

Synthesis of 2,7-Carbazolenevinylene-Based Copolymers and Characterization of Their Photovoltaic Properties**

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New electroactive and photoactive conjugated copolymers consisting of alternating 2,7-carbazole and oligothiophene moieties linked by vinylene groups have been developed. Different oligothiophene units have been introduced to study the relationship between the polymer structure and the electronic properties. The resulting copolymers are characterized by UV-vis spectroscopy, size-exclusion chromatography, and thermal and electrochemical analyses. Bulk heterojunction photovoltaic cells from different copolymers and a soluble fullerene derivative, [6,6]-phenyl-C₆₁ butyric acid methyl ester, have been fabricated, and promising preliminary results are obtained. For instance, non-optimized devices using poly(*N*-(4-octyloxyphenyl)-2,7-carbazolenevinylene-*alt*-3'',4''-dihexyl-2,2';5',2'';5'',2''';5''',2''''-quinquethiophenevinylene 1'',1''-dioxide) as an absorbing and hole-carrier semiconductor exhibit power conversion efficiency up to 0.8% under air mass (AM) 1.5 illumination. These features make 2,7-carbazolenevinylene-based and related polymers attractive candidates for solar-cell applications.

1. Introduction

In recent years, considerable effort has been directed towards the development of new polymer-based photovoltaic devices. Polymeric solar cells are becoming more and more attractive because they represent a green and renewable energy alternative to fossil energy or nuclear power. They show many potential advantages over traditional silicon-based solar cells such as relatively low cost, tunable electronic properties, good mechanical properties, and ease of processing. Their main limitations are low power-energy conversion efficiency (η_e) and relative instability compared to silicon-based solar cells. However, their performance is still improving, and recently η_e values around 5% have been reported for polymeric solar cells.^[1,2]

To increase the photocurrent and the device efficiency, the active layer should absorb as many of the incident photons as possible to generate a maximum of excitons.^[3] Thus, a good overlap of the active layer with the solar spectrum (visible and near-infrared) is required. Therefore, in the last few years, chemists have synthesized various low-bandgap polymers (bandgap $E_g < 1.8$ eV) able to harvest more photons at long wavelengths. Also, considerable efforts have been devoted to

obtaining a better understanding of the relationships between the energy levels of polymers and the performance of solar cells.

For all these reasons, many conjugated polymers have been investigated so far. Among them, polythiophenes,^[1,2] fluorene-based copolymers,^[4] and poly(*p*-phenylenevinylene) derivatives^[5] have shown the best features for solar-cell applications. Interestingly, Morin and co-workers have reported the synthesis of new electroactive and photoactive polycarbazoles linked at the 2,7-positions.^[6–8] These polymers allow the design of highly conjugated materials that were difficult, if not impossible, to obtain from poly(3,6-carbazole) derivatives. Very recently, Müllen and co-workers have reported the first photovoltaic cell based on poly(*N*-alkyl-2,7-carbazole), with an efficiency of 0.6%.^[9] In parallel, the synthesis of new 2,7-carbazolenevinylene-based polymers and oligomers were also reported.^[10,11] These materials have been successfully utilized in polymeric light-emitting diodes (PLEDs) and organic field-effect transistors (OFETs). Moreover, 2,7-carbazolenevinylene-based copolymers should also exhibit interesting features as active polymeric layers in solar cells. Indeed, carbazole is well-known to be a good hole-transporting unit, and the introduction of 2,7-carbazole groups as a building block yields a linear structure with a high degree of conjugation along the backbone of the macromolecules, allowing easier charge transport. In addition, the introduction of the vinylene linkage in π -conjugated systems has been an effective strategy for modulating their electronic properties by lowering the bandgap.^[12] It is a good method to form coplanar molecules with extended π -conjugation lengths because of the relatively low dihedral angle between the vinylene and aryl groups, leading to an increase of the absorption maxima.^[13] Finally, different comonomer units can be easily introduced to fine tune the electronic properties.

Therefore, we report the synthesis and characterizations of a new class of 2,7-carbazolenevinylene-based copolymers used as

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p-type semiconductors in solar cells. In order to study the effects of the molecular design (conjugation length, substituent effects, etc.) on the photovoltaic properties, we used several oligothiophene comonomers, also well known for their relatively low bandgaps and good hole-transporting properties.^[14]

2. Results and Discussion

2.1. Synthesis of 2,7-Functionalized Carbazole Monomers

All copolymers studied here have been synthesized starting from 2,7-bis(methyltrityloxy)carbazole (compound **1**), the synthesis of which was previously described.^[10] As shown in Figure 1, compound **1** was first substituted on the nitrogen atom with an octyloxybenzene unit using the Ullmann procedure to provide compound **3**. The low yield obtained for this reaction can be attributed to the low solubility of compound **3**, rendering chromatographic purification difficult. It is worth noting that an aryl unit was used in the preparation of polymers to provide sufficient resonance stabilization in order to increase their ability to transport hole carriers.^[15] On the other hand, we have chosen to introduce a linear alkoxy chain instead of a branched one to promote good intermolecular interactions and molecular self-organization. The trityl group was removed in a mixture of dichloromethane and methanol containing few drops of concentrated hydrochloric acid, yielding *N*-(4-octyloxyphenyl)-2,7-bis(hydroxymethyl)carbazole (compound **4**). The hydroxymethyl groups of compound **4** can be transformed into chloromethyl groups by using thionyl chloride

in toluene with a catalytic amount of pyridine to provide *N*-(4-octyloxyphenyl)-2,7-bis(chloromethyl)carbazole (compound **5**). The latter compound seems to be moisture sensitive and must be used in the hours following its synthesis. The phosphonate derivative (compound **6**) can be obtained by treating compound **5** with hot triethyl phosphite for several hours. This monomer is particularly suitable for a subsequent Horner–Emmons reaction. Compound **4** can also be transformed into dialdehyde moieties (compound **7**) by oxidation with pyridinium chlorochromate (PCC) in dichloromethane in the presence of silica gel and molecular sieves.

2.2. Synthesis of the Thiophene-Based Comonomers

To prepare the targeted 2,7-carbazolevinylene-based copolymers, some dialdehyde oligothiophenes were synthesized. The complete synthetic pathways for these comonomers are described in Figure 2.

4,4'-Dioctyl-2,2'-bithiophene (compound **8**) was synthesized from the corresponding thiophene by lithiation with *n*-BuLi/*N,N,N',N'*-tetramethylethylenediamine (TMEDA), followed by oxidative coupling with copper chloride.^[16] In order to obtain 5,5'-diformyl-4,4'-dioctyl-2,2'-bithiophene (compound **9**), a dilithiation with BuLi/TMEDA followed by a formylation reaction with dimethylformamide (DMF)^[17] is required to overcome the low yield of a classical Vilsmeier–Haak reaction.

The synthesis of larger substituted oligothiophenes requires some intermediate steps. In the case of the cross-coupling reaction between thiophene units, it is well known that the Stille re-

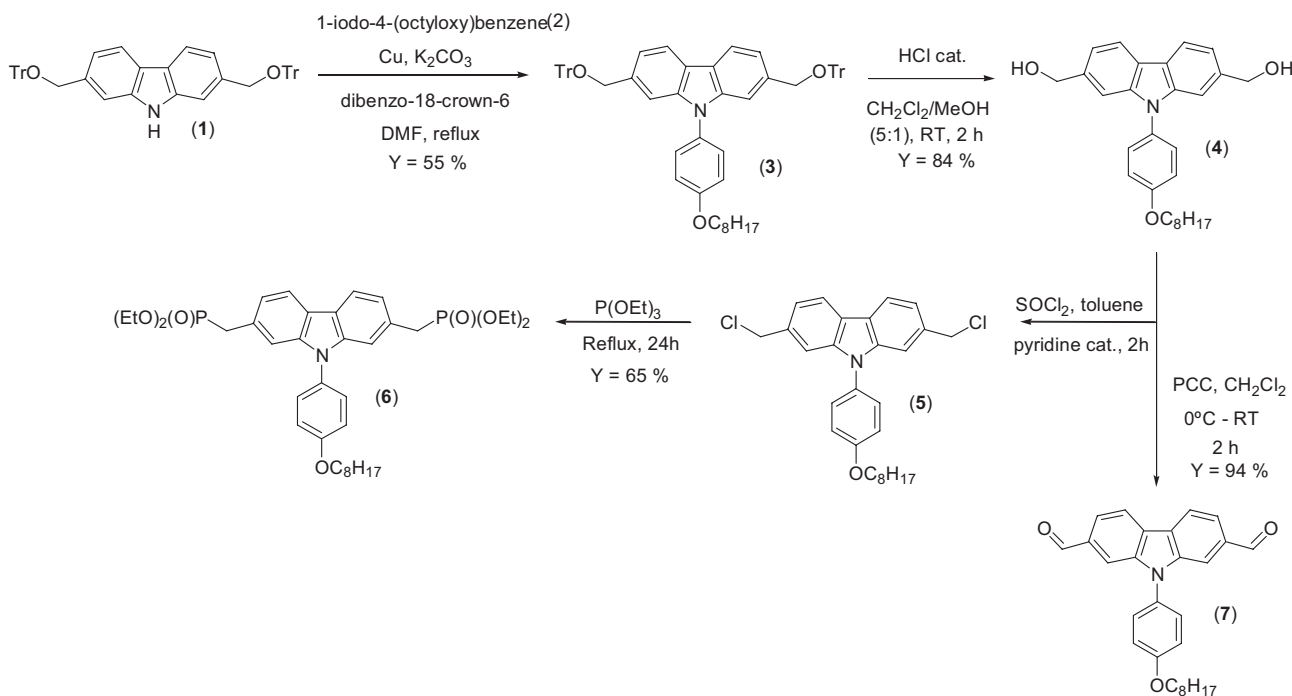


Figure 1. Synthesis of the 2,7-carbazolevinylene-based comonomers. Tr: trityl; DMF: dimethylformamide; RT: room temperature; Y: yield; PCC: pyridinium chlorochromate.

