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Synthesis and Characterization of Highly Fluorescent Indenofluorenes

Samuel Merlet, Maria Birau, and Zhi Yuan Wang*

*Nortel Networks-Carleton University Laboratory for Advanced Materials Research,
Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa,
Ontario, Canada K1S 5B6*

wangw@ccs.carleton.ca

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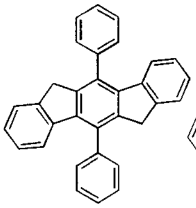
ABSTRACT



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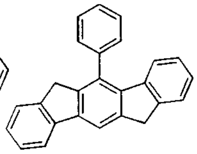

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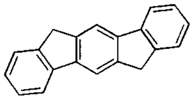

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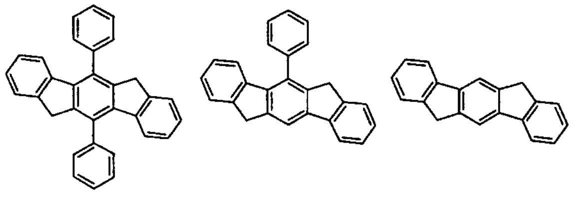
Described here are the synthesis and optical and electrochemical properties of a series of indenofluorenes as new building blocks for electronic and optoelectronic materials.

Organic materials such as the semiconducting π-conjugated compounds (e.g., pentacene)[1,2] suitable for applications in electronics (e.g., thin film transistor) and optoelectronics (e.g., organic light emitting diodes, OLED) have received increasing attention during the past years. The research currently focuses on the development of organic semiconductors with a good stability to high temperature, air, and chemicals.

Alkylated fluorenes and indenofluorenes are known to have good fluorescence properties and have also been investigated for the OLED applications.[3−5] A major problem encountered in fluorescent planar molecules or polymers is the formation of π-aggregates/excimers, which leads to an additional emission band in long wavelength and a decrease in electroluminescence. This problem is mainly solved by introduction of long or branched side chains (e.g., octyl groups on the bridging methylene of fluorene and indenofluorene) and copolymerization with a suitable bulky comonomer. For example, it has been demonstrated that incorporation of the octyl groups at 6,6′,12,12′-positions and a small amount of 9,10-anthracendiyl moiety into a rigid-rod indenofluorene polymer can effectively suppress the aggregation tendency of the indenofluorene segments.[6]

To increase the steric hindrance, we have designed a new substituted indenofluorene, 5,11-diphenyl-6,12-dihydroindeno[1,2b]fluorene **(1)**. It is also of great interest to synthesize the monosubstituted and unsubstituted analogues (**2** and **3**) to complete the series (Scheme 1). Moreover, it should be feasible to further functionalize these indenofluorene compounds for thin-film transistor and OLED applications.

Scheme 1



1 **2** **3**

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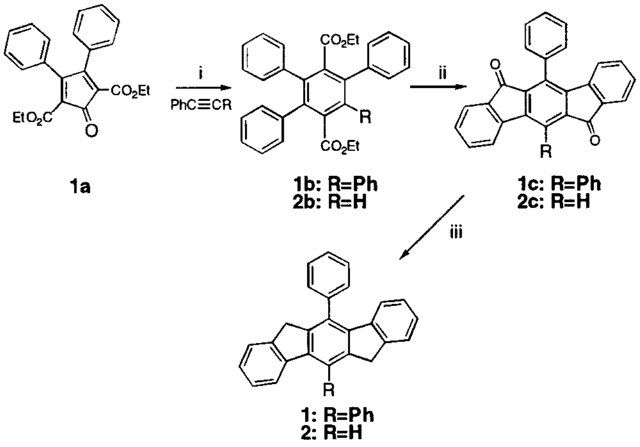
Scheme 2[a]



[a] Reagents and conditions: (i) dichlorobenzene, reflux, 12 h, 90%; (ii) glacial AcOH, HBr, reflux, 48 h, (**1b**, 78%; **2b**, 78%); then concentrated H_2SO_4, 3 h, rt, (**1c**, 90%; **2c**, 88%); (iii) N_2H_4·H_2O, KOH, diethylene glycol, reflux, 24 h, (**1**, 95%; **2**, 98%).

