Supplementary Information (SI) for Nanoscale.

# Supplementary Information

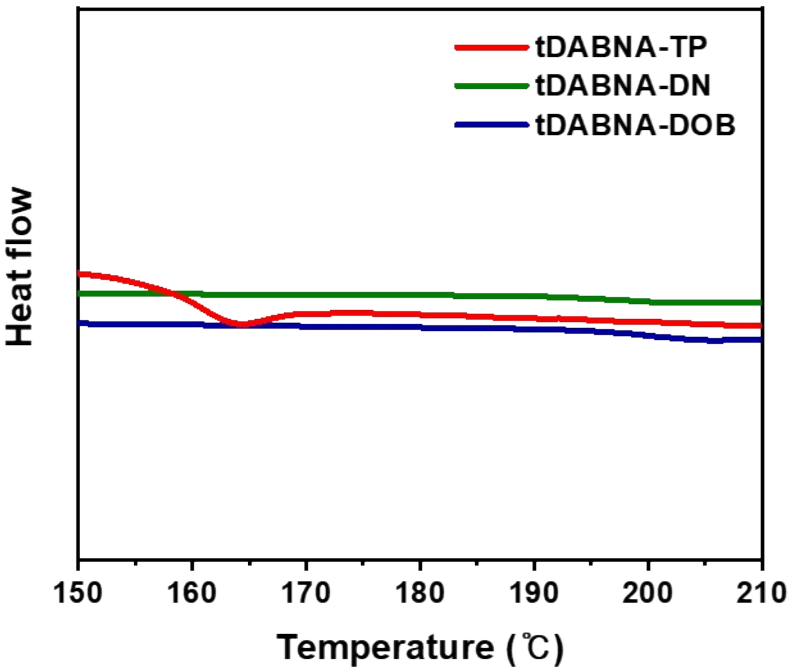
# Pendant engineering in multiple-resonance thermally activated delayed fluorescence to yield charge-transfer and locally excited-state characteristics

**Jeong Yeol Yoo,[†] Tae Hoon Ha,[†] and Chil Won Lee ***

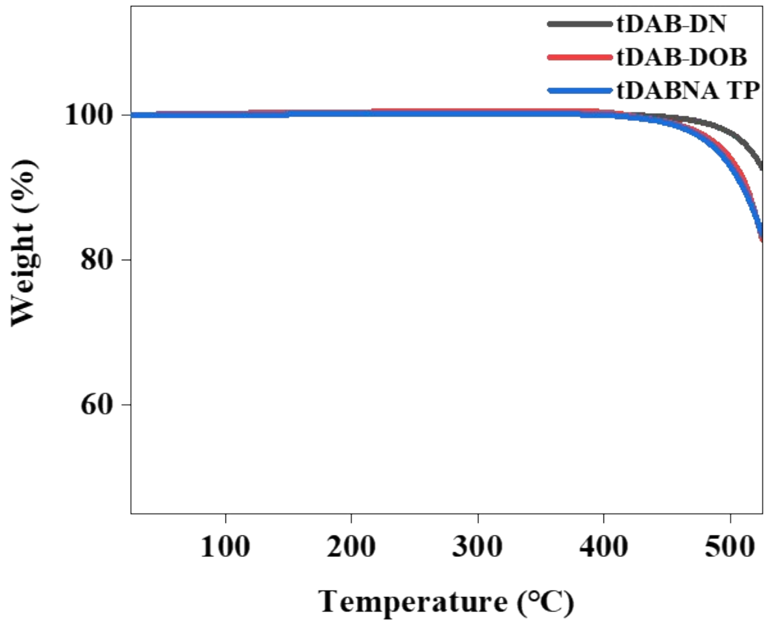
*Department of Chemistry, Dankook University, Cheonan 31116, South Korea*

[†] These authors contributed equally to this work.

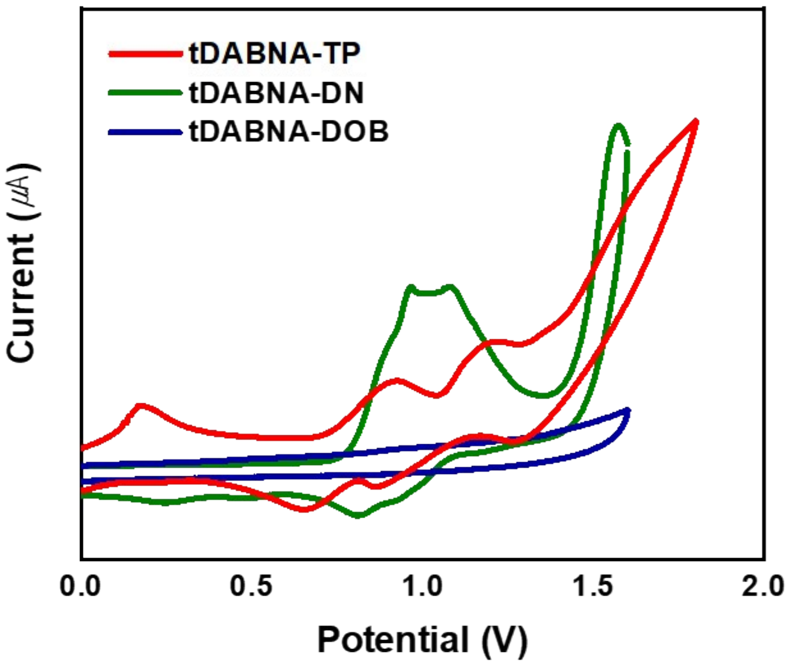
[*] Corresponding author email: chili@dankook.ac.kr



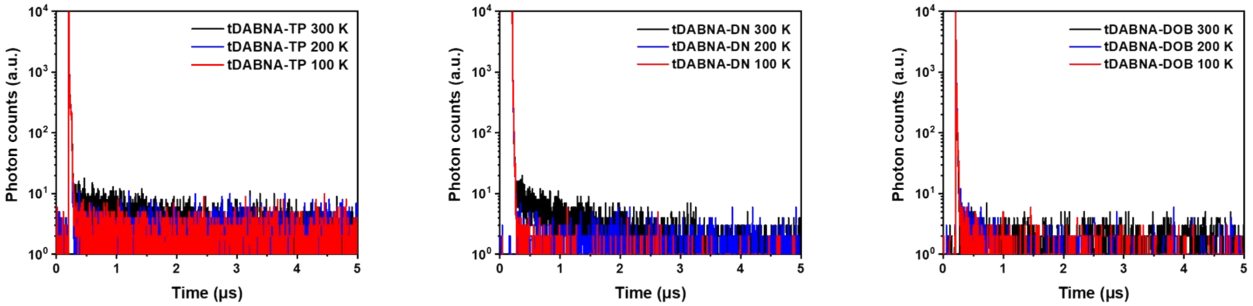
**Supplementary Fig. S1.** Thermal properties: Differential scanning calorimetry thermograms of the MR-TADF emitters.



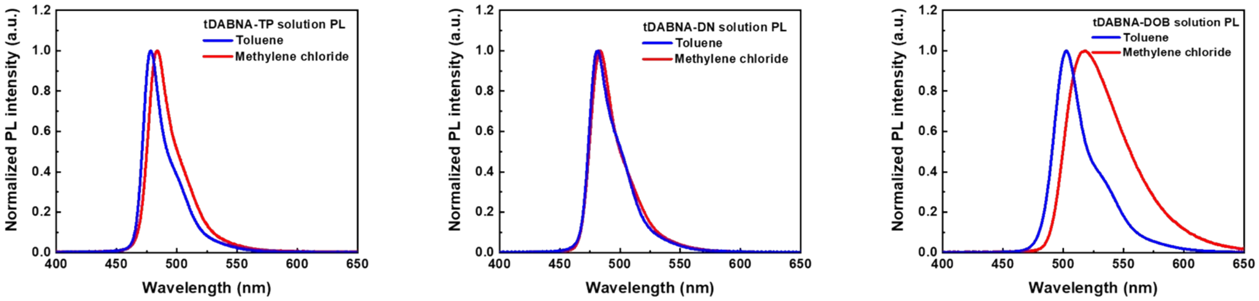
**Supplementary Fig. S2.** The thermal gravimetric analysis (TGA) measurement of MR-TADF emitters.



