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n-Channel Semiconductor Materials Design for Organic Complementary Circuits

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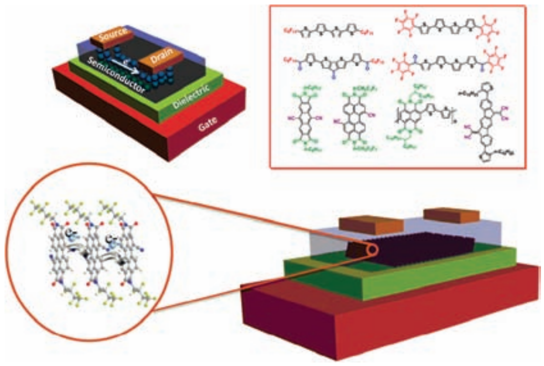

Organic semiconductors have unique properties compared to traditional inorganic materials such as amorphous or crystalline silicon. Some important advantages include their adaptability to low-temperature processing on flexible substrates, low cost, amenability to high-speed fabrication, and tunable electronic properties. These features are essential for a variety of next-generation electronic products, including low-power flexible displays, inexpensive radio frequency identification (RFID) tags, and printable sensors, among many other applications. Accordingly, the preparation of new materials based on π-conjugated organic molecules or polymers has been a central scientific and technological research focus over the past decade. Currently, *p*-channel (hole-transporting) materials are the leading class of organic semiconductors. In contrast, high-performance *n*-channel (electron-transporting) semiconductors are relatively rare, but they are of great significance for the development of plastic electronic devices such as organic field-effect transistors (OFETs).

In this Account, we highlight the advances our team has made toward realizing moderately and highly electron-deficient *n*-channel oligomers and polymers based on oligothiophene, arylenediimide, and (bis)indenofluorene skeletons. We have synthesized and characterized a "library" of structurally related semiconductors, and we have investigated detailed structure–property relationships through optical, electrochemical, thermal, microstructural (both single-crystal and thin-film), and electrical measurements. Our results reveal highly informative correlations between structural parameters at various length scales and charge transport properties.

We first discuss oligothiophenes functionalized with perfluoroalkyl and perfluoroarene substituents, which represent the initial examples of high-performance *n*-channel semiconductors developed in this project. The OFET characteristics of these compounds are presented with an emphasis on structure–property relationships. We then examine the synthesis and properties of carbonyl-functionalized oligomers, which constitute second-generation *n*-channel oligothiophenes, in both vacuum- and solution-processed FETs. These materials have high carrier mobilities and good air stability. In parallel, exceptionally electron-deficient cyano-functionalized arylenediimide derivatives are discussed as early examples of thermodynamically air-stable, high-performance *n*-channel semiconductors; they exhibit record electron mobilities of up to 0.64 $cm^2/V \cdot s$. Furthermore, we provide an overview of highly soluble ladder-type macromolecular semiconductors as OFET components, which combine ambient stability with solution processibility. A high electron mobility of 0.16 $cm^2/V \cdot s$ is obtained under ambient conditions for solution-processed films.

Finally, examples of polymeric *n*-channel semiconductors with electron mobilities as high as 0.85 $cm^2/V \cdot s$ are discussed; these constitute an important advance toward fully printed polymeric electronic circuitry. Density functional theory (DFT) computations reveal important trends in molecular physicochemical and semiconducting properties, which, when combined with experimental data, shed new light on molecular charge transport characteristics. Our data provide the basis for a fundamental understanding of charge transport in high-performance *n*-channel organic semiconductors. Moreover, our results provide a road map for developing functional, complementary organic circuitry, which requires combining *p*- and *n*-channel transistors.

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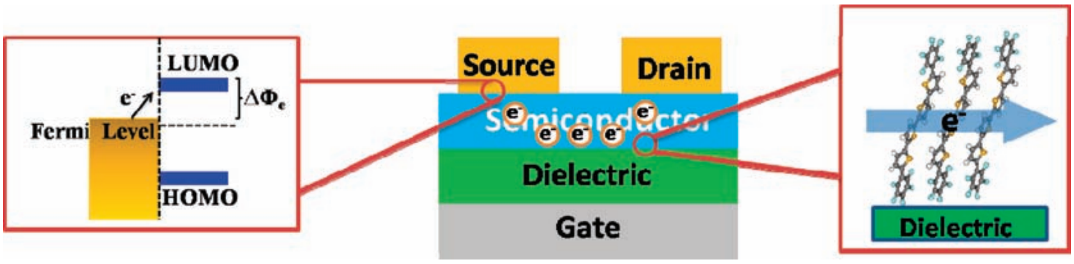

FIGURE 1. Schematic of an *n*-channel top-contact/bottom-gate field-effect transistor (FET) showing the charge-injection process and favorable electron transport direction.

