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Supporting information for

Bis(Benzothiophene-*S,S*-Dioxide) Fused Small Molecules Realize Solution-Processible, High-Performance and Non-Doped Blue Organic Light-Emitting Diodes

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1. Experimental

2.1. Materials and characterization.

^{1}H and ^{13}C NMR spectra were measured on a Bruker 500 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS; δ=0) as internal reference. Elemental analyses were recorded on a Vario Elelemental analysis instrument (Elementar Co.). The mass spectra were performed with a Bruker Autoflex III smartbeam MALDI-TOF/TOF mass spectrometer. Thermal stabilities were evaluated by measuring thermo-gravimetric analysis (TGA) thermograms on a Netzsch TG 209 at 20 ^oC min^{-1} and differential scanning calorimetry (DSC) on a Netzach DSC 204 at 10 ^oC min^{-1}. The cyclic voltammetry (CV) test of the compounds were measured by using a CHI630E electrochemical work-station (CH Instruments Ins.), and performed in an electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile at a scan rate of 50 mV s^{-1} at room temperature under the protection of nitrogen. A Pt wire was used as the counter electrode and a saturated calomel electrode was used as the reference electrode. UV-vis absorption spectra were obtained by using the spectrophotometer (SHIMADZU UV-2600) and Photoluminescence (PL) spectra were carried out with a fluorospectrophotometer (HORIBA Scientific Fluoromax-4). Fluorescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus-QY. Photoelectron yield spectroscopy (PYS) was measured at atmospheric ultraviolet photoelectron spectroscopy (Rikken Keiki AC-3). Atomic force microscopy (AFM) measurements were performed on a Bruker Multimode 8 microscope in Scan Asyst in air mode. The films for AFM measurement were spin-coated on the top of the

ITO/PEDOT:PSS surface.

2.2. Synthesis

2.2.1 Synthesis of 9,9-bis(2-ethylhexyl)-2,7-bis(2-methylsulfinyl)phenyl)-9H-fluorene(3)

2,2'-(9,9-bis(2-ethylhexyl-9H-fluorene-2,7-diyl)-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9.64 g, 15 mmol), 1-bromo-2-(methyl-sulfinyl)benzene (7.23 g, 33 mmol), catalyst of tetrakis(triphenylphosphine)platinum ($Pd(PPh_3)_4$) (0.87 g, 0.75 mmol), phase transfer catalyst of tetrabutylammonium bromide (TBAB) (0.24 g, 0.75 mmol) were completely dissolved in 200 ml toluene under nitrogen. Then, 20.7 ml fresh K_2CO_3 (20.7 g, 0.15 mol) aqueous solution (50 wt%) was injected and reacted at 80 ^{o}C for 24 h. When it cooled to room temperature, the organic layer was separated and the aqueous layer was extracted with DCM, washed by water, and then concentrated by a rotary evaporator. The crude product was purified by a silica gel column chromatography using petroleum ether/DCM mixture (1:3 by volume) as eluent. Yellow oil of 1 was obtained in 51.5% yield (4.517 g). ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 8.16 (d, J=5.15 Hz, 2H),7.82 (d, J=4.75 Hz, 2H), 7.61 (m, 4H), 7.45 (m, 6H), 2.34 (s, 6H), 2.16 (m, 4H), 0.85 (m, 18H), 0.61 (m, 6H), 0.52 (t, J=6.25 Hz, 6H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ (ppm): 151.60, 143.91, 140.52, 139.68, 137.03, 130.67, 130.35, 128.71, 128.07, 123.70, 123.52, 120.44, 56.14, 44.55, 44.31, 34.82, 33.56, 27.98, 27.01, 22.60, 13.90, 10.11. Element Anal. Calcd for [$C_{43}H_{54}O_2S_2$] (%): C 77.43, H 8.16, S 9.61; Found: C 75.82, H 8.54, S 9.88. MS (APCI): m/z (%): 667.7.

2.2.2 Synthesis of 9,9-bis(2-ethylhexyl) bis[2,3-b;6,7-b]benzo[d]thiophene(4)

9,9-bis(2-ethylhexyl)-2,7-bis(2- methylsulfinyl)phenyl)-9H-fluorene (468.9 mg, 0.668 mmol), trifluoromethanesulfonic acid (4.2 mL) and phosphorus pentoxide (254.5 mg, 1.336 mmol) were added into a 250 mL round-bottom flask. The mixture stirred at room temperature for 12 h and then poured into ice water. After collecting the precipitate and drying under vacuum, it was dissolved in 50 ml pyridine under nitrogen and reacted at 90 ℃ for 8 h. When it cooled to room temperature, the mixture was extracted with DCM and washed by water, concentrated by a rotary evaporator. The crude product was purified by a silica gel column chromatography using petroleum ether as eluent. White solid of 2 was obtained in 51.5% yield (4.517 g). ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 8.20 (d, J=5.15 Hz, 2H), 8.19 (s, 2H), 8.09 (s, 2H), 7.86 (d, J=4.75 Hz, 2H), 7.45 (m, 4H), 2.16 (m, 4H), 0.84 (m, 18H), 0.60 (m, 6H), 0.52 (t, J=6.15 Hz, 6H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ (ppm): 148.56, 140.42, 140.03, 138.78, 135.75, 135.37, 126.61, 124.47, 123.08, 121.64, 115.81, 114.00, 56.24, 44.56, 34.79, 33.55, 27.97, 27.00, 22.61, 13.88, 10.12. Element Anal. Calcd for [$C_{41}H_{46}S_2$] (%): C 81.86, H 7.69, S 10.63; Found: C 82.06, H 7.84, S 10.23. MS (APCI): m/z (%): 603.7.

