Stepwise and Directional Synthesis of End-Functionalized Single-Oligomer OPVs and Their Application in Organic Solar Cells

Mikkel Jørgensen* and Frederik C. Krebs

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

mikkel.joergensen@risoe.dk

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A new stepwise directional synthetic route to single-oligomer *p*-phenylenevinylenes (OPVs) has been developed. The first step in the reaction sequence is the condensation of a functionalized benzaldehyde with a novel monomer having a methyl phosphonate ester group in one end and an acetal-protected aldehyde at the other end of a stilbene core. Oligomerization then proceeds stepwise by alternating reaction of the previous aldehyde-terminated OPV fragment with the monomer and deprotection of the acetal. Thus, a series of OPVs with 3, 5, 7, 9, and 11 phenylene vinylene units has been prepared that has an electron-donating methoxy group at one end and an electron-accepting aldehyde group at the other end. Some examples where a dimethylamino group replaced the methoxy group were also prepared. The oligomer with seven phenylene vinylene units was then further derivatized at the aldehyde position to create a series of OPVs with a range of substituents from strongly electron-accepting nitrophenyl to electron-donating methoxyphenyl. Photovoltaic cells were assembled with the synthesized OPVs as the photoactive layer. Illumination under simulated sunlight (AM1.5) gave short circuit currents (I_{sc}) in the range 0.015−0.5 mA cm^{-2} and typical open circuit voltages (V_{oc}) of 0.4−0.8 V. The maximum efficiency obtained was ~0.1%.

Introduction

Single oligomers of *p*-phenylenevinylenes (OPVs) are of interest in many areas of materials research, in some cases as models for the corresponding poly-*p*-phenylenevinylenes (PPVs) that are used in organic light-emitting displays (PLEDs),[1,2] field-effect transistors (FETs),[3−5] and photovoltaics (solar cells).[6−8] Single oligomers may be advantageous in these applications because polymers are rather broad distributions in terms of molecular weight and may also contain impurities that are hard to determine and quantify. Single molecule compounds are of course much better defined, and the properties can therefore be correlated more easily with the structure.[9,10] Conjugated oligomers of definite length have also been proposed as electronic wires for the construction of circuits and even computers in a “bottom-up” technology.[11,12] Another advantage of single oligomers is the ability to modify the end groups to obtain OPVs with an electron donor in one end and an acceptor in the other end, resulting in *donor-wire-acceptor*-type compounds.[13]

In an earlier approach to OPVs produced by a stepwise and directional route, Yu et al. utilized a scheme with alternate coupling of two different monomers.[14,15] The Heck reaction and the Horner−Wadsworth−Emmons reaction were then used to connect the growing OPV with the monomers. The oligomer that was produced in these experiments had an alternating substitution pattern with two alkoxy or alkyl groups on every second benzene ring (see Chart 1).

In the course of investigating the charge carrier mobilities of some conducting polymers for photovoltaic devices, we independently prepared a range of PPVs very similar to the OPVs studied by Yu's group with linear alkyl chains from C6 to C12.[16] The mobilities found were

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* To whom correspondence should be addressed.

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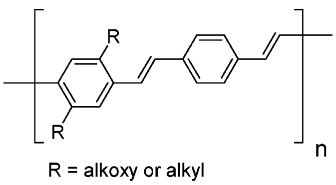
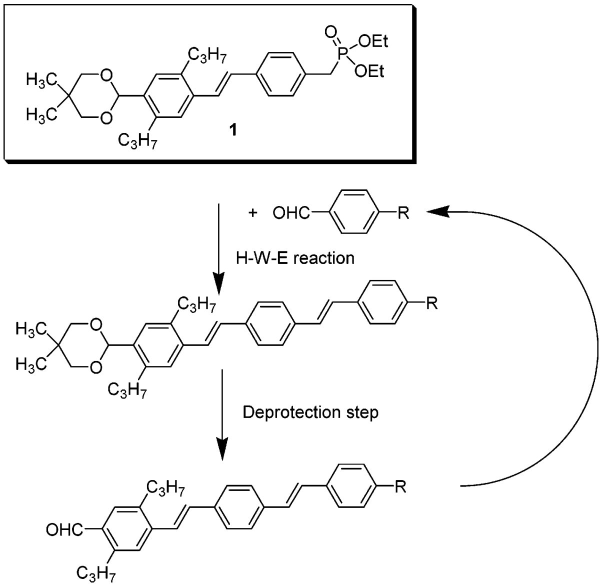
10.1021/jo049111x CCC: $27.50

CHART 1



SCHEME 1. Stepwise Oligomerization of the Acetal Protected Monomer 1[a]



[a] In the first step, the substituent R denotes methoxy, *N*,*N*-dimethylamino, or halogen. Subsequently, R becomes the remaining part of the extended OPV.

very high indeed, and together with the other interests mentioned above, this prompted us to undertake a new investigation of single oligomer OPVs. On the other hand, we also recently found that when palladium-catalyzed reactions are used for polymerization this almost invariably leads to the incorporation of small palladium nanoparticles that are very hard or impossible to remove.[17] Even very small amounts of these particles degrade the properties of thin film devices prepared from these polymers by creating electrical shorts or preferred conduction paths. We have therefore developed an alternative and somewhat simpler reaction scheme to these OPVs utilizing only one monomer with a phosphonate ester group in one end and an acetal-protected aldehyde in the other. The oligomerization then proceeds in two alternating steps: the Horner−Wadsworth−Emmons reaction followed by deprotection of the aldehyde as depicted in Scheme 1.

The finished OPVs contain a terminal aldehyde group that is ideally suited for further functionalization. In a related paper, Xue and Luo[18] have prepared a monomer very similar to **1**, but with alkoxy groups instead of alkyl. They used this rather “hard to come by” monomer to obtain symmetrical oligomers in a stepwise fashion, whereas the present paper describes the uncommon unidirectional oligomerization. We also investigated the end-group functionalization using the HWE reaction with a series of electron-donating and -accepting benzylphosphonate esters or Knoevenagel-type condensation with malodinitrile. Finally, condensation with 2,3-dimethylbenzothiazolium hexafluorophosphate has been carried out to obtain cyanine-type dyes. Cyanine and merocyanine dyes have been utilized both as photosensitizers of silver halide in photographic films and as dye sensitizers of TiO_2-based photovoltaics.[19] These single-oligomer OPVs with different end groups were then investigated in organic photovoltaic cells.

Results and Discussion

Synthesis. The crucial part of the OPV synthesis outlined above is the preparation of the acetal-protected monomer **1**. Several different routes to this compound were investigated. One could, e.g., envisage adding the phosphonate ester group as the last step via an Arbuzov reaction, but it proved impossible to prepare the required bromomethyl precursor for this route without destroying the aldehyde or acetal functionality in the other end of the molecule. It was therefore decided to build the central vinyl group using the Heck reaction as the last step. An obvious commercial starting material was 4-vinylbenzyl chloride that can be converted to the diethyl phosphonate ester **2** via the Arbuzov reaction as described previously by Boutevin et al.[20] We found that this compound was rather sensitive and partly destroyed under the reaction conditions published. Adding 1 equiv of sodium iodide and running the reaction in acetonitrile as solvent was found to improve the yield somewhat.

