Journal Name

COMMUNICATION

Highly efficient non-doped deep blue fluorescent emitter with horizontal emitting dipoles using interconnecting unit between chromophores

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Kwon-Hyeon Kim[+a], Jang Yeol Baek[+b], Chan Woo Cheon[c], Chang-Ki Moon[a], Bomi Sim[a], Myeong Yong Choi[b], Jang-Joo Kim[a]*, and Yun-Hi Kim[c]*

Supporting figures

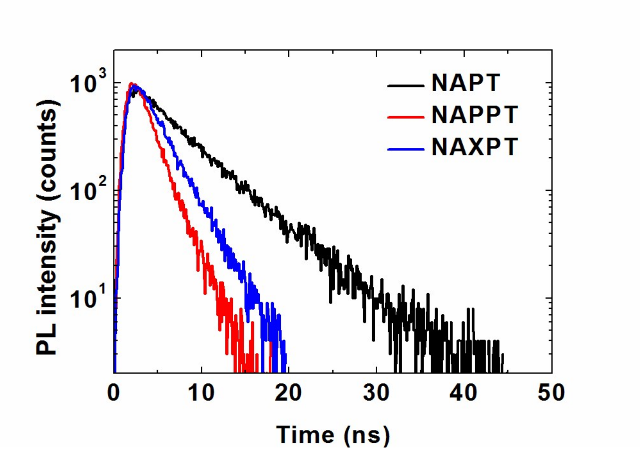


Figure S1. Transient PLs of 50nm thick NAPT, NAPPT and NAXPT film on fused silica.

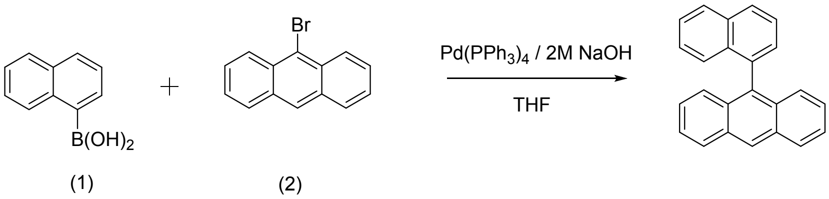
Experimental Section

All starting materials were purchased from Aldrich and TCI. Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) was purchased from Umicore. All starting materials were used without further purification. And all solvents were further purified prior to use.

***Materials characterization*:** 1H NMR was recorded using Avance 300 MHz and DRX 500MHz NMR Bruker spectrometers, and chemical shifts are reported in ppm units with tetramethylsilane as the internal standard. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instruments 2050 thermogravimetric analyzer. The sample was heated at 10 °C.min^{-1} from 50 to 800 °C. The differential scanning calorimeter (DSC) was conducted under nitrogen in a TA Instruments 2100 differential scanning calorimeter. The sample was heated at 10 °C·min^{-1} from 30 to 350 °C. Mass spectra were measured using a Jeol JMS-700 mass spectrometer. UV−vis absorption spectra were measured using a Perkin-Elmer LAMBDA-900 UV−vis−NIR spectrophotometer and an LS-50B luminescence spectrophotometer, respectively. The cyclic voltammogram of the materials were recorded on an epsilon E3 at room temperature in a 0.1 M solution of tetrabutylammonium perchlorate (Bu_4NClO_4) in acetonitrile under nitrogen gas at a scan rate of 50 mV/s. A Pt wire was used as the counter electrode and an $Ag/AgNO_3$ electrode as the reference electrode.

