New Synthesis, Electroluminescence, and Photophysical Properties of Poly[(formylphenyl)methylsilanediyl] and Its Derivatives

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ABSTRACT: A new one-step synthesis of formylated poly[methyl(phenyl)silanediyl] (PMPSi) is reported. The aldehyde groups were incorporated into the parent polymer by the reaction with dichloromethyl methyl ether in the presence of Lewis acid (SnCl₄). The reaction takes place via an unstable aryl(methoxy)methyl chloride intermediate. The new procedure is an important simplification of the known four-step synthesis of the poly[(formylphenyl)methylsilanediyl] via chloromethylation in the first step. The presence and reactivity of aldehyde groups in the polymer were proved by means of ¹H NMR, UV-vis, and FT IR spectroscopies. The reduction in relative molecular weight of the parent polysilane after reaction was not so pronounced as in the multistep synthesis. Model compounds N-benzylidene-1-aminopyrene, N-benzylidene-4-phenylaniline, and N-benzylidene-4-phenylazoaniline were synthesized for spectral characterization of the substituted polysilanes. The π -conjugated systems (pyrene, biphenyl, azobenzene) were attached to the σ -conjugated polysilane backbone. Photophysical properties, photostability, charge photogeneration, and photoluminescence of these materials were studied. Single- and double-layer lightemitting devices (LEDs) with emission in visible spectral region were fabricated. Their spectral and electrical characteristics were studied. Electroluminescence efficiency in double-layer LEDs reached the value of 0.03-0.06% and was more than 1 order of magnitude higher than that in single-layer devices (\sim 0.005%). Modified polysilanes exhibited better photostability than PMPSi and are particularly intended for the use in multilayer or blend devices.

Introduction

In the past years polysilanes have attracted considerable attention as a new class of σ -conjugated polymers.^{1,2} Although the synthesis of high-molecular-weight soluble polysilanes was reported nearly 20 years ago,³⁻⁵ the functionalization or modification of such polymers is still a subject of investigation. The problem is that not all reactive functional groups present in the dichlorosilane monomer ($\mathbb{R}^1\mathbb{R}^2$ Si $\mathbb{C}I_2$; \mathbb{R}^1 , \mathbb{R}^2 = alkyl or aryl) before polymerization can withstand drastic conditions of the Wurtz coupling reaction. Although the toluene-sodium dispersion reflux conditions are often replaced by reductive coupling at lower temperatures (using crown ethers⁶ or graphite-potassium⁷ as a phase-transfer or heterogeneous catalyst, respectively), the main problem still remains. Hence, the direct syntheses of functionalized polysilanes have been restricted to dichlorosilane monomers with functional groups, which are resistant to the reaction conditions (aryloxy,^{1,8} dimethylamino,^{8,9} and trimethylsilyl¹⁰ groups). The trimethylsilyl group has been used to protect the hydroxy group in dichloro[1-(4-hydroxy-3-methoxyphenyl)propyl]phenylsilane prior to polymerization.¹¹ Chemical modification of the polymer affords another possibility of introducing a reactive functional group into parent polysilanes. However, the choice of suitable reactions is limited because of a low oxidation potential of the σ -conjugated silicon backbone.¹ Chlorine- or bromine-containing polymers were prepared by addition of HCl or HBr in the presence of Lewis acid to silane copolymers carrying 2-(cyclohex-3-en-1yl)ethyl substituents.¹² A very useful chemical modification of aryl-containing polysilanes is the Friedel-Crafts chloromethylation¹³ using chloromethyl methyl ether and stannic chloride as a catalyst. The reaction was recently studied in more detail¹⁴ with poly[methyl(phenyl)silanediyl] (PMPSi) and chloromethyl methyl ether generated in situ from dimethoxymethane and thionyl chloride. The chloromethyl group can undergo a host of reactions. The transformation of chloromethyl into aldehyde groups enabled preparation of polysilanes¹⁵ bearing directly attached π -conjugated chromophores, which can be useful in many applications. Four reaction steps, however, were necessary to accomplish the synthesis of poly[(formylphenyl)methyl-silanediyl] from the parent PMPSi.

Our previous studies of charge transport and photogeneration in substituted PMPSi showed that these processes were strongly influenced by the nature of substituents. We have shown¹⁶ that aromatic ring substitution with an electron-withdrawing group increased the quantum efficiency of charge photogeneration by a factor higher than 1 order of magnitude. The substitution of PMPSi also influenced the hole mobility, which depends on electron affinities and dipole moments of the attached chromophores. In contrast to the charge photogeneration and charge transport data, there is no information concerning electroluminescence in such PMPSi derivatives. PMPSi was used as a hole-transporting layer in multilayer LEDs.^{17,18} PMPSi,^{19,20} dialkyl,^{21–24} diaryl,^{23,25–27} silole-incorporated,²⁸ and oxygen-cross-linked²⁹ polysilanes, and PMPSi copolymers containing thiophene^{30,31} or anthracene³² units in the polymer backbone were reported as emitting layers in polymer LEDs. Recently,³³ we have shown an improved performance of polymer LEDs based on blends composed of poly[2,5-bis(isopentyloxy)-1,4-phenylene] (SPPP) and PMPSi compared to the single-component LEDs made of SPPP.

In this paper we developed a one-step synthesis of formylated PMPSi, which was further used as a functionalized polymeric precursor for the attachment of



Figure 1. Structures of the polymers under study.

 π -conjugated systems (Figure 1). Single-layer and doublelayer light-emitting devices (LEDs) were fabricated, and their electric and optical characteristics were measured and discussed.

Experimental Section

Materials. Sodium (~30% dispersion of Na in toluene), dichloro(methyl)phenylsilane, 1-aminopyrene, 4-aminoazobenzene, 4-aminobiphenyl, 4-methylbenzene-1-sulfonic acid, benzaldehyde, 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), and dichloromethyl methyl ether were the commercial products (Fluka, Aldrich) and were used as received. Toluene p.a. (Lachema Brno, Czech Republic) was dried by 24 h refluxing over sodium metal and distilled.

Syntheses of Model Compounds. N-Benzylidene-1-aminopyrene (NB-Pyr). 1.30 g (0.006 mol) of 1-aminopyrene, 5.31 g (0.05 mol) of benzaldehyde, and 0.05 g of 4-methylbenzene-1sulfonic acid (catalyst) were dissolved in 80 mL of toluene. The mixture was refluxed 5 h using a Dean–Stark adapter for water removing. After cooling the toluene was evaporated and methanol (50 mL) was added. The yellow crystals were filtered off, recrystallized from ethanol, and dried. Yield 1.35 g (74%); mp 99–100 °C. Anal. Calcd for C₂₃H₁₅N (305.39): C, 90.46; H, 4.95; N, 4.59%. Found: C, 90.41; H, 5.11; N, 4.56%. ¹H NMR (THF- d_8): 7.47 (t, 5H, C₆H₅), 7.75–8.16 (m, 8H, C₁₆H₉), 8.65 (d, 1H, C₁₆H₉), 8.76 (s, 1H, N=CH) ppm (Figure 2). UV-vis (THF): $\lambda_{\text{max}} = 382 \text{ nm}, \epsilon = 24 300 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Figure 3). FT-IR (film on KBr): 3040 (aromatic C-H); 1620 (C=N); 1582, 1453 (pyrene ring stretching); 1180 (aryl-N, stretching); 1100 (aromatic C-H, bending); 970 (azomethine C-H, in-plane); 840 (pyrene ring deformation); 757, 719, and 688 cm⁻¹ (aromatic C-H, out-of-plane).

