Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis and Electroluminescence Properties of Novel Deep Blue Emitting 6,12-Dihydro-diindeno[1,2-b;1',2'-e]pyrazine Derivatives

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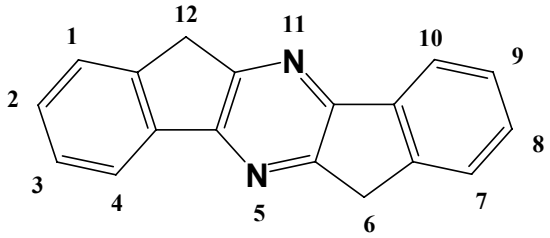
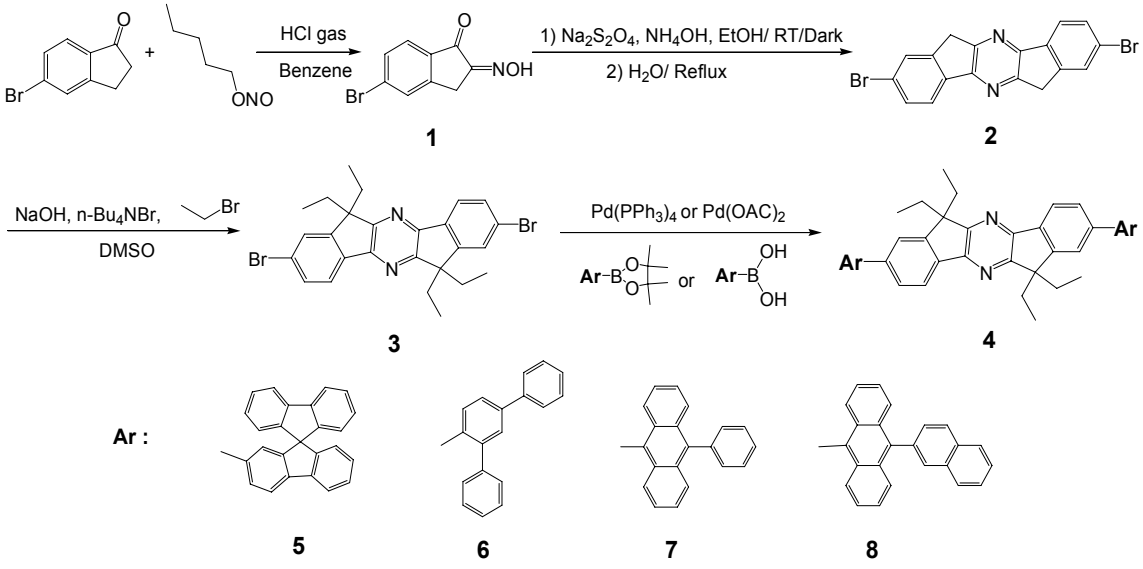


Scheme S1. The molecular structure of indenopyrazine (IPY), with relevant position numbered.



Scheme S2. Synthetic routes of SF-EPY, TP-EPY, PA-EPY, and NA-EPY.

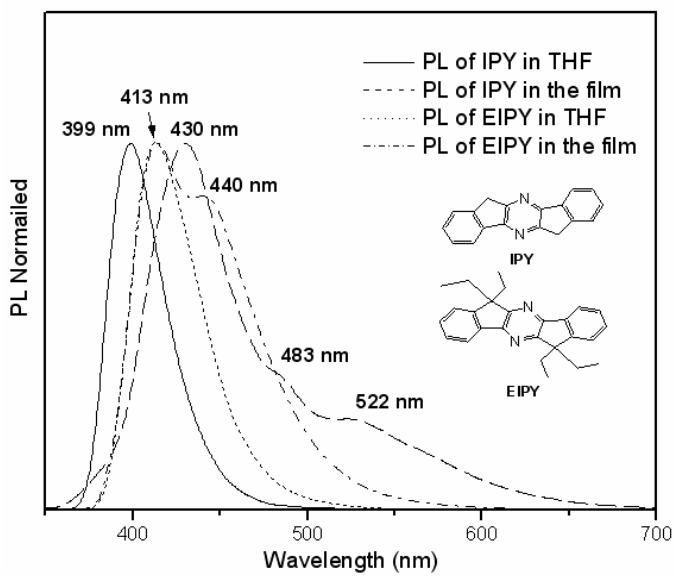


Figure S1. PL spectra of indenopyrazine(IPY) & ethyl indenopyrazine(EIPY)

