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 OLEDs

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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°C. Potassium carbonate and N,N-dimethylformamid were purchased from [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) Sigma Aldrich. and 3,4,5trimethoxyphenylboronic acid were purchased from Fluorochem. 4-(9-Carbazolyl)benzeneboronic acid pinacol ester was purchased from Alfa Aesar. Compounds 4-Br-SBF¹ and 4-Ph-SBF² 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® Rf 400 (UV detection 200-360nm), over standard silica cartridges (Redisep[®] Isco, GraceResolv[™] Grace or Puriflash[®] columns Interchim). ¹H and ¹³C NMR spectra were recorded using Bruker 300 MHz instruments (¹H frequency, corresponding ¹³C frequency: 75 MHz); chemical shifts were recorded in ppm and J values in Hz. In the 13 C NMR spectra, signals corresponding to C, CH, CH₂ or CH₃ 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 CD₂Cl₂. 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 (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 N₂ on a APEX II Brucker AXS or a D8 VENTURE Bruker AXS diffractometer for X-ray data collection (Mo K α radiation, λ = 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)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°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.

Spectroscopic studies

Cyclohexane (analytical grade, VWR) and 2-methyltetrahydrofuran (analytical grade, Sigma Aldrich), 1N 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 ΔE^{opt} (eV) = hc/ λ , λ being the absorption edge (in meter). With h = 6.62606x10⁻³⁴ J.s (1 eV = 1.60217x10⁻¹⁹ J) and c = 2.99792x10⁸ m.s⁻¹, this equation may be simplified as: ΔE^{opt} (eV) = 1239.84/ λ (in nm). Triplet energy level E_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 (ϵ) were calculated from the gradients extracted from the plots of absorbance *vs* concentration with five solutions of different concentrations for each sample.

$$A = \varepsilon \times l \times \ell$$

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 (ϕ sol) were calculated relative to quinine sulfate (ϕ ref = 0.546 in H₂SO₄ 1N). ϕ sol was determined according to the following equation,

$$\phi sol = \phi ref \times \frac{(Grad_S)}{(Grad_r)} \times \left(\frac{\eta_s}{\eta_r}\right)^2$$

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, η is the refracting index of the solvent (η_s = 1.426 for cyclohexane). Five solutions of different concentration (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 μ L of a THF solution (10 mg/mL) on a sapphire plate (10 mm x 10 mm) at 2500 tr/min on a Süss₊MicroTec Lab Spin 6/8.

IR spectra were recorded on a Bruker Vertex 7 0 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 M AgNO₃ solution in CH_3CN when studies are performed in CH_2Cl_2 or a silver wire covered by AgI (silver wire in Bu_4NI 0.1 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 (Fc/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 Al_2O_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. Fc/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) = -[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 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 (S0) 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 6-31G(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, PBE0, 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-C²,*N*](picolinato)iridium(III) (FIrpic) and the green dopant: tris[2-phenylpyridinato-C²,*N*]iridium(III) Ir(ppy)₃, the hole-injection material copper(II) phthalocyanine (CuPc), the hole-transporting materials *N*,*N*'-di(1-naphthyl)-*N*,*N*'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) and 4,4',4''-tris(carbazole-9-yl)triphenylamine (TCTA) and the electron-transporting/electron-injection/hole-blocking material 1,3,5-tris(1-phenyl-1*H*-benzimidazol-2-yl)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 mVs⁻¹ in CH₂Cl₂/[NBu₄][PF₆] 0.2 M in the presence of **4-PhCz-SBF** (red line) and of **4-Ph(OMe)₃-SBF** (blue line).



Figure S 3. Differential pulse voltammetry in $CH_2Cl_2/[NBu_4][PF_6]$ 0.2 M in the presence of **4-Ph(OMe)₃-SBF** (left, blue line) and of **4-PhCz-SBF** (right, red line)



Figure S 4. Cyclic voltammetry at 100 mVs⁻¹ in $CH_2Cl_2/[NBu_4][PF_6]$ 0.2 M in the presence of **Ph(OMe)**₃ (2.5 10⁻³ M): reduction (left) and oxidation (right).



Figure S 5. Cyclic voltammetry at 100 mVs⁻¹ in $CH_2CI_2/[NBu_4][PF_6]$ 0.2 M in the presence of **N-PhCz** (2.5 10⁻³ M): reduction (left) and oxidation (right).

