The Synthesis and Properties of Modified Oligopentafulvenes

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CONTENTS

Chapter One

General Introduction

1-1. General Purpose of the Present Study

The science of polymers (macromolecules), whether natural or artificial ones, has extensively developed in this century and we have been benefited from it in numerous ways. Artificial polymers in use are essentially mixtures of compounds with different polymerization degree of rather simple monomer molecules. Simple structures of monomers place limitation on the properies of polymers. Recent advance of science and technology, however, demand development of new materials with sophisticated properties.

Useful organic compounds owe their properties mainly to π-electrons of unsaturated bonds and unshared electrons of heteroatoms. Therefore, polymers with high conjugation or heteroatoms should have wide possibilities for devoloping new materials with novel physicochemical properties; a good example is electron-conducting property of doped polyacetylene[1]. A large problem is, however, poor solubility of conjugated polymers when complex molecules more than acetylene are used as monomers, and the poor solubility has long prevented detailed studies on the structure and properties of polymers of conjugated molecules.

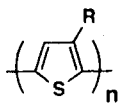
Oligomers are polymers with low polymerization degree (number of monomer unit n = 2 - 20). Synthesis and characterization of oligomers with distinct number of monomer unit are much easier than polymers, and in addition oligomers can be modified so as to be more soluble in organic solvents than polymers. Therefore, oligomers of conjugated molecules can be suitably designed and synthesized in direction for certain properties such as electron conductivity and functional dyes. In addition, the results of studies on such oligomers would open ways for devising novel and highly conjugated polymers with useful properties.

Indeed, studies on oligomers of conjugated molecules, in particular cyclic conjugated molecules, has recently been active and blooming . The general purpose of studies in this thesis is to develop a new type of oligomers or polymers which would be of interest from structural and

physicochemical points of view. Although electron conducting or paramagnetic property is one of the indirect goals, emphasis is primarily laid on the creation of new conjugated oligomers and studies of their fundamental properties.

1-2. Recent Development of Oligomers and Polymers of Conjugated Molecules

Polythiophene and its derivatives **1**[2], poly(*p*-phenylenevinylene) **2**[3] and poly(2,5-thienylenevinylene) **3**[4] have been well studied as electron-conducting polymers. It is known that these polymers develop charged defects in the oxidized state, polarons (radical cations) and bipolarons (dications), which seem to be responsible for the conducting properties of these systems[5]. A number of oligothiophenes were synthesized[6] and the preparation and characterization of polarons and bipolarons of some oligothiophenes were examined to describe the distribution of polarons over the chain[7]. Oligo(*p*-phenylenevinylene) **4** (n = 1 - 6)[8] and oligo(2,5-thienylenevinylene) **5** (n = 1 - 4)[9] were also synthesized and their electronic properties in the reduced and oxidized states were investigated.



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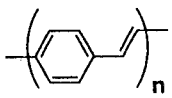

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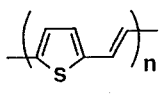

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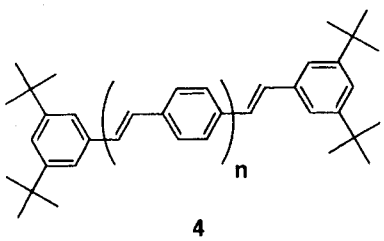

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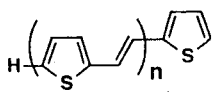

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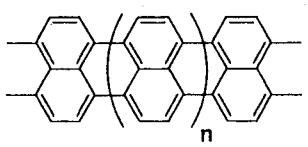
On the other hand, a variety of novel conjugated polymers, which are expected to possess interesting properties and functions, have been proposed by theoretical chemists, and are challenging molecules for synthetic organic chemists. Synthesis and characterization of the oligomers of such unknown polymers will afford a good deal of suggestive information. Poly(*peri*-naphthylene)s **6** have been theoretically predicted to have an extremely low band-gap



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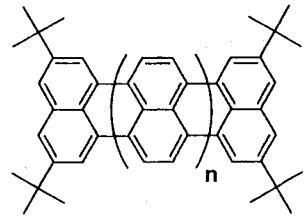

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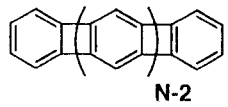
which is characteristic to electron-conducting metals[10]. Müllen *et al.* synthesized oligo(*peri*-naphthylene)s **7** up to pentamer (n = 3) and investigated their properties by spectroscopic methods[11]. [N]Phenylenes, general formula **8**, in which the antiaromatic cyclobutadienes are juxtaposed to the aromatic benzene, have several interesting features. When N is odd, the π-electron count is (4n+2), while it is (4n) when N = even. Therefore, an alternation of properties is expected as a reflection of the total electron count, just as observed in the annulenes. Vollhardt *et al.* synthesized not only linear [N]phenylenes **8** but also angular isomers **9**, up to N = 5, and



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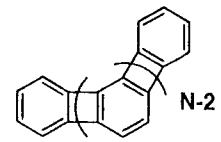

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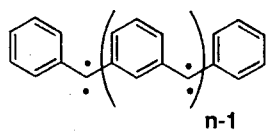
investigated their properties from NMR and electronic spectra, X-ray structual analysis, reduction to the dianion, complexation with metals, and so on[12]. Poly(*m*-phenylenecarbene)s **10** were proposed by Mataga as ground state multiplet molecules which possess ferromagnetic properties[13]. Iwamura and Itoh succeeded in generating tetracarbene **11** (n = 4) from the corresponding tetrakis-diazo compound[14]. This is well known as the first organic nonet molecule in ground state, and the chemistry of such high-spin molecules is now one of the most actively investgated area of science. The ionic derivatives of oligo(9, 10-anthrylene)s **12** are



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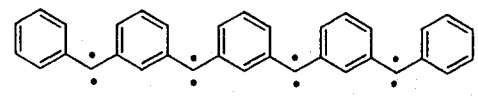

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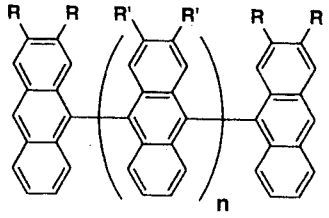
predicted to be able to form high-spin states. Müllen *et al.* synthesized **12** up to heptamer[15]. Their cyclovoltammetric and ESR characterization provide evidence for the possibility of forming high-spin states.



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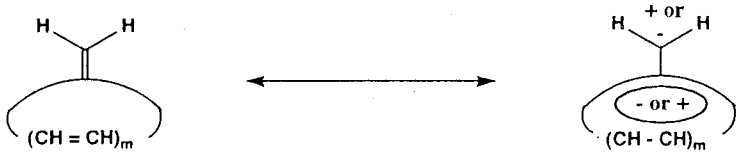
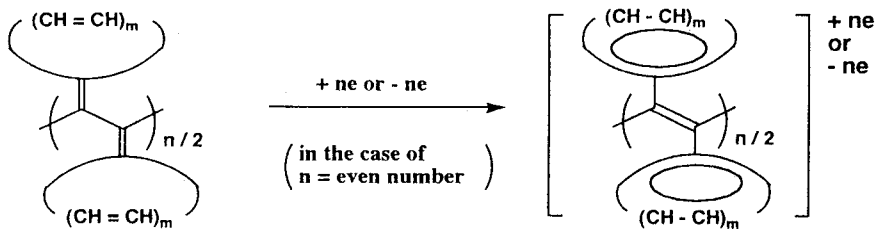
1-3. Oligofulvenes and Oligopentafulvenes as Novel Conjugated Oligomers

Fulvene **13** is a common name of cross-conjugated molecules, methylenecyclopolyalkene. Although fulvenes rather behave as polyolefins, they can receive resonance contribution of aromatic dipolar structure **14**. Thus, the larger the contribution of **14** is, the more stable a



13 **14**

fulvene is. In view of this characteristic electronic property of cross-conjugated fulvenoid compounds, their polymers at the exomethylene terminal carbons, general formula **15**, are interesting synthetic targets from the view points of both organic and macromolecular chemistry. They should generate poly-cations or -anions having polyacetylene spine **16**, upon electronic oxidation or reduction depending on their ring size. It would be of interest to examine this possibility not only as an access to novel polyacetylenes but also as a potential entry into electron-conducting polyacetylenes. There have been no studies on oligofulvenes except on some dimers. Based on several considerations, I decided to study on modified oligopentafulvenes in order to explore this new field of oligomers.



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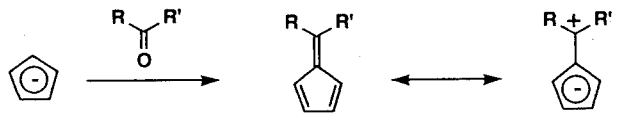
1-4. On Pentafulvenes

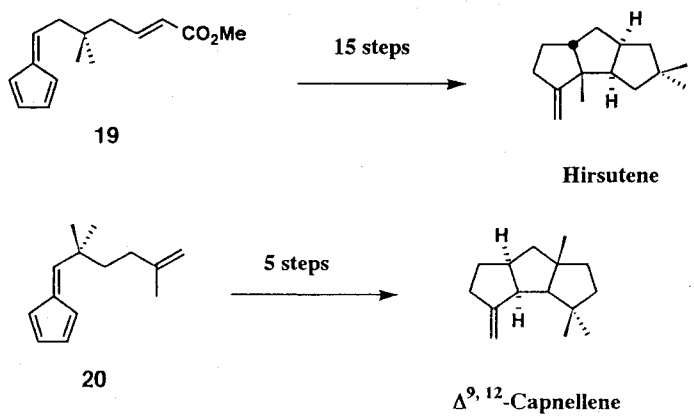
Pentafulvenes, general formula **17**, are among the simplest cross-conjugated fulvenoid compounds, and are theoretically and synthetically useful compounds as evidenced by the fact that they have served as the subject of many investigations and that the numerous papers have been published since Thiele first described about them in 1900[16].

Pentafulvenes are expected to show aromaticity, if they receive a sizable contribution of the dipolar resonance structure **18** which shares aromatic stabilization of 6π-electron of cyclopentadienyl anion. However, every evidence obtained from a variety of measurements suggests that pentafulvene is best represented by a formula with defined single and double bonds and that a dipolar structure makes at most no more than 10% contribution to overall nature of the molecule[17, 18]. In fact, the parent compound (R = R' = H) is highly reactive, polymerizes and undergoes autooxidation readily[16]. But the presence of an electron-donating group or a heteroatom substituent at 6-position stabilizes the molecule to an appreciable extent. This is due to increase of the contribution of dipolar structure. A good number of such derivertives of pentafulvene have been synthesized in simple ways from ketones and cyclopentadienyl anion[19].

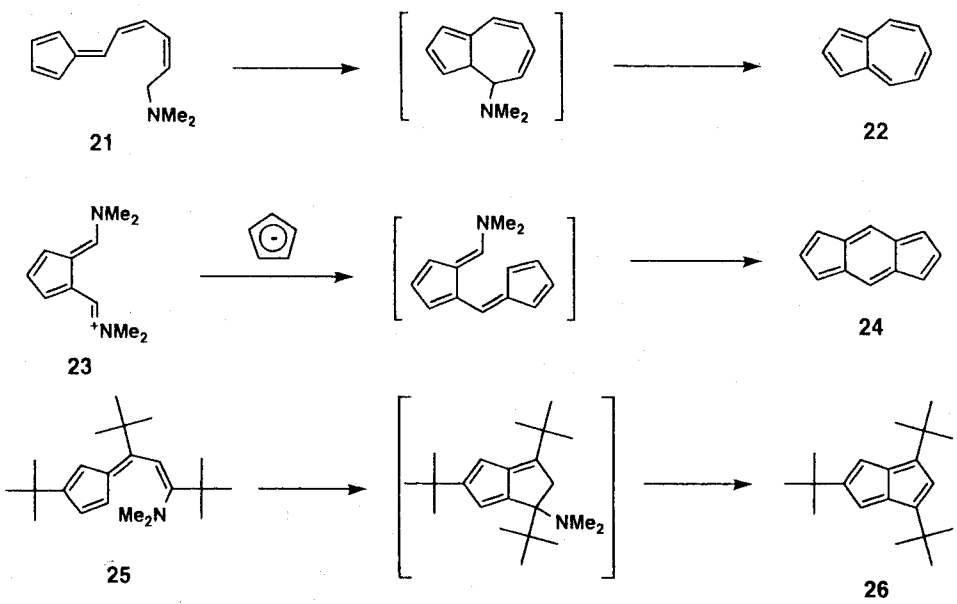


17 18

Owing to the easiness of preparation, moderate stability and reactivity, pentafulvenes have been useful synthetic intermediates for both the total synthesis of natural products and the synthesis of π-conjugated compounds. For example, pentafulvenes **19** and **20** have served as

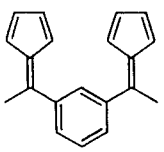


key intermediates in the total synthesis, by Little *et al.*, of *d, l*-hirsutene[20] and *d, l*-$\Delta^{9,12}$-capnellene[21], respectively. On the other hand, azulene **22**[22], *s*-indacene **24**[23], and t-butyl



substituted pentalene **26**[24] were synthesized by Hafner *et al.* through pentafulvenes **21**, **23** and

25, respectively. Furthermore, bis-pentafulvenes **27** - **30** have been recently prepared[25] as the synthetic intermediates for new hydrocarbon tetraradicals composed of two triplet trimethylenemethane subunits, such as **31**; thus, pentafulvenes can be useful for the synthetic approach to high-spin organic molecules.



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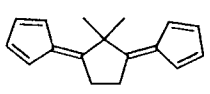

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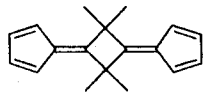

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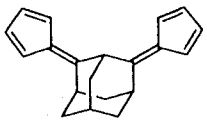

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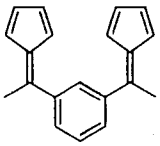

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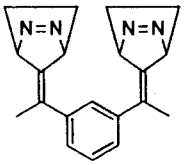

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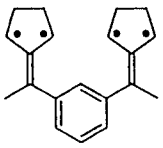

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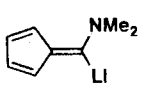
According to MO calculations, pentafulvenes have appreciably low LUMO, and indeed they are readily reduced electrochemically to an anion radical and further to a dianion when substituents at 6-position are capable of stabilizing a negative charge. This ready reduction of pentafulvene is, in another sense, a reflection of the aromatic stabilization of cyclopentadienyl anion. Alkali metal reduction of pentafulvenes had been reported[26, 27], but hardly showed synthetic utilities. Recently in our laboratry, however, effective use of alkali metal reduction of pentafulvenes has been developed. Pentafulvenes having dimethylamino group as a leaving group at 6-position afford useful reactive intermediate such as 6-dimethylamino-6-lithiopentafulvene **32**[28] and dianion of 6-dimethylamino-6-phenylpentafulvene **33**[29], or novel conjugated molecules, such as 6, 6'-bipentafulvenyl **34**[30] and 2-cyclopentadienylidene-2H-thiapyran **35**[31]. The formation of **35** involves a novel rearrangement.



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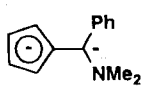

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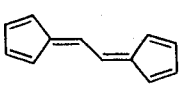

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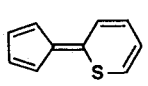

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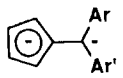
Reactions of 6, 6-diarylpentafulvene dianions **36**[29] with dichloromethane yield 1, 1-diaryl-spiro[2,4]hepta-4, 6-dienes **37**, and alkali metal reduction of the diphenylspiroheptadiene (Ar = Ar' = Ph) in turn genarates a novel homopentafulvene dianion **38**[32]. Compound **38** and diphenylpentafulvene dianion (Ar = Ar' = Ph in **36**) are characterized by NMR spectroscopy. These investigations shed new light on the chemistry of pentafulvenes.



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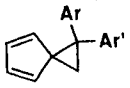

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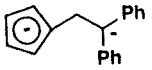

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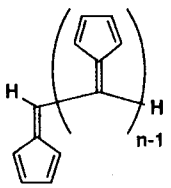
1-5. Modified Oligopentafulvenes as Actual Target Molecules

As described above, pentafulvenes are fundamental compounds as cross-conjugated π-systems, and their high electron affinity gives attractive possibilities of new developments in the synthesis and chemistry of novel conjugated molecules. Thus, oligomers of pentafulvenes, namely oligopentafulvenes **39**, are interesting as a typical model for polymers of cross-comjugated fulvenoids **15**. However, 6, 6-bipentafulvenyl **34** undergoes air-oxidation and intramolecular electrocyclization to afford tricyclic conpound **40** at around room temperature[30, 33]. This suggests synthetic difficulties for **39** from the viewpoint of stability. Incidentaly, 8, 8-biheptafulvenyl **41** also shows similar behavior[34]. Some modification is required for the



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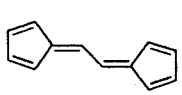

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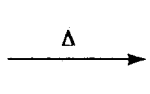

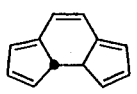

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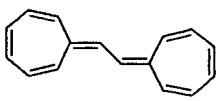
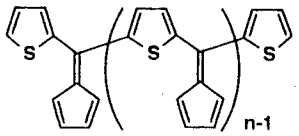


41

preparation of such oligomers.

I therefore designed oligopentafulvenes inserted with 2-thienyl groups, namely oligo-6-(2-thienyl)pentafulvenes **42**, as an alternative model system. The 2-thienyl group here provides two advantages; first, its electron-donating property contributes to stabilization of the dipolar pentafulvene π-system; second, the easy metalation of thiophene at 2(5)-position furnishes sites for oligomer extention.



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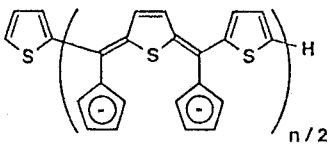
Electronic reduction of **42** should generate polyanions **43**, which have oligoacetylene spine modified with thienoquinoid extention. Polyacetylenes have been well studied for the electron-conducting polymers; the highly doped polyacetylene shows metallic conductivity. On the other hand, the thienoquinoid structure also plays an important role in the electronic conducting polymers. The electron conduction of doped polythiophene has been attributed to the formation of the thienoquinoid structure in the polymer. Theoretically, co-polymers of thiophene and thienoquinoid, general formula **44**, are predicted to possess a small band gap necessary for good electron conduction[35]. Therefore, studies on the synthesis and physical properties of the oligomer **42** is significant for the science of novel functionalized materials as well as a new development of pentafulvene chemistry.



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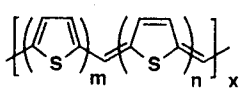
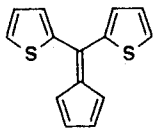
(in the case of n = even number)



44

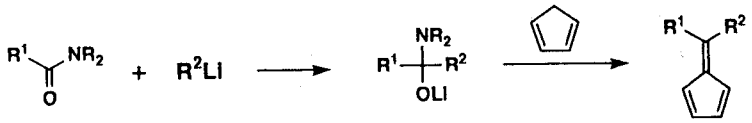
1-6. Contents of the Present Thesis

The present doctoral thesis consists of six chapters. Chapter Two describes the selective lithiation and functionalization of 6, 6-di-(2-thienyl)pentafulvene **42a** (n = 1 in **42**). Compound **42a** is considered as a building block for **42**, and lithiation and functionalization of 5'-position of the 2-thienyl group is essential for the synthesis of **42**. To avoid nucleophilic attack at 6-position of pentafulvenes arising from their dipolar properties, lithiating reagent having less nucleophilic character is required. I searched for suitable lithiating agents which selectively lithiate at 5'-position of the 2-thienyl group. As a result, phenyllithium and lithium diisopropylamide (LDA) were found to be successful for the present purpose, whereas n-butyllithium and t-butyllithium gave very poor results. The lithiated dithienylpentafulvenes were proved to be good intermediates for the synthesis of a variety of derivatives of **42a** including oligomers.

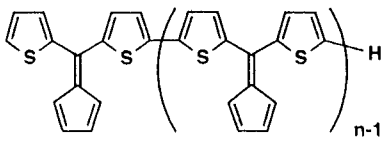


42a

Chapter Three describes a new and efficient synthesis of pentafulvenes. In the course of my attempts to synthesize **42**, I encountered with some difficulties because the precursor ketones tended to become hardly soluble or unstable as the number of the repeating unit increased. Therefore, development of a new method for the synthesis of pentafulvenes which does not require isolation of precursor ketones became desirable, and I found that reactions of N, N-dialkylamides with organolithium compounds followed by addition of cyclopentadiene furnish 6-mono or 6, 6-disubstituted pentafulvenes in moderate to high yields.



Chapter Four describes the synthesis and physical properties of oligo-6-(2-thienyl) pentafulvenes **42**. They were synthesized up to tetramer (n = 4) by application of the new pentafulvene synthesis described in Chapter Three. The obtained oligomers have fair to moderate stability and show considerably low reduction potentials on cyclic voltammetry to suggest ready formation of polyanions or polyanion radicals with oligoacetylene spine. The anionic species of **42** were generated by alkali metal reduction, and characterized by UV-Vis. and NMR spectroscopy. Their structure agrees with the expected one, *i.e.* such a structure **43** having oligoacetylene spine attached with cyclopentadienyl anion. Oligopentafulvenes inserted with bithiophene, namely oligo[6, 6-(2-thienyl)pentafulvene]s, **45**, and oligothienylpentafulvenes having hydrogen atoms on the terminals, **46**, were also synthesized and are described in this chapter.



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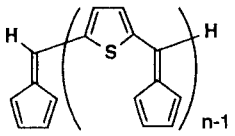

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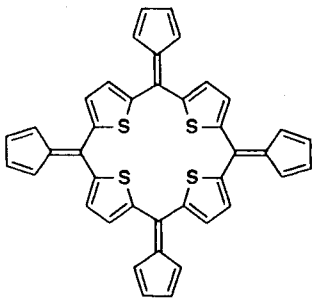
Chapter Five describes the synthesis and properties of cyclic-tetramer **47** and cyclic-hexamer **48** of oligo-6-(2-thienyl)pentafuvene. These compounds were prepared concurrently



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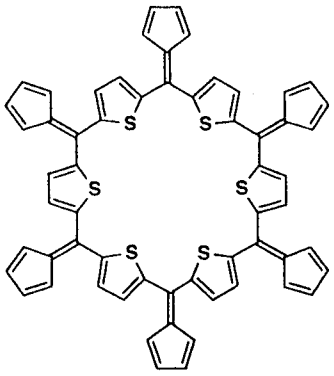
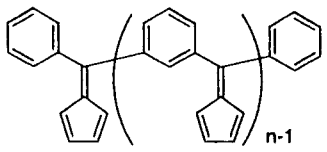


48

by application of the oligothienylpentafulvene synthesis described in Chapter Four under high dilution conditions. They are not only novel macrocycles containing thiophene rings, but also precursors for novel anionic species of great structural and physicochemical interest in relation with annulene chemistry.

Chapter Six describes the synthesis and properties of oligopentafulvenes inserted with benzene ring, namely oligo(phenylene)pentafulvenes. The *meta*-linked isomers, oligo(*m*-phenylene)pentafulvenes **49**, are expected to form multiplet poly(anion radical) by electronic reduction. The new pentafulvene synthesis enabled to prepare **49** up to tetramer. The branched isomer **50** was also prepared. Reduction potentials of **49** and **50** by cyclic voltammetry suggest the formation of poly(anion radical). The corresponding *para*-isomers **51**, which have t-butyl groups at the terminal phenyl groups for improvement of solubility, were also synthesized up to tetramer.



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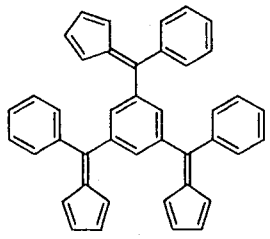

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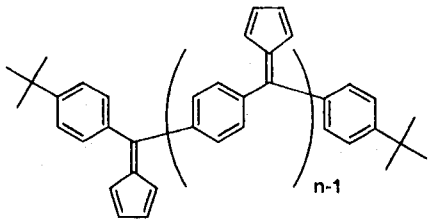

51

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Chapter Two

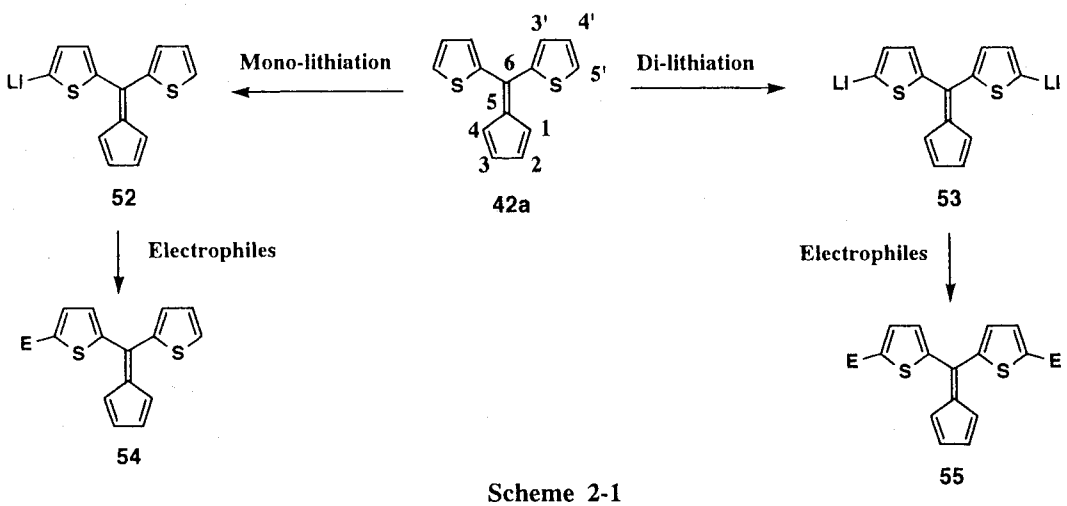
Selective Lithiation and Functionalization of 6, 6-Di(2-thienyl)pentafulvenes

2-1. Introduction

There are two reasons to choose 6, 6-di(2-thienyl)pentafulvene **42a** as a building block for synthesizing oligo-6-(2-thienyl)pentafulvenes.

1) The electron-donating 2-thienyl group should contribute to stabilization of the pentafulvene π-system.
2) 5-Position of the thienyl group can be readily metallated and functionalized, and hence would be a linking site for synthesizing oligo-6-(2-thienyl)pentafulvenes.

Generally, pentafulvenes are susceptible to nucleophilic attack at 6-position owing to their dipolar properties[11]. Use of a base having nucleophilic character may cause competitive reactions between the lithiation of 5'-position of **42a** and the nucleophilic attack at 6-position; thus suitable lithiating agents which selectively lithiate at 5-position of the 2-thienyl group were required. Phenyllithium and lithium diisopropylamide (LDA) were found to work for the present purpose. The successfully lithiated species could be functionalized by reaction with a variety of electrophiles to give 5'-substituted 6, 6-di(2-thienyl)pentafulvenes **54** and **55** (Scheme 2-1).

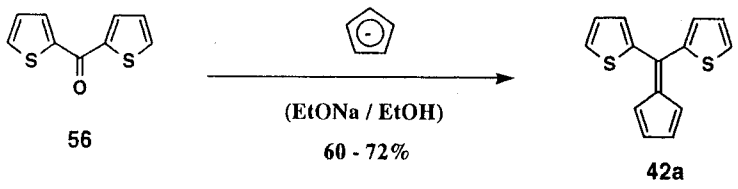


Scheme 2-1

In this chapter, I describe the details of the selective lithiation and functionalization of **42a** which can be a useful method for the synthesis of novel conjugated compounds having pentafulvene structure.

2-2. Results and Discussion

6, 6-Di(2-thienyl)fulvene **42a** , though it has a simple structure, was unknown and here first synthesized by the condensation of cyclopentadienyl anion and di-2-thienyl ketone **56**[2] in 60 - 72 % yields (Scheme 2-2). Compound **42a** is a wine red crystalline substance and fairly stable in air at room temperature, differing from the high instability of the parent pentafulvene[3].

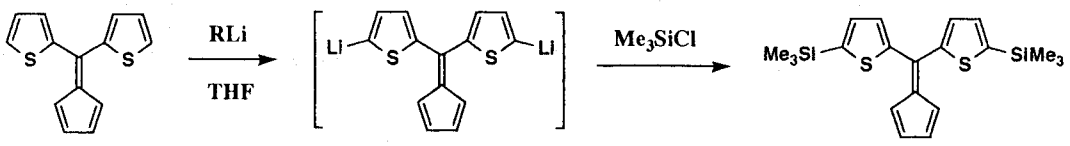


56 **42a**

Scheme 2-2

At first, the di-lithiation of **42a** was examined by several organolithium reagents (Table 2-1). The lithiation was monitored by quenching the reaction mixture with chlorotrimethylsilane leading to bis(trimethylsilyl) compound **55a** (Scheme 2-3). n-Butyllithium afforded only complex mixtures, and **55a** was not detected at all in the mixture. This may be due to attack of n-butyllithium at 6-position of **42a** to destroy pentafulvene π-framework. t-Butyllithium also gave very poor results.

On the other hand, lithium diisopropylamide (LDA) , which has a low nucleophilicity, worked well. Upon addition of 2.5 equivalents of LDA to **42a** in tetrahydrofuran (THF), the reaction mixture turned to orange suspension as the temperature gradually rose to 0 °C from -70 °C. Bis-trimethylsilylated product **55a** was obtained in 95 % yield after quenching with chlorotrimethylsilane.



42a 53 55a

Scheme 2-3

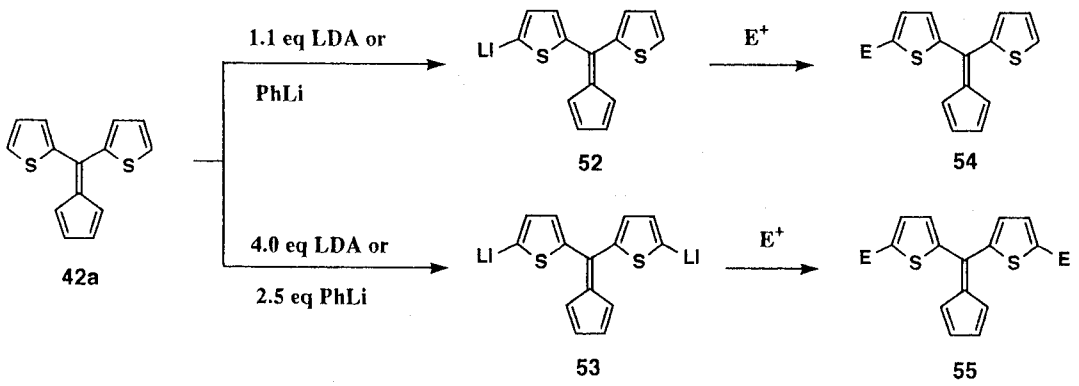
Table 2-1. Lithiation of **42a** by Various Organolithium Compounds Followed by Quenching with Chlorotrimethylsilane[a]

Entry	RLi[b]	Yield of **55a** (%)
1	n-BuLi	0
2	t-BuLi	0
3	Lithium diisopropylamide[c]	95
4	PhLi	88
5	2-Thienyllithium[c]	83

[a] Reactions were carried out at -70 °C in THF. [b] 2.5 equivalents, [c] Warmed up to 0 °C,

Phenyllithium also effected the selective lithiation. The lithiation with this reagent proceeded even at -70 °C. Similar to the case of LDA, the reaction mixture turned to orange suspension after addition of phenyllithium, suggesting that dilithio-derivative **55** is poorly soluble in THF.

Furthermore, use of 2-thienyllithium as a base also resulted in the lithiation of 5'-position of **42a**; thus the acidity of the proton at 5'-position of **42a** is higher than that at 2-position of thiophene itself, probably due to the electron-withdrawing property of 6-pentafulvenyl group. Accordingly, functionalization of **42a** could be attained via lithiation with LDA or phenyllithium. Table 2-2 summarizes the results of mono- and di-lithiation and functionalization of **42a**. The selective monolithiation was carried out by use of 1.1 equivalents of LDA or phenyllithium at -70 - 0 °C for 1 hour in THF, giving dark red solutions. The di-lithiation was carried out by 2.2 - 4.0



Scheme 2-4

Table 2-2. Lithiation and Functionalization of **42a**[a]

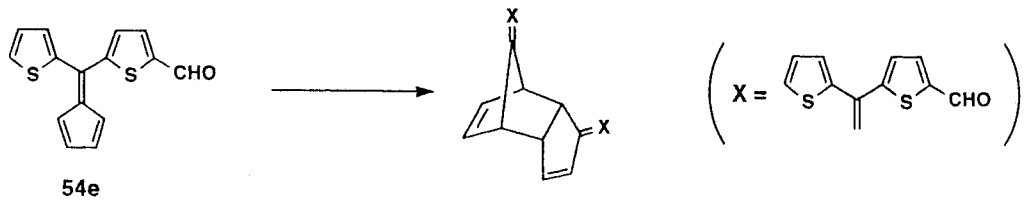
Entry	RLi	Equiv.	Electrophile	Product(E=)	Yield %
1	LDA	1.1	Me_3SiCl	**54a**($SiMe_3$)	95
2	LDA	1.1	PhSSPh	**54b**(SPh)	97[b]
3	PhLi	1.1	PhSSPh	**54b**(SPh)	99
4	LDA	1.1	Ph_2CO	**54c**(Ph_2COH)	81
5	PhLi	1.1	$BrCH_2CH_2Br$	**54d**(Br)	99[c]
6	LDA	1.1	Me_2NCHO	**54e**(CHO)	75
7	LDA	4.0	Me_3SiCl	**55a**($SiMe_3$)	99
8	LDA	4.0	PhSSPh	**55b**(SPh)	88
9	PhLi	2.5	PhSSPh	**55b**(SPh)	96
10	LDA	4.0	PhSeSePh	**55f**(SePh)	78
11	LDA	4.0	Ph_2CO	**55c**(Ph_2COH)	97
12	LDA	4.0	$BrCH_2CH_2Br$	**55d**(Br)	28[d]
13	PhLi	2.2	$BrCH_2CH_2Br$	**55d**(Br)	44

[a] Reactions were carried out at -50 °C to 0 °C for 1 h in THF. [b] Warmed up to r. t. and the yield is based on 27 % recovery. [c] Based on 14 % recovery. [d] The monobromide (45 %) and starting material (22 %) were also obtained.

equivalents of the reagents (Scheme 2-4). Phenylsulfenylation and phenylselenylation of the lithio compounds, **52** and **53**, proceeded in high yields (Entry 2-3 and 8-10). Reaction with benzophenone gave the diphenylhydroxymethyl derivatives, **54c** and **55c,** in good yields (Entry 4 and 11). While the monobromination of **42a** with 1, 2-dibromoethane through monolithiation afforded monobromide **54d** in good yield accompanied with some recovery of **42a** (Entry 5), the dibromination through dilithiation resulted in only poor to moderate yields of dibromide **55d** with concomitant formation of monobromide **54d** and starting material **42a** (Entry 12 and 13).

In general, pentafulvenes are electronically destabilized by introduction of an electron-withdrawing group at 6-position owing to the antiaromatic destabilization of cyclopentadienyl cation[4]. For the same reason, cyclopentadienone is extremely unstable to form rapidly a dimer as it is formed[5]. Similar may be the case when electron-withdrawing group(s) is introduced into the thiophene ring of **42a**.

Formylation of monolithio compound **52** by N, N-dimethylformamide gave monoformyl compound **54e** in good yield in solutions (Entry 6); however, concentration of the solution led to the formation of isomeric mixture of dimers **57** [MS(FAB); m/z 541 $(M+H)^+$] (Scheme 2-5). Di-formyl compound was too unstable to exist as a monomer even in solutions.



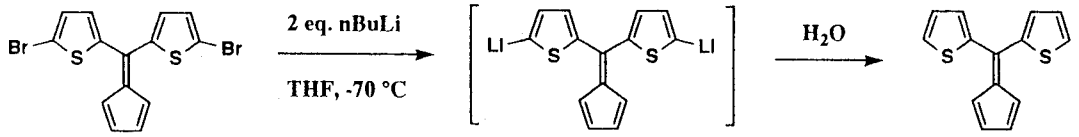
54e **57**

Scheme 2-5

Relatively weak electron-withdrawing groups, such as bromine atom, seem not to destabilize the π-system of **42a**, appreciably. Monobromide **54d** and dibromide **55d** are fairly stable without formation of the corresponding dimers.

Selective lithiation and functionalization were also possible for **54d** and **55d** by halogen-lithium exchange. Thus, treatment of **55d** with 2.5 equivalents of n-butyllithium at -70 °C

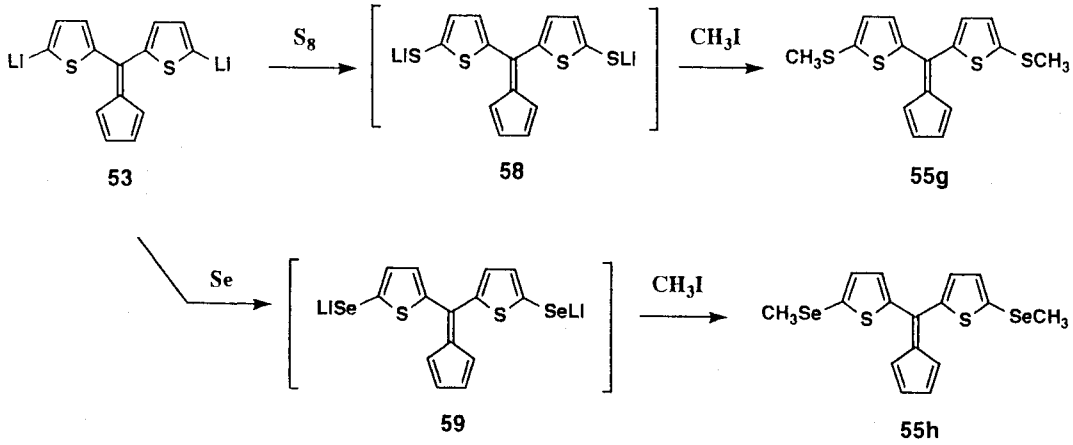
afforded dilithio derivative **53** without decomposition of the pentafulvene π-skeleton and quenching with water gave **42a** in 77% yield (Scheme 2-6).



55d **53** **42a**

Scheme 2-6

Reaction of **53** with solid sulfur (S8) and metallic selenium generated the thiolate and selenolate anion, **58** and **59**, in deep purple solutions, respectively. They should give alkylchalcogeno derivatives by quenching with alkyl halides. In fact, methylthio compound **55g** was obtained by quenching with methyl iodide in 54 % yield, and selenomethyl derivative **55h** in 50 % yield in similar way (Scheme 2-7).



53 **58** **55g**

59 **55h**

Scheme 2-7

Thus, although there is a problem on the stability of the functionalized derivatives of **42a** depending on the elecronic nature of substituents, the present results should offer good opportunities for synthesizing novel pentafulvenoid compounds of structural and physicochemical interest, especially, oligo-6-(2-thienyl)pentafulvenes.

2-3. Experimental Section

General Remarks . Melting points were determined on a Yanaco MP 500D apparatus and uncorrected. Mass spectral analysis (MS) were performed on a JEOL JMS-SX102 instrument. ^{1}H and ^{13}C-NMR spectra were recorded on JEOL JNM-PMX60Si, JEOL EX-270, and JEOL GSX-400 instruments. Unless otherwise noted, spectra are reported in δ value referenced to Me_4Si. IR spectra were observed on Hitachi EPI-G3 and Perkin-Elmer 1650 spectrometers. Characters written behind wavenumbers are represented as follows; s = strong, m = medium, w = weak. Electronic (UV-Vis) spectra were obtained on a Hitachi U-3400 instrument and are reported in nanometers (log ε)(sh = shoulder). Elemental analysis were performed by the elemental analysis laboratory, Faculty of Science, Osaka University. Column chromatography was carried out with the use of Merck Art. 7734 Kieselgel 60, 70 -230 mesh ASTM, or neutral alumina Merck Art. 1097 Aluminiumoxid 90, activity II-III, 70-230 mesh ASTM. Analytical TLC was performed by using plates (0.25 mm) prepared from Merck Art. GF-254. Tetrahydrofuran was freshly distilled under a nitrogen atmosphere from sodium-benzophenone immediately prior to use. Cyclopentadiene was prepared from dicyclopentadiene by distillation according to the literature[6], and the distilled cyclopentadiene was stored in a deep-freezer until it was used. 1.5 M n-Butyllithium in hexane (Mitsuwa Pure Chemicals, Inc.) and 1.8 M phenyllithium in cyclohexane/diethyl ether = 70/30 v/v (Aldrich Chemical Co., Inc) are purchased and used as it is. All solvents were distilled before use.

Materials. Di(2-thienyl)ketone was prepared according to the literature[2]. Diisopropylamine was distilled from calcium hydride under a nitrogen atmosphere. Chlorotrimethylsilane, diphenyl disulfide, diphenyl diselenide, benzophenone, 1, 2-dibromoethane, sulfur (sublimed), selenenium (powder), and iodomethane are all commercially available and were used without further purification. N, N-Dimethylformamide was distilled from calcium hydride under reduced pressure.

6, 6-Di(2-thienyl)pentafulvene ***42a***. In a 200-mL, round-bottomed, four-necked flask equipped with a magnetic stirring bar, a rubber septum, a thermometer, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 70 mL anhydrous ethanol and 3 g (131 mmol) of sodium chips under nitrogen flow. The mixture was stirred at room temperature until the sodium was consumed completely. The flask was allowed to cool to 0 °C, 20 mL (242 mmol) of cyclopentadiene was added via syringe through the septum, and the mixture was stirred at room temperature for 1 hour. The mixture was cooled again to -30 °C (a dry ice / ethanol bath), and added with 5 g (25.7 mmol) of di(2-thienyl)ketone **56** in one portion. The cooling bath was removed and the mixture was allowed to warm up to room temperature, and stirred at 40 °C for additional 1 h. The contents of the reaction flask were poured into 200 mL of water and extracted with hexane (50 mL x 3). The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was evaporated in vacuo, and the residue was passed through a short column of Al_2O_3 (30 g) eluted with 10 % benzene/hexane. Crystals, precipitated by consentration of the solution, were collected by filtration to give **42a** (3.74 g, 60 %).

42a: Wine red prisms (hexane); m.p. 95-96 °C; MS (EI, 70 eV) m/z 242 (M^+); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 5.1, 1.1 Hz, 2H), 7.26 (dd, J = 3.7, 1.1 Hz, 2H), 7.10 (dd, J = 5.1, 3.7 Hz, 2H), 6.57-6.59 (m, 2H), 6.53-6.54 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.44, 143.22, 136.17, 132.83, 132.48, 130.06, 127.16, 124.05; UV-Vis. (EtOH) λ_{max}/nm (log ε) 369 (4.32), 307sh (3.87), 280 (3.90), 222sh (4.09); IR (KBr) ν 3083m, 3067m, 1806w, 1669w, 1620w, 1558s, 1509m, 1456m, 1416s, 1364s, 1303m, 1266m, 1226m, 1161w, 1142m, 1083m, 1043m, 993m, 900m, 849m, 834m, 819m, 786m, 766s, 714s, 677s, 619m, 578m, 550m, 495w cm^{-1}; Anal. Calcd. for $C_{14}H_{10}S_2$: C, 69.38; H, 4.16. Found: C, 69.34; H, 4.19.

General Procedure for Monolithiation and Functionalization of ***42a****: With Lithium Diisopropylamide.* A 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, was purged with dry nitrogen. Anhydrous THF (3 mL) and 0.2 mL (1.4 mmol) of diisopropylamine were added via syringe through the septum. The mixture was cooled to -50 °C,

and 0.7 mL (1.1 mmol) of 1.5 M n-butyllithium in hexane was added dropwise. After the addition was complete, the mixture was stirred at 0 °C for 30 min and was cooled to -90 °C. A solution of 242 mg (1.0 mmol) of **42a** in 5 mL of anhydrous THF was added via syringe through the septum in one portion. The mixture was allowed to warm up to 0 °C and stirred for 1 h. The solution turned to dark red and was again cooled to -70 °C, 3 mmol of electrophiles (neat or in THF solution) was added, and the stirring continued at 0 °C for additional 1 h. The reaction mixture was added with water and extracted with hexane or benzene/hexane. The organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C; A column fitted with an ice-cooled jacket was used.) to give 5'-substituted-6, 6-di(2-thienyl)pentafulvenes **54a-c** in yields given in Table 2-2.

*General Procedure for Monolithiation and Functionalization of **42a**: With Phenyllithium.* In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 242 mg (1.0 mmol) of **42a** and 6 mL of anhydrous THF under nitrogen flow. The mixture was cooled to -70 °C, 0.6 mL (1.1 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added dropwise via syringe through the septum, and the stirring continued at -70 °C for 1 h. An electrophile (3 mmol, neat or in THF solution) was added, and the reaction mixture was allowed to warm up to 0 °C and then stirred for additional 1 h. A work-up and chromotography were performed in similar way described above to give **54b** and **54d** in yields given in Table 2-2.

*5'-Trimethylsilyl-6, 6-di(2-thienyl)pentafulvene **54a**.* Dark red oil; MS (EI, 70 eV) m/z 314 (M^+); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.50 (dd, J = 5.1, 1.3 Hz, 1H), 7.30 (d, J = 3.5 Hz, 1H) 7.25 (dd, J = 3.7, 1.3 Hz, 1H), 7.21 (d, J = 3.5 Hz, 1H), 7.08 (dd, J = 5.1, 3.6 Hz, 1H), 6.50-6.58 (m, 4H), 0.34 (s, 9H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 145.23, 146.38, 143.28, 143.26, 136.16, 133.96, 133.86, 132.71, 132.36, 132.28, 129.85, 127.08, 124.14, 124.09, -0.13.

*5'-Phenylthio-6, 6-di(2-thienyl)pentafulvene **54b**.* Dark red oil; MS (EI, 70 eV) m/z 350 (M^+, 80 %), 322 (35%), 256 (35%), 241 [$(M-SPh)^+$, 100 %], 208 (60%), 185 (15%), 171

(10%), 129 (20%), 111 (10%), 73 (20%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.49 (dd, J = 5.1, 1.3 Hz, 1H), 7.15-7.33 (m, 8H), 7.07 (dd, J = 5.1, 3.6 Hz, 1H), 6.52-6.58 (m, 3H), 6.46-6.49 (m, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 147.33, 143.73, 142.49, 137.87, 137.17, 135.21, 134.32, 133.17, 132.97, 132.80, 132.78, 130.12, 129.17, 128.56, 127.21, 126.87, 124.12, 123.67; IR (neat) ν 3050m, 2910m, 1582s, 1565s, 1480s, 1441s, 1418s, 1379s, 1220m, 1083m, 1022m, 995w, 908w, 757s, 690s cm^{-1}.

5'-Diphenylhydroxylmethyl-6, 6-di(2-thienyl)pentafulvene ***54c***. Orange crystals (ether-hexane); m.p. 58-59 °C; MS (EI, 70 eV) m/z 424 (M^+, 0.4%), 279 (30%), 265 (5%), 167 (35%), 149 (45%), 113 (10%), 71 (10%), 57 (20%), 28 (30%), 18 (100%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.49 (d, J = 5.1, 1.2 Hz, 1H), 7.28-7.40 (m, 10H), 7.25 (dd, J = 3.7, 1.2 Hz, 1H), 7.10 (d, J = 3.8 Hz, 1H), 7.07 (dd, J = 5.1, 3.7 Hz, 1H), 6.74 (d, J = 3.8 Hz, 1H), 6.53-6.58 (m, 3H), 6.45-6.48 (m, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 157.13, 146.07, 143.32, 143.16, 142.83, 136.17, 132.77, 132.57, 132.51. 132.28, 129.94, 128.12, 127.82, 127.23, 127.12, 126.96, 124.15, 123.89, 80.28; IR (KBr) ν 3748m. 3010w, 1556s, 1435m, 1363m, 1220w, 998m, 904m, 855m, 820m, 768s, 698s, 644m cm^{-1}; Anal. Calcd. for $C_{27}H_{20}OS_2$: C, 76.38; H, 4.75. Found: C, 76.18; H, 4.85.

5'-bromo-6, 6-di(2-thienyl)pentfulvene ***54d***. Dark red oil; MS (EI, 70 eV) m/z 322/320 (M^+, 55%, 55%), 241 [$(M-Br)^+$, 100%], 208 (70%), 195 (15%), 139 (10%), 120 (13%), 69 (10%), 45 (10%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.53 (dd, J = 5.1, 1.3 Hz, 1H), 7.25 (dd, J = 3.6, 1.3 Hz, 1H), 7.10 (dd, J = 5.1, 3.6 Hz, 1H), 7.06 (d, J = 4.0 Hz, 1H), 7.00 (d, J = 4.0 Hz, 1H), 6.57-6.66 (m, 2H), 6.47-6.52 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 144.61, 143.68, 142.35, 134.88, 133.01, 132.92, 132.87, 130.31, 130.26, 127.29, 124.08, 123.56, 117.54; IR (neat) ν 3050m, 2910s, 2840m, 1565s, 1470s, 1415s, 1364s, 1330w, 1260w, 1210w, 1080m, 968s, 905m, 762s, 703s, 678s, 640m, 624m cm^{-1}.

General Procedure for Dilithiation and Functionalization of ***42a****: With Lithium Diisopropylamide.* A 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, was purged with dry nitrogen. Anhydrous THF (6 mL) and 0.6 mL (4.2 mmol) of

diisopropylamine were added via syringe through the septum under nitrogen flow. The mixture was cooled to -50 °C, and 2.5 mL (4.0 mmol) of 1.5 M n-butyllithium in hexane was added dropwise. After the addition was complete, the the mixture was stirred at 0 °C for 30 min, and then cooled to -50 °C. A solution of 242 mg (1.0 mmol) of **42a** in 5 mL of anhydrous THF was added dropwise via syringe through the septum. The mixture was allowed to warm up to 0 °C and stirred for 1 h. The solution turned to orange suspension and was again cooled to -70 °C, 10 mmol of an electrophile (neat or in THF solution) was added, and the stirring continued at 0 °C for 1 h. The reaction mixture was added with water and extracted with hexane or benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C) to give 5', 5"-disubstituted-6, 6-di(2-thienyl)pentafulvenes **55a-f** in yields given in Table 2.

*General Procedure for Dilithiation of **42a**: With Phenyllithium.* In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 242 mg (1.0 mmol) of **42a** and 6 mL of anhydrous THF under nitrogen flow. The mixture was cooled to -70 °C, added with 1.4 mL (2.5 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 V/V) dropwise via syringe through the septum, and the stirring continued at -70 °C for 1 h. An electrophile (10 mmol, neat or in THF solution) was added, the rection mixture was allowed to warm up to 0 °C, and then stirred for additional 1 h. A work-up and chromotography were performed in similar way described above to give **55a-55d** in yields given in Table 2-2.

*5', 5"-Bis(trimethylsilyl)-6, 6-di(2-thienyl)pentafulvene **55a**.* Dark red oil; MS (EI, 70 eV) m/z 386 (M^+, 15%), 313 [$(M-SiMe_3)^+$, 10%], 226 (60%), 182 (100%), 169 (15%), 111 (20%), 72 (35%), 18 (15%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.30 (d, J = 3.5 Hz, 2H), 7.22 (d, J = 3.5 Hz, 2H), 6.57 (brs, 4H), 0.35 (s, 18H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 148.32, 146.18, 143.11, 136.26, 133.87, 133.82, 132.15, 124.23, -0.10.

