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Synthesis and characterization of X-shaped oligo(*para*-phenylene) derivatives functionalized with fluorene ethynylene

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Abstract

A series of linear and X-shaped oligo(*para*-phenylene) derivatives functionalized with fluorene ethynylenes **1**, **3** and **4** were synthesized through sequent Sonogashira coupling and Suzuki–Miyaura reaction in high yield. The electron-donating group –OCH_3 and electron-withdrawing counterparts –CF_3 were introduced to tune the spectra properties of compounds **3** and **4**. The detail investigation of their photophysical properties in solution and film indicated that the introduction of both –OCH_3 and –CF_3 makes maximum emission distinct red-shift in comparison with parent compound **1**, but the latter more prominently.

Keywords: Sonogashira coupling; Suzuki coupling; Oligo(fluorene ethynylene); Electronic effect; Photophysical property

Monodisperse and well-defined π-conjugated oligomers have recently become a subject of intensive research in material science due to their potential applications in electrical circuits [1], switches and sensors [2], organic light-emitting diodes (OLEDs) [3–5], solar cells [5], organic field-effect transistors (OFETs) [6], multiphoton absorbing materials [7] and models to understand the fundamental properties of their analogous polydisperse polymers [8].

Poly(arylene ethynylene)s (PAEs) can be viewed as the dehydro analogues of poly(arylene vinylene) (PAVs) in which the ethyne groups impart additional rigidity to the conjugated framework. The polymer and oligomer based on arylene ethylene have shown better photostability [9,10], higher PL efficiency and more facile to synthesis than PAVs [11]. Oligofluorenes are important model compounds for polyfluorenes, which are the promising blue light-emitting materials with high photoluminescence quantum yields, and thermal and oxidative stability [12]. Development of various synthetic methodologies makes it possible to design and synthesize a variety of soluble monodisperse oligo(fluorene ethynylene) derivatives, 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 systems [13–16].

Herein, we primarily report the synthesis of a series of linear and X-shaped compounds **1**, **3** and **4** and the investigation of electronic effects on the photophysical properties. Compounds **1**, **3** and **4** were synthesized through sequent Sonogashira coupling and Suzuki–Miyaura reaction in high yield (Scheme 1). All three compounds were

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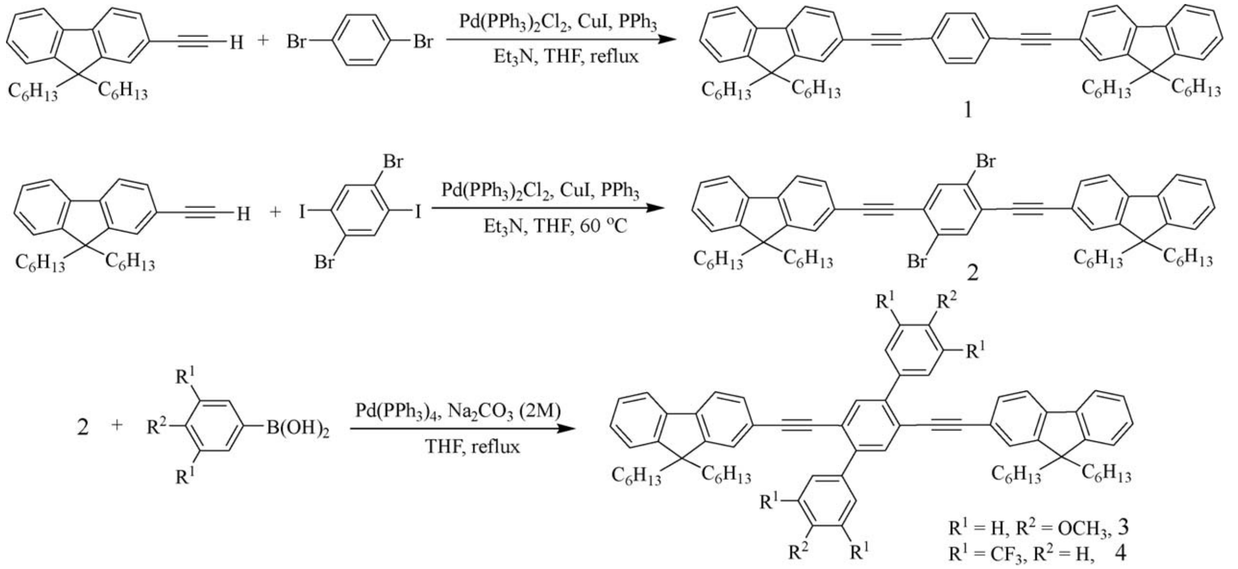

Scheme 1. Synthesis of X-shaped oligo(*para*-phenylene) derivatives **1**, **3** and **4**.

readily soluble in common solvents, such as hexane, CH_2Cl_2, $CHCl_3$, and THF, which allow us to conveniently obtain their ^{1}H and ^{13}C NMR spectra, and MALDI-TOF MS characterization data to verify their structure and purity.

1. Experimental

All chemicals, reagents, and solvents were used as received from commercial sources without further purification except tetrahydrofuran (THF), triethylamine (Et_3N), and toluene that had been distilled over sodium/benzophenone, CaH_2, and sodium, respectively. All nonaqueous operations were carried out under a dry, oxygen-free, nitrogen atmosphere. Pd-catalyzed Sonogashira and Suzuki–Miyaura couplings of aryl halides with terminal alkynes and aryl boronic acid respectively were conducted according to reported procedures [13,17]. All reactions were monitored by TLC with silica gel. Column chromatography was carried on silica gel (160–200 m). ^{1}H and ^{13}C NMR spectra were recorded on a Mercury plus 300 MHz or Bruker 400 MHz using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard in all cases. Mass spectra were obtained with a JEOL JMS-70 spectrometer in EI mode and a MALDI-TOF (Matrix assisted laser desorption ionization/time-of-flight)-MS mass spectrometer Bruker BIFLEX III. UV–vis spectra were recorded on PerkinElmer Lambda 35 UV–vis spectrometer. PL spectra were carried out on PerkinElmer LS 55 Luminescence Spectrometer.

2. Result and discussion

Compound **1** was obtained from 2-ethynyl-9,9-dihexyl-2-fluorene [15] and commercially available 1,4-dibromobenzene under standard Sonogashira condition. Compounds **3** and **4** were prepared through sequent Sonogashira coupling and Suzuki–Miyaura reaction. Firstly, 2-ethynyl-9,9-dihexyl-2-fluorene was coupled to 1,4-dibromo-2,5-diidobenzene at room temperature utilizing the different reactivity between aryl bromide and aryl iodide, which provided the important intermediate **2** in 76% yield. Then **3** and **4** were synthesized *via* Suzuki–Miyaura coupling reaction between **2** and 4-methoxyphenylboronic acid, 3,5-bis(trifluoromethyl)phenyl boronic acid in 83% and 79% yield respectively (Scheme 1). Their structures and purity were fully characterized and verified by ^{1}H and ^{13}C NMR, elemental analysis, and MALDI-TOF MS [18].

The normalized absorption and fluorescence spectra of compounds **1**, **3** and **4** in THF solution and in neat film are shown in Fig. 1a and c respectively. The absorption features of **1**, **3** and **4** with two major absorption bands were all similar to the previously reported oligo(fluorene ethynylene) [13–15]. Their absorption maximum λ_{max} in solution peaked at 355 nm for **1**, 371 nm for **3**, and 375 nm for **4** respectively, displaying a distinct red-shift 16 nm for **3** and