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# A chiral conjugated oligomer based on 1,1′-binaphthol with 3,3′-acetylene spacer

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## Summary

A 1,1'-binaphthol based optically active oligomer **6** with 3,3'-acetylene spacer was prepared from 2,2'-dimethoxy-1,1'-binaphthalene **3** through the palladium-catalyzed Stille coupling reaction. The high optical rotation and CD spectrum varified the main chain chirality of the oligomer. The photophysical properties of **6**, absorption, excitation and fluorescent spectra, demonstrated that the oligomer molecule had a conjugated structure, but twisting and rigid conformation would reduce the delocalization along the backbone.

## Introduction

Recently, optically active synthetic polymer derived from a chiral monomer has generated tremendous interest.[1] In general, when a chiral monomer is employed, there often results in a preference for helix formation in one direction, i.e., with a main chain chirality.[2] Such polymers have been used as adsorbing 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 investigation on the conjugated polymer with main chain chirality has been reported.[3] Recently, we proposed the synthesis of optically active binaphthol-based polymers. Chiral binaphthyl moiety shows stable chirality at high temperature and structural rigidity leading to ease of helix formation. We have reported the synthesis of the dimer (**1**) of a binaphthol derivative connecting by acetylene.[4] At the same time, the synthesis of polymers or oligomers linked at 4,4'-position of 1,1'-binaphthol giving a linear structure with screwlike segment[5] and at 6,6'-position with chiral conjugated structure[3,6] was

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reported. Herein, we would like to release the synthesis of a chiral oligomer linked by acetylene at 3,3'-position of 1,1'-binaphthyl moiety. In the view of the molecular structure, a chiral conjugated oligomer is expected. The investigation on the photophysical properties of the oligomer is helpful to understand its structural characteristics and able to provide a clue to modify the structure of the polymer for meeting the requirement in special photophysical properties.

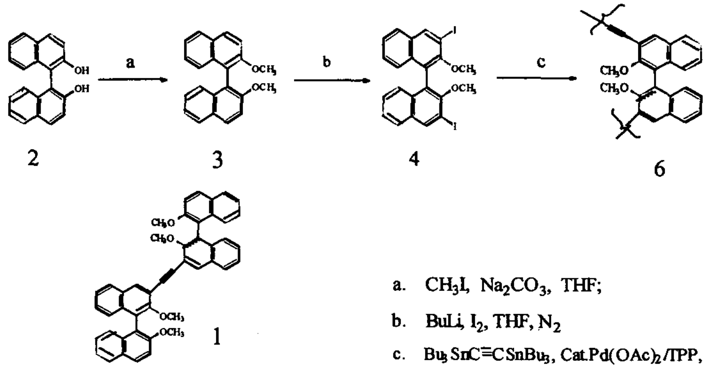
## Experimental

### *Synthesis and Oligomerization*

The oligomer preparation started from 1,1'-binaphthol (BINOL). Both enantiomers of BINOL are available commercially or easily prepared through a variety of methods.[7] For the present study, optically pure (S)-binaphthol (**2**) was used. The same strategy described herein can be applied to the preparation of (R)-binaphthol derivatives and its oligomer. The synthetic route to the monomer **4** is shown on Scheme 1. Methylation of **2** with methyl iodide and NaH in THF generated the dimethyl ether **3**. Ortholithiation-iodination of the **3** using the Sniekus's procedure[8] produced the bis-iodo-BINOL derivative **4** (in 70% isolated yield). For performing the oligomerization, the palladium-catalyzed Stille reaction[9] between aryl halides and organotin compounds was employed (Scheme 1). Based on a modified procedure,[10] the (S)-(-)-**4** reacted with bis(tributylstannyl)acetylene (**5**) in refluxing 1,4-dioxane for 3 days to give the oligomer **6**.

**6**: $^1$H NMR, δ(ppm): 3.78(bs, 6H); 7.09(bd, 2H); 7.10-7.23(m, 2H); 7.40(m, 2H); 7.82(bd, 2H); 8.24(bs, 2H). $^{13}$C NMR, δ(ppm): 60.16, 90.80, 117.43, 124.93, 125.37, 125.72, 127.29, 127.84, 130.25, 133.91, 134.42, 155.60. FT-IR, ν(cm$^{-1}$): 749, 1013, 1409, 1637, 1970, 2849, 2918, 3400.

