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Quadrupolar donor–acceptor substituted oligo(phenylenevinylene)s—synthesis and solvatochromism of the fluorescence[†,‡]

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ABSTRACT: The electronic spectra of oligo(phenylenevinylene)s with five benzene rings and an acceptor–donor–acceptor substitution pattern were investigated. Although the absorption spectra are mostly unaffected by an increasing solvent polarity, both bathochromic shifts and reduced efficiencies of the fluorescence arise with the quadrupolar electronic structure. The chromophores with the lowest oxidation or reduction potentials are the most sensitive towards the environment. The synthesis of the centrosymmetrical oligomers was performed in a sequence of two two-fold Wittig–Horner olefinations. Copyright © 2004 John Wiley & Sons, Ltd.
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KEYWORDS: fluorescence; solvatochromism; cyclic voltammetry; oligo(phenylenevinylene)

INTRODUCTION

Organic compounds with extended π-systems, conjugated polymers, polymers with conjugated segments, and well defined oligomers have become an important class of electronic materials.[1–3] The application profile, based on their unusual semiconducting and luminescent properties, includes photoconductivity, non-linear optical devices, sensors, field effect transistors and light emitting diodes.[4] Phenylene, hetarylene, vinylene and ethinylene are the fundamental components of most of the materials investigated. Optimisation of the electrooptical properties of a given system and their adjustment to other materials in different devices is possible by choice of the conjugation length.[5,6] A more flexible approach is the introduction of (anti-)auxochromic groups, which strongly affect conductivity,[7] redox potentials and the band gap, often combined with improvement of the solubility, thermal and solid state properties.[3,8,9] Arylamines[10,11] and alkyloxy groups are the most important electron donating substituents, and cyanide and fluorine are widely used to enhance the electron affinity.[9,12–15]

The combination of donors and acceptors on a chromophore may result in non-linear optical properties,[16] such as solvatochromism, dual fluorescence, or high two-photon absorptivity.[17–19] Chromophores with a pronounced dipolar donor–acceptor substitution have been used as the active layer in photovoltaic cells.[20,21] The relative positions of donors and acceptors on a conjugated system are decisive for these characteristics, the simple shift of an (anti-)auxochrome to a neighbouring position can have dramatic effects, e.g. extensive quenching of the fluorescence.[22–24] We are interested in organic materials for electrooptical applications, such as monodisperse oligo(phenylenevinylene)s (OPVs) and the manipulation of their properties. Centrosymmetrical compounds with quadrupolar arrangements of donor and acceptor groups can be efficient and environment-dependent fluorophores,[25] and we have found two-photon absorption cross sections as high as $4.1 \times 10^{-46}\,\mathrm{cm}^4\,\mathrm{photons}^{-1}$.[19] Fluorophors with strong solvatochromic responses (shift of emission spectra or change of efficiencies) are attractive as fluorescent probes, e.g. for sensing applications for low-cost CCD spectrometers. Both non-linear optical processes, two-photon absorption and solvatochromism, are tuned by the strength and the position of donor and acceptor groups on a chromophore. This paper presents a comparative study of the fluorescence of OPVs with five rings and a pronounced acceptor–donor–acceptor structure.

SYNTHESIS

The synthesis of these symmetrical five-ring OPVs **1–11** (Scheme 1, Table 1) with electron donors on the central nucleus and acceptors attached to the lateral rings has

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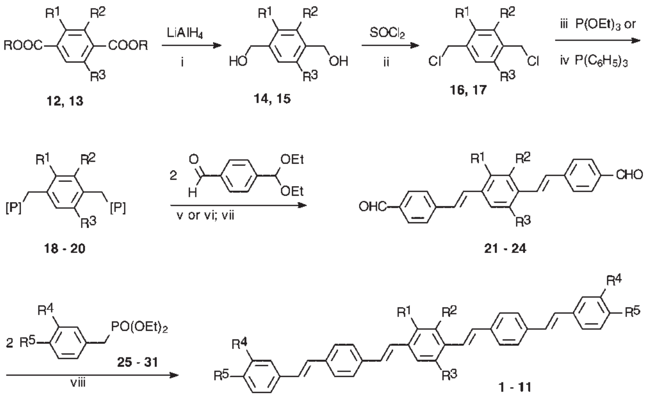

