Pergamon

Tetrahedron Letters 43 (2002) 3313–3317

TETRAHEDRON
LETTERS

Zr-promoted cyclization of diynes bearing C_2-chirality: synthesis and properties of new chiral conjugated molecules

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Received 10 January 2002; revised 28 February 2002; accepted 15 March 2002

Abstract—Conjugated oligomers bearing 4,5,6,7-tetrahydro-5*S*,6*S*-dioctyloxybenzothiophene as a central linkage were synthesized by Negishi's reagent (n-Bu_2ZrCp_2) promoted intramolecular cyclization of a diyne and subsequent Suzuki coupling reactions. The chirality in the central linkage originated from tartaric acid, which induced the conjugated backbone of oligomers to exhibit interesting optical activity. © 2002 Elsevier Science Ltd. All rights reserved.

Conjugated organic materials with well-defined structures and properties are of interest for electronic devices. Over the last decade, intensive investigations on π-conjugated systems have resulted in the successful development of new synthetic methodologies.[1] Among these efficient strategies for constructing π-conjugated oligomers with precise conjugation length, the zirconocene diyne-coupling pathway has been used to synthesize conjugated systems with novel architecture. Zirconocene-promoted intramolecular cyclization of diynes generates synthetic intermediates containing zirconacyclopentadiene unit(s) which can be subsequently transformed into a variety of structures, for example thiophene,[2] thiophene-1-oxide,[3] thiophene-1,1-dioxide,[3] phosphole,[4] germole[5] and highly functionalized benzene derivatives.[6] These subsequent chemical transformations can be used to tailor the structure of conjugated backbones, giving new options for efficiently tuning the electronic and optical properties. In addition, the physical properties of a π-conjugated system not only rely on the main chain structure, but are also governed by the attached side chains. The nature of the side chains has a substantial impact on the physical properties of the conjugated oligomer and polymers. For example, the hexyl side chains of regioregular poly(3-hexylthiophene), P3HT, play an important role on the molecular ordering, resulting in the highest field-effect mobility reported for polymer transistors.[7] In contrast, many optically active polymers have been obtained by introducing side chains carrying chirality center(s). The resulting polymers exhibit interesting optical behavior induced by the chiral side chains.[8] It is generally accepted that studies on the fundamental properties of oligomeric species often provide specific information enabling prediction of the behavior of their corresponding polymeric analogs.[9] Along this line, we took advantage of the Zr-promoted cyclization of diynes as a versatile tool to introduce side chains with C_2-chirality originating from tartaric acid, giving a series of interesting precursors for new conjugated systems.

Intramolecular zirconocene coupling of diynes for the synthesis of new dibromide building blocks is outlined in Scheme 1. The C_2 chirality in the diyne precursor used for zirconocene-promoted intramolecular cyclization originates from natural L-tartaric acid. Following a literature procedure,[10] diethyl L-tartrate was converted to the bis-mesylate **1**, which was further converted to the diyne **2** with an excess amount of lithium acetylide–ethylenediamine complex.[11] Alkylation of the 1,2-dihydroxy group of **2** with 1-bromoctane was accomplished by the modified Williamson's ether synthesis,[12] using phase transfer catalysis to give the dioctyloxydiyne **3** in 62% yield. Further modification on the terminal acetylene is necessary, because the zirconocene coupling cyclization is not applicable for unprotected terminal diynes. The deprotonation of the terminal alkyne with n-butyllithium followed by trapping of the lithium acetylide with trimethylsilyl chloride cleanly afforded the bistrimethylsilylated diyne compound **4** in 99% yield. Treatment of **4** with Negishi's reagent (n-Bu_2ZrCp_2), generated in situ from zirconocene dichloride and n-butyllithium, gave the zirconocycle intermediate which was subsequently quenched with sulfur monochloride, S_2Cl_2, affording a new chiral

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Keywords: zirconocene; C_2-chirality; chiral conjugated oligomer.

