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Synthesis and Characterization of Oligo(9,9-dihexyl-2,7-fluorene ethynylene)s: For Application as Blue Light-Emitting Diode

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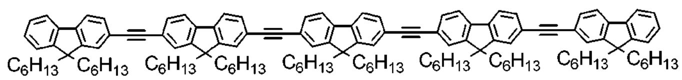
ABSTRACT



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Highly soluble and strongly blue fluorescent oligo(9,9-dihexyl-2,7-fluorene ethynylene)s (OFEs) were synthesized by a Pd/Cu-catalyzed Sonogashira coupling reaction. An organic light-emitting diode using pentamer 15 as the emitting material was successfully fabricated and emitted a bright blue light.

Monodisperse, well-defined π-conjugated oligomers have recently become a subject of intense research in material science.[1] For example, they can be used as nondefected structures for electronic devices such as organic light-emitting diodes (OLEDs),[2] solar cells,[3] and field-effect transistors (FETs)[4] and as models[1c] to understand the fundamental properties of their analogous polydisperse polymers. Development of synthetic methodology makes it possible to design a variety of soluble monodisperse oligomers, which permit color and charge injection tuning through their conjugation length control, as well as the introduction of electron-donating or -withdrawing groups to the parent π-conjugated system.[5]

Oligofluorenes are important model compounds for polyfluorenes, which are the promising blue light-emitting materials with extremely high photoluminescence, quantum yields, and thermal and oxidative stability.[6] The structure−property relationship of polyfluorene was obtained by investigating the electronic properties of each type of oligofluorene.[7] However, there were, to our knowledge, no reports on determination of the effective conjugation length for poly(2,7-fluorene ethynylene) (PFE). Herein we report a successful synthesis of a series of OFEs and their optical properties and offer the possibility of an OLED application using pentamer **15** as blue light-emitting material.

The syntheses of OFEs started from commercially available fluorene. Electrophilic monoiodination[8] of fluorene afforded 2-iodofluorene, which was subsequently alkylated to give 2-iodo-9,9-dihexylfluorene (**2**) in 57% overall yield.

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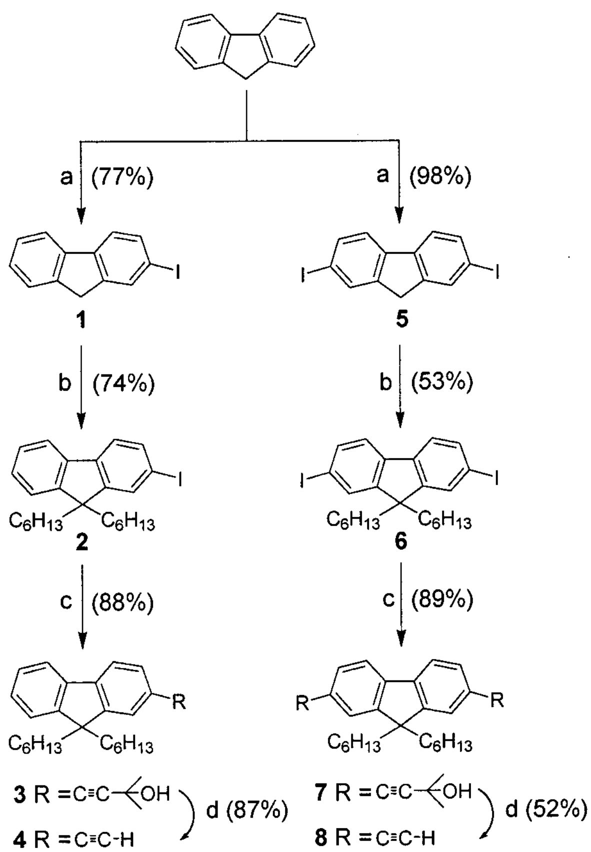
Pd/Cu-catalyzed cross-coupling of **2** and 3-methyl-1-butyn-3-ol provided **3** (88%), which was then converted to 2-ethynyl-9,9-dihexylfluorene (**4**) by a base-promoted deprotection in 87% yield. The long dihexyl moieties provide good solubility for the longer oligomers. 2,7-Diethynyl-9,9-dihexylfluorene (**8**), which is a monomer to construct the longer OFEs, was prepared by diiodination of fluorene, a displacement reaction with hexyl bromide, cross-coupling using Pd/Cu catalyst, and finally deprotection (Scheme 1).

