Pergamon

Tetrahedron, Vol. 53, No. 30, pp. 10357-10400, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00629-7

The Preparations and Some Properties of Mixed Aryl-Thienyl Oligomers and Polymers

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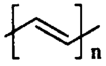
Abstract: The syntheses by transition metal coupling reactions of a large number of oligomers constructed from benzene and thiophene rings are described. The first use of arylcadmium chlorides for such coupling reactions is reported. The routes chosen allow for rational variation in the modes of linkage, the substitution and the proportions of the two units. The benzene and thiophene rings are always joined in a known order and may bear a wide variety of regularly spaced functional groups. Additionally the shape of the oligomers may be varied at will. In all cases p-type doping with iodine or ferric chloride leads to large enhancements in conductivity.

1. INTRODUCTION

As long ago as 1910,[1] the lustrous bronze appearance of poly(sulfurnitride),$(SN)_x$, implied that this non-metallic polymer might have metal-like properties. This inference was confirmed sixty years later[2] and it was further shown that the polymer became superconducting at below 0.26°K.[3,4] Exposure of $(SN)_x$ to bromine or similar oxidising agents, a process known as 'doping', enhanced the room temperature conductivity of $(SN)_x$ by an order of magnitude.[5]

The discovery of semi-conducting polyacetylene (**1**)(PA),[6-9] has focused attention on organic polymers capable of extended electron delocalisation. These include polyaromatics such as poly(*p*-phenylene)(**2**)(PPP),[10] polythiophene(**3**)(PT),[11] polypyrrole(**4**)(PP),[12] polyfuran(**5**)(PF)[13] and polyselenophene(**6**).[14] Polyarylvinylenes such as poly(phenylenevinylene)(**7**)(PPV)[15] and poly(thienylenevinylene)(**8**)(PTV)[16] are similar to polyaromatics and show good stability, processibility and mechanical properties. Heteroatoms may be incorporated into the polymer backbone in polymers such as polyaniline[17](**9**) and poly(*p*-phenylenesulfide)[18,19](**10**)(PP5).



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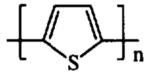

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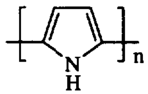

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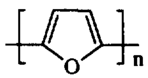

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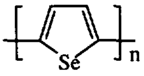

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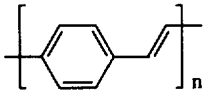

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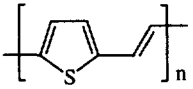

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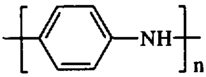

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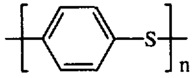


(10)

There are many potential applications of (**1**)-(**10**) and their derivatives and this has generated intense interest in the synthesis and properties of these and related systems.[20] The materials offer alternatives for a variety of applications including batteries,[21-24] electrochromic displays,[25] the protection of semi-conductor photoanodes,[26-29] information storage,[30] photoenergy conversion,[31] electrocatalysis,[32,33,34] as sensors,[35-39] for molecular electronics[20d] and for the controlled release of drugs.[38] The situation has been reviewed.[39,40]

With this wide range of possible applications there is a need for versatile, flexible syntheses of polyaromatics of precise structure containing functional or other organyl groups which allow for the tuning of the physical and chemical properties of the polymers or oligomers.

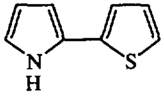
1.1. Appraisal of synthetic methodology for polyaromatics

At the commencement of this work all the synthetic strategies available had strong drawbacks. There were two general approaches - the electrochemical and the chemical.

1.1.1. Electrochemical Synthesis

The electrochemical method for the oxidative polymerisation of aromatic monomers can frequently be manipulated so as to give films which are tough enough for a wide variety of applications.[39] An important feature of this approach is the control of the incorporation and release of ions (doping - undoping).[41,42] However, electrochemical synthesis depends on surface couplings of cation radicals, such couplings becoming increasingly less regioselective as the polymer grows.[29] As a result, though electrochemically produced polypyrrole is drawn with regular α,α'-linkages (2,5-linkages) between the rings as in (**4**), this is an idealised structure, and XPS studies[43] show that as many as one in three pyrrole rings suffers from a structural disorder, part of which is due to linkages other than 2,5. Another indication of the lack of regularity is a comparison of PT when derived from thiophene or 2,2′-bithienyl.[29,43,44] If the polymer were as shown in (**3**), then regardless of its origin, the product polymer from each source would be the same. In fact, they are not identical. A 1-µm film derived from thiophene has a peak width at half height (PWHH) of ~ 300-350mV at the peak oxidation potential (E_{pa}) of +1.0V. The film derived from 2,2′-bithienyl also has $E_{pa} = +1.0V$ but with a much sharper oxidation peak with a PWHH of only ~ 90mV for a 1μm thick film. It was proposed that this was due to the fact that the film derived from α,α′-bithienyl was more regular in terms of α,α′-linkages than that derived from thiophene, as the joining of each unit of α,α′-bithienyl *ipso facto* involves two clearly defined α,α′-linkages. This more uniform structure for the polymer chains in turn confers more desirable electrochemical properties.

In case of monomers such as **(11)**[45] and **(12)**,[46] the *order* of the units is unknown as well as the linkages and their electrochemically produced polymers, **(13)** and **(14)**, represent an enormous set of structures.



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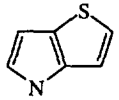

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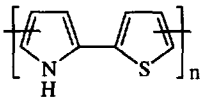

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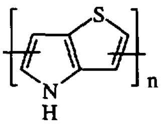
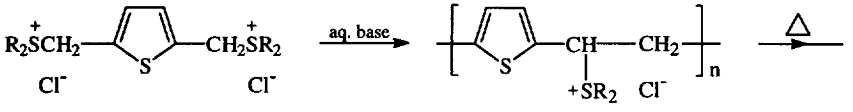


(14)

A further point is that in unsymmetrical units it is not possible to control the topicity of the polymer by electrochemical polymerisation. Thus there could be poly(*meta*-phenylene) and poly(*ortho*-phenylene) as well as poly(*para*-phenylene), and also polymers containing controlled proportions of 1,4- , 1,3 and 1,2- linkages in a known order. The situation with regard to more complex aromatic systems such as naphthalene is even more unsatisfactory.

1.1.2 Chemical synthesis of polymers containing a single aromatic group

At the inception of this work,[47,48] the situation with regard to chemical polymerisations[49] was little better than with regard to electrochemical polymerisations. Polymerisations could be carried out either directly on a monomer to give the desired polymer or indirectly to give a polymer precursor that could be cast or otherwise undergo morphological modification before conversion to the final polyaryl. Examples of the former methods are the oxidative production of PPP[50,51] **(2)** and PP **(4)**[52] from benzene and pyrrole respectively. The favoured method for the preparation of **(2)** is by the polymerisation of benzene by oxygen or a high valent metal salt in the presence of Lewis acids.[50,51] The products always contain cross-linked polymer, the proportion varying with the specific method used. The oxidative polymerisation of pyrrole whether at a vapour liquid interface[52] to give a film or by halogens[53] or by Fe(III) and Cu(II)[12,54,55] leads to a product as undefined as that produced electrochemically. Indirect routes[49] include the bacterial oxidation of benzene, Ziegler-Natta catalysis of the resultant protected cyclohexadienediol, followed by elimination to give PPP.[56] This method is somewhat similar to the polymerisation of 1,3-cyclohexadiene followed by pyrolysis or chemical manipulation.[57,58] Polymer **(8)** has been prepared using the process in equation (1). The precursor polymer **(16)** is prepared from **(15)** using aqueous base, and can be cast into thin films from its aqueous solution. Thermolysis then yields PTV **(8)** (eq. 1).[59]


(8) (1)

(15) (16)

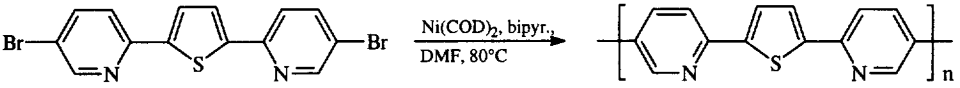
Variations on this theme using methoxy rather than dialkylsulfonium substituents have been successfully investigated.[60,61] This type of synthesis gives polymers of good chemical structure but is currently limited to the production of regular polymers containing only one repeating aromatic unit. It has been applied to the production of poly(2-butoxy-5-methoxyphenylenevinylene),[62] and poly(2-methoxy-5-methylthiophenylene vinylene).[63]

More germane to the work described in this paper is the self coupling of aromatic dihalides under the influence of a variety of metals. Thus the Fittig reaction,[64] Ullmann coupling,[65] the nickel(II) catalysed coupling of Grignard reagents[66] and the oxidative coupling of dilithioarenes[67] have all been utilised to make (**2**). All of these reactions are summarised in equation (2).

