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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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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/m^2 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.

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-

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* 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).

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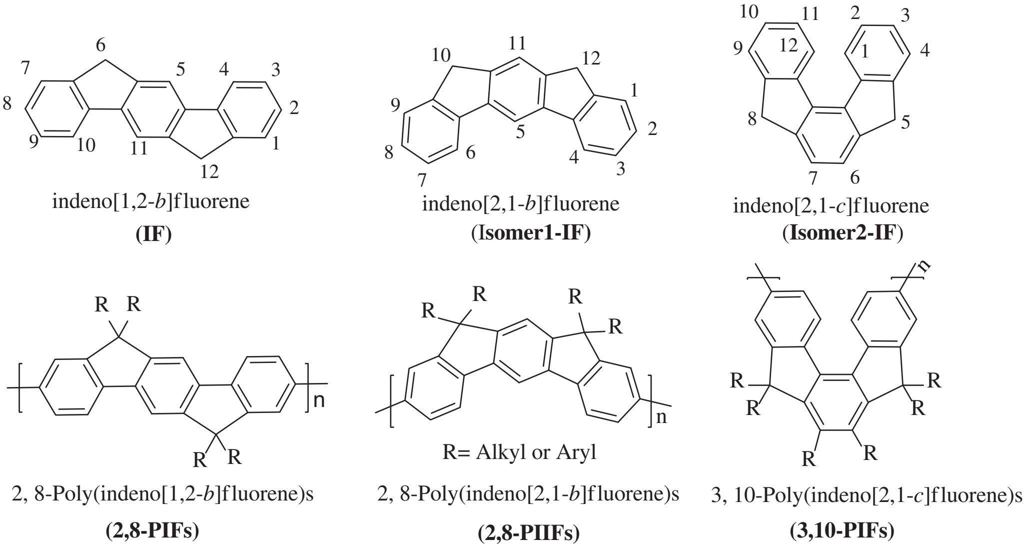


Scheme 1. Chemical structures of polyphenylene-based polymers.

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

^{1}H 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). EI-MS were recorded on a LCQ DECA XP Liquid Chromatograph–Mass Spectrometer (Thremo 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 °C on a Rigaku RAXIS RAPID IP diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). 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 precleaned ITO-glass substrates, which was followed by drying in a vacuum oven at 80 °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 otherwise specified, were obtained from Aldrich and Beida Syn Chem Co, and were used as received.

*2.3.1. Diethyl-4′,5′-dipropyl-[1,1′:2′,1″-terphenyl]-3′,6′-dicarboxylate (**2**)*

Diethoxycarbonyldiphenylcyclopentadienone **1** (3.76 g, 10.0 mmol) and 4-octyne (1.65 g, 15.0 mmol) were dissolved in mesitylene (20 mL), and the mixture was then heated at 180 °C for 24 h under argon atmosphere. The mixture was allowed to cool down to room temperature. After removal of mesitylene under reduced pressure, the residue was purified by silica gel column chromatography with petroleum ether and ethyl acetate as eluents to afford **2** as a white solid (yield: 50%). ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.11–6.99 (m, 10H, Ar–H), 3.94–3.87 (m, 4H, CH_2), 2.66–2.61 (m, 4H, CH_2), 1.73–1.63 (m, 4H, CH_2), 1.04–0.85 (m, 12H, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 169.3, 1 38.3, 136.9, 136.7, 136.3, 130.1, 127.1, 126.6, 60.73, 32.8, 24.8, 14.8, 13.5. MS (EI), *m/z*: 458 (M^+, 100%). Elemental analysis: Anal. Calcd for $C_{30}H_{34}O_4$: C, 78.57; H, 7.47. Found: C, 78.95; H, 7.63.

*2.3.2. 6,7-Dipropyl-indeno[2,1-c]fluorene-5,8-dione (**3**)*

A mixture of **2** (4.58 g, 10.0 mmol) and polyphosphoric acid (40 mL) was stirred vigorously for 2 h at 100 °C. The mixture was poured slowly into ice water and yellow precipitation was filtered off. The resulting solid was purified by a flash column chromatography using dichloromethane as eluant to afford **3** as a yellow-orange solid (yield: 60%). ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.10–8.07 (m, 2H, Ar–H), 7.76–7.74 (m, 2H, Ar–H), 7.64–7.57 (m, 2H, Ar–H), 7.41–7.36 (m, 2H, Ar–H), 3.15–3.10 (m, 4H, CH_2), 1.59–1.52 (m, 4H, CH_2), 1.13–1.08 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 193.3, 145.7, 142.6, 136.7, 135.6, 135.1, 134.4, 128.9, 124.2, 123.3, 28.3, 24.2, 14.6. MS (EI), *m/z*: 366 (M^+, 100%). Elemental analysis: Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.54; H, 6.43.

*2.3.3. 6,7-Dipropyl-5,8-dihydroindeno[2,1-c]fluorene (**4**)*

With a vigorous stirring, **3** (3.66 g, 10.0 mmol) was dissolved in 2,2′-oxydiethanol (50 mL) and hydrazine (14.5 g, 40.0 mmol) was added to the mixture. The mixture was heated at 70 °C for 1 h. NaOH (4.0 g, 40.0 mmol) was added to the mixture and then the mixture was refluxed overnight. The resultant was poured into 2 M HCl solution and extracted with chloroform. The combined organic phase was dried over anhydrous $MgSO_4$. After removal of the solvents under reduced pressure, the residue was purified by column chromatography using petroleum ether and dichloromethane as eluents to afford **4** as a white solid (yield: 45%). ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.55–8.48 (m, 2H, Ar–H), 7.62–7.59 (m, 2H, Ar–H), 7.46–7.41 (m, 2H, Ar–H), 7.38–7.32 (m, 2H, Ar–H), 3.98–3.95 (s, 4H, CH_2), 2.85–2.79 (m, 4H, CH_2), 1.75–1.54 (m, 4H, CH_2), 1.15–1.10 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 144.0, 142.8, 142.7, 135.3, 134.7, 126.4, 126.0, 125.0, 123.3, 43.6, 32.4, 23.8, 15.0. MS (EI), *m/z*: 338 (M^+, 100%). Elemental analysis: Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.55; H, 7.49.

*2.3.4. 5,5,6,7,8,8-Hexapropyl-5,8-indeno[2,1-c]fluorene (**5**)*

With a vigorous stirring, *n*-BuLi (10 mL, 2.5 M in hexane, 0.025 mol) was added dropwise to a suspension of **4** (3.38 g, 0.010 mol) in anhydrous THF under argon at 0 °C. The mixture was stirred at 0 °C for 1 h, followed by adding 1-bromopropane (3.0 g, 0.025 mol) dropwise, and then the mixture was stirred for another 1 h. *n*-BuLi (10 mL, 2.5 M in hexane, 0.025 mol) was added dropwise at 0 °C and the mixture was stirred for 1 h. Finally, 1-bromopropane (3.0 g, 0.025 mol) was added dropwise. The mixture was allowed to cool down to room temperature slowly and stirred overnight. The resultant was poured into saturated aqueous NH_4Cl and extracted with dichloromethane and then the combined organic phase was dried with $MgSO_4$. After removal of the solvents under reduced pressure, the residue was purified by column chromatography using petroleum ether as eluant to afford **5** as a white solid (yield: 86%). ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.40–8.30 (m, 2H, Ar–H), 7.38–7.28 (m, 6H, Ar–H), 2.86–2.31 (m, 4H, CH_2), 2.29–2.02 (m, 4H, CH_2), 1.99–1.63 (m, 4H, CH_2), 1.50–1.40 (m, 4H, CH_2), 1.12–0.65 (m, 26H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 152.1, 145.7, 141.2, 136.8, 134.8, 126.1, 125.7, 122.1, 121.5, 56.5, 42.4, 30.7, 25.0, 16.9, 14.8, 14.1. MS (EI), *m/z*: 506 (M^+, 100%). Elemental analysis: Anal. Calcd for $C_{26}H_{26}$: C, 90.06; H, 9.94. Found: C, 90.64; H, 9.79.

