# Dithienosilole− and Dibenzosilole−Thiophene Copolymers as Semiconductors for Organic Thin-Film Transistors

Hakan Usta, Gang Lu, Antonio Facchetti,* and Tobin J. Marks*

Department of Chemistry and the Materials Research Center, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

Received May 4, 2006; E-mail: a-facchetti@northwestern.edu; t-marks@northwestern.edu

The design and realization of new π-conjugated organic semiconductors has been a topic of great research interest for the past decade.[1] The most prominent examples of such materials are polycondensed benzenoids, polyacetylenes, and (oligo)polyheteroaromatics.[1,2] Among these, the silole (silacyclopentadiene) moiety has recently been investigated as a novel conjugated system in which the σ^*-orbital of the silicon−carbon bond effectively interacts with the π^*-orbital of the butadiene fragment, leading to a low-lying LUMO.[3] In particular, since Tamao et al. reported that 2,5-bis(2-pyridyl)silole derivatives exhibit electron-transporting properties,[4] a number of applications of silole-containing small molecules and polymers have emerged, including new conducting polymers,[5] OLEDs,[6] and solar cells.[7] Very recently, silole-containing polymers have also been used to fabricate organic field-effect transistors (OFETs[8]).[9]
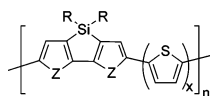

TS6T1 (1) : Z = S, R = C_6H_{13}, x = 1
TS6T2 (2) : Z = S, R = C_6H_{13}, x = 2
BS8T1 (3) : Z = CH=CH, R = C_8H_{17}, x = 1
BS8T2 (4) : Z = CH=CH, R = C_8H_{17}, x = 2
F8T1   (5) : Z = CH=CH, R = C_8H_{17}, x = 1
              C instead of Si
F8T2   (6) : Z = CH=CH, R = C_8H_{17}, x = 2
              C instead of Si

The above considerations and the possibility that incorporation of electron-withdrawing silacycles might enhance π-electron overlap along conjugated polymer backbones, without compromising environmental stability, prompted us to synthesize new silole-containing π-conjugated polymers and to investigate their properties in OFETs. Note that from literature diffraction and computational studies, silole-containing molecular cores are expected to be planar, and the bulkiness of the silicon substituents should have little impact on the ring planarity.[10] In this communication, we report the realization of four new silolearene−thiophene copolymers, **1**−**4**, and compare their properties with new fluorene−thiophene-based polymer **F8T1** (**5**) and widely investigated **F8T2** (**6**). It is seen that the silole-based materials can be synthesized in high yields, are environmentally stable, and yield solution-processable films which act as efficient hole transporters in FET devices. Carrier mobilities as high as ∼0.06 cm^2/Vs and current on/off ratios of ∼10^5−10^6 for unaligned films are measured in devices functioning in ambient conditions.

Polymer synthetic details can be found in Supporting Information. Briefly, polymers **1** and **2** were prepared via Stille coupling sequences by reacting silole precursor **10** with thiophene reagents **11** and **12**, respectively (Scheme 1, top), in refluxing THF using Pd(PPh₃)₂Cl₂ as the catalyst. The synthesis of polymers **3**−**6** was then carried out using a modified Suzuki polycondensation (Scheme 1, bottom for **3** and **4**) in a biphasic reaction with Pd[PPh₃]₄ as the catalyst. The solvents were toluene and aqueous sodium bicarbonate, and Aliquat 336 was used as the phase transfer agent to maximize

