



Synthesis and photophysical properties of monodisperse oligo(9,9-di-*n*-octylfluorene-2,7-vinylene)s functionalized anthracenes

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ABSTRACT

Four new well-defined monodisperse linear oligofluorenes with anthracene core **An-OFV_n** ($n = 1-4$) have been synthesized through Heck and Wittig reaction. These conjugated oligomers exhibit good solubility in common organic solvents. It is found that the conjugation length of the oligomers can be extended and the formation of excimers can be suppressed with increasing the number of fluorene–vinylene units linked in the 9,10-positions of anthracene.

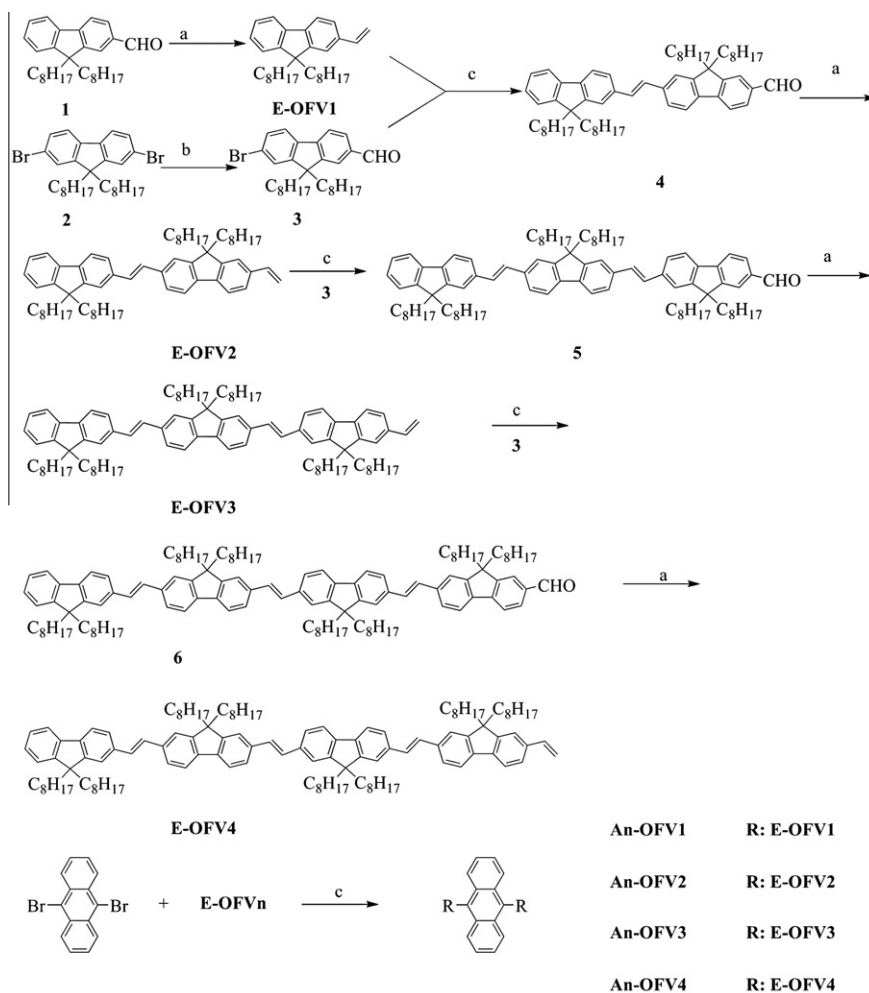
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Monodisperse, well-defined π -conjugated oligomers, have attracted much current attention in terms of molecular, electronic, and optoelectronic materials because they can be used as nondefected structures for electronic devices,¹ such as organic light-emitting diodes (OLEDs),² solar cells,³ electrical conductors,⁴ and field-effect transistors (FETs),⁵ and as models for understanding the structure–property relationship as well as the fundamental properties of their analogous polydisperse polymers.⁶ A number of functionalized oligomers have been synthesized, including oligothiophenes,⁷ oligocarbazoles,⁸ oligophenothiazine,⁹ oligoanilines,¹⁰ and oligophenylenes¹¹. Especially, since Miller and Klaerner reported the first monodisperse oligo(9,9-di-*n*-hexylfluorenes),¹² many kinds of oligofluorenes¹³ have been prepared as model compounds of poly(alkylfluorene)s, which have emerged as leading electroluminescent materials due to their high photoluminescence quantum efficiencies, high hole mobility, high thermal stability, and good solubility. For example, Chen and co-workers have synthesized a series of monodisperse chiral oligofluorenes with chiroptical activities.¹⁴ Tsutsui and co-workers have reported the monodisperse oligo(9,9-dihexyl-2,7-fluoreneethynylene)s as light-emitting layer in LEDs. Geng and co-workers have found that the photophysical properties and the thermal properties varied with the molecular length of the monodisperse oligo(9,9-di-*n*-octylfluorene-2,7-vinylene)s. In addition, oligofluorene-functionalized star-shaped architectures have also been prepared by several groups.¹⁵ On the other hand, anthracene derivatives are also one of the promising candidates in blue fluorescent materials.¹⁶ However,

