Pergamon

Tetrahedron: Asymmetry, Vol. 7, No. 8, pp. 2251-2262, 1996

0957-4166/96 $15.00 + 0.00

PII: S0957-4166(96)00280-7

Synthesis, Chiroptical and Redox Properties of Axially Chiral Binaphthol-based Oligomers

Hak-Fun Chow* and Man-Kit Ng

Department of Chemistry, The Chinese Univesity of Hong Kong, Shatin, NT, Hong Kong

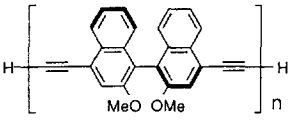
Abstract: Linearly-aligned, axially chiral, enantiomerically pure binaphthyl-based oligomers **1** - **3** were synthesized from enantiomerically pure monomer **4** by an oxidative Hay coupling procedure. The higher oligomers exhibited moderate optical rotation enhancement as compared to the lower analogues, but this effect quickly reached a plateau with the tetramer. Cyclic voltammetry studies of these oligomers showed that there was little electronic interactions between the naphthol units. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

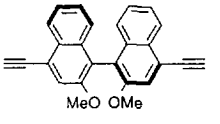
Conjugated organic polymers exhibit many remarkable electrical and optical properties, and have potential applications as electroluminescence, nonlinear optical and conducting devices.[1] With few exceptions, most conjugated polymers reported were optically inactive. The surging interest in optically active polymers stemmed from their potential usefulness in ferroelectric, nonlinear optical, liquid-crystal applications, enantiomeric resolutions, host guest recognitions and asymmetric syntheses.[2] While most optically active polymers have their chirality derived from chiral side groups,[3] only a few conjugated polymers with the chiron units resided on the backbone have been synthesized.[4] Conjugated polymers with main chain chirality had been expected to provide enhanced optical rotation[4c] and improved chiral induction in asymmetric synthesis.[4d] In order to design optically active conjugated polymers with novel applications, the relationship between the chiroptical properties and the number as well as the stereospatial arrangement of the constituent chiral units of the polymer needed to be clarified. Unfortunately, most of the main chain chiral polymers reported so far are polydisperse, stereochemically heterogenous mixtures and it is thus extremely difficult to quantify this important relationship. Furthermore, conjugated polymers with rigid π-systems often possess poor solubility, which seriously inhibits full structural elucidations and property investigations.

Structurally defined conjugated oligomers with solubilizing groups had been successfully employed as models for conjugated polymers.[5] Many optical and electrical properties of high molecular weight conjugated polymers had been shown to closely correspond to those of oligomers containing a few conjugating units. Moreover, oligomers can be easily prepared as monodisperse species, allowing one to follow systematically

their physical properties as a function of chain length. Our interest in this area led to the discovery[6] that linearly-aligned, bis(acetylene)-linked, axially chiral binaphthyl-based oligomers **1** - **3** exhibited moderate molar rotation enhancement compared to that of the monomeric unit **4** on a per binaphthol unit basis. This molar rotation enhancement turned out to be closely related to the linearly disposition of the chiral binaphthol units along the backbone. This report, on the other hand, focused the redox properties of these oligomers, together with a full account of their preparation. To the best of our knowledge, the redox properties of conjugated oligomers with main chain chirality has never been disclosed before.



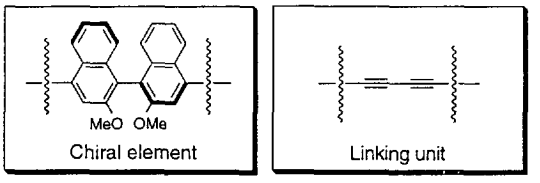
1 - 3 n = 2 - 4



4

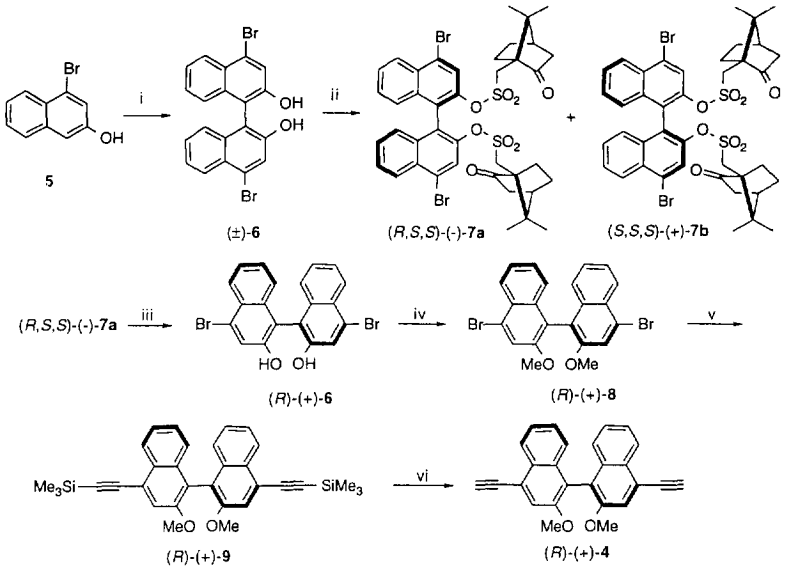
RESULTS AND DISCUSSIONS

The optically active oligomers **1** - **3** consist of two structural elements: (a) a chiral unit based on an axially chiral binaphthol and (b) a conjugative bis(acetylenic) functionality as the linker between two consecutive chiral elements. The binaphthol unit was chosen as the chiron because of its outstanding asymmetric differentiation properties and its widespread usefulness in asymmetric synthesis. In order to have the chiral axis coaligned with the polymer backbone, the bis(acetylene) linker has to be connected to the 4,4' positions of the binaphthol units. This conjugated functionality also enables electronic or resonance delocalization across two adjacent binaphthol units.



