Polyindolo[3,2-*b*]carbazoles: A New Class of p-Channel Semiconductor Polymers for Organic Thin-Film Transistors

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ABSTRACT: The synthesis and field-effect transistor (FET) properties of a novel class of indolocarbazole-based conjugated polymers, poly(indolo[3,2-*b*]carbazole)s, are described. Dehalogenative coupling polymerization of dichloroindolo[3,2-*b*]carbazoles with $Zn/NiCl_2/PPh_3$/2.2′-dipyridil gave the corresponding poly(indolo[3,2-*b*]-carbazole)s, while oxidative coupling polymerization of indolo[3,2-*b*]carbazoles with $FeCl_3$ proceeded regioselectively, affording poly(indolo[3,2-*b*]carbazole-2,8-diyl)s. Crystallization and optical properties of these polymers were different, depending on the regiochemistry of backbone linkages and peripheral substitutions. Thin film transistor devices using these polymer semiconductors exhibited p-channel FET behavior, dictated predominantly by nature of substitution and backbone linkages (2,8- or 3,9-linkage). Solution-processed polyindolo[3,2-*b*]carbazole thin-film semiconductors obtained from $FeCl_3$ polymerization generally provided better FET performance.

Introduction

The phenomenal explosion in research activities in organic thin-film transistors (OTFTs) in recent years is driven by the expectation that these are potentially very low-cost alternatives to silicon-based technologies for use in large-area, flexible, and ultra low-cost electronic applications.[1,2] OTFTs may be fabricated by common solution deposition/patterning techniques (e.g., coating, stamping, offset printing, inkjet printing, etc.) and on plastic substrates to enable flexible electronics. However, many organic semiconductors (e.g., pentacene,[3] regioregular poly(3-hexylthiophene)[4]) are sensitive to photoinduced oxidative interactions with atmospheric oxygen, leading to adversely degraded semiconductor properties. To overcome the photooxidative sensitivity, we recently developed a new class of indolo[3,2-*b*]-carbazole-based semiconductors, which exhibited significantly enhanced photostability by virtue of their relatively low-lying HOMOs and larger optical band gaps.[5,6] OTFTs using vacuum-evaporated indolo[3,2-*b*]carbazole thin-film semiconductors afforded field-effect transistor (FET) mobility up to ~0.14 $cm^2/(V\ s)$, manifesting efficient charge carrier injection and transport. As with most small-molecule organic semiconductors such as sexithiophenes, however, solution-processed indolo[3,2-*b*]-carbazole thin-film semiconductors yielded much lower mobility—a consequence attributable to difficulties in controlling thin-film quality of solution-processed small molecules as well as inefficiency of small molecules to establish optimum molecular ordering in thin films from solution. From this perspective, we envisioned that a polymeric system based on an indolo[3,2-*b*]-carbazole building block would be an ideal approach and offer a scalable process to stable, solution-processed semiconductors for OTFTs.

Results and Discussion

The indolo[3,2-*b*]carbazole units can be coupled at C-3/C-9 or C-2/C-8 positions to give poly(indolo[3,2-*b*]carbazole-3,9-diyl) (**I**) or poly(indolo[3,2-*b*]carbazole-2,8-diyl) **(II)**, respectively (Figure 1). Polymer **I** has an extended π-conjugation along its backbone, which resembles those of poly(*p*-arylene)s, while polymer **II** has a greatly restricted π-conjugation not along its backbone and resembles those of polyarylamines. In view of their different geometric and electronic structures, these polymers[7] are expected to exhibit different molecular organization behaviors and display distinctly different optoelectronic and electrical properties.

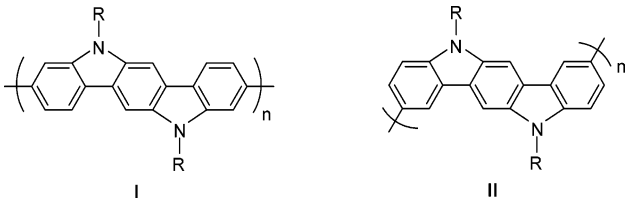

Figure 1. General structures of poly(indolo[3,2-*b*]carbazole-3,9-diyl), **I**, and poly(indolo[3,2-*b*]carbazole-2,8-diyl), **II**.

Polymers **I** and **II** were synthesized via a dehalogenative coupling polymerization of dihaloindolo[3,2-*b*]carbazole monomers, as described in Scheme 1. 3,9-Dichloroindolo[3,2-*b*]-carbazole (**1**) and 2,8-dichloroindolo[3,2-*b*]carbazole (**2**) were prepared respectively from condensation of 3- and 4-chlorophenylhydrazine with 1,4-cyclohexanedione, followed by double Fischer indolization. Subsequent alkylation or arylation with 1-bromododecane or 1-dodecyl-4-iodobenzene gave the corresponding 5,11-disubstituted monomers **3** and **4**. Dehalogenative coupling polymerization of **3** and **4** using $Zn/NiCl_2/PPh_3$/2,2′-dipyridyl in dimethylacetamide (DMAc)/toluene gave the respective poly(indolo[3,2-*b*]carbazole)s **I** and **II**. Gel permeation chromatography (GPC) analysis showed that these polymers had number-average molecular weights ranging from 3300 to 9200 against polystyrene standards (Table 1). The observed relatively low molecular weights of isolated polymer products were primarily due to their poor solubility characteristics in the polymerization medium (gelation or precipitation occurred in the late stage of polymerization). In THF solutions (Figure 2A and Table 1), polymers **Ia** and **Ib** showed strong UV−vis absorptions with λ_{max} at 421 and 410 nm, respectively, while polymers **IIa** and **IIb** exhibited absorptions at significantly shorter wavelengths with λ_{max} at 357 and 355 nm, respectively, and only very weak absorptions beyond 400 nm. These differ-

