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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 – OCH₃ and electron-withdrawing counterparts –CF₃ 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 –OCH₃ and –CF₃ makes maximum emission distinct red-shift in comparison with parent compound **1**, but the latter more prominently. \bigcirc 2010 Ming Zhang. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

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 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, CH₂Cl₂, CHCl₃, and THF, which allow us to conveniently obtain their ¹H and ¹³C 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 (Et₃N), and toluene that had been distilled over sodium/benzophenone, CaH₂, 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). ¹H and ¹³C NMR spectra were recorded on a Mercury plus 300 MHz or Bruker 400 MHz using CDCl₃ 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 1,4dibromobenzene 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 1,4dibromo-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 ¹H and ¹³C 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



Fig. 1. Normalized absorption and fluorescence spectra of compounds 1, 3 and 4 in THF solution (a) and (b); solid film (c) and (d).

20 nm for **4** in comparison with the parent compound **1**. Meanwhile, the shoulder peak corresponding to maximum effective conjugation length was measured at 372, 392 and 393 nm, respectively for compounds **1**, **3**, and **4**. It suggested that the extended conjugation lengths were obtained by introducing electron-donating or -withdrawing groups in the middle benzene ring. The absorption behaviors in film were very similar to that in solution except for small red-shifts (Table 1), indicating unobvious aggregation formed which was attributed to their X-shaped skeleton.

To investigate the substitution effect in excited state, the photoluminescence (PL) spectra of compounds 1, 3 and 4 were also studied (Fig. 1b and d). All PL spectra were obtained upon excitation at the corresponding absorption maximum. The PL spectra of all compounds are also strongly influenced by the substitution patterns of the central phenyl rings. First, in diluted solution $(1.0 \times 10^{-6} \text{ mol/L})$, the emission peaks of compounds 3 and 4 have obvious redshift relative to that of 1, indicating extended conjugation lengths by substitution. The emission peaks at 426 and 423 nm for 3 and 4 respectively showed similar substitution effect by electron donating and withdrawing groups. Furthermore, the well-defined vibronic structure of 3 that was modified by methoxy phenyl groups means higher rigidity than that of 4 in excited state. However, in film state, long wavelength emission band assigned to emission from excimer occurred at 472, 514 and 519 nm for compounds 1, 3, and 4, respectively. Obviously, the formation of excimers was attributed to strong π - π stacking interaction of planar and shape-persistent π -conjugated system.

In conclusion, we have synthesized a series of linear and X-shaped oligo(*para*-phenylene) derivatives functionalized with fluorone ethynylene by sequent Sonogashira and Suzuki–Miyaura coupling reaction. Spectroscopy investigation indicated that the substitution manner has a distinct influence on their photophysical

Table 1 Photophysical properties of compounds 1, 3 and 4.

λ_{abs} [nm] (THF)	λ_{abs} [nm] (film)	λ_{PL} [nm] (THF)	λ_{PL} [nm] (film)
355, 378 (sh)	359, 386 (sh)	389, 408 (sh)	450, 472 (sh)
371, 392 (sh)	378, 399 (sh)	406, 426 (sh)	434, 514 (sh)
375, 393 (sh)	382, 401 (sh)	423	462 (sh), 519
	$\lambda_{abs} \text{ [nm] (THF)}$ 355, 378 (sh) 371, 392 (sh) 375, 393 (sh)	$\begin{array}{c c} \lambda_{abs} \ [nm] \ (THF) & \lambda_{abs} \ [nm] \ (film) \\ \hline 355, 378 \ (sh) & 359, 386 \ (sh) \\ 371, 392 \ (sh) & 378, 399 \ (sh) \\ 375, 393 \ (sh) & 382, 401 \ (sh) \\ \hline \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

properties in both dilute solution and film state. In addition, the electron-donating/withdrawing groups prove an effective way to tune their absorption and emission behaviors.

