

## Supplementary Information

# Bridged Triphenylamine as Novel Host Material for Highly Efficient Blue and Green Phosphorescent OLEDs

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**General Information.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were measured on Varian Unity 300 MHz spectrometer using  $\text{CDCl}_3$  as solvent and tetramethylsilane as an internal reference. Elemental analyses of carbon, hydrogen, and nitrogen were performed on Vario EL-III microanalyzer. MALDI-TOF mass spectrometric measurement was performed on Bruker Biflex III MALDI TOF instrument. EI-MS spectra were recorded on VJ-ZAB-3F-Mass spectrometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  from  $30\text{ }^\circ\text{C}$  to  $600\text{ }^\circ\text{C}$  under argon. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of  $15\text{ }^\circ\text{C min}^{-1}$  from  $25\text{ }^\circ\text{C}$  to  $700\text{ }^\circ\text{C}$ . UV-Vis absorption spectra were recorded on Shimadzu UV-2550 spectrophotometer. PL spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Pt button

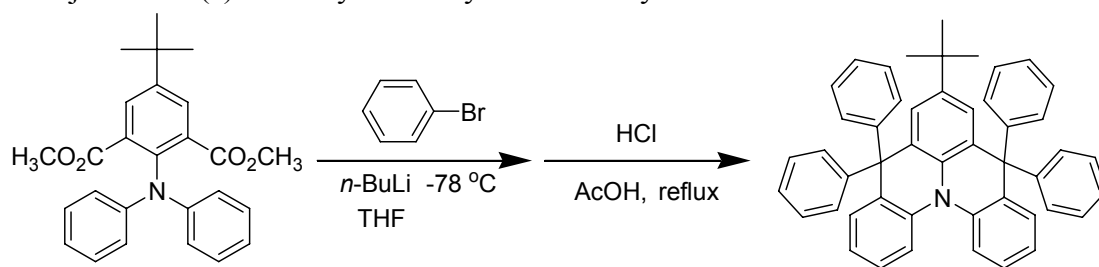
working electrodes of 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled CHI660C instruments at room temperature.

*n*-Butyllithium in hexane was purchased from Alfa Asia Chemical Co. Tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>), 5-*t*-butyl-*m*-xylene were purchased from Aldrich. The intermediate 5-*t*-butyl-2-diphenylamino-isophthalic acid dimethyl ester was prepared according to the literature. All reagents commercial available were used as received unless otherwise stated. The solvents (THF, diethyl ether, dichloromethane) were purified by conventional procedure and distilled under dry argon before using. All reactions were carried out using Schlenk techniques in an argon atmosphere.

***Device fabrication and measurement*** The hole-injection MoO<sub>3</sub>, hole-transporting materials NPB (1,4-bis(1-naphthylphenylamino)-biphenyl), mCP (1,3-bis(9-carbazolyl)benzene), hole-blocking and electron-transporting material TAZ (3-(4-biphenyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole) were commercially available. Commercial indium tin oxide (ITO) coated glass with sheet resistance of 10Ω/□ was used as the starting substrates. Before device fabrication, the ITO glass substrates were pre-cleaned carefully and treated by UV/O<sub>3</sub> for 2 min. Then the sample was transferred to the deposition system. 10 nm of MoO<sub>3</sub> was firstly deposited to ITO substrate, followed by 80 nm NPB, 5 nm mCP, emissive layer, 40 nm TAZ. Finally, a cathode composed of 1 nm of lithium fluoride and 100 nm of aluminum were sequentially deposited onto the substrate in the vacuum of 10<sup>-6</sup> Torr to construct the device. The I-V-B of EL devices was measured with a Keithley 2400 Source meter and a Keithley 2000 Source multimeter equipped with a calibrated silicon photodiode. The EL spectra were measured by JY SPEX CCD3000 spectrometer. All measurements were carried out at room temperature under ambient conditions.

