Synthesis of new dipyridylphenylaminosiloles for highly emissive organic electroluminescent devices†

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High-performance organic electroluminescent devices based on two new siloles, 1,1-dimethyl-2,5-bis(p-2,2'-dipyridylaminophenyl)silole (5) and 1,1-dimethyl-2,5-bis(p-2,2'-dipyridylaminophenyl)-3,4-diphenylsilole (8), acting as both electron- and hole-transporting material, are described. The best performance is attained with silole 8, which displays a luminescence of 10^4 Cd m⁻² at 10 V for a current density of less than 0.2 A cm⁻², which is as efficient as tris(8-hydroxyquinoline)aluminium (Alq3), one of the best candidates for electroluminescent materials under the same conditions.

Electroluminescent (EL) organic and coordination compounds have been the subject of very active research for some years because of their various potential applications in advanced materials devoted to the design of light, flat and sometimes soft displays.^{1,2} Light-emitting diodes based on evaporated molecules are often multi-layer devices consisting of a hole-injecting layer (HIL), a hole-transporting layer (HTL), an emissive layer, and possibly an electron-transporting layer (ETL), the whole sandwiched between two properly chosen electrodes. These structures can be restricted to one, two or three-layer devices if a molecule has the ability to transport electrons and/or holes and at the same time emit light. In this sense, the development of molecules able to transport either holes and electrons is still a challenge. Amongst the various EL organic compounds recently described in the literature, silole-based ones have occupied a growing position since Tamao et al. reported a general onepot synthesis of 2,5-diaryl-3,4-diphenylsiloles and discovered their high efficiency in EL devices owing to their efficient electron-transporting properties.^{3,4} This very interesting property originates from a low-lying LUMO, which is the consequence of an effective interaction between the σ^* orbital of the silole silicon atom with the π^* orbital of the butadiene fragment.⁵ In the course of their investigations to increase the electron-transporting properties of siloles and therefore their efficiency in EL devices, Tamao *et al.* have found that 2,5-dipyridyl-3,4-diphenylsiloles gave excellent results when used in multilayer EL devices, showing performances that sometimes exceed those of the well-known tris(quinolinato)aluminium (Alq) with a high durability. Moreover, by adding diphenylamino groups to the above mentioned 2,5-dipyridylsiloles, they have been able to remove the hole-transporting layer to achieve single-layer organic EL devices. The design of other siloles having both hole- and electron-transporting abilities is, therefore, an interesting path to follow.

We report in this communication the synthesis and the use in EL devices of two new diarylsiloles having di-2-pyridylaminophenyl as aryl groups. The design of these molecules was motivated by the idea that, besides being potential hole transporters, the di-2-pyridylaminophenyl side groups can act as metal chelates, which is not the case for the previously described triarylamino groups. Indeed, as shown by Wang *et al.*, the coordination of metal salts by di-2-pyridylamino based ligands leads to blue luminescent and/or electroluminescent complexes.^{8,9}

Compounds 5 and 8 were prepared by the methods shown in Schemes 1 and 2, respectively. The preparation of compound 5 involves the synthesis of 1,1-dimethyl-2,5-(4-phenyl)silole 4, that may be used as the starting molecule for various 3,4unsubstituted-2,5-diarylsiloles. Thus, the formation of the silacyclopentadiene 2 was achieved by reacting 4-(trimethylsilyl)styrene 1 with lithium in the presence of dimethyldichlorosilane. 10 The trimethylsilyl side-groups was readily and selectively replaced by bromine to yield the bis(4-bromophenyl) derivative 3. Only Me₃Si-C bond cleavage occurred and no product arising from the cleavage of the ring Si-C bonds was obtained. Treatment of 3 by 2 equiv of N-bromosuccinimide in the presence of benzoyl peroxide, followed by refluxing of the mixture in the presence of a weak base, yields the silole 4 (overall yield: 15%). The introduction of the 2-pyridylamino groups was achieved by following the procedure described by Wang et al.,11 which involves the solvent-free thermally activated reaction of 4 with 2-dipyridylamine in the presence of

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Scheme 1 Synthesis of silole 5: (i) Li, Me₂SiCl₂; (ii) Br₂; (iii) NBS, benzoyl peroxide; (iv) AcOK–AcOH; (v) di-2-pyridylamine, CuSO₄, K₂CO₃.

