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Stepwise Unidirectional Synthesis of Oligo Phenylene Vinylenes with a Series of Monomers. Use in Plastic Solar Cells

Mikkel Jørgensen* and Frederik C. Krebs

The Polymer Department, Risø National Laboratory, P.O. Box 49, DK-4000 Roskilde, Denmark

mikkel.joergensen@risoe.dk

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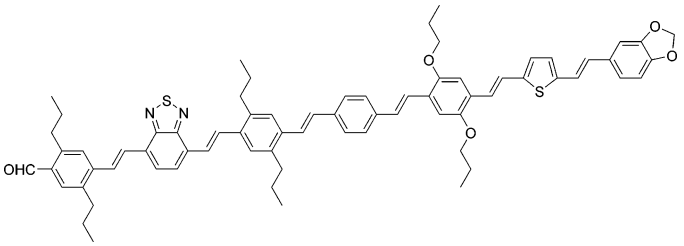

Four new monomers for directional stepwise synthesis of oligophenylenevinylenes (OPVs) (4-{2-[4-(5,5-dimethyl[1,3]dioxan-2-yl)-2,5-dipropoxyphenyl]vinyl}benzyl)phosphonic acid diethyl ester, (5-{2-[4-(5,5-dimethyl[1,3]dioxan-2-yl)-2,5-dipropylphenyl]vinyl}thiophene-2-ylmethyl)phosphonic acid diethyl ester, (5-{2-[4-(5,5-dimethyl[1,3]dioxan-2-yl)-2,5-dipropoxyphenyl]vinyl}thiophene-2-ylmethyl)phosphonic acid diethyl ester, and (7-{2-[4-(5,5-dimethyl[1,3]dioxan-2-yl)-2,5-dipropylphenyl]-vinyl}benzo[1,2,5]thiadiazol-4-ylmethyl)phosphonic acid diethyl ester have been prepared. Trimeric OPVs were then synthesized and tested as active materials in photovoltaic cells. Conversion efficiencies in the range of 0.5−1% were obtained in blends with the soluble C_{60} derivative PCBM. A terpyridine end-functionalized trimer and a heterotrimer with a mixed composition of monomers were also prepared.

Introduction

Phenylene vinylene oligomers (OPVs) and the corresponding polymers (the PPVs) have been extensively investigated both in regard to their synthesis and material properties as conducting elements and as light harvesting antennas.[1−6] A smaller subset of these interesting materials are OPVs of a unidirectional nature that can be prepared using a stepwise strategy, as we have shown in a previous paper.[7] Such a strategy allows us to fine-tune the properties to the level that have only been realized in natural oligomers such as peptides and oligonucleotides, which are also prepared using similar methods (Figure 1). Single oligomers are much better defined than polymers, and properties can therefore be correlated with structure far easier.[1] To realize this potential, we need a toolbox of diverse monomers and a reliable sequential reaction scheme to assemble them. The latter requirement is fulfilled by monomers that can be joined using a two-step procedure. An obvious choice is to create the vinylene groups using the Horner−Wadsworth−Emmons (HWE) reaction (also called the Horner−Wittig reaction) between a benzyl phosphonate ester and a benzaldehyde. To avoid uncontrolled polymerization, the requisite aldehyde functionality must be protected as an acetal until needed. Each cycle in our synthesis thus has a HWE reaction followed by a deprotection step as outlined in Scheme 1.

Stepwise and unidirectional oligomerization of OPVs has not been widely exploited presumably due to the added work required to prepare monomers such as **1**. Some groups have prepared a number of both symmetrical and unsymmetrical OPVs with varying end groups with 6−12 phenylene vinylene fragments using the HWE,[8] Siegrist,[9] Heck,[10] and Suzuki−Miyaura[11] type reactions. The group of Yu et al. has prepared OPVs through stepwise reactions with two different monomers

(1) (a) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, 1998. (b) Wong, M. S.; Li, Z. H. *Pure Appl. Chem.* **2004**, *76*, 1409−1419.
(2) Granström, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Anderson, M. R.; Friend, R. H. *Nature* **1998**, *395*, 257−260.
(3) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15−26.
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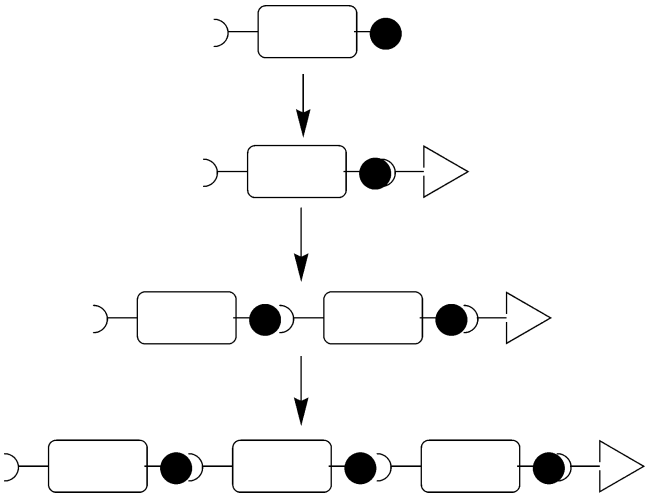
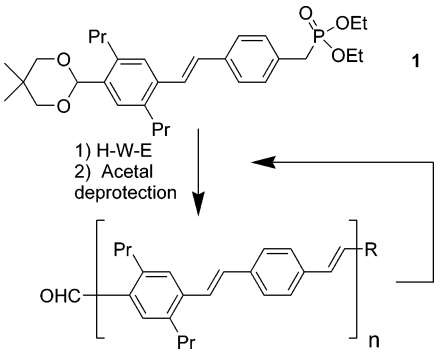


FIGURE 1. Concept of unidirectional stepwise oligomerization. A monomer has two different end groups that can be coupled in a sequential manner. One group is protected during coupling and then deprotected to allow the next cycle. In the first reaction, the monomer is end-capped with a monofunctional reagent.

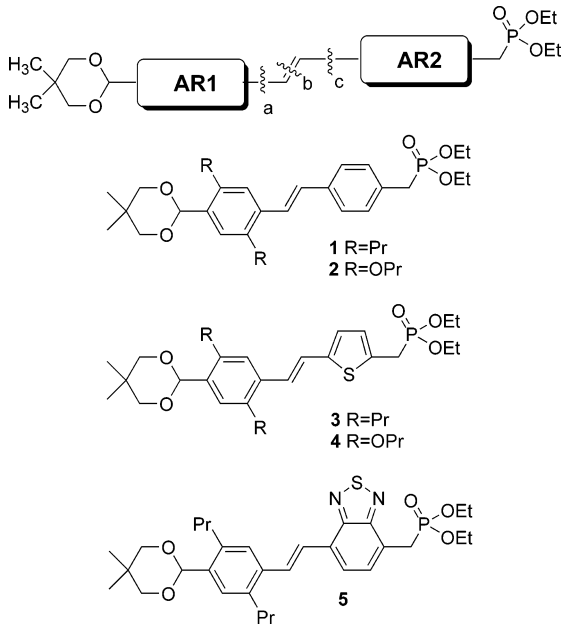
SCHEME 1. Unidirectional and Stepwise Synthesis of OPV Oligomers Based on HWE Reactions with Monomer 1 Followed by Deprotection of the Acetal Group[a]



[a] In the first step, the monomer is typically reacted with 4-methoxybenzaldehyde which then becomes the R group.

utilizing the Heck and HWE reactions alternately.[12] Previously, we have described the simpler strategy using only one type of monomer summarized in Scheme 1, where the extension of the oligomer is carried out with a HWE reaction followed by deprotection of the acetal function. The unidirectional nature allows end-functionalization to study the effects of attaching functional groups that can interact, e.g., with a surface or with other molecules. This concept have previously been explored

CHART 1. Generalized Monomer Structure Where AR1 Is a Dipropyl- or Dipropoxyphenyl Group and AR2 Can Be 1,4-Phenyl, Thiophenyl, or Benzothiadiazole Substituents[a]



[a] Three general synthetic strategies have been investigated with the principal disconnections (a−c) shown around the central double bond.

in the context of organic solar cells.[13] Another interesting possibility is to use the control over the synthesis to create molecules with a gradual change in electronic levels along the conjugated backbone. Compounds such as these could find widespread use as active materials in polar devices such as organic light emitting diodes and plastic solar cells. Materials with a directional buildup may be much more appropriate to use in contact with electrode surfaces or with a variation of the electronic levels that sets a preferred orientation for electron/hole transport or even charge separation.

Results and Discussion

Monomer Synthesis. Chart 1 shows the general layout of the monomer stilbene type structure composed of two aryl groups linked by a vinylene bridge. At one end is a methyl phosphonate ester group and at the other an acetal-protected aldehyde group. Also shown in Chart 1 are the three possible bond disconnections of the central vinylene fragment in the monomer. The syntheses of the monomers **1** and **2** using the Heck reaction are examples of the (a) type disconnection. Since our first paper on the subject we have extended the list of monomers to members with more electron-donating/accepting groups. Two types of AR1 groups, either dipropyl- or dipropoxy-substituted, have been utilized. The alkyl groups give the OPVs some degree of solubility at least up to the "trimer" stage with seven benzene rings. Three different AR2 groups were investigated with either benzene, thiophene

(8) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402−428. (b) Yang, J. P.; Heremens, P. L.; Haefnagels, R.; Tachelet, W.; Dielteens, P.; Blockhuys, F.; Giese, H. J.; Borghs, G. *Synth. Met.* **2000**, *108*, 95−100. (c) Meier, H.; Gerold, J.; Kolshorn, H.; Baumann, W.; Bletz, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 292−295.

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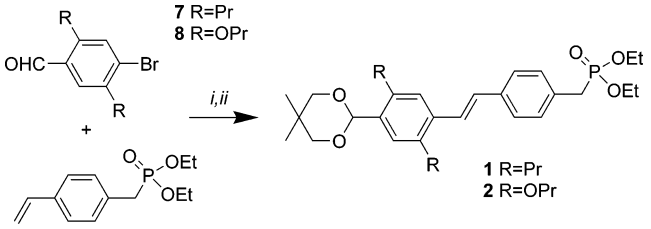
SCHEME 2. Synthesis of the Monomers 1 and 2[a]



[a] Key: (i) Pd_2dba_3, Et_3N, P(*t*-Bu)$_3$·HBF_4, dioxane; (ii) 2,2-dimethylpropanediol, TsOH, toluene.

or benzothiadiazole moieties totaling in all five different monomers (**1**−**5**). Both the AR1 and AR2 groups influence the OPV electronic structure, which allow us to vary, e.g., the optical band gap. The diverse nature of these monomers also prompted us to investigate a number of different synthetic routes that will be discussed in the following. These routes explore the principal disconnections (a), (b), and (c) to form the double bond using the Heck-, HWE-, and the Stille-type reactions.

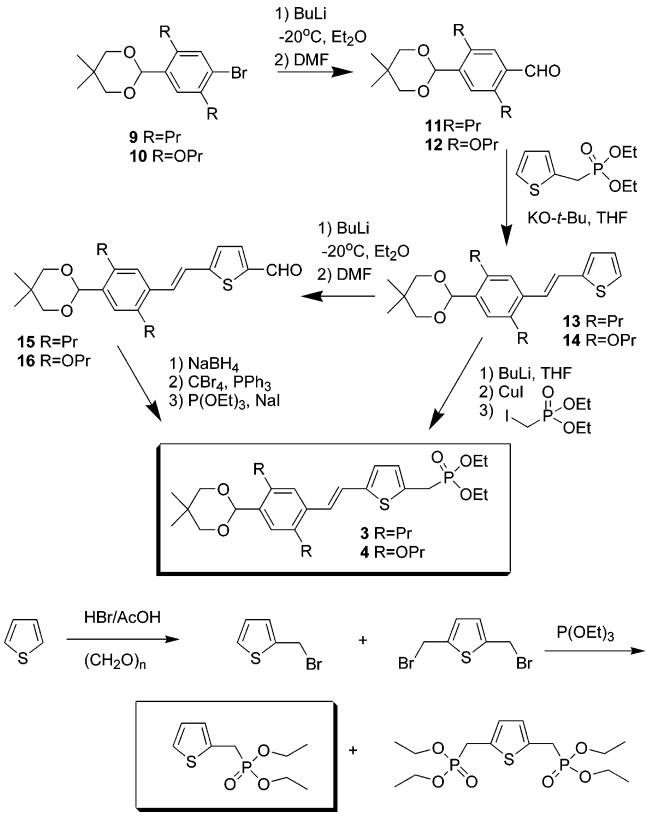
Disconnection (a). As described previously, the monomer **1** with a stilbene motif was prepared via the Heck reaction from 4-bromo-2,5-dipropylbenzaldehyde **7** and diethyl 4-vinyl-benzyl phosphonate ester followed by acetalization with 2,2-dimethylpropane-1,3-diol as shown in Scheme 2. The best conditions for the Heck reaction were optimized in the previous study to be Pd_2dba_3 and tri-*tert*-butylphosphine as the catalyst system in dioxane as solvent and triethylamine as the base at reflux similar to the system devised by Litke and Fu.[14]

This method has now been extended to prepare the monomer **2** with propoxy groups instead of propyl on the AR1 ring. The 4-bromo-2,5-dipropoxybenzaldehyde (**8**), needed for this step, was prepared from 1,4-dibromo-2,5-dipropoxybenzene by halogen-to-lithium exchange followed by reaction with dimethylformamide as described by Meier and Aust.[15] Careful control over the reaction conditions are necessary, especially the choice of diethyl ether as solvent, to limit the amount of dilithiation resulting in an inseparable mixture of aldehydes and starting material. Otherwise, the concomitant Heck reaction with diethyl 4-vinylbenzyl phosphonate ester followed by acetalisation to prepare monomer **2** was completely analogous to the synthesis of monomer **1**. Purification was achieved by chromatography.

