JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2000; **13:** 587–590

Review Commentary

Synthesis and electronic spectra of substituted oligo(phenylenevinylene)s

Heiner Detert* and Erli Sugiono

Institut für Organische Chemie, Duesbergweg 10–14, D-55099 Mainz, Germany

Received 27 August 1999; revised 1 March 2000; accepted 17 March 2000

ABSTRACT: A series of substituted oligo(*p*-phenylenevinylene)s (OPVs) with five benzene rings was prepared via PO-activated olefinations and Knoevenagel condensations. The central ring is substituted with two octyloxy groups to ensure good solubility of the OPVs and the lateral styrene units carry further substituents, with either electron-accepting or donating character and also combinations thereof. The spectral features of these OPVs are dominated by the basic chromophore; further auxochrome groups on the lateral rings (*meta* and *para* positions) shift the absorption and emission spectra only slightly to longer wavelengths. Significant bathochromic shifts (absorption ca 20 nm, emission ca 40 nm) are observed for OPVs with cyano groups on the terminal vinylene segments. The absorption spectra are independent from the concentration and solvatochromism is very small. The OPVs are photochemically stable to near-UV irradiation (366 nm) in neutral solution, whereas mid-UV irradiation (254 nm) causes decomposition of the chromophore. The presence of traces of acids or amines leads to different photochemical pathways. Copyright © 2000 John Wiley & Sons, Ltd.

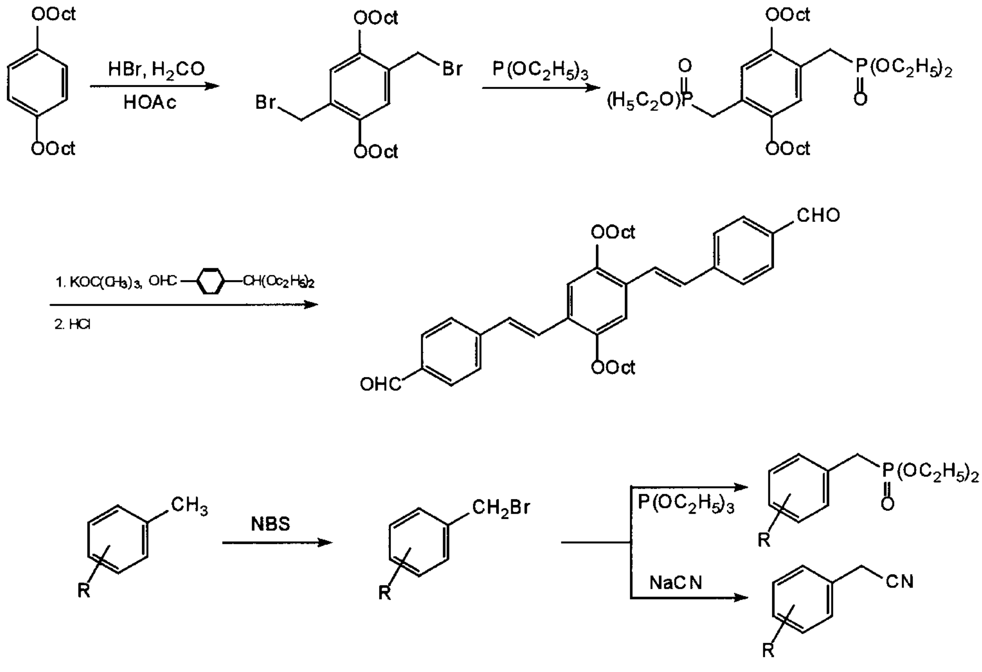
KEYWORDS: oligo(phenylenevinylene)s; electronic spectra

