

Note

CHIRAL CONJUGATED OLIGOMER BASED ON 1,1'-BINOL WITH 3,3'-ACETYLENE-PHENYLENE-ACETYLENE SPACER*

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Abstract The 1,1'-binaphthol based oligomers **3** and **7** with 3,3'-acetylene-phenylene-acetylene spacer were prepared from BINOL **1**. The high optical rotation value and CD spectra demonstrated the main chain chirality of the oligomer molecule. The UV-VIS and fluorescent spectra evidence the characteristics of conjugated structure. In comparison with oligomer **2** bearing 3,3'-acetylene spacer, the oligomers **3** and **7** have longer efficient conjugation segment, and their fluorescent quantum yields (ϕ) increased (0.60–0.65 versus 0.14). Extending the effective conjugation segment would improve the photophysical properties of chiral conjugated polymers.

Keywords Chiral conjugated oligomer, BINOL, 3,3'-Acetylene-phenylene-acetylene spacer

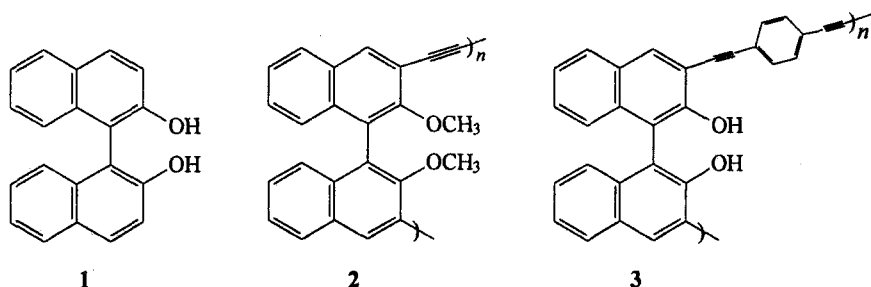
INTRODUCTION

Recently, optically active synthetic polymers derived from the chiral monomers have received tremendous interest^[1]. In general, when a chiral monomer is employed, there often results a preference for helix formation in one direction, i.e., with a main chain chirality^[2]. Such polymers have been used as the absorbing material for chromatography and have other potential applications based on their piezoelectric, ferroelectric, or nonlinear optical properties. Several conjugated polymers with chiral side chain substituents are known, but few investigations on the conjugated polymer with main chain chirality have been reported^[3]. 1,1'-bi-2-naphthol (BINOL) (**1**) is an important chiral auxiliary and a ligand for many asymmetric transformation^[4]. 1,1'-binaphthyl dimer, oligomer and polymer have been studied extensively due to their unique properties in molecular recognition, asymmetric catalysts and materials^[5]. It was reported that the synthesis of polymers or oligomers linked to the 4,4'-position of BINOL would give a linear structure with screwlike segment^[6] and to the 6,6'-position with chiral conjugated structure^[7]. In the meantime, we synthesized a BINOL based oligomer (**2**) connecting to acetylene at 3,3'-position with main chain chirality^[8]. The oligomer molecule has a conjugated structure, but with a short effective conjugation segment which would reduce the delocalization along the backbone. Herein, we wish to report photophysical studies of a chiral oligomer **3** linked by an acetylene-phenylene-acetylene spacer at 3,3'-position of 1,1'-binaphthyl moiety. The oligomer was expected to have longer effective conjugation segment to improve the photophysical properties of the chiral conjugated polymer.