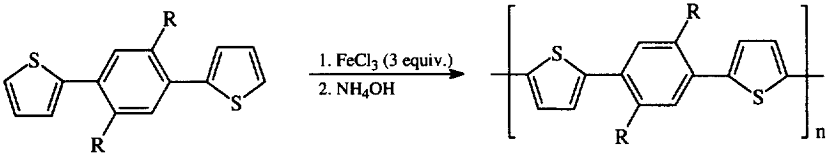
$$ArX_2 \longrightarrow Y\text{—}(Ar)_n\text{—}Z \qquad (2)$$

1.1.3 The chemical synthesis of regular mixed polyaromatics

If the aromatic group to be polymerised is itself of a mixed nature then chemical methods can yield regular polyaromatics containing more than one type of unit. An example, utilising equation (2) is given in equation (3).[68]


(3)

Another approach, giving compounds of the type we report here was provided by Reynolds as shown in equation (4).[69,70]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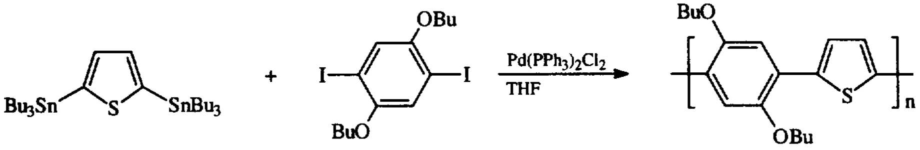
Two recent papers[71,72] have analogies with the work reported here and previously by us (equation 5).[47,48]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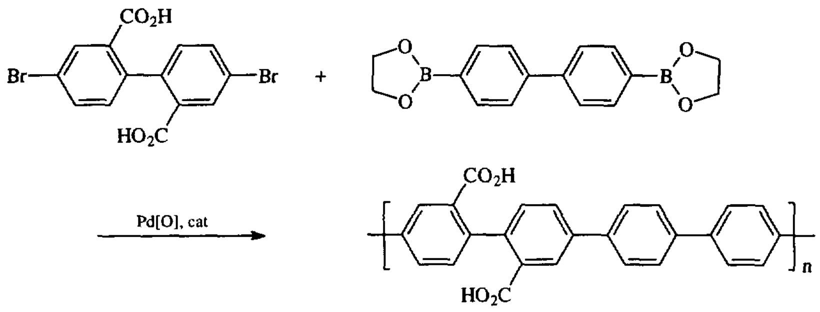
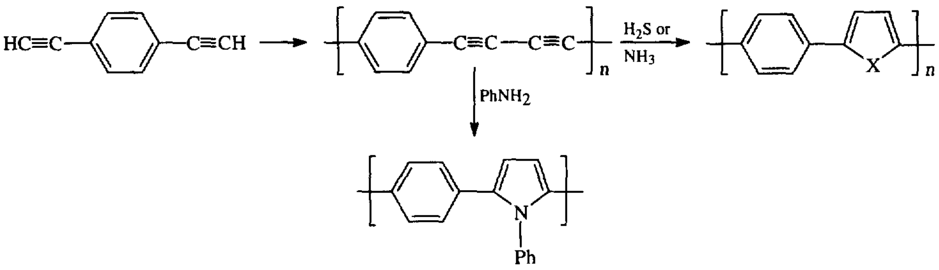


(6)

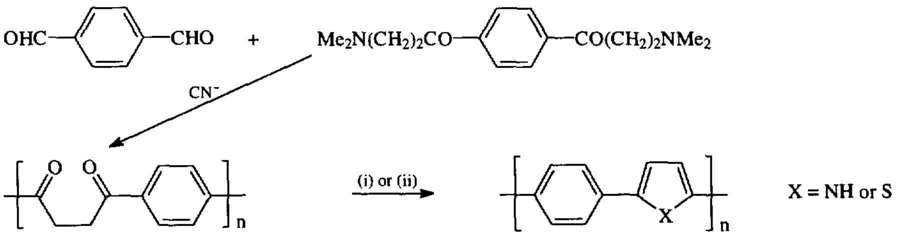
Another approach is to make a polymer with functionality suitable for conversion either to a benzene ring or to a heteroaromatic. The first example was the preparation of high molecular weight poly(diethynylbenzenes)[72] by oxidative coupling[73] of 1,3- and 1,4-diethynylbenzenes, followed by transformation to pyrroles or thiophenes.[72] (Scheme 1).



Scheme 1

However the addition of either H_2S or NH_3 resulted in much cross linking and 1,3- additions,[72] and only the addition of aniline gave a reasonable polymer containing the two required units. We have further explored this approach[40] and will report on it separately. It has also been utilised for the production of oligomers.[74]

A similar approach (Scheme 2) involves the production of poly-1,4-diketones followed by reaction with either Lawesson's reagent[75] or ammonia.[76] A similar series of reactions was used to prepare thiophene oligomers.[77]



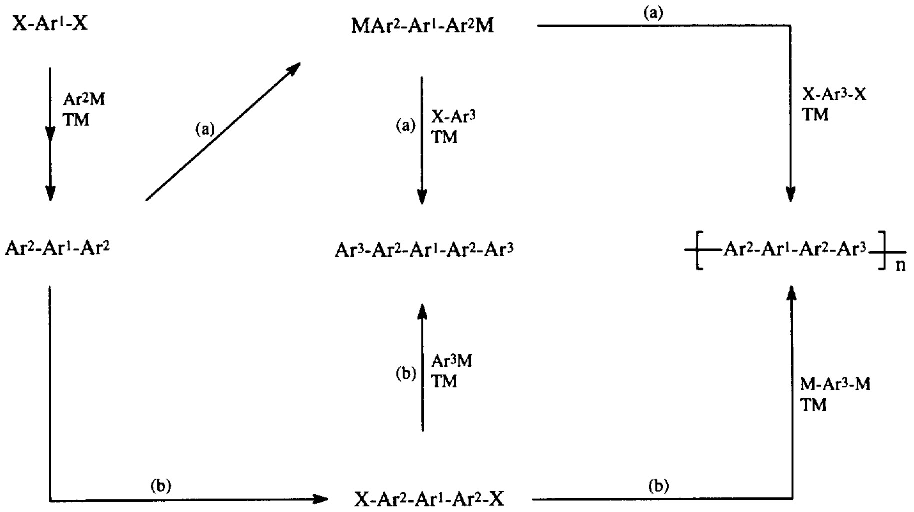
(i) Lawesson's reagent; (ii) NH_3

Scheme 2

2. Current Work

2.1 *Basic approach to the production of mixed aromatic polymers/oligomers of defined structures*

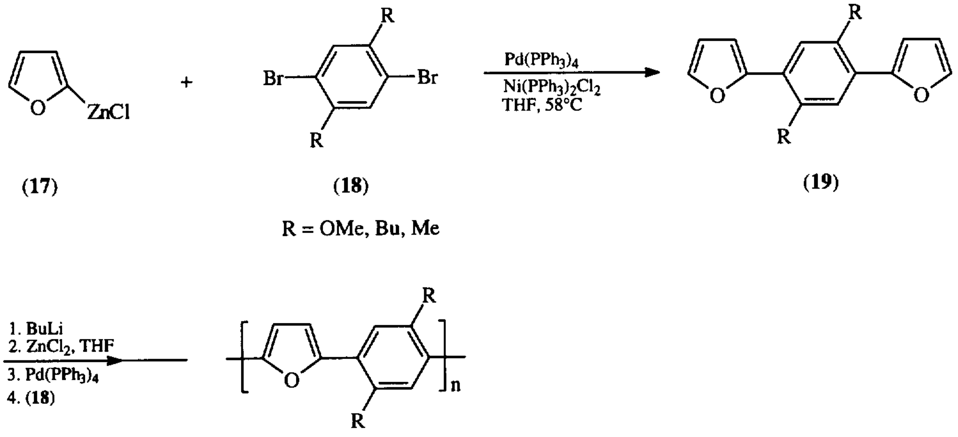
Our methodology for the synthesis of mixed aromatic polymers/oligomers of defined structures is shown in its simplest form in Scheme 3, which sets out two approaches (a) and (b) which are illustrated in the text.



X = Br, I; M = ZnCl, SnR_3, CdCl, $B(OR)_2$; TM = transition metal catalyst.

Scheme 3

This approach was first actualised by us[47] in the following simplified sequence (Scheme 4) (Ar^1=Ar^3).



(17) **(18)** **(19)**

R = OMe, Bu, Me

(20)

Scheme 4

Polymers (**20**) have the following attributes: (i) all the units are joined unequivocally by 1,4- and 2′,5′-linkages;[78,79] (ii) the *order* of the units is defined; (iii) the stoichiometry of the units relative to each other is defined and (iv) there is no cross linking.[47,48]

The theoretical advantages of Scheme 3 are as follows.

(i) The polymer chains can carry a variety of units such as phenylene and thiophenylene in varying orders and proportions.

(ii) The units are joined by known and specific linkages.

(iii) The order of the units is unequivocal.

(iv) Isomeric polymers with different topicities can be produced.

