



## Spiro-configured dibenzosuberene compounds as deep-blue emitters for organic light-emitting diodes with a CIEy of 0.04

Clement Brouillac, Wan-Shan Shen, Joelle Rault-Berthelot, Olivier Jeannin, Cassandre Quinton, Zuo-Quan Jiang, Cyril Poriel

### ► To cite this version:

Clement Brouillac, Wan-Shan Shen, Joelle Rault-Berthelot, Olivier Jeannin, Cassandre Quinton, et al.. Spiro-configured dibenzosuberene compounds as deep-blue emitters for organic light-emitting diodes with a CIEy of 0.04. *Materials Chemistry Frontiers*, 2022, 6 (13), pp.1803-1813. 10.1039/d2qm00287f . hal-03715050

**HAL Id: hal-03715050**

**<https://hal.science/hal-03715050>**

Submitted on 20 Sep 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

# Spiro-Configured Dibenzosuberenes as Deep-Blue Emitters for Organic Light-Emitting Diodes with CIEy of 0.04

Clément Brouillac,<sup>a</sup> Wan-Shan Shen,<sup>b</sup> Joëlle Rault-Berthelot,<sup>a</sup> Olivier Jeannin,<sup>a</sup> Cassandre Quinton,<sup>a</sup> Zuo-Quan Jiang<sup>b</sup> and Cyril Poriel<sup>\*a</sup>

a. Univ Rennes, CNRS, ISCR-UMR CNRS 6226, F-35000 Rennes, France-  
email: cyril.poriel@univ-rennes1.fr

b. Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu 215123, China.

Keywords: Dibenzosuberene, deep-blue emitter, organic light-emitting diode, *spiro* compounds

## Abstract

Deep blue electroluminescence is highly required for organic light-emitting diode (OLED) technology. However, designing fluorophores displaying adequate CIE coordinates and particularly a low CIEy is far from an easy task. We report in this work the synthesis, the physico-chemical properties and the application in OLED of deep blue emitters constructed on the dibenzosuberene (DBS) molecular fragment. Three emitters, **SPA-DBS**, **SIA-DBS** and **SQPTZ-DBS**, have been constructed following a similar molecular design strategy that is the *spiro* connection of an electron rich unit, namely *N*-phenylacridine (PA), indoloacridine (IA) or quinolinophenothiazine (QPTZ) to the DBS core. The PA, IA and QPTZ fragments are known to be efficient hole injectors due to their strong electron-rich character. Through a structure/properties relationship study, we analyse the electrochemical, photophysical and thermal behaviours of these three emitters. When used as emitter in an OLED, a deep-blue emission with CIE of (0.16, 0.04) is obtained with **SPA-DBS**, reaching an EQE of ca 1% and a  $V_{on}$  of 4V. The CIEy coordinate of 0.04 appears to be particularly low and fits the NSTC, ITU and EBU standards.

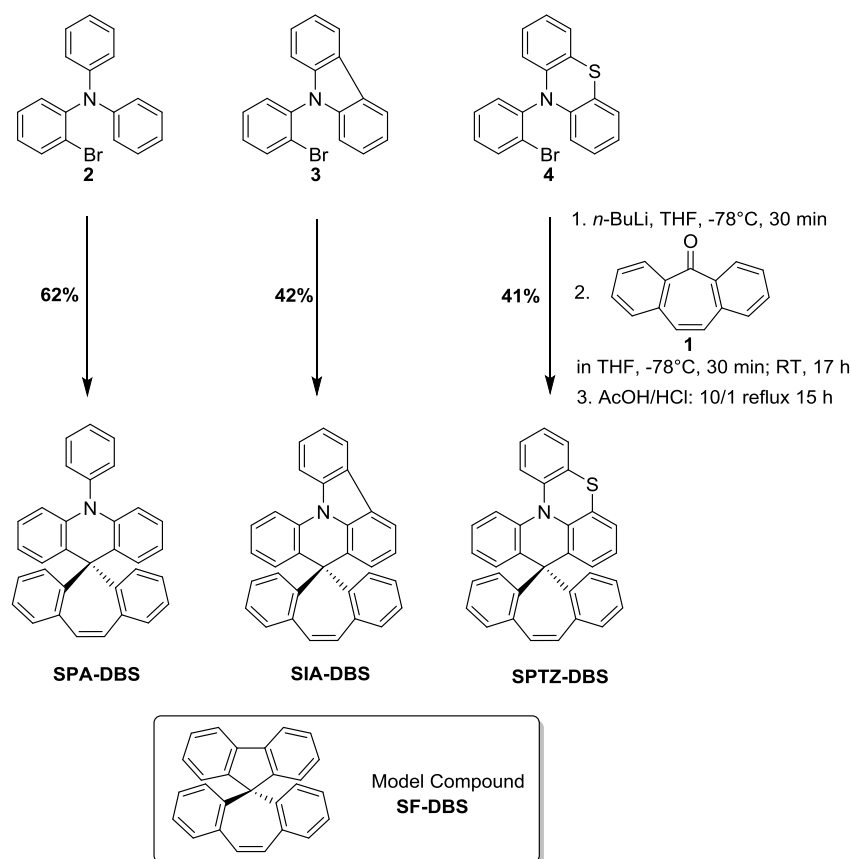
## Introduction

In the past three decades, organic light-emitting diodes (OLEDs) technology has encountered a fantastic development and is now released on the market.<sup>1-3</sup> The efforts of chemists, physicists, electronicians and materials scientists have allowed reaching very high efficiency OLEDs. On many aspects, the technology has significantly evolved since the pioneer works of Tang in 1987.<sup>4</sup> One of the most important feature is undoubtedly the different generations of emitters, which have been used to improve the devices performance from fluorescent materials (TADF, Generation I)<sup>5-7</sup> to phosphorescent materials (Generation II)<sup>8-13</sup> and to thermally activated delayed fluorescent materials (Generation III).<sup>14-15</sup> Reaching an efficient emission on both ends of the visible spectrum i.e., the violet<sup>16-19</sup> and near-infrared<sup>20</sup> regions, has always been a major challenge in the field. These wavelengths can open up novel applications for future OLEDs. For example, light source with a wavelength of 405 nm is particularly awaited because of a variety of bacteria are sensible to this wavelength (antibacterial blue light).<sup>21</sup> Efficient and stable emission in the violet/deep blue region has always been an important field of research in the OLED technology.<sup>5, 12, 22-25</sup> However, whatever the nature of the emitters, reaching high efficiency OLEDs in this range of wavelengths has been one of the most difficult problem to solve for the last twenty years. For example, in Phosphorescent OLEDs, which is the most mature technology in the field, very high efficiency red, green and sky-blue devices have been reached (EQE above 25%)<sup>22-25 13, 26-27</sup> but deep blue and violet OLEDs are still deeply lacking. In term of CIE coordinates, different standards can be found in literature. According to the National Television Standards Committee (NTSC) standard, the Commission Internationale de l'Eclairage (CIE) color coordinates for a pure blue light are  $x=0.14$  and  $y=0.08$ , respectively. The  $y$  coordinate is even lowered by the recommendations of the European Broadcasting Union (EBU) ( $x=0.15/ y=0.06$ )<sup>24, 28</sup> and the International Telecommunication Union (ITU) (ITU-R Recommendation BT.2020:  $x=0.131/y=0.046$ ).<sup>29</sup> Reaching these CIE coordinates in an OLED is far from an easy task, especially the CIEy, and needs very precise molecular designs. The challenge of deep-blue emitting OLEDs mainly relies on the difficulty to reach efficient emitters fulfilling all the characteristics desired. Indeed, a deep-blue emitter should have a wide bandgap ( $>3$  eV), which is detrimental for charge injection within an OLED device. Incorporation of electron-rich (electron donor) and

electron-poor (electron acceptor) in the molecular structure is an interesting strategy to reduce the carrier injection barrier with a better fit with the electrode Fermi levels. However, the incorporation of donor and acceptor functional units can lead to a red shift of the emission wavelength due to intramolecular charge transfer (ICT). In order to avoid this red shift, the molecular construction should separate the emitter to the charge injection group. In addition, the emission in the solid state should be efficient and not be shifted compare to solution as often observed when  $\pi$ - $\pi$  interactions occur.<sup>28</sup> As the study of elementary building units has been one of the driving force of organic electronics for the last thirty years, we wish to report herein a barely studied molecular fragment, in the field of blue emitters, that is dibenzosuberene (DBS).<sup>30-32</sup> DBS is a double bridged biphenyl unit, one double bond on one side and a methylene unit on the other. There is a clear analogy between this fragment and the widely known fluorene and phenylacridine fragment in which the double bond is replaced by a direct carbon-carbon bond for the latter and a nitrogen bridge for the former.

