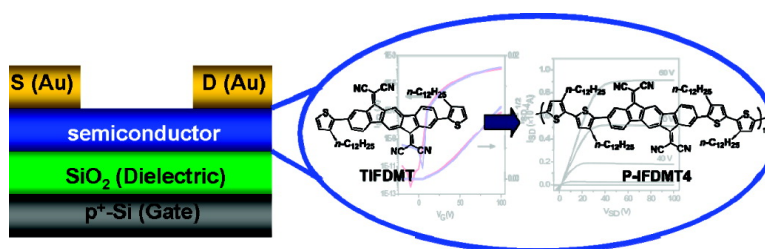


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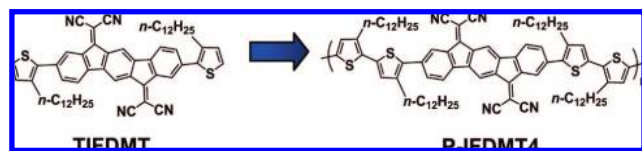
Air-Stable, Solution-Processable *n*-Channel and Ambipolar Semiconductors for Thin-Film Transistors Based on the Indenofluorenebis(dicyanovinylene) Core

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

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

Received March 27, 2008; E-mail: a-facchetti@northwestern.edu; t-marks@northwestern.edu

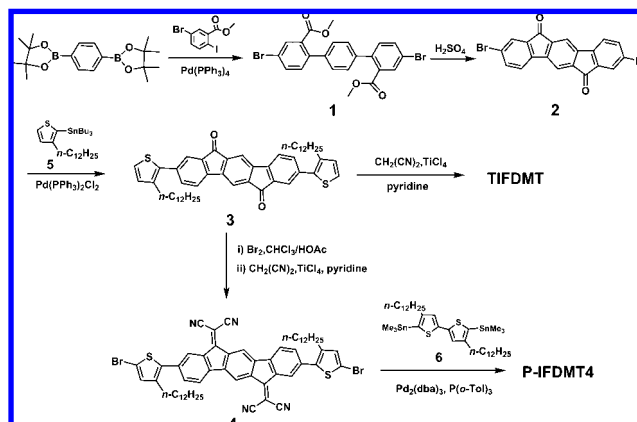
The development of solution-processable small-molecule and polymeric semiconductors for field-effect transistors (FETs) exhibiting high carrier mobility and good ambient stability is crucial to realizing low-cost and mechanically flexible printed electronics.¹ During the past decade, intense research efforts have yielded a number of air-stable p-channel (hole-transporting)² and n-channel (electron-transporting)³ semiconductors. Nevertheless, very few solution-processable, air-stable n-channel materials are known.³ Furthermore, known examples generally exhibit modest FET performance ($\mu_e \approx 0.01\text{--}10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)⁴ versus the corresponding vacuum-deposited films ($\mu_e \approx 0.64\text{--}0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), likely reflecting microstructural irregularities in the solution-processed films.³ Realization of air-stable, solution-processable, n-channel molecules and polymers is important for p–n junctions, bipolar transistors, organic complementary circuitry (CMOS), and for stimulating fundamental research on OFET charge transport.^{1,5} Recently, a solution-processable dicyanomethylene-substituted terthienoquinoid derivative was reported to exhibit $\mu_e \approx 0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in air, however it suffers from a low $I_{\text{on}}/I_{\text{off}}$ ratio (ca. $10^3\text{--}10^4$) and μ_e drops to ca. $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ over time in ambient conditions.⁶ Importantly, the paucity of air-stable n-channel polymers has significantly hindered utilizing the superior rheological properties of polymers in printing processes.⁷