(v) Regularly spaced functional groups can be introduced.

(vi) Because both routes (a) and (b) (Scheme 3) are available, functional groups that can withstand zinc or tin reagents but not lithiation, can be introduced on either Ar^1 or Ar^3.

(vii) By making Ar^1 and Ar^3 symmetrical 2,5-disubstituted benzenoids, problems of 'head-tail' linkages are obviated, and not only the order of the units but also the order of substituents is clear.

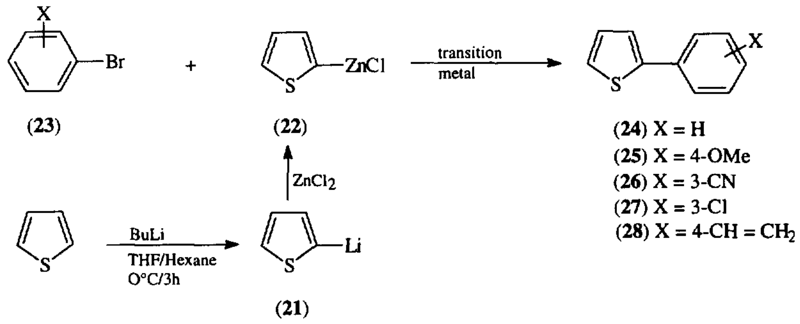
(vii) Completely two dimensional polymers containing heteroatoms can be produced.

(viii) Three dimensional polymers can be made by the use of novel cross linking agents such as 1,3,5-trithienylbenzene (*vide infra*).

This paper limits itself to the production of mixed aryl-thienyl polymers, and related oligomers made as models and also for electrochemical polymerisations.

2.2 *Synthesis of two ring compounds*

Two ring compounds (**24**) - (**28**) were readily produced by the process shown in Scheme 5.



Scheme 5

Quantitative lithiation of thiophene in the 2-position to give (**21**)[80] was confirmed by deuteriation studies (Scheme 5). Transmetallation with anhydrous zinc chloride gave the zinc derivative (**22**) used to couple with (**23**). We initially used Pd(PPh$_3$)$_4$ as catalyst for all our reactions, to give (**24**)-(**27**) in >80% isolated yields (Table 1). When a nickel catalyst was used with 1-bromo-3-chlorobenzene as substrate, then

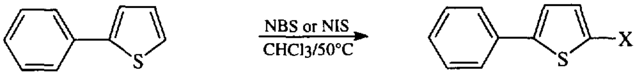
1,3-dithienylbenzene was the main product, only 5% of the mono-coupled product (**27**) being produced (Table 1, entry 4). *This differentiation between the palladium and nickel catalysed reactions opens the way for the step-wise introduction of two different aromatic or heteroaromatic groups into a bromochlorobenzene.* Another point of great interest was that a cyano group, (entry 3), possible precursor of either a carboxyl or a benzylamine functionality, was successfully carried through the coupling process. A 4-vinyl group, a precursor of polystyrene polymers was also incorporated, though in poor yield to give (**28**).

Table 1. Couplings to yield 2-arylthiophenes according to Scheme 5

Entry	Aryl halide (**21**)	Conditions[a]	Time (h)	Product	Yield[b](%)
1	X = H	THF, 50°C, $Pd(PPh_3)_4$	24	(**24**)	80
2	X = 4-OMe	THF, r.t., $Pd(PPh_3)_4$	3	(**25**)	88
3	X = 3-CN	THF, 50°C, $Pd(PPh_3)_4$	10	(**26**)	80
4	X = 3-Cl	THF, r.t., $Cl_2Ni(PPh_3)_2$	16	(**27**)	5
5	X = 3-Cl	THF, r.t. $Pd(PPh_3)_4$	6	(**27**)	82
6	X = 4-vinyl	50°C, $Pd(PPh_3)_2Cl_2$	20	(**28**)	26[c]

[a]All reactions in THF. [b]Isolated, purified yields. [c]26% 4-Bromostyrene (26%) recovered.

Compound (**24**) was readily halogenated[81] by NBS or NIS (equation 7) to give (**29**) and (**30**) which are useful for oligomer preparations.

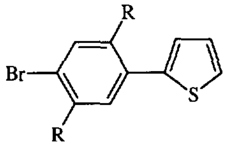


(7)

(**24**)

(**29**) X = Br (88%)
(**30**) X = I (77%)

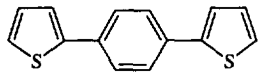
Other halogenated 2-arylthiophenes (**31**), (**32**) and (**33**) were produced as by-products from the attempted couplings of the corresponding 1,4-dibromoarenes with (**22**) to give three-ring compounds, as in 2.3.



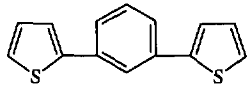
(**31**) R = Me (20%) (**33**) R = Pr^i (40%)
(**32**) R = Bu^n (14%)

2.3 *The synthesis of three ring compounds*

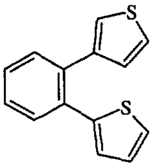
Compounds (**34**), (**35**) and (**36**) were produced by the transition metal catalysed coupling of (**22**) with 1,4-, 1,3- and 1,2-dibromobenzenes respectively.



(34) (72%)

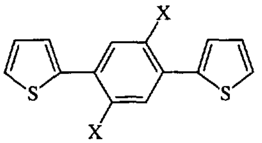


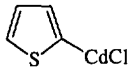
(35) (65%)



(36) (34%)

The reactions to give (**34**) and (**35**) proceeded in the usual fashion for unhindered aryl bromides, but the reaction of 1,2-dibromobenzene was considerably slower, and reaction was incomplete even after 24h at 50°C. Compound (**34**) was also made in 65% yield from the palladium catalysed coupling of 1,4-dibromobenzene with 2-thienyl*bis*(isobutoxy)borane in Suzuki conditions.[82] Electrochemical polymerisations of (**34**) and (**35**) could be carried out on plate electrodes to give films that are chemically and physically very stable, and which we have shown elsewhere may prove suitable for electrochromic devices.[83,84]





(47)

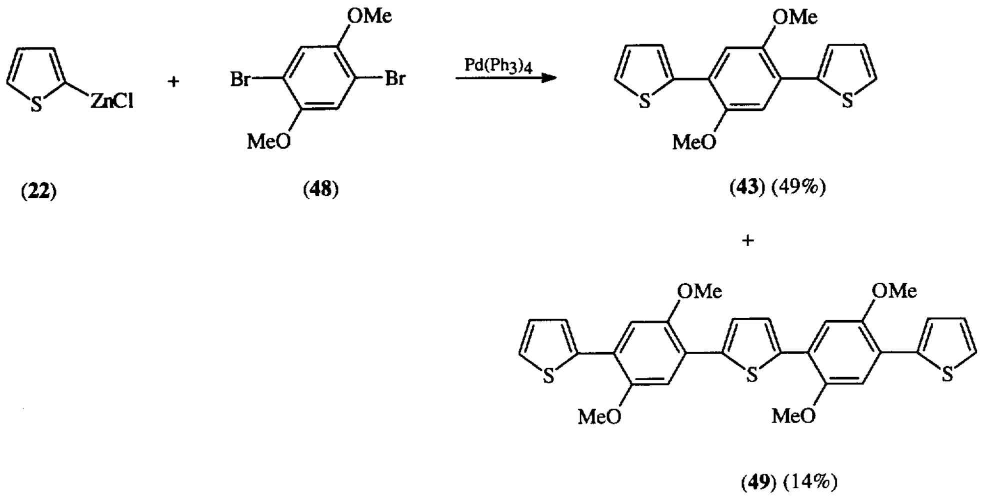
(**37**) X = Me (57%)
(**38**) X = Pr^i (2%)
(**39**) X = Bu (66%)
(**40**) X = Oct (3.4%)

(**41**) X = CN (62%)
(**42**) X = CO_2Me (28%)
(**43**) X = OMe (49%)
(**44**) X = OBu (66%)

