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Molecular engineering to improve the balance of charge carrier in single-layer silole-based OLEDs.

Laurent Aubouy, a Nolwenn Huby, b Lionel Hirsch, b Arie van der Lee, c and Philippe Gerbier a * 

We report a molecular engineering study on optical, structural and electrical properties of seven silole derivates aiming at enhancing the balance of charge carrier in single-layer devices. By functionalizing two hole-transporting groups, dipyridylamine or anthracene, on the silole ring, we have investigated the influence of both entity types on the hole current. We have concluded that in contrast to dipyridylamine groups, anthracene groups decrease the balance of charge carrier since the latter groups not only increase the hole current but also electron contribution. Doubling the number of hole transporting groups lead the silole D to become a very efficient emissive layer exhibiting threshold voltage below 3 V and luminous efficiency \( L_\text{e} = 0.8 \text{ cd/A at 7 V} \).

Introduction

Organic light-emitting diodes (OLEDs) using small molecules or polymers have been intensively pursued after the initial works by Tang, Van Slyke and Burroughes 1, 2 because of their enormous potential in flat, flexible panels lighting and displays. The search for efficient and stable new emitting materials with appropriate emission spectrum remains as one of the most active areas of these studies. Different strategies have been developed to enhance the efficiency of the devices such as the assisted singlet-triplet internal conversion and the balance of charge carriers in the emissive zone. Among them, the approach involving the incorporation of heavy metal complexes has attracted a great attention since it allows to obtain both very high efficiencies and white emission. 3-8 On the other hand, the balance of charge carriers in the emissive zone has attracted much less attention due to the development of multilayer structures as a response to this issue. 9, 10 Indeed, in organic semi-conductors, one of both charge-carriers presents a higher mobility compared to the other one. This leads to several drawbacks such as, for instance, the location of the recombination zone close to an electrode, leading to a huge quenching of excitons. Therefore it is possible to overcome this problem by using PIN OLEDs structures.11 Nevertheless, this approach suffers of some drawbacks due to a large number of interfaces and/or segregation phase apperition.


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The aim of this paper is to design a fluorescent molecule able to transport both charge carriers. In this way, we focussed on silole derivatives since they appear to possess all the requirements to achieve single-layer OLEDs. The siloles or silacyclopentadienes are a group of five-membered silacycles that possess σ*-π* conjugation arising from the interaction between the σ* orbital of two exocyclic σ bonds on the silicon atom and the π* orbital of the butadiene moiety. As a consequence, the calculated LUMO level of a silole ring is lower than those of other heterocyclopentadienes, such as pyrrole, furan, and thiophene. Moreover, thanks to its nonaromatic character the π-system of the silole ring is more prone to allow electron delocalization when compared with its thiophene cousins. From a structural point of view, because of the non-coplanar structure of 2,3,4,5-tetraarylsiloles, the distances between silole cores of any two adjacent molecules, even in the solid state, are far from the normal π–π interaction distance (ca. 3–4 Å). This gives rise to a very interesting photophysical property called aggregation-induced photoluminescence (PL) emission (AIE). Because of the AIE characteristics, 2,3,4,5-tetraphenylsiloles can show extremely high PL quantum yields (up to 100%), even in a crystalline form. Thereby, 2,3,4,5-tetraphenylsiloles are excellent emitters in the fabrication of electroluminescence (EL) devices, an external quantum efficiency (ηEL) up to 8%, close to the theoretical limit for a singlet emitter, was realized with such derivatives in the emissive layer. Finally, siloles exhibit very high electron mobility, exceeding the well-known tris-(8-hydroxyquinoline) aluminum (Alq3), and have been utilized as the electron-transporting layer for EL devices.

The results presented in this paper follow previous reports concerning the silole A (Scheme 1). This molecule is based on a silacyclopentadiene core, which acts both as emissive and electron-transporting component, and two dipyridylamino functionalities grafted on each side, which act as hole-transporting groups. By associating those two functionalities, we have achieved a sufficient balance of charge to make light from single-layer OLEDs. However, the temperature dependence and the electron injection barrier dependence investigations have highlighted the weak hole contribution in hole-only devices that is only three orders of magnitude lower than the electron one. Since it may be expected that a better balance of charge should improve greatly the efficiency of the devices, we have designed the siloles shown in Schemes 1 and 3 with increasing their hole-transporting properties. On the one hand, the dipyridylamino hole-transporting groups were changed by anthracenyl ones that are well known as good hole-transporting group in molecular films. On the other hand, we changed the hole-carriers to electron-carriers ratio that is 1:1 for silole E, 2:1 for siloles A, A’, B, B’ and 4:1 for siloles C and D. The effect of the conjugation between electron- and hole-transporting moieties was also studied by inserting a disrupting ether bridge between the two (siloles A vs A’ and B vs B’). Optical and structural properties are systematically correlated to the device performances in order to highlight the influence of the number of hole-transporting group on the balance of charge carriers.

