

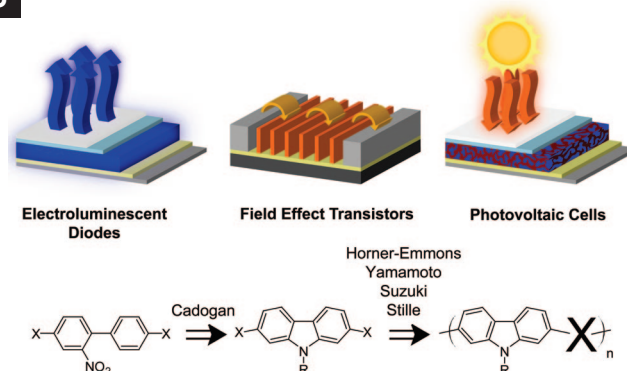
Poly(2,7-carbazole)s: Structure–Property Relationships

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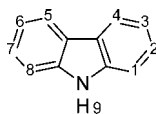
Conjugated polymers combine the interesting optical and electrical properties of metals with the processing advantages and mechanical properties of traditional synthetic polymers. With clever use of a variety of synthetic tools, researchers have prepared highly pure polymers with optimized physical properties during the past 30 years. For example, the synthesis of well-defined polyacetylenes, polyphenylenes, polythiophenes, polyfluorenes, and other conjugated polymers have significantly improved the performance of these polymeric materials. However, one important class of conjugated polymers was missing from this chemical inventory: easy access to well-defined poly(2,7-carbazole)s and related polymers. This Account highlights advances in the synthesis of poly(2,7-carbazole) derivatives since they were first reported in 2001.

Starting from 2-nitro-biphenyl derivatives, 2,7-functionalized carbazoles are typically obtained from Cadogan ring-closure reactions. In a second step, Yamamoto, Stille, Suzuki, or Horner–Emmons coupling polymerization leads to various poly(2,7-carbazole) derivatives. We discuss the characterization of their optical and electrical properties with a strong emphasis on the structure–property relationships. In addition, we carefully evaluate these polymers as active components in light-emitting diodes, transistors, and photovoltaic cells. In particular, several low band gap poly(2,7-carbazole) derivatives have revealed highly promising features for solar cell applications with hole mobilities of about $3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and power conversion efficiencies up to 4.8%. Finally, we show how these new synthetic strategies have led to the preparation of novel poly(heterofluorene) derivatives and ladder-type conjugated polymers.

Introduction

For many years, carbazole-based materials have been investigated for their electrical and optical properties. For instance, as good photoconductors and hole-transporting materials, poly(*N*-vinylcarbazole) and other derivatives have been extensively utilized in xerographic applications.¹ In 1977, the first evidence of high electrical conductivity in doped polyacetylene^{2,3} triggered a sec-

ond life for polycarbazole derivatives. As were many other aromatic polymers (polyanilines, poly(*p*-phenylene)s, polythiophenes, polypyrroles, poly(2,7-fluorene)s, etc.), poly(3,6-carbazole)s were intensively investigated.^{1,4} Indeed, carbazole has many advantages as an organic material: (1) 9*H*-carbazole (Scheme 1) is a cheap starting material; (2) the nitrogen atom can be easily functionalized with a large variety of substituents to

SCHEME 1. Carbazole Structure and Numeration

modulate the carbazole properties without increasing the steric interactions near the backbone; (3) carbazole units can be linked at different positions; (4) its fully aromatic configuration provides good chemical and environmental stabilities. Despite these promising features, conjugated poly(2,7-carbazole)s remained unavailable for a long time. This is related to the fact that, in contrast to many other conjugated polymers (including poly(3,6-carbazole) derivatives), the synthesis of poly(2,7-carbazole)s is not straightforward.^{1,4} For instance, direct oxidative polymerization or electropolymerization of carbazoles only results in oligomeric materials linked at the 3,6-positions. Alternative synthetic pathways have since been found to prepare well-defined poly(2,7-carbazole) derivatives. This Account describes these recent developments on the synthesis of poly(2,7-carbazole)s and related polymers, their structure–property relationships, and their utilization in various electronic and optical devices, such as polymeric light-emitting diodes (PLEDs), organic field-effect transistors (OFETs), and photovoltaic cells (PCs). It is anticipated that this class of materials might lead to exciting applications in the near future.

Synthesis of Poly(2,7-carbazole)s

As mentioned in the preceding, the 3,6- (para position from the nitrogen atom, Scheme 1) and 1,8-positions (ortho position from the nitrogen atom, Scheme 1) on the carbazole unit are highly activated. The electron-rich nature of carbazole therefore inhibits direct and specific aromatic substitution at the 2,7-positions. Therefore, 2,7-functionalized carbazoles have been obtained from indirect approaches. These methodologies usually require a 4,4'-functionalized biphenyl unit bearing an activated group at the 2(-2') position(s) for a subsequent ring-closing reaction, leading then to the desired 2,7-functionalized carbazoles (Scheme 2). This principle was first illustrated by Smith and Brown in 1951.⁵ Using azide derivatives, they converted them into carbazoles by a thermal cyclization reaction. A more practical methodology was reported in 1953 by Heinrich⁶ where 2,7-functionalized carbazoles are directly obtained from 2,2'-diamino-biphenyls under acidic conditions at high temperatures. In 1965, Cadogan reported what is still today a very useful ring-closure reaction for the preparation of functionalized carbazoles.^{7,8} From 2-nitro-biphenyl derivatives refluxed in P(OEt)₃, 2,7-functionalized carbazoles can be obtained in

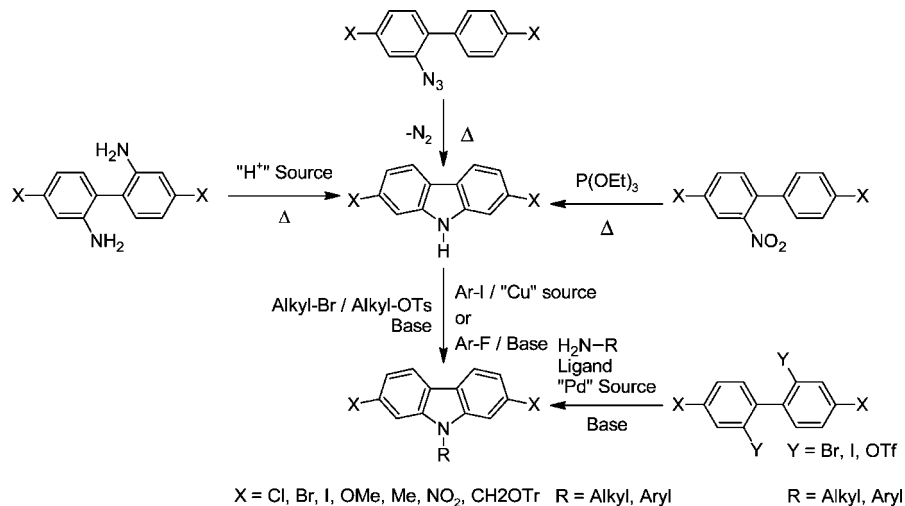
50–60% yields, usually in only two or three steps from commercially available starting compounds.^{9,10} To enhance the solubility and other properties of the resulting 2,7-functionalized carbazoles (and subsequent polymers), the synthesis is generally completed with an alkylation or arylation reaction on the nitrogen atom. Recently, novel methodologies^{11–13} have taken advantage of palladium cross-coupling reactions developed by Buchwald and Hartwig (Scheme 2). These methods offer two main advantages: (1) milder reaction conditions tolerant to a wider variety of functional groups and (2) 2,7-functionalized carbazoles directly obtained in an N-alkylated or N-arylated form. However, the scope of these methods is limited by the additional steps required to prepare the 2,2'-difunctionalized (iodide, bromide, or triflate) biphenyl precursors.

