### Supplementary Information

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<u>S 1</u> Structures 4-substituted 9,9'-SpiroBiFluorene (4-SBF): 4 Phenyl substituted SBF (**4-Ph-SBF**), 2pyridine substituted 4-SBF (**4-2Py-SBF**), 3-pyridine substituted 4-SBF (**4-3Py-SBF**), 4-pyridine substituted 4-SBF (**4-4Py-SBF**), and 4-pyridine-2-substituted SBF (**2-4Py-SBF**) investigated in this work

#### MATHERIALS AND METHODS

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique. Commercially available reagents and solvents were used without further purification other than those detailed below. THF was distilled from sodium/benzophenone prior to use. Light petroleum refers to the fraction with bp 40-60°C. 2.5M solutions of n-BuLi in hexanes or THF were purchased from Sigma Aldrich. 2,2'-dibromobiphenyl was purchased from Fluorochem. Reactions were stirred magnetically, unless otherwise indicated. Analytical thin layer chromatography was carried out using aluminum backed plates coated with Merck Kieselgel 60 GF254 and visualized under UV light (at 254 and 360 nm). Chromatography was carried out using Teledyne Isco CombiFlash® Rf 400 (UV detection 200-360nm), over standard silica cartridges (Redisep® Isco, GraceResolv<sup>™</sup> Grace or Puriflash® columns Interchim). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Bruker 300 MHz instruments (<sup>1</sup>H frequency, corresponding <sup>13</sup>C frequency: 75 MHz); chemical shifts were recorded in ppm and J values in Hz. In the <sup>13</sup>C NMR spectra, signals corresponding to C, CH, CH<sub>2</sub> or Me groups, assigned from DEPT, are noted. The residual signals for the NMR solvents are: CDCl<sub>3</sub>; 7.26 ppm for the proton and 77.00 ppm for the carbon,  $CD_2Cl_2$ ; 5.32 ppm for the proton and 53.80 ppm for the carbon. The following abbreviations have been used for the NMR assignment: s for singlet, d for doublet, t for triplet and m for multiplet. High resolution mass spectra were recorded at the Centre Régional de Mesures Physiques de l'Ouest (Rennes) on (i) Bruker MicrO-Tof-Q II (Source: Atmospheric Pressure Chemical Ionization (APCI - direct introduction) (ASAP-Atmospheric Solids Analysis Probe) at a temperature of 30°C - positive mode) or on (ii) Waters Q-Tof II.

#### <u>X-Ray :</u>

Crystal was picked up with a cryoloop and then frozen at 150 K under a stream of dry N<sub>2</sub> on a APEX II Brucker AXS diffractometer for X-ray data collection (Mo Ka radiation,  $\lambda = 0.71073$  Å). **4-Ph-SBF** structure was published previouly.<sup>18</sup>

**4-4Py-SBF** (C<sub>30</sub>H<sub>19</sub>N)); M = 393.46. APEXII, Bruker-AXS diffractometer, Mo-Ka radiation ( $\lambda$  = 0.71073 Å), T = 150(2) K; monoclinic, P2<sub>1</sub>/c, a = 9.9614(3), b = 9.8012(3), c = 20.6471(7) Å, a = 90°,  $\beta$  = 97.0710(10)°,  $\gamma$  = 90°, V = 2000.52(11) Å<sup>3</sup>.Z = 4, d = 1.306 g.cm<sup>-3</sup>,  $\mu$  = 0.075 mm<sup>-1</sup>. The structure was solved by direct methods using the SIR97 program,<sup>52</sup> and then refined with full-matrix least-square methods based on F<sup>2</sup> (SHELXL-97)<sup>53</sup> with the aid of the WINGX<sup>54</sup> program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F<sup>2</sup> with 4588 unique intensities and 280 parameters converged at  $\omega$ R(F<sup>2</sup>) = 0.1004 (R(F) = 0.0417) for 3805 observed reflections with I > 2 $\sigma$ (I).

**2-4Py-SBF** 2(C<sub>30</sub>H<sub>19</sub>N)); M =786.92. APEXII, Bruker-AXS diffractometer, Mo-Ka radiation ( $\lambda$  = 0.71073 Å), T = 150(2) K; monoclinic, P2<sub>1</sub>/c, a = 10.7952(3), b = 9.3404(2), c = 40.8653(11) Å, a = 90°,  $\beta$  = 94.0020(10)°,  $\gamma$  = 90°, V = 4110.46(18) Å<sup>3</sup>.Z = 4, d = 1.272 g.cm<sup>-3</sup>,  $\mu$  = 0.073 mm<sup>-1</sup>. The structure was solved by direct methods using the SIR97 program,<sup>52</sup> and then refined with full-matrix

least-square methods based on F<sup>2</sup> (SHELXL-97)<sup>53</sup> with the aid of the WINGX<sup>54</sup> program. All nonhydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F<sup>2</sup> with 9403unique intensities and 559 parameters converged at  $\omega R(F^2) = 0.11$  (R(F) = 0.04453) for 7254 observed reflections with I >  $2\sigma(I)$ .

The figures were generated with Mercury software 3.3.

#### **Spectroscopic studies:**

Cyclohexane (analytical grade, VWR) was used without further purification. Standard 1N solution of sulfuric acid was purchased from Alfa Aesar. UV-visible spectra were recorded using an UV-Visible spectrophotometer SHIMADZU UV-1605. The energy gap was calculated from the absorption edge of the UV-vis absorption spectra in solution in cyclohexane, using the formula  $\Delta E^{opt}$  (eV) = hc/ $\lambda$ ,  $\lambda$  being the absorption edge (in meter). With h =  $6.6 \times 10^{-34}$  J.s ( $1eV = 1.6 \times 10^{-19}$  J) and c =  $3.0 \times 10^8$  m.s<sup>-1</sup>, this equation may be simplified as:  $\Delta E^{opt}$  (eV) =  $1237.5/\lambda$  (in nm). Triplet energy level E<sub>T</sub> was calculated from the maximum of the first phosphorescence emission peak, and conversion in electron volt was obtained with the previous formula. Emission spectra were recorded with a PTI spectrofluorimeter (PTI-814 PDS, MD 5020, LPS 220B) using a xenon lamp. Quantum yields in solution ( $\emptyset_{sol}$ ) were calculated relative to quinine sulfate ( $\emptyset_{sol} = 0.546$  in H<sub>2</sub>SO<sub>4</sub> 1N).  $\emptyset_{sol}$  was determined according to the following equation,

where, subscripts s and r refer respectively to the sample and reference. The integrated area of the emission peak in arbitrary units is given as T, n is the refracting index of the solvent ( $n_s = 1.426$  for cyclohexane) and A is the absorbance. Three solutions of different concentration of the substrate (A<0.1) and 3 solutions of the reference (quinine sulfate) were prepared. The quinine sulfate concentration was chosen so as the absorption of the reference and the substrate were the same at the excitation wavelength. 3 quantum yields were then calculated at this wavelength and the average value is reported. IR spectra were recorded on a Bruker Vertex 70 using a diamond crystal MIRacle ATR (Pike). Thin films were prepared by spin-coating ca 300 µL of a THF solution (10 mg/mL) on a sapphire plate (10 mm x 10 mm) at 2500 tr/min on a Süss MicroTech Labspin 6.