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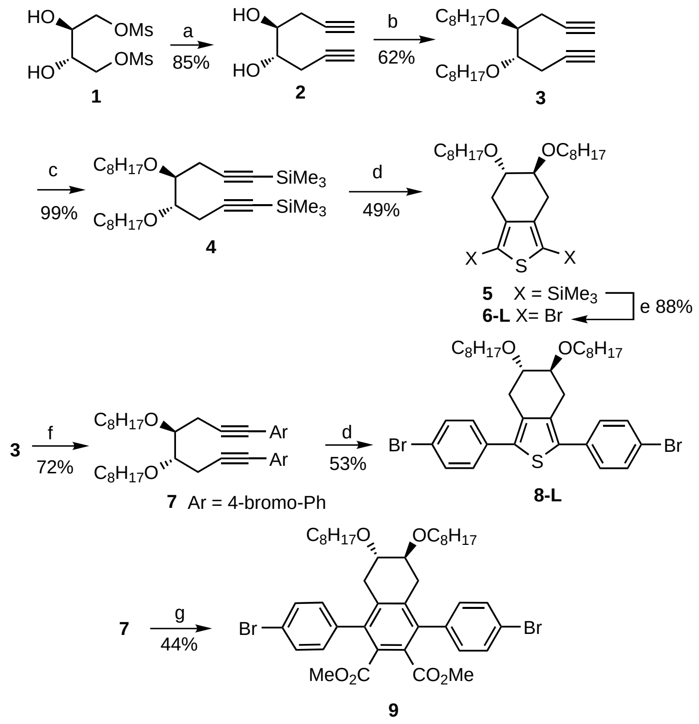
PII: S0040-4039(02)00520-8



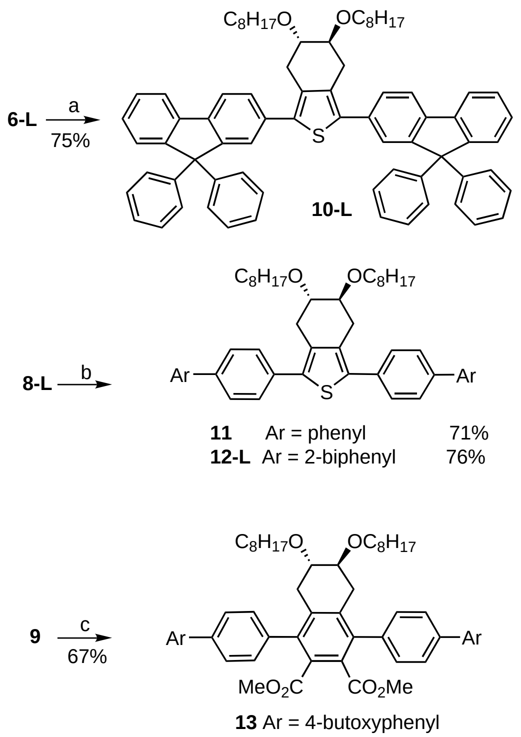
Scheme 1. *Reagents and conditions*: (a) lithium acetylide ethylenediamine complex, DMSO/THF; (b) 1-bromooctane, NaOH, CTAB, THF; (c) *n*-BuLi, $(CH_3)_3SiCl$; (d) (i) Cp_2ZrCl_2, *n*-BuLi, THF (ii) S_2Cl_2; (e) Br_2, CCl_4; (f) 1-bromo-4-iodobenzene, $PdCl_2(PPh_3)_2$, CuI, Et_2NH; (g) (i) Cp_2ZrCl_2, *n*-BuLi (ii) CuCl, DMAD, THF.

molecule **5**. The trimethylsilyl groups in **5** were displaced by treating **5** with bromine under electrophilic substitution conditions to give a 49% yield of 2,9-dibromo-4,5,6,7-tetrahydro-5*S*,6*S*-dioctyloxylbenzothiophene (**6-L**).[13] To probe the influences of the side chain chirality on the physical properties, **6-D**, which is an enantiomer of **6-L**, was synthesized in a similar manner but starting from diethyl D-tartrate.