Scheme 2 Synthesis of silole 8: (i) NpLi; (ii) ZnCl₂·TMEDA; (iii) PdCl₂(PPh₃)₂.

copper sulfate and potassium carbonate to yield compound 5 as a bright yellow solid (32%).

Compound **8** was more conveniently prepared by the method described by Tamao *et al.*, which involves the one-pot intramolecular reductive cyclization of bis(phenylethynyl) silane **6** and subsequent Pd(0) catalyzed cross-coupling reaction with an aryl bromide, as depicted in Scheme 2. The synthesis of 4-(2,2'-dipyridylamino)bromobenzene **7** that was originally described by Wang *et al.* ¹¹ was improved by carrying out the Ullmann condensation in sealed tubes. Silole **8** was recovered as a bright yellow solid with 24% yield.

UV-visible absorption and fluorescence spectra of both materials have been measured in solution as well as on evaporated films. In solution, the spectra of **5** and **8** are characterized by the presence of two intense absorption bands in the 280 and 380 nm regions (Table 1); the emission spectra show an emission peak centered at ca. 520 nm. As discussed previously, the absorption band observed at ca. 280 nm originates from π - π * transitions of the aryl groups, whereas the absorption band observed at ca. 380 nm is characteristic of

 π - π * transitions in the silole ring.³ When compared with the values reported for 1,1-dimethyl-2,3,4,5-tetraphenyl silole (TPS; absorption: $\lambda_{\text{max}} = 359$ nm, emission: $\lambda_{\text{max}} = 467$ nm, $\Phi_{\rm em} = 0.0014)^3$ and 1,1-dimethyl-2,5-diphenyl silole (DPS; $\lambda_{\text{max}} = 376 \text{ nm}$, emission: $\lambda_{\text{max}} = 463 \text{ nm}$, $\Phi_{\text{em}} = 0.29$), 12 the red-shift that is observed for 5 and 8 in both absorption and emission is indicative of a substantial perturbation of the HOMO-LUMO levels provided by the presence of the terminal dipyridylamino groups. Moreover, as observed with parents DPS and TPS, a red-shift is also observed when the phenyl located at the 3,4-positions are removed. One of the more striking effects afforded by the presence of the dipyridylamino groups is reflected by the quantum yields measured for 8 $(\Phi_{\rm em} = 0.06)$, which is much higher than that of the related TPS (see above). In the solid state, the near-UV-visible film spectra (Fig. 1) show the intense absorption due to the π - π * transitions of the silole ring. The λ_{max} values (Table 1) are close to those measured in solution; a maximal shift of 10 nm is observed for silole 8. This difference may be due to the apparently superior ability of silole 8 to crystallize when deposited on glass slides.

Table 1 Photophysical and electrochemical data for siloles 5 and 8

Silole	UV-Vis $\lambda_{max}/nm \ (\epsilon/mol^{-1} \ cm^{-1})$		PL $\lambda_{\rm max}/{\rm nm} \; (\Phi_{\rm em})^c$		Cyclic voltammetry ^d			
	Solution ^a	Film ^b	Solution ^a	Film ^b	$E_{ m pa}/{ m V}$	$E_{ m pc}/{ m V}$	$E_{ m a}/{ m V}$	$E_{ m c}/{ m V}$
5	410 (29 308)	413	522 (0.19)	553	0.9	-1.90	0.71	-1.55
8	391 (20 225)	401	516 (0.06)	540	1.0	-1.59	0.89	-1.44

^a Measured in dichloromethane. ^b For evaporated thin film on glass. ^c Relative to perylene ($\Phi_{em} = 0.94$). ^d In nBu_4PF_6 (0.1 M) in CH₃CN, electrodes: glassy carbon, Ag/Ag⁺, Pt. E_{pa} and E_{pc} are the anodic and cathodic peak potentials.

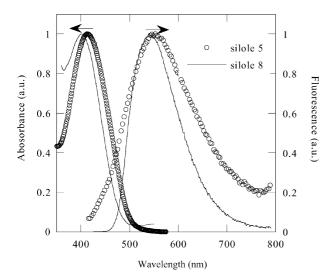


Fig. 1 Normalized absorption and fluorescence spectra of evaporated films of siloles 5 and 8 on glass slides.

