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Design, Synthesis, and Characterization of Ultralow Bandgap Molecular Semiconductors for Ambient-Stable and Solution-Processable Ambipolar Organic Field-Effect Transistors

Resul Ozdemir,^{1#} Donghee Choi,^{2#} Mehmet Ozdemir,¹ Guhyun Kwon,² Hyekyoung Kim,² Unal Sen,³ Choongik Kim*,² and Hakan Usta*¹

¹ Department of Materials Science and Nanotechnology Engineering, Abdullah Gül University, Kayseri, Turkey

² Department of Chemical and Biomolecular Engineering, Sogang University, Mapo-gu, Seoul, Korea

³ Department of Mechanical Engineering, Abdullah Gül University, Kayseri, Turkey

[#] These authors contributed equally to this work.

^{*}Correspondence to: Prof. Hakan Usta (E-mail:hakan.usta@agu.edu.tr), Prof. Choongik Kim (E-mail: choongik@sogang.ac.kr).

Abstract



The design and development of novel ambipolar semiconductors is very crucial to advance various optoelectronic technologies including organic complementary (CMOS) integrated circuits. Although numerous high-performance ambipolar polymers have been realized to date, small molecules have been unable to provide high ambipolar performance in combination with ambient-stability and solution-processibility. In this study, by implementing highly π -electron deficient, ladder-type IFDK/IFDM acceptor cores with bithiophene donor units in D-A-D π -architectures, two novel small molecules, **20D**-TTIFDK and 20D-TTIFDM, were designed, synthesized and characterized in order to achieve ultralow band-gap (1.21-1.65 eV) semiconductors with sufficiently balanced molecular energetics for ambipolarity. The HOMO/LUMO energies of the new semiconductors are found to be -5.47/-3.61 and -5.49/-4.23 eV, respectively. Bottomgate/top-contact OFETs fabricated via solution-shearing of **2OD-TTIFDM** yield perfectly ambient stable ambipolar devices with reasonably balanced electron and hole mobilities of 0.13 cm²/V s and 0.01 cm²/V s, respectively with I_{on}/I_{off} ratios of ~10³-10⁴, and 20D-**TTIFDK**-based OFETs exhibit ambipolarity under vacuum with highly balanced ($\mu_e/\mu_h \sim 2$) electron and hole mobilities of 0.02 cm²/V s and 0.01 cm²/V s, respectively with I_{on}/I_{off} ratios of $\sim 10^5$ - 10^6 . Furthermore, complementary-like inverter circuits were demonstrated with the current ambipolar semiconductors resulting in high voltage gains of up to 80. Our findings clearly indicate that ambient-stability of ambipolar semiconductors is a function of molecular orbital energetics without being directly related to bulk π -backbone structure. To the best of our knowledge, considering the processing, charge-transport and inverter characteristics, the current semiconductors stand out among the best performing ambipolar small molecules in the OFET and CMOS-like circuit literature. Our results provide an efficient approach in designing ultralow band-gap ambipolar small molecules with good solution-processibility and ambient-stability for various optoelectronic technologies including CMOS-like integrated circuits.

Introduction

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Ambipolar organic semiconductors are attractive functional materials as potential alternatives to conventional inorganic semiconductors (i.e., Si, Ge, GaAs, etc.) both for fundamental research and for the fabrication of flexible, low-cost, and light-weight optoelectronic devices such as single-component CMOS (complementary metal-oxide semiconductor)-type transistor circuits and light-emitting transistors (OLETs).^[1-8] Device optimizations such as dielectric surface treatments,^[9] electrode surface modifications,^[10] and using non-symmetric work-function electrodes,^[11] or depositing bilayer/blend semiconductor films^[12-14] have been successfully employed to realize ambipolar charge-transport in organic field-effect transistors (OFETs). However, the most ideal approach would be to have an intrinsically ambipolar π -system, regardless of the device architecture.^[1,15] The ability of an intrinsic ambipolar semiconductor to transport both electrons and holes, as an initial approximation, usually requires energetically close HOMO and LUMO frontier orbitals (energy gap < 2.0 eV), which are symmetrically positioned around the metal electrode fermi level, and also requires good solid-state orbital overlaps between neighboring π systems.^[12,16,17] In order to utilize ambipolar semiconductors in ideal optoelectronic applications, charge transport of electrons and holes should be balanced ($\mu_e/\mu_h \approx 1$) with good mobility and ambient-stability. This is particularly important to achieve maximum gains in logic circuits and light-emission efficiencies in OLETs. In addition, in order to enable lowcost, facile device fabrications via spin-coating, solution-shearing, and printing, the semiconductors should exhibit good solubilities in common organic solvents.

To date, ambient-stable and solution-processable ambipolar semiconductors have been mainly reported with π -conjugated polymers, and charge carrier mobilities exceeding those of amorphous silicon ($\mu_{e,h} > 0.5 \text{ cm}^2/\text{V}\cdot\text{s}$) have been achieved in polymer-based organic field-effect transistors (OFETs).^[18–20] Most of these polymers have highly extended donor-acceptor (D-A) type π -backbones, which leads to π -electronic structures with small HOMO-LUMO

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energy gaps (< 2.0 eV) and low LUMO energies (<-4.0 eV) to facilitate charge injection/transport of both electrons and holes under ambient conditions.^[21-23] Nevertheless, very few solution-processed small molecules with ambipolar charge-transport are known to operate in ambient.^[24–26] This is mainly due to the difficulty of achieving such low HOMO-LUMO energy gaps and sufficiently low LUMOs within a limited π -extension of a molecular backbone. When compared with polymers, small molecular π -conjugated systems offer advantageous properties including enhanced solubility, higher crystallinity, better synthetic reproducibility, and higher degree of purity.^[27-31] Since the early studies on hole-transporting thiophene-based small molecules in OFETs,^[32] the design and development of novel molecular π -architectures with solution-processibility and ambient-stability have been quite important for the realization of printed electronic circuits which can operate in ambient.^[33–37] To date, many high mobility (>1.0 cm²/V·s) unipolar (*p*-channel or *n*-channel) molecular semiconductors have been developed,^[38,39] however, there are very few ambipolar small molecules exhibiting good solution-processibility and ambient stability.^[40-42] In addition, the majority of these ambipolar small molecules are based on diketopyrrolopyrrole (DPP) acceptor core, and they typically have electron/hole mobilities in the range of ~0.001-0.1 cm²/V·s.^[43,44] To the best of our knowledge, the highest ambient-stable electron mobility reported to date was for an ambipolar DPP-based small molecule with $\mu_e = 0.6-0.8 \text{ cm}^2/\text{V} \cdot \text{s}$; however, this molecule exhibited much lower hole mobility of $\sim 10^{-3}$ cm²/V s for the same device.^[45] Therefore, the continued research efforts to design and develop new ambipolar small molecules are crucial to realize high and balanced charge carrier mobilities, to fully reveal their technological potential and to elucidate the fundamentals of electron vs. hole transport processes in novel molecular solids.