The above considerations prompted us to pursue new polymerizable, electron-deficient architectures and to investigate their properties as semiconducting polymer building blocks. In this Communication, we report the synthesis, characterization, and field-effect response of a novel *n*-channel semiconducting molecule **TIFDMT** and of the corresponding thiophene-based copolymer **P-IFDMT4**. In these structures, the highly electron-deficient, ladder-type indenofluorenebis(dicyanovinylene) skeleton is utilized to depress LUMO energies, providing ambient stability to the gate field-induced electron carriers. Furthermore, the donor–acceptor backbone enhances core rigidity and π -conjugation, affording low band gap semiconductors. We report here that solution-processed **TIFDMT** FETs exhibit $\mu_e = 0.10\text{--}0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in ambient, while **P-IFDMT4**-based devices are interestingly ambipolar, having electron and hole mobilities of ca. $2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. To the best of our knowledge, this is the first ambipolar OFET polymer which operates in air.⁸

The syntheses of **TIFDMT** and **P-IFDMT4** are shown in Scheme 1. Suzuki coupling of 1,4-benzenediboronic acid dipinacol ester with methyl 5-bromo-2-iodobenzoate yields compound **1** (89%

Scheme 1. Synthetic Routes to **TIFDMT** and Polymer **P-IFDMT4**



yield). Intramolecular Friedel–Crafts acylation of **1** is achieved by H_2SO_4 treatment at 120°C (91% yield). $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ -catalyzed Stille coupling of **2** and **5** in DMF then yields compound **3** (35% yield) which undergoes reaction with excess malononitrile in the presence pyridine and TiCl_4 to afford **TIFDMT** in 40% yield. Polymer building block **4** is prepared in 45% yield by bromination of compound **3**, followed by condensation with malononitrile. Monomer **4** and **TIFDMT** are very soluble in common organic solvents, allowing convenient purification by flash chromatography. Monomer **4** is copolymerized with **6** via microwave-assisted $\text{Pd}_2(\text{dba})_3/\text{P}(\text{o-Tol})_3$ -catalyzed Stille coupling. The resulting polymer is purified by multiple dissolution/precipitation (60% yield). Final products are characterized by ^1H and ^{13}C NMR, EA, IR, GPC, and MS.

Thin-film cyclic voltammetry reveals five reversible reductions for **TIFDMT** with the first half-wave potential ($E_{1/2}^{\text{red-1}}$) at -0.12 V , whereas **P-IFDMT4** exhibits six reversible reductions and one oxidation ($E_{1/2}^{\text{red-1}} = -0.29 \text{ V}$ and $E_{1/2}^{\text{ox-1}} = 1.07 \text{ V}$; Supporting Information, Figure S1). Thin-film optical band gaps are estimated from the low energy band edges in the optical spectra as 1.52 and 1.36 eV for **TIFDMT** and **P-IFDMT4**, respectively (Figure S2). Consequently, the solid-state HOMO/LUMO energy levels are at $-5.84\text{--}4.32 \text{ eV}$ for **TIFDMT** and $-5.51\text{--}4.15 \text{ eV}$ for **P-IFDMT4**.⁹ The combined low LUMO energies and small band gaps are indicative of the highly electron-deficient and π -conjugated nature of these new structures. These are among the lowest LUMO energies reported to date for a semiconducting polymer, approaching those of air-stable *n*-channel core-cyanate perylene-, anthracene-, and naphthalene-based small molecule semiconductors.³

Top-contact FETs were fabricated by spin-coating **TIFDMT** or **P-IFDMT4** solutions in CHCl_3 (5.0 mg/mL) on OTS (octadecyltrichlorosilane) treated $\text{p}^+\text{-Si}/\text{SiO}_2$ (300 nm) substrates. Next, the semiconductor films (60–65 nm) were annealed at 150°C for 30

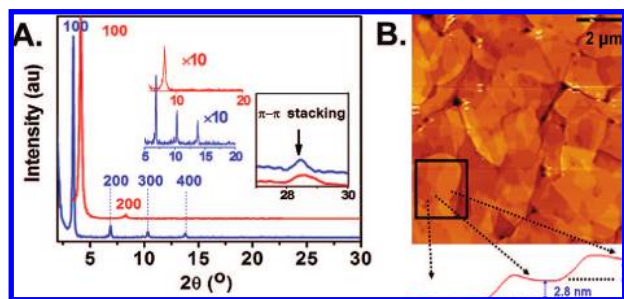


Figure 1. (A) θ - 2θ XRD and grazing-incidence XRD (inset) scans for spin-coated **TIFDMT** (blue line) and **P-IFDMT4** (red line) films; (B) tapping mode AFM image of a spin-coated **TIFDMT** film.

