

## Electroluminescence from Double Layer Organic Light-emitting Diodes Using Dehydrocoupled Polysilanes as Hole Transport Layers

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In this article, four polysilanes are used as hole transporting materials, together with the electroluminescent metal complex 8-hydroxyquinoline aluminium (Alq<sub>3</sub>), in organic double layer light emitting diodes (LED). It appears that the side chain substituents strongly influence the device performance. Amino-substituted polysilanes show stable device performance and a power efficiency of 0.33 lm W<sup>-1</sup>. This is an increase by more than 100% compared to the Alq<sub>3</sub> single layer LED (0.15 lm W<sup>-1</sup>).

*Key words:* electroluminescence, polysilanes, double layer light-emitting diode, LED.

### INTRODUCTION

Light emitting diodes (LEDs) based on thin conjugated polymer films<sup>1–5</sup> and/or sublimed thin molecular<sup>6</sup> or oligomer<sup>7–9</sup> layers have attracted much interest because of their possible application in flat, flexible and large-area displays<sup>10</sup>. In such devices, light emission occurs due to the recombination of singlet excitons formed by the combination of negative and positive

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polarons,<sup>11</sup> which are injected from the cathode and the anode, respectively, and subsequently drift towards each other under the applied electric field. Obviously, it is important to achieve well balanced charge carrier injection<sup>12</sup> and good charge carrier transport<sup>13</sup> in order to obtain equal numbers of positive and negative charge carriers in the emissive region. In case of an unbalanced charge carrier injection, the majority of carriers will partly reach the counter electrode without recombination. This leads to ohmic losses and faster device degradation due to Joule heating.<sup>14</sup>

Since the first demonstration of organic thin film electroluminescence (EL),<sup>6</sup> the combination of electron transporting layers (ETL) and/or hole transporting layers (HTL) together with an emissive layer has been shown to be essential for improved device performance.<sup>15</sup> These layers provide a more efficient charge carrier injection due to smaller barriers at the electrode/transport layer interface and/or gain better charge carrier transport due to higher charge carrier mobilities. Additionally, introduction of an ETL and/or a HTL leads to a band offset at the interface to the emitting layer, where charge carriers can accumulate. The excitons generated at this interface are kept away from the electrodes, where several quenching mechanisms can occur.<sup>16</sup>

In this article, we present the results of investigations of four polysilanes used as hole transporting materials in combination with the electroluminescent metal complex 8-hydroxyquinoline aluminium ( $\text{Alq}_3$ ), which is well known as a good electron transporting material with a high intrinsic trap density.<sup>17,18</sup>

Polysilanes with  $\sigma$ -conjugated Si main chains have been investigated in several LED configurations.<sup>19–22</sup> In these materials, the hole drift mobilities have been estimated to be in the order of  $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>23</sup> The charge carrier transport within the polysilanes is a thermally activated hopping process involving states associated with the silicon backbone. It has been shown<sup>24</sup> that the hole mobility along a polysilane chain is not sensitive to side-group substituents. On the other hand, the side-chains influence the electronic transport properties strongly due to their geometric arrangement of the silicon backbone, and the substituents are crucial for the film forming properties, *e.g.* solubility and morphology. At least, they effect the stability in ambient atmosphere and under device operation.

## SYNTHESIS AND EXPERIMENTAL

The transition metal catalyzed polymerization of primary hydrosilanes allows the preparation of structurally new polymers that are difficult to synthesize by classical Wurtz type coupling.<sup>25,26</sup> The resulting polymers can easily be functionalized by

