

Syntheses and Characterization of Electroactive and Photoactive 2,7-Carbazolenevinylene-Based Conjugated Oligomers and Polymers

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This study reports the first syntheses and characterization of 2,7-carbazolenevinylene-based oligomers and polymers. Their relatively straightforward syntheses are mainly based on Horner–Emmons or Knoevenagel coupling reaction leading to well-defined oligomers and polymers. As expected, introduction of vinylene and cyanovinylene unit into the polymer backbone decreases the band gap allowing a fine-tuning of the optical and electrical properties. These electroactive and photoactive organic materials exhibit promising performances in light-emitting devices and field-effect transistors. For instance, preliminary measurements using poly(*N*-(2-ethylhexyl)-2,7-carbazolenevinylene-*alt*-2,5-diethoxy-1,4-phenylenevinylene) (PCCVP) have revealed orange-red emission with an intensity of 245 cd/m² at 10 V, whereas *p*-type mobility of about 3.7×10^{-2} cm²/V·s and an on/off ratio as high as 10⁶ were reached with 1,4-bis(vinylene-(*N*-hexyl-2-carbazole))phenylene (CPC).

1. Introduction

Conjugated oligomers and polymers are subjected to important investigations from both academic and industrial laboratories¹ because of their great potential for the development of chemo- and biosensors² and electronic devices (light-emitting diodes,³ field-effect transistors,⁴ solar cells,⁵ etc.). The advantages of organic electroactive and photoactive materials over inorganic ones are their ease of processing and the tunability of their properties through simple chemical modifications. Significant developments in modern synthetic chemis-

try, especially the chemistry of carbon–carbon bond formation (through Kumada, Stille, Yamamoto, Suzuki, Heck, and Sonogashira couplings, etc.), have allowed the synthesis of various well-defined conjugated oligomers and polymers with optimized physical properties. Depending on the aimed applications, different conjugated building blocks, such as thiophene, pyrrole, phenylene, and fluorene moieties, have been utilized. However, the development of new conjugated building blocks is still a challenge for the synthesis of optimized materials for future plastic electronic devices.

In this regard, we have recently prepared well-defined, conjugated, poly(2,7-carbazole) derivatives.^{6–8} In contrast to the partially conjugated 3,6-carbazole-based polymers, this new class of aromatic polymers has led us to prepare luminescent polymers spanning the entire visible range,⁹ useful in light-emitting diodes.^{10,11} However, the development of 2,7-carbazole-based polymers for electronic applications such as photovoltaic cells and field-effect transistors, which require materials having planar structure with low band-gap and good hole transport properties, is not straightforward. Moreover, introduction of alkyl chains on comonomers (helping polymer solubility) induces some steric hindrance leading to an increase of the band gap and limited

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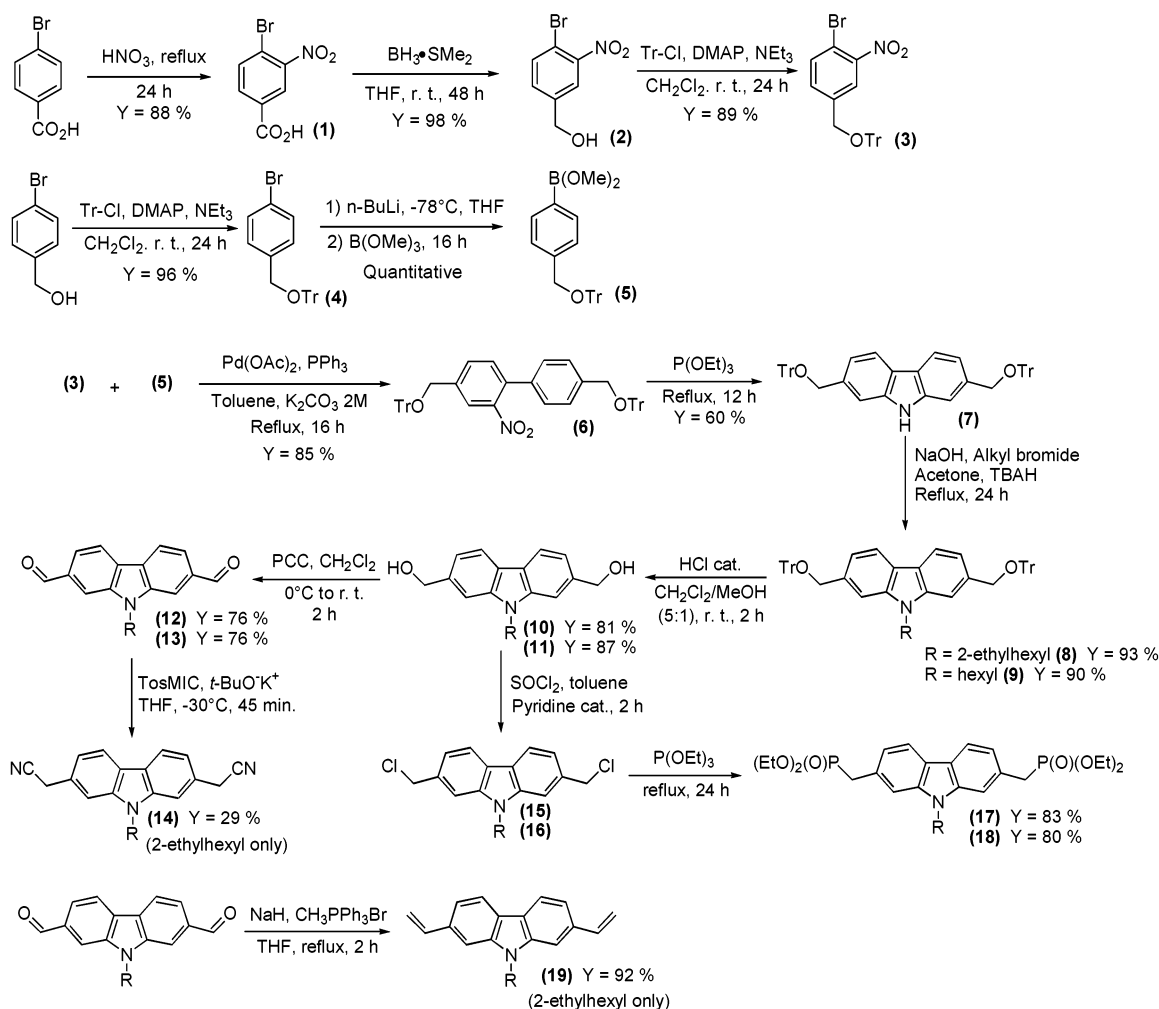
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Scheme 1. Synthesis of the 2,7-Difunctionalized Carbazoles



