

Supplementary Information Section

Semi-Transparent Organic Solar Cells Based on Large Bandgap Star-shaped Small Molecules as Mixed Donors with PM6

Minming Yan,^a Peter J. Skabara^{a,*} and Hong Meng^{*,b}

^a School of Chemistry, University of Glasgow, G12 8QQ, UK.

^b Peking University Shenzhen Graduate School, Shenzhen 518055, P.R.China

Corresponding authors: menghong@pku.edu.cn (H. Meng);
peter.skabara@glasgow.ac.uk (P. J. Skabara);

General experimental details

Unless stated otherwise, all reagents were purchased from Sigma Aldrich, TCI, Alfa Aesar or Fluorochem and used without further purification. Tetrakis(triphenylphosphine)palladium(0) was synthesised and stored under an inert atmosphere.

Dry solvents were obtained from a solvent purification system (SPS 400 Innovative Technologies) with alumina as a drying agent. Glassware was dried in an oven at 120 °C overnight.

Solvents were removed using a rotary evaporator with a vacuum supplied by a low vacuum pump, and, when necessary, a high vacuum was used to remove residual solvent.

Thin layer chromatography (TLC) was performed using Merck Silica gel 60 F254 TLC plates. Column chromatography was carried out on silica gel Zeoprep 60 Hyd (40-63 µm mesh).

¹H and ¹³C NMR spectra were recorded on a Bruker AVIII 400 apparatus at 400 MHz and 100 MHz, respectively, or a Bruker AV500 at 500MHz and 125MHz, respectively. NMR data are presented in the following order: chemical shifts (δ) in ppm; multiplicity as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m); coupling constants (J) in Hz. Multiples are reported over the range they appeared (in ppm). Signals were sharp unless stated as broad. Samples were referenced to residual solvent peaks.

The elemental analysis (the micro analyse) is on an Exeter CE-440 Elemental Analyser including interpreting the presentation of carbon, hydrogen, and nitrogen.

The Mass Spectrometry Service utilises Jeol M-STATION and Bruker microTOFq Mass Spectrometers to produce quality low- and high-resolution spectra using Electron Ionisation (EI), Chemical Ionisation (CI) and Electrospray (ESI) techniques. The service also incorporates Shimadzu Gas Chromatography-Mass Spectrometry (GCMS) and Shimadzu Liquid Chromatography Mass Spectrometry (LCMS) instruments facilitating trace organics analysis of volatile, semi-volatile and non-volatile mixtures. MS MALDI-TOF analyses were run on a Shimadzu Axima-CFR spectrometer (mass range 20-150000Da); GCMS were run on a Thermo Finnigan Polaris Q spectrometer using electron ionization (EI) mode (mass range 50-650Da). The high-resolution mass measurements were performed on a Waters Xevo G2S instrument (ASAP-TOF-MS) or a Finnigan MAT 95XP (EI).

Thermal analysis

Melting points were determined using Stuart Scientific SMP1 Melting Point apparatus.

Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer Thermogravimetric Analyser TGA7 or a NETZSCH TG 209 F3 - Tarsus thermogravimeter under a constant flow of Argon or Nitrogen (20 mL/min). The temperature was increased at a rate of 10 °C/min from 40°C to 500°C.

Differential scanning calorimetry (DSC) was carried out on a TA Instruments Q1000 with a RC-90 refrigerated cooling unit attached or on a NETZSCH DSC 214 – Polyma differential scanning calorimeter. The test procedure was a standard Heat-Cool-Reheat, and the temperature range was from 20°C to 300 °C at 10°C min⁻¹.

Electrochemical characterisation

Cyclic voltammetry measurements were performed using a CH Instruments 660E electrochemical workstation with iR compensation at a scan rate of 0.1 V s⁻¹. The electrochemical cell is comprised of glassy carbon, platinum wire and silver wire as working, counter and reference electrodes respectively. The experiments were conducted at room temperature in degassed (Ar) 0.1 M solutions of tetrabutylammonium tetrafluoroborate in an anhydrous solvent with ca. 5 × 10⁻⁴ M concentrations of the studied compounds.

All measurements were referenced against the half-wave potential ($E_{1/2}$) of the F/F_{c+} redox couple. The cathodic and anodic peaks are shown for reversible and irreversible (irr) processes. The HOMO and LUMO levels were determined according to the following equations:

$$\text{LUMO} = -(E_{\text{ox}} - E_{1/2} + 4.8) \text{ (eV)};$$

$$\text{HOMO} = -(E_{\text{red}} - E_{1/2} + 4.8) \text{ (eV)}$$

E_{ox} and E_{red} are presented with a threshold voltage of oxidation or reduction individually.

Optical properties

UV-Vis absorption spectra were recorded on a Shimadzu 2600 spectrophotometer fitted with an integrating sphere and results were normalised to λ_{max} . Fluorescence spectroscopy measurements were conducted on the Perkin Elmer LS45 fluorescence spectrometer, the Edinburgh Instruments FLS980 fluorescence spectrometer or the Horiba Duetta Bio Fluorescence and Absorbance spectrometer (the short excitation time can reduce lights exposure for materials). Thin films for recording PL spectra were prepared by spin-coating technique utilizing a SPS-Europe Spin150 Spin processor using 2.5 mg ml^{-1} solutions of compounds in soluble solvent (in chloroform mostly) on pre-cleaned quartz substrates (UQG optics) or by drop casting of 5 mg ml^{-1} solutions on quartz substrates.

SCLC analysis

Devices used for SCLC analysis were fabricated by a spin-coating / evaporation hybrid method. Pre-patterned ITO slides ($7 \text{ } \Omega/\text{sq}$, $15 \text{ mm} \times 15 \text{ mm} \times 1.1 \text{ mm}$, KINTEC) were cleaned with deionised water, acetone and isopropanol in an ultrasonic bath for 5 minutes before treatment with UV–ozone for 15 mins. The architecture of the devices was ITO/PEDOT:PSS (30 nm)/BFN and BFSN (100 nm) /Ag(60-100 nm). For all devices, the devices were fabricated using pre-cleaned indium-tin-oxide (ITO) coated glass substrates after ozone plasma treatment. PEDOT:PSS (Xi'an polymer light technology Corp, Al 4083) was spin-coated and annealed on a hotplate at 120°C for 20 minutes. After the substrate cooled down to room temperature, the BFN or BFSN was spun at 1000 rpm from chloroform solution at a concentration of 10 mg/ml . Ag was thermally evaporated using a Kurt J. Lesker Spectros II deposition system at 10^{-6} bar at a deposited rate of $1\text{--}1.5 \text{ } \text{Å/s}$. A Keithley Semiconductor Characterisation System (SCS) 4200 were used for recording the J-V curves.

