

## Supporting Information

### **Spirobifluorene modified electron transport materials for high efficiency in phosphorescent organic light-emitting diodes**

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## **Experimental**

### **General information**

2-Bromo-1,1'-biphenyl (Combi-Blocks, Ins), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (GOM), phenylboronic acid (Alfa), 2,7-dibromo-9H-fluorene-9-one (Samyoung Ino. Co), 2,4-dichlorobenzo[4,5]thieno[3,2-d]pyrimidine, and 2,4-dichlorobenzofuro[3,2-d]pyrimidine were used as received. 2-Chloro-4,6-diphenyl-1,3,5-triazine, tris(dibenzylideneacetone)dipalladium(0), tetrakis(triphenylphosphine)palladium(0), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (P&H tech.), n-butyllithium solution (Acros organic), potassium acetate, potassium carbonate, cesium carbonate, hydrochloric acid, acetic acid, 1,4-dioxane, and 1,2-dichlorobenzene (Daejung) were used with no further purification. Dehydrated tetrahydrofuran (TCI), ethanol, and toluene (Samchun) were used as solvents.

The PL spectrum was measured by using PerkinElmer, LS-55. The UV-vis spectrum was

obtained by UV-vis spectrophotometer (JASCO, V-730) using a transmittance mode. Cyclic voltammetry was developed by Iviumstat from Ivium Tech with 0.1 M tetrabutylammonium perchlorate in acetonitrile (ACN) electrolyte in 10 mV / s .

. The electrostatic potential map was calculated by Avogadro surface function with iso value of 0.1 and the electrostatic potential values were measured by mulfiwfn. The refractive index was measured by spectroscopic ellipsometer (ISA Jobin-Yvon Co.) and calculated with elliptic constant (Psi, Delta). The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were obtained by Bruker 500 MHz and 700 MHz NMR, respectively, using deuterated chloroform solvent.

0.1 M tetrabutylammonium perchlorate in acetonitrile (ACN)

## **Synthesis**

### **Synthesis of 2,7-dibromo-9,9'-spirobi[fluorene] (P2)**

Firstly, a solution of 2-bromo-1,1'-biphenyl (2.43 g, 10.4 mmol) in anhydrous tetrahydrofuran (21 ml, 0.5 M) was stirred in a two-necked flask for 1 h at -78 °C after cooling with dry ice. Then, 5 ml of n-butyllithium (2.5 M in hexane, 12.5 mmol) was injected by slow dropping under a nitrogen condition and stirred at -78 °C for 1 h. At the same time, a solution of 2,7-dibromo-9H-fluorene-9-one (4.2 g, 12.5 mmol) in anhydrous tetrahydrofuran (60 ml, 0.21 M) was stirred in a two necked flask at 0 °C after cooling with ice. After 1 h, the solution of 2,7-dibromo-9H-fluorene-9-one was added into the 2-bromo-1,1'-biphenyl mixed solution. The reaction mixture was gradually heated to room temperature with stirring. After 5 h, acetic acid (50 ml) and HCl (5 ml) were dropped slowly to the reaction mixture and refluxed overnight at 80°C. After quenching the reaction mixture with sodium hydroxide solution and extracted with dichloromethane (MC) and deionized water (DW), the organic layer was stirred with magnesium sulfate. After filtering, the filtrate was dried under vacuum by evaporator. The filtrate was purified by silica column chromatography (MC : n-hexane (HEX) (1:10)).

Yield 69%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.89 – 7.80 (m, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.48 (dd, J = 8.2 Hz, 1.8, 2H), 7.39 (td, J = 7.5, 1.1 Hz, 2H), 7.14 (td, J = 7.5, 1.1 Hz, 2H), 6.83 (d, J = 1.8 Hz, 2H), 6.74 – 6.68 (m, 2H). MS (APCI) (*m/z*): [(M+H)<sup>+</sup>] calculated as C<sub>25</sub>H<sub>14</sub>Br<sub>2</sub> 475.19 ; found 474.95.

