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Syntheses of Conjugated Oligomers and Macrocycles Containing Thiophene, Pyrrole, Furan, 1,3,4-Thiadiazole and Thiazolo[5,4-d]thiazole

presented by

Seaver Shieh

has been accepted towards fulfillment
of the requirements for

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Eugene E. Hoff
Major professor

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Syntheses of Conjugated Oligomers and Macrocycles Containing Thiophene, Pyrrole, Furan, 1,3,4-Thiadiazole and Thiazolo[5,4-d]thiazole

By

Seaver Shieh

A Dissertation

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ABSTRACT

Synthesis of Conjugated Oligomers and Macrocycles Containing Thiophene, Pyrrole, Furan, 1,3,4-Thiadiazole and Thiazolo[5,4-d]thiazole

By

Seaver Shieh

Study of the structural influences of conducting polymers is one of the most important research in this area. Because conducting polymers containing carbon-nitrogen double bonds in the conduction pathway still have not thoroughly been explored[36] and study on this aspect can provide information on the heteroatom (nitrogen) influence on the properties of the conductive polymers, preparation of conductive polymers and oligomers with C=N bond in the conductive main chain have been studied and discussed in this thesis. Several new mixed oligomers which contain thiophene, furan, pyrrole, 1,3,4-thiadiazole and thiazolo[4,5-d]thiazole have been synthesized and some spectroscopic properties have been studied. The results show that 1,3,4-thiadiazole increases the bandgaps because of the electron withdrawing properties of this heterocycle. Thiazolo[4,5-d]thiazole decreases the bandgaps because of the bigger conjugation property of the π-electrons in it.

In the course of synthesis of mixed thiophene oligomers containing 1,3,4-thiadiazole an efficient and practical method for the

preparation of 2,5-diaryl-1,3,4-thiadiazoles in one pot has been developed. The value of this reaction has been shown by the syntheses of a variety of 2,5-diaryl-1,3,4-thiadiazoles with high yield (>90% yield for most reactions). By using this method, 2,5-di(4-hydroxylphenyl)-1,3,4-thiadiazole and 2,5-dipyridyl-1,3,4-thiadiazoles have been synthesized in one pot with high yield. The traditional syntheses of these two kinds of compounds usually require several steps and use expensive reagents[42,43].

1,4-Diketones are important intermediate compounds for the syntheses of thiophenes, pyrroles, furans and other heterocycles. In the search for a good method for the preparation of 1,4-diketones, oxidative coupling of trimethylsilyl enol ethers with Ceric Ammonium Nitrate(CAN) has been shown to be a practical method for the syntheses of 3,4-dialkyl-1,4-(2-thienyl)-1,4-butanediones. $VOCl_3$/Pyridine has been found to be a good oxidative reagent for the oxidative coupling of trimethylsilyl enol ethers to 1,4-diketones. By using $VOCl_3$/Pyridine as an oxidation reagent the reaction time is shorter compared to that with CAN.

In the approaches of syntheses of conjugated macrocycles a hexathiophene macrocycle has been synthesized with low yield (1.5%). The formation of this compound was confirmed by mass spectrum, ^{1}H-NMR and UV-Vis. The results show that there is only a little aromatic property of this compound, which is inconsistent with that predicted by Huckel rule and MM2 calculation. Further research in the structure of this compound is necessary.

This thesis is dedicated with love to

my Father, Shu-Lin Xie

and

my Mother, Qiao-Ying Chi

To my wife, Lillian H. Shieh
for her love, support and understanding

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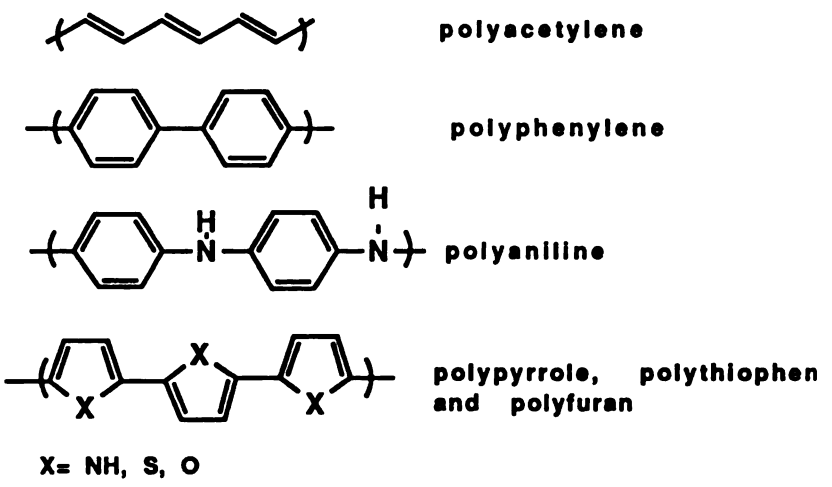
INTRODUCTION

Since the 1970's a number of special polymers have been found which exhibit electrical conductivity when they are submitted to oxidation or reduction. These kinds of special materials are called conducting polymers. They are new materials with many potential applications[1-4], such as rechargeable polymer battery[5,6], electrochromic displays[7,8], antistatic and transparent conducting material[9], chemical sensors[10,11], memory devices[12], polymer based diodes and transistors[13-15].

The common feature of conducting polymers is that they are structurally conjugated. Some conducting polymer structures are shown in Figure I-1.

Neutral conjugated organic polymers can not conduct electricity because of the lack of electrical carriers. In order to become a conductor or semiconductor, it is necessary to introduce charge carriers into neutral polymers. These typical processes are called doping. Generally, there are two methods to introduce charge

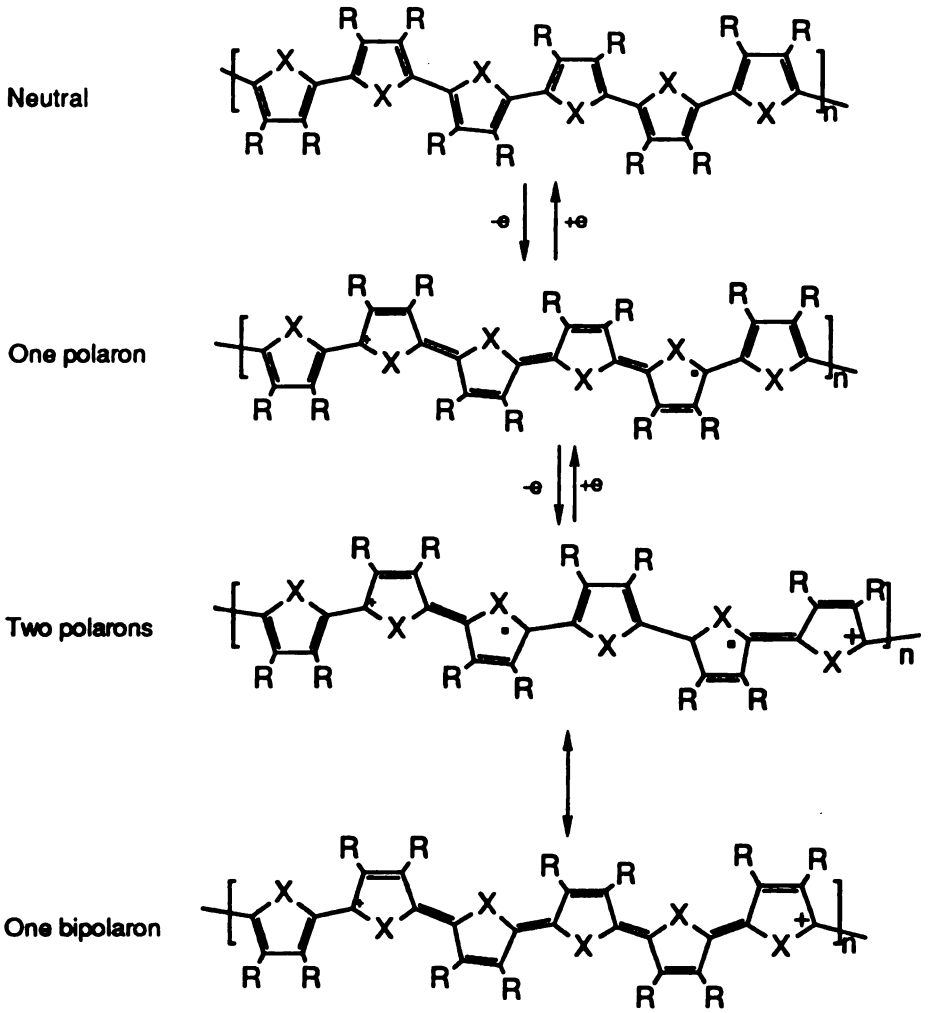
Figure I-1



carriers. One is to take off one or more electrons from the neutral polymers by oxidation, which introduces positive charges in the polymers. This process is called p-doping. The other is to introduce negative charges by the addition of electrons (reduction), which is described as n-doping. Scheme I-1 shows some p-doped conducting polymer structures.

Although there has been much progress in the research of conducting polymers, the conductive mechanism is still unclear. Generally, in analogy to inorganic conductors or semiconductors, band theory is utilized to explain the conductive mechanisms. In a conjugated polymer, the highest occupied electronic orbitals constitute the valence band (VB) and the lowest unoccupied orbitals form the conduction band (CB). The width between the VB and CB is called the bandgap(Eg). The intrinsic conductivity of an organic conducting polymer is determined by the bandgap. Neutral

Scheme I-1

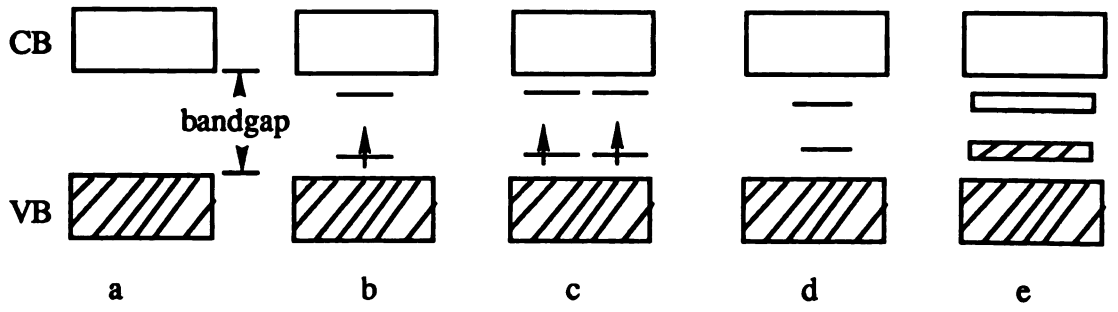


x= NH, S, O; R= H, Alkyl groups etc

conjugated polymers are intrinsically insulators because of large bandgaps. The result of doping lowers the bandgap so as to increase the electrical conductivity[16]. The band structures of neutral and doped conductive polymers are shown in Figure I-2.

Polyacetylene is the first and most electrically conductive polymer reported so far. Its conductivity has been reported as high

Figure I-2



a. The bandgap of neutral conjugated polymers
b. The bandgap of one polaron
c. The bandgap of two polarons
d. The bandgap of one bipolaron
e. The bandgap of doped conductive polymers

as 16000S/cm per unit weigh[17]. However, its applications have been limited by its low stability and poor processing properties. In contrast, polypyrrole, polythiophene, polyfuran and some other polyheteroaromatic compounds show reasonable electrical conductivity and high stability[18]. Another advantage of polyheteroaromatic compounds over polyacetylene is the ease of modifying the polymer chains to achieve the processing requirement by simple substitutions. Many conductive polymers, soluble in both organic solvent and water, have been synthesized in this way[19-24].

Generally speaking, the knowledge of the relationship between the chemical structures of monomers and the electrical properties of the resulting polymers is important both in the understanding of electrical conduction mechanisms of conductive polymers and in the

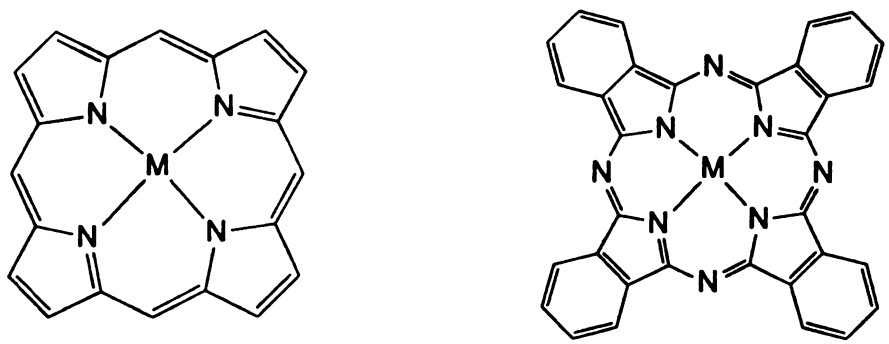
preparation of new kinds of conductive polymers. Although there has been lots of progress in understanding the monomer structural influences on the conductivity and other properties of the corresponding polymers, the reported results so far are not enough to understand the conductive mechanisms or functions of some heteroatoms *e.g.* sulfur and nitrogen in the conductivity or other properties of polyheteroaromatic systems. If we consider polyacetylene as a basic conjugated system, polypyrrole, polythiophene and polyfuran can be rationalized as NH, S, and O functionalized polyacetylene derivatives.

Structural modifications are commonly used strategies in the study of monomer structural influences on the properties of the resulting polymers. For the polyheteroaromatic systems there are two ways to modify the conductive polymer structures. One is to synthesize heteroaromatic monomers with different substituents and then study the substituent influences on the properties of resulting polymers. The other is to synthesize monomers with special structures so that the resulting polymers will have different main chain structures. By this way, the relationship of the monomer structures with the properties of the conducting polymers can be easily studied. Conducting polymers synthesized from 3- and/or 4-alkyl substituted pyrroles, thiophenes and furans belong to the first kind but polyisothianaphthene (PITP)[25], polythieno[3,2-b]thiophene(PTT)[26], *etc.* can be considered as the second. Considering that studies on the influences of the main chain structures on the properties of the conducting polymers are less than those on the side chain influences, the syntheses of new structural monomers and

oligomers is one of the goals in my Ph.D. thesis research. In Chapter 1 and 2 of this thesis the syntheses of some new conjugated oligomers containing thiophene, pyrrole, furan, 1,3,4-thiadiazole and thiazolo[5,4-d]thiazole will be presented.

Conjugated macrocyclic compounds are other kinds of organic conductors with the metalloporphyrins and metallophthalocyanines as two common compounds for this purpose (Figure I-3)[27].

Figure I-3



The basic requirement for these kinds of organic conductors is that the constituent molecules must be essentially planar. The planar structure allows them to stack close enough to be a conductor or semiconductor. This basic requirement allows chemists to design and synthesize new macrocyclic compounds which are structurally planar or nearly planar and then study the molecular size effects on the conductivity and other properties. Expanded porphyrins are one of these kinds of macrocyclic compounds. In Chapter 3 of this thesis the attempted syntheses of some new conjugated macrocyclic compounds will be presented and discussed.

Chapter 1

Syntheses of Some Tricyclic Compounds as Monomers for the Syntheses of New Conductive Polymers

1.1 Attempt at the Synthesis of a Phenylene Bridged Tricycle

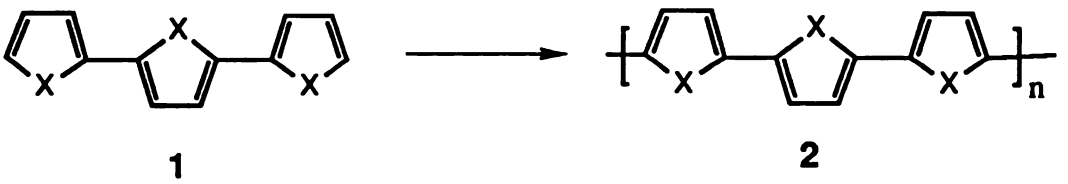
Although there are lots of reports on the monomer structure influences on electrical properties of the conductive polymers[27-30], research on the study of structural influences of the properties of conductive polymers is still an interesting area, and there is still lot of work to be done in understanding the relationship of monomer structures and the electrical conductivity.

Generally, polypyrrole, polythiophene, polyfuran and some other polyheteroaromatic compounds can form linear, one-dimensional chains. Monomers with three or more reactive positions can form conductive polymers with multi-dimensions. Scheme 1-1 shows one of the possible multi-dimension conductive polymers.

Preparation and electrical property studies of multi-dimensional conductive polymers are important both in the understanding of conductive mechanisms and in the exploration of new kinds of conductive polymers. The heteroaromatic tricycles with a phenylene

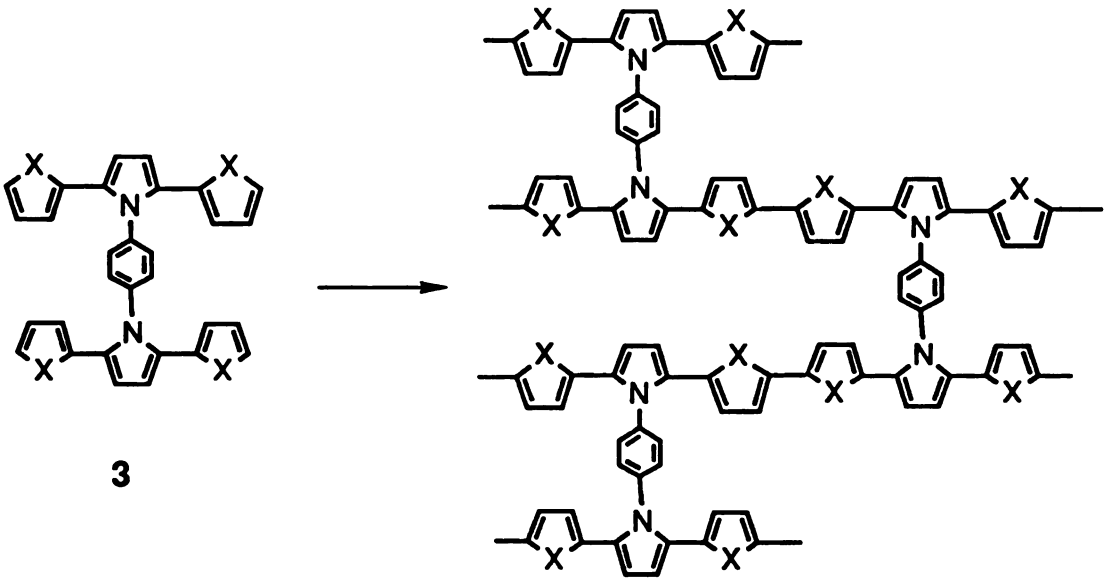
bridge have been suggested[31] as monomers of multi-dimensional conductive polymers (Scheme 1-1).

Scheme 1-1



1 2

one-dimension

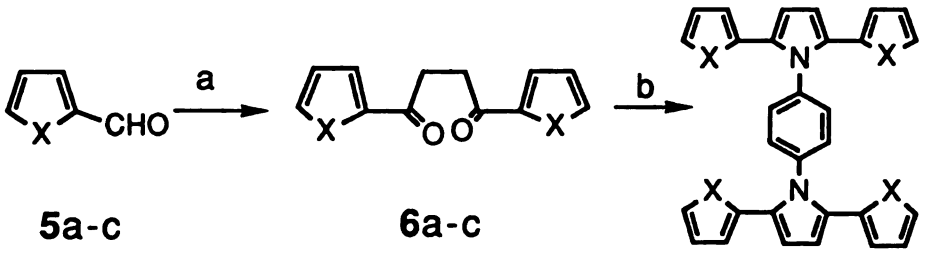


3 4

multi-dimensions

The synthesis of symmetric heteroaromatic tricycles with a phenylene bridge has been achieved by Merrill in this laboratory by using Stetter's reaction to prepare the correspondent 1,4-diketones and then condensed with p-phenylene diamine (Scheme 1-2)[31].

Scheme 1-2



5a-c 6a-c 3a-c

a, X=NH; b, X=S; c, X=O

a. thiazolium salt (cat.), Et_3N, divinyl sulfone, dioxane, 80 °C

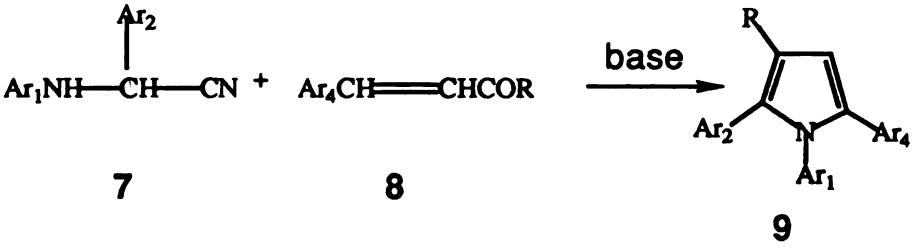
b. phenylene diamine, HOAc, reflux

Although the above route seems to be a good one to the synthesis of this kind of system there still are some problems which have to be solved. First, the electrically rich property of pyrrole ring makes Stetter's reaction not good for the unsubstituted 2-formyl pyrrole[31]. When unsubstituted 2-formyl pyrrole is used protection with an electron withdrawing group is necessary. Second, although condensation of the 1,4-diketone with phenylene diamine in two steps gave moderate yield of the expected p-phenylene bridged tricyclic compound **3**, one step condensation resulted in very low yield[31]. Third, Stetter's reaction requires expensive reagents such as divinyl sulfone and only symmetric monomers can be synthesized in this method. Therefore, to find another route for the synthesis of compound **3** is still necessary.

Miller and Ploechel[32] in 1898 reported that the addition of anilinophenylacetonitrile(7)(Ar_1=Ph) to cinnamaldehyde(8) yields

1,2,5- triphenylpyrrole (9)(Ar_1=Ph, Ar_2, Ar_4=Ph, R=H) (Scheme 1-3). A similar reaction has also been reported by Clark and Lapworth[33]. Further research and the applications of this reaction has been demonstrated by Treibs and Derra[34].

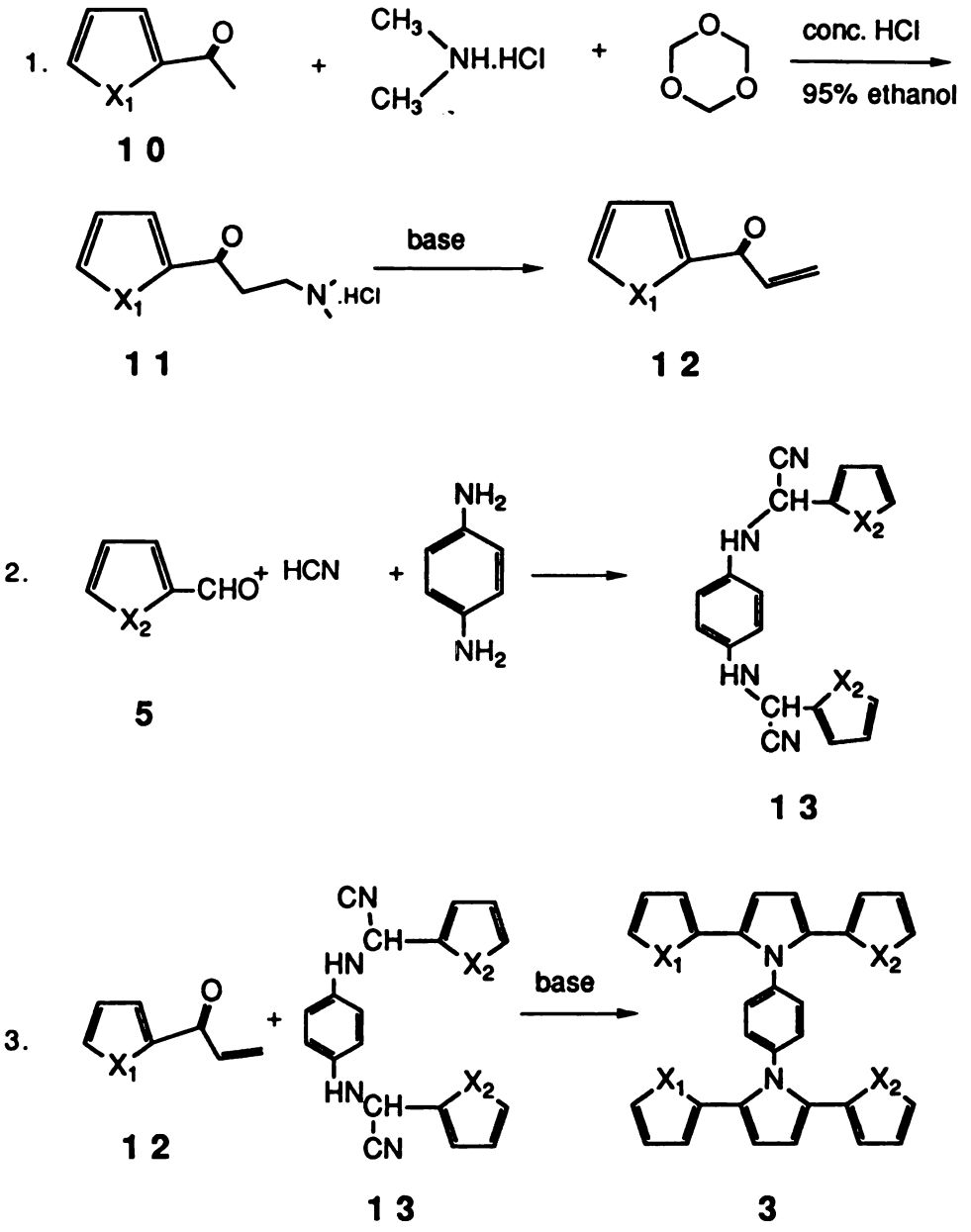
Scheme 1-3



7 8 9

As an application of the Miller-Ploechel reaction, the following project has been proposed (Scheme 1-4). Starting with 2-acetyl derivatives of thiophene, furan or pyrrole and using Mannich reaction followed by treating with bases the unsaturated ketones(12) can be synthesized (reaction 1 in Scheme 1-4). Synthesis of the corresponding aminonitriles(13) can be achieved by the condensations of the 2-formyl thiophene, furan or pyrrole with hydrogen cyanide and p-phenylene diamine (reaction 2 in Scheme 1-4). If the Miller-Ploechel reaction can be utilized in this system the reaction of the unsaturated ketones(12) with the aminonitrile(13) will lead to the expected compound 3 (reaction 3 in Scheme 1-4).

Scheme 1-4



10 11 12 5 13 3

X_1, X_2= NH, S,O

While this research work was being conducted, we thought that one would want to know whether the Miller-Ploechel reaction is a

reliable reaction, and whether it can be applied to this system. As a model reaction the aminonitrile **13** with X=S has been synthesized and reacted it with acrolein in the reported standard condition. The reasons for choosing it as a model reaction are:

(1). The thiophene ring is relatively more stable than pyrrole and furan.

(2). Conducting polymers synthesized from thiophene derivatives show higher conductivity than those from pyrrole or furan analogs.

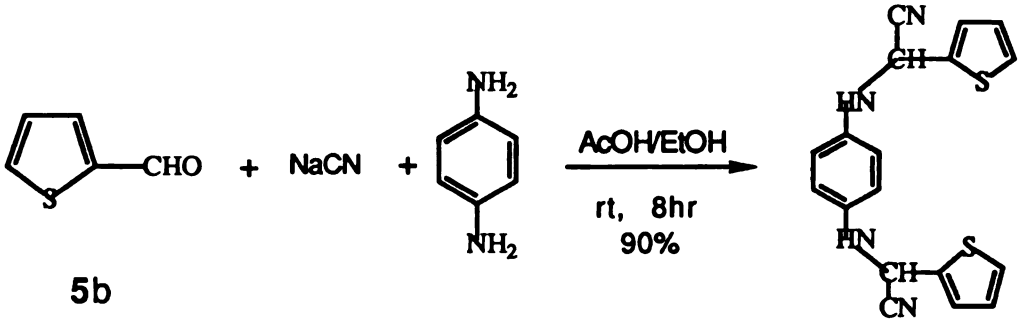
(3) Acrolein has been reported as a good reagent for the Miller-Ploechel reaction. Unknown compound **15** was the expected product in this model synthesis.

Compound **13b**(X_2=S) has been synthesized by the condensation of 2-formyl thiophene, NaCN, AcOH, p-phenylene diamine in ethanol with 90% yield (Scheme 1-5). When compound **13b** reacted with acrolein in the reported reaction condition, it had been found that the imine compound **16** was the only isolated product. This result indicates that before the Miller-Ploechel reaction occurs the aminonitrile loses two molecules of hydrogen cyanide in the basic reaction conditions (Scheme 1-6). Considering the reaction mechanism of the Miller-Ploechel reaction (Scheme 1-7) and this unexpected result we thought that Miller-Ploechel reaction might not be a general reaction as it is difficult to apply to the synthesis of compound **3**.

Because of the unsuccessful application of the Miller-Ploechel reaction to the synthesis of compound **15** further research on above project has not been attempted. Research has been guided to the

syntheses of new kinds of conductive polymers which contain C=N double bonds or other heterocycles aside from pyrroles, thiophenes and furans in the conductive pathway.

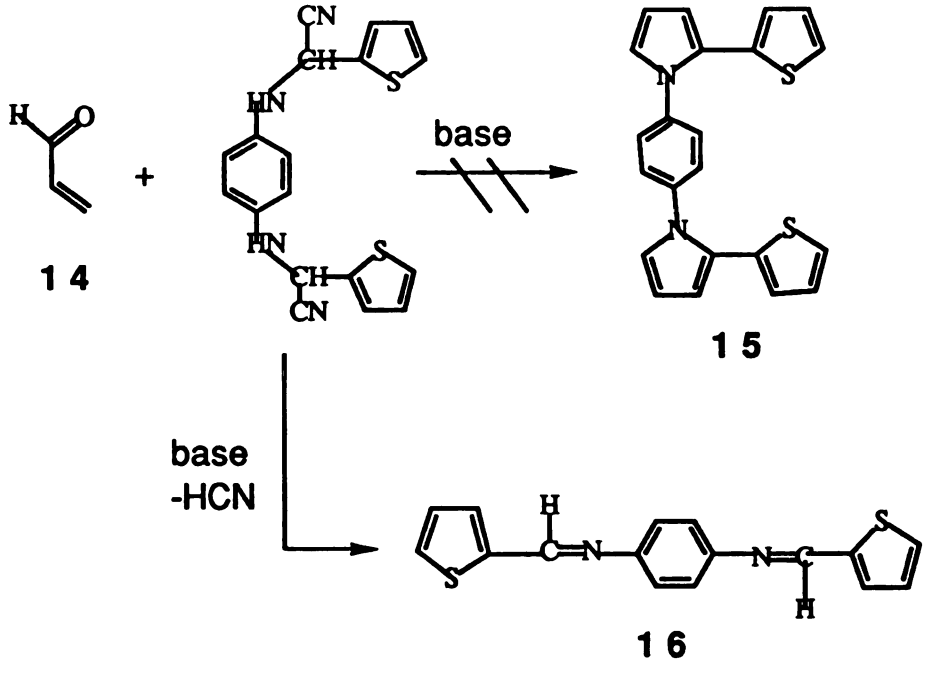
Scheme 1-5



5b

13b

Scheme 1-6

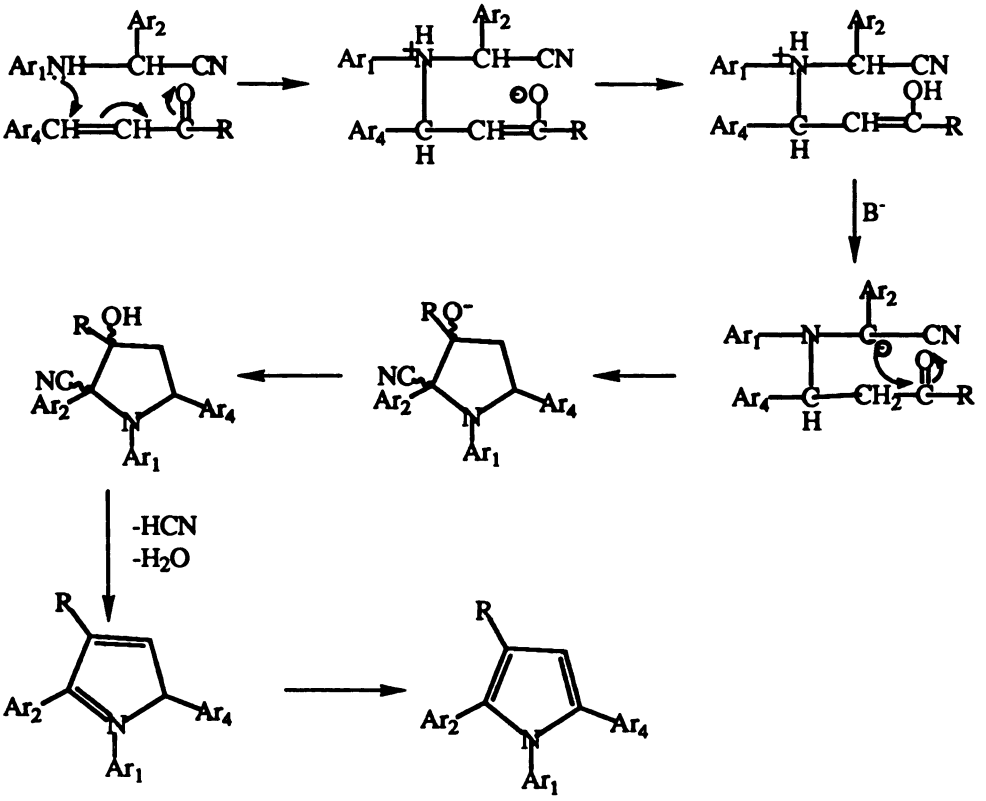


14

15

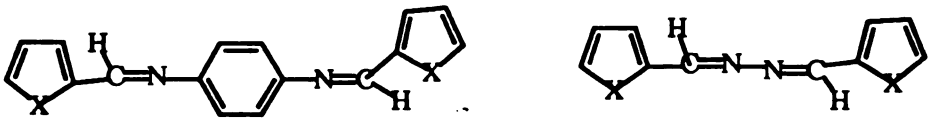
16

Scheme 1-7



Considering that conducting polymers containing carbon-nitrogen double bond in the conduction pathway still have not thoroughly been studied[36] and study on the conductive polymers containing C=N double bond might provide information on the heteroatom (nitrogen) influence on the properties of the conductive polymers, preparation of conductive polymers with C=N double bond in the conductive main chain is necessary. In order to synthesize conductive polymers with C=N double bond in the conduction pathway, monomers **16, 17** (Figure 1-1) are the simplest candidates.

Figure 1-1



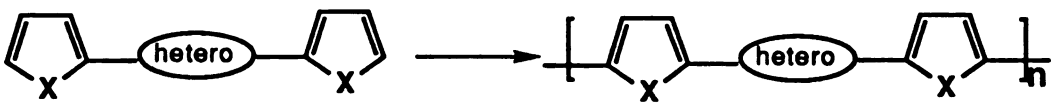
16 17

Monomers **16** and **17** with X=S have been prepared by the reaction of 2-formyl thiophene with p-phenylene diamine and hydrazine in benzene in the presence of HCl catalyst (best yield can be obtained when pH value is controlled between 5 and 6). Unfortunately when they are submitted to the electrical polymerization monomers **16** and **17** do not polymerize in normal electrical polymerization conditions. Chemical polymerization by $FeCl_3$ in dried CH_2Cl_2 also fails to synthesize conductive polymers by using the imine compounds **16** and **17** as monomers. Generally, electrically inactive monomers are difficult to polymerize by using common chemical oxidation methods and the reactivity of C=N double bonds with Grignard reagents excludes the possibility of using a Grignard coupling reaction to synthesize the conjugated polymers with these imine monomers. No further attempts have been made to synthesize conductive polymers from these imine monomers and research was immediately turned to other kinds of monomers which contain C=N double bond or other heterocyclic compounds in the conductive polymer main chains.

Monomers **16** and **17** contain two pyrrole, thiophene or furan rings at the ends and the middle parts are structurally different fragments. It was thought that if the middle parts are modified in a

proper way, many monomers with different structures can be synthesized and electrical or chemical polymerization of these monomers will lead to many new kinds of conductive polymers. In this way the structural influences of the monomers on the properties of the resulted conductive polymers can be easily studied. Following this strategy and considering the chemical reactivity of monomers **16** and **17**, we think that one of the choices for the middle parts is to incorporate a special heterocyclic compound between two pyrroles, thiophenes or furans. Scheme 1-8 shows this strategy.

Scheme 1-8



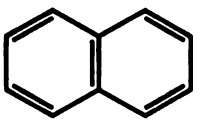
X= NH, S, O

With this strategy in hand the next step was to choose which heterocyclic compounds were to be used. The guideline is to choose a heterocyclic compound which contains special groups or atoms whose importance to the conductivity are to be studied. In the following sections, how this strategy has been used for the synthesis of some tricyclic compounds as candidates for the syntheses of new conductive polymers and higher oligomers will be presented.

1.2 Syntheses of 2,5-Diaryl-thiazolo[5,4-d]thiazoles

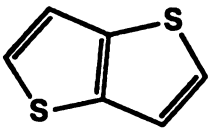
Thiazolo[5,4-d]thiazole(**20**) is an aromatic compound with 10 π-electrons. The chemical structure of thiazolo[5,4-d]thiazole is isoelectronic with that of naphthalene and that of thieno[3,2-b] thiophene (Figure 1-2).

Figure 1-2



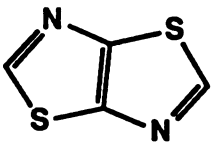
18

Naphthalene



19

Thieno[3,2-b]thiophene



20

Thiazolo[5,4--d]thiazole

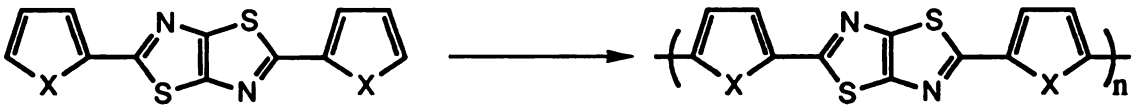
Thiazolo[5,4-d]thiazole(**20**) is thought to be a good candidate as a heterocyclic compound for the incorporation in the thiophene oligomers because of its structural similarity to thieno[3,2-b]thiophene(**19**) and it contains two C=N double bonds. Syntheses and studies of conjugated oligomers or polymers containing thiazolo[5,4-d] thiazole may provide some information on the influence of a nitrogen atom or a C=N double bond on the properties of conductive polymers.

From literature, it was known that thiazolo[5,4-d]thiazole itself can not polymerize electrochemically[35]. Lithiation of thiazolo[5,4-d]thiazole followed by oxidation with $CuCl_2$ gave a completely disordered polymer[36]. In our opinion, it is difficult to use this

homopolymerization result to study the influence of structure on the properties of conductive polymers.

As an attempt to study the influence of thiazolo[5,4-d]thiazole on the properties of the thiophene based oligomers or polymers one part of my research was to synthesize some tricyclic compounds which contain thiazolo[5,4-d]thiazole, and then use these tricyclic compounds as monomers for the syntheses of new conductive polymers (Scheme 1-9). Compounds **21b** and **21c** are known but **21a** is an unknown compound. All the expected polymers **22a**, **22b** and **22c** are new.

Scheme 1-9



21a-c **22a-c**

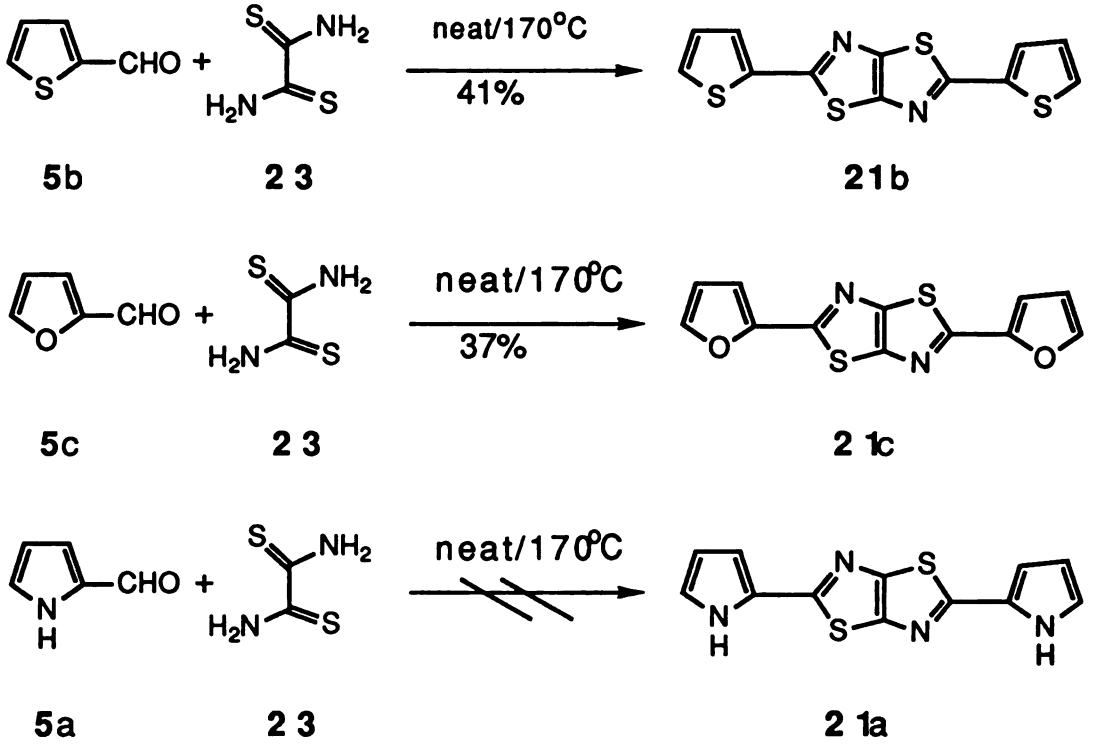
a, X=NH; b, X=S; c, X=O

Compounds **21b** and **21c** have been prepared by the condensation of 2-formyl thiophene and 2-formyl furan with dithiooximide via the reported procedure (Scheme 1-10)[37,38].

Condensation of 2-formyl thiophene with dithiooximide in the absence of solvent at 170 °C gave 41% yield of 2,5-di(2-thienyl)thiazolo[5,4-d]thiazole **21b**. Similarly, reaction of 2-formyl furan with dithiooximide gave 2,5-di(2-furanyl)thiazolo[5,4-d]thiazole **21c** in 37% yield (Scheme 1-10). However, the reaction of 2-formyl pyrrole with dithiooximide in the same condition fails to

give the expected product, 2,5-dipyrryl thiazolo[5,4-d]thiazole, **21a** (Scheme 1-10).

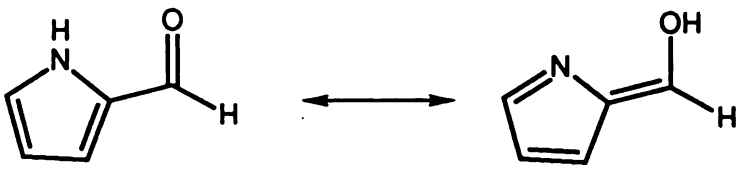
Scheme 1-10



Changing reaction condition by using DMF as solvent does not improve the yield of 2,5-di(2-thienyl)thiazolo[5,4-d]thiazole **21b** and 2,5-di(2-furanyl)thiazolo[5,4-d]thiazole **21c**. It also failed to give any isolated yield of 2,5-dipyrryl thiazolo[5,4-d]thiazole, **21a**. The failure of the condensation of 2-formyl pyrrole with dithiooximide might be attributed to the most electronically rich character of 2-formyl pyrrole among these three 2-formyl compounds which makes

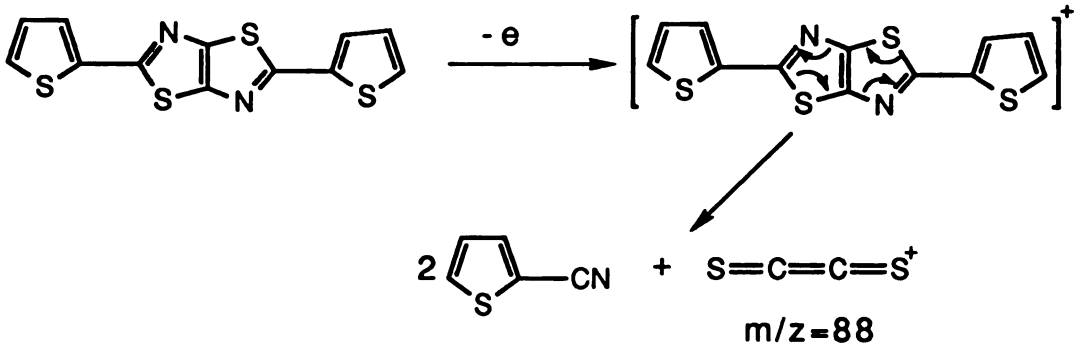
it unstable. Another reason for this failure might be attributed to the hydrogen in the 1-position of 2-formyl pyrrole. The resonance hybrid structure[39] of 2-formyl pyrrole make the condensation difficult (Figure 1-3).

Figure 1-3



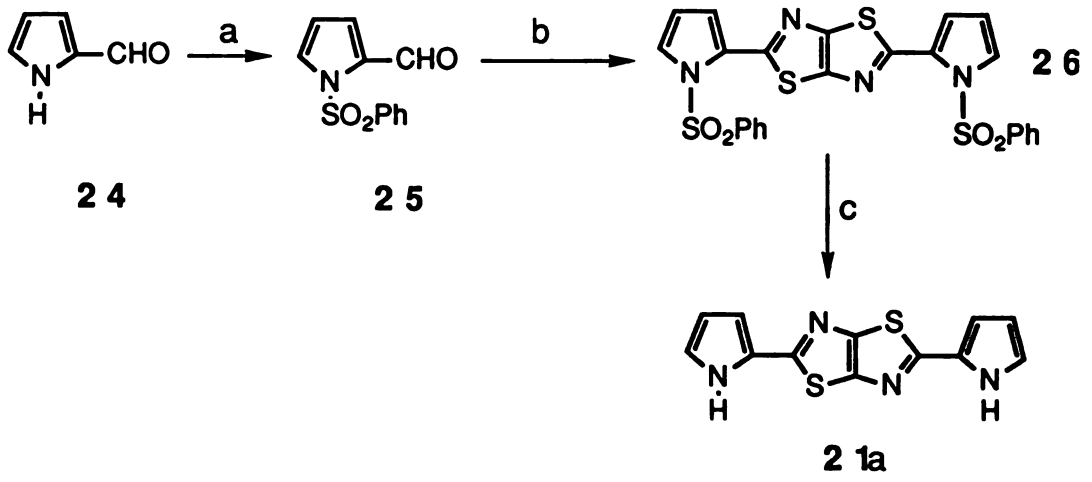
The structures of **21b** and **21c** confirmed by ^{1}H-NMR, mass spectra, UV-Vis spectra and other spectroscopies. For example, the three sets of doublet doublet peaks with chemical shift of 7.58 (J=4.1, 1.0Hz), 7.47(J=5.4, 1.0Hz) and 7.12ppm (J=5.4, 4.1Hz) shows the characteristic of the pattern of α-monosubstituted thiophene. EI-mass spectra shows a strong molecular ion peak at m/z=306 (relatively intensity 61.4) which is in support of the structure of **21b**. The base-line at m/z=88 corresponds to the structure of $C_2S_2^+$ which is consistent with the loss of two α-cyanothiophene (Scheme 1-10.1). The UV-Vis maximum absorption at 388nm shows a bathochromic shift of about 30nm of α-terthiophene, another indication of extended conjugated structure of **21b**.

Scheme 1-10.1



In order to synthesize 2,5-di(2-pyrryl)thiazolo[5,4-d]thiazole(**21a**) it is necessary to protect the pyrrole ring with an electron withdrawing group. Reaction of 2-formyl pyrrole with $ClSO_2Ph$ in CH_2Cl_2 with the presence of NaOH gave the expected 2-formyl-1-phenylsulfonyl pyrrole(**25**) in 91% yield. Condensation of 2-formyl-1-phenylsulfonyl pyrrole(**25**) dithiooximide in DMF lead to the formation of the expected 2,5-di(1-phenylsulfonyl-2-pyrryl) thiazolo[5,4-d]thiazole(**26**) in 25% yield. Hydrolysis of 2,5-di(1-phenylsulfonyl-2-pyrryl)thiazolo[5,4-d]thiazole(**26**) with NaOH in refluxing EtOH for 8 hours gave a 72% yield of the 2,5-di(2-pyrryl)thiazolo[5,4-d]thiazole(**21a**) (Scheme 1-11).