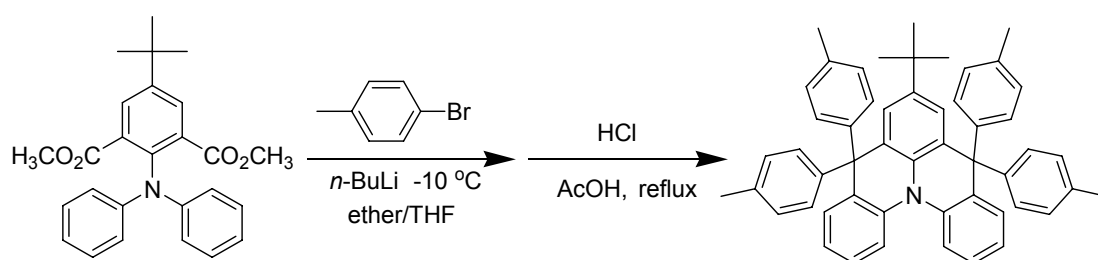
## ***Synthesis***

**7-*t*-Butyl-5,5,9,9-tetraphenyl-13b-aza-naphtho[3,2,1-de]anthracene (1, BTPA 1)**



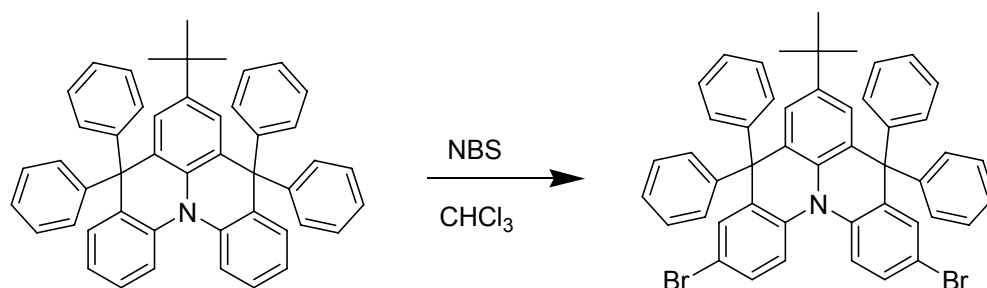
To a solution of 1-bromobenzene (1.4 g, 8.8 mmol) in dry THF (10 ml) was added slowly a 2.5 M *n*-butyllithium/hexane solution (3.5 ml, 8.8 mmol) at  $-78\text{ }^{\circ}\text{C}$ . The resulting mixture was allowed to stir at this temperature for 1 h, then a solution of 5-*t*-butyl-2-diphenylamino-isophthalic acid dimethyl ester (0.83 g, 2 mmol) in 10 ml dry THF was added dropwise. After the addition, the mixture was allowed to warm to room temperature and stirred for 3 h. Then the reaction mixture was quenched with dilute solution of ammonium chloride, extracted with ether, and the organic layers were washed with brine, dried over anhydrous sodium sulfate, and evaporated to yield a yellow solid; the solid was washed with hexane and used for the next reaction without purification. The dried solid was dissolved in boiling acetic acid (30 ml), and concentrated  $\text{HCl}_{(\text{aq})}$  (3 ml) was added dropwise. After refluxed for 3 hours, the mixture was poured into ice water (200 ml). The precipitate was collected and washed twice with ethanol, then purified by column chromatography on silica gel using 3:1(v:v) petroleum/chloroform as the eluent to afford the product as a white solid (0.8 g, Yield: 64%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.29-7.26 (m, 6H), 7.12-7.03 (m, 14H), 6.91-6.83 (m, 8H), 6.76 (d,  $J = 7.8$  Hz, 2H), 1.08 (s, 9H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 145.92, 143.64, 139.08, 135.14, 131.56, 129.99, 129.00, 127.60, 127.37, 126.46, 126.07, 124.59, 121.80, 116.93, 57.343, 34.28, 31.34. Anal. Calcd. for  $\text{C}_{48}\text{H}_{39}\text{N}$  (%): C, 91.53; H, 6.24; N, 2.22. Found: C, 91.50; H, 6.63; N, 2.15. MS (EI)  $m/z$  629.7 [ $\text{M}^+$ ]