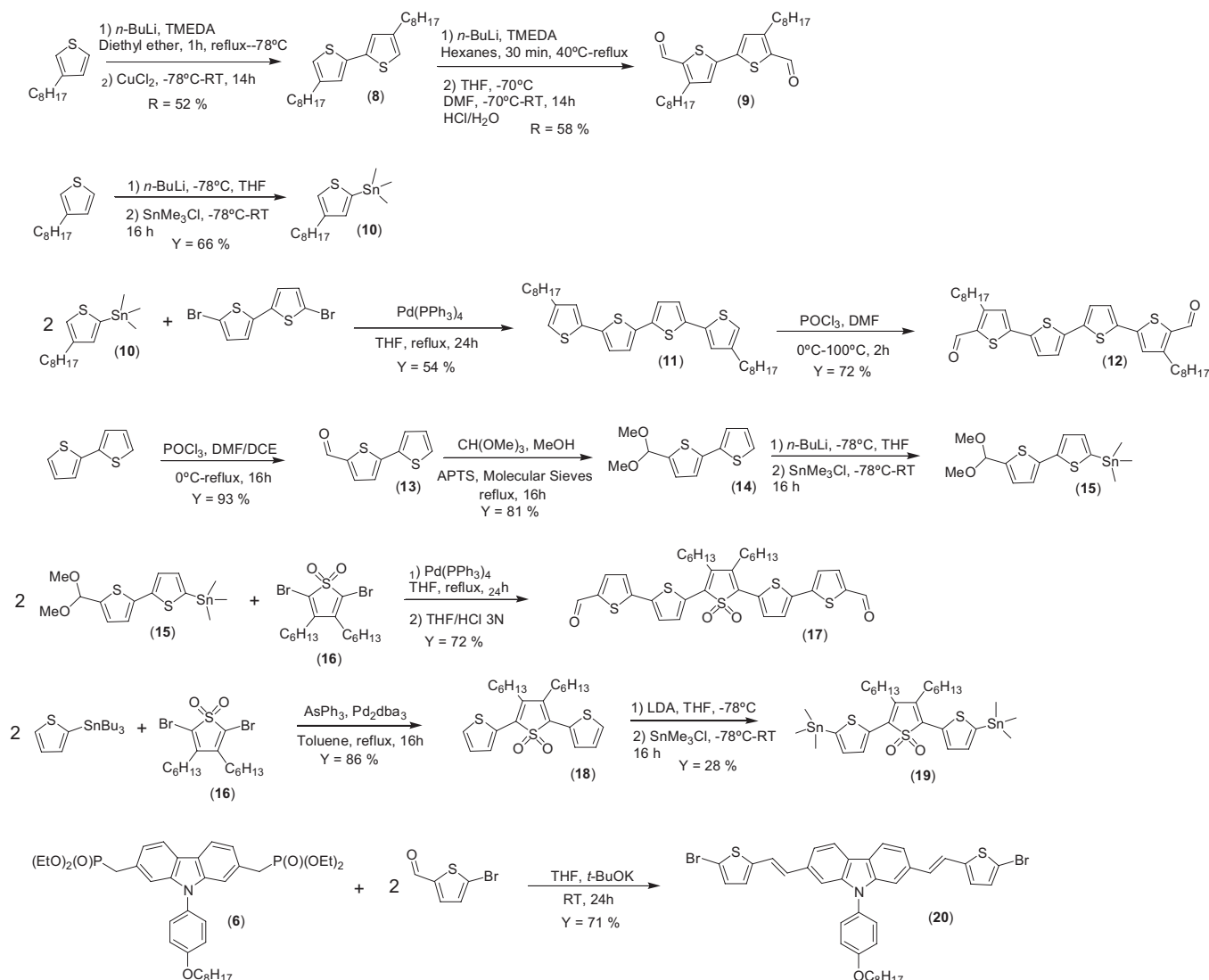


Figure 2. Synthesis of the thiophene-based comonomers. TMEDA: *N,N,N',N'*-tetramethylethylenediamine; THF: tetrahydrofuran; DCE: dichloroethane; APTS: *p*-toluenesulfonic acid; dba: dibenzylideneacetone; LDA: lithium diisopropylamide.

action is more effective than the Suzuki reaction. Thus, 2-trimethyltin-4-octylthiophene (compound **10**) was synthesized from the reaction of the lithium salt of the 3-octylthiophene with trimethyltin chloride. This compound, purified by distillation under reduced pressure, was used as starting material for the Stille cross-coupling reaction with 5,5'-dibromo-2,2'-bithiophene to provide compound **11**. Compound **12** was obtained in good yield by using an excess of two equivalents of DMF/phosphoryl chloride reagent in the Vilsmeier reaction. The side product of this reaction is 5-formyl-4,4''-dioctyl-2,2':5',2'':5'',2'''-quarterthiophene, the monoformyl derivative of compound **11**, which can be used in a second Vilsmeier reaction to provide a new batch of compound **12**. As for 4,4'-dioctyl-2,2'-bithiophene, an octyl chain was used to enhance the solubility of the corresponding polymer.

On the basis of previous studies from Barbarella et al.^[18] and our group,^[19] it is possible to tailor the frontier orbitals of thio-

phene-based copolymers through the oxidation of the thiophene ring to give the corresponding thiophene *S,S*-dioxide. Thiophene *S,S*-dioxide is no longer aromatic, has two localized carbon-carbon double bonds and two sulfur-oxygen double bonds, and has different optical and redox properties from those of their aromatic counterpart. The insertion of the thienyl *S,S*-dioxide unit into the molecular skeleton of thiophene-based copolymers leads to an increase in the electron affinity of these compounds and, consequently, to a decrease of the bandgap, with almost no change of the ionization potential value.

To synthesize a 2,7-carbazolenevinylene-based copolymer incorporating the quinquethiophene-*S,S*-dioxide moiety, two different strategies were considered. The first one was based on the Horner-Emmons copolymerization involving a dialdehyde quinquethiophene dioxide (compound **17**). The second one was based on the Stille copolymerization utilizing a di(trimethyl)tin derivative (compound **19**).

The dialdehyde derivative (compound **17**) was obtained in good yield by a Stille cross-coupling reaction between two equivalents of (5'-dimethoxymethyl-[2,2']bithiophenyl-5-yl)-trimethylstannane (compound **15**) and one equivalent of 2,5-dibromo-3,3-dihexylthiophene 1,1-dioxide^[18b] (compound **16**), followed by a simultaneous in situ hydrolysis of the acetals in a 3 N tetrahydrofuran (THF)/HCl mixture at room temperature. The strategy, where the aldehyde functions are first formed and then protected, was required because of the difficulty in post-formylating the quinquethiophene-*S,S*-dioxide compound. Three steps were necessary to obtain compound **15**. First, the 2,2'-bithiophene was formylated by a Vilsmeier reaction (compound **13**). Then, the aldehyde function was protected by a conversion into the dimethyl acetal. The corresponding acetal compound **14** was monolithiated with one equivalent of *n*-BuLi and then treated with trimethyltin chloride to obtain compound **17**.

Tin-functionalized compound **19** was synthesized in a good yield from the reaction of 3',4'-dihexyl-2,2':5,2'-terthiophene-1',1'-dioxide^[18b] (compound **18**) with lithium diisopropylamide (LDA), followed by the reaction of this dilithio anion with two equivalents of trimethyltin chloride. The crude product was

purified by two successive recrystallizations from hexanes at -25°C .

