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From Donor and Acceptor Substituted *meta*- and *para*-Xylenes to *para*-Quinodimethanes and Poly(*meta*-phenylenevinylene)s [1)]

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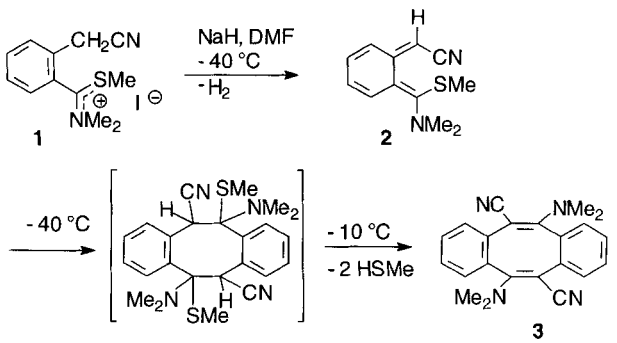
Abstract. *Ortho*-, *meta*- and *para*-xylenes **1**, **13a**, **13b** and **13c**, with donor and acceptor substituents at the α- and α' positions, lead to a remarkable variety of intermediates and reaction products after deprotonation of the benzylic proton. Thus, the reaction of *para*-(cyanomethyl)dialkyl[(methylthio)phenylmethylene]ammonium tetrafluoroborates **13a** and **13b** with sodium hydride affords the *para*-quinodimethanes **14a** and **14b**. Poly(*meta*-phenylenevinylene) **14c** can be obtained when starting from **13c**. We report the synthesis of *para*-quinodimethanes **14a** and **14b** and poly(*meta*-phenylenevinylene) **14c** and describe a successive approach towards *meta*-phenylenevinylenes of definite length **16b** and **17b** starting from **12d**. Moreover, we compare the stability and reactivity of *para*-quinodimethane **14a** and **14b** with those of the *ortho*-quinodimethane **2** and we focus on the characterization of the resulting donor and acceptor substituted compounds.

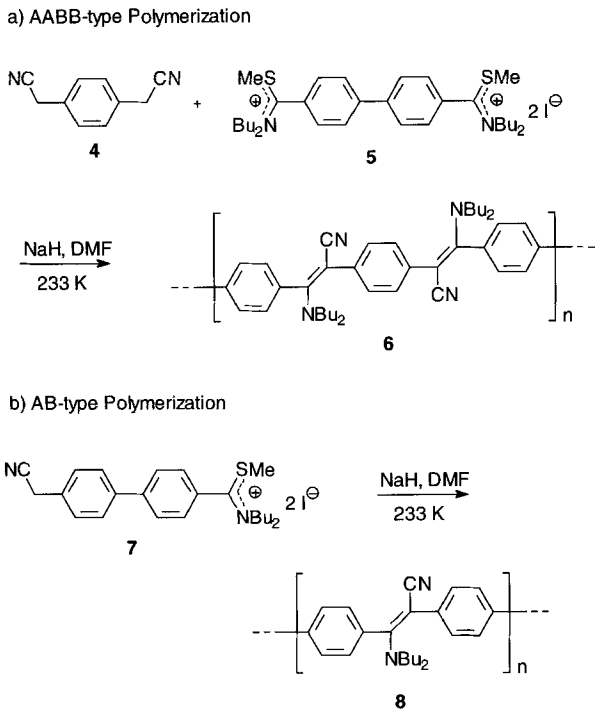
Quinodimethanes were investigated in detail in the past [1–10], whereby the characterization of their structures was hindered by their high reactivity. For instance, the existence of unsubstituted *para*-quinodimethane could only be proven at 77 K by UV- and IR-spectroscopy [10]. Nevertheless, it is possible to improve the stability of quinodimethanes by introducing alkyl chains in 2,6-positions at the phenylene ring [6] or by push-pull stabilization *via* donor and acceptor substituents. A well known example of this class is the 7,7,8,8-tetracyanoquinodimethane (TCNQ) [5]. Donor and acceptor substituted *ortho*-quinodimethanes have also been studied by Gompper *et al.* [1–2]. The authors describe the deprotonation of *ortho*-(cyanomethyl)dimethyl[(methylthio)-phenylmethylene]ammonium iodide (**1**) at 223 K (with sodium hydride or potassium *tert*-butoxide) [1], providing *ortho*-quinodimethane **2**, which is stable until 253 K (Scheme 1). Upon warming the solution to about 260 K, dimerization of *ortho*-quinodimethane **2** takes place, methanethiol is eliminated and 5,11-dicyano-6,12-bis(dimethylamino)dibenzo-[*a*,*e*]cyclooctatetraene (**3**) can be isolated in 50% yield.

In a similar approach, we were able to couple dianions of type **4** with dications of type **5** and, after elimination of methanethiol, we obtained new poly(arylenevinylene)s with donor and acceptor substituents at each double bond, as for example **6** (Scheme 2 (a)) [11]. According to this investigation, we considered polymerizing not only AA-(dication) and BB-(dianion) building blocks, but also introducing AB-compounds, combining cation- and anion-functions in one monomer. In fact, we were able to polymerize monomer **7**. The latter contains a biphenylylene spacer between the anionic and cationic reaction centers, which inhibits an annihilation of the charges. Accordingly, we could obtain the polyarylenevinylene **8** (Scheme 2 (b)) [11].