The other reaction partner in the central Heck reaction, 4-bromo-2,5-dipropyl-benzaldehyde **3**, was prepared from 2,5-dipropyl-1,4-dibromobenzene as previously described for the similar dioctyl compound[16] in three steps from commercially available 1,4-dichlorobenzene. Several versions of the Heck reaction were then tried out with different catalyst/phosphine and base mixtures in polar solvents. It was found to be essential that both reactants **2** and **3** were distilled immediately before the reaction. The best conditions found were essentially those described by Littke and Fu using Pd_2dba_3, tri-*tert*-butylphosphine, and excess triethylamine as the base.[21] Other amine bases also worked, but it was observed that with dicyclohexylmethylamine partial cleavage of the ester groups in the ethyl phosphonate moiety took place. The aldehyde-terminated monomer was finally protected by acetalization with 2,2-dimethyl-1,3-propandiol to form **1** (Scheme 2).

Stepwise Oligomerization. The stepwise oligomerization starts as shown in Scheme 1 with the HWE reaction between an aldehyde and the monomer **1**. This aldehyde can in principle have one or more substituents

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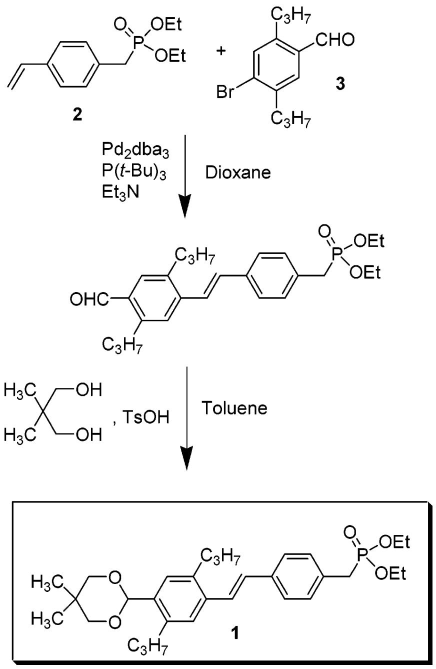
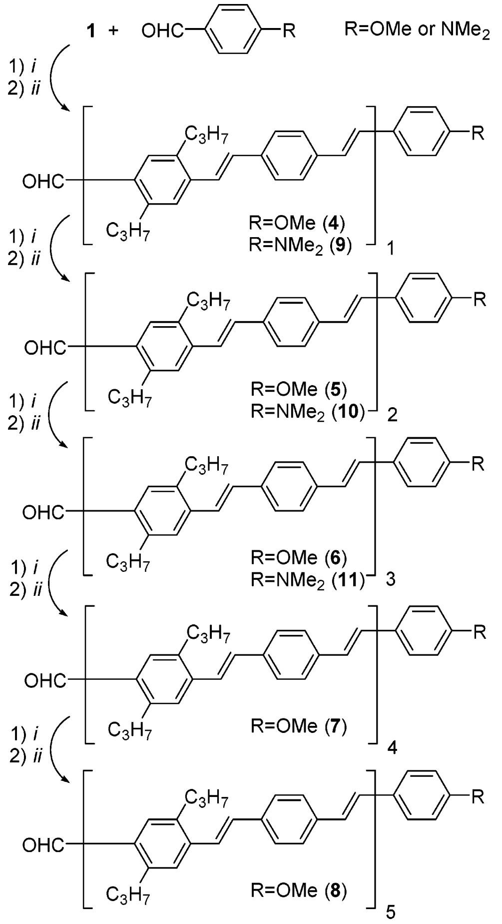
SCHEME 2. Synthesis of the Acetal-Protected Monomer 1



SCHEME 3. Synthesis of the OPV Oligomers 4−8 with Methoxy Groups and Oligomers 9−11 with Dimethylamino Groups[a]



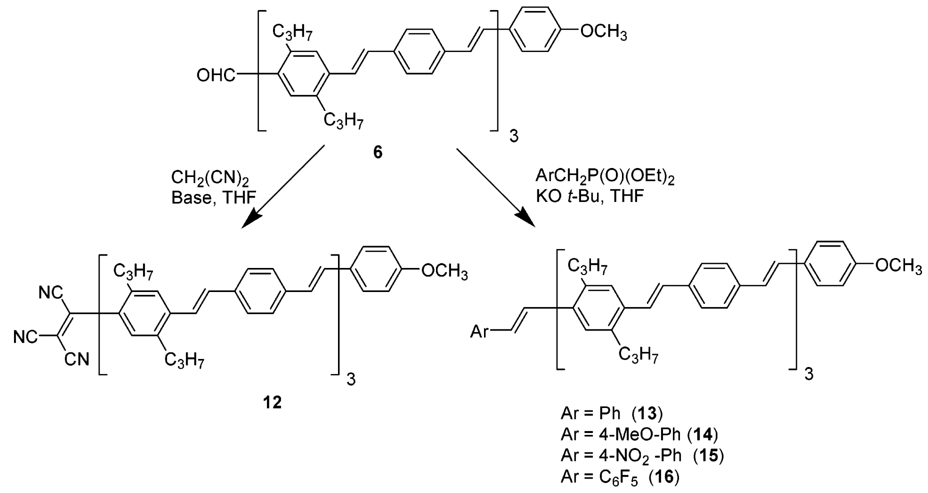
[a] Reaction conditions: (*i*) HWE reaction with **1** in dioxane with potassium *tert*-butoxide; (*ii*) acetal hydrolysis with dilute hydrochloric acid.

that can be used for further elaboration at a later stage. Presently, we have used 4-iodo-, 4-bromo-, 4-dimethylamino-, or 4-methoxybenzaldehyde as the starting point for the oligomerization. The product of this HWE reaction is an end-capped "monomer" that consists of three benzene rings separated by two vinylene groups. Simply pouring the reaction mixture from the HWE reaction directly into dilute hydrochloric acid cleaved the acetal-protecting group. Repeating the HWE reaction with monomer **1** and the previous product, followed by deacetalization in one pot, then effected the elongation of the oligomer by two more phenylene vinylene residues. Both the HWE-reaction and the deprotection step are fast, clean, and high yielding. These factors are of course important considerations when little purification is performed between each step in the oligomerization; otherwise, byproducts will rapidly accumulate. Each monomer unit extends the oligomer by about 13 Å so with end groups the pentamer (**8**), which is the longest prepared, is approximately 70 Å long. Many properties, such as the absorption maximum and extinction coefficient, scale with the size of the conjugated system. Thus, the color of the oligomers in the solid state changes from the almost colorless monomer over yellow to orange and finally to orange-red for the pentamer (**8**). Unfortunately, the solubility of the oligomers decreases with the size making them increasingly difficult to prepare and derivatize. The trimer (**6**) is still readily soluble in, e.g., chloroform while the pentamer (**8**) is only soluble in solvents such as hot 1,2-dichlorobenzene. Using larger and/or branched alkyl chains could perhaps alleviate this problem. Attempts in that direction were investigated, but preparation of sufficiently pure monomers such as **1** was unsuccessful.

