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Synthesis and Characterization of Electron-Deficient and Highly Soluble (Bis)Indenofluorene Building Blocks for n-Type Semiconducting Polymers

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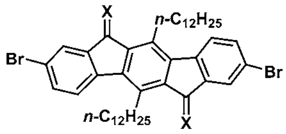
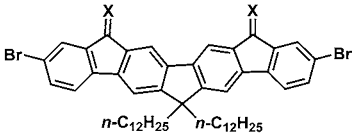
ABSTRACT



1, X = O
2, X = C(CN)$_2$



3, X = O
4, X = C(CN)$_2$

New electron-deficient and soluble indenofluorene-based and bisindenofluorene-based ladder-type building blocks embedding carbonyl and dicyanovinylene functionalities were synthesized, and their optical and electrochemical properties were characterized. These derivatives exhibit optical band gaps of 1.83 to 2.44 eV and low LUMO energies of −3.24 to −4.30 eV, representing a promising new building block class for n-type polymeric electronic materials.

During the past several decades, π-conjugated polymers have received major scientific and technological attention due to their potential as electro-active materials in organic electronics, particularly in printed thin-film transistors, photovoltaic cells, and light-emitting displays.[1] Among these applications, organic thin-film transistors (OTFTs) are considered attractive alternatives to conventional inorganic transistors in functions that require low-cost, low-temperature, solution-phase device processing and mechanical flexibility.[2] As one important OTFT figure-of-merit, large charge carrier mobilities exceeding 1 cm^2 V^{-1} s^{-1} have been reported for p-channel (hole transporting) and n-channel (electron transporting) OTFT small-molecule semiconductors.[3] However, typical mobilities for polymeric semiconductors are far below these optimized, single-crystal or vapor-deposited film values.[4] Among known polymeric semiconductors, soluble n-channel polymers are rare, with the highest reported mobility being 0.01−0.03 cm^2 V^{-1} s^{-1}.[5] A critical goal then is to realize polymers possessing high n-type mobility (>0.1 cm^2 V^{-1} s^{-1}) and air stability along with good OFET current modulation (>10^5) characteristics. A polymer exhibiting these characteristics would be an excellent candidate for practical OTFT applications, reflecting the intrinsic technological attractions of polymers, such as facile film formation and compatibility with low-cost manufacturing and direct-write printing techniques on flexible plastic substrates.[6] These

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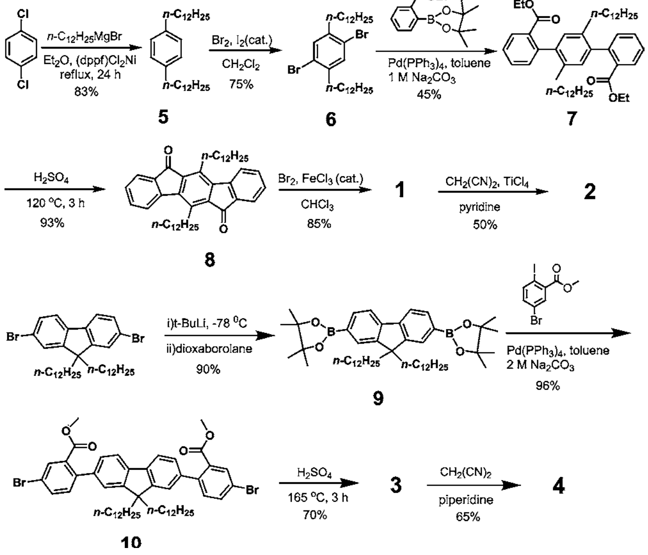
considerations prompted us to seek new electron-depleted (low LUMO) molecular building blocks as polymer precursors based on ladder-type cores.[7] Here we report the synthesis and characterization of a new family of difunctionalized ladder-type molecules (**1**−**4**) in which highly electron-deficient carbonyl and dicyanovinylene groups are introduced into the planar indenofluorene and bisindenofluorene structures along with solubilizing alkyl chains. The design considerations for building blocks **1**−**4** are: (i) Highly π-conjugated planar cores to facilitate efficient π-electron delocalization and to favor good intermolecular $\pi-\pi$ stacking.[8] (ii) Electron-withdrawing carbonyl and dicyanovinylene functionalities to lower LUMO energies, which is crucial for achieving electron transport.[9] (iii) Alkyl side chains (n-$C_{12}H_{25}$) to increase core solubility without disrupting backbone π-conjugation.[10] (iv) Since Suzuki, Stille, and Yamamoto polymerizations will be employed to synthesize the corresponding polymers, all building blocks are designed to accommodate aryl bromide functionalities at the molecular termini.