Results and Discussion
The siloles A-D were conveniently prepared by the method described by Tamao and Yamaguchi that involves the one-pot reductive intramolecular cyclization of bis(phenylethynyl)silane and the subsequent Pd(0)-catalyzed cross-coupling reaction with the desired arylbromide (Scheme 1). The synthesis of 9-(4-bromophenyl)anthracene and [4-(4-bromo-phenoxy)-phenyl]anthracene was achieved starting from anthrone by using the procedure described by Murphy et al. 3,5-bis(2,2'-dipyridylamino)-bromobenzene and [4-(4-bromo-phenoxy)-phenyl]di-pyridyn-2-yl-amine were synthesized through a modification of the original Ullman’s reaction. The preparation of the asymmetrically 9,10-diarylanthracene was achieved through an adaptation of the procedure described by Smet et al. It involves firstly the lithiation of the compound followed by the addition of the resulting lithio derivative on anthraquinone to afford the monoadduct in 43% yield. To this compound, a two-fold excess of 4-bromophenyllithium was added yielding the diol. The excess of 4-bromophenyllithium was necessary to react with the OH group present in the monoadduct 8. Reduction of the latter using NaH2PO2 and KI in refluxing acetic acid afforded a light yellow solid in 20% yield.

The synthesis of silole E involves firstly the preparation of the bis-silole derivative through the Tamao-Yamaguchi’s reaction between the dizincic intermediate 2 and 1.5 equiv. of 1,4-dibromobenzene. The bis(bromophenyl)silole 12 which is formed along with 11 is easily isolated by column chromatography and will serve as starting material for other syntheses. The subsequent Suzuki coupling between 11 and the boronic acid derivative afforded the expected bis-silole E in good yield.

(ii) Geometries of siloles

The determination of the conformational preferences of these molecules is of outmost importance for the understanding of their electronic behaviour. Since crystals suitable for a X-ray structure determination could only be obtained for A, B, and 11, we turned to density functional theory (DFT) calculations with the B3LYP functional to obtain information about the molecular conformations for the rest of siloles. Due to the size of the molecules, geometry optimizations without symmetry constrains were performed with the 6-31G basis set to the standard convergence criteria as implemented in Gaussian98. Such calculations were followed by single point runs using a 6-31+G* basis to obtain accurate energies. Structurally characterized siloles, dipyrdyldamines, and diphenylethers served as benchmarks to test how well the experimentally determined geometry is reproduced by the calculations, and some relevant torsion angles are collected in Table 1. As exemplified with A (Figure 1), all compounds have a propeller-like arrangement of the four phenyl rings, as found in the crystal structures, while the two methyl substituents on the silicon atom are nearly perpendicular to the mean plane of the SiC ring. The torsion angles of the substituted phenyl rings at the 2- and 5-positions of the central silole ring (φ1) are in the range of what is usually observed with tetraarylsiloles (ca. 30-60°).

Table 1. Torsion angles [°] in siloles

<table>
<thead>
<tr>
<th></th>
<th>A°</th>
<th>B°</th>
<th>C°</th>
<th>D°</th>
<th>E°</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ1</td>
<td>43.4 (44.7)</td>
<td>49.1 (58.4)</td>
<td>38.6</td>
<td>47.8</td>
<td>43.5 (45.1)</td>
</tr>
<tr>
<td>φ2</td>
<td>45.4 (34.3)</td>
<td>---</td>
<td>46.8</td>
<td>50.8 (50.4)</td>
<td>55.5</td>
</tr>
<tr>
<td>φ3</td>
<td>---</td>
<td>77.0 (68.5)</td>
<td>---</td>
<td>71.6 (74.2)</td>
<td>---</td>
</tr>
</tbody>
</table>

* Average values. † Values from crystal structures (see text) are between parentheses. ‡ See scheme 5. § see 44.
The torsion angles between the anthracene main plane and the adjacent phenyl ring ($\phi_3$) fall as well in the range of what is usually observed with related molecules (ca. 70°). This is expected to induce a strong reduction of the conjugation between the electron-transporting silole ring and the lateral hole-transporting groups. The same is expected when an ether bridge is inserted between the two electroactive components since the planar planes of the phenyl ring on both sides of the oxygen atom are nearly perpendicular (see figure 1). Though no crystal suitable for X-ray diffraction were obtained for the bis-silole $E$, we were able to solve the structure of its precursor $11$. This compound crystallizes along with one $\text{CH}_2\text{Cl}_2$ molecule in the $C2/c$ space group. As seen in Figure 2, the molecule possesses an axis of symmetry that passes through the middle of the central phenyl ring. The torsion angles $\phi_1$ between this ring and the two adjacent siloles have a value of 45.14°. As a result, the two silole rings are nearly perpendicular, which contrasts very strongly with the thiophene analogues that are nearly planar. This situation is also encountered in the optimized geometry of silole $E$.

### (iii) Optical and electronic properties

The UV-visible absorption, photoluminescence (PL) spectra have been measured both in solution and thin films. Electroluminescence (EL) spectra were obtained from single layer devices with a structure: ITO/PEDOT:PSS/ silole 50 nm/ Ca. The most relevant data obtained from these spectra are collected in Table 2. Figures 3 and 4 are representative of the two behaviours that are encountered in this series of molecules. As it is seen in figure 3, compound $A$, $A'$, $C$ or $E$ display a broad absorption band in the range of 368 nm and 389 nm which is characteristic of the $\pi \rightarrow \pi^*$ transition in the silole ring. However, as it is seen in Figure 4, in the compounds $B$, $B'$ or $D$, this transition is overlapped by the well recognizable pattern of phenylanthracenes. The comparison of Figures 3 and 4 reveals that the siloles without anthracene side groups behave differently than those bearing ones. In the first family (siloles $A$, $A'$, $C$ and $E$) all the emission spectra are nearly superimposable whatever the excitation mode or the physical state (solution vs thin film). The most important deviation is found with silole $C$ in which a shift of ca. 9 nm is found between the PL and the EL spectra (Table 2). In the second family (siloles $B$, $B'$ and $D$), the PL and EL spectra show differences both in the position of their emission maxima and in their shape, as exemplified in figure 4 with silole $D$. In solution, the anthracene moieties appear to

**Figure 1.** DFT-optimized (B3LYP-6/31G) molecular structures of siloles $A$ (top) and $B'$ (bottom).

**Figure 2.** X-ray structure of silole $11$. The $\text{CH}_2\text{Cl}_2$ crystallization molecule has been removed for sake of clarity.

