

Supporting information

Pyrimidine-5-carbonitrile acceptor combined with an ortho linked donor for long lifetime through facilitated reverse intersystem crossing in thermally activated delayed fluorescent emitters

Ji Seon Jang¹⁺, Ha Lim Lee¹⁺, Kyung Hyung Lee¹⁺, Jun Yeob Lee^{1*}, Wan Pyo Hong^{2*}

¹School of Chemical Engineering, Sungkyunkwan University

2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggi, 16419, Korea

²School of Advanced Materials and Chemical Engineering, Daegu Catholic University,

13-13, Hayang-ro, Hayang-eup, Gyeonsan-si, Gyeongbuk, 38430, Korea

E-mail: leej17@skku.edu, wphongw@cu.ac.kr

+ Ji Seon Jang, Ha Lim Lee, and Kyung Hyung Lee contributed equally.

Experimental

General information

All starting materials were commercially available and used without any further purification. Benzaldehyde, piperdine and phosphorus(V) oxychloride (POCl₃) were purchased from Sigma Aldrich Co. Benzamidine was a product of J&H Chemical Co. 9-Phenyl-9H,9'H-3,3'-bicarbazole was supplied from LG Chem. Ltd. Ethyl 2-cyanoacetate was bought from Combi-Blocks Inc. (2-Fluorophenyl)boronic acid and sodium methoxide were supplied from Alfa Aesar, Thermo Fisher Scientific Inc. Potassium carbonate, cesium carbonate, 1,4-dioxane, N,N-dimethylacetamide and magnesium sulfate (MgSO₄) were products of Duksan Sci. Co. Tetrakis(triphenylphosphine) palladium(0) was purchased from P&H tech Co. Ethyl alcohol,

n-hexane, chloroform, methylene chloride (MC) and toluene were products of Samchun Pure Chemical Co. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded for structures analysis with NMR spectrometer (Bruker, Avance-500). The mass spectra of intermediates were measured by using Advion, Expression^L CMS spectrometer in APCI mode and the mass spectra of final product was recorded by using JMS-700 (JEOL) with high resolution fast atom bombardment (FAB) mode. The HOMO and LUMO energy levels were estimated by cyclic voltammetry measurement (Ivium Tech., Iviumstat). The absorption spectra and emission spectra were measured using a UV-vis spectrophotometer (JASCO, V-730) and fluorescence spectrophotometer (PerkinElmer, LS-55), respectively. The PL quantum yield was measured using Quantaury-QY Absolute PL quantum yield spectrometer (HAMAMATSU, C11347-11). The transient PL decay data were obtained by Quantaury-Tau Fluorescence lifetime spectrometer (HAMAMATSU, C11367-31) under a nitrogen atmosphere.

Synthesis

(E)-ethyl 2-cyano-3-phenylacrylate

Ethyl 2-cyanoacetate (100 g, 0.88 mol) and benzaldehyde (103 g, 0.97 mol) were added in 1,000 ml round-bottomed flask and dissolved using ethyl alcohol. Then, piperidine (3.76 g, 0.04 mol) was slowly added into the mixture dropwisely under a nitrogen atmosphere. The reaction was proceeded with stirring and heating for 12 h. The reaction mixture was cooled down to room temperature. The crude product was filtered and purified with recrystallization. The product was obtained as a yellow powder (142 g, Yield 80%).

^1H NMR (500 MHz, CDCl_3): δ 8.25 (s, 1H), 7.99-7.98 (d, $J = 7.00$ Hz, 2H), 7.57-7.51 (m, 1H), 7.51-7.48 (t, $J_1 = 8.00$ Hz, $J_2 = 7.00$ Hz, 2H), 4.40-4.36 (q, 2H), 1.41-1.38 (t, 3H).

MS (APCI) m/z Found 202.34 $[(\text{M} + \text{H})^+]$, Calculated from $\text{C}_{12}\text{H}_{11}\text{NO}_2$: 201.22.