N-Benzylidene-4-phenylazoaniline (NB-Azo) was prepared by the same procedure as NB-Pyr above, using 4-aminoazobenzene (3.0 g, 0.015 mol), benzaldehyde (10.62 g, 0.1 mol), and 4-methylbenzene-1-sulfonic acid (0.1 g) as a reaction mixture. Yield 3.47 g (80%); mp 130 °C (lit.³⁴ 130–131 °C). Anal. Calcd for C₁₉H₁₅N₃ (285.34): C, 79.98; H, 5.30; N, 14.73%. Found: C, 79.95; H, 5.38; N, 14.69%. ¹H NMR (THF-*d*₈): 7.29–7.45 (m, 8H, i.e., 5H of C₆H₅ and 3H of C₆H₅–N), 7.83–7.93 (m, 6H, i.e., 2H of C₆H₅–N and 4H of N–C₆H₄–N), 8.54 ppm (s, 1H, N=CH) (Figure 2). UV–vis (THF): $\lambda_{max} = 360$ nm, $\epsilon = 29 200$ L mol⁻¹ cm⁻¹ (Figure 3). FT IR (film on KBr): 3055, 3025 (aromatic C–H); 1621 (C=N); 11445 (N=N); 1187 (aryl–N, stretching); 967 (azomethine C–H, in-plane); 875 (azomethine C–H, out-of-plane).

N-Benzylidene-4-phenylaniline (NB–BiPh) was prepared by the same procedure as NB-Pyr above, using 4-aminobiphenyl (3.05 g, 0.018 mol), benzaldehyde (10.62 g, 0.1 mol), and 4-methylbenzene-1-sulfonic acid (0.1 g) as a reaction mixture. Yield 3.01 g (65%); mp 148 °C (lit.³⁵ 147 °C, lit.³⁶ 148–149 °C). Anal. Calcd for C₁₉H₁₅N (257.34): C, 88.68; H, 5.88; N, 5.44%. Found: C, 88.59; H, 6.03; N, 5.43%. ¹H NMR (THF-*d*₈): 7.21– 7.40 (m, 8H, i.e., 5H of C₆H₅ and 3H of C₆H₅–Ph), 7.55–7.60 (m, 4H, i.e., 2H of C₆H₅–Ph and 2H of Ph–C₆H₄–N), 7.84– 7.90 (m, 2H, Ph–C₆H₄–N), 8.51 ppm (s, 1H, N=CH). UV–vis (THF): $\lambda_{max} = 331$ nm, $\epsilon = 16$ 700 L mol⁻¹ cm⁻¹ (Figure 3). FT IR (film on KBr): 3055, 3030 (aromatic C–H); 1624 (C=N); 1169 (aryl–N, stretching); 970 (azomethine C–H, in-plane); 880 (azomethine C–H, out-of-plane); 838, 760, 721, and 689 cm⁻¹ (aromatic C–H, out-of-plane).

Syntheses of Polymers. Poly[methyl(phenyl)silanediyl]. PMPSi-1. The polymer was prepared by Wurtz coupling polymerization of dichloromethyl(phenyl)silane. A sulfonation flask (1500 mL) with reflux condenser, pressure equalizing addition funnel, and a motor-driven glass stirrer was charged under argon with sodium dispersion (33 g, 1.43 mol of Na) in toluene (400 mL) excluding light from the reaction mixture. The stirred sodium dispersion was heated to a gentle reflux and a solution of dichloromethyl(phenyl)silane (120 g, 0.63 mol) in toluene (100 mL) was added quickly enough to maintain the reflux. The reaction mixture was refluxed for 3 h, then cooled to room temperature, and quenched with ethanol (150 mL) and water (700 mL). The toluene layer was separated and washed with water (2 \times 750 mL), and the solvent was evaporated. The greasy residue was dissolved in tetrahydrofuran (THF, 250 mL) and the addition of a propan-2-olmethanol mixture (2 L, 1:1 by vol) precipitated the PMPSi as a white powder; yield 51.9 g (68%). The oligomers were further removed by extraction with boiling diethyl ether; yield 29.6 g (39%). The purified polymer possessed a largely unimodal but very broad molar mass distribution ($M_w = 39900$, $M_n = 8600$). ¹H NMR (CDCl₃): -1.1 to 0.2 (broad peak, 3H, CH₃), 6.1-7.3 (broad peak, 5H, C₆H₅) ppm. UV–vis (THF): $\lambda_{max} = 338$ nm, $\epsilon = 8200$ L mol⁻¹ cm⁻¹ (characteristic $\sigma \rightarrow \sigma^*$ transition for the silicon backbone of PMPSi). FT-IR (film on KBr): 3070, 3050, and 3020 (aromatic C-H); 2960 and 2895 (aliphatic C-H); 1950, 1890, and 1815 (aromatic); 1485 (skeletal ring breathing); 1430 and 1100 (Si-Ph); 1250 (Si-Me); 730 (aromatic C-H, out-of-plane); 696 (Si-C); 462 cm⁻¹ (Si-Si).

PMPSi-2. Poly[methyl(phenyl)silanediyl] was also prepared using sodium dispersion in toluene at 65 °C and 18-crown-6 as a phase-transfer catalyst. Addition of the crown ether to the heterogeneous Wurtz reaction promotes the synthesis of a high-molecular-weight polymer.⁶ Sodium dispersion (3.9 g, 0.17 mol of Na) and 18-crown-6 (0.012 g, 4.54×10^{-5} mol) were stirred under argon in dry toluene (75 mL) at 65 °C. Dichloromethyl(phenyl)silane (14.09 g, 0.074 mol) in dry toluene (75 mL) was added dropwise (30 min), and the reaction mixture was heated at 65 °C for 3 h with strong mixing. After cooling, the reaction was quenched with methanol (50 mL), and toluene (100 mL) and water (100 mL) were added. The toluene layer was washed with water (3 \times 150 mL) and dried over anhydrous magnesium sulfate (2 h). The solvent was evaporated; the residue was dissolved in THF (150 mL) and precipitated into propan-2-ol (900 mL); yield 2.82 g (32%). The polymer showed a bimodal molar mass distribution. The low-molecularweight fraction was removed by stirring (2 h) with hexane (50 mL). The high-molecular-weight fraction was filtered and reprecipitated from THF into propan-2-ol; yield 1.09 g (12%). $M_{\rm w} = 321\,000, M_{\rm n} = 205\,000.$ ¹H NMR and FT IR spectra confirmed the structure of PMPSi (see above). UV-vis (THF): $\lambda_{max} = 338 \text{ nm}, \epsilon = 9200 \text{ L mol}^{-1} \text{ cm}^{-1}$.