**Figure 3.** Normalized UV-visible ($\circlearrowright$), photoluminescence (in solution: $\triangledown$ and thin film: $\triangledown$) and electroluminescence ($\bigcirc$) spectra of silole $A$.

**Figure 4.** Normalized UV-visible ($\circlearrowright$), photoluminescence (in solution: $\triangledown$ and thin film: $\triangledown$) and electroluminescence ($\bigcirc$) spectra of silole $D$. 
the AIE phenomenon, 20, 21 the siloles display a very strong absorption and the emission spectra. Moreover this indicates that the two silole rings behave independently, is in good agreement with their perpendicular arrangement in the molecular structure (see above). Interestingly, the presence of either 9-phenylanthracene or 9,10-diphenylanthracene highly fluorescent subunits (see below) in the molecular structures of siloles B, B' and D has no positive effect on their quantum yields. Along with what is observed in the fluorescence spectra, this indicates that a large amount of energy is transferred from the anthracene chromophores to the silole and then released via non-radiative processes. Finally, semi-quantitative measurements of the fluorescence quantum yields on thin films have been also performed. The following sequence have been found: B > B' > D > A > A' > C > DPA > Perylene ≈ E where DPA (9,10-diphenylanthracene, \( \Phi_{\text{em}} \) (solution) = 1.00) and Perylene (\( \Phi_{\text{em}} \) (solution) = 0.94) are given for comparison. On account to the AIE phenomenon, 20, 21 the siloles display a very strong fluorescence in the solid state that exceeds both DPA and Perylene which possess nearly quantitative quantum yields in solution.

To better understand the optical data, we now turn to a description of the main characteristics of the HOMO and LUMO levels as calculated at the DFT level. The analysis of the HOMO and LUMO wave functions shown for siloles A and B in Figure 5 show the typical pattern of tetraphenylsiloles. 46, 47 The HOMO wavefunctions show a very similar spatial distribution with an antibonding character between the silole ring and the phenyl rings located at the 2,5-positions. The same similarity is found with the LUMO wavefunctions which bonding character is observed between the silole ring and the adjacent phenyl rings. The energies of the HOMO and LUMO orbitals (Table 2), which do not vary on a large extend upon modification of the substituents, are in the range of what is usually reported for tetraarylsiloles. The examination of the wavefunctions calculated for siloles A' and B' (Figure 6 for B') show a nearly identical orbital distribution on the tetraphenylsilole core. However, in contrast to their parents A and B, very few electron probability density is found on either the dipryridylamino or the phenylanthracene moieties. This illustrates the expected disruption of the conjugation brought about by the diphenylether bridges, and the reason why the emission maximum of these two molecules is blue-shifted of 20 nm when compared with their parents A and B.

Table 2. Main values of the optical properties (UV-Visible and fluorescence spectra) in solution and in thin films.

<table>
<thead>
<tr>
<th>Silole</th>
<th>Absorption* ( \lambda_{\text{max}} ) [nm]</th>
<th>PL* ( \lambda_{\text{max}} ) [nm]</th>
<th>Quantum yield*</th>
<th>EL* ( \lambda_{\text{max}} ) [nm]</th>
<th>HOMO and (LUMO) levels [eV]*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>388 (403)</td>
<td>526 (542)</td>
<td>0.040</td>
<td>545</td>
<td>-5.20 (2.04)</td>
</tr>
<tr>
<td>B</td>
<td>389 (394)</td>
<td>428 (507)</td>
<td>0.015</td>
<td>521</td>
<td>-5.39 (2.00)</td>
</tr>
<tr>
<td>C</td>
<td>379 (385)</td>
<td>503 (511)</td>
<td>0.038</td>
<td>520</td>
<td>-5.32 (1.79)</td>
</tr>
<tr>
<td>D</td>
<td>404 (437)</td>
<td>455 (503)</td>
<td>0.040</td>
<td>518</td>
<td>-5.09 (1.85)</td>
</tr>
<tr>
<td>E</td>
<td>419 (-)</td>
<td>538 (557)</td>
<td>0.002</td>
<td>586</td>
<td>-5.11 (1.89)</td>
</tr>
<tr>
<td>A'</td>
<td>378 (375)</td>
<td>505 (505)</td>
<td>0.006</td>
<td>504</td>
<td>-5.00 (2.01)</td>
</tr>
<tr>
<td>B'</td>
<td>388 (392)</td>
<td>407 (507)</td>
<td>0.020</td>
<td>517</td>
<td>-5.16 (2.32)</td>
</tr>
</tbody>
</table>

* The values recorded with thin solid films are between parentheses. 4 Measured in CH2Cl2. 5 Measured in solution, quantum yield relative to perylene (\( \Phi_{\text{em}} \) = 0.94). 6 From B3LYP/6-31G* DFT calculations.