One of the obvious attractive starting groups is 4-iodo- and 4-bromobenzaldehyde, which should then give access to oligomers substituted at one end with the halogen and at the other with an aldehyde functionality. The oligomerization reactions proceeded efficiently to the trimer with these aldehydes, but when the products were analyzed by ^{1}H NMR and mass spectrometry (MALDI-TOF) it was revealed that the halogens had been eliminated. In the case of iodine, only the trimer with no halogen was detected, while in the case of bromine a varying amount remained. A possible explanation is that under the HWE reaction conditions potassium *tert*-butoxide may attack the halogen atom. The resulting OPV anion then abstracts a proton, e.g., from the solvent, to give the observed product. 4-Methoxybenzaldehyde was then used as the starting aldehyde to react with the monomer **1**. The methoxy group provides a convenient reference signal in NMR and illustrates that some functionality is possible in the starting end of the OPV. Later, dimethylaminobenzaldehyde was used to create a smaller series of OPVs (see Scheme 3).

End-Group Functionalization. The terminal aldehyde group in the OPV **6** was used as starting point for end-group functionalization. Knoevenagel condensation with malodinitrile gave the tricyanovinylene OPV **12** as evidenced by mass spectrometry. Probably, malodinitrile is first condensed with the aldehyde forming the dinitrile. Excess malodinitrile then reacts with this product under

SCHEME 4. End Functionalization of the OPV 6 Using Either a Knoevenagel-Type Condensation with Malodinitrile or an HWE Reaction with Arylmethylphosphonate Esters

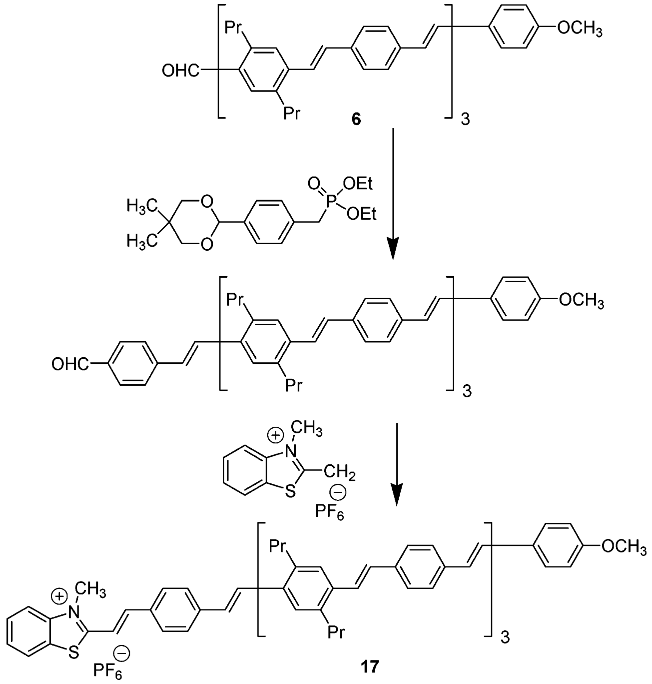


oxidative conditions to form the product. Tricyanovinylenes have been observed in a number of malodinitrile condensations.[22] Benzyl phosphonate esters substituted with electron-donating or -accepting groups were used in HWE reactions to prepare the OPVs **13** to **16** (see Scheme 4).

Another interesting possibility is to react the aldehyde group of the OPVs with, e.g., an *N*-alkylbenzothiazolium salt to form cyanine dye terminated oligomers. *N*-Methyl-2-methyl-1,3-benzothiazolium hexafluorophosphate did indeed react with the OPVs to give deeply red-violet colored materials, but definite products could not be obtained. A possible explanation could be that sterical hindrance from the propyl group ortho to the aldehyde makes the reaction less favorable. Test reactions with 4-bromobenzaldehyde, on the other hand, could be readily controlled to give the cyanine using 1 equiv of the *N*-methylbenzothiazolium salt. Since this unhindered aldehyde reacted so well, a possible solution was to extend the OPVs with one phenylvinylene group. To this end, an acetal-protected diethyl phosphonylbenzaldehyde was prepared according to Accorsi et al.[23] This reagent reacted successfully with the OPV **6** under HWE conditions, and the acetal function was deprotected as previously described. The cyanine-derivatized OPV **17** were now prepared in a straightforward manner as depicted in Scheme 5.

The cyanine-terminated OPV precipitated directly from the reaction mixture and could be separated by simple filtration. To enhance the solubility for device fabrication, the hexafluorophosphate ion was exchanged with the novel tetrabiphenylborate anion. The synthesis of sodium tetrabiphenylborate is presented in the Experimental Section.

SCHEME 5. Synthesis of the Cyanine-Terminated OPV 17[a]



[a] The OPV **6** was first extended with the reagent diethyl 4-(5,5-dimethyl-1,3-dioxan-2-yl)-benzylphosphonate ester to create an unhindered aldehyde and then condensed with 1 equiv of 2,3-dimethylbenzothiazolium hexafluorophosphate to create the cyanine-OPV **17**.

Characterization of the OPV Oligomers. The oligomers were conveniently characterized by their ^{1}H NMR spectra. In Figure 1, a stacked plot of ^{1}H spectra of the methoxy-terminated OPVs **4**, **5**, **6**, and **7** are shown. The most notable change occurs for the signals due to the methylene groups neighboring the aryl group(s) occurring as triplets at 2.9 and 3.1 ppm. The signal at 3.1 ppm is due to the methylene group ortho to the aldehyde group, and the signal at 2.9 ppm is due to the methylene group(s) ortho to the vinylene group(s). As the oligomer is enlarged the relative intensity of these two signals changes accordingly from 1:1 in **4** to 1:5 in **6**. Size exclusion chromatography (SEC), normally used for characterization of polymers, is well suited for assessing the purity of the OPV oligomers. In this chromatographic technique, the molecules are simply separated according to their hydrodynamic volume with the largest molecules being eluted first. As seen in Figure 1, the oligomers **4**−**8** are easily separated by this system and the purities are