6-Oxo-2,4-diphenyl-1,6-dihydropyrimidine-5-carbonitrile

(E)-ethyl 2-cyano-3-phenylacrylate (50 g, 0.25 mol) and benzimidamide (36 g, 0.30 mol) were poured into a 500 ml 2-neck round-bottomed flask and distilled dimethylacetamide (DMAc) was added into the mixture. Then, sodium methoxide solution (25 wt% in methanol) was slowly added into the reaction mixture under a nitrogen atmosphere, until the color of mixture was changed to yellow with a solid precipitation. The reaction mixture was refluxed for 3 h and filtered using hot ethyl alcohol. The mixture with benzimidamide was obtained as a white powder. MS (APCI) m/z Found 274.36 [(M + H)⁺], Calculated from C₁₇H₁₁N₃O : 273.29

4-Chloro-2,6-diphenylpyrimidine-5-carbonitrile

6-Oxo-2,4-diphenyl-1,6-dihydropyrimidine-5-carbonitrile (10 g, 0.04 mol) was added into a round-bottomed flask and 1,4-dioxane was added into the flask. The mixture was stirred until the starting material was well dissolved. Then, phosphorus (V) oxychloride (11 g, 0.07 mol) was added to the mixture dropwisely. After addition, the reaction mixture was stirred and refluxed for 5 h and cooled down to room temperature. The mixture was quenched by sodium bicarbonate solution. The quenched solution was extracted with methylene chloride and deionized water. The extracted organic layer was dried over MgSO₄ and concentrated using a rotary evaporator. The crude solid was washed several times with MC and re-precipitated with methylene chloride and methanol. The product was obtained as a white powder (3.1 g, Yield 28%).

¹H NMR (500 MHz, CDCl₃): δ 8.58-8.56 (dd, J₁= 8.00 Hz, J₂=1.50 Hz, 2H), 8.18-8.17 (dd, J₁= 7.00 Hz, J₂=2.00 Hz, 2H), 7.65-7.52 (m, 6H), 7.55-7.52 (m, J₁= 8.00 Hz, J₂=7.00 Hz, J₃=1.50 Hz, J₄=1.00 Hz, 2H).

MS (APCI) m/z Found 292.83 [(M + H)⁺], Calculated from C₁₇H₁₀ClN₃ : 291.73

4-(2-Fluorophenyl)-2,6-diphenylpyrimidine-5-carbonitrile

4-Chloro-2,6-diphenylpyrimidine-5-carbonitrile (3.0 g, 0.01 mol) and (2-fluorophenyl)boronic acid (1.73 g, 0.12 mol) dissolved in tetrahydrofuran (THF) were added into a 250 mL 2-neck round-bottomed flask and then the mixture was stirred. The 2M potassium carbonate solution was poured into a slightly heated mixture. Then, tetrakis(triphenylphosphine)palladium(0) (0.35g, 0.0003 mol) was added to the mixture and the reaction was refluxed and stirred for 10 h. The organic layer was extracted with methylene chloride and deionized water. The separated organic layer was concentrated with rotary evaporator. The crude product was reprecipitated with methylene chloride and methanol, and filtered with n-hexane. The product was obtained as a white powder (3.20 g, Yield 91%).

¹H NMR (500 MHz, CDCl₃): δ 8.66-8.64 (dd, J₁= 8.00 Hz, J₂= 1.50 Hz, 2H), 8.22-8.20 (dd, J₁= 7.50 Hz, J₂= 2.00 Hz, 2H), 7.79-7.76 (td, J₁=J₂= 7.50 Hz, J₃= 2.00 Hz, 1H), 7.63-7.52 (m, 7H), 7.40-7.37 (td, J₁=J₂= 7.50 Hz, J₃= 1.00 Hz, 1H), 7.33-7.29 (m, 1H).

MS (APCI) m/z Found 352.42 [(M + H)⁺], Calculated from C₂₃H₁₄FN₃ : 351.38

2,4-Diphenyl-6-(2-(9'-phenyl-9H,9'H-[3,3'-bicarbazol]-9-yl)phenyl)pyrimidine-5-carbonitrile (PyCNoBCz)

4-(2-Fluorophenyl)-2,6-diphenylpyrimidine-5-carbonitrile (1.0 g, 0.003 mol), 9-phenyl-9H,9'H-3,3'-bicarbazole (1.45 g, 0.0034 mol) and cesium carbonate (2.78 g, 0.0085 mol) were added into a pressure tube. Then DMAC (10 ml) was added into the mixture. The mixture was refluxed and stirred for 3 h and cooled down to room temperature. Small amount of deionized water was added into a cooled reaction mixture and the mixture was extracted with chloroform. The extracted organic layer was concentrated and adsorbed into silica gel for column purification. The adsorbed product was loaded into a column chromatography and purified

using eluent of n-hexane:chloroform (1:4). The final product was obtained as a yellow powder (1 g, Yield 48%).