excimer with bathochromic-shifted emission is often detected in some anthracene-based emitting materials.¹⁷ Miller and co-workers have suggested that the formation of excimers can be suppressed by the introduction of small amounts of anthracene into the main chain linked via the 9,10-positions.¹⁸ In order to reveal the effect of the oligofluorene linked to anthracene on the formation of excimer, herein, a series of new monodisperse linear oligofluorenes-functionalized anthracenes **An-OFV_n** ($n = 1-4$) have been synthesized. It is found that the emission of excimer is quite strong for **An-OFV1** and it can be suppressed effectively for **An-OFV4**. Therefore, the formation of excimers can be gradually suppressed with increasing the number of fluorene–vinylene units linked to the 9,10-positions of anthracene, which will be helpful for the design of novel blue-emitting materials with high fluorescence efficiency.

The synthetic routes for monodisperse oligo(9,9-di-*n*-octylfluorene-2,7-vinylene)s-functionalized anthracenes **An-OFV_n** are sketched in Scheme 1. The precursors of oligo(9,9-di-*n*-octylfluorene-2,7-vinylene)s with terminal vinylene groups **E-OFV_n** were first prepared by alternate Heck reaction and Wittig reaction.^{11a,19} For example, **E-OFV1** was obtained through Wittig reaction between methyltriphenylphosphoniumiodide and 2-formyl-9,9-di-*n*-octylfluorene (**1**), which was synthesized according to the method reported in the Ref. 13a in a yield of 95%. Then, compound **4** was readily obtained from **E-OFV1** and 2-bromo-7-formyl-9,9-di-*n*-octylfluorene (**3**), which was an important intermediate for extending the fluorene units in **E-OFV_n** and prepared in accordance with the literature,^{13a} catalyzed by Pd(OAc)₂ in *N,N*-dimethylformamide (DMF) at 110 °C for 10 h via the Heck reaction in a yield of 78%. The Wittig reaction between compound **4** and meth-

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Scheme 1. Synthesis of **An-OFVn**. Reagents and conditions: (a) $[\text{Ph}_3\text{PCH}_3]^+ \Gamma^-$, *t*-BuOK, THF, 0 °C to rt; (b) (1) *n*-BuLi, THF, –78 °C; (2) DMF, –78 °C; (c) Pd(OAc)₂, K₂CO₃, DMF, Bu₄NBr, 110 °C, 10 h.

yltriphenylphosphoniumiodine could afford **E-OFV2** in a yield of 85%. Accordingly, by using alternate Heck reaction and Wittig reaction, we gained **E-OFV3** and **E-OFV4** in good yields. Finally, the linear monodisperse π -conjugated oligomers of **An-OFVn** were synthesized by Heck reaction between **E-OFVn** and 9,10-dibromoanthracene. The yields for the compounds **An-OFV1**, **An-OFV2**, **An-OFV3**, and **An-OFV4** are 75%, 70%, 68%, and 65%, respectively. All the intermediates and the final products were purified by column chromatography followed by recrystallization, and the new compounds were characterized with FT-IR, ¹H NMR, ¹³C NMR, elemental analysis, and MALDI/TOF mass spectroscopy [24]. The compounds **An-OFVn** exhibited a vibration absorption band around 960 cm⁻¹ arising from the wagging vibration of the *trans*-double bond (C=C) in the IR spectrum.^{13b,20} In addition, the ¹H NMR spectra of **An-OFVn** also confirmed that all the ethenyl groups adopted the *trans*-conformation on account of the absence of the signal at ~6.5 ppm assigned to protons in *cis*-double bonds (–CH=CH–).^{20,21} Due to the introduction of long carbon chains **An-OFVn** were readily dissolved in many organic solvents, including dichloromethane, chloroform, toluene, ethyl acetate, and tetrahydrofuran.

