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Stepwise synthesis and characterization of oligomers based on 1,1′-binaphthol with 3,3′-acetylene spacer[1]

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Abstract

A selective mono de-iodination led to an alternative preparation of a mono-iodo binaphthol-derivative in high yield. With the mono-iodo compound, several structurally well-defined, 1,1′-binaphthol-based optically active oligomers with a 3,3′-acetylene spacer were synthesized through palladium catalyzed, stepwise-coupling methods. The electrical and photo-physical properties of the oligomers have been examined. The electrical, photo-absorption, excitation and fluorescent data for various oligomers indicated that there is a very limited conjugation present between the naphthylene rings. The atropic of 1,1′-binaphthyl moiety led to twist and rigid main chain in the oligomers and polymers. With the changes of the external environment such as solvents, solvent viscosity and ambient temperature, the wavelengths of absorption and fluorescence and the intensities of absorption are changed slightly, but the fluorescent intensity and quantum yield can be influenced. The luminescent behaviors of the longer chain oligomer exhibit the twisted intramolecular charge transfer characteristic, which has a potential application in wavelength-stable light emitting material adaptable to ambient temperature and the solvent used in wide range.

1. Introduction

Chiral recognition plays an important role in biological systems. Such a recognition is also the basis of enantio-differentiation for asymmetric organic synthesis.[2] Chiral and helical properties are also common to biopolymers, such as polysaccharides, nucleic acids and some polypeptides.[3] Recently, optically active synthetic polymers with stable helices derived from a chiral monomer have generated considerable interest.[4] Such polymers have been used as adsorbing materials for chromatography

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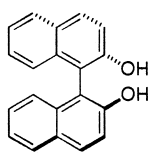
and have other potential applications based on their piezoelectric, ferroelectric, or nonlinear optical properties. 1,1′-Bi-2-naphthol (BINOL, **1**) is an important chiral auxiliary and a ligand for many asymmetric transformations.[5] Its 3,3′-di-substituted derivatives **2** were synthesized[6] and used as chiral catalysts,[7] through complexation with Lewis acids, in a variety of reactions. These compounds have also been used widely in molecular recognition studies.[8] The preparation and synthetic utilities of the unsymmetrical, 3-substituted derivatives **3** have also been explored recently by Snieckus and others.[9,10]



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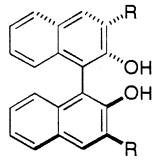

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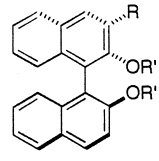

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Several years ago, we proposed and started the design and synthesis of binaphthol-based polymers and structurally well-defined oligomers (Fig. 1).[11] The polymers and oligomers proposed should have potential uses as nonlinear optical materials, as novel conducting materials, as hosts for molecular recognition, and as chiral ligands for asymmetric catalysis. In addition, the protecting group can be changed (e.g. to form crown ethers) to accommodate various needs; the acetylene linkage between the binaphthols can be replaced by other linkers and the location of halogens can be varied through different halogenation methods.[12] Electronically push–pull functional groups can also be attached to the aromatic ring to induce second order nonlinear optical properties.[13] Towards this goal, we have recently reported the study of the polymer.[14] Related to this study, we have also developed a palladium catalyzed acetylene gas reaction in an aqueous medium.[15] The reaction was subsequently applied to the synthesis of a binaphthol-based chiral polymer and other poly(arene ethynylene)s.[16] In contrast, established by Tour, the stepwise synthesis of structurally well-defined conjugated oligomers has recently received considerable attention.[17] The significance of the study lies in the following facts: these oligomers and polymers serve as the model for the study of their corresponding polydispersed macromolecular analogs and they provide information concerning the electronic, photonic, thermal, and morphological properties of related polydispersed polymers on the molecular level. Thus, in order to understand the relationship between the chain length and the electrical and photophysical properties of 3,3′-acetylene linked binaphthol-based polymers and oligomers, we have investigated the stepwise synthesis of several structurally well-defined 1,1′-binaphthol-based optically active oligomers with a 3,3′-acetylene spacer. The properties were examined and compared with the corresponding polymers. Previously, Tour has synthesized a spiral oligomer with a 4,4′-connection through a stepwise synthesis.[18]

2. Results and discussions:

Optically active 1,1′-bi-2-naphthol is readily available commercially.[19] It can also be obtained from the racemic compounds through enzymatic[20] and chemical resolution.[21] In the present study, the chemical resolution by De Lucchi[22] and Merck's[23] crystallization procedures were used to obtain the optically active 1,1′-bi-2-naphthol. A variety of protecting groups can be used for the derivatization of binaphthol. As the starting point, we chose methylated derivatives in our study.

To synthesize oligomers with controlled length, we adopted Tour's stepwise method.[17] For the synthesis of a dimeric derivative (Scheme 1), binaphthol (*S*-isomer) (**1**) is methylated in 78–80% yield by reaction with methyl iodide and sodium carbonate in DMF or sodium hydride in THF in the presence