2.3. Synthesis of Copolymers

Most of the 2,7-carbazolenevinylene-containing polymers were synthesized from Horner–Emmons reactions between dialdehyde and diphosphonate derivatives (Fig. 3). The Horner–Emmons coupling reaction seems to be the best method to synthesize well-defined polymers because it provides strict regioselectivity and an all-trans configuration,^[20] in contrast to the standard Wittig reaction (between dialdehyde and diphosphonium salt), which generally gives molecules having a mixture of *cis* and *trans* isomers.^[21] The synthesis of oligomers having well-defined structures is very important to maximize solid-state intermolecular interactions. The Horner–Emmons reaction does not lead to side reactions such as incomplete eliminations during double-bond formation or crosslinking leading to insoluble polymers with undesirable optical, electrical, and mechanical properties.^[19] Furthermore, the problem of contamination of the conjugated-polymer materials by palla-

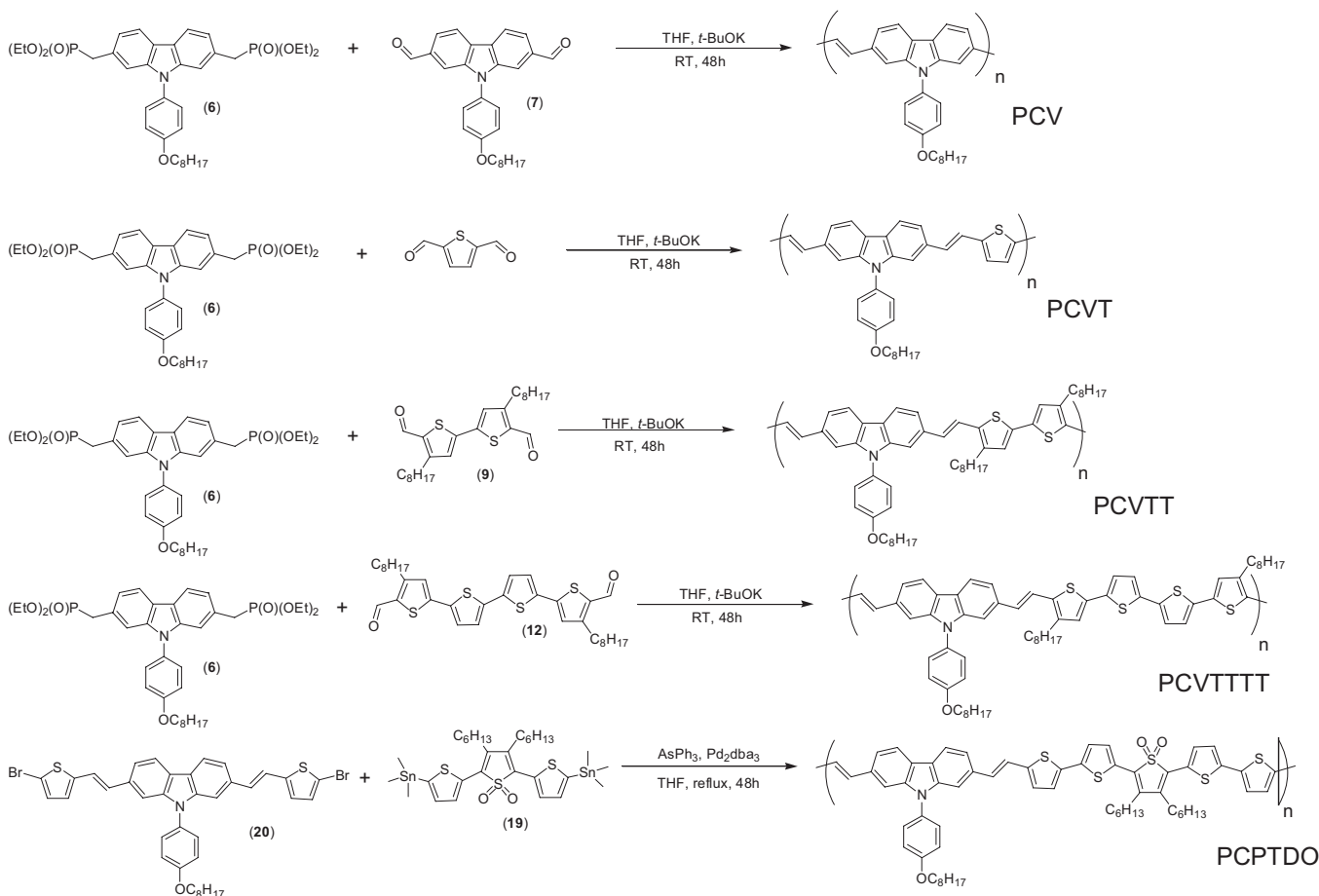


Figure 3. Synthesis and chemical structure of the 2,7-carbazolenevinylene-based copolymers: poly(*N*-(4-octyloxyphenyl)-2,7-carbazolenevinylene) (PCV), poly(*N*-(4-octyloxyphenyl)-2,7-carbazolenevinylene-*alt*-2,5-thiophene) (PCVT), poly(*N*-(4-octyloxyphenyl)-2,7-carbazolenevinylene-*alt*-4,4'-dioctyl-5,5';2,2'-bithiophene) (PCVTT), poly(*N*-(4-octyloxyphenyl)-2,7-carbazolenevinylene-*alt*-4,4''-dioctyl-5,5'';2,2';5',2'';5'',2'''-quaterthiophene) (PCVTTTT), and poly(*N*-(4-octyloxyphenyl)-2,7-carbazolenevinylene-*alt*-3'',4''-dihexyl-2,2';5',2'';5'',2'''-quinquethiophenevinylene 1'',1''-dioxide) (PCPTDO).

dium catalysis resulting from the palladium catalyst is prevented by the use of this palladium-free reaction.^[22] Finally, Horner–Emmons chemistry seems to give higher molecular weights than the standard Wittig reaction.^[23] PCV, PCVT, PCVTT, and PCVTTTT were synthesized using the standard Horner–Emmons reaction using equimolar ratios of dialdehyde and compound **6** in the presence of an excess of potassium *tert*-butoxide in anhydrous THF. In the case of poly(N-(4-octyloxyphenyl)-2,7-carbazolenevinylene-*alt*-3'',4''-dihexyl-2,2';5',2'';5'',2''';5''',2''''-quinquethiophenevinylene 1'',1''-dioxide) (PCPTDO), the use of the Horner–Emmons reaction did not lead to the desired polymer. After 24 h of reaction, a black powder was obtained that exhibits an UV-vis absorption maximum at 420 nm. At this point, we do not yet really understand why this reaction did not work properly. To avoid the use of the Horner–Emmons reaction, compound **19** was utilized to provide the polymer by a Stille cross-coupling polymerization with the compound **20**. This comonomer, which is an oligomer with a central carbazole unit, was obtained by a standard Horner–Emmons reaction using two equivalents of 2-bromo-5-thiophenecarboxaldehyde and compound **6** (see Fig. 2). On the basis of previous studies performed by the Barbarella group,^[24] the Stille cross-coupling reaction was carried out using Pd(AsPh₃)₄ generated in situ as catalyst in refluxing THF. In that particular case, Pd(AsPh₃)₄ has proven to be more effective than Pd(PPh₃)₄.^[24]

2.4. Polymer Characterization

All polymers presented here are soluble in common organic solvents such as THF or chloroform. The good solubility of these copolymers can be explained by the relatively high degree of substitution of the comonomers.

2,7-Carbazolenevinylene-based copolymers have low molecular weights (see Table 1) but exhibit good film-forming properties. All polymeric materials are amorphous with glass-transition temperatures between 60 and 90 °C and relatively good thermal stability (see Table 1).

Table 1. Number-average molecular weight (M_n), polydispersity (M_w/M_n , where M_w is the weight-average molecular weight), degree of polymerization (DP), glass-transition temperature (T_g), and thermal gravimetric analysis results of the 2,7-carbazolenevinylene-based copolymers.

Polymer	M_n [kg mol ⁻¹]	M_w/M_n	DP	T_g [°C]	T for 5% weight loss [°C]
PCV	2.8	1.4	7	62	400
PCVT	4.1	1.4	8	63	360
PCVTT	3.7	2.1	4	60	220
PCVTTTT	4.3	1.9	4	70	145
PCPTDO	3.3	1.3	3	90	275

2.5. Optical Properties

UV-vis absorption spectra (both in solution and as thin film) of all these polymers are presented in Table 2 and Figure 4. As expected, the absorption wavelength maximum is red-shifted

Table 2. UV-vis maximum absorption wavelength (λ_{max}) and bandgap energy (E_g) for 2,7-carbazolenevinylene-based copolymers.

Polymer	Solution absorption λ_{max} [a] [nm]	Film absorption λ_{max} [nm]	E_g [b] [eV]
PCV	426	436	2.3
PCVT	462	466	2.2
PCVTT	487	507	2.1
PCVTTTT	491	513	2.0
PCPTDO	514	579	1.7

[a] Measurements performed in CH₂Cl₂. [b] Determined from the onset of the UV-vis absorption in the solid state.