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

| | 4-Ph(OMe) ₃ -SBF | 4-PhCz-SBF | Ph(OMe)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 mVs⁻¹ in DMF/[NBu₄][PF₆] 0.2 M in the presence of **4-Ph-SBF** (black), **4-Ph(OMe)**₃-SBF (blue), **4-PhCz-SBF** (red), **N-PhCz** (pink)

Table S 2. LUMO levels of **4-Ph(OMe)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 |
|--|----------------|------------|----------|--------|
| E _{peak potential} ^{red} (V) | -2.57 | -2.44 | -2.55 | -2.78 |
| E _{onset} ^{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 mVs⁻¹ in $CH_2Cl_2/[NBu_4][PF_6]$ 0.2 M in the presence of **4-PhCz-SBF** (left) and of **4-Ph(OMe)_3-SBF** (right).



Figure S 8. Cyclic voltammetry at 100 mV.s⁻¹ in $CH_2Cl_2/[Bu_4N][PF_6]$ 0.2 M. Platinum disk working electrode (diameter 1mm), left: electropolymerization in presence of **N-PhCz** [2.5 10⁻³ M], 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 mV s⁻¹ in $CH_2Cl_2/[NBu_4][PF_6]$ 0.2 M. Working electrodes: platinum disk electrode (diameter 1mm) covered with **poly(N-PhCz**) in black, **poly(4-PhCz-SBF)** in red, **poly(4-Ph-SBF)** in green or **poly(4-Ph(OMe)_3-SBF)** 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. Re | eporting of the | significant | angles for | 4-PhCz-SBF, | 4-Ph(OMe) ₃ -SBF | and 4-Ph-SBF |
|---------------|-----------------|-------------|------------|-------------|-----------------------------|--------------|
|---------------|-----------------|-------------|------------|-------------|-----------------------------|--------------|

| | Angle (deg) between Ph₄ and Ph₅ planes | deg)Angle (deg)Angle (deg) Ph_4 andbetween Ph_3 andbetween Ph_1 andines Ph_4 planes 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-SBF² molecule 1 51.2 | | 12.7 | 4.2 | 88.3 |
| 4-Ph-SBF² molecule 2 | 56.6 | 4.8 | 2.2 | 89.7 |

1. 4-(N-phenylcarbazole)-9,9'-spirobifluorene of 4-PhCz-SBF

| Identification code | shelx |
|-----------------------------------|---|
| Empirical formula | C ₄₃ H ₂₇ N |
| Formula weight | 557.65 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P 21/n |
| Unit cell dimensions | a = 8.9157(12) Å |
| | b = 13.655(2) Å |
| | c = 24.229(4) Å |
| Volume | 2904.4(7) Å ³ |
| Z | 4 |
| Density (calculated) | 1.275 Mg/m ³ |
| Absorption coefficient | 0.073 mm ⁻¹ |
| F(000) | 1168 |
| Crystal size | 0.09 x 0.06 x 0.01 mm ³ |
| Theta range for data collection | 2.267 to 26.402°. |
| Index ranges | -11<=h<=11, -16<=k<=17, -30<=l<=30 |
| Reflections collected | 30446 |
| Independent reflections | 5937 [R(int) = 0.1134] |
| Completeness to theta = 25.242° | 99.8% |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 5937 / 0 / 398 |
| Goodness-of-fit on F ² | 1.050 |
| Final R indices [I>2sigma(I)] | R1 = 0.0603, wR2 = 0.1290 |
| R indices (all data) | R1 = 0.1056, wR2 = 0.1465 |
| Extinction coefficient | 0.0217(16) |
| Largest diff. peak and hole | 0.482 and -0.237 e.Å ⁻³ |

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



Figure S 10. Angle between cycles 4 and 5: 45.4°



Figure S 11. Angle between cycles 3 and 4: 11.2°



Figure S 12. Angle between cycles 1 and 2: 4.0°



Figure S 13. Angle between the two five membered cycles of the fluorene units: 84.1°

Some short C/C intermolecular distances are observed ($d_{C/C=}3.32$ Å, $d_{C/C=}3.28$ Å, see below) in the **4-PhCz-SBF** packing. These short distances are shorter than the sum of the Van der Walls radii, ie 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 ($d_{C/H=}2.84$ Å, $d_{C/H=}2.88$ Å, $d_{C/H=}2.89$ Å, 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 Å.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-Ph(OMe)₃-SBF

