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

Laurent Aubouy,<sup>a</sup> Nolwenn Huby,<sup>b</sup> Lionel Hirsch,<sup>\*b</sup> Arie van der Lee,<sup>c</sup> and Philippe Gerbier<sup>\*a</sup>

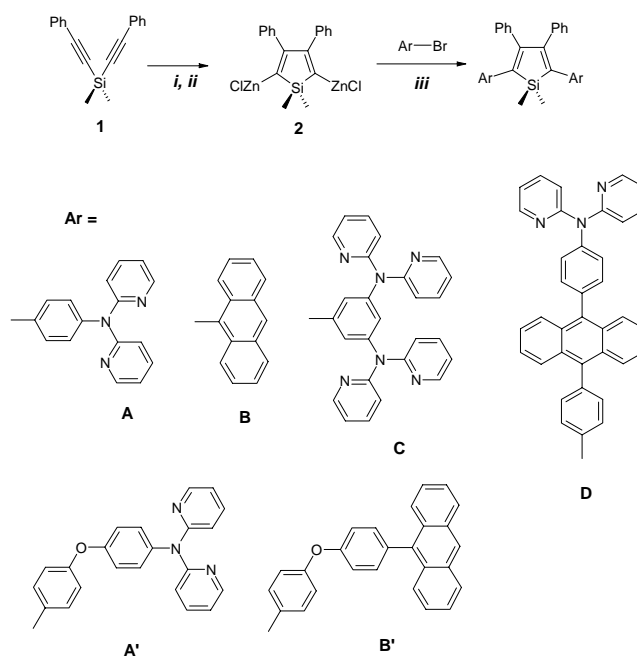
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We report a molecular engineering study on optical, structural and electrical properties of seven silole derivatives aiming at enhancing the balance of charge carrier in single-layer devices. By functionalizing two hole-transporting groups, dipyrindylamine 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 dipyrindylamine 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  $L_e = 0.8$  cd/A at 7 V.

## 15 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<sup>1, 2</sup> 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.<sup>3-8</sup> 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.<sup>9, 10</sup> 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<sup>11</sup>. Nevertheless, this approach suffers of some drawbacks due to a large number of interfaces and/or segregation phase apparition. The main text of the article should appear here. Headings and subheadings should be formatted using the

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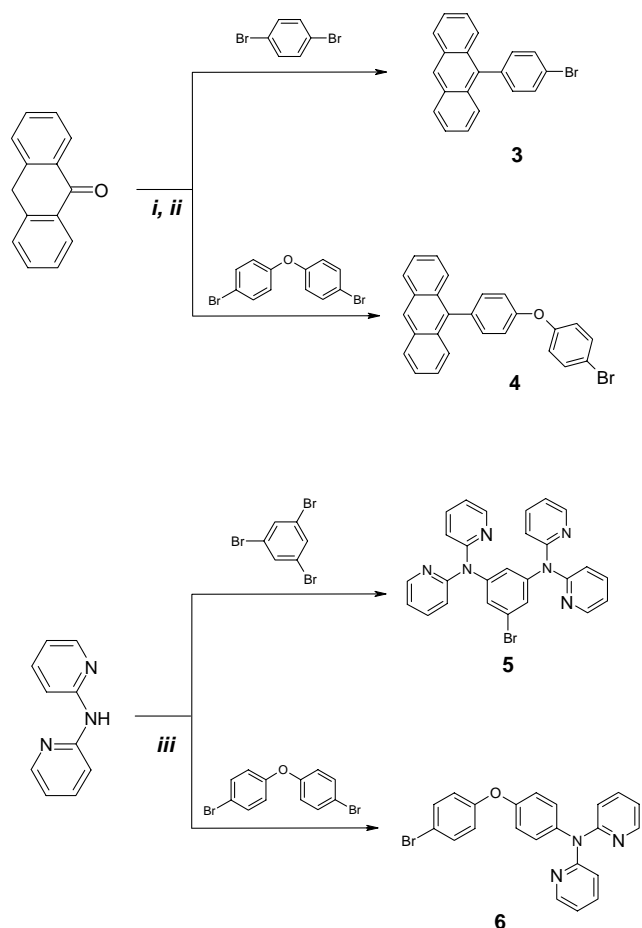
**Scheme 1.** Tamao's synthetic route to 2,5-difunctionalized siloles: *i*) 4 equiv. LiNp, *ii*) 4 equiv. ZnCl<sub>2</sub>.TMEDA, *iii*) 2 equiv. ArBr, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.

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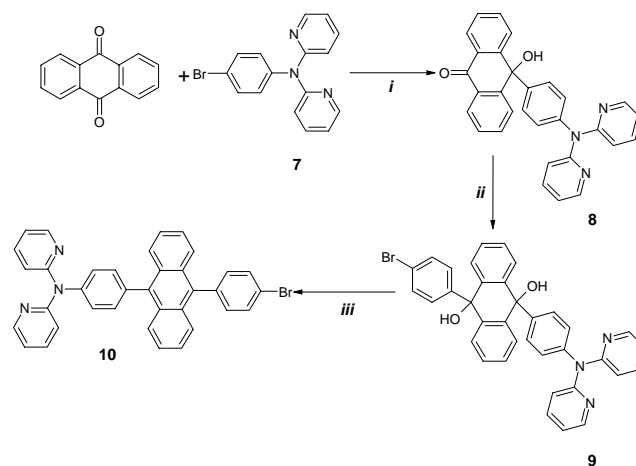
The aim of this paper is to design a fluorescent molecule able to transport both charge carriers. In this way, we focussed on silole derivatives since they appear to possess all the requirements to achieve single-layer OLEDs. The siloles<sup>12-15</sup> or silacyclopentadienes are a group of five-membered silacycles that possess  $\sigma^*-\pi^*$  conjugation arising from the interaction between the  $\sigma^*$  orbital of two exocyclic  $\sigma$  bonds on the silicon atom and the  $\pi^*$  orbital of the butadiene moiety.<sup>16</sup> 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  $\pi$ -system of the silole ring is more prone to allow electron delocalization when compared with its thiophene cousins.<sup>17, 18</sup> 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  $\pi-\pi$  interaction distance (*ca.* 3–4 Å).<sup>19</sup> This gives rise to a very interesting photophysical property called aggregation-induced photoluminescence (PL) emission (AIE).<sup>20, 21</sup> 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.<sup>22, 23</sup> Thereby, 2,3,4,5-tetraphenylsiloles are excellent emitters in the fabrication of electroluminescence (EL) devices, an external