Disconnection (b). A few symmetrical OPVs with alternating benzene and thiophene groups have been described by Xue and Luo as promising red light-emitting materials in OLED's.[16] Thiophene is not so easy to introduce since a thiophene analogue to diethyl 4-vinylbenzyl phosphonate ester is not known. Somewhat different strategies were therefore adopted for the monomers **3** and **4** as shown in Scheme 3.

The partially acetal protected dipropyl- or dipropoxyterephthaldehydes **11** and **12** were prepared from the bromophenyldioxolanes **9** and **10** via bromine-to-lithium exchange with butyllithium in THF followed by reaction with dimethyl formamide. A HWE reaction with diethyl thiophene methyl phosphonate ester gave the compounds

SCHEME 3. Synthesis of the Thiophene-Containing Monomers 3 and 4 through Two Different Routes (Top)[a]



[a] The syntheses of 2-(diethylphosphonylmethyl)thiophene and 2,5-bis(diethylphosphonylmethyl)thiophene are also shown (bottom).

13 and **14** as light yellow recrystalizable solids. While diethyl thiophene methyl phosphonate ester[17a] and the bis phosphonate ester[17b] are known compounds, a modified procedure was used in this study and details of the synthetic procedure can be found in the Experimental Section. An unusual type of alkylation procedure was then employed to add the methyl phosphonate ester group at the thiophene moiety. Dalton and Wang[18] and later Frère et al.[19] developed a reaction where a thiophene-copper reagent is derivatized with diethyl iodomethyl phosphonate ester. We applied this reaction to the thiophene derivatives **13** and **14** to obtain the monomers **3** and **4**. Unfortunately, it was rather difficult to obtain pure materials by this procedure because the reaction did not go to completion and also due to difficulties in removing dark-colored copper impurities. A somewhat longer route also shown in Scheme 3 was therefore explored. The compounds **13** and **14** were transformed into the crystalline aldehydes **15** and **16** by lithiation with butyllithium followed by reaction with dimethyl formamide. Reduction to the corresponding hydroxymethyl

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(15) Meier, H.; Aust, H, *J. Prakt. Chem.* **1999** *341*, 466−471.
(16) Xue, C.; Luo, F.-T. *Tetrahedron* **2003**, *59*, 5193−5198.
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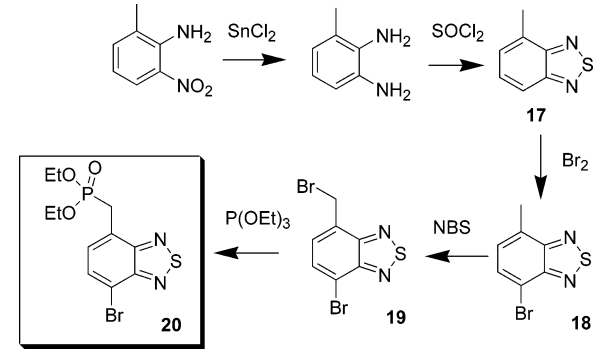
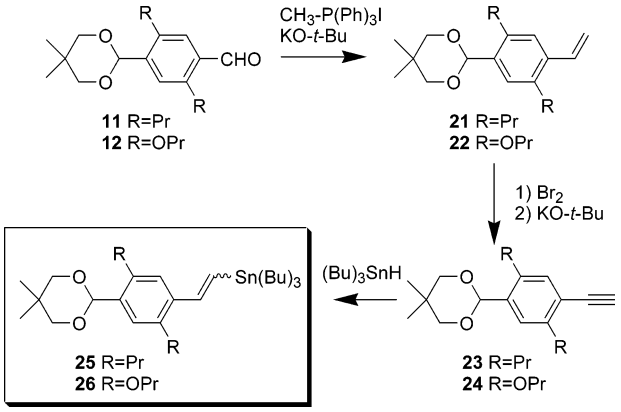
thiophene compounds was accomplished with sodium borohydride in a mixture of ethanol and THF. A Mitsunobu reaction with carbon tetrabromide and triphenyl phosphine was then used to convert the hydroxymethyl group into the corresponding thiophenylmethyl bromide. Finally, the phosphonate ester groups were introduced by an Arbusov reaction with triethyl phosphite. Purification of the monomers **3** and **4**, using column chromatography with diethyl ether as eluent and then became much easier.

Disconnection (c). Work on the synthesis of 4-methyl-2,1,3-benzothiadiazole (**17**) was reported by Michaelis as early as 1893 by reaction of 3-methylphenylene-1,2-diamine and thionyl chloride in benzene followed by steam distillation.[20] Later work by Pilgram et al. on the preparation of **17** used thionylaniline with good yield.[21] Vanelle et al. compared the thionyl chloride route and the thionylaniline route and while the latter generally gives a higher yield the workup is tedious.[22] Recent work on derivatization of the benzothiadiazole skeleton includes amination using both nitration and palladium catalysis.[23] We prepared **17** by a combination of the Michaelis and the Vanelle route employing stannous chloride reduction of 2-amino-3-nitrotoluene followed by reaction with thionyl chloride and subsequent steam distillation of the product. The bromination of **17** in HBr(aq) using bromine gave **18** by a procedure similar to the one described.[21,22] The use of excess bromine has been reported to give **19** directly[21] while allylic bromination using NBS in CCl_4 is preferable.[22] All of the literature procedures[20−23] have analytical data limited to elemental analysis and boiling points/melting points. Except for **18** where ^{1}H NMR data is given there are no reported ^{1}H NMR and ^{13}C NMR data for these compounds. Reaction of **19** with triethyl phosphite gave the phosphonic ester **20** directly. The preparations of the ethynyl compounds **23** and **24** were attempted in different ways. The simplest approach was a Sonogashira coupling using trimethylsilyl acetylene and copper/palladium catalysis followed by removal of the TMS groups using either Bu_4NF or K_2CO_3 in $MeCl_2$/MeOH. The latter method proved to be most efficient allowing for easy workup. The Sonogashira reaction was, however, very sluggish, and attempts to convert the bromine into iodine gave no improvement. It was then decided to prepare the acetylene from the vinyl compound by bromine addition and elimination using potassium *tert*-butoxide instead. Addition of tributyltin hydride to arylacetylenes have been studied in the literature and gives rise to both α and β addition and *cis* and *trans* addition.[24−27] The best method for the addition was found to be the mixing of the two components neat and stirring gently under argon while following the progress of the reaction using NMR.

SCHEME 4. Synthesis of the Thiadiazole Moiety of Monomers 5 and 6



SCHEME 5. Synthesis of the Dipropyl- and Dipropoxyphenylvinylstannane Reagents



The coupling of stannanes with aryl halides has been reported with the use of copper,[28] palladium,[29] nickel,[30] and manganese[31] catalysis. We chose copper catalysis with sodium chloride as cocatalyst for the subsequent coupling of the vinylstannane with **20** in NMP (Scheme 4). While the addition of Bu_3SnH to the acetylene was about 60% *trans*, this was reflected in the product after coupling as being a mixture of *cis* and *trans* (Scheme 5). To overcome this, $(PPh_3)_4Pd(0)$ was added at the end of the coupling reaction followed by heating to reflux. This efficiently transformed all the double bonds into the *trans* form. Monomer **5** was prepared sufficiently pure using this route, while it proved impossible to separate **6** from a larger amount of starting materials and byproducts (Scheme 6).

Synthesis and Characterization of OPV Oligomers. With the monomers (**1**−**5**) in hand it was now possible to explore a number of different experiments with oligomers. A simple extension of our previous work was to make trimers of each of the monomers and investigate the difference in absorption maxima. The

(20) Michaelis, A. *Ann. Chem.* **1893**, *273*, 173−268 (p 263).
(21) Pilgram, K.; Zupan, M.; Skiles, R. *J. Heterocycl. Chem.* **1970**, *7*, 629−633.
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(31) Kang, S.-K.; Kim, J.-S.; Choi, S.-C. *J. Org. Chem.* **1997**, *62*, 4208−4209.

SCHEME 6. Final Assembly of the Thiadiazole-Type Monomers 5 and 6 through Stille Coupling of the Components 20 with 25 or 26

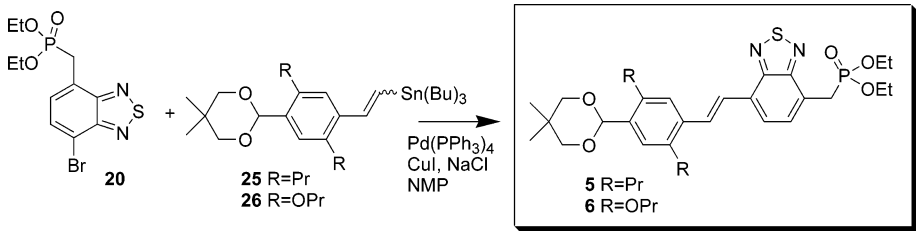
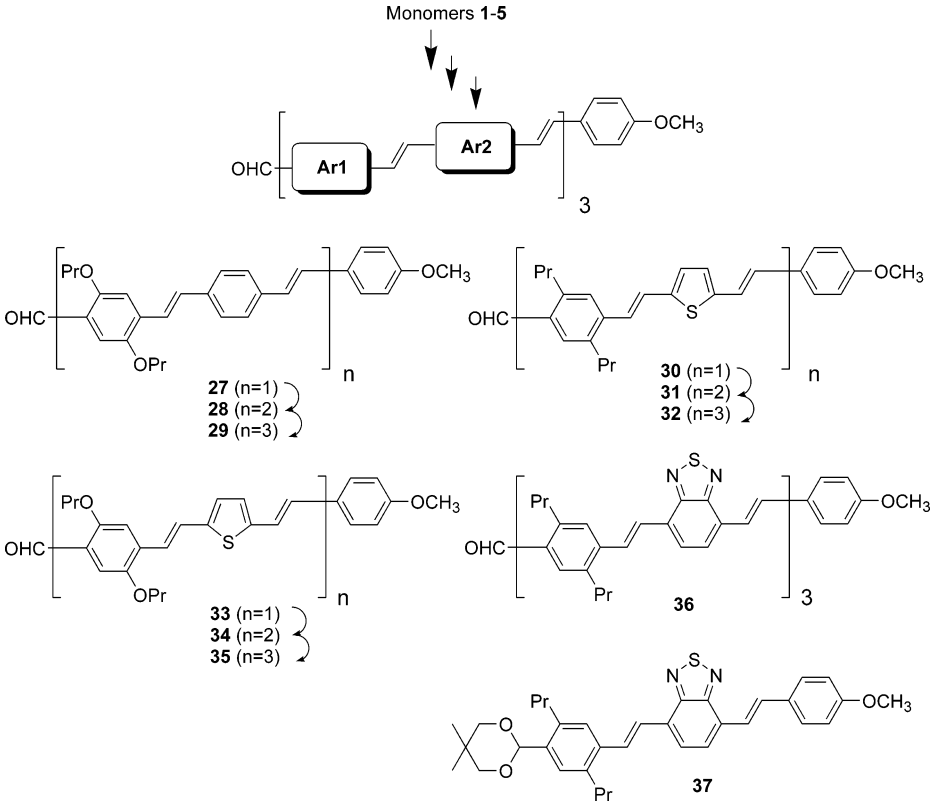


CHART 2. Structures of the Four Different Types of "Homo" Oligomers Prepared in This Study Based on the Monomers 2−5[a]



[a] In the first step, each of the monomers was end-capped by a HWE reaction with 4-methoxybenzaldehyde followed by hydrolysis of the acetal function. Stepwise elongation with the monomers then gave the corresponding dimers and trimers.

maxima are an expression of the optical band gap that is related to the various donor/acceptor groups in the molecules.

