Supporting information

Development of Blue Multiresonance Thermally Activated Delayed Fluorescence Host Materials Including Ge-Based Bulky Group

Sangwook Park [a], Hyukmin Kwon [a], Hayoon Lee [a], Kiho Lee [a], Seokwoo Kang [a], Ki Ju Kim [b], Taekyung Kim [b,c], Jongwook Park *[a]

[a]Integrated Engineering, Department of Chemical Engineering, Kyung Hee University,

Gyeonggi, 17104, Republic of Korea

[b]Department of Information Display, Hongik University,

Seoul, 04066, Republic of Korea

[c] Department of Materials Science and Engineering, Hongik University,

Sejong, 30016, Republic of Korea

* Corresponding author

E-mail : Jongwook Park (jongpark@khu.ac.kr), Taekyung Kim (taekyung.kim@hongik.ac.kr)

Experimental

General information

Reagents and solvents were purchased as reagent grade and used without further purification. Analytical TLC was carried out on Merck 60 F254 silica gel plate, and column chromatography was performed on Merck 60 silica gel (230-400 mesh). The ^{1}H-NMR spectra were recorded on Bruker Avance 400 and ^{13}C-NMR spectra were recorded on JEOL JNM-AL300. The FAB+-mass was recorded on a JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were obtained by using a Lambda 1050 UV/Vis/NIR spectrometer (PerkinElmer). A PerkinElmer luminescence spectrometer LS55 (Xenon flash tube) was used to perform photoluminescence (PL) spectroscopy and excitation curves. Absolute photoluminescence quantum yield (PLQY) values were obtained by using Quantaurus-QY (Hamamatsu). Transient PL decay time values were obtained by using Quantaurus-Tau (Hamamatsu). The values of singlet and triplet energies were obtained by using JASCO FP-8500 fluorescence spectrometer. The glass transition temperatures (T_g) of the compounds were determined using differential scanning calorimetry (DSC) under a N_2 atmosphere by using a Q-1000 (TA instruments). Degradation temperatures (T_d) were determined with thermogravimetric analysis

(TGA) by using a TGA Q5000 IR (TA instruments).nThe HOMO energy levels were determined with ultraviolet photoelectron yield spectroscopy (Riken Keiki AC-2). The LUMO energy levels were derived from the HOMO energy levels and the band gaps.

Synthesis
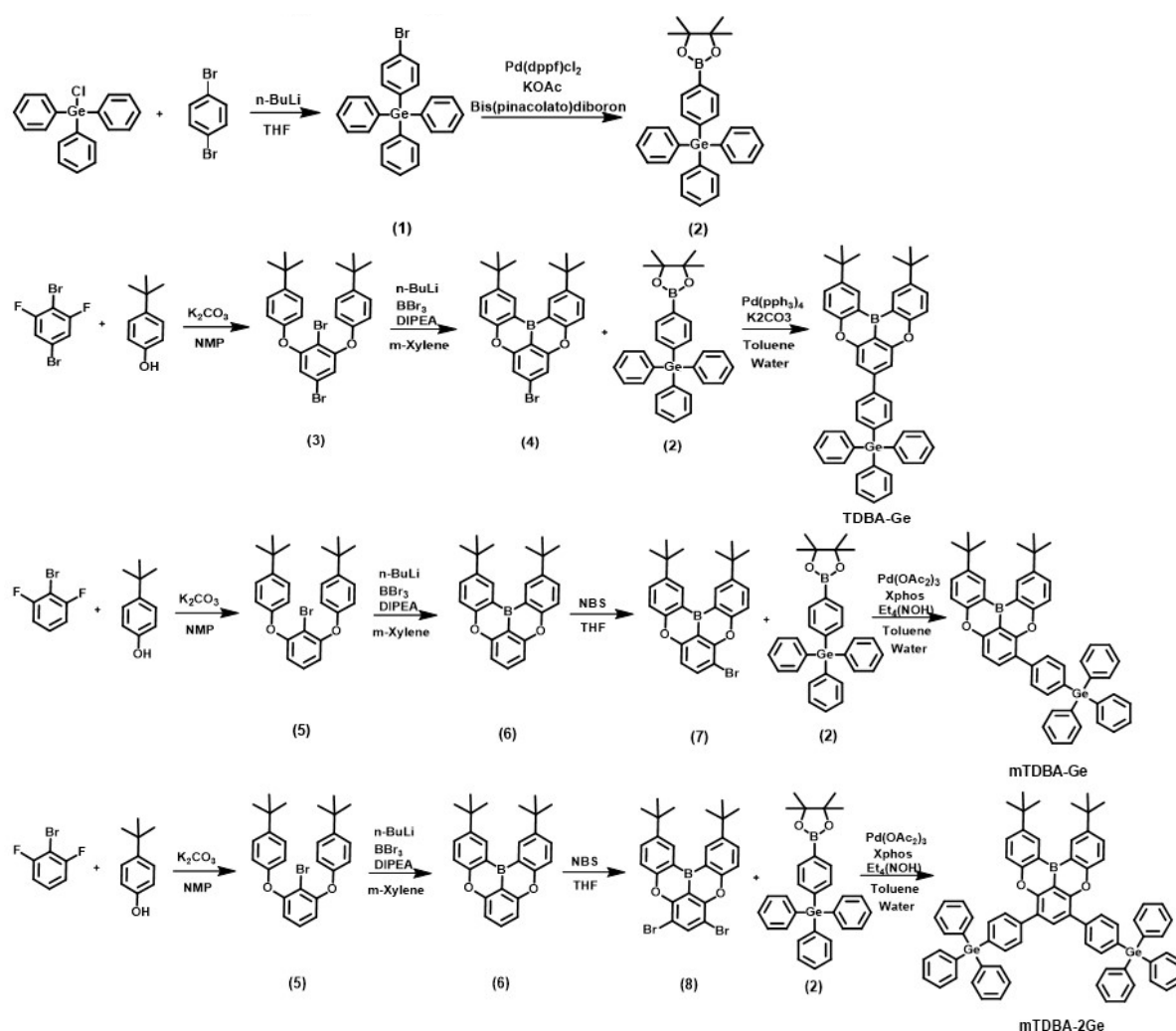
Scheme S1. Synthetic route of TDBA-based host materials.

(4-bromophenyl)triphenylgermane (1)

In a 2-neck round flask, 1,4-dibromobenzene (3.0 g, 12.71 mmol) and anhydrous THF (10 ml) were combined, and the mixture was stirred under a nitrogen atmosphere for 30 minutes. An ice bath (acetone) was set up, maintaining a temperature of -78°C. 2.5M n-BuLi (5.05 ml) was then added dropwise, and the reaction was stirred for 1 hour. In a dropping funnel, triphenylgermanium chloride (3.94 g, 11.60 mmol) and anhydrous THF (20 ml) were placed under a nitrogen atmosphere and added dropwise to the reaction mixture. After removing the ice bath, the reaction progress was

monitored by TLC over approximately 4 hours. Extraction was performed using a mixture of chloroform and deionized water, followed by drying with $MgSO_4$ to remove moisture. After solvent removal, the obtained white solid was adsorbed and subjected to column chromatography(dichloromethane:n-hexane=1:9 v/v). The solvent was evaporated to yield a white solid, which was further precipitated and filtered using methanol to obtain the pure white solid substance (yield:80%). ^1H NMR (400 MHz, Chloroform-d) δ 7.53 – 7.46 (m, 8H), 7.43 – 7.35 (m, 11H) ppm.

triphenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)germane (2)

In a 2-neck round flask, (4-bromophenyl)triphenylgermane (2.56 g, 5.57 mmol), KOAc (1.64 g, 16.7 mmol), Bis(pinacolato)diboron (1.55 g, 6.12 mmol), and 1,4-dioxane(60 ml) were combined under a nitrogen atmosphere. The mixture was stirred for 30 minutes. Pd(dppf)Cl$_2$ (0.204 g, 0.28 mmol,) was added, and the temperature was set to 110°C. The reaction was carried out for 6 hours, with the reaction progress monitored intermittently by TLC. Extraction was performed using a mixture of dichloromethane and deionized water, followed by drying with $MgSO_4$ to remove moisture. After maximum solvent removal, the obtained white solid was adsorbed and subjected to column chromatography(Ethyl acetate:n-hexane=1:9 v/v). The solvent was evaporated, yielding a white solid, which was then precipitated with methanol and subjected to vacuum filtration, obtaining pure white solid 1.42 g (yield: 50%). ^1H NMR (400 MHz, Chloroform-d) δ 7.83 – 7.77 (m, 2H), 7.56 – 7.49 (m, 8H), 7.42 – 7.34 (m, 9H), 1.33 (s, 12H) ppm.

4,4'-((2,5-dibromo-1,3-phenylene)bis(oxy))bis(tert-butylbenzene) (3)

2,5-dibromo-1,3-difluorobenzene (10.0 g, 36.8 mmol), 4-(tert-butyl)phenol (16.6 g, 110.4 mmol), and potassium carbonate (15.3 g, 110.4 mmol) were dissolved in anhdrous N-Methyl-2-pyrrolidone (NMP) (45mL) under a nitrogen atmosphere. After stirring at 170 ℃ 20h, the reaction mixture was cool to room temperature and the solution extracted with dichloromethane and water three times. The organic phase was dried with anhydrous $MgSO_4$ and filtered. The solvent was condensed by evaporation under a vacuum and precipitated with methanol and subjected to vacuum filtration, obtaining pure white solid (yield:78%). ^1H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.36 (m, 4H), 7.00 – 6.93 (m, 4H), 6.72 (s, 2H), 1.33 (s, 18H) ppm.

7-bromo-2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (4)

4,4'-((2,5-dibromo-1,3-phenylene)bis(oxy))bis(tert-butylbenzene) (5.0 g, 11.0 mmol) were dissolved in anhydrous m-xylene(60 mL) under an argon atmosphere. After stirring 30minutes, a solution n-butyllithium (5.3 mL, 2.5 M) was added slowly to the solution at -50℃. Then, the mixture was stirred at room temperature for 1h. Then boron tribromide (1.57 mL, 16.5 mmol) was slowly added at -50℃, and the reaction mixture was then maintained at room temperature (RT) for 30 minutes, followed by a 1hour reaction at 45 °C. Then N,N-diisopropylethylamine (3.84 mL, 22.1 mmol) was slowly added at -15 ℃. The mixture was stirred at room temperature for 30 minutes, and 140℃ for 20h. Upon completion of the reaction, the solution was cooled to room temperature and extracted with dichloromethane and water three times. The organic phase was dried with anhydrous $MgSO_4$ and filtered. The solvent was condensed by evaporation under a vacuum and the crude was purified through the silica gel column chromatography (dichloromethane: n-hexane=1:4 v/v) to afford white solid (yield43%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.72 (d, J = 2.5 Hz, 2H), 7.78 (dd, J = 8.8, 2.5 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.37 (s, 2H), 1.47 (s, 18H) ppm.

(4-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-7-yl)phenyl)triphenylgermane (TDBA-Ge)

triphenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)germane (0.66 g, 1.30 mmol), 7-bromo-2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (0.5 g, 1.08 mmol), 2M potassium carbonate (2.764 g), and tetrakis(triphenylphosphine)palladium(0) (0.125 g, 0.108 mmol) were dissolved in 20 mL of toluene and 10mL of distilled water at room temperature under an argon atmosphere. After stirring at 110 ℃ 24 hours, the reaction mixture was cool to room temperature and the solution extracted with ethylacetate and water three times. The organic phase was dried with anhydrous $MgSO_4$ and filtered. The solvent was condensed by evaporation under a vacuum and the crude was purified through the silica gel column chromatography (ehthylacetate: n-hexane=1:9 v/v) to afford white solid (yield:59%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.76 (dd, J = 4.8, 2.5 Hz, 2H), 7.88 (d, J = 8.5 Hz, 1H), 7.81 – 7.76 (m, 3H), 7.73 (dd, J = 8.8, 2.5 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.66 – 7.58 (m, 6H), 7.51 (d, J = 8.8 Hz, 1H), 7.46 – 7.38 (m, 10H), 7.30 (d, J = 8.4 Hz, 1H), 1.48 (d, J = 5.9 Hz, 18H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ:158.91, 157.96, 147.44, 145.09, 141.27, 138.47, 138.09, 138.00, 135.53, 131.59, 130.33, 129.34, 128.48, 118.09, 107.13, 34.88, 31.85 ppm ; HRMS(FAB+): calcd for $C_{50}H_{45}BGeO_2$ 762.2724, found: 762.2734.

