Summary

This thesis describes the synthesis and the spectroscopic and nonlinear optical characterization of a large series of donor- and acceptor-substituted diphenylsilanes with the structure DPh-(SiMe₂)n-PhA and fragments thereof.

Nonlinear optics (NLO) deals with the interaction of electromagnetic fields (light) with matter so as to generate new electromagnetic fields altered from the incident field with respect to phase, frequency, amplitude or other propagation characteristics. One of the applications involving nonlinear optical phenomena is frequency doubling of near infrared laser light (frequency $\omega$) by a nonlinear optical material into blue light ($2\omega$). In this way, information can be recorded with a density four times as high as that attainable when the fundamental wavelength is used.

Optical transparency of the NLO material at the generated double frequency (410 nm for a red 820 nm diode laser) is therefore a major requirement. The nonlinear optical behaviour of such materials is the result of the nonlinear relation between the induced polarization, $P_i$, and the applied electric field caused by the asymmetry of the polarizability of the molecules of which the material consists of. On the molecular scale this is represented by the hyperpolarizability, $\beta$; on a macroscopic scale, by the nonlinear susceptibility, $\chi^{(2)}$. Large values of the hyperpolarizability are usually found for organic compounds that consist of a (polarizable) delocalized $\pi$-system with an electron donor (D) and an electron acceptor (A) grafted onto both sides of the conjugated path. The induced polarization, when an alternating electromagnetic field impinges on a material, is larger in the direction from the donor to the acceptor than vice versa. Thus, in order to have a non-zero value of a materials' optical nonlinearity ($\beta \neq 0; \chi^{(2)} \neq 0$), the NLO-molecules must be organized in a non-centrosymmetric way.

One of the major drawbacks of increasing a materials' nonlinearity is the loss of transparency; the aim of this research, therefore, has been the synthesis of nonlinear optical materials that are transparent in the visible spectrum while still having moderate nonlinear optical properties. Instead of a completely $\pi$-conjugated system, we have chosen a ($\sigma$-$\pi$)-conjugated frame consisting of a permethylsilanylene $\sigma$-bridge connecting two phenyl-rings (so called D$\sigma$A-compounds). Another approach (in combination with the $\sigma$-bridge) is the use of inductive-type acceptors, such as the perfluorobutylsulfonyl group (SO₂C₄F₉), because of their strong electron-attracting character and the improved transparency of compounds that contain this acceptor compared to those with mesomeric-type acceptors, such as the nitro or dicyanovinyl group.

One of our aims has been the understanding of the electronic transitions, the extent of ($\sigma$-$\pi$)-conjugation occurring in the D$\sigma$A-compounds and the interaction
between donor and acceptor substituents through the \((\sigma-\pi)\)-conjugated frame. To this end, we have studied the absorption and emission properties of these compounds by UV-Vis and fluorescence spectroscopy and also the relation between NMR chemical shift trends and ground state electronic properties. Furthermore, we have synthesized and characterized 'fragment' compounds consisting of a mono- or disil(ane)ylbenzene moiety \(para\)-substituted with either a donor or an acceptor.

Finally, we have aimed at incorporating D\(\sigma\)A-compounds in a polymer matrix, either dispersed or covalently linked through a functionalized donor (or acceptor) group, in order to obtain a nonlinear optical material.

In **Chapter 1** a general introduction about nonlinear optics (background, theory and materials) and about \((\sigma-\pi)\)-conjugation and excited-state properties of phenylpermethyloligosilanes has been given.

**Chapter 2** describes the synthesis of the D\(\sigma\)A-compounds and fragments thereof. The general route to the synthesis of D\(\sigma\)A-compounds is the successive coupling of the Grignard reagents of the \(para\)-acceptor- and donor-substituted bromobenzenes with a dichlorosilane. By specific reactions at the acceptor side, new acceptor groups could be created. Also the synthesis of a diol-functionalized dialkylamino donor- and perfluorobutylsulfonyl-acceptor-substituted diphenyldisilane, to be used as a (co)monomer in an NLO-polymer, has been presented. The crystallographic structures of two sulfonyl-acceptor-substituted diphenyldisilanes were resolved. These molecules possess a \(trans\)-conformation in which the donor and acceptor substituents are found at positions with the largest possible distance between them.