Figure 1. The chemical structures of **2OD-TTIFDK** and **2OD-TTIFDM** showing the α -substituted bithiophene donor units in yellow, indeno[1,2-b]fluorene-6,12-dione (IFDK) acceptor unit in green, and indeno[1,2-b]fluorene-6,12-diylidene)dimalononitrile (IFDM) acceptor unit in red.

To achieve reasonably balanced ambipolarity in a small molecular backbone, we utilized the strategy of building very strong D-A-D π -architecture using ladder-type indeno[1,2-b]fluorene-6,12-dione (IFDK) and indeno[1,2-b]fluorene-6,12dividene)dimalononitrile (IFDM) π -acceptors and α -substituted bithiophene terminal π donor units.^[46] This approach can yield very small HOMO-LUMO gaps since HOMO is dominated by π -donor unit while LUMO is dominated by π -acceptor unit. In addition, structural and electronic properties of cyclopenta-fused scaffolds can be favorable to stabilize both positive and negative charges on these new molecular backbones.^[47] Specifically. IFDM was used due to its great coplanarity and extremely strong electron-accepting ability in a proper sized π -core.^[48] Swallow-tailed alkyl substitutents, 2-octyldodecyl (2-OD), are placed at molecular termini (α, ω -positions) to ensure good solubility while minimizing inter-ring twists.^[49] We report herein the design, synthesis and characterization of two new ladder-type small molecules, 2,8-bis(5'-(2-octyldodecyl)-2,2'-bithiophen-5-yl)indeno[1,2-b]fluorene-6,12dione (2OD-TTIFDK) and 2,2'-(2,8-bis(5'-(2-octyldodecyl)-2,2'-bithiophen-5-yl)indeno[1,2b]fluorene-6,12-divlidene)dimalononitrile (2OD-TTIFDM) (Figure 1). The chemical

structures, physicochemical and optoelectronic properties of the new compounds were characterized by ¹H/¹³C NMR, TGA, DSC, UV-Vis and CV. Our design yields ultra-low solid-state band gaps of 1.65 eV for 2OD-TTIFDK and 1.21 eV for 2OD-TTIFDM with favorable HOMO/LUMO energy levels of -5.47/-3.61 eV and -5.49/-4.23 eV, respectively, for balanced ambipolarity. Specifically, the sufficiently low LUMO of dicyanovinylenefunctionalized molecule, **2OD-TTIFDM**, enables ambient-stable electron-transport, while properly aligned HOMO level facilitates hole injection/transport. Top-contact/bottom-gate OFETs fabricated via solution-shearing of **2OD-TTIFDM** yield perfectly ambient-stable ambipolar devices with relatively balanced electron and hole mobilities of 0.13 cm^2/V s and 0.01 cm²/V·s, respectively, and I_{on}/I_{off} ratios of $10^3 - 10^4$. On the other hand, the carbonylfunctionalized molecule, **20D-TTIFDK**, exhibits highly balanced ambipolarity ($\mu_e/\mu_h \sim 2$) under vacuum with electron and hole mobilities of 0.02 $\text{cm}^2/\text{V}\cdot\text{s}$ and 0.01 $\text{cm}^2/\text{V}\cdot\text{s}$. respectively and I_{off} ratios of $10^5 - 10^6$. We have also successfully demonstrated the application of the new ambipolar transistors to complementary-like inverters, which is the building block of integrated circuits for data processing. The new inverters exhibit high voltage gains of 30 in ambient for 2OD-TTIFDM and 223 in vacuum for 2OD-TTIFDK. Our findings indicate that although D-A-D π -skeleton stays the same for both small molecules, energetic stabilization of LUMO (-3.61 eV \rightarrow -4.23 eV) as a result of functional group modification is key to the ambient stability of the corresponding OFETs. The theoretical calculations explain the differences in molecular energetics and provide insights into the current functionalization strategies. Our results clearly indicate that IFDM π -core is a proper-sized, favorable acceptor unit for building efficient, soluble ambipolar small molecules to operate in ambient. Considering the processing, charge-transport and inverter characteristics, the current molecular semiconductors are among the best performing ambipolar small molecules in the OFET and CMOS-like inverter literature.

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EXPERIMENTAL

Materials and Methods

The reagents were purchased from commercial sources and used as received unless otherwise noted. Conventional vacuum/nitrogen manifold system was used, and all the reactions were carried out under N₂. The ¹H/¹³C NMR spectra were recorded on a Bruker 400 spectrometer (¹H, 400 MHz; ¹³C, 100 MHz), and elemental analyses were performed on a Leco Truspec Micro model instrument. Thermogravimmetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on Perkin Elmer Diamond model instruments under nitrogen at a heating rate of 10 °C/min. Cyclic voltammetry measurements were performed on a C3 Cell Stand equipped with the Epsilon potentiostat/galvanostat (Bioanalytical Systems, Inc., Lafayette, IN). UV-vis absorption measurements were performed on a UV-vis spectrophotometer (Shimadzu, UV-1800). MALDI-TOF was performed on a BrukerMicroflex LT MALDI-TOF-MS instrument. The total energy minimizations and the optimization of the molecular geometries were carried out using density functional theory (DFT) at the B3LYP/6-31G** level with Gaussian 09.^[50] The synthesis of 2-octyldodecylbromide and 2,8-dibromoindeno[1,2-b]fluorene-6,12-dione (IFDK-Br2) were conducted in accordance with the reported procedures (See Supporting Information).^[49]