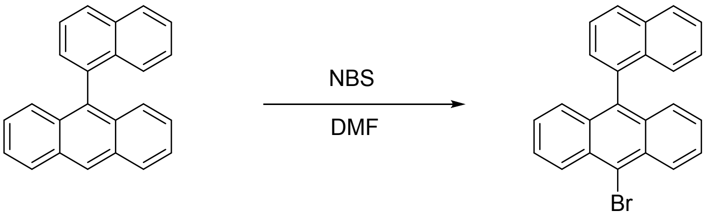
***Synthesis*:**

Synthesis of 9-(naphthalen-1-yl)anthracene



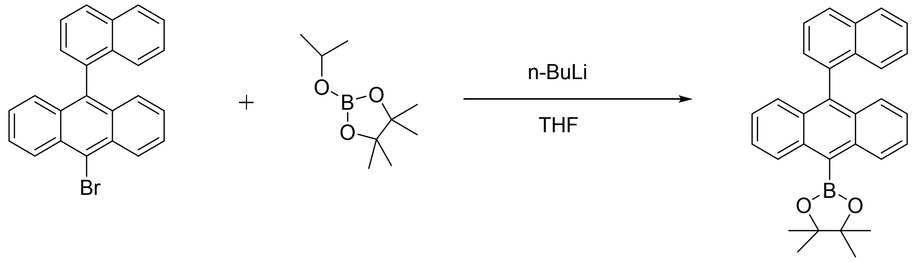
Naphthalene-1-ylboronic acid (3.5 g, 20.42 mmol) and 9-bromo anthracene (3.5 g, 13.61 mmol) were mixed in dry THF (50 mL). NaOH (2M solution, 12 mL) was added, and the mixture was stirred. Tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$ (0.47 g, 3 mol%) was added and stirred for 12h at 80~90 °C. The crude solid product was filtered and washed with CH_2Cl_2. The product was purified by a column with n-hexane. Yield:5.1 g (68.9%), ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.54 (s, 1H), 8.09-7.98 (m, 4H), 7.95-7.89 (m, 2H), 7.72-7.69 (m, 2H), 7.61-7.57 (m, 3H), 7.50-7.44 (m, 2H), 7.34-7.30 (m, 2H).

Synthesis of 9-bromo-10-(1-naphthalenyl)anthracene



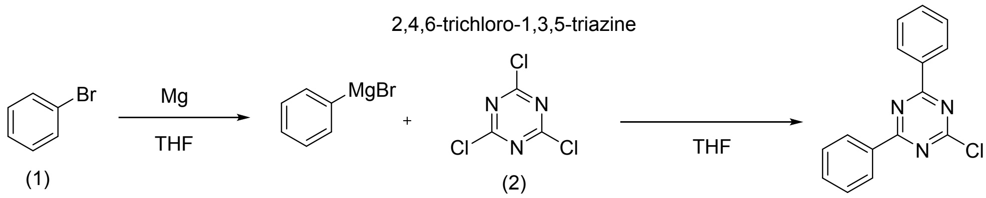
9-(Naphthalen-1-yl)anthracene (5 g , 16.4 mmol) was added to dimethylformamide (60 mL) , and the mixture was stirred. After the mixture was completely dissolved, slowly added n-bromosuccinimide (3.51 g, 19.7 mmol). The reaction mixture was refluxed at 80 °C for 2h. After the mixture was cooled, water was added to it. The crude solid product was filtered , washed and dried. Yield: 5.8 g (92.2 %), ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.67-8.65 (d, 2H), 8.07-7.99 (m, 2H), 7.89-7.84 (m, 2H), 7.66-7.64 (d, 2H), 7.60-7.56 (m, 4H), 7.52-7.50 (m, 1H), 7.35-7.32 (m, 2H).

Synthesis of 4,4,5,5-tetramethyl-2-(10-(naphthalen-1-yl)anthracen-9-yl)-1,3,2-dioxaborolane



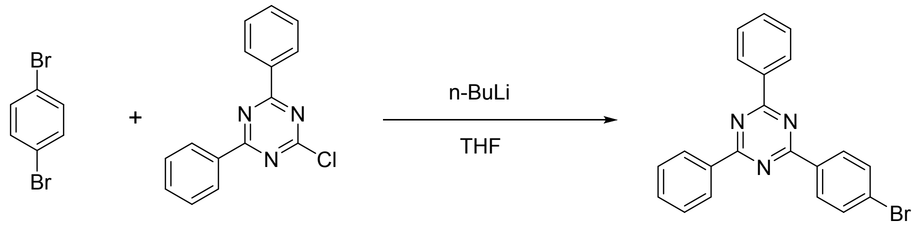
n-Butyllithium (2.5 M solution in hexane, 23.18 g, 57.95 mmol) was added to a solution of 9-bromo-10-(1-naphthalenyl)anthracene (10 g , 48.29 mmol) in anhydrous THF (60 mL) at -78 °C. The mixture was stirred at -78 °C for 40 min. After 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.75 g, 53.11 mmol) was added to the reaction mixture, the mixture was heated at room temperature for 12h. The product was purified by a column with hexane and EA (Hex:EA=7:3). Yield: 5.1 g (68.9%) ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.50-8.47(d, 2H), 8.07-7.99 (m, 2H), 7.69-7.66 (m, 1H), 7.51-7.41 (m, 6H), 7.38-7.19 (m, 3H), 7.03(m, 1H), 1.65 (s, 12H).

