Pergamon

SCIENCE DIRECT®

Tetrahedron Letters 44 (2003) 1915–1918

TETRAHEDRON
LETTERS

The effect of 2,2-dicyanovinyl groups as electron acceptors in push–pull substituted oligo(1,4-phenylenevinylene)s

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Received 5 October 2002; accepted 7 January 2003

Abstract—The newly synthesized oligo(1,4-phenylenevinylene) series **2a**–**d** with bis(2-hexyloctyl)amino groups as electron donors and 2,2-dicyanovinyl groups as electron acceptors represents conjugated oligomers with strong push–pull effects. Due to the decrease of the intramolecular charge transfer with increasing numbers of repeat units (n = 1–4), the long-wavelength transition shows a particularly great *hypsochromic* shift for the extension of the chromophore. © 2003 Elsevier Science Ltd. All rights reserved.

Oligo(phenylenevinylene)s (OPV) attract a lot of attention, because of their excellent properties as photoconductors and electroluminophores; moreover, various applications in the field of nonlinear optics (NLO) are known.[1–11] Large second order hyperpolarizabilities have been found for compounds with terminal donor–acceptor substitution.[2,11] Normally, OPVs show a monotonous *bathochromic* shift of the absorption and the fluorescence maxima with increasing numbers n of repeat units. The convergence for $n \rightarrow \infty$ can be predicted on the basis of exponential functions.[8,10,12] However, we recently established the unexpected result, that a monotonous *hypsochromic* effect can occur with increasing numbers n, provided that the intramolecular charge transfer (ICT) is strongly reduced with growing extension of the chromophore. An example in the OPV series was found for terminal dialkylamino and nitro groups.[13] This surprising behaviour encouraged us to look for other OPV systems with strong push–pull effects.

Starting with the aldehydes **1a**–**d**, we prepared the 2,2-dicyanovinyl derivatives **2a**–**d** by the condensation reaction with malononitrile in boiling $CHCl_3$ (Scheme 1). The introduction of a third cyano substituent on the vinyl group proved to be very difficult. The addition of HCN (**2a**→**3a**) works almost quantitatively and with the regioselecivity expected for a nucleophilic addition; however, the subsequent oxidation (dehydrogenation) failed under many reaction conditions. Traces of **4a** could be detected in the process with $Pb(OAc)_4$ in CH_2Cl_2. Finally, we succeeded with a radical process with NBS in the presence of azoisobutyronitrile (AIBN). The solid target compound **4a**[14] was obtained in moderate yields; until now the reaction could not be applied to higher OPV systems.

The highly branched dialkylamino group in **1a**–**d**, **2a**–**d**, **3a** and **4a** guarantees a reasonably good solubility in chlorinated hydrocarbons as CH_2Cl_2, $CHCl_3$ and CCl_4.

In comparison to the purely donor substituted compound **5a** (n = 1), a significant bathochromic shift is observed for the (E)-stilbenes with terminal donor–acceptor substitution (Scheme 2 and Table 1). The effect increases from the yellow cyano compound **6a** (n = 1) via the orange formyl compound **1a**, the red nitro compound **7a** (n = 1), and the dark red vinyl system **2a** to the deep blue compound **4a**.

Obviously, the intramolecular charge transfer (ICT) plays a dominant role in this series. Therefore one can expect for the compounds **2a**–**d** a hypsochromic effect with increasing numbers n. The extension of the conjugation should not be able to compensate the decrease of ICT. Figure 1 illustrates the result of the UV/vis measurement in $CHCl_3$. The series **2a**–**d** exhibits in fact a strong hypsochromic shift with increasing numbers n of repeat units. The effect is even more pronounced as in the nitro series **7a**–**d**. In contrast to the 2,2-dicyanovinyl group as strong acceptor, the cyano group is a relatively weak acceptor and permits a bathochromic effect with growing numbers n. Thus Figure 1 comprises the

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Keywords: oligomers; conjugation; push–pull effect; UV/vis spectra.