### **Synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-spirobi[fluorene] (P1)**

A mixture of 2,7-dibromo-9,9'-spirobi[fluorene] (5 g, 10.54 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (8.0 g, 31.62 mmol), potassium acetate (8.23 g, 84.3 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.77 g, 1.05 mmol) in 1,4-dioxane (80 ml, 0.25 M) was refluxed under a nitrogen atmosphere for 6 h and cooled down to room temperature. The purification method was the same as with that 2,7-dibromo-9,9'-spirobi[fluorene] except the ratio of eluent in silica column chromatography (MC : HEX (1:4)).

Yield 74%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.84 (dt, J = 7.6, 5.6 Hz, 6H), 7.33 (dd, J = 10.9, 4.1 Hz, 2H), 7.12 (d, J = 0.5 Hz, 2H), 7.06 (t, J = 7.5 Hz, 2H), 6.67 (dd, J = 7.6, 0.5, 2H), 1.22 (s, 24H). MS (APCI) (*m/z*): [(M+H)<sup>+</sup>] calculated as C<sub>37</sub>H<sub>38</sub>B<sub>2</sub>O<sub>4</sub> 569.30 ; found 569.30.

### **Synthesis of 2-chloro-4-phenylbenzo[4,5]thieno[3,2-d]pyrimidine**

2-chloro-4-phenylbenzo[4,5]thieno[3,2-d]pyrimidine was synthesized according to our previous work.<sup>32-34</sup>

### **Synthesis of 2-chloro-4-phenylbenzofuro[3,2-d]pyrimidine**

The synthesis and purification of 2-chloro-4-phenylbenzofuro[3,2-d]pyrimidine was the same as that of 2-chloro-4-phenylbenzo[4,5]thieno[3,2-d]pyrimidine except that 2,4-

dichlorobenzofuro[3,2-d]pyrimidine was used instead of 2,4-dichlorobenzo[4,5]thieno[3,2-d]pyrimidine.

Yield 80%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.60 – 8.56 (m, 2H), 8.28 – 8.20 (m, 1H), 7.78 – 7.69 (m, 2H), 7.63 – 7.47 (m, 4H). MS (APCI) (*m/z*): [(M+H)<sup>+</sup>] calculated as C<sub>16</sub>H<sub>9</sub>ClN<sub>2</sub>O 281.05 ; found 281.05.

### **Synthesis of 2,7-bis(4,6-diphenyl-1,3,5-triazin-2-yl)-9,9'-spirobi[fluorene] (SBFTrz)**

A mixture of 2-chloro-4,6-diphenyl-1,3,5-triazine (4.3 g, 16 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-spirobi[fluorene] (3 g, 5.3 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.93 g, 0.80 mmol) in THF(48 ml, 0.3 M) with 2.5 M potassium carbonate (7.3 g, 52.8 mmol) was refluxed under a nitrogen atmosphere for overnight and cooled down to room temperature. After extraction purification with MC and DW, firstly the MC, acetone and THF washing was used as a purification method. After that, the recrystallization was executed with 1,2-dichlorobenzene. Finally, the final product was purified through vacuum sublimation.

Yield 81%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.91 (dd, J = 8.0, 1.4, 1H), 8.66 – 8.62 (m, 4H), 8.15 (d, J = 8.0, 1H), 8.08 (d, J = 1.0, 1H), 8.01 (d, J = 7.9, 1H), 7.60 – 7.55 (m, 2H), 7.53 (t, J = 7.4, 4H), 7.45 (t, J = 7.6, 1H), 7.16 (td, J = 7.5, 0.9, 1H), 6.85 (d, J = 7.6, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, δ/ppm) : 171.55, 171.49, 150.52, 147.70, 145.14, 142.14, 136.93, 136.12, 132.46, 129.47, 128.96, 128.60, 128.12, 128.05, 124.61, 124.17, 120.85, 120.41. MS (HR-FAB) (*m/z*) : [(M+H)<sup>+</sup>] calculated as C<sub>55</sub>H<sub>34</sub>N<sub>6</sub> 779.2918 ; found 779.2930