Morphology characterisation.

The morphology of active layers is determined by AFM, which was conducted on a Bruker Multiple 8.

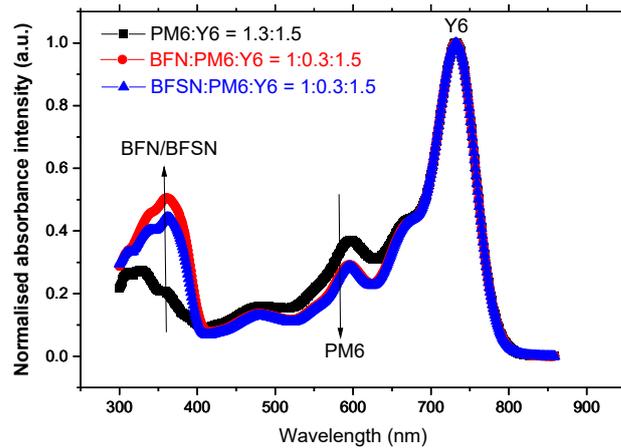


Fig. S1. Normalised absorbance intensity of active materials in CH_3Cl solution ($10^{-5}\sim 10^{-4}\text{M}$).

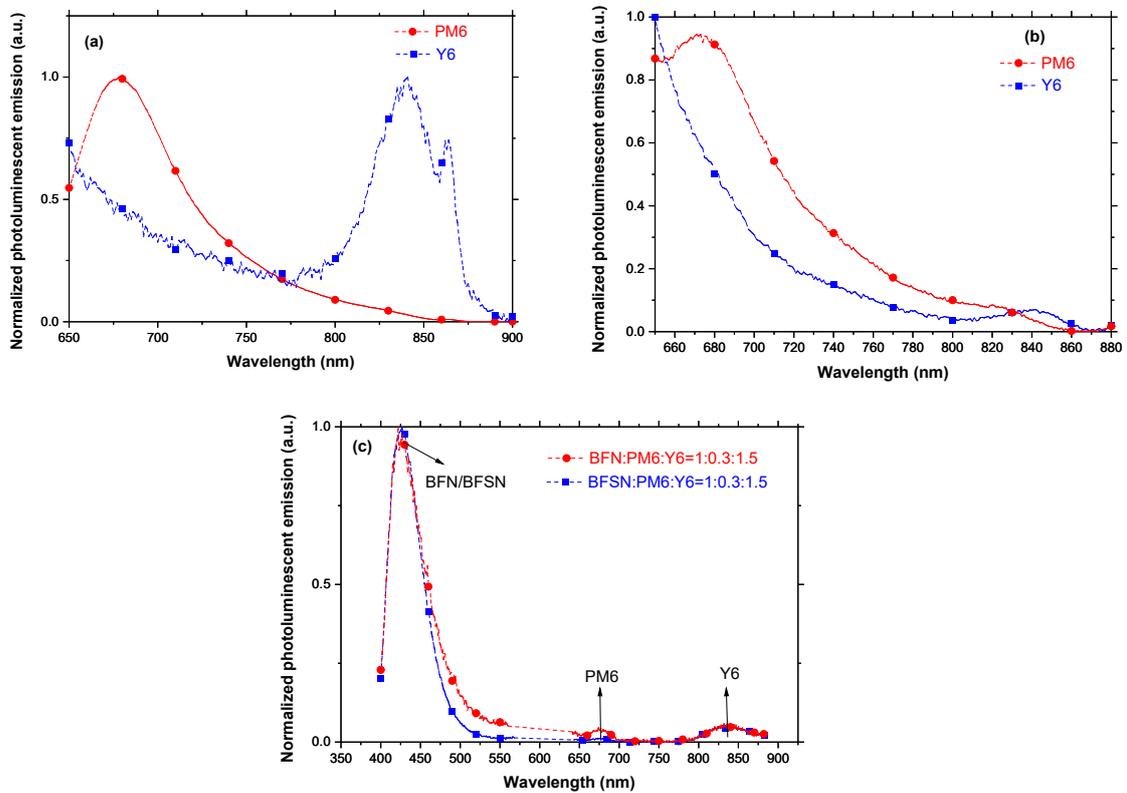


Fig. S2. Normalised photoluminescent intensity of films in quartz with a thickness of 100 nm, (a) PM6 and Y6 were excited at 575 nm; (b) PM6 and Y6 were excited at 300 nm; (c) BFN/BFSN blended active layer film excited at 300 nm.

Photoluminescence was used to investigate the charge separation in ternary active films, as shown in Fig. S2. In Fig S2(a) and (b), the individual PM6 and Y6 were excited at 575 nm and 300 nm, and the PL peaks of PM6 and Y6 were measured at 680 nm and 840 nm. In PM6 and Y6 blended film (PM6:Y6 = 1.3:1.5), negligible PL peaks were found for either of the excitation wavelengths of 300 nm or 575 nm. In Fig. S2(c), BFN, PM6 and Y6 blended films (BFN/BFSN:PM6:Y6 = 1:0.3:1.5) were excited at 300 nm, leading to an observation of BFN, BFSN, PM6 and Y6 emission peaks, which indicates less efficient charge separation in ternary films, unlike the binary films.