Herein, three emitters, **SPA-DBS**, **SIA-DBS** and **SQPTZ-DBS**, have been constructed following a similar molecular design strategy that is the *spiro* connection of an electron rich unit, namely *N*-phenylacridine (PA),<sup>33-35</sup> indoloacridine (IA)<sup>36</sup> or quinolinophenothiazine (QPTZ)<sup>37-39</sup> to the DBS core. The PA, IA and QPTZ fragments are known to be efficient hole injectors due to their strong electron rich character, in other words they possess high HOMO levels. On the other hand, the *spiro* connection is known to be a very efficient structural feature to improve the thermal and morphological properties and also allows to control the interactions between the two orthogonal functional units.<sup>3, 40-43</sup> In this work, we report the synthesis, the physico-chemical properties and the application in OLED of three blue emitters based on the DBS core. In the solid state, these emitters display an emission in the deep-blue region. When used as emitter in an OLED, a blue emission with CIE of (0.16, 0.04) is obtained with **SPA-DBS**, reaching an EQE of ca 1% and possessing an  $\gamma$  CIE coordinate below 0.1, fitting the NSTC, ITU and EBU standards.

## Synthesis



Scheme 1. Synthesis of **SQPTZ-DBS**, **SPA-DBS** and **SIA-DBS**

When designing an organic semi-conductor for electronics, thinking to its synthetic approach is a mandatory step.<sup>43-44</sup> The present target molecules have been synthesized at the multi-gram scale, from commercially available starting

material dibenzosuberone **1**, through an efficient two-step approach (Scheme 1). The nucleophilic addition reaction on dibenzosuberone of the corresponding lithiated intermediate derivatized from PA (**2**), IA (**3**) or QPTZ (**4**) were first performed. Electrophilic intramolecular cyclization of the resulting suberenol (not isolated) in acidic media (HCl/AcOH) afforded the corresponding materials with 62% yield for **SPA-DBS**, 42% yield for **SIA-DBS** and 41% yield for **SQPTZ-DBS**. Thus, this synthetic approach is short, efficient and low cost as it uses cheap starting materials (less than 5 €/g for both **SIA-DBS** and **SQPTZ-DBS** and 8 €/g for **SPA-DBS**) and no palladium catalyst. In order to precisely study the impact of the association of the electron-rich fragments with the DBS core, a model compound will also be studied, namely dibenzosuberene-fluorene **SF-DBS**.

## Structural properties

**SPA-DBS** (CCDC 2149596) and **SIA-DBS** (CCDC 2149597) have been crystallised by vapour diffusion of pentane in  $\text{CDCl}_3$  in order to confirm their molecular structure by X-Ray crystallography and to study the structural characteristics (see X-Ray data in the SI). Unfortunately, despite intensive scouting, it was not possible to grow crystals of **SQPTZ-DBS**. Oppositely to the two others, this compound does not display any crystallization transition phase as observed in DSC (see Figure 6). **SPA-DBS** crystallizes in an orthorhombic system,  $P2_12_12_1$  containing two molecules (see Fig S18 in SI). **SIA-DBS** crystallizes in a monoclinic system,  $P2_1/c$ . In the two molecules, the PA or IA unit and the DBS unit are almost orthogonal with a twist angle (value in orange in Figure 1) of  $90^\circ$  for **SPA-DBS** and  $87^\circ$  for **SIA-DBS**. The presence of a *spiro* carbon leads to this orthogonality between the two fragments, which is at the origin of the absence of significant  $\pi$ -conjugation between them. This structural characteristic is the base of the present design. Additionally, in **SPA-DBS**, the angle between the acridine unit and the attached phenyl (indicated in purple in Figure 1) is  $80^\circ$ , which indicates a second  $\pi$ -conjugation interruption at the nitrogen atom. It also changes the molecular radius (distance from the *spiro* carbon atom to the farthest carbon atom, green arrow in Figure 1). It has been evaluated at 7.2 Å and 7.0 Å for **SPA-DBS** and **SIA-DBS** respectively. The bond between the two phenyl rings in IA fragment reduces the molecular radius due to a more folded structure.

For each aromatic unit, a torsion angle has been defined as the dihedral angle between the two external benzene rings of each unit (values in blue for the IA and PA units and in red for the DBS unit, Figure 1). The acridine moiety of the PA core has a smaller torsion angle of  $3.8^\circ$  compared to that of the IA fragment, which presents a torsion angle of  $7.2^\circ$ . This is caused by the presence of a single bond between the two phenyls rings in the IA fragment, which decreases the planarity of the acridine core. For the DBS unit, the torsion angle has been measured at  $8.2^\circ$  and  $7.2^\circ$  for **SPA-DBS** and **SIA-DBS** respectively. For both molecules, this moiety is not flat due to the presence of the central C=C bond linking the two phenyl rings, which causes some deviations from planarity.

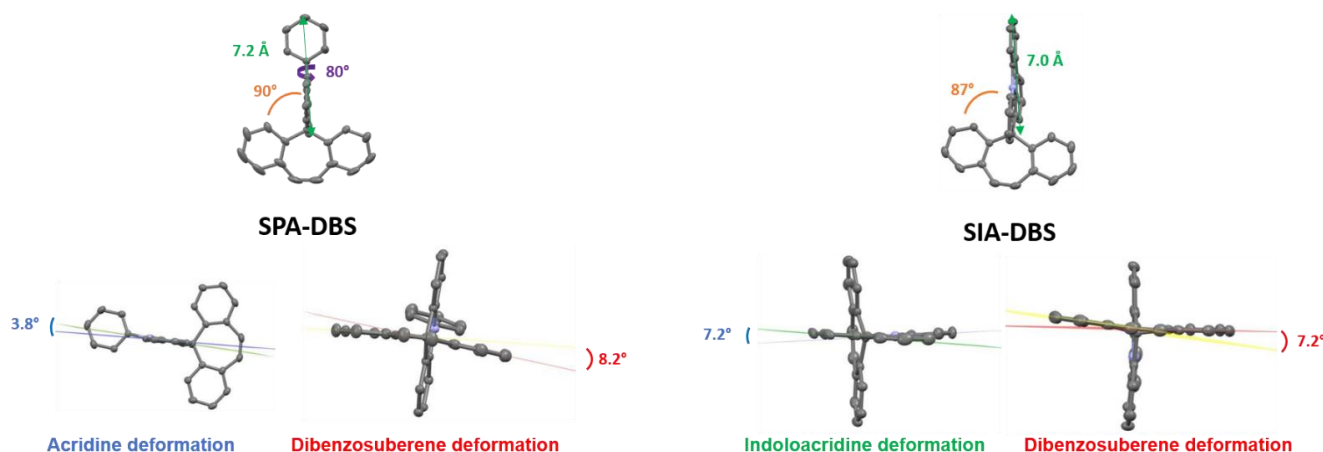


Figure 1. Molecular structure from X-ray crystallography of **SPA-DBS** (left) and **SIA-DBS** (right) (ellipsoid probability at 50% level). Hydrogen atoms have been omitted for clarity.

## Electrochemistry

The electrochemical properties of **SQPTZ-DBS**, **SPA-DBS** and **SIA-DBS** have been investigated by cyclic voltammetry (CV) in  $\text{CH}_2\text{Cl}_2$  for oxidation and in DMF for reduction; potentials are given versus a saturated calomel electrode (SCE).

In reduction, the three compounds present a first reversible reduction wave peaking at -2.18, -2.22 and -2.17 V for **SQPTZ-DBS**, **SPA-DBS** and **SIA-DBS** respectively (Figure 2A). From their onset reduction potentials, the LUMO

were calculated close to -2.3 eV for the three compounds (-2.33, -2.29, -2.35 eV for **SQPTZ-DBS**, **SPA-DBS** and **SIA-DBS** respectively), indicating a reduction centered on the DBS core for the three compounds with only a weak effect of the *spiro*-linked donor part. This is in accordance with the molecular modelling, which shows a LUMO energy level spread out on the DBS core with only a very small contribution of the donor unit (Figure 2E). This is also confirmed by the model compound **SF-DBS**, which also presents a first reversible reduction wave at -2.28 V and a LUMO energy level evaluated at -2.30 eV. Moreover, compared to its parent fluorene, one can note that DBS unit allows to significantly decrease the LUMO energy level by 0.42 eV, from -1.81 eV in spirobifluorene **SBF** to -2.23 eV in **SF-DBS**. This also holds true for the other couples spirophenylacridine-fluorene **SPA-F**<sup>35</sup> / **SPA-DBS** (-1.94 vs -2.29 eV), spiroindoloacridine-fluorene **SIA-F**<sup>36</sup> / **SIA-DBS** (-1.88 vs -2.35 eV), and spiroquinolinophenothiazine-fluorene **SQPTZ-F**<sup>38</sup> / **SQPTZ-DBS** (-1.89 vs -2.33 eV). This is an important consideration to allow an efficient electron injection within a device.

Exploring the electrochemical behaviour up to more negative potential reveals two additional irreversible reduction waves with maxima at -2.80 and -2.93 V for **SQPTZ-DBS** and at -2.74 and -2.90 V for **SIA-DBS** and only one irreversible reduction wave peaking at -2.86 V for **SPA-DBS** and at -2.79 V for **SF-DBS** (Figure 2B). Those additional reductions do not modify the reversibility of the first reduction wave indicating the stability of the different negatively charged species.