*2.3.5. 3,10-Dibromo-5,5,6,7,8,8-hexapropyl-5,8-indeno[2,1-c] fluorene (**6**)*

Compound **5** (5.1 g, 0.010 mol) was dissolved in tetrachloromethane, and 20 g of $Al_2O_3/CuBr_2$ (2:1) was added with a vigorous stirring. The mixture was kept at reflux overnight. The resultant was cooled to room temperature and filtered off. After removal of the solvents under reduced pressure, the residue was purified by column chromatography using petroleum as eluant to afford **6** as a white solid (yield: 95%). ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.13–8.11 (m, 2H, Ar–H), 7.47–7.42 (m, 4H, Ar–H), 2.86–2.28 (m, 4H, CH_2), 2.21–1.99 (m, 4H, CH_2), 1.97–1.89 (m, 4H, CH_2), 1.39–1.37 (m, 4H, CH_2), 1.12–0.58 (m, 26H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 154.9, 145.9, 140.1, 137.7, 134.0, 129.1, 125.2, 123.4, 120.4, 57.1, 42.4, 30.9, 25.2, 17.1, 15.0, 14.2. MALDI-TOF MS, *m/z*: 664.1 (M^+). Elemental analysis: Anal. Calcd for $C_{38}H_{48}Br_2$: C, 68.67; H, 7.28. Found: C, 68.25; H, 7.19.

*2.3.6. 3,10-Bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-5,5,6,7,8,8-hexapropyl-5,8-indeno[2,1-c]fluorene (**7**)*

To a stirred solution of 3,10-dibromo-5,5,6,7,8,8-hexapropyl-indeno[2,1-*c*]fluorene (0.66 g, 1.0 mmol) in DMSO (10 mL), 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi(1,3,2-dioxaborolane) (0.25 g, 2.0 mmol), KOAc (0.90 g, 8.0 mmol) and Pd(dppf)Cl_2 (0.06 g, 0.06 mmol) were added. The mixture was heated to 80 °C overnight with vigorous stirring under argon atmosphere. After removal of the solvents under reduced pressure, the residue was extracted with chloroform and the combined organic phase was dried over anhydrous $MgSO_4$. After removal of the solvents under reduced pressure, the residue was purified by flash chromatography to afford **7** as a white solid (yield: 80%). ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.36–8.34 (m, 2H, Ar–H), 7.79–7.76 (m, 4H, Ar–H), 2.83–2.81 (m, 4H, CH_2), 2.21–2.05 (m, 8H, CH_2), 1.41 (s, 24H, CH_3), 1.39–1.37 (m, 4H, CH_2), 1.13–0.53 (m, 26H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 151.5, 146.6, 144.3, 137.7, 135.2, 132.9, 127.8, 121.7, 83.6, 56.8, 42.3, 30.9, 25.2, 24.9, 17.1, 15.0, 14.3. MS (ESI), *m/z*: 759.40 (M^+, 100%). Elemental analysis: Anal. Calcd for $C_{50}H_{72}B_2O_4$: C, 79.15; H, 9.56. Found: C, 79.35; H, 9.18.

*2.3.7. 3-Bromo-5,5,6,7,8,8-hexapropyl-indeno[2,1-c]fluorene(**8**)*

To a mixture of 5,5,6,7,8,8-hexapropyl-indeno[2,1-*c*]fluorene (0.5 g, 1.0 mmol), chloroform (10 mL) and acetic acid (10 mL), NBS (0.18 g, 1.0 mmol) in chloroform (15 mL) was added dropwise with a vigorous stirring. The reaction mixture was stirred overnight. The organic phase was extracted with chloroform and the combined organic phase was dried over anhydrous $MgSO_4$. After removal of the solvents under reduced pressure, the residue was purified by flash column chromatography to afford **8** as a white solid (yield: 95%). ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.37–8.35 (m, 2H, Ar–H), 7.81–7.75 (m, 2H, Ar–H), 7.36–7.30 (m, 3H, Ar–H), 2.87–2.80 (m, 4H, CH_2), 2.25–2.02 (m, 8H, CH_2), 1.35–1.30 (m, 4H, CH_2), 1.14–1.10 (m, 26H, CH_2CH_3). MS (EI), *m/z*: 585, (M^+, 100%).

*2.3.8. 3-(4′,4′,5′,5′-Tetramethyl-1′,3′,2′-dioxaborolan-2-yl)-5,5,6,7,8,8-hexapropyl-indeno[2,1-c]fluorene(**9**)*

To a stirred solution of **8** (0.58 g, 1.0 mmol) in DMSO (10 mL), 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi(1,3,2-dioxaborolane) (0.25 g, 1.0 mmol), KOAc (0.45 g, 4.0 mmol) and Pd(dppf)Cl_2 (0.03 g, 0.03 mmol) was added. The mixture was heated to 80 °C overnight with vigorous stirring under argon atmosphere. The mixture was cooled to room temperature. After removal of the solvents under reduced pressure, the residue was extracted with chloroform and the combined organic phase was dried over anhydrous $MgSO_4$. After removal of the solvents under reduced pressure, the residue was purified by flash chromatography to give **9** as a white solid (yield: 87%): ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.37–8.35 (m, 2H, Ar–H), 7.81–7.75 (m, 2H, Ar–H), 7.36–7.30 (m, 3H, Ar–H), 2.87–2.80 (m, 4H, CH_2), 2.25–2.02 (m, 8H, CH_2), 1.41 (s, 12H, CH_3), 1.14–1.10 (m, 6H). 0.55–0.48 (m, 24H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 152.4, 151.4, 146.5, 145.9, 144.4, 141.4, 137.7, 135.1, 135.4, 134.8, 132.9, 127.7, 126.4, 125.9, 122.4, 121.8, 121.6, 83.6, 56.8, 56.7, 42.6, 42.4, 30.9, 30.9, 25.2, 25.0, 17.2, 17.1, 15.1, 14.3, 14.3. Elemental analysis: Anal. Calcd for $C_{44}H_{61}BO_2$: C, 83.52; H, 9.72. Found: C, 83.41; H, 9.56.

