

## Supporting Information

### **Extremely Deep Blue and Highly Efficient non-doped Organic Light Emitting Diodes using Asymmetric Anthracene Derivative with Xylene unit**

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## S1. Experimental Section

**Materials:** All reagents and chemicals were purchased from Aldrich and used without further purification. All reactions were carried out under a N<sub>2</sub> atmosphere.

**Instrument:** <sup>1</sup>H NMR spectra were recorded using a Bruker Avance-300MHz FT-NMR spectrometer, and chemical shifts were reported in ppm with tetramethylsilane(TMS) as internal standard. Thermogravimetric analysis (TGA) was performed under nitrogen using a TA instruments 2050 thermogravimetric analyzer. The sample was heated from 35 °C to 800 °C with a heating rate of 10 °C per minute. Differential scanning calorimeter (DSC) was conducted under nitrogen using a TA instrument DSC Q10. The sample was heated from 40 °C to 330 °C with a heating rate of 10 °C/min. UV-visible spectra and photoluminescence (PL) spectra were measured by Shimadzu UV-1065PC UV-visible spectrophotometer and Perkin Elmer LS50B fluorescence spectrophotometer, respectively. The electrochemical properties of the materials were measured by cyclic voltammetry (Epsilon C3) in a 0.1 M solution of tetrabutyl ammonium perchlorate in acetonitrile. A Jeol JMS-700 high-resolution mass spectrometer (HR-MS) was used to obtain the mass spectra of the samples.

**Synthesis of 9-(naphthalene-2-yl)anthracene (1a):** The compound was synthesized according to the literature procedure.<sup>[1b]</sup>; Yield: 10.5 g (67%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 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-(naphthalen-2-yl)anthracene (1b):** The compound was synthesized according to the literature procedure.<sup>[4g]</sup>; Yield: 12.6 g (93%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 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 9-(2-naphthylanthracene)-10-boronic acid (1c):** The compound was synthesized according to the literature procedure.<sup>[4h]</sup>; Yield: 8.9 g (78%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.15-8.05 (m, 4H), 7.85 (m, 2H), 7.70-7.67 (m, 4H), 7.51-7.47 (m, 3H), 7.40 (m, 2H), 5.19 (s, 2H).

**Synthesis of *N,N*-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (2a):** The synthetic procedure is similar to that of 1c. A solution of 4-bromo-*N,N*-diphenylaniline (24.00 g, 74.08 mmol) in THF (250 mL) was cooled to -78 °C. *n*-BuLi (2.5 M in hexanes, 32.6 mL, 81.49 mmol) was added dropwise over 30 minute. After 1 h, 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16.6 mL, 81.49 mmol) was added. The mixture was stirred at -78 °C for 30 min and then at room temperature for 6 h. The reaction was quenched with 2 M HCl. The layers were separated, and the aqueous layer was extracted 3 times with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were combined, washed once with saturated aqueous NaCl, dried over MgSO<sub>4</sub>, and evaporated to yield an off-white solid. The solid was washed with *n*-hexane to yield 2a as a white powder.; Yield: 17.11 g (65%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> δ): 7.86-7.83 (d, 2H), 7.38-7.33 (m, 4H), 7.26-7.12 (m, 8H), 1.47 (s, 12H).