#### 7-*t*-Butyl-5,5,9,9-tetra-*p*-tolyl-13b-aza-naphtho[3,2,1-de]anthracene (2, BTPA 2)



To a solution of 1-bromo-4-methylbenzene (3.25 g, 20 mmol) in dry diethyl ether (20 ml) was added slowly a 2.5 M *n*-butyllithium/hexane solution (7.9 ml, 19 mmol) at  $-10\text{ }^{\circ}\text{C}$  (ice-salt bath). The resulting mixture was allowed to stir at  $-10\text{ }^{\circ}\text{C}$  for 1 h, then a solution of 5-*t*-butyl-2-diphenylamino-isophthalic acid dimethyl ester (1.33 g, 3.2 mmol) in 20 ml dry THF was added dropwise. After the addition, the mixture was allowed to warm to room temperature and stirred for 3 h. Then the reaction mixture was quenched with dilute solution of ammonium chloride, then extracted with ether; the organic layers were washed with brine, dried over anhydrous sodium sulfate, and evaporated to give a yellow solid; the solid was washed with hexane and used for the next reaction without purification. The dried solid was dissolved in boiling acetic acid (30 ml), and concentrated HCl (aq) (3 ml) was added dropwise. After refluxed for 3 hours, the mixture was poured into ice water (200 ml). The precipitate was collected and washed twice with ethanol, then purified by column chromatography on silica gel using 3:1(v:v) petroleum/chloroform as the eluent to afford the product as a white solid (1.39 g, Yield: 64%). m. p.:  $324\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.09-7.01 (m, 6H), 6.91 (s, 6H), 6.92-6.89 (m, 12H), 6.72-6.68 (m, 6H), 2.37 (s, 6H), 2.22 (s, 6H), 1.09 (s, 9H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 143.70, 143.49, 143.39, 139.39, 136.06, 135.66, 135.54, 134.69, 131.87, 131.71, 130.29, 129.10, 128.54, 128.257, 126.51, 124.68, 121.90, 117.20, 56.95, 34.57, 31.66, 21.29, 21.13. Anal. Calcd. for  $\text{C}_{52}\text{H}_{47}\text{N}$  (%): C, 91.05; H, 6.91; N, 2.04. Found: C, 91.01; H, 6.88; N, 1.92. MS (EI)  $m/z$  685.8 [ $\text{M}^+$ ]

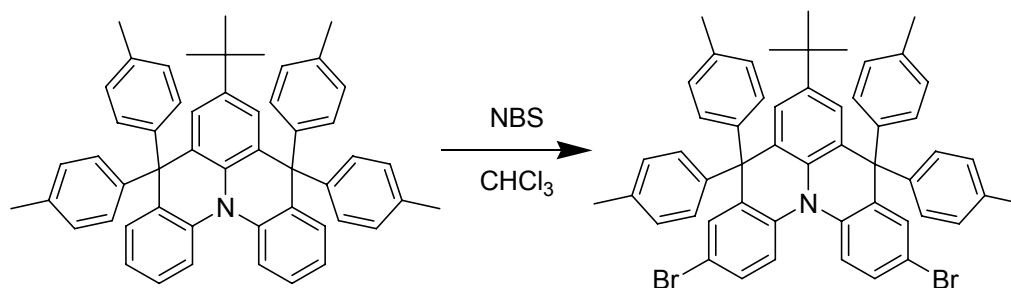
**3,11-Dibromo-7-*t*-butyl-5,5,9,9-tetraphenyl-13b-aza-naphtho[3,2,1-de]anthracene (3)**



A solution of **1** (0.49 g, 0.78 mmol) in 20 ml of chloroform was cooled to  $0\text{ }^{\circ}\text{C}$ , then NBS (0.31 g, 1.7 mmol) was added. The mixture was stirred for 24 h at room