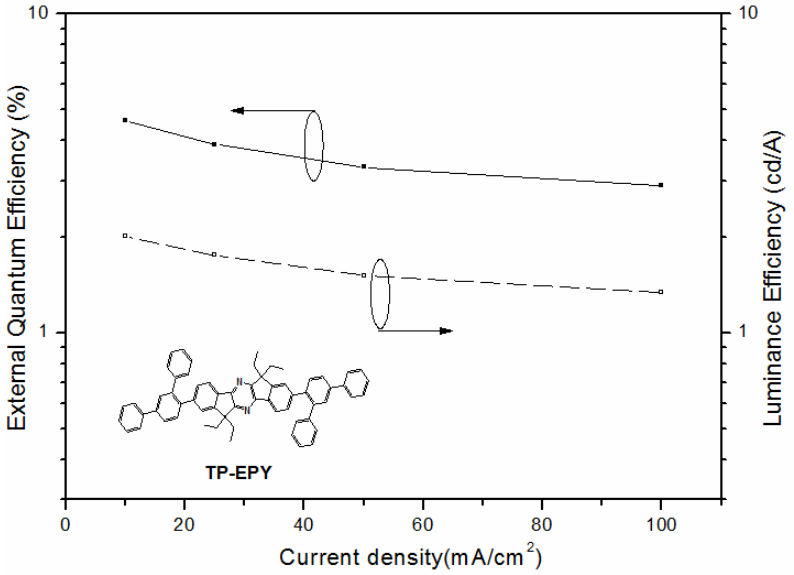


Figure S2. Plots of external quantum efficiency and luminance efficiency as functions of the current density for TP-EPY

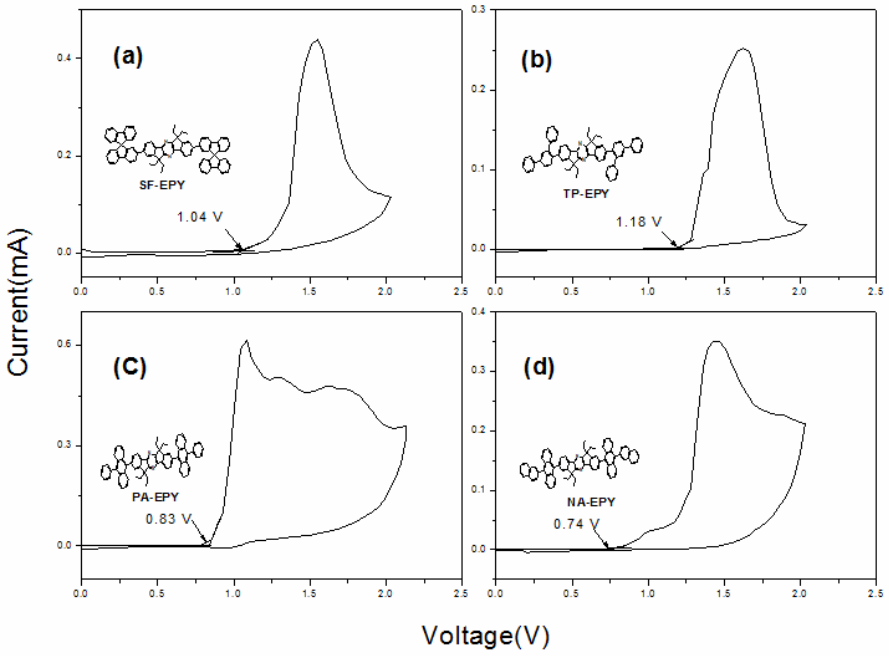


Figure S3. Cyclic voltammograms of thin films of (a) SF-EPY (b) TP-EPY (c) PA-EPY (d) NA-EPY.

Table S1. Thermal properties and AFM data of SF-EPY, TP-EPY, PA-EPY, and NA-EPY

	Tg	Tm	Td	Ra (nm)		
	(℃)	(℃)	(℃)	Untreatment	@ 25℃	@ 65℃
SF-EPY	-	-	393	0.4	1.0	2.7
TP-EPY	-	340	437	0.8	0.7	0.9
PA-EPY	112	-	383	0.5	0.7	1.1
NA-EPY	-	295	518	0.4	3.4	3.5
DPVBi	64	204	-	1.3	44.1	43.0

1) Untreatment : just after evaporation, @ 25℃ : 25□ treatment for 24 h under N_2 @ 65℃ : 65□ treatment for 24 h under N_2

2) Ra means an average surface roughness.