4,4'-((2-bromo-1,3-phenylene)bis(oxy))bis(tert-butylbenzene) (5)

2-bromo-1,3-difluorobenzene (10.0g, 51.8mmol), 4-(tert-butyl)phenol (23.35g, 155mmol), and potassium carbonate (21.48g, 155mmol) were dissolved in N-Methyl-2-pyrrolidone(120mL) under a nitrogen atmosphere. After stirring at 150 ℃ 20h, the reaction mixture was cool to room temperature and the solution extracted with dichloromethane and water three times. The organic phase was dried with anhydrous $MgSO_4$ and filtered. The solvent was condensed by evaporation under a vacuum and the crude was purified through the silica gel column chromatography (dichloromethane: n-hexane=1:9 v/v) to afford white solid (yield:78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 4H), 7.12 (t, *J* = 8.3 Hz, 1H), 7.00 – 6.93 (m, 4H), 6.65 (d, *J* = 8.2 Hz, 2H), 1.31 (s, 18H) ppm.

2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (TDBA) (6)

4,4'-((2-bromo-1,3-phenylene)bis(oxy))bis(tert-butylbenzene) (5.0 g, 11.0 mmol) were dissolved in anhydrous *m*-xylene(60 mL) under an argon atmosphere. After stirring 30minutes, a solution n-butyllithium (5.3 mL, 2.5 M) was added slowly to the solution at -50℃. Then, the mixture was stirred at room temperature for 1h. Then boron tribromide (1.57 mL, 16.5 mmol) was slowly added at -50℃, and the reaction mixture was then maintained at room temperature (RT) for 30 minutes, followed by a 1hour reaction at 45 °C. Then N,N-diisopropylethylamine (3.84 mL, 22.1 mmol) was slowly added at -15 ℃. The mixture was stirred at room temperature for 30 minutes, and 140℃ for 20h. Upon completion of the reaction, the solution was cooled to room temperature and extracted with dichloromethane and water three times. The organic phase was dried with anhydrous $MgSO_4$ and filtered. The solvent was condensed by evaporation under a vacuum and the crude was purified through the silica gel column chromatography (dichloromethane: n-hexane=1:4 v/v) to afford white solid (yield:53%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 2.6 Hz, 2H), 7.80 – 7.72 (m, 3H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 1.47 (s, 18H) ppm.

8-bromo-2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (7)

In a 3-neck round flask, TDBA (1.4 g, 3.66 mmol) and anhydrous THF 20 ml were combined under a nitrogen atmosphere for 30 minutes. N-bromosuccinimide (NBS) (0.782 g, 4.39 mmol) in anhydrous THF 20 ml was added dropwise. The reaction mixture was stirred at room temperature (RT) for 8 hours, and the progress of the reaction was monitored by TLC. Extraction was performed

using a mixture of dichloromethane (MC) and deionized water, followed by drying with $MgSO_4$ to remove moisture. After maximum solvent removal, the obtained solid was adsorbed and subjected to column chromatography (dichloromethane: n-hexane=1:9 v/v). The solvent was evaporated to yield a solid, which was then precipitated with methanol and filtered to obtain white solid (yield:83%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (t, *J* = 2.4 Hz, 2H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.80 (ddd, *J* = 8.8, 5.4, 2.5 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 1H), 1.48 (s, 18H) ppm.

(4-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-8-yl)phenyl)triphenylgermane (mTDBA-Ge)

In a 3-neck round flask, 8-bromo-2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (0.5 g, 1.08 mmol) and triphenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)germane (0.66 g, 1.30 mmol) were combined with anhydrous toluene (20 ml) under a nitrogen atmosphere for 30 minutes. Palladium(II) acetate (Pd(OAc)$_2$) (0.024 g, 0.108 mmol) and Xphos (0.062 g, 0.130 mmol) were added, followed by the addition of a 1.37M Et$_4$(NOH) aqueous solution (10 ml) dropwise. The temperature was set to 110°C, and the reaction progress was monitored by TLC for 3 hours. Extraction was performed using a mixture of dichloromethane (MC) and deionized water, followed by drying with $MgSO_4$ to remove moisture. After maximum solvent removal, the obtained white solid was adsorbed and subjected to column chromatography (dichloromethane: n-hexane=3:7 v/v). The solvent was evaporated, yielding a white solid, which was then precipitated with methanol and filtered to obtain the pure white solid (yield:30%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 (dd, *J* = 4.7, 2.5 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.81 – 7.77 (m, 3H), 7.73 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.64 – 7.60 (m, 6H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.42 (qd, *J* = 4.3, 3.8, 1.1 Hz, 10H), 7.30 (d, *J* = 8.5 Hz, 1H), 1.48 (d, *J* = 5.8 Hz, 18H) ppm.^{13}C NMR (126 MHz, CDCl$_3$) δ:158.55, 158.48, 157.19, 153.67, 145.17, 145.09, 138.57, 136.29, 135.84, 135.60, 135.34, 134.52, 131.66, 131.56, 130.39, 130.15, 129.48, 129.27, 128.43, 121.32, 118.37, 118.03, 108.91, 34.67, 31.66 ppm ; HRMS(FAB+): calcd for $C_{50}H_{45}BGeO_2$ 762.2724, found: 762.2723.

6,8-dibromo-2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (8)

In a 3-neck round flask, TDBA (1.0 g, 2.62 mmol) and anhydrous THF (10 ml) were combined under a nitrogen atmosphere for 30 minutes. NBS (1.117 g, 6.28 mmol) in anhydrous THF (28 ml) was added dropwise. The reaction was allowed to proceed at room temperature (RT) for 5-6 hours, and

the reaction progress was monitored by TLC. Extraction was performed using a mixture of ethyl acetate (EA) and deionized water, followed by drying with $MgSO_4$ to remove moisture. After maximum solvent removal, a white solid was obtained. A small amount of dichloromethane (MC) was added, and excess methanol was used for re-precipitation. The mixture was then subjected to vacuum filtration, yielding pure white solid 1.04 g(yield:74%). ^{1}H NMR (300 MHz, Chloroform-d) δ 8.79 (d, J = 2.5 Hz, 2H), 8.22 (s, 1H), 7.86 (dd, J = 8.9, 2.5 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 1.52 (s, 18H) ppm.

((2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene-6,8-diyl)bis(4,1-phenylene))bis(triphenylgermane) (mTDBA-2Ge)

