

Supporting Information

Two Channel Emission Controlled by Conjugation Valve for Color Switching of Thermally Activated Delayed Fluorescence

Emission

*Rajendra Kumar Konidena, Kyung Hyung Lee, and Jun Yeob Lee**

School of Chemical Engineering, Sungkyunkwan University, 2066 Seobu-ro, Jangan-gu,
Suwon, Gyeonggi 440-746, Korea

Email: leej17@skku.edu

	Experimental section	S2
Fig. S1.	a) TGA and b) traces observed for the compounds.	S5
Fig. S2	¹ H NMR spectra of 2 recorded in CDCl ₃	S5
Fig. S3	¹ H NMR spectra of 3 recorded in CDCl ₃	S6
Fig. S4	¹ H NMR spectra of 5 recorded in CDCl ₃	S6
Fig. S5	¹ H NMR spectra of 6 recorded in CDCl ₃	S7
Fig. S6	¹ H NMR spectra of 34CzBN recorded in CDCl ₃	S7
Fig. S7	¹³ C NMR spectra of 34CzBN recorded in CDCl ₃	S8
Fig. S8	¹ H NMR spectra of 44CzBN recorded in CDCl ₃	S8
Fig. S9	¹³ C NMR spectra of 44CzBN recorded in CDCl ₃	S9

Experimental section

Materials and methods

The chemicals and solvents received from commercial suppliers were used as received. The intermediates 3-chloro-2,6-difluorobenzonitrile (**1**) and 4-bromo-2,6-difluorobenzonitrile (**4**) were purchased from TCI chemicals. All the reactions were performed under inert atmosphere. The general experimental methods used for the characterization of materials such as nuclear magnetic resonance spectroscopy (NMR), mass spectroscopy (MS), UV-visible absorption and emission spectroscopy, PLQY, transient PL analysis, thermal properties and cyclic voltammetry measurements were presented in our previous report.¹

Synthesis

2,6-difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (2). A mixture of 3-chloro-2,6-difluorobenzonitrile (5.00 g, 28.8 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (8.30 g, 31.6 mmol), [bis(diphenylphosphino)ferrocene]palladium(II) dichloride (0.84 g, 0.78 mmol), potassium acetate (4.68 g, 46.83 mmol) was dissolved in 50 mL of 1,4-dioxane. The reaction mixture was refluxed at 100 °C for 6 h. The progress of reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, extraction with dichloromethane, drying over magnesium sulfate and evaporation of the solvent were carried out. A crude product was purified by column chromatography using dichloromethane (DCM):hexanes (1:3) as an eluent, which produced the intermediate **2** as a colorless solid (4.56 g, 60%). ¹H NMR (500 MHz, CDCl₃, δ ppm): 8.01-7.97 (m, 1H), 7.07-7.03 (m, 1H). ¹³C NMR (CDCl₃, δ ppm): 168.99, 166.66, 164.31, 142.84, 112.15, 109.50, 84.85, 25.63. MS (APCI) *m/z* 266.10 [(M+H)⁺].

2,3',4,5'-tetrafluoro-[1,1'-biphenyl]-3,4'-dicarbonitrile (3). A mixture of **2** (3.00 g, 11.0 mmol), 4-bromo-2,6-difluorobenzonitrile (2.62 g, 12.1 mmol), potassium carbonate (4.58 g, 33.0 mmol), and tetrakis(triphenylphosphine)-palladium(0) (0.63 g, 0.55 mmol) was dissolved

in tetrahydrofuran:H₂O (3:1) and degassed with N₂ for 15 min. The reaction mixture was refluxed at 80 °C for 4 h. After completion of the reaction, extraction with dichloromethane, drying over magnesium sulfate and evaporation of the solvent were carried out. The crude mixture was purified on column chromatography using DCM:hexanes (1:4) as an eluent to get the intermediate **3** in yellow solid (2.4 g, 80%). ¹H NMR (500 MHz, CDCl₃, δ ppm): 7.73-7.69 (m, 1H), 7.26-7.22 (m, 3H). ¹³C NMR (CDCl₃, δ ppm): 164.48, 162.53, 160.92, 158.67, 140.30, 135.62, 113.65, 112.84, 108.70. MS (APCI) *m/z* 277.01 [(M+H)⁺].