The syntheses of indenofluorene-based compounds **1** and **2**, and bisindenofluorene-based compounds **3** and **4**, are shown in Scheme 1.

Scheme 1. Synthesis of (Bis)Indenofluorene-Based Monomers **1**−**4**



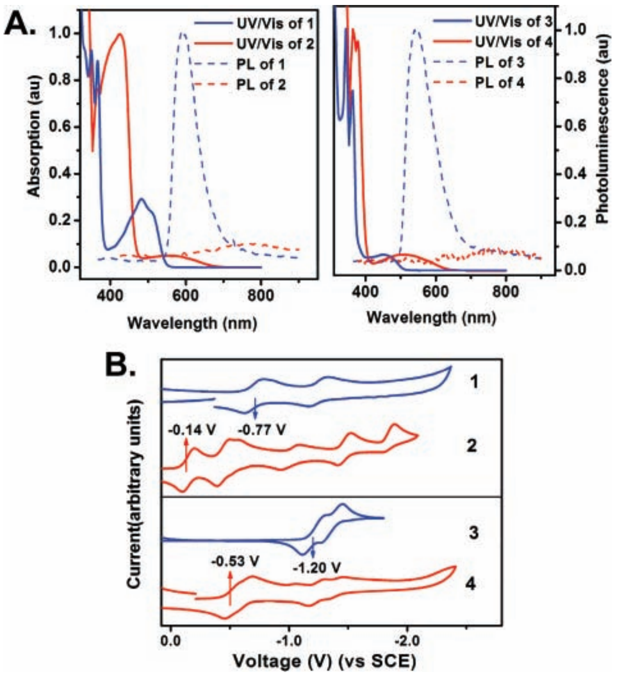


Figure 1. (A) Normalized UV−vis absorption (solid lines) and photoluminescence (dashed lines) spectra. (B) Cyclic voltammograms of compounds **1**, **2**, **3**, and **4** in THF.

Kumada coupling of n-dodecylmagnesium bromide with 1,4-dichlorobenzene affords 1,4-di-n-dodecylbenzene (**5**) in 83% yield, which is then selectively brominated in CH_2Cl_2 under rigorous exclusion of light to afford 2,5-dibromo-1,4-di-n-dodecylbenzene (**6**) in 75% yield. Suzuki coupling of **6** with 2-(ethoxycarbonyl)phenylboronic acid pinacol ester gives compound **7** as a colorless oil in 45% yield. The moderate yield obtained for this Suzuki coupling is due to the presence of the electron-withdrawing ester group in the boronic ester reagent.[11] Double intramolecular Friedel−Crafts acylation is next achieved by treatment of the diester **7** with concentrated sulfuric acid at 120 °C for 3 h. Indenofluorenedione product **8** is isolated as an orange solid in 93% yield. Compound **8** is then regioselectively brominated at the 2 and 8 positions using $FeCl_3/Br_2$ with rigorous exclusion of light to afford monomer **1** in 85% yield. Knoevenagel condensation of **1** to form dimalononitrile structure **2** is achieved in 50% yield using excess malononitrile along with pyridine and $TiCl_4$. Due to the substantial steric hindrance of the carbonyl groups in compound **1**, $TiCl_4$ is used as the Lewis acid for this reaction, but is not necessary for the synthesis of **4** from less sterically hindered **3** (vide infra). Fluorene boronic ester **9** is synthesized in 90% yield starting from 2,7-dibromo-9,9-didodecylfluorene which is double-lithiated

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with *t*-butyllithium and subsequently reacted with 2-isopropoxy- 4,4,5,5-tetramethyl[1,3,2]dioxaborolane. Compound **10** is prepared by Suzuki coupling of **9** with methyl 2-iodo-5-bromobenzoate in high yield (96%). Treatment of **10** with concentrated sulfuric acid at 165 °C for 3 h induces double intramolecular acylation, yielding the target bisindenofluorene diketone **3**. The yield obtained for this ring closure is 70%, with high selectivity at each reaction site (84%). Knoevenagel condensation of **3** with malononitrile and piperidine as the base affords **4** in 65% yield as a purple solid. The new monomers are very soluble in common organic solvents ($CHCl_3$, CH_2Cl_2, THF, toluene), which allows convenient purification by flash columnn chromatography. Compounds **1**−**4** were characterized by ^{1}H NMR, ^{13}C NMR, elemental analysis, IR, and mass spectroscopy (EI/ESI/MALDI-TOF).