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Experimental Details

1. General information

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 500 and Avance 600 spectrometers. Fast atom bombardment (FAB) Mass spectra were recorded on a JEOL, JMS-AX505WA, HP5890 series II. Atomic force microscopy (AFM) imaging was performed in air using a PicoScan system (Molecular Imaging) equipped with a 5×5 μm scanner. Magnetic-ac(Mac) mode (a non-contact mode) was used for all the AFM images. The optical absorption spectra were obtained with a HP 8453 UV-VIS-NIR spectrometer. The melting temperatures (T_m), glass-transition temperatures (T_g), and degradation temperatures (T_d) of the compounds were measured by carrying out differential scanning calorimetry (DSC) under a nitrogen atmosphere using a DSC2910 (TA Instruments) and thermogravimetric analysis (TGA) using a SDP-TGA2960 (TA Instruments). A Perkin Elmer luminescence spectrometer LS50 (xenon flash tube) was used for photo- and electro-luminescence spectroscopy. The redox potentials of the compounds were determined with cyclic voltammetry (CV) using a WBCS 3000 system with a scanning rate of 100 mV/s. The synthesized materials were dissolved in acetonitrile (AN) with 0.1M tetrabutylammonium perchlorate as an electrolyte. We used a platinum working electrode and a saturated $Ag/AgNO_3$ reference electrode. Ferrocene was used for potential calibration and for reversibility criteria. For the EL devices, all organic layers were deposited under 10^{-6} Torr, with a rate of deposition of 1 Å/s to give an emitting area of 4 mm^2. The LiF and aluminium layers were continuously deposited under the same vacuum conditions. The current–voltage (I–V) characteristics of the fabricated EL devices were obtained with a Keithley 2400 electrometer. Light intensity was obtained with a Minolta CS-100A and CS-1000A.

2. Synthesis of SF-EPY, TP-EPY, PA-EPY, and NA-EPY

These compounds were synthesized by Suzuki aryl-aryl coupling reaction using Pd catalyst. A typical synthetic procedure was as follows : 2,8-dibromo-6,6,12,12-tetraethyl-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine (6.7 g, 13 mmol) and 4,4,5,5-tetramethyl-2-9H-spirobifluoren-2-yl-1,3,2-dioxaborolane (13 g, 31 mmol) were mixed in a round flask of 500 mL and then tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) (1.5g, 1.3 mmol) was added, which was stirred by using anhydrous THF of 350 mL as solvent. Afterwards, 2M K_2CO_3 (100 mL) was added and refluxed. The reaction was checked with TLC, and when the reaction was completed, extraction was performed by using water and EA (ethyl acetate), and moisture was removed by using anhydrous $MgSO_4$. After removing solvent, recrystallization was performed with THF and ethanol; and as a result, pure yellow SF-EPY was obtained.

2-1. Synthesis of 6,6,12,12-tetraethyl-2,8-bis(9',9''-spirobifluorene-2-yl)-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine (SF-EPY)

The final yield was 35%. ^{1}H NMR (500 MHz, THF-d_8) : δ 0.29 (t, 12H), 2.07 (m, 4H), 2.30 (m, 4H),

6.62 (d, 2H), 6.74 (d, 4H), 7.11 (m, 8H), 7.37 (m, 6H), 7.50 (d, 2H), 7.64 (s, 2H), 7.80 (d, 2H), 7.94 (m, 8H), 8.03 (d, 2H). ^{13}C NMR(500MHz, $CDCl_3$) : 163.0, 152.1, 150.3, 149.6, 148.9, 142.1, 142.0, 141.3, 138.5, 128.1, 127.9, 127.5, 126.7, 124.4, 124.1, 122.8, 121.6, 121.3, 120.5, 120.3, 54.2, 31.4, 29.9, 8.8. FT-IR (KBr cm^{-1}) : 3061, 2962, 2928, 2875, 1713, 1614, 1446, 1367, 776, 752, 730. Fab^+-MS *m/e* : 997, High-resolution mass spectra (HRMS) Calcd. for C76 H57 N2 (M+) 997.4522, found : 997.4512.

2-2. Synthesis of 6,6,12,12-Tetraethyl-2,8-bis-[1,1';3',1'']terphenyl-4'-yl-6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine (TP-EPY)

The yield was 56%. ^{1}H NMR (500 MHz, THF-d_8) : δ (ppm) 0.20 (t, 12H), 1.83 (s, 4H), 2.17 (s, 4H), 7.1 (s, 2H), 7.27 (m, 10H), 7.35 (t, 2H), 7.48 (m, 6H), 7.63 (d, 2H), 7.74 (m, 8H), 7.95 (d, 2H), ^{13}C NMR(500MHz, $CDCl_3$) : 162.9, 152.2, 149.1, 142.2, 141.8, 141.4, 140.8, 140.7, 139.9, 137.9, 131.2, 130.1, 129.7, 129.0, 128.3, 127.7, 127.4, 126.9, 126.4, 125.5, 121.0, 53.9, 31.3, 8.9. FT-IR(KBr cm^{-1}) : 3060, 2962, 2930, 2873, 1713, 1613, 1478, 1441, 1369, 830, 773, 749, 697. Fab^+-MS *m/e* : 824, HRMS Calcd for C62 H52 N2 (M+) 824.4130, found : 824.4124.