As for many other aromatic conjugated polymers, advances in metal-catalyzed polycondensation in the 1990s made possible the first synthesis of poly(2,7-carbazole)s.⁹ For such polymerization reactions, the syntheses of various monomers (2,7-dichloro-,⁹ 2,7-ditriflate-,¹⁴ and 2,7-dibromocarbazole¹⁰) using the previously described Cadogan reaction have been optimized. Indeed, using Yamamoto,^{15,16} Stille,^{17,18} or Suzuki^{19,20} coupling polymerization, 2,7-difunctionalized carbazoles are efficiently converted into well-defined poly(2,7-carbazole)s (Scheme 3). Taking advantage of either Yamamoto^{15,16} or Stille^{17,18} coupling polymerization, these monomers generated several interesting homopolymers and copolymers. However, it is important to note that Yamamoto copolymerization is restricted to random copolymers, whereas Stille copolymerization is limited by the difficult synthesis of pure organotin derivatives. Suzuki^{19,20} polycondensation solved these two important issues. Based on methodologies reported for the synthesis of poly(2,7-fluorene)s,^{21–24} efficient syntheses of 2,7-diboronic ester derivatives (Scheme 3) were developed from halogen-lithium exchange and palladium-catalyzed borylation.^{14,25,26} These 2,7-diboronic ester derivatives are generally easily purified from recrystallization or flash chromatography, resulting in high purity monomers. Combined with any dibromo- or diiodoarene, these key 2,7-diboronic ester derivatives lead to various alternating and random copolymers.

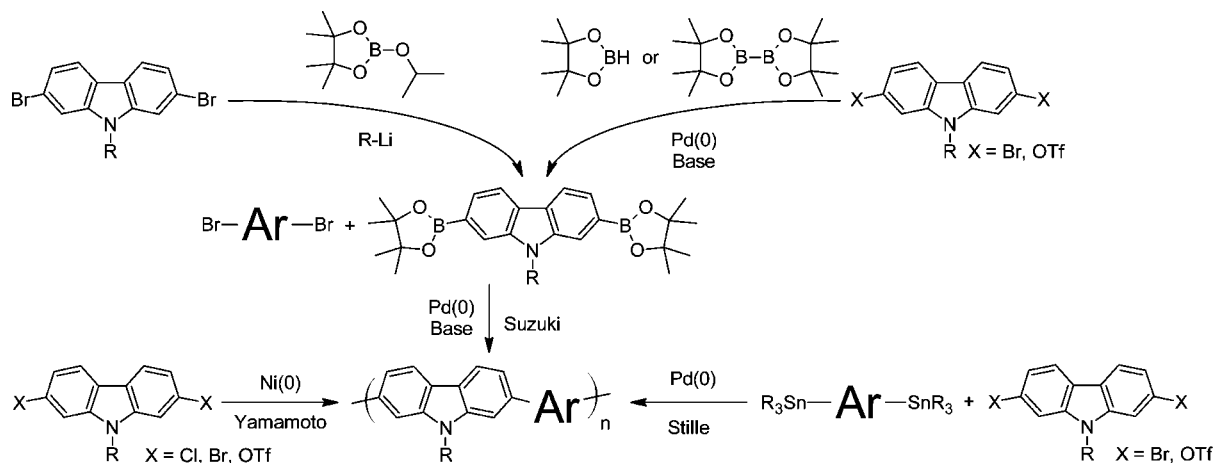
Poly(2,7-carbazole)s as PLED Materials

Initial studies on poly(2,7-carbazole) derivatives indicated great potential as blue-light-emitting materials. For instance, homopolymers exhibit blue fluorescence with a maximum of emission near 415–440 nm with relatively high quantum yields.^{9,27} Taking advantage of the chemical versatil-

SCHEME 2. Generic Synthetic Pathways to 2,7-Functionalized Carbazoles



SCHEME 3. Generic Synthetic Pathways to Poly(2,7-carbazole) Derivatives



ity of the carbazole unit, many poly(2,7-carbazole) derivatives were specifically developed to maximize their electroluminescence properties. Two main solutions have been explored (Scheme 4): substitution at the nitrogen atom with various alkyl^{9,27–30} or aryl^{30–34} groups or copolymerization^{35,36} with specifically designed comonomers. These poly(2,7-carbazole) derivatives are generally synthesized from Suzuki^{19,20} or Yamamoto^{15,16} coupling polymerization with number-average molecular weights (M_n) ranging from 2 kDa up to 93 kDa. Over the years, several important conclusions have been drawn from these optimization processes. Large bulky alkyl chains (especially **P1-C**,³⁰ **P1-E**,²⁷ **P1-F**²⁹) or aryl groups bearing multiple alkyl chains (**P1-G** to **P1-J**)^{30–34} on the carbazole nitrogen atom seem to be necessary to increase the polymer's solubility and molecular weight (M_n between 30–93 kDa). Copolymerization with substituted comonomers (**P2**, **P3**) gave similar effects. Finally, *N*-aryl-substituted poly(2,7-car-

bazole)s generally show higher fluorescence quantum yields in the solid state (up to 0.40).^{33,34}

Several poly(2,7-carbazole) derivatives (**P1-D**,^{37,38} **P1-H**,^{33,34,39} **P1-I**,³⁹ and **P3**³⁸) have been more extensively studied for blue PLED applications. Their properties are summarized in Table 1. Even after some optimization, the overall performances of these poly(2,7-carbazole) derivatives in PLEDs remain modest. Some polymers (**P1-D**, **P1-I**, **P3**) show proper CIE coordinates but moderate efficiencies. Other polymers^{33,34,39} (**P1-H**) may exhibit better luminance ($B_{\max} = 18\,800 \text{ cd} \cdot \text{m}^{-2}$; $E = 0.95 \text{ cd} \cdot \text{A}^{-1}$) but slowly turns greenish afterward (CIE (x, y) = 0.22, 0.36). In fact, PLEDs made of poly(2,7-carbazole)s generally suffer from improper balance of charge injection and charge transport (p-type transport being favored), limiting the overall device performances. In parallel, to improve poly(2,7-carbazole) stability,¹⁴ protection of the 3,6-positions^{40,41} with methyl or nitrile groups (**P1-Me**, **P1-CN**, **P4**) have been proposed.

SCHEME 4. Synthetic Pathways to Blue-Light-Emitting Poly(2,7-carbazole) Derivatives

