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The Synthesis and Condensation of Oligo(phenylenevinylene)s with Alkoxysilyl End Groups

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Summary: Monodisperse alkoxylated oligo(phenylenevinylene)s with 3, 4, or 5 benzene rings were connected to reactive di- and triethoxysilanes, either directly or via flexible spacers. Aminopropylsilanes were condensed with stilbenoid aldehydes and subsequently reduced to amines, for the direct, rigid connection, the Heck reaction and also cross-metathesis with vinyl silanes proved to be successful routes. Hydrolysis of the ethoxysilanes leads to polymerisable cyclosiloxanes or curable three-dimensional networks with pendent chromophores.

Introduction

During the past decade, luminescent organic semiconductors have gained considerable attention due to promising applications as active materials in non linear optical and light emitting devices.[1,2] Among the different classes of compounds with extended π-sytems chromophores, like polythiophenes or polyphenylenes, conjugated polymers based on phenylenevinylene repeat units are one of the most intensively investigated materials.[3] Besides the polymers, well defined oligomers containing only a few repeat units have been synthesised and thoroughly studied. These monodisperse molecular species serve as model compounds for a reliable correlation of the structure and the electrical and optical properties of the corresponding polymers.[4-6] Moreover, they are attractive as electronic materials in their own right.[7] A major drawback for the application of these well-defined, low molecular weight oligomers is their strong tendency towards crystallisation. Oligo(phenylenevinylene)s (OPVs) have been applied as evaporated films,[8] in polymeric matrices[9] and as conjugated units in the main chain[10,11] or as side groups of a flexible polymer backbone.[12,13] A different approach for the immobilisation of these π-systems is based on the sol-gel process of alkoxysilanes. Fluorescent organic-inorganic hybrid materials containing poly(phenylenevinylene) (PPV) have been reported as early as 1991 by Karasz et al.[14,15] and chromophores with covalent bonds to reactive alkoxysilanes have been used for the fabrication

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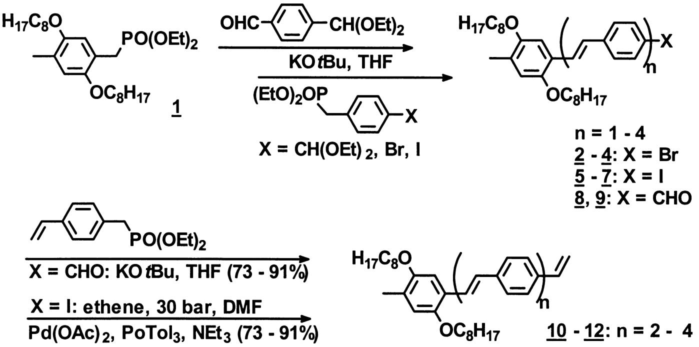
nanostructured hybrid materials.[16,17] Recently, the promising potential of electrooptically active compounds with curable chloro- or alkoxysilanes has been pointed out for light harvesting[18] and photorefractive materials,[19,20] hole conducting[21] and light emitting layers.[22] In this paper, we focus on the synthesis, condensation and optical spectra of monodisperse OPVs with covalent bonds to alkoxysilanes, either directly or via flexible spacers.

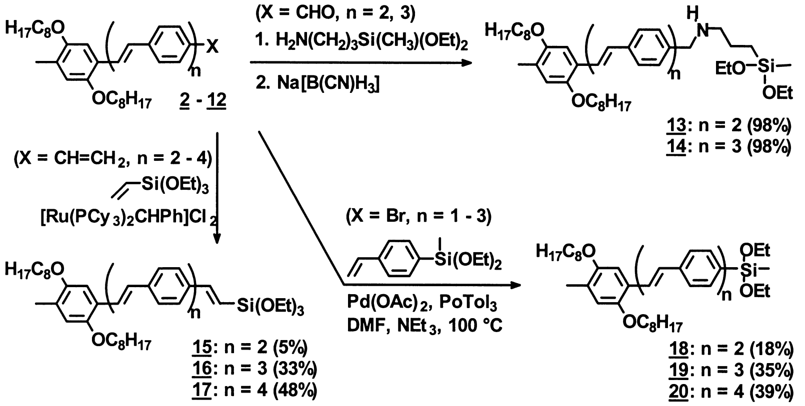
Synthesis

The connection of oligo(phenylenevinylene)s with alkoxysilyl moieties was performed on three different routes, condensation with aminopropylsilanes, Heck reaction with an alkoxysilyl styrene and by cross-metathesis of vinyl-OPVs with vinylsilanes. Chromophores composed of three to five benzene rings connected via *trans*-vinylene linkages were prepared via subsequent Horner olefination steps using monoprotected terephthal dialdehyde and a benzyl phosphonate with an acetal in the *p*-position as a key synthons. Starting from 2,5-bis(2-ethylhexyloxy)benzyl phosphonate 1,[23,24] this sequence led to molecules 2 - 9 with reactive moieties (iodine, bromine, or carbaldehyde) on the opposite side of the chromophore (scheme 1). Oligomers with terminal vinylene groups 10 - 12 were prepared by Horner olefinations using 4-vinyl benzylphosphonate as well as by the Heck reaction of the iodo-OPVs with compressed ethene.[25]