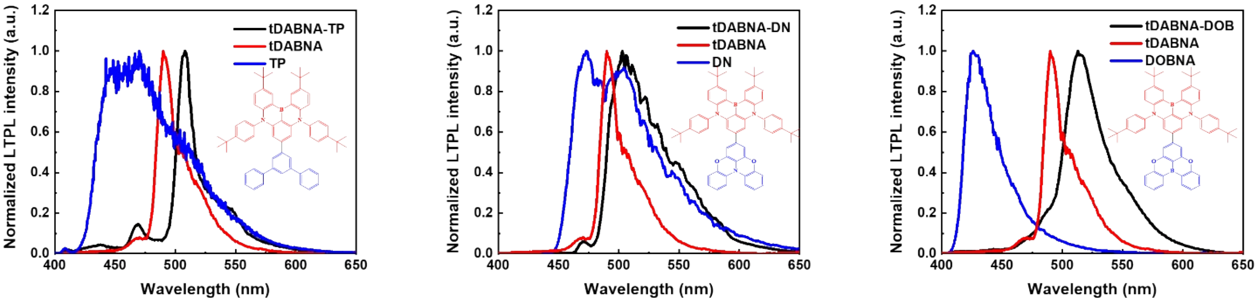
**Supplementary Fig. S3.** Electrochemical properties: Cyclic voltammograms of the MR-TADF emitters.



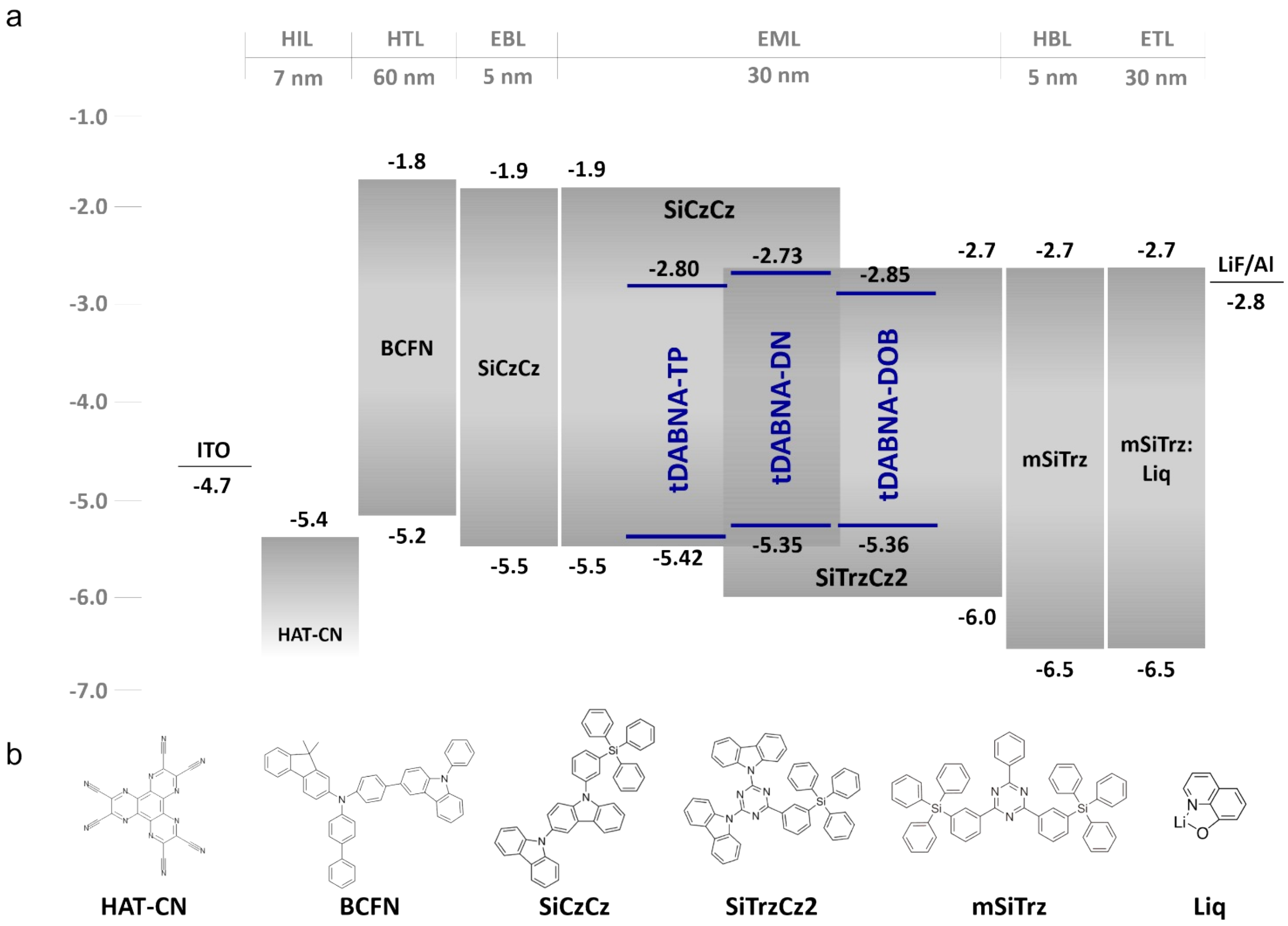
**Supplementary Fig. S4.** Levels of temperature-dependent transient PL decay of the MR-TADF emitters (1 wt.%) in the SiCzCz:SiTrzCz2 co-host films (black: 300 K; red: 200 K; blue: 100 K).



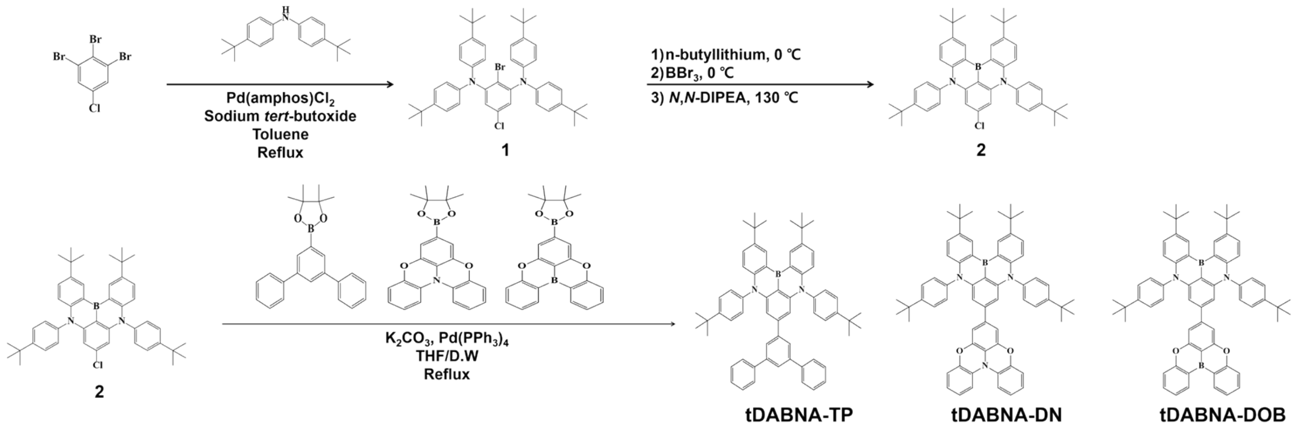
**Supplementary Fig. S5.** Room-temperature PL spectra of the MR-TADF emitters in different solvents (blue line: toluene; red line: dichloromethane).