transport ability. One of the most popular strategies to overcome these problems is the introduction of vinylene units along the conjugated backbone, which is a well-known technique to allow a decrease of the band gap and a fine-tuning of the electrical properties.¹² This concept has been well illustrated by Siove et al.¹³ with poly(*N*-alkyl-3,6-carbazole) derivatives which have shown a strong bathochromic shift of their UV–visible absorption maximum after the addition of a cyanovinylene moiety.

Along these lines, we report the syntheses and properties of 2,7-carbazolenevinylene-based conjugated oligomers and polymers. The characterization of these materials into different electronic and electrooptical devices should allow a better understanding of the structure–property relationships in this new class of organic materials.

2. Experimental Section

Chloroform (spectrograde) and tetrahydrofuran (HPLC grade) were purchased from Aldrich and used as received. 3,4-Diethyl-

2,5-bis(methylphosphonate)thiophene,¹⁴ [4-(2-ethylhexyloxy)-phenyl]-bis-(4'-formylphenyl)amine,¹⁵ and 2,5-diethyloxy-1,4-diformylbenzene¹⁶ were synthesized as previously described in the literature. All other monomers, oligomers, and polymers have been synthesized following procedures described in the Supporting Information. Procedures for the characterization of the oligomers and polymers as well as those describing device fabrication are also included in the Supporting Information.

3. Results and Discussion

3.1 Synthesis of 2,7-Functionalized Monomers.

Because the introduction of functional groups at the 2- and 7-positions cannot be achieved directly from a carbazole unit, a synthetic scheme based on a pre-functionalized biphenyl unit containing functions at the 4 and 4'-positions, followed by a ring closure reaction, was utilized.^{6,7} Therefore, as shown in Scheme 1, 4-bromobenzoic acid was first treated with boiling nitric acid overnight yielding a mononitration reaction in the alpha position of the bromine atom to give compound 1 in a good yield. The carboxylic group was reduced in

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mild conditions using a borane–dimethyl sulfide complex in anhydrous THF to give the corresponding benzyl alcohol (compound **2**). The alcohol groups were protected using trityl chloride in dichloromethane in the presence of DMAP and triethylamine leading to 4-bromo-3-nitromethyltrityloxybenzene (**3**) in a very good yield. The choice of trityl group as a protecting group was motivated by its good tolerance to alkaline conditions used later for the alkylation of carbazole derivative. Also, trityl-containing molecules have great ability to crystallize, helping purification through recrystallization or trituration. In the same way, 4-bromobenzyl alcohol was treated with trityl chloride to give the corresponding protected compound **4**. This compound was treated with *n*-butyllithium and trimethylborate to give compound **5** in a quasi-quantitative yield. It is important to avoid hydrolysis of boronic ester with acid, as commonly achieved to obtain boronic acid function, because of the great sensitivity of the trityl protecting group to acidic conditions. A Suzuki cross-coupling reaction using Pd(OAc)₂ and PPh₃ between compounds **3** and **5** provided 4,4'-bis(methyltrityloxy)-2-nitrobiphenyl (**6**) in good yield. A Cadogan ring closure reaction was carried out onto compound **6** leading to 2,7-bis(methyltrityloxy)carbazole (**7**). Compound **7** was substituted on the nitrogen atom with a branched or linear alkyl chain using common procedures to provide compounds **8** and **9**, respectively. It is important to note that a branched alkyl chain was used in the preparation of polymers to decrease π -stacking in the solid state and to increase their solubility in common organic solvents. On the other hand, a linear alkyl chain was used in case of oligomers to favor good intermolecular interactions. The trityl group was removed in a mixture of dichloromethane and methanol containing few drops of concentrated hydrochloric acid yielding *N*-alkyl-2,7-bis(hydroxymethyl)carbazole (compounds **10** and **11**). These compounds are the starting points for the syntheses of carbazole precursors, ultimately leading to 2,7-carbazolevinylene moieties.

First, compounds **10** and **11** can be transformed into dialdehyde moieties (compounds **12** and **13**) by oxidation with pyridinium chlorochromate (PCC) in dichloromethane in the presence of silica gel and molecular sieves. Dialdehyde compounds are very useful for the preparation of oligomers and polymers having vinylene units as they can be used in several types of reactions such as Wittig, Horner–Emmons, and Knoevenagel reactions. An aldehyde group can be transformed into a cyanomethyl group by treating compound **12** with tosylmethyl isocyanide in the presence of base in dry THF to give bis(cyanomethyl) derivative (**14**). The low yield of this reaction is due to the formation of several side-products leading to difficult purification. Many attempts to synthesize compound **14** from *N*-(2-ethylhexyl)-2,7-bis(chloromethyl)carbazole using a cyanide salt in polar solvents gave overall yields similar to those obtained when starting from dialdehyde derivatives. Compound **12** can also be transformed into 2,7-bis(vinylene)carbazole by a simple Wittig reaction using methylphosphonium bromide in the presence of NaH in anhydrous THF to give compound **19**. This compound allows the synthesis of oligomers and polymers having vinylene units by the Heck cross-coupling reaction in which common dibromoarylene compounds are used

instead of the more tedious dialdehyde compounds.