Scheme 1-11



a) $PhSO_2Cl$(1.1 eq), NaOH, CH_2Cl_2/H_2O, rt, 24hrs, 91%;

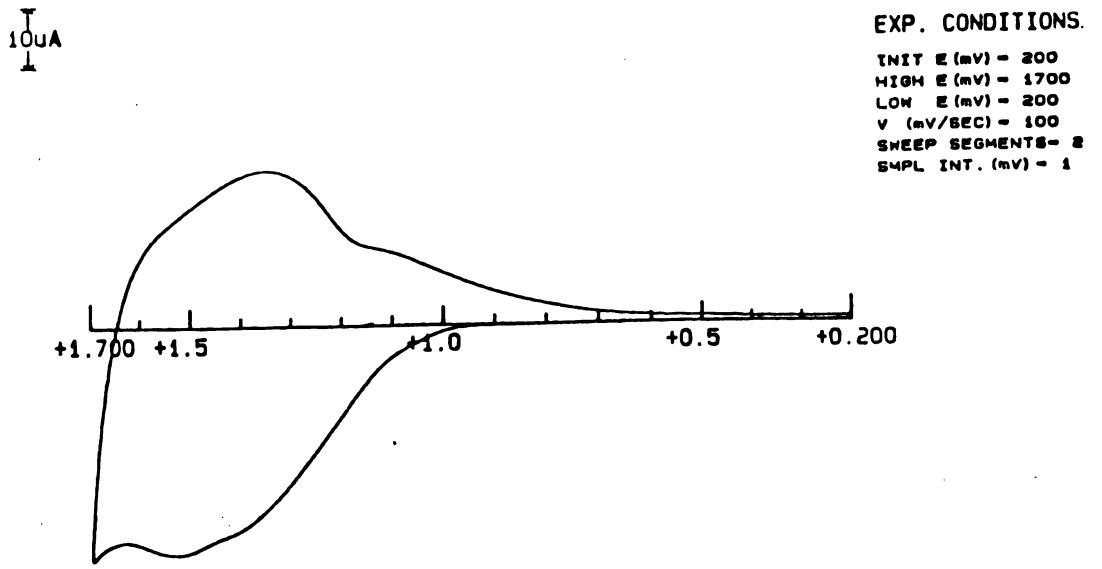
b) DMF, 150 °C, 40min, 25%;

c) NaOH, EtOH, reflux, 8hrs, 72%.

Chemical polymerization of 2,5-di(2-thienyl)thiazolo[5,4-d] thiazole with $FeCl_3$ in CH_2Cl_2 fails to give a high molecular weight polymer. The resultant products are orange colored low molecular weight oligomers. The molecular weight were determined by end-group of H^1-NMR with about 3,000 to 6,000. UV-Vis spectra show a maximum absorption at 497nm.

When monomers **21b** & c were submitted to electrical polymerization they polymerize easily under normal conditions. Figure 1-4 shows the cyclic voltamgram result of **21c**.

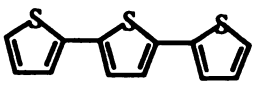
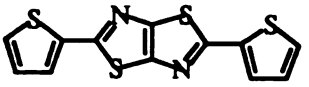
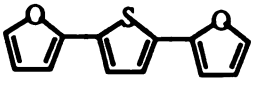
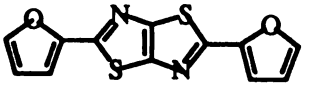
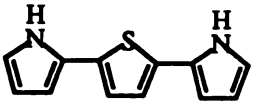
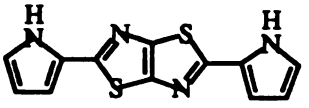
Figure 1-4



From Figure 1-4 the oxidation peak covers a broad range centered at about 1.53V which corresponds to the oxidation potential of the monomer, the formed oligomers or the polymer. This low oxidation potential indicates monomer **21b** might be a good candidate for the synthesis of new conducting polymer **22b** and could be used as a component for copolymerization with other monomers e.g. pyrrole, thiophene, *etc.*

The UV-absorption of 2,5-di(2-thienyl)thiazolo[5,4-d]thiazole has been determined and compared with that of α -terthienyl. The results are presented in Table 1-1. These results show that the heterocycle thiazolo[4,5-d]thiazole cause a bathochromic shift of about 30nm for the π-π^* absorption band (Table 1-1). Similar results are obtained for the furan and pyrrole oligomers systems (Table 1-1).

Table 1-1

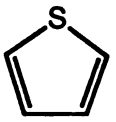
Structures	UV-Vis(nm)	Structures	UV-Vis(nm)
 (28)	356	 (21b)	388
 (29)	351	 (21c)	380
 (27)	360	 (21a)	391

If we compare these results with the p-phenyl analogs[40], the long wavelength absorption band means that the conjugated polymers containing thiazolo[4,5-d]thiazole will have a lower bandgap.

1.3 Syntheses of Tricyclic Compounds Containing 1,3,4-Thiadiazole

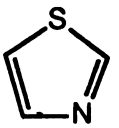
1,3,4-Thiadiazole(**32**) is a heterocyclic compound with 6 π-electrons. It is structurally similar to the thiophene and thiazole except that it contains two nitrogen atoms. The structural similarity of thiophene, thiazole and 1,3,4-thiadiazole are shown in Figure 1-5.

Figure 1-5



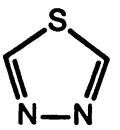
30

Thiophene



31

Thiazole

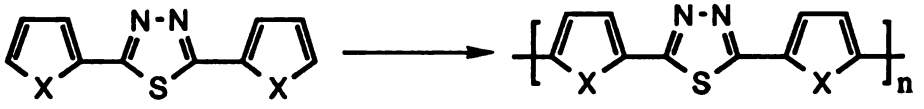


32

1,3,4-thiadiazole

In a study of the influence of heterocyclic compounds on the properties of polythiophene, polypyrrole and polyfuran we thought that the incorporation of 1,3,4-thiadiazole into the thiophene, pyrrole or furan oligomers or polymers may provide some information on the influence of the nitrogen atom on the properties of these systems. For example, if we use the tricyclic compounds 2,5-di(2-thienyl)-1,3,4-thiadiazole, 2,5-di(2-pyrryl)-1,3,4-thiadiazole or 2,5-di(2-furryl)-1,3,4-thiadiazloe as a monomers, chemical or electrochemical polymerization of these monomers will give polymers containing 1,3,4-thiadiazole. Study of these polymers and comparison with the homopolypyrrole, polythiophene or polyfuran will give us an understanding of the influence of 1,3,4-thiadiazole to the properties of polypyrrole, polythiophene or polyfuran.

Scheme 1-12

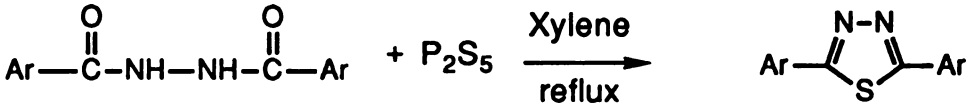


X= NR, S, O, Te, etc

Based on this consideration, a part of my research has been involved in the syntheses and property studies of tricyclic compounds which contains a 1,3,4-thiadiazole.

A common route to the syntheses of 2,5-diaryl-1,3,4-thiadiazoles is the reaction of a precursor hydrazide with P_2S_5 or Lawesson's reagent[41] (Scheme 1-13).

Scheme 1-13

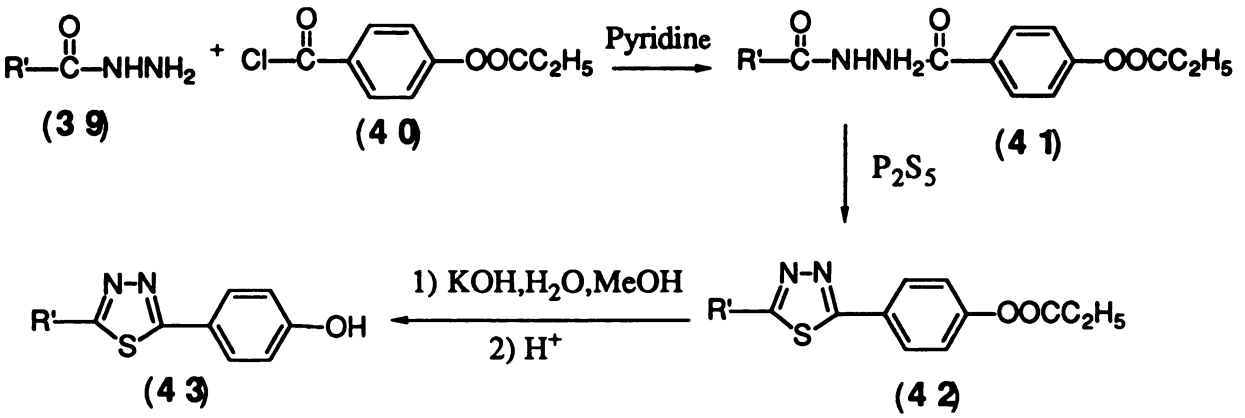


Although this route is classical and has been used to synthesize many 1,3,4-thiadiazole derivatives, the precursor hydrazides are not common reagents and sometimes must be synthesized via several steps. For example, the syntheses of arylhydrazides containing hydroxyl, amino or other functional groups which can react with acyl chlorides generally need protection of the functional groups. Protection and deprotection increase the number of reaction steps. For instance, 2,5-di(4-hydroxylphenyl)-1,3,4-thiadiazole is an important precursor for the syntheses of liquid crystals or biological active compounds. The synthesis of the hydrazide requires the protection of hydroxyl group[42] (Scheme 1-14).

Another example of the difficulty of the syntheses of 2,5-diaryl-1,3,4-thiadiazoles by the route of using hydrazides as the precursors is the syntheses of 2,5-dipyridyl-1,3,4-thiadiazoles. The

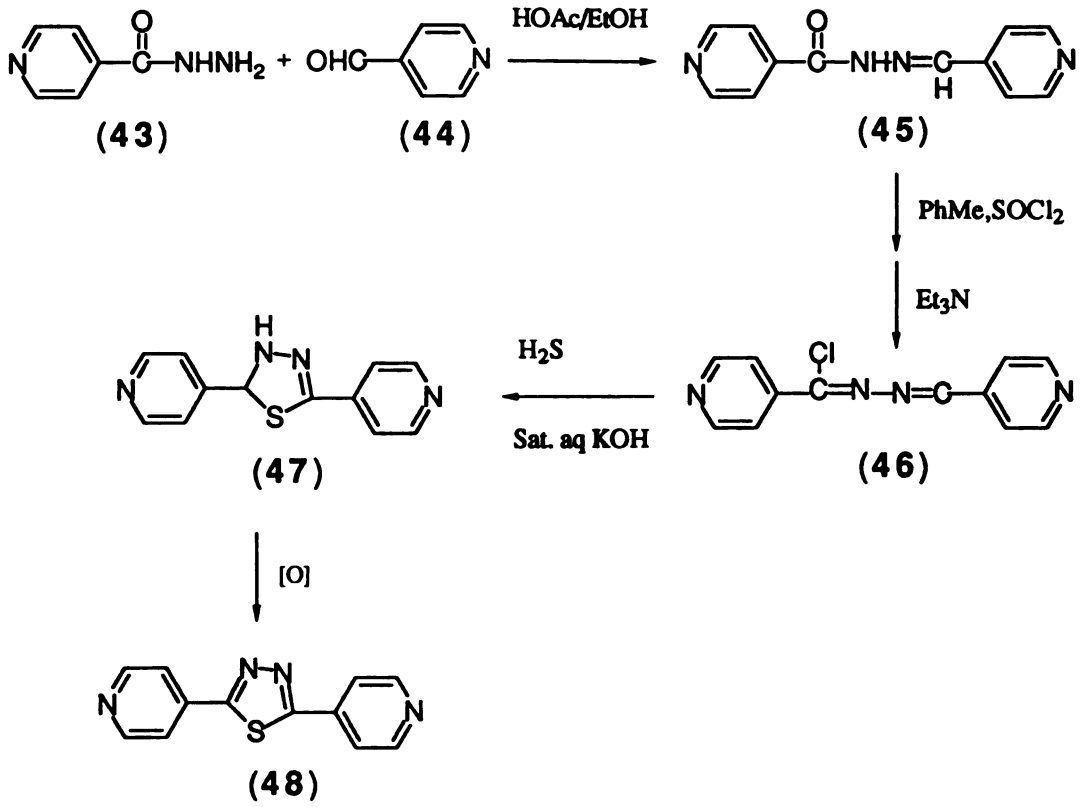
reactivity of pyridine with acyl chlorides make this route impractical. Scheme 1-15 shows a patented route to the synthesis of 2,5-dipyridyl-1,3,4-thiadiazole[43].

Scheme 1-14[42]



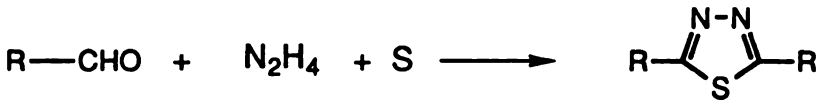
a) R'=$C_{10}H_{21}$; b) OC_9H_{19}

Scheme 1-15[43]



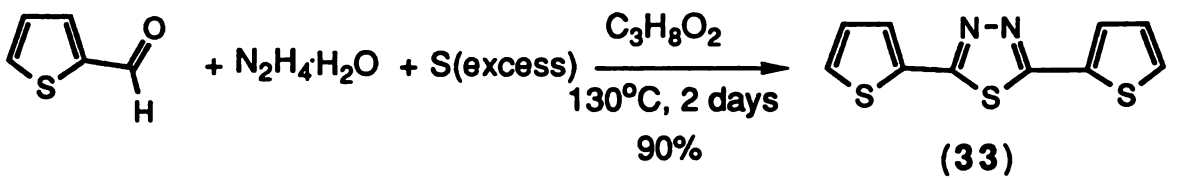
Reaction of an aromatic aldehyde with hydrazine and elemental sulfur is another route for the synthesis of 2,5-diaryl-1,3,4-thiadiazole (Scheme 1-16). As we know, aldehydes, hydrazine and sulfur are all common and inexpensive reagents, and this one-pot procedure make it a promising route to the syntheses of 2,5-diaryl substituted 1,3,4-thiadiazoles. Although it has been claimed that this method has been used for the syntheses of some 2,5-diaryl-1,3,4-thiadiazoles[44], in our hand, the reported procedure[45] is only good for the syntheses of 2,5-dialkyl-1,3,4-thiadiazoles. There is no published procedure to synthesize 2,5-diaryl-1,3,4-thiadiazoles by the reaction of aromatic aldehydes, hydrazine and sulfur.

Scheme 1-16



Use of a similar procedure and reaction condition to the condensation of thiophene 2-carboxylaldehyde, hydrazine monohydrate and two equivalent sulfur at 90 °C for 24 hours failed to give the expected 2,5-di(2-thienyl)-1,3,4-thiadiazole. The major product isolated is the imine compound with a less than 10% yield of the 2,5-di(2-thienyl)-1,3,4-thiadiazole. This unexpected result indicates that the reaction condition might be too mild. Increase of the temperature to 110-130 °C and extension of the reaction time to two days in the presence of a high boiling amine (e.g, tributylamine) and an excess sulfur (four or more equivalents) allow the reaction to go smoothly. For example, reaction of thiophene 2-carboxylaldehyde, hydrazine monohydrate and excess sulfur (6 equivalents) in propylene glycol at 130 °C for 2 days in the presence of tributylamine gave 2,5-di(2-thienyl)-1,3,4-thiadiazole in a 90% yield (Scheme 1-17).

Scheme 1-17

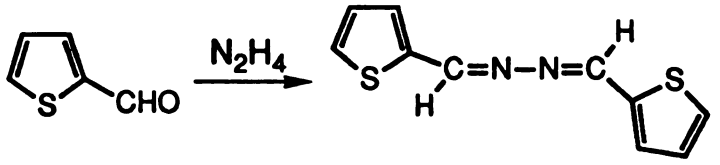


(33)

This procedure provides a convenient synthesis of 2,5-di(2-thienyl)-1,3,4-thiadiazole. Although the details of the reaction mechanisms are not known, one of the possible mechanisms is shown in Scheme 1-18.

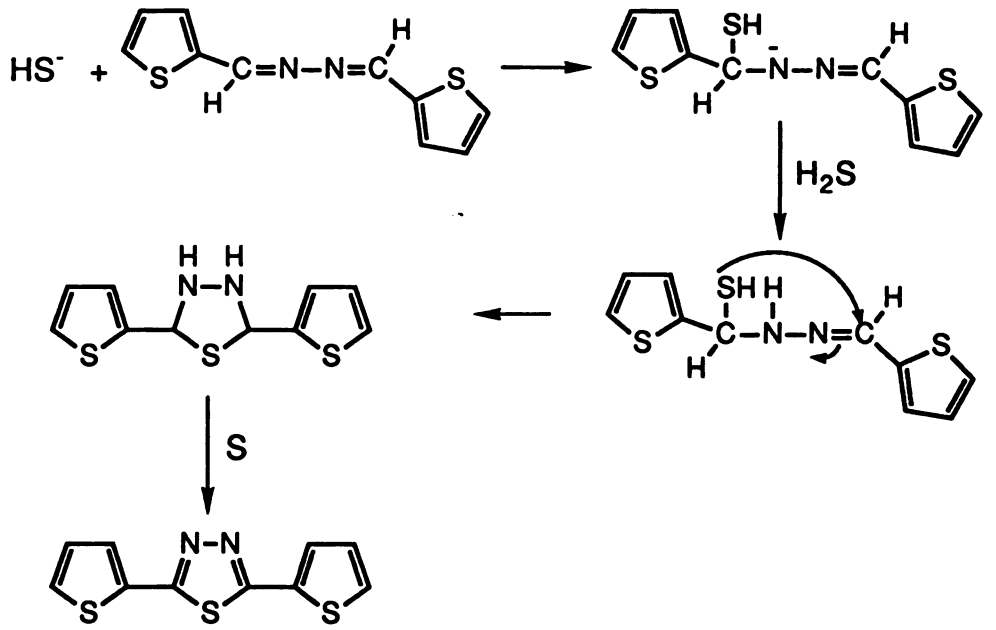
Reaction of the thiophene 2-carboxaldehyde with hydrazine forms the imine product. Reduction of sulfur with hydrazine give to the formation of hydrogen sulfide which then reacts with amine to form hydrogen sulfide anion. Nucleophilic addition of the hydrogen sulfide anion with the imine to form the intermediate imine thiol which then cyclizes to form the tetrahydro-1,3,4-thiadiazole derivative. Oxidation of the tetrahydro-1,3,4-thiadiazole by sulfur lead to the formation of the expected 2,5-di(2-thienyl)-1,3,4-thiadiazole (Scheme 1-18).

Scheme 1-18



$$2S + N_2H_4 \longrightarrow 2H_2S + N_2$$

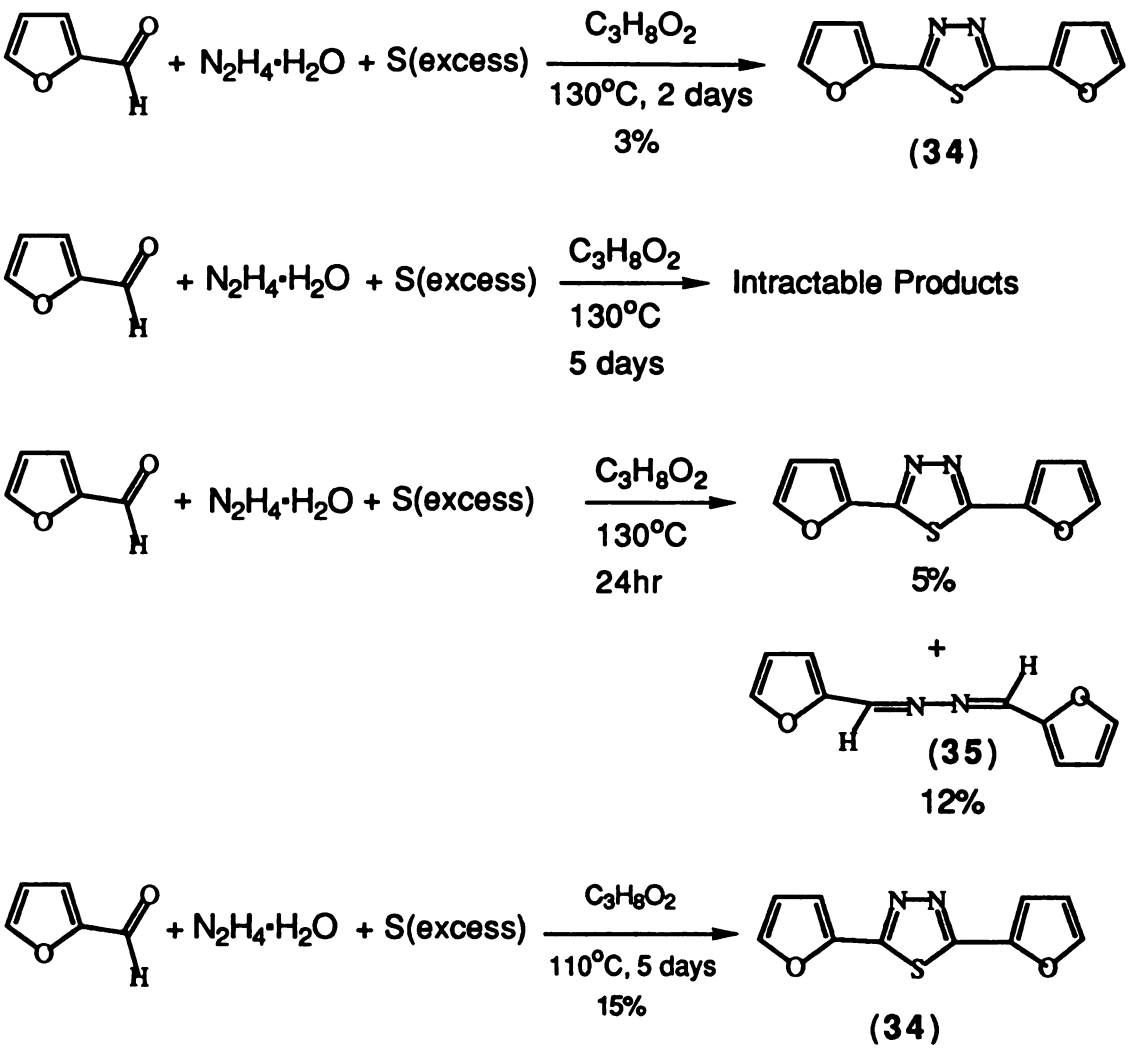
$$H_2S + NBu_3 \longrightarrow HS^- + HN^+Bu_3$$



As an extension of this procedure, the syntheses of 2,5-di(2-pyrryl)-1,3,4-thiadiazole and 2,5-di(2-furryl)-1,3,4-thiadiazoles by the condensation of the correspondent carboxaldehydes with hydrazine monohydrate and elemental sulfur have been attempted.

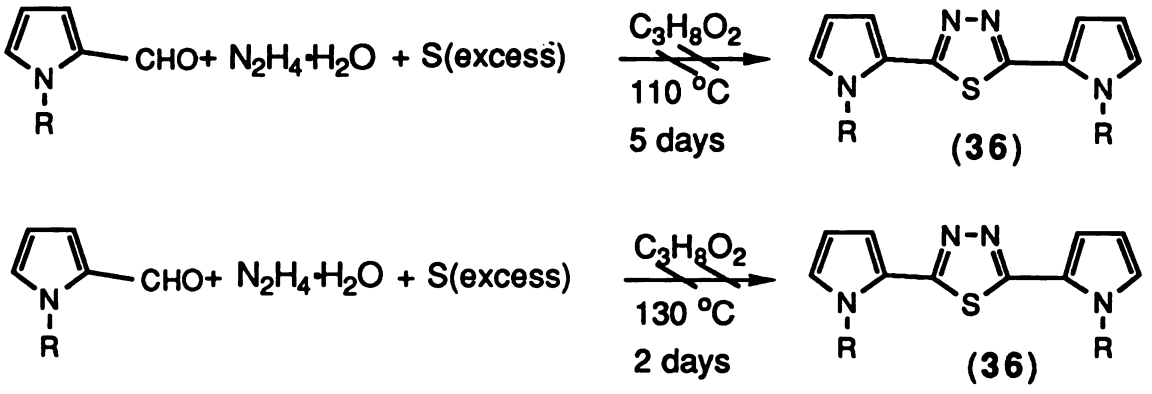
Condensation of 2-furan carboxaldehyde with hydrazine monohydrate and excess elemental sulfur in propylene glycol at 130 °C for two days gave only a very low yield (about 3%) after several trials. Extension of reaction time to five days gave only intractable materials. Shortening the reaction time to one day gave a 5% of product and 12% of the imine intermediate. Decreasing the temperature to 110 °C and lengthening the reaction time to five days gave 15% of the isolated 2,5-di(2-furryl)-1,3,4-thiadiazole (Scheme 1-19). Further attempts to improve the product yield by changing the reaction conditions (e.g. temperature, reaction time and the ratio of reagents) did not succeed.

Scheme 1-19



The condensation of 2-formylpyrrole or 2-formyl-1-methyl-pyrrole with hydrazine monohydrate and elemental sulfur at 130 °C for two days or at 110 °C for five days both failed to give 2,5-di(2-pyrryl)-1,3,4-thiadiazole or 2,5-di(1-methyl-2-pyrryl)-1,3,4-thiadiazole (Scheme 1-20).

Scheme 1-20



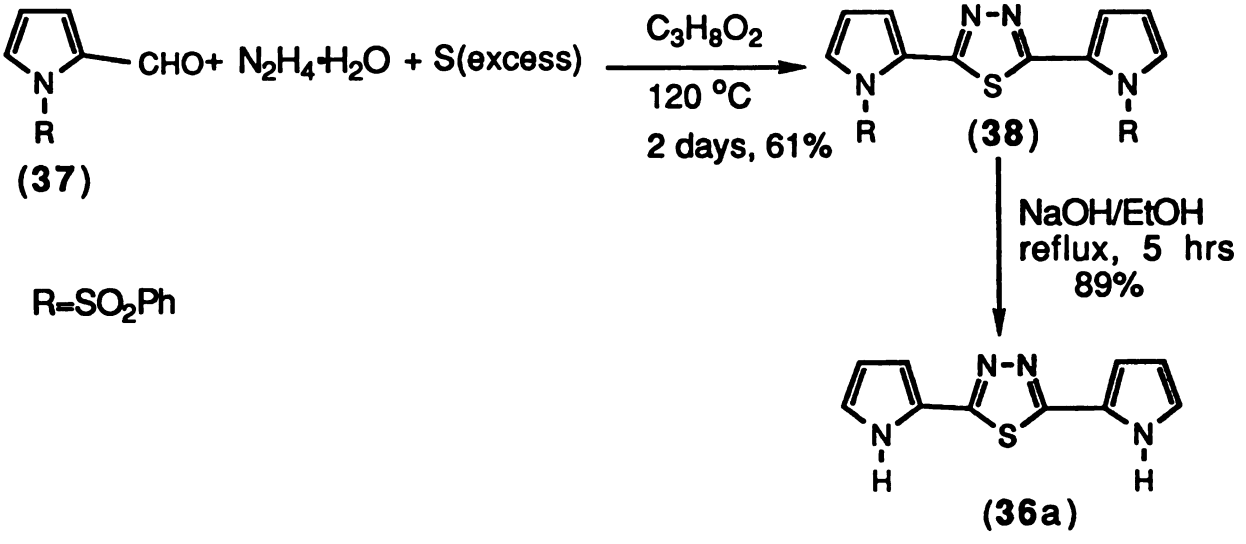
a, R=H; b, R=Methyl

The differences of the condensation reactions of 2-formyl pyrrole and 2-formyl furan from that of the thiophene analog may be attributed either to the electron richer characters of pyrrole and furan rings which reduce the reactivity of the corresponding aldehydes, imines and other relative derivatives to form the expected thiadiazoles or to the instability of pyrrole and furan derivatives which make the side reactions (e.g. oxidation, ring opening etc.) more competitive. In order to overcome the above difficulties and explore the possibility of the above reaction for the synthesis of 2,5-di(2-pyrryl)-1,3,4-thiadiazole protection of the pyrrole 1-nitrogen with an electron withdrawing group has been investigated.

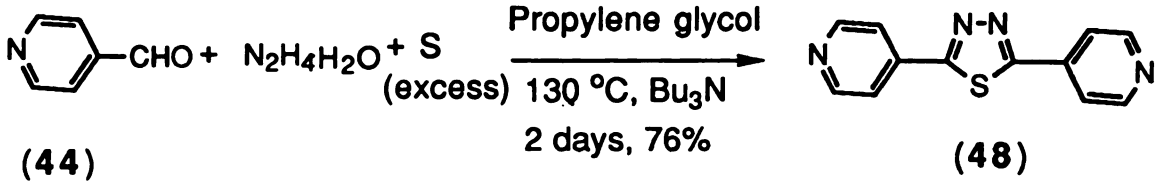
Condensation of 2-formyl-phenylsulfonepyrrole with hydrazine monohydrate and excess sulfur gave the expected product, 2,5-di(1-phenylsulfone-2-pyrryl)-1,3,4-thiadiazole(**38**) in 61% yield. Base hydrolysis of 2,5-di(1-phenylsulfone-2-pyrryl)-1,3,4-thiadiazole(**38**) gave the 2,5-di(2-pyrryl)-1,3,4-thiadiazole in 89% yield (Scheme 1-21).

The generality of this synthesis of 2,5-diaryl-1,3,4-thiadiazoles has also been investigated by the use of different arylaldehydes. For example, reaction of 4-pyridinecarboxaldehyde or 6-methyl-2-pyridinecarboxaldehyde with hydrazine monohydrate and elemental sulfur gave good yield of the correspondent 2,5-di(4-pyridyl)-1,3,4-thiadiazole and 2,5-di(6-methyl-2-pyridyl)-1,3,4-thiadiazole (Scheme 1-22).

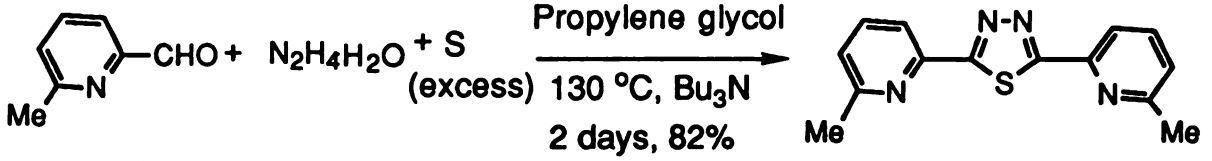
Scheme 1-21



Scheme 1-22



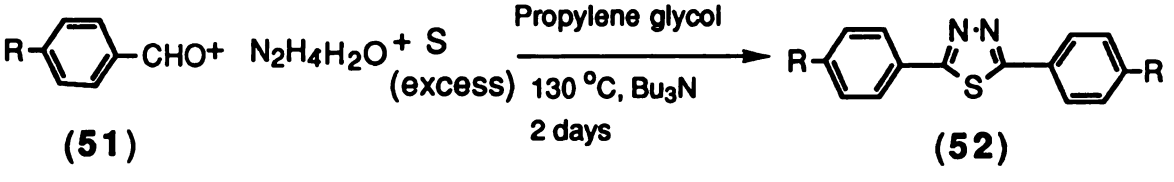
(44) (48)



(49) (50)

Some other 2,5-diaryl-1,3,4-thiadiazoles have also been synthesized by the condensation of the correspondent aryl aldehydes with hydrazine monohydrate and elemental sulfur. Scheme 1-23 shows some of the results.

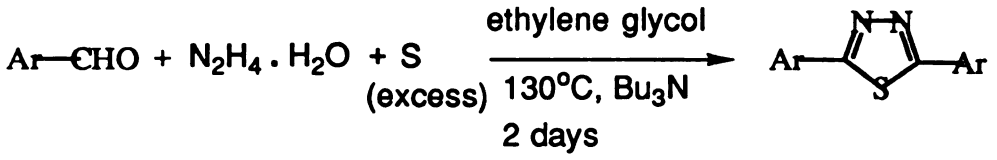
Scheme 1-23

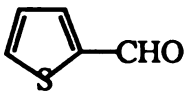
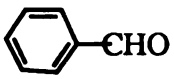
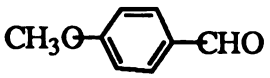


(51) (52)

Aldehydes	Yield (isolated thiadiazoles %)
a, R = H	83%
b, R = OCH_3	84%
c, R = OH	79%

Scheme 1-24



Aldehydes	Yield of Thiadiazoles
	71%
	66%
	60%

The solvent effect has also been investigated briefly. Generally, an alcoholic solvent is necessary. The low boiling point alcohols, e.g. methanol, ethanol or propanol are not very good solvents because the cyclization reaction requires high temperature. The use of high boiling solvent, e.g. DMF, DMSO, *etc.* gave a very low yield of product (10-20%). Change of solvent from propylene glycol to ethylene glycol results in a slightly lower yield of products. Scheme 1-24 shows some of the results. The low yield of product in ethylene glycol may be attributed to the lower solubility of the starting aldehydes, the

intermediate imines and the products in ethylene glycol than those in propylene glycol.

The above results indicate that the condensation of arylaldehydes with hydrazine monohydrate and elemental sulfur is a general, efficient and most convenient route to the syntheses of 2,5-diaryl-1,3,4-thiadiazoles. The value of this reaction has been shown by the high yield of the syntheses of 2,5-dipyridyl-1,3,4-thiadiazoles, which can not been synthesized by the classical route or need several steps by a patented route. Propylene glycol is a good solvent for this reaction.

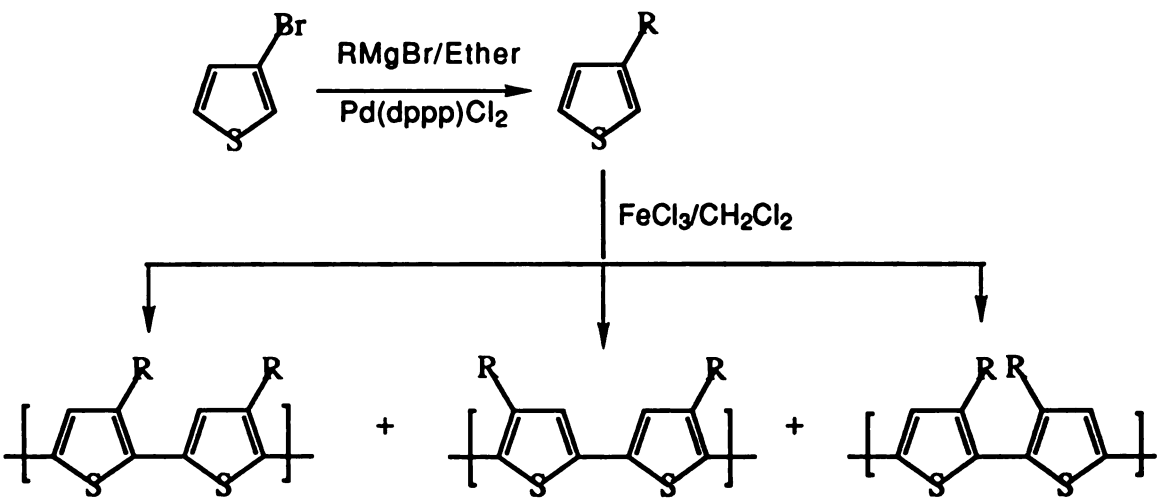
1.4 Synthesis of 3,4-Dialkyl-2,5-di(2-thienyl) Thiophenes, Pyrroles and Furans

Although polythiophene, polypyrrole and polyfuran are good organic conductors, their β-unsubstituted polymers show low solubility in common organic solvents. The low solubility of β-unsubstituted thiophene, pyrrole and furan results in the low processibility so as to limit their applications.

In order to improve the solubility and processibility of polythiophene, polypyrrole and polyfuran, generally, C_4-C_{18} alkyl substitution in the 3- and/or 4- positions of the thiophene[46-48], pyrrole[49] or furan[50] rings has been used as monomers. Poly-3-alkylthiophenes are the most common soluble and processible conductive polymers. Although poly-3-alkylthiophene can improve

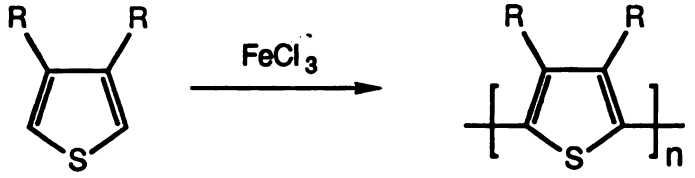
the solubility and processibility to some extent the polymerization of 3-alkylthiophene may occur in head to head, head to tail or tail to tail manners. The resulting poly-3-alkylthiophenes are complicated mixtures (Scheme 1-25). The lack of regularity of the alkyl substituents in poly-3-alkylthiophene make it difficult to study the structural influences on the properties of correspondent conducting polymers.

Scheme 1-25[47]



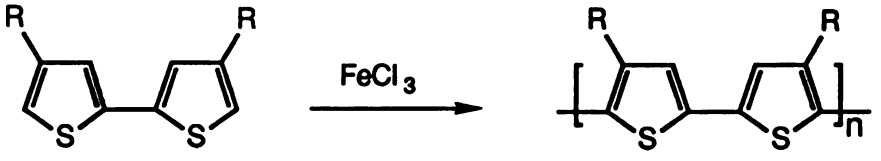
In order to solve the regularity and solubility problems of polythiophene, several other monomers have been used. For example, the use of 3,4-dialkylthiophene as monomer can lead to the formation of a regular polythiophene (Scheme 1-26). However, the steric effects of the bulky alkyl groups reduce the conjugation of the polymers so as to reduce the conductivity[51].

Scheme 1-26[51]



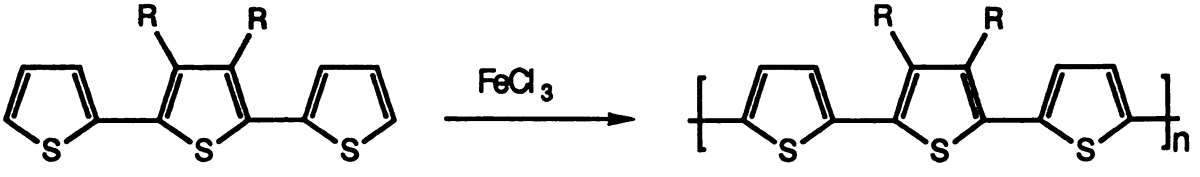
The use of 3,3'-dialkyl-2,2'-bithienyl as a monomer can also lead to the formation of regular polythiophenes. However, synthesis of the monomer generally require several steps[52] (Scheme 1-27).

Scheme 1-27[52]



Another method of solving the solubility and regularity problems is the use of 3,4-dialkyl-2,5-di(2-thienyl) thiophene as monomer which has been synthesized by Dr. Michael Benz in our laboratory[53,54].

Scheme 1-28[54]

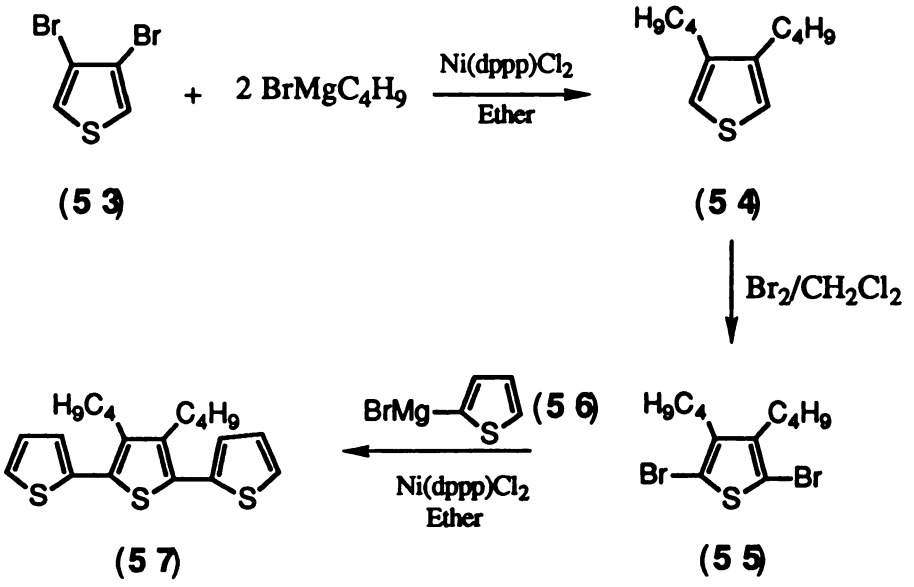


Because 3,4-dialkyl-2,5-di(2-thienyl) thiophene, pyrrole and furan are good monomers for the syntheses of soluble and regular conducting polymers and can be also used as precursors for the construction of some new polythiophene macrocyclic compounds a reliable and practical route to the syntheses of these compounds has to be developed. A part of my research has been involved in this and the results are presented in the following sections.

1.4.1 Synthesis of 3,4-Dialkyl-2,5-di(2-thienyl) thiophene by Grignard Coupling Reaction

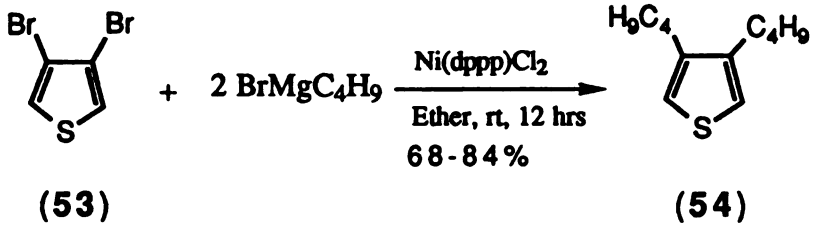
One of the obvious route to the synthesis of 3,4-dialkyl-2,5-di(2-thienyl)thiophene is the use of a Grignard's coupling reaction as a key step. This route has been described by Michael Benz[53] as a good route to the synthesis of 3,4-dibutyl-2,5-di(2-thienyl)thiophene (Scheme 1-29).

Scheme 1-29[53]



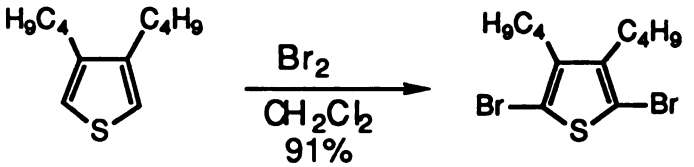
Grignard coupling of 3,4-dibromothiophene with n-butyl magnesium bromide in anhydrous ether at room temperature with the catalysis of [1,3-di(diphenylphosphino)propane]Ni(II) chloride ($Ni(dppp)Cl_2$) gave good yield of 3,4-dibutylthiophene (Scheme 1-30). This result is consistent with the reported result[53].

Scheme 1-30



Bromination of 3,4-dibutylthiophene with bromine in CH_2Cl_2 gave a good yield of 2,5-dibromo-3,4-dibutyl-thiophene (Scheme 1-31).

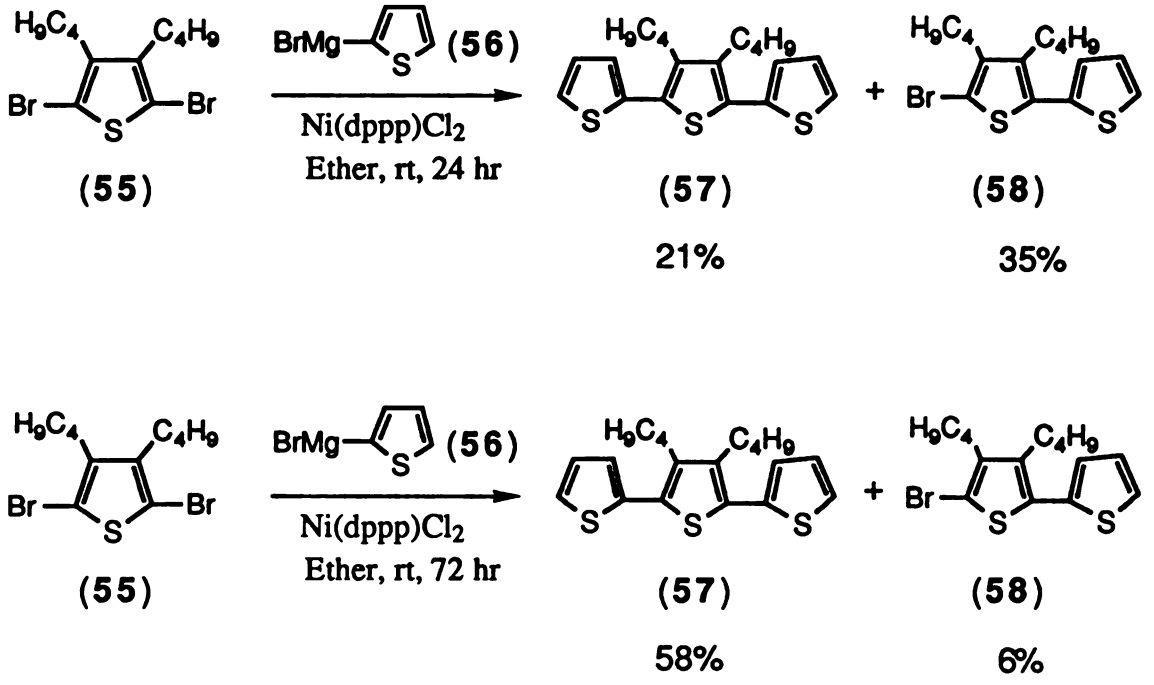
Scheme 1-31



(54) (55)

Grignard coupling of 2,5-dibromo-3,4-dibutyl-thiophene with 2-thienyl magnesium bromide by the catalysis of $Ni(dppp)Cl_2$ in ether at room temperature for 24 hours gave a 21% yield of 3,4-dibutyl-2,5-di(2-thienyl)thiophene(57) and 35% of the monocoupling product 2-bromo-3,4-dibutyl-5-(2-thienyl)thiophene(58). Lengthen the reaction time to 72 hours to give 58% yield of 3,4-dibutyl-2,5-di(2-thienyl)thiophene and 6% of 2-bromo-3,4-dibutyl-5-(2-thienyl)thiophene (Scheme 1-32). It is difficult to eliminate the formation of 2-bromo-3,4-dibutyl-5-(2-thienyl)thiophene. This result shows some difference from that reported by M. Benz[53].

Scheme 1-32



The formation of the monocoupling product 2-bromo-3,4-dibutyl-5-(2-thienyl)thiophene(58) indicates that the coupling of 2,5-dibromo-3,4-dibutyl-thiophene with 2-thienyl magnesium bromide is a step-wise reaction and the second-step of the coupling reaction is a slow reaction.