Scheme 1. Synthetic Route to Polymers **1**−**4**
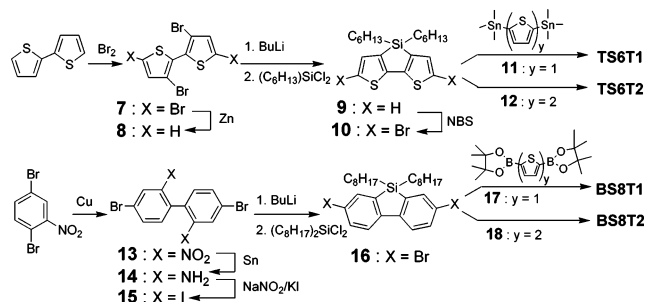
Table 1. Physicochemical Properties [Molecular Weight (M_w, KD), Polydispersity (PD), Solution and Film Optical Absorption Maxima (λ, nm),[a] Energy Gaps (E_g, eV)], OFET Charge Carrier Mobilities (μ, cm^2 V^{-1} s^{-1}),[b] and Current On/Off Ratios (I_{on}:I_{off}) in Air for Polymers **1**−**6**

polymer	M_w (PD)	λ_{sol} (E_g)	λ_{film} (E_g)	μ_h	I_{on}:I_{off}
TS6T1	30 (2.9)	521 (2.0)	574 (1.8)	0.02	2×10^5
TS6T2	41 (3.0)	544 (1.9)	545 (1.9)	0.06	5×10^5
BS8T1	112 (3.1)	473 (2.5)	484 (2.5)	6×10^{-5}	3×10^4
BS8T2	127 (3.7)	503 (2.3)	493 (2.3)	0.006	2×10^6
F8T1	17 (2.6)	427 (2.6)	440 (2.5)	9×10^{-5}	2×10^5
F8T2	80 (3.3)	456 (2.4)	460 (2.4)	0.006	2×10^5

[a] λ_{max} at the longest wavelengths. [b] Calculated in saturation for device structure n^{2+}−Si/SiO₂−HMDS (300 nm)/polymer (20−30 nm)/Au contacts (50 nm). OFETs tested in ambient conditions.

product molecular weight. All of the polymers were purified by dissolution in minimal amounts of THF or TCB and precipitation from large amounts of boiling methanol, cooled to room temperature, stirred overnight, and then collected by centrifugation. The dissolution−precipitation process was repeated multiple times. The polymer structures were verified by ¹H and ¹³C NMR spectroscopy and elemental analysis. Polymer molecular weights were determined by GPC versus polystyrene, and results are summarized in Table 1. Note that the M_w values of copolymers **3** and **4** are greater than those of **1** and **2**, and we are currently optimizing the synthesis of **1** and **2** following the Suzuki protocol.

The thermal properties of the present polymers were examined by differential scanning calorimetry (Figure S1). Polymers **2**, **3**, and **5** exhibit a single broad endotherm centered at 250−300 °C without apparent exothermic return peaks. In contrast, polymers **1** and **4** exhibit single reversible endothermic (260 and 330 °C, respectively) and exothermic (230 and 290 °C, respectively) transitions, whereas **F8T2** (**6**) behaves as previously reported.[11] Thermogravimetric analysis scans of **1**−**4** (Figure S2) exhibit negligible weight loss below 400 °C, demonstrating excellent thermal stability. Optical absorption data for polymers **1**−**6** in THF solutions and as thin films are summarized in Table 1, and spectra are shown in Figure S3.
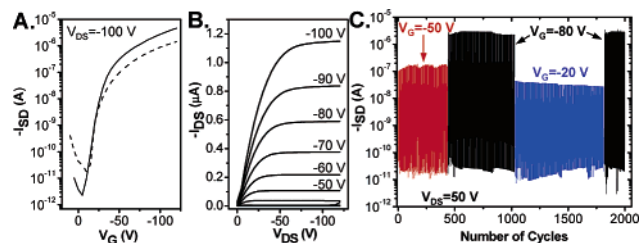
Figure 1. **BS8T2**-based FETs. (A) Transfer plots before (dotted line) and after film annealing (solid line). (B) Output plot of an annealed device. (C) ON−OFF cycles (0.03 Hz) under ambient conditions for the annealed device at $V_{DS} = -50$ V for different gate biases.

