4386 *Chem. Mater.* **2004,** *16,* 4386−4388

Organic Microelectronics: Design, Synthesis, and Characterization of 6,12-Dimethylindolo[3,2-*b*]Carbazoles

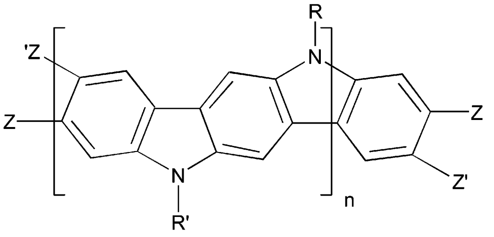
Salem Wakim,[†] Jimmy Bouchard,[†] Michel Simard,[§]
Nicolas Drolet,[†,‡] Ye Tao,[‡] and Mario Leclerc[*,†]

Canada Research Chair in Electroactive and Photoactive Polymers, Department of Chemistry, Université Laval, Quebec City, Quebec, Canada, G1K 7P4, Institute for Microstructural Sciences, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6, and Laboratory of X-ray Diffraction, Department of Chemistry, Université de Montréal, Montreal, Quebec, Canada, H3C 3J7

Received February 11, 2004
Revised Manuscript Received May 13, 2004

Although researchers have been working in the field of organic microelectronics for more than 20 years, novel electroactive molecules are still required to solve important remaining problems: stability and processability together with good charge transport properties.[1−3] In the particular case of organic p-type field-effect transistors, the best candidates are polythiophenes,[4] oligothiophenes,[5] oligofluorenes,[2] oligo(2,6-anthrylene)s,[6] and pentacenes.[7] Among these materials, pentacene thin-film field-effect transistors have received particular attention since they have shown hole mobilities about 5 $cm^2 V^{-1} s^{-1}$ with on/off current ratios up to 10^8 in some cases.[7] However, pentacene is only moderately stable to oxygen as a dense solid and is unstable under illumination. Pentacene also has a very high melting point and is virtually insoluble, even in hot aromatic solvents.[6,8] It could therefore be interesting to develop pentacene-like oligomers which show similar coplanar ladder structures and favorable packing geometry together with improved stability and processability. Organic synthesis allows great flexibility at the molecular scale together with the possibility of fine-tuning the physical and chemical properties according to the aimed applications. Starting from this point, a new class of pentacene-like semiconducting organic materials has been designed using phenyl-capped ladder oligo(*p*-aniline) derivatives (Scheme 1). Interestingly, depending upon the nature of the R and R′ groups, it may be possible to develop amphiphilic molecules that could lead to well-defined thin films through Langmuir−Blodgett processing or self-assembly procedures. Moreover, for the emerging nanoelectronics, these molecules have the potential to make connections with different nanoelectrodes and to function as conducting and semiconducting nanowires as well as three-way nanoconnectors or molecular transistors.

Scheme 1. Phenyl-Capped Conjugated Ladder Oligo(*p*-aniline)s



Z and Z′ = H; alkyl; Cl; Br; SAc; Ph-SAc; Ph-NC.
R and R′ = alkyl; alkyl-TEO; alkyl-SAc; Ph-SAc.
n = 1; 1.5; 2; 2.5.

To start a general synthesis of this new class of materials, we focused on the Cadogan procedure as the ring closure reaction.[9] To synthesize the corresponding dimer (e.g., [3,2-*b*]indolocarbazole or $n = 1$ and $Z = Z'$ $= H$ in Scheme 1), we started with a double reductive cyclization[10] of 2′,5′-dinitro-1,1′;4′,1″-terphenyl induced by $P(OEt)_3$ but were unable to isolate a pure product. Several other synthetic methods have also been described for the preparation of indolocarbazoles, but all these methods suffer from low yields, limited synthetic versatility, and/or the formation of many side-products.[11] One general aspect mentioned throughout the literature refers to the insolubility of indolocarbazoles in common organic solvents which leads to isolation problems and low yields.[12] To solve this problem, we decided to use a soluble *N*-alkyl substituted carbazole precursor. As we recently reported,[13] it is now possible to prepare, in good yields, *N*-alkyl-2,7-disubstituted

---

[*] To whom correspondence should be addressed. Tel: 1-418-656-3452. Fax: 1-418-656-7916. E-mail: Mario.leclerc@chm.ulaval.ca.