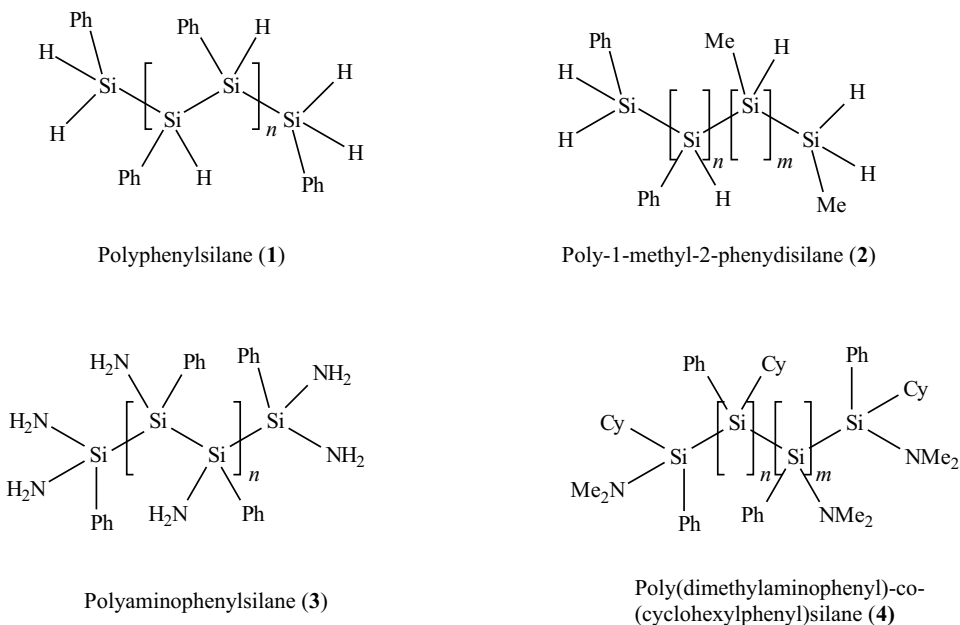


Figure 1. Molecular structures of polyphenylsilane (PS-1), poly-1-methyl-2-phenyldisilane (PS-2), polyaminophenylsilane (PS-3) and poly(dimethylaminophenyl)-co-(cyclohexylphenyl)silane (PS-4).

halogenation or hydrosilylation,<sup>27</sup> while copolymerization of primary hydrosilanes with amines leads to amino substituted polysilanes (Figure 1).<sup>28</sup>

*Polyphenylsilane (PS-1)* was synthesised by coupling of phenylsilane using  $\text{Cp}_2\text{ZrCl}_2/2\text{BuLi}$  as a catalyst.<sup>29</sup> The polymer was dissolved in toluene and filtered over a short Florisil column to separate it from the catalyst ( $M_w = 3800$  Da).

*Poly-1-methyl-2-phenyldisilane (PS-2)* was synthesized in an analogous way by polymerization of 1-methyl-2-phenyldisilane ( $M_w = 50000$  Da).<sup>30</sup>

*Polyaminophenylsilane (PS-3)* was synthesized by catalytic copolymerization of phenylsilane and ammonia under pressure using  $\text{Cp}_2\text{TiMe}_2$  as a catalyst. Removal of the volatiles yielded a viscous grey oil ( $M_w = 1060$  Da).

*Poly(dimethylaminophenyl)-co-(cyclohexylphenyl)silane (PS-4)*:  $\text{PhSiH}_3$  and dimethylamine were copolymerized under pressure using  $\text{Cp}_2\text{TiMe}_2$  as a catalyst in the presence of cyclohexene as hydrogen acceptor.<sup>31</sup> 50% of silicon atoms of the resulting polymer were cyclohexyl substituted due to hydrosilylation ( $M_w = 2090$  Da).

The polymers were characterized by nuclear magnetic resonance spectroscopy, IR spectroscopy and gel permeation chromatography. All reactions were carried out under a dry argon atmosphere using Schlenk techniques.

All double layered LEDs, *i.e.*: ITO / PS-*i* (*i* = 1,...,4) /  $\text{Alq}_3$  / Al, were produced as follows: polysilanes were dissolved in oxygen free toluene at concentrations from 1.2 to 1.5 mg mL<sup>-1</sup>. Under inert conditions the solutions were spin-coated on indium-

tin-oxide (ITO) coated glass substrates. The thickness of the films (30 to 70 nm) was determined by Tolansky's interferometric method. The Alq<sub>3</sub> layers (70 nm) were vacuum deposited onto the PS layers at  $3 \times 10^{-6}$  mbar at an evaporation rate of 0.6 to  $1.5 \text{ \AA s}^{-1}$ , monitoring the thickness with a quartz microbalance. Finally, the Al cathodes were evaporated on top of the double layer structures at a pressure less than  $5 \times 10^{-6}$  mbar. The active areas of the devices were about  $3 \times 2.5 \text{ mm}^2$ . The external quantum efficiency was measured with a calibrated photodiode in an integrating sphere. The EL spectra were recorded with a CCD-spectrometer (Oriel 77400). All measurements were performed in an argon atmosphere.