Scheme 1[a]



[a] (a) I_2, H_5IO_6, AcOH, H_2SO_4, H_2O, reflux, 4 h; (b) $C_6H_{13}Br$, triethylbenzylammonium chloride, 50% aqueous NaOH, DMSO, rt, 6 h; (c) 3-methyl-1-butyn-3-ol, $PdCl_2(PPh_3)_2$, PPh_3, CuI, triethylamine, reflux, 6 h; (d) KOH, 2-propanol, reflux, 3 h.

Our strategy for the potential blue light-emitting OFEs was based on the synthetic route above (Scheme 2). Pd/Cu-catalyzed cross-coupling of **2** and **4** generated dimer **9** in 62% yield. Treatment of **4** with **6** in the presence of Pd/Cu catalyst afforded trimer **10** (28%) and byproduct iodo dimer **11** (24%) after purification of silica gel, respectively. The latter further reacted with 3-methyl-1-butyn-3-ol to give **12**, followed by the cleavage of the polar group to afford dimer **13** with the terminal acetylene unit. Treatment of **11** with **13** or **8** using **a** Sonogashira coupling reaction gave the desired tetramer **14** (67%) or pentamer **15** (19%), respectively. Pentamer **15**, which is the longest monodisperse OFEs in the present π-conjugated system, is still highly soluble in common organic solvents such as chloroform, dichloromethane, and THF. This is necessary not only to prepare oligomers with the sufficiently long rod length but also to fabricate organic light-emitting diodes (OLEDs) by the spin-coating method.

To investigate the electronic properties of each type of oligomer structure and to determine the effective conjugation length for the corresponding polymer, absorption spectra for each oligomer were examined. The OFEs exhibit a distinct red shift as their rod lengths increase (Figure 1a). The