[†] Université Laval.

[‡] Institute for Microstructural Sciences, National Research Council of Canada.

[§] Université de Montréal.

(1) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.

(2) Meng, H.; Zheng, J.; Lovinger, A. J.; Wang, B. C.; Patten, P. G. V.; Bao, Z. *Chem. Mater.* **2003**, *15*, 1778.

(3) Babel, A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 13656.

(4) (a) Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 4108. (b) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741.

(5) (a) Videlot, C.; Ackermann, J.; Blanchard, P.; Raimundo, J. M.; Frère, P.; Allain, M.; Bettignies, R.; Levillain, E.; Roncali, J. *Adv. Mater.* **2003**, *15*, 306. (b) Dimitrakopoulos, C. D.; Furman, B. K., Graham, F.; Hedge, S.; Purushothaman, S. *Synth. Met.* **1998**, *92*, 47. (c) Horowitz, G.; Garnier, F.; Yassar, A.; Hajlaoui, R.; Kouki, F. *Adv. Mater.* **1996**, *8*, 52.

(6) Ito, K.; Suzuki, T.; Sakamoto, Y.; Kubota, D.; Inoue, Y.; Sato, F.; Tokito, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1159.

(7) (a) Gundlach, D. J.; Lin, Y. Y.; Jackson, T. N.; Nelson, S. F.; Schlom, D. G. *IEEE Electron Device Lett.* **1997**, *18*, 87. (b) Lin, Y. Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. *IEEE Electron Device Lett.* **1997**, *18*, 606. (c) Meng H.; Bendikov, M.; Mitchell, G.; Helgeson, R.; Wudl, F.; Bao, Z.; Siegrist, T.; Kloc, C.; Chen, C.-H. *Adv. Mater.* **2003**, *15*, 1090. (d) Klauk, H.; Halik, M.; Zschieschang, U.; Schmid, G.; Radlik, W.; Weber, W. *J. Appl. Phys.* **2002**, *92*, 5259. (e) Kelley, T. W.; Muyres, D. V.; Baude, P. F.; Smith, T. P.; Jones, T. D. *Mater. Res. Soc. Symp. Ser.* **2003**, *771*, 169.

(8) (a) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359. (b) Herwing, P. T.; Müllen, K. *Adv. Mater.* **1999**, *11*, 480.

(9) Cadogan, J. I. G.; Carmeron-Wood, M.; Makie, R. K.; Searle, R. J. G. *J. Chem. Soc.* **1965**, 4831.

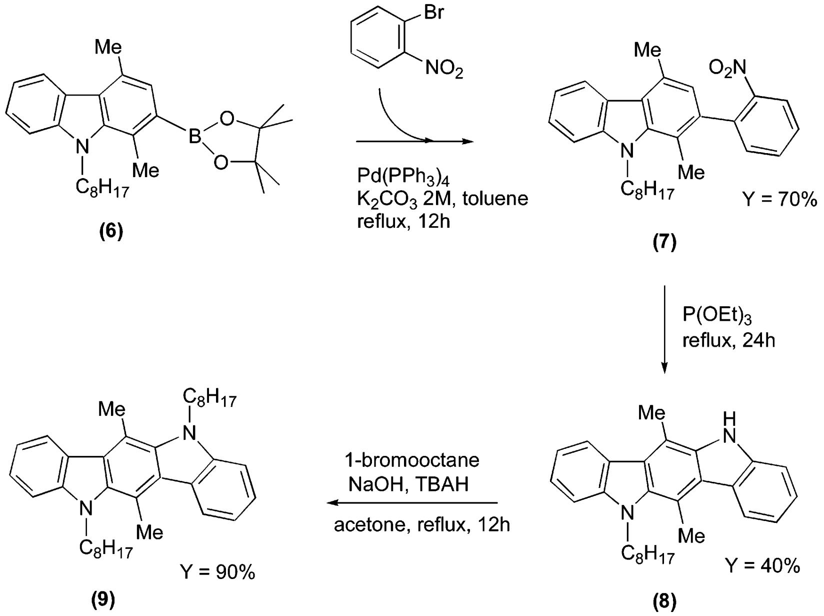
(10) Kistenmacher, A.; Müllen, K. *J. Heterocycl. Chem.* **1992**, *29*, 1237.