## RESULTS AND DISCUSSION

Figure 2 shows the current ( $I$ ) and integrated light emission (EL) as a function of the applied electric field ( $E$ ) in forward direction (*i.e.* ITO as the anode) of an ITO/PS-3/Alq<sub>3</sub>/Al and an ITO/PS-2/Alq<sub>3</sub>/Al device compared to a single layer ITO/Alq<sub>3</sub>/Al LED. The onset field of the PS-3/Alq<sub>3</sub> device occurs at  $1 \text{ MV cm}^{-1}$  whereas the turn on the fields for the ITO/Alq<sub>3</sub>/Al single layer device and the LED with PS-2 as the HTL are above  $1.5 \text{ MV cm}^{-1}$ . For a current density of  $40 \text{ mA cm}^{-2}$ , the single layer device yields a brightness of  $275 \text{ cd m}^{-2}$  and the ITO/PS-3/Alq<sub>3</sub>/Al LED  $650 \text{ cd m}^{-2}$ . The latter yields a maximum brightness of  $1500 \text{ cd m}^{-2}$  at  $145 \text{ mA cm}^{-2}$ . The double layer LED using PS-2 as the HTL permits only current densities up to  $18 \text{ mA cm}^{-2}$  yielding a brightness of  $45 \text{ cd m}^{-2}$ .

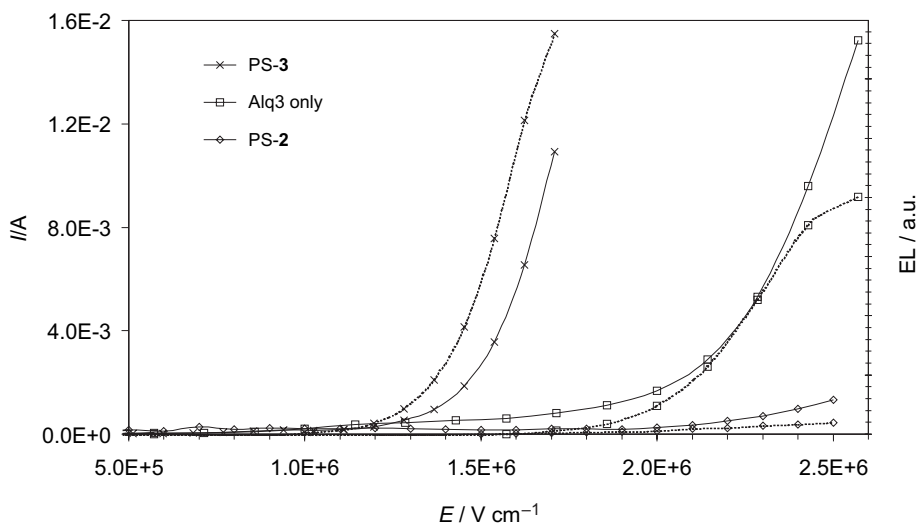


Figure 2. Current (solid line) and EL (dashed line) vs. electric field of an ITO/PS-2/Alq<sub>3</sub>/Al and an ITO/PS-3/Alq<sub>3</sub>/Al device in comparison with a single layer Alq<sub>3</sub> LED.

Figure 3 shows the power efficiency *versus* the applied electric field of the single layer device and the double layer LEDs using PS-2 and PS-3 as HTL. Since the PS-3/Alq<sub>3</sub> device requires considerably less current for equal or even higher EL compared to the Alq<sub>3</sub> single layer LED, the efficiency has been considerably improved. For example, the power efficiency for the maximum achievable brightness has been increased from 0.15 lm W<sup>-1</sup> (Alq<sub>3</sub> single layer LED) to 0.33 lm W<sup>-1</sup> (PS-3/Alq<sub>3</sub> double layer LED).