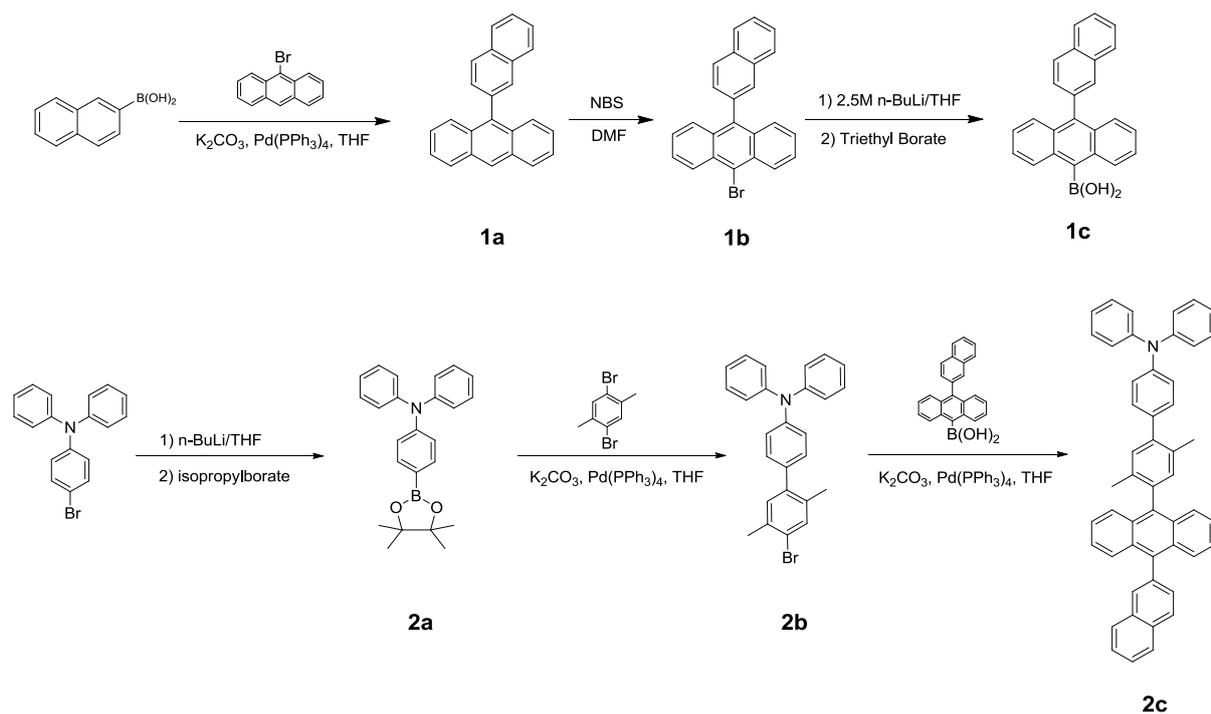
**Synthesis of 4'-bromo-2',5'-dimethyl-*N,N*-diphenyl-[1,1'-biphenyl]-4-amine (2b):** The synthetic procedure is similar to that of 1a. Under a nitrogen atmosphere, a mixture of 2a (10 g, 26.93 mmol) and 2,5-dibromo-1,4-dimethylbenzene (9.24 g, 35.02 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.13 g, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> solution (2 M, 30 mL) in THF (20 mL) and toluene (100 mL) was stirred for 48 h at 80 °C. After being cooled to room temperature, the mixture was extracted

with  $\text{CHCl}_3$ . The organic layer was washed with water and dried over magnesium sulfate, filtered, and evaporated under reduced pressure. After removal of the solvents, the residue was purified by column chromatography on silica gel using a solvent of hexane.; Yield: 6.2 g (54%);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.44(s, 1H), 7.32-7.28 (m, 3H), 7.17-7.05 (m, 12H), 2.40 (s, 3H), 2.27 (s, 3H).