Synthesis and Characterization

Synthesis of 5-(2-octyldodecyl)-2,2'-bithiophene (1). To a solution of 2,2'-bithiophene (1.353 g, 8.14 mmol) in THF (25 mL) at -78 °C was added 3.41 mL (8.52 mmol) of *n*-butyllithium (2.5 M in *n*-hexane) dropwise under nitrogen. The resulting mixture was stirred at -78 °C for 30 min and at room temperature for an additional 1 h. Then, 2-octyldodecylbromide (3.11 g, 8.95 mmol) was added to this mixture slowly at -78 °C. The resulting reaction mixture was stirred at room temperature for 1 h and then heated to 85 °C

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for 12 h. The reaction was quenched with water, and the product was extracted with chloroform. The organic phase was washed with water, dried over Na₂SO₄, filtered, and evaporated to dryness to yield a crude product, which was purified by column chromatography on silica gel using hexane as the eluent to give the pure product (1.415 g, 38.8% yield). ¹H NMR (400 MHz, CDCl₃): δ 0.89 (m, 6H), 1.27-1.35 (m, 33H), 2.72 (d, 2H, J = 6.8 Hz), 6.66 (d, 1H, J = 3.2 Hz), 6.99 (m, 2H), 7.11 (d, 1H, J = 3.2 Hz), 7.17 (d, 1H, J = 5.2 Hz).

Synthesis of trimethyl(5'-(2-octyldodecyl)-[2,2'-bithiophen]-5-yl)stannane (2). To a solution of 5-(2-octyldodecyl)-2,2'-bithiophene (1) (1.415 g, 3.17 mmol) in THF (30 mL) at -78 °C was added 1.33 mL (3.33 mmol) of *n*-butyllithium (2.5 M in *n*-hexane) under nitrogen. The mixture was stirred at -78 °C for 30 min and then at room temperature for 1 h. Then, trimethyltin chloride (0.695 g, 3.49 mmol) was added slowly at -78 °C, and the resulting reaction mixture was allowed to warm to room temperature and stirred at room temperature overnight. The reaction was quenched with water, and the product was extracted with hexane. The organic phase was washed with water, dried over Na₂SO₄, filtered, and evaporated to dryness to give the pure product (1.889 g, 97.7% yield). ¹H NMR (CDCl₃, 400 MHz): δ 0.39 (s, 9H), 0.89 (m, 6H), 1.27-1.35 (m, 33H), 2.72 (d, 2H, J = 6.4 Hz), 6.65 (d, 1H, J = 3.2 Hz), 6.98 (d, 1H, J = 3.2 Hz), 7.07 (d, 1H, J = 3.6 Hz), 7.22 (d, 1H, J = 3.6 Hz).

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Synthesis of 2,8-bis(5'-(2-octyldodecyl)-2,2'-bithiophen-5-yl)indeno[1,2-b]fluorene-6,12dione (2OD-TTIFDK). The reagents 2,8-dibromo-indeno[1,2-b]fluorene-6,12-dione(IFDK-Br₂) (0.282 g, 0.641 mmol), trimethyl(5'-(2-octyldodecyl)-[2,2'-bithiophen]-5-yl)stannane (2) (0.860 g, 1.41 mmol), and Pd(PPh₃)₂Cl₂ (45.0 mg, 0.0641 mmol) in anhydrous DMF (40 mL) were heated at 125 °C under nitrogen for 2 days. Then, the mixture was then cooled to room temperature and quenched with water. The reaction mixture was extracted with chloroform, and the organic phase was washed with water, dried over Na₂SO₄, filtered, and evaporated to

dryness to give the crude product. The crude was then purified by column chromatography on silica gel using chloroform as the eluent to afford the pure product as a dark green solid (0.230 g, 30.6% yield). m.p. 217-218 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.90 (m, 6H), 1.28-1.32 (m, 33H), 2.72 (d, 2H, J = 6.4 Hz), 6.64 (d, 1H, J = 3.6 Hz), 6.98 (m, 2H), 7.18 (d, 1H, J = 3.6 Hz), 7.41 (d, 1H, J = 7.6 Hz), 7.62 (d, 1H, J = 8.5 Hz), 7.64 (s, 1H), 7.73 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 14.1, 22.7, 26.6, 29.4, 29.5, 29.6, 29.7, 30.0, 31.9, 33.2, 34.6, 40.0, 115.6, 120.5, 120.8, 123.5, 123.7, 124.4, 125.9, 130.9, 134.4, 134.6, 135.3, 138.2, 139.2, 140.2, 141.3, 144.4, 145.2, 192.1. MS (MALDI-TOF) *m/z* (M⁺): calcd. for C₇₆H₉₈O₂S₄: 1170.64, found: 1171.74 [M+H]⁺. Anal. calcd. for C₇₆H₉₈O₂S₄: C, 77.90; H, 8.43, found: C, 77.98; H, 8.64.

Synthesis of 2,2'-(2,8-bis(5'-(2-octyldodecyl)-2,2'-bithiophen-5-yl)indeno[1,2-b]fluorene-6,12-diylidene)dimalononitrile (2OD-TTIFDM). The reagents 2,8-bis(5'-(2-octyldodecyl)-2,2'-bithiophen-5-yl)indeno[1,2-b]fluorene-6,12-dione (2OD-TTIFDKTT) (0.100 g, 0.085 mmol) and dicyanomethane (79 mg, 1.19 mmol) were dissolved in 12 mL of dry chlorobenzene under nitrogen. Then, pyridine (0.131 mL, 1.62 mmol) and TiCl₄ (0.094 mL, 0.853 mmol) were added and the resulting reaction mixture was heated at 110 °C for 5 h. Then, the reaction was cooled to room temperature and quenched with water. The reaction mixture was extracted with chloroform, and the organic phase was washed with water, dried over Na₂SO₄, filtered, and evaporated to dryness to give the crude product. The crude was then purified by column chromatography on silica gel using chloroform as the eluent to give the pure product as a dark solid (63 mg, 58.8% yield). m.p. 320-321 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.90 (m, 6H), 1.27-1.35 (m, 33H), 2.57 (d, 2H, J = 6.0 Hz), 6.50 (d, 1H, J = 3.6 Hz), 6.81 (m, 2H), 7.01 (d, 1H, J = 3.6 Hz), 7.24 (d, 1H, J = 8.0 Hz), 7.42 (d, 1H, J = 8.0 Hz), 8.02 (s, 1H), 8.04 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 14.2, 22.7, 26.5, 29.3, 29.4, 29.6, 29.7, 29.8, 30.0, 32.0, 33.1, 34.5, 39.9, 112.6, 112.7, 117.4, 121.1, 122.3, 123.6, 123.9, 124.8, 126.0, 129.9, 130.2, 134.0, 134.4, 135.4, 138.4, 138.5, 138.9, 139.1, 142.4, 145.0, 158.5. MS (MALDI-TOF) *m/z* (M⁺): calcd. for C₈₂H₉₈N₄S₄: 1266.67, found: 1267.19 [M+H]⁺. Anal. calcd. for C₈₂H₉₈N₄S₄: C, 77.68; H, 7.79; N, 4.42, found: C, 77.96; H, 7.95; N, 4.56.