1. Introduction

The design, synthesis, and characterization of new organic molecular/polymeric π-conjugated materials is an important aspect of the scientific development of next-generation optoelectronic devices.[1−3] Structurally, these materials consist of conjugated units with highly delocalized π-systems, imbuing them with unique electrical and optical properties that can be easily tuned via rational structural modifications.[4−6] Among the diverse applications envisioned for these functional materials, such as conductors, semiconductors, insulators, and light-absorbers/-emitters, field-effect transistors (FETs; Figure 1) are key building blocks and have attracted great interest.[7,8] Although organic semiconductors may exhibit comparable or lower electrical performance than inorganics such as amorphous or crystalline silicon, they offer unique attractions such as low-temperature processing on flexible (rollable) substrates, large area coverage, tunable optoelectronic properties, low-cost, high-speed fabrication, and facile synthetic modification.[9] Such features should enable next-generation electronic products such as low-power consumption flexible diplays, inexpensive plastic RFID tags, smart cards, electronic paper, printable sensors, plastic solar cells, to name a few.[10,11] The solubility, stability, and rheological properties of organic materials are compatible with high-throughput printing, patterning, and spin-coating of active materials over large areas under ambient conditions, a marked contrast to silicon microelectronics fabrication which requires highly capital-intensive lithographic techniques.[12] In addition, organic semiconductors can be easily modified via chemical synthesis, affording new materials with tunable chemical, optical, and electrical properties. This flexibility allows efficient screening of structural series to define the required criteria for any particular property or application.

Since the first report of a *p*-channel (hole-transporting) organic FET (OFET) based on an electrochemically grown polythiophene film in 1986, electronic and structural criteria governing charge transport characteristics have been widely investigated to elucidate fundamental relationships between molecular solid-state properties and device performance.[13,14] Today, *p*-channel materials represent the leading class of organic semiconductors, due principally to their synthetic accessibility and relatively air-stable charge transport characteristics.[1,2] In contrast, there has been a paucity of electron transporting semiconductors. Efficient *n*-channel conduction in organic materials is crucial to the function of *p*−*n* junction diodes, organic photovoltaics, and complementary organic circuits, where the combination of *p*- and *n*-channel transistors enables greater circuit speeds, lower power dissipation, and more stable operation.[15] Organic complementary circuits are currently at an early stage of development due to the scarcity of *n*-channel semiconductors with good processability, ambient stability, and high electrical performance. However, through rational molecular design and synthesis, many new *n*-channel semiconductors have been realized via functionalization of acene, arylene, thiophene, phenylene, and fluorene-based π-structures with electron-deficient constitutents such as perfluoroalkyl, −CN, −F, perfluoroaryl, carbonyl (−C=O), and imide (−C(O)NHC(O)−) groups.[16,17] Additionally, ambipolar materials, which simultaneously transport both electrons and holes, have recently been realized from bilayers or blends of *p*- and *n*-channel semiconductors, from low band gap donor−acceptor compounds, and from arylenediimide-based small molecules.[18−21]

Neverthless, there are few *n*-channel semiconductors today that fully meet the performance/processing criteria for real-world applications ($\mu_e \geq 0.1$ cm^2/V·s, $I_{on}/I_{off} \geq 10^5-10^6$), and the principal challenges remain ambient stability and solution-processability. Ambient stability in *n*-channel semiconductors was first addressed by de Leeuw in 1997, and degradation was attributed to reaction of the charge-carrying electrons (organic π-radical anions) with O_2 and H_2O.[22] Although several different strategies, such as

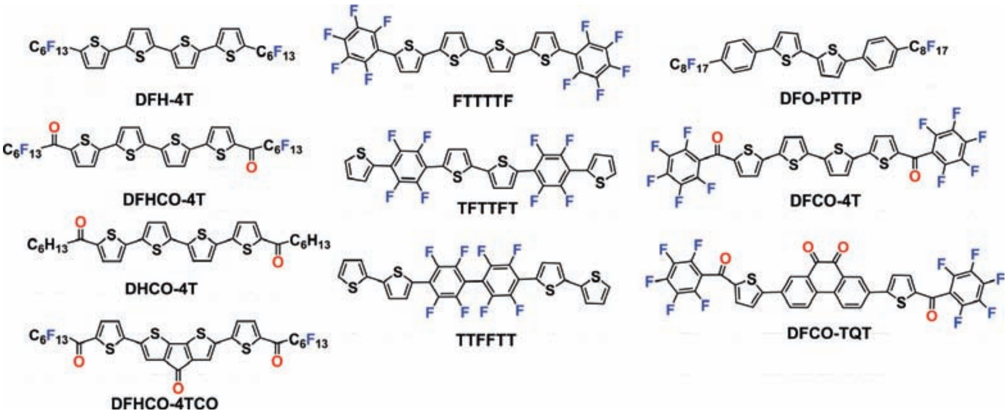

FIGURE 2. Structures of perfluoroalkyl/arene-modified oligothiophene semiconductors.

lowering frontier MO energies or introducing kinetic O_2/H_2O barriers, have been pursued to enhance device durability, the number of materials with desired properties has been inadequate until recently, and the fundamental limitations not well-established.[23] Regarding processability, the required strong π-interactions and rigid conjugated backbones would seem to contradict those factors which enhance solubility in common organic solvents: lipophilic substituents and segmental mobility. This requirement of balancing solid-state packing and solubility introduces significant synthetic challenges; however, sustained efforts to develop molecular and polymeric *n*-channel semiconductors combining ambient stability and solution processability have borne fruit. This Account describes efforts in our team over the past decade to design, synthesize, characterize, and introduce into devices moderately and highly electron-deficient oligothiophene-, arylenediimide-, (bis)indenofluorene-based molecules and polymers as *n*-channel semiconductors for high-performance OFETs.