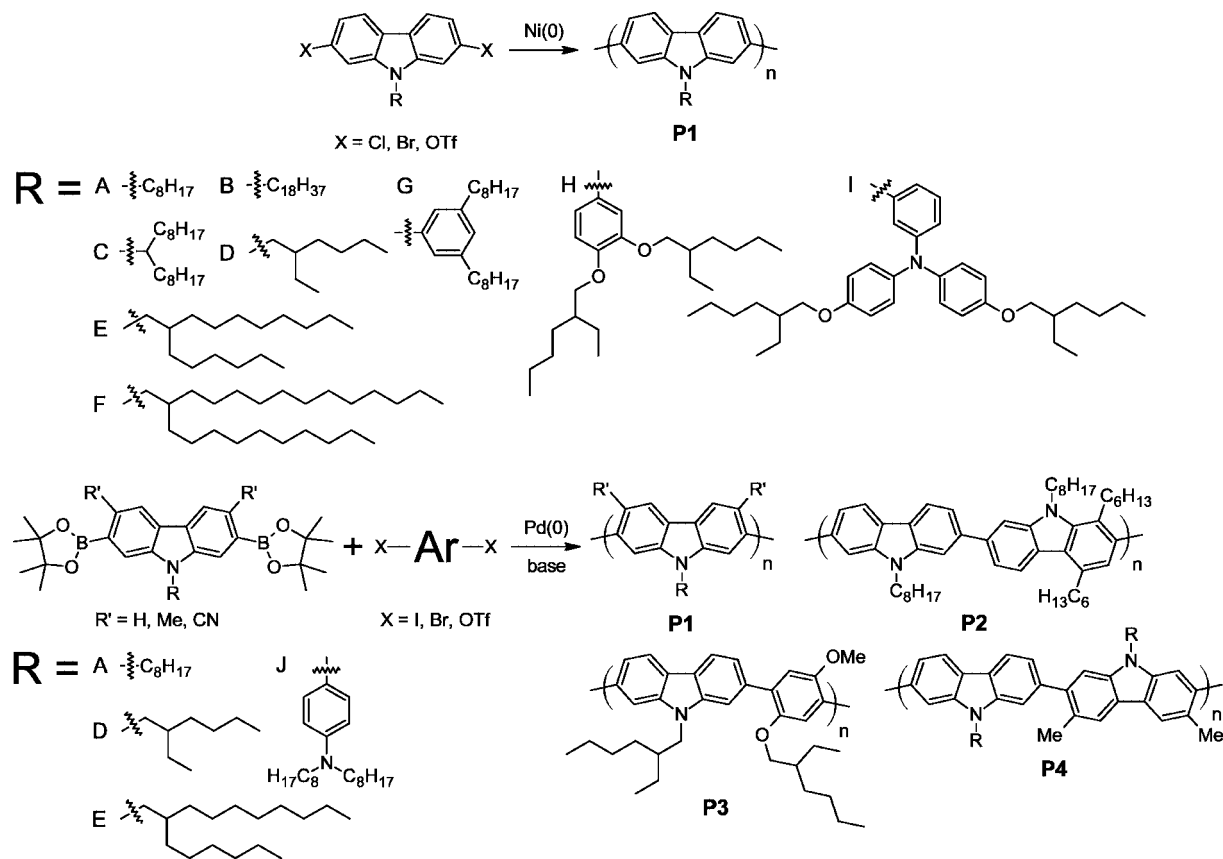


TABLE 1. Electroluminescent Properties of Blue-Light-Emitting Poly(2,7-carbazole) Derivatives

polymer	ϕ_{F}^a %	λ_{PL}^b nm	λ_{EL}^c nm	V_{ON}^d V	B_{max}^e $\text{cd} \cdot \text{m}^{-2}$	E_{max}^f $\text{cd} \cdot \text{A}^{-1}$	CIE ^g (x, y)
P1-D	26	448	440	4	1000	0.67	0.17, 0.19
P1-H	40	455	484	3	5000	0.57	0.17, 0.14
P1-I	32	450	450	4	4000	0.74	0.16, 0.17
P3	32	425	424	4	1500	0.53	0.16, 0.09

^a Fluorescence quantum yields in the solid state. ^b Maximum photoluminescence wavelength. ^c Maximum electroluminescence wavelength. ^d Turn-on voltage. ^e Maximum brightness. ^f Maximum efficiency. ^g CIE coordinates according to 1931 chart.

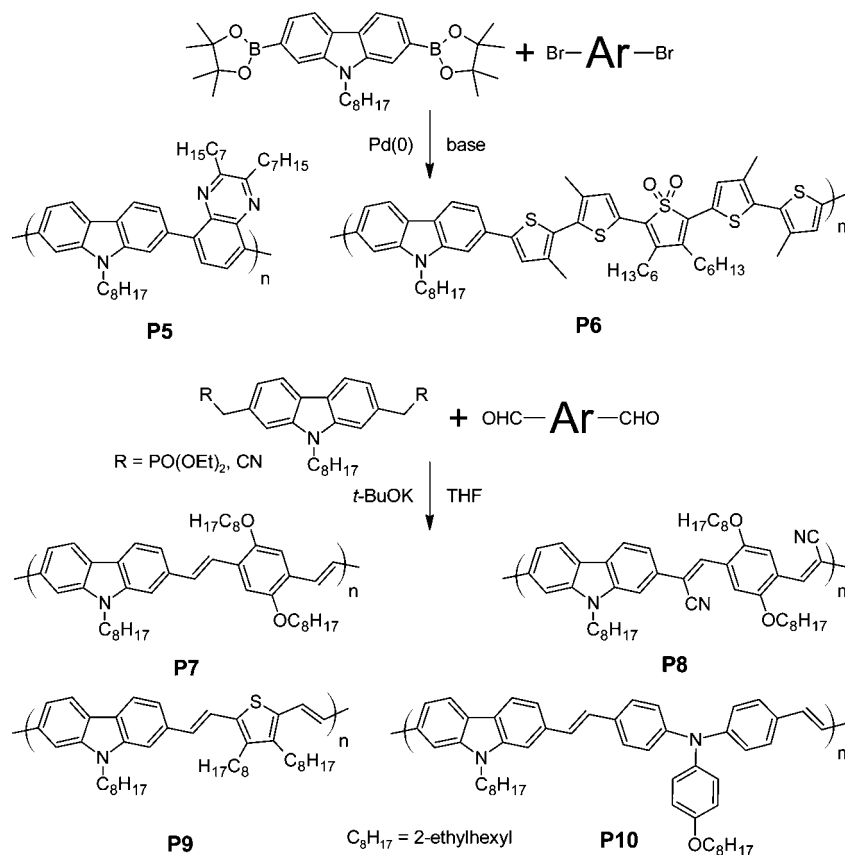
To complete a full color display, green- and red-light-emitting materials are also required. Usually, copolymerization with electron-deficient comonomers generates an internal charge transfer (ICT)^{42,43} that results in low band gap poly(2,7-carbazole) derivatives (Scheme 5). Along these lines, quinoxaline comonomer (**P5**)²⁸ led to green-light-emitting polymer, whereas copolymerization with thiophene dioxide-based pentamer (**P6**)²⁸ gave a red-light-emitting polymer. Alternatively, low band gap poly(2,7-carbazole) derivatives can also be obtained by the introduction of vinylene units along the backbone (Scheme 5).⁴⁴ Being prepared from Horner–Emmons or Knoevenagel reaction, these polymers are metal-free, a good criteria for microelectronic applications.⁴⁵ In solution, luminescence with maxima between 487 and 581 nm is observed for these poly(2,7-carbazolenevinylene)⁴⁴ derivatives. How-

ever, only **P8** shows some luminescence in the solid state. Strong interchain interactions may enhance nonradiative deactivation pathways for the other polymers, prohibiting the fabrication of efficient PLEDs.