(**45**) X = OMOM (55%)
(**46**) X = OH

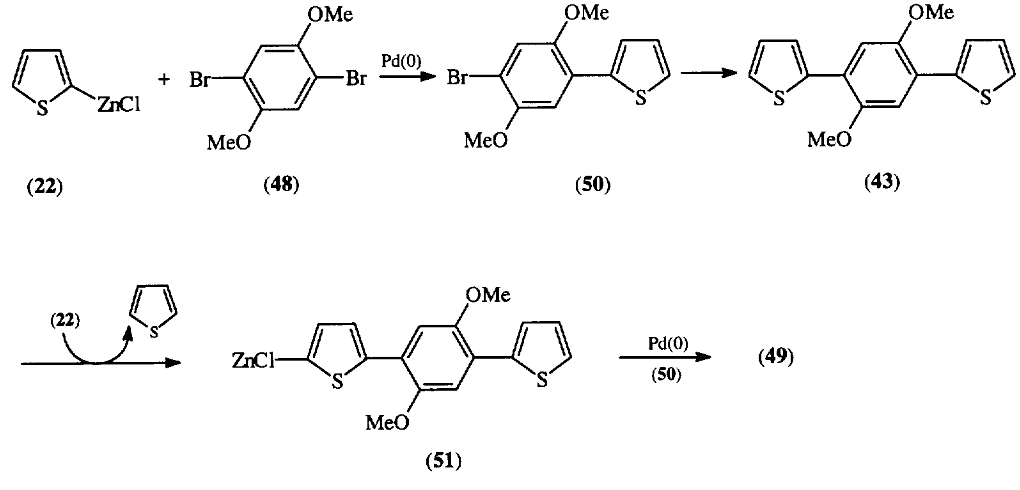
Compounds (**37**) to (**45**) were made by coupling the appropriate 1,4-dibromides with (**22**). Certain points of interest emerged. Compound (**37**) was produced in 57% yield using not 2-thienylzinc chloride (**22**) but 2-thienylcadmium chloride (**47**). To our knowledge this is the first use of cadmium salts in transition metal ($Pd(PPh_3)_4$) catalysed aromatic coupling, and has certain advantages. The main one is that cadmium chloride is far easier to dry (120°C, laboratory oven, 3h) than is zinc chloride (140°C, 0.5 mmHg, P_2O_5) and can be stored much more easily. However cadmium salts may be more toxic and must be handled carefully. In this reaction the mono-coupled salt (**31**) was also obtained in 20% yield. The *n*-butyl compound (**39**) was produced without difficulty, together with 14% of (**32**). However in our standard conditions, (**38**) was produced in only 1% yield (together with 40% of mono-coupled product (**33**)) and (**40**) could be made in only 2% yield. The latter yield was improved to 3.4% by use of $Pd[0](PPh_3)_2$.[85]

Compound (**42**) was produced in rather low yield (28%), with the mass balance being made up by starting material, (1,4-dibromo-2,5-dicarbomethoxybenzene). The cyano groups however, perhaps due to their lower bulk, did not inhibit coupling and (**41**) was synthesised in reasonable yield. Compound (**43**) was produced in only moderate yields (20-35%) using either $Ni(dppp)Cl_2$ or $Ni(PPh_3)_2Cl_2$ and therefore the coupling of **22** and **48** was carried out using $Pd(PPh_3)_4$ with 2.5 equivalent of (**22**) to give the results shown in equation 8.



(8)

The production of 5-ring compound (**49**) shows that the couplings are not quite so straightforward as we had initially assumed. We suppose that (**49**) is formed, by an exchange reaction followed by coupling as in Scheme 6. We have obtained similar results with furanyl compounds.[79]



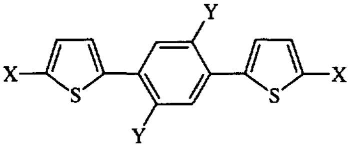
Scheme 6

The first step must be the production of (**50**). If (**50**) builds up, due to slow further reaction to give (**43**), then an exchange reaction of (**43**) with excess (**22**) can occur so as to give (**51**) which reacts with (**50**) to give (**49**).

When almost exactly two equivalents of (**22**) were reacted with 1,4-dibromo-2,5-di-*n*-butoxybenzene using $Pd(PPh_3)_2Cl_2$ as catalyst, a 66% yield of (**44**) was isolated, without any analogue of (**49**) being produced.

The MOM ether (**45**) was readily made and it was shown that the MOM groups did not direct lithiation to their *o*-positions,[86] but that α, α′- lithiation of the thienyl rings occurred as usual. Brief acid hydrolysis of (**45**) gave (**46**)(100%), which could not be produced by direct coupling.

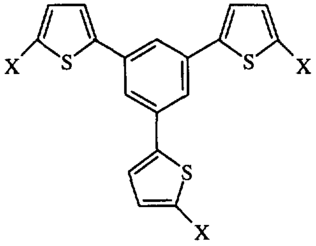
Halogenated compounds (**52**), (**53**) and (**54**) were produced from the parent compounds (**34**) and (**44**) by halogenation with either NBS or NIS.



(**52**), X = Br, Y = H (88%)
(**53**), X = I, Y = H (60%)
(**54**), X = I, Y = OBu (71%)

2.4 *Four ring compounds*

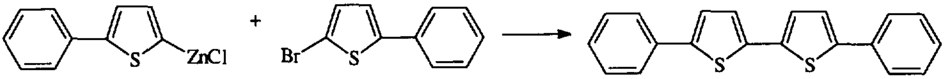
The coupling of 1,3,5-tribromobenzene with (**22**) proceeded well using $Pd(PPh_3)_4$ to give (**55**) in 65% yield. Compound (**55**) was later used as a novel cross linking agent in polymerisation reactions. Lithiation of (**55**) occurred readily to give the α,α′,α′′-trilithio derivative (**56**) from which (**57**) was made for cross linking and for further couplings.



(**55**) X = H; (**56**) X = Li; (**57**) X = ZnCl

Compound (**59**) has an α,α′-bithienyl linkage similar to those produced by the electrochemical polymerisation of (**34**) and (**35**). We had difficulty in its synthesis, and therefore the coupling was used as a template to develop suitable methodology.

We first tried variations on our normal methodology as in equation 9, with the results given in Table 2.

 (9)

(**58**) (**29**) (**59**)

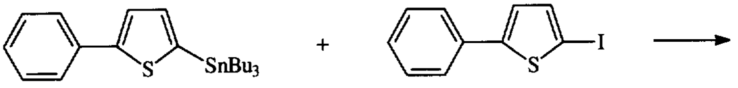
Table 2. The preparation of (**59**) according to equation 9

Entry	Solvent	Catalyst	Temp. °C	Time (h)	Yield (%)[a]
1	DME[b]	Pd(dppf)Cl_2[c]	80	96	21
2	DME	$Pd(PPh_3)_2Cl_2$	80	96	29
3	DME	$Pd(PPh_3)_2Cl_2$, CuI, NEt_3	80	96	58
4	DME	$Pd(PPh_3)_4$	80	96	29
5	THF	$Pd(PPh_3)_4$	60	120	48
6	Diglyme	$Pd(PPh_3)_4$	140	96	15
7	Diglyme	$Pd(PPh_3)Cl_2$	140	96	32
8	Diglyme	Pd(dppf)Cl_2	140	96	17

[a)]Precipitates from reaction mixture. [b)]DME = $MeOCH_2CH_2OMe$. [c)]dppf = bis(diphenylphosphino)ferrocene. [d)]Diglyme = $MeOCH_2CH_2OCH_2CH_2OMe$.

As the results of the palladium catalysed coupling of arylzinc chlorides with aryl bromides were unsatisfactory for the synthesis of (**59**), other methodology was sought. Coupling of organotin reagents with aryl halides tolerates a large number of functional groups.[86] In general, when alkyl and aryl groups are both attached to the tin, it is the aryl group that preferentially couples using palladium catalysis. Aryl-[87] or alkenyl iodides[88] are generally superior to the corresponding bromides, and dimethyl formamide appears to be a good solvent for the reactions.[89]

Based on the above findings and some preliminary experiments, we concentrated on the coupling of (**30**) and (**60**) to yield (**59**) (equation 10).



(**59**) (10)

(**60**) (**30**)

The results of a series of exploratory experiments are given in Table 3, from which it is clear that DMF is a better solvent for the coupling than THF, regardless of catalyst,. Furthermore a nickel catalyst (entry 9), gave a lower yield compared with a comparable palladium catalyst (entry 1). Pd(II) (entries 1, 2) gave a better or comparable yield to Pd(0) (entries 3, 4).

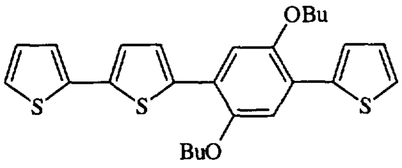
Table 3. The preparation of (**59**) according to equation 10[a]

Entry	Solvent	Catalyst	Temp. (°C)	Yield (%)[b]
1	DMF	$Pd(PPh_3)_2Cl_2$	130	61
2	DMF	$Pd(PPh_3)_2Cl_2$. PPh_3	130	74
3	DMF	$Pd(PPh_3)_4$	130	68
4	DMF	$Pd(PPh_3)_4$. PPh_3	130	69
5	THF	$Pd(PPh_3)_4$	50	33
6	THF	$Pd(PPh_3)_4$. PPh_3	50	26
7	THF	$Pd(PPh_3)_4$. CuI. NEt_3	50	46
8	THF	$Pd(PPh_3)_4$. PPh_3. CuI. NEt_3	50	26
9	DMF	$Ni(PPh_3)_2Cl_2$	100	45

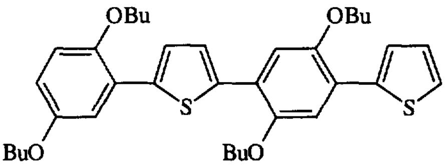
[a])All reactions carried out for 48h. [b])Isolated yields.