2. Perfluoroalkyl/aryl-Modified Oligothiophenes

Among the organic semiconductor classes used in OFETs, oligo-/polythiophenes have been central due to their chemical and electrochemical stability, synthetic accessibility, and straightforward chemical modification.[24,25] The first reported *p*-channel OFET was based on a polythiophene film, and other early examples included α,ω-dialkyloligothiophenes, representing the first high mobility π-conjugated semiconductors.[26] In an effort to invert the majority carrier sign, we introduced strongly electron-withdrawing perfluoroalkyl (-*n*-C_6F_{13}) and perfluoroarene ($-C_6F_4-$ and $-C_6F_5$) substituents at either the molecular termini or β, β' positions, and showed that efficient thin-film electron transport can be achieved in oligothiophene derivatives of varied core sizes (bithiophene → sexithiophene). This new class of oligothiophenes was synthesized via Stille coupling reactions (Figure 2).[27] Note that thermogravimetric analysis indicates excellent thermal stability and volatility for these compounds, which is crucial for efficient vapor-phase growth of the corresponding thin films. However, the oligomers with less than four conjugated thiophene units are found to be either FET inactive or poorly active, which is primarily attributable to their poor film-forming tendencies.[26,30] Additionally, density functional theory (DFT) level theoretical modeling of the electronic structures of the oligomers reveals excellent agreement between computed geometries/frontier molecular orbitals and experimental crystal structures/electrochemical potentials.

Although initial electrical characterization of the perfluoroalkyl-substituted oligothiophenes indicated that lowered LUMO energies were responsible for electron injection/stabilization, further studies on perfluoroarene-substituted structures (FTTTTF, TFTTFT, and TTFFTT) showed that backbone regiochemistry has a profound effect on the carrier polarity via altered intermolecular LUMO$\cdots$LUMO electronic coupling (bandwidth), polaronic charge localization, and fluorinated core screening effects.[28,29] For example, although all of the aforementioned perfluoroarene-substituted structures exhibit lower LUMO energies ($\Delta = 0.2-0.3$ eV) than their nonfunctionalized oligothiophene counterparts, only FTTTTF shows *n*-channel behavior with $\mu_e = 0.08$ cm^2/V$\cdot$s, while enclosing the perfluoroaryl fragments within the thiophene core *inverts* the carrier polarity to *p*-type, resulting in lower hole mobilities of 0.01 and 4.10^{-5} cm^2/V$\cdot$s for TFTTFT and TTFFTT, respectively. High FET electron mobilities of 0.08$-$0.22 cm^2/V$\cdot$s with current I_{on}/I_{off} ratios $> 10^5-10^6$ were achieved for these

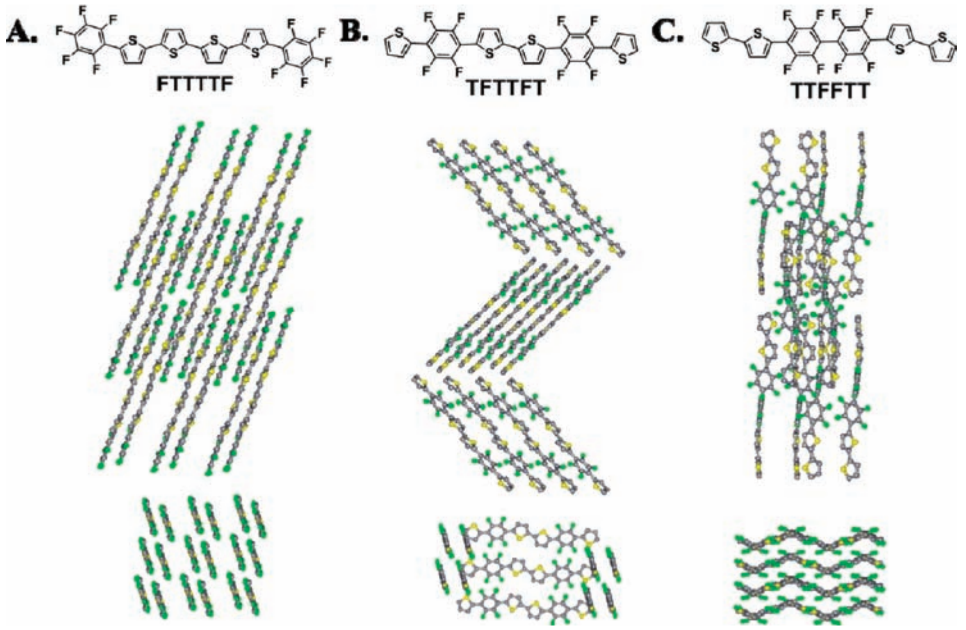

FIGURE 3. Single-crystal X-ray structures of the semiconductors (A) FTTTTF, (B) TFTTFT, and (C) TTFFTT, viewed along selected crystallographic axes.

semiconductors, some of the highest reported in *n*-channel thiophenes. In contrast, for perfluoroalkyl-substituted oligothiophenes, when the *n*-C_6F_{13} substitution is changed from the terminal (α,ω) to lateral skeletal positions (β, β'), electron mobilities fall to $5 \times 10^{-4}-10^{-6}$ $cm^2/V \cdot s$, attributable principally to decreased core conjugation and limited $\pi-\pi$ intermolecular overlap due to the increased inter-ring torsions. Another informative molecular class is the mixed phenylene−thiophene oligomers functionalized with perfluorooctyl chains at the molecular termini. These semiconductors exhibit *n*-channel behavior with electron mobilities approaching 0.1 $cm^2/V \cdot s$ (for DFO-PTTP) with very high I_{on}/I_{off} ratios of $\sim 10^7$.[30] Furthermore, OFETs fabricated from some of these materials exhibit exceptionally high, reversible, tunable, and stable memory effects.