The hydroxymethyl groups of compounds **10** and **11** can also be transformed into chloromethyl groups by using thionyl chloride in toluene with a catalytic amount of pyridine to provide *N*-alkyl-2,7-bis(chloromethyl)carbazole (compounds **15** and **16**). The latter compounds seem to be moisture sensitive and must be used in the hours following their synthesis. Phosphonate derivatives (compounds **17** and **18**) can be obtained by treating compounds **15** and **16** with hot triethyl phosphite for several hours. These monomers are particularly suitable for subsequent Horner–Emmons reaction.

3.2 Synthesis of 2-Functionalized Monomers. The strategies used for the synthesis of monosubstituted carbazole units are more or less the same as those utilized for disubstituted derivatives (see Scheme 2). Once again, standard Pd-catalyzed reaction between compound **3** and phenylboronic acid gave 4-(methyltrityloxy)-2-nitrobiphenyl (**20**) in a good yield. Cadogan ring closure reaction was carried out on compound **20**, leading to 2-(methyltrityloxy)carbazole (**21**). *n*-Hexyl chain was added onto the nitrogen atom in the same manner used for the syntheses of compounds **8** and **9**, then the trityl group was removed in acidic media to yield compound **22**. In the case of all monosubstituted carbazole derivatives, only linear *n*-hexyl chain was introduced as these precursors have been designed for transistor applications. As described above, hydroxymethyl group can be oxidized leading to aldehyde (compound **23**) or replaced by a chloromethyl group (compound **24**) which can be treated with triethyl phosphite to give the phosphonate derivative (compound **25**).

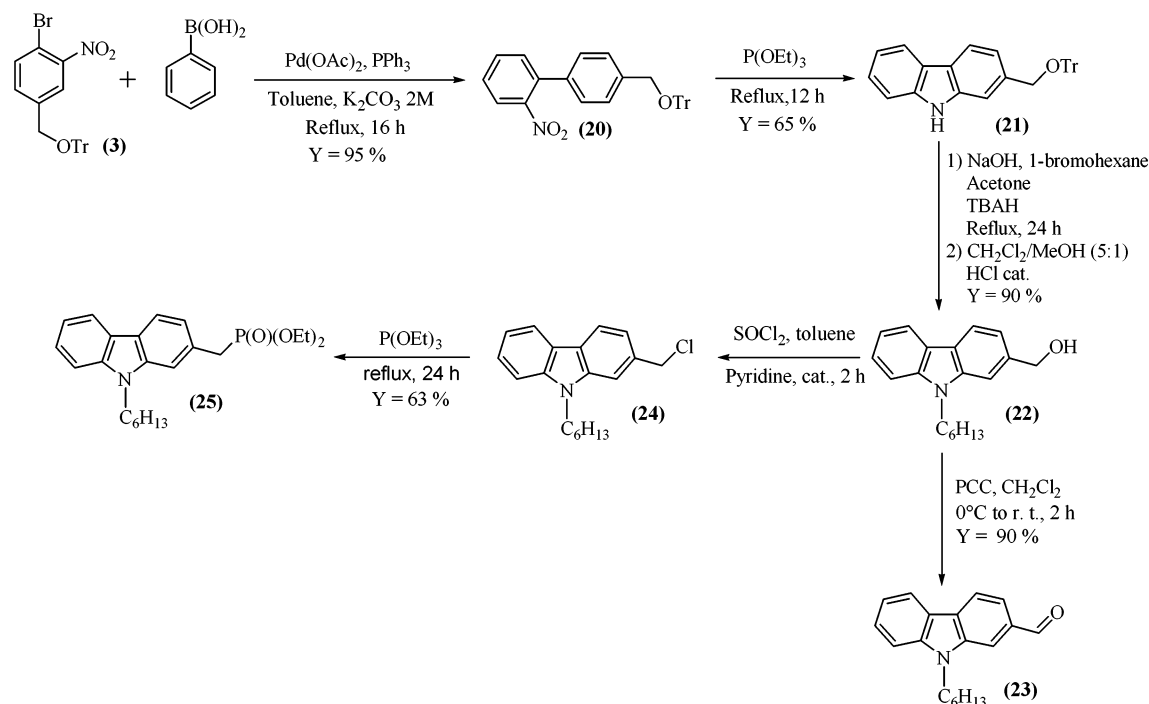
3.3 Synthesis of the Oligomers. Most of the 2,7-carbazolevinylene-containing oligomers were synthesized from Horner–Emmons reactions between dialdehyde and diphosphonate derivatives (Scheme 3). The Horner–Emmons coupling reaction seems to be the best way to synthesize well-defined oligomers and polymers because it provides strict regioselectivity and all-trans configuration,¹⁷ in contrast to the standard Wittig reaction (between dialdehyde and diphosphonium salt) which generally gives molecules having a mixture of *cis* and *trans* isomers.¹⁸ The synthesis of oligomers having well-defined structure is very important to maximize solid-state intermolecular interactions. Moreover, a Horner–Emmons reaction does not lead to side reactions such as incomplete eliminations during double bond formation or cross-linking leading to insoluble polymers with undesirable optical, electrical, and mechanical properties.¹⁷