(11) (a) Yudina, L. N.; Bergman, J. *Tetrahedron* **2003**, *59*, 1265. (b) Katritzky, A. R.; Li, J.; Stevens, C. V. *J. Org. Chem.* **1995**, *60*, 3401. (c) Van der Auweraer, M.; Dederen, C.; Palmans-Windels, C.; De Schryver, F. C. *J. Am. Chem. Soc.* **1982**, *104*, 1800. (d) Hünig, S.; Steinmetzer, H. C. *Tetrahedron Lett.* **1981**, *8*, 645. (e) Bergman, J. *Tetrahedron* **1970**, *26*, 3353. (f) Grotta, H. M.; Riggle, C. J.; Bearse, A. E. *J. Org. Chem.* **1961**, *26*, 1509.

(12) Tholander, J.; Bergman, J. *Tetrahedron* **1999**, *55*, 12577. (b) Black, D. St. C.; Ivory, A. J.; Kumar, N. *Tetrahedron* **1995**, *51*, 11801.

10.1021/cm049786g CCC: $27.50 © 2004 American Chemical Society
Published on Web 07/07/2004

Scheme 2. Synthesis of 5,11-Dioctyl-6,12-dimethylindolo[3,2-*b*]Carbazole



carbazoles. Along these lines, we first tried a Cadogan reductive ring closure of *N*-octyl-2-(2′-nitrobenzene)-carbazole but only obtained a mixture of unsymmetrical and symmetrical indolocarbazoles, corresponding to the ortho and para ring closure. Another approach, based on 3- and 3,6-nitrocarbazole derivatives, was also tested, but Cadogan reactions did not work well with these precursors.

To obtain the formation of the targeted isomer, a new *N*-octyl-2-substituted carbazole derivative **6** with methyl protecting groups at the 1- and 4-positions was synthesized based on well-established methodologies[13b] in 6 steps (see Supporting Information). As described in Scheme 2, the Suzuki coupling reaction of compound **6** with commercially available 1-bromo-2-nitrobenzene using $Pd(PPh_3)_4$ provides compound **7** with a 70% isolated yield. Then, Cadogan ring closure in hot triethyl phosphite was performed regioregularly on compound **7** to offer the desired soluble para isomer, 5-hydro-11-octyl-6,12-dimethylindolo[3,2-*b*]carbazole **8**, which was isolated in 40% yield. This compound is an excellent intermediate because it offers an opportunity to develop different kinds of 6,12-dimethylindolo[3,2-*b*]carbazoles depending on the nature of the substituent. In our strategy to develop a new family of totally symmetrical 6,12-dimethylindolo[3,2-*b*]carbazoles, compound **8** was alkylated[13b] with 1-bromooctane under reflux in acetone using NaOH and TBAH as a phase transfer agent to give 5,11-dioctyl-6,12-dimethylindolo[3,2-*b*]carbazole **9** with 90% isolated yield. This compound is soluble in THF, $CHCl_3$, and CH_2Cl_2, etc. and can be easily recrystallized from acetone to give thin yellow needles.