The UV–vis absorption spectra of **An-OFVn** and **E-OFVn** in solutions are shown in Figure 1. It was clear that in dilute solution (2.0×10^{-6} M, Fig. 1b) **E-OFV1** gave three absorption bands at 286, 298, and 318 nm, which red shifted significantly with increasing the number of fluorene–vinylene units on account of the

extending of π -conjugation. For instance, the absorption maximum shifted to 398, 425, and 438 nm for **E-OFV2**, **E-OFV3**, and **E-OFV4**, respectively (Table S1). Whereas, the absorption of **An-OFVn** exhibited red-shift compared with that of **E-OFVn**. For instance, **An-OFV1** showed three absorption peaks at 325, 336, and 423 nm, in which the two former ones due to fluorene units gave a little red shift compared with those of **E-OFV1** and the latter one was ascribed to the electronic transition of the anthracene-based conjugated system. Because of the overlap of the absorption of the conjugated difluorene units and anthracene core the absorption bands of **An-OFV2** are merged into a broad band between 350 and 450 nm and a feeble hump around 430 nm was observed. With increasing the fluorene–vinylene units, the absorption of oligofluorene units became dominating, so we could find two absorption bands at 409 and 434 nm for **An-OFV3** as well as the ones at 420 and 444 nm for **An-OFV4** which were similar to those of **E-OFV3** and **E-OFV4**, and further red shifted compared to **An-OFV2** (Table S1). Meanwhile, the absorption bands of **An-OFVn** in the films red shifted compared with those in solutions. From Figure S1, we could find that the absorption maxima of **An-OFV1** in the film red shifted to 438 nm from 423 nm in the solution, indicating the occurrence of the intermolecular interaction in the solid states.

Figure 2 shows the concentration-dependent fluorescent emission spectra of **An-OFVn** in chloroform. It is obvious that **An-OFV1** exhibits three emission bands at 412, 439, and 459 nm in dilute solution below 1.0×10^{-8} M. With increasing the concentra-

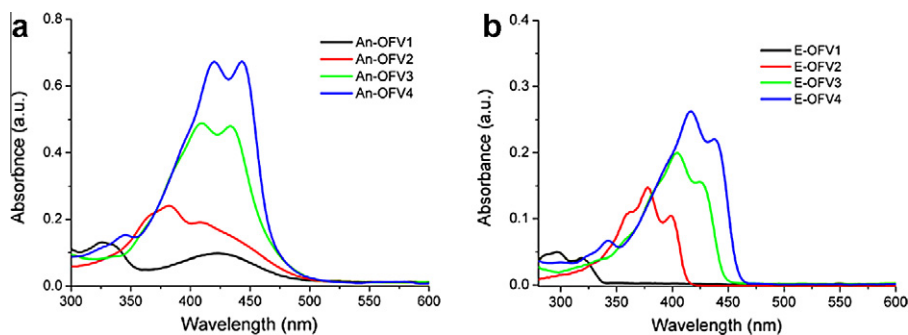


Figure 1. UV-vis absorption spectra of (a) **An-OFVn** in chloroform (1.0×10^{-6} M) and (b) **E-OFVn** in chloroform (2.0×10^{-6} M).

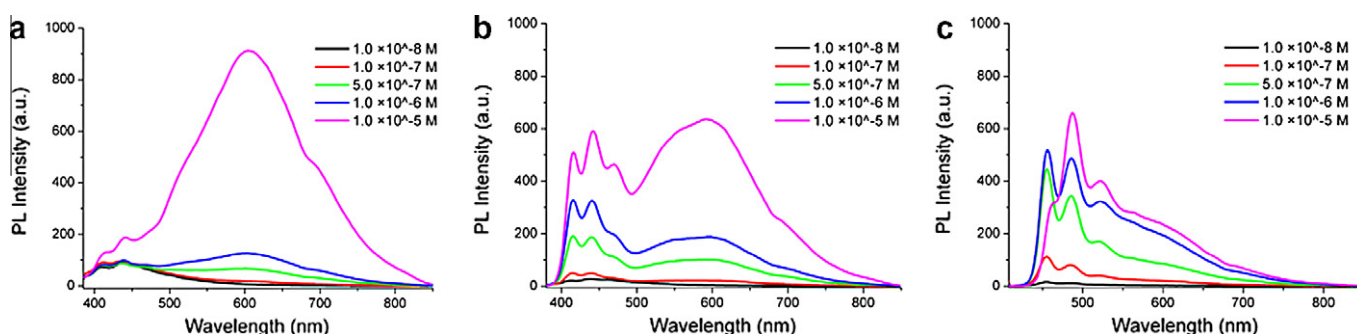


Figure 2. Concentration-dependent fluorescent emission spectra of (a) **An-OFV1**, (b) **An-OFV2**, and (c) **An-OFV4** in chloroform ($\lambda_{\text{ex}} = 365$ nm).