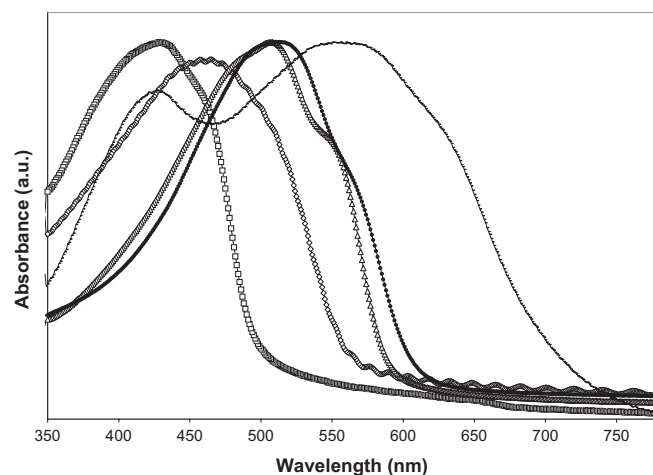


Figure 4. Normalized UV-vis absorbance of thin films of the 2,7-carbazolenevinylene-based copolymers: PCV (□), PCVT (◇), PCVTT (△), PCVTTTT (●), and PCPTDO (-).

as the number of thiophene units increases. This indicates that the bandgap can be easily tuned by addition of thiophene units in the backbone. Moreover, the addition of *S,S*-dioxide thiophene induces a significant bathochromic shift of the absorption spectrum. These results are in good agreement with those already published for *S,S*-dioxide-containing oligomers.^[18] Details of the orbital levels are presented in the electrochemical properties section below.

The small shifts (4–22 nm) measured between the solution and solid-state data suggest that these polymers (except PCPTDO) have similar conformations in both states. In the case of PCPTDO, the larger shift can be explained by the presence of the *S,S*-dioxide moiety in the backbone, which plays an important role in solid-state packing, thus changing the optical properties.^[25]

2.6. Electrochemical Properties

The electrochemical properties of these processable 2,7-carbazolenevinylene-based copolymers are summarized in Table 3. A good approximation for the ionization potential (highest occupied molecular orbital, HOMO) and electron affinity (lowest unoccupied molecular orbital, LUMO) of these

Table 3. Electrochemical oxidation ($E_{\text{peak ox}}$), reduction ($E_{\text{peak red}}$), ionization potential (E_{HOMO}), electron affinity (E_{LUMO}), and bandgap energy (E_g) of 2,7-carbazolenevinylene-based copolymers. SCE: saturated calomel electrode. HOMO: highest occupied molecular orbital. LUMO: lowest unoccupied molecular orbital.

Polymer	$E_{\text{peak ox}}$ ($E_{\text{onset ox}}$) [a] [V vs. SCE]	$E_{\text{peak red}}$ ($E_{\text{onset red}}$) [a] [V vs. SCE]	E_{HOMO} [b] [eV]	E_{LUMO} [c] [eV]	E_g [eV]
PCV	1.06 (0.91)	−1.99 (−1.87)	5.61	2.83	2.78
PCVT	0.97 (0.82)	−1.86 (−1.78)	5.52	2.92	2.60
PCVTT	0.94 (0.79)	−1.87 (−1.68)	5.49	3.02	2.47
PCVTTT	0.80 (0.70)	−1.84 (−1.74)	5.40	2.96	2.44
PCPTDO	0.89 (0.80)	−1.33 (−1.20)	5.50	3.50	2.00

[a] The values in parentheses correspond to the oxidation peak onset. [b] E_{HOMO} measured from the cathodic onset. [c] E_{LUMO} measured from the anodic onset.

polymers can be calculated from electrochemical measurements,^[26] but, as it is often the case for dynamic electrochemical measurements, the measured electrochemical bandgaps are about 0.3–0.4 eV larger than those obtained from optical measurements.

All polymers exhibit a monoelectronic, partially reversible oxidation process between 0.80 and 1.06 V versus standard calomel electrode (SCE); for a typical example, see Figure 5 for PCPTDO. The HOMO energy level decreases proportionally with the increase of the conjugation length of the copolymer, except in the case of PCPTDO. This behavior is in good agree-

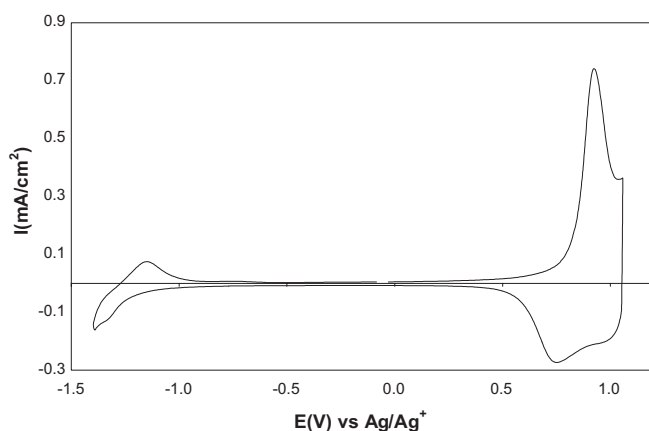


Figure 5. Cyclic voltammogram (current I vs. potential E) of PCPTDO at a scan rate of 50 mV s^{−1}.

ment with the observations of the Barbarella group.^[18b] It is interesting to note that the oxidation potential of PCPTDO is higher than that of regioregular polythiophenes (0.6 V versus SCE),^[27] thus indicating higher oxidative stability. The energy level of the HOMO of the donor polymers in a photovoltaic cell is very important and must be fine-tuned for high device efficiency. Indeed, the HOMO level must allow a good open-circuit potential (V_{oc}) value.^[28] All polymers show a partial reversibility in this monoelectronic reduction process. As ex-

pected, the reduction potential of PCPTDO is remarkably less negative ($E_{\text{red}} = -1.33$ V vs. SCE) than those observed for all other polymers. Hence, PCPTDO has a lower bandgap than all others, but a comparable HOMO level.

A complete picture of the band structure is presented in Figure 6. The first dashed line indicates the threshold for air stability^[29,30] (5.2 eV), and the second dashed line represents the threshold value for an effective charge transfer to [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) (3.8 eV),^[30] which is the electron acceptor.

2.7. Photovoltaic Cells

Having characterized all these physical properties for these new copolymers, bulk heterojunction photovoltaic cells having the sandwich structure ITO/PEDOT:PSS/polymer:PCBM/Al (ITO: indium tin oxide; PEDOT:PSS: poly(3,4-ethylenedioxythiophene:poly(styrene sulfonate))) were fabricated. A layer of PEDOT:PSS was first spin-coated to provide a more uniform contact and to improve hole injection.^[31] The photovoltaic active blend of carbazole-based polymer:PCBM (in a weight ratio of 20:80) was then spin-coated from a chloroform solution. The devices were coated by deposition of a 100 nm aluminum layer as the cathode top electrode.

To standardize and control the quality of the photovoltaic cells, cells containing poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV) as the active polymeric layer were fabricated along with the tested polymers. In our non-optimized systems, efficiencies from devices containing MEH-PPV were about 0.6 %.

All devices were tested under illumination with simulated solar light air mass (AM) 1.5G, light intensity 90 mW cm^{−2}). An example current–voltage curve is presented in Figure 7, which shows the current–voltage behavior of PCPTDO–PCBM solar cells.

The overall energy conversion efficiency, η_e , has been calculated using

$$\eta_e = \frac{V_{\text{oc}} I_{\text{sc}} FF}{P_{\text{inc}}} \quad (1)$$

where V_{oc} [V], I_{sc} [A cm^{−2}], FF , and P_{inc} [W cm^{−2}] are the open-circuit potential, short-circuit current, fill factor, and incident light power, respectively. The value of the fill factor of the device was determined by calculating the area of the maximum power rectangular area under the I – V curve in the fourth quadrant. Therefore, the FF is given by

$$FF = \frac{V_{\text{max}} I_{\text{max}}}{V_{\text{oc}} I_{\text{sc}}} \quad (2)$$

where V_{max} and I_{max} are voltage and current at the point of maximum power output.

The performances of photovoltaic devices are summarized in Table 4. Except for PCPTDO, all I_{sc} values were in the same range. This means that the number of thiophene units did not greatly influence the solar-cell performance, which could indi-

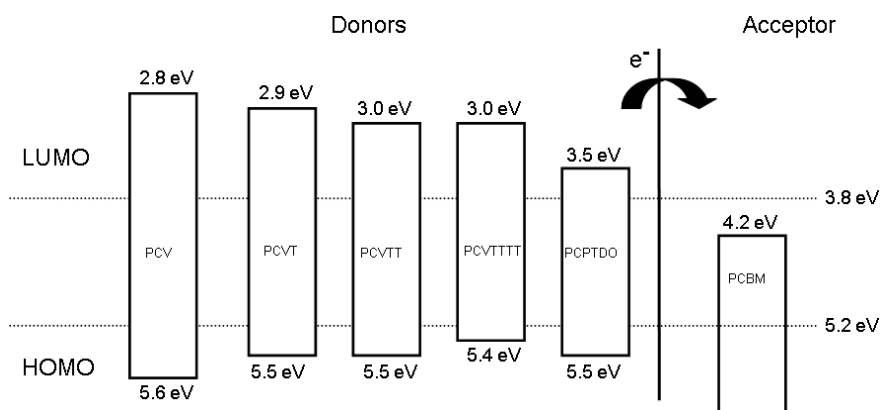


Figure 6. Band diagram for accepting PCBM and donor PCV, PCVT, PCVTT, PCVTTT, and PCPTDO copolymers. Dashed lines indicate the thresholds for air stability (5.2 V) and effective charge transfer to PCBM (3.8 V) according to Reynolds and co-workers [30].