**Scheme 2.** Syntheses of the hole-transporting functionalities: *i*) 1 equiv. *n*BuLi, *ii*) MeOH, HCl 6 M, *iii*)  $K_2CO_3$ ,  $CuSO_4 \cdot 5H_2O$ .

quantum efficiency ( $\eta_{EL}$ ) up to 8%, close to the theoretical limit for a singlet emitter, was realized with such derivatives in the emissive layer.<sup>24, 25</sup> 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.<sup>26-28</sup>

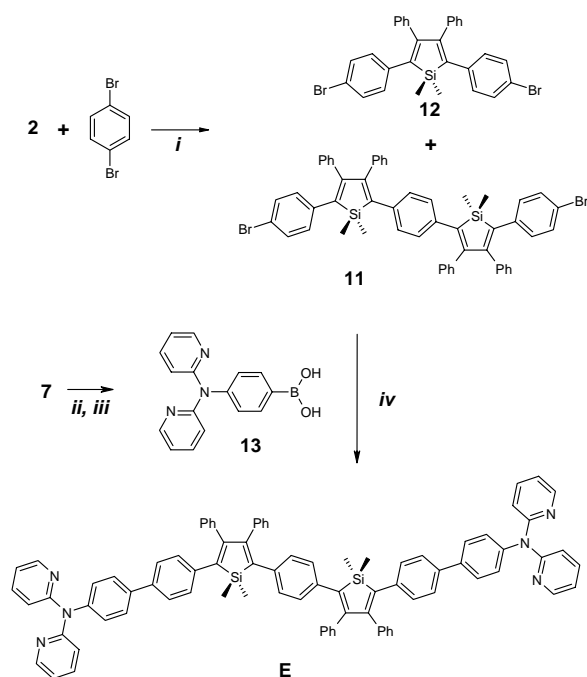
The results presented in this paper follow previous reports concerning the silole **A** (Scheme 1).<sup>25, 27</sup> This molecule is based on a silacyclopentadiene core, which acts both as emissive and electron-transporting component, and two dipyridylamino functionalities grafted on each side, which act as hole-transporting groups.<sup>29, 30</sup> By associating those two



**Scheme 3.** Synthesis of **10**: *i*) *n*BuLi, *ii*) 2 equiv. 1-bromo, 4-lithiobenzene, *iii*)  $NaH_2PO_4$ , KI, glacial acetic acid.

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.<sup>27</sup> 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 (siloles **B** and **B'**).<sup>31, 32</sup> 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



**Scheme 4.** Synthesis of **E**: i)  $\text{PdCl}_2(\text{PPh}_3)_2$ , ii) 1 equiv.  $n\text{BuLi}$ ,  $\text{B}(\text{OMe})_3$ , iii)  $\text{H}_2\text{O}$ ,  $\text{NH}_4\text{Cl}$ , iv)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{K}_2\text{CO}_3$ .

### (i) Syntheses

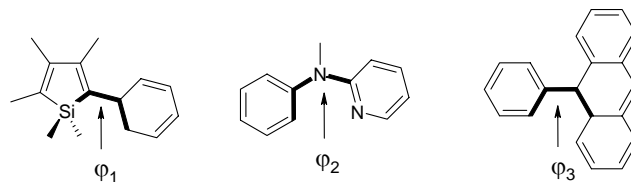
The siloles **A-D** were conveniently prepared by the method described by Tamao and Yamaguchi<sup>33</sup> that involves the one-pot reductive intramolecular cyclization of bis(phenylethynyl)silane and the subsequent Pd(0)-catalyzed cross-coupling reaction with the desired arylbromide (Scheme 1). The synthesis of 9-(4-bromophenyl)-anthracene **3** and 9-[4-(4-bromo-phenoxy)-phenyl]anthracene **4** was achieved starting from anthrone by using the procedure described by Murphy *et al.*<sup>34</sup> 3,5-bis(2,2'-dipyridylamino)-bromobenzene **5** and [4-(4-bromo-phenoxy)-phenyl]di-pyridyn-2-yl-amine **6** were synthesized through a modification of the original Ullman's reaction.<sup>35, 36</sup> The preparation of the asymmetrically 9,10-diarylanthracene **10** was achieved through an adaptation of the procedure described by Smet *et al.*<sup>37, 38</sup> It involves firstly the lithiation of the compound **7**<sup>25, 39</sup> followed by the addition of the resulting lithio derivative on anthraquinone to afford the monoadduct **8** in 43% yield. To this compound, a two-fold excess of 4-bromophenyllithium was added yielding the diol **9**. The excess of 4-bromophenyllithium was necessary to react with the OH group present in the monoadduct **8**. Reduction of the latter using  $\text{NaH}_2\text{PO}_2$  and KI in refluxing acetic acid afforded **10** as a light yellow solid in 20% yield.

The synthesis of silole **E** involves firstly the preparation of the bis-silole derivative **11** 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 **13**<sup>39</sup> afforded the expected bis-silole **E** in good yield.

### (ii) Geometries of siloles

The determination of the conformational preferences of these molecules is of utmost importance for the understanding of their electronic behaviour. Since crystals suitable for a X-ray structure determination could only be obtained for **A**,<sup>40</sup> **B**,<sup>41</sup> 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.<sup>42</sup> 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.<sup>43</sup> Such calculations were followed by single point runs using a 6-31+G\* basis to obtain accurate energies. Structurally characterized siloles, dipyridylamines, 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.<sup>19</sup> 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  $\text{SiC}_4$  ring. The torsion angles of the substituted phenyl rings at the 2- and 5-



**Scheme 5.** Location of the torsion angles reported in table 1.

positions of the central silole ring ( $\phi_1$ ) are in the range of what is usually observed with tetraarylsiloles (*ca.* 30-60°).