*5', 5"-Di(phenylthio)-6, 6-di(2-thienyl)pentafulvene **55b**.* Orange leaflets (ether-hexane); m.p. 90-91 °C, MS (EI, 70 eV) m/z 458 (M^+, 5%), 410 (5%), 349 (7%), 279 (7%), 256 (6%),

149 (20%), 81 (30%), 69 (95%), 57 (30%), 41 (40 %), 32 (70%), 28 (100%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.16-7.35 (m, 14H), 6.56-6.59 (m, 2H), 6.47-6.51 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 144.61, 144.01, 138.17, 134.39, 134.28, 133.24, 133.20, 129.24, 128.68, 126.97, 123.80; IR (KBr) ν 3040w, 1555s, 1480m, 1440s, 1421s, 1370s, 1323m, 1211m, 1022m, 999m, 922m, 898m, 811s, 770s, 750s, 689s, 653m, 578m, 512m cm^{-1}; Anal. Calcd. for $C_{26}H_{18}S_4$: C, 68.08; H, 3.96. Found: C, 67.55; H, 3.90.

5', 5"-Bis(diphenylhydroxylmethyl)-6, 6-di(2-thienyl)pentafulvene ***55c***. Orange leaflets (ether-hexane); m.p. 69-70 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.29-7.40 (m, 20H), 7.11 (d, J = 3.8 Hz, 2H), 6.72 (d, J = 3.8 Hz, 2H), 6.50-6.55 (m, 4H), 2.98 (s, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 157.01, 146.08, 143.22, 142.84, 136.18, 132.44, 132.40, 128.14, 127.83, 127.25, 126.98, 124.02, 80.29; IR (KBr) ν 3440m, 3056, 1558s, 1491m, 1363s, 1133m, 1083w, 1000s, 911m, 866m, 805m, 759s, 698s, 650m cm^{-1}; Anal. Calcd. for $C_{40}H_{30}S_2$: C, 79.17; H, 4.98. Found: C, 78.62; H, 5.18.

5', 5"-Dibromo-6, 6-di(2-thienyl)pentafulvene ***55d***. Wine-red crystals (CH_2Cl_2-hexane); m.p. 88.5-89 °C; MS (EI, 70 eV) m/z 402/400/398 (M^+, 35%, 70%, 35%), 321/319 [$(M-Br)^+$, 100%], 240 [$(M-2Br)^+$, 50%]. 195 (38%), 139 (15%), 120 (25%), 98 (10%), 69 (10%), 28 (10%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.09 (d, J = 3.9 Hz, 2H), 7.01 (d, J = 3.9 Hz, 2H), 6.58-6.61 (m, 2H), 6.45-6.48 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 143.93, 143.73, 133.61, 133.44, 132.98, 130.39, 123.60, 117.82; IR (KBr) ν 3080w, 1539s, 1403s, 1364s, 1322m, 1001m, 978m, 919m, 810s, 763s, 685s, 664m cm^{-1}; Anal. Calcd. for $C_{14}H_8S_2Br_2$: C, 42.02; H, 2.02. Found: C, 41.78; H, 2.01.

5', 5"-Di(phenylseleno)-6, 6-di(2-thienyl)pentafulvene ***55f***. Orange leaflets (ether-hexane); m.p. 100-101 °C; MS (EI, 70 eV) m/z 554(M^+, Se = 80, 50%), 387 (100%), 317 (30%), 284 (20%), 240 (50%), 195 (30%), 157 (20%), 121 (10%), 77 (25%), 51 (10%), 18 (10%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.40-7.49 (m, 4H), 7.23-7.31 (m, 8H), 7.14 (d, J = 3.7 Hz, 2H), 6.55-6.59 (m, 2H), 6.47-6.51 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 148.02, 143.82, 135.67, 134.22, 133.53, 133.10, 13219, 131.16, 129.93, 129.43, 127.43, 123.82; UV-Vis. (cyclohexane) λ_{max}/nm (log ε) 383 (4.29), 280 (4.14), 237 (4.30); IR (KBr) ν 3025w, 1553s, 1476m, 1440m, 1412s, 1369s, 1321m, 1209m, 1020m, 999m, 921m, 895w,

824s, 768s, 740s, 685s, 647m, 557m, 486m cm^{-1}; Anal. Calcd. for $C_{26}H_{18}S_2Se_2$: C, 56.52; H, 3.28. Found: C, 56.35; H, 3.38.

Dilithiation of ***55d*** *with n-Butyllithium. Synthesis of* ***42a***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 200 mg (0.5 mmol) of **55d** and 8 mL of anhydrous THF under nitrogen flow. The solution was cooled to -70 °C, 0.8 mL (1.2 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum and stirring continued at -70 °C for 1 h. The reaction mixture was quenched with water and extracted with hexane. The combined extracts were washed with water and brine, dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C, eluted with 10% benzene/hexane) to give 93 mg of **42a** in 77% yield.

5', 5"-Di(methylthio)-6, 6-di(2-thienyl)pentafulvene ***55g***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 0.6 mL (4.3 mmol) of diisopropylamine and 5 mL of anhydrous THF under nitrogen flow. The mixture was cooled to -50 °C, and 2.2 mL (3.3 mmol) of 1.5 M n-butyllithium in hexane was added dropwise. After the addition was complete, the mixture was stirred at 0 °C for 30 min and then cooled to -50 °C. A solution of 388 mg (1.6 mmol) of **42a** in 5 mL of anhydrous THF was added dropwise via syringe through the septum. The mixture was stiirred at 0 °C for 1 h, and 122 mg (3.8 mmol) of solid sulfur was added in one portion. The solution turned to deep purple, and stirred for additional 1 h at the same temperature. Iodomethane (1 mL, 16.1 mmol) was added dropwise, and the mixture was allowed to warm up to room temperature. After being stirred for 1 h, the reaction mixture was added with water and extracted with hexane. The combined extracts were washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C, eluted with hexane to 10% benzene/hexane) to give 286 mg of **55g** in 54% yield. 5', 5"-Di(methylseleno)-6, 6-di(2-thienyl)pentafulvene **55h** was also prepared in similar way (50% yield).

55g: Orange crystals (ether-hexane); m.p. 41-42 °C; MS (EI, 70 eV) m/z 334 (M^+. 100%), 319 [$(M-CH_3)^+$, 10%], 287 [$(M-SCH_3)^+$, 30%], 272 [$(M-SCH_3-CH_3)^+$, 10%], 240 [$(M-2SCH_3)^+$, 15%], 228 (10%), 195 (5%), 91 (5%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.12 (d, J = 3.8 Hz, 2H), 7.00 (d, J = 3.9 Hz, 2H), 6.56-6.59 (m, 2H), 6.50-6.52 (m, 2H), 2.56 (s, 6H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 144.07, 143.28, 142.70, 135.11, 133.34, 132.36, 128.76, 123.73, 20.75; IR (KBr) ν 2916w, 1558s, 1541s, 1457m, 1411s, 1362m, 1315m, 1082w, 963m, 806m, 765m, 680m cm^{-1}; Anal. Calcd. for $C_{16}H_{14}S_4$: C, 57.79; H, 4.24. Found: C, 57.37; H, 4.21.

55h: Dark red oil; MS (EI, 70 eV) m/z 430 (M^+, Se = 80, 70%), 335 [$(M-SeCH_3)^+$, 100%], 240 [$(M-2SeCH_3)^+$, 45%]; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.13 (d, J = 3.8 Hz, 2H), 7.11 (d, J = 3.8 Hz, 2H), 6.57-6.59 (m, 2H), 6.50-6.53 (m, 2H), 2.43 (s, 6H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 145.99, 142.98, 134.78, 133.55, 132.54, 132.48, 132.43, 123.81, 11.42; IR (neat) ν 3040w, 2980w, 2910w, 1550m, 1408s, 1360m, 1330w, 1270w, 1205w, 1073w, 990w, 900m, 800m, 753s, 676m, 638w, 470w cm^{-1}.

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Chapter Three

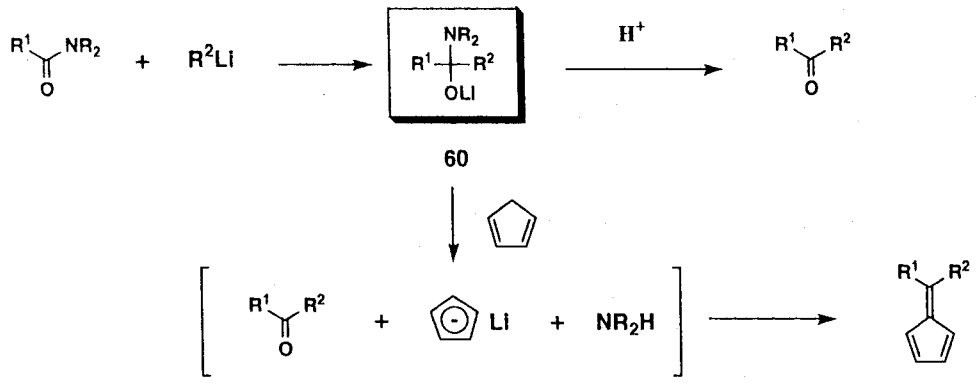
Tandem Reactions of N, N-Dialkylamides with Organolithium Compounds and Cyclopentadiene. A New Efficient Synthesis of Pentafulvenes

3-1. Introduction

Base-catalyzed condensation of aldehydes and ketones with cyclopentadiene has been a most useful method for the synthesis of pentafulvenes[1]. The scope and limitation of this method depends on the availability and reactivity of the carbonyl compounds as well as on the stability of the pentafulvenes to be formed.

During my attempts to synthesize oligo-6-(2-thienyl)pentafulvenes, I encountered some difficulties because the precursor ketones tended to become hardly soluble or unstable as the number of pentafulvene units increased; the details will be discussed in the next chapter. Therefore, a new synthetic method of pentafulvenes was required, particularly, a method which does not need isolation of precursor ketones.

Reactions of organolithium compounds with N, N-dialkylamide, chlorocarbamates and carbamate esters have been reported to yield aldehydes or ketones after hydrolysis[2]. The intermediate adduct of an organolithium compound and a dialkylamide is a N, N-dialkylamino-alkoxide **60** which can be regarded as a protected form carbonyl compounds. Quenching of this



Scheme 3-1

intermediate with cyclopentadiene instead of water should generate a ketone and cyclopentadienyl anion (and dialkylamine) *in situ*, and accordingly yield a pentafulvene by their condensation (Scheme 3-1).

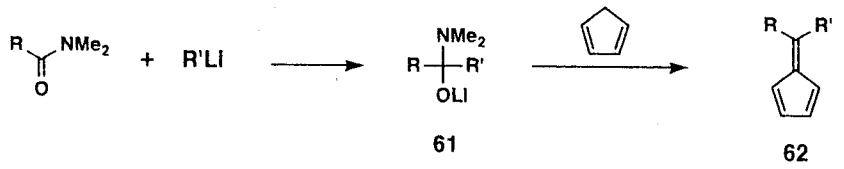
This chapter describes the detail of this new pentafulvene synthesis as well as the scope and limitation, and the application to other reactions.

3-2. Result and Discussion

At first, the reactions of N, N-dimethylamides with several organolithium compounds and cyclopentadiene were examined (Scheme 3-2). The general procedure is as follows. To a solution of an organolithium compound in THF was added an N, N-dimethylamide in THF at -70 to -50 °C, and the mixture was stirred at 0 °C for 1 h. Cyclopentadiene was added at the same temperature, and stirring was continued at 0 °C or room temterature. The reaction mixture was added with water and extracted with hexane or benzene/hexane, and worked up as usual. The product was isolated by chromatography on silica gel.

Table 3-1 summarizes the one-pot synthesis of 6-substituted pentafulvenes **62**. Reactions of N, N-dimethylbenzamide with aryllithium afforded **62a-d** in moderate to high yields under mild conditions (Entry 1 - 4). Methyllithium also gave **62f** in a good yield, while butyllithium needed longer reaction time at room temperature to give **62g** (Entry 6 and 7). 6-(1-Naphthyl)-6-phenylpentafulvene **62e** was obtained in a good yield from 1-naphthamide and phenyllithium, but in a poor yield from 1-naphtyllithium and N, N-dimethylbenzamide (Entry 5 and 8). Preparation of **62e** from the corresponding ketone and cyclopentadienyl anion gave rather poor yield (17%)[3]. 6-(2-Naphthyl)-6-phenylpentafulvene **62h** was also prepared in a high yield (Entry 9). On the other hand, use of N, N-dimethylformamide as an amide afforded mono-6-substituted pentafulvenes (Entry 10 - 13). Relatively low yield of **62i** may be due to the instability of the product.

In the case of N, N-dimethylacetamide, 6-methyl substituted pentafulvenes **62n** and **62f** were obtained in rather poor yields (Entry 14 and 15). Deprotonation from the methyl group of acetamide by the organolithium reagent may have occurred in competition with nucleophillic attack



Scheme 3-2

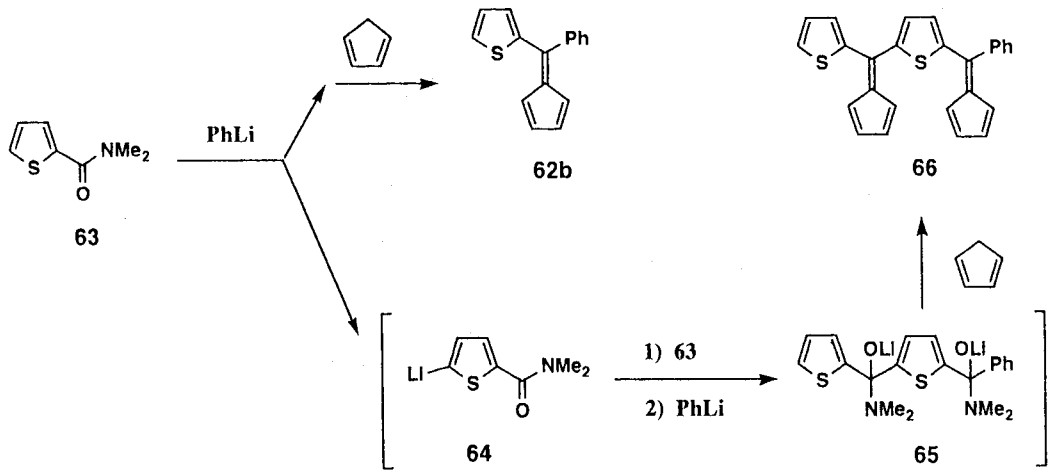
Table 3-1. Synthesis of 6-Substituted Pentafulvenes by Successive Reactions of N, N-Dimethylamides with Organolithium Compounds and Cyclopentadiene

Entry	$RCONMe_2$ R =	R'Li R' =	Temperature and time[a]	Pentafulvene **62**	Yield (%)
1	Phenyl	Phenyl	0 °C, 3 h	**62a**	85
2	"	2-Thienyl	"	**62b**	64
3	"	p-Anisyl	"	**62c**	81
4	"	4-Bromophenyl	"	**62d**	79
5	"	1-Naphthyl	20 °C, 24 h	**62e**	20[b]
6	"	Methyl	0 °C, 3 h	**62f**	99
7	"	Butyl	20 °C, 24 h	**62g**	51[c]
8	1-Naphthyl	Phenyl	20 °C, 8 h	**62e**	80
9	2-Naphthyl	Phenyl	20 °C, 3 h	**62h**	92
10	H	Phenyl	0 °C, 3 h	**62i**	56
11	"	p-Tolyl	"	**62j**	62
12	"	p-Anysil	"	**62k**	74
13	"	2-Thienyl	"	**62m**	59
14	Methyl	Butyl	"	**62n**	33
15	"	Phenyl	"	**62f**	30

[a] Conditions after addition of cyclopentadiene. [b] 1-Naphthyl phenyl ketone was obtained in 60% yield. [c] Butyl phenyl ketone was obtained in 26% yield.

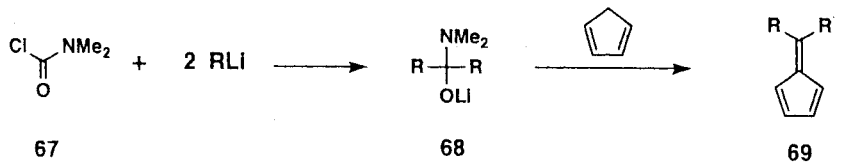
to the amide carbonyl group. Similar may be the following case of 2-thienyl carbamide, because hydrogen at 5-position of the thiophene ring can be deprotonated fairly easily.

The reaction of N, N-dimethyl-2-thienylcarbamide **63** with phenyllithium and then cyclopentadiene gave bispentafulvene **66** in 21% yield in addition to monopentafulvene **62b** in 28% (Scheme 3-3). The intermediacy of **64** and **65** explains the formation of **66**. Appreciably easy metalation of **64** to **65** owing to the presence of electron-withdrawing amide group and less easy metalation of **65** for the lack of any electron-withdrawing group probably play key roles in this transformation.



Scheme 3-3

N, N-Dimethylcarbamyl chloride **67**[4] is also a useful synthon, in particular, for the synthesis of symmetrically 6, 6-disubstituted pentafulvenes **69** by use of two molar equivalents of organolithium compounds (Scheme 3-4). Table 3-2 summarizes the results of the synthesis of **69** from several organolithium compounds. Relatively low yield of **42a** (Entry 2) is probably due to some transmetalation between 2-thienyllithium and the intermediate adduct **68a** (R = 2-thienyl), because 5-positions of the thienyl groups in **68a** are open to metalation. Indeed, **69**, which has methyl groups at 5-positions of the thienyl groups, was prepared in 75% yield (Entry 3). While dimethylacetamide afforded 6-alkylpentafulvenes in poor yields, carbamyl chloride **67** gave 6, 6-dibutylpentafulvene **69e** in a good yield of 69% (Entry 5).



67 68 69

Scheme 3-4

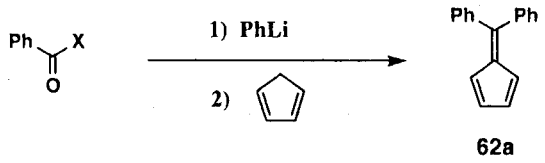
Table 3-2. Synthesis of 6, 6-Disubstituted Pentafulvenes by Reactions of N, N-Dimethyl Carbamyl Chloride **67** with Organolithium Compounds and Cyclopentadiene

Entrry	RLi[a] R =	Temperature and time[b]	Pentafulvene **69**	Yield (%)
1	Ph	0 °C, 3 h	**62a**	83
2	2-Thienyl	"	**42a**	50
3	5-(2-Methyl)thienyl	"	**69c**	75
4	2, 2'-Bithienyl	"	**69d**	70
5	n-Butyl	20 °C, 12 h	**69e**	69

[a] 2-2.5 equivalents of RLi was used. [b] Conditions after addition of cyclopentadiene.

3-2. Scope and Limitation

Effects of solvents and of substituents in the amide group on the present pentafulvene synthesis were examined to get some insights into the scope and limitation. Synthesis of diphenylpentafulvene **62a** was selected as a model reaction (Scheme 3-5 and Table 3-3). When ether was used as a solvent, the yield of **62a** was considerably lower (34%) than the case of THF (Entry 1), and an appreciable amount of benzophenone (50%) was obtained. This result suggests that ether is unfavorable at the reaction either between cyclopentadiene and intermediate



62a

Scheme 3-5

Table 3-3. Synthesis of 6, 6-Diphenylpentafulvene **62a** under Several Conditions

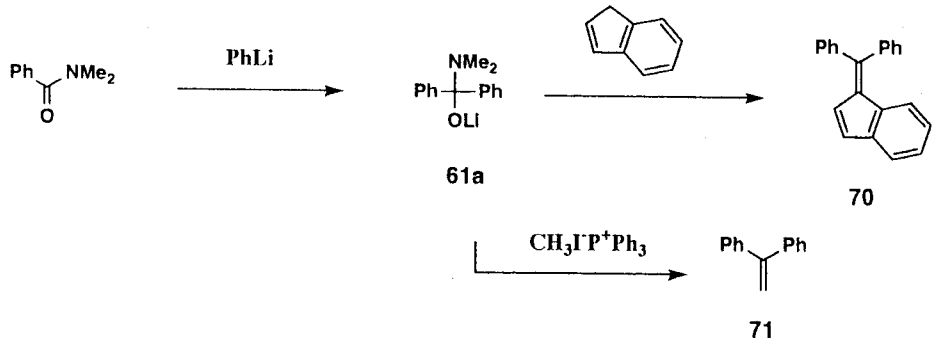
Entry	X in PhCOX	Solvent	Tempepature and time[a]	Yield of **62a**
1	NMe_2	ether	20 °C, 3 h	34[b]
2	NEt_2	THF	0 C, 3 h	76
3	$N(-(CH_2)5-)$[c]	"	"	91
4	OEt	"	20 °C, 12 h	9

[a] Conditions after addition of cyclopentadiene. [b] Benzophenone was obtained in 50% yield.
[c] Benzoyl piperidine.

aminoalkoxide or between cyclopentadienyl anion and benzophenone. The latter may be main reason, because less polar ether is not suitable for the usual pentafulvene synthesis. N, N-Diethylbenzamide and benzoyl piperidine could be also employed in this method (Entry 2 and 3), though they might be less favorable when nucleophiles become bulkier. As anticipated, use of ethyl benzoate in place of amides failed to afford pentafulvenes (Entry 4), owing to the instability of intermediate alkoxyalkoxide, which in turn favors the Grignard synthesis of tertiary alcohols.

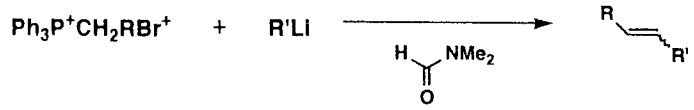
The key point of this new pentafulvene synthesis is that carbonyl compounds and cyclopentadienyl anion are generated *in situ.* Therefore, other proper precursors of carbanion, instead of cyclopentadiene, should be used in this method. In fact, addition of indene to N, N-dimethylaminodiphenylalkoxide **61a** afforded diphenylbenzopentafulvene **70**[5] in 75% yield. Intermediate aminoalkoxide were also found to effect the Wittig reaction: a reaction of

methyltriphenylphosphonium iodide with **61a** gave diphenylolefin **71** in 94% yield (Scheme 3-6). Further applications are expected and remain to be explored.

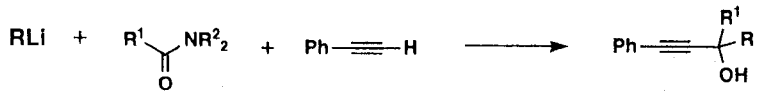


Scheme 3-6

In the course of this study, two papers based on a similar strategy have recently been reported. One is the Wittig reactions using phosphonium salts and organolithium reagents in N, N-dimethylformamide[6] (Scheme 3-7), and the other is one-flask synthesis of propargylic alcohols from oraganolithium reagents, N, N-disubstituted amides and acetylenes[7] (Scheme 3-8). These papers, however, did not mention the formation of the intermediate adducts, such as **61** and **68**, which play a key role in the present new pentafulvene synthesis.



Scheme 3-7



Scheme 3-8

In conclusion, the present new procedure provide a simple and good yield one-pot pentafulvene synthsis. The reaction does not require isolation of a precursor ketone and proceeds under mild conditions. Thus this method, together with the lithiation and functionalization of

dithienylpentafulvene described in Chapter 2, should be suitable for the synthesis of pentafulvenoid compounds with complex structure, such as, oligopentafulvenes.

3-4. Experimental Section

Materials. N, N-Dimethylarylcarbamides were prepared from the corresponding acid chlorides and N, N-dimethylformamide[8]. N, N-Diethylbenzamide was prepared from benzoyl chloride and diethylamine. Benzoyl piperidine was synthesized according to literature[9]. N, N-Dimethylacetamide and dimethylcarbamyl chloride were commercially available and used without further purification. 2, 2'-Bithiophene was synthesized according to literature[10]. Indene was commercially available, and methyltriphenylphosphonium iodide was prepared according to literature[11]. Most of the products were identified by comparison of the physical data either with literature or with those of samples prepared by known methods.

General Procedure for Table 3-1. Synthesis of ***62****.* A 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, was purged with dry nitrogen. In this flask, a THF (5 mL) solution of organolithium reagent (5 mmol) was prepared from the corresponding aryl bromide and 1.5 M n-butyllithium (5 mmol) in hexane in conventional manner. To the stirred solution was added a solution of N, N-dimethylamide (5-6 mmol) in THF (5 mL) via syringe through the septum at -50 °C under nitrogen flow, and the mixture was stirred for 1 h at 0 °C. In the cases of phenyllithium, methyllithium and n-butyllithium, a commercial solution was added to the solution of N, N-dimethylamide. Cyclopentadiene (1 mL, 12 mmol) was added and the stirring continued at 0 °C or room temperature. The reaction mixture was added with water and extracted with hexane or benzene/hexane. The organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C; A column fitted with an ice-cooled jacket was used.) to give **62a-62n** in yields given in Table 3-1.

6, 6-Diphenylpentafulvene **62a**: Orange crystals; m.p. 80.5-81 °C (lit.[12] m.p. 81.5-82 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.35-7.42 (m, 6H), 7.29-7.34 (m, 4H), 6.59-6.62 (m, 2H), 6.28-6.31 (m, 2H)

6-Phenyl-6-(2-thienyl)pentafulvene **62b**: Dark red crystals; m.p. 44-45 °C; MS (EI, 70 eV) m/z 236 (M^+, 15%), 203 (5%), 84 (10%), 49 (10%), 28 (15%), 18 (100%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.46 (dd, J = 5.0, 1.3 Hz, 1H), 7.33-7.39 (m, 5H), 7.08 (dd, J = 3.6, 1.3 Hz, 1H), 7.03 (dd, J = 5.0, 3.6 Hz, 1H), 6.76-679 (m, 1H), 6.58-6.62 (m, 1H), 6.47-6.50 (m, 1H), 6.04-6.07 (m, 1H). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 143.96, 143.92, 143.04, 141.09, 133.05, 132.94, 131.65, 131.62, 130.41, 128.85, 127.53, 127.41, 125.09, 123.06.

6-(p-Anisyl)-6-phenylpentafulvene **62c**: Orange crystals; m.p. 82-82.5 °C (lit.[13] 83.5-84.5 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.30-7.39 (m, 5H), 7.27 (dt, J = 8.9, 2.8 Hz, 2H), 6.90 (dt, J = 8.9, 2.8 Hz, 2H), 6.56-6.62 (m, 2H), 6.33-6.37 (m, 1H), 6.23-6.26 (m, 1H), 3.85 (s, 3H).

6-(4-Bromophenyl)-6-phenylpentafulvene **62d**: Orange crystals; m.p. 91-92 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.50 (d, J = 8.6 Hz, 2H), 7.33-7.38 (m, 3H), 7.27-7.31 (m, 2H), 7.17 (d, J = 8.6 Hz, 2H), 6.58-6.61 (m, 2H), 6.22-6.30 (m, 2H).

6-(1-Naphthyl)-6-phenylpentafulvene **62e**: Orange crystals; m.p. 101-102 °C (lit.[3] 104-104.5 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.87 (t, 8.4 Hz, 1H), 7.67 (d, J= 7.9 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.36-7.45 (m, 4H), 7.28-7.35 (m, 5H), 6.64-6.68 (m, 1H), 6.56-6.59 (m, 1H), 6.43-6.47 (m, 1H), 5.86-5.90 (m,1H).

6-Methyl-6-phenylpentafulvene **62f**: Yellow oil[14]; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.38-7.41 (m, 5H), 6.65-6.68 (m, 1H), 6.58-6.60 (m, 1H), 6.49-6.51 (m, 1H), 6.22-6.23 (m, 1H), 6.20-6.21 (m, 1H), 2.56 (s, 3H).

6-Butyl-6-phenylpentafulvene **62g**: Yellow oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.27-7.34 (m 5H), 6.61-6.64 (m, 1H), 6.52-6.56 (m, 1H), 6.43-6.46 (m, 1H), 6.09-6.12 (m, 1H), 2.89 (t. J = 7.4 Hz, 2H), 1.23-1.46 (m, 4H), 0.84 (t, J = 7.1 Hz, 3H).

6-(2-Naphthyl)-6-phenylpentafulvene **62h**: Orange crystals (ether-hexane); m.p. 89-89.5 °C; MS (EI, 70 eV) m/z 280 (M^+, 100%), 265 (25%), 252 (10%), 202 (20%), 189 (5%), 138 (10%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.85-7.88 (m, 3H), 7.80 (d, J = 8.6 Hz, 1H), 7.49-7.56 (m, 2H), 7.33-7.42 (m, 6H), 6.61-6.65 (m, 2H), 6.34-6.36 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 151.92, 144.30, 141.22, 138.72, 133.24, 132.70, 132.46, 132.43, 132.21, 129.15, 128.79, 128.59, 127.78, 127.66, 127.23, 126.88, 126.45, 124.49, 124.40; IR (KBr)

ν 3055m, 1560s, 1458s, 1363s, 1085m, 1001m, 921m, 684m, 818s, 751s, 700s, 662m, 591m, 556m, 480m cm^{-1}; Anal. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.20; H, 5.68.

6-Phenylpentafulvene **62i**: Red leaflets; m.p. 31-32 °C (lit.[15] 32.5-33 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.56-7.61 (m, 2H), 7.31-7.44 (m, 3H), 7.22 (s, 1H), 6.64-6.71 (m, 2H), 6.49-6.53 (m, 1H), 6.31-6.34 (m, 1H).

6-(p-Tolyl)pentafulvene **62j**: Orange leaflets; m.p. 54-55 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.50 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.19 (s, 1H), 6.70-6.72 (m, 1H), 6.63-6.67 (m, 1H), 6.48-6.50 (m, 1H), 6.30-6.33 (m, 1H), 2.39 (s, 3H).

6-(p-Anisyl)pentafulvene **62k**: Orange crystals; m.p. 65-66 °C (lit.[14] 70.5 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.57 (dt, J = 8.7, 2.4 Hz, 2H), 7.16 (s, 1H), 6.94 (dt, J = 8.7, 2.4 Hz, 2H), 6.71-6.73 (m, 1H), 6.64-6.67 (m, 1H), 6.46-6.49 (m, 1H), 6.30-6.33 (m, 1H), 3.85 (s, 3H).

6-(2-Thienyl)pentafulvene **62m**: Orange leaflets; m.p. 81.5-82 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.46 (dt, J = 5.2, 1.0 Hz, 1H), 7.28 (dd, J = 3.7, 1.0 Hz, 1H), 7.23 (s, 1H), 7.06 (dd, J = 5.2, 3.7 Hz, 1H), 6.85-6.87 (m, 1H), 6.61-6.64 (m, 1H), 6.43-6.45 (m, 1H), 6.25-6.28 (m, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 142.53, 140.61, 135.13, 133.16, 130.72, 130.51, 129.84, 127.72, 127.23, 119.51.

6-Butyl-6-methylpentafulvene **12n**: Yellow oil; ^{1}H-NMR (60 MHz, CCl_4) δ 6.5-6.8 (m, 4H), 2.8 (t, J = 7 Hz, 2H), 1.6-2.2 (m, 4H), 1.3 (t, J = 7 Hz, 3H).

Reaction of N, N-Dimethyl-2-thienylcarbamide ***63*** *with Phenyllithium and Cyclopentadiene. Synthesis of 5'-(6-Phenylfulvenyl)-6, 6-di(2-thienyl)pentafulvene* ***66***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 365 mg (2.4 mmol) of **63** and 6 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -70 °C, 1.6 mL (2.5 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added dropwise via syringe through the septum. The mixture was allowed to warm up to 0 °C, and stirried for 1 h. Cyclopentadiene (1 mL, 12 mmol) was added and the stirring continued at the same temperature for 3 h. The reaction mixture was added with water

and extracted with benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C, eluted with hexane to 10% benzene/hexane) to give 158 mg of **62b** (28%) from the first fraction and 97 mg of **66** (21%) from the second fraction.

66: Red crystals (ether-hexane); m.p. 111-112 °C; MS (EI, 70 eV) m/z 394 (M^+, 100%), 361 (25%), 242 (15%), 208 (15%), 149 (15%), 81 (30%), 69 (60%), 49 (40%), 28 (50%), 18 (65%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.54 (dd, J = 5.0, 1.0 Hz, 1H), 7.41 (brs, 5H), 7.29 (dd, J = .6, 1.0 Hz, 1H), 7.23 (d, J = 4.0 Hz, 1H), 7.11 (dd, J = 5.0 Hz, 1H), 7.08 (d, J = 4,0 Hz, 1H), 6.80-6.83 (m, 1H), 6.62-6.65 (m, 1H), 6.57-6.59 (m, 3H), 6.47-6.52 (m, 2H), 6.01-6.05 (m, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 148.14, 147.80, 144.07, 143.80, 143.04, 142.47, 140.50, 135.41, 133.72, 133.11, 133.06, 132.90, 132.88, 132.83, 132.05, 131.61, 130.15, 128.97, 127.65, 127.23, 125.18, 124.21, 123.68, 122.74; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 418 (4.42), 360 (4.37), 287 (4. 14); IR (KBr) ν 3086w 1543s, 1507s, 147m, 1410m, 1361s, 1008w, 1278m, 1172w, 1078m, 985m, 911m, 838m, 818m, 765s, 718s, 700s, 670s, 627m, 551m cm^{-1}; Anal. Calcd. for $C_{26}H_{18}S_2$: C, 79.15; H, 4.60. Found: C, 78.51; H, 4.60.

General Procedure for Table 3-2. Synthesis of ***69***. A 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, was purged with dry nitrogen. In this flask, a THF (5 mL) solution of organolithium reagent (5 mmol) was prepared from the corresponding aryl bromide and 1.5 M n-butyllithium in hexane (5 mmol) in conventional manner. To the stirred solution was added 0.23 mL (2.5 mmol) dimethylcarbamyl chloride **67** via syringe through the septum below -70 °C under nitrogen flow, and the mixture was stirred at 0 °C for 1 h. Cyclopentadiene (0.5 mL, 6 mmol) was added and the stirring continued at 0 °C or room temperature. The reaction mixture was added with water and extracted with hexane or benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C) to give **62a**, **42a**, and **69c-e** in yields given in Table 3-2.

6, 6-Di[5-methyl-(2-thienyl)]pentafulvene **69c**: Wine red needles (hexane); m.p. 66-67 °C; MS (EI, 70 eV) m/z 270 (M^+, 38%), 255 [$(M-CH_3)^+$, 20%], 240 [$(M-2CH_3)^+$, 10%], 222 (5%), 44 (5%), 28 (30%), 18 (100%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.10 (d, J = 3.6 Hz, 2H), 6.78 (dd, J = 3.6, 1.0 Hz, 2H), 6.54-6.57 (m, 4H), 2.54 (d, J = 1.0 Hz, 6H), ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 145.50, 141.92, 140.89, 137.20, 133.36, 131.55, 125.83, 123.95, 15.63. IR (KBr) *v* 3066w, 1556s, 1507s, 1456s, 1430s, 1363s, 1273m, 1221m, 1165m, 1076m, 1052m, 999m, 912m, 814s, 740s, 768s, 689s, 666s, 553m, 472m cm^{-1}; Anal. Calcd. for $C_{16}H_{14}S_2$: C, 71.07; H, 5.22. Found: C, 70.92; H, 5.18.

6, 6-Di(2, 2'-bithienyl)pentafulvene **69d**: Orange leaflets (CH_2Cl_2-hexane); m.p. 100.5-101 °C; MS (EI, 70 eV) m/z 406 (M^+, 100%), 373 (30%), 354 (10%), 279 (5%), 179 (10%), 127 (30%), 99 (42%), 81 (18%), 44 (5%), 18 (5%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.20-7.25 (m, 6H), 7.17 (d, J = 4.0 Hz, 2H), 7.01 (dd, J = 5.0, 3.7 Hz, 2H), 6.57-6.61 (m, 4H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 143.14, 142.42, 141.35, 136.77, 135.44, 133.93, 132.43, 128.04, 125.37, 124.47, 123.84, 123.72; IR (KBr) *v* 3100m, 1558s, 1431s, 1362s, 1224m, 1082m, 1046m, 997m, 912m, 842s, 805s, 787s, 768s, 697s, 464m cm^{-1}; Anal. Calcd. for $C_{22}H_{14}S_4$: C, 64.99; H, 3.47. Found: C, 64.81; H, 3.40.

6, 6-Di(n-butyl)pentafulvene **69e**: Pale yellow oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.44-6.51 (m, 4H), 2.53 (t, J = 7.7 Hz, 4H), 1.49-1.60 (m, 4H), 1.30-1.43 (sextet, J = 6.9 Hz, 4H), 0.93 (t, J = 7.3 Hz, 6H).

1, 2-Benzo-6, 6-diphenylpentafulvene ***70***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 710 mg (4.8 mmol) of N, N-dimethylbenzamide and 10 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -70 °C, and 3 mL (5.4 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added dropwise via syringe through the septum. The mixture was allowed to warm up to 0 °C, and stirried for 1 h. Indene (1.5 mL, 12 mmol) was added at 0 °C, and the mixture was allowed to warm up to room temperature, and stirred overnight. The reaction mixture was added with water and extracted with hexane. The combined organic layer was washed with water and

brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C, eluted with 10% benzene/hexane) to give 1003 mg of **70** (75%).

70: Yellow crystals; m.p. 109-110 °C (lit.[5] 111-112 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.28-7.45 (m, 11H), 7.13 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 5.6 Hz, 1H), 6.83 (d, J = 7.3 Hz, 1H), 6.65 (d, J = 5.6 Hz, 1H), 6.59 (d, J = 7.9 Hz, 1H).

Application to the Wittig Reaction. 1, 1-Diphenylethylene ***71***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 350 mg (2.3 mmol) of N, N-dimethylbenzamide and 8 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -70 °C, and 1.5 mL (2.4 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added dropwise via syringe through the septum. The mixture was allowed to warm up to 0 °C, and stirried for 1 h. Methyltriphenylphosphonium iodide (950 mg, 2.3 mmol) was added in one portion. The colorless suspension was allowed to warm up to room temperature, and stirred overnight. Hexane was added, and the mixture was filtered. The filtrate was evapolated in vacuo, and the residue was separated by column chromatography on silica gel (30 g, eluted with hexane) to give 389 mg of **71** (94%).

71: colorless oil; ^{1}H-NMR (60 MHz, CCl_4) δ 7.2 (brs, 10H), 5.2 (s, 2H).

3-5. References

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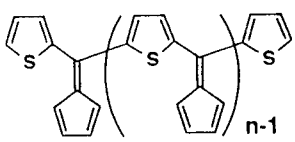
Chapter Four

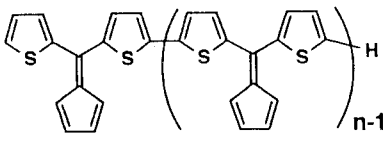
Synthesis and Properties of Oligo-6-(2-thienyl)pentafulvenes and Related Oligothienylpentafulvenes

4-1. Introduction

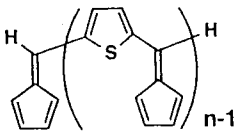
Based on the information obtained in the previous two chapters, I designed the synthetic route to oligo-6-(2-thienyl)pentafulvenes **42**, and was successful in synthesizing systematically up to tetramer **42d.** Furthermore, both oligofulvenes inserted with bithiophene, namely oligo[6, 6-di(2-thienyl)pentafulvene]s **45**, and oligothienylfulvenes having hydrogen atom on the terminals **46** were also prepared up to tetramer and trimer, respectively. In this chapter, I describe the details of the synthesis and properties of these oligofulvenes.



42



45



46

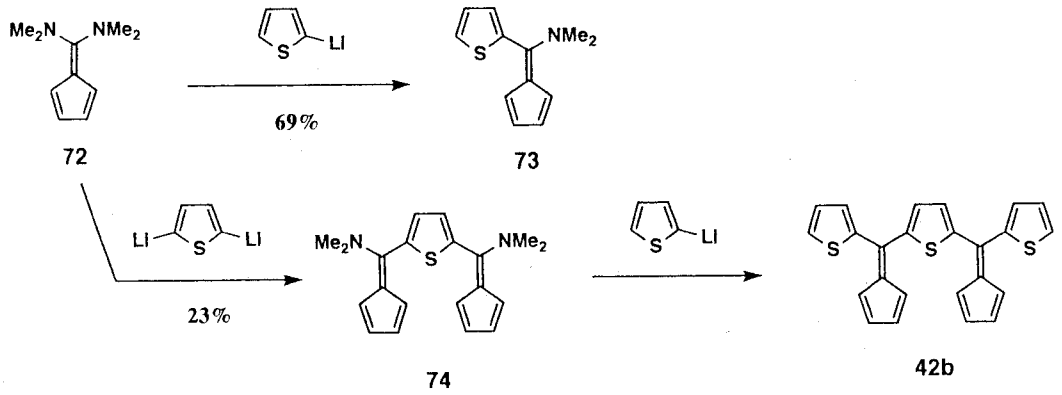
a : n = 1, b : n = 2, c : n = 3, d : n = 4

4-2. Synthetic Strategies

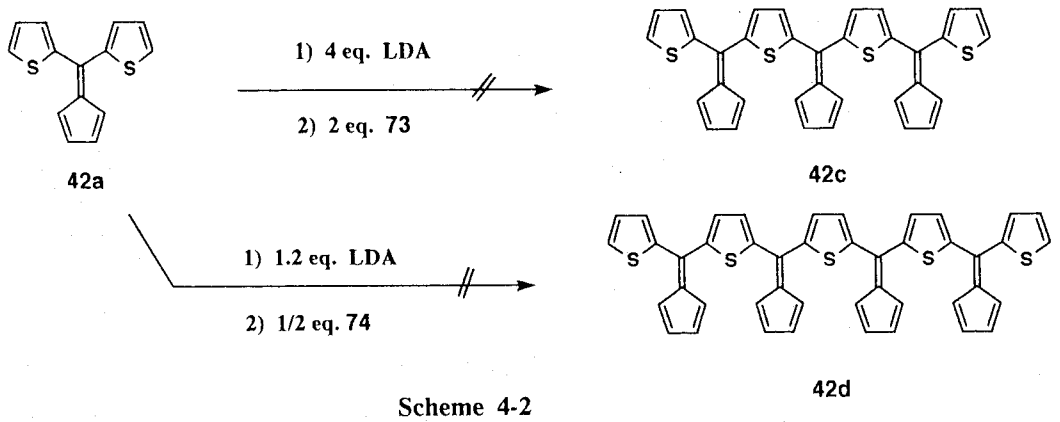
There can be considered three pathways for the synthesis of oligo-6-(2-thienyl)pentafulvene **42**. The key reactions of these pathways are (1) the nucleophilic substitution on 6-dimethylaminopentafulvenes, (2) the condensation of ketones with cyclopentadienyl anion, and (3) the new pentafulvene synthesis described in the previous chapter.

Hafner *et al.* reported that 6-dimethylaminopentafulvenes are useful precursors to 6-substituted pentafulvenes through formally nucleophilic substitution reactions because of their polarized properties[1]. Morikawa in our laboratory examined an application of this method in the synthesis of **42**[2]. 6-Dimethylamino-6-(2-thienyl)pentafulvene **73**[3] was prepared from 6, 6-

bis(dimethylamino)pentafulvene **72**[14] and 2-thienyllithium in 69% yield; however, bis-pentafulvene **74** was obtained in only 23% yield from **72** and 2, 5-dilithiothiophene. Transformation of **74** to **42b** by reaction with two equivalents of 2-thienyllithium was possible, but the yield was poor (Scheme 4-1). In addition, attempted syntheses of **42c** by reaction of **73** and the dilithio compound from **42a**, and **42d** by reaction of **74** and the monolithio compound from **42a** were unsuccessful (Scheme 4-2). The reason for the failure may be ascribed to rather poor reactivity of **73** and **74** toward nucleophiles (the dimethylamino group electronically stabilizes pentafulvene systems and hence decreases the reactivity of these compounds) as well as poor nucleophilicity of the mono- and di-lithio derivatives of **42a**.

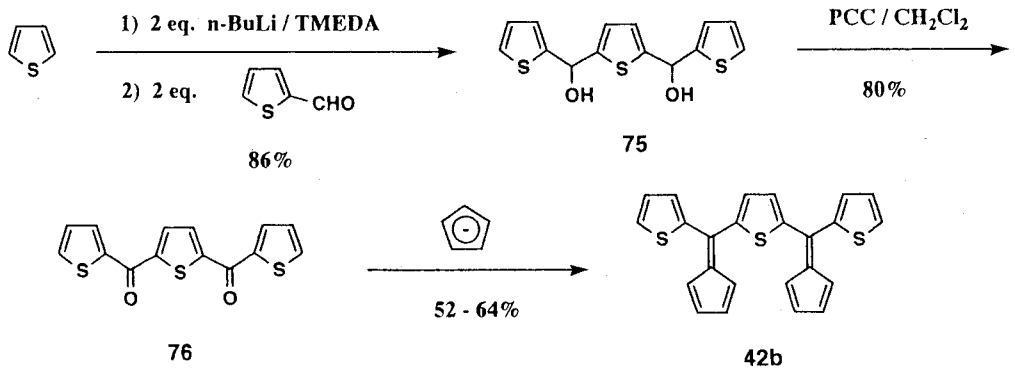


Scheme 4-1

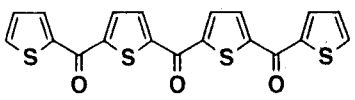


Scheme 4-2

The synthetic strategy based on the condensation of ketones and cyclopentadienyl anion also met some difficulties. Diketone **76**[5], prepared by reaction of 2, 5-dilithiothiophene and 2-formylthiophene followed by oxidation of resulting diol **75** with pyridinium chlorochromate (PCC), afforded **42b** in 52-64% yield (Scheme 4-3). A problem was much lower solubility of **76** than that of di(2-thienyl)ketone in organic solvents; thus, triketone **77**[6] would be even less soluble and have solubility problem in the condensation with cyclopentadienyl anion. In fact, the synthesis of **77** gave poorly soluble solids which were difficult to purify.



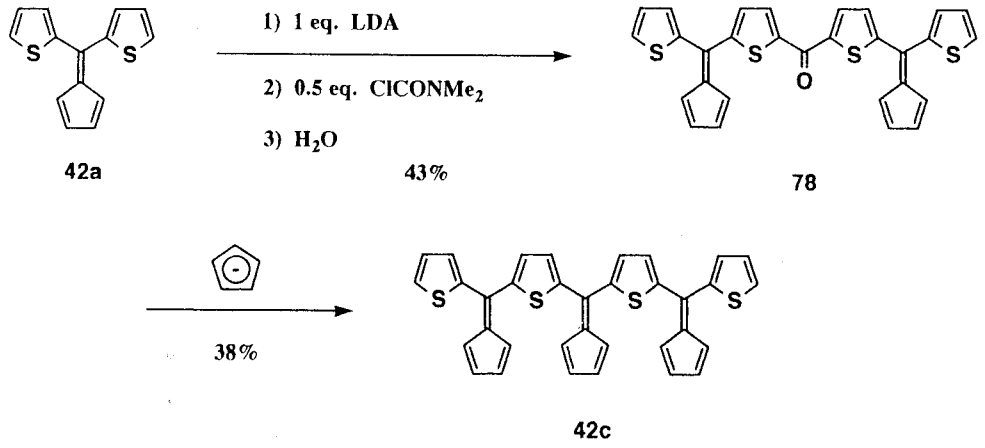
Scheme 4-3



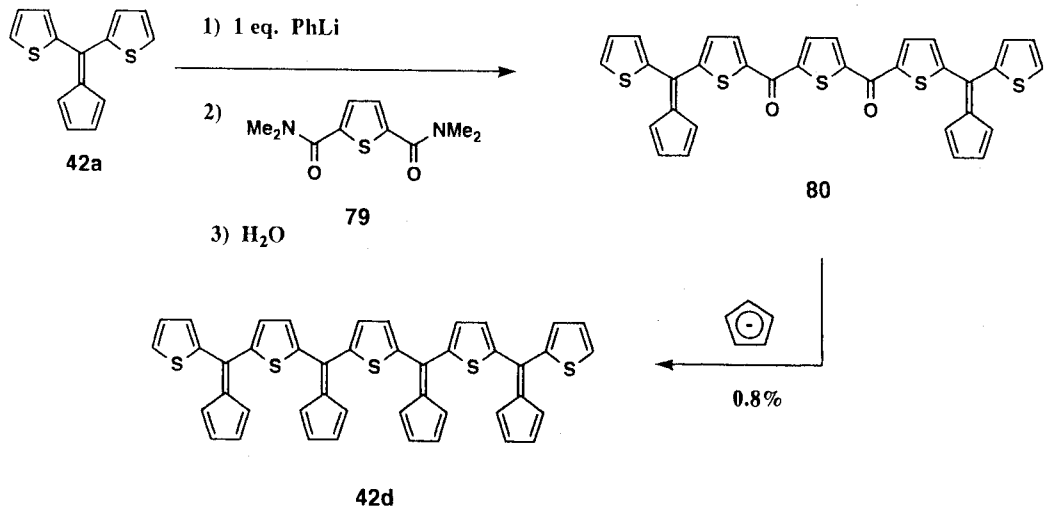
77

Therefore, an application of the ketone synthesis through the reaction of N, N-dialkylamides[7] was next examined using **42a**. The reaction of dimethylcarbamyl chloride and two equivalents of monolithio derivative of **42a** gave monoketone **78** in 43% yield. Compound **78** afforded trimer **42c** in 38% yield by condensation with cyclopentadienyl anion (Scheme 4-4)[2b]. Owing to electron-withdrawing property of the carbonyl group, however, **78** is rather unstable and has difficulties in handling; this suggests a stability problem of precursor ketones for the synthesis of higher oligomers by this method. In fact, diketone **80** prepared from **42a** and N, N, N', N'-tetramethyl-2, 5-thiophenedicarbamide **79** was too unstable to be isolated.

Addition of cyclopentadienyl anion to the crude product mixture produced **42d** in only 0.8% yield (Scheme 4-5).



Scheme 4-4

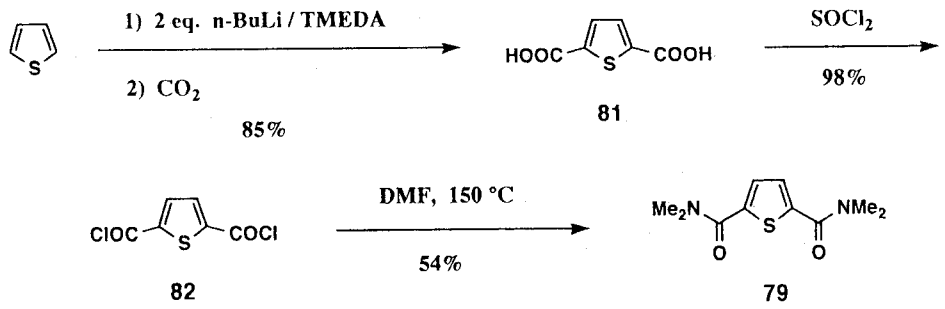


Scheme 4-5

It was for this reason why the new pentafulvene synthesis described in Chapter 3, which does not require isolation of the precursor ketones, was developed, and the method turned out most successful for the present purpose. This method allowed one-pot synthesis of **42b**, **42c**, and **42d**. The details are described in the following section.

4-3. Synthesis of Oligo-6-(2-thienyl)pentafulvenes

N, N, N', N'-Tetramethyl-2, 5-thiophenedicarbamide **79**, which can be, together with 6, 6-di(2-thienyl)pentafulvene **42a**, an useful building block, was prepared as shown in Scheme 4-6. Dilithiation of thiophene with 2.2 equivalents of n-butyllithium/N, N, N', N'-tetramethylethylenediamine complex[8] followed by quenching with carbon dioxide (dry ice) afforded 2, 5-thiophenedicarboxylic acid **81**[9] in 85% yield. Compound **81** was transformed to the corresponding bis(acid chloride) **82**[9] with thionyl chloride (98% yield). Heating of **82** in N, N-dimethylformamide gave **79** as colorless crystals (54% yield).