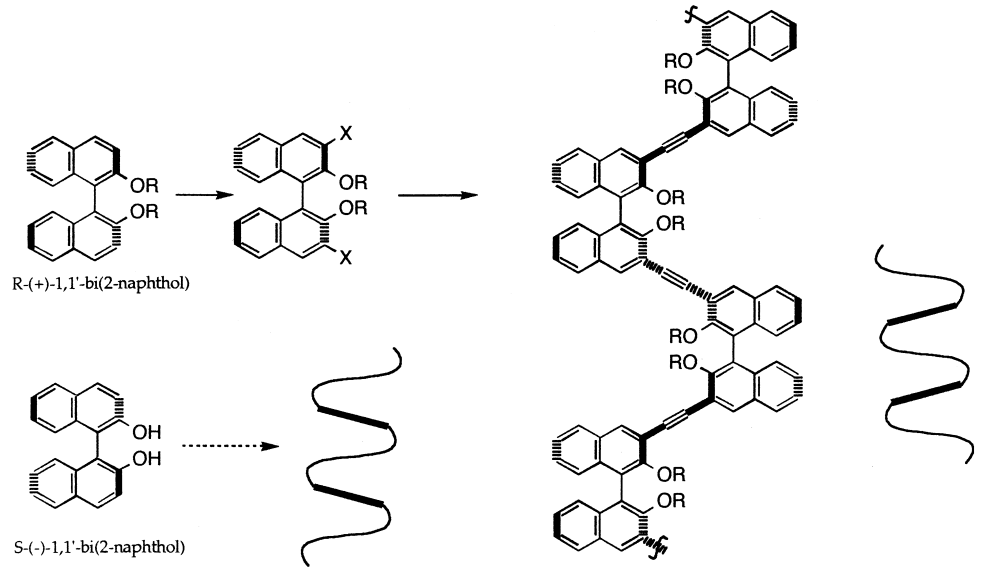
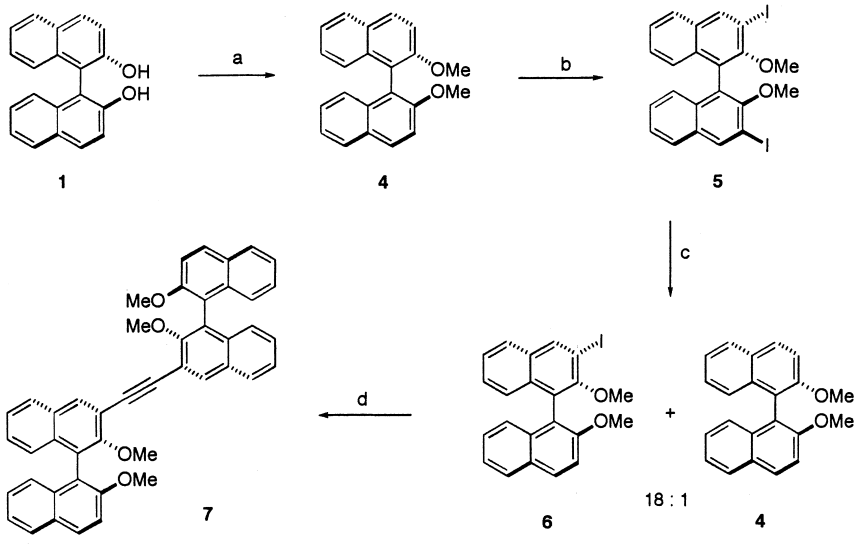


Fig. 1.

of a catalytic amount of 18-crown-6.[24] Following the literature procedure,[9] 3,3′-di-iodo derivative **5** was obtained in 76% yield from BINOL dimethyl ether (**4**) by reaction with butyllithium in the presence of tetramethylethylenediamine (TMEDA) followed by quenching with iodine.

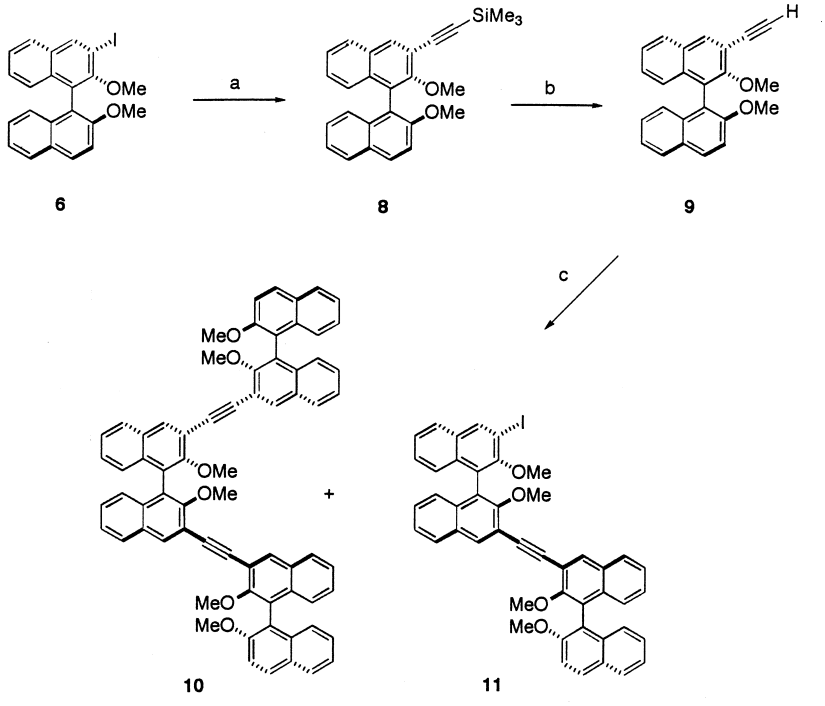


Scheme 1. Synthesis of pseudo binaphthol dimer. Conditions: (a) NaH/CH_3I/THF/18-crown-6/rt/70–80%; (b) n-BuLi (2 equiv.)/TMEDA/Et_2O/−78°C/4 h; then, I_2/−78°C/5 h, yield 76%; (c) n-BuLi/THF/−78°C/1 h, 73% (yield of **6**); (d) bis(tributylstannyl)acetylene/BTH/$Pd(OAc)_2$/PPh_3/dioxane/reflux/5.5 h, 66%

At this point, a key obstacle that we encountered is the selective mono-iodination of binaphthol. Attempts to prepare the mono-iodo compound through the Snieckus–Beak lithiation–iodination reaction by controlling the amount of reactants led to a mixture of the starting material, mono-iodination and di-iodination products, in which the mono-iodination compound often consisted of the minor product.