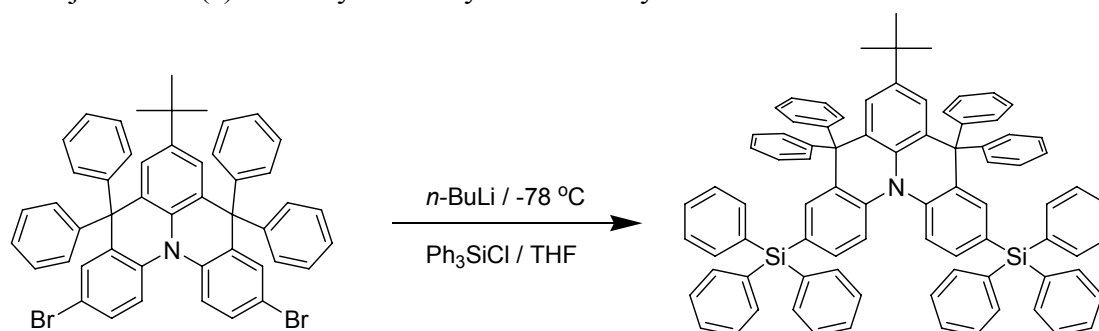
temperature. After filtered, the filtrate was washed with water, and the organic layers were dried with sodium sulfate, filtered, and recrystallized from ethanol to give a white solid (0.54 g, Yield: 88%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.33-7.26 (m, 6H), 7.14-7.08 (m, 8H), 7.01-6.77 (m, 14H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 145.32, 144.76, 138.18, 137.88, 134.25, 132.69, 132.65, 131.72, 131.64, 130.00, 129.08, 128.04, 127.94, 127.28, 126.69, 125.02, 118.54, 115.03, 57.64, 34.60, 31.53. Anal. Calcd. for  $\text{C}_{48}\text{H}_{37}\text{Br}_2\text{N}$  (%): C, 73.20; H, 4.73; N, 1.78. Found: C, 73.11; H, 4.23; N, 1.61. MS (EI)  $m/z$  785.4 [ $\text{M}^+$ ]

### 3,11-Dibromo-7-*t*-butyl-5,5,9,9-tetra-*p*-tolyl-13b-aza-naphtho[3,2,1-de]anthracene (4)



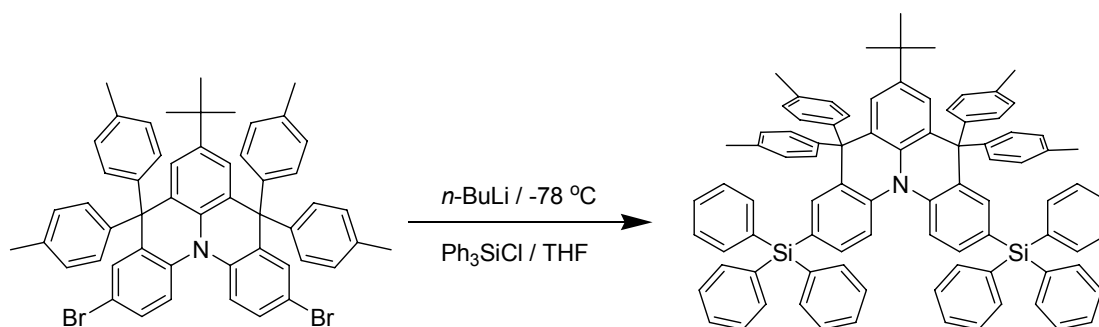
A solution of **2** (0.69 g, 0.78 mmol) in 20 ml of chloroform was cooled to 0 °C, then NBS (0.40 g, 1.7 mmol) was added. The mixture was stirred for 24 h at room temperature. After filtered, the filtrate was washed with water, and the organic layers were dried with sodium sulfate, filtered, and recrystallized from ethanol to give a white solid (0.71 g, Yield: 84%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.11(d, 6H), 6.93-6.87(m, 14H), 6.65 (d, 4H), 2.38 (s, 6H), 2.23 (s, 6H), 1.07 (s, 9H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 144.49, 142.56, 142.00, 138.19, 136.59, 135.97, 134.06, 132.67, 131.75, 131.49, 129.77, 128.90, 128.69, 128.57, 124.84, 118.54, 114.83, 56.97, 34.60, 31.59, 21.34, 21.14. Anal. Calcd. for  $\text{C}_{52}\text{H}_{45}\text{Br}_2\text{N}$  (%): C, 74.02; H, 5.38; N, 1.66. Found: C, 74.36; H, 5.27; N, 1.42. MS (EI)  $m/z$  843.9 [ $\text{M}^+$ ].