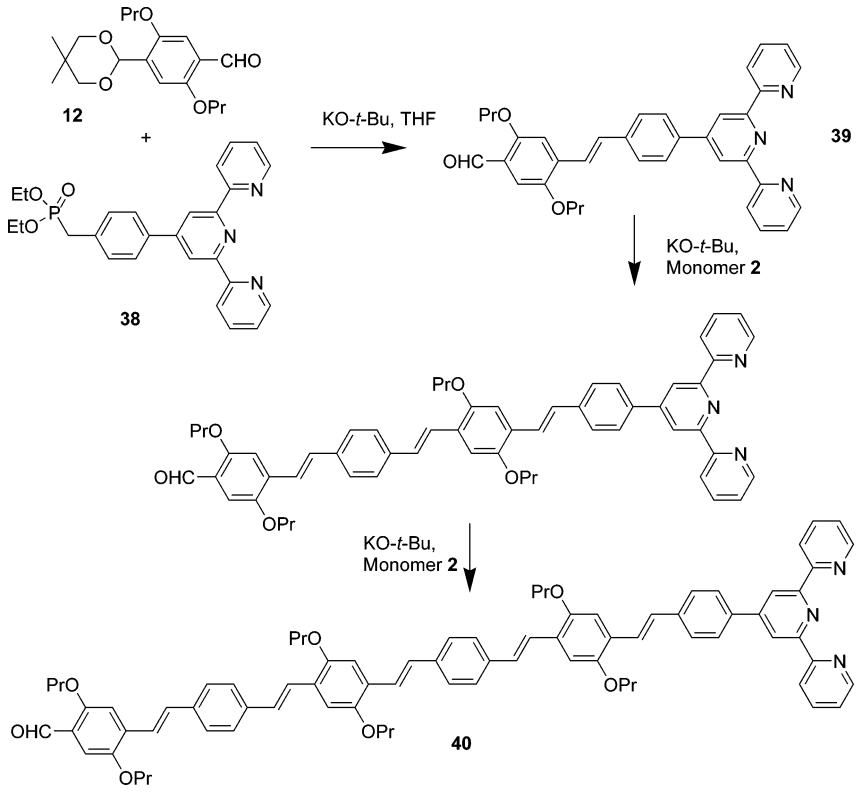
The monomers **3** and **4** were designed to give oligomers with alternating benzene and thiophene moieties. Smaller symmetrical OPVs of this type have recently been studied by Xue and Luo for their potential as red light-emitting materials.[16] Thiophene-containing conducting polymers and oligomers are of interest as low band-gap materials. Reactions with the monomer **5** proved to be difficult and gave only low yields (20−30%) of products in the HWE reaction. A possible side reaction is nucleophilic attack on the benzothiadiazole moiety and as a consequence sodium hydride was used as the base in the reactions with **5** instead of potassium *tert*-butoxide. The trimer **36** was obtained in very low yield and contaminated with both dimeric and tetrameric products. It could be purified by size exclusion chromatography (SEC) to show that it is a low band gap material with absorption maximum at 500 nm extending out to 600 nm. To prove the identity of the product in the HWE reaction between monomer **5** and 4-methoxybenzaldehyde the 4-{2-[4-(5,5-dimethyl-[1,3]dioxan-2-yl)-2,5-dipropyl-phenyl]-vinyl}-7-[2-(4-methoxy-phenyl)-vinyl]-benzo[1,2,5]thiadiazole **37** was isolated and characterized as described in the Experimental Section (Chart 2).

End-Functionalization. The present synthetic strategy makes it straightforward to add end-groups that can give further functionality to the molecules. Adding a ligand group such as a terpyridine moiety would allow us to create metal complexes attached to a conjugated "wire" OPV. A similar terpyridine-OPV architecture has been reported recently.[32]

The synthesis of the terpyridine end-functionalized trimer **40** began with a HWE reaction between the terpyridine phosphonate ester **38** and the aldehyde **12**

(32) El-ghayoury, A.; Schenning, A. P. H. J.; van Hal, P. A.; Weidl, C. H.; van Dongen, J. L. J.; Janssen, R. A. J.; Schubert, U. S.; Meijer, E. W. *Thin Solid Films* **2002**, *403−404*, 97−101.

SCHEME 7. Synthesis of a "Trimer" OPV with a Terpyridine End Group 40



resulting in the end-capped monomer **39** (Scheme 7). Although Zang et al. and others have described terpyridine phosphonate ester **38** previously, no specific details on the synthesis and compound properties were given.[33−35] These have therefore been included in the Experimental Section. Extension of compound **39** with the monomer **2** was carried out twice using the HWE reaction followed by deprotection of the acetal function to give the target terpyridine trimer **40**.

Tapering the Electronic Levels. In principle it is possible to control the nature and substituents of each aromatic ring along the OPV. This level of specificity is similar to that found in peptide synthesis where the order of amino acid residues can be controlled. Choosing different monomers with different electronic levels would allow us to create OPVs were these properties vary along the backbone. A preferred direction of electron or hole conduction could be envisaged. To demonstrate the present level of control that is possible with the set of monomers and the stepwise oligomerization reactions we prepared a "hetero-trimer" **43** using three different monomers as shown in Scheme 8. The assembly began with the end capping of monomer **4** with piperonal creating the electron-rich part of the molecule. In the second step, monomer **1** was chosen as a bridge and finally, the monomer **5** was added to create the electron deficient region. Inspection will show that each of the seven aromatic rings in the structure is substituted differently. A disconnection scheme would show that virtually every bond with the exception of the rings themselves and the propyl groups have been created along the synthetic pathway. Only the last step adding monomer **5** proved to be troublesome resulting in a very low yield.

Spectral Properties. The absorption spectra of the trimers, measured in chloroform solution, seen in Figure 2 show the effect of the substitutions on the optical band gap. Changing the propyl substituents on the AR1 ring into propoxy groups when, AR2 is a benzene or a thiophene ring, red shifts the absorption maximum 44 and 63 nm, respectively (original trimer → **29** and **32** → **35**). Exchanging benzene for thiophene in AR2 similarly affects red shifts of 57 and 50 nm (original trimer → **32** and **29** → **35**). The effect of substituting the AR2 benzene ring in the original trimer with a benzothiadiazole ring is more dramatic with a red shift of 91 nm (original trimer → **36**). Changing the end group from a 4-methoxyphenyl to a terpyridine group (**29** → **40**) on the other hand has almost no effect. The absorption maximum is still at 451 nm with a slightly broader shoulder toward higher wavelengths.

Photovoltaic Behavior. The materials prepared here were also investigated with respect to their photovoltaic properties. It was, however, found that the materials with propoxy sidegroups formed very poor films and it was only possible to prepare photovoltaic devices of **32** and **35**. One reason for this observation could be that the torsion angle between the aryl group and the alkoxy substituent is close to 0° whereas the torsion angle between the aryl group and an alkyl group is close to 90°.[36] In the solid a planar geometry is more easily achieved with alkoxy groups and packing is easier. This could explain the poor solubility for the alkoxy com-

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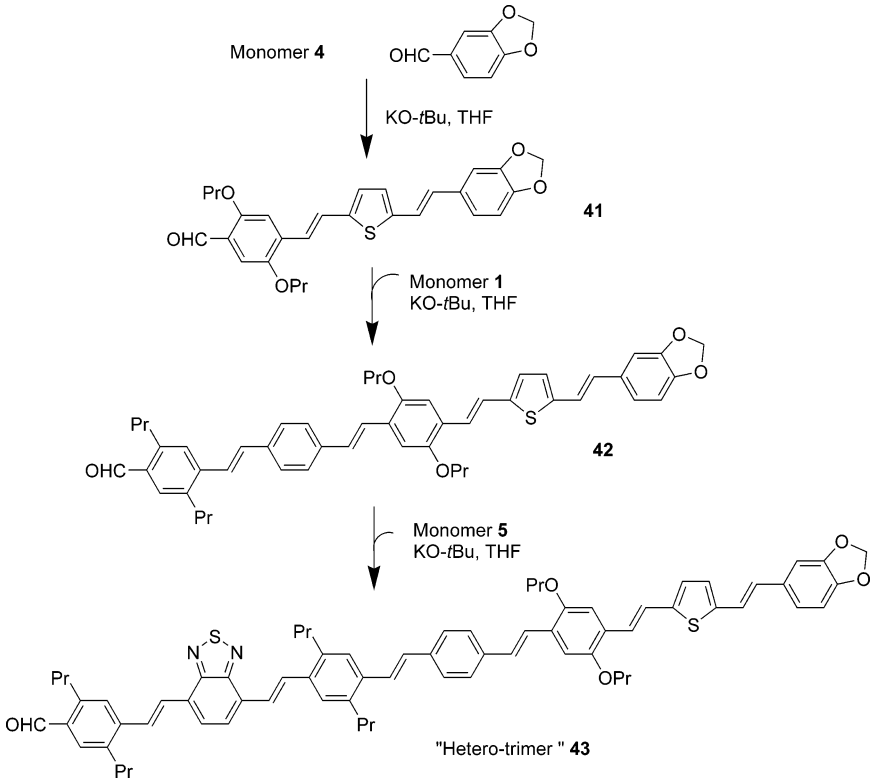
(35) Spahni, W.; Calzaferri, G. *Helv. Chim. Acta* **1984**, *67*, 450.

SCHEME 8. Synthesis of the Hetero Trimer 43 Starting from Piperonal[a]



[a] All seven aromatic rings in this compound are differently substituted showing the versatility of the stepwise oligomerization scheme.

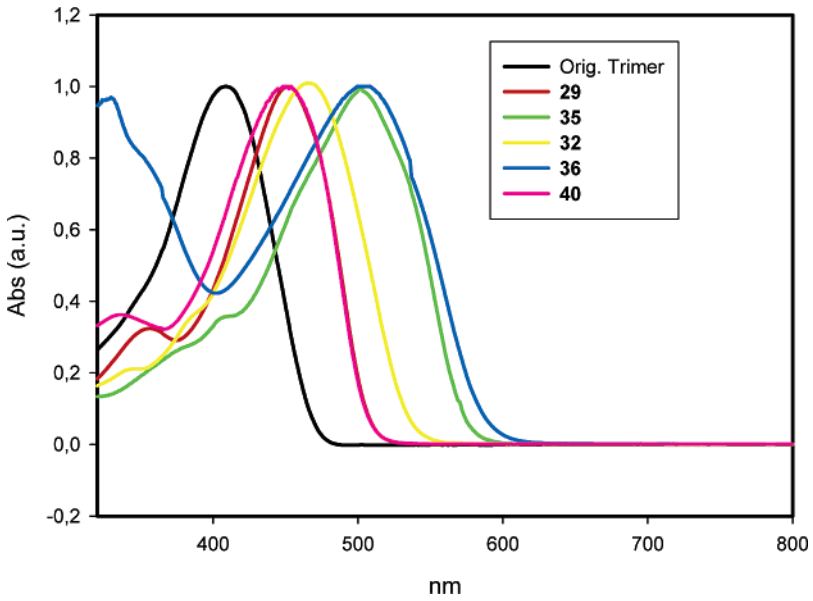


FIGURE 2. Normalized absorption spectra of the original trimer prepared from monomer **1** and the trimers **29**, **32**, **35**, **36**, and **40** dissolved in chloroform.

pounds based on a PPV backbone. Fortunately, this is not the case for the oligophenylenevinylenethienylenevinylene backbone. Photovoltaic cells based on **32** and **35** and their mixtures with the soluble fullerene derivative PCBM[37] were prepared on glass substrates with a layer of PEDOT/PSS covered ITO. The active layer was coated on top by spin-coating and the device was completed by evaporation of an aluminum electrode. The devices were then tested under a sun simulator (AM1.5) with an incident power in the range of 1000 W m^{-2} and the IV-curves were recorded. The results have been summarized in Table 1.

Good dark rectification characteristics and diode behavior were only obtained with a high concentration of

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(37) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60*, 532–538.

TABLE 1. Photovoltaic Data for the Materials Studied

material	rectification |1V|	V_{oc} (V)	I_{sc} (mA cm^{-2})	FF (%)	$P_{Incident}$ (W m^{-2})	η (%)
32	0.92	0.155	−0.005	25	931	0.0002
32/PCBM (1:1)	1.04	0.290	−0.596	27	931	0.0500
32/PCBM (1:4)	9.84	0.499	−2.639	34	970	0.4662
35	0.94	0.080	−0.007	24	945	0.0001
35/PCBM (1:1)	3.46	0.625	−1.875	34	945	0.4216
35/PCBM (1:4)	12.4	0.505	−3.926	38	935	0.8140

[a] The device geometry was ITO/PEDOT:PSS/material/aluminum. The devices were tested under a sun simulator with a spectrum approximating AM1.5 and were not corrected for mismatch. The active area of the devices was 3 cm^2.

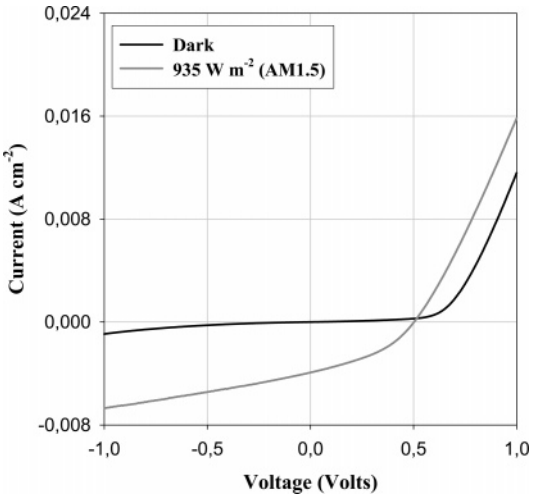

FIGURE 3. IV curves of the device based on **35** and PCBM (1:4) in the dark and under illumination with a sun simulator at 935 W m^{-2} approximating AM1.5 conditions.