Fluorescence intensity decays were obtained by the time-correlated single-photon counting (TCSPC) method with femtosecond laser excitation using a set-up composed of a Titanium Sapphire laser (Tsunami, Spectra-Physics) pumped by a doubled Nd:YVO<sub>4</sub> laser (Millennia, Spectra-Physics), pumped itself by two laser diode arrays. Light pulses at 900 nm were selected by acousto-optic crystals at a repetition rate of 4 MHz, and the third harmonics at 300 nm was obtained through non-linear crystals. Fluorescence photons were detected at 90° through a monochromator by means of a Hamamatsu MCP R3809U photomultiplier, connected to a SPC-630 TCSPC module from Becker & Hickl. The instrumental response function was recorded before each decay measurement. The fluorescence data were analyzed by a nonlinear least-squares global method using the Globals software package

developed at the Laboratory for Fluorescence Dynamics at the University of Illinois at Urbana-Champaign, which includes reconvolution analysis and non-linear least-squares minimization method.

**Electrochemical studies.** Electrochemical experiments were performed under argon atmosphere using a Pt disk electrode (diameter 1 mm), the counter electrode was a vitreous carbon rod and the reference electrode was a silver wire in a 0.1M AgNO<sub>3</sub> solution in CH<sub>3</sub>CN. Ferrocene was added to the electrolyte solution at the end of a series of experiments. The ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple served as internal standard. The three electrodes cell was connected to a PAR Model 273 potentiostat/galvanostat (PAR, EG&G, USA) monitored with the ECHEM Software. Activated Al<sub>2</sub>O<sub>3</sub> was added in the electrolytic solution to remove excess moisture. For a further comparison of the electrochemical and optical properties, all potentials are referred to the SCE electrode that was calibrated at -0.405 V vs. Fc/Fc<sup>+</sup> system. Following the work of Jenekhe,<sup>37</sup> we estimated the electron affinity (EA) or lowest unoccupied molecular orbital (LUMO) and the ionisation potential (IP) or highest occupied molecular orbital (HOMO) from the redox data. The LUMO level was calculated from: LUMO (eV) =  $-[E_{onset}^{red}$  (vs SCE) +4.4] and the HOMO level from: HOMO (eV) =  $-[E_{onset}^{ox}$  (vs SCE) + 4.4], based on an SCE energy level of 4.4 eV relative to the vacuum. The electrochemical gap was calculated from:  $\Delta E^{el} = |HOMO-LUMO|$  (in eV).

**Theoretical modeling.** Full geometry optimization with Density Functional Theory (DFT)<sup>55,56</sup> and Time-Dependent Density Functional Theory (TD-DFT) calculations were performed with the hybrid Becke-3 parameter exchange<sup>57-59</sup> functional and the Lee-Yang-Parr non-local correlation functional<sup>60</sup> (B3LYP) implemented in the Gaussian 09 (Revision B.01) program suite<sup>61</sup> using the 6-311G+(d,p) basis set and the default convergence criterion implemented in the program. The figures were generated with GaussView 5.0. S<sub>0</sub> to T<sub>1</sub> energy transition (E<sub>T</sub>) was calculated from the difference between the total energy of the molecule in its respective singlet and triplet state.

#### **Thermal analysis:**

Thermal Gravimetric Analysis (TGA) was carried out by using TA SDT Q600 instrument, at the Ecole Nationale Superieure de Chimie de Rennes or at the "Institut des Sciences Analytiques" (UMR CNRS 5280) of Villeurbanne. TGA curves were measured at 10°C/min from 0 to 600°C under nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out by using NETZSCH DSC 200 F3 instrument equipped with an intracooler. DSC traces were measured at 10°C/min. 2 heating/cooling cycles were successively carried out and the glass transition was determined from the 2<sup>nd</sup> heating cycle.

#### **Device fabrication and characterization:**

OLEDs based on a multilayer structure have been fabricated onto patterned ITO coated glass substrates from XinYan Tech (thickness: 100 nm and sheet resistance: less of 20 W/m). The organic materials (from Aldrich and Lumtec) are deposited onto the ITO anode by sublimation under high vacuum (<  $10^{.6}$  Torr) at a rate of 0.2 – 0.3 nm/s. The structure of the device is the following: ITO/CuPc(10 nm)/NPB (40 nm)/TCTA (10 nm)/Hosts:dopant (20 nm)/TPBi (40 nm)/LiF (1.2 nm)/Al (100 nm). In this device, ITO is used as the anode, CuPc (copper phtalocyanine) is the hole injecting layer, NPB (N,N'-di(1-naphtyl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine) is the hole-transporting layer, TCTA (4,4',4"-Tris(carbazol-9-yl)-triphenylamine) is the electron/exciton blocking layer, TPBI (1,3,5-Tris(1-phenyl-1H-benzimidazol-2-yl)benzene) is both the electron transporting layer and the hole blocking layer and a thin film of lithium fluoride covered with aluminum is the cathode. The entire device is fabricated in the same run without breaking the vacuum. In this study, the thicknesses of the different organic layers were kept constant for all the devices. The active area of the devices defined by the overlap of the ITO anode and the metallic cathode was 0.3 cm<sup>2</sup>. The current-voltage-luminance (I-V-L) characteristics of the devices were measured with a regulated power supply (Laboratory Power Supply EA-PS 3032-10B) combined with a multimeter and a 1 cm<sup>2</sup> area silicon calibrated photodiode (Hamamatsu). The spectral emission was recorded with a SpectraScan PR650 spectrophotometer. All the measurements were performed at room temperature and at ambient atmosphere with no further encapsulation of devices.