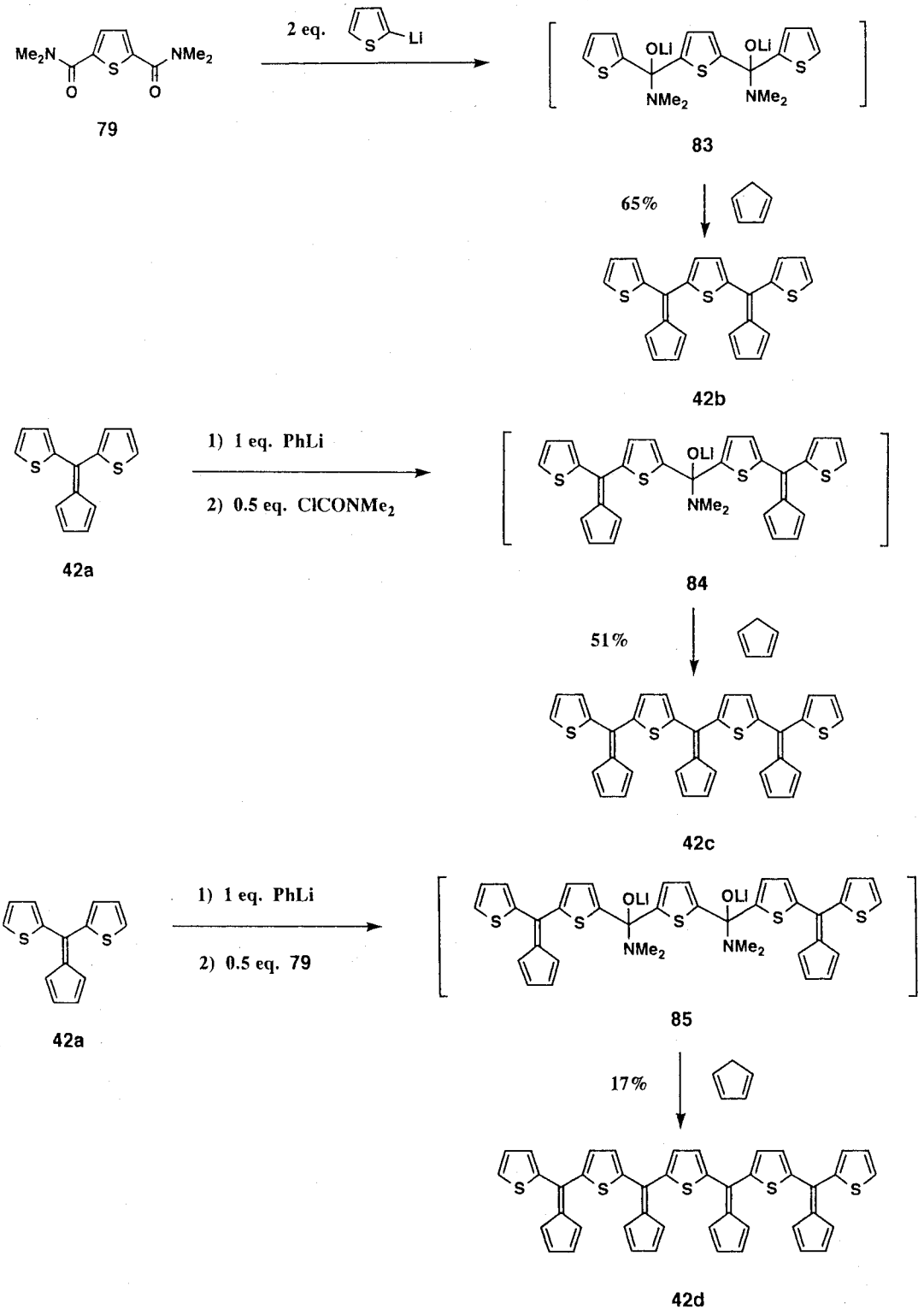


Scheme 4-6

Scheme 4-7 shows the successful synthesis of dimer **42b**, timer **42c**, and tetramer **42d** by the application of the new pentafulvene synthesis using **42a** and **79**.

Reaction of **79** and two equivalents of 2-thienyllithium followed by addition of excess cyclopentadiene gave **42b** in 65% yield. Quenching with water, instead of cyclopentadiene, gave diketone **76** to indicate the intermediate formation of **83**.

For the synthesis of **42c**, monomer **42a** was first monolithiated by reaction with one equivalent of phenyllithium. Addition of a half equivalent of dimethylcarbamyl chloride and then cyclopentadiene to this solution afforded **28c** in 51% yield. Dimethylaminoalokoxyl group of intermediate **84** should little affect electronically on pentafulvene π-system, differing from destabilization effect of carbonyl group; thus **42c** was obtained in moderate yield.


Me2N
NMe2
O
O
S
79
2 eq.
Li
OLi
NMe2
83
65%
42b
1) 1 eq. PhLi
2) 0.5 eq. ClCONMe2
42a
84
51%
42c
1) 1 eq. PhLi
2) 0.5 eq. 79
42a
85
17%
42d

Scheme 4-7

In similar way, **42d** could be synthesized via reaction of **79** and two equivalents of the monolithio derivative of **42a**, through **85**, in 17% yield. Compound **42d** is rather unstable, and tends to decompose upon concentration of its solution above room temperature; thus, **42d** was purified by column chromatography on silica gel at 0 °C and separated as crystalline substance from the carefully concentrated solution without external heating. Because of the increased instability and the decreased yield of **42d**, no attempt to synthsize higher oligomers has been made.

4-4. Physical Properties of Oligo-6-(2-thienyl)pentafulvenes

The oligofulvenes **42b-d** are dark red crystalline substances with fair to moderate stability, and were identified by mass and ^{1}H-NMR spectra. The stability, however, decreases with increase of unit number, and in particular, **42d** is considerably unstable as described in the previous section. The decrease of stability may be due to the electron-withdrawing property of cyclopentadienylidene group. Because cyclopentadienyl anion shares aromatic stabilization as a 6π-electron system, cyclopentadienylidene group has a property of electron acceptor.

^{1}H-NMR Spectra

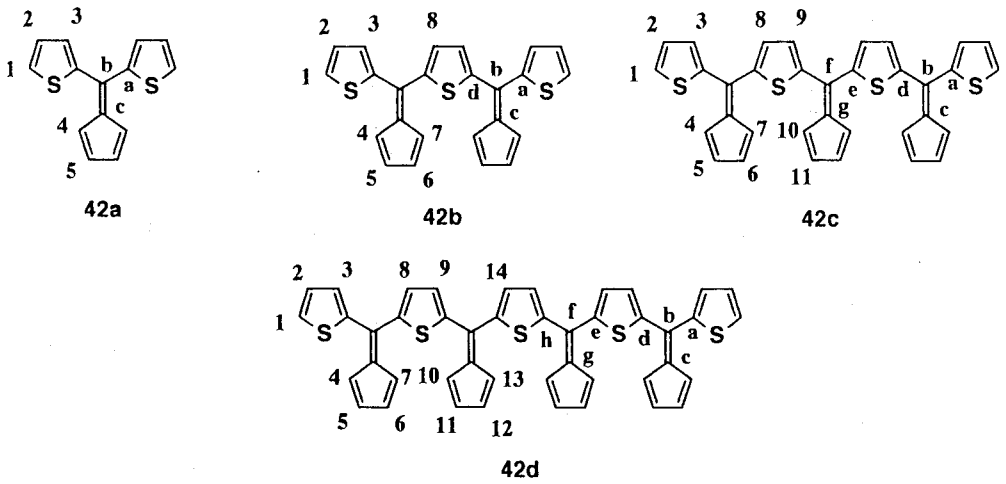


Figure 4-1. Numbering for NMR assignments.

Table 4-1. ^{1}H-NMR Chemical Shifts (δ/ppm) and Assignments[a] of Oligo-6-(2-thienyl)pentafulvene **42a-d**

Compounds	H_1	H_3, H_{8-9}, H_{14}	H_2	H_4, H_{6-7} H_{10-13}	H_5
42a[b]	7.52 (dd, J = 5.1, 1.1 Hz, 2H)	7.26 (dd, J = 3.7, 1.1 Hz, 2H)	7.10 (dd, J = 5.1, 3.7 Hz, 2H)	6.57-6.59 (m, 2H)	6.53-6.54 (m, 2H)
42b[c]	7.56 (dd, J = 5.0, 1.3 Hz, 2H)	7.30 (dd, J = 3.6, 1.3 Hz, 2H) 7.27 (s, 2H)	7.13 (dd, J = 5.0, 3.6 Hz, 2H)	6.58-6.61 (m, 6H)	6.49-6.51 (m, 2H)
42c[d]	7.61 (dd, J = 5.1, 1.3 Hz, 2H)	7.34 (d, J = 3.8 Hz, 2H) 7.33 (dd, J = 3.7, 1.3 Hz, 2H) 7.31 (d, J = 3.8 Hz, 2H)	7.16 (dd, J = 5.1, 3.7 Hz, 2H)	6.57-6.63 (m, 10H)	6.49-6.51 (m, 2H)
42d[d]	7.60 (dd, J = 5.1, 1.3 Hz, 2H)	7.41 (d, J = 4.0 Hz, 2H) 7.35 (s, 2H) 7.34 (d, J = 4.0 Hz, 2H) 7.33 (dd, J = 3.7, 1.3 Hz, 2H)	7.16 (dd, J = 5.1, 3.7 Hz, 2H)	6.58-6.63 (m, 14H)	6.49-6.51 (m, 2H)

[a] See Fig. 4-1 for numbering of the protons. [b] 400MHz, $CDCl_3$. [c] 270 MHz, $CDCl_3$. [d] 400 MHz, CD_2Cl_2.

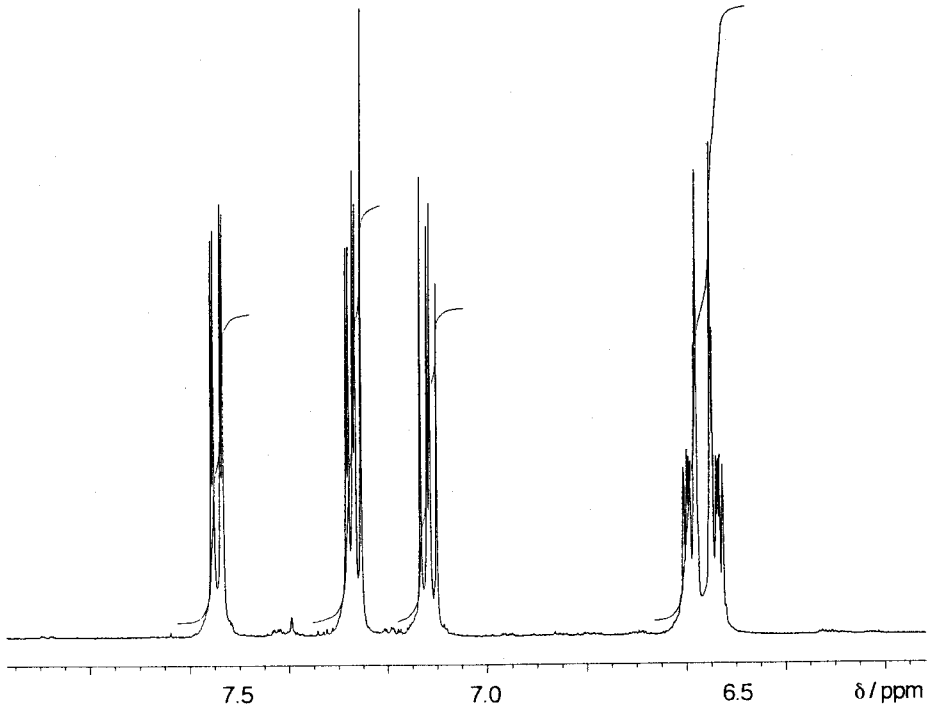


Figure 4-2. ^{1}H-NMR spectrum of **42a**.

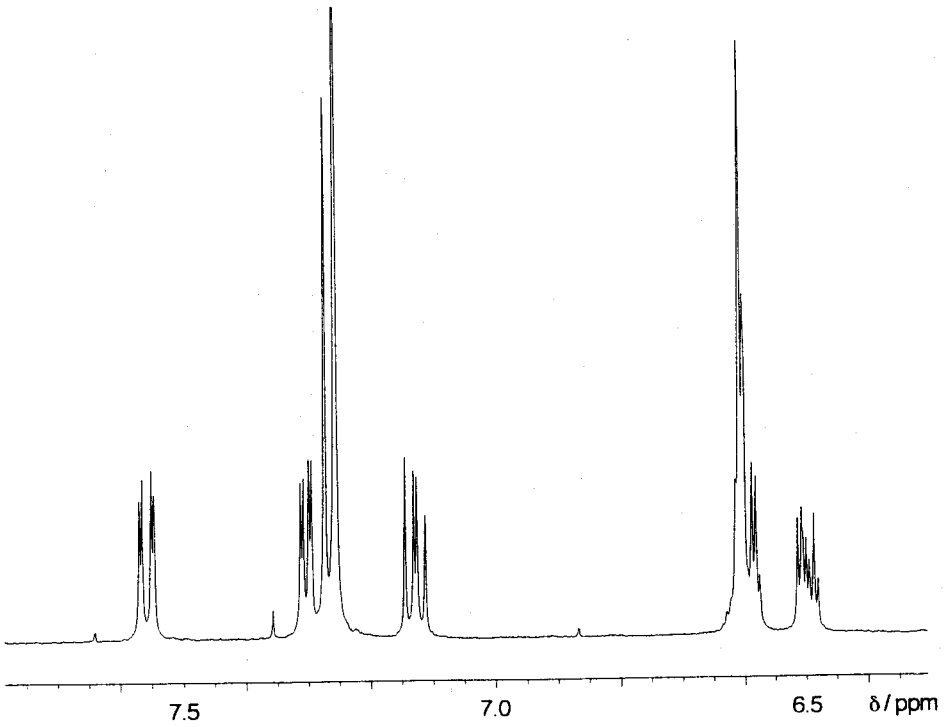


Figure 4-3. ^{1}H-NMR spectrum of **42b**.

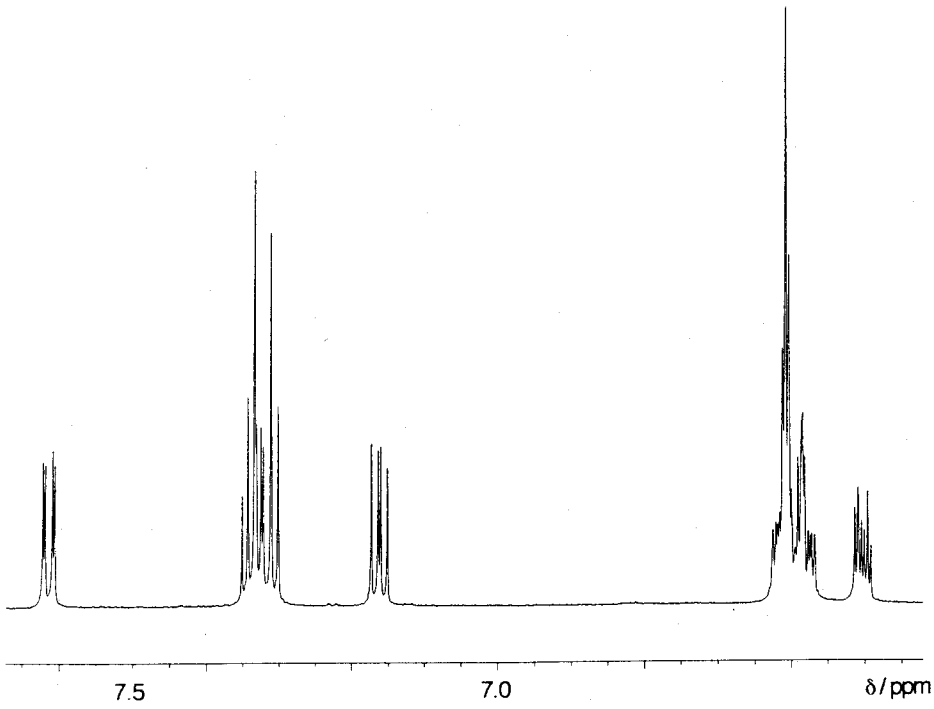


Figure 4-4. ^{1}H-NMR spectrum of **42c**.

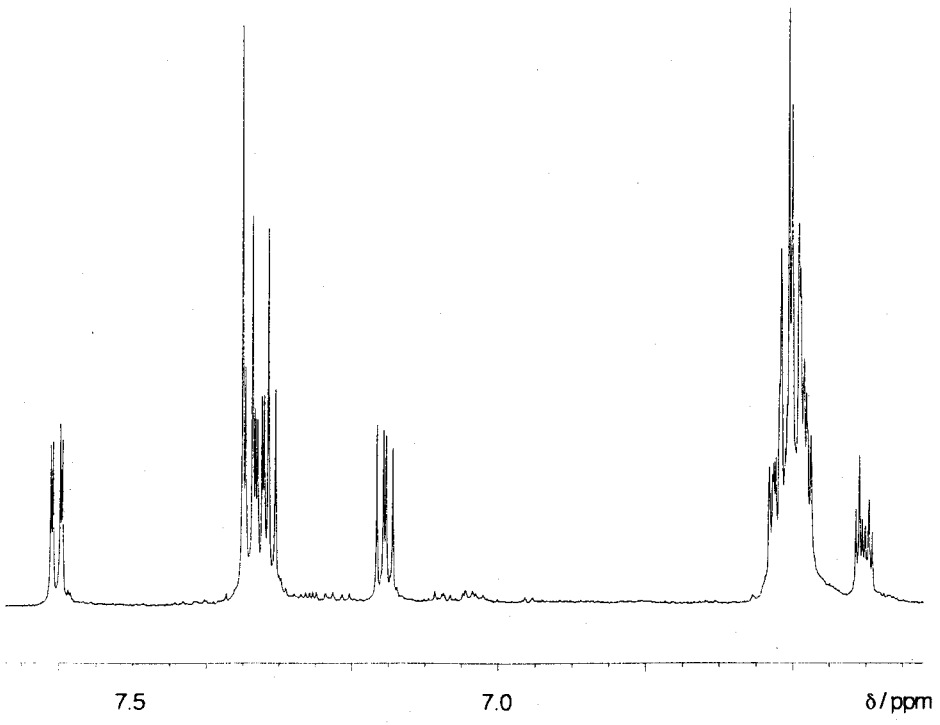


Figure 4-5. ^{1}H-NMR spectrum of **42d**.

Table 4-1 summarizes ^{1}H-NMR data and assignment of **42a - d** and Figure 4-2 to 4-5 show their spectra. The numbering for the assignments are shown in Figure 4-1. ^{1}H-NMR spectra support the C_2 symmetry of the molecules, and show similarity each other. The signals of double-doublet observed at the lowest magnetic field (7.5-7.6 ppm) are assigned to the protons at 5-position of the terminal thiophene rings (H_1). The double-doublets at 7.1-7.2 ppm are assigned to 3-position protons of the terminal thiophene rings (H_2). The other protons of thiophene rings (H_3, $H_{8\text{-}9}$, H_{14}) appear closely at 7.25-7.4 ppm. The protons on the pentafulvene moieties are observed at 6.5-6.7 ppm region. In **42b-d**, signals corresponding to two hydrogens appear out of other pentafulvene protons at higher field. These signals can be assigned to the outer-2-positon protons of the terminal pentafulvene moieties (H_5). It is generally known that 2-position protons appear at higher field than 1-position protons in 6, 6-disubstituted pentafulvenes[10]. The inner-2-position protons should shift to lower magnetic field owing to larger anisotropic effect by other pentafulvene rings.

^{13}C-NMR Spectra

^{13}C-NMR spectra also well reflect the structure of the oligomers **42a-d.** Figure 4-6 to 4-9 show their proton-decoupled spectra. In **42a**, **42b** and **42c**, the number of observed signals agrees with the expected number for these C_2 symmetric molecules: eight, twelve and eighteen signals are observed, respectively. Although twenty-two signals are expected for **42d**, the observed number is twenty. This is probably due to overlapping of signals because of the similarity of partial structures.

Table 4-2 summarizes ^{13}C-NMR chemical shifts and assignments of **42a-d**. The assignments of the tertialy carbons of **42a-c** are achieved by their 2D CH-COSY spectra. The signals of **42d** are assigned by the analogy from **42a-c**. In **42d**, the two signals are probably overlapped on the signal at 133.59 ppm, and the signal at 132.97 ppm may also involve the two signals, judging from their half widths and the comparison with the spectrum of **42c**. Almost no difference in the chemical shifts is seen among the oligomers.

Table 4-2. ^{13}C-NMR Chemical Shifts[a] and Assignments[b] of **42a - d**

	42a	**42b**	**42c**	**42d**
C_1	130.06	130.17	130.23	130.24
C_2	127.16	127.25	127.28	127.30
C_3	132.83	132.93	132.90	132.91
C_8, C_9 or C_{14}		132.18	132.98 132.81	132.97[c], 132.87 132.81
C_4, C_7, C_{10} or C_{13}	132.48	133.17 132.88	133.49, 133.22 132.93	133.59[d], 133.29 132.97[c]
C_5	124.05	124.24	124.23	124.25
C_6, C_{11}, or C_{12}		123.72	123.85 123.68	123.91, 123.89 123.69
C_a	143.22	142.55	142.45	142.51
C_d, C_e, or C_h		147.58	147.70 146.80	147.79, 146.99 146.75
C_b or C_f	143.44	144.10	144.59 144.11	144.75 144.22
C_c or C_g	136.17	135.43	135.28, 134.67	135.28 134.57

[a] 67.8 MHz, in $CDCl_3$, at 30 °C, δ / ppm, referenced to the solvent signal; 77.02 ppm. [b] See Fig 4-1 for numbering of the carbons. [c] The overlapping signal. [d] Involving two signals.

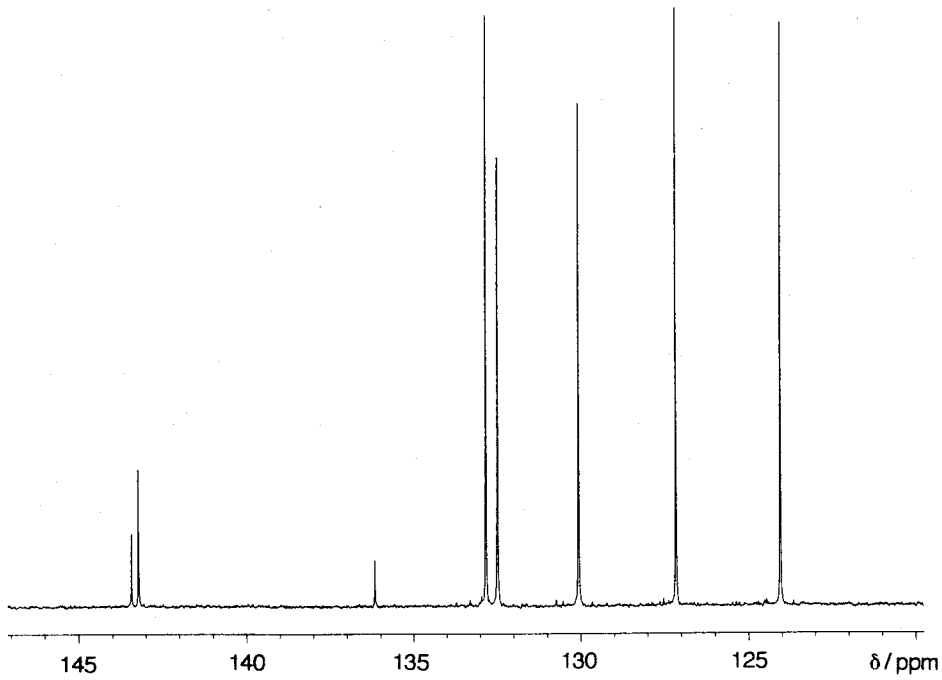


Figure 4-6. ^{13}C-NMR spectrum of **42a**.

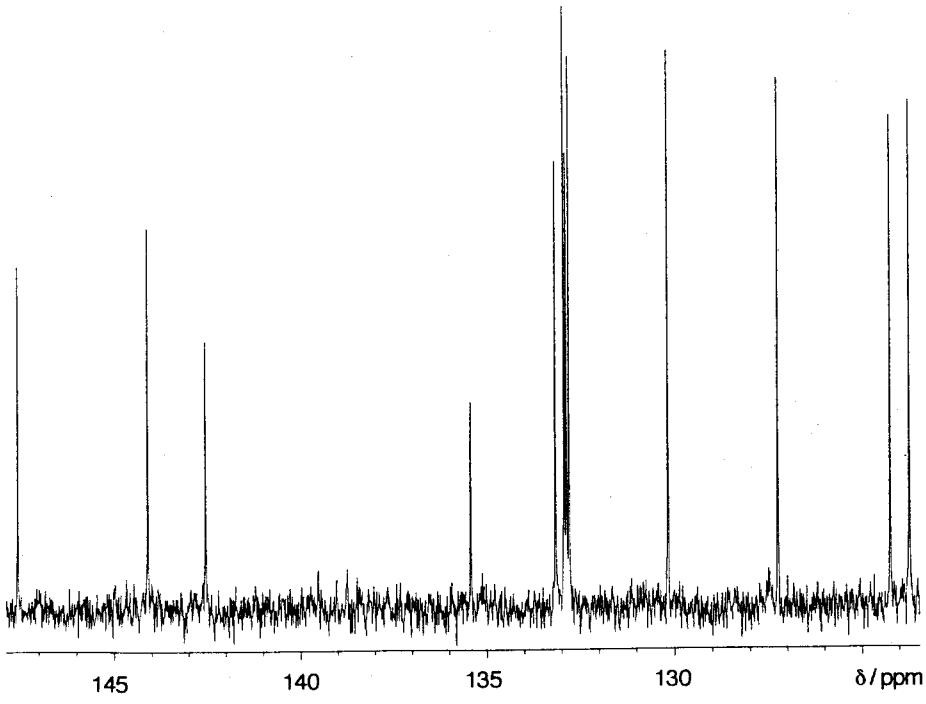


Figure 4-7. ^{13}C-NMR spectrum of **42b**.

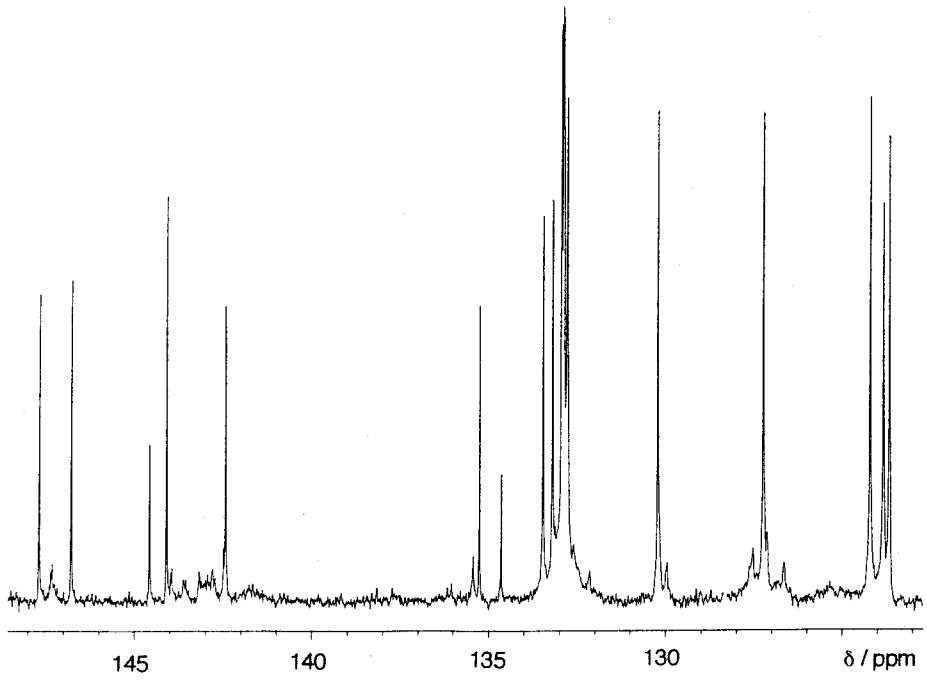


Figure 4-8. ^{13}C-NMR spectrum of **42c**.

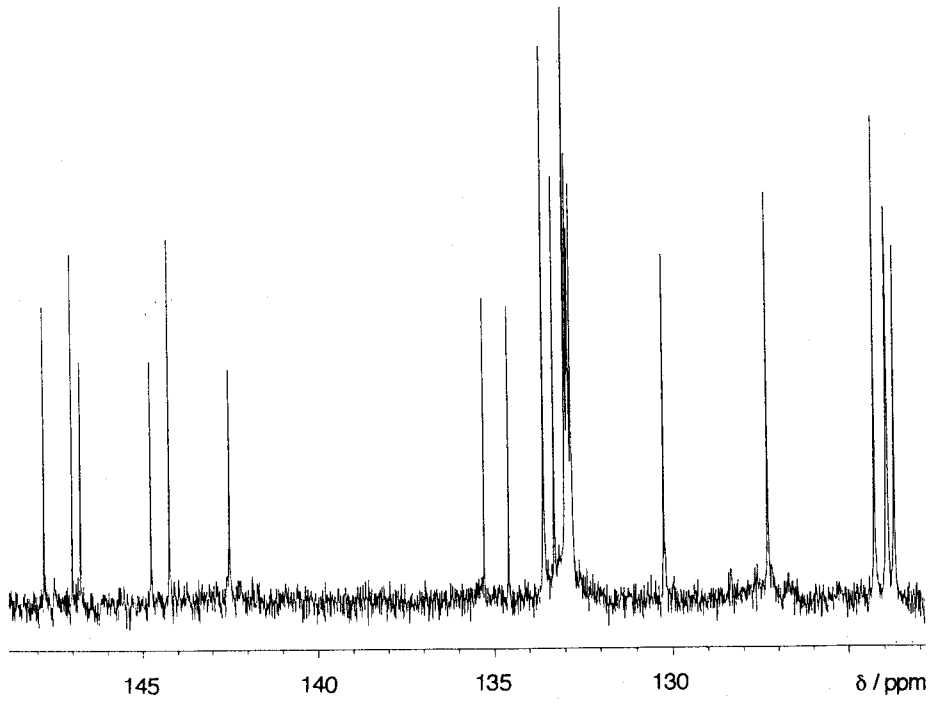


Figure 4-9. ^{13}C-NMR spectrum of **42d**.

The tertialy carbons of pentafulvene moieties are observed at clearly separated two regions: the signals at 123-125 ppm which are assigned to the carbons of 2-position of the five-membered rings and the signals at 132-134 ppm which are assigned to the carbons of 1-position. The difference of these chemical shifts ($\Delta\delta \cong 9$ ppm) is larger than those of 6, 6-diphenylpentafulvene (129.6 and 125.4 ppm, $\Delta\delta = 4.2$ ppm) to reflect that the charge destribution of **42a-d** slightly differ from diphenylpentafulvene. Degree of contribution of dipolar structure to pentafulvenoids can be estimated from the averaged chemical shifts of tertialy carbons of cyclopentadienylidene moiety[11]. Resonance contribution of dipolar structure increases electron density of the five-membered ring leading to smaller values (higher fields) of the averaged chemical shift. The corresponding values of **42a-d** are 128.0-128.6 ppm. This is larger than those of 6, 6-dimethylpentafulvene[11] ($\delta_{av} = 125.7$) and sesquifulvalene[12] ($\delta_{av} = 124.3$), and is comparable to 6, 6-diphenylpentafulvene[11, 13] ($\delta_{av} = 127.5$). Therefore, the contribution of dipolar structure is estimated to be small judging from the avaraged chemical shifts of the pentafulvene moieties.

All of the quaternary carbons appear at the region of 135-150 ppm. The signals observed at the regions of 135-136 ppm and 144-145 ppm can be assigned to the carbons of the exocyclic double bond of pentafulvene framework, because the number of signals increases from each one in **42a** and **42b** to each two in **42c** and **42d**. Taking account of a dipolar structure of pentafulvene, the signals at lower magnetic field are assigned to C_b or C_f (See Fig. 4-1), and the signals at higher magnetic field to C_c or C_g. Similarly, the signals at 147-150 ppm region are assigned to the inner-thiophene ring carbons, C_d, C_e, or C_h, bacause of the increase of the number of signals; **42a**: none, **42b**: one, **42c**: two, **42d**: three. The signals at 142-143 ppm are asigned to the terminal-thiophene ring carbons, C_a, because of no change of the number of signals through **42a** to **42d**.

Electronic spectra

Table 4-4 and Figure 4-10 show electronic spectral data and spectra of **42a-d**. Electronic spectra of pentafulvenes have been well investigated, and it is known that they have two

Table 4-4. Electronic Spectral Data of Oligo-6-(2-thienyl)pentafulvenes **42a - d**

compound	λ_{max} (log ε) in CH_2Cl_2		
42a	373 (4.30)	277(3.90)	
42b	415 (4.36)	368 (4.40)	287 (4.05)
42c	409 (4.62)	368 (4.57)	290 (4.26)
42d	408 (4.76)	365sh (4.67)	289 (4.38)

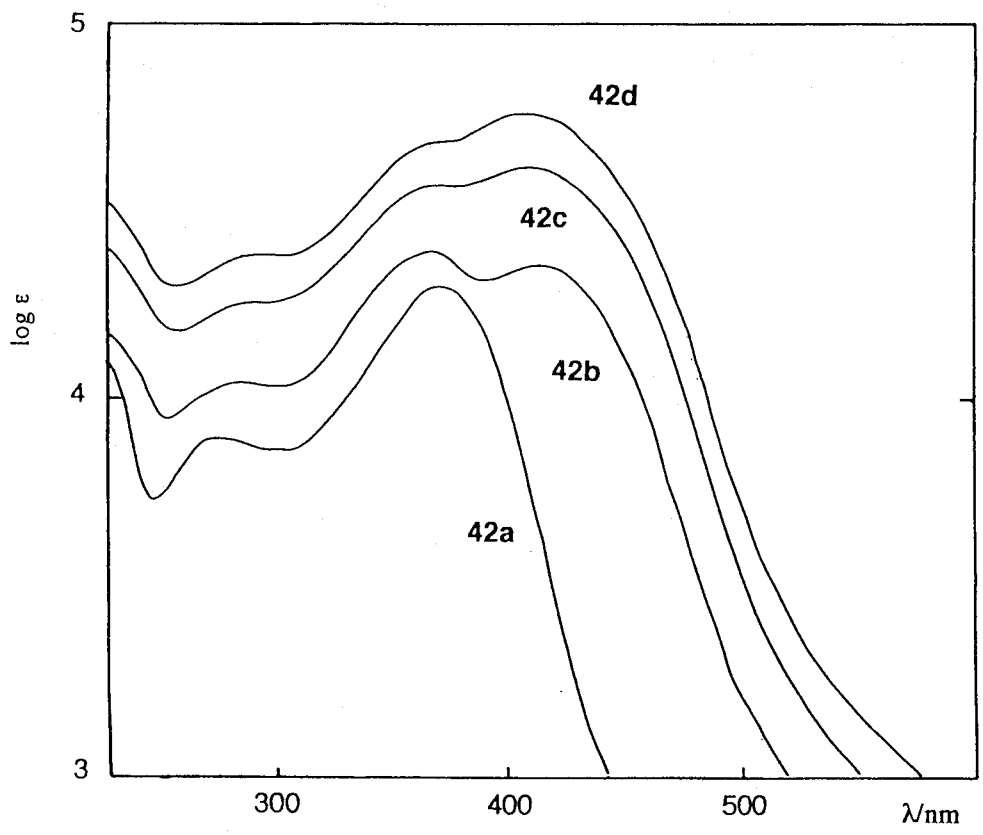


Figure 4-10. Electronic spectra of **42a-d.**

characteristic absorption bands: A_1 band is strong at 240-300 nm (log $\varepsilon \cong$ 4-4.5) and B_2 band is weak at 360-400 nm (log$\varepsilon \cong$ 2-3)[14]. The absorptions correspond to a SHOMO-LUMO and a HOMO-LUMO transition, respectively. The electronic spectrum of **42a** [373 nm (log ε = 4.3) and 277 (log ε = 3.9)], however, shows a considerably different absorption pattern from the typical pattern. The weak B_2 band seems to be hidden in the strong A_1 band at 373 nm. The strongest absorption of **42a** is at about 40 nm longer than that of 6, 6-diphenylpentafulvene (λ_{max} = 327, 244 nm in dichloromethane). This bathochromic shift is probably due to the electron-donating property of 2-thienyl group which extends the conjugation through the sulfur atom. The dimer **42b** absorbs visible light at about 40 nm longer wave length (λ_{max} = 415 nm) than **42a** does (373 nm), suggesting that conjugation between the two pentafulvenes through the central thiophene ring is appreciable. However, further extension of the oligomer does not appreciably affect the absorption wavelengths and only increases absorption intensity. The lack of appreciable change may be due to the cross-conjugated structure of pentafulvene unit and the conformational mobility of the oligomer system. It is generally known that conjugation in cross-conjugated systems is less effective than in linearly conjugated systems.

It may be valuable to analyse conformations of oligomers **42b-d** either in solutions or in crystals. The amalysis in solutions will be difficult for these compounds, and unfortunately attempts to obtain single crystals suitable for X-ray crystallographic anlysis have been unsuccessful.

Electrochemical behavior

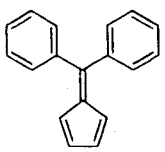
The most notable feature was observed in the redox potentials of **42a-d**. The electrochemical behaviors were studied by means of cyclic voltammetry. Table 4-5 summarizes reduction potentials of **42a-d** together with data of the related compounds and 5', 5"-disubstituted dithienylpentafulvene derivatives described in Chapter 2 and 3. Figure 4-11 shows cyclic voltammograms of **42a-d**. The monomer **42a** shows two pairs of reversible redox waves at -1.28 and -1.83 V, which should correspond to the formation of its radical anion and dianion, respectively. These values are smaller than those of 6, 6-diphenylpentafulvene **62a** (- 1.44 and

Table 4-5. Reduction Potentials[a] of **42a-d** and the Related Compounds by Cyclic Voltammetry

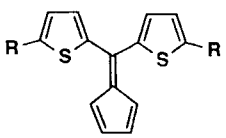
Compound	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$
42a[b]	- 1.28	- 1.83	
42b[b]	- 0.93	- 1.03	
42c[c]	- 0.81	- 1.29	-1.85
42d[c]	- 0.84	- 1.05	
62a[b]	- 1.44	- 2.01	
69c[b]	- 1.32	- 1.91*	- 2.30[d]
55g[b]	- 1.14	- 1.65	
55b[b]	- 1.06	- 1.53	
55d[b]	- 1.17	- 1.32	
69d[b]	- 1.16	- 1.61	- 2.04[d]
86	- 1.11[e]		

[a] V vs Ag/AgCl (calibration with ferrocene/ferrocenyl cation taken to have +0.52 V), in 0.1 M n-Bu4NClO4/DMF, sweep rate 100 mV/sec. [b] Measured at 20 °C.

[c] Measured at - 70 °C. d Peak potential. [e] - 1.63 V in the original paper (Fc/Fc^+ = 0.00 V)[16].



62a



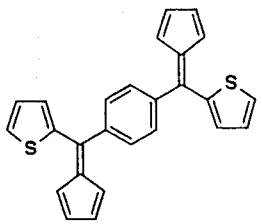
R = Me : 69c

R = SMe : 55g

R = SPh : 55b

R = Br : 55d

R = 2-thienyl : 69d



86

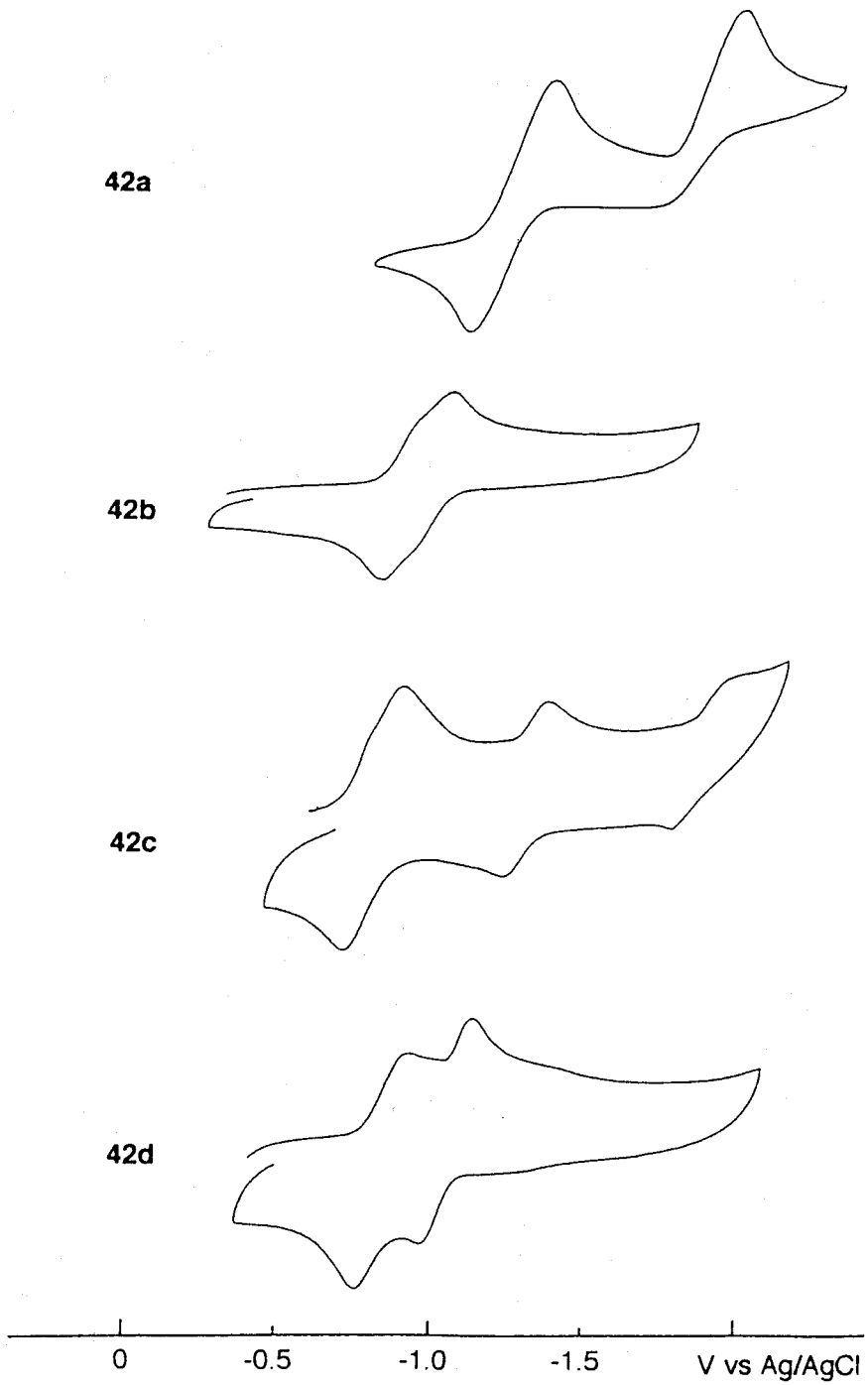
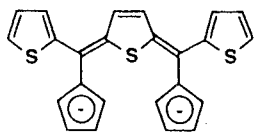


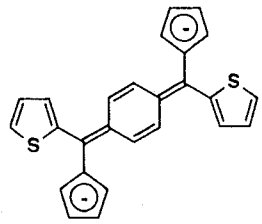
Figure 4-11. Cyclic voltammograms of **42a-d**.

-2.01 V)[15] to indicate stabilizing effects of the 2-thienyl groups on negative charge. Introduction of π-system (**55b** and **69d**) or weakly electron-withdrawing group (**55d**) at 5'-position of **42a** lowers reduction potentials in accordance with stabilizing effect of these groups. Particularly, the small E^2 value of the dibromo derivative **55d** suggests formation of a relatively stable dianion by decrease of electronic repulsion. On the other hand, introduction of alkyl group (**69c**) destabilizes the anionic species.

While **42a** shows well separated two reduction potentials, the redox waves of **42b** are nearly overlapping and their values, -0.93 and -1.03 V, are appreciably smaller than those of **42a**. This suggests ready formation of dianion $\mathbf{42b^{2-}}$. Quite recently, compound **86** was also reported to show one reversible redox wave at -1.11 V involving two electron migration to form of dianion $\mathbf{86^{2-}}$[16]. The lower potentials of **42a** indicate that dianion $\mathbf{42b^{2-}}$ having a thienoquinoid structure is more stable than dianion $\mathbf{86^{2-}}$ which has a benzoquinoid structure.

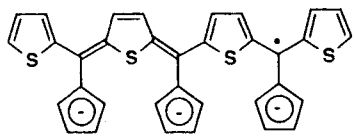


$\mathbf{42b^{2-}}$

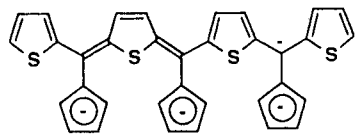


$\mathbf{86^{2-}}$

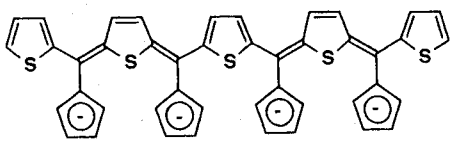
For the trimer **42c**, E^1 is even lower (- 0.81 V) with almost simultaneous two electron transfer, and E^2 and E^3 correspond to the formation of trianion radical $\mathbf{42c^{3-\bullet}}$ and tetraanion $\mathbf{42c^{4-}}$. Tetramer **42d** shows, similar to **42b**, only two redox waves of here each two electron transfer to indicate easy formation of tetraanion $\mathbf{42d^{4-}}$ having an oligoacetylene spine attached with cyclopentadienyl anions.



$\mathbf{42c^{3-\bullet}}$



$\mathbf{42c^{4-}}$

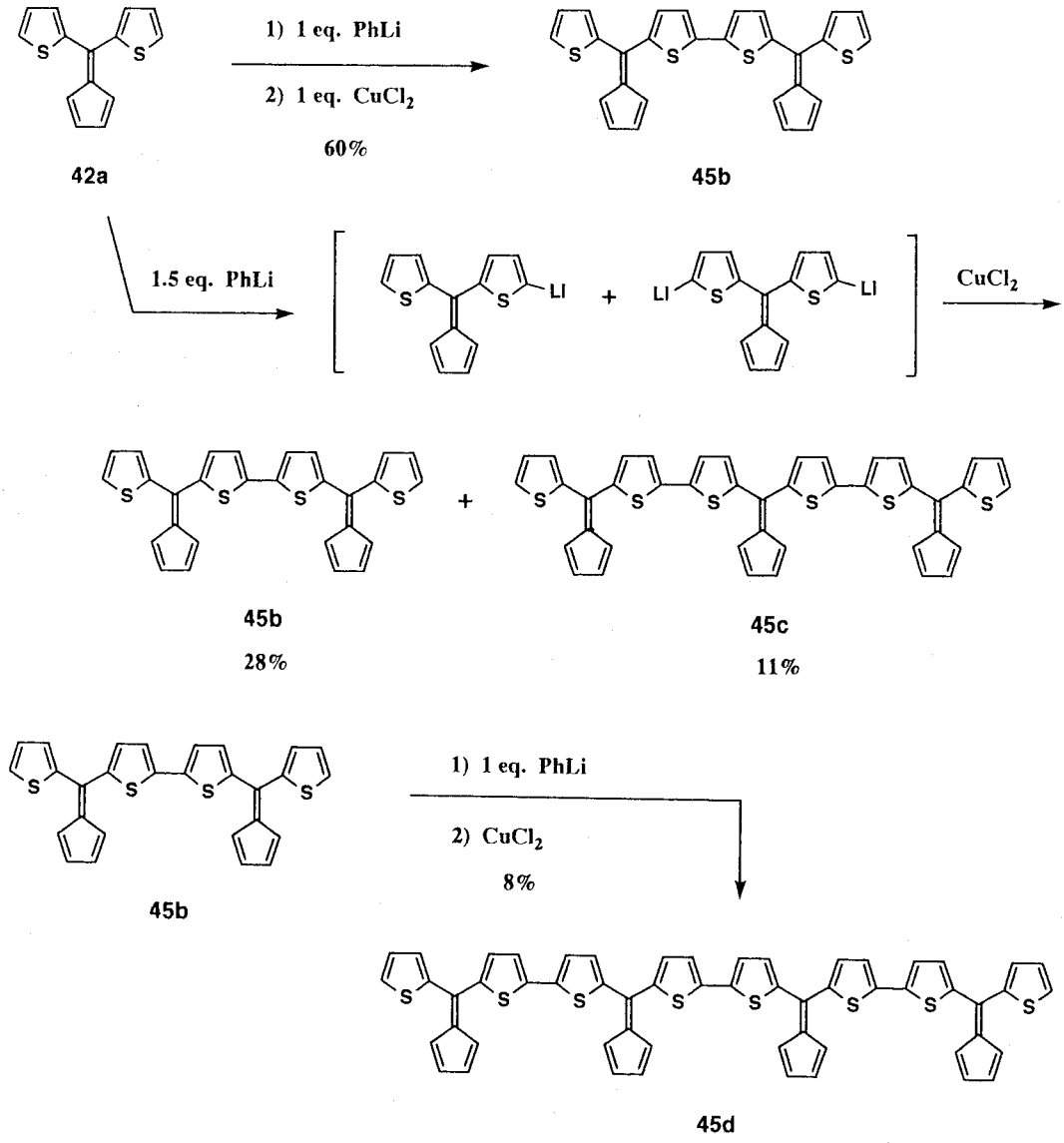


42d^{4-}

These results lead to the conclusion that oligo-6-(2-thienyl)pentafulvenes can indeed be reduced to polyanions with a modified polyacetylene spine. Thus, chemical reductions of **42a-d** are next of interest. In Section 4-9, generation and characterization of the anionic species from **42a-d** by alkali metal reduction will be described.

4-5. Synthesis of Oligo[6, 6-di(2-thienyl)pentafulvene]s

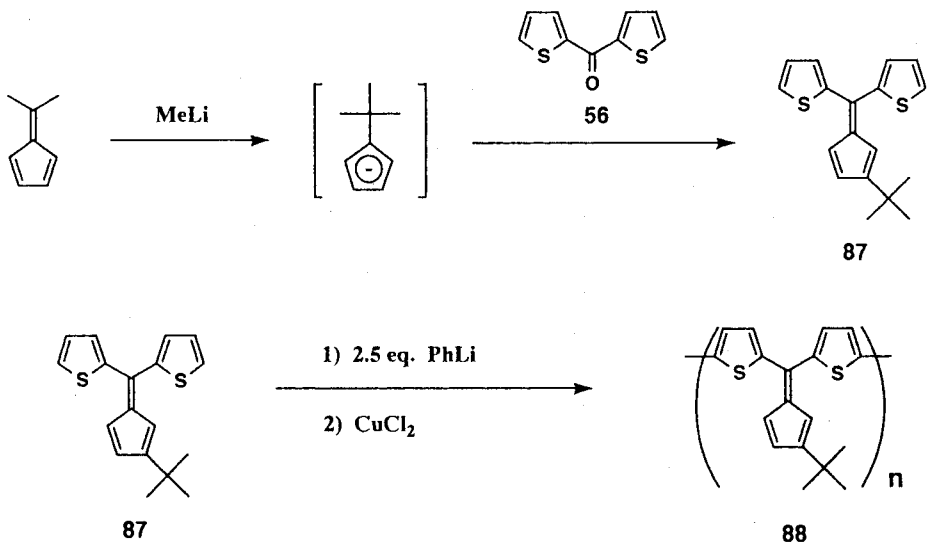
Oligo[6, 6-di(2-thienyl)pentafulvene]s **45** were synthesized by an oxidative coupling of **42a** via organocopper derivatives. Scheme 4-8 outlines the synthetic routes.