The UV−vis absorption and fluorescence spectra of compounds **1**−**4** in THF are shown in Figure 1A, and optical data are collected in Table 1. The absorption spectra of diketone-functionalized monomers **1** and **3** exhibit three maxima, two of them located below 400 nm, and the third one at 450−485 nm. The higher energy maxima (368 nm (**1**) and 365 nm (**3**)) correspond to the $\pi-\pi^*$ transitions of the indenofluorene and bisindenofluorene backbones, respectively, whereas the weaker absorptions at lower energies (484 nm (**1**) and 455 nm (**3**)) are attributed to the symmetry-forbidden carbonyl group n-π^* transition.[12] The absolute absorption maxima of all compounds are shifted to longer wavelengths by ~100 nm compared to that of fluorenone (258 nm in THF).[13] This bathochromic shift is indicative of enhanced π-conjugation of the molecular backbone and is attributed to the highly planar, ladder-type structure of these cores embedding two electron-withdrawing carbonyl groups. When the carbonyl functionalities are replaced with the dicyanovinylene groups, the absolute absorption maxima shift to 426 nm for **2** and 378 nm for **4**, and long-wavelength absorptions are now observed at 579 and 513 nm for **2** and **4**, respectively. The bathochromic shift upon dicyanovinylene functionalization is ~58 nm for the indenofluorene and ~13 nm for the bisindenofluorene core and is consistent with the reported shifts for similar ladder structures.[14,15] This behavior is attributed to LUMO energetic stabilization due to the stronger electron-withdrawing nature of the dicyanovinylene compared to the carbonyl group, resulting in a band gap contraction from 2.28 eV (**1**) to 1.83 eV (**2**), and from 2.44 eV (**3**) to 1.95 eV (**4**).[15] These gaps are considerably smaller than those of typical non-functionalized indenofluorene cores (~3.7 eV).[7d]

Table 1. Electrochemical and Optical Absorption/Emission Properties of Compounds **1**, **2**, **3**, and **4**, and Corresponding Estimated Frontier Molecular Orbital Energies

compd	λ_{abs} (nm)	λ_{em} (nm)	E_g[c] (eV)	$E_{1/2}^{red-1}$ (V)	E_{HOMO}[d]/E_{LUMO}[e] (eV)
1	368,484[a]	590	2.28	−0.77	−5.95/−3.67
2	426,579[a]	762[b]	1.83	−0.14	−6.16/−4.30
3	365,455[a]	540	2.44	−1.20	−5.68/−3.24
4	378,513[a]	768[b]	1.95	−0.53	−5.86/−3.91

[a] n−π^* transition assigned to carbonyl groups. [b] Broad, weak emission peak. [c] Band gap estimated from the low-energy band edge of the UV−vis spectrum. [d] E_{HOMO} calculated from: E_g = LUMO − HOMO.[19] [e] E_{LUMO} calculated as: $-(E^{1/2}{}_{red-1} + 4.44\ \mathrm{eV})$.[19]

The fluorescence emission maxima of carbonyl-containing cores **1** and **3** are located at 590 and 540 nm, respectively. The large observed Stokes shifts are attributable to the occurrence of internal energy transfers between two chromophore units in these molecules: the indenofluorene/bisindenofluorene core and the aryldiketone system.[7c] For dicyanovinylene compounds **2** and **4**, very broad, weak emissions centered at 762 and 768 nm, respectively, are observed. The fluorescence quenching in these highly electron-deficient molecules may be due to the existence of nonradiative internal energy/electron transfers before the radiative emission process.[16] Further detailed studies including polarized absorption and emission measurements will be required to fully define the nature of this emission quenching.

To investigate the redox properties of these new ladder-type molecules, cyclic voltammetry measurements were performed in THF by using Pt as the working electrode, Ag as the pseudo reference electrode, and ferrrocene (0.54 V vs SCE) as the internal standard. The cyclic voltammograms of **1**−**4** are shown in Figure 1B, and electrochemical data are collected in Table 1. For all molecules, multiple reversible reductions but no oxidations are observed, suggesting that all building blocks are substantially electron-dopable.[17] Analysis of the half-wave potentials reveals the importance of carbonyl and dicyanovinylene functionalizations in modulating the **1**−**4** frontier molecular orbitals.