### **Synthesis of 2,7-bis(4-phenylbenzo[4,5]thieno[3,2-d]pyrimidin-2-yl)-9,9'-spirobi[fluorene] (SBFBTP)**

The synthesis and purification of SBFBTP was the same as that of 2,7-bis(4,6-diphenyl-1,3,5-

triazin-2-yl)-9,9'-spirobi[fluorene] except that 2-chloro-4-phenylbenzo[4,5]thieno[3,2-d]pyrimidine was used instead of 2-chloro-4,6-diphenyl-1,3,5-triazine.

Yield 68%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.11 (d, J = 8.0, 4H), 8.07 (d, J = 1.3, 4H), 7.98 (d, J = 7.7, 4H), 7.88 (d, J = 8.0, 4H), 7.67 – 7.62 (m, 4H), 7.61 – 7.56 (m, 8H), 7.44 – 7.40 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, δ/ppm) : 159.11, 158.90, 149.86, 148.14, 141.80, 138.35, 137.97, 135.72, 130.71, 129.66, 128.91, 128.68, 128.64, 127.99, 125.51, 125.24, 124.97, 124.42. MS (HR-FAB) (m/z) : [(M+H)<sup>+</sup>] calculated as C<sub>57</sub>H<sub>32</sub>N<sub>4</sub>S<sub>2</sub> 837.2141 ; found 837.2151

### **Synthesis of 2,7,-bis(4-phenylbenzofuro[3,2-d]pyrimidin-2-yl)-9,9'-spirobi[fluorene] (SBFBFP)**

A mixture of 2-chloro-4-phenylbenzofuro[3,2-d]pyrimidine (2 g, 7.12 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-spirobi[fluorene] (1.84 g, 3.24 mmol) and tris(dibenzylideneacetone)dipalladium(0) (0.16 g, 0.18 mmol) in ethanol (7 ml) and toluene (14 ml) with 6 M cesium carbonate solution(13.9 g, 42.75 mmol) was refluxed under a nitrogen atmosphere for overnight and cooled down to room temperature. The purification method was the same as that of 2,7-bis(4,6-diphenyl-1,3,5-triazin-2-yl)-9,9'-spirobi[fluorene].

Yield 61%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.83 (dd, J = 8.0, 1.5, 1H), 8.64 (dt, J = 8.0, 1.7, 2H), 8.28 (dt, J = 5.8, 2.8, 2H), 8.04 (d, J = 1.0, 2H), 8.00 (d, J = 7.9, 1H), 7.69 – 7.64 (m, 2H), 7.62 – 7.59 (m, 2H), 7.58 – 7.54 (m, 1H), 7.47 – 7.42 (m, 2H), 7.16 (ddd, J = 8.4, 6.5, 1.1, 1H), 6.91 (d, J = 7.6, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, δ/ppm) : 141.80, 135.72, 130.71, 130.47, 128.91, 128.80, 128.69, 128.64, 128.00, 126.01, 125.24, 124.97, 124.00, 123.68, 122.83, 120.59, 120.46. MS (HR-FAB) (m/z) : [(M+H)<sup>+</sup>] calculated as C<sub>57</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub> 805.2598 ; found 805.2598

## Supporting Figures

**Fig. S1** Energy levels and chemical structures of materials fabricated device

**Fig. S2** EL spectra of device (a) SBFTTrz (b) SBFBTP (c) SBFBFP and (d) DBFTTrz with increasing voltage

**Fig. S3** (a)  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$ -NMR of 2,7-bis(4,6-diphenyl-1,3,5-triazin-2-yl)-9,9'-spirobi[fluorene] (SBFTTrz)