The synthesis of PCP was achieved by the reaction of an excess of benzaldehyde reacting with compound **18** in the presence of an excess of potassium *tert*-butoxide in anhydrous THF at room temperature. In the same way, CCC, CTC, and CTTC were synthesized using an excess of compound **25** with compound **13**, 2,5-thiophenedicarboxaldehyde, and 5,5'-diformyl-2,2'-bithiophene (**26**), respectively. It is worth nothing that the

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Scheme 2. Synthesis of the 2-Functionalized Carbazoles



lower yield obtained for thiophene-containing oligomers can be attributed to their more difficult purification compared to that of other oligomers because they do not crystallize easily. CPC was synthesized using compound **23** and 1,4-bis(methylphosphonate)benzene. The use of aldehyde **23** is motivated by the easiest purification of the resulting CPC compared to CPC synthesized from *N*-hexyl-2-methylphosphonatecarbazole (**25**) and terephthalaldehyde. In fact, when compound **25** is used, the dimeric intermediate possesses an aldehyde group and tends to precipitate rapidly in the reaction mixture, decreasing the amount of the desired trimer and, consequently, making purification more difficult. For the synthesis of BPCBP, a Heck coupling reaction was carried out between compound **19** and 4-bromo-1,1'-biphenyl using palladium (II) acetate as catalyst with $P(o\text{-tolyl})_3$ as ligand and triethylamine as a base in anhydrous DMF at 110 °C. In this specific case, a carbazole unit having a branched chain was used to enhance solubility. Finally, a Knoevenagel coupling reaction was used to synthesize PCP-CN. The reaction did occur between an excess of phenylacetonitrile and compound **13** in the presence of a catalytic amount of potassium *tert*-butoxide in an anhydrous mixture of *tert*-butyl alcohol and THF.

3.4 Synthesis of the Polymers. As for the oligomers, polymers having 2,7-carbazolenevinylene units were synthesized from a Horner–Emmons reaction (Scheme 4). Many attempts were made to synthesize these polymers by standard Wittig reaction but the molecular weight of the resulting polymers was very low, probably due to a very fast precipitation of polymers in the chloroform/ethanol mixture. Tributyl phosphonium salt could be used instead of triphenyl phosphonium salt to improve solubility of monomers in chloroform and minimize the amount of ethanol in the reaction mixture.¹⁹ PCVP, PCVT, and PCVPA were synthesized following standard Horner–Emmons reaction using equimolar ratios of dialdehyde and compound **17** in the

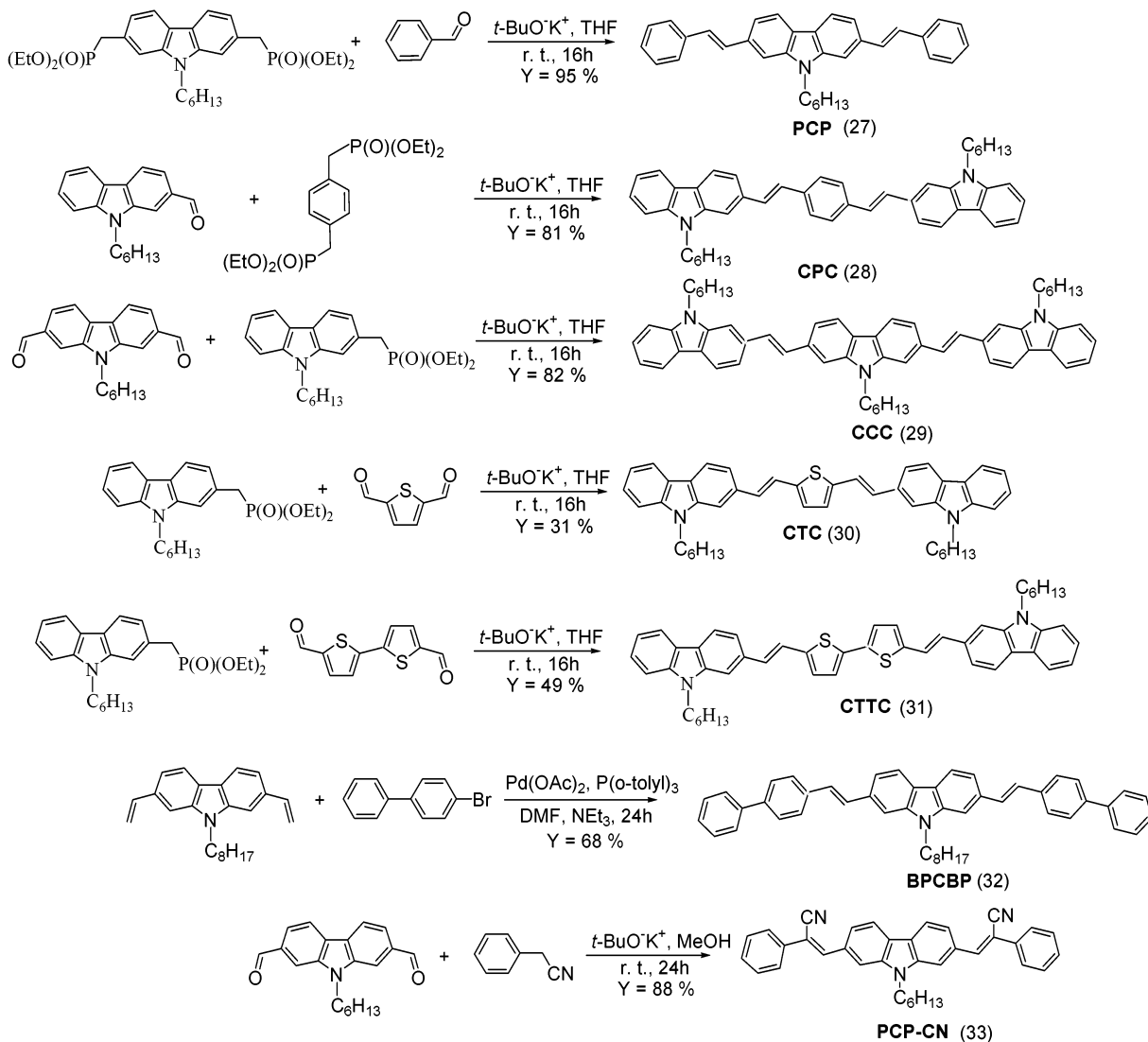
presence of an excess of potassium *tert*-butoxide in anhydrous THF. In the case of PCCVP, Knoevenagel reaction was carried out using compound **14** and 2,5-diethoxy-1,4-diformylbenzene in the presence of a catalytic amount of potassium *tert*-butoxide in an anhydrous mixture of *tert*-butyl alcohol and THF, at room temperature.