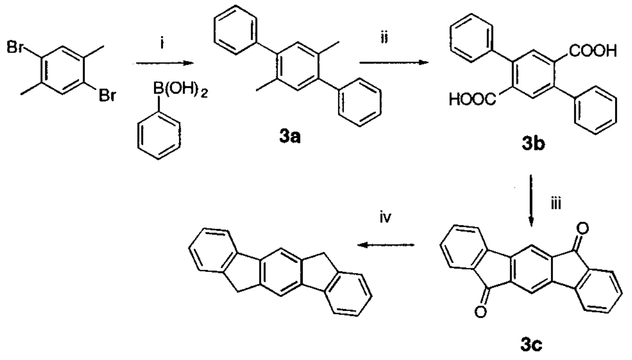
As described in Scheme 2, compound **1** was synthesized starting with a Diels–Alder addition of the cyclone **1a**[7] and diphenylacetylene to give the tetraphenyl diester **1b** in 90% yield. The hydrolysis of **1b** was performed in acetic acid with hydrobromic acid to give the corresponding acid, which was cyclized quantitatively in the diketone **1c**. It was noticed that the cyclization was regiospecific and gave only one isomer. The steric hindrance and torsion angles of the terphenyl moiety probably play a dominant role in this cyclization. The subsequent Wolf–Kirshner reduction afforded **1** in 86% yield.

Compound **2** was synthesized via the same route as **1** using phenylacetylene instead of diphenylacetylene. In this case the cyclization gave two isomers, which had to be separated by fractional recrystallization.

As shown in Scheme 3, compound **3** was synthesized using a modified Ebel method.[8] The aqueous Suzuki coupling between 2,5-dibromo-*p*-xylene and phenylboronic acid gave **3a** in 98% yield,[9] which was oxidized using potassium permanganate in aqueous pyridine to yield the corresponding acid. The cyclization and the subsequent reduction afforded **3** in overall 64%.

Figure 1 displays the UV–vis and photoluminescence (PL) spectra of **1**–**3** in solution. The absorption spectra of **1**–**3** are similar, displaying an absorption maximum around 329–334 nm (Table 1). It is expected that the absorbance from the indenofluorene moiety remains the same while the peak at 220 nm decreases as the number of pendent phenyl groups decreases from 2 to 1 and 0.

Scheme 3[a]



[a] Reagents and conditions: (i) water, K_2CO_3, Bu_4NBr, $Pd(OAc)_2$, 70 °C, 2 h, 98%; (ii) $KMnO_4$, pyridine, water, reflux, 24 h, 96%; (iii) concentrated H_2SO_4, 25 °C, 2 h, 90%; (iv) N_2H_4·H_2O, KOH, diethylene glycol, reflux, 48 h, 76%.

Compounds **1**–**3** are highly fluorescent with a quantum yield of 73–78%. These results indicate that the absorption λ_{max} and the photoluminescence efficiency are relatively insensitive to the phenyl substituent and mainly arise from the indenofluorene moiety. However, the pendent phenyl groups could influence the emission wavelength, as compounds **1** and **2** with one and two phenyl groups showed a red-shifted emission compared with that of **3** (Table 1). The longer emission wavelength of **1** and **2** reveals the contribution of phenyl substituents to a more conjugated excited state, in contrast with a twisted ground state. It can also be seen that the sharpness of emission peak is affected by the phenyl substituent (Figure 1).

Cyclic voltammograms of **3** exhibited two quasi-reversible reduction peaks of respective potential (vs SCE) E_1^{red} = −2.6 V and E_2^{red} = −2.9 V and one quasi-reversible oxidation peak of potential E_1^{ox} = 1.25 V (Figure 2 and Table 1), whereas **1** and **2** exhibited only one quasi-reversible