| Identification code | shelx |
|-----------------------------------|--|
| Empirical formula | C ₃₄ H ₂₆ O ₃ |
| Formula weight | 482.55 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P 21/c |
| Unit cell dimensions | a = 9.3340(6) Å |
| | b = 23.1087(16) Å |
| | c = 12.5077(8) Å |
| Volume | 2557.3(3) Å ³ |
| Z | 4 |
| Density (calculated) | 1.253 Mg/m ³ |
| Absorption coefficient | 0.079 mm ⁻¹ |
| F(000) | 1016 |
| Crystal size | 0.25 x 0.21 x 0.01 mm ³ |
| Theta range for data collection | 1.762 to 27.510°. |
| Index ranges | -12<=h<=12, -29<=k<=28, -15<=l<=16 |
| Reflections collected | 18674 |
| Independent reflections | 5853 [R(int) = 0.0294] |
| Completeness to theta = 25.242° | 100.0% |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 5853 / 0 / 337 |
| Goodness-of-fit on F ² | 1.041 |
| Final R indices [I>2sigma(I)] | R1 = 0.0881, wR2 = 0.2445 |
| R indices (all data) | R1 = 0.1252, wR2 = 0.2783 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.574 and -0.417 e.Å ⁻³ |

Table S 5. Crystal data and structure refinement for 4-Ph(OMe)₃-SBF



Figure S 16. Angle between cycles 4 and 5: 78.0°



Figure S 17. Angle between cycles 3 and 4: 2.7°



Figure S 18. Angle between cycles 1 and 2: 3.2°



Figure S 19. Angle between the two five membered cycles of the fluorene units: 89.4°

Some short C/H intermolecular distances are observed ($d_{C/H=}2.64$ Å, $d_{C/H=}2.72$ Å, $d_{C/H=}2.84$ Å, $d_{C/H=}2.85$ Å, $d_{C/H=}2.88$ Å, see below) in the **4-Ph(OMe)₃-SBF** packing. These short distances are shorter than the sum of the Van der Walls radii, ie d=2.9 Å.⁷



Figure S 20. Short C/H intermolecular distances in the **4-PhCz-SBF** packing

A short O/H intermolecular distances is observed ($d_{O/H=}2.63$ Å, 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=2.72 Å.⁷



Figure S 21. Short O/H intermolecular distance in the 4-PhCz-SBF packing

A short H/H intermolecular distances is observed ($d_{H/H=}2.28$ Å, 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 Å.⁷



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





Figure S 23. Absorption molar coefficient spectra of **4-Ph-SBF** (black), **4-PhCz-SBF** (red), **N-PhCz** (pink), **4-Ph(OMe)**₃-**SBF** (blue) and **Ph(OMe)**₃ (sky blue) in cyclohexane



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

The comparison of the spectrum of **4-PhCz-SBF** and the sum of spectra of **N-PhCz** and **4-Ph-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 **N-PhCz** and **4-Ph-SBF**

Information regarding the absorption spectrum of 4-PhCz-SBF

The band at 340 nm of 4-PhCz-SBF is due to a transition from the HOMO to the L+2 orbital, both localized on the phenylcarbazole unit. It corresponds to a locally excited transition on the carbazole unit from the ground state (S_0) to a locally excited state (S_{LE}), noted \mathbb{D}_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 (S₀) to a charge transfer state (S_{CT}), noted λ_2 on the figure below. As can be seen on this figure, the smaller bandgap (in blue) corresponds to the higher wavelength (λ_1). However, the excited state $(S_{LE} \text{ in blue})$ reached by this wavelength (λ_1) is higher in energy than the other one $(S_{CT} \text{ in orange})$ reached by λ_2) at their respective relaxed geometries. In other words, the crossing between the potential curves of S_{CT} and S_{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)



Figure S 26. Potential energy curves of the S_0 , S_{LE} and S_{CT} states in cyclohexane (left) and in ethanol (right)

In order to validate the hypothesis of the existence of a charge transfer state (S_{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 (S_0 , S_{LE} , S_{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 λ_3 =345 nm comes from the S_{LE} excited state (which is not influenced by the solvent, as expected)

-the emission wavelength at λ_4 (361 and 383 nm dependent on the solvent) comes from the S_{CT} excited state. Note that λ_4 (ethanol) is higher than λ_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_{LE} in blue) gives $\Delta E = E(S_{LE})-E(S_0) = 4.46$ 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, S_{CT} in orange) gives $\Delta E = E(S_{CT})-E(S_0) = 4.33$ 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_{LE} (sky blue) states of **4-PhCz-SBF**; right: Superposition of the structures obtained by molecular modelling of the S_0 (dark blue) and S_{CT} (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)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 S0 (sky blue) and S1 (green) states of **4-Ph(OMe)₃-SBF** clearly concerns the trimethoxyphenyl substituent.