2-3. Synthesis of 6,6,12,12-tetraethyl-2,8-(10-Phenyl-9-anthracyl)-6,12-dihydrodiindeno(1,2-b;1,2-e)pyrazine(PA-EPY)

The yield was about 35 %. ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 0.61(t, 12H), 2.17 (m, 4H), 2.48 (m, 4H), 7.38 (m, 8H), 7.52 (t, 4H), 7.57~-7.64 (m, 10H), 7.74 (t, 4H), 7.81 (t, 4H), 8.39 (d, 2H). ^{13}C NMR(500MHz, $CDCl_3$) : 163.3, 152.1, 140.4, 139.2, 137.6, 131.5, 130.9, 130.1, 128.6, 127.7, 127.3, 127.0, 126.6, 126.5, 125.4, 125.2, 121.4, 54.4, 31.6, 9.1. FT-IR(KBr cm^{-1}) : 3060, 2961, 2928, 2874, 1654, 1617, 1458, 1440, 1364, 769, 702. FAB^+-MS *m/e* : 873, HRMS Calcd for C66 H53 N2 (M+) 873.4209, found : 873.4185.

2-4. Synthesis of 6,6,12,12-Tetraethyl-2,8-bis-(10-naphthalen-2-yl-anthracen-9-yl)-6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine(NA-EPY)

The yield was 24 %. ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 0.63 (t, 12H), 2.25 (s, 4H), 2.50 (s, 4H), 7.39 (m, 8H), 7.64-7.61 (m, 10H), 7.77 (d, 4H), 7.83 (d, 4H), 7.95 (d, 2H), 8.01 (d, 2H), 8.05 (d, 2H), 8.11 (d, 2H), 8.41 (d, 2H). FT-IR(KBr cm^{-1}) : 3059, 2961, 2928, 2875, 1714, 1614, 1456, 1441, 1364, 821, 763, 747. FAB^+-MS *m/e* : 973, HRMS Calcd for C74 H57 N2 (M+) 973.4522, found : 973.4508.

3. Synthesis of 2,8-dibromo-6,6,12,12-tetraethyl-6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine (3)

3-1. Synthesis of 5-Bromo-2,3-dihydro-2-(hydroxyimino)inden-1-one (1)

To a 500 mL round flask, 5-bromo-indanone (10 g, 47 mmol) and benzene(160 mL) were mixed and stirred at a normal temperature. After bubbling dry HCl gas for 5 minutes, amylnitrite (6.66 g, 56 mmol) was slowly added. While dry HCl gas was bubbled, the mixture was heated until 40□ and stirred for 5

hours. After it was again stirred for 12 hours at room temperature, the reactant was filtered and rinsed with MeOH, MC to obtain pure **1**. The yield was 84%. ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm) 3.78 (s, 2H), 7.68 (s, 2H), 7.9 (s, 1H), 12.72 (s, 1H)

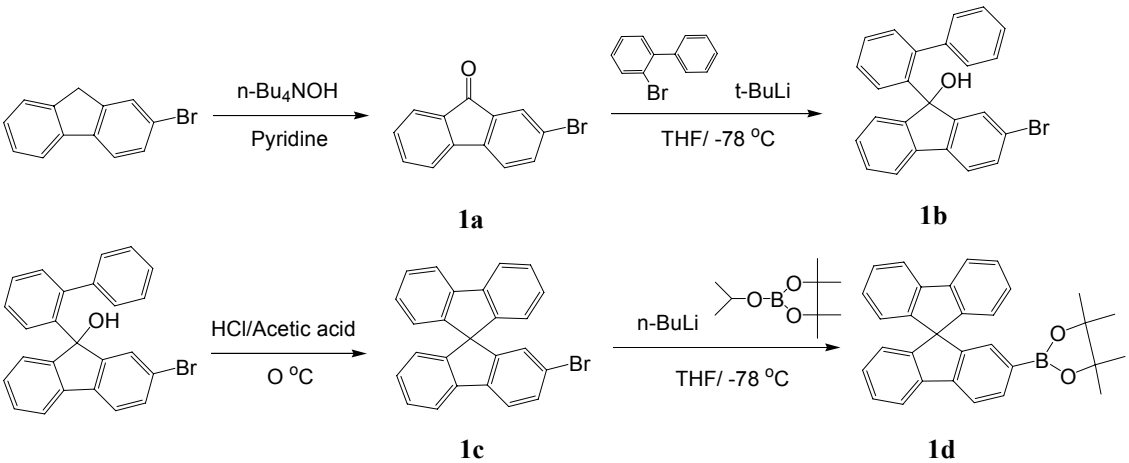
3-2. Synthesis of 2,8-Dibromo-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine (2)