Figure 5. B3LYP/6-31G*-calculated highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals for siloles A and B.

Figure 6. B3LYP/6-31G*-calculated HOMO and LUMO molecular orbitals for silole B'.

(iv) Electroluminescence properties and balance of charge carriers

In order to study the EL properties, single layer devices have been investigated, with the following structure: ITO/PEDOT:PSS/ silole 50 nm/ Ca. The electroluminescent spectra are shown in Figure 7. As observed during the photoluminescence studies, only the silole ring contributes to the emission and device based on molecule A is 20 nm...
recombination probability of injected holes and electrons, is the ratio of singlet and triplet excitons contributing to the charge-carriers in this series of molecules, one has to consider the factors that determine the efficiency of an OLED. Actually, this may approximately be calculated by the following equation:  

\[ \eta_{\text{external}} = \gamma \cdot \eta_{\text{recomb}} \cdot \eta_{\text{ST}} \cdot \eta_{\text{optical}} \cdot \Phi_{\text{PL}} \]  

where \( \eta_{\text{external}} \) is the total power efficiency of the device, \( \gamma \) is the balance of charge-carrier, \( \eta_{\text{recomb}} \) represents the recombination probability of injected holes and electrons, \( \eta_{\text{ST}} \) is the ratio of singlet and triplet excitons contributing to the radiative recombination, \( \eta_{\text{optical}} \) is the efficiency of the optical outcoupling from the device, and \( \Phi_{\text{PL}} \) is the quantum yield of fluorescence of the emissive material. By spin statistics, \( \eta_{\text{ST}} \), which is the ratio of singlet to triplet excitons, should be \( \eta_{\text{ST}} = 0.25 \), since parallel spin pairs will recombine to triplet excitons while antiparallel spin pairs will recombine to singlet and triplet excitons. Thus, for fluorescent emitters, we find \( \eta_{\text{ST}} = 0.25 \), which is a severe limitation of quantum efficiency of an OLED. Concerning the optical outcoupling efficiency, a simple estimation regarding the OLED as classical optics device shows that a flat device with typical refractive index of the organic layers of 1.7, deposited on ITO/glass, achieves approximately 20% outcoupling. Therefore, the first factor that defines the efficiency of an OLED on which we can play from a molecular engineering point of view is the balance of charge-carrier (\( \gamma \)).

To analyze the result of molecular engineering on the silole core in terms of balance of charge-carriers, one has still to take into account both the charge transport processes and the quantum yield of fluorescence in the solid state of each molecule. Concerning the first issue, at least two parameters have to be taken into consideration: the orbital energy levels and the organization of the molecules in the thin film. In previous works we have studied the transport properties of siloles A and B. Actually, they have a very close behaviour on account to their similarities both in terms of molecular organization (they form amorphous films) and in terms of energy levels and orbital distribution (see above). Therefore, it seems reasonable to set the factor \( \eta_{\text{recomb}} \) in Eq. 1 to a same arbitrary value for all the series of molecules studied here. In this way, the comparison of the luminous efficiencies corrected by the relative solid-state \( \Phi_{\text{PL}} \) value should allow to estimate the effect of molecular engineering on the balance of charge carriers.

**Table 3.** The luminance (L), luminous efficiency (Le) and energetic efficiency (R) of siloles operating in ITO/PEDOT-PSS/Silole/Ca OLEDs.

<table>
<thead>
<tr>
<th>Silole</th>
<th>Vth [V]</th>
<th>L [cd/m²]</th>
<th>Le [cd/A]</th>
<th>R [lm/W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.5</td>
<td>26 (370)</td>
<td>0.17 (0.20)</td>
<td>0.095 (0.066)</td>
</tr>
<tr>
<td>B</td>
<td>3.1</td>
<td>25 (350)</td>
<td>0.16 (0.18)</td>
<td>0.100 (0.099)</td>
</tr>
<tr>
<td>C</td>
<td>9</td>
<td>8 (74)</td>
<td>0.05 (0.056)</td>
<td>0.012 (0.015)</td>
</tr>
<tr>
<td>D</td>
<td>2.9</td>
<td>80 (1550)</td>
<td>0.32 (0.35)</td>
<td>0.320 (0.35)</td>
</tr>
<tr>
<td>E</td>
<td>4.5</td>
<td>- (86)</td>
<td>(0.09)</td>
<td>-</td>
</tr>
<tr>
<td>A'</td>
<td>18</td>
<td>5 (5)</td>
<td>0.03 (0.03)</td>
<td>0.003 (0.003)</td>
</tr>
<tr>
<td>B'</td>
<td>4.2</td>
<td>21 (290)</td>
<td>0.14 (0.19)</td>
<td>0.060 (0.060)</td>
</tr>
</tbody>
</table>

* Values measured at a current density of 200 mA/cm². Values measured at 20 mA/cm².
From semi-quantitative measurements we have found the following sequence for the solid-state photoluminescence quantum yield $\Phi_{PL}$: $B > B' > D > A > A' > C > E$. By using the procedure of normalization described in the experimental part, we have found that the photoluminescence intensity of the procedure of normalization described in the experimental part, we have found that the photoluminescence intensity of the device and the hole carrier moieties ($h$) is not given since it is of the same order than the error on the measurement. Therefore, the ratio $L_e$ over $\Phi_{PL}$ should give a good indication on the correlation between the balance of charge carriers in the device and the hole carrier moieties ($h$). The disruption of the conjugation in silole $A$ allows us now to evaluate the importance of the fact that the silole $A$ possesses a weak solid-state $\Phi_{PL}$ when compared to $D$, and $ii)$ the four dipirydilamino groups generate a strong steric hindrance which disfavors the electron transfert between the silole rings in the device.