The conditions of the best yielding small scale experiment (entry 2) were adopted for larger experiments (see Experimental) and gave an 88% yield of (**59**). These conditions were used elsewhere.

Two further linear four-ring compounds (**61**) and (**62**) were made, the former being of particular interest as a potential monomer for electrochemical polymerisation.



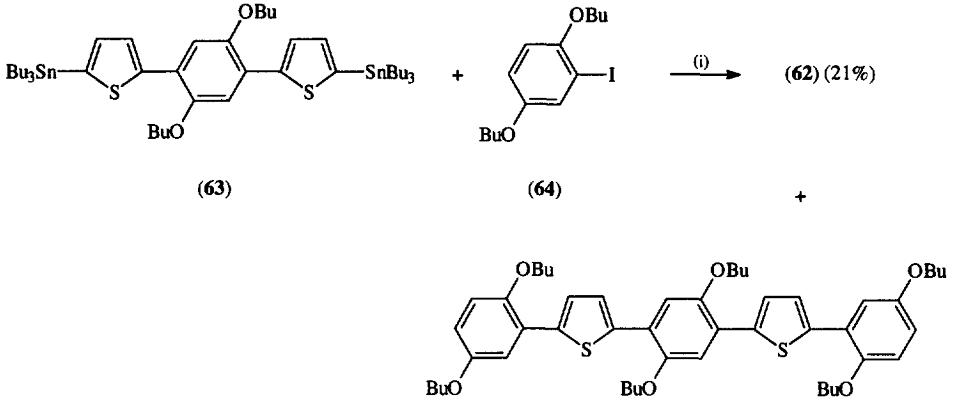
(**61**)



(**62**)

Compound (**61**) in fact was a small biproduct (0.6%) of the reaction of 4 equivalents 2-thienyltri-*n*-butylstannane with (**53**) but if one equivalent of 2-thienyltri-n-butylstannane were used then the yield of (**61**) was enhanced.

Compound (**62**) was best prepared by the reaction shown in equation (11).



(63) **(64)** **(65)**

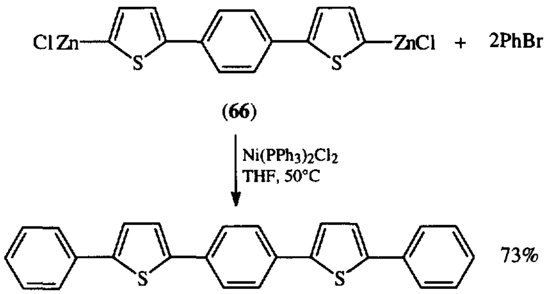
(11)

(i) $Pd(PPh_3)_2Cl_2$, DIBAH, DMF
60°C, 20h.

Compound (**63**), made in the usual way from (**44**) (Section 2.3), was reacted with (**64**), using a highly active Pd(0) catalyst produced by the reduction of $Pd(PPh_3)_2Cl_2$ with DIBAH.[85] The 21% yield of (**62**) is a minimum yield, as a large proportion of (**62**) was admixed with some (**65**). Time did not permit a full purification, and the presence of (**65**), which was not isolated pure, was established by CI mass spectrometry.

2.5 *Five ring compounds*

Compound (**67**) was readily obtained in 73% yield *via* the Ni(II) catalysed coupling of two equivalents of bromobenzene with the zinc reagent (**66**) prepared *in situ* from (**34**).

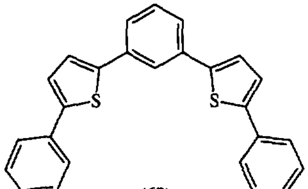


(66) **(67)**

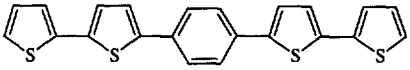
(12)

Compound (**67**) was obtained as a brick red powder which was poorly soluble in all common solvents, its identity being confirmed by accurate mass spectrometry. Compound (**67**) could also be prepared by an alternative strategy whereby two equivalents of (**58**) were coupled with 1,4-dibromobenzene using $Pd(PPh_3)_4$ as catalyst giving (**67**) as yellow crystals in a somewhat reduced (55%) yield.

Palladium catalysed coupling of 2 equivalents of (**58**) with 1,3-dibromobenzene gave (**68**) in 48% yield, this compound again, exhibiting very poor solubility in common organic solvents.



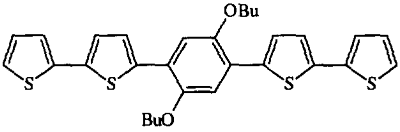
(68)



(69)

Synthesis of (**69**) was achieved in 35% yield by coupling 2 equivalents of thienylzinc chloride, (**22**), with the dibromide (**52**) using the catalyst prepared by reduction of $Pd(PPh_3)_2Cl_2$ with DIBAH.[85] Previous attempts to prepare (**69**) *via* (**52**) but using $Pd(PPh_3)_4$ as catalyst in the same conditions had failed. This result demonstrates the superior activity of the reduced catalyst. Compound (**69**) exhibited very poor solubility in all common organic solvents.

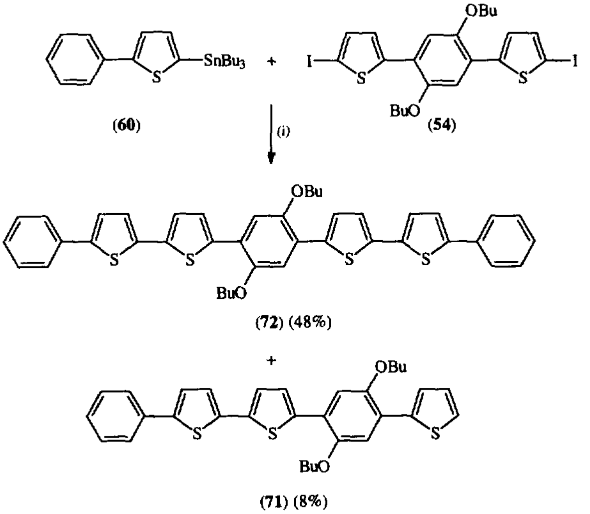
Reaction of 4 equivalents of 2-tributylstanylthiophene with (**54**) using $Pd(PPh_3)_2Cl_2$/DIBAH gave a 40% isolated yield of (**70**) which was significantly more soluble than its counterpart, (**69**) which allowed us to obtain a solution nmr spectrum. A low yield (0.6%) of (**61**) was also isolated from this reaction (Section 2.4).



(**70**)

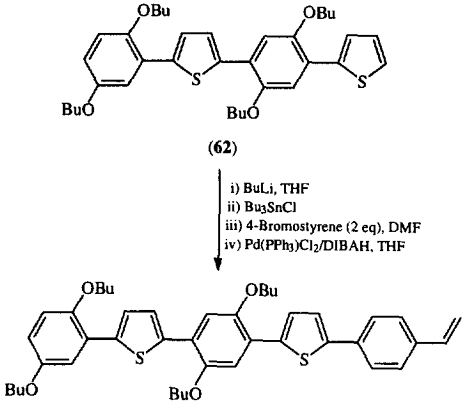
Methoxy substituted 5 ring oligomer (**49**) was obtained as a side product in the reaction of 2.5 equivalents of (**22**) with 1,4-dibromo-2,5-dimethoxybenzene (equation 8). The mechanism for the formation of (**49**) is discussed above (Scheme 6).

Three equivalents of (**60**) reacted with (**54**) in accordance with equation (13) to give (**71**) as a side product in 8% yield along with 48% of (**72**).



(13)

Five ring oligomer (**73**) was prepared according to equation (14).



(73) (26%)

(14)

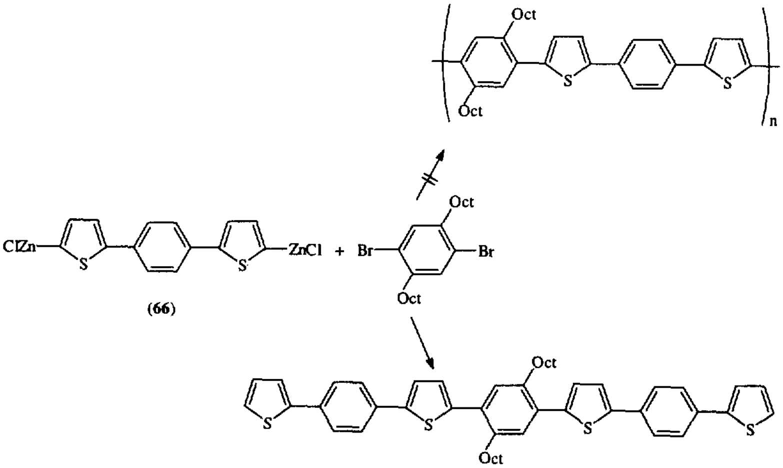
The actual yield of (**73**) should be higher than the 26% isolated since the compound did not separate cleanly from unreacted (**62**) and a significant proportion of the reaction product remained as an unseparated mixture of (**73**) and (**62**).

