## Supporting Information for

## Electron-rich 4-substituted spirobifluorenes:

# Towards a new family of high triplet energy host materials for high-efficiency green and sky blue 

 phosphorescent OLEDsCassandre Quinton, ${ }^{\text {a }}$ Sébastien Thiery, ${ }^{\text {a }}$ Olivier Jeannin, ${ }^{a}$ Denis Tondelier, ${ }^{\text {b }}$ Bernard Geffroy, ${ }^{\text {b,c }}$ Emmanuel Jacques, ${ }^{\text {d }}$ Joëlle Rault-Berthelot, ${ }^{\mathrm{a}^{*}}$ Cyril Poriel ${ }^{\mathrm{a}^{*}}$
a. Institut des Sciences Chimiques de Rennes-UMR CNRS 6226-Université Rennes 135042 Rennes-France
b. LPICM, CNRS, École Polytechnique, Université Paris Saclay, 91128, Palaiseau, France
c. LICSEN, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-surYvette Cedex, France
d. UMR CNRS 6164-Institut d'Électronique et des Télécommunications de RennesDépartement Microélectronique \& Microcapteurs, Bât.11B, Université Rennes 1, Campus de Beaulieu 35042 Rennes Cedex, France

## Corresponding Author

*e-mail: cyril.poriel@univ-rennes1.fr, joelle.rault-berthelot@univ-rennes1.fr

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## Materials and methods

All manipulations of oxygen-sensitive 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. Tetrahydrofuran was purchased from Sigma Aldrich and was distilled from sodium/benzophenone prior to use. Light petroleum refers to the fraction with boiling point of $40-60^{\circ} \mathrm{C}$. Potassium carbonate and $\mathrm{N}, \mathrm{N}$-dimethylformamid were purchased from Sigma Aldrich. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) and 3,4,5trimethoxyphenylboronic acid were purchased from Fluorochem. 4-(9-Carbazolyl)benzeneboronic acid pinacol ester was purchased from Alfa Aesar. Compounds 4-Br-SBF ${ }^{1}$ and $4-\mathrm{Ph}^{-S B F^{2}}$ were synthetized as previously described. 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 ${ }^{\circledR}$ Rf 400 (UV detection $200-360 \mathrm{~nm}$ ), over standard silica cartridges (Redisep ${ }^{\circledR}$ Isco, GraceResolv ${ }^{\text {m }}$ Grace or Puriflash ${ }^{\circledR}$ columns Interchim). ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded using Bruker 300 MHz instruments ( ${ }^{1} \mathrm{H}$ frequency, corresponding ${ }^{13} \mathrm{C}$ frequency: 75 MHz ); chemical shifts were recorded in ppm and J values in Hz . In the ${ }^{13} \mathrm{C}$ NMR spectra, signals corresponding to $\mathrm{C}, \mathrm{CH}, \mathrm{CH}_{2}$ or $\mathrm{CH}_{3}$ groups, assigned from DEPT, are noted. 2D NMR spectra allow the complete interpretation and the numbering is in SI (Figures S45 and S47). The residual signals for the NMR solvents used are 5.32 ppm (proton) and 54.00 ppm (carbon) for $\mathrm{CD}_{2} \mathrm{Cl}_{2}$. 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 I'Ouest (CRMPO-Rennes) on Waters Q-Tof II.

## X-Ray

Crystals were picked up with a cryoloop and then frozen at 150 K under a stream of dry $\mathrm{N}_{2}$ on a APEX II Brucker AXS or a D8 VENTURE Bruker AXS diffractometer for X-ray data collection (Mo K $\alpha$ radiation, $\lambda=0.71073$ Å).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 1514247 (4-PhCz-SBF) and 1514246 (4-Ph(OMe) $\mathbf{3}_{3}$-SBF). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Figures were generated with Mercury software 3.3.

## Thermal analysis

Thermal Gravimetric Analysis (TGA) was carried out at the "Institut des Sciences Analytiques" (UMR CNRS 5280) of Villeurbanne. TGA curves were measured at $10^{\circ} \mathrm{C} / \mathrm{min}$ from 0 to $600^{\circ} \mathrm{C}$ 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 $10^{\circ} \mathrm{C} / \mathrm{min}, 2$ heating/cooling cycles were successively carried out.

## Spectroscopic studies

Cyclohexane (analytical grade, VWR) and 2-methyltetrahydrofuran (analytical grade, Sigma Aldrich), 1 N solution of sulfuric acid in water (Standard solution, Alfa Aesar), and quinine sulfate dihydrate (99+\%, ACROS organics) were used without further purification.

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 $\Delta \mathrm{E}^{\mathrm{opt}}(\mathrm{eV})=\mathrm{hc} / \lambda, \lambda$ being the absorption edge (in meter). With $\mathrm{h}=$ $6.62606 \times 10^{-34} \mathrm{~J} . \mathrm{s}\left(1 \mathrm{eV}=1.60217 \times 10^{-19} \mathrm{~J}\right)$ and $\mathrm{c}=2.99792 \times 10^{8} \mathrm{~m} \cdot \mathrm{~s}^{-1}$, this equation may be simplified as: $\Delta \mathrm{E}^{\mathrm{opt}}(\mathrm{eV})=1239.84 / \lambda$ (in $n m$ ). Triplet energy level $\mathrm{E}_{\mathrm{T}}$ was calculated from the maximum of the first phosphorescence emission peak, and conversion in electron volt was obtained with the previous formula.
Molar attenuation coefficients $(\varepsilon)$ were calculated from the gradients extracted from the plots of absorbance vs concentration with five solutions of different concentrations for each sample.

$$
A=\varepsilon \times l \times C
$$

Above, $I$ and $C$ refer respectively to the pathlength and the sample concentration.
Emission spectra were recorded with a PTI spectrofluorimeter (PTI-814 PDS, MD 5020, LPS 220B) using a Xenon lamp.
Quantum yields in solution ( $\varnothing$ sol) were calculated relative to quinine sulfate ( $\varnothing \mathrm{ref}=0.546$ in $\mathrm{H}_{2} \mathrm{SO}_{4}$ 1 N ). $\varnothing$ sol was determined according to the following equation,

$$
\phi s o l=\phi r e f \times \frac{\left(\operatorname{Grad}_{S}\right)}{\left(\operatorname{Grad}_{r}\right)} \times\left(\frac{\eta_{s}}{\eta_{r}}\right)^{2}
$$

where subscripts $s$ and $r$ refer respectively to the sample and reference, Grad is the gradient from the plot of integrated fluorescence intensity vs absorbance, $\eta$ is the refracting index of the solvent ( $\eta_{s}$ $=1.426$ for cyclohexane). Five solutions of different concentration ( $\mathrm{A}<0.1$ ) of the sample and five solutions of the reference (quinine sulfate) were prepared. The integrated area of the fluorescence peak was plotted against the absorbance at the excitation wavelength for both the sample and reference. The gradients of these plots were then injected in the equation to calculate the reported quantum yield value for the sample.

Low temperature ( 77 K ) measurements were performed in 2-methyltetrahydrofuran which freezes as a transparent glassy matrix. Measurements were carried using a singleblock quartz cuvette containing the solution, which was placed in an Oxford Optistat cryostat cooled with liquid nitrogen, equipped itself with three quartz optical windows.

Thin films were prepared by spin-coating ca $300 \mu \mathrm{~L}$ of a THF solution ( $10 \mathrm{mg} / \mathrm{mL}$ ) on a sapphire plate ( $10 \mathrm{~mm} \times 10 \mathrm{~mm}$ ) at $2500 \mathrm{tr} / \mathrm{min}$ on a Süss+MicroTec Lab Spin 6/8.

IR spectra were recorded on a Bruker Vertex 70 using a diamond crystal MIRacle ATR (Pike).

## Electrochemical studies

All electrochemical experiments were performed under an argon atmosphere, using a Pt disk electrode (diameter 1 mm ), the counter electrode was a vitreous carbon rod. The reference electrodes were either a silver wire in a $0.1 \mathrm{M} \mathrm{AgNO}_{3}$ solution in $\mathrm{CH}_{3} \mathrm{CN}$ when studies are performed in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ or a silver wire covered by Agl (silver wire in $\mathrm{Bu}_{4} \mathrm{NI} 0.1 \mathrm{M}$ in DMF) when studies are
performed in DMF. Ferrocene was added to the electrolytic solutions at the end of a series of experiments. The ferrocene/ferrocenium ( $\mathrm{Fc} / \mathrm{Fc}^{+}$) 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 $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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 . $\mathrm{Fc} / \mathrm{Fc}^{+}$system. Following the work of Jenekhe, ${ }^{3}$ we estimated the electron affinity (EA) or lowest unoccupied molecular orbital (LUMO) and the ionization potential (IP) or highest occupied molecular orbital (HOMO) from the redox data. The LUMO level was calculated from: LUMO (eV) $=-\left[\mathrm{E}_{\text {onset }}{ }^{\text {red }}\right.$ (vs SCE) + 4.4] and the HOMO level from: $\mathrm{HOMO}(\mathrm{eV})=-\left[\mathrm{E}_{\text {onset }}{ }^{\mathrm{ox}}(v s \mathrm{SCE})+4.4\right]$, based on an SCE energy level of 4.4 eV relative to the vacuum. The electrochemical gap was calculated from: $\Delta \mathrm{E}^{\mathrm{el}}=|\mathrm{HOMO}-\mathrm{LUMO}|$ (in eV ).

## Theoretical modelling

Calculations were carried out with the Gaussian 09 software on the OCCIGEN calculator of the Centre Informatique National de l'Enseignement Supérieur (CINES (Montpellier) under project c2016085032). Molecules were drawn and figures were generated with the GaussView 5.0 software.

Full geometry optimization of the ground state (SO) and frequency calculation were performed with Density Functional Theory (DFT) ${ }^{4,5}$ CAM-B3LYP implemented in the Gaussian 09 (Revision B.01) program suite ${ }^{6}$ using the $6-31 \mathrm{G}(\mathrm{d})$ basis set and the default convergence criterion implemented in the program.

Geometry optimization of the first excited triplet state (T1) was performed using Time-Dependent Density Functional Theory (TD-DFT) calculations using the CAM-B3LYP functional and the 6-311+G(d,p) basis set.

Transition diagrams were obtained through TD-DFT calculations performed using the B3LYP, PBEO, CAM-B3LYP and M06-2X functionals and the extended 6-311+G(d,p) basis set on the geometry of S0.

Spin density (SD) representation was obtained through TD-DFT calculations performed using the CAM-B3LYP functional and the extended $6-311+G(d, p)$ basis set and a triplet spin on the previously optimized geometry of T1.

## Devices fabrication and characterization

The sky-blue dopant: bis[2-(4,6-difluorophenyl)pyridinato- $\mathrm{C}^{2}, N$ ](picolinato)iridium(III) (FIrpic) and the green dopant: tris[2-phenylpyridinato- $\left.\mathrm{C}^{2}, N\right]$ iridium (III) $\operatorname{Ir}(\mathrm{ppy})_{3}$, the hole-injection material copper(II) phthalocyanine (CuPc), the hole-transporting materials $N, N^{\prime}-\mathrm{di}\left(1\right.$-naphthyl)- $N, N^{\prime}$-diphenyl-(1, $1^{\prime}$ -biphenyl)-4, $4^{\prime}$-diamine (NPB) and $4,4^{\prime}, 4^{\prime \prime}$-tris(carbazole-9-yl)triphenylamine (TCTA) and the electron-transporting/electron-injection/hole-blocking material 1,3,5-tris(1-phenyl-1H-benzimidazol-2yl )benzene ( TPBi ) were commercially available. Commercial indium tin oxide (ITO) coated glass was used as the starting substrates. Before device fabrication, the ITO glass substrates were pre-cleaned carefully. Then the sample was transferred to the deposition system and each layer was sequentially evaporated: CuPc (10 nm), NPB ( 40 nm ), TCTA (10 nm), emissive layer (EML, 20 nm ), TPBi ( 40 nm ) and, finally, a cathode composed of 1.2 nm of lithium fluoride and 100 nm of aluminum. In the deposition of the EML, the host and guest were placed into different evaporator sources.