2.3.9. 5,5,5′,5′,6,6′,7,7′,8,8,8′,8′-Dodecapropyl-3,3′-bis(indeno[2,1-c]fluorene)s (dimer)

Compound **8** (5.85 g, 0.010 mol), **9** (6.32 g, 0.010 mol), and $Pd(PPh_3)_4$ (0.34 g, 0.30 mmol) were dissolved in a mixture of THF (100 mL) and aqueous 2 M Na_2CO_3 (20 mL). The mixture was refluxed with vigorous stirring for 2 d under argon atmosphere. After the mixture was cooled to room temperature, it was extracted with ethyl acetate and the combined organic phase was dried over anhydrous $MgSO_4$. After removal of the solvents under reduced pressure, the residue was purified by column chromatography using petroleum ether as eluant to afford white solids, which was dissolved in chloroform and precipitated in methanol to afford dimer as a white solid (yield: 70%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.49–8.44 (m, 3H, Ar–H), 7.73–7.71 (m, 3H, Ar–H), 7.59–7.58 (m, 1H, Ar–H), 7.37–7.35 (m, 1H, Ar–H), 7.34–7.24 (m, 6H, Ar–H), 2.85–2.80 (m, 8H, CH_2), 2.29–2.02 (m, 16H, CH_2), 1.47–1.45 (m, 8H, CH_2), 1.16–0.64 (m, 52H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 153.2, 152.4, 146.3, 146.0, 141.5, 140.7, 139.3, 137.2, 137.1, 135.0, 134.7, 128.8, 127.1, 126.4, 126.0, 124.9, 122.7, 122.4, 121.9, 121.8, 120.0, 56.9, 56.8, 56.7, 42.8, 42.7, 31.0, 29.7, 25.3, 17.3, 17.2, 15.1, 14.4, 14.3. MALDI-TOF MS, *m/z*: 1012.8 (M^+).

2.3.10. 5,5,5′,5′,5″,5″,6,6′,6″,7,7′,7″,8,8,8′,8′,8″,8″-Octadecapropyl-3,3′:10′,3″-ter(indeno[2,1-c]fluorene)s (trimer)

Compound **6** (6.64 g, 0.010 mol), **9** (6.32 g, 0.010 mol), and $(PPh_3)_4Pd$ (0.34 g, 0.30 mmol) were dissolved in a mixture of THF (80 mL) and aqueous 2 M Na_2CO_3 (20 mL). The mixture was refluxed with vigorous stirring for 2 d under argon atmosphere. After the mixture was cooled to room temperature, it was extracted with ethyl acetate and the combined organic phase was dried over anhydrous $MgSO_4$. After removal of the solvents under reduced pressure, the residue was purified by column chromatography using petroleum ether as eluant to afford white solids, which was dissolved in chloroform and precipitated in methanol for two times to afford trimer as a white solid (yield: 63%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.56–8.44 (m, 6H, Ar–H), 7.73–7.61 (m, 8H, Ar–H), 7.38–7.31 (m, 6H, Ar–H), 2.87 (m, 12H, CH_2), 2.32–2.02 (m, 24H, CH_2), 1.55–1.48 (m, 12H, CH_2). 1.16–0.66 (m, 78H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 153.3, 153.2, 152.4, 146.4, 146.3, 146.0, 141.5, 140.7, 139.4, 139.3, 137.2, 137.1, 135.0, 134.7, 126.3, 125.9, 125.0, 122.7, 120.0. 57.0, 56.9, 56.8, 42.8, 42.7, 31.9, 31.0, 29.7, 29.4, 25.3, 22.7, 17.3, 17.2, 15.1, 14.4, 14.3, 14.1. MS MALDI-TOF MS, *m/z*: 1515.9 (M^+).

*2.3.11. 2-Bromo-5,5,10,10,15,15-hexahexyl-truxene (**M3**)*

To a mixture of 5,5,10,10,15,15-hexahexyltruxene (10.00 g, 11.81 mmol) and 20 mg of anhydrous $FeCl_3$ as catalyst in 60 mL of chloroform was added dropwise a solution of bromine (1.05 mL, 20.00 mmol) in 10 mL of chloroform at 0 °C over 1 h. The mixture was then allowed to return to room temperature. After stirring 24 h, the mixture was washed with saturated sodium thiosulfate solution and brine to remove excess bromine. The precipitate was filtered and washed with water for three times. The filtrate was washed with brine and extracted with chloroform. Removal of the solvent gave a yellow residue, which was then combined with the white precipitate. Recrystallization of the combined solid from EtOH afforded **M3** as a white solid (yield: 96%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.10–8.08 (m, 1H, Ar–H), 8.01–7.94 (m, 2H, Ar–H), 7.35–7.14 (m, 7H, Ar–H), 2.78–2.58 (m, 6H, CH_2), 1.86–1.74 (m, 6H, CH_2), 0.75–0.60 (m, 36H, CH_2), 0.41–0.34 (m, 18H, CH_2), 0.27–0.20 (m, 12H, CH_3).

2.3.12. General procedures for the synthesis of polymers

With **P1** as an example 3,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,5,6,7,8,8-hexapropyl-indeno[2,1-*c*]fluorene **7** (759 mg, 1.0 mmol), 3,10-dibromo-5,5,6,7,8,8-hexapropyl-indeno[2,1-*c*]fluorene **6** (664 mg, 1.0 mmol), and tetrakis(triphenylphosphine) palladium (5 mg) were dissolved in toluene/THF (10 mL, 3:1) and stirred for 0.5 h, and then 2 M Na_2CO_3 aqueous solution (4 mL) was added. The mixture was heated to 100 °C and stirred for 2 d under argon atmosphere. Then the resultant was poured into stirred methanol (200 mL) to generate plenty of light-yellow precipitates. The solid was collected by filtration and then dissolved in toluene and washed twice with dilute $NaHCO_3$ solution. The careful reprecipitation procedure in acetone/methanol was repeated several times. The polymer was further purified by washing with acetone at reflux in a Soxhlet for 2 days. The light-yellow solid was dried in vacuum at room temperature (yield: 52%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.57–8.55 (m, 2H), 7.79–7.73 (m, 4H), 2.89 (m, 4H), 2.35 (m, 4H), 2.15 (m, 4H), 1.53–1.50 (m, 4H), 1.18–1.15 (m, 8H), 0.88–0.72 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 153.3, 146.4, 140.8, 139.4, 137.2, 134.7, 128.8, 127.1, 125.0, 122.7, 120.1, 57.0, 42.8, 31.9, 31.0, 29.8, 29.7, 29.4, 25.3, 22.7, 17.3, 15.1, 14.4, 14.4, 14.1. Elemental analysis: Anal. Calcd for $C_{39}H_{50}$: C, 90.29; H, 9.71. Found: C, 89.69; H, 9.58. M_n: 6968, PDI: 1.57.