Scheme 1 Synthesis of donor and acceptor substituted *ortho*-quinodimethane **2** and subsequent dimerization to cyclooctatetraene **3**

[1)] Presented in part at the third conference on iminium salts, Stimpfach-Rechenberg (Germany), September 17–19, 1997

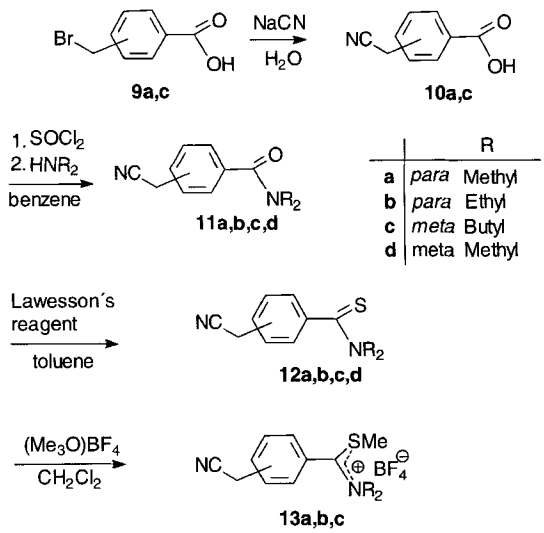


Scheme 2 AABB-type (a) and AB-type (b) polymerization routes for the synthesis of donor and acceptor substituted poly(*para*-phenylenevinylene)s **6** and **8**

In this article we describe the synthesis of *meta*- and *para*-xylenes **13a**, **13b** and **13c**, which constitute isomers of *ortho*-(cyanomethyl)dimethyl[(methylthio) phenyl-methylene]ammonium iodide (**1**), and test their suitability for the synthesis of oligomers and polymers. Firstly, we consider compounds **13a** and **13b** with regard to *para*-quinodimethane formation and subsequent polymerization, and in a following step, we discuss the synthesis and polymerization of the *meta*-bifunctional ammonium salt **13c**.

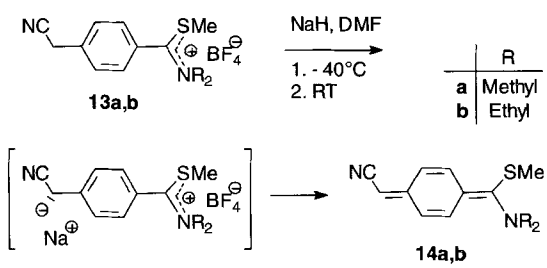
Results and Discussion

For the formation of *para*-quinoid π-systems, the ammonium salts **13a** and **13b** were chosen as starting compounds, which differ only in the alkyl substituents (methyl (**13a**), ethyl (**13b**)) at the ammonium-nitrogen. The synthesis of these ammonium salts succeeds in good yields in four steps (Scheme 3): Starting from *para*-(bromomethyl)benzoic acid (**9a**) with sodium cyanide in water, it is possible to synthesize *para*-(cyanomethyl) benzoic acid (**10a**) in 79% yield. After treatment of **10a** with thionyl chloride in benzene, we obtain the acid chloride which can be converted with dimethyl- or diethylamine in benzene into the corresponding amides (**11a** and **11b**) in good yields (85% and 72%). The reaction of **11a** and **11b** with Lawesson's Reagent (4-methoxyphenylthionophosphine sulfide dimer) in toluene under reflux leads to the thioamides **12a** and **12b**, which can be purified by column chromatography (65 and 70% yield, respectively). In a final step, the ammonium salts **13a** and **13b** can be obtained by methylation with trimethyloxonium tetrafluoroborate in dichloromethane at room temperature in quantitative yields.



Scheme 3 Synthesis of *ortho*-, *meta*- and *para*-xylenes **13a**, **b**, **c**, starting from *meta*- and *para*-(bromomethyl)benzoic acid (**9a,c**)

The deprotonation reactions of **13a** and **13b** with sodium hydride in dimethylformamide are carried out in deuterated DMF and observed by ^1H NMR spectroscopy (Scheme 4). This approach also allows characterization of less stable intermediates at low temperatures. For the investigation of the formation of *para*-quinodimethane **14a**, **13a** is placed in an NMR tube in DMF and cooled to 223 K. After addition of two equivalents of sodium hydride, a change of the color from colorless to yellow can be immediately observed, which is a possible hint for a *para*-quinodimethane structure.



Scheme 4 Formation of the donor and acceptor substituted *para*-quinodimethanes **14a** and **14b**

Convincing evidence for the formation of *para*-quinodimethane, 3-(cyanomethyl)-6-(dimethylaminomethylthiomethylene)-1,4-cyclohexadiene (**14a**), is provided by the ^{1}H NMR spectrum (Figure 1). It is known from the literature, that the formation of a quinoid structure is accompanied by a shift of the NMR signals to higher field [8, 9]. Accordingly, the signals of the aromatic protons (Ha, Ha', Hb, and Hb') of **13a** appear as doublets at δ/ppm = 8.01 and 7.55, those of **14a** as four doublets at δ/ppm = 7.29, 7.15, 6.42 and 6.12 (Figure 1). The signal of the benzylic proton of **14a** (δ/ppm = 3.25) is shifted by 1.2 to higher field as compared to the signal of the benzylic protons of **13a** (δ/ppm = 4.45). To investigate the thermal stability of **14a**, the sample is warmed up in 10 K steps. Surprisingly, we observe that the donor and acceptor substituents are able to stabilize the *para*-quinodimethane up to a temperature of 353 K. Warming to temperatures above 353 K gives a number of ^{1}H NMR signals which broaden upon further warming and finally, unidentified decomposition products occur, however, phenylenevinylene formation, as in the case of the *ortho*-quinodimethane **2**, is not observed.