Efforts to improve the yield of the mono-iodination compound by changing the ratio of lithiation reagents or reaction conditions were not successful, with either predominant formation of bis-iodination products or recovered starting material occurring in most cases. In contrast, we found the Snieckus lithiation–iodination to be very effective in generating bis-iodination products. After many failures in preparing the mono-iodo BINOL derivative, we decided to examine de-iodination of the readily accessible bis-iodo derivative (**5**). This led us to develop a very efficient method for preparing mono-iodo binaphthol derivatives through highly selective mono-de-iodination of di-iodo binaphthol. The reaction gave virtually a single product, the desired one, each time we ran the reaction. This highly selective mono-de-iodination gave us ready access to the target bis-binaphthol derivative (**7**). Thus, treatment of the di-iodo compound **5** with one equivalent of butyllithium at −78°C led to the formation of the mono iodo-binaphthol derivative **6** in 73% isolated yield together with 6–7% recovered starting material. The yield discrepancy is primarily a result of isolation loss. The formation of a minute amount of compound **4** (ca. 5%) was a result of the bis-lithiation of **5**. Finally, reaction of the mono-iodo derivative **6** with bis-(tributylstannyl)acetylene, catalyzed by palladium and triphenylphosphine,[25] produced the dimeric derivative **7** in 66% yield after column chromatography.

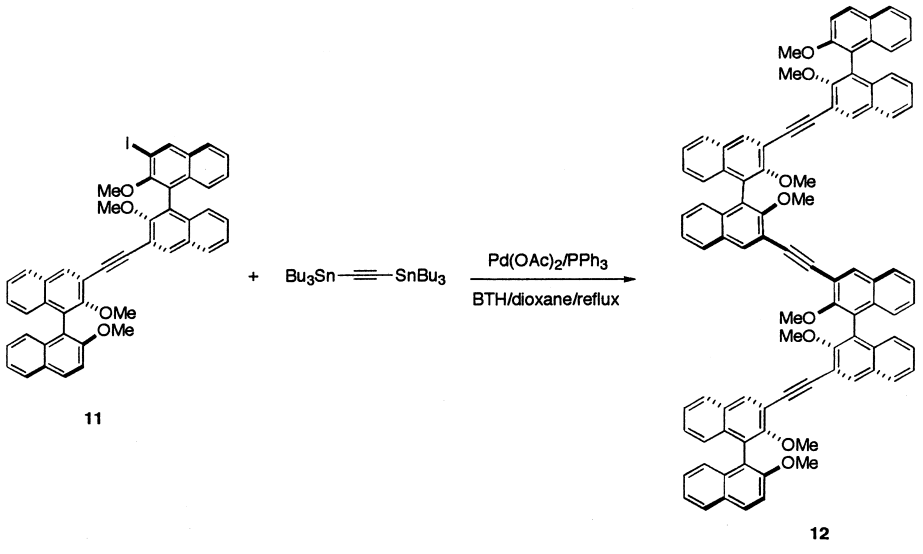
In order to synthesize the pseudo binaphthol trimer, the mono-iodo compound **6** was coupled with trimethylsilylacetylene through the Sonogashira–Cassar–Heck coupling to give compound **8**.[26] The trimethylsilyl group in **8** was then removed with tetrabutylammonium fluoride in THF to give a mono-acetylene derivative **9**. Reacting two equivalents of **9** with one equivalent of the di-iodide **5** through the palladium catalyzed coupling reaction generated the corresponding trimeric product **10** together with the dimeric mono-iodide **11** (Scheme 2).



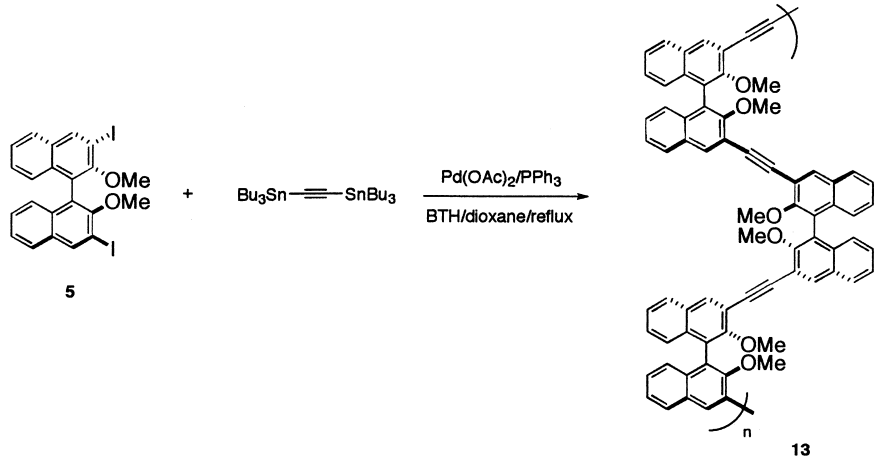
Scheme 2. Synthesis of pseudo binaphthol trimer. Conditions: (a) trimethylsilylacetylene/$Pd(OAc)_2$/PPh_2/CuI/Et_3N/H_2O:CH_2CN (1:5)/rt/overnight, 93%; (b) TBAF/THF/rt/1 h, 95%; (c) **5**/$Pd(OAc)_2PPh_3$/CuI/Et_3N/H_2O:CH_3CN (1:5)/rt/72 h, 25% (**10**), 57% (**11**)

For the synthesis of the pseudo tetramer, the reaction of two equivalents of the iodo-dimeric derivative

11 with one equivalent of bis(tributylstannyl)acetylene in dioxane through the Stille coupling generated the corresponding tetrameric compound **12** (Scheme 3). In principle, the method that we used for the stepwise syntheses of lower oligomers can be used for the syntheses of higher oligomeric compounds, such as pentamers and hexamers, if necessary. However, cross-coupling between the di-iodide **5** and bis(tributylstannyl)acetylene through the Stille coupling resulted in the formation of the polymer **13** (Scheme 4). The compounds thus synthesized, were characterized with various electrical and photophysical methods.



Scheme 3. Synthesis of pseudo binaphthol tetramer



Scheme 4. Synthesis of binaphthol polymer

Table 1
Redox potentials of oligomers determined by cyclic voltammetry

	Monomer (R)	Dimer (R)	Trimer (R)	Tetramer (R)	Polymer (R)
$E_{1/2}$	-	-0.98	-1.01	-0.99	-0.94

Concentration: 0.45-51. mM for the oligomers, 8.7 mg/5 mL for the polymer; conducting salt: n-$Bu_4N^+BF_4^-$; solvent: THF; working, counter and reference electrode: Pt disc, Pt wire, Ag wire respectively; redox potential vs SEC ($Fecp_2$ as internal standard); scan rate = 100 mVs^{-1}, T = 0°C.