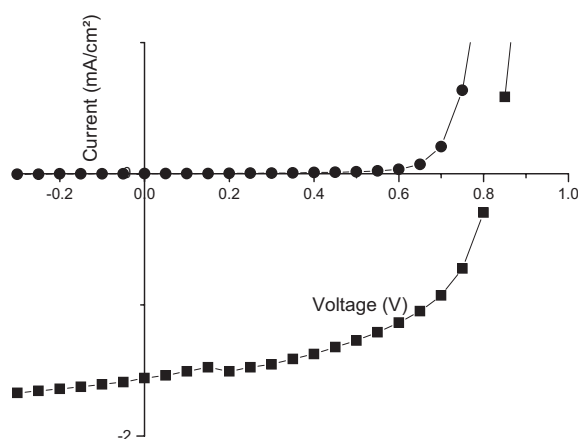


Figure 7. Current–voltage curves for PCPTDO/PCBM solar cells in the dark (●) and under illumination (■) with 90 mW cm^{−2}, AM 1.5 simulated

Table 4. Short-circuit current (I_{sc}), open-circuit potential (V_{oc}), voltage and current at the point of maximum power output (I_{max} and V_{max}), fill factor (FF), and overall energy conversion efficiency (η_e) of 2,7-carbazolenevinylene-based copolymers in solar-cell devices.

Polymer	I_{sc} [mA cm ^{−2}]	V_{oc} [V]	I_{max} [mA cm ^{−2}]	V_{max} [V]	FF [%]	η_e AM1.5 [%]
PCV	0.889	0.850	0.584	0.60	46.4	0.4
PCVT	1.076	0.700	0.670	0.50	44.5	0.4
PCVTT	0.859	0.550	0.572	0.40	48.4	0.3
PCVTTT	0.761	0.500	0.470	0.35	43.2	0.2
PCPTDO	1.558	0.800	1.048	0.65	54.6	0.8

cate that relatively small variations in the fraction of absorbed light was not critical compared to the mobility of the charge carriers through, possibly, the carbazole moieties. Furthermore, as discussed above, the V_{oc} is directly governed by the difference between the energy levels of the HOMO of the donor and the LUMO of the acceptor. Except for PCPTDO, when the bandgap decreases, the HOMO level increases (see Table 4). Thus, the highest V_{oc} (0.850 V) was reached with the

homopolymer PCV, which has the lowest HOMO level. PCPTDO has a satisfying V_{oc} (0.800 V), higher than PCVTTT (0.500 V). As a consequence of this good compromise found in the molecular design of PCPTDO, high fill-factor and overall energy conversion efficiency values of 55 % and 0.8 %, respectively, were calculated for this solar cell. This latter value is four times higher than that obtained with PCVTTT ($\eta_e = 0.2$ %), and is also higher than the performances obtained from the well-characterized MEH–PPV (0.6 %) under our device fabrication conditions. However, these results are not as good as those obtained by Inganäs and co-workers for a photovoltaic cell based on an alternating copolymer based on fluorene and PCBM, where a power-conversion efficiency of 2.2 % was reported.^[4c]

However, further improvements can be expected for our carbazole-based photovoltaic systems by increasing the molecular weights, the solubility, and by creating more organized morphologies. It can also be anticipated that various combinations of acceptors may lead to improved performance. Such optimizations will be the subject of future studies.

3. Conclusions

New, well-defined 2,7-carbazolenevinylene-based copolymers have been successfully synthesized. These copolymers were characterized by size-exclusion chromatography, UV-vis spectroscopy, thermal analyses, and cyclic voltammetry. The fabrication and characterization of photovoltaic cells from these various copolymers have shed some light on the interplay between the structure of the copolymers and their optical properties. Interestingly, a very good value of $\eta_e = 0.8$ % was obtained with PCPTDO in photovoltaic cells for which no parameters were optimized. These results indicate that 2,7-carbazolenevinylene-based copolymers are very attractive materials for photovoltaic cell applications. Much better efficiencies should be obtained by optimizing the polymer/PCBM ratio, device configurations, and thin-film morphology. This latter parameter should be improved by changing the spin-coating conditions and/or by creating crystalline or liquid-crystalline polycarbazole derivatives.

4. Experimental

Characterization: ¹H and ¹³C NMR spectra were recorded using a Varian AS400 in deuterated chloroform, methyl sulfoxide, acetone, or THF solutions at 298 K. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) with a high-pressure liquid chromatography (HPLC) pump using a Waters UV-vis detector. The calibration curve was made with a series of monodisperse polystyrene standards in THF (HPLC grade, Aldrich). UV-vis absorption spectra were recorded using a Hewlett–Packard diode-array spectrophotometer (model 8452A) using

1 cm path-length quartz cells. Optical bandgaps were calculated from the onset of the visible-absorption band. For solid-state measurements, polymer solutions in chloroform were cast on quartz plates. Electrochemical analysis of polymers was carried out in a two-compartment cell with a Solartron potentiostat (model 1287) using platinum electrodes at a scan rate of 50 mV s⁻¹ against Ag/Ag⁺ (0.100 M of AgNO₃ in acetonitrile) reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) in acetonitrile. Acetonitrile was dried over CaH₂ under an inert atmosphere (argon) for 24 h. Bu₄NBF₄ was dried at 100 °C under reduced pressure. In these conditions, the oxidation potential (*E*_{ox}) of ferrocene was 0.151 V versus Ag/Ag⁺, whereas the *E*_{ox} of ferrocene was 0.457 V versus SCE in 0.1 M Bu₄NBF₄/MeCN solution. As reported by Reynolds and co-workers, [30], the SCE electrode was assumed to be at 4.7 eV from vacuum. Thermogravimetric analyses were performed using a Mettler Toledo TGA SDTA 851e at a heating rate of 20 °C min⁻¹ under a nitrogen flow. Differential scanning calorimetry analyses were performed using a Perkin-Elmer DSC-7 instrument at 10 °C min⁻¹ under a nitrogen atmosphere.

Materials: Tetrahydrofuran (ACS grade), toluene (ACS grade), and methylene chloride (ACS grade) were distilled over potassium, CaH₂, and sodium, respectively, prior to use. All other chemicals were purchased from Aldrich and used without further purification. 3-Octylthiophene, <productlargeclass>5,5'-dibromo-2,2'-bithiophene, 2,2'-bithiophene, 2-(tributylstannyl)thiophene, and 5-bromo-2-thiophenecarboxaldehyde were purchased from Aldrich and used without further purification<productlargeclass>. The synthesis of 2,7-bis(trityloxymethyl)carbazole (**1**) [9], 1-iodo-4-octyloxybenzene (**2**) [32], and 2,5-dibromo-3-3-dihexylthiophene 1,1-dioxide (**16**) [18b] have been described previously.

***N*-(4-Octyloxy-phenyl)-2,7-bis(trityloxymethyl)carbazole (3):** A 250 mL flask was charged with 2,7-bis(trityloxymethyl)carbazole (**1**) (20 g, 28.1 mmol), 1-iodo-4-octyloxybenzene (**2**) (14 g, 42.1 mmol), K₂CO₃ (7.8 g, 56.2 mmol), copper powder (3.6 g, 56.2 mmol, Aldrich), dibenzo-18-crown-6 (743 mg, 2.8 mmol), and 90 mL of DMF. The resulting mixture was refluxed under argon for 20 h and then cooled at room temperature. Water was then added under vigorous stirring. The organic product was extracted with dichloromethane. The aqueous layer was removed, and the organic layer was washed three times with distilled water. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (15 % ethyl acetate in hexanes as eluent) to provide 14.1 g of the title product as a white solid. Melting point (mp) 158–159 °C (Yield: 55 %). ¹H NMR (400 MHz, CDCl₃, ppm): 8.07 (d, 2H, *J* = 7.9 Hz); 7.51 (m, 12H); 7.44 (d, 2H, *J* = 8.6 Hz); 7.27 (m, 22H); 7.10 (d, 2H, *J* = 8.7 Hz); 4.29 (s, 4H); 4.03 (t, 2H, *J* = 6.5 Hz); 1.86 (q, 2H, *J* = 6.5 Hz); 1.51 (m, 2H); 1.34 (m, 8H); 0.89 (t, 3H, *J* = 7 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): 144.40; 141.85; 137.22; 130.24; 128.97; 128.65; 128.15; 128.13; 128.04; 127.19; 122.37; 120.15; 119.05; 115.67; 108.37; 110.00; 87.22; 68.59; 66.53; 32.06; 29.61; 29.53; 29.50; 26.35; 22.90; 14.35. High-resolution mass spectrometry (HRMS): Calculated for C₆₆H₆₁N₁O₃; 915.4651; found: 915.4669.