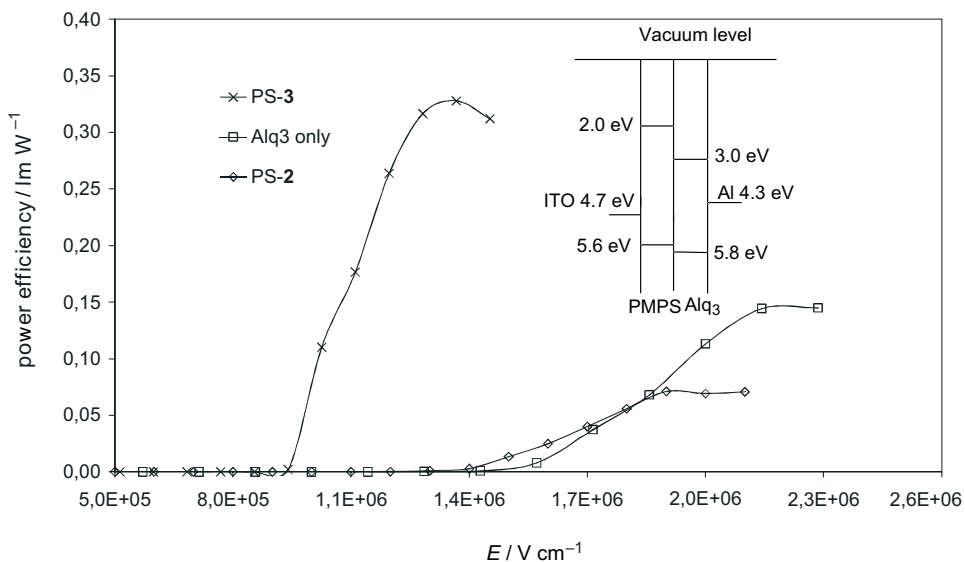


Figure 3. Power efficiency *vs.* electric field of an ITO/PS-2/Alq<sub>3</sub>/Al and an ITO/PS-3/Alq<sub>3</sub>/Al device in comparison with a single layer Alq<sub>3</sub> LED.

The feature of the EL spectra and thereby the average emission wavelength of the emission is the same for the single and all the double layer devices (Figure 4). Therefore, we conclude that negligible light originates from the polysilanes, but mainly from Alq<sub>3</sub>.

Obviously, PS-2 and PS-3 effect the device performance in a different manner. While the achievable brightness and efficiency increases for the PS-3/Alq<sub>3</sub> LED compared to the single layer device, the introduction of PS-2 as the HTL has a negative effect on the device performance, *i.e.*, lower efficiency and faster device degradation compared to the single layer LED. In a very similar way, PS-1 and PS-4 do not improve the device performances.

Differences between the several devices appear distinct in double logarithmic *I-E* characteristics (Figure 5). Characteristics of the devices using