2,3',4,5'-tetra(9*H*-carbazol-9-yl)-[1,1'-biphenyl]-3,4'-dicarbonitrile (34CzBN). A mixture of **3** (1.00 g, 3.6 mmol), 9*H*-carbazole (2.43 g, 14.4 mmol) and cesium carbonate (14.0 g, 43.2 mmol) were added to a pressure tube containing 10 ml of dimethylformamide. The reaction mixture was kept for heat at 150 °C for 3 h. Progress of the reaction was examined by TLC analysis. After completion of the reaction, extraction with DCM and drying over MgSO₄ and the evaporation of solvent gave the yellow residue. The crude reaction mixture was purified on column chromatography using DCM:hexanes (1:1) as an eluent to get **34CzBN** (2.60 g, 85% yield) in colorless solid. ¹H NMR (500 MHz, CDCl₃, δ ppm): 8.15 (d, *J* = 10.0 Hz, 2H), 8.12 (d, *J* = 10.0 Hz, 4H), 8.05 (d, *J* = 10.0 Hz, 1H), 7.92-7.87 (m, 3H), 7.50-7.34 (m, 18H), 7.27-7.24 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 4H). ¹³C NMR (CDCl₃, δ ppm): 143.83, 143.37, 143.01, 140.42, 140.28, 139.16, 136.16, 135.07, 133.32, 130.00, 128.07, 126.76, 126.40, 124.55, 124.08, 121.75, 121.35, 121.01, 120.69, 115.36, 112.85, 112.74, 109.85, 109.59, 101.33. MS (APCI) *m/z* 865.30 [(M+H)⁺]. Elemental analysis (%): calculated for C₆₂H₃₆N₆; C, 86.09; N, 9.72; H, 4.19. found: C, 86.27; N, 9.51; H, 4.39.

2,6-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrile (5). The intermediate **5** were prepared from **1** (3.00 g, 13.8 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (4.00 g, 15.8 mmol), [bis(diphenylphosphino)ferrocene]palladium(II)

dichloride (0.49 g, 0.41 mmol) and potassium acetate (4.09 g, 41.4 mmol) according to the above procedure described for **2**. Colorless solid (2.00 g, 55%). ¹H NMR (500 MHz, CDCl₃, δ ppm): 7.44-7.42 (m, 2H). ¹³C NMR (CDCl₃, δ ppm): 164.91, 163.54, 162.38, 161.63, 117.42, 111.09, 109.72, 108.34, 85.47, 25.15. MS (APCI) *m/z* 266.12 [(M+H)⁺].

3,3',5,5'-tetrafluoro-[1,1'-biphenyl]-4,4'-dicarbonitrile (6). The intermediate **6** were prepared from **5** (1.50 g, 5.4 mmol), 4-bromo-2,6-difluorobenzonitrile (1.40 g, 6.48 mmol), potassium carbonate (2.20 g, 16.2 mmol), and tetrakis(triphenylphosphine)-palladium(0) (0.31 g, 0.27 mmol) using similar procedure described for **3**. Colorless solid (1.05 g, 75%). ¹H NMR (500 MHz, CDCl₃, δ ppm): 7.29 (s, 4H). ¹³C NMR (CDCl₃, δ ppm): 165.13, 162.79, 144.86, 110.94, 108.26, 93.68. MS (APCI) *m/z* 277.03 [(M+H)⁺].

3,3',5,5'-tetra(9H-carbazol-9-yl)-[1,1'-biphenyl]-4,4'-dicarbonitrile (44CzBN). The compound **44CzBN** were prepared from **6** (1.00 g, 3.6 mmol), 9H-carbazole (2.43 g, 14.4 mmol) and cesium carbonate (14.0 g, 43.2 mmol) using similar procedure described for **34CzBN**. Green solid (2.1g, 74%). ¹H NMR (500 MHz, CDCl₃, δ ppm): 8.56 (s, 1H), 8.14-8.12 (m, 1H), 7.90-7.88 (m, 2H), 7.56-7.53 (m, 2H), 7.37-7.34 (m, 2H), 1.45 (s, 1H). ¹³C NMR (CDCl₃, δ ppm): 144.43, 144.24, 140.56, 127.38, 126.80, 124.42, 121.71, 121.09, 109.68. MS (APCI) *m/z* 865.32 [(M+H)⁺]. Elemental analysis (%): calculated for C₆₂H₃₆N₆; C, 86.09; N, 9.72; H, 4.19. found: C, 86.28; N, 9.63; H, 3.98.

Device fabrication

The employed device structure is indium tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 60 nm)/4,40-cyclohexylidenebis[*N,N*-bis(4-methylphenyl)aniline] (TAPC, 20 nm)/1,3-bis(*N*-carbazolyl)benzene (mCP, 10 nm)/DPEPO: **CzBN** or **34CzBN** or **44CzBN** (25 nm, 10%)/diphenylphosphine oxide-4-(triphenylsilyl) phenyl (TSPO1, 5 nm)/2,20,200-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBi) (20 nm)/LiF(1.5 nm)/Al(200 nm).

Vacuum evaporation process was used as fabrication method of the devices. All devices were optically and electrically tested using a CS 2000 spectroradiometer and Keithley 2400 after compressing all devices.