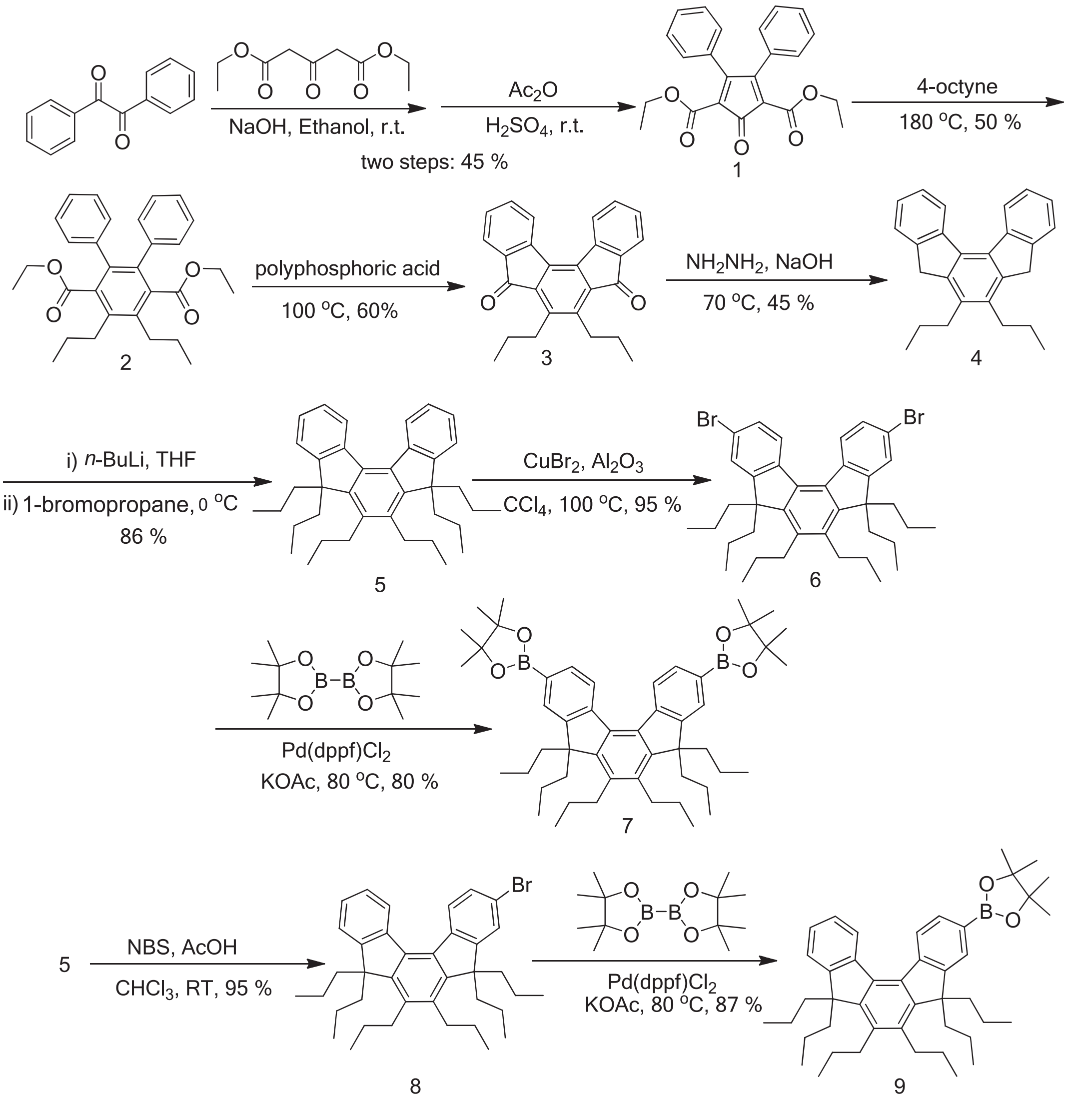
P2 (yield: 58%): ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.42–8.40 (m, 2H), 7.90–7.88 (m, 2H), 7.77–7.56 (m, 8H), 7.32–7.24 (m, 4H), 6.85–6.78(m, 4H), 3.94–3.92 (m, 4H), 2.85 (m, 4H), 2.28 (m, 4H), 2.06 (m, 4H), 1.78–1.73 (m, 4H), 1.55 (m, 8H), 1.32–1.25 (m, 4H), 1.14–1.12 (m, 10H), 0.88–0.66 (m, 26H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 158.0, 153.1, 152.9, 146.3, 141.0, 140.8, 139.2, 138.8, 138.0, 137.2, 134.6, 129.4, 129.3, 128.7, 127.2, 126.5, 125.2, 124.6, 122.6, 120.4, 120.1, 114.2, 67.9, 64.5, 42.7, 31.9, 31.6, 29.7, 29.6, 29.4, 29.3, 25.7, 25.3, 22.7, 22.6, 17.2, 15.1, 14.4, 14.3, 14.1, 14.0. Elemental analysis: Anal. Calcd for $C_{76}H_{90}O_2$: C, 88.15; H, 8.76. Found: C, 88.49; H, 9.27. M_n: 9124, PDI: 1.67.

P3 (yield: 42%): ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.61–8.43 (m, 4H), 7.86–7.77 (m, 8H), 7.44–7.24 (m, 4H), 3.05–2.81 (m, 16H), 2.37–2.10 (m, 20H), 1.53–1.43 (m, 4H), 1.01–0.94 (m, 46H), 0.73–0.63 (m, 38H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 154.5, 154.4, 153.6, 153.3, 146.4, 145.2, 145.1, 144.9, 140.9, 140.4, 139.6, 139.3, 139.1, 138.5, 138.1, 137.3, 134.4, 127.1, 125.1, 125.0, 57.0, 55.9, 55.8, 42.8, 37.1, 31.6, 31.5, 29.7, 29.6, 29.5, 24.0, 22.4, 22.3, 22.2, 17.3, 15.1, 14.4, 14.0, 13.9. Elemental analysis: Anal. Calcd for $C_{102}H_{138}$: C, 89.71; H, 10.29. Found: C, 90.25; H, 9.68. M_n: 11,575, PDI: 1.92.