1. Synthesis of enantiomerically pure monomer 4

The enantioselective preparation of the chiral monomer (*R*)-(+)-**4** started from the known 4-bromo-2-naphthol **5** (Scheme 1).[7] The bromine atoms at the 4,4' positions serve as the connecting points for the oligomers to propagate along the chiral axis *via* organometallic coupling reactions. Copper(I) catalyzed oxidative coupling of **5** by Koga's method[8] afforded racemic 4,4'-dibromo substituted binaphthol (±)-**6** in 90% yield as a pale brown solid. This racemic mixture was then converted into a diastereomeric mixture of bis-(*S*)-camphorsulfonates (*R*,*S*,*S*)-(−)-**7a** and (*S*,*S*,*S*)-(+)-**7b** by treatment with (*S*)-(+)-camphorsulfonyl chloride in triethylamine in 95% yield. Although compounds (*R*,*S*,*S*)-(−)-**7a** and (*S*,*S*,*S*)-(+)-**7b** co-crystallized together in a number of solvent systems, fortunately they were readily separable by silica gel chromatography using ethyl acetate-toluene (1 : 50) as the eluting solvent. The more polar bis-sulfonate (*R*,*S*,*S*)-(−)-**7a** had an (*R*)-chiral axis, whose absolute configuration was determined on the basis of X-ray crystallographic analysis (Figure 1).[6] The dihedral angle between the two naphthol rings was 82°, preventing extensive π-π overlapping between the



Scheme 1. *Reagents and conditions:* i) CuCl(OH)-TMEDA, O_2, CH_2Cl_2; ii) (*S*)-camphorsulfonyl chloride, NEt_3, CH_2Cl_2; iii) NaOH, MeOH/H_2O; iv) MeI, Cs_2CO_3, acetone; v) TMSCCH, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3; vi) K_2CO_3, MeOH/THF

two naphthol rings. Both diastereomers (*R*,*S*,*S*)-(–)-**7a** and (*S*,*S*,*S*)-(+)-**7b** could be desulfonylated with sodium hydroxide in aqueous methanol solution to give enantiomerically pure (*R*)-(+)-**6** and (*S*)-(–)-**6** respectively with >97% enantiomeric excess. To ensure no racemization took place during base treatment, the binaphthol (*R*)-(+)-**6** obtained after base hydrolysis was treated with (*S*)-(+)-camphorsulfonyl chloride to regenerate the bis-sulfonate. Examination of the crude reaction mixture indicated the presence of only (*R*,*S*,*S*)-(–)-**7a**, the other diastereomer (*S*,*S*,*S*)-(+)-**7b** was not detectable by ^{1}H-NMR spectroscopy (250 MHz). This reaction sequence could be performed on a 10 g scale. As a result, a reliable preparative route for both enantiomers (*R*)-(+)-**6** and (*S*)-(–)-**6** was secured. The antipodal relationship of compounds (*R*)-(+)-**6** and (*S*)-(–)-**6** could also be confirmed by the mirror-image relationship of their respective CD spectra (Figure 2).

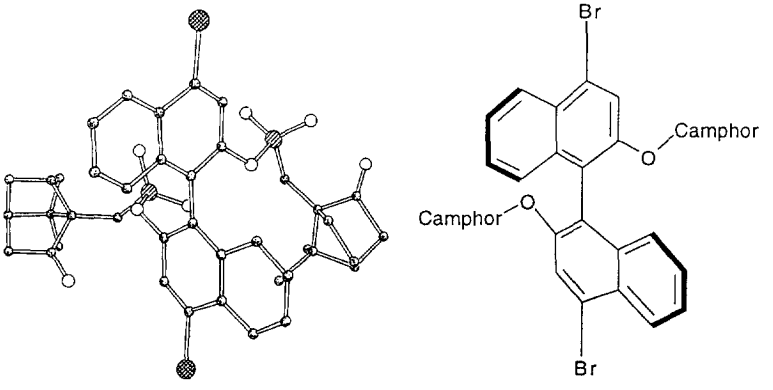


Figure 1. X-ray structure of compound (*R*,*S*,*S*)-(-)-**7a**

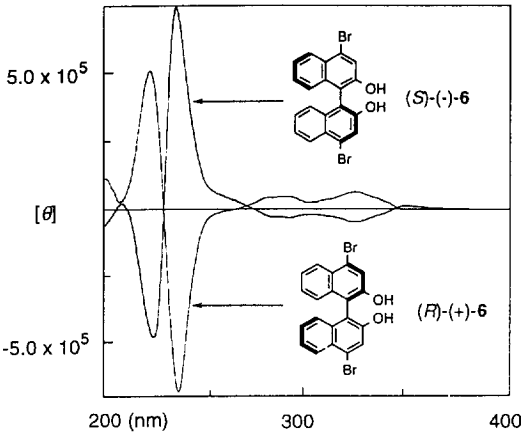
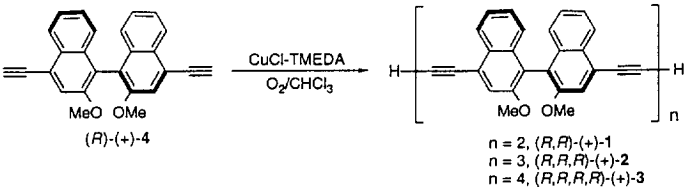


Figure 2. CD spectra (in $ClCH_2CH_2Cl$) of enantiomeric binaphthols (*R*)-(+)-**6** and (*S*)-(-)-**6**

The enantiomerically pure (*R*)-(+)-**6** was then converted into the corresponding methyl ether (*R*)-(+)-**8** by reaction with MeI and Cs_2CO_3. No *C*-alkylation product was isolated from this reaction. The acetylenic moiety was then anchored to the 4 and 4' positions of (*R*)-(+)-**8** by palladium(0)-catalyzed coupling[9] with trimethylsilylacetylene to give the bis(trimethylsilylacetylene) derivative (*R*)-(+)-**9**. The coupling of the first acetylene was relatively fast. However, attachment of the second acetylene turned out to be very sluggish and the reaction required prolonged heating at 75°C to ensure complete reaction. Treatment of compound (*R*)-(+)-**8** with tetrabutylammonium fluoride gave a complex mixture of products. On the other hand, the two trimethylsilyl groups could be removed cleanly with K_2CO_3 to give the terminal bis(acetylene) derivative (*R*)-(+)-**4** in 99% yield.