^1H NMR (500 MHz, CDCl_3): δ 8.38-8.37 (d, J = 2.00 Hz, 1H), 8.23-8.23 (d, J = 1.50 Hz, 1H), 8.22-8.20 (d, J = 7.50 Hz, 1H), 8.01-7.98 (t, J_1 = 7.00 Hz, J_2 =7.50 Hz, 2H), 7.95-7.93 (dd, J_1 = 7.00 Hz, J_2 =1.50 Hz, 2H), 7.90-7.85 (m, 2H), 7.80-7.76 (m, 2H), 7.72-7.70 (dd, J_1 = 8.50 Hz, J_2 =1.50 Hz, 1H), 7.66-7.61 (m, 4H), 7.56-7.28 (m, 14H), 7.21-7.18 (t, J_1 = J_2 = 7.50 Hz, 1H), 7.15-7.12 (t, J_1 = J_2 = 8.00 Hz, 2H).

^{13}C NMR (125 MHz, CDCl_3): δ 169.35, 168.71, 164.37, 142.19, 141.52, 141.25, 140.19, 137.95, 136.53, 135.95, 135.91, 135.62, 134.57, 134.45, 132.52, 131.97, 131.78, 131.68, 130.56, 130.10, 129.34, 129.21, 128.99, 128.92, 128.49, 127.64, 127.26, 126.23, 126.13, 125.95, 125.93, 124.14, 124.05, 123.74, 123.62, 120.63, 120.59, 120.25, 120.17, 119.13, 119.07, 117.02, 110.47, 110.18, 110.08, 102.23, 68.17, 25.80.

MS (HR-FAB) m/z Found 739.2739 $[(M + H)^+]$. Calculated from $\text{C}_{53}\text{H}_{33}\text{N}_5$: 739.2736

Device fabrication and measurements

Before deposition, indium tin oxide (ITO) substrate was washed with acetone, deionized water and isopropyl alcohol several times. The deposition of all fabricated devices was performed a high vacuum condition of 5.0×10^{-7} torr. The device structure was summarized below.

ITO (50 nm)/DNTPD (60 nm)/BPBPA (20 nm)/PCZAC (10 nm)/CzTrz:Emitter(30 nm)/DBFTrz (5 nm)/ZADN (30 nm)/LiF (1.5 nm)/Al (200 nm)

DNTPD is *N,N'*-diphenyl-*N,N'*-bis-[4-(phenyl-*m*-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine and used as hole injection material. BPBPA is as a role of hole transport layer, and its full name is $\text{N}_4, \text{N}_4, \text{N}_4, \text{N}_4$ -tetra([1,1'-biphenyl]-4-yl)-[1,1'-biphenyl]-4,4'-diamine. PCZAC and DBFTrz is used as exciton blocking layer with different carrier character. PCZAC is 9,9-dimethyl-10-(9-phenyl-9H-carbazol-3-yl)-9,10-dihydroacridine and hole type exciton blocking layer.

DBFTrz is 2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[b,d]furan used as a hole blocking layer and electron type exciton blocking layer. ZADN is 2-[4-(9,10-di-naphthalen-2-yl-anthracene-2-yl)-phenyl]-1-phenyl-1H-benzimidazole used as an electron transport layer. CzTrz is 9-(3'-(4,6-diphenyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-3-yl)-9H-carbazole, which is bipolar host. Device evaluation was performed by using Keithley2400 source measurement unit and CS2000 spectroradiometer for electrical and optical measurements, respectively.