2.2.3 Synthesis of 9,9-bis(2-ethylhexyl)bis[2,3-b;6,7-b]benzo[d]thiophene-S,Sdioxide (5)

9,9-bis(2-ethylhexyl) bis[2,3-b;6,7-b]benzo[d] thiophene (2.89 g, 4.8 mmol) was dissolved in

40 ml anhydrous DCM entirely at room temperature, m-chloroperbenzoic acid (m-CPBA) (4.14 g, 24 mmol) was added in three times. After stirred at room temperature for 8 h, saturated sodium hydroxide aqueous solution was added to stop the reaction. The mixture was extracted with DCM and washed by water, concentrated by a rotary evaporator. The crude product was purified by a silica gel column chromatography using petroleum ether/DCM mixture (2:1 by volume) as eluent. White solid of 3 was obtained in 84% yield (2.69 g). ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) : 8.19 (s, 2H), 7.87 (t, J=7.05 Hz, 4H), 7.80 (t, J=4.00 Hz, 2H), 7.69 (t, J=6.30 Hz, 2H), 7.57 (t, J=6.25 Hz, 2H), 2.15 (m, 4H), 0.83 (m, 18H), 0.61 (m, 6H), 0.53 (t, J=6.15 Hz, 6H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ (ppm):157.62, 141.70, 139.70, 137.74, 134.12, 132.20, 131.85, 130.56, 122.78, 121.89, 116.00, 114.52, 56.23, 44.55, 34.80, 33.56, 27.98, 27.01, 22.62, 13.89, 10.13. Element Anal. Calcd for [$C_{41}H_{46}O_4S_2$] (%): C 73.84, H 6.95, S 9.61; Found: C 75.27, H 7.10, S 9.72. MS (APCI) ($C_{41}H_{46}O_4S_2$): m/z (%): 668.1.

2.2.4 Synthesis of M1(FBTO-Br)

A solution of NBS (1.05 g, 5.88 mmol) in trifluoroacetic acid and concentrated sulfuric acid (1:1 by volume) (6 ml) was added dropwise to a stirred mixture of 9,9-bis(2-ethylhexyl) bis[2,3-b;6,7-b] benzo[d] thiophene-S,S-dioxide (1.86 g, 2.67 mmol) in $CHCl_3$/ trifluoroacetic acid (1:6 by volume) (28 mL) under nitrogen. The reaction mixture was stirred for 12 h and extracted with DCM. The organic layer was concentrated. The residue was purified by a silica gel column chromatography using petroleum ether/DCM mixture (2:1 by volume) as eluent. White solid of compound M1 was obtained in 86% yield (1.89 g). ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 8.19 (s, 2H), 8.00 (s, 2H), 7.80 (m, 4H), 7.73 (d, J=8.10 Hz, 2H), 2.14 (d, J=4.45 Hz, 4H), 0.89-0.75 (m, 18H), 0.61 (m, 6H), 0.53 (t, J=7.15 Hz, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm): 157.65, 141.64, 139.89, 137.55, 137.03, 130.55, 130.41, 125.71, 124.45, 122.62, 116.90, 114.51, 56.22, 44.59, 34.78, 33.58, 27.95, 26.96, 22.61, 13.88, 10.13. Element Anal. Calcd for [$C_{41}H_{44}Br_2O_4S_2$] (%): C 59.71, H 5.38, S 7.77; Found: C 56.37, H 5.02, S 7.46. MS (APCI) ($C_{41}H_{44}Br_2O_4S_2$): m/z (%): 824.9.