#### SYNTHESIS



Ethyl 2'-bromo-[1,1'-biphenyl]-2-carboxylate (1)

1-bromo-2-iodobenzene (2.01 g, 7.12 mmol), (2-(ethoxycarbonyl)phenyl)boronic acid (1.78 g, 9.16 mmol, 1.29 eq), K<sub>2</sub>CO<sub>3</sub> (4.83 g, 34.95 mmol, 4.91 eq) and Pd(dppf)Cl<sub>2</sub><sup>1</sup> (0.17 g, 0.21 mmol, 0.03 eq) were dissolved in dry toluene (20 mL). The mixture was warmed to 100°C and stirred overnight. After cooling to room temperature, water (50 mL) was added, and organic layer was extracted three times with dichloromethane (3x30 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (light petroleum/ethyl acetate 95/5) to afford a colorless oil (1.41 g, 4.63 mmol), [column conditions: Silica cartridge 24 g (Serlabo); solid deposit on Celite®;  $\lambda_{detection}$ : (254 nm, 280 nm); ethylacetate in light . <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.04 (ddd, J = 7.7, 1.5, 0.5 Hz, 1H, ArH), 7.66 – 7.57 (m, 2H, ArH), 7.50 (td, J = 7.6, 1.4 Hz, 1H, ArH), 7.41 – 7.34 (m, 1H, ArH), 7.30 – 7.21 (m, 3H, ArH), 4.15 – 4.04 (m, 2H, CH<sub>2</sub>), 1.04 (t, J = 7.1 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  167.2 (C=O), 143.5 (C), 142.5 (C), 132.5 (CH), 132.2 (CH), 131.5 (CH), 131.2 (C), 130.8 (CH), 130.6 (CH), 129.1 (CH), 128.4 (CH), 127.5 (CH), 123.5 (C), 61.3 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>). HRMS calculated for C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>BrNa: 326.9996, found 326.9995 [M+Na]<sup>+</sup>.



4-bromo-9H-fluoren-9-one (2)

Ethyl 2'-bromo-[1,1'-biphenyl]-2-carboxylate (1.02 g, 3.33 mmol) was dissolved in methanesulfonic acid (10 mL). The mixture was warmed to 100°C, for two hours. The hot mixture was poured in cold water (100 mL) and crude product was extracted with dichloromethane (3x30 mL). The combined organic extracts were dried over magnesium sulfate; filtered, and concentrated under reduced pressure. The residue was purified by recrystallisation in ethanol to afford a yellow solid (0.86 g, 3.31 mmol). Yield: 99%. mp (ethanol):  $125-126^{\circ}C.^{51}$  <sup>1</sup>H NMR (300 MHz,  $CD_2Cl_2$ )  $\delta$ : 8.40 (dt, J = 7.7, 0.8 Hz, 1H, ArH), 7.71 (ddd, J = 7.3, 1.3, 0.7 Hz, 1H, ArH), 7.69 – 7.57 (m, 3H, ArH), 7.41 (td, J = 7.5, 0.9 Hz, 1H), 7.21 (dd, J = 8.0, 7.3 Hz, 1H, ArH); <sup>13</sup>C NMR (75 MHz,  $CD_2Cl_2$ )  $\delta$ : 192.6 (C), 144.2 (C),

<sup>&</sup>lt;sup>1</sup> Pd(dppf)Cl<sub>2</sub> : [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride complex with dichloromethane

142.8 (C), 139.9 (CH), 137.2 (C), 135.2 (CH), 134.6 (C), 130.7 (CH), 130.1 (CH), 124.7 (CH), 124.0 (CH), 123.4 (CH), 118.0 (C). HRMS calculated for C<sub>13</sub>H<sub>8</sub>OBr 258.9758, found 258.9758 [M+H]<sup>+</sup>.



#### 4-bromo-9,9'-spirobi[fluorene] (4-Br-SBF)

2-bromo-1,1'-biphenyl (0.78 g, 3.34 mmol) was dissolved in dry THF (30 mL) under argon atmosphere, cooled to -78°C and stirred during 10 minutes at this temperature. A 2.5M n-BuLi solution in THF (1.47 mL, 3.67 mmol, 1.10 eq) was then slowly injected via a syringe, at -78°C. The resulting yellow mixture was stirred at the same temperature for one hour. 4-bromo-9H-fluoren-9-one **(2)** (1.00 g, 3.86 mmol, 1.15 eq) in solution in dry THF (35 mL) was then added dropwise, the mixture was stirred for another 30 min at -78°C, and allows warming up to room temperature gradually overnight. Saturated brine solution (10 mL) was added, and the mixture was extracted twice with dichloromethane (2x30 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure.

Without other purification, the crude was dissolved into a mixture of acetic acid/hydrochloric acid (50 mL/5 mL) and warmed at 70°C during 2 h under stirring. Then, the mixture was poured into water/ice (200 mL), and the solution was neutralized with solid sodium hydroxide until pH reach 7. Then, the organic layer was extracted three times with dichloromethane (3x50 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (light petroleum) to afford a colorless solid (2.84 g, 7.19 mmol). [column conditions: Silica cartridge 24 g (Serlabo); solid deposit on Celite®; detection : (254 and 280 nm); light petroleum at 18 mL/min; collected fraction: 15-35 min]. Yield: 75%. spectroscopic characterization and purity is in agreement with the literature.<sup>19, 41</sup>



#### 2-(9,9'-spirobi[fluoren]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3)

4-bromo-9,9'-spirobi[fluorene] (0.50 g, 1.26 mmol) was dissolved in dry THF (15 mL) under Argon. A 2.5M THF solution of n-BuLi (0.61 mL, 1.52 mmol, 1.2 eq) was added dropwise into the solution at - 78°C via syringe. The resulting pink mixture was stirred at the same temperature for 1 h, and then 2isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.35 mL, 1.71 mmol, 1.35 eq) was added in one portion. The resulting mixture was stirred for another 30 min at -78°C, and allowed warming to room temperature gradually and stirred overnight. Saturated brine solution (10 mL) was added, and the mixture was extracted three times with dichloromethane (3x30 mL). The combined organic layer were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (light petroleum/dichloromethane, 75/25) to afford a colorless solid (0.41 g, 0.93 mmol). Yield: 74 %. mp: 223°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.79 (d, J= 7.8 Hz, 1H, ArH), 7.85-7.81 (m, 3H, ArH), 7.39-7.33 (m, 3H, ArH), 7.12-7.06 (m, 4H, ArH), 6.79-6.77(dd, J= 7.5, 1.5 Hz, 1H, ArH), 6.74-6.69 (m, 3H, ArH), 1.52 (s, 12H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 149.7 (C), 149.6 (C), 149.4 (C), 147.0 (C), 143.5 (C), 142.4 (C), 136.4 (CH), 128.4 (2xCH, observed from DEPT), 128.3 (CH), 128.1 (CH), 127.20 (CH), 126.9 (CH), 124.8 (CH), 124.3 (CH), 124.0 (CH), 120.7 (CH), 84.8 (C-B), 66.2 (C spiro), 25.4 (CH<sub>3</sub>). HRMS calculated for C<sub>31</sub>H<sub>28</sub>O<sub>2</sub>B: 443.2182, found: 443.2179 [M+H]<sup>+</sup>. IR (ATR, cm<sup>-1</sup>): v = 555, 577, 625, 636, 648, 669, 683, 727, 758, 787, 806, 837, 858, 958, 983, 1005, 1032, 1072, 1090, 1124, 1141, 1209, 1232, 1271, 1286, 1311, 1346, 1378, 1412, 1446, 1479, 1589, 2931, 2978, 3039, 3057.