3. Cyclic voltammetry studies of the oligomers

The electrical properties of the oligomers that we obtained were determined by cyclic voltammetry techniques through the measurement of their redox potentials (Table 1). Dimer **7**, trimer **10**, tetramer **12** and the polymer **13** all showed an irreversible signal at approximately −1.00 V. Thus, the observed reduction potential seems independent of the length of the oligomer. The results indicated a negligible conjugative interaction between adjacent naphthol units, which is different from the electrical properties of simple conjugated oligomers such as poly(p-phenylenevinylene)s.[27] In those cases, the absolute values of the first reductive potential decrease with the increase in chain length. In the present study, steric effects prohibited the conjugative aryl–aryl interactions between the two naphthol rings. The results were similar to the 4,4′-linked binaphthol oligomers reported earlier.[28]

4. Photophysical studies

The photophysical properties of the oligomers and polymers have been examined by a variety of methods. Extensive photophysical property studies have been focused on the dimer and the polymer since both are more readily available. The circular dichroism (CD) spectrum's studies and optical rotation measurements were reported earlier, and show a helical conformation of the polymer.[16] The absolute optical rotation value of the polymer is much higher than that of the short chain oligomers. The absorptions (Fig. 2) were observed at 350 nm (ε_{max} 6.9×10^4) for the polymer and 345 nm (ε_{max} 2.0×10^4) for the dimer. The result indicated that although a twisting conformation exists in the oligomer molecule, there are some conjugation characteristics present in the polymer. However, the nearly identical maximum wavelengths of the oligomer and the dimer show that they have the same effective conjugation segment, the naphthyl–acetylene–naphthyl (NAN) moiety. The excitation properties of the oligomer were measured at various conditions and the spectra (Fig. 3) exhibit different intensities for each peak. Under excitation at different wavelengths, the oligomer had almost the same emission wavelength. The shapes of the absorption and emission spectra seem to have a macroscopic symmetry, but with slight differences in detail. This implies that the conformations between ground state and the excited state are somewhat different. Relative to the ground state, some bond twisting, solution relaxation and changes in the electronic structure in the excited state probably occur. This exhibits a general characteristic of rigid chromophore, since the fluorescent quantum yield of the polymer in toluene is only 0.14. Obviously, the twisting conformation of the 1,1′-binaphthyl moiety would interfere with the extension of the conjugation existing in the NAN segment, reducing the delocalization along the molecular backbone.

To understand the photophysical properties of the longer oligomer **13** further, the fluorescent properties of the oligomer have been examined under a variety of conditions. Fig. 4 shows the fluorescent spectra of the polymer (or longer oligomer) **13** in different solvents. It is interesting to note that the fluorescent

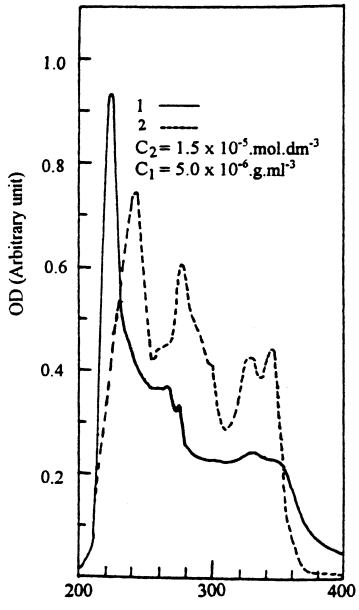


Fig. 2. Absorption spectra of **7** and **13**

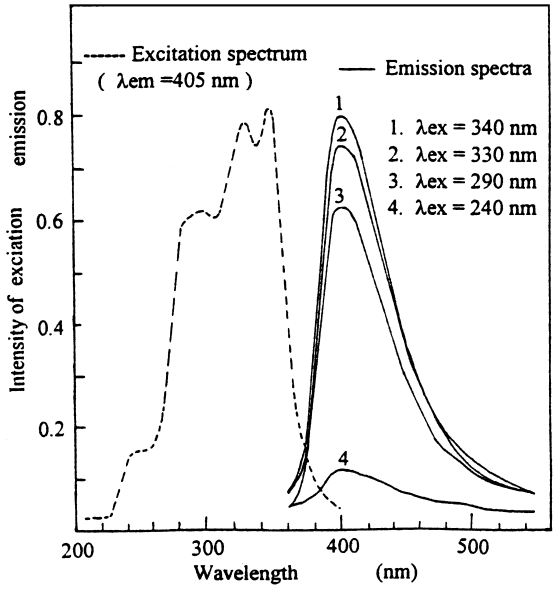


Fig. 3. Excitation and emission spectra of **13**

wavelength has slightly shifted in different solvents used, excited at 342 nm with emission at 402–406 nm. Table 2 shows that the molar extinction coefficient (ε_{max}) and wavelength (λ_{max}) of UV absorption at long wavelengths are also changed slightly when different solvents are used. As indicated earlier, the polymer has a highly ordered and rigid structure. The interaction between the solvents and the polymer molecules is not great enough to influence the effective conjugation segment in the main chain of the polymer, so that the λ_{em} of fluorescence and the λ_{max} and ε_{max} of absorption spectra are solvent-independent. However, the emission intensities and quantum yields (ϕ) in fluorescence spectra would

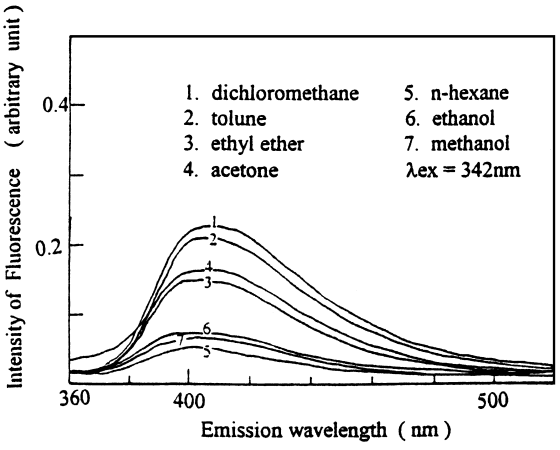


Fig. 4. Fluorescence spectra of **13** in various solvents

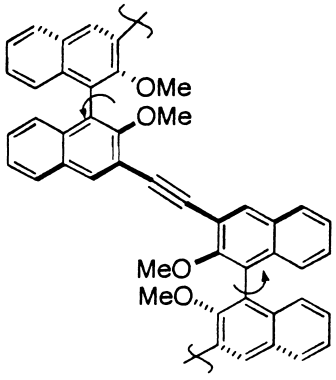
Table 2
Absorption and fluorescent data of **13** in different solvents[a]