**Chapter 3** reports about several relationships between NMR chemical shifts and other molecular properties of D\(\sigma\)A-compounds and their fragments. A linear correlation has been found between the \(^{29}\text{Si}\) NMR chemical shift difference of the two silicon atoms in the disilanes, their calculated ground-state dipole moments and the sum of the Hammett substituent constants of the donor and acceptor substituents. The \(^1\text{H}\) NMR chemical shifts could be related to the reactivity of (di)chlorosilanes towards Grignard reagents: the reactivity of a silicon-chloride bond in \((\text{Cl}-(\text{SiMe}_2)_6\text{-Cl})\) has been found to be as large as that of the Si-Cl bond in the monochlorohexasilane \((\text{Cl}-(\text{SiMe}_2)_6\text{PhBr})\). The results obtained by the \(^{29}\text{Si}\) and \(^1\text{H}\) NMR data imply that the substituent effect through the silicon chain is small (at least in the ground state) and decreases with increasing silicon chain length. \(^{13}\text{C}\) NMR chemical shifts of carbon atoms that are bonded to silicon were shown to be linearly, but inversely related to the substituent effect of the donor or acceptor group at the other side of the silicon atom. This means that these \(^{13}\text{C}\) NMR chemical shifts are inversely related to electron density at the nucleus, in disagreement with the general interpretation of NMR chemical shifts.
Chapter 4 presents the absorption and emission properties of $\text{D}_{\text{O}}\text{A}$-compounds and fragments thereof, measured in solution by UV-Vis and fluorescence spectroscopy, respectively. In contrast to fully $\pi$-conjugated $\text{D}_{\pi}\text{A}$-molecules, which show one major absorption band (the so-called Intramolecular Charge Transfer (ICT) band), the $\text{D}_{\text{O}}\text{A}$-compounds show at least two major absorption bands. These can be ascribed to transitions in the separate donor and acceptor fragments. In the former case, the silicon bridge acts as an acceptor; in the latter case it is an electron donor. Furthermore, the disilanyl group seems to be a much better donor group than the monosilyl group, especially in combination with a strong inductive electron acceptor like the $\text{SO}_2\text{C}_4\text{F}_9$-group. The absorption spectra of compounds with the mesomeric dicyanovinyl acceptor are considerably red-shifted from those of the inductive-acceptor-containing compounds. The $\text{Me}_2\text{N}$-donor- and $\text{CH}=$C(CN)$_2$-acceptor-substituted disilanyl compound shows, besides the two 'local' absorptions, a ICT band at the red side of the spectrum. This can also be observed for the analogous compound with the $\text{SO}_2\text{C}_4\text{F}_9$-acceptor when the absorption spectra of the fragment compounds are substracted from that of the whole molecule. A red shift of the absorption spectra is observed when going from one to two silicon atoms in the bridge, but not when the chain length is further increased to six silicon atoms.

The emission spectra of some $\text{D}_{\text{O}}\text{A}$-compounds with the dimethylamino donor and with various acceptors have been measured in solvents of different polarity. Except for a local non-solvent-dependent emission band, a solvent-dependent one can be observed at lower frequencies for compounds with an inductive sulfonyl ($\text{SO}_2\text{C}_4\text{F}_9$ or $\text{SO}_2\text{Ph}$) or a trifluoromethyl ($\text{CF}_3$) acceptor. This emission arises from a polar charge-transfer excited state that is formed by electron transfer from a locally excited state in the donor fragment to the charge-separated state. The change in dipole moment, calculated from the solvatochromic shifts, from the ground to the charge-separated excited state amounts to 25 and 40 Debye for the $\text{CF}_3^-$ and the $\text{SO}_2\text{C}_4\text{F}_9$-acceptor, respectively. This agrees well with the displacement of the unit charge of an electron from the donor phenyl ring to the acceptor phenyl ring of the molecule in the extended form. The polar excited state of the compound with the $\text{SO}_2\text{Ph}$-acceptor ($\Delta\mu = 26$ D) probably belongs to a folded conformation that arises from an extended charge-separated excited state after a second electron transfer, from the inner to the outer phenyl ring of the acceptor, has occurred. This compound can therefore be classified as a trichromophoric $\text{D}_{\text{O}}\text{A}_{\text{sA}}$-compound (s: spacer).

The $\text{F}$- and $\text{CF}_3$-acceptor compounds are photochemically unstable: this is shown by the change in absorption and emission spectra upon irradiation in solution. The emission spectra of the sulfonyl-acceptor containing compounds show a second, non-solvatochromic emission band, which can be assigned to a transition from a
locally-excited acceptor-fragment of the DσA-compound or, most probably, from a photodissociation product.

Chapter 5 presents the values of the first hyperpolarizability, $\beta$, of the DσA-compounds and their fragments, obtained by the hyper-Rayleigh scattering (HRS) technique. For some of these compounds, the $\beta$ values are very well reproduced by theoretical calculations. The largest $\beta$ values were found for compounds with the dicyanovinyl acceptor. This is not surprising since the absorption spectra of these compounds are the most red-shifted in our series. The $\beta$ value of a $\pi$-conjugated molecule is usually determined mainly by the contribution of the ICT-transition. The DσA-compounds, on the contrary, have $\beta$ values that are not much larger than the sum of the contributions from the separate fragment nonlinearities. However, for the disilanyl compound with the Me$_2$N-donor and CH=C(CN)$_2$-acceptor a charge-transfer contribution of 50% can be observed.

It can be concluded that the silicon-bridged DσA-compounds have very interesting optical properties. This class of compounds can be classified as bichromophoric donor-acceptor compounds with the silicon bridge being only a weak charge-transmitter in the ground state. A correlation between transparency and nonlinearity for this type of compounds exists; a $\beta$ value similar to that of $p$-nitroaniline could be observed for a perfluorobutylsulfonyl-acceptor-containing disilane, while it has a better transparency. This means that this type of compounds certainly can be considered for frequency doubling applications. The large volume of these molecules will reduce the nonlinearity density compared to that of donor-acceptor-substituted benzenes, but this property, together with the large dipole moments, will probably favour the orientational stability when these molecules are oriented in a polymer matrix. Hence, the incorporation of the functionalized DσA-compound into a polymer in order to study the macroscopic nonlinear optical behaviour will be an interesting future research topic.