The terminal alkyne could be further modified via a transition metal catalyzed reaction. The selective $PdCl_2(PPh_3)_2$-catalyzed Sonogashira coupling reaction of **3** with 4-iodobromobenzene in the presence of a co-catalyst, CuI, in diethylamine at room temperature afforded the dibromide compound **7** in a yield of 72%. Compound **7** was further cyclized in a similar manner as **4** by treatment with Negishi's reagent and followed by trapping the zirconocycle intermediate with S_2Cl_2 to give 53% of the dibromide compound **8-L**, an interesting chiral building block possessing a 4,5,6,7-tetrahydro-5*S*,6*S*-dioctyloxylbenzothiophene unit as the central linkage. The enantiomer **8-D** was isolated via a similar synthetic pathway to **8-L**. Another interesting building block with a highly functionalized phenylene core was obtained according to the Takahashi's method;[6] the zirconacyclopentadiene intermediate derived in situ from **7** with Negishi's reagent was converted to the diester **9** in an isolated yield of 44% in the presence of CuCl and dimethyl acetylenedicarboxylate (DMAD).

The viability of the synthesis of conjugated molecules based on these chiral dibromide cores was investigated. The extension of the conjugation of the chiral core by Suzuki coupling reactions of dibromides **6**, **8**, and **9** with arylboronic esters or various arylboronic acids is outlined in Scheme 2. A catalytic amount of the bulky phosphine ligand, P^tBu_3, was added to improve the efficiency of the Suzuki coupling reaction. For dibromide **6-L**, a bulky aryl group, 9,9-diphenylfluorene, was introduced to the C2 and C9 positions of the 4,5,6,7-tetrahydrobenzothiophene by using 2-(9,9-diphenylfluorenyl) pinacol boronate as the coupling reagent. Consequently, oligomer **10-L** was isolated in 75% yield. The enantiomeric oligomer **10-D** was also isolated in a similar manner from **6-D**. Two different arylboronic acids were tested for coupling with the chiral dibromide **8** to afford oligomers **11** and **12-L** in 71 and 76% yields, respectively. For a comparison, the enantiomer **12-D** was also synthesized. In addition, the conjugation of dibromide **9** was extended by reacting with 4-butoxyphenyl boronic acid under standard Suzuki coupling conditions, giving the oligomer **13** in an isolated yield of 67%.

UV–vis absorption and photoluminescence (PL) of chiral molecules **10**, **12**, and **13** in dilute $CHCl_3$ solution were investigated to probe their electronic properties. The HOMO–LUMO energy band gap was estimated according to the absorption onsets. Intense blue fluorescence for **10**–**13** with quantum yields ranging from 0.15 to 0.32 was detected upon irradiating at the corresponding absorption maximum. The photophysical properties are summarized in Table 1. A comparison of the UV–vis and PL spectra of **10**–**13** is shown in Fig. 1. As we can see from Fig. 1, **10** exhibits evident



Scheme 2. *Reagents and conditions*: (a) 2-(9,9-diphenylfluorenyl) pinacol boronate, $\mathrm{Pd(PPh_3)_4}$, $\mathrm{K_2CO_3}$, $\mathrm{P}^t\mathrm{Bu_3}$, DME; (b) arylboronic acids, $\mathrm{Pd(PPh_3)_4}$, $\mathrm{K_2CO_3}$, $\mathrm{P}^t\mathrm{Bu_3}$, toluene; (c) 4-butoxyphenyl boronic acid, $\mathrm{Pd(PPh_3)_4}$, $\mathrm{K_2CO_3}$, $\mathrm{P}^t\mathrm{Bu_3}$, toluene.

