SUPPORTING INFORMATION

Synthesis and characterization of heteroatom-bridged bispirofluorenes for the application of organic light-emitting diodes

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Experimental Section

General Instrumentation

¹H and ³¹P NMR spectra were measured on a Bruker AVA-300 NMR spectrometer and the latter used H₃PO₄ (85% in H₂O) as the internal standard. ¹³C NMR spectra and DEPT spectra were recorded on a Bruker AV-500 NMR spectrometer. High resolution mass spectrometric measurements were obtained on JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan) from Mass Spectroscopic Laboratory in-house service of the Institute of Chemistry. Infrared absorption spectra were recorded on a PerkinElmer Spectrum 100 FT-IR Spectrometer. UV-visible electronic absorption spectra were recorded on a Hewlett-Packard 8453 Diode Array Spectrophotometer. Fluorescence spectra were obtained on Hitachi F-4500 fluorescence spectrophotometer with a scan rate of 1200 nm/min. The ionization potentials (or HOMO energy levels) of SP₂X series were determined by a low energy photo-electron spectrometer (Riken-Keiki AC-2). LUMO energy levels were estimated by subtracting the optical band-gap energy (ΔE) from HOMO energy levels. ΔE was determined by the on-set absorption energy from the absorption spectra of the materials as thin film. The differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere on a Perkin-Elmer DSC-7 differential scanning calorimeter, using a scan rate of 10 °C/min. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer DSC-7 thermogravimetric analyzer to determine the decomposition temperatures (T_d) of the compounds under nitrogen atmosphere, using a heating rate of 10 °C/min. To measure the triplet energy gap of a thin film sample, we established a system with a temperature control of Model 350 (LakeShore Company) as low as 10 K by Model 22C/350C Cryodyne Refrigerators (Janis Research Company) and a tunable laser with excitation wavelengths of 355,

532, and 1064 nm (Brilliant B laser, Quantel Company), which is coupled to a time-delay controller of a LP920 flash photolysis spectrometer (Edinburgh Instruments). Except SP₂N, the absorption wavelength of SP₂X series was too short to being excited by Brilliant B Laser. Hence, we measured the triplet energy gap of a frozen sample in 2-Me-THF by using Fluorolog III photoluminescence spectrometer which equipped a xenon lamp as excitation light source. Electrochemical potentials of the compounds were determined by cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) using a BAS 100B electrochemical analyzer with a scanning rate at 100 mV/s. For the scanning of redox potentials of SP₂X series, the studied compounds were dissolved in deoxygenated dry CH₂Cl₂ (for oxidation potential scans) or THF (for reduction potential scans) with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte. We used a platinum and carbon working electrode for oxidation and reduction electrochemical study, respectively. In both studies, a saturated nonaqueous Ag/AgNO₃ referenced electrode was used. Ferrocene was used for potential calibration (all reported potentials were referenced against Ag/Ag⁺) and for reversibility criteria.

Device fabrication and performance measurements

OLED devices were fabricated by thermal vacuum deposition. The substrate was an indium-tin-oxide (ITO) coated glass (Shin An SNP, Taiwan) with a sheet resistance of $\leq 30 \Omega/\text{sq}$. The pretreatment of ITO includes a routine chemical cleaning using detergent, deionized water, acetone and isopropyl alcohol in sequence, followed by oxygen plasma cleaning. The thermal evaporation of organic materials was carried out using CRYOTEC-10 at a chamber pressure of 10^{-6} Torr. The thickness of each layer was determined by quartz thickness monitor (STM-100/MF and STM-2XM). The cathode of LiF/Al was prepared first thermally deposited a LiF thin film (10 Å) followed by the deposition of Al metal (1000 Å) as the top layer. The thickness of each layer material was determined similarly as before. The devices were all encapsulated with glass slides, which were attached to the device by UV-cured epoxy glue. The effective size of the emitting diode was 4.00 mm^2 , which is significantly smaller than the active area of the photodiode detector. Current-voltage-luminance (*I-V-L*) measurements were made simultaneously using a Keithley 2400 source meter and a Newport 1835C optical meter equipped with a Newport 818-ST silicon photodiode, respectively. The measurements for devices were made at room temperature under ambient condition. The EL spectra of devices were measured using the fluorescence spectrophotometer by blocking the incident light.