Scheme 1. Synthesis of centrosymmetrical OPVs. (i) $LiAlH_4$, ether, 35 °C, 4 h; (ii) $SOCl_2$, CH_2Cl_2, 0 °C, 20 h; (iii) $P(OEt)_3$, 165 °C, 4 h; (iv) CH_3CN, 80 °C, 24 h; (v) $[P] = PO(OEt)_2$: THF, KOtBu, 0 °C, 15 min; (vi) $[P] = (C_6H_5)_3P^+$: DMF, NaH, 0 °C, 2 h; (vii) HCl (2 M), 25 °C, 20 h; 57–84%; (viii) THF, KO*t*-Bu, 0 °C, 30 min, 33–92%

been perfomed via two two-fold Wittig–Horner reactions. The starting materials, donor-substituted bis(phosphonates) **18**–**20** or bis(phosphonium salt) **21** have been reported[24,26] or were prepared from the corresponding terephthalic diesters **12**, **13**. A reduction of these esters with $LiAlH_4$ followed by OH–chlorine exchange with thionyl chloride and Michalis–Arbusov reaction or alkylation of triphenylphosphine led to **20**, **21**. The distyrylbenzene dicarbaldehydes **22**–**25** were obtained in a two-fold olefination of the bifunctional **18**–**21** with mono-protected terephthaldialdehyde and subsequent hydrolysis of the acetals. The title compounds **1**–**11** were assembled in a second set of PO-activated olefinations of the dialdehydes **22**–**25** and acceptor-substituted benzyl phosphonates **26**–**32**. Flexible side chains attached to the central ring ensure good to excellent solubilities in common solvents and allow purification via chromatography followed by crystallisation from dichloromethane–methanol. The pure compounds were obtained in moderate (**4**, **6**, **7**, **8**) to good yields and form yellow to brick-red solids. The all-*trans* configuration of the vinylene linkages was confirmed by H-NMR spectroscopy.

Table 1. Substitution pattern of donor–acceptor substituted OPVs **1**–**11**

OPV	R^1	R^3	R^4	R^5	m.p. (°C)
1	C_6H_{13}	C_6H_{13}	H	CH_3	222
2	C_6H_{13}	C_6H_{13}	H	CN	228
3	OC_8H_{17}	OC_8H_{17}	H	CN	208
4	NRR′	NRR′[a]	H	CN	208
5	$R^1 = R^2 = OC_8H_{17}$	H	H	CN	150
6	C_6H_{13}	C_6H_{13}	H	NO_2	241
7	OC_8H_{17}	OC_8H_{17}	H	NO_2	216
8	OC_8H_{17}	OC_8H_{17}	NO_2	H	172
9	OC_8H_{17}	OC_8H_{17}	CF_3	H	168
10	OC_8H_{17}	OC_8H_{17}	OXD[b]	H	177
11	OC_8H_{17}	OC_8H_{17}	NO_2	OC_6H_{13}	155

[a] NRR′ = *N*-hexyl-*N*-propylamino.

[b] OXD = 5-heptafluorpropyl-1,3,4-oxadiazolyl-2.

ELECTROCHEMISTRY

Electron withdrawing or donating groups are (anti)-auxochromes on a chromophore and at the same time modulators of the electrochemical properties. A substitution of chromophore **1** with donors or acceptors will alter the electron distribution preferentially in the vicinity of the substituent and facilitate redox processes (Table 2). Oxidation potentials are reduced by about 0.17 V through changing alkyl to ether (**2** → **3**) and by a further 0.24 V upon replacing ether (**3**) by a secondary amine (**4**). [Cyclic voltammetry: 100 mV s^{-1}, tetrabutylammonium tetrafluoroborate (0.1 M) in CH_2Cl_2, WE: Pt disc, CE Pt wire, RE Ag/AgCl/LiCl/EtOH, 27 °C. All potentials are referenced to ferrocene/ferrocenium as the internal standard ($E_{1/2} = 0.352$ V).] Acceptors such as cyanides promote the reduction (**1** → **2**), but in this series only irreversible processes have been found. The nitro-group proved to be a much more powerful acceptor giving reversible reduction waves at low potentials, the reduction potentials are shifted about 0.9 V to lower potentials, whereas the influence on the oxidation potentials is only small. Some interaction of the donor-substituted centre of the conjugated system and the nitrobenzene subunits is visible: compare the reduction potentials of **6**, **7** and **8**. A donor on the same ring (**8** → **11**) shifts the reduction potential by about 0.16 V to a lower potential. Other acceptors such as trifluoromethyl (**9**) or 1,3,4-oxadiazole (**10**) are less effective, but are still stronger than the cyanide. By substitution of the five-ring OPV **1** with strong donors and acceptors the electrochemical bandgap can be reduced from 3 V to less than 2 V.