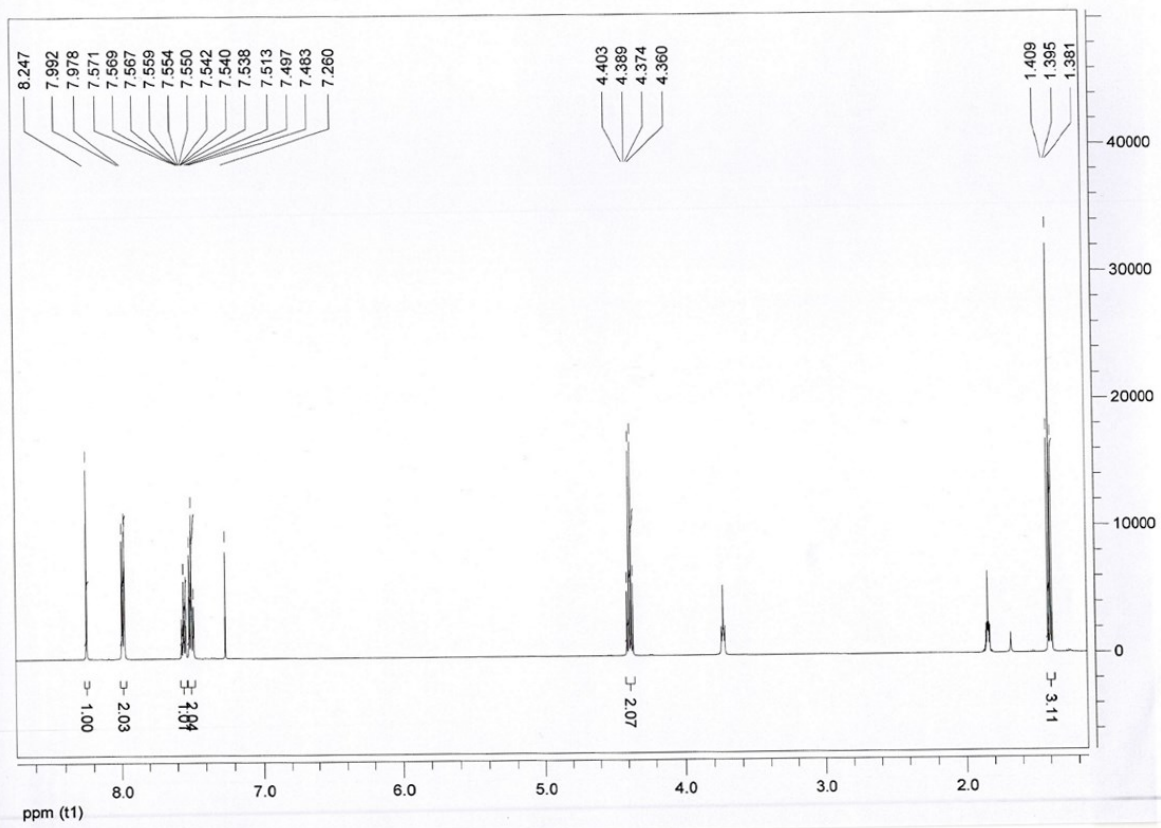
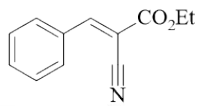
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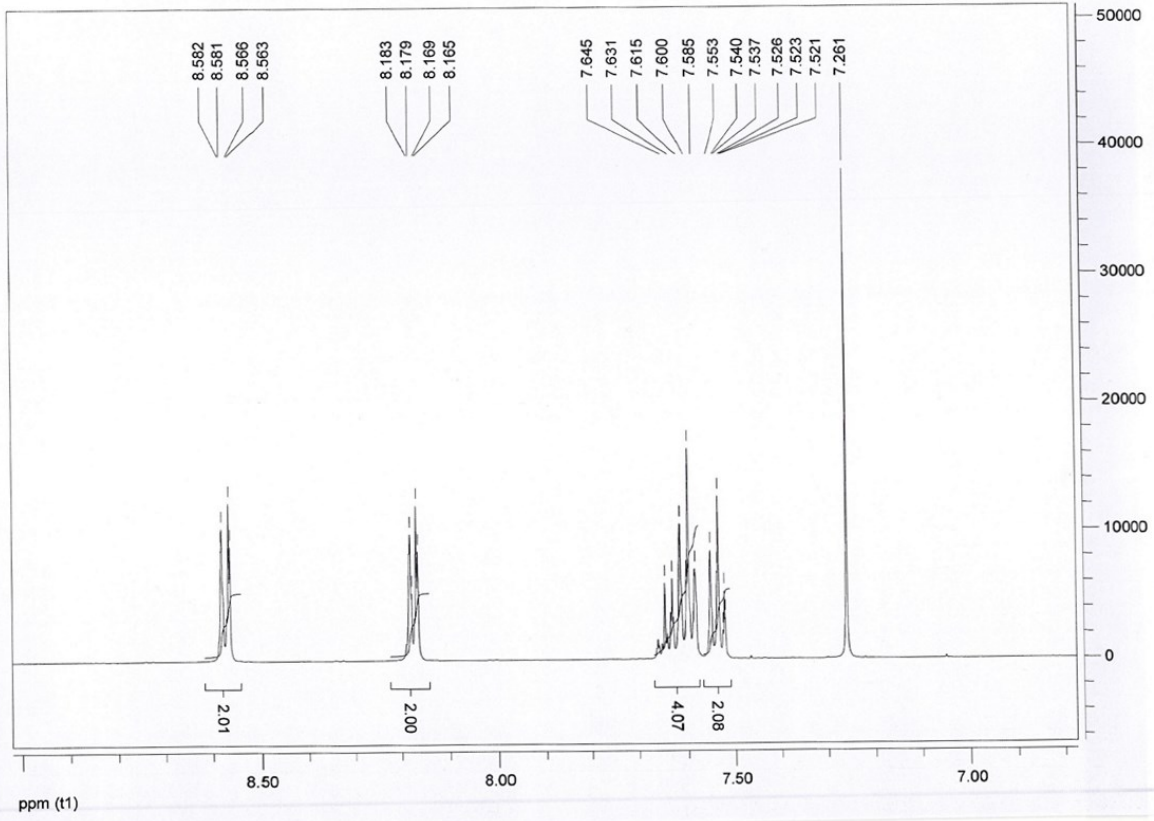
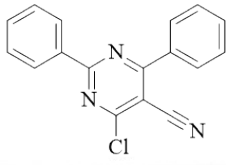
Figure S1. ^1H NMR spectra of intermediates and final compound