Figure S 31. Superposition of the structures obtained by molecular modelling of the SO (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 SO (pink) and S1 (orange) states of **4-PhCz-SBF**



Figure S 33. Superposition of the structures obtained by molecular modelling of the SO (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-PhCz-SBF** obtained by TD-DFT M06-2X/6-311+G(d,p), shown with an isovalue of 0.04 [e bohr⁻³]^{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 |
|---|-----|
|---|-----|

| λ (nm) | Oscillator strength | Major contribs |
|-----------|------------------------|---|
| 287 | 0.05 | HOMO→L+2 (84%) |
| 278 | 0.43 | HOMO→LUMO (54%) |
| 268 | 0.12 | H-3→LUMO (10%), H-1→LUMO (49%) |
| 263 | 0.17 | H-1→L+1 (65%) |
| 261 | 0.09 | HOMO→L+3 (39%) |
| 258 | 0.13 | H-2→L+2 (68%) |
| 255 | 0.06 | H-3→L+3 (13%), H-1→L+3 (27%), HOMO→L+4 (10%) |
| 252 | 0.08 | H-3→L+5 (14%), H-1→L+1 (11%), H-1→L+5 (50%) |
| 243 | 0.02 | H-5→LUMO (33%) |
| 238 | 0.004 | H-6→L+1 (48%) |
| 237 | 0.06 | H-4→LUMO (12%), H-3→LUMO (39%), H-1→L+3 (15%) |
| 236 | 0.06 | H-2→LUMO (30%), HOMO→L+14 (10%) |
| 233 | 0.002 | HOMO→L+4 (24%), HOMO→L+6 (22%), HOMO→L+7 (11%), HOMO→L+8 (12%) |
| 227 | 0.01 | H-3→LUMO (14%), HOMO→LUMO (23%), HOMO→L+3 (10%), HOMO→L+4 (13%) |
| 227 | 0.08 | H-3→L+1 (66%) |
| 226 | 0.27 | H-2→LUMO (25%), HOMO→L+14 (14%) |
| 224 | 0.21 | H-3→L+3 (18%), H-1→LUMO (13%), H-1→L+3 (11%) |
| 222 | 0.18 | H-4→LUMO (20%), H-3→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 [e bohr⁻³]^{1/2}. For clarity purpose, only the main contribution of each transition is shown.

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

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



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 PBE0/6-311+G(d,p), shown with an isovalue of 0.04 [e bohr⁻³]^{1/2}. For clarity purpose, only the main contribution of each transition is shown.

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

| Table S 8. | TD-DFT | PBF0/6-31 | 1+G(d.p) | of 4-PhCz-S | BF |
|------------|--------|-------------|-----------|-------------|----|
| 10010 0 0. | | 1 DE0/ 0 31 | ±. ((a)b) | | |



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 [e bohr⁻³]^{1/2}. For clarity purpose, only the main contribution of each transition is shown.

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



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

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

Table S 10. TD-DFT M06-2X/6-311+G(d,p) of **4-Ph(OMe)₃-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 [e bohr⁻³]^{1/2}. For clarity purpose, only the main contribution of each transition is shown.

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

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

Atomic coordinates

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

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

| С | -5.625157 | 1.131763 | 0.006941 |
|---|-----------|-----------|-----------|
| С | -5.845517 | -1.118624 | 0.016474 |
| С | -5.141847 | 2.438013 | 0.046873 |
| С | -6.977229 | 0.854242 | -0.276418 |
| С | -5.637263 | -2.491988 | 0.125971 |
| С | -7.118641 | -0.586359 | -0.26854 |
| С | -6.043077 | 3.466057 | -0.185107 |
| Н | -4.096693 | 2.645256 | 0.24692 |
| С | -7.863726 | 1.905664 | -0.505303 |
| С | -6.726433 | -3.326821 | -0.073268 |
| Н | -4.65958 | -2.895412 | 0.364207 |
| С | -8.19767 | -1.446981 | -0.4653 |
| С | -7.392916 | 3.207944 | -0.455331 |
| Н | -5.691193 | 4.492766 | -0.158418 |
| Н | -8.908387 | 1.704654 | -0.723764 |
| С | -7.995815 | -2.81452 | -0.369924 |
| Н | -6.589762 | -4.400957 | 0.005535 |
| Н | -9.183607 | -1.048846 | -0.68634 |
| Н | -8.072378 | 4.035727 | -0.630522 |
| Н | -8.826768 | -3.495704 | -0.521843 |
| N | -4.94124 | -0.070506 | 0.1838 |