red-shifts both in absorption and emission maxima when compared to those of **11**, which is expected to have a similar effective conjugation length as **10** based on the structural analysis. The bathochromic shifts in **10** could be ascribed to the coplanar structure in the rigid 9,9-diphenylfluorene moieties. It is intriguing that **11** and **12** exhibit very similar absorption and emission behaviors, although **12** is expected to have a shorter conjugation length due to the twisted conformation of the 2-biphenyl moiety. However, the absorption maximum of **11** is red-shifted only by 10 nm when compared with that of 2,5-diphenylthiophene.[14] In other aspects, the UV–vis and PL spectra of **13** are strongly blue-shifted when compared to those of **10** and **11**. In molecule **13**, the significant *ortho–ortho* steric interactions between the *ortho*-hydrogens and the ester groups as well as the methylene ($\mathrm{CH_2}$) groups are expected, which would prevent the formation of a coplanar conformation of the conjugated backbone in the ground state. The highly twisted conformation completely blocks the extension of the π-conjugation along the molecular axis, resulting in an increased band gap and the blue-shifts, both in absorption and emission maxima. The distinct Stokes shift of **13** further confirms the existence of a highly twisted ground state. The redox behavior of molecules **10**–**13** was investigated by cyclic voltammetry in $\mathrm{CH_2Cl_2}$. These chiral molecules, except for **13**, exhibit a reversible cathodic oxidation redox couple. The radical cation is believed to be generated first on the thiophene ring and subsequently delocalized over the whole molecule. The lower oxidation potential of **10** compared to that of **11** and **12** is consistent with the assumption of a more coplanar ground state conformation in **10**. The thermal properties of chiral molecules **10**–**13** were investigated by means of thermogravimetric analysis (TGA). The temperatures corresponding to 5% weight loss ranged from 340 to 417°C were observed upon heating **10**–**13** under a nitrogen atmosphere. The morphological properties were studied by differential scanning calorimetry (DSC) analysis. The glass transition temperature (T_g) of **10** was determined to be 69°C by heating the liquid nitrogen quenched melt sample. The rigidity of 9,9-diphenylfluorene makes a significant contribution to the high morphological stability of **10**. In contrast to **10**, molecules **12** and **13** exhibit lower T_g values, which could be due to the introduction of two morphological flexible long alkyl chains. The redox and thermal properties are also summarized in Table 1.

To probe the influence of the chirality on the photophysical behavior of **10** and **12**, the two pairs of enantiomers were subjected to circular dichroism (CD) analysis (Fig. 2). There is no CD effect associated with the backbone chromophore absorption of the enantiomeric pair of **10**. In contrast to **10**, the enantiomeric pair of **12** demonstrated a weak CD effect, which could be due to the exciton coupling of the conjugated main chain and the twisted biphenyl subunit. The appearance of a mirror image CD spectra of **10-L** versus **10-D** and **12-L** vs **12-D** indicates that the optical behavior of the conjugated backbone is strongly reliant on the chirality

Table 1. The physical properties of chiral conjugated molecules **10**–**13**

Compound	λ_{max} (nm)[a]	λ_{em} (nm)[b]	Φ_{FL}[c]	Band gap (eV)[d]	CV (V)[e]	T_g (°C)[f]	TGA[g]
10	354	424	0.27	3.1	0.69	69	417
11	336	418	0.32	3.2	0.76	−6	340
12	335	415	0.31	3.2	0.75	21	370
13	283	406	0.15	3.6	–	12	375

[a] 1.5×10^{-5} M in $\mathrm{CHCl_3}$.

[b] 1.5×10^{-5} M in $\mathrm{CHCl_3}$, excitation at absorption maximum.

[c] In EtOAc with Coumarin I as a standard.

[d] Determined by the absorption onset.

[e] In anhydrous $\mathrm{CH_2Cl_2}$, $\mathrm{TBAPF_6}$ was used as a supporting electrolyte, potential was recorded relative to ferrocene/ferrocenium oxidation.

[f] By DSC analysis of the liquid nitrogen quenched melt sample.

[g] Temperature corresponding to 5% weight loss upon heating under nitrogen.