Indenofluorenedione **1** undergoes two reversible reductions with the half-wave potentials of −0.77 and −1.31 V versus SCE, which are assigned as reduction of the diketone to the quinonoidal dianion.[7c] Ladder-type diketone structure **1** can be reduced much more easily than non-ladder type terphenylene and quaterphenylene compounds which show reversible reductions at −2.40 V and −2.28 V (vs SCE), respectively.[18] Thus, it is evident that the reduction potential is shifted to more positive values with increasing degree of planarity and electron deficiency of the core. The reversibility of both reductions demonstrates the redox stability of the new diketone structure. The estimated LUMO energy is −3.67 eV using the vacuum level energy of the standard calomel electrode as 4.44 eV.[19]

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Upon dicyanovinylene functionalization, compound **2** exhibits six reversible one-electron reductions with the first reduction located at −0.14 V. The greater electron-accepting capacity of **2** is attributable to the highly electron-withdrawing character of the dicyanovinylene groups. The LUMO energy is estimated as −4.30 eV. To our knowledge, this is one of the lowest LUMO energies reported for an electron-deficient, soluble polymer building block, and is comparable to those of air-stable n-channel core-cyanated perylene and naphthalene semiconductors.[20] Bisindenofluorenedione **3** exhibits two reversible electron reductions at −1.20 and −1.39 V. Upon dicyanovinylene functionalization, the reduction potentials exhibit anodic shifts, with the first reduction now located at −0.53 V. Compound **4** exhibits five one-electron reductions. It can be seen that dicyanovinylene functionalization at either indenofluorene and bisindenofluorene position decreases the voltage gap between the first two reductions by 0.1−0.2 V, doubtless reflecting the more electron-accepting nature of these derivatives, and rendering the second reduction more facile. This similarity of the first two potentials suggests that these reductions are largely malononitrile-centered as previously observed for tricyanovinyl-capped oligothiophenes.[21]

The anodic shift in the reduction potential from the diketone to dicyanovinylene structure is ∼0.65 V for both systems, which suggests that the dicyanovinylene substituent electronically affects both cores in the same way. The potential difference between successive reduction events [$\Delta E_{1/2} = E_{1/2-2} - E_{1/2-1}$] for bisindenofluorene-based compounds **3** and **4** is ∼0.19 V, whereas the difference is almost three times that (∼0.52 V) in indenofluorene-based structures **1** and **2**. Here, the second reduction becomes more difficult than the first due to less effective radical anion delocalization and increased Coulombic repulsion within the smaller indenofluorene π-system compared to the bisindenofluorene π-system. A similar trend is observed for the α-nT and phenylene (p-nP) series.[18,22]

Top-contact OFETs were fabricated by vapor deposition of compound **4** on OTS-treated n^{++}-Si/SiO$_2$(300 nm) substrates. Preliminary measurements reveal an unoptimized electron mobility of 0.002 cm^2 V^{-1} s^{-1} with a current on/off ratio of ∼10^6 (Figure 2). Note that although soluble, bromo/iodo functionalized monomeric building blocks are generally poor OFET semiconductors, the corresponding polymers can exhibit far greater performance. For example, within the polythiophene family, although β-alkylsubstituted oligothiophenes exhibit negligible/low carrier mobilities, the corresponding polymers (e.g., PQT, P3HT) are among the highest mobility organic semiconductors reported to date.[3,4c] The observed electron mobility for **4** is therefore very promising for the further optimization of these building blocks as n-channel polymers.

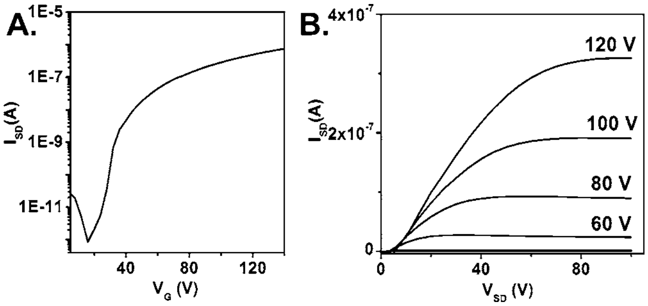

Figure 2. OFET plots of devices (n++-Si/SiO$_2$−OTS (300 nm)/**4** (50 nm)/Au contacts (50 nm)) fabricated with monomer **4**. (A) Transfer curve for V_{SD} = 100 V. (B) Output curve for various gate voltages.

In summary, we have successfully designed and synthesized a new family of ladder-type organic semiconductor building blocks. These structures exhibit high electron affinities and solubilities, crucial requirements for n-channel semiconducting polymers. The homo- and copolymerization reactions of these monomers are currently under investigation and will be reported in due course.

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Supporting Information Available: Detailed experimental procedures, device fabrication /characterization details, spectroscopic characterizations; ^{1}H NMR, ^{13}C NMR, IR, and EI/ESI/MALDI-MS spectra of **1**, **2**, **3**, **4**, and **8** (Figures S1−S16). This material is available free of charge via the Internet at http://pubs.acs.org.

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