Table 2. Redox potentials of **1**–**11** in solution[a]

OPV	$E^0_{2,red}$(V)	$E^0_{1,red}$(V)	$E^0_{1,ox}$(V)
1		−2.08 p	0.98 r
2	−2.25 p	−2.01 p	0.94 r
3	−2.23 p	−2.02 p	0.77 p
4		−2.21 p	0.53 r
5			0.71 r
6	−2.25 p	−1.13 r	0.91 r
7	−1.92 p	−1.18 r	0.65 p
8	−2.18 p	−1.21 r	0.73 r
9	−2.29 r	−1.98 r	0.77 r
10	−2.09 p	−1.87 p	0.86 p
11	−2.29 p	−1.37 r	0.76 r

[a] p: peak potential, r: reversible wave, half-wave potential.

ELECTRONIC SPECTRA AND SOLVATOCHROMISM

Compound **1** represents the fundamental chromophore of all OPVs investigated here, five benzene rings are connected via four vinylene units and two side chains are attached to the central ring. Absorption ($\lambda_{\max} = 393$ nm) and fluorescence ($\lambda^{F}_{\max} = 449$ nm) are almost independent of the solvent polarity (solvatochromic shifts $\Delta\lambda = +4$ nm, $\Delta\lambda^{F} = +8$ nm) and excitation and emission are separated by large Stokes shifts ($\Delta\nu = 3173$–$3387\ \mathrm{cm^{-1}}$). [Electronic spectra were recorded at ambient temperature, using an MCS320/340 UV/Vis spectrometer (Zeiss) ($c \approx 10^{-5}\ \mathrm{mol\,l^{-1}}$) for absorption and an LS 50B (PerkinElmer) for fluorescence spectra ($c \approx 10^{-5}$–$10^{-8}\ \mathrm{mol\,l^{-1}}$).] Exchanging the terminal methyl groups for cyanides (**2**) results in a red shift of ≈ 10 nm of all spectra (Table 2). A quadrupolar substitution pattern (**3**) is obtained when the electronically almost neutral alkyl side chains in **2** are replaced by alkoxy chains. The donor effect of the oxygen combined with donor–acceptor interaction and aided by the improvement of conjugation due to reduced sterical hindrance on the central ring add to a red shift of 29 nm of the absorption maximum. As with **1** and **2**, the excitation spectra of **3** are almost independent of the solvent. In non-polar solvents, absorption and the strong fluorescence ($\Phi_F = 0.67$ in dioxane) are separated by comparably small Stokes shifts ($\Delta\nu = 2476$–$2757\ \mathrm{cm^{-1}}$), the Stokes shifts are substantially higher in CH_2Cl_2 or ethanol as the emission of **3** is positively solvatochromic. [Fluorescence quantum yields were obtained by comparison with quinine sulfate in 0.1 M H_2SO_4 ($\Phi_F = 0.577$) and corrected for the refractive index according to Lackowicz.] An even more pronounced acceptor–donor–acceptor structure and therefore further reduced excitation energy should result from the substitution of the ether groups in **3** by dialkylamines. Nevertheless, a hypsochromic shift (**4**: $\lambda_{\max} = 423$ nm, $\Delta\lambda = -10$ nm) is obtained. Although they are much stronger donors, the voluminous dialkylamines force the molecule to distort the adjacent dihedral angles, thus reducing the efficiency of the conjugation. Irradiated solutions of diamino-dicyano-OPV **4** emit light, the colour and the efficiency of the fluorescence (Fig. 1) are strongly dependent on the solvent.[28] Huge Stokes shifts ($\Delta\nu$ 4900–6500 $\mathrm{cm^{-1}}$) and moderate efficiencies ($\Phi_F = 0.3$–0.6) are obtained in non-polar solvents (cyclohexane, dioxane, toluene). In the polar solvents dichloromethane and ethanol, this positive solvatochromic, low-energy fluorescence is quenched. A negative solvatochromic, inefficient ($\Phi_F \approx 0.06$–0.03), short-wavelength emission is observed instead. As with **4**, the absorption maximum of **5** is shifted to a higher energy compared with its isomer **3**, an effect known from dyes and conjugated polymers.[8,29]. Except for the hypsochromism of excitation and emission, the optical properties of **5** are close to **3** (Table 3).