3. Results and discussion

3.1. Synthesis and characterization

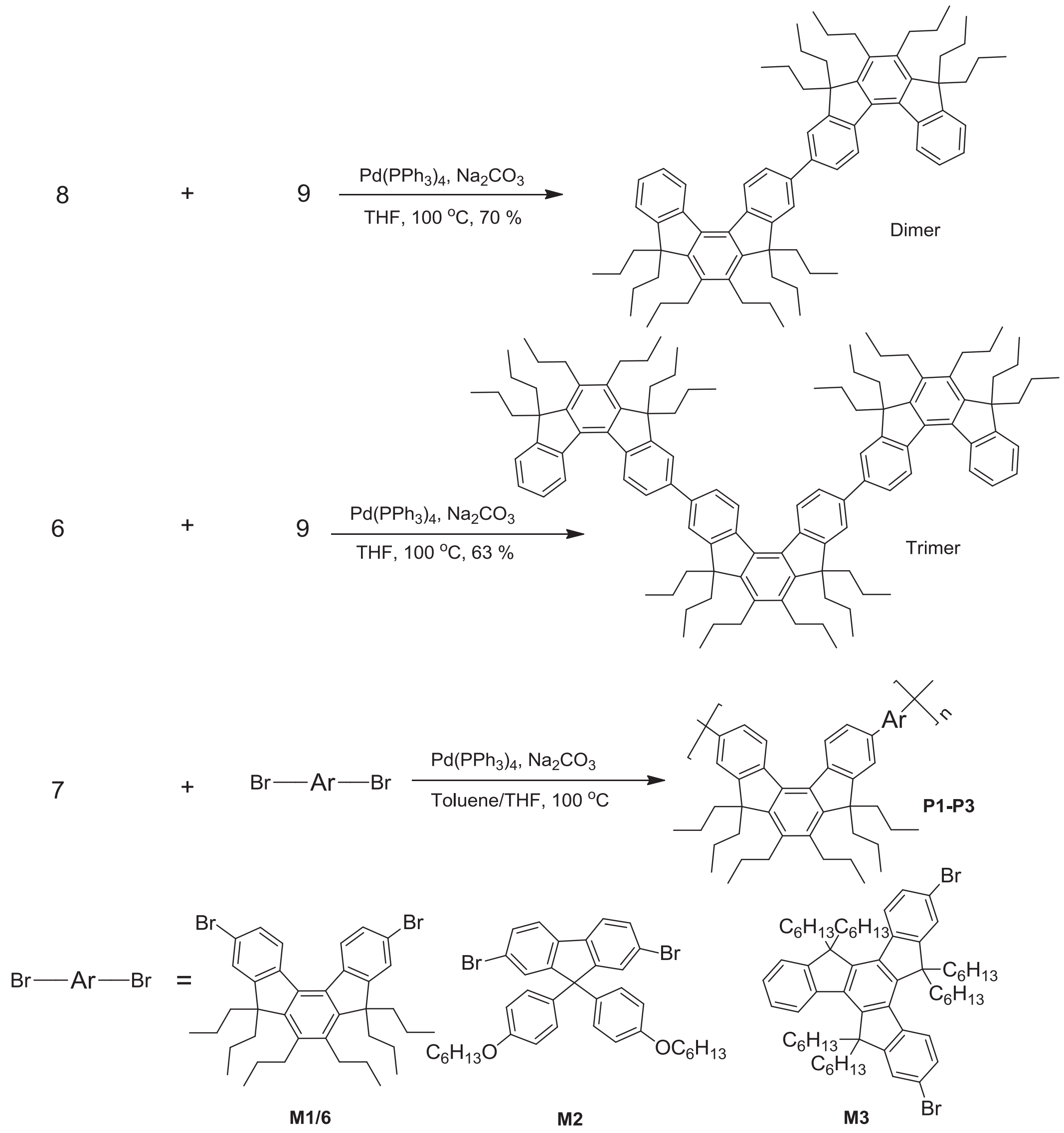
The synthetic approaches for monomers and polymers **P1**–**P3** are illustrated in Schemes 2 and 3. Compound **1** was prepared according to the typical procedures [14] by the condensation reaction



Scheme 2. The synthetic routes of the compounds **1**–**9**.

between 1,3-diethoxycarbonaylacetone and benzil in the presence of NaOH, followed by an acid-promoted dehydration using the concentrated H_2SO_4 in 45% yield. The subsequent Diels–Alder reaction between **1** with 4-octyne afforded diester **2** in 50% yield. Compound **2** underwent an intramolecular double Friedel–Crafts acylation to form 6,7-dipropyl-indeno[2,1-*c*]fluorene-5,8-dione **3** with 60% yield in hot polyphosphoric acid. A Wolff–Kishner reduction of compound **3** afforded 6,7-dipropyl-5,8-dihydro-indeno[2,1-*c*]fluorene **4** in 45% yield. An alkylation of **4** with *n*-BuLi and 1-bromopropane led to 5,5,6,7,8,8-hexapropyl-indeno[2,1-*c*] fluorene **5** in 86% yield. Subsequent alumina-supported $CuBr_2$ bromination afforded 3,10-dibromo-5,5,6,7,8,8-hexapropyl-indeno [2,1-*c*]fluorene **6**. A Miyaura coupling between **6** and two equivalent of bis(pinacolato)diboron catalyzed by $Pd(dppf)Cl_2$ produced boronic diester **7** in 80% yield. Monobromination of **5** with NBS generated bromide **8** in 95% yield. Boronic ester **9** was obtained from **8** through a Miyaura reaction in 87% yield. To more precisely assess the mode of conjugated polymer, indeno[2,1-*c*]fluorene-based dimer and trimer were prepared. Compound **8** was coupled with boronic ester **9** to give dimer under the standard Suzuki reaction condition in 70% yield. The Suzuki coupling reaction between **6** and **9** afforded trimer in 63% yield. The palladium-catalyzed Suzuki coupling polymerization was employed to produce the desired polymers (**P1**, **P2**, and **P3**) in moderate yields. The crude polymers were washed with methanol, water, and methanol again, successively, and were placed in a Soxhlet apparatus and extracted with acetone for 48 h. The structures of the dimers, trimers, and the resultant polymers were confirmed by ^1H and ^{13}C NMR characterization, as well as elemental analysis. All polymers were readily soluble in common organic solvents such as chloroform, tetrahydrofuran, and toluene. The number average molecular weights (M_n) of **P1**–**P3** were 6968, 9124 and 11,575, respectively, determined by gel permeation chromatography (**GPC**) using THF as the eluant and polystyrene as standard.

To elucidate molecular structure, single crystal of compound **7** was obtained by slow diffusion of methanol into a solution of the sample in dichloromethane (Fig. 1). There are two molecules in the unit cell with different configurations. Close H–H contacts occur in the crowded region of molecules, and two kinds of distances of the hydrogen atoms are observed (1.944 Å and 2.041 Å). The distances are significantly shorter than twice the van der Waals radius of the hydrogen atom (2.4 Å). Therefore, the strong repulsive interaction between the hydrogen atoms leads to the spatial distortion of the conjugated indeno[2,1-*c*]fluorene π-system which provides



Scheme 3. Synthetic routes of dimer, trimer and polymers.

significant molecular stabilization [15]. The dihedral angles between two fluorenyl planes (through the central phenyl ring) are 16.37° (between the plane {C10, C11, C12, C13, C14, C15, C16, C17, C5, C6, C7, C8, C9} and plane {C5, C6, C7, C8, C16, C17, C18, C19, C20, C1, C2, C3, C4}), 19.06° (between the plane {C51, C52, C53, C54, C55, C56, C57, C58, C65, C66, C67, C68, C69} and the plane {C55, C56, C57, C58, C100, C59, C60, C61, C62, C63, C64, C65, C66}), respectively.

3.2. Absorption and photoluminescence properties

Normalized absorption and emission spectra of **P1**, **P2**, and **P3** in chloroform (10^{-6} M) are shown in Fig. 2. The photophysical properties are summarized in Table 1. All polymers showed very strong π–π^* transition attributed to the conjugated backbone, which progressively blue-shifted (in web version), indicating the decrease of the effective conjugation length. The absorption maximum (λ_{max}) peaked at 385 nm for **P1**, 381 nm for **P2**, and 364 nm for **P3**, implicating that the incorporation of truxene unit into polymer backbone can decrease the electronic conjugation degree in comparison with fluorene and twisted indeno[2,1-*c*] fluorene counterparts. **P1** and **P2** showed almost identical photoluminescent (**PL**) behaviors, which peaked at around 428 nm with a shoulder at about 450 nm. In general, the presence of well defined vibronic structures in the emission spectra indicates that the polymers have rigid and well-defined backbone structures. In comparison with **P1**, the emission maximum (λ_{max}) of **P3** showed a blue-shift (in web version) of 21 nm. The obvious blue-shift maybe attributed to the *meta*-conjugation of truxene cores. All polymers show large stokes shift (ca. 50 nm) between absorption and emission maximum, indicating large structural differences between the ground states and excited states [7]. Furthermore, the absorption and emission behaviors of **P1** in chloroform were different with those of *n*-alkyl-substituted poly(indeno[1,2-*b*]fluorene)s (**2,8-PIFs**, Scheme 1) [7]. For **2,8-PIFs**, the absorption and emission maxima peaked at 416 and 432 nm, respectively, with small Stokes shift of 16 nm, which is similar to ladder-type polymers. The differences might be caused by enhanced torsion angle of the twisted-indenofluorene repeating units in polymer backbone, leading to the decrease of conjugation length. The absorption ($\lambda_{max} = 385$ nm) and emission peaks ($\lambda_{max} = 428$ nm) of **P1** red-shifted (in web version) in comparison with those of **PF** ($\lambda_{max} = 383$ nm, $\lambda_{max} = 415$ nm), implying enhanced conjugation. The Φ_{PL} of polymers **P1**, **P2**, and **P3** in THF are 0.46, 0.69 and 0.50, respectively.