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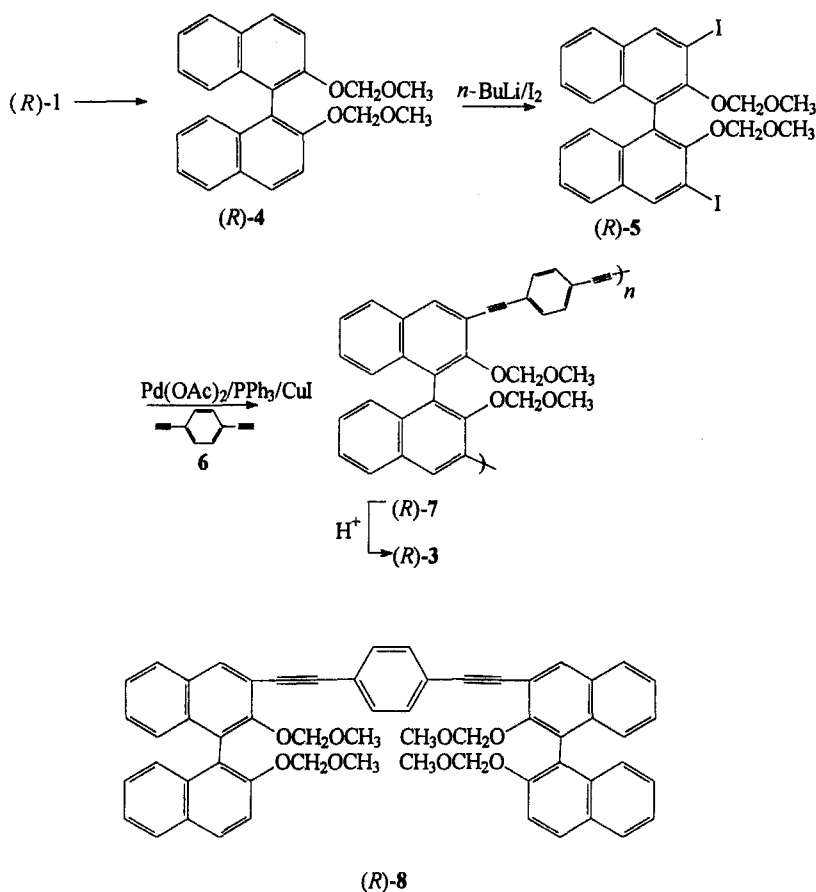
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EXPERIMENTAL

Materials and Synthesis

The oligomers were prepared from BINOL. Its enantiomers were available commercially or easily prepared through a variety of methods. For the present study, optically pure (*R*)-1 was used. The same strategy described here can be applied to the preparation of (*S*)-binaphthol derivatives and their oligomers. Ortholithiation of the dimethoxymethyl ether 4 using the Sniekus's procedure^[9] produced the bis-iodo-BINOL derivative 5 with 76% yield). According to the Hay's procedure^[10], 1,4-diethynylbenzene 6 was prepared from 1,4-divinylbenzene. For performing the oligomerization, the palladium-catalyzed Sonogashira-Cassar-Heck coupling reaction^[11] between aryl acetylene and bis-iodide compound was employed.



Scheme 1

(R)-3,3'-Diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (R)-(+)-5

To a solution of *(R)-(+)-4* (1.87 g, 5 mmol) in anhydrous THF (40 mL), *n*-BuLi (1.6 mol/L in hexane, 12.5 mL) was added dropwise at -78°C under nitrogen atmosphere, with stirring for 4 h at -78°C . A solution of iodine (3.2 g) in 20 mL of THF was added to the mixture, and stirred for 3 h at room temperature. Then, 20% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution (20 mL) was added and stirred for another 2 h. The water phase was extracted with CH_2Cl_2 (20 mL $\times$ 3) and the combined organic layer was dried over Na_2SO_4 . After evaporation, the residue was purified by flash chromatography (silica gel, eluent: 20% of ethyl acetate in petroleum ether) to give a white solid (**5**, 2.4 g, 76.2%). mp $125\text{--}127^{\circ}\text{C}$ (Ref. [12] $127\text{--}128^{\circ}\text{C}$). $[\alpha]_{\text{D}} = 115.8$ (*c* 0.4, THF). $^1\text{H-NMR}$ (CDCl_3 , δ): 2.6 (s, 6H), 4.7 (d, 2H), 4.8 (d, 2H), 7.1–7.5 (m, 6H), 7.8 (d, 2H) and 8.58 (s, 2H).

Oligomer (R)-(-)-7

In a flame-dried flask, a mixture of *(R)-(+)-5* (0.47 g, 0.75 mmol), 1,4-diethynylbenzene **6** (0.096 g, 0.75 mmol) and triethylamine (4 mL) in THF (7 mL) and DMF (7 mL) was purged with nitrogen for 15 min. The flask was then placed in an oil-bath, and palladium (II) acetate (5.6 mg, 0.025 mmol), triphenylphosphine (19 mg, 0.075 mmol) and cuprous iodide (10 mg, 0.05 mmol) were added consecutively. After the reaction mixture was refluxed under nitrogen for 72 h, the cooled mixture was poured into 100 mL methanol to precipitate out the polymer. The precipitate was redissolved in THF (10 mL), and reprecipitated from 50 mL methanol again to give a yellow solid (**7**, 0.45 g), then dried under vacuum. $[\alpha]_{\text{D}} = -429$ (*c* 0.15, THF). FTIR (KBr, cm^{-1}): 3057, 2959, 1970, 1618, 1440, 1260, 1099, 971 and 840. $^1\text{H-NMR}$ (CDCl_3 , δ): 2.87 (s, 3H), 2.95 (s, 3H), 4.94–5.02 (m, 4H), 7.05–7.42 (m, 8H), 7.64–7.88 (m, 4H) and 8.23 (m, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , δ): 57.7, 68.0, 76.3, 77.8, 99.9, 111.8, 125.3, 125.5, 125.7, 126.0, 127.6, 127.8, 128.4, 128.8, 129.6, 131.5, 131.8 and 132.0.