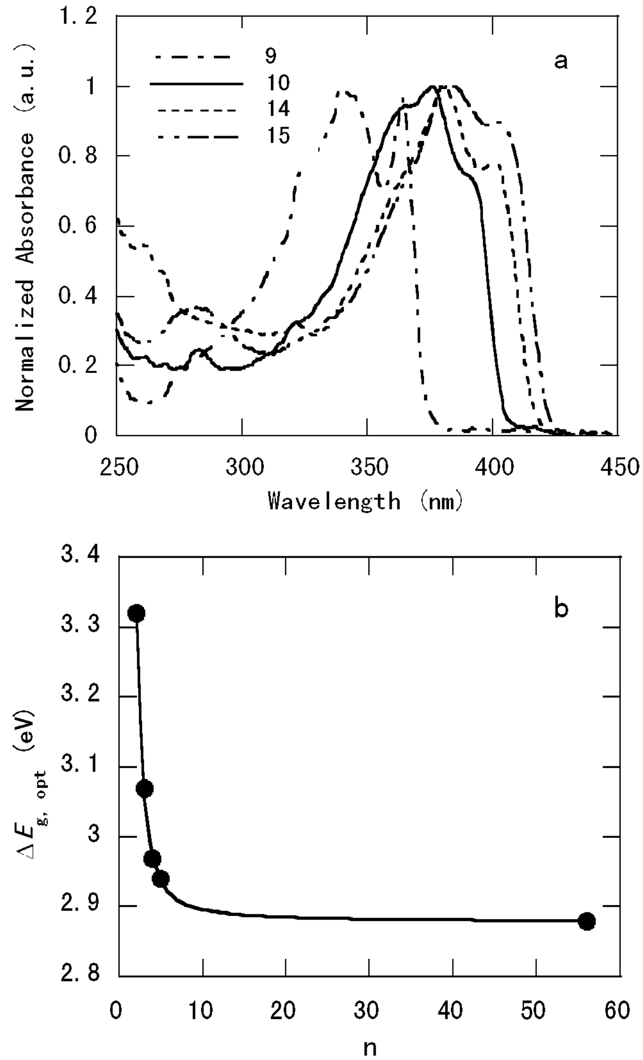
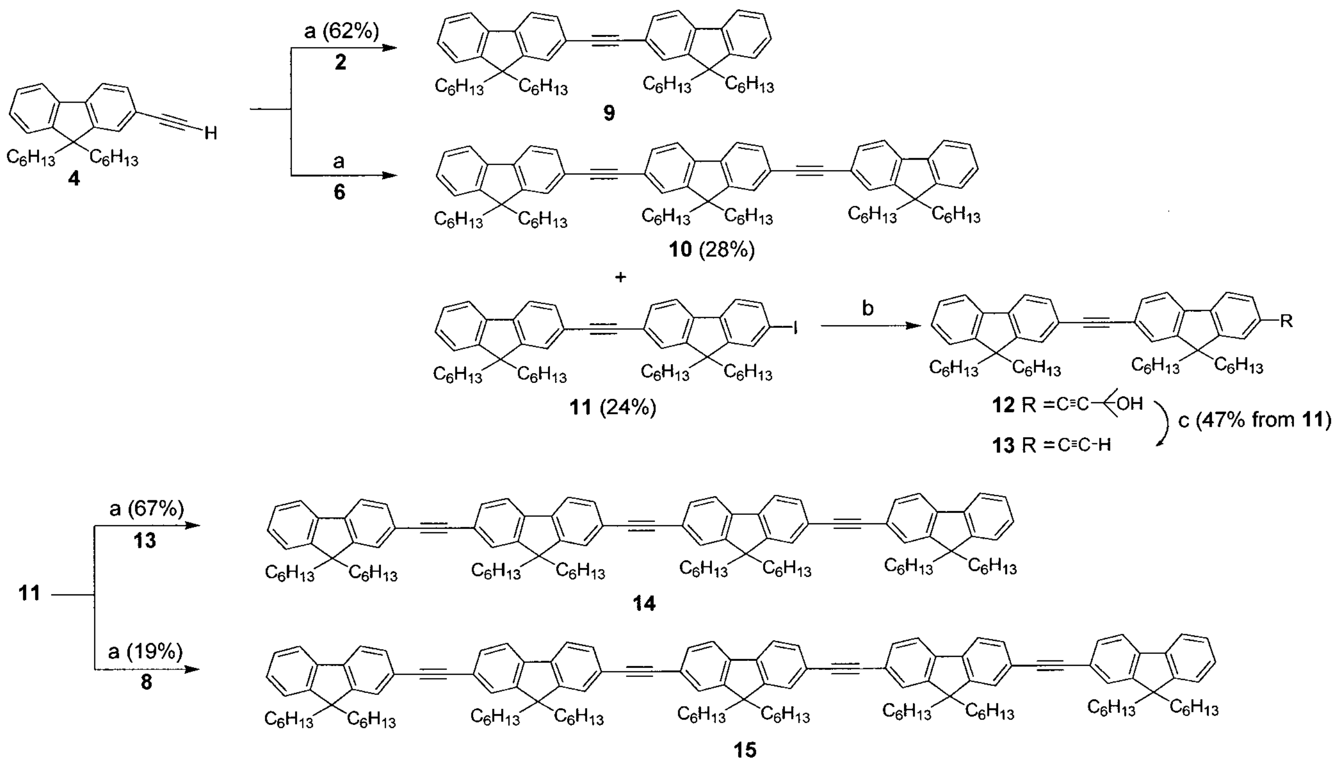