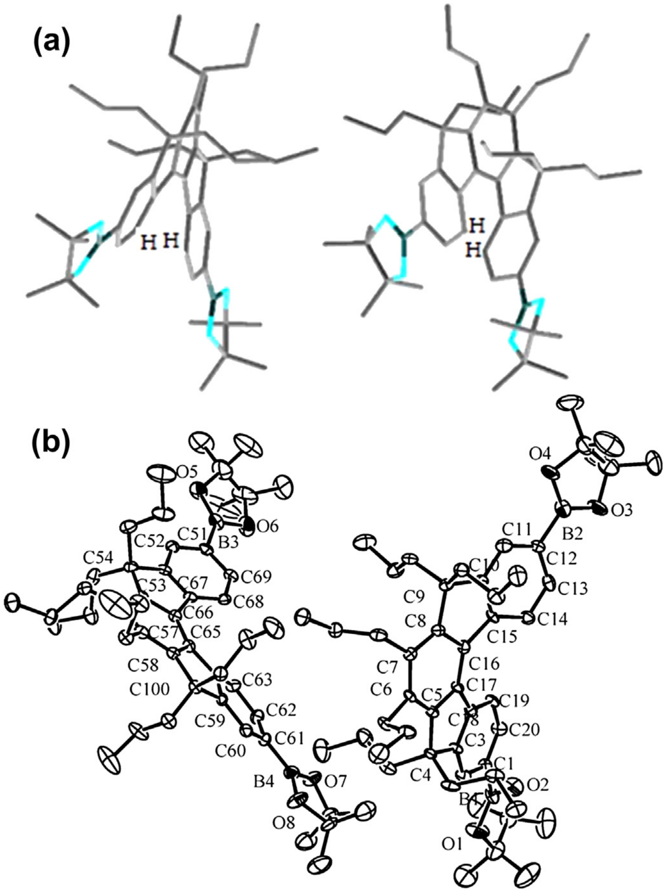


Fig. 1. Single crystal structure of compound **7**: (a) wireframe representation and (b) **ORTEP** views of the crystal structure with thermal ellipsoids at the 50% probability level (hydrogen atoms have been omitted for clarity).

Normalized absorption and emission spectra of polymers **P1**, **P2**, and **P3** in films are shown in Fig. 3. The structured absorption bands of polymers observed in solution were also exhibited in the solid state. The *UV*-vis absorption maxima of the polymers in thin films appeared slightly blue-shifted (in web version) compared to those in solutions, suggesting that the aggregation of the chromophores was suppressed in solid state. However, the PL spectra of the polymers behaved differently when came from solution to film. As shown in Fig. 3, the peaks of the zigzag polymers did not show much red-shift (in web version), but the shoulder peaks decreased significantly, even disappeared in solid state. **P1** and **P2** showed almost identical emission features, which peaked at around 450 nm without the vibronic structure. In the case of **P1**, it did not exhibit a long-wavelength emission peaked at around 530 nm, which was frequently observed in straight-alkyl-substituted **2,8-PIFs** in solid states, probably attributing to the aggregation of **2,8-PIFs** [15,16]. It is also indicative that incorporating kinked indeno[2,1-*c*]fluorene is probably effective to suppress the aggregation in the solid state.

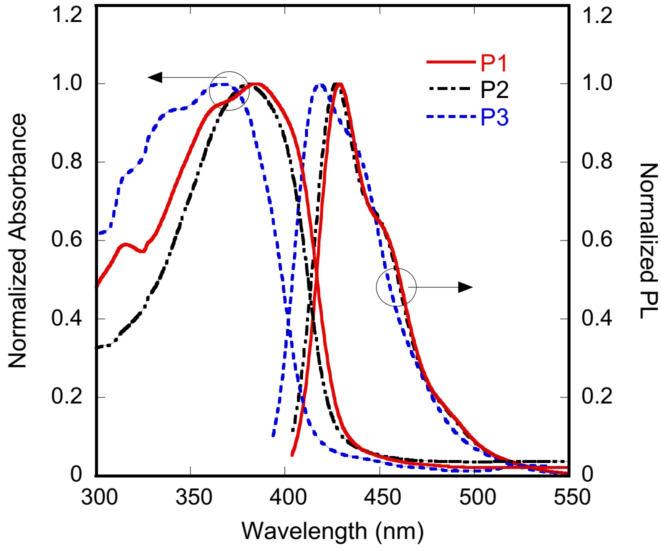


Fig. 2. Absorption and emission spectra of polymers in chloroform (1×10^{-6} M).

To determinate the effective conjugation of **P1**, the absorption and emission features of dimer, trimer and homopolymer **P1** in chloroform were investigated. As shown in Fig. 4, the electronic absorption behaviors of twisted oligo(indeno[2,1-*c*]fluorene)s exhibited a direct correlation to the conjugation length, i.e., the absorption maximum continuously red-shifted (in web version) as the number of the indeno[2,1-*c*]fluorene units increased. Dimer, trimer, and **P1** exhibited maximum absorptions at 354, 378, and 385 nm, respectively. Their PL features revealed typical characteristics of conjugated oligoindenofluorenes derivatives and exhibited maximum emissions at 410 nm for dimer, 424 nm for trimer, and 428 nm for **P1**, with well-defined vibronic features. For these values, the effective conjugation length of **P1** is estimated to be about 4 units of indeno[2,1-*c*]fluorene.

3.3. Electrochemical properties

Electrochemical properties of the polymers were investigated by cyclic voltammetry (CV). As shown in Fig. 5, all polymers except **P3** exhibited reversibility in both *n*-doping and *p*-doping processes. For **P1**, it is observed that upon cathodic sweeping of the polymer, the onset of the reduction occurred at −2.15 V with a cathodic peak at −2.48 V. In the anodic scan, the oxidation (*p*-doping) process gave a sharp peak at 1.60 V with the onset of the oxidation occurred at 1.25 V. Accordingly, the HOMO and LUMO energy levels were estimated to be −5.65 eV and −2.25 eV, respectively. The electrochemical properties of **P2** showed only slightly differences and a smaller bandgap than that of **P1**. For **P3**, by insertion of the truxene unit into the polymer main chain, a decrease in oxidation potential was expected initially because of the decrease in effective conjugation of the polymer main chain together with the steric hindrance of the alkyl groups. However, **P3** showed almost the same oxidation peak potential as that of **P1**. On the other hand, there was an obvious difference in the onset potential of the *n*-doping process between the two polymers, which caused a decrement of 0.4 eV of LUMO energy level for **P3** in comparison with **P1**. The reason of this inconsistency between absorption spectra and electrochemical results is unknown, possibly due to some dynamic problems in CV measurement.