Materials Preparation

All chemical and reagents were obtained from commercial suppliers and used without further purification. Solvents were purified according to the standard procedures. Unless specified condition, all reaction were performed under nitrogen atmosphere using standard Schlenk techniques. The compounds were readily purified by silica gel column chromatography. Further purification by gradient sublimation is necessary for materials prior to device fabrication.

For materials synthesis, the starting materials 2-bromo-9,9'-spirobifluorene (**1**)¹, 2-hydroxyl-9,9'-spirobifluorene (**4**)², and 4-trimethylsilyl-2'-bromobiphenyl (**7**)³ were synthesized according to reported literature. For the materials used in device fabrication, BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) was commercially available; NPB (4,4'-bis[*N*-(1-naohthyl)-*N*-phenylamino]-buphenyl),⁴ TPBI (2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole))⁵ and TCTA (tris(4-carbazoyl-9-ylphenyl)amine)⁶ were prepared via published methods.

2-Amino-9,9'-spirobifluorene, **2**

A mixture of **1** (4.0 g, 10.15 mmol), copper(I) oxide (0.73 g, 5.07 mmol), palladium(II) acetate (11.4 mg, 0.051 mmol) and *N*-methyl-2-pyrrolidone (0.4 mL) in Parr bomb reactor was cooled to -78 °C and then NH_{3(l)} (20 mL) condensed from NH_{3(g)} was added. The Parr bomb reactor was heated up to 130 °C and the internal pressure was over 800 psi. The reaction was completed after 24 hours. After the reactor cooling to room temperature, NH_{3(g)} was vented. The reaction residue was extracted with dichloromethane and ammonia water solution. The organic layer was collected and dried over magnesium sulfate. After removal of drying agent, the organic solution was evaporated till dryness under reduced pressure and a brown solid (3.30 g, 98%) was obtained. The solid product was pure enough and used in the following reaction without further purification. m.p. (°C): 234. FT-IR (λ , cm⁻¹): 3454, 3377, 3039, 1617, 1454, 1307, 1120, 821, 751, 735, 638. ¹H NMR (300 MHz, CDCl₃): δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.34 (td, *J* = 7.5 Hz, 0.9 Hz, 2H), 7.26 (td, *J* = 7.5 Hz, 0.9 Hz, 1H), 7.09 (td, *J* = 7.5 Hz, 0.9 Hz, 2H), 6.97 (td, *J* = 7.5 Hz, 0.9 Hz, 1H), 6.75 (d, *J* = 7.5 Hz, 2H), 6.68-6.62 (m, 2H), 6.01 (d, *J* = 0.9 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 150.54, 149.27, 147.80, 146.48, 142.28, 141.60, 132.73, 127.74, 127.54 (x2), 126.03, 124.15, 123.71, 120.77, 119.80, 118.61, 114.68, 110.49, 65.76. EI-HRMS: calcd 331.1361, *m/z* = 331.1370 (M⁺).

Figure S1. The ^1H NMR spectrum of compound **2** isolated from the reaction solution without further purification.

Bis(9,9'-spirobifluorene-2-yl)amine, **3**

To a mixture of **2** (3.0 g, 9.06 mmol), 2-bromo-9,9'-spirobifluorene (3.9 g, 9.96 mmol), cesium carbonate (3.54 g, 10.86 mmol), and palladium acetate (102 mg, 0.456 mmol) in toluene (90 mL) was added tri-*tert*-butylphosphine (0.44 mL, 1.80 mmol). The reaction solution was stirred at 110 °C for 36 hours. After the reaction cooling to room temperature, toluene was removed under reduced pressure. The residue solid was extracted with dichloromethane and water. The organic layer was collected and dried over magnesium sulfate. After removal of drying agent, the organic solution was evaporated till dryness under reduced pressure. The residue was purified by column chromatography (silica gel, 50% CH_2Cl_2 /hexanes) to afford a light yellow solid (2.0 g, 34%). m.p. (°C): 302. FT-IR (λ , cm^{-1}): 3389, 3039, 1602, 1518, 1447, 1310, 817, 752, 740, 725, 635. ^1H NMR (300 MHz, CD_3OD): δ 7.86 (d, J = 7.5 Hz, 4H), 7.72 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 8.1 Hz, 2H), 7.35 (t, J = 7.5 Hz, 4H), 7.28 (t, J = 7.5 Hz, 2H), 7.09 (t, J = 7.5 Hz, 4H), 7.02-6.94 (m, 4H), 6.62 (d, J = 7.5 Hz, 4H), 6.51 (d, J = 7.8 Hz, 2H), 6.16 (d, J = 2.1 Hz, 2H). ^{13}C NMR (125 MHz, CD_3Cl_3): δ 151.47, 150.28, 149.05, 144.54, 143.32, 142.71, 135.01, 128.48, 128.41, 128.36, 126.98, 124.86, 124.56, 121.33, 120.67, 119.67, 116.64, 113.72, 66.88. EI-HRMS: calcd 645.2456, m/z = 645.2475 (M^+).