Oligomer (R)-(-)-3

To a solution of oligomer **7** (0.2 g) in THF (20 mL), isopropanol (6 mL) and hydrochloric acid (6 mol/L, 5 mL) were added. After the mixture was stirred for 36 h at room temperature, the volatiles were expelled under reduced pressure. The solid was filtered and washed with 100 mL water. After being dried under vacuum, the residue was extracted with 10 mL THF. The solution was filtered and the filtrate was evaporated to give a yellow solid (**3**, 0.11 g). $[\alpha]_{\text{D}} = -443$ (*c* 0.1, THF). FTIR (KBr, cm^{-1}): 3506, 3058, 2954, 1970, 1620, 1437, 1245, 1101, 953 and 842. $^1\text{H-NMR}$ (CDCl_3 , δ): 7.05–7.59 (m, 8H), 7.66–8.39 (m, 6H) and 10.0 (bs, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , δ): 98.9, 106.3, 111.8, 125.3, 125.6, 125.9, 127.8, 128.6, 128.8, 129.6, 131.5, 131.8 and 132.0.

According to the same procedure, starting from monoiodide, *(R)-(+)-3-iodo-1,1'-bi-2-naphthylol* dimethoxymethyl ether, the dimer, *(R)-(+)-8* was synthesized in 71% yield as a yellow solid. $[\alpha]_{\text{D}} = 202$ (*c* 0.15, THF). $^1\text{H-NMR}$ (CDCl_3 , δ): 2.65 (s, 6H), 3.15 (s, 6H), 4.91 (d, *J* = 5.64 Hz, 2H), 5.00 (m, 4H), 5.16 (d, *J* = 6.9 Hz, 2H), 7.18–7.31 (m, 6H), 7.35–7.44 (m, 6H), 7.52–7.60 (m, 6H), 7.86 (d, *J* = 8.1 Hz, 3H), 7.96 (d, *J* = 9.0 Hz, 3H) and 8.22 (s, 2H). *m/z* (FAB-MS): 870.8 (M^+).

Measurements

Molecular weights were measured on a Knauer vapour pressure osmometer (Germany). The optical rotation was measured with a Perkin-Elmer 241 MC and circular dichroism spectrum with a Jasco J-715 Polarimeter. ^1H and $^{13}\text{C-NMR}$ were performed on Varian XL-300 NMR spectrometer. FTIR was recorded on a Perkin-Elmer FTIR 1760X spectrometer. The UV-VIS spectra were recorded by a Hitachi-330 absorption spectrophotometer. The excitation and the fluorescent spectra were recorded with a Hitachi-MPF-4 Fluorescent spectrophotometer. The concentration of sample solution was adjusted to be sufficiently dilute (5×10^{-6} g/mL) to avoid the remission and reabsorption. The photoluminescent lifetime of oligomer was determined by the method of phase-deviation adjustment on SImomjinco Hardware 4800s spectrophotometers. The reference sample was an aqueous solution of glycogen. The fluorescent quantum yields were determined by the following equation: $\phi = \phi_0(n_x^2 S_F^x OD^x) / (n_r^2 S_F^r OD^r)$ with Rodamine B ($\phi = 0.95$, solvent: ethanol) as the reference, where ϕ and ϕ_0 are the fluorescent quantum yields of oligomer and reference samples, n_x and n_r are the refractive indexes, S_F^x and S_F^r are the integral areas of the fluorescent spectra of oligomer and reference samples. *OD* is the optical density of the corresponding absorption.