tion, the bands in the region of 400–460 nm were intensified without shift, but another broad band at 602 nm appeared and became stronger and stronger, whose intensity was ca. five times higher than that at 439 nm at 1.0×10^{-5} M. We deemed that the emission at 602 nm of **An-OFV1** should be ascribed to the emission of the excimer formed in the excited state,^{22,23} which can be further confirmed by the absorbance-concentration diagram of **An-OFVn** in solution. From Figure S2, a well linear relationship between the absorption maximum and the concentration for **An-OFV1**, **An-OFV2**, and **An-OFV3** can be detected, suggesting that no aggregates are formed in ground state when the concentration was less than 1.0×10^{-5} M. Similarly, **An-OFV2** and **An-OFV3** also gave the emission at 400–500 nm, which red shifted compared with those of **An-OFV1** on account of the enlargement of the conjugation. On the other hand, when the concentrations are higher than 1.0×10^{-7} M, the emission at ca. 600 nm ascribed to the excimer emerged. It should be notable that the emission intensity at ca. 600 nm is comparable to that at 441 nm for **An-OFV2** when the concentration reached 1.0×10^{-5} M, meaning that the emission from excimer is not as strong as that in **An-OFV1**. In the case of **An-OFV4**, as shown in Figure 2c, the emission of the excimer is quite lower than that at ca. 450 nm. Thus, with increasing the length of oligofluorene linked to the 9,10-positions of anthracene, the formation of excimer can be suppressed on account of the steric effect as well as the interaction between fluorene-vinylene units, and the emission of excimer decreases significantly when the number of fluorene-vinylene units in the arms reached four. It should be noticed that the emission intensity at ca. 455 nm for **An-OFV4** at 1.0×10^{-5} M decreased compared with that at lower concentration, which might be due to the molecular aggregation at higher concentration (Figs. S2 and S3). In addition, **An-OFVn** showed similar asymmetrical emission peaks located at ca. 570 nm in the films, which might be due to the emission of the molecular aggregates and the excimers (Fig. S1). The fluorescence quantum yields (Φ_F) of **An-OFVn** ($n = 1-4$) in toluene were mea-

sured by using quinine sulfate ($\Phi_F = 0.546$, $\lambda_{\text{ex}} = 365$ nm) as a standard, and they were 0.21, 0.34, 0.77, and 0.85, respectively.

In conclusion, we have synthesized four new well-defined monodisperse linear oligofluorenes-functionalized anthracenes **An-OFVn** ($n = 1-4$) by alternate Heck and Wittig reactions in good yields. The absorption bands exhibited red shift with increasing the number of fluorene-vinylene units because of the enlargement of the conjugation. Meanwhile, the strong emission at 602 nm assigned to the electronic transition of the excimer for **An-OFV1** can be detected, but decreases significantly when the number of fluorene units in the arms reached four, suggesting that the formation of excimer can be suppressed with increasing the number of fluorene-vinylene units linked in the 9,10-positions of anthracene. The strategy of restraint of the excimer formation will be helpful for fabrication of novel blue-emitting materials with high fluorescence efficiency.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.07.155.