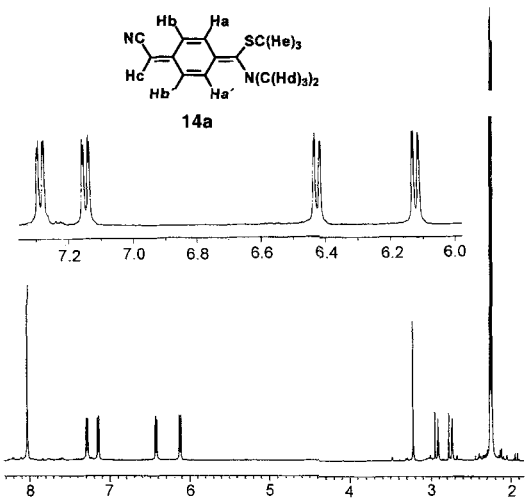


Fig. 1 ^{1}H NMR spectrum (500 MHz, DMF-d_7, 223 K) of **14a**

By carrying out the analogous experiment at 223 K in an NMR-tube with **13b**, we also obtain a quinoid structure. Here, the four doublets that belong to the aromatic protons appear at δ/ppm = 6.92, 6.82, 6.36, and 6.05. While raising the temperature from 223 K to room temperature, the shape of the four aromatic signals changes from doublets to broad singlets which is shown in Figure 2. Remarkably, in this case, further warming leads to a shift of these signals. As a result, those of Ha and Ha' coalesce at 323 K to one doublet at δ/ppm = 6.87 and those of Hb and Hb' coalesce at 338 K to one broad signal at δ/ppm = 6.23. Obviously, above room temperature isomerization occurs by rotation about the *para*-quinodimethane double bonds. With the aid of NOE (Nuclear Overhauser Effect) difference measurements at room temperature, it is possible to relate the signals at lower field to the aromatic protons neighboring the amino- and methylthiofunctions (Hb, Hb'). We conclude, that, due to different double bond strength on both *para*-quinodimethane sides, the mobility of the methylene units with amino- and methylthio-substituents is higher than that of the cyanomethylene unit. If the reaction mixture is cooled from 373 K to room temperature, the *para*-quinodimethane ^{1}H NMR spectrum of **14b**, containing four doublets, is again observed, which is proof of the stability of this compound. Further heating leads to decomposition products, and no phenylenevinylene formation is seen.

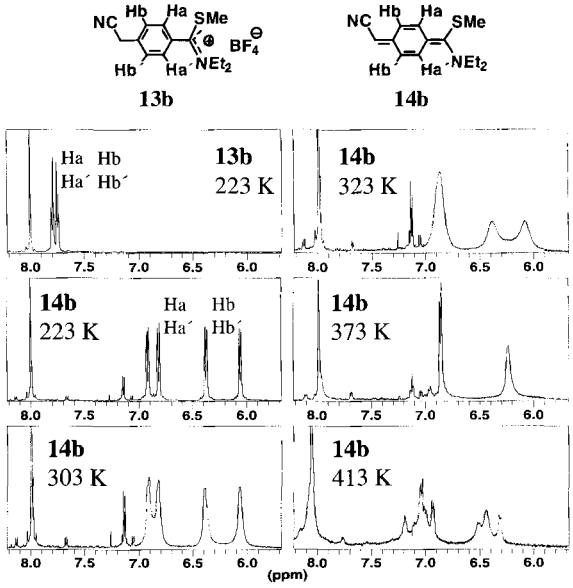
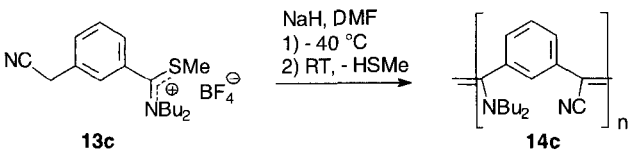


Fig. 2 ^{1}H NMR spectra (500 MHz, DMF-d_7) of **13b** (223 K) and **14b** (223, 303, 323, 373 and 413 K)

It is evident that the reaction products of sodium hydride and the xylenes **1**, **13a** and **13b**, depend on the *ortho*- and *para*-positions of the reactive groups. Whereas the *para*-quinodimethanes **14a** and **14b** are stable over a large temperature range, the donor and acceptor substituted *ortho*-quinodimethane **2** of Gompper *et al.* represents an intermediate that dimerizes easily under formation of the phenylenevinylene **3**. Obviously, the ground state of **14a** and **14b** is only represented by the charge compensated *para*-quinoid structure, due to the donor and acceptor stabilization, and further reactions are prevented. In comparison, the lower stability of the *ortho*-isomer **2** can be attributed to the steric hindrance of its substituents.

A quinodimethane structure should become impossible by separation of the nucleophilic and electrophilic reaction center *via* a *meta*-phenylene unit. In this case, a compensation of the charges could only be described through a biradical structure. We consider *meta*-(cyanomethyl)dibutyl[(methylthio)phenyl-methylene]ammonium tetrafluoroborate (**13c**) as representative for the investigation of the reactivity of donor and acceptor substituted *meta*-xylenes. After deprotonation with sodium hydride in deuterated DMF at 223 K, the color changes from bright yellow to brown (Scheme 5). A great variety of signals occurs in the ^{1}H NMR-spectrum which merge to broad unstructured signals after warming to room temperature. More information can be obtained from Field-Desorption-Mass-Spectrometry (FD-MS) of the crude reaction product. Here, the distances of the observed signals correspond exactly to the molecular weight of one repetition unit of **14c**, which is 254.2 g/mol, and macromolecules with up to ten repetition units are detectable. The transformation of **13c**, when performed on a preparative scale, affords the dibutylamino- and cyano- substituted poly(*meta*-phenylenevinylene) **14c** as bright yellow, glassy powder in 65% yield.