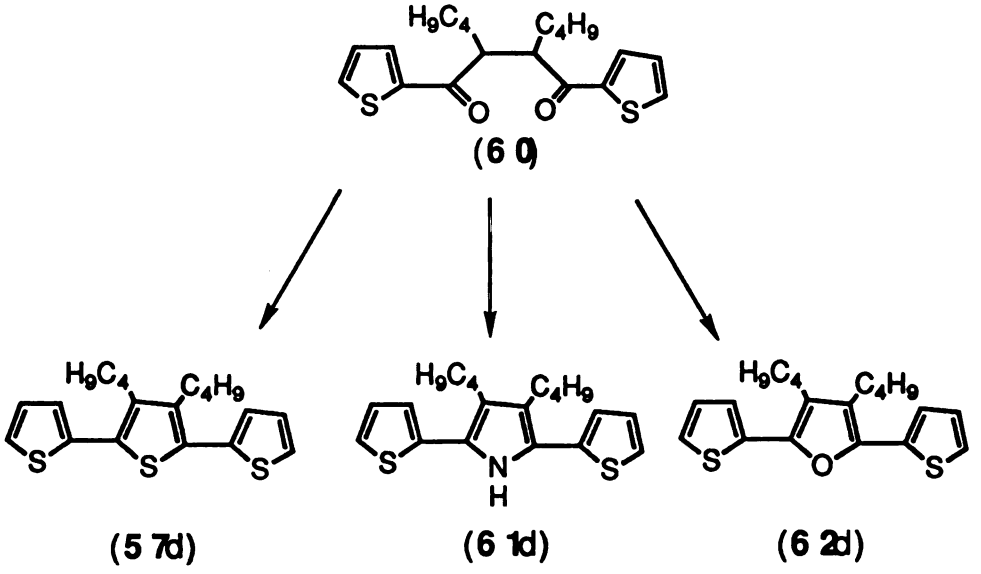
1.4.2 Synthesis of 3,4-Dialkyl-2,5-di(2-thienyl)thiophenes, Pyrroles and Furans by the 1,4-Diketone Route

1,4-Diketones are versatile intermediates for the syntheses of thiophenes, pyrroles, furans and many other heterocyclic compounds. Although many synthetic routes have been reported for the syntheses of 1,4-diketones[46-50], one of the most promising routes is the oxidative coupling of ketones. Oxidative coupling of ketone enolates with Cu^{2+} and other transition metal ions[51,52] has been reported and has become one of the most useful methods. However, the syntheses of 1,4-diketones from ketones by oxidative coupling of silyl enol ether usually can provide more reliable results and lead to a good yield of 1,4-diketones. So far, Ce^{4+}, Cu^{2+}, $Pb(OAc)_4$ and hypervalent iodide[53-56] have been reported as good oxidants for this purpose. Recently, a new procedure for the syntheses of 1,4-diketones by the treatment of silyl enol ether with $VO(OEt)Cl_2$ in dichloromethane has also been reported[57]. In Sections 1.4.2.1-3 the syntheses of 3,4-dialkyl-1,4-(2-thienyl)-1,4-butanediones will be presented and the results will be discussed.

1.4.2.1 Synthesis of 3,4-Dibutyl-1,4-(2-Thienyl)-1,4-Butanedione by the Oxidative Coupling of Dimethylsilyl bis-enol ether

The importance of 3,4-dibutyl-2,5-di(2-thienyl)thiophene, pyrrole and furan as precursors for the syntheses of conductive polymers and macrocyclic compounds has encouraged us to search for a general and practical route to synthesize these compounds. Because of the easy transformation of 1,4-diketone to thiophene, pyrrole and furan, synthesis of 3,4-dibutyl-1,4-(2-thienyl)-1,4-butanedione is the key step (Scheme 1-33).

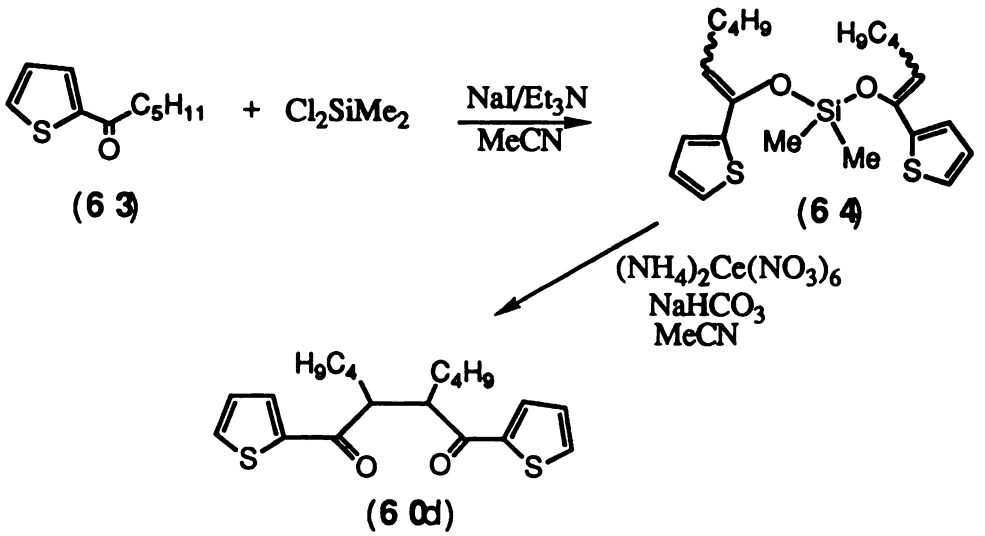
Scheme 1-33



The first synthesis of 2,3-dibutyl-1,4-di(2-thienyl) butanedione was reported by Wiepart[58] in 1990. The author used

the oxidative coupling of the dimethylsilyl bis-enol ether with ceric ammonium nitrate(CAN) (Scheme 1-34). The reported yield is 48% and the reaction was run in small scale.

Scheme 1-34

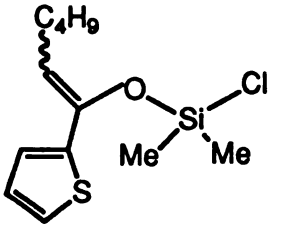


This method had been used by Dr. Michael Benz[59] to synthesize 3,4-dibutyl-2,5-di(2-thienyl)thiophene, pyrrole and furan. In order to make full use of this reaction to synthesize a large quantity of 2,3-dibutyl-1,4-di(2-thienyl) butanedione some questions still must be answered. First, how general is this coupling reaction? Second, can the yield be improved and the reaction be run on a large scale (e.g. 100 grams or more)? In order to answer the above questions, one of my efforts was on the study of the influences of reaction conditions on the coupling of dimethylsilyl bis-enol ether with ceric ammonium nitrate(CAN).

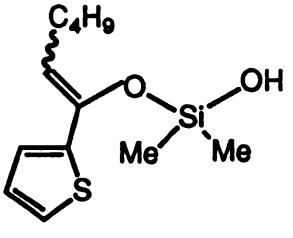
After several trials, it was found that the oxidative coupling reaction is highly depended on the quality of the starting dimethylsilyl bis-enol ether. Then, research was concentrated on the preparation of good quality dimethylsilyl bis-enol ether. Unfortunately, the use of excess of dimethylsilyl chloride or the change of reaction conditions, e.g. change the reagent addition procedure or run the reaction at different temperature (-20, 0, and 40 °C) did not give any better results.

It was latter found that the crude dimethylsilyl bis-enol ether was still contaminated with some dimethyl chlorosilyl mono-enol ether(**65**) . The dimethyl chlorosilyl mono-enol ether(**65**) hydrolyzes during the work-up to form the silicone hydroxyl compound(**66**) (Figure 1-6). The hydroxyl group in the hydrolyzed product(**66**) might affect the oxidative coupling reaction of dimethylsilyl bis-enol ether to form the 1,4-diketones. And indeed, the use of purified dimethylsilyl bis-enol ether as starting material increased the yield of 1,4-diketons from 48% to 57% in one experiment.

Figure 1-6



(65)



(66)

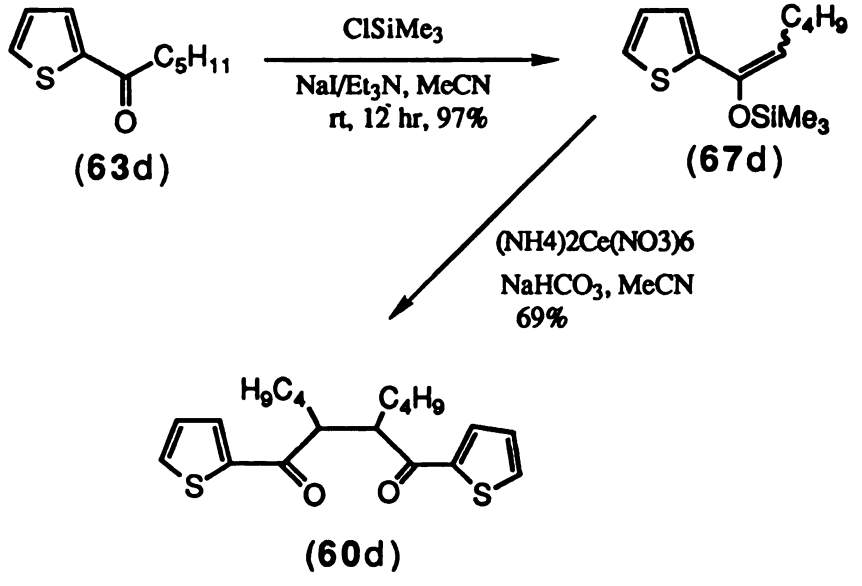
Because of the difficulty of purification of dimethylsilyl bis-enol ether, a further attempt to improve this reaction has not been made and research was turned to use trimethylsilyl enol ether instead of dimethylsilyl bis-enol ether and the results are presented in section 1.4.2.2.

1.4.2.2 Synthesis of 3,4-Dialkyl-1,4-(2-thienyl)-1,4-butanedione by the Oxidative Coupling of Trimethylsilyl Enol Ethers With Ceric Ammonium Nitrate(CAN)

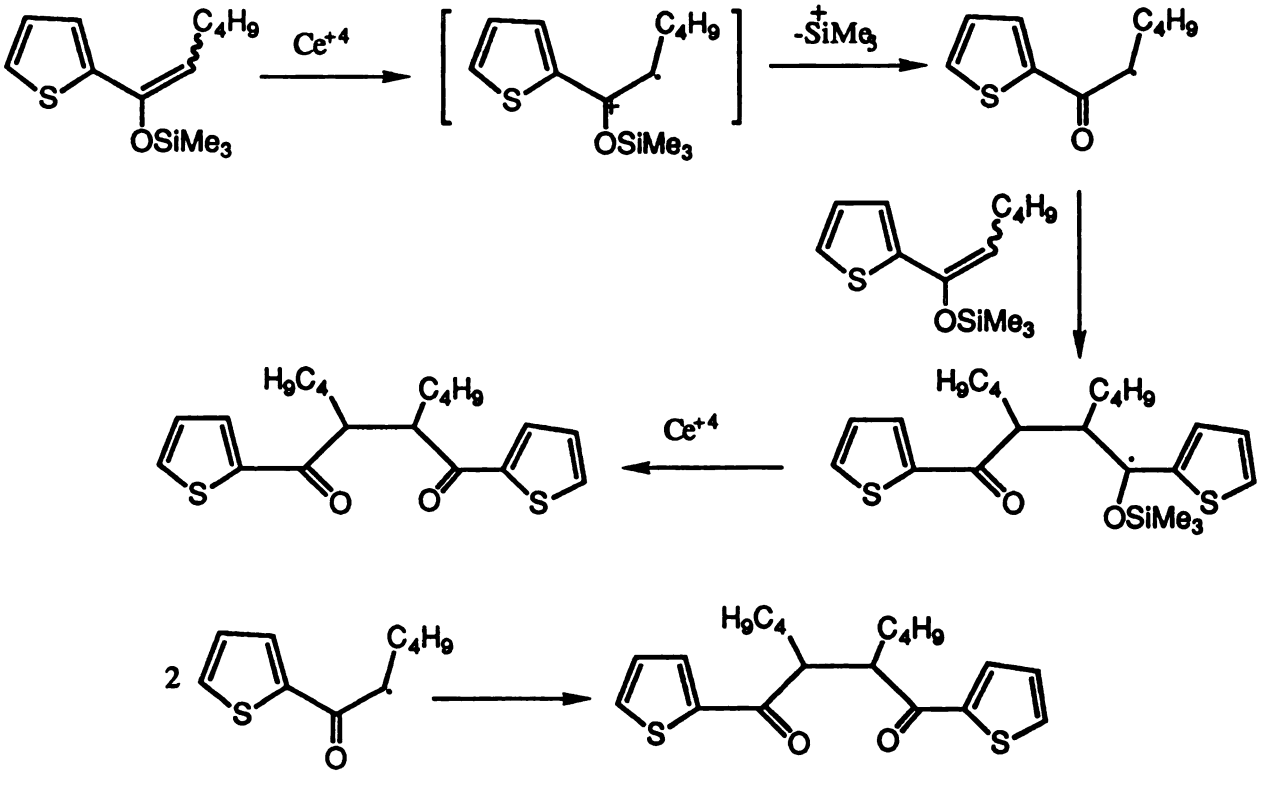
During the search of reaction conditions useful for the preparation of good quality silyl enol ether it was found that a good quality of silyl enol ether can be easily prepared by the reaction of cholorotrimethylsilane with a ketone by using a slight excess of the former reagent. By this route it is easy to prepare a crude silyl enol ether with >95% purity (by NMR data) which can be used as a starting material for oxidative coupling with high isolated yield of the 1,4-diketones (55%-67% based on the starting ketone) (Scheme 1-35).

Scheme 1-36 shows one of the possible reaction mechanisms. Oxidation of silyl enol ether by Ce^{+4} with one electron transferred leads to the formation of a radical cation which then loses a trimethyl silyl cation and forms a carbonyl radical. Then, the carbonyl radical can be self-coupled or reacts with another molecule of silyl enol ether to form another radical which is then oxidized by Ce^{+4} with the lost of $^{+}SiMe_3$ to form the expected 1,4-diketone.

Scheme 1-35



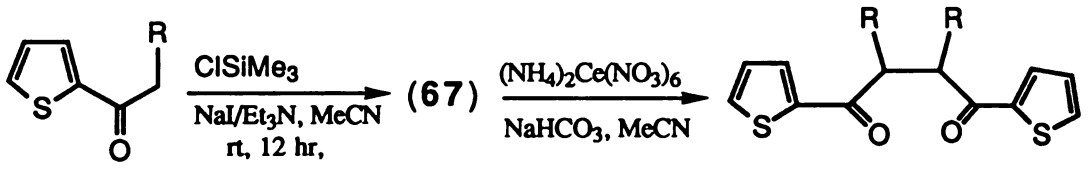
Scheme 1-36



The generality of this synthesis of 1,4-diketones has also been investigated by using different alkyl groups and the results are summarized in Scheme 1-37. All the structures of the 1,4-diketones have been characterized by ^{1}H-NMR, ^{13}C-NMR, mass spectra and IR spectra.

Generally speaking, the reaction is reliable for different alkyl groups and the yield is quite stable. This is consistent with the proposed radical reaction mechanism (Scheme 1-36).

Scheme 1-37



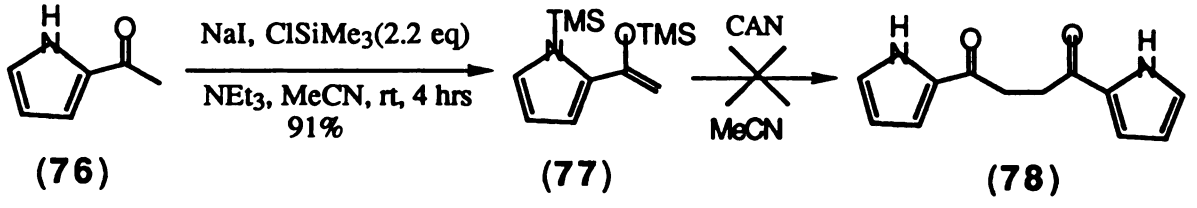
(63) (60)

Starting Ketones	Yield of 1,4-diketones(isolated,%)
R = H	55
R = Me	65
R = Et	60
R = Butyl	67
R = Hexyl	63

In general, the use of trimethylsilyl enol ether instead of dimethylsilyl bis-enol ether usually can give a better yield of 1,4-diketones. This provides a general and practical route to the synthesis of 1,4-di(2-thienyl)-2,3-dialkyl-1,4-butanediones.

As an extension of this reaction, an attempt at the synthesis of 1,4-di(2-pyrryl)-1,4,-butanedione has been conducted. Reaction of 2-acetyl pyrrole with 2.2 equivalents of chlorotrimethylsilane in the presence of NaI(2.2 eq.) and Et_3N (2.2 eq) gave 2-(1-trimethylsilyl pyrryl)-trimethylsilyl ethenol ether(77) in 91% yield. Oxidation with ceric ammonium nitrate(CAN) gave an intractable product. No 1,4-di(2-pyrryl)-1,4,-butanedione(78) was isolated (Scheme 1-38).

Scheme 1-38



(76) (77) (78)

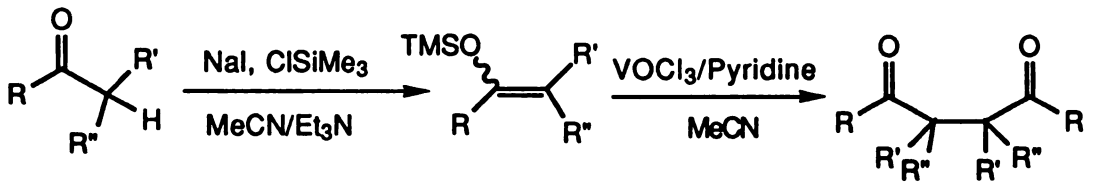
Failure of oxidative coupling of 2-(1-trimethylsilyl pyrryl)-trimethylsilyl ethenol ether to form the 1,4-di(2-pyrryl)-1,4-butanedione by the use of CAN as oxidant might be attributed either to the acidity of proton of the ammonium ion in the reagent or the instability of the starting silyl enol ether, the intermediates or the product in the oxidative condition. Because of this unexpected result, some of my efforts have been involved in the use of different

oxidants as coupling reagents and the results are presented in section 1.4.2.3.

1.4.2.3 Synthesis of 3,4-Dialkyl-1,4-(2-thienyl)-1,4-butanedione by the Oxidative Coupling of Trimethylsilyl Enol Ethers with $VOCl_3$/Pyridine

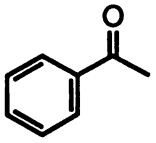
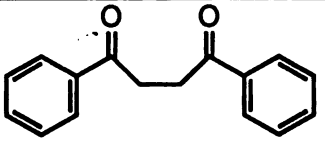
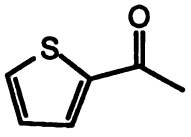
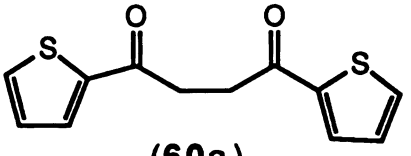
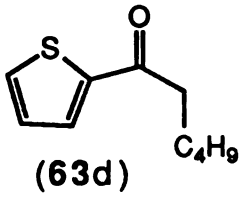
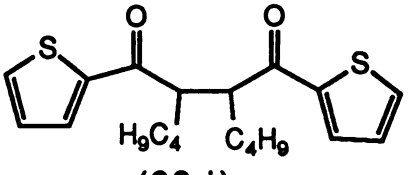
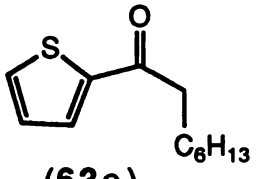
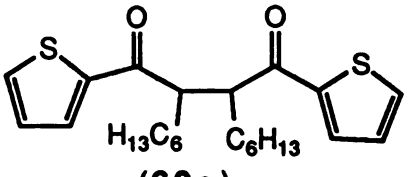
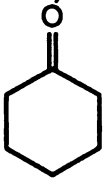
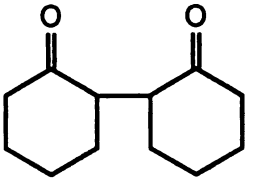
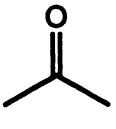
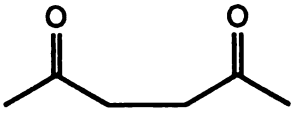
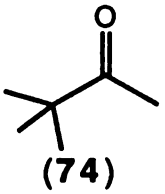
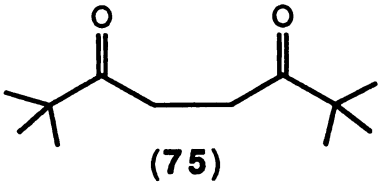
In the previous section, a convenient synthesis of 2,3-dialkyl-1,4-di(2-thienyl)-1,4-butanediones by the oxidative coupling of the silyl enol ethers with ceric ammonium nitrate(CAN) was described. In the search for new oxidative reagents for the syntheses of 1,4-diketones from ketones we found that $VOCl_3$/pyridine can also bring about the oxidative coupling reaction of silyl enol ethers to form the expected 1,4-diketones.

Scheme 1-39



Some of the results are listed in table 1-2.

Table 1-2

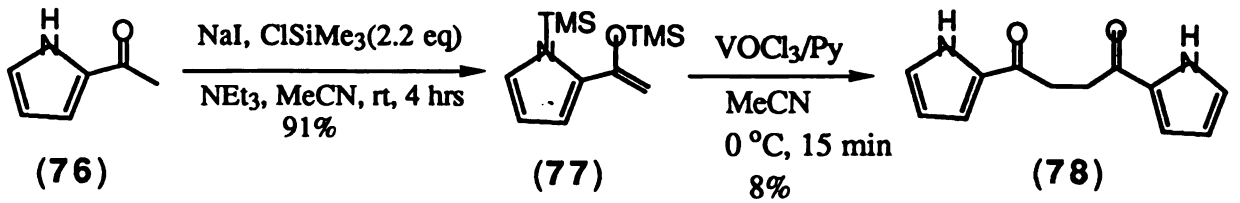
Starting Ketones	1,4-Diketones	Yield(Overall, %)
 (68)	 (69)	49
 (63a)	 (60a)	50
 (63d)	 (60d)	55
 (63e)	 (60e)	54
 (70)	 (71)	51
 (72)	 (73)	67
 (74)	 (75)	61

The reaction mechanism is thought to be similar to that obtained by using CAN as oxidant. The use of pyridine as a base makes the reaction in a milder condition so as to increase the yield of products. Acetonitrile is a good solvent for this reaction. The use of other solvents e.g. THF and CH_2Cl_2 leads to a lower yield.

By this procedure, the synthesis of 1,4-di(2-pyrryl)-1,4-butanedione by the oxidative coupling of the silyl enol ether has been attempted by using several different conditions. Oxidation of the protected silyl enol ether, 2-(1-trimethylsilyl pyrryl)-trimethylsilyl ethenol ether, with vanadium oxytrichloride and 1.0 eq of pyridine in acetonitrile at 0 °C for 15 minutes gave a low yield of the expected 1,4-diketone (Scheme 1-43). Both lowering the temperature to -40 °C and extending the reaction time to one hour both did not lead to a higher yield of product. Nor did the use of $VO(OEt)Cl_2$ as an oxidation reagent in dichloromethane improve the yield of 1,4-diketone.

The lower yield of 1,4-di(2-pyrryl)-1,4-butanedione from the oxidative coupling reaction of 2-(1-trimethylsilyl pyrryl)-trimethylsilyl ethenol ether with $VOCl_3$, or $VO(OEt)Cl_2$ reagents might be attributed to the instability of the starting material, the intermediates and the product. The shorter reaction time assures the survival of some of the product, which lead to the isolation of a low yield of 1,4-di(2-pyrryl)-1,4-butanedione.

Scheme 1-40



(76) (77) (78)

In summary, a new procedure for the synthesis of 1,4-diketones from ketones by the oxidative coupling of the silyl enol ether with $VOCl_3$/pyridine has been developed. By this method an alternative route to the syntheses of 3,4-dialkyl-2,5-di(2-thienyl)thiophenes, pyrroles and furans has also been achieved and the results are presented and discussed in section 1.4.2.4. Generally speaking, the synthesis of 1,4-diketones by the oxidation of silyl enol ethers with CAN is more convenient and suitable for large scale synthesis, but oxidative coupling of silyl enol ethers with $VOCl_3$/pyridine is more convenient for small scale synthesis.

1.4.2.4 Synthesis of 3,4-Dialkyl-2,5-di(2-thienyl)thiophenes, Pyrroles and Furans

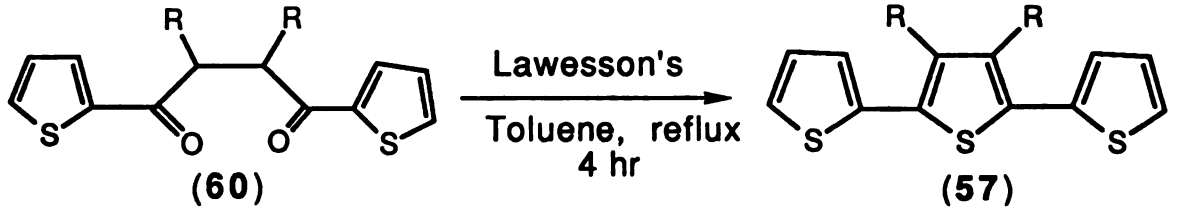
In section 1.4.1 the synthesis of 3,4-dibutyl-2,5-di(2-thienyl)thiophene by the Grignard coupling reaction was discussed and the results are compared with those reported. Generally speaking, the reaction is good only for small scale synthesis

of 3,4-dibutyl-2,5-di(2-thienyl)thiophene. It is difficult to synthesize 3,4-dialkyl-2,5-di(2-thienyl)pyrroles because of the acidity of the proton on pyrrole nitrogen.

Because large quantity of 1,4-di(2-thienyl)-2,3-dialkyl-1,4-butanediones have been synthesized by the oxidative coupling of silyl enol ether with ceric ammonium nitrate or $VOCl_3$/pyridine as described in Sections 1.4.2.2 and 1.4.2.3 it is reasonable to synthesize 3,4-dialkyl-2,5-di(2-thienyl)thiophenes, pyrroles and furans by the use of these 1,4-diketone precursors.

Reaction of 1,4-di(2-thienyl)-2,3-dialkyl-1,4-butanediones with P_2S_5 or Lawesson's reagent gave high yield of 3,4-dialkyl-2,5-di(2-thienyl) thiophene. Some of the results are summarized in Scheme 1-41. The structures of the terthiophenes have been characterized by ^{1}H-NMR, ^{13}C-NMR, mass spectra, UV-Vis and compared with the results from Grignard coupling products.

Scheme 1-41



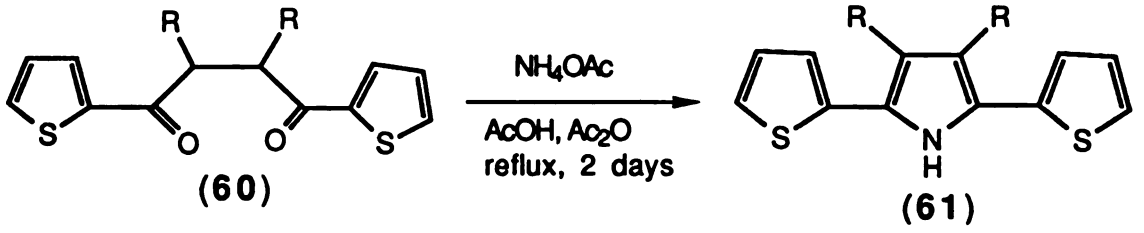
(60) (57)

Starting 1,4-diketones	Isolated Yield of Terthiophenes(%)
a, R=H	82
b, R=Me	84
c, R=Et	88
d, R=Butyl	81
e, R=Hexyl	89

The high yield of thiophene formation plus the easy synthesis of 2,3-dialkyl-1,4-di(2-thienyl)-1,4-butanediones it a practical route to the synthesis of 3,4-dialkyl-2,5-di(2-thienyl) thiophenes. It also makes the synthesis of 3,4-dialkyl-2,5-di(2-thienyl) pyrroles and furans ease.

For instance, reaction of the 2,3-dialkyl-1,4-di(2-thienyl)-1,4-butanediones with NH_4Ac, AcOH, $(Ac)_2O$ gave good yield of 3,4-dialkyl-2,5-di(2-thienyl)pyrroles. Scheme 1-42 shows some of the results. The structures for the formation of the pyrrole derivatives is characterized by ^1H-NMR, ^{13}C-NMR, mass spectra, UV-Vis.

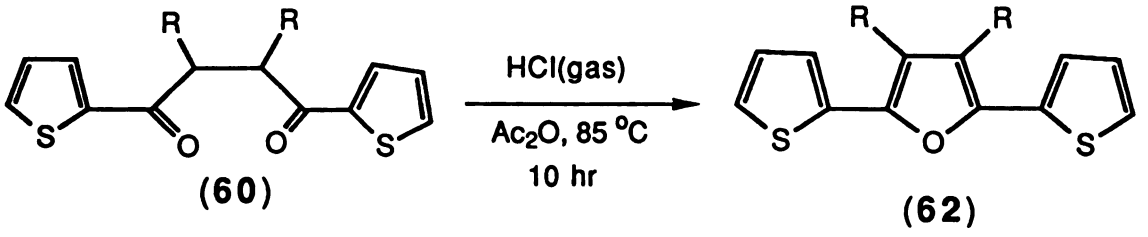
Scheme 1-42



Starting 1,4-Diketones	Isolated Yield of Products(%)
a, R=H	78
b, R=Me	75
c, R=Et	74
d, R=Butyl	80
e, R=Hexyl	81

Reaction of the 2,3-dialkyl-1,4-di(2-thienyl)-1,4-butanediones(**60**) in HCl/Ac_2O at 80 °C for 15 hours gave good to moderate yield of 3,4-dialkyl-2,5-di(2-thienyl)furans. Some of the results are summaried in Scheme 1-41. The structures of the furan derivatives is characterized by ^{1}H-NMR, ^{13}C-NMR, mass spectra, UV-Vis *etc.*.

Scheme 1-43



(60) (62)

Starting 1,4-Diketones	Yield of Products(%)
a, R = H	71
b, R = Me	65
c, R = Et	64
d, R = Butyl	69
e, R = Hexyl	61

In summary, the oxidative coupling of trimethylsilyl enol ethers with ceric ammonium nitrate(CAN) is a general and practical route for the synthesis of 2,3-dialkyl-1,4-di(2-thienyl)-1,4-butanediones. By this method the syntheses of several 3,4-dialkyl-2,5-di(2-thienyl)thiophenes, pyrroles and furans have been achieved. In addition, the oxidative coupling of trimethylsilyl enol ethers with $VOCl_3$/pyridine reagent provides a convenient route to the syntheses of variety of 1,4-diketones.

Chapter 2

Syntheses and Spectroscopic Studies of Thiophene and Mixed Thiophene Oligomers

Synthesis and property study of conductive oligomers is another interesting research area. The information from the study of conductive oligomers can help us to understand the conductive mechanisms of conjugated organic polymers.

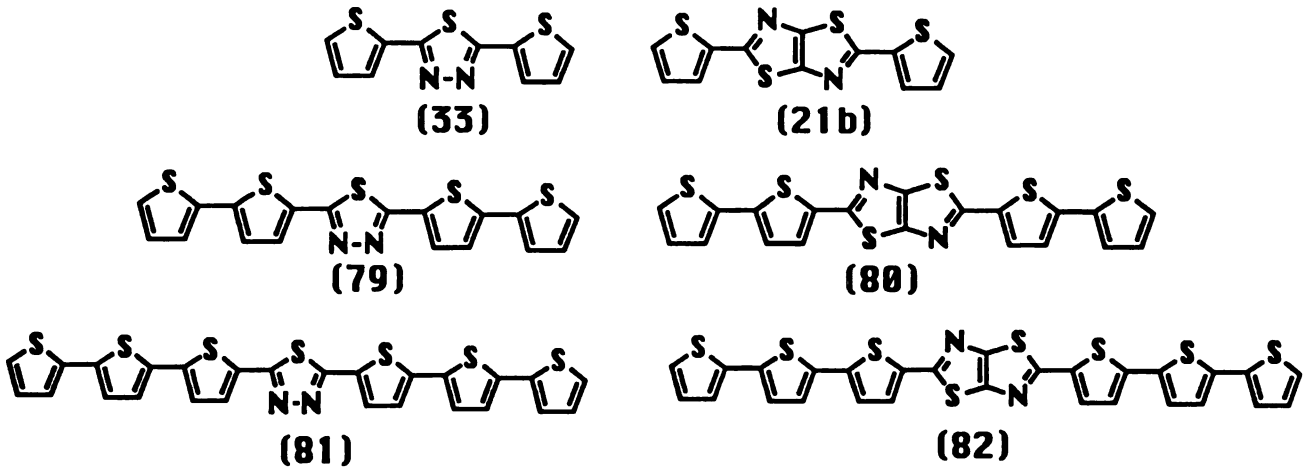
So far, one of the major problems in this research area is the difficulty of synthesizing specific molecular weight of conjugated oligomers or single oligomer. In this chapter, the synthesis and property study of some new conjugated thiophene and mixed thiophene oligomers will be presented.

The study of the influence of thiazolo[5,4-d]thiazole and 1,3,4-thiadiazole on the properties of thiophene oligomers has encouraged us to synthesize mixed thiophene oligomers which contain thiazolo[5,4-d]thiazole and 1,3,4-thiadiazole rings. Several β-unsubstituted mixed thiophene oligomers have been synthesized (Figure 2-1).

During the research, one of the major problems was the low solubility of the oligomers. For example, although unsubstituted pentathiophene still shows some solubility in organic solvent, the analog heptathiophene shows very low solubility in most organic solvents, e.g. $CHCl_3$, CH_2Cl_2, acetone, acetonitrile, *etc*.. The mixed thiophene oligomers show ever lower solubility in common organic

solvents. For instance, although terthiophene is very soluble in most organic solvents the analogs 2,5-di(2-thienyl)thiazolo[5,4-d]thiazole and 2,5-di(2-thienyl)-1,3,4-thadiazole show low solubility in hexanes, CH_2Cl_2, *etc*. The higher oligomers are only slightly soluble in $CHCl_3$, CH_2Cl_2, acetone, acetonitrile, etc. The low solubility of these unsubstituted thiophene oligomers make it difficult to study relationship of structures and properties.

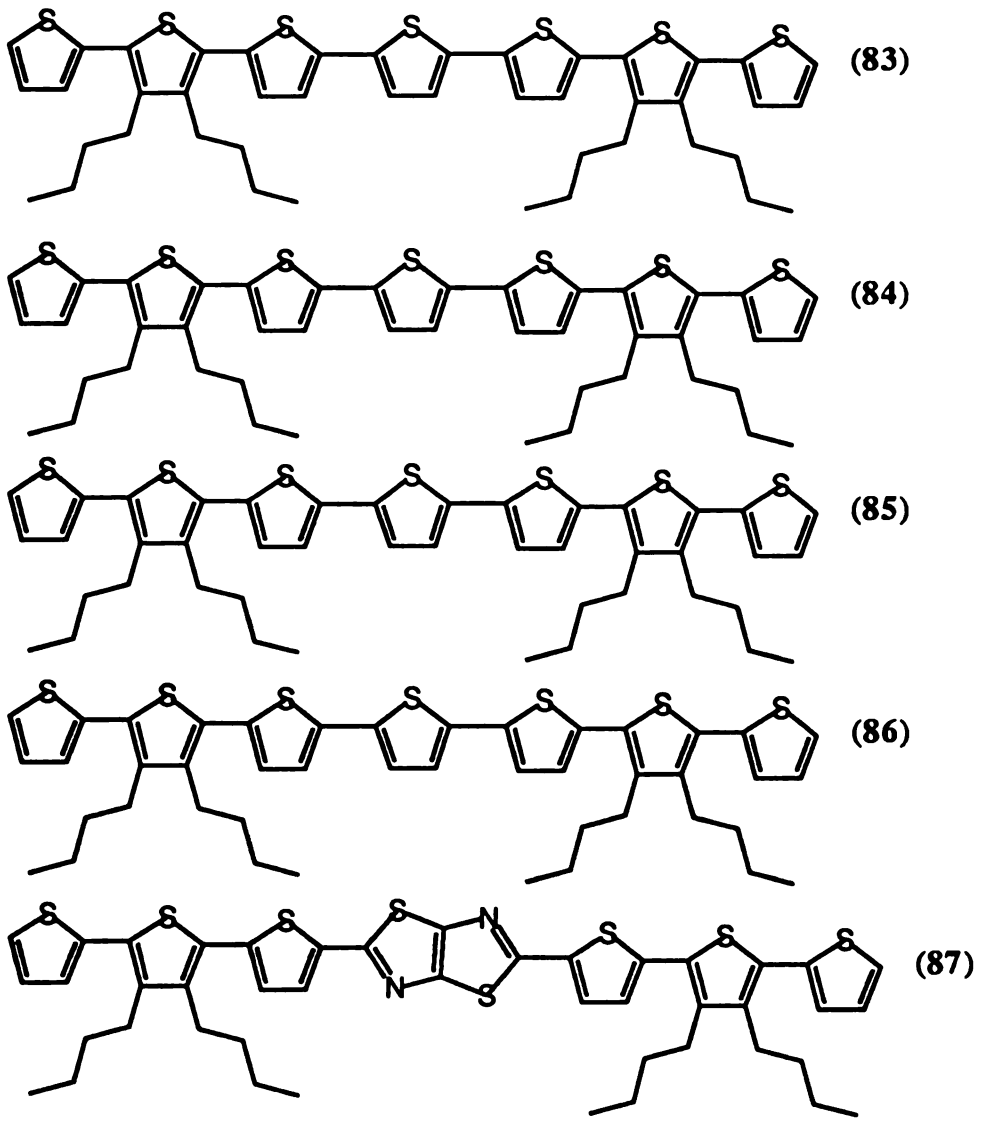
Figure 2-1



In order to improve the solubility of these thiophene oligomers, butyl groups have been introduced in the thiophene β-positions. In Section 1.4 of this thesis an improved and practical route to the synthesis of 3,4-dialkyl-2,5-di(2-thienyl)thiophene, pyrrole and furan has been described. By this route large quantity of 3,4-dibutyl-2,5-di(2-thienyl)thiophene were synthesized. The high solubility and regularity of this thiophene oligomer make it a good precursor for the syntheses of higher thiophene oligomers.

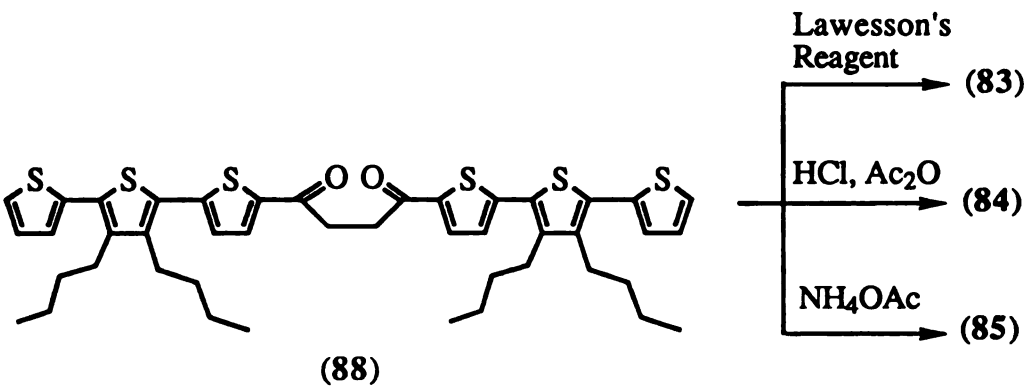
Although there are many reports on the study of thiophene oligomers[71-74] research on the influence of heterocyclic systems to the thiophene oligomers is relatively spare[75]. In order to provide more information on the influence of heterocycles to the properties of polythiophene, the following oligomers **83-87** were chosen as candidate model oligomers (Figure 2-2).

Figure 2-2



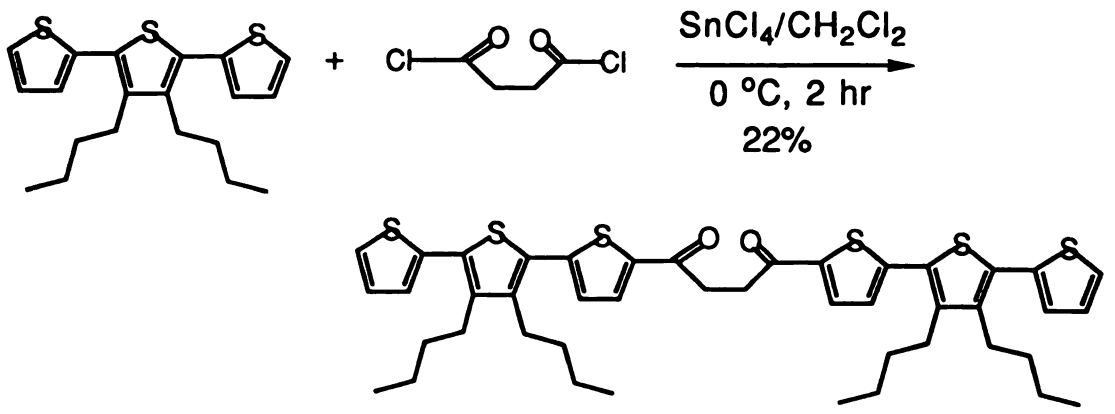
Considering that thiophene, pyrrole and furan can be easily synthesized by the reaction of 1,4-diketone with Lawesson's reagent (or P_2S_5), NH_4OAc, HCl/Ac_2O, one of the key steps in the syntheses of compounds **83-85** is to synthesize the precursor 1,4-diketone **88** (Scheme 2-1).

Scheme 2-1



The synthesis of the 1,4-diketone(**88**) has been achieved by two different methods. One is Friedel-Crafts acylation of the α-terthiophene with succinyl chloride. Reaction of 3',4'-dibutyl-2,2',5',2"-terthiophene with succinyl chloride by using tin(IV) chloride as a catalyst in dichloromethane at 0 °C gave 22% yield of the expected 1,4-diketone **88** (Scheme 2-2).

Scheme 2-2

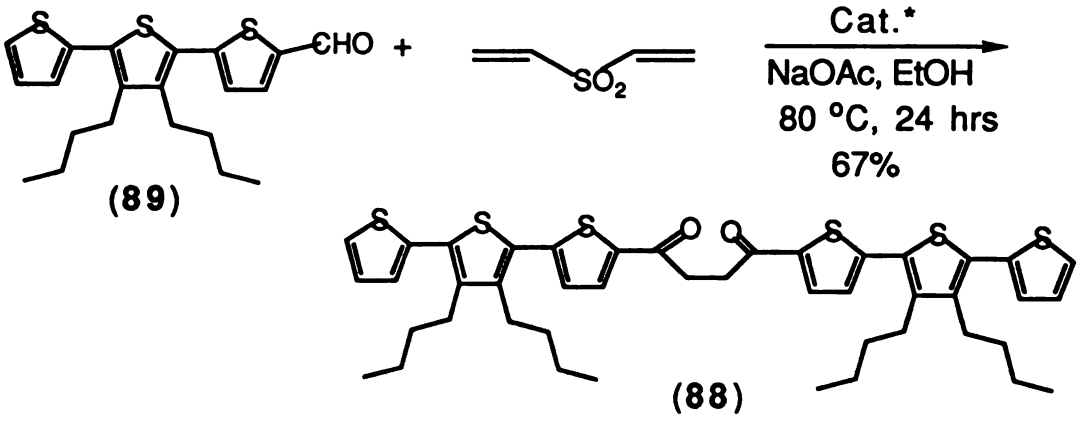


The 1,4-diketone(88) is a stable yellow needle compound with a melting point 178-179 °C. UV-Vis shows a maximum absorption at 390nm. ^{1}H-NMR shows the two b-protons of the thiophene rings which are close to the carbonyl groups with chemical shift at 7.73 and 7.17 ppm respectively and coupling each other. The coupling constant is 4.4Hz. The three protons on the terminal thiophene rings show a typical pattern of an α-substituted thiophene. The chemical shifts are 7.32, 7.14, and 7.05 and the coupling constants 5.3, 4.4 and 1.3Hz respectively. The mass spectrum shows a relatively stable molecular ion with the relatively intensity 55.7. The base line is at m/z=415. The peak with m/z=401 may correspond to the molecular ion with two positive charges. This compound may be used as a model compound for the study of polaron formation by doping and polaron interaction through a non conjugated carbon-carbon chain.

Another route for the synthesis of 1,4-diketones is the use of Stetter's reaction[56]. Reaction of 5-formyl-3',4'-dibutyl-2,2',5',2"-terthiophene with divinyl sulfone catalyzed by 3,4-dimethyl-5-(2-

hydroxyethyl)-thiazolium iodide gave 67% of the 1,4-diketone **88** (Scheme 2-3).

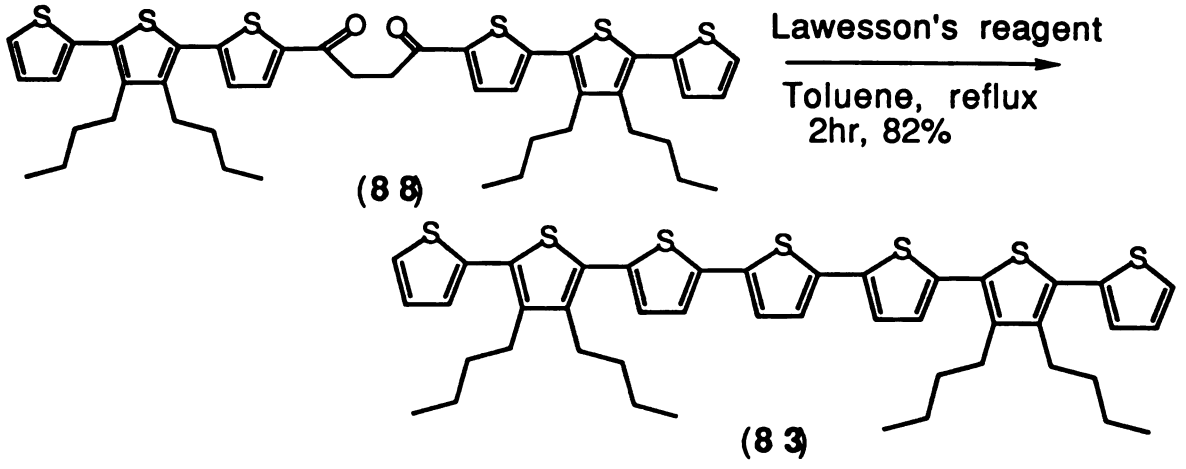
Scheme 2-3



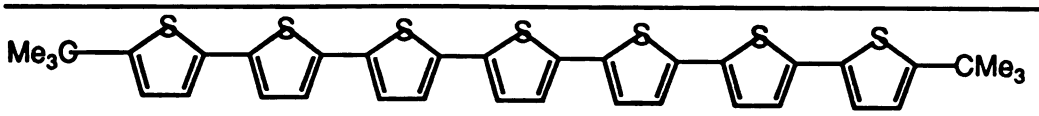
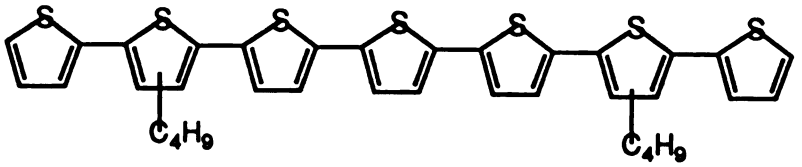
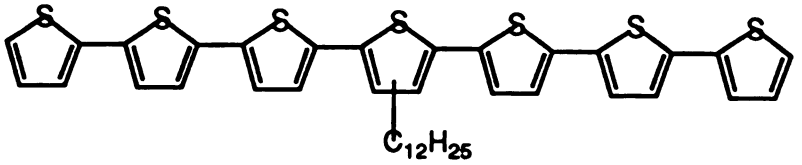
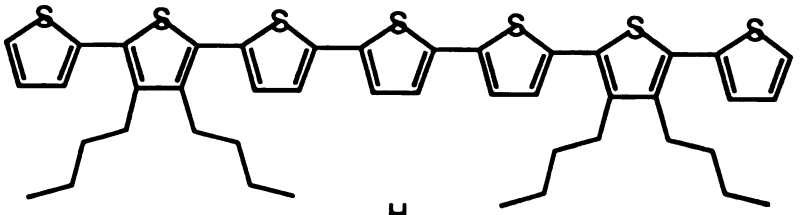
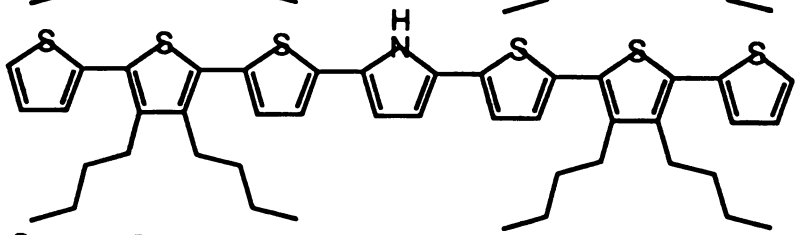
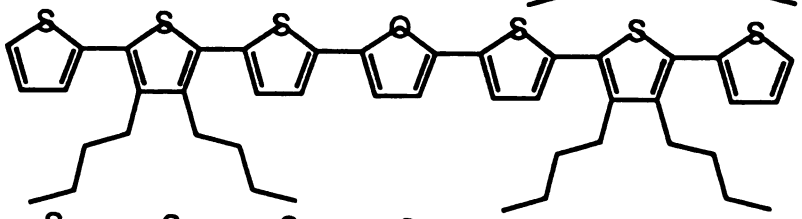
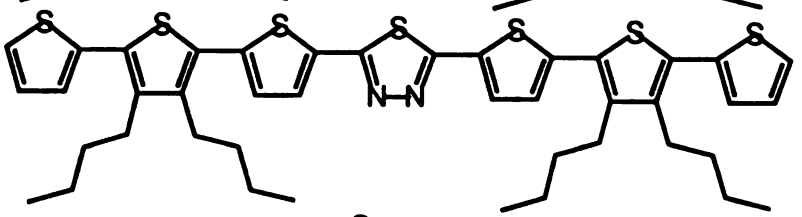
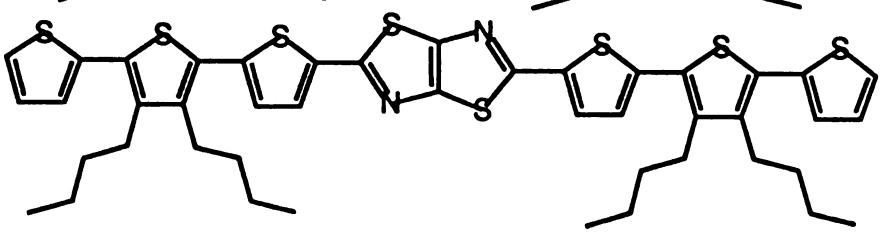
Cat. = 3,4-Dimethyl-5-(2-hydroxyethyl)-thiazolium iodide

The synthesis of the α-heptathiophene(**83**) have been accomplished by treatment of the 1,4-diketone(**88**) with P_2S_5 or Lawesson's reagent in toluene. For example, reaction of **88** with 1.2 equivalent Lawesson's reagent (excess) in refluxing toluene for two hours gave the heptathiophene(**83**) in 82% yield (Scheme 2-4).