9-(4-Trimethylsilyl-biphenyl-2'-yl)-9-fluorenol, **8**

To a dry THF solution (360 mL) of **7** (33.0 g, 108.10 mmol) was added *n*-BuLi (44.6 mL, 111.50 mmol, 2.5M in hexane) slowly at -78 °C. The mixture was stirred for 60 minutes under nitrogen atmosphere. After stirring for 60 minutes, a dry THF solution (150 mL) of 9-fluorenone (15.0 g, 83.25 mmol) was added dropwise at -78 °C. The reaction mixture was then stirred at room temperature for 18 hours. After the reaction quenched by adding water, the mixture was extracted with dichloromethane. After drying over magnesium sulfate, the separated organic layer was evaporated till dryness under reduced pressure. The residue was purified by column chromatography (silica gel, 50% CH₂Cl₂/hexanes) to afford a white solid (21.8 g, 65%). m.p. (°C): 77. FT-IR (λ , cm⁻¹): 3443, 3063, 2954, 1637, 1449, 1248, 1163, 1111, 1018, 915, 842, 751, 732, 663. ¹H NMR (300 MHz, CDCl₃): δ 8.60 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.39-7.25 (m, 4H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 7.8 Hz, 2H), 6.13 (d, *J* = 7.8 Hz, 2H), 0.38 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 150.54, 140.87, 140.59, 140.08, 139.66, 136.12, 130.97, 130.81, 128.47, 128.12, 127.77, 127.02, 126.79, 126.20, 124.28, 119.86, 82.34, -1.28. EI-HRMS: calcd 406.1753, *m/z* = 406.1752 (M⁺).

2-Iodo-9,9'-spirobifluorene, **5**

Stirring at 70 °C under nitrogen atmosphere, to a mixture of **8** (21.8 g, 53.64 mmol), *N*-chlorosuccinimide (7.9 g, 59.00 mmol) and sodium iodide (8.8 g, 59.00 mmol) in acetic acid (220 mL) was added 5 drops of concentrated HCl_(aq) dropwise. The reaction mixture was stirred for 18 hours. After the reaction quenched by adding water, it was cooled to room temperature and the resulting precipitate was collected by filtration. The obtained solid was dissolved in dichloromethane and dried over magnesium sulfate. After removal of drying agent, the organic solution was evaporated till dryness under reduced pressure. The residue was further purified by column chromatography (silica gel, 10% CH₂Cl₂/hexanes) to afford a white solid (19.8 g, 83%). m.p. (°C): 195. FT-IR (λ , cm⁻¹): 3063, 1643, 1446, 822, 749, 729, 636.

^1H NMR (300 MHz, CDCl_3): δ 7.83 (d, $J = 7.8$ Hz, 2H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.57 (d, $J = 8.1$ Hz, 1H), 7.40-7.31 (m, 3H), 7.11 (t, $J = 7.5$ Hz, 3H), 7.02 (s, 1H), 6.74-6.65 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 150.94, 148.45, 147.95, 141.76, 141.45, 140.72, 136.81, 133.10, 128.44, 127.98, 127.96, 127.89, 124.07, 124.03, 121.65, 120.12, 120.09, 92.84, 65.76. MALDI-HRMS: calcd 442.0219, $m/z = 442.0239$ (M^+).

Figure S2. The ^1H NMR spectrum of compound **5** isolated from the reaction solution before purification by column chromatography.