OFET Device Fabrication and Characterization

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All OFETs were fabricated on highly *n*-doped silicon wafers having thermally oxidized 300 nm SiO₂ dielectric (capacitance per unit area $C_i = 11.4 \text{ nF/cm}^2$) by adopting the topcontact/bottom-gate (TC/BG) device architecture. The substrates were cleaned via sonication in acetone sonication for 10 min and followed by oxygen plasma cleaning for 5 min (Harrick plasma, PDC-32G, 18 W). The PS (polystyrene)-brush treatment was performed in accordance with the reported procedures ($M_w = 1.7 - 10$ kg/mol) to achieve favorable dielectric-semiconductor interfaces.^[51-53] The organic semiconductor layers (2OD-TTIFDK and 2OD-TTIFDM) were deposited via solution-shearing method on PS-brush-treated substrates. The solution-shearing method was performed based on the reported procedure, and the conditions were optimized with respect to solvent, concentration of solution, temperature of substrate, shearing speed, and thermal annealing temperature.^[54] The solutionsheared substrates were kept in a vacuum oven at 150 °C for 30 min, and then placed in a desiccator for 24 h to remove the residual solvent. The profilometer (DEKTAK-XT, Brucker) was used to measure the OSC film thicknesses (30 - 60 nm). The top electrodes were thermally evaporated (deposition rate = 0.2 Å/s) as Au layers (50 nm) with various channel widths (W; 1000 and 500 µm) and lengths (L; 100 and 50 µm). Keithley 4200-SCS was used to characterize the electronic performances of OFETs in ambient or in a vacuum probe station $(< 10^{-2} \text{ Torr})$ at room temperature. The electronic performance in the saturation region such as charge carrier mobilities (μ) and threshold voltages (V_T) were extracted from the equation:

$$\mu_{sat} = (2I_{DS}L)/[WC_i(V_G - V_T)^2]$$

where I_{DS} is the drain current, L and W are the channel length and width, respectively, C_i is the areal capacitance of the gate dielectric, V_G is the gate voltage, and V_T is the threshold voltage. The reported OFET characteristics are the average of 10 different devices with standard deviations of less than 5-10%. The surface morphology and microstructure of thinfilms were measured by atomic force microscopy (AFM, NX10, Park systems) and X-ray diffraction (XRD, Smartlab, Rigaku), respectively.

Fabrication and Characterization of Complementary-like Inverters

The complementary-like inverters were fabricated on the PS-brush treated n^{++} -Si/SiO₂ gate-dielectric substrate using two identical ambipolar OFETs based on **2OD-TTIFDK** or **2OD-TTIFDM** with a common gate as the input voltage (V_{IN}). The top electrodes with various channel widths (W; 2000, 1000, and 500 µm) and lengths (L; 100 and 50 µm) were deposited through shadow mask to define the electrode of supply bias (V_{DD}), the common electrode of output voltage (V_{OUT}), and the ground electrode. The channel dimensions for the two ambipolar OFETs were identical. The complementary-like inverters were characterized with the Keithley 4200-SCS instrument in ambient or under vacuum (< 10^{-2} Torr).

RESULTS AND DISCUSSIONS

Computational Modeling, Synthesis and Characterizations

Density-Functional Theory (DFT) study was performed on the model compounds **M1** and **M2** prior to the synthesis to gain initial insights into the molecular and electronic structures of the new molecules (Figure 2). In these model compounds, shorter chains (isobutyl) were employed instead of longer alkyl chains (2-octyldodecyl) to ease the calculations by reducing degrees of freedom. Based on the energy-minimized geometries, **IFDK** and **IFDM** π -cores are found to adopt high co-planarity while some degree of acceptable inter-ring twists exist between these cores and outer thiophene units ($\theta < 22^{\circ}$). For both compounds, HOMO is

highly delocalized along the molecular backbone and LUMO is more localized on the acceptor cores. However, the proper size of the acceptor unit may still ensure efficient intra-/inter-molecular π -delocalization and therefore good electron transport. The theoretical HOMO-LUMO energy gaps are estimated as 2.27 eV for **M1** and 1.45 eV for **M2**. The large reduction in the energy gap originates mainly from the LUMO level reduction (-2.90 eV \rightarrow - 3.87 eV) as a result of functional group modification from carbonyl to dicyanovinylene. The origin of this reduction is a result of favorable inductive and mesomeric effects of dicyanovinylene *vs.* carbonyl ensuring very low LUMO level with minimal influences on HOMO energy level. The low LUMO energy level of **M2** is ideal for air-stable electron transport, which, when combined with its still relatively high HOMO, should enable ambipolarity in ambient. It is noteworthy that although ambipolarity may also be expected from **M1**, based on its relatively high LUMO, the electron-transport is not expected to be stable in ambient.

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Figure 2. Chemical structures of the model compounds **M1** and **M2**. Optimized molecular geometries showing inter-ring dihedral angles, computed HOMO and LUMO energy levels, and topographical orbital representations (DFT, B3LYP/6-31G**).