To a 500 mL round flask, the synthesized **1** (6 g, 25 mmol) and sodium dithionite (13 g, 75 mmol) were mixed with EtOH (50 mL). In the nitrogen atmosphere, 14.5% ammonia solution (50 mL) was added and stirred at a room temperature with no roomlight for 3 days. After distilled water (50 mL) was added to reaction mixture, it was heated and refluxed for 24 hours in the air. When the reaction was finished, it was cooled and then more distilled water (100 mL) was added. After stirring, the mixture was filtered and sufficiently rinsed with MeOH, diethyl ether and then **2** was obtained. The yield was 62 %. ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm) 4.06 (s, 4H), 7.35 (d, 2H), 7.6 (s, 2H), 7.96 (d, 2H)

3-3. Synthesis of 2,8-Dibromo-6,6,12,12-tetraethyl-6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine (3)

To a 500 mL round flask, the synthesized **2** (5 g, 12 mmol), KOH (2.71 g, 48 mmol), and *n*-Bu_4NBr (0.77 g, 2.4 mmol) were added, which were stirred with DMSO of 300 mL at a room temperature. And then, bromoethane (7.3 mL, 67 mmol) was slowly added. This mixture was stirred at a room temperature for 24 hours, and when the reaction was completed, extraction was performed with water and benzene, and then anhydrous $MgSO_4$ was added before filtering and decompressing and concentrating. With additional benzene and methanol, the mixture was left in sonicator for thirty minutes. When this was filtered, white solid matter was created. The yield was 54%. ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm) 0.38 (t, 12H) 2.07 (s, 4H), 2.33 (s, 4H), 7.58 (m, 4H), 7.95 (d, 2H), Fab^+-MS m/e : 526

4. Synthesis of Side Groups (SF, TP, PA, and NA)



Scheme S3. Synthetic routes of 4,4,5,5-Tetramethyl-2-9H-spirobifluoren-2-yl-1,3,2-dioxaborolane

4-1-1. Synthesis of 2-Bromo-9H-fluoren-9-one (1a)

2-Bromo-9H-fluorene (5 g, 20 mmol) was dissolved in pyridine of 19 mL Under a nitrogen atmosphere, tetrabutylammonium hydroxide in methanol (5 mL, 5 mmol) was added slowly and stirred. After the reaction was done, extraction was carried out by using water and EA and moisture was removed by using anhydrous $MgSO_4$. After eliminating a solvent, re-crystallization was performed with MeOH to obtain pure **1a**. The yield was 90%. ^{1}H NMR (300MHz, $CDCl_3$) : δ (ppm) 7.41 (m, 2H), 7.51 (m, 2H), 7.67 (m, 3H)

4-1-2. Synthesis of 2-Bromo-9-(biphenyl-2-yl)-9H-fluoren-9-ol (1b)

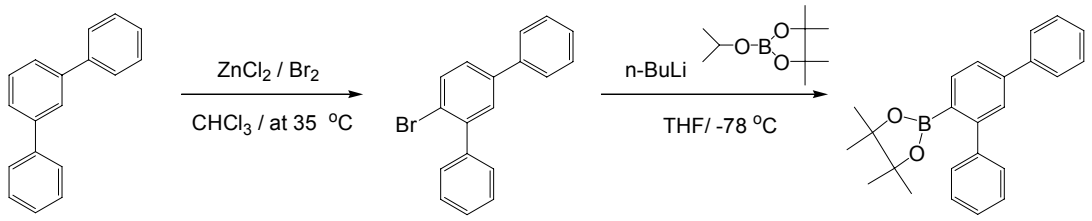
Anhydrous tetrahydrofuran(THF) of 300 mL was added to 2-bromobiphenyl (7 mL, 43 mmol) in a round flask of 500 mL under a nitrogen, which was stirred. After cooling to -78℃, *t*-butyllithum (60 mL, 103 mmol) was added and stirred for about one hour, and then a synthesized material, **1a** (13.2g, 51mmol) was slowly dissolved in anhydrous THF. After confirming the reaction with TLC, extraction was performed with water and EA and moisture was removed by using anhydrous $MgSO_4$. After removing a solvent, column was performed under the condition of n-hexane : EA = 50 : 1 to obtain pure **1b**. The yield was 54%. ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm) 2.23 (s, 1H), 5.96 (d, 1H), 6.14 (d, 1H), 6.67 (m, 2H), 6.82 (t, 1H), 6.97 (d, 1H), 7.00 (d, 1H), 7.14 (m, 1H), 7.19 (m, 3H), 7.32 (m, 3H), 7.52 (t, 1H), 8.41 (d, 1H).