Thermal properties


Figure S 1. DSC curves of 4-PhCz-SBF (left) and of 4-Ph(OMe) ${ }_{3}$-SBF (right)

## Electrochemistry



Figure S 2. Cyclic voltammetry at $100 \mathrm{mVs}^{-1}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2} /\left[\mathrm{NBu}_{4}\right]\left[\mathrm{PF}_{6}\right] 0.2 \mathrm{M}$ in the presence of 4-PhCz-SBF (red line) and of $4-\mathrm{Ph}(\mathrm{OMe})_{3}-\mathrm{SBF}$ (blue line).


Figure S 3 . Differential pulse voltammetry in $\mathrm{CH}_{2} \mathrm{Cl}_{2} /\left[\mathrm{NBu}_{4}\right]\left[\mathrm{PF}_{6}\right] 0.2 \mathrm{M}$ in the presence of 4- $\mathrm{Ph}(\mathrm{OMe})_{3}-\mathrm{SBF}$ (left, blue line) and of 4-PhCz-SBF (right, red line)


Figure S 4. Cyclic voltammetry at $100 \mathrm{mVs}^{-1}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2} /\left[\mathrm{NBu}_{4}\right]\left[\mathrm{PF}_{6}\right] 0.2 \mathrm{M}$ in the presence of $\left.\mathbf{P h ( O M e )}\right)_{3}$ ( $2.510^{-3} \mathrm{M}$ ): reduction (left) and oxidation (right).


Figure S5. Cyclic voltammetry at $100 \mathrm{mVs}^{-1}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2} /\left[\mathrm{NBu}_{4}\right]\left[\mathrm{PF}_{6}\right] 0.2 \mathrm{M}$ in the presence of $\mathrm{N}-\mathrm{PhCz}\left(2.510^{-3} \mathrm{M}\right)$ : reduction (left) and oxidation (right).

Table S 1. Energy levels of the frontier orbitals of 4-Ph(OMe) $)_{3}-\mathrm{SBF}, 4-\mathrm{PhCz}-\mathrm{SBF}, \mathrm{Ph}(\mathrm{OMe})_{3}$ and $\mathrm{N}-\mathrm{PhCz}$ obtained by electrochemical measurements in DCM

|  | 4-Ph(OMe) $\mathbf{3}^{-}$-SBF | 4-PhCz-SBF | Ph(OMe) $\mathbf{3}_{3}$ | N-PhCz |
| :--- | :--- | :--- | :--- | :--- |
| LUMO (eV) | -1.91 | -1.97 | -1.9 | -1.9 |
| HOMO (eV) | -5.62 | -5.52 | -5.66 | -5.59 |
| Energy gap (eV) | 3.7 | 3.6 | 3.8 | 3.7 |



Figure S 6. Cyclic voltammetry at $100 \mathrm{mVs}^{-1}$ in DMF/[ $\left.\mathrm{NBu}_{4}\right]\left[\mathrm{PF}_{6}\right] 0.2 \mathrm{M}$ in the presence of 4-Ph-SBF (black), 4-$\mathrm{Ph}(\mathrm{OMe})_{3}$-SBF (blue), 4-PhCz-SBF (red), $\mathrm{N}-\mathrm{PhCz}$ (pink)

Table S 2. LUMO levels of 4-Ph(OMe) $\mathbf{3}_{3}$-SBF, 4-PhCz-SBF, 4-Ph-SBF and N-PhCz obtained by electrochemical measurements in DMF

|  | 4-Ph(OMe) ${ }_{3}$-SBF | 4-PhCz-SBF | 4-Ph-SBF | N-PhCz |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{E}_{\text {peak potential }}{ }^{\text {red }}$ (V) | -2.57 | -2.44 | -2.55 | -2.78 |
| $E_{\text {onset }}{ }^{\text {red }}$ (V) | -2.42 | -2.30 | -2.40 | -2.65 |
| LUMO (eV) | -1.98 | -2.10 | -2.00 | -1.75 |



Figure S 7. Cyclic voltammetry at $100 \mathrm{mVs}^{-1}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2} /\left[\mathrm{NBu}_{4}\right]\left[\mathrm{PF}_{6}\right] 0.2 \mathrm{M}$ in the presence of 4-PhCz-SBF (left) and of 4-Ph(OMe) ${ }_{3}$-SBF (right).



Figure S 8. Cyclic voltammetry at $100 \mathrm{mV} . \mathrm{s}^{-1}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2} /\left[\mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right] 0.2 \mathrm{M}$. Platinum disk working electrode (diameter 1 mm ), left: electropolymerization in presence of $\mathrm{N}-\mathrm{PhCz}\left[2.510^{-3} \mathrm{M}\right], 15$ recurrent sweeps between 0.24 and 2.24 V ; right: study of the modified working electrode (previously prepared) in a monomer free solution, 3 recurrent sweeps between 240 and 1100 mV .


Figure S 9. Cyclic voltammetries (CVs) at $100 \mathrm{mV} \mathrm{s}^{-1}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2} /\left[\mathrm{NBu}_{4}\right]\left[\mathrm{PF}_{6}\right] 0.2 \mathrm{M}$. Working electrodes: platinum
 green or poly $\left(4-\mathrm{Ph}(\mathrm{OMe})_{3}-\mathrm{SBF}\right)$ in blue. Each polymer has been prepared by oxidation of its monomer solution. Each CV has been normalized towards the maximum current value.

## Structural properties



Chart S 1. Numeration of the phenyl rings for the 4-substituted-SBF derivatives
Table S 3. Reporting of the significant angles for 4-PhCz-SBF, 4-Ph(OMe) $\mathbf{3}_{\mathbf{3}}$-SBF and 4-Ph-SBF

|  | Angle (deg) <br> between $\mathrm{Ph}_{4}$ and <br> $\mathrm{Ph}_{5}$ planes | Angle (deg) <br> between $\mathrm{Ph}_{3}$ and <br> $\mathrm{Ph}_{4}$ planes | Angle (deg) <br> between $\mathrm{Ph}_{1}$ and <br> $\mathrm{Ph}_{2}$ planes | Spiro angle (deg) |
| :---: | :---: | :---: | :---: | :---: |
| 4-PhCz-SBF | 45.4 | 11.002 | 4.0 | 84.1 |
| 4-Ph(OMe)3-SBF | 78.0 | 2.7 | 3.2 | 89.4 |
| 4-Ph-SBF <br> molecule 1 | 51.2 | 12.7 | 4.2 | 88.3 |
| 4-Ph-SBF |  |  |  |  |
| molecule 2 $^{2-5.6}$ | 56.8 | 2.2 | 89.7 |  |

## 1. 4-( $N$-phenylcarbazole)-9,9'-spirobifluorene of $4-\mathrm{PhCz}-\mathrm{SBF}$

Table S 4. Crystal data and structure refinement for 4-PhCz-SBF

| Identification code | shelx |
| :---: | :---: |
| Empirical formula | $\mathrm{C}_{43} \mathrm{H}_{27} \mathrm{~N}$ |
| Formula weight | 557.65 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group <br> Unit cell dimensions | P 21/n |
|  | $\mathrm{a}=8.9157(12) \AA$ |
|  | $\mathrm{b}=13.655(2) \AA$ |
|  | $\mathrm{c}=24.229(4) \AA$ |
| Volume | 2904.4(7) ${ }^{3}$ |
| Z | 4 |
| Density (calculated) | $1.275 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.073 \mathrm{~mm}^{-1}$ |
| F(000) | 1168 |
| Crystal size | $0.09 \times 0.06 \times 0.01 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.267 to $26.402^{\circ}$. |
| Index ranges | $-11<=\mathrm{h}<=11,-16<=\mathrm{k}<=17,-30<=1<=30$ |
| Reflections collected | 30446 |
| Independent reflections | 5937 [ R ( int ) $=0.1134$ ] |
| Completeness to theta $=25.242^{\circ}$ | 99.8\% |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5937 / 0/398 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.050 |
| Final R indices [ $1>2$ sigma $(1)$ ] | $\mathrm{R} 1=0.0603, \mathrm{wR2}=0.1290$ |
| R indices (all data) | $R 1=0.1056, w R 2=0.1465$ |
| Extinction coefficient | 0.0217(16) |
| Largest diff. peak and hole | 0.482 and -0.237 e. $\AA^{-3}$ |



Figure S 10. Angle between cycles 4 and 5: $45.4^{\circ}$


Figure S 11. Angle between cycles 3 and 4: 11.2 ${ }^{\circ}$


Figure S 12. Angle between cycles 1 and 2: 4.0 ${ }^{\circ}$


Figure S 13. Angle between the two five membered cycles of the fluorene units: $84.1^{\circ}$
Some short C/C intermolecular distances are observed ( $d_{C / C=} 3.32 \AA \AA^{\prime} d_{C / C=} 3.28 \AA$, see below) in the 4-PhCz-SBF packing. These short distances are shorter than the sum of the Van der Walls radii, ie $\mathrm{d}=3.4$ Å. ${ }^{7}$


Figure S 14. Short C/C intermolecular distances in the 4-PhCz-SBF packing
Some short C/H intermolecular distances are observed ( $d_{C / H} 2.84 \AA \AA_{C / H}=2.88 \AA \AA_{C / H}=2.89 \AA$, see below) in the 4-PhCz-SBF packing. These short distances are shorter than the sum of the Van der Walls radii, ie $d=2.9 \AA \AA^{7}$


Figure S 15. Short C/H intermolecular distances in the 4-PhCz-SBF packing

## 2. 4-(3,4,5trimethoxyphenyl)-9,9'-spirobifluorene of $4-\mathrm{Ph}(\mathrm{OMe})_{3}-\mathrm{SBF}$

Table S 5. Crystal data and structure refinement for 4-Ph(OMe) $\mathbf{3}_{3}$-SBF

| Identification code | shelx |
| :---: | :---: |
| Empirical formula | $\mathrm{C}_{34} \mathrm{H}_{26} \mathrm{O}_{3}$ |
| Formula weight | 482.55 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group <br> Unit cell dimensions | P 21/c |
|  | $\mathrm{a}=9.3340(6) \AA$ |
|  | $\mathrm{b}=23.1087(16) \AA$ |
|  | $\mathrm{c}=12.5077(8)$ A |
| Volume | 2557.3(3) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.253 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.079 \mathrm{~mm}^{-1}$ |
| F(000) | 1016 |
| Crystal size | $0.25 \times 0.21 \times 0.01 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.762 to $27.510^{\circ}$. |
| Index ranges | -12<=h<=12, -29<=k<=28, -15<=\|<=16 |
| Reflections collected | 18674 |
| Independent reflections | 5853 [R(int) $=0.0294$ ] |
| Completeness to theta $=25.242^{\circ}$ | 100.0\% |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5853 / 0/337 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.041 |
| Final R indices [ $1>2$ sigma( 1 ]] | $R 1=0.0881, w R 2=0.2445$ |
| R indices (all data) | $\mathrm{R} 1=0.1252, \mathrm{wR} 2=0.2783$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 1.574 and -0.417 e. $\AA^{-3}$ |