Solvent	λ_{max}(nm)[b]	ε_{max}(x10^{4}mol^{-1}dm^3)[c]	λ_{em}(nm)[d]	ϕ [e]
Hexane	350.0	6.2	402.0	0.080
Toluene	348.0	7.0	406.0	0.14
CH_2Cl_2	348.0	6.9	406.0	0.11
Acetone	348.0	6.4	404.0	0.13
Et_2O	346.0	6.8	402.0	0.20
THF	348.0	6.4	404.0	0.14
Ethanol	348.0	6.1	404.0	0.090
Methanol	348.0	6.0	404.0	0.080

a: at 22°C; b. absorption wavelength; c. molar extinction coefficient constants at λ_{max}; d. fluorescent wavelength; e. fluorescent quantum yield.

change with the solvents used (Fig. 4 and Table 2). It is suggested that there are two main competitive non-radiation paths for energy relaxation in the polymer **13** (Fig. 5). One is the rotation of the two naphthyl groups around the C_1–$C_{1'}$ bond (path A) and the other is the vibration of the methoxy group (path B). The change of the ϕ with various solvents used can be ascribed to the solvent molecule clathrating or intercalating into the screw-sense structure of the polymer. Since the screw-sense structure could get inclusion with some solvent molecules, this interaction has a great influence on the rotation of the binaphthyl and the vibration of the methoxy groups. Both of them are directly related to fluorescent intensity and quantum yield. Different solvent molecules have different abilities to enter into the screw-sense structure of the polymer molecule, leading to the appearance of the solvent dependence of the fluorescent intensity and quantum yield.

These twisted intramolecular charge transfer (TICT)[29] fluorescent characteristics were also verified by the dependence of the viscosity of the solvents used on the oligomer fluorescent intensity. Fig. 6 shows that the fluorescent intensity of the polymer decreases with an increasing proportion of glycol in the glycol–methanol co-solvent system, i.e. with increasing the viscosity of the co-solvent used. When the solvent system with low viscosity was employed, the fluorescent intensity decreased greatly (cf. CH_3OH:glycol from 1:0 to 9:1). Obviously, viscose solvent systems would slow down the rotation of the 1,1′-binaphthyl group (path A) and reduce the interaction between oligomer and solvent molecules,



Path A: Rotation of naphthyl Moieties

Path B: Vibration of MeO groups

Fig. 5. Scheme of two relaxation paths

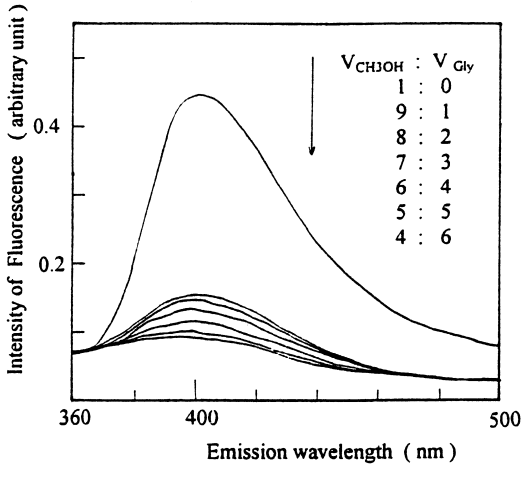


Fig. 6. Viscosity dependence of intensity in fluorescent spectra of **13**

leading to lower fluorescent intensity. However, the structure of the oligomer is so rigid that the interaction between oligomer and solvent molecules does not change significantly with the increase in solvent viscosity, once the solvent system becames viscous enough.

The temperature dependence of the fluorescent intensity in **13** was examined. The λ_{em} does not change with ambient temperature; only fluorescent intensity changes with the ambient temperature. Experimental results show that when the ambient temperature increases from 0°C to 15°C, the fluorescent intensity enhances. However, when the temperature is over 15°C, the fluorescent intensity decreases with increasing the temperature of the system (Fig. 7). For the photophysical behavior of the TICT state, at temperatures below 15°C, increasing the temperature could promote the rotation of the twisted moiety (Path A), which results in enhancement of the fluorescent intensity. However, when the temperature overpasses a critical point (over 15°C), increasing the temperature would be more favorable to the vibration of the methoxy group (path B), enhancing the collisions between molecules of the solvents and polymer. It is suggested that path B, as well as enhancing the collisions would lead to decrease of the fluorescent intensity.