***N*-(4-Octyloxy-phenyl)-2,7-bis(hydroxymethyl)carbazole (4):** A 500 mL flask was charged with compound **3** (6.4 g, 7.0 mmol), dichloromethane (200 mL), methanol (50 mL), and concentrated HCl (0.8 mL). The resulting mixture was stirred for 2 h, and then saturated aqueous NaHCO₃ (70 mL) was added. The aqueous layer was removed, and the organic layer was washed three times with distilled water. The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure. The resulting solid was recrystallized in toluene to provide 2.53 g of the title product as a white solid. mp 140–141 °C (Yield: 84 %). ¹H NMR (400 MHz, acetone-*d*₆, ppm): 8.10 (d, 2H, *J* = 8.0 Hz); 7.48 (d, 2H, *J* = 8.9 Hz); 7.34 (s, 2H); 7.23 (m, 4H); 4.76 (d, 4H, *J* = 5.9 Hz); 4.22 (t, 2H, *J* = 5.8 Hz); 4.14 (t, 2H, *J* = 6.5 Hz); 1.86 (m, 2H); 1.55 (m, 2H); 1.38 (m, 8H); 0.91 (t, 3H, *J* = 7.0 Hz). ¹³C NMR (100 MHz, acetone-*d*₆, ppm): 158.92; 142.04; 140.90; 130.17; 128.81; 122.12; 119.89; 118.80; 115.86; 107.69; 68.28; 64.53; 31.91; 29.42; 29.36; 26.14; 22.65; 13.69. (The two missing peaks are hidden by the residual signal of acetone). HRMS: Calculated for C₂₈H₃₃N₁O₃; 431.2460; found: 431.2469.

***N*-(4-Octyloxy-phenyl)-2,7-bis(chloromethyl)carbazole (5):** To a solution of compound **4** (2.53 g, 5.4 mmol) in dry toluene (100 mL) containing a few drops of pyridine was slowly added thionyl chloride (3.17 mL, 43.5 mmol, Aldrich) at 0 °C. The mixture was stirred at 0 °C for 1 h and then at room temperature for 2 h. The excess of thionyl chloride and toluene was removed under reduced pressure. The yellow oil obtained was used without further purification.

***N*-(4-Octyloxy-phenyl)-2,7-bis(methylphosphonate)carbazole (6):** In a 100 mL flask, compound **5** and triethylphosphite (30 mL) were mixed and heated to reflux under argon for 24 h. The solution cooled at room temperature and excess of triethylphosphite was removed under reduced pressure. The resulting orange oil was purified by column chromatography (50 % acetone in hexanes as eluent) to provide 2.39 g of the title product as a yellow oil. (Yield: 65 %). ¹H NMR (400 MHz, CDCl₃, ppm): 7.98 (d, 2H, *J* = 8 Hz); 7.36 (d, 2H, *J* = 8.9 Hz); 7.17 (m, 4H); 7.05 (d, 2H, *J* = 8.9 Hz); 3.95 (m, 10H); 3.23 (d, 4H, *J* = 21.5 Hz); 1.81 (q, 2H, *J* = 6.7 Hz); 1.49 (m, 2H); 1.33 (m, 8H); 1.18 (t, 12H, *J* = 7 Hz); 0.87 (t, 3H, *J* = 6.8 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): 158.83; 142.12; 129.91; 129.53; 129.44; 128.72; 122.02; 121.91; 121.85; 120.36; 115.91; 111.21; 111.13; 68.64; 62.36; 62.29; 35.24; 33.87; 32.08; 29.61; 29.51; 26.33; 22.92; 16.63; 16.57; 14.36. (Many peaks result from carbon coupling with phosphorous). HRMS: Calculated for C₃₆H₅₁N₁O₇P₂; 671.3141; found: 671.3154.

***N*-(4-Octyloxyphenyl)-2,7-bis(formyl)carbazole (7):** In a 100 mL flask, compound **4** (1.50 g, 3.48 mmol), pyridinium chlorochromate (3.75 g, 17.4 mmol, Aldrich), molecular sieves 4 Å (750 mg), silica gel (750 mg), and dichloromethane (35 mL) were mixed at room temperature. The resulting mixture was stirred 2 h at room temperature and then filtered through silica gel (using dichloromethane as eluent) to provide 1.4 g of the title product as a bright yellow solid. mp 133–134 °C (Yield: 94 %). ¹H NMR (400 MHz, CDCl₃, ppm): 10.08 (s, 2H); 8.29 (d, 2H, *J* = 8.1 Hz); 7.86 (s, 2H); 7.83 (dd, 4H, *J* = 8.0 and 1.3 Hz); 7.41 (d, 2H, *J* = 8.9 Hz); 7.14 (d, 2H, *J* = 8.9 Hz); 4.08 (t, 2H, *J* = 6.6 Hz); 1.87 (m, 2H); 1.53 (m, 2H); 1.36 (m, 8H); 0.91 (t, 3H, *J* = 6.8 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): 192.47; 159.60; 143.05; 135.63; 128.82; 128.48; 127.15; 121.95; 121.76; 116.29; 112.32; 68.72; 32.05; 29.56; 29.49; 29.44; 26.29; 22.90; 14.34. HRMS: Calculated for C₂₈H₂₉N₁O₃; 427.2147; found: 427.2145.

4,4'-Diocetyl-2,2'-bithiophene (8): A solution of *N,N,N',N'*-tetramethylethylenediamine (4.22 mL, 28 mmol, Aldrich) and of 2.5 M *n*-butyllithium solution (11.2 mL, 28 mmol) in 55 mL of anhydrous ether was added into a solution of 3-octylthiophene (5.0 g, 25.4 mmol) in 130 mL of anhydrous ether under stirring and then refluxed for about 1 h. After cooling down to –78 °C, CuCl₂ (4.44 g, 33 mmol) was added in one portion and the mixture was stirred overnight, during which period the temperature rose to room temperature. Acidification, extraction, washing, and drying provided a dark oil. This resulting oil was then purified by column chromatography (hexanes as eluent). Recrystallization from diethyl ether at dry-ice temperature gave 2.6 g of the title product as a white solid. mp 32 °C (Yield: 52 %). ¹H NMR (400 MHz, CDCl₃, ppm): 6.95 (s, 2H); 6.74 (s, 2H); 2.54 (t, 4H, *J* = 7.6 Hz); 1.59 (t, 4H, *J* = 6.6 Hz); 1.28 (m, 20H); 0.85 (t, 3H, *J* = 7.1 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): 144.20; 137.56; 125.01; 118.90; 32.10; 30.73; 30.61; 29.64; 29.53; 29.48; 22.90; 14.34. HRMS: Calculated for C₂₄H₃₈S₂; 390.2415; found: 390.2418.

5,5'-Diformyl-4,4'-diocetyl-2,2'-bithiophene (9): Under nitrogen atmosphere, to a solution of **8** (2.5 g, 6.4 mmol) and TMEDA (2 mL, 13.4 mmol) in dry hexanes was added dropwise a 2.5 M hexanes solution of *n*-butyllithium (5.4 mL, 13.4 mmol) at room temperature. The mixture was stirred for 30 min at 40 °C and then refluxed for 2 h more. After addition of anhydrous THF (120 mL), the solution was cooled at –78 °C. An excess of dry DMF (2.5 mL, 32 mmol) was added dropwise. The reaction mixture was left to reach room temperature, and the obtained solution was poured into a 3.7 % aqueous HCl solution (1000 mL), under vigorous stirring and kept below 0 °C. After neutralization with NaHCO₃ solution, the organic layer was extracted several times with diethyl ether and dried with magnesium sulfate. Then solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (10 % THF in hexanes as eluent). Recrystallization from diethyl ether provided 1.7 g of the title product

as a yellow solid. mp 76 °C (Yield: 58 %). ¹H NMR (400 MHz, CDCl₃, ppm): 9.99 (s, 2H); 7.16 (s, 2H); 2.91 (t, 4H, *J* = 7.5 Hz); 1.65 (t, 4H, *J* = 6.7 Hz); 1.25 (m, 20H); 0.85 (t, 3H, *J* = 7.0 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): 181.99; 153.88; 144.24; 137.98; 128.82; 32.01; 31.57; 29.51; 29.49; 29.37; 28.73; 22.84; 14.29. HRMS: Calculated for C₂₄H₃₈O₂S₂: 446.2313; found: 446.2322.

2-Trimethyltin-4-octylthiophene (10): Under an argon atmosphere, to a solution of 3-octylthiophene (4 g, 20.4 mmol) in anhydrous THF was added dropwise a 2.5 M hexanes solution of *n*-butyllithium (8.96 mL, 22.4 mmol) at –78 °C. The mixture was stirred at –78 °C for 2 h. Then, 1 M trimethyltin chloride solution in dry THF (24 mL, 22.4 mmol) was added, and the solution was stirred at –78 °C for an additional 2 h, and then overnight at room temperature. Water was then added under vigorous stirring. The aqueous layer was removed, and the organic layer was washed three times with distilled water. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The resulting dark oil was purified by distillation under reduced pressure (135 °C under 1.1 mm Hg; 1 mm Hg ~ 133 Pa) to provide 4.9 g of the title product as a brown oil (Yield: 66 %). ¹H NMR (400 MHz, CDCl₃, ppm): 6.84 (s, 1H); 6.66 (s, 1H); 2.29 (t, 2H, *J* = 7.3 Hz); 1.27 (t, 2H, *J* = 6.8 Hz); 0.94 (m, 10H); 0.35 (t, 3H, *J* = 7.1 Hz); 0.002 (s, 9H).