Figure S 16. Angle between cycles 4 and 5: 78.0 ${ }^{\circ}$


Figure S 17. Angle between cycles 3 and 4: 2.7 ${ }^{\circ}$


Figure S 18. Angle between cycles 1 and 2: 3.2 ${ }^{\circ}$


Figure S 19. Angle between the two five membered cycles of the fluorene units: $89.4^{\circ}$
Some short C/H intermolecular distances are observed ( $\mathrm{d}_{\mathrm{C} / \mathrm{H}=2.64} \AA \mathrm{~A}_{\mathrm{C} / \mathrm{H}}=2.72 \AA$, $\mathrm{d}_{\mathrm{C} / \mathrm{H}=2.84} \AA \mathrm{~A}_{\mathrm{C} / \mathrm{H}=2.85}$ $\AA$, $\mathrm{d}_{\mathrm{C} / H=} 2.88 \AA$, see below) in the $4-\mathrm{Ph}(\mathrm{OMe})_{3}$-SBF packing. These short distances are shorter than the sum of the Van der Walls radii, ie $d=2.9 \AA \AA^{7}$


Figure S 20. Short C/H intermolecular distances in the 4-PhCz-SBF packing
A short O/H intermolecular distances is observed ( $\mathrm{d}_{\mathrm{O} / \mathrm{H}=2.63} \AA$, see below) in the 4-Ph(OMe) $\mathbf{3}_{\mathbf{3}}$-SBF packing. This short distance is shorter than the sum of the Van der Walls radii, ie $d=2.72 \AA .{ }^{7}$


Figure S 21. Short O/H intermolecular distance in the 4-PhCz-SBF packing
A short H/H intermolecular distances is observed ( $\mathrm{d}_{\mathrm{H} / \mathrm{H}=2.28} \AA$, see below) in the 4-Ph(OMe) ${ }_{3}$-SBF packing. This short distance is shorter than the sum of the Van der Walls radii, ie d=2.4 $\AA$. ${ }^{7}$


Figure S 22. Short H/H intermolecular distance in the 4-PhCz-SBF packing

## Photophysical properties



Figure S 23. Absorption molar coefficient spectra of 4-Ph-SBF (black), 4-PhCz-SBF (red), N-PhCz (pink), 4-Ph(OMe) $\mathbf{3}^{-S B F}$ (blue) and $\mathrm{Ph}(\mathrm{OMe})_{3}$ (sky blue) in cyclohexane



Figure S 24. Normalized emission spectra of 4-Ph-SBF (black, $\lambda_{\text {exc }}=309 \mathrm{~nm}$ ), 4-PhCz-SBF (red, $\lambda_{\text {exc }}=295$ nm ), $\mathrm{N}-\mathrm{PhCz}$ (pink, $\lambda_{\mathrm{exc}}=280 \mathrm{~nm}$ ), 4-Ph(OMe) -SBF (blue, $\lambda_{\mathrm{exc}}=309 \mathrm{~nm}$ ) and $\mathrm{Ph}(\mathrm{OMe})_{3}$ (sky blue, $\lambda_{\text {exc }}=264 \mathrm{~nm}$ ) in cyclohexane

The comparison of the spectrum of 4-PhCz-SBF and the sum of spectra of $\mathbf{N}-\mathrm{PhCz}$ and $4-\mathrm{Ph}-\mathrm{SBF}$ shows a charge transfer band between 300 and 330 nm (see below).


Figure S 25. Comparison of the absorption spectrum of 4-PhCz-SBF and the sum of the absorption spectra of $\mathrm{N}-\mathrm{PhCz}$ and 4-Ph-SBF

## Information regarding the absorption spectrum of 4-PhCz-SBF

The band at 340 nm of $4-\mathrm{PhCz}-\mathrm{SBF}$ is due to a transition from the HOMO to the $\mathrm{L}+2$ orbital, both localized on the phenylcarbazole unit. It corresponds to a locally excited transition on the carbazole unit from the ground state $\left(\mathrm{S}_{0}\right)$ to a locally excited state $\left(\mathrm{S}_{\mathrm{LE}}\right)$, noted $\mathrm{T}_{1}$ on the figure 1 . In addition, the band at 325 nm is due to a transition from the HOMO (localized on the carbazole unit) to the LUMO (localized on the phenylfluorene unit). It corresponds to a charge transfer transition from the ground state $\left(\mathrm{S}_{0}\right)$ to a charge transfer state $\left(\mathrm{S}_{\mathrm{CT}}\right)$, noted $\lambda_{2}$ on the figure below. As can be seen on this figure, the smaller bandgap (in blue) corresponds to the higher wavelength $\left(\lambda_{1}\right)$. However, the excited state ( $S_{\text {LE }}$ in blue) reached by this wavelength $\left(\lambda_{1}\right)$ is higher in energy than the other one ( $\mathrm{S}_{\mathrm{CT}}$ in orange reached by $\lambda_{2}$ ) at their respective relaxed geometries. In other words, the crossing between the potential curves of $\mathrm{S}_{\mathrm{CT}}$ and $\mathrm{S}_{\mathrm{LE}}$ induces an inversion of their relative energy between the geometry at the ground state and their respective relaxed geometries. In short, the geometry of the ground state promotes the locally excited state transition compared to the charge transfer one. Furthermore, if one considers the frontier orbitals, the LUMO is localized on the accepting part (phenylfluorene unit) and the L+2 and HOMO are both localized on the carbazole unit. Due to the destabilization of the charge transfer state at the geometry of the ground state, it is hence easier to promote an electron from the HOMO localized on the carbazole unit to an orbital also localized on the carbazole unit (ie $L+2$ ) than an orbital localized on the phenylfluorene unit (ie LUMO)
cyclohexane
ethanol


Figure S 26.Potential energy curves of the $S_{0,} S_{L E}$ and $S_{C T}$ states in cyclohexane (left) and in ethanol (right)

In order to validate the hypothesis of the existence of a charge transfer state ( $\mathrm{S}_{\mathrm{CT}}$ in orange), we recorded the absorption and the emission spectra in a non-polar solvent (cyclohexane) and in a polar solvent (ethanol), as shown below). On the one hand, the absorption spectra are really similar, showing that the solvent has almost no influence on the relative energy of the three states $\left(\mathrm{S}_{0}, \mathrm{~S}_{\mathrm{LE}}\right.$, $\mathrm{S}_{\mathrm{CT}}$ ) at the geometry of the ground state. On the other hand, the emission spectra are different. They both display two bands: one is at the same wavelength ( 345 nm ) for the two solvents, the other one is bathochromically shifted for the ethanol compare to the cyclohexane (from 361 nm to 383 nm ). One explanation could be:
-the emission wavelength at $\lambda_{3}=345 \mathrm{~nm}$ comes from the $S_{L E}$ excited state (which is not influenced by the solvent, as expected)
-the emission wavelength at $\lambda_{4}$ (361 and 383 nm dependent on the solvent) comes from the $\mathrm{S}_{\mathrm{CT}}$ excited state. Note that $\lambda_{4}$ (ethanol) is higher than $\lambda_{4}$ (cyclohexane) since the charge transfer state is stabilized by a polar solvent.

Thus, there is a charge transfer state (in orange) which is more stable than a locally excited state (in blue) in their respective relaxed geometries (due to an important geometrical reorganization of the charge transfer state). But, at the geometry of the ground state, the charge transfer state is destabilized compared to the locally excited state.


Figure S 27.Absorption (left) and emission (right) spectra of 4-PhCz-SBF in cyclohexane and ethanol
Some theoretical calculations have been performed in order to support the inversion of the energy levels of the locally excited state and the charge transfer state. On the one hand, the optimization of the first excited state at the geometry of the ground state (root=1, the one needed the weaker energy, $S_{\mathrm{LE}}$ in blue) gives $\Delta \mathrm{E}=\mathrm{E}\left(\mathrm{S}_{\mathrm{LE}}\right)-\mathrm{E}\left(\mathrm{S}_{0}\right)=4.46 \mathrm{eV}$, each state being at its respective relaxed geometry in vacuum. On the other hand, the optimization of the second excited state at the geometry of the ground state (root=2, the one needed the larger energy, $\mathrm{S}_{\mathrm{CT}}$ in orange) gives $\Delta \mathrm{E}=$ $\mathrm{E}\left(\mathrm{S}_{\mathrm{CT}}\right)-\mathrm{E}\left(\mathrm{S}_{0}\right)=4.33 \mathrm{eV}$, each state being at its respective relaxed geometry in vacuum. Thus, at their respective relaxed geometries, the charge transfer state is actually more stable than the locally excited state whereas, at the geometry of the ground state, the charge transfer state is destabilized compare to the locally excited state.

Furthermore, we can note in the figure below (left) that, as assumed above, the ground (deep blue) and the locally excited (sky blue) state are really very similar (weak reorganization). Oppositely, the geometrical reorganization between ground (deep blue) and charge transfer (orange) state is important (see figure below right).


Figure S 28.Left: Superposition of the structures obtained by molecular modelling of the SO (dark blue) and $S_{L E}$ (sky blue) states of 4-PhCz-SBF; right: Superposition of the structures obtained by molecular modelling of the $S_{O}$ (dark blue) and $S_{C T}$ (orange) states of 4-PhCz-SBF

## Molecular modelling

## Geometry optimization

The major difference between the structures obtained by X-Ray (blue) and molecular modelling (sky blue) concerns the methoxy group in para position which is impacted by an O/H intermolecular interaction in the crystal structure.


Figure S 29. Superposition of the structures obtained by X-Ray (blue) and molecular modelling (sky blue) of 4-Ph(OMe) $\mathbf{3}_{3}$-SBF


Figure S 30. Superposition of the structures obtained by X-Ray (red) and molecular modelling (pink) of 4-PhCz-SBF

The major difference between the structures obtained molecular modelling of the SO (sky blue) and S1 (green) states of 4-Ph(OMe) $\mathbf{3}_{\mathbf{3}}$-SBF clearly concerns the trimethoxyphenyl substituent.


Figure S 31. Superposition of the structures obtained by molecular modelling of the S0 (sky blue) and S1 (green) states of 4-Ph(OMe) ${ }_{3}$-SBF

The structures obtained molecular modelling of the S0 (pink) and S1 (orange) states of 4-PhCz-SBF are really similar, showing the high rigidity of 4-PhCz-SBF.


Figure S 32. Superposition of the structures obtained by molecular modelling of the S0 (pink) and S1 (orange) states of 4-PhCz-SBF


Figure S 33. Superposition of the structures obtained by molecular modelling of the S0 (grey) and S1 (black) states of 4-Ph-SBF

## TD-DFT

## 4-PhCz-SBF



Figure S 34. Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of $4-\mathrm{PhCz-SBF}$ obtained by TD-DFT M06-2X/6-311+G(d,p), shown with an isovalue of $0.04\left[\mathrm{e} \mathrm{bohr}^{-3}\right]^{1 / 2}$. For clarity purpose, only the main contribution of each transition is shown.