**Scheme 1**



2

3

4

6

1

a. $CH_3I$, $Na_2CO_3$, THF;
b. BuLi, $I_2$, THF, $N_2$
c. $Bu_3SnC\equiv CSnBu_3$, Cat.Pd$(OAc)_2$/TPP,

### *Measurement and Instruments*

The molecular weight measurements were done by gel permeation chromatography using a 25 cm Jordi Gel DVB mixed bed column, a Perkin-Elmer Binary pump (model 250) and a Perkin-Elmer diode array detector (model 235). The eluent was THF, and the column was operated under the eluent head pressure adjusted to maintain a flow rate of 0.75 m/min. The dry oligomer was dissolved in THF at a concentration of 0.1% (wt/vol), and 20 microliters of this solution was used. Polystyrene samples in the molecular weight range of 600-200,000 were used as calibration standards.

The optical rotation was measured on Perkin-Elmer 241 MC and CD spectrum was on Jasco J-715 Polarimeter. $^1$H and $^{13}$C NMR were performed on GE-OMEGA 400. FT-IR was recorded by Perkin-Elmer 2000 FT-IR Photospectrometer.

The absorption spectra were recorded by the Hitachi-330 U.V.-Visible absorption spectrophotometer, the excitation and the fluorescent spectra were recorded by the Hitachi-MPF-4 Fluorescent spectrophotometer. The concentration of sample solution was adjusted in enough dilute ($5x10^{-6}$g/mL) to avoid the remission and reabsorption. The photoluminescent lifetime of the oligomer was determined by the method of phase-deviation adjustion on SLMOMJINCO Hardware 4800s spectrophotometers. The reference sample was an aqueous solution of glycogen.

## Results and Discussion

The molecular weight measurement of oligomer **6** indicated a number average molecular weight (Mn) of 1882 (Mw=3029) with a polydispersity index of 1.6. It was assumed that the steric effect at the 3,3'-position of 1,1'-binaphthyl moiety could obstruct further extension of oligomer chain. The oligomer is soluble in THF, $CH_2Cl_2$, $CHCl_3$ and so on. It was characterized by $^1$H and $^{13}$C NMR, where the corresponding signals were assigned to aromatic, methoxy and acetylene moieties, even there was some broadening in the signals. FT-IR showed a relatively weak peak at 1970 cm$^{-1}$ assigned to a conjugated acetylene bond.

As well known, the optical rotations of the optically active polymer show enormous enhancements over that of the individual monomer used because of the registry-induced helicity. The value of the optical rotation of the oligomer **6**, $[\alpha]_D$: -332 (c=0.5, THF), was much bigger than that of 2,2'-dimethoxy-1,1'-binaphthalene **3** ($[\alpha]_D$: -79.5, THF)[11] and the dimer **1** ($[\alpha]_D$: -120, THF)[4]. The enormous enhancement of the optical rotation for **6** is attributed to the main chain chirality.

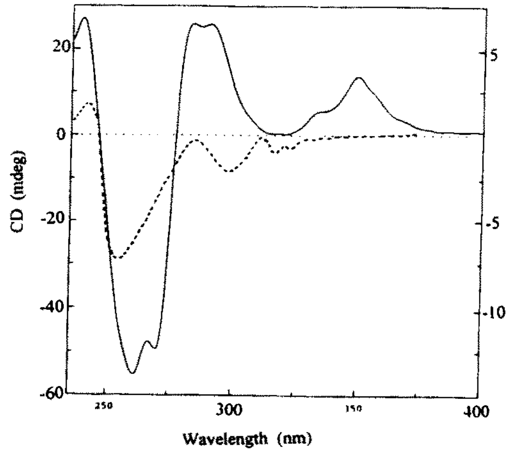


Fig 1. CD spectrum of 6 ( solid line, left axis) and 2 (dashed line, right axis)