The comparison of siloles $A$ and $B$ allows in which the $h^+/e^-$ ratio is equal to 2 allows us to estimate the relative ability of the side-group to transport holes. They are both equivalently efficient in OLEDs but $A$ is characterized by a $L_e/\Phi_{PL}$ ratio of 0.39 whereas the one of $B$ that is 0.16. In other words, the dipirydilamino groups appear to be more efficient than anthracenyl ones as hole carriers to correct the balance of charges in silole-based devices. This may originate from the fact that anthracene entities not only enhance the holes current compared to the dipirydilamine ones, but also increase the electron current, leading to a smallest correction of the balance of charge carriers. The comparison of siloles $A$, $A'$, $B$ and $B'$ allows us now to evaluate the importance of the conjugation between both the charge carriers since the presence of the diphenyl bridge has been shown to isolate both the moieties from an electronic point of view (see above). The disruption of the conjugation in silole $A'$ is accompanied by a marked decrease of the efficiency when compared to $A$, while the solid-state $\Phi_{PL}$ of both are close enough. In contrast to that, the same modification only weakly affects the efficiency of the devices based on siloles $B$ and $B'$.

### Conclusions

From the examination of Table 4, it appears that the major trend is that the more the $h^+/e^-$ ratio is high, the more the balance of charges appears to be improved. This result is well in line with the fact that the silole ring possesses an exceptional electron carrier ability that widely exceeds the hole carrier ability of the organic groups grafted to it. As a consequence a large number of hole-transporting groups are needed to correct the balance of charge. Therefore, the silole $D$ in which the $h^+/e^-$ ratio is equal to 4 displays the best luminous efficiency. In the case of the silole $C$, in spite of a similar ratio, the performances are disappointing since luminance and efficiencies (see Table 2) are one order of magnitude lower than $A$ and $B$ at 20 mA/cm². Moreover the current density is considerably lowered than the one observed with the other molecules at a considered applied voltage. This phenomenon may be attributed to two main reasons: $i)$ this silole posses a weak solid-state $\Phi_{PL}$ when compared to $D$, and $ii)$ the four dipirydilamino groups generate a strong steric hindrance which disfavors the electron transfert between the silole rings in the device.

### Table 4

<table>
<thead>
<tr>
<th>Silole</th>
<th>$L_e$ [cd/A]</th>
<th>Relative solid-state $\Phi_{PL}$</th>
<th>$L_e/\Phi_{PL}$ [cd/A]</th>
<th>$h^+/e^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.17</td>
<td>0.44</td>
<td>0.39</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>0.16</td>
<td>1.00</td>
<td>0.16</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>0.05</td>
<td>&lt;0.05</td>
<td>1.00</td>
<td>4</td>
</tr>
<tr>
<td>D</td>
<td>0.52</td>
<td>0.67</td>
<td>0.78</td>
<td>4</td>
</tr>
<tr>
<td>E</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>$A'$</td>
<td>0.03</td>
<td>0.36</td>
<td>0.08</td>
<td>2</td>
</tr>
<tr>
<td>$B'$</td>
<td>0.14</td>
<td>1.00</td>
<td>0.14</td>
<td>2</td>
</tr>
</tbody>
</table>

* Values measured at a current density of 20 mA/cm². * Silole accounts for $1 e^-$ whereas either an anthracenyl or a dipirydilamino side-group accounts for $1 h^+$. 

Figure 8. (a) Current-density-voltage characteristics for devices based on PEDOT:PSS/Silole (50 nm)/Ca, and (b) Corresponding luminance-voltage characteristics.
In this paper we showed that the balance of charge carriers can be improved by assembling different entities. The central silole ring has been functionalized by hole transporting groups. Two solutions have been investigated. On the one hand, dipyrirdlamino have been compared to anthracene groups. Performances had not been improved due to enhancement of both charge carriers transport. On the other hand, two new molecules have been synthesized containing four hole transporting groups for one silole ring. Finally, the energetic efficiencies have been enhanced by a factor six using the same device structure using suited hole transporting groups and appropriate grafted positions.