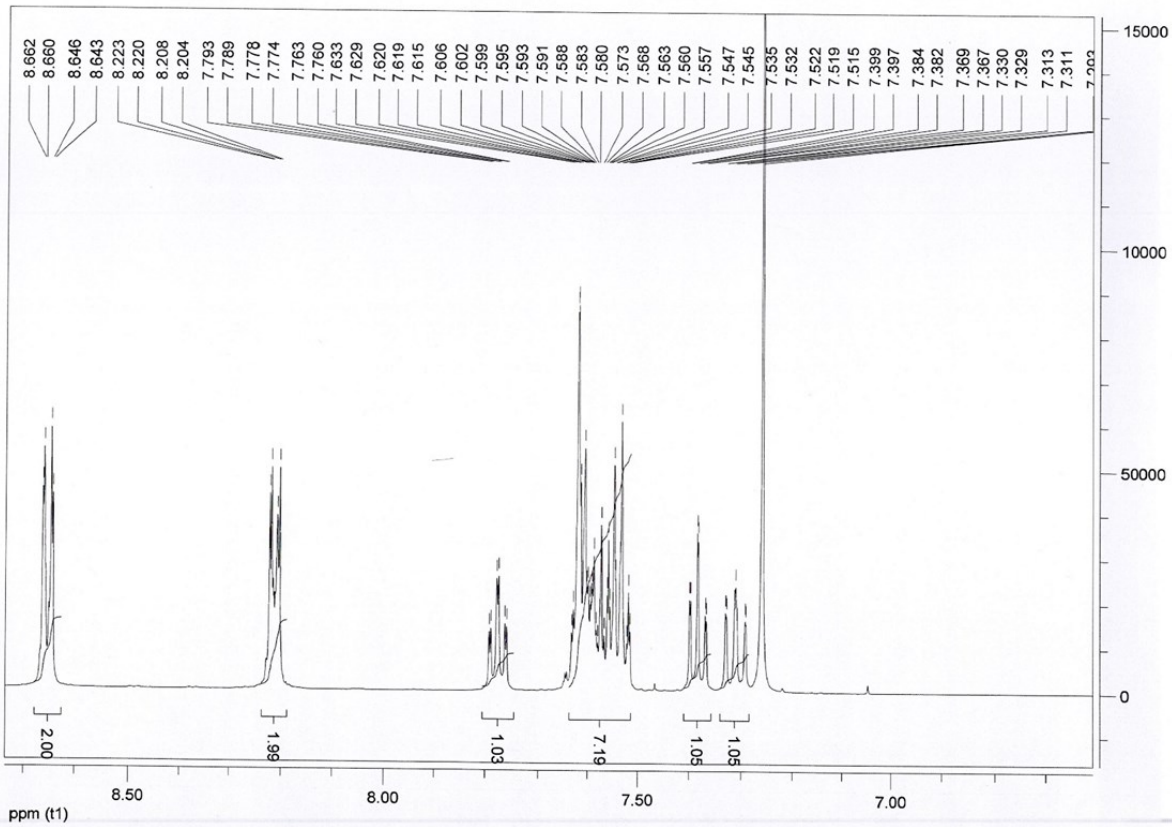
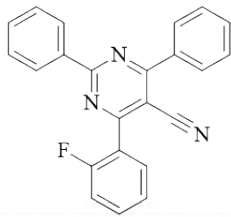
Figure S2. ^{13}C NMR spectrum of PyCNoBC