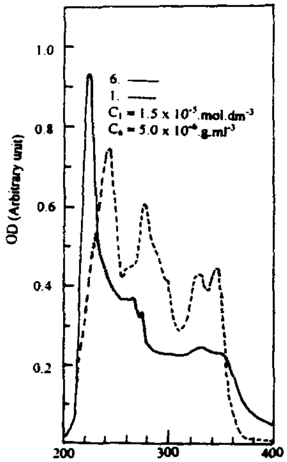


Fig 2. The absorption spectra of 1 and 6 in ethanol solution

The Circular Dichroism (CD) spectrum of **6** (Fig. 1) shows two resemble bisignals (292 and 283nm, 270 and 261nm) with some overlap, which are assigned to the CD effect of the binaphthyl moiety, due to a splitting of the excited state into two exciton levels via a Davydov interaction.[12] The positive CD effect also was found at 350nm originated from the chirality of the main chain in the oligomer molecule. However, for dimer **1** there were the small negative CD effect observed at 320nm and the CD effect in 250-300nm stemming from the binaphthyl moiety. Fig 2 displayed the absorption spectra of the oligomer **6** and dimer **1**. The absorptions were observed at 350nm ($\varepsilon_{max}$: $6.9x10^4$) for **6** and 345nm ($\varepsilon_{max}$: $2.0x10^4$) for **1** respectively. It indicated that although twisting conformation existed in the oligomer molecule, some conjugated characteristic still appeared at longer wavelength, which was suggested to be mainly from the effective conjugation segment, naphthyl-acetylene-naphthyl moiety. Comparing CD and absorption spectra of **1** with these of **6**, it is worthy to note that only the oligomer has distinct CD effect at 350nm. It also proved that the oligomer has main chain chirality and conjugated structure along the molecule backbone.[13]

The excitation spectra of **6** (Fig. 3) exhibit vibronic excitations at the same five wavelengths as in the absorption spectra, but with the different intensity in each peaks. The difference of maximum wavelength between 0-0 transition of absorption and emission is defined as Stokes shift, ($\Delta\lambda = \lambda em - \lambda ex$ ).[14] The magnitude of $\Delta\lambda$ describes the structure reorganization between ground and excited state. For some kind of conjugated polymer, Stocks shift is only 20-30nm, expressing a little of structure reorganization. In contrast, the oligomer **6** has very high Stocks shift, $\Delta\lambda$=405nm-343nm=62nm, indicating a large structure reorganization involved. Otherwise, the shape of the absorption and the emission spectra is very different, that implies the conformation between ground state and excited state is very different. Relative to the ground state, some bond twisting, solution relaxation and the change of the electronic structure in the excited state probably occurred.

The photoluminescent lifetime is able to characterize the decay process in the excited state and the number of the excited species. For the oligomer **6**, fluorescence in dichloromethane decayed in the biexponential mode and excitation at identical wavelength gave two different photoluminescent lifetimes, $\tau_1$ and $\tau_2$ (Table 1). Two lifetimes observed indicated that two excited species should exist in **6**. According to Mataga's suggestion,[15] the fast one of the lifetimes is ascribed to charge transfer in locally excited (LE) state and the slow one to twist intramolecular charge transfer (TICT) in delocalized excited state. The wavelength dependence of the luminescent lifetime can be interrupted as an indication of the presence of either two equilibrum ground state conformations with different excited state decaytimes or two overlapping excited electronic states with different decay times.[16] Due to the oligomer **6** can be considered as a symmetry-disturbed system, LE fluorensent and TLCT fluorescent bands overlap considerably,[15] so that the wavelength dependence

Table 1. Photoluminescent lifetimes measured at different excitation wavelength*

| $\lambda$ex, nm | 350 | 330 | 290 |
|---|---|---|---|
| $\tau_1$,ns (Fi) | 11.539 (0.232) | 23.965 (0.126) | 52.367 (0.127) |
| $\tau_2$,ns (Fi) | 2.549 (0.768) | 3.137 (0.874) | 3.211 (0.851) |

* in $CH_2Cl_2$, $\lambda$em=403nm

was not observed in the emission spectrum (Fig. 3).

The shape of absorption, excitation and emission spectra also correlates tightly with the rigidity of molecular backbone. Both absorption and excitation spectra of the oligomer **6** have the fine structure, indicating a highly ordered structure. The fluorescent spectra are very smooth, this also implies that the backbone of the oligomer is too stiff to make the binaphathyl moiety rotate to nearly planar. On the other hand, the absorption, excitation and fluorescent spectra of the oligomer **6** are similar to that of the dimer **1** in the shape of the curves, splitting and the position of the peaks. The basic functional segment in photophysical behavior of the oligomer **6** should be the same as in the dimer **1**. Otherwise, the fluorescent quantum yield of **6** in toluene was only 0.14. Relatively lower value exhibited that the delocalization along the molecule backbone was not strong. Obviously, the twisting conformation of the binaphthyl moiety would interfere the extension of the conjugation existed in the naphthyl-acetylene-naphthyl segment, reducing the delocalization along the molecule backbone. In summary, the oligomer molecule should have a main chain with entire chirality, composed of effective conjugation segments, where the connecting point of each segments is 1,1'-position of 2,2'-methoxy-1,1'-binaphthyl moiety as shown on Fig 4.