***N,N*-Bis(9,9'-spirobifluorene-2-yl)phenylamine, **6a** (**SP₂N**)**

A mixture of **3** (0.27 g, 0.42 mmol), iodobenzene (0.2 mL, 1.68 mmol), potassium carbonate (0.23 g, 1.68 mmol), and copper (11 mg, 0.17 mmol) in 1,2-dichlorobenzene (4.2 mL) was stirred at 180 °C for 18 hours. After cooling to room temperature, the reaction solution was first filtered through a pad of celite and then 1,2-dichlorobenzene was removed under reduced pressure. The residue was extracted with dichloromethane and water. The organic layer was collected and dried over magnesium sulfate. After removal of drying agent, the organic solution was evaporated till dryness under reduced pressure. The residue was purified by column chromatography (silica gel, 30% CH_2Cl_2 /hexanes) to afford **SP₂N** as a light yellow solid (0.24 g, 80%). m.p. (°C): 346. FT-IR (λ , cm^{-1}): 3061, 1598, 1489, 1447, 1292, 1024, 824, 750, 727, 695. ^1H NMR (300 MHz, CDCl_3): δ 7.73-7.62 (m, 6H), 7.55 (d,

$J = 7.5$ Hz, 2H), 7.35-7.20 (m, 7H), 7.06 (t, $J = 7.8$ Hz, 4H), 7.04-6.96 (m, 2H), 6.94-6.78 (m, 4H), 6.78-6.64 (m, 6H), 6.59 (d, $J = 7.2$ Hz, 2H), 6.42 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 149.93 (C), 148.90 (C), 148.67 (C), 147.44 (C), 147.24 (C), 141.61 (C), 141.35 (C), 136.88 (C), 128.68 (CH), 127.70 (CH), 127.57 (CH, CH), 126.96 (CH), 124.06 (CH), 123.85 (CH), 123.78 (CH), 122.65 (CH), 121.96 (CH), 120.46 (CH), 120.16 (CH), 119.91 (CH), 119.33 (CH), 65.89 (C). MALDI -HRMS: calcd 721.2769, $m/z = 721.2788$ (M^+).

Figure S3. ^1H -NMR spectrum (CDCl_3) of SP_2N .

Figure S4. ^{13}C -NMR spectrum (CDCl_3) of SP_2N .

Figure S5. DEPT spectra of **SP₂N**.

Figure S6. MALDI-HR Mass spectrum of **SP₂N**.

Bis(9,9'-spirobifluorene-2-yl)diphenylsilane, 6b (SP₂Si)

To a dry THF solution (150 mL) of **1** (2.0 g, 5.08 mmol) was added *n*-BuLi (2.14 mL, 5.35 mmol, 2.5 M in hexane) slowly at -78 °C. The mixture was stirred for 60 minutes under nitrogen atmosphere. Dichlorodiphenylsilane (0.49 mL, 2.31 mmol) was added dropwise at -78 °C and the mixture was stirred at room temperature for 12 hours. After the reaction quenched by adding water, the mixture was extracted with dichloromethane. The organic layer was collected and dried over magnesium sulfate. After removal of drying agent, the organic solution was evaporated till dryness under reduced pressure. The residue was purified by column chromatography (silica gel, 20% CH₂Cl₂/hexanes) to afford **SP₂Si** as a white solid (0.19 g, 10%). m.p. (°C): 283.

FT-IR (λ , cm^{-1}): 3064, 1601, 1446, 1428, 1105, 831, 750, 729, 700. ^1H NMR (300 MHz, CDCl_3): δ (ppm): 7.79 (d, $J = 7.5$ Hz, 2H), 7.73 (d, $J = 7.5$ Hz, 4H), 7.67 (d, $J = 7.5$ Hz, 2H), 7.37-7.25 (m, 8H), 7.23-7.13 (m, 6H), 7.12-7.01 (m, 10H), 6.93 (s, 2H), 6.69 (dd, $J = 7.8$ Hz, 0.9 Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 149.31 (C), 148.60 (C), 148.04 (C), 143.23 (C), 141.73 (C), 141.40 (C), 136.03 (CH, CH), 134.12 (C), 133.43 (C), 131.09 (CH), 129.23 (CH), 128.19 (CH), 127.62 (CH, CH), 127.53 (CH, CH), 124.02 (CH), 123.82 (CH), 120.24 (CH), 119.97 (CH), 119.44 (CH), 66.00 (C). MALDI-HRMS: calcd 835.2797, $m/z = 835.2824$ ($\text{M} + \text{Na}^+$).

Figure S7. ^1H -NMR spectrum (CDCl_3) of SP_2Si .

Figure S8. ^{13}C -NMR spectrum (CDCl_3) of SP_2Si .

Figure S9. DEPT spectra of **SP₂Si**.