Since the discovery of the electroluminescence of poly(*p*-phenylenevinylene) (PPV) by Burroughes *et al.*[1] a broad variety of conjugated polymers have been prepared and investigated for use in light-emitting diodes (LEDs). In addition to PPV, polythiophenes and poly(*p*-phenylene)s have been used extensively;[2] solubility has been obtained by substitution with flexible side-chains[3] or sterically demanding groups.[4] Model compounds proved to be very useful for the elucidation of the photochemical and photophysical properties of the polymers,[5,6] since they can be prepared with monodisperse chain lengths, in high purity, and are often much more soluble than the polymers. Furthermore, oligomeric compounds can be used as luminescent building blocks in alternating copolymers[7] and as electronic materials in their own right.[8] For the use of conjugated materials such as PPV in LEDs, low-lying LUMO levels are favourable,[9] since then the injection of electrons from metals with higher work functions such as aluminium to the organic semiconductor requires low activation energies and the performance of the diode is improved. Unfortunately, most PPV-type materials are predominantly hole conducting;[10] a few polymers and oligomers with higher electron affinity have been described bearing cyano groups at the vinylene linkage or electron-deficient heterocycles in the main chain.[11–13] We have prepared a series of oligo(phenylenevinylene)s (OPVs) with five benzene rings and a variety of substituents of different character on the lateral rings and studied the influences of substitution on the absorption and emission spectra and the photostability of these model compounds.

The fundamental chromophore of the title compounds is a linear OPV with five benzene rings and two octyloxy groups in the 2,5-positions of the central ring; further auxochrome groups are symmetrically located on the terminal styrene units. The synthetic strategy for these compounds started with the central distyrylbenzene segment carrying two carbaldehyde functionalities and the two octyloxygroups which are essential for the solubility of the intermediate and the final compounds. Hydroquinone dioctyl ether was chloromethylated or bromomethylated and a twofold Michaelis–Arbusov reaction led to the bisphosphonate (31% via chloromethylation, 38% via bromomethylation) (Scheme 1). The distyrylbenzenedicarbaldehyde was prepared in a twofold Horner reaction with terephthaldialdehyde monodiethylacetal followed by acidic cleavage of the acetals. This synthon was used for the preparation of all OPVs reported here. The aldehydes were converted to styrene units via a second twofold Horner reaction with a variety of substituted benzylphosphonates or to α-cyanostyrenes with benzyl cyanides in a twofold

---

**Correspondence to:* H. Detert, Institut für Organische Chemie, Duesbergweg 10–14, D-55099 Mainz, Germany.
E-mail: detert@mail.uni-mainz.de

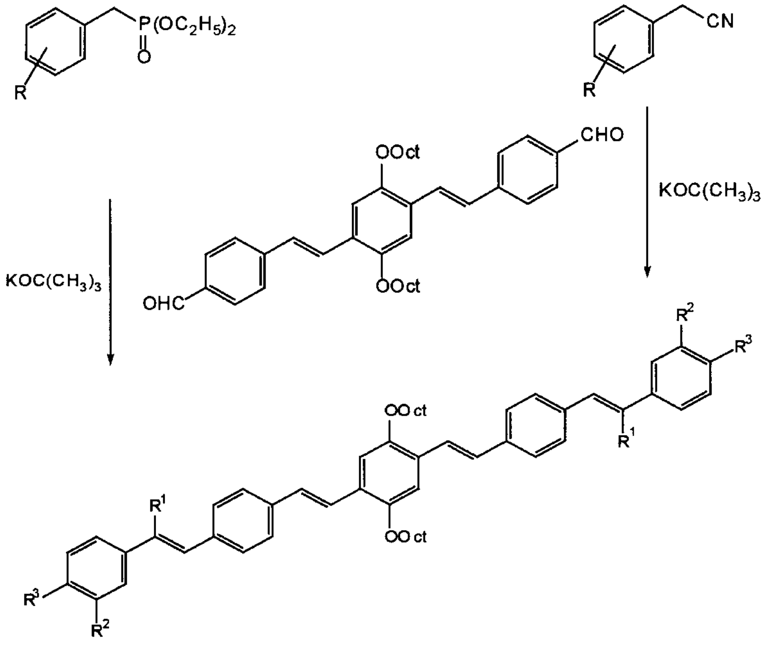


Scheme 1. Synthesis of starting materials

Knoevenagel condensation (Scheme 2). The yields in the final step were in the range 57–96% (except OPV **5**, 17%). Synthetic details will be reported elsewhere. All OPVs were readily soluble with melting-points in the range 153–203 °C; a small mesophase was observed only for **1** (155–162 °C).