Compound (**73**) is of interest as the vinyl group could be used either as a precursor to a *polystyrene* type polymer or as an anchor onto a polysiloxane backbone thus providing two variations of an inert polymer backbone featuring regularly spaced polyaromatic pendant groups. The butyloxy groups confer good solubility characteristics on (**73**) and should therefore facilitate both the polymerisation and subsequent processing of the polymers.

2.6 *Seven ring Compounds*

Compound (**72**) was obtained as outlined in equation (13) in 48% yield along with 8% of (**71**).

Attempted polymerisation according to equation (15) yielded the oligomer (**74**).



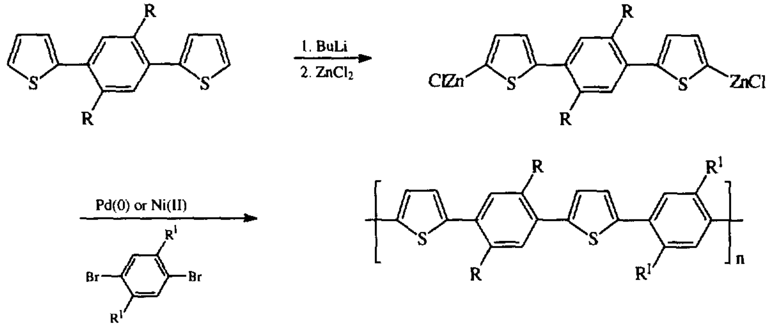
74

(15)

3. Preparation of polymers by transition metal catalysed cross coupling reactions

3.1 Simple polymers via *strategy (a), Scheme 3*

Strategy (a), Scheme 3 with $Ar^1 = Ar^3$ was adopted as a convenient method to make aryl-thienyl polymers of known stoichiometry, order and topicity as shown in Scheme 7.



(75) $R = R^1 = H$
(76) $R = R^1 = Me$
(77) $R = R^1 = Bu^n$
(78) $R = R^1 = OMe$
(79) $R = H, R^1 = OMe$
(80) $R = H, R^1 = Bu^n$
(81) $R = H, R^1 = CO_2Me$

Scheme 7

Polymer (**75**) was obtained from (**34**) and 1,4-dibromobenzene as a brown solid which precipitated from the reaction. It was insoluble in all the solvents tried and did not melt below 360°C. X-ray analysis showed it to be highly crystalline, like its furan analogue.[90] Polymer (**76**) was green, insoluble and did not melt below 360°C. Polymer (**77**) (from **43** and 1,4-dibromo-2,5-di-*n*-butylbenzene) was obtained as a rather sticky green solid mass (39%) after column chromatography. It had good solubility in chloroform, dichloromethane and hot toluene. GPC analysis suggested a maximum molecular weight of 2000-3000 which translates to a chain length of between 7-11 units.

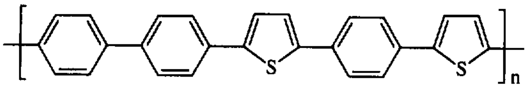
Polymer (**78**) was made (55%) as usual and was a green powder, slightly soluble in polar solvents in which it gave an intense green fluorescence. By g.p.c. it had a molecular weight of between 2000-3000.

The versatility of the methodology was next demonstrated by the preparation of (**79**), (**80**) and (**81**) which are polymers with alternating substituted and unsubstituted benzene rings.

Polymer (**79**) was a yellow material slightly soluble in chloroform to give yellow solutions that, unlike its analogue (**77**) did not fluoresce. Polymer (**80**) was a yellow powder, not melting below 360°C and soluble in chlorinated hydrocarbon solvents. Polymer (**81**) was obtained as a green powder that was slightly soluble in DMSO, DMF, THF and chloroform.

3.2. Demonstration of variation of the ratio of benzene and thienyl rings

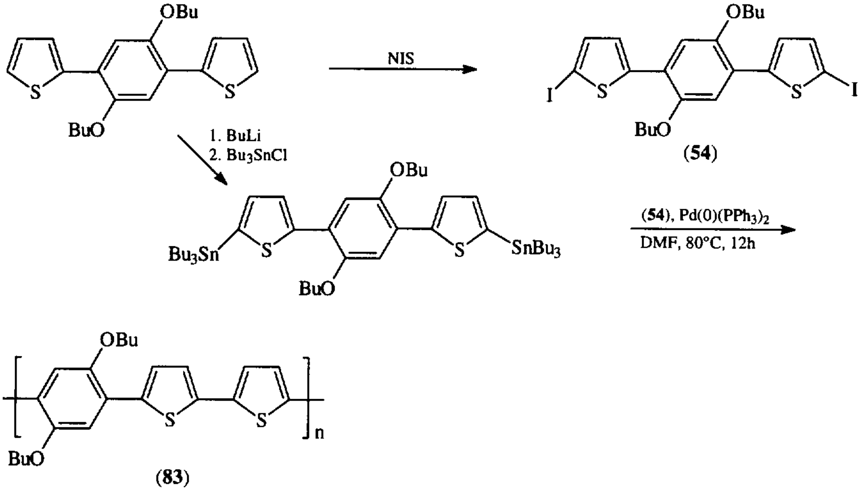
The ratio of benzene to thienyl rings was altered by using the methodology of Scheme 7, but substituting 4,4′-dibromobiphenyl for a 1,4-dibromobenzene. The product (**82**) has *three* benzene rings for every *two* thienyl rings, but maintains the high degree of structural order associated with this methodology.



(82)

Substance (**82**) was a brown powder which did not soften below 360°C and was completely insoluble in all solvents tried.

The ratio of phenyl to thienyl rings was also varied as shown in Scheme 8 (approach (b), Scheme 3).

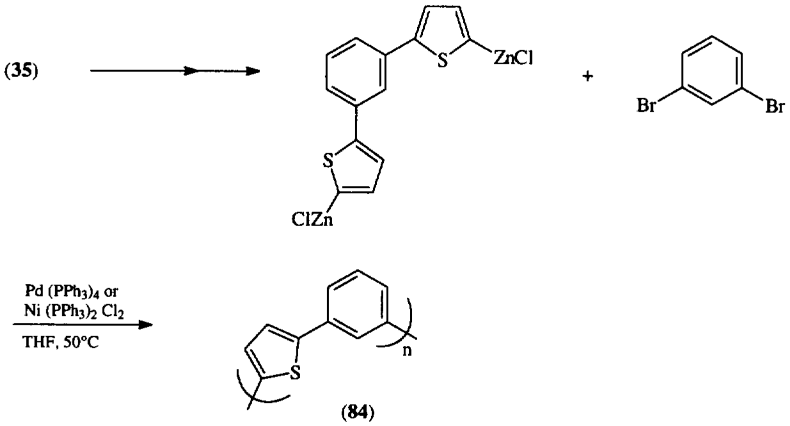


Scheme 8

Polymer (**83**) was a bright red powder produced in 62% yield.

3.3. *Variation in the shape of the polymer*

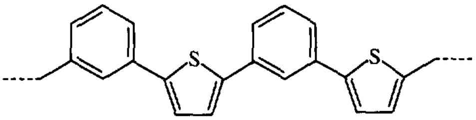
The approach shown in Scheme 7 was adapted as shown in Scheme 9 to give polymer (**84**).



Scheme 9

Polymer (**84**) is the 1,3- analogue of (**75**), and although the radical(s) produced on doping cannot delocalise along the chain in the same way as (**75**) and other 1,4-diaryl polymers such as PPP (**2**), nevertheless (**84**) gives an increase in conductivity on doping very comparable with (**75**).

The shape of (**84**) is not known. It could of course be spiral, but a pseudo-linearity (ripple linearity) as shown in (**85**) is also possible and this would allow ready chain hopping, which may also be a major phenomenon for the truly linear (**75**).



(**85**)

One point that should be noted is that the 1,3-linked precursor (**35**) could be coupled with a linear 1,4-dibromide, such as 1,4-dibromobenzene to give yet more shape control.

3.4. *Use of a novel cross linker*

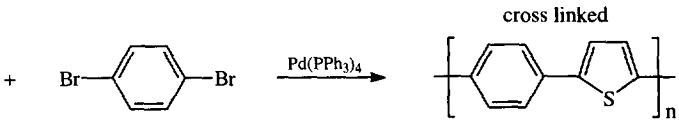
We have previously shown that (**57**) is readily produced and, as a trivalent organometallic containing the same units as polymers (**75**) and (**85**) linked in the α-position as usual, it should prove an unusual but highly apposite cross linking agent.

Therefore the reaction shown in equation (16) was carried out.