2.2.5 Synthesis of 4,4,5,5-tetramethyl-2-(9,9,9',9'-tetraoctyl-9H,9'H-[2,2'-difluoren]-7-yl) - 1,3,2-dioxa-borolane (FF-Bor)

2,2'-(9,9-bisoctyl-9H-fluorene-2,7-diyl)-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5) (9.64 g, 15 mmol), 2-bromo-9,9-dioctylfluorene (5.63 g, 12 mmol), $Pd(PPh_3)_4$ (0.69 g, 0.6 mmol), TBAB (0.19 g, 0.6 mmol)were completely dissolved in 200 ml under nitrogen. Then, 16.6 ml fresh K_2CO_3 (16.6 g, 0.12 mol) aqueous solution (50 wt%) was injected and reacted at 80 ℃ for 24 h. When it cooled to room temperature, the organic layer was separated and the aqueous layer was extracted with DCM, washed by water, and then concentrated by a rotary evaporator. The crude product was purified by a silica gel column chromatography using petroleum ether/DCM mixture (1:5 by volume) as eluent. Yellow oil of FF-Bor was obtained in 60.4% yield (6.56 g). ^{1}H-NMR

(500 MHz, $CDCl_3$) δ (ppm): 7.81 (m, 1H), 7.76 (m, 3H), 7.66 (m, 2H), 7.59 (m, 4H), 7.38 (m, 3H), 2.04 (m, 8H), 1.44 (s, 12H), 1.23 (m, 40H), 0.82 (m, 12H), 0.60 (br, 8H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) : 152.07, 151.43, 150.99, 150.18, 143.82, 141.01, 140.77, 140.45, 140.35, 140.10, 133.81, 128.89, 126.98, 126.77, 126.04, 122.90, 121.46, 121.42, 120.31, 119.85, 119.70, 119.01, 83.68, 55.23, 55.15, 40.36, 40.23, 31.78, 30.02, 29.97, 29.20, 24.94, 23.80, 23.74, 22.58, 14.06. Element Anal. Calcd for [$C_{157}H_{206}O_4S_2$] (%): C 84.89, H 9.35, S 2.89; Found: C 85.58, H 9.63, S 2.88. MS-APCI m/z, calcd for $C_{64}H_{93}B_2O$ (M^+): 904.73; found: 905.9.

2.2.6 Synthesis of FBTO-EHNa

A 15 mL Schlenk tube were full of monomers of M1 (1.65 g, 2.0 mmol), 1-naphthylboronic acid (1.12 g, 4.4 mmol) and $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol). After being evacuated and refilled with nitrogen three times, THF (8.0 mL) and tetraethyl ammonium hydroxide aqueous solution (Et_4NOH, 20 wt/v%, 0.5 mL) was successively injected into the tube. The mixture was stirred at 75 ℃ for 24 h. After cooled to room temperature, the THF was evaporated and the crude product was purified by a silica gel column chromatography using petroleum ether/DCM mixture (2:1 by volume) as eluent. Light-yellow solid of *FBTO-EHNa* was obtained in 68% yield (1.25 g). ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) : 8.25 (s, 2H), 8.14 (s, 2H),8.04 (d, J=7.85 Hz, 2H), 7.98 (m, 6H), 7.91 (d, J=8.1 Hz 2H), 7.86 (t, J=3.25 Hz, 2H), 7.78 (m, 2H), 7.56 (m, 2H), 2.20 (d, J=5.05 Hz, 4H), 0.95-0.81 (m, 18H), 0.66 (t, J=6.05 Hz, 6H), 0.58 (t, J=7.45 Hz, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) : 157.52, 143.96, 141.51, 139.36, 138.09, 135.98, 133.56, 133.18, 132.82, 131.27, 130.52, 130.35, 129.09, 128.42, 127.75, 126.83, 126.34, 124.67, 121.79, 121.11, 116.92, 114.45, 56.17, 44.70, 34.81, 33.67, 28.04, 27.01, 22.69, 13.96, 10.19. Element Anal. Calcd for [$C_{61}H_{58}O_4S_2$] (%): C 79.70, H 6.36, S 6.98; Found: C 79.91, H 6.75, S 7.01. [MS] MALDI-MS m/z Calcd: 919.25; found, 920.85.

2.2.7 Synthesis of FBTO-EHSF

A procedure similar to that used for *FBTO-EHNa* was followed but with 2-(9,9'-spirobi[fluoren]- 2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan (1.95 g, 4.4 mmol) instead of 1-Naphthylboronic acid. Light-yellow solid of *FBTO-EHSF* was obtained in 76% yield (1.97 g). ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) : 8.11 (s, 2H), 7.96 (d, J=7.95 Hz, 2H), 7.90 (m, 8H), 7.74 (m, 6H), 7.68 (m, 2H), 7.41 (t, J=7.45 Hz, 6H) , 7.14 (m, 6H) , 6.99 (t, J=5.05 Hz, 2H) , 6.77 (t, J=6.25 Hz, 6H), 2.12 (d, J=5.2 Hz, 4H), 0.79 (m, 18H), 0.58 (t, J=6.2 Hz, 6H), 0.50 (t, J=7.28 Hz, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) : 157.40, 150.12, 149.32, 148.25, 143.68, 142.49, 141.84, 141.33, 140.84, 139.02, 138.16, 137.88, 132.39, 131.14, 130.99, 128.37, 127.98, 126.76, 124.15, 124.01, 122.49, 121.41, 120.66, 120.32, 116.77, 114.23, 66.00, 56.07, 44.52, 34.69, 33.59, 27.93, 26.95, 22.58, 13.88, 10.10. Element Anal. Calcd for [$C_{91}H_{74}O_4S_2$] (%): C 84.36, H 5.76, S 4.95; Found: C 84.93, H 5.65, S 4.87. [MS] MALDI-MS m/z Calcd: 1295.71; found, 1295.43.