The crystal structures of the highest mobility perfluoroalkyl-substituted oligomers reveal close $\pi-\pi$ intermolecular interactions between the aromatic cores and lamellar arrays of segregated fluorocarbon chains.[27,31] Single-crystal diffraction characterization reveals substantially planar cores (e.g., FTTTTF and TFTTFT in Figure 3) with the common feature of close interleaving of electron-rich and electron-deficient subunits at $\pi-\pi$ stacking distances of $\sim$3.20 Å, in contrast to previously reported herringbone motifs for other oligothiophenes.[31] The observed packing arrangement enhances intermolecular orbital overlap and reduces the barrier to charge transport, resulting in high-mobility semiconductors.[32]

Following an approach similar to that for tuning oligothiophene properties, a series of a,ω-carbonyl-functionalized quaterthiophenes was prepared with acyl, perfluoroacyl, benzoyl, and perfluorobenzoyl substituents (Figure 2).[33] Synthetic access includes Friedel−Crafts acylation and Stille coupling, with final products purified by recrystallization and gradient sublimation. DFT calculations and physicochemical characterizations indicate that carbonyl-functionalization substantially lowers the HOMO and LUMO energies and reduces the band gaps. Additionally, thermal (differential scanning calorimetry) and single-crystal diffraction structural characterizations indicate that carbonyl incorporation enhances mesophase formation tendencies and changes the molecular packing arrangement from typical herringbone motif for alkyl/perfluoroalkyl-substituted and unsubstituted oligothiophenes to slipped cofacial packing, which ultimately enhances film-forming characteristics as evident from XRD and SEM data. OFET measurements indicate that these materials are active as *p*-channel, *n*-channel, and ambipolar semiconductors. High FET electron mobilities of $\sim$0.6 $cm^2/V \cdot s$ are obtained for DFHCO-4T films. Additionally, DHCO-4T operates as an ambipolar semiconductor with high electron and hole mobilities of 0.1 and 0.01 $cm^2/V \cdot s$, respectively, resulting from balanced electron and hole injection barriers. Recently, after appropriate gate dielectric surface modification and optimization of the film growth conditions (substrate temperature, evaporation rate, post-deposition thermal/solvent annealing), electron mobilities

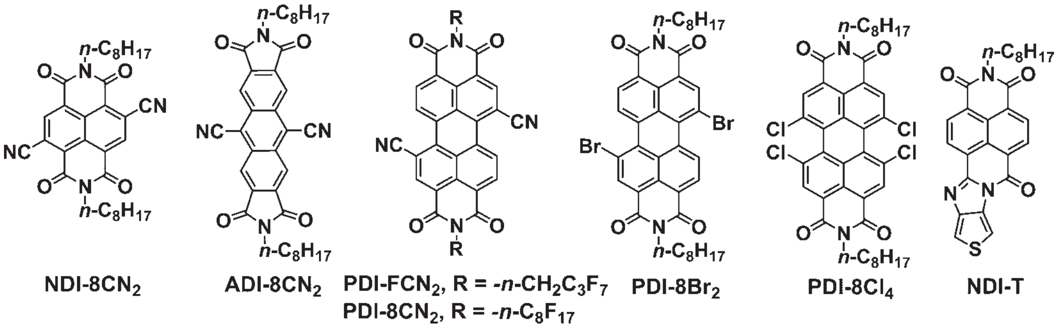

FIGURE 4. Structures of electron-deficient *N,N′*-substituted arylenediimide semiconductors.

were increased to 0.67 cm^2/V·s for DHCO-4T, 1.7 cm^2/V·s for DFHCO-4T, and 0.43 cm^2/V·s for FTTTTF.[34] Note that these values are among the highest *n*-type mobilities reported for thin-film organic semiconductors.

The first examples of air-stable *n*-channel oligothiophene semiconductors are highly electron-deficient DFHCO-4T and DFHCO-4TCO, the TFTs of which operate in air with somewhat lower electron mobilities (~5−10×) than those under vacuum (0.01 vs 0.08 cm^2/V·s). Another material with good ambient stability is phenanthrenedione-functionalized DFCO-TQT which exhibits an electron mobility of 0.02 cm^2/V·s and $I_{on}/I_{off} \sim 10^5$.[35] Ambient stability appears to reflect a combination of low-lying LUMOs (electrochemical $E_{1/2} = -0.30$ to -0.65 V vs SCE) and close packing of fluorinated units to form an O$_2$/H$_2$O kinetic barrier.

In general, most oligothiophenes exhibit lower FET performance as solution-processed films than as vacuum-deposited films ($\mu_e \approx 1.7-0.01$ vs $0.01-10^{-5}$ cm^2/V·s), likely reflecting diminished microstructural regularity in the former. Note however that DFCO-4T-based OFETs exhibit very high electron mobilities of 0.51 and 0.25 cm^2/V·s for vapor-deposited and solution-cast films, respectively; the latter is the highest reported for a solution-processed organic semiconductor measured under vacuum. Thin film and single-crystal XRD analyses reveal close $C_6F_5\cdots C_6F_5$ $\pi-\pi$ stacking which promotes highly ordered film microstructures having preferential "edge-on" molecular orientation ($\pi-\pi$ stacking parallel to the dielectric surface), favoring facile in-plane source → drain charge transport.