# General procedure for Suzuki coupling from 4-Br-SBF and 2-Br-SBF: synthesis of 4-3Py-SBF, 4-4Py-SBF and 2-4Py-SBF

9,9'-spirobi[fluorene] brominated compound (**4-Br-SBF** or **2-Br-SBF**), boronic acid derivative (3pyridylboronic acid or 4-pyridylboronic acid), K<sub>2</sub>CO<sub>3</sub> and Pd(dppf)Cl<sub>2</sub> were dissolved in dry DMF. The mixture was warmed to 150°C and stirred overnight. After cooling to room temperature, saturated solution of chloride ammonium (50 mL) was added, and organic layer was extracted three times with dichloromethane (3x30 mL) and washed with brine (3x30 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (see conditions for each compound).



#### 3-(9,9'-spirobi[fluoren]-4-yl)pyridine (4-3Py-SBF)

3-(9,9'-spirobi[fluoren]-4-yl)pyridine was prepared according to the general procedure between 4bromo-9,9'-spirobi[fluorene] (0.70 g, 1.78 mmol), 3-pyridylboronic acid (0.33 g, 2.67 mmol, 1.50 eq),  $K_2CO_3$  (2.61 g, 18.88 mmol, 10.61 eq), Pd(dppf)Cl<sub>2</sub> (0.09 g, 0.11 mmol, 0.06 eq) and DMF (60 mL). The residue was purified by flash chromatography on silica gel (light petroleum/ethyl acetate 8/2) to afford a colorless solid (0.60 g, 1.53 mmol), [column conditions: Silica cartridge 24 g (Serlabo); solid deposit on Celite®;  $\lambda_{detection}$ : (254 nm, 280 nm); dichloromethane in ethyl acetate (8/2) at 25 mL/min; collected fraction: 9-18 min]. Yield: 86 %. mp: 146°C. <sup>1</sup>H NMR (300MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.86 (d, J= 1.5 Hz, 1H, ArH), 8.75 (dd, J= 4.8, 1.2 Hz, 1H, ArH), 7.97 (dt, J= 7.8, 2.1 Hz, 1H, ArH), 7.89 (dt, J= 7.8, 0.6 Hz, 2H, ArH), 7.55-7.50 (m, 1H, ArH), 7.40 (dt, J= 7.5, 1.2 Hz, 2H, ArH), 7.25-7.11 (m, 4H, ArH), 7.09-6.99 (m, 3H, ArH), 6.76 (d, J= 7.5 Hz, 2H, ArH), 6.71 (dd, J= 7.2, 1.8 Hz, 1H, ArH), 6.66 (m, 1H, ArH); <sup>13</sup>C NMR (75MHz,CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  150.5 (CH), 150.3 (C), 149.8 (C), 149.6 (CH), 149.3 (C), 142.4 (C), 141.8 (C), 139.5 (C), 137.2 (CH), 137.1 (C), 134.7 (C), 130.6 (CH), 128.4 (2xCH, observed from HSQC), 128.3 (CH), 128.1 (CH), 127.9 (CH), 124.4 (CH), 124.3 (CH), 124.1 (CH), 123.9 (CH), 123.3 (CH), 120.8 (CH), 66.2 (C spiro); IR (ATR, cm<sup>-1</sup>): v = 615, 646, 711, 727, 739, 750, 764, 783, 800, 818, 872, 920, 949, 1003, 1022, 1078, 1107, 1153, 1253, 1282, 1398, 1427, 1444, 1471, 1562, 1581, 1599, 3016, 3041. HRMS calculated for C<sub>30</sub>H<sub>20</sub>N: 394.1596, found: 394.1589 [M+H]<sup>+</sup>;  $\lambda_{abs}$  [nm] ( $\epsilon$ [10<sup>4</sup> L.mol<sup>-1</sup>.cm<sup>-1</sup>]) = 297 (0.9), 308 (1.4).



#### 4-(9,9'-spirobi[fluoren]-4-yl)pyridine (4-4Py-SBF)

4-(9,9'-spirobi[fluoren]-4-yl)pyridine was prepared according to the general procedure between 4bromo-9,9'-spirobi[fluorene] (0.74 g, 1.88 mmol), 4-pyridylboronic acid (0.35 g, 2.87 mmol, 1.52 eg), Pd(dppf)Cl<sub>2</sub> (0.09 g, 0.11 mmol, 0.05 eq), K<sub>2</sub>CO<sub>3</sub> (2.64 g, 19.10 mmol, 10.13 eq), DMF (55 mL). The residue was purified by flash chromatography on silica gel (light petroleum/ethyl acetate 8/2) to afford a colorless solid (0.66 g, 1.68 mmol), [column conditions: Silica cartridge 12 g (Serlabo); solid deposit on Celite®;  $\lambda_{detection}$ : (254 nm, 280 nm); ethyl acetate in light petroleum (2/8) at 30 mL/min; collected fraction: 5-15 min. Yield: 89%. mp: 188-189°C. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.78 (dd, J= 6, 1.5 Hz, 2H, ArH), 7.89 (dt, J= 7.5, 1.2 Hz, 2H, ArH), 7.58 (dd, J= 6, 1.5 Hz, 2H, ArH), 7.41 (dt, J= 7.5, 0.9 Hz, 2H, ArH), 7.02-7.21 (m, 7H, ArH), 6.75 (dt, J= 7.5, 0.9 Hz, 2H, ArH), 6.71 (dd, J= 6.3, 2.4 Hz 1H, ArH), 6.66 (m, 1H, ArH); <sup>13</sup>C NMR (75MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 150.7 (CH), 150.4 (C), 149.8 (C), 149.3 (C), 149.2 (C), 142.4 (C), 141.5 (C), 138.7 (C), 135.6 (C), 129.9 (CH), 128.47 (CH), 128.45 (2xCH, observed from HSQC), 128.1 (CH), 127.9 (CH), 124.9 (CH), 124.4 (CH), 124.32 (2xCH, observed from DEPT), 123.4 (CH), 120.78 (CH), 66.18 (C spiro); IR (ATR, cm<sup>-1</sup>): v = 505, 569, 596, 615, 638, 646, 654, 684, 727, 741, 752, 768, 804, 833, 991, 1030, 1157, 1214, 1282, 1403, 1444, 1475, 1542, 1583, 1599, 1676, 3010, 3026, 3053, 3064. HRMS calculated for C<sub>30</sub>H<sub>20</sub>N: 394.1596, found: 394.1590  $[M+H]^+$ ;  $\lambda_{abs}$  [nm] ( $\epsilon$ [10<sup>4</sup> L.mol<sup>-1</sup>.cm<sup>-1</sup>]) = 297 (0.7), 308 (1.2).