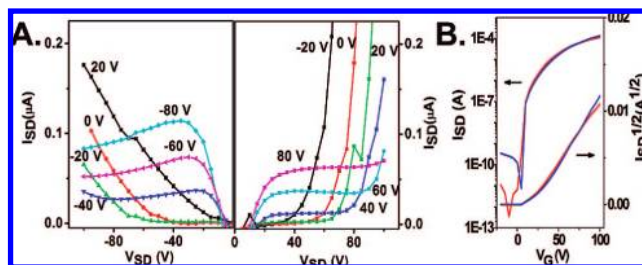


Figure 2. OFET plots of devices measured in air. (A) Output curves as a function of gate bias for **P-IFDMT4**-based devices; (B) transfer curve ($V_{SD} = 100$ V) for fresh **TIFDMT**-based device (red line) and after 5 months storage in air (blue line).

min under vacuum, followed by Au electrode (50 nm) deposition. Thin-film microstructural order was assayed by out-of plane θ - 2θ XRD and grazing-incidence X-ray diffraction (GIXRD) scans. As shown in Figure 1A, **TIFDMT** and **P-IFDMT4** thin films are highly crystalline, exhibiting Bragg reflections up to the fourth (400) and second (200) order, respectively. Primary reflections are observed at $2\theta = 3.46^\circ$ (d -spacing = 25.6 Å) for **TIFDMT** and at $2\theta = 4.12^\circ$ (d -spacing = 21.4 Å) for polymer **P-IFDMT4**. These data are consistent with well-organized lamellar microstructures having the common preferential molecular/chain “edge-on” orientation relative to the substrate surface (Figure S3).^{2d,10} The assigned π - π stacking repeat distance is 3.1 Å ($2\theta = 28.5^\circ$, inset Figure 1A), significantly smaller than typically observed for oligo/polythiophenes (3.4–3.8 Å).^{1,10} As shown in Figure 1B, AFM characterization of **TIFDMT** films reveals very large plate-like grains (3–5 μm sizes) of terraced islands with step heights of ~ 2.8 nm, corresponding to the d -spacing along the lamellar layers. In contrast, **P-IFDMT4** films exhibit small grains (<0.1 μm sizes; Figure S4).

FET device characteristics were measured in ambient conditions. Typical transfer and output plots for **TIFDMT** are shown in Figure 2 and S5. These devices exhibit n-channel operation with $\mu_e = 0.10$ – 0.16 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, $I_{\text{on}}/I_{\text{off}} = 10^7$ – 10^8 , and $V_T = 0$ to ca. +5 V. Note that these devices exhibit negligible variations in TFT characteristics after 5 months storage in air without exclusion of light or humidity (Figure 2B). Interestingly, **P-IFDMT4**-based FETs are ambipolar in ambient conditions and exhibit similar electron and hole mobilities ($\sim 2 \times 10^{-4}$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) and $I_{\text{on}}/I_{\text{off}}$ ratios ($\sim 10^4$; Figure 2A and S5) with V_T values of ca. +5 V (n -channel) and ca. -10 V (p -channel). Although the present unoptimized mobilities are moderate, to the best of our knowledge this is the very first example of an air-stable, highly soluble ambipolar semiconducting polymer.