X-ray crystallographic analyses of a single crystal of compound **9** show a triclinic crystal system with a coplanar molecular structure. This suggests that the π-conjugation is effectively extended over the entire molecule. The X-ray structure of molecule **9** is shown in Figure 1 and the detailed crystallographic data are given in the Supporting Information. Packing diagrams of molecule **9** demonstrate a π-stacking arrangement of molecules along the *a*-axis of the single-crystal unit cell. The intermolecular distance between two molecules is 3.45 Å. This type of orientation is very interesting to produce high charge carrier mobility along the direction of $\pi-\pi$ stacking,[1,14] and could be related to favorable attractive interactions between the side chains. Dif-

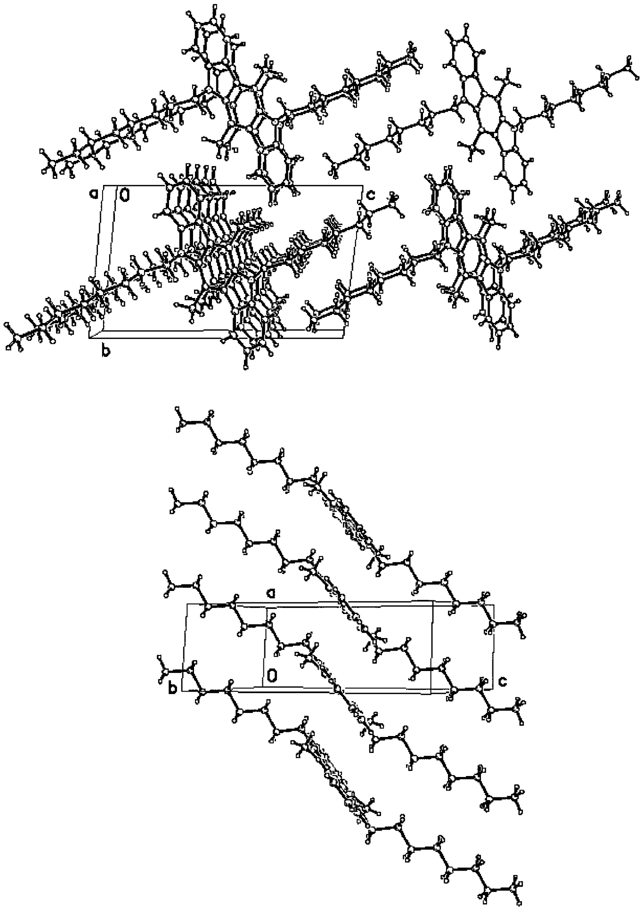


Figure 1. X-ray structure of compound **9**. View of packing, down *a* axis (top) and perpendicular to *a* axis (bottom).

---

[13] (a) Morin, J. F.; Leclerc, M. *Macromolecules* **2001**, *34*, 4680. (b) Zotti, G.; Schiavon, G.; Zecchin, S.; Morin, J. F.; Leclerc, M. *Macromolecules* **2002**, *35*, 2122.

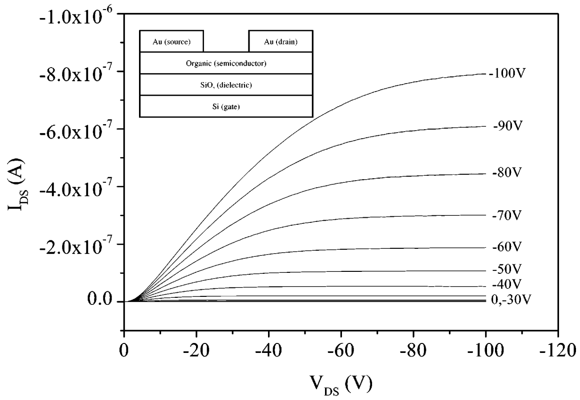


Figure 2. Source-drain current (I_{DS}) versus source-drain voltage (V_{DS}) at various gate voltages (V_G) from a top-contact geometry OFET with *W*/*L* = 40:1 using compound **9** as semiconducting material deposited at a substrate temperature of 25 °C.

ferential scanning calorimetry (DSC) measurements on compound **9** showed melting endotherms and recrystallization exotherms at 151 and 118 °C, respectively.