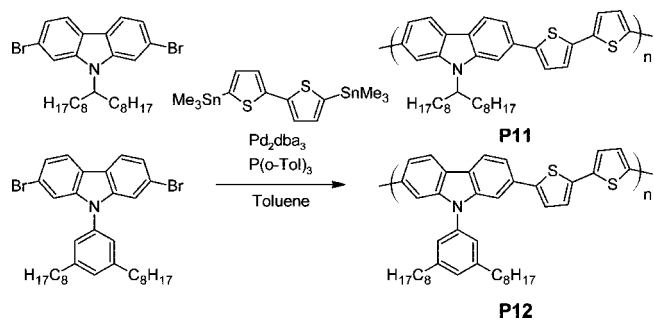
Poly(2,7-carbazole)s as OFET Materials

Two major conclusions from these PLED studies motivated the development of carbazole-based materials for OFET applications: (1) the carbazole moiety is a good hole transport unit; (2) with an appropriate structure, carbazole-based materials may have strong intermolecular interactions in the solid state. Excluding polythiophene derivatives^{46–48} and poly(2,7-fluorene) derivatives,^{48,49} few other classes of polymers exhibit good performance in OFETs. To mimic fluorene's structure,^{50,51} a branched side chain was designed and placed on

SCHEME 5. Synthetic Pathways to Low Band Gap Poly(2,7-carbazole) Derivatives for Light-Emitting Diodes

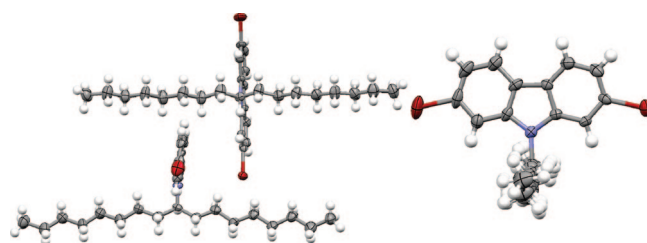


SCHEME 6. Synthetic Pathways to Poly(2,7-carbazole) Derivatives for Field-Effect Transistors

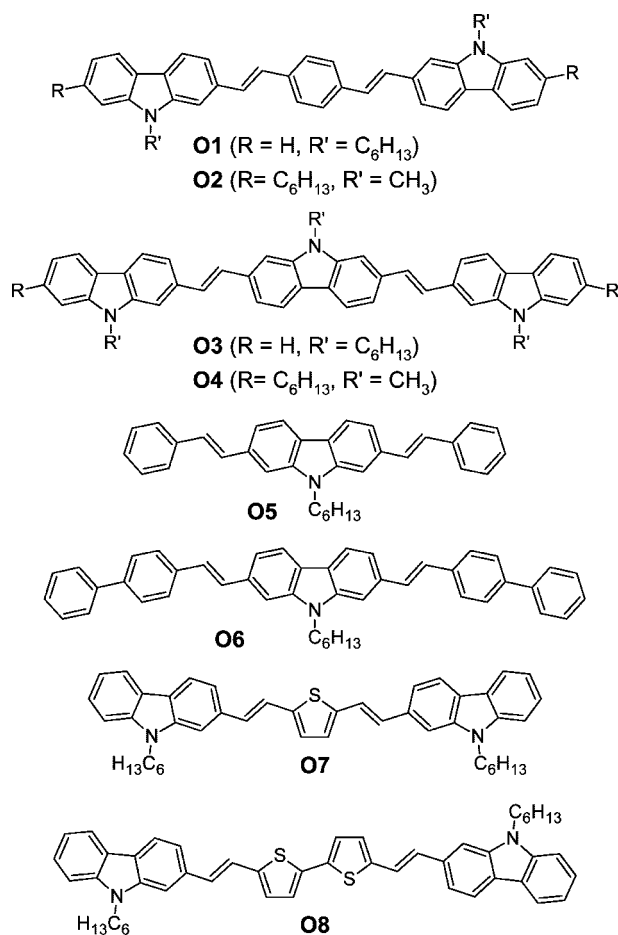


the carbazole nitrogen atom³⁰ (Scheme 6). X-ray analyses of single-crystal of *N*-9'-heptadecanyl-2,7-dibromocarbazole (Figure 1) clearly confirm this analogous structure. To ensure relatively high molecular weight materials (M_n ca. 20 kDa), optimized Stille copolymerization reactions were developed (Scheme 6). Despite some structural organization (as revealed from DSC and X-ray diffraction data), **P11** and **P12** exhibit modest hole mobilities (10^{-4} – 10^{-3} $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) in OFET devices. However, these polymers show stable performance, attributed to good air stability.³⁰

Oligomeric materials generally present better structural organization than their polymeric analogs.^{52,53} Based on this

FIGURE 1. X-ray single-crystal ORTEP view of *N*-9'-heptadecanyl-2,7-dibromocarbazole.

concept, 2,7-carbazolenevinylene-based oligomers^{44,54} (Scheme 7) have been also investigated. The Horner–Emmons reaction involved in the synthesis of such molecules offers two main advantages. First, as previously noted, metal-free materials are obtained. Furthermore, this chemistry offers easy access to a wide variety of oligomers in only a few synthetic steps from commercially available products. Indeed, the carbazole unit can be placed either at the end or in the middle of the oligomers to modulate the resulting physical and chemical properties. A good and compact solid-state organization was particularly evident for **O1** and **O2**. However, other compounds, such as **O3**, show an amorphous state. In fact, the symmetry of the molecules seems to greatly influence their solid-state organization. Through substrate and temperature

SCHEME 7. Chemical Structure of 2,(7)-Carbazolevinylene Oligomers

optimizations, mobility as high as $0.3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ in OFET was obtained with **O1**.⁵⁴ Moreover, the relatively high oxidation potential (0.80 V vs SCE) of this oligomer leads to air-stable material, resulting in a large and stable $I_{\text{on}}/I_{\text{off}}$ ratio (10^6 – 10^7).

Poly(2,7-carbazole)s as PC Materials

Fundamental parameters discovered in PLED and OFET studies highlighted the great potential of poly(2,7-carbazole)s for bulk heterojunction (BHJ) PCs. First, poly(2,7-carbazole) derivatives exhibit low highest occupied molecular orbital (HOMO) energy levels, resulting in air-stable polymers and, possibly, high open circuit potential (V_{oc}) values. Second, with proper structure and organization, these materials exhibit good hole mobility values. Finally, like poly(2,7-fluorene) derivatives,²⁴ the absorption spectrum of poly(2,7-carbazole) derivatives can be easily modified through copolymerization for optimal solar spectral match. Müllen²⁹ and co-workers first reported a PC based on **P1-F** (Scheme 4) and perylene tetracarboxydiimide (PDI) blends. These PCs exhibit high V_{oc} values but relatively low performances (Table 2), probably related to the poor

solar spectral match of the devices. About the same time, low band gap poly(2,7-carbazolevinylene)s⁵⁵ (Scheme 8) were also developed to better fit the solar spectral emission. Except for **P17**, Horner–Emmons reaction was used to obtain these polymers, leading to high purity materials as previously noticed. These polymers present band gaps ranging from 2.3 to 1.7 eV and relatively low HOMO energy levels (–5.6 to –5.5 eV). However, device performances (Table 2) still remained relatively low. In fact, these polymers have low solubility and low molecular weight, possibly limiting the performances of the devices. Furthermore, the possibility of vinylene bond degradation through photooxidation^{56,57} may also affect these performances.

As our understanding of the BHJ solar cells improved, design rules for optimal polymeric materials blended with [6,6]-phenyl- C_{61} butyric acid methyl ester (PCBM) emerged.^{58–60} However, before these new rules could be applied, new poly(2,7-carbazole) derivatives with better solubility and molecular weight had to be developed. Initially, both alkyl and aryl side chains developed for OFET (Scheme 7) were tested.³⁰ It turns out that polymers bearing alkyl side chains show higher power conversion efficiencies (PCE). Optimized Suzuki polymerization reaction (Scheme 9) gave **P19** samples with a relatively high molecular weight and good film-forming properties and mobility (up to $3 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$). These features led to high PCE values (Table 2).^{61,62} To further improve device performances, new polymers (Scheme 9) were synthesized taking into account design rules and DFT calculations.⁶² Despite optimized LUMO energy levels for some polymers (**P21**, **P22**, and **P23**), the better structural organization in symmetric polymers (**P18**, **P19**, and **P20**) leads to better hole mobilities and PCE values (Table 2).⁶² As for **P1-F** and **P17**, the low HOMO energy level of these polymers (ca. –5.6 to –5.4 eV) provides an excellent environmental stability and high V_{oc} values (between 0.71 and 0.96 V).