In a 3-neck round flask, 6,8-dibromo-2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (0.3 g, 0.555 mmol) and triphenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)germane (0.845 g, 1.666 mmol) were combined with anhydrous toluene (30 ml) under a nitrogen atmosphere for 30 minutes. Palladium(II) acetate (Pd(OAc)$_2$) (0.0125 g, 0.0555 mmol) and Xphos (0.0318 g, 0.0667 mmol) were added, followed by the addition of a 1.37M Et$_4$(NOH) aqueous solution (15 ml) dropwise. The temperature was set to 110°C, and the reaction progress was monitored by TLC for 2 hours. Extraction was performed using a mixture of dichloromethane (MC) and deionized water, followed by drying with $MgSO_4$ to remove moisture. After maximum solvent removal, the obtained white solid was adsorbed and subjected to column chromatography(dichloromethane: n-hexane=3:7 v/v). The solvent was evaporated, yielding a white solid, which was then precipitated with methanol and filtered to obtain the pure white solid(yield:83%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.78 (d, J = 2.6 Hz, 2H), 8.00 (s, 1H), 7.85 – 7.81 (m, 4H), 7.74 (dd, J = 8.8, 2.4 Hz, 2H), 7.70 – 7.66 (m, 4H), 7.63 – 7.60 (m, 12H), 7.46 – 7.40 (m, 20H), 1.54 (s, 18H) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ: 158.32, 153.27, 145.27, 138.41, 136.26, 135.59, 135.49, 134.71, 131.63, 130.23, 129.52, 129.27, 128.43, 121.88, 34.69, 31.66ppm ; HRMS(FAB+): calcd for $C_{74}H_{63}BGe_2O_2$ 1140.3354, found: 1140.3338.
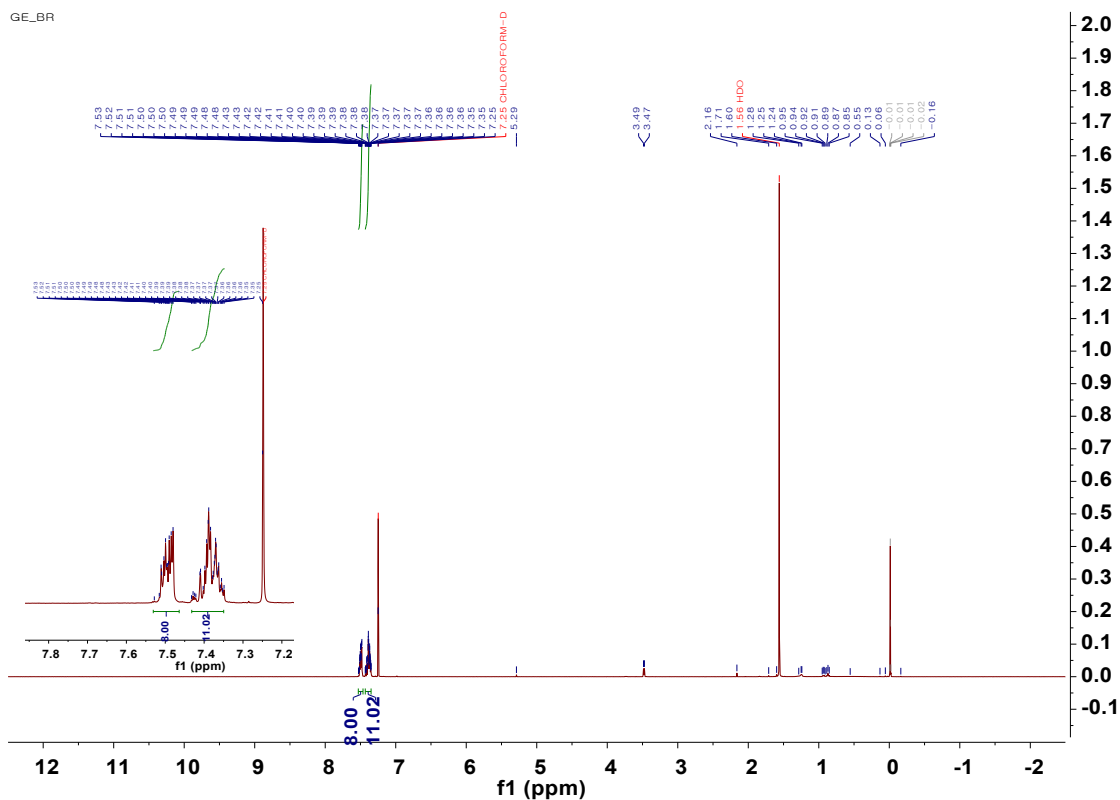
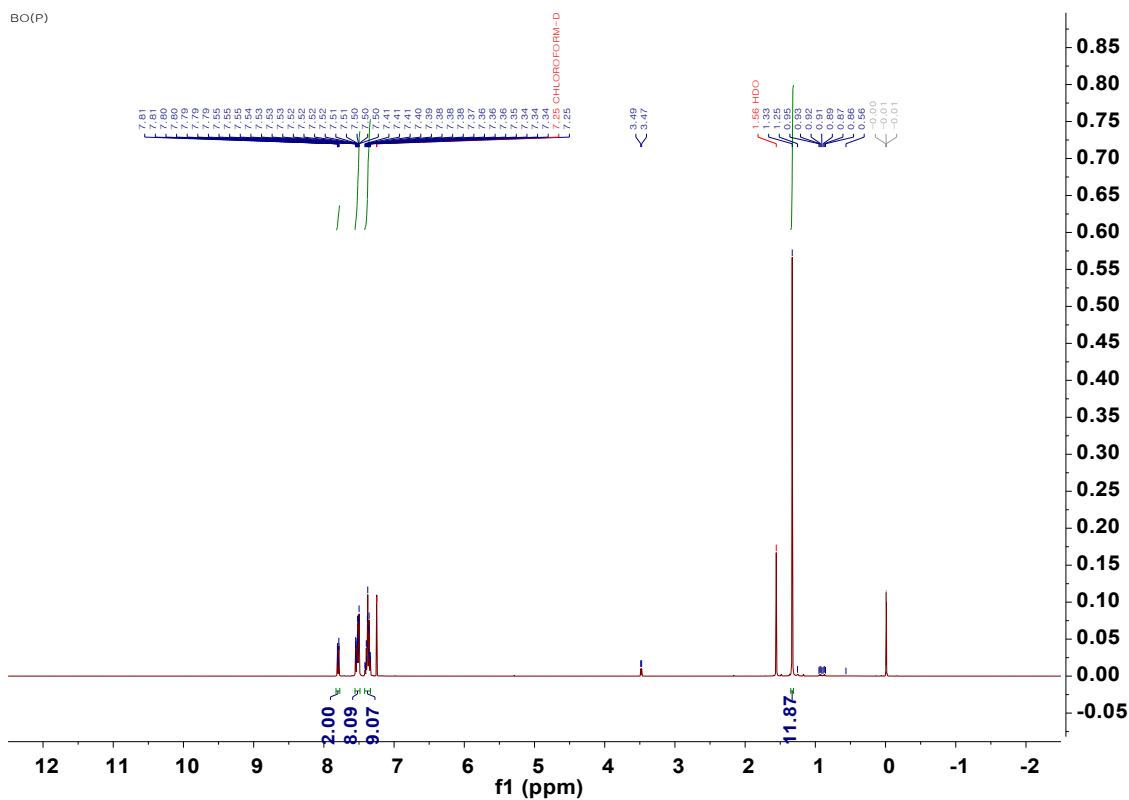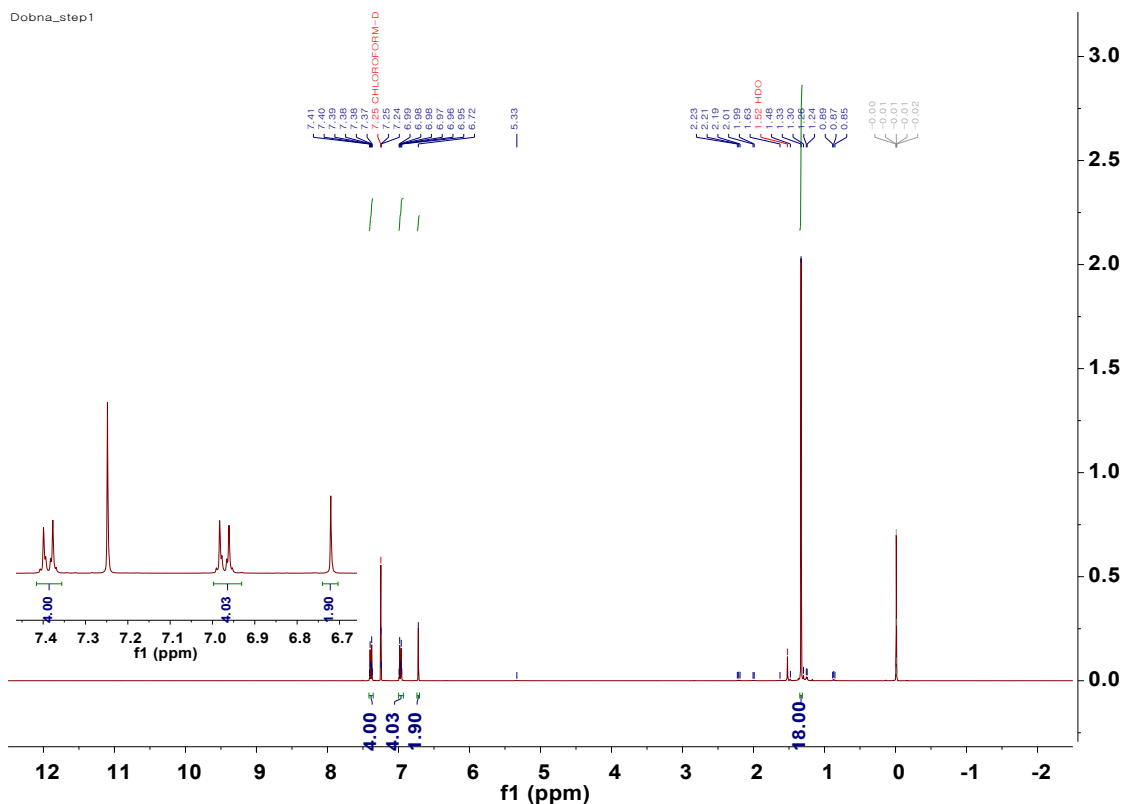**Figure S1**. ^{1}H-NMR spectra of (4-bromophenyl)triphenylgermane (1).

Figure S2. ^{1}H-NMR spectra of triphenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)germane (2).

re S3. ¹H-NMR spectra of 4,4'-((2,5-dibromo-1,3-phenylene)bis(oxy))bis(tert-butylbenzene) (3).
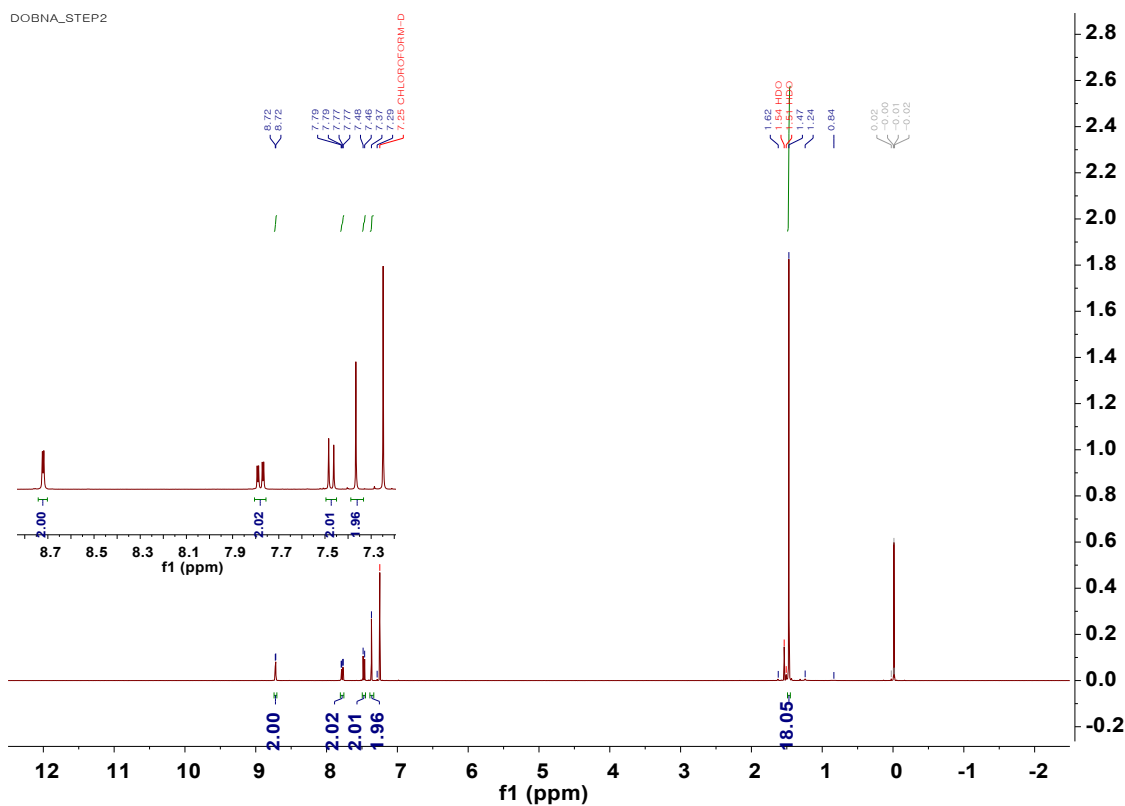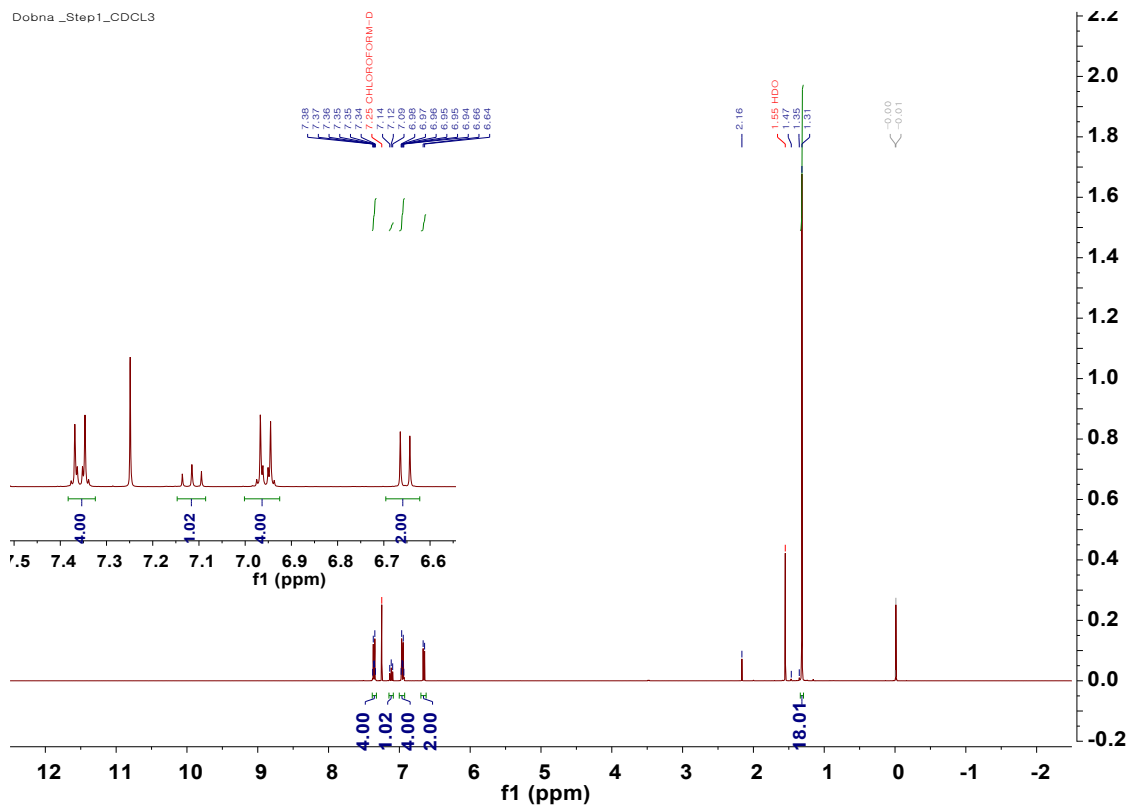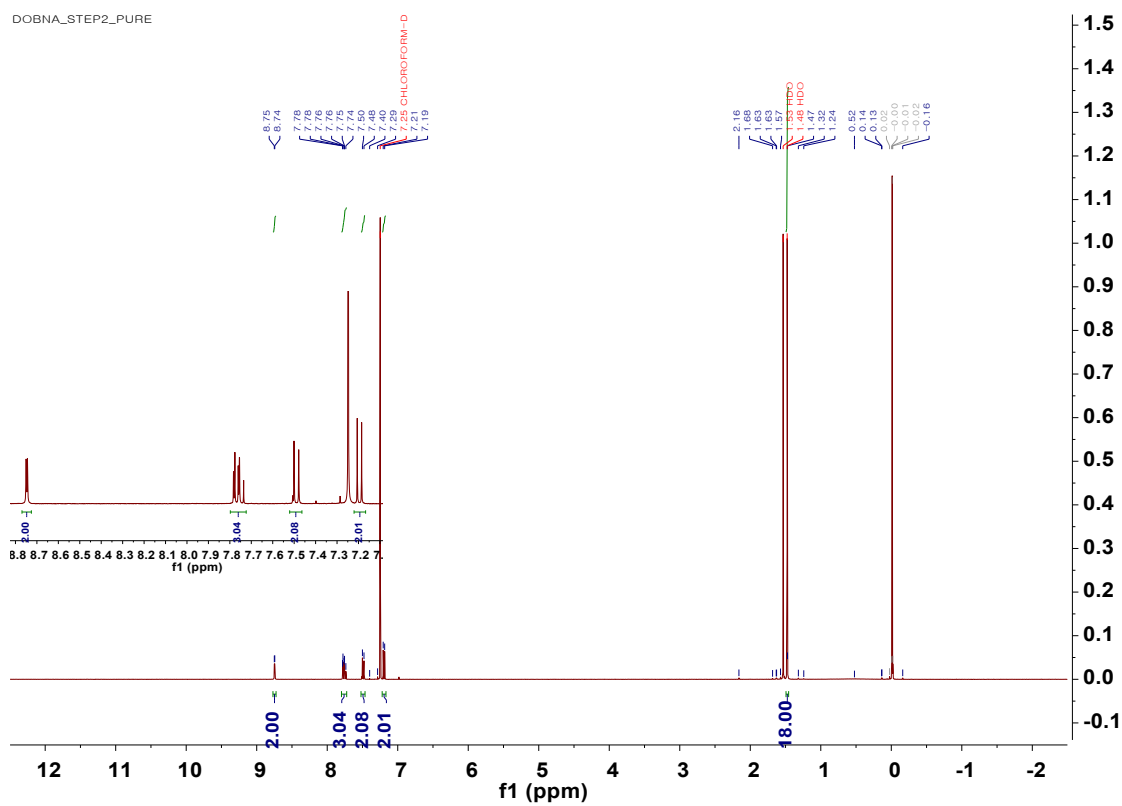