**Experimental**

**General methods and device performance measurements**

Solvents were distilled prior to use. THF and ether were dried over sodium/benzophenone, and distilled under Argon. All the reactions were carried out under argon atmosphere. $^1$H, $^{13}$C and $^{29}$Si NMR spectra were recorded on a Bruker Advance 200 DPX spectrometer, the FT-IR spectra on a Thermo Nicolet Avatar 320 spectrometer, the UV-visible spectra on a Seocam Anthelie instrument and the MS spectra on a Jeol JMS-DX 300 spectrometer. I-V characteristics were recorded with a Keithley 2400 Sourcemeter, $\gamma$-V with a photodiode placed under the OLED and coupled to an HP multimeter. Electroluminescence spectra were measured using an Ocean Optics PC2000 CCD spectrometer. All electroluminescent devices were kept are characterized in a glove box under nitrogen. Fluorescence spectra in thin film were recorded with an Edinburgh Instruments Ltd spectrofluorimeter. Absorption spectra in thin film were realized with an UV-visible SAFAS Monaco 190 DES spectrometer. Current-voltage (I-V) characteristics were recorded using a Keithley 4200 Semiconductor analyser and luminance-voltage (L-V) with a photodiode calibrated with a Minolta CS-100 luminancemeter. Electroluminescence (EL) spectra were measured using an Ocean Optics HR2000 CCD spectrometer. All electroluminescent devices were fabricated and characterized in a glove box under nitrogen. Absorption spectra were recorded with a Perkin Elmer Lambda 35 and ex situ using a Tencor AS-IQ profilometer. Finally, a 80 nm-thick calcium layer capped by 100 nm thick aluminium was evaporated under secondary vacuum (10$^{-6}$ mbar). The deposition rate of the silole layer was set at about 1 nm/s with a thickness of 50 nm measured in situ using a quartz balance and ex situ using a Tencor AS-IQ profilometer. Finally, a 80 nm-thick calcium layer capped by 100 nm thick aluminium layer were evaporated through a shadow mask on top of the silole derivative. Each step of their preparation and characterization took place in glove box under inert atmosphere.

**Preparation of 9-[4-(4-Bromo-phenoxy)-phenyl]anthracene (4)**

A solution of n-BuLi 2.5 M in hexane (7.7 mL, 19 mmol) was added to an ethereal solution (70 mL) of 4,4’ dibromodiphenylether (6.25 g, 19 mmol) cooled at –78 °C. The reaction mixture was left under stirring for 0.5 h at this temperature and anthrone was added by small portions (3 g, 15 mmol). This mixture was left under stirring for 3 h at -78°C and the temperature is allowed to reach slowly the room temperature. An aqueous solution of HCl (0.5 M) was then added to the reaction mixture until a pH of 4-5 was reached and extracted with Et$_2$O. After the usual processing, the resulting residue was subjected to a silicagel column chromatography (CH$_2$Cl$_2$/pentane : 10/90) to give 4 as a
white-yellow solid (yield: 50%). Mp: 149 °C. $^1$H NMR (CDCl$_3$, δ, ppm): 8.54 (s, 1H), 8.09 (d, $^3$(H,H) = 8, 2H), 7.75 (d, $^3$(H,H) = 8 Hz, 1H), 7.60-7.37 (m, 8H), 7.23 (d, $^3$(H,H) = 9 Hz, 2H), 7.12 (d, $^3$(H,H) = 9 Hz, 2H).$^{13}$C NMR (CDCl$_3$, δ, ppm): 158.81, 156.71, 134.35, 133.27, 133.15, 131.79, 130.79, 128.83, 127.13, 127.07, 125.86, 125.55, 121.33, 119.01, 116.45. HRMS (FAB+, m-nitrobenzyl alcohol matrix) m/z: calcd for [M+H]$^+$ C$_{26}$H$_{17}$BrO: 424.0463; found: 424.0456.

Preparation of [4-(4-bromo-phenoxy)-phenyl]di-pyridyn-2-yl-amine (6)

A mixture of 4,4'-dibromodiphenylether (7.14 g, 21.7 mmol), di-2-pyridylamine (1.50 g, 8.70 mmol), K$_2$CO$_3$ (1.40 g, 10.4 mmol) and CuSO$_4$·5H$_2$O (0.217 g, 0.87 mmol) in water (20 mL) was stirred well and evaporated to dryness in vacuum. The mixture was ground in a mortar and 3-5 drops of CH$_2$Cl$_2$ were added to this mixture. The mixture was heated in a schlenk tube at 210 °C for 6 h.

After being cooled at room temperature, the mixture was dissolved in CH$_2$Cl$_2$ (100 mL) and water (100 mL) and extracted. After evaporation of the solvents, the residue was subjected to column chromatography CH$_2$Cl$_2$/THF (95/5) to afford compound 6 as a white solid (yield: 80%). Mp: 102 °C. $^1$H NMR (CDCl$_3$, δ, ppm): 8.33 (dd, $^3$(H,H) = 6.5, $^3$(H,H) = 2 Hz, 2H), 7.62 (td, $^3$(H,H) = 7, 3H), 7.47 (d, $^3$(H,H) = 9 Hz, 2H), 7.21 (d, $^3$(H,H) = 6 Hz, 2H). 7.00-6.81 (m, 8H).$^{13}$C NMR (CDCl$_3$, δ, ppm): 157.99, 156.17, 136.56, 134.35, 133.27, 133.15, 131.54, 148.50, 148.47, 140.33, 137.63, 128.92, 120.82, 119.84, 118.15, 116.71, 115.95. HRMS (FAB+, m-nitrobenzyl alcohol matrix) m/z: calcd for [M+H]$^+$ C$_{26}$H$_{17}$BrN$_3$O: 418.0550; found: 418.0547.

