

Indeno[2,1-*c*]fluorene-based blue fluorescent oligomers and polymers: Synthesis, structure, photophysical and electroluminescence properties

Bin Du^a, Lei Wang^c, Si-Chun Yuan^{a,**}, Ting Lei^b, Jian Pei^{b,*}, Yong Cao^c

^a Food Science and Engineering College, Department of Fundamental Science, Beijing University of Agriculture, Beijing 102206, China

^b Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

^c State Key Laboratory of Luminescent Materials and Devices, Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Guangzhou 510640, China

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ABSTRACT

An alkylated skeleton of indeno[2,1-*c*]fluorene, viewed as a positional isomerism of indeno[1,2-*b*]fluorene, was developed to construct several conjugated oligomers and polymers through a Pd-catalyzed Suzuki coupling reaction for organic light-emitting diodes. Single crystal analysis indicated that the structure of indeno[2,1-*c*]fluorene was twisted due to close H–H contacts in the crowded region of molecules. **P1–P3** showed good solubility in common organic solvents as well as facile film forming properties. In comparison with linear *n*-alkyl-substituted oligo(indeno[1,2-*b*]fluorene)s and poly(indeno[1,2-*b*]fluorene)s (**2,8-PIFs**), the absorption and emission features of twisted *n*-alkyl-substituted oligo(indeno[2,1-*c*]fluorene)s and poly(indeno[2,1-*c*]fluorene) (**P1**) in dilute solution exhibited a correlation to the conjugation length and obviously blue-shifted due to the distorted backbones. All polymers emitted strong blue fluorescence with very narrow full widths at half-maximum (fwhm) (about 50 nm) in dilute solution and in thin film. Electroluminescent (EL) devices with the configuration of ITO/PEDOT:PSS/PVK/polymers/Ba/Al were fabricated to achieve blue EL emission with maximum brightness up to 2800 cd/m² at a bias of 10 V. The EL devices using **P2** as the active materials showed a maximum external quantum efficiency of 1.2% and a maximum luminous efficiency of 1.5 cd/A. Our investigations demonstrate that indeno[2,1-*c*]fluorene moiety might be regarded as a potential building skeleton to develop the effective blue and UV light-emitting materials.

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1. Introduction

Blue light-emitting polymers and copolymers are drawing wide interest, notably for applications in large-area flexible and tunable polymeric light-emitting diodes (**PLEDs**) [1]. In this respect, considerable efforts have been devoted to the development of solution-processable poly(*p*-phenylene)s (**PPPs**) [2], polyfluorene (**PF**) [3], ladder-type PPPs (**LPPPs**) [4], poly(tetrahydropyrene)s [5], poly(2,7- or 3,6-phenanthrylene)s [6], poly(2,8-indenofluorene)s (2,8-**PIFs**, Scheme 1) [7], poly(2,7-pyrenylene)s [8] and their derivatives due to the suited **HOMO–LUMO** energy gaps required for obtaining blue emission. Of these, linear polycyclic indenofluorene-based **PIFs** and their derivatives continue to attract considerable attention [9]. Indenofluorenes have unique geometries that allow

the methylene bridges to be either on the opposite side (indeno[1,2-*b*]fluorene and indeno[2,1-*c*]fluorene, Scheme 1) or on the same side (indeno[2,1-*b*]fluorene) of the terphenyl core [10].

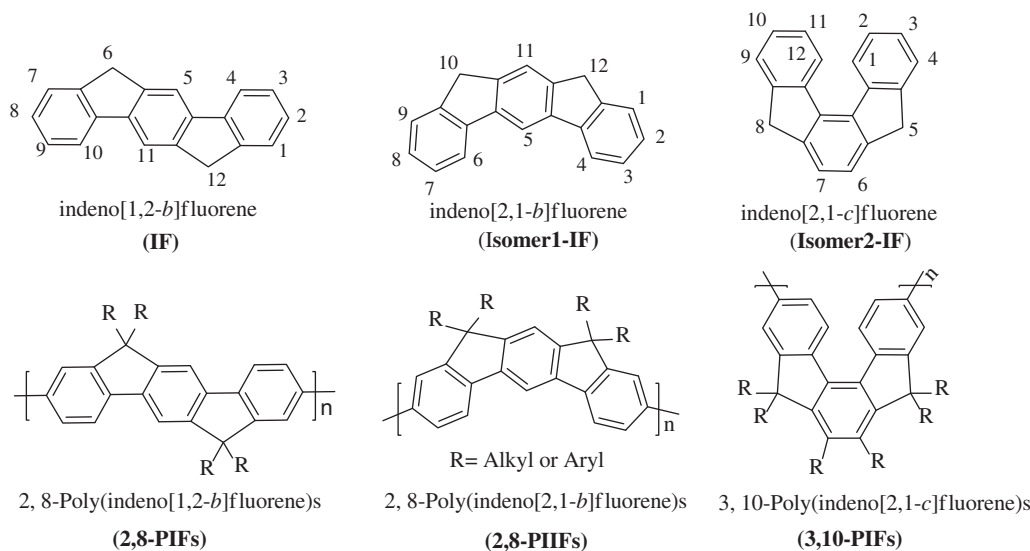
Polycyclic oligomers and polymers based on indeno[1,2-*b*]fluorene (**IF**) are of inherent high fluorescent emission yields with the maximum emission peaks ranging from 410 to 450 nm [11]. However, the blue emission of these derivatives in the solid state appears to be unstable due to the rapid appearance of long-wavelength emission bands. A variety of strategies toward achieving their spectrum stability and color purity have been utilized in the literatures through copolymerization, appending aryl groups onto methylenes, functionalization with dispiro-chromophores, and others [12].