3. Highly Electron-Deficient Core-Functionalized Arylene Diimides

Electron-withdrawing diimide substituents, when combined with π-conjugated aromatic units such as naphthalene, anthracene, and perylene cores, afford promising architectures with impressive *n*-channel semiconducting characteristics.[36] As one early example of arylenediimide semiconductors, N-fluorocarbon naphthalenediimides exhibited air-stable electron mobilities of ~0.1 cm^2/V·s with $I_{on}/I_{off} \sim 10^5$.[37] In contrast, N-hydrocarbon arylenediimide OFETs generally operate only under inert atmosphere due to the absence of densely packed fluorocarbon groups, which act as a kinetic barrier to O$_2$/H$_2$O trap penetration. Similar effects are observed with copper perfluorophthalocyanine and fluorocarbon-substituted oligothiophenes (e.g., DFCO-4TCO).[38] Although some of these fluorinated semiconductors exhibit initial ambient operational stability, depending on the O$_2$ partial pressure and film methodology, OFET performance degrades over periods of hours to days.[39] Our group demonstrated that functionalizing arylenediimide cores with electron−withdrawing substituents such as Br, Cl, and CN results in highly electron-deficient semiconductors having low LUMO energies and favorable molecular packing (Figure 4).[40,41] The strategy is to stabilize charge-carrying electrons in low-lying LUMOs against O$_2$ and H$_2$O, so that intrinsically (i.e., thermodynamically) air-stable devices are realized, even without fluorocarbon barriers. Note that Schmidt et al. showed that perylenediimides functionalized with fluorines in the bay region can also exhibit efficient *n*-channel transport in air (μ_e = 0.34 cm^2/V·s).[42] In contrast, end-substitutions on the imide nitrogen of arylenediimides have minimal effects on the molecular energetics due to the presence of a nodal plane in their corresponding HOMOs and LUMOs that bisects the molecules through the imide nitrogen atoms.[43,44] However, substituents on the imide nitrogen atoms alter the thermal behavior, crystal packing, and solubility of the materials, and the morphology of the corresponding thin films.[39,40]

As first-generation materials, perylenediimide single-crystal structures reveal nearly planar polycyclic cores (torsion angles ~ 5°) for the dicyanated molecules (e.g., PDI-8CN$_2$) and highly distorted core structures (torsion angles ~ 25−40°) for the dibromo and tetrachloro derivatives (e.g., PDI-8Br$_2$, PDI-8Cl$_4$). The core planarity affects the electrical properties of the corresponding thin films: μ_e = 10^{-5}–10^{-3} cm^2/V·s for PDI-8Br$_2$ and PDI-8Cl$_4$ → 0.64 cm^2/V·s for PDI-FCN$_2$ via alterations in intermolecular $\pi-\pi$ orbital overlap and molecular packing. Note that PDI-FCN$_2$ exhibits exceptionally high air-stable electron mobility (0.64 cm^2/V·s) in combination with a low threshold voltage and substantial processing versatility. Additionally, through extensive optimization, solution-processed PDI-8CN$_2$ FETs were fabricated with μ_e = 0.01–0.2 cm^2/V·s and $I_{on}/I_{off} \sim 10^6$.[45] Using these materials, solution-processed bottom-gate and top-gate complementary organic logic and frequency-generating devices with unprecedented performance were fabricated.[46] Following a similar approach, anthracenediimides were structurally optimized to yield good ambient stability and high current modulation; for ADI-8CN$_2$, μ_e = 0.01–0.03 cm^2/V·s and $I_{on}/I_{off} = 10^7$, which is attributed to the balanced electron affinity ($E_{1/2} = -0.33$ V) of the semiconductor providing both efficient electron stabilization and minimal carrier-generating ambient doping ($I_{off} \sim 10^{-11}$–10^{-12} A). Furthermore, core-cyanated naphthalenediimides with large optical band gaps ($E_g \sim 3.0$ eV) were synthesized and shown to be the first examples of air-stable, high-mobility, optically transparent organic *n*-channel semiconductors. Thus, NDI-8CN$_2$ thin films were grown on overhead transparency film coated with a spin-cast PEDOT:PSS polymeric gate electrode and a polymer dielectric, affording air-stable, flexible, and transparent OFETs with mobilities as high as 0.03 cm^2/V·s. Recently, catenated arylenediimide-oligothiophenes were reported as a new class of high-performance *n*-channel semiconductors.[47] In addition to the instructive correlations between molecular physicochemical features and FET performance, one of the naphthalenediimide derivatives, NDI-T (Figure 4), exhibits an electron mobility of 0.35 cm^2/V·s under vacuum and a slightly reduced but stable value of 0.10 cm^2/V·s in air. Analysis of the redox properties, air stabilities, and FET threshold voltages of arylene/oligothiophene-based semiconductors developed in this laboratory yields an empirical first reduction potential onset criterion of ~ -0.1 V for ambient OFET stability (Figure 5), indicating an overpotential of ~0.6 V for reaction of the corresponding π-anion with O$_2$/H$_2$O. Although the concept of overpotential was initially suggested for organic semiconductors by de Leeuw (0.5–1.0 V), the present estimate is the first for *n*-channel OFETs.

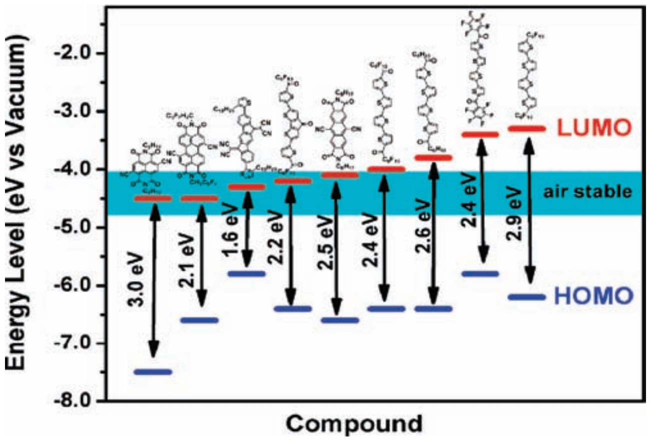

FIGURE 5. Energy level diagram for representative organic small-molecule semiconductors showing experimentally estimated LUMO energies. The blue region indicates FET devices with ambient stability.