Scheme 2-4

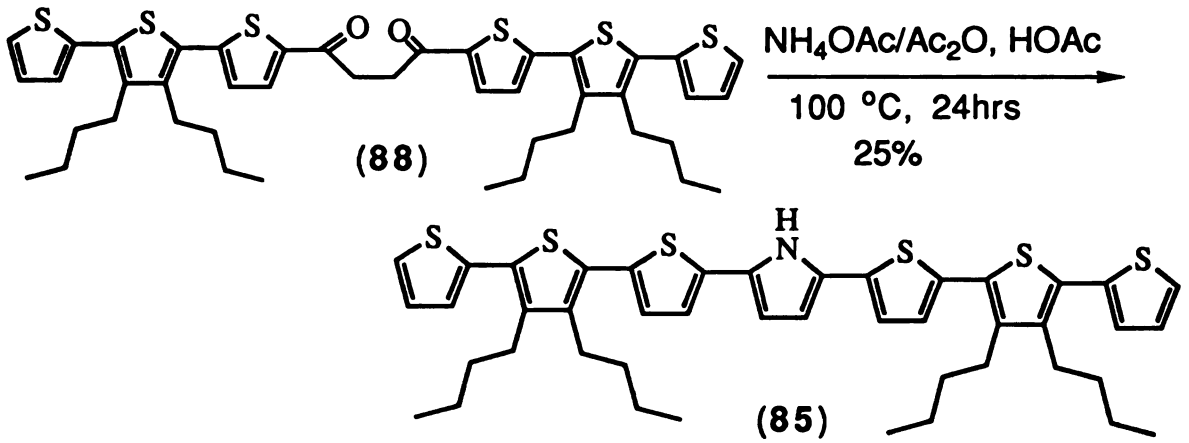


The orange needles of heptathiophene **83** melts at 129-130 °C. The UV-Vis spectra show a maximum absorption at 429nm. Compared with other alkyl substituted heptathiophene, it seems the two butyl groups on the β-positions of the same thiophene ring lower the conjugation of the oligomer. For instance, the α, α'-di-terbutyl-heptathiophene shows a UV-maximum absorption at 451nm, and the β-monobutyl-substituted heptathiophene shows a UV-maximum absorption at 440nm (Table 2-1). The mass spectrum shows that the molecular ion peak is the base line, which means that removal of one electron from the heptathiophene leads to a relatively stable radical cation. Removal of one more electron from the original formed molecular ion radical lead to the formation of a new molecular ion with two positive charges. This is indicated by relatively strong peak at m/z=400 (relative intensity 25.15%). This result shows that heptathiophene may be a good candidate as a model compound for the study of polaron and bipolaron formation by doping. Further research with this compound may provide more interesting results.

Compounds	UV(nm) Maximum Absorption
	451[4]
	440[4]
	435[4]
	429
	437
	431
	417
	466

The transformation of the 1,4-diketone(**88**) to pyrrole derivative(**85**) has been achieved by the reaction of the 1,4-diketone with $NH_4OAc/AcOH/Ac_2O$ at 100 °C under N_2 for 24 hours. The isolated yield is relatively low(25%) (Scheme 2-5). The low isolated yield of the pyrrole derivative **85** might be attributed to the instability of the starting diketone **88** and/or the product **85** in the acidic condition. Attempts to improve the yield by changing the reaction conditions (e.g. temperature or reaction time) failed.

Scheme 2-5

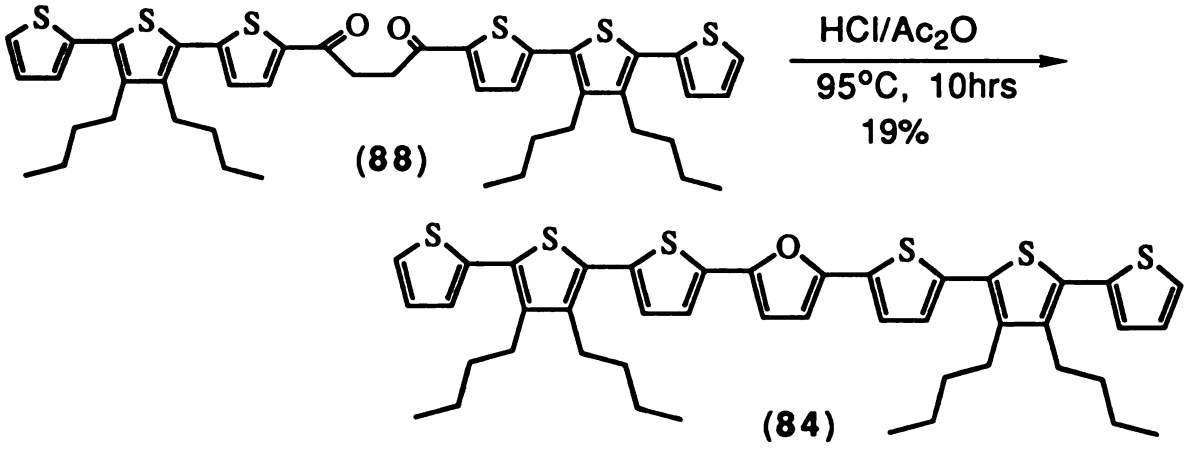


Compound **85** is an orange solid with melting point of 141-142 °C. The UV-Vis spectrum shows a maximum absorption at 437nm($CHCl_3$), which corresponds to a bathochromic shift of 8nm compared with that of the thiophene analog **83**. This indicates that the replacement of a thiophene ring with a pyrrole in the thiophene oligomers increases the conjugation so as to lower the bandgap. The mass spectrum shows that the molecular peak is the base line, which means

that the removal of one electron from the neutral molecule forms a relatively stable radical cation. This is similar to the result of heptathiophene **83**.

The furan derivative **85** has been synthesized by the acid induced cyclization of the 1,4-diketone(**88**) with 19% yield (Scheme 2-6). This unusually low yield of furan may be attributed to the instability of the starting 1,4-diketone **88** and the product **85** in the acidic environment. Attempts to improve the yield by changing the reaction temperature and reaction time or by using different acids (e.g. H_2SO_4, H_3PO_4) were not successful.

Scheme 2-6

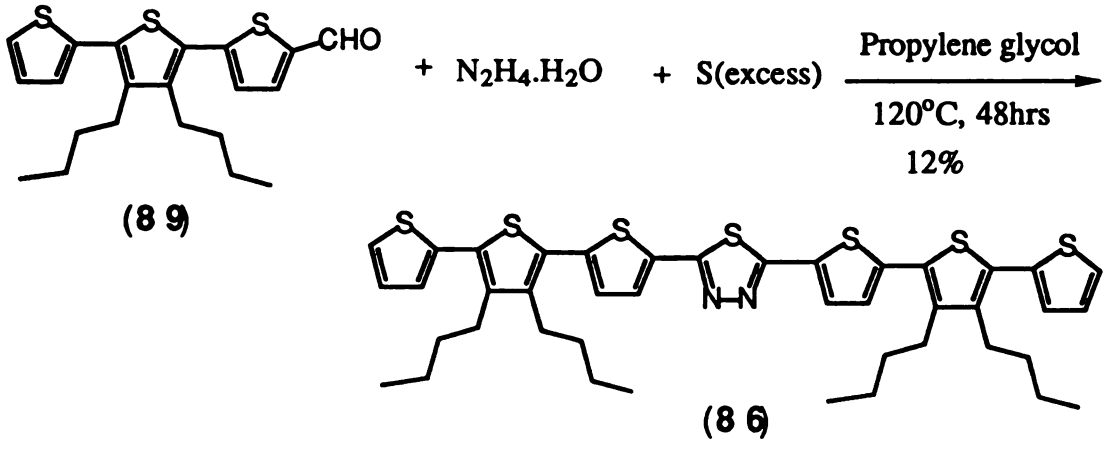


Compound **84** is an orange solid with melting point 112-114 °C. The UV-Vis spectrum shows a maximum absorption at431nm ($CHCl_3$), a 2nm bathochromic shift compared to that of the thiophene analog **83** (see Table 2-1). The mass spectrum shows the base-line at m/z=784 which corresponds to the molecular ion peak.

The successful syntheses of the thiophene oligomer **83** and the pyrrole and furan derivatives **85** and **84** encouraged us to search for the possibility of syntheses of the 1,3,4-thiadiazole and thiazolo[5,4-d] thiazole derivative oligomers **86** and **87**.

The synthesis of the 1,3,4-thiadiazole derivative(**86**) has been achieved by the condensation of the α-terthiophene monoaldehyde (**89**) with hydrazine monohydrate and elemental sulfur. The isolated yield is low (12%) (Scheme 2-7). This low yield may be attributed to the instability of the starting material and/or the product in the reaction conditions. Attempts to improve the yield by changing the reaction conditions (reaction time, temperature, and ratio of sulfur) failed.

Scheme 2-7

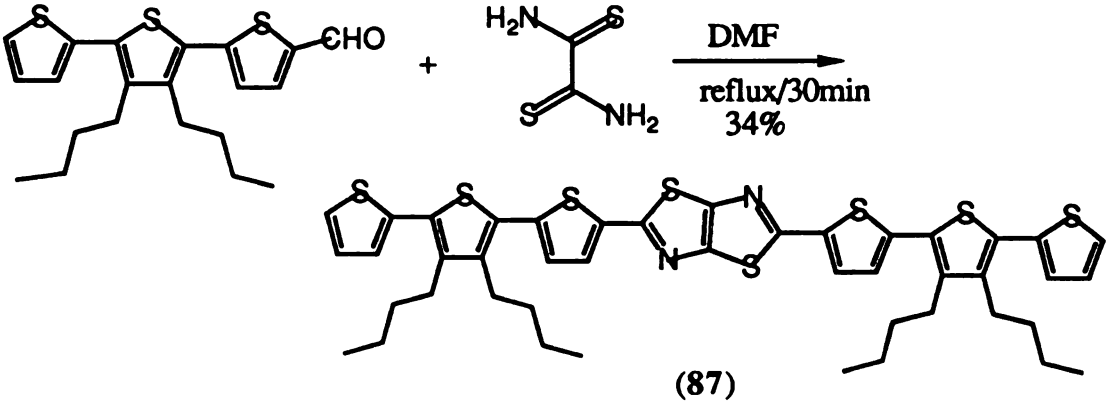


Compound **86** crystallizes as orange needles which melts at 206-208 °C(decomp.). The UV-Vis spectrum shows the maximum absorption at 417nm, which is a12nm shift to shorter wavelength

compared with the result of the thiophene analog(**83**) (see Table 2-1). This means that the replacement of a thiophene ring in the heptathiophene with a 1,3,4-thiadiazole ring reduces the conjugation and increases the bandgap.

The synthesis of the thiazolo-[5,4-b]thiazole has been achieved by the condensation of the terthiophene monoaldehyde with dithiooximide. Condensation of the α-terthiophene monoaldehyde (**89**) with dithiooximide in refluxing DMF under N_2 for 30 minutes gave a 34% yield of the expected thiazolo-[5,4-b]thiazole derivative(**87**) (Scheme 2-8).

Scheme 2-8



(**87**)

The thiazolo[5,4-b]thiazole derivative(**87**) is an orange-red needle compound with a melting point 178 °C(decomp). The UV-Vis spectrum shows the maximum absorption at 466nm. The mass

spectrum shows that the molecular ion is not as stable as that of the corresponding thiophene oligomer. Further study may provide more information on the influence of thiazolo[5,4-b]thiazole on properties of the thiophene oligomers.

Chapter 3

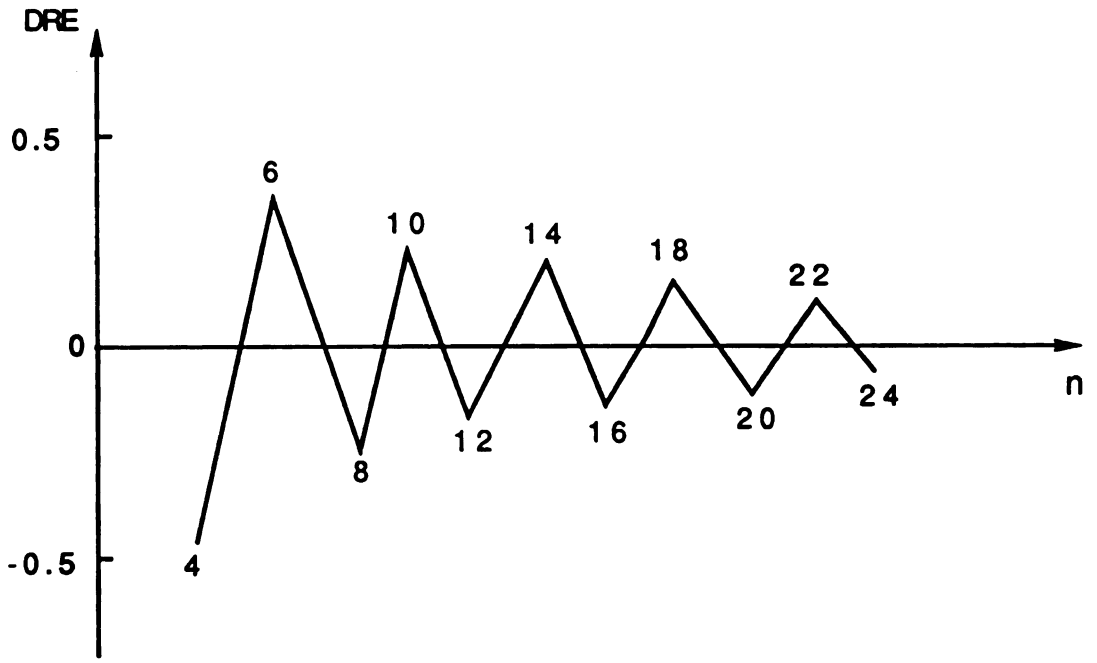
Synthetic Approachs of Some New Conjugated Macrocyclic Compounds

Synthesis and study of conjugated macrocyclic compounds with 18 or more π–electrons is one of the promising research areas that evolve from the traditional annulenes chemistry[76], to relatively new applications in photo therapy[77], organic conductors and organic superconductors[78].

Annulene chemistry is one of the branchs of chemistry that deals with conjugated cyclic polyenes. The central role of annulene chemistry is to study the aromatic and antiaromatic properties of conjugated cyclic compounds. According to Huckel's theory a planar conjugated cyclic compound is aromatic if the number of π-electrons in the conjugated system is 4n+2, where n is an integer. Whereas, a planar conjugated cyclic compound with 4n π-electrons is known as antiaromatic. Theoretical calculations of the resonance energy show that planar conjugated cyclic compounds with [4n+2] π-electrons possesses positive resonance energy which stabilizes the systems while those with [4n] π–electrons possess negative resonance energy which destabilizes the systems. The calculations also predicted that the resonance energies might vanish when the number of π-electrons

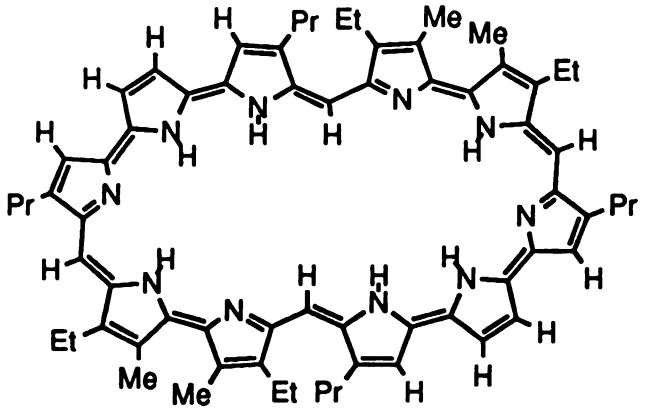
exceeds 26[79] and the molecule is planar. The change of resonance energy with the number of π-electrons is shown in Figure 3-1.

Figure 3-1



The Huckel aromatic theory is still meeting the challenge of experimentalists. Synthetic organic chemists are still interested in the synthesis and study of new annulenes. So far, the largest antiaromatic annulene synthesized and characterized is the 40 π-electrons expanded porphyrin, turcasarin[80] (Figure 3-2).

Figure 3-2



Turcasarin

The successful synthesis of turcasarin indicates that the resonance energy of aromatic and antiaromatic may be not significant when the π-electrons of the conjugated macrocycles exceed 26.

Medical use and bioactivity are other important impetus to the research of conjugated macrocycles. Photo dynamic therapy of cancer by the use of expanded porphyrins is one of the examples. Porphyrin is a well-known heteroannulene compound with 18 π-electrons. Hematoporphyrin derivatives (HPD) have been used as photo sensitizers for the photoradiation therapy of cancer since 1975[2]. Hematoporphyrin derivatives photoradiation therapy of cancer relies on the discovery of that hematoporphyrin derivatives are selectively retained by the cancer cells. When a human body affected with cancer is injected with a certain dose of HPD in vein the HPD will be selectively retained by the cancer cells for 2-3 days. If the body is exposed to a laser light with the wavelength of 625-635nm (red

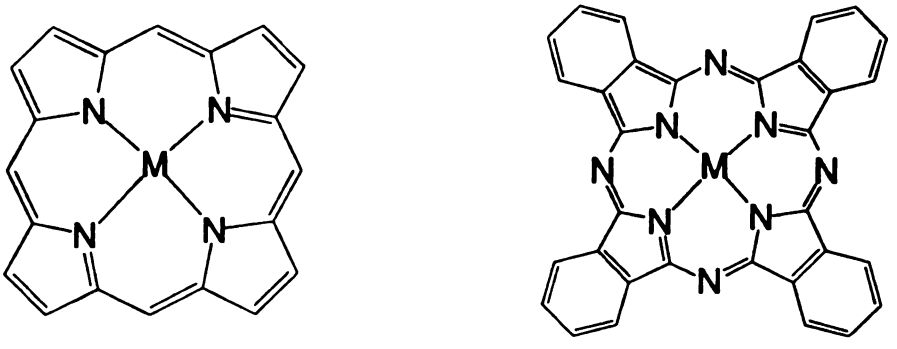
light), the HPD will be excited by the light. Then, the excited state of HPD transfer the energy to the ground triplet state of the oxygen($^3O_2$) to form the excited singlet state of oxygen($^1O_2$) in the cells. The excited singlet state of oxygen($^1O_2$) in the cells in turn oxidizes the substrate of the cancer cells and kills them.

Although HPD photo radiation therapy of cancer have many advantages over chemotherapy, the similarity of the adsorption wavelength of hematoporphyrin derivatives to that of the natural heme porphyrins of the human body limit its clinical applications. One of the improved methods is the use of expanded metalloporphyrins which have different adsorption wavelength from the heme porphyrins in the human body. The potential application of expanded metalloporphyrins in photo therapy of cancer makes the synthesis and property study of expanded porphyrins and other conjugated macrocyclic compounds one of the promising research areas.

The use of conjugated macrocyclic compounds as potential organic conductors and superconductors is another interesting research area. Several conjugated metallomacrocyclic compounds and their low-dimensional polymeric compounds have been extensively investigated. Similar to the linear conjugated polymers, the stack of undoped conjugated macrocyclic compounds behaves as an insulator and the doped form shows a conductivity as high as 100S[81]. For this kind of organic conductors, one of the most important things is the regularity of stack. Good conductivity has been found if the metallomacrocycles can form good and regular stacks. In order to form a good and regular stack the macrocyclic compounds should be

planar or almost planar. Of all the macrocyclic compounds, metalloporphyrins and phthalocyanines are two kinds of common compounds which have been more extensively investigated (Figure 3-3).

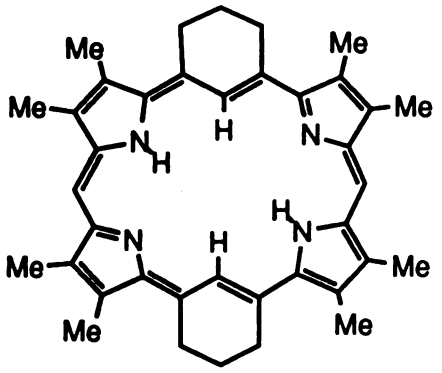
Figure 3-3



The importance of conjugated macrocyclic compounds have inspired many chemists to do research on the synthesis and studies of these compounds, and a large number of conjugated macrocyclic compounds have been synthesized and characterized. For example, expansion of the porphyrin macrocycles by inserting odd numbers of carbon atoms alternately between the pyrrolic rings gives rise to a family of expanded porphyrins. These kind of compounds has been named platyrins by Professor E. LeGoff in Michigan State University, and [1,3,1,3]platyrin(**91**)[82], and [1,5,1,5]platyrin(**92**)[83] have been synthesized. By a similar strategy, several other analogs of this kind of expanded porphyrins, [22]porphyrin(1,3,1,3)(**93**)[84], [26]porphyrin(1,5,1,5)(**95**)[85], 14-aza[26]porphyrin(1,51,5)(**96**)[85], [26]porphyrin(3,3,3,3)(**94**)[86] and [34]porphyrin(5,5,5,5)(**97**)[87] have also been reported by different groups with the

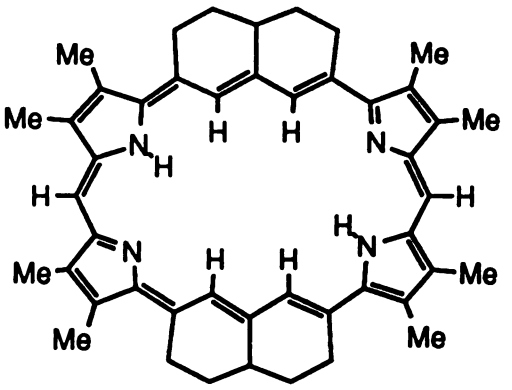
[34]porphyrin(5,5,5,5)(97) as the largest aromatic system (Figure 3-4).

Figure 3-4



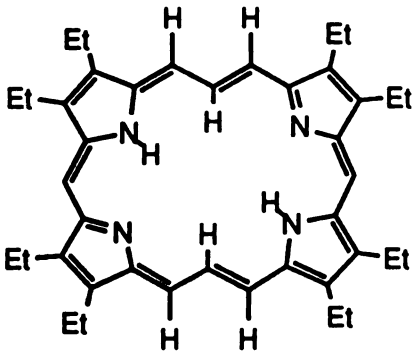
(91)

[1,3,1,3]Platyrin



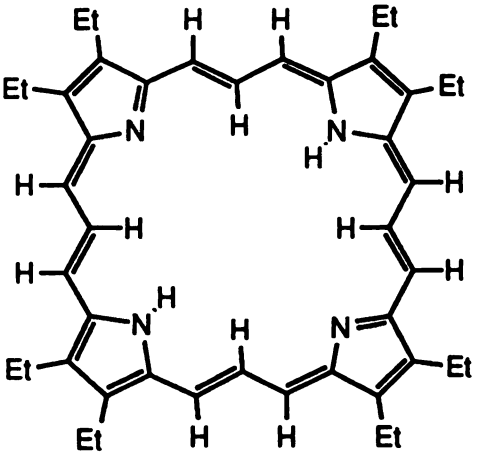
(92)

[1,5,1,5]Platyrin



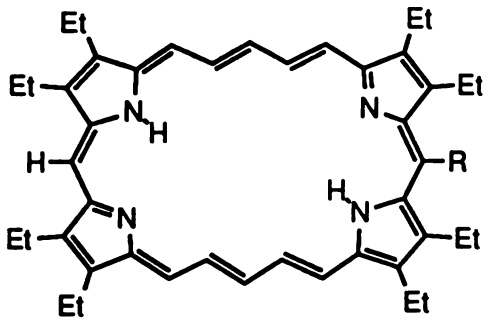
(93)

[22]Porphyrin(1,3,1,3)



(94)

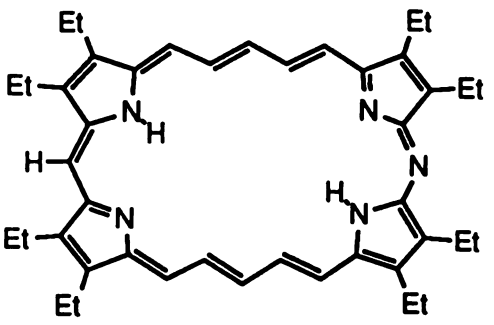
[26]Porphyrin(3,3,3,3)



(95)

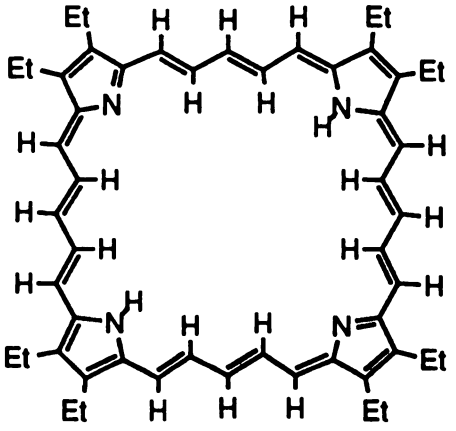
[26]porphyrin(1,5,1,5)

R=H, Ph, Et



(96)

14 aza[26]porphyrin(1,5,1,5)



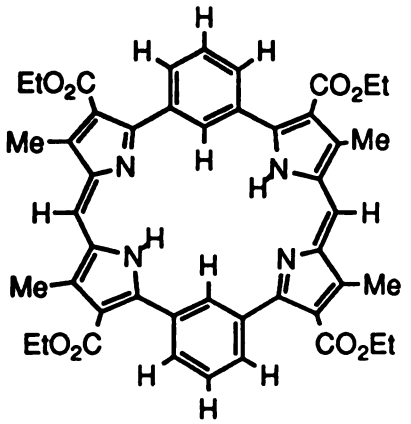
(97)

[34]Porphyrin(5,5,5,5)

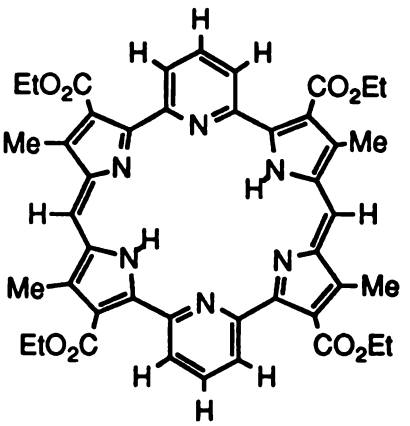
By inserting a benzene, pyridine or other heterocyclic rings between the pyrrolic rings of porphyrin macrocycle several other expanded porphyrins have also been synthesized recently. For instance, the syntheses of new expanded porphyrins(**98**, **99**)[88] and the porphocyanine(**100**)[89] have been reported. Structurally, expanded porphyrins **100** is similar to [1,3,1,3]platyrin **91** but **98** and **99** are different (Figure 3-5). Actually, compounds **98** and **99**

are not conjugated in the macrocyclic system, but [1,3,1,3]platyrin and porphocyanine(**100**) are conjugated.

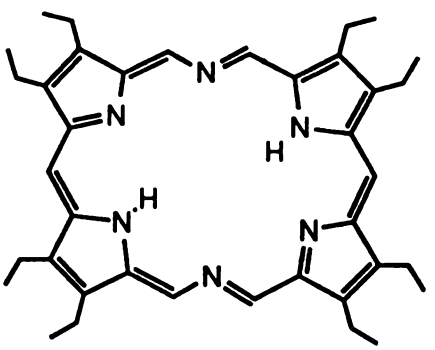
Figure 3-5



(**98**)



(**99**)



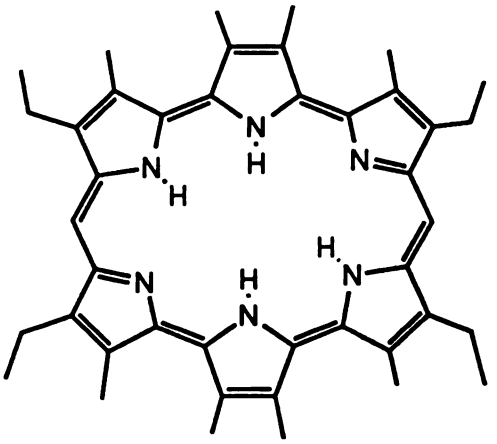
(**100**)

Porphocyanine

Footballene(**101**)[90] is another expanded porphyrin with the replacement of two pyrrolic rings to the two methine group in porphyrin. Footballene **101** an antiaromatic annulene with 24 π-

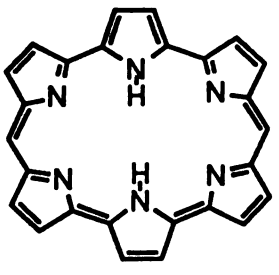
electrons. It can be named as [24]porphyrin(1,4,1,4). Molecular calculation of force field by the program MM2 has predicted that footballene **101** might be present in three different oxidation states with 22, 24, and 26 π-electrons respectively[31] (Figure 3-6). Research on the possibility of these different oxidation states may provide direct evidence of aromatic and antiaromatic properties of heteroanullenes.

Figure 3-6

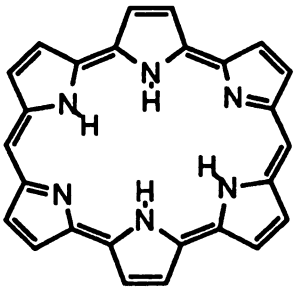


(101)

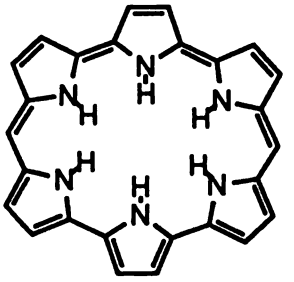
Footballene



.. 22-π



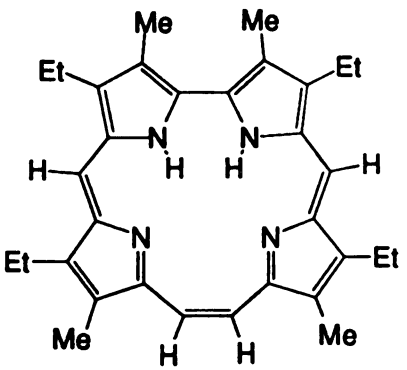
24-π



26-π

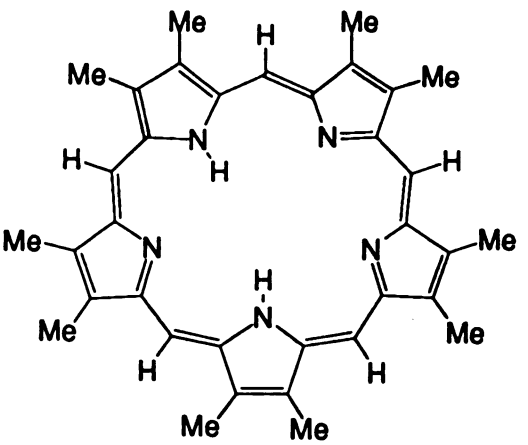
Sapphyrin(**104**)[91] is a modified structure of pentaphyrin(**103**)[92]. It contains five pyrrolic rings and four methine groups in the macrocyclic system, one methine group short compared with that of pentaphyrin. Sapphyrin can be also thought as the expanded ring system of porphyrin(2,1,0,1)(**102**)[91]. By the replacement of one or two pyrrolic rings of sapphyrin with furan or thiophene, oxasapphyrin(**107**)[92], thiasapphyrin(**105**)[92] and dioxasapphyrin(**106**)[92] have also been reported (Figure 3-7).

Figure 3-7



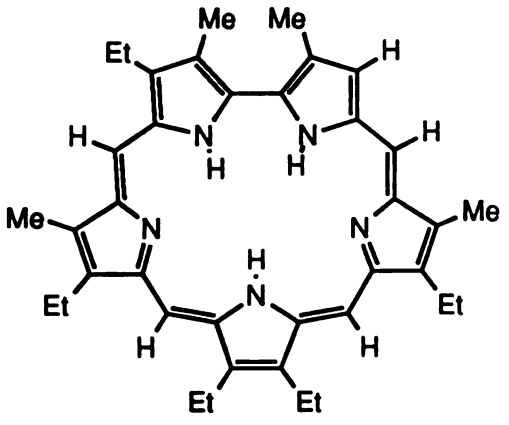
(102)

Porphyrin(2,1,0,1)



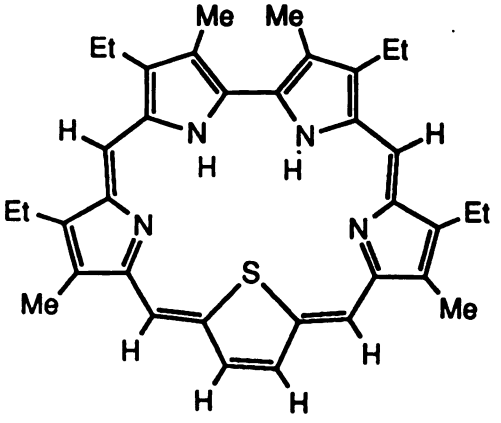
(103)

Pentaphyrin



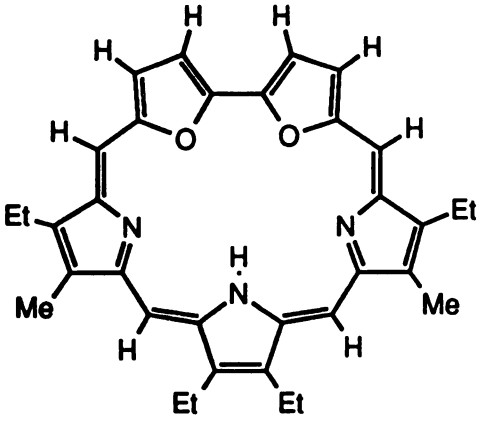
(104)

Sapphyrin



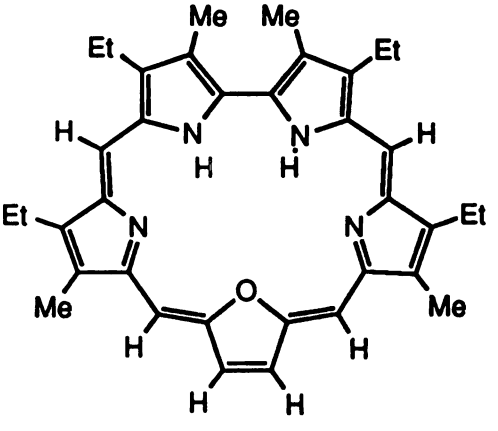
(105)

Thiasapphyrin



(106)

Dioxasapphyrin



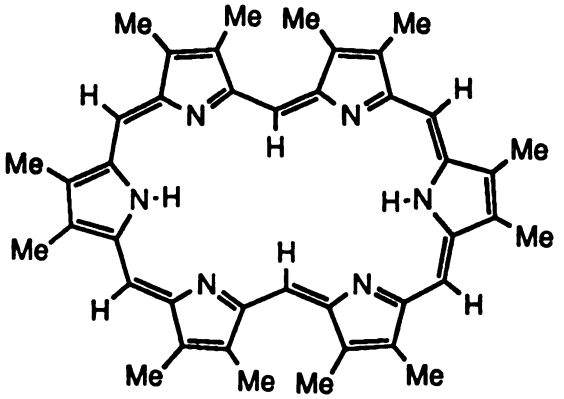
(107)

Oxasapphyrin

Other expanded porphyrins reported includes hexaphyrin (**108**)[93] rubyrin(**109**)[94], and rosarin(**110**)[95]. Hexaphyrin(**108**)[93] is an expanded porphyrin which contains six pyrrolic rings and six methine groups in the macrocyclic ring system. Rubyrin(**109**)[94] contains six pyrrolic rings and four methine groups which is two methine groups short compared with that of hexaphyrin **108**.

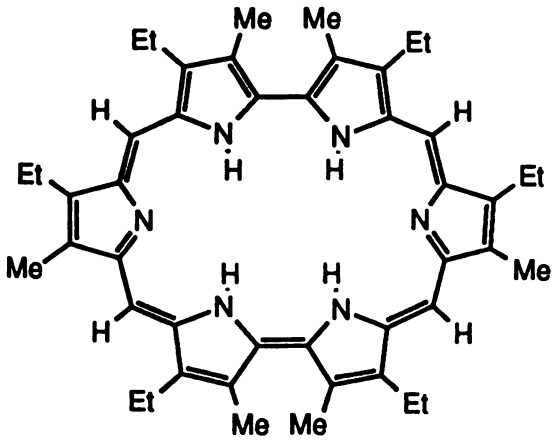
Because there are two pairs of pyrrolic rings connected together directly rubyrin can be thought as an expanded porphycene (see below). Rosarin(**110**)[95] contains six pyrrolic rings and three methine groups (Figure 3-8).

Figure 3-8



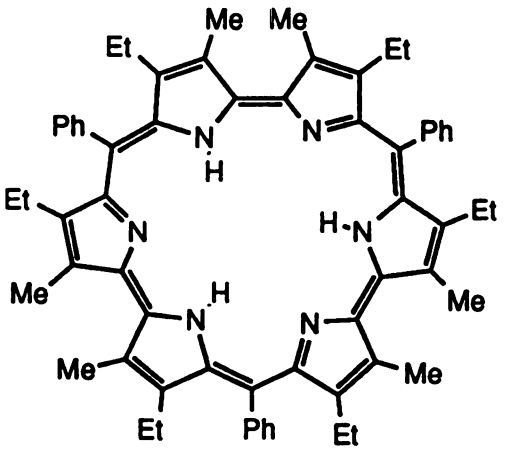
(108)

Hexaphyrin



(109)

Rubyrin

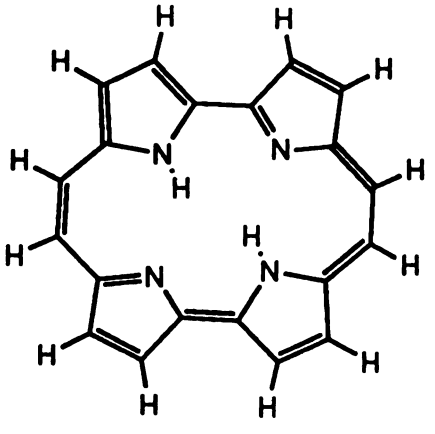


(110)

Rosarin

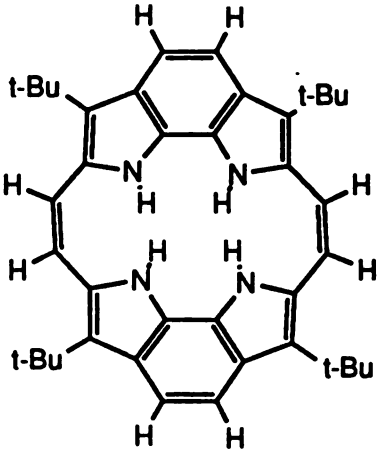
In addition to the many reports on the syntheses and studies of conjugated macrocycles based on the expansion of porphyrins, there are many interests on the systems of expanded isomeric porphyrins. For example, porphycene(**111**)[96] is an isomeric porphyrin with 18 π-electrons. It can be identified as porphyrin(2,0,2,0). The ethylene bridged porphycene-like(**112**) is a [20]heteroannulene[97]. By inserting a certain number of methine groups or a five or six member cyclic ring between the connected pyrrolic rings of the porphycene, several new macrocyclic compounds, expanded porphycenes, have been synthesized. For example, [22]porphyrin(2,2,2,2)(**113**)[97] and the acetylene-cumulene porphyrinoid(**114**)[97], the expanded porphycene [26]porphyrin(6,0,6,0)(**115**)[98], as well as the heterocyclic expanded porphycenes (**116**)[99], (**117**)[100] have been synthesized (Figure 3-9).

Figure 3-9



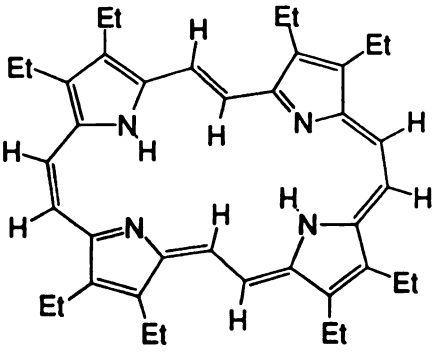
(**111**)

Porphycene



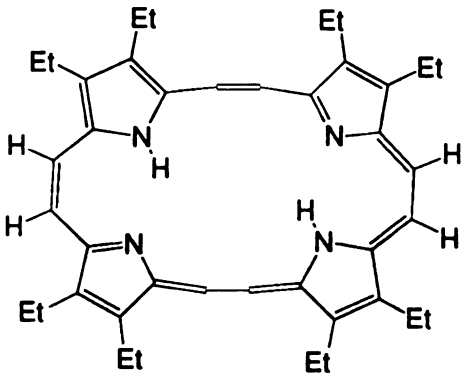
(**112**)

Bridged Porphycene



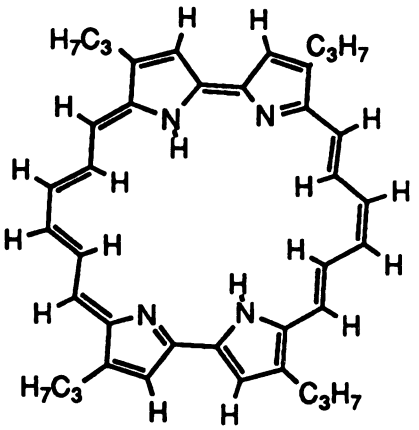
(113)

[22]Porphyrin(2,2,2,2)



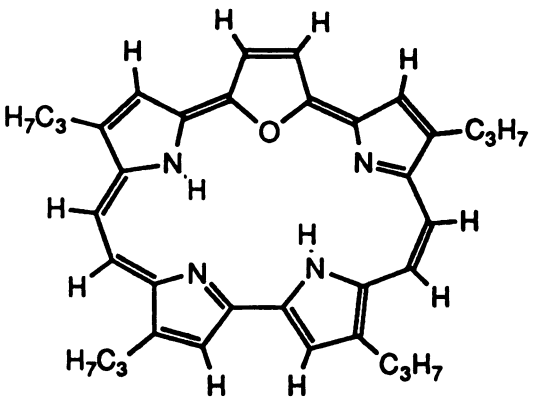
(114)

Acetylene-Cumulene Porphyrinoids

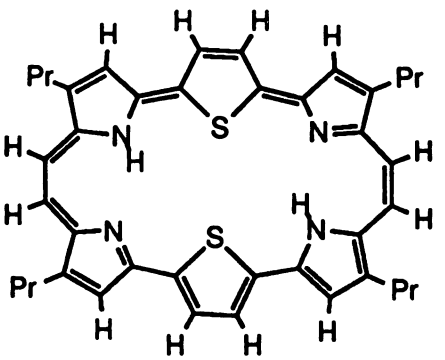


(115)

[26]Porphyrin(6,0,6,0)



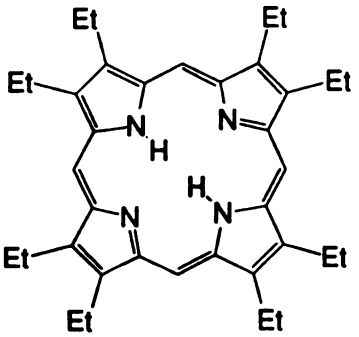
(116)



(117)

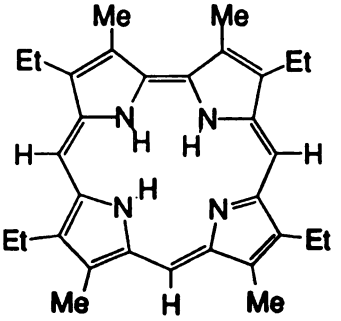
Corrole(**119**)[101], the aromatic basic structure of the ring framework of vitamin B_{12}, and its isomer, isocorrole(**120**)[102] both contain four pyrrolic rings and three methine groups, one methine group short compared to the structure of porphyrins(**118**) (Figure 3-10). The conjugated pentapyrrolic macrocycle(**121**)[103] can be thought as the expanded isocorrole. The furan analogs(**122, 123**)[104] of macrocycle **121** have also been reported in the literature (Figure 3-10).

Figure 3-10



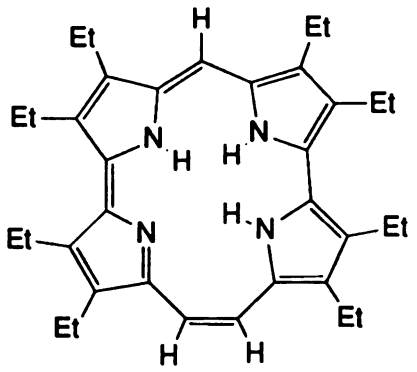
(118)

Tetraethylporphyrin



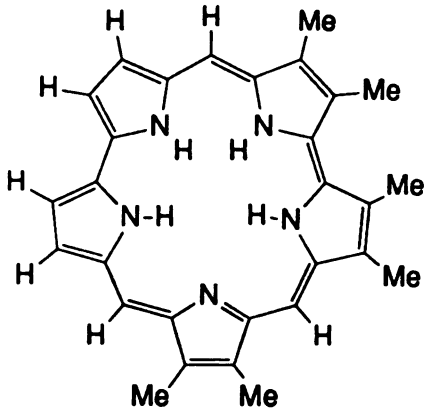
(119)

Corrole

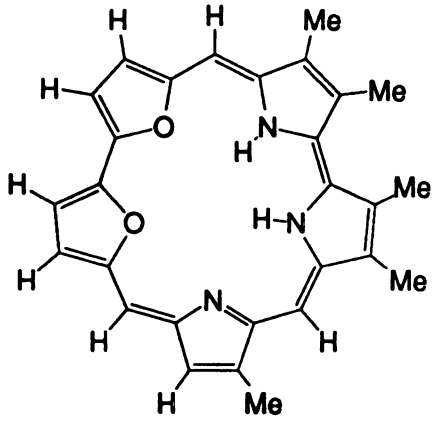


(120)

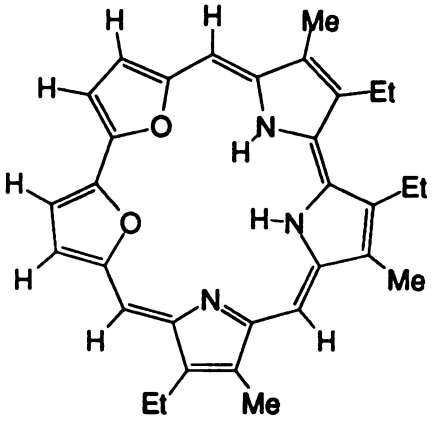
Isocorrole



(121)



(122)

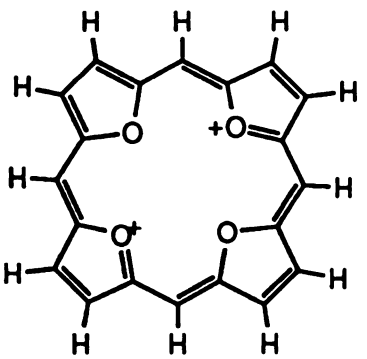


(123)

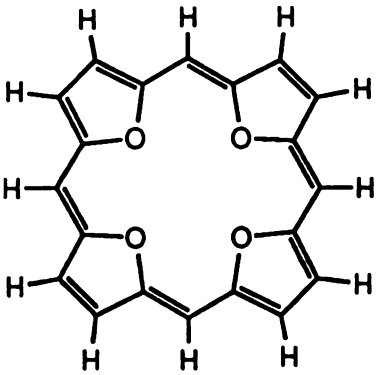
Another area of research on the syntheses and studies of porphyrin analogs and their expanded systems is the use of furan, thiophene, pyridine or other heterocyclic compounds in place of the pyrrole ring of porphyrins. Because of the similar structure and chemical reactivity of furan and thiophene with pyrrole, many efforts have been involved in the syntheses and studies of furan and thiophene analogs of porphyrin, porphycene and their expanded systems. For instance, although the oxygen or sulfur-bridged

[20]annulene tetraoxaisophlorin(**125**) and tetrathiaisophlorin(**127**) are unknown, their oxidized dications, the furan and thiophene analogs of porphyrin, (**124**)[105] and (**126**)[106] have been reported. The furan analogous of porphycene (**128**) and (**129**) have also been synthesized[107]. Because of the size of sulfur atom the thiophene analog of porphycene (**130**) is still unknown. However, a mixed thiophene and pyrrole containing porphycene analog (**131**)[108] has been reported recently. The expanded tetraoxaporphycene (**133**) and it's dication (**132**) have also reported[109]. A tetraoxa[26]-porphyrin(3,3,3,3)(**136**) and the expanded tetrathiaporphycene (**134**) and (**135**) have also been synthesized[110] (Figure 3-11).