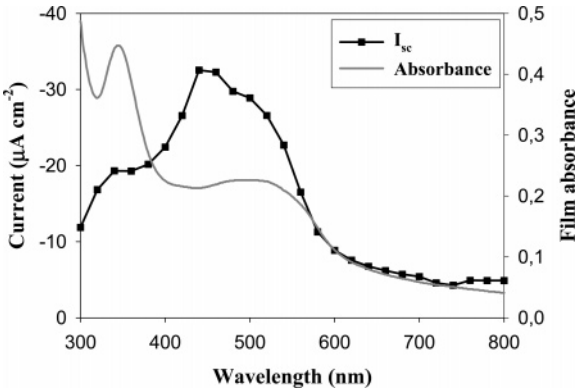

FIGURE 4. Photovoltaic action spectrum in terms of the short circuit current (I_{sc}) for a photovoltaic cell based on a mixture of **35** and PCBM (1:4) with an active area of 3 cm^2. The UV−vis spectrum of the device film is also shown.

PCBM (80 wt %) as shown in Figure 3 for **35**. The fill factors (FF) obtained increased with increasing PCBM concentration as expected. The maximum value obtained was 38% and thus considerably lower than typical literature values exceeding 50% for small area devices (active areas of a few mm^2). Our devices had a large active area (3 cm^2) and the sheet resistance of the electrodes could contribute significantly to the serial resistance of the device. A higher serial device resistance leads to a lowering of the FF. The presence of film imperfections and parasitic or shunt resistances lowers the parallel device resistance and would thus also lead to a lowering of the FF. We attribute the low values for FF to the choice of a large device area. The possibility of achieving functional devices over large area are however paramount for future applications and an active area of a few square centimeters must be considered as an absolute minimum for devices when considering the future potential of the technology.

The photovoltaic action spectrum was symbatic with the absorption spectrum as shown in Figure 4.

The maximum incident photon current efficiency (IPCE) that is a measure of how many of the incident photons that are converted into electrons in the external circuitry was 16% for a 1:4 mixture of **35** and PCBM at the maximum (440 nm). This shows that the photovoltaic conversion is highly efficient in a narrow range. All photovoltaic characterization was performed in the ambient atmosphere.

Conclusion

Four new stilbene-type monomers with an acetal masked aldehyde group connected to a dipropyl- or dipropoxy-substituted benzene ring, and a phosphonate ester group connected to either benzene, thiophene, or a benzothiadiazole ring, have been prepared. Several new synthetic strategies had to be developed to be able to obtain the monomers. With these at hand together with an existing monomer from a previous study, directional stepwise synthesis of oligomers up to the trimer stage were made having seven aryl groups connected by six ethylene bridges. End group functionalization was investigated using a terpyridine group with the promise of easy access to metal coordinated OPVs. Access to the five different monomers also made it possible to prepare a mixed trimer with differently substituted rings in effect a tapering of the electronic levels along the molecule. The convergent synthetic strategy chosen allows for the preparation of gram quantities of the trimers where many of the bonds have been created during the synthetic pathway. The varied nature of the different trimers was reflected in the UV−vis absorption spectra with maxima in the 400−500 nm range. Exchanging the propyl groups in the AR1 ring for propoxy groups and benzene to thiophene in the AR2 ring thus affects a redshift of 100 nm allowing some control over the optical band gap. Photovoltaic devices could be made from two of the trimers **32** and **35** with alternating benzene and thiophene groups. Mixed with the soluble C_{60} derivative PCBM these cells converted the incident light to electric power with efficiencies in the range of 0.5 to 1% with trimer **35** having the highest efficiency and the lowest band gap.

Experimental Section

(4-{2-[4-(5,5-Dimethyl[1,3]dioxan-2-yl)-2,5-dipropoxyphenyl]vinyl}benzyl)phosphonic Acid Diethyl Ester (2) (Monomer 2). 4-Bromo-2,5-dipropoxybenzaldehyde (30 g, 0.1 mol) and 4-vinylbenzylphosphonic acid diethyl ester (25,5 g, 0.10 mol) were dissolved in dioxane (200 mL) together with triethylamine (40 mL) and purged with argon for 5 min. Then catalyst $Pd_2(dba)_3$ (0.4 g) and tri-*tert*-butylphosphine tetrafluoroboric acid salt (0.55 g) were added, and the dark mixture was heated to reflux under argon for 3 h. The next day, dioxane and excess triethylamine was removed in a vacuum, the remaining dark oil was partitioned between diethyl ether (400 mL) and dilute hydrochloric acid (200 mL), the water phase was extracted once with diethyl ether (200 mL), and the combined organic phase was washed with dilute hydrochloric acid, dried over magnesium sulfate, filtered, and evaporated. The oil was dissolved in diethyl ether, silica (ca. 100 mL) was added, and the ether was evaporated. Meanwhile, a large column of silica (ca. 300 mL) slurried in diethyl ether was made up. The crude product/silica mixture was placed on top and eluted with diethyl ether (ca. 2L) to remove a dark band (catalyst and starting material). The product was the eluted with THF. The solvent was removed in a vacuum to give ca. 41 g of yellow oil.

The oil was dissolved in toluene (300 mL) together with 2,2-dimethyl-1,3-propanediol (10.5 g, 0.1 mol) and a catalytic amount of *p*-toluenesulfonic acid and heated to reflux for 1h in a flask equipped with a water separator. The mixture was cooled and filtered through a small layer of potassium carbonate to remove the acid and a small amount of palladium black. The toluene was removed in a vacuum to give a tan oil. Yield: 47.8 g, 99%. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.87 (s, 3H), 1.05 (t, 3H, $J = 7$ Hz), 1.07 (t, 3H, $J = 7$ Hz), 1.24 (t, 6H, $J = 7$ Hz), 1.32 (s, 3H), 1.84 (heptuplet, 4H, $J = 7$ Hz), 3.14 (d, 2H, $J_{PH} = 22$ Hz), 3.65 (d, 2H, $J = 11$ Hz), 3.75 (d, 2H, $J = 11$ Hz), 3.9−4.0 (m, 8H), 5.74 (s, 1H), 7.06 (d, 1H, $J = 16$ Hz), 7.08 (s, 1H), 7.18 (s, 1H), 7.26 (dd, 2H, $J_1 = 2$ Hz, $J_2 = 8$ Hz), 7.45 (d, 1H, $J = 16$ Hz), 7.46 (d, 2H, $J = 8$ Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 10.6, 10.7, 16.3, 16.4, 21.4, 21.8, 22.6, 22.8, 23.2, 30.3, 32.4, 34.6, 36.5, 62.2, 62.3, 70.9, 71.2, 77.9, 97.0, 110.8, 111.6, 123.6, 126.6, 126.7, 127.4, 127.7, 128.6, 129.9, 130.1, 130.5, 130.6, 136.6, 136.7, 150.3, 151.1 ppm. MS: *m/z* 583.2818, calcd for $C_{31}H_{45}O_7P$ (MNa^+) 583.2795.

(5-{2-[4-(5,5-Dimethyl[1,3]dioxan-2-yl)-2,5-dipropylphenyl]vinyl}thiophene-2-ylmethyl)phosphonic Acid Diethyl Ester (Monomer 3). Compound **15** (10 g, 24 mmol) was dissolved in THF (100 mL) and ethanol (50 mL) and treated with sodium borohydride (5 g, excess) for 30 min. The solvents were removed in a vacuum, and the oily residue was separated between water (100 mL) and diethyl ether (100 mL) the organic phase was dried over magnesium sulfate, filtered, and evaporated to dryness. The semisolid was taken up in THF (100 mL) and treated with carbon tetrabromide (8.8 g, 1.1 equiv) and triphenylphosphine (6.9 g, 1.1 equiv) for 1 h. The solvent was removed, and the residue taken up in diethyl ether and filtered through a 5 cm layer of silica to remove most of the triphenylphosphine oxide. Diethyl ether was then removed in a vacuum, and the remaining oil was mixed with an excess of triethyl phosphite. The reaction mixture was heated to reflux for 10 min and the excess triethyl phosphite removed in a vacuum. The raw product was purified by chromatography on silica with diethyl ether as eluent. Yield: 3.2 g, 25% as oil. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.77 (s, 3H), 0.95 (t, 3H, $J = 7$ Hz), 0.97 (t, 3H, $J = 7$ Hz), 1.28 (t, 6H, $J = 8$ Hz), 1.31 (s 3H), 1.61 (heptuplet, 4H, $J = 7$ Hz), 2.64 (p, 4H, $J = 7$ Hz), 3.31 (d, 2H, $J_{HP} = 21$ Hz), 3.62 (d, 2H, $J = 11$ Hz), 3.75 (d, 2H, $J = 11$ Hz), 4.08 (p, 4H, $J = 7$ Hz), 5.48 (s, 1H), 6.8−6.9 (m, 2H), 6.98 (d, 1H, $J = 16$ Hz), 7.06 (d, 1H, $J = 16$ Hz), 7.30 (s, 1H), 7.40 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.1, 14.2, 16.3, 21.8, 23.2, 24.4, 24.6, 25.4, 30.1, 34.2, 35.2, 77.9, 100.0, 122.7, 124.3, 125.4, 125.7, 126.3, 127.6, 127.8, 128.0, 131.3, 132.0, 132.1, 132.5, 132.8, 135.2, 135.5, 137.8, 138.0, 138.2, 140.7. MS: *m/z* 534.2457, calcd for $C_{29}H_{43}O_5PS$ (MNa^+) 534.2461. Anal. Calcd for $C_{29}H_{43}O_5PS$: C, 65.14; H, 8.11. Found: C, 65.41; H, 8.22.

(5-{2-[4-(5,5-Dimethyl[1,3]dioxan-2-yl)-2,5-dipropoxyphenyl]vinyl}thiophene-2-ylmethyl)phosphonic Acid Diethyl Ester (Monomer 4). Prepared from the aldehyde **16** as above. Yield: 37%. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.80 (s, 3H), 1.06 (t, 3H, $J = 7$ Hz), 1.08 (t, 3H, $J = 7$ Hz), 1.30 (t, 6H, $J = 7$ Hz), 1.33 (s, 3H), 1.83 (heptuplet, 4H, $J = 8$ Hz), 3.34 (d, 2H, $J_{HP} = 21$ Hz), 3.65 (d, 2H, $J = 11$ Hz), 3.76 (d, 2H, $J = 11$ Hz), 3.96 (t, 3H, $J = 7$ Hz), 3.99 (t, 3H, $J = 7$ Hz), 4.09 (pentuplet, 4H, $J = 8$ Hz), 5.74 (s, 1H), 6.84−6.89 (m, 2H), 7.00 (s, 1H), 7.17 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 10.6, 10.7, 16.3, 21.8, 22.8, 23.2, 28.5 ($J_{CP} = 2$ Hz), 30.2, 63.0 ($J_{CP} = 1$ Hz), 70.8, 71.1, 77.8, 97.0, 110.6, 111.6, 122.4, 123.2, 125.8, 127.3, 127.8, 131.4, 143.2, 150.3, 151.0 ppm. MS: *m/z* 589.2336, calcd for $C_{29}H_{43}O_7PS$ (MNa^+) 589.2350.

(7-{2-[4-(5,5-Dimethyl[1,3]dioxan-2-yl)-2,5-dipropylphenyl]vinyl}benzo[1,2,5]thiadiazol-4-ylmethyl)phosphonic Acid Diethyl Ester (Monomer 5). The crude product mixture of compound **25** (26.6 mmol) was mixed with NaCl (1.6 g, 26.6 mmol) in NMP (60 mL) and CuI (0.506 g, 2.66 mmol, 10 mol %). The mixture was heated to 90 °C and became dark brown. The phosphonate ester (9.71 g, 26.6 mmol) dissolved in NMP (60 mL) was added slowly. The color soon changed to light yellow/brown and was stirred overnight at 90 °C while adding the phosphonate slowly over about 1 h. The following day, $(PPh_3)_4Pd$ (300 mg) was added and the mixture heated to reflux. The mixture was poured into water and extracted with ether. The ether phase was passed through silica and washed with ether (2 L). It was then washed with THF (2 L). Evaporation of the THF gave a dark red oil. Yield: 6.5 g (42%). ^{1}H NMR (250 MHz, 300 K, TMS, $CDCl_3$) δ: 0.80 (s, 3H), 1.01 (t, 3H, $J = 7$ Hz), 1.18 (t, 3H, $J = 7$ Hz), 1.66 (heptuplet, 4H, $J = 8$ Hz), 2.69 (t, 2H, $J = 7$ Hz), 2.78 (t, 2H, $J = 7$ Hz), 3.65 (d, 2H, $J = 11$ Hz), 3.74 (d, 2H, $J_{PH} = 22$ Hz), 3.78 (d, 2H, $J = 11$ Hz), 4.04 (pentet, 4H, $J = 7$ Hz), 5.53 (s, 1H), 7.41 (d, 1H, $J = 16$ Hz), 7.47 (s, 1H), 7.51 (s, 1H), 7.60 (s, 2H), 8.31 (d, 1H, $J = 16$ Hz); ^{13}C NMR (63 MHz, 300 K, TMS, $CDCl_3$) δ: 14.2, 16.2, 16.3, 17.6, 21.9, 23.2, 24.6, 24.7, 30.3, 34.3, 35.8, 49.3, 62.1, 62.2, 77.9, 99.9, 123.7, 123.9, 125.2, 126.6, 127.0, 129.8, 129.9, 131.6, 135.7, 136.1, 137.9, 138.8, 153.2, 155.4. MS: *m/z* 609.2508, calcd for $C_{31}H_{43}N_2O_5PS$ (MNa^+) 609.2523.