Note that the λ_{max} values of silole-based polymers **3** and **4** are red-shifted by ∼40−50 nm versus fluorene-based analogues **5** and **6**, demonstrating Si σ*-orbital involvement in the π-conjugation. Furthermore, note that $1 \rightarrow 3$ and $2 \rightarrow 4$ λ_{max} trends reflect both the effects of the π electron-donating S atom versus simple −C≡C− and the more planar conformation of five-five versus five-six inter-ring linkages in contributing to the large bathochromic shifts [40−50 nm (THF), 60−90 nm (film)]. Thus, the polymer band gaps (Table 1) are found on average to decrease going from **5**, **6** (2.4−2.6 eV) to **3**, **4** (2.3−2.5 eV) to **1**, **2** (1.8−2.0 eV).

OFETs were fabricated as described in Supporting Information with semiconductor films deposited by spin-coating from THF (**1** and **2**) or 1,2,4-trichlorobenzene (**3−6**) solutions. That good OFET response is achieved using low-boiling THF[12] is unprecedented and appears to reflect the substantial microstructural ordering (vide infra). After spin-coating and before Au contact deposition, the films were annealed at 230−250 °C for 30 min under N_2. Annealing significantly improves device performance as shown in Figure 1A for **BS8T2**. Output/transfer plots for **1−6** are shown in Figures 1 and S4−6.

Polymers **TS6T1** (**1**) and **TS6T2** (**2**) exhibit high saturation hole carrier mobilities of ∼ 0.02 and 0.06 cm²/Vs, respectively, and I_{on}:$I_{off} > 10^5$ when measured in air (Figure S4). This is remarkable considering the modest molecular weights and is likely a consequence of the high degree of microstructural order as supported by film X-ray diffraction data (Figure S7). Spin-coated or solution-cast films of regioregular polythiophenes, such as **P3HT** and **PQT**, *but not* **F8T2**, are known to self-organize into π-stacked/edge-on lamellar structures parallel to the HMDS−SiO$_2$ substrate normal, resulting in very efficient charge transport.[13] Bithiophene-based polymers **BS8T2** (**4**) and **F8T2** (**6**) also exhibit appreciable field-effect mobilities (∼0.006 cm²/Vs) and I_{on}:I_{off} ratios ($>10^6$ and $>10^5$, respectively). The FET parameters for **F8T2** are very similar to literature values for unaligned films.[14] Note that OFETs based on silole-based polymers **TS6T2** (Figure S8) and **BS8T2** (Figure 1C) can be ON−OFF cycled repeatedly under ambient conditions at different V_G values with negligible degradation of output characteristics, demonstrating impressive stability. When deposited and annealed under similar conditions, **BS8T1** (**3**) and **F8T1** (**5**) exhibit far lower performance ($\mu \sim 10^{-4}$ cm²/Vs and I_{on}:$I_{off} \sim 10^5$), probably the combined result of lower π-conjugation and poor crystallinity, verified by film XRD.

In conclusion, four new silolearene copolymers have been synthesized and characterized in OFET devices. Carrier mobilities approaching 0.1 cm²/Vs and I_{on}:$I_{off} > 10^5-10^6$ have been achieved for *unaligned* films. To better study and understand their physicochemical/OFET properties, the fluorenyl analogues **F8T1** and **F8T2** were also synthesized. The results clearly demonstrate that silole-arene copolymer films are highly textured and can exhibit substantial hole mobilities and I_{on}:I_{off} ratios, rivalling those of comparably processed and more widely investigated/optimized

F8T2 and polythiophenes. It is likely that OFET performance can be further improved via optimization of polymer M_w and film deposition/processing conditions.

Supporting Information Available: Polymers **1−6** syntheses/spectroscopic data and FET device fabrication. Figures S1−S8. This material is available free of charge via the Internet at http://pubs.acs.org.

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