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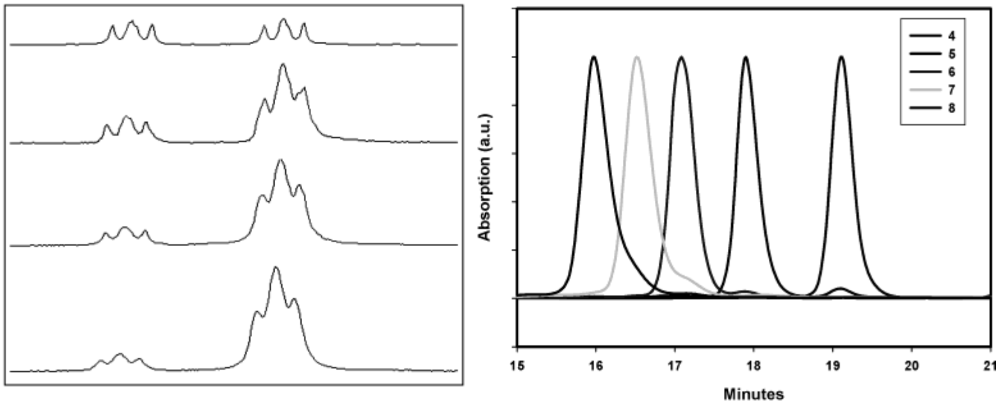

FIGURE 1. Characterization of the oligomers with ^{1}H NMR and SEC. (Left) an overlay of the ^{1}H NMR spectra in the region 2.5−3.2 ppm, with the signals from the two types of methylene groups connected to the aryl groups, of the OPV monomer (**4**), dimer (**5**), trimer (**6**), and tetramer (**7**) (from top to bottom). (Right) the normalized size exclusion Chromatograms of the OPVs **4**−**8**.

TABLE 1. Summary of PR-TRMC Data Obtained for the Oligomers 4−6[a]

OPV	$\Delta\sigma_{\mathrm{eop}}/\rho D$ (S m^2 J^{-1})	$\Sigma\mu_{\min}$ (cm^2 V^{-1} s^{-1})	$\tau_{1/2}$ (μs)
4	7.5×10^{-8}	1.9×10^{-2}	9
5	7.0×10^{-8}	1.8×10^{-2}	11
6	8.5×10^{-8}	2.1×10^{-2}	12

[a] Dose-normalized conductivity changes are shown along with the corresponding minimum sum of charge carrier mobilities based on a pair formation energy of 25 eV and a survival probability of 1 taken at 1 μs post end-of-pulse (eop). The first half-life is also quoted.

high. The pentamer **8** does, however, contain small amounts of **6** and **7**.

Charge Carrier Mobilities Studied by PR-TRMC. The minimum sum of carrier mobilities was determined using the pulse radiolysis time-resolved microwave conductivity technique developed by Warman et al.[24] and applied to PPVs with alkyl substituents on every second benzene ring.[16] The technique is contactless and independent of experimental parameters such as thin film preparation, etc.[16,24] A high carrier mobility $\Sigma\mu_{\min}$ is an important parameter for materials destined for semiconductor applications to allow the carriers to reach external electrodes rather than being trapped internally and lost. The results are summarized in Table 1. While the values of the carrier mobilities are high and in the same range as those found for the similar PPVs, the lifetimes reported as the half-lives $\tau_{1/2}$ are considerably shorter.

Photovoltaic Cell Characterization. Photovoltaic cells based on a selection of the OPVs synthesized above were assembled using a standard technique described in detail elsewhere.[25] The OPVs were spin-coated from chloroform solution onto indium−tin oxide (ITO) glass slides, covered with PEDOT-PSS. An aluminum electrode was then evaporated onto the organic layer in a high vacuum chamber. The electrical resistances of the photovoltaic cells were then measured to ascertain that the devices were functional and free from defects creating electrical short circuits. Typically, the device resistance was found to be in the 10−100 kΩ range. The cells were then illuminated with a sun simulator (AM1.5) with an incident power of 1000 W m^{-2} and the short circuit current (I_{sc}) and open circuit voltage (V_{oc}) measured. In a simplistic view of the operation of an organic photovoltaic cell, the light that is absorbed by the OPV layer creates an exited state (exciton), which can then evolve into a charge-separated state by exciton dissociation which is a requirement for photovoltaic action. The binding energy of the exciton is large in organic materials, and due to their low dielectric constant the attractive force between the electron−hole pair acts over long distances. Exciton dissociation has been shown to take place preferably at domain boundaries,[26] and for single component photovoltaic devices this implies that most of the excitons that dissociate into separate charge carriers do so at the electrode interfaces. Conjugated materials such as PPVs and OPVs are generally hole conductors, and this implies that it is the OPV−aluminum electrode interface at which the majority of exciton dissociation takes place by way of electron injection into the aluminum electrode as demonstrated by selective illumination of the two different electrode interfaces.[27] The hole that is liberated can then travel to the ITO−PEDOT electrode. As a result, the fate of the exciton for single component solar cells is often recombination (and loss) and values for I_{sc} are generally low as one would expect. Typically, single-component devices exhibit current densities of the order of 1−10 μA cm^{-2}.[28] The I_{sc} generated is thus a measure of the efficiency in a number of steps in the process of light absorption, exciton dissociation, and carrier transport. Table 2 summarizes the photovoltaic cell characterization data together with the calculated dipole moments. It is clear that the I_{sc} values are subject to large uncertainties since they are dependent on a large number of device-related properties. Two of the OPVs gave photovoltaic cells with much

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TABLE 2. Photovoltaic Cell Characterization of the OPVs (Active Area ca. 3 cm^2)

compd	I_{sc} (μA cm^{-2})	V_{oc} (V)	calcd dipole moment (D)
6	2.2	0.105	3.0
10	9.7	0.889	4.4
11	**478**	0.748	4.1
12	**105**	0.565	5.5
13	10	0.145	1.5
14	16	0.420	0.2
15	21	0.155	7.9
16	5	0.805	3.8
17	1.7	0.022	-

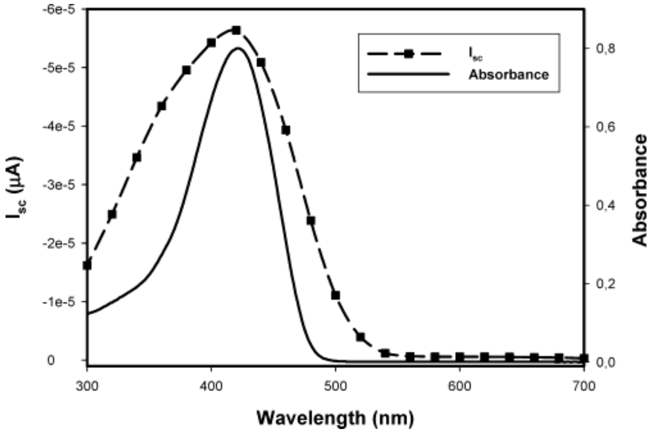

FIGURE 2. Photovoltaic action spectrum in terms of the short circuit current (I_{sc}) for a photovoltaic cell based on the OPV **11** with an active area of 2.8 cm^2. The UV–vis spectrum of the device is also shown with a $\lambda_{max} = 421$ nm and $\epsilon_{max} = 138.400$ M^{-1} cm^{-1}.