As a result, the different conformations that may be found, either in the solid state or in solution, give rise to the difference observed in the $\lambda_{\rm max}$ values. This assumption is also supported by solid state fluorescence spectra since the intense emission that is observed at ca. 545 nm (see Table 1) is broader for silole 5 than for silole 8.

An important point for the interpretation of the spectroscopic data is based on a knowledge of the conformational preference of the siloles. Since crystals suitable for an X-ray structure determination could not be obtained, we turned to density functional theory (DFT) calculations with the UB3LYP functional to get some relevant information about the molecular conformations. Due to the size of the molecules, the geometry calculations were performed with the 6-31 basis set to the standard convergence criteria as implemented in Gaussian 98. 13 Structurally characterized siloles served as a benchmark to see how well the experimentally determined geometry could be reproduced by the calculations.¹⁴ The geometry of siloles 5 and 8 virtually approaches a C_2 symmetry, even though the optimizations were done without constraints (Fig. 2). Silole 5 displays a nearly coplanar arrangement of the adjacent phenyl rings with respect to the central silole ring, with torsion angles of 11.1°. Silole 8 has a propeller-like arrangement of the four phenyl rings in which the torsion angles of the unsubstituted phenyl rings in the 3and 4-positions (83.4°) with respect to the central silole ring are larger than those of the dipyridylamino bearing phenyl rings in the 2- and 5-positions (48.3°). As a result the degree of conjugation expected for 5 should be greater than the one

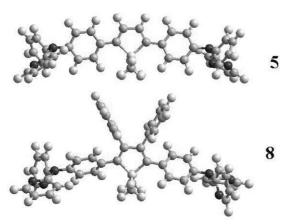


Fig. 2 DFT optimized geometries of siloles 5 and 8

expected for **8**, at least in solution. This assumption is fully supported, firstly by the red-shift that is observed in their UV-visible spectra and secondly by the fact that **5** displays a much higher quantum yield than **8**. However, one has to take into account the fact that the substantial quantum yield decrease that is afforded by the phenyl groups at the 3,4-positions may also originate from nonradiative decay processes due to the rotational motion of these groups.

Cyclic voltammetry was performed on the two molecules to estimate the HOMO and LUMO energy levels and to confirm the optical band gap obtained from the UV-visible absorption measurements. For efficient electron-transporting materials, a low reduction potential is preferred in order to facilitate electron injection from the cathode. On the other hand, for efficient hole-transporting materials, a low oxidation potential will favor hole injection from the anode. From the onset potentials of the oxidation and reduction processes (see Table 1), the band gap of silole 5 is estimated to be 2.26 eV, while it is 2.33 eV for silole 8, which is in good agreement with the values obtained from the optical absorption spectrum (2.34 eV for silole 5 and 2.48 eV for silole 8). The HOMO and LUMO energy levels were calculated assuming that the energy level corresponding to the electrochemical potential of the saturated calomel electrode ($E_{\rm SCE}$) is -4.4 eV. ¹⁵ The HOMO and LUMO levels were estimated to be -5.02 and -2.76 eV for silole 5 and -5.2 and -2.87 eV for silole 8.

Electroluminescent devices based on siloles 5 and 8 were fabricated, with the structure shown on Fig. 3. The electrodes were chosen in order to match the HOMO and LUMO levels of the organic materials. ITO is a commonly used anode because it is transparent and has a relatively high work function (4.8 eV), which matches quite well the HOMO level of the siloles. Between ITO and the silole a thin layer of PEDOT/PSS was inserted. PEDOT/PSS is a conducting polymer acting as a buffer to reduce the shorting problems caused by the ITO deposition process; it also acts as a barrier to oxygen and indium diffusion from the ITO. Moreover, it slightly increases the work function of the anode, lowering the barrier to holes. A 50 nm thick silole layer was then thermally evaporated and calcium was used as the cathode since its work function (2.9 eV) is close to the electron affinity of the siloles. In the ITO/PEDOT/silole/Ca device the silole acts as the emitter but also as the electron- and hole-transporting layer.