3.4. Electroluminescent properties

Initially, single-layer devices with the configuration of ITO/PEDOT:PSS(50 nm)/polymers(75 nm)/Ba(4 nm)/Al(150 nm) were fabricated to investigate their EL properties. As depicted in Fig. 6, EL features showed blue (in web version) emission maxima peaked at 430 nm for **P1**, 432 nm for **P2**, and 426 nm for **P3**, respectively. A maximum external quantum efficiency of 0.08% and a luminous efficiency of 0.10 cd/A were achieved from **P2**, with the EL onset at about 5.4 V in the forward bias direction. The low efficiencies were attributed to the imbalance of electron and hole injection and

Table 1
The photophysical and electrochemical properties of polymers.

Polymers	In $CHCl_3$ solution				In film[a]					
	$\lambda_{abs,max}$ (nm)	$\lambda_{PL,max}$nm)	Stokes shift (nm)	Φ_{PL}[b]	$\lambda_{abs,max}$ (nm)	$\lambda_{PL,max}$ (nm)	E_g (eV)	E_{ox} (eV)	HOMO (eV)	LUMO (eV)
P1	385	428	43	0.46	378	450	3.40	1.25	−5.65	−2.25
P2	381	427	46	0.69	377	451	3.45	1.35	−5.75	−2.30
P3	364	418	54	0.50	361	436	2.90	1.15	−5.55	−2.65

[a] measured as film spin-coated from chloroform solution.
[b] measured in THF solution.

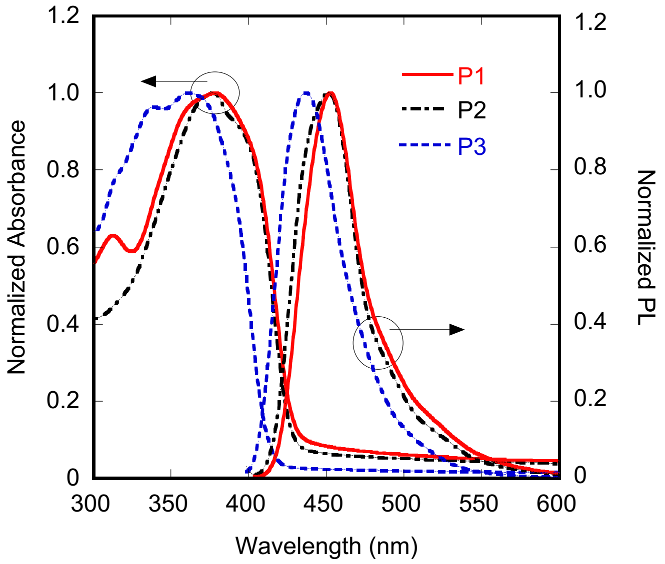


Fig. 3. The absorption and emission spectra of polymers in thin film.

transportation. The detailed device performances are shown in Table 2. and Fig. 7.

In order to improve the device performances, PVK was introduced to balance the electron and hole injection. With a low electron affinity (ca. −2.2 eV) and ionization potential (ca. −5.8 eV), PVK was used as a hole-transporting and electron-blocking material in OLEDs. The multilayed devices with the configuration of ITO/PEDOT:PSS (50 nm)/PVK(40 nm)/polymers (80 nm)/Ba (4 nm)/Al (150 nm) were fabricated. The maximal external quantum efficiency for **P3** was increased to 1.2% and a maximum luminous efficiency of 1.5 cd/A was achieved with EL onset at about 7 V. The onset voltage was significantly increased, in accordance with the

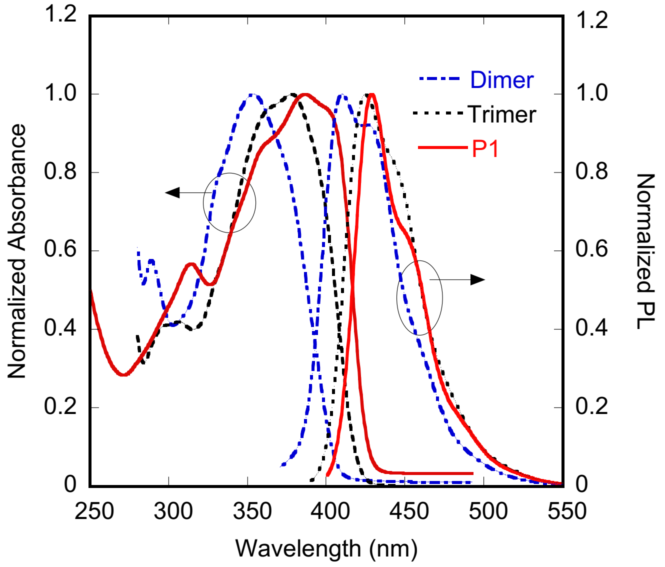


Fig. 4. The absorption and emission spectra of **P1** and oligo(indeno[2,1-*c*]fluorene)s in chloroform (1×10^{-6} M).

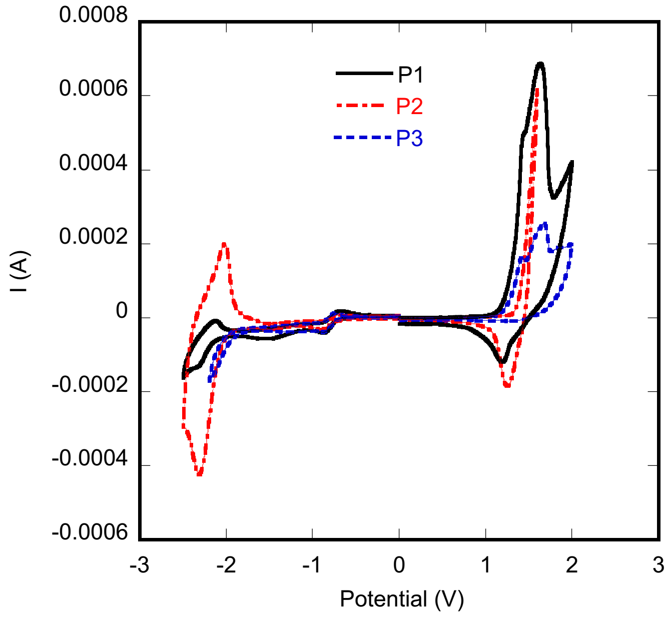


Fig. 5. Cyclic voltammograms of polymers in CH_3CN solution.