4-1-3. Synthesis of 2-Bromo-9-spirobifluorene (1c)

A synthesized compound, **1b** (8.7 g, 21 mmol) was dissolved in acetic acid of 200 mL and it was cooled down to 0～5℃. Afterwards, HCl (10 mL) was slowly dropped. After the reaction was completed, crystals were filtered to obtain pure **1c**. The yield was 72%. ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm) 6.73 (d, 3H), 6.84 (s, 1H), 7.14 (t, 3H), 7.40 (m, 3H), 7.49 (d, 1H), 7.71 (d, 1H), 7.85 (m, 3H)

4-1-4. Synthesis of 4,4,5,5-Tetramethyl-2-9H-spirobifluoren-2-yl-1,3,2-dioxaborolane (1d)

A synthesized compound, **1c** (7.11 g, 18 mmol) was put in a 500 mL round flask under a nitrogen and then anhydrous THF of 300 mL was added to the flask and stirred. After cooling it to -78℃, n-butyllithum (24 mL, 40 mmol) was dropped slowly, followed by stirring for 30 minutes, and then 2-isopropoxy-4,4,5,5- tetramethyl-1,3,2-dioxaborolane (8 mL, 40 mmol) was added. The reaction was confirmed with TLC, extraction was done with water and EA, and moisture was removed by using anhydrous $MgSO_4$. When a solvent was removed and recrystallization was performed with MeOH, pure **1d** was obtained. The yield was 71%. ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm) 1.25 (s, 12H), 6.93 (d, 3H), 7.01 (s, 1H),7.10 (t, 3H), 7.47 (m, 3H), 7.63 (d, 1H), 7.85 (d, 1H), 7.92 (m, 3H).



2a **2b**

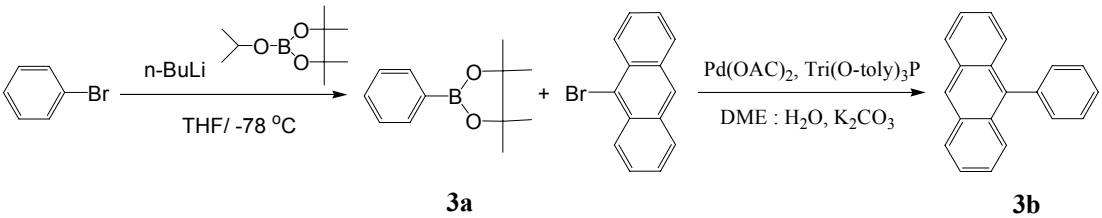
Scheme S4. Synthetic routes of 4,4,5,5-Tetramethyl-2-[1,1';3',1'']terphenyl-4'-yl-[1,3,2]dioxaborolane

4-2-1. Synthesis of 4'-Bromo-[1,1';3',1'']terphenyl (2a)

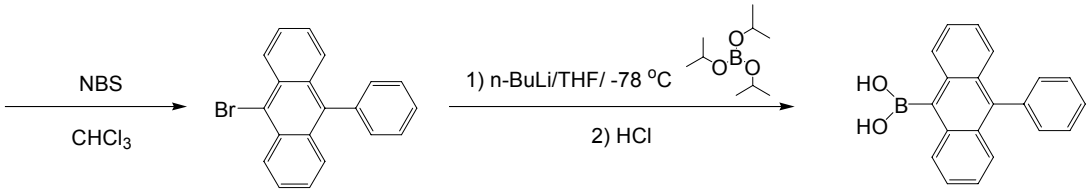
To a 500 mL round flask, [1,1';3',1'']terphenyl (11.52 g, 50.0 mmol) and $ZnCl_2$ (6.82 g, 50.0 mmol) were mixed with chloroform of 300 mL. The temperature was cooled down to -78℃ and then increased until 35℃. Br_2 of 2.53 mL diluted with chloroform of 76 mL were slowly dropped into the reaction solution for 2 hours. The reaction was confirmed with TLC, extraction was done with water and chloroform, and moisture was removed by using anhydrous $MgSO_4$. This compound was used for the next reaction without further purification.

4-2-2. Synthesis of 4,4,5,5-Tetramethyl-2-[1,1';3',1'']terphenyl-4'-yl-[1,3,2]dioxaborolane (2b)

2a was put in a 500 mL round flask. And then anhydrous THF of 300 mL was added to the flask and stirred under a nitrogen atmosphere. This was cooled down to –78℃ and then *n*-butyllithum (31.14 mL, 1.6 M in Hexane) was slowly mixed to create light green sediment. After stirring it for about 30 minutes, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12.44 mL, 59.7 mmol) was slowly added. The reaction was confirmed with TLC, extraction was done with water and EA, and moisture was removed by using anhydrous $MgSO_4$. When column was performed in the condition of EA : n-hexane = 1:20, pure white **2b** was obtained. The yield was 56 %. ^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) 1.25 (s, 12H), 7.38 (m, 4H), 7.45 (m, 4H), 7.57 (d, 1H), 7.63(m, 3H), 7.81(d, 1H), EI^+-MS m/e : 356