The normalized EL spectra (Fig. 4) recorded for siloles 5 and 8 operating in the EL device described above are almost superimposable with an emission peak in the yellow-green region at 545 nm. The EL and solid-state PL spectra are very close for compound 8 based devices, whereas with compound 5 the PL spectrum is broader. This can be explained in terms of crystallinity, assuming that silole 5 tends to crystallize faster inside an operating device. To evaluate the performance of the two silole derivatives as electroluminescent materials, we examined the current density-voltage (J-V) and luminance-voltage (L-V) characteristics (Fig. 5) of ITO/PEDOT/silole/Ca devices. For both compounds, above a threshold voltage of 3 V a significant current flows, giving rise to light emission. Silole 5 exhibits excellent performances, reaching a luminance of 3×10^3 Cd m⁻² at 10 V and a maximum efficiency of 1.2

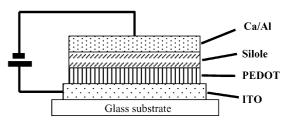


Fig. 3 Structure of the electroluminescent devices.

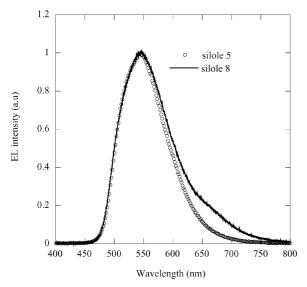


Fig. 4 Normalized electroluminescence spectra of ITO/PEDOT/silole/ Ca devices

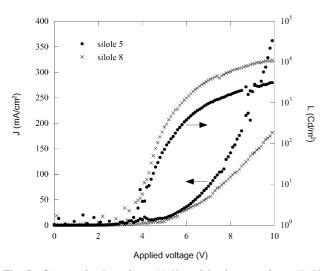


Fig. 5 Current density-voltage (J-V) and luminance-voltage (L-V) characteristics of ITO/PEDOT/silole/Ca devices

Cd A⁻¹ (Table 2). However, the best performance is attained with silole **8**, which displays a luminance of 10⁴ Cd m⁻² at 10 V and a maximum efficiency of 6.3 Cd A⁻¹ (obtained at 50 mA cm⁻²). For comparison, silole **8** is more efficient than Alq, one of the most efficient electroluminescent materials reported so far, ^{16,17} which exhibits an efficiency of 2.2 Cd A⁻¹ under the same conditions (devices made with the same structure). Moreover, the incorporation of the dipyridylamino group into the diarylsilole skeleton appears to be of crucial importance since the EL efficiency of **8** is about ten times the one measured for its diphenylamino cousin.⁷

In conclusion, we have reported in this communication the synthesis and the use in EL devices of new diarylsiloles having di-2-pyridylaminophenyl aryl groups. Both compounds were found to be very efficient in single-layer light emitting diodes. The best performance is observed with silole 8, which displays

 Table 2
 Performance of ITO/PEDOT/silole/Ca electroluminescent devices

Silole		$J/\text{mA cm}^{-2}$ at 10 V	<i>L</i> /Cd m ⁻² at 10 V	Max efficiency/ Cd A ⁻¹
5	544 (2.28)	363	3×10^3 1×10^4	1.2
8	546 (2.27)	183		6.3

a maximum efficiency of more than 6 Cd A⁻¹, which is more efficient than Alq3, one of the best candidate for electroluminescent materials, and is certainly the best value reported up-to-date for silole-based EL devices. The design of these molecules was motivated by the main reason that besides being potentially both electron- and hole-transporters, the di-2-pyridylaminophenyl side groups can act as metal chelates.¹⁸

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. ¹H, ¹³C and ²⁹Si 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 and characterized in a glove box under nitrogen.

Device fabrication

EL devices based on siloles **5** and **8** as both emitting and transporting layer were fabricated on an ITO (indium tin oxide) substrate covered with a 60 nm thick layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT/PSS) deposited by the usual spin-coating technique and cured at 80° for about 1 h. A 50 nm thick silole layer was then thermally evaporated under secondary vacuum (around 10⁻⁶ mbar). The calcium cathode was evaporated through a shadow mask on top of the silole and capped with a layer of aluminum to minimize its oxidation.

