

A General Synthetic Route to Indenofluorene Derivatives as New Organic Semiconductors

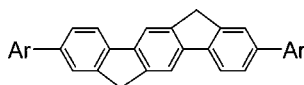
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ABSTRACT



A series of 2,6-disubstituted indenofluorene derivatives were obtained in high purity via a general route involving the Suzuki coupling reaction. The potential of these conjugated indenofluorenes as new organic semiconductors was demonstrated by the light-emitting diode reaching a high luminance of 1400 Cd/m² below 10 V.

Conjugated aromatic compounds are potential candidates as organic semiconductors for use in thin-film transistors (TFTs) and light-emitting diodes (LEDs). By incorporation of strongly electronegative substituents such as fluorine¹ and cyano groups² into certain aromatic molecules, some important n-type compounds have been obtained for TFT applications. To develop organic LED devices (OLEDs) with

uniform luminescence, saturated color, and low driving voltages, many material factors must be considered, such as emission efficiency, color purity, carrier mobility, thermal and chemical stability, and processability (for vapor-phase deposition).³

Among those organic semiconductors known for transistor and OLED applications, the fluorene-based compounds,⁴ oligomers,⁵ and polymers⁶ have received most attention, owing to their unique properties, availability, and processability. Since the substituted fluorenes are known to have relatively high band gaps and low HOMO levels, they are

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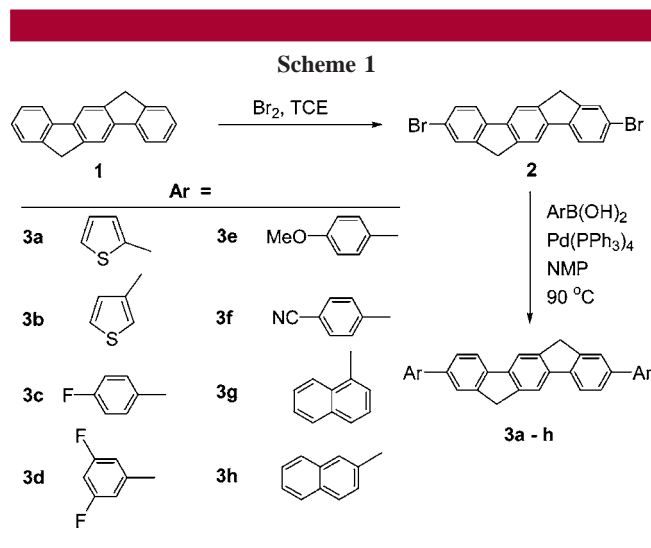
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stable to photo- and electro-oxidation and the related devices have shown high on/off ratios with good aging characteristics.^{4d}

Fluorene is a rigid and planar molecule, due to the methylene bridging unit at the 2,2'-positions of the biphenyl moiety, with high thermal stability.⁷ Since its electronic and optical properties arise from its planar biphenyl moiety, it is conceivable that the structurally related compound, indenofluorene, should have some unique electronic and optical characteristics attributable to a planar, longer conjugated *p*-terphenyl moiety.

A number of different synthetic routes are available for the syntheses of indenofluorene derivatives that are mainly functionalized at the 9,9'-positions with the alkyl groups.⁸ Each one is unique, but not general enough to allow for the synthesis of a series of structurally related indenofluorenes for probing the structure–property relationships. We report herein a facile synthetic route to a new series of indenofluorene derivatives with aryl groups at the terminal 2,6-positions and the preliminary results of organic LED using one of eight indenofluorene derivatives synthesized.