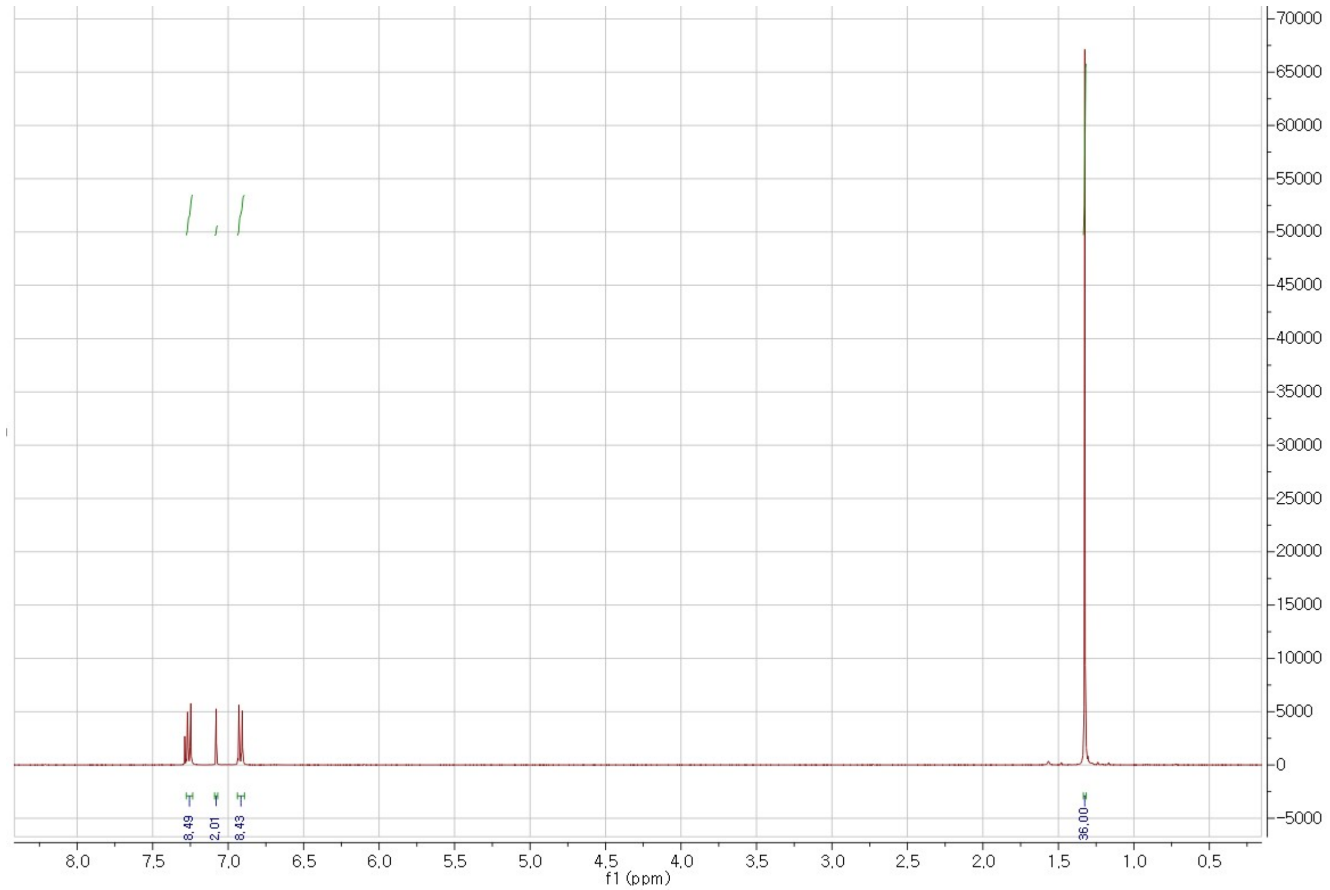
**Supplementary Fig. S6.** Low-temperature PL spectra of the MR-TADF emitters (black line: MR-TADF; red line: tDABNA; blue line: substituent).



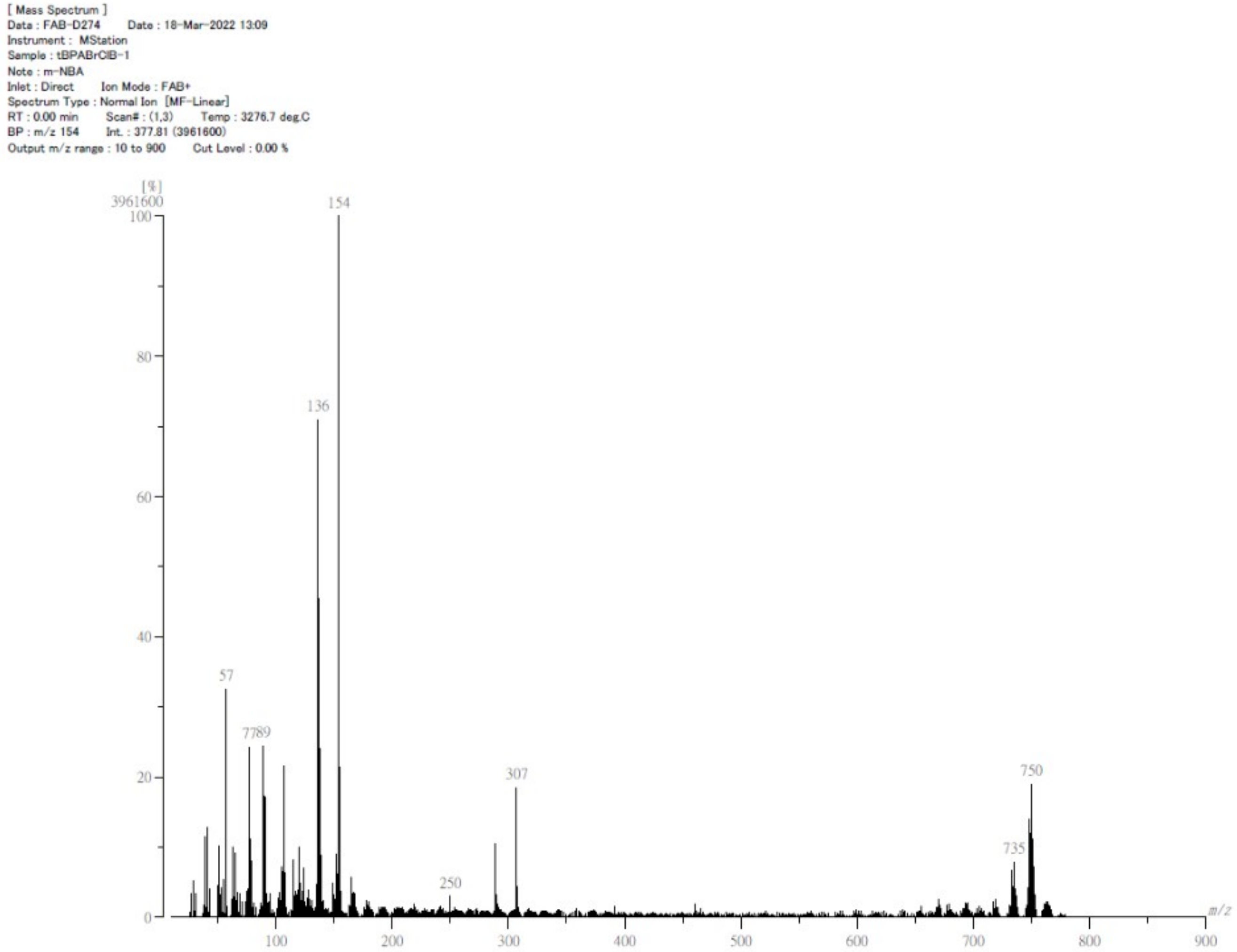
**Supplementary Fig. S7.** OLED device configuration: (a) Energy level diagram and thickness of the device. (b) Molecular structures of the OLED materials.