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- [18] Selected data: 1: ¹H NMR (300 MHz, CDCl₃): δ 7.71–7.66 (m, 4H, Ar–H), 7.56 (s, 4H, Ar–H), 7.52–7.50 (m, 4H, Ar–H), 7.35–7.30 (m, 6H, Ar-H), 2.00–1.95 (t, 8H, J = 8.1 Hz, -CH₂-), 1.15–1.08 (m, 24H, -CH₂-), 0.79–0.74 (t, 12H, J = 7.2 Hz, -CH₃), 0.70–0.60 (m, 8H, -CH₂-). ¹³C NMR (75 MHz, CDCl₃,): δ 151.04, 150.80, 141.64, 140.35, 131.50, 130.63, 127.57, 126.88, 125.96, 123.15, 122.88, 121.13, 120.02, 119.65, 92.49, 89.17, 55.20, 40.39, 31.51, 29.71, 23.71, 22.59, 13.99. EI MS (*m/z*): 790 (M⁺, 100%). 2: ¹H NMR (300 MHz, CDCl₃): δ 7.84 (s, 2H, Ar-H), 7.73–7.68 (m, 4H, Ar-H), 7.58–7.53 (m, 4H, Ar-H), 7.36–7.34 (m, 6H, Ar-H), 2.01–1.96 (t, 8H, J = 8.1 Hz, -CH₂-), 1.15–1.06 (m, 24H, -CH₂-), 0.79-0.74 (t, 12H, J = 6.9 Hz, -CH₃), 0.63-0.60 (m, 8H, -CH₂-). ¹³C NMR (75 MHz, CDCl₃); δ 151.12, 150.88, 142.32, 140.19, 136.00, 130.95, 127.77, 126.92, 126.43, 1226.01, 123.57, 122.91, 120.38, 120.14, 119.72, 98.00, 86.96, 55.18, 40.32, 31.49, 29.66, 23.69, 22.56, 13.99. MALDI-TOF MS (*m*/*z*): 946.4. **3**: ¹H NMR (300 MHz, CDCl₃): δ 7.77–7.74 (s + d, 6H, *J* = 9.0 Hz, Ar–H), 7.69–7.62 (m, 4H, Ar-H), 7.36–7.31 (m, 10H, Ar-H), 7.08–7.05 (d, 4H, J = 9.0 Hz, Ar-H), 3.92 (s, 6H, -CH₃), 1.97–1.91 (t, 8H, J = 8.1 Hz, -CH₂-), 1.14– 1.04 (m, 24H, -CH₂-), 0.78-0.74 (t, 12H, J = 6.9 Hz, -CH₃), 0.60 (s, br, 8H, -CH₂-). ¹³C NMR (75 MHz, CDCl₃): δ 159.36, 150.99, 150.68, 141.48, 140.34, 133.58, 132.03, 130.56, 130.37, 127.49, 126.84, 125.74, 122.85, 121.54, 121.44, 119.96, 119.56, 113.39, 94.93, 89.63, 55.32, 55.02, 40.33, 31.47, 29.68, 23.67, 22.57, 13.98. MALDI-TOF MS (m/z): 1002.6. 4: ¹H NMR (300 MHz, CDCl₃): δ 8.32 (s, 4H, Ar-H), 8.02 (s, 2H, Ar-H), 7.86 (s, 2H, Ar-H), 7.70-7.64 (m, 4H, Ar-H), 7.39-7.31 (m, 10H, Ar-H), 1.98-1.93 (t, 8H, J = 6.6 Hz, -CH₂-), 1.09-1.03 (m, 24H, -CH₂-), 0.78-0.73 (t, 12H, J = 7.2 Hz, -CH₃), 0.59-0.55 (m, 8H, -CH₂-). ¹³C NMR (75 MHz, CDCl₃): δ 151.13, 150.92, 142.37, 141.05, 140.16, 140.05, 134.13, 131.92, 131.49, 130.68, 129.53, 127.81, 126.92, 125.71, 125.22, 122.90, 122.32, 121.85, 121.60, 120.14, 120.08, 119.74, 97.31, 87.04, 55.20, 40.30, 31.49, 29.64, 23.66, 22.57, 13.95. MALDI-TOF MS (m/z): 1214.6.