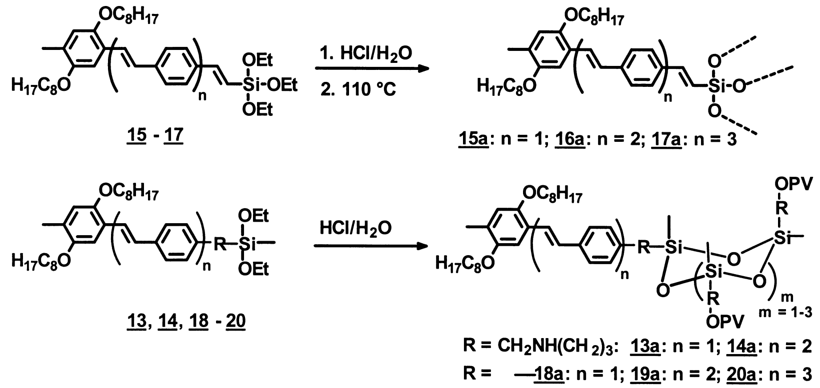
Scheme 1. Synthesis of alkoxylated OPVs with terminal reactive centres.

These chromophores were used for the final reactions with functional alkoxysilanes. The condensation of the stilbenoid aldehydes with aminopropylsilanes to imines and their reduction to secondary amines was a straightforward and high yielding route[24] to the title compounds with a flexible spacer linking the fluorescent and the reactive subunits (Scheme 2). For a rigid connection between these functional components, two strategies were studied: the Heck reaction of bromo-OPVs with p-diethoxymethylsilyl styrene[26,27] and the ruthenium-catalysed cross-metathesis of OPVs with a terminal vinyl group and vinyl triethoxysilane.[23,28] Both routes for the connection of the OPVs to the alkoxysilane unit gave only poor results for distyrylbenzene (15: 5%; 18: 16%), but the yields increased considerably upon extension of the conjugated system to chromophores with four (16: 33%; 19: 35%) and five (17: 48%; 20: 39%) aromatic rings (scheme 2).



Scheme 2. Connection of OPVs with alkoxysilanes.

The hydrolysis of the alkoxysilanes and condensation to oligosiloxanes (Scheme 3) was performed with the diethoxymethylsilyl-substituted OPVs 13, 14, 18 - 20 and also with triethoxysilanes 15 – 17. The silanes 13 – 20 were dissolved in chloroform/ethanol 1/1, dil. hydrochloric acid was added and the mixture stirred for 2 days, followed by neutralizing with $NaHCO_3$, drying, and evaporation of the solvent. The diethoxysilanes 13, 14, 18 - 20 were transformed into (inseparable) mixtures of good soluble cyclotri-, -tetra-, and –pentasiloxanes 13a, 14a, 18a – 20a with pendant chromophores (Maldi-tof). Even the "early" condensation products 15a – 17a from triethoxysilans 15 - 17 were soluble in chloroform. Transparent films on glass were obtained from the solutions by casting chloroform solutions of siloxanes 13a – 20a. The films of 15a – 17a were cured by annealing in vacuo for 3 h at 110 °C to insoluble, transparent films.



Scheme 3. Oligomerisation of di- and triethoxysilanes linked to OPVs via acid-catalysed hydrolysis and condensation.

Electronic Spectra

The electronic spectra of the oligosiloxanes were measured in dichloromethane solution (ca. 10^{-5} mol/L absorption, ca 10^{-7} mol/L emission) and as films on glass (fluorescence and fluorescence excitation spectra).

In dilute solution, the increasing conjugation length of the OPVs is strongly reflected in the bathochromic shifts of the absorption maxima. Compounds with a distyrylbenzene chromophore (13, 18) are characterised by an absorption maximum at 375 nm, an extension of the conjugated system by a vinylene linkage results in a bathochromic shift of about 10 nm (15: λ_{max}= 386 nm), already half the effect of a phenylene vinylene repeat unit (14, 19: λ_{max} = 395 nm, 397nm). The extent of the red shift is reduced upon further elongations of the π-systems (16: λ_{max} = 401 nm; 17, 20: λ_{max} = 409 nm, 410 nm). A comparison of the fluorescence spectra shows a different trend: again, the distyrylbenzenes display fluorescence maxima at highest energies in this series (13, 18: $\lambda_{f,max}$ = 409 nm, 410 nm) and an elongation of the π-system by a vinyl group results in a red shift of the emission of about 10 nm (15: $\lambda_{f,max}$ = 479 nm), but in contrast to the absorption spectra, the fluorescence maxima are only slightly shifted upon further extension of the conjugated system (16, 17, 19, 20: $\lambda_{f,\,max}$ = 481 - 482 nm, 14: $\lambda_{f,\,max}$ = 484 nm). This indicates that the exciton is confined to a π-system consisting of only three phenylenevinylene repeat units. As the effective conjugation length of oligo(phenylenevinylene)s is reached with chromophores containing ten benzene rings,[29] this early convergence can be attributed to the energetic effect of the terminal 2,5-dialkoxy substitution.