The UV−visible absorption properties of compound **9** were also studied. The UV−visible spectrum of **9** in CH_2Cl_2 shows two absorption maxima at 394 and 413 nm. Solid-state absorption spectrum reveals two absorption maxima at 404 and 431 nm. Cyclic voltammetry was performed in THF solution (with 0.1 M tetrabutylammonium perchlorate) to investigate the redox behavior of compound **9** and to assess the HOMO and LUMO energy levels. Compound **9** shows a reversible oxidation at 0.89 V (vs SCE) and a quasi-reversible reduction at −2.67 V (vs SCE). The HOMO and LUMO energy levels estimated from the onset potentials of oxidation ($E_{ox}{}^{onset}$, 0.71 V vs SCE) and reduction ($E_{red}{}^{onset}$, −2.45 V vs SCE) are at −5.11 and −1.95 eV, respectively. These spectroscopic and electrochemical data indicate that the neutral semiconducting form of this compound should be stable in air. The band gap energy calculated from electrochemical data is 3.16 eV, which agrees with the value obtained from UV−vis spectroscopy (2.88 eV).

An organic field-effect transistor (OFET) using oligomer **9** as the active material was fabricated on SiO_2/Si substrates by high-vacuum evaporation using a top-contact geometry at a substrate temperature of 25 °C. Figure 2 represents the source-drain current (I_{DS}) versus source-drain voltage (V_{DS}) characteristics for an OFET with compound **9** at various gate voltages (V_G) and the schematic cross-sectional view of the fabricated device. This graph shows that **9** behaves as a p-type organic semiconductor with well-defined linear and saturation regimes. The hole mobility and the on/off ratio calculated[15] in the saturation regime at $V_{DS} = -90$ V are 10^{-3} cm^2 V^{-1} s^{-1} and 10^5, respectively, and the threshold voltage is −18 V.

In conclusion, we have described an efficient method to prepare soluble 6,12-dimethylindolo[3,2-*b*]carbazoles by Cadogan ring closure from an *N*-alkyl-2-substituted carbazole precursor. This synthetic methodology offers great flexibility at the molecular scale to develop oligomers having different chemical structures and physical properties. X-ray structure of compound **9** demonstrates an interesting π-stacking arrangement of molecules along the *a*-axis with 3.45 Å as intermolecular ring distance. The first OFET using 5,11-dioctyl-6,12-dimethylindolo[3,2-*b*]carbazole **9** as an active layer has been successfully fabricated. It shows *p*-channel characteristics with a hole mobility of 10^{-3} cm^2 V^{-1} s^{-1} and I_{on}/I_{off} ratio of 10^5. These preliminary results are highly promising considering the simplicity of the conjugated oligomers and of the experimental setup. We firmly believe that device performances can be improved by using longer oligomers or different side-chain patterns or by using optimized device configurations. These studies are currently in progress in our laboratories.

Acknowledgment. This work was supported by the Canada Research Chair program and NSERC grants.

Supporting Information Available: Detailed experimental procedures, ^{1}H and ^{13}C NMR of compounds **1**−**9**, and X-ray structural information on compound **9** (PDF) and X-ray crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM049786G

---

(14) Kunugi, Y.; Takimiya, K.; Yamane, K.; Yamashita, K.; Aso, Y.; Otsubo, T. *Chem. Mater.* **2003**, *15*, 6.

(15) See Supporting Information for semilogarithmic plot of source-drain current versus gate voltage and plot of square root of source-drain current versus gate voltage, for OFET using **9** as semiconducting material, from which field-effect mobility, I_{on}/I_{off} ratio, and threshold voltage can be calculated.