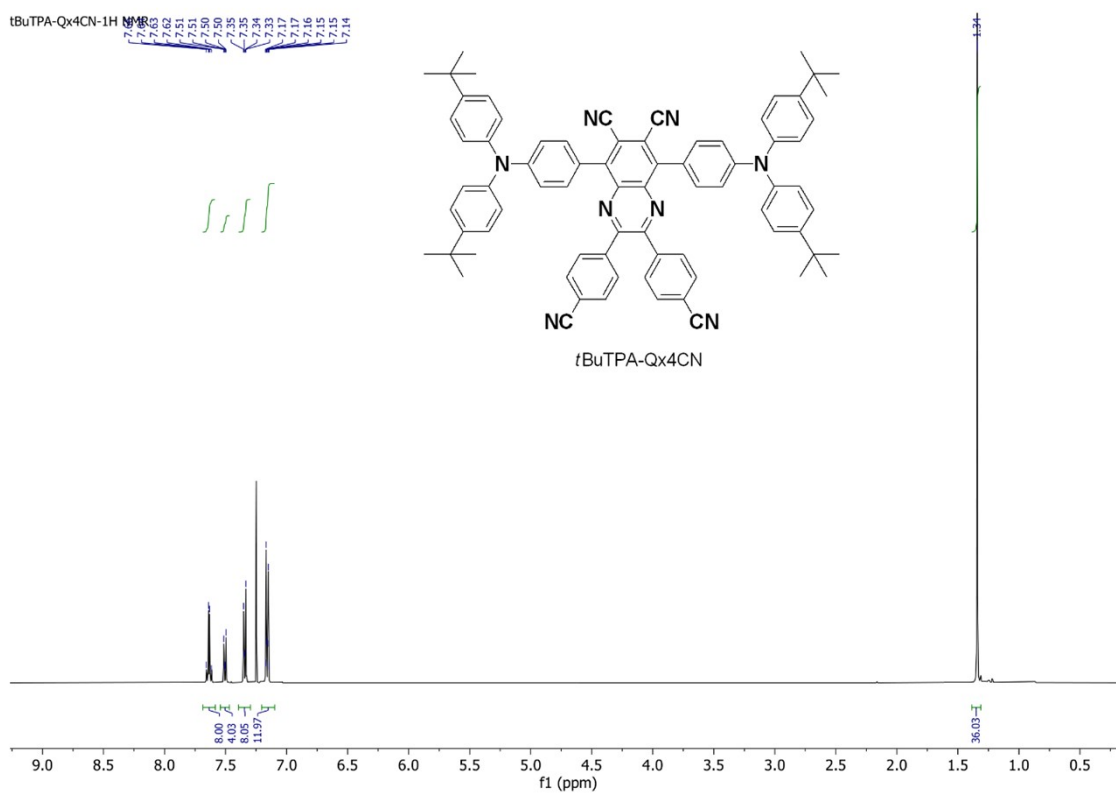


Figure S11. ¹H NMR spectrum of *t*BuTPA-Qx4CN.

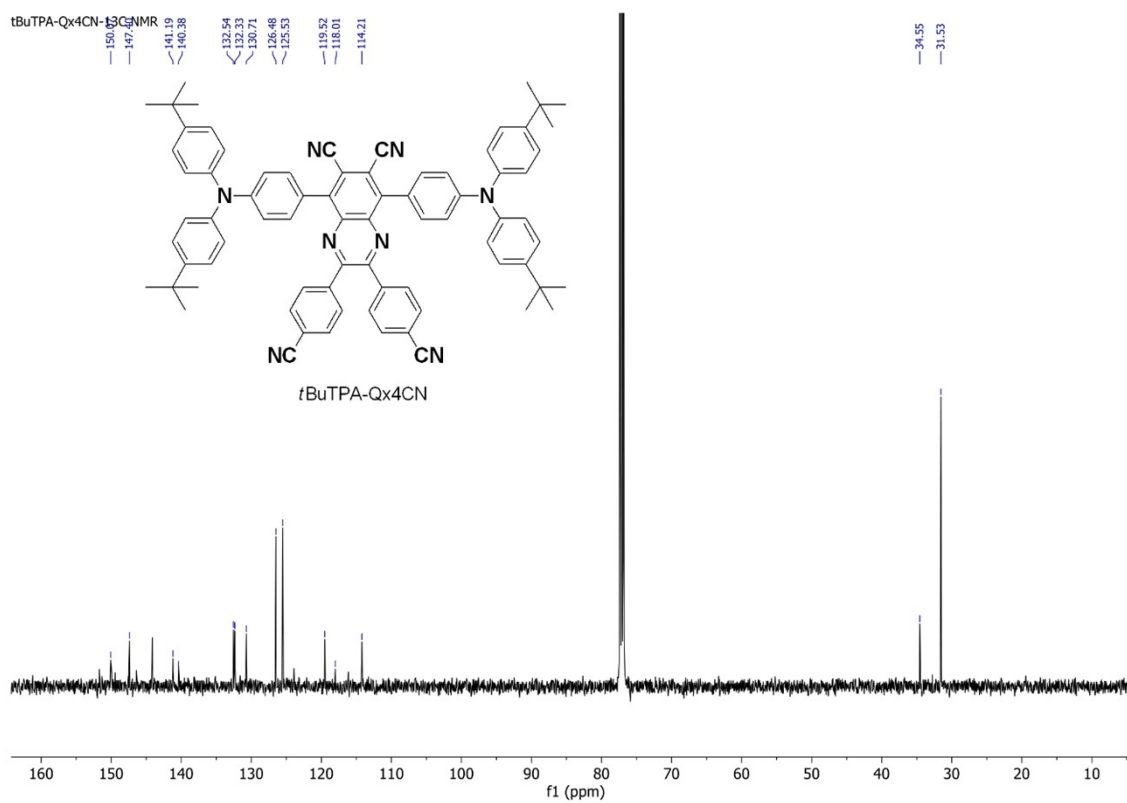


Figure S12. ¹³C NMR spectrum of *t*BuTPA-Qx4CN.