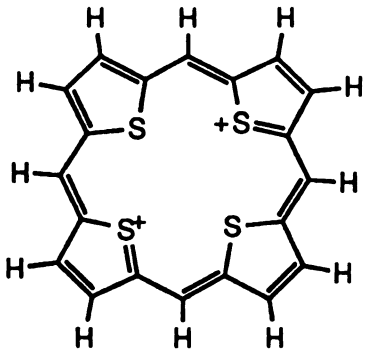
Figure 3-11



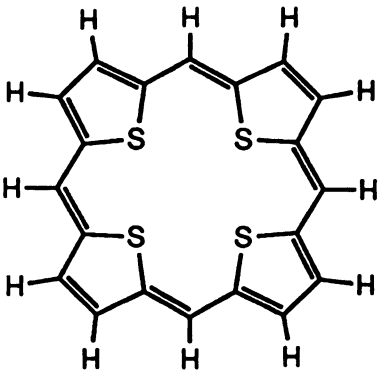
(**124**)



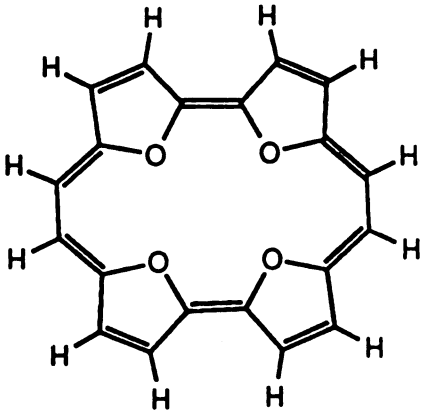
(**125**)



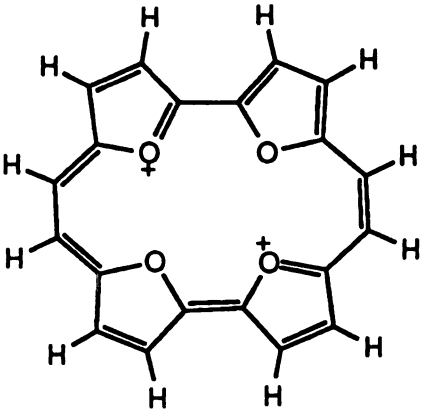
(126)



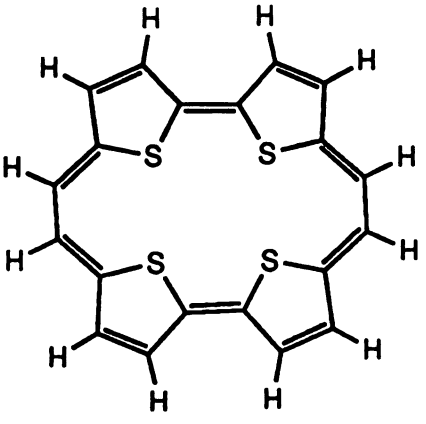
(127)



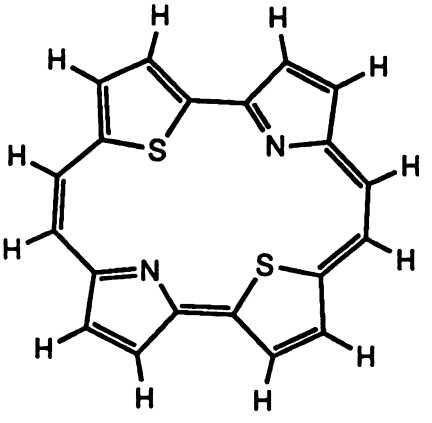
(128)



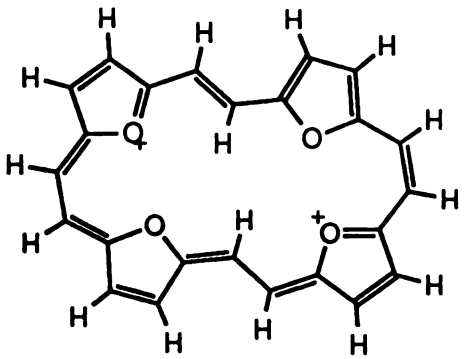
(129)



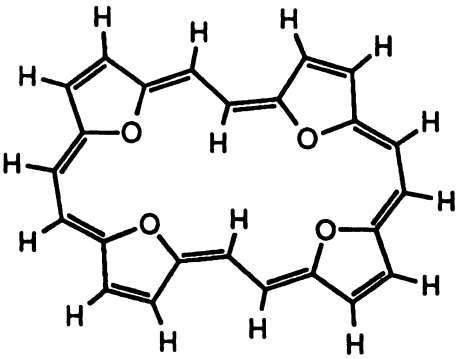
(130)



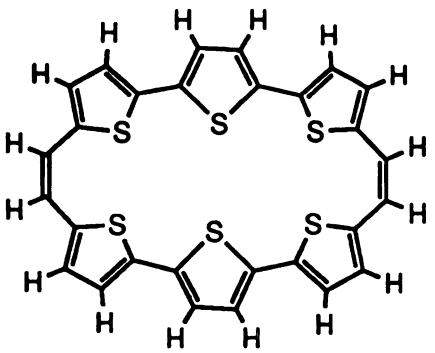
(131)



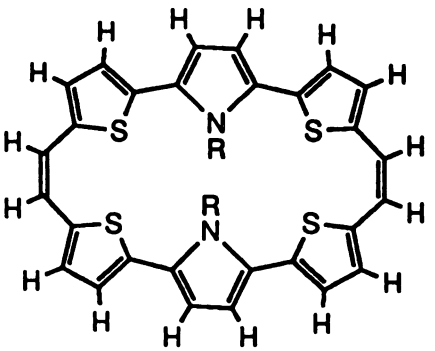
(132)



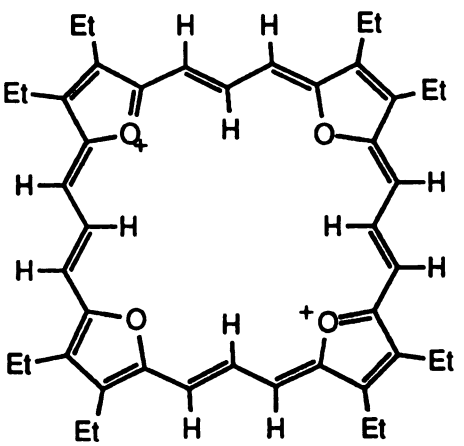
(133)



(134)



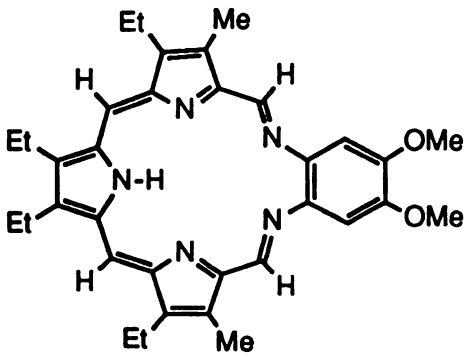
(135)



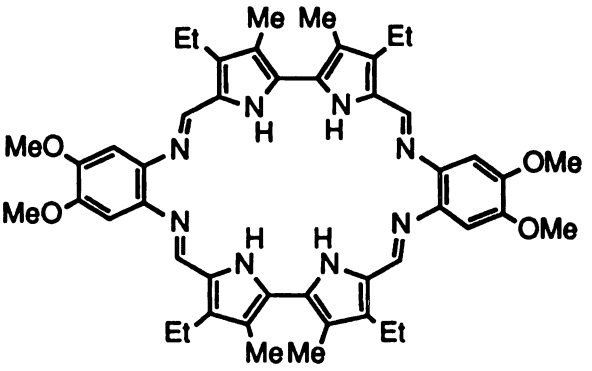
(136)

Some other conjugated macrocyclic compounds which contain heterocyclic compounds other than pyrrole, furan and thiophene have been also synthesized. For example, texaphyrin(**137**, **138**)[111] is a kind of conjugated macrocyclic compounds which contain imine groups in the conjugated systems, and may be used as photo-sensitizers in the photo dynamic therapy. Other macrocyclic compounds synthesized include the macrocyclic ketone (**139**)[111] and the imidazole containing coronand(**140**)[112], *etc*. (Figure 3-12).

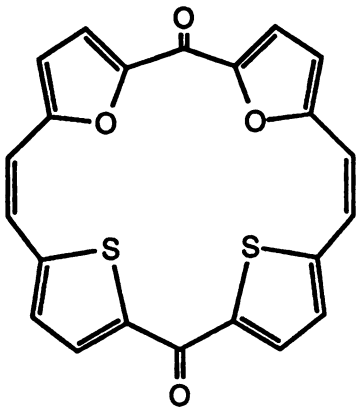
Figure 3-12



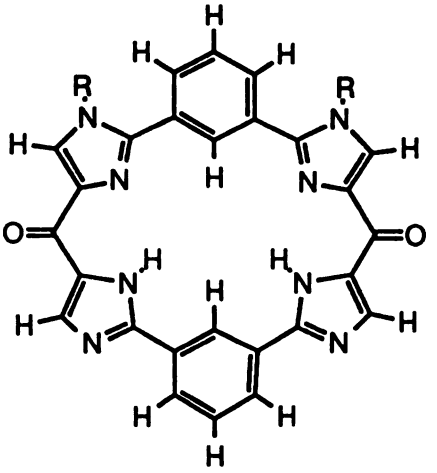
(**137**)



(**138**)



(**139**)



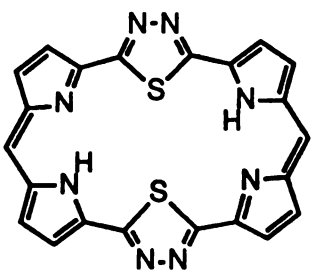
(**140**)

1,3,4-Thiadiazole is a heterocyclic compound with a broad range of bioactivities[113-115]. In Chapter 1 Section 1.3 a convenient, and efficient one-pot procedure for the synthesis of 2,5-diary-1,3,4-thiadiazole has been described. Considering that the shape similarity of 1,3,4-thiadiazole with pyrrole, thiophene and furan, and there is no report in the syntheses of macrocyclic compounds containing 1,3,4-thiadiazole part of my efforts has been involved in the attempted syntheses of several new conjugated macrocyclic compounds which contain 1,3,4-thiadiazole rings. The results will be described in Sections 3.1 and 3.2. Another part of my research is on the syntheses of new conjugated hexathiophene macrocyclic compounds and the results will be reported on Sections 3.3 and 3.4.

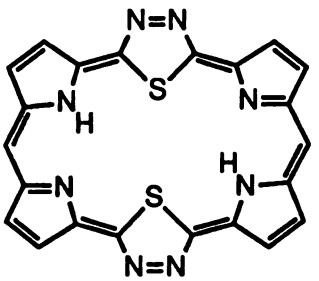
3.1 Synthetic Approaches of A New Tetrapyrrolic Macrocycle Containing 1,3,4-Thiadiazole

The convenient procedure for the synthesis of 2,5-diaryl-1,3,4-thiadiazoles which has been described in Section 1.3 of this thesis encouraged us to do research on the application of this procedure to the synthesis of a new 1,3,4-thiadiazole containing tetrapyrrolic macrocyclic compound(**141**). It can be predicted that compound **141** can resonance to another unknown macrocyclic compound(**142**) (Figure 3-13). Molecular modeling with MM2 shows that compound **142** is the lower energy state.

Figure 3-13



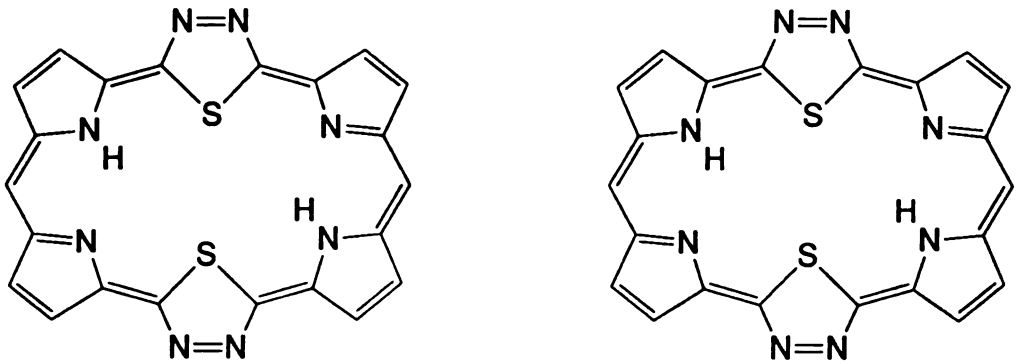
(**141**)



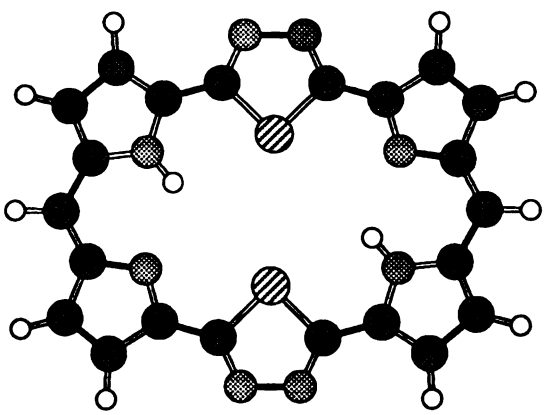
(**142**)

The molecule is expected to be essentially planar by force field calculation. The three dimensional structrue and space-filling structures of compound **142** are shown in Figure 3-14.

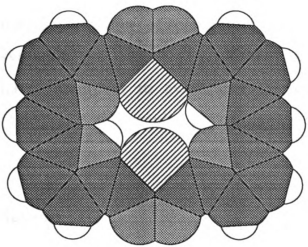
Figure 3-14



(142a)



(142b)

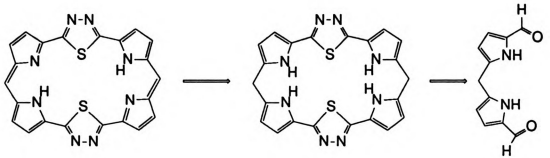


(142c)

(142d)

Retrosynthetic analysis shows compound **141** might be synthesized by the oxidation of the unknown macrocyclic compound **143** which in turn might be synthesized by the condensation of 5,5'-bisformyl dipyrrylmethane with hydrazine monohydrate and elemental sulfur (Scheme 3-1).

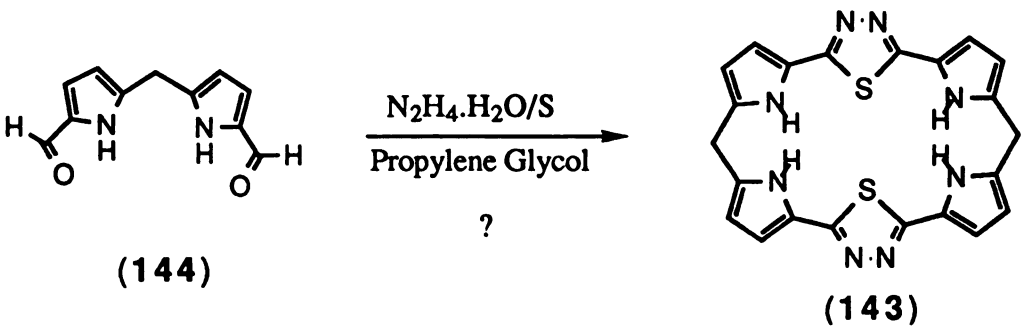
Scheme 3-1



(141) (143) (144)

Obviously, the key step in this synthetic strategy is the macrocyclization of compound **143** (Scheme 3-2). By the use of the synthetic procedure of 1,3,4-thiadiazole described in Section 1.3 we have attempted to synthesize the unknown macrocyclic compound (**143**) and the results are presented and discussed as follows.

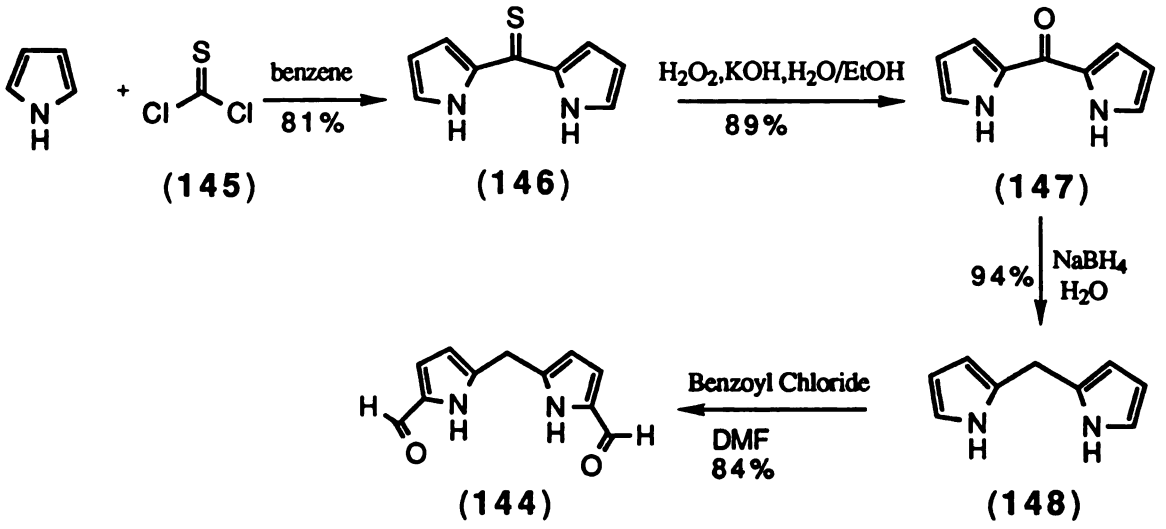
Scheme 3-2



(144) **(143)**

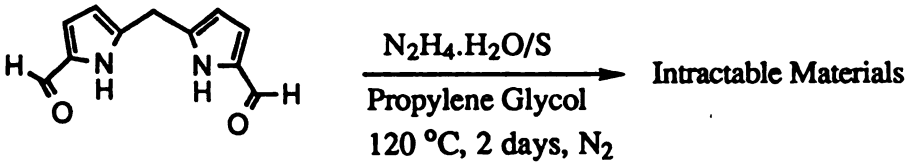
The precursor 5,5'-bisformyl-dipyrrylmethane **144** has been synthesized in four steps starting with pyrrole by a modified experimental procedure described by Clezy and coworker[113] (Scheme 3-3).

Scheme 3-3



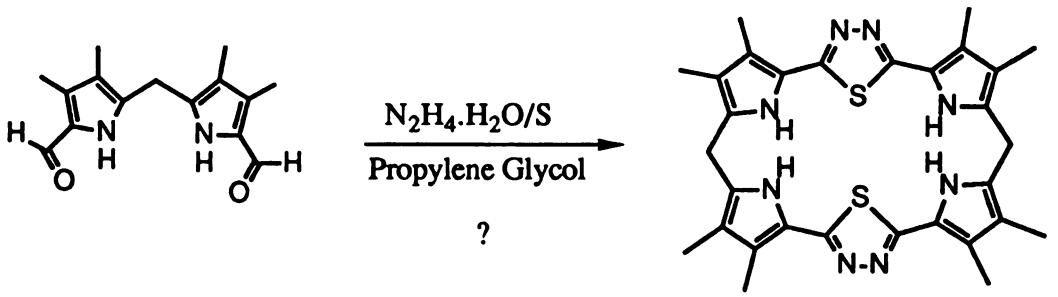
When 5,5'-bisformyl-2,2'-dipyrrylmethane(**144**) was submitted to the reaction with hydrazine monohydrate and elemental sulfur, only intractable tar-like materials were formed and flash column chromatography failed to isolate any cyclized product. Changing reaction conditions by reducing the reaction temperature and/or shortening the reaction time did not give any isolable cyclization product either(Scheme 3-4). One major reason for the failure of this reaction might be attributed to the instability of the starting material, 5,5'-bisformyl-2,2'-dipyrrylmethane(**144**) and/or product in the reaction conditions.

Scheme 3-4



Considering that that β-substituent alkyl groups might favor the macrocyclization and stabilize the pyrrole rings, research was turned to the synthesis of the macrocyclic compound **150** with methyl groups on the β-positions of pyrroles (Scheme 3-5).

Scheme 3-5

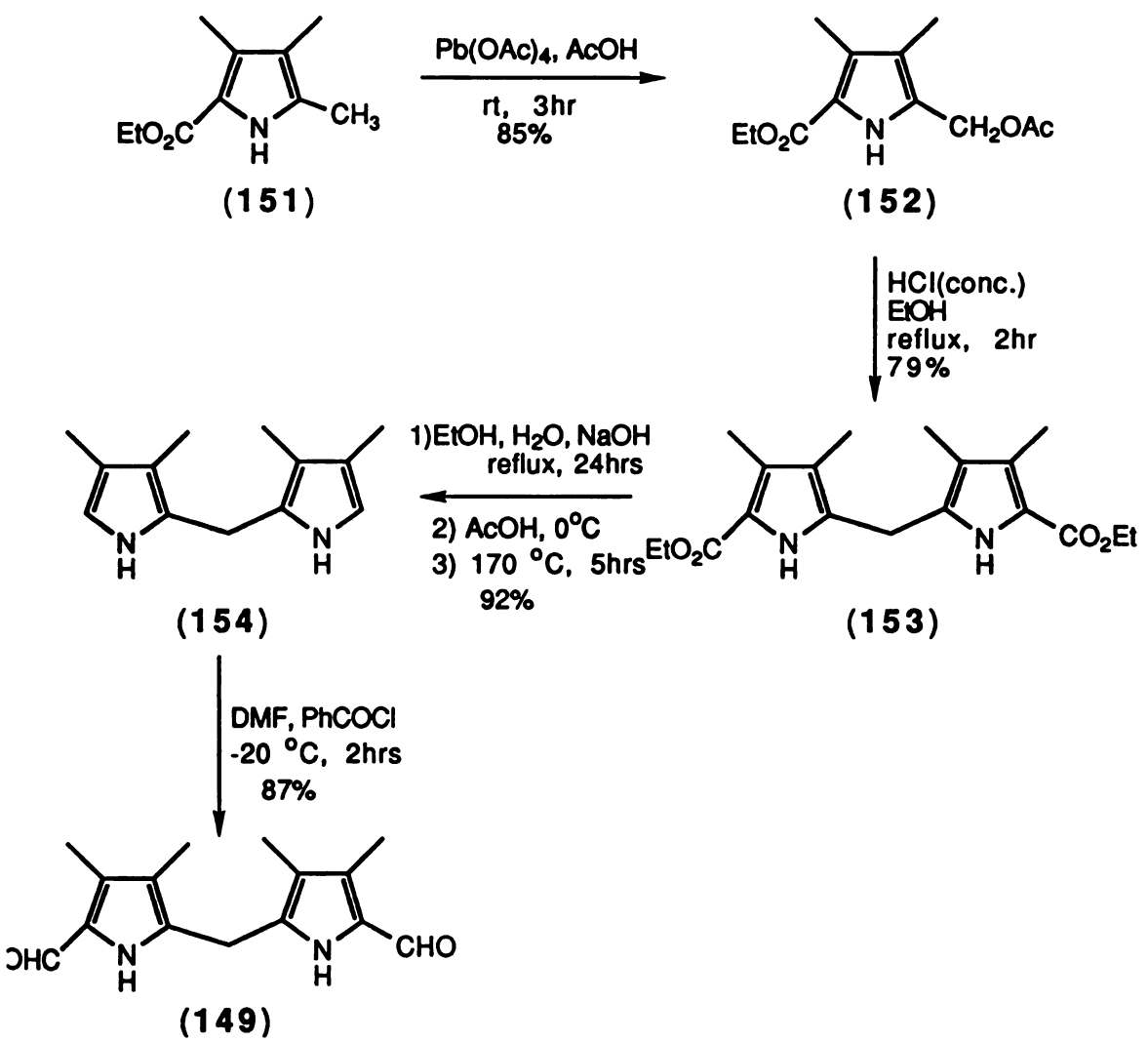


(149) **(150)**

5,5'-Bisformyl-3,3',4,4'-tetramethyl-2,2'-dipyrrylmethane**149** was synthesized by six steps(Scheme 3-6). Reaction of 2-ethoxycarbonyl-3,4,5-trimethylpyrrole(**151**) with $Pb(OAc)_4$ in acetic acid at room temperature for three hours gave the 2-ethoxycarbonyl-3,4-dimethyl-5-acetyloxylmethylpyrrole(**152**) in 85% yield. Refluxing 2-ethoxycarbonyl-3,4-dimethyl-5-acetyloxylmethylpyrrole(**152**) in ethanol with the catalysis of concentrated HCl for two hours gave the 5,5'-ethoxycarbonyl-3,3',4,4'-tetramethyldipyrrylmethane(**153**) in 79% yield. Hydrolysis of 5,5'-ethoxycarbonyl-3,3',4,4'-tetramethyldipyrrylmethane(**153**) followed by decarboxylation gave the 3,3',4,4'-tetramethyl-2,2'-dipyrrylmethane(**154**) in 92% yield. Formylation of the 3,3',4,4'-tetramethyl-2,2'-dipyrrylmethane(**154**) with DMF and benzoyl

chloride gave the 5,5'-bisformyl-3,3',4,4'-tetramethyl-2,2'-dipyrrylmethane(**149**) in 87% yield (Scheme 3-6).

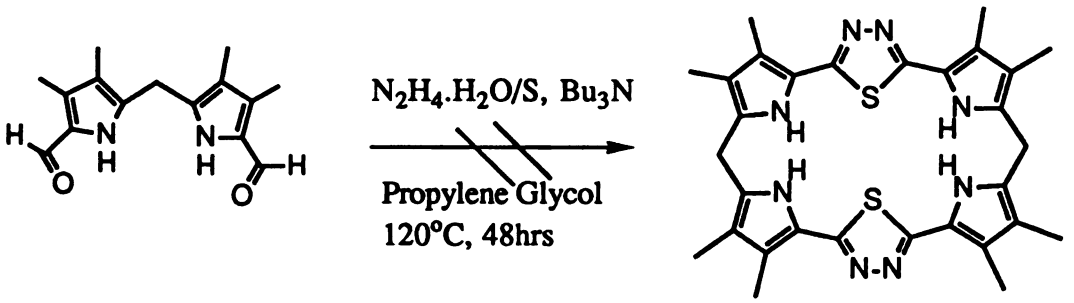
Scheme 3-6



Reaction of 5,5'-bisformyl-3,3',4,4'-tetramethyl-2,2'-dipyrrylmethane(**149**) with hydrazine monohydrate and elemental

sulfur in the presence of small amount of tributylamine at 120 °C for two days led to the formation of an intractable tar-like material, and no cyclized product was isolated by flash column chromatography (Scheme 3-7). The change of reaction conditions by reducing the temperature and/or shortening the reaction time failed to give an isolable yield of cyclized product. Because of this failure of the synthesis of compound **142**, further research on the synthesis of compound **140** was not attempted. Other efforts were expended on the attempted synthesis of other new conjugated macrocyclic compounds and the results are presented in Sections 3.2-3.4.

Scheme 3-7

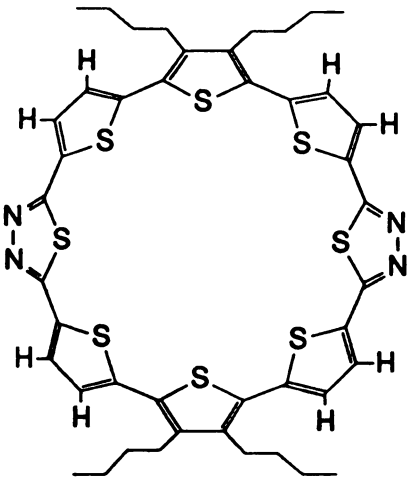


3.2 Synthesis of A New Hexathiophene Macrocycle Containing 1,3,4-Thiadiazole

In Section 1.4 of this thesis, an improved and practical route to the synthesis of 3',4'-dialkyl-2,2',5',2"-terthiophene was described. By this method, a large quantity of 3',4'-dibutyl-2,2',5',2"-terthiophene has been synthesized in this laboratory. By the

combination with the efficient procedure for the synthesis of 2,5-diaryl-1,3,4-thiadiazoles described in Section 1.3 of this thesis, a new macrocyclic compound which contains six thiophene rings and two 1,3,4-thiodiazole rings **154** has been chosen as a target compound. And part of my research work has been involved in the synthesis of this new compound (Figure 3-15).

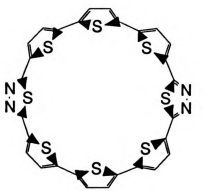
Figure 3-15



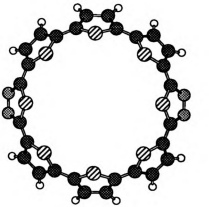
154

Molecular calculation of force field shows that the structure of this compound is not planar, but like a crown. MM2 energy minimized molecular structure, three dimensional structure and space-filling structures are shown in Figure 3-16.

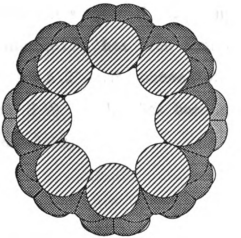
Figure 3-16



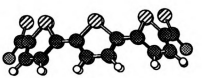
154a



154b



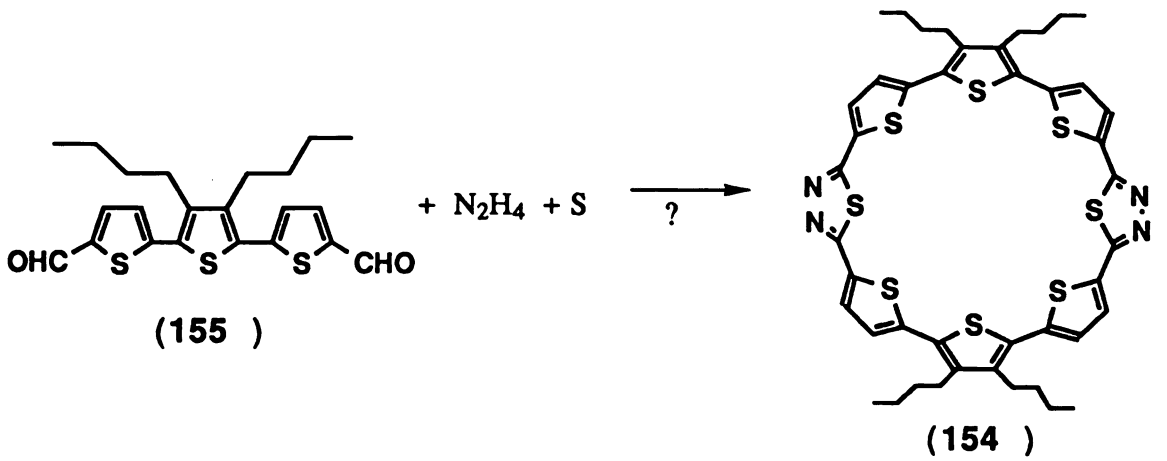
154c



154d

Retrosynthetic analysis shows macrocycle **154** might be synthesized by the condensation of 5,5''-bisformyl-3',4'-dibutyl-2,2',5',2''-terthiophene with hydrazine monohydrate and elemental sulfur (Scheme 3-8).

Scheme 3-8

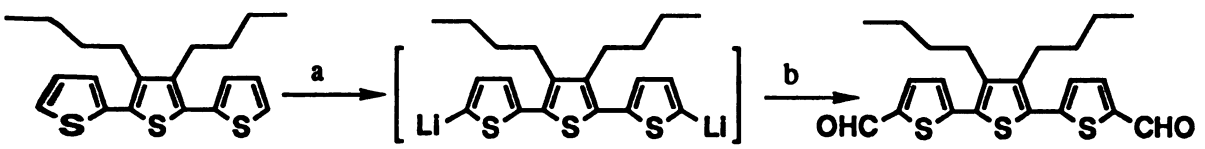


(155)

(154)

Synthesis of 5,5''-bisformyl-3',4'-dibutyl-2,2',5',2''-terthiophene**155** has been achieved by the lithiation of the 3',4'-dibutyl-2,2',5',2''-terthiophene followed by the reaction with DMF (Scheme 3-9). It also has been synthesized by a Vilsmeier reaction (Scheme 3-10).

Scheme 3-9

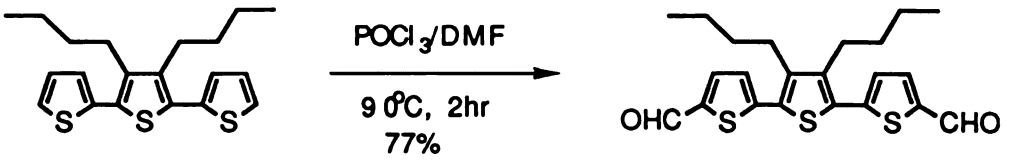


(57)

(155)

a, BuLi(2.1 eq), hexane/THF b, DMF(2.4 eq), THF, Yield 81%

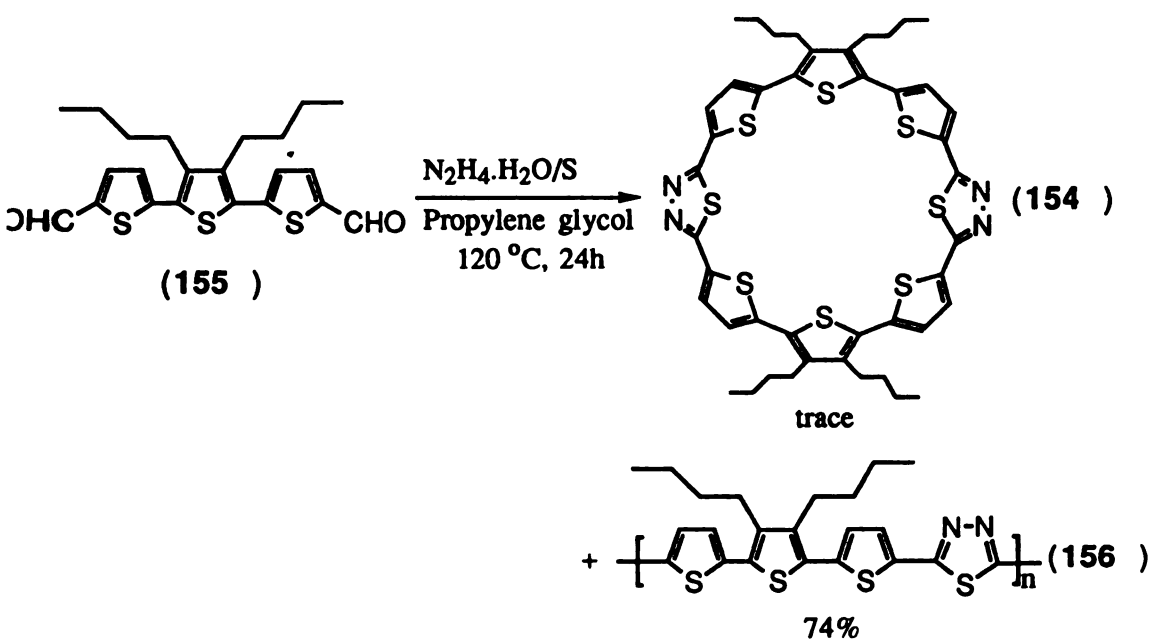
Scheme 3-10



(57) (155)

Condensation of the 5,5''-bisformyl-3',4'-dibutyl-2,2',5',2''-terthiophene with hydrazine monohydrate and elemental sulfur at 120°C for two days gave only a polymeric product with no isolable yield of cyclized product. Shortening the reaction time to 24 hours led to the formation of polymeric product as the major product with a trace of cyclized product which was determined by mass spectrum to be **154** (Scheme 3-11).

Scheme 3-11

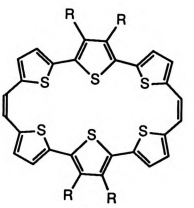


Attempts to improve the yield of the macrocyclic compound **154** by the use of two step synthesis or high dilution technique failed.

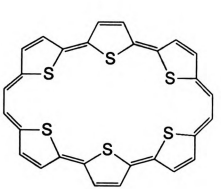
3.3 Synthetic Approaches of A New Hexathiophene Macrocycle

When my effort was on the syntheses of new macrocyclic compounds by the use of 3',4'-dibutyl-2,2',5',2"-terthiophene as a precursor, one of the target compounds was compound **157**. Compound **157** is a thiophene-derived annulene with 28 π-electrons and force field molecular calculation shows that it is not a planar molecule (Figure 3-17). Unfortunately, when I was going to synthesize this new macrocyclic compound, a synthesis of a similar macrocycle appeared in Tetrahedron Letter[109]. At this time, my research was guided to the synthesis of a new hexathiophene macrocyclic compound **158**. Compound **158** contains six thiophene rings and six methine groups in the macrocyclic system and is a 30 π-electron annulene (Figure 3-18).

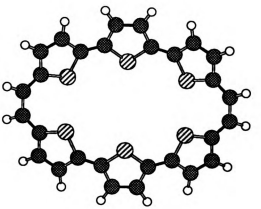
Figure 3-17



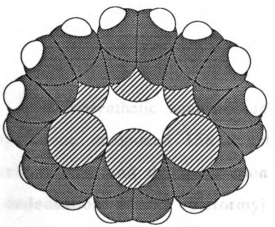
(157)



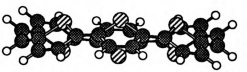
(157a)



(157b)

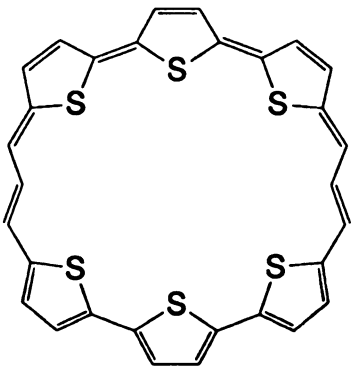


(157c)

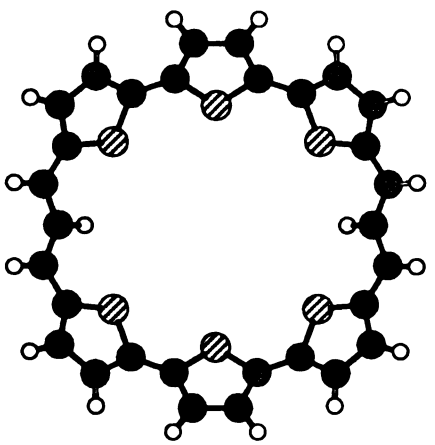


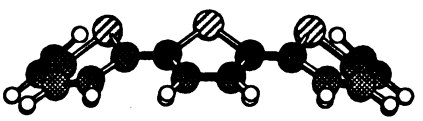
(157d)

Figure 3-18



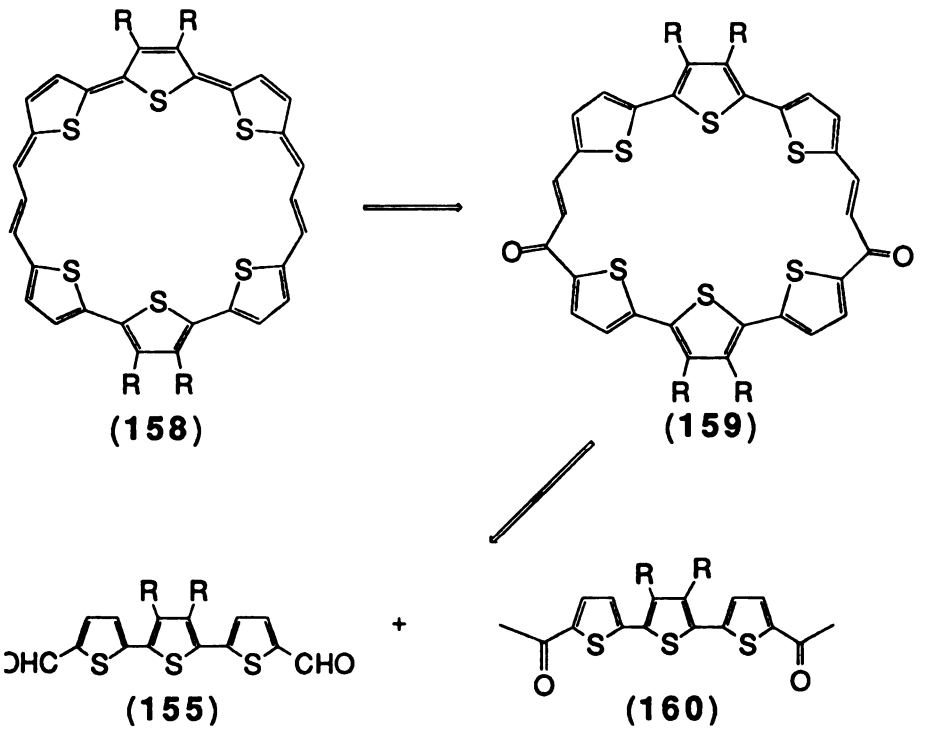
(158)





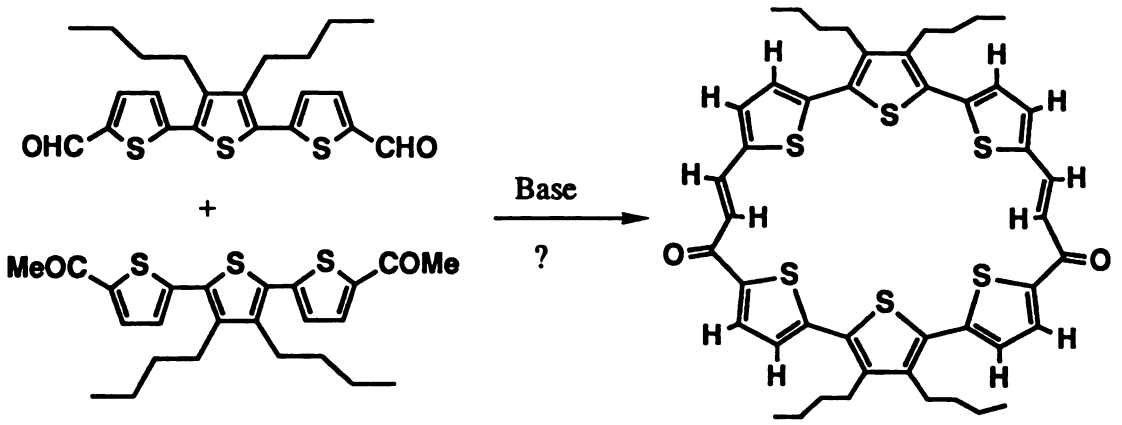
Retrosynthetic analysis suggests that one of the approaches to synthesize compound **158** might be from the unknown macrocyclic ketone **159**, and the preparation of compound **159** might be by the condensation of 5,5"-bisformyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**155**) with 5,5"-bisacetyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**160**) (Scheme 3-12).

Scheme 3-12



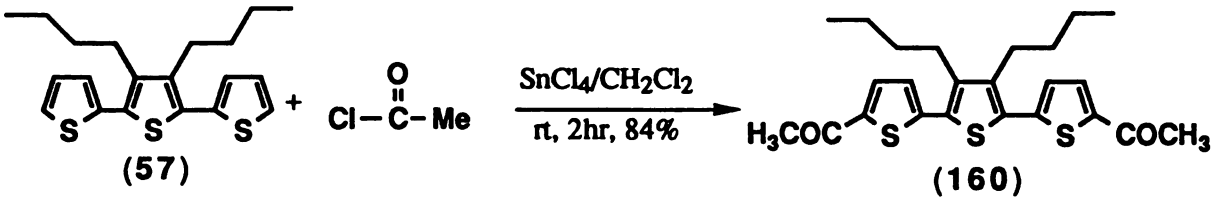
By this strategy, one of the key steps is to synthesize the unknown macroketone **159** by condensation of 5,5"-bisformyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**155**) with 5,5"-bisacetyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**160**). Therefore, part of my effort has been involved in the synthesis of macrocyclic ketone **159** (Scheme 3-13).

Scheme 3-13



The 5,5"-bisacetyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**160**) has been synthesized by a Lewis's acid catalyzed acetylation of 3',4'-dibutyl-2,2',5',2"-terthiophene with 84% yield (Scheme 3-14). 5,5"-Bisacetyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**160**) is a stable orange colored needle solid compound with a melting point of 96-96.5 °C (uncorrected). The UV-Vis maximum absorption is 395nm.

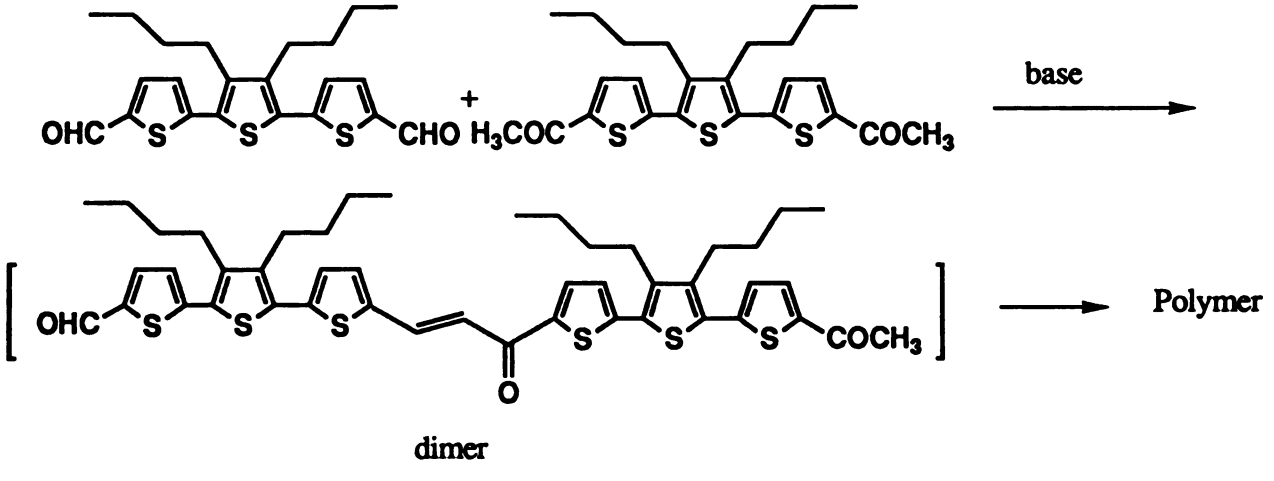
Scheme 3-14



Condensation of the 5,5"-bisacetyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**160**) with the 5,5"-bisformyl-3',4'-dibutyl-2,2',5',2"-

terthiophene(**155**) has been attempted in several different conditions(NaOEt/EtOH, Na_2CO_3/EtOH and NaH/DMSO). Unfortunately, the only product isolated was polymeric materials. There was no trace of cyclization products isolated by flash column chromatography. It seems that the condensation reaction of 5,5"-bisacetyl-3',4'-dibutyl-2,2',5',2"-terthiophene and 5,5"-bisformyl-3',4'-dibutyl-2,2',5',2"-terthiophene is a step wise reaction. The two ends hardly react at the same time. When one end of 5,5"-bisacetyl-3',4'-dibutyl-2,2',5',2"-terthiophene reacts with one end of the 5,5"-bisformyl-3',4'-dibutyl-2,2',5',2"-terthiophene a rigid dimeric compound formed which make the cyclization of the other ends difficult (Scheme 3-15).