#### 4-(9,9'-spirobi[fluoren]-2-yl)pyridine (2-4Py-SBF)

4-(9,9'-spirobi[fluoren]-2-yl)pyridine was prepared according to the general procedure between 2bromo-9,9'-spirobi[fluorene] (0.75 g, 1.89 mmol), 4-pyridylboronic acid (0.33 g, 2.65 mmol, 1.40 eq), K<sub>2</sub>CO<sub>3</sub> (1.78 g, 12.88 mmol, 6.79 eq), Pd(dppf)Cl<sub>2</sub> (0.08 g, 0.09 mmol, 0.05 eq), DMF (20 mL). The residue was purified by flash chromatography on silica gel (light petroleum/ethyl acetate 9/1) to afford a colorless solid (0.61 g, 1.55 mmol), [column conditions: Silica cartridge 24 g (Serlabo); solid deposit on Celite®;  $\lambda_{detection}$ : (254 nm, 280 nm); ethyl acetate in light petroleum (1/9) at 35 mL/min; collected fraction: 10-20 min. Yield: 82 %. mp: 140°C. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.51 (d, J= 4.8 Hz, 2H, ArH), 7.94 (dd, J= 7.8, 0.6 Hz, 1H, ArH), 7.86 (tt, J= 7.5, 0.6 Hz, 3H, ArH), 7.66 (dd, J= 8.1, 1.8 Hz, 1H, ArH), 7.41-7.33 (m, 3H, ArH), 7.24 (dd, J= 6, 1.5 Hz, 2H, ArH), 7.12 (m, 3H, ArH), 6.99 (dd, J= 1.8, 0.6 Hz, 1H, ArH), 6.75 (tt, J= 7.5, 0.9 Hz, 3H, ArH); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 150.5 (CH), 150.4 (C), 149.9 (C), 148.9 (C), 148.2 (C), 143.4 (C), 142.4 (C), 141.5 (C), 138.2 (C), 128.9 (CH), 128.5 (2xCH, observed from DEPT), 128.4 (CH), 127.4 (CH), 124.3 (2xCH, observed from DEPT), 122.8 (CH), 121.8 (CH), 121.29(CH), 121.0 (CH), 120.7 (CH), 66.5 (C spiro); IR (ATR, cm<sup>-1</sup>): v = 526, 552, 617, 660, 698, 729, 752, 777, 814, 1005, 1068, 1105, 1153, 1405, 1446, 1544, 1593, 3053, 3061. HRMS calculated for C<sub>30</sub>H<sub>20</sub>N: 394.1596, found 394.1596 [M+H]<sup>+</sup>; λ<sub>abs</sub> [nm] (ε[10<sup>4</sup> L.mol<sup>-1</sup>.cm<sup>-1</sup>]) = 297 (2.2), 308 (2.1), 321 (1.6).

#### Specific Suzuki coupling from 2-bromopyridine: synthesis of 4-2Py-SBF



2-(9,9'-spirobi[fluoren]-4-yl)pyridine (4-2Py-SBF)

2-(9,9'-spirobi[fluoren]-4-yl)pyridine was prepared by reaction between (9,9'-spirobi[fluoren]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**) (0.75 g, 1.70 mmol), 2-bromopyridine (0.29 g, 1.85 mmol, 1.09 eq), K<sub>2</sub>CO<sub>3</sub> (1.17 g, 8.50 mmol, 4.99 eq), Pd(Ph<sub>3</sub>)<sub>4</sub> (0.10 g, 0.12 mmol, 0.07 eq) and THF/water (30 mL/12 mL). The residue was purified by flash chromatography on silica gel (light petroleum/ethyl acetate 9/1) to afford a colorless solid (0.37 g, 0.95 mmol), [column conditions: Silica cartridge 24 g (Serlabo); solid deposit on Celite®;  $\lambda_{detection}$ : (254 nm, 280 nm); ethylacetate in light petroleum (1/9) at 20 mL/min; collected fraction: 12-30 min]. Yield: 56 %. mp: 201°C. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.85-8.82 (m, 1H, ArH), 7.95-7.88 (m, 3H, ArH), 7.71-7.68 (dt, J= 7.8, 0.9 Hz, 1H, ArH), 7.47-7.43 (m, 1H, ArH), 7.43-7.37 (td, J= 7.5, 0.9Hz, 2H, ArH), 7.35-7.32 (dd, J= 7.5, 0.9 Hz, 1H, ArH), 7.20-7.12 (m, 3H, ArH), 7.08-7.01 (m, 3H, ArH), 6.78-6.76 (d, J= 7.8 Hz, 2H, ArH), 6.74-6.71 (dd, J= 7.5, 1.2 Hz, 1H, ArH), 6.67-6.64 (m, 1H, ArH); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  159.73 (C), 150.22 (CH),150.22 (C), 149.70 (C), 149.43 (C), 142.42 (C), 141.79 (C), 139.42 (C), 137.57 (C), 137.19 (CH), 130.09 (CH), 128.42 (CH), 128.38 (CH), 128.26 (CH), 127.94 (CH), 127.78 (CH), 124.89 (CH), 124.42 (CH), 124.22 (CH), 124.18 (CH), 123.80 (CH), 123.24 (CH), 120.71 (CH), 66.28 (C spiro). IR (ATR, cm<sup>-1</sup>): v = 540, 569, 619, 644, 656, 731, 746, 779, 814, 922, 951, 991, 1030, 1147, 1281, 1413, 1425, 1446, 1470, 1485, 1560, 1579, 2926, 3012, 3057. HRMS calcd for C<sub>30</sub>H<sub>20</sub>N: 394.1596, found: 394.1595 [M+H]<sup>+</sup>. Elemental analysis calculated for C<sub>30</sub>H<sub>19</sub>N: C, 91.57 %; H, 4.87 %; N, 3.56 %. Found: C, 91.19 %; H, 4.98 %; N, 3.41 %;  $\lambda_{abs}$  [nm] ( $\epsilon$ [10<sup>4</sup> L.mol<sup>-1</sup>.cm<sup>-1</sup>]) = 297 (2.2), 309 (3.1).

Empirical formula	$C_{30}H_{19}N$
Formula weight	393.46
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P2 <sub>1</sub> /c
Unit cell dimensions	$a = 9.9614(3) \text{ Å}, \alpha = 90 \circ$
	b = 9.8012(3) Å, β = 97.0710(10) °
	$c = 20.6471(7) \text{ Å}, \gamma = 90 ^{\circ}$
Volume	$2000.52(11) \text{ Å}^3$
Z, Calculated density	4, 1.306 (g.cm <sup>-3</sup> )
Absorption coefficient	$0.075 \text{ mm}^{-1}$
F(000)	824
Crystal size	0.39 x 0.35 x 0.31 mm
Crystal color	colorless
Theta range for data collection	1.99 to 27.53 °
h_min, h_max	-12, 10
k_min, k_max	-12, 12
I_min, I_max	-26, 26
Reflections collected / unique	17499 / 4588 [R(int) = 0.0306]
Reflections [I>2o]	3805
Completeness to theta_max	0.996
Absorption correction type	multi-scan
Max. and min. transmission	0.977, 0.971
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	4588 / 0 / 280
Goodness-of-fit	1.046
Final R indices [I>2σ]	R1 = 0.0417, wR2 = 0.1004
R indices (all data)	R1 = 0.052, WR2 = 0.1119
Largest diff. peak and hole	0.24 and -0.213 eÅ <sup>-3</sup>