Number of imaginary frequencies: 0

Table S 13. Atomic coordinates of **4-Ph(OMe₃)-SBF** at the fundamental state after geometry optimization

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

| С | 5.87843 | -1.555704 | 0.298985 |
|---|-----------|-----------|-----------|
| Н | 6.889227 | -1.249834 | 0.045164 |
| С | 4.799652 | -0.710372 | 0.067924 |
| С | 4.739645 | 0.642436 | -0.503696 |
| С | 5.744071 | 1.475622 | -0.981644 |
| Н | 6.782473 | 1.157406 | -0.971161 |
| С | 5.396996 | 2.728963 | -1.475683 |
| Н | 6.170058 | 3.391538 | -1.852656 |
| С | 4.065933 | 3.142134 | -1.491239 |
| Н | 3.811664 | 4.123296 | -1.880145 |
| С | 3.059024 | 2.307089 | -1.012073 |
| Н | 2.021827 | 2.628813 | -1.024348 |
| С | 3.403603 | 1.059911 | -0.519976 |
| С | -2.40424 | -0.352174 | -0.65865 |
| С | -2.857625 | 0.953825 | -0.473975 |
| Н | -2.176976 | 1.777773 | -0.645564 |
| С | -4.174123 | 1.182792 | -0.076569 |
| С | -5.040998 | 0.106573 | 0.141268 |
| С | -4.588155 | -1.198448 | -0.071111 |
| С | -3.269372 | -1.427686 | -0.466314 |
| Н | -2.900889 | -2.434047 | -0.618241 |
| С | -3.873122 | 3.535271 | -0.021052 |
| Н | -3.026844 | 3.492333 | 0.674754 |
| Н | -4.489159 | 4.403806 | 0.213485 |
| Н | -3.491372 | 3.629045 | -1.044963 |
| С | -7.268442 | 0.516826 | -0.43446 |
| Н | -7.021565 | 1.39295 | -1.044735 |
| Н | -8.227274 | 0.681009 | 0.060569 |
| Н | -7.338963 | -0.370569 | -1.073961 |
| С | -5.102955 | -3.51412 | -0.026194 |
| Н | -4.776736 | -3.716651 | -1.053632 |
| Н | -5.978974 | -4.122921 | 0.19928 |
| Н | -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 | X | Y | Z |
|------|-----------|-----------|-----------|
| С | -2.83005 | -3.060398 | -1.677283 |
| С | -4.155885 | -2.63208 | -1.640031 |
| С | -4.488722 | -1.406009 | -1.073062 |
| С | -3.475325 | -0.615489 | -0.544276 |
| С | -2.144548 | -1.04804 | -0.582912 |
| С | -1.814046 | -2.268082 | -1.147438 |
| С | -3.520124 | 0.701398 | 0.10715 |
| С | -2.216435 | 1.066363 | 0.463119 |
| С | -1.220857 | -0.014706 | 0.055529 |
| С | -4.588983 | 1.544677 | 0.386795 |
| С | -4.338665 | 2.754876 | 1.025666 |
| С | -3.039569 | 3.115797 | 1.379203 |
| С | -1.968031 | 2.270838 | 1.098837 |

