SYNTHESIS.......................................................................................................................................................................................... 1
X-RAY DIFFRACTION.................................................................................................................................................................................. 2
PHOTOPHYSICAL PROPERTIES................................................................................................................................................................. 9
THEORETICAL MODELING ............................................................................................................................................................................. 16
THERMAL PROPERTIES.............................................................................................................................................................................. 18
ELECTROCHEMICAL PROPERTIES.......................................................................................................................................................... 20
DEVICES FABRICATION ............................................................................................................................................................................ 21
2D NMR STUDIES..................................................................................................................................................................................... 22
COPY OF NMR SPECTRA ............................................................................................................................................................................ 26
COPY OF MASS SPECTRA............................................................................................................................................................................ 32

\[ \text{S} \text{1 Structures of 9,9'}\text{-SpiroBiFluorene (SBF) and 4-Phenyl-9,9'}\text{-SpiroBiFluorene (4-Ph-SBF)} \]

investigated in this work

SYNTHESIS

\[ \text{4-bromo-9,9'}\text{-spirobi[fluorene] (1)} \]

2,2'-dibromo-1,1'-biphenyl (3.03 g, 9.70 mmol) was dissolved in dry THF (40 mL) under argon atmosphere, cooled at -78°C, and stirred during 10 minutes at this temperature. A 2.5M n-ButLi solution in THF (4.31 mL, 10.78 mmol, 1.11 eq) was then slowly injected via a seringue, at -78°C. The
resulting yellow mixture was stirred at the same temperature for 30 min. 9-fluorenone (2.03 g, 11.24 mmol, 1.16 eq) 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 ethyl acetate (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®; \(\lambda_{\text{detection}}\): (254 nm and 280 nm); light petroleum at 18 mL/min; collected fraction: 15-35 min]. Yield: 75%. mp: 148-150°C; \(^1\)H NMR (300Mhz, CDCl\(_3\)): \(\delta\) 8.66 (d, \(J = 8.1\), 1H, ArH), 7.83 (d, \(J = 7.5\), 2H, ArH), 7.50 (dd, \(J = 8.1, 0.9\) Hz, 1H, ArH), 7.44-7.35 (m, 3H, ArH), 7.19-7.09 (m, 3H, ArH), 6.94 (t, \(J = 7.5\) Hz, 1H, ArH), 6.72 (m, 3H, ArH), 6.64 (d, \(J = 7.5\), 1H, ArH); \(^{13}\)C NMR (75Mhz, CDCl\(_3\)): \(\delta\) 151.7 (C), 149.1 (C), 148.5 (C), 141.9 (C), 141.1 (C), 140.1 (C), 132.8 (CH), 128.7 (CH), 128.6 (CH), 128.10 (CH), 128.07 (CH), 127.6 (CH), 124.2 (CH), 124.0 (CH), 123.7 (CH), 123.1 (CH), 120.2 (CH), 116.9 (C), 66.0 (C spiro).

X-RAY DIFFRACTION

4-Ph-SBF :

\(C_{62}\) \(H_{40}\); \(M = 784.94\). APEXII, Bruker-AXS diffractometer, Mo-K\(\alpha\) radiation (\(\lambda = 0.71073\) Å), \(T = 150(2)\) K; triclinic \(P-1\) (I.T.#2), \(a = 9.7817(3)\), \(b = 13.8740(5)\), \(c = 16.0080(5)\) Å, \(\alpha = 106.1120(10)\), \(\beta = 91.4330(10)\), \(\gamma = 92.9300(10)\) °, \(V = 2082.65(12)\) Å\(^3\), \(Z = 2\), \(d = 1.252\) g.cm\(^{-3}\), \(\mu = 0.071\) mm\(^{-1}\). The structure was solved by direct methods using the SIR97 program\(^2\), and then refined with full-matrix least-square methods based on \(F^2\) (SHELXL-97)\(^3\) with the aid of the WINGX\(^4\) 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 \(F^2\) with 9483 unique intensities and 559 parameters converged at \(wR(F^2) = 0.1549\) (\(R(F) = 0.0581\)) for 8364 observed reflections with \(I > 2\sigma(I)\).
Table 1 Crystal data and structure refinement for 4-Ph-SBF