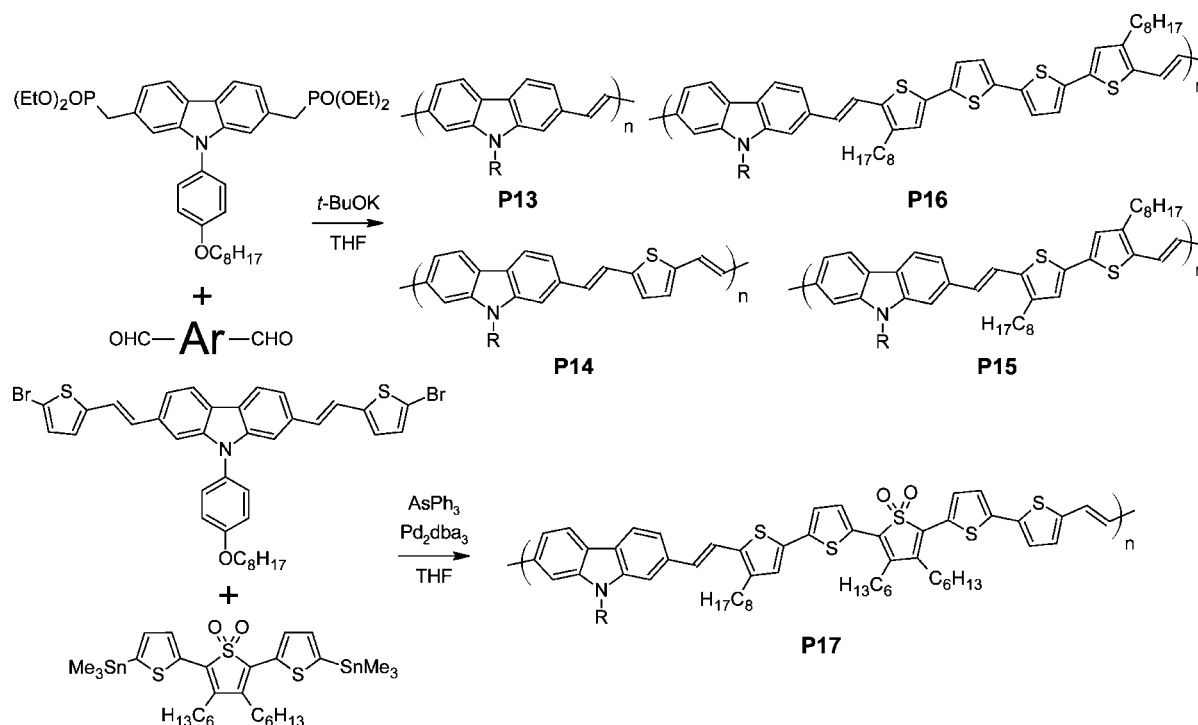
Conclusions and Outlook

Since the original synthesis of poly(2,7-carbazole)s⁹ in 2001, these materials have emerged as one important class of π -conjugated polymers. As demonstrated in this Account, good environmental stability (i.e., low HOMO energy levels), good p-type charge transport, and easy modulation of the physical properties are key features of poly(2,7-carbazole) derivatives. In particular, polymeric bulk heterojunction photovoltaic cells based on poly(2,7-carbazole) derivatives seem to be the most promising field of applications. Along these lines, it is worth noting that recent studies in our group have

TABLE 2. Electronic and Photovoltaic Properties of Poly(2,7-carbazole) Derivatives

polymer	E_{HOMO}^a eV	E_{LUMO}^b eV	$E_{\text{g}}^{\text{opt},c}$ eV	V_{oc}^d V	I_{sc}^e mA · cm ⁻²	FF ^f	η_{e}^g %
P1-F	-5.6	-2.6	3.0	0.71	-0.26	0.37	0.6 ^h
P13	-5.61	-2.83	2.3	0.60	-0.58	0.46	0.4 ⁱ
P14	-5.52	-2.92	2.2	0.50	-0.67	0.45	0.4 ⁱ
P15	-5.49	-3.02	2.1	0.40	-0.57	0.48	0.3 ⁱ
P16	-5.40	-2.96	2.0	0.35	-0.47	0.43	0.2 ⁱ
P17	-5.50	-3.50	1.7	0.80	-1.0	0.55	0.8 ⁱ
P18	-5.46	-3.42	2.02	0.95	-3.0	0.56	1.8 ⁱ
P21	-5.52	-3.67	1.89	0.90	-2.6	0.44	1.1 ⁱ
P19	-5.45	-3.60	1.88	0.86	-6.8	0.56	3.6 ⁱ
P22	-5.53	-3.80	1.75	0.71	-2.9	0.32	0.7 ⁱ
P20	-5.47	-3.65	1.87	0.96	-3.7	0.60	2.4 ⁱ
P23	-5.55	-3.93	1.67	0.85	-1.4	0.60	0.8

^a Ionization potential (E_{HOMO} ; HOMO = highest occupied molecular orbital). ^b Electron affinity (E_{LUMO} ; LUMO = lowest unoccupied molecular orbital). ^c Solid state optical band gap. ^d Open-circuit potential. ^e Short-circuit current. ^f Fill factor. ^g Power conversion efficiency. ^h Test under AM1.5G at 100 W · m⁻². ⁱ Test under AM1.5G at 900 W · m⁻².

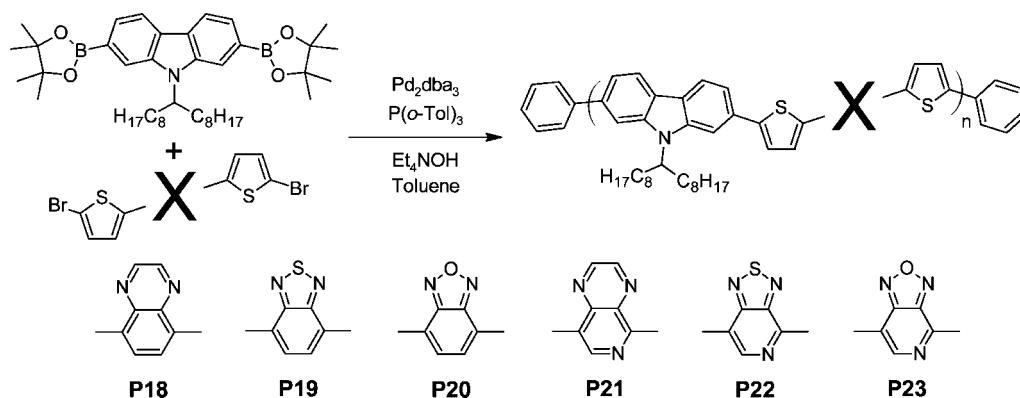
SCHEME 8. Synthetic Pathways to Low Band Gap Poly(2,7-carbazolevinylene) Derivatives

revealed a power conversion efficiency up to 4.8% with **P19**. Furthermore, taking advantage of easy band gap and LUMO energy level modulations, one can expect to synthesize better materials for solar cells, including tandem configurations.^{58–60} Commercial applications can be anticipated with a power conversion efficiency around 6–10%.

