

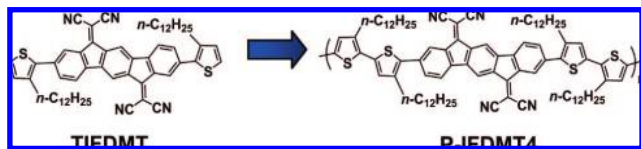
Air-Stable, Solution-Processable *n*-Channel and Ambipolar Semiconductors for Thin-Film Transistors Based on the Indenofluorenebis(dicyanovinylene) Core

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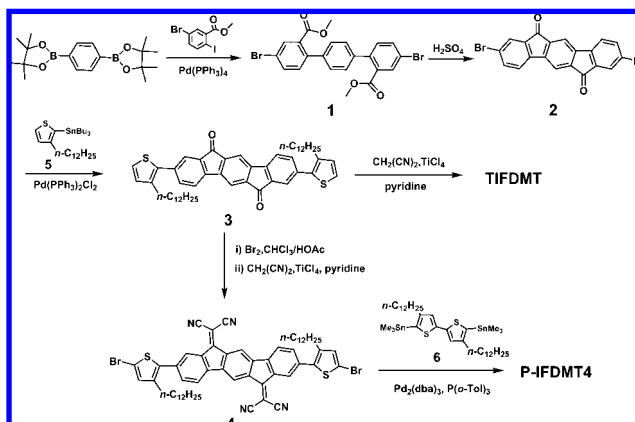
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The development of solution-processable small-molecule and polymeric semiconductors for field-effect transistors (FETs) exhibiting high carrier mobility and good ambient stability is crucial to realizing low-cost and mechanically flexible printed electronics.¹ 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-cyanated 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

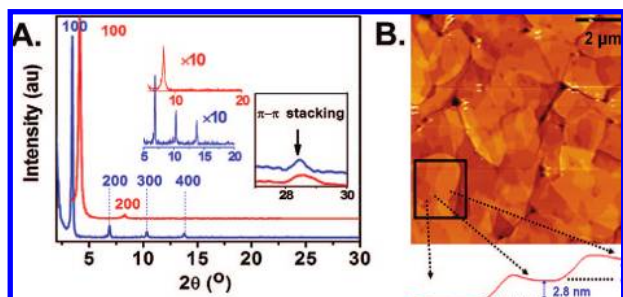


Figure 1. (A) θ - 2θ XRD and grazing-incidence XRD (inset) scans for spin-coated **TIFDMT** (blue line) and **P-IFDMT4** (red line) films; (B) tapping mode AFM image of a spin-coated **TIFDMT** film.

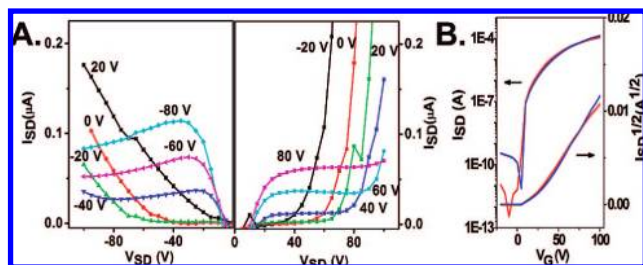


Figure 2. OFET plots of devices measured in air. (A) Output curves as a function of gate bias for **P-IFDMT4**-based devices; (B) transfer curve ($V_{SD} = 100$ V) for fresh **TIFDMT**-based device (red line) and after 5 months storage in air (blue line).

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>.

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