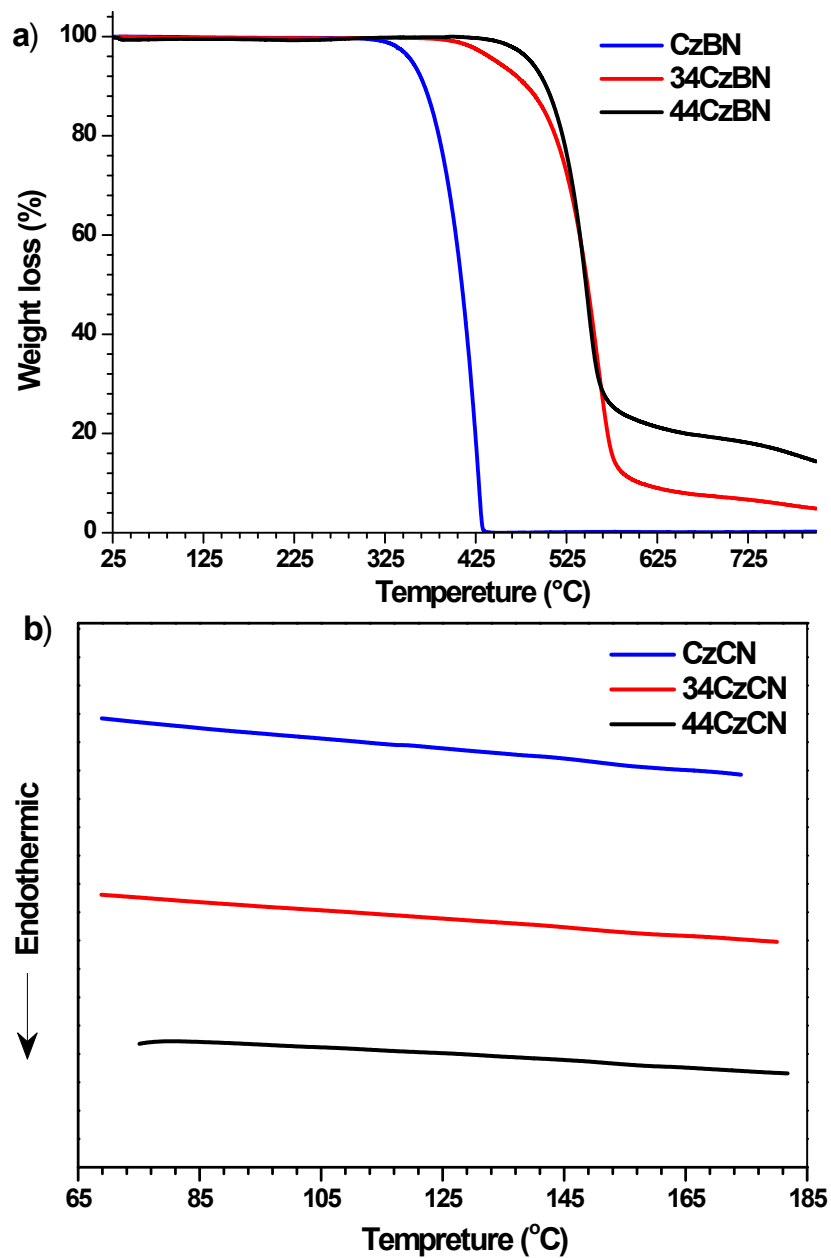


Fig. S1 a) TGA and b) DSC traces observed for the compounds.