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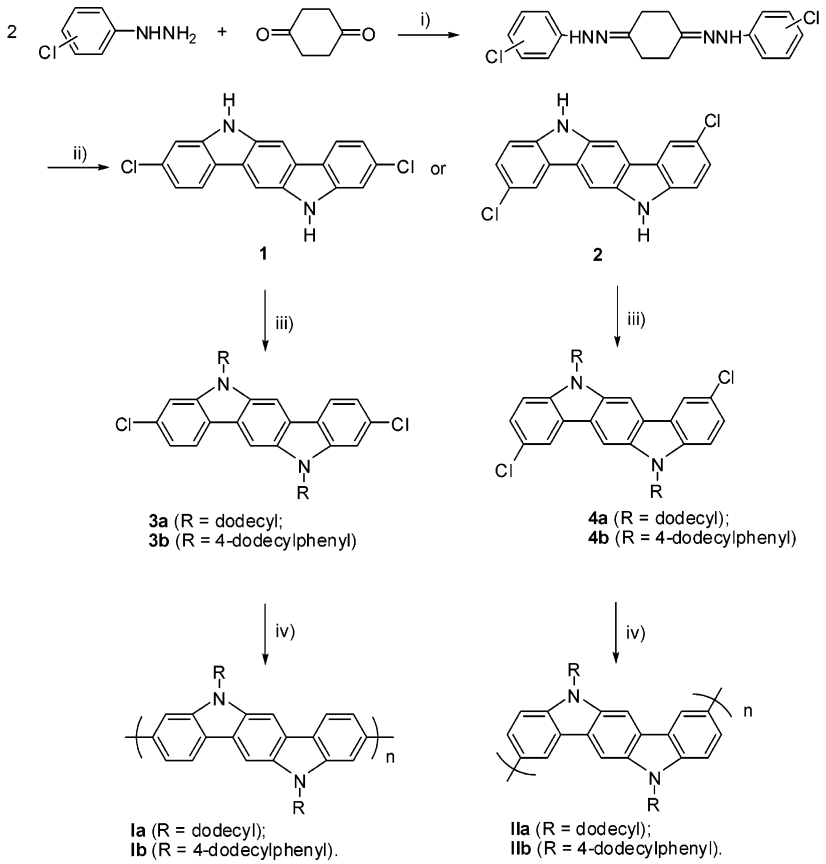
Scheme 1. Synthesis of Polyindolo[3,2-*b*]carabzoles via Dehalogenative Coupling Polymerization[a]



[a] (i) EtOH/50 °C, 1 h; (ii) H_2SO_4/AcOH/65 °C; (iii) $C_{12}H_{15}Br$/NaOH/DMSO/50 °C (**3a** and **4a**) or $C_{12}H_{25}C_6H_4I$, K_2CO_3, 1,2-dichlorobenzene/reflux (**3b** and **4b**); (iv) Zn/$NiCl_2$/2,2′-dipyridyl/DMAc.

Table 1. Properties of Polyindolo[3,2-*b*]carbazoles

					absorption λ_{max}, nm	
polyindolo[3,2-*b*]carbazole	polymerization methods	yield, %	M_n	M_w/M_n	THF solution	film
Ia	Zn-mediated dehalogenative coupling polymerization	80.9	9200	1.25	421, 400 (s)	477 (s), 438, 396 (s)
Ib		56.0	5700	1.15	410, 392 (s)	444 (s), 415
IIa		37.1	3300	1.44	428, 408, 357	435 (s), 414, 359
IIb		89.9	5700	1.16	418, 401, 355	423 (s), 403, 358
IIa	$FeCl_3$-mediated oxidative coupling polymerization	53.9	11200	2.63	428, 409, 360	425, 365
IIb		38.8	7000	2.08	418, 400, 354	422, 403, 356
IIc		81.2	4930	3.34	427, 407, 358	425, 362

ences in spectral properties reflected the extensive π-conjugation along the polymer backbone of **I** and the restricted π-conjugation systems of **II**. In fact, the spectral features of **II** are essentially similar to those of the corresponding monomeric indolo[3,2-*b*]-carbazoles.[5,6] In addition, **I** also exhibited 20−30 nm bathochromic shifts from solution to thin-film spectra (Figure 2B), indicative of the establishment of higher structural orders in the solid state through intermolecular $\pi-\pi$ interactions. In sharp contrast, the thin-film spectrum of **II** showed little bathochromic shifts over its solution spectral properties, revealing its inability to achieve higher molecular orders in the solid state.

An alternate synthesis of **II** could be realized by a regioselective oxidative coupling of indolo[3,2-*b*]carbazole since its C-2/C-8 positions are highly activated toward oxidative reaction owing to their para relationship to the amino functions. Accordingly, when 5,11-disubstituted indolo[3,2-*b*]carbazole **5** was treated with excess $FeCl_3$ in chlorobenzene at 50 °C for 24 h, oxidative coupling polymerization leading to the formation of **II** occurred in good yields (Scheme 2). The polymer products obtained from this polymerization process possessed higher molecular weight than those by dehalogenative polymerization (Table 1), primarily because of higher solubility characteristics of **II** in chlorobenzene reaction medium. ^{1}H NMR spectral analysis showed that these polymers were structurally similar to those obtained by dehalogenative coupling method (e.g., **IIa**; Figure 3), indicating that the present oxidative coupling reactions were highly regioselective. This was further supported by similarities in their other spectral properties (UV−vis and IR spectra).