| С | -0.126699 | 0.48028 | -0.880137 |
|---|-----------|-----------|-----------|
| С | 1.147635 | 0.220664 | -0.353635 |
| С | 0.97284 | -0.411023 | 0.973338 |
| С | -0.400145 | -0.557622 | 1.215093 |
| С | -0.295108 | 1.119991 | -2.094762 |
| С | 0.835945 | 1.516448 | -2.800123 |
| С | 2.103615 | 1.253528 | -2.293486 |
| С | 2.289989 | 0.593192 | -1.074914 |
| С | 1.888462 | -0.811706 | 1.944195 |
| С | 1.417517 | -1.368853 | 3.128963 |
| С | 0.052163 | -1.526962 | 3.353082 |
| С | -0.86719 | -1.116136 | 2.39238 |
| Н | -2.586821 | -4.019872 | -2.123153 |
| Н | -4.936066 | -3.261273 | -2.057373 |
| Н | -5.523117 | -1.075928 | -1.045798 |
| Н | -0.780999 | -2.601806 | -1.176699 |
| Н | -5.602805 | 1.267146 | 0.113241 |
| Н | -5.162952 | 3.424534 | 1.251212 |
| Н | -2.861129 | 4.063547 | 1.877668 |
| Н | -0.955904 | 2.551492 | 1.374833 |
| Н | -1.290598 | 1.313032 | -2.482932 |
| Н | 0.732435 | 2.02494 | -3.753586 |
| Н | 2.981303 | 1.547514 | -2.861216 |
| Н | 2.953211 | -0.692257 | 1.789523 |
| Н | 2.127165 | -1.682686 | 3.888474 |
| Н | -0.29701 | -1.965888 | 4.282622 |
| Н | -1.934108 | -1.224328 | 2.563949 |
| С | 3.681812 | 0.310399 | -0.626836 |
| С | 4.572961 | 1.35717 | -0.383258 |
| С | 4.141789 | -1.003117 | -0.50067 |
| С | 5.887247 | 1.099576 | -0.009552 |
| Н | 4.225533 | 2.381433 | -0.480082 |
| С | 5.455156 | -1.262175 | -0.129416 |
| Н | 3.460342 | -1.825032 | -0.698664 |
| С | 6.331929 | -0.210874 | 0.119248 |
| Н | 6.564513 | 1.926229 | 0.182629 |
| Н | 5.796705 | -2.288935 | -0.039176 |
| Н | 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 | Х | Y | Z |
|------|----------|-----------|-----------|
| С | 5.404635 | -3.349369 | -1.28 |
| С | 6.757888 | -3.052407 | -1.128059 |
| С | 7.161956 | -1.805341 | -0.662176 |
| С | 6.191788 | -0.860355 | -0.350445 |
| С | 4.833414 | -1.161483 | -0.503443 |
| С | 4.431889 | -2.402362 | -0.967319 |
| С | 6.312278 | 0.516219 | 0.150531 |
| С | 5.026889 | 1.049772 | 0.300797 |
| С | 3.967006 | 0.028471 | -0.099191 |

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

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

Table S 16. Atomic coordinates of **4-Ph(OMe)**₃-**SBF** at the S1 state after geometry optimization (TD-DFT)

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

| С | -6.239176 | 1.735885 | 1.218314 |
|---|-----------|-----------|-----------|
| Н | -7.222667 | 2.115965 | 1.477349 |
| С | -6.113361 | 0.77 | 0.224985 |
| Н | -6.99222 | 0.395854 | -0.292026 |
| С | -4.845638 | 0.296555 | -0.091803 |
| С | -4.407284 | -0.699129 | -1.079844 |
| С | -5.129622 | -1.46242 | -1.989254 |
| Н | -6.210675 | -1.37783 | -2.051443 |
| С | -4.443271 | -2.339684 | -2.822956 |
| Н | -4.993312 | -2.942366 | -3.539189 |
| С | -3.055925 | -2.451316 | -2.748369 |
| Н | -2.535433 | -3.139138 | -3.407659 |
| С | -2.33152 | -1.687059 | -1.836317 |
| Н | -1.250072 | -1.770236 | -1.77972 |
| С | -3.014199 | -0.814475 | -1.006776 |
| С | 2.381026 | 0.878606 | -0.236862 |
| С | 2.535879 | -0.539117 | -0.080966 |
| Н | 1.659933 | -1.163973 | -0.159499 |
| С | 3.794413 | -1.108099 | 0.041398 |
| С | 4.940905 | -0.305232 | 0.020409 |
| С | 4.799193 | 1.10043 | -0.153636 |
| С | 3.556006 | 1.67826 | -0.285489 |
| Н | 3.460265 | 2.751321 | -0.371026 |
| С | 2.895114 | -3.297529 | 0.273129 |
| Н | 2.225826 | -2.997489 | 1.08617 |
| Н | 3.293243 | -4.292869 | 0.471783 |
| Н | 2.333063 | -3.314926 | -0.668435 |
| С | 6.704997 | -1.634036 | -0.820661 |
| Н | 6.091072 | -2.526366 | -0.962783 |
| Н | 7.707538 | -1.921864 | -0.500906 |
| Н | 6.77086 | -1.072273 | -1.75947 |
| С | 5.924356 | 3.177009 | -0.322501 |
| Н | 5.456911 | 3.45659 | -1.274166 |
| Н | 6.961086 | 3.513694 | -0.313864 |
| Н | 5.379395 | 3.654797 | 0.500028 |
| 0 | 4.018256 | -2.440694 | 0.188434 |
| 0 | 6.183 | -0.809604 | 0.217291 |
| 0 | 5.969406 | 1.775265 | -0.163475 |