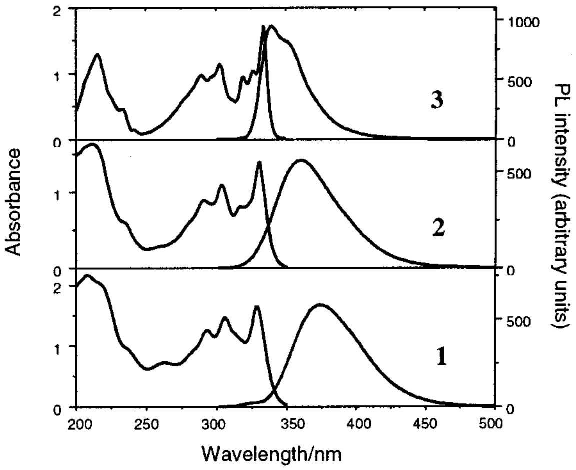


Figure 1. UV-vis absorption (24 μM in cyclohexane for **1** and **2**, in Decalin for **3**) and PL of **1** (0.6 μM in cyclohexane), **2** (0.6 μM in cyclohexane), and **3** (0.6 μM in Decalin) excited at 329–334 nm.

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Table 1. Optical and Electrochemical Properties of **1**−**3**

	λ_{max}abs (nm)/log ϵ	λ_{max}em (nm)	quantum yield (%)[a]	ΔE_{abs} (eV)	E_1^{red} (V)[b] vs SCE	E_2^{red} (V)[b] vs SCE	E_1^{ox} (V)[d] vs SCE	ΔE_{ec} (V)
1	329/4.83	375	74	3.77	−2.2	−2.40[c]		
2	331/4.76	364	78	3.75	−1.8	−2.2[c]		
3	333/4.83	340, 356	73	3.71	−2.6	−2.9	1.25	3.85

[a] Calculated in reference to quinine sulfate (1 μM in 1 N H_2SO_4). [b] Performed in 0.1 M solution of *n*-Bu_4NPF_6 in DMF, carbon electrode as the working electrode, scan rate of 200 mV s^{-1}, ferrocene as an internal standard. [c] E_{pc}. [d] Performed in 0.1 M $LiClO_4$ in acetonitrile.

reduction wave of potential E_1^{red} = −2.2 and −1.8 V, respectively. They both showed an irreversible second reduction step, suggesting that the ionic species are either very stable or transformed into the electro-inactive species. It is likely that the radical anion obtained after the first reduction is transformed into a dianion that is protonated in DMF, which may contain a trace amount of water.

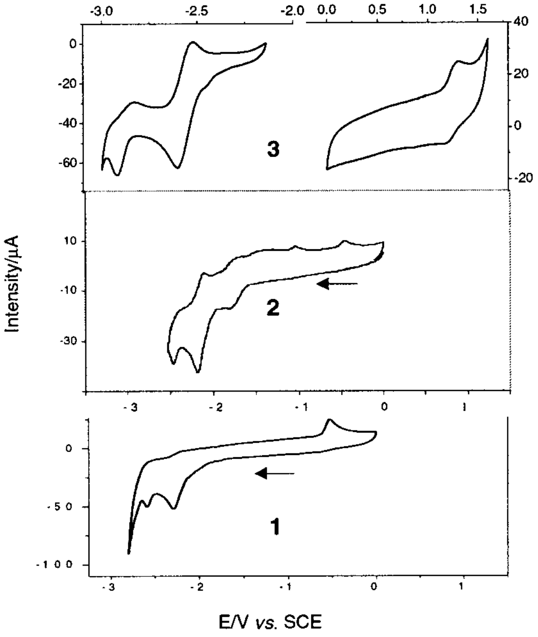

Figure 2. Cylcic voltammograms of **1**−**3**: reduction peaks for **1** and **2**; reduction and oxidation peaks for **3**.

The presence of the phenyl group obviously made the electrochemical reduction much easier, as reduction potentials are increased from −2.6 to −2.2 V for **3** and **1**, respectively.

Furthermore, compounds **1**−**3** have a similar optical band gap of 3.7 eV (Table 1). It is of interest to compare the electrochemical band gap with the optical one,[10] as the two ΔE values are quite close for **3**. Unfortunately ΔE_{ec} cannot be obtained for both **1** and **2,** since their oxidation potentials are out of the solvent window.

In summary, we have demonstrated efficient methods for the synthesis of a new series of indenofluorenes. These indenofluorenes are large band-gap compounds with high PL in solution and thus show a great potential as optoelectronic materials. Further electrochemical and solid-state studies are under way and will be reported in due course. Improvements of physical properties are under investigation, along with the functionalization of such compounds.

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Supporting Information Available: Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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