Table S1 Crystal data and structure refinement for 4-4Py-SBF

#### 4-4Py-SBF X-Ray structure



<u>S 2</u> Angle between the mean plane of the pendant pyridinyl ring and that of its attached phenyl ring (of the fluorene) in **4-4Py-SBF**: 42.19°



**<u>S 3</u>** Angle between the two phenyl rings of the substituted fluorene unit in **4-4Py-SBF**: 16.81 °



**<u>S 4</u>** Angle between the two phenyl rings of the non substituted fluorene unit in **4-4Py-SBF**: 4.10 °



<u>S 5</u> Angle between the two five membered cycles of the fluorene units in **4-4Py-SBF**: 87.79  $^{\circ}$ 



<u>**S 6**</u> Short contacts (C-H and N-H, distance < (sum of  $r_{vdw}$ -0.1)) in **4-4Py-SBF** 

Empirical formula	$C_{60}H_{38}N_2$
Extended formula	$2(C_{30}H_{19}N)$
Formula weight	786.92
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P2 <sub>1</sub> /c
Unit cell dimensions	$a = 10.7952(3)$ Å, $\alpha = 90$ °
	$b = 9.3404(2) \text{ Å}, \beta = 94.0020(10) \circ$
	$c = 40.8653(11) \text{ Å}, \gamma = 90 \circ$
Volume	4110.46(18) Å <sup>3</sup>
Z, Calculated density	4, 1.272 (g.cm <sup>-3</sup> )
Absorption coefficient	$0.073 \text{ mm}^{-1}$
F(000)	1648
Crystal size	0.58 x 0.36 x 0.15 mm
Crystal color	colorless
Theta range for data collection	1 to 27.53 °
h_min, h_max	-13, 14
k_min, k_max	-12, 11
I_min, I_max	-48, 52
Reflections collected / unique	35440 / 9403 [R(int) = 0.0338]
Reflections [I>2σ]	7254
Completeness to theta_max	0.994
Absorption correction type	multi-scan
Max. and min. transmission	0.989 , 0.969
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	9403 / 0 / 559
Goodness-of-fit	1.028
Final R indices [I>2σ]	R1 = 0.0453, wR2 = 0.11
R indices (all data)	R1 = 0.0638, $wR2 = 0.1235$
Largest diff. peak and hole	0.269 and $-0.27 \text{ e-}.\text{Å}^{-3}$

 $\underline{\textbf{Table S2}}$  Crystal data and structure refinement for 2-4Py-SBF

#### 2-4Py-SBF Molecule 1 X-Ray structure



<u>S 7</u> Angle between the mean plane of the pendant pyridinyl ring and that of its attached phenyl ring (of the fluorene) in **2-4Py-SBF molecule 1**: 37.54°



<u>S 8</u> Angle between the two phenyl rings of the substituted fluorene unit in **2-4Py-SBF molecule 1**:  $3.21^{\circ}$ 



S 9 Angle between the two phenyl rings of the non substituted fluorene unit in 2-4Py-SBF molecule 1:  $6.06^{\circ}$ 



 $\underline{S\,10}$  Angle between the two five membered cycles of the fluorene units in **2-4Py-SBF molecule 1**:  $$88.10^\circ$ 



<u>**S 11**</u> Short contacts (C-H distance < (sum of  $r_{vdw}$ ) + 0.1)) in **2-4Py-SBF molecule 1** 

#### 2-4Py-SBF Molecule 2 X-Ray structure.



<u>S 12</u> Angle between the mean plane of the pendant pyridinyl ring and that of its attached phenyl ring (of the fluorene) in **2-4Py-SBF molecule 2**: 32.78°



<u>S 13</u> Angle between the two phenyl rings of the substituted fluorene unit in 2-4Py-SBF molecule 2: 4.97°



<u>S 14</u> Angle between the two phenyl rings of the non substituted fluorene unit in 2-4Py-SBF molecule 2: 7.38°



 $\underline{S\,15}$  Angle between the two five membered cycles of the fluorene units in **2-4Py-SBF molecule 2**:  $89.52^\circ$ 



<u>**S 16**</u> Short contacts (C-H and N-H, distance < (sum of  $r_{vdw}$ )) in **2-4Py-SBF molecule 2** 

### THEORETICAL MODELING



**<u>S 17</u>** Experimental absorption spectrum (top) and calculated Absorption spectrum from TD-DFT (bottom) of four 4-substituted SBF derivatives (the same color code is used for an easiest comparison).



<u>S 18</u> Experimental Absorption spectrum (top) and calculated Absorption spectrum from TD-DFT (bottom) of **2-Ph-SBF** (in black) and **2-4Py-SBF** (in red).



**<u>S 19</u>** Calculated frontier molecular orbitals by DFT and the 6<sup>th</sup> first calculated electronic transitions by TD-DFT of **4-Ph-SBF**, after geometry optimization with DFT B3LYP/6-311G+(d,p), show with an isovalue of 0.04 <sup>1</sup>

## 4-2Py-SBF



LUMO+1: -1.20 eV



LUMO+2: -1.16 eV



**S 20** Calculated frontier molecular orbitals by DFT and the 11<sup>th</sup> first calculated electronic transitions by TD-DFT of **4-2Py-SBF**, after geometry optimization with DFT B3LYP/6-311G+(d,p), show with an isovalue of 0.04



<u>S 21</u> Calculated frontier molecular orbitals by DFT and the 8<sup>th</sup> first calculated electronic transitions by TD-DFT of **4-3Py-SBF**, after geometry optimization with DFT B3LYP/6-311G+(d,p), show with an isovalue of 0.04



## 4-4Py-SBF



LUMO+2: -1.18 eV

LUMO+1: -1.34 eV



### LUMO+3: -1.18 eV

Excited state 1 λ: 311.32 nm f: 0.0553 Excited state 2 λ: 295.42 nm f: 0.0726 **Excited state 7** λ: 271.37 nm f: 0.129 Excited state 10 λ: 261.83 nm f: 0.0591 Excited state 11 λ: 259.54 nm f: 0.0695 Excited state 19 λ: 244.17 nm f: 0.0955 Excited state 20 λ: 243.14 nm f: 0.0965



HOMO-1: -6.37 eV

<u>S 22</u> Calculated frontier molecular orbitals by DFT and the 9<sup>th</sup> first calculated electronic transitions by TD-DFT of **4-4Py-SBF**, after geometry optimization with DFT B3LYP/6-311G+(d,p), show with an isovalue of 0.04