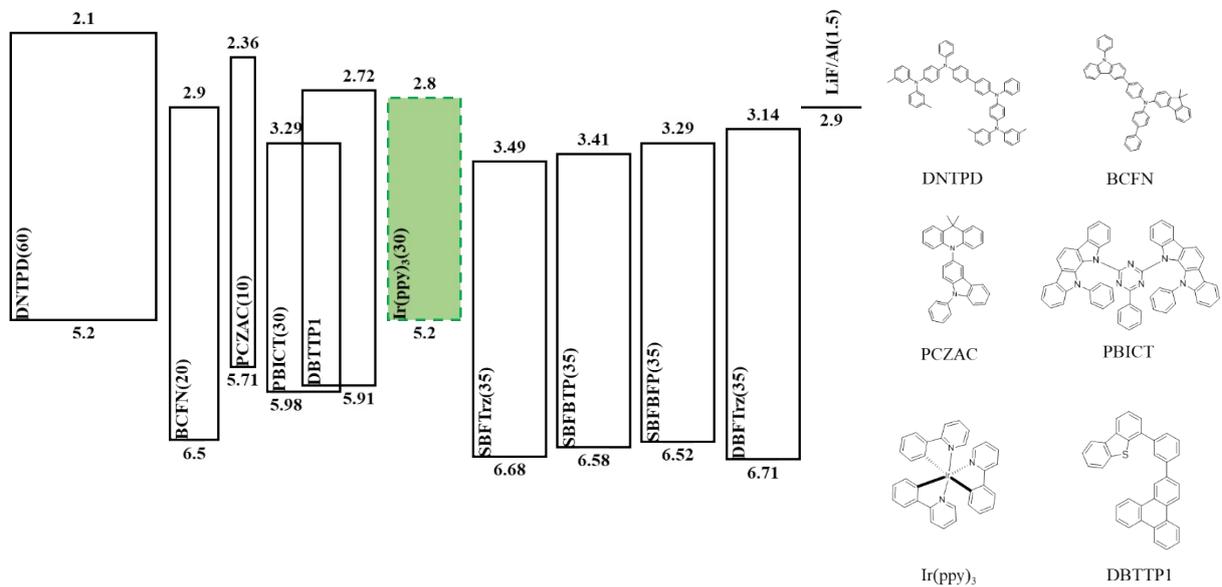
**Fig. S4** (a)  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$ -NMR 2,7-bis(4-phenylbenzo[4,5]thieno[3,2-d]pyrimidin-2-yl)-9,9'-spirobi[fluorene] (SBFBTP)

**Fig. S5** (a)  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$ -NMR 2,7-bis(4-phenylbenzofuro[3,2-d]pyrimidin-2-yl)-9,9'-spirobi[fluorene] (SBFBFP)