In this two-step approach (Scheme 1), a key step involves the Suzuki coupling reaction, and 2,6-dibromoindenofluorene (**2**) is a building block for a variety of indenofluorene derivatives. Indenofluorene was readily available in tens or even hundreds of grams in four steps, starting with the Suzuki reaction of 2,5-dibromo-*p*-xylene with phenylboronic acid in quantitative yield. Oxidation of 2,5-diphenyl-*p*-xylene by potassium permanganate yielded 2,5-diphenylterephthalic acid (92% yield), which was treated in concentrated H₂SO₄ to afford the corresponding diketone in 96% yield, which was then reduced to indenofluorene by the modified Wolf–Kishner reduction.^{8a} Indenofluorene was easily brominated with Br₂ in 1,1,2,2-tetrachloroethane (TCE) at room temperature to afford 2,6-dibromoindenofluorene (**2**) in 77%

yield (see the Supporting Information). Compound **2** can be prepared in tens of grams and becomes a building block for a series of indenofluorene derivatives.

The subsequent Suzuki reaction was carried out to couple compound **2** with the corresponding boronic acids in the presence of Pd(PPh₃)₄ in NMP at 90 °C (see the Supporting Information). The resulting products were filtered and washed with water. Compounds **3a–h** were obtained in modest yields (7–44%), without optimization, after purification by vacuum sublimation.

Thermogravimetric analysis confirmed good thermal stability of these indenofluorene derivatives, as 5% weight loss of **3a** was observed at 411 °C in nitrogen. The differential scanning calorimetry (DSC) revealed the melting transition of 392 °C for **3c**, while the crystallization temperature upon cooling was found to be 338 °C. High melting behavior was also observed for other compounds (Table 1). Despite their

Table 1. Properties of Compounds **3a–h**

	mp ^a (<i>T</i> _c , °C)	λ _{abs} , ^b nm	λ _{PL} , ^b nm	Φ ^c
3a	362	365, 381	396, 416, 443	44
3b	> 400	350, 365	378, 398, 421	34
3c	392 (338)	346, 356	376, 394, 417	48
3d	397 (385)	350, 360	383–401, 430	43
3e	> 400	353	385, 403, 432	59
3f	389 (380)	358	428	78
3g	337 (281)	311, 345	393	18
3h	> 400	355	394, 403, 432	55

^a Melting points are measured by DSC. *T*_c = crystallization temperature. ^b In DMF. ^c Quantum yield (%) in reference to quinine sulfate (1 μM in 1 N H₂SO₄).

high melting characteristics, these compounds can be readily sublimed under vacuum at elevated temperatures.

The UV–vis absorption and photoluminescence (PL) of all eight compounds in solution (DMF) were studied (Table 1). Two absorption peaks (λ_{max}) were observed for **3a–d** and **3g**, whereas **3e**, **3f**, and **3h** had only one broad peak. The peaks at the longer wavelength (345–381 nm) correspond to the π–π* transition of the conjugated aromatic rings, and those at a shorter wavelength (311–365 nm) are attributed to the electronic transition of each aromatic unit. The presence of the thienyl rings caused a red shift (Figure 1). Correspondingly, PL peaks appeared around 400 nm for the samples in solution.

Energy level of **3a** and **3b** could be determined using the data from cyclic voltammetry and absorption spectra.⁹ However, like many conjugated organic compounds, the electrochemical processes of **3a** and **3b** were not reversible. By calculating with the HOMO–LUMO band gap measured from the absorption spectra, the LUMO level is 2.0 eV for **3a** and 2.6 eV for **3b** (Table 2). The HOMO levels of **3a–h** are ~5.1–5.8 eV.

The electroluminescent (EL) properties of compound **3a** were tested in the following OLED structure: ITO/**3a** (500

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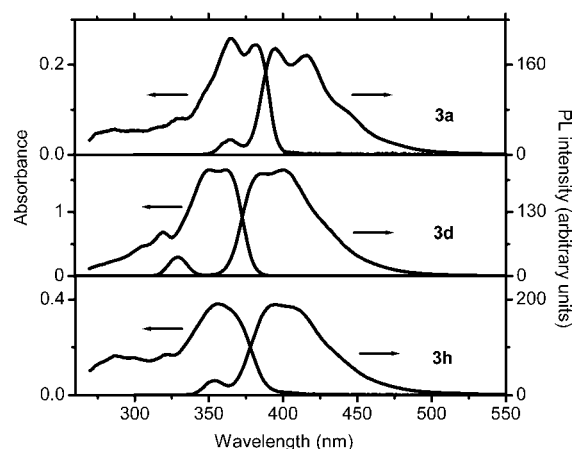


Figure 1. UV absorption ($25\ \mu\text{M}$ for all) and PL of **3a** ($0.5\ \mu\text{M}$), **3d** ($0.25\ \mu\text{M}$), and **3h** ($0.5\ \mu\text{M}$) in DMF, excited at 350, 355, and 365 nm, respectively.