Hydrolysis of the alkoxysilanes and condensation results in negligible changes (+/- 1 – 3 nm) of the electronic spectra of the chromophores in dilute solutions. But interactions of the chromophores in the pure, solid films have a distinct effect on the optical properties, as can bee seen from the spectra of these compounds (13a – 20a) in the pure films on glass (Figure 1, Table 1). In the fluorescence excitation spectra, the maxima of the four- and five-ring compounds 14a, 16a, 17a, 19a, 20a are hypsochromically shifted to 388 – 392 nm (compared to the absorption spectra in dil. solution) and also the distyrylbenzenes 13a (λ_{max} = 349 nm), 15a, 18a (λ_{max} = 342 nm) show a second, intense maximum or shoulder at about 388 nm. Comparing the emission spectra of solid oligomers (13a – 20a) with the fluorescence of the corresponding monomer, hypsochromic shifts of 8 – 10 nm were recorded for the distyrylbenzenes (13a, 18a), changing to red shifted emissions regarding π-systems with four or five benzene rings (14a, 19a, 20a). In the series of the OPVs connected to siloxane networks (15a – 17a), much more pronounced bathochromic shifts of the fluorescene maxima were recorded ($\Delta\lambda$ = 14 – 29 nm). This can be attributed to a different aggregation behaviour of chromophores connected (18a – 20a, via flexible spacers 13a, 14a) to flexible oligosiloxanes in contrast to these OPVs linked to rigid siloxane networks (15a – 17a).

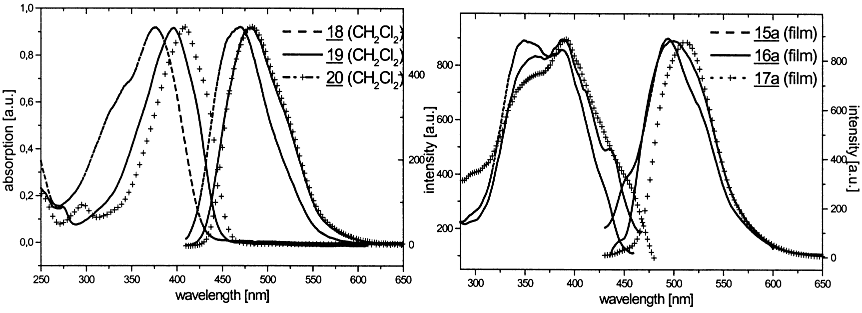


Figure 1. Normalised electronic spectra of homologous series of monomeric ethoxysilyl-OPVs 18 – 20 in solution and of OPVs bound to siloxane networks (15a – 17a) as solid film.

Table 1. Absorption and emission maxima of ethoxysilyl-OPVs and cyclosiloxanes / siloxane networks with pendent stilbenoid chromophores 13(a) – 20(a).

	Monomers (CH_2Cl_2)			Oligomers (neat film)	
	$\lambda_{abs.\ max}$ [nm]	$\lambda_{fluo,\ max}$ [nm]		$\lambda_{ecx,\ max}$ [nm]	$\lambda_{fluo,\ max}$ [nm]
13	375	469	13a	342 (384sh)	458
14	395	484	14a	(350sh) 391	498
15	386	479	15a	349 (388)	493
16	401	482	16a	(360) 388	501
17	410	482	17a	392	511
18	376	470	18a	342 (388 sh)	462
19	397	481	19a	391 (355 sh)	482
20	409	482	20a	392	507

Conclusion

Monodisperse alkoxylated oligo(phenylenevinylene)s with three to five benzene rings have been connected to di- and triethoxysilyl moieties Heck reactions and cross-metathesis with vinylsilanes lead to a direct, rigid connection of chromophore and reactive moiety, compounds with a flexible spacers were obtained by condensation of aldehydes with aminopropylsilanes. Acid-catalysed hydrolysis and condensation of these luminescent compounds led to oligosiloxanes with pendent conjugated units, transforming small molecules into (temporarily) soluble materials with well defined chromophores. Cross-linking the siloxanes did not change the absorption/emission behaviour remarkably, a strong blue-green luminescence is emitted from solution as well as from transparent films.

Acknowledgements

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