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Poly(2,7-carbazole) Derivatives as Semiconductors for Organic Thin-Film Transistors

Salem Wakim[a,b], Nicolas Blouin[a], Emilie Gingras[a], Ye Tao[b] and Mario Leclerc[a]*

a) Canada Research Chair on Electroactive and Photoactive Polymers,
Département de Chimie, Université Laval, Quebec City, Quebec, Canada, G1K 7P4
Fax: +1-418-656-7916; E-mail: mario.leclerc@chm.ulaval.ca
b) Institute of Microstructural Sciences, National Research Council of Canada, Ottawa, Ontario,
Canada, K1A 0R6

Contents for Supporting Information:

Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on a Varian AS400 apparatus in an appropriated deuterated solvent solution at 298 K unless other specifications. Chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) with an HPLC Waters 515 pump, two Shodex KF-804 columns (Particle size 7μ, 8.0 mm ID x 300 mm), and chloroform as eluent using a Waters 441 UV-Vis detector. The calibration curve was made with a series of monodispersed polystyrene standards (Shodex). UV-visible absorption spectra were taken using a Varian Cary 500 UV-VIS-NIR spectrophotometer. Differential scanning calorimetry (DSC) analysis was performed on a Mettler Toledo DSC823e instrument, calibrated with ultrapure indium. DSC traces were measured at a scanning rate of 10 °C/min, under a nitrogen flow. Cyclic voltammograms (CVs) were recorded on a Solartron 1287 potentiostat using platinum electrodes at a scan rate of 50 $mV.s^{-1}$ and a Ag/Ag^{+} (0.10 M of $AgNO_3$ in acetonitrile) reference electrode in an anhydrous and argon saturated solution of 0.1 M of tetrabutylammonium tetrafluoborate (Bu_4NBF_4) in acetonitrile. Tetrabutylammonium tetrafluoborate (98 %, Aldrich) was recrystallized three times in 50:50 mixture of methanol/water and dried at 100°C under reduced pressure, as reported in the literature*[1]*. In these conditions, the oxidation potential ($E_{ox}^{½}$) of ferrocene was 0.11 V versus Ag/Ag^{+}, whereas the $E_{ox}^{½}$ of ferrocene was 0.41 V versus SCE. The HOMO and LUMO energy levels were determined from the oxidation and reduction onset of the second scan from CV data taking into account the SCE level at -4.7 eV *[2, 3]*. Out-of-plane X-ray diffraction (XRD) measurements were recorded at room temperature with a Siemens (D5000) diffractometer using Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 30 mA. The XRD patterns were obtained using Bragg-

Brentano geometry (θ-2θ) from thin films prepared in the same way as for the device on OTS-treated SiO_2/Si substrates.

Synthesis

Materials. All starting organic compounds were purchased from Aldrich, Alfa Aesar or TCI America and used without further purification. All reactions were carried out under argon at 1 atmosphere unless mentioned otherwise. Some reaction solvents were distilled before use (acetonitrile, chloroform, methanol and toluene from CaH_2). Column chromatography was carried out on silica gel (Size 40 - 63 µm, Pore size 60 Å, Silicycle). The 3,5-dibromo-1-trimethylsilylbenzene*[4]* purified by high vacuum distillation*[5]* (**1**), 2,7-dibromo-9-H-carbazole*[6]* (**4**), *N*-9'-heptadecanyl-2,7-dibromocarbazole*[7]* (**6**) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene*[8, 9]* (**7**) have been already reported in the literature. All other compounds have been synthesized following procedures described below.

3,5-Dioctyl-1-trimethylsilylbenzene **(2).** A flame-dried three neck flask fitted with a condenser and containing a magnetic stir bar was charged with 21.83 g (70.86 mmol) of 3,5-dibromo-1-trimethylsilylbenzene (**1**), 28.00 g (177.2 mmol) of fresh octyl boronic acid, 65.27 (283.4 mmol) of $K_3PO_4 \cdot H_2O$, 0.273 (1.417 mmol) of $Pd(OAc)_2$ and 1.164 g (2.834) of 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) then carefully evacuated and backfilled with argon (this sequence was repeated three times). Carefully degassed toluene (140 mL) with argon over 30 minutes was added via a syringe through the septum and the resulting mixture was heated at 100 °C with vigorous stirring overnight. The black reaction mixture was allowed to cool to room temperature, filtered through a thin pad of silica gel (eluting with hexanes) and concentrated under reduced pressure. Hexanes (500 mL) was added to the resulting oil and removed under reduced pressure to eliminate remaining toluene. This operation was repeated two times to afford 21.80 g (58.18 mmol) of a colorless oil. (Yield : 82 %).