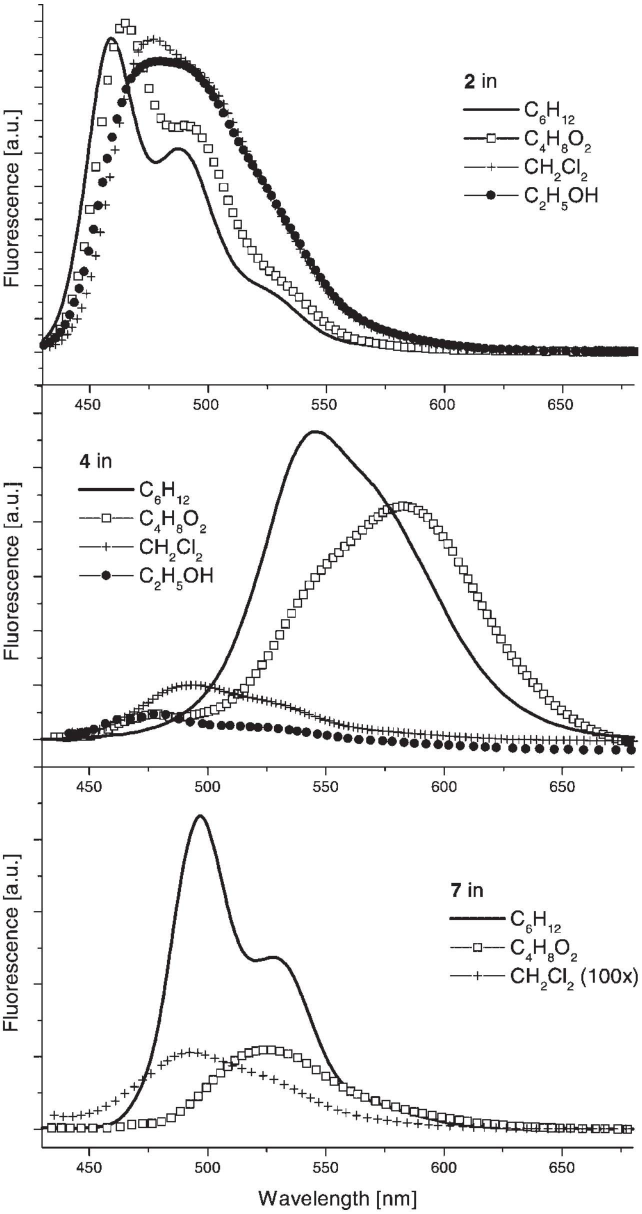

Figure 1. Emission spectra of **2**, **4** and **7** in different solvents

Cyanides have been used widely as acceptors for light-emitting chromophores,[8,12,13] but the nitro group, which is an even stronger acceptor has received less attention.[30] The small number of fluorescent nitro-compounds has been attributed to fluorescence quenching via predissociation[31] and to the existence of low lying n–π^* states and fast inter-system crossing.[32] Replacing the cyanides in **2** and **3** by nitro groups gives OPVs **6** and **7**. The higher strength of the nitro acceptor results in bathochromic shifts of the absorption maxima and of the fluorescence. Solvents have only minor effects on the excitation spectra but a strong impact on the emission: their fluorescence efficiencies in cyclohexane and toluene are moderate to high ($\Phi_F = 0.4$–0.8) but negligible in dichloromethane or ethanol ($\Phi_F < 0.01$). As is observed with amino–cyano