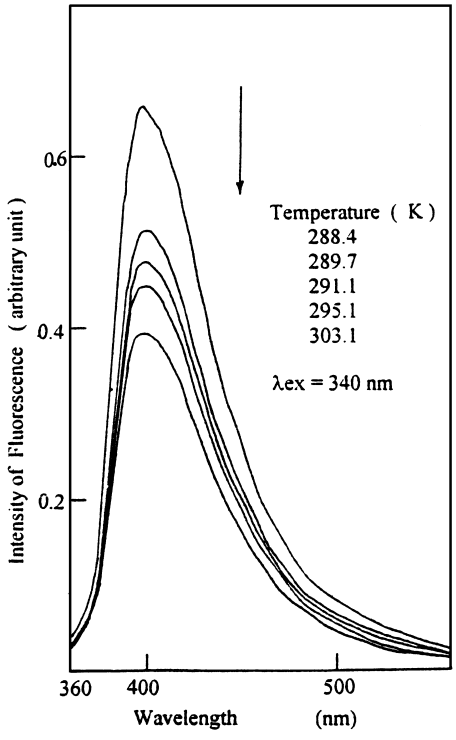


Fig. 7. Temperature dependence of intensity in fluorescent spectra of **13**

It is clear from the results of this investigation that as a twist conjugated polymer, the electrical and photophysical properties of **13** are very different from that of linear conjugated polymers, such as polyphenylethylenes[30] and polythiophenes.[31] For linear conjugated polymers, their effective conjugation segments are sensitive to the external environment. This is ascribed to the changes of external elements being able to induce the planar–nonplanar conversion along the conjugated chain, leading to the change of absorption and fluorescent wavelength. However, for the polymer, the NAN segments are connected with each other at 1,1′-position of 1,1′-binaphthyl moiety, forming a twist and rigid structure, which results in the TICT luminescent characteristics of the polymer **13**. Therefore, the NAN segment could not be changed with external environment, such as the changes in solvents used, solvent viscosity and ambient temperature. These TICT luminescent characteristics indicate a potential application as a light emitting material adaptable to the ambient temperature and a wide range of solvents.

5. Conclusion

Structurally well-defined oligomers based on 1,1′-binaphthol with a 3,3′-acetylene spacer have been synthesized through stepwise chain growth. The electronic and photophysical properties of binaphthol-based polymers and oligomers have been found to be the electronic and photophysical properties of a single binaphthol monomer unit. The study shows that the effective conjugation segment of the oligomers and polymer is a NAN moiety, which resulted from a twist and rigid conformation. With a change in external environment, such as solvents, solvent viscosity and ambient temperature, the change in the effective conjugated segment is minimal, leading to only a minute change in redox potential and in the fluorescent and absorption wavelengths. However, the external environment would influence the rotation

of the 1,1′-binaphthyl group around the C_1–$C_{1'}$ bond, resulting in a change in the fluorescent intensity and quantum yield. This study provides the basis for designing and modifying related organic materials in responding to the desired properties on the molecular level.

6. Experimental

Commercially available compounds were used without further purification. TMEDA was freshly distilled over CaH_2. Reactions were generally conducted under a positive pressure of dry N_2 within glassware which had been flame-dried under a stream of dry N_2. Anhydrous solvents and reaction mixtures were transferred by oven-dried syringe or cannula. Flash chromatography employed E. Merck silica gel (Kiesegel 60, 230–400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a G.E. Omega 400 (400 MHz) instrument, with TMS as an internal standard. Infra-red spectra were performed on an FT-IR (Mattson Cygnus 100). Elemental analyses were measured with a Heraeus CHN-RAPID instrument. Optical rotations were determined on PE 241 MC at 589 nm. Mass spectra and elemental analyses were performed at the Center of Instrumental Facility of Tulane University, and at the Chemistry Institute of the Chinese Academy of Sciences. The optical rotations were measured on a Perkin–Elmer 241 MC and CD spectra were taken using a Jasco J-715 polarimeter. The absorption spectra were recorded on a Hitachi-330 UV–visible absorption spectrophotometer; the excitation and the fluorescent spectra were recorded on a Hitachi MPF-4 fluorescent spectrophotometer. The concentration of the sample solution was adjusted (5×10^{-6}g ml^{-1}) to be dilute enough to avoid re-emission and re-absorption. The photoluminescent lifetime of the oligomer was determined by the method of phase-deviation adjusting on SLMOMJINCO Hardware 4800s spectrophotometers. The reference sample was an aqueous solution of glycogen. The solvents used were purified according to the literature methods.[32]

Cyclic voltammetric studies were carried out on a CV-50W voltammetric analyzer (Bioanalytical Systems Inc., IN, USA) using a cell comprising of a platinum disc working electrode, a platinum counter electrode and a silver reference electrode. Tetra-n-butylammonium tetrafluoroborate was used as a supporting electrolyte. Samples were purged with nitrogen for 3 min before carrying out the CV experiments. Unless otherwise mentioned, measurements were conducted at a scan rate of 100 mV s^{-1} at 0°C in dry THF.

The molecular weight measurements of the oligomers from the non-stepwise syntheses were performed 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 for the GPC measurements was THF, and the column was operated under the eluent head pressure adjusted to maintain a flow rate of 0.75 m min^{-1}.

6.1. 3,3′-Di-iodo-1,1′-bi-2-naphthol dimethyl ether (5)

To a mixture of 1,1′-bi-2-naphthol dimethyl ether (*S*) (**4**, 0.7 g, 2.2 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (0.8 g, 6.9 mmol) in 30 ml ether at room temperature, n-BuLi (4.9 ml, 1.6 M in hexane, 7.84 mmol) was added dropwise via a syringe under nitrogen. After stirring for 4 h, the mixture was cooled to −78°C with a dry ice/acetone bath, and then a solution of I_2 (2.2 g, 8.6 mmol) in 30 ml ether was added and stirred for 5 h. The reaction mixture was slowly warmed to room temperature, quenched with saturated aqueous $Na_2S_2O_3$ solution (20 ml) and stirred for 30 min. The organic layer was separated, and the aqueous phase was extracted with methylene chloride (3×20 ml). The combined organic layer was dried over magnesium sulfate and concentrated. The residue was

purified by flash chromatography on silica gel (eluent: hexane:methylene chloride, 4:1) to give the di-iodo product **5** as a white solid (0.95 g, 76%). [α] +16.8 (*c* 1.5; $CHCl_3$). FTIR ($CDCl_3$): 3055, 1561, 1495, 1454, 1386, 1348, 1233, 1149, 1042, 1020 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.41 (s, 6H), 7.07 (d, 2H), 7.26 (t, *J*=8.4 Hz, 2H), 7.40 (t, *J*=8.4 Hz, 2H), 7.79 (d, *J*=7.6 Hz, 2H), 8.53 (bs, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 61.14, 92.40, 125.38, 125.69, 125.77, 126.98, 127.11, 132.17, 133.84, 139.91, 154.45 ppm. Anal. calcd for $C_{22}H_{16}O_2I_2$: C, 46.67; H, 2.85. Found: C, 46.95; H, 3.09.