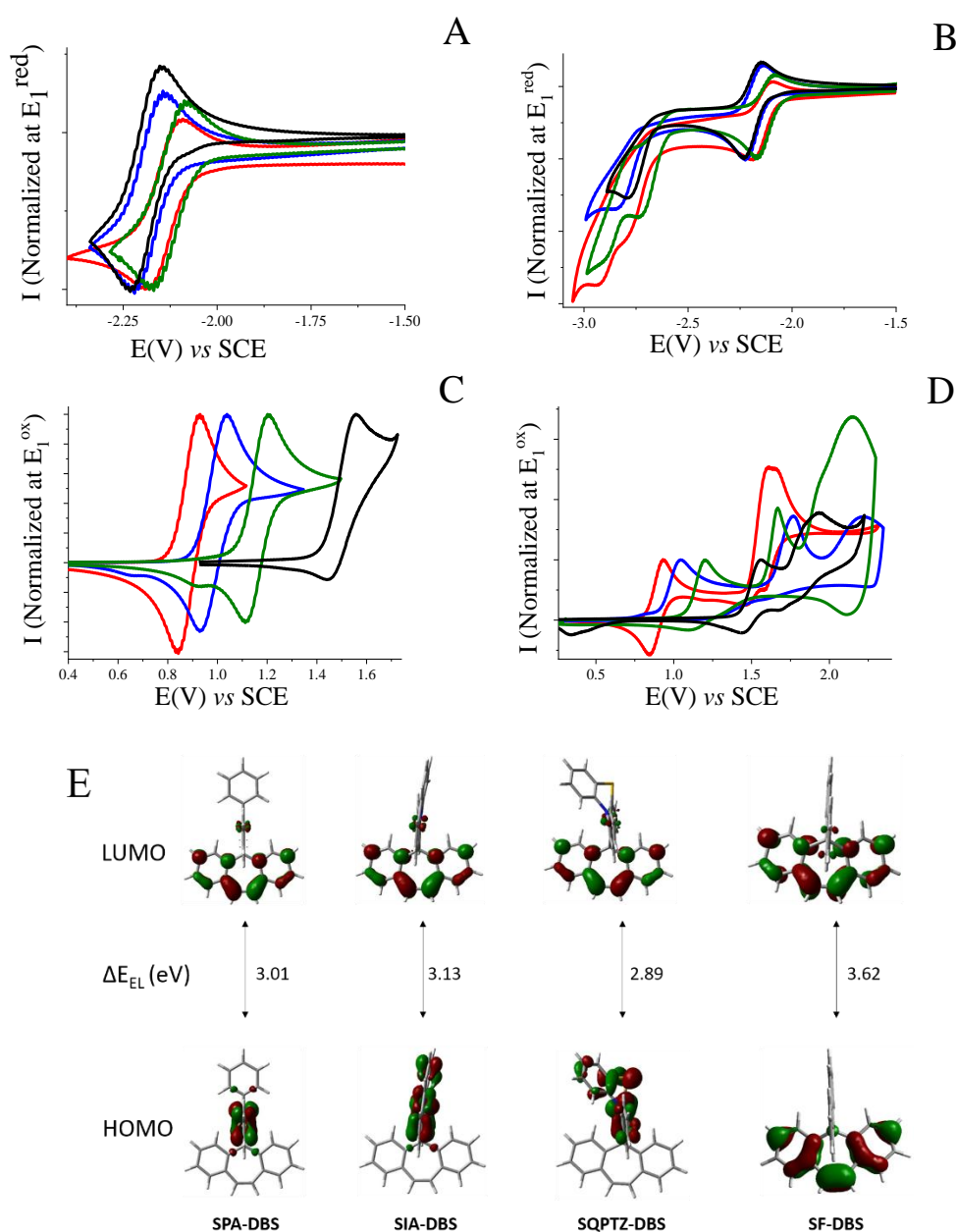


Figure 2. Normalized cyclic voltammograms of **SQPTZ-DBS** (red lines), **SPA-DBS** (blue lines), **SIA-DBS** (green lines) and **SF-DBS** (black line) in the cathodic (A&B, DMF +  $\text{Bu}_4\text{NPF}_6$  0.1 M) or the anodic (C&D,  $\text{CH}_2\text{Cl}_2$  +

Bu<sub>4</sub>NPF<sub>6</sub> 0.2 M) range. Sweep-rate of 100 mV.s<sup>-1</sup>, platinum disk (diameter 1 mm) working electrode. E. Representations of HOMO and LUMO orbitals obtained by DFT in B3LYP/6-311+G(d,p).

In oxidation, **SQPTZ-DBS**, **SPA-DBS** and **SIA-DBS** present a quasi-reversible first oxidation wave with a maximum at 0.94, 1.05 and 1.20 V respectively (Figure 2C). This first electron transfer is fully driven by the strength of the donor unit as the HOMO is exclusively spread out on this fragment (Figure 2E). These results are in accordance with previously reported electrochemical data, which have highlighted the different electron rich nature of the structurally related PA, IA and QPTZ fragments.<sup>36-38</sup> As the HOMO of **SF-DBS** is spread out on the DBS unit (Figure 2E), this model compound displays a drastically different behaviour with a first oxidation wave only partially reversible and shifted to higher potential (1.56 V). The HOMO energy levels were evaluated from the onset potential of the first oxidation wave at -5.22, -5.30, -5.48 and -5.83 eV for **SQPTZ-DBS**, **SPA-DBS**, **SIA-DBS** and **SF-DBS** respectively. The second and third oxidation processes (Figure 2D) are dependent to the donor unit and erase the reversibility of the first oxidation except for **SQPTZ-DBS**, which first oxidation remains reversible even after reaching high potential values, showing the stability of the different charged species. QPTZ building block is indeed known in literature for the high stability of its cation radical and dication.<sup>38</sup> It should be noted that **SF-DBS**, when oxidized up to its second oxidation wave, is submitted to an electrodeposition process, involving carbon-carbon coupling at C2 of the fluorene units as usually observed for other fluorene based compounds.<sup>45-47</sup> However, no carbon-carbon coupling occurs on the DBS unit.

## Photophysics

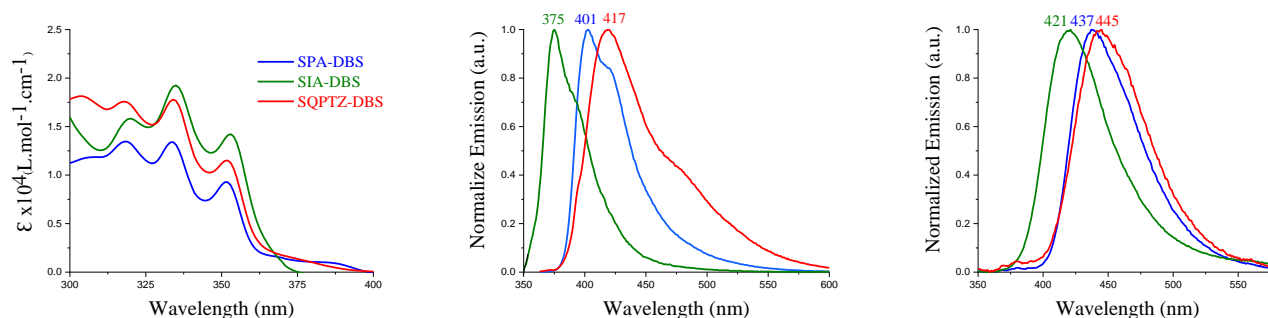


Figure 3. Absorption (Left) and emission (Middle,  $\lambda_{\text{exc}} = 300$  nm) in cyclohexane and emission in spin-coated thin film (Right,  $\lambda_{\text{exc}} = 300$  nm) of **SQPTZ-DBS** (red line), **SPA-DBS** (blue line) and **SIA-DBS** (green line)

UV–Vis absorption and emission spectra of **SQPTZ-DBS** (red line), **SPA-DBS** (blue line) and **SIA-DBS** (green line) were recorded in dilute cyclohexane solution at room temperature (Figure 3). The optical properties are summarized in Table 1. For all these three molecules, the absorption ranges from 300 to 400 nm (Figure 3-left), which could be assigned to  $\pi$ - $\pi^*$  transitions (see SI). TD-DFT calculations indicate that the band experimentally found at 352-353 nm for the three compounds is due to a HOMO-1  $\rightarrow$  LUMO transition involving orbitals both localized on the DBS part (Figure 4-left). This transition is modeled at 354-355 nm for the three compounds, showing a good agreement between theoretical and experimental results. Furthermore, the calculations show that the HOMO  $\rightarrow$  LUMO transition is almost forbidden (oscillator strengths of 0.004-0.014 for the three compounds). Indeed, the spiro carbon allows a good spatial separation between the HOMO localized on the donor (IA, PA or QPTZ) and the LUMO localized on the accepting DBS. In addition, it has been shown above that **SIA-DBS** displays a lower HOMO level than the two other compounds. Its weaker donor ability induces a weaker charge transfer character of the HOMO  $\rightarrow$  LUMO transition compared to the PA and QPTZ counterparts. Thus, the HOMO  $\rightarrow$  LUMO band of **SIA-DBS** is modeled at the lowest wavelength in the series ( $\lambda_{\text{th}} = 395, 422$  and  $418$  nm for **SIA-DBS**, **SPA-DBS** and **SQPTZ-DBS** respectively). For this reason, this band, in the UV-Vis absorption spectrum, is hidden by the HOMO-1  $\rightarrow$  LUMO band in the case of **SIA-DBS** but can be detected as a shoulder for **SPA-DBS** and **SQPTZ-DBS**.