RESULTS AND DISCUSSION

Characterization

The molecular weights of the oligomers **3** and **7** are 5700 and 2380, respectively. It is assumed that the steric effect at the 3,3'-position of 1,1'-binaphthyl moiety could restrict further extension of the oligomer. Oligomers **3** and **7** are soluble in THF, CH_2Cl_2 , and CHCl_3 . They were characterized by ^1H and ^{13}C -NMR spectra, in which the corresponding signals are assigned to aromatic, methoxymethyl and acetylene moieties.

As is well known, the optical rotation of optically active polymers shows enormous enhancements over that of the individual monomers used because of the regio-induced helicity. The values of the optical rotation of the oligomers (*R*)-**3** and (*R*)-**7**, $[\alpha]_{\text{D}} = -429$ and $[\alpha]_{\text{D}} = -443$, are much bigger than those of (*R*)-**1** ($[\alpha]_{\text{D}} = 34.0$), (*R*)-**4** ($[\alpha]_{\text{D}} = 97.8$)^[12] and dimer (*R*)-**8** ($[\alpha]_{\text{D}} = 202$), but in opposite rotation direction. The tremendous optical rotations of **3** and **7** are attributed to their main chain chiralities.

The CD spectra of the oligomers (*R*)-**3** and (*R*)-**7** (Fig. 1) show a set of signals in the range of 200–250 nm, which are assigned to the CD effect of the binaphthyl moiety. Negative CD effects were also found at 421 and 392 nm for (*R*)-(-)-**3** and (*R*)-(-)-**7**, respectively, which originate from the helical nature of oligomer molecules. In comparison with (*S*)-(-)-**2**, a positive CD effect at 350 nm, the CD effects of **3** and **7** located at longer wavelength with a difference of 42–71 nm show the characteristic of longer effective conjugation segment.

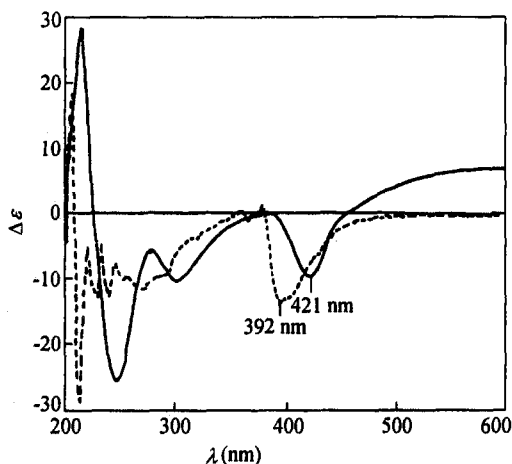


Fig. 1 CD spectra of oligomers (*R*)-**3** (----) and (*R*)-**7** (—)

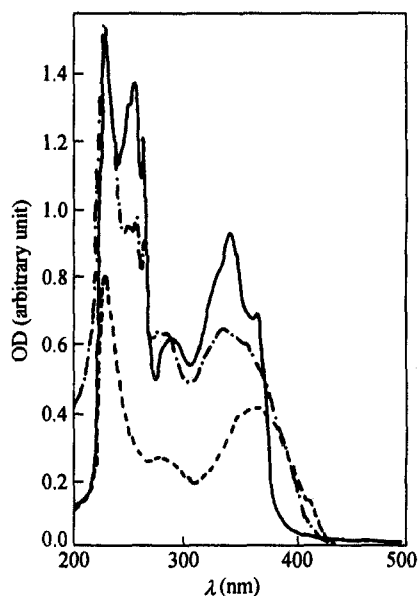


Fig. 2 The UV-VIS spectra of oligomers **3** (----), **7** (—) and dimer **8** (- · -)

Photophysical Properties

Figure 2 displays the absorption spectra of oligomers. The absorptions were observed at 370 nm for oligomers **3** and 365 nm for **7**. In comparison with the absorptions of the dimer **8** ($\lambda_{\text{max}} = 355$ nm), the absorptions of **3** and **7** red-shifted to longer wavelength, which indicates that although twisting conformation exists in the oligomer molecule, some conjugated characteristic still appears at longer wavelength. On the other hand, the shape of absorption spectra of the oligomer **7** is similar to that of the dimer **8**, indicating that the oligomer and dimer have the same effective conjugation segment, naphthyl-acetylene-phenylene-acetylene-naphthyl. Meanwhile, the red-shifts of the absorption spectra of oligomers **3** and **7** relative to the absorption at 350 nm of oligomer **2** are observed, which stems mainly from the relatively long effective conjugation segment. The wavelengths of UV absorption at longer wavelength range changed slightly with various solvents, indicating that the interaction

between the solvent and oligomer molecules is not great enough to influence the effective conjugation segment in the molecule backbone.

