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Electroluminescent diode utilizing poly[(diphenylsilanediyl)ethynediyl]

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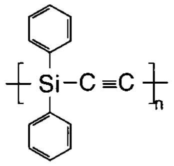
1. Introduction

An attempt was done in the last time to synthesize polymers whose backbone main chain structure consists of both the σ-conjugated Si structures and π-conjugated oligophenylene unit [1]. It was found that optical absorption is influenced by both the oligosilane and oligophenylene part and photoluminescence (PL) is shifted to the visible region in comparison with that of π- and σ-conjugated part of the backbone. The large Stokes shift of the PL (up to 1.3 eV) indicates that this type of substances is a good candidate for lasing material. A remarkable spectral narrowing upon the irradiation with THG light (355 nm) of Nd:YAG laser was observed on poly[(tetraethyldisilane-1,2-diyl)-*p*-quaterphenyldiyl]. In this paper we report on spectral and electroluminescent properties of a polymer consisting of carbon and silicon atoms in the main chain with the carbon atoms bonded by a π-electron containing triple bond, poly[(diphenylsilanediyl)ethynediyl] (PDPSiEt). The silicon atoms are substituted with π-conjugated phenyls.



Scheme 1: Chemical structure of poly[(diphenylsilanediyl)ethynediyl]

2. Experimental

PDPSiEt (see Scheme 1) was prepared by condensation of dichloro(diphenyl)silane with tetrachloroethane in a similar way to that described by Fang et al. [2]. The polymer possessed a unimodal but broad molar mass distribution, $\overline{M}_w = 4 \times 10^3$ g mol^{-1}. Films for photoluminescence measurements were prepared from a toluene solution by spin coating (2000 rpm, 50 s) or by casting on stainless steel substrates. EL diodes consisted of an indium-tin-oxide (ITO) coated quartz substrate, an emission layer of PDPSiEt, and an indium-containing magnesium (In:Mg) electrode. The conditions of spin coating were: 250 rpm for the first 5 s and then 2000 rpm for 30 s.

Optical absorption and photoluminescence spectra were measured using a Hitachi 330 spectrophotometer and a Hitachi F-2000 fluorescence spectrophotometer, respectively. Current-voltage characteristics were measured by a conventional method using a power supply and electrometer. The emission intensity was determined with a photomultiplier (R 928, Hamamatsu Photonics Co.).

3. Quantum chemical calculations

Calculations were performed using ab initio and semiempirical quantum chemical methods (Gaussian 98 computer program [3]). The molecular conformations of hexamers were determined by means of the minimization of the total energy calculated using the Becke three-parameter hybrid method with the correlation functional of Lee, Yang, and Paar (B3LYP) using the 3–21G$^{(*)}$ basis set of atomic orbitals. Atomic charges were calculated at B3LYP/6-31G* level, UV–VIS spectra were calculated by ZINDO method.

4. Results and discussion

The shape of the molecule, is given in Fig. 1. The C – Si – C angles are around 108°, the angle C[Ph(4a)] – Si(4) – C[Ph(4b)] was determined as 111°. The Si – C bond lengths in the main chain are about 1.82 Å, whereas the C ≡ C bond length are around 1.22 Å.

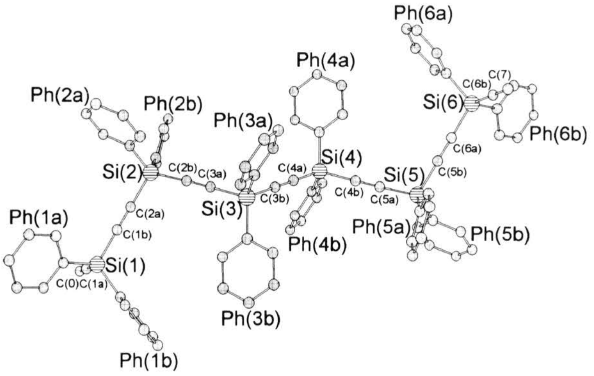


Fig. 1. Geometry of oligo[(diphenylsilanediyl)ethynediyl] as obtained by the B3LYP/3-21G$^{(*)}$ quantum chemical method. Numbering of atoms is given.

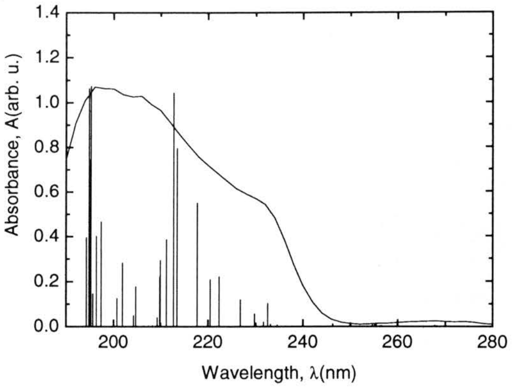


Fig. 2. Absorption spectrum of thin PDPSiEt film. Discrete lines are calculated electronic transitions; their heights represent relative values of the oscillator strength.