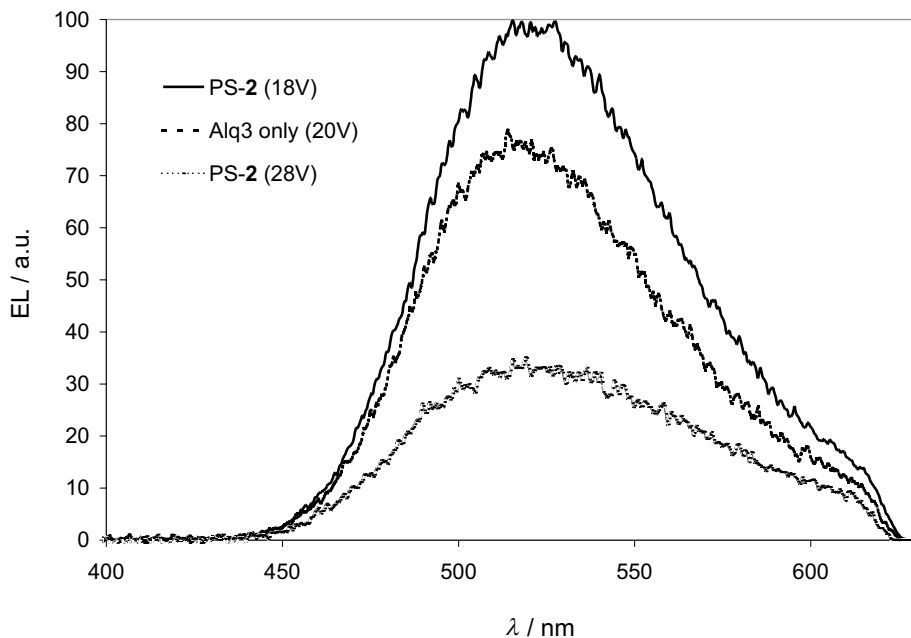


Figure 4. EL spectra of an  $\text{Alq}_3$  single layer device in comparison with the double layer LEDs using PS-2 and PS-3, respectively, as the HTL.

PS-1, PS-2 or PS-4, as the HTL are qualitatively comparable: the double logarithmic plot of the devices containing these HTLs can be divided into four regimes with respect to different power laws ( $I \propto E^{m+1}$ ), whereas the single layer LED and the LED using PS-3 as the HTL do not show regions II and III.

I) In the case of the double layer devices using PS-1, PS-2 or PS-3 as the HTL at low voltages, there is a space-charge-limited current (SCLC) regime,  $I \propto E^2$ , as it is usually observed in the case of charge transport in organic materials, because the injection of a small amount of charge carriers at low voltages gives rise to an internal space charge distribution due to the low mobility of the charge carriers.

II) At a certain voltage, the traps are filled up completely and a steep increase of the current ( $m \approx 13$ ) can be noticed due to the higher charge carrier mobility. In some devices, we observed a partial or complete destruction of the device due to the sudden increase of the current.

III) In the third region, the current is quite constant ( $\approx 0.1$  mA) and independent of the voltage. We are not aware of any similar device behaviour published and we suggest that this is mainly due to instabilities in the poly-

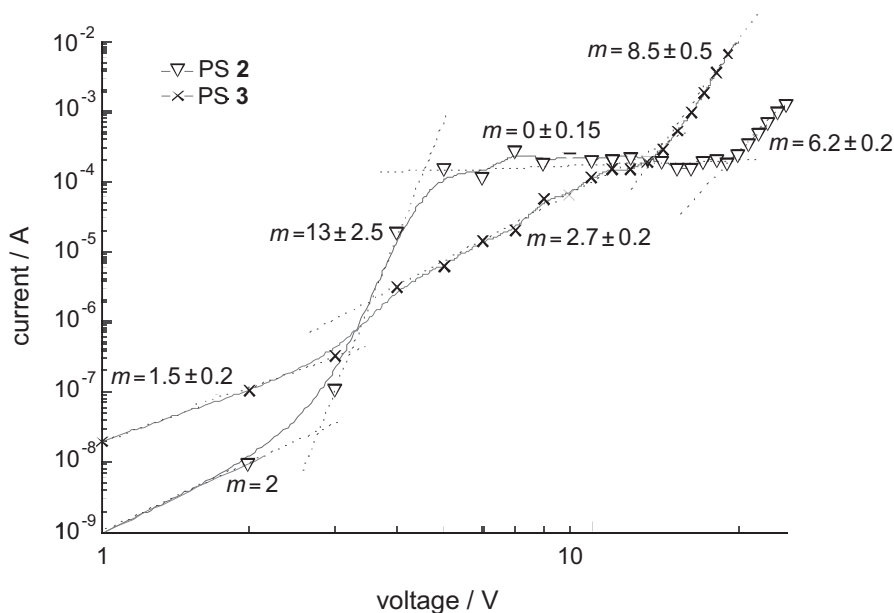


Figure 5. Current-voltage characteristics of an ITO/PS-3/Alq<sub>3</sub>/Al and an ITO/PS-2/Alq<sub>3</sub>/Al device. Added  $m$ -values mark different regimes with the corresponding power laws,  $I \propto V^{m+1}$ .

silane layers, PS-1, PS-2 or PS-4. DSC/TGA measurements of the pure polysilanes show that PS-1, PS-2 and PS-4 become unstable at temperatures above 150 °C, whereas amino-substituted polysilanes, such as PS-3, are notably more stable, *i.e.*, up to 300 °C.