**Supplementary Fig. S8.** Synthetic route used in preparing the MR-TADF emitters.

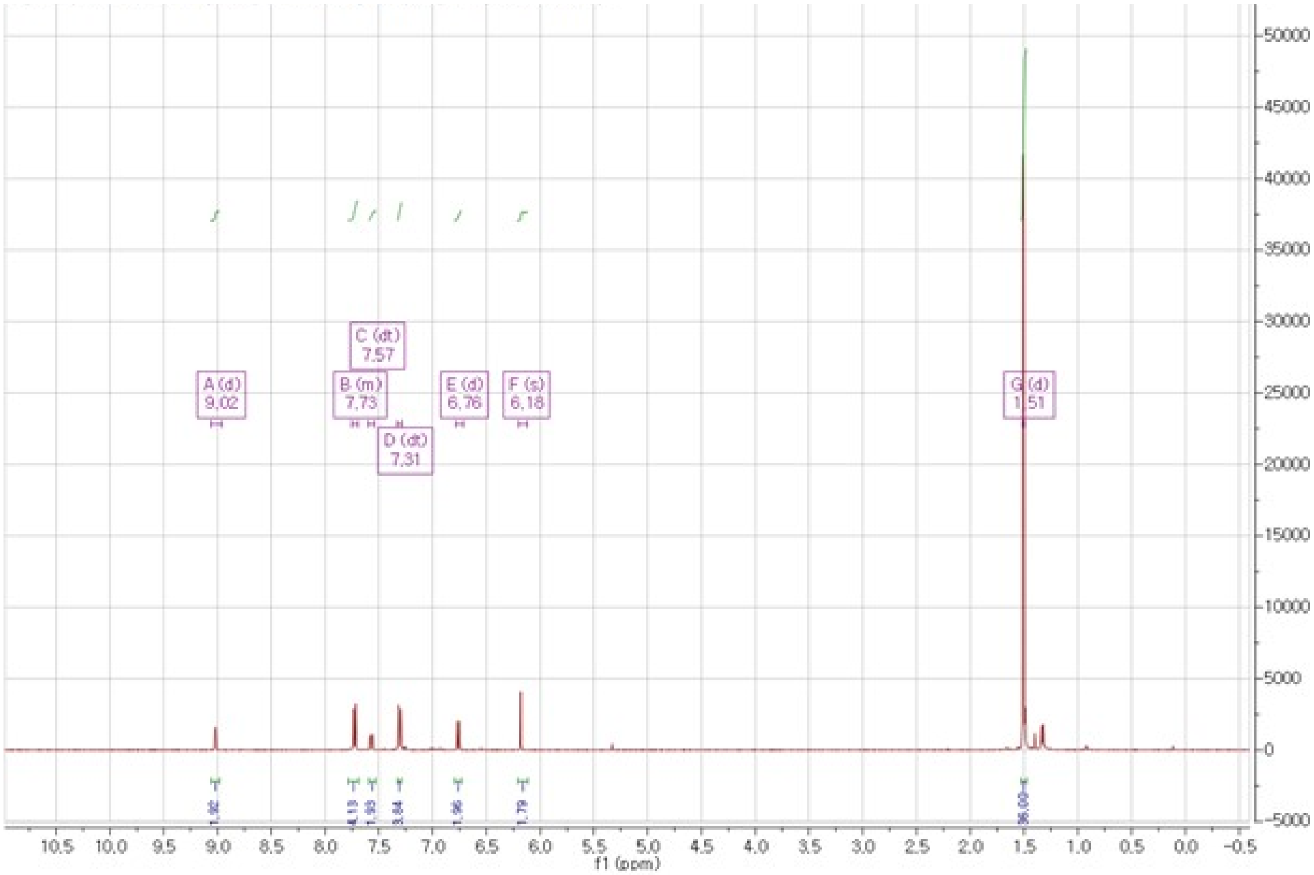


**Supplementary Fig. S9.** $^1$H-NMR spectrum of **1**.

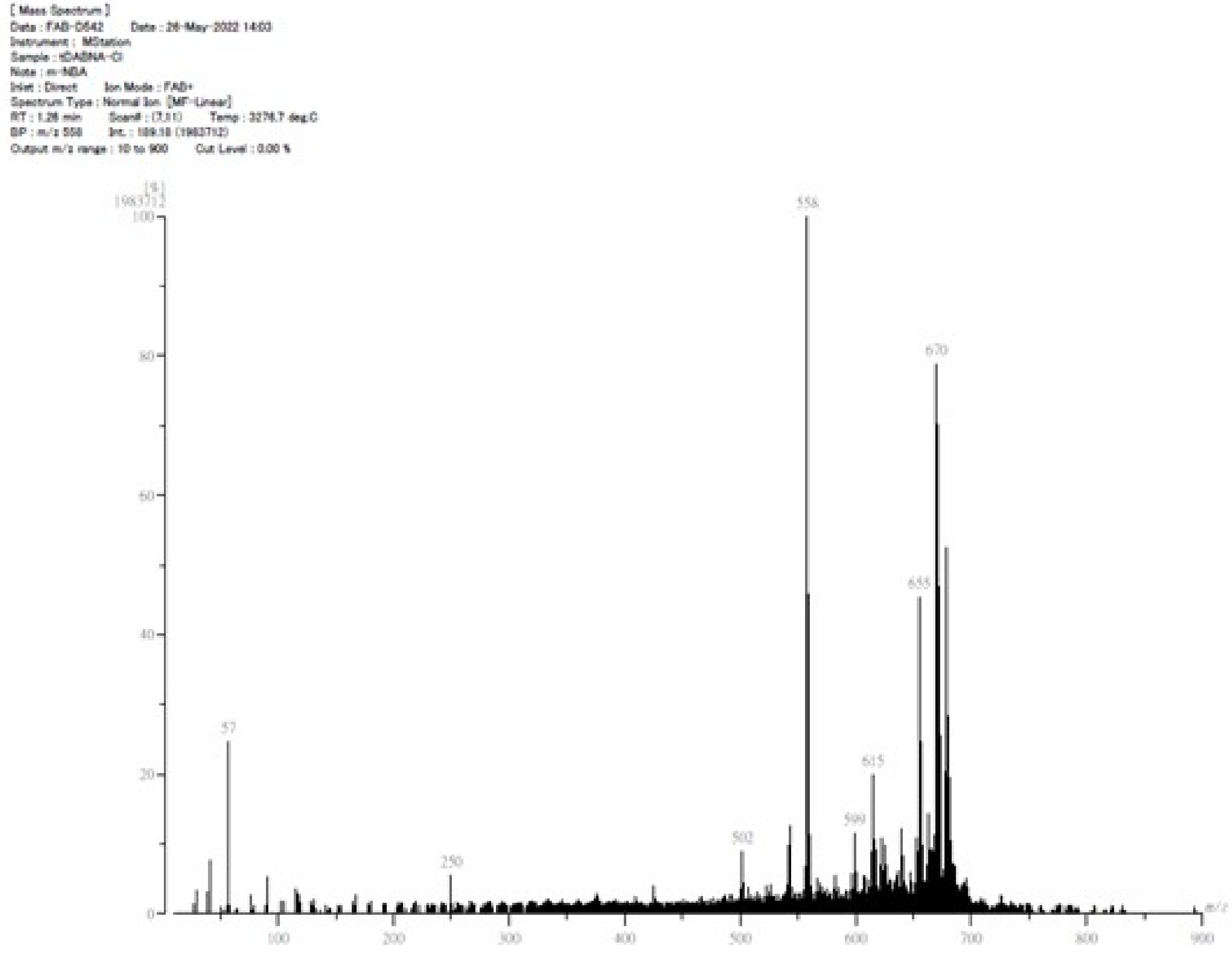


[ Mass Spectrum ]
Data : FAB-D274 Date : 18-Mar-2022 13:09
Instrument : MStation
Sample : tBPABrClB-1
Note : m-NBA
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.00 min Scan# : (1,3) Temp : 3276.7 deg.C
BP : m/z 154 Int. : 377.81 (3961600)
Output m/z range : 10 to 900 Cut Level : 0.00 %