Preparation of [4-(di-pyridin-2-yl-amino)-phenyl]-10-hydroxy-anthracen-9-one (8)

A solution of n-BuLi 2.5 M in hexane (10.5 mL, 26 mmol) was added to a THF solution (100 mL) of 4-(2,2'-dipiryridylamino)bromobenzene $^{34}$ (7 g, 21 mmol) THF cooled at –78 °C. The reaction mixture was left under stirring for 1 h at this temperature. A THF solution (150 mL) of antraquinone (8.73 g, 42 mmol) was then added to this mixture and left under stirring for 8 h while allowing the temperature reach slowly the room temperature. An aqueous solution of HCl (1 M) was added to this mixture until a pH of 4-5 was reached and extracted with EtO$_2$. After the usual processing, the resulting residue was subjected to a silicagel column chromatography (CH$_2$Cl$_2$/MeOH; 99:1) to give 8 as a light yellow powder (yield: 20%). Mp: 267 °C. $^1$H NMR (CDCl$_3$, δ, ppm): 8.42 (dd, $^3$(H,H) = 6, $^3$(H,H) = 2 Hz, 2H), 7.93-7.62 (m, 8H), 7.53-7.39 (m, 10H), 7.21 (d, $^3$(H,H) = 7 Hz, 2H), 7.08 (d, $^3$(H,H) = 7, $^3$(H,H) = 2 Hz, 2H).$^{13}$C NMR (CDCl$_3$, δ, ppm): 158.66, 148.85, 144.99, 138.46, 138.05, 136.04, 135.86, 133.49, 132.73, 132.06, 130.31, 130.16, 127.39, 127.07, 126.95, 125.73, 125.59, 122.05, 118.86, 117.81, 116.41. HRMS (FAB+, m-nitrobenzyl alcohol matrix) m/z: calcd for [M+H]$^+$ C$_{36}$H$_{24}$N$_3$Br: 577.5097; found: 578.1204.

Preparation of 2-[4-(5-(4-bromo-phenyl)-1,1-dimethyl-3,4-diphenylsilol-2-yl)phenyl]-1,1-dimethyl-3,4-diphenyl-silole (11)

A mixture of lithium (0.055 g, 8 mmol) and naphthalene (1.03 g, 8 mmol) in THF (15 mL) was stirred at room temperature under argon for 5 h to form a deep green solution of lithiumnaphthalenide. To the this solution was added bis[phenylthiyl]dimethylsilane 1 (0.50 g, 2 mmol) in THF (10 mL). After stirring for 10 min, the reaction mixture was cooled to 0 °C and [ZnCl$_2$(tmen)] (tmen = bis(phenylethynyl)dimethylsilane) 2 (5.00 g, 2 mmol) in THF in glacial acetic acid (60 mL), treated with NaH$_2$PO$_4$ (8.44 g, 64 mmol) and KI (4.22 g, 25 mmol), and heated to reflux for 20 min. After cooling, the reaction mixture was treated with cold water (300 mL) and extracted with CH$_2$Cl$_2$. After the usual processing, the resulting residue was subjected to a silicagel column chromatography (CH$_2$Cl$_2$/MeOH; 99:1) to give 11 as a white solid (yield: 50 %). Mp: 149 °C. UV-Visible (λmax, nm, log ε): 255 (5.46), 399 (5.20). $^1$H NMR (CDCl$_3$, δ, ppm): 7.15 (d, $^3$(H,H) = 9 Hz, 4H), 6.96-6.86 (m, 12H), 6.74-6.64 (m, 12H), 6.58 (s, 4H), 0.03 (s, 1H).$^{13}$C NMR (CDCl$_3$, δ, ppm): 153.14, 153.86, 142.14, 140.60, 139.26, 139.15, 138.84, 137.38, 131.46, 130.82, 130.32, 130.25, 128.93, 127.92, 127.82, 126.77, 126.63.
199.72, -3.31. $^{29}$Si NMR (CDCl$_3$, δ, ppm) : 8.09. HRMS (FAB+, m-nitrobenzyl alcohol matrix) m/z: calculated for [M+H]$^-$ C$_{54}$H$_{44}$Br$_2$Si$_2$: 906.1348; found: 906.1330. Characterization of silole 1: the synthesis of this compound was previously described starting from 1-bromo, 4-iodobenzene.$^{55}$ Mp: 224 °C. UV-Visible (λmax, nm, log ε): 250 (5.54), 361 (5.23). $^1$H NMR (CDCl$_3$, δ, ppm): 7.28 (d, 1J(H,H) = 9 Hz, 4H), 7.10-7.02 (m, 6H), 6.81-6.75 (m, 8H ), 0.47 (s, 1H).$^{13}$C NMR (CDCl$_3$, δ, ppm): 154.90, 141.17, 139.04, 138.57, 131.56, 130.78, 130.24, 128.02, 126.94, 119.95, -3.52. $^{29}$Si NMR (CDCl$_3$, δ, ppm): 8.23. HRMS (FAB+, m-nitrobenzyl alcohol matrix) m/z: calculated for [M+H]$^-$ C$_{54}$H$_{44}$Br$_2$Si$_2$: 906.1396; found: 906.1396.