**Table 1.** Torsion angles [°] in siloles<sup>d</sup>

	<b>A</b> <sup>b</sup>	<b>B</b> <sup>b</sup>	<b>C</b>	<b>D</b> <sup>b,d</sup>	<b>E</b>
$\phi_1$ <sup>c</sup>	43.4 (44.7)	49.1 (58.4)	38.6	47.8	43.5 (45.1)
$\phi_2$ <sup>c</sup>	45.4 (34.3)	---	46.8	50.8 (50.4)	55.5
$\phi_3$ <sup>c</sup>	---	77.0 (68.5)	---	71.6 (74.2)	---

<sup>a</sup> Average values. <sup>b</sup> Values from crystal structures (see text) are between parentheses. <sup>c</sup> See scheme 5. <sup>d</sup> see<sup>44</sup>.

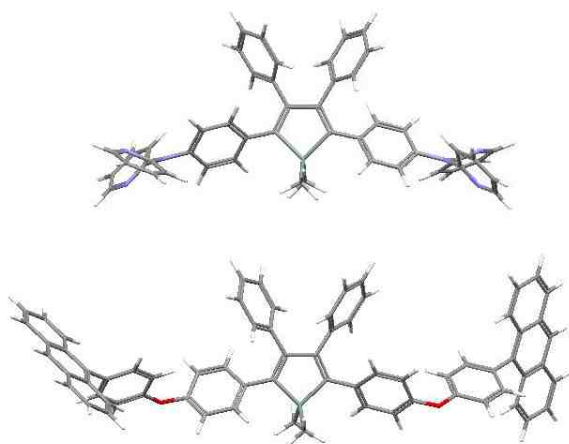


Figure 1. DFT-optimized (B3LYP-6/31G) molecular structures of siloles **A** (top) and **B'** (bottom).

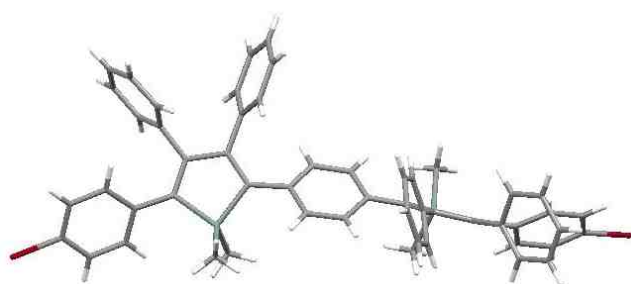


Figure 2. X-ray structure of silole **11**. The  $\text{CH}_2\text{Cl}_2$  crystallization molecule has been removed for sake of clarity.

The torsion angles between the anthracene main plane and the adjacent phenyl ring ( $\varphi_3$ ) fall as well in the range of what is usually observed with related molecules (*ca.*  $70^\circ$ ). 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 plain 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  $\varphi_1$  between this ring and the two adjacent siloles have a value of  $45.14^\circ$ . 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**.

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/ $\text{Ca}$ . 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.<sup>33</sup> 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

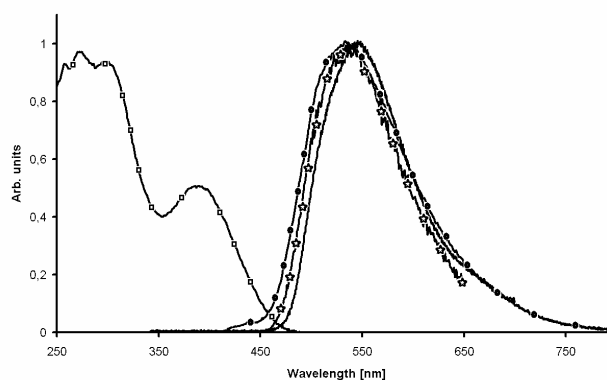


Figure 3. Normalized UV-visible ( $\square$ ), photoluminescence (in solution:  $\bullet$  and thin film:  $\star$ ) and electroluminescence ( $\longrightarrow$ ) spectra of silole **A**.

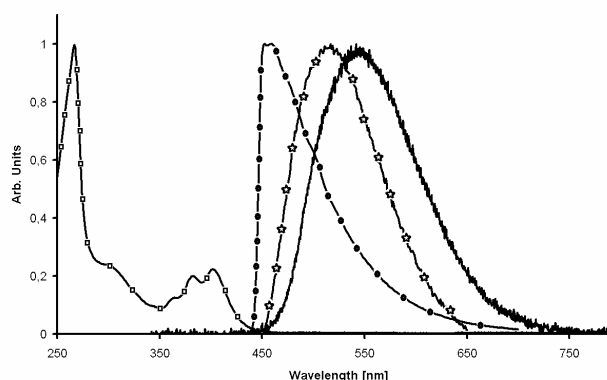


Figure 4. Normalized UV-visible ( $\square$ ), photoluminescence (in solution:  $\bullet$  and thin film:  $\star$ ) and electroluminescence ( $\longrightarrow$ ) spectra of silole **D**.

**Table 2.** Main values of the optical properties (UV-Visible and fluorescence spectra) in solution and in thin films.<sup>a</sup>

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

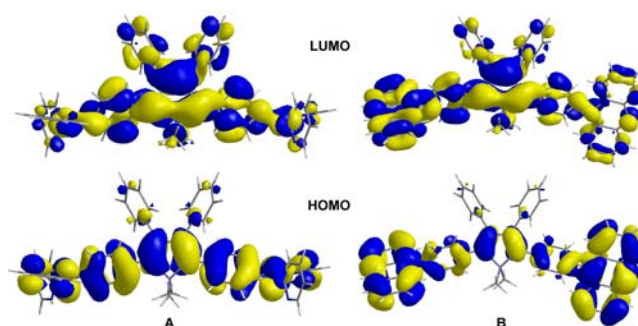
<sup>a</sup> The values recorded with thin solid films are between parentheses. <sup>b</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Measured in solution, quantum yield relative to perylene ( $\phi_{em} = 0.94$ ). <sup>d</sup> From B3LYP/6-31G\* DFT calculations.