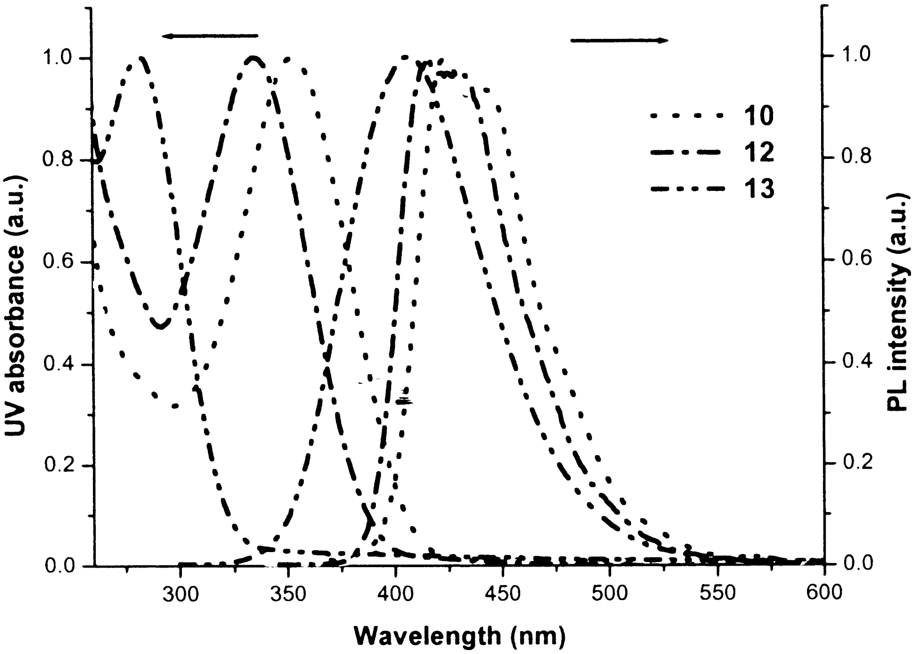


Figure 1. UV–vis absorption spectra and emission spectra of **10**, **12**, and **13**.

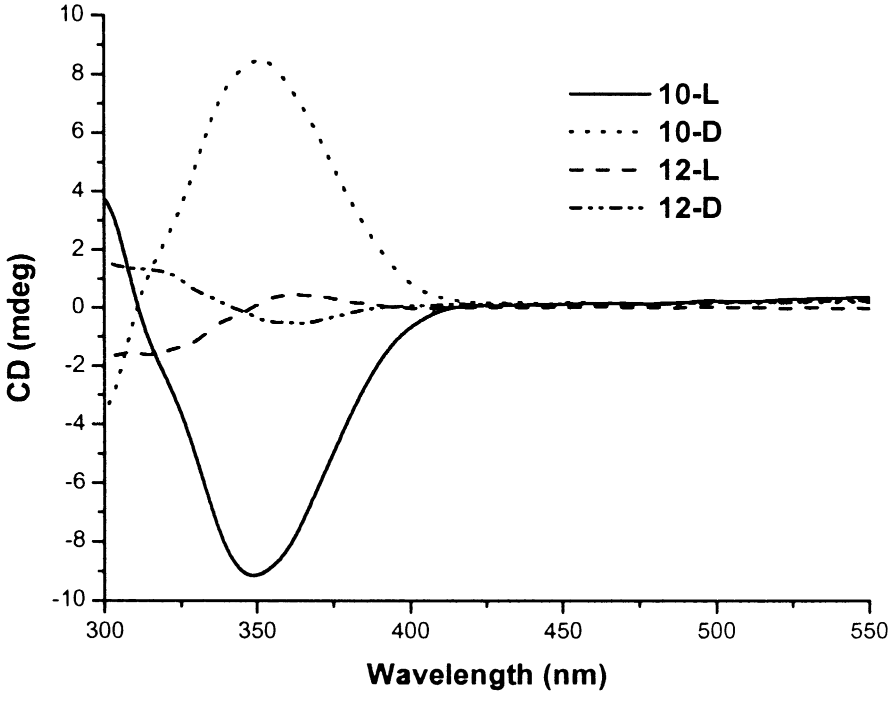


Figure 2. A comparison of the circular dichroism spectra of **10-L**, **10-D**, **12-L**, and **12-D** (2 mg in 5 mL $CHCl_3$).

of the side chain. We suggest at this point that the chiral information of the conjugated chromophore could be induced by the stereogenic centers in the side chain. The chiral molecules synthesized thus exhibit interesting optical activity.

In summary, we have successfully synthesized a new class of chiral conjugated molecules based on 4,5,6,7-tetrahydro-5*S*,6*S*-dioctyloxylbenzothiophene as a central linkage by zirconocene promoted intramolecular cyclization of diynes and subsequent Suzuki coupling reactions. The chiral information originated from the natural tartaric acid is effectively transferred to the conjugated chromophore, resulting in interesting optical activities.

Acknowledgements

We thank the National Science Council and the Ministry of Education of Taiwan for the financial support.