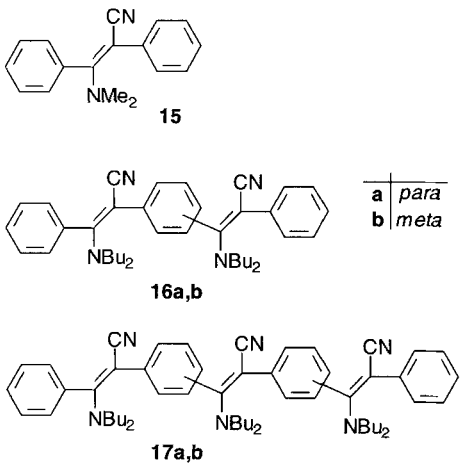
13c **14c**

Scheme 5 Synthesis of poly(*meta*-phenylenevinylene) **14c**

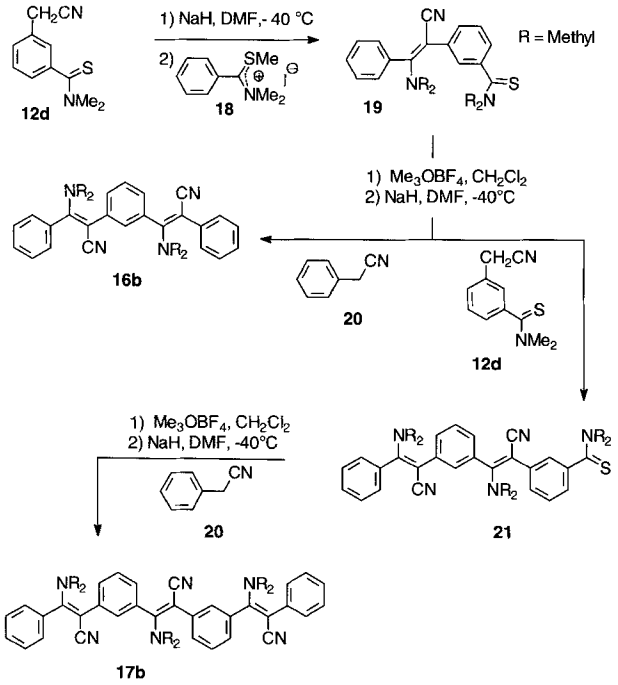
A common method for the characterization of polymers is gel-permeation-chromatography (GPC) analysis. With DMF as eluent and using polystyrene calibration, an average degree of polymerization of 10 is obtained. However, the shape of the elugramm indicates adsorption effects of the very polar material on the column so that the obtained molecular weight data is not reliable. We already observed similar problems regarding molecular weight determination with polymers **6** and **8** which possess related structures to **14c** [11]. Because of this, we did not spend further effort on the determination of the molecular weight. Moreover, it could be shown, that the optical properties and the processability of donor and acceptor phenylenevinylenes do not change markedly with increasing polymer length [11]. Further investigation of polymer **14c** reveals, that it is soluble in most organic solvents. By applying the spincoating technique it is possible to obtain films of 0.1 to 1 µm thickness, which are transparent and possess yellow color. In chloroform solution a UV-VIS absorption maximum at λ_{max} = 352 nm and an absorption edge of 470 nm is observed. Compared to the donor and acceptor substituted poly(*para*-phenylene-vinylene)s **6** and **8** (λ_{max} = 386 and 380 nm) [11], this is a hypsochromic shift of the absorption maximum of **14c** of 34 and 28 nm. In poly(*meta*-phenylenevinylene) **14c** the extended π-conjugation is interrupted by any *meta*-bridge and the "effective conjugation length" comprises more or less one donor and acceptor stilbene **15** (λ_{max} = 340 nm [12]) (Scheme 6). The good processability and its low light absorption qualify polymer **14c**, together with polymers **6** and **8**, for the investigation of its electrooptical properties, which we will report separately [13].

Considering investigation of nonlinear optical properties, not only the processability and absorption but also the dipole moments are of major interest [14]. Polymer **14c** contains conformationally mobile donor and acceptor vinylene subunits with a strong dipole and this raises the question of additivity of the dipole moments in the polymer. Preliminary information is available for the α-dimethylamino-β-cyanostilbene (**15**) (Scheme 6), which constitutes a building block of polymer **14c**. Starting from a crystal of the pure *trans*-isomer of **15**, it could be shown that at equilibrium in solution, *cis*- and *trans*-isomers coexist in the ratio 57:43, indicating a remarkably fast isomerization [12]. The dipole moment μ of this compound in solution is 6.12 Debye [12], whereby a AM1 calculation shows, that the *trans*- und *cis*-stilbenes **15** possess similar dipole moments [12]. The *para*-phenylenevinylene oligomers **16a** und **17a** (Scheme 6), which contain two and three dipolar vinylene units, possess dipole moments of 6.24 und 7.73 Debye, respectively [12].