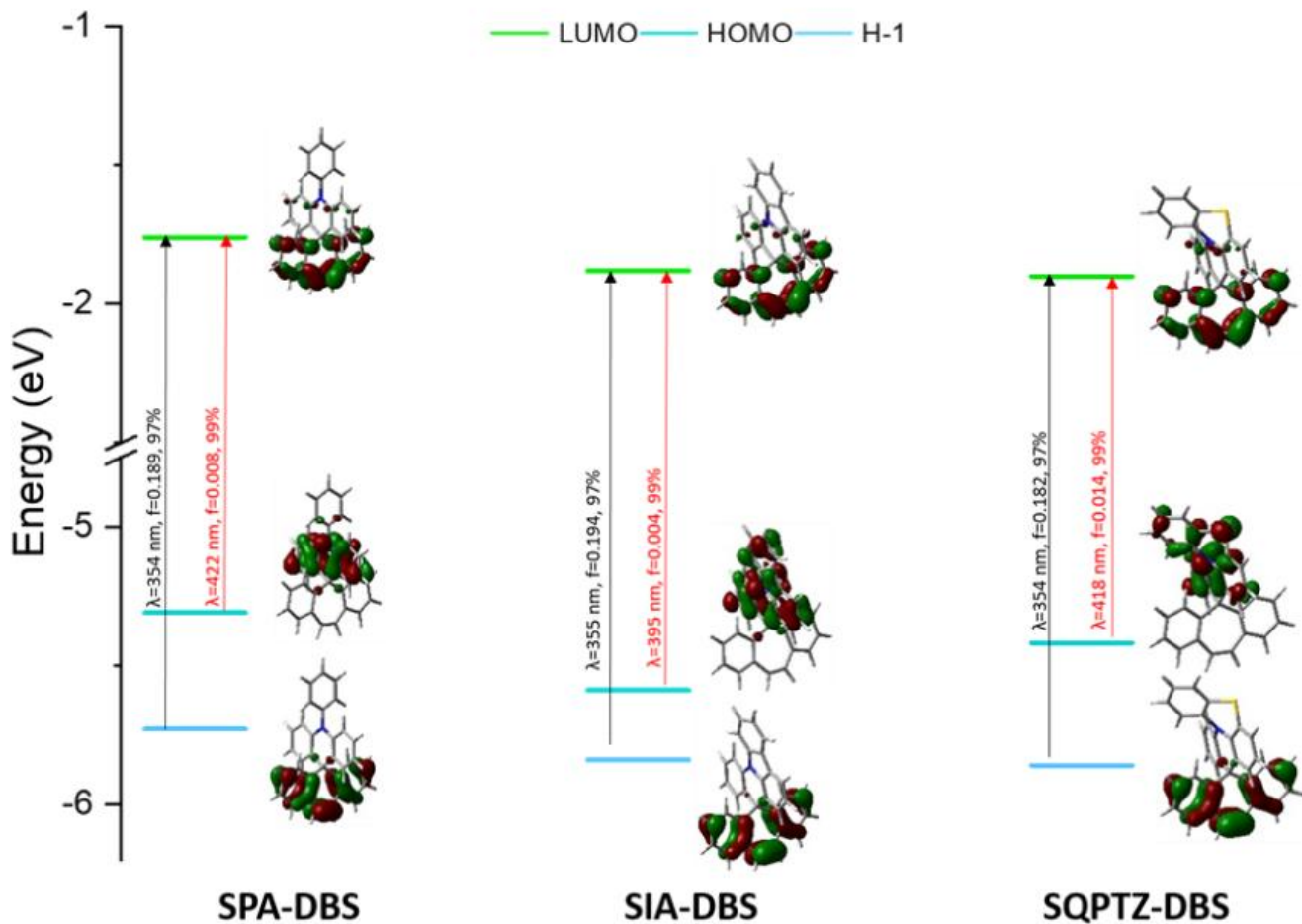


Figure 4. Representation of the energy levels and the main molecular orbitals involved in the electronic transitions of **SPA-DBS** (left), **SIA-DBS** (middle) and **SQPTZ-DBS** (right) obtained by TD-DFT b3lyp and the 6-311+G(d, p) basis set on the geometry of  $S_0$ , shown with an isovalues of 0.04 [ $e \text{ bohr}^{-3}$ ]<sup>1/2</sup> (for clarity purpose, only the main contribution for each transition is shown, details provided in SI).

Table 1. Selected electronic and physical properties of **SPA-DBS**, **SIA-DBS**, **SQPTZ-DBS**

	SPA-DBS	SIA-DBS	SQPTZ-DBS
$\lambda_{\text{abs}}$ [nm ( $\times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$ )] <sup>a</sup>	318 (1.35); 334 (1.34); 352 (0.93)	320 (1.58); 335 (1.92); 353 (1.42)	318 (1.76); 334 (1.78); 352 (1.15)
$\lambda_{\text{em sol}}$ (nm) <sup>a, b</sup>	401	375	417
$\text{QY}_{\text{sol}}$ <sup>a, b, c</sup>	0.12	0.12	0.02
$\lambda_{\text{em film}}$ (nm) <sup>b, d</sup>	437	421	445
$\text{QY}_{\text{film}}$ <sup>d, e</sup>	0.06	0.07	0.02
FWHM (nm) <sup>a, b, f</sup>	47	38	62
FWHM <sub>film</sub> (nm) <sup>b, d, f</sup>	60	58	64
$\tau_f$ (at $\lambda_{\text{em sol}}$ ) [ns] <sup>a, g</sup>	7.1 (401)	3.4 (375)	1.6 (417)
$k_r$ [ns <sup>-1</sup> ] <sup>h</sup>	0.018	0.035	0.015
$k_{\text{nr}}$ [ns <sup>-1</sup> ] <sup>h</sup>	0.12	0.26	0.67

$E_{\text{ox}}$ (V vs SCE) <sup>i</sup>	1.05, 1.76, 2.21	1.20, 1.67, 1.94, 2.15	0.94, 1.61, 1.65
$E_{\text{red}}$ (V vs SCE) <sup>j</sup>	-2.22, -2.86	-2.17, -2.74, -2.90*	-2.18, -2.80, -2.93
HOMO <sub>exp</sub> (eV) <sup>k</sup>	-5.30	-5.48	-5.22
LUMO <sub>exp</sub> (eV) <sup>k</sup>	-2.29	-2.35	-2.33
$\Delta E_{\text{EL}}$ (eV) <sup>l</sup>	3.01	3.13	2.89
HOMO <sub>theo</sub> (eV) <sup>m</sup>	-5.31	-5.59	-5.42
LUMO <sub>theo</sub> (eV) <sup>m</sup>	-1.76	-1.88	-1.90
$S_1$ (eV) <sup>n</sup>	3.33	3.54	3.30
$T_d$ (°C) <sup>o</sup>	303	328	346
$T_g$ (°C) <sup>p</sup>	/	105	117
$T_c$ (°C) <sup>p</sup>	158	127	/
$T_f$ (°C) <sup>q</sup>	243	257	210

a. in cyclohexane at RT; b.  $\lambda_{\text{exc}}=300$  nm; c. quantum yield (QY) determined with sulfate quinine in  $H_2SO_4$  1M as reference; d. In spin-coated film; e. QY determined in integration sphere f. FWHM: Full width at half maximum. g.  $\lambda_{\text{exc}}=310$  nm; h.  $k_r=QY/\tau_f$  and  $k_{nr}=(1/\tau_f)*(1-QY_{\text{sol}})$ ; i. in dichloromethane; j. in DMF; k. from electrochemical data; l.  $\Delta E_{\text{EL}}=|HOMO-LUMO|$ ; m. from theoretical calculations, TD-DFT B3LYP/6-311+G(d,p); n. from onset of emission spectrum in cyclohexane; o. from TGA; p. from DSC (2<sup>nd</sup> heating cycle); q. from DSC (1<sup>st</sup> heating cycle). \*Shoulder

The emission properties of these three molecules were then determined in cyclohexane (Figure 3, middle). The three compounds display fluorescent features in the deep blue region with a red shift of the maximum emission, from 375 nm for **SIA-DBS**, to 401 nm for **SPA-DBS** and to 417 nm for **SQPTZ-DBS** (Corresponding  $S_1$  values of 3.54, 3.33 and 3.30 eV). Thus, oppositely to their absorption spectra, which were similar, the emission spectra appear to be very different with a 42 nm red shift between **SIA-DBS** and **SQPTZ-DBS**. This can be assigned to electronic and structural features. Indeed, the more electron rich nature of the QPTZ fragment induces a stronger photoinduced intramolecular charge transfer (ICT), which causes a red shift. In addition, due to the presence of the sulphur bridge, the QPTZ fragment is significantly more flexible than the rigid IA unit, causing more important geometry modification between  $S_0$  and  $S_1$ , which in turn leads to a red shift of the emission. Compare to fluorene-based counterparts, **SPA-F**, **SIA-F** and **SQPTZ-F** previously reported in literature (see structures in SI), which possess an emission wavelength at 345, 361 and 417 nm respectively,<sup>35-36, 38, 48</sup> one can note, for the DBS compounds, an extension of the conjugation pathway, induced by the presence of the double bond between the two phenyl rings, causing a significant red shift of the emission maxima. This allows reaching fluorophores with an emission in the deep-blue region.