Poly[(formylphenyl)methylsilanediyl]. PMPSi-CHO-(12 mol %). Under argon and with exclusion of light, PMPSi-1 (4.81 g, 0.04 mol) was dissolved in dichloromethane (100 mL) and cooled to 0 °C. SnCl₄ (20.84 g, 0.08 mol) and dichloromethyl methyl ether (9.20 g, 0.08 mol) were added, and the mixture was stirred at 0 $^\circ C$ for 2 h and then poured onto crushed ice (\sim 150 g). The organic layer was separated and washed with water $(2 \times 100 \text{ mL})$. The solvent was evaporated; the residue was dissolved in THF (80 mL) and precipitated into methanol (700 mL). The white polymer was filtered off and dried; yield 2.90 g. $M_{\rm w} = 21\,000$, $M_{\rm n} = 7500$. ¹H NMR (CDCl₃): -1.1 to 0.6 (broad peak, 3H, CH₃), 6.1-7.6 (broad peak, 5H, C₆H₅), 9.5-9.9 ppm (peak, 1H, CHO) (Figure 4). From ¹H NMR spectrum the content of aldehyde groups in PMPSi-CHO was determined as 12 mol %. UV-vis (THF): $\lambda_{\text{max}} = 330 \text{ nm}, \epsilon = 6500 \text{ L mol}^{-1} \text{ cm}^{-1}$. FT IR (film on KBr): vibration bands of PMPSi and 2926 (aldehyde C-H), 1702 cm^{-1} (aldehyde C=O).



Figure 2. ¹H NMR spectra of model compounds (NB–Pyr, NB–Azo) and corresponding modified polymers PMPSi–Pyr(12 mol %) and PMPSi–Azo(12 mol %) in deuterated tetrahydrofuran.



Figure 3. UV-vis spectra of model compounds NB-Azo (dashed line), NB-Pyr (solid line), and NB-BiPh (dashed and dotted line) in tetrahydrofuran.

PMPSi–*CHO*(6 mol %). Under argon and with exclusion of light, PMPSi-1 (4.81 g, 0.04 mol) was dissolved in dichloromethane (100 mL) and cooled to 0 °C. SnCl₄ (15.63 g, 0.06 mol) and dichloromethyl methyl ether (6.90 g, 0.06 mol) were added, and the mixture was stirred at 0 °C for 30 min and then poured onto crushed ice (~150 g). Then the procedure was the same as above; yield 3.45 g. $M_w = 33\ 000$, $M_n = 8200$. ¹H NMR and FT IR spectra confirmed the presence of aldehyde groups, and their content was determined as 6 mol %. UV–vis (THF): $\lambda_{max} = 335\ nm$, $\epsilon = 7300\ L\ mol^{-1}\ cm^{-1}$.



Figure 4. ¹H NMR spectrum of PMPSi–CHO(12 mol %) in CDCl₃. The sharp signal at 0 ppm belongs to the internal standard (hexamethyldisiloxane). The numbers denote the integrated intensities for aldehyde (1H, CHO, 1.184) and aromatic (5H, C_6H_5 , 53.867) protons.

Various reaction conditions were studied, and the results are summarized in Table 1.

Modification of PMPSi–CHO with 1-Aminopyrene. *PMPSi–Pyr(12 mol %).* 0.71 g (0.7 mmol of –CHO groups) of PMPSi–CHO (12 mol %) was refluxed with 0.76 g (3.5 mmol) of 1-aminopyrene and 0.05 g of 4-methylbenzene-1-sulfonic acid in toluene (60 mL) for 30 min. After cooling, the reaction mixture was precipitated into methanol (500 mL). The bright yellow polymer was filtered off and dried. The raw material was three times reprecipitated from THF (30 mL) into methanol (500 mL); yield 0.65 g (76%). $M_w = 23 000$, $M_n = 8100$. ¹H NMR (THF- d_8): –1.1 to 0.6 (broad peak, 3H, CH₃), 6.1–7.6 (broad peak, 5H, C₆H₅), 7.6–8.25 (m, 9H, C₁₆H₉), 8.4–8.8 (peak, 1H, N=CH), 9.5–9.9 (traces, 1H, CHO) ppm (Figure 2). UV–vis (THF): $\lambda_{max} = 330$ nm ($\sigma \rightarrow \sigma^*$), $\epsilon_{330} = 7600$ L mol⁻¹

 Table 1. Reaction Conditions for Formylation of PMPSi-1 with Dichloromethyl Methyl Ether (Cl₂CHOCH₃) in the Presence of Lewis Acids (SnCl₄, TiCl₄) at 0 °C (Related per 1 mol of PMPSi-1)

						UV-vis content (mol %)	
expt no.	SnCl ₄ (mol)	TiCl ₄ (mol)	Cl ₂ CHOCH ₃ (mol)	time (min)	¹ H NMR CHO content (mol %)	UV-vis cor PMPSi-Pyr (382 nm) <0.5 6 12 10 11 b b 1 1	PMPSi-Azo (360 nm)
1	0.5		0.5	10	0	< 0.5	<0.5
2	1.5		1.5	30	6	6	5
3	2.0		2.0	120	12	12	11
4 ^a	2.0		2.0	270	10	10	9
5	2.0		2.0	480	10	11	10
6		1.7	0.8	30	b	b	b
7		0.9	0.4	30	b	b	b
8		0.5	1.5	20	1	1	1

^a At 20 °C. ^b The aldehyde content was not determined because oily oligomeric products were formed.



Figure 5. UV-vis spectra of PMPSi-1 (solid line) and polymers modified with pyrene structural units, PMPSi-Pyr-(6 mol %) (dashed and dotted line) and PMPSi-Pyr(12 mol %) (dashed double dotted line), and polymers modified with azobenzene structural units, PMPSi-Azo(6 mol %) (dotted line) and PMPSi-Azo(12 mol %) (dashed line), in tetrahydrofuran.

cm⁻¹; $\lambda_{max} = 384$ nm ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$), $\epsilon_{384} = 3020$ L mol⁻¹ cm⁻¹ (Figure 5). FT IR (film on KBr): vibration bands of PMPSi and 1620 (C=N), 1589 (pyrene ring stretching), 1183 (aryl–N, stretching), 841 (pyrene ring deformation), 756 cm⁻¹ (aromatic C–H, out-of-plane).

PMPSi−Pyr(6 mol %). The same procedure as above but with 0.71 g (0.35 mmol of −CHO groups) of PMPSi−CHO (6 mol %) and 0.39 g (1.8 mmol) of 1-aminopyrene as starting materials; yield 0.58 g (74%). $M_{\rm w} = 30~000$, $M_{\rm n} = 8100$. UV-vis (THF): $\lambda_{\rm max} = 335~{\rm nm}~(\sigma \to \sigma^*)$, $\epsilon_{335} = 7800$ L mol⁻¹ cm⁻¹; $\lambda_{\rm max} = 384~{\rm nm}~(\pi \to \pi^*,~{\rm n} \to \pi^*)$, $\epsilon_{384} = 1490$ L mol⁻¹ cm⁻¹ (Figure 5). ¹H NMR and FT IR data are identical with those for PMPSi−Pyr(12 mol %), but the peaks responsible for pyrene substitution are reduced in their intensity approximately to one-half.