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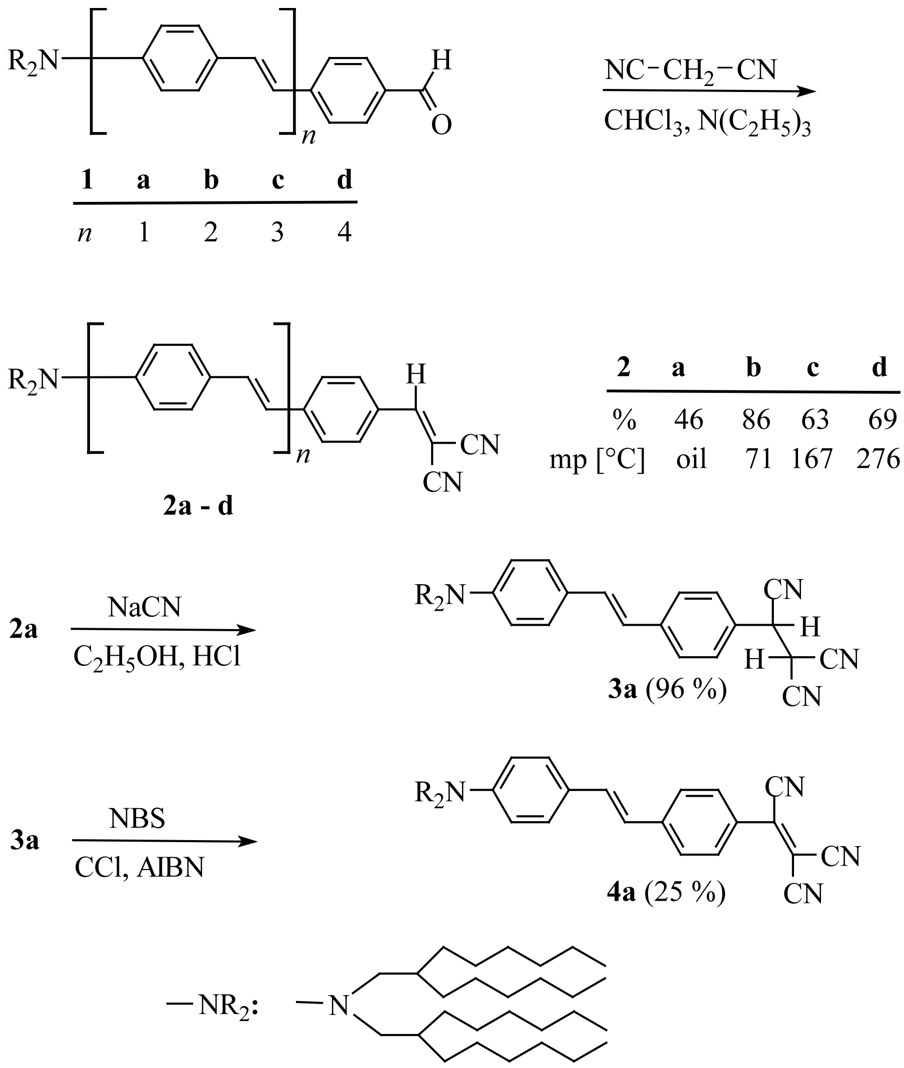
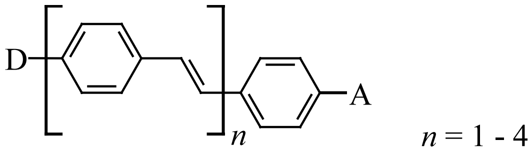
doi:10.1016/S0040-4039(03)00120-5



Scheme 1. Transformation of the OPV aldehydes **1a**–**d** to the 2,2-dicyanovinyl derivatives **2a**–**d** and of **2a** to the tricyanovinyl compound **4a**.



	5	**6**	**1**	**7**	**2**	**4a** ($n = 1$)
A	H	CN	CHO	NO_2	$CH{=}C(CN)_2$	$C(CN){=}C(CN)_2$
D	$N[CH_2{-}CH(C_6H_{13})_2]_2$					

Scheme 2. OPVs with terminal donor–acceptor substitution.

total behaviour of push–pull substituted OPVs, namely hypsochromic and bathochromic OPV series and the formyl series, in which the absorption maxima are almost independent of the extension of the π system (chromophore).

The characterization of the members of the novel OPV series **2** by ^{1}H NMR data is summarized in Table 2. A complete correlation of the ^{13}C NMR signals of **2a** was achieved by heteronuclear shift correlation measurements. The result is shown in Figure 2.

Table 1. Long-wavelength absorption maxima of donor–acceptor substituted (*E*)-stilbenes. (Measurement in $CHCl_3$)

Compound	**5a**	**6a**	**1a**	**7a**	**2a**	**4a**
λ_{max} [nm]	366	401	423	461	525	670
log ε	4.3	4.3	4.3	4.7	4.5	4.6