IV) Finally, the turn on EL voltage gives rise to a further steep current increase due to the significant injection of the negative charge carriers into the conducting band (*i.e.*, the lowest unoccupied molecular orbital [LUMO]).

The double logarithmic  $I/E$ -characteristic of the ITO/PS-3/Alq<sub>3</sub>/Al LED differs from the former by the absence of the second and third regime, which is replaced by a gradual current increase between the SCLC regime and the onset field of the EL. When interpreting the improved device performance of the ITO/PS-3/Alq<sub>3</sub>/Al LED compared to the single layer device, one has to consider the positions of the highest occupied molecular orbital (HOMO) and LUMO levels of the organic materials as well as the workfunctions of the electrodes (ITO:  $\sim 4.8$  eV, Al: 4.3 eV) in the device (see inset Figure 3). The levels of polymethylphenylsilane were determined by cyclic voltametry measurements and are around 2.0 eV (LUMO) and 5.6 eV (HOMO), which is close to the Alq<sub>3</sub>-HOMO level of about 5.8 eV (lowest unoccupied molecular [LUMO] level  $\approx 3.0$  eV).<sup>21</sup>

Applying a low bias voltage, the current is dominated by positive polarons, which are injected from the ITO into the PS-**3**. This is due to the fact that the barrier height at the ITO/PS-**3** interface ( $\approx 0.8$  eV) is lower than that at the Alq<sub>3</sub>/Al interface ( $\approx 1.3$  eV). Positive polarons traverse the PS-**3** layer and build up a positive sheet charge at the PS-**3**/Alq<sub>3</sub> interface and a space charge in the Alq<sub>3</sub> bulk. Thereby, the local electric field at the Alq<sub>3</sub>/Al interface is increased, which facilitates a higher electron injection, whereas the electric field at the anode decreases, so that the charge carrier injection becomes better balanced.

Electroluminescence occurs as soon as the voltage is high enough for a significant injection of negative polarons. Because of the high LUMO level offset at the PS-**3**/Alq<sub>3</sub> interface ( $\approx 1.0$  eV), negative polarons are blocked before reaching the anode. This leads to less ohmic losses, stabilized performance and increased efficiency, due to higher probability of singlet exciton formation from positive and negative polarons. Additionally, excitons are generated at the internal interface and they recombine radiatively away from the electrodes, where several quenching mechanisms can lead to non-radiative losses.

## CONCLUSION

We have investigated the performances of organic double layer devices using different polysilanes, generated by transition metal catalyzed dehydrocoupling reactions, as the HTL together with Alq<sub>3</sub> as the emitting layer. The results prove that side-chain substituents are crucial for the ability to use polysilanes as HTLs in LEDs. Insertion of polyaminophenylsilane (PS-**3**), as the HTL, leads to stabilized device performance and increases the power efficiency by more than 100% compared to the single layer LED.

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**SAŽETAK****Elektroluminescencija dvoslojne svijetleće diode sastavljene od dehidrovezanih polisilana, koji služe za transport šupljina**

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Prikazani su rezultati ispitivanja diode, koja emitira svjetlost (LED), a sastoji se od organskog dvosloja. Pri tome su korištena četiri polisilana kao materijali, koji transportiraju šupljine. 8-Hidroksikinolin aluminijev kompleks ( $Alq_3$ ) upotrijebljen je kao elektroluminescentni spoj. Pokazano je da performacije diode ovise o pobočnim lancima i supstituentima na njima. Amino-supstituirani polisilani pokazali su se izuzetno efikasima u tom pogledu.