Scheme 1 shows the synthesis of the stannylated π -donor moiety, trimethyl(5'-(2-octyldodecyl)-[2,2'-bithiophen]-5-yl)stannane (2) and the corresponding α,ω -disubstituted

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molecules **2OD-TTIFDK** and **2OD-TTIFDM**. The synthesis of the ladder-type acceptor core IFDK-Br2 was carried out via Suzuki cross-coupling and intramolecular Friedel-Crafts acylation reactions in accordance with the established procedure by our group (Scheme S1). Donor unit, 2, was prepared from bithiophene in two steps: in the first step, bithiophene was monolithiated and capped with 2-octyldodecylbromide to yield 1 in 39% yield, and subsequently, 2 was synthesized from 1 in 98% yield via a conventional lithiation/stannylation reaction. The synthesis of the new carbonyl functionalized ladder type compound **2OD-TTIFDK** was carried out via conventional Stille cross-coupling reaction by reacting IFDK-Br2 and 2 in DMF using Pd(PPh₃)₂Cl₂ catalyst in 31% yield. Since the solubility of IFDK-Br2 was very low in common organic solvents, the success of this reaction relies on using highly polar solvent (DMF) at high temperature (125 °C). During the course of this reaction, the coupling of the first π -donor moiety having 2-OD chain enhances the solubility of the mono-coupled adduct significantly so that the second coupling proceeds more easily. Dicyanovinylene functionalized molecule, **20D-TTIFDM**, was synthesized via Knoevenagel condensation between **20D-TTIFDK** and malononitrile in the presence of pyridine and TiCl₄ in 59% yield. Thanks to the presence of swallow-tailed 2-OD alkyl substituents, the new D-A-D molecules are found to be very soluble in common organic solvents (CHCl₃, THF, Toluene, etc.) and purifications were performed by flash column chromatography using Silica gel and chloroform as the stationary phase and eluent, respectively. The good solubilities of the new molecules also enable the fabrication of OFETs via solution-processing. The chemical structures and purities of the intermediate and final products were confirmed by ¹H/¹³C NMR (Figures S1, S2, S4, and S5), mass spectroscopy (MALDI-TOF) (Figures S3 and S6), elemental analysis, and ATR-FTIR (Figure S7). Based on thermogravimetric analysis (TGA), both compounds exhibited good thermal stabilities with onset decomposition temperatures over 350 °C (Figure S8A). Differential scanning

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calorimetry (DSC) measurements of 2OD-TTIFDK and 2OD-TTIFDM exhibited hightemperature endotherms at 218 °C and 320 °C, respectively, which are in accord with the conventional melting temperature measurements (Figure S8B). Surprisingly, higher-energy endothermic thermal transitions (179/208 °C for 2OD-TTIFDK and 209 °C for 2OD-**TTIFDM**) were observed for both compounds prior to the major melting process, which is typical characteristics of liquid-crystalline materials.^[55] On cooling, the DSC traces of both compounds displayed the same behavior of their heating cycle. Although the π -skeleton remains the same for both compounds, the melting temperature significantly increases (ΔT_m) = +102 °C) when the functional group is changed from carbonyl ("C=O" in **20D-TTIFDK**) to dicyanovinylene ("C=C(CN)₂" in **2OD-TTIFDM**). This indicates more effective cohesive forces in the solid-state packing for the latter molecule, which is likely a combined result of larger local/molecular dipole moments and enhanced dipole-dipole/ π - π interactions as a result of stronger donor-acceptor characteristics. When compared with our previously reported compound, **2OD-TIFDKT** (Figure S9),^[49] the introduction of additional thiophenes at molecular termini significantly increased T_m by ~80 °C in 20D-TTIFDK as a result of enhanced π -core rigidity.



Scheme 1. Synthesis of 2OD-TTIFDK and 2OD-TTIFDM.

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As shown in Figure 3, when the concentrations of **2OD-TTIFDK** and **2OD-TTIFDM** in CDCl₃ increased from 1.0 mg/mL to 16.0 mg/mL, the chemical shifts of the aromatic and

α-aliphatic protons moved upfield (- $\Delta\delta = 0.1-0.4$ ppm), indicating the presence of shielding effect. This shielding is due to enhanced electron-density on individual protons as a result of molecular stacking in organic solvents via intermolecular π-π stacking and van der Waals interactions. The aromatic protons that show chemical shifts originated both from **IFDK/IFDM** π-cores and bithiophene units, as well as the *alpha*-methylene proton (Ar-<u>CH₂-</u> CH(C₈H₁₇)C₁₀H₂₁) adjacent to the thiophenes, indicating that all these protons are involved in the intermolecular interactions in the molecular stacks. The aromatic peaks were broadened with increasing concentration, which further supports the stacking model since intermolecular attractions widen the local electronic profile around each proton. Similar stacking behaviors were observed for a number of π-conjugated small molecules in the literature.^[56–58] This indicates the existence of favorable intermolecular interactions for the present D-A-D π-cores even in the solution-phase, which may potentially render the formation of favorable supramolecular architecture after solvent removal in the solid-state (*vide infra*).



Figure 3. The concentration dependent ¹H NMR spectra of **2OD-TTIFDK** (A) and **2OD-TTIFDM** (B) in CDCl₃. Inset is the schematic model of molecular stacking in solution as a result of concentration. (The blue and green units represent π -backbone and flexible hydrocarbon chains, respectively.)

Optical and Electrochemical Properties

UV-vis absorption spectra (Figures 4A and 4B) of **2OD-TTIFDK** and **2OD-TTIFDM** in dichloromethane solutions exhibit similar higher energy maxima at 410 nm and

400 nm, respectively, corresponding to π - π * transitions of the bithiophene-indeno[1,2blfluorene core, which remains the same for both compounds although the functional groups are different. However, lower-energy peaks appear at 568 nm and 740 nm for **20D-TTIFDK** and 2OD-TTIFDM, respectively, reflecting the differences in the chemical nature of carbonyl vs. dicyanovinylene functional groups. Therefore, these relatively weaker lowerenergy transitions are most likely to be governed by the functional groups and originates from symmetry forbidden n- π^* transitions.^[59,60] The optical band gaps in solution are calculated from the low-energy absorption edges as 1.89 eV (2OD-TTIFDK) and 1.31 eV (2OD-**TTIFDKM**). Both compounds exhibit significant bathochromic shifts ($\Delta \lambda = 16-216$ nm) and reductions in optical band gaps when going from dilute solution to solid-state. This is indicative of molecular planarization and enhanced π - π stacking/donor-acceptor interactions in the solid-state. The solid-state optical band gaps are estimated as 1.65 eV for 2OD-**TTIFDK** and 1.21 eV for **2OD-TTIFDM**, which are, to the best of our knowledge, among the lowest in the literature for π -conjugated small molecules. It is noteworthy that the optical band-gap and absorption maxima observed for the present compound, **20D-TTIFDM**, is ~ 0.15 eV smaller and ~ 30 nm red-shifted, respectively, compared to those of structurally related compound, β -C12-TTIFDM (1.44 eV; $\lambda_{max} = 410$, 711 nm).^[48] This is due to repositioning of the hydrocarbon chains from β - to α, ω -positions (Figure S9) in the new semiconductor, which minimizes the inter-ring twists between donor and acceptor units (θ_{Ph}) The = 45-46° \rightarrow 16-17°) and further extends the π -conjugation on the present compound. This is found to be very advantageous to the charge carrier mobilities in the corresponding OFET devices (vide infra).