**Supplementary Fig. S10.** Gas chromatography (GC)-mass spectrum of **1**.

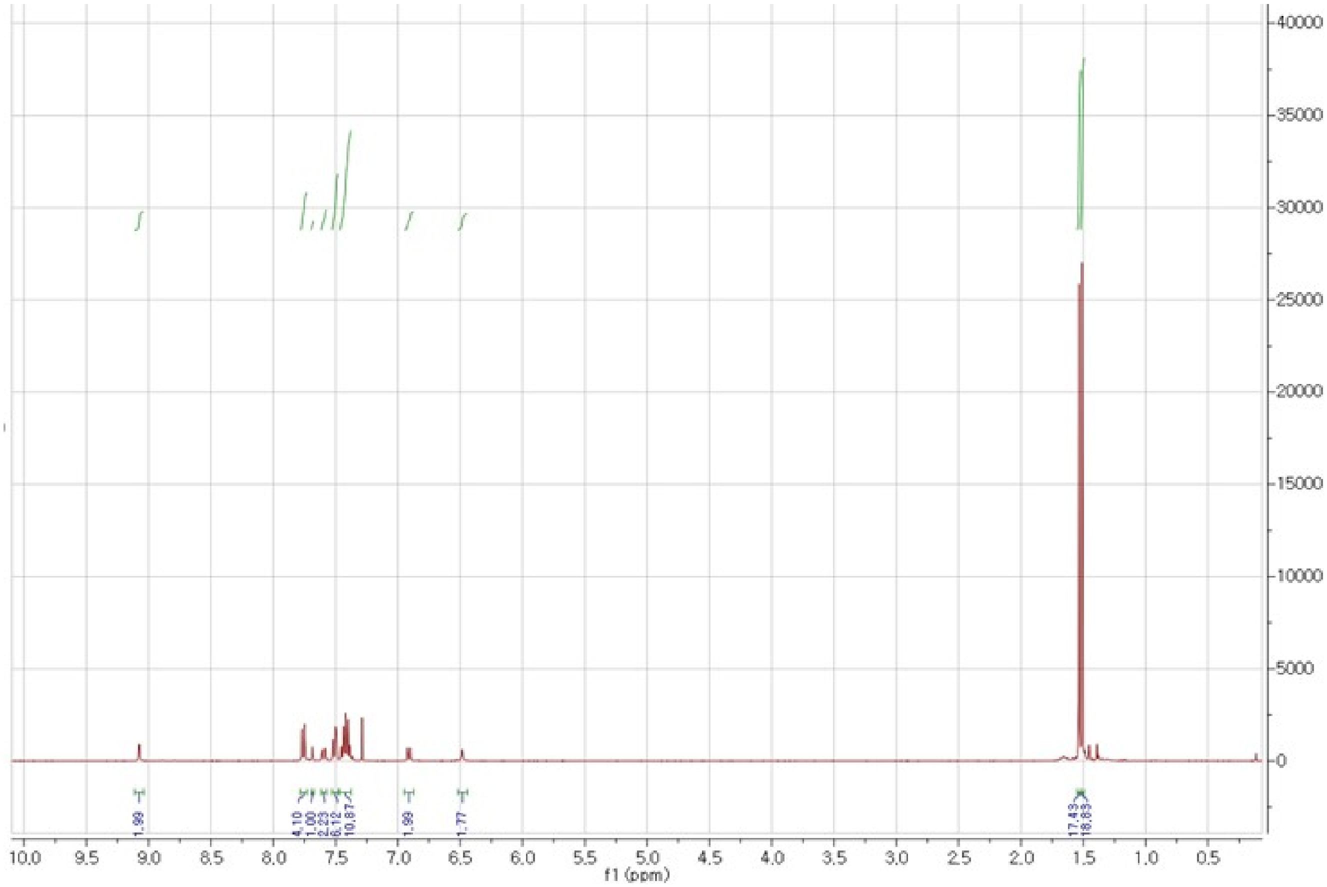


**Supplementary Fig. S11.** $^1$H-NMR spectrum of **2**.

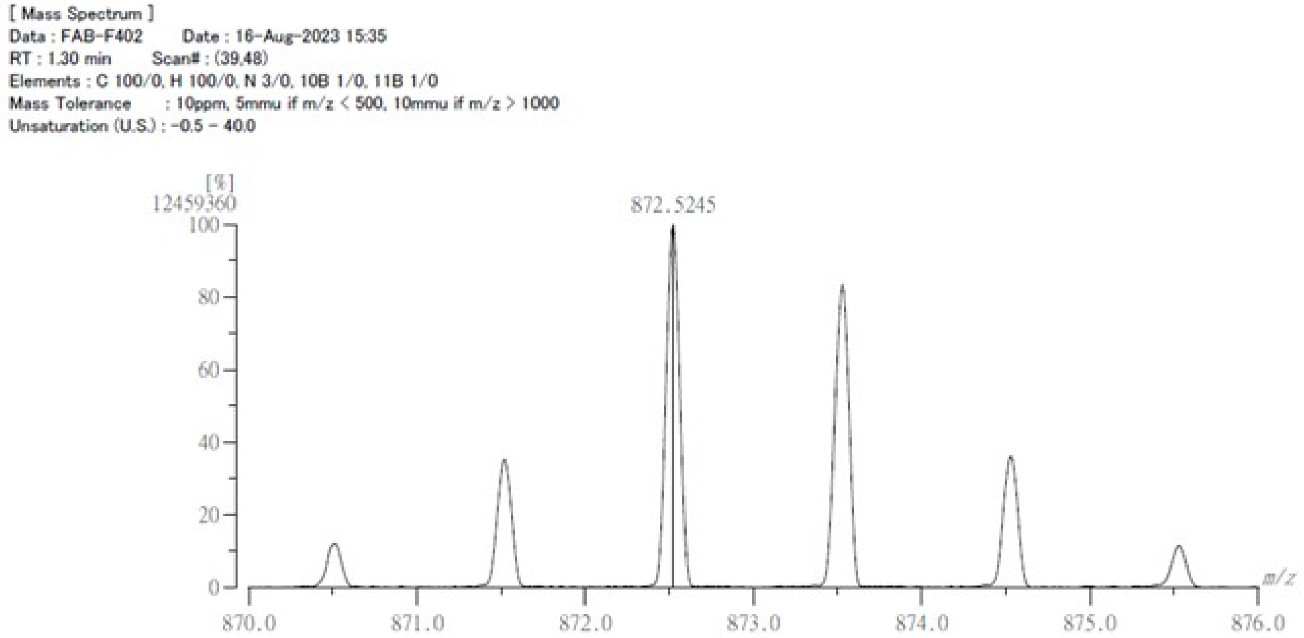


```
[ Mass Spectrum ]
Data : FAB-0542       Date : 26-May-2022 14:03
Instrument :  MStation
Sample : tDABNA-Cl
Note : m-NBA
Inlet : Direct       Ion Mode : FAB+
Spectrum Type : Normal Ion  [MF-Linear]
RT : 1.28 min       Scan# : (7,11)       Temp : 3276.7 deg.C
BP : m/z 558       Int. : 169.18 (1983712)
Output m/z range : 10 to 900       Cut Level : 0.00 %
```