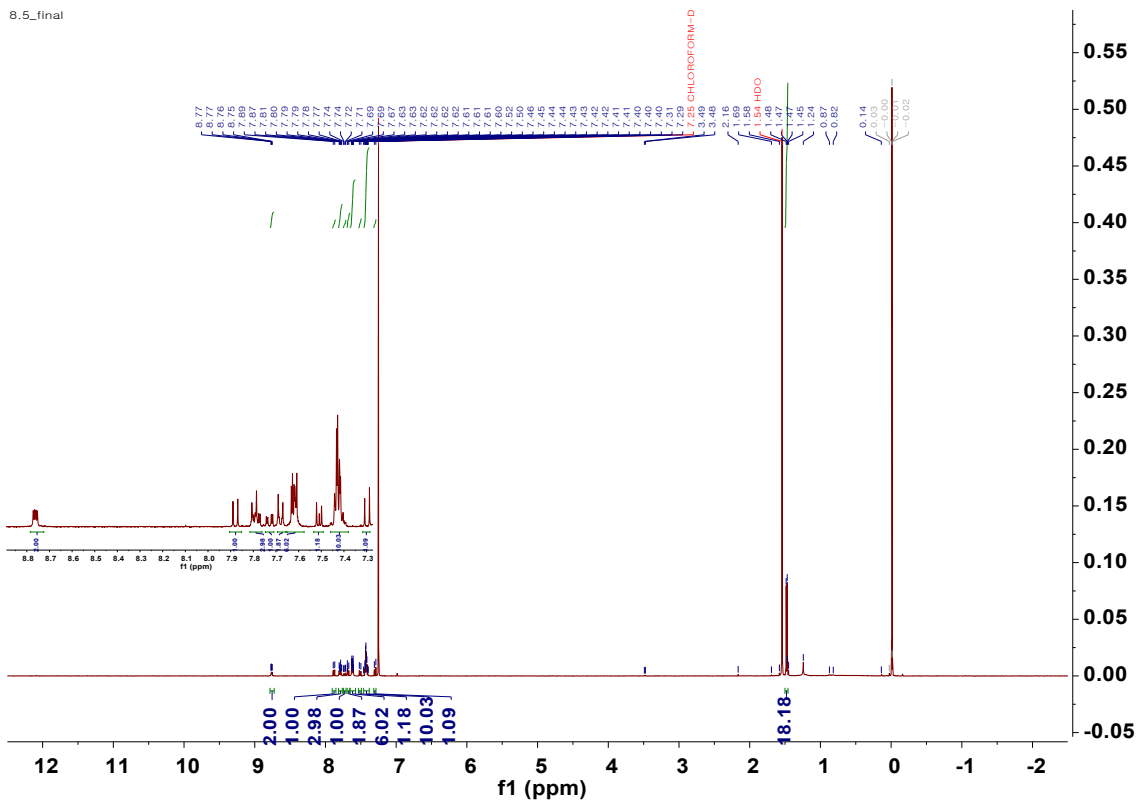**Figure S4**. ¹H-NMR spectra of 7-bromo-2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (4).

**Figure S5**. ^{1}H-NMR spectra of 4,4'-((2-bromo-1,3-phenylene)bis(oxy))bis(tert-butylbenzene) (5).

Figure S6. ^{1}H-NMR spectra of 2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (TDBA) (6).

Figure S7. ¹H-NMR spectra of 8-bromo-2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (7).

Figure S8. ¹H-NMR spectra of 6,8-dibromo-2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (8).
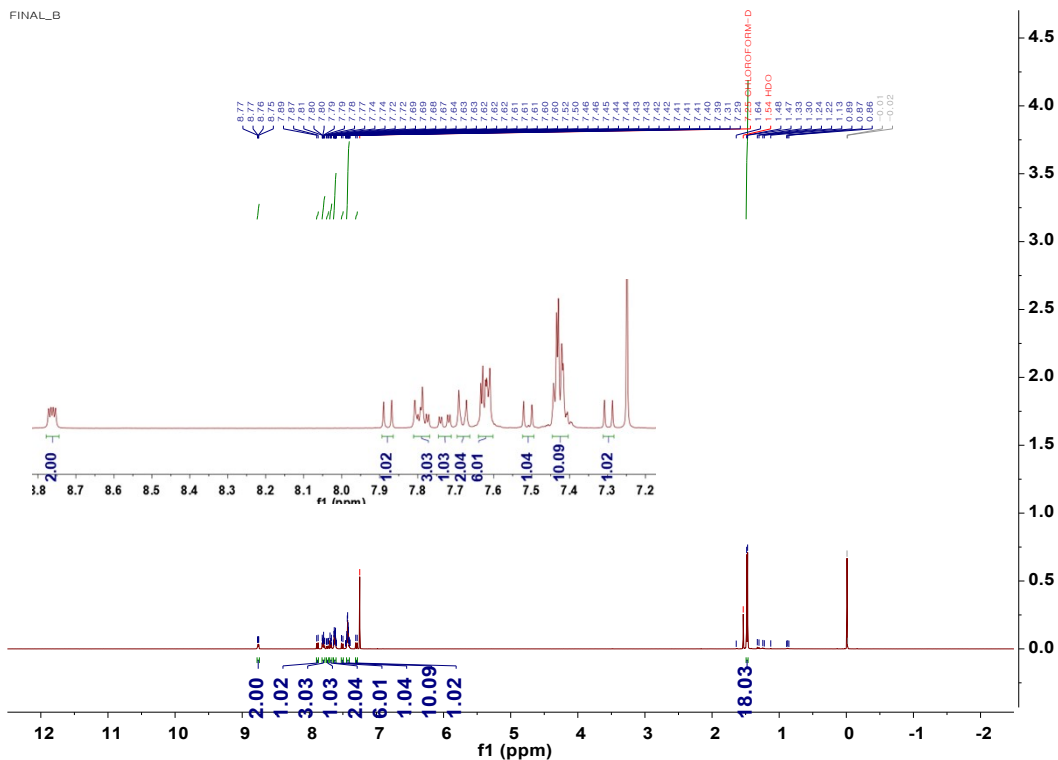
Fig

ure S9. ¹H-NMR spectra of (4-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-7-yl)phenyl)triphenylgermane (TDBA-Ge).
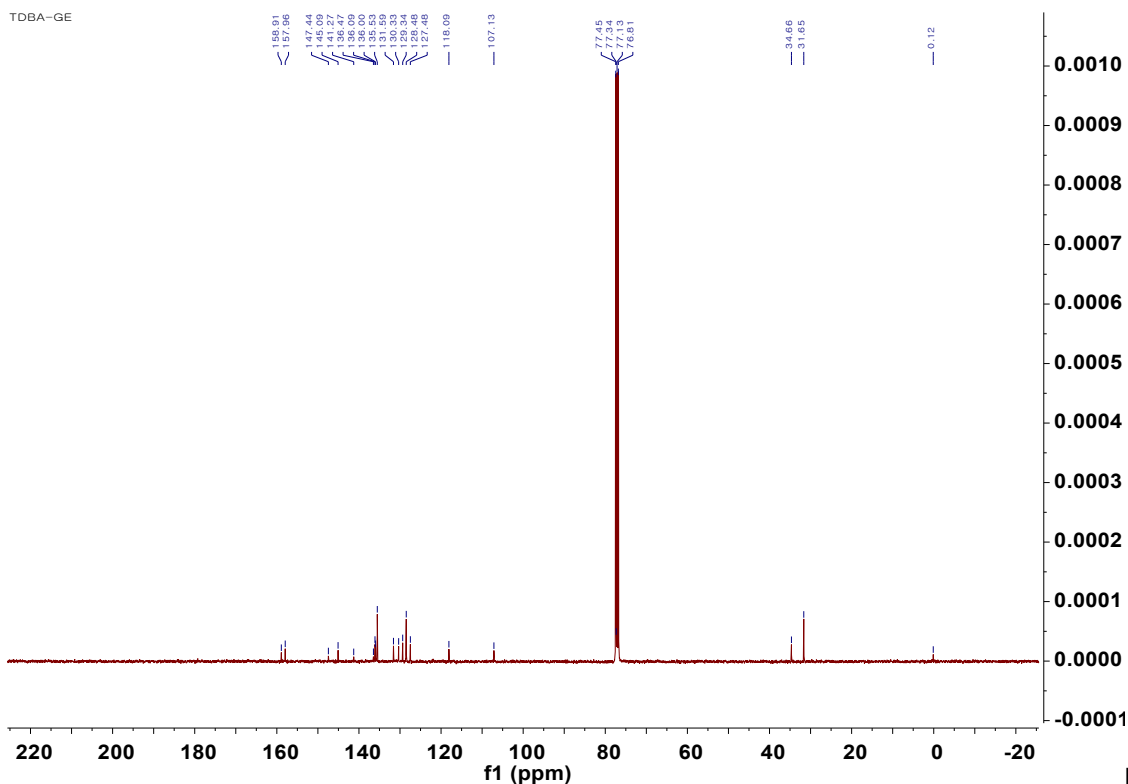
Figur

e S10. ¹³C-NMR spectra of (4-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-7-

yl)phenyl)triphenylgermane (TDBA-Ge).