2. *Oligomerization of the monomer 4*



The oligomerization of terminal bis(acetylene) monomer (*R*)-(+)-**4** was conducted according to the Hay procedure[10] (CuCl-TMEDA, O_2) in chloroform solution (0.05 M). Upon initial addition of the catalyst, the reaction mixture turned immediately yellow and gradually became dark green with the formation of highly fluorescent compounds. Examination of the crude product by thin layer chromatography (tlc) showed the presence of the starting material (*R*)-(+)-**4**, together with the desired dimer (*R,R*)-(+)-**1**, trimer (*R,R,R*)-(+)-**2** and tetramer (*R,R,R,R*)-(+)-**3** with increasing polarities. A highly fluorescent, tlc immobile component, which we believed to be the insoluble higher oligomers was also noted at the base line of tlc plate. Longer reaction time led to the formation of yellow precipitates which could not be dissolved and characterized in any organic solvent. The lower soluble oligomers **1** - **3** were then separated by silica gel column chromatography. We were unable to isolate the pentamer and the hexamer from the reaction mixture, presumably due to their poor

solubility properties. Increasing the reaction temperature or changing the catalytic system to copper(II) acetate-pyridine again failed to isolate the pentamer and hexamer. We believed that they were actually formed during the coupling reaction but their poor solubilities hampered their isolation. The dimer, trimer and tetramers were yellow solids, showing strong fluorescence in solution. As expected, the solubility of these oligomers decreased with increasing numbers of the binaphthol units. Thus, while the monomer and the dimer showed reasonable solubility in chloroform, the trimer and especially the tetramer were sparingly soluble in both chlorinated and non-chlorinated solvents.

The structural identities of these oligomers were supported by their ^{1}H-NMR and mass spectral data. The methoxy groups in each oligomers had slightly different chemical shift values. Thus, two (δ 3.80 and 3.79) and three methoxy singlets (δ 3.83, 3.80 and 3.79) were observed for the dimer (*R*,*R*)-(+)-**1** and trimer (*R*,*R*,*R*)-(+)-**2**, respectively. The tetramer (*R*,*R*,*R*,*R*)-(+)-**3** gave three methoxy signals (δ 3.84, 3.81 and 3.79) with relative intensity ratio of 2 : 1 : 1, suggesting that two of the four methoxy groups, which were tentatively assigned as the internal ones, had the same chemical environment. On the other hand, the acetylenic proton of all oligomers had nearly the same chemical shift value at around δ 3.6 (Figure 3).

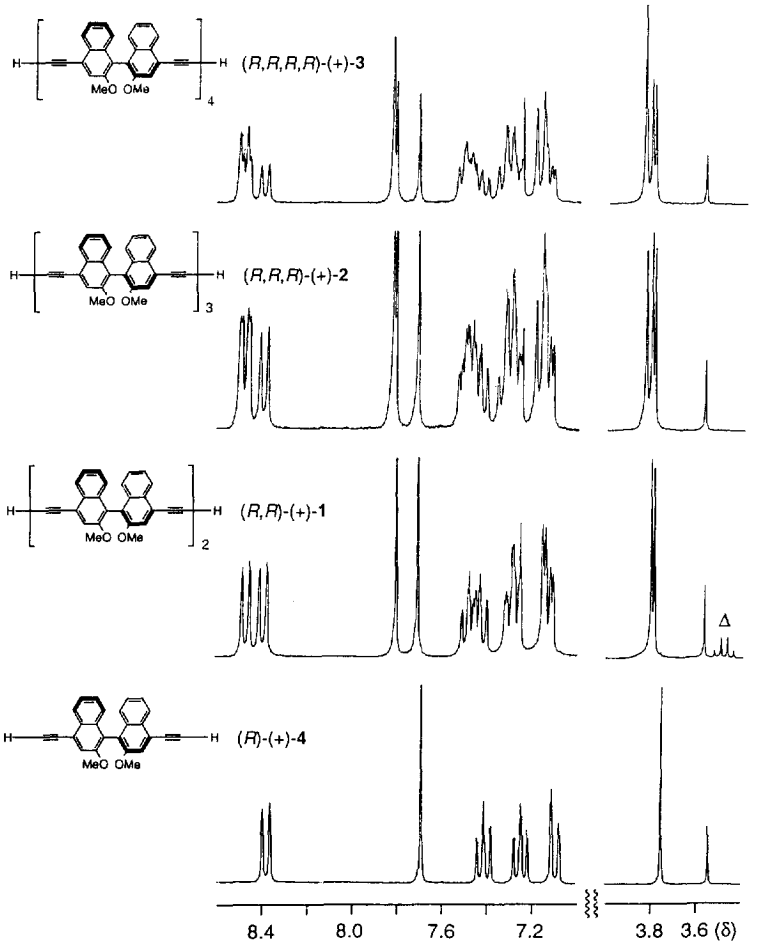


Figure 3. ^{1}H-NMR spectra of compounds **1** - **4** (Δ = solvent peaks).

3. Ultraviolet spectroscopic and chiroptical properties of compounds 1 - 4

Table 1. Specific rotation[a] and UV[b] data of compounds **1** - **4**.