**Supplementary Fig. S12.** GC-mass spectrum of **2**.

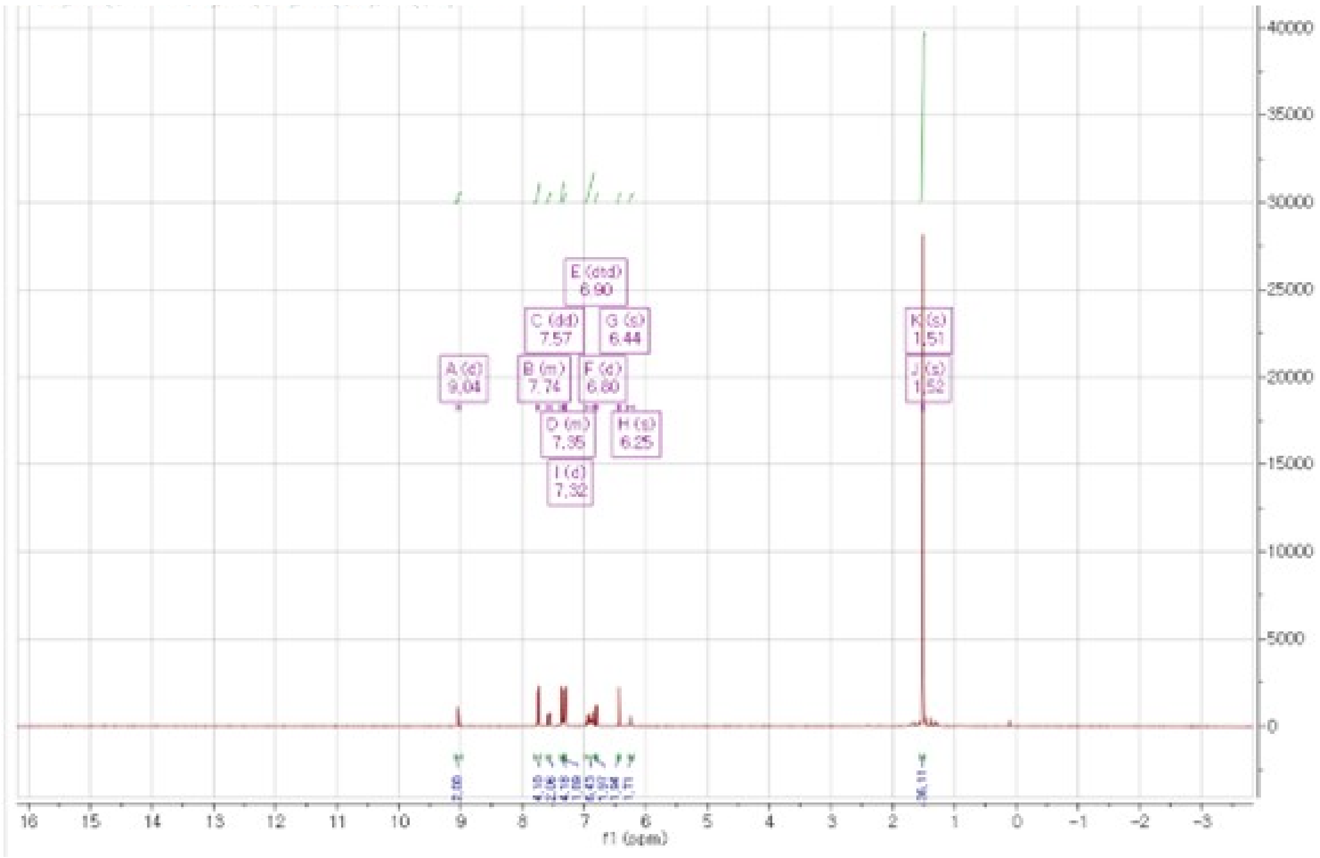


**Supplementary Fig. S13.** $^1$H-NMR spectrum of tDABNA-TP.

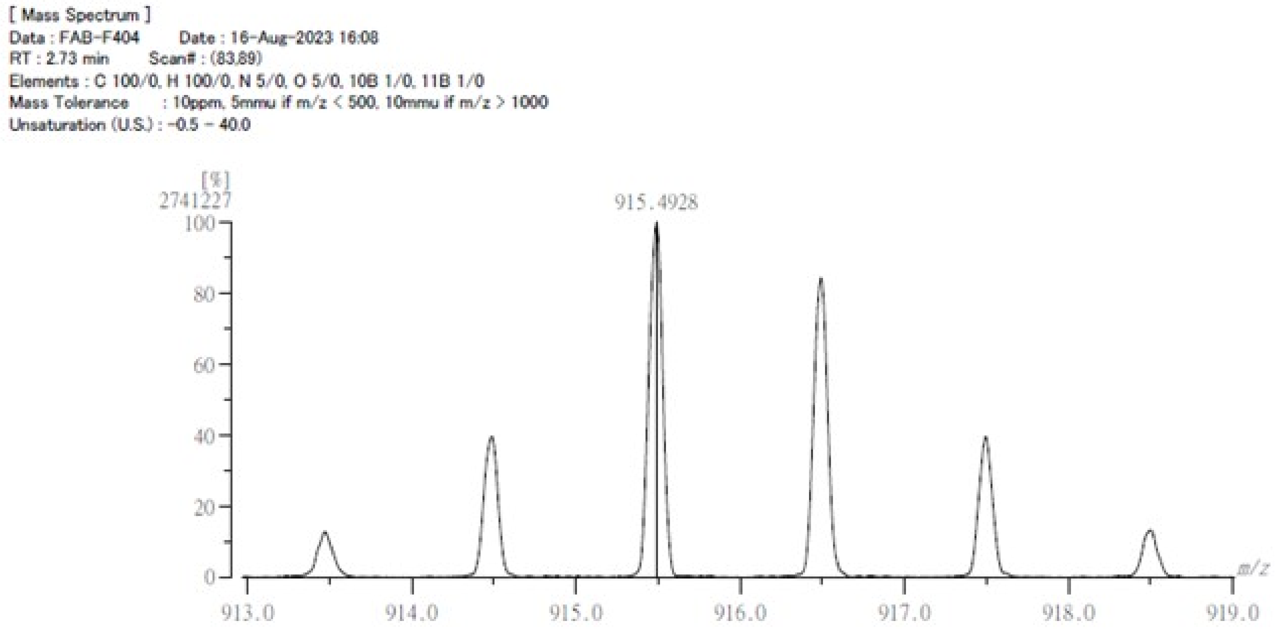


[ Mass Spectrum ]
Data : FAB-F402 Date : 16-Aug-2023 15:35
RT : 1.30 min Scan# : (39,48)
Elements : C 100/0, H 100/0, N 3/0, 10B 1/0, 11B 1/0
Mass Tolerance : 10ppm, 5mmu if m/z < 500, 10mmu if m/z > 1000
Unsaturation (U.S.) : -0.5 - 40.0