### 3,11-Ditriphenylsilyl-7-*t*-Bbutyl-5,5,9,9-tetraphenyl-13b-aza-naphtho[3,2,1-de]anthracene (5, BTPASi1)



The solution of **3** (0.46 g, 0.59 mmol) in THF (15 ml) were treated with 2.5 M *n*-BuLi (0.71 mL, 1.8 mmol) at  $-78\text{ }^{\circ}\text{C}$  and stirred for 1 h, then quenched with a solution of chlorotriphenylsilane (0.37 g, 1.26 mmol) in THF (5 ml). The mixture was washed with water and extracted with dichloromethane. The product was purified by column chromatography on silica gel using 3:1(v:v) petroleum/chloroform as the eluent to afford a white solid (0.31 g, Yield: 43%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.34 (d,  $J = 7.2$  Hz, 12H), 7.29 (d,  $J = 6.6$  Hz, 6H), 7.20 (t,  $J = 7.2$  Hz, 12H), 7.14-7.01 (m, 18H), 6.86-6.79 (m, 10H), 0.99 (s, 9H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 146.29, 146.00, 140.10, 138.98, 136.41, 134.70, 131.67, 131.54, 129.54, 129.30, 127.94, 127.51, 126.68, 126.63, 126.31, 125.25, 116.91, 57.49, 34.52, 31.54. Anal. Calcd. for  $\text{C}_{84}\text{H}_{67}\text{NSi}_2$  (%): C, 87.99; H, 5.89; N, 1.22. Found: C, 88.14; H, 6.27; N, 0.91. MS (MALDI-TOF)  $m/z$  1146.4 [ $\text{M}^+$ ].

### 3,11-Ditriphenylsilyl-7-*t*-butyl-5,5,9,9-tetra-*p*-tolyl-13b-aza-naphtho[3,2,1-de]ant hracene (**6**, BTPASi<sub>2</sub>)



The solution of **3** (0.35 g, 0.42 mmol) in THF (15 ml) were treated with 2.5 M *n*-BuLi (0.5 mL, 1.25 mmol) at  $-78\text{ }^{\circ}\text{C}$  and stirred for 1 h, then quenched with a solution of chlorotriphenylsilane (0.37 g, 1.26 mmol) in THF (5 ml). The mixture was washed with water and extracted with dichloromethane then dried ( $\text{Na}_2\text{SO}_4$ ). The

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product was purified by column chromatography on silica gel using 3:1(v:v) petroleum/chloroform as the eluent to afford a white solid (0.25 g, Yield: 47%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.42-7.34 (m, 18H), 7.30-7.25 (m, 16H), 7.01-6.90 (m, 12H), 6.80-6.73 (m, 8H), 2.31 (s, 6H), 2.25 (s, 6H), 1.08 (s, 9H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 144.04, 143.56, 143.30, 140.15, 139.12, 136.43, 135.65, 135.54, 134.79, 134.39, 131.39, 129.44, 129.13, 128.61, 128.15, 127.89, 126.38, 125.06, 116.96, 99.83, 56.83, 34.55, 31.60, 21.29, 21.12. Anal. Calcd. for  $\text{C}_{88}\text{H}_{75}\text{NSi}_2$  (%): C, 87.88; H, 6.29; N, 1.16. Found: C, 88.26; H, 5.96; N, 0.85. MS (MALDI-TOF)  $m/z$  1201.9  $[\text{M}^+]$ .