*6.2. 3-Iodo-1,1′-bi-2-napthol dimethyl ether (**6**)*

To a solution of **5** (0.62 g, 1.1 mmol) in 30 ml THF, n-BuLi (0.73 ml, 1.6 M, 1.17 mmol) was added dropwise at −78°C under N_2. After stirring for 1 h at −78°C, saturated aqueous NH_4Cl solution (10 ml) was added to quench the reaction and the reaction mixture was warmed to room temperature. The organic layer was separated and the aqueous phase was extracted with methylene chloride. The combined organic layer was dried over magnesium sulfate and concentrated. The residue was purified by flash chromatography on silica gel (eluent: hexane:methylene chloride from 4:1 to 3:1) to give the mono-iodo compound **6** as a white solid (0.35 g, yield 73%). [α] −54.6 (*c* 0.5; $CHCl_3$). FTIR ($CDCl_3$): 3055, 1622, 1593, 1508, 1454, 1393, 1261, 1148, 1081 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.40 (s, 3H), 3.80 (s, 3H), 7.09 (t, *J*=7.2 Hz, 2H), 7.25 (m, 1H), 7.33 (t, *J*=8.4 Hz, 1H), 7.38 (t, *J*=8.4 Hz, 1H), 7.76 (d, *J*=7.2 Hz, 1H), 7.88 (d, *J*=7.6 Hz, 1H), 8.03 (d, *J*=8.8 Hz, 1H), 8.49 (bs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 56.52, 60.87, 92.71, 113.32, 118.55, 123.74, 125.02, 125.49, 125.77, 125.91, 126.74, 126.90, 126.93, 128.02, 128.95, 130.14, 130.18, 132.42, 134.05, 139.12, 154.41, 154.81 ppm. Anal. calcd for $C_{22}H_{17}O_2I$: C, 60.02; H, 3.89. Found: C, 60.22; H, 3.88.

*6.3. Synthesis of the pseudo-dimer **7***

A mixture of PPh_3 (10 mg, 0.038 mmol) and $Pd(OAc)_2$ (2.1 mg, 0.008 mmol) was flushed for 5 min with nitrogen gas. To the mixture, freshly distilled dioxane (2.5 ml) was added via syringe under nitrogen. The resulting reaction mixture was stirred at 40–50°C for 30 min. Then, a solution of 3-iodo-1,1′-bi-2-napthol dimethyl ether (**6**) (84 mg, 0.19 mmol), a few crystals of BTH, and bis(tributylstannyl)acetylene (58 mg, 0.096 mmol) in dioxane (3 ml) was added via syringe. The mixture was refluxed under nitrogen for 5.5 h, cooled to room temperature, and extracted with water/CH_2Cl_2. The organic phase was dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (eluent: hexane:CH_2Cl_2, 3:1) to give product **7** (41 mg, yield 66%). [α] −120 (*c* 0.5; THF). FTIR ($CDCl_3$): 2936, 1954, 1734, 1622, 1593, 1510, 1458, 1411, 1356, 1250, 1148, 1011, 750 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.75 (s, 6H), 3.80 (s, 6H), 7.09 (d, *J*=8.2 Hz, 2H), 7.14 (d, *J*=8.2 Hz, 2H), 7.23 (m, 2H), 7.32 (t, *J*=8.0 Hz, 2H), 7.39 (t, *J*=8.0 Hz, 2H), 7.46 (d, *J*=9.2 Hz, 2H), 7.87 (t, *J*=7.6 Hz, 4H), 8.01 (d, *J*=8.8 Hz, 2H), 8.24 (bs, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 56.50, 61.16, 90.71, 113.45, 113.49, 118.66, 123.63, 125.18, 125.23, 125.51, 125.70, 126.67, 127.03, 127.84, 127.95, 129.02, 129.81, 130.41, 134.02, 154.84, 155.65 ppm. HRMS: calcd for $C_{46}H_{35}O_4$ (M+H), 651.2535. Found, 651.2538.

*6.4. Preparation of mono-trimethylsilylacetylene-binaphthol **8***

A mixture of PPh_3 (13 mg, 0.05 mmol), CuI (9 mg, 0.05 mmol) and palladium acetate (5 mg, 0.025 mmol) in 1.2 ml of H_2O:CH_3CN (5:1) was stirred for 15 min under nitrogen. To the reaction mixture, a solution of the mono-iodo compound **6** (440 mg, 1 mmol), trimethylsilylacetylene (147 mg, 1.5 mmol) and triethylamine (253 mg, 2.5 mmol) in 2 ml of acetonitrile was added via syringe under nitrogen. After

stirring overnight at room temperature, the mixture was diluted with methylene chloride, washed with brine and dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (eluent: hexane:ethyl acetate, 10:1) to give compound **8** (314 mg, 93%). FTIR ($CDCl_3$): 2957, 2153, 1622, 1593, 1510, 1458, 1406, 1356, 1265, 907, 849, 754 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.27 (s, 9H), 3.62 (s, 3H), 3.78 (s, 3H), 7.05–7.12 (m, 2H), 7.17–7.25 (m, 2H), 7.29–7.41 (m, 2H), 7.45 (d, *J*=7.3 Hz, 1H), 7.91–7.81 (m, 2H), 8.0 (d, *J*=7.3 Hz, 1H), 8.16 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 58.2, 62.8, 99.6, 104.5, 114.6, 114.8, 119.2, 119.7, 124.9, 127.1, 127.3, 127.9, 128.4, 128.7, 129.0, 129.2, 129.8, 131.9, 132.1, 134.5, 135.1, 135.3, 157.8, 158.2 ppm. HRMS: calcd for $C_{27}H_{27}SiO_2$ (M+H): 411.1780. Found, 411.1779.