2-(4-Bromo-2,5-dipropylphenyl)-5,5-dimethyl[1,3]-dioxane (9). 4-Bromo-2,5-dipropylbenzaldehyde (52 g, 0.19 mol) was mixed with 2,2-dimethyl-1,3-propanediol (22 g, 1.1 equiv) and *p*-toluenesulfonic acid (200 mg, cat) in toluene (500 mL) in a flask equipped with a Dean−Stark water separator and heated to reflux for 2 h. The cooled mixture was washed with a solution of sodium hydrogen carbonate, dried over magnesium sulfate, filtered, and evaporated to dryness. Yield: 66 g, 96%. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 7.51 (s, 1H), 7.35 (s,1H), 5.49 (s, 1H), 3.78 (d, 2H, $J = 11$ Hz), 3.64 (d, 2H, $J = 11$ Hz), 2.70 (t, 2H, $J = 7$ Hz), 2.63 (t, 2H, $J = 8$ Hz), 1.65 (m, 4H), 1.33 (s, 3H), 0.99 (double triplet, 6H, $J = 8$ Hz), 0.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.0, 14.2, 21.9, 23.3, 24.4, 30.2, 33.7, 37.9, 77.9, 99.5, 124.8, 128.1, 133.4, 135.3, 139.4, 139.6.

2-(4-Bromo-2,5-dipropoxyphenyl)-5,5-dimethyl[1,3]-dioxane (10). 4-Bromo-2,5-dipropoxybenzaldehyde (47 g, 0.15 mol) was dissolved in toluene (300 mL together with 2,2-dimethyl-1,3-propanediol (16 g, 0.15 mol) and *p*-toluenesulfonic acid (cat.) and heated to vigorous reflux for 1 h in flask equipped with a Dean−Stark trap to remove water. The cooled reaction mixture was washed with sodium hydrogencarbonate solution dried over $MgSO_4$, filtered, and finally evaporated. Yield: 57 g, 98%. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 7.21 (s, 1H), 7.07 (s, 1H), 5.69 (s, 1H), 3.99 (t, 2H, $J =$ Hz), 3.88 (t, 2H, $J =$ Hz), 3.75 (d, 2H, $J =$ Hz), 3.64 (d, 2H, $J =$ Hz), 1.7−1.9 (m, 4H), 1.31 (s, 3H), 1.06 (t, 3H, $J =$ Hz), 1.03 (t, 3H, $J =$ Hz), 0.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 150.5, 149.9,

127.2, 117.8, 113.1, 112.6, 96.7, 77.84, 71.6, 71.1, 30.3, 23.2, 22.7, 22.6, 21.8, 10.6, 10.6.

4-(5,5-Dimethyl[1,3]dioxan-2-yl)-2,5-dipropylbenzaldehyde (11). Compound **9** (114 g, 0.321 mol) was dissolved in dry THF and cooled to −78 °C on a dry ice acetone bath under argon. Butyllithium (1.5 M in hexanes, 240 mL) was added in one portion, and the reaction mixture was stirred in the cold for another 10 min to complete the reaction. Then DMF (100 mL, excess) was added, and the cooling bath was removed. After 1 h at ambient temperature, water (200 mL) was added, and the solvents were removed in a vacuum. The remaining oil water mixture was taken up in diethyl ether, dried over magnesium sulfate, filtered, and evaporated again. The oil was distilled. Yield: 84.6 g, 74%. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.82 (s, 3H), 0.99 (t, 3H, J = 7 Hz), 1.34 (s, 3H), 1.61−1.7 (m, 4H), 2.70 (t, 2H, J = 8 Hz), 2.98 (t, 2H, J = 8 Hz), 3.66 (d, 2H, J = 11 Hz), 3.79 (d, 2H, J = 11 Hz), 5.55 (s, 1H), 7.57 (s, 1H), 7.64 (s, 1H), 10.27 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.0, 14.1, 21.8, 23.2, 24.3, 25.6, 30.2, 33.8, 34.0, 77.9, 99.2, 128.9, 132.0, 133.7, 138.4, 141.2, 143.1, 192.1.

4-(5,5-Dimethyl[1,3]dioxan-2-yl)-2,5-dipropoxybenzaldehyde (12). Prepared from **10** as above. Yield: 82% as a white solid. Could be recrystallized with loss from ethanol. Mp: 76−77 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 10.47 (s, 1H), 7.30 (broad s, 2H), 5.74 (s, 1H), 4.06 (t, 2H, J = 8 Hz), 3.95 (t, 2H, J = 8 Hz), 3.75 (d, 2H, J = 11 Hz), 3.69 (d, 2H, J = 11 Hz), 1.84 (m, 4H), 1.32 (s, 3H), 1.06(t, 3H, J = 7 Hz), 1.03 (t, 3H, J = 7 Hz), 0.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 189.580, 156.304, 150.115, 134.652, 125.293, 112.140, 110.299, 96.505, 77.875, 70.641, 70.596, 30.349, 23.210, 22.596, 22.555, 21.830, 10.577, 10.527. Anal. Calcd for $C_{19}H_{28}O_5$: C, 67.83; H, 8.39. Found: C, 67.69; H, 8.40.

2-[2,5-Dipropyl-4-(2-thiophene-2-ylvinyl)phenyl]-5,5-dimethyl[1,3]dioxane (13). Prepared using the same procedure as for compound **14** (below). Yield: 45%. Mp: 80−81 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.82 (s, 3H), 1.00 (t, 3H, J = 7 Hz), 1.01 (t, 3H, J = 7 Hz), 1.35 (s, 3H), 1.66 (heptuplet, 4H, J = 7 Hz), 2.6−2.75 (m, 4H), 3.65 (d, 2H, J = 11 Hz), 3.79 (d, 2H, J = 11 Hz), 5.53 (s, 1H), 7.01 (dd, 1H, J = 4 Hz, J = 5 Hz), 7.09 (d, 1H, J = 16 Hz), 7.07 (dd, 1H, J = 1.0 Hz, J = 4 Hz), 7.18 (d, 1H, J = 16 Hz), 7.19 (d, 1H, J = 5 Hz), 7.35 (s, 1H), 7.41 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.2, 14.3, 21.9, 23.3, 24.5, 24.7, 30.2, 34.3, 35.3, 77.9, 100.0, 122.7, 124.1, 125.7, 126.2, 126.5, 127.6, 135.2, 135.7, 137.8, 138.2, 143.4. Anal. Calcd for $C_{24}H_{32}O_2S$: C, 74,95; H, 8,39. Found: C, 75,-04; H, 8,47.

2-[2,5-Dipropoxy-4-(2-thiophene-2-ylvinyl)phenyl]-5,5-dimethyl[1,3]dioxane (14). Dioxolane aldehyde starting material (43.5 g, 0.129 mol) and thiophenemethyl phosphonate ester (30 g, 1 equiv) were mixed in THF (500 mL) under argon. Potassium *tert*-butoxide (20 g, excess) was dissolved in THF and added to the reaction mixture in small portions. The reaction was exothermic and a gel formed. The mixture was then heated to reflux for 1 h during which time the mixture became a thin slurry. The cooled reaction mixture was diluted with water and the solvent evaporated. The yellow oil was partitioned between water (100 mL) and diethyl ether (250 mL). The organic phase was dried over $MgSO_4$, filtered, and evaporated to give 52 g oil that solidified on standing. The solid was triturated with methanol (150 mL) and filtered to give 34 g of moist yellow crystalline material. ^{1}H NMR showed that this material was slightly impure with a small amount of the starting aldehyde. The raw material was therefore recrystallized from 150 to 200 mL methanol. Yield: 23 g, 42%. Mp: 113−114 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.81 (s, 3H), 1.07 (t, 3H, J = Hz), 1.10 (t, 3H, J = Hz), 1.34 (s, 3H), 1.85 (m, 4H), 3.67 (d, 2H, J = Hz), 3.77 (d, 2H, J = Hz), 4.00 (m, 4H), 5.75 (s, 1H), 6.99−7.06 (m, 3H), 7.18 (d, 1H, J = Hz), 7.20 (s, 1H), 7.27 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 151.1, 150.3, 143.7, 127.5, 127.4, 125.6, 125.6, 124.1, 123.7, 122.4, 115.2, 111.7, 110.9, 97.1, 77.9, 77.030, 76.9, 76.5, 71.1, 71.0, 30.3, 23.2, 22.8, 21.9, 10.8, 10.7 ppm. Anal. Calcd for $C_{24}H_{32}O_4S$: C, 69.20; H, 7.74. Found: C, 69.15; H, 7.75.

5-{2-[4-(5,5-Dimethyl[1,3]dioxan-2-yl)-2,5-dipropylphenyl]vinyl}thiophene-2-carbaldehyde (15). Compound **13** (16 g, 42 mmol) was dissolved in THF (250 mL) and cooled on a dry ice−acetone bath. At −50 °C, butyllithium (30 mL, 1.5 M in hexanes) was added, and the temperature was allowed to reach 0 °C in 30 min. Cooling was applied while adding DMF (25 mL, excess) to keep the temperature below −30 °C. Stirring at ambient temperature was continued for 1 h to complete the reaction, and water (100 mL) was added. The solvents were removed in a vacuum, and the residue was taken up in diethyl ether. The ether phase was separated and evaporated to give a tan oil that was triturated with methanol (50 mL) and scratched to induce crystallization. Yield: 13.4 g, 78%. Mp: 113−115 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.82 (s, 3H), 0.99 (t, 3H, J = 7 Hz), 1.01 (t, 3H, J = 7 Hz), 1.34 (s, 3H), 2.6−2.7 (m, 4H), 3.66 (d, 1H, J = 11 Hz), 3.79 (d, 1H, J = 11 Hz), 5.52 (s, 1H), 7.10 (d, 1H, J = 16 Hz), 7.14 (d, 2H, J = 4 Hz), 7.38 (s, 1H), 7.41 (d, 1H, J = 16 Hz), 7.47 (s, 1H), 7.66 (d, 2H, J = 4 Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.1, 14.2, 21.9, 23.2, 24.7, 30.2, 35.2, 77.9, 99.8, 121.7, 126.3, 126.7, 127.9, 130.7, 134.5, 136.4, 137.1, 138.1, 138.9, 141.4, 153.0, 182.5. MS: m/z 327.1423, calcd for $C_{20}H_{22}O_2S$ (MH^+) 327.1413.

5-{2-[4-(5,5-Dimethyl[1,3]dioxan-2-yl)-2,5-dipropoxyphenyl]vinyl}thiophene-2-carbaldehyde (16). Prepared from **14** as above. Yield: 76%. Mp: 128−129 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.80 (s, 3H), 1.04 (t, 3H, J = 7 Hz), 1.09 (t, 3H, J = 7 Hz), 1.33 (s, 3H), 1.85 (heptuplet, 4H,J = 8 Hz), 3.66 (d, 2H, J = 11 Hz), 3.76 (d, 2H, J = 11 Hz), 5.74 (s, 1H), 7.02 (s, 1H), 7.12 (d, 2H, J = 4 Hz), 7.21 (s, 1H), 7.25 (d, 1H, J = 16 Hz), 7.50 (d, 1H, J = 16 Hz), 7.64 (d, 2H, J = 4 Hz), 9.84 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 10.6, 10.7, 21.8, 22.8, 23.7, 30.3, 70.8, 71.1, 77.9, 111.2, 111.6, 121.3, 126.0, 126.1, 128.3, 137.2, 141.3, 150.3, 151.6, 153.5, 182.5.

4-Methylbenzo-2,1,3-thiadiazole (17). 3-Methyl-1,2-phenylenediamine (0.66 mol), prepared by reduction of 2-amino-3-nitrotoluene using $SnCl_2$ in concentrated HCl, was stirred in benzene (500 mL) when $SOCl_2$ (200 mL, excess) was added over 30 min with vigorous stirring. HCl(g) was evolved, and the evaporation cooled the solution. The mixture was heated gently. After 3 days, the black mixture with a yellow transmission color was hydrolyzed carefully with water. The benzene was evaporated, and the mixture was steam distilled. After 2 L of steam had distilled, the distillation was stopped and the distillate was saturated with NaCl and extracted with ether. Evaporation gave 65 g (65%). ^{1}H NMR (250 MHz, 300 K, TMS, $CDCl_3$): δ 2.65 (s, 3H), 7.10 (d, J = 7 Hz, 1H), 7.36 (dd, J_1=7 Hz, J_2=9 Hz, 1H), 7.30 (d, J = 9 Hz, 1H); ^{13}C NMR (63 MHz, 300 K, TMS, $CDCl_3$): δ 17.6, 118.8, 127.7, 129.3, 131.5, 154.9, 155.4. Elemental analysis in accordance with ref 20.