\AA)/PBD ($500\ \text{\AA}$)/LiF ($15\ \text{\AA}$)/Al. PBD or 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole is an electron transport material with a lower HOMO than that of **3a**, which should facilitate the charge recombination in **3a**.¹⁰ The combination of a thin LiF layer and Al has been shown to form an efficient cathode.¹¹ The ITO surface was treated in a UV–ozone oven for 10 min, and then the structure was thermally evaporated without exposure to air in an Edwards Auto-306 multisource chamber with a base vacuum better than 10^{-6} Torr. A quartz substrate was placed beside the OLED substrate to collect the deposited **3a**, for comparison of thin film PL with its EL spectrum.

Table 2. HOMO and LUMO Level of **3a** and **3b**

	$E^{\text{ox } a}$ (V)	HOMO (eV)	λ_{onset} (nm)	E_g (eV)	LUMO (eV)
3a	0.55	5.1	399	3.1	2.0
3b	1.18	5.8	383	3.2	2.6

^a Redox potential versus NHE; performed in propylene carbonate containing $0.1\ \text{M LiClO}_4$.

The OLED was tested using a programmable Keithley 2400 SourceMeter unit and a Minolta LS-110 Luminance

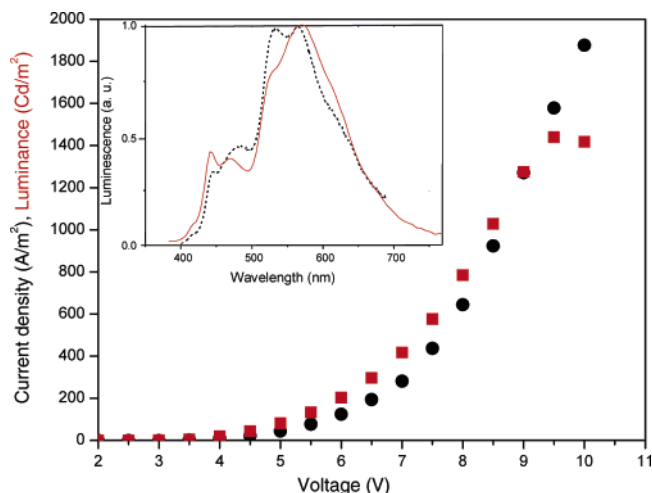


Figure 2. JLV (current density in black circles, luminance in red squares) characteristics of an ITO/**3a**/PBD/LiF/Al OLED. Inset: EL (taken at 9 V, solid red line) of OLED and PL of **3a** (350 nm excitation, dashed black line).

meter. Figure 2 shows typical current density–voltage and luminance–voltage characteristics of the OLED. The OLED reaches a high luminance of $1400\ \text{Cd/m}^2$ below 10 V for a current density around $1600\ \text{A/m}^2$. The quantum luminous efficiency is about 1 Cd/A at 9 V but decreases at higher voltages. The inset of Figure 2 shows the EL spectrum taken at 9 V, which is independent of the voltage and is in agreement with the PL taken on the quartz witness sample excited at 350 nm. Due to the polycrystalline nature of the deposited film of **3a**, the observed absorption was broader, have multiple bands and shifted to longer wavelengths in comparison with the spectrum of **3a** in solution (Figure 1). As a result, the PL spectrum of thin film was also broader and the device emitted the whitish yellow color.

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Supporting Information Available: Syntheses and characterizations of compounds **2** and **3** and CV of thin films of **3a** and **3b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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