Figure S10. MALDI–HR Mass spectrum of **SP₂Si**.

Bis(9,9'-spirobifluorene-2-yl)phenylphosphinoxide, 6c (SP₂PO)

To a dry THF solution (8.5 mL) of **1** (1.0 g, 2.54 mmol) was added *n*-BuLi (1.22 mL, 3.05 mmol, 2.5M in hexane) slowly at -78 °C. The mixture was stirred for 60

Chemical structure of the cation: c1ccc(cc1)[P+](c2ccccc2)(c3ccccc3)c4ccccc4

¹H NMR spectrum (CDCl₃) showing peaks from 0 to 8 ppm. Integration values are provided below the baseline and above the peaks. A list of peak chemical shifts is shown at the top.

Chemical shifts (ppm): 7.831, 7.806, 7.754, 7.729, 7.7372, 7.7348, 7.7323, 7.7298, 7.7272, 7.7258, 7.7253, 7.7226, 7.7188, 7.7155, 7.7130, 7.7107, 7.7061, 7.036, 7.011, 7.155, 7.188, 7.130, 7.107, 7.061, 7.036, 7.011, 6.715, 6.690, 6.631, 6.606, 6.581, 6.606.

Integration values (from left to right): 2.222, 6.182, 19.782, 2.380, 4.252, 2.188, 4.000, 2.188, 4.000.

Acquisition parameters:

- NAME: CLW-SP2P-sub1
- EXPNO: 1
- PROCNO: 1
- Date_: 20120319
- Time: 14.58
- INSTRUM: spect
- PROBHD: 5 mm QNP 1H/13
- PULPROG: zg30
- TD: 16384
- CDCl3: 16
- NS: 0
- DS: 0
- SWH: 4807.692 Hz
- FIDRES: 0.293438 Hz
- AQ: 1.7038950 sec
- RG: 1440
- DW: 104.000 usec
- DE: 6.50 usec
- TE: 300.0 K
- D1: 2.00000000 sec
- TDO: 1

Channel f1 parameters:

- NUC1: 1H
- P1: 9.10 usec
- PL: -4.00 dB
- PL1W: 26.37401772 W
- SFO1: 300.1319508 MHz
- SI: 0162
- SF: 300.1300128 MHz
- WVN: no
- SSB: 0
- LB: 0.00 Hz
- GB: 0
- PC: 1.00

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Figure S12. ^{13}C -NMR spectrum (CDCl₃) of SP_2PO .

Figure S13. DEPT spectra of SP_2PO .

Figure S14. ³¹P-NMR spectrum (CDCl₃) of SP₂PO.

Figure S15. MALDI-HR Mass spectrum of SP₂PO.

Bis(9,9'-spirobifluorene-2-yl)ether, 6d (SP₂O)

To a mixture of **4** (1.0 g, 3.01 mmol), copper(I) oxide (43 mg, 0.30 mmol), **5** (2.7 g, 6.10 mmol), cesium carbonate (2.9 g, 9.03 mmol), and salicyldoxime (82 mg, 0.60 mmol) in sulfolane (5 mL) was added dry 4 Å molecular sieve (1 g). The reaction mixture was stirred at 140 °C for 3 days. The temperature was raised to 180 °C for

next 18 hours. After cooling to room temperature, the reaction solution was poured into water and the resulting precipitate was collected by filtration. The obtained solid was extracted with dichloromethane and water. The organic layer was dried over magnesium sulfate. After removal of drying agent, the organic solution was evaporated till dryness under reduced pressure. The residue was purified by column chromatography (silica gel, 20% CH₂Cl₂/hexanes) to afford the **SP₂O** as a white solid (1.2 g, 62%). m.p. (°C): 255. FT-IR (λ , cm⁻¹): 3054, 1603, 1581, 1447, 1261, 1200, 878, 751, 739. ¹H NMR (300 MHz, CDCl₃): δ 7.77 (d, *J* = 7.5 Hz, 4H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.36-7.26 (m, 6H), 7.10-6.98 (m, 6H), 6.79 (dd, *J* = 8.1 Hz, 2.4 Hz, 2H), 6.68 (d, *J* = 7.5 Hz, 4H), 6.64 (d, *J* = 7.5 Hz, 2H), 6.32 (d, *J* = 7.5 Hz, 2.1 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 157.00 (C), 150.80 (C), 148.75 (C), 148.47 (C), 141.64 (C), 141.15 (C), 137.04 (C), 127.82 (CH), 127.72 (CH), 127.68 (CH), 127.17 (CH), 123.97 (CH), 123.90 (CH), 120.67 (CH), 119.93 (CH), 119.45 (CH), 117.70 (CH), 114.98 (CH), 65.87 (C). MALDI-HRMS: calcd 646.2297, *m/z* = 646.2314 (M⁺).