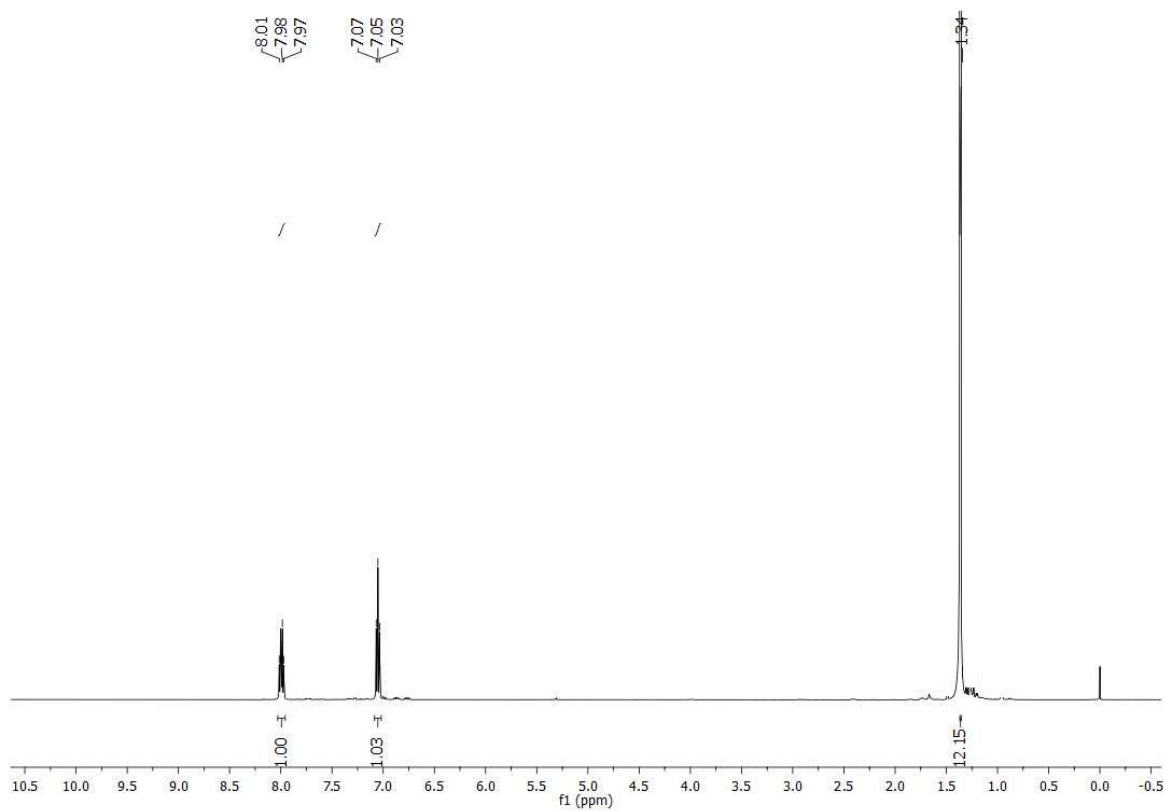


Fig. S2 ^1H NMR spectra of **2** recorded in CDCl_3

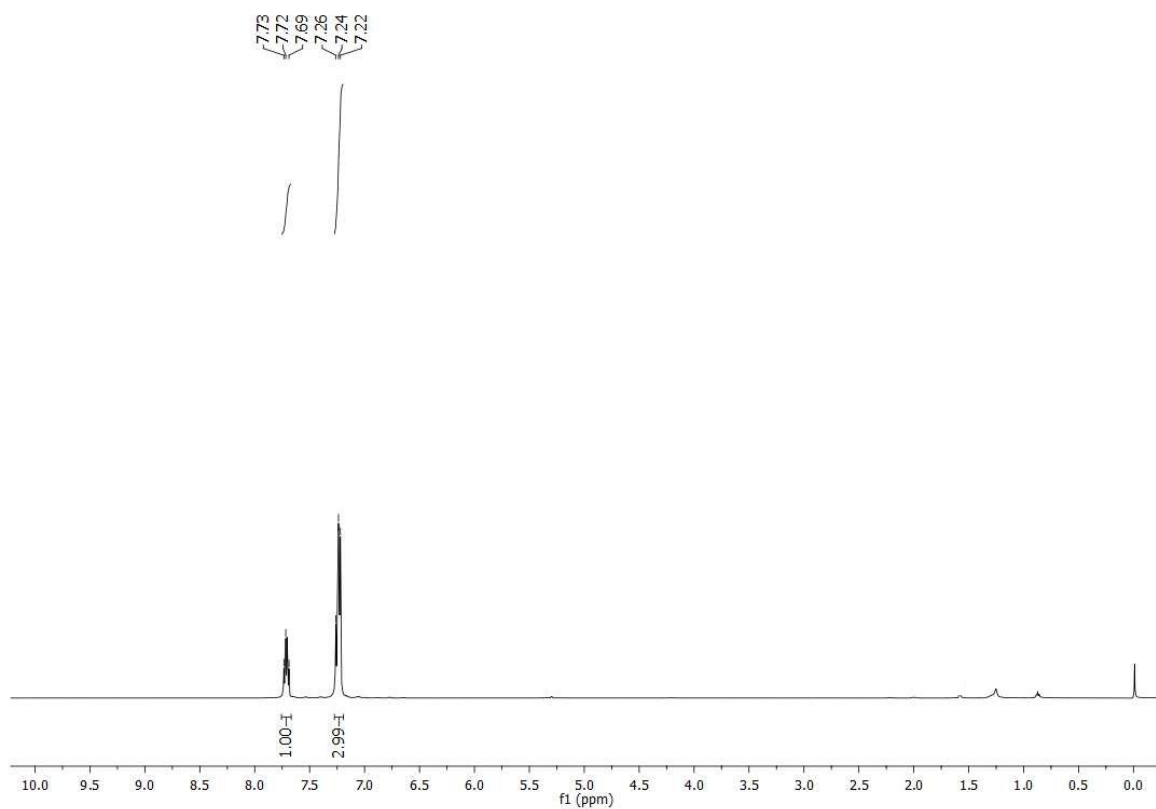


Fig. S3 ^1H NMR spectra of **3** recorded in CDCl_3