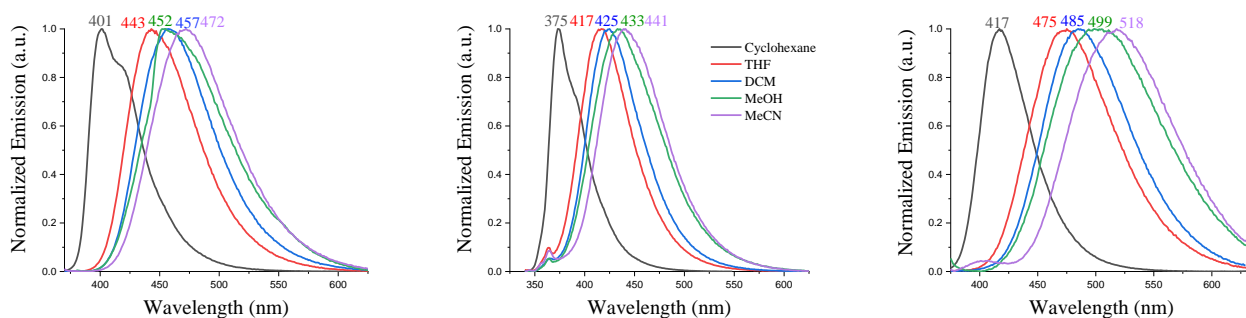


Figure 5. Emission spectra in different solvents of **SPA-DBS** (left), **SIA-DBS** (middle) and **SQPTZ-DBS** (right),  $\lambda_{\text{exc}}=330$  nm

The quantum yields of both **SIA-DBS** and **SPA-DBS** are measured at 0.12 whereas that of **SQPTZ-DBS** is 6 times lower, 0.02 in accordance with a more important ICT in the former (see below solvatochromatic experiments). This is expected in view of the very low oscillator strength arising from the spatial separation of the electron rich and the electron poor fragments, which promotes a vanishingly small transition dipole moment between the  $S_1$  and  $S_0$  states. The three compounds exhibit single lifetimes, dependent of the donor unit. Thus, **SPA-DBS** displays a long lifetime of 7.1 ns, whereas those of **SIA-DBS** and **SQPTZ-DBS** are significantly reduced (3.4 and 1.5 ns respectively). The analysis of the radiative ( $k_r$ ) and the non-radiative ( $k_{nr}$ ) constants provides interesting data on the deexcitation of excited states. Indeed, for the three compounds, the  $k_r$  are very weak, in accordance with the small oscillator strength observed between the  $S_0$  and  $S_1$  states. The  $k_{nr}$  of **SQPTZ-DBS** is the highest in the series, six times higher than that of **SPA-DBS** (0.67 and 0.12 ns<sup>-1</sup> respectively). As their  $k_r$  are almost identical (0.018 and 0.015 ns<sup>-1</sup> respectively), this shows that the presence of the sulphur bridge in **SQPTZ-DBS** and the flexibility induced increases vibrational deactivation pathways (and increase the ISC as previously reported<sup>37</sup>), leading to a decrease of the quantum yield. This is in accordance with the conclusions exposed above in term of wavelength emission. Thus, the sulphur bridge of the QPTZ fragment (which is a building unit only recently investigated for organic electronic applications<sup>37-39</sup>) leads to very appealing electrochemical properties (high HOMO and stability of the cation radical), but increases non-radiative pathways. It is finally important to mention that no phosphorescence contribution is observed at 77 K in Me-THF for all compounds.

Solvatochromic experiments allow to visualize the strength of the three donor units through the intensity of the ICT occurring in these systems, Figure 5. For the three compounds, there is a significant red shift from apolar cyclohexane to highly polar MeCN, 68 nm for **SIA-DBS**, 71 nm **SPA-DBS** and 101 nm for **SQPTZ-DBS**. The red shift translates a more intense ICT and follows the strength of the donor highlighted in the electrochemical part. In the case of **SIA-DBS**, the presence of a small band at low wavelength is detected as soon as the polarity of the solvent increased. This band is assigned to a locally excited state as it is not dependent of the polarity of the medium and recorded at ca 363 nm, almost identical to the maximum observed in cyclohexane (375 nm, Figure 5). Such a behaviour is sometimes detected for Donor/Acceptor compounds.<sup>36</sup>

The differences ( $\Delta\mu$ ) between the dipole moment at the ground state ( $\mu$ ) and at the first excited state ( $\mu^*$ ) have been evaluated using the Lippert-Mataga formalism.  $\Delta\mu$  of 16.3, 15.9 and 17.9 D have been measured (the dipole moments at the ground state have been obtained by DFT calculations, 2.2, 0.6 and 1.4 D) for **SPA-DBS**, **SIA-DBS** and **SQPTZ-DBS** respectively (see in SI). These  $\Delta\mu$  data translate the different polarities of the three fluorophores in their excited states ( $\mu^* = 18.5$ , 16.5 and 19.3 D resp.). The solvatochromic effect (Figure 5) and the corresponding high  $\Delta\mu$  observed for **SPA-DBS**, **SIA-DBS** and **SQPTZ-DBS** are indicative of a significant photoinduced ICT. Thus, one can note that the QPTZ fragment provides the highest  $\Delta\mu$  due to its electron-rich behaviour stronger than that of the PA and IA analogues **SPA-DBS** and **SIA-DBS**.

Solid state fluorescence has finally been recorded before any OLED applications. From solution to film, there is a red shift detected for the three emitters, 46 nm for **SIA-DBS**, 36 nm for **SPA-DBS** and 28 nm for **SQPTZ-DBS** due to the different environment (Figure 3, right). However, the emission remains in the deep-blue region with maxima at 421, 437 and 445 nm respectively, which is highly beneficial for the targeted application (see below).

## Thermal Properties

Before any possible OLED application, thermal properties should be evaluated by means of thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC), Figure 6. In the present case, the three emitters possess a high decomposition temperature  $T_d$  (5% mass loss), above 300°C. More importantly, **SQPTZ-DBS** presents a higher glass transition temperature  $T_g$  (117°C determined by DSC during the 2nd heating run, between 20 and 260°C) compared to **SIA-DBS**, which presents a  $T_g$  detected at 105°C. It is important to notify that no  $T_g$  were observed is the same conditions for **SPA-DBS**. Both high  $T_g$  and high  $T_d$  parameters are important to reach highly stable devices. Thus, incorporation of a sulfur atom in **SQPTZ-DBS** is beneficial for further OLED applications in terms of thermal properties. **SPA-DBS** and **SIA-DBS** present a crystallization temperature  $T_c$  at ca. 158°C and 127°C respectively which is suppressed in the QPTZ based compounds. As amorphous materials are highly desired in this field, this is an important characteristic of the QPTZ fragment.