Figure S16. ¹H-NMR spectrum (CDCl₃) of **SP₂O**.

Figure S17. ^{13}C -NMR spectrum (CDCl₃) of SP_2O .

Figure S18. DEPT spectra of SP_2O .

Figure S19. MALDI–HR Mass spectrum of **SP₂O**.

Bis(9,9'-spirobifluorene-2-yl)-sulfone, 6e (SP₂SO₂)

To a mixture of **5** (8.0 g, 18.08 mmol), copper(I) iodine (0.16 g, 0.83 mmol), potassium *tert*-butoxide (0.23 g, 16.50 mmol), cesium carbonate (10.8 g, 33.0 mmol) and salicylaldoxime (0.23 g, 1.68 mmol) in sulfolane (40 mL) was carefully added thioacetamide (0.62 g, 8.25 mmol). The reaction mixture was stirred at 140 °C for 24 hours. For the following 48 hours reaction, another batch of thioacetamide (0.31 g, 4.13 mmol) was added. After cooling to room temperature, the reaction solution was poured into water and the resulting precipitate was collected by filtration. The obtained solid was extracted with dichloromethane and water. The organic layer was dried over magnesium sulfate. After removal of drying agent, the organic solution was evaporated till dryness under reduced pressure. The residue was purified by column chromatography (silica gel, 20% CH₂Cl₂/hexanes) to afford the diarylsulfide intermediate (3.1 g, 52%) as a white solid. The intermediate was dissolved in dichloromethane (100 mL) and treated with hydrogen peroxide (20 mL, 30 wt% aqueous solution). The reaction mixture was stirred for the next 24 hours at room temperature. The separated organic layer was dried over magnesium sulfate. After removal of drying agent, the organic solution was evaporated till dryness under reduced pressure. The residue was purified by column chromatography (silica gel, 50% CH₂Cl₂/hexanes) to afford **SP₂SO₂** as a white solid (2.5 g, 77%). m.p. (°C): 289. FT-IR (λ , cm⁻¹): 3061, 1599, 1446, 1409, 1320, 1141, 1073, 803, 753, 728, 689, 607.

^1H NMR (300 MHz, CDCl_3): δ 7.86-7.72 (m, 8H), 7.62 (dd, $J = 8.1$ Hz, 1.5 Hz, 2H), 7.40-7.30 (m, 6H), 7.26 (d, $J = 1.5$ Hz, 2H), 7.14 (t, $J = 7.5$ Hz, 2H), 7.05 (t, $J = 7.5$ Hz, 4H), 6.70 (d, $J = 7.5$ Hz, 2H), 6.55 (d, $J = 7.5$ Hz, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 150.13 (C), 149.87 (C), 147.00 (C), 146.60 (C), 141.89 (C), 140.50 (C), 139.50 (C), 129.53 (CH), 128.14 (CH), 128.01 (CH), 127.94 (CH), 127.90 (CH), 124.24 (CH), 123.74 (CH), 123.22 (CH), 120.92 (CH), 120.47 (CH), 120.28 (CH), 65.93 (C). MALDI-HRMS: calcd 717.1864, $m/z = 717.1883$ ($\text{M} + \text{Na}^+$).

Figure S20. ^1H -NMR spectrum (CDCl_3) of SP_2SO_2 .

Figure S21. ^{13}C -NMR spectrum (CDCl_3) of SP_2SO_2 .

Figure S22. DEPT spectra of SP_2SO_2 .

Figure S23. MALDI-HR Mass spectrum of SP_2SO_2 .

The absorption (UV) and photoluminescence (PL) spectra of SP_2X series in dichloromethane and 2-Me-THF.

Figure S24. The absorption (UV) and photoluminescence (PL) spectra of SP and SP₂X series.

Electrochemical voltammogram of SP and SP₂X series

Figure S25. Cyclic and differential pulsed voltammograms of ferrocene, SP and SP₂X series.

Thermal properties of SP₂X series

Figure S26. DSC thermograms of SP and SP_2X series.

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