Although indeno[1,2-*b*]fluorene with a planar and long conjugated terphenylene moiety has been intensively explored as a promising building skeleton to develop linear blue light-emitting oligo(2,8-indenofluorene)s and **PIFs** with the structures intermediate between **PFs** and totally ladder-type **PPPs**, to the best of our knowledge, less was known about its positional isomer indeno[2,1-

* Corresponding author. Tel./fax: +86 10 62758145.

** Corresponding author. Tel./fax: +86 10 80799170.

E-mail addresses: ysc@bac.edu.cn (S.-C. Yuan), jianpei@pku.edu.cn (J. Pei).



Scheme 1. Chemical structures of polyphenylene-based polymers.

c]fluorene (**Isomer 2-IF**, **Scheme 1**) [13], and the photophysical properties of indeno[2,1-*c*]fluorene-based polymers in the applications of optoelectronic devices has not been reported. Indeno[2,1-*c*]fluorene, by virtue of its unique zigzag topology, is considered as an attractive building skeleton and functionalized at C-3, C-5, C-6, C-7, C-8, and C-10 positions via readily available reactions. A polycyclic polymer containing the indeno[2,1-*c*]fluorene moiety can be expected to offer two major advantages: (1) the attachment of alkyl groups at the 6,7-positions enhances solubility without disturbing the conjugation along the chain; (2) the interruption of the planarity attributed to the disordered skeleton within the stepladder polymers would reduce the unwanted low energy emission band, which has been observed for **IF**-based PLEDs.

Herein, we wish to report the synthesis of indeno[2,1-*c*]fluorene-based polymers, which can be viewed either as **PIF** or **PF** analogs. To the best of our knowledge, no report has described the approach for the synthesis of poly(indeno[2,1-*c*]fluorene)s. Indeno[2,1-*c*]fluorene is polymerized through a Pd-catalyzed Suzuki coupling reaction from a 3,10-substituted monomer to generate a kinked **PIF** analog. Additionally, the synthesis of 3,10-linked bis(indeno[2,1-*c*]fluorene)s and tris(indeno[2,1-*c*]fluorene)s (trimer), which serve as model compounds for the spectroscopic characterization of the corresponding polymers, is described.

2. Experimental section

2.1. Measurement and characterization

^1H and ^{13}C NMR spectra were collected on a Bruker DRX 300 and 400 spectrometer in deuterated chloroform solution, with tetramethylsilane (TMS) as internal standard in all cases. Elemental analyses were carried out on an Elementar Vario EL (Germany). EIMS were recorded on a LCQ DECA XP Liquid Chromatograph–Mass Spectrometer (Thermo Group). UV-vis spectra were recorded on Perkin–Elmer Lambda 35 UV-vis spectrometer and PL spectra were carried out on a Perkin–Elmer LS55 Luminescence spectrometer. Cyclic voltammetry was carried out on a CHI660A electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in CH_3CN at a scan rate of 10 mV s^{-1} at room temperature under argon atmosphere. A Pt wire was used as the counter electrode, and a saturated calomel electrode was used as the reference electrode. The molecular weight of

the polymers was determined with a Waters GPC 2410 instrument in tetrahydrofuran (THF) by use of a calibration curve of polystyrene standards. The single crystals of compound **7** was performed at $20\text{ }^\circ\text{C}$ on a Rigaku RAXIS RAPID IP diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The determination of crystal class and unit cell parameters was carried out by the Rapid-AUTO (Rigaku 2000) program package. The structures were solved by use of SHELXTL program.

2.2. Device fabrication

Device configurations are ITO/PEDOT:PSS/polymers/Ba/Al and ITO/PEDOT:PSS/PVK/polymers/Ba/Al, respectively. The fabrication of electroluminescent devices was carried out by the standard procedure below. A 50 nm thick layer of poly(ethylene dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS, Baytron P 4083, purchased from Bayer AG) was spin-coated on the pre-cleaned ITO-glass substrates, which was followed by drying in a vacuum oven at $80\text{ }^\circ\text{C}$ for 8 h. A thin film of the polymers was spin-coated on the top of PEDOT in chlorobenzene. A 50 nm PVK film was placed between the PEDOT and the emitting layer. The film thicknesses of the active layers were around 75–80 nm, measured by an Alfa Step 500 surface profiler (Tencor). A layer of Ba (4–5 nm), and a layer of Al (150 nm) were subsequently vacuum-evaporated onto the top of the EL polymer layer under vacuum. Device fabrication was carried out in a controlled dry-box (Vacuum Atmosphere Co.) in N_2 circulation. Current density (J)–voltage (V)–luminance (L) data was collected using a Keithley 236 source measurement unit and a calibrated silicon photodiode. External EL quantum efficiencies (EQE) were obtained by measuring the total light output in all directions in an integrating sphere (IS-080, Labsphere). The luminance (cd/m^2) was measured by a Si photodiode, and calibrated by a PR-705 SpectraScan Spectrophotometer (Photo Research). Photoluminescence quantum yields were obtained by nanolog infrared fluorescence test system (HORIBA J. Y.). Photoluminescence (PL) spectra and electroluminescence (EL) spectra were recorded by a CCD spectrophotometer (Instaspec 4, Oriel).

2.3. Materials

All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All reagents, unless

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