3a **3b**



3c **3d**

Scheme S5. Synthetic routes of 9-Phenylanthracen-10-yl-10-boronic acid

4-3-1. Synthesis of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (3a)

Bromobenzene (4 mL, 37.68mmol) in a 250 mL round flask was mixed with anhydrous THF under a nitrogen atmosphere. It was cooled down to -78℃ and *n*-butyllithum (28.26 mL, 45.22 mmol) was added slowly into the reaction solution. After stirring it for 30 minutes, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9.41 mL, 45.22 mmol) was added. After confirming the reaction with TLC, extraction was performed with water and chloroform to obtain pure **3a**. The yield was 98%. ^{1}H-NMR (300MHz, $CDCl_3$): δ (ppm) 1.31 (s, 12H), 7.34 (t, 2H), 7.43 (t, 1H), 7.82 (d, 2H) EI^+-MS *m/e* : 204

4-3-2. Synthesis of 9-Phenylanthracene (3b)

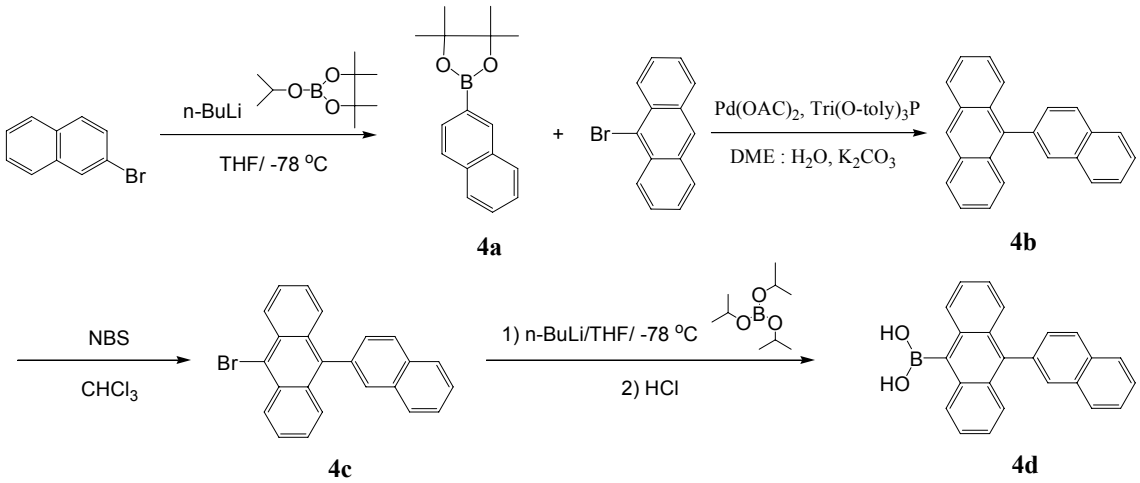
In a nitrogen air current, 9-bromoanthracene (7.93g, 0.029mol), palladium (II) acetate (1.95 g, 8.7 mmol) , and tris(2-methylphenyl) phosphine (2.73 g, 8.7 mmol) were mixed in a 500 mL round flask. The reaction mixtures were stirred with 1,2-dimethoxyethene of 300 mL used as a solvent. Then, K_2CO_3 (20.14 g, 0.145 mol) was dissolved in a mixed solution of water and DME, which was added as well. **3a** (7.1 g, 0.035 mol) dissolved in dimethoxyethene of 50 mL was slowly dropped into the reaction solution and then refluxed for 12 hours. The reaction was confirmed with TLC, and when the reaction was finished, extraction was performed by using water and chloroform. Anhydrous $MgSO_4$ was put into an organic layer to remove moisture and the solvent was concentrated. When recrystalization was done with THF and methanol, pure **3b** could be obtained. The yield was 87 %. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.46 (m, 10H), 7.58 (m, 4H), 7.67 (d, 2H), 8.06 (d, 2H), 8.49 (s, 1H)

4-3-3. Synthesis of 10-Bromo-9-phenylanthracene (3c)

To a round flask of 500 mL charged with chloroform of 300 mL, **3b** (5g, 0.020mol) and *N*-bromosuccin imide (NBS) (3.53g, 0.020 mol) were added and smoothly refluxed for 2 hours while the temperature was maintained at 40 ~ 50℃. When the reaction was completed, evaporation was carried to remove NBS, and with column in the condition of n-hexane : $CHCl_3$ = 5 : 1, pure **3c** was obtained. The yield was about 85%. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ (ppm) 7.34~7.41 (m, 4H), 7.56~7.65 (m, 7H), 8.62 (d, 2H), EI^+-MS *m/e* :335