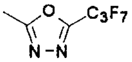
The absorption and emission spectra were recorded in dichloromethane under ambient conditions; the concentrations were about 10^{-5} mol l^{-1} (absorption) and 10^{-8} mol l^{-1} (fluorescence). For the photochemical experiments the solvents were purified by additional filtration through basic alumina and the solutions were thoroughly degassed. The essential spectroscopic data are collected in Table 1.

The intensely coloured OPVs can be divided into two groups: the yellow compounds with substituents on the benzene rings (**1**–**9**, except **5**) and the orange to dark-red OPVs with propenenitrile segments. Upon UV irradia-



Scheme 2. Synthesis and substitution pattern of OPVs **1–12**

Table 1. Substituents and spectral data

Compound	R^1	R^2	R^3	λ_{max} (nm)	$\lambda_{0.1}$ (nm)	$\epsilon \times 10^{-4}$ ($l\,mol^{-1}\,cm^{-1}$)	λ^f_{max} (nm)
1	H	H	CH_3	424	478	8.3	483
2	H	H	OC_6H_{13}	426	478	9.1	500
3	H	H	Br	425	477	9.1	501
4	H	H	CN	434	491	8.6	504
5	H	H	NO_2	450	514	7.4	499
6	H	CF_3	H	425	478	8.5	502
7	H	CN	H	425	480	6.7	490
8	H		H	427	480	9.3	489
9	H	$SO_2C_{10}H_{21}$	OC_3H_7	426	478	9.8	487
10	CN	H	H	445	508	8.3	524
11	CN	CF_3	H	451	519	7.1	531
12	CN	H	Cl	450	528	9.3	533

tion, the solids exhibit intense fluorescence, and again the red, non-fluorescent nitro-substituted OPV **5** is different.

This division into two groups holds also for the OPVs in solution. Both types (ring substitution in **1**–**9** and vinylene substitution in **10**–**12**) showed very similar UV–visible spectra with two small maxima at 305 and 360 nm and an intense maximum at 424–434 nm for the first group (except **5**) and at 445–451 nm for the second group. Exemplary spectra (OPVs **1, 5, 9** and **11**) are depicted in Fig. 1. It was found that *meta* substitution of the terminal rings with electron acceptors (6–8) results in small changes in the electronic spectra, whereas *para*-substitution (**4** and **5** and, more pronounced, the vinylene cyanides **10**–**12**) induces strong bathochromic shifts.

In the emission spectra of **1**–**4** and **6**–**9** the maximum of the fluorescence intensity was found in the range 483–504 nm, followed by a characteristic shoulder ($\Delta\lambda \approx 30$ nm) on the red side. This shoulder was lost in the emission spectra of the α-cyano-substituted OPVs **10**–**12** and the maxima were shifted to the red (524–533 nm). Compared with the other investigated OPVs, the fluorescence intensity of the dinitro compound **5** was about 0.01%. Two effects are responsible for the reduced intensity: the quenching of the fluorescence by the nitro groups and the bathochromic shift of the absorption spectrum ($\lambda_{max} = 450$ nm) leading to strong reabsorption of the emitted light.