2.2.8 Synthesis of FBTO-EHFF

A procedure similar to that used for *FBTO-EHNa* was followed but with 4,4,5,5-tetramethyl-2-(9,9,9',9'-tetraoctyl-9H,9'H-[2,2'-difluoren]-7-yl)-1,3,2-dioxa-borolane (2.17 g, 2.4 mmol) instead of 1-Naphthylboronic acid. Light-yellow solid of *FBTO-EHFF* was obtained in 69% yield (1.84 g). ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) : 8.24 (s, 2H), 8.20 (s, 2H), 7.99 (d, J=7.9 Hz, 2H), 7.95 (d, J=7.95 Hz, 2H), 7.84 (m, 6H), 7.80 (d, J=7.75 Hz, 2H) , 7.75 (d, J=7.3 Hz, 2H), 7.66 (m, 12H), 7.35 (m, 6H), 2.11 (m, 20H), 1.20-1.09 (m, 80H), 0.96-0.76 (m, 56H), 0.68 (m, 8H), 0.59 (t, 6H, J=7.15 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) : 157.50, 152.24, 151.89, 151.51, 151.01, 144.54, 141.65, 141.42, 141.15, 140.73, 140.47, 140.27, 139.39, 139.23, 138.01, 137.31, 132.57, 131.36, 129.98, 127.04, 126.79, 126.29, 126.07, 126.00, 123.93, 121.66, 121.49, 121.40, 120.81, 120.38, 120.26, 119.89, 119.73, 116.84, 114.37, 56.17, 55.51, 55.17, 44.67, 40.43, 40.35, 34.80, 33.71, 33.76, 30.02, 29.21, 28.04, 27.02, 23.89, 23.81, 22.68, 22.58, 14.05, 13.96, 10.18. Element Anal. Calcd for [$C_{157}H_{206}O_4S_2$] (%): C 84.89, H 9.35, S 2.89; Found: C 85.58, H 9.63, S 2.88. [MS] MALDI-MS m/z Calcd: 2221.49; found, 2221.67.

2.3. OLEDs fabrication

The ITO coated glass substrate was preliminarily cleaned in deionized (DI) water, acetone and ethanol in an ultrasonic bath, respectively, and dried with N_2. After treatment with UV-ozone (UVO) chamber for 20 min, the ITO substrate was coated with a layer of PEDOT:PSS (4083) at 4000 rpm for hole injection, and then the PEDOT:PSS layer was annealed at 120 ^oC for 10 min in air. Subsequently, the substrate was transferred into a N_2 filled glovebox. The emitting materials dissolved in chlorobenzene solution (10 mg ml^{-1}) were then spin-coated onto the PEDOT:PSS layer at 1000 rpm. After baking the emitting layer at 50 ^oC for 10 min, the sample was loaded into a vacuum chamber. The electron transporting layer (TmPyPB), the electron injecting layer (Liq) and Al cathode were consecutively evaporated in the vacuum chamber, consecutively. Then, the device was sealed with curable UV resin in N_2-filled glove-box. The EL properties of the devices were measured in ambient air after encapsulation. A PR735 SpectraScan Spectroradiometer (Photo Research) combined with a Keithley 2400 SourceMeter unit was controlled with a customized software to simultaneously determine the current-voltage-luminous intensity characteristics and the EL spectra.