Scheme 4-8

Monolithio derivative of **42a**, prepared by the reaction with one equivalent of phenyllithium, was subjected to oxidative homo-coupling by treating with one equivalent of copper (II) chloride ($CuCl_2$)[17] to give bis[6, 6-di(2-thienyl)pentafulvene] **45b** in 60% yield. When 1.5 equivalents of phenyllithium, which should form a mixture of the mono- and di-lithio derivatives of **45a**, were used, similar treatment with $CuCl_2$ afforded trimer **45c** (11%) along with dimer **45b** (28%). In similar way, monolithiation and oxidative coupling of **45b** gave tetramer **45d** in 8% yield. The considerably low yield of **45d** may be due to poor stability and reactivity of the monolitio derivative of **45b**. The actual reason is not certain since no attempt for optimization of the reaction condition has been made.

Polymerization of **42a** should proceed by action of $CuCl_2$ to the dilithio derivative of **42a**. The polymerization was examined by use of t-butyl substituted dithienylpentafulvene **87** as a monomer, in order to increase stability[18] and solubility of the polymer to be formed (Scheme 4-9). Product analyses in regard to the degree of polymerization were undertaken by Prof. K. Müllen (Max-Planck-Institute for Polymer Research, Germany), and it turned out that the product **88** polymerized up to at most octamer (M_W = 2258) and pentamer was the major product (peak molecular weight = 1421). Now, synthesis of higher polymers is under attempt.



Scheme 4-9

4-6. Physical Properties of Oligo[6, 6-di(2-thienyl)pentafulvene]s

Oligopentafulvenes **45b-d** are dark red crystalline substances and fairly stable. Even tetramer **45d** is stable enough for usual handling at room temperature. Probably, the bithiophene unit inhibits conjugation through it and hence decreases destabilization caused by the electron-withdrawing property of cyclopentadienylidene group. This conversely suggests less favorable structure for generating polyanions with a modified polyacetylene spine.

^{1}H and ^{13}C-NMR data support the structure of the oligomers, and their spectral patterns tend to be similar to those of **42a-d** described in Section 4-4. However, defined ^{13}C-NMR data of **45d** were not obtained because of its extremely poor solubility.

Electronic Spectra

Figure 4-12 and Table 4-6 show electronic spectra and spectral data of **45b-d**, together with those of **42a**. The tendency of these spectra is similar to those of the oligomers **42a-d**; while the dimer absorbs at longer wavelength than the monomer, the trimer and tetramer display no bathochromic shift from the dimer.

Dimer **45b** absorbs at 33 nm longer than **42b** does (**45b**; λ_{max} =448 nm, **42b**; 415 nm). The bathochromic shift is apparently due to the extension of the π-system caused by insertion of a bithiophene unit. There is no appreciable difference in wavelength among dimer **45b**, trimer **45c**, and tetramer **45d** except for their absorption coefficient. This suggests that the bis-pentafulvene units in the oligomers would behave almost independently from an electronic structural point of view.

Electrochemical behavior

Table 4-7 summarizes reduction potentials of **45a-d** together with the data of the monomer **42a**. In dimer **45b**, only one reversible redox wave was observed at -0.93 V. This wave probably corresponds to a two-electron process similar to **42b**; accordingly dianion **45b**$^{2-}$

Table 4-6. Electronic Spectral Data of Oligo[6, 6-di(2-thienyl)pentafulvene]s **45b-d** and **42a**

Compound	λ_{max} (log ε) in CH_2Cl_2			
42a	373 (4.30)	277(3.90)		
45b	448 (4.57)	391 (4.44)	334 (4.36)	295 (4.16)
45c	446 (4.77)	365sh (4.5)	281 (4.32)	
45d	449 (4.98)	277 (4.48)		

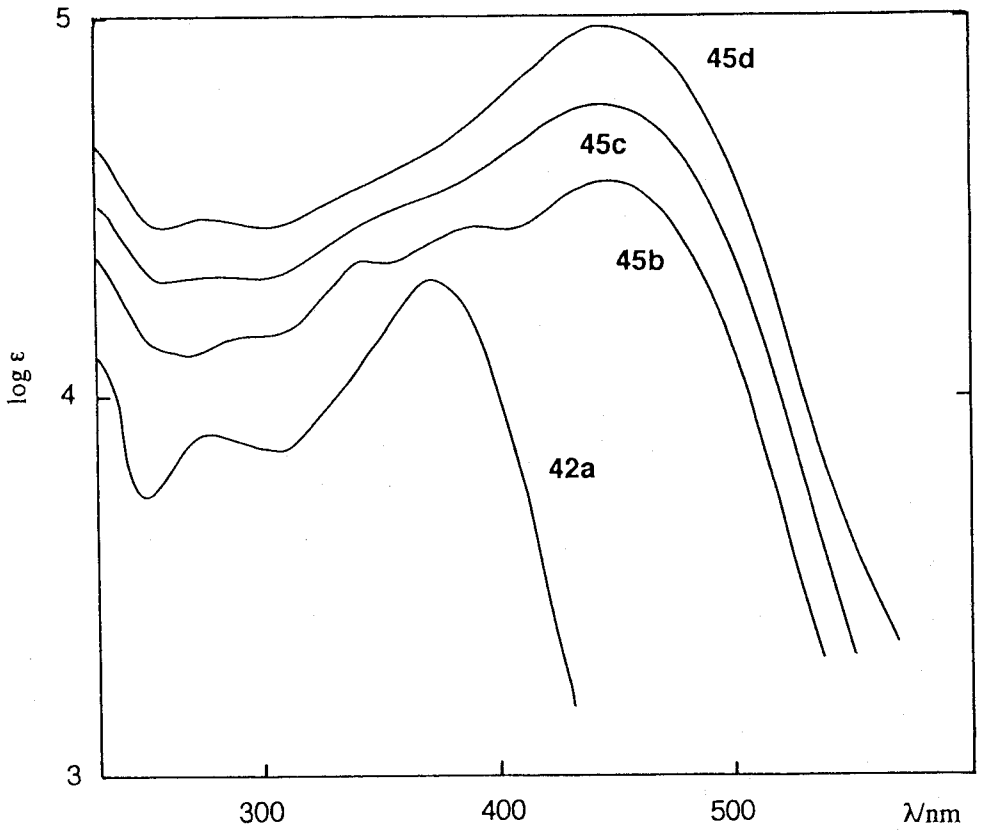


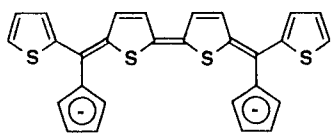
Figure 4-12. Electronic spectra of **45b-d** and **42a**.

should also be fairly stable. Trimer **45c** and tetramer **45d** also provided the results similar to **42c** and **42d**, respectively. E^2 and E^3 in **45c** correspond to the formation of trianion radical **45c**$^{3-\bullet}$ and tetraanion **45c**$^{4-}$, and E^2 in **45d** suggest the formation of the tetraanion **45d**$^{4-}$. As a whole, reduction behavior of **45b-d** are similar to those of **42b-d**.

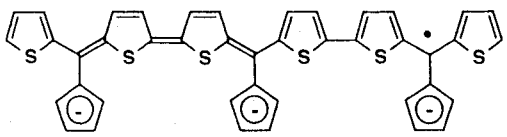
Table 4-7. Reduction Potentials of Oligo[6, 6-di(2-thienyl)pentafulvene]s **45b-d** and **42a** by Cyclic Voltammetry

Compound	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$
42a[b]	- 1.28	- 1.83	
45b[b]	- 0.93		
45c[c]	- 0.87	- 1.12	-1.56
45d[c]	- 0.85	- 1.04	

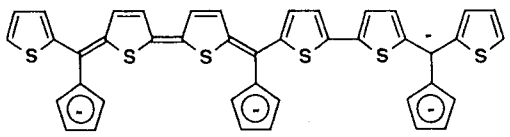
[a] V vs Ag/AgCl (calibration with ferrocene/ferrocenyl cation taken to have +0.52 V), in 0.1 M n-Bu4NClO4/DMF, sweep rate 50 mV/sec. [b] Measured at 20 °C. [c] Measured at - 70 °C.



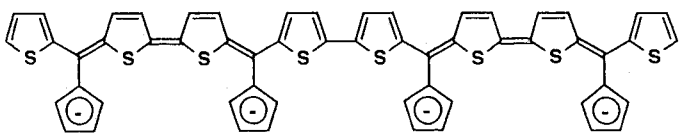
45b^{2-}



45c$^{3-\bullet}$



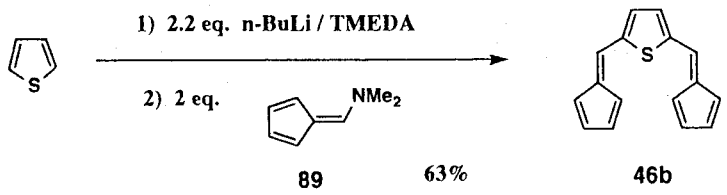
45c^{4-}



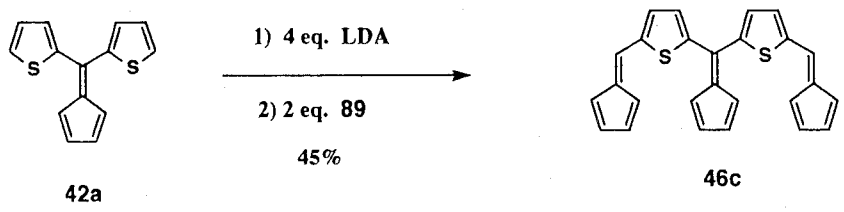
45d^{4-}

4-7. Synthesis of Oligothienylpentafulvenes Having Hydrogen Atoms on the Terminals

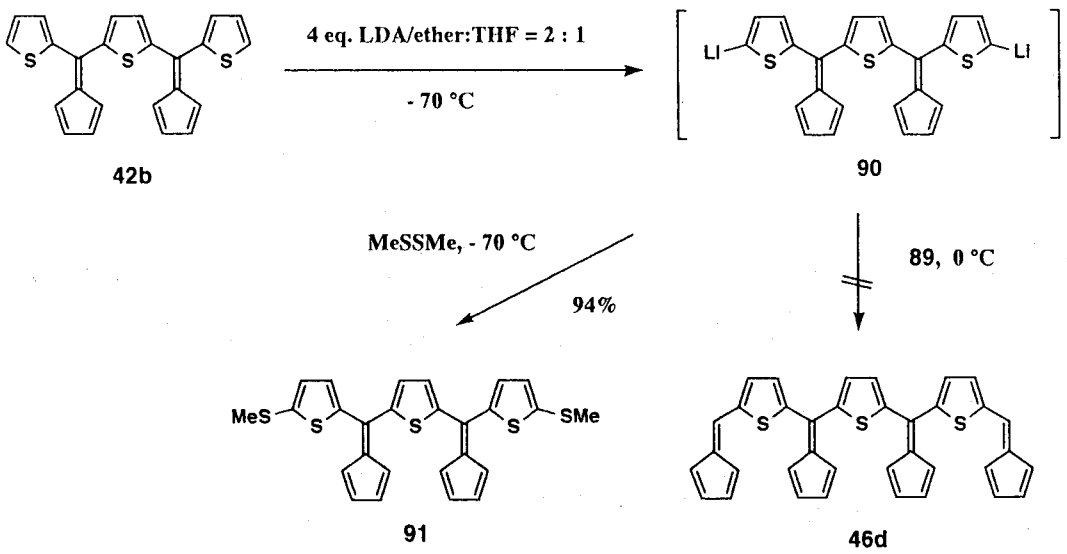
By virture of higher reactivity of 6-dimethylaminopentafulvene **89**[19] than 6, 6-bis(dimethylamino)pentafulvene **72**, an application of nucleophilic substitution reaction on **89** provided oligomers **46**. Dimer **46b** was prepared by the reaction of 2, 5-dilithiothiophene and



Scheme 4-10



Scheme 4-11



Scheme 4-12

two equivalents of **89** in 63% yield (Scheme 4-10). Condensation of 2, 5-diformylthiophene and cyclopentadienyl anion failed to give **46b**. Similar reaction of dilithio derivative of **42a** and two equivalents of **89** afforded trimer **46c** in 45% yield (Scheme 4-11). Synthesis of tetramer **46d** through dilithiation of **42b** was unsuccessful. Dilithiation of **42b** required considerably demanding conditions. Only the case of treating **42b** with four equivalents of LDA in THF and ether (1/2 = V/V) at -70 °C gave dilithio derivative **90**, but it tends to decompose even at 0 °C. Therefore, the reaction of **90** with a relatively reactive electrophile, such as dimethyl disulfide, provided bis-methylthio derivative **91** in 94% yield, whereas the reaction with less reactive **89** failed to give **46d** (Scheme 4-12).

4-8. Physical Properties of Oligothienylpentafulvenes Having Hydrogen Atoms on the Terminals

Compound **46b-c** are dark red crystalline substances and are identified by mass and NMR spectra. In spite of the lack of an electron-donating 2-thienyl group at the terminal carbons, **46b-c** are fairly stable.

Electronic spectra

Table 4-8 and Figure 4-13 show electronic spectra of **46b-c**, **42a** and 6-(2-thienyl)pentafulvene **62m** in cyclohexane. The longest absorption wavelength of **46b** is about 70 -100 nm longer than those of monopentafulvenes. Thus, electronic spectral behavior of **46b** is similar to **42b** and **45b**. On the other hand, the shape of the spectra is appreciably different between **46b** and **46c**. The spectrum of **46c** rather resemble that of **42a**; thus **46c** seems to be regarded as a dithienylpentafulvene perturbed by two pentafulvenyl groups from electronic structural point of view.

Table 4-8. Electronic Spectral Data of Oligopentafulvenes **46b-c**, **42a** and 6-Thienyl-pentafulvene **62m**

Compound	λ_{max} (log ε) in cyclohexane			
46b	449 (4.45)	423 (4.57)	291 (4.45)	281sh (4.3)
46c	436sh (4.6)	404 (4.68)	339sh (4.2)	293 (4.22)
	282sh (4.2)			
62m	344 (4.41)	286(3.74)	224sh (3.7)	
42a	369 (4.32)	307sh (3.9)	280 (3.90)	222sh (4.1)

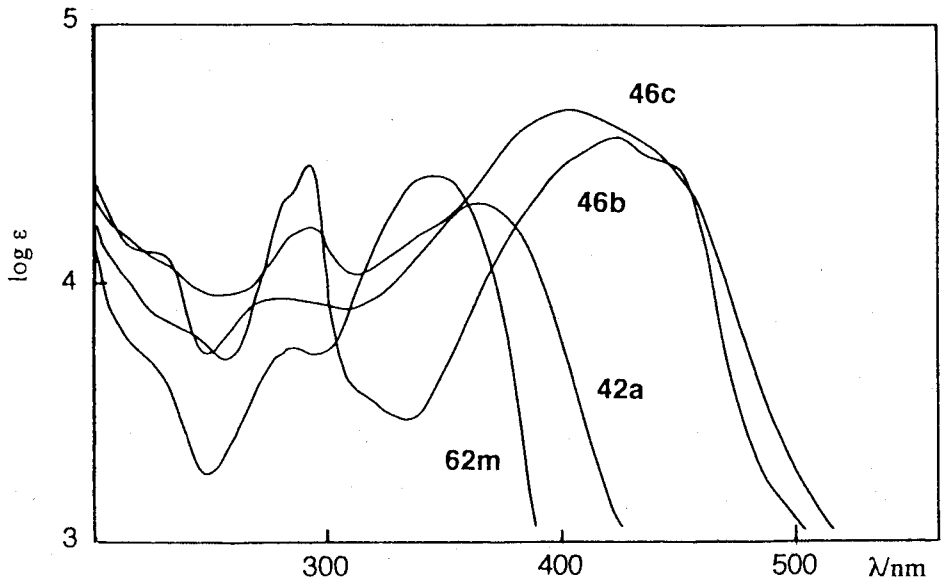
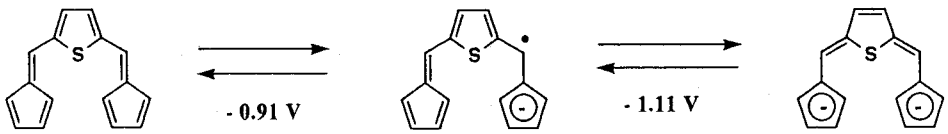


Figure 4-13. Electronic spectra of **46b-c**, **42a** and **62m**.

Electrochemical behavior

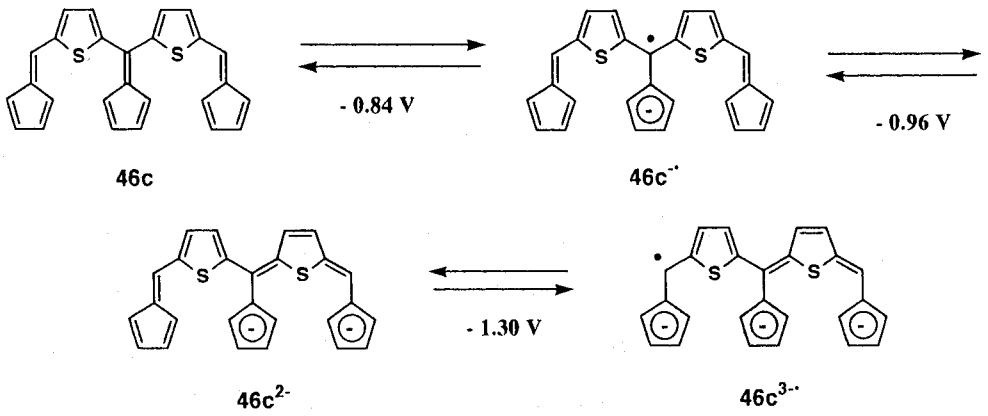
Table 4-9 and Figure 4-14 show reduction potentials and cyclic voltammograms of **46b-c** and **62m**. Their redox behavior slightly differ from those of **42b-d** and **45b-d**. Although **42b** and **45b** give two pairs of very close redox waves which almost appear to be two-electron transfer in one wave, the cyclic voltammogram of **46b** shows two pairs of clearly separated redox waves. Although the first reduction potential (E^1) of **46b** is almost the same with that of **42b**, the second reduction potential (E^2) is higher than that of **42b** and **45b**. Thus, the absence of 2-thienyl group at the terminals slightly decreases the stability of dianion **46b**$^{2-}$ (Scheme 4-13).



46b **46b**$^{\cdot-}$ **46b**$^{2-}$

Scheme 4-13

On the other hand, **46c** gave three reversible redox waves, corresponding to the formation of its radical anion, dianion, and trianion radical, respectively (Scheme 4-14). The difference between the first reduction potential and the second is smaller than that of **46b**. This may suggest that the dianion **46c**$^{2-}$ is more stabilized by the extended π-system. No reduction peak was observed up to - 2.0 V to suggest less stability of tetraanion **46c**$^{4-}$. Similarly, monothienyl-pentafulvene **62m** does not show the reduction potential leading to its dianion; therefore, dianion of **62m** should be unstable.



46c $46c^{\cdot-}$ $46c^{2-}$ $46c^{3-\cdot}$

Scheme 4-14

Table 4-9. Reduction Potentials[a] of Oligopentafulvenes **46b - c**, and 6-Thienylpentafulvene **62m** by Cyclic Voltammetry

Compound	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$
62m	- 1.37		
46b	- 0.91	- 1.11	
46c	- 0.84	- 0.96	- 1.30

[a] V vs Ag/AgCl (calibration with ferrocene/ferrocenyl cation taken to have +0.52 V), in 0.1 M n-Bu_4NClO_4/DMF, sweep rate 100 mV/sec, measured at 20 °C.

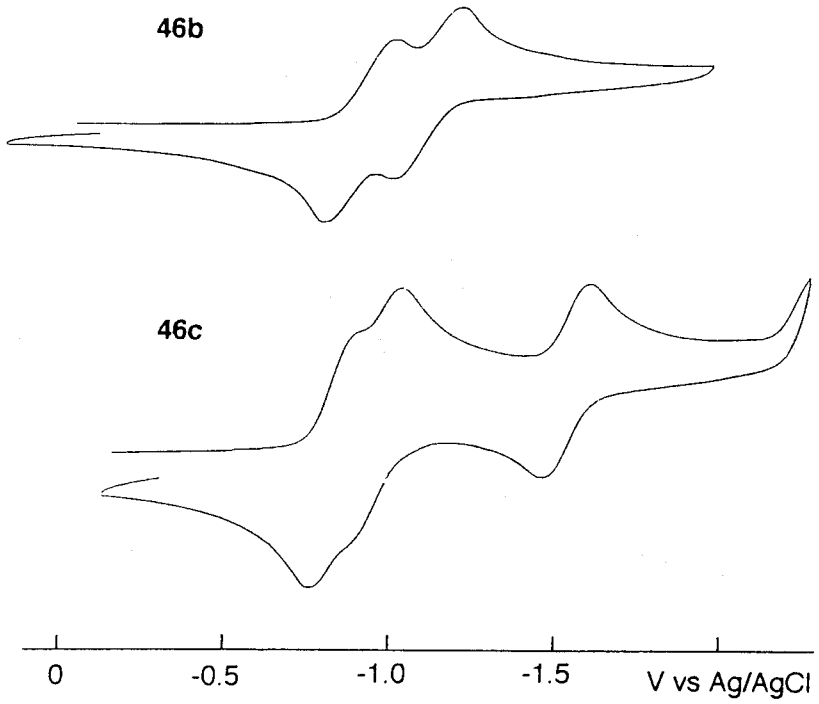


Figure 4-14. Cyclic voltammograms of **46b** and **46c**.

To summarize of Section 4-2 to 4-8, oligo-6-(2-thienyl)pentafulvens **42a-d**, oligo[6, 6-di(2-thienyl)pentafulvene]s **45b-d** and oligothienylpentafulvenes having hydrogen atoms at the terminals **46b-c** were obtained as crystalline substances with fair to moderate stability. In NMR and electronic spectra, no appreciable changes were observed among the oligomers. Their redox hehavior by cyclic voltammetry, however, showed appreciable difference by the change of the number of pentafulvene unit. These oligomers possess considerably high electron affinities and the reversible redox waves suggest the formation of stable anionic species which have oligoacetylenes spine attached with cyclopentadienyl anions.

Therefore, I next studied the generation and characterization of the anionic species of oligothienylpentafulvenes by alkali metal reduction. The details will be described in the next section.

Alkali metal reduction of bis-6-(2-thienyl)pentafulvene **42b**

The behavior of alkali metal reduction of **42b** in THF was monitored by the change of electronic spectra. To avoid excessive reduction and for the easiness of handling, 3% sodium amalgam, which is relatively weak reductant, was used as the alkali metal for reduction of **42b**. The details for the measurement of electronic spectra are described in the experimental section.

Figure 4-15 shows the change of the electronic spectra of **42b** upon contacts at brief intervals with sodium amalgam. While the absorptions at 415 and 368 nm became weak, new absorptions appeared at 551 and 341 nm and increased as the reaction proceeded,. An isosbestic

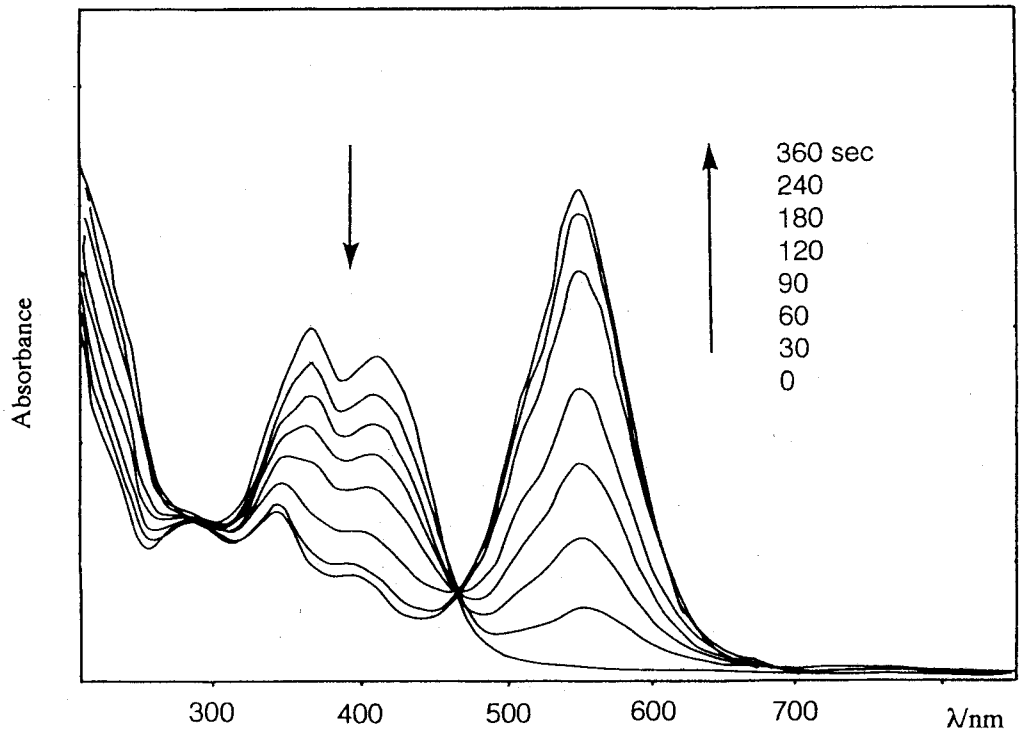
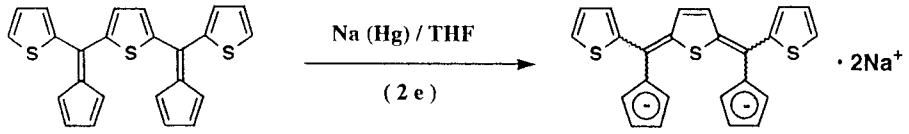


Figure 4-15. Change of electronic spectra of **42b** upon reduction with Na (Hg) in THF.

point was observed at 468 nm. The change of the spectra almost stopped after the total contact time of 360 seconds, and the solution became deep purple. An additional contact with the metals for more than 30 minutes did not change the spectrum. The observed new spectra may be attributed to the formation of dianion **92**. This change of electronic spectra suggests that the reduction of **42b** with sodium proceeds in alomst one step involving two electrons (Scheme 4-15), although two slightly different reduction potentials are observed by cyclic voltammetry .



42b **92**

Scheme 4-15

To confirm the formation of dianion **92**, NMR spectra of the reduced mixture were measured. Tetrahydrofuran-d8 was used as solvent, and again 3% sodium amalgam as alkali metal. The apparatus and experimental procedure for the reduction in a NMR tube are described in the experimental section. The resulting solution was deep purple. This dianion was stable in the solution at room temperature under degassed condition and regenerated **42b** on exposure to air (82%). ^{1}H- and ^{13}C-NMR data of **92** are consistent with the expected dianion structure. Figure 4-16 and 4-17 show ^{1}H- and ^{13}C-NMR spectra of **92**. ^{1}H-NMR spectrum shows the formation of one major product with good symmetry and one minor product with lower symmetry. Table 4-10 summarizes NMR data of the major component of **92**. In ^{1}H-NMR, the protons of pentafulvene moieties are observed as two pairs of triplets (J = 2.8 Hz), which shows typical patterns of mono-substituted cyclopentadienyl anion[15, 20, 21]. The signals of double-doublets at 7.15 ppm are assigned to the protons at 5-position of the terminal thiophene rings, and the multiplets at 6.86 - 6.90 ppm to the protons at 3- and 4-positions of the terminal thiophene rings. The singlet at 6.29 ppm is assigned to the protons of the central thienoquinoid moiety , and shows a ralatively large degree (ca. 1 ppm from **28b**) of high field shift.

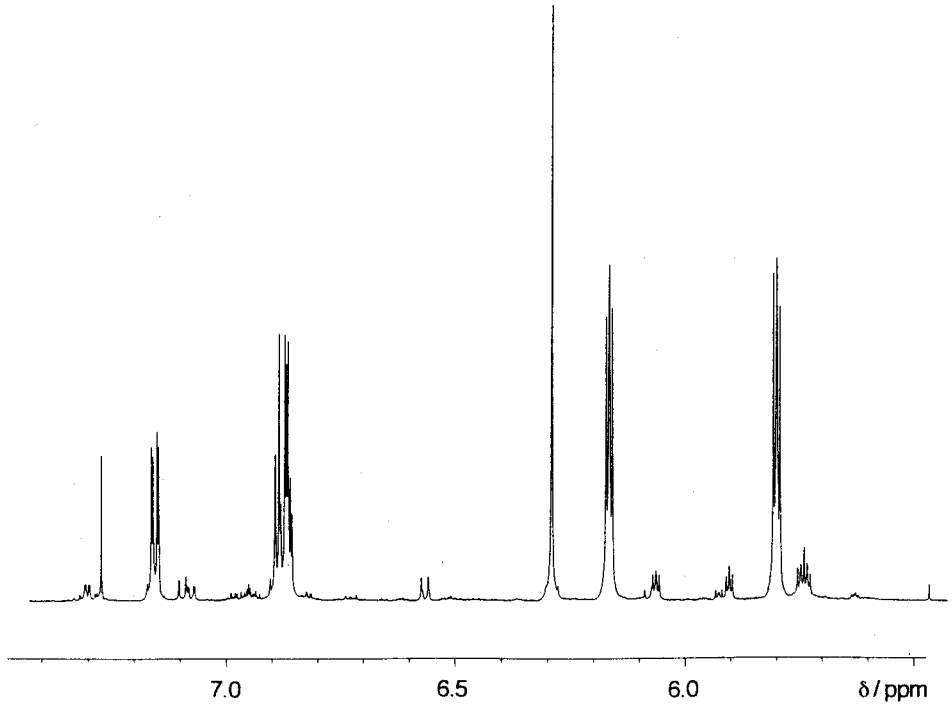


Figure 4-16. ^{1}H-NMR spectrum of **92**.

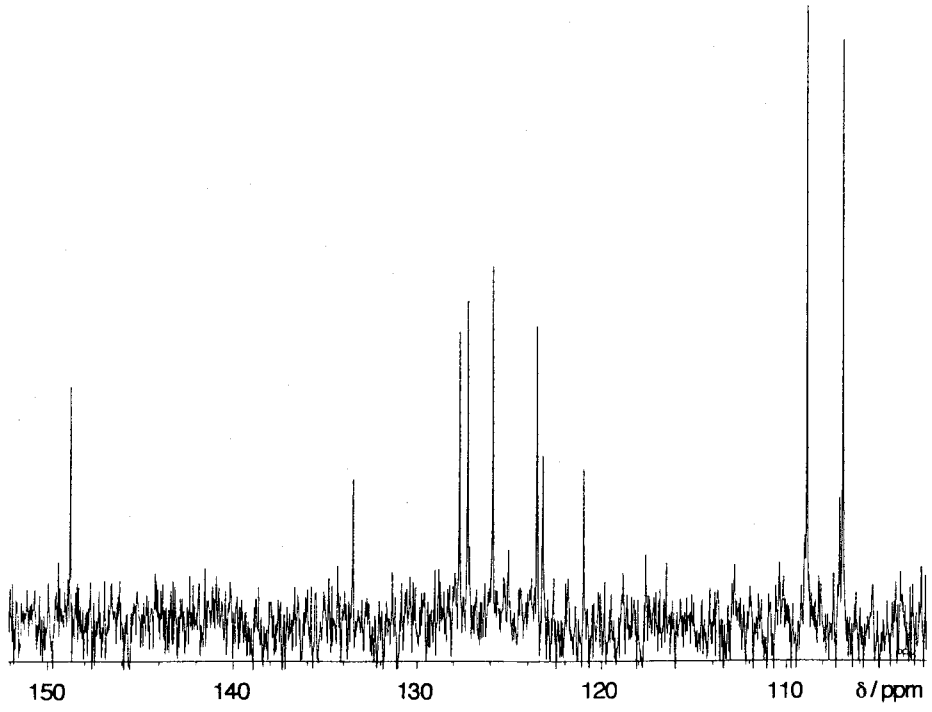


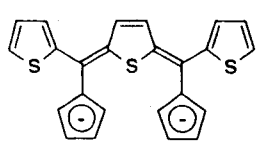
Figure 4-17. ^{13}C-NMR spectrum of **92**.

Table 4-10. ^{1}H- and ^{13}C-NMR Data[a] of Dianion **92** and **93**

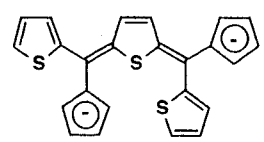
Compound	^{1}H chemical shifts[b] (δ)	^{13}C chemical shifts[c] (δ)
92 (**42b**$^{2-}$•2Na^{+})	7.15 (dd, J = 4.8, 1.5 Hz, 2H)	148.78, 133.50, 127.66
	6.86-6.90 (m, 4H)	127.22, 125.87, 123.53
	6.29 (s, 2H)	123.19, 120.99, 108.87
	6.17 (t, J = 2.8 Hz, 4H)	106.92
	5.80 (t, J = 2.8 Hz, 4H)	
93 (**42b**$^{2-}$•2Li^{+})	7.19 (t, J = 3.2 Hz, 2H)	148.18, 135.54, 128.89
	6.93 (brd,-like, 4H)	127.50, 126.16, 124.02
	6.44 (s, 2H)	122.83, 121.14, 108.64
	6.11 (t, J = 2.5 Hz, 4H)	105.86
	5.75 (t, J = 2.5 Hz)	

[a] In THF-d8, at 30 °C. [b] At 270 MHz , referenced to the solvent signal: 1.70 ppm. [c] At 67.8 MHz, referenced to the solvent signal: 25.30 ppm.

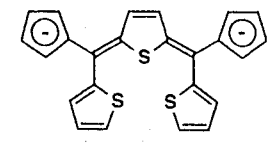
There can be considered three geometric isomers for the structure of **92**, as shown in Figure 4-18. From the observed spectra, the structure of major product is determined to be **92A** having C_2 symmetry because a nuclear Overhauser effect (NOE) is observed between the singlet at 6.29 ppm and the muliplets at 6.86 - 6.90 ppm, If the major product were **92C**, NOE



92A



92B



92C

Figure 4-18. Possible isomers of dianion **92**.

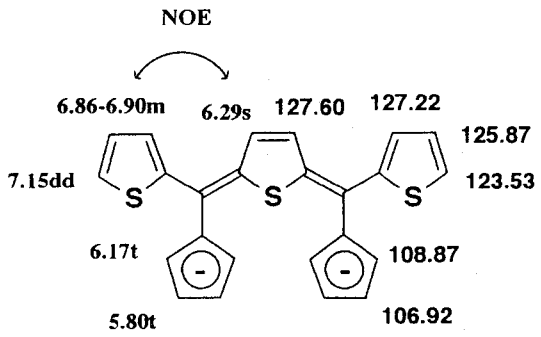
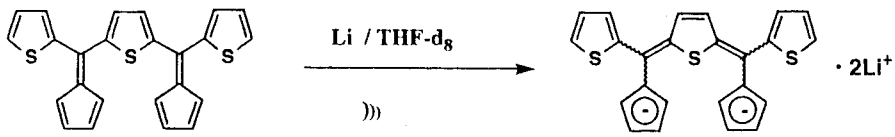


Figure 4-19. ^{1}H and ^{13}C assignments of **92**.

must have been observed between the singlet at 6.29 ppm and the triplets at 6.17 or 5.80 ppm. The minor product can be assigned to **92B** from its non-symmetric spectrum. The ratio of **92A** and **92B** is estimated to be about 10 : 1 from the intensity of the singlet at 6.29 ppm and the doublet at 6.57 ppm. Assignment of the signals of tertiary carbons are made by its C-H COSY spectrum and shown in Figure 4-19. The carbons of the thienoquinoid moiety appear at 127.60 ppm. This chemical shift is lower than those of the terminal thiophene carbons to indicate that the electoron density at the thienoquinoid moiety is relatively low; therefore, the negative charges of **92** nearly localize on cyclopentadienylanion moieties. Molecular orbital calculation may provide further insight into the electronic structure of **92** if proper parameters for sulfur atoms are given.

Dianion of **42b** was also obtained by reduction with lithium metal. Treatment of **42b** with a small excess of lithium powder in THF-d8 for 20 min under sonication afforded a deep purple solution of dianion **93** (Scheme 4-16). Figure 4-20 shows ^{1}H-NMR spectrum of **93**. The observed spectrum is similar to **92**, and the structure of major product is also determined to be **92A** by NOE measurement. NMR data of **93** are also listed in Table 4-10.



42a **93**

Scheme 4-16

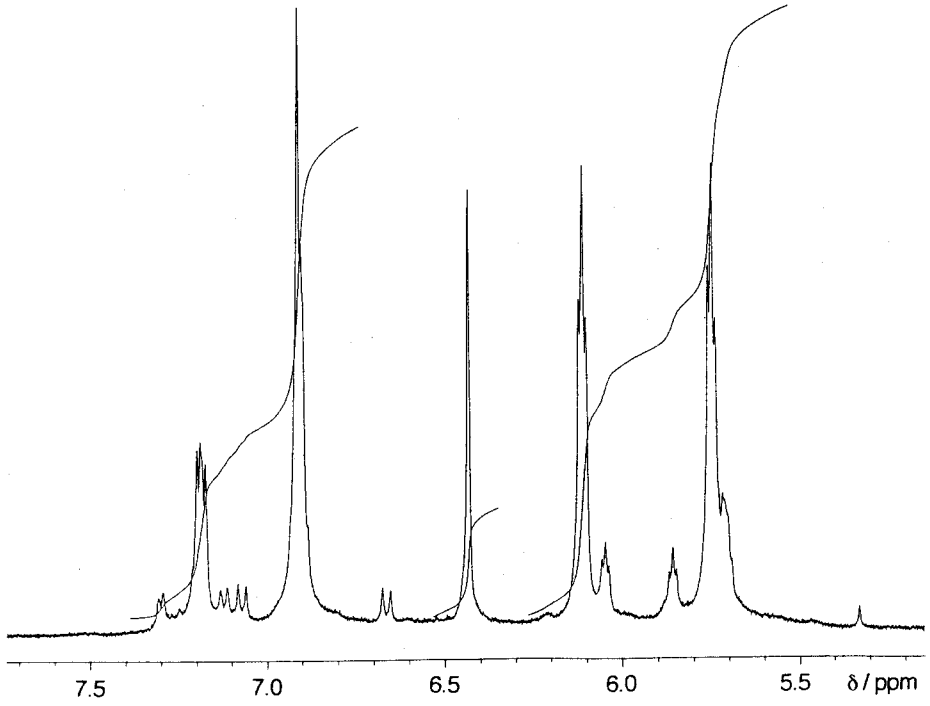
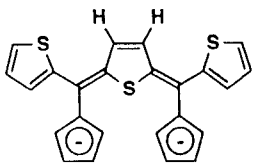
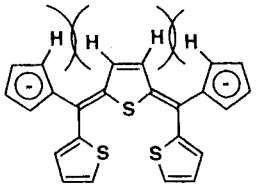


Figure 4-20. ^{1}H-NMR spectrum of **93**.

The selective formation of isomer **92A** can be explained from the steric point of view. When the dianion took the configuration of **92C**, the hydrogen atoms of the thienoquinoid moiety and the cyclopentadienyl anion would interact each other. In the structure **92A**, steric interaction between the sulfur atom of the thienyl group and the hydrogen atoms of the thienoquinoid moiety would be smaller, and therefore **92A** may be thermodinamically more stable



92A



92C

than **92C**. It is, however, not certain at this moment whether **92A** and **92C** isomerize each other at higher temperature. Variable temperature NMR spectra should give an answer to this question, but anionic nature of **92A** and co-existence of reducing agent make the measurement at higher temperatures difficult.

Alkali metal reduction of bis[6. 6-di(2-thienyl)pentafulvene] **45b**

The reduction of **45b** was carried out by treatment of 3% sodium amalgam in similar way to **42b**, and monitored by the change of electronic spectra. Figure 4-21 shows their spectral change. As the reduction proceeds, a new absorption at 681 nm increased while the absorption of the starting material **45b** decreased. An isosbestic point was observed at 527 nm. The color of solution changed from orange to green. The reduction completed in about 240 seconds, and no

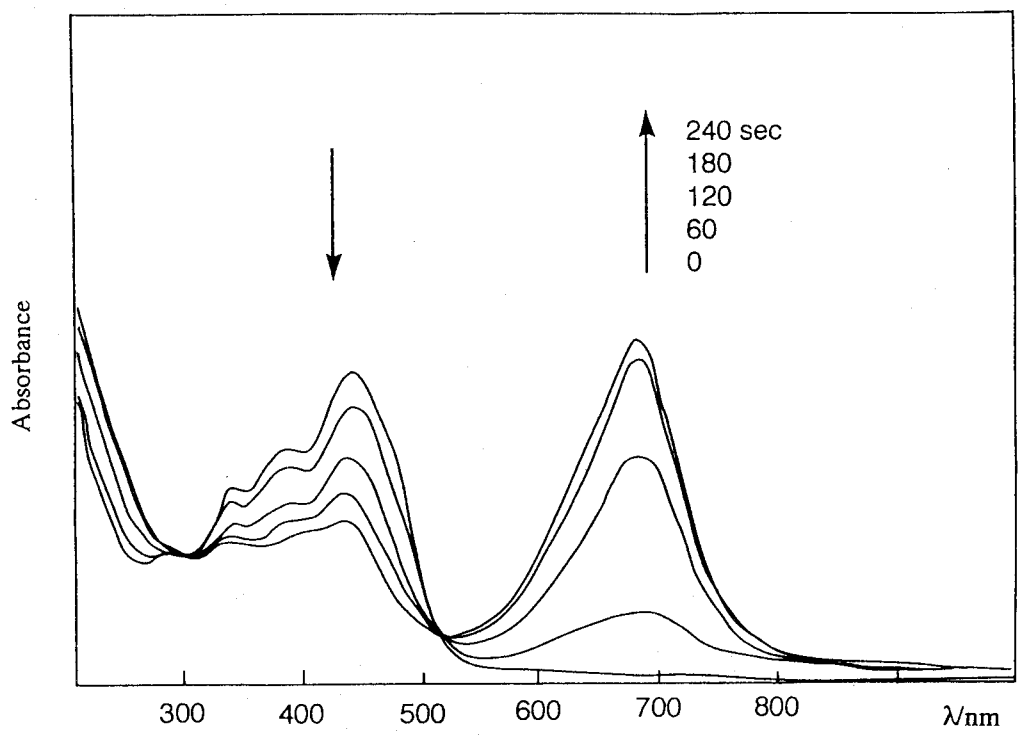
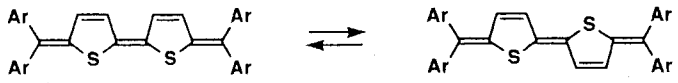


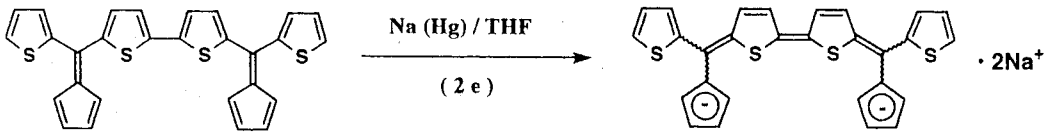
Figure 4-21. Change of electronic spectra of **45b** upon reduction with Na (Hg) in THF.

appreciable change in the spectra was observed after standing overnight. The observed spectra correspond to the formation of dianion **94**. Dianion **94** absorbs 130 nm longer than **74**. The long-wavelength absorptions are reasonable when compared with the absorption of **95** which recently prepared in our laboratory[22] and shows the longest absorption maxima at 530 - 660 nm.



95

According to this change of the spectra, **45b** is reduced to dianion **94** again almost in one step, and **94** presumably take the structure of bis(thienoquinoid) form (Scheme 4-17). Therefore, I measured NMR spectra of **94**, but the observed spectra suggested **94** to be a complex mixture of geometrical isomers. Because there can be six geometrical isomers for **94**.



45b **94**

Scheme 4-17

Alkali metal reduction of 2, 5-bis(6-pentafulvenyl)thiophene **46b**

Figure 4-22 shows the change of electronic spectra when **46b** was reduced with 3% sodium amalgam in THF. Compound **46b** showed a slightly different reduction behavior from **42b** and **45b**. At the begining of the contact with sodium amalgam, the new absorption at 689 and 495 nm appeared accompanied with decrease of absorptions of the starting material. The solution became green at once. The absorption corresponding to the band at 689 nm was not observed in the case of **42b** and **45b**. This may be due to the formation of the radical species. During the additional contact with the metals, the absorptions at 495 and 320 nm increased. The

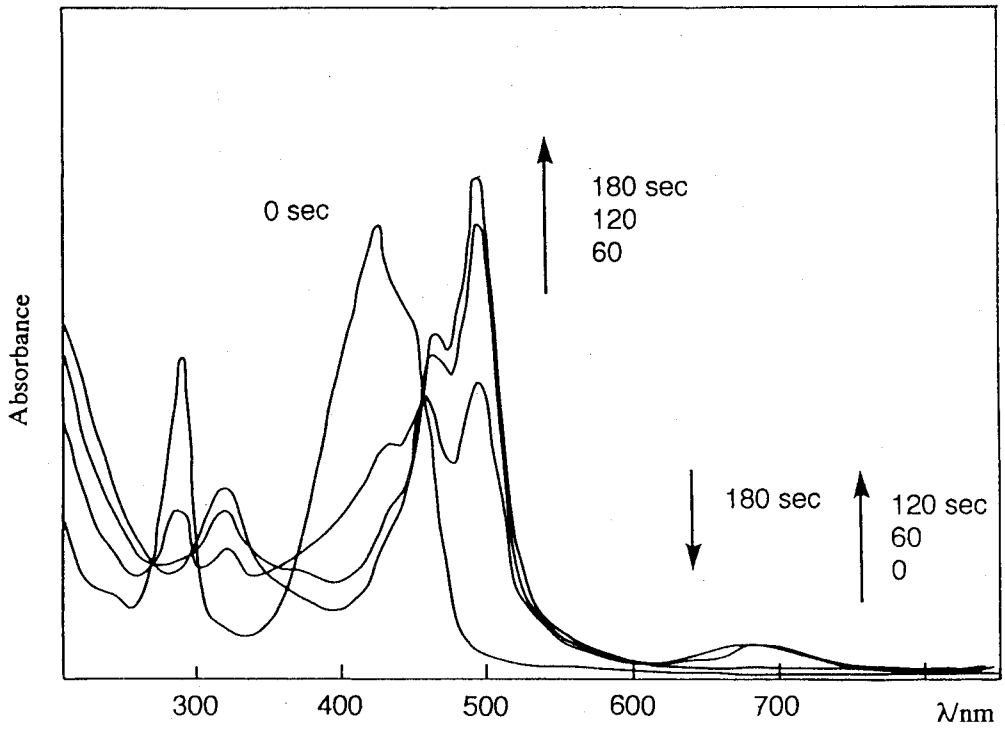
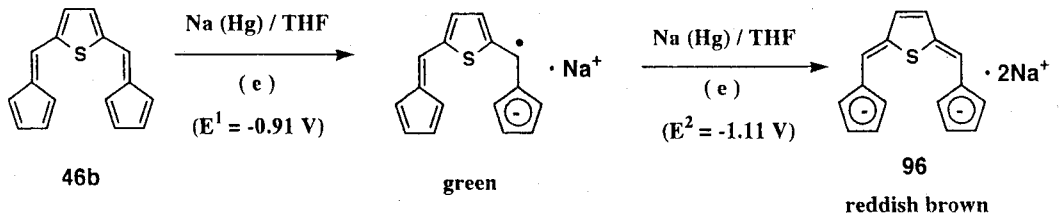


Figure 4-22. Change of electronic spectra of **46b** upon reduction with Na (Hg) in THF.

absorption at 689 nm remained to be observed until the contact time of 120 seconds, but disappeared after further 60 seconds. After disappearance of the absorption at 689 nm, any appreciable change of the spectra was not observed to indicate the complete formation of dianion



Scheme 4-18

96. The solution was finally reddish brown. From this spectral change, the reduction process of **46b** involves two steps in agreement with the larger difference between the first and second reduction potentials obtained by cyclic voltammetry (Scheme 4-18). The intensity of the spectra decreased when the solution was allowed to stand overnight at room temperature; thus, the stability of dianion **96** is inferior to **92** and **94**.

NMR measurements were carried out to determine the structure of the dianion. Figure 4-23 shows ^{1}H-NMR spectrum of **96**. Similar to **92**, two isomers are observed: the major product with C_2 symmetry and the minor without symmetry. ^{13}C-NMR spectrum could not be obtained because **96** decomposed during the measurement.

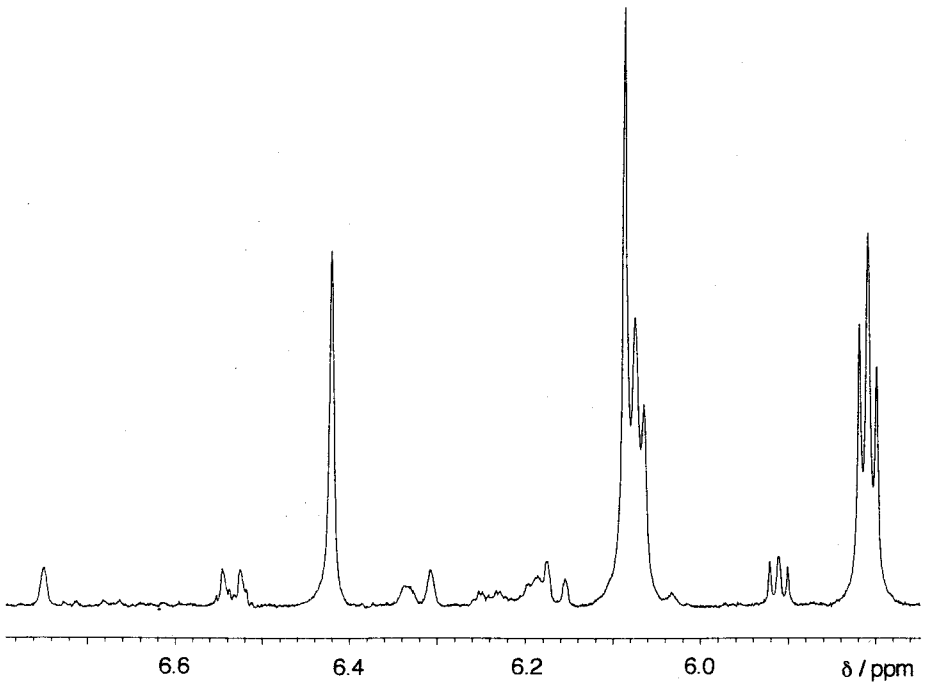
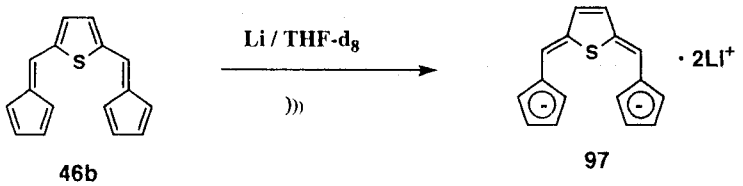


Figure 4-23. ^{1}H-NMR spectrum of **96**.

On the other hand, the lithium salt of the dianion, *i.e.* compound **97**, was stable enough for the measurement of ^{13}C-NMR spectra. Treatment of **46b** with a small excess of lithium powder in THF-d8 for 30 min under sonication afforded a dark orange solution of dianion **97** (Scheme 4-18). Table 4-11 lists ^{1}H and ^{13}C chemical shifts of **96** and **97**. Figure 4-24 and 25 show ^{1}H- and ^{13}C-NMR spectra of **97**.



46b **97**

Scheme 4-19

Table 4-11. ^{1}H- and ^{13}C-NMR Data[a] of Dianion **96** and **97**

Compound	^{1}H chemical shifts[b] (δ)	^{13}C chemical shifts[c] (δ)
96 (**46b**$^{2-}$•2Na^{+})	6.42 (s, 2H)	
	6.09 (s, 2H)	
	6.07 (t, J = 2.7 Hz, 4H)	
	5.81 (t, J = 2.7 Hz, 4H)	
97 (**46b**$^{2-}$•2Li^{+})	6.41 (s, 2H)	133.33, 129.55, 120.18
	6.17 (s, 2H)	116.12, 106.65, 106.17
	6.05 (t, J = 2.7 Hz, 4H)	
	5.77 (t, J = 2.7 Hz, 4H)	

[a] In THF-d8, at 30 °C. [b] At 270 MHz, referenced to the solvent signal; 1.70 ppm. [c] At 67.8 MHz, referenced to the solvent signal; 25.30 ppm.