4-Bromo-7-methylbenzo-2,1,3-thiadiazole (18). Compound **17** (15 g, 0.1 mol) was dissolved in HBr(aq) 47% (100 mL). The mixture was stirred while bromine (16 g (0.1 mol) was added. The mixture was stirred and heated. After 5 min, a solid precipitated. After 30 min, the color of bromine had disappeared and a colorless sticky adduct had formed. The mixture was heated to vigorous reflux with vigorous stirring. A sudden evolution of HBr(g) was observed indicating the elimination of HBr. Crystals gradually formed on the sides of the flask. After 16 h, the reaction was stopped. Some of the product had deposited in the condenser. The colorless product was extracted with CH_2Cl_2, and the organic phase was dried ($MgSO_4$) and evaporated to give the pure product. Yield: 19.75 g (86%). Mp: 135−137 °C. ^{1}H NMR (250 MHz, 300 K, TMS, $CDCl_3$) δ: 2.57 (s, 3H), 7.06 (d, J = 7 Hz, 1H), 7.56 (d, J = 7 Hz, 1H). ^{13}C NMR (63 MHz, 300 K, TMS, $CDCl_3$) δ: 17.4, 111.1, 128.3, 131.1, 131.8, 153.0, 155.0. Anal. Calcd for $C_7H_5BrN_2S$: C, 36.70; H, 2.20; N, 12.24. Found: C, 36.74; H, 1.79; N, 11.96.

4-Bromo-7-bromomethylbenzo-2,1,3-thiadiazole (19). Compound **18** (19.7 g, 0.086 mol) was mixed with NBS (15.3

g, 0.086 mol) and benzoyl peroxide (50 mg) in CCl_4 (500 mL). The mixture was heated to reflux when 33% HBr in AcOH (1 mL) was added. The reaction usually started within a few minutes and was complete in 30 min. The mixture was evaporated, and the solids were dissolved in CH_2Cl_2 (1 L). The organic phase washed with water (3 × 500 mL), dried over $MgSO_4$, and evaporated to dryness. The solid could be recrystallized from CCl_4 but was sufficiently pure for use in the subsequent step. Yield: 25.6 g (97%). Mp: 138−140 °C. ^{1}H NMR (250 MHz, 300 K, TMS, $CDCl_3$) δ: 4.92 (s, 2H), 7.51 (d, J = 7 Hz, 1H), 7.79 (d, J = 7 Hz, 1H). ^{13}C NMR (63 MHz, 300 K, TMS, $CDCl_3$) δ: 27.6, 114.8, 129.8, 130.3, 131.9, 152.9, 153.5. Anal. Calcd for $C_7H_4Br_2N_2S$: C, 27.30; H, 1.31; N, 9.10. Found: C, 27.51; H, 1.05; N, 9.06.

4-Bromo-7-(diethylphosphonomethyl)benzo-2,1,3-thiadiazole (20). Compound **19** (25.6 g, 0.083 mol) was refluxed in triethyl phosphite (100 mL) for 1 h. Evaporation of the triethyl phosphite gave a yellow oil that was distilled using a microdistillation apparatus. The product was collected as a yellow oil discarding two prefractions. Bp: 220−232 °C/0.01 × 10^{-3} bar. Yield: 22.9 g (73%). ^{1}H NMR (250 MHz, 300 K, TMS, $CDCl_3$) δ: 1.07 (t, J = 7 Hz, 6H), 3.57 (d, J = 22 Hz, 2H), 3.94 (q, J = 7 Hz, 4H), 7.36 (dd, J_1 = 7 Hz, J_2 = 4 Hz, 1H), 7.65 (d, J = 7 Hz, 1H). ^{13}C NMR (63 MHz, 300 K, TMS, $CDCl_3$) δ: 16.68 (d, J = 6 Hz), 29.30 (d, J = 140 Hz), 62.65 (d, J = 6 Hz), 113.06 (d, J = 5 Hz), 125.54 (d, J = 10 Hz), 130.38 (d, J = 7 Hz), 132.35 (d, J = 4 Hz), 153.40 (d, J = 2 Hz), 154.73 (d, J = 6 Hz). Anal. Calcd for $C_{11}H_{14}BrN_2O_3PS$: C, 36.18; H, 3.86; N, 7.67. Found: C, 35.80; H, 3.39; N, 7.69.

2,5-Dipropyl-4-(5,5-dimethyl-1,3-dioxan-2-yl)styrene (21). Compound **11** (45.6 g, 150 mmol) was mixed with triphenylphosphonium bromide (60 g, excess) in dry THF (500 mL) under argon. tBuOK (20 g, excess) was added slowly in portions. The mixture acquired a yellow color and became warm. The mixture was stirred under argon for 24 h. The mixture was poured into water (1 L), and the THF was evaporated. The mixture was extracted with ether, and the ether phase was dried and evaporated to a volume of 250 mL and passed through a column packed with silica (10 cm Ø × 10 cm). The product eluted first and was obtained as a light yellow oil. Yield: 36.75 g (81%). ^{1}H NMR (250 MHz, 300 K, TMS, $CDCl_3$) δ: 0.81 (s, 3H), 0.95−1.03 (m, 6H), 1.34 (s, 3H), 1.5−1.7 (m, 4H), 2.58−2.70 (m, 4H), 3.65 (d, J = 11 Hz, 2H), 3.78 (d, J = 11 Hz, 2H), 5.25 (dd, J_1 = 2 Hz, J_2 = 11 Hz, 1H), 5.62 (dd, J_1=2 Hz, J_2=17 Hz, 1H), 5.53 (s, 1H), 6.96 (dd, J_1 = 11 Hz, J_2 = 17 Hz, 1H), 7.28 (s, 1H), 7.43 (s, 1H). ^{13}C NMR (63 MHz, 300 K, TMS, $CDCl_3$) δ: 14.18, 14.23, 21.9, 23.2, 24.3, 24.7, 30.2, 34.2, 35.1, 77.9, 100.0, 114.9, 126.8, 127.2, 134.7, 135.2, 136.6, 137.7, 137.8. Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 78.55; H, 10.19.

2,5-Dipropoxy-4-(5,5-dimethyl-1,3-dioxan-2-yl)-styrene (22). Compound **12** (50 g, 149 mmol) was mixed with triphenylphosphonium bromide (60 g, excess) in dry THF (500 mL) under argon. tBuOK (20 g, excess) was added slowly in portions. The mixture became a little more yellow and warm. The mixture was stirred under argon for 24 h. Water (100 mL) was added, and the mixture was evaporated. Ether was added, and the mixture was washed with water. A solid was sometimes observed to crystallize from the aqueous phase (this was found to be triphenylphosphine oxide). The ether phase was passed through silica. The product runs in the front and triphenylphosphine oxide was retained. The pure product was obtained as a yellow oil. Yield: 45 g (90%). ^{1}H NMR (250 MHz, 300 K, TMS, $CDCl_3$) δ: 0.79 (s, 3H), 1.05 (t, J = 8 Hz, 6H), 1.33 (s, 3H), 1.74−1.86 (m, 4H), 3.65 (d, J = 11 Hz), 3.76 (d, J = 11 Hz), 3.89−4.00 (m, 4H), 5.25 (dd, J_1 = 2 Hz, J_2 = 11 Hz, 1H), 5.72 (dd, J_1 = 2 Hz, J_2 = 18 Hz, 1H), 5.75 (s, 1H), 7.00 (s, 1H), 7.06 (dd, J_1 = 11 Hz, J_2 = 18 Hz, 1H), 7.18 (s, 1H); ^{13}C NMR (63 MHz, 300 K, TMS, $CDCl_3$) δ: 10.63, 10.67, 21.8, 22.8, 23.2, 30.2, 70.7, 71.0, 77.8, 97.0, 110.8, 111.3, 114.2, 127.5, 128.0, 131.7, 150.2, 150.8. Anal. Calcd for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.49; H, 9.12.

2,5-Dipropyl-4-(5,5-dimethyl-1,3-dioxan-2-yl)phenylacetylene (23). Compound **21** (34.5 g, 114 mmol) was dissolved in ether (500 mL) containing pyridine (0.5 mL). The mixture was cooled to 0 °C. Bromine (5.85 mL, 114 mmol) was added with stirring. After 10 min, the mixture was evaporated. THF (500 mL) was added and the product dissolved under argon. tBuOK (30 g, excess) was added and the mixture heated to reflux. After 1 h, the reaction was complete. The mixture was cooled, and water (500 mL) was added. The organic phase was separated and dried. Evaporation gave an oil that was distilled on a microdistillation apparatus. A prefraction (1 g) boiling up to 170 °C was discarded. The fraction boiling at 170−176 °C/0.007mbar was collected. Yield: 17.25 g (40%). ^{1}H NMR (250 MHz, 300 K, TMS, $CDCl_3$) δ: 0.81 (s, 3H), 0.99 (t, J = 8 Hz, 6H), 1.34 (s, 3H), 1.60−1.75 (m, 4H), 2.63 (t, J = 7 Hz, 2H), 2.77 (t, J = 7 Hz, 2H), 3.21 (s, 1H), 3.65 (d, J = 11 Hz, 2H), 3.79 (d, J = 11 Hz, 2H), 5.55 (s, 1H), 7.31 (s, 1H), 7.51 (s, 1H). ^{13}C NMR (63 MHz, 300 K, TMS, $CDCl_3$) δ: 14.09, 14.15, 21.8, 23.2, 23.9, 24.3, 30.2, 33.7, 36.3, 77.9, 80.1, 82.6, 99.6, 121.7, 126.5, 133.8, 136.5, 137.4, 142.9. Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.96; H, 9.39. Found: C, 80.12; H, 9.60.

2,5-Dipropoxy-4-(5,5-dimethyl-1,3-dioxan-2-yl)phenylacetylene (24). Compound **22** (38.1 g, 114 mmol) was dissolved in ether (500 mL) containing pyridine (0.5 mL). The mixture was cooled to 0 °C, and bromine (5.83 mL, 114 mmol) was added slowly. The color of the bromine disappeared immediately. A solid precpipitated. The mixture was evaporated and dissolved in THF (500 mL). tBuOK (30 g, excess) was added with cooling. The mixture was heated to reflux. After 1 h, the reaction was complete. The mixture was cooled, and water was added. The organic phase was separated and dried. Evaporation gave an oil that was distilled on a microdistillation apparatus discarding a small prefraction boiling below 160 °C/4 × 10^{-3} mbar. The fraction boiling at 160−180 °C/4 × 10^{-3} mbar was collected. Yield: 18.5 g (54%). ^{1}H NMR (250 MHz, 300 K, TMS, $CDCl_3$) δ: 0.77 (s, 3H), 0.99−1.07 (m, 6H), 1.30 (s, 3H), 1.73−1.86 (m, 4H), 3.26 (s, 1H), 3.63 (d, J = 11 Hz, 2H), 3.73 (d, J = 11 Hz, 2H), 3.88 (t, J = 6 Hz, 2H), 4.01 (t, J = 6 Hz, 2H), 5.71 (s, 1H), 6.96 (s, 1H), 7.19 (s, 1H); ^{13}C NMR (63 MHz, 300 K, TMS, $CDCl_3$) δ: 10.48, 10.54, 21.8, 22.6, 23.1, 30.2, 70.8, 71.0, 77.8, 80.1, 81.1, 96.7, 111.7, 112.6, 117.7, 129.0, 149.6, 154.7. Anal. Calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 71.94; H, 8.74.

1-Tributylstannyl-2-(2,5-dipropyl-4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)ethylene (25). The ethyne (8 g, 26.6 mmol) was mixed with tributylstannyl hydride (8 g, slight excess) neat and heated under argon to 50 °C. The reaction was followed using NMR and was found to proceed smoothly over a few hours. The appearance of two doublets and disappearance of the acetylenic proton is easy to follow. After 3 h, tributylstannyl hydride (1.5 g) was added and the temperature increased to 100 °C for 30 min. This completed the reaction that would seem to be a 2:1 mixture of *cis* and *trans* (or *trans* and *cis*). The mixture was used directly.

HWE Reactions of the Monomers (1−5) with Aromatic Aldehydes and Extension to the Dimers and Trimers. General Procedure. 4-(2-{4-[2-(4-Methoxyphenyl)vinyl]-phenyl}vinyl)-2,5-dipropoxybenzaldehyde (27). Monomer **2** (1.3 g, 2.3 mmol) and 4-methoxybenzaldehyde (0.52 g, 3.8 mmol, excess) were dissolved in THF (50 mL), and the mixture was heated to reflux and treated with potassium *tert*-butoxide (0.7 g, excess). The reaction mixture was stirred at reflux for 30 min to complete the HWE reaction. Concentrated hydrochloric acid (5 mL) was added and reflux continued for 30 min to hydrolyze the acetal function. The solvent was removed in a vacuum and the residue mixed with water (25 mL). The solid product was filtered off, washed with water (2 × 25 mL) and ethanol (2 × 25 mL), and finally dried in a vacuum. Yield: 0.81 g, 76%. A small sample was recrystallized from acetonitrile. Mp: 168−9 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.10 (t, 6H, J = 7 Hz), 1.89 (p, 4H, J = 7 Hz), 3.83 (s, 3H), 4.00 (t, 2H, J = 7 Hz), 4.07 (t, 2H, J = 6 Hz), 6.91, (d, 2H, J = 9 Hz), 6.97 (d,

1H, J = 16 Hz), 7.10 (d, 1H, J = 16 Hz), 7.17 (s, 1H), 7.24 (d, 1H, J = 16 Hz), 7.33 (s, 1H), 7.4−7.6 (m, 7H), 10.47 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 10.6, 10.7, 22.6, 55.3, 70.6, 70.7, 110.1, 110.5, 114.2, 122.5, 124.2, 126.0, 126.6, 127.2, 127.8, 128.5, 130.0, 131.9, 134.4, 136.2, 137.7, 150.7, 156.2, 159.4, 189.0. MS: *m/z* 456.2312, calcd for $C_{30}H_{32}O_4$ (MH^+) 456.2301.