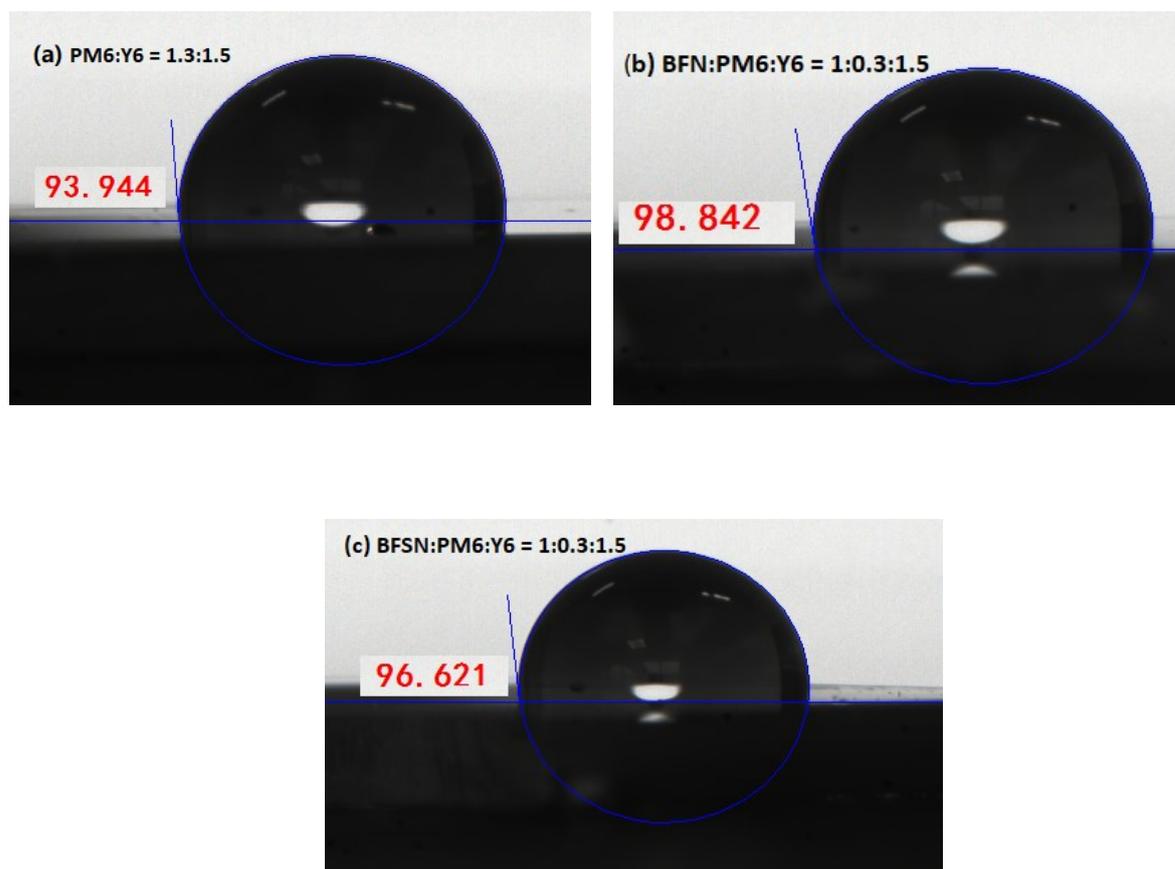
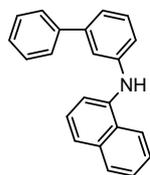


Fig. S3. Contact angle measurements, (a)PM6:Y6 = 1.3:1.5; (b) BFN:PM6:Y6 = 1:0.3:1.5; (c) PM6:Y6 = 1.3:1.5.

The contact angle measurements given in Fig. S3 are used to observe any changes in hydrophobicity of the blended films, and it can be seen that there is very little variation in hydrophobicity between compositions of the binary and ternary films.

Compound 1

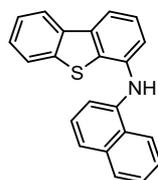
N-(Naphthalene-1-yl)- N-1,1'-biphenyl-3-amine



3-Bromobiphenyl (10 g, 43 mmol, 1 eq), 4-naphthylamine (7.37 g, 51.5 mmol, 1.2, eq), Pd₂(dba)₃ (1.2 g, 1.29 mmol, 0.03 eq) and NaOtBu (8.25 g, 85.8 mmol, 2 eq) were added to the flask. Then 80 mL dry toluene was added to the flask after degassing. Before adding P(t-bu)₃ (1.74 g, 8.6 mmol, 0.2 eq), the mixture was stirred in N₂ for 30 mins. The mixture was refluxed at 80°C overnight. After aqueous workup the crude product was subjected to column chromatography on silica gel, eluting with petroleum ether: CH₂Cl₂ (8:1) for **the yellow oily** product (yield 70%). The characterisation is consistent with the published patent.¹

Compound 2

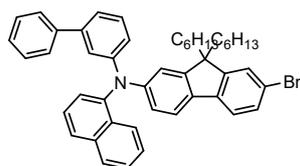
N-(Naphthalene-1-yl)-N-dibenzothiophene-4-amine



4-Bromodibenzothiophene (27 g, 102.6 mmol, 1 eq), 4-naphthylamine (17.6 g, 123.2 mmol, 1.2 eq), Pd₂(dba)₃ (2.8 g, 3.1 mmol, 0.03 eq) and NaOtBu (19.7 g, 205.2 mmol, 2 eq) were added in the flask. Then 150 mL dry toluene was added into the flask after degassing. Before adding P(t-bu)₃ (4.15 g, 20.5 mmol, 0.2 eq), the mixture was stirred in N₂ for 30 mins. The mixture was refluxed at 80°C overnight. After aqueous workup the crude product was subjected to column chromatography on silica gel, eluting with petroleum ether: DCM (7:1) for the pale pink solid product. (yield 93%) The characterisation is consistent with the published patent ¹

Compound 3.

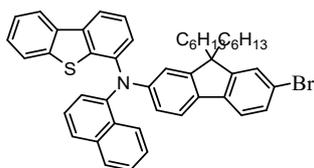
7-Bromo-N-(naphthalene-1-yl)-N-(1,1'-biphenyl-3-yl)-9,9-dihexyl-9H-fluoren-2-yl amine



Compound 9 (5.46 g, 18.5 mmol, 0.7 eq), 2,7-dibromo-9,9-dihexylfluorene (13 g, 26.4 mmol, 1.0 eq), Pd₂(dba)₃ (362 mg, 0.40 mmol, 1.5 % eq), 1,1'-bis(diphenylphosphino)ferrocene (dppf, 229 mg, 0.4 mmol, 1.5% eq) and NaOtBu (2.54 g, 26.40 mmol, 1 eq) were added in the flask. Then dry toluene was added into the flask after degassing. The mixture was refluxed at 100 °C overnight. After aqueous workup the crude product was subjected to column chromatography on silica gel, eluting with petroleum ether to remove 2,7-dibromo-9,9-dihexylfluorene followed petroleum ether: CH₂Cl₂ (10:1) to isolate a pale yellow product (**M.P.** = 108 – 102°C yield 90%), **ESI MS** calculated for C₄₇H₄₈BrN 706, found 730 (M+Na⁺); **microanalysis** calculated for C₄₇H₄₈BrN C, 79.9, H, 6.9 %, found C, 80.1, H, 7.0 %; **¹H NMR** (500 MHz, DMSO) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.89 (t, *J* = 9.0 Hz, 2H), 7.65 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.49 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.46 – 7.42 (m, 3H), 7.40 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.32 – 7.26 (m, 2H), 7.25 – 7.19 (m, 2H), 7.16 (d, *J* = 2.1 Hz, 1H), 6.87 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.83 – 6.78 (m, 1H), 1.86 (td, *J* = 12.6, 12.1, 4.9 Hz, 2H), 1.75 (td, *J* = 12.3, 4.6 Hz, 2H), 1.11 – 0.80 (m, 10H), 0.77 – 0.35 (m, 12H). **¹³C NMR** (101 MHz, C₆D₆) δ 153.35, 152.34, 149.82, 149.02, 144.45, 143.03, 141.37, 140.62, 135.96, 134.73, 131.49, 130.44, 130.20, 129.05, , 127.34, 126.78, 126.70, 126.69, 126.52, 126.28, 124.84, 121.80, 121.46, 121.31, 121.21, 120.88, 120.60, 117.05, 55.62, 40.36, 31.78, 29.98, 24.18, 23.02, 14.30.