higher I_{sc} values, 105 μA cm^{-2} for OPV **12** and 478 μA cm^{-2} for OPV **11**. The low I_{sc} values for most of the OPVs in this study are equivalent to or better than those measured in devices based on PPVs alone, indicating no significant effect of the end groups. For the OPVs **11** and **12**, however, the end groups impart some as yet unexplained increased efficiency. This “end group effect” is not wholly unprecedented. In a previous study, a terphenylenevinylene polymer end-capped with a dye also increased the efficiency of a photovoltaic cell 100-fold.[29] A possible role of the end groups on the OPVs may be to create a dipole in the molecules that can assist this charge separation. To classify the substituted OPVs, the ground-state dipole moments were calculated at the AM1 level using the MOPAC program package. The values obtained should only be taken as a relative scale. Unfortunately, there seems to be no clear correlation with most of the I_{sc} values in the range of 5–50 μA cm^{-2} irrespective of the dipole moment.

The photovoltaic action spectrum as shown in Figure 2 for OPV **11** is as expected symbatic with the absorption spectrum. The plot of the I_{sc} as a function of wavelength is broader than the absorption spectrum due to the large bandwidth of the high power spectrometer as described earlier (~25 nm).[25] The fill factor for the devices based on OPV **11** was found to be 26%, and this translates into a photovoltaic conversion efficiency of ~0.1% under AM1.5 conditions with an incident white light intensity of 1000 W m^{-2}. The efficiency is still remarkable when considering that OPV **11** only absorbs in a very narrow wavelength range (essentially limited to a 100 nm wavelength range).

The most efficient polymer photovoltaics consist of a mixture of a conjugated polymer material and a fullerene derivative with the fullerene being the major component in the active layer (typically 80 wt %). In this manner, an efficiency of 3.8% has been reported and the possibility of 5% has been indicated.[30] While our value for the efficiency is 30–50 times lower it is noticeable that we achieve this without the addition of a fullerene material and in a much smaller absorption range. Finally, when comparing the incident photon current efficiency at optimal wavelength (IPCE) values reported for the best systems (80%)[31] and the value obtained here (8%) our system is only a factor of 10 times lower (at wavelength of maximum absorption). While a factor of 10 times lower is not competitive from a technological point of view, our results demonstrate that it is likely that efficient non-fullerene-based photovoltaic materials will be developed soon.

Conclusion

A rational and efficient synthesis of single OPV oligomers has been presented. The directional nature of the synthetic scheme naturally offers two different end groups—one end comes from the starting aldehyde, while the other is simply an aldehyde or a later derivative. Strongly donating methoxy and dimethylamino groups in one end together with a range of mostly electron-withdrawing derivatives of the terminal aldehyde have been utilized in this study to create a series of well-defined donor-wire-acceptor-type compounds. An example of a donor-wire-dye compound was also prepared with cyanine dye obtained by condensation of an extended version of the OPV **6** with 1,2-dimethylbenzothiazolium hexafluorophosphate.

Size-exclusion chromatography was used as a supplementary form of characterization that is very well suited to establish the purity of the oligomers, and it showed that the particular reactions for coupling the monomer **1** to the growing OPV the HWE reaction and acetal deprotection used in this study gave easy access to oligomers of high purity.

The carrier mobilities obtained from the PR-TRMC study were similar to those measured for the corresponding PPVs. Although this method does not distinguish between positive and negative carriers, it is most probable that only hole conduction is relevant.

The photovoltaic cells constructed from the OPVs generated in this study had efficiencies roughly comparable to those obtained for, e.g., cells prepared from the popular MEH–PPV alone, except in the case of the OPVs **11** and **12** that gave improvements of 1–2 orders of magnitude. Although it is difficult to assess, it seems that these values rival those of cells constructed from short stretches of OPV covalently linked to C$_{60}$ studied by Nierengarten et al.[32] and Peeters et al.[33] A simple

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explanation of this "end-group effect" in terms of the dipole moment of the OPV has not been found, but the magnitude of the effect seems to warrant further exploration and perhaps lead the way toward efficient nonfullerene photovoltaics.

Experimental Section

Elemental analysis could not be carried out reliably on a number of the high molecular weight oligomers. Different analytical laboratories found lower and varying amounts of carbon in the samples, while hydrogen and nitrogen usually were within range. Mass spectra (MALDI-TOF) were therefore used as additional proof of the identity of the compounds.

Size-Exclusion Chromatography (SEC). SEC was performed in chloroform using a preparative gel column system comprised of a guard column and two gel columns in succession. The column dimensions were 25 mm Ø × 600 mm, and the pore diameters were, respectively, 100 and 1000 Å. Polystyrene standards were used for the molecular weight determination or MALDI-TOF.

Photovoltaic Characterization. Photovoltaic devices were prepared on PEDOT/PSS-coated ITO substrates[34] by spin-coating microfiltered (0.45 μm) chloroform solutions at a rotational speed of 1500 rpm. The concentration of the solution was typically 10 mg mL^{-1} and adjusted to give a film absorbance of 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 $<8 \times 10^{-6}$ 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, the samples were mounted with silver epoxy, and the thermosetting silver epoxy was hardened in an oven at 94 °C for 3 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 150 W water-cooled Xenon lamp, a blazed diffraction grating, and a movable arm with the sample. The setup has been described earlier.[25] 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 approximate AM1.5 conditions in the wavelength range relevant for this study. The simulated sunlight was then adjusted to 1000 W m^{-2} using a pyranometer and was not corrected for mismatch of the spectral response. The photovoltaic response degrades quickly in the atmosphere under illumination (1000 W m^{-2}), and measurements were performed within 20 min of preparation. We ascribe this to a photoreaction with molecular oxygen leading to bleaching as shown for similar PPVs in an earlier study.[16]

4-Bromo-2,5-dipropylbenzaldehyde (3). 1,4-Dibromo-2,5-dipropylbenzene[35] (0.3 mol, 96 g) was dissolved in THF (ca 200 mL) and added to a solution of *n*-BuLi in THF at −70 °C (200 mL, 0.16 M mixed with 500 mL THF at −70 °C). The solution was stirred with dry ice/acetone cooling until the temperature reached −60 °C again, DMF (100 mL, excess) was added, and the cooling bath was removed. Stirring at room temperature was continued for 1 h. The reaction mixture was acidified with dilute hydrochloric acid and the solvent evaporated in a vacuum. The remaining oil was partitioned between petrol (300 mL) and water (300 mL). The petrol was removed on the rotary evaporator, and the remaining oil was distilled in a vacuum, using an oil pump, at 130−140 °C. Yield: 64.5 g, 0.24 mol, 80%. ^{1}H NMR (CDCl$_3$, 250.1 MHz) δ: 0.95 (t, 6H, J = 8 Hz), 1.61 (p, 4H, J = 8 Hz), 2.69 (t, 2H, J = 8 Hz), 2.89 (t, 2H, J = 8 Hz), 7.42 (s, 1H), 7.61 (s, 1H), 10.18 (s, 1H). ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ: 13.7, 13.8, 22.8, 25.2, 33.4, 37.5, 130.9, 132.5, 132.8, 135.0, 140.2, 144.1, 191.2.