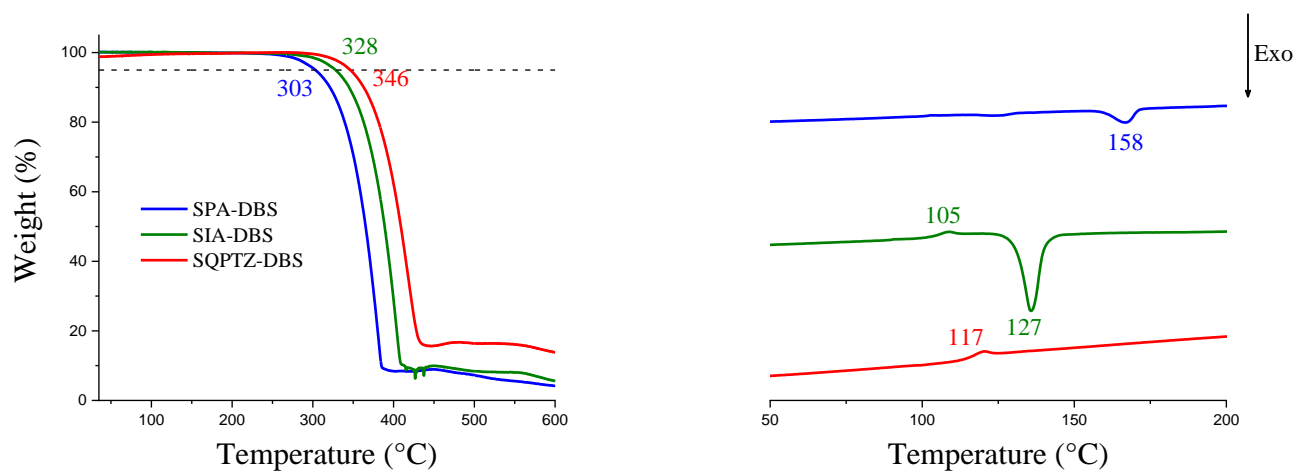
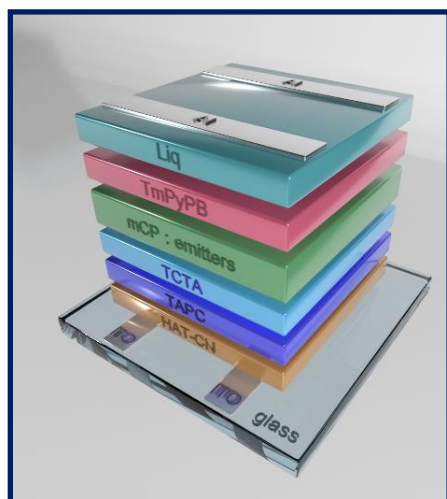
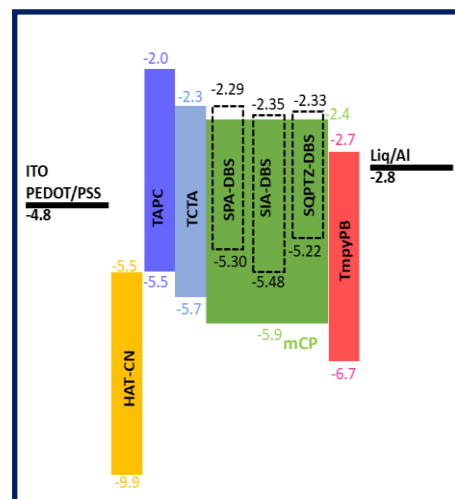


Figure 6. TGA (Left) and DSC (Right, 2<sup>nd</sup> heating cycle only) of **SPA-DBS** (blue lines), **SIA-DBS** (green lines) and **SQPTZ-DBS** (red lines).

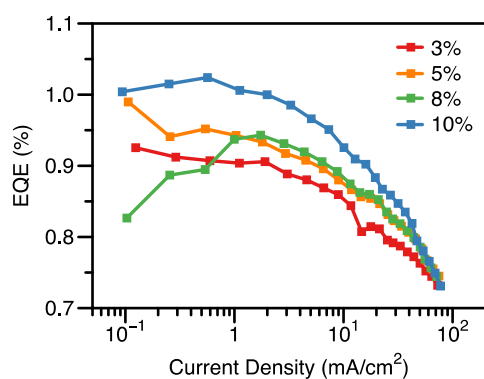
A)



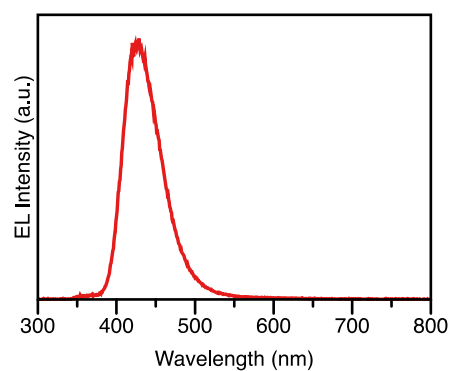
B)



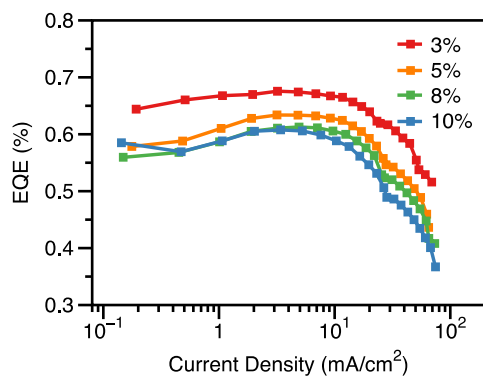
C)



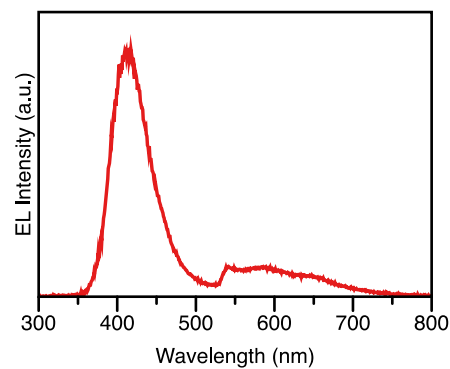
D)



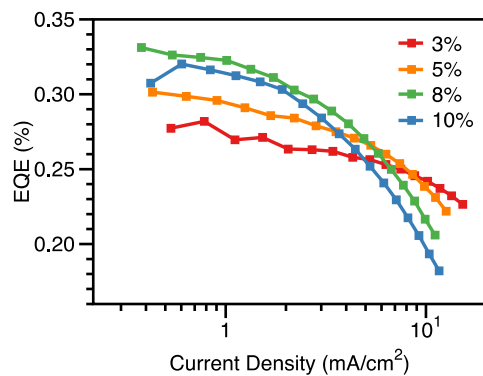
E)



F)



G)



H)

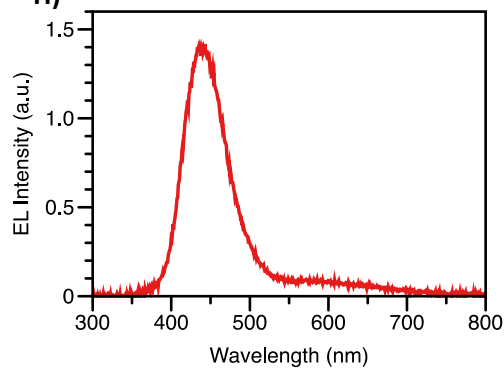


Figure 7: Device structure (A), Energy level diagram (B). Electroluminescent spectra and EQE vs current density of **SPA-DBS** (C-D), **SIA-DBS** (E-F) and **SQPTZ-DBS** (G-H)

Finally, the compounds were incorporated as emitter in OLED devices. As shown in Figure 7, the optimal device configuration was ITO/HAT-CN (10 nm)/ TAPC (40 nm)/ TCTA (10 nm)/ mCP: emitters (x%, 20 nm)/ TmPyPB (40 nm)/ Liq (2 nm)/ Al (120 nm). The concentration of the emitter in the emissive layer was evaluated between 3 and 10% (See Figures S15, S16 and S17).

The electroluminescent (EL) spectra, measured at a current density of 5 mA/cm<sup>2</sup>, appears to be very different and dependent on the electron rich fragment (Figure 7, D, F, H). Indeed, in the case of both **SIA-DBS** and **SQPTZ-DBS**, a large band between 500 and 700 nm is observed, in addition to the blue contribution respectively observed at 414 and 442 nm. Such a band in the green region has been the subject of intense researches in the field of blue OLEDs in order to find its origin ( $\pi$ - $\pi$  interactions, keto defect etc).<sup>17, 49-51</sup> Due to this parasite band, the CIE, respectively measured at (0.24, 0.14) and (0.18, 0.10) for **SIA-DBS** and **SQPTZ-DBS** do not fit with the chromatic standards exposed above. However, **SPA-DBS** does not present this parasite green emission band and its EL spectrum only possesses the blue contribution at 428 nm, very similar to that measured in solid thin film, 437 nm (Figure 3, right). This device possesses a good colour purity as its full width at half-maximum (FWHM) is estimated to be 55 nm, almost identical to that measured in thin-solid film (60 nm, Table 1). The difference observed between the three compounds may arise from the extended cores of IA and QPTZ vs PA, which may favour  $\pi$ - $\pi$  stacking. Thus, the CIE coordinates of the **SPA-DBS** based device (0.16, 0.04) appears to be very interesting for display, with a particularly low CIEy value of 0.04. The current density versus EQE plots for these devices are presented in Figure 7 and the device performance is summarized in Table 2 (detailed performance is shown in SI). These devices display turn-on voltages ( $V_{on}$  at 1 Cd.cm<sup>-2</sup>) ranging from 3.5 to 5.1 V in the same range than those obtained with the best fluorescent violet OLEDs reported to date in literature (3.6-3.8 V).<sup>29</sup> This is directly related to the presence of electron rich units in these structures. These values appear nevertheless a little bit high due to the low concentration of emitter in the large bandgap material mCP. In term of performance, the highest EQE is measured for **SPA-DBS** with an EQE of 1.02 % (10% of emitter). Thus, the performance of **SPA-DBS** based OLEDs with a  $V_{on}$  of 4V, an EQE of ca 1% and CIE coordinate of (0.16, 0.04) is a first step towards the development of violet DBS based emitters with low CIEy. These CIE coordinates closely approach the ITU-R Recommendation BT.2020 (Rec. 2020) standard of (0.131, 0.046).<sup>29</sup>

Table 2. Best OLED performances using **SPA-DBS**, **SIA-DBS** and **SQPTZ-DBS** as emitter with different percentage of doping and mCP as the host material.