Figure 1. (a) Normalized absorption spectra of **9**, **10**, **14**, and **15** in chloroform. (b) Plot of optical band gap versus the number of repeating units (*n*) for **9**, **10**, **14**, **15**, and PFE.

maximum peaks observed for these oligomers approach that (2.88 eV)[9] for PFE. By inspecting the edge of the absorption spectra, the energy band gaps were plotted as a function of oligomer length (Figure 1b). This saturated curve indicates that the oligomers prepared are well defined and largely nondefected, and the calculated effective conjugation length of PFE is about 10 fluorene units, which corresponds to a

(9) Lee, S. H.; Nakamura, T.; Tsutsui, T., unpublished results.

Scheme 2[a]



[a] (a) $PdCl_2(PPh_3)_2$, PPh_3, CuI, triethylamine, reflux, 24 h; (b) 3-methyl-1-butyn-3-ol, $PdCl_2(PPh_3)_2$, PPh_3, CuI, triethylamine, reflux, 6 h; (c) KOH, 2-propanol, reflux, 6 h.

total of 20 aromatic rings. As shown in Figure 2, pentamer **15** exhibits strong blue fluorescence with an emission maximum at 402 nm and a weaker peak centered on 445 nm, which is bathochromically shifted by 50 nm compared to dimer **9**. The PL efficiencies of **9**, **10**, **14**, and **15** are 49, 52, 63, and 64, respectively. Apparently, increasing conjugation length in the π-conjugated system increases the quantum yield of fluorescence. Pentamer **15**, with the highest quantum efficiency in this study, was tried to fabricate OLED.[10] The electroluminescence (EL) spectrum of pentamer **15** shows blue light emission with a maximum peak at 424 nm and a weaker peak at 449 nm, in which the maximum peak is red-shifted by 22 nm compared to the PL spectrum of pentamer **15** in $CHCl_3$. This result indicates strong intermolecular interaction in the solid state.

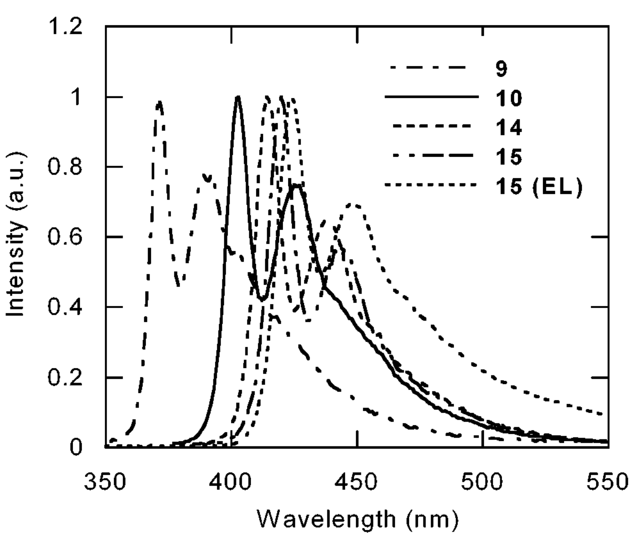


Figure 2. Normalized photoluminescence spectra of **9**, **10**, **14**, and **15** in chloroform and electroluminescence (EL) spectrum of **15**.

In summary, we have synthesized a new series of soluble oligo(9,9-dihexyl-2,7-fluorene ethynylene)s with strong blue fluorescence and successfully fabricated an organic light-emitting diode (OLED) using pentamer **15**, yielding blue light emission.

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

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(10) OLED was fabricated on an indium tin oxide (ITO)-coated glass substrate by spin-coating of pentamer **15** in chloroform as the emitting layer (60 nm) and then by vacuum thermal deposition (below $1 \times \sim 10^{-6}$ Torr) of Ca as the cathode.