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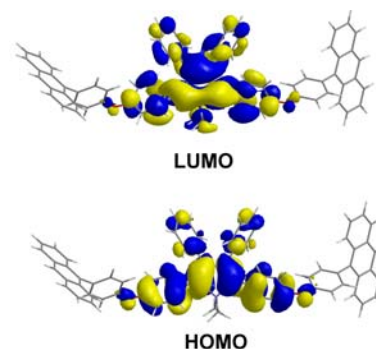
be mainly responsible of the emission, as attested by the vibronic coupling seen on the curves. Moreover, it is worthy to note that the Stocke's shift that is observed with this second family (*ca.* 20-50 nm) is substantially smaller than with the first one (*ca.* 120-140 nm). As usually observed for the 2,3,4,5-tetraphenylsiloles, the quantum yields in solution are rather low (Table 2), the lowest value being found with **E** in which two silole rings are presents in the structure. This behaviour likely originates from resonant photon absorption phenomenon, since there is a substantial overlap between the absorption and the emission spectra. Moreover this observation, which indicates that the two siloles 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**  $\approx$  **B'** > **D** > **A** > **A'** > **C** > **DPA** > Perylene  $\approx$  **E** where **DPA** (9,10-diphenylanthracene,  $\phi_{em}$  (solution) = 1.00) and **P** Perylene ( $\phi_{em}$  (solution) = 0.94)<sup>45</sup> are given for comparison. On account to the AIE phenomenon,<sup>20, 21</sup> 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.<sup>46, 47</sup> 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 in 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 dipyridylamino 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**.



**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

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redshift compared to the others. All the emissions correspond to the yellow-green domain on the chromatic diagram of the

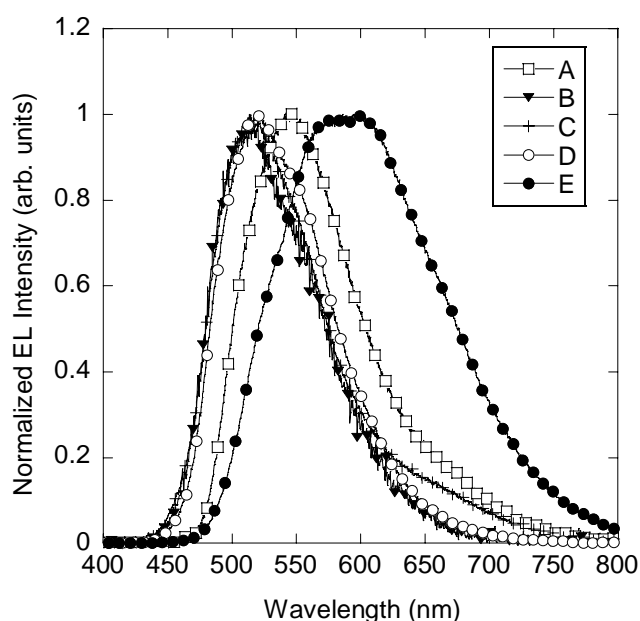


Figure 7. EL spectra from devices ITO/PEDOT:PSS/Silole (50 nm)/Ca.

*Commission Internationale de l'Eclairage*. Their corresponding current density–voltage and luminance–voltage are presented in figure 3 (a) and figure 3 (b) respectively. When compared with the calculated HOMO and LUMO energy levels of the siloles (see Table 2), the high work function of the anode ITO/PEDOT:PSS (-5.2 eV) and the low one of the calcium cathode (-2.9 eV) are suitable to favour the injection of both charge-carriers in the active layer. As a consequence, threshold voltage values generally below 4V are necessary to start of detection of luminance of the device (Table 3). Moreover, with the exception of siloles **C** and **E**, all the molecules presented here display quite good luminous efficiencies ( $L_e$ ) for single-layer devices. In terms of performances, **D** exhibits the best values with a threshold voltage below 3 V and a luminous efficiency  $L_e$  of 0.75 cd/A at 7 V. At the opposite, **C** and **E** are weakly electroluminescent. Indeed, these molecules need high applied voltages to reach the same order of current density than with **A**, **B** or **D**.

To better understand the origin of these different behaviours and to try to outline the relationships that may exist between the molecular structure and the balance of 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:<sup>48, 49</sup>

$$\eta_{\text{external}} = \gamma \cdot \eta_{\text{recomb}} \cdot \eta_{\text{ST}} \cdot \eta_{\text{optical}} \cdot \Phi_{\text{PL}} \quad (1)$$

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 organics 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

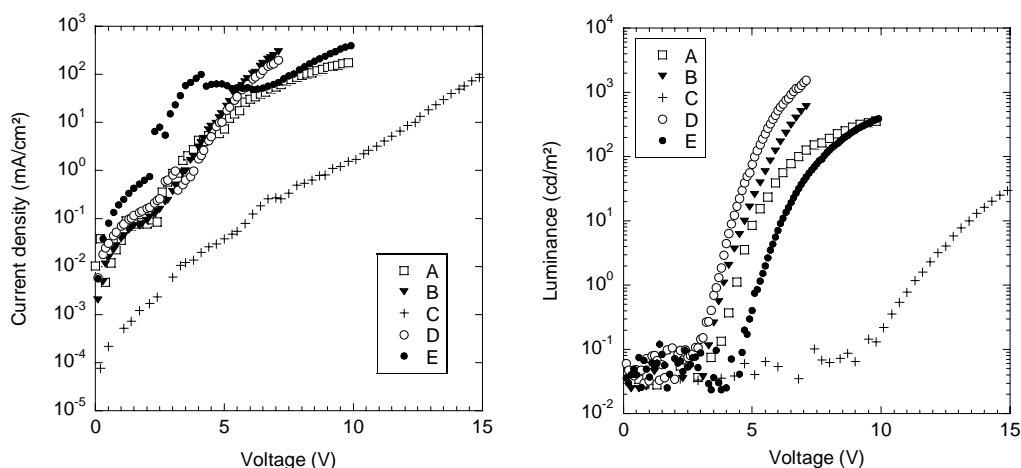
Table 3. The luminance (L), luminous efficiency ( $L_e$ ) and energetic efficiency ( $R_e$ ) of siloles operating in ITO/PEDOT:PSS/Silole/Ca OLEDs.<sup>a</sup>