Synthesis of 2-chloro-4,6-diphenyl-1,3,5-triazine



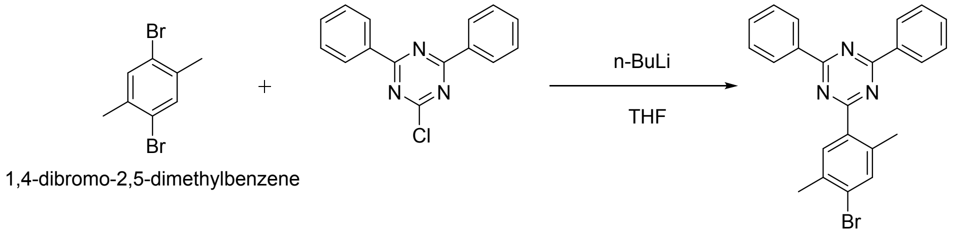
Dry magnessium(15.81 g , 650.72 mmol) was added THF(220 mL) at 70°C. Bromo benzene (85.18 g, 455.50 mmol) was slowly added, and the mixture was stirred for 1.5h. In the solution of 2,4,6-trichloro-1,3,5-triazine (30 g, 162 mmol) in THF (230 mL), the obtained mixture was slowly added. After the reaction mixture was stirred for overnight at 35 °C, the mixture extracted with MC anhydrous $MgSO_4$. The product was purified by a column with Hexane and MC (Hex:MC=2:1). Yield: 9.68 g (22.3 %) %. ^{1}H-NMR (300MHz, CD_2Cl_2, ppm): 8.68-8.51 (m, 4H), 7.75-7.52 (m, 6H). [M+], 267

Synthesis of 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine



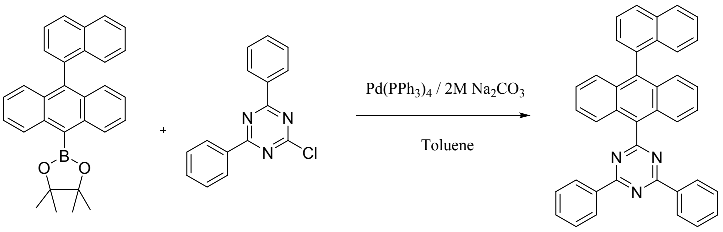
n-Butyllithium (2.5 M solution in hexane, 9.70 g, 24.27 mmol) was added to a solution of 1,4-dibromo benezene (4.40 g ; 18.67 mmol) in anhydrous tetrahydrofuran THF (120 mL) at -78 °C. The mixture was stirred at -78 °C for 30min. After 2-chloro-4,6-diphenyl-1,3,5-triazine (5 g, 18.67 mmol) was added to the reaction mixture, the mixture was heated at room temperature for 1.5h. The mixture was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. The product was purified by a column with hexane and MC (5:1). Yield:1.9 g (26.4%), ^{1}H-NMR (300MHz, CD_2Cl_2, ppm): 8.80-8.74 (m, 4H), 8.21-8.19 (d, 2H), 7.74-7.72 (d, 2H), 7.65-7.60 (m, 6H)