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

| Х | Y | Z |
|----------|---|---|
| 4.390916 | -3.73032 | -0.530044 |
| 5.783059 | -3.789435 | -0.507388 |
| 6.539273 | -2.63149 | -0.354646 |
| 5.8814 | -1.414537 | -0.224159 |
| | X 4.390916 5.783059 6.539273 5.8814 | X Y 4.390916 -3.73032 5.783059 -3.789435 6.539273 -2.63149 5.8814 -1.414537 |

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

| С | -5.810073 | 0.98879 | -0.097665 |
|---|-----------|-----------|-----------|
| С | -5.593681 | -1.251579 | 0.116788 |
| С | -5.589045 | 2.362609 | -0.171129 |
| С | -7.072537 | 0.429468 | -0.378434 |
| С | -5.129741 | -2.542973 | 0.35881 |
| С | -6.934299 | -1.004763 | -0.239767 |
| С | -6.662674 | 3.170988 | -0.51302 |
| Н | -4.610798 | 2.786169 | 0.026167 |
| С | -8.136126 | 1.2636 | -0.719671 |
| С | -6.030201 | -3.588152 | 0.218417 |
| Н | -4.102483 | -2.725659 | 0.653155 |
| С | -7.820065 | -2.072805 | -0.37487 |
| С | -7.927116 | 2.632053 | -0.782011 |
| Н | -6.516185 | 4.244921 | -0.575477 |
| Н | -9.114053 | 0.844396 | -0.937411 |
| С | -7.362692 | -3.361094 | -0.148542 |
| Н | -5.692696 | -4.603828 | 0.400518 |
| Н | -8.855605 | -1.895203 | -0.649762 |
| Н | -8.746676 | 3.292868 | -1.045155 |
| Н | -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 | Х | Y | Z |
|------|-----------|-----------|-----------|
| С | 3.108447 | 2.74578 | -2.441057 |
| С | 4.493418 | 2.644642 | -2.55837 |
| С | 5.196377 | 1.67961 | -1.843838 |
| С | 4.492611 | 0.81771 | -1.011548 |
| С | 3.101503 | 0.921249 | -0.895087 |
| С | 2.403067 | 1.882336 | -1.605425 |
| С | 4.952363 | -0.282009 | -0.151801 |
| С | 3.839138 | -0.84552 | 0.483486 |
| С | 2.560817 | -0.130082 | 0.07346 |
| С | 6.227386 | -0.782924 | 0.083151 |
| С | 6.375789 | -1.853167 | 0.959439 |
| С | 5.266343 | -2.414005 | 1.590086 |
| С | 3.98849 | -1.911642 | 1.354726 |
| С | 1.496331 | -1.025081 | -0.551911 |
| С | 0.182402 | -0.702569 | 0.025425 |
| С | 0.374261 | 0.098371 | 1.140673 |
| С | 1.778813 | 0.477386 | 1.233105 |
| С | 1.651907 | -2.059268 | -1.411491 |
| С | 0.491393 | -2.808322 | -1.820766 |
| С | -0.791953 | -2.437405 | -1.393614 |
| С | -1.022195 | -1.364833 | -0.538243 |

| С | -0.519857 | 0.547605 | 2.183359 |
|---|-----------|-----------|-----------|
| С | -0.030304 | 1.354896 | 3.181854 |
| С | 1.330811 | 1.741927 | 3.225176 |
| С | 2.236507 | 1.278429 | 2.241154 |
| Н | 2.574716 | 3.503786 | -3.006071 |
| Н | 5.028679 | 3.325112 | -3.213498 |
| Н | 6.275802 | 1.604223 | -1.938125 |
| Н | 1.323654 | 1.96168 | -1.515099 |
| Н | 7.094494 | -0.349924 | -0.407034 |
| Н | 7.365109 | -2.256149 | 1.153522 |
| Н | 5.39928 | -3.249453 | 2.270444 |
| Н | 3.124166 | -2.349343 | 1.845211 |
| Н | 2.633792 | -2.335965 | -1.782574 |
| Н | 0.605871 | -3.630705 | -2.518288 |
| Н | -1.646347 | -2.955385 | -1.817691 |
| Н | -1.552546 | 0.224445 | 2.18903 |
| Н | -0.697141 | 1.688157 | 3.971735 |
| Н | 1.684571 | 2.380707 | 4.027183 |
| Н | 3.285609 | 1.554383 | 2.292824 |
| С | -2.377034 | -0.866323 | -0.299696 |
| С | -3.467582 | -1.736872 | -0.249579 |
| С | -2.617661 | 0.51592 | -0.178903 |
| С | -4.767456 | -1.263518 | -0.086599 |
| Н | -3.332984 | -2.810277 | -0.308952 |
| С | -3.906479 | 0.992385 | -0.001898 |
| Н | -1.784556 | 1.20197 | -0.237311 |
| С | -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 |
| С | -7.021667 | -1.998425 | -0.521631 |
| Н | -7.464367 | -2.98893 | -0.645647 |
| Н | -7.639137 | -1.397822 | 0.147545 |
| Н | -6.9662 | -1.509519 | -1.501288 |
| С | -6.860065 | 1.408878 | -0.669978 |
| Н | -7.864461 | 1.635333 | -0.307896 |
| Н | -6.295993 | 2.33498 | -0.793705 |
| Н | -6.932294 | 0.891309 | -1.634652 |
| С | -3.147211 | 3.232825 | 0.247439 |
| Н | -3.605179 | 4.200206 | 0.455719 |
| Н | -2.455164 | 2.973403 | 1.05645 |
| Н | -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'-di(1-naphtyl)-N,N'-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/AI: Lithium fluoride covered with aluminum is the cathode