Host	Dopant	$V_{on}^a$ (V)	$CE_{max}$ (cd/A)	$EQE_{max}$ (%)	$\lambda_{max}$ (nm)	FWHM (nm)	CIE (x, y) <sup>b)</sup>
	<b>SPA-DBS</b> (10%)	4.0	0.439	1.024	428	55	(0.16, 0.04)
mCP	<b>SIA-DBS</b> (3%)	3.5	0.668	0.676	414	60	(0.24, 0.14)
	<b>SQPTZ-DBS</b> (8%)	5.1	0.205	0.331	442	61	(0.18, 0.10)

a) Recorded at a luminance of 1 cd/m<sup>2</sup>. b) Measured at a driving current density of 5 mA/cm<sup>2</sup>

## Conclusion

To conclude, we report in this work the synthesis, the physico-chemical properties and the application in OLED of deep blue emitters constructed on the dibenzosuberene molecular fragment. As the charge injection is particularly important in deep-blue emission, electron rich units, namely *N*-phenylacridine, indoloacridine and quinolinophenothiazine have been connected to the DBS core. The resulting organic materials display similar LUMO levels lying at ca -2.30 eV and different HOMO levels driven by the donor unit comprised between -5.22 and -5.48 eV. The spiro-configuration allows maintaining high  $T_g$  and  $T_d$  in accordance with OLED application. **SPA-DBS** displays a deep-blue emission with CIE of (0.16, 0.04), reaching an EQE of ca 1% and possessing a very low CIEy coordinate

of 0.04. This CIEy coordinate fits the NSTC, ITU and EBU standards. This work not only reports a deep blue emitter for OLED but also shed light on interesting properties displayed by the DBS fragment, such as its low LUMO energy level, ca -2.3 eV, which is significantly decreased compared to its counterpart fluorene. This particularity can be advantageously used in further designs to favour the electron injection in electronic devices.

There are no conflicts to declare.

## Supporting Information

Details on the materials synthesis, their thermal, photophysical and electrochemical properties, theoretical modeling and device data are provided in the supporting Information. Copies of NMR spectra are also included. The Supporting Information is available free of charge on the Publications website.

## Acknowledgments

The authors would like to thank the ANR (SPIROQUEST, n°19-CE05-0024) for financial support of this project, the Agence de l'Environnement et de la Maitrise de l'Energie (ADEME) for PhD grand (CB, EcoElec Project). We would like to thank Bruno Lafitte (ADEME), Dr Maxime Romain to have initiated dibenzosuberene compounds in the group and the CRMPO (Rennes) for mass analysis. This work was granted access to the HPC resources of CINES under the allocation 2021-A0100805032 awarded by GENCI. The authors thank Dr J. F. Bergamini (Rennes) for the TOC material.

Received: ((will be filled in by the editorial staff))

## References

1. Hong, G.; Gan, X.; Leonhardt, C.; Zhang, Z.; Seibert, J.; Busch, J. M.; Bräse, S., A Brief History of OLEDs—Emitter Development and Industry Milestones *Adv. Mater.* 2021, **33**, 2005630.
2. Mertens, R., *The OLED Handbook: A Guide to OLED Technology, Industry & Market*. 2019 edition: 2019.
3. Qu, Y.-K.; Zheng, Q.; Fan, J.; Liao, L.-S.; Jiang, Z.-Q., Spiro Compounds for Organic Light-Emitting Diodes *Accounts of Materials Research* 2021, **2**, 1261.
4. Tang, C. W.; Vanslyke, S. A., Organic electroluminescent diodes *App. Phys. Lett.* 1987, **51**, 913.
5. Poriel, C.; Rault-Berthelot, J., Blue Single-Layer Organic Light-Emitting Diodes Using Fluorescent Materials: A Molecular Design View Point *Adv. Funct. Mat.* 2020, **30**, 1910040.
6. Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller, J.; Moon, R.; Roitman, D.; Stocking, A., Organic Electroluminescent Devices *Science* 1996, **273**, 884.
7. Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Lögdlund, M.; Salaneck, W. R., Electroluminescence ds les polymere conjugue ref DEA *Nature* 1999, **397**, 121.
8. Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R., Highly efficient phosphorescent emission from organic electroluminescent devices *Nature* 1998, **395**, 151.
9. Tao, Y.; Yang, C.; Qin, J., Organic host materials for phosphorescent organic light-emitting diodes *Chem. Soc. Rev.* 2011, **40**, 2943.
10. Yook, K. S.; Lee, J. Y., Small Molecule Host Materials for Solution Processed Phosphorescent Organic Light-Emitting Diodes *Adv. Mater.* 2014, **26**, 4218.
11. Poriel, C.; Rault-Berthelot, J., Structure–property relationship of 4-substituted-spirobifluorenes as hosts for phosphorescent organic light emitting diodes: an overview *J. Mater. Chem. C* 2017, **5**, 3869.
12. Poriel, C.; Rault-Berthelot, J., Designing Host Materials for the Emissive Layer of Single-Layer Phosphorescent Organic Light-Emitting Diodes: Toward Simplified Organic Devices *Adv. Funct. Mat.* 2021, **31**, 2010547.
13. Wang, Q.; Lucas, F.; Quinton, C.; Qu, Y.-K.; Rault-Berthelot, J.; Jeannin, O.; Yang, S.-Y.; Kong, F.-C.; Kumar, S.; Liao, L.-S.; Poriel, C.; Jiang, Z.-Q., Evolution of pure hydrocarbon hosts: simpler structure, higher performance and universal application in RGB phosphorescent organic light-emitting diodes *Chem. Sci.* 2020, **11**, 4887.
14. Endo, A.; Ogasawara, M.; Takahashi, A.; Yokoyama, D.; Kato, Y.; Adachi, C., Thermally Activated Delayed Fluorescence from Sn4+—Porphyrin Complexes and Their Application to Organic Light Emitting Diodes — A Novel Mechanism for Electroluminescence *Adv. Mater.* 2009, **21**, 4802.
15. Wong, M. Y.; Zysman-Colman, E., Purely Organic Thermally Activated Delayed Fluorescence Materials for Organic Light-Emitting Diodes *Adv. Mater.* 2017, **29**, 1605444.