(4-{2-[4-(5,5-Dimethyl-1,3-dioxan-2-yl)-2,5-dipropylphenyl]vinyl}benzyl)phosphonic Acid Diethyl Ester (1). 4-Bromo-2,5-dipropylbenzaldehyde (**3**) (28.5 g, 0.106 mol), 4-vinylbenzyl phosphonate ester[20] (26.2 g, 0.103 mol), and triethylamine (40 mL) were mixed in a 500 mL round-bottomed flask with dioxane (250 mL) and purged with argon for 5 min. Then Pd$_2$dba$_3$ (180 mg, 0.2 mmol) and P(t-Bu)$_3$ HBF$_4$ (260 mg, 0.9 mmol) were added, and the flask was fitted with a reflux condenser. The reaction mixture was heated to reflux under argon. A precipitate (Et$_3$N·HBr) began to form almost immediately. After 4 h, the reaction mixture was allowed to cool. The solvent was removed in a vacuum and the remaining dark oil was partitioned between dilute hydrochloric acid and diethyl ether (250 mL each). The organic phase was washed once with water and dried over MgSO$_4$. The ether was filtered through silica and eluted with more ether and then with acetone. A small amount of dark material was removed. Yield after evaporation of the solvents: 41.0 g, 92.6 mmol, 90.0%. ^{1}H NMR was in accordance with the product structure. The crude product was used immediately to prepare the acetal-protected monomer.

2,2-Dimethyl-1,3-propandiol (11 g, 0.106 mol) was added to the crude aldehyde together with a small amount of *p*-toluenesulfonic acid and toluene (150 mL). The mixture was heated to reflux for 1 h in a flask equipped with a Dean−Stark trap to remove the water. The mixture was cooled and extracted with an equal volume of sodium carbonate in water (emulsion), and the organic phase was dried with a large amount of magnesium sulfate, filtered, and evaporated in a vacuum to give colorless oil. Yield: 42.9 g, 81.1 mmol, 79%. ^{1}H NMR (CDCl$_3$, 250.1 MHz) δ: 0.80 (s, 3H), 0.96−1.04 (m. 6H), 1.26 (t, 6H, J = 8 Hz), 1.34 (s, 3H), 1.6−1.7 (m, 4H), 2.6−2.7 (m, 4H), 3.15 (d, 2H, =22 Hz), 3.65 (d, 2H, J = 9 Hz), 3.78 (d, 2H,J = 9 Hz), 4.0−4.1 (m, 4H), 5.52 (s, 1H), 6.95 (d, 1H, J = 16 Hz), 7.3−7.5 (m, 7H). ^{13}C NMR (CDCl3, 62.9 MHz) δ: 14.2, 14.3, 16.3, 16.4, 21.9, 23.3, 24.4, 24.7, 30.2, 32.5, 34.3, 34.7, 35.3, 77.9, 126.3, 126.6, 126.7, 128.2, 129.0, 129.3, 130.1, 130.8, 135.2, 136.1, 136.5, 137.8, 138.2. Anal. Calcd for C$_{31}$H$_{45}$O$_5$P: C, 70.43; H, 8.58. Found: C, 70.04; H, 8.80.

MeO-OPV-aldehyde 4. Acetal-protected monomer **1** (5.0 g, 9.5 mmol) and 4-methoxybenzaldehyde (3 g, 22 mmol, large excess) were dissolved in THF (150 mL), purged with argon, and heated to reflux. Potassium *tert*-butoxide (2 g, 17 mmol) was added and reflux continued for 30 min. The reaction mixture was quenched in dilute hydrochloric acid (100 mL) and heating continued for 20 min to hydrolyze the acetal function. The solvent was then removed in a vacuum, and the remaining solid was filtered and washed with water (2 × 100 mL), ethanol (2 × 100 mL), and finally petroleum ether. The yellow product was dried in a vacuum to remove traces of solvent. Yield: 3.13 g, 7.37 mmol, 78%. Mp: 193−5 °C. UV−vis [chloroform, $\lambda_{\max}$ (ϵ)]: 395 (55 900); ^{1}H NMR (CDCl$_3$, 250.1 MHz) δ 1.01 (t, 3H, J = 6 Hz), 1.03 (t, 3H, J = 6 Hz), 1.6−1.75 (m, 4H), 2.78 (t, 2H, J = 6 Hz), 3.01 (t, 2H, J = 6 Hz), 3.84 (s, 3H), 6.92 (d, 2H, J = 9 Hz), 6.99 (d, 1H, J = 16 Hz), 7.12 (d, 1H, J = 16 Hz), 7.13 (d, 1H, J = 16 Hz), 7.36 (d, 1H, J = 16 Hz), 7.48 (d, 2H, J = 9 Hz), 7.50 (s, 1H), 7.53 (s, 4H), 7.65

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(s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.1, 24.4, 24.6, 55.3, 114.2, 125.5, 126.2, 126.6, 126.9, 127.8, 127.9, 128.2, 129.6, 130.2, 130.3, 134.2, 135.2, 136.0, 136.7, 137.1, 138.4, 138.8, 144.0, 159.4, 191.5. Anal. Calcd for $C_{30}H_{32}O_2$: C, 84.87; H, 7.60. Found: C, 84.9; H, 7.8.

General Procedure for the Preparation of the OPVs 5−8. Monomer **1** and an equal amount of aldehyde-terminated OPV (**4**, **5**, **6**, or **7**) was mixed in dry THF and purged with argon. Then potassium *tert*-butoxide (2 equiv, excess) was added, and the mixture was refluxed for 30 min to complete the reaction. The cooled mixture was diluted with water and acidified with hydrochloric acid. The precipitate was filtered and washed with water and ethanol. The moist product was then dissolved in THF, and concentrated hydrochloric acid was added to hydrolyze the acetal at reflux for 30 min. The mixture was diluted with an equal volume of water and the solvent removed in a vacuum. The precipitated product was filtered and washed thoroughly with water and ethanol.