Table 3. Optical spectra of OPVs **1–11** in different solvents

	Cyclohexane		1,4-Dioxane		Toluene		Dichloromethane		Ethanol	
	λ_{max} (nm)	λ^f_{max} (nm) $\Delta\nu^a$ (cm^{-1})	λ_{max} (nm)	λ^f_{max} (nm) $\Delta\nu$ (cm^{-1})	λ_{max} (nm)	λ^f_{max} (nm) $\Delta\nu$ (cm^{-1})	λ_{max} (nm) $\log\varepsilon$	λ^f_{max} (nm) $\Delta\nu$ (cm^{-1})	λ_{max} (nm)	λ^f_{max} (nm) $\Delta\nu$ (cm^{-1})
1	393	449 3173	395	453 3241	395	456 3387	397 4.939	457 3307	393	452 3321
2	404	459 2997	405	465 3186	405	466 3232	407 4.920	476 3561	409	480 3617
3	433	485 2476	434	493 2757	434	493 2757	434 4.928	540 3434	433	517 3752
4	423	535 4949	423	583 6488	425	576 6168	425 4.836	495 3327	420	479 2932
5	408	455 2531	411	460 2591	413	461 2521	413 5.013	473 2981	409	483 3746
6	413	472 3026	422	506 3934	422	489 3247	424 4.924	481 2795	423	481 2851
7	442	497 2504	445	525 3424	448	514 2866	449 4.955	494 2029	446	493 —
8	423	478 2730	428	486 2788	430	476 2247	429 4.952	471 2079	430	474 2159
9	422	475 2644	424	481 2795	425	483 2825	426 4.914	489 3024	421	482 3006
10	423	478 2720	425	483 2825	429	486 2733	428 4.916	492 3039	423	484 2979
11	423	476 2632	424	483 2881	425	484 2869	427 4.824	471 2188	427	482

[a] $\Delta\nu$ = Stokes shift.

OPV **4**, initial bathochromism of the fluorescence (cyclohexane → dioxane: ≈ 30 nm) is followed by a very weak and hypsochromically shifted emission from solutions in ethanol or CH_2Cl_2.

A change in the positions of the nitro groups in **7** from the *p*-position to the neighbouring *m*-positions gives OPV **8**. Braking the conjugation between donors and acceptors shifts absorption and emission about 20 nm to the blue (in cyclohexane). A solvent-independent absorption and, as for **4**, **6** and **7** an initially positive and then inverted solvatochromism adds to a switch of the fluorescence efficiency from moderate in hydrocarbons ($\Phi_F = 0.35$) to low ($\Phi_F = 0.05$) in dioxane, CH_2Cl_2, or ethanol. The latter results only from the nitro group, their replacement by other electron withdrawing groups such as CF_3 (**9**) or 1,3,4-oxadiazol (**10**) results in highly fluorescent OPVs ($\Phi_F \approx 0.7$), in non-polar as well as in polar solvents. The mitigation of the quadrupolar electronic structure of brick-red **8** by attaching alkoxy donors to the nitrobenzene subunits gives orange **11**, with nearly identical spectra in solution. Although the spectra of **11** are essentially independent of the solvent, the fluorescence quantum yield is not. Efficient in hydrocarbons ($\Phi_F \approx 0.5$), the fluorescence declines in dioxane or dichloromethane ($\Phi_F \approx 0.1$) and vanishes in alcohol ($\Phi_F = 0.001$).

The optical properties of the fundamental chromophore **1** are virtually unaffected by solvent polarity. Quadrupolar substitution of the chromophore with electron acceptors and donors shifts the absorption spectra to lower energies, these shifts are mainly controlled by the increasing acceptor or donor strength of the substituents [e.g. **1** → **2** → **6**: λ_{max} (C_6H_{12}) = 393 nm, 404 nm, 413 nm]. Although dialkylamines are much stronger donors than ether groups, an exchange of the latter by dialkylamines (**3** → **4**) provokes a hypsochromic shift. This can be attributed to reduced conjugation along the backbone due to the steric effect of the voluminous dialkylamines. Contrary to dipolar substituted oligomers,[32] solvatochromism of the absorption of quadrupolar OPVs **2–11** is only small ($\Delta\lambda = 11$ nm).