Syntheses

1,1-Dimethyl-2,5-bis(4-trimethylsilylphenyl)silacyclopentane

(2). To a suspension of lithium (0.46 g, 66 mmol) in THF (40 mL) was added few drops of a solution of Me₂SiCl₂ (2.84 g, 22 mmol) and 4-trimethylsilylstyrene (1; 7.76 g, 44 mmol) in THF (10 mL) to initiate the reaction. Once the reaction had started, the temperature was lowered to 0 °C and maintained through the rest of the addition. After the addition, the reaction mixture was left for 0.5 h at room temperature under stirring, hydrolyzed with a saturated NH₄Cl solution and extracted with ether. The viscous yellow oil that was obtained upon evaporation of the solvent was subjected to a column chromatography (silica gel) to afford 2 as a colourless solid (3.20 g, 36%). ¹H NMR (CDCl₃, δ): 7.49–7.45 (m, 4H), 7.17–7.11 (m, 4H), 2.70–2.16 (m, 6H), 0.38 (s, 1.5H), 0.30 (s, 18H), –0.04 (s, 3H), –0.54 (s, 1.5H). MS (FAB+, *m*-nitrobenzyl alcohol matrix): m/z 410 [C₃₀H₃₈Si₃]⁺.

1,1-Dimethyl-2,5-bis(4-bromophenyl)silacyclopentane (3). To a stirred solution of **2** (2.91 g, 7.1 mmol) in ether (250 mL) at -80 °C was slowly added Br₂ (0.75 mL, 14.5 mmol). After the addition was complete, the temperature was slowly increased to room temperature and left to stir for 0.5 h. The solvent was then evaporated under vacuum to afford a brown-red semisolid, which was chromatographed on a short silica column to lead to compound **3** as a pale yellow crystalline product with a yield of 83% (2.49 g). ¹H NMR (CDCl₃, δ): 7.42 (d, J = 7.5 Hz, 4H), 7.02 (d, J = 7.5 Hz, 4H), 2.72–2.02 (m, 6H), 0.37 (s, 1.5H),

0.05 (s, 3H), -0.54 (s, 1.5H). MS (FAB+, *m*-nitrobenzyl alcohol matrix): m/z 424 $[C_{18}H_{20}Br_2Si]^+$.

1,1-Dimethyl-2,5-bis(4-bromophenyl)silole (4). N-Bromosuccinimide (2.09 g, 11.7 mmol) and benzoyl peroxide (10 mg) in CCl₄ (10 mL) were heated to reflux. Compound 3 was then added rapidly and the reaction mixture left under reflux for 1 h. After cooling, the mixture was then filtered and poured into a solution of CH₃CO₂K (1.44 g, 14.7 mmol) and acetic acid (0.1 mL) in acetonitrile (25 mL). The mixture was refluxed for 1 h, cooled, hydrolyzed with a saturated NH₄Cl solution and extracted with ether. Evaporation of the solvents yielded a brown-yellow solid, which was washed several times with pentane to afford 2.00 g of 4 as a bright yellow solid (yield: 41%). M.p. 207 °C. ¹H NMR (CDCl₃, δ): 7.54 (d, J = 6.5 Hz, 4H), 7.37 (s, 2H), 7.35 (d, J = 6.5 Hz, 4H), 0.55 (s, 6H). ¹³C NMR (CDCl₃, δ): 138.81, 132.30, 132.08, 128.67, 128.08, 121.06. ²⁹Si NMR (CDCl₃, δ): 8.21. MS (FAB+, *m*-nitrobenzyl alcohol matrix): m/z 420 $[C_{18}H_{16}Br_2Si]^+$.

1,1-Dimethyl-2,5-bis(4-phenyl-di-2-pyridylamine)silole (5). A mixture of 4 (0.8 g, 2 mmol), di-2-pyridylamine (1.23 g, 7.14 mmol), K₂CO₃ (0.956 g, 7.14 mmol) and CuSO₄ (0.100 g, 0.4 mmol) in water (20 mL) and CH₂Cl₂ (100 mL) was thoroughly stirred and then evaporated to dryness in vacuum. The mixture was ground in a mortar and 3-5 drops of CH₂Cl₂ were added to this mixture. The mixture was heated in a Schlenk tube at 210 °C for 6 h. After being cooled to room temperature, the mixture was dissolved in CH₂Cl₂ (100 mL) and water (100 mL), then extracted. After evaporation of the solvent, the residue was subjected to column chromatography with CH₂Cl₂ -THF (90:10) to afford compound 5 (yield: 32%). M.p. 260 °C. ¹H NMR (CDCl₃, δ): 8.38 (dd, $J_1 = 7$, $J_2 = 2$ Hz, 4H), 7.61 (td, $J_1 = 7$, $J_2 = 2$ Hz, 4H), 7.47 (d, J = 9 Hz, 4H), 7.32 (s, 2H), 7.18 (d, J = 9 Hz, 4H), 7.07 (d, J = 7 Hz, 4H), 6.97 (dd, $J_1 = 7$, $J_2 = 2$ Hz, 4H), 0.56 (s, 6H). ¹³C NMR (CDCl₃, δ): 158.60, 154.70, 149.03, 138.96, 137.89, 134.80, 130.32, 129.69, 127.62, 118.56, 117.61, -2.86. ²⁹Si NMR (CDCl₃, δ): 8.14. HRMS (FAB+, *m*-nitrobenzyl alcohol matrix): *m*/*z* 601.2526; calcd for $C_{38}H_{32}N_6Si\ [M+H]^+$: 601.2536.