These studies on the synthesis of poly(2,7-carbazole)s inspired also the preparation of several new polymeric materials. For instance, it is worth noting the recent reports on poly(1,8-carbazole) derivatives⁶³ and well-defined nanostructured macrocycles.⁶⁴ In parallel, extended ladder-type carbazoles have been extensively studied in the past few years for applications in PLEDs and OFETs. These ladder carbazole

derivatives are divided into two different classes: alternating nitrogen- and carbon-bridged compounds and fully nitrogen-bridged compounds. Based on the work of Müllen and Scherf on ladder-type polyphenylenes,⁶⁵ carbazole-based precursors have been readily converted into semi- or full-ladder polymers with alternating nitrogen- and carbon-bridged units.^{26,66,67} These polymers show good air stability and promising performance as PLED materials. The development of full nitrogen-bridged compounds presented additional challenges and different synthetic methodologies were developed for these purposes.^{25,68–71} These studies notably led to the first synthesis of diindolo[3,2-*b*:2',3'-*h*]carbazole^{25,69} and various indolo[3,2-*b*]carbazole- and diindolo[3,2-*b*:2',3'-*h*]carba-

SCHEME 9. Synthetic Pathways to Low Band Gap Poly(2,7-carbazole) Derivatives for Photovoltaic Cells



zole-based polymers.^{72–75} Due to their highly symmetric and crystalline nature, indolo[3,2-*b*]carbazole-based oligomers^{76–78} and polymers^{74,75} proved to be promising air-stable p-type materials in OFETs. Finally, other heterofluorenes (dibenzosilole, dibenzoborole, etc.) also recently emerged as promising materials for organic electronic applications.^{79–82} Despite all these recent contributions, many aspects of carbazole's chemistry and related systems are still unexplored and many opportunities and discoveries remain to be made. A bright future is foreseen for poly(2,7-carbazole)s and related polymers.

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BIOGRAPHICAL INFORMATION

Nicolas Blouin was born in Quebec City. He received his B.Sc. degree in chemistry from Université Laval in 2004 and then joined the research group of Pr. M. Leclerc. He is currently a fourth-year graduate student in the chemistry Ph.D. program. During that time, he received several scholarships, notably the NSERC Postgraduate Scholarships (PGS M), the Canada Graduate Scholarships (CGS D), and the FQRNT Energy research scholarship (A7). His research interests include the development of new heterocycles and conjugated polymers and their applications in organic field-effect transistors and photovoltaic cells.

Mario Leclerc was awarded a Ph.D. in chemistry from Université Laval, Quebec City, Canada, in 1987. After a short postdoctoral stay at INRS-Energie et Matériaux near Montréal, he joined the Max-Planck-Institute for Polymer Research, in Mainz, Germany, as a postdoctoral fellow in the research group of Prof. Dr. G. Wegner. In 1989, he accepted a position of professor at the department of chemistry of Université de Montréal. In 1998, he moved to Université Laval to join the Centre de Recherche en Sci-

ences et Ingénierie des Macromolécules (CERSIM). Since 2001, he has been the recipient of the Canada Research Chair (Tier 1) on Electroactive and Photoactive Polymers. His current research activities include the synthesis and characterization of new conjugated oligomers and polymers for applications in micro- and nanoelectronics, electro-optics, genomics, and proteomics.

FOOTNOTES

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REFERENCES

- Grazulevicius, J. V.; Strohriegel, P.; Pielichowski, J.; Pielichowski, K. Carbazole-Containing Polymers: Synthesis, Properties and Applications. *Prog. Polym. Sci.* **2003**, *28*, 1297–1353.
- Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. Synthesis of Electrically Conducting Organic Polymers - Halogen Derivatives of Polyacetylene, $(CH)_x$. *J. Chem. Soc., Chem. Commun.* **1977**, 578–580.
- Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; MacDiarmid, A. G. Electrical-Conductivity in Doped Polyacetylene. *Phys. Rev. Lett.* **1977**, *39*, 1098–1101.
- Morin, J.-F.; Leclerc, M.; Adès, D.; Siove, A. Polycarbazoles: 25 Years of Progress. *Macromol. Rapid Commun.* **2005**, *26*, 761–778.
- Smith, P. A. S.; Brown, B. B. The Synthesis of Heterocyclic Compounds from Aryl Azides. I. Bromo and Nitro Carbazoles. *J. Am. Chem. Soc.* **1951**, *73*, 2435–2437.
- Heinrich, L. Über eine vereinfachte Täubersche Carbazol-Synthese. *Chem. Ber.* **1953**, *86*, 522–524.
- Cadogan, J. I. G.; Cameron-Wood, M.; Makie, R. K.; Searle, R. J. G. The Reactivity of Organophosphorus Compounds. *J. Chem. Soc.* **1965**, *483*, 1–4837.
- Cadogan, J. I. G. Phosphite-Reduction of Aromatic Nitro-Compounds as a Route to Heterocycles. *Synthesis* **1969**, 11–17.
- Morin, J. F.; Leclerc, M. Syntheses of Conjugated Polymers Derived from *N*-Alkyl-2,7-carbazoles. *Macromolecules* **2001**, *34*, 4680–4682.
- Dierschke, F.; Grimsdale, A. C.; Müllen, K. Efficient Synthesis of 2,7-Dibromocarbazoles as Components for Electroactive Materials. *Synthesis* **2003**, 2470–2472.
- Nozaki, K.; Takahashi, K.; Nakano, K.; Hiyama, T.; Tang, H.-Z.; Fujiki, M.; Yamaguchi, S.; Tamao, K. The Double *N*-Arylation of Primary Amines: Toward Multisubstituted Carbazoles with Unique Optical Properties. *Angew. Chem., Int. Ed.* **2003**, *42*, 2051–2053.
- Kuwahara, A.; Nakano, K.; Nozaki, K. Double *N*-Arylation of Primary Amines: Carbazole Synthesis from 2,2'-Biphenyldiols. *J. Org. Chem.* **2005**, *70*, 413–419.
- Kitawaki, T.; Hayashi, Y.; Ueno, A.; Chida, N. One-Step Construction of Carbazoles by Way of the Palladium-Catalyzed Double *N*-Arylation Reaction and its Application to the Total Synthesis of Murrastifoline-A. *Tetrahedron* **2006**, *62*, 6792–6801.
- Zotti, G.; Schiavon, G.; Zecchin, S.; Morin, J. F.; Leclerc, M. Electrochemical, Conductive, and Magnetic Properties of 2,7-Carbazole-Based Conjugated Polymers. *Macromolecules* **2002**, *35*, 2122–2128.
- Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z. H.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. Preparation of π -Conjugated Poly(thiophene-2,5-diyl), Poly(*p*-phenylene), and Related Polymers Using Zerovalent