Silole	V <sub>th</sub> [V]	L [cd/m <sup>2</sup> ]	$L_e$ [cd/A]	$R_e$ [lm/W]
A	3.5	26 (370) <sup>b</sup>	0.17 (0.20) <sup>b</sup>	0.095 (0.06) <sup>[b]</sup>
B	3.1	25 (350) <sup>[b]</sup>	0.16 (0.18) <sup>[b]</sup>	0.100 (0.09) <sup>[b]</sup>
C	9	8 (74) <sup>[c]</sup>	0.05 (0.036) <sup>[c]</sup>	0.012 (0.015) <sup>[c]</sup>
D	2.9	80 (1550) <sup>[c]</sup>	0.52 (0.75) <sup>[c]</sup>	0.320 (0.35) <sup>[c]</sup>
E	4.5	-(86) <sup>[c]</sup>	-(0.09) <sup>[c]</sup>	-
A'	18	5 (5) <sup>[b]</sup>	0.03 (0.03) <sup>[b]</sup>	0.003 (0.003) <sup>[b]</sup>
B'	4.2	21 (290) <sup>[c]</sup>	0.14 (0.19) <sup>[c]</sup>	0.060 (0.060) <sup>[c]</sup>

<sup>a</sup> Values measured at a current density of 20 mA/cm<sup>2</sup>. <sup>b</sup> Value between parentheses measured at 100 mA/cm<sup>2</sup>. <sup>c</sup> Value between parentheses measured at 200 mA/cm<sup>2</sup>.

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.<sup>27, 41, 50, 51</sup> In previous works we have studied the transport properties of siloles **A** and **B**.<sup>41</sup> 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).<sup>27, 41, 50</sup> 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.



**Figure 8.** (a) Current-density-voltage characteristics for devices based on ITO/PEDOT:PSS/Silole (50 nm)/Ca, and (b) Corresponding luminance-voltage characteristics.

From semi-quantitative measurements we have found the following sequence for the solid-state photoluminescence quantum yield  $\Phi_{PL}$ :  $\mathbf{B} \approx \mathbf{B}' > \mathbf{D} > \mathbf{A} > \mathbf{A}' > \mathbf{C} > \mathbf{E}$ . By using the procedure of normalization described in the experimental part, we have found that the photoluminescence intensity of **B** is *ca.* 1.5 times higher than the one of **D**, *ca.* 2.3 times higher than the one of **A**, *ca.* 2.8 times higher than the one of **A'** and more than 20 times higher than the one of **C** (the value for **E** 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 ( $h^+$ : dipyrrodamino or anthracenyl side-groups) over the electron carrier moieties ( $e^-$ : silole ring) present in the molecular

structure (Table 4). 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/cm<sup>2</sup>. 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 possesses a weak solid-state  $\Phi_{PL}$  when compared to **D**, and *ii*) the four dipyrrodamino groups generate a strong steric hindrance which disfavours the electron transfer between the silole rings in the device.

**Table 4.** The luminous efficiency ( $L_e$ ), relative solid-state PL quantum yield ( $\Phi_{PL}$ ) and the hole carrier to the electron carrier formal ratio ( $h^+/e^-$ ) of siloles operating in ITO/PEDOT:PSS/Silole/Ca OLEDs.

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

<sup>a</sup> Values measured at a current density of 20 mA/cm<sup>2</sup>. <sup>b</sup> A silole ring accounts for 1  $e^-$  whereas either an anthracenyl or a dipyrrodamino side-group accounts for 1  $h^+$ .

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 dipyrrodamino 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 dipyrrodamine 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



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, dipyrindylamino 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.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  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 Secomam Anthelie instrument and the MS spectra on a Jeol JMS-DX 300 spectrometer. I-V characteristics were recorded with a Keithley 2400 Sourcemeter, L-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 a 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 with  $[\text{O}_2]$  and  $[\text{H}_2\text{O}]$  less than 0.1 ppm. The semi-quantitative solid state quantum yields have been measured on evaporated films of the same thickness and corrected by the corresponding absorption coefficient at the excitation wavelength (380 nm). In order to compare materials, cares have been taken for experimental conditions. Spectrofluorimetre parameters were kept unchanged from a sample to another, thickness of the thin films were the same and the fluorescence spectrum of each molecule has been corrected by the corresponding absorption coefficient at the excitation wavelength. An excitation wavelength at 380 nm has been selected, since all maxima absorption bands are localized in this domain.

### X-ray diffraction

The diffraction intensities for silole **11** were collected at the joint X-ray Scattering Service of the Institut Charles Gerhardt and the Institut Européen des Membranes of the University of Montpellier II, France, at 175 K using an Oxford Diffraction Xcalibur-I diffractometer. The structure

was solved by *ab-initio* (charge-flipping) methods using SUPERFLIP<sup>52</sup> and refined by least-squares methods on F using CRYSTALS,<sup>53</sup> against  $|F|$  on data having  $I > 2\sigma(I)$ ;  $R$ -factors are based on these data. Hydrogen atoms were located from difference Fourier synthesis. The  $\text{CH}_2\text{Cl}_2$  crystallization molecule was found to be heavily disordered. Two carbon positions and seven chlorine position were found. The total site occupancy of the carbon positions were strongly restrained to 1 and that of the chlorine positions to 2. Restraints were also put on the  $U_{\text{iso}}$  parameters of carbon and chlorine in order to have them approximately equal. No attempts were made to place the proton sites for the two solvent carbon atoms. Basic structural data for silole **11** ( $\text{C}_{27}\text{H}_{22}\text{BrSi}, \text{CH}_2\text{Cl}_2$ ; two solvent hydrogens not placed):  $a=13.8694(8)$  Å,  $b=14.3213(8)$  Å,  $c=26.3741(14)$  Å,  $\alpha=90^\circ$ ,  $\beta=98.256(4)^\circ$ ,  $\gamma=90^\circ$ ,  $V=5184.4(5)$  Å<sup>3</sup>, space group  $C2_1/c$ , 50775 reflections measured, 3634 independent reflections with  $I > 2\sigma(I)$  used for refinement with 307 parameters and two restraints.  $R=0.0391$ .  $wR=0.0383$ . Full details can be found in the accompanying cif-file.