Table S 6. TD-DFT M06-2X/6-311+G(d,p) of 4-PhCz-SBF

| $\begin{aligned} & \hline \lambda \\ & (\mathrm{nm}) \end{aligned}$ | Oscillator strength | Major contribs |
| :---: | :---: | :---: |
| 287 | 0.05 | HOMO $\rightarrow$ L+2 (84\%) |
| 278 | 0.43 | HOMO $\rightarrow$ LUMO (54\%) |
| 268 | 0.12 | H-3 $\rightarrow$ LUMO (10\%), H-1 $\rightarrow$ LUMO (49\%) |
| 263 | 0.17 | H-1 $\rightarrow$ L+1 (65\%) |
| 261 | 0.09 | $\mathrm{HOMO} \rightarrow \mathrm{L}+3$ (39\%) |
| 258 | 0.13 | $\mathrm{H}-2 \rightarrow \mathrm{~L}+2$ (68\%) |
| 255 | 0.06 | $\mathrm{H}-3 \rightarrow \mathrm{~L}+3$ (13\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (27\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+4$ (10\%) |
| 252 | 0.08 | $\mathrm{H}-3 \rightarrow \mathrm{~L}+5$ (14\%), H-1 $\rightarrow \mathrm{L}+1$ (11\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+5$ (50\%) |
| 243 | 0.02 | H-5 $\rightarrow$ LUMO (33\%) |
| 238 | 0.004 | $\mathrm{H}-6 \rightarrow \mathrm{~L}+1$ (48\%) |
| 237 | 0.06 | H-4 $\rightarrow$ LUMO (12\%), H-3 $\rightarrow$ LUMO (39\%), H-1 $\rightarrow$ L+3 (15\%) |
| 236 | 0.06 | $\mathrm{H}-2 \rightarrow \mathrm{LUMO}$ (30\%), HOMO $\rightarrow$ L+14 (10\%) |
| 233 | 0.002 | $\begin{aligned} & \mathrm{HOMO} \rightarrow \mathrm{~L}+4(24 \%), \mathrm{HOMO} \rightarrow \mathrm{~L}+6(22 \%), \mathrm{HOMO} \rightarrow \mathrm{~L}+7 \text { (11\%), HOMO } \rightarrow \mathrm{L}+8 \\ & (12 \%) \end{aligned}$ |
| 227 | 0.01 | H-3 $\rightarrow$ LUMO (14\%), HOMO $\rightarrow$ LUMO (23\%), HOMO $\rightarrow$ L+3 (10\%), HOMO $\rightarrow$ L+4 (13\%) |
| 227 | 0.08 | $\mathrm{H}-3 \rightarrow \mathrm{~L}+1$ (66\%) |
| 226 | 0.27 | $\mathrm{H}-2 \rightarrow \mathrm{LUMO}$ (25\%), HOMO $\rightarrow$ L+14 (14\%) |
| 224 | 0.21 | $\mathrm{H}-3 \rightarrow \mathrm{~L}+3$ (18\%), $\mathrm{H}-1 \rightarrow \mathrm{LUMO}$ (13\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (11\%) |
| 222 | 0.18 | $\mathrm{H}-4 \rightarrow \mathrm{LUMO}$ (20\%), H-3 $\rightarrow$ L+4 (19\%) |



Figure S 35. Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of 4-PhCz-SBF obtained by TD-DFT CAM-B3LYP/6-311+G(d,p), shown with an isovalue of $0.04\left[\mathrm{e} \text { bohr } \mathrm{r}^{-3}\right]^{1 / 2}$. For clarity purpose, only the main contribution of each transition is shown.

Table S 7. TD-DFT CAM-B3LYP/6-311+G(d,p) of 4-PhCz-SBF

| $\lambda(\mathrm{nm})$ | Oscillator strength | Major contribs |
| :---: | :---: | :---: |
| 288 | 0.06 | $\mathrm{HOMO} \rightarrow \mathrm{L}+2$ (85\%) |
| 275 | 0.38 | $\mathrm{H}-3 \rightarrow$ LUMO (11\%), H-1 $\rightarrow$ LUMO (20\%), HOMO $\rightarrow$ LUMO (38\%) |
| 267 | 0.19 | H-1 $\rightarrow$ LUMO (35\%), HOMO $\rightarrow$ LUMO (17\%) |
| 265 | 0.18 | $\mathrm{H}-3 \rightarrow \mathrm{~L}+1$ (12\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+1$ (64\%) |
| 261 | 0.17 | $\mathrm{H}-2 \rightarrow \mathrm{~L}+2$ (72\%) |
| 259 | 0.06 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (12\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+3$ (29\%) |
| 255 | 0.03 | $\mathrm{H}-3 \rightarrow \mathrm{~L}+3$ (10\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (19\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+5$ (23\%) |
| 254 | 0.06 | $\mathrm{H}-3 \rightarrow \mathrm{~L}+4$ (15\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+4$ (45\%) |
| 245 | 0.01 | H-5 $\rightarrow$ LUMO (34\%) |
| 240 | 0.004 | $\mathrm{H}-6 \rightarrow \mathrm{~L}+1$ (47\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+9$ (11\%) |
| 237 | 0.08 | $\mathrm{H}-7 \rightarrow \mathrm{~L}+2$ (12\%), H-2 $\rightarrow$ LUMO (16\%), HOMO $\rightarrow \mathrm{L}+13$ (22\%) |
| 234 | 0.08 | $\mathrm{H}-4 \rightarrow \mathrm{LUMO}$ (17\%), H-3 $\rightarrow$ LUMO (38\%), H-1 $\rightarrow$ L+3 (20\%) |
| 225 | 0.04 | $\mathrm{H}-3 \rightarrow \mathrm{~L}+1$ (21\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+6$ (13\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+8$ (10\%) |
| 225 | 0.05 | H-3 $\rightarrow$ L+1 (39\%) |
| 223 | 0.29 | $\mathrm{H}-2 \rightarrow \mathrm{LUMO}$ (31\%), HOMO $\rightarrow$ L+13 (20\%) |
| 222 | 0.06 | H-3 $\rightarrow$ LUMO (15\%), H-1 $\rightarrow$ LUMO (13\%), HOMO $\rightarrow$ LUMO (14\%) |
| 220 | 0.23 | $\mathrm{H}-3 \rightarrow \mathrm{~L}+3$ (25\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (10\%) |
| 220 | 0.17 | $\mathrm{H}-4 \rightarrow \mathrm{LUMO}$ (12\%), H-3 $\rightarrow$ L+5 (11\%) |



Figure S 36. Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of 4-PhCz-SBF obtained by TD-DFT PBEO/6-311+G(d,p), shown with an isovalue of 0.04 [e bohr $\left.\mathrm{e}^{-3}\right]^{1 / 2}$. For clarity purpose, only the main contribution of each transition is shown.

Table S 8. TD-DFT PBEO/6-311+G(d,p) of 4-PhCz-SBF

| $\lambda(\mathrm{nm})$ | Oscillator strength | Major contribs |
| :---: | :---: | :---: |
| 317 | 0.20 | HOMO $\rightarrow$ LUMO (87\%) |
| 307 | 0.10 | HOMO $\rightarrow$ L+2 (86\%) |
| 295 | 0.03 | $\mathrm{H}-1 \rightarrow \mathrm{LUMO}$ (60\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+3$ (21\%) |
| 292 | 0.04 | $\mathrm{H}-1 \rightarrow \mathrm{LUMO}$ (27\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+3$ (44\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+5$ (18\%) |
| 284 | 0.08 | H-1 $\rightarrow$ L+1 (80\%) |
| 279 | 0.008 | H-2 $\rightarrow$ LUMO (82\%) |
| 279 | 0.01 | $\mathrm{HOMO} \rightarrow \mathrm{L}+1$ (91\%) |
| 278 | 0.04 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (17\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+3$ (10\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+5$ (55\%) |
| 273 | 0.007 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (56\%), HOMO $\rightarrow \mathrm{L}+5$ (15\%) |
| 272 | 0.06 | $\mathrm{H}-3 \rightarrow \mathrm{LUMO}$ (74\%), $\mathrm{H}-2 \rightarrow \mathrm{~L}+2$ (12\%) |
| 272 | 0.13 | $\mathrm{H}-3 \rightarrow$ LUMO (17\%), $\mathrm{H}-2 \rightarrow \mathrm{~L}+2$ (51\%), HOMO $\rightarrow$ L+8 (18\%) |
| 269 | 0.01 | H-1 $\rightarrow$ L+4 (77\%) |
| 260 | 0.11 | H-3 $\rightarrow$ L+1 (86\%) |
| 259 | 0.05 | $\mathrm{H}-3 \rightarrow \mathrm{~L}+3$ (27\%), HOMO $\rightarrow$ L+6 (17\%) |
| 258 | 0.00 | $\mathrm{H}-2 \rightarrow \mathrm{~L}+3$ (76\%), H-2 $\rightarrow \mathrm{L}+5$ (13\%) |
| 257 | 0.007 | HOMO $\rightarrow$ L+4 (77\%) |
| 256 | 0.05 | $\mathrm{H}-5 \rightarrow \mathrm{LUMO}$ (40\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+5$ (13\%) |
| 255 | 0.004 | HOMO $\rightarrow$ L+6 (63\%) |



Figure S 37. Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of 4-PhCz-SBF obtained by TD-DFT B3LYP/6-311+G(d,p), shown with an isovalue of $0.04\left[\mathrm{e} \text { bohr } \mathrm{r}^{-3}\right]^{1 / 2}$. For clarity purpose, only the main contribution of each transition is shown.

Table S 9. TD-DFT B3LYP/6-311+G(d,p) of 4-PhCz-SBF

| Wavelength (nm) | Oscillator strength | Major contribs |
| :---: | :---: | :---: |
| 332 | 0.18 | HOMO $\rightarrow$ LUMO (93\%) |
| 316 | 0.07 | HOMO $\rightarrow$ L+2 (86\%) |
| 308 | 0.01 | $\mathrm{H}-1 \rightarrow \mathrm{LUMO}$ (27\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+3$ (53\%) |
| 304 | 0.05 | $\mathrm{H}-1 \rightarrow \mathrm{LUMO}$ (63\%), HOMO $\rightarrow$ L+3 (20\%) |
| 299 | 0.003 | HOMO $\rightarrow$ L+1 (92\%) |
| 294 | 0.002 | H-2 $\rightarrow$ LUMO (93\%) |
| 293 | 0.07 | H-1 $\rightarrow$ L+1 (81\%) |
| 291 | 0.06 | $\mathrm{HOMO} \rightarrow \mathrm{L}+3$ (10\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+5$ (75\%) |
| 284 | 0.004 | $\mathrm{H}-3 \rightarrow \mathrm{LUMO}$ (16\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (58\%) |
| 282 | 0.09 | $\mathrm{H}-3 \rightarrow \mathrm{LUMO}$ (75\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (16\%) |
| 279 | 0.08 | $\mathrm{H}-2 \rightarrow \mathrm{~L}+2$ (66\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+8$ (24\%) |
| 277 | 0.002 | H-1 $\rightarrow$ L+4 (78\%) |
| 274 | 0.002 | $\mathrm{HOMO} \rightarrow \mathrm{L}+4$ (87\%) |
| 272 | 0.0003 | H-2 $\rightarrow$ L+3 (80\%) |
| 270 | 0.06 | $\mathrm{H}-3 \rightarrow \mathrm{~L}+3$ (17\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+6$ (45\%) |
| 270 | 0.11 | H-3 $\rightarrow$ L+1 (79\%) |
| 269 | 0.0001 | H-2 $\rightarrow$ L+1 (99\%) |
| 268 | 0.01 | H-3 $\rightarrow$ L+3 (29\%), H-1 $\rightarrow$ L+5 (10\%), HOMO $\rightarrow$ L+6 (36\%) |

## 4-Ph(OMe) ${ }_{3}$-SBF



Figure S 38. Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of 4-Ph(OMe) $\mathbf{3}^{-S B F}$ obtained by TD-DFT M06-2X/6-311+G(d,p), shown with an isovalue of $0.04\left[\mathrm{e} \text { bohr } \mathrm{r}^{-3}\right]^{1 / 2}$. For clarity purpose, only the main contribution of each transition is shown.