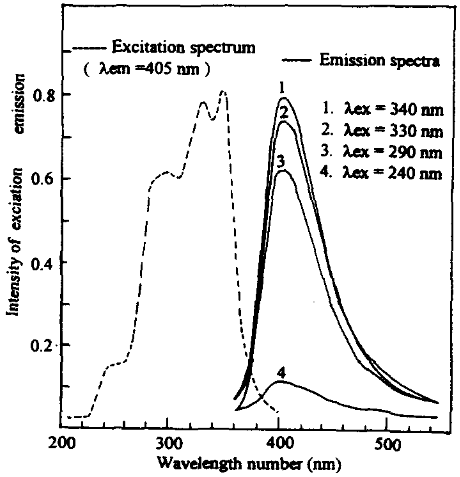


Fig. 3 The excitation and emission spectra of oligmer 6. in ethanol solution.

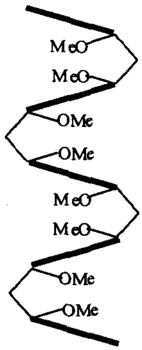


Fig 4 Illustrative diagram of oligomer molecule

## Conclusion

A 1,1'-binaphthol based optically active oligomer **6** with 3,3'-acetylene spacer was prepared from BINOL through the palladium-catalyzed Stille coupling reaction. The high optical rotation and CD spectrum exhibited main chain chirality of the oligomer **6**. The dependence of the photophysical behavior on the molecular structure of the oligomer revealed that the oligomer **6** had a conjugated structure, but the rigid and twisting conformation would reduce the delocalization along the backbone. The effective conjugation segments were connected each other in 1,1'-position of 1,1'-binaphthyl moiety. It is suggested that extending the effective conjugation segment and alterring the substitute on the 1,1'-binaphthalene molecule would be favorable to increase effective conjugation without losing the main chain chirality. The research project on improving the molecular structure of this kind of polymer is in progress.

## Acknowledgment

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## References

[1] For the review on the optically active polymer from chiral monoer, see: Okamoto Y, Nakano T (1994) Chem Rev 94: 349 and Wulff G (1995) Angrew Chem Int Ed 34: 1812

[2] For some recent example, see: Green M M, Peterson N C, Sato T, Teramoto A, Cook R, Lifson S (1995) Science 268: 1860; Puts R D, Sogah D Y (1995) Macromolecules 28: 390; Li L S, Strupp S I (1995) Macromolecules 28: 2618; Kakuchi T, Kamimura H., Matsunami S, Yokota K, Tsuda K (1995) Macromolecules 28: 658; Moore J S, Gorman C B, Grubbs R H (1991) J Am Chem Soc 113:1704; Coates G W, Waymouth R M (1991) J Am Chem Soc 113: 6270

[3] Hu Q, Vitharana D, Liu G Y, Jain V, Wagaman M W, Zhang L, Lee T R, Pu L (1996) Macromolecules 29: 1082

[4] Li C J, Wang D, Slaven IV W T (1996) Tetrahedron Letters 26: 4459

[5] Bedworth P V, Tour J M (1994) Macromolecules 27: 622

[6] a)Hu Q S, Vitharana D, Zheng X F, Wu C, Kwan C M S, Pu L (1996) J Org Chem 61: 8370; b)Hu Q S, Zheng X F, Pu L (1996) J. Org. Chem.61: 5200

[7] For recent example, see: Sakamoto T,Yonehara H, Pac C (1994) J Org Chem 59: 6859; Niji M, Nakajima M, Koga K (1994) Tetrahedron Letters 35: 7983

[8] Cox P J, Wang W, Snieckus V (1992) Tetrahedron Letters 17: 2253

[9] For review, see: Stille J E (1986) Angew Chem Int Ed Engl 25: 508

[10] Cummins C H (1994) Tetrahedron Letters 35: 857

[11] Lingenfelter D S, Helgeson R C, Cram D J (1981) J Org Chem 46: 393

[12] Langeveld-Voss B M W, Janssen R A J, Christiaans M P T, Meskers S C J, Dekkers H P J M, Meijier E W (1996) J Am Chem Soc 118: 4908

[13] Moore J S, Gorman C B, Grubbs R H (1991) J Am Chem Soc 113: 1704

[14] Hagler T W, Pakbaz K, Voss K F, Heeger A L (1991) Phys Rev B 8562

[15] Mataga N, Yao H, Okada T, Rettig W (1989) J Phys Chem 93: 3383

[16] Amotz D B, Harris C B (1987) J Chem Phys 86: 4856