### Device fabrication

Devices of *ca.* 10 mm<sup>2</sup> were fabricated on ITO-coated glass substrates (Merck, thickness  $\approx$  115 nm, sheet resistance  $\rho \approx 17 \Omega/\square$ ). After the cleaning process in trichloroethylene, ethanol and deionised water, an UV-ozone treatment was performed during 15 min. Then, a 50 nm-thick layer of PEDOT-PSS was spun coated at 5000 rpm on top of ITO and baked at 80 °C for about 1 hour. PEDOT-PSS is a conducting polymer, acting as a buffer, in reducing short circuit problems induced by the ITO roughness. It weakly increases the work-function of the anode and acts as a barrier to oxygen and indium diffusion from ITO.<sup>54</sup> On the PEDOT-PSS layer, the organic compounds as well as the cathodes were thermally 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  $-78^\circ\text{C}$ . 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  $-78^\circ\text{C}$  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  $\text{Et}_2\text{O}$ . After the usual processing, the resulting residue was subjected to a silicagel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{pentane}$  : 10/90) to give **4** as a

white-yellow solid (yield : 50 %). Mp: 149 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) : 8.54 (s, 1H), 8.09 (d, <sup>3</sup>J(H,H) = 8, 2H), 7.75 (d, <sup>3</sup>J(H,H) = 8 Hz, 1H), 7.60-7.37 (m, 8H), 7.23 (d, <sup>3</sup>J(H,H) = 9 Hz, 2H), 7.12 (d, <sup>3</sup>J(H,H) = 9 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) : 158.81, 156.71, 136.56, 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]<sup>+</sup> C<sub>26</sub>H<sub>17</sub>BrO : 424.0463; found : 424.0456.

#### Preparation of [4-(4-bromo-phenoxy)-phenyl]di-pyridin-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<sub>2</sub>CO<sub>3</sub> (1.40 g, 10.4 mmol) and CuSO<sub>4</sub>·5H<sub>2</sub>O (0.217g, 0.87 mmol) in water (20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was stirred well and evaporated to dryness in vacuum. The mixture was ground in a mortar and 3-5 drops of CH<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>Cl<sub>2</sub> (100 mL) and water (100 mL) and extracted. After evaporation of the solvent, the residue was subjected to column chromatography CH<sub>2</sub>Cl<sub>2</sub>/THF (95/5) to afford compound **6** as a white solid (yield: 80%). Mp: 102 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) : 8.33 (dd, <sup>3</sup>J(H,H) = 6, <sup>3</sup>J(H,H) = 2 Hz, 2H), 7.62 (td, <sup>3</sup>J(H,H) = 7, <sup>3</sup>J(H,H) = 2 Hz, 2H), 7.47 (d, <sup>3</sup>J(H,H) = 9 Hz, 2H), 7.21 (d, <sup>3</sup>J(H,H) = 6 Hz, 2H), 7.00-6.81 (m, 8H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) : 157.99, 156.17, 154.50, 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]<sup>+</sup> C<sub>22</sub>H<sub>16</sub>BrN<sub>3</sub>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'-dipyridylamino)bromobenzene **7**<sup>25, 39</sup> (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 anthraquinone (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 then added to the reaction mixture until a pH of 4-5 was reached and extracted with Et<sub>2</sub>O. After the usual processing, the resulting residue was subjected to a silicagel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/THF gradient: 97/3 to 90/10) to give **8** as a light yellow powder (yield: 43 %). Mp: 265-267 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) : 8.35-8.09 (m, 4H), 7.77 (dd, <sup>3</sup>J(H,H) = 8, <sup>3</sup>J(H,H) = 1 Hz, 2H), 7.62 (td, <sup>3</sup>J(H,H) = 7, <sup>3</sup>J(H,H) = 2 Hz, 2H), 7.58-7.48 (m, 4H), 7.37 (d, <sup>3</sup>J(H,H) = 9 Hz, 2H), 7.10 (d, <sup>3</sup>J(H,H) = 9 Hz, 2H), 7.00-6.89 (m, 4H), 2.93 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) : 182.32, 151.40, 148.71, 147.94, 138.45, 134.53, 130.75, 130.36, 128.71, 128.60, 127.37, 127.21, 126.65, 118.83, 117.04, 116.57, 73.5. HRMS (FAB+, m-nitrobenzyl alcohol matrix) *m/z*: calcd for [M+H]<sup>+</sup> C<sub>30</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub> : 455.5227; found: 456.1704.

#### Preparation of (4-[10-(4-Bromo-phenyl)-anthracen-9-yl]-phenyl)di-pyridin-2-yl-amine (10)

A solution of n-BuLi 2.5 M in hexane (10 mL, 25 mmol) was added to a THF solution (50 mL) of 1,4-dibromobenzene (5.92 g, 25 mmol) cooled at -78 °C. The reaction mixture was left under stirring for 1 h at this temperature and added via a cannula to a THF solution (100 mL) of **8** (3.26 g, 7.1 mmol) also cooled at -78 °C. This mixture was left under stirring for 8 h while allowing the temperature reach slowly the room temperature, then treated with aqueous HCl (1 M) to pH 4-5 and extracted with ether. The combined organic layers are dried over MgSO<sub>4</sub> and evaporated under vacuum to afford compound **9** as a viscous oil. The residue was then dissolved in glacial acetic acid (60 mL), treated with NaH<sub>2</sub>PO<sub>4</sub> (8.44 g, 95 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<sub>2</sub>Cl<sub>2</sub>. After the usual processing, the resulting residue was subjected to a silicagel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 99/1) to give **10** as a light yellow powder (yield: 20 %). Mp: 267 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) : 8.42 (dd, <sup>3</sup>J(H,H) = 6, <sup>3</sup>J(H,H) = 2 Hz, 2H), 7.93-7.62 (m, 8H), 7.53-7.39 (m, 10H), 7.21 (d, <sup>3</sup>J(H,H) = 7 Hz, 2H), 7.08 (td, <sup>3</sup>J(H,H) = 7, <sup>3</sup>J(H,H) = 2 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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]<sup>+</sup> C<sub>36</sub>H<sub>24</sub>N<sub>3</sub>Br : 577.5097; found: 578.1204.