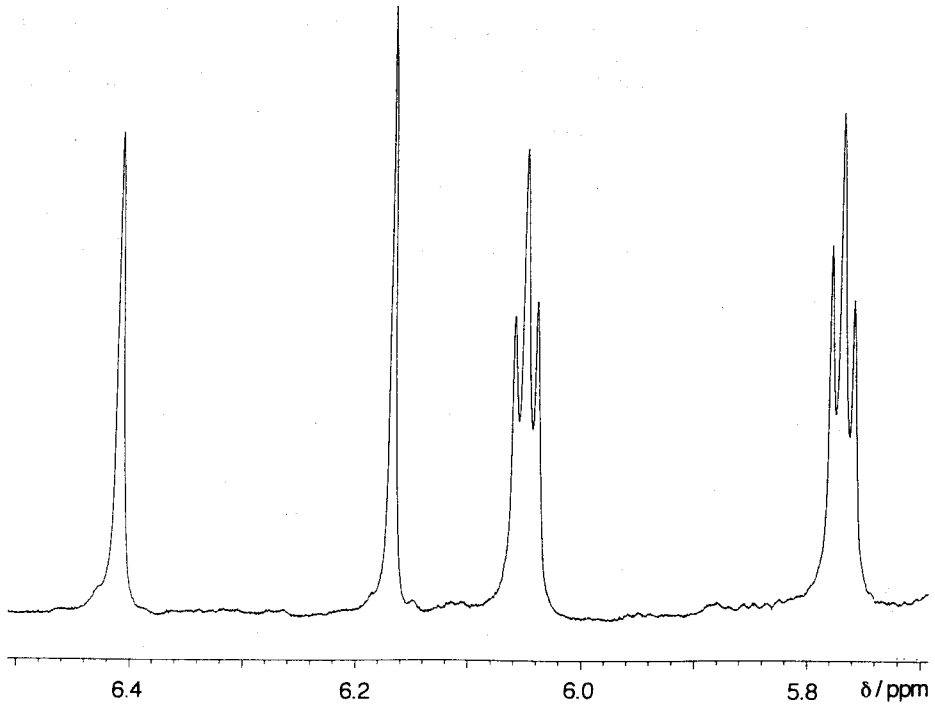


Figure 4-24. ^{1}H-NMR spectrum of **97**.

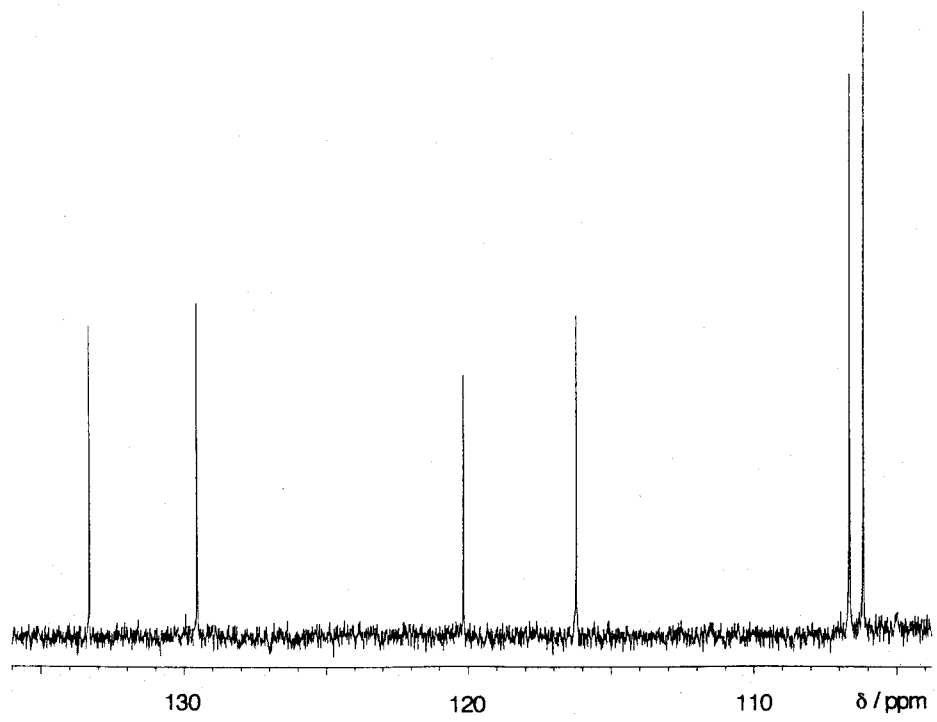
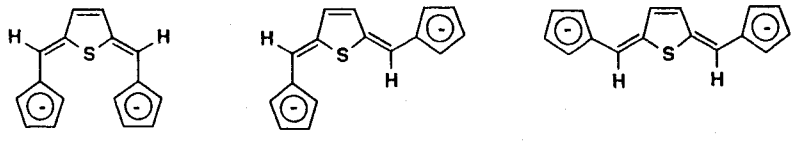


Figure 4-25. ^{13}C-NMR spectrum of **97**.

It is noteworthy that only one isomer is observed for the lithium salt **97**. From the differential NOE spectra, the structure of **97** is determined to be **97A**, but neither **97B** nor **97C**. Figure 4-26 summarizes the assignment of ^1H chemical shifts. The selective formation of **97A** may be also explained from the steric point of view. The structure **97A** is much less conjested than **97C**. Compound **97** is not so stable and gradually decomposed in a NMR tube giving rise to uncharacterizable signals with decrease of the dianion's signals.



97A **97B** **97C**

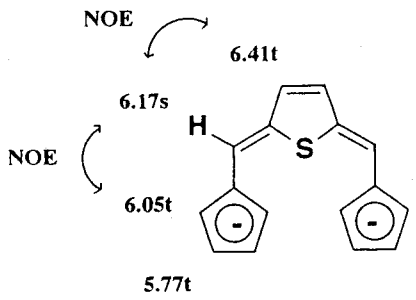


Figure 4-26. ^1H assignments of **97**.

Alkali metal reduction of tris-6-(2-thienyl)pentafulvene **42c**

Reduction hehavior of trimer **42c** was also examined. According to the reduction potentials by cyclic voltammetry, dianion, trianion radical, and tetraanion should be generated successively. It is interesting whether these species can be detected spectroscopically or not. Figure 4-27 shows the change of electronic specra upon the reduction of **42c** with Na (Hg). The spectrum after 30 sec contact with Na (Hg) showed a small absorption at 985 nm. Further

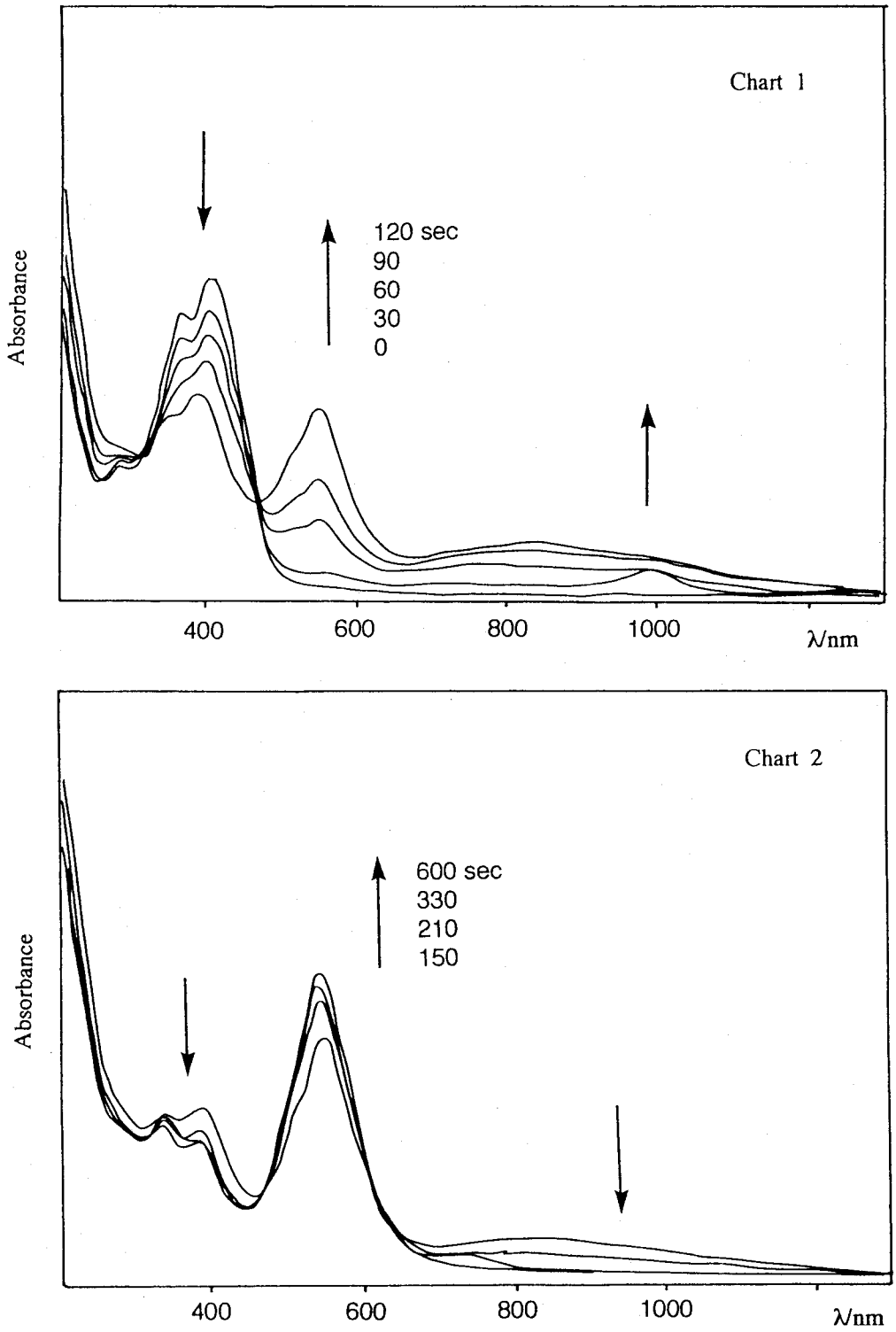
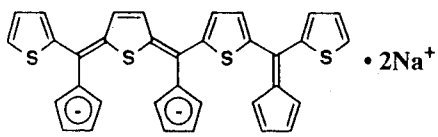


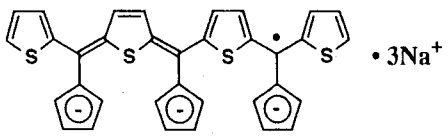
Figure 4-27. Change of electronic spectra of **42c** upon reduction with Na (Hg) in THF.

contact at intervals led to appearance of a very broad absorption at 700 - 1200 nm with concomitant increase of a stronger absorption at 547 nm band (Chart 1 in Figure 4-27). The solution was brownish at this point. The broad absorption began to decrease after 120 seconds, while the 547 nm absorption continued to increase (Chart 2). The solution was finally deep purple. This purple solution was fairly stable and the intensity of absorption did not decrease during standing overnight at room temperature. According to the observed change of electronic spectra, the reduction of **42c** by sodium amalgam seems to involve three stages. The final product which is probably responsible for the deep purple color is fairly stable. Therefore, NMR measurements were carried out to get information about the structure of the final product.

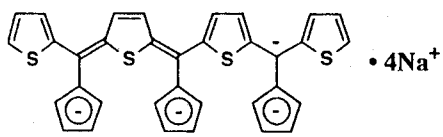
Figure 5-28 shows the observed ^{1}H-NMR spectrum, and Table 4-12 summarizes ^{1}H- and ^{13}C-NMR data. Although the spectrum is condiderably complicated, it indicates the formation of one major product. This spectrum should correspond to either dianion **98** or tetraanion **100**, not to trianion radical **99**, because it gives well-definable signals. If the product be tetraanion **100**, the signals of the thiophene ring-protons in the dithienylpentafulvene dianion moiety should appear at higher magnetic field than the observed signals (6.7-7.2 ppm), since the signals of di(2-thienyl)methyl anion **101**, of which NMR spectrum was recently observed in our labolatry[23], appear in the region of 5.4-6.5 ppm, and since the signals of the phenyl region of diphenylpentafulvene dianion **36**[15] were also observed at relatively high field (H_{para} = 5.67 ppm, H_{meta} = 6.39 ppm, H_{ortho} = 7.25 ppm; The ortho protons were rather at low field due to the anisotropy effect of the cyclopentadienyl anion moiety.). Futhermore, 3% sodium amalgam is



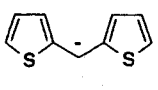
98



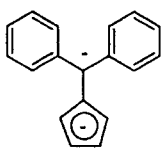
99



100

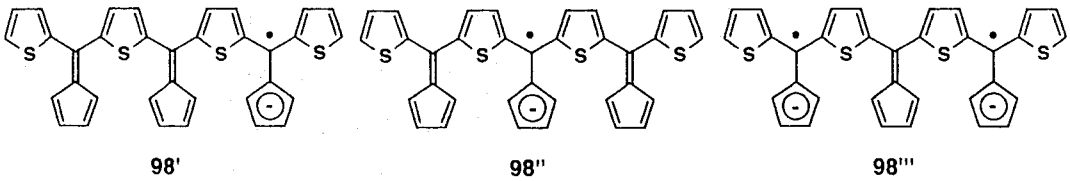


101



36

rather weak reagent for reduction and hardly afford anionic species which have relatively high reduction potentials. In fact, it was impossible to generate benzophenone ketyl radical ($E_{1/2}$ = - 1.73 V)[24] and 6, 6-bis(2-thienyl)pentafulvene dianion ($E_{1/2}$ = - 1.83 V)by reduction with 3% sodium amalgam; thus, tetraanion **100** ($E_{1/2}$ = -1.85 V) would be hard to be generated under the condition. Therefore, I assign the stable anionic species to dianion **98** at present. Then, how can be explained the three-step change of the electronic spectra? A possible explanation is as follows. The first reduction gives anion radical 98' or 98". The second reduction of 98' forms bis(anion radical) 98''' which slowly isomerises to dianion 98. This is only a speculation and needs further studies for clear elucidation.



98' 98" 98'''

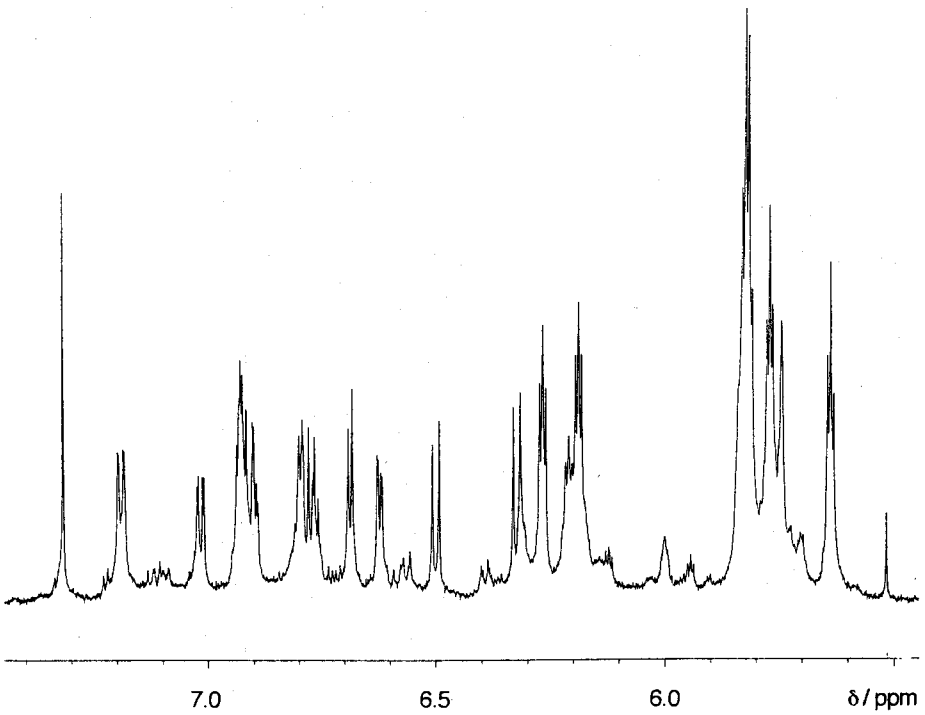


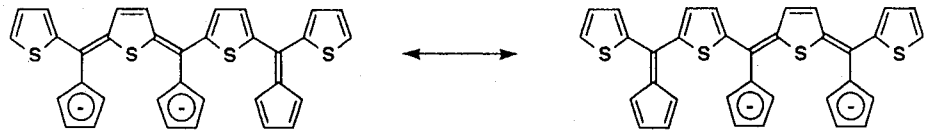
Figure 4-28. ^{1}H-NMR spectrum of **98**.

Table 4-12. ^{1}H- and ^{13}C-NMR Data[a] of Dianion **98** (**42c**$^{2-}$•2Na^{+})

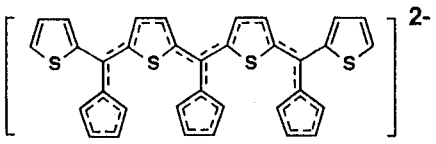
	Chemical shifts[b] (δ)
^{1}H-NMR (400 MHz)	7.19 (dd, J = 5.1, 1.3 Hz, 1H)
	7.02 (dd, J = 5.0, 1.4 Hz, 1H)
	6.84 - 6.94 (m, 2H)
	6.76 - 6.81 (m, 2H)
	6.69 (d, J = 3.7 Hz, 1H)
	6.62 (dd, J = 3.3, 0.9 Hz, 1H)
	6.50 (d, J = 5.9 Hz, 1H)
	6.32 (d, J = 6.0 Hz, 1H)
	6.27 (t, J = 2.8 Hz, 1H)
	6.21 (t, J = 2.8 Hz, 1H)
	6.19 (t, J = 2.8 Hz, 2H)
	5.81 - 5.83 (m, 4H)
	5.75 - 5.78 (m, 2H)
	5.64 (t, J = 2.7 Hz, 2H)
^{13}C-NMR (100 MHz)	155.83, 153.06, 149.00
	146.05, 133.90, 133.37
	130.35, 129.02, 128.31
	127.46, 127.15, 126.07
	126.02, 125.90, 124.38
	123.40, 123.18, 122.89
	122.60, 120.45, 119.59
	117.17, 109.10, 108.95
	108.75, 106.95, 106.69
	106.66, 104.17, 102.69

[a] In THF-d8, at 30 °C. [b] Refereced to the solvent signal; ^{1}H: 1.70 ppm, ^{13}C: 25.3 ppm.

If partially localized dianion structures **98A** and **98B** contributed equally, **98** would be represented by the delocalized structure **98C**, With this structure, its ^{1}H-NMR spectrum would show C_2 symmetry. The observed spectrum, however, apparently indicates a non-symmetrical structure and is more reasonably assignd to the structure **98A** (or **98B**) which consists of the partial structure of bis-pentafulvene dianion and dithienylpentafulvene.



98A **98B**



98C

The assignment of each proton and determination of the configuration of dianion moiety were based on the differential NOE measurements. The doublets at 6.50 ppm is assigned to the proton of thienoquinoid moiety from its coupling constant (J = 5.9 Hz). On the basis of this signal, other signals are assigned as shown in Figure 4-29.

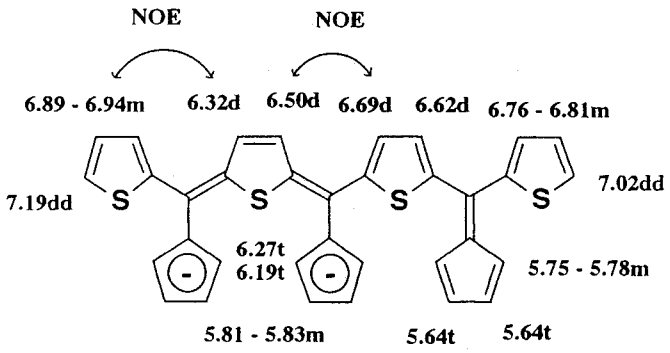


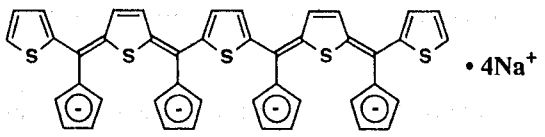
Figure 4-29. Tentative ^{1}H assignments of **98**.

It is noteworthy that the protons of pentafulvene moiety appear at higher magnetic field (5.64 - 5.78 ppm) than ordinary pentafulvenoids. This indicates that the pentafulvene moiety is suffered relatively large perturbation of the bis-pentafulvene dianion.

However, there are still some questions about the structure of this anionic species. If it is really dianion **98A**, what makes it take such partially localized structure rather than delocalized structure **98C**? A possible reason is that resonance energy of a thiophene must be more sacrified by the delocalization of negative charge. Then, there should be an equilibrium between **98A** and **98B** with certain energy barrier. Do NMR spectra at higher temperature show an averaged spectrum with C_2 symmetry? Unfortunately, instability of the anionic species at higher temperature has so far prevented such measurements. Further studies will be anyway necessary for definite conclusion.

Alkali metal reduction of tetrakis-6-(2-thienyl)pentafulvene **42d**

According to the cyclic voltammogram, the reduction of tetramer **42d** consists of two steps each involving two electrons. It is interesting whether similar behavior is detected or not in the chemical reduction of **42b**. Figure 4-30 shows the change of electronic spectra on the reduction of **42d** with Na (Hg). Two steps in the reduction are apparentry observed. In the first step (from 0 to 120 seconds), an absorption at 553 nm and a very broad absorption at 600-1400 nm appeared, while the absorbance of 405 nm absorption of the starting material decreased (Chart 1). The spectral change has the isobestic point at 460 nm. The solution changed from orange to reddish brown. In the second step (120s - 270s), the broad absorption at 600-1400 nm decreased and the absorption at 553 nm increased. The change of the spectra finished after 270 seconds, and the solution was deep purple (Chart 2). The final spectra should correspond to tetraanion **102**. Thus, the broad absorption after 120 seconds may be ascribed to the compound arisen from two electron reduction, and its structure may be assumed as 'bis(anion radical) structure', such as



102

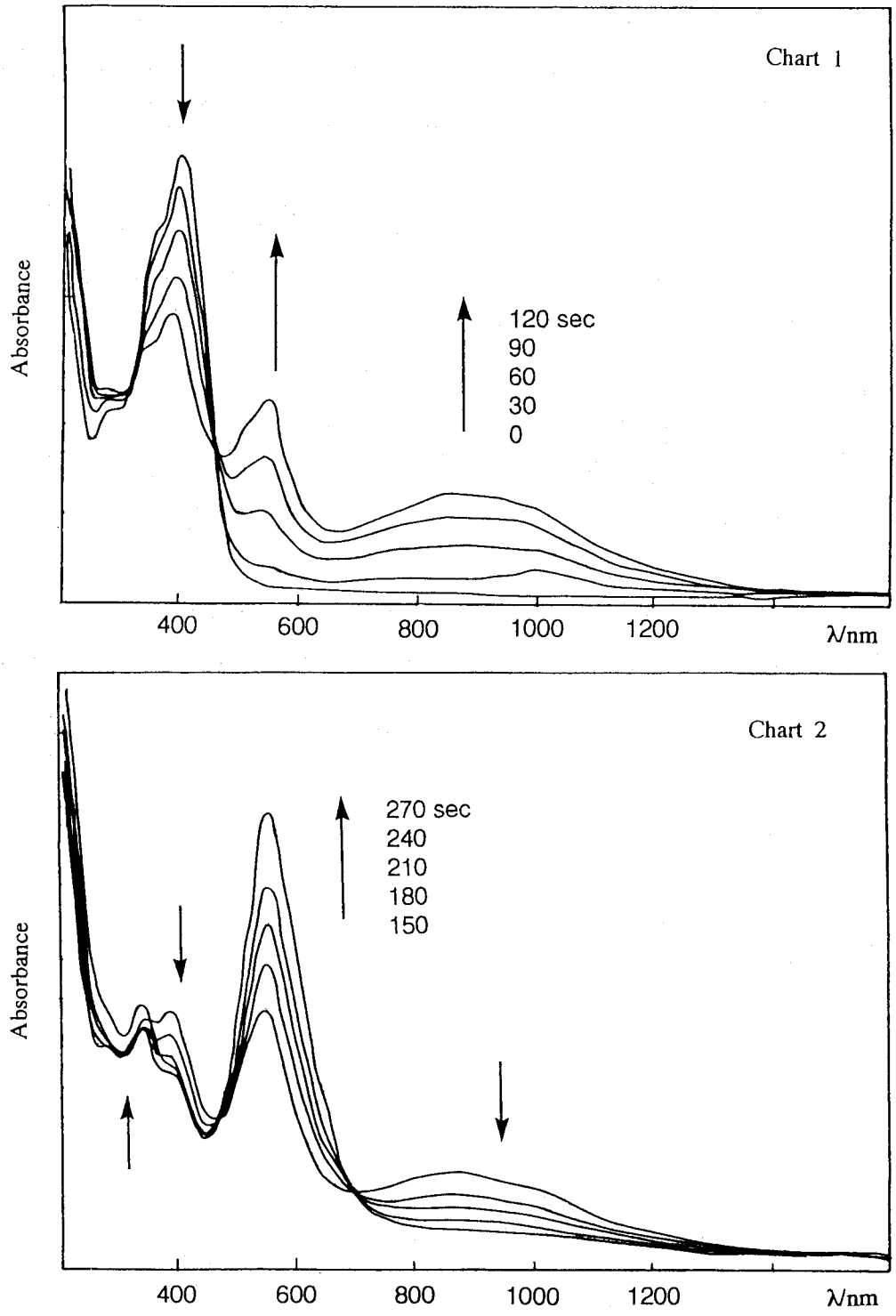
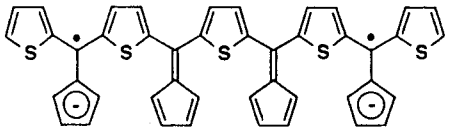
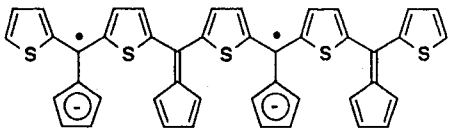


Figure 4-30. Change of electronic spectra of **42d** upon reduction with Na (Hg) in THF.

103 and **104**, rather than dianion structure, such as **105** and **106**, in consideration of the broad absorption at 600-1400 nm. But it is just tentative, and further investigations by means of ESR spectroscopy and so on would be required for elucidation of the intermediate.



104



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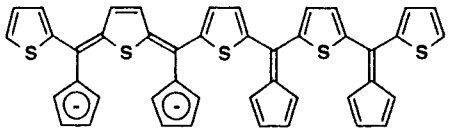
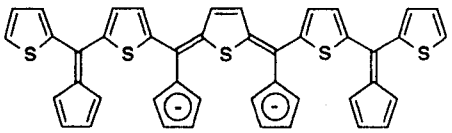


105



106

Measurement of NMR spectra of tetraanion **102** was successful. Figure 4-31 shows its ^{1}H-NMR spectrum. Although the solution contains some impurities, the expected signals for

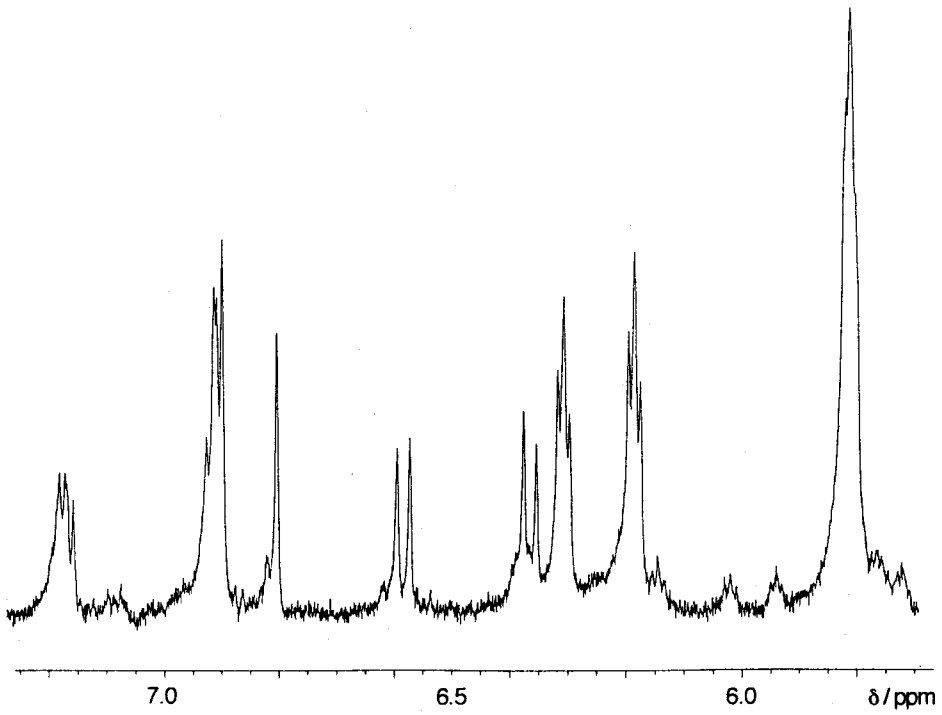


Figure 4-31. ^{1}H-NMR spectrum of **102**.

Table 4-13. ^{1}H- and ^{13}C-NMR Data[a] of Tetraanion **102** (**42d**$^{4-}$•4Na^{+})

	Chemical shifts[b] (δ)
^{1}H-NMR (400 MHz)	7.19 (dd, J = 3.9, 2.4 Hz, 1H)
	6.92 - 6.93 (m, 4H)
	6.82 (s, 2H)
	6.60 (d, J = 6.0 Hz, 2H)
	6.39 (d, J = 6.0 Hz, 2H)
	6.33 (t, J = 2.8 Hz, 4H)
	6.21 (t, J = 2.8 Hz, 4H)
	5.82 - 5.84 (m, 8H)
^{13}C-NMR (100 MHz)	149.10, 146.49, 134.13
	133.30, 128.51, 127.40
	127.15, 126.03, 125.85
	123.36, 122.83, 122.57
	120.49, 106.60, 106.47
	104.14, 102.69

[a] In THF-d$_8$, at 30 °C. [b] Referenced to the solvent signal; ^{1}H: 1.70 ppm, ^{13}C: 25.3 ppm.

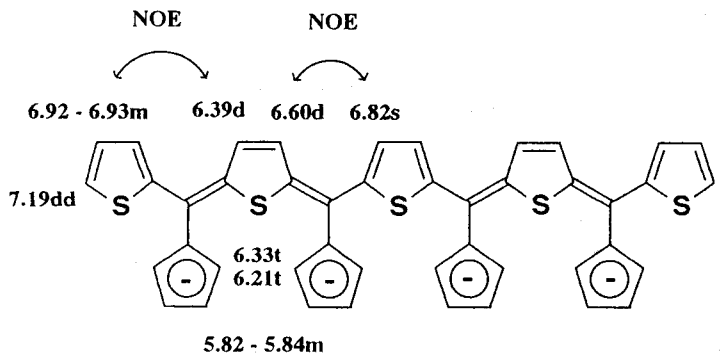


Figure 4-32. ^{1}H assignments of **102**.

102 are clearly observed. The singlet at 6.82 ppm can be assigned to the proton at the central thiophene ring. Thus, **102** has a C_2 symmetry. The configurations of the dianion moieties were determined by measurement of differential NOE spectra to be similar to **92** and **98**; that is, the structure of **102** is the one as depicted. The assignment of other signals are indicated in Figure 4-32. The chemical shifts do not show any large differences from **90** and **93**. These data well reflect the structure **102** in which two 'bis-pentafulvene dianion' units are linked at both sides of the central thiophene ring. ^{13}C-NMR also indicated the C_2 symmetrical structure. Table 4-13 summarizes ^{1}H- and ^{13}C-NMR data.

In conclusion of this section, chemical reductions of oligothienylpentafulvenes **42a-d**, together with **45b** and **46b**, were successful. Their reduction behaviors could be monitered by means of electronic spectra. Table 4-14 summarizes the absorption wavelength of dianion **92**, **98** and tetraanion **102**. NMR spectra of dianion **92**, **97**, **98** and tetraanion **102** could be obtained. These anionic species are relatively stable, and it is proved that they possess a structure of formal oligoacetylene spine attached with cyclopentadienyl anions. However, the results from **98** and **102** seem to suggest that the spines of polyanions of higher oligomers and polymers do not have full conjugation, but rather have structures of alternate thienoquinoid and thiophene moieties.

Table 4-14. Electronic Spectral Data of **92**, **98**, and **102**

Compound	λ_{max} / nm (log ε^a) in THF			
92	551 (4.6)	13sh (4.4)	393sh (4.0)	341 (4.2)
98	551 (4.9)	389sh (4.6)	341 (4.6)	
102	553 (4.7)	386sh (4.4)	343 (4.5)	

[a] The ε values are calculated on the assumption of quantitative formation of the dianions or the tetraanion.

4-10. Experimental Section

Materials N, N, N', N'-Tetramethylethylenediamine was distilled from calcium hydride under nitrogen atmosphere. 2-Formylthiophene[25] and pyridinium chlorochromate (PCC)[26] were prepared according to literature. Thionyl chloride is commercially available and used without further purification. Anhydrous copper (II) chloride was prepared from its dihydrate by heating under reduced pressure[27]. 6, 6-Dimethylpentafulvene was synthesized by condensation of acetone and cyclopentadienyl anion. Methyllithium was perchased and used as it is. 6-Dimethylaminopentafulvene was synthesized according to literature[19b]. Tetrahydrofuran and tetrahydrofuran-d8 for generation of the anionic species were dried over sodium-pottasium alloy and degassed immediatry before use. Sodium amalgam (3%) was prepared accrding to literature[28] and stored in a desiccator.

Electrochemical Measurements. The cyclic voltammetry system used in the present thesis was composed of a Yanaco Model P-1000 voltammetric analyzer, a Yanaco Model FG-121B function generator, and a Yanaco Model WX-4401 X-Y recorder. The working electrode was a glassy-carbon stick. The counter electrode was a Pt wire. The reference electrode was an Ag wire, on which AgCl had been deposited electrolytically, and was immersed in the electrolyte solution. The measurements were performed in DMF containing 0.1 M n-Bu_4NClO_4 under nitrogen atomosphere. Potentials were calibrated using the ferrocene/ferrocenyl cation couple (+0.52 V vs Ag/AgCl) as a standard.

On the Results of Elemental Analyses Although new compounds in this chapter gave correct mass and NMR spectral data, their elemental analyses were not all satisfactory enough because of their some decomposition during recrystalizations. Anyway, not only satisfactory results of elemental analyses but also unsatisfactry results are described for information.

2, 5-Di[hydroxy(2-thienyl)methyl]thiophene ***75***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, a reflux condenser, and a Y-

shaped adaptor for nitrogen inlet and outlet attached to a bubbler, was placed 2.3 mL (15 mmol) of N, N, N', N'-tetramethylethylenediamine (TMEDA) under nitrogen flow, and stirring was started. The flask was cooled to 0 °C in an ice-water bath, and 10 mL (15 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum. After stirring at 0 °C for 30 min, 0.6 mL (7.5 mmol) of thiophene was added, and the mixture was allowed to warm up to room temperature, then refluxed for 30 min. The mixture was cooled to -70 °C, and added with 1.7 g (15 mmol) of 2-formylthiophene in 15 mL of THF dropwise via syringe through the septum. The mixture was allowed to warm up to room temperature and stirred for additional 5 h. The reacton mixture was added with 20% aqueous ammonium chloride solution and extracted with ether. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (50 g, eluted with 10% ether/benzene) to give 2.0 g of **75** (86%). The crude product was used for the next oxidation without further purification.

75: Pale yellow oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.25 (dd, J = 5.0, 1.0 Hz, 2H), 6.98 (ddd, J = 3.6, 1.2, 0.9 Hz, 2H), 6.94 (dd, 5.0, 3.5 Hz, 2H), 6.83/6.82 (s, 2H), 6.18/6.16 (s, 2H), 2.86/2.84 (s, 2H).

2, 5-Di(2-thienoyl)thiophene ***76***. In a 500 mL round-bottomed, one-necked flask equipped with a magnetic stirring bar and a calcium chloride drying tube, were placed 3.6 g (11.7 mmol) of **75** and 200 mL of dry benzene. The mixture was added with 58 g of PCC/alumina[26] and stirred at room temperature for 8 h. The reaction mixiture was filtered, and the solid was washed with dichloromethane until the product was not detected by TLC. The combined filterate was evapolated in vacuo, and the residue was recrystallized from dichloromethane-hexane to give 2.8 g of **76** (80%).

76: Pale yellow crystals (CH_2Cl_2-hexane); m.p. 179-180 °C (lit.[5] 182.5 -183 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.97 (dd, J = 3.4, 1.7 Hz, 2H), 7.91 (s, 2H), 7.77 (dd, J = 4.4, 1.7 Hz, 2H), 7.23 (dd, J = J = 4.4, 3.4 Hz, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 178.57, 147.42, 142.49, 134.65, 133.96, 132.48, 128.30; IR (KBr) *v* 3093w, 1600s, 1516m, 1412s, 1352m, 1289s, 1054m, 807, 723s cm^{-1}.

2, 5-Thiophenedicarboxylic acid ***81***. In a 500-mL round-bottomed, four-necked flask equipped with a magnetic stirring bar, a rubber septum, a reflux condenser, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, was placed 12 mL (80 mmol) of TMEDA under nitrogen flow, and stiring was started. The flask was cooled to 0 °C in an ice-water bath, and 50 mL (75 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum. After stirring at 0 °C for 30 min, 2.4 mL (30 mmol) of thiophene was added, and the mixture was allowed to warm up to room temperature, then refluxed for 30 min. The mixture was cooled to -70 °C, and added with 100 mL of anhydrous ether. Large excess of finely divided dry ice (4-5 g) was added into the reaction flask, and the mixture was allowed to warm up to room temperature. The contents of the flask were poured into 200mL of 10% aqueous sodium hydroxide solution. The aqueous layer was twice washed with ether. The crude dicarboxylic acid was precipitated from the aqueous layer by addition of conc. hydrochloric acid, and filtered in vacuo and washed with water until the filtrate became neutral to give 4.4 g of **81** (85%) as colorless powder . The crude product was used for the next reaction without further purification.

2, 5-Thiophenedicarbonyl dichloride ***82***. In a 30 mL round-bottomed, one-necked flask equipped with a magnetic stirring bar and a reflux condenser fittrd with a calcium chloride drying tube, were placed 4.3 g (25 mmol) of **81** and 10 mL of thionyl chloride. The mixture was refluxed for 8 h. The extra thionyl chloride was removed in vacuo, and the residue was washed with hexane and filtered to give 5.1 g of **82** (98%). The crude product was used for the next reaction without further purification.

82: Colorless crystals; m.p. 34-35 °C; ^{1}H-NMR (60 MHz, CCl_4) δ 7.9 (s).

N, N, N', N'-Tetramethyl-2, 5-thiophenedicarbamide ***79***. In a 50-mL round-bottomed, one-necked flask equipped with a magnetic stirring bar and a reflux condenser fitted with a calcium chloride drying tube, was placed 3.1 g (14.8 mmol) of 2, 5-thiophenedicarbonyl dichloride **82** and 15 mL of N, N-dimethylformamide. The mixture was heated at 150 °C for 10 h under stirring. After cooling to room temperature, the reaction mixture was added with water

and extracted with dichloromethane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was crystalized by addition of a small amount of dichloromethane followed by hexane. The crystals were collected by filtration to give 1.6 g of **79** (48%).

79: Colorless crystals (benzene-hexane); m.p. 115 °C; MS (EI, 70 eV) m/z 226 (M^+, 25%), 182 [$(M\text{-}NMe_2)^+$, 40%], 84 (25%), 49 (20%), 28 (20%), 18 (100%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.27 (s, 2H), 3.18 (s, 6H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 163.93, 140.07, 128.68, 39.15, 36.65; IR (KBr) ν 1710m, 1600s, 1532s, 1393s, 1270s, 1198s, 1055m, 1027m, 732m, 688m cm^{-1}.

Bis-[6-(2-thienyl)pentafulvene] ***42b***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 0.3 mL (3.7 mmol) of thiophene and 7 mL of anhydrous THF under nitrogen flow. The stirred mixture was cooled below -50 °C by immersion in a dry ice-ethanol bath, and 1.3 mL (2.0 mmol) of 1.5 M n-butyllithium in hexane was added via syringe through the septum, The mixture was stirred at -50 °C for 1 h, and added with 230 mg (1.0 mmol) of **79** in one portion. The resulting colorless suspension was allowed to warm to 0 °C (an ice-water bath), and stirred for an additional 1 h. The mixture turned into a pale-yellow solution, and was added with 1 mL (12 mmol) of cyclopentadiene at the same temperature. The stirring was continued at 0 °C for 2 h. The dark-blue reaction mixture was added with water and extracted with dichloromethane. The organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. After removal of $MgSO_4$ by filtration, the filtrate was passed through a short column of Al_2O_3 (30 g) eluted with dichloromethane. Solvent was removed in vacuo, and the residue was separated by column chromatography on silica gel (40 g, 0 °C; A column fitted with an ice-cooled jacket was used.) using benzene/hexane as eluent. The crude crystals , precipitated by concentration of the solution, were collected by filtration, and washed with ether/hexane to give 261 mg of **42b** (65%).

42b: Wine red needles (CH_2Cl_2-hexane); m.p. 156 °C; MS (EI, 70 eV) m/z 400 (M^+, 100%), 367 (20%), 333 (15%), 302 (10%), 282 (10%), 240 (10%), 184 (10%), 171 (12%), 139

(12%), 115 (12%), 28 (25%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.56 (dd, J = 5.0, 1.3 Hz, 2H), 7.30 (dd, J = 3.6, 1.3 Hz, 2H), 7.27 (s, 2H), 7.13 (dd, J = 5.0, 3.6 Hz, 2H), 6.58-6.61 (m, 6H), 6.48-6.51 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 147.58, 144.10, 142.55, 135.43, 133.17, 132.93, 132.88, 132.80, 130.17, 127.25, 124.24, 123.72; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 415 (4.36), 368 (4.40), 287 (4.05); IR (KBr) ν 3086w, 1550s, 1457m, 1411m, 1363s, 1307w, 1279m, 1230w, 1081m, 1069m, 995m, 908m, 817m, 783m, 765s, 709m, 683m, 624w cm^{-1}; Anal. Calcd. for $C_{24}H_{16}S_3$: C, 71.97; H, 4.03. Found: C, 71.50; H, 3.97.

*Tris-[6-(2-thienyl)pentafulvene] **42c***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 732 mg (3.0 mmol) of 6, 6-di(2-thienyl)-pentafulvene **42a** and 10 mL of anhydrous THF under nitrogen flow. The stirred mixture was cooled below -50 °C, and 1.7 mL (3.0 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added dropwise via syringe through the septum, and the stirring was continued at -50 °C for 1 h. To the dark red solution was added 0.15 mL (1.5 mmol) of dimethylcarbamyl chloride via syringe through the septum at -70 °C. The mixture was allowed to warm up to 0 °C, and stirred at 0 °C for an additional 1 h. Cyclopentadiene (2 mL, 24 mmol) was added and the stirring continued at the same temperature for 2 h. The reaction mixture was added with water and extracted with dichloromethane. The organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. After removal of $MgSO_4$ by filtration, the filtrate was passed through a short column of Al_2O_3 (30 g) eluted with dichlromethane. Solvent was removed in vacuo, and the residue was separated by column chromatography on silica gel (40 g, 0 °C) using benzene/hexane as eluent. The crude crystals , precipitated by concentration of the solution, were collected by filtration, and washed with ether/hexane to give 398 mg of **42c** (51%).

42c: Wine red crystals (CH_2Cl_2-hexane); m.p. ca. 160 °C (decomp.); MS (FAB) m/z 559 [(M+H)$^+$]; ^{1}H-NMR (400 MHz, CD_2Cl_2) δ 7.61 (dd, J = 5.1, 1.3 Hz, 2H), 7.34 (d, J = 3.8 Hz, 2H), 7.33 (dd, J = 3.7, 1.3 Hz, 2H), 7.31 (d, J = 3.8 Hz, 2H), 7.16 (dd, J = 5.1, 3.7 Hz, 2H), 6.57-6.63 (m, 10H), 6.49-6.51 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 147.70,

146.80, 144.59, 144.11, 142.45, 135.28, 134.67, 133.49, 133.22, 132.98, 132.93, 132.90, 132.81, 130.23, 127.28, 124.23, 123.85, 123.68; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 409 (4.62), 368 (4.57), 290 (4.26); IR (KBr) ν 3073w, 1555s, 1459m, 1415m, 1365s, 1304w, 1278m, 1084w, 1044w, 994m, 906w, 806w, 768s, 707m, 682s, 625w cm^{-1}; Anal. Calcd. for $C_{34}H_{22}S_4$: C, 73.08; H, 3.97. Found: C, 71.72; H, 4.00.

*Tetrakis-[6-(2-thienyl)pentafulvene] **42d**.* In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 242 mg (1.0 mmol) of **42a** and 10 mL of anhydrous THF under nitrogen flow. The stirred mixture was cooled below -50 °C, and 0.6 mL (1.0 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added dropwise via syringe through the septum, and the stirring was continued at -50 °C for 1 h. The reaction mixture turned dark red and was added with 110 mg (0.5 mmol) of **79** in one portion. The mixture was allowed to warm up to 0 °C, and stirred at 0 °C for additional 1 h. Cyclopentadiene (1 mL, 12 mmol) was added and the stirring continued at the same temperature for 2 h. The mixture was added with water and extracted with dichloromethane, the organic layer washed with water and brine, and dried over anhydrous $MgSO_4$. After removal of $MgSO_4$ by filtration, the filtrate was passed through a short column of Al_2O_3 (30 g) eluted with dichlromethane. Solvent was removed in vacuo without external heating, and the residue was separated by column chromatography on silica gel (40 g, 0 °C) using dichloromethane/hexane as eluent. The fractions containing **42d** were combined and evaporated carefully without external heating (Complete evaporation of solvent led to decomposition of the product.). Crystals were precipitated during the evaporation, and the concentration of the solutions was stopped when the solvent volume became ca. 100 mL. The wine red crystals were collected by filtration, and washed with ether/ hexane to give 60 mg of **42d** (17%).

42d: Wine red crystals (CH_2Cl_2-hexane); m.p. ca 200 °C (decomp.); MS (FAB) m/z 717 $[(M+H)^+]$; ^{1}H-NMR (400 MHz, CD_2Cl_2) δ 7.60 (dd, J = 5.1, 1.3 Hz, 2H), 7.35 (s, 2H), 7.34 (d, J = 4.0 Hz, 2H), 7.33 (dd, J = 3.7, 1.3 Hz, 2H), 7.31 (d, J = 4.0 Hz, 2H), 7.16 (dd, J = 5.1, 3.7 Hz, 2H), 6.58-6.63 (m, 14H), 6.49-6.51 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$)

δ 147.79, 146.99, 146.75, 144.75, 144.22, 142.51, 135.28, 134.58, 133.59, 133.29, 132.97, 132.91, 132.87, 132.81, 130.24, 127.30, 124.25, 123.92, 123.89, 123.69; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 408 (4.76), 365sh (4.67), 289 (4.38); IR (KBr) ν 2918w, 1559m, 1424m, 1363s, 1083w, 767s, 701m, 580w, 503w cm^{-1}; Anal. Calcd. for $C_{44}H_{28}S_5$: C, 73.70; H, 3.94. Found: C, 72.87; H, 4.46.

Bis[6, 6-di(2-thienyl)pentafulvene] ***45b***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 485 mg (2.0 mmol) of **42a** and 15 mL of anhydrous THF under nitrogen flow. The stirred mixture was cooled below -70 °C, and 1.2 mL (2.2 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added dropwise via syringe through the septum. The mixture was stirred at -70 °C for 1 h, and added with 310 mg (2.3 mmol) of anhydrous copper (II) chloride in one portion. The suspension was stirred at -70 °C for 30 min, then allowed to warm to 0 °C, and stirred for additional 2 h. Benzene/hexane (1/1 v/v) was added, and the mixture was passed through a short column of Al_2O_3 (30 g) eluted with benzene/hexane. Solvent was removed in vacuo, and the residue was separated by column chromatography on silica gel (40 g, 0 °C) using benzene/hexane as eluent. The crude crystals, precipitated by concentration of the solution, were collected by filtration, and washed with ether/hexane to give 202 mg of **45b** (51%).

45b: Wine red needles (CH_2Cl_2-hexane); m.p. 175-176 °C (decomp.); MS (EI, 70 eV) m/z 482 (M^+, 100%), 449 (10%), 415 (10%), 354 (10%), 240 (10%), 208 (10%), 18 (10%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.56 (dd, J = 5.0, 1.2 Hz, 2H), 7.30 (dd, J = 3.6, 1.2 Hz, 2H), 7.24 (d, J = 4.0 Hz, 2H), 7.20 (d, J = 4.0 Hz, 2H), 7.13 (dd, J = 5.0, 3.6 Hz, 2H), 6.57-6.64 (m, 6H), 6.45-6.50 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 143.66, 142.93, 142.60, 141.56, 135.48, 134.00, 132.92, 132.85, 132.52, 130.09, 127.22, 124.50, 124.22, 123.48; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 448 (4.57), 391 (4.44), 343 (4.36), 295 (4.16); IR (KBr) ν 3065w, 1793w, 1616w, 1540s, 1458m, 1421s, 1358s, 1311m, 1228m, 1080s, 998s, 766s, 708s, 678m cm^{-1}; Anal. Calcd. for $C_{28}H_{18}S_4$: C, 69.67; H, 3.76. Found: C, 69.30; H, 3.71.

*Tris[6, 6-di(2-thienyl)pentafulvene] **45c**.* In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 1000 mg (4.1 mmol) of **42a** and 20 mL of anhydrous THF under nitrogen flow. The stirred mixture was cooled below -70 °C, and 3.4 mL (6.1 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added dropwise via syringe through the septum. The mixture was stirred at -70 °C for 1 h, and added with 850 mg (6.3 mmol) of anhydrous copper (II) chloride in one portion. The suspension was stirred at -70 °C for 30 min, then allowed to warm up to 0 °C, and stirred for additional 2 h. Benzene/hexane (1/1 v/v) was added, and the mixture was passed through a short column of Al_2O_3 (30 g) eluted with benzene/hexane. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (40 g, 0 °C, eluted with 10% benzene/hexane to 20% benzene/hexane) to give 276 mg of **45b** (28%) from the first fraction and 128 mg of **45c** (11%) from the second fraction.

45c: Dark red crystals (CH_2Cl_2-hexane); m.p. 145 °C (decomp.); MS (FAB) m/z 723 [$(M+H)^+$)]; ^{1}H-NMR (400 MHz, CD_2Cl_2) δ 7.61 (dd, J = 5.1, 1.1 Hz, 2H), 7.32 (dd, J = 3.8, 1.1 Hz, 2H), 7.31 (d, J = 3.9 Hz, 2H), 7.30 (d, J = 3.9 Hz, 2H), 7.27 (d, J = 3.9 Hz, 2H), 7.23 (d, J = 3.9 Hz, 2H), 7.16 (dd, J = 5.1, 3.8 Hz, 2H), 6.57-6.64 (m, 10H), 6.46-6.48 (m, 2H); ^{13}C-NMR (100 MHz, CD_2Cl_2) δ 147.17, 144.07, 143.37, 142.86, 142.67, 142.00, 141.82, 135.85, 135.18, 134.60, 134.55, 133.37, 133.27, 132.89, 130.63, 127.72, 125.11, 125.08, 124.50, 123.97, 123.80; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 446 (4.77), 365sh (4.51), 281 (4.32); IR (KBr) ν 3067w, 1651w, 1552s, 1424s, 1363s, 1314m, 1082m, 998s, 909s, 802m, 766m, 678m cm^{-1}; Anal. Calcd. for $C_{42}H_{26}S_6$: C, 69.77; H, 3.62. Found: C, 69.76; H, 3.87.