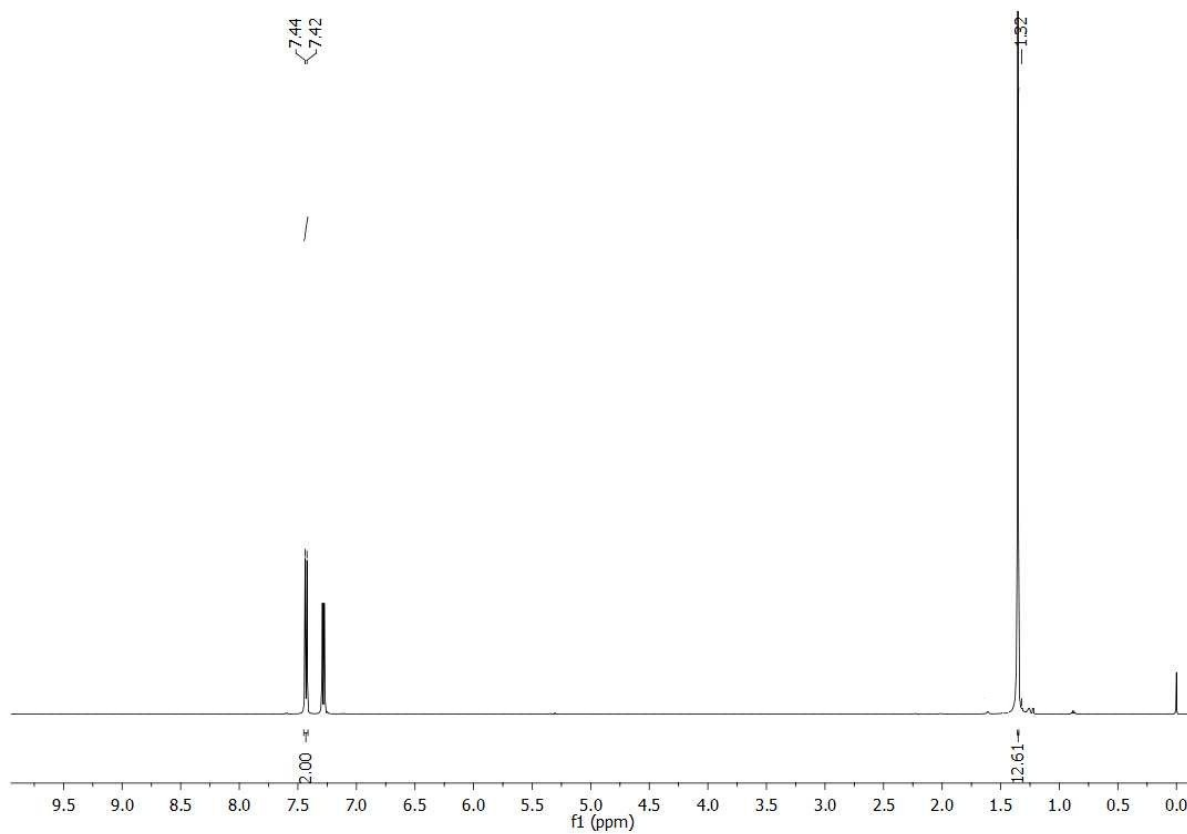


Fig. S4 ^1H NMR spectra of **5** recorded in CDCl_3

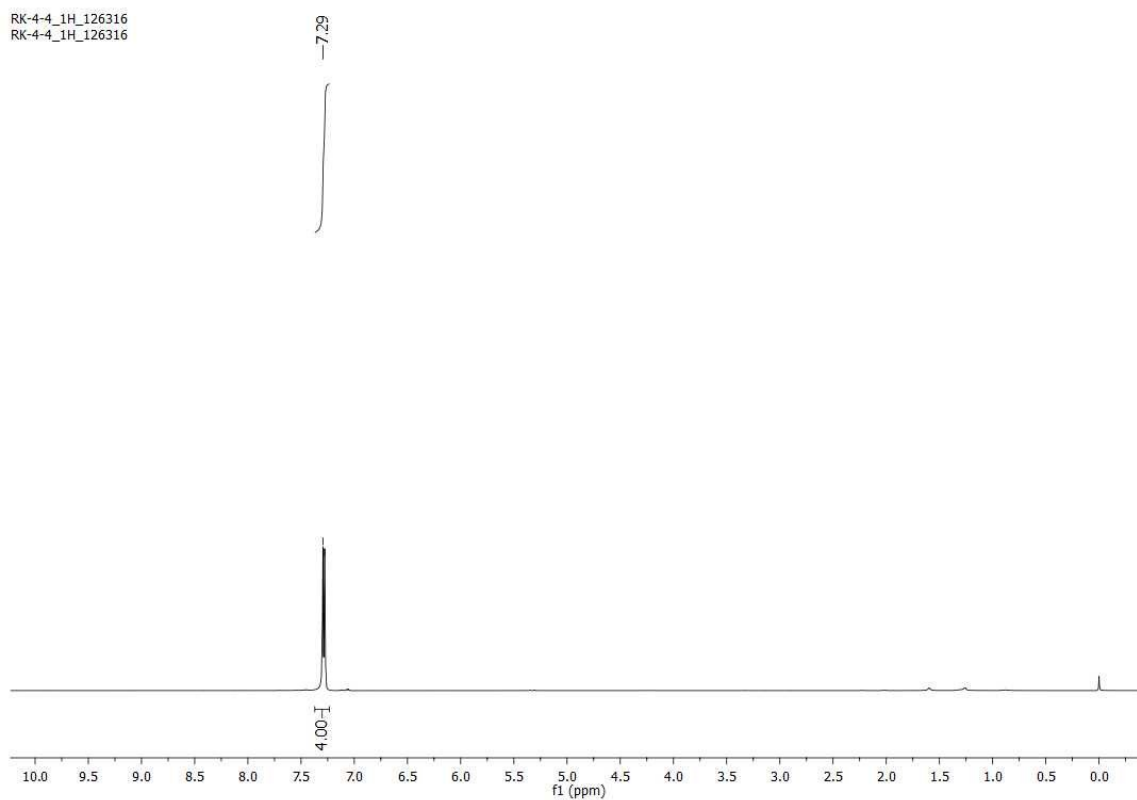


Fig. S5 ^1H NMR spectra of **6** recorded in CDCl_3