Figure S3. Amplified UV-Vis absorption spectra of PyCNoBC

Figure S4. The PyCNoBC (a) and TrzoBC (b) TADF emitter of the J-V data to dependence on the doping concentration.







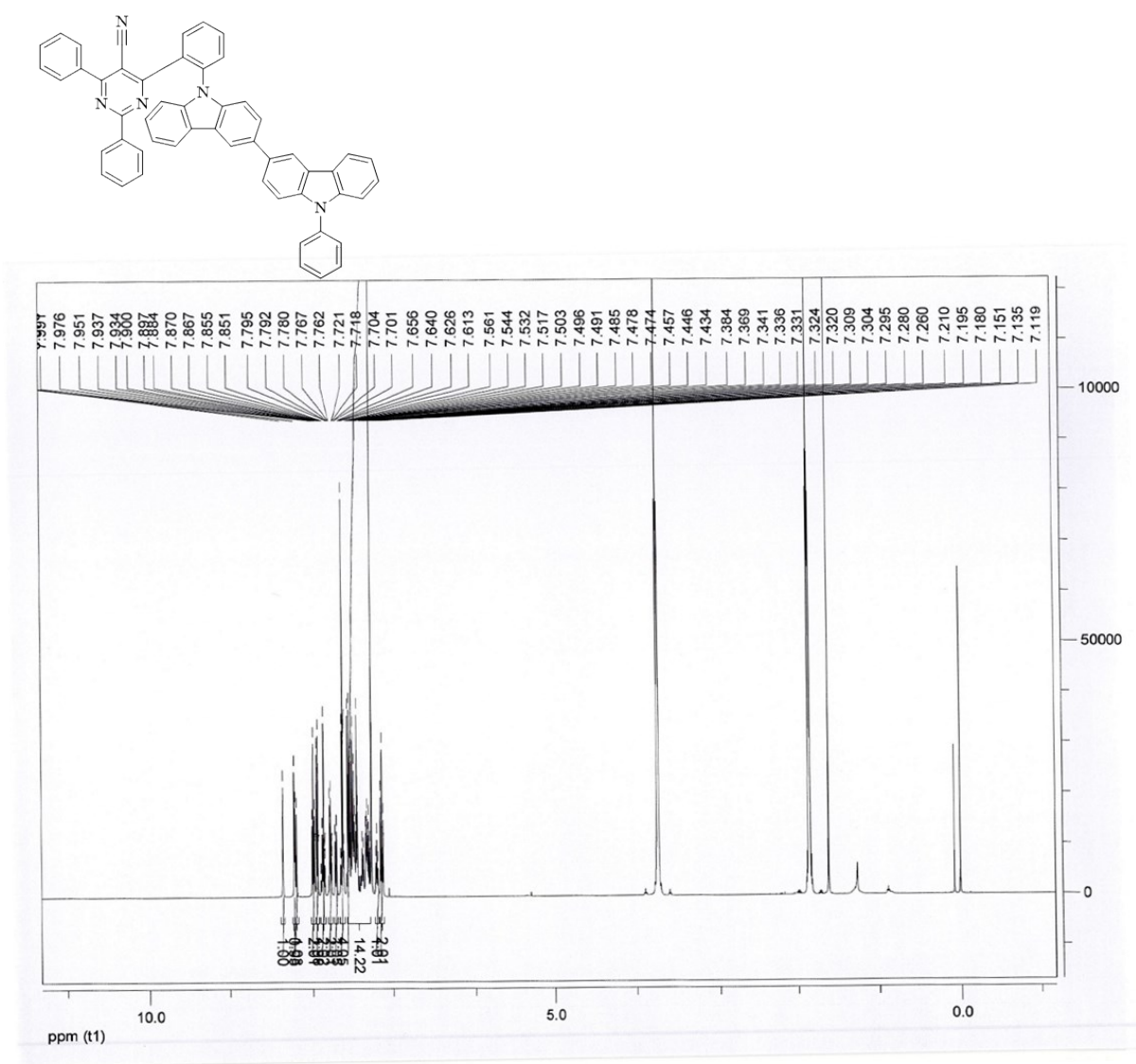


Figure S1.

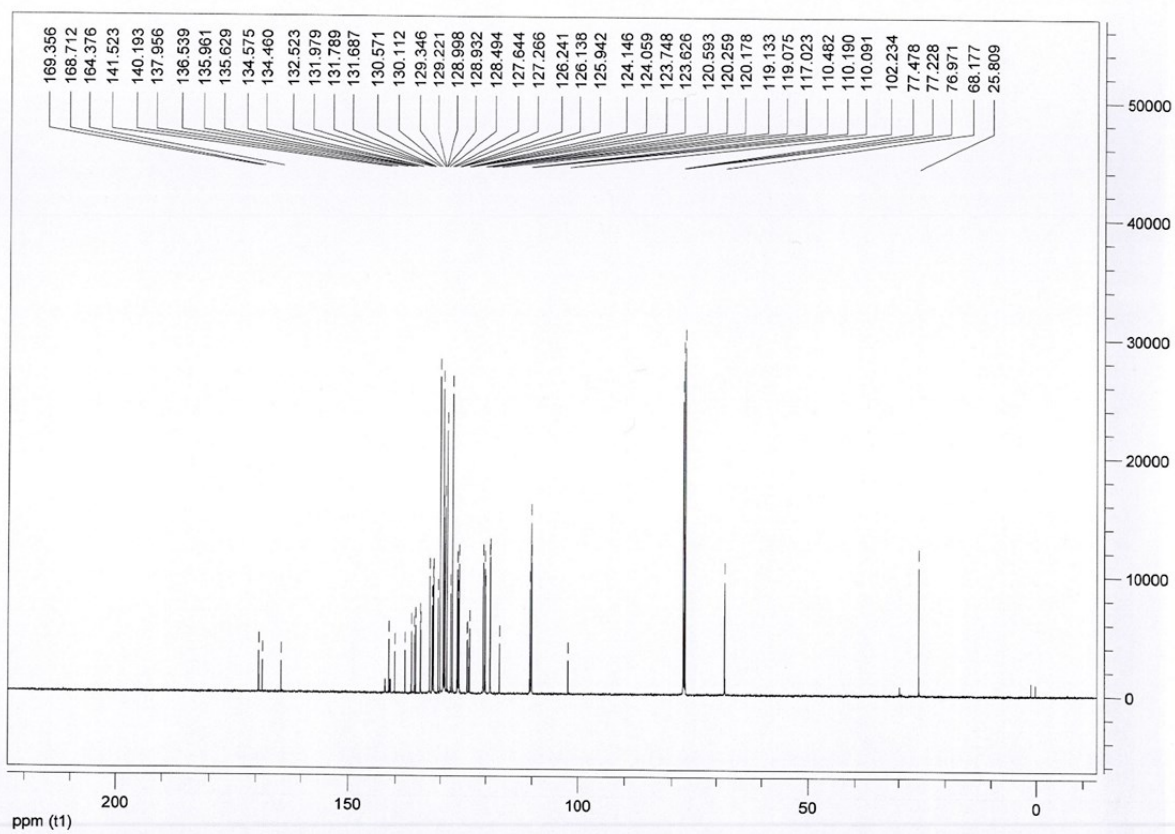
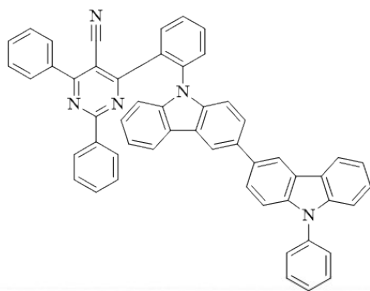


Figure S2.