^{1}H NMR (400MHz, $CDCl_3$, ppm) : δ 7.16 (s, 2H); 7.01 (s, 1H); 2.59 (t, *J* = 7.8 Hz, 4H); 1.63 (m, 4H); 1.32 (m, 20H); 0.90 (t, *J* = 6.9 Hz, 6H); 0.28 (s, 9H)

^{13}C NMR (100MHz, $CDCl_3$, ppm) : δ 142.19; 140.15; 130.86; 129.29; 36.27; 32.07; 31.89; 29.70; 29.66; 29.46; 22.85; 14.28; -0.85

HRMS : Calculated for $C_{25}H_{46}Si$: 374.3369 Found: 374.3372 ± 0.0011

3,5-dioctyl-1-iodobenzene **(3).** In a flame-dried round bottom flask, 20.00 g (53.37 mmol) of compound **2** was dissolved in anhydrous methanol (535 mL) and anhydrous chloroform (535 mL) then, 24.92 g (112.8 mmol) of silver trifluoroacetate was added. The reaction was cooled down to 0 °C and 27.49 g of iodine (106.7 mmol) added all at once. Within 30-60 min the reaction was completed by TLC analysis and filtered through Celite (washing with 750 - 1000 mL of additional hexanes). The solvent was evaporated and the crude product dissolved in hexanes (300 mL) then washed three times with saturated sodium thiosulfate (450 mL) then two times with water (450 mL). The organic layer was dried with $MgSO_4$ and the solvent removed under reduced pressure. The resulting oil was purified by short column chromatography (silica gel, hexanes as eluant) to obtain 22.32 g (51.77 mmol) of a colorless oil. (Yield : 97 %).

^{1}H NMR (400MHz, $CDCl_3$, ppm) : δ 7.36 (s, 2H); 6.94 (2, 1H); 2.51 (t, *J* = 7.8 Hz, 4H); 1.57 (m, 4H); 1.30 (m, 20H); 0.89 (t, *J* = 7.0 Hz, 6H)

^{13}C NMR (100MHz, $CDCl_3$, ppm) : δ 145.27; 134.77; 128.21; 94.57; 35.68; 32.03; 31.50; 29.57; 29.43; 29.39; 22.82; 14.27

HRMS : Calculated for $C_{22}H_{37}I$: 428.1940 Found: 428.1931 ± 0.0013

N(3',5'-Dioctylbenzene)-2,7-dibromocarbazole **(5).** A flame-dried three neck flask fitted with a condenser and a thermometer was charged with 2.890 g (8.893 mmol) of 2,7-dibromo-9-H-carbazole (**4**), 141 mg (0.741 mmol) of CuI, 170 mg (1.482 mmol) of L-Proline, 2.561 g (18.53 mmol) of anhydrous K_2CO_3 and 3.175 g (7.411 mmol) of 3,5-dioctyl-1-iodobenzene **(3)** then carefully evacuated and backfilled with argon (this sequence was repeated three times). Degassed anhydrous dimethylsulfoxide (8.9 mL) was added through the septum and the mixture heated at 85 °C (90 °C maximum) with an oil bath for 72 hours. The reaction mixture was then allowed to cool to room temperature, poured in 250 mL of distillated water and extracted three times with hexanes. The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was dissolved in dichloromethane, preadsorbed on silica gel and purified by column chromatography (silica gel, hexanes as eluent) to afford 1.203 g (1.923 mmol) of a colorless oil. (Yield : 26 %).

^{1}H NMR (400MHz, $CDCl_3$, ppm) : δ 7.93 (d, *J* = 8.3 Hz, 2H); 7.49 (d, *J* = 1.8 Hz, 2H); 7.39 (dd, J_1 = 8.3 Hz and J_2 = 1.7 Hz, 2H); 7.15 (m, 1H); 7.10 (d, *J* = 1.5 Hz, 2H); 2.70 (t, *J* = 7.7 Hz, 4H); 1.68 (m, 4H); 1.32 (m, 20H); 0.88 (t, *J* = 7.0 Hz, 6H)

^{13}C NMR (100MHz, $CDCl_3$, ppm) : δ 145.33; 142.15; 136.21; 128.86; 124.26; 123.49; 121.68; 121.53; 120.00; 113.35; 35.96; 32.04; 31.52; 29.63; 29.49; 29.42; 22.82; 14.27

HRMS : Calculated for $C_{34}H_{43}Br_2N$: 623.1762 Found: 623.1773 ± 0.0019

General Yamamoto polymerization procedure. In a three-necked flame-dried round bottom flask fitted with a condenser were added, in order, 2.4 eq of 2,2′-bipyridyl (BiPy), 2.4 eq of bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$), 2.4 eq of 1,5-cyclooctadiene (COD), anhydrous *N,N*-dimethylformamide (DMF) degassed via three freeze – pump – thaw cycles and anhydrous toluene.