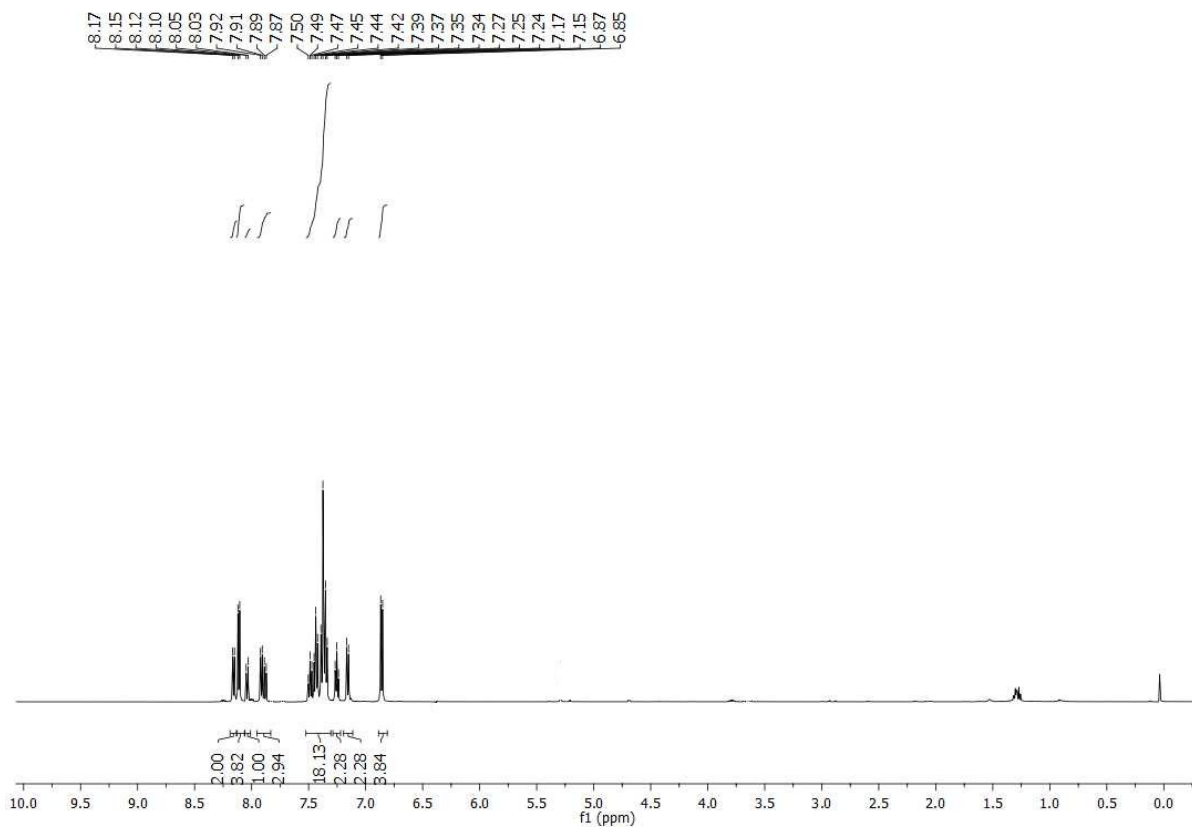


Fig. S6 ^1H NMR spectra of **34CzBN** recorded in CDCl_3

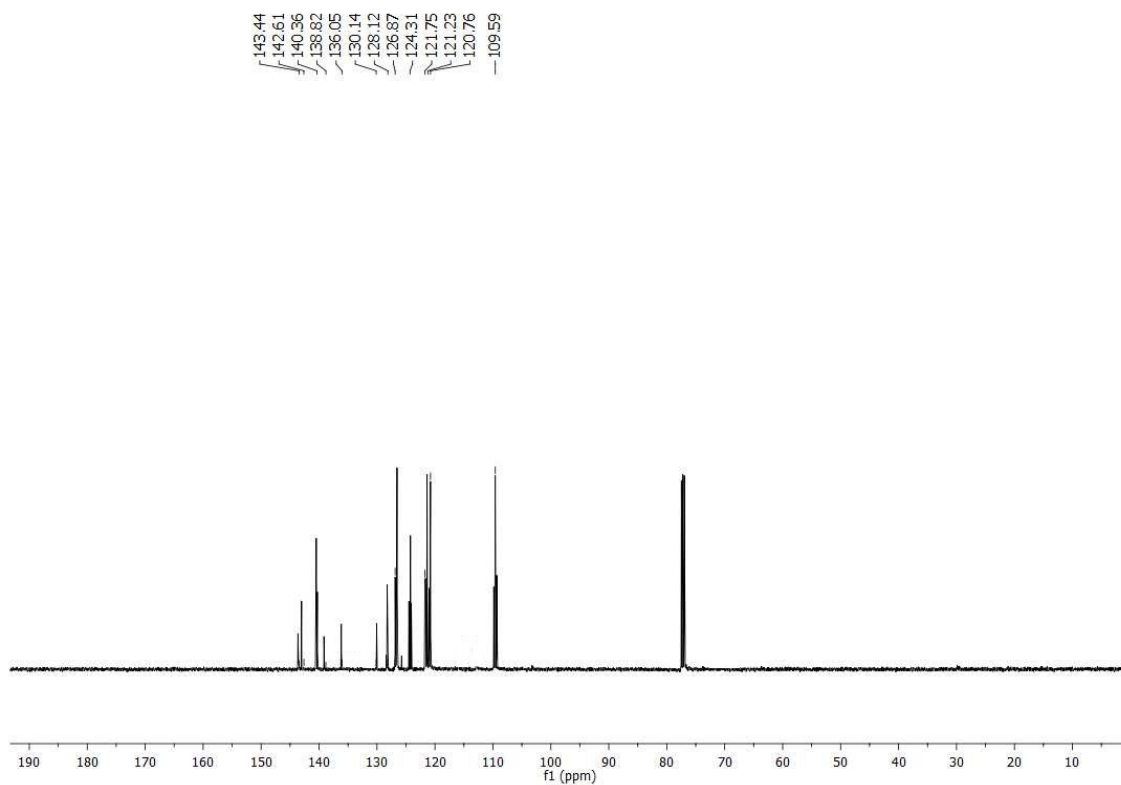