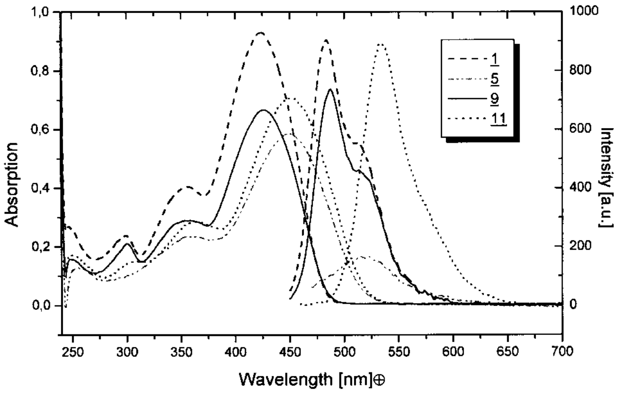


Figure 1. UV–visible and fluorescence spectra of selected OPVs

The introduction of electron-withdrawing substituents into the *meta* positions of the lateral rings offers the possibility of tuning the electron affinity of the chromophore with only slight changes in the electronic spectra (OPVs **6**–**9** compared with **1**). Birckner *et al.* investigated the electronic spectra of substituted 1,4-distyrylbenzenes[14] and observed strong bathochromic shifts of the absorption ($\Delta\lambda \approx 40$ nm) and emission ($\Delta\lambda \approx 70$ nm) upon introduction of cyano groups to the vinylene linkages. Additional electron donors increased the red shift of the absorption maximum, wheras the fluorescence maximum was preserved. Notable is compound **9**: the bathochromic shift of the fluorescence ($\Delta\lambda = 17$ nm compared with **1**) due to the terminal auxochrome alkoxy groups can be levelled out by the introduction of electron-withdrawing sulfones. The emission spectrum is shifted about 13 nm to the blue, close to OPV **1**. Combinations of this type, vicinal auxochrome and anti-auxochrome groups, offer the opportunity to fine-tune the emission properties and the electron affinity of the chromophore. Sulfones and 1,3,4-oxadiazoles are powerful electron acceptors with an additional binding site, useful for the introduction of solubilizing side-chains.

Changing the solvent from cyclohexane to dichloromethane, acetonitrile and ethanol caused shifts of the absorption maxima of less than 3 nm, but the extinctions were changed significantly: the extinction coefficients increased in the sequence ethanol, cyclohexane, acetonitrile for compounds with electron-withdrawing substituents (**7, 9, 11**), whereas this order was reversed for OPV **1**.

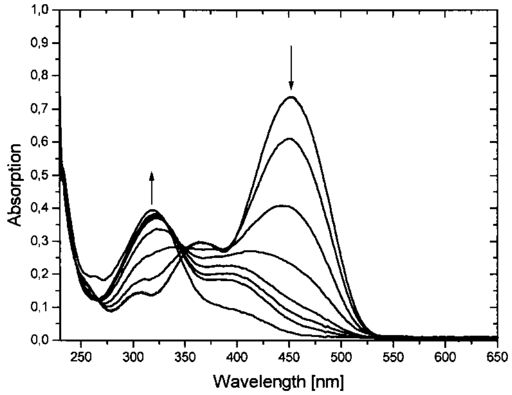


Figure 2. Irradiation of OPV **11** in cyclohexane

For use in electrooptical devices, a high photostability of the chromophore is required. OPV **11**, bearing two electron-withdrawing groups, was irradiated in different media with near-UV(NUV) (366 nm) and mid-UV-(MUV) radiation (254 nm). In cyclohexane, **11** was inert towards NUV, whereas MUV caused a uniform photoreaction with a decrease in the absorption maximum (451 nm), an isosbestic point at 352 nm and the build-up of a maximum at 320 nm (Fig. 2), indicating a *trans–cis* isomerization of one of the four vinylene linkages. Traces of acids are known to destroy oligo(2,5-dialkoxyphenylenevinylene)s in a slow dark reaction and very much accelerated by irradiation with NUV and even more pronounced, with MUV.[15] A solution of **11** in CH_2Cl_2 containing 0.5% trifluoroacetic acid was stable in the dark for prolonged times; irradiation with NUV caused a slow decomposition of the chromophore, accompanied by a small increase in the absorption at 301 nm. With MUV, the rate of the decrease in the absorption maximum was comparable to the rate observed in cyclohexane in the absence of acid, but the acid induced a different photochemical pathway, presumably by protonation of the excited chomophore and subsequent addition reactions.