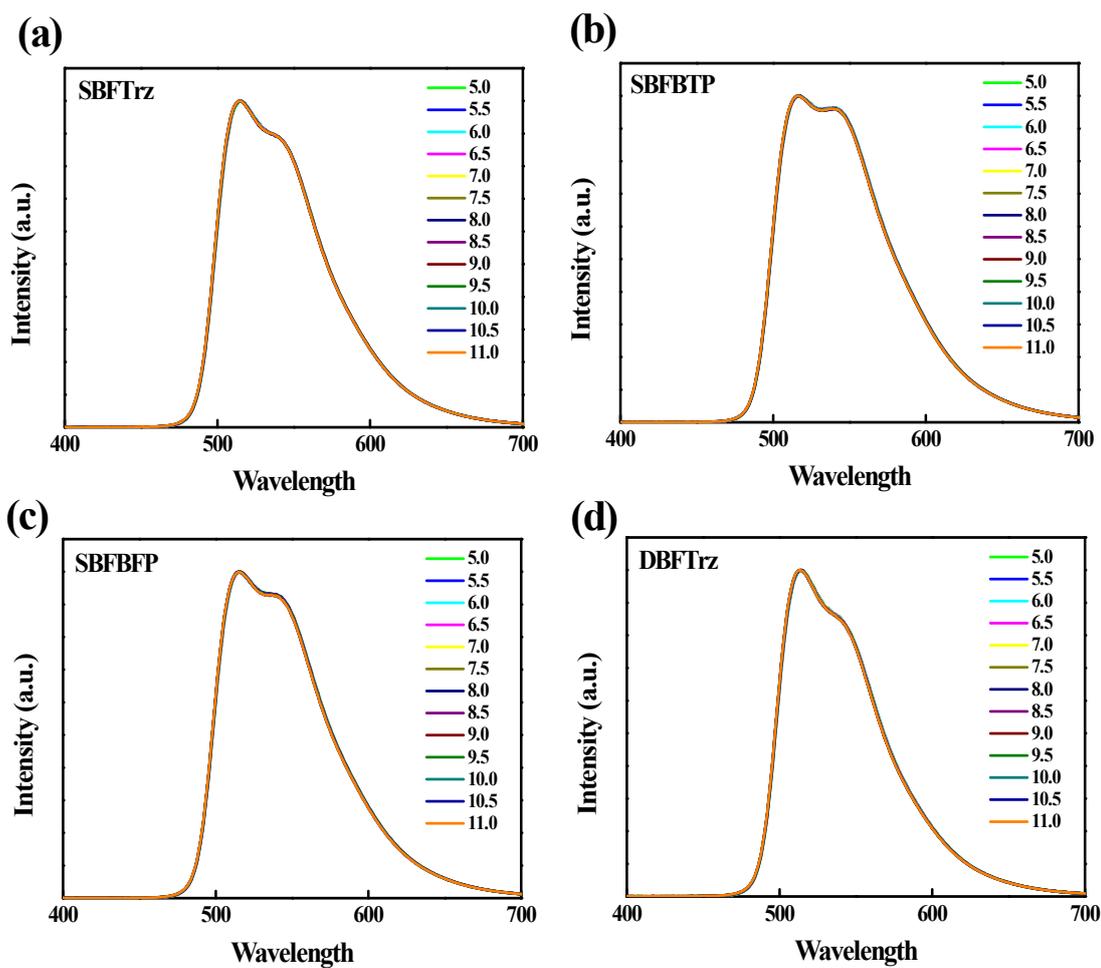


Device structure :

ITO (50 nm) / DNTPD (60 nm) / BCFN (20 nm) / PCzAc (10 nm) / PBICT:DBTTP1:Ir(ppy)<sub>3</sub> (30 nm, 25:75, 5% doping ) / ETL (35 nm) / LiF (1.5 nm) / Al (200 nm)