16. Zhang, Y.; Cheng, G.; Zhao, Y.; Hou, J.; Liu, S.; Tang, S.; Ma, Y., Organic pure-blue-light-emitting devices based on terfluorenes compounds *App. Phys. Lett.* 2005, **87**, 241112.
17. Poriel, C.; Cocherel, N.; Rault-Berthelot, J.; Vignau, L.; Jeannin, O., Incorporation of Spiroxanthene Units in Blue-Emitting Oligophenylene Frameworks: A New Molecular Design for OLED Applications *Chem. Eur. J.* 2011, **17**, 12631.
18. Cocherel, N.; Poriel, C.; Vignau, L.; Bergamini, J.-F.; Rault-Berthelot, J., DiSpiroXanthene-IndenoFluorene: A New Blue Emitter for Nondoped Organic Light Emitting Diode Applications *Org. Lett.* 2010, **12**, 452.
19. Lee, H. L.; Chung, W. J.; Lee, J. Y., Narrowband and Pure Violet Organic Emitter with a Full Width at Half Maximum of 14 nm and y Color Coordinate of Below 0.02 *Small* 2020, **16**, 1907569.
20. Yuan, Y.; Hu, Y.; Zhang, Y.-X.; Lin, J.-D.; Wang, Y.-K.; Jiang, Z.-Q.; Liao, L.-S.; Lee, S.-T., Over 10% EQE Near-Infrared Electroluminescence Based on a Thermally Activated Delayed Fluorescence Emitter *Adv. Funct. Mater.* 2017, **27**, 1700986.
21. Maclean, M.; Murdoch, L. E.; MacGregor, S. J.; Anderson, J. G., Sporicidal effects of high-intensity 405 nm visible light on endospore-forming bacteria *Photochem. Photobiol.* 2013, **89**, 120.
22. Lee, J.-H.; Chen, C.-H.; Lee, P.-H.; Lin, H.-Y.; Leung, M.-k.; Chiu, T.-L.; Lin, C.-F., Blue organic light-emitting diodes: current status, challenges, and future outlook *J. Mater. Chem. C* 2019, **7**, 5874.
23. Wang, Y.; Yun, J. H.; Wang, L.; Lee, J. Y., High Triplet Energy Hosts for Blue Organic Light-Emitting Diodes *Adv. Funct. Mater.* 2020, **31**, 2008332.
24. Yang, X.; Xu, X.; Zhou, G., Recent advances of the emitters for high performance deep-blue organic light-emitting diodes *J. Mater. Chem. C* 2015, **3**, 913.
25. Monkman, A., Why Do We Still Need a Stable Long Lifetime Deep Blue OLED Emitter? *ACS Appl. Mater. Interfaces* 2022, 10.1021/acsaami.1c09189.
26. Poriel, C.; Rault-Berthelot, J.; Jiang, Z.-Q., Are pure hydrocarbons the future of host materials for blue phosphorescent organic light-emitting diodes? *Mater. Chem. Front.* 2022.
27. Poriel, C.; Rault-Berthelot, J., Pure hydrocarbons: An efficient molecular design strategy for the next generation of host materials for Phosphorescent Organic Light-Emitting Diodes *Acc. Mater. Res.* 2022, **3**, 379.
28. Dumur, F., Deep-blue Organic Light-emitting Diodes: From Fluorophores to Phosphors for High-efficiency Devices In *Advanced Surface Engineering Materials*, Scrivener Publishing: 2016, 561.
29. Zou, S. N.; Chen, X.; Yang, S. Y.; Kumar, S.; Qu, Y. K.; Yu, Y. J.; Fung, M. K.; Jiang, Z. Q.; Liao, L. S., Efficient Violet Organic Light- Emitting Diodes with CIEy of 0.02 Based on Spiro Skeleton *Adv. Opt. Mater.* 2020, **8**, 2001074.
30. Wei, Y.; Chen, C.-T., fDoubly Ortho-Linked cis-4,4'-Bis(diarylamino)stilbene/Fluorene Hybrids as Efficient Nondoped, Sky-Blue Fluorescent Materials for Optoelectronic Applications *J. Am. Chem. Soc.* 2007, **129**, 7478.
31. Jou, J.-H.; Su, Y.-T.; Hsiao, M.-T.; Yu, H.-H.; He, Z.-K.; Fu, S.-C.; Chiang, C.-H.; Chen, C.-T.; Chou, C.-h.; Shyue, J.-J., Solution-Process-Feasible Deep-Red Phosphorescent Emitter *J. Phys. Chem. C* 2016, **120**, 18794.
32. Chen, C.-T.; Wei, Y.; Lin, J.-S.; Moturu, M. V. R. K.; Chao, W.-S.; Tao, Y.-T.; Chien, C.-H., Doubly Ortho-Linked Quinoxaline/Diphenylfluorene Hybrids as Bipolar, Fluorescent Chameleons for Optoelectronic Applications *J. Am. Chem. Soc.* 2006, **128**, 10992.
33. Romain, M.; Tondelier, D.; Geffroy, B.; Jeannin, O.; Jacques, E.; Rault-Berthelot, J.; Poriel, C., Donor/Acceptor Dihydroindeno[1,2-a]fluorene and Dihydroindeno[2,1-b]fluorene: Towards New Families of Organic Semiconductors *Chem. Eur. J.* 2015, **21**, 9426.
34. Romain, M.; Tondelier, D.; Jeannin, O.; Geffroy, B.; Rault-Berthelot, J.; Poriel, C., Properties modulation of organic semi-conductors based on a donor-spiro-acceptor (D-spiro-A) molecular design: new host materials for efficient sky-blue PhOLEDs *J. Mater. Chem. C* 2015, **3**, 97010.
35. Lucas, F.; Quinton, C.; Fall, S.; Heiser, T.; Tondelier, D.; Geffroy, B.; Leclerc, N.; Rault-Berthelot, J.; Poriel, C., Universal host materials for red, green and blue high-efficiency single-layer phosphorescent organic light-emitting diodes *J. Mater. Chem. C* 2020, **8**, 16354.
36. Thiery, S.; Tondelier, D.; Geffroy, B.; Jeannin, O.; Rault-Berthelot, J.; Poriel, C., Modulation of the Physicochemical Properties of Donor–Spiro–Acceptor Derivatives through Donor Unit Planarisation: Phenylacridine versus Indoloacridine—New Hosts for Green and Blue Phosphorescent Organic Light-Emitting Diodes (PhOLEDs) *Chem. Eur. J.* 2016, **22**, 10136.
37. Poriel, C.; Rault-Berthelot, J.; Thiery, S.; Quinton, C.; Jeannin, O.; Biapo, U.; Geffroy, B.; Tondelier, D., 9H-Quinolino[3,2,1-k]phenothiazine: A New Electron-Rich Fragment for Organic Electronics *Chem. Eur. J.* 2016, **22**, 17930.
38. Lucas, F.; Tondelier, D.; Geffroy, B.; Heiser, T.; Ibraikulov, O. A.; Quinton, C.; Brouillac, C.; Leclerc, N.; Rault-Berthelot, J.; Poriel, C., Quinolophenothiazine as Electron Rich Fragment for RGB Single-Layer Phosphorescent Organic Light-Emitting Diodes *Mater. Chem. Front.* 2021, **5**, 8066.

39. Quinton, C.; Sicard, L.; Jeannin, O.; Vanthuyne, N.; Poriel, C., Confining Nitrogen Inversion to Yield Enantiopure Quinolino[3,2,1-k]Phenothiazine Derivatives *Adv. Funct. Mat.* 2018, **28**, 1803140.
40. Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J., Spiro Compounds for Organic Optoelectronics *Chem. Rev.* 2007, **107**, 1011.
41. Xie, L.-H.; Liang, J.; Song, J.; Yin, C.-R.; Huang, W., Spirocyclic Aromatic Hydrocarbons (SAHs) and their Synthetic Methodologies *Curr. Org. Chem.* 2010, **14**, 2169.
42. Liu, S.; Xia, D.; Baumgarten, M., Rigidly-Fused Spiro-Conjugated  $\pi$ -Systems *ChemPlusChem* 2021, **21**, 36.
43. Poriel, C.; Sicard, L.; Rault-Berthelot, J., New generations of spirobifluorene regioisomers for organic electronics: tuning electronic properties with the substitution pattern *Chem. Comm.* 2019, **55**, 14238.
44. Poriel, C.; Rault-Berthelot, J., Dihydroindenofluorene positional isomers *Acc. Chem. Res.* 2018, **51**, 1818.
45. Ferrand, Y.; Poriel, C.; Le Maux, P.; Rault-Berthelot, J.; Simonneaux, G., Asymmetric Heterogeneous Carbene Transfer Catalyzed by Optically Active Ruthenium Spirobifluorenylporphyrin Polymers. *Tetrahedron Asymmetry* 2005, **16**, 1463.
46. Poriel, C.; Ferrand, Y.; Le Maux, P.; Rault-Berthelot, J.; Simonneaux, G., Organic Cross-Linked Electropolymers as Supported Oxidation Catalysts: Poly((tetrakis(9,9'-spirobifluorenyl)porphyrin)manganese) Films *Inorg. Chem.* 2004, **43**, 5086.
47. Poriel, C.; Ferrand, Y.; Le Maux, P.; Paul-Roth, C.; Simonneaux, G.; Rault-Berthelot, J., Anodic oxidation and physicochemical properties of various porphyrin-fluorenes or -spirobifluorenes: Synthesis of new polymers for heterogeneous catalytic reactions *J. Electroanal. Chem.* 2005, **583**, 92.
48. Lucas, F.; Ibraikulov, O. A.; Quinton, C.; Sicard, L.; Heiser, T.; Tondelier, D.; Geffroy, B.; Leclerc, N.; Rault-Berthelot, J.; Poriel, C., Spirophenylacridine-2,7-(diphenylphosphineoxide)-fluorene: A Bipolar Host for High-Efficiency Single-Layer Blue Phosphorescent Organic Light-Emitting Diodes *Adv. Opt. Mater.* 2020, **8**, 1901225.
49. Chan, K. L.; Sims, M.; Pascu, S. I.; Ariu, M.; Holmes, A. B.; Bradley, D. D. C., Understanding the Nature of the States Responsible for the Green Emission in Oxidized Poly(9,9-dialkylfluorene)s: Photophysics and Structural Studies of Linear Dialkylfluorene/Fluorenone Model Compounds *Adv. Funct. Mater.* 2009, **19**, 2147.
50. Grimsdale, A. C., In search of stable blue emission from phenylene-based conjugated polymers *Curr. Org. Chem.* 2010, **14**, 2196.
51. Cocherel, N.; Poriel, C.; Rault-Berthelot, J.; Barrière, F.; Audebrand, N.; Slawin, A. M. Z.; Vignau, L., New  $3\pi$ -2Spiro Ladder-Type Phenylene Materials: Synthesis, Physicochemical Properties and Applications in OLEDs *Chem. Eur. J.* 2008, **14**, 11328.