Whereas the solvent effects on the absorption spectra are only small, the fluorescence is influenced strongly. The former can be attributed to similar stabilisation of ground states and Franck–Condon states by polar solvents. In the excited states it is likely that a stabilisation via intramolecular charge transfer (ICT) from strong donors (OR, NR_2) to strong acceptors (CN, NO_2) occurs, followed by a reorganisation of the solvent cage. Increasing solvent polarity stabilises these ICT excited states relative to the ground-state molecules resulting in bathochromic shifts of the fluorescence. Additionally, the lowered energies of the ICT states may lead to severe fluorescence quenching.

This explains the higher fluorescence efficiency of **3** in polar solvents compared with **4** or **7** where either the strength of the donor or of the acceptor are enhanced. In particular, nitro-substituted chromophores (**6**, **7**, **8**, **11**) show the strong impact of increasing solvent polarity on the fluorescence efficiency. Though luminescent in hydrocarbons, their fluorescence is almost completely quenched in CH_2Cl_2 or ethanol. Cyclic voltammetry revealed that the reduction potential is shifted about 0.8 V to lower potentials, much more than the cyanide-induced shift of 0.07 V. This extraordinary high ability of NO_2 to accept electrons favours the formation of ICT excited states, the stabilisation of these charged species in polar solvents facilitates non-radiative processes and quenches the fluorescence. Addition or omission of donor groups modulates the band gap (**6**: 2.04 V, **8**: 1.94 V, **11**: 2.13 V) but the optical properties are mainly controlled by the nitro group. The effects of other acceptors, oxadiazole, CF_3 and CN on the band gap are much smaller ($\Delta E = 2.9$–2.7 V). This less pronounced stabilisation of the negative charge correlates with a lower sensitivity of the excited states towards the environment. Although some stabilisation of the excited states by solvent polarity is visible as positive solvatochromism of the fluorescence, it is not sufficient to provoke extensive fluorescence quenching.

Amino-cyano OPV **4** appears to be a special case. Although the difference in the redox potentials ($\Delta E \approx 2.7$ V) is in the range of the band gap of cyano–alkoxy OPVs, the impact of solvent polarity on the excited state and its consequences on the fluorescence resemble to the properties of nitro-OPVs but with a much smaller band gap. In addition to the electronic effects of the withdrawing cyanide and strong donor dialkylamine (**2** → **4**: $\Delta E_{ox} = -0.41$ V) the steric effect of the big NR_2 has to be taken into account. Compared with **2** and **3** with weaker but less voluminous donors, the absorption of **4** is shifted to higher energies, but the excited state is strongly stabilised even in non-polar solvents. The huge Stokes shift ($\Delta\nu = 4949\ \mathrm{cm}^{-1}$ in C_6H_{12}) can be attributed to a severe change of the geometry resulting in a distinctly improved conjugation along the π-system and interaction of electron donating and withdrawing groups in the excited state. The limited degree of conjugation in the ground state and its change in the excited state restricts a correlation of the electrical and optical properties of **4** and the comparison with the other quadrupolar OPVs.

CONCLUSION

A straightforward synthesis of quadrupolar substituted oligo(phenylenevinylene)s has been described. Alkyl, alkoxy and dialkylamino groups on the central ring improve solubility and reduce the oxidation potential. Acceptors on the terminal rings, CN, CF_3 and NO_2, provoke a quadrupolar electronic structure and reduced band gap. This results in positive solvatochromism of the emission. With dialkylamine as the donor or acceptor nitro the highest impacts on the fluorescence have been observed, strong red shifts and positive solvatochromism, but vanishing efficiencies in polar solvents, including the anomalous solvent dioxane.[18] Compared with the moderate acceptors CN or CF_3, the powerful NO_2 strongly facilitates the formation of ICT excited states and their non-radiative decay. Although the electrical properties of dialkylamino OPV **4** are closer to the alkoxy-analogues, the effect of solvent polarity on the emission is similar to the nitro-substituted OPVs. Excitation results in extensive alteration of the geometry prohibiting a correlation of the band gap and optical properties of the excited state. The solvatochromism and preliminary experimental results with **3**, **7** suggest high two-photon absorptivities (Z. Kotler, Beer-Sheva, unpublished work).

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