MeO-OPV 5. Yield: 4.36 g, 6.11 mmol 69%. Mp: 185−9 °C. UV−vis [chloroform, λ_{max} (ϵ)]: 402 (84 400). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.05 (t, 12H, $J = 8$ Hz), 1.70 (p, 8H, $J = 8$ Hz), 2.78 (t, 6H, $J = 8$ Hz), 3.03 (t, 2H, $J = 8$ Hz), 3.84 (s, 3H), 6.9−7.7 (m, 22H), 10.26 (s, 1H). Anal. Calcd for $C_{52}H_{56}O_2$: C, 87.60; H, 7.92. Found: C, 87.8; H, 8.1.

MeO-OPV 6. Yield: 5.52 g, 5.5 mmol, 96%. Mp: 230−2 °C. UV−vis [chloroform, λ_{max} (ϵ)]: 408 (132 000). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.05 (t, 18H, $J = 8$ Hz), 1.73 (m, 12H), 2.78 (t, 8H, $J = 8$ Hz), 3.02 (t, 2H, $J = 8$ Hz), 3.84 (s, 3H), 6.9−7.7 (m, 34H), 10.26 (s, 1H). Anal. Calcd for $C_{74}H_{80}O_2$: C, 88.75; H, 8.05. Found: C, 88.6; H, 8.1.

MeO-OPV 7. Yield: 87%. Mp > 250 °C. UV−vis [chloroform, λ_{max} (ϵ)]: 416 (135 000). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.06 (t, 24H, $J = 8$ Hz), 1.71 (m, 16H), 2.79 (t, 14H, $J = 7$ Hz), 3.03 (t, 2H, $J = 8$ Hz), 3.84 (s, 3H), 6.9−7.7 (m, 44H), 10.26 (s, 1H). Anal. Calcd for $C_{96}H_{104}O_2$: C, 89.39; H, 8.13. Found: C, 89.0; H, 8.2.

MeO-OPV 8. Yield: 57%. Mp > 250 °C. UV−vis [chloroform, λ_{max} (ϵ)]: 420 (144 000). ^{1}H NMR (*o*-$C_6D_4Cl_2$, 250.1 MHz, 400 K) δ: 1.09 (t, 30H, $J = 8$ Hz), 1.78 (m, 20H), 2.87 (broad, 18H), 3.03 (broad, 2H), 3.72 (s, 3H), 6.9−7.7 (m, 54H), 10.30 (s, 1H). Anal. Calcd for $C_{118}H_{128}O_2$: C, 89.80; H, 8.17. Found: C, 89.6; H, 8.4.

Me$_2$N-OPV 9. Monomer **1** (3.0 g, 5.7 mmol) and *N*,*N*-dimethylbenzaldehyde (1.0 g, 6.7 mmol) were dissolved in THF (100 mL). Then potassium *tert*-butoxide (2 equiv, excess) was added, and the mixture was refluxed for 30 min to complete the reaction. The cooled mixture was hydrolyzed with 25 mL of concentrated hydrochloric acid for 30 min at ambient temperature. The mixture was cautiously neutralized by pouring it into a beaker containing a solution of sodium carbonate in water. The orange product was filtered off and washed with water and ethanol. Yield: 2.35 g, 94%. Mp: 158−9 °C. UV−vis [chloroform, λ_{max} (ϵ)]: 407 (46 200). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.00 (t, 3H, $J = 7$ Hz), 1.03 (t, 3H, $J = 7$ Hz), 1.61−1.77 (m, 4H), 2.78 (t, 2H, $J = 7$ Hz), 3.01 (s + t, 8H), 6.72 (d, 2H, $J = 8$ Hz), 6.93 (d, 1H, $J = 16$ Hz), 7.11 (d, 1H, $J = 16$ Hz), 7.13 (d, 1H, $J = 16$ Hz), 7.34 (d, 1H, $J = 16$ Hz), 7.44 (d, 2H, $J = 8$ Hz), 7.51 (s + s, 4 + 1H), 7.65 (s, 1H), 10.25 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.0, 23.9, 25.5, 34.2, 34.9, 40.4, 112.5, 123.8, 124.4, 125.7, 126.4, 126.8, 127.7, 127.9, 129.3, 132.4, 132.5, 132.7, 135.5, 138.4, 141.4, 143.1, 150.2. Anal. Calcd for $C_{31}H_{35}NO$: C, 85.08; H, 8.06; N, 3.20. Found: C, 85.1; H, 8.2; N, 3.1.

General Procedure for the Preparation of the OPVs 10 and 11. Monomer **1** and an equal amount of aldehyde-terminated OPV (**9** or **10**) were dissolved in THF (100 mL). Then potassium *tert*-butoxide (2 equiv, excess) was added, and the mixture was refluxed for 30 min to complete the reaction. The cooled mixture was hydrolyzed with 25 mL of concentrated hydrochloric acid for 30 min at ambient temperature. The mixture was cautiously neutralized by pouring it into a beaker containing a solution of sodium carbonate in water. The orange product was filtered off and washed with water and ethanol.

Me$_2$N-OPV 10. Yield: 85%. Mp: 195−8 °C. UV−vis [chloroform, λ_{max} (ϵ)]: 414 (82 100). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.04 (t, 12H, $J = 7$ Hz), 1.69 (m, 8H), 2.78 (t, 6H, $J = 8$ Hz), 3.00 (s, 3H), 6.74 (d, 2H, $J = 8$ Hz), 6.9−7.6 (m, 21H), 7.67 (s, 1H), 10.26 (s, 1H). MS (MALDI-TOF): *m*/*z* 725.56, calcd for $C_{53}H_{59}NO$ 725.4597.

Me$_2$N-OPV 11. Yield: 89%. Mp > 250 °C. UV−vis [chloroform, λ_{max} (ϵ)]: 421 (138 400). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.05 (t, 18H, $J = 8$ Hz), 1.69 (m, 12H), 2.78 (t,10H, $J = 7$ Hz), 3.00 (s + t, 3H + 2H), 6.73 (d, 2H, $J = 8$ Hz), 6.9−7.6 (m, 31H), 7.66 (s, 1H), 10.26 (s, 1H). MS (MALDI-TOF): *m*/*z* 1013.86, calcd for $C_{75}H_{83}NO$ 1013.6475.

MeO-OPV Adduct with Malodinitrile (12). MeO-OPV **6** (500 mg, 0.5 mmol) was dissolved in THF (25 mL) together with an excess of malodinitrile (300 mg). Piperidine (1 mL) and ethanol (5 mL) were added, and the reaction mixture was heated to reflux for 1 h. The solvents were removed in a vacuum, the residue was triturated with ethanol (50 mL), and the solid product was filtered off and washed with more ethanol and petroleum ether. Yield: 480 mg, 96%. Mp: 235 °C dec. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.01 (m, 18H), 1.67 (m,12H), 2.76 (m,12H), 3.84 (s, 6H), 6.92 (d, 2H, $J = 8$ Hz), 7.0−7.5 (m, 32H), 8.03 (d, 2H, $J = 7$ Hz). MS (MALDI-TOF): *m*/*z* 1073.66, calcd for $C_{78}H_{79}N_3O$ 1073.6223.