	Monomer (*R*)-(+)-**4** (*c* = 1.18)	Dimer (*R*,*R*)-(+)-**1** (*c* = 0.55)	Trimer (*R*,*R*,*R*)-(+)-**2** (*c* = 0.28)	Tetramer (*R*,*R*,*R*,*R*)-(+)-**3** (*c* = 0.20)
λ = 589 nm				
[α]	92	111	115	127
[*M*]	333	802	1246	1833
[*M*]/binaphthol unit	333	401	415	458
λ = 578 nm				
[α]	98	119	124	133
[*M*]	355	860	1343	1920
[*M*]/binaphthol unit	355	430	448	480
λ = 546 nm				
[α]	122	149	153	164
[*M*]	442	1077	1657	2368
[*M*]/binaphthol unit	442	539	552	592
UV				
λ_{max} (nm)	356	380	409	411
ε ($mol^{-1}dm^3cm^{-1}$)	20000	45000	98000	225000

[a] Specific rotation measurements (error ± 1%) were performed in chloroform solution at 25.0 ± 0.1°C. [b] UV measurements were performed in 1,2-dichloroethane solution at 22°C.

The chiroptical properties of the monomer and oligomers were examined by polarimetry studies (Table 1). The specific rotations [α] increased gradually with increasing number of binaphthol units. This trend was also observed in polarized light at different wavelength. The molar optical rotations [*M*], which represented the chiroptical property of a compound on a per mole basis, again increased steadily from the monomer (+333, λ = 589 nm) to the tetramer (+1833). Because monomer (*R*)-(+)-**4** has a different chromophoric structure[11] than those of oligomers **1** - **3**, thus a direct comparison of rotational values with reference to the monomer is misleading. Nonetheless, it was noticed that the molar rotation contribution per binaphthol units was largest for the tetramer and gradually decreased towards the dimer. Due to the dependence of specific rotation values on the increasing bathochromic shift of the absorptions with increasing oligomer length, we decided to look at the circular dichroism (CD) spectra of these compounds (Figure 4). As it turned out, compounds **1** to **4** all gave similar CD pattern with a negative Cotton effect at λ = 240 nm and a positive effect at λ = 226 nm. There was an additional positive dichroism maximum at 340 nm which was not apparent in the UV spectra. Detailed examination of the CD spectra revealed that the monomer (*R*)-(+)-**4** exhibited consistently smaller molar ellipiticity [θ] than the dimer (*R*,*R*)-(+)-**1** in the 200 - 400 nm absorption region, which in turn was consistently smaller than that of the trimer (*R*,*R*,*R*)-(+)-**2**. However, the trimer (*R*,*R*,*R*)-(+)-**2** and tetramer (*R*,*R*,*R*,*R*)-(+)-**3** had almost identical CD spectra. It was clear that observed specific rotation enhancement due to increasing chain length began to level off with the tetramer. The lack of significant specific rotation enhancement in this series of compounds, in contrast to chiral polymers with helical backbone,[12] could be due to the rotational freedom of the diacetylene spacer, which allowed individual chiral binaphthol units to rotate independently and not arrange in a coherent manner to exert cooperative chiroptical amplification.

It was noted that Vasella[13] and Diederich[14] had recently reported two different series of optically active bis(acetylene)-containing oligomers having chiral sugar and binaphthol units, respectively, as part of the main chain, but there was little correlation between the molar rotation power and the number of chiral units. Tours also reported the preparation of a diastereomeric mixture of axially chiral conjugated polymers based on

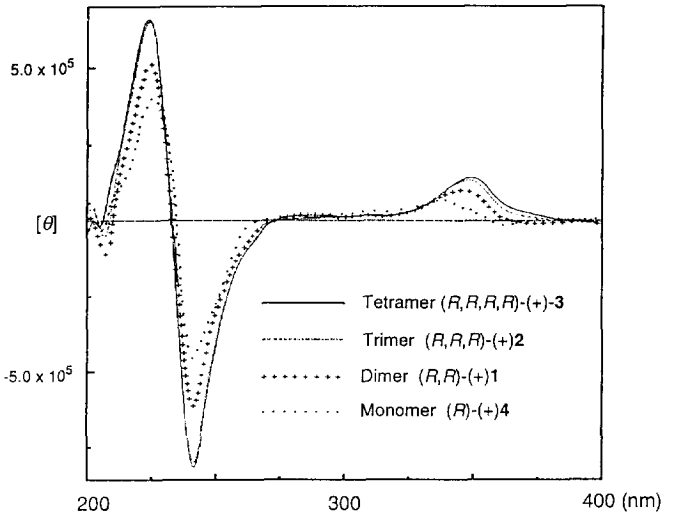


Figure 4. CD spectra of compounds **1** - **4** (in $ClCH_2CH_2Cl$, [θ] = molar ellipiticity)

binaphthyl units,[4c] however no specific rotation enhancement could be observed for the resulting polymer. We believed that the moderate rotational enhancement detected here could be due to the linear alignment of the chiral axes along with the oligomer backbone. No such effect was observed when the chiral axes were arranged in a cyclic array.[14]

A close look at the ultraviolet spectra of these oligomers suggested that despite of the orthogonality of the two naphthol rings, there was still electronic delocalization between them (Table 1). The monomer (*R*)-(+)-**4** had a λ_{max} at 356 nm while those of the dimer (*R*,*R*)-(+)-**1** had a value at 380 nm. This significant shift of λ_{max} was due to a change of chromophoric structure from the monomer (*R*)-(+)-**4** to the dimer (*R*,*R*)-(+)-**1**. On the other hand, only a small shift of λ_{max} value was observed between the trimer and tetramer, further confirming that there was little conjugative interaction between the naphthol units.

4. Cyclic voltammetry studies of compounds 1 - 4

Table 2. Redox potentials of compounds **1** - **4** determined by cyclic voltammetry[a]

	Monomer (*R*)-(+)-**4**	Dimer (*R*,*R*)-(+)-**1**	Trimer (*R*,*R*,*R*)-(+)-**2**	Tetramer (*R*,*R*,*R*,*R*)-(+)-**3**
$E_{1/2}$	–	−1.94	−1.93	−1.9[b]

[a] Concentration: 0.4 – 4.0 mM; conducting salt: n-$Bu_4N^+BF_4^-$ (150 mM); solvent: THF; working, counter and reference electrode: Pt disc, Pt wire, Ag respectively; redox potentials *vs* SCE ($FeCp_2$ as internal standard at 0.31 V); scan rate = 100 mVs^{-1}, T = 0°C. [b] Partially overlapped with redox signals arising from solvent.