Compound 4

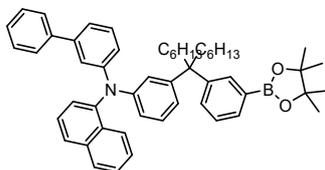
7-Bromo-N-(naphthalene-1-yl)-N-(dibenzothiophene-4-yl)-9,9-dihexyl-9H-fluoren-2-yl amine



Compound 10 (9.42 g, 28.44 mmol, 0.7 eq), 2,7-dibromo-9,9-dihexylfluorene (20 g, 40.6 mmol, 1.0 eq), Pd₂(dba)₃ (557 mg, 0.61 mmol, 1.5 % eq), 1,1'-bis(diphenylphosphino)ferrocene (dppf, 352 mg, 0.61 mmol, 1.5 % eq) and NaOtBu (3.9 g, 40.6 mmol, 1 eq) were added in the flask. Then dry toluene was added to the flask after degassing. The mixture was refluxed at 100°C overnight. After aqueous workup the crude product was subjected to column chromatography on silica gel, eluting with petroleum ether to remove 2,7-dibromo-9,9-dihexylfluorene followed petroleum ether: DCM (10:1) to collect a **pale yellow solid** product (yield 80%). (**M.P.** = 80 – 84°C, **ESI MS** calculated for C₄₇H₄₆BrNS 737, found 760 (M+Na⁺); **microanalysis** calculated for C₄₇H₄₆BrNS C, 76.6, H, 6.3 %, found C 77.7, H, 6.48 %; ¹H NMR (500 MHz, DMSO) δ 8.40 – 8.28 (m, 1H), 8.15 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.75 (m, 3H), 7.69 – 7.63 (m, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 1.9 Hz, 1H), 7.53 – 7.39 (m, 6H), 7.30 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.24 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.82 – 6.73 (m, 2H), 1.78 (td, *J* = 12.7, 4.6 Hz, 2H), 1.62 (ddd, *J* = 16.4, 12.2, 4.4 Hz, 2H), 1.07 – 0.94 (m, 6H), 0.94 – 0.65 (m, 16H); ¹³C NMR (101 MHz, C₆D₆) δ 153.46, 152.27, 148.02, 143.66, 140.69, 140.41, 138.35, 136.08, 135.84, 134.89, 131.13, 130.41, 126.73, 126.61, 126.54, 126.47, 126.23, 125.98, 125.76, 124.78, 124.59, 122.87, 122.04, 121.17, 120.96, 120.62, 117.66, 116.96, 55.61, 40.32, 31.82, 29.97, 24.12, 23.02, 14.33.

Compound 5

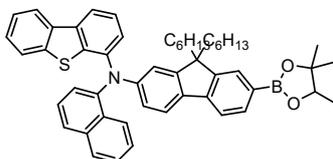
7-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(naphthalene-1-yl)-N-(1,1'-biphenyl-2-yl)-9,9-dihexyl-9H-fluoren-2-yl amine



To a solution of Compound 11 (3.8g, 5.37 mmol, 1 eq) in THF at -80°C, a solution of butyllithium (2.48 M) in hexane (2.58 ml, 1.2 eq) was added dropwise under Ar. The reaction was cooled down to -100°C, and (1.64 mL, 8.05 mmol, 1.5 eq) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added and after removing the bath the stirring continued overnight. The reaction was quenched by water and the crude product was extracted with CH₂Cl₂ and dried over MgSO₄. Then the product was purified by column chromatography silica gel, eluting in hexane CH₂Cl₂ (5:1) to collect a pale yellow product. The boronic acid pinacol ester was compared with its starting material in proton NMR spectroscopy to identify the new structure and used for further reactions without other characterisations.

Compound 6

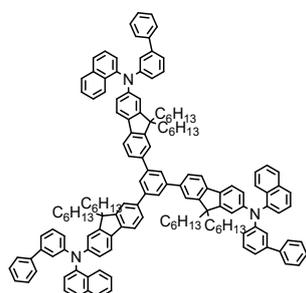
7-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(naphthalene-1-yl)-N-(dibenzothiophene-4-yl)-9,9-dihexyl-9H-fluoren-3-yl amine



To a solution of Compound 12 (2 g, 2.71 mmol, 1 eq) in THF at -80°C , a solution of butyllithium (2.48 M) in hexane (1.63 ml, 1.5 eq) was added dropwise under Ar. The reaction was cooled down to -100°C , and (1.1 mL, 5.42 mmol, 2 eq) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added and after removing the bath the stirring continued overnight. The reaction was quenched by water and the crude product was extracted with DCM and dried over MgSO_4 . Then the product was purified by column chromatography silica gel, eluting in hexane CH_2Cl_2 (5 1) to collect a pale grey solid product. The boronic acid pinacol ester was compared with its starting material in proton NMR spectroscopy to identify the new structure and used for further reactions without other characterisations.

BFN

1,3,5-Tri(N-(naphthalene-1-yl)-N-(1,1'-biphenyl-3-yl)-9,9-dihexyl-9H-fluorene-2-yl-amine) benzene



Compound 13 (1.5 g, 1.99 mmol, 4 eq), 1,3,5-tribromobenzene (156 mg, 0.50 mmol, 1 eq), $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (1.18 g, 3.73 mmol, 7.5 eq) and $\text{Pd}(\text{PPh}_3)_4$ (115 mg, 0.1 mmol, 0.2 eq) was added into the flask. Then the mixture was refluxed in dry THF (25 mL) and degassed DI water (2.5 mL) at 80°C overnight. 5% hydrochloric acid was added to the solution for 2 h and NaHCO_3 solution was used to neutralize the solution. After aqueous workup the crude product was subjected to column chromatography on silica gel, ramping petroleum ether: toluene (8:1) to petroleum ether: toluene (4:1) to collect a white solid product. (yield 57%, **M.P.** = **126 – 132 $^{\circ}\text{C}$**). **BFB MS** calculated for $\text{C}_{147}\text{H}_{147}$, 1954. found 1955 [(M+H)+]; **Microanalysis** C 90.3, H 7.6, N 2.2 %, found C 90.4, H 6.2, N 2.3 %; (**$^1\text{H NMR}$** (400 MHz, CD_2Cl_2) δ 8.00 (dd, $J = 8.6, 1.1$ Hz, 1H), 7.96 – 7.86 (m, 2H), 7.82 (d, $J = 8.3$ Hz, 1H), 7.70 (d, $J = 15.2$ Hz, 3H), 7.62 – 7.32 (m, 10H), 7.31 – 7.14 (m, 4H), 6.99 (d, $J = 8.2$ Hz, 2H), 2.07 – 1.79 (m, 4H), 1.08 (dq, $J = 39.2, 6.1, 5.4$ Hz, 12H), 0.78 (t, $J = 7.2$ Hz, 10H). **$^{13}\text{C NMR}$** (101 MHz, CD_2Cl_2) δ 140.97, 128.69, 128.48, 127.36, 126.93, 126.40, 126.20, 124.27, 120.38, 55.27, 54.03, 53.76, 53.49, 53.22, 52.95, 40.36, 31.58, 29.70, 23.92, 22.63, 13.87, -0.37.