The structural orderings of polyindolo[3,2-*b*]carbazoles in thin films were studied by X-ray diffraction (XRD). Thin films of these polymers were prepared on a silicon wafer by drop-casting from their hot 1 wt % solutions in chlorobenzene and then annealed at 80 °C for 2 h in vacuo before their XRD patterns were recorded (Figure 4). Poly(indolo[3,2-*b*]carbazole)s **Ia**, **Ib**, and **IIa** prepared by dehalogenative polymerization exhibited highly crystalline patterns with distinct primary diffraction peaks, while **IIb** showed broad and weak diffraction peaks, revealing

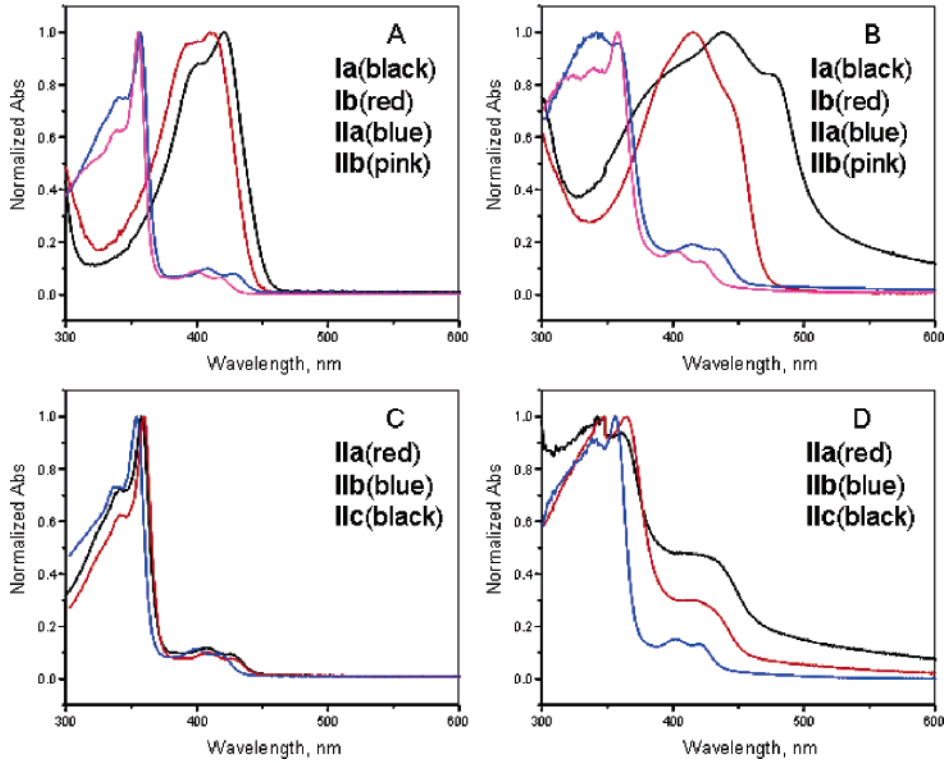
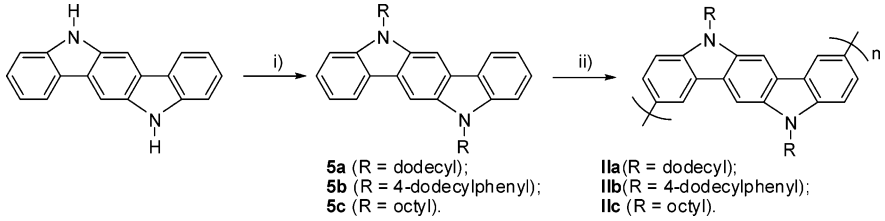


Figure 2. UV−vis absorption properties of polyindolocarbazoles **I** and **II**: A (THF solutions) and B (thin films) from polymers prepared by dehalogenative polymerization; C (THF solutions) and D (thin films) from polymers prepared via $FeCl_3$ polymerization.

Scheme 2. Synthesis of Polyindolocarabzoles via Oxidative Coupling Polymerization[a]



[a] (i) RBr/NaOH/DMSO/50 °C (**5a** and **5c**) or $C_{12}H_{25}C_6H_4I$, K_2CO_3, 1,2-dichlorobenzene/reflux (**5b**); (ii) $FeCl_3$/chlorobenzene/50 °C.

its poor crystallinity. **IIa** and **IIc** prepared by $FeCl_3$ polymerization also displayed high crystallinity, with strong primary diffraction peaks at $2\theta = 7.24°$ and 5.22°, corresponding to *d* spacing of 12.2 and 16.9 Å, respectively. However, the *d* spacing of the primary diffraction peak (16.9 Å) for **IIa** from $FeCl_3$ polymerization was significantly shorter than that from dehalogenative polymerization ($d = 22.3$ Å), which was likely due to markedly different molecular weights and thus different molecular orderings. **IIb** from $FeCl_3$ polymerization showed similar poor crystallinity as that from dehalogenative polymerization.

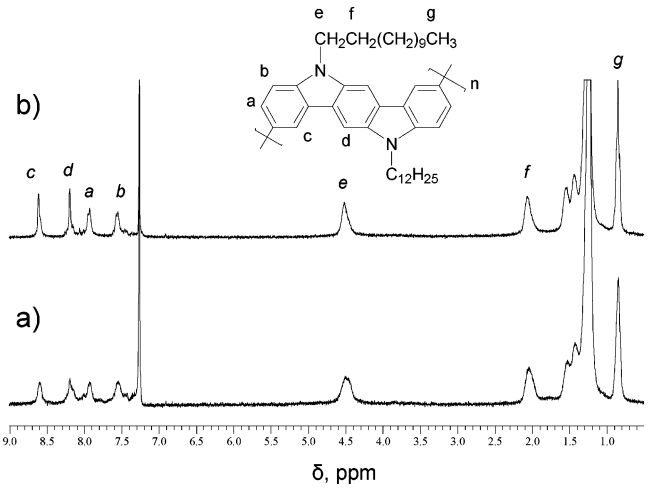


Figure 3. ^{1}H NMR spectra of polyinodolocarbazole **IIa** (a) from dehalogenative polymerization and (b) from $FeCl_3$ polymerization.