Table S 10. TD-DFT M06-2X/6-311+G(d,p) of 4-Ph(OMe) ${ }_{3}$-SBF

| $\lambda(\mathrm{nm})$ | Oscillator strength | Major contribs |
| :---: | :---: | :---: |
| 267 | 0.20 | HOMO $\rightarrow$ LUMO (70\%) |
| 264 | 0.17 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+1$ (33\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+1$ (38\%) |
| 258 | 0.08 | $\mathrm{H}-1 \rightarrow$ LUMO (22\%), HOMO $\rightarrow$ LUMO (11\%), HOMO $\rightarrow$ L+2 (33\%) |
| 252 | 0.07 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (24\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+3$ (25\%) |
| 246 | 0.09 | $\mathrm{H}-3 \rightarrow$ LUMO (12\%), H-1 $\rightarrow$ LUMO (23\%), HOMO $\rightarrow$ L+2 (19\%) |
| 245 | 0.08 | H-3 $\rightarrow$ LUMO (24\%), H-2 $\rightarrow$ LUMO (11\%), H-1 $\rightarrow$ LUMO (10\%) |
| 240 | 0.05 | $\mathrm{H}-5 \rightarrow$ LUMO (20\%), H-1 $\rightarrow$ LUMO (17\%), HOMO $\rightarrow$ L+2 (10\%) |
| 238 | 0.005 | H-6 $\rightarrow$ L+1 (45\%) |
| 229 | 0.09 | $\mathrm{H}-2 \rightarrow \mathrm{~L}+1$ (40\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+1$ (12\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+1$ (31\%) |
| 227 | 0.14 | $\mathrm{H}-2 \rightarrow \mathrm{LUMO}$ (53\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+2$ (16\%) |
| 224 | 0.14 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+2$ (52\%) |
| 222 | 0.03 | $\mathrm{H}-3 \rightarrow \mathrm{LUMO}$ (12\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+3$ (17\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+4$ (13\%) |
| 221 | 0.07 | $\mathrm{H}-2 \rightarrow \mathrm{~L}+3$ (17\%), HOMO $\rightarrow$ L+3 (23\%), HOMO $\rightarrow$ L+4 (12\%) |
| 219 | 0.03 | $\mathrm{H}-3 \rightarrow$ LUMO (26\%), HOMO $\rightarrow$ L+4 (32\%) |
| 217 | 0.004 | $\mathrm{H}-2 \rightarrow \mathrm{~L}+2$ (12\%), H-1 $\rightarrow \mathrm{L}+4$ (14\%) |
| 215 | 0.02 | $\mathrm{H}-2 \rightarrow \mathrm{~L}+2$ (16\%) |
| 214 | 0.03 | $H-5 \rightarrow L+1$ (10\%), $\mathrm{H}-4 \rightarrow \mathrm{~L}+1$ (25\%), $\mathrm{H}-2 \rightarrow \mathrm{~L}+1$ (12\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+1$ (16\%) |
| 213 | 0.002 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+4$ (11\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+6$ (17\%), HOMO $\rightarrow$ L+6 (10\%) |

## 4-Ph-SBF



Figure S 39. Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of 4-Ph-SBF obtained by TD-DFT M06-2X/6-311+G(d,p), shown with an isovalue of $0.04\left[\mathrm{e} \text { bohr } \mathrm{r}^{-3}\right]^{1 / 2}$. For clarity purpose, only the main contribution of each transition is shown.

Table S 11. TD-DFT M06-2X/6-311+G(d,p) of 4-Ph-SBF

| $\lambda(\mathrm{nm})$ | Oscillator strength | Major contribs |
| :---: | :---: | :---: |
| 267 | 0.17 | H-1 $\rightarrow$ LUMO (10\%), HOMO $\rightarrow$ LUMO (67\%) |
| 264 | 0.18 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+1$ (15\%), HOMO $\rightarrow \mathrm{L}+1$ (60\%) |
| 256 | 0.09 | $\mathrm{H}-1 \rightarrow$ LUMO (13\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+2$ (15\%), HOMO $\rightarrow$ L+2 (42\%) |
| 252 | 0.08 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (19\%), HOMO $\rightarrow$ L+3 (45\%) |
| 243 | 0.05 | $\mathrm{H}-3 \rightarrow$ LUMO (29\%), H-2 $\rightarrow$ LUMO (17\%) |
| 238 | 0.005 | H-4 $\rightarrow$ L+1 (48\%) |
| 236 | 0.11 | $\mathrm{H}-2 \rightarrow$ LUMO (10\%), $\mathrm{H}-1 \rightarrow$ LUMO (45\%), HOMO $\rightarrow$ L+2 (18\%) |
| 231 | 0.004 | H-5 $\rightarrow$ LUMO (15\%) |
| 228 | 0.11 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+1$ (64\%), $\mathrm{HOMO} \rightarrow \mathrm{L}+1$ (16\%) |
| 222 | 0.11 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+2$ (33\%), HOMO $\rightarrow$ LUMO (13\%), HOMO $\rightarrow$ L+2 (19\%) |
| 221 | 0.17 | $\mathrm{H}-2 \rightarrow$ LUMO (40\%), H-1 $\rightarrow$ LUMO (17\%), H-1 $\rightarrow$ L+2 (17\%) |
| 220 | 0.10 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (33\%), HOMO $\rightarrow$ L+3 (34\%) |
| 217 | 0.007 | $\mathrm{HOMO} \rightarrow \mathrm{L}+4$ (63\%) |
| 213 | 0.008 | $\mathrm{H}-1 \rightarrow \mathrm{~L}+4$ (22\%), HOMO $\rightarrow$ L+5 (31\%) |
| 212 | 0.04 | $\mathrm{H}-2 \rightarrow \mathrm{~L}+1$ (44\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+3$ (12\%), $\mathrm{H}-1 \rightarrow \mathrm{~L}+4$ (10\%) |
| 211 | 0.17 | $\mathrm{H}-3 \rightarrow \mathrm{~L}+2$ (13\%), $\mathrm{H}-2 \rightarrow \mathrm{~L}+2$ (24\%), HOMO $\rightarrow$ L+9 (16\%) |
| 209 | 0.48 | $\mathrm{H}-3 \rightarrow$ LUMO (28\%), HOMO $\rightarrow$ L+6 (19\%), HOMO $\rightarrow$ L+9 (10\%) |
| 208 | 0.008 | H-4 $\rightarrow$ LUMO (24\%), HOMO $\rightarrow$ L+6 (11\%) |

## Atomic coordinates

Table S 12. Atomic coordinates of 4-PhCz-SBF at the fundamental state after geometry optimization

| Atom | X | Y | Z |
| :---: | :---: | :---: | :---: |
| C | 5.505106 | -3.104318 | -1.746889 |
| C | 6.849526 | -2.795544 | -1.547419 |
| C | 7.218466 | -1.618584 | -0.903851 |
| C | 6.222237 | -0.755786 | -0.462802 |
| C | 4.872703 | -1.068477 | -0.664127 |
| C | 4.506263 | -2.239588 | -1.304914 |
| C | 6.304155 | 0.535302 | 0.234947 |
| C | 5.004227 | 1.004996 | 0.456183 |
| C | 3.973318 | 0.025289 | -0.095073 |
| C | 7.401879 | 1.274357 | 0.65983 |
| C | 7.183971 | 2.486213 | 1.307375 |
| C | 5.888483 | 2.951756 | 1.526012 |
| C | 4.788015 | 2.211332 | 1.100022 |
| C | 2.99082 | -0.481457 | 0.951387 |
| C | 1.665058 | -0.227636 | 0.568642 |
| C | 1.693626 | 0.498475 | -0.720857 |
| C | 3.030736 | 0.641084 | -1.117111 |
| C | 3.296119 | -1.104806 | 2.147631 |
| C | 2.253493 | -1.480542 | 2.98762 |
| C | 0.935522 | -1.2448 | 2.613758 |
| C | 0.611028 | -0.629946 | 1.400206 |
| C | 0.681818 | 1.042092 | -1.509654 |
| C | 1.021202 | 1.698238 | -2.68869 |
| C | 2.351196 | 1.81857 | -3.083576 |
| C | 3.366996 | 1.290682 | -2.292232 |
| H | 5.233814 | -4.026561 | -2.251226 |
| H | 7.615995 | -3.479909 | -1.897929 |
| H | 8.267302 | -1.381635 | -0.750837 |
| H | 3.458755 | -2.480163 | -1.460679 |
| H | 8.413023 | 0.915551 | 0.491129 |
| H | 8.031033 | 3.07524 | 1.64538 |
| H | 5.735628 | 3.899811 | 2.032286 |
| H | 3.778618 | 2.57442 | 1.269249 |
| H | 4.329583 | -1.289188 | 2.42473 |
| H | 2.465206 | -1.967384 | 3.934383 |
| H | 0.127214 | -1.561399 | 3.266116 |
| H | -0.357418 | 0.964425 | -1.216848 |
| H | 0.235836 | 2.122501 | -3.306749 |
| H | 2.597323 | 2.3317 | -4.008027 |
| H | 4.407698 | 1.390888 | -2.58587 |
| C | -0.827157 | -0.45656 | 1.057281 |
| C | -1.663503 | 0.31017 | 1.870557 |
| C | -1.389557 | -1.104551 | -0.04555 |
| C | -3.0186 | 0.432594 | 1.592761 |
| H | -1.245359 | 0.814584 | 2.736143 |
| C | -2.738528 | -0.972235 | -0.341988 |
| H | -0.756513 | -1.710428 | -0.686317 |
| C | -3.56282 | -0.203346 | 0.479238 |
| H | -3.662842 | 1.016487 | 2.241489 |
| H | -3.160905 | -1.461056 | -1.21351 |


| C | -5.625157 | 1.131763 | 0.006941 |
| :--- | :--- | :--- | :--- |
| C | -5.845517 | -1.118624 | 0.016474 |
| C | -5.141847 | 2.438013 | 0.046873 |
| C | -6.977229 | 0.854242 | -0.276418 |
| C | -5.637263 | -2.491988 | 0.125971 |
| C | -7.118641 | -0.586359 | -0.26854 |
| C | -6.043077 | 3.466057 | -0.185107 |
| H | -4.096693 | 2.645256 | 0.24692 |
| C | -7.863726 | 1.905664 | -0.505303 |
| C | -6.726433 | -3.326821 | -0.073268 |
| H | -4.65958 | -2.895412 | 0.364207 |
| C | -8.19767 | -1.446981 | -0.4653 |
| C | -7.392916 | 3.207944 | -0.455331 |
| H | -5.691193 | 4.492766 | -0.158418 |
| H | -8.908387 | 1.704654 | -0.723764 |
| C | -7.995815 | -2.81452 | -0.369924 |
| H | -6.589762 | -4.400957 | 0.005535 |
| H | -9.183607 | -1.048846 | -0.68634 |
| H | -8.072378 | 4.035727 | -0.630522 |
| N | -8.826768 | -3.495704 | -0.521843 |