Figure 4. For compounds **2OD-TTIFDK** and **2OD-TTIFDM**, (A) Optical absorption in dichloromethane solution, (B) Optical absorption as thin-films, and (C) Cyclic voltammograms in dichloromethane $(0.1 \text{M Bu}_4\text{N}^+\text{PF}_6^-, \text{ scan rate} = 50 \text{ mV}\cdot\text{s}^{-1})$.

As shown in Figure 4C, cyclic voltammetry (CV) measurements of **2OD-TTIFDK** and **2OD-TTIFDM** in dichloromethane solutions exhibit reversible oxidation and reduction peaks with the first half-wave potentials located at 1.07 V/-0.79 V (vs. Ag/AgCl) and 1.09 V/-0.17 V (vs. Ag/AgCl), respectively. The existence of both oxidative and reductive electrochemical processes with good reversibility indicates the intrinsic redox-stable ambipolar nature of the present compounds. Due to the stronger electron accepting nature of dicyanovinylene in **20D-TTIFDM** compared to carbonyl in **20D-TTIFDK**, reduction potential shows significant anodic shift (-0.79 V \rightarrow -0.17 V) with minimal change on the oxidation potentials. The corresponding HOMO/LUMO energy levels are estimated as -5.47 eV/-3.61 eV for **2OD-TTIFDK** and -5.49 eV/-4.23 eV for **2OD-TTIFDM**, using the vacuum level energy of Ag/AgCl as -4.40 eV. These observations are consistent with our theoretical findings (vide supra) that for both compounds, HOMOs are delocalized along the same molecular backbone and LUMOs are localized on the acceptor core functionalities. On the basis of the oxidation and reduction potentials, the electrochemical band gaps for **2OD**-TTIFDK and 2OD-TTIFDM are estimated as 1.86 eV and 1.26 eV, respectively, which are in perfect agreement with the optical band gaps. Based on the molecular orbital energetics

and low band gaps, the HOMO (-5.47- -5.49 eV) and LUMO (-3.61- -4.23 eV) energies of the current compounds should favor concurrent electron and hole injection/transport (ambipolarity) in the corresponding thin-films. Specifically, the LUMO level of **2OD**-**TTIFDM** is highly favorable for ambient-stable electron-transport.

Field-Effect Transistor and Complementary-like Inverter Fabrication and Characterization

Top-contact/bottom-gate (TC/BG) OFETs were fabricated by solution-shearing 30-60 nm thick films of **2OD-TTIFDK** and **2OD-TTIFDM** on PS-brush treated n⁺⁺-Si/SiO₂(300 nm) substrates to achieve favorable semiconductor-dielectric interfaces with higher semiconductor film quality and better control on the microstructure/morphology, as compared to conventional solution-based methods such as drop casting and spin coating.^[61,62] For both semiconductors, the most ideal solution-shearing condition was identified as applying 1.0 mg/mL (in chlorobenzene) semiconductor formulations on substrates maintained at 50-60 °C at a shearing speed of ~1.0 mm/min. OFET devices were characterized under positive and negative gate biases in ambient and under vacuum to explore the ambipolarity, device performance, and ambient stability. Typical transfer and output curves are shown in Figures 5 and S10-S13, and the corresponding OFET data are summarized in Table 1.



Figure 5. (A, B) Ambipolar (P-channel (in red) and N-Channel (in blue)) transfer curves of the OFET devices based on solution-sheared thin-films of **2OD-TTIFDK** and **2OD-TTIFDM**, and (C) Top-contact/bottom-gate OFET device structure and the band lineups of the molecular orbital energy levels with respect to O_2/H_2O electrochemical redox couple at the air-thin film interface.

As expected from the optical/electrochemical and theoretical characterizations (*vide supra*), all OFET devices fabricated with the current semiconductors, **2OD-TTIFDM** and **2OD-TTIFDK**, were found to exhibit typical ambipolar characteristics. This indicates intrinsic ambipolar semiconducting nature of the present compounds and can be attributed to their low solid-state band gaps (1.21-1.65 eV), which render both HOMO and LUMO levels energetically accessible for hole and electron injection/transport, respectively. Consistent with its highly stabilized LUMO energy level of -4.23 eV, **2OD-TTIFDM** is found to be perfectly ambient-stable as semiconductor thin-film in OFETs with electron and hole mobilities of 0.13 cm²/V·s and 0.01 cm²/V·s, respectively, and I_{on}/I_{off} ratios of ~10³–10⁴ in ambient conditions (Figure 5). These devices are found to exhibit negligible variations in