Having examined the chiroptical properties of the oligomers, we focused our attention on their redox behavior by cyclic voltammetry technique (Table 2). None of the oligomers showed any redox peaks from –2.5 V to +2.0 V in dichloromethane. On switching to tetrahydrofuran as the solvent, the monomer (*R*)-(+)-**4** again

did not give any observable peaks in the cyclic voltammogram. On the other hand, oligomers **1** - **3** gave a single redox signal at approximately the same redox potential (–1.9 V *vs* SCE), which was attributed as the first reduction potential. However, the second reduction process could not be observed. Hence, the observed reduction potential was independent to the the degree of oligomerization, implying that there was little conjugative interactions between adjacent naphthol units. This invariance of redox potential upon oligomerization was in sharp contrast to those behavior of simple conjugated oligomers such as oligo-(*p*-phenylenevinylene)s,[15] where the absolute values of the first redox potential decreased with increasing chain length—a normal trend usually followed by conjugated oligomers.[5] The redox potential trend reported here, however, was in line with those observed for the oligo(9,10-anthrylene)s.[16] In our examples, the orthogonal disposition of the two naphthol rings and the strong steric repulsion arising between these two units if they were to adopt co-planarity prohibited any conjugative aryl-aryl interactions. As a result, each naphthol-diacetylene-naphthol unit behaved as an independent redox centre.

CONCLUSIONS

We have shown that enhanced optical rotatory property of structurally rigid, chiral oligomers could be achieved if the optically active units were aligned linearly along the main axis. The effect, however, was moderate and leveled off rapidly with increasing oligomer length. This result was different from those of Diederich and Tours, in which no molar rotational enhancement was observed when the binaphthol units were arranged in a cyclic array,[14] or when the chiral elements were not homogeneously pure.[4c] In terms of redox properties, the orthogonal disposition of the two naphthol units prevented extensive electronic delocalization along the oligomer backbone. As a consequence, each chiral subunit behaved as an independent redox active center and hence the first reduction potential was independent of the oligomer length. The conjugation barrier with nearly independent redox active behaviour of the chiral subunits makes this kind of chiral oligomers a possible candidate for organic ferromagnets.[17] Finally, the potential use of these optically active oligomers in enantioselective host-guest recognition and catalysts is also being investigated in our laboratories.

EXPERIMENTAL SECTION

Melting points were measured on a Reichert Microscope apparatus and are uncorrected. Brüker WM 250 spectrometer was used to obtain ^{1}H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra unless otherwise stated. Coupling constants were reported in Hertz. UV spectra were recorded on a Hitachi U-2000 Spectrophotometer. Mass spectra were obtained on a Bruker APEX 47e FTMS by fast atom bombardment (FAB), electron ionization (EI) or electrospray ionization (ESI) technique, and unless otherwise stated, are mass of most abundant isotopic peak. Optical rotational data were measured on a Perkin-Elmer Polarimeter 341 at 25.0 ± 0.1°C. Circular dichroism measurements were carried out on a JASCO J-720 Spectropolarimeter at 22°C. Cyclic voltametric 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*-butyl-ammonium 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 done at a scan rate of 100 mVs^{-1} at 0°C. Elemental analyses were carried out

either at MEDAC Ltd., Middlesex, United Kingdom or Shanghai Institute of Organic Chemistry, PRC. Unless otherwise stated, all chemicals were purchased from commercial suppliers and used without further purification.

Oligomers (*R,R*)-(+)-**1**, (*R,R,R*)-(+)-**2** and (*R,R,R,R*)-(+)-**3**. To a mixture of copper (I) chloride (9.6 mg, 0.097 mmol) and *N,N,N',N'*-tetramethylethylenediamine (14.8 µl, 0.098 mmol) in chloform (4.5 cm^3) was added a solution of the bis-acetylenic monomer (*R*)-(+)-**4** (353 mg, 0.97 mmol) in chloroform (15 cm^3). The resulting mixture was stirred at 25°C in air for 1 h. The dark green solution was diluted with chloroform (25 cm^3) and washed with saturated NH_4Cl solution, dried (Na_2SO_4), filtered and evaporated *in vacuo*. The yellowish green residue was purified by flash chromatography on silica gel (hexane/CH_2Cl_2 = 10/1 gradient to 1/3) to afford monomer (20%), dimer (30%), trimer (10%) and tetramer (4%) as yellow fluorescent solids.

(*R,R*)-(+)-**1**: yellow solid; m.p. > 230°C (decomp.); ^{1}H-NMR (250 MHz, $CDCl_3$) 8.47 (d, *J* = 8.3 Hz, 2 H), 8.39 (d, *J* = 8.2 Hz, 2 H), 7.80 (s, 2 H), 7.71 (s, 2 H), 7.51 - 7.39 (m, 4 H), 7.33 - 7.25 (m, 4 H), 7.14 (d, *J* = 8.4 Hz, 4 H), 7.13 (d, *J* = 8.3 Hz, 2 H), 3.80 (s, 6 H), 3.79 (s, 6 H), 3.57 (s, 2 H); ^{13}C-NMR (62.5 MHz, $CDCl_3$) 154.3, 154.2, 133.9, 133.8, 130.2, 129.6, 127.2, 127.1, 126.3, 125.8, 125.5, 125.0, 124.7, 122.3, 121.4, 121.2, 121.0, 120.9, 119.5, 119.0, 82.2, 81.9, 81.5, 79.1, 56.9; *m/z* (ESI) 723.3 (*M* + H^+, 80%, $C_{52}H_{34}O_4$ + H^+ requires 723.3).