Number of imaginary frequencies: 0
Table S 13. Atomic coordinates of 4-Ph( $\mathrm{OMe}_{3}$ )-SBF at the fundamental state after geometry optimization

| Atom | X | Y | Z |
| :---: | :---: | :---: | :---: |
| C | 2.49169 | -0.020802 | 0.053509 |
| C | 1.405448 | -0.472243 | -0.913241 |
| C | 1.583441 | -1.034428 | -2.164337 |
| H | 2.581777 | -1.191839 | -2.561223 |
| C | 0.458015 | -1.398908 | -2.895695 |
| H | 0.569164 | -1.846384 | -3.878491 |
| C | -0.813656 | -1.180291 | -2.377831 |
| H | -1.687373 | -1.446823 | -2.964776 |
| C | -1.009603 | -0.598037 | -1.121638 |
| C | 0.127144 | -0.259769 | -0.375348 |
| C | 0.291513 | 0.291768 | 0.988043 |
| C | -0.631542 | 0.618104 | 1.979625 |
| H | -1.693782 | 0.490905 | 1.814388 |
| C | -0.170123 | 1.108206 | 3.197386 |
| H | -0.885163 | 1.363079 | 3.973733 |
| C | 1.192677 | 1.272319 | 3.433426 |
| H | 1.534218 | 1.658251 | 4.388969 |
| C | 2.119377 | 0.933567 | 2.451841 |
| H | 3.184416 | 1.0453 | 2.632617 |
| C | 1.661986 | 0.441418 | 1.241516 |
| C | 3.49997 | -1.111987 | 0.398163 |
| C | 3.265587 | -2.355339 | 0.960186 |
| H | 2.256585 | -2.66423 | 1.216808 |
| C | 4.347041 | -3.202409 | 1.191764 |
| H | 4.179602 | -4.180389 | 1.632301 |
| C | 5.642119 | -2.80511 | 0.863408 |
| H | 6.474291 | -3.476888 | 1.050369 |


| C | 5.87843 | -1.555704 | 0.298985 |
| :---: | :---: | :---: | :---: |
| H | 6.889227 | -1.249834 | 0.045164 |
| C | 4.799652 | -0.710372 | 0.067924 |
| C | 4.739645 | 0.642436 | -0.503696 |
| C | 5.744071 | 1.475622 | -0.981644 |
| H | 6.782473 | 1.157406 | -0.971161 |
| C | 5.396996 | 2.728963 | -1.475683 |
| H | 6.170058 | 3.391538 | -1.852656 |
| C | 4.065933 | 3.142134 | -1.491239 |
| H | 3.811664 | 4.123296 | -1.880145 |
| C | 3.059024 | 2.307089 | -1.012073 |
| H | 2.021827 | 2.628813 | -1.024348 |
| C | 3.403603 | 1.059911 | -0.519976 |
| C | -2.40424 | -0.352174 | -0.65865 |
| C | -2.857625 | 0.953825 | -0.473975 |
| H | -2.176976 | 1.777773 | -0.645564 |
| C | -4.174123 | 1.182792 | -0.076569 |
| C | -5.040998 | 0.106573 | 0.141268 |
| C | -4.588155 | -1.198448 | -0.071111 |
| C | -3.269372 | -1.427686 | -0.466314 |
| H | -2.900889 | -2.434047 | -0.618241 |
| C | -3.873122 | 3.535271 | -0.021052 |
| H | -3.026844 | 3.492333 | 0.674754 |
| H | -4.489159 | 4.403806 | 0.213485 |
| H | -3.491372 | 3.629045 | -1.044963 |
| C | -7.268442 | 0.516826 | -0.43446 |
| H | -7.021565 | 1.39295 | -1.044735 |
| H | -8.227274 | 0.681009 | 0.060569 |
| H | -7.338963 | -0.370569 | -1.073961 |
| C | -5.102955 | -3.51412 | -0.026194 |
| H | -4.776736 | -3.716651 | -1.053632 |
| H | -5.978974 | -4.122921 | 0.19928 |
| H | -4.293257 | -3.776025 | 0.66519 |
| 0 | -4.715417 | 2.411733 | 0.119884 |
| 0 | -6.310643 | 0.327226 | 0.594753 |
| 0 | -5.509365 | -2.173069 | 0.136405 |

Number of imaginary frequencies: 0
Table S 14. Atomic coordinates of 4-Ph-SBF at the fundamental state after geometry optimization

| Atom | $\mathbf{X}$ | $\mathbf{Y}$ | $\mathbf{Z}$ |
| :--- | :--- | :--- | :--- |
| C | -2.83005 | -3.060398 | -1.677283 |
| C | -4.155885 | -2.63208 | -1.640031 |
| C | -4.388722 | -1.406009 | -1.073062 |
| C | -3.475325 | -0.615489 | -0.544276 |
| C | -2.144548 | -1.04804 | -0.582912 |
| C | -1.814046 | -2.268082 | -1.147438 |
| C | -3.520124 | 0.701398 | 0.10715 |
| C | -2.216435 | 1.066363 | 0.463119 |
| C | -1.220857 | -0.014706 | 0.055529 |
| C | -4.588983 | 1.544677 | 0.386795 |
| C | -4.338665 | 2.754876 | 1.025666 |
| C | -3.039569 | 3.115797 | 1.379203 |
| C | -1.968031 | 2.270838 | 1.098837 |


| C | -0.126699 | 0.48028 | -0.880137 |
| :---: | :---: | :---: | :---: |
| C | 1.147635 | 0.220664 | -0.353635 |
| C | 0.97284 | -0.411023 | 0.973338 |
| C | -0.400145 | -0.557622 | 1.215093 |
| C | -0.295108 | 1.119991 | -2.094762 |
| C | 0.835945 | 1.516448 | -2.800123 |
| C | 2.103615 | 1.253528 | -2.293486 |
| C | 2.289989 | 0.593192 | -1.074914 |
| C | 1.888462 | -0.811706 | 1.944195 |
| C | 1.417517 | -1.368853 | 3.128963 |
| C | 0.052163 | -1.526962 | 3.353082 |
| C | -0.86719 | -1.116136 | 2.39238 |
| H | -2.586821 | -4.019872 | -2.123153 |
| H | -4.936066 | -3.261273 | -2.057373 |
| H | -5.523117 | -1.075928 | -1.045798 |
| H | -0.780999 | -2.601806 | -1.176699 |
| H | -5.602805 | 1.267146 | 0.113241 |
| H | -5.162952 | 3.424534 | 1.251212 |
| H | -2.861129 | 4.063547 | 1.877668 |
| H | -0.955904 | 2.551492 | 1.374833 |
| H | -1.290598 | 1.313032 | -2.482932 |
| H | 0.732435 | 2.02494 | -3.753586 |
| H | 2.981303 | 1.547514 | -2.861216 |
| H | 2.953211 | -0.692257 | 1.789523 |
| H | 2.127165 | -1.682686 | 3.888474 |
| H | -0.29701 | -1.965888 | 4.282622 |
| H | -1.934108 | -1.224328 | 2.563949 |
| C | 3.681812 | 0.310399 | -0.626836 |
| C | 4.572961 | 1.35717 | -0.383258 |
| C | 4.141789 | -1.003117 | -0.50067 |
| C | 5.887247 | 1.099576 | -0.009552 |
| H | 4.225533 | 2.381433 | -0.480082 |
| C | 5.455156 | -1.262175 | -0.129416 |
| H | 3.460342 | -1.825032 | -0.698664 |
| C | 6.331929 | -0.210874 | 0.119248 |
| H | 6.564513 | 1.926229 | 0.182629 |
| H | 5.796705 | -2.288935 | -0.039176 |
| H | 7.358218 | -0.413391 | 0.409672 |

Number of imaginary frequencies: 0
Table S 15. Atomic coordinates of 4-PhCz-SBF at the S1 state after geometry optimization (TD-DFT)

| Atom | X | Y | Z |
| :--- | :--- | :--- | :--- |
| C | 5.404635 | -3.349369 | -1.28 |
| C | 6.757888 | -3.052407 | -1.128059 |
| C | 7.161956 | -1.805341 | -0.662176 |
| C | 6.191788 | -0.860355 | -0.350445 |
| C | 4.833414 | -1.161483 | -0.503443 |
| C | 4.431889 | -2.402362 | -0.967319 |
| C | 6.312278 | 0.516219 | 0.150531 |
| C | 5.026889 | 1.049772 | 0.300797 |
| C | 3.967006 | 0.028471 | -0.099191 |


| C | 7.431965 | 1.278969 | 0.460408 |
| :---: | :---: | :---: | :---: |
| C | 7.250799 | 2.579338 | 0.920543 |
| C | 5.969855 | 3.108609 | 1.067981 |
| C | 4.847219 | 2.344181 | 0.757964 |
| C | 2.978494 | -0.297926 | 1.011003 |
| C | 1.656038 | -0.087663 | 0.591922 |
| C | 1.694916 | 0.448722 | -0.787296 |
| C | 3.034032 | 0.511074 | -1.197891 |
| C | 3.276764 | -0.739083 | 2.287372 |
| C | 2.230853 | -0.97182 | 3.173901 |
| C | 0.915816 | -0.782827 | 2.766584 |
| C | 0.598104 | -0.355732 | 1.472563 |
| C | 0.692782 | 0.900147 | -1.644076 |
| C | 1.042324 | 1.381266 | -2.901698 |
| C | 2.373641 | 1.419171 | -3.308557 |
| C | 3.380408 | 0.98593 | -2.451095 |
| H | 5.105911 | -4.326955 | -1.645393 |
| H | 7.503648 | -3.801328 | -1.376194 |
| H | 8.21754 | -1.57772 | -0.546074 |
| H | 3.377539 | -2.633965 | -1.086345 |
| H | 8.431995 | 0.871015 | 0.346023 |
| H | 8.115459 | 3.188082 | 1.166395 |
| H | 5.845749 | 4.125511 | 1.427038 |
| H | 3.849269 | 2.757287 | 0.871483 |
| H | 4.308138 | -0.893206 | 2.58945 |
| H | 2.437535 | -1.313534 | 4.183092 |
| H | 0.10478 | -0.995331 | 3.456577 |
| H | -0.347378 | 0.888762 | -1.344433 |
| H | 0.264354 | 1.73365 | -3.571941 |
| H | 2.627905 | 1.795763 | -4.294394 |
| H | 4.422391 | 1.026548 | -2.754141 |
| C | -0.837665 | -0.243471 | 1.104259 |
| C | -1.698558 | 0.575936 | 1.839599 |
| C | -1.377056 | -1.006794 | 0.063435 |
| C | -3.05052 | 0.648179 | 1.54134 |
| H | -1.298766 | 1.167369 | 2.657068 |
| C | -2.726804 | -0.950032 | -0.241879 |
| H | -0.724309 | -1.651152 | -0.516475 |
| C | -3.571148 | -0.117216 | 0.496809 |
| H | -3.713411 | 1.276347 | 2.125017 |
| H | -3.133898 | -1.532248 | -1.060441 |
| C | -5.667987 | 1.131213 | 0.005686 |
| C | -5.781604 | -1.159614 | 0.02226 |
| C | -5.219385 | 2.438687 | 0.019718 |
| C | -7.018939 | 0.760955 | -0.288537 |
| C | -5.491136 | -2.502665 | 0.173812 |


| C | -7.089048 | -0.661724 | -0.280302 |
| :--- | :--- | :--- | :--- |
| C | -6.169183 | 3.45953 | -0.228023 |
| H | -4.178321 | 2.680196 | 0.196831 |
| C | -7.942779 | 1.788797 | -0.529462 |
| C | -6.544508 | -3.427241 | -0.028323 |
| H | -4.500711 | -2.841512 | 0.452674 |
| C | -8.116748 | -1.595852 | -0.477781 |
| C | -7.496072 | 3.121071 | -0.491001 |
| H | -5.858598 | 4.497342 | -0.218375 |
| H | -8.98053 | 1.564658 | -0.750058 |
| C | -7.819875 | -2.963833 | -0.349557 |
| H | -6.355568 | -4.489049 | 0.073978 |
| H | -9.124221 | -1.273564 | -0.716387 |
| H | -8.213741 | 3.914068 | -0.681421 |
| H | -8.619194 | -3.683975 | -0.499989 |
| N | -4.945713 | -0.051662 | 0.188882 |