4. Carbonyl-/Dicyanovinylene-Functionalized (Bis)indenofluorenes

To address the substantial challenges of creating ambient-stable and solution-processable *n*-channel FETs, a new family of highly electron-deficient carbonyl-/dicyanovinylene-functionalized (bis)indenofluorene-based ladder-type building blocks was invented with the design rationale of combining core planarity, electron-deficiency, and solubility (Figure 6).[48,49] Although ladder-type structures were previously used in OLEDs, our research first demonstrated their applicability in *n*-channel/ambipolar OFETs.[50] These compounds are freely soluble in common organic solvents, allowing efficient chromatographic purification. This is a significant advantage over many organic semiconductors where poor solubility necessitates high-temperature vacuum sublimation for purification and film growth.[51]

Substituent variation enables HOMO/LUMO energetic tuning in these ladder-type molecules in steps of ~0.1 eV over a 1.0 eV window, thus eliciting *p*-channel, *n*-channel, and ambipolar transport characteristics, and identifying the MO energetic windows governing majority carrier polarity and air stability. For this family of ladder-type semiconductors, DFT calculations are consistent with the experimental results and fully explain the observed electronic structure trends associated with core structure and functional group alterations. The LUMO energy onset for carrier electron stabilization is estimated as −4.0 to −4.1 eV, indicating an overpotential of 0.9–1.0 eV.[52] One of these compounds, TIFDMT, forms thin films with a well-organized lamellar microstructure having preferential alkyl chain "edge-on" orientation relative to the substrate, with short $\pi-\pi$ stacking distances of 3.1 Å. Exceptionally large platelike, highly crystalline grains (~3–5 μm) with terraces of ~2.8 nm are realized in solution-cast films, introducing the possibility of fabricating grain-boundary-free, single-crystal-like solution-cast *n*-channel FETs. TIFDMT consists of a highly planar

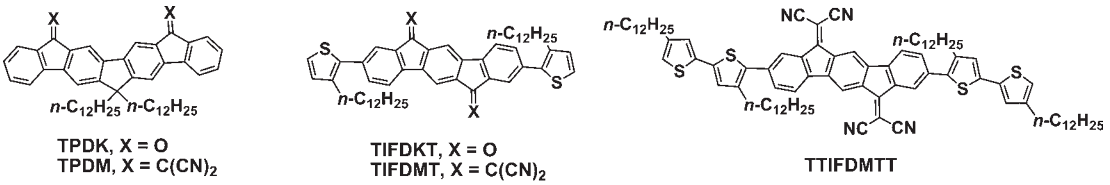

FIGURE 6. Molecular structures of representative carbonyl/dicyanovinylene-functionalized (bis)indenofluorene semiconductors.

indenofluorene core with dicyanovinylene substituents inducing local dipole moments, a low-lying LUMO, and good crystal packing properties, while terminal thiophene units with lateral substituents provide good solubility for spin-coating processes and enhance packing in thin films via alkyl chain interdigitation. Solution-cast films exhibit an electron mobility of 0.16 $cm^2/V \cdot s$, $I_{on}/I_{off} = 10^7 - 10^8$, and $V_T \sim 0$ V, one of the best device performances to date for solution-cast air-stable *n*-channel semiconductors. Note that all FETs exhibit negligible variation in response characteristics after 5 months storage in air without exclusion of light or humidity, reflecting excellent ambient stability, and consistent with the low LUMO energy ($E_{1/2} = -0.12$ V). Another interesting member of this family is TTIFDMTT (Figure 6) which exhibits air-stable ambipolar behavior with electron and hole mobilities of $\sim 10^{-4} - 10^{-3}$ $cm^2/V \cdot s$ and I_{on}/I_{off} $\sim 10^4$, representing the first example of an ambipolar oligomeric semiconductor to function in air. The unique electronic structure of TTIFDMTT provides a very small band gap of 1.44 eV, rendering the HOMO (-5.66 eV) accessible for hole injection by Au contacts while maintaining a low LUMO energy ($E_{1/2} = -0.20$ V).

5. Electron-Deficient Semiconducting Polymers

Over the past two decades, limited progress has been made in developing *n*-channel polymers, largely due to the synthetic challenges of optimizing the delicate balance between adequate solubility and close condensed-state $\pi - \pi$ packing. Polymers exhibiting efficient electron transport and high electron affinities are attractive in CMOS, organic photovoltaics, and OLEDs, since polymer rheological properties lend themselves well to printing processes. Additionally, fundamental questions about long-range electron transport can be addressed with these materials.[53]

The first example of an *n*-channel FET-active polymer was BBL (Figure 7), a ladder-type polymer processed from methanesulfonic acid and exhibiting $\mu_e = 0.03 - 0.1$ $cm^2/V \cdot s$ and $I_{on}/I_{off} = 5 - 10^5$.[54] More recently, highly soluble perylenediimide copolymer P(PDI-DTT) was synthesized and shown to exhibit an electron mobility of 0.013 $cm^2/V \cdot s$ and $I_{on}/I_{off} = 10^4$ with aluminum electrodes under inert atmosphere.[55] In related research, well-known *p*-channel polymers were shown to exhibit *n*-channel behavior ($\mu_e = 10^{-4} - 10^{-3}$ $cm^2/V \cdot s$) after hydrophobic dielectric surface treatment and using low work-function alkali metal electrodes.[56]