Synthesis of 2-(4-bromo-2,5-dimethylphenyl)-4,6-diphenyl-1,3,5-triazine



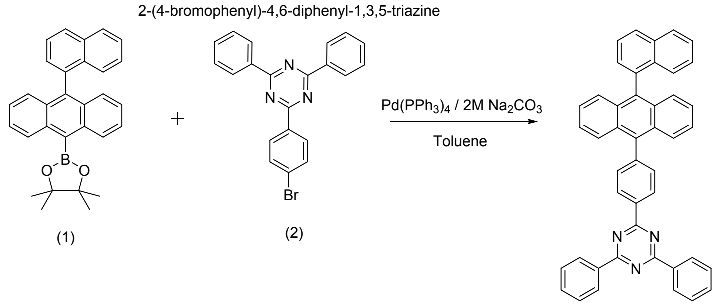
n-Butyllithium (2.5 M solution in hexane, 6.2 g) was added to a solution of 1,4-dibromo-2,5-dimethylbenzene (3.85 g, 14.57 mmol) in anhydrous THF (50 mL) at -78 °C. The mixture was stirred at -78 °C for 30 min. After 2-chloro-4,6-diphenyl-1,3,5-triazine (3 g, 11.21 mmol) was added to the reaction mixture, the mixture was heated at room temperature for 24h. The mixture was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. The product was purified by a column with Hexane and MC (Hex:MC=2:1). Yield: 1.9 g (38.4%). ^{1}H-NMR (300MHz, CD_2Cl_2, ppm): 8.76-8.73 (m, 4H), 8.21 (s, 1H), 7.64-7.59 (m, 7H), 2.82 (s, 3H), 2.52 (s, 3H)

Synthesis of 2-(10-(naphthalen-1-yl)anthracen-9-yl)-4,6-diphenyl-1,3,5-triazine (NAPT)



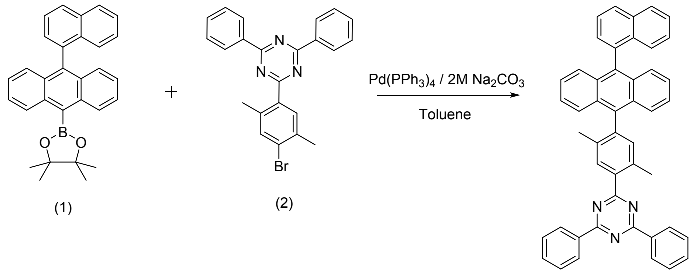
4,4,5,5-Tetramethyl-2-(10-(naphthalen-1-yl)anthracen-9-yl)-1,3,2-dioxaborolane (1 g, 2.32 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (1.24 g, 4.63 mmol), and Na_2CO_3 (2M solution, 13 mL) were mixed in dry THF (50 mL). Tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$ (0.23 g, 3 mol%) was added and stirred for 24h at 80~90 °C. The reaction mixture extracted with ethyl acetate and dried over anhydrous $MgSO_4$. The product was purified by a column with Hexane and MC (Hex:MC=2:1). Yield :0.6 g (41.3%), ^{1}H-NMR (300MHz, CD_2Cl_2, ppm): 8.83-8.80 (m, 4H), 8.17-8.08 (m, 2H), 7.97-7.94 (d, 2H), 7.82-7.77 (t, 1H), 7.73-7.43 (m, 12H), 7.34-7.27 (m, 3H), 7.22-7.19 (d, 1H) [M+]=535, ^{13}C-NMR (500MHz, CD_2Cl_2, ppm): 172,04 137.63, 136.48, 135.88, 133.47, 132.93, 130.79, 129.34, 129.20, 129.10, 128.81, 128.28, 127.43, 126.78, 126.37, 126.33, 126.10, 125.66, 125.59, 125.41

Synthesis of 2-(4-(10-(naphthalen-1-yl)anthracen-9-yl)phenyl)-4,6-diphenyl-1,3,5-triazine (NAPPT)