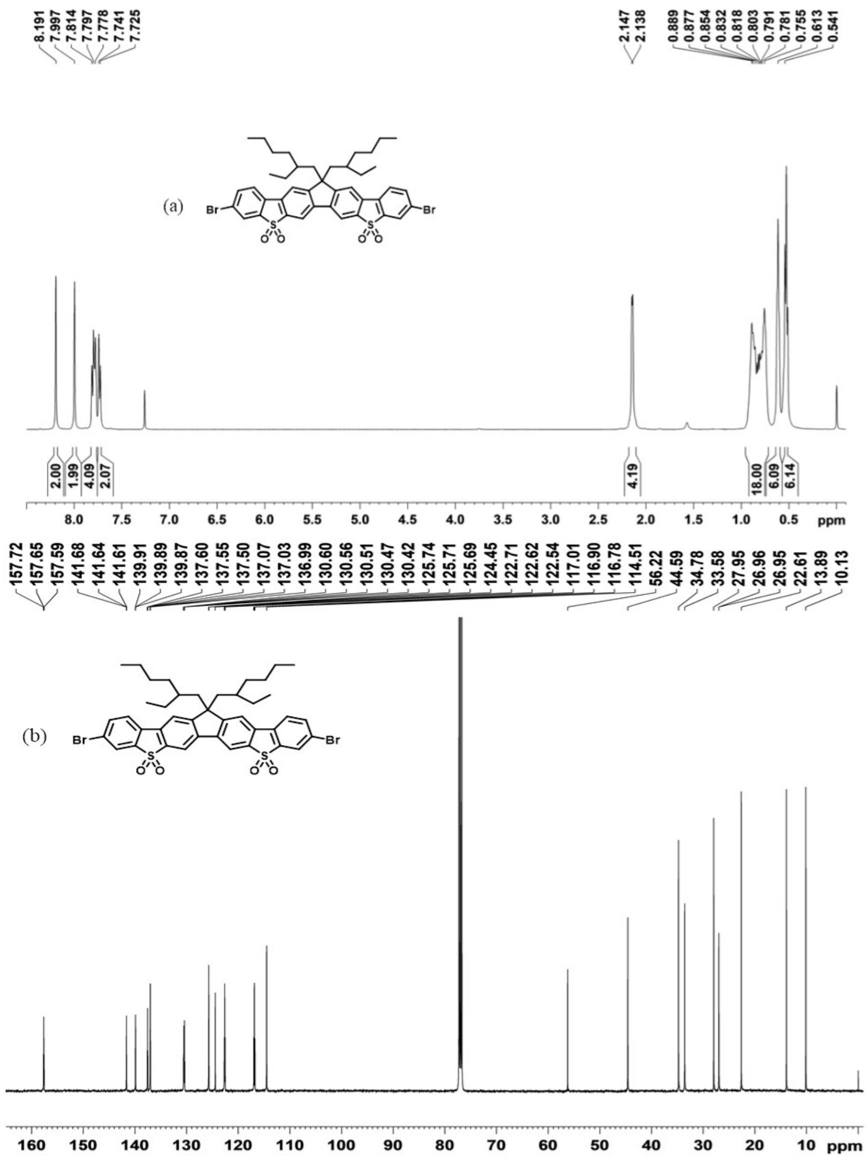

Figure S1. ^{1}H-NMR and ^{13}C-NMR spectra of compound FBTO-2Br

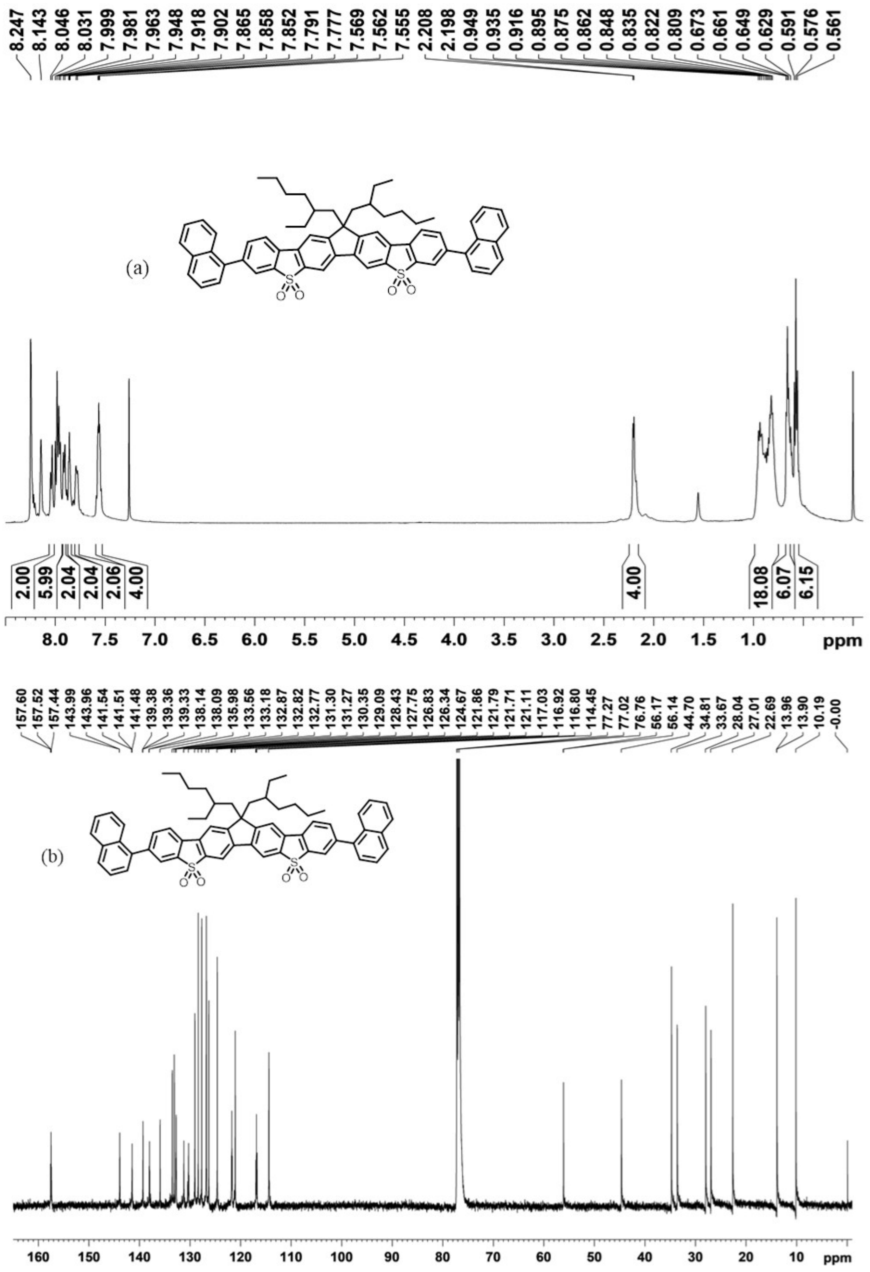

Figure S2. ^{1}H-NMR and ^{13}C-NMR spectra of compound FBTO-EHNa

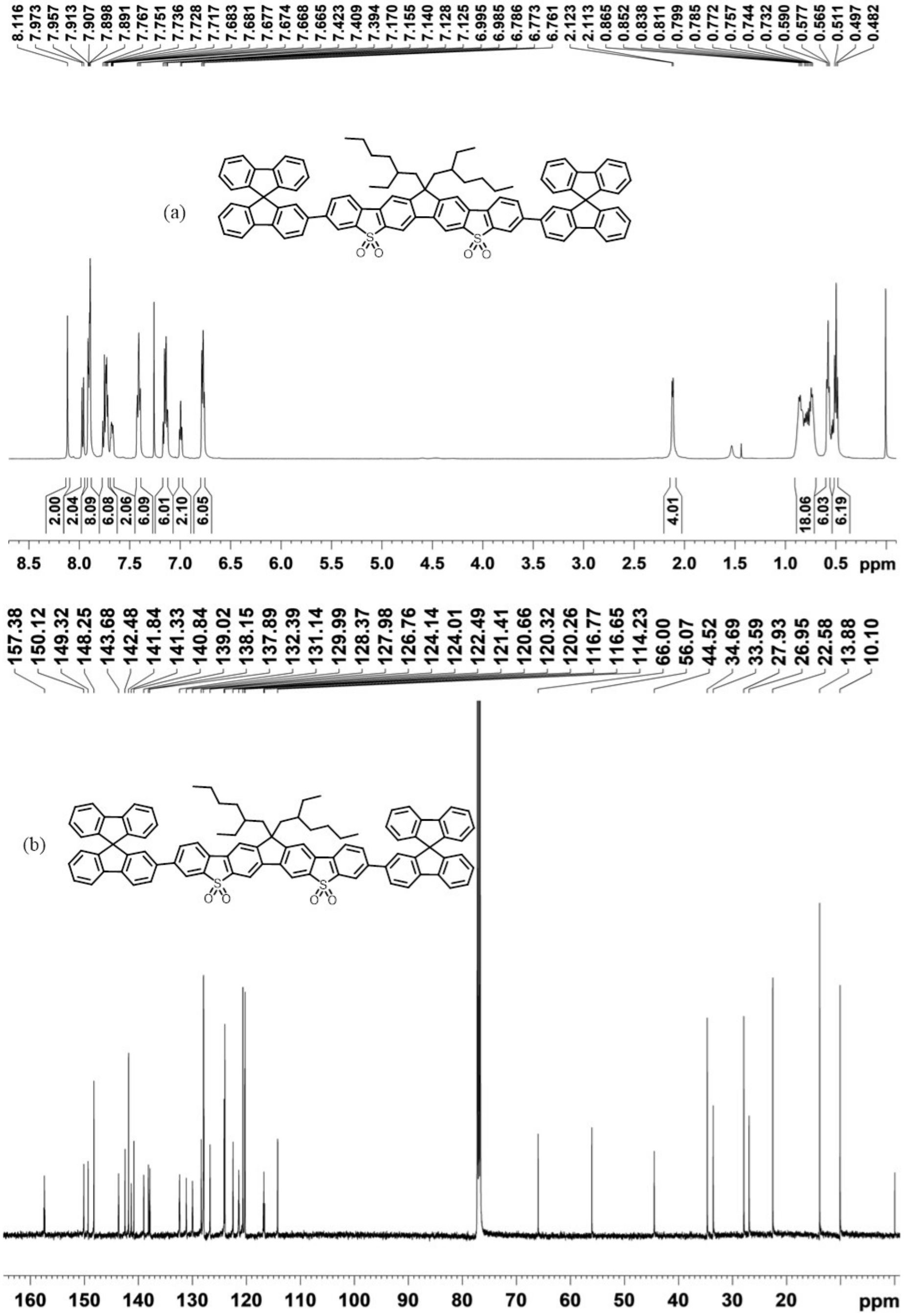

Figure S3. ^{1}H-NMR and ^{13}C-NMR spectra of compound FBTO-EHSF

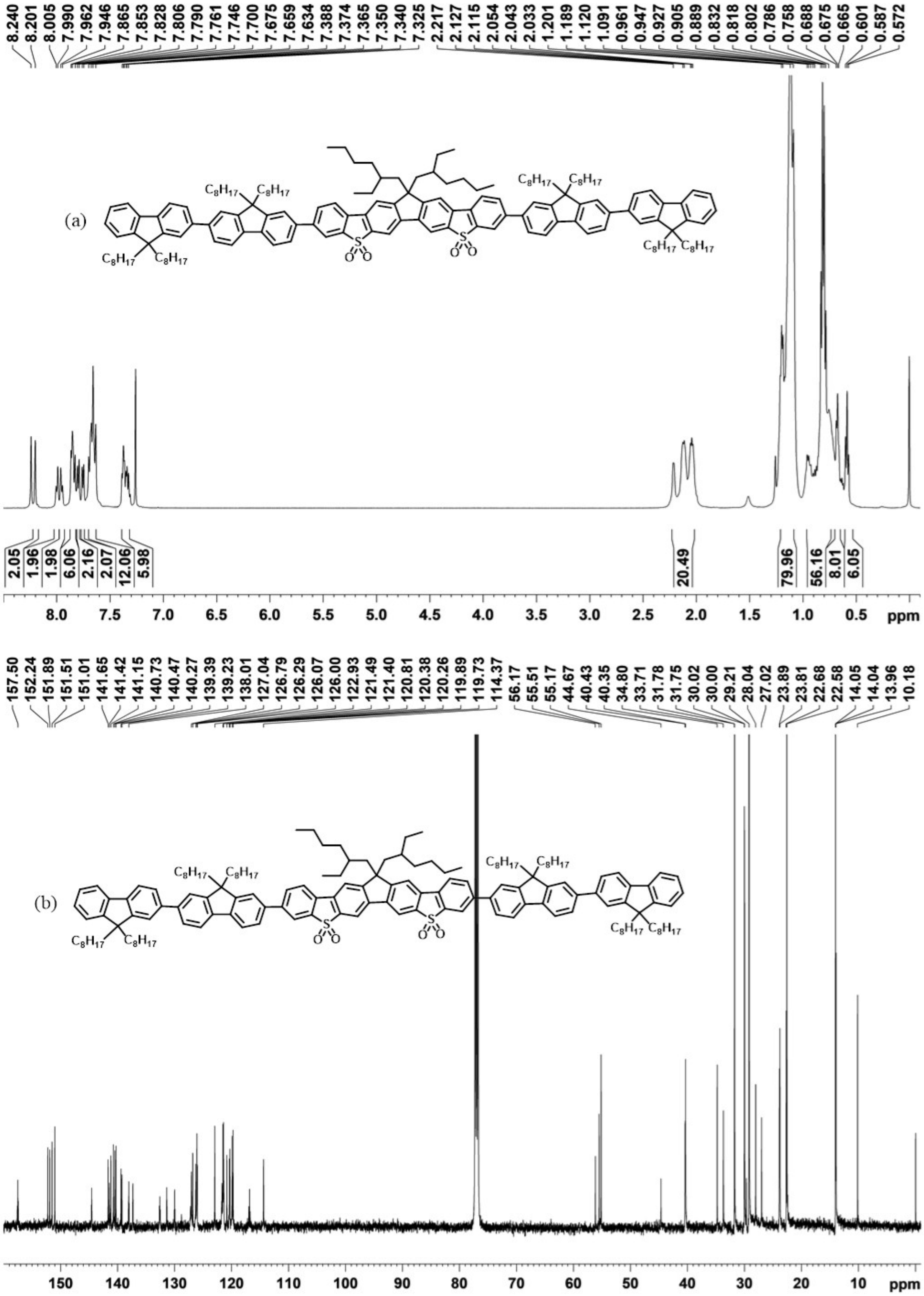