2-4Py-SBF



LUMO+1: -1.36 eV



LUMO+2: -1.07 eV



**<u>S 23</u>** Calculated frontier molecular orbitals by DFT and the 6<sup>th</sup> first calculated electronic transitions by TD-DFT of **2-4Py-SBF**, after geometry optimization with DFT B3LYP/6-311G+(d,p), show with an isovalue of 0.04

## 2-Ph-SBF



**<u>S 24</u>** Calculated frontier molecular orbitals by DFT and the 7<sup>th</sup> first calculated electronic transitions by TD-DFT of **2-Ph-SBF**, after geometry optimization with DFT B3LYP/6-311G+(d,p), show with an isovalue of 0.04 <sup>2</sup>

## THERMAL PROPERTIES



**<u>S 25</u>** TGA spectrum of **4-2Py-SBF** 



**<u>S 26</u>** DSC curves of **4-2Py-SBF** 



**<u>S 27</u>** TGA spectrum of **4-3Py-SBF** 



S 28 DSC curves of 4-3Py-SBF

![](_page_31_Figure_0.jpeg)

**<u>S 29</u>** TGA spectrum of **4-4Py-SBF** 

![](_page_32_Figure_0.jpeg)

**<u>S 30</u>** DSC curves of **4-4Py-SBF** 

![](_page_33_Figure_0.jpeg)

**<u>S 31</u>** TGA spectrum of **2-4Py-SBF** 

![](_page_34_Figure_0.jpeg)

**<u>S 32</u>** DSC curves of **2-4Py-SBF** 

![](_page_35_Figure_0.jpeg)

<u>S 33</u> TGA spectra (left) and DSC curves from second heating cycle (right) of **4-2Py-SBF** (black line), **4-3Py-SBF** (red line), **4-4Py-SBF** (blue line) and **2-4Py-SBF** (green line).
	4-Ph-SBF	4-4Py-SBF	4-3Py-SBF	4-2Py-SBF	2-4Py-SBF	2-Ph-SBF
m.p.(°C)	213*	188-189*	147*	201*	140**	100-108*
T <sub>d</sub> (°C)	254	217	220	242	181	238
T <sub>g</sub> (°C)	76	84	81	81	92	78
Tc (°C)	115	-	-	140	-	-

\*: Measured from DSC, \*\*: Measured with the electrothermal melting point apparatus.

## PHOTOPHYSICAL PROPERTIES



<u><b>S 34</b></u> Qu	antum yield	measurements	: Absorption of	solution of	of <b>4-2Py</b>	-SBF	in cycloh	exane a	and q	uinine
			sulfate (QS)	in $H_2SO_4$	1N					

Solution	$\lambda$ (nm)	А	Ts	T <sub>QS</sub>	$n_D^{25}$ (cyclohexane)	$n_D^{25}$ (H <sub>2</sub> SO <sub>4</sub> 1N)	Φ
1	311,5	0,1192	34974,8	127629	1,42662	1,3325	17%
2	310,5	0,0942	31025,4	116812	1,42662	1,3325	17%
3	310,5	0,0586	25061,1	96133,6	1,42662	1,3325	16%

Table S4 Quantum yield calculation of 4-2Py-SBF



 $\underline{\textbf{S 35}}$  Quantum yield measurements : Absorption of solution of 4-3Py-SBF in cyclohexane and quinine sulfate (QS) in  $H_2SO_4$  1N

Solution	λ (nm)	А	$T_{S}$	$T_{QS}$	$n_D^{25}$ (cyclohexane)	$n_D^{25}$ (H <sub>2</sub> SO <sub>4</sub> 1N)	Φ
1	309	0,083	79707,2	123370	1,42662	1,3325	40%
2	309	0,042	62185,4	93764,3	1,42662	1,3325	42%
3	309	0,016	51410	84392,2	1,42662	1,3325	38%

Table S5 Quantum yield calculation of 4-3Py-SBF



<u>S 36</u>	Quantum yield measurements	: Absorption of	solution of	f 4-4Py-SBF	in cyclohexane	and quinir	٦e
		sulfate (QS)	in $H_2SO_4$ 1	.N			

Solution	$\lambda$ (nm)	А	Ts	T <sub>QS</sub>	$n_D^{25}$ (cyclohexane)	$n_D^{25}$ (H <sub>2</sub> SO <sub>4</sub> 1N)	Φ
1	310,5	0,084	68281,4	109998	1,42662	1,3325	39%
2	309,5	0,038	60377,9	90114,5	1,42662	1,3325	42%
3	310	0,021	36602,1	56620,9	1,42662	1,3325	40%

Table S6 Quantum yield calculation of 4-4Py-SBF



 $\underline{\textbf{S 37}}$  Quantum yield measurements : Absorption of solution of 2-4Py-SBF in cyclohexane and quinine sulfate (QS) in  $H_2SO_4$  1N

Solution	λ (nm)	А	Ts	T <sub>QS</sub>	$n_D^{25}$ (cyclohexane)	$n_D^{25}$ (H <sub>2</sub> SO <sub>4</sub> 1N)	Φ
1	309,5	0,0465	32394,7	36498,3	1,42662	1,3325	56%
2	308,5	0,0688	42578,2	48999,8	1,42662	1,3325	54%
3	309	0,1075	61127,1	69029,1	1,42662	1,3325	55%

Table S7 Quantum yield calculation of 2-4Py-SBF



<u>**S 38**</u> UV-Vis absorption spectrum of **4-2Py-SBF** in various solvents ( $10^{-6}$  M)



**<u>S 39</u>** Fluorescence emissions spectrum of **4-2Py-SBF** in various solvents ( $\lambda_{exc}$  = 310nm)



**<u>S 40</u>** UV-Vis spectrum of **4-3Py-SBF** in various solvents  $(10^{-6} \text{ M})$ 



<u>S 41</u> Fluorescence emissions spectrum of **4-3Py-SBF** in various solvents ( $\lambda_{exc}$  = 310 nm, except for toluene:  $\lambda_{ex}$  = 312 nm)



<u>**S 42**</u> UV-Vis spectrum of **4-4Py-SBF** in various solvents ( $10^{-6}$  M)



<u>S 43</u> Fluorescence emissions spectrum of **4-4Py-SBF** in various solvents ( $\lambda_{exc}$  = 309 nm, except for toluene:  $\lambda_{exc}$  = 311 nm)



**<u>S 44</u>** UV-Vis spectrum of **2-4Py-SBF** in various solvents (10<sup>-6</sup> M)



**<u>S 45</u>** Fluorescence emissions spectrum of **2-4Py-SBF** in various solvents ( $\lambda_{exc}$  = 309 nm (cyclohexane, MeCN),  $\lambda_{exc}$  = 311nm (Toluene, DCM),  $\lambda_{exc}$  = 312 nm (THF))

	Cyclohexane	Toluene	THF	DCM	MeCN
4-2Py-SBF	17%	13%	16%	15%	15%
4-3Py-SBF	40%	33%	39%	43%	37%
4-4Py-SBF	40%	32%	39%	39%	37%
2-4Py-SBF	55%	50%	70%	120%	76%