Modification of PMPSi–CHO with 4-Aminoazobenzene. *PMPSi–Azo(12 mol %).* 0.92 g (0.9 mmol of –CHO groups) of PMPSi–CHO(12 mol %) was refluxed with 3.0 g (15.2 mmol) of 4-aminoazobenzene and 0.1 g of 4-methylbenzene-1-sulfonic acid in toluene (120 mL) for 30 min. After cooling, the reaction mixture was precipitated into methanol (800 mL). The yellow polymer was filtered off and dried. The raw material was three times reprecipitated from THF (50 mL) into methanol (700 mL); yield 0.71 g (66%). $M_w = 22500$, M_n = 7800. ¹H NMR (THF- d_8): –1.0 to 0.5 (broad peak, 3H, CH₃), 6.1–7.2 (broad peak, 5H, C₆H₅–Si), 7.2–7.35 (peak, 4H, C−C₆H₄−Si), 7.35−7.5 (peak, 3H, C₆H₅−N), 7.75−8.0 (peak, 2H of C₆H₅−N and 4H of N−C₆H₄−N), 8.2−8.5 (peak, 1H, N=CH), 9.5−9.9 (traces, 1H, CHO) ppm (Figure 2). UV−vis (THF): $\lambda_{max} = 335 \text{ nm} (\sigma \rightarrow \sigma^*)$, $\epsilon_{335} = 7800 \text{ L mol}^{-1} \text{ cm}^{-1}$; $\lambda = 360 \text{ nm}$ (shoulder, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$), $\epsilon_{360} \sim 3000 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Figure 5). FT IR (film on KBr): vibration bands of PMPSi and 1620 (C=N), 1444 (N=N), 1182 (aryl−N, stretching), 756 cm⁻¹ (aromatic C−H, out-of-plane).

PMPSi-Azo(6 mol %). The same procedure as above but with 0.92 g (0.45 mmol of -CHO groups) of PMPSi-CHO(6 mol %), 1.50 g (7.6 mmol) of 4-aminoazobenzene, and 0.1 g of 4-methylbenzene-1-sulfonic acid as starting materials; yield 0.58 g (59%). $M_{\rm w} = 34~000, M_{\rm n} = 8500.$ UV-vis (THF): $\lambda_{\rm max} = 335$ nm ($\sigma \rightarrow \sigma^*$), $\epsilon_{335} = 7800$ L mol⁻¹ cm⁻¹; $\lambda = 360$ nm (shoulder, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$), $\epsilon_{360} \sim 1500$ L mol⁻¹ cm⁻¹ (Figure 5). ¹H NMR and FT IR data are identical with those for PMPSi-Azo(12 mol %), but the peaks responsible for azobenzene substitution are reduced in their intensity approximately to one-half.

Modification of PMPSi-CHO with 4-Aminobiphenyl. PMPSi-BiPh(3 mol %). 0.71 g (0.7 mmol of -CHO groups) of PMPSi-CHO (12 mol %) was refluxed with 1.20 g (7 mmol) of 4-aminobiphenyl and 0.1 g of 4-methylbenzene-1-sulfonic acid in toluene (100 mL) for 30 min. After cooling, the reaction mixture was precipitated into methanol (700 mL). The white polymer was filtered off and dried. The raw material was three times reprecipitated from THF (50 mL) into methanol (700 mL); yield 0.41 g (51%). $M_{\rm w} = 20\ 000,\ M_{\rm n} = 7900.\ ^1{\rm H}\ {\rm NMR}$ (THF-d₈): -1.1 to 0.4 (broad peak, 3H, CH₃), 6.1-7.25 (broad peak, 5H of C₆H₅-Si and 3H of C₆H₅-Ph), 7.25-7.5 (peak, 2H of C₆H₅-Ph and 2H of Ph-C₆H₄-N), 7.55-7.75 (peak, 2H, Ph-C₆H₄-N), 8.2-8.4 (broad peak, 1H, N=CH), 9.5-9.9 ppm (broad peak, 1H, CHO). The ratio of the integrated intensities of aldehyde (CHO) and azomethine (N=CH) hydrogens was found to be 3:1. It means that a quarter of aldehyde groups of PMPSi-CHO(12 mmol %) was reacted with 4-aminobiphenyl to give PMPSi–BiPh(3 mol %). UV–vis (THF): $\lambda_{max} = 335$ nm $(\sigma \rightarrow \sigma^*)$, $\epsilon_{335} = 8100$ L mol⁻¹ cm⁻¹; should r at $\lambda = 360-400$ nm. FT IR (film on KBr): vibration bands of PMPSi and 1699 (aldehyde C=O), 1620 (C=N), 1170 (aryl-N, stretching), 756 cm^{-1} (aromatic C–H, out-of-plane).

Polymer Characterization. Molecular weights of the polymers were determined using GPC/SEC chromatograph (Laboratory Instruments, CZ) equipped with RI and UV 254 nm detectors, column 8 \times 600 mm (PSS 10 000, PSS, Germany) and data collection and treatment (Data Monitor, Watrex, CZ). Polystyrene standards (PL Laboratories, UK) were used for calibration. The samples were measured in THF, which was dried over molecular sieve 4A and distilled.

UV–vis spectra were taken on a Perkin-Elmer Lambda 20 spectrometer. Both solutions and films on fused silica substrates were measured. The contents of azobenzene or pyrene structural units in polysilanes (Table 1) were determined by spectrometry in THF using molar absorption coefficients of model compounds NB–Azo ($\epsilon_{360} = 29\ 200\ L\ mol^{-1}\ cm^{-1}$) or NB–Pyr ($\epsilon_{382} = 24\ 300\ L\ mol^{-1}\ cm^{-1}$).

 1 H NMR spectra were taken on a Bruker ACF-300 spectrometer at 300.1 MHz in CDCl₃ or deuterated THF using

hexamethyldisiloxane as an internal standard. The content of aldehyde groups in PMPSi–CHO was determined from the integrated intensity of the CHO signal at 9.5-9.9 ppm (1H) by comparison with a broad signal of aromatic protons at 6.1-7.6 ppm (5H).

FT IR spectra were measured using a Perkin-Elmer Paragon 1000 PC Fourier transform infrared spectrometer in KBr pellets or as a film on KBr pellet.

Sample Preparation. Thin polymer films were prepared by spin-coating from toluene solutions. All solutions were filtered with 0.45 μ m Millex-FH₁₃ Millipore syringe filters prior the spin-coating. Thin films for optical studies were spin-coated onto fused silica substrates. All films exhibited a good optical quality. Polymer LEDs with a hole-injecting indium tin oxide (ITO) electrode and an electron-injecting aluminum electrode were fabricated. Two types of the devices were prepared: the polymer layers were spin-coated (1) onto ITO-covered glass substrates and (2) onto ITO substrates covered with thin layer of poly[3,4-(ethylenedioxy)thiophene]/poly(styrenesulfonate) (PEDT:PSS). The ITO glass substrates were purchased from Merk (Germany) and PEDT:PSS Baytron-P from Bayer AG (Germany). The 50 nm thick PEDT:PSS layers were prepared by spin-coating and dried in a vacuum at 396 K for 3 h prior the polymer film deposition. Finally, 60-80 nm thick top aluminum (Al) electrodes were vacuum-evaporated on the top of polymer films to form LED devices. Typical active areas of the LEDs were 4 or 8 mm². Samples for charge photogeneration measurements (film thicknesses from 700 to 1300 nm) were prepared by spin-coating of the polymer solution in toluene onto stainless steel substrates. All polymer films were dried in a vacuum (10⁻³ Pa) at 323 K for 6 h. Layer thicknesses were measured using a KLA-Tencor P-10 profilometer. All thin-film preparation and the LED fabrication were done under ambient laboratory conditions.

Cyclovoltammetric Measurements. Cyclic voltammetry (CV) was measured using a PA4 polarographic analyzer (Laboratory Instruments, CZ) with a tree-electrode cell in dichloromethane containing *tert*-butylammonium perchlorate (0.1 mol L⁻¹) as an electrolyte. Platinum strip electrodes were used as the working and counter electrodes, and Ag/AgCl electrode was used as the reference electrode. Polymer concentration in the measured solution was 10^{-3} mol L⁻¹. Typical scan rates were 20-100 mV s⁻¹.