#### Preparation of 2-[4-(5-(4-bromo-phenyl)-1,1-dimethyl-3,4-diphenyl)silol-2-yl)phenyl]-5-(4-bromo-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 mixture was added bis(phenylethynyl)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<sub>2</sub>(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 1,4-dibromobenzene (0.80 g, 34 mmol) in THF (20mL) and [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (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<sub>2</sub>O. After evaporation of the solvents, the resulting residue was subjected to a silicagel column chromatography (pentane/CH<sub>2</sub>Cl<sub>2</sub> : 95/5) to yield **11** and the silole **12** as separate solids. The siloles were each recrystallized from a hexane/ CH<sub>2</sub>Cl<sub>2</sub> mixture to give **11** as dark yellow crystals (yield: 30 %) and **12** as light yellow crystals (yield: 20 %). Characterizations of silole **11**: Mp: 310 °C. UV-Visible (λ<sub>max</sub>, nm, log ε): 255 (5.46), 399 (5.20). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) : 7.15 (d, <sup>3</sup>J(H,H) = 9 Hz, 4H), 6.96-6.86 (m, 12H), 6.74-6.64 (m, 12H), 6.58 (s, 4H), 0.35 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) : 155.14, 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,

119.72, -3.31. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ, ppm) : 8.09. HRMS (FAB+, m-nitrobenzyl alcohol matrix) *m/z*: calcd for [M+H]<sup>+</sup> C<sub>54</sub>H<sub>44</sub>Br<sub>2</sub>Si<sub>2</sub> : 906.1348; found: 906.1330. Characterizations of silole **11**: the synthesis of this compound was previously described starting from 1-bromo, 4-iodobenzene.<sup>55</sup> Mp: 224 °C. UV-Visible (λ<sub>max</sub>, nm, log ε): 250 (5.54), 361 (5.23). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) : 7.28 (d, <sup>3</sup>J(H,H) = 9 Hz, 4H), 7.10-7.02 (m, 6H), 6.81-6.75 (m, 8H), 0.47 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) : 154.90, 141.17, 139.04, 138.57, 131.56, 130.78, 130.24, 128.02, 126.94, 119.95, -3.52. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ, ppm) : 8.23. HRMS (FAB+, m-nitrobenzyl alcohol matrix) *m/z*: calcd for [M+H]<sup>+</sup> C<sub>30</sub>H<sub>18</sub>Br<sub>2</sub>Si : 571.9996; found: 571.9985.

#### Preparation of 2,5-[Bis-(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 lithiumnaphthalenide. To this mixture was added bis(phenylethynyl)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<sub>2</sub>(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**<sup>34</sup> (1.59 g, 4.8 mmol) in THF (20 mL) and [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (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<sub>2</sub>O. After evaporation of the solvents, the resulting residue was subjected to a silicagel column chromatography (pentane/CH<sub>2</sub>Cl<sub>2</sub> : 85/15) and recrystallized from a hexane/CH<sub>2</sub>Cl<sub>2</sub> mixture to give **B** as a yellow crystalline powder (yield: 35 %). Mp : 333 °C. UV-Visible (λ<sub>max</sub>, nm, log ε): 254 (6.37), 352 (5.22), 368 (5.43), 386 (5.50). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 8.51 (s, 2H), 8.07 (d, <sup>3</sup>J(H,H) = 8 Hz, 4H), 7.72 (d, <sup>3</sup>J(H,H) = 8 Hz, 4H), 7.53-7.37 (m, 8H), 7.28-7.00 (m, 18H), 0.77 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 155.02, 146.18, 142.73, 139.58, 139.39, 137.53, 135.22, 133.80, 131.31, 130.62, 130.55, 129.18, 128.72, 127.90, 127.33, 126.81, 125.61, 125.47, -3.07. <sup>29</sup>Si (CDCl<sub>3</sub>, δ, ppm): 2.80. MS (FAB+, m-nitrobenzyl alcohol matrix) *m/z*: 766 [M]<sup>+</sup>. Analysis calcd for C<sub>58</sub>H<sub>42</sub>Si : 90.82 %C, 5.52 %H; found: 89.94 %C, 5.64 %H.

#### Preparation of Silole **A**'

Same procedure as for silole **B**, using a solution of p-2,2'-dipyridylaminophenyl-4-bromophenylether **6**<sup>50</sup> (1.87 g, 4.4 mmol) in THF (20 mL). After evaporation of the solvents, the resulting residue was firstly subjected to a silicagel column chromatography (MeOH/CH<sub>2</sub>Cl<sub>2</sub> : 3/97) followed by an alumina column (THF/CH<sub>2</sub>Cl<sub>2</sub> : 5/95 to give **A**' as a bright yellow powder (yield: 42 %). Mp: 128 °C. UV-Visible (λ<sub>max</sub>, nm, log ε) : 277 (5.70), 377 (5.20). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) : 8.35 (dd, <sup>3</sup>J(H,H) = 6, <sup>3</sup>J(H,H) = 2 Hz, 4H), 7.58 (td, <sup>3</sup>J(H,H) = 7, <sup>3</sup>J(H,H) = 2 Hz, 4H), 7.16 (d, <sup>3</sup>J(H,H) = 9 Hz, 4H), 7.14-6.86 (m, 30H), 0.52 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) : 158.13, 155.05, 154.67, 153.77, 148.47, 140.48, 139.84,

138.88, 137.50, 135.11, 132.16, 132.06, 128.86, 127.53, 126.28, 119.69, 118.68, 117.98, 116.66, -3.60. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ, ppm) : 7.87. MS (FAB+, m-nitrobenzyl alcohol matrix) *m/z*: 937 [M+H]<sup>+</sup>. Analysis calcd for C<sub>62</sub>H<sub>48</sub>N<sub>6</sub>O<sub>2</sub>Si : 79.46 %C, 5.16 %H, 8.97 %N; found : 78.18 %C, 5.34 %H, 8.81 %N.