3.5 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 high degree of substitution of the comonomers. As observed for 2,7-carbazole-based polymers,^{8,9} utilization of comonomers with one or more alkyl side chains is necessary to obtain soluble 2,7-carbazolenevinylene-based polymers with high molecular weights. For example, only a very small fraction (presumably of low molecular weight) of the homopolymer (poly[(*N*-2-ethylhexyl)-2,7-carbazolenevinylene]) is soluble in hot chloroform (unpublished results). Many copolymers that contain unsubstituted comonomer unit were synthesized but none of them were soluble. Also, 2,7-carbazolene-(cyanovinylene)-containing polymers are generally more soluble in polar organic solvents. This behavior is not fully understood but can be reasonably attributed to the polar character of the cyanovinylene moiety. Other parameters, such as chain conformation, can also be responsible for this difference of solubility.

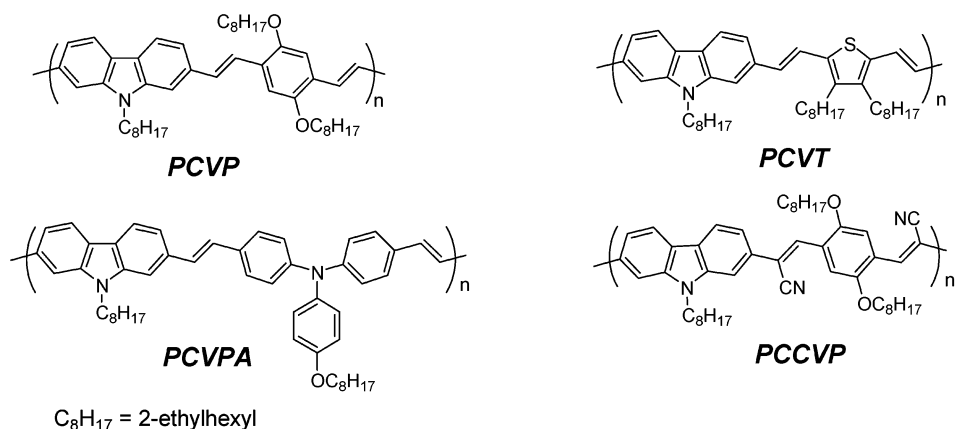
2,7-Carbazolenevinylene-based copolymers have moderate molecular weight (between 7 900 and 14 300 g/mol, see Table 1) and exhibit good film-forming properties. Moreover, they are amorphous with glass-transition temperatures between 60 °C for PCVT and 132 °C for PCVPA. Interestingly, the introduction of a cyano group onto the vinylene unit seems to induce some rigidity in the polymer backbone, as indicated by the higher glass transition temperature of PCCVP (72 °C)

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Scheme 3. Chemical Structure of the Oligomers



Scheme 4. Synthesis and Chemical Structure of the Polymers



compared to that of PCVP (61 °C). This difference could be greater because the molecular weight of PCCVP is half of that of PCVP.

3.6 Optical Properties. UV–visible absorption and photoluminescence properties of 2,7-carbazolenevinylene-based polymers are presented in Table 2. As expected, the introduction of vinylene and cyanovinylene bound into the backbone leads to relatively low band gaps.

Moreover, the incorporation of an electron-rich unit, such as thiophene, instead of a phenylene moiety significantly decreases the band gap (see the difference between band gaps of PCVP and PCVT in Table 2). Moreover, the addition of cyano group onto the vinylene bond induces a bathochromic shift in the absorption spectrum as shown by the difference in the maximum of absorption (29 nm) between PCVP and PCCVP. This

Table 1. Polymerization Yields, Molecular Weights, and Thermal Properties of the Polymers

polymer	yield (%)	M_n (kg/mol)	M_w/M_n	T_g (°C)
PCVP	61	14.3	3.2	61
PCVT	72	10.5	3.2	60
PCVPA	52	13.4	3.4	132
PCCVP	68	7.9	4.5	72

Table 2. Optical Properties of the Polymers

polymer	solution λ_{\max} (nm) ^a		thin film λ_{\max} (nm)		Φ_F	E_g (eV) ^c
	abs.	emi.	abs.	emi. ^b		
PCVP	455	508 (538)	469		0.40	2.37
PCVT	485	581 (547)	497		0.16	2.15
PCVPA	450	487	460		0.31	2.38
PCCVP	484	552 (582)	505	656 (701)	0.67	2.20

^a Measurements performed in CHCl_3 . ^b Only PCCVP shows fluorescence in the solid state. ^c E_g values were determined from UV-visible absorption spectra in the solid state.