Figure S4. ^{1}H-NMR and ^{13}C-NMR spectra of compound FBTO-EHFF

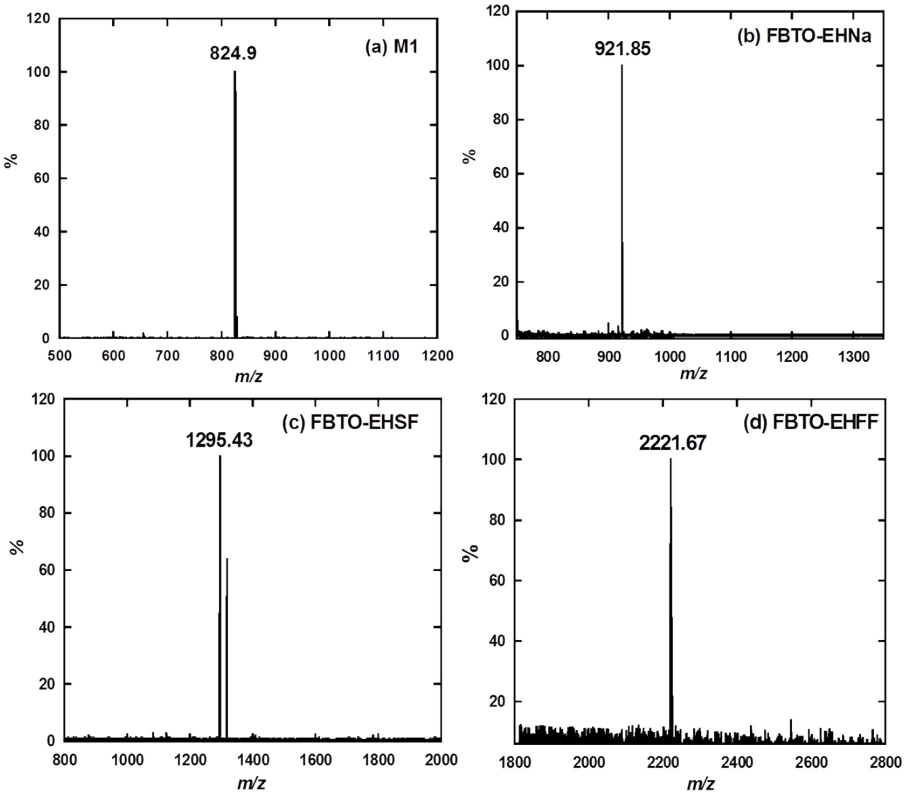

Figure S5. MALDI-TOF spectra of the compounds

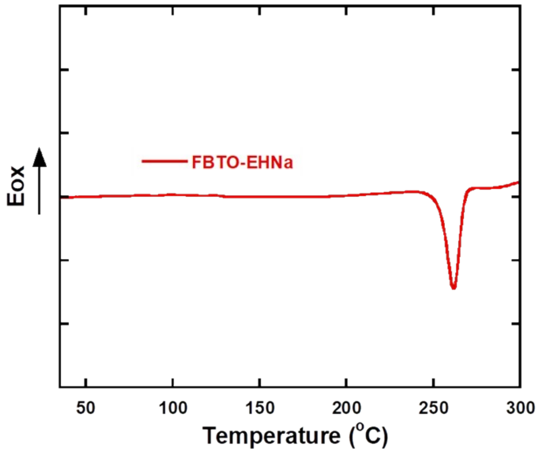

Figure S6. DSC curve of FBTO-EHNa

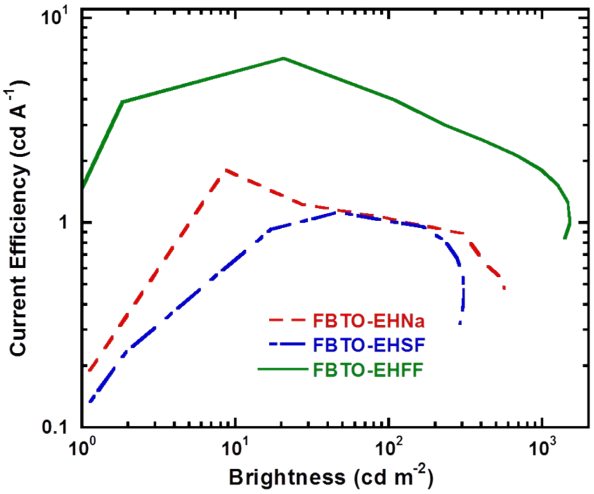

Figure S7. The efficiency-luminance curves for the FBTO-EHNa, FBTO-EHSF and FBTO-EHFF

Table S1. The data summary of absorption and PL spectra of FBTO-EHNa, FBTO-EHSF and FBTO-EHFF in different solvents

solvents	Δf(ε,n)	FBTO-EHNa				FBTO-EHSF				FBTO-EHFF			
		ϕ_{PL} (%)	UV	PL	Δv	ϕ_{PL} (%)	UV	PL	Δv	ϕ_{PL} (%)	UV	PL	Δv
Hexane	0.0012	52.4	371	418	3030.7	64.5	376	421	2842.8	90.5	388	436	2837.4
Toluene	0.014	65.5	372	420	3072.2	69.8	382	426	2703.8	93.7	392	445	3038.3
$CHCl_3$	0.147	59.0	373	421	3056.7	68.1	383	434	3068.2	89.4	394	463	3782.4
THF	0.21	59.7	375	426	3192.5	66.7	382	430	2922.2	79.8	393	486	4869.2
DCM	0.217	60.9	375	429	3356.6	66.0	383	436	3173.9	76.3	395	489	4866.6
DMF	0.276	61.2	377	433	3430.5	63.8	384	438	3210.6	62.1	397	495	4986.9