Scheme 3-15



dimer

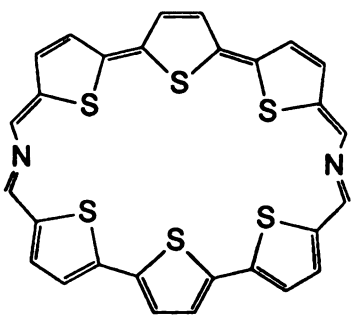
The failure for the synthesis of the macrocyclic ketone by the condensation of 5,5"-bisacetyl-3',4'-dibutyl-2,2',5',2"-terthiophene with the 5,5"-bisformyl-3',4'-dibutyl-2,2',5',2"-terthiophene made us

to search for an alternate route to the synthesis of macrocyclic compound **158**.

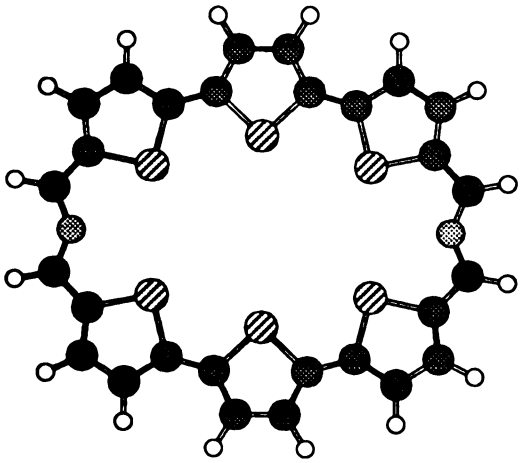
3.4 Synthesis of A New Hexathiophene Macrocyclic Compound

Another macrocyclic compound which is interesting to us is the new macrocyclic compound **161**. Molecular mechanic calculation shows it is an aromatic compound with 30 π-electrons. MM2 molecular modeling shows that it has a perfect planar structure. The tetrahedral angles are calculated all less than 0.5°. The bond distances and bond angles are shown in **161d** and **161e** of Figure 3-19.

Figure 3-19

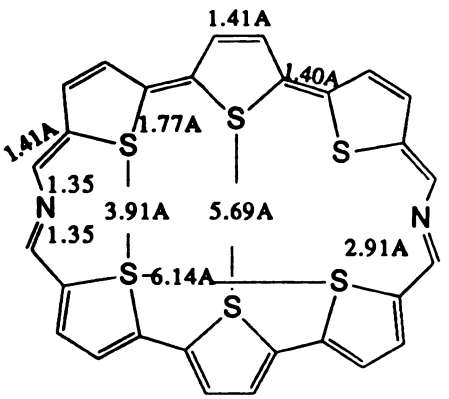


161a

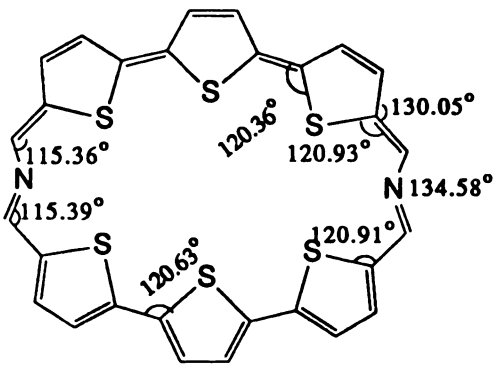


161b

161c



161d

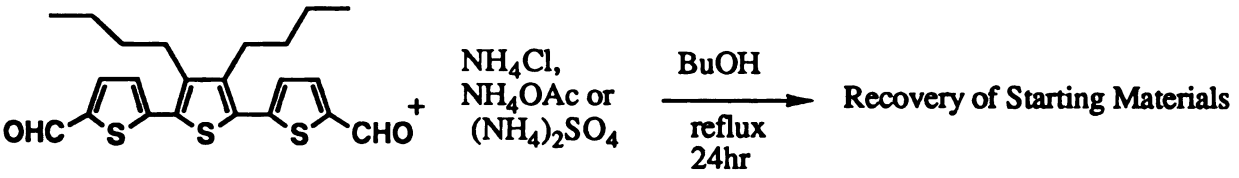


161e

The first attempt at the synthesis of this new compound was on the condensation of 5,5"-bisformyl-3,4-3',4'-dibutyl-2,2',5',2"-terthiophene with an ammonium salt. However, all the results showed the ammonium salt is not as reactive as expected. For example, refluxing 5,5"-bisformyl-3',4'-dibutyl-2,2',5',2"-terthiophene with 2.0 equivalents of ammonium chloride in butanol

for 24 hours gave 85% of recovery of starting 5,5"-bisformyl-3',4'-dibutyl-2,2',5',2"-terthiophene. Extension of reaction time to 3 days leads to the formation of some intractable tarry materials with the recovery of 30% of starting materials. The use of ammonium acetate or ammonium sulfate in place of ammonium chloride did not improve the results (Scheme 3-16).

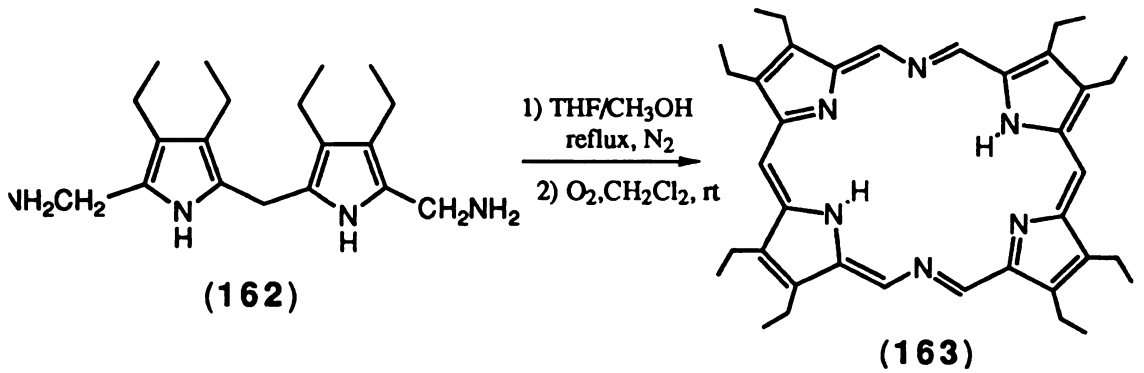
Scheme 3-16



(155)

Condensation of the bismethylene amine was thought as an alternate route and it had been used by Dolphin and coworkers[89] for the synthesis of porphocyanine(163) by the self condensation of 5,5'-bis(aminomethyl)dipyrrylmethane(162) (Scheme 3-17). Some of research efforts was involved in the synthesis of the unknown macrocyclic compound 161 by the self condensation of 5,5"-bis(aminomethyl)-3',4'-dibutyl-2,2',5',2"terthiophene(164) (Scheme 3-18).

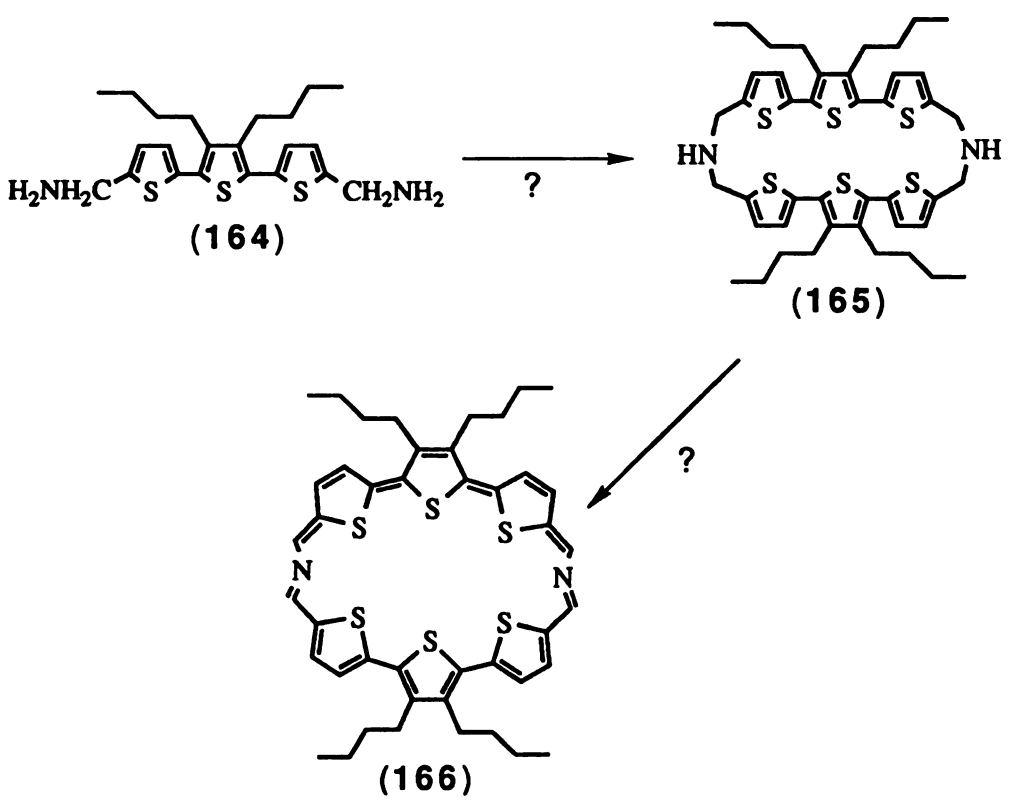
Scheme 3-17



(162)

(163)

Scheme 3-18



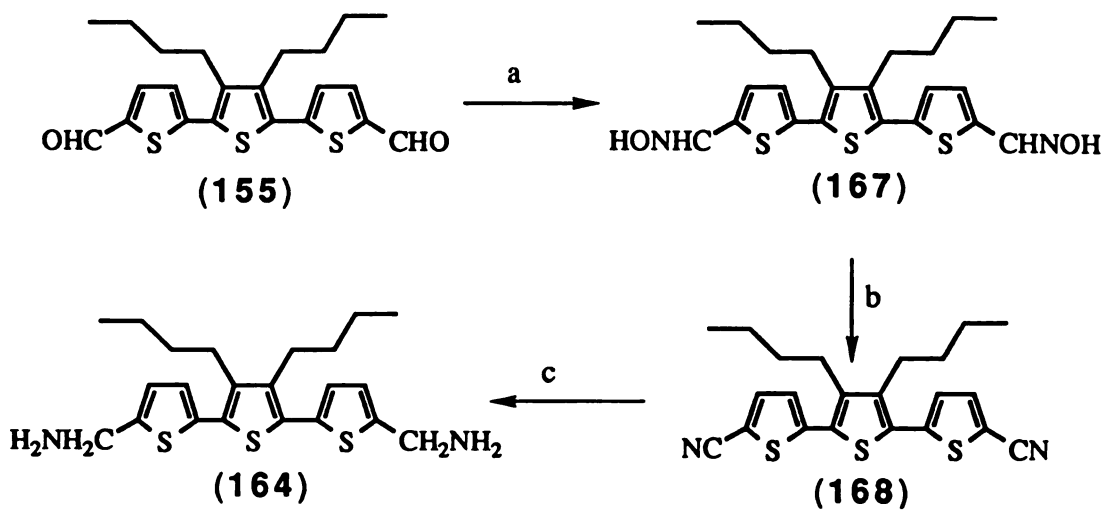
(164)

(165)

(166)

5,5"-Bis(aminomethyl)-3',4'-dibutyl-2,2',5',2"-terthiophene has been synthesized in three steps in an overall yield of 59% (Scheme 3-19).

Scheme 3-19

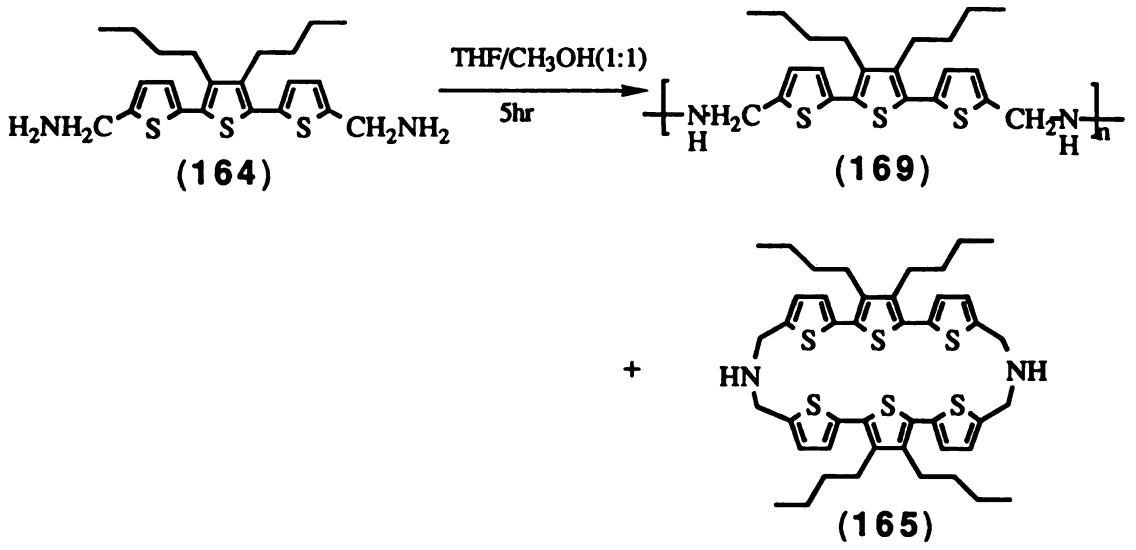


a, NH_2OH, EtOH; b, Ac_2O; c, $LiAlH_4$, THF

5,5''-Bis(aminomethyl)-3',4'-dibutyl-2,2',5',2''-terthiophene **164** is an orange oil which solidified when cooled in a refrigerator. The solid looks like wax and it is difficult to recrystalize. When treated with dilute HCl/H_2O solution a dark-orange crystal formed which can be purified by recrystalization from ethanol.

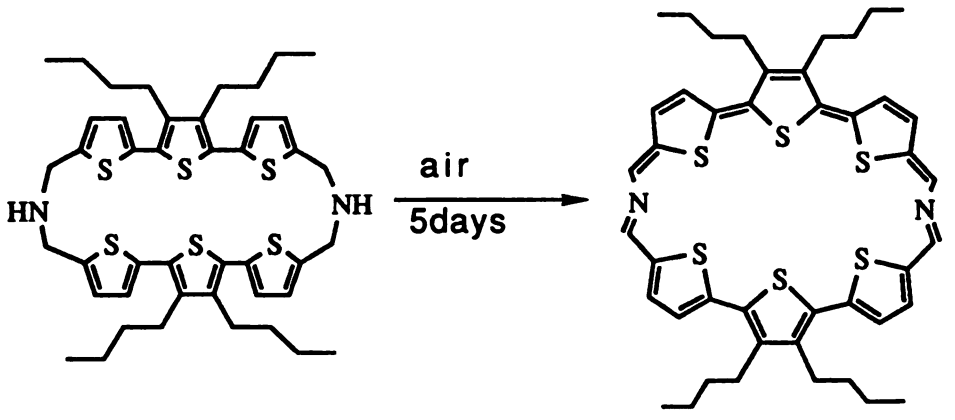
When 5,5''-bis(aminomethyl)-3',4'-dibutyl-2,2',5',2''-terthiophene was refluxed in THF/CH_3OH (1:1) for 5 hours under N_2, one of the products isolated is thought to be the high molecular weight polymeric material because it shows very dark-colored and low solubility (yield 45%). The other products are wax-like solids which was thought to be a mixture of low molecular weight polymer and some cyclized macrocycles (yield 41%) (Scheme 3-20).

Scheme 3-20



Air oxidation of the low molecular portion followed by double column chromatography and recrystalization from CH_2Cl_2/hexane gave the macrocyclic compound **166** in low yield (1.5%). Compound **166** is a purple luster crystal with a melting point of 254-255 °C (uncorrected). The UV-Vis maximum absorption is at 483nm.

Scheme 3-21



Structurally, compound **166** is an azaannulene with 30 π-electrons. By Huckel rule it is an aromatic compound and should exhibit diamagnetic ring current in ^{1}H-NMR spectrum. However, our experiments showed that the diamagnetic ring current is very small because the chemical shifts of protons in compound **166**, 8.21 (s, 4H), 7.54 (d, J=4.4Hz, 4H) and 7.38(d, 4.4Hz, 4H) ppm. This low diamagnetic ring current is inconsistent with the prediction of aromatic nature of this compound. This might be correspondent to a nonplanar structure. Further research on elucidation of the structure of this compound is still necessary.

Conclusions

(1). Studies of the influence of heteroatom such as S, N, etc. on the properties of conductive polymers are very important for search of low bandgap organic conductors. In the studies of C=N double bound influences on the properties of conducting polymers, it has been shown that the incorporation of thiazolo[4,5-d]thiazole can lower the bandgap. In order confirm this effect, several new mixed thiophene oligomers containing thiazolo[4,5-d]thiazole have been synthesized and UV-Vis and other spectroscopic properties have been studied.

(2). 1,4-Diketones are important intermediate compounds for the syntheses of thiophenes, pyrroles, furans and other heterocyclic compounds. In the search of efficient and practical methods for the syntheses of 1,4-diketones, it has been demonstrated that 1,4-diketones can be synthesized by the oxidative coupling of trimethylsilyl enol ethers with ceric ammonium nitrate (CAN). This method has been shown to be a practical method for the syntheses of a variety of 1,4-diketones.

$VOCl_3$/Pyridine has been shown to be a new and efficient oxidation reagent for the syntheses of 1,4-diketones via oxidative coupling of trimethylsilyl enol ethers. The reaction time is shorter compared with that using ceric ammonium nitrate as oxidation reagent.

(3). 1,3,4-Thiadiazoles based conductive polymers are important compounds which are stable at high temperature. During the research of syntheses of mixed thiophene oligomers and polymers which contain 1,3,4-thiadiazole, an efficient and practical method of one step synthesis of 2,5-diary-1,3,4-thiadiazoles has been discovered. The application of this method has been shown by the syntheses of several new mixed thiophene, furan and pyrrole oligomers which contain 1,3,4-thiadiazole. UV-Vis and other spectroscopic properties of these new compounds have been also studied. And UV-Vis spectra show that 1,3,4-thiadiazole increases the bandgap.

(5). A new hexathiophene macrocycle which contains C=N bound has been synthesized in low yield (1.5%). ^{1}H-NMR shows there is not much aromatic property of this compound, which is inconsistent with the predictions of Huckel rule and MM2 calculation. Further research on the structure of this new compound is necessary.

Experimental Section

General:

Pentane, hexane and petroleum ether were dried by distillation over $CaCl_2$, discarded the first 10% forerun and stored in 500ml glass-stoppered bottles. Toluene was dried by distillation under argon over sodium-benzophenone ketyl. Triethylamine was dried by distillation under argon over calcium hydride. Ethanol was dried by distillation over magnesium. Acetonitrile was dried by distillation from calcium hydride and fractionated from P_2O_5 and stored over activated molecular sieves 3A in 100ml bottles. Dichloromethane and chloroform were dried by distillation over calcium hydride and redistillation from P_2O_5. Tetrahydrofuran was dried by distillation over calcium hydride and redistillation from potassium under argon. N,N-Dimethylformamide(DMF) was dried by stirring overnight with CaO and vacuum distillation (the first 10% forerun was discarded).

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained on a Varian Gemini 300 MHz and/or Varian VXR 500 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) using the residual solvent proton resonance as the internal reference (acetone, 2.04; acetonitrile, 1.93; chloroform, 7.24; dichloromethane, 5.32; DMSO, 2.49; methanol, 3.30; tetrahydrofuran, 1.73). ^{1}H-NMR data are

reported as follows: chemical shift multiplicity (s, singlet; br s, broad singlet; d, doublet, dd, doublet of doublets; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), number of protons. ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a Varian Gemini (75.4 MHz) spectrometer. Chemical shift values are reported in parts per million using the solvent peak as the internal reference (acetone, 29.8; chloroform, 77.0; DMSO, 39.5; methanol, 49.0; tetrahydrofuran, 67.4). Infrared(IR) spectra were obtained from Nujol mull for solids or neat for liquids and recorded on a Nicolet IR/42 spectrometer. Ultraviolet and visible (UV-vis) spectra were recorded in dichloromethane or chloroform solution by using 1cm matched quartz cells with a Shimadzu UV-160 spectrophotometer. EI mass spectra were obtained on a TRIO-1 spectrometer with EI at 70 eV. High resolution mass spectra were obtained on JOEL HX110 high resolution mass spectrometer in the mass facility at the department of biochemistry at Michigan State University.

Synthesis of N,N'-dicyano(2-thienyl)methyl phenylene diamine(13b):

To a mixture of 2-thiophenecarboxaldehyde(2.24 g, 20.0 mmole), sodium cyanide(1.33 g, 20.5 mmole) and p-phenylene diamine(1.08 g, 10.0 mmole) in 20 ml of dry benzene was added 5 ml of acetic acid. The reaction mixture was stirred at room temperature for 24 hours and than quenched with saturated sodium bicarbonate solution. The yellow precipitate was filtered, washed with 5% aqueous sodium bicarbonate solution (2x20ml),

water(2x20 ml) and saturated sodium chloride solution (2x15 ml). The resulting yellow solid was dried in vacuum. Flash column chromatographic purification from silica gel with ethyl acetate/hexanes (35/65) as eluent gave **13b** as a white solid. Yield 3.15 g (90%). m.p. 157-158 °C (uncorrected). ^{1}H-NMR(DMSO-d_6): 7.61(d, J=5.7Hz, 2H), 7.30(d, J=1.0Hz, 2H), 7.08(dd, J=5.7Hz, 1.0Hz, 2H), 6.77(s, 4H), 6.36(d, 11.3Hz, 2H), 6.14(d, 11.3Hz, 2H); ^{13}C-NMR(DMSO-d_6): 45.6, 115.7, 119.1, 122.3, 126.3, 126.9, 127.0, 138.6; EI-MS, m/z(relative intensity): 350(M^+, 1.06), 296(base), 147(14.1), 134(5.63), 115(19.5), 102(7.04), 77(5.41).

Synthesis of 2,5-di(2-thienyl)thiazolo[5,4-d]thiazole(**21b**):

a) A mixture of 2-thiophenecarboxaldehyde (2.0 g, 17.8 mmole) and dithiooximide(1.0 g, 8.3 mmole) was heated neat at 170 °C under N_2 for 30 min. The dark red reaction mixture was cooled to room temperature and the solid product was collected by filtration, washed with ice-cold methanol(2x10ml) and dried in vacuum. Column chromatographic purification over silica gel with ethyl acetate/hexanes(35/65) as eluent followed by crystallization from ethyl acetate/ethanol(50/50) gave the 2,5-di(2-thienyl)thiazolo[5,4-d]thiazole(**21b**) as yellow needles. Yield, 1.04 g (41%). m.p.=236-238 °C (uncorrected). ^{1}H-NMR(DMSO-d_6): 7.58(dd, J=4.1Hz, 1.0Hz, 2H), 7.47(dd, J=5.4Hz, 1.0Hz, 2H), 7.12(dd, J=5.4Hz, 4.1Hz); EI-MS, m/z(relative intensity): 308(M^++2, 11.2), 307(M^++1, 10.7), 306(M^+, 61.4), 153(4.35), 127(4.38), 109(14.9), 90(13.8),

89(5.04), 88(base), 69(7.73), 45(11.4); UV-Vis(maximum absorption): 388nm ($CHCl_3$).

b) A mixture of 2-thiophene carboxaldehyde (6.0 g, 53.3 mmole) and dithiooximide (1.0 g, 8.3 mmole) in 10 ml DMF was heated at reflux under N_2 for 40 minutes. The dark red reaction mixture was cooled and the precipitated product was collected by filtration, washed with water (2x20 ml) and ice-cold methanol (3x10 ml). Then the yellow solid was dried in vacuum. Column chromatographic purification over silica gel with ethyl acetate/hexanes(35/65) as eluent followed by crystallization from ethyl acetate/ethanol (50/50) gave the product as yellow needles. Yield, 2.45 g (32%). All the spectroscopic characterizations are the same as those from method(a).

Synthesis of 2,5-di(2-furanyl)thiazolo[5,4-d]thiazole(**21c**):

a) A mixture of 2-furan carboxaldehyde (1.21 g, 12.6 mmole) and dithiooximide (0.74 g, 6.17 mmole) was heated neat at 170 °C under N_2 for 35min. The dark red reaction mixture was cooled and the solid product had been collected by filtration, washed with ice-cold MeOH (2x10 ml) and dried in vacuum. Column chromatographic purification over silica gel with ethyl acetate/hexanes(35/65) as eluent followed by crystallization from ethyl acetate/ethanol(50/50) gave the product as yellow needles. Yield, 0.63 g (37%). m.p.=240-241 °C (lit.[5] 238-240 °C). ^{1}H-NMR(DMSO-d_6): 7.55(dd, J=3.4Hz, 0.7Hz,

2H), 7.08(dd, J=4.8Hz, 0.7Hz, 2H), 6.59(dd, J=4.8Hz, 3.4Hz); EI-MS, m/z(relative intensity): 276(M^++2, 10.4), 275(M^++1, 15.8), 274(M^+, base), 246(7.55), 137(12.3), 111(14.9), 93(11.4), 88(98.8), 64(9.32), 39(11.0). UV-Vis(maximum absorption): 380nm ($CHCl_3$).

b) A mixture of 2-furan carboxaldehyde (3.0 g, 31.3 mmole) and dithiooximide(1.8 g, 15.0 mmole) in 10 ml DMF was heated at reflux under N_2 for 30 min. The dark red reaction mixture was cooled and the precipitated product was collected by suction filtration, washed with water(2x20ml) and ice-cold methanol (3x10 ml). Then the yellow solid was dried in vacuum. Column chromatographic purification over silica gel with ethyl acetate/hexanes (35/65) as eluent followed by crystallization from ethyl acetate/ethanol (50/50) gave the product as yellow needles. Yield, 1.29 g (31%). All the physical properties are the same as those from method (a).

Synthesis of 2,5-di(1-phenylsulfonyl-2-pyrryl)thiazolo[5,4-d]thiazole(26):

A mixture of 1-phenylsulfonyl-2-pyrrole carboxaldehyde(25) (2.35 g,10.0 mmole) and dithiooximide (0.59 g, 4.9 mmole) in 20 ml DMF was heated at reflux under N_2 for 40 min. The dark red reaction mixture was cooled and the precipitated product was collected by suction filtration, washed with water (2x20 ml) and ice-cold methanol (3x10 ml). Then the solid was dried in vacuum to give a

tan solid as crude product. Column chromatographic purification over silica gel with ethyl acetate/hexanes/CH_2Cl_2 (50/20/30) as eluent followed by crystallization from ethyl acetate/ethanol/hexanes (60/25/15) gave the product as light tan solid. Yield, 2.70 g (25%). m.p. 276-278 °C (decomp.). ^{1}H-NMR(DMSO-d_6): 7.90(d, J=7.4Hz, 4H), 7.76(dd, J=4.1Hz, 1.6Hz, 2H), 7.50-7.39(m, 6H), 7.07(dd, J=3.9Hz, 1.6Hz, 2H), 6.32(dd, J=4.1Hz, 3.9Hz, 2H). ^{13}C-NMR(DMSO-d_6): 159.1, 148.7, 137.9, 133.0, 132.4, 129.5, 128.1, 127.8, 123.2, 110.1; high resolution mass spectra: calcd for $C_{24}H_{16}N_4O_4S_4$, 552.648, found: 552.496.

Synthesis of 2,5-di(2-pyrryl)thiazolo[5,4-d]thiazole(**21a**):

A mixture of 2,5-di(1-phenylsulfonyl-2-pyrryl)thiazolo[5,4-d]thiazole(**26**)(1.5 g, 2.7 mmole), sodium hydroxide (0.3 g, 7.5 mmole) in 100ml of ethanol was refluxed for 12 hours. Then the reaction mixture was cooled and the ethanol was removed by a rotary evaporator. The residue was extracted with chloroform (4x25 ml) and the combined chloroform was washed with water (3x15 ml) and saturated aqueous sodium chloride solution (20 ml), dried over sodium sulfate. The organic solvent was removed by a rotary evaporator to give a dark brown solid as the crude product. Column chromatographic purification over silica gel with ethyl acetate/hexanes (25/75) as the eluent followed by crystallization from ethyl acetate/ethanol (50/50) gave the product as yellow powders. Yield, 0.53 g (72%). m.p.=251-253 °C

(uncorrected). ^{1}H-NMR(DMSO-d_6): 12.1(s, br., 2H), 7.21(m, 2H), 7.01(m, 2H), 6.28(m, 2H); ^{13}C-NMR(DMSO-d_6): 153.8, 147.6, 132.8, 128.4, 120.1, 110.3; high resolution mass spectra: calculated for $C_{12}H_8N_4S_2$, 272.344, found: 272.391; UV-Vis maximum absorption: 391nm ($CHCl_3$).

Synthesis of 2,5-di(2-thienyl)-1,3,4-thiadiazole(**33**):

A mixture of 2-thiophene carboxaldehyde (3.6 g, 32.1 mmole), hydrazine monohydrate (0.77 g, 15.5 mmole), elemental sulfur (1.1 g, 34.4 mmole), and tributylamine (0.3 g, 1.6 mmole) in 20ml of propylene glycol was heated at 130 °C for 48 hours. Then, the reaction mixture was cooled to room temperature and the precipitate was filtered by suction filtration. The solid was washed with ice-cold methanol (3x20 ml) and carbon disulfide (3x15 ml); dried in vacuum to give a yellow solid as crude product. Column chromatographic purification over silica gel with ethyl acetate/hexanes (35/65) as eluent followed by crystallization from ethanol/ethyl acetate (50/50) gave the 2,5-di(2-thienyl)-1,3,4-thiadiazole(**33**) as yellow needles. Yield: 3.49 g (90%). m.p.=155-156 °C (uncorrected). ^{1}H-NMR(DMSO-d_6): 7.86(dd, J=5.6Hz, 1.3Hz, 2H), 7.77(dd, J=4.2Hz, 1.3Hz, 2H), 7.24(dd, J=5.6Hz, 4.2Hz, 2H); ^{13}C-NMR(DMSO-d_6): 160.3, 130.5, 130.3, 130.1, 128.1; EI-MS, m/z(relative intensity): 252(M^++2, 18.2), 251(M^++1, 19.1), 250(M^+, base), 221(5.6), 178(7.7), 177(10.5), 143(8.9), 142(7.3), 141(84.8), 129(11.6), 127(94.9), 114(9.3), 109(23.4), 97(15.2), 96(11.6), 83(21.1), 82(11.5), 71(18.1), 70(13.5),

69(57.6), 58(14.3), 45(31.4), 39(19.7). UV-Vis(maximum absorption): 342nm ($CHCl_3$).

Synthesis of 2,5-di(2-furanyl)-1,3,4-thiadiazole(**34**):

A mixture of 2-furan carboxaldehyde (3.0 g, 31.2 mmole), hydrazine monohydrate(0.78 g, 15.6 mmole), elemental sulfur (1.1 g, 34.4 mmole), and tributylamine (0.3 g, 1.6 mmole) in 20ml of propylene glycol was heated at 110°C for 5 days. Then, the light brown colored reaction mixture was cooled to room temperature and the precipitate was filtered by suction filtration. The solid was washed with ice-cold methanol (3x20 ml) and carbon disulfide (3x15 ml); dried in vacuum. Column chromatographic purification of the crude product from silica gel with ethyl acetate/CH_2Cl_2/hexanes (20/10/70) as the eluent followed by crystallization from ethanol/ethyl acetate (50/50) gave the 2,5-di(2-furanyl)-1,3,4-thiadiazole(**34**) as yellow needles. Yield: 0.51 g (15%). m.p.=148-151 °C. ^{1}H-NMR(DMSO-d_6): 8.01(dd, J=2.3, 0.6Hz, 2H), 7.38(dd, J-4.0Hz, 0.6Hz, 2H), 6.79(dd, J=4.0Hz, 2.3Hz, 2H); ^{13}C-NMR(DMSO-d_6): 156.0, 145.9, 143.6, 112.4, 112.0; EI-MS, m/z(relative intensity): 218(M^+, base), 189(4.7), 125(70.4), 111(15.6), 93(17.4).

Synthesis of 2,5-di(1-phenylsulfonyl-2-pyrryl)-1,3,4-thiadiazole(**38**):

A mixture of 1-phenylsulfonyl-2-pyrrole carboxaldehyde(**25**) (3.1 g, 13.2 mmole), hydrazine monohydrate(0.33 g, 6.6 mmole), elemental sulfur (1.54 g, 48.1 mmole) and tributylamine (0.2 g, 1.1 mmole) in 50 ml propylene glycol was kept at 120 °C with magnetic stirring for two days. The dark colored reaction mixture was cooled and the precipitate was collected by suction filtration. The solid was washed with ice-cold methanol (3x20 ml) and carbon disulfide (3x15 ml); dried in vacuum. Column chromatographic purification of the crude product over silica gel with ethyl acetate/CH_2Cl_2/hexanes (40/10/50) as the eluent followed by crystallization from ethanol gave a light tan solid product. Yield: 2.0 g (61%). m.p. 240-242 °C (decomp.). ^{1}H-NMR(DMSO-d_6): 7.86(dd, J=7.3Hz, 2.0Hz, 4H), 7.72(dd, J=4.1Hz, 1.5Hz, 2H), 7.45-7.21(m, 6H), 7.01(dd, J=3.9Hz, 1.5Hz, 2H), 6.29(dd, J=4.1Hz, 3.9Hz, 2H); ^{13}C-NMR(DMSO-d_6): 160.4, 142.3, 138.7, 132.9, 128.6, 128.0, 124.6, 118.1; high resolution mass spectra, calculated for $C_{22}H_{16}N_4O_4S_3$, 496.568; Found: 496.497.

Synthesis of 2,5-di(2-pyrryl)-1,3,4-thiadiazole(**36a**):

A mixture of 2,5-di(1-phenylsulfonyl-2-pyrryl)-1,3,4-thiadiazole(**38**) (2.0 g, 4.0 mmole), sodium hydroxide (0.6 g, 15.0 mmole) in 50 ml of ethanol was kept at reflux for 12 hours. Then the reaction mixture was cooled and the ethanol was removed by a rotary evaporator. The residue was extracted with chloroform

(4x25 ml) and the combined chloroform was washed with water (3x15 ml) and saturated NaCl, dried over sodium sulfate. The organic solvent was removed by a rotary evaporator to give a dark brown solid as the crude product. Column chromatographic purification over silica gel with ethyl acetate/hexanes (25/75) as the eluent followed by crystallization from ethyl acetate/ethanol (50/50) gave the product as yellow needles. Yield: 0.77 g (89%). m.p.=168-169 °C (uncorrected). ^{1}H-NMR($CDCL_3$): 12.0(s, br., 2H), 7.09(m, 2H), 6.98(m, 2H), 6.30(m, 2H); ^{13}C-NMR($CDCL_3$): 158.1, 137.8, 129.1, 124.0, 114.5; high resolution mass spectra, calculated. for $C_{10}H_8N_4S$, 216.264, found, 216.304. UV-Vis maximum absorption: 351nm ($CHCl_3$).

Synthesis of 2,5-di(4-pyridyl)-1,3,4-thiadiazole(**48**):

A mixture of 4-pyridine carboxaldehyde (3.4 g, 31.8 mmole), hydrazine monohydrate (0.79 g, 15.8 mmole), elemental sulfur (1.95 g, 61.0 mmole), and tributylamine (0.3 g, 1.6 mmole) in 40 ml of propylene glycol was heated at 130 °C for 48 hours. Then, the reaction mixture was cooled to room temperature and the precipitate was filtered by suction filtration. The solid was washed with ice-cold methanol (3x20 ml) and carbon disulfide (3x15 ml); dried in vacuum to give a yellow solid as crude product. Column chromatographic purification over silica gel with ethyl acetate/hexanes (40/60) as eluent followed by crystallization from ethanol/ethyl acetate (50/50) gave the 2,5-di(4-pyridyl)-1,3,4-thiadiazole(**48**) as yellow plates. Yield: 2.88 g (76%). m.p.=229-230 °C (decomp.). ^{1}H-NMR(DMSO-d_6):

8.82(d, J=7.7Hz, 2H), 8.02(d, J=7.7Hz, 2H); ^{13}C-NMR(DMSO-d_6): 166.8, 150.4, 135.4, 120.9; EI-MS, m/z(relative intensity): 242(M^++2, 6.35), 241(M^++1, 18.4), 240(M^+, base), 138(4.66), 137(7.94), 136(92.3), 122.0(35.1), 109(13.1), 104(32.2), 78(58.0), 77(15.6), 63(11.6), 51(53.0), 50(16.3). UV-Vis(maximum absorption): 292nm ($CHCl_3$).

Synthesis of 2,5-di(6-methyl-2-pyridyl)-1,3,4-thiadiazole(**50**):

A mixture of 6-methyl-2-pyridine carboxaldehyde (3.8 g, 31.4 mmole), hydrazine monohydrate (0.78 g, 15.6 mmole), elemental sulfur (2.0 g, 62.5 mmole), and tributylamine (0.31 g, 1.7 mmole) in 30ml of propylene glycol was heated at 130 °C for 48 hours. Then, the reaction mixture was cooled to room temperature and the precipitate was filtered by suction filtration. The solid was washed with ice-cold methanol (3x20 ml) and carbon disulfide (3x15 ml); dried in vacuum to give a yellow solid as crude product. Column chromatographic purification over silica gel with ethyl acetate/hexanes (30/70) as eluent followed by crystallization from ethanol/ethyl acetate (50/50) gave the 2,5-di(3-methyl-2-pyridyl)-1,3,4-thiadiazole(**50**) as yellow needles. Yield: 3.43 g (82%). m.p.=156-157 °C (uncorrected). ^{1}H-NMR(DMSO-d_6): 8.09(d, J=8.4Hz, 2H), 7.91(t, J=8.5Hz, 2H), 7.44(d, J=8.5Hz, 2H), 2.56(s, 6H); ^{13}C-NMR(DMSO-d_6): 170.6, 158.3, 146.9, 137.4, 125.0, 116.9, 23.2; EI-MS, m/z(relative intensity): 268(M^+, 9.33), 258(26.8), 256(73.7), 194(8.76), 192(33.2), 162(12.9), 160(56.2), 130(12.8), 128(65.9), 96(30.4), 66(13.6), 64(base). UV-Vis(maximum absorption):264nm, 282nm(shoulder) ($CHCl_3$).

Synthesis of 2,5-diphenyl-1,3,4-thiadiazole(**52a**):

A mixture of benzaldehyde (5.2 g, 49 mmole), hydrazine monohydrate (1.2 g, 24 mmole), elemental sulfur (3.0 g, 94 mmole), and tributylamine (0.5 g, 1.7 mmole) in 30ml of propylene glycol was heated at 130 °C for 48 hours. Then, the reaction mixture was cooled to room temperature and the precipitate was filtered by suction filtration. The solid was washed with ice-cold methanol (3x20 ml) and carbon disulfide (3x15 ml); dried in vacuum to give a yellow solid as crude product. Column chromatographic purification over silica gel with ethyl acetate/hexanes (35/65) as eluent followed by crystallization of the crude product from ethanol/ethyl acetate (50/50) gave the 2,5-diphenyl-1,3,4-thiadiazole(**52a**) as white plates. Yield: 4.74 g (83%). m.p.=138-139 °C (uncorreted). ^{1}H-NMR(DMSO-d_6): 8.02(m, 4H), 7.58(m, 6H); ^{13}C-NMR(DMSO-d_6): 167.3, 130.9, 128.9, 128.8, 127.0; EI-MS, m/z(relative intensity): 240(M^++2, 7.21), 239(M^++1, 20.8), 238(M^+, 96.5), 165(8.66), 137(7.02), 136(12.9), 135(base), 121(50.0), 119(6.13), 108(10.2), 103(24.0), 91(10.8), 89(5.94), 78(7.92), 77(90.6), 76(14.4), 63(11.0), 51(28.0); UV-Vis(maximum absorption): 307nm ($CHCl_3$).

Synthesis of 2,5-di(4-methoxylphenyl)-1,3,4-thiadiazole(**52b**):

A mixture of 4-methoxylbenzaldehyde (3.3 g, 24.3 mmole), hydrazine monohydrate(0.6 g, 12.0 mmole), elemental sulfur (1.63 g, 50.9 mmole), and tributylamine (0.4 g, 2.2 mmole) in 30 ml of

propylene glycol was heated at 130 °C for 48 hours. Then, the reaction mixture was cooled to room temperature and the precipitate was filtered by suction filtration. The solid was washed with ice-cold methanol (3x20 ml) and carbon disulfide (3x15 ml); dried in vacuum to give a yellow solid as crude product. Column chromatographic purification over silica gel with ethyl acetate/hexanes (35/65) as eluent followed by crystallization from ethanol/ethyl acetate (50/50) gave the 2,5-di(4-methoxylphenyl)-1,3,4-thiadiazole(**52b**) as yellow solid. Yield: 3.0 g (84%). m.p.=159-160 °C (uncorrected). ^{1}H-NMR(DMSO-d_6): 7.95(dd, J=7.6Hz, 2.2Hz, 4H), 7.12(dd, J=7.6Hz, 2.2Hz, 4H), 3.86(s, 6H); ^{13}C-NMR (DMSO-d_6): 166.3, 160.9, 129.2, 121.7, 114.9; EI-MS, m/z (relative intensity): 300(M^++2, 9.56), 299(M^++1, 26.4), 298(M^+, base), 165(44.4), 152(10.8), 151(59.6), 150(69.3), 149(10.6), 136(13.0), 133(32.0), 122(28.2), 108(12.2), 90(13.4),. 76(9.11), 63(11.8); UV-Vis(maximum absorption): 329nm ($CHCl_3$).

Synthesis of 2,5-di(4-hydroxylphenyl)-1,3,4-thiadiazole(**52c**):

A mixture of 4-hydroxylbenzaldehyde (2.8 g, 23.0 mmole), hydrazine monohydrate (0.58 g, 11.6 mmole), elemental sulfur (1.6 g, 23.0 mmole), and tributylamine (0.4 g, 2.1 mmole) in 25 ml of propylene glycol was heated at 130 °C for 48 hours. Then, the reaction mixture was cooled to room temperature and the precipitate was filtered by suction filtration. The solid was washed with ice-cold methanol (3x20 ml) and carbon disulfide (3x15 ml); dried in vacuum to give a yellow solid as crude product. Column chromatographic

purification over silica gel with ethyl acetate/hexanes (35/65) as eluent followed by crystallization from ethanol/ethyl acetate (50/50) gave the 2,5-di(4-hydroxylphenyl)-1,3,4-thiadiazole(**52c**) as yellow solid. Yield:2.63 g (84%). m.p.=206-208 °C (uncorrected). ^{1}H-NMR(DMSO-d_6): 10.2(s, 2H), 7.81(dd, J=7.5, 2.3Hz, 4H), 6.92(dd, J=7.5, 2.3Hz, 4H); ^{13}C-NMR (DMSO-d6): 166.0, 160.2, 129.3, 120.7, 116.2; EI-MS, m/z(relative intensity): 272(M^++2, 6.43), 271(M^++1, 18.2), 270(M^+, base), 153(5.67), 152(10.4), 151(95.7), 139(3.10), 140(4.50), 137(56.8), 122(5.80), 120(7.33), 119(43.2), 105(5.22), 93(6.43), 65(37.4), 64(11.9), 63(10.9), 51(12.1), 39(16.2); UV-Vis (maximum absorption): 349nm ($CHCl_3$).

Synthesis of 1-(2-thienyl)ethenyl-1-oxytrimethylsilane(**67a**):

In a 250 ml round bottom flask was charged 5.1 g dry NaI (35.2 mmole) and 100 ml dry acetonitrile. The mixture was stirred at room temperature until all the sodium iodide dissolved. Then 3.8 g of trimethylchlorosilane (35.2 mmole) was added by a syringe and the mixture was stirred at room temperature for about 10 minutes. Then 3.56 g of dry triethyl amine (35.2 mmole) was added to the flask at one batch with vigorously stirring, followed by dropwise addition of 3.9 g of thienyl methyl ketone (31.0 mmole) in 5 ml dry acetonitrile. The brown-colored mixture was continually stirred at room temperature overnight. Then, 100 ml 5% sodium bicarbonate solution was added. The organic layer was separated and the aqueous layer was extracted with ether (3x20 ml). The combined

ether extracts were washed with 2% ice-cold HCl (2x20 ml), H_2O (2x20 ml) and saturated NaCl (30 ml), dried with Na_2SO_4. Removal of the solvent with rotary evaporator gave a brown oil as a crude product. ^{1}H-NMR shows that it contains 97.3% silyl enol ether (**67a**) and 2.7% of the starting ketone. Yield: 5.83 g (96% based on the conversion of 2-thienyl methyl ketone). ^{1}H-NMR($CDCl_3$): 7.15(d, J=4.9Hz, 2H), 6.97(t, J=4.9Hz, 1H), 4.83(d, J=2.1Hz, 1H), 4.33(d, J=2.1Hz, 1H), 0.29(s, 9H).

Synthesis of 1-(2-thienyl)propenyl-1-oxytrimethylsilane(**67b**):

In a 250 ml round bottom flask was charged 6.5 g dry NaI (44.8 mmole) and 150 ml dry acetonitrile. The mixture was stirred at room temperature until all the NaI dissolved. Then 4.86 g of trimethylchlorosilane (44.8 mmole) was added by a syringe and the mixture stirred at room temperature for about 10 minutes. Then 4.53 g of dry Et_3N (44.8 mmole) was added to the flask at one batch with vigorously stirred, followed by dropwise addition of 4.9 g of thienyl ethyl ketone (35 mmole) in 10 ml dry acetonitrile. The brown-colored mixture was continually stirred at room temperature overnight. Then, 50 ml of 5% $NaHCO_3$ was added. The organic layer was separated and the aqueous layer was extracted with ether (3x30 ml). The combined ether extracts were washed with 2% ice-cold HCl (2x25 ml), H_2O (2x25 ml) and saturated NaCl (30 ml), dried with Na_2SO_4. Removal of the solvent with a rotary evaporator gave a brown oil as the crude product. ^{1}H-NMR shows that it contains 95.0%

silyl enol ether(**67**b) and 5.0% of the starting ketone. Yield: 6.92 g (94.7% based on the conversion of 2-thienyl ethyl ketone). ^{1}H-NMR($CDCL_3$): 7.09(dd, J=4.3Hz, 0.9Hz), 7.01(dd, J=3.7Hz, 0.9Hz, 1H), 6.92(dd, J=4.3Hz, 3.7Hz, 1H), 5.31(q, J=7.7Hz, 1H), 1.70(d, J=7.8Hz, 3H), 0.21(s, 9H).