(*R,R,R*)-(+)-**2**: yellow solid; m.p. > 230°C; ^{1}H-NMR (250 MHz, $CDCl_3$) 8.48 (d, *J* = 8.2 Hz, 2 H), 8.47 (d, *J* = 8.4 Hz, 2 H), 8.39 (d, *J* = 8.4 Hz, 2 H), 7.82 (s, 2 H), 7.81 (s, 2 H), 7.71 (s, 2 H), 7.53 - 7.40 (m, 6 H), 7.35 - 7.24 (m, 6 H), 7.19 - 7.10 (m, 6 H), 3.83 (s, 6 H), 3.80 (s, 6 H), 3.79 (s, 6 H), 3.57 (s, 2 H); ^{13}C-NMR (62.5 MHz, $CDCl_3$) 154.3 (2 x), 154.2, 133.9 (2 x), 133.8, 130.2 (2 x), 129.6, 127.3 (2 x), 127.1, 126.3 (2 x), 125.8 (2 x), 125.5, 125.1, 124.7, 122.3, 122.0, 121.4, 121.0, 120.9, 119.5 (2 x), 119.0, 82.3, 81.9, 81.6, 81.5, 79.2, 79.1, 56.9; *m/z* (ESI) 1083.4 (*M* + H^+, 100%, $C_{78}H_{50}O_6$ + H^+ requires 1083.4).

(*R,R,R,R*)-(+)-**3**: yellow solid; m.p. > 230°C; ^{1}H-NMR (250 MHz, $CDCl_3$) 8.49 (d, *J* = 8.4 Hz, 4 H), 8.48 (d, *J* = 8.4 Hz, 2 H), 8.39 (d, *J* = 8.5 Hz, 2 H), 7.83 (s, 4 H), 7.81 (s, 2 H), 7.71 (s, 2 H), 7.54 - 7.40 (m, 8 H), 7.36 - 7.25 (m, 8 H), 7.20 - 7.11 (m, 8 H), 3.84 (s, 12 H), 3.81 (s, 6 H), 3.79 (s, 6 H), 3.57 (s, 2 H); *m/z* (ESI) 1444.5 (M^+, 100%, $C_{104}H_{66}O_8$ requires 1444.5).

4,4'-Bis-(ethynyl)-2,2'-binaphthol-bis-methyl ether (*R*)-(+)-**4**. To a solution of (*R*)-(+)-**9** (1.55 g, 3.06 mmol) in methanol (50 cm^3) and tetrahydrofuran (50 cm^3) was added potassium carbonate (1.0 g, 7.2 mmol). The resulting mixture was stirred at 25°C under nitrogen for 1 h and excess solvent evaporated *in vacuo*. The residue was taken up in ethyl acetate (300 cm^3) and washed with water (75 cm^3), dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the optically pure monomer (*R*)-(+)-**4** (1.10g, 3.04 mmol, 99%) as a pale brown solid, m.p. 192 - 194°C; ^{1}H-NMR (250 MHz, $CDCl_3$) 8.37 (d, *J* = 8.3 Hz, 2 H), 7.69 (s, 2H), 7.41 (ddd, *J* = 8.1, 6.7 and 1.3 Hz, 2 H), 7.25 (ddd, *J* = 8.4, 6.9 and 1.3 Hz, 2 H), 7.09 (d, *J* = 8.5 Hz, 2 H), 3.75 (s, 6 H), 3.55 (s, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) 154.0, 133.7, 129.5, 127.0, 126.1, 125.5, 124.6, 121.1, 121.0, 118.8, 82.2, 81.8, 56.8; *m/z* (HRMS) 362.1313 (M^+, 100%, $C_{26}H_{18}O_2$ requires 362.1307). Anal. Calcd. for $C_{26}H_{18}O_2$: C, 86.17; H, 5.01. Found: C, 86.44; H, 5.10.

4,4'-Dibromo-2,2'-binaphthol (±)-**6.** A mixture of 4-bromo-2-naphthol (7.0 g, 31 mmol) and CuCl(OH)-TMEDA (0.70 g, 3 mmol) in dry dichloromethane (200 cm^3) was stirred at 25°C for 4 h. The dark brown mixture was diluted with dichloromethane (100 cm^3), washed with saturated NH_4Cl solution (2 x 150 cm^3),

dried (Na_2SO_4), filtered and evaporated *in vacuo* to give binaphthol (±)-**6** (6.3 g, 14 mmol, 90%) as a pale brown solid, m.p. 214 - 216°C.