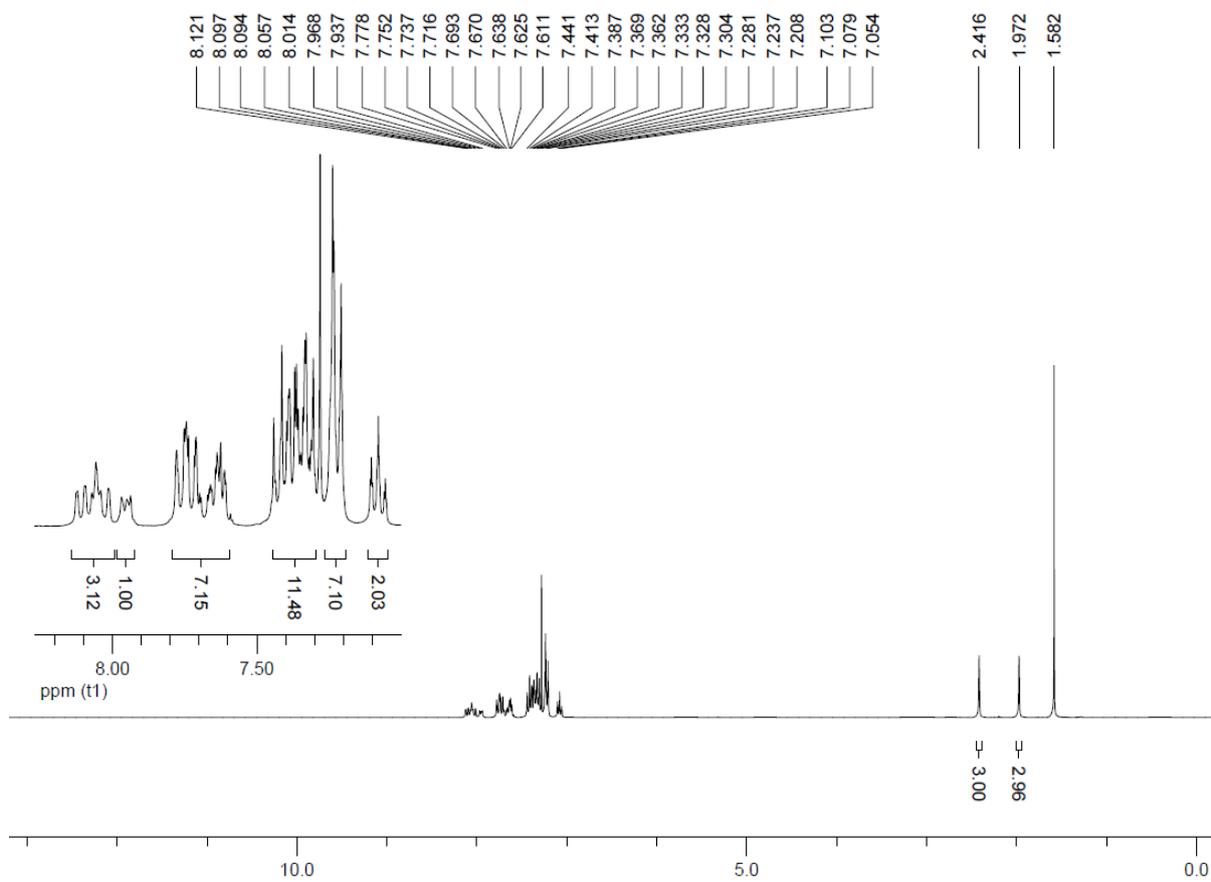
**Synthesis of 2',5'-dimethyl-4'-(10-(naphthalen-2-yl)anthracen-9-yl)-N,N-diphenyl-[1,1'-biphenyl]-4-amine, TPAXAN (2c):** The synthesis of TPAXAN is similar to that of 1a. Compound 2b (5.0 g, 11.67 mmol), 1c (6.06 g, 17.51 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (0.2 g, 0.12 mmol) were mixed in toluene (100 mL).  $\text{K}_2\text{CO}_3$  solution (2 M, 20 mL) were added during stirring. The mixture was refluxed under a nitrogen atmosphere for 48 h at 80 °C. After being cooled to room temperature, the mixture was extracted with  $\text{CHCl}_3$ . The organic layer was washed with water and dried over magnesium sulfate, filtered, and evaporated under reduced pressure. After removal of the solvents, the residue was purified by silica column chromatography (eluent: n-hexane/EA=20:1) to yield a powder.; Yield: 2.3 g (30%);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.12-8.01 (m, 3H), 7.97-7.94 (m, 1H), 7.78-7.61 (m, 7H), 7.44-7.30 (m, 11H), 7.24-7.21 (m, 7H), 7.10-7.05 (t, 2H), 2.42 (s, 3H), 1.97 (s, 3H);  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 150.49, 149.19, 143.53, 139.66, 139.29, 139.25, 138.67, 137.79, 136.06, 135.89, 135.39, 135.20, 134.04, 132.94, 132.79, 132.76, 132.38, 132.31, 132.30, 131.92, 130.73, 130.56, 130.53, 129.77, 129.54, 129.04, 128.83, 127.75, 127.05, 125.99, 125.46, 22.89, 22.01; HR-MS (EI) m/z calcd for  $\text{C}_{50}\text{H}_{37}\text{N}$  ( $\text{M}^+$ ): 651.2926; found 651.2925.