When discussing the occurrence of dipolar moieties in polymer **14c**, it should be helpful to include *meta*-phenylenevinylene oligomers. These enable a systematic investigation of molecules with raising length, con-



Scheme 6 Oligomeric donor and acceptor substituted *para*- (a) and *meta*- (b) phenylenevinylenes **15**, **16a,b** and **17a,b**



Scheme 7 Successive build-up of *meta*-phenylenevinylenes **16b** and **17b**

taining dipoles perpendicular to a π-conjugated chain The synthesis can be performed starting from *meta*-(cyanomethyl)-*N*,*N*-dimethylthiobenzamide (**12d**) in a successive build-up. This method has already been used for the "one-pot"-preparation of *para*-oligophenylenevinylenes [12]. The synthesis of compounds **16b** and **17b** is demonstrated in Scheme 7. Starting from the thioamide **12d**, deprotonation in DMF at 233 K with sodium hydride and coupling with one equivalent of ammonium salt **18** leads to the thioamide **19** in 95% yield. Without further purification, it is possible to alkylate quantitatively with trimethyloxonium tetrafluoroborate in dichloromethane. Addition of the resulting ammonium salt to a DMF solution of benzyl cyanide (**20**) and sodium hydride at 233 K leads to *meta*-distyrylbenzene **16b**. Addition to a solution of **12d** instead of **20** at 233 K leads to the thioamide **21** (91% yield), which can in a new reaction sequence be alkylated and coupled with benzyl cyanide, to give oligomer **17b** containing three local dipoles. Compounds **16b** and **17b** can be purified by chromatography on silica gel with an eluent mixture of petrol ether/ethyl acetate 1:3. Finally, the oligo(*meta*-phenylenevinylenes) **16b** and **17b** can be isolated in glassy state in 62 and 44% total yield, respectively. It has to be mentioned, that the structures of **16a**,**b**, **17a**,**b**, **19** and **21** are simplified (all *trans*), because for donor and acceptor substituted phenylenevinylenes we always find a mixture of *cis*- and *trans*-isomers in solution. It can be assumed, that the equilibrium of each stilbene unit is about 57:43 (*trans*:*cis*), as in the case of the donor and acceptor stilbene **15** [12]. This thesis is underlined by the ^1H and ^{13}C NMR spectra of **16b** and **17b**, which show a lot of signals, which belong to different isomers. However, an exact relation of these signals to the different isomers is not possible.

The longest wavelength absorption maxima of the UV-VIS spectra of **16b** and **17b** are determined to 344 and 345 nm. As expected, they do not deviate much from those of the donor and acceptor stilbene **15** (340 nm) and the polymer **14c** (352 nm).

Conclusion

Three new donor and acceptor substituted xylenes have been obtained. In a first approach, the *para*-xylenes **13a** and **13b** have been synthesized, which possess different substituents at the ammonium nitrogen (methyl (**13a**) and ethyl (**13b**)). The deprotonation of these compounds with sodium hydride at 223 K in DMF leads to a compensation of the positive and negative charges and formation of the *para*-quinodimethanes **14a** and **14b** which are stable until 373 K. Their ^1H NMR spectra exhibit dynamic line broadening effects. With the help of NOE difference measurements, the relevant dynamic process can be identified as rotation of donor and acceptor substituted methylene units about the double bonds, which possess a partial single bond character. In a second approach, we have attempted to prevent compensation of the charges by generating the *meta*-bridged system **13c**, which cannot form a quinoid structure. Indeed, we obtain the donor and acceptor substituted poly(*meta*-phenylenevinylene) **14c**. Furthermore, the oligomeric *meta*-phenylenevinylenes **16b** and **17b**, which represent model compounds for polymer **14c**, have been synthesized in a successive build-up, starting from **12d**. By measuring the dipole moments of these oligomers in solution, we will monitor the dipole moments of donor and acceptor *meta*-phenylenevinylene chains as a function of chain length. We will report separately on these dipole moment measurements and on possible applications of polymer **14c** [13, 15].

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Experimental

NMR spectra were recorded on Bruker AMX 500 or Bruker AC 300 spectrometers. Chemical shifts are given in δ scale in parts per million relative to tetramethylsilane as internal standard. The calibration of the ^1H and ^{13}C NMR spectra was

carried out by means of solvent peaks: $CDCl_3$: δ (^{1}H) = 7.24; δ (^{13}C) = 77.0; DMF-d_7: δ (^{1}H) = 8.01; δ (^{13}C) = 162.7. – IR spectra were obtained on a Nicolet 320 FT-IR spectrometer. UV-VIS spectra were recorded on a Perkin-Elmer Lambda 15. Mass spectrometry was performed on a VG ZAB 2-SE-FPD by means of FD. Melting points (uncorrected) were obtained on a Büchi 510 apparatus.

para-(Cyanomethyl)benzoic acid (10a) (General Procedure)

para-(Bromomethyl)benzoic acid (**9a**)

(20.00 g, 93.0 mmol) is placed in a 1 l flask and stirred with sodium cyanide (13.67 g, 279.0 mmol) in 650 ml water for 12 h under reflux. After cooling, the reaction mixture is filtered and hydrochloric acid is added to the filtrate to precipitate the acid. The bright yellow acid is filtered off, washed with water and dried at 323 K under vacuo, *para*-(Cyanomethyl)benzoic acid (**10a**) is obtained in 79% yield (11.96 g), *m.p.* 416 K. – ^{1}H NMR (300 MHz, DMF-d_7) δ/ppm= 8.14, 7.50 (4H, 2d, ArH), 3.85 (2H, s, CH_2–CN). – ^{13}C NMR (75 MHz, DMF-d_7) δ/ppm= 167.2, 136.6, 130.4, 129.6, 128.6, 126.5, 119.2, 22.8.

meta-(Cyanomethyl)benzoic acid (**10c**)

Yield 11.23 g (75%), *m.p.* 408 K. – ^{1}H NMR (300 MHz, DMF-d_7) δ/ppm = 7.96, 7.58 (4H, 2m, ArH), 4.14 (2H, s, CH_2–CN). – ^{13}C NMR (75 MHz, DMF-d_7) δ/ppm = 168.0, 136.9, 130.5, 129.2, 126.3, 119.4, 23.0.