Table 3. Optical and Electrochemical Properties of the Carbazolevinylene-Based Oligomers

oligomer	λ_{\max} sol.	$E_{\text{peak ox}}$ ($E_{\text{onset ox}}$) V vs SCE	$\pi-\pi^*$ transition (eV)
PCP	376	1.26 (1.09)	2.92
CPC	395	1.04 (0.80)	2.80
CCC	402	1.03 (0.91)	2.73
CTC	433	0.97 (0.83)	2.53
CTTC	453	0.92, 1.12 (0.81)	2.36
BPCBP	392	1.24 (1.03)	2.78
PCP-CN	399	1.58 (1.41)	2.63

shift can be attributed to the presence of an intramolecular donor-acceptor phenomenon between the cyanovinylene unit, an electron-withdrawing group, and the carbazole moiety, an electron-rich unit, which decreases the $\pi-\pi^*$ energy gap. Solid-state absorption spectra are only slightly bathochromically shifted compared to those of solution which seems to indicate that 2,7-carbazolevinylene-based polymers exhibit very similar conformation in both states. Photoluminescence of these polymers shows a green to yellow emission with maximum of emission varying from 487 to 581 nm, in solution. The large Stokes shift observed for many of those polymers may indicate that conformations of the polymer main chain are different from ground state (more twisted) to excited state (coplanar). Interestingly, only PCCVP shows measurable photoluminescence in the solid state with a maximum at 656 nm. The quenching behavior observed in the solid state may be attributed to a coplanar conformation which favors strong interchain interactions which are known to enhance nonradiative deactivation pathways.²⁰ The introduction of a cyano group on the vinylene bond can induce steric interactions into the polymer main chain leading to a more twisted conformation, reducing thereby the $\pi-\pi$ stacking in the solid state.

Absorption spectra of oligomers in chloroform solution were also recorded and the results are summarized in Table 3. As typically observed for conjugated molecules, the maximum of absorption of oligomers are bathochromically shifted when the conjugation length increases. As an example, BPCBP shows a maximum of absorption at 392 nm whereas PCP exhibits an absorption maxi-

Table 4. Electrochemical Properties of the Carbazolevinylene-Based Polymers

polymer	$E_{\text{peak ox}}$ ($E_{\text{onset ox}}$) V vs SCE	$E_{\text{peak red}}$ ($E_{\text{onset red}}$) V vs SCE	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^a (eV)
PCVP	0.71 (0.63)	-1.94 (-1.70)	5.03	2.70	2.33
PCVT	0.64 (0.56)	-1.84 (-1.57)	4.96	2.83	2.13
PCVPA	0.71 (0.59)	-2.14 (-1.77)	4.99	2.63	2.36
PCCVP	1.33 (1.15)	-1.29 (-1.08)	5.55	3.32	2.23

^a Band-gap measured from cathodic and anodic peak onset.

mum at 376 nm. As observed with the polymers, addition of a cyano group onto the vinylene unit induces a red shift of the absorption spectrum, as revealed by the difference of 23 nm in the absorption maximum between PCP and PCP-CN. This red shift can be attributed to the presence of an intramolecular charge-transfer complex between carbazole and the cyano group.

3.7 Electrochemical Properties. The electrochemical properties of these processable 2,7-carbazolevinylene-based conjugated polymers are summarized in Table 4. All polymers present a partially reversible oxidation process around 0.70 V vs SCE, except for PCCVP which exhibits an oxidation peak potential (E_{ox}) of 1.33 V vs SCE. This behavior can be explained by the presence in the polymer backbone of an electron-withdrawing cyano group which is known to increase the oxidation potential. In the reduction process, only PCCVP shows some (partial) reversibility. Moreover, the reduction peak potential (E_{red}) of this polymer is significantly higher ($E_{\text{red}} = -1.29$ V vs SCE) than all others, probably due to its high electron affinity as observed for cyano-MEH-PPV.²¹ A good approximation for ionization potential (HOMO) and electron affinity (LUMO) of polymers can be calculated from electrochemical measurements using the method reported by Brédas and co-workers.²² Polymers having vinylene units (PCVP, PCVT, and PCVPA) exhibit HOMO energy levels between 4.96 and 5.03 eV, which is close to that of the ITO anode (~ 4.7 eV) used in light-emitting diodes and photovoltaic cells, whereas LUMO energy levels are between 2.63 and 2.83 eV. Interestingly, band gaps calculated from electrochemical data are in excellent agreement with those calculated from optical measurements.

Electrochemical properties of oligomers are summarized in Table 3. All oligomers show a partially reversible oxidation process between 0.92 and 1.26 V vs SCE. The oxidation potential of oligomers decreases as conjugation length increases, as generally observed with π -conjugated molecules. For example, CTTC exhibits an oxidation potential of 0.92 V vs SCE, which is 50 mV lower than that of CTC. Interestingly, CTTC shows two distinct oxidation processes which can be reasonably associated with 2,7-carbazolevinylene segment and bithiophene unit.

3.8 Polymeric Light-Emitting Devices. The electroluminescence (EL) properties of PCCVP were examined in a simple device configuration (ITO/PEDOT-PSS/PCCVP/LiF/Al/Ag), where PEDOT-PSS was used as the

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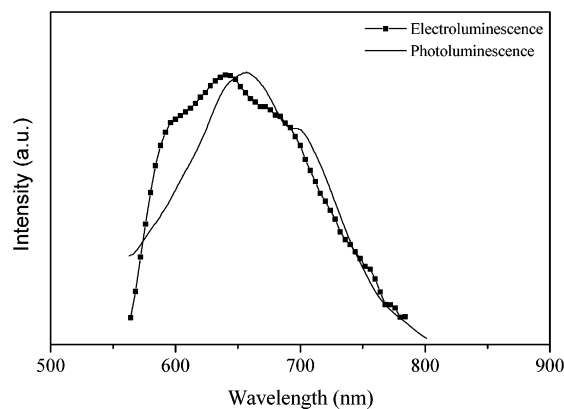


Figure 1. Normalized PL and EL spectra of PCCVP in solid state.