4-3-4. Synthesis of 9-Phenylanthracen-10-yl-10-boronic acid (3d)

Synthesized **3c** (3g, 9mmol) were mixed with anhydrous THF in a 250 mL round flask under a nitrogen air. It was cooled down to -78□ and after adding *n*-butyllithum (6.75 mL, 11 mmol), it was stirred for about 30 minutes. Then, triethylborate (1.86 mL, 11 mmol) was added and stirred until it reached a room temperature. Then, after adding 1N HCl, it was stirred for additional 30 minutes and then extraction was performed with water and diethyl ether to obtain pure **3d**. The yield was 78%. ^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) 7.37 (t, 2H), 7.41 (t, 2H), 7.52 (t, 5H), 7.64 (m, 2H), 8.04 (d, 2H), 8.84 (s, 2H)



Scheme S6. Synthetic routes of 10- naphthalene-2-yl-anthracen-9-boronic acid

4-4-1. Synthesis of 4,4,5,5-Tetramethyl-2-naphthalen-2-yl-[1,3,2]dioxaborolane (4a)

To a 250 mL round flask, 2-bromo-naphthalene (10 g, 48.2 mmol) was mixed with THF in a nitrogen atmosphere. When this was cooled down to –78□ and *n*-butyllithum (36.15 mL 1.6 M in Hexane) was slowly added, black sediment was generated. After stirring for about 30 minutes, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2- dioxaborolane (11.99 mL, 57.8 mmol) was slowly added. The reaction was confirmed with TLC, extraction was done with water and EA, and moisture was removed by using anhydrous $MgSO_4$. This compound was used for the next reaction without further purification.

4-4-2. Synthesis of 9-Naphthalen-2-yl-anthracene (4b)

To a 500 mL round flask, **4a** (8.29 g, 32.6 mmol) and 9-bromoanthracene (7 g, 27.2 mmol) were put under a nitrogen atmosphere. And then, palladium (II) acetate (0.18g, 0.81mmol) and tris(2-methylphenyl) phosphine (0.25 g, 0.81 mmol) were added into the flask and stirred with 1,2-dimethoxyethene used as a solvent. The temperature was increased up to 50□, K_2CO_3 (27.64g, 0.2mol) dissolved in water of 100 mL was added to the reaction mixture. and the reaction solution was refluxed for 6 hours. The reaction process was checked with TLC and when the reaction was completed, extraction was performed with water and chloroform. Moisture was removed by adding anhydrous $MgSO_4$ and a solvent was concentrated. Chloroform and methanol was used for recrystallization, which allowed obtaining pure white **4b**. The yield was 87%. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ (ppm) 7.34 (t, 2H), 7.49 (t, 2H), 7.60-7.54 (m, 3H) 7.69 (d, 2H), 7.93-7.88 (m, 2H), 8.08-7.99 (m, 4H), 8.53 (s, 1H)

4-4-3. Synthesis of 9-Bromo-10-naphthalen-2-yl-anthracene (4c)

4b (5.3g, 17.4 mmol) and *N*-bromosuccin imide (NBS) (4.02 g, 20.88 mmol) were mixed in a 500 mL round flask and chloroform of 300 mL was used as a solvent while the temperature was maintained at 60 □. The reaction process was checked with TLC and when the reaction was completed, after

evaporation, column was carried out in the condition of n-hexane : $CHCl_3$ = 10 : 1 to obtain pure white **4c**. The yield was about 85%. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ (ppm) 7.36-7.31 (m, 2H),7.50 (d, 1H), 7.67-7.56 (m, 6H), 7.90-7.87 (m, 2H), 8.06-7.99 (m, 2H), 8.64 (d, 2H)

4-4-4. Synthesis of 10- naphthalene-2-yl-anthracen-9-boronic acid (4d)

To a 250 mL round flask, **4c** (5.5 g, 12.7 mmol) was mixed with anhydrous tetrahydrofuran under a nitrogen atmosphere. It was cooled down to -78□ and then *n*-butyllithum (11.18 mL, 17.89 mmol) was slowly added, the reaction solution changed to black. After stirring for about 30 minutes, triethylborate (3.04 mL, 17.89 mmol) was added and stirred until the temperature went up to a room temperature. And then, 2N HCl of 1mL was added and stirred for additional 30 minutes. The reaction was confirmed with TLC, extraction was done with water and EA, and moisture was removed by using anhydrous $MgSO_4$. After recrystallization with EA and *n*-hexane, white **4d** was obtained. The yield was 90%. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ (ppm) 5.25 (s, 2H), 7.35 (t, 2H), 7.51-7.47 (m, 3H), 7.67 (t, 2H), 7.70 (d, 2H), 7.89 (m, 2H), 8.06-8.00 (m, 2H), 8.19 (d, 2H)