para-(Cyanomethyl)-*N,N*-dimethylbenzamide (11a) (General Procedure)

para-(Cyanomethyl)benzoic acid (**10a**)

(11.96 g, 74.3 mmol) is dissolved under an argon atmosphere in benzene (200 ml) in a 500 ml flask. After addition of thionyl chloride (88.4 g, 743 mmol), the solution is stirred for 24 h under reflux. The solvent and the remaining thionyl chloride are removed *in vacuo* and, without further purification, the residue is placed together with 150 ml benzene in a 500 ml flask with gas inlet under argon atmosphere and cooled to 278 K. Dimethylamine (10.05 g, 223 mmol) is added within 30 min, followed by stirring for 6 h at room temperature and addition of 250 ml of water. The organic phase is washed with 200 ml hydrochloric acid (36% aq. soln) and with 200 ml water. After removal of the solvent, **11a** is isolated as a brownish oil. Purification can be achieved through a silica gel column with ethyl acetate as eluent, and *para-(cyanomethyl)-N,N-dimethylbenzamide* (**11a**) can be obtained as a colorless oil (11.88 g, 85%). – ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm = 7.43–7.24 (4H, m, ArH), 3.72 (2H, s, CH_2–CN), 3.00, 2.91 (6H, 2m, $N(CH_3)_2$). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 170.4, 136.9, 129.6, 128.9, 128.6, 127.8, 127.2, 124.8, 35.0, 23.1.

para-(Cyanomethyl)-N,N-diethylbenzamide (**11b**)

Yield 72%. – ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm = 7.36 (4H, m, ArH), 3.72 (2H, s, CH_2–CN), 3.55, 3.20 (4H, 2m, $N(CH_2CH_3)_2$), 1.17, 1.07 (6H, 2s, $N(CH_2CH_3)_2$). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 171.1, 137.2, 129.4, 129.0, 128.6, 127.9, 125.0, 41.6, 41.0, 23.1, 13.7, 10.5.

meta-(Cyanomethyl)-N,N-dibutylbenzamide (**11c**)

Yield 78%. – ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm = 7.31 (4H, m, ArH), 3.72 (2H, s, CH_2–CN), 3.44, 3.16 (6H, 2m, N–CH_2–CH_2–CH_2–CH_3), 1.75–0.55 (14H, m, N–CH_2–CH_2–CH_2–CH_3). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 172.0, 137.7, 129.3, 129.1, 128.7, 126.8, 124.7, 49.1, 44.8, 31.1, 30.0, 22.8, 20.6, 20.1, 14.3, 14.0. – MS(FD, 8kV) *m/z*: 272.4 (M^+).

meta-(Cyanomethyl)-N,N-dimethylbenzamide (**11d**)

Yield 65%. – ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm = 7.34 (4H, m, ArH), 3.73 (2H, s, CH_2–CN), 3.05, 2.93 (6H, 2s, $N(CH_3)_2$). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 170.1, 136.9, 129.4, 128.8, 127.8, 127.4, 125.0, 35.1, 23.0.

para-(Cyanomethyl)-*N,N*-dimethylthiobenzamide (12a) (General Procedure)

To a solution of *para*-(cyanomethyl)-*N,N*-dimethylbenzamide (**11a**) (11.88 g, 63.2 mmol) in toluene (150 ml), Lawesson's Reagent (4-methoxyphenylthionophosphine sulfide dimer) (6.42 g, 15.9 mmol) is added and refluxed for 24 h. After cooling, the solvent is removed and purification by chromatography on silica gel with an eluent mixture dichloromethane/ethyl acetate of 3:1 yields 8.39 g (65%) of the orange oil.

para-(cyanomethyl)-N,N-dimethylthiobenzamide (**12a**)

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm = 7.32 (4H, m, ArH), 3.76 (2H, s, CH_2–CN), 3.61, 3.18 (6H, 2s, $N(CH_3)_2$). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 200.0, 144.5, 130.0, 129.5, 128.2, 125.7, 125.5, 117.8, 43.8, 42.9, 23.4.

para-(Cyanomethyl)-N,N-diethylthiobenzamide (**12b**)

Yield 70%. – ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm = 7.36 (4H, m, ArH), 3.72 (2H, s, CH_2–CN), 3.55, 3.20 (4H, 2m, $N(CH_2CH_3)_2$), 1.17, 1.07 (6H, 2t, $N(CH_2CH_3)_2$). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 199.2, 143.7, 137.2, 131.0, 128.0, 127.1, 125.8, 117.5, 47.8, 46.1, 23.4, 14.1, 11.2.

meta-(Cyanomethyl)-N,N-dibutylthiobenzamide (**12c**)

Yield 74%. – ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm = 7.46–7.03 (4H, m, ArH), 3.73 (2H, s, CH_2–CN), 4.03, 3.35 (6H, 2t, N–CH_2–CH_2–CH_2–CH_3), 1.85, 1.51, 1.42, 1.15, 1.00, 0.77 (14H, 6m, N–CH_2–CH_2–CH_2–CH_3). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 199.3, 144.9, 130.3, 129.2, 127.4, 124.6, 117.4, 53.4, 51.6, 30.6, 28.1, 23.5, 20.3, 19.8, 10.2, 13.4. – MS(FD, 8kV) *m/z*: 288.4 (M^+).

meta-(Cyanomethyl)-N,N-dimethylthiobenzamide (**12d**)