Electroluminescence and Photoluminescence Measurements. Electroluminescence (EL) and photoluminescence (PL) spectra were measured using a homemade spectrofluorometer with single photon-counting detection (SPEX, RCA C31034 photomultiplier). LEDs were supplied from a Keithley 237 source measure unit, which served for the simultaneous recording of the current flowing trough the sample. PL spectra were taken perpendicular to the sample surface, and the angle of incidence for the excitation beam was 30° relative to the sample surface normal to minimize reabsorption. A 300 W xenon lamp (Oriel) was used as the excitation source. The measured EL and PL emission spectra were corrected for the spectral response of the detection system. Current-voltage and luminance-voltage characteristics were recorded simultaneously using the Keithley 237 source measure unit and a silicon photodiode with integrated amplifier (EG&G HUV-4000B) for the detection of total light output. A voltage signal from the photodiode was recorded with Hewlett-Packard 34401A multimeter. The LED characteristics were measured in a vacuum chamber to prevent any electrode degradation. Photostability was followed by UV-vis spectroscopy. PL and absorption measurements were performed under ambient laboratory conditions.

The EL quantum efficiencies were evaluated from the measurements of EL spectra and the total light output. The external EL efficiency is expressed by the relation $\eta_{\text{ext}} = n_{\text{ph}}/n_{\text{el}}$, where n_{ph} and n_{el} are the total number of photons emitted from LED and the total number of electrons injected into the polymer per second, respectively. n_{el} was evaluated from the current *I* passing trough LED as $n_{\text{el}} = I/e$, where $e = 1.6 \times 10^{-19}$ C. The total light output was measured with calibrated silicon photodiode with built-in amplifier. n_{ph} was determined

from the photocurrent $I_{\rm ph}$ caused by the emitted photons using the relation

$$n_{\rm ph} = \frac{I_{\rm ph}}{\int n(\lambda) \frac{hc}{\lambda} S(\lambda) \, \mathrm{d}\lambda} \tag{1}$$

where λ is the wavelength of the emitted photons, $n(\lambda)$ the fraction of photons with wavelength λ , hc/λ the photon energy, and $S(\lambda)$ the sensitivity of the photodiode (A W⁻¹). $I_{\rm ph}$ was evaluated from the measured voltage signal U using $I_{\rm ph} = U/G$, where G (V A⁻¹) is the gain of the built-in amplifier. $n(\lambda)$ was calculated from the EL spectrum. For the estimation of the internal EL quantum efficiency, $\eta_{\rm EL}$, the external EL efficiency was multiplied by the factor $2n^2$, where n is the refractive index of the polymer.³⁷ The value n = 1.67 was used in our evaluation of the $\eta_{\rm EL}$.

Charge Photogeneration Measurements. The measurements of the photogeneration efficiencies were carried out using the technique of emission-limited photoinduced discharge.³⁸ A sample was charged to the initial surface potential $U_0 = Q_0/C(Q_0)$ is the surface charge density and *C* is the sample capacitance per unit area) by a corona and then discharged upon irradiation. The photoinduced discharge quantum efficiency η' was calculated from the formula

$$\eta' = -(1/e\Phi)(dQ/dt)_0 = -(1/e\Phi)C(dU/dt)_0$$
(2)

where Φ is the absorbed photon flux density, $(dQ/dt)_0$ the rate of change of the surface charge density, and $(dU/dt)_0$ the initial photoinduced discharge slope. Under emission-limited conditions, the η' is independent both of the sample thickness and of the light intensity and is equal to the photogeneration efficiency $\eta_{\rm ph}$. The surface potentials were measured with a homemade rotary electrodynamic condenser electrometer. The measurements were performed with irradiation incident upon the positively charged surface, using a 300 W xenon lamp (Oriel) with a band filter maximum at 358 nm (a bandwidth of 65 nm). To ensure emission-limited conditions, the discharge was measured with photon fluxes as low as possible (10¹⁷photons $m^{-2} s^{-1}$). Light-induced discharge rates were 1018 corrected for the dark discharge rate. The sample capacitances C were determined from capacitance measurements at the frequency 1 kHz.

Results and Discussion

Syntheses and Modification of PMPSi-CHO. The modification of PMPSi by the attachment of π -conjugated chromophores (Figure 1) drove the effort to simplify the known four-step synthesis of poly[(formylphenyl)methylsilanediyl].¹⁵ The previous authors used the Kroehnke method for the synthesis of chemically sensitive aldehydes, where the pyridinium salt of the chloromethylated arene was reacted with a nitroso compound yielding the corresponding nitrone, which could be hydrolyzed to the aldehyde. The attempts to convert chloromethylated PMPSi directly to the aldehyde using either high-temperature oxidation with dimethyl sulfoxide³⁹ or the Sommelet reaction¹⁰ were not successful. Vilsmeier-Haack, Gattermann-Koch, and Gattermann reactions are relatively simple and the most frequently used procedures for formylation of aromatic hydrocarbons. Unfortunately, the catalysts (AlCl₃, ZnCl₂, POCl₃) employed are too aggressive to preserve the silicon backbone; the less aggressive TiCl₄, SnCl₄, and SbCl₄ were found to be inefficient.⁴⁰

On the other hand, in the synthesis of aromatic aldehydes using dichloromethyl alkyl ethers, the catalysts $AlCl_3$, $TiCl_4$, and $SnCl_4$ have been used successfully. One-step formylations of benzene, toluene, cumene, naphthalene, fluorene, pyrene, phenanthrene, thiophene,

 $Ar-H + Cl-CH-O-R \xrightarrow{-HCl} [Ar-CH-OR] \xrightarrow{H_2O} Ar-CHO + ROH + HCl$ $\downarrow \Delta$ Ar-CHO + RCl

etc., were performed⁴¹ using either dichloromethyl methyl ether or butyl dichloromethyl ether in the yields of 60–90%. The reaction takes place via an unstable aryl(alkoxy)methyl chloride intermediate. On heating, this decomposes to an aromatic aldehyde and the corresponding alkyl chloride, with water yielding an aromatic aldehyde, alcohol, and hydrochloric acid (Scheme 1; Ar = aryl, R = methyl or butyl). This synthetic method was also successfully used for formylation of polystyrene⁴² where the aldehyde functionalization of aromatic rings reached 50%.