The FET characteristics of poly(indolo[3,2-*b*]carbazole) semiconductors were studied using a bottom-gate, top-contact TFT configuration. The fabrication and characterization of TFT devices were carried out under ambient conditions without taking any precautions to insulate the materials and devices from exposure to air, moisture, and light. The test TFT devices were built on an n-doped silicon wafer with the wafer itself serving as the gate electrode and its 110 nm surface thermal SiO_2 layer as the gate dielectric. The dielectric surface was modified with various modification agents [octyltrichlorosilane (OTS-8), phenyltrichlorosilane (PTS), and polystyrene] to improve device performance. For silane modification, the wafer SiO_2 surface was first cleaned with argon plasma and then washed with distilled water and 2-propanol. Subsequently, the wafer was immersed in 0.1 M solution of silane modification agent in toluene at 60 °C for 20 min, rinsed with toluene and 2-propanol, and then dried with an air stream. For polystyrene modification, a 0.5 wt % solution of polystyrene in *o*-xylene was spin-coated on the cleaned wafer surface at 3000 rpm for 30 s and dried to provide a thin polystyrene film, which was cross-linked by exposure to a 250 nm UV lamp at an intensity of 0.16 W/cm^2

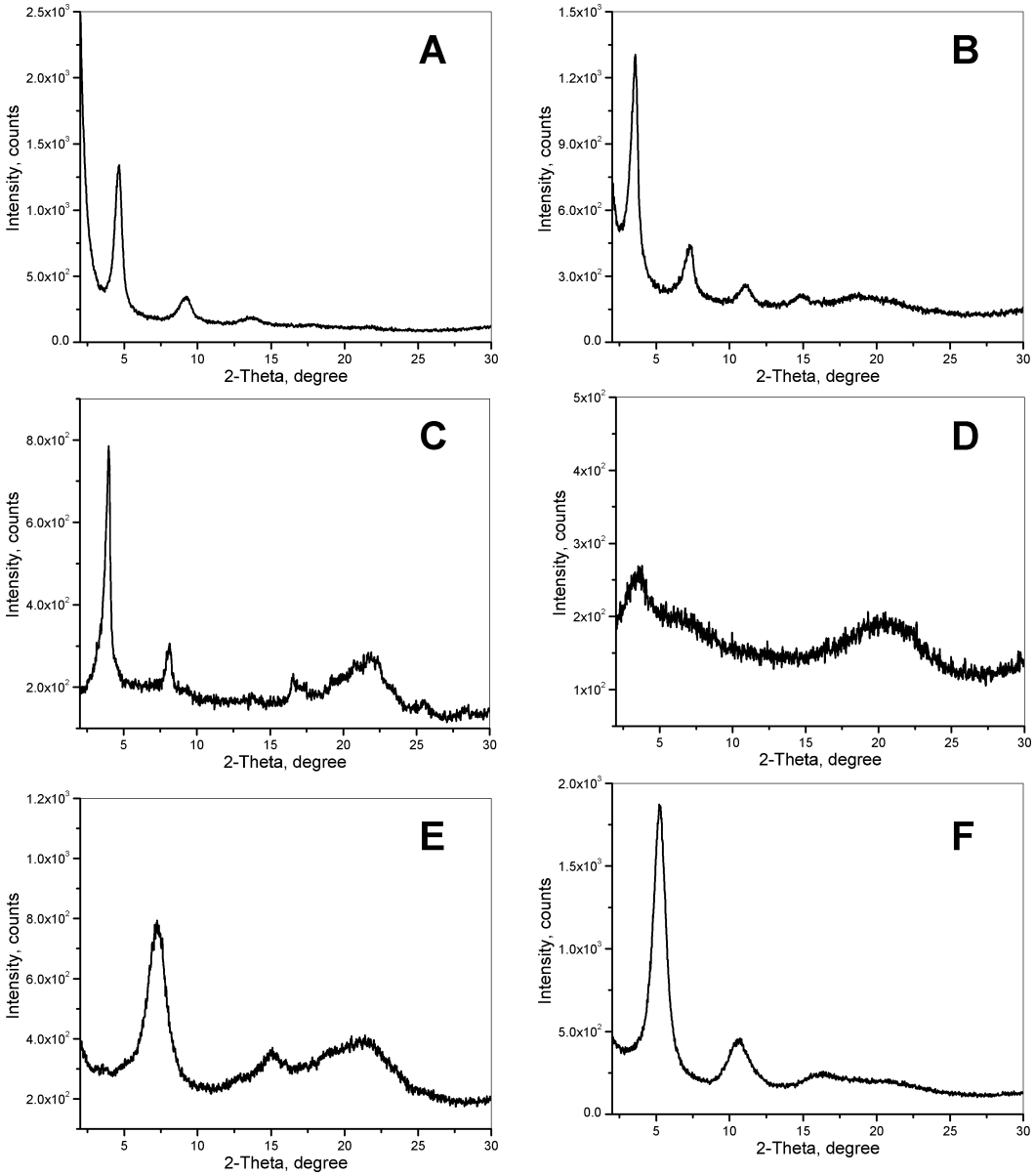


Figure 4. X-ray diffractions of drop-cast thin films of polyindolocarbazoles: A, B, C, and D were respectively from **Ia**, **Ib**, **IIa**, and **IIb** prepared by dehalogenative polymerization; E and F were respectively from **IIa** and **IIc** prepared by $FeCl_3$ polymerization.

for 12 s. The irradiated film was immersed in toluene at 60 °C for 20 min to remove the non-cross-linked fractions, followed by drying before use. The poly(indolo[3,2-*b*]carbazole) semiconductor was deposited on the nonmodified and modified wafer by spin-coating a 0.3−1 wt % solution of the polymer in 1,2-dichlorobenzene at 1000 rpm for 120 s and vacuum-dried to give a 20−50 nm thick semiconductor layer. Subsequently, the gold source/drain electrodes were deposited by vacuum evaporation through a shadow mask, thus creating a series of TFTs with various channel length (L) and width (W) dimensions.