<table>
<thead>
<tr>
<th>Identification code</th>
<th>4-Ph-SBF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{62}H_{40}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>784.94</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>\begin{align*} \text{a} &amp; = 9.7817(3) \text{ Å} \quad \alpha = 106.1120(10)^\circ \ \text{b} &amp; = 13.8740(5) \text{ Å} \quad \beta = 91.4430(10)^\circ \ \text{c} &amp; = 16.0080(5) \text{ Å} \quad \gamma = 92.9300(10)^\circ \end{align*}</td>
</tr>
<tr>
<td>Volume</td>
<td>2082.65(12) Å^{3}</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.252 Mg/m^{3}</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.071 mm^{-1}</td>
</tr>
<tr>
<td>F(000)</td>
<td>824</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.32 x 0.29 x 0.23 mm^{3}</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.33 to 27.50°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-12 \leq h \leq 12, -18 \leq k \leq 16, -20 \leq l \leq 20</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>34015</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>9483 [R(int) = 0.0191]</td>
</tr>
<tr>
<td>Completeness to theta = 27.50°</td>
<td>99.1 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.984 and 0.978</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F^2</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>9483 / 0 / 559</td>
</tr>
<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.057</td>
</tr>
<tr>
<td>Final R indices [I&gt;2\sigma(I)]</td>
<td>\begin{align*} R_1 &amp; = 0.0581, \text{ wR}2 = 0.1549 \end{align*}</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>\begin{align*} R_1 &amp; = 0.0660, \text{ wR}2 = 0.1676 \end{align*}</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.903 and -0.389 e.Å^{-3}</td>
</tr>
</tbody>
</table>
The X-ray diffraction data of single crystals of 4-Ph-SBF reveal an asymmetric unit containing two independent molecules (see below). The angle between the mean plane of the pendant phenyl ring and that of its attached phenyl ring (of the fluorene) is of 51.2° for molecule 1 and 56.6° for molecule 2.

**S 2**

**MOLECULE 1**

**S 3** Angle between the mean plane of the pendant phenyl ring and that of its attached phenyl ring (of the fluorene): 51.2°
S.4 Angle between the two phenyl rings of the substituted fluorene unit: 12.7°

S.5 Angle between the two phenyl rings of the non-substituted fluorene unit: 4.2°
**MOLECULE 2**

**S.6** Angle between the mean plane of the pendant phenyl ring and that of its attached phenyl ring (of the fluorene): $56.6^\circ$

**S.7** Angle between the two phenyl rings of the substituted fluorene unit: $4.8^\circ$
Angle between the two phenyl rings of the non-substituted fluorene unit: 2.2°

Some short intermolecular distances are revealed mainly C-H distances but also one short C-C distance of 3.35 Ångströms (See below).

\[ d_{cc} : 3.35 \, \text{Å} \]
**S 10** Selected C/H, C/C and CH/π distances in the intermolecular packing of **4-Ph-SBF**
Quantum yield measurements: Absorption of solutions of SBF in cyclohexane and quinine sulfate (QS) in H₂SO₄ 1N

**Table 2 Quantum yield calculation of SBF**

<table>
<thead>
<tr>
<th>Solution</th>
<th>λ (nm)</th>
<th>A</th>
<th>Tₛ</th>
<th>Tₚₛ</th>
<th>nₛ'D₂₅ (cyclohexane)</th>
<th>nₛ'D₂₅ (H₂SO₄ 1N)</th>
<th>φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>297</td>
<td>0.0475</td>
<td>46949</td>
<td>74590</td>
<td>1.42662</td>
<td>1.3325</td>
<td>39%</td>
</tr>
<tr>
<td>2</td>
<td>298</td>
<td>0.0337</td>
<td>38263</td>
<td>59663.7</td>
<td>1.42662</td>
<td>1.3325</td>
<td>40%</td>
</tr>
<tr>
<td>3</td>
<td>298.5</td>
<td>0.0205</td>
<td>26534.5</td>
<td>42274.6</td>
<td>1.42662</td>
<td>1.3325</td>
<td>39%</td>
</tr>
</tbody>
</table>
Fluorescence decay curves of SBF and 4-Ph-SBF recorded in cyclohexane solution. Excitation wavelength = 300nm. Emission wavelength = 320nm and 360nm for SBF and 4-Ph-SBF, respectively. Full width at half maximum (FWHM) of the instrumental response function (IRF) = 60ps.
**S13** Quantum yield measurements: Absorption of solutions of **4-Ph-SBF** in cyclohexane and quinine sulfate (QS) in H$_2$SO$_4$ 1N