We applied different reaction conditions for formylation of parent PMPSi-1 with dichloromethyl methyl ether in the presence of Lewis acids (Table 1). TiCl₄ was found to be too aggressive for the silicon backbone; only oily oligomeric products were isolated (Table 1, experiments 6 and 7). When the amount of $TiCl_4$ was decreased, the polymer could be isolated, but the degree of formylation was low (Table 1, experiment 8). On the other hand, the use of SnCl₄ (a weaker Lewis acid) appeared to be more convenient, and the reaction proceeded smoothly. The aldehyde protons (1H) in PMPSi-CHO were clearly detected by ¹H NMR spectroscopy at 9.75 ppm (Figure 4), and by comparison with a broad signal of aromatic protons (5H) at 6.1–7.6 ppm, the content of aldehyde groups in the polymer could be determined (Table 1). The aldehyde $\tilde{C}-H$ (2926 cm⁻¹) and C=O (1702 cm⁻¹) vibrations in addition to those of PMPSi were detected by FT IR spectroscopy. The aldehyde groups are assumed to be attached in the para positions of the benzene rings for steric reasons, similarly to chloromethylation.^{14,15} We reached the maximum degree of formylation, i.e., 12 mol % (lit.¹⁵ 14-16 mol %), for a reaction time 120 min at 0 °C (Table 1, experiment 3). The extent of formylation did not increase either with increasing temperature or reaction time (Table 1, experiments 4 and 5, respectively), in contrast to chloromethylation.¹⁴ Approximately 50% reduction in molecular weight was observed for PMPSi-CHO(12 mol %) ($M_w = 21\,000$, $M_n = 7500$) in comparison with parent PMPSi-1 ($M_w = 39\ 000,\ M_n = 8600$). The formylation reaction is probably in competition with the silicon backbone degradation (cleavage), and the process is time-dependent. Consequently, the molecular weight decrease for PMPSi-CHO(6 mol %) was found to be lower ($M_w = 33\ 000$, $M_n = 8200$). This is a very good result because in the four-step synthesis of PMPSi-CHO substantially larger molecular weight decreases (90%) were reported. In particular, it is the highmolecular-weight fraction of the initial PMPSi that seems to degrade preferentially, thereby giving rise to a formylated polymer with lower molecular weight and a narrower distribution. In general, the random degradation cleavage of a polymer with $M_w/M_n > 2$ leads to the material with polydispersity limiting to 2. In an attempt to reach a higher degree of formylation, we synthesized high-molecular-weight PMPSi-2 using a phase-transfer catalyst, 18-crown-6. Even with this material, we were not able to prepare PMPSi-CHO containing more than 12 mol % of aldehyde groups. For

many electrooptical applications, such an amount of reactive groups in the polymer is sufficient.

The π -conjugated systems (1-aminopyrene, 4-aminoazobenzene, and 4-aminobiphenyl) were attached to PMPSi-CHO(6 or 12 mol %) by acid-catalyzed condensation of the aldehyde with amino groups yielding Schiff bases (PMPSi-Pyr, PMPSi-Azo, PMPSi-BiPh). In the case of PMPSi-Pyr and PMPSi-Azo almost total conversion of aldehyde groups to the corresponding Schiff bases was observed and proved by spectral analysis. ¹H NMR spectra of modified polymers (Figure 2) show that the azomethine hydrogens (N=CH) around 8.5 ppm are accompanied by traces of aldehyde hydrogens (CHO) around 9.7 ppm. From integrated intensities of these protons a conversion higher than 95% could be calculated. If we compare the spectrum of PMPSi-CHO (Figure 4) and the spectra of PMPSi-Pyr and PMPSi–Azo (Figure 2), the aromatic protons of pyrene and azobenzene structural units are clearly visible. (The spectra of model compounds NB-Pyr and NB-Azo are shown for convenience.) Using molar absorption coefficient of NB-Pyr and NB-Azo (Figure 3), the content of pyrene units in PMPSi-Pyr and azobenzene units in PMPSi-Azo (Figure 5) was determined by UV-vis spectrometry in THF. The results are in very good agreement with the aldehyde content in PMPSi-CHO calculated from ¹H NMR data (Table 1). Finally, FT IR spectra of modified polymers show that the carbonyl vibration band at 1702 cm⁻¹ completely disappeared during these reactions, and the new C=N vibration band at 1620 cm⁻¹ and other bands (see Experimental Section) responsible for the attachment of either pyrene or azobenzene structural units appeared. In the case of PMPSi-BiPh the conversion of aldehyde groups was incomplete. Integrated intensities of aldehyde (CHO) and azomethine (N=CH) protons of ¹H NMR spectrum have shown that approximately 25% of aldehyde groups was reacted with 4-aminobiphenyl. This estimation could not be supported by UV-vis spectrometry because the absorption maximum of NB-BiPh (331 nm) coincides with the maximum of $\sigma \rightarrow \sigma^*$ absorption band (335 nm) of PMPSi-BiPh, and only a shoulder at 360-400 nm was visible. But FT IR data of PMPSi-BiPh supported the results received from ¹H NMR. The carbonyl vibration band at 1700 cm⁻¹ of unreacted aldehyde groups was detected in addition to the bands at 1620 cm⁻¹ (C=N) and 1170 cm⁻¹ (aryl-N). In contrast to formylation, the condensation reaction yielding the Schiff bases proceeded without degradation of the main chain. Molecular weight characteristics of starting PMPSi-CHO and modified polymers were found to be nearly unchanged (see Experimental Section). The condensation process does not cause further degradation of synthesized polymers in accordance with reported results.¹⁵

Optical Absorption and Photoluminescence of Thin Films. Absorption spectra of modified polysilane films exhibited a maximum at about 330–340 nm corresponding to the σ -conjugation on the silicon backbone and were similar to those measured in solutions (cf. Figure 5). Photostability was followed from the change of $\sigma \rightarrow \sigma^*$ absorption maximum during the illumination with a mercury lamp. The molar absorption coefficient per silicon atom increases with molecular weight of polysilanes,¹ and consequently the chain degradation can be evaluated by means of UV–vis spectroscopy. Measurements were performed on several



Figure 6. Normalized absorbance measured at the maximum corresponding to the σ -conjugation of the silicone backbone vs the time of irradiation with a mercury lamp for PMPSi-1 (solid circles) and modified polysilanes: PMPSi–Azo(6 mol %) (open triangles), PMPSi–Azo(12 mol %) (solid triangles), PMPSi–Pyr(6 mol %) (open circles), PMPSi–Pyr(12 mol %) (crosses), and PMPSi–BiPh(3 mol %) (solid squares).

sets of the thin layers, and Figure 6 shows typical data. All modified polysilanes exhibited significantly better photostability than PMPSi. A very good stabilization effect was obtained in polysilanes modified by the pyrene even at low pyrene content.

PMPSi exhibits a sharp photoluminescence with high quantum efficiency in the near-ultraviolet (NUV) region located at 354 nm, characteristic of quasi-one-dimensional excitons delocalized on the silicon backbone. It emerges from the longest segments and gives the energy of the singlet state for these segments.⁴³ Phonon sidebands are absent, indicating weak phonon coupling. The photoluminescence study of thin films of the prepared polymers has shown that the modification of PMPSi quenched the PL emission peak of PMPSi at 354 nm. An example is shown for modification with azobenzene (Figure 7a). In comparison with PMPSi an increase in visible PL emission intensity was observed for PMPSi-BiPh. The PL spectrum was analyzed by multiple Gaussian function (Figure 7b). The contribution of the NUV emission with the band maximum at 360 nm to the whole PL intensity is 5% only, whereas the visible bands with maxima located at 470 and 524 nm contribute by 52% and 43%, respectively. Compared to PMPSi, the integral PL intensity in the visible region increased by a factor of 3. The PL spectra of PMPSi-Pyr indicate that the excitation energy is trapped by pyrene. The fluorescence spectrum of the pyrene consists of a structured band of the monomer and a broad structureless band of excimer. The monomer fluorescence of pyrene exhibits vibrational bands with maxima at 377, 397, and 419 nm and the maximum of the excimer band located at about 470 nm. PL spectra of the PMPSi-Pyr (Figure 7c) consist of the NUV emission and a broad band in the visible region typical of the pyrene excimer. The NUV emission could be assigned to the pyrene monomer bands and the NUV emission of excitons delocalized on the silicon backbone. The intensity of the excimer emission increased with the increasing concentration of the pyrene, which indicates molecular association of pyrene in polysilane. The PL behavior in



Figure 7. Photoluminescence emission spectra of thin films of (a) PMPSi (solid line), PMPSi-Azo(0.6 mol %) (dashed line) and PMPSi-Azo(6 mol %) (dotted line); (b) PMPSi-BiPh(3 mol %, circles), solid line is the best fit using multiple Gaussian function with components displayed by dashed lines; (c) PMPSi-Pyr (6 mol %, solid line) and PMPSi-Pyr (12 mol %, dashed line). Excitation wavelength was 310 nm.