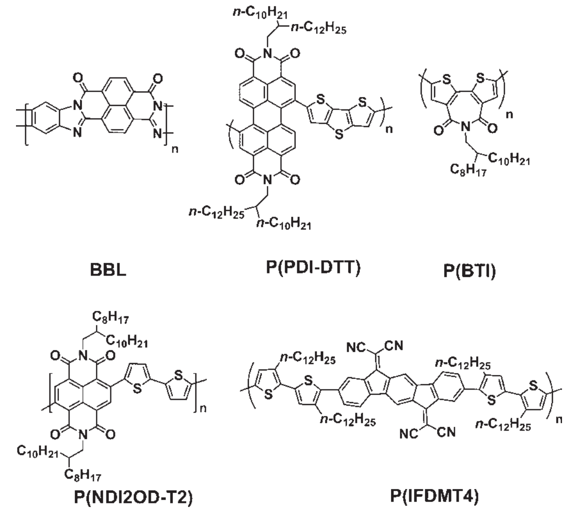

FIGURE 7. Examples of polymeric *n*-channel/ambipolar semiconductors.

We recently demonstrated a computationally guided design strategy for developing the new electron-transporting polymer P(BTI) based on the *N*-alkyl-2,2′-bithiophene-3,3′-dicarboximide unit (Figure 7).[57] Presynthetic computational analysis and electrochemical considerations revealed that introducing the π-electron-deficient imide moiety significantly increases the polymer electron affinity ($E_{1/2} = -1.01$ V) and introduces local dipole moments, yielding cofacial *antiparallel* intra- and interchain orientations. During the synthesis of this polymer, the bithiophenedicarboximide substituents were screened from linear (-n-C_6H_{13}, -n-C_8H_{17}, and -n-$C_{12}H_{25}$) to branched alkyl chains ($-(CH_2)_3CH(CH_3)$-$(CH_2)_3CH(CH_3)CH_3$, $-CH_2CH(C_2H_5)C_4H_9$, and $-CH_2CH(C_8H_{17})$-$C_{10}H_{21}$) to evaluate the interplay of solubility, crystallinity, and charge transport. The polymer functionalized with the 2-octyldodecyl chain exhibited good solubility and enabled highly crystalline films with short cofacial $\pi - \pi$ stacking

TABLE 1. Summary of the Field-Effect Mobilities (μ), Threshold Voltages (V_T), Current I_{on}/I_{off} ratios, Electrochemical Reduction Potentials ($E_{red\text{-}1}$), and OFET Device Structure/Film-Deposition Method for *n*-Channel Semiconductors

semiconductor	$E_{red\text{-}1}$(V)	μ (cm^2/V s)^a	I_{on}/I_{off}	V_T (V)	device structure (deposition technique)^b	ref
DFH4T	−1.53	0.24 (vacuum)	10^8	20−30	BG-TC (vacum dep.)	27
DFHCO-4T	−0.88	0.32−0.6 (vacuum)	10^5	38	BG-TC (vacum dep.)	33
		1.7 (vacuum)	10^9	24	BG-TC (SiO$_2$/PS dielectric, vacum dep.)	34
DHCO-4T	−1.06	0.12 (e$^-$, vacuum)	10^7	35	BG-TC (vacum dep.)	33
		0.01 (h$^+$, vacuum)	10^7	−54		
		0.67 (e$^-$, vacuum)	10^7	50	BG-TC (SiO$_2$/PS dielectric, vacum dep.)	34
		0.002 (h$^+$, vacuum)	10^3	−60 to −70		
DFHCO-4TCO	−0.65	0.08 (vacuum)	10^7	9	BG-TC (vacum dep.)	33
		0.005−0.01 (air)	10^5−10^6	10−20		
FTTTTF	−1.51	0.43 (vacuum)	10^8	30−40	BG-TC (vacum dep.)	34
DFO-PTTP	NA	0.03−0.07 (vacuum)	10^6−10^7	50−55	BG-TC (vacum dep.)	30
DFCO-4T	−1.05	0.45 (vacuum)	10^8	30	BG-TC (vacum dep.)	35
		0.21 (vacuum)	10^5	50−70	BG-TC (solution dep.)	
DFCO-TQT	−0.45	0.02 (air)	10^5 −10^6	25−30	BG-TC (vacum dep.)	35
NDI-8CN2	+0.08	0.15 (vacuum)	10^3	−37	BG-TC (vacum dep.)	40
		0.11 (air)	10^3	−55		
ADI-8CN2	−0.33	0.03 (vacuum)	10^6−10^7	10	BG-TC (vacum dep.)	41
		0.01 (air)	10^6−10^7	15		
PDI-8CN2	−0.06	0.06−0.1 (air)	10^7	0−10	BG-TC (vacum dep.)	40
		0.01−0.06 (air)	10^5−10^7	0−10	BG-TC (solution dep.)	
PDI-FCN2	+0.04	0.64 (air)	10^4	−20 to −30	BG-TC (vacum dep.)	40
NDI-T	−0.65	0.35 (vacuum)	10^6	28	BG-TC (vacum dep.)	47
		0.10 (air)	10^7	50		
TPDM	−0.53	0.02 (vacuum)	10^6	20	BG-TC (vacuum dep.)	52
TIFDMT	−0.12	0.16 (air)	10^7−10^8	0−5	BG-TC (solution dep.)	49
TTIFDMTT	−0.20	0.001 (e$^-$, air)	10^5	20	BG-TC (solution dep.)	52
		10^{-4} (h$^+$, air)	10^5	−25		
P(BTI)	−1.11	0.01 (vacuum)	10^7	75	BG-TC (solution dep.)	57
P(IFDMT4)	−0.29	2×10^{-4} (e$^-$, air)	10^4	5 (e$^-$)	BG-TC (solution dep.)	52
		2×10^{-4} (h$^+$, air)	10^4	−10 (h$^+$)		
P(NDI2ODT2)	−0.49	0.01−0.08 (air)	10^6−10^7	−20	BG-TC (solution dep.)	59
		0.45−0.85 (air)	10^6−10^8	0−5	TG-BC (solution dep.)	60