**Table 3** Quantum yield calculation of **4-Ph-SBF**

<table>
<thead>
<tr>
<th>Solution</th>
<th>$\lambda$ (nm)</th>
<th>A</th>
<th>$T_s$</th>
<th>$T_{QS}$</th>
<th>$n_D^{25}$ (cyclohexane)</th>
<th>$n_D^{25}$ (H$_2$SO$_4$ 1N)</th>
<th>$\varphi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>309.5</td>
<td>0.0792</td>
<td>103003</td>
<td>154233</td>
<td>1.42662</td>
<td>1.3325</td>
<td>42%</td>
</tr>
<tr>
<td>2</td>
<td>310.5</td>
<td>0.044</td>
<td>72068.1</td>
<td>108069</td>
<td>1.42662</td>
<td>1.3325</td>
<td>42%</td>
</tr>
<tr>
<td>3</td>
<td>309</td>
<td>0.0175</td>
<td>56909.3</td>
<td>89577.4</td>
<td>1.42662</td>
<td>1.3325</td>
<td>40%</td>
</tr>
</tbody>
</table>
Quantum yield measurements: Absorption of solutions of 4-Ph-SBF in cyclohexane and quinine sulfate (QS) in H$_2$SO$_4$ 1N

**Table 4** Quantum yield calculation of 4-Ph-SBF

<table>
<thead>
<tr>
<th>Solution</th>
<th>$\lambda$ (nm)</th>
<th>$A$</th>
<th>$T_S$</th>
<th>$T_QS$</th>
<th>$n_D^{25}$ (cyclohexane)</th>
<th>$n_D^{25}$ (H$_2$SO$_4$ 1N)</th>
<th>$\varphi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>297</td>
<td>0,0739</td>
<td>127369</td>
<td>165870</td>
<td>1,42662</td>
<td>1,3325</td>
<td>48%</td>
</tr>
<tr>
<td>2</td>
<td>298,5</td>
<td>0,0634</td>
<td>100148</td>
<td>132413</td>
<td>1,42662</td>
<td>1,3325</td>
<td>47%</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>0,0474</td>
<td>64462,2</td>
<td>83593,7</td>
<td>1,42662</td>
<td>1,3325</td>
<td>48%</td>
</tr>
</tbody>
</table>
**S15** Emission spectrum of Fluorene, fluorescence and phosphorescence contributions recorded in a frozen matrix of methylcyclohexane/2-methylpentane (1:1) at 77 K, $\lambda_{\text{exc}} = 295$ nm
**S 16** Emission spectra of SBF, fluorescence and phosphorescence contributions recorded in a frozen matrix of methylcyclohexane/2-methylpentane (1:1) at 77 K, \( \lambda_{\text{exc}} = 297 \text{ nm} \).
S.17 Emission spectrum of 4-Ph-SBF, fluorescence and phosphorescence contributions recorded in a frozen matrix of methylcyclohexane/2-methylpentane 1:1 at 77 K, $\lambda_{\text{exc}} = 297$ nm. Inset a zoom in phosphorescence emission.
THEORETICAL MODELING

SBF

LUMO+1: -1.25 eV  
LUMO+2: -0.84 eV  
LUMO+3: -0.84 eV

LUMO: -1.25 eV

HOMO: -5.99 eV

HOMO-2: -6.79 eV

HOMO-1: -6.26 eV

Excited state 1
\[ \lambda: 297.6 \text{ nm} \]
\[ f: 0.064 \]
Excited state 2
\[ \lambda: 297.59 \text{ nm} \]
\[ f: 0.064 \]
Excited states 3 and 4
\[ f: 0 \]
Excited state 5
\[ \lambda: 271.95 \text{ nm} \]
\[ f: 0.1449 \]
Excited state 6
\[ \lambda: 271.95 \text{ nm} \]
\[ f: 0.1449 \]
Excited state 7
\[ \lambda: 261.09 \text{ nm} \]
\[ f: 0.0905 \]
Excited state 8
\[ \lambda: 261.09 \text{ nm} \]
\[ f: 0.0906 \]

S 18 Calculated frontier molecular orbitals by DFT and the 6th first calculated electronic transitions by TD-DFT of SBF, after geometry optimization with DFT B3LYP/6-311G+(d,p), show with an isovalue of 0.04
**4-Ph-SBF**