4,4''-Diocetyl-2,2':5',2'':5'',2'''-quarterthiophene (11): A solution of **10** (3.3 g, 9.2 mmol) and 5,5'-dibromo-2,2'-bithiophene (1 g, 3.1 mmol) in THF (30 mL) was deaerated twice with argon followed by the addition of tetrakis(triphenylphosphine) palladium (2 mol %). The reaction mixture was heated at reflux for 24 h under argon. Then, saturated NaHCO₃ aqueous solution was added. The aqueous layer was removed, and the organic layer was washed three times with distilled water. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The resulting yellow solid was purified by column chromatography (hexanes as eluent) to provide 930 mg of the title product as a yellow solid. mp 90–91 °C (Yield: 54 %). ¹H NMR (400 MHz, CDCl₃, ppm): 7.02 (s, 2H); 6.98 (d, 1H, *J* = 1.3 Hz); 6.78 (d, 1H, *J* = 0.9 Hz); 2.55 (t, 4H, *J* = 7.8 Hz); 1.61 (m, 4H); 1.25 (m, 20H); 0.86 (t, 6H, *J* = 7.1 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): 144.43; 136.83; 135.87; 125.31; 125.01; 124.31; 124.23; 119.42; 32.11; 30.72; 30.61; 29.64; 29.54; 29.47; 22.89; 14.34. HRMS: Calculated for C₃₂H₄₂S₄: 554.2169; found: 554.2178.

5,5'''-Diformyl-4,4''-diocetyl-2,2':5',2'':5'',2'''-quarterthiophene (12): DMF (40 mL, 12.9 mmol) and phosphorous oxychloride (POCl₃) (5 mL, 34 mmol) were mixed together and stirred for 20 min at 0 °C. To the yellow DMF-POCl₃ complex, a solution of **11** (0.9 g, 1.6 mmol) in DMF (20 mL) was added dropwise at 0 °C. The reaction mixture was heated at 100 °C for 2 h under argon. Then, the reaction mixture was poured into dilute HCl solution (150 mL), and the organic layers were extracted with dichloromethane. The organic layer was washed with an aqueous solution of sodium bicarbonate and subsequently with distilled water. After drying over magnesium sulfate and removal of organic solvent under reduced pressure, the crude product was purified by column chromatography (70 % chloroform in hexanes as eluent) to provide 700 mg of the title product as a yellow solid. mp 147–148 °C (Yield: 72 %). ¹H NMR (400 MHz, CDCl₃, ppm): 9.97 (s, 2H); 7.24 (d, 2H, *J* = 3.9 Hz); 7.13 (d, 2H, *J* = 3.9 Hz); 7.04 (s, 2H); 2.90 (t, 4H, *J* = 7.7 Hz); 1.66 (m, 4H); 1.26 (m, 20H); 0.87 (t, 6H, *J* = 7.1 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): 181.74; 154.15; 145.42; 137.99; 136.29; 135.87; 127.06; 126.86; 125.46; 32.03; 31.59; 29.54; 29.52; 29.38; 28.77; 22.85; 14.31. HRMS: Calculated for C₃₄H₄₂O₂S₄: 610.2067; found: 610.2070.

5-Formyl-2,2'-bithiophene (13): Phosphorous oxychloride (6.3 mL, 42.7 mmol) was added to a solution of 2,2'-bithiophene (6.3 g, 38.0 mmol) and DMF (3.3 mL, 42.7 mmol) in 1,2-dichloroethane (62 mL) cooled in an ice bath. The solution was then warmed up to room temperature and heated to reflux. After refluxing overnight, the yellow suspension was cooled to room temperature and poured into a saturated aqueous sodium acetate solution (250 mL) and stirred for several hours to complete the hydrolysis. The yellow suspension formed was extracted with dichloromethane. The organic layers were combined and washed with water, dried over magnesium sulfate, and concentrated. The crude product was purified by column chromatography

(10 % ethyl acetate in hexanes as eluent) to provide 6.8 g of the title product as a brown solid. mp 48–49 °C (Yield: 93 %). ¹H NMR (400 MHz, CDCl₃, ppm): 9.82 (s, 1H); 7.63 (d, 1H, *J* = 3.9 Hz); 7.32 (d, 2H, *J* = 4.9 Hz); 7.22 (d, 1H, *J* = 3.9 Hz); 7.04 (t, 1H, *J* = 4.3 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): 182.84; 147.42; 141.92; 137.65; 136.27; 128.63; 127.38; 126.42; 124.51. HRMS: Calculated for C₉H₆O₂S₂: 193.9860; found: 193.9856.

5-Dimethoxymethyl-2,2'-bithiophene (14): A solution of **13** (2.0 g, 10.3 mmol), *p*-toluenesulfonic acid monohydrate (0.196 mg, 1.03 mmol), molecular sieves (catalytic amount), and trimethyl orthoformate (5.6 mL, 51.5 mmol) in anhydrous methanol (10 mL) was refluxed under argon for 16 h. Then, the solution was poured into a 5 % sodium hydroxide solution and extracted with dichloromethane. The crude product was purified by column chromatography (15 % ethyl acetate in hexanes as eluent) treated with 1 % of triethylamine to provide 2.0 g of the title product as a yellow oil. (Yield: 81 %). ¹H NMR (400 MHz, CDCl₃, ppm): 7.18 (dd, 1H, *J* = 1.1 Hz, *J* = 4.0 Hz); 7.13 (dd, 1H, *J* = 1.1 Hz, *J* = 3.9 Hz); 7.04 (d, 1H, *J* = 3.7 Hz); 6.98 (q, 1H, *J* = 3.6 Hz, *J* = 1.5 Hz); 6.94 (dd, 1H, *J* = 0.8 Hz, *J* = 3.7 Hz); 5.58 (s, 1H); 3.36 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): 140.55; 137.95; 137.52; 128.01; 126.30; 124.67; 123.94; 123.50; 100.12; 52.79. HRMS: Calculated for C₁₁H₁₂O₂S₂: 240.3412; found: 240.3421.

(5'-Dimethoxymethyl-[2,2'-bithiophenyl-5-yl)-trimethyl-stannane (15): Under an argon atmosphere, to a solution of **14** (1.98 g, 8.2 mmol) in anhydrous THF (30 mL) was added dropwise a 2.5 M hexanes solution of *n*-butyllithium (3.32 mL, 8.3 mmol) at –78 °C. The mixture was stirred at –78 °C for 2 h. Then, a solution of trimethyltin chloride (1.66 g, 8.3 mmol) in anhydrous THF (8 mL) was added and the solution was stirred at –78 °C for an additional 2 h and then overnight at room temperature. Water was then added under vigorous stirring. The aqueous layer was removed, and the organic layer was washed three times with distilled water. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The dark oil obtained was used without further purification. ¹H NMR (400 MHz, CDCl₃, ppm): 6.88 (d, 1H, *J* = 3.0 Hz); 6.69 (d, 1H, *J* = 3.4 Hz); 6.67 (d, 1H, *J* = 3.7 Hz); 6.58 (dd, 1H, *J* = 0.9 Hz, *J* = 3.7 Hz); 5.22 (s, 1H); 3.00 (s, 6H); 0.002 (s, 9H).

3',4''-Dihexyl-5,5'''-dicarbaldehyde-2,2':5',2'':5'',2'''-quin-quethiophene 1'',1'-dioxide (17): A solution of **15** (2.8 g, 6.95 mmol) and 2,5-dibromo-3-3-dihexylthiophene 1,1-dioxide (1.4 g, 3.16 mmol) in anhydrous THF (45 mL) was deaerated twice with argon followed by the addition of tetrakis(triphenylphosphine) palladium (2 mol %). The reaction mixture was heated at reflux for 24 h under argon. Then, a saturated NaHCO₃ aqueous solution was added. The aqueous layer was removed, and the organic layer was washed three times with distilled water. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The resulting red solid was put back in THF (25 mL) and treated with a 3 N HCl solution. This mixture was stirred for 1.5 h at room temperature. Then, the solution was poured into water (250 mL) and the resulting precipitate was filtered. The resulting red solid was purified by recrystallization in dichloromethane to provide 1.52 g of the title product as a red solid. Decomposition temperature > 150 °C (Yield: 72 %). ¹H NMR (400 MHz, CDCl₃, ppm): 9.86 (s, 2H); 9.67 (dd, 4H, *J* = 3.97 Hz, *J* = 9.0 Hz); 7.39 (d, 2H, *J* = 4.0 Hz); 7.30 (d, 2H, *J* = 3.9 Hz); 2.68 (t, 4H, *J* = 7.8 Hz); 1.55 (m, 8H); 1.35 (m, 8H); 0.91 (t, 6H, *J* = 7.0 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): 182.65; 154.70; 142.92; 138.68; 138.51; 137.34; 130.46; 130.32; 129.98; 127.03; 125.33; 31.51; 29.82; 28.69; 27.46; 22.75; 14.24. HRMS: Calculated for C₃₄H₃₆O₄S₂: 668.1217; found: 668.1213.