Fig. S7 ^{13}C NMR spectra of **34CzBN** recorded in CDCl_3

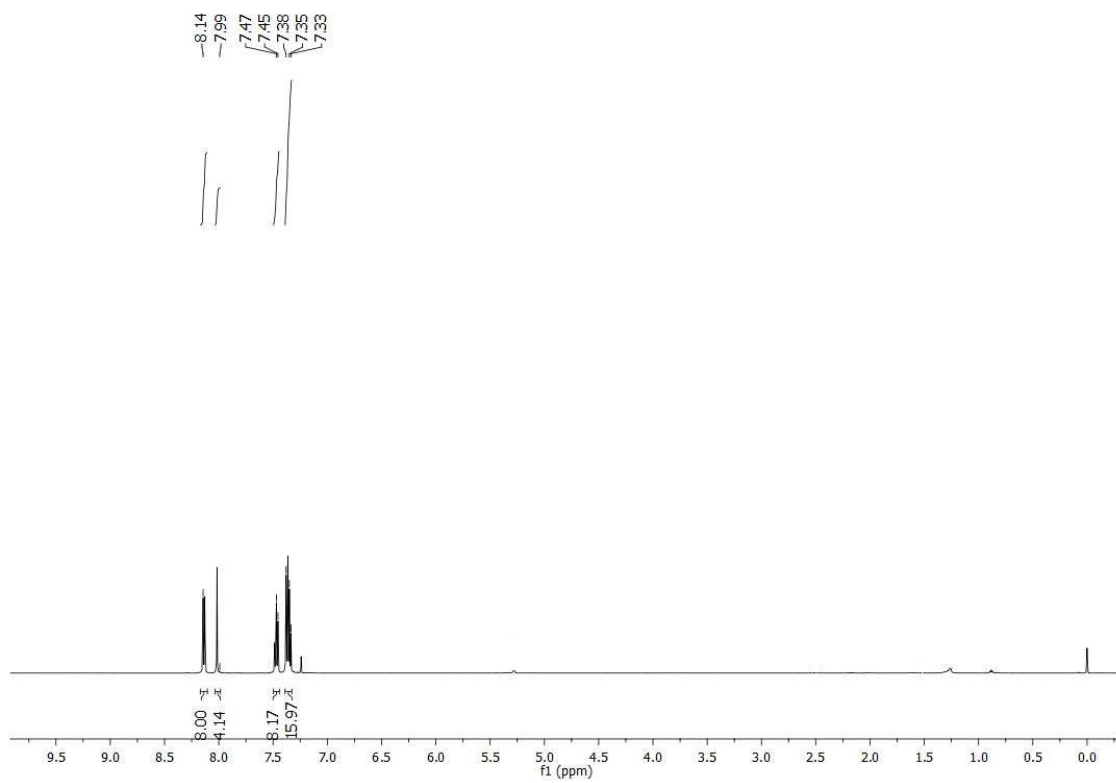


Fig. S8 ^1H NMR spectra of **44CzBN** recorded in CDCl_3

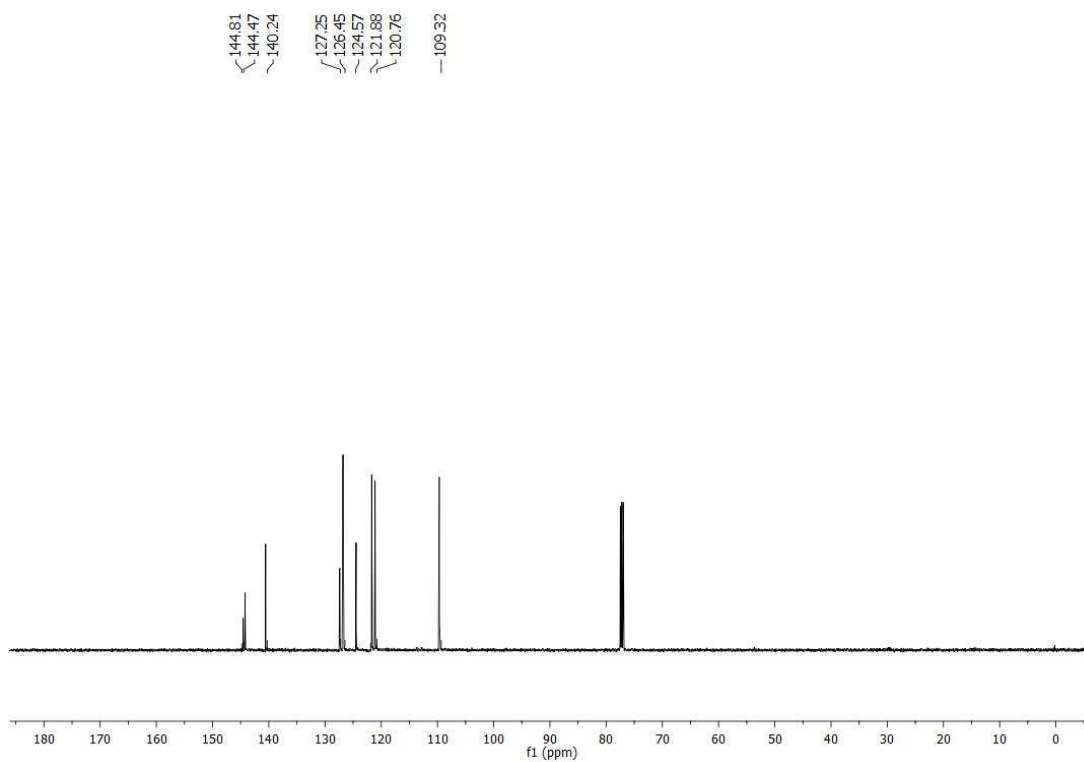


Fig. S9 ^{13}C NMR spectra of **44CzBN** recorded in CDCl_3

References

1. S. Y. Byeon, J. Kim, D. R. Lee, S. H. Han, S. R. Forrest and J. Y. Lee, *Adv. Optical Mater.* 2018, **6**, 1701340.