Synthesis of 1-(2-thienyl)butenyl-1-oxytrimethylsilane(**67**c):

In a 500 ml round bottom flask was charged 9.0 g dry NaI (62.1 mmole) and 150 ml dry acetonitrile. The mixture was stirred at room temperature until all the NaI dissolved. Then 6.73 g of trimethylchlorosilane (62.1 mmole) was added by a syringe and the mixture was stirred at room temperature for about 10 minutes. Then 6.37 g of dry triethyl amine (63.0 mmole) was added to the flask at one time with vigorously stirring, followed by dropwise addition of 8.47 g of thienyl propyl ketone (55.0 mmole) in 10 ml dry acetonitrile. The brown-colored mixture was continually stirred at room temperature overnight. Then 100 ml of 5% $NaHCO_3$ was added and the organic layer was separated. The aqueous layer was extracted with ether (3x30 ml) and the combined ether layers were washed with 2% ice-cold HCl (2x30 ml), H_2O (2x30 ml) and saturated NaCl (35 ml), dried with Na_2SO_4. Removal of the solvent in rotary evaporator gave a brown oil as the crude product. ^{1}H-NMR shows that it contains 94.9% silyl enol ether(**67**c) and 5.1% of the starting ketone. Yield: 11.38 g (92.8% based on the conversion of 2-thienyl

propyl ketone). ^{1}H-NMR($CDCl_3$): 7.10(dd, J=4.4Hz, 0.9Hz, 1H), 7.03(dd, J=3.6Hz, 0.9Hz, 1H), 6.91(dd, J=4.4Hz, 3.6Hz, 1H), 5.32(t, J=7.7Hz, 1H), 2.14(m, 2H), 1.37(t, J=7.8Hz, 3H), 0.25(s, 9H).

Synthesis of 1-(2-thienyl)hexenyl-1-oxytrimethylsilane(**67d**):

In a 500 ml round bottom flask was charged 10.7 g dry NaI (73.8 mmole) and 250 ml dry acetonitrile. The mixture was stirred at room temperature until all the NaI dissolved. Then 8.0 g of trimethylchlorosilane (73.8 mmole) was added by a syringe and the mixture was stirred at room temperature for about 10 minutes. Then 7.46 g of dry triethyl amine (73.8 mmole) was added to the flask at one time with vigorously stirring, followed by dropwise addition of 12 g of 2-thienyl pentyl ketone (66.0 mmole) in 20 ml dry acetonitrile. The brown-colored mixture was continually stirred at room temperature overnight. Then, 100ml of 5% $NaHCO_3$ aqueous solution was added and the organic layer was separated. The aqueous layer was extracted with ether (3x30 ml), and the combined ether layers were washed with 2% ice-cold HCl (2x50 ml), H_2O (2x50 ml) and saturated NaCl (50 ml); dried with Na_2SO_4. Removal of the solvent by a rotary evaporator gave a brown oil as the crude product. ^{1}H-NMR shows that it contains 95.7% silyl enol ether(**67d**) and 4.3% of the starting ketone. Yield: 15.7 g (95% based on the conversion of 2-thienyl pentyl ketone). ^{1}H-NMR($CDCl_3$): 7.13(dd, J=4.2Hz, 1.1Hz, 1H), 7.05(dd, J=3.6Hz, 1.1Hz, 1H), 6.97(dd, J=4.0Hz,

3.6Hz, 1H), 5.26(t, J=8.0Hz, 1H), 2.18(m, 2H), 1.49-1.34(m, 4H), 0.95(t, J=7.8Hz, 3H), 0.27(s, 9H).

Synthesis of 1-(2-thienyl)octenyl-1-oxytrimethylsilane(**67e**):

In a 500 ml round bottom flask was charged 8.7 g dry NaI (60.0 mmole) and 200 ml dry acetonitrile. The mixture was stirred at room temperature until all the NaI dissolved. Then 6.5 g of trimethylchlorosilane (60.0 mmole) was added by a syringe and the mixture was stirred at room temperature for about 10 minutes. Then 6.06 g of dry triethyl amine (60.0 mmole) was added to the flask at one time with vigorously stirring, followed by dropwise addition of 11.1 g of thienyl heptyl ketone (52.8 mmole) in 20ml dry acetonitrile. The brown-colored mixture was continually stirred at room temperature overnight. Then, 100 ml of 5% $NaHCO_3$ aqueous solution was added and the organic layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined ether layers were washed with 2% ice-cold HCl (2x40 ml), H_2O (2x40 ml) and saturated NaCl (50 ml); dried with Na_2SO_4. Removal of solvent with a rotary evaporator gave a brown oil as the crude product. ^{1}H-NMR shows that it contains 96.0% of the silyl enol ether(**67e**) and 4.0% of the starting ketone. Yield: 13.95 g (94.5% based on the conversion of 2-thienyl heptyl ketone). ^{1}H-NMR($CDCl_3$): 7.06(dd, J=4.4Hz, 0.8Hz, 1H), 7.00(dd, J=3.7Hz, 0.8Hz, 1H), 6.95(dd, J=4.4Hz, 3.7Hz, 1H), 5.28(t, J=7.8Hz, 1H), 2.16(m, 2H), 1.79(m, 2H), 1.39(m, 6H), 0.94(t, J=7.7Hz, 3H), 0.24(s, 9H).

Synthesis of 1,4-di(2-thienyl)-1,4-butanedione(**60a**):

a) Synthesis of 1,4-di(2-thienyl)-1,4-butanedione(**60a**) by the oxidation of 2-thienyl silyl ethenol ether(**67b**) with ceric ammonium nitrate.

A silyl enol ether(**67a**) (4.3 g, 21.7 mmole) in 20 ml dry acetonitrile was added dropwise with vigorously stirring to a mixture of 12 g ceric ammonium nitrate (22.0 mmole), 3.77 g $NaHCO_3$ (44.7 mmole) and 150 ml dry acetonitrile in a 500 ml round bottom flask under N_2. After addition the reaction was continued at room temperature for four more hours and then quenched with water. The product was extracted with chloroform (4x30 ml) and the combined chloroform layers were washed with water (2x30 ml) and dried with Na_2SO_4. Removal of the solvent by rotary evaporator gave a light-brown residue as the crude 1,4-diketone. Column chromatographic purification over silica gel with ethyl acetate/hexanes (25/75) as the eluent followed by crystallization from hexanes/CH_2Cl_2 (90/10) gave the product as colorless needles. m.p. 131-132 °C (uncorrected) (lit.[73e] 130-131 °C). Yield: 1.50 g (55% based on the starting ketone). ^{1}H-NMR($CDCl_3$): 7.81(dd, J=4.3Hz, 1.2Hz, 2H), 7.64(dd, J=5.1Hz, 1.2Hz, 2H), 7.13(dd, J=5.1Hz, 4.3Hz), 3.38(s, 4H); ^{13}C-NMR($CDCl_3$): 190.0, 143.3, 133.2, 131.7, 127.7, 32.7; EI-MS, m/z(relative intensity): 250(M^+, 11.7), 139(17.0), 113(5.99), 112(7.66), 111(base), 83(8.51), 55(4.22), 39(20.7).

b) Synthesis of 1,4-di(2-thienyl)-1,4-butanedione(**60a**) by the oxidation of 2-thienyl silyl ethenol ether(**67a**) with vanadium trichloride oxide

Silyl enol ether(**67a**) 1.85 g (with 94.5% pure) (9.3 mmole) in 5 ml dry acetonitrile was added to a mixture of 1.62 g of $VOCl_3$ (1.0 e.q) in 20 ml dry acetonitrile at room temperature under N_2. After the addition, the reaction was continued for 15 more minutes. Then, the dark-red mixture was quenched with 10ml ice-cold 5% $NaHCO_3$ aqueous solution. The organic layer was separated and the aqueous layer extracted with ether (2x10 ml). The combined organic layers were washed with H_2O (2x10 ml), saturated NaCl (10 ml) and dried with Na_2SO_4. Removal of the solvent gave a light brown colored crude 1,4-diketone. Column chromatographic purification over silica gel with ethyl acetate/hexanes (25/75) as the eluent followed by crystallization from hexanes gave the expected 1,4-diketone(**60a**) as colorless needles. All the physical properties are the same as those from method(a). Yield: 0.57 g (49% based on the starting ketone).

Synthesis of 2,3-dimethyl-1,4-di(2-thienyl)-1,4-butanedione(**60b**):

a) Synthesis of 2,3-dimethyl-1,4-di(2-thienyl)-1,4-butanedione(**60b**) by the oxidation of thienyl silyl-1-propenol ether(**67b**) with ceric ammonium nitrate.

A silyl enol ether(**67b**) (6.15 g, 29.0 mmole) in 20 ml dry acetonitrile was added dropwise with vigorously stirring to a mixture of 16 g ceric ammonium nitrate (29.3 mmole), 5.02 g $NaHCO_3$ (59.6 mmole) and 200 ml dry acetonitrile in a 500 ml round bottom flask under nitrogen. After the addition of the reagents, the reaction was continued at room temperature for four more hours. Then the reaction was quenched with water. The product was extracted with chloroform (4x30 ml). The combined organic layers were washed with water (3x30 ml) and dried with Na_2SO_4. Removal of the solvent by a rotary evaporator gave a light-brown residue as the crude product. ^{1}H-NMR shows that it is a mixture of diasteromers. Column chromatographic purification over silica gel with ethyl acetate/hexanes (20/80) as the eluent followed by crystallization from hexanes gave one of the diastereomers as colorless needdles. m.p.=124-126 °C (uncorrected) (lit.[73c)]123-125 °C). Continuing eluting with the same solvent gave the other isomers. Total yield of 1,4-diketones: 2.53 g (65% based on the starting ketone). ^{1}H-NMR($CDCl_3$): 7.84(dd, J=4.3Hz, 1.2Hz, 2H), 7.69(dd, J=5.4Hz, 1.2Hz, 2H), 7.17(dd, J=5.4, 4.3Hz, 2H), 3.76(m, 2H), 1.17(d, J=7.3Hz, 6H); ^{13}C-NMR($CDCl_3$): 196.4, 146.0, 134.6, 132.6, 128.3, 49.8, 30.1; EI-MS, m/z(relative intensity): 278(M^+, 6.96), 263(1.36), 167(9.80), 153(9.02), 140(75.3), 128(11.5), 111(base), 83(38.0), 68(5.98), 56(34.1), 45(19.4), 39(69.0);

b) Synthesis of 2,3-dimethyl-1,4-di(2-thienyl)-1,4-butanedione(**60**b) by the oxidation of thienyl silyl-1-propenol ether(**67**b) with vanadium trichloride oxide

A silyl enol ether(**67**b) 2.26 g (with 97.1% pure) (10.6 mmole) in 5 ml dry MeCN was added to a mixture of 1.84 g of $VOCl_3$ (1.0 e.q) in 20 ml dry acetonitrile at room temperature under N_2. After the addition, the dark-red mixture was quenched with 20 ml ice-cold 5% $NaHCO_3$ aqueous solution. The organic layer was separated and the aqueous layer was extracted with ether (2x20 ml). The combined organic layers were washed with H_2O (2x20 ml), saturated NaCl (20 ml) and dried with sodium sulfate. Removal of the solvent gave a light brown colored crude 1,4-diketone as a mixture of diasteromers; Column chromatographic purification over silica gel with ethyl acetate/hexanes (20/80) as the eluent followed by crystallization from hexanes gave the expected 1,4-diketone. All the physical properties are the same as those from method(a). Total yield: 0.84 g 57% based on the starting ketone).

Synthesis of 2,3-diethyl-1,4-di(2-thienyl)-1,4-butanedione(**60**c):

a) Synthesis of 2,3-diethyl-1,4-di(2-thienyl)-1,4-butanedione(**60**c) by the oxidation of thienyl silyl-1-butenol ether(**67**c) with ceric ammonium nitrate.

A silyl enol ether(67c) (10.0 g, 44.2 mmole) in 30 ml dry acetonitrile was added dropwise with vigorously stirring to a mixture of 24 g ceric ammonium nitrate (44.0 mmole), 7.53 g $NaHCO_3$(89.3 mmole) and 200 ml dry acetonitrile in a 500 ml round bottom flask under nitrogen. After the addition the reaction was continued at room temperature for four more hours and then quenched with water. The product was extracted with chloroform (4x30 ml) and the combined organic layers were washed with water (3x20 ml) and dried with sodium sulfate. Removal of the solvent by a rotary evaporator gave a light-brown residue as the crude 1,4-diketone. ^1H-NMR shows it is a mixture of diastereomers. Column chromatographic purification over silica gel with ethyl acetate/hexanes (18/82) followed by crystallization from hexanes/CH_2Cl_2 (85/15) and recrystallization from hexanes gave one of the diastereomers as colorless needdles. Yield: 1.4 g. m.p.=147-149 °C (uncorrected). Continued eluting with the same solvent gave the other isomers. Total yield of 1,4-diketones: 4.06 g (60% based on the starting ketone). ^1H-NMR($CDCl_3$): 7.84(dd, J=4.3, 1.2Hz), 7.70(dd, J=5.5, 1.2Hz, 2H), 7.16(dd, J=5.5, 4.3Hz), 3.75(m, 2H), 1.64(m, 2H), 1.35(m, 2H), 1.07(t, J=7.9Hz, 6H); ^{13}C-NMR($CDCl_3$): 196.5, 146.1, 134.6, 132.5, 128.4, 49.7, 31.2, 27.0; EI-MS, m/z(relative intensity): 306(M^+, 1.96), 277(1.87), 195(8.90), 167(9.74), 154(47.3), 111(base), 83(17.4). IR:

b) Synthesis of 2,3-diethyl-1,4-di(2-thienyl)-1,4-butanedione(**60c**) by the oxidation of thienyl silyl-1-butenol ether(**67c**) with vanadium trichloride oxide

A silyl enol ether(**67c**) 2.08 g (with 96.4% pure) (9.2 mmole) in 5 ml dry acetonitrile was added to a mixture of 1.60 g of $VOCl_3$ (1.0 e.q.) in 20 ml dry acetonitrile at room temperature under N_2. After the addition, the dark-red mixture was quenched with 10 ml ice-cold 5% $NaHCO_3$ aqueous solution. The organic layer was separated and the aqueous layer was extracted with ether (2x20 ml). The combined organic layers were washed with H_2O (2x20 ml), saturated NaCl (20 ml) and dried with sodium sulfate; Removal of the solvent gave a light brown colored crude 1,4-diketone as a mixture of diastereomers; Column chromatographic purification over silica gel with ethyl acetate/hexanes (18/82) as the eluent followed by crystallization from hexanes/CH_2Cl_2 (85/15) and recryctallization from hexanes gave one of the diastereoisomers as colorless needle. All the physical properties are the same as those from method (a).Total yield of 1,4-diketones: 0.73 g (52% based on the starting ketone).

Synthesis of 2,-3-dibutyl-1,4-di(2-thienyl)-1,4-butanedione(**60d**):

a) Synthesis of 2,-3-dibutyl-1,4-di(2-thienyl)-1,4-butanedione(**60d**) by the oxidation of thienyl silyl-1-hexenol ether(**67d**) with ceric ammonium nitrate.

A silyl enol ether(67d) (16.0 g, 62.5 mmole) in 30ml dry acetonitrile was added dropwise with vigorously stirring to a mixture of 36 g ceric ammonium nitrate (66.0 mmole), 11.3 g $NaHCO_3$ (134 mmole) and 250 ml dry acetonitrile in an one litter round bottom flask under nitrogen. After the addition the reaction was continued at room temperature for four more hours and then quenched with water. The product was extracted with chloroform (4x30 ml) and the combined organic solvent was washed with water (3x20 ml) and dried with sodium sulfate. Removal of the solvent by a rotary evaporator gave a light-brown residue as the crude product. ^{1}H-NMR shows it is a mixture of diasteromers. Column chromatographic purification over silica gel with ethyl acetate/hexanes (10/90) as the eluent followed by crystallization from hexanes/CH_2Cl_2 (85/15) and recrystallization from hexanes gave one of the diastereomers as colorless needdle. m.p. 161-162 °C (uncorrected). Further eluting with the same solvent gave the other diastereomers. Total yield of 1,4-diketones: 7.58 g (67% based on the starting ketone). ^{1}H-NMR($CDCl_3$): 7.84(dd, J=4.3, 1.2Hz, 2H), 7.71(dd, J=5.2, 1.2Hz, 2H), 7.16(dd, J=5.2, 4.3Hz, 2H), 3.72(d, 2H), 1.56-1.79(m, 2H), 1.29-1.44(m, 2H), 1.04-1.19(m, 8H), 0.68(t, 6H); ^{13}C-NMR($CDCl_3$): 196.6, 146.3, 134.7, 132.6, 128.4, 50.7, 32.2, 29.7, 22.7, 13.7; EI-MS m/z (relative intensity): 41(6.69), 43(2.59), 55(14.14), 69(3.44), 83(8.71), 85(2.05), 97(5.74), 111(100), 126(10.48), 139(37.37), 149(9.34), 154(5.8), 168(20.33), 181(12.12), 182(46.97), 195(26.52), 251(2.56), 306(1.25), 362(M^+, 0.62).

b) Synthesis of 2,3-dibutyl-1,4-di(2-thienyl)-1,4-butanedione(**60**d) by the oxidation of thienyl silyl-1-hexenol ether(**67**d) with vanadium trichloride oxide

A silyl enol ether(**67**d) 1.74 g (with 95.2% pure) (6.6 mmole) in 5 ml dry acetonitrile was added to a mixture of 1.15 g of $VOCl_3$ (1.0 e.q) in 20 ml dry acetonitrile at room temperature under N_2. After the addition, the dark-red mixture was quenched with 10ml ice-cold 5% $NaHCO_3$ aqueous solution. The organic layer was separated and the aqueous layer was extracted with ether (2x10 ml). The combined organic layers were washed with H_2O (2x10 ml), saturated NaCl (10 ml) and dried with sodium sulfate; Removal of the solvent gave a light brown colored crude 1,4-diketone. ^{1}H-NMR shows it is a mixture of diastereomers. Column chromatographic purification over silica gel with ethyl acetate/hexanes (10/90) as the eluent followed by crystallization and recrystallization gave one of the diastereomers as colorless needles. m.p.=161-162 °C(uncorrected). All other physical properties are the same as those from method (a). Total yield of 1,4-diketones: 0.65 g (55% based on the starting ketone).

Synthesis of 2,3-dihexyl-1,4-di(2-thienyl)-1,4-butanedione(**60**e):

a) Synthesis of 2,3-dihexyl-1,4-di(2-thienyl)-1,4-butanedione(**60**e) by the oxidation of thienyl silyl-1-octenol ether(**67**e) with ceric ammonium nitrate.

A silyl enol ether(**67e**) (8.0 g, 28.4 mmole) in 30 ml dry acetonitrile was added dropwise with vigorously stirring to a mixture of 15.5 g ceric ammonium nitrate (28.4 mmole), 4.86 g $NaHCO_3$ (57.6 mmole) and 150 ml dry MeCN in a 500 ml round bottom flask under nitrogen. After the addition the reaction was continued at room temperature for four more hours and then quenched with water. The product was extracted with chloroform (4x30 ml) and the combined organic solvent was washed with water and dried over sodium sulfate. Removal of the solvent by a rotary evaporator gave a light-brown residue as the crude product. ^{1}H-NMR shows it is a mixture of diastereomers. Column chromatographic purification over silica gel with ethyl acetate/hexanes (8/92) as the eluent followed by crystallization from hexanes/CH_2Cl_2 (90/10) and recrystallization from hexanes gave one of the diastereomers as colorless needles. m.p.=127-128 °C (uncorrected). Further eluting with the same solvent gave the other diastereomers. Total yield of 1,4-diketones: 3.70 g (63% based on the starting ketone). ^{1}H-NMR($CDCl_3$): 7.82(2H, dd, J=4.3, 1.2Hz), 7.69(2H, dd, J=5.2, 1.2Hz), 7.16(2H, dd, J=5.2, 4.3Hz), 3.70(2H, m), 1.65-1.68(2H, m), 1.35-1.38(2H, m), 0.96-1.18(16H, m), 0.73(6H, t, J=7.9Hz); ^{13}C-NMR($CDCl_3$): 196.5, 146.3, 134.7, 132.6, 128.4, 50.7, 32.6, 31.4, 29.3, 27.6, 22.4, 13.9; EI-MS, m/z(relatively intensity): 418(M^+, 0.37), 334(1.45), 307(2.00), 223(16.71), 210(29.14), 196(12.15), 139(37.57), 126(19.20), 111(base), 55(14.92).

b) Synthesis of 2,3-dihexyl-1,4-di(2-thienyl)-1,4-butanedione(**60e**) by the oxidation of thienyl silyl-1-octenol ether(**67e**) with vanadium trichloride oxide

A silyl enol ether(**67e**) 2.35 g (with 96.0% pure) (8.3 mmole) in 5 ml dry acetonitrile was added to a mixture of 1.45 g of $VOCl_3$ (1.0 e.q) in 20 ml dry acetonitrile at room temperature under N_2. After the addition, the dark-red mixture was quenched with 10 ml ice-cold 5% $NaHCO_3$ aqueous solution. The organic layer was separated and the aqueous layer was extracted with ether (2x10 ml). The combined organic layers were washed with H_2O (2x20 ml), saturated NaCl (20 ml) and dried with sodium sulfate. Removal of the solvent gave a light brown colored crude 1,4-diketones as a mixture of the diastereomers. Column chromatographic purification over silica gel with ethyl acetate/hexanes (8/92) as the eluent followed by crystallization from hexanes/CH_2Cl_2 (90/10) and recrystallization from hexanes gave one of the diastereomers as colorless needles. All the physical properties are the same as those from method (a). Total yield of 1,4-diketones: 0.93 g (54% based on the starting ketone).

Synthesis of 3',4'-dimethyl-2,2',5',2"-terthiophene(**57b**)

A mixture of 2,3-dimethyl-1,4-di(2-thienyl)-1,4-butanedione (2.0 g, 7.2 mmole), P_2S_5 (1.5 g, 6.7 mmole) (or Lawesson's reagent 1.8 g, 4.5 mmole), $NaHCO_3$ (2.5 g, 29.8 mmole) and dry toluene (50 ml) was refluxed gently for two hours. The resulting dark mixture

was then cooled to room temperature; poured into water (100 ml) and extracted with CH_2Cl_2 (3x20 ml). The combined organic layers were washed with water (2x30 ml), saturated NaCl (30 ml) and dried with magnesium sulfate. Removal of the solvent in vacuo gave a dark-green residue as the crude product. Column chromatographic purification over silica gel with hexanes/ether (95/5) as the eluent and crystallization from hexanes gave the 3',4'-dimethyl-2,2',5',2"-terthiophene(57b) as a light yellow solid. Yield: 1.67 g (84%). m.p.=127-128 °C (uncorrected) (lit.[73d] 128 °C). ^{1}H-NMR($CDCl_3$): 7.32(dd, J=5.7, 1.3Hz, 2H), 7.17(dd, J=4.0, 1.3Hz, 2H), 7.09(dd, J=5.7, 4.0Hz, 2H), 2.28(s, 6H); ^{13}C-NMR(CDCl3): 135.9, 134.7, 132.8, 127.0, 125.5, 124.9, 13.7; EI-MS, m/z(relative intensity): 278(M^++2, 15.3), 277(M^++1, 19.5), 276(M^+, base), 275(M^+-1, 11.6), 261(13.1), 243(7.06), 227(7.1), 184(5.32), 139(4.11), 138(12.1), 127(14.2), 121(11.1), 109(5.65), 97(5.44), 69(10.5), 45(12.6); UV-Vis(maximum absorption): 335nm ($CHCl_3$).

Synthesis of 3',4'-diethyl-2,2',5',2"-terthiophene(57c)

A mixture of 2,3-diethyl-1,4-di(2-thienyl)-1,4-butanedione (3.06 g, 10.0 mmole), P_2S_5 (2.2 g, 9.83 mmole) (or Lawesson's reagent 3.4 g, 8.5 mmole), $NaHCO_3$ (3.5 g, 41.7 mmole) and dry toluene (60 ml) was refluxed gently for two hours. The dark reaction mixture was then cooled to room temperature; poured into water (100 ml) and extracted with CH_2Cl_2 (3x20 ml). The combined organic layers were washed with water (2x30 ml), saturated NaCl (30 ml) and dried

with magnesium sulfate. Removal of the solvent in vacuo gave a dark-green residue as the crude product. Column chromatographic purification over silica gel with hexanes as eluent followed by crystallization from hexanes gave the 3',4'-diethyl-2,2',5',2"-terthiophene(57c) as a light yellow solid. Yield: 2.67 g (88%). m.p.=97-98 °C (uncorrected). ^{1}H-NMR($CDCl_3$): 7.32(dd, J=5.7, 1.3Hz, 2H), 7.16(dd, J=4.1, 1.3Hz, 2H), 7.10(dd, J=5.7, 4.1Hz, 2H), 2.61(q, J=8.0Hz, 4H), 1.59(t, J=8.0Hz, 6H). ^{13}C-NMR($CDCl_3$): 138.2, 135.7, 131.6, 127.2, 125.6, 124.5, 30.1, 13.8; EI-MS, m/z(relative intensity): 306(M^++2, 14.7), 305(M^++1, 20.9), 304(M^+, base), 277(12.8), 271(5.1), 241(5.71), 139(4.56), 138(11.8), 127(15.1). UV-Vis(maximum absorption): 335nm ($CHCl_3$).

Synthesis of 3',4'-dibutyl-2,2',5',2"-terthiophene(57d)

A mixture of 2,3-dibutyl-1,4-di(2-thienyl)-1,4-butanedione (2.5 g, 6.9 mmole), P_2S_5 (1.4 g, 6.25 mmole) (or Lawesson's reagent 1.65 g, 4.1 mmole), $NaHCO_3$ (3.6 g, 42.9 mmole) and dry toluene (50 ml) was refluxed gently for two hours. The reaction mixture was then cooled to room temperature and poured into water (100 ml). The product was extracted with CH_2Cl_2 (3x30 ml) and the combined organic layers were washed with water (2x30 ml), saturated NaCl (30 ml) and dried with magnesium sulfate. Removal of the solvent in vacuo gave a dark-green residue as the crude product. Column chromatographic purification over silica gel with hexanes as

eluent followed by crystallization from hexanes gave the 3',4'-dibutyl-2,2',5',2"-terthiophene(**57d**) as a light yellow solid. Yield: 2.01 g (81%). m.p.= 36-37 °C (uncorrected) (lit.[53] 36-36.5 °C). ^{1}H-NMR($CDCl_3$): 7.32(dd, J=5.7, 1.4Hz, 2H), 7.16(dd, J=4.0, 1.4Hz, 2H), 7.07(dd, J=5.7, 4.0Hz, 2H), 2.72(t, J=8.8Hz, 4H), 1.57(m, 4H), 1.46(m, 4H), 0.97(t, J=8.8Hz, 6H); ^{13}C-NMR(CDCl3): 140.0, 135.7, 129.7, 127.4, 125.8, 125.3, 32.9, 27.8, 23.0, 13.9; EI-MS, m/z(relative intensity): 362(M^++2, 18.1), 361(M^++1, 24.7), 360(M^+, base), 319(7.09), 318(12.2), 317(39.6), 303(13.7), 277(8.88), 276(13.9), 275(56.1), 273(8.65), 260(9.76), 242(11.4), 241(10.9), 227(10.8), 138(5.18), 127(19.2); UV-Vis(maximum absorption): 335nm ($CHCl_3$).

Synthesis of 3',4'-dihexyl-2,2',5',2"-terthiophene(**57e**)

A mixture of 2,3-dihexyl-1,4-di(2-thienyl)-1,4-butanedione (2.18 g, 5.2 mmole), P_2S_5 (1.2 g, 5.36 mmole) (or Lawesson's reagent 1.5 g, 3.75 mmole), $NaHCO_3$ (3.5 g, 41.7 mmole) and dry toluene (50 ml) was refluxed gently for two hours. The dark reaction mixture was then cooled to room temperature and poured into water (100 ml). The product was extracted with CH_2Cl_2 (3x30 ml) and the combined organic layers were washed with water (2x30 ml), saturated NaCl (30 ml) and dried with magnesium sulfate. Removal of the solvent in vacuo gave a dark-green residue as the crude product. Column chromatographic purification over silica gel with hexanes as the eluent followed by crystallization from hexanes gave the 3',4'-dihexyl-2,2',5',2"-terthiophene(**57e**) as a light yellow oil.

Yield: 1.92 g (89%). ^{1}H-NMR($CDCl_3$): 7.33(dd, J=5.8, 1.4Hz, 2H), 7.17 (dd, J=4.0, 1.4Hz, 2H), 7.09(dd, J=5.8, 4.0Hz, 2H), 2.73(t, J=8.1Hz, 4H), 1.61(m, 4H), 1.45(m, 4H), 1.36(m, 8H), 0.94(t, J=7.8Hz, 6H). ^{13}C-NMR($CDCl_3$): 140.1, 135.7, 129.6, 127.3, 125.8, 125.2, 31.5, 30.7, 29.6, 28.1, 22.6, 14.1; EI-MS, m/z(relative intensity): 416(M^+, base), 401(12.7), 400(56.1), 346(8.63), 345(33.7), 331(8.92), 289(5.90), 277(14.3), 276(18.7), 275(97.3), 261(9.12), 242(8.04), 227(6.57), 127(5.02), 43(10.3); UV-Vis(maximum absorption): 335nm ($CHCl_3$).

Synthesis of 3,4-dimethyl-2,5-di(2-thienyl)pyrrole(**61b**)

A mixture of 2,3-dimethyl-1,4-di(2-thienyl)-1,4-butanedione(**60b**) (1.57 g, 5.6 mmole), anhydrous NH_4OAc (1.54 g, 20.0 mmole), acetic anhydride (2.0 ml) in 50ml acetic acid was refluxed gently for 48 hours. Then the dark-red reaction mixture was cooled and the acetic acid/acetic anhydride was removed by vacuum distillation. The residue was extracted with ether (4x30 ml) and the combined ether layers were washed with 5% sodium bicarbonate solution (3x20 ml), water (2x20 ml), saturated NaCl (2x15 ml), and dried with sodium sulfate. The solvent was removed by a rotary evaporator. Column chromatographic purification over silica gel with hexanes/ether (95/5) as the eluent followed by crystallization from hexanes/CH_2Cl_2 (85/15) gave the 3,4-dimethyl-2,5-di(2-thienyl)pyrrole(**61b**) as a pale yellow solid. Yield: 1.01 g (75%). m.p.=132-133 °C (uncorrected). ^{1}H-NMR($CDCl_3$): 7.98 (s, br., 1H), 7.23 (m, 2H), 7.08-7.01 (m, 4H), 2.29 (s, 6H). ^{13}C-NMR($CDCl_3$):

135.4, 127.3, 123.4, 123.0, 122.7, 122.1, 14.4; EI-MS, m/z (relative intensity): 261 (M^++2, 10.1), 260 (M^++1, 17.1), 259 (M^+, base), 258 (M^+-1, 17.2), 244 (10.2), 147(5.76), 110 (7.15). UV-Vis (maxmum absorption): 345nm ($CHCl_3$).

Synthesis of 3,4-diethyl-2,5-di(2-thienyl)pyrrole(**61c**)

A mixture of 2,3-diethyl-1,4-di(2-thienyl)-1,4-butanedione(**60c**) (1.72 g, 5.6 mmole), anhydrous NH_4OAc (1.50 g, 19.5 mmole), acetic anhydride (2.0 ml) in 50 ml acetic acid was kept at gentle reflux for 48 hours. Then the dark-red reaction mixture was cooled and the acetic acid/acetic anhydride was removed by vacuum distillation. The residue was extracted with ether (4x30 ml) and the combined ether layers were washed with 5% sodium bicarbonate solution (3x20 ml), water (2x20 ml), saturated NaCl (2x15 ml) and dried with sodium sulfate. The solvent was removed by a rotary evaporator. Column chromatographic purifucation over silica gel with hexanes/ether (97/3) as eluent followed by crystallization from hexanes/CH_2Cl_2 (90/10) gave the 3,4-diethyl-2,5-bis(2-thienyl)pyrrole(**61c**) as a pale yellow solid. Yield: 1.20 g (74%). m.p.=103-104 °C (uncorrected). ^{1}H-NMR($CDCl_3$): 8.00(s, br., 1H), 7.22(d, J=5.3Hz, 2H), 7.10-7.02(m, 4H), 2.61(q, J=8.2Hz, 4H), 14.8(t, J=8.1Hz, 6H); ^{13}C-NMR($CDCl_3$): 135.6, 127.3, 123.2, 123.0, 122.7, 122.3, 31.0, 13.8; EI-MS, m/z(relative intensity): 289(M^++2, 10.6), 288(M^++1, 18,0), 287(M^+, base), 272(14.2), 258(9.3),

244(6.97), 147(6.81), 110(7.09); UV-Vis(maximum absorption): 345nm ($CHCl_3$).

Synthesis of 3,4-dibutyl-2,5-di(2-thienyl)pyrrole(**61d**)

A mixture of 2,3-dibutyl-1,4-di(2-thienyl)-1,4-butanedione(**60d**) (2.1 g, 5.8 mmole), anhydrous NH_4OAc (1.60 g, 20.8 mmole), acetic anhydride (2.0 ml) in 50 ml acetic acid was refluxed gently for 48 hours. Then, the dark-red reaction mixture was cooled and the acetic acid/acetic anhydride was removed by vacuum distillation. The residue was extracted with ether (4x30 ml) and the combined ether layers were washed with 5% sodium bicarbonate solution (3x20 ml), water (2x20 ml), saturated NaCl (2x15 ml) and dried with sodium sulfate. The solvent was removed by a rotary evaporator. Column chromatography purification over silica gel with hexanes as the eluent gave the 3,4-dibutyl-2,5-di(2-thienyl)pyrrole(**61d**) as a pale yellow solid. Yield: 1.60 g (80%). m.p.=47-48 °C (uncorrected). ^{1}H-NMR($CDCl_3$): 7.97(s, br., 1H), 7.21(d, J=5.4Hz, 2H), 7.08-7.02(m, 4H), 2.63(t, J=8.6Hz, 4H), 1.56(m, 4H), 1.45(m, 4H), 0.96(t, J=7.8Hz, 6H); ^{13}C-NMR($CDCl_3$): 135.5, 127.4, 123.3, 123.1, 122.8, 122.2, 33.5, 24.7, 23.0, 13.9; EI-MS, e/z(relative intensity): 345(M^++2, 10.4), 344(M^++1, 20.8), 343(M^+, base), 301(11.6), 300(50.3), 260(7.6), 259(15.5), 258(76.4), 256(13.2), 244(6.13), 17(5.05), 147(6.33), 129(13.0), 110(6.02), 43(5.05), 41(9.12); UV-Vis(maximum absorption): 345nm ($CHCl_3$).

Synthesis of 3,4-dihexyl-2,5-di(2-thienyl)pyrrole(**61e**)

A mixture of 2,3-dihexyl-1,4-di(2-thienyl)-1,4-butanedione (**60e**) (1.65 g, 3.9 mmole), anhydrous NH_4OAc (1.20 g, 15.6 mmole), acetic anhydride (2.0 ml) in 50 ml acetic acid was refluxed gently for 48 hours. Then the dark-red reaction mixture was cooled and the acetic acid/acetic anhydride were removed by vacuum distillation. The residue was extracted with ether (4x30 ml) and the combined ether layers were washed with 5% sodium bicarbonate solution (3x20 ml), water (2x20 ml), saturated NaCl (2x15 ml) and dried with sodium sulfate. The solvent was removed by a rotary evaporator. Column chromatographic purification over silica gel with hexanes as the eluent gave the 3,4-dihexyl-2,5-di(2-thienyl)pyrrole(**61e**) as a pale yellow solid. Yield: 1.26 g (81%). m.p.=31-32 °C(uncorrected). ^{1}H-NMR($CDCl_3$): 7.98(s, br., 1H), 7.22(d, J=5.4, 2H), 7.09-7.02(m, 4H), 2.67(t, J=8.2Hz, 4H), 1.59(m, 4H), 1.42(m, 4H), 1.34(m, 8H), 0.95(t, J=7.7Hz, 6H); ^{13}C-NMR($CDCl_3$): 135.7, 129.6, 124.0, 123.1, 122.8, 122.0, 31.8, 29.7, 29.0, 27.3, 22.1, 13.8; EI-MS, m/z(relative intensity): 401(M^++2, 10.9), 400(M^++1, 26.8), 399(M^+, base), 384(10.9), 329(28.7), 314(7.45), 258(67.8), 244(5.18), 147(6.51), 110(5.91); UV-Vis(maximum absorption): 345nm ($CHCl_3$).

Synthesis of 3,4-dimethyl-2,5-di(2-thienyl)furan(**62b**)

A solution of 2,3-dimethyl-1,4-di(2-thienyl)-1,4-butanedione(**60b**) (2.51 g, 9.03 mmole) in 30 ml acetic anhydride was kept in an acetone-dry-ice bath(-15 to -20°C) with magnetic stirring. Gaseous HCl was bubbled through this cold solution for 15 min and then the acetone-bath was removed and the reaction mixture was allowed to warm up to room temperature. The mixture was stirred at 85°C for 8 hours. Then the dark reaction mixture was cooled and acetic anhydride was removed by vacuum distillation. The residue was extracted with ether (4x30 ml) and the combined ether layers were washed with 5% sodium bicarbonate solution (3x20 ml), water (2x20 ml), saturated NaCl (2x15 ml) and dried with sodium sulfate. The solvent was removed by a rotary evaporator. Column chromatographic purification over silica gel with hexanes/ether (95/5) as the eluent gave the 3,4-dimethyl-2,5-di(2-thienyl)furan(**62b**) as a pale yellow solid. Yield: 1.52 g (65%). m.p.=108-109 °C(uncorrected). ^{1}H-NMR($CDCl_3$): 7.31(d, J=4.1Hz, 2H), 7.26(d, J=5.5Hz, 2H), 7.08(dd, J=5.5Hz, 4.1Hz, 2H), 2.23(s, 6H); ^{13}C-NMR($CDCl_3$): 142.1, 133.6, 128.0, 123.8, 123.5, 122.4, 13.7; EI-MS, m/z(relative intensity): 262(M^++2, 3.17), 261(M^++1, 8.26), 260(M^+, 67.4), 259(17.5), 245(4.1), 231(5.60), 176(3.91), 162(4.76), 134(5.14), 111(base), 83(10.9); UV-Vis (maximum absorption) 337nm ($CHCl_3$).

Synthesis of 3,4-diethyl-2,5-di(2-thienyl)furan(**62c**)

A solution of 2,3-diethyl-1,4-di(2-thienyl)-1,4-butanedione (**60c**) (2.08 g, 6.8 mmole) in 30 ml acetic anhydride was kept in an acetone-dry-ice bath(-15 to -20 °C) with magnetic stirring. Gaseous HCl was bubbled through this cold solution for 15 min. Then the acetone-bath was removed and the reaction was allowed to warm up to room temperature. Then the reaction mixture was stirred at 85°C for 8 hours. The dark mixture was cooled and the acetic anhydride was removed by vacuum distillation. The residue was extracted with ether (4x30 ml) and the combined ether layers were washed with 5% aqueous sodium bicarbonate solution (3x20 ml), water (2x20 ml), saturated NaCl (2x15 ml) and dried with sodium sulfate. The solvent was removed by a rotary evaporator. Column chromatographic purification over silica gel with hexanes/ether (97/3) as eluent gave the 3,4-diethyl-2,5-di(2-thienyl)furan(**62c**) as a pale yellow solid. Yield: 1.25 g (64%). m.p.=69-70 °C(uncorrected). ^{1}H-NMR($CDCl_3$): 7.31(d, J=4.1Hz, 2H), 7.25(d, J=5.6Hz, 2H), 7.07(dd, J=5.6, 4.1Hz, 2H), 2.61(q, J=8.1Hz, 4H), 1.04(t, J=8.1Hz, 6H); ^{13}C-NMR($CDCl_3$): 142.8, 133.7, 128.4, 123.9, 123.5, 122.4, 29.7, 13.6; EI-MS, m/z(relative intensity): 290(M^++2, 4.96), 289(M^++1, 11.8), 288(M^+, 72.1), 273(10.9), 259(5.7), 245(20.7), 162(4.08), 134(5.16), 111(base), 83(14.7); UV-Vis(maximum absorption): 337nm ($CHCl_3$).

Synthesis of 3,4-dibutyl-2,5-di(2-thienyl)furan(**62d**)

A solution of 2,3-dibutyl-1,4-di(2-thienyl)-1,4-butanedione (**60d**) (2.41 g, 6.6 mmole) in 30 ml acetic anhydride was kept in

an acetone-dry-ice bath (-15 to -20 °C) with magnetic stirring. Gas HCl was bubbled through this cold solution for 15 min. Then the cold-bath was removed and the solution was allowed to warm up to room temperature. The reaction mixture was stirred at 85 °C for 8 hours. The dark reaction mixture was cooled and the acetic anhydride was removed by vacuum distillation. The residue was extracted with ether (4x30 ml) and the combined ether extracts were washed with 5% sodium bicarbonate solution (3x20 ml), water (2x20 ml), saturated NaCl (2x15 ml) and dried with sodium sulfate. The solvent was removed by a rotary evaporator. Column chromatographic purification over silica gel with hexanes as the eluent gave the 3,4-dibutyl-2,5-di(2-thienyl)furan(**62d**) as a pale yellow oil. Yield: 1.58 g (69%). ^{1}H-NMR($CDCl_3$): 7.30(d, J=4.0Hz, 2H), 7.26(d, J=5.6Hz, 2H), 7.09(dd, J=5.6, 4.0Hz, 2H), 2.64(t, J=8.2Hz, 4H), 1.61(m, 4H), 1.50(m, 4H), 1.01(t, J=7.8Hz, 6H); ^{13}C-NMR($CDCl_3$): 143.2, 133.5, 127.4, 123.7, 123.5, 122.6, 32.1, 23.9, 23.0, 13.9; EI-MS, m/z(relative intensity): 346(M^++2, 8.6), 345(M^++1, 17.0), 344(M^+, 73.3), 301(10.9), 273(6.0), 259(14.6), 231(8.7), 191(4.6), 184(5.6), 147(8.9), 129(8.6), 115(5.1), 113(8.4), 112(9.9), 111(base), 97(21.5), 85(15.5), 83(15.4), 77(5.2), 57(11.5), 43(12.6), 41(22.2), 39(20.6); UV-Vis(maximum absorption): 337nm ($CHCl_3$).

Synthesis of 3,4-dihexyl-2,5-di(2-thienyl)furan(**62e**)

A solution of 2,3-dihexyl-1,4-di(2-thienyl)-1,4-butanedione(**60e**) (1.94 g, 4.6 mmole) in 30 ml acetic anhydride was

kept in an acetone-dry-ice bath (-15 to -20 °C) with magnetic stirring. Gaseous HCl was bubbled through this cold solution for 15 min. Then the acetone-bath was removed and the reaction was allowed to warm up to room temperature. The reaction mixture was stirred at 85°C for 8 hours. Then, the mixture was cooled and the acetic anhydride was removed by vacuum distillation. The residue was extracted with ether (4x30 ml) and the combined ether layers were washed with 5% sodium bicarbonate solution (3x20 ml), water (2x20 ml), saturated NaCl (2x15 ml) and dried with sodium sulfate. The solvent was removed by a rotary evaporator. Column chromatographic purification over silica gel with hexanes as the eluent gave the 3,4-dihexyl-2,5-di(2-thienyl)furan(**62e**) as a pale yellow oil.Yield: 1.13 g (61%). ^{1}H-NMR($CDCl_3$): 7.30(d, J=4.0Hz, 2H), 7.25(d, J=5.6Hz, 2H), 7.09(dd, J=5.6, 4.0Hz, 2H), 2.63(t, J=8.1Hz, 4H), 1.61(m, 4H), 1.43(m, 4H), 1.30(m, 8H), 0.94(t, J=7.8Hz, 6H); ^{13}C-NMR($CDCl_3$): 143.0, 133.8, 128.6, 124.0, 123.7, 122.5, 31.2, 29.8, 29.3, 27.5, 22.4, 13.5; EI-MS, m/z(relative intensity): 402(M^++2, 7.9), 401(M^++1, 20.9), 400(M^+, 78.1), 385(8.24), 329(9.7), 315(2.87), 245(18.6), 111(base), 83(12.8). UV-Vis(maximum absorption): 337nm ($CHCl_3$).

Synthesis of 2-(1-trimethylsilyl pyrryl) trimethylsilyl ethenol ether(**77**):

To a mixture of NaI (3.75 g, 25 mmole), $ClSiMe_3$ (2.70 g, 24.9 mmole) and Et_3N (2.52 g, 25 mmole) in acetonitrile (30 ml) was

added dropwise the 2-acetyl pyrrole (1.09 g, 10.0 mmoles) in 5 ml dry acetonitrile. The resulted opaque mixture was stirred at room temperature under N_2 for two hours and then the reaction was quenched with saturated $NaHCO_3$ solution. The mixture was extracted with petroleum ether (bp=35 - 60 °C) (3x30 ml) and the combined organic layers were washed with water (2x20 ml), saturated NaCl (2x15 ml) and dried with sodium sulfate. The solvent was removed by a rotary evaporator to give an orange oil residue as the crude product. Vacuum distillation gave the product as a colorless oil. Yield: 2.30 g (91%). ^{1}H-NMR($CDCl_3$): 6.75(dd, J=3.0, 1.7Hz, 1H), 6.32(dd, J=3.5, 1.7Hz, 1H), 6.13(dd, J=3.5, 3.0Hz, 1H), 4.55(d, J=1.1Hz, 1H), 4.30(d, J=1.1Hz, 1H), 0.29(s, 9H);

Synthesis of 1,4-di(2-pyrryl)-1,4-butanedione(**78**):

A solution of 2-(1-trimethylsilyl pyrryl) trimethylsilyl ethenol ether(**77**) (2.30 g, 9.09 mmole) in 2ml dried acetonitrile was added dropwise to a mixture of $VOCl_3$ (10.0 mmoles) and pyridine (10.0 mmoles) in dry acetonitrile (20 ml) at 0 °C under N_2. After the addition the reaction mixture was stirred at 0 °C for 15 min. The reaction was quenched with saturated aqueous sodium bicarbonate solution. Then, the mixture was extracted with ether (3x20 ml) and the combined ether layers were washed with 5% $NaHCO_3$ (2x20 ml), H_2O (30 ml), saturated NaCl (20 ml) and dried with Na_2SO_4. The solvent was removed by a rotary evaporator to give a light brown colored residue as the crude product. Column chromatographic

purification over silica gel with ether/ethyl acetate:/hexanes (5/3/92) as the eluent, followed by crystallization from ethanol gave the expected 1,4-di(2-pyrryl)-1,4-butanedione(78) as colorless needles. Yield: 8%. mp=154 -156 °C(uncorrected). ^{1}H-NMR($CDCl_3$): 10.2(2H, s, broad), 7.14(2H, m), 6.98(2H, m), 6.29(2H, m), 3.41(4H, s); EI-MS, m/z(relatively intensity): 216(M^+, 21.4), 122(52.3), 94(base), 66(31.4).

Synthesis of 2,5-di(5-(2,2'-bithienyl))-1,3,4-thiadiazole(79):

A mixture of 5-(2,2'-bithienyl) carboxaldehyde (2.50 g, 12.9 mmole), hydrazine monohydrate (320 mg, 6.4 mmole), elemental sulfur (500 mg, 15.6 mmole), and tributylamine (150 mg, 0.8 mmole) in 20 ml of propylene glycol was heated at 120 °C for 48 hours. Then, the reaction mixture was cooled to room temperature and the precipitate was collected by suction filtration. The solid was washed with ice-cold methanol (3x20 ml), carbon disulfide (3x15 ml) and dried in vacuum to give a light tan solid as crude product. Column chromatographic purification over silica gel with ethyl acetate/hexanes (40/60) as eluent followed by crystallization from ethanol/ethyl acetate (50/50) gave the 2,5-di(5-(2,2'-bithienyl))-1,3,4-thiadiazole(79) as orange needles. Yield: 390 mg (28%). m.p.=259-261 °C(uncorrected). ^{1}H-NMR(DMSO-d_6): 7.63(d, J=4.4Hz, 2H), 7.35(m, 4H), 7.23(d, J=4.4Hz, 2H), 7.08(m, 2H); ^{13}C-NMR(DMSO-d_6): 164.1, 146.6, 141.5, 137.2, 135.7, 128.3, 127.1, 126.1, 124.2; EI-MS, m/z(relative intensity): 414(M^+, 10.7), 223(base), 191(4.6); High

resolution mass spectra, calculated. for $C_{18}H_{10}N_2S_5$: 414.580, found: 414.495; UV-Vis(maximum absorption): 379nm ($CHCl_3$).