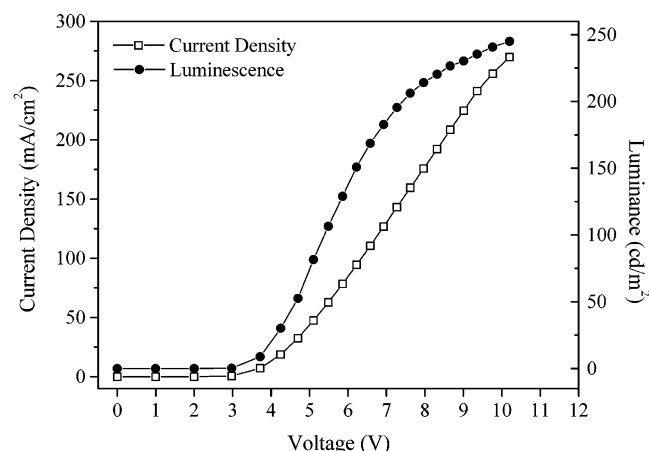


Figure 2. Current density–voltage–luminescence (I – V – L) characteristics of ITO/PEDOT-PSS/PCCVP/LiF/Al/Ag device.

hole-injecting layer, and LiF/Al served as the electron-injecting electrode. A typical EL spectrum from this device is shown in Figure 1 along with its photoluminescence spectrum. The relatively low band gap of 2,7-carbazolenevinylene polymeric materials allows PCCVP to emit light into the orange-red region with a maximum of emission at 640 nm (C. I. E. coordinates: $u' = 0.40$ and $v' = 0.54$). When compared with PL maximum, the EL maximum of the resulting device is blue-shifted by about 15 nm. The EL spectrum of PCCVP shows an additional shoulder around 590 nm. The I – V – L characteristics of this device are shown in Figure 2. The current increases with increasing forward bias, according to typical diode behavior. In this device configuration, the maximum luminescence value obtained is 245 cd/m^2 at 10 V. The light emission starts at 3 V, which is a relatively low turn-on voltage. An efficiency of 0.17 cd/A has been reached at 5 V. It should be noted here that the efficiency decreases by adding a thin layer of hole-blocking materials, such as Bu-PBD, between the emitting material and LiF/Al cathode. These preliminary results lead us to believe that holes and electrons are relatively well transported in PCCVP, probably due to the bipolar properties of this polymer.

3.9 Organic Field-Effect Transistors. The typical I_{DS} (source-drain current) vs V_{DS} (source-drain voltage) for different V_{G} (gate voltage) having CPC as the semiconductor material is reported in Figure 3. The schematic cross-sectional view of the fabricated device is also shown in the inset of Figure 3. This graph shows

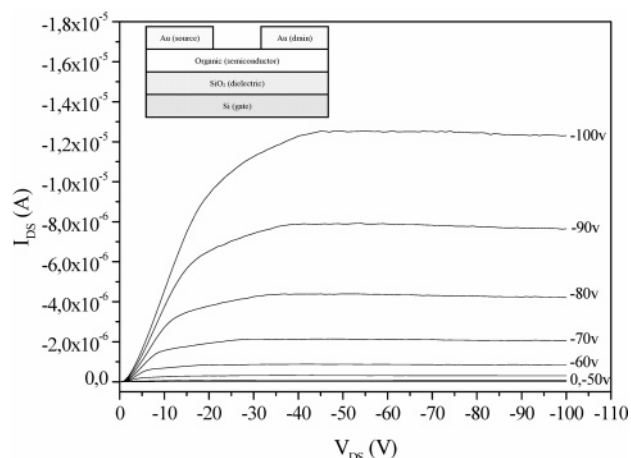


Figure 3. Source-drain current (I_{DS}) versus source-drain voltage (V_{DS}) at various gate voltages (V_{G}) from a top-contact geometry OFET using 2,7-carbazolenevinylene oligomer CPC as semiconductor material evaporated at a substrate temperature of 195 °C on a HMDS-treated surface.

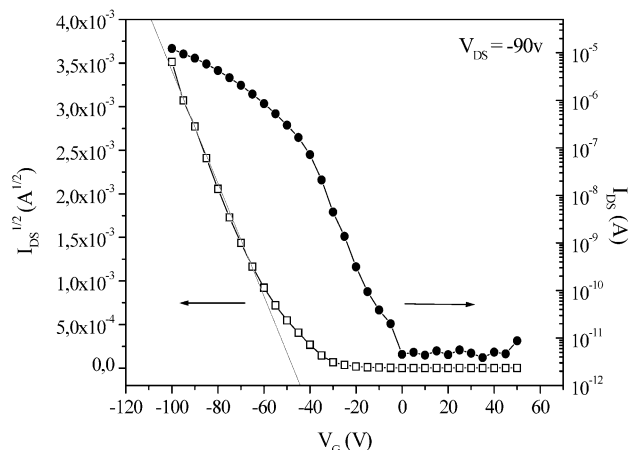


Figure 4. Plot of $I_{\text{DS}}^{1/2}$ vs V_{G} and semilogarithmic plot of I_{DS} vs V_{G} OFET using 2,7-carbazolenevinylene oligomer CPC as semiconductor material evaporated at a substrate temperature of 195 °C on a HMDS-treated surface.