Preparation of 2,5-Bis-[4-(4-anthracen-9-yl-phenyl)-1,1-dimethyl-3,4-diphenyl]-silole (B')

A mixture of lithium (0.055 g, 8 mmol) and naphthalene (1.03 g, 8 mmol) in THF (15 mL) was stirred at room temperature under argon for 5 h to form a deep green solution of lithiomnaphthalene. To this mixture was added bis(phenylethynyl)dimethylsilane I (0.50 g, 2 mmol) in THF (10 mL). After stirring for 10 min, the mixture was cooled to 0 °C and [ZnCl$_2$(tmen)] (tmen = N,N,N',N'-tetramethylenediamine) (2.01 g, 8 mmol) was added, followed by an addition of THF (20 mL). After stirring for an hour at room temperature, a solution of 9-(4-bromophenyl)-anthracene 3$^{+}$ (1.59 g, 4.8 mmol) in THF (20mL) and [PdCl$_2$(PPh)$_3$I] (0.10 g, 0.13 mmol) were successively added. The mixture was heated under reflux and stirred for 20 h. After hydrolysis by water, the mixture was extracted with Et$_2$O. After evaporation of the solvents, the resulting residue was subjected to a silicagel column chromatography (pentane/CH$_2$Cl$_2$: 85/15) and recrystallized from an hexane/CH$_2$Cl$_2$ to give B’ as a yellow solid (yield: 89 %). Mp: 264 °C. UV-Visible (λmax, nm, log ε): 257 (6.47), 350 (4.95), 362 (5.13), 385 (5.10). $^1$H NMR (CDCl$_3$, δ, ppm): 8.54 (s, 2H), 8.09 (d, 1J(H,H) = 8 Hz, 4H), 7.76 (d, 1J(H,H) = 8 Hz, 4H), 7.55-7.38 (m, 12H), 7.24 (d, 1J(H,H) = 8 Hz, 4H). 7.12-7.60 (m, 16H), 6.92-6.82 (m, 8H), 6.72-6.64 (m, 16H), 6.51 (d, 1J(H,H) = 8 Hz, 4H), 0.27 (s, 6H). $^{13}$C NMR (CDCl$_3$, δ, ppm): 157.18, 155.30, 154.27, 140.97, 139.39, 136.84, 135.57, 133.75, 132.95, 130.83, 130.77, 130.44, 128.79, 128.00, 127.21, 127.01, 126.73, 125.79, 125.53, 119.21, 118.94, -3.10. $^{29}$Si NMR (CDCl$_3$, δ, ppm): 7.99. MS (FAB+, m-nitrobenzyl alcohol matrix) m/z: 951 [M+H]$^-$ Analysis calculated for C$_{70}$H$_{50}$O$_2$: 88.39 %C, 5.35 %H; found: 86.69 %C, 5.48 %H.

Preparation of [5-(1,1-dimethyl-3,4-diphenyl-silol-2,5-yl)bis(N,N,N',N'-tetra-pyridin-2-yl-benzene-1,3-diamine) (C)

Same procedure as for silole B, using a solution of 4 (2.04 g, 4.8 mmol) in THF (20mL). After evaporation of the solvents, the resulting residue was firstly subjected to a silicacgel column chromatography (pentane/CH$_2$Cl$_2$: 80/20) and recrystallized from hexane/CH$_2$Cl$_2$ to give B’ as a yellow powder (yield: 89 %). Mp: 264 °C. UV-Visible (λmax, nm, log ε): 257 (6.47), 350 (4.95), 362 (5.13), 385 (5.10). $^1$H NMR (CDCl$_3$, δ, ppm): 8.54 (s, 2H), 8.09 (d, 1J(H,H) = 8 Hz, 4H), 7.76 (d, 1J(H,H) = 8 Hz, 4H), 7.55-7.38 (m, 12H), 7.24 (d, 1J(H,H) = 8 Hz, 4H). 7.12-7.60 (m, 16H), 6.92-6.82 (m, 8H), 6.72-6.64 (m, 16H), 6.51 (d, 1J(H,H) = 8 Hz, 4H), 0.27 (s, 6H). $^{13}$C NMR (CDCl$_3$, δ, ppm): 157.56, 154.46, 148.20, 145.25, 142.38, 139.04, 138.76, 136.76, 132.51, 127.41, 126.16, 123.49, 121.87, 118.33, 117.24, -4.11. $^{29}$Si NMR (CDCl$_3$, δ, ppm): 8.67. MS (FAB+, m-nitrobenzyl alcohol matrix) m/z: 1091 [M+H]$^-$ Analysis calculated for C$_{70}$H$_{50}$O$_2$: 77.03 %C, 5.16 %H, 15.40 %N; found : 76.56 %C, 5.37 %H, 15.99 %N.

Preparation of 10-[4-(1,1-Dimethyl-3,4-diphenyl-silol-2,5-yl)phenyl]-anthracen-9-yl-bis-(dipyridin-2-yl-amine) (D)

Same procedure as for silole B, using a solution of 10 (2.76 g, 4.8 mmol) in THF (20mL). The residue was purified by silicacgel column chromatography (CH$_2$Cl$_2$/THF gradient : 80/20 to 70/30) and crystallized from an hexane/CH$_2$Cl$_2$ mixture to afford D as a yellow solid (yield: 15 %). Mp: 376 °C. UV-Visible (λmax, nm, log ε): 268 (6.30), 389 (5.57), 407 (5.63). $^1$H NMR (CDCl$_3$, δ, ppm): 8.45 (dd, 1J(H,H) = 6, 1J(H,H) = 2 Hz, 4H), 7.91-7.86 (m, 4H), 7.77-7.86 (m, 8H), 7.50-7.39 (m, 16H), 7.28-7.19 (m, 10H), 7.19-7.08 (m, 8H),