*Tetrakis[6, 6-di(2-thienyl)pentafulvene] **45d**.* In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 240 mg (0.5 mmol) of **41b** and 10 mL of anhydrous THF under nitrogen flow. The stirred mixture was cooled below -70 °C, an 0.3 mL (0.6 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added

dropwise via syringe through the septum. The mixture was stirred at -70 °C for 1 h, and added with 70 mg (0.5 mmol) of anhydrous copper (II) chloride in one portion. The suspension was stirred at -70 °C for 30 min, then allowed to warm up to 0 °C, and stirred for additional 2 h. Dichloromethane was added, and the mixture was passed through a short column of Al_2O_3 (30 g) eluted with dichloromethane. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (40 g, 0 °C, eluted with 20% benzene/hexane to benzene/hexane = 1/2 v/v) to give 20mg of **45d** (8%).

45d: Dark red crystals (CH_2Cl_2-hexane); m.p. ca. 230 °C (decomp.); MS (FAB) m/z 963 [$(M+H)^+$)]; ^{1}H-NMR (400 MHz, CD_2Cl_2) δ 761 (dd, J = 5.0, 1.3 Hz, 2H), 7.30-7.34 (m, 8H), 7.283 (d, J = 3.8 Hz, 2H), 7.280 (d, J = 4.0 Hz, 2H), 7.24 (d, J = 4.0 Hz, 2H), 7.17 (dd, J = 5.0, 3.7 Hz, 2H), 6.57-6.64 (m, 14H), 6.46-6.48 (m, 2H); UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 449 (4.98), 277 (4.48); IR (KBr)ν 3068w, 1621m, 1555s, 1462m, 1424s, 1361s, 1316m, 1081m, 997m, 906m, 801s, 768s, 707m, 677m cm^{-1}; Anal. Calcd. for $C_{56}H_{34}S_8$: C, 69.82; H, 3.56. Found: C, 68.34; H, 3.43.

2-t-Butyl-6, 6-di(2-thienyl)pentafulvene ***87***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 2.4 g (22.6 mmol) of 6, 6-dimethylpentafulvene and 10 mL of anhydrous THF under nitrogen flow. The stirred mixture was cooled below -50 °C, and 15 mL (22.5 mmol) of 1.5 M methylllithium in diehtyl ether was added dropwise via syringe through the septum. The mixture was allowed to warm up to 0 °C, and stirred for 1 h. The mixture was again cooled to -50 °C, and a solution of 2.0 g(10.0 mmol) of di(2-thienyl)ketone **56** in 10 mL of anhydrous THF was added via syringe through the septum. The mixture was allowed to warm up to 0 °C, and stirred for additional 2 h. The reaction mixture was added with water and extracted with hexane. The organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (50g, hexane as eluent) to give 1.4 g of **87** (46%).

87: Dark red crystals (hexane); m.p. 104 -105 °C; MS (EI, 70 eV) m/z 963 (M^+, 5%), 283 [$(M-Me)^+$, 15%], 28 (20%), 18 (100%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.50 (dd, J = 5.0,

1.3 Hz, 1H), 7.48 (dd, J = 5.0, 1.3 Hz, 1H), 7.24 (dd, J = 3.6, 1.3 Hz, 1H), 7.21 (dd, J = 3.6, 1.3 Hz, 1H), 7.10 (dd, J = 5.0, 3.6 Hz, 1H), 7.08 (dd, J = 5.0, 3.6 Hz, 1H), 6.63 (dd, J = 5.4, 2.0 Hz, 1H), 6.49 (dd, J = 5.4, 2.0 Hz, 1H), 6.21 (t, J = 2.0 Hz, 1H), 1.21 (s, 9H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 159.19, 143.78, 143.58, 143.42, 133.60, 132.42, 132.10, 131.92, 129.32, 129.07, 127.06, 126.91, 125.03, 115.02, 32.45, 29.64; IR (KBr) ν 3074w, 2956s, 1554s, 1463w, 1415s, 1357s, 1250m, 1074m, 1018m, 930w, 845w, 816m, 790w, 704s, 660m cm^{-1}; Anal. Calcd. for $C_{18}H_{18}S_2$: C, 72.43; H, 6.08. Found: C, 72.79; H, 6.03.

Polymerization of ***87***. In a 100-mL round-bottomed, four-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 4 g (13.4 mmol) of **70** and 40 mL of anhydrous THF under nitrogen flow. The stirred mixture was cooled below -70 °C, and 19 mL (34.2 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added dropwise via syringe through the septum. The mixture was stirred at -70°C for 1 h, and added with 4.6 g (34.1 mmol) of anhydrous copper (II) chloride in one portion. The suspension was stirred at -70 °C for 30 min, then allowed to warm up to 0 °C, and stirred for additional 2 h. Dichloromethane was added, and the mixture was passed through a short column of Al_2O_3 (150 g) eluted with CH_2Cl_2. Dark red powders, precipitated by concentration of the solution, were collected by filtration, and washed with hexane to give 1.9 g of **71**. This sample was analyzed in the laboratory of Prof. K. Müllen (See Text, Section 4-5).

2, 5-Bis(6-pentafulvenyl)thiophene ***46b***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, a reflux condenser, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, was placed 1.3 mL (8.3 mmol) of N, N, N', N'-tetramethylethylenediamine (TMEDA) under nitrogen flow, and stirring was started. The flask was cooled to 0 °C in an ice-water bath, and 5.5 mL (8.3 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum. After stirring at 0 °C for 30 min, 0.3 mL (3.8 mmol) of thiophene was added, and the mixture was allowed to warm up to room temperature, then refluxed for 30 min. The mixture was cooled to -60 °C, and added

with 30 mL of anhydrous THF, followed by 1070 mg (8.4 mmol) of 6-dimethylamino-pentafulvene **89** in one portion. The mixture was allowed to warm up to 0°C, and the stirring was continued for additional 3 h. The reaction mixture was added with water and extracted with benzene/hexane. The organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. After removal of $MgSO_4$ by filtration, the filtrate was passed through a short column of Al_2O_3 (30 g) eluted with benzene/hexane. Solvent was removed in vacuo, and the residue was separated by column chromatography on silica gel (40 g, 0 °C) using benzene/hexane as eluent. The crude crystals , precipitated by concentration of the solution, were collected by filtration, and washed with ether/hexane to give 640 mg of **46b** (87%).

46b: Wine red needles (CH_2Cl_2-hexane); m.p. 114-115 °C; MS (EI, 70 eV) m/z 236 (M^+, 10%), 63 (10%), 28 (17%), 18 (100%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.20 (s, 2H), 7.15 (s, 2H), 6.84-6.86 (m, 2H), 6.62-6.66 (m, 2H), 6.44-6.46 (m, 2H), 6.22-6.25 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 145.18, 144.14, 135.88, 133.58, 131.33, 128.85, 127.14, 119.48; UV-Vis. (cyclohexane) λ_{max}/nm (log ε) 449sh (4.45), 423 (4.57), 291 (4.45), 281sh (4.32); IR (KBr) ν 3071w, 1597s, 1459m, 1424m, 1377m, 1334m, 1228m, 1086m, 988m, 898s, 755s, 615m cm^{-1}; Anal. Calcd. for $C_{16}H_{12}S$: C, 81.31; H, 5.12. Found: C, 80.85; H, 5.08.

5', 5"-Di(6-pentafulvenyl)-6, 6-di(2-thienyl)pentafulvene ***46c***. A 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, was purged with dry nitrogen. Anhydrous THF (6 mL) and 0.4 mL (2.8 mmol) of diisopropylamine were added via syringe through the septum under nitrogen flow. The mixture was cooled to -50 °C, and 1.3 mL (2.0 mmol) of 1.5 M n-butyllithium in hexane was added dropwise. After the addition was complete, the mixture was stirred at 0 °C for 30 min, and then cooled to -50 °C. A solution of 120 mg (0.5 mmol) of **42a** in 5 mL of anhydrous THF was added dropwise via syringe through the septum, and the mixture was allowed to warm up to 0 °C. After stirring for 1 h, 250 mg (2.0 mmol) of **89** was added in one portion, and the mixture was stirred at 0 °C for additional 3 h. The reaction mixture was added with water and extracted with benzene/hexane. The organic layer was washed

with water and brine, and dried over anhydrous $MgSO_4$. After removal of $MgSO_4$ by filtration, the filtrate was passed through a short column of Al_2O_3 (30 g) eluted with benzene/hexane. Solvent was removed in vacuo, and the residue was separated by column chromatography on silica gel (40 g, 0 °C) using benzene/hexane as eluent. The crude crystals , precipitated by concentration of the solution, were collected by filtration, and washed with ether/hexane to give 89 mg of **46c** (87%).

46c: Dark red prisms (CH_2Cl_2-hexane); m.p. 155 °C (decomp.); MS (FAB) m/z 395 [$(M+H)^+$)], 394 (M^+); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.29 (dd, J = 3.9, 0.7 Hz, 2H), 7.22 (d, J = 3.9 Hz, 2H), 7.18 (d, J = 0.7 Hz, 2H), 6.78-6.82 (m, 2H), 6.56-6.64 (m, 2H), 6.53-6.56 (m, 2H), 6.44-6.47 (m, 2H), 6.24-6.43 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 147.03, 145.10, 144.91, 144.02, 135.88, 134.31, 133.73, 133.42, 133.06, 131.30, 128.87, 127.14, 123.75, 119.50; UV-Vis. (cyclohexane) λ_{max}/nm (log ε) 436sh (4.6), 404 (4.68), 339sh (4.2), 293 (4.22), 282sh (4.2); IR (KBr) ν 3067w, 1606s, 1552s, 1464m, 1325m, 1231m, 1080m, 990m, 900s, 864m, 759s, 616m cm^{-1}; Anal. Calcd. for $C_{26}H_{18}S_3$: C, 79.15; H, 4.60. Found: C, 78.30; H, 4.61.

*Dilithiation of **42b**. Synthesis of **91**.* A 100-mL round-bottomed, four-necked flask equipped with a magnetic stirring bar, a rubber septum, a thermometer, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, was purged with dry nitrogen. Anhydrous ether (5 mL) and 0.3 mL (2.1 mmol) of diisopropylamine were added via syringe through the septum under nitrogen flow. The mixture was cooled to -50 °C, and 1.3 mL (2.0 mmol) of 1.5 M n-butyllithium in hexane was added dropwise. After the addition was complete, the mixture was stirred at 0 °C for 30 min, and again cooled to -70 °C. A solution of 190 mg (0.5 mmol) of **42b** in 10 mL of anhydrous THF and 15 mL of anhydrous ether was added dropwise via syringe through the septum, and the mixture was stirred at -70 °C for 1 h. Dimethy disulfide (0.2 mL, 1.8 mmol) was added and the stirring continued at -70 °C for 40 min. The reaction mixture was added with water and extracted with ether. The organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was

chromatographed on silica gel (30g, 0 °C, eluted with hexane to 20% benzene/hexane) to give 219 mg of **91** (94%).

91: Red oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.28 (s, 2H), 7.15 (d, J = 3.8 Hz, 2H), 7.01 (d, J = 3.8 Hz, 2H), 6.59-6.62 (m, 4H), 6.52-6.55 (m, 4H), 2.57 (s, 6H).

*General Procedure for Measurements of the Electronic Spectral Change of **42b-d**, **45b** and **46b** upon Reduction with Sodium Amalgam.* Fig. 4-33 shows the apparatus for the present experiments. About 1 mg of a sample was put into the vessel C with a long-necked spatula from A, and excees amounts of 3% sodium amalgam and a magetic stirring bar were put into the vessel F from D. The glass tube was sealed at E, and the apparatus was connected to a vacuum line at A. Anhydrous THF (5 mL) was distilled into C, and the glass tube was sealed at B. The solution was first transfered to the quartz cell (1 mm in thickness) to measure the spectrum of the neutral molecule. After the measurement, the solution was tranfered to F through the filter (porosity No. 2). The mixture was stirred at rooom temperature for 30 seconds, then was transfered to the cell as quickly as possible. The spectrum of the resultant solution was measured. The solution was again transfered to F, and stirred for 30 seconds. These procedures were repeated until the spectra did not show any appreciable change.

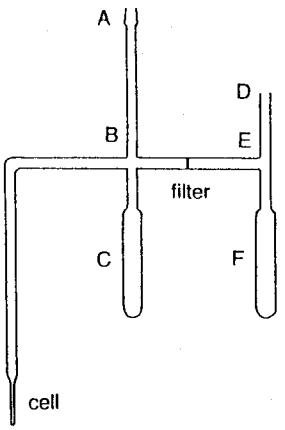


Figure 4-33. Apparatus for mesurements of electronic spectra.

*General Procedure for Measurements of NMR Spectra of the Anionic Species **42b-d**, and **46b**.* Figure 4-34 shows the apparatus for measurements of NMR spectra of dianions **42b**$^{2-}$, **42c**$^{2-}$ and **46b**$^{2-}$, and tetraanion **42d**$^{4-}$. A sample was put into the vessel C with a long-necked spatula from A, and excess amounts of 3% sodium amalgam was put into F from D. The glass tube was sealed at E, then the apparatus was connected to a vacuum line at A. Anhydrous THF-d8 (0.6 mL) was distilled into C, and the glass tube was sealed at B. The solution was transfered to the NMR tube through the filter (porosity No. 2). After sealing the tube at G, the NMR tube was turned upside down to contact with the sodium amalgam. The ^{1}H-NMR spectra were measured at brief intervals to monitor the proceeding of the reduction. When the spectrum exhibited sharp signals, the NMR tube was sealed at H.

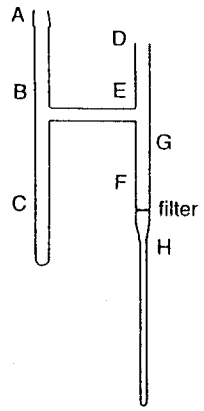


Figure 4-34. Apparatus for mesurements of NMR spectra.

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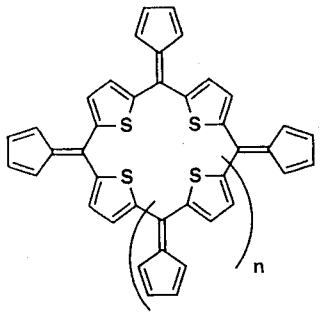
Chapter Five

Synthesis and Properties of Cyclic Oligo-6-(2-thienyl)pentafulvenes

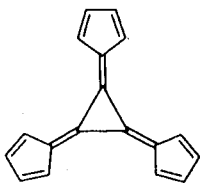
5-1. Introduction

Cyclic compounds of oligo-6-(2-thienyl)pentafulvene, depicted below, are also interesting substances from the view points of structural and physicochemical properties associated with their cyclic symmetrical structures. Cyclic oligomers larger than tetramer **47** (n = 1) would not suffer high strain in the structures, and must be obtainable as fairly stable substances.

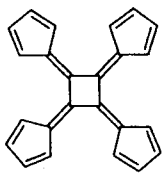


47 : n = 1

Compound **47** can be regarded as a 'thiophene-extended' [4] radialene. Radialenes (polymethylenecycloalkanes) have aroused the interest of both theorists and experimentalists owing to their unusual topology and electronic structures[1]. Tris(cyclopentadienylidene) cyclopropane **107** and tetrakis(cyclopentadienylidene)cyclobutane **108** are still unkown. Tris(9-



107



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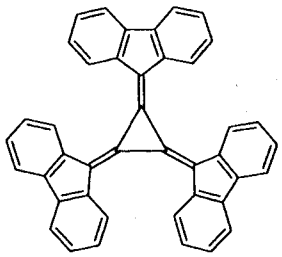
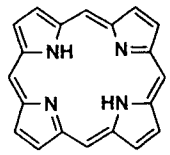


109

fluorenylidene) cyclopropane **109** was synthesized in our laboratry [2], and I described in the master thesis of mine the generation of dianion of **109** and the characterization of its unique electronic properties[3].

Moreover, **47** is also regarded as a tetrathia analogue of porphynoids because the four thiophene rings are annulated with the four sp^2 carbons.



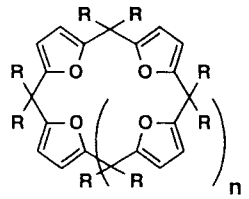
110

Porphyn **110** and its derivatives such as porphyrins, which contain four pyrrole rings, have been actively investigated in various area of science; metallo-organic chemistry, inorganic chemistry, biochemistry, photochemistry, synthetic organic chemistry and so on. From the aspect of structural organic chemistry, **110** behaves as a cyclic 18π–electron system with aromaticity. In other word, **110** is an NH-bridged diaza[18]annulene. However, there have not been so many investigations of porphynoid compounds in which the nitrogen atoms are replaced by oxygen and chalcogen atoms.

Johnson and his co-workers synthesized the first chalcogen porphyrins [4]. By Ulman and Manassen et al. and other groups, porphyrins in which one or two of the nitrogen atoms are replaced by sulfur, selenium and tellurium atoms were prepared through the established methodology of porphyrin synthesis, and some of their physical properties were studied [5-12]. While many of these novel macrocycles exhibit peculiar features, virtually all of them retained the spectral and structural characteristics associated with porphyrins.

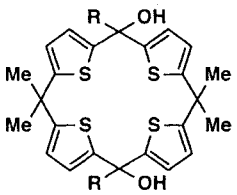
Furan analogues of porphyrinogen (tetrahydroporphyrin) type compounds **111** are known since 1955 [13]. This type of macrocycles were prepared up to octamers by acid catalysed condensations [13-16] or the reaction of dilithiated 2, 2-di(2-furyl)propane with N, N-dimethylcarbamate [17]. However, the thiophene analogues of porphyrinogens could not be prepared by acid catalysed condensations [13]. Only three compounds of tetrathia-porphyrinogen

are known: **112a-b** by Ahmed and Meth-Cohn[18] , and **113** by Vogel [19] (**113** was derived from tetraoxaporphyrinogen by treatment with H_2S/HCl.).



111

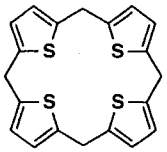
R = H or Me



112

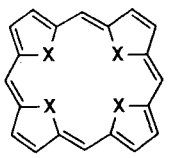
a : R = H

b : R = Me



113

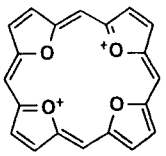
Full-conjugated macrocycles **114**, which are regarded as the oxygen or sulfur bridged-[20]annulene, are also interesting compounds. Oxygen analogue **114a** was prepared by Vogel *et el.*[20], but **114b** remains still unknown. Compounds **114** may suffer antiaromatic instability of 20π systems; in fact, **114a** is probably prone to polymerize owing to the presence of two *o*-quinoid furan units [20]. Dications and dianions of **114**, however, should show aromatic properties expected for $[4n+2]\pi$ electron systems, and indeed Vogel *et al.* recently reported the syntheis and characterization of tetraoxa-, tetrathia-, tetraselena-porphyrin dications **115-117**[15, 19, 21]. While these ionic species are similar to pyrylium ions chemically, they clearly qualify as porphyrinoid in terms of spectral properties and molecular structure.



114

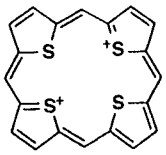
a : X = O

b : X = S



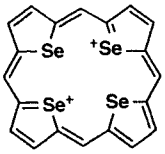
$2\ ClO_4^-$

115



$2\ ClO_4^-$

116



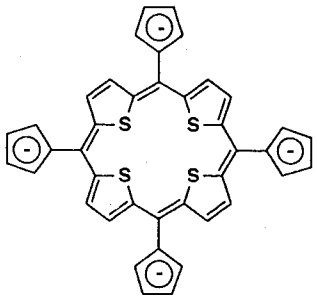
(in H_2SO_4)

117

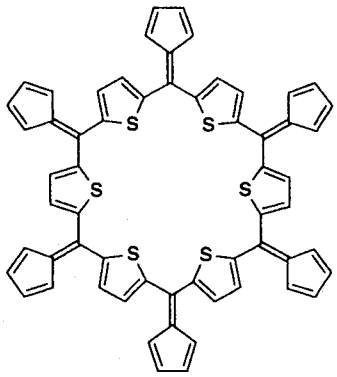
According to the aspects described above, the cyclic tatrafulvene **47** would be valuable as a novel tetrathia-porphyrinoid if it could be synthesized. Furthermore, the tetraanion of **47**, to be

represented as $\mathbf{47}^{4-}$ which is drawn below, possesses an isoelectronic structure of [20]annulene. Thus, the redox behavior of **47** is of great interest.

Therefore, I examined the synthesis of **47** from **42a** by the application of the new pentafulvene synthesis described in the previous chapters. Better than expectation, I was able to obtain not only **47**, but also cyclic hexamer **48**, although the yields were poor. Compound **48** is also an attractive macrocycle; its hexaanion would be a [30]annulene. In this chapter, I describe the details of the synthesis and physical properties of these two novel cyclic oligomers.



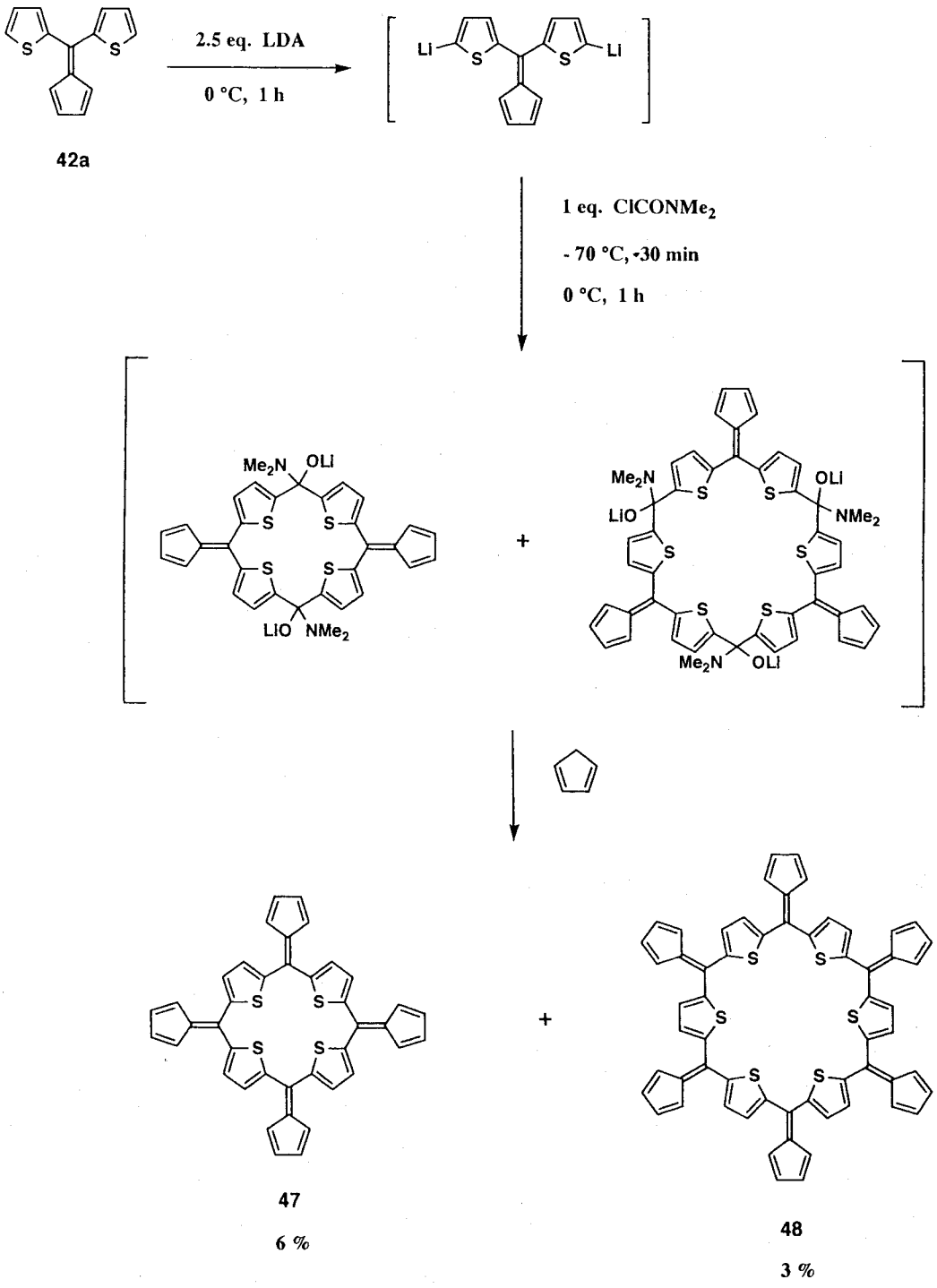
$\mathbf{47}^{4-}$



48

5-2. Synthesis

The concurrent syntheses of cyclic tetramer **47** and cyclic hexamer **48** were achieved as shown in Scheme 5-1 by the application of the new pentafulvene synthesis described in the previous chapters. The reaction was carried out under relatively high dilution condition. A THF solution of **42a** was treated with 2.5 equivalents of lithium diisopropylamide (LDA) at 0 °C. The resultant dark red solution of dilithio derivative was reacted with a THF solution of equimolar amount of dimethylcarbamyl chloride, followed by further treatment with excess amount of cyclopentadiene. After usual work-up, the reaction mixture was chromatographed on silica gel (benzene/hexane as eluent) to give **47** and **48** in 6% and 3% yield, respectively. An important



Scheme 5-1

point of this reaction is the use of 2.5 equivalents of LDA for dilithiation of **42a**. When a large excess amount of LDA (*e. g.* 4 equivalents) was used, no cyclic product was obtained.

5-3. Physical Properties

Compound **47** and **48** are orange crystalline substances and their solubilities in organic solvents are slightly poorer than the linear oligomers. Clear melting points were not observed because **47** and **48** began to decompose when the temperature rose to about 200 °C. FAB-mass spectra show a correct molecular ion peak [$(M+H)^+$] at 633 for **47**, and at 949 for **48**.

NMR spectra

Table 5-1 lists NMR data, and Figure 5-1 and 5-2 show NMR spectra of **47** and **48**. ^{1}H-NMR are similar each other and seem not to show any particular properties as peripheral conjugated systems. Only three signals appear: one singlet at 7.35 ppm and two multiplets at 6.5 - 6.7 ppm region. ^{13}C-NMR spectra show only six signals for both compounds. This simplicity

Table 5-1. ^{1}H and ^{13}C-NMR Data of **47** and **48**

	47	**48**
^{1}H-NMR[a] (δ / ppm)	7.35 (s, 8H)	7.35 (s, 12H)
	6.66-6.68 (m, 8H)	6.63-6.65 (m, 12H)
	6.53-6.56 (m, 8H)	6.52-6.55 (m, 12H)
^{13}C-NMR[b] (δ / ppm)	148.00, 144.18,	147.10, 144.84,
	134.47, 133.83,	134.50, 133.68,
	133.06, 123.32.	133.12, 123.85.

[a] In $CDCl_3$, 270 MHz. [b] In $CDCl_3$, 67.8 MHz.

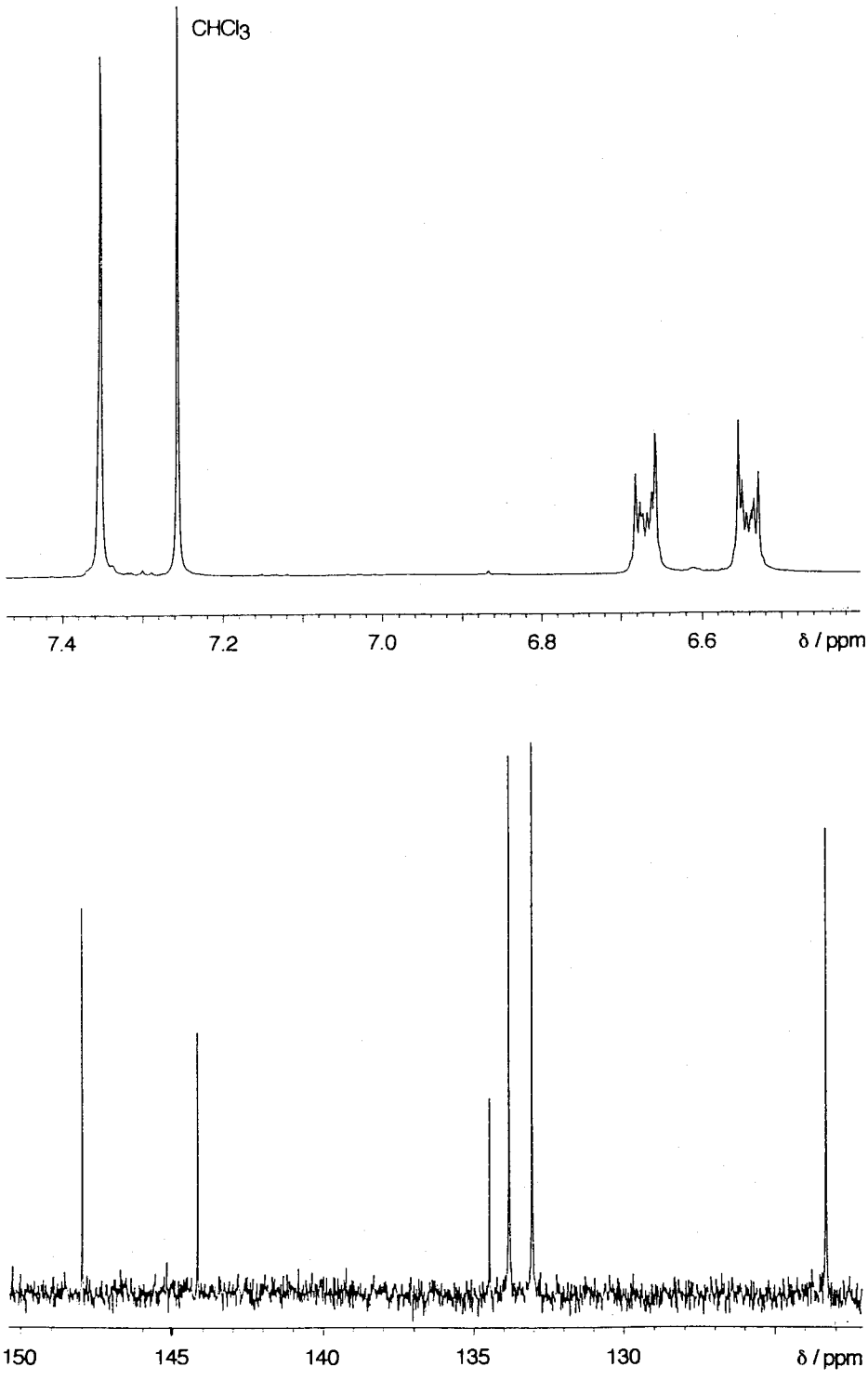


Figure 5-1. ^{1}H- and ^{13}C-NMR spectra of **47**.

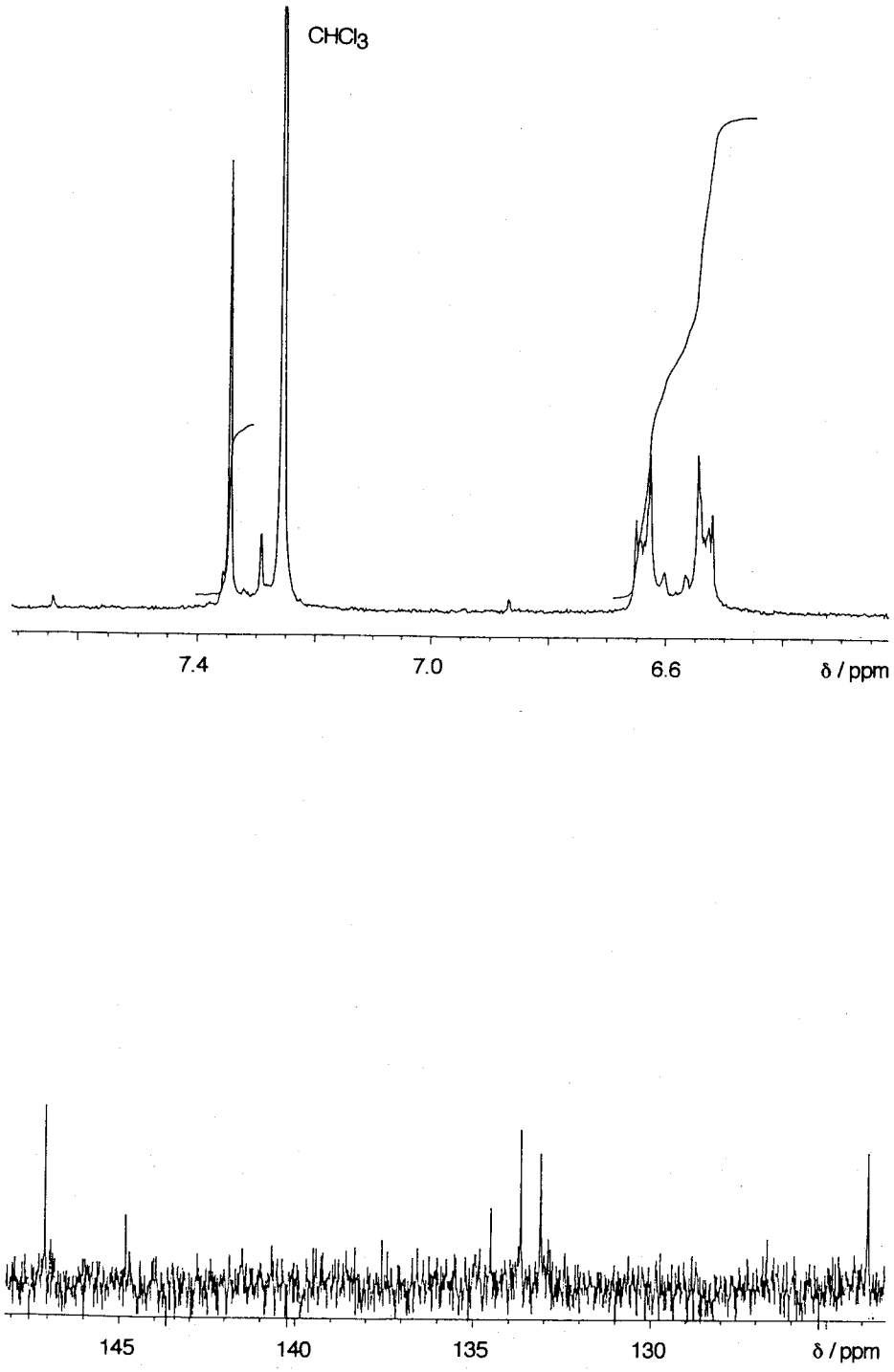


Figure 5-2. ^{1}H- and ^{13}C-NMR spectra of **48**.

of NMR spectra agree with the symmetrical cyclic structures: **47** has D_{4h} and **48** has D_{6h} symmetry in solution.

Electronic spectra

Figure 5-3 shows the electronic spectra of **47** and **48**. While the linear oligomers have three absorption bands at ca. 410, 370, and 290 nm, **47** has two distinct bands at 412 (log ε = 4.95) and 287 (4.45) nm. Except for the number of the bands, they are essentially similar and therefore **47** seems to hardly possess properties as a cyclic conjugated system in neutral state. Compound **48** shows also two peaks at 407 (log ε = 5.06) and 291 (4.51) nm, similar to **47** except intensity. The absorption coefficient (ε value) of **48** is appreciably higher than **47**; in particular, the ε value at 407 nm exceeds 100,000.

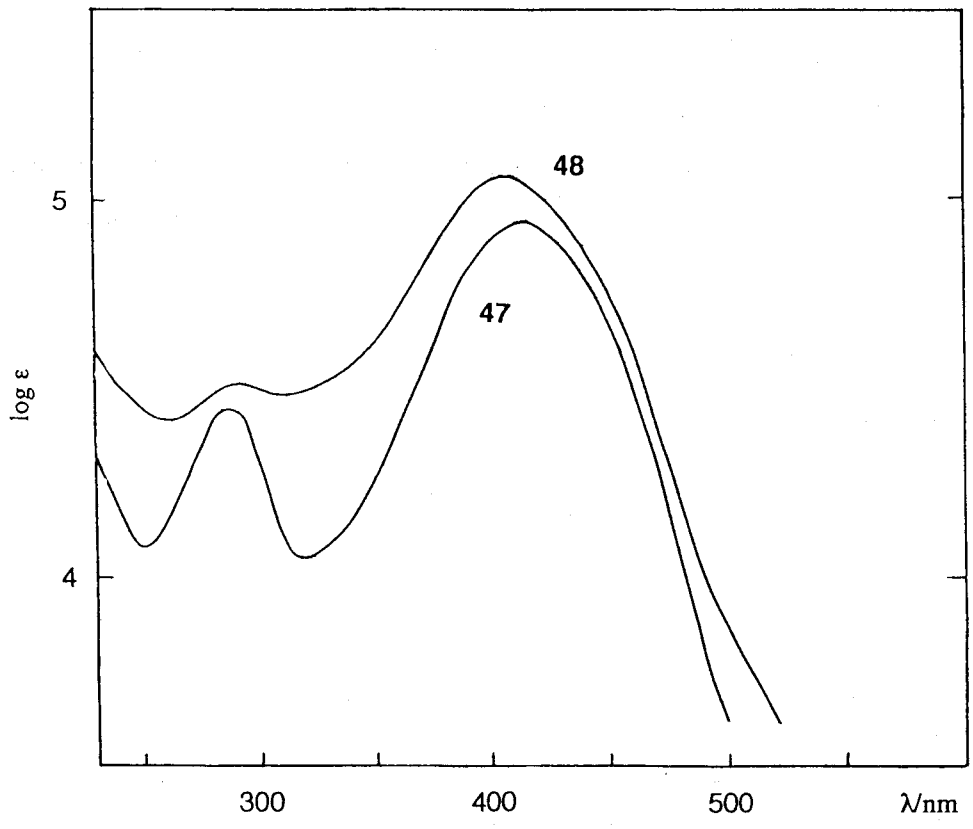


Figure 5-3. Electronic spectra of **47** and **48**.

Electrochemical behavior

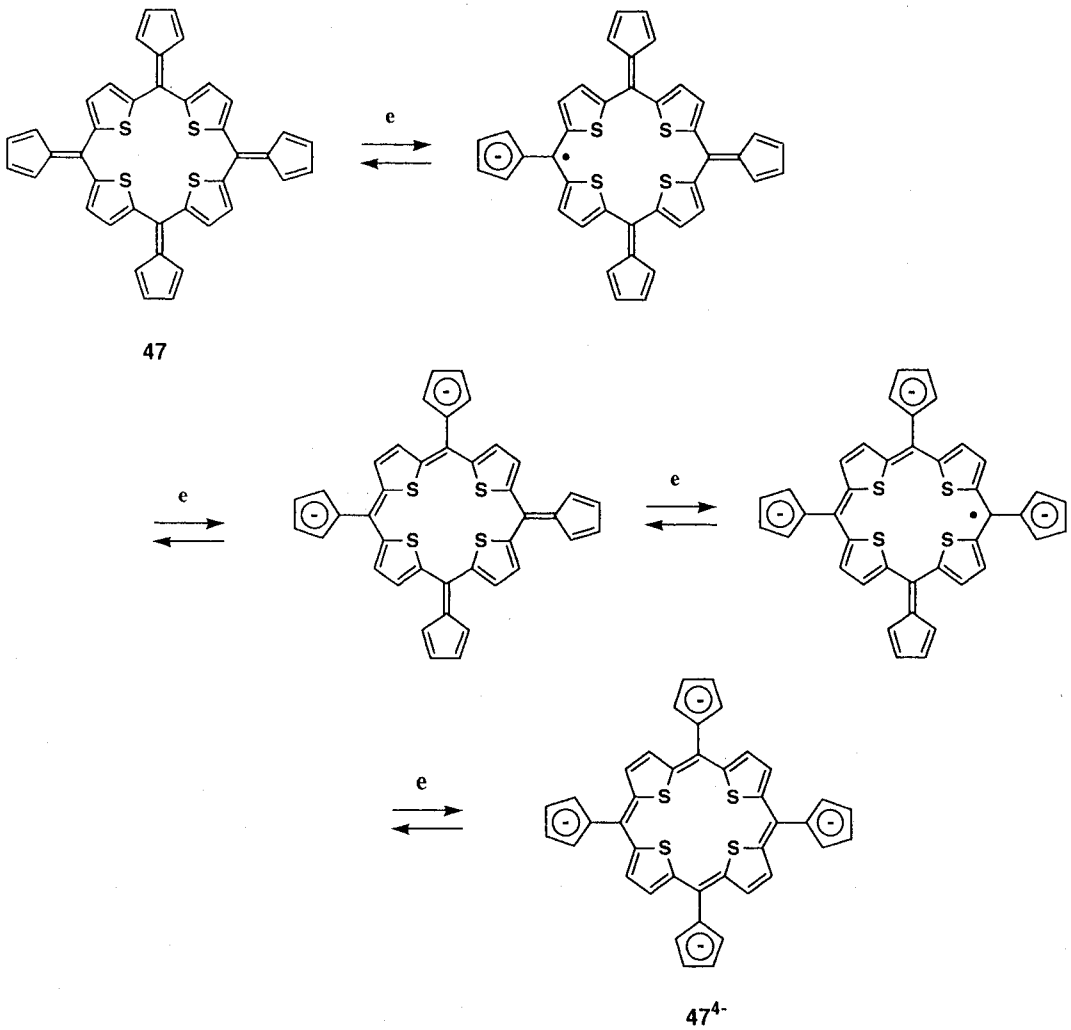
Electrochemical behavior was studied by cyclic voltammetry. Table 5-2 shows the reduction potentials and Figure 5-4 the cyclic voltammograms. Two reversible redox waves at -0.70 and -1.08 V were observed for **47**. The first wave is estimated to involve transfer of three electrons and the second wave one electron as judged from the intensity of waves; they should correspond to the formation of trianion radical and tetraanion, respectively. Scheme 5-2 shows the reduction process of **47**. The three-electron process of the first wave indicates that the potentials of the first, second and third reduction steps should be very close. The introduction of the fourth electron seems to be influenced by antiaromatic destabilization of the tetraanion $\mathbf{47}^{4-}$ to be formed.

On the other hand, **48** surprisingly shows only one reversible redox wave at - 0.77 V, although transfer of electrons up to six must be involved. This reduction potential is considerably low similar to the first reduction potential of **47** (-0.70 V) and the linear dimer **42b** (-0.93 V). Accordingly, the properties of anionic species of **48** are of great interest. If this wave really corresponds to transfer of six electrons (Scheme 5-3), hexaanion $\mathbf{48}^{6-}$ would be resonance stabilized to some extent either by virtue of the 30π–electron periphery or by other peculiar structures. To get further insight into the structure of the redution product, alkali metal reduction of **48** was carried out.

Table 5-2. Reduction Potentials[a] of **47** and **48** by Cyclic Voltammetry

Compound	$E^1_{1/2}$	$E^2_{1/2}$
47	- 0.70	- 1.08
48	- 0.77	

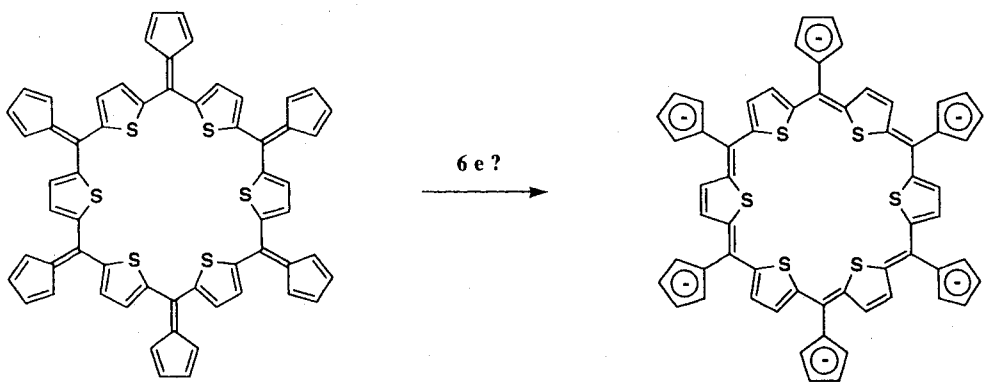
[a] V vs Ag/AgCl (calibration with ferrocene/ferrocenyl cation taken to have +0.52 V), in 0.1 M n-Bu_4NClO_4/DMF, sweep rate 50 mV/sec. Measured at 0 °C.



47

47^{4-}

Scheme 5-2



48

48^{6-}

Scheme 5-3

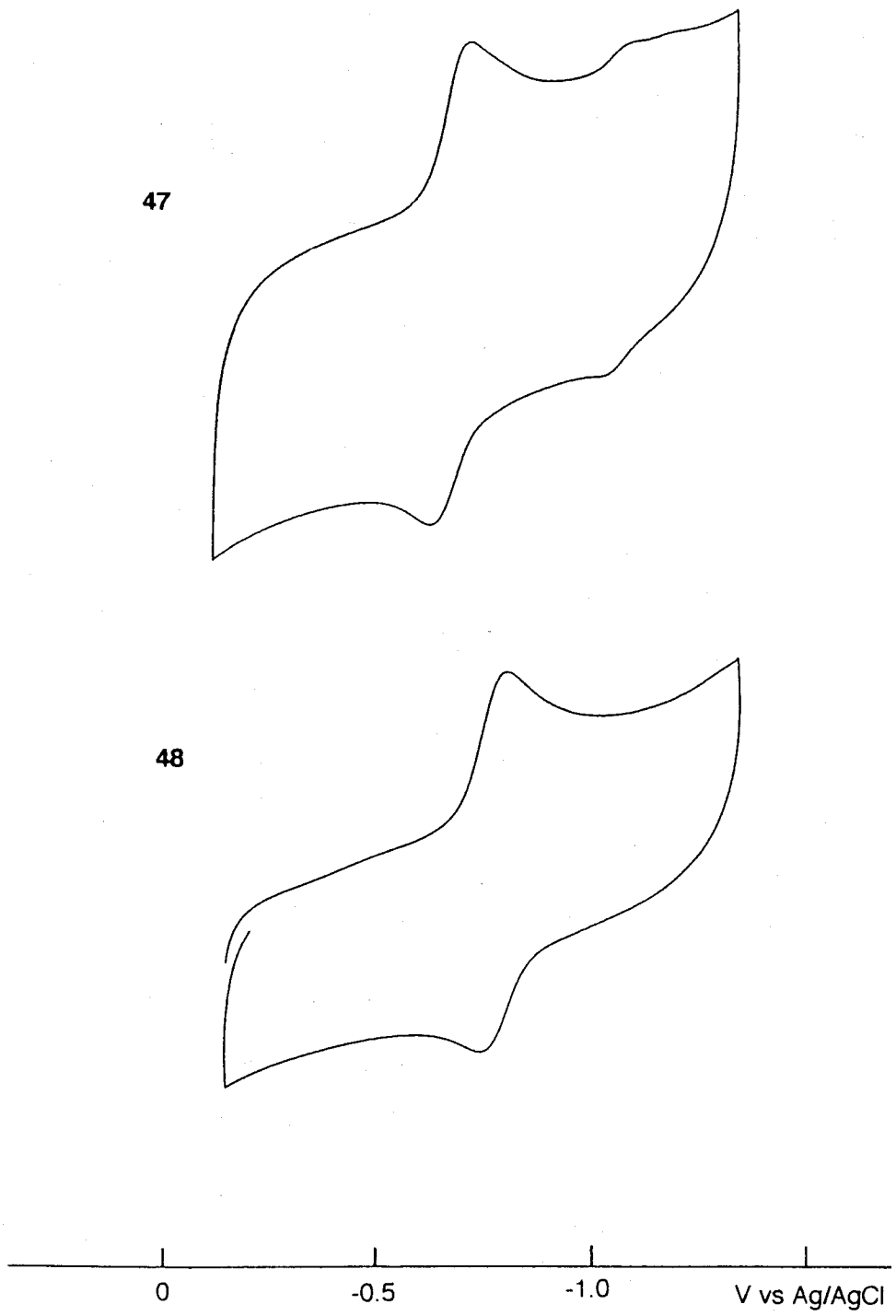
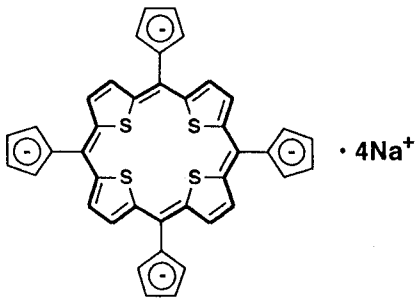


Figure 5-4. Cyclic voltammograms of **47** and **48**.

Chemical reductions of **47** and **48** were examined with 3% sodium amalgam in the similar manner for **42b-d** described in Chapter Four, Section 4-9. While the absorption of the starting material became weak, no new absorptions appeared in the reduction of **47** at room temperature. The color of the solution changed from orange to subdued brown, then turned purple, but the purple color disappeared in short time. This may be attributed to the extraordinary instability of tetraanion **118** ($\mathbf{33}^{4-}\bullet 4Na^{+}$). As described in the introduction, this instability may be ascribed to the contribution of antiaromatic [20] annulene structure. Thus, tetraanion once formed might be subject to ready polymerization similar to compound **114b** described by Vogel[21]. Indeed, black precipitates were deposited on the bottom of the cell after the measurement. More mild conditions would be required to generate the tetraanion. Further attempts are now under progress.



118

On the other hand, alkali metal reduction of cyclic-hexamer **48** proceeded successfully. Figure 5-5 shows the change of the electronic spectra of **48** upon contacts at brief intervals with sodium amalgam. As the reduction proceeded new absorptions apppeared at about 550 nm and 800nm, the latter's tailing 1200 nm (Chart 1). An isosbetic point was observed at 442 nm. When the total contact time was over 120 seconds, the broad band became weak and the abosorption at 537 nm increased (Chart 2). The reduction almost completed in about 240 seconds. The solution turned deep purple. The resultant spectrum has two bands at 537 and 340 nm, but their intensities slowly decreased during standing overnight.