6.5. *Preparation of mono-acetylene-binaphthol **9***

To a solution of compound **8** (80 mg, 0.2 mmol) in dry THF (20 ml), tetrabutylammonium fluoride (0.27 ml, 0.27 mmol, 1.0 M in THF) was added at room temperature. The reaction mixture was stirred at room temperature for 1 h. After evaporation of the solvent in vacuo, the residue was dissolved in 40 ml of methylene chloride, washed with brine and dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (eluent: hexane:ethyl acetate, 4:1) to give the mono-acetylene **9** (63 mg, 95%). FTIR ($CDCl_3$): 3287, 2933, 2247, 1622, 1593, 1508, 1458, 1408, 1358, 1238, 1248, 909, 808, 735 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.35 (s, 1H), 3.59 (s, 3H), 3.79 (s, 3H), 7.12 (d, *J*=7.2 Hz, 2H), 7.21–7.25 (m, 2H), 7.32–7.41 (m, 2H), 7.46 (d, *J*=7.3 Hz, 1H), 7.82–7.90 (m, 2H), 8.01 (d, *J*=7.3 Hz, 1H), 8.19 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 57.7, 61.8, 81.9, 81.2, 114.1, 117.3, 119.3, 124.5, 125.9, 126.2, 126.6, 126.9, 127.5, 128.1, 128.7, 128.9, 129.6, 130.9, 131.2, 134.2, 134.8, 135.9, 156.8, 157.2 ppm. MS (EI): for $C_{24}H_{18}O_2$ (M): 338 (100%). HRMS: calcd for $C_{24}H_{18}O_2$ (M), 338.1301. Found, 338.1297.

6.6. *Synthesis of the pseudo-trimer **10***

A mixture of PPh_3 (7 mg, 0.025 mmol), CuI (5 mg, 0.025 mmol) and palladium acetate (2.5 mg, 0.0125 mmol) in acetonitrile (1 ml) and water (0.2 ml) was stirred under nitrogen for 15 min. To the reaction mixture, a solution of the mono-acetylene **9** (120 mg, 0.5 mmol), the di-iodo compound **6** (283 mg, 0.5 mmol) and triethylamine (127 mg, 1.25 mmol) in acetonitrile (2 ml) was added via syringe under nitrogen. After stirring for 72 h at room temperature, the reaction mixture was diluted with methylene chloride (50 ml), washed with brine, dried over magnesium sulfate and concentrated. The crude product was purified by flash chromatography on silica gel (eluent: hexane:ethyl acetate, 4:1) to give the trimer **10** (41 mg, 25%) together with the iodo-dimer **11** (222 mg, 57%). (**10**): [α] 72.3 (*c* 1.3; $CHCl_3$). FTIR (KBr): 3010, 2952, 2844, 1603, 1489, 1174, 1050, 778 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 375 (s, 6H), 3.86 (s, 6H), 3.88 (s, 6H), 7.10–7.51 (m, 20H), 7.81–7.92 (m, 6H), 8.04 (d, *J*=7.3 Hz, 2H), 8.31 (d, *J*=7.3 Hz, 4H) ppm. Anal. calcd for $C_{70}H_{50}O_6$: C, 85.19; H, 5.07. Found: C, 85.17; H, 5.11.

6.7. *Synthesis of the pseudo-tetramer **12***

A mixture of PPh_3 (10 mg, 0.04 mmol) and palladium acetate (2.1 mg, 0.009 mmol) in 1 ml of dioxane was stirred under nitrogen for 30 min at 40–50°C. A solution of the iodo-dimer **11** (50 mg, 0.065 mmol), bis(tributylstannyl)acetylene (30 mg, 0.05 mmol) and a few crystals of BTH in dioxane (2 ml) was added via syringe under nitrogen. The reaction mixture was refluxed for 5.5 h, cooled to room temperature, diluted with water and extracted with methylene chloride. The organic solution was washed with brine,

dried over magnesium sulfate and concentrated. After removing the solvent, the residue was purified by flash chromatography on silica gel (eluent: hexane:ethyl acetate, 4:1) to give the tetramer **12** (22 mg, 51%). [α] −42.3 (*c* 0.6; CH_3Cl). FTIR (KBr): 2987, 2851, 1612, 1510, 1245, 1030, 785 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.78 (s, 6H), 3.79 (s, 6H), 3.71 (s, 6H), 3.66 (s, 6H), 7.06–7.18 (m, 8H), 7.21–7.31 (m, 8H), 7.28–7.33 (m, 2H), 7.35–7.42 (m, 6H), 7.48 (d, *J*=7.3 Hz, 2H), 7.82–7.91 (m, 8H), 7.98–7.04 (d, *J*=7.3 Hz, 2H), 8.18 (s, 2H), 8.24 (s, 2H), 8.28 (s, 2H) ppm. FAB-MS for $C_{94}H_{65}O_8Na_2$ (M+2Na−H): 1367.

*6.8. Synthesis of the polymer **13***

A mixture of PPh_3 (4.3 mg, 0.016 mmol) and $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) was flushed with nitrogen gas. To the mixture, freshly distilled dioxane (1.5 ml) was added via syringe. The resulting reaction mixture was stirred at room temperature for 30 min followed by the dropwise addition of a solution of **5** (40 mg, 0.07 mmol), a few crystals of BTH, and bis(tributylstannyl)acetylene (42 mg, 0.073 mmol) in dioxane (1 ml) via a syringe. The mixture was refluxed (bath temperature: 110–120°C) under nitrogen for 3 days, forming a dark colored solution with some dark deposit. After cooling to room temperature, methylene chloride was added to dissolve any solid formed. The solution was then filtered through silica gel. After evaporation of the solvent, hexane was added to the residue. The mixture was filtered and washed with acetone to give a dark brown solid **13** (5.1 mg, 44%). M_n: 1882 (M_w=3029); PDI=1.6. [α] −332 (*c* 0.5; THF). FTIR ($CDCl_3$): 3400, 2918, 2849, 1970, 1637, 1409, 1013, 749 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.78 (bs, 2H), 7.09 (bd, 2H), 7.10–7.23 (m, 2H), 7.40 (m, 2H), 7.82 (bd, 2H), 8.24 (bs, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 60.16, 90.80, 117.43, 124.93, 125.37, 125.72, 127.29, 127.84, 130.25, 133.91, 134.42, 155.60 ppm. Elemental anal. calcd for $(C_{24}H_{16}O_2)_n$: C, 85.69; H, 4.79. Found: C, 76.09; H, 4.68. The discrepancy (calculated–found) is due to the presence of low molecular weight oligomers.

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