Synthesis of 2,5-di(5-(2,2',5',2"-terthienyl))-1,3,4-thiadiazole(**81**):

A mixture of 5-(2,2',5',2"-terthienyl) carboxaldehyde (500 mg, 1.8 mmole), hydrazine monohydrate (45 mg, 0.9 mmole), elemental sulfur (150 mg, 4.69 mmole), and tributylamine (50 mg, 0.27 mmole) in 20 ml of propylene glycol was heated at 120 °C for 48 hours. Then, the reaction mixture was cooled to room temperature and the precipitate was collected by suction filtration. The solid was washed with ice-cold methanol (3x20 ml), carbon disulfide (3x15 ml) and dried in vacuum to give a tan solid as crude product. Column chromatographic purification over silica gel with ethyl acetate/hexanes (50/50) as eluent followed by crystallization from ethanol/ethyl acetate (50/50) gave the 2,5-di(5-(2,2',5',2"-terthienyl))-1,3,4-thiadiazole(**81**) as orange needles. Yield: 57 mg (11%). m.p.=309-310 °C (uncorrected). ^{1}H-NMR(DMSO-d_6): 7.61(d, J=4.1, 2H), 7.22(m, 8H), 7.11(d, J=4.1Hz, 2H), 7.05(dd, J=4.4, 3.9Hz, 2H); ^{13}C-NMR(DMSO-d_6): 162.4, 145.1, 142.3, 140.8, 139.8, 136.5, 135.8, 132.5, 129.4, 128.0, 126.3, 125.7, 125.2. EI-MS, m/z(relative intensity): 578(M^+, base), 305(49.6), 289(6.74), 273(8.76). High resolution mass spectra, calculated for $C_{26}H_{14}N_2S_7$: 578.812, found 578.719. UV-Vis(maximum absorption): 432nm ($CHCl_3$).

Synthesis of 2,5-di(5-(2,2'-bithienyl))thiazolo[5,4-d]thiazole(**80**):

A mixture of 5-(2,2'-bithienyl) carboxaldehyde (1.50 g, 7.7 mmole) and dithiooximide (0.46 g, 3.8 mmole) in 20 ml DMF was heated at gentle reflux under N_2 for 30 min. The dark red reaction mixture was cooled and the precipitate was collected by suction filtration. The solid was washed with water (2x20 ml), ice-cold methanol (3x10 ml) and then dried in vacuum. Column chromatographic purification over silica gel with ethyl acetate/hexanes (50/50) as eluent followed by crystallization from ethyl acetate/etnanol (50/50) gave the 2,5-di(5-(2,2'-bithienyl))thiazolo[5,4-d]thiazole(**80**) as orange needles. Yield:370 mg (22%). m.p.=276-277 °C (uncorrected). ^{1}H-NMR(DMSO-d_6): 7.54(d, J=4.2Hz, 2H), 7.31(m, 4H), 7.19(d, J=4.2Hz, 2H), 7.02(m, 2H); EI-MS, m/z(relative intensity): 470(M^+, base), 279(2.71), 191(10.8), 88(78.6), 83(6.90). High resolution mass spectra, calculated for $C_{20}H_{10}N_2S_6$: 470.660, found: 470.459. UV-Vis(maximum absorption): 407nm ($CHCl_3$).

Synthesis of 2,5-di(5-(2,2',5',2"-terthienyl))thiazolo[5,4-d]thiazole(**82**):

A mixture of 5-(2,2',5',2"-terthienyl) carboxaldehyde (400 mg, 1.45 mmole) and dithiooximide (87 mg, 0.72 mmole) in 20 ml DMF was heated at gentle reflux under N_2 for 30 minutes. The dark red reaction mixture was cooled and the precipitate was collected by

suction filtration. The solid was washed with water (2x20 ml), ice-cold methanol (3x10 ml) and then dried in vacuo to give a tan solid as the crude product. Column chromatographic purification over silica gel with ethyl acetate/hexanes (60/40) as eluent followed by crystallization from ethyl acetate/ethanol (50/50) gave the 2,5-di(5-(2,2',5',2"-terthienyl))thiazolo[5,4-d]thiazole(**82**) as orange needles. Yield: 65 mg (15%). m.p.=326-328 °C (uncorrected). ^{1}H-NMR(DMSO-d_6): 7.60(d, J=4.0, 2H), 7.23(m, 8H), 7.10(d, J=4.0Hz, 2H), 7.04(dd, J=4.5, 3.9Hz, 2H). ^{13}C-NMR(DMSO-d_6): 158.6, 148.0, 146.5, 145.4, 142.6, 141.0, 140.1, 136.9, 135.7, 132.8, 130.0, 128.5, 127.1, 126.4, 126.0. EI-MS, m/z(relative intensity): 634(M^+, base), 361(5.16), 273(11.29), 88(57.6); High resolution mass spectra, calculated for $C_{28}H_{14}N_2S_8$: 634,892, found 634.816. UV-Vis(maximum absorption): 478nm ($CHCl_3$).

Synthesis of 5-formyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**89**):

a), Synthesis of 5-formyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**89**) by the lithiation of the 2,2',5',2"-terthiophene followed by the reaction of the lithiated compound with DMF:

BuLi (0.7 ml of 1.6M in hexanes solution,1.1 eq.) was added to a cooled (-50 °C) mixture of 3',4'-dibutyl-2,2',5',2"-terthiophene (360 mg, 1.0 mmole), tetramethylethenediamine (TMEDA, 100 mg) and 15 ml hexanes by a syringe under N_2. After the addition, the reaction mixture was stirred at -50 °C for 30 minutes and then stirred at

room temperature for another 30 minutes. The reaction mixture was then recooled to -78 °C and 1.2 eq. of dimethyformamide(DMF) in 5 ml ether was added slowly by a syringe. After the addition the reaction was slowly raised to room temperature and the mixture was stirred for one more hour. Then, the mixture was poured into 50 ml 2% ice cold aqueous HCl solution with vigorously stirring. Then the mixture was extracted with ether (3x15 ml). The combined organic extracts were washed with water (2x20 ml), saturated $NaHCO_3$ (2x20 ml), saturated NaCl (20 ml) and dried with $MgSO_4$. Removal of the solvent gave a dark-oil which solidify when cooled. Column chromatographic purification over silica gel with hexanes/ether/ CH_2Cl_2 (85/10/5) as eluent followed by crystallization from hexanes gave the 5-formyl-3',4'-dibutyl-2,2'5',2"-terthiophene(**89**) as a light green yellow solid product. Yield:279 mg(72%). mp=41-42 °C (uncorrected). ^{1}H-NMR ($CDCl_3$): 9.86(1H, s), 7.67(1H, d, J=4.5Hz), 7.33(1H, dd, J=5.7 and 1.3Hz), 7.21(1H, d, J=4.5Hz), 7.16(1H, dd, J=4.0 and 1.3Hz), 7.07(1H, dd, J=5.7 and 4.0Hz), 2.74(4H, m), 1.35-1.60(8H, m), 0.93(6H, m); ^{13}C-NMR($CDCl_3$): 182.6, 146.5, 142.5, 142.1, 140.7, 136.8, 135.5, 132.3, 128.8, 127.5, 126.4, 126.1, 32.8, 32.6, 28.1, 27.7, 23.0, 22.9, 13.8(2). EI-MS m/z(relative intensity): 388(M^+, base), 345(17.5), 331(9.9), 317(10.9), 303(28.6), 275(28.4), 274(14.7), 273(7.6), 240(11.0), 227(11.1), 126(18.8), 111(21.4). UV-Vis($CHCl_3$): 393nm.

b), Synthesis of 5-formyl-3',4'-dibutyl-2,2'5',2"-terthiophene(**89**) by a Vilsmier reaction:

To a stirred solution of 3',4'-dibutyl-2,2',5',2"-terthiophene (1.48 g, 4.1 mmole) in dry N,N-dimethylformamide (314 mg, 4.3 mmole, 1.05 eq.) at 60 °C, $POCl_3$ (0.7 g, 4.5 mmole) was added dropwise by a syringe over 10 minutes under nitrogen. After the addition, the reaction mixture was stirred at this temperature for 2 hours and then at 80 °C for 2 more hours. Then an excess of aqueous sodium acetate solution (20 ml, 10%) was added and the mixture was stirred at room temperature for 5 hours and heated on a steam-bath for 30 minutes. The mixture was cooled to room temperature and extracted with ether (3x15 ml). The combined organic layers were washed with water (2x20 ml), saturated $NaHCO_3$ (2x20 ml), brine (30 ml) and dried with $MgSO_4$. Removal of the solvent gave a dark-oil which solidified when cooled. Column chromatographic purification over silica gel with hexanes/ether/CH_2Cl_2 (85/10/5) as eluent followed by crystallization from hexanes gave the expectd 5-formyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**89**) as a light green yellow solid. Yield:1.21 g (76%). All the spectroscopic characterizations are the same as those from Method (a).

Synthesis of 1,4-di(5-(3',4'-dibutyl-2,2',5',2"-terthienyl))-1,4-butanedione(88):

a), Synthesis of 1,4-di(5-(3',4'-dibutyl-2,2',5',2"-terthienyl))-1,4-butanedione(**88**) by a Friedel-Crafts acylation reaction:

A solution of 3',4'-dibutyl-2,2',5',2"-terthiophene (3.60 g, 10 mmole), succinyl chloride (0.77 g, 5.0 mmole) in 10 ml of CH_2Cl_2 was added dropwise over 60 minutes to a vigorously stirred mixture of $SnCl_4$ (2.60 g, 10 mmoles) in 20 ml CH_2Cl_2 at 0 °C under N_2. After the addition the reaction mixture was stirred continuously at the same temperature for one more hour. The dark-red reaction mixture was quenched with ice cold 3% HCl aqueous solution. The organic layer was separated and the aqueous layer was extrated with CH_2Cl_2 (2x20 ml). The combined organic layers were washed with water (2x20 ml), saturated $NaHCO_3$ (20 ml), brine (20 ml) and then dried with sodium sulfate. The solvent was removed by a rotary evaporator to give a dark color solid crude product. Column chromatographic purification over silica gel with ethyl acetate/CH_2Cl_2/hexanes (20/15/65) as eluent followed by crystallization from CH_2Cl_2/hexanes (20/80) gave the product as yellow needles. Yield: 880 mg (22%). m.p.=175-176 °C (uncorrected). ^{1}H-NMR ($CDCl_3$): 7.73(2H, d, J=4.4Hz); 7.32(2H, dd, J=4.4 and 1.3Hz); 7.17(2H, d, J=4.4Hz); 7.14(2H, dd, J=5.3 and 1.3Hz); 7.05(2H, dd, J=5.3 and 4.4Hz); 3.37(4H, s); 2.75(4H, t); 2.69(4H, t); 1.53(8H, m); 1.43(8H, m); 0.95(6H, t); 0.93(6H,t). ^{13}C-NMR($CDCl_3$): 190.6, 144.9, 142.1, 141.9, 140.5, 135.7, 132.5, 131.7, 129.0, 127.4, 126.3, 126.1, 125.8, 32.9, 32.8, 32.6, 28.0, 27.7, 23.0, 22.9, 13.9, 13.8; EI-MS, m/z(relative intensity): 802(M^+, 55.7), 415(base), 402(13.8), 401(M^{2+},12.1), 387(43.75), 317(10.3), 274(14.8), 147(70.74), 75(10.9), 55(14.2). UV-Vis($CHCl_3$): 390nm.

b). Synthesis of 1,4-di(5-(3',4'-dibutyl-2,2',5',2"-terthienyl))-1,4-butanedione(88) by a Stetter's reaction:

A mixture of 5-formyl-3',4'-dibutyl-2,2',5',2"-terthiophene(89) (388 mg, 1.0 mmole), 3,4-dimethyl-5-(2-hydroxyethyl)-thiazolium iodide 28.5 mg, 0.1 mmole)(cat.), NaOAc (16.4 mg, 0.2 mmoles) in 5 ml absolute ethanol was refluxed gently under N_2 for 6 hours. The reaction mixture was then cooled to room temperature and poured into 50 ml of water. The mixture was extracted with $CHCl_3$ (3x15 ml) and the combined organic layers were washed with water (2x20 ml) and saturated NaCl (30 ml). The solvent was removed by a rotary evaporator to give an orange solid as the crude product. Column chromatographic purification over silica gel with ethyl acetate/CH_2Cl_2/Hexanes(20:15:65) as eluent gave the 1,4-di(5-(3',4'-dibutyl-2,2'5',2"-terthienyl))-1,4-butanedione(88) as light yellow needles. Yield:268 mg (67%). m.p.=175-176 °C (uncorrected). ^{1}H-NMR ($CDCl_3$): 7.73(2H, d, J=4.4Hz); 7.32(2H, dd, J=4.4 and 1.3Hz); 7.17(2H, d, J=4.4Hz); 7.14(2H, dd, J=5.3 and 1.3Hz); 7.05(2H, dd, J=5.3 and 4.4Hz); 3.37(4H, s); 2.75(4H, t); 2.69(4H, t); 1.53(8H, m); 1.43(8H, m); 0.95(6H, t); 0.93(6H,t). ^{13}C-NMR($CDCl_3$): 190.6, 144.9, 142.1, 141.9, 140.5, 135.7, 132.5, 131.7, 129.0, 127.4, 126.3, 126.1, 125.8, 32.9, 32.8, 32.6, 28.0, 27.7, 23.0, 22.9, 13.9, 13.8; EI-MS, m/z(relative intensity): 802(M^+, 55.7), 415(base), 402(13.8), 401(M^{2+},12.1), 387(43.75), 317(10.3), 274(14.8), 147(70.74), 75(10.9), 55(14.2). UV-Vis(maximum absorption): 390nm ($CHCl_3$).

Synthesis of 3',3'''',4',4''''-tetrabutyl-2,2',5',2",5",2"',5"',2"",5"",2""',5""',2""'-heptathiophene(**83**):

A mixture of 1,4-di(5-(3',4'-dibutyl-2,2',5',2"-terthiophene))-1,4-butanedione (80 mg, 0.1 mmoles), Lawesson's reagent (50 mg, 0.124 mmoles) and 5 ml toluene was refluxed gently for two hours under N_2. The dark reaction mixture was cooled to room temperature and poured into 20 ml of water. The mixture was then extracted with CH_2Cl_2 (3x10 ml) and the combined organic layers were washed with water (2x15 ml), dried with $MgSO_4$. Removal of the solvent by a rotary evaporator gave a tan color solid as the crude product. Column chromatographic purification over silica gel with hexanes/ether (95/5) as the eluent followed by crystallization from hexanes gave the 3',3'''',4',4''''-tetrabutyl-2,2',5',2",5",2"',5"',2"",5"",2""',5""',2""'-heptathiophene(**83**) as orange needles. Yield 65 mg (82%). m.p.=129-130 °C (uncorrected). ^{1}H-NMR($CDCl_3$): 7.30(2H, dd, J=5.4 and 1.2Hz), 7.02-7.14(10H, m), 2.64-2.77(8H, m), 1.48-1.60(8H, m), 1.38-1.48(8H, m), 0.88-0.95(12H, m); ^{13}C-NMR($CDCl_3$): 140.24(2), 136.6, 136.1, 136.0, 135.4, 130.1 129.6, 127.4, 126.4, 125.9, 125.4, 124.3, 124.0, 32.9, 32.8, 27.9, 27.8, 23.04, 23.00, 13.87(2); EI-MS, m/z(relative intensity): 800(M^+, base), 400(M^{2+}, 25.15), 315(24.24), 308(11.06), 97(13.48), 84(22.58), 69(17.42), 55(22.88). UV-Vis($CHCl_3$): 429nm.

Synthesis of 2,5-di(5-(3',4'-dibutyl-2,2',5',2"-terthienyl))furan(**84**):

A solution of 1,4-di(5-(3',4'-dibutyl-2,2',5',2"-terthienyl))-1,4-butanedione (60 mg, 0.075 mmole) in 10 ml acetic anhydride was kept in an acetone-dry-ice bath(-15 to -20 °C) with magnetic stirring. Gaseous HCl was bubbled through this cold solution for 15 minutes. Then the cold-bath was removed and the solution was allowed to warm up to room temperature. Then, the reaction mixture was stirred at 95 °C for 10 hours. The dark reaction mixture was cooled and the acetic anhydride was removed by vacuum distillation. The residue was extracted with ether (4x30 ml) and the combined ether layers were washed with 5% sodium bicarbonate solution (3x20 ml), water (2x20 ml), saturated NaCl (2x15 ml) and dried with sodium sulfate. Removal of the solvent by a rotary evaporator gave a dark colored residue as the crude product. Column chromatographic purification over silica gel with hexanes/ether (97/3) as the eluent gave the 2,5-di(5-(3',4'-dibutyl-2,2',5',2"-terthienyl))furan(**84**) as orange solid. Yield: 58 mg (19%). m.p.=112-114 °C (uncorrected). ^{1}H-NMR($CDCl_3$): 7.31(dd, J=5.2, 1.2Hz, 2H), 7.15-7.02(m, 10H), 2.59-2.70(m, 8H), 1.46-1.61(m, 8H), 1.37-1.45(m, 8H), 0.90-0.95(m, 12H); ^{13}C-NMR($CDCl_3$): 140.1, 139.8, 136.4, 136.0, 135.7, 135.2, 130.0, 129.2, 127.0, 126.1, 125.4, 125.1, 124.0, 123.6, 32.7, 32.6, 27.7, 27.6, 23.0(2), 13.5(2); EI-MS, m/z(relative intensity): 784(M^+, base), 741(30.4), 713(5.1), 699(14.1), 392(2.10), 344(18.4), 302(4.79). High resolution mass spectra, calculated for $C_{44}H_{48}OS_6$: 785.184, found: 785.149. UV-Vis(maximum absorption): 431nm ($CHCl_3$).

Synthesis of 2,5-di(5-(3',4'-dibutyl-2,2',5',2"-terthienyl))pyrrole(**85**):

A mixture of 1,4-di(5-(3',4'-dibutyl-2,2',5',2"-terthienyl))-1,4-butanedione (56 mg, 0.07 mmole), anhydrous NH_4OAc (60 mg, 0.78 mmole), acetic anhydride (1.0 ml) in 5 ml acetic acid was kept at 100 °C for 24 hours. The dark-red reaction mixture was cooled and the acetic acid/acetic anhydride was removed by vacuum distillation. The residue was extracted with ether (4x10 ml) and the combined ether was washed with 5% sodium bicarbonate solution (3x15 ml), water (2x15 ml), saturated NaCl (2x10 ml) and dried with sodium sulfate. Removal of the solvent by a rotary evaporator gave a tan colored residue as the crude product. Column chromatographic purification over silica gel with hexanes/ether (97/3) as eluent gave the 2,5-di(5-(3',4'-dibutyl-2,2',5',2"-terthienyl))pyrrole(**85**) as an orange solid. Yield: 14 mg (25%). m.p.= 141-142 °C (uncorrected). ^{1}H-NMR($CDCl_3$):7.28-6.94(m, 12H), 2.69-2.57(m, 8H), 1.60-1.44(m, 8H), 1.40-1.35(m, 8H), 0.95-0.90(m, 12H); ^{13}C-NMR($CDCl_3$): 140.9, 140.2, 138.7, 136.9, 136.2, 135.8, 135.0, 130.1, 129.0, 127.1, 126.4, 125.5, 125.1, 123.0; EI-MS, m/z(relative intensity): 783(M^+, base), 740(12.6), 712(9.7), 698(21.8), 343(9.6), 301(4.09). High resolution mass spectra, calculated for $C_{44}H_{49}NS_6$: 784.202, found: 784.147. UV-Vis(maximum absorption): 437nm ($CHCl_3$).

Synthesis of 2,5-di(5-(3',4'-dibutyl-2,2',5',2"-terthienyl))-1,3,4-thiadiazole(86):

A mixture of 5-formyl-3',4'-dibutyl-2,2',5',2"-terthiophene (120 mg, 0.31 mmole), hydrazine monohydrate (7.7 mg, 0.15 mmole), elemental sulfur (60 mg, 1.87 mmole), and tributyl amine (20 mg, 0.11 mmole) in 10 ml of propylene glycol was heated at 120 °C for 48 hours. Then, the reaction mixture was cooled to room temperature and the precipitate was collected by suction filtration. The solid was washed with ice-cold methanol (3x10 ml), carbon disulfide (3x10 ml) and then dried in vacuum to give a dark-red solid as crude product. Column chromatographic purification over silica gel with hexanes/ether/ethyl acetate (85/5/10) as the eluent followed by crystallization from hexanes/ethyl acetate (90/10) gave the expected 2,5-di(5-(3',4'-dibutyl-2,2',5',2"-terthienyl))-1,3,4-thiadiazole(86) as orange needles. Yield: 14 mg (12%). m.p.=206-208 °C (decomp.). ^{1}H-NMR($CDCl_3$): 7.50(d, J=4.3Hz, 2H), 7.30(dd, J=6.8, 1.1Hz, 2H), 7.16(dd, J=3.9, 1.1Hz, 2H), 7.10(d, J=4.3Hz, 2H), 7.05(dd, J=6.8, 3.9Hz, 2H), 2.75(t, J=8.1Hz, 4H), 2.70(t, J=8.1Hz, 4H), 1.60-1.52(m, 8H), 1.49-1.43(m, 8H), 0.96-0.93(m, 12H); ^{13}C-NMR($CDCl_3$): 161.3, 142.7, 141.0, 140.2, 135.1, 134.6, 131.9, 129.4, 127.0, 125.8, 125.4, 124.6, 124.0, 32.4, 32.1, 28.3, 28.0, 22.7(2), 13.6(2). EI-MS, m/z(relative intensity): 802(M^+, 7.4), 759(5.1), 417(base), 385(20.7), 359(4.7), 344(8.1). High resolution mass spectra, calculated for $C_{42}H_{46}N_2S_7$: 803.228, found: 803.169. UV-Vis(maximum absorption): 417nm ($CHCl_3$).

Synthesis of 2,2'-di(5-(3',4'-2,2':5',2"-terthienyl))-thiazolo[5,4-d]thiazole(87):

A mixture of 5-formyl-3',4'-dibutyl-2,2',5',2"-terthiophene(89) (388 mg, 1.0 mmoles), dithiooxamide (60 mg, 0.5 mmoles) and DMF (5 ml) was refluxed gently under N_2 for 30 minutes. Then the dark-red reaction mixture was cooled to room temperature and poured into water (20 ml), and extracted with $CHCl_3$ (3x15 ml). The combined organic layers was washed with water (2x15 ml) and dried with sodium sulfate. Removal of the solvent by a rotary evaporator gave a dark-red solid as the crude product. Column chromatographic purification over silica gel with hexanes/ethyl acetate (92/8) as the eluent followed by crystallization from hexanes/CH_2CL_2 (90/10) gave the 2,2'-di(5-(3',4'-2,2':5',2"-terthienyl))thiazolo[4,5-b]thiazole(87) as orange-red solid. Yield: 146 mg (34%). m.p.=178 °C (decomp.). ^{1}H-NMR($CDCl_3$): 7.47(2H, d, J=4.3Hz), 7.31(2H, dd, J=5.6, 1.1Hz); 7.14(2H, dd, J=4.0, 1.1Hz), 7.11(2H, d, J=4.3Hz), 7.06(2H, dd, J=5.6, 4.0Hz), 2.77(4H, t), 2.70(4H, t), 1.55(8H, m), 145(8H, m), 0.94(12H, m). EI-MS, m/z (relatively intensity): 858(M^+, 30.06), 429(M^{2+}, 9.01), 374(23.47), 344(13.96), 331(10.74), 300(11.20), 289(11.66), 127(17.79), 121(11.35), 111(10.43), 97(19.33), 69(41.72), 64(43.56), 55(33.74), 44(base). UV-Vis($CHCl_3$): 466nm.

Synthesis of 2,2'-dipyrrylthione(**146**):

A solution of pyrrole (5.0 g, 74.5 mmole) in dry ether (40 ml) was added dropwise to a vigorously stirred solution of thiophosgene (4.2 g, 36.5 mmole) in benzene (80 ml) at 0 °C. The addition took about 20 minutes. After the addition, the red reaction mixture was continuously stirred at 0 °C for 30 more minutes. Then 100 ml of aqueous methanol (80%) was added and the mixture was stirred at room temperature for one hour. The solvent was removed by a rotary evaporator and the dark-red residue was dissolved in CH_2Cl_2 (20 ml). Chromatographic purification on neutral alumina with hexanes/ether(80/20) as the eluent followed by crystallization from aqueous ethanol gave the 2,2'-dipyrrylthione as lustrous red needles. Yield, 3.78g(59%). m.p=97-98 °C(lit.[113] 96 - 98 °C). ^{1}H-NMR ($CDCl_3$): 9.76(s., br., 2H), 7.18(m, 2H), 7.03(m, 2H), 6.40(m, 2H); ^{13}C-NMR ($CDCl_3$): 193.1, 138.3, 127.7, 114.8, 112.5; EI-MS(e/z, relative intensity): 178(M^++2, 5.58), 177(M^++1, 13.7), 176(M^+, base), 175(M^+-1, 34.4), 143(18.4), 109(58.2), 89(7.3), 83(8.7), 67(20.3), 39(14.3).

Synthesis of 2,2'-dipyrrylketone(**147**):

20 ml 5% aqueous hydrogen peroxide was added portion-wise to a vigorously stirred solution of 2,2'-dipyrrylthione (1.0 g, 5.7

mmole) in ethanol (95%; 120 ml) containing 2.0 g (35.7 mmole) potassium hydroxide. After the addition, the mixture was continuously stirred at room temperature for 30 minutes and then heated on a steam bath for 30 more minutes. The reaction mixture was then poured into 300 ml of water. The white precipitate was collected by suction filtration and dried in vacuum. Further purification by sublimation (200 °C/1 mm) gave the 2,2'-dipyrrylketone as white powder. Yield 0.69 g (76%). m.p.=159-160 °C. ^{1}H-NMR($CDCl_3$): 9.92(s, br., 2H), 7.14(m, 2H), 7.07(m, 2H), 6.34(m, 2H); ^{13}C-NMR($CDCL_3$): 110.5, 115.6, 123.6, 130.1, 171.8; EI-MS(e/z, relative intensity): 161(M^++1, 9.75), 160(M^+, base), 104(10.9), 94(72.4), 67(81.3), 66(42.2), 51(6.1), 39(31.3).

Synthesis of 2,2'-dipyrrylmethane(**148**):

Sodium borohydride (1 g each, 6 g total) was added portionwise over 3 hours to a solution of 2,2'-dipyrrylketone (2.0 g, 12.5 mmole) in refluxing ethanol (95%, 50 ml) containing 2.0 ml of morpholine under nitrogen. Every time after the addition of a portion of borohydride 3.0 ml of water was added. After the addition of all the sodium borohydride the reaction mixture was refluxed for two hours, then cooled to room temperature and poured into 100 ml of water. The solvent was removed by vacuum distillation and the residue was extracted with petroleum ether. The combined petroleum extracts were concentracted and cooled in -10 °C to give

2,2'-dipyrrylmethane as colorless needles (yield, 1.68 g, 92%). m.p.=72-73 °C(lit.[113] 73 °C). ^{1}H-NMR($CDCl_3$): 7.82(s, br., 2H), 6.65(m, 2H), 6.16(m, 2H), 6.05(m, 2H), 3.97(s, 2H); ^{13}C-NMR($CDCL_3$): 128.8, 117.3, 108.3, 106.4, 26.3; EI-MS(e/z, relative intensity): 147(M^++1, 10.4), 146(M^+, base), 145(M^+-1), 73.6), 118(17.5), 117(17.5), 80(40.2), 67(28.4), 53(11.6), 39(10.5).

Synthesis 5,5'-diformyl-2,2'-dipyrrylmethane(**149**):

To a stirred solution of 2,2'-dipyrrylmethane (1.2 g, 8.2 mmole) in dry N,N-dimethylformamide (10 ml) at 0°C, 6.0 ml of benzoyl chloride was added dropwise over 10 minutes under nitrogen. After the addition, the reaction mixture was stirred at this temperature for 2 hours and then at room temperature for 5 hours. Then an excess of 10% aqueous sodium acetate solution (20 ml) was added and the mixture was stirred at room temperature for five hours and heated on a steam-bath for 20 minutes. The mixture was diluted with water (30 ml) and the precipitate was collected by filtration. Recrystallization from ethanol gave the 5,5'-diformyl-2,2'-dipyrrylmethane as colorless needles. Yield, 1.39 g (84%). m.p.=231-232 °C(dec.) (lit.[113] 229-231 °C). ^{1}H-NMR(Acetone-d_6): 11.2(s, br., 2H), 9.41(s, 2H), 6.90(d, J=4.0Hz, 2H), 6.13(d, J=4.0Hz, 2H), 4.16(s, 2H); ^{13}C-NMR(DMSO-d_6): 178.4, 138.2, 132.3, 121.3, 109.6, 25.6; EI-MS(e/z, relative intensity): 203(M^++1, 11.5), 202(M^+, base), 173(23.9), 145(41.7), 117(11.3), 108(17.4), 94(10.2), 80(12.6), 67(6.4), 53(9.62), 51(8.5), 39(8.4).

Synthesis of ethyl 5-acetoxymethyl-3,4-dimethylpyrrole-2-carboxylate(152):

Lead tetra-acetate (12.0 g, 27.1 mmole) was added to a solution of ethyl 2,3,4-trimethylpyrrole-5-carboxylate (4.9 g, 27.1 mmole) in 120 ml glacial acetic acid at room temperature over 10 minutes with vigorously stirring. After the addition, stirring was continued for two more hours. Then, the acetic acid was removed by vacuum distillation. The residue was poured into water (200 ml) and the precipitate was collected by filtration, washed with water and dried in vacuum. Crystallization from aqueous acetone gave the ethyl 5-acetoxymethyl-3,4-dimethylpyrrole-2-carboxylate(152) as colorless needles. Yield: 5.47 g (85%). m.p.=132-133 °C (lit.[116] 132 °C). ^{1}H-NMR ($CDCl_3$): 11.8(s, br., 2H), 4.97(s, 2H), 4.30(q, J= Hz, 2H), 2.31(s, 3H), 2.02(s, 3H), 1.97(s. 3H), 1.36(t, J= Hz, 3H).

Synthesis of diethyl 3,3',4,4'-tetramethyldipyrrylmethane-5,5'-dicarboxylate(153):

A solution of ethyl 5-acetoxymethyl-3,4-dimethylpyrrole-2-carboxylate (4.2 g, 17.6 mmole) in ethanol (120 ml) containing 3 ml concentrated hydrochloric acid was kept at reflux for two hours. Then the reaction mixture was cooled in ice-bath and the precipitate was collected by suction filtration. The solid crude product was washed with ethanol and dried in vaccum. Recrystallization from

ethanol gave the diethyl 3,3',4,4'-tetramethyldipyrrylmethane-5,5'-dicarboxylate(**153**) as white solid. Yield: 2.40 g (79%). m.p.=196-198 °C(lit.[116] 198 °C). ^{1}H-NMR($CDCl_3$): 12.1(s, br., 2H), 4.34(q, 4H), 4.06(s, 2H), 2.07(s. 6H), 1.98(s, 6H);

Synthesis of 3,3',4,4'-tetramethyldipyrrylmethane(**154**):

A mixture of diethyl 3,3',4,4'-tetramethyldipyrromethane-5,5'-dicarboxylate (1.5 g, 4.3 mmole) and sodium hydroxide (0.69 g, 17.2 mmole) in 20 ml ethanol (95%) was heated at reflux under nitrogen for 24 hours. Then, the reaction mixture was cooled in ice water and acidified with acetic acid. The ethanol/acetic acid was removed by vacuum distillation. Then 5 ml of ethylene glycol was added to the residue and the mixture was stirred at 170°C under N_2 for 5 hours, cooled to room temperature and poured into 100 ml of water. The mixture was extracted with ether (3x30 ml) and the combined ether extracts was washed with water (2x20 ml), 5% aqueous sodium bicarbonate solution (2x20 ml) and dried with sodium sulfate. Column chromatographic purification over nutral alumina with hexanes/CH_2Cl_2 (80/20) as the eluent gave the expected 3,3',4,4'-tetramethyldipyrrylmethane(**154**) as white solid. Yield: 396 mg (92%). m.p.=88-89 °C (lit.[116] 87-88 °C). ^{1}H-NMR($CDCl_3$): 8.27(s. br. 2H), 6.38(s, 2H), 4.10(s, 2H), 1.96(s, 6H), 1.84(s, 6H). ^{13}C-NMR($CDCl_3$): 130.2, 127.4, 119.7, 108.5, 27.0, 14.1, 13.9.

Synthesis of 5,5'-diformyl-3,3',4,4'-tetramethyl-2,2'-dipyrrylmethane(**149**):

Benzoyl chloride(6ml) was added to a stirred solution of 3,3',4,4'-tetramethyl-2,2'-dipyrrylmethane (3.0 g) in N,N-dimethylformamide(DMF) (20 ml) at 0 °C. The reaction mixture rapidly turned to a thick paste. After the addition the mixture was kept at 0 °C with magnetically stirred for one hour. Then, the reaction mixture was diluted with ether (50 ml) and poured into water (10 ml). An excess sodium acetate in ethanol/water (70/30) was added and the mixture was warmed on a water-bath at 30 °C for two hours. The precipitate 5,5'-diformyl-3,3',4,4'-tetramethyl-2,2'-dipyrrylmethane was collected by suction filtration. Recrystallization from ethyl acetate/$CHCl_3$(20/80) gave the 5,5'-diformyl-3,3',4,4'-tetramethyl-2,2'-dipyrrylmethane as cream needles. Yield (84%). m.p.=296-298 °C (lit.[116] 293 °C). ^{1}H-NMR($CDCl_3$): 12.3(s, br., 2H), 9.46(s, 2H), 4.27(s, 2H), 2.05(s, 6H), 1.97(s, 6H); ^{13}C-NMR($CDCl_3$): 176.9, 139.7, 134.2, 129.1, 121.8, 25.9, 13.8, 13.5.

Synthesis of 5,5''-bisformyl-3',4'-dibutyl-2,2',5',2''-terthiophene(**155**):

(a), Synthesis of 5,5''-diformyl-3',4'-dibutyl-2,2',5',2''-terthiophene(**155**) by the lithiation of the 2,2',5',2''-terthiophene followed by the reaction of the lithiated compound with N,N-dimethylformide(DMF):

BuLi (2.8 ml of 1.6M in hexanes solution,2.2 eq.) was added to a cooled (-50 °C) mixture of 3',4'-dibutyl-2,2',5',2"-terthiophene (720 mg, 2.0 mmole), tetramethylethenediamine (TMEDA, 400 mg) and 40 ml haxanes by a syringe under N_2. After the addition, the reaction mixture was stirred at -50 °C for 30 minutes and then stirred at room temperature for another 30 minutes. The reaction mixture was recooled to -78 °C and 2.2 eq. of dimethyformamide (DMF) in 5 ml of ether was added slowly by a syringe. After the addition the reaction mixture was warmed slowly to room temperature, and stirred for one hour and then poured into 200 ml of 2% ice cold aqueous HCl solution with vigorously stirring. The mixture was extracted with CH_2Cl_2 (4x30 ml) and the combined organic extracts were washed with water, saturated sodium bicarbonate and brine. Dried with $MgSO_4$. Removal of the solvent by a rotary evaporator gave a dark-colored residue as the crude product. Column chromatographic purification over silica gel with hexanes/ether/CH_2Cl_2 (65/20/15) as the eluent gave the expected 5,5"-diformyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**155**) as orange needles. Yield, 674 mg (81%). m.p.=92-93 °C (uncorrected). ^{1}H-NMR($CDCl_3$): 9.91(s, 2H), 7.73(d, J=4.5Hz, 2H), 7.27(d, J=4.5Hz, 2H), 2.78(t, J=8.9Hz, 4H), 1.54(m, 4H), 1.48(m, 4H), 0.97(t, J=7.9Hz, 6H); ^{13}C-NMR($CDCl_3$): 13.8, 22.9, 28.0, 32.5, 126.7, 130.5, 136.7, 142.8, 142.9, 145.6, 182.6; EI-MS(e/z, relative intensity): 418(M^++2, 16.4, 417(M^++1, 25.2), 416(M^+, base), 345(23.9), 331(7.3), 303(42.0), 288(6.1), 275(5.6), 270(5.5), 240(6.6), 227(5.6), 127(6.6), 41(7.1). UV-Vis(maximum absorption): 404nm ($CHCl_3$).

(b), Synthesis of 5,5"-diformyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**155**) by Vilsmeier reaction:

To a stirred solution of 3',4'-dibutyl-2,2',5',2"-terthiophene(1.8 g, 5.0 mmole) in dry N,N-dimethylformamide (10 ml) at 60 °C, an excess of $POCl_3$ (2.50 g, 16.3 mmole) was added dropwise over 10 minutes under nitrogen. After the addition, the reaction mixture was stirred at this temperature for two hours and at 80 °C for two more hours. Then an excess aqueous sodium acetate solution (20 ml, 10%) was added. The mixture was stirred at room temperature for five hours and heated on a steam-bath for 30 minutes. Then the mixture was diluted with 30 ml of water and the precipitate was collected by filtration. Coluum chromatographic purification over silica gel with hexanes/CH_2Cl_2 (50/50) as the eluent followed by crystallization from ethanol gave the 5,5"-diformyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**155**) as orange needles. Yield, 1.60 g (77%). All the physical properties are the same as those from the lithiation procedure(a).

Synthesis of 5,5"-bisacetyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**160**):

To a mixture of 3',4'-dibutyl-2,2',5',2"-terthiophene (360 mg, 1.0 mmole) and acetyl chloride (173 mg, 2.2 mmole) in 20 ml dry dichloromethane was added $SnCl_4$ (570 mg, 2.2 mmole, in 2 ml of dichloromethane). The resulting red mixture was stirred at room temperature for two hours. Then, the reaction was quenched with

10ml 3% HCl aqueous solution. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2x10 ml). The combined organic layers were washed with H_2O (2x20 ml), 5% $NaHCO_3$ (2x20 ml) and saturated NaCl (20 ml), dried with magnesium sulfate. Removal of the solvent gave an orange solid residue as the crude product. Column chromatographic purification over silica gel with hexanes/ethyl acetate (85/15) as the eluent followed by crystallization from hexanes/CH_2Cl_2 (90/10) gave the expected 2,5"-bisacetyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**160**) as orange needles. Yield:373 mg (84%). m.p.=96.0-96.5 °C (uncorrected). ^{1}H-NMR ($CDCl_3$): 7.61(d, J=4.5Hz, 2H), 7.15(d, J=4.5Hz, 2H), 2.77(t, J=8.2Hz, 4H), 2.55(s, 6H), 1.54(m, 4H), 1.50(m, 4H), 0.94(t, J=8.1Hz, 6H); ^{13}C-NMR ($CDCL_3$): 190.5, 144.2, 143.4, 142.2, 132.8, 130.5, 126.5, 32.6, 27.9, 26.6, 22.9, 13.8; EI-MS, e/z(relative intensity): 446(M^++2, 14.5), 445(M^++1, 24.6), 444(M^+, base), 401(5.6), 361(8.5), 360(12.9), 359(57.9), 318(7.1), 317(30.0), 316(13.5), 301(5.2), 274(6.1), 259(2.7), 227(3.3), 207(6.0), 169(3.6), 127(8.6), 97(2.2), 43(88.6). UV-Vis(maximum absorption): 395nm ($CHCl_3$).

Synthesis of 5,5"-bisformyloxime-3',4'-dibutyl-2,2',5',2"-terthiophene(**167**):

A mixture of 5,5"-bisformyl-3',4'-dibutyl-2,2',5',2"-terthiophene (300 mg, 0.72 mmole), hydroxyamine hydrochloride (200 mg, 2.88 mmole), sodium acetate (200 mg, 2.44 mmole) and 100 ml absolute ethanol was kept at 65 °C for two hours. Then the

ethanol was removed by a rotary evaporator to give a yellow colored residue which was subsequently extracted with CH_2Cl_2 (4x20 ml). The combined CH_2Cl_2 extracts were washed with water (2x20 ml) and dried with sodium sulfate. Removal of the solvent gave a yellow solid as the crude product which was determined by ^{1}H-NMR to be >96% pure. ^{1}H-NMR results show that it is a mixture of three isomers. Yield is quantitative. Column chromatographic purification over silica gel with ethyl acetate/hexanes (50/50) as the eluent followed by crystallization from ethanol gave one of the isomers as yellow needles. m.p.=169-170 °C (decomp.). ^{1}H-NMR(DMSO-d_6): 7.86(s, 2H), 7.46(d, J=4.5Hz, 2H), 7.24(d, J=4.5Hz, 2H), 2.70(m, 4H), 1.54(m. 4H), 1.48(m, 4H), 0.91(t, J=7.9Hz, 6H). ^{13}C-NMR(DMSO-d_6): 142.6, 139.8, 139.1, 134.7, 131.0, 129.1, 124.3, 31.6, 26.6, 21.7, 12.9; EI-MS(e/z, relative intensity): 446(M^+, 15.5), 428(M^+-18, 62.7), 410(M^+-36, base), 385(6.25), 367(12.8), 353(10.4), 343(19.5), 325(82.6), 310(14.8), 300(20.1), 292(14.5), 266(11.1), 252(10.1), 152(30.0), 146(10.6), 134(10.1), 69(12.8), 55(17.1), 43(21.3), 41(31.0);

Synthesis of 5,5''-biscyanol-3',4'-dibutyl-2,2',5',2''-terthiophene(**168**):

The 5,5''-bisformyloxime-3',4'-dibutyl-2,2',5',2''-terthiophene (**167**) (305 mg, 0.68 mmole) in 50 ml acetic anhydride was stirred at 100 °C under N_2 for ten hours. Then, the acetic anhydride was removed by vacuum distillation. 50 ml of water was added to the residue and the mixture was stirred at room temperature for 30

minutes. The product was extracted with CH_2Cl_2 (2x30 ml) and the combined organic layers were washed with water (2x15 ml), 5% sodium bicarbonate solution (2x15 ml), saturated NaCl solution (20 ml) and dried with sodium sulfate. Removal of the solvent by a rotary evaporator gave a dark-orange solid as the crude product. Column chromatographic purification over silica gel with ethyl acetate/hexanes (15/85) as the eluent gave the first orange band as the expected 5,5"-biscyanol-3',4'-dibutyl-2,2',5',2"-terthiophene (**168**). Yield: 187 mg (67%). m.p.=77-78 °C (uncorrected). ^{1}H-NMR ($CDCl_3$): 7.56(d, J=4.4Hz, 2H), 7.12(d, J=4.4Hz, 2H), 2.70(t, J=7.7Hz, 4H), 1.38-1.56(m, 8H), 0.95(t, J=7.8Hz, 6H); ^{13}C-NMR($CDCL_3$): 182.0, 142.1, 137.3, 128.9, 125.6, 113.5, 108.6, 32.2, 27.5, 22.5, 13.4; EI-MS(e/z, relative intensity): 412(M^++2, 14.8), 411(M^++1, 23.9), 410(M^+, base), 353(8.32), 327(10.9), 326(17.4), 352(76.2), 312(5.46), 311(7.73), 310(11.2), 292(11.2), 291(7.32), 151(28.3), 122(12.3), 57(7.53), 55(14.0), 43(14.4). UV-Vis(maximum absorption): 371nm ($CHCl_3$).

Further elution with the same solvent gave 5,5"-bisformyl-3',4'-dibutyl-2,2',5',2"-terthiophene (5.7 mg, 2%) as by-product with a recovery of starting material 5,5"-bisformyloxime-3',4'-dibutyl-2,2',5',2"-terthiophene (9.0 mg, 3%).

Synthesis of 5,5"-bisaminomethyl-3',4'-dibutyl-2,2',5',2"-terthiophene(**164**):

A mixture of the 2,5''-biscyanol-3',4'-dibutyl-2,2',5',2''-terthiophene(**168**) (200 mg. 0.49 mmole), $LiAlH_4$ (100 mg, 2.63 mmole) in 10 ml tetrahydrofuran was stirred at room temperature under N_2 for two hours. Then, the reaction was quenched with water (50 ml) and the product was extracted with ether (4x20 ml). The combined ether extracts were washed with 5% sodium bicarbonate solution (2x20 ml), saturated NaCl solution (20 ml) and dried with sodium sulfate. Removal of the solvent by a rotary evaporator gave a wax-like residue as the crude product. Column chromatographic purification over neutral alumina with hexanes/ether (60/40) as the eluent followed by crystallization from hexanes gave the 5,5''-bisaminomethyl-3',4'-dibutyl-2,2',5',2''-terthiophene(**164**) as orange solid. Yield: 187 mg (92%). m.p.=37-38 °C (uncorrected). ^{1}H-NMR ($CDCl_3$): 6.92(d, J=4.0Hz, 2H), 6.80(d, J=4.0Hz, 2H), 4.0(s, 4H), 2.66(t, J=8.5Hz, 4H), 1.71(s, br., 4H), 1.50(m, 4H), 1.41(m, 4H), 0.92(t, J=7.9Hz, 6H); ^{13}C-NMR(CDCL3): 147.1, 139.6, 134.2, 129.6, 125.3, 123.8, 41.4, 32.8, 27.6, 22.8, 13.7; EI-MS, e/z(relative intensity): 420(M^++2, 13.7), 419(M^++1, 22.2), 418(M^+, base), 404(4.07), 403(6.07), 402(23.8), 385(4.16), 375(3.27), 358(4.27), 346(5.72), 331(5.37), 330(6.93), 329(28.9), 285(7.16), 112(6.46), 97(4.87), 68(4.75), 56(6.54), 41(5.90);

Synthesis of macrocycle tetrabutylhexathiophenecine(**166**):

The 5,5''-bisaminomethyl-3',4'-dibutyl-2,2',5',2''-terthiophene(**164**) (150 mg, 0.36 mmole) in 200 ml methanol was kept at reflux under N_2 for 24 hours. Then the methanol was removed by a rotary evaporator, and 30 ml of CH_2Cl_2 and 20 ml of water was added to the brown colored residue. The insoluble dark colored resin-like product was separated by filtration, washed with water and cold methanol, and dried in vacuum. Yield: 67 mg (45% by weight). This compound was identified as a polymeric material by ^{1}H-NMR and mass spectra.

The CH_2Cl_2 layer was separated from the filtrate and the aqueous layer was extracted with CH_2Cl_2 (3x10 ml). The combined CH_2Cl_2 extracts were washed with water (2x20 ml), 5% $NaHCO_3$ aqueous solution (2x20 ml), saturated NaCl aqueous solution (20 ml) and dried with sodium sulfate. The solvent was removed by a rotary evaporator until about 5 ml left. Then, about 20 ml of ethanol was added and the mixture was kept in dark with air bubbling through it for five days. Then the solvent was removed by a rotary evaporator to give a dark-colored residue. Column chromatography over neutral alumina with hexanes/ethyl acetate/CH_2Cl_2 (65/20/15) as the eluent gave the first dark-orange band which was collected. The solvent was removed and the residue was further purified by column chromatography over silica gel with hexanes/ethyl acetate/CH_2Cl_2 (60/15/25) as the eluent. Recrystallization from ethanol/ethyl acetate(85/15) gave the expected macrocycle (**166**) as purple lustre needles. m.p.=254-255 °C (uncorrected). Yield: 2.15 mg(1.5% based on the starting 5,5''-bisaminomethyl-3',4'-dibutyl-2,2',5',2''-terthiophene(**164**)). ^{1}H-NMR($CDCl_3$): 8.21(s, 4H), 7.54(d, J=4.4Hz, 4H),

7.38(d, 4.4Hz, 4H), 2.63(t, J=6.9Hz, 8H), 1.31-1.68(m, 16H), 0.91(t, J=7.8Hz, 12H). ^{13}C-NMR($CDCl_3$): 158.4, 143.5, 140.2, 135.8, 131.9, 127.2, 124.0. High resolution mass spectra, calculated for $C_{44}H_{48}N_2S_6$, 797.204, found: 797.158. UV-Vis(maximum absorption): 483nm ($CHCl_3$).

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