p-2,2'-Dipyridylaminobromophenyl (7). A mixture of 1,4dibromobenzene (4.939 g, 2.09 mmol), di-2-pyridylamine (1.2 g, 6.96 mmol), K₂CO₃ (1.12 g, 8.37 mmol) and CuSO₄ (0.174 g, 0.697 mmol) in water (20 mL) and CH₂Cl₂ (100 mL) was stirred well and evaporated to dryness in vacuum. The mixture was ground in a mortar and 3-5 drops of CH₂Cl₂ were added to this mixture. The mixture was heated in a sealed tube at 200 °C for 6 h. After being cooled to room temperature, the mixture was dissolved in CH₂Cl₂ (100 mL) and water (100 mL), then extracted. After evaporation of the solvent, the residue was subjected to column chromatography with CH₂Cl₂ to afford compound 7 (yield: 83%). M.p. 124 °C. ¹H NMR (CDCl₃, δ): 8.35 (dd, $J_1 = 7$, $J_2 = 2$ Hz, 4H), 7.60 (td, $J_1 = 7$, $J_2 = 2$ Hz, 4H), 7.51 (d, J = 9 Hz, 2H), 7.09 (d, J = 9 Hz, 2H), 7.05–6.95 (m, 4H). ¹³C NMR (CDCl₃, δ): 157.32, 149.06, 144.81, 138.11, 133.14, 129.03, 118.93, 118.93, 117.44, 114.31. HRMS (FAB+, *m*-nitrobenzyl alcohol matrix): *m*/*z* 326.0271; calcd for C₁₆H₁₂N₃Br: 326.0293...

1,1-Dimethyl-2,5-bis(4-phenyldi-2-pyridylamine)-3,4-diphenyl-silole (8). 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 give a deep green solution of lithium naphthalenide. To this mixture was added bis(phenylethynyl)dimethylsilane (0.5 g, 2 mmol) in THF (10 mL). After stirring for 10 min, the reaction mixture was cooled to 0° C and [ZnCl₂(tmen)] (tmen = N, N, N', N'-tetramethylene-

diamine; 2.01 g, 8 mmol) was added, followed by addition of THF (20 mL). After stirring for 1 h at room temperature, a solution of 4-(2,2'-dipyridylamino)bromobenzene (7; 1.304 g, 4 mmol) in THF (20 mL) and [PdCl₂(PPh₃)₂] (0.100 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 Et₂O. After evaporation of the solvents, the resulting residue was subjected to a column chromatography with CH₂Cl₂-THF (85:15) to give 0.560 g of 8 as a bright yellow crystalline solid (yield: 40 %). ¹H NMR (CDCl₃, δ): 8.35 (dd, $J_1 = 7$, $J_2 = 2$ Hz, 4H), 7.56 (td, $J_1 = 7$, $J_2 = 2$ Hz, 4H), 7.07–7.02 (m, 6H), 6.97–6.95 (m, 20H), 0.57 (s, 6H). 13 C NMR (CDCl₃, δ): 158.54, 154.58, 148.93, 142.85, 139.65, 137.89, 137.03, 130.55, 130.27, 127.93, 126.65, 126.47, 123.49, 118.56, 117.62, -2.72. ²⁹Si NMR (CDCl₃, δ): 8.038. HRMS (FAB+, *m*-nitrobenzyl alcohol matrix): m/z 753.3196; calcd for $C_{38}H_{32}N_6Si [M + H]^+$: 753.3162.

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