The absorption spectrum is given in Fig. 2. It consists of the strong peak at about 200 nm, a shoulder at 232 nm, and a very weak absorption in the region around 270 nm. The main absorptions at 213 nm (oscilator strength 0.35) and 195 nm (0.36) are associated with π (phenyl and C≡C) → π (phenyl) and π (C≡C) → σ (main chain) and π (phenyl) transitions, respectively. From analysis of the experimental absorption edge on assumption of direct electronic transitions using the relationship $(h\nu \times \alpha)^2$ vs. $h\nu$, where $h\nu$ is the photon energy and α is the absorption coefficient, the band-gap energy was evaluated to be 5.2 eV. By the calculation, the HOMO-LUMO energy gap was determined as 5.33 eV in good agreement with the experimental value.

Figure 3 shows photo- and electroluminescence emission spectra of PDPSiEt films 180 nm thick. The EL spectrum was nearly independent of the applied voltage and also of the PDPSiEt film thickness. The photoluminescence spectrum is a good mirror image of the absorption spectrum, keeping even the shoulder. The Stokes shift of the fluorescence spectrum from the absorption spectrum is about 154 nm in the solid state. The peak in the EL spectrum (λ = 361 nm) almost coincides with that in the photoluminescence spectrum (λ = 354 nm, measured at room temperature), including a tail up to 570 nm, but excluding the shoulder part in the short-wavelength region. Thus, the main peak of the EL is narrower than that of the photoluminescence (cf. the values of FWHM: 0.48 eV vs. 0.69 eV).

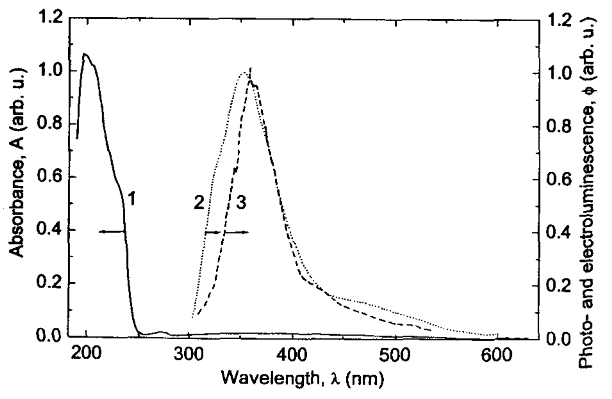


Fig. 3. Absorption (curve 1), photo- (curve 2) and electroluminescence (curve 3) spectra of thin PDPSiEt film.

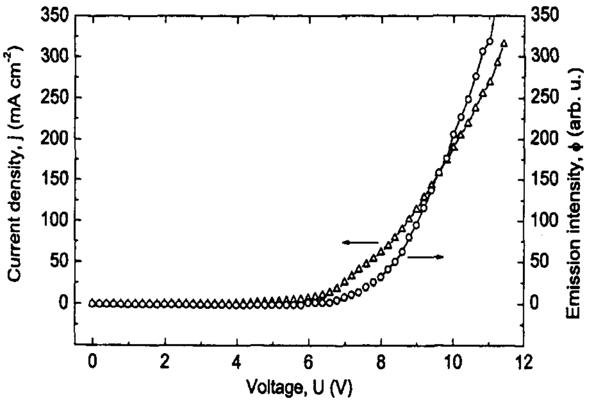


Fig. 4. Current - voltage and light intensity - voltage characteristics for thin PDPSiEt film measured at 77 K.

The current-voltage characteristic of EL diodes ITO/PDPSiEt/In:Mg is given in Fig. 4. The forward bias corresponds to a positive bias voltage on the ITO electrode. The current increases with increasing forward bias voltage, but the reverse bias current remains small; the diode exhibits a rectifying characteristic. The light started at about 8 V at the sample thickness 180 nm. The emission intensity increases monotonically with increasing injection current showing almost a linear dependence in the voltage range 3 - 11 V.

The charge carrier injection from the electrodes leads to the formation of positive and negative polarons, with an important charge redistribution. Whereas in the formation of the positive polaron, Si atoms become more positive and C atoms in the main chain carry approximately the same charge as the neutral molecule in the formation of the negative polaron all the above mentioned atoms are more negative. Charges on phenyls are more positive or negative in the formation of the positive or negative polaron, respectively.

5. Conclusion

The electroluminescence spectrum of the ITO/PDPSiEt/In:Mg diode was nearly independent of the applied voltage and of the film thickness. The peak in the EL spectrum (λ_{max} = 361 nm) almost coincides with that in the photoluminescence spectrum. The absorption spectrum is a good mirror image of the luminescence spectrum. The electric characteristics are determined by space-charge-limited injection of holes through an interface barrier at the contact.

Acknowledgements

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