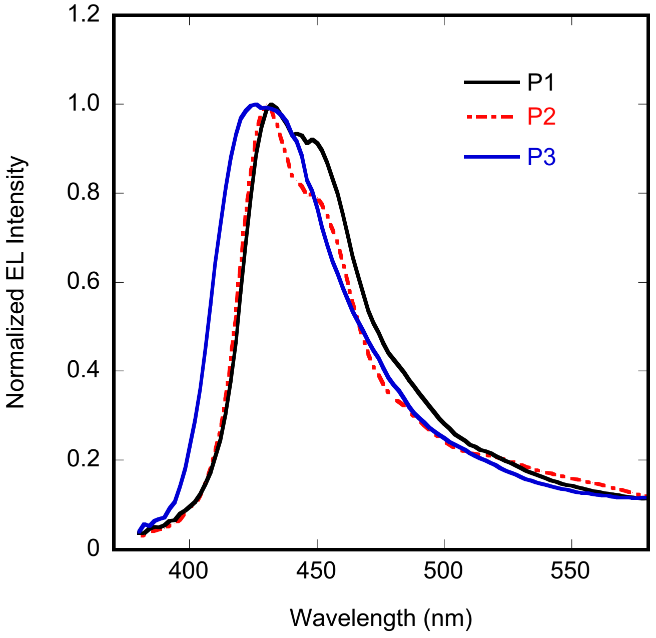


Fig. 6. Electroluminescent spectra of polymers in devices.

Table 2
OLED device performances of **P1**, **P2** and **P3**.

Materials	Device configuration[a]	Turn-on (V)	QE_{max} (%)	LE_{max} (cd/A)	L_{max} (cd/m^2)	CIE (*x*, *y*)
P1	A	6.8	0.93	1.10	2780	0.204, 0.150
	B	5.4	0.06	0.07	500	0.208, 0.227
P2	A	7.7	0.73	0.87	2340	0.201, 0.157
	B	5.4	0.08	0.10	490	0.278, 0.204
P3	A	6.2	1.20	1.50	1820	0.215, 0.149
	B	5.6	0.06	0.07	330	0.200, 0.187

[a] A: ITO/PEDOT:PSS/PVK/polymers/Ba/Al. B: ITO/PEDOT:PSS/polymers/Ba/Al.

general observations that the PVK layer would cause a substantial increase in the operating voltage, as shown in Fig. 7a. Certain important device characteristics have been dramatically improved by inserting a PVK layer between PEDOT:PSS and the emitting layer, probably due to the effective electron-blocking as suggested by Jenekhe et al. [17].

In comparison, PLED from **2,8-PIFs**, showed a greenish-blue (in web version) emission with CIE coordinates (x = 0.380, y = 0.448). However, in above-mentioned devices with twisted indeno[2,1-*c*]fluorene-based polymers (**P1**–**P3**) as emitting layers, the green-blue emission was absent, probably due to the differences in the packing of conjugated chains. The unplanar twisted indeno[2,1-*c*]fluorene along the polymer backbone may globally lead to less dense chain-packing and a subsequent decrease in the rate of excited-state interchain migration [15–18]. Despite the enhanced device performances by inserting PVK layer, the efficiencies are not high and the EL stability under thermal annealing and electric field are still unknown. To solve this problem, utilizing proper thermal annealing treatment to adjust the morphology, copolymerization with other potential building blocks, and selection of a good electron injection-cathode could be good choices. The efforts are in progress and will be reported in a forthcoming paper.

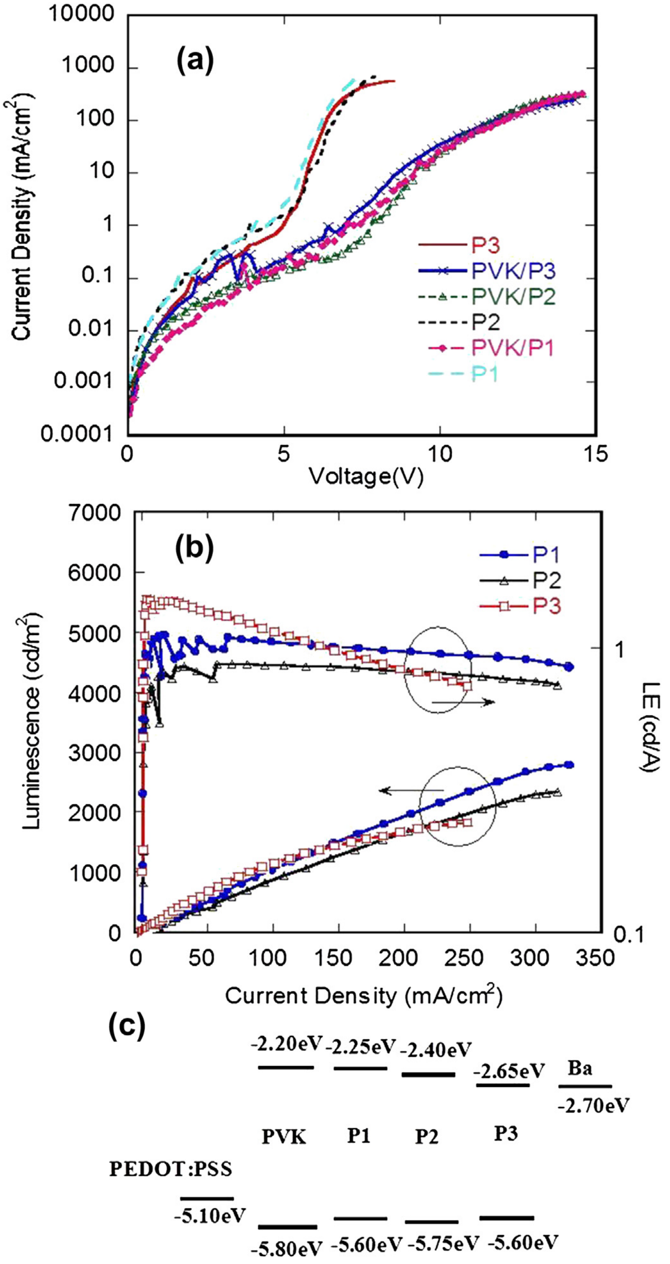


Fig. 7. (a) The current density–voltage curves of devices. (b) The current density–efficiency curves of the devices. (c) The energy level diagram of the device components.

4. Conclusions

A conjugated skeleton, indeno[2,1-*c*]fluorene, has been developed to construct new conjugated polymer for organic light-emitting diodes. Single crystal analysis of its structure shows that this molecule exhibits interesting twisted structures. A series of novel conjugated polymers and oligomers containing twisted indeno[2,1-*c*]fluorene unit have been synthesized through the Pd-catalyzed Suzuki coupling polymerization and their electroluminescent properties have been characterized. In comparison with *n*-alkyl-substituted **2,8-PIFs**, the absorption and emission behaviors of alkyl-substituted **P1** in solution and in solid film are different, probably caused by the distorted backbone. The electronic absorption and emission behaviors of these distorted oligo(indeno[2,1-*c*]fluorene)s and polymers exhibit a direct correlation to the conjugation length, and substantially blue-shifted relative to the linear oligo(indeno[1,2-*b*]fluorene)s and **2,8-PIFs**. Electroluminescent devices with the configuration of ITO/PEDOT:PSS/PVK/polymers/Ba/Al show blue EL emission spectrum with luminance values of typically 1800–2800 cd/m^2 at a bias of 10 V. The maximal external device efficiency of 1.2% and a maximum luminous efficiency of 1.5 cd/A are achieved. The formation of long wavelength emission bands, typically attributed to polymer aggregation in *n*-alkyl-substituted **2,8-PIFs** in electroluminescent devices, is not observed in our polymers. Our investigations demonstrate that twisted indeno[2,1-*c*]fluorene moiety might be utilized as a potential building skeleton to generate the effective blue light-emitting materials.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.03.044.

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