More interestingly, the fluorescent spectra of oligomer 7 (Fig. 3) exhibit two emission peaks between 385 and 410 nm either in polar solvents or in non-polar solvents. However, the fluorescent spectra of oligomer 2 are very smooth with one broad peak at 405 nm^[8]. On the other hand, for oligomers 3 and 7, the fluorescence in dichloromethane decayed by the excitation at identical wavelength gave two different photoluminescent lifetimes, τ_1 and τ_2 (Table 1). The fluorescent quantum yields of the oligomers 3 and 7 ($\phi = 0.60$ and 0.65 , respectively) are listed in Table 1. It is interesting to compare them with that of the oligomer 2 ($\phi = 0.14$). These results probably imply that the oligomer 3 and 7 could have some restricted rotation of binaphthyl moieties due to the longer spacer, which could change the torsion between two naphthyl rings of binaphthyl moiety, leading to the π - π interaction. Furthermore, the longer effective conjugation segment in the molecule backbone would markedly improve the photophysical properties of the chiral 1,1'-binaphthol-based polymer with 3,3'-conjugated spacer.

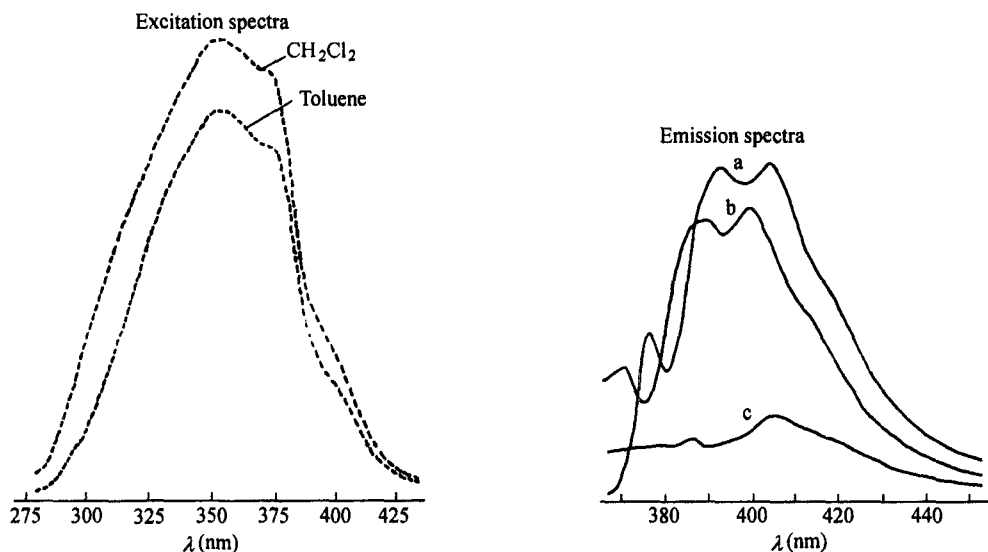


Fig. 3 The excitation and emission spectra of 7

a) $\lambda_{\text{ex}} = 348$ nm; b) $\lambda_{\text{ex}} = 370$ nm; c) $\lambda_{\text{ex}} = 400$ nm

Table 1. Photoluminescent lifetimes^a and quantum yields

Oligomer	τ_1 (ns)	τ_2 (ns)	ϕ
3	6.59	1.38	0.60
7	6.13	1.18	0.65
2	11.54	2.55	0.14

^a in CH_2Cl_2 , $\lambda_{\text{em}} = 403$ nm

CONCLUSION

Starting from chiral BINOL 1 and 1,4-diethynylbenzene 6, 1,1'-binaphthol-based optically active oligomers 3 and 7 with 3,3'-acetylene-phenylene-acetylene spacer were prepared. The high optical rotation and CD spectrum revealed main chain chirality of the oligomers. In comparison with the oligomer 2 bearing 3,3'-acetylene spacer, the oligomers 3 and 7 have longer efficient conjugation segments, resulting in the changes of the photophysical behaviors evidenced in UV-VIS and fluorescent spectra. The fluorescent quantum yields (ϕ) of the oligomers 3 and 7 increased markedly. Extending the effective conjugation segment would be favorable to the increase of effective conjugation without losing the main chain chirality. This investigation provides a clue to improve the photophysical properties of chiral conjugated polymers.

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