Figure 8. Electric field dependences of the photogeneration efficiency (T = 300 K) in PMPSi (open circles) and modified polysilanes: PMPSi–Azo(6 mol %) (solid circles), PMPSi–Pyr(6 mol %) (open squares), PMPSi–Pyr(12 mol %) (solid squares), and PMPSi–BiPh(3 mol %) (crosses). Dashed and solid lines were calculated using the Onsager theory with the distribution of CT radii given by the δ - and Gaussian function, respectively, with the parameters given in Table 2.

modified polysilanes is a consequence of exciton mobility in PMPSi, which was demonstrated by Tokura et al.⁴⁴ They showed that defects produced by the introduction of a bond connecting two polysilane chains efficiently quenched the NUV emission and gave rise the visible PL.

Charge Carrier Photogeneration. The charge photogeneration efficiency, $\eta_{\rm ph}$, was measured with light incident upon the positively charged surface and with the intensity of light as low as possible to avoid photodegradation. Reproducible values of η_{ph} were obtained, and photodegradation was not observed during the measurements. Compared to PMPSi, in all modified polysilanes a decrease in the $\eta_{\rm ph}$ was observed. The electric field dependencies of $\eta_{\rm ph}$ are shown in Figure 8. They were explained by the Onsager model.⁴⁵ According to this model, the charge photogeneration takes place in two steps; in the first step bound electron-hole (e-h) pairs are formed, and in the second step the e-h pairs dissociate into free charges. For spherically symmetrical distribution of bound pairs, the overall photogeneration efficiency $\eta_{\rm ph}$ is expressed as

$$\eta_{\rm ph}(r, F, T) = \eta_0 \int 4\pi r^2 f(r, F, T) g(r) \, \mathrm{d}r \tag{3}$$

where η_0 is the primary quantum yield, i.e., the fraction of absorbed photons that results in e-h pairs and is assumed to be independent of the electric field *F*, *g*(*r*) an initial spatial distribution of e-h pairs, and *f*(*r*,*F*,*T*) the Onsager's dissociation probability^{45,46} of the pairs separated by a distance *r* in the presence of an external electric field *F*. If the usual Onsager model is assumed,



Figure 9. Electroluminescence spectrum (open circles) of polymer LED: ITO/PEDT:PSS/PMPSi/Al fitted by multiple Gaussian function (solid line) with components displayed by dashed lines.

Table 2. Parameters Obtained from the Experimental Dependences $\eta_{\rm ph}$ vs *F* (See Figure 8) Using the Onsager Model with the Distribution of CT Radii Given by the δ -Function (r_0 , η_0) and the Gaussian Function (α , $\eta_{0\alpha}$)

polymer	<i>r</i> ₀ (nm)	η_0	α (nm)	$\eta_{0\alpha}$
PMPSi	2.6	0.05	1.20	0.50
PMPSi-Pyr(6 mol %)	2.2	0.03	1.00	0.30
PMPSi-Pyr(12 mol %)	2.0	0.02	0.90	0.28
PMPSi-BiPh(3 mol %)	2.6	0.005	1.20	0.05
PMPSi-Azo(6 mol %)	2.4	0.03	1.10	0.28

all the pairs are separated by the same distance r_0 ; i.e., the initial spatial distribution of bound pairs is given by the δ -function, $g(r) = (4\pi r^2)^{-1} \delta(r - r_0)$. The usual Onsager model represents a first approximation only and is valid at low electric fields (see dashed lines in Figure 8). The full lines in Figure 8 represent the best theoretical fits to our experimental data obtained for the Gaussian distribution function of e-h pair radii, $g(r) = (\pi^{-3/2}\alpha^{-3}) \exp(-r^2/\alpha^2)$. The parameters of the theoretical fits are given in Table 2. The most effective separation distance of electron-hole pairs for their dissociation at low electric fields is close to r_0 , and at high electric fields it approaches the value of α . It is evident that the lower η_{ph} in PMPSi–BiPh than in PMPSi is caused by a lower value of the primary quantum yield $\eta_{0\alpha}$ (η_0) only, whereas the separation distances or distribution of the pair distances is the same. In PMPSi-Pyr both shortening of the separation distances and a decrease in the primary quantum yield $\eta_{0\alpha}$ (η_0) were observed. These results indicate a decrease in the geminate recombination quenching at an electric field, which could be favorable for EL. Correlation of these results with the results of the photostability and photoluminescence studies suggests the existence of additional deactivation channels in the modified polysilanes. In PMPSi-Azo, the azobenzene isomerization could be one of the effective channels.

Electroluminescence. Single-layer ITO/polysilane/ Al LEDs exhibited weak white EL emission with the highest efficiency, $\eta_{\rm EL} \sim 0.005\%$ photons/electrons, detected on the ITO/PMPSi–Pyr(6 mol %)/Al devices, which is slightly higher than that of 0.002% reported



Figure 10. Electroluminescence spectrum (open circles) of polymer LED: ITO/PEDT:PSS/PMPSi-BiPh(3 mol %)/Al fitted by multiple Gaussian function (solid line) with components displayed by dashed lines.

for the LEDs made of pyrene single crystal.⁴⁷ Our $\eta_{\rm EL}$ is higher than those ($\eta_{\rm ext} \sim 0.0001\%$) reported in LEDs (ITO and Al electrodes) made of PMPSi^{19,28} or oxygencross-linked polysilanes²⁹ and is similar to those reported for LEDs (ITO and Mg:Ag electrodes) made of silole-incorporated polysilane²⁸ ($\eta_{\rm ext} \sim 0.001\%$) or poly-[2-naphthyl(phenyl)silanediyl] doped with 2-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole²⁰ ($\eta_{\rm EL} \sim$ 0.002–0.008%). Recently, higher values of $\eta_{\rm ext}$ (=0.1%) were reported for LEDs (ITO and Al electrodes) made of poly[bis(4-butylphenyl)silanediyl].^{25,26}

Double-layer devices, ITO/PEDT:PSS/polysilane/Al, exhibited more than 1 order of magnitude higher $\eta_{\rm EL}$ than those in the single-layer LEDs. The EL spectrum of ITO/ PEDT:PSS/PMPSi/Al, shown in Figure 9, consists of a NUV sharp emission peak located at 353 nm (3.52 eV), the position of which is in good agreement with the PL peak position, and of broad emission bands in the visible region at 419 and 558 nm. Contrary to Suzuki,¹⁹ who observed the sharp NUV peak at low temperatures only, we detected such emission at room temperature. $\eta_{\rm EL}$ up to 0.1% photons/electrons, determined on freshly prepared LEDs, decayed after several runs to the value of 0.02%. As the time of LED operation increased, the contribution of NUV emission decreased, the contribution of visible bands increased, and the difference in the shapes of PL and EL spectra was more pronounced. Double-layer LEDs based on substituted polysilanes exhibited a broad white emission. In EL spectra of LEDs made of PMPSi-BiPh, the bands at 420 and 552 nm are dominant (Figure 10). EL spectra of LEDs made of PMPSi-Pyr consisted of broad bands, which could be assigned to the emission of the pyrene excimers with a different conformation and to the recombination centers of the structural origin. The band at 590 nm dominates (Figure 11). The EL spectra differ from PL ones due to different excitation, which indicates that different recombination centers are dominant in PL and EL. In EL, the charge trapping in the radiative recombination centers plays an important role. $\eta_{\rm EL}$ in double-layer LEDs made of PMPSi-BiPh or PMPSi-Pyr were in the range of 0.03–0.06% photons/electrons.