- Nickel Complexes. Linear Structure and Properties of the π -Conjugated Polymers. *Macromolecules* **1992**, *25*, 1214–1223.
- 16 Yamamoto, T. Synthesis of π -Conjugated Polymers Bearing Electronic and Optical Functionalities by Organometallic Polycondensations. Chemical Properties and Applications of the π -Conjugated Polymers. *Synlett* **2003**, 425–450.
- 17 Babudri, F.; Cicco, S. R.; Farinola, G. M.; Naso, F.; Bolognesi, A.; Porzio, W. Synthesis, Characterization and Properties of a Soluble Polymer with a Poly(phenylenevinylene) Structure. *Macromol. Rapid Commun.* **1996**, *17*, 905–911.
- 18 Bao, Z.; Chan, W. K.; Yu, L. Exploration of the Stille Coupling Reaction for the Synthesis of Functional Polymers. *J. Am. Chem. Soc.* **1995**, *117*, 12426–12435.
- 19 Rehahn, M.; Schluter, A.-D.; Wegner, G.; Feast, W. J. Soluble Poly(para-phenylene)s. 2. Improved Synthesis of Poly(para-2,5-di-n-hexylphenylene) via Pd-Catalysed Coupling of 4-Bromo-2,5-di-n-hexylbenzeneboronic Acid. *Polymer* **1989**, *30*, 1060–1062.
- 20 Schlüter, A. D. The tenth anniversary of Suzuki polycondensation (SPC). *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1533–1556.
- 21 Ranger, M.; Rondeau, D.; Leclerc, M. New Well-Defined Poly(2,7-fluorene) Derivatives: Photoluminescence and Base Doping. *Macromolecules* **1997**, *30*, 7686–7691.
- 22 Woo, E. P.; Inbasekaran, M.; Shiang, W. R.; Roof, G. R. 9-Substituted Fluorenes and 9-Substituted Fluorene Oligomers and Polymers. US Patent 5,708,130, 1997.
- 23 Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. Progress with Light-Emitting Polymers. *Adv. Mater.* **2000**, *12*, 1737–1750.
- 24 Leclerc, M. Polyfluorenes: Twenty Years of Progress. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2867–2873.
- 25 Bouchard, J.; Wakim, S.; Leclerc, M. Synthesis of Diindolocarbazoles by Cadogan Reaction: Route to Ladder Oligo(p-anilines). *J. Org. Chem.* **2004**, *69*, 5705–5711.
- 26 Dierschke, F.; Grimsdale, A. C.; Müllen, K. Novel Carbazole-Based Ladder-Type Polymers for Electronic Applications. *Macromol. Chem. Phys.* **2004**, *205*, 1147–1154.
- 27 Iraqi, A.; Wataru, I. Preparation and Properties of 2,7-Linked N-Alkyl-9H-carbazole Main-Chain Polymers. *Chem. Mater.* **2004**, *16*, 442–448.
- 28 Morin, J. F.; Leclerc, M. 2,7-Carbazole-Based Conjugated Polymers for Blue, Green, and Red Light Emission. *Macromolecules* **2002**, *35*, 8413–8417.
- 29 Li, J.; Dierschke, F.; Wu, J.; Grimsdale, A. C.; Müllen, K. Poly(2,7-carbazole) and Perylene Tetracarboxydiimide: A Promising Donor/Acceptor Pair for Polymer Solar Cells. *J. Mater. Chem.* **2006**, *16*, 96–100.
- 30 Wakim, S.; Blouin, N.; Gingras, E.; Tao, Y.; Leclerc, M. Poly(2,7-carbazole) Derivatives as Semiconductors for Organic Thin-Film Transistors. *Macromol. Rapid Commun.* **2007**, *28*, 1798–1803.
- 31 Iraqi, A.; Simmance, T. G.; Yi, H.; Stevenson, M.; Lidzey, D. G. Preparation and Properties of 4-Dialkylamino-phenyl N-Functionalized 2,7-Linked Carbazole Polymers. *Chem. Mater.* **2006**, *18*, 5789–5797.
- 32 Yi, H.; Iraqi, A.; Stevenson, M.; Elliott, C. J.; Lidzey, D. G. A New Class of Blue-Emitting Materials for LED Applications: Triarylamine N-Functionalised 2,7-Linked Carbazole Polymers. *Macromol. Rapid Commun.* **2007**, *28*, 1155–1160.
- 33 Kobayashi, N.; Koguchi, R.; Kijima, M. Novel Blue Light Emitting Poly(N-arylcarbazole-2,7-ylene) Homopolymers: Syntheses and Properties. *Macromolecules* **2006**, *39*, 9102–9111.
- 34 Koguchi, R.; Kobayashi, N.; Shinnai, T.; Oikawa, K.; Tsuchiya, K.; Kijima, M. Synthesis of Poly(N-aryl-2,7-carbazole)s for Efficient Blue Electroluminescence Materials. *Macromol. Chem. Phys.* **2008**, *209*, 439–449.
- 35 Morin, J.-F.; Boudreault, P.-L.; Leclerc, M. Blue-Light-Emitting Conjugated Polymers Derived From 2,7-Carbazoles. *Macromol. Rapid Commun.* **2002**, *23*, 1032–1036.
- 36 Fu, Y.; Bo, Z. Synthesis, Optical, and Electrochemical Properties of the High-Molecular-Weight Conjugated Polycarbazoles. *Macromol. Rapid Commun.* **2005**, *26*, 1704–1710.
- 37 Morin, J.-F.; Beaupre, S.; Leclerc, M.; Levesque, I.; D'lorio, M. Blue Light-Emitting Devices from New Conjugated Poly(N-substituted-2,7-carbazole) Derivatives. *Appl. Phys. Lett.* **2002**, *80*, 341–343.
- 38 Drolet, N. Ph.D Thesis, Université Laval, Quebec City, 2006.
- 39 Kobayashi, N.; Kijima, M. Blue Electroluminescent Properties of Poly(N-arylcarbazole-2,7-ylene) Homopolymers. *Appl. Phys. Lett.* **2007**, *91*, 081113.
- 40 Iraqi, A.; Pegington, R. C.; Simmance, T. G. Postmodification of Poly(9-alkyl-9H-carbazole-2,7-diy)s as a Route to New Main-Chain-Functionalized Carbazole Polymers. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3336–3342.
- 41 Iraqi, A.; Pickup, D. F.; Yi, H. Effects of Methyl Substitution of Poly(9-alkyl-9H-carbazole-2,7-diy)s at the 3,6-Positions on Their Physical Properties. *Chem. Mater.* **2006**, *18*, 1007–1015.
- 42 Müllekorn, H. A. M. v.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. Developments in the Chemistry and Band Gap Engineering of Donor-Acceptor Substituted Conjugated Polymers. *Mater. Sci. Eng., R* **2001**, *32*, 1–40.
- 43 Roncali, J. Molecular Engineering of the Band Gap of π -Conjugated Systems: Facing Technological Applications. *Macromol. Rapid Commun.* **2007**, *28*, 1761–1775.
- 44 Morin, J. F.; Drolet, N.; Tao, Y.; Leclerc, M. Syntheses and Characterization of Electroactive and Photoactive 2,7-Carbazolevinylene-Based Conjugated Oligomers and Polymers. *Chem. Mater.* **2004**, *16*, 4619–4626.
- 45 Krebs, F. C.; Nyberg, R. B.; Jorgensen, M. Influence of Residual Catalyst on the Properties of Conjugated Polyphenylenevinylene Materials: Palladium Nanoparticles and Poor Electrical Performance. *Chem. Mater.* **2004**, *16*, 1313–1318.
- 46 Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. Two-Dimensional Charge Transport in Self-Organized, High-Mobility Conjugated Polymers. *Nature* **1999**, *401*, 685–688.
- 47 McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; MacDonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. Liquid-Crystalline Semiconducting Polymers with High Charge-Carrier Mobility. *Nat. Mater.* **2006**, *5*, 328–333.
- 48 Salleo, A. Charge Transport in Polymeric Transistors. *Mater. Today* **2007**, *10*, 38–45.
- 49 Sirringhaus, H.; Wilson, R. J.; Friend, R. H.; Inbasekaran, M.; Wu, W.; Woo, E. P.; Grell, M.; Bradley, D. D. C. Mobility Enhancement in Conjugated Polymer Field-Effect Transistors through Chain Alignment in a Liquid-Crystalline Phase. *Appl. Phys. Lett.* **2000**, *77*, 406–408.
- 50 Leclerc, M.; Ranger, M.; Bélanger-Gariépy, F. 2,7-Dibromo-9,9-dioctylfluorene-Chloroform (1/0.25). *Acta Crystallogr.* **1998**, *C54*, 799–801.
- 51 Ranger, M.; Leclerc, M. New Base-Doped Polyfluorene Derivatives. *Macromolecules* **1999**, *32*, 3306–3313.
- 52 Dimitrakopoulos, C. D.; Malenfant, P. R. L. Organic Thin Film Transistors for Large Area Electronics. *Adv. Mater.* **2002**, *14*, 99–117.
- 53 Murphy, A. R.; Frechet, J. M. J. Organic Semiconducting Oligomers for Use in Thin Film Transistors. *Chem. Rev.* **2007**, *107*, 1066–1096.
- 54 Drolet, N.; Morin, J. F.; Leclerc, N.; Wakim, S.; Tao, Y.; Leclerc, M. 2,7-Carbazolevinylene-Based Oligomer Thin-Film Transistors: High Mobility Through Structural Ordering. *Adv. Funct. Mater.* **2005**, *15*, 1671–1682.
- 55 Leclerc, N.; Michaud, A.; Sirois, K.; Morin, J. F.; Leclerc, M. Synthesis of 2,7-Carbazolevinylene-Based Copolymers and Characterization of Their Photovoltaic Properties. *Adv. Funct. Mater.* **2006**, *16*, 1694–1704.
- 56 Alstrup, J.; Norrman, K.; Jorgensen, M.; Krebs, F. C. Lifetimes of Organic Photovoltaics: Design and Synthesis of Single Oligomer Molecules in Order to Study Chemical Degradation Mechanisms. *Sol. Energy Mater.* **2006**, *90*, 2777–2792.
- 57 Pacios, R.; Chatten, A. J.; Kawano, K.; Durrant, J. R.; Bradley, D. D. C.; Nelson, J. Effects of Photo-oxidation on the Performance of Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene]:[6,6]-Phenyl C₆₁-Butyric Acid Methyl Ester Solar Cells. *Adv. Funct. Mater.* **2006**, *16*, 2117–2126.
- 58 Koster, L. J. A.; Mihailetechi, V. D.; Blom, P. W. M. Ultimate Efficiency of Polymer/Fullerene Bulk Heterojunction Solar Cells. *Appl. Phys. Lett.* **2006**, *88*, 093511.
- 59 Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. Design Rules for Donors in Bulk-Heterojunction Solar Cells - Towards 10% Energy-Conversion Efficiency. *Adv. Mater.* **2006**, *18*, 789–794.
- 60 Thompson, Barry, C.; Fréchet, Jean, M. J. Polymer-Fullerene Composite Solar Cells. *Angew. Chem., Int. Ed.* **2008**, *47*, 58–77.
- 61 Blouin, N.; Michaud, A.; Leclerc, M. A Low-Bandgap Poly(2,7-Carbazole) Derivative for Use in High-Performance Solar Cells. *Adv. Mater.* **2007**, *19*, 2295–2300.
- 62 Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, E.; Neagu-Plesu, R.; Belletete, M.; Durocher, G.; Tao, Y.; Leclerc, M. Toward a Rational Design of Poly(2,7-Carbazole) Derivatives for Solar Cells. *J. Am. Chem. Soc.* **2008**, *130*, 732–742.
- 63 Michinobu, T.; Osako, H.; Shigehara, K. Alkyne-Linked Poly(1,8-carbazole)s: A Novel Class of Conjugated Carbazole Polymers. *Macromol. Rapid Commun.* **2008**, *29*, 111–116.
- 64 Jung, S.-H.; Pisula, W.; Rouhanipour, A.; Räder, H. J.; Jacob, J.; Müllen, K. A Conjugated Polycarbazole Ring around a Porphyrin. *Angew. Chem., Int. Ed.* **2006**, *45*, 4685–4690.
- 65 Scherf, U.; Müllen, K. Polyarylenes and Poly(arylenevinylene)s. 7. A Soluble Ladder Polymer via Bridging of Functionalized Poly(p-phenylene)-Precursors. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 489–497.
- 66 Patil, S. A.; Scherf, U.; Kadashchuk, A. New Conjugated Ladder Polymer Containing Carbazole Moieties. *Adv. Funct. Mater.* **2003**, *13*, 609–614.
- 67 Mishra, A. K.; Graf, M.; Grasse, F.; Jacob, J.; List, E. J. W.; Müllen, K. Blue-Emitting Carbon- and Nitrogen-Bridged Poly(ladder-type tetraphenylene)s. *Chem. Mater.* **2006**, *18*, 2879–2885.