Oligomeric aryl amines and polyvinylcarbazole are typical hole conducting compounds in electrooptical devices and amines are used as auxochrome groups for the colour tuning of conjugated compounds.[8,14] The photostability of **11** towards daylight and NUV was not influenced by the presence of triethylamine (5% in cyclohexane). Upon irradiation with MUV (254 nm), a slow photochemical reaction was observed. The rate of the decrease in the absorption maximum of **11** in the absence of triethylamine was about 10 times higher than in the presence of the base. The amine led to a different photochemistry, substantiated by increasing absorptions at 365-nm and much more pronounced at 311 nm. The initial step in this reaction might be a photochemical electron transfer process, as has been proposed for the addition of amines to stilbene.[16]

OPVs with five benzene rings and a variety of different substituents were prepared from a distyrylbenzene with two terminal carbaldehyde groups and benzyl phosphonates and benzyl cyanides. Whereas vinyl cyanides caused strong red shifts of the absorption and emission and are known to reduce the fluorescence quantum yields strongly, only small changes in the spectral features were observed when electron-withdrawing substituents were linked to the aromatic rings. An increase in the electron affinity of the chromophore by substitution with electron acceptors is probable and will be quantified by cyclic voltammetry.

REFERENCES

1. Burroughes JH, Bradley DDC, Brown AR, Marks RN, MacKay K, Friend RH, Burn PL, Holmes AB. *Nature (London)* 1990; **347**: 539–541.
2. Kraft A, Grimsdale AC, Holmes AB. *Angew. Chem.* 1998; **110**: 417–443.
3. Braun D, Heeger AJ. *Appl. Phys. Lett.* 1991; **58**: 1982–1984.
4. Greiner A, Heitz W. *Macromol. Chem., Rapid Commun.* 1988; **9**: 581–586.
5. Müllen K, Wegner G. *Electronic Materials: the Oligomer Approach*. Wiley-VCH: Weinheim, 1998; Martin RE, Diederich F. *Angew. Chem.* 1999; **111**: 1440–1469; *Angew. Chem., Int. Ed. Engl.* 1999; **38**: 1350–1377.
6. Brédas JL. *Adv. Mater.* 1995; **7**: 263–274.
7. Yang Z, Sokolik I, Karasz FE. *Macromolecules* 1993; **26**: 1188–1190; Yang Z, Hu B, Karasz FE. *Macromolecules* 1995; **28**: 6151–6154.
8. Stalmach U, Detert H, Meier H, Gebhardt V, Haarer D, Bacher A, Schmidt H-W. *Opt. Mater.* 1998; **9**: 77–81.
9. Yakovlev YuO, Zolin VF. *Synth. Met.* 1997; **91**: 205–206.
10. Greczmiel M, Pösch P, Schmidt H-W, Strohriegl P. *Macromol. Symp.* 1996; **102**: 371–380.
11. Greenham NC, Moratti SC, Bradley DDC, Friend RH, Holmes AB. *Nature (London)* 1993; **365**: 628–630.
12. Detert H, Schollmeier D. *Synthesis* 1999; 999–1004.
13. (a) Gill RE, van Hutten PF, Meetsma A, Hadziioannou G. *Chem. Mater.* 1996; **8**: 1341–1346; (b) Stalmach U, Detert H. *J. Prakt. Chem.* 2000; **341**: 10–16.
14. Birckner E, Grummt U-W, Rost H, Hartmann A, Pfeiffer S, Tillmann H, Hörhold H-H. *J. Fluoresc.* 1998; **8**: 73–80.
15. Stalmach U. *PhD Thesis*, Mainz, 1996.
16. Lewis FD, DeVoe RJ. *Tetrahedron* 1982; **38**: 1096.