**Supplementary Fig. S14.** High-resolution mass spectrum of tDABNA-TP.

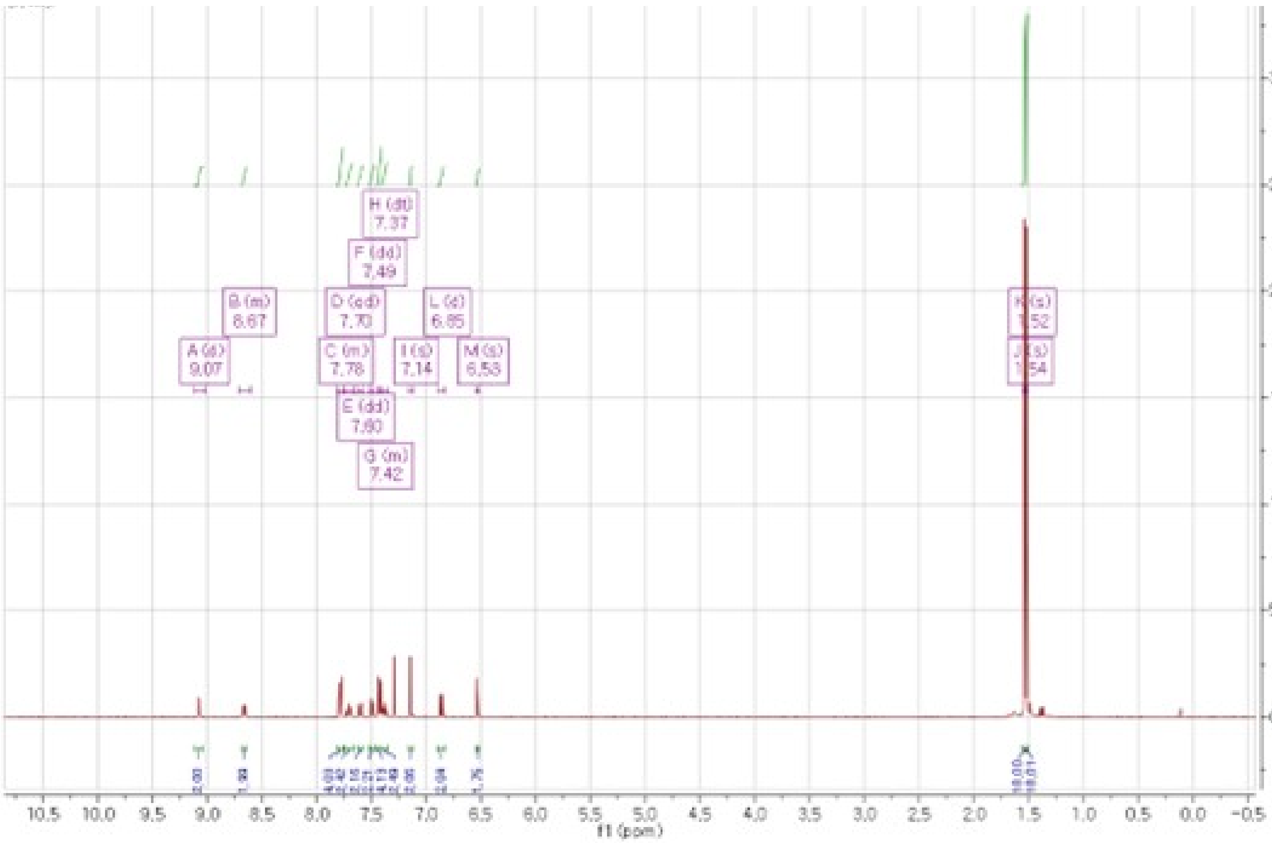


**Supplementary Fig. S15.** $^1$H-NMR spectrum of tDABNA-DN.

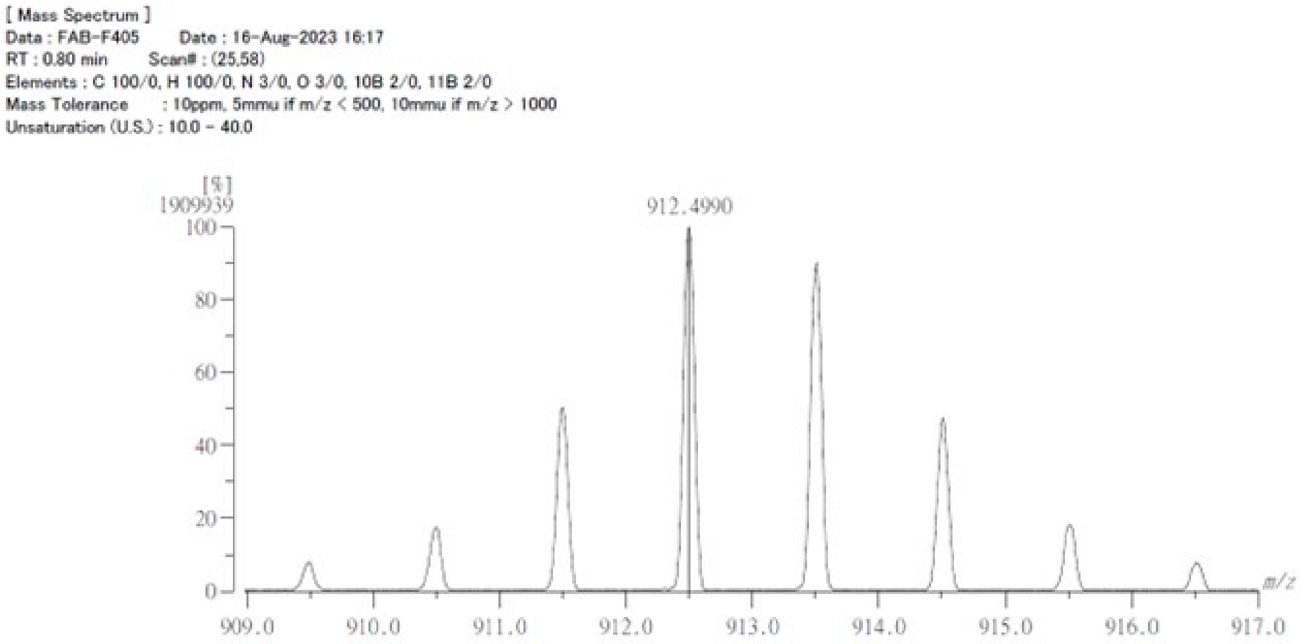


[ Mass Spectrum ]
Data : FAB-F404 Date : 16-Aug-2023 16:08
RT : 2.73 min Scan# : (83,89)
Elements : C 100/0, H 100/0, N 5/0, O 5/0, 10B 1/0, 11B 1/0
Mass Tolerance : 10ppm, 5mmu if m/z < 500, 10mmu if m/z > 1000
Unsaturation (U.S.) : -0.5 - 40.0

**Supplementary Fig. S16.** High-resolution mass spectrum of tDABNA-DN.



**Supplementary Fig. S17.** $^1$H-NMR spectrum of tDABNA-DOB.



[ Mass Spectrum ]
Data : FAB-F405 Date : 16-Aug-2023 16:17
RT : 0.80 min Scan# : (25,58)
Elements : C 100/0, H 100/0, N 3/0, O 3/0, 10B 2/0, 11B 2/0
Mass Tolerance : 10ppm, 5mmu if m/z < 500, 10mmu if m/z > 1000
Unsaturation (U.S.) : 10.0 - 40.0