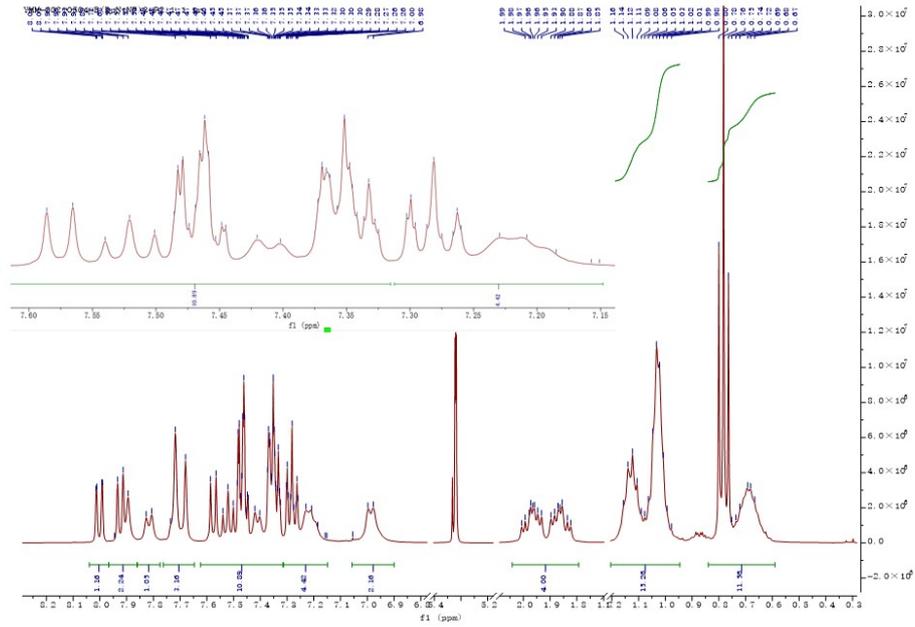


Fig. S4. ¹H NMR spectrum of BFN.

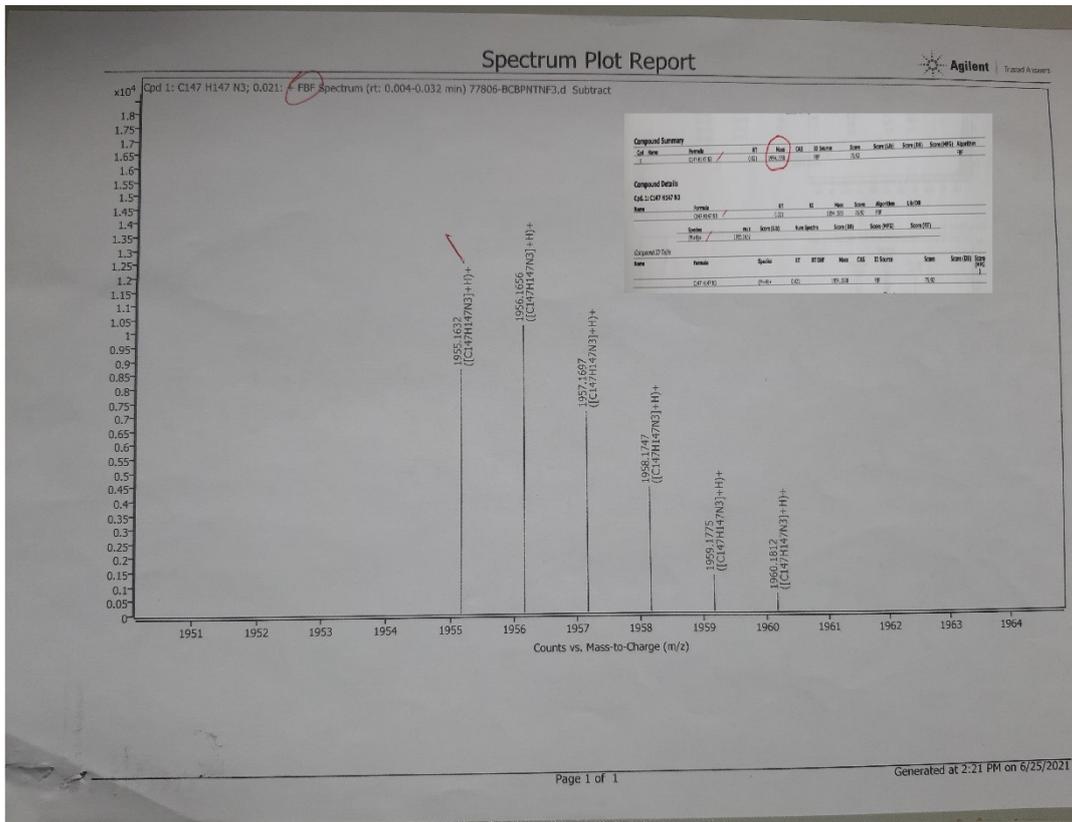


Fig. S5. Mass spectrum of BFN.