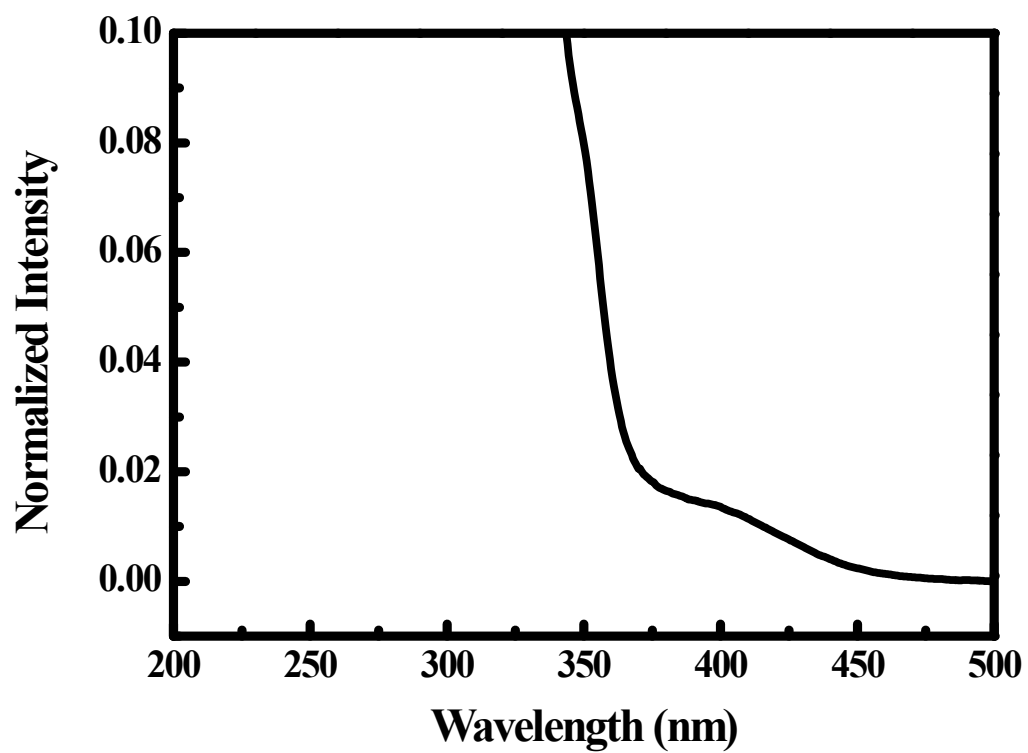


Figure S3.

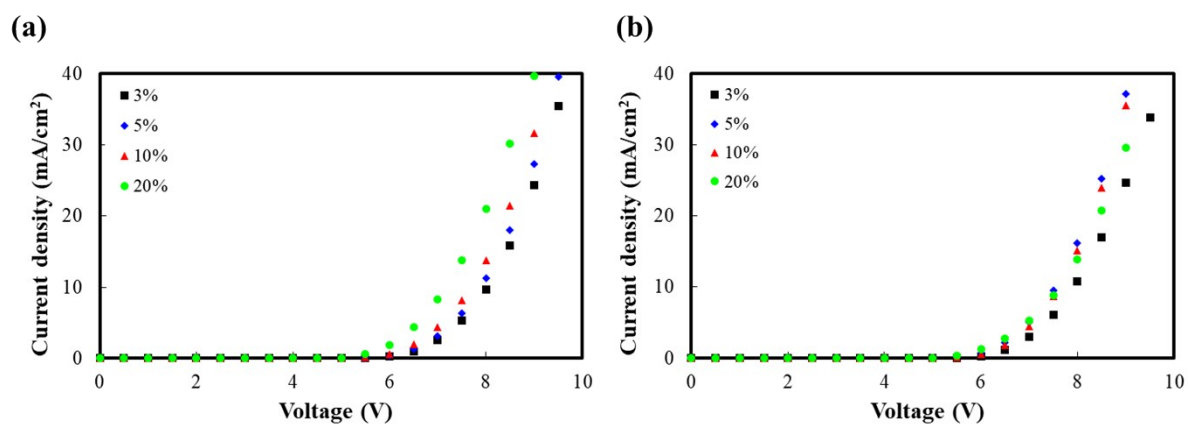


Figure S4.