Bis-(*S*)-camphorsulfonates (*R,S,S*)-(–)-**7a** and (*S,S,S*)-(+)-**7b**. To a solution of (±)-**6** (4.5 g, 10 mmol) in dry dichloromethane (200 cm^3) was added (1*S*)-camphor-10-sulfonyl chloride (7.5 g, 30 mmol) at 0°C followed by dry triethylamine (5.60 cm^3, 40 mmol). The mixture was stirred at 0°C under nitrogen for 2 h and poured into water (100 cm^3). The aqueous phase was then extracted with dichloromethane (2 x 50 cm^3). The combined extracts were washed with saturated NaCl solution, dried, filtered and evaporated *in vacuo* to give the diastereomeric (*R,S,S*)-(–)-**7a** and (*S,S,S*)-(+)-**7b** (8.3 g, 9.5 mmol, 95%) as a pale yellow solid. Flash chromatography on silica gel (toluene/EtOAc = 100/2) afforded the less polar (*S,S,S*)-(+)-**7b** (3.1 g, 71% based on (*S*)-**6** as a pale yellow glassy substance, and the mole polar (*R,S,S*)-(–)-**7a** (3.0 g, 68% based on (*R*)-**6** as a pale yellow solid. (*R,S,S*)-(–)-**7a**: m.p. 189 - 191°C; $[\alpha]_D^{25}$ = - 9.4 (*c* = 1.4 in $CHCl_3$); ^{1}H-NMR (250 MHz, $CDCl_3$) 8.37 - 8.33 (m, 2 H), 8.15 (s, 2 H), 7.65 - 7.58 (m, 2 H), 7.44 - 7.37 (m, 2 H), 7.26 - 7.22 (m, 2 H), 3.34 (d, *J* = 15.0 Hz, 2 H), 2.43 (d, *J* = 15.0 Hz, 2 H), 2.28 - 2.17 (m, 2 H), 1.95 - 1.92 (m, 2 H), 1.80 - 1.62 (m, 4 H), 1.28 - 1.14 (m, 6 H), 0.58 (s, 6 H), 0.54 (s, 6 H); ^{13}C-NMR (62.5 MHz, $CDCl_3$) 194.8, 144.7, 133.6, 130.5, 128.3, 127.8, 127.5, 126.9, 125.1, 124.7, 122.7, 57.6, 49.5, 47.6, 42.6, 42.1, 26.7, 24.4, 19.1, 19.0; *m/z* (FAB) 874 (M^+, 6%, $C_{40}H_{40}Br_2O_8S_2$ requires 874). (*S,S,S*)-(+)-**7b**: m.p. 92 - 94°C; $[\alpha]_D^{25}$ = +15.2 (*c* = 1.8 in $CHCl_3$); ^{1}H-NMR (250 MHz, $CDCl_3$) 8.37 - 8.33 (m, 2 H), 8.13 (s, 2 H), 7.66 - 7.60 (m, 2 H), 7.47 - 7.41 (m, 2 H), 7.32 - 7.29 (m, 2 H), 2.95 (d, *J* = 14.9 Hz, 2 H), 2.48 (d, *J* = 14.9 Hz, 2 H), 2.28 - 2.18 (m, 2 H), 1.99 - 1.77 (m, 8 H), 1.39 - 1.22 (m, 4 H), 0.76 (s, 6 H), 0.55 (s, 6 H); ^{13}C-NMR (62.5 MHz, $CDCl_3$) 194.9, 144.8, 133.5, 130.4, 128.4, 127.8, 127.4, 126.9, 125.2, 124.7, 122.7, 57.6, 49.3, 47.6, 42.7, 42.1, 26.7, 24.7, 19.2 (2 x); *m/z* (FAB) 874 (M^+, 6%, $C_{40}H_{40}Br_2O_8S_2$ requires 874).

4,4'-Dibromo-2,2'-binaphthol (*R*)-(+)-**6**. To a suspension of diastereomerically pure (*R,S,S*)-(–)-**7a** (2.45 g 2.8 mmol) in methanol (120 cm^3) was added an aqueous solution of sodium hydroxide (1.2 M, 15 cm^3). The resulting mixture was warmed to 60°C for 20 h and cooled to 0°C. The solution was acidified with diluted HCl solution and excess methanol evaporated *in vacuo*. The residue was taken up in dichloromethane (200 cm^3), washed with diluted HCl solution, saturated NaCl solution, dried (Na_2SO_4), filtered and evaporated *in vacuo* to give the optically pure (*R*)-(+)-**6** (0.87 g, 2.0 mmol, 70%) as a pale yellow solid, m.p. 214 - 216°C; $[\alpha]_D^{25}$ = +24.2 (*c* = 3.1 in $CHCl_3$); ^{1}H-NMR (250 MHz, $CDCl_3$) 8.31 - 8.28 (m, 2 H), 7.75 (s, 2 H), 7.52 - 7.46 (m, 2 H), 7.39 - 7.32 (m, 2 H), 7.16 - 7.12 (m, 2 H), 5.07 (s, 2 H); ^{13}C-NMR (62.5 MHz, $CDCl_3$) 152.5, 134.0, 128.5, 128.4, 127.9, 126.0, 125.6, 124.6, 122.1, 110.7; *m/z*: (FAB) 444 (M^+, 76%, $C_{20}H_{12}Br_2O_2$ requires 444); Anal. Calcd. for $C_{20}H_{12}Br_2O_2$: C, 54.09; H, 2.72. Found: C, 54.06; H, 2.77. (*S*)-(–)-**6**: m.p. 214 - 216°C; $[\alpha]_D^{25}$ = – 24.3 (*c* = 1.9 in $CHCl_3$); ^{1}H-NMR (250 MHz, $CDCl_3$) 8.31 - 8.27 (m, 2 H), 7.74 (s, 2 H), 7.52 - 7.46 (m, 2 H), 7.39 - 7.33 (m, 2 H), 7.16 - 7.12 (m, 2 H), 5.06 (s, 2 H); ^{13}C-NMR (62.5 MHz, $CDCl_3$) 152.4, 133.9, 128.5, 128.3, 127.9, 126.0, 125.5, 124.5, 122.0, 110.6; *m/z* (FAB) 444 (M^+, 76%, $C_{20}H_{12}Br_2O_2$ requires 444).

4,4'-Dibromo-2,2'-binaphthol-bis-methyl ether (*R*)-(+)-**8**. A mixture of (*R*)-(+)-**6** (2.73 g, 6.1 mmol), methyl iodide (5.8 cm^3, 93 mmol) and cesium carbonate (8.4 g, 26 mmol) in acetone (90 cm^3) was stirred at 25°C for 2 h. The mixture was filtered and the filtrate concentrated on a rotary evaporator to afford bis-methyl

ether (*R*)-(+)-**8** (2.6 g, 5.5 mmol, 90%) as a yellow solid, m.p. 205 - 207°C; $[\alpha]_D^{25}$ = + 78.3 (*c* = 1.2 in $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 250 MHz) 8.24 (dd, *J* = 9.0 and 0.7 Hz, 2 H), 7.76 (s, 2 H), 7.42 (ddd, *J* = 7.5, 7.8 and 1.3 Hz, 2 H), 7.25 (ddd, *J* = 7.7, 7.5 and 1.2 Hz, 2 H), 7.09 (ddd, *J* = 8.4, 0.7 and 0.6 Hz, 2 H), 3.76 (s, 6 H); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) 154.5, 134.5, 127.8, 127.2, 127.2, 125.4, 123.8, 118.8, 118.4, 56.9; *m/z* (FAB) 472 (M^+, 22%). Anal. Calcd. for $C_{22}H_{16}Br_2O_2$: C, 55.96; H, 3.42. Found: C, 55.92; H, 3.45.