Table S 16. Atomic coordinates of 4-Ph(OMe) $\mathbf{3}^{-S B F}$ at the S 1 state after geometry optimization (TDDFT)

| Atom | $\mathbf{X}$ | $\mathbf{Y}$ | $\mathbf{Z}$ |
| :--- | :--- | :--- | :--- |
| C | -2.451146 | 0.116466 | 0.064554 |
| C | -1.392629 | 1.072924 | -0.477221 |
| C | -1.555683 | 2.168284 | -1.272073 |
| H | -2.533962 | 2.450454 | -1.647424 |
| C | -0.411754 | 2.976648 | -1.562758 |
| H | -0.536795 | 3.86332 | -2.176219 |
| C | 0.840872 | 2.629998 | -1.127929 |
| H | 1.688339 | 3.225148 | -1.451177 |
| C | 1.07847 | 1.435108 | -0.389493 |
| C | -0.119812 | 0.7384 | 0.066895 |
| C | -0.304206 | -0.179232 | 1.132985 |
| C | 0.585829 | -0.653838 | 2.134445 |
| H | 1.573963 | -0.225817 | 2.242766 |
| C | 0.125119 | -1.61978 | 3.023289 |
| H | 0.792504 | -1.992221 | 3.795444 |
| C | -1.18455 | -2.090621 | 2.968831 |
| H | -1.519052 | -2.837424 | 3.682013 |
| C | -2.09685 | -1.568444 | 2.029994 |
| H | -3.129839 | -1.903242 | 2.022573 |
| C | -1.662926 | -0.618695 | 1.142469 |
| C | -3.717471 | 0.78422 | 0.579369 |
| C | -3.843719 | 1.746912 | 1.566714 |
| H | -2.96726 | 2.124804 | 2.08448 |
| C | -5.114454 | 2.221399 | 1.883606 |
| H | -5.229891 | 2.975977 | 2.655522 |


| C | -6.239176 | 1.735885 | 1.218314 |
| :--- | :--- | :--- | :--- |
| H | -7.222667 | 2.115965 | 1.477349 |
| C | -6.113361 | 0.77 | 0.224985 |
| H | -6.99222 | 0.395854 | -0.292026 |
| C | -4.845638 | 0.296555 | -0.091803 |
| C | -4.407284 | -0.699129 | -1.079844 |
| C | -5.129622 | -1.46242 | -1.989254 |
| H | -6.210675 | -1.37783 | -2.051443 |
| C | -4.443271 | -2.339684 | -2.822956 |
| H | -4.993312 | -2.942366 | -3.539189 |
| C | -3.055925 | -2.451316 | -2.748369 |
| H | -2.535433 | -3.139138 | -3.407659 |
| C | -2.33152 | -1.687059 | -1.836317 |
| H | -1.250072 | -1.770236 | -1.77972 |
| C | -3.014199 | -0.814475 | -1.006776 |
| C | 2.381026 | 0.878606 | -0.236862 |
| C | 2.535879 | -0.539117 | -0.080966 |
| H | 1.659933 | -1.163973 | -0.159499 |
| C | 3.794413 | -1.108099 | 0.041398 |
| C | 4.940905 | -0.305232 | 0.020409 |
| C | 4.799193 | 1.10043 | -0.153636 |
| C | 3.556006 | 1.67826 | -0.285489 |
| H | 3.460265 | 2.751321 | -0.371026 |
| C | 2.895114 | -3.297529 | 0.273129 |
| H | 2.225826 | -2.997489 | 1.08617 |
| H | 3.293243 | -4.292869 | 0.471783 |
| H | 2.333063 | -3.314926 | -0.668435 |
| C | 6.704997 | -1.634036 | -0.820661 |
| H | 6.091072 | -2.526366 | -0.962783 |
| H | 7.707538 | -1.921864 | -0.500906 |
| H | 6.77086 | -1.072273 | -1.75947 |
| H | 5.924356 | 3.177009 | -0.322501 |
|  | 5.456911 | 3.45659 | -1.274166 |
|  | 6.961086 | 3.513694 | -0.313864 |
|  | -018256 | -2.440694 | 0.188434 |
|  | -0.809604 | 0.217291 |  |
|  | 1.775265 | -0.163475 |  |

Table S 17. Atomic coordinates of 4-PhCz-SBF at the T1 state after geometry optimization (TD-DFT)

| Atom | $\mathbf{X}$ | $\mathbf{Y}$ | $\mathbf{Z}$ |
| :--- | :--- | :--- | :--- |
| C | 4.390916 | -3.73032 | -0.530044 |
| C | 5.783059 | -3.789435 | -0.507388 |
| C | 6.539273 | -2.63149 | -0.354646 |
| C | 5.8814 | -1.414537 | -0.224159 |


| C | 4.482952 | -1.357851 | -0.246564 |
| :---: | :---: | :---: | :---: |
| C | 3.731232 | -2.509958 | -0.40006 |
| C | 6.401349 | -0.050791 | -0.051631 |
| C | 5.317561 | 0.831703 | 0.032106 |
| C | 3.998708 | 0.082998 | -0.08612 |
| C | 7.705081 | 0.423712 | 0.031855 |
| C | 7.911842 | 1.78911 | 0.200097 |
| C | 6.831739 | 2.666237 | 0.283961 |
| C | 5.525035 | 2.190573 | 0.200114 |
| C | 3.052094 | 0.264101 | 1.095286 |
| C | 1.689148 | 0.5026 | 0.599339 |
| C | 1.752868 | 0.767381 | -0.760892 |
| C | 3.111019 | 0.542716 | -1.237186 |
| C | 3.343674 | 0.33604 | 2.415128 |
| C | 2.277655 | 0.58326 | 3.353334 |
| C | 0.948818 | 0.686875 | 2.922832 |
| C | 0.578985 | 0.584509 | 1.58384 |
| C | 0.77196 | 1.244478 | -1.706411 |
| C | 1.138564 | 1.419522 | -3.019506 |
| C | 2.45627 | 1.16083 | -3.463237 |
| C | 3.446411 | 0.730084 | -2.548668 |
| H | 3.815444 | -4.642947 | -0.650309 |
| H | 6.282193 | -4.748045 | -0.610409 |
| H | 7.624101 | -2.682183 | -0.338278 |
| H | 2.646277 | -2.465278 | -0.418765 |
| H | 8.549763 | -0.255989 | -0.032207 |
| H | 8.924301 | 2.175403 | 0.267039 |
| H | 7.010343 | 3.728928 | 0.415449 |
| H | 4.683656 | 2.873929 | 0.266105 |
| H | 4.36295 | 0.224872 | 2.771162 |
| H | 2.500606 | 0.628747 | 4.413618 |
| H | 0.169187 | 0.757687 | 3.67493 |
| H | -0.230796 | 1.483852 | -1.377468 |
| H | 0.404297 | 1.780868 | -3.733298 |
| H | 2.7124 | 1.307933 | -4.506829 |
| H | 4.463092 | 0.555779 | -2.888253 |
| C | -0.824445 | 0.458894 | 1.199927 |
| C | -1.838636 | 1.129636 | 1.909398 |
| C | -1.223096 | -0.382137 | 0.143964 |
| C | -3.174333 | 0.963557 | 1.590442 |
| H | -1.568306 | 1.80401 | 2.715126 |
| C | -2.559281 | -0.542214 | -0.185667 |
| H | -0.469984 | -0.925032 | -0.41575 |
| C | -3.548793 | 0.126814 | 0.535621 |
| H | -3.941248 | 1.480865 | 2.15715 |
| H | -2.845245 | -1.186305 | -1.010489 |


| C | -5.810073 | 0.98879 | -0.097665 |
| :--- | :--- | :--- | :--- |
| C | -5.593681 | -1.251579 | 0.116788 |
| C | -5.589045 | 2.362609 | -0.171129 |
| C | --7.072537 | 0.429468 | -0.378434 |
| C | -5.129741 | -2.542973 | 0.35881 |
| C | -6.934299 | -1.004763 | -0.239767 |
| C | -6.662674 | 3.170988 | -0.51302 |
| H | -4.610798 | 2.786169 | 0.026167 |
| C | -8.136126 | 1.2636 | -0.719671 |
| C | -6.030201 | -3.588152 | 0.218417 |
| H | -4.102483 | -2.725659 | 0.653155 |
| C | -7.820065 | -2.072805 | -0.37487 |
| C | -7.927116 | 2.632053 | -0.782011 |
| H | -6.516185 | 4.244921 | -0.575477 |
| H | -9.114053 | 0.844396 | -0.937411 |
| C | -7.362692 | -3.361094 | -0.148542 |
| H | -5.692696 | -4.603828 | 0.400518 |
| H | -8.855605 | -1.895203 | -0.649762 |
| H | -8.746676 | 3.292868 | -1.045155 |
| H | -8.041208 | -4.201712 | -0.25138 |
| N | -4.913999 | -0.036757 | 0.202428 |

Table S 18. Atomic coordinates of 4-PhCz-SBF at the T1 state after geometry optimization (TD-DFT)

| Atom | $\mathbf{X}$ | $\mathbf{Y}$ | $\mathbf{Z}$ |
| :--- | :--- | :--- | :--- |
| C | 3.108447 | 2.74578 | -2.441057 |
| C | 4.493418 | 2.644642 | -2.55837 |
| C | 5.196377 | 1.67961 | -1.843838 |
| C | 4.492611 | 0.81771 | -1.011548 |
| C | 3.101503 | 0.921249 | -0.895087 |
| C | 2.403067 | 1.882336 | -1.605425 |
| C | 4.952363 | -0.282009 | -0.151801 |
| C | 3.839138 | -0.84552 | 0.483486 |
| C | 2.560817 | -0.130082 | 0.07346 |
| C | 6.227386 | -0.782924 | 0.083151 |
| C | 6.375789 | -1.853167 | 0.959439 |
| C | 5.266343 | -2.414005 | 1.590086 |
| C | 3.98849 | -1.911642 | 1.354726 |
| C | 1.496331 | -1.025081 | -0.551911 |
| C | 0.182402 | -0.702569 | 0.025425 |
| C | 0.374261 | 0.098371 | 1.140673 |
| C | 1.778813 | 0.477386 | 1.233105 |
| C | 1.651907 | -2.059268 | -1.411491 |
| C | 0.491393 | -2.808322 | -1.820766 |
| C | -0.791953 | -2.437405 | -1.393614 |
| C | -1.022195 | -1.364833 | -0.538243 |