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO+1</td>
<td>-1.27 eV</td>
</tr>
<tr>
<td>LUMO+2</td>
<td>-0.94 eV</td>
</tr>
<tr>
<td>LUMO+3</td>
<td>-0.84 eV</td>
</tr>
<tr>
<td>HOMO</td>
<td>-5.97 eV</td>
</tr>
<tr>
<td>HOMO-1</td>
<td>-6.25 eV</td>
</tr>
</tbody>
</table>

Excited states:

- **Excited state 1**
  - $\lambda$: 300.25 nm
  - $f$: 0.06

- **Excited state 2**
  - $\lambda$: 298.49 nm
  - $f$: 0.059

- **Excited states 3 and 4**
  - $f$: 0

- **Excited state 5**
  - $\lambda$: 276.78 nm
  - $f$: 0.1519

- **Excited state 6**
  - $\lambda$: 274.41 nm
  - $f$: 0.1249

- **Excited state 7**
  - $\lambda$: 266.68 nm
  - $f$: 0.06

- **Excited state 8**
  - $f$: 0

- **Excited state 9**
  - $\lambda$: 263.08 nm
  - $f$: 0.01

**S 19** Calculated frontier molecular orbitals by DFT and the 6th 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
THERMAL PROPERTIES

\[ T_d = 234 \]

S 20 TGA curve of SBF
S 21 TGA curve of 4-Ph-SBF
ELECTROCHEMICAL PROPERTIES

S 22 Cyclic voltammetry at 100 mV s$^{-1}$ in CH$_2$Cl$_2$/[NBu$_4$][PF$_6$] 0.2 M in presence of 4-Ph-SBF (5.2 $10^{-3}$ M) (left) or of SBF (10$^{-2}$ M) (right), ten recurrent sweeps. Platinum disk working electrode (diameter 1mm).

S 23 Cyclic voltammetry at 100 mV s$^{-1}$ in CH$_2$Cl$_2$/[NBu$_4$][PF$_6$] 0.2 M. Working electrodes: platinum disk electrode (diameter 1mm) covered with poly(4-Ph-SBF) or poly(SBF) during the ten cycles presented figure S 19.

S 24 Cyclic voltammetry at 100 mV s$^{-1}$ in CH$_2$Cl$_2$/[NBu$_4$][PF$_6$] 0.2 M in presence of 4-Ph-SBF (5.2 $10^{-3}$ M) (left) or of SBF (10$^{-2}$ M) (right), ten recurrent sweeps. Platinum disk working electrode (diameter 1mm).
**Devices Fabrication**

**Green OLED Energy Diagram**

ITO/CuPc(10 nm)/NPB (40 nm)/TCTA (10 nm)/ (4-Ph-SBF or SBF) doped with Ir(ppy)$_3$ (20 nm)/TPBI (40 nm)/LiF (1.2 nm)/Al (100 nm).

**Blue OLED Energy Diagram**

ITO/CuPc(10 nm)/NPB (40 nm)/TCTA (10 nm)/ (4-Ph-SBF or SBF) doped with FIrpic (20 nm)/TPBI (40 nm)/LiF (1.2 nm)/Al (100 nm).

Host materials: either 4-Ph-SBF (HOMO:-5.95 eV; LUMO:-1.95 eV) or SBF HOMO:-5.94 eV; LUMO:-1.89 eV). The two diagrams presented above were drawn with 4-Ph-SBF energy levels.

The HOMO/LUMO energy levels have been reported from ALDRICH for Ir(ppy)$_3$ and FIrpic and from Yang et al, Chem. Soc Rev. 2011, 40 2943-2970 for all organic compounds.
4-Ph-SBF-HMBC (C spiro)-CD$_2$Cl$_2$
COPY OF NMR SPECTRA

$1^1$H-CDCl$_3$

Solvent residual peak

Chemical structure with a Br label.
$\text{1}^{13}\text{C-CDCl}_3$

Solvent residual peak
$4$-Ph-SBF$-^1$H-CD$_2$Cl$_2$
4-Ph-SBF-$_{13}$C-CD$_2$Cl$_2$
4-Ph-SBF-DEPT-CD₂Cl₂
COPY OF MASS SPECTRA

S 26 High Resolution Mass Spectra of 4-Ph-SBF