that 2,7-carbazolenevinylene oligomers form a typical p-channel transistor operating in two different modes. The so-called linear regime where the current follows Ohm's law drives the device at low source-drain voltage and can be described by eq 1. As the source-drain voltage increases, the device enters into the so-called saturation regime, which can be described by eq 2.

$$I_{\text{DS}} = \left(\frac{W}{L}\right) \mu C_i (V_{\text{G}} - V_{\text{T}}) V_{\text{DS}} \quad (1)$$

$$I_{\text{DS}} = \left(\frac{W}{2L}\right) \mu C_i (V_{\text{G}} - V_{\text{T}})^2 \quad (2)$$

Here, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the SiO_2 layer (5.68 nF/cm^2), V_{G} is the gate voltage, V_{T} is the threshold voltage, and V_{DS} is the source-drain voltage. On the basis of the experimental data, the field-effect mobility, μ , was calculated into the saturation regime at $V_{\text{DS}} = -90$ V (eq 2) using the slope of a plot of $I_{\text{DS}}^{1/2}$ vs V_{G} , which is equal to the square root of $W\mu C_i/(2L)$. Figure 4 shows a graph that contains a plot of $I_{\text{DS}}^{1/2}$ vs V_{G} and a semilogarithmic plot of I_{DS} vs V_{G} , from which the

Table 5. Characteristics of 2,7-Carbazolenevinylene Oligomeric Semiconductors Used in This Study^a

compound	mobility (cm ² /V·s)	$I_{\text{on}}/I_{\text{off}}$	V_t (V)
CPC ^b	2.2×10^{-4} (3.5×10^{-3} at 195 °C)	10^4 (10^5)	-55 (-23)
CPC ^c	8.4×10^{-4} (3.7×10^{-2} at 195 °C)	10^4 (10^6)	-50 (-46)
BPCBP ^b	1.8×10^{-7} (2.6×10^{-6} at 100 °C)	10^2 (10^2)	-13 (-30)
BPCBP ^c	1.4×10^{-6} (6.6×10^{-6} at 100 °C)	10^2 (10^3)	-28 (-22)

^a Values in parentheses were obtained on films deposited at 100–200 °C. ^b Plain substrate. ^c HMDS-treated substrate.

threshold voltage can be found by extrapolating the curve to $V_G = 0$. Table 5 lists mobilities, $I_{\text{on}}/I_{\text{off}}$ ratios, and threshold voltages for CPC and BPCBP oligomers. Depending on the chemical structure, the oligomeric 2,7-carbazolenevinylene derivatives show relatively low hole mobilities ranging from 10^{-4} to 10^{-7} cm²/V·s and relatively low $I_{\text{on}}/I_{\text{off}}$ ratios ranging from 100 to 10 000 when oligomers are evaporated at a substrate temperature of 25 °C. Under these conditions, the threshold voltages are approximatively -50 and -28 V for CPC and BPCBP, respectively. The performances are well improved for these two compounds when the surface is treated with HMDS prior to oligomer evaporation and/or when the substrate is heated to 100–200 °C during oligomer deposition. The best performance has been obtained with CPC evaporated on an HMDS-treated surface and on a substrate temperature of 195 °C, which shows a high mobility of 3.7×10^{-2} cm²/V·s and a very high $I_{\text{on}}/I_{\text{off}}$ ratio of 10^6 , 1 order of magnitude higher than those obtained for sexithiophene derivatives in optimized device configuration.²³ This high value of $I_{\text{on}}/I_{\text{off}}$ ratio can be attributed in part to the relatively high oxidation potential of CPC (1.04 V vs SCE), making this oligomer relatively insensitive to oxidation upon exposure to oxygen, meaning that few residual charges are present in material when $V_G = 0$ compared to 6T which is prone to atmospheric doping.²⁴ The higher mobility of CPC can be attributed to their relative coplanar structure as compared to BPCBP that possess a twisted 1,1'-biphenyl unit (dihedral angle $\sim 44^\circ$)²⁵ which could prevent molecules from forming well-organized film through π - π interactions. Considering the organization

is an important parameter for high mobility in organic materials, it is not surprising that BPCBP gives lower mobilities.

4. Conclusions

This study reports the first syntheses and characterization of electroactive and photoactive 2,7-carbazolenevinylene-based oligomers and polymers. The introduction of vinylene unit at positions 2 and 7 of the carbazole moiety has allowed the formation of relatively low-band-gap materials. Using Horner–Emmons and Knoevenagel reactions, well-defined oligomers and polymers can be obtained. These types of cross-coupling reactions are particularly suitable for electronic applications compared to palladium-catalyzed cross-coupling reactions because they do not require metallic catalysts which can lead to metallic residues that may alter the device performances. Moreover, poly(*N*-(2-ethylhexyl)-2,7-carbazolenevinylene-*alt*-2,5-diethoxy-1,4-phenylenevinylene) (PCCVP) has shown interesting performances in light-emitting devices with relatively balanced hole and electron transport properties, whereas 1,4-bis(vinylene-(*N*-hexyl-2-carbazole))phenylene CPC has demonstrated a very high mobility of 3.7×10^{-2} cm²/V·s and an $I_{\text{on}}/I_{\text{off}}$ ratio of 10^6 when used as a *p*-type semiconducting material in field-effect transistors. From these preliminary results, it is firmly believed that device performances can be improved by using more adapted device configurations. Future work will focus on these issues and on a better understanding of device performances versus film morphologies for applications in *plastic* electronics.

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Supporting Information Available: Details of syntheses, characterization, and device fabrication and testing (pdf). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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