The resulting solution was stirred at 60 – 65 °C for 30 min in absence of light. In the second flame-dried round bottom flask, 1.0 eq of monomer (**5)** or (**6)** was dissolved in anhydrous toluene. The monomer solution was added to the purple catalyst solution and the black resulting mixture was stirred at 60 – 70 °C for three days in absence of light. When needed, 2 or 3 mL of toluene were added to ensure a constant solvent concentration. After 72 hours, 1.0 eq of bromobenzene was added to the reaction. Sixteen hours later, the mixture was cooled and quenched into a 500 mL MeOH / HCl (4:1) solution. After a few minutes, the color of the suspension changed from black to light yellow. The resulting solution was stirred for two hours to destroy any residual catalyst before it was filtered through a 0.45 µM Teflon filter to afford a solid. The resulting polymer was put into a Soxhlet apparatus and was washed with acetone, hexanes and chloroform. The chloroform fraction (550-600 mL) was reduced to 40-50 mL under reduced pressure, precipitated in methanol/water (10:1, 500 mL), filtered through 0.45 µm nylon filter and finally air dried overnight.

Poly[N(3',5'-dioctylbenzene)-2,7-carbazole] **(P1)**. Following the general Yamamoto polymerization procedure, the polymer was synthesized using 210.3 mg (1.347 mmol) of BiPy, 370.4 mg (1.347 mmol) of Ni(COD)$_2$, 287 µL (1.347 mmol) of COD, 7.0 mL of DMF and 7.0 ml of toluene and 351.0 mg (0.5611 mmol) of monomer (**5**) dissolved into 14 mL of toluene. The title polymer was obtained as a light yellow powder. (181 mg; Yield : 69 %).

Poly[N-9'-heptadecanyl-2,7-carbazole] **(P2)**. Following the general Yamamoto polymerization procedure, the polymer was synthesized using 166.3 mg (1.065 mmol) of BiPy, 292.9 mg (1.065 mmol) of Ni(COD)$_2$, 227 µL (1.065 mmol) of COD, 5.5 mL of DMF and 5.5 mL of toluene and

250.0 mg (0.4437 mmol) of monomer (**6**) dissolved into 11 mL of toluene. The title polymer was obtained as a light yellow powder. (163 mg; Yield : 91 %).

General Stille polymerization procedure. In a 50 mL flame dried flask, 1.00 eq of monomer (**5**) or (**6**), 1.00 eq of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**7**), 0.02 eq of tris(dibenzylideneacetone)dipalladium(0) and 0.08 eq of tri(o-tolyl)phosphine were dissolved in degassed toluene. The reaction mixture was vigorously stirred at 90-95 °C. After 72 hours, 1.00 eq of bromobenzene was added to the reaction; then, one hour later, 1.00 eq of trimethyl(phenyl)tin was added and the reaction refluxed overnight to complete the end-capping reaction. The polymer was purified by precipitation in methanol/water (10:1), filtered through 0.45 µm nylon filter and washed on Soxhlet apparatus with acetone, hexanes, and chloroform. The chloroform fraction (550-600 mL) was reduced to 40-50 mL under reduced pressure, precipitated in methanol/water (10:1, 500 mL), filtered through 0.45 µm nylon filter and finally air dried overnight.

Poly[N(3',5'-dioctylbenzene)-2,7-carbazole-alt-2,2'-(5,5'-bithienylene)] (**P3**). Following the general Stille polymerization procedure, the polymer was synthesized using 321.8 mg (0.5145 mmol) of compound (**5**) and 253.0 mg (0.5145 mmol) of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**7**) in 5.1 mL of toluene to obtain 261 mg of an orange solid (81 % yield).

Poly[N(9'-heptadecanyl)-2,7-carbazole-alt-2,2'-(5,5'-bithienylene)] (**P4**). Following the general Stille polymerization procedure, the polymer was synthesized using 250.0 mg (0.4437 mmol) of compound (**6**) and 218.2 mg (0.4437 mmol) of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**7**) in 4.4 mL of toluene to obtain 231 mg of an orange solid (92 % yield).