Figure S11. ¹H-NMR spectra of (4-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracen-8-yl)phenyl)triphenylgermane (mTDBA-Ge).
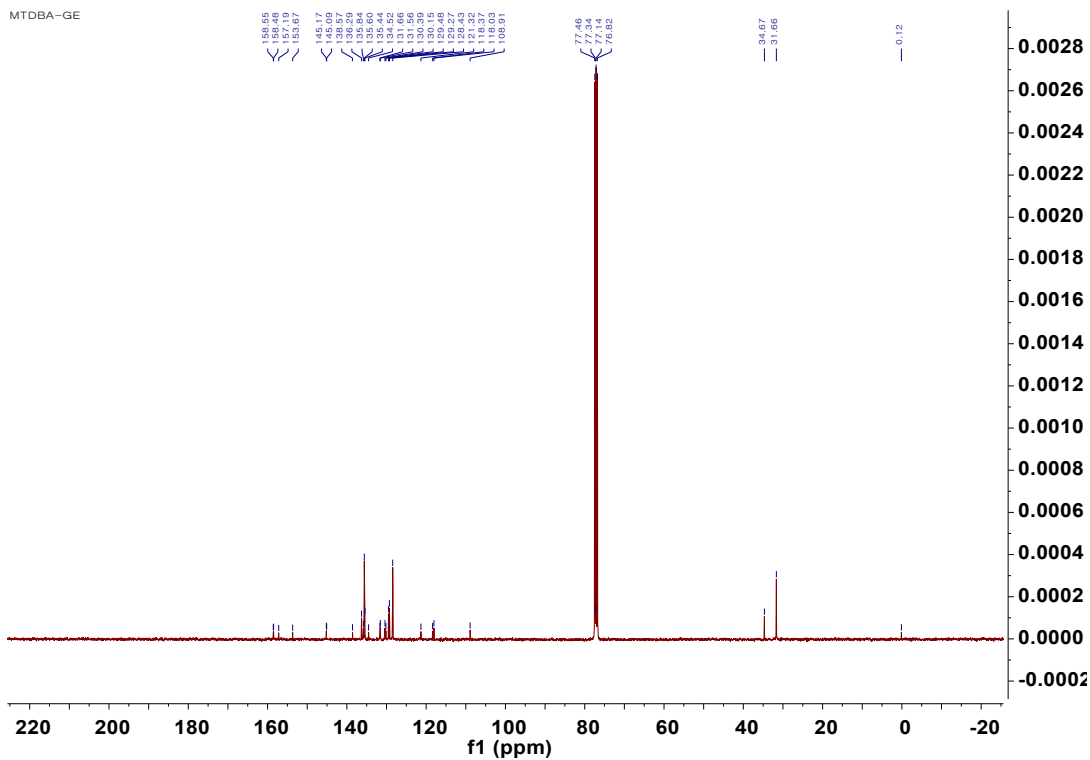

Figure S12. ¹³C-NMR spectra of (4-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-

de]anthracen-8-yl)phenyl)triphenylgermane (mTDBA-Ge).

Figure S13. ¹H-NMR spectra of ((2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene-6,8-diyl)bis(4,1-phenylene))bis(triphenylgermane) (mTDBA-2Ge).

Figure S14. ¹³C-NMR spectra of ((2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1-

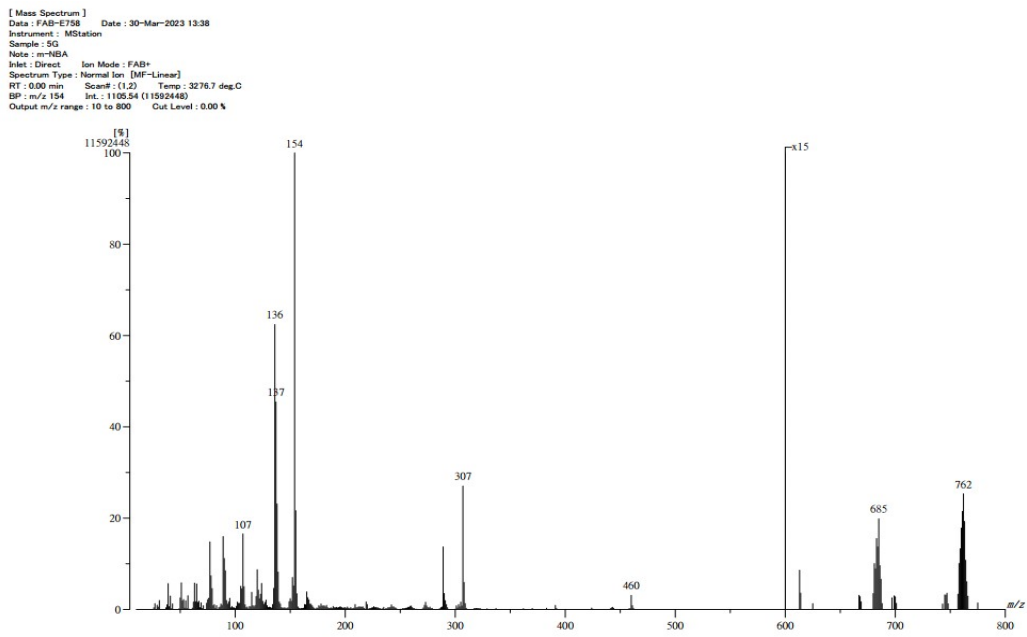de]anthracene-6,8-diyl)bis(4,1-phenylene))bis(triphenylgermane) (mTDBA-2Ge).
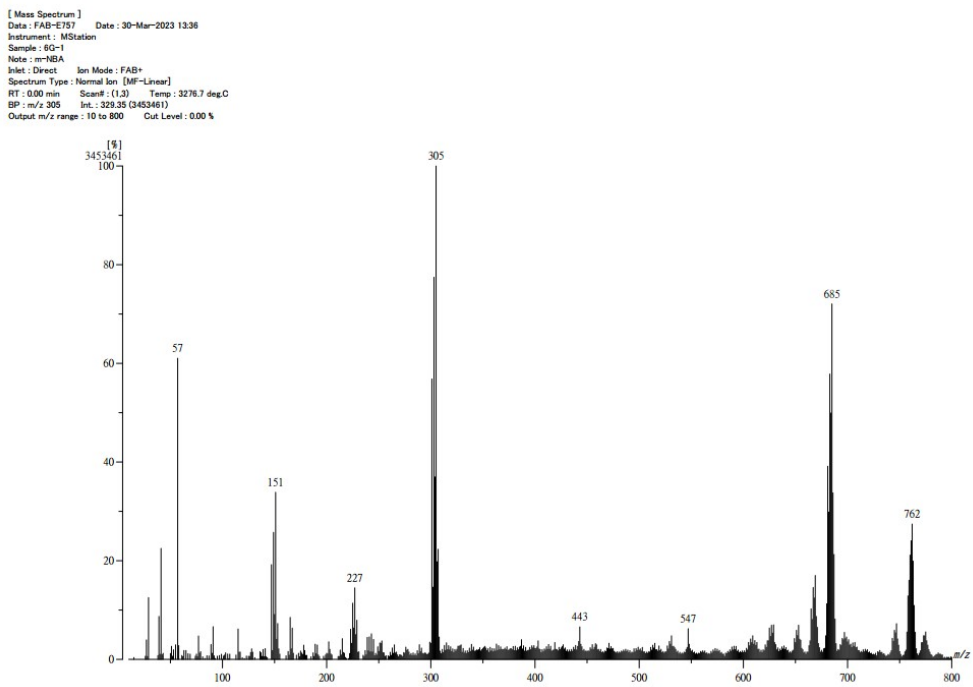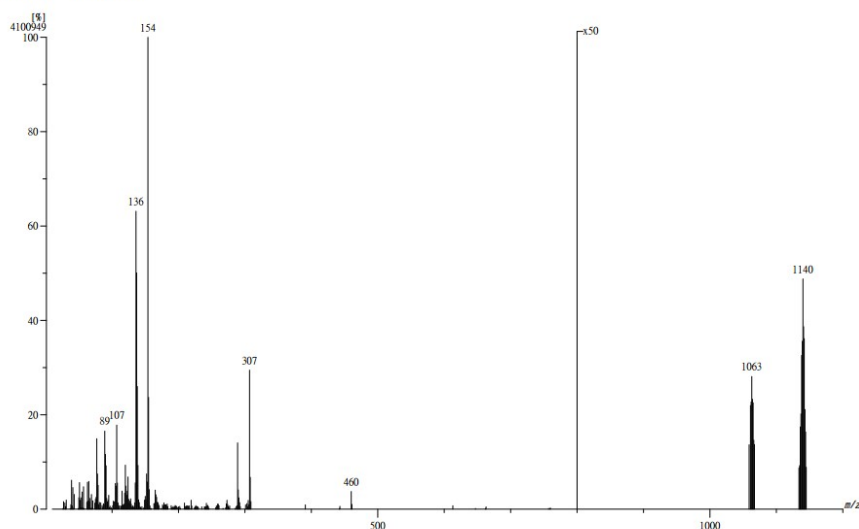

Figure S15. GC-HRMS of TDBA-Ge.

Figure S16. GC-HRMS of mTDBA-Ge.

[Mass Spectrum]
Data : FAB-E714   Date : 22-Mar-2023 10:47
Instrument : MStation
Sample : 7GE_1
Note : m-NBA
Inlet : Direct   Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.21 min   Scan# : (2,4)   Temp : 3276.7 deg.C
BP : m/z 154   Int. : 391.10 (4100949)
Output m/z range : 10 to 1200   Cut Level : 0.00 %

Figure S17. GC-HRMS of mTDBA-2Ge.

| LUMO+2 | LUMO+1 | LUMO | HOMO | HOMO-1 | HOMO-2 |
| -0.656 | -0.978 | -1.951 | -5.768 | -6.433 | -6.540 |
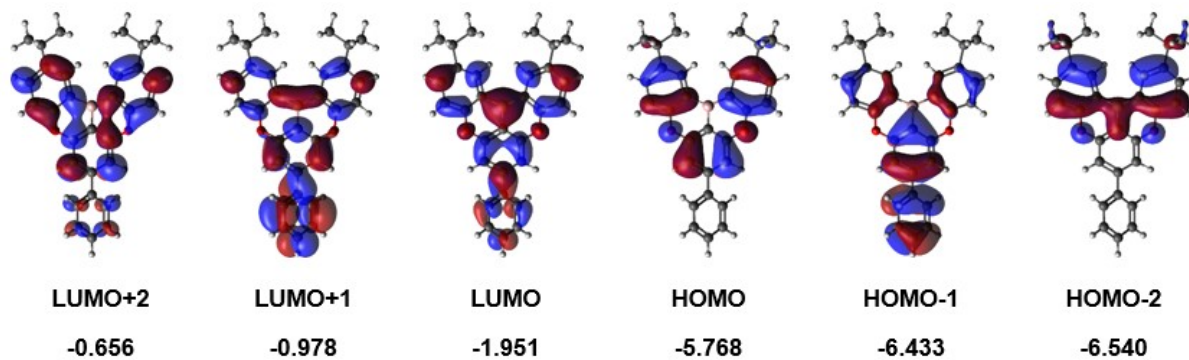
Figure S18. Calculated electronic transitions of TDBA-Ph.

Table S1. Calculated transition character of TDBA-Ph.