General Procedure for the OPVs 13−16. MeO-OPV **6** was dissolved in THF (25 mL) together with diethyl benzylphosphonate ester, diethyl 4-methoxybenzylphosphonate ester, diethyl 4-nitrobenzylphosphonate ester, or diethyl 2,3,4,5,6-pentaflurobenzylphosphonate ester (500 mg, excess). Potassium *tert*-butoxide (0.25 g, excess) was added, and the mixture was heated to reflux for 30 min. The cooled mixture was mixed with dilute hydrochloric acid and the THF removed in a vacuum. The residue was filtered off and washed with water (2 × 200 mL) and ethanol (2 × 100 mL). After drying, the crude solid was taken up in chloroform and filtered through a layer of silica. The solvent was again removed in a vacuum.

OPV 13. From **6** and diethyl benzylphosphonate ester. Yield: 88%. Mp: 247−9 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.06 (t, 18H, $J = 8$ Hz), 1.6−1.8 (m, 12H), 2.79 (t, 12H, $J = 7$ Hz), 3.84 (s, 3H), 6.92 (d, 2H, $J = 7$ Hz), 7.0−7.6 (m, 39H). MS (MALDI-TOF): *m*/*z* 1074.69, calcd for $C_{81}H_{86}O$ 1074.6679.

OPV 14. From **6** and diethyl 4-methoxybenzylphosphonate ester. Yield: 70%. Mp: 246−50 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.05 (t,18H,$J = 7$ Hz), 1.74 (m, 12H), 2.79 (t, 12H, $J = 7$ Hz), 3.85 (s, 3H), 3.86 (s, 3H), 6.9−7.6 (m, 40H). MS (MALDI-TOF): *m*/*z* 1104.63, calcd for $C_{82}H_{88}O_2$ 1104.6784.

OPV 15. From **6** and diethyl 4-nitrobenzylphosphonate ester. Yield: 66%. Mp > 250 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.05 (t, 18H, $J = 8$ Hz), 1.73 (m, 12H), 2.78 (t, 12H, $J = 7$ Hz), 3.84 (s, 3H), 6.92 (d, 2H, $J = 9$ Hz), 7.0−7.6 (m, 34H), 7.65 (d, 2H, $J = 9$ Hz), 8.25 (d, 2H, $J = 9$ Hz). MS (MALDI-TOF): *m*/*z* 1119.78, calcd for $C_{81}H_{85}NO_3$ 1119.6529.

OPV 16. From **6** and diethyl 2,3,4,5,6-pentaflurobenzylphosphonate ester. Yield: 94%. Mp: 245−8 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.05 (t, 18H, $J = 7$ Hz), 1.70 (m, 12H), 2.78 (t, 12H, $J = 7$ Hz), 3.85 (s, 3H), 6.92 (d, 2H, $J = 8$ Hz), 7.0−7.6 (m, 34H). MS (MALDI-TOF): *m*/*z* 1164.67, calcd for $C_{81}H_{81}F_5O$ 1164.6207.

Cyanine Derivative of OPV 6 (17). Compound **6** (1.0 mmol) was dissolved in hot dioxane (100 mL) together with acetal-protected ethyl phosphonylmethylbenzaldehyde (1 g, 2.9 mmol), and then potassium *tert*-butoxide (1.1 g, 10 mmol) was added and the mixture heated to reflux for 30 min. The cooled reaction mixture was poured into dilute hydrochloric acid and filtered. The filter cake was redissolved in dioxane and added to concentrated hydrochloric acid and stirred for 30 min to hydrolyze the acetal. The solvent was removed in a vacuum and the residue filtered, washed with ethanol, and dried.

The extended oligomer was dissolved in dioxane (100 mL) at reflux. An equal amount of 1,2-dimethylbenzothiazolium hexafluorophosphate was added together with piperidine (1 mL) and ethanol (10 mL). Reflux was continued for 30 min until the product separated as a very dark solid. Hot filtration afforded the cyanine-terminated OPV as the hexafluorophosphate salt. Yield = 520 mg, 37%. Mp > 250 °C. ^{1}H NMR (DMSO-d_6, 250.1 MHz) δ: 1.00 (t, 6H, $J = 7$ Hz), 1.63 (p, 4H, $J = 7$ Hz), 2.82 (m, 4H), 3.59 (s, 3H), 3.80 (s, 3H), 6.97 (d, 2H, $J = 8$ Hz), 7.0−7.4 (m, 4H), 7.43 (d, 1H, $J = 16$ Hz), 7.5−7.7 (m, 9H), 7.6−7.9 (m, 4H), 8.0−8.1 (m, 3H), 8.2−8.3 (m, 2H), 8.44 (d, 1H, $J = 8$ Hz). Anal. Calcd for $C_{91}H_{94}F_6NOPS$: C, 78.4; H, 6.8; N. 1.0. Found: C, 78.7; H, 7.0; N, 1.2

Sodium Tetrabiphenylborate. 4-Bromobiphenyl (39 g, excess) was dissolved in dry THF (300 mL) and cooled to −78 °C. *n*-BuLi (100 mL, 1.6M) was added. The temperature rose to −40 °C, and a solid precipitated. The mixture was allowed to stir for 5 min. $BF_3\cdot Et_2O$ (5 g) was added, the cooling bath was removed, and the mixture was left to reach rt overnight. A clear colorless solution was obtained. Na_2CO_3 (100 g) was added followed by water (500 mL). The mixture was stirred for 1 h, and the phases were allowed to settle in a separating funnel. The lower aqueous phase with some fine fluoride sludge was discarded, and the THF phase was dried over Na_2CO_3 and evaporated to give a semisolid. NMR showed it to contain butyl groups and a solid insoluble in $CDCl_3$. The semisolid was shaken with light petroleum ether, filtered, washed with benzene and chloroform, and dried to obtain a white solid. Yield: 4.91 g (19%). Mp > 275 °C. ^{1}H NMR (250 MHz, DMSO-d_6, 300 K, TMS): δ 7.27 (t, 1H, $J = 7$ Hz), 7.35−7.48 (m, 6H), 7.66 (d, 2H, $J = 7$ Hz); ^{11}B NMR (80 MHz, DMSO-d_6, 300 K, $BF_3\cdot Et_2O$): δ −6.68 (s). ^{13}C NMR (63 MHz, DMSO-d_6, 300 K, TMS): δ 123.9, 126.0, 126.1, 128.7, 133.7, 136.0, 141.9, 162.8 (q, $J = 49$ Hz). Anal. Calcd for $C_{48}H_{36}BNa\cdot {}^1/_2H_2O$: C, 87.94; H, 5.69. Found: C, 87.8; H, 5.70.

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Supporting Information Available: ^{1}H NMR spectra of the compounds **4**, **5**, **7**−**13**, **15**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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