**Supplementary Fig. S18.** High-resolution mass spectrum of tDABNA-DOB.

## Supplementary Methods

**2-Bromo-*N*$^1$,*N*$^1$,*N*$^3$,*N*$^3$-tetrakis(4-(*tert*-butyl)phenyl)-5-chlorobenzene-1,3-diamine (1).** 1,2,3-Tribromo-5-chlorobenzene (10.0 g, 28.6 mmol), bis(4-*tert*-butylphenyl)amine (16.9 g, 60.1 mmol), sodium *tert*-butoxide (11.0 g, 114 mmol), and bis(di-*tert*-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II) (0.60 g, 0.86 mmol) were dissolved in toluene (100 mL) under an $N_2$ atmosphere. After stirring at 150 °C in an oil bath for 12 h, the mixture was cooled to room temperature, and the catalyst and base were removed first via filtration. The collected filtrate was purified via recrystallization to generate 12.0 g of white powder. Yield: 56%. $^1$H nuclear magnetic resonance (NMR, 400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.8 Hz, 8H), 7.08 (s, 2H), 6.92 (d, *J* = 8.8 Hz, 8H), 1.33 (s, 36H). Mass spectrometry (MS, field desorption (FD)) *m/z* 750.

**2,12-Di-*tert*-butyl-5,9-bis(4-(*tert*-butyl)phenyl)-7-chloro-5,9-dihydro-5,9-diaza-13*b*-boranaphtho[3,2,1-de]anthracene (2).** Compound **1** (14.1 g, 33.5 mmol) and *tert*-butylbenzene (100 mL) were added to a 250 mL round-bottom flask equipped with a condenser and stirrer. The mixture was cooled to 0 °C before a solution of *n*-butyllithium in pentane (14.1 g, 33.5 mmol) was added slowly to the mixture, which was then allowed to warm to room temperature. After stirring at room temperature for 1 h, the mixture was cooled to 0 °C. After the addition of $BBr_3$ (1.00 mL, 10.5 mmol) at 0 °C, the mixture was stirred at room temperature for 0.5 h. *N*,*N*-Diisopropylethylamine (2.87 mL, 16.8 mmol) was added at 0 °C and then the mixture was heated at 130 °C for 12 h. After the completion of the reaction, methanol (400 mL) was poured into the mixture to quench the reaction, and the resulting product was extracted using dichloromethane and purified via recrystallization. Yield: 26% (3.0 g, 11.0 mmol). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, *J* = 2.4 Hz, 1H), 7.75–7.69 (m, 2H), 7.57 (dt, *J* = 6.1, 3.1 Hz, 1H), 7.31 (dt, *J* = 4.7, 2.7 Hz, 2H), 6.76 (d, *J* = 9.0 Hz, 1H), 6.18 (s, 1H), 1.51 (d, *J* = 2.0 Hz, 17H). MS (FD) *m/z* 679.

**7-(2,12-Di-*tert*-butyl-5,9-bis(4-(*tert*-butyl)phenyl)-5,9-dihydro-5,9-diaza-13*b*-boranaphtho[3,2,1-de]anthracen-7-yl)benzo[5,6][1,4]oxazino[2,3,4-*kl*]phenoxazine (tDABNA-TP).** Compound **2** (1.50 g, 2.21 mmol), [1,1':3',1''-terphenyl]-5'-ylboronic acid (0.73 g, 2.65 mmol), aqueous $K_2CO_3$, $Pd(PPh_3)_4$ ($PPh_3$ = triphenylphosphine), and tetrahydrofuran (THF, 60 mL) were added to a 250 mL round-bottom flask equipped with a condenser and stirrer, and the mixture was heated at 100 °C for 15 h. After the completion of the reaction, 50 mL of $H_2O$ was poured into the mixture to quench the reaction, and the resulting product was extracted with dichloromethane, purified using silica gel column chromatography (10 vol.% ethyl acetate in *n*-hexane used as the eluent), and further purified via recrystallization. Yield: 44% (0.84 g, 0.96 mmol). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 2H), 7.79–7.73 (m, 4H), 7.69 (s, 1H), 7.59 (dt, *J* = 8.4, 2.7 Hz, 2H), 7.51 (ddd, *J* = 4.1, 3.2, 1.6 Hz, 6H), 7.46–7.34 (m, 10H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.48 (s, 2H), 1.53 (s, 18H), 1.51 (s, 18H). High-resolution MS (FD) *m/z* 872.5245.

**7-(2,12-Di-*tert*-butyl-5,9-bis(4-(*tert*-butyl)phenyl)-5,9-dihydro-5,9-diaza-13*b*-boranaphtho[3,2,1-de]anthracen-7-yl)benzo[5,6][1,4]oxazino[2,3,4-*kl*]phenoxazine (tDABNA-DN).** Compound **2** (2.00 g, 2.94 mmol), 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[5,6][1,4]oxazino[2,3,4-*kl*]phenoxazine (1.41 g, 3.53 mmol), aqueous $K_2CO_3$, $Pd(PPh_3)_4$, and THF (60 mL) were added to a 250 mL round-bottom flask equipped with a condenser and stirrer, and the mixture was heated at 100 °C for 15 h. After the completion of the reaction, distilled $H_2O$ (50 mL) was poured into the mixture to quench the reaction, and the resulting product was extracted with dichloromethane, purified using silica gel column chromatography (20 vol.% dichloromethane in *n*-hexane used as the eluent), and further purified via recrystallization. Yield: 57% (1.55 g, 1.69 mmol). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 2.4 Hz, 1H), 7.77–7.72 (m, 2H), 7.57 (dd, *J* = 9.1, 2.4 Hz, 1H), 7.39–7.33 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 1H), 6.90 (dtd, *J* = 24.0, 7.6, 1.8 Hz, 3H), 6.80 (d, *J* = 9.0 Hz, 1H), 6.44 (s, *J* = 8.3 Hz, 1H), 6.25 (s, 1H), 1.52 (s, 9H), 1.51 (s, 9H). MS (FD) *m/z* 915.4928.

**7-(5,9-Dioxa-13*b*-boranaphtho[3,2,1-de]anthracen-7-yl)-2,12-di-*tert*-butyl-5,9-bis(4-(*tert*-butyl)phenyl)-5,9-dihydro-5,9-diaza-13*b*-boranaphtho[3,2,1-de]anthracene (tDABNA-DOB).** Compound **2** (1.50 g, 2.21 mmol), 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,9-dioxa-13*b*-boranaphtho[3,2,1-de]anthracene (1.05 g, 2.65 mmol), aqueous $K_2CO_3$, $Pd(PPh_3)_4$, and THF (60 mL) were added to a 250 mL round-bottom flask equipped with a condenser and stirrer, and the mixture was heated at 100 °C for 15 h. After the completion of the reaction, distilled $H_2O$ (50 mL) was poured into the mixture to quench the reaction, and the resulting product was extracted with dichloromethane, purified using silica gel column chromatography (10 vol.% ethyl acetate in *n*-hexane used as the eluent), and further purified via recrystallization. Yield: 61.8% (1.25 g, 1.37 mmol). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, *J* = 2.4 Hz, 2H), 8.70–8.60 (m, 2H), 7.81–7.74 (m, 4H), 7.70 (qd, *J* = 7.3, 3.8 Hz, 2H), 7.60 (dd, *J* = 9.0, 2.4 Hz, 2H), 7.49 (dd, *J* = 8.4, 0.9 Hz, 2H), 7.44–7.40 (m, 4H), 7.37 (dt, *J* = 12.1, 2.6 Hz, 2H), 7.14 (s, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.53 (s, 2H), 1.54 (s, 18H), 1.52 (s, 18H). MS (FD) *m/z* 912.4990.