State	Absorption energy (eV) & wavelength (nm)	Characteristic of transition	Contribution (%)
T_1	2.818 eV (440.0 nm)	HOMO → LUMO	96.9
T_2	3.366 eV (368.3 nm)	HOMO-1 → LUMO	72.0
S_1	3.381 eV (366.7 nm)	HOMO → LUMO	94.4

LUMO+2	LUMO+1	LUMO	HOMO	HOMO-1	HOMO-2
-0.846	-1.066	-1.966	-5.770	-6.399	-6.537
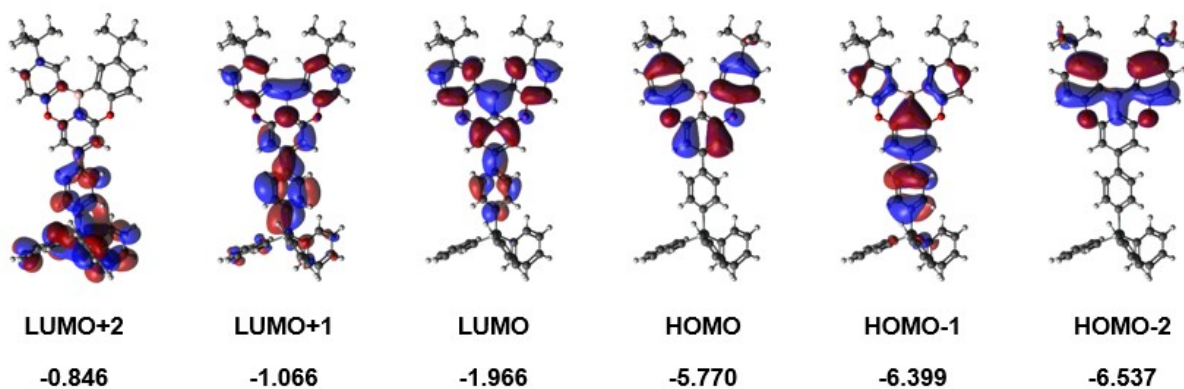
Figure S19. Calculated electronic transitions of TDBA-Ge.

Table S2. Calculated transition character of TDBA-Ge.

State	Absorption energy (eV) & wavelength (nm)	Characteristic of transition	Contribution (%)
T_1	2.811 eV (441.0 nm)	HOMO → LUMO	96.7
T_2	3.330 eV (372.4 nm)	HOMO-1 → LUMO	73.0
S_1	3.372 eV (367.6 nm)	HOMO → LUMO	94.4

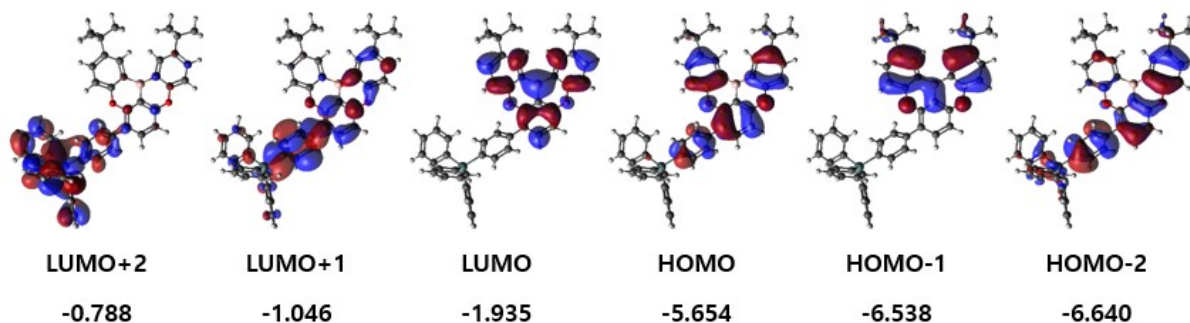| LUMO+2	LUMO+1	LUMO	HOMO	HOMO-1	HOMO-2
-0.788	-1.046	-1.935	-5.654	-6.538	-6.640

Figure S20. Calculated electronic transitions of mTDBA-Ge.

Table S3. Calculated transition character of mTDBA-Ge.

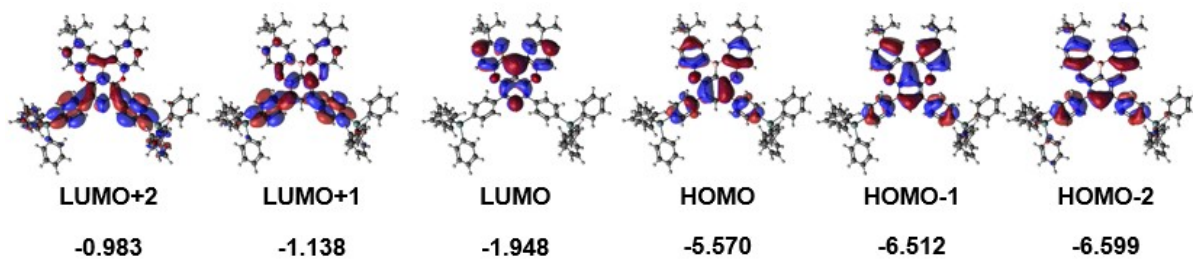| State	Absorption energy (eV) & wavelength (nm)	Characteristic of transition	Contribution (%)
T_1	2.749 eV (451.0 nm)	HOMO → LUMO	95.9
T_2	3.382 eV (366.6 nm)	HOMO-1 → LUMO / HOMO → LUMO+1	13.6/ 56.8
S_1	3.259 eV (380.5 nm)	HOMO → LUMO	95.4

Figure S21. Calculated electronic transitions of mTDBA-2Ge.

Table S4. Calculated transition character of mTDBA-2Ge.

State	Absorption energy (eV) & wavelength (nm)	Characteristic of transition	Contribution (%)
T_1	2.681 eV (462.5 nm)	HOMO → LUMO	95.9
T_2	3.239 eV (382.8 nm)	HOMO → LUMO+1	74.1
S_1	3.157 eV (392.8 nm)	HOMO → LUMO	95.7

$\Delta E_{ST} = 0.515\ eV$, $f(S_0 - S_1) = 0.1309$

	$\langle S_1|\hat{H}_{SOC}|T_1\rangle$ (cm^{-1})	$\langle S_1|\hat{H}_{SOC}|T_2\rangle$ (cm^{-1})	$\langle S_1|\hat{H}_{SOC}|T_3\rangle$ (cm^{-1})	$\langle S_1|\hat{H}_{SOC}|T_4\rangle$ (cm^{-1})
TDBA-Ge	**0.040**	0.323	0.041	0.030

$\Delta E_{ST} = 0.471\ eV$, $f(S_0 - S_1) = 0.1139$

	$\langle S_1|\hat{H}_{SOC}|T_1\rangle$ (cm^{-1})	$\langle S_1|\hat{H}_{SOC}|T_2\rangle$ (cm^{-1})	$\langle S_1|\hat{H}_{SOC}|T_3\rangle$ (cm^{-1})	$\langle S_1|\hat{H}_{SOC}|T_4\rangle$ (cm^{-1})
mTDBA-Ge	**0.102**	0.479	0.190	0.081

0.1162

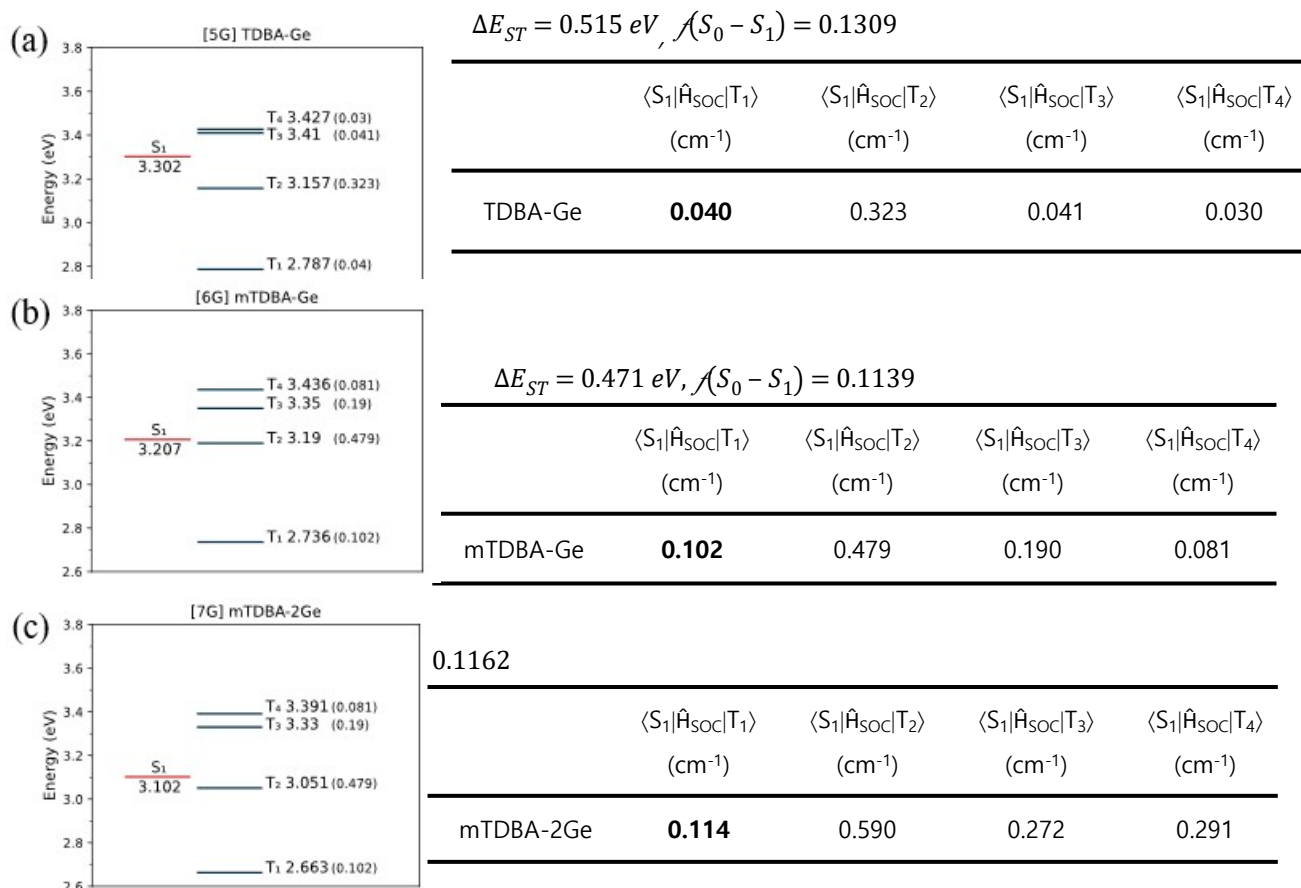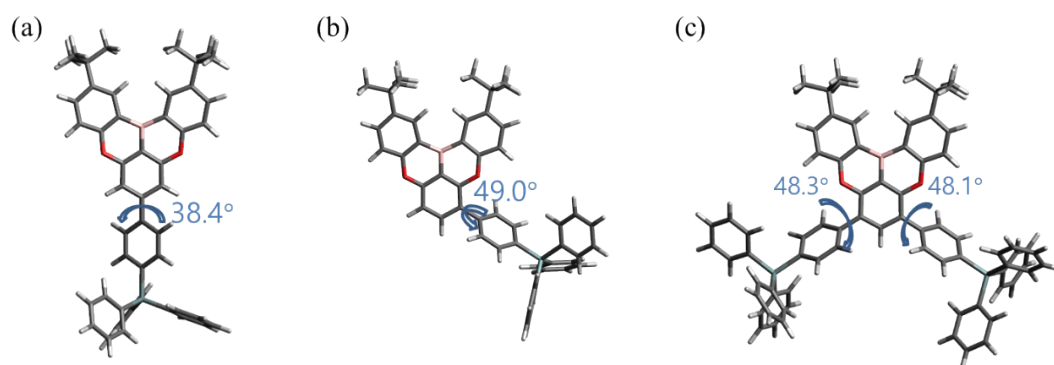|	$\langle S_1|\hat{H}_{SOC}|T_1\rangle$ (cm^{-1})	$\langle S_1|\hat{H}_{SOC}|T_2\rangle$ (cm^{-1})	$\langle S_1|\hat{H}_{SOC}|T_3\rangle$ (cm^{-1})	$\langle S_1|\hat{H}_{SOC}|T_4\rangle$ (cm^{-1})
mTDBA-2Ge	**0.114**	0.590	0.272	0.291

Figure S22. Isosurface of HOMO and LUMO composing S0→S1 transition (isovalue = 0.02) with representative electronic transition energies with SOC values of (a) TDBA-Ge, (b) mTDBA-Ge, (c) mTDBA-2Ge. TD-B3LYP calculation was conducted at the level of 6-31G(d,p).