Yield 74%. – ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm = 7.10 (4H, m, ArH), 3.54 (2H, s, CH_2–CN), 3.39, 2.94 (6H, 2s, $N(CH_3)_2$). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 199.8, 144.2, 130.3, 129.1, 127.9, 125.3, 117.3, 44.0, 43.1, 23.4.

para-(Cyanomethyl)dimethyl[(methylthio)phenylmethylene]ammonium tetrafluoroborate (13a) (General Procedure)

para-(Cyanomethyl)-*N,N*-dimethylthiobenzamide (**12a**) (837 mg, 4.1 mmol) is dissolved in dichloromethane (5 ml) in a 50 ml flask under argon atmosphere. After addition of trimethyloxonium tetrafluoroborate (606 mg, 4.1 mmol), the solution is stirred for 48 h at room temperature. The solvent is

removed *in vacuo* and the colorless ammonium salt **13a** is obtained in quantitative yield (1.255 g). – ^{1}H NMR (500 MHz, DMF-d_7) δ/ppm = 8.01, 7.55 (4H, 2d, ArH), 4.45 (2H, s, CH_2–CN), 2.87 (6H, s, N(CH_3)$_2$), 2.45 (3H, s, SCH_3). – ^{13}C NMR (75 MHz, DMF-d_7) δ/ppm = 186.2, 131.5, 130.9, 129.1, 128.7, 128.3, 127.3, 119.5, 58.9, 58.3, 56.8, 33.5. – MS(FD, 8kV) *m/z*: 219.3 (M^+ – 86.8(BF_4^-)). – IR ν/cm^{-1} = 3059, 2965, 2937, 2876, 2254, 1580, 1471, 1422, 1267, 1068, 745.

para-(Cyanomethyl)diethyl[(methylthio)phenylmethylene] ammonium tetrafluoroborate (**13b**)

Yield 100%. – ^{1}H NMR (500 MHz, DMF-d_7) δ/ppm = 7.80, 7.74 (4H, 2d, ArH), 4.32 (2H, s, CH_2–CN), 4.20, 3.75 (4H, 2m, N–CH_2), 2.33 (3H, s, SCH_3), 1.51, 1.28 (6H, 2t, CH_2–CH_3). – ^{13}C NMR (75 MHz, DMF-d_7) δ/ppm = 191.4, 135.5, 130.4, 129.6, 127.6, 117.3, 53.7, 51.1, 23.9, 18.6, 13.8. 11.4. – MS(FD, 8kV) *m/z*: 247.4 (M^+ – 86.8(BF_4^-)). – IR: ν/cm^{-1} = 3059, 2965, 2937, 2876, 2254, 1580, 1471, 1422, 1267, 1068, 745.

meta-(Cyanomethyl)dibutyl[(methylthio)phenylmethylene] ammonium tetrafluoroborate (**13c**)

Yield 100%. – ^{1}H NMR (500 MHz, DMF-d_7) δ/ppm = 7.61 (2H, d, ArH), 7.42 (1H, s, ArH), 7.35 (1H, t, ArH), 3.93, 3.51 (4H, 2t, N–CH_2), 3.91 (2H, s, CH_2–CN), 2.15 (3H, s, SCH_3) 1.87, 1.60 (4H, 2m, N–CH_2–CH_2), 1.44, 1.08 (4H, 2m, N–CH_2–CH_2–CH_2), 0.95, 0.67 (6H, 2t, CH_2–CH_3). – ^{13}C NMR (75 MHz, DMF-d_7) δ/ppm = 191.3, 133.8, 132.0, 131.2, 127.5, 126.4, 126.0, 117.8, 58.4, 55.9, 30.1, 27.5, 23.2, 20.7, 19.7, 18.4, 13.6, 13.3. – MS(FD, 8kV) *m/z*: 303.5 (M^+ – 86.8 (BF_4^-)). – IR: ν/cm^{-1} = 3059, 2965, 2937, 2876, 2254, 1580, 1471, 1422, 1267, 1068, 745.

3-(Cyanomethyl)-6-(dimethylaminomethylthiomethylene)-1,4-cyclohexadiene (14a) (General Procedure)

para-(Cyanomethyl)dimethyl[(methylthio)phenylmethylene] ammonium tetrafluoroborate (**13a**)

(10 mg, 0.03 mmol) is placed in an NMR tube in deuterated DMF (0.75 ml) and cooled to 223 K. After addition of 4 equivalents (3 mg) of sodium hydride (95% w/w dispersion in mineral oil), the reaction mixture is warmed up in 10 K steps and simultaneously observed by ^{1}H NMR spectroscopy. – ^{1}H NMR (500 MHz, DMF-d_7, 273 K) δ/ppm = 7.29, 7.15, 6.42, 6.12 (4H, 4d, ArH, J = 8.7 Hz), 3.25 (1H, s, =CH–CN), 2.25 (6H, s, N–CH_3), 2.23 (S–CH_3).

3-(Cyanomethyl)-6-(diethylaminomethylthiomethylene)-1,4-cyclohexadiene (**14b**)

^{1}H NMR (500 MHz, DMF-d_7, 273 K) δ/ppm = 6.92, 6.82, 6.36, 6.05 (4H, 4d, ArH, J = 8.6 Hz), 3.81 (4H, m, N–CH_2), 2.87 (1H, s, =CH–CN), 1.21 (6H, t, CH_3), 1.23 (S–CH_3).