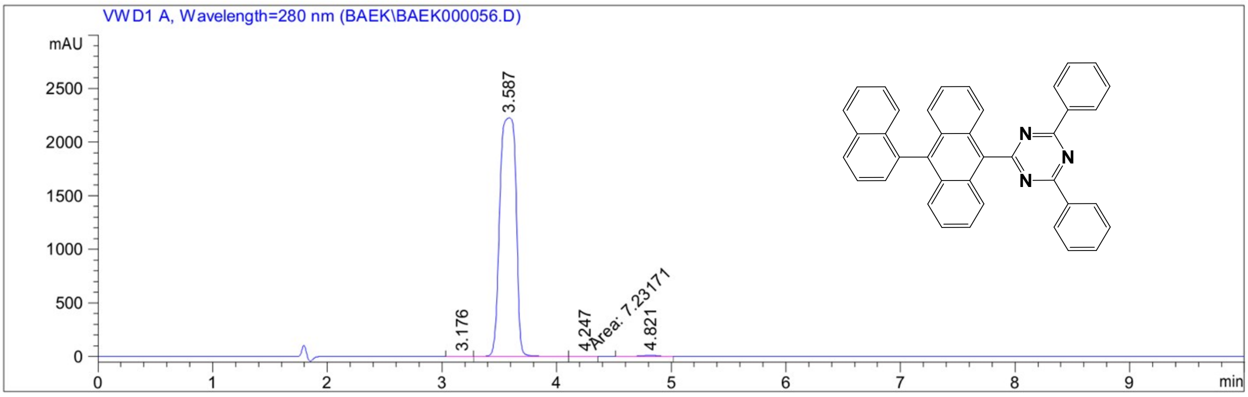
4,4,5,5-Tetramethyl-2-(10-(naphthalen-1-yl)anthracen-9-yl)-1,3,2-dioxaborolane (0.5 g, 1.16 mmol) and 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (0.58 g, 1.51 mmol) were mixed in dry toluene (50 mL). Na_2CO_3 (2M) and tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$ (0.06 g, 3 mol%) was added and stirred for 24h at 80~90 °C. The reaction mixture was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. The product was purified by a column with Hexane and MC (Hex:MC=2:1). Yield: 0.3 g (42.9%), ^{1}H-NMR (300MHz, CD_2Cl_2, ppm): 9.11-9.09 (m, 2H), 8.92-8.89 (m, 3H), 8.14-8.08 (m, 3H), 7.88-7.70 (m, 5H), 7.69-7.63 (m, 7H), 7.57-7.52 (m, 1H), 7.49-7.40 (m, 2H), 7.38-7.30(m, 2H), 7.29-7.26 (m, 3H), 7.18-7.15 (d, 1H) [M+]=611, %), ^{13}C-NMR (500MHz, CD_2Cl_2, ppm): 171,89 143.07.63, 138.91, 136.82, 136.27, 134.66, 132.64, 132.35, 131.94, 129.99, 129.72, 129.06, 128.73, 128.29, 126.09, 126.06, 125.39, 125.30, 122.63.

Synthesis of 2-(2,5-dimethyl-4-(10-(naphthalen-1-yl)anthracen-9-yl)phenyl)-4,6-diphenyl-1,3,5-triazine (NAXPT)



4,4,5,5-Tetramethyl-2-(10-(naphthalen-1-yl)anthracen-9-yl)-1,3,2-dioxaborolane (2.5 g, 5.8 mmol) and 2-(4-bromo-2,5-dimethylphenyl)-4,6-diphenyl-1,3,5-triazine (2.19 g, 5.27 mmol) were mixed in dry toluene (50 mL). Na_2CO_3 (2M) and tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$ (0.23 g, 3 mol%) was added and stirred for 24h at 80~90 °C. The reaction mixture was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. The product was purified by a column with hexane and MC (Hex:MC=2:1). Yield: 1.2 g (32.4%), ^{1}H-NMR (300MHz, CD_2Cl_2, ppm): 8.83-8.80 (m, 4H), 8.54-8.52 (d, 1H), 8.16-8.08 (m, 2H), 7.79-7.64 (m, 10H), 7.57-7.30 (m, 6H), 7.29-7.26 (m, 3H), 7.17-7.14 (m, 1H), 3.04 (s, 3H), 2.98(s, 3H) [M+]=639, ^{13}C-NMR (500MHz, CD_2Cl_2, ppm): 171.46, 141.76, 136.33, 135.62, 133.74, 132.86, 132.61, 130.71, 129.49, 129.27, 129.23, 129.08, 128.76, 128.14, 127.26, 126.75, 125.62, 125.40, 125.31, 19.56

Purification of Materials : NAPT, NAPPT, and NAXPT were purified by sublimation. The purity of sublimated NAPT, NAPPT, and NAXPT were characterized by HPLC.