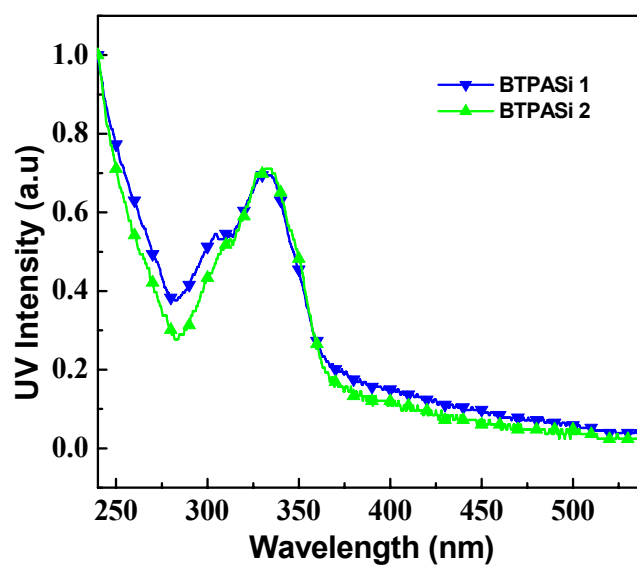
### ***X-Ray structural analysis.***

Single-crystal X-ray diffraction data were obtained from a Bruker AXS Smart CCD diffractometer using a graphite-monochromated  $\text{MoK}\alpha$  ( $\lambda=0.71073\text{\AA}$ ) radiation. The data were collected using the  $\omega/2\theta$  scan mode and corrected for Lorentz and polarization effects as well as the absorption during data reduction using Shelxtl 97 software.

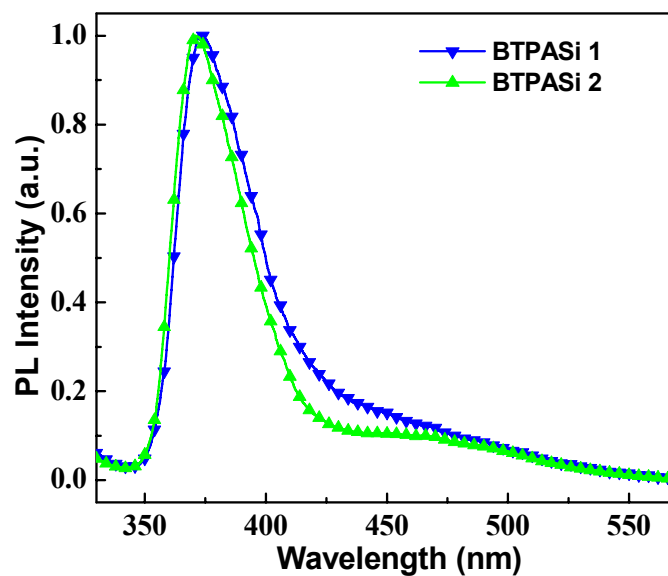
The ethyl acetate was seriously disordered during the refinement. Attempts were made to model the disorder of the solvate molecule, but failed every time. Then some related bond lengths and bond angles are restrained during the refinement using commands 'DFIX' and 'SADI' ( for example, the C-O single bond = 1.256  $\text{\AA}$  and the C=O double bond = 1.245  $\text{\AA}$ ).

Crystal data of  $\text{BTPASi}_2$  at 293(2) K:  $\text{C}_{92}\text{H}_{83}\text{NO}_2\text{Si}_2$ ,  $M_r = 1290.77$ , monoclinic, space group  $\text{P}2(1)/c$ ,  $D_c = 1.144 \text{ g cm}^{-3}$ ,  $Z = 4$ ,  $a = 14.6954(5) \text{\AA}$ ,  $b = 19.5226(5) \text{\AA}$ ,  $c = 26.3298(9) \text{\AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 97.2890(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 7492.8 (4) \text{\AA}^3$ ,  $\mu = 0.097 \text{ mm}^{-1}$ . Bruker AXS Smart CCD diffractometer, Mo- $\text{K}_\alpha$  radiation,  $\lambda = 0.71073 \text{\AA}$ , number of reflections measured = 59952, number of independent reflections = 13230,  $R_{\text{int}} = 0.0746$ , final  $R(F) = 0.0659$  ( $I > 2\sigma(I)$ ),  $wR(F^2) = 0.1657$ .

The crystallographic data of  $\text{BTPASi}_2$  (excluding structure factors) has been deposited to the Cambridge Crystallographic Data Centre with the deposition number CCDC-714843. This data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