**Fig. S1** Energy levels and chemical structures of materials fabricated device

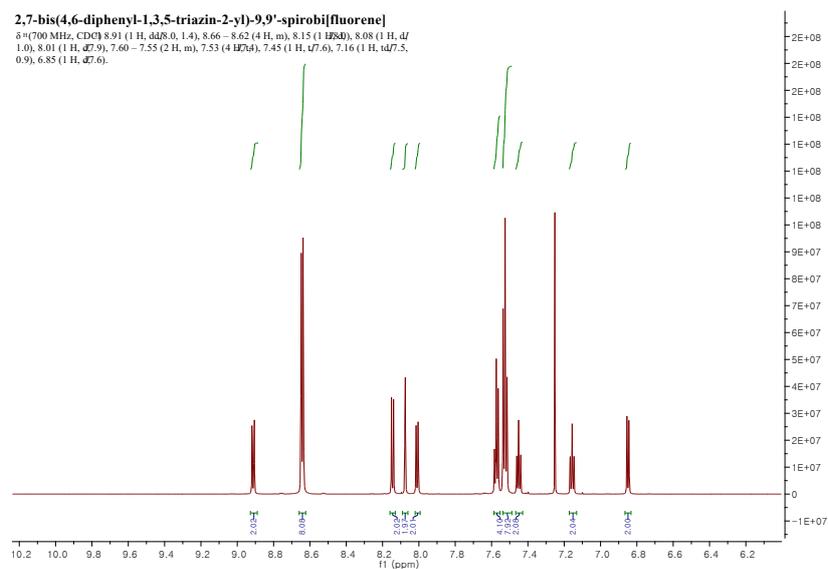


**Fig. S2** EL spectra of device (a) SBFTrz (b) SFBTP (c) SFBFP and (d) DBFTrz with increasing voltage

(a)

**2,7-bis(4,6-diphenyl-1,3,5-triazin-2-yl)-9,9'-spirobi[fluorene]**

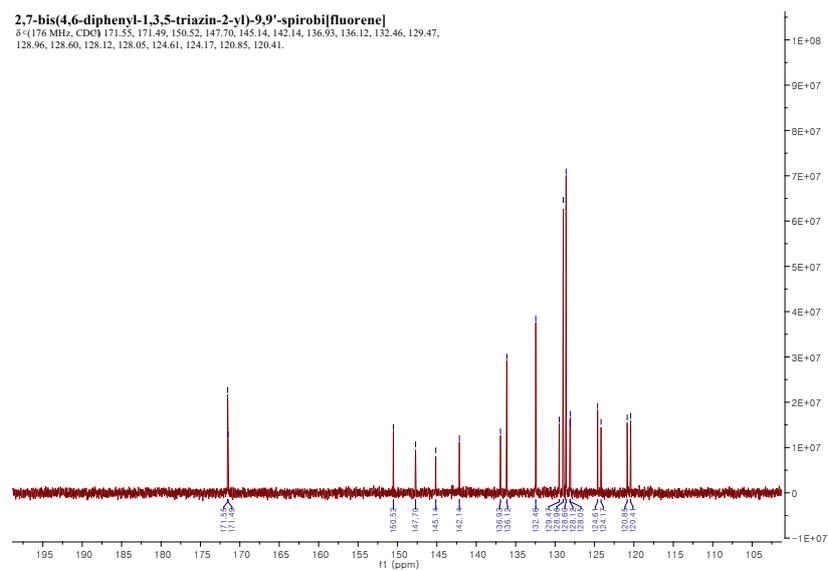
$\delta$ =(700 MHz, CDCl<sub>3</sub>) 8.91 (1 H, dd(8.0, 1.4), 8.66 – 8.62 (4 H, m), 8.15 (1 H, s(d)), 8.08 (1 H, d/1.0), 8.01 (1 H, d(7.9)), 7.60 – 7.55 (2 H, m), 7.53 (4 H, t(7.4)), 7.45 (1 H, t(7.6)), 7.16 (1 H, t(7.5, 0.9)), 6.85 (1 H, d(7.6)).



(b)