transistor characteristics after few months of storage in ambient, showing prolonged stability of the corresponding semiconductor thin-films (Figure S12). When the semiconductor performance of **2OD-TTIFDM** is compared with that of structurally related **B-C12-TTIFDM**^[48] (Figure S9), which includes additional linear alkyl chains at thiophenes' β positions, two orders of magnitude (×100) higher electron ($\mu_e = 1 \times 10^{-3} \text{ cm}^2/\text{V} \cdot \text{s} \rightarrow 0.13$ cm²/V·s) and hole ($\mu_h = 1 \times 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s} \rightarrow 0.01 \text{ cm}^2/\text{V} \cdot \text{s}$) mobilities were achieved with the current semiconductor, **2OD-TTIFDM**. The substantial mobility improvements observed for the new semiconductor probably reflects a combination of D-A-D π -core planarization as a result of reducing inter-ring D-A twists (vide supra) and improved thin-film microstructure/morphology due to the solution-shearing process. From a structural design standpoint, in the development of ambipolar small molecules employing donor-acceptor linkages, we can suggest that it's important to minimize the inter-ring twists between donor and acceptor units. On the other hand, due to its relatively higher LUMO energy level of -3.61 eV, OFETs fabricated with **2OD-TTIFDK** were only active under vacuum; they exhibit highly balanced ($\mu_e/\mu_h \sim 2$) ambipolar behavior with mobilities of 0.02 cm²/V·s (for *n*channel) and 0.01 cm²/V·s (for *p*-channel) with $I_{on/off}$ ratios of ~10⁵-10⁶, respectively. When 20D-TTIFDK-based OFETs were measured in ambient conditions, although p-channel performance remained at the same level, *n*-channel performance showed significant initial drop ($\times 100$) and eventually became inactive (Figure S13). The transition of electron transport from being unstable to ambient-stable was clearly observed for the present semiconductors when the functional group was changed from *carbonyl* to *dicyanovinylene*, even though the π -backbone (bithiophene-indeno[1,2-b]fluorene-bithiophene) remains the same. This indicates the importance of molecular orbital energetics stabilization for ambient-stable electron-transport in semiconductor thin-films and an electrochemical threshold exists between -3.6 eV and -4.2 eV. This is consistent with earlier reports, and corresponds to a

required stabilization of LUMO energy level against electrochemical trapping by O_2 - H_2O redox couple.^[48,63] To the best our knowledge, the OFET characteristics of **2OD-TTIFDM** are among the best solution-processed, small molecular ambipolar performances in terms of reasonably balanced and ambient-stable charge carrier mobilities. It's noteworthy that further device structure optimizations such as using ferroelectric dielectrics^[20] and adding graphene oxide (GO)^[64] or single-walled carbon nanotube (SWNT)^[65] interlayers can be employed to further balance electrical characteristics of hole- *vs* electron-transport with the current ambipolar semiconductors.

 Table 1. Electrical Performance of OFETs based on 2OD-TTIFDK and 2OD-TTIFDM

 developed in this study.^a

| Material | N-channel | | | P-channel | | |
|------------|--------------------------------|------------------------------------|---------------------|--------------------------|------------------------------------|---------------------|
| | μ_e (cm ² /V·s) | V _T (V) | I_{on}/I_{off} | $\mu_h (cm^2/V \cdot s)$ | V _T (V) | I_{on}/I_{off} |
| 20D-TTIFDK | 0.02 ± 0.002 | 34±3 | 1.4×10 ⁵ | 0.01±0.001 | -55±4 | 2.2×10 ⁶ |
| 20D-TTIFDM | 0.13±0.012 | 13±2 | 1.0×10^{4} | 0.01±0.002 | -33±2 | 1.1×10 ³ |

^a The OFETs based on **20D-TTIFDK** and **20D-TTIFDM** were measured under vacuum and in ambient, respectively.

Complementary-like inverter is an essential building block of integrated circuits for data processing, and it typically requires the fabrication of separate *p*- and *n*-channel transistors. However, when an ambipolar semiconducting material is used, only a single layer of organic semiconductor is required without the need for separate patterning of unipolar *p*- and *n*-channel semiconductors. Therefore, given the promising high-performance, well-balanced ambipolar OFET characteristics of the new semiconductors, complementary-like inverters were fabricated from **20D-TTIFDK** or **20D-TTIFDM** semiconductor solutions and characterized on single substrates using two identical ambipolar transistors with the shared gold electrode (Figure 6-inset). As shown in Figures 6 and S14, complementary-like inverters based on **20D-TTIFDK** and **20D-TTIFDM** operated well under vacuum and in

ambient, respectively, in the first and third quadrants with sharp switchings of V_{OUT}'s at supplied voltages (V_{DD}) of +100 and -100 V, respectively. The voltage gain is calculated from $|dV_{OUT}/dV_{IN}|$, where V_{OUT} and V_{IN} are the output and input voltages, respectively. The ability of the current inverters to operate in both quadrants is the specific advantage of having ambipolar OFETs.^[66,67] For **20D-TTIFDK**-based inverters, very high voltage gain of 80 V/V was achieved at positive V_{IN} along with a maximum gain of 28 V/V at negative V_{IN} . To the best of our knowledge, the high voltage gain in the first quadrant is among the highest gains achieved with a solution-processed, single-component ambipolar voltage semiconductor.^[68-70] High voltage gain from sharp voltage inversion demonstrates the reliability of the current inverter devices, and can be attributed to the highly balanced ambipolar charge-transport behavior of **2OD-TTIFDK** (vide supra).^[71] On the other hand, inverters based on ambient-stable semiconductor, **2OD-TTIFDM**, were characterized in ambient, and they exhibited good voltage gains of 30 V/V (Figure S14). Our results show that the current solution-processable ambipolar small molecules are ideal semiconductors not only for ambipolar OFETs but also for single-component CMOS-like organic circuits. However, it's noteworthy that the observed Z-shaped voltage transfer characteristics (VTC) for both semiconductors are typical for unoptimized ambipolar transistor-based inverters, since both the pull-up (p-channel) and pull-down (n-channel) transistors cannot be completely switched off at low and high V_{IN}'s.^[64] These features will cause limited noise margin and large static power consumption, and further inverter device optimizations such as semiconductor film doping or incorporating interlayers are needed to further match charge carrier mobilities (μ) and threshold voltages (V_T) in the *p*- and *n*-channel regions.^[65]



Figure 6. Voltage transfer characteristics (VTC) of a complementary-like inverter fabricated by two identical **2OD-TTIFDK**-based ambipolar transistors in first (A) and third (B) quadrants with supplied voltages of +100 V and -100 V. Inset shows the circuit diagram and the plots of gains ($-dV_{OUT}/dV_{IN}$) are given in red.