FIrpic: bis[2-(4,6-difluorophenyl)pyridinato-C²,N](picolinato)iridium(III), blue phosphorescent emitter

Ir(ppy)₃: tris[2-phenylpyridinato-C²,N]iridium(III), green phosphorescent emitter



Figure S 40. Normalized electroluminescent spectrum at 10 mA/cm² of the green device using **4**-**Ph(OMe)**₃-SBF as host doped with $Ir(ppy)_3$ (10% in mass) as emitting layer







Figure S 42. Normalized electroluminescent spectrum at 10 mA/cm² of the blue device using **4-Ph(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 mA/cm² of the green device using **4**-**PhCz-SBF** as host doped with $Ir(ppy)_3$ (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 $Ir(ppy)_3$ (10% in mass) as emitting layer



Figure S 46. Normalized electroluminescent spectrum at 10 mA/cm² of the blue device using **4-PhCz-SBF** 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)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 J-V² characteristics of Au/OSC/Au devices with thickness e^{\sim}40 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 (Θ =1) of the space-charge-limited current regime using the Mott-Gurney relation (1)

$$J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \Theta \mu \frac{V^2}{L^3}$$
(1)
$$\Theta = \frac{n_f}{n_f + n_t}$$
(2)

Where ϵ_r is the dielectric constant of the semiconductor extracted from C-V measurement, the factor Θ is the ratio between free and total charge carriers given by the relation 2, V is the applied voltage across a length L and J_{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 1fA 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.

 $J_D = qn\mu E (3)$

4-PhCz-SBF

 T_{sub} =135°C – Rate speed=0.8A/s - P=3.10⁻⁷ mbar





Figure S 50.J_D=f(E)

4-Ph(OMe)₃-SBF

 T_{sub} =105°C - rate Speed=0.3A/s - P=4.10⁻⁷ mbar



Figure S 52.J_D=f(E)

NMR studies



Figure S 53. Labelling of 4-PhCz-SBF



Figure S 54. COSY NMR of **4-PhCz-SBF** (CD₂Cl₂)



Figure S 55. HSQC NMR of **4-PhCz-SBF** (CD₂Cl₂)



Figure S 56. HMBC NMR of 4-PhCz-SBF (CD₂Cl₂)



Figure S 57. Labelling of 4-Ph(OMe)₃-SBF



Figure S 58. COSY NMR of 4-Ph(OMe)₃-SBF (CD₂Cl₂)



Figure S 59. HSQC NMR of **4-Ph(OMe)₃-SBF** (CD₂Cl₂)



Figure S 60. HMBC NMR of 4-Ph(OMe)₃-SBF (CD₂Cl₂)



Figure S 61. Comparison of the chemical shift of H3 for **4-PhCz-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)



Figure S 63. ¹H NMR spectrum of **4-PhCz-SBF** (CD₂Cl₂)



Figure S 64. ¹³C NMR spectrum of **4-PhCz-SBF** (CD₂Cl₂)



Figure S 65. DEPT135 spectrum of 4-PhCz-SBF (CD₂Cl₂)



Figure S 66. ¹H NMR spectrum of **4-Ph(OMe)₃-SBF** (CD₂Cl₂)



Figure S 67. ¹³C NMR spectrum of **4-Ph(OMe)₃-SBF** (CD₂Cl₂)



Figure S 68. DEPT135 spectrum of 4-Ph(OMe)₃-SBF (CD₂Cl₂)

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