**2,7-bis(4,6-diphenyl-1,3,5-triazin-2-yl)-9,9'-spirobi[fluorene]**

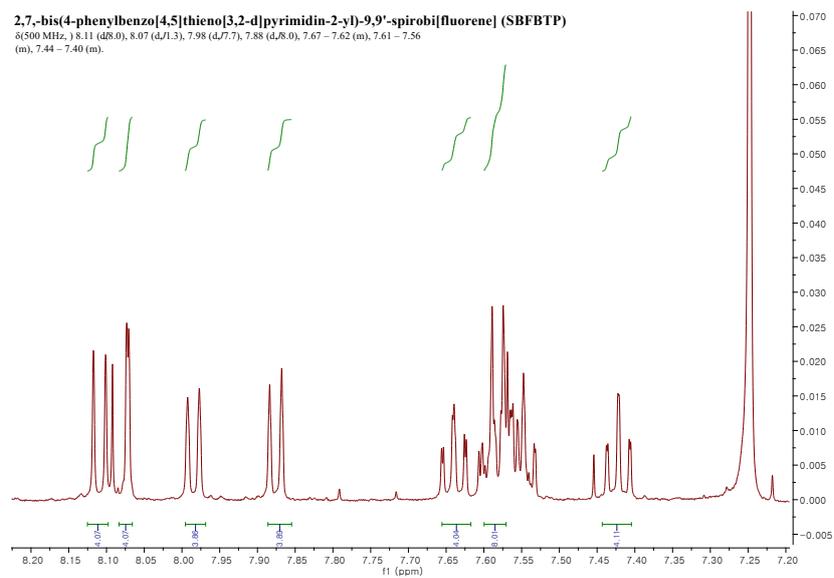
$\delta$ =(176 MHz, CDCl<sub>3</sub>) 171.55, 171.49, 150.52, 147.70, 145.14, 142.14, 136.93, 136.12, 132.46, 129.47, 128.96, 128.60, 128.12, 128.05, 124.61, 124.17, 120.85, 120.41.



**Fig. S3** (a) <sup>1</sup>H-NMR and (b) <sup>13</sup>C-NMR of 2,7-bis(4,6-diphenyl-1,3,5-triazin-2-yl)-9,9'-spirobi[fluorene] (SBFTrz)

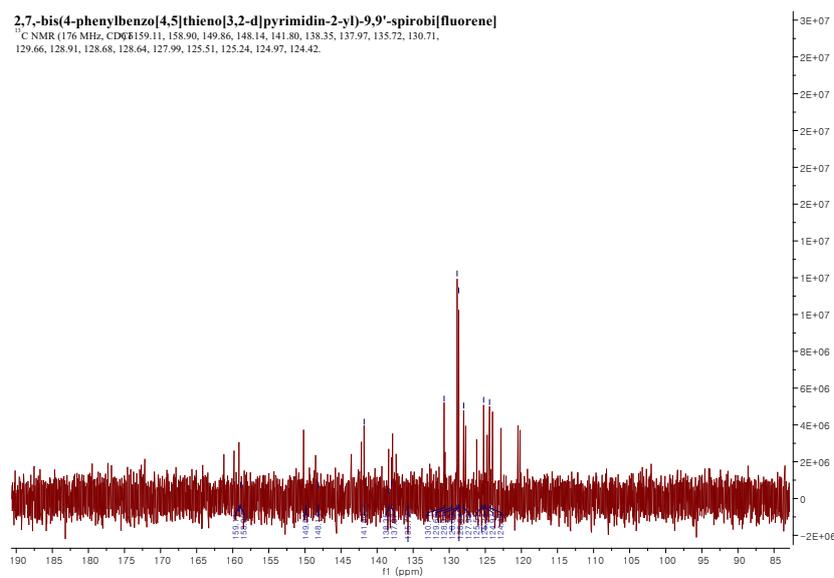
(a)

**2,7-bis(4-phenylbenzo[4,5]thieno[3,2-d]pyrimidin-2-yl)-9,9'-spirobi[fluorene] (SBFBTP)**  
 $\delta$ (500 MHz, ) 8.11 (d $\delta$ 0), 8.07 (d $\delta$ 1.3), 7.98 (d $\delta$ 7.7), 7.88 (d $\delta$ 8.0), 7.67 – 7.62 (m), 7.61 – 7.56 (m), 7.44 – 7.40 (m).