| C | -0.519857 | 0.547605 | 2.183359 |
| :---: | :---: | :---: | :---: |
| C | -0.030304 | 1.354896 | 3.181854 |
| C | 1.330811 | 1.741927 | 3.225176 |
| C | 2.236507 | 1.278429 | 2.241154 |
| H | 2.574716 | 3.503786 | -3.006071 |
| H | 5.028679 | 3.325112 | -3.213498 |
| H | 6.275802 | 1.604223 | -1.938125 |
| H | 1.323654 | 1.96168 | -1.515099 |
| H | 7.094494 | -0.349924 | -0.407034 |
| H | 7.365109 | -2.256149 | 1.153522 |
| H | 5.39928 | -3.249453 | 2.270444 |
| H | 3.124166 | -2.349343 | 1.845211 |
| H | 2.633792 | -2.335965 | -1.782574 |
| H | 0.605871 | -3.630705 | -2.518288 |
| H | -1.646347 | -2.955385 | -1.817691 |
| H | -1.552546 | 0.224445 | 2.18903 |
| H | -0.697141 | 1.688157 | 3.971735 |
| H | 1.684571 | 2.380707 | 4.027183 |
| H | 3.285609 | 1.554383 | 2.292824 |
| C | -2.377034 | -0.866323 | -0.299696 |
| C | -3.467582 | -1.736872 | -0.249579 |
| C | -2.617661 | 0.51592 | -0.178903 |
| C | -4.767456 | -1.263518 | -0.086599 |
| H | -3.332984 | -2.810277 | -0.308952 |
| C | -3.906479 | 0.992385 | -0.001898 |
| H | -1.784556 | 1.20197 | -0.237311 |
| C | -5.005268 | 0.110731 | 0.039686 |
| 0 | -5.727571 | -2.222165 | 0.013375 |
| 0 | -6.266129 | 0.569846 | 0.313092 |
| 0 | -4.212431 | 2.30844 | 0.164688 |
| C | -7.021667 | -1.998425 | -0.521631 |
| H | -7.464367 | -2.98893 | -0.645647 |
| H | -7.639137 | -1.397822 | 0.147545 |
| H | -6.9662 | -1.509519 | -1.501288 |
| C | -6.860065 | 1.408878 | -0.669978 |
| H | -7.864461 | 1.635333 | -0.307896 |
| H | -6.295993 | 2.33498 | -0.793705 |
| H | -6.932294 | 0.891309 | -1.634652 |
| C | -3.147211 | 3.232825 | 0.247439 |
| H | -3.605179 | 4.200206 | 0.455719 |
| H | -2.455164 | 2.973403 | 1.05645 |
| H | -2.590972 | 3.292517 | -0.695772 |

## Device fabrication and characterization

## OLED structure:

Glass/ITO/CuPc 10 nm/NPB 40 nm/TCTA 10 nm/ Host + Dopant: 10-20\% 20 nm/TPBi 40 nm/ LiF 1.2 nm/Al 100 nm .

ITO: Indium Tin Oxide: anode
CuPc: copper phtalocyanine: hole injecting layer
NPB: $N, N^{\prime}$-di(1-naphtyl)- $N, N^{\prime}$-diphenyl-[1,10-biphenyl]-4,4'-diamine: hole transporting layer
TCTA: 4,4',4"'tris(carbazole-9-yl)triphenylamine: electron/exciton blocking layer
TPBi: 1,3,5-Tris(1-phenyl-1H-benzimidazol-2-yl)benzene: electron transport/hole blocking layer
LiF/Al: Lithium fluoride covered with aluminum is the cathode
Flrpic: bis[2-(4,6-difluorophenyl)pyridinato- $\left.\mathrm{C}^{2}, N\right]$ (picolinato)iridium(III), blue phosphorescent emitter
$\operatorname{Ir}(\mathrm{ppy})_{3}$ : tris[2-phenylpyridinato- $\mathrm{C}^{2}, N$ ]iridium(III), green phosphorescent emitter


Figure S 40. Normalized electroluminescent spectrum at $10 \mathrm{~mA} / \mathrm{cm}^{2}$ of the green device using 4$\mathbf{P h}(\mathbf{O M e})_{3}-\mathbf{S B F}$ as host doped with $\operatorname{Ir}(\mathrm{ppy})_{3}(10 \%$ in mass) as emitting layer


Figure $S$ 41. Current efficiency (CE, Cd/A, blue) and power efficiency ( $\mathrm{PE}, \mathrm{Im} / \mathrm{W}$, black) versus current density of the green device using $4-\mathrm{Ph}(\mathrm{OMe})_{3}$-SBF as host doped with $\operatorname{Ir}(\mathrm{ppy})_{3}(10 \%$ in mass) as emitting layer


Figure S 42. Normalized electroluminescent spectrum at $10 \mathrm{~mA} / \mathrm{cm}^{2}$ of the blue device using 4$\mathbf{P h}(\mathrm{OMe})_{3}$-SBF as host doped with FIrpic ( $20 \%$ in mass) as emitting layer


Figure $S$ 43. Current efficiency (CE, Cd/A, blue) and power efficiency (PE, Im/W, black) versus current density of the blue using 4-Ph(OMe) $)_{3}$-SBF as host doped with FIrpic ( $20 \%$ in mass) as emitting layer


Figure S 44. Normalized electroluminescent spectrum at $10 \mathrm{~mA} / \mathrm{cm}^{2}$ of the green device using 4-PhCz-SBF as host doped with $\operatorname{Ir}(\mathrm{ppy})_{3}$ ( $10 \%$ in mass) as emitting layer


Figure S 45. Current efficiency (CE, Cd/A, red) and power efficiency (PE, Im/W, black) versus current density of the green device using 4-PhCz-SBF as host doped with $\operatorname{Ir}(\mathrm{ppy})_{3}(10 \%$ in mass) as emitting layer


Figure S 46. Normalized electroluminescent spectrum at $10 \mathrm{~mA} / \mathrm{cm}^{2}$ of the blue device using 4-PhCzSBF as host doped with FIrpic (17\% in mass) as emitting layer


Figure S 47. Current efficiency (CE, Cd/A, red) and power efficiency (PE, Im/W, black) versus current density of the blue device using 4-PhCz-SBF as host doped with FIrpic (17\% in mass) as emitting layer


Figure S 48. JVL curves for green (top) and blue (bottom) devices using 4-PhCz-SBF and 4-Ph(OMe) $\mathbf{3}^{-}$ SBF as host

## Mobilities Determinations

Hole carrier mobility has been estimated using vertical structure with gold electrodes (work function of 5.1 eV ). The third regime (trap free region) of experimental $\mathrm{J}-\mathrm{V}^{2}$ characteristics of $\mathrm{Au} / \mathrm{OSC} / \mathrm{Au}$ devices with thickness $\mathrm{e}^{\sim} 40 \mathrm{~nm}$ shows a quadratically dependence. This behavior is characteristic for a space-charge limited current (SCLC).

We determined the hole carrier mobility using space-charge-limited current (SCLC) measurements. The mobility was extracted from the trap-free region $(\Theta=1)$ of the space-charge-limited current regime using the Mott-Gurney relation (1)
$J_{S C L C}=\frac{9}{8} \varepsilon_{0} \varepsilon_{r} \Theta \mu \frac{V^{2}}{L^{3}}$
$\Theta=\frac{n_{f}}{n_{f}+n_{t}}$
Where $\varepsilon_{\mathrm{r}}$ is the dielectric constant of the semiconductor extracted from C-V measurement, the factor $\Theta$ is the ratio between free and total charge carriers given by the relation $2, \mathrm{~V}$ is the applied voltage across a length $L$ and $J_{\text {sclc }}$ is the current density in the trap-free regime. In the relation $2 n_{f}$ and $n_{t}$ are the free and the trapped carrier density in the OSC.

The Mott-Gurney law was applied on Au-OSC SCL diode with resistivity calculated from the J-V Characteristics slope. The thickness of the OSC layer is about 40 nm . According to the very high resistivity of the OSC, the measurement was performed in dark conditions, under vacuum with a Keithley 2636A with current resolution of 1 fA and maximum applied voltage of 200 V . The hole carrier mobility has been extracted from the Mott-Gurney law (experimental J-V² slope).

Carrier density has been extracted from the J-E characteristic slope with the following relation in the linear regime and from the hole carrier mobility extracted from experimental J-V² slope.
$J_{D}=q n \mu E(3)$

## 4-PhCz-SBF

$\mathrm{T}_{\text {sub }}=135^{\circ} \mathrm{C}$ - Rate speed $=0.8 \mathrm{~A} / \mathrm{s}-\mathrm{P}=3.10^{-7} \mathrm{mbar}$


Figure S 49. $\mathbf{J}_{\mathbf{D}}=\mathbf{f}\left(\mathbf{V}^{\mathbf{2}}\right)$


Figure S $50 . \mathbf{J}_{\mathrm{D}}=\mathbf{f}(\mathbf{E})$

## 4-Ph(OMe) ${ }_{3}$-SBF

$\mathrm{T}_{\text {sub }}=105^{\circ} \mathrm{C}$ - rate Speed $=0.3 \mathrm{~A} / \mathrm{s}-\mathrm{P}=4.10^{-7} \mathrm{mbar}$


Figure $\mathrm{S} 51 . \mathbf{J}_{\mathbf{D}}=\mathbf{f}\left(\mathbf{V}^{\mathbf{2}}\right)$


Figure $\mathrm{S} 52 . \mathbf{J}_{\mathbf{D}}=\mathbf{f}(\mathbf{E})$

## NMR studies



Figure S 53. Labelling of 4-PhCz-SBF


Figure S 54. COSY NMR of 4-PhCz-SBF $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$


Figure S 55. HSQC NMR of 4-PhCz-SBF $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$


Figure S 56. HMBC NMR of 4-PhCz-SBF $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$


Figure S 57. Labelling of $4-\mathrm{Ph}(\mathrm{OMe})_{3}-\mathrm{SBF}$


Figure S 58. COSY NMR of 4-Ph(OMe) $\mathbf{3}_{\mathbf{3}} \mathbf{- S B F}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$


Figure S 59. HSQC NMR of 4- $\mathrm{Ph}(\mathrm{OMe})_{3}-\mathrm{SBF}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$


Figure S 60. HMBC NMR of 4- $\mathrm{Ph}(\mathrm{OMe})_{3}-\mathrm{SBF}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$


Figure S 61. Comparison of the chemical shift of H 3 for $4-\mathrm{PhCz}-\mathrm{SBF}$ ( 7.36 ppm , in red), 4-Ph(OMe) ${ }_{3}$-SBF (7.21, in blue), 4-Ph-SBF (7.21, in black)


Figure S 62. Comparison of the chemical shift of H1 for 4-PhCz-SBF ( 6.73 ppm , in red), 4-Ph(OMe) ${ }_{3}$-SBF ( 6.65 , in blue), 4-Ph-SBF (6.67, in black)

## Copy of NMR spectra



Figure $\mathrm{S} 63 .{ }^{1} \mathrm{H}$ NMR spectrum of 4-PhCz-SBF $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$


Figure S 64. ${ }^{13} \mathrm{C}$ NMR spectrum of 4-PhCz-SBF $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$


Figure S 65. DEPT135 spectrum of 4-PhCz-SBF $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$


Figure $\mathrm{S} 66 .{ }^{1} \mathrm{H}$ NMR spectrum of $4-\mathrm{Ph}(\mathrm{OMe})_{3}-\mathrm{SBF}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$


Figure $\mathrm{S} 67 .{ }^{13} \mathrm{C}$ NMR spectrum of $4-\mathrm{Ph}(\mathrm{OMe})_{3}-\mathrm{SBF}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$


Figure S 68 . DEPT135 spectrum of 4-Ph(OMe) $\mathbf{3}_{\mathbf{3}}$-SBF $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$

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