Table S8 Quantum yields measured in various solvents of 4-2Py-SBF, 4-3Py-SBF, 4-4Py-SBF and 2-4Py-SBF



<u>**S** 46</u> Emission spectra of **4-2Py-SBF**, fluorescence and phosphorescence contributions recorded in a frozen matrix of 2-methyltetrahydrofuran at 77 K,  $\lambda_{exc} = 309$  nm



<u>**S 47**</u> Emission spectra of **4-3Py-SBF**, fluorescence and phosphorescence contributions recorded in a frozen matrix of 2-methyltetrahydrofuran at 77 K,  $\lambda_{exc} = 309$  nm



<u>**S**</u> 48 Emission spectra of **4-4Py-SBF**, fluorescence and phosphorescence contributions recorded in a frozen matrix of 2-methyltetrahydrofuran at 77 K,  $\lambda_{exc} = 309$  nm



<u>S 49</u> Emission spectra of **2-4Py-SBF**, fluorescence and phosphorescence contributions recorded in a frozen matrix of 2-methyltetrahydrofuran at 77 K,  $\lambda_{exc} = 300$  nm









<u>S 51</u> Current efficiency (black) and Power efficiency (blue) versus current density of the non-doped **4-4Py-SBF**, Ir(ppy)<sub>3</sub> doped **4-4Py-SBF** and FIrpic doped **4-4Py-SBF** devices.









<u>S 53</u> Current efficiency (black) and Power efficiency (blue) versus current density of the non-doped **4-3Py-SBF**, Ir(ppy)<sub>3</sub> doped **4-3Py-SBF** and FIrpic doped **4-3Py-SBF** devices.









<u>S 55</u> Current efficiency (black) and Power efficiency (blue) versus current density of the non-doped **4**-**2Py-SBF**, Ir(ppy)<sub>3</sub> doped **4-2Py-SBF** and FIrpic doped **4-2Py-SBF** devices.









<u>S 57</u> Current efficiency (black) and Power efficiency (blue) versus current density of the non-doped 2-4Py-SBF, Ir(ppy)<sub>3</sub> doped 2-4Py-SBF and FIrpic doped 2-4Py-SBF devices.

## ELECTROCHEMICAL PROPERTIES



**<u>S 58</u>** Cyclic voltammetry of **4-2Py-SBF** (5  $10^{-3}$  M) in CH<sub>2</sub>Cl<sub>2</sub> + Bu<sub>4</sub>NPF<sub>6</sub> 0.2 M, sweep-rate 100 mV.s<sup>-1</sup>. Platinum disk ( $\emptyset$ : 1mm) working electrode.



**<u>S 59</u>** Cyclic voltammetry of **4-3Py-SBF** (5  $10^{-3}$  M) in CH<sub>2</sub>Cl<sub>2</sub> + Bu<sub>4</sub>NPF<sub>6</sub> 0.2 M, sweep-rate 100 mV.s<sup>-1</sup>. Platinum disk ( $\emptyset$ : 1mm) working electrode.



<u>**S 60**</u> Cyclic voltammetry of **4-4Py-SBF** (5  $10^{-3}$  M) in CH<sub>2</sub>Cl<sub>2</sub> + Bu<sub>4</sub>NPF<sub>6</sub> 0.2 M, sweep-rate 100 mV.s<sup>-1</sup>. Platinum disk ( $\emptyset$ : 1mm) working electrode.



<u>**S 61**</u> Cyclic voltammetry of **2-4Py-SBF** (5  $10^{-3}$  M) in CH<sub>2</sub>Cl<sub>2</sub> + Bu<sub>4</sub>NPF<sub>6</sub> 0.2 M, sweep-rate 100 mV.s<sup>-1</sup>. Platinum disk ( $\emptyset$ : 1mm) working electrode.



<u>**S 62</u>** Cyclic voltammetry of **4-2Py-SBF** (5  $10^{-3}$  M) in CH<sub>2</sub>Cl<sub>2</sub> + Bu<sub>4</sub>NPF<sub>6</sub> 0.2 M, ten successive sweeps. Sweep-rate 100 mV.s<sup>-1</sup>. Platinum disk ( $\emptyset$ : 1mm) working electrode.</u>

















4-3Py-SBF-HMBC-CD<sub>2</sub>Cl<sub>2</sub> (zoom in C Spiro)















2-4Py-SBF-HMBC-CD<sub>2</sub>Cl<sub>2</sub> (zoom on C Spiro)














2-DEPT-CD<sub>2</sub>Cl<sub>2</sub>



























4-4Py-SBF-DEPT-CD<sub>2</sub>Cl<sub>2</sub>









## COPY OF MASS SPECTRA

4-2Py-SBF

Instrument : Waters G-Tot 2 Fichier : ASAP\_1386\_MS\_01 raw Date/Heure : 28-Nov-2013 / 1247;48 Scans : (11: 60) de m/z 60 à 600 Lockmass : 411 Description : S. THÉRY 42 Py B FL Température : 425°C



Instrument : Waters G-Tot 2 Fichier : ASAP\_1386\_M5\_01 raw Date/Heure : 28-Nov-2013 / 12-47:48 Scans : (11: 60) de m/z 382 à 388 Lockmass : 411 Description : 6. THÉRY 42 Py B FL Température : 425°C



Séparation : 10 Seuil : 0.01 mmu Charge : 1 Résolution : 10000 Formule brute : C30 H20 N





## 4-3Py-SBF



4-4Py-SBF

2-4Py-SBF

394.1598 [M+H]+ 393.1544 319.0153 271.2858 295.2927 || 328.1207 375.1629 129.0543 156.0804 424.1743 п 800 m/z Instrument : Waters G-Tot 2 Fichier : ASAP\_487\_MS\_01.raw Date/Heure : 18-Apr-2013 / 10:03:05 Scans : (105 : 156) de m/z 392 à 399 Lockmass : 149 Description : S. THÉRY 24 Py SBF AM Température : 300°C 394.1598 [N++-]+ 393.1544 395.1674 396,1714 397.1752 398.1726 Δ 299 m/z Séparation : 10 Seuil : 0.01 mmu Charge : 1 Résolution : 10000 Formule brute : C30 H20 N 394.1598 Arnas isotopique théorique de [M+H]+ : C30 H20 N 395.1629 396.1882 397.1695 0 + 392 Δ 299 m/z

Instrument : Waters G-Tot 2 Fichler : ASAP\_487\_MS\_01.raw DateHeure : 18-Apr-2013 / 10.03/05 Scians : (105 : 156) de m/z 80 à 800 Lockmass : 148 Description : S. THÉRY 24 Py SBF AM Température : 300°C

- <sup>1</sup> S. Thiery et al., *J. Mater. Chem. C.*, **2014**, 2, 4156 <sup>2</sup> S.Thiery et al., *Tetrahedron*, **2014**, 70, 6337