4-[2-(4-{2-[4-(2-{4-[2-(4-Methoxyphenyl)vinyl]phenyl}-vinyl)-2,5-dipropoxyphenyl]vinyl}phenyl)vinyl]-2,5-dipropoxybenzaldehyde (28). The methoxy-terminated monomer **27** from above (0.81 g, 1.7 mmol) and monomer **2** (1.3 g, 2.3 mmol, excess) were reacted as above with potassium *tert*-butoxide to give the methoxy-terminated dimer product. Yield: 1.1 g, 82%. Mp: 191−3 °C. Could be recrystallized from a small amount of benzene. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.11 (t, 6H, J = 7 Hz), 1.15 (t, 6H, J = 7 Hz), 1.92 (p, 8H, J = 7 Hz), 3.84 (s, 3H), 3.99−4.12 (m, 8H), 6.89 (d, 2H, J = 8 Hz), 6.97 (d, 1H, J = 16 Hz), 7.10 (d, 1H, J = 16 Hz), 7.12−7.22 (m, 5H), 7.26 (d, 1H, J = 16 Hz), 7.34 (s, 1H), 7.37 (s, 1H), 7.5−7.6 (m, 12H), 10.48 (s, 1H). MS: *m/z* 776.3923, calcd for $C_{52}H_{56}O_6$ (MH^+) 776.4077.

4-{2-[4-(2-{4-[2-(4-{2-[4-(2-{4-[2-(4-Methoxyphenyl)vinyl]-phenyl}vinyl)-2,5-dipropoxyphenyl]vinyl}phenyl)vinyl]-2,5-dipropoxyphenyl}vinyl)phenyl]vinyl}-2,5-dipropoxybenzaldehyde (29). Compound **28** (1.0 g, 1.3 mmol) and monomer **2** (1,3 g, 2.3 mmol, excess) were reacted as above to give the trimer product as an orange powder. Yield: 1.20 g, 83%. Mp: 236−8 °C. UV−vis [chloroform, $\lambda_{max}(\epsilon)$]: 452 (142 000). Could be recrystallized from DMF. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.08−1.20 (m, 18H), 1.92 (p, 12H, J = 7 Hz), 3.83 (s, 3H), 3.99−4.1 (m, 12H), 6.91 (d, 2H, J = 9 Hz), 6.97 (d, 1H, J = 16 Hz), 7.09 (d, 1H, J = 16 Hz), 7.1−7.2 (m, 9H), 7.29 (s, 1H), 7.35 (s, 1H), 7.4−7.6 (m, 19 H), 10.48 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 10.6, 10.7, 10.8, 22.7, 22.9, 55.3, 70.6, 70.8, 71.1, 110.2, 110.6, 114.2, 123.2, 124.3, 126.3, 126.6, 126.8, 127.0, 127.2, 127.7, 128.0, 128.5, 130.2, 134.4, 136.4, 136.8, 137.0, 137.1, 137.3, 138.1, 150.8, 151.1, 156.2, 159.3, 189.0 ppm. MS: *m/z* 1110.6213, calcd for $C_{75}H_{83}NO_7$ (MH^+) 1110.6242.

4-(2-{5-[2-(4-Methoxyphenyl)vinyl]thiophene-2-yl}vinyl)-2,5-dipropylbenzaldehyde (30). Prepared as above from 4-methoxybenzaldehyde and monomer **3**. Recrystallized from ethanol. Yield: 54%. Mp: 98−100 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.02 (t, 6H, J = 7 Hz), 1.59−1.78 (m, 4H), 2.76 (t, 2H, J = 8 Hz), 3.00 (s, 2H, J = 8 Hz), 3.84 (s, 3H), 6.9−7.1 (m, 10H), 7.24 (d, 1H, J = 16 Hz), 7.4−7.5 (m, 3H), 7.64 (s, 1H), 10.23 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 13.9, 14.0, 24.0, 25.5, 34.2, 34.9, 55.3, 114.3, 119.7, 124.3, 125.5, 126.5, 127.4, 127.7, 128.3, 128.8, 129.6, 132.5, 132.8, 138.3, 140.8, 141.0, 143.1, 143.4, 159.5, 191.7 ppm. MS: *m/z* 430.1962, calcd for $C_{28}H_{30}O_2S$ (MH^+) 430.1967.

4-[2-(5-{2-[4-(2-{5-[2-(4-Methoxyphenyl)vinyl]thiophene-2-yl}vinyl)-2,5-dipropylphenyl]vinyl}thiophene-2-yl)-vinyl]-2,5-dipropylbenzaldehyde (31). Prepared from the methoxyterminated monomer **30** and monomer **3**. Used directly in the next step. Yield: 52%. Mp: 167 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.02 (t, 6H, J = 7 Hz), 1.04 (t, 6H, J = 6 Hz), 1.61−1.76 (m, 8H), 2.7−2.8 (m, 6H), 3.00 (t, 2H, J = 7 Hz), 3.84 (s, 3H), 6.8−7.4 (m, 14H), 7.4−7.5 (m, 5H), 7.64 (s, 1H), 7.24 (s, 1H).

4-{2-[5-(2-{4-[2-(5-{2-[4-(2-{5-[2-(4-Methoxyphenyl)vinyl]-thiophene-2-yl}vinyl)-2,5-dipropylphenyl]vinyl}thiophene-2-yl)vinyl]-2,5-dipropylphenyl}vinyl)thiophene-2-yl]vinyl}-2,5-dipropylbenzaldehyde (33). Prepared from the dimer **32** and monomer **3**. Yield: 67%. Mp: 195−8 °C. UV−vis [chloroform, $\lambda_{max}(\epsilon)$]: 465 (146 000). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.97−1.08 (m, 18H), 1.6−1.8 (m, 12H), 2.7−2.8 (m, 10H), 3.01 (t, 2H, J = 8 Hz), 3.84 (s, 3H), 6.8−7.3 (m, 23H), 7.4−7.5 (m, 7H), 7.65 (s, 1H), 10.24 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.0, 24.1, 25.5, 34.3, 34.9, 35.3, 55.3, 114.2, 119.9, 122.2, 122.6, 124.6, 125.5, 126.5, 126.6, 127.0, 127.6, 128.2, 128.3, 129.8, 132.5, 132.8, 134.4, 134.5, 134.7, 134.8, 138.3, 138.4, 140.8, 141.5, 142.2, 142.4, 142.5, 143.1, 143.6, 159.4, 191.7. MS: *m/z* 1019.4937, calcd for $C_{68}H_{74}O_2S_3$ (MH^+) 1019.4924.

4-(2-{5-[2-(4-Methoxyphenyl)vinyl]thiophene-2-yl}vinyl)-2,5-dipropoxybenzaldehyde (33). Prepared from 4-methoxybenzaldehyde and monomer **4** as above. Recrystallized from ethanol to give red powder. Yield: 67%. Mp: 134−135 °C. UV−vis [chloroform, $\lambda_{max}(\epsilon)$]: 440 (42 700). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.09 (t, 3H, J = 7 Hz), 1.11 (t, 3H, J = 7 Hz), 1.81−1.96 (m, 4H), 3.82 (s, 3H), 3.99 (t, 2H, J = 6 Hz), 4.05 (t, 2H, J = 6 Hz), 6.49 (d, 1H, J = 4 Hz), 6.91 (d, 2H, J = 4 Hz), 6.98−7.01 (m, 3H), 7.08 (broad singlet, 1H), 7.20 (d, 1H, J = 16 Hz), 7.31 (s, 1H), 7.37 (d, 1H, J = 16 Hz), 7.41 (d, 2H, J = 9 Hz), 10.44 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 10.6, 10.7, 22.6, 55.3, 70.6, 70.7, 110.2, 110.5, 114.2, 119.7, 122.3, 124.1, 125.6, 126.4, 127.7, 128.2, 128.7, 129.6, 133.9, 141.4, 143.5, 150.7, 156.2, 159.5, 188.9. MS: *m/z* 463.1935, calcd for $C_{28}H_{30}O_4S$ (MH^+) 463.1938.

4-[2-(5-{2-[4-(2-{5-[2-(4-Methoxyphenyl)vinyl]thiophene-2-yl}vinyl)-2,5-dipropoxyphenyl]vinyl}thiophene-2-yl)-vinyl]-2,5-dipropoxybenzaldehyde (34). Prepared from compound **33** and monomer **4**. Yield: 76%. Mp 119−120 °C. UV−vis [chloroform, $\lambda_{max}(\epsilon)$]: 484 (82 200). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.05−1.18 (m, 12H), 1.91 (heptuplet, 8H, J = 7 Hz), 3.83 (s, 3H), 3.99−4.01 (m, 8H), 6.84−7.01 (m, 11H), 7.21−7.28 (m, 5H), 6.86 (d, 2H, J = 8 Hz), 7.42 (d, 2H, J = 9 Hz), 10.45 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 10.6, 10.7, 10.8, 22.6, 22.9, 55.3, 70.7, 70.8, 71.1, 110.7, 114.2, 119.9, 122.5, 124.2, 126.9, 127.6, 129.8, 134.0, 141.8, 142.3, 144.1, 150.8, 151.1, 151.2, 156.2, 159.4, 188.9. MS: *m/z* 788.3166, calcd for $C_{48}H_{52}O_6S_2$ (MH^+) 788.3205.

4-{2-[5-(2-{4-[2-(5-{2-[4-(2-{5-[2-(4-Methoxyphenyl)vinyl]-thiophene-2-yl}vinyl)-2,5-dipropoxyphenyl]vinyl}-thiophene-2-yl)vinyl]-2,5-dipropoxyphenyl}vinyl)-thiophene-2-yl]vinyl}-2,5-dipropoxybenzaldehyde (35). Prepared from compound **34** and monomer **4**. Yield: 89%. Mp: 120−125 °C. UV−vis [chloroform, $\lambda_{max}(\epsilon)$]: 502 (118 000). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.04−1.2 (m, 18H), 1.8−2.0 (m, 12H), 3.83 (s, 3H), 4.0−4.1 (m, 12H), 6.8−7.1 (m, 15H), 7.2−7.4 (m, 13H), 10.45 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 10.6, 10.7, 10.8, 22.7, 22.9, 55.3, 70.6, 70.7, 71.1, 110.2, 110.5, 114.2, 120.0, 122.5, 123.3, 123.4, 124.1, 125.6, 126.8, 127.6, 128.0, 129.8, 134.0, 141.8, 142.2, 142.3, 144.1, 150.7, 151.1, 151.2, 156.2, 159.4, 188.9. MS: *m/z* 1115.4611, calcd for $C_{68}H_{74}O_8S_3$ (MH^+) 1115.4619.

4-[2-(7-{2-[4-(2-{7-[4-(2-{7-[2-(4-Methoxyphenyl)vinyl]-benzo[1,2,5]thiadiazol-4-yl}vinyl)-2,5-dipropylphenyl]-vinyl}benzo[1,2,5]thiadiazol-4-yl}vinyl)-2,5-dipropyl-phenyl]vinyl}benzo[1,2,5]thiadiazol-4-yl)vinyl]-2,5-di-propylbenzaldehyde (36). Prepared from monomer **5** and 4-methoxybenzaldehyde in three steps using sodium hydride as the base. Unfortunately, the yield in each step was rather poor and the final product was contaminated with some lower and higher molecular weight components, presumably the dimer and tetramer. This crude product was purified using size-exclusion chromatography which left only enough material for mass spectroscopy and absorption spectroscopy. UV−vis [chloroform, $\lambda_{max}(\epsilon)$]: 310, 499. MS: *m/z* 1174.5081, calcd for $C_{74}H_{74}N_6O_2S_3$ (MH^+) 1174.5030.