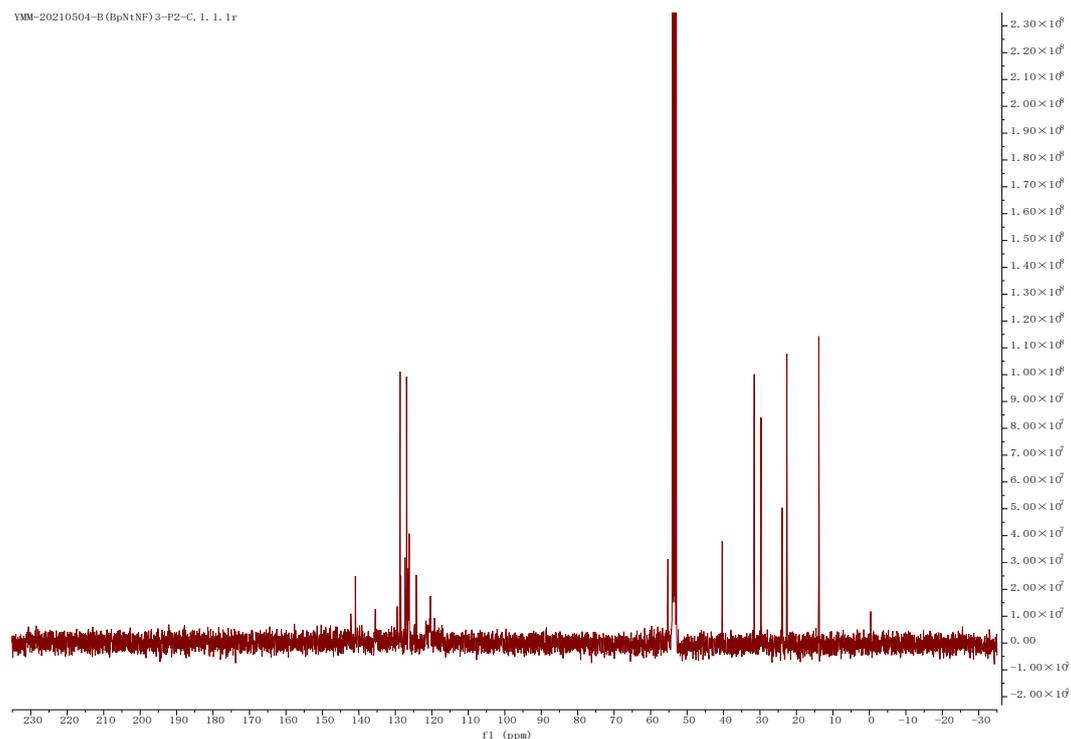
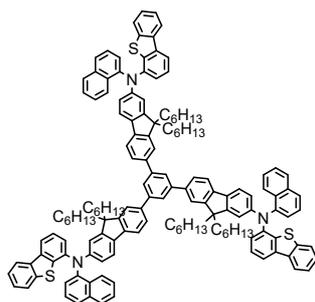


Fig. S6. ^{13}C NMR spectrum of BFN.

BFSN

1,3,5-Tri(N-(naphthalene-1-yl)-N-(dibenzothiophene-4-yl)-9,9-dihexyl-9H-fluorenyl-2-yl-amine) benzene



Compound 14 (1.5 g, 191 mmol, 4 eq), 1,3,5-tribromobenzene (150 mg, 0.48 mmol, 1 eq), $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (1.13 g, 3.59 mmol, 7.5 eq) and $\text{pd}(\text{pPh}_3)_4$ (110 mg, 0.1 mmol, 0.2 eq) was added into the flask. Then the mixture was refluxed in dry THF (25 mL) and degassed DI water (2.5 mL) at 80°C overnight. 5% hydrochloric acid was added to the solution for 2h and NaHCO_3 solution was used to neutralize the solution. After aqueous workup the crude product was subjected to column chromatography on silica gel, eluting with petroleum ether: toluene (8:1) ramping to petroleum ether: toluene (4:1) to collect a white solid product. (yield 57%, M.P. = $174 - 182^\circ\text{C}$). **BFB MS** calculated for $\text{C}_{147}\text{H}_{141}\text{N}_3\text{S}_3$ 2044.0, found 2044 [(M+H)⁺]; **Microanalysis** calculated for $\text{C}_{147}\text{H}_{141}\text{N}_3\text{S}_3$ C, 86.30, H, 6.95, N 2.05 %, found C 86.75, H 5.64, N 2.17 %; **^1H NMR** (400 MHz, CD_2Cl_2) δ 8.24 – 8.14 (m, 1H), 8.02 – 7.86 (m, 3H), 7.79 (d, $J = 8.2$ Hz, 1H), 7.74 – 7.64 (m, 4H), 7.58 (d, $J = 8.2$ Hz, 1H), 7.51 – 7.36 (m, 5H), 7.35 – 7.26 (m, 2H), 7.15 (d, $J = 7.7$ Hz, 1H), 7.00 – 6.80 (m, 2H), 1.99 – 1.68 (m, 4H), 1.16 – 0.84 (m, 12H), 0.76 (t, $J = 7.2$ Hz,

10H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 139.86, 135.63, 128.44, 126.87, 126.16, 124.40, 124.19, 122.60, 121.71, 55.23, 54.03, 53.76, 53.49, 53.22, 52.95, 40.31, 31.58, 29.65, 23.83, 22.60, 13.87.

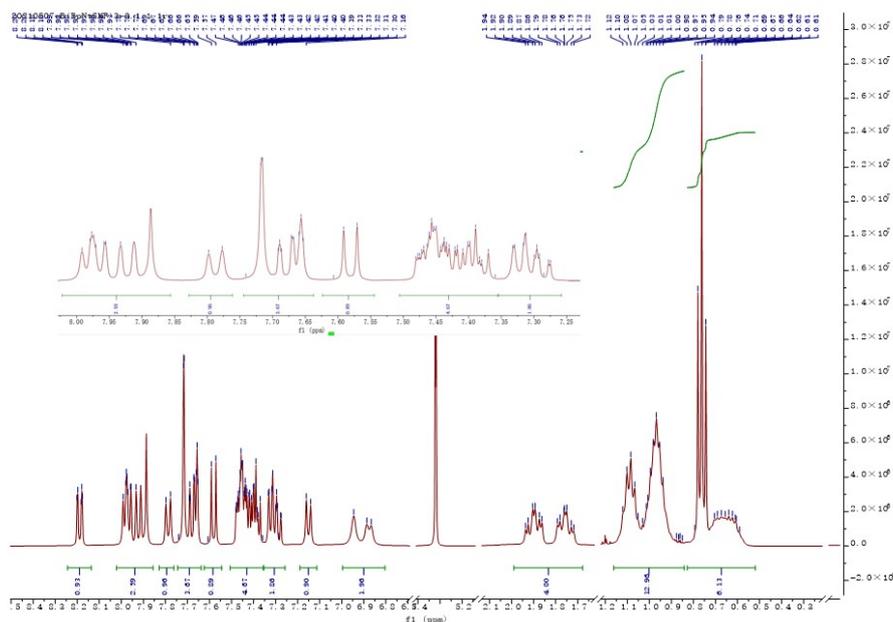


Fig. S7. ^1H NMR spectrum of BFSN.