(**66**) (0.9 equivalent)

+

(**57**) (0.1 equivalent)



(16)

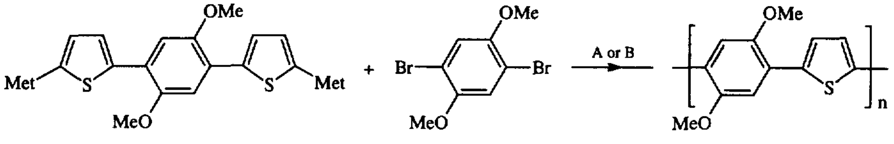
(**86**)

We had previously shown[91] that (**57**) undergoes metal catalysed cross coupling in the usual fashion, and therefore it should participate in the polymerisation shown in equation (16) to give a highly complex three dimensional set of structures. The polymer (**86**) that resulted was the usual insoluble powder that results from the production of unsubstituted polymer. It had no solubility in any solvent tried and also it had no special enhancement of conductivity in either the doped or undoped state as compared with similar polymers which are not cross linked.

3.5. *Effect of metal on molecular weight*

A study of reaction (17) shown in Table 4 was undertaken to investigate the effect on the reaction of the metal used to give the soluble polymer, (**78**).

Table 4. The effect of the metal on the coupling reaction of equation 16



(87) **(48)** **(78)**

(17)

	Met	Conditions	Average n of (78)	M. Wt
(a)	MgBr	A[1]	2-4	388-766
(b)	ZnCl	A	6-8	1164-1552
(c)	CdCl	A	6-8	1164-1552
(d)	$B(OH)_2$	B[2]	10-12	1940-2328

[1] A = $Pd(PPh_3)_4$, THF, 24h, 50°C. [2] B = $Pd(PPh_3)_4$, THF/H_2O, Na_2CO_3, 24h, 62°C.

Compounds (**87a-c**) were all made by salt exchange from the corresponding α,α'-dilithio compound and were used directly. Compound (**87d**) was made by the reaction of a large excess of $B(OPr^i)_3$ with the dilithio-compound, followed by gentle acid hydrolysis. It was used directly without full characterisation.

Clearly the bis-Grignard reagent (**87a**) was inferior to the zinc and cadmium reagents (**87b**) and (**87c**) which were comparable. The reagent that gave the highest molecular weight was the boronic acid (**87d**).[92] However in our hands the thienylboronic acids were difficult to produce and keep and therefore zinc and cadmium reagents were used for our initial investigations. However further investigations of the boronic acids are justified.

4. *Electrical properties of chemically produced aryl-thienyl polymers*

The electrochemical polymerisations of dithienylbenzenes and the properties of the films produced have been reported elsewhere,[83,84] and are the subject of active investigation and will not be discussed here. Only the parent compounds (**34**) and (**35**) gave useable films on plates.

We decided that we would subject our polymers to acceptor (p-type) doping by oxidants,[93] expecting that our mixed aryl-thienyl compounds would behave as Class I polymers like PA, PPP and PP[94] which simply undergo electron transfer upon doping to produce the conducting complex. All conductivities were measured by converting the dried powders to discs of 1 cm diameter and 0.5-1 mm of thickness, and then small slabs of material are used for the resistance measurements on a Keithley-617 programmable electrometer.

We first studied the parent polymer, (**75**) with the results shown in Table 5.

Table 5. Effect of dopant and conditions on conductivity of poly(1,4-phenylene-2′,5′-thienylene) (**75**)

Experiment	Doping Agent	Method	Conductivity (S cm^{-1})
1.	None	---	4.0 x 10^{-11}
2.	$FeCl_3$	$CHCl_3$	4.0 x 10^{-5}
3.	$FeCl_3$	glyme	2.6 x 10^{-4}
4.	$FeCl_3$	CH_3NO_2	1.2 x 10^{-3}
5.	$CuBr_2$	CH_3NO_2	3.0 x 10^{-7}
6.	$CuBr_2$	THF	9.2 x 10^{-6}
7.	Benzoquinone	$CHCl_3$	3.3 x 10^{-8}
8.	I_2	vapour (I Torr)	2.3 x 10^{-3}
9.	I_2	$CHCl_3$	5.0 x 10^{-5}
10.	Bu_4NIO_3	THF	1.8 x 10^{-6}

The effective dopants, dry, dark green $FeCl_3$ in CH_3NO_2, (experiment 4),[95] and iodine vapour (experiment 8) caused a colour change to an intense black either in the solution or the powder. We found that over a period the $FeCl_3/CH_3NO_2$ method was better as iodine is lost slowly from the iodine doped powders. The $FeCl_3$ doped powders when pressed into a disc had an almost metallic lustre, whilst the less effective dopants gave green or brown discs.

Using the established conditions we examined the effect of doping on our polymers (Table 6).

Table 6. Acceptor doping of phenylene-thienylene polymers

Experiment	Polymer	Dopant[a]	Conductivity (S cm^{-1})
1.	(**75**)	Undoped	4.0 x 10^{-11}
2.	(**75**)	$FeCl_3$	1.2 x 10^{-3}
3.	(**75**)	I_2[b]	2.3 x 10^{-3}
4.	(**84**)	Undoped	2.0 x 10^{-11}
5.	(**84**)	$FeCl_3$	2.0 x 10^{-4}
6.	(**82**)	Undoped	2.0 x 10^{-11}
7.	(**82**)	$FeCl_3$	1.9 x 10^{-4}
8.	(**82**)	DDQ[c]	2.0 x 10^{-8}
9.	(**76**)	Undoped	1.3 x 10^{-10}
10.	(**76**)	$FeCl_3$	1.9 x 10^{-4}
11.	(**77**)	Undoped	3.6 x 10^{-11}
12.	(**77**)	I_2	1.6 x 10^{-3}
13.	(**78**)	Undoped	1.0 x 10^{-7}
14.	(**78**)	$FeCl_3$	1.6 x 10^{-3}
15.	(**79**)	Undoped	4.2 x 10^{-8}
16.	(**79**)	I_2	2.1 x 10^{-4}
17.	(**80**)	Undoped	3.2 x 10^{-11}
18.	(**80**)	I_2	6.1 x 10^{-4}
19.	(**81**)	Undoped	4.12 x 10^{-11}
20.	(**81**)	I_2	2.5 x 10^{-7}
21.	(**86**)	Undoped	3.0 x 10^{-11}
22.	(**86**)	I_2	5.0 x 10^{-5}

[a] Unless otherwise stated $FeCl_3$ was used in a freshly made up solution in CH_3NO_2 and iodine was used as a freshly made up solution in chloroform. [b] Iodine vapour used. [c] Used in ethanol solution.

For completeness experiments 1, 4 and 8 in Table 5 have been included in Table 6 as experiments 1, 2 and 3. For the experiments in Table 6, for convenience we generally used iodine in chloroform for doping. However this procedure is *ca.* 2 x 10^{-2} times less effective than iodine vapour (compare experiments 8 and 9 of Table 5) and so the conductivities of Table 3 are far from optimal as regards the iodine doping.

The unsubstituted 1,4- and 1,3- polymers (**75**) and (**83**) show an increase of *ca.* 3 x 10^8 and 1 x 10^7 in conductivity on doping in the same conditions. The 1,3- polymer (**83**) cannot form quinonoid forms and *this implies that the polaron mechanism is not the main conduction mechanism in those cases.* Polymer (**82**) with a different ratio of phenylene to thienyl rings from any other polymer in the Table, nevertheless shows a comparable level of enhancement of conductivity of 10.[7] DDQ was far less effective, although we could obtain fairly concentrated solutions, despite the report that when uncorporated into films of (**8**) it gave a very marked increase in conductivity.

The undoped conductivities of the methoxypolymers (**77**) and (**79**) were high at 1.0 x 10^{-7} and 4.2 x 10^{-8} respectively. This is in line with our other work on their polyfuran analogues[48] and is not unexpected in that a reduction in the band gaps and ionisation energies of polymers containing strong electron donating groups have been observed, for example with poly(3-alkoxy-2,5-thienylene vinylene).[96] Doping was successful with *all* the polymers however, whether they had electron donating or electron withdrawing (CO_2Me) on the phenyl rings.

ACKNOWLEDGEMENT We thank Dr G Coles (University of Wales, Swansea) for conductivity measurements and the EPSRC for financial support.