OFETS preparation and measurements

A heavily p-doped Si wafers (resistivity 5-10 Ω cm) with a 6077 Å thermal SiO_2 (unit area capacitance, C = 5.68 nF cm^2) were used both as the substrate and as the gate electrode. First, all the substrates were cleaned by subsequent soaking in acetone (5 min), isopropanol in an ultrasonic bath at 80°C (5 min), and de-ionized (DI) water (10 min). Three kinds of surface treatments were used. In the case of plain SiO_2, the substrates were taken from the DI water, dried with nitrogen (contact angle H_2O = 30 ± 3°). In the case of HMDS- and OTS-treated SiO_2, the substrates were taken from DI water and activated by successive soakings in a $NH_4OH/H_2O_2/H_2O$ (2:2:100) solution in an ultrasonic bath at 80°C (5 min); DI water (1 min); $HCl/H_2O_2/H_2O$ (2:2:100) solution in an ultrasonic bath at 80°C (5 min); DI water (5 min) and dried with nitrogen. Then, the substrates were treated with UV/ozone photoreactor for one hour to remove any residual organic materials and to create a high density of silanol groups at the surface (contact angle H_2O about 3°). To improve the chemical and electrical properties of the gate dielectric, the SiO_2/Si substrates were modified with a self-assembled monolayer (SAM) of HMDS (hexamethyldisilazane) or OTS (octyltrichlorosilane). Thus, the substrates were treated with HMDS in a vapour prime system at 550 mT and 135°C for 12 min (contact angle H_2O = 78 ± 3°) or with OTS in a 5 mM octyltrichlorosilane solution in dry hexanes at room temperature for 24 h. After the OTS SAM formation, the substrates were removed and rinsed with hexanes, ultrasonicated in a clean vial in chloroform, acetone, isopropanol and DI water for 5 minutes each, and then heated at 100°C for 5 min (contact angle H_2O = 104 ± 3°). Films of **P1**, **P2**, **P3** and **P4** (with a thickness of 60, 50, 40 and 35 nm, respectively) were deposited on pre-treated SiO_2/Si substrates by spin-coating a 10 mg/mL solution of the polymer in chloroform or chlorobenzene. Then, films were heated under nitrogen at 55°C for 10 min in order to remove the residual solvent or annealed at a temperature between

120°C and 200°C for 30 min. The source and drain electrodes were defined by thermally evaporating gold (700 Å) through a shadow mask (channel width = 2600 μm, channel length = 45 μm) on top of the organic thin film forming top-contact geometry transistors. The OFETs were characterized under ambient conditions with an Agilent (4155c) semiconductor parameter analyser. The hole mobilities were calculated in the saturation regime *[10]* at V_{DS} = -100 V using the following equation $I_{DS} = (W/2L)\mu C_i(V_G-V_T)^2$, where V_{DS} is the source-drain voltage, I_{DS} is the source-drain current, W and L are, respectively, the channel width and length, μ is the field-effect mobility, C_i is the capacitance per unit area of the SiO_2 layer, and V_G and V_T are, respectively, the gate voltage and threshold voltage.

Thermal characterization

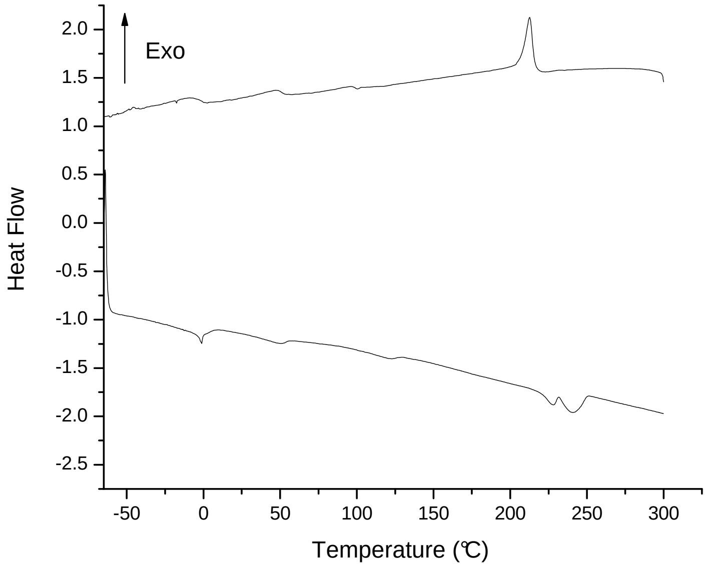

Figure S1. Differential scanning calorimetry thermogram for polymer P1.