Figure 11. Electroluminescence spectra of polymer LEDs: ITO/PEDT:PSS/PMPSi-Pyr(6 mol %)/Al (solid line) and ITO/ PEDT:PSS/PMPSi-Pyr(12 mol %)/Al (dashed line).



Figure 12. Dependence of the current and spectrally integrated EL intensity on the applied electric field measured on polymer light-emitting devices: ITO/PEDT:PSS/PMPSi–BiPh-(3 mol %)/Al (crosses), ITO/PEDT:PSS/PMPSi–Pyr(6 mol %)/ Al (open circles), and ITO/PEDT:PSS/PMPSi–Pyr(12 mol %)/ Al (solid circles).

In PMPSi–Pyr devices, higher values of $\eta_{\rm EL}$ were measured for a lower pyrene content. The measured $\eta_{\rm EL}$ values are in the same range as the values reported for LEDs based on π -conjugated polymer such as poly[2,5bis(isopentyloxy)-1,4-phenylene]⁴⁸ and are also comparable with the EL efficiency measured in double-layer devices composed of hole-transporting (triphenylamine) and light-emitting (random copolymer of 9,9-dihexylfluorene and anthracene) layers.⁴⁹ Similar EL efficiencies were reported for the devices based on PMPSi containing anthracene units.³²

The onset of the EL emission was at ca. 1.5×10^8 V m⁻¹, being connected with a current increase at high electric fields (see Figure 12). The hole mobility of PMPSi (10^{-8} m² V⁻¹ s⁻¹) is not significantly modified by low substitution and the barrier height at the ITO/

polysilane interface is small, so the polysilane LEDs are typical hole-only devices. The ionization potential $(I_{\rm P})$, which corresponds to the HOMO energy level, was determined from the cyclovoltammetric measurements. In PMPSi the onset of oxidation potential (E_{ox}) was 0.7 V relative to the Ag/AgCl reference electrode. The E_{ox} of modified polysilanes ($E_{ox} \sim 0.72 - 0.78$ V) was slightly shifted to higher voltages compared with PMPSi. Similar to PMPSi and other polysilanes,9 the modified polysilanes oxidized irreversibly. Using an empirical relationship,⁵⁰ $I_{\rm P} = 4.4 + E_{\rm ox}$ (eV), the $I_{\rm P}$ values of 5.1– 5.2 eV were estimated. The ITO work function usually varies from 4.7 to 4.9 eV, so the expected height of the injection barrier for holes is lower than 0.5 eV and could further be reduced by using PEDT:PSS. On the other hand, the injection barrier for electrons in polysilanes is several times higher. However, significant hole trapping at the radiative centers near the polysilane/Al interface can improve the electron injection due to the space charges produced by trapped holes. The analysis of the current characteristics shows the influence of the space charges. Two regimes can be distinguished. At lower electric fields (F), the quadratic dependence of the current on F is characteristic of the spacecharge-limited current (SCLC) behavior.⁵¹ At higher F, when EL emission starts, the current I increases more steeply, $I \sim F^m$, with *m* at about 9–10, which can be explained in the frame of SCLC with an exponential trap distribution.⁵¹ While the current is dominated by holes, the EL intensity $I_{\rm EL}$ is determined by electron supply. The dependence of $I_{\rm EL}$ on F shows a Fowler-Nordheim behavior due to tunneling of minority carriers (electrons).52

As follows from the discussion above, the limiting factor in polysilane LEDs is electron injection. Therefore, better device performances are expected using metals with low work functions such as Ca or by introducing an electron-transporting layer. The EL efficiencies of polysilane LEDs are low; therefore, these materials are particularly intended for the use in multilayer or blend devices as hole transporting polymers to modify transport and injection properties. Recently, we have shown an improved performance (an increase in η_{EL} up to 25 times and improved stability) of blend LEDs made of an EL polymer (substituted poly-(terphenyl-4,4"-divlvinylene)) and a hole-transporting polymer (poly[biphenyl-4-yl(phenyl)silanediyl])⁵³ compared to the device made of neat EL polymer. Further, we achieved an increase in $\eta_{\rm EL}$ (up to 30 times) and improvement of the stability of blue emission in LEDs made of blends composed of poly[2,5-bis(isopentyloxy)-1,4-phenylene] (SPPP) and PMPSi, compared to the case of SPPP LEDs.³³ The results of our present research showed that blending of PMPSi-Pyr with poly(9,9dihexadecylfluorene-2,7-diyl) (SPF) leads to an increase in $\eta_{\rm EL}$ (ca. 2 orders of magnitude) and stability, compared to the case of SPF LEDs.

Conclusions

We have developed a one-step synthesis of poly-[(formylphenyl)methylsilanediyl], which was utilized as the functionalized polymer precursor for the attachment of π -conjugated systems to the polysilane backbone. ¹H NMR, UV-vis, and FT IR spectroscopies proved the presence of the aldehyde functionality. We reached the maximum content of reactive aldehyde groups in the functionalized polymer, 12 mol %. The molecular weight reduction caused by formylation is less (50%) than that in the multistep procedure (90%). The attachment of aromatic amines yielding Schiff bases proceeded smoothly and without further degradation of the main chain. For PMPSi–Pyr and PMPSi–Azo, almost total conversion of aldehyde groups to the corresponding Schiff bases was observed, but in the case of PMPSi–BiPh, the aldehyde groups conversion was only 25%.

Photophysical properties (photostability, photoluminescence, and charge photogeneration) of modified polysilanes were studied, and polymer light-emitting devices were fabricated and characterized. In comparison with PMPSi, quenching of NUV emission and an increase in the visible PL emission intensity were observed in modified polysilanes. LEDs emitted white light, and the electroluminescence spectra differed from photoluminescence spectra. Charge trapping in the radiative recombination centers plays an important role in EL emission. The EL efficiency up to 0.06% photon/electron was detected in double-layer LEDs, which is 1 order of magnitude higher than that in single-layer devices. Chemical substitution improved the photostability of PMPSi; therefore, the modified polysilanes are promising for use in polymer-blend LEDs to modify transport and injection properties and/or to prevent aggregation of the conjugated polymers. The Onsager model with the initial distribution of separation distances of electron-hole pairs given by the Gaussian function is a suitable model for description of the electron-hole pair dissociation during the photogeneration process in polysilanes. The most effective separation distances of electron-hole pairs in the charge photogeneration process were determined to be 2.0–2.6 and 0.9–1.2 nm at low and high electric fields, respectively.

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