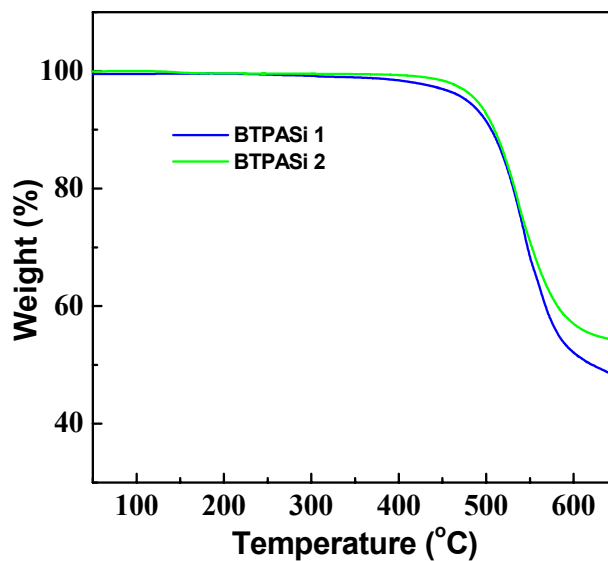


**Figure S1.** Normalized UV-vis absorption spectra of **BTPASi 1** and **BTPASi 2** in film.

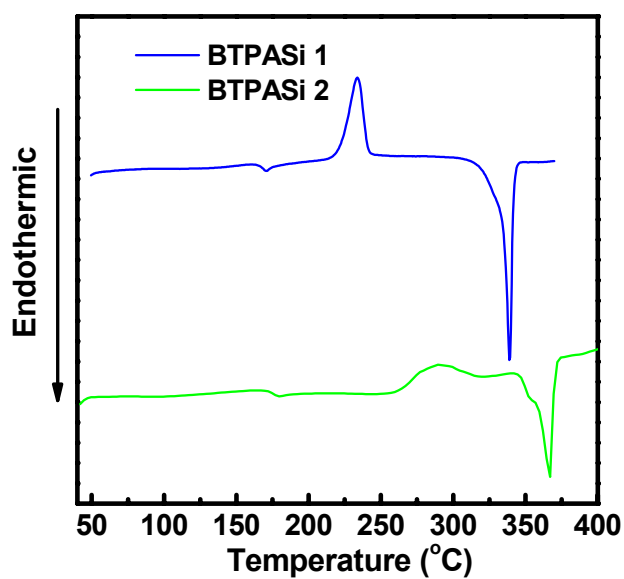


**Figure S2.** Normalized PL spectra of **BTPASi 1** and **BTPASi 2** in film.

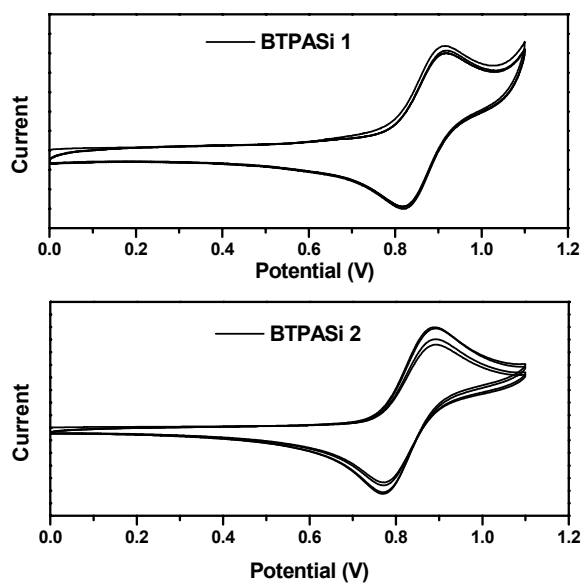




**Figure S3.** TGA thermograms of **BTPASi 1** and **BTPASi 2** recorded at a heating rate of  $15\text{ }^{\circ}\text{C min}^{-1}$ .



**Figure S4.** DSC thermograms of **BTPASi 1** and **BTPASi 2** recorded at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ .



**Figure S5.** Cyclic voltammograms of **BTPASi 1** and **BTPASi 2**.

**Table S1.** Electrochemical data of the host materials.

	HOMO <sup>a</sup> [eV]	LUMO <sup>b</sup> [eV]	$E_g^{\text{opt } c}$ [eV]
BTPASi1	5.30	2.00	3.30
BTPASi2	5.28	1.98	3.30

<sup>a</sup> Estimated from the onset oxidation potential. <sup>b</sup> LUMO = HOMO +  $E_g$ . <sup>c</sup> Estimated from the onset of absorption edge.