Thin-Film Microstructure and Morphology

The microstructural and morphological characteristics of the solution-sheared thinfilms of the current semiconductors were investigated by out-of-plane θ -2 θ X-ray diffraction (XRD) technique and atomic force microscopy (AFM). As shown in Figure 7, both semiconductor thin-films showed crystalline patterns with distinct (00*l*) diffraction peaks up to the third order along with broad (0*k*0) peaks. The primary diffraction peaks (001) were observed at $2\theta = 3.05^{\circ}$ (*d*-spacing = 29.0 Å) for **2OD-TTIFDK** and at $2\theta = 2.37^{\circ}$ (*d*-spacing = 37.2 Å) for **2OD-TTIFDM**, indicative of the formation of well-organized lamellar microstructure having molecular/alkyl-chain edge-on orientation relative to the dielectric surface. Further weak diffraction peaks were observed at $2\theta = 4.24^{\circ}$ (001') and 5.34° (001'') for **2OD-TTIFDK**-based thin-film, which do not belong to the primary diffraction family, indicating the existence of additional minor crystalline phases.



Figure 7. θ -2 θ X-ray diffraction (XRD) scans and AFM topographic images (inset) of **2OD**-**TTIFDK** (A) and **2OD-TTIFDM** (B) thin-films fabricated by solution shearing method. The scale bar denotes 1-2 μ m and the arrow shows the shearing direction.

The *d*-spacings for both compounds are shorter than the computed molecular lengths (~57.0 Å) with fully extended (all-trans conformation) alkyl chains. This indicates that significant alkyl chain interdigitation and/or molecular tilting from the substrate normal are likely to occur in thin-film phases. Considering that the alkyl chains remain the same for both semiconductors, the larger *d*-spacing observed for **2OD-TTIFDM** reflects more vertically oriented molecular π -cores relative to the dielectric surface, probably as a result of stronger intermolecular interactions between D-A-D π -cores (*vide supra*). **2OD-TTIFDM** thin-film exhibited much stronger (001) diffraction peak intensity (×7 for the same film thickness) with smaller FWHM (full width at half maximum) (~0.20° *vs.* ~0.35°) when compared with that of **2OD-TTIFDK**. This shows that **2OD-TTIFDM** thin-films have higher crystallinity with larger mean crystallite size.^[72] Broad diffraction peaks observed at $2\theta \sim 22^\circ$ (010) were ascribed to π - π stacking interactions with distances of ~4.1 Å between molecular backbones, which is somewhat larger than the typical π - π stacking observed for oligo-/polythiophenes (3.4-3.9 Å).^[48,73,74] This points to relatively weaker π - π stacking interactions for the current semiconductors and it can be attributed to the presence of sterically bulky, swallow-tailed 2-

octyldodecyl substituents, which may preclude the π -cores from approaching each other effectively. AFM characterizations provide more information on the morphological aspects of the current films, and, therefore, allow us to better understand the correlations with the electrical performances. Both films reveal highly homogeneous morphologies with surface roughness below 4-5 nm for $10 \times 10 \ \mu m$ scan areas. Although **2OD-TTIFDK** films exhibited small highly-interconnected isotropic spherulites (~100-200 nm diameter sizes), 20D-**TTIFDM** films revealed two-dimensional micron-size (\sim 1-2 µm) plate-like grains of terraced islands with step-heights of \sim 3.9 nm, which corresponds to the *d*-spacing measured from the XRD characterization (~3.7 nm). The observed highly crystalline and edge-on π -oriented microstructure, and layer-by-layer grown 2-D morphology of **2OD-TTIFDM** film favors efficient charge-transport OFETs. Furthermore, when these favorable in microstructural/morphological features are compared with those of **2OD-TTIFDK**-based thin-film, it seems to significantly enhance the field-effect electron mobility (\times 6) with minimal influence on the field-effect hole mobility. This shows that thin-film morphological and microstructural characteristics may have totally different effects on electron and hole charge-transport characteristics of molecular solids.

Conclusions

Two new solution-processable ambipolar small molecules, **2OD-TTIFDK** and **2OD-TTIFDM**, have been designed, synthesized and fully characterized. The new semiconductors having strong D-A-D π -architectures employ ladder-type π -acceptors of **IFDK/IFDM** and α substituted bithiophene π -donors, which results in ultralow band gaps of 1.21-1.65 eV. The HOMO/LUMO frontier orbital energies of the new molecules (-5.47/-3.61 eV for **2OD-TTIFDK** and -5.49/-4.23eV for **2OD-TTIFDM**) are found to be highly favorable for balanced ambipolar charge-transport and ambient-stability for **2OD-TTIFDM**. The resulting bottom-gate/top-contact OFET devices fabricated by solution-shearing **2OD-TTIFDM** show Journal of Materials Chemistry C Accepted Manuscript

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clear ambipolar characteristics in ambient with reasonably balanced carrier mobilites of 0.13 cm²/V·s for electron and 0.01 cm²/V·s for hole with I_{on}/I_{off} ratios of ~10³-10⁴. **2OD**-**TTIFDK**-based OFETs exhibit ambipolarity under vacuum with highly balanced ($\mu_{c}/\mu_{h} \sim 2$) electron and hole mobilities of 0.02 cm²/V·s and 0.01 cm²/V·s, respectively with I_{on}/I_{off} ratios of ~10⁵-10⁶. Most importantly, complementary-like inverters were demonstrated based on the new ambipolar small molecules, which showed sharp signal switching with very high gains of up to 80. When the charge transport stability of the current semiconductors are compared, our observations show that the ambient-stability of charge-transport in ambipolar semiconductors is governed mainly by the stabilization of conducting electrons in LUMO energy level. To the best of our knowledge, the current D-A-D π -structures are among the best performing ambipolar small molecules for OFET and complementary-like inverter devices. Our findings clearly provide an efficient approach for the preparation of ultralow band-gap small molecules as ambient-stable and solution-processable ambipolar semiconductors for various organic optoelectronic technologies including CMOS-like integrated circuits.

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Supporting Information

SI includes synthetic procedures and characterizations for compounds 2-octyldodecyl bromide and 2,8-dibromoindeno[1,2-b]fluorene-6,12-dione (**IFDK-Br2**) shown in Scheme S1, Figures S1-S8 (¹H/¹³C NMR, MALDI-TOF, and ATR-FTIR spectra, TGA/DSC curves of **2OD-TTIFDK** and **2OD-TTIFDM**), Figures S9 (Chemical structures and optimized geometries of some reference compounds), and Figures S10-S14 (OFET and Inverter electrical curves).

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