4,4'-Bis-(trimethylsilylethynyl)-2,2'-binaphthol-bis-methyl ether (*R*)-(+)-**9**. A mixture of (*R*)-**7** (1.6 g, 3.4 mmol), trimethylsilylacetylene (6.0 cm^3, 42 mmol), bis(triphenylphosphine)palladium(II) chloride (140 mg, 0.20 mmol) and copper(I) iodide (70 mg, 0.37 mmol) in dry benzene (20 cm^3) and triethylamine (18 cm^3) was heated at 75°C for 36 h. The mixture was filtered through a short pad of silica gel and washed with ethyl acetate (100 cm^3). After concentration of the filtrate on a rotary evaporator, the crude compound was chromatographed on silica gel (hexane/EtOAc = 30/1) to give (*R*)-(+)-**9** (1.37 g, 2.7 mmol, 80%) as a yellow solid, m.p. 223 - 225°C; $[\alpha]_D^{25}$ = + 71.8 (*c* = 1.8 in $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 250 MHz) 8.34 (d, *J* = 8.2 Hz, 2 H), 7.64 (s, 2 H), 7.40 (ddd, *J* = 7.6, 7.5 and 1.1 Hz, 2 H), 7.23 (ddd, *J* = 7.5, 1.4 and 1.2 Hz, 2 H), 7.06 (d, *J* = 8.3 Hz, 2 H), 3.74 (s, 6 H), 0.37 (s, 18 H); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) 153.1, 132.7, 128.4, 125.9, 125.2, 124.4, 123.5, 121.0, 119.9, 117.3, 102.1, 98.8, 55.7, -0.9; *m/z* (HRMS) 506.2048 (M^+, 100%). Anal. Calcd. for $C_{32}H_{34}O_2Si_2$: C, 75.84; H, 6.76. Found: C, 75.89; H, 6.63.

ACKNOWLEDGMENTS

We thank the Research Grants Council, Hong Kong for the financial support.

REFERENCES AND NOTES

1. For reviews, see a) Skotheim, T. A. Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; b) Bredas, J. L.; Silbey, R. *Conjugated Polymers: the Novel Science and Technology of Highly Conducting and Nonlinear Optically Active Materials*; Kluwer Academic Publishers: Bostson, 1991; c) Kiess, H. G., Ed. *Conjugated Conducting Polymers*; Springer-Verlag: New York, 1992.
2. For reviews, see a) Wulff, G. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 21; b) Chapoy, L. L. *Recent Advances in Liquid Crystalline Polymers*; Elsevier: Amsterdam, 1985.
3. For examples, see a) Ciardelli, F.; Lanzillo, S.; Pieroni, O. *Macromolecules* **1974**, *2*, 174; b) Lemaire, M.; Delabouglise, D.; Garreau, R.; Guy, A.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1988**, 658; c) Kotkar, D.; Joshi, V.; Ghosh, P. K. *J. Chem. Soc., Chem. Commun.* **1988**, 917; d) Tang, B.-Z.; Kotera, N. *Macromolecules* **1989**, *22*, 4388; e) Moore, J. S.; Gorman, C. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 1704; f) Yashima, E.; Huang, S.; Matsushima, T.; Okamoto, Y. *Macromolecules* **1995**, *28*, 4184.
4. a) Ito, Y.; Ihara, E.; Murakami, M.; Shiro, M.; *J. Am. Chem. Soc.* **1990**, *112*, 6446; b) Ito, Y.; Ihara, E.; Murakami, M. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1509; c) Bedworth, P. V.; Tour, J. M. *Macromolecules* **1994**, *27*, 622; d) Hu, Q.-S.; Vitharana, D.; Liu, G.-Y.; Jain, V.; Wagaman, M. W.; Zhang, L.; Lee, T. R.; Pu, L. *Macromolecules* **1996**, *29*, 1082.
5. Baumgarten, M.; Müllen, K. *Top. Curr. Chem.* **1994**, *169*, 1.

6. Ng, M.-K.; Chow, H.-F.; Chan, T.-L.; Mak, T. C. W. *Tetrahedron Lett.* **1996**, *37*, 2979.
7. Newman, M. S.; Sankaran, V.; Olson, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 3237.
8. Noji, M.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1994**, *35*, 7983.
9. Takahashi, S.; Kuroyama, Y.; Sonogashira, N.; Hagihara, N. *Synthesis* **1980**, 627.
10. Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275.
11. Monomer **4** could be considered as having of two 'independent' naphthol-monoacetylene chromophores due to the orthogonal disposition of the two naphthol rings. However, a new type of naphthol-diacetylene-naphthol chromophore unit was inserted between the two terminal naphthol-monoacetylene chromophores for oligomers **1** - **3**.
12. For examples, see a) Green, M. M.; Andreola, C.; Muñoz, B.; Reidy, M. P. *J. Am. Chem. Soc.* **1988**, *110*, 4063; b) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Wilson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452.
13. Alzeer, J.; Vasella, A. *Helv. Chim. Acta* **1995**, *78*, 1219 and references cited therein.
14. In one of the cyclic binaphthol-containing oligomer series, the molar rotation was proportional to the number of chiral binaphthol groups inside the molecule. However, in another related series, no relationship could be established, see Anderson, S.; Neidlein, U.; Gramlich, V.; Diederich, F. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1596.
15. Schenk, R.; Gregorius, H.; Meerholz, K.; Heinze, J.; Müllen, K. *J. Am. Chem. Soc.* **1991**, *113*, 2634.
16. Baumgarten, M.; Müller, U.; Bohnen, A.; Müllen, K. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 448.
17. Müller, U.; Baumgarten, M. *J. Am. Chem. Soc.* **1995**, *117*, 5840.

(*Received in Japan* 7 *May* 1996; *accepted* 12 *June* 1996)