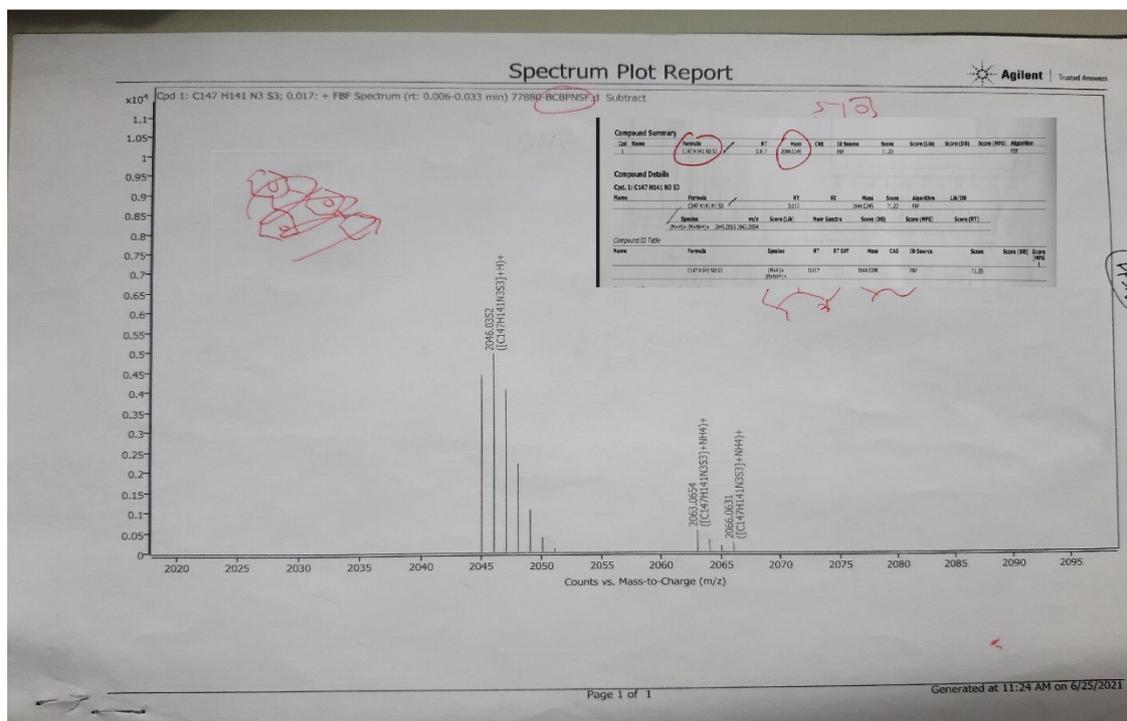


Fig. S8. Mass spectrum of BFSN.

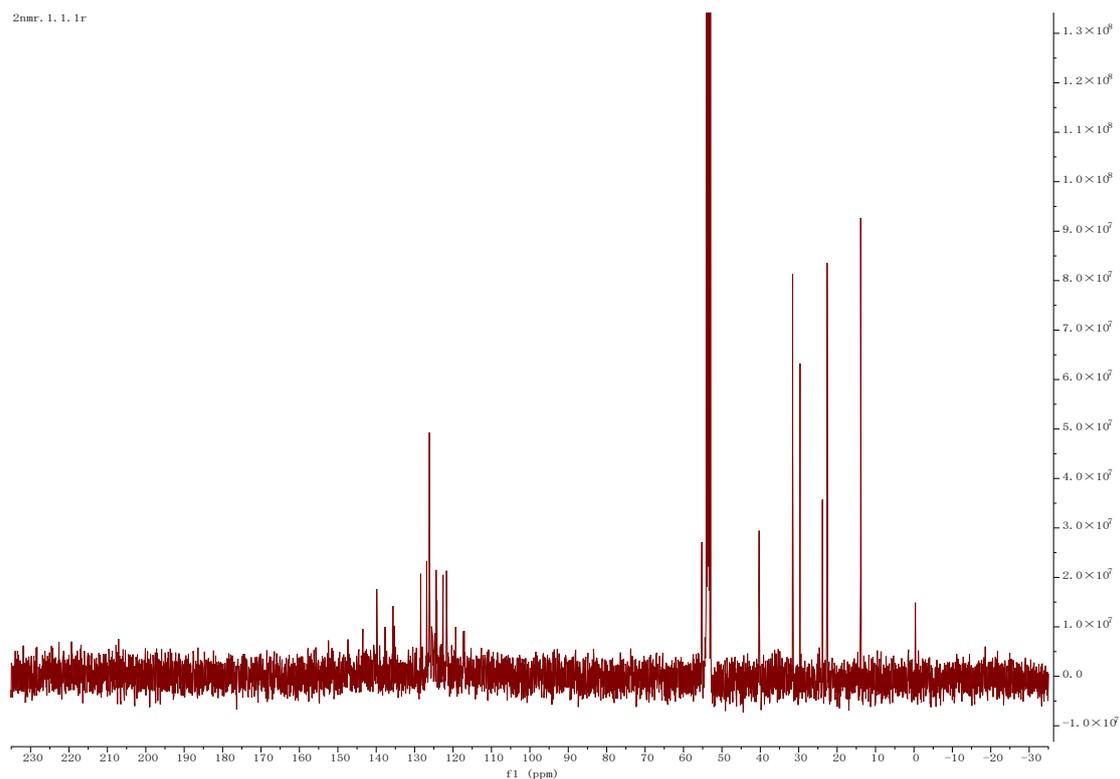


Fig. S9. ^{13}C NMR spectrum of BFSN.

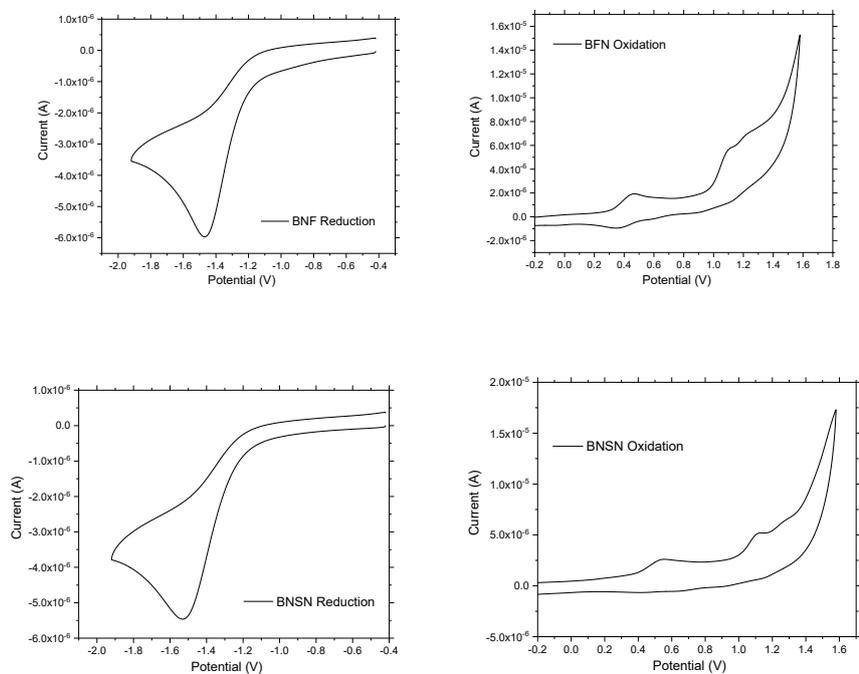


Fig. S10. Reduction (left) and oxidation (right) curves from cyclic voltammetry of compounds related to amines referenced against the $E_{1/2}$ of the Fc/Fc^+ redox couple; 5×10^{-4} M solutions in 0.01 M $n\text{-Bu}_4\text{NPF}_6$.