Figure S23. Optimized (B3LYP/6-311G(d,p)) geometries at the ground state and dihedral angle between TDBA core and peripheral side groups (phenyl and tetraphenylgermanium) of (a) TDBA-Ge, (b) mTDBA-Ge, (c) mTDBA-2Ge.

a-axis

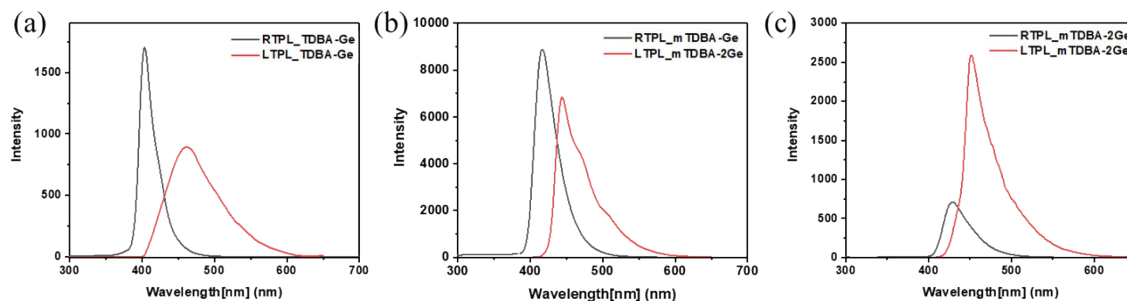b-axis

c-axis

a-axis

b-axis

c-axis
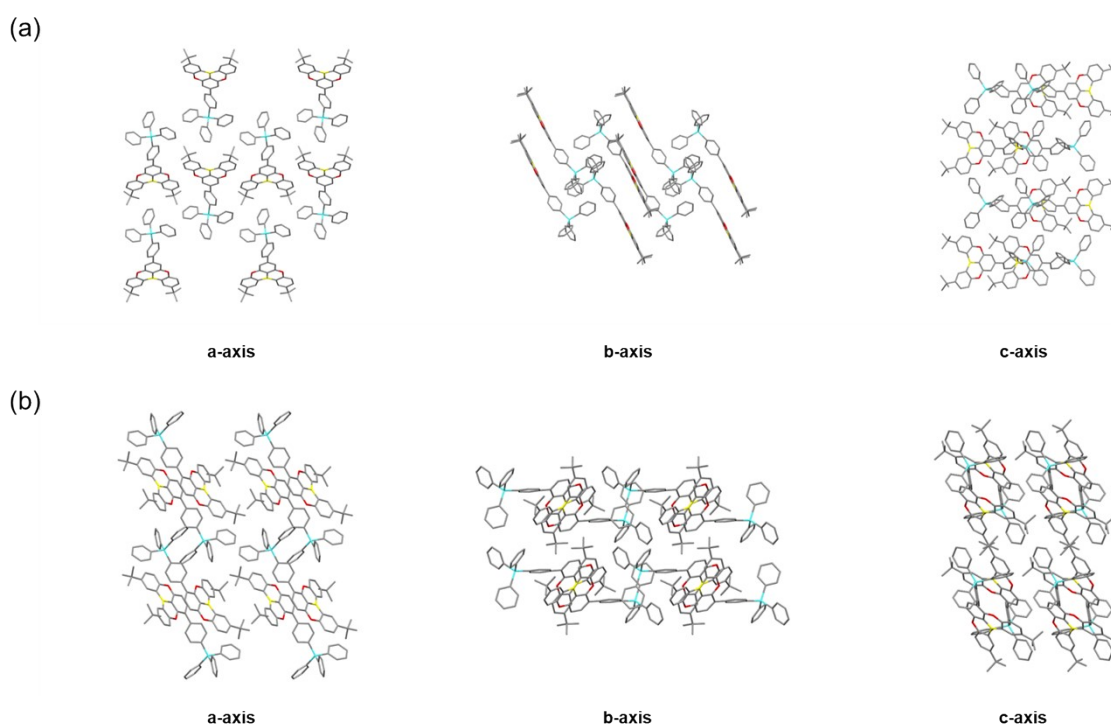
**Figure S24.** Single crystal XRD analysis. (a) TDBA-Ge, (b) mTDBA-Ge.
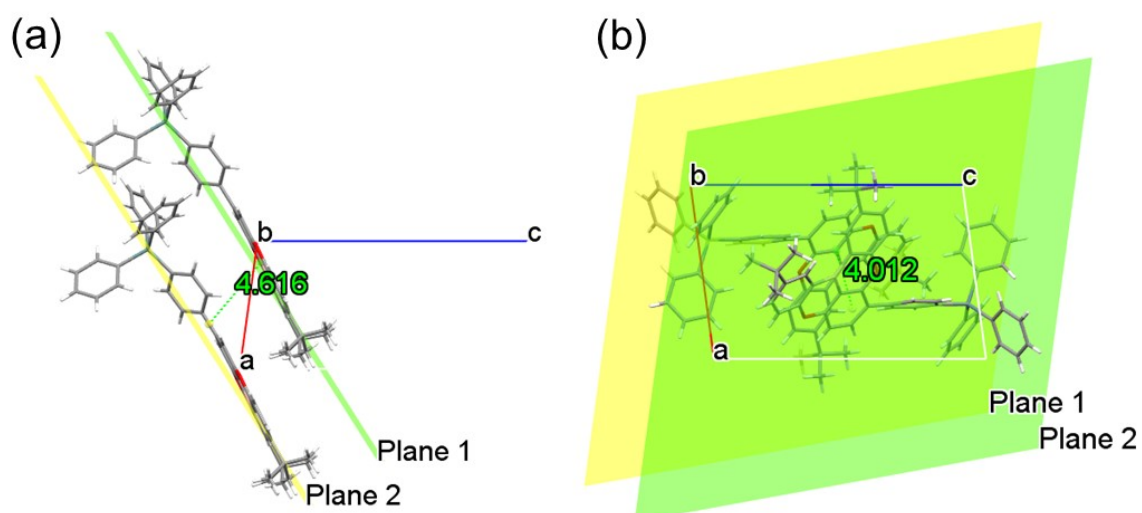
Figure S25. Single crystal XRD data for average distance of plane to plane (b-axis). (a) TDBA-Ge, (b) mTDBA-Ge.
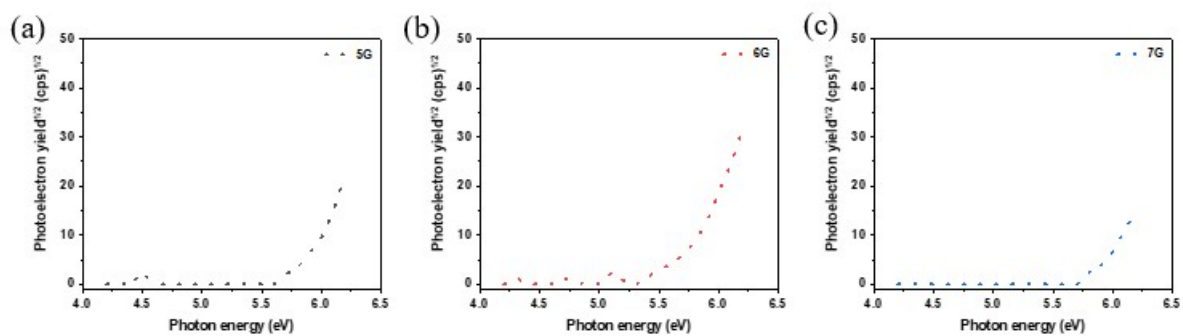

Figure S26. Photoelectron spectroscopy (AC-2) of TDBA-based host materials. (a) TDBA-Ge, (b) mTDBA-Ge, (c) mTDBA-2Ge.

Figure S27. Photoluminescence (black) at room temperature, low temeperature photoluminescence with delay (Red) at 77K spectra of neat film. (a) TDBA-Ge, (b) mTDBA-Ge, (c) mTDBA-2Ge.
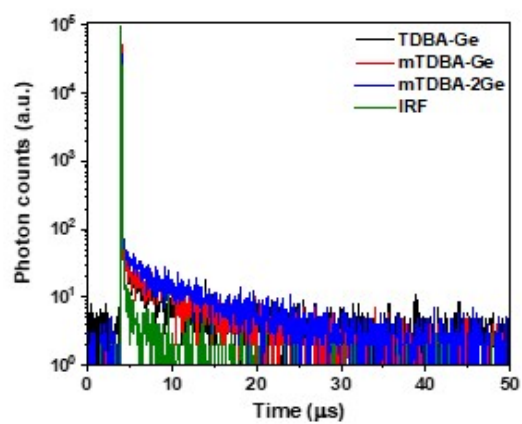
Figure S28. Transient photoluminescence decay spectra of the neat films (IRF: instruments response function). Range : 50 μs.
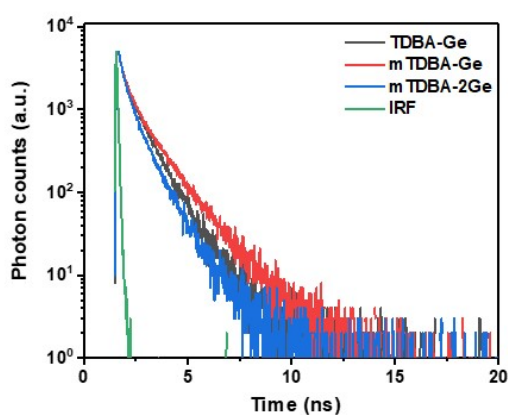

Figure S29. Transient photoluminescence decay spectra of the neat films (IRF: instruments response function). Range : 20 ns.

Table S5. Rate constant for TDBA based host materials (non-doped film) at room temperature.

	TDBA-Ge	mTDBA-Ge	mTDBA-2Ge
Φ	0.18	0.20	0.25
Φ_F	0.172	0.201	0.244
Φ_{TADF}	0.003	0.003	0.009
τ_f (ns)	11.50	14.74	10.30
τ_{TADF} (µs)	6.98	6.95	6.29
k_F ($\times 10^7$)	1.49	1.36	2.37
k_{IC} ($\times 10^7$)	7.04	5.31	7.00
k_{ISC} ($\times 10^7$)	1.62	1.07	3.28
Φ_{IC}	0.810	0.783	0.722
Φ_{ISC}	0.02	0.02	0.03
k_{TADF} ($\times 10^4$)	2.50	2.93	4.02
k_{RISC} ($\times 10^3$)	4.38	5.98	10.17
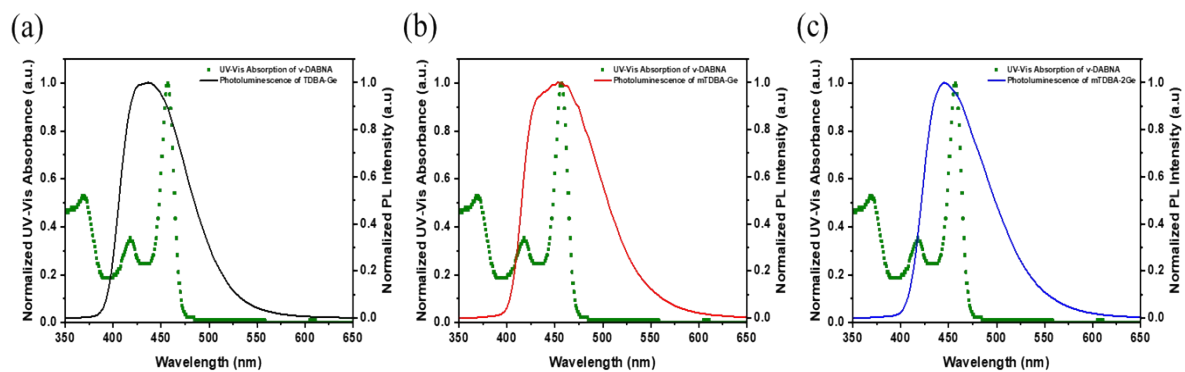
Figure S30. Spectral overlap between ν-DABNA and TDBA-based host. (a) TDBA-Ge, (b) mTDBA-Ge, (c) mTDBA-2Ge.
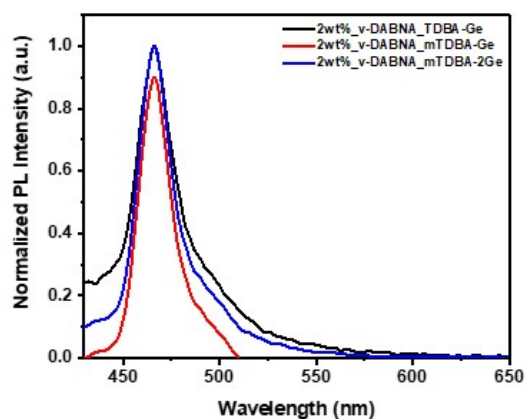
Figure S31. Photoluminescence spectra of the 2 wt% ν-DABNA-doped TDBA-based films.