The test TFT devices with channel length of 90 or 190 μm and channel width of 1 or 5 mm were used for $I-V$ measurements. The mobility in the saturated regime was extracted from the following equation:

$$\text{saturated regime } (V_D > V_G): \quad I_D = C_i\mu(W/2L)(V_G - V_T)^2$$

where I_D is the drain current, C_i is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are respectively the gate voltage and threshold voltage. V_T of the device was determined from the relationship between the square root of I_D at the saturated regime and V_G of the device by extrapolating the measured data to $I_D = 0$.

The FET performance of poly(indolo[3,2-*b*]carbazole) semiconductor in the TFT test devices depended on its backbone linkage positions (i.e., C-2/C-8 or C-3/C-9), nature of side chains, and polymerization methods. Poly(indolo[3,2-*b*]carbazole)s prepared by Zn-mediated dehalogenative coupling polymerization showed little or no FET properties. On the other hand, poly(indolo[3,2-*b*]carbazole)s obtained from $FeCl_3$-mediated oxidative coupling polymerization exhibited significant FET behaviors, with extracted mobility in the saturation regime up to 0.02 $cm^2/(V\ s)$. Figure 5 depicts the $I-V$ characteristics of a typical OTFT with poly(indolo[3,2-*b*]carbazole) **IIc**, which conformed to the conventional transistor models in both the linear and saturated regimes. The output curves showed good saturation behaviors with no observable contact resistance while the transfer curve in the saturated regime exhibited a near-quadratic increase in current as a function of gate bias; slight deviations at high voltages, which were likely due to bias stress effects, were however noted. The extracted mobility in the linear

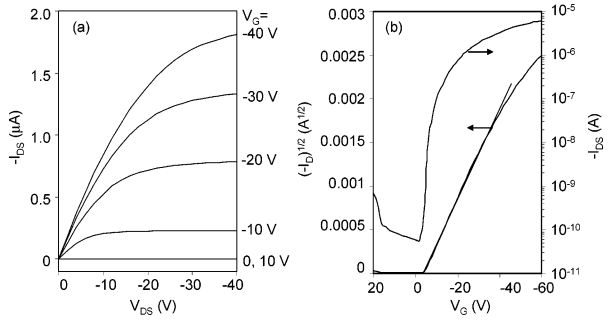


Figure 5. FET characteristics of an exemplary OTFT with **IIc** on polystyrene-modified substrate (channel length = 90 μm, channel width = 5000 μm): (a) output curves at different gate voltages and (b) transfer curve in saturated regime at constant source-drain voltage of −60 V and square root of the absolute value of current as a function of gate voltage.

regime was slightly lower than that in the saturated regime, and this was quite similar to OTFTs with most organic semiconductors. Table 2 summarizes the maximum saturation mobility values, threshold voltages, and current on/off ratios of OTFTs with solution-processed poly(indolo[3,2-*b*]carbazole) semiconductors on various dielectric surfaces. Both poly(indolo[3,2-*b*]-carbazole)s **Ia** and **Ib** prepared from dehalogenative polymerization at C-3/C-9 formed poor-quality thin films on hydrophobic surfaces (e.g., silane- and polystyrene-modified SiO_2 surface). Although they did form excellent films on nonmodified SiO_2 surface, no significant FET activity was detected. Similarly, while poly(indolo[3,2-*b*]carbazole)s **IIa** and **IIb** from dehalogenative polymerization also formed uniform semiconductor thin films on OTS-8-modified SiO_2 surface, their TFTs provided low mobility. This was not however the case with poly(indolo[3,2-*b*]carbazole)s prepared by $FeCl_3$ polymerization. Specifically, **IIa** and **IIc** exhibited better FET characteristics on polystyrene-modified SiO_2 surface, providing mobility as high as 0.02 cm^2 V^{-1} s^{-1}. On the other hand, poly(indolo[3,2-*b*]carbazole) **IIb** afforded much lower mobility due to the amorphous nature of its semiconductor film. The above results clearly showed that the FET performance of poly(indolo[3,2-*b*]carbazole)s depended not only on the regiochemistry and substutuents of the polymers but also on the processes by which they were synthesized.

In addition, the surface chemistry of gate dielectric also played a critical role on FET performance. As can be noted, with poly(indolo[3,2-*b*]carbazole) **IIc** as the semiconductor, OTS-8 modification of SiO_2 dielectric surface provided a conducive surface chemistry for semiconductor molecules to achieve optimum molecular ordering for charge carrier transport. The extracted mobility in this case was as much as 5 times higher than those of TFTs built on nonmodified SiO_2 surface. A further mobility improvement by a factor of 5 was achieved when polystyrene was used as surface modification layer. Polystyrene offered an optimum surface chemistry for poly(indolo[3,2-*b*]carbazole **IIc** likely because of its phenyl groups which provided better interaction with the fused-ring aromatic poly(indolo[3,2-*b*]-carbazole) semiconductor. This was partly supported by the finding that when OTS-8 was replaced with PTS (which as a phenyl group) as the modification agent for the SiO_2 dielectric in the TFT devices, a higher mobility was also observed.

The TFT devices using solution-processed thin-film semiconductors of poly(indolo[3,2-*b*]carbazole) **II** were stable under ambient conditions even when exposed to visible light. The HOMO levels of polymers **IIa**−**c**, as determined by cyclic voltammetry, are 5.1−5.2 eV from vacuum, almost identical to their small molecule counterparts. Their low-lying HOMOs and larger optical band gaps may explain for the resistance of these polymer semiconductors to photoinduced oxidative doping and degradation.