4-{2-[4-(5,5-Dimethyl-[1,3]dioxan-2-yl)-2,5-dipropyl-phenyl]vinyl}-7-[2-(4-methoxyphenyl)vinyl]benzo-[1,2,5]thiadiazole (37). Monomer **5** (300 mg, 0.5 mmol) and 4-methoxybenzaldehyde (150 mg, 1.1 mmol) were dissolved in THF (50 mL), sodium hydride (100 mg, 60% dispersion in mineral oil) was added, and the mixture was heated to reflux for 1 h. The cooled reaction mixture was then filtered through a layer of silica to remove excess monomer and basic residues. The solvent was removed in a vacuum, and the orange red residue was triturated with hot ethanol (50 mL) and cooled. The product was filtered off, washed with ethanol (25 mL) and petroleum ether (2 × 50 mL), and finally dried in a vacuum. Yield: 80 mg 28%. Mp: 126−128 °C. ^{1}H NMR ($CDCl_3$, 250.1

MHz) δ: 0.83 (s, 3H), 1.04 (t, 6H, J = 7 Hz), 1.36 (s, 3H), 1.71 (heptuplet, 4H, J = 7 Hz), 2.73 (t, 2H, J = 8 Hz), 2.82 (t, 2H, J = 8 Hz), 3.68 (d, 2H, J = 11 Hz), 3.81 (d, 2H, J = 11 Hz), 3.86 (s, 3H), 5.56 (s, 1H), 6.94 (d, 2H, J = 8 Hz), 7.4−7.6 (m, 6H), 7.65 (s, 2H), 7.93 (d, 1H, J = 16 Hz), 8.34 (d, 1H, J = 16 Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.3, 21.9, 23.3, 24.6, 24.8, 30.2, 34.3, 35.5, 55.3, 77.9, 100.0, 114.2, 122.5, 125.5, 126.2, 126.5, 127.3, 127.7, 128.2, 129.4, 129.6, 130.4, 131.1, 132.7, 135.6, 136.3, 137.9, 138.9, 153.9, 159.8.

(4-[2,2′;6′,2″]Terpyridin-4′-yl-benzyl)phosphonic Acid Diethyl Ester (38).[33] 4′-*p*-Tolyl[2,2′;6′,2″]terpyridine was prepared according to the solventless method developed by Cave and Raston[38] and subsequently reacted with *N*-bromosuccinimide (NBS). The 4′-(4-bromomethylphenyl)[2,2′:6′,2″]terpyridine[34] (6.2 g, 15.4 mmol) was mixed with triethyl phosphite (10 mL, excess) and heated to reflux for 30 min. On cooling, the product separated as an off-white powder that was triturated with petroleum ether and filtered off. Yield: 6.3 g, 89%. Mp: 93−94 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.24 (t, 6H, J = 7 Hz), 3.18 (d, 2H, J = 21 Hz), 4.01 (heptuplet, 4H, J = 7 Hz), 7.28 (ddd, 2H, J = 1 Hz, J = 5 Hz, J = 7 Hz), 7.41 (dd, 2H, J = 2 Hz, J = 8 Hz), 7.77−7.84 (m, 4H), 8.61 (D, 2H, J = 8 Hz), 8.68 (d, 2H, J = 8 Hz), 8.69 (s, 2H).

2,5-Dipropoxy-4-[2-(4-[2,2′;6′,2″]terpyridin-4′-ylphenyl)-vinyl]benzaldehyde (39). Prepared from terpyridine benzyl phosphonate ester and aldehyde **12**. Recrystallized from ethanol. Yield: 87%. Mp: 222−224 °C. ^{1}H NMR (250 MHz, 300 K, DMSO-d_6−$CDCl_3$ 1:1) δ: 1.04 (t, 3H, J = 7 Hz), 1.06 (t, 3H, J = 7 Hz), 1.81 (pentuplet, 4H, J = 7 Hz), 3.96 (t, 2H, J = 6 Hz), 4.09 (t, 2H, J = 6 Hz), 7.17 (s, 1H), 7.44 (d, 1H, J = 17 Hz), 7.52 (d, 1H, J = 17 Hz), 8.02 (t, 2H, J = 6 Hz), 8.05 (s, 1H), 8.16 (d, 2H, J = 8 Hz), 8.59 (t, 2H, J = 7 Hz), 9.02 (d, 2H, J = 5 Hz), 9.07 (s, 2H), 9.24 (d, 2H, J = 8 Hz), 10.32 (s, 1H). ^{13}C NMR ($CDCl_3$ with 4 dr CF_3COOH, 62.9 MHz) δ: 10.4, 22.4, 71.0, 107.7, 112.3, 116.8, 121.3, 123.0, 123.3, 124.9, 125.2, 127.9, 128.0, 134.0, 135.6, 140.0, 142.5, 146.2, 146.8, 148.0, 150.8, 153.6, 157.5, 158.4, 159.1, 159.7, 160.4. MS: *m/z* 556.2590, calcd for $C_{36}H_{33}N_3O_3$ (MH^+) 556.2595.

4-[2-(4-{2-[4-(2-{4-[2-(2,5-Dipropoxy-4′-[2,2′;6′,2″]terpyridin-4′-yl-biphenyl-4-yl)vinyl]phenyl}vinyl)-2,5-dipropoxyphenyl]vinyl}phenyl)vinyl]-2,5-dipropoxybenzaldehyde (40) (Trimer Terpyridin). Prepared from compound **39** and monomer **2** in two HWE reaction/acetal deprotection cycles in 43% yield as an orange powder. Mp: 267−268 °C. UV−vis [chloroform, $\lambda_{max}(\epsilon)$]: 451 (126 000). ^{1}H NMR (250 MHz, 300 K, $CDCl_3$) δ: 1.0−1.2 (m, 18H), 1.8−2.0 (m, 12H), 4.0−4.1 (m, 12H), 7.1−7.4 (m, 14H), 7.47−7.69 (m, 14H), 7.86−7.96 (m, 4H), 8.67−8.78 (m, 6H) 10.47 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 10.6, 10.7, 10.8, 22.6, 22.9, 70.7, 71.2, 110.8, 118.5, 121.3, 123.7, 123.7, 126.9, 127.0, 127.2, 127.5, 128.6, 134.4, 136.8, 137.2, 138.9, 149.1, 149.7, 151.2, 156.0, 156.2, 156.4. MS: *m/z* 1196.6162, calcd for $C_{80}H_{81}N_3O_7$ (MH^+) 1196.6147.

4-{2-[5-(2-Benzo[1,3]dioxol-5-ylvinyl)thiophene-2-yl]-vinyl}-2,5-dipropoxybenzaldehyde (41). Prepared from piperonal and monomer **4**. Yield: 82%. Mp: 137−138 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.09 (t, 3H, J = 7 Hz), 1.11 (t, 3H, J = 7 Hz), 1.87 (p, 2H, J = 7 Hz), 1.90 (p, 2H, J = 7 Hz), 4.00 (t, 2H, J = 6 Hz), 4.06 (t, 2H, J = 6 Hz), 5.98 (s, 2H), 6.79 (d, 1H, J = 8 Hz), 6.85 (d, 1H, J = 16 Hz), 6.89−7.05 (m, 5H), 7.08 (s, 1H), 7.20 (d, 1H, J = 16 Hz), 7.31 (s, 1H), 7.37 (d, 1H, J = 16 Hz), 10.45 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 10.6, 10.7, 22.6, 70.6, 70.7, 101.2, 105.3, 108.5, 110.2, 110.5, 120.2, 121.5, 122.5, 124.1, 125.6, 126.7, 128.2, 128.8, 131.4, 133.9, 141.6, 143.1, 147.5, 148.2, 150.7, 156.2, 188.9 ppm. MS: *m/z* 477.1724, calcd for $C_{28}H_{28}O_5S$ (MH^+) 477.1730.

4-(2-{4-[2-(4-{2-[5-(2-Benzo[1,3]dioxol-5-ylvinyl)thiophene-2-yl]vinyl}-2,5-dipropoxyphenyl)vinyl]phenyl}-vinyl)-2,5-dipropylbenzaldehyde (42). Prepared from the product above and monomer **1**. Yield: 85%. Mp: 144−146 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.02 (t, J = 7 Hz), 1.04 (t, J = 7 Hz), 1.15 (t, J = 7 Hz), 1.16 (t, J = 7 Hz), 1.6−1.8 (m, 4H), 19−2.0 (m, 4H), 2.78 (t, 2H, J = 8 Hz), 3.02 (t, 2H, J = 8 Hz), 4.0−4.1 (m, 4H), 5.98 (s, 2H), 6.8−7.2 (m, 11H), 7.26 (s + s, 2H), 7.37 (d, 1H, J = 16 Hz), 7.5−7.6 (m, 6H), 7.66 (s, 1H), 10.25 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 10.8, 14.0, 22.9, 24.0, 25.6, 34.2, 34.9, 71.0, 71.1, 101.2, 105.3, 108.5, 110.6, 120.4, 121.4, 126.7, 126.9, 127.2, 127.9, 128.1, 131.6, 132.5, 132.7, 136.2, 138.1, 138.4, 141.3, 141.9, 142.5, 143.1, 147.4, 148.2, 151.1, 151.2, 191.8 ppm. MS: *m/z* 764.3530, calcd for $C_{50}H_{52}O_5S$ (MH^+) 764.3535

Hetero Trimer (43). Prepared from compound **42** and monomer **5**. Yield: 21%. Mp: 198 °C dec. UV−vis [chloroform, $\lambda_{max}(\epsilon)$]: 460 (86 000). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.8−1.2 (m, 18H), 1.6−2.0 (m, 12H), 4.0 (m, 12H), 5.96 (s, 2H), 6.7−7.7 (m, 28H), 8.41 (d, 1H, J = 9 Hz), 10.27 (s, 1H). MS: *m/z* 1111.5112, calcd for $C_{72}H_{74}N_2O_5S_2$ (MH^+) 1111.5112.

Diethyl 2-Thiophene-yl-2-methylphosphonate Ester and Bisester. Thiophene (84 g, 1 mol) was mixed with paraformaldehyde (33 g, 1.1 mol) in acetic acid (250 mL) and cooled using an ice−ethanol bath. HBr (185 mL, ca. 1 mol, 33% in acetic acid) was added in one portion with vigorous stirring. The temperature increased to 30 °C and then declined back to 5 °C. After being stirred at that temperature for 1 h, the mixture was allowed to reach ambient temperature and then poured into water (2 L). The organic phase was separated, diluted with chloroform (300 mL), washed with saturated sodium hydrogen carbonate solution (1 L), dried over magnesium sulfate, filtered, and dried. The solvent was removed in a vacuum to give an oil (110 g) with the approximate composition 85/15 of 2-bromomethylthiophene and 1,4-bis-bromomethylthiophene that was mixed directly with triethyl phosphite (200 g, excess) and heated to reflux for 1 h and then distilled in a vacuum. Yield: 95.3 g of diethyl 2-thiophene-yl-2-methylphosphonate ester, 40% based on thiophene, bp 112−6 °C at 3×10^{-3} mbar. Continued distillation gave the tetraethyl thiophene 2,5-bis (methylphosphonate ester). Yield: 24 g. Bp: 210−45 °C at 3×10^{-3} mbar.

Photovoltaic Characterization. Photovoltaic devices were prepared on PEDOT/PSS-coated ITO substrates as reported elsewhere.[7] The concentration of the solutions were typically 20 mg mL^{-1} in chlorobenzene. In the case of the oligomer/PCBM mixtures this implied a varying absorption intensity of the oligomer component for the device (see the Supporting Information). The film absorbencies were in the range 0.7−0.2. All manipulations were carried out in air. The samples were then transferred to the vacuum chamber of the evaporator and pumped to a pressure $<2 \times 10^{-6}$ mbar and left for 1 h before the aluminum electrode (100 nm) was applied by thermal evaporation. After cooling, the system was purged with argon and the samples were mounted with silver epoxy and the thermosetting silver epoxy hardened in an oven at 75 ± 5 °C for 15 min. The samples were then analyzed immediately after hardening the silver epoxy. The active area of the devices was 3 cm^{-2}. The electrical measurements were carried out using a Keithley 2400 Sourcemeter. The wavelength dependence of the photovoltaic response was measured using a high power spectrometer comprised of a 150W water-cooled Xenon lamp, a blazed diffraction grating, and a movable arm with the sample. The setup has been described earlier (see also the Supporting Information).[39] The photovoltaic response under simulated sunlight (AM1.5) was performed using a Solar Constant 575 from Steuernagel Lichttechnik GmBH, Germany. The spectrum of the solar simulator was determined in the wavelength range 180−1100 nm using an optical spectrum analyzer and was found to have larger abundance of UV-photons and a smaller abundance of IR photons. The use of a UV filter was found necessary to

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approximate AM1.5 conditions in the wavelength range relevant for this study. The simulated sunlight was then adjusted to approximately 900−1000 W m^{-2} using a bolometric precision pyranometer from Eppley laboratories. The exact incident power was recorded during each experiment. The temperature of the devices during measurement was 72 ± 2 °C. The results were not corrected for mismatch of the spectral response. The photovoltaic response degraded quickly in the atmosphere for the pure oligomers and somewhat slower for the oligomer/PCBM mixtures (see the Supporting Information). In the latter case, half-lives of the order of 24 h were observed under illumination (1000 W m^{-2}, AM1.5). The degradation of the photovoltaic response with time is well-known and mechanistic studies have been reported recently.[40] Reaction with both oxygen from the atmosphere and the aluminum electrode is responsible for the degradation.[41] Other possible factors include humidity from the atmosphere.

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Supporting Information Available: IV curves, wavelength scans, and device film UV−vis spectra for all devices studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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