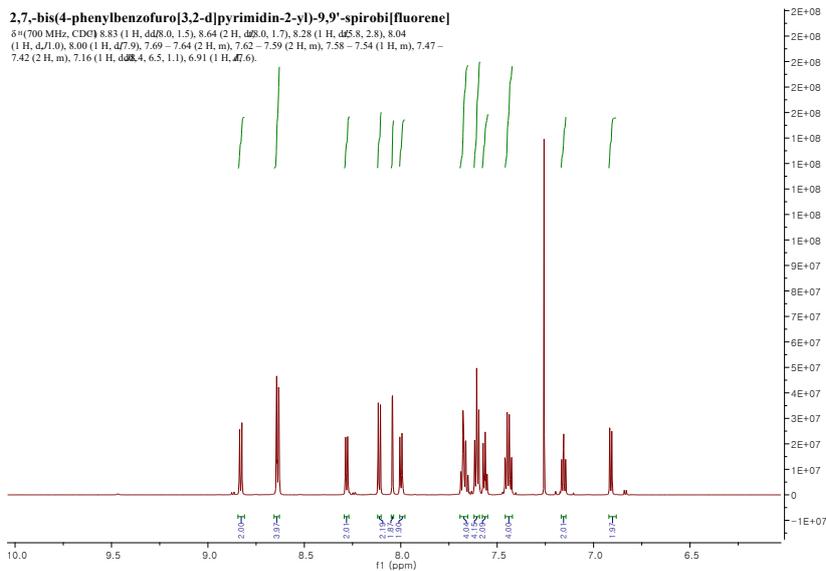
(b)

**2,7-bis(4-phenylbenzo[4,5]thieno[3,2-d]pyrimidin-2-yl)-9,9'-spirobi[fluorene]**  
 $^{13}$ C NMR (176 MHz, CDCl<sub>3</sub>) 159.11, 158.90, 149.86, 148.14, 141.80, 138.35, 137.97, 135.72, 130.71, 129.66, 128.91, 128.68, 128.64, 127.99, 125.51, 125.24, 124.97, 124.42.

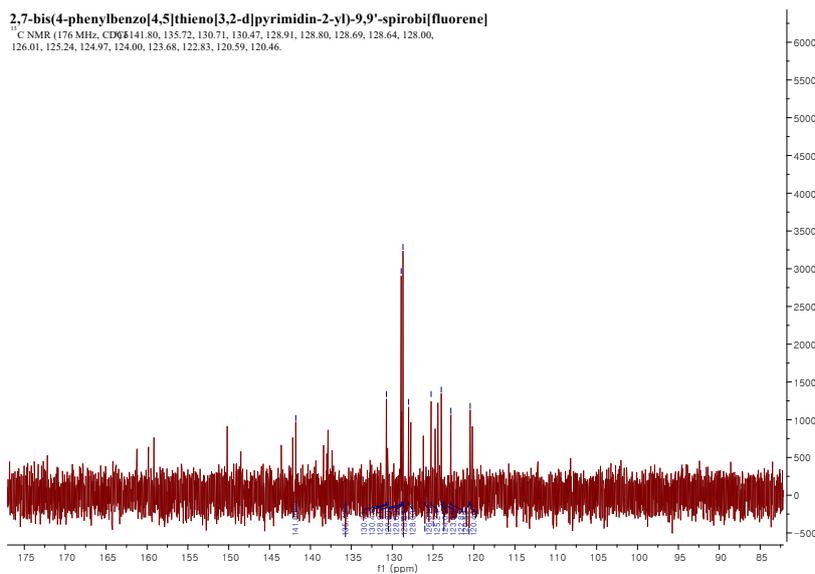


**Fig. S4** (a)  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$ -NMR 2,7-bis(4-phenylbenzo[4,5]thieno[3,2-d]pyrimidin-2-yl)-9,9'-spirobi[fluorene] (SBFBTP)

(a)



(b)



**Fig. S5** (a) <sup>1</sup>H-NMR and (b) <sup>13</sup>C-NMR 2,7-bis(4-phenylbenzofuro[3,2-d]pyrimidin-2-yl)-9,9'-spirobi[fluorene] (SBFBFP)