Polymer **14c**

meta-(Cyanomethyl)dibutyl[(methylthio)phenylmethylene] ammonium tetrafluoroborate (**13c**) (200 mg, 0.513 mmol) is placed in a 100 ml reaction flask under argon atmosphere in DMF (5 ml) and cooled to 243 K. After addition of 2 equivalents (26 mg) of sodium hydride (95% w/w dispersion in mineral oil) and a reaction time of 8 h, the solution is allowed to warm to room temperature. Distillation of the brownish reaction mixture to remove DMF and purification by solving of the residue in dichloromethane, washing with water and distillation of the dichloromethane leads to 85 mg of the bright yellow, glassy polymer **14c** (65% yield). – ^{1}H NMR (500 MHz, DMF-d_7) δ/ppm = 7.75–6.55 (4H, m, ArH), 3.85–2.50 (4H, m, N–CH_2), 1.80–1.00 (8H, m, N–CH_2–CH_2–CH_2), 1.00–0.65 (6H, m, -CH_2 -CH_3). – ^{13}C NMR (75 MHz, DMF-d_7) δ/ppm = 137.8, 137.6, 130.6, 130.5, 129.2, 129.0, 128.2, 127.9, 51.9, 51.7, 30.5, 30.0, 28.7, 20.6, 20.2, 14.2, 14.1. – IR ν/cm^{-1} = 3054, 2963, 2933, 2873, 2306, 2187, 1676, 1422, 1265, 1064, 733. – UV-VIS ($CHCl_3$): λ_{max}/nm (ε_{max} l/mol cm) = 352 (7890).

Successive Build-up of Oligomers 16b and 17b

The following reactions are performed under argon atmosphere in dry solvents. Firstly, *meta*-(cyanomethyl)-*N,N*-dimethylthiobenzamide(**12d**) (5.0 g, 24.5 mmol) is placed in a 100 ml flask in DMF (25 ml) and cooled to 233 K, after which sodium hydride (95% w/w dispersion in mineral oil) (1.238 g, 49 mmol) and dimethyl[(methylthio)phenylmethylene] ammonium iodide (**18**) [12] (7.178 g, 24.5 mmol) are added. The solution is allowed to warm to room temperature after 6 h. The solvent is removed *in vacuo* (yield 95%) and dichloromethane (30 ml) and trimethyloxonium tetrafluoroborate (3.626 g, 24.5 mmol) are added to the brownish residue **19**. After 24 h the solvent is removed and about one half of the resulting ammonium salt (5.00 g,11.4 mmol) is added to a solution of benzyl cyanide (1.334 g, 11.4 mmol) and sodium hydride (95% w/w dispersion in mineral oil) (576 mg, 22.8 mmol) at 233 K in DMF (20 ml). After a reaction time of 6 h the mixture is allowed to warm to room temperature and the donor and acceptor distyrylbenzene **16b** is obtained as a brownish oil, which can be purified by chromatography on silica gel with an eluent mixture ethyl acetate/petrol ether of 3:1. The glassy, yellow product **16b** is obtained in 62% total yield (2.955 g).

For the preparation of oligomer **17b**, the alkylated compound **19** (5.00 g,11.4 mmol) is added to a solution of **12d** (2.326 g, 11.4 mmol) and sodium hydride (95%) (580 mg, 23.0 mmol) at 233 K in DMF (15 ml). After 6 h and warming to room temperature, the solvent is distilled and **21** obtained in 91% yield. **21** can be alkylated quantitatively with trimethyloxonium tetrafluoroborate (1.687 g, 11.4 mmol) in dichloromethane (30 ml) within 24 h. Coupling with benzyl cyanide is performed analogously to the synthesis of **16b** (with **20** (1.334 g, 11.4 mmol) and NaH (576 mg, 22.8 mmol)) to give the donor and acceptor oligomer **17b**. This can also be purified by chromatography on silica gel with an eluent mixture ethyl acetate/petrol ether of 3:1 and the glassy, yellow product **17b** is isolated in 44% total yield (2.950 g).

16b: – ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm = 7.45–6.63 (14H, m, ArH) 3.02, 2.83, 2.64, 2.60, 2.39, 2.21 (12H, 6s, N–CH_3). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 164.2, 162.7, 162.4 161.5, 137.2, 136.3, 136.0, 129.9, 128.4, 128.3, 127.9, 127.7, 127.5, 125.9, 125.7, 124.8, 124.5, 43.4, 42.9, 42.7, 42.5. – MS (FD, 8kV) *m/z*: 418.3 (M^+). – IR ν/cm^{-1} = 3054, 2977, 2933, 2863, 2185, 1545, 1394, 1266, 1063, 736 – UV-VIS ($CHCl_3$): λ_{max}/nm (ε_{max} l/mol cm) = 344 (16190).

$C_{28}H_{26}N_4$	Calcd.:	C 80.35	H 6.26	N 13.38
(418.54)	Found	C 80.16	H 6.18	N 13.27.

17b: – ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm = 7.55–6.70 (18H, m, ArH) 3.13, 3.11, 3.10, 3.05, 2.95, 2.92, 2.67, 2.65, 2.53, 2.43, 2.28, 2.09 (18H, 12s, N-CH_3). – ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm = 163.8, 162.2, 162.0, 161.4, 137.5, 136.2, 134.5, 130.0, 128.5, 128.0, 126.5, 125.6, 123.6, 123.4, 121.9, 121.7, 43.3, 42.9, 42.9, 42.8. – MS(FD, 8kV) *m/z* = 588.4 (M^+). – IR ν/cm^{-1} = 3054, 2986, 2931, 2305, 2186, 1559, 1445, 1395, 885, 737. – UV-VIS ($CHCl_3$): λ_{max}/nm (ε_{max} l/mol cm) = 345 (24100).

$C_{39}H_{36}N_6$ (588.75) Calcd.: C 81.60 H 6.16 N 14.27
Found: C 81.40 H 6.19 N 14.14.

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