In conclusion, we have synthesized a new class of poly(indolo[3,2-*b*]carbazole)s with backbone linkages at C-2/C-8 and C-3/C-9 using a Zn-mediated dehalogenative coupling polymerization of dichloroindolo[3,2-*b*]carbazole. Poly(indolo[3,2-*b*]-carbazole)s with backbone linkages at C-2/C-8 were also synthesized by an $FeCl_3$-mediated oxidative coupling polymerization of indolo[3,2-*b*]carbazole. TFTs using solution-processed poly(indolo[3,2-*b*]carbazole) thin-film semiconductors with C-2/C-8 backbone linkages provided better FET performance, which may be attributed to the capability of the polymer to provide sufficient resonance stabilization to the ammonium radical cations formed in the charge carrier transport process.[6] In addition, poly(indolo[3,2-*b*]carbazole)s obtained from $FeCl_3$ polymerization were found to be better thin-film semiconductors, affording FET mobility to 0.02 cm^2 V^{-1} s^{-1}. The low-lying HOMOs and relatively large optical band gaps of poly(indolo-[3,2-*b*]carbazole)s also rendered these semiconductors unusually stable under ambient conditions even in the presence of visible light. These poly(indolo[3,2-*b*]carbazole)s therefore represent a useful class of solution-processable semiconductors for fabrication of stable OTFT circuits for printed electronics.

Experimental Section

1. Measurements. ^1H NMR spectra were recorded in $CDCl_3$ on a 300 MHz Bruker Spectrospin 300 spectrometer with tetramethylsilane as an internal standard. IR spectra were obtained on a Nicolet Magna-IR 500 Series II spectrophotometer. UV−vis absorption spectra were carried out on a Varian Cary 5 UV−vis NIR spectrophotometer. Thermal analysis was performed on TA Instruments DSC 2910 differential scanning calorimeter (DSC) at a heating rate of 5 °C/min under a nitrogen atmosphere. X-ray diffraction was recorded at room temperature on a Rigaku MiniFlex diffractometer using Cu Kα radiation (λ 1.54 18 Å) with a $\theta-2\theta$ scans configuration. OTFTs were characterized using Keithley SCS-4200 characterization system in ambient conditions.

Table 2. Summary of FET Properties of Poly(indolo[3,2-*b*]carbazole)s

poly(indolo[3,2-*b*]-carbazole)s	polymerization method	surface modification agent	mobility (cm^2 V^{-1} s^{-1})	threshold voltage (V)	on/off ratio
Ia	Zn-mediated dehalogenative coupling polymerization	none	N.A.	N.A.	N.A.
Ib		none	N.A.	N.A.	N.A.
IIa		OTS-8	1.5×10^{-5}	−12	10^2
IIb		OTS-8	8.0×10^{-4}	−10	10^3
IIa	$FeCl_3$-mediated oxidative coupling polymerization	polystyrene	9.6×10^{-3}	−8	10^5
IIb		polystyrene	1.8×10^{-3}	−10	10^3
IIc		none	7.0×10^{-4}	−20	10^3
		OTS-8	3.8×10^{-3}	−14	10^4
		PTS	5.3×10^{-3}	−8	10^5
		polystyrene	2.0×10^{-2}	−4	10^5

Cyclic voltammetric measurements were performed on a BAS 100 voltammetric system with a three-electrode cell in a solution of tetrabutylammonium perchlorate (Bu_4NClO_4) (0.10 M) in acetonitrile at a scanning rate of 40 mV s^{-1}. An Ag/AgCl electrode, a platinum wire, and a sealed platinum rod were used as the reference electrode, counter electrode, and working electrode, respectively. The working platinum electrode was coated with a 0.5 wt % solution of poly(indolo[3,2-*b*]carbazole) in chlorobenzene and heated in a vacuum oven at 150 °C for 10 min to give a thin poly(indolo[3,2-*b*]carbazole) film on the electrode. The HOMO energy levels were estimated using the equations $E_{HOMO} = Ep' + 4.38$ eV, where Ep' is the onset potential for oxidation relative to the Ag/AgCl reference electrode.[8]

2. Materials Synthesis. All reagents were used as received from Sigma-Aldrich. 5,11-Indolo[3,2-*b*]carbazole,[9] 3,9-dichloroindolo-[3,2-*b*]carbazole (**1**),[6] 2,8-dichloroindolo[3,2-*b*]carbazole (**2**),[6] 3,9-dichloro-5,11-didodecylinodolo[3,2-*b*]carbazole (**3a**),[6] 2,8-dichloro-5,11-didodecylindolo[3,2-*b*]carbazole (**4a**),[6] 5,11-dioctylinodolo[3,2-*b*]carbazole (**5a**),[5] and 5,11-didodecylinodolo[3,2-*b*]carbazole (**5b**)[5] were synthesized according to the procedures in the literature.

3,9-Dichloro-5,11-bis(4-dodecylphenyl)indolo[3,2-*b*]carbazole (3b). 1-Dodecyl-4-iodobenzene which was used in the condensation reaction was prepared as follows. A mixture of 1-phenyldodecane (26.33 g, 106.84 mmol), iodine (10.85 g, 42.75 mmol), H_5IO_6 (4.87 g, 21.37 mmol), acetic acid (54 mL), deionized water (9.6 mL), and 98% sulfuric acid (3.53 g) in a 250 mL flask was heated at 80 °C for ~3 h until the purple iodine color disappeared. The resulting mixture was extracted with dichloromethane, neutralized with saturated aqueous $NaHCO_3$ solution, and washed three times with water. The organic layer was separated, dried over $MgSO_4$, and filtered, and the solvent was removed using a rotary evaporator. After column chromatography on silica gel using hexane as an eluent, 38.80 g of a colorless viscous liquid was obtained. ^{1}H NMR indicated that the crude product was a mixture of 1-dodecyl-4-iodobenzene (69%), 1-dodecyl-2-iodobenzene (24%), and unreacted 1-phenyldodecane (7%). This crude product was used in subsequent preparation of 5,11-bis(4-dodecylphenyl)-indolo[3,2-*b*]carbazole, **3b**, without purification. ^{1}H NMR data for 1-iodo-4-dodecylbenzene ($CDCl_3$): δ 7.58 (d, J = 8.3 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 2.53 (t, J = 7.8 Hz, 2H), 1.57 (m, 2H), 1.20−1.40 (m, 18H), 0.88 (t, J = 6.5 Hz, 3H).