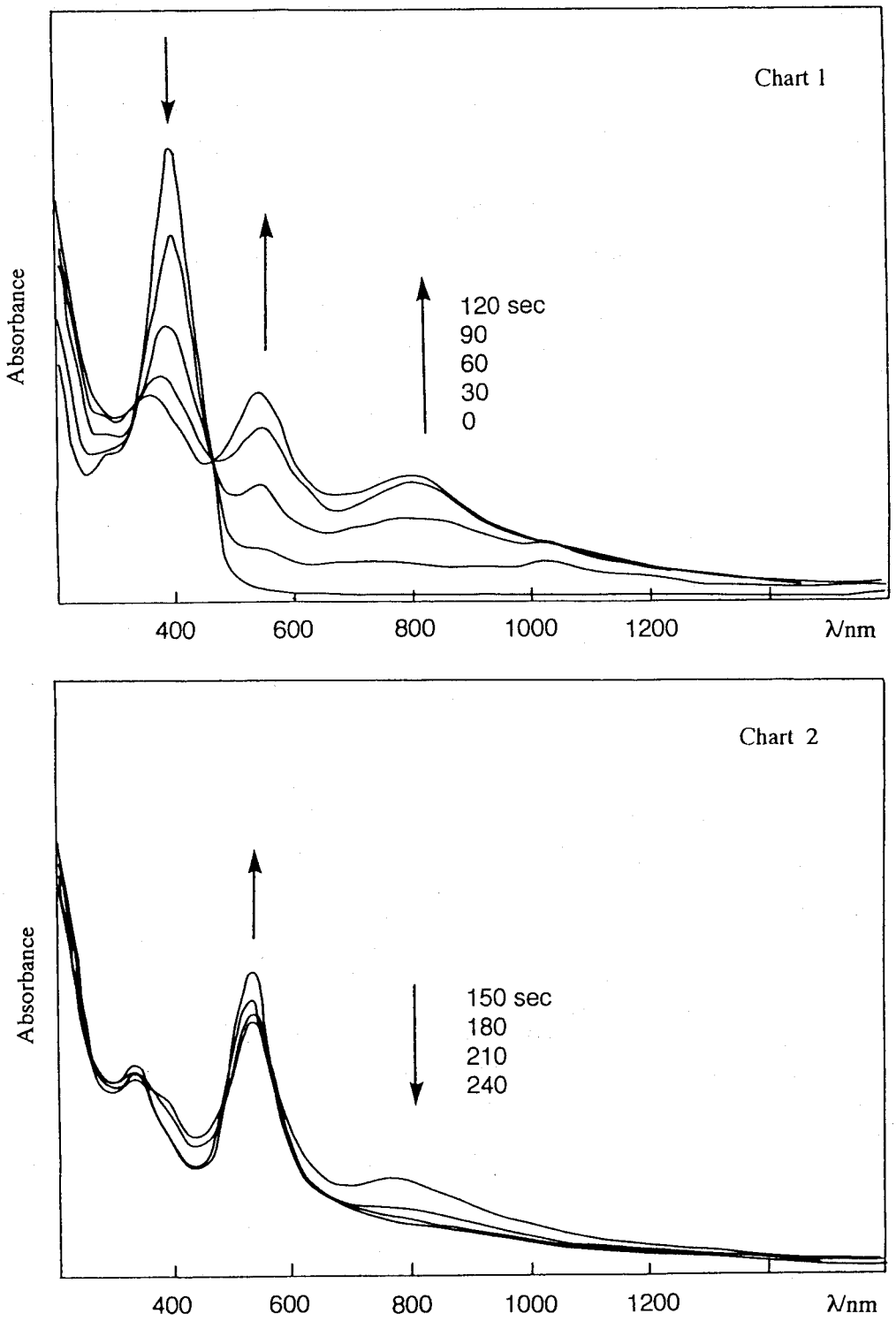
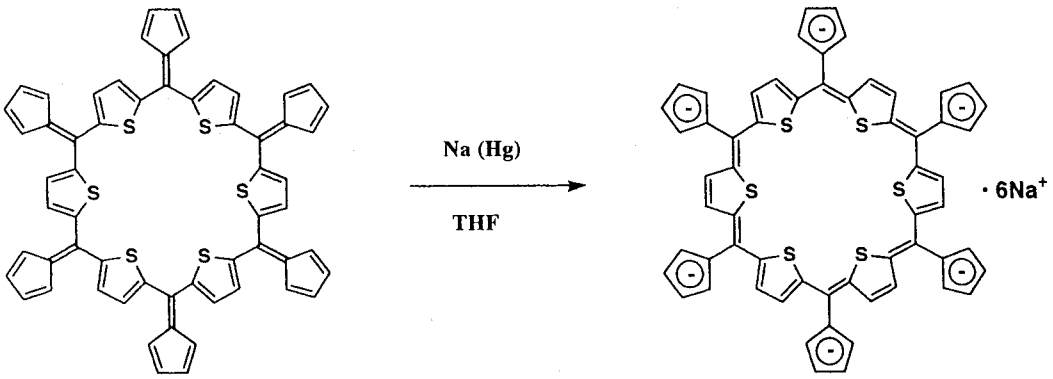


Figure 5-5. Change of electronic spectra of **48** upon reduction with Na (Hg) in THF.

This spectrum may be attributed to the formation of haxaanion **119** ($\mathbf{48}^{6-}\cdot 6Na^{+}$) (Scheme 5-4). To confirm this, the reduction of **48** was monitored by the change of ^{1}H-NMR spectra. After few seconds of reduction, no signal was observed except that of the solvent. As the solution turned purple, a broard signals appeared and gradually became sharp. Finally, a spectrum exhibiting two singlets and two triplets was obtained . Figure 5-6 displays the obtained ^{1}H-NMR spectrum, and Table 5-3 lists its chemical schifts. The spectrum suggests either the formation of a molecule with D_3 symmetry (not D_6 symmetry) or a rapid equilibrium among molecules with lower symmetry.

The dianion and tetraanion do not seem to explain the spectrum well. Because aromatic stabilization of 6π cyclopentadienyl anion is appreciably large, the negative charges should localize in the five membered rings. This makes it unable to form a full conjugated periphery in the central part of the molecule for the dianion and tetraanion. Both the structures of fully perpheral conjugation and rapid equilibrium of localized structure should require appearance of all the thiophene protons as one singlet. Therefore, the possibilities of the formation of dianion or tetraanion are ruled out. The spectrum should be attributed to hexaanion **119**.



48 **119**

Scheme 5-4

For hexaanion **119**, principally two structures are conceivable: one is partially delocalized structure **119A**, the other fully delocalized structures **119B**. The observation of two different singlets means that **119** hardly shows significant contribution of the peripheral conjugated

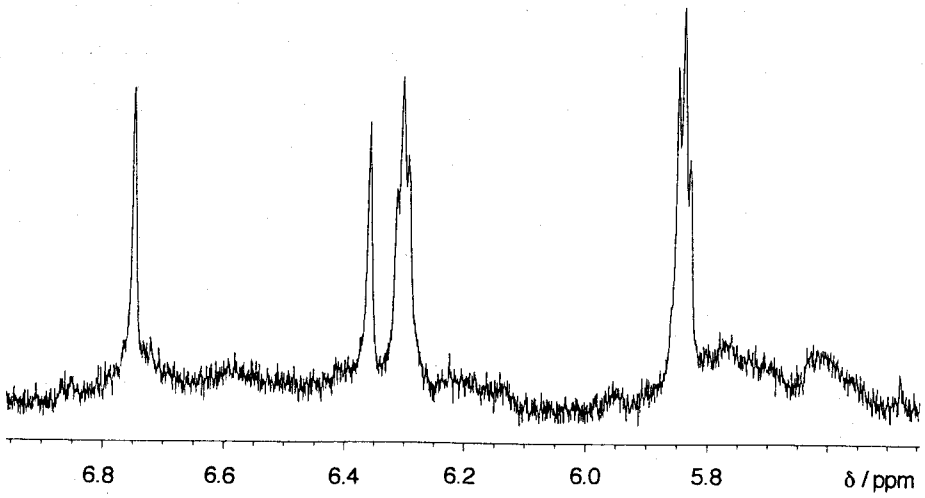


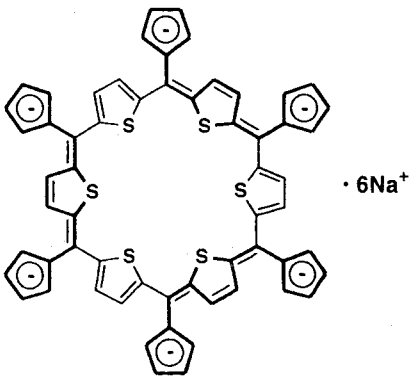
Figure 5-6. ^{1}H-NMR spectrum of **119** ($\mathbf{48}^{6-}\bullet 6Na^+$).

Table 5-3. ^{1}H-NMR Data[a] of Cyclic-hexaanion **119** ($\mathbf{48}^{6-}\bullet 6Na^+$)

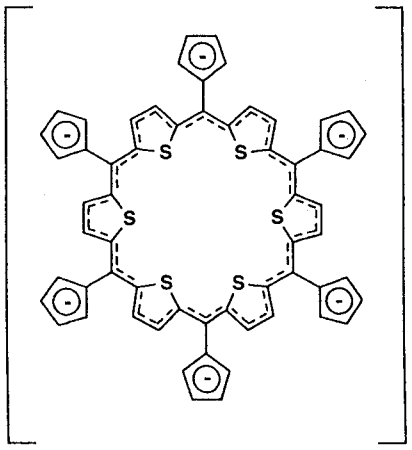
Compound	Chemical shifts[b] (δ)
119	6.75 (s, 6H)
	6.36 (s, 6H)
	6.30 (t, J = 2.8 Hz, 12H)
	5.84 (t, J = 2.8 Hz, 12H)

[a] In THF-d8, at 30 °C. [b] At 270 MHz, referenced to the solvent signal: 1.70 ppm.

system, *i.e.* [30] annulene **119B**. The structure of **119** is best represented by formula **119A**, which consists of localized three thiophene rings and three bis-pentafulvenyl dianion inserted with thienoquinoid. In this structure, the singlet at 6.36 ppm can be assigned to the thienoquinoid protons (6H) and the singlet at lower field of 6.75 ppm to the thiophene ring protons (6H) by comparison with ^{1}H-NMR spectra of dianions of linear pentafulvenyl-dimers **42b** (**92**) and **46b** (**97**). The electronic spectra which is similar to that of **42b** also suggest the structure **119A**. Absorption maxima of **119B** must be much at longer wavelength than the obtained data.



119A



119B

Why does **119** take the structure **119A** rather than **119B**? A possible reason is as follows. To take delocalized structure **119B**, the resonance energy gained by the [30] annulene must exceed the some loss of resonance energy of three thiophenes. On the basis of theoretical works, however, resonance energy of [4n+2] annulenes decreases as the number of π–electron increases[22]. Thus, it seems to be energitically favored to retain three thiophenes in the structure of **119** like **119A**. Therefore, resonance stabilization of [30] annulene **119B** is estimated to be not very large. If this is true, ^{1}H-NMR of **119A** should show an averaged spectra of equilibrium between 119A and its equivalent double bond isomer at elevated temperatures. However, measurements at varied temperature seemed to be difficult because of the instability of **119** at high temperatures and remains to be reexamined.

^{13}C-NMR spectra should also provide valuable information about the structure of **119**. However, attempts of the measurement have been unsuccessful probably because of either decomposition during the measurement and poor solubility of **119**.

According to the consideration by molecular models, **119** can be either almost planar or non-planer with slight deviation of the three thiophenes from the overall plane, and the radius of the cavity is estimated about 1.8 Å. It seems to be an interesting question whether the three sulfur atoms on thienoquinoid moietiy can chelate a metal, for example the counter sodium cation, or not. To examine such phenomena, the solubility of the compound must be improved.

Synthesis of Cyclic-tetra-[6-(2-thienyl)pentafulvene] ***47*** *and Cyclic-hexa-[6-(2-thienyl) pentafulvene]* ***48***. A 200 mL, round-bottomed, four-necked flask equipped with a magnetic stirring bar, a rubber septum, a thermometer, a 50 mL pressure-equalizing droppng funnel sealed with a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, was charged with 20 mL of anhydrous THF and 0.4 mL (2.8 mmol) of diisopropylamine. The reaction flask was cooled to -50 °C in a dry ice-ethanol bath, and 1.7 mL (2.5 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum. The mixture was stirred at 0 °C for 30 min, and then cooled to -70 °C. A solution of 242 mg (1.0 mmol) of 6, 6-di(2-thienyl)pentafulvene **42a** in 50 mL anhydrous THF was transfered to the dropping funnel through the septum, and added dropwise to keep the temperature below -50 °C. After the addition was complete, the dropping funnel was rinsed with 10mL of anhydrous THF. The solution was allowed to warm up to 0 °C and stirred for 1h, and again cooled below -70°C. A solution of 0.1 mL (1.0 mmol) of dimethylcarbamyl chloride in 20 mL anhydrous THF was transfered to the dropping funnel. and added dropwise over a period 30 min to keep the reaction temperature below -70 °C. After the addition was complete, the dropping funnel was again rinsed with 10 mL of anhydrous THF, and the stirred solution was maintained -70 °C for addtional 30 min, then allowed to warm up to 0 °C. The stirring was continued at 0 °C for 1 h, and then 1 mL (12.0 mmol) of cyclopentadiene was added via syringe through the septum, and the reaction mixture was stirred at 0 °C for additionl 3 h. A small amount of water (ca. 2 mL) was added and the mixture was allowed to warm up to room temperature. The tetrahydrofuran was evaporated in vacuo, and the residue was dissolved in 150 mL of dichloromethane. After washing with water and brine, the dichloromethane layer was dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was passed through a short column of alumina (30 g) eluted with benzene/haxane (1/1 v/v). After removal of the solvent in vacuo, the residue was chromatographed on silica gel (30 g, 0 °C, eluted with 10% benzene/hexane to 20% benzene/hexane; A column fitted with an ice-cooled jacket was used.) to give 18 mg of **47** (6%) from the first fraction and 9 mg of **48** (3%) from the second fraction.

47: Orange needles (CH_2Cl_2-hexane); m.p. ca. 200 °C (decomp.); MS (FAB) m/z 633 [$(M+H)^+$]; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.35 (s, 8H), 6.66 - 6.68 (m, 8H), 6.53 - 6.56 (m, 8H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 148.00, 144.18, 134.47, 133.83, 133.06, 123.32; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 412 (4.95), 287 (4.45); IR (KBr) ν 3065w, 1564s, 1467s, 1359s, 1245m, 1075m, 1041m, 990m, 900m, 821m, 764s, 675s cm^{-1}; Anal. Calcd. for $C_{40}H_{24}S_4$: C, 75.91; H, 3.82. Found: C, 75.17; H, 3.83.

48: Reddish-orange crystals (CH_2Cl_2-hexane); m.p. ca. 200 °C (decomp.); MS (FAB) m/z 949 [$(M+H)^+$]; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.35 (s, 12H), 6.63 - 6.65 (m, 12H), 6.52 - 6.55 (m, 12H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 147.10, 144.84, 134.50, 133.68, 133.12, 123.85; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 407 (5.06), 291 (4.54); IR (KBr) ν 2925w, 1564m, 1430m, 1362s, 1272m, 1081s, 1040s, 903w, 767s, 677m cm^{-1}; Anal. Calcd. for $C_{60}H_{36}S_6$: C, 75.91; H, 3.82. Found: C, 75.28; H, 4.03.

Procedures for Measurements of the Electronic and NMR Spectra of Cyclic Hexaanion ***119***. These experimental procedures are similar to those for **42b-d**, **45b** and **46b**. See the Experimental Section of Chapter Four.

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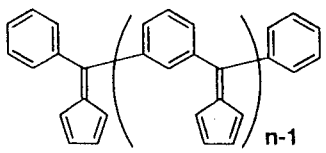
Chapter Six

Synthesis and Properties of Oligo(phenylene)pentafulvenes

6-1. Inrtoduction

As described in Chapter 2 to 5, I succeeded in synthesizing the linear and cyclic oligothienylpentafulvenes and revealed their fundamental physicochemical properties. Futhermore, I developed the new pentafulvene synthesis, which was particularly effective for the synthesis of pentafulvene oligomers. There can also be oligopentafulvenes inserted with benzene rings instead of thiophene, namely *oligo(phenylene)pentafulvenes*.

Three structural isomers can be envisioned for oligo(phenylene)pentafulvenes. One is oligo(*m*-phenylene)pentafulvenes **49** of which pentafulvene units connect with benzene rings at *meta*-position, and the second is oligo(*p*-phenylene)pentafulvenes **120**. The former oligomer **49** is particularly expected to show some interesting physical properties. The third is oligo(*o*-phenylene)pentafulvenes; however, the molecules will suffer steric crowding and may not be suitable for exploring the synthesis and properties.



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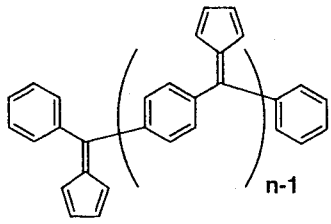
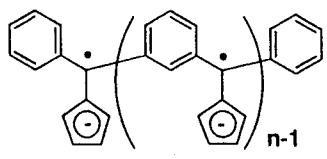


120

Meta and *para*-compounds are expected to show distinctly different properties. Reduction of a pentafulvene with one electron generates an anion radical having the highest unshared-



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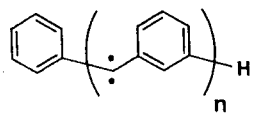

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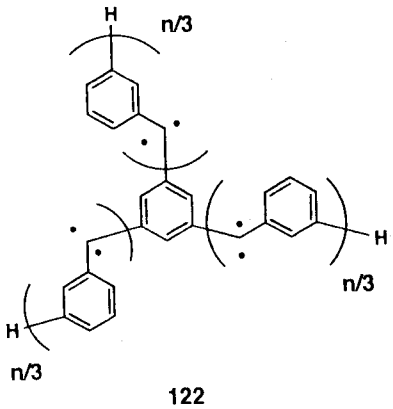

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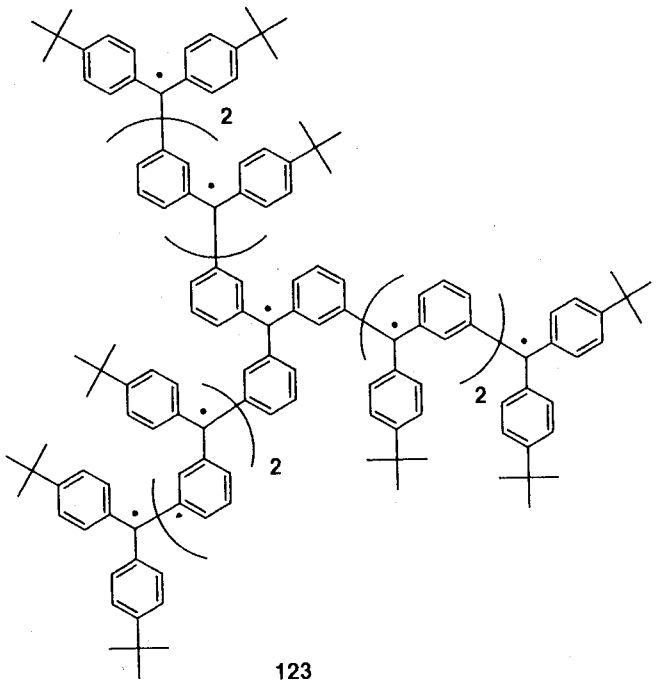
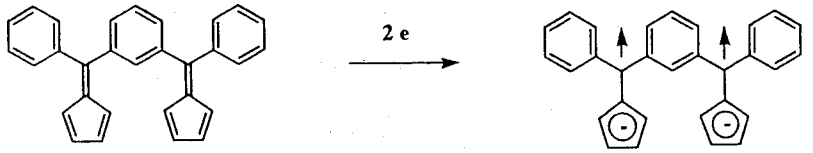
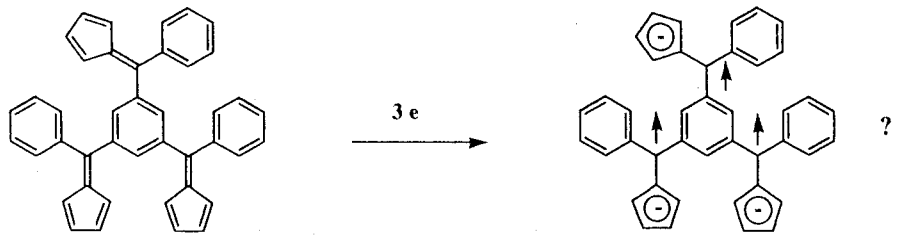


123

electron density at 6-position[1]. Therefore, reduction of **49** should proceed to form poly(anion radical), such as **121**, so called 'non-Kekule' molecule[2]. Polyradicals and polycarbenes linked with *meta*-phenylene unit have been revealed to behave as high spin organic molecules. As described in Chapter One, polycarbenes **10**[3-5] and **122**[6, 7] were prepared by H. Iwamura and K. Itoh *et al.*, and the maximum multiplisity of nonadecet has been observed[7]. A. Rajka *et al.* synthesized a series of polyarylmethyl radicals by oxidation of the corresponding polyanions[8], and compound **123** was obtained as undecet decaradical[9]. These polycarbenes and polyradicals owe their multiplicity to the topological symmetry of *meta*-phenylene unit. Similar to these precedents, poly(anion radical) **121** can be multiplet molecules; *e.g.* triplet diradical **121b** is expected from compound **49b** and quintet triradical **124** from branched tris(m-phenylene)pentafulvene **50**.

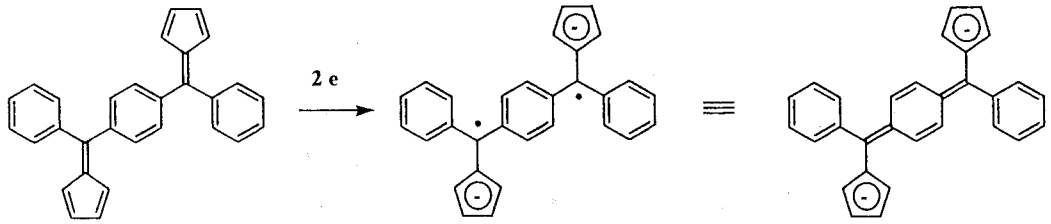


49b **121b**



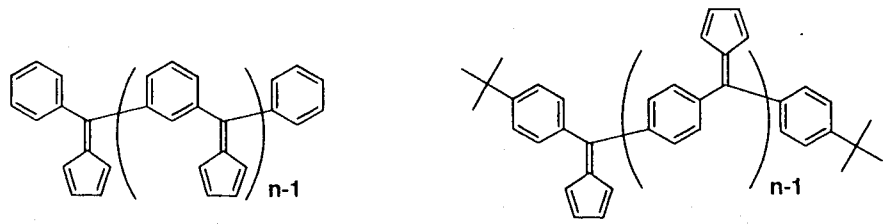
50 124

On the other hand, two-electron reduction of **120b** (n = 2) would not produce triplet species **125**, but *para*-quinoid dianion **126**.



120b 125 126

In this chapter, the synthesis and fundamental physicochemical properties of **49a-d** and **50** are described. Although, generation of multiplet radical anions has not been examined yet and remains as a future task, the preliminary information about the formation of poly(radical anion) were obtained by the measurement of cyclic voltammetry. In addition, synthesis of oligo(*p*-phenylene)pentafulvenes was also examined, and oligomers with one t-butyl group at terminal benzene rings **51** were successfully prepared up to tetramer **51d**. I also describe these results herein.

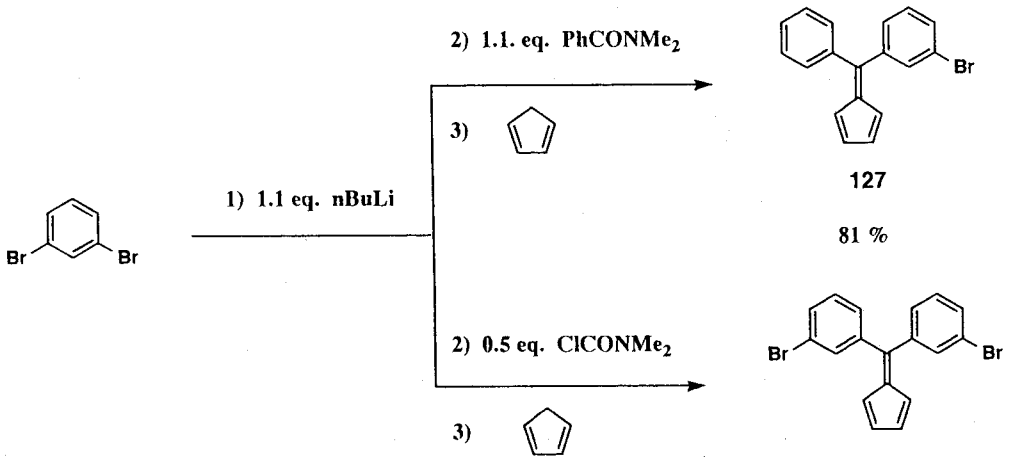


49 51

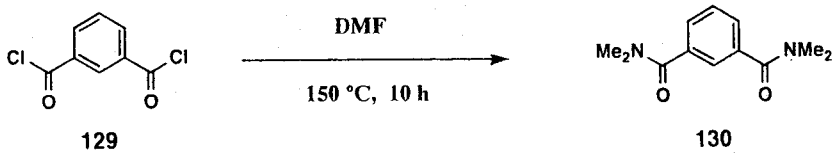
a : n = 1, b : n = 2, c : n = 3, d : n = 4

6-2. Synthesis of Oligo(m-phenylene)pentafulvenes

For synthesizing oligo(*m*-phenylene)pentafulvenes **49**, 6-(3-bromophenyl)-6-phenyl-pentafulvene **127**, 6, 6-di(3-bromophenyl)pentafulvene **128**, and N, N, N', N'-tetramethyl-isophthalamide **130**[10] are required as building blocks, as 6, 6-dithienylpentafulvene **42a** and N, N, N', N'-tetramethy-2, 5-thiophenedicarbamide **79** were building blocks for oligothienyl-pentafulvene **42**. Compound **127** and **128** were prepared from 1, 3-dibromobenzene by application of the new pentafulvene synthesis in 81% and 42% yield, respectively (Scheme 6-1). Diamide **130** was prepared from isophthaloyl chloride **129** by heating with DMF in 73% yield (Scheme 6-2).



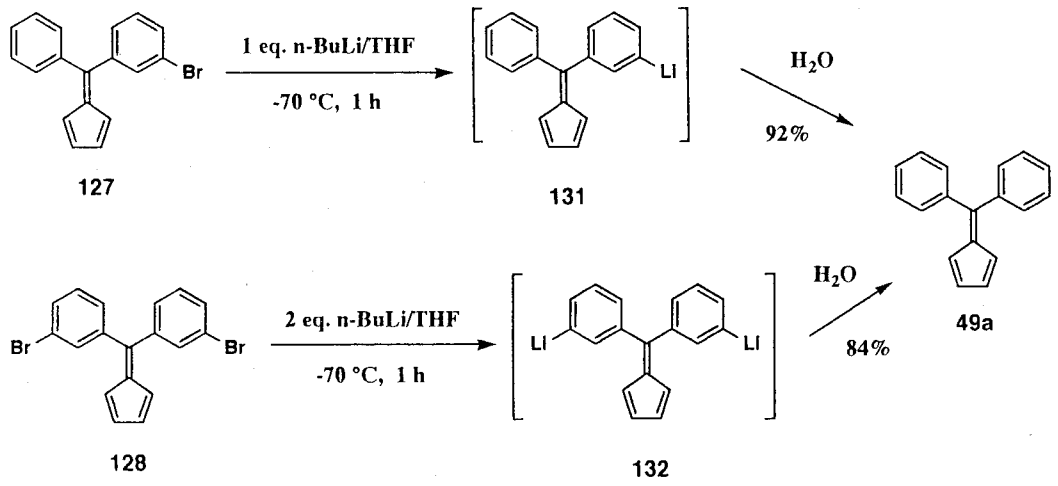
Scheme 6-1



Scheme 6-2

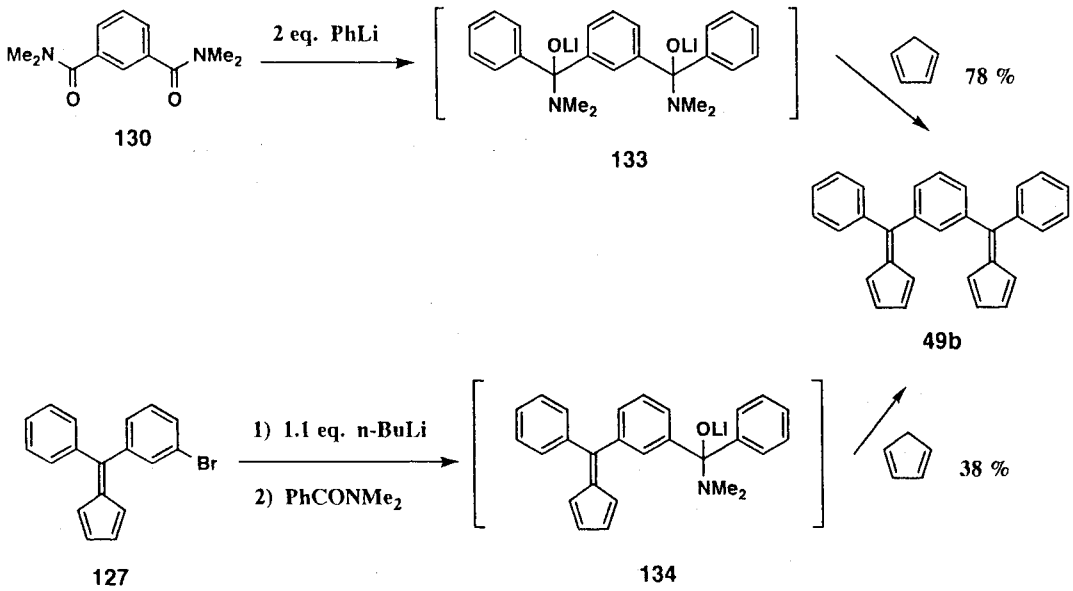
A selective lithiation of **127** and **128** could be achieved with n-butyllithium through halogen-lithium exchange. Upon addition of one equivalent of n-butyllithium to **127** in THF at -70 °C for 1 h, the orange reaction mixture turned to a dark red solution of **131**. When quenched

with water, the reaction mixture gave 6, 6-diphenylpentafulvene **49a** in 92% yield. Dilithiation was also possible by action of two equivalents of n-butyllithium to **128** at - 70°C for 1 h in THF, giving dark red solutions. Dilithio derivative **132** also afforded **49a** in 84% yield by quenching with water (Scheme 6-3).



Scheme 6-3

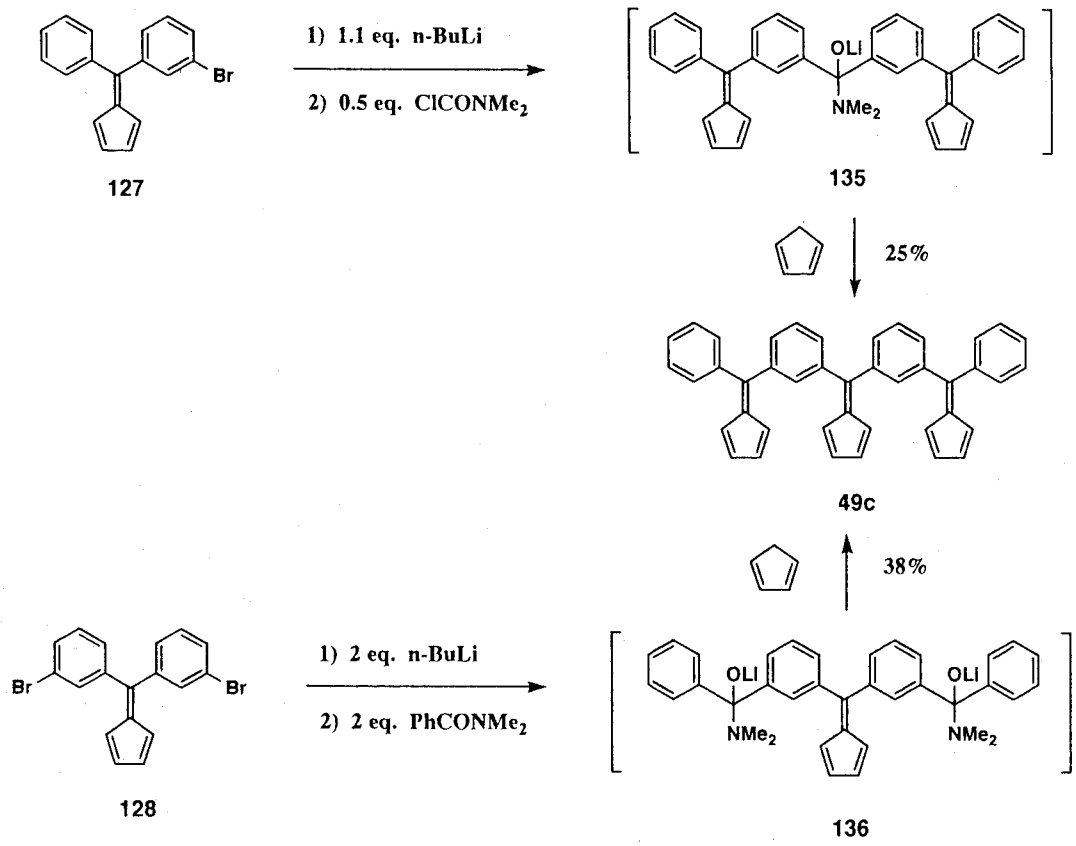
Bis(*m*-phenylene)pentafulvene **49b** was synthesized in two ways (Schem 6-4). Treatment of **130** with two equivalents of phenyllithium in THF at 0 °C, followed by addition of



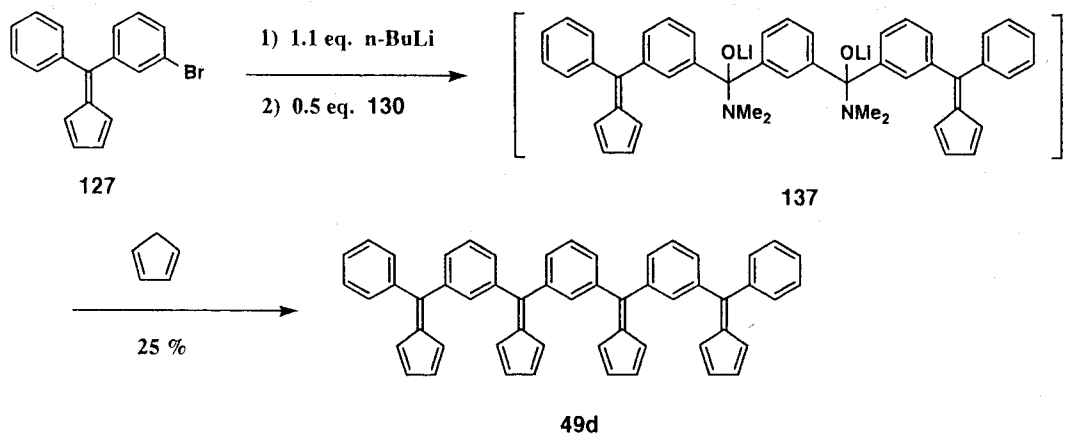
Scheme 6-4

excess cyclopentadiene gave **49b** in 78% yield presumably by the intermediacy of **133**. On the other hand, the reaction of **127** with N, N-dimethylbenzamide and then cyclopentadiene also afforded **49b** via **134**, but the yield (38%) was poorer. This poor yield may be due to either relatively low nucleophilicity of **131** to dimethylamide or instability of 6-(3-benzoylphenyl)-6-phenylpentafulvene formed *in situ*.

The two strategies are also applicable to the synthesis of tris(*m*-phenylene)pentafulvene **49c** (Scheme 6-5). Monolithiation of **127**, reaction with half equivalent of dimethycarbamyl chloride, and addition of cyclopentadiene afforded **49c** in 25% yield. Another way starting from **128** by way of bis-aminoalkoxide **136** resulted in a better yield of 38%.



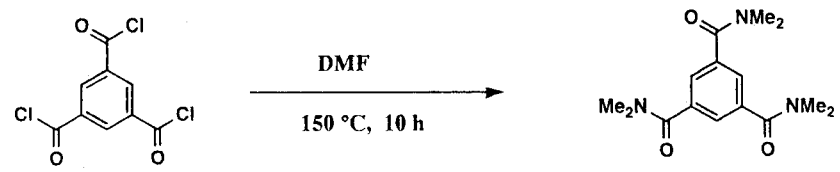
Similarly, tetrakis(*m*-phenylene)pentafulvene **49d** was synthesized by the combination of two molar amount of **127** and one molar of **130** in 25% yield, as shown in Scheme 6-6.



127 137 49d

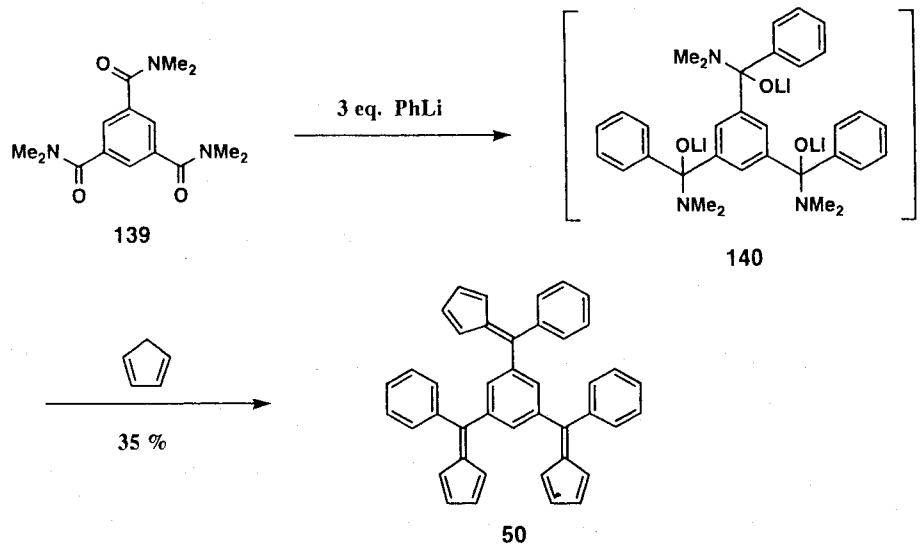
Scheme 6-6

Branched tris(*m*-phenylene)pentafulvene **50** could be prepared from N, N, N', N', N", N"-hexamethyl-1, 3, 5-benzenetricarbamide **139** which was obtained from 1, 3, 5-



138 139

Scheme 6-7

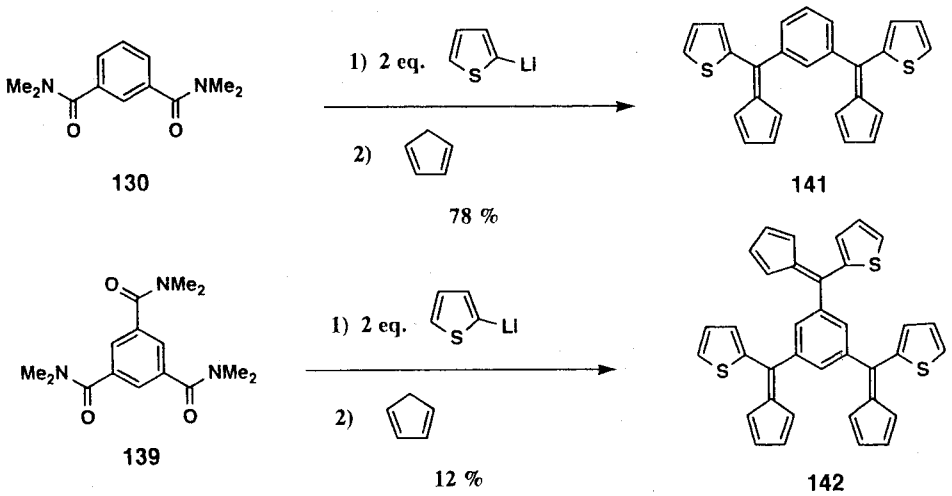


139 140 50

Scheme 6-8

benzenetricarbonyl trichloride **138** by heating in DMF in 31% yield (Scheme 6-7). Treatment of **108** with three equivalents of phenyllithium in THF at 0 °C followed by addition of excess cyclopentadiene afforded **50** in 35% yield (Scheme 6-8).

To examine the effect of substituents at 6-position of pentafulvene moieties on the properties of oligo(*m*-phenylene)pentafulvenes having 2-thienyl groups at the terminals *i.e.* **141** and **142** were synthesized (Scheme 6-9). Their synthesis were carried out in similar way to **49b** and **50** except for use of 2-thienyllithium in place of phenyllithium, in 78% and 12% yield, respectively.



Scheme 6-9

6-3. Physical Properties of Oligo(m-phenylene)pentafulvenes

The oligomers **49b-d** are orange crystalline substances, and **141** and **142** are reddish-orange. They are all fairly stable. Even tetramer **49d** is stable enough for usual handling, differing a little from the decreasing stability of oligo-6-(2-thienyl)pentafulvenes with increase of unit number. This may be ascribed to the poorer electronic interaction between substituents in *meta*-disubstituted benezenes than those of 2, 5-disubstituted thiophenes.

All oligomers were identified by mass spectra and ^{1}H and ^{13}C-NMR spectra. While **49c** shows ^{13}C signals fewer by one signal than expected for the C_2 symmetry, **49d** and **50** does by two probably due to some overlapping of the signals. From the NMR spectra, the linear

oligomers **49b-d** and **141** have C_2 symmetry and the branched compounds **50** and **142** have C_3 symmetry in solutions.

Electronic spectra

Table 6-1 lists electronic spectral data of the oligo(*m*-phenylene)pentafulvenes prepared. Figure 6-1 shows the spectra of **49a-d**. All of **49a-d** and **50** have two peaks at 327 - 330 nm and 243 - 248 nm. Among them, no change in wavelength is observed by the increase of pentafulvene unit. This indicates that conjugation hardly exist between the intramolecular pentafulvene units because of 1, 3-linkage of the units on the benzene ring: each pentafulvene unit is nearly independent from the electronic structural point of view.

Figure 6-2 shows the spectra of **141** and **142** together with those of **49c** and **50**. Compound **141** and **142** show bathochromic shifts of 20 - 27 nm as compared with **49c** and **50**. This is in line with the longer-wave absorption of 6, 6-di(2-thienyl)pentafulvene **42a** (λ_{max} = 373, 277 nm) than 6, 6-diphenylpentafulvene **49a**.

Table 6-1. Electronic Spectral Data of Oligo(*m*-phenylene)pentafulvenes

Compound	λ_{max} (log ε) in CH_2Cl_2	
49a	327 (4.33)	243 (4.16)
49b	329 (4.60)	247 (4.43)
49c	329 (4.77)	247 (4.60)
49d	328 (4.82)	248 (4.70)
50	330 (4.76)	247 (4.61)
141	357 (4.60)	268 (4.31)
142	357 (4.76)	268 (4.51)

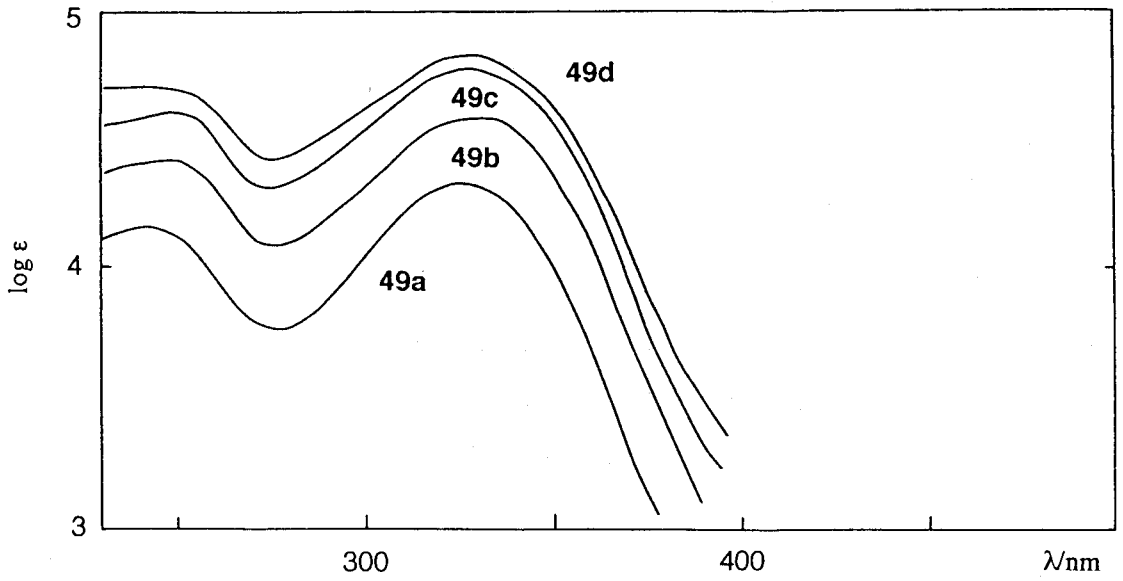


Figure 6-1. Electronic spectra of **49a-d**.

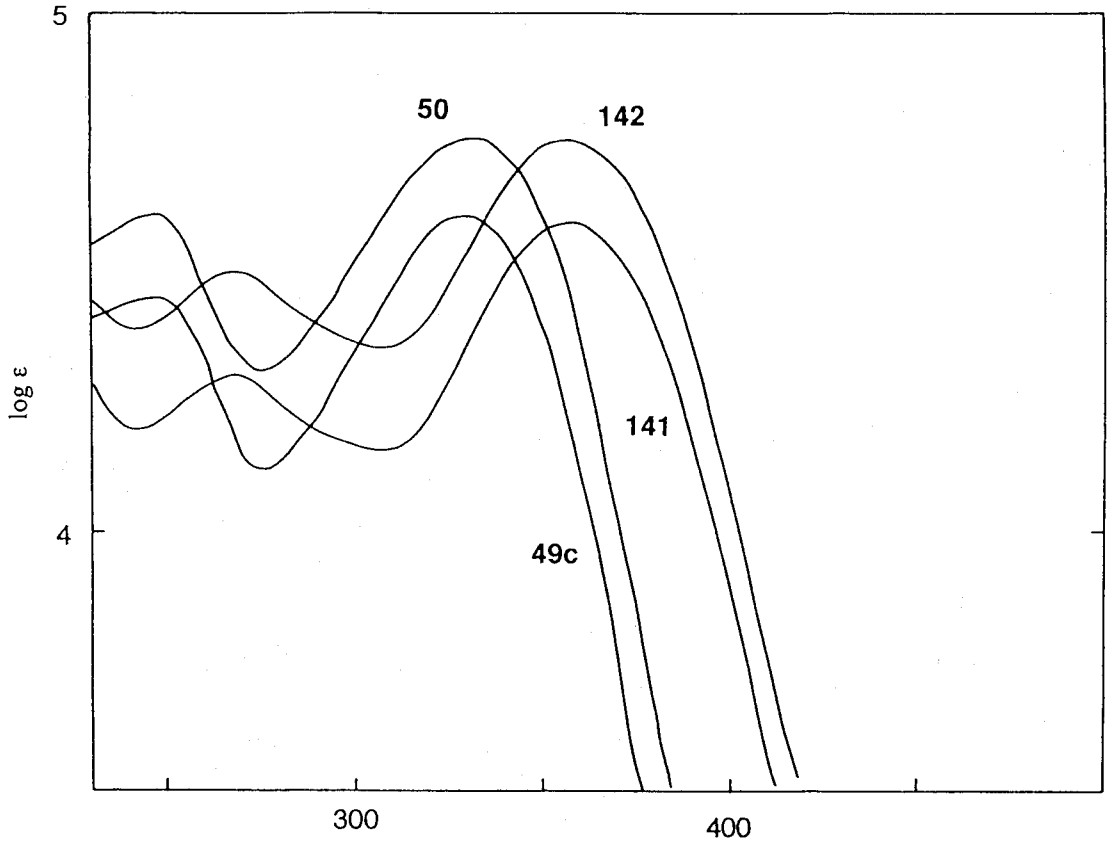
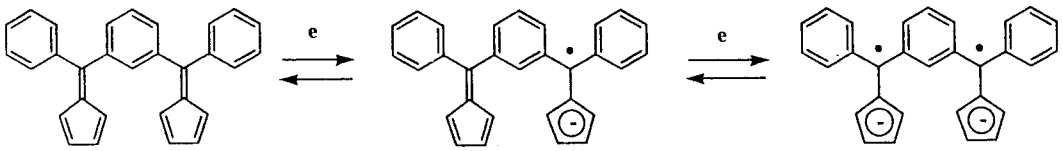


Figure 6-2. Electronic spectra of **49c**, **50**, **141** and **142**.

Electrochemical behavior

The electrochemical behavior was studied by using cyclic voltammetry. Table 6-2 lists the reduction potentials of the oligomers, and Figure 6-3 shows cyclic voltammograms of **49b-d**.

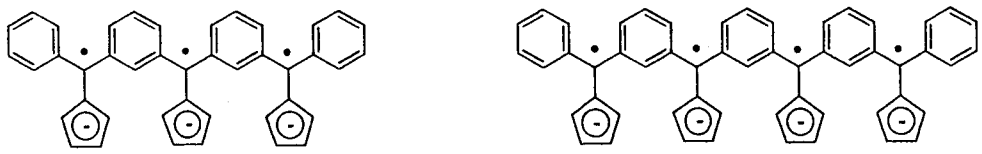
Compounds **49b** showed two reversible redox waves at -1.42 and -1.58 V, and one irreversible wave at -2.16 V. Taking into consideration that the second reduction potential of **49a** is -2.01 V, which corresponds to the formation of diphenylpentafulvene dianion, the appreciably lower potentials of the first two waves indicate the formation of mono-(anion radical) **143** and bis-(anion radical) **121b**, respectively (Scheme 6-10).



49b **143** **121b**

Scheme 6-10

Similarly, the three pairs of reversible redox waves of **49c** indicate the formation of tris-(anion radical) **121c**, and the four successive waves of **49d** indicate the formation of tetrakis-(anion radical) **121d**. Branched trimer **50** also showed three reversible waves corresponding to the formation of tris(anion radical) **124** when it was measured at -70 °C, but reversibility was poor when measured at 25 °C. Peak potentials of **49b** at -2.16 V and of **49c** at - 2.35 V are due to further reduction. Compounds **141** and **142** gave slightly lower reduction potentials than the phenyl derivatives, and further reduction did not detected. Here again, 2-thienyl group stabilizes the anion radcals to be formed more than phenyl group[12].

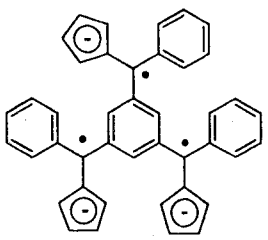


121c **121d**

Table 6-2. Reduction Potentials[a] of Oligo(*m*-phenylene)pentafulvenes by Cyclic Voltammetry

Compound	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$E^4_{1/2}$
49a[d]	- 1.44	- 2.01		
49b	- 1.42	- 1.58	- 2.16[b]	
49c	- 1.35	- 1.47	-1..70	- 2.35[b]
49d	- 1.39	- 1.47	- 1.60	- 1.78
50[c]	- 1.37	- 1.55	- 1.74	
141	- 1.36	- 1.51		
142	- 1.29	- 1.44	- 1.57	

[a] V vs Ag/AgCl (calibration with ferrocene/ferrocenyl cation taken to have +0.52 V), in 0.1 M n-Bu_4NClO_4/DMF, sweep rate 50 mV/sec, measured at 25 °C. [b] Peak potential. [c] Measured at - 70 °C. [d] Ref. 13.



124

As the properties and structure of these oligo-(anion radcal) are of interest, ESR studies for the reductant of **49b** and **50** are now under collaboration with Prof. K. Müllen.