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24. **An-OFV1**: ^1H NMR (500 MHz, CDCl_3) δ 8.49 (dd, $J = 6.8, 3.3$ Hz, 4H), 8.00 (d, $J = 16.5$ Hz, 2H), 7.77 (dd, $J = 13.9, 7.5$ Hz, 4H), 7.70 (d, $J = 7.9$ Hz, 2H), 7.61 (s, 2H), 7.52 (dd, $J = 6.9, 3.2$ Hz, 4H), 7.38–7.30 (m, 6H), 7.05 (d, $J = 16.5$ Hz, 2H), 2.03 (s, 8H), 1.26–1.10 (m, 40H), 0.85–0.77 (m, 12H), 0.79–0.63 (m, 8H) (Fig. S18). ^{13}C NMR (125 MHz, CDCl_3) δ 151.90, 151.51, 141.70, 141.18, 138.54, 136.65, 130.11, 127.53, 127.22, 127.00, 125.86, 125.62, 124.68, 123.37, 121.45, 120.35, 120.18, 55.53, 40.77, 32.19, 30.45, 29.63, 24.23, 23.01, and 14.47 ppm (Fig. S19). IR (KBr, cm^{-1}): 2926, 2853, 1468, 1453, 1376, 963, 775, and 740. Elemental analysis calculated for $\text{C}_{76}\text{H}_{94}$: C, 90.60; H, 9.40. Found: C, 90.47, H, 9.30. MS, m/z : cal: 1007.6, found: 1007.7 (Fig. S20). Mp: 94.0–95.0 °C. **An-OFV2**: ^1H NMR (500 MHz, CDCl_3) δ 8.51 (dd, $J = 6.8, 3.2$ Hz, 4H), 8.02 (d, $J = 16.5$ Hz, 2H), 7.78 (d, $J = 7.8$ Hz, 2H), 7.75 (d, $J = 7.8$ Hz, 2H), 7.72 (s, 1H), 7.70 (d, $J = 7.5$ Hz, 5H), 7.62 (s, 2H), 7.55 (dt, $J = 9.9, 7.0$ Hz, 12H), 7.36–7.28 (m, 10H), 7.06 (d, $J = 16.3$ Hz, 2H), 2.11–1.97 (m, 16H), 1.26–1.03 (m, 80H), 0.90–0.70 (m, 32H), 0.70–0.60 (m, 8H) (Fig. S21). ^{13}C NMR (125 MHz, CDCl_3) δ 151.26, 150.96, 140.87, 136.42, 128.47, 127.02, 126.78, 125.59, 122.85, 120.61, 120.25, 119.88, 119.65, 55.02, 40.52, 31.79, 30.07, 29.23, 23.76, 22.59, and 14.06 ppm (Fig. S22). IR (KBr, cm^{-1}): 2926, 2854, 1466, 1376, 965, 829, 758, and 740. Elemental analysis calculated for $\text{C}_{138}\text{H}_{178}$: C, 90.23; H, 9.77. Found: C, 90.11, H, 9.65. MS, m/z : cal: 1836.9, found: 1837.4 (Fig. S23). Mp: 111.0–113.0 °C. **An-OFV3**: ^1H NMR (500 MHz, CDCl_3) δ 8.51 (s, 4H), 8.03 (d, $J = 16.1$ Hz, 2H), 7.88–7.65 (m, 14H), 7.65–7.48 (m, 22H), 7.32 (dd, $J = 22.4, 10.2$ Hz, 14H), 7.07 (d, $J = 14.5$ Hz, 2H), 2.17–1.95 (m, 24H), 1.22–0.91 (m, 120H), 0.82–0.67 (m, 60H) (Fig. S24). ^{13}C NMR (125 MHz, CDCl_3) δ 151.78, 151.70, 151.55, 151.26, 150.97, 140.88, 138.15, 136.48, 132.87, 129.73, 128.72, 128.64, 128.56, 127.01, 126.78, 126.61, 125.72, 125.59, 125.26, 124.33, 122.85, 121.05, 120.71, 120.61, 120.06, 119.91, 119.64, 55.03, 40.54, 31.81, 30.09, 29.26, 23.77, 22.60, and 14.06 ppm (Fig. S25). IR (KBr, cm^{-1}): 2925, 2851, 1466, 1375, 966, 827, 758, and 740. Elemental analysis calculated for $\text{C}_{200}\text{H}_{262}$: C, 90.10; H, 9.90. Found: C, 89.93, H, 9.79. MS, m/z : cal: 2666.2, found: 2667.1 (Fig. S26). Mp: 147.0–149.0 °C. **An-OFV4**: ^1H NMR (500 MHz, CDCl_3) δ 8.51 (dd, $J = 6.8, 3.3$ Hz, 4H), 8.03 (d, $J = 16.4$ Hz, 2H), 7.85–7.65 (m, 18H), 7.63 (s, 2H), 7.61–7.47 (m, 28H), 7.39–7.27 (m, 18H), 7.07 (d, $J = 16.2$ Hz, 2H), 2.33–1.96 (m, 32H), 1.23–0.92 (m, 160H), 0.85–0.63 (m, 80H) (Fig. S27). ^{13}C NMR (125 MHz, CDCl_3) δ 151.55, 140.88, 140.63, 136.49, 130.65, 128.57, 127.01, 126.78, 125.71, 122.85, 120.61, 119.91, 55.03, 40.53, 31.80, 30.09, 29.24, 23.77, 22.59, and 14.06 ppm (Fig. S28). IR (KBr, cm^{-1}): 2926, 2852, 1467, 1376, 962, 827, 756, and 740. Elemental analysis calculated for $\text{C}_{262}\text{H}_{346}$: C, 90.02; H, 9.98. Found: C, 89.87, H, 9.89. MS, m/z : cal: 3495.5, found: 3496.2 (see Fig. S29). Mp: 170.0–172.0 °C.