[a] Vacuum, measured in a vacuum probe station; air, measured in air. [b] BG-TC, bottom-gate/top-contact; TG-BC, top-gate/bottom-contact; PS, polystyrene.

distances of 3.43 Å. A high electron mobility of 0.014 cm^2/V·s ($I_{on}/I_{off} = 10^7$) was measured in OFET devices. Other studies have addressed systematically the role of alkyl substituents on thiophene-based semiconductors and found that the solubility of the materials and charge carrier mobility of the corresponding OFETs can vary by several orders of magnitude.[58] The breakthrough in *n*-channel polymers came with the synthesis of regioregular P(NDI2OD-T2), a copolymer of 2,6-naphthalenediimide and 2,2′-bithiophene.[59,60] This polymer can be prepared with high molecular mass (~250 kDa) and exhibits a low band gap of 1.45 eV. Top gate/bottom contact OFETs on plastic, fabricated via spin-coating and/or gravure/flexo/inkjet printing, achieve ambient-stable electron mobilities of 0.45−0.85 cm^2/V·s after optimization. Additionally, the first example of an all-printed polymeric CMOS inverter with gain of 25−65 was demonstrated. In another study, we demonstrated one of the first examples of an air-stable, highly soluble donor−acceptor ambipolar semiconducting polymer P(IFDMT4) which exhibits a very low band gap of 1.36 eV and a first reduction potential of −0.29 V. P(IFDMT4) OFETs exhibit ambipolar behavior in air with balanced electron and hole mobilities ~2×10^{-4} cm^2/V·s and $I_{on}/I_{off} = 10^4$. These findings demonstrate that electron transport and ambient stability concepts developed above for molecular semiconductors can be effectively extended to polymeric materials. Further synthetic efforts promise even higher performance levels.

6. Conclusions

Computationally aided materials design combined with exploratory synthesis have advanced the OFET field enormously since 1990. During the past decade, as presented in this Account, electron-withdrawing unit/substituent introduction into π-electron frameworks has proven to be a promising approach to enhance electron injection into, and transport through, the condensed state structures of these materials. Many π-conjugated architectures have now been rationally designed, synthesized, and validated as efficient *n*-channel semiconductors. Today, in addition to the advances achieved in *n*-channel semiconductors in terms of materials diversity, device processing, and device performance (Table 1), detailed explorations of structure−property relationships have yielded compelling guidelines for understanding fundamental aspects of *n*-channel semiconduction. Based upon combined studies from this and other research groups, *n*-channel materials design guidelines include: (i) incorporation and arrangement of electron withdrawing substituents on π-conjugated frameworks to enhance electron injection/stabilization/transport, (ii) proper π-conjugated backbone regiochemistry, (iii) structural planarity both for charge stabilization and molecular packing, (iv) tuning LUMO energies to specified levels ($<-4.0-4.1$ eV) to enhance ambient stability and optimize transistor threshold voltages, (v) incorporation of β-substituents into π-conjugated backbone of ladder type cores to increase solution-processability while maintaining close thin-film packing via alkyl chain interdigitation, and (vi) introducing local dipole moments in polymers to induce cofacial antiparallel molecular arrangements while keeping high solubility via swallow-tailed alkyl substituents. Although some fundamental issues are still unresolved and these guidelines do not guarantee high performance, since every material has unique properties, these guidelines are extremely useful for the knowledge-based realization of new *n*-type structures. Materials combining all these desired physical and chemical features are still sparse, with the principal challenges being solution-processability and air-stability. Among all the materials developed in our research program, it is noteworthy that dicyanated perylenediimide small molecules and naphthalenediimide based polymers represent the two most attractive classes of semiconductors considering both their facile synthetic accessibility and stable, high device performance. We believe that concurrent theoretical design/simulation and synthesis/characterization studies must be pursued vigorously to enhance existing structures and to develop entirely new π-conjugated platforms.

BIOGRAPHICAL INFORMATION

Hakan Usta was born in 1982. He graduated from Bilkent University (Ankara, Turkey) in 2004 and received his Ph.D. degree in chemistry at Northwestern University in 2008 with Prof. Tobin J. Marks. His thesis focused on the design, synthesis, and characterization of novel organic small molecules and polymers as semiconductors and dielectrics for OFETs. Then he joined Polyera Corporation, Skokie, IL, where he is currently a Senior Research Scientist and his responsibilities include development of high-performance functional organic molecules and polymers for organic optoelectronic applications.

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FOOTNOTES

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