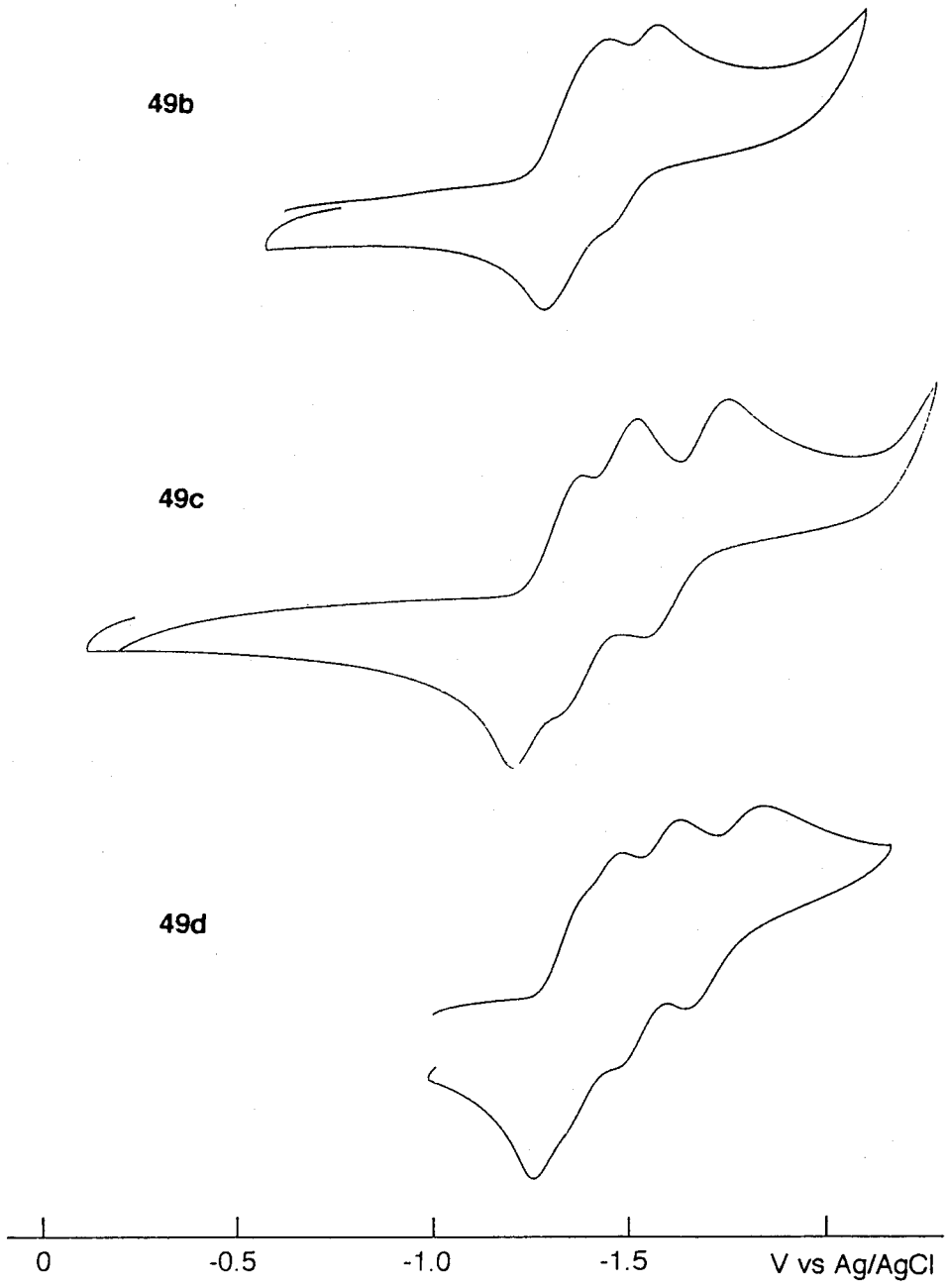
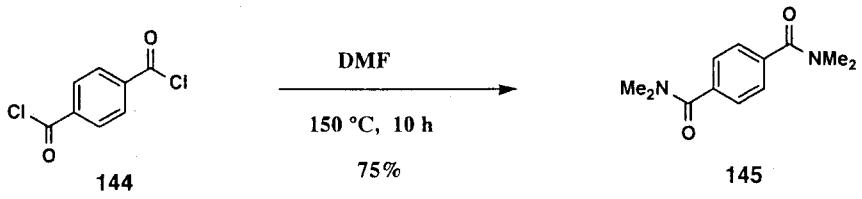
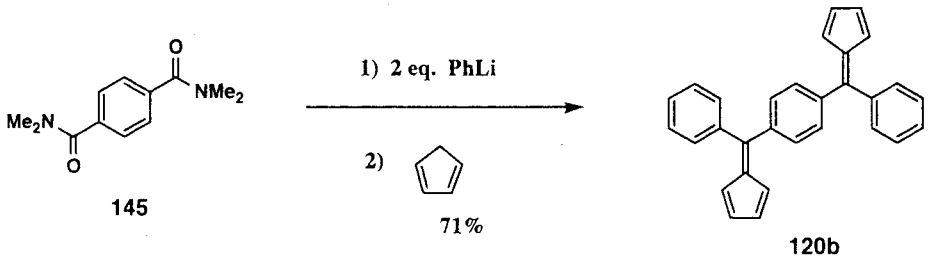


Figure 6-3. Cyclic voltammograms of **49b-d**.

The synthesis of dimer **120b** was recently reported by Adam *et al.*[14]; however, its synthesis required a severe condition and the yield was moderate (56% yield from 1, 4-di(benzoyl)benzene by refluxing with cyclopentadienyl anion in ethanol for 2 h.). Our new pentafulvene synthesis is also useful for the synthesis of **120b**: treatment of N, N, N', N'-tetramethylterephthalamide **145**[15], prepared from terephthaloyl chloride **144** and DMF (Scheme 6-11), with two equivalents of phenyllithium followed by addition of cyclopentadiene afforded **120b** in 71% yield under mild conditions (Scheme 6-12).

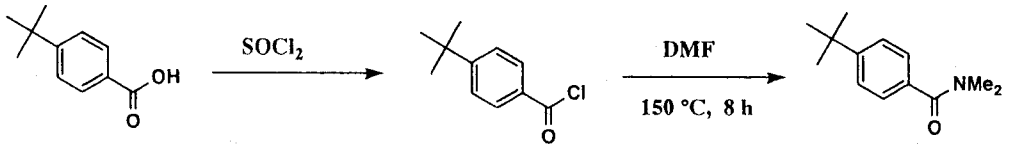


Scheme 6-11



Scheme 6-12

The dimer **120b** is considerably less soluble than diphenylpentafulvene in organic solvents, suggesting that the trimer and tetramer would be much less soluble and characterization of them be difficult even if their syntheses could be achieved. To improve solubility, t-butyl group was introduced at terminal benzene rings. Thus, N, N-dimethyl-4-t-butylbenzamide **148**[16] prepared from 4-t-butylbenzoic acid **146** (Scheme 6-12) was used for the synthesis of the trimer and tetramer having t-butyl groups.

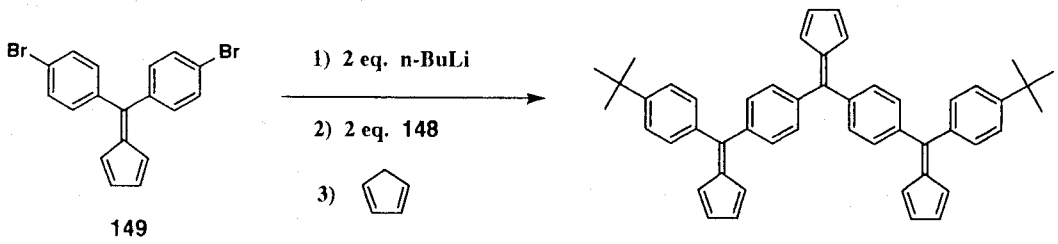


146 147 148

overall 43%

Scheme 6-13

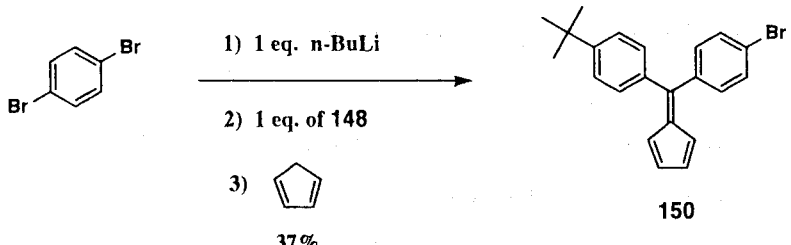
6, 6-Di(4-bromophenyl)pentafulvene **149**[17] was first dilithiated by two equivalents of n-butyllithium. The reaction of the dilithio compound with **148** followed with cyclopentadiene afforded trimer **51c** in 12% yield. As expected, **51c** is more soluble than **120b**.



149 12% 51c

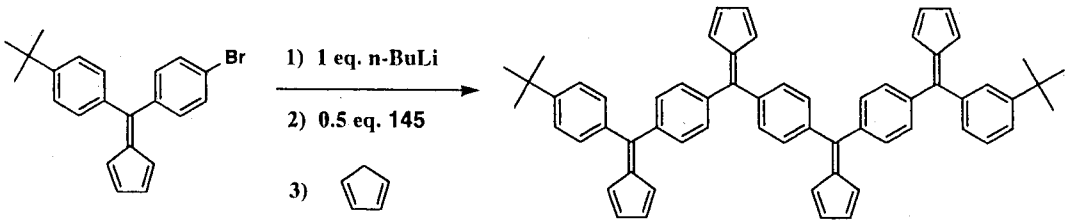
Scheme 6-14

For the synthesis of tetramer **51d**, 6-(4-bromophenyl)-6-(4-tbutylphenyl)pentafulvene **150** was required and prepared in 37% yield from **148** and 1, 4-dibromobenzene as shown in Scheme 6-15. Further examination of reaction conditions may improve the yield. Tetramer **51d** was obtained by the combination of two equivalents of mono-lithiated **150**, one equivalent of **145** and cyclopentadiene in 18% yield (Scheme 6-16).



37% 150

Scheme 6-15

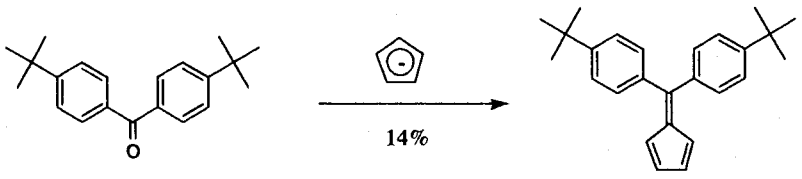


150

51d

Scheme 6-16

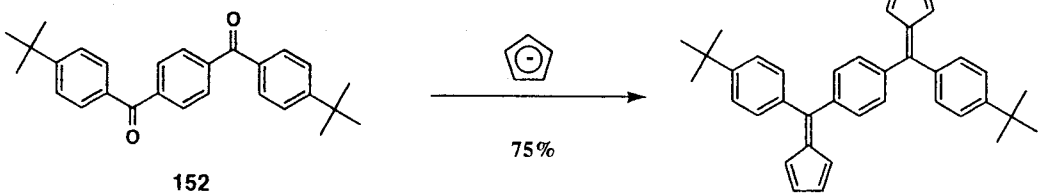
To compare physical properties of **51c** and **51d**, monomer **51a** and dimer **51b** were also prepared. Synthesis were achieved by condensation of the corresponding ketones **151**[18] and **152**, with cyclopentadienyl anion in 14% and 75% yield, respectively (Scheme 6-17 and 6-18).



151

51a

Scheme 6-17



152

51b

Scheme 6-18

6-5. Physical Properties of Oligo(p-pheylene)pentafulvenes

Compounds **51a-d** are orange crystalline substances and relatively stable. Solubility in organic solvents tends to decrease as the fulvene unit increases; however, even tetramer **51d**, is well soluble in benzene and dichloromethane. Identification of these compounds were carried out by measurement of mass spectra and ^{1}H- and ^{13}C-NMR spectra.

Table 6-3. Electronic Spectral Data of Oligo(*p*-phenylene)pentafulvenes

Compound	λ_{max} (log ε) in CH_2Cl_2			
51a	341 (4.37)	243 (4.22)		
51b	358sh (4.5)	333 (4.56)	294sh (4.34)	244 (4.39)
51c	350 (4.71)	330sh (4.7)	297sh (4.5)	249 (4.51)
51d	348 (4.84)	326sh (4.8)	298sh (4.6)	249 (4.61)

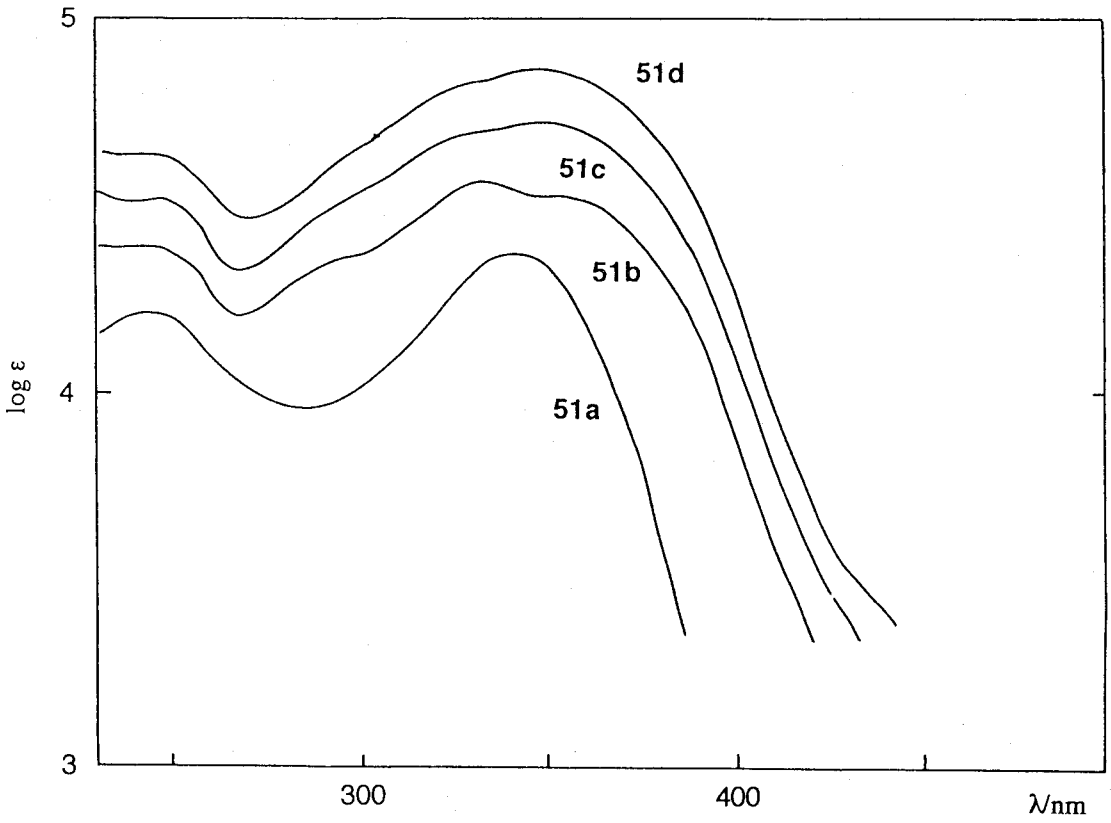


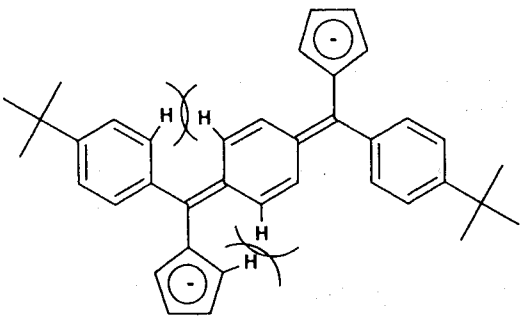
Figure 6-4. Electronic spectra of **51a-d**.

Table 6-3 and Figure 6-4 show electronic spectral data and the spectra of **51a-d.** The tendency of the spectral change from **51a** to **51d** is similar to that of oligo-6-(2-thienyl)pentafulvenes. Dimer **51b** absorbs at 17 nm longer wavelength than monomer **51a**. The

bathochromic shift is smaller than that of the corresponding oligo-6-(2-thienyl)pentafulvenes (33 nm). This may suggest that the conjugation between two pentafulvene units through the central benzene ring is inhibited to higher extent in **51a** by the steric interaction of hydrogen atoms attached to the central benzene and pentafulvenes.

Table 6-4 summarizes the reduction potentials and Figure 6-5 shows the cyclic voltammograms of **51b-d**. Compound **51b** gave one reversible redox wave involving two electrons at -1.22 V, and it corresponds to the formation of dianion **153**. As compared with bis-6-(2-thienyl)pentafulvene **42b** (E_1 = -0.93, and E_2 = -1.03 V), **51b** is less easily reduced than **42b**, and similar behaviors were observed for trimer **51c** and tetramer **51d**. Each of the four reduction potentials of **51c** must corresponds to the formation of anion radical, dianion, trianion radical, and tetraanion, respectively. The two-step electron transfer for the formation of dianion should reflect to the different symmetry of the molecule from **51b**. On the other hand, reduction of **51d** seems again to involve two-electron trnsfer each at -1.19 and -1.33 V to form a tetraanion. The third potential of weak wave(- 1.53 V) may be due to further reduction, to a pentaanion.

The structure of dianion **153** is considered as a quinoid-type compound as depicted below. The steric hindrance would arise among the hydrogen atoms of the quinoid, cyclopentadienyl and terminal benzene moieties, and therfore the molecule considerably deviate from coplanarity. The difference in electrochemical behavior of oligo(*p*-phenylene)pentafulvenes and oligo-6-(2-thienyl)pentafulvenes is probably induced by this destabilization of dianion **153**, as well as larger aromatic stabilization of benzene than thiophene.



153

Table 6-4. Reduction Potentials[a] of Oligo(*p*-phenylne)pentafulvenes by Cyclic Voltammetry

Compound	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$E^4_{1/2}$
51a	- 1.42	- 2.01[b]		
51b	- 1.22			
51c	- 1.22	- 1.27	-1.58	- 1.97
51d	- 1.19	- 1.33	- 1.53	
42b	- 0.93	- 1.03		

[a] V vs Ag/AgCl (calibration with ferrocene/ferrocenyl cation taken to have +0.52 V), in 0.1 M n-Bu_4NClO_4/DMF, sweep rate 50 mV/sec, measured at 25 °C. [b] Peak potential.

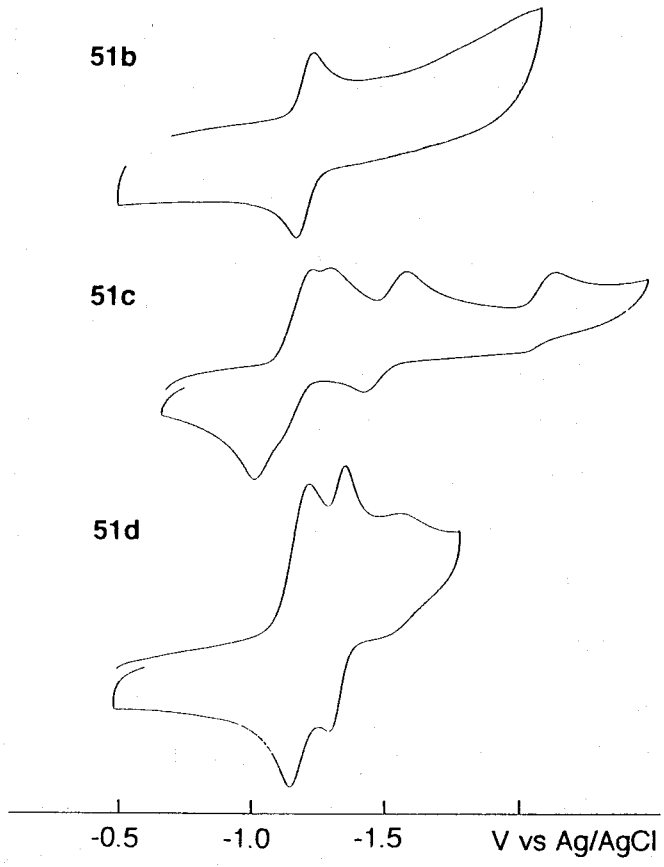


Figure 6-5. Cyclic voltammograms of **51b-d**.

6-6. Experimental Section

Materials. 1, 3-Dibromobenzene, 1, 4-dibromobenzene, thiophene, dimethylcarbamyl chloride, isophthaloyl chloride, 1, 3, 5-benzenetricarbonyl trichloride, terephthaloyl chloride, and 4-t-buthylbenzoic acid were all commercially available and used without further purification. 6, 6-Di(4-bromophenyl)pentafulvene **149** was prepared from 1, 4-dibromobenzene and dimethylcarbamyl chloride by the new pentafulvene synthesis (52% yield). 4, 4'-Di-t-butylbenzophenone **151** was prepared according to literature[18]. 1, 4-Di(4-t-butylbenzoyl) benzene **152** was prepared from t-butylbenzene and terephthaloyl chloride. Sodium hydride was commercially available as 60% oil suspension and used as it is.

6-(3-Bromophenyl)-6-phenylpentafulvene ***127.*** In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 3.5 g (15 mmol) of 1, 3-dibromobenzene and 25 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -70 °C, 10 mL (15 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum, and the mixture was stirred at -70 °C for 1 h. A solution of 2.2 g (14.8 mmol) of N, N-dimethylbenzamide in 5 mL of anhydrous THF was added. The reaction mixture was allowed to warm up to 0 °C, and stirred for 1 h. Cyclopentadiene (4 mL, 48 mmol) was added and the stirring continued at 0 °C for additional 3 h. The reaction mixture was added with water and extracted with hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C; A column fitted with an ice-cooled jacket was used.) using hexane as eluent to give 3.7 g of **127** (81%).

127: Orange crystals (hexane); m.p. 64-65 °C; MS (EI, 70 eV) m/z 308/310 (M^+, 30 %, 30%), 229 [$(M - Br)^+$, 100%], 202 (25%), 189 (5%), 152 (20%), 113 (15%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.48-7.55 (m, 1H), 7.47 (m, 1H), 7.36-7.40 (m, 3H), 7.27-7.31 (m, 2H), 7.23-7,25 (m, 2H), 6.58-6.61 (m, 2H), 6.22-6.29 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 149.62, 144.56, 143.26, 140.54, 134.49, 132.98, 132.92, 131.93, 131.53, 130.51,

129.18, 127.86, 127.85, 124.31, 123.88, 121.93; IR (KBr) ν 3059m, 1598s, 1551s, 1472s, 1440m, 1399m, 1360s, 1323m, 1290w, 1086m, 995m, 938m, 788s, 698s, 672s cm^{-1}; Anal. Calcd. for $C_{18}H_{13}Br$: C, 69.92; H, 4.24, Found: C, 70.82; H, 4.26.

6, 6-Di(3-bromophenyl)pentafulvene ***128***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 3.5 g (15 mmol) of 1, 3-dibromobenzene and 20 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -70 °C, 10 mL (15 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum, and the mixture was stirred at -70 °C for 1 h. To the stirred solution was added 0.5 mL (5.4 mmol) dimethylcarbamyl chloride via syringe through the septum beolw -70 °C, and the mixture stirred at 0 °C for 1 h. Cyclopentadiene (4 mL, 48 mmol) was added and the stirring continued at 0 °C for additional 2 h. The reaction mixture was added with water and extracted with hexane. The combined organic layer was washed with water and brine, and dried over anhydrous MgSO4. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C, eluted with hexane) to give 1.2 g of **128** (42%).

128: Orange crystals (hexane); m.p. 102-103 °C; MS (EI, 70 eV) m/z 386/388/390 (M^+, 35%, 70 %, 35%), 307/309 [$(M-Br)^+$, 75 %, 75%], 228 [$(M-2Br)^+$, 100 %], 202 (15%), 187 (5%), 152 (10%), 113 (10%), 63 (8%), 39 (5%); ^{1}H-NMR (270 MHz / $CDCl_3$) δ 7.54 (dt, J = 1.7, 7.6Hz, 2H), 7.45 (t, J = 1.7 Hz, 2H), 7.26 (t, J = 7.6 Hz, 2H), 7.22 (dt, J = 1.7, 7.6 Hz, 2H), 6.60-6.63 (m, 2H), 6.20-6.23, (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 147.61, 145.29, 142.61, 134.45, 133.64, 131.86, 130.43, 129.43, 123.94, 122.13; IR (KBr) ν 3061w, 1587m, 1552s, 1471m, 1399m, 1356m, 1320m, 1183m, 1089m, 999m, 936s, 882m, 788s, 700s, 663m, 621m cm^{-1}; Anal. Calcd. for $C_{18}H_{12}Br_2$: C, 55.71; H, 3.12, Found: C, 56.13; H, 3.14.

N, N, N', N'-Tetramethylisophthalamide ***130***. In a 50-mL round-bottomed, one-necked flask equipped with a magnetic stirring bar and a reflux condenser fitted with a calcium chloride drying tube, were placed 10 g (50 mmol) of isophthaloyl chloride and 10 mL of N, N-

dimethylformamide. The mixture was heated at 150 °C for 10 h under stirring. After cooling to room temperature, the reaction mixture was added with water and extracted with dichloromethane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was crystallized by addition of hexane to give 7.9 g of **130** (73%).

130: Colorless crystals; m.p. 92-93 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.46 (brs, 4H), 311 (brs, 6H), 2.97 (brs, 6H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 170.66, 136.35, 128.45, 128.03, 125.48, 39.43, 35.24; IR (KBr) *v* 2935m, 1627s, 1502m, 1397s. 1256m, 1203w, 1074m, 920w, 823m, 740m, 636m cm^{-1}.

*Bis(m-phenylene)pentafulvene **49b** From **130**.* In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 220 mg (1.0 mmol) of **99** and 8 mL of anhydrous THF under nitrogen flow. The stirred mixture was cooled below -50 °C, and 1.6 mL (2.5 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added dropwise via syringe through the septum. The mixture was allowed to warm up to 0 °C, and stirred for 1 h. Cyclopentadiene (1 mL, 12 mmol) was added and the stirring continued at 0 °C for additional 3 h. The reaction mixture was added with water and extracted with benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C, eluted with hexane to 10% benzene/hexane) to give 305 mg of **49b** (78%).

*Bis(m-phenylene)pentafulvene **49b** From **127**.* In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 300mg (1.0 mmol) of **127** and 7 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -70 °C, 0.7 mL (1.1 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum, and the mixture was stirred at -70 °C for 1 h. A solution of 2.2 g (14.8 mmol) of N, N-dimethylbenzamide in 5 mL of anhydrous THF was added. The reaction mixture was allowed to warm up to 0 °C, and stirred for 1 h. Cyclopentadiene (1 mL, 12 mmol) was added and the

stirring continued at 0 °C for additional 3 h. The reaction mixture was added with water and extracted with benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C, eluted with hexane to 10% benzene/hexane) to give 145 mg of **49b** (38%) and 76 mg of recovery of **127** (25%).

49b: Orange crystals (ether-hexane); m.p. 136-137 °C; MS (EI, 70 eV) m/z 382 (M^+); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.29-7.37 (m, 14H), 6.55-6.58 (m, 4H), 6.24-6.30 (m, 4H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 151.14, 144.12, 140.98, 140.89, 135.38, 132.54, 132.21, 132.03, 128.76, 128.31, 127.77, 127.16, 124.31, 124.11; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 329 (4.60), 247 (4.43); IR (KBr) ν 3042m, 1594s, 1440s, 1360s, 1320m, 1087m, 931m, 798s, 777s, 699s, 670s, 639m, 321m cm^{-1}; Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80, Found: C, 93.74; H, 5.97.

*Tris(m-phenylene)pentafulvene **49c** From **127**.* In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 640 mg (2.1 mmol) of **127** and 8 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -70 °C, 1.5 mL (2.2 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum, and the mixture was stirred at -70 °C for 1 h. To the stirred solution was added 0.1 mL (1.0 mmol) dimethylcarbamyl chloride via syringe through the septum beolw -70 °C, and the mixture stirred at 0 °C for 1 h. Cyclopentadiene (1 mL, 12 mmol) was added and the stirring continued at 0 °C for additional 2 h. The reaction mixture was added with water and extracted with benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C, eluted with 10% CH_2Cl_2/hexane) to give 133 mg of **49c** (25%).

*Tris(m-phenylene)pentafulvene **49c** From **128**.* In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 384mg (1.0 mmol) of **128** and 7 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -70 °C, 0.7 mL (1.1

mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum, and the mixture was stirred at -70 °C for 1 h. A solution of 350 mg (2.3 mmol) of N, N-dimethylbenzamide in 5 mL of anhydrous THF was added. The reaction mixture was allowed to warm up to 0 °C, and stirred for 1 h. Cyclopentadiene (1 mL, 12 mmol) was added and the stirring continued at 0 °C for additional 3 h. The reaction mixture was added with water and extracted with benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C, eluted with 10% benzene/hexane to 20% benzene/hexane) to give 204 mg of **49c** (38%).

49c: Orange crystals (ether-hexane); m.p. 159 °C; MS (FAB) m/z 535 [$(M+H)^+$]; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.26-7.42 (m, 18H), 6.54-6.60 (m, 6H), 6.20-6.30 (m, 6H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 151.10, 150.46, 144.36, 144.14, 140.98, 140.63, 135.23, 132.81, 132.62, 132.57, 132.37, 132.11, 132.08, 128.80, 127.80, 127.28, 124.36, 124.13, 124.07; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 329 (4.77), 247 (4.60); IR (KBr) ν 3059w, 1583m, 1442m, 1360s, 1085w, 999w, 928w, 850w, 802m, 744s, 755m, 706s, 668s, 623m, 584m cm^{-1} ; Anal. Calcd. for $C_{42}H_{30}$: C, 94.34; H, 5.66, Found: C, 93.13; H, 5.72.

Tetrakis(m-phenylene)pentafulvene ***49d***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 315mg (1.0 mmol) of **127** and 10 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -70 °C, 0.7 mL (1.1 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum. The mixture was stirred at -70 °C for 1 h, and added with 110 mg (0.5 mmol) of **130** in one portion. The suspension was allowed to warm up to 0 °C , and stirred for additional 1 h. Cyclopentadiene (0.8 mL, 7.3 mmol) was added and the stirring continued at 0 °C for additional 4 h. The reaction mixture was added with water and extracted with dichloromethane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (40 g, 0 °C, eluted with 10% benzene/hexane to 20% benzene/hexane) to give 87 mg of **49d** (25%).

49d: Orange crystals (ether-hexane); m.p. 257-258 °C; MS (FAB) m/z 687 [$(M+H)^+$]; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.22-7.39 (m, 22H), 6.54-6.58 (m, 8H), 6.17-6.29 (m, 8H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 151.07, 150.35, 144.44, 144.19, 141.01, 140.70, 140.61, 135.29, 135.13, 132.90, 132.85, 132.67, 132.60, 132.42, 132.28, 132.08, 128.83, 127.82, 127.39, 127.32, 124.37, 124.12; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 328 4.82), 248 (4.70); IR (KBr) ν 3059m, 2923m, 1592s, 1471s, 1359s, 1086s, 1004m, 903w, 775s, 704s cm^{-1}.

N, N, N', N', N", N"-Hexamethyl-1, 3, 5-benzenetricarbamide ***139***. In a 100-mL round-bottomed, one-necked flask equipped with a magnetic stirring bar and a reflux condenser fitted with a calcium chloride drying tube, were placed 14.4 g (54.2 mmol) of 1, 3, 5-benzenetricarbonyl trichloride **138** and 20 mL of N, N-dimethylformamide. The mixture was heated at 150 °C for 10 h under stirring. After cooling to room temperature, the reaction mixture was added with water and extracted with dichloromethane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvents were removed in vacuo. The residue was a brown oil, and recryctallized from benzene-hexane to give 1.9 g of **139** as colorless crystals. Concentration of the filtrate and further recrystallization of the residue from benzene-hexane gave additional 3.0 g of **139**. The combined yield was 4.9 g (31%).

139: Colorless crystals (benzene-hexane); m.p. 149 - 150 °C; MS (EI, 70 eV) m/z 291 (M^+, 20%), 247 [$(M-NMe_2)^+$, 35%], 167 (20%), 149 (60%), 57(20%), 28 (20%), 18 (100%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.53 (s, 3H), 3.11 (brs, 9H), 3.00 (brs, 9H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 169.69, 136.70, 126.80, 39.46, 35.31; IR (KBr) ν 2936m, 1628s, 1502m, 1404s, 1258m, 1189m, 1095s, 884w, 741w, 696m, 672m cm^{-1}.

Branched tris(m-phenylene)pentafulvene ***50***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 292 mg (1.0 mmol) of **108** and 15 mL of anhydrous THF under nitrogen flow. The stirred mixture was cooled below -50 °C, and 2.0 mL (3.0 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added dropwise via syringe through the septum. The mixture was allowed to warm up to 0 °C, and stirred for 1 h.

Cyclopentadiene (1 mL, 12 mmol) was added and the mixture was stirred at 0 °C for 2 h. Stirring was continued at room temperature for 2 h. The reaction mixture was added with water and extracted with benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C, eluted with 10% benzene/hexane) to give 186 mg of **50** (35%).

50: Orange prisms (ether-hexane); m.p. 170 °C; MS (EI, 30 eV) m/z 534 (M^+, 60%), 457 (25%), 121 (45%), 119 (60%), 117 (75%), 82 (40%), 57 (20%), 28 (70%), 18 (100%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.29-7.40 (m, 15H), 7.28 (s, 3H), 6.52-6.57 (m, 6H), 6.25-6.28 (m, 3H), 6.18-6.21 (m, 3H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 150.49, 144.33, 140.70, 140.52, 135.38, 132.76, 132.00, 128.89, 127.89, 124.31, 123.93; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 330 (4.76), 247 (4.61); IR (KBr) ν 3058w, 1596s, 1467m, 1441m, 1359s, 1264m, 1158m, 1085m, 1019m, 989m, 927m, 780s, 697s, 665m, 640m cm^{-1}; Anal. Calcd. for $C_{42}H_{30}$: C, 94.34; H, 5.66, Found: C, 94.07; H, 5.64.

1, 3-Bis(6-(2-thienyl)pentafulvenyl)benzene ***141***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 0.5 mL (6.2 mmol) of thiophene and 10 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -50 °C, 3.0 mL (4.5 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum. The mixture was stirred at -50 °C for 1 h, and added with 450 mg (2.0 mmol) of **130** in one portion. The suspension was allowed to warm up to 0 °C, and stirred for additional 1 h. Cyclopentadiene (0.8 mL, 7.3 mmol) was added and the stirring continued at 0 °C for additional 3 h. The reaction mixture was added with water and extracted with benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (40 g, 0 °C, eluted with 10% benzene/hexane) to give 505 mg of **141** (78%).

141: Reddish-orange needls (ether-hexane); m.p. 103 °C; MS (EI, 70 eV) m/z 394 (M^+, 3%), 234 (2%),219 (5%),186 (2%), 105 (4%), 28 (15%), 18 (100%); ^{1}H-NMR (270 MHz,

$CDCl_3$) δ 7.53 (dd, J = 5.0, 1.3 Hz, 2H), 7.41-7.47 (m, 4H), 7.13 (dd, J = 3.6, 1.3 Hz, 2H), 7.08 (dd, J = 5.0, 3.6 Hz, 2H), 6.78 (dt, J = 5.3, 1.8 Hz, 2H), 6.62 (dt, J = 5.3, 1.8 Hz, 2H), 6.52 (dt, J = 5.3, 1.8 Hz, 2H), 6.09 (dt, J = 5.3, 1.8 Hz, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 143.72, 143.22, 143.10, 140.55, 134.26, 133.33, 132.93, 132.04, 131.91, 130.59, 127.53, 126.85, 124.89, 123.01; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 357 (4.60), 268 (4.31); IR (KBr) ν 3071m, 1557s, 1459m, 1411m, 1360s, 1264m, 1226w, 1080m, 1002w, 895m, 840w, 768m, 702s cm^{-1}; Anal. Calcd. for $C_{26}H_{18}S_2$: C, 79.15; H, 4.60, Found: C, 78.93; H, 4.53.

1, 3, 5-Tris(6-(2-thienyl)pentafulvenyl)benzene ***142***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 0.4 mL (5.0 mmol) of thiophene and 10 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -50 °C, 2.2 mL (3.3 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum. The mixture was stirred at -50 °C for 1 h, and added with 290 mg (1.0 mmol) of **138** in one portion. The suspension was allowed to warm to 0 °C , and stirred for additional 1 h. Cyclopentadiene (0.8 mL, 7.3 mmol) was added and the stirring continued at 0 °C for additional 3 h. The reaction mixture was added with water and extracted with benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (40 g, 0 °C, eluted with 10% benzene/hexane to 20% benzene/hexane) to give 64 mg of **142** (12%).

142: Reddish-orange prisms (ether-hexane); m.p. ca. 200 °C (decomp.); MS (EI, 30 eV) m/z 552 (M^+, 40%), 368 (50%), 267 (20%), 236 (50%), 208 (10%), 175 (10%), 84 (95%), 69 (90%), 57 (100%), 49 (80%), 43 (90%), 28 (20%), 18 (50%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.53 (dd, J = 4.9, 1.3 Hz, 3H), 747(s, 3H), 7.17 (dd, J = 3.6, 1.3 Hz, 3H), 7.09 (dd, J = 4.9, 3.6 Hz, 3H), 6.77 (dt, J = 5.3, 1.8 Hz, 3H), 6.61 (dt, J = 5.3, 1.8 Hz, 3H), 6.52 (dt, J = 5.3, 1.8 Hz, 3H), 6.10 (dt, J = 5.3, 1.8 Hz, 3H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 143.56, 143.36, 142.31, 140.06, 134.52, 133.60, 132.88, 132.22, 130.74, 127.67, 124.67, 122.98; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 357 (4.76), 268 (4.51); IR (KBr) ν 3062m, 1567s,

1460m, 1412s, 1358s, 1263m, 1086m, 899m, 770s, 701s, 545w, 514w cm^{-1}; Anal. Calcd. for $C_{36}H_{24}S_3$: C, 78.22; H, 4.38, Found: C, 77.98; H, 4.31.

N, N, N', N'-Tetramethylterephthalamide ***145***. In a 50-mL round-bottomed, one-necked flask equipped with a magnetic stirring bar and a reflux condenser fitted with a calcium chloride drying tube, were placed 11 g (54.2 mmol) of terephthaloyl chloride and 20 mL of N, N-dimethylformamide. The mixture was heated at 150 °C for 10 h under stirring. After cooling to room temperature, the reaction mixture was added with water and extracted with dichloromethane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was crystallized by addition of hexane to give 8.9 g of **145** (75%).

145: Colorless crystals; m.p. 145-146 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.45 (s, 4H), 3.12 (brs, 6H), 2.97 (brs, 6H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 170.60, 137.20, 126.87, 39.23, 35.08; IR (KBr) ν 2935m, 1630s, 1526m, 1478m, 1400s, 1266m, 1228m, 1088m, 858m, 736m, 599m cm^{-1}.

1, 4-Bis(6-phenylpentafulvenyl)benzene ***120b***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 230 mg (1.0 mmol) of **145** and 8 mL of anhydrous THF under nitrogen flow. The stirred mixture was cooled below -50 °C, and 1.6 mL (2.5 mmol) of 1.8 M phenyllithium in cyclohexane/diethyl ether (70/30 v/v) was added dropwise via syringe through the septum. The mixture was allowed to warm up to 0 °C, and stirred for 1 h. Cyclopentadiene (1 mL, 12 mmol) was added and the stirring continued at 0 °C for additional 3 h. The reaction mixture was added with water and extracted with benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C, eluted with 20% benzene/hexane) to give 290 mg of **120b** (71%).

120b: Orange crystals; m.p. 154-155 °C (lit.[14] 156-157 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.34 - 7.42 (m, 10H), 7.33 (s, 4H), 6.59 - 6.64 (m, 4H), 6.34 - 6.37 (m, 2H), 6.27 - 6.30 (m, 2H).

N, N-Dimethyl-4-t-butylbenzamide ***148***. In a 100-mL round-bottomed, one-necked flask equipped with a magnetic stirring bar and a reflux condenser fitted with a calcium chloride drying tube, were placed 10g (56.1 mmol) of 4-t-butylbenzoic acid **146** and 20mL of thionyl chloride. The mixture was refluxed for 18 h. The extra thionyl chloride was removed by distillation under normal pressure. To the residue was added 20 mL of DMF, and the mixture was heated at 150 °C for 8 h. The product was distilled under reduced pressure (b.p. 120 °C, 5 mmHg) and yielded 5 g of **148** (43%).

148: Colorless crystals; m.p. 84 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.38 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 3.02 (brs, 3H), 3.00 (brs, 3H), 1.30 (s, 9H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 171.74, 152.65, 133.35, 126.90, 125.14, 39.64, 35.30, 334.70, 31.16; IR (KBr) ν 2964s, 1624s, 1491m, 1388s, 1266m, 1113m, 1079m, 855m, 771m, 716m, 580m, 505m cm^{-1}.

Tris(p-phenylene)pentafulvene ***51c***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 428 mg (1.1 mmol) of 6, 6-di(4-bromophenyl)-pentafulvene **149** and 8 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -70 °C, 1.7 mL (2.5 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum, and the mixture was stirred at -70 °C for 1 h. A solution of 518 mg (2.5 mmol) of **148** in 5 mL of anhydrous THF was added. The reaction mixture was allowed to warm up to 0 °C, and stirred for 1 h. Cyclopentadiene (1 mL, 12 mmol) was added and the mixture was stirred at 0 °C for 2 h, and at room temperature for 2 h. The reaction mixture was added with water and extracted with benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (40 g, 0 °C, eluted with 10% benzene/hexane to 20%

benzene/hexane). The crude product was an orange oil. Recrystallization from ether-hexane gave 88 mg of **51c** as orange crystals (38%).

51c: Orange crystals (ether-hexane); m.p. ca. 200 °C (decomp.); MS (FAB) m/z 647 [$(M+H)^+$]; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.32 (d, J = 8.4Hz, 4H), 7.37 (brs, 8H), 7.29 (d, J = 8.4 Hx, 4H), 6.60 - 6.65 (m, 6H), 6.32 - 6.37 (m, 6H), 1.37 (s, 18H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 152.18, 151.33, 150.51, 144.74, 144.08, 141.92, 141.28, 138.05, 132.79, 132.32, 132.21, 132.03, 131.59, 131.40, 124.79, 124.58, 124.33, 124.24, 34.79, 31.32; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 350(4.71), 330sh (4.7)297sh (4.5), 249 (4.51); IR (KBr) ν 3066w, 2957s, 1585s, 1466m, 1403w, 1360s, 1321w, 1266w, 1086m, 1020m, 998m 917m, 844m, 804s 772s, 674s, 552m cm^{-1}; Anal. Calcd. for $C_{50}H_{46}$: C, 92.83; H, 7.17, Found: C, 92.04; H, 7.46.

6-(4-Bromophenyl)-6-(4-t-butylphenyl)pentafulvene **150**. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 2.8 g (12 mmol) of 1, 4-dibromobenzene and 20 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -70 °C, 10 mL (15 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum, and the mixture was stirred at -70 °C for 1 h. A solution of 2.5 g (12.2 mmol) of **148** in 5 mL of anhydrous THF was added. The reaction mixture was allowed to warm up to 0 °C, and stirred for 1 h. Cyclopentadiene (3 mL, 36 mmol) was added and the stirring continued at 0 °C for additional 4 h. The reaction mixture was added with water and extracted with hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (30 g, 0 °C, eluted with hexane). The crude product was orange oil. Recrystallization from hexane in a deep-freezer gave 1.6 g of **150** (36%).

150: Orange leaflets (hexane); m.p. 87.5-88 °C; MS (EI, 70 eV) m/z 364/366 (M^+, 50%, 50%), 307/309 [$(M-t-Bu)^+$, 100%, 100%], 285 (10%), 247 (20%), 228 (50%), 202 (10%), 152 (15%), 121 (45%), 69 (10%), 57 (20%), 28 (10%), 18 (80%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.50 (dt, J = 8.6, 2.1 Hz, 2H), 7.38 (dt, J = 8.6, 2.1 Hz, 2H), 7.22 (dt, J =

8.5, 2.1 Hz, 2H), 7.19 (dt, J = 8.5, 2.1 Hz, 2H), 6.58-6.60 (m, 2H), 6.32-6.35 (m, 1H), 6.20-6.23 (m, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 152.27, 150.59, 143.858, 140.37, 137.80, 133.63, 132.42, 132.36, 132.00, 130.92, 124.81, 124.50, 123.96, 123.26, 34.77, 31.30; IR (KBr) ν 3066w, 2959s, 2864m, 1585s, 1483s, 1393m, 1360s. 1323w, 1266w, 1072m, 1010s, 914m, 839s, 810s, 776s, 669s, 560m cm^{-1}; Anal. Calcd. for $C_{22}H_{21}Br$: C, 72.33; H, 5.79, Found: C, 72.87; H, 5.89.

Tetrakis(p-phenylene)pentafulvene ***51d***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 777 mg (2.1 mmol) of **150** and 10 mL of anhydrous THF under nitrogen flow. The mixture was cooled below -70 °C, 1.7 mL (2.3 mmol) of 1.5 M n-butyllithium in hexane was added dropwise via syringe through the septum. The mixture was stirred at -70 °C for 1 h, and added with 220 mg (0.5 mmol) of **145** in one portion. The suspension was allowed to warm to 0 °C , and stirred for an additional 1 h. Cyclopentadiene (1 mL, 12 mmol) was added and the stirring continued at 0 °C for additional 3 h. The reaction mixture was added with water and extracted with benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (40 g, 0 °C, eluted with 10% benzene/hexane to 20% benzene/hexane) to give 141 mg of **51d** (18%).

51d: Reddish-orange crystals (CH_2Cl_2-hexane); m.p. ca. 200 °C (decomp.); MS (FAB) m/z 799.8 [(M+H)$^+$]; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz, 4H), 7.37 (brs, 12H), 7.29 (d, J = 8.4 Hz, 4H), 6.60-6.65 (m, 8H), 6.32-6.37 (m, 8H), 1.36 (s, 18H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 152.18, 151.30, 150.34, 144.84, 144.09, 141.97, 141.47, 141.21, 138.06, 132.88, 132.85, 132.33, 132.21, 132.02, 131.60, 131.54, 131.39, 124.79, 124.58, 124.35, 124.29, 124.22, 34.79, 31.32; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 348 (4.84), 326sh (4.8)298sh (4.6); IR (KBr) ν 3067w, 2957s, 2899m, 1282s, 1500m, 1466s, 1400m, 1359s, 1319m, 1084m, 997m, 914m, 841m, 800s, 772s, 743m, 672s, 554m cm^{-1}; Anal. Calcd. for $C_{64}H_{54}$: C, 93.19; H, 6.81, Found: C, 92.66; H, 6.81.

6, 6-Di(4-t-butylphenyl)pentafulvene ***51a***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 400 mg (10.8 mmol) of sodium hydride(60% oil dispersion) and 8 mL of anhydrous THF under nitrogen flow. The suspension was cooled to -30 °C, and 1 mL (12 mmol) of cyclopentadiene was added. The mixture was allowed to warm up to room temperature, and stirred for 1 h. The mixture was again cooled to -50 °C, and a solution of 740mg (2.5 mmol) of 4, 4'-di-t-butylbenzophenone **151** in 8 mL of anhydrous THF was added. The reaction mixture was allowed to warm up to room temperature, and stirred for additional 3 h. The mixture was added with water and extracted with hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (40 g, 0 °C, eluted with hexane to 10% benzene/hexane). The crude product was recrystallized from hexane to yield 122 mg of **51a** (14%).

51a: Orange needles (hexane); m.p. 153-154 °C; MS (EI, 70 eV) m/z 342 (M^+, 10%), 385 [(M - t-Bu)$^+$, 20%], 256 (20%), 228 (7%), 185 (5%), 129 (7%), 57 (25%), 43 (30%), 28 (20%), 18 (100%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.39 (dt, J = 8.6, 2.0 Hz, 4H), 7.26 (dt, J = 8.6, 2.0 Hz, 4H), 6.58-6.60 (m, 2H), 6.32-6.35 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 152.55, 151.91, 143.23, 138.52, 132.09, 131.54, 124.58, 124.53, 34.75, 31.32; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 341 (4.37), 243 (4.22); IR (KBr) ν 3068w, 2962s, 2865m, 1586s, 1504m, 1465s, 1396m, 1361s, 1327m, 1268m, 1108m, 1082w, 1017w, 919m, 841s, 816s, 776m, 747m, 677s, 634w, 556m cm^{-1}; Anal. Calcd. for $C_{26}H_{30}$: C, 91.17; H, 8.83, Found: C, 90.72; H, 8.78.

Bis(p-phenylene)pentafulvene ***51b***. In a 50-mL round-bottomed, two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, were placed 360 mg (9.0 mmol) of sodium hydride(60% oil dispersion) and 8 mL of anhydrous THF under nitrogen flow. The suspension was cooled to -30 °C, and 1 mL (12 mmol) of cyclopentadiene was added. The mixture was allowed to warm up to room temperature, and stirred for 1 h. The mixture was again cooled to -50 °C, and a solution of

400 mg (1.0 mmol) of 1, 4-di(4-t-butylbenzoyl)benzene **152** in 8 mL of anhydrous THF was added. The reaction mixture was allowed to warm up to room temperature, and stirred for additional 6 h. The mixture was added with water and extracted with benzene/hexane. The combined organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (40 g, 0 °C, eluted with hexane to 10% benzene/hexane). The crude product was washed with hexane and filterted to give 370 mg of **51b** (75%).

51b: Orange crystals (CH_2Cl_2-hexane); m.p. 213-214 °C; MS (EI, 70 eV) m/z 494 (M^+, 35%), 437 [$(M\text{-t-Bu})^+$, 10%], 57 (10%), 28 (15%), 18 (100%); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.41 (d, J = 8.6 Hz, 4H), 7.33 (s, 4H), 7.28 (d, J = 8.6 Hz, 4H), 6.59-6.62 (m, 4H), 6.32-6.37 (m, 4H), 1.36 (s, 18H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 152.13, 151.50, 143.99, 141.75, 138.10, 132.22, 132.13, 132.04, 131.44, 124.76, 124.57, 124.30, 34.79, 31.33; UV-Vis. (CH_2Cl_2) λ_{max}/nm (log ε) 358sh (4.5), 333 (4.56), 294sh (4.3), 244 (4.39); IR (KBr) ν 3072w, 2963s, 2867m, 1584s, 1467m, 1408m, 1361s, 1321m, 1107m, 1085m, 1003m, 921s, 843m, 808s, 774m, 678s, 555m cm^{-1}; Anal. Calcd. for $C_{38}H_{38}$: C, 92.26; H, 7.74, Found: C, 91.81; H, 7.70.

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List of Publications

1. Selective Lithiation and Functionalization of 6, 6-Bis(2-thienyl)pentafulvene
   Hiroyuki Kurata, Tatsuya Morikawa, Takashi Kumagai, Takeshi Kawase, and Masaji Oda
   Chemistry Express, **1991**, *6*, 853.

2. Synthesis and Alkali Metal Reduction of 1, 1-Diarylspiro[2, 4]hepta-4, 6-dienes. Generation of Homopentafulvene Dianions
   Takeshi Kawase, Hiroyuki Kurata, Shin-ichi Fujino, Tatsuya Ekinaka, and Masaji Oda
   Tetrahedron Lett. **1992**, *33*, 7201.

3. Tandem Reactions of N, N-Dialkylamides with Organolithium Compounds and Cyclopentadienes. A New Efficient Synthesis of Pentafulvenes
   Hiroyuki Kurata, Tatsuya Ekinaka, Takeshi Kawase, and Masaji Oda
   Tetrahedron Lett., **1993**, *34*, 3445.

4. Synthesis and Properties of Oligo-6-(2-thienyl)pentafulvenes
   Takeshi Kawase, Hiroyuki Kurata, Tatsuya Morikawa, and Masaji Oda
   Tetrahedron Lett. **1993**, *34*, 3449.

5. Cyclic Oligo-6-(2-thienyl)-pentafulvenes
   Hiroyuki Kurata, Takeshi Kawase, and Masaji Oda
   in preparation

Related Papers

5. Tetra(2-thienyl)butatrienes: New Butatriene Derivatives with Highly Amphoteric Multistage Redox Properties and a Short Central Double Bond

Takeshi Kawase, Seiji Muro, Hiroyuki Kurata, and Masaji Oda

J. Chem. Soc., Chem. Commun., **1992**, 778.

6. Novel Cyclo-oligomerization of Nickel Carbenoids: a Simple and Efficient Synthesis of Radialenes

   Masahiko Iyoda, Akira Mizusuna, Hiroyuki Kurata, and Masaji Oda

   J. Chem. Soc., Chem. Commun., **1989**, 1690.

7. Synthesis of the Tris(9-fluorenylidene)cyclopropane Dianion and Related Dianions: [3]Radialenes with Novel Electronic Properties

   Masahiko Iyoda, Hiroyuki Kurata, Masaji Oda, Chiaki Okubo, and Kichisuke Nishimoto

   Angew. Chem. Int. Ed. Engl., **1993**, *32*, 89.

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