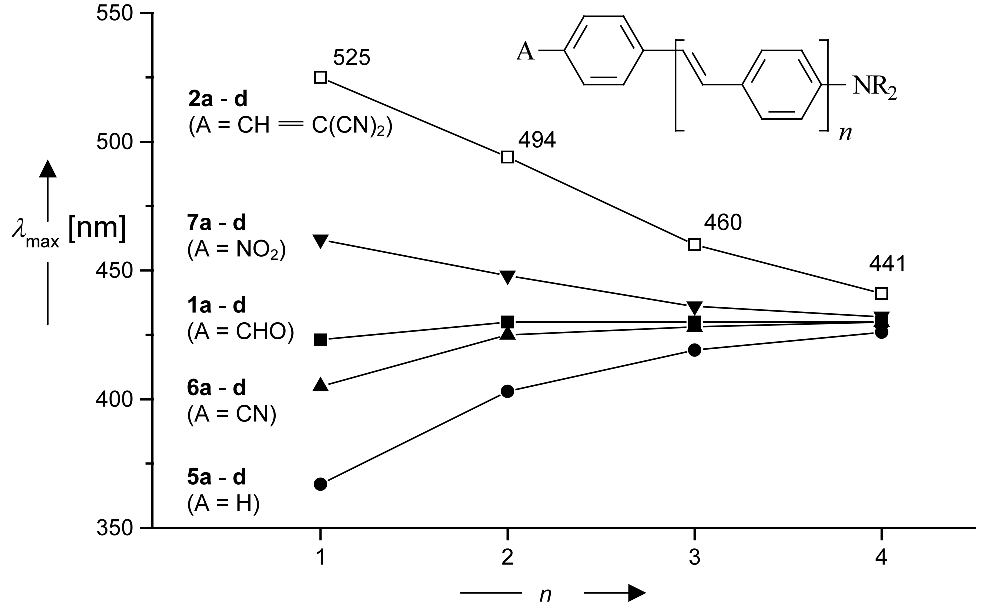


Figure 1. Long–wavelength absorption maxima of the OPV series **2a–d** (□) in comparison to the OPV series **1a–d**, **5a–d**, **6a–d** and **7a–d**.[15] (Measurement in $CHCl_3$).

Table 2. ^{1}H NMR data of the compounds **2a–d** (δ values in $CDCl_3$ with TMS as internal standard)

CH_3 (t, 12 H)	0.87±0.01
CH_2 (m, 40 H)	1.24±0.01
CH (m, 2 H)	1.83±0.01
N–CH_2 (d, 4 H)	3.22±0.01
CH=CH (AB, 2 H) ^3J=(16.2±0.2) Hz	6.85–7.28
CH=C$(CN)_2$ (s, 1 H)	7.66±0.03
C_6H_4	
Donor side (AA′BB′, 4 H)	6.63±0.01/7.34±0.02
Acceptor side (AA′BB′, 4 H)	7.58±0.04/7.87±0.03
Middle (AA′BB′, 4 H)	7.45±0.01/7.48±0.02
Middle (s, 4 H)	7.51±0.02

The donor–acceptor interaction is diminished, when the OPV chain is extended. Consequently, the δ values of the C atoms in *para* position to the donor group are increased and the δ values of the C atoms in *para* position to the acceptor group are decreased. Moreover, the high polarization of the olefinic double bond is strongly reduced; the $\Delta\delta$ difference, which amounts to 12.8 ppm in **2a**, is for the two terminal double bonds in the OPV scaffold reduced with increasing chromophore length to 6–7 ppm. A complete characterization of the new compounds by elemental analyses, NMR and MS data shall be given in a full paper.

Interestingly the absorption of push–pull polyenes with terminal 4-dibutylaminophenyl and dicyanovinyl groups shows a bathochromic shift for increasing numbers of repeat units.[16] Obviously the structure of the conjugated chain between donor and acceptor groups has a decisive influence.

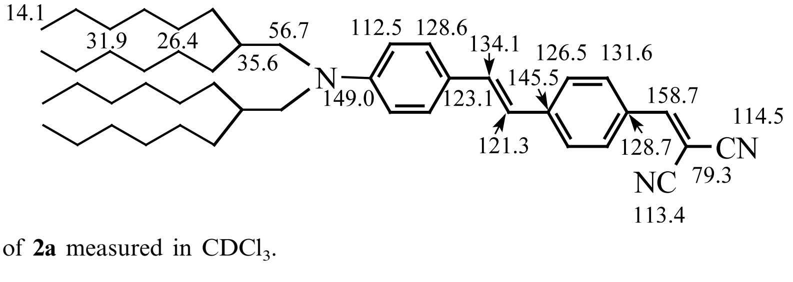


Figure 2. ^{13}C NMR data of **2a** measured in $CDCl_3$.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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14. The crude product **3a** can be used for the preparation of **4a** in boiling CCl_4. Column chromatography [SiO_2, hexane/toluene (7:3)] gives a blue solid, which start to decompose above 200°C. ^1H NMR data of **4a**: $\delta = 0.86$ (t, 12 H, CH_3), 1.24 (m, 40 H, CH_2), 1.83 (m, 2 H, CH), 3.24 (d, 4 H, NCH_2), 6.63/7.40 (AA′BB′, 4 H, N–C_6H_4), 6.88/7.30 (AB, $^3J = 16.0$ Hz, olefin H), 7.58/8.03 (AA′BB′, 4 H, C_6H_4). FD-MS 689 ($M^{+\bullet}$, 100%).
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