A mixture of 3,9-dichloroindolo[3,2-*b*]carbazole, **1** (0.69 g, 2.12 mmol), 18-crown-6 (0.11 g, 0.42 mmol), K_2CO_3 (2.34 g, 17.0 mmol), 1-iodo-4-octylbenzene (3.43 g, 6.37 mmol, 69% of purity) as prepared above, copper (0.54 g, 8.5 mmol), and 1,2-dichlorobenzene (8.5 mL) was charged into an argon-filled 50 mL flask fitted with a condenser. The mixture was heated under reflux in an argon atmosphere for 24 h. Subsequently, the reaction mixture was cooled to room temperature, diluted with tetrahydrofuran, and filtered. A viscous liquid, which was obtained after removal of solvent using a rotary evaporator, was added to 100 mL of methanol with vigorous stirring. The precipitated yellow solid was filtered, washed several times with water and methanol, then dissolved in 100 mL of hexane by heating, and filtered to remove the insoluble materials. The filtrate was concentrated to about 50 mL, allowed to cool to room temperature, and then chilled at 0 °C overnight. The crystallized yellow product was filtered, washed with a small amount of hexane, and dried to yield 1.23 g (71.4%) of 5,11-bis-(4-dodecylphenyl)indolo[3,2-*b*]carbazole, **3b**; mp 151.7 °C. ^{1}H NMR ($CDCl_3$): δ 7.99 (d, J = 8.3 Hz, 2H), 7.95 (s, 2H), 7.50 (m, 8H), 7.35 (d, J = 1.8 Hz, 2H), 7.18 (dd, J_1 = 8.3 Hz, J_2 = 1.8 Hz, 2H), 2.78 (t, J = 7.7 Hz, 4H), 1.77 (pent, J = 7.5 Hz, 4H), 1.25−1.60 (m, 36H), 0.89 (t, J = 6.6 Hz, 6H). IR (NaCl): 2923, 2852, 1614, 1517, 1502, 1463, 1438, 1375, 1337, 1304, 1235, 1068, 960, 799 cm^{-1}. MS (TOF): m/z 812.4595 (812.4603 calcd for $C_{54}H_{66}N_2Cl_2$).

2,8-Dichloro-5,11-bis(4-dodecylphenyl)indolo[3,2-*b*]carbazole (4b). This compound was prepared from 2,8-dichloroindolo-[3,2-*b*]carbazole (**1b**) and 1-dodecyl-4-iodobenzene using a similar synthetic procedure for **3b**; yield 68.5%, mp 165.8 °C. ^{1}H NMR ($CDCl_3$): δ 8.07 (dd, J_1 = 1.8 Hz, J_2 = 0.9 Hz, 2H), 7.97 (s, 2H), 7.49 (m, 8H), 7.32 (d, J = 1.8 Hz, 2H), 7.31 (d, J = 0.9 Hz, 2H), 2.78 (t, J = 7.8 Hz, 4H), 1.77 (pent, J = 7.4 Hz, 4H), 1.25−1.60 (m, 36H), 0.89 (t, J = 6.6 Hz, 6H). IR (NaCl): 2922, 2851, 1605, 1518, 1465, 1456, 1375, 1319, 1261, 1235, 1179, 1074, 835, 797 cm^{-1}. MS (TOF): m/z 812.4578 (812.4603 calcd for $C_{54}H_{66}N_2Cl_2$).

5,11-Bis(4-dodecylphenyl)indolo[3,2-*b*]carbazole (5b). This compound was prepared from indolo[3,2-*b*]carbazole and 1-dodecyl-4-iodobenzene using a similar synthetic procedure for **3b**; yield 48.3%, mp 126.5 °C. ^{1}H NMR ($CDCl_3$): δ 8.12 (d, J = 7.7 Hz, 2H), 8.05 (s, 2H), 7.58 (d, J = 8.3 Hz, 4H), 7.47 (d, J = 8.3 Hz, 4H), 7.40 (m, 4H), 7.22 (m, 2H), 2.78 (t, J = 7.7 Hz, 4H), 1.77 (m, 4H), 1.25−1.60 (m, 36H), 0.89 (t, J = 6.5 Hz, 6H). IR (NaCl): 3047, 2955, 2920, 2851, 1607, 1517, 1476, 1451, 1324, 1236, 839, 731 cm^{-1}. MS (TOF): m/z 744.5340 (744.5383 calcd for $C_{54}H_{68}N_2$).