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Peak RetTime  Type   Width     Area       Area
  #   [min]          [min]   [mAU*s]       %
----|-------|------|-------|----------|--------
  1   2.004          0.0000    0.00000   0.0000
  2   3.176 VV       0.0918   11.43200   0.0525
  3   3.587 VV       0.1604 2.16297e4   99.3951
  4   4.247 MM T     0.1542    7.23171   0.0332
  5   4.821 BV       0.1875  112.97044   0.5191
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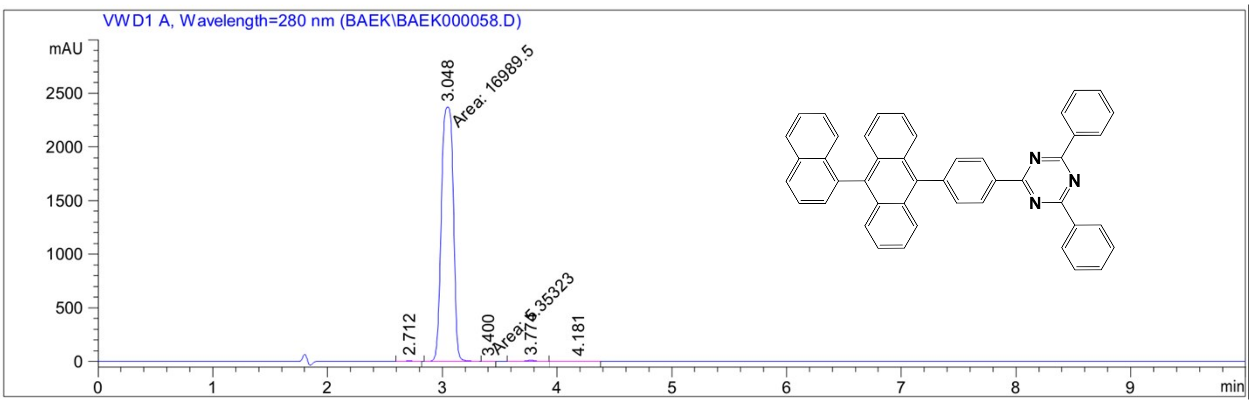

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Peak RetTime  Type   Width     Area      Area
 #    [min]          [min]   [mAU*s]      %
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   1   2.004          0.0000    0.00000   0.0000
   2   2.712 BB       0.0685   28.71358   0.1677
   3   3.048 MM T     0.1194 1.69895e4   99.2497
   4   3.400 MM T     0.0626    5.35323   0.0313
   5   3.774 VB       0.0970   67.47844   0.3942
   6   4.181 BB       0.1174   26.89638   0.1571
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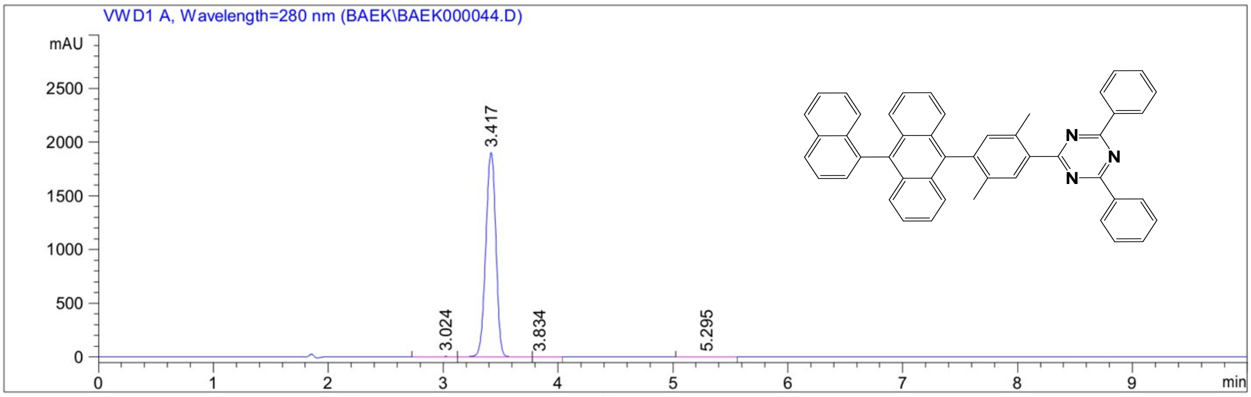