3',4''-Dihexyl-2,2':5',2'':5'',2'''-terthiophene 1'',1'-dioxide (18): To a 14 mL toluene solution of Pd₂dba₃ (81 mg, 0.088 mmol) and AsPh₃ (0.107 g, 0.35 mmol) was added 2,5-dibromo-3-3-dihexylthiophene 1,1-dioxide (**16**) (1.37 g, 3.1 mmol) in 5 mL of toluene. At reflux, 2-tributylstannylthiophene (8.85 mL, 27.9 mmol) was added. After refluxing for 16 h, the solution was cooled at room temperature and poured into water (50 mL). The product was extracted with dichloromethane, and the organic layer was washed three times with distilled water. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (10 % ethyl acetate in hexanes as eluent) to pro-

vide 1.2 g of the title product as a yellow solid. mp 49–50 °C (Yield: 86 %). ¹H NMR (400 MHz, CDCl₃, ppm): 7.74 (dd, 2H, *J* = 1.1 Hz, *J* = 3.8 Hz); 7.51 (dd, 2H, *J* = 1.1 Hz, *J* = 5.1 Hz); 7.19 (q, 2H, *J* = 3.8 Hz, *J* = 1.4 Hz); 2.67 (t, 4H, *J* = 8.0 Hz); 1.56 (m, 8H); 1.36 (m, 8H); 0.91 (t, 6H, *J* = 7.0 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): 137.62; 130.50; 129.04; 128.74; 128.30; 128.26; 31.59; 29.86; 28.74; 27.29; 22.79; 14.27. HRMS: Calculated for C₂₄H₃₂O₂S₃: 448.1564; found: 448.1574.

5,5'-Trimethylstannyl-3,4'-dihexyl-2,2':5',2''-terthiophene 1',1'-dioxide (19): Under an argon atmosphere, to a solution of **18** (1.15 g, 2.57 mmol) in anhydrous THF (30 mL) was added dropwise a 2 M solution of LDA (2.83 mL, 5.66 mmol) in hexanes at –78 °C. The mixture was stirred at –78 °C for 2 h. Then, a solution of trimethyltin chloride (1.66 g, 8.3 mmol) in anhydrous THF (3 mL) was added and the solution was stirred at –78 °C for an additional 2 h, and then overnight at room temperature. Water was then added under vigorous stirring. The aqueous layer was removed, and the organic layer was washed three times with distilled water. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was put back in methanol (110 mL), and the mixture was cooled at –78 °C and then warmed up to 0 °C. The yellow suspension was then filtered. The resulting yellow solid was purified by two successive recrystallizations in hexanes to provide 560 mg of the title product as a yellow–brown crystalline product. mp 91–92 °C (Yield: 28 %). ¹H NMR (400 MHz, CDCl₃, ppm): 7.82 (d, 2H, *J* = 3.6 Hz); 7.25 (d, 2H, *J* = 3.6 Hz); 2.69 (t, 4H, *J* = 8.0 Hz); 1.56 (m, 8H); 1.37 (m, 8H); 0.93 (t, 6H, *J* = 7.0 Hz); 0.41 (s, 9H). ¹³C NMR (100 MHz, CDCl₃, ppm): 142.20; 137.20; 136.14; 134.17; 130.26; 129.53; 31.53; 29.79; 28.62; 27.30; 22.76; 22.75; 14.28; –7.90. HRMS: Calculated for C₃₀H₄₈O₂S₃Sn₂: 776.0860; found: 776.0850.

N-(4-Octyloxyphenyl)-2,7-bis(-2-(5-bromothiophen-2-yl)vinyl)carbazole (20): In a 250 mL round-bottomed flask, compound **6** (1.5 g, 2.23 mmol), 2-bromo-5-thiophenecarboxaldehyde (1.28 g, 6.7 mmol, Aldrich), dry THF (130 mL), and potassium *tert*-butoxide (3 g, 26.8 mmol, Aldrich) were added. The mixture was stirred at room temperature for 24 h and poured into cold methanol (300 mL). The yellow precipitate was filtered and rinsed thoroughly with water, followed by methanol. The yellow solid was purified by column chromatography (60 % chloroform in hexanes as eluent). A final recrystallization in a mixture of 6:1 hexanes and chloroform gave 1.18 g of the title product as a yellow crystalline solid. mp 123–124 °C (Yield: 71 %). ¹H NMR (400 MHz, CDCl₃, ppm): 8.03 (d, 2H, *J* = 8.1 Hz); 7.44 (d, 2H, *J* = 8.8 Hz); 7.39 (dd, 2H, *J* = 8.1 Hz, *J* = 1.3 Hz); 7.30 (s, 2H); 7.16 (d, 2H, *J* = 8.6 Hz); 7.13 (d, 2H, *J* = 15.3 Hz); 6.95 (d, 2H, *J* = 3.8 Hz); 6.91 (d, 2H, *J* = 16.0 Hz); 6.78 (d, 2H, *J* = 3.9 Hz); 4.11 (t, 2H, *J* = 8.1 Hz); 1.89 (m, 2H); 1.47 (m, 10H); 0.93 (t, 3H, *J* = 7.0 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): 159.04; 145.02; 142.82; 134.96; 130.74; 129.87; 129.73; 129.03; 126.27; 123.04; 120.96; 120.70; 118.78; 115.99; 111.11; 107.85; 68.68; 32.10; 29.65; 29.57; 29.54; 26.38; 22.95; 14.39. HRMS: Calculated for C₃₈H₃₅BrN₂O₂S₂: 743.0527; found: 743.0510.

General Procedure for Horner–Emmons Polymerization: In a 50 mL flask, a diphosphonate derivative (500 mg, 0.7 mmol), a dialdehyde derivative (0.7 mmol), and anhydrous THF (20 mL) were mixed under argon. Potassium *tert*-butoxide (335 mg, 3.0 mmol) was slowly added, and the solution was stirred at room temperature under argon for 48 h. The resulting solution was poured into 300 mL of methanol and the precipitate was filtered, rinsed thoroughly with methanol, and washed in a Soxhlet apparatus using acetone for 48 h to provide the polymer.

Poly(N-(4-octyloxyphenyl)-2,7-carbazolenevinylene-alt-3'',4''-dihexyl-2,2':5',2''-quinoxithiophenevinylene 1',1''-dioxide) (PCP-TDO) by Stille Reaction: In a 25 mL flask, tris(dibenzylideneacetone)-dipalladium (Pd₂dba₃, 3.6 mg, 3.87 × 10^{–3} mmol) was dissolved in 5.5 mL of freshly distilled THF, and AsPh₃ (4.74 mg, 1.55 × 10^{–2} mmol) was added. The solution was stirred for about 30 min, and then compound **20** (192.6 mg, 0.26 mmol) was added. Then the temperature was increased to reflux, and, at this temperature, compound **19** (200 mg, 0.26 mmol) was added. The solution was stirred and refluxed under argon for 48 h. The resulting solution was poured into 300 mL of methanol, and the precipitate was filtered, rinsed thoroughly with methanol, and washed in a Soxhlet apparatus using acetone for 48 h to provide the title polymer with good film-forming properties.

Photovoltaic Cells Fabrication and Testing: The organic photovoltaic cells devices (OPC) were prepared on a commercial ITO-coated glass substrate (25 mm × 25 mm) with a sheet resistance of ≤ 10 Ohms square^{–1} (Präzisions Glas & Optic GmbH, Germany). Each substrate had been patterned using photolithographic techniques to produce a segment with active area of 100 mm². Prior to use, the substrate were cleaned sequentially with detergent, deionized water, and ultrasonicated isopropanol. ITO substrates were then spin-coated (2000 rpm, 60 s) with a thin film of PEDOT:PSS (Baytron P, Bayer AG, Germany) from its water solution to promote hole injection and dried at 120 °C for 10 min. A blend of carbazole-based polymer and [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) (BuckyUSA, Houston, TX) (20:80) was solubilized in chloroform, filtered through a 0.2 μm polytetrafluoroethylene filter, spin-coated at 2000 rpm for 60 s, and dried at 50 °C for 15 min and then, at room temperature, under vacuum for 12 h. The devices were completed by deposition of a 100 nm aluminum layer (the layer was thermally evaporated at a pressure of 1 × 10^{–6} Torr (1 Torr ~ 133 Pa) at room temperature).

Current–voltage (*I*–*V*) curves were measured using a Keithley 2400 Digital SourceMeter under a collimated beam. Illumination of the cells was performed through the ITO side by white light from a solar simulator (Oriental Instruments 150 W Solar Simulator with appropriate filters to provide AM 1.5G) with an intensity of 90 mW cm^{–2}.

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