**OLED fabrication and evaluation:** The OLEDs were fabricated by thermal evaporation onto cleaned glass substrates precoated with 30 nm-thick ITO. Prior to the deposition of

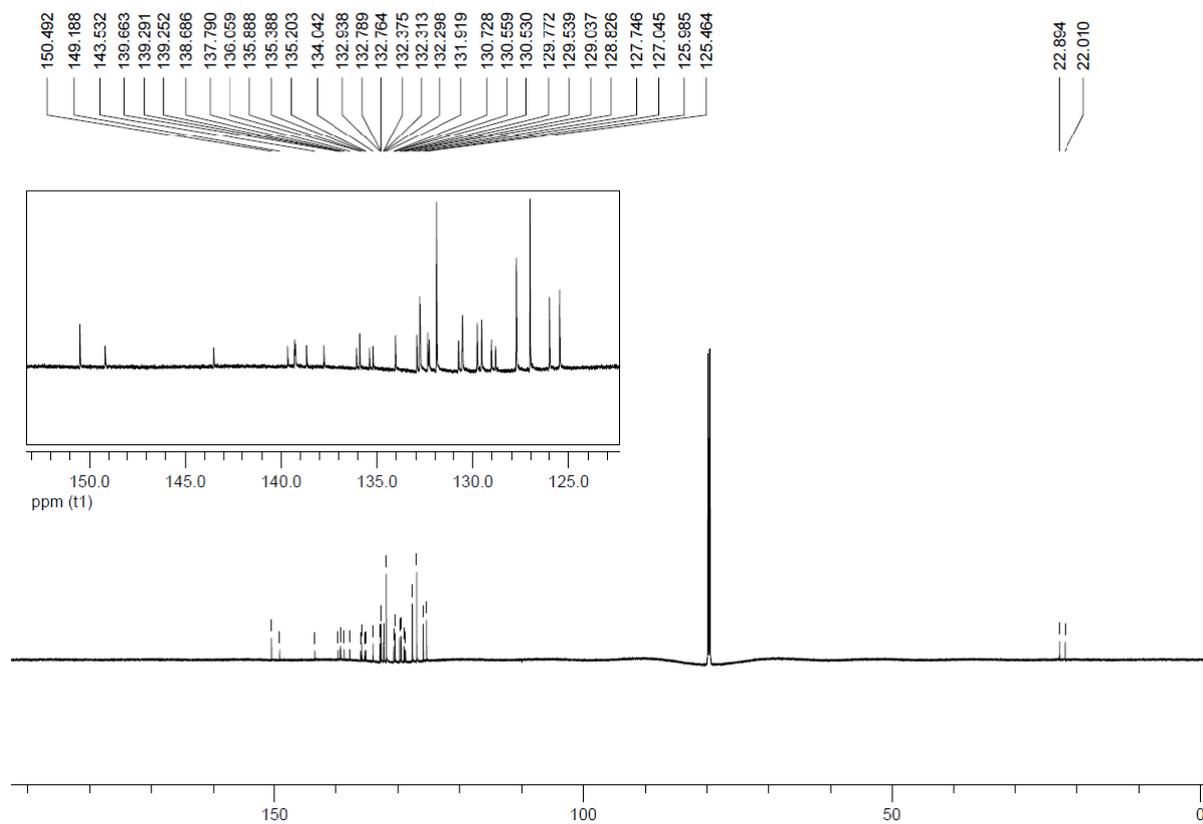
organic layers, the ITO substrates were exposed to UV-ozone flux for 10 min following degreasing in acetone and isopropylalcohol. All layers were deposited by thermal evaporation at the base pressure of  $< 5 \times 10^{-7}$  Torr without breaking vacuum. The current density, the luminance, and the EL spectra were measured using a Keithley 2400 programmable source meter and a SpectraScan PR650 (Photo Research). The EQE of the OLEDs were calculated from the current density, the luminance, and the EL spectra using Lambertian angular distribution approximation.