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Peak RetTime  Type   Width     Area       Area
 #    [min]          [min]   [mAU*s]       %
----|-------|------|-------|-----------|--------|
   1   2.004          0.0000    0.00000    0.0000
   2   3.024 BV       0.1118   29.95036    0.2552
   3   3.417 VV       0.0966 1.16846e4   99.5533
   4   3.834 VB       0.1077    3.27137    0.0279
   5   5.295 BB       0.1612   19.20531    0.1636
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Figure S2. HPLC plot of NAPT, NAPPT and NAXPT

Density functional theory (DFT) calculation method: Optimization of geometry, energy level, and Kohn-Sham orbitals were calculated by DFT calculation and singlet transition energies were calculated by time-dependent DFT calculation using Gaussian09 program. The calculations were performed using B3LYP, and the 6-31G(d) for all atoms.

***Measurement of PL quantum yield*:** PL quantum yields of the organic materials were measured using samples thermally deposited on fused silica under a vacuum of 5×10^{-7} Torr. The samples in an integration sphere were excited with a He/Cd laser (Melles Griot, 325 nm) to detect PL using a photomultiplier tube attached to a monochromator.

***Transient PL and EL measurement*:** Transient PL was measured by using a pulsed N2 laser (KEN-2X, USHO) as the excitation light source and a streak camera (C10627, Hamamatsu) as the optical detection system. Transient EL measurements were obtained by applying a voltage pulse with a duration of 100 µs with repetition rate of 100 Hz using an 8114A pulse generator (Agilent) and Emission was detected by a streak camera (C10627, Hamamatsu)

***Analysis orientation of transition dipoles of compounds*:** Orientation of transition dipoles was determined from the analysis of variable angle spectroscopic ellipsometry (VASE, J. A. Woolam M-2000) and angle dependent photoluminescence of the film. Optical constants were analyzed using J. A. Woolam Complete EASE software. Analysis of the optical constants (refractive index n and extinction coefficient k) of organic films deposited on the silicon substrate was initiated using the Cauchy model at the transparent region, expanded to the whole region by the B-spline model satisfying the Kramers-Krönig consistency, and completed by inserting Gaussian oscillators into the result of the B-spline model. The uniaxial model was applied using separate analyses for the ordinary and the extraordinary axes.

The dipole orientations of emitting layers were determined by analyzing the angle-dependent PL of the film using the classical dipole model. This model allows for the separate calculation of the p- and s-polarized light emission from horizontally and vertically oriented dipoles in a non-absorbing anisotropic medium. According to the dipole model, the horizontally and vertically oriented dipoles, p_x and p_z, emit p-polarized light, whereas the other horizontally oriented dipole, p_y, emits s-polarized light. The angle-dependent emission intensity of the p-polarized light is significantly different for the p_x and p_z dipoles, allowing the proportion of horizontal dipoles to be determined by fitting the simulated p-polarized intensity for various ratios of p_x and p_z to the experimental data. Using this method, the ratio of horizontal ($p_{\mathrm{P}} = p_x + p_y$) to vertical ($p_\perp = p_z$) dipoles can be evaluated.

The experimental setup has been reported previously was composed of a half cylinder lens with a sample holder on a motorized rotation stage, a dichroic mirror to filter the excitation beam, a polarizer to select the polarization of the emitted light and a fiber optic spectrometer (Ocean Optics Maya2000). A He-Cd continuous wave laser (325 nm, Melles Griot) used as a excitation source was guided by a optical fiber fixed behind the sample holder at an angle of 45 °. Emitting layer films were thermally deposited on a 1-mm-thick fused silica substrate and encapsulated under N_2 atmosphere before use, were used for the angle-dependent PL measurements. P-polarized light was used to analyze the orientation of the dipoles in the films.

***Device fabrication and characterization*:** The OLEDs were fabricated on clean glass substrates that were pre-patterned with 70-nm-thick ITO under a pressure of 5×10^{-7} Torr by thermal evaporation without breaking the vacuum. Current density, luminance, and electroluminescence spectra were measured using a programmable source meter (Keithley 2400) and a spectrophotometer (Spectrascan PR650, Photo Research). The angular distribution of the EL was measured with a programmable source meter (Keithley 2400), a goniometer, and a fiber optic spectrometer (Ocean Optics S2000)