The observed high mobility for **TIFDMT** probably reflects a combination of enhanced intermolecular π -orbital overlap, highly

textured thin films, and large film grain sizes. Furthermore, the preferential “edge-on” molecular orientation doubtless favors in-plane source-to-drain ($S \rightarrow D$) transport.¹⁰ The excellent air-stability of **TIFDMT** and **P-IFDMT4** is likely related to the low LUMO energies (-4.15 and -4.32 eV).³ The unique electronic structure of the present polymer provides a very small band gap (1.36 eV), rendering the HOMO level (-5.51 eV) accessible for hole injection by Au contacts, thus enhancing p -channel operation.

In summary, we report the synthesis and characterization of new air-stable molecular and polymeric semiconductors based on indenofluorenebis(dicyanovinylene). Solution-processed FETs exhibit high electron mobility with excellent ambient stability. The first example of an air-stable, ambipolar polymer (**P-IFDMT4**) is reported. Studies are underway to further optimize the polymer architecture and device-processing characteristics.

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Supporting Information Available: Synthetic procedures for **1**–**6**, device fabrication details; UV-vis/electrochemical/FET/AFM data; Figures S1–S5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Facchetti, A. *Mater. Today* **2007**, *10*, 28. (b) Murphy, A. R.; Frechet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066. (c) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296. (d) Vardeny, Z. V.; Heeger, A. J.; Dodabalapur, A., Eds. *Summary of the Fundamental Research Needs in Organic Electronic Materials*; Elsevier B.V.: Amsterdam, 2005. (e) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.
- (2) (a) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; Macdonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W. M.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nat. Mater.* **2006**, *5*, 328. (b) Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9034. (c) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028. (d) Ong, B. S.; Wu, Y. L.; Liu, P.; Gardner, S. *J. Am. Chem. Soc.* **2004**, *126*, 3378.
- (3) (a) Schmidt, R.; Ling, M. M.; Oh, J. H.; Winkler, M.; Könemann, M.; Bao, Z.; Würthner, F. *Adv. Mater.* **2007**, *19*, 3692. (b) Wang, Z.; Kim, C.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 13362. (c) Jones, B. A.; Ahrens, M. J.; Yoon, M. H.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Angew. Chem., Intl. Ed. Engl.* **2004**, *43*, 6363. (d) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Seigrist, T.; Li, W.; Lin, Y.-Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478.
- (4) A solution-processed electron mobility of $0.21 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (on/off ratio = 10^5) was reported, however the device only operates in vacuum: Letizia, J. A.; Facchetti, A.; Stern, C. L.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 13476.
- (5) Chesterfield, R. J.; McKeen, J. C.; Newman, C. R.; Ewbank, P. C.; da Silva Filho, D. A.; Brédas, J.-L.; Miller, L. L.; Mann, K. R.; Frisbie, C. D. *J. Phys. Chem. B* **2004**, *108*, 19281.
- (6) Handa, S.; Miyazaki, E.; Takimiya, K.; Kunugi, Y. *J. Am. Chem. Soc.* **2007**, *129*, 11684.
- (7) A mobility of $0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (on/off ratio ca. 5–10) has been reported for an n-type polymer, processed from methanesulfonic acid, a solvent which is not attractive for large-scale applications: Babel, A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 13656.
- (8) Ambipolar behavior was reported for several polymers by using various gate dielectric surface treatments, but measurements were carried out under nitrogen: Chua, L. L.; Zaumseil, J.; Chang, J. F.; Ou, E. C. W.; Ho, P. K. H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194.
- (9) E_{LUMO} is calculated as $-(E_{1/2}^{\text{red-1}} + 4.44 \text{ eV})$ assuming that Koopmans' theorem holds ($EA^{\text{red}} \approx -E_{\text{LUMO}}$). SCE energy level is taken to be -4.44 eV below the vacuum level. E_{HOMO} is calculated from: $\text{HOMO} = \text{LUMO} - E_g$ (estimated from optical absorption spectra). Bard, A. J.; Faulkner, L. R. *Electrochemical Methods-Fundamentals and Applications*; Wiley: New York, 1984.
- (10) (a) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Hutchison, G. R.; Ratner, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 13480. (b) 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. *Nature* **1999**, *401*, 685.

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