**Fig. S1.** Full Synthetic routes to TPAXAN.



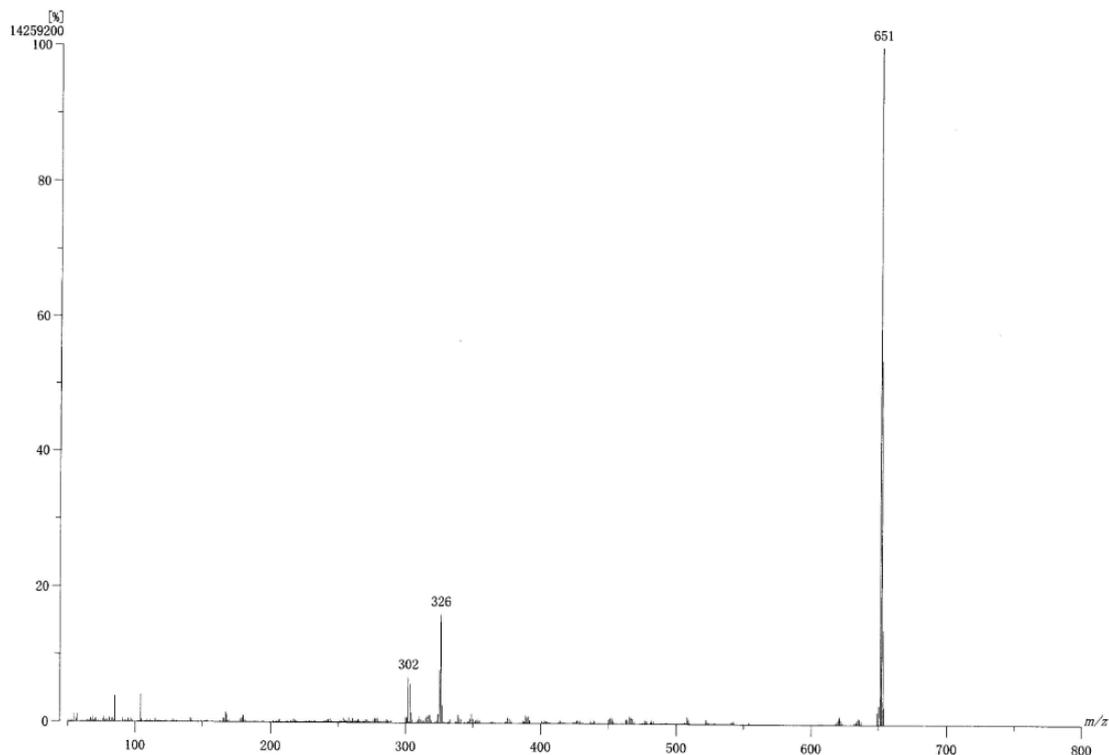
(a)  $^1\text{H-NMR}$  spectrum



(b)  $^{13}\text{C}$ -NMR spectrum

Fig. S2. NMR spectra of TPAXAN.

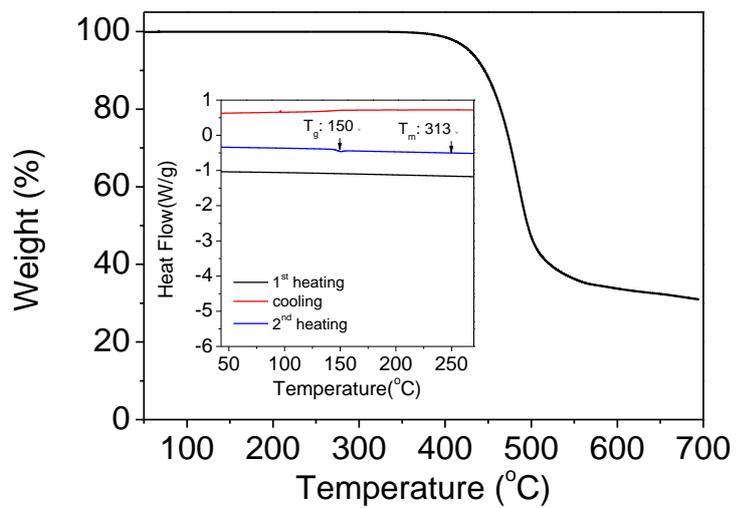
[Mass Spectrum]  
Data : 20130320\_TPAXAN-LR Date : 20-Mar-2013 12:57  
Inlet : Direct Ion Mode : EI+  
RT : 1.40 min Scan# : 43



Data : 20130320\_TPAXAN-HR Date : 20-Mar-2013 13:11  
Instrument : MStation  
Sample : -  
Note : -  
Inlet : Direct Ion Mode : EI+  
RT : 1.47 min Scan# : 45  
Elements : C 100/1, H 100/1, N 10/1  
Mass Tolerance : 1000ppm, 3mmu if m/z > 3  
Unsaturation (U.S.) : -0.5 - 50.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
1 651.2925	100.00	-0.2 / -0.1	33.0 C50 H37 N

**Fig. S3.** Mass spectrum of TPAXAN.



**Fig. S4.** TGA and DSC thermograms of TPAXAN.