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

Same procedure as for silole **B**, using a solution of **4** (2.04g, 4.8 mmol) in THF (20 mL). After evaporation of the solvents, the resulting residue was firstly subjected to a silicagel column chromatography (pentane/CH<sub>2</sub>Cl<sub>2</sub> : 80/20) and recrystallized from hexane/CH<sub>2</sub>Cl<sub>2</sub> to give **B**' as a yellow powder (yield: 89 %). Mp: 264 °C. UV-Visible (λ<sub>max</sub>, nm, log ε) : 257 (6.47), 350 (4.95), 362 (5.13), 385 (5.10). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) : 8.54 (s, 2H), 8.09 (d, <sup>3</sup>J(H,H) = 8 Hz, 4H), 7.76 (d, <sup>3</sup>J(H,H) = 8 Hz, 4H), 7.55-7.38 (m, 12H), 7.24 (d, <sup>3</sup>J(H,H) = 8 Hz, 4H), 7.12-76.90 (m, 18H), 0.62 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) : 157.18, 155.30, 154.27, 140.97, 139.39, 136.84, 135.57, 133.75, 132.95, 131.81, 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. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ, ppm) : 7.99. MS (FAB+, m-nitrobenzyl alcohol matrix) *m/z*: 951 [M+H]<sup>+</sup>. Analysis calcd for C<sub>70</sub>H<sub>50</sub>O<sub>2</sub>Si : 88.39 %C, 5.30 %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 3,5-bis(2,2'-dipyridylamino)bromobenzene<sup>36</sup> **5** (1.43 g, 4.4 mmol) in THF (20 mL). After evaporation of the solvents, the resulting residue was subjected to a silicagel column chromatography (MeOH/CH<sub>2</sub>Cl<sub>2</sub> : 10/90) and recrystallized from a hexane/CH<sub>2</sub>Cl<sub>2</sub> mixture to give **C** as a bright yellow powder (yield: 28 %). Mp: 135-137 °C. UV-Visible (λ<sub>max</sub>, nm, log ε) : 282 (5.80), 303 (5.79), 379 (5.10). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) : 8.31 (dd, <sup>3</sup>J(H,H) = 6, <sup>3</sup>J(H,H) = 2 Hz, 8H), 7.53 (td, <sup>3</sup>J(H,H) = 7, <sup>3</sup>J(H,H) = 2 Hz, 8H), 6.92-6.82 (m, 22H), 6.72-6.66 (m, 6H), 6.51 (d, <sup>3</sup>J(H,H) = 2 Hz, 4H), 0.27 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) : 157.56, 154.46, 148.20, 145.25, 142.38, 141.19, 138.25, 137.76, 120.51, 127.41, 126.16, 123.49, 121.87, 118.33, 117.24, -4.11. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ, ppm) : 8.67. MS (FAB+, m-nitrobenzyl alcohol matrix) *m/z*: 1091 [M+H]<sup>+</sup>. Analysis calcd for C<sub>70</sub>H<sub>54</sub>N<sub>12</sub>Si : 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 (20 mL). The residue was purified by silicagel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/THF gradient : 80/20 to 70/30) and crystallized from a hexane/CH<sub>2</sub>Cl<sub>2</sub> mixture to afford **D** as a yellow solid (yield: 15 %). Mp: 376 °C. UV-Visible (λ<sub>max</sub>, nm, log ε) : 268 (6.30), 389 (5.57), 407 (5.63). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) : 8.45 (dd, <sup>3</sup>J(H,H) = 6, <sup>3</sup>J(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),

7.05-7.02 (m, 8H), 0.88 (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm) : 159.81, 159.33, 155.16, 148.90, 144.84, 141.53, 139.74, 139.29, 138.57, 137.56, 136.75, 136.29, 135.81, 133.48, 130.80, 130.42, 130.33, 129.50, 128.82, 127.85, 127.23, 127.03, 125.26, 125.14, 119.73, 118.37, 117.15, -4.54.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm) : 8.27. MS (FAB+, m-nitrobenzyl alcohol matrix)  $m/z$ : 1257  $[M+H]^+$ . Analysis calcd for  $\text{C}_{90}\text{H}_{64}\text{N}_6\text{Si}$  : 85.95 %C, 5.09 %H, 6.68 %N; found : 85.12 %C, 5.27 %H, 6.56 %N.

#### Preparation of (4-[5-((1,1-Dimethyl-3,4-diphenyl)silol-2,5-yl)phenyl]-1,1-dimethyl-3,4-diphenyl-silol-2-yl)-biphenyl-4-yl)-bis-(di-pyridin-2-yl-amine) (E)

A mixture of bisilole 11 (0.40 g, 0.44 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.05 g, 0.044 mmol), and toluene (50 mL) was stirred for 10 min. The boronic acid  $13^{39}$  (0.76 g, 26 mmol) in 20 mL of EtOH and NaOH (0.18 g) in 20 mL of  $\text{H}_2\text{O}$  were subsequently added. The mixture was stirred and refluxed for 72 h and allowed to cool to room temperature. The water layer was separated and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{MgSO}_4$ , and the solvents were evaporated under reduced pressure. Purification of the crude product was carried out by silicagel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{THF}$  : 85/15) followed by the recrystallization of the solid from a  $\text{CH}_2\text{Cl}_2$ /pentane mixture to afford E as a dark yellow solid in 86% yield. Mp: 334 °C. UV-Visible ( $\lambda_{\text{max}}$ , nm,  $\log \epsilon$ ) : 284 (5.77), 311 (5.79), 419 (5.65).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm) : 8.41 (dd,  $^3J(\text{H,H}) = 6$ ,  $^3J(\text{H,H}) = 2$  Hz, 4H), 7.66-7.57 (m, 8H), 7.39 (d,  $^3J(\text{H,H}) = 8.5$  Hz, 4H), 7.24 (d,  $^3J(\text{H,H}) = 8.5$  Hz, 4H), 7.07-6.96 (m, 24H), 6.88-6.83 (m, 4H), 6.72 (s, 4H), 0.53 (s, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm) : 157.62, 154.31, 153.68, 148.18, 141.58, 140.80, 139.04, 139.01, 138.96, 138.01, 137.14, 137.05, 129.98, 129.96, 129.37, 128.56, 128.13, 127.51, 127.41, 127.36, 126.36, 126.23, 126.15, 118.30, 116.95, -3.45.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm) : 7.95. MS (FAB+, m-nitrobenzyl alcohol matrix)  $m/z$ : 1241  $[M+H]^+$ . Analysis calcd for  $\text{C}_{86}\text{H}_{68}\text{N}_6\text{Si}_2$  : 83.18 %C, 5.51 %H, 6.78 %N; found : 82.43 %C, 5.66 %H, 6.78 %N.

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