Poly(5,11-didodecylindolo[3,2-*b*]carbazole-3,9-diyl) (Ia). To a 25 mL flask were added **3a** (0.662 g, 1 mmol), zinc powder (0.262 g, 4 mmol), triphenylphosphine (0.131 g, 0.5 mmol), 2,2′-dipyridil 10.9 mg, 0.07 mmol), anhydrous nickel(II) chloride (9.1 mg, 0.07 mmol), and DMAc (2 mL). The flask containing the mixture was degassed and then filled with argon, and the procedure was repeated two more times. The reaction mixture was heated to 80 °C and maintained at this temperature for 10 min. Toluene (1 mL) was added, and the heating was continued for 40 min until the mixture became viscous and some insoluble materials formed. At this time, additional toluene (2 mL) was added, and the mixture was stirred for 40 min until the mixture became viscous again. Then toluene (3 mL) was added and stirred for another 24 h. The reaction mixture was cooled to room temperature and poured into methanol (200 mL) containing 2 N aqueous HCl solution (20 mL). After stirring for 30 min, 2 N aqueous ammonia solution (30 mL) was added. The precipitated solid was filtered, washed with water and methanol, and dried. The solid was extracted with heptane in a Soxhlet apparatus for 24 h to remove oligomer materials. The resulting solid was dissolved in chlorobenzene and precipitated from methanol (200 mL); yield 0.478 g (80.9%). GPC: M_n = 9200, M_w/M_n = 1.25. ^{1}H NMR ($CDCl_3$): δ 8.32 (2H), 8.09 (2H), 7.76 (2H), 7.65 (2H), 4.53 (4H), 2.05 (4H), 1.25−1.60 (m, 36H), 0.86 (6H). IR (NaCl): 2921, 2851, 1619, 1510, 1468, 1445, 1375, 1340, 1247, 1120, 832, 798 cm^{-1}.

Poly(5,11-bis(4-dodecylphenyl)indolo[3,2-*b*]carbazole-3,9-diyl) (Ib). This polymer was prepared in accordance with the synthetic procedure for **Ia** using **3b** as the monomer; yield 56.0%. GPC: M_n = 5700, M_w/M_n = 1.15. ^{1}H NMR ($CDCl_3$): δ 8.14, 8.05, 7.64, 7.50, 2.80 (4H), 1.80 (4H), 1.29−1.52 (m, 36H), 0.88 (6H). IR (NaCl): 3033, 2923, 2852, 1610, 1518, 1459, 1340, 1230, 1190, 840, 794 cm^{-1}.

Poly(5,11-didodecylindolo[3,2-*b*]carbazole-2,8-diyl) (IIa). This polymer was prepared in accordance with the synthetic procedure for **Ia** using **4a** as the monomer; yield 37.1%. GPC: M_n = 3300, M_w/M_n = 1.44. ^{1}H NMR ($CDCl_3$): δ 8.59 (2H), 8.19 (2H), 7.92 (2H), 7.55 (2H), 4.50 (4H), 2.04 (4H), 1.23−1.60 (m, 36H), 0.84 (6H). IR (NaCl): 2923, 2851, 1616, 1509, 1468, 1314, 1232, 834, 794 cm^{-1}.

Poly(5,11-bis(4-dodecylphenyl)indolo[3,2-*b*]carbazole-2,8-diyl) (IIb). This polymer in accordance with the synthetic procedure for **Ia** using **4b** as the monomer; yield 89.9%. GPC: M_n = 5700, M_w/M_n = 1.16. ^{1}H NMR ($CDCl_3$): δ 8.43 (2H), 8.18 (2H), 7.74 (2H), 7.64 (4H), 7.51 (6H), 2.81 (4H), 1.80 (4H), 1.26−1.55 (m, 36H), 0.87 (6H). IR (NaCl): 3033, 2923, 2852, 1608, 1516, 1453, 1320, 1232, 840, 801 cm^{-1}.

Poly(5,11-dioctylindolo[3,2-*b*]carbazole-2,8-diyl)-$FeCl_3$ (IIc). **5a** (0.481 g, 1 mmol) in chlorobenzene (10 mL) was added to a mixture of $FeCl_3$ (0.681 g, 4.2 mmol) and chlorobenzene (20 mL) in a 50 mL flask under an argon atmosphere. The reaction mixture was heated to 50 °C and stirred for 24 h. After cooling to room temperature, the reaction mixture was poured into methanol (200 mL). The precipitated solid was washed with water and methanol

for many times. The solid was then suspended in 2 N aqueous ammonia solution (100 mL) for 1 h, filtered, and subjected to Soxhlet extraction with methanol for 24 h and then heptane for 24 h. The residue in the Soxhlet apparatus was dissolved with chlorobenzene and precipitated from methanol; yield 0.40 g (81.2%). GPC (THF-soluble fraction): $M_n = 4930$, $M_w/M_n = 3.34$. ^{1}H NMR ($CDCl_3$): δ 8.61 (2H), 8.19 (2H), 7.93 (2H), 7.55 (2H), 4.51 (4H), 2.06 (4H), 1.23−1.60 (m, 20H), 0.88 (6H). IR (NaCl): 3045, 2923, 2852, 1618, 1507, 1467, 1313, 1227, 833, 788 cm^{-1}.

Poly(5,11-didodecylindolo[3,2-*b*]carbazole-2,8-diyl)-$FeCl_3$ (IIa). This polymer was in accordance with the synthetic procedure for **IIc** using **5b** as the monomer; yield 53.9%. GPC: $M_n = 11\,200$, $M_w/M_n = 2.63$. ^{1}H NMR ($CDCl_3$): δ 8.61 (2H), 8.19 (2H), 7.92 (2H), 7.55 (2H), 4.52 (4H), 2.06 (4H), 1.23−1.60 (m, 36H), 0.85 (6H). IR (NaCl): 3036, 2922, 2852, 1619, 1507, 1467, 1314, 1228, 834, 789 cm^{-1}.

Poly(5,11-bis(4-dodecylphenyl)indolo[3,2-*b*]carbazole-2,8-diyl)-$FeCl_3$ (IIb). This polymer was prepared in accordance with the synthetic procedure for **IIc** using **5c** as a monomer; yield 38.8%. GPC: $M_n = 7000$, $M_w/M_n = 2.08$. ^{1}H NMR ($CDCl_3$): δ 8.43 (2H), 8.18 (2H), 7.75 (2H), 7.65 (2H), 7.50 (4H), 7.42 (2H), 2.80 (4H), 1.79 (4H), 1.26−1.55 (m, 36H), 0.87 (6H). IR (NaCl): 3033, 2924, 2852, 1608, 1516, 1452, 1320, 1233, 841, 802 cm^{-1}.

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