We also thank Professor T. C. Chang for providing the CD/ORD spectropolarimeter.

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13. New compounds were characterized by spectroscopic techniques. Selected data for: Compound **10-L**: $[\alpha]_D^{18}$ −48.8 (*c* 1.67, $CHCl_3$), **10-D**: $[\alpha]_D^{18}$ 47.9 (*c* 1.67, $CHCl_3$); mp 101–103°C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.79 (d, $J=8.0$ Hz, 4H), 7.55 (d, $J=1.4$ Hz, 2H), 7.50 (dd, $J=7.9$, 1.5 Hz, 2H), 7.44 (d, $J=7.6$ Hz, 2H), 7.38 (td, $J=7.4$, 0.9 Hz, 2H), 7.29 (td, $J=7.5$, 1.0 Hz, 2H), 7.26–7.19 (m, 20H), 3.62–3.60 (m, 2H), 3.50 (d, $J=7.0$ Hz, 4H), 3.08 (dd, $J=16.5$, 4.0 Hz, 2H), 2.73 (dd, $J=16.3$, 7.2 Hz, 2H), 1.56–1.51 (m, 4H), 1.33–1.27 (m, 20H), 0.89 (t, $J=7.1$ Hz, 6H); HRMS (*m*/*z*, FAB^+) calcd for $C_{74}H_{74}O_2S$ 1026.5410, Found 1026.5419. Compound **11**: $[\alpha]_D^{26}$ 14.6 (*c* 1.67, $CHCl_3$); mp 95–97°C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.68–7.60 (m, 12H), 7.49 (t, $J=7.3$ Hz, 4H), 7.38 (tt, $J=7.4$, 1.9 Hz, 2H), 3.79–3.75 (m, 2H), 3.60 (t, $J=6.7$ Hz, 4H), 3.24 (dd, $J=16.5$, 3.9 Hz, 2H), 2.95 (dd, $J=16.5$, 6.5 Hz, 2H), 1.58 (quin., $J=6.9$ Hz, 4H), 1.35–1.27 (m, 20H), 0.88 (t, $J=7.1$ Hz, 6H). Anal. calcd for $C_{48}H_{58}O_2S$: C, 82.47; H, 8.36. Found: C, 82.65; H, 8.25. Compound **12-L**: $[\alpha]_D^{20}$ 9.85 (*c* 1.67, $CHCl_3$), **12-D**: $[\alpha]_D^{20}$ −10.1 (*c* 1.67, $CHCl_3$); mp 141–142°C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.49–7.43 (m, 8H), 7.36 (dt, $J=8.4$, 1.9 Hz, 4H), 7.25–7.17 (m, 14H), 3.71–3.70 (m, 2H), 3.61–3.52 (m, 4H), 3.13 (dd, $J=16.7$, 4.0 Hz, 2H), 2.82 (dd, $J=16.5$, 6.6 Hz, 2H), 1.58–1.53 (m, 4H), 1.33–1.27 (m, 20H), 0.88 (t, $J=7.1$ Hz, 6H). Anal. calcd for $C_{60}H_{66}O_2S$: C, 84.66; H, 7.82. Found: C, 84.66; H, 7.94. Compound **13**: $[\alpha]_D^{26}$ 21.4 (*c* 1.67, $CHCl_3$); mp 128–129°C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.63–7.59 (m, 8H), 7.29 (d, $J=8.3$, 4H), 7.01 (dt, $J=8.7$, 1.9, 4H), 4.04 (t, $J=6.5$ Hz, 4H), 3.61–3.59 (m, 2H), 3.47 (s, 6H), 3.39 (t, $J=6.7$ Hz, 4H), 2.83 (dd, $J=17.5$, 3.6 Hz, 2H), 2.63 (dd, $J=17.1$, 5.0 Hz, 2H), 1.85–1.78 (m, 4H), 1.59–1.45 (m, 8H), 1.31–1.24 (m, 20H), 1.01 (t, $J=7.4$ Hz, 6H), 0.87 (t, $J=6.7$ Hz, 6H). Anal. calcd for $C_{62}H_{80}O$: C, 78.11; H, 8.46. Found: C, 78.20; H, 8.40.
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