- 68 Wakim, S.; Bouchard, J.; Simard, M.; Drolet, N.; Tao, Y.; Leclerc, M. Organic Microelectronics: Design, Synthesis, and Characterization of 6,12-Dimethylindolo[3,2-*b*]carbazoles. *Chem. Mater.* **2004**, *16*, 4386–4388.
- 69 Wakim, S.; Bouchard, J.; Blouin, N.; Michaud, A.; Leclerc, M. Synthesis of Diindolocarbazoles by Ullmann Reaction: A Rapid Route to Ladder Oligo(*p*-aniline)s. *Org. Lett.* **2004**, *6*, 3413–3416.
- 70 Wakim, S.; Leclerc, M. Towards the Synthesis of Ladder Oligo(*p*-aniline)s. *Synlett* **2005**, 1223–1234.
- 71 Bergman, J.; Janosik, T.; Wahlstrom, N. Indolocarbazoles. *Advances Heterocyclic Chemistry*; Academic Press: New York, 2001; Vol *80*, pp 1–71.
- 72 Blouin, N.; Michaud, A.; Wakim, S.; Boudreault, P.-L. T.; Leclerc, M.; Vercelli, B.; Zecchin, S.; Zotti, G. Optical, Electrochemical, Magnetic, and Conductive Properties of New Polyindolocarbazoles and Polydiindolocarbazoles. *Macromol. Chem. Phys.* **2006**, *207*, 166–174.
- 73 Blouin, N.; Leclerc, M.; Vercelli, B.; Zecchin, S.; Zotti, G. Optical, Electrochemical, Magnetic, and Conductive Properties of New Poly(indolocarbazole-*alt*-bithiophene)s. *Macromol. Chem. Phys.* **2006**, *207*, 175–182.
- 74 Li, Y.; Wu, Y.; Ong, B. S. Polyindolo[3,2-*b*]carbazoles: A New Class of *p*-Channel Semiconductor Polymers for Organic Thin-Film Transistors. *Macromolecules* **2006**, *39*, 6521–6527.
- 75 Blouin, N.; Wakim, S.; Tao, Y.; Leclerc, M. Poly(2,7-carbazole)s and Polyindolo[3,2-*b*]carbazoles as Field Effect Transistor. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2007**, *48*, 292–293.
- 76 Li, Y.; Wu, Y.; Gardner, S.; Ong, B. S. Novel Peripherally Substituted Indolo[3,2-*b*]carbazoles for High-Mobility Organic Thin-Film Transistors. *Adv. Mater.* **2005**, *17*, 849–853.
- 77 Wu, Y.; Li, Y.; Gardner, S.; Ong, B. S. Indolo[3,2-*b*]carbazole-Based Thin-Film Transistors with High Mobility and Stability. *J. Am. Chem. Soc.* **2005**, *127*, 614–618.
- 78 Boudreault, P. L. T.; Wakim, S.; Blouin, N.; Simard, M.; Tessier, C.; Tao, Y.; Leclerc, M. Synthesis, Characterization, and Application of Indolo[3,2-*b*]carbazole Semiconductors. *J. Am. Chem. Soc.* **2007**, *129*, 9125–9136.
- 79 Yamaguchi, S.; Shirasaka, T.; Akiyama, S.; Tamao, K. Dibenzoborole-Containing π -Electron Systems: Remarkable Fluorescence Change Based on the “On/Off” Control of the $p_{\pi}-\pi^*$ Conjugation. *J. Am. Chem. Soc.* **2002**, *124*, 8816–8817.
- 80 Chen, R. F.; Fan, Q. L.; Zheng, C.; Huang, W. A General Strategy for the Facile Synthesis of 2,7-Dibromo-9-heterofluorenes. *Org. Lett.* **2006**, *8*, 203–205.
- 81 Chen, J.; Cao, Y. Silole-Containing Polymers: Chemistry and Optoelectronic Properties. *Macromol. Rapid Commun.* **2007**, *28*, 1714–1742.
- 82 Wakamiya, A.; Mishima, K.; Ekawa, K.; Yamaguchi, S. Kinetically Stabilized Dibenzoborole as an Electron-Accepting Building Unit. *Chem. Commun.* **2008**, 579–581.