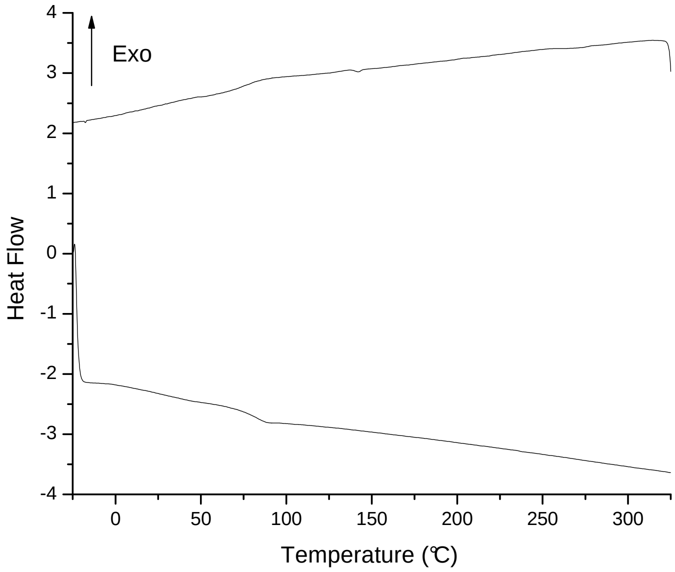

Figure S2. Differential scanning calorimetry thermogram for polymer P2.

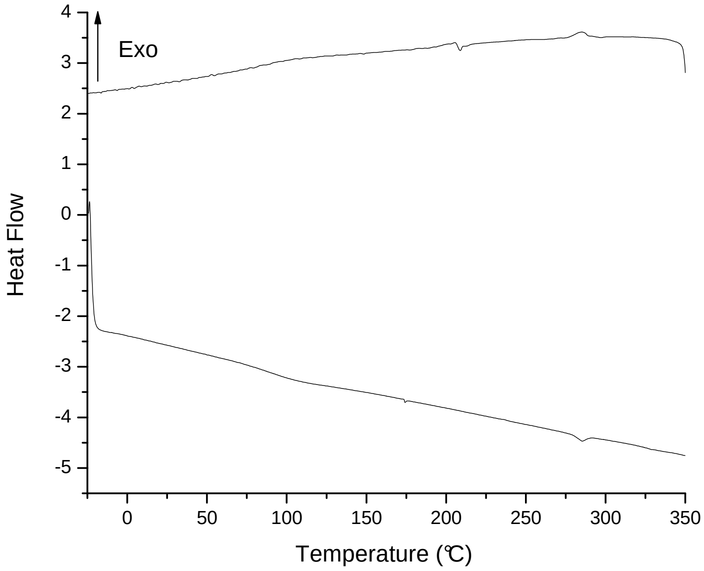

Figure S3. Differential scanning calorimetry thermogram for polymer P3.

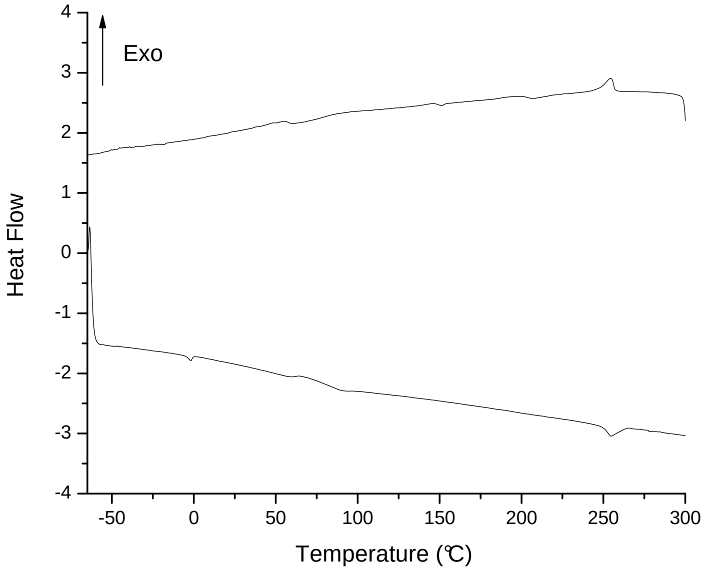

Figure S4. Differential scanning calorimetry thermogram for polymer P4.

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