Table S1 HOMO and LUMO energy levels for the amine compounds.

	HOMO (eV)	LUMO (eV)	E_g (eV)	E_{ox} (eV)	E_{red} (eV)
BFN	5.12	2.08	3.04	0.47, 1.10(irr)	-1.48(irr)
BFSN	5.17	2.09	3.08	0.55(irr), 1,11(irr)	-1.54(irr)

Table S2 Thermal properties of star-shaped amine compounds.

	M.P. (°C)	T_d , 5% (°C)	T_g , (°C)
BFN	126-132	437	N/A
BFSN	174-182	440	N/A

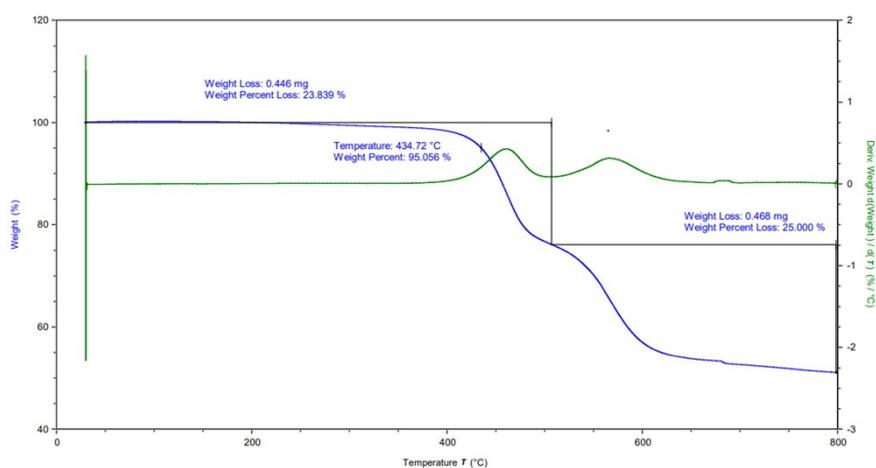


Fig. S11. TGA of BFN

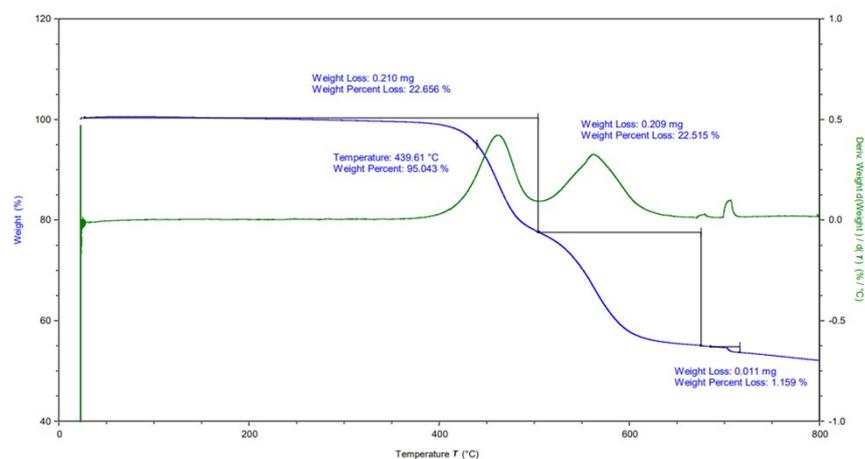


Fig. S12. TGA of BFSN

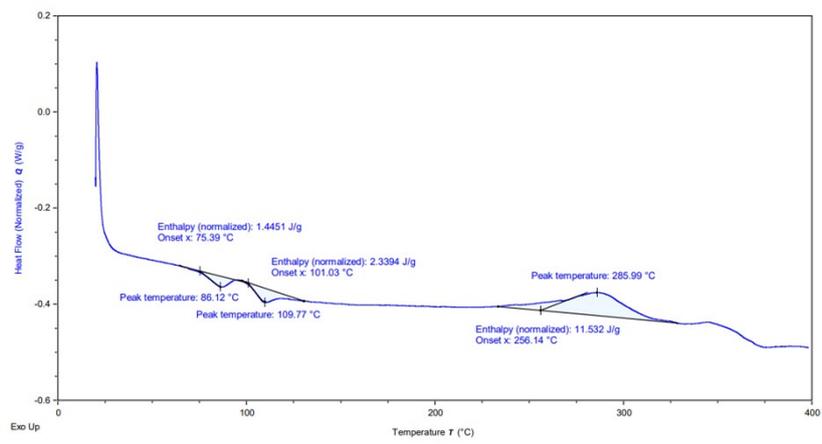


Fig. S13. DCS of BFN.

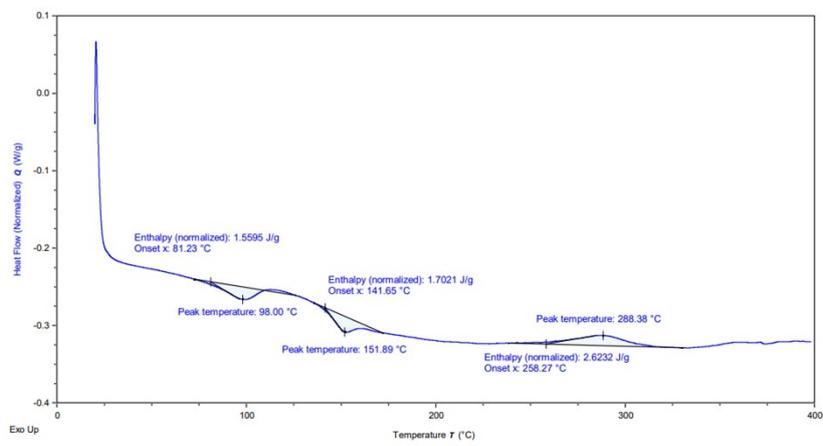


Fig. S14. DSC of BFSN.

1. Z. Jia; J. Guo; and Y. Li, CN113121588A, 2015.