Table S6. Summary of the photophysical properties of the 2wt% doped TDBA-based materials.

	Doped Film			
	λ_{em}[a] (nm)	FWHM (nm)	PLQY (%)	τ_d [b] (µs)
2wt%_v-DABNA_TDBA-Ge	465	18	29	2.73
2wt%_v-DABNA_mTDBA-Ge	465	18	24	3.22
2wt%_v-DABNA_mTDBA-2Ge	465	18	37	2.53

[a] Maximum wavelength in UV–Vis absorption and photoluminescence spectra. [b] Delayed lifetime calculated by PL decay for a vacuum-deposited neat film.

Figure S32. Transient photoluminescence decay spectra of the doped films (IRF: instruments response function). Range : 100 µs.
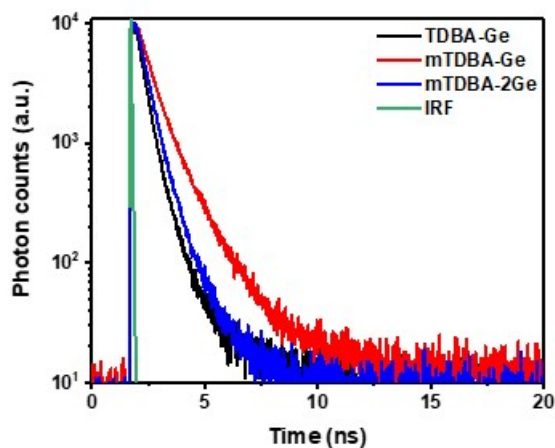
Figure S33. Transient photoluminescence decay spectra of the doped films (IRF: instruments response function). Range : 20 ns.

Table S7. Rate constant for ν-DABNA in TDBA based host materials (2wt% doped) at room temperature.

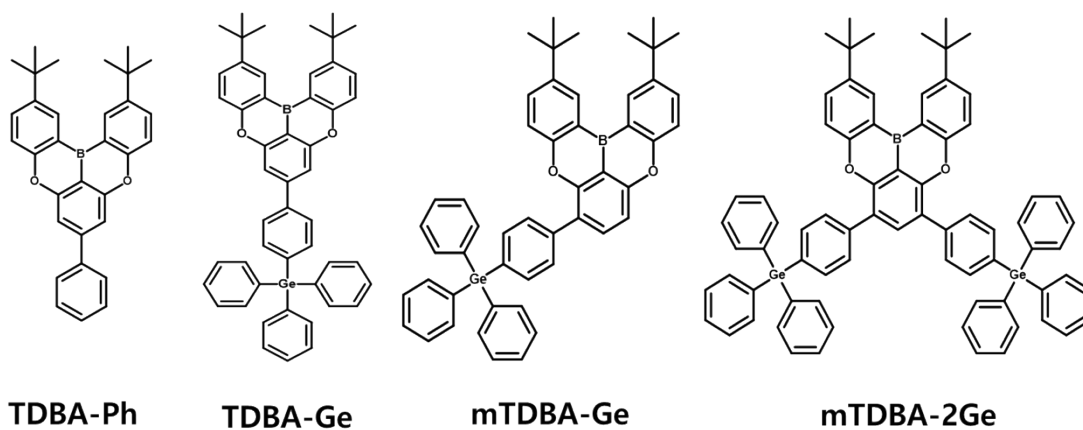|	TDBA-Ge	mTDBA-Ge	mTDBA-2Ge
Φ	0.29	0.24	0.37
Φ_F	0.223	0.198	0.284
Φ_{TADF}	0.067	0.042	0.090
τ_f (ns)	11.15	11.60	10.97
τ_{TADF} (μs)	2.73	3.22	2.53
k_F ($\times 10^7$)	1.99	1.70	2.58
k_{IC} ($\times 10^7$)	4.88	5.39	4.32
k_{ISC} ($\times 10^7$)	2.08	1.51	2.20
Φ_{IC}	0.545	0.627	0.475
Φ_{ISC}	0.23	0.18	0.24
k_{TADF} ($\times 10^4$)	10.59	7.43	14.75
k_{RISC} ($\times 10^4$)	3.07	1.78	5.51
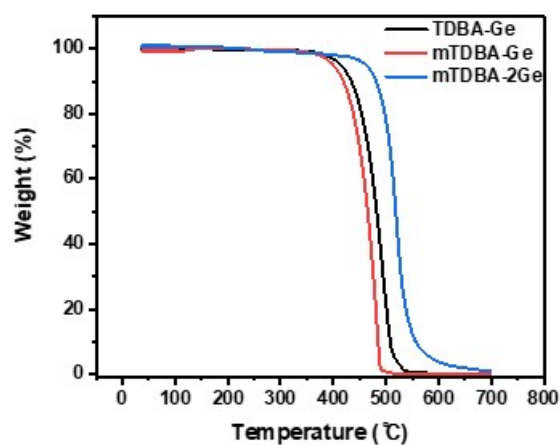
Figure S34. Thermo gravimetric analyzer (TGA) results of TDBA-based host materials.
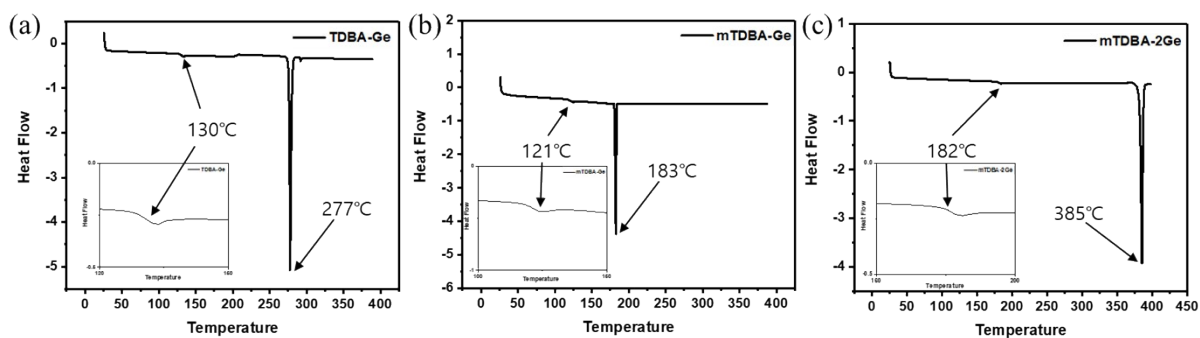
Figure S35. Differential scanning calorimetry (DSC) results of TDBA-based host materials. (a) TDBA-Ge, (b) mTDBA-Ge, (c) mTDBA-2Ge.

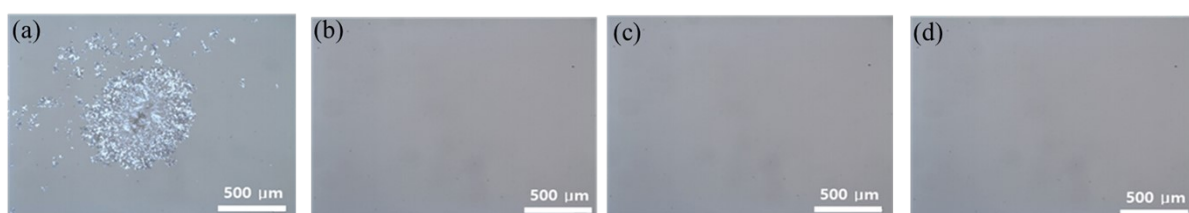**TDBA-Ph**   **TDBA-Ge**   **mTDBA-Ge**   **mTDBA-2Ge**

Scheme S2. Device performance of host materials.

Table S8. Rate constant of energy transfer between host and dopant based on Stern-Volmer equation.

	TDBA-Ph	TDBA-Ge	mTDBA-Ge	mTDBA-2Ge
Slope	**0.13**	**0.54**	**0.53**	**0.77**
$\mathbf{k_q{}^a}$	**3.43 x 10^7**	**5.25 x 10^7**	**4.99 x 10^7**	**11.20 x 10^7**

^{a} Energy transfer that occurs between host and dopant.

Figure S36. Optical microscopy image of the 2 wt% ν-DABNA-doped TDBA-based film. (a) TDBA-Ph, (b) TDBA-Ge, (c) mTDBA-Ge, (d) mTDBA-2Ge.

Table S9. Crystal data and structure refinement for TDBA-Ge.

Identification code	TDBA-Ge
Empirical formula	C50 H45 B Ge O2
Formula weight	761.26
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2$_1$
Unit cell dimensions	a = 7.3514(7) Å a= 90°.
	b = 17.756(2) Å b= 97.767(4)°.
	c = 15.1936(16) Å g = 90°.
Volume	1965.0(4) Å^3
Z	2
Density (calculated)	1.287 Mg/m^3
Absorption coefficient	0.820 mm^{-1}
F(000)	796
Crystal size	0.362 x 0.101 x 0.037 mm^3
Theta range for data collection	1.353 to 27.554°.
Index ranges	-7<=h<=9, -23<=k<=22, -19<=l<=19
Reflections collected	35014

Independent reflections	8895 [R(int) = 0.0507]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6716
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8895 / 1 / 493
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1041
R indices (all data)	R1 = 0.0684, wR2 = 0.1126
Absolute structure parameter	0.5
Extinction coefficient	n/a
Largest diff. peak and hole	0.710 and -0.549 e.Å^{-3}

Table S10. Crystal data and structure refinement for mTDBA-Ge.

Identification code	mTDBA-Ge	
Empirical formula	C50 H45 B Ge O2	
Formula weight	761.26	
Temperature	98(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.6818(3) Å	a= 87.307(2)°.
	b = 13.8617(4) Å	b= 82.169(2)°.
	c = 14.9707(4) Å	g = 86.075(2)°.
Volume	1984.31(10) Å^3	
Z	2	
Density (calculated)	1.274 Mg/m^3	
Absorption coefficient	0.812 mm^{-1}	
F(000)	796	
Crystal size	0.228 x 0.210 x 0.116 mm^3	
Theta range for data collection	1.474 to 27.528°.	
Index ranges	-12<=h<=12, -18<=k<=18, -19<=l<=19	
Reflections collected	53904	
Independent reflections	9122 [R(int) = 0.0329]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6877	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	9122 / 0 / 487
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0296, wR2 = 0.0694
R indices (all data)	R1 = 0.0352, wR2 = 0.0717
Extinction coefficient	n/a
Largest diff. peak and hole	0.457 and -0.308 e.Å^{-3}