EXPERIMENTAL

General Conditions

Acetic acid, 1,4 dibromobenzene, 4-bromostyrene, N-iodosuccinimide 1,4-diisopropylbenzene, 1,4-dibromo-2,5-dimethylbenzene, 1,4-dimethoxybenzene, mercuric oxide, iodine, cuprous iodide, triphenylphosphine, *tetrakis*(triphenylphosphine)palladium, *bis*(triphenylphosphine)palladium dichloride, *bis*(triphenylphosphine)nickel dichloride and diisobutylaluminium hydride (DIBAH, 1.0M in THF) were used as received from the suppliers. (1,1′-Diphenylphosphinoferrocenyl)palladium dichloride ($Pd(dppf)Cl_2$) was prepared from *bis*(acetonitrile)palladium dichloride ($Pd(MeCN)_2Cl_2$) and dppf according to Hagartu.[93] *n*-Butyllithium was purchased as a 2.5 M solution in hexanes and estimated prior to use.[94] Bromobenzene and toluene were both purified by shaking with conc. H_2SO_4 (ice-cooled in the case of toluene), washing with water, 10% aqueous NaOH, then water again before pre-drying over calcium chloride, refluxing over calcium hydride and distillation. THF and diethyl ether were filtered through alumina then refluxed over and distilled from calcium hydride under argon. 1,2-Dimethoxyethane (glyme) and *bis*(2-methoxyethyl)ether (diglyme) were stirred over calcium hydride and distilled under reduced pressure. Dimethylformamide was stirred with dried magnesium sulfate and distilled under reduced pressure. Thiophene and furan were stirred over and distilled from calcium hydride under argon. Chloroform was washed with water, pre-dried with calcium chloride, refluxed over phosphorous pentoxide and distilled. Pentane was distilled from P_2O_5. N-Bromosuccinimide was recrystallised from water then dried in a desiccator over P_2O_5 under reduced pressure. Zinc chloride was weighed into a flask and dried at 140°C under reduced pressure (5 mm Hg) for at least 4h. The flask was then immediately sealed with a rubber septum and flushed with dry nitrogen until cool. Tetrahydrofuran was added *via* a double ended needle under nitrogen pressure and the zinc chloride dissolved. The solution was used immediately. Cadmium chloride was dried in an oven at 120°C for at least 4h. Tri-*n*-butyltin chloride was distilled under reduced pressure. Chromatographic purifications were performed on columns of silica gel (230-400 mesh) under medium pressure, using mixtures of pentane and chloroform (solvent gradient) as eluent. All procedures involving air sensitive reagents were performed in oven dried glassware, assembled whilst hot and cooled in a slow stream of dry nitrogen. Transfer of reagents between flasks was achieved *via* double ended needles using nitrogen or argon pressure or by graduated syringes, all reaction vessels being under a positive pressure of nitrogen or argon. Melting points were recorded on a Gallenkamp hot stage apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a WM 250 Bruker instrument at 250.1 MHz and 62.9 MHz respectively. DEPT/135 spectra were also obtained on this instrument. NMR spectra were recorded in $CDCl_3$ unless otherwise stated and are reported relative to tetramethylsilane ($\delta = 0$). J values are quoted in Hz. Infrared spectra were recorded on a Perkin-Elmer 1420 ratio recording spectrometer and a UNICAM SP 1050 spectrometer as KBr discs unless otherwise stated. UV/visible spectra were recorded on a Phillips PV 8720 UV/Vis scanning spectrophotometer with absorption maxima reported in nm along with ($\log_{10} \varepsilon$). Mass spectra were obtained using a VG MASSLAB 12-250 quadrupole instrument using alternating chemical/electron impact ionisation (ACE) conditions. Accurate masses were recorded on a ZAB-E VG analytical reverse geometry magnetic instrument. Elemental analyses were provided by the Microanalytical Service at the University of Wales Cardiff. Molecular weight determinations were carried out at the RARDE (MoD) establishment, Waltham Abbey using a Waters GPC system equipped with Waters Expert Version 4.0 analytical software.

Typical procedure for the preparation of 1,4-dibromo-2,5-diorganylbenzenes.

*1,4-Dibromo-2,5-di-*n*-octylbenzene.* A solution of 1-bromooctane (158.8g, 0.8 mol) in diethyl ether (250 ml) was added slowly to a mixture of magnesium turnings (20g, 0.8 mol) and iodine (0.2g, 1.6 mmol) with stirring and occasional heating. Once addition was complete, the mixture was heated under reflux for 30min to complete formation of the Grignard reagent. A mixture of 1,4-dichlorobenzene (59 g, 0.4 mol) and $Ni(Ph_2PCH_2CH_2CH_2PPh_2)Cl_2$ (0.5 g, 0.9 mmol) in diethyl ether (300 ml) and THF (50 ml) was added slowly to the well stirred solution of *n*-octylmagnesium bromide with occasional cooling in ice-water if the reaction became too violent. Upon completion of addition and when the reaction appeared to have stabilised, the reaction mixture was heated under reflux for 24h, then cooled in ice-water, carefully quenched with distilled water then shaken with aqueous hydrochloric acid (3M, 250 ml). The aqueous phase was extracted with diethyl ether (2 x 200 ml) and the combined organic phases washed with water (100 ml), dried over $MgSO_4$, filtered and the solvent evaporated. Distillation (192°C/ 0.13mmHg) of the crude material gave 1,4-di-*n*-octylbenzene (105 g, 86%) as a clear oil. δ_H 7.07 (4H, s), 2.55 (4H, b.rt), 1.59 (4H, m), 1.30 (20H, m), 0.88 (6H, b.rt); δ_C 140.1, 128.3, 32.0, 31.6, 29.8, 29.6, 29.5, 29.4, 22.7, 14.1; m/z 302 (M^+, 100), (b) Neat bromine (49.5 g, 0.31 mol) was added dropwise with stirring to neat 1,4-di-*n*-octylbenzene, (146.8 g, 0.155 mol) containing iodine (0.2 g, 1.6 mmol) at 0°C, with rigorous exclusion of light. The reaction was stirred for 24h after completion of addition then quenched with aqueous sodium hydroxide (3M, 50 ml). The aqueous layer was extracted with ether (2 x 100 ml), and the combined organic phases were washed with water (2 x 50 ml), dried over $MgSO_4$, filtered and the solvent evaporated. Recrystallisation of the crude product from ethanol gave the title product (61.5 g, 84%) mp 38°-40°C (lit[95] 40°C); ν_{max} (KBr) (cm^{-1}), 850, 1010, 1050, 1120, 1370, 1420, 1470; δ_H (100 MHz) 7.35 (2H, s), 2.63 (4H, t), 1.57-1.50 (4H, m), 1.36 (4H, m), 0.88 (6H, t); δ_C (25.2 MHz) 141.3, 133.7, 123.1, 35.6, 31.9, 30.8, 29.9, 29.4, 29.3, 22.7, 14.1; m/z 462 (50); 460 (100), 458 (51).

*1,4-Di-*n*-butylbenzene.* Using the general conditions above 1,4-Dichlorobenzene (59 g, 0.4 mol) gave the title compound (58 g, 77%); bp 71°C/0.66 mm/Hg; δ_H 7.04 (4H, s), 2.54 (4H, t), 1.56 (4H, quintet), 1.34 (4H, sextet), 0.90 (6H, t); δ_C 140.0, 128.3, 35.4, 33.9, 22.5, 14.0; m/z 190 (M^+, 100).

*1,4-Dibromo-2,5-di-*n*-butylbenzene.* Bromination of 1,4-di-*n*-butylbenzene (58g, 0.31 mol) as in the general method, gave the title compound (67g, 61%) mp 27°-28°C; ν_{max} (KBr) (cm^{-1}) 1050, 1380, 1475; δ_H 7.35 (2H, s), 2.63 (4H, t), 1.53 (4H, m), 1.40 (4H, m), 0.94 (6H, t); δ_C 141.3, 133.8, 123.1, 35.2, 32.0, 22.4, 13.9; m/z 350 (M^+, 45), 348 (M^+, 89), 346 (M^+, 43), 307 (50), 305 (100), 303 (52), 227 (41), 225 (42). Found C, 48.45; H, 5.64% $C_{14}H_{20}Br_2$ requires C, 48.30; H, 5.79%

1,4-Dibromo-2,5-diisopropylbenzene. Bromination of 1,4-diisopropylbenzene (24.0 g, 0.15 mol) gave the title compound (35.0 g, 73%); mp 35°-37°C; ν_{max} (KBr) (cm^{-1}) 695, 805, 1040, 1070, 1110, 1200, 1250, 1330, 1370, 1390, 1480; δ_H (100 MHz) 7.44 (2H, s), 3.28 (2H, m), 1.20 (12H, d, J, 7); δ_C (25.2 MHz) 146.3, 130.6, 123.4, 32.5, 22.6; m/z 322 (M^+, 12), 320 (M^+, 31), 305 (100), 128 (56). Found C, 45.33; H, 5.00%; M^+, 319.9599; $C_{12}H_{16}Br_2$ requires C, 45.0; H, 5.02%; M^+, 319.9599 for $C_{12}H_{16}{}^{79}Br^{81}Br$.

1,4-Dibromo-2,5-dimethoxybenzene (**48**). Concentrated sulfuric acid (12.5 ml of sp. gr 1.83, 18 M) was added to a solution of potassium bromide (17.75 g, 150 mmol) and 1,4-dimethoxybenzene (100 g, 72.5 mol) in water (50 ml) and ethanol. Hydrogen peroxide (30% v/v, 30 ml) was added over 15 min whilst the solution was gently heated under reflux. Heating was then continued for 5 minutes during which pale red needles precipitated from solution. Water was added slowly to the hot mixture and the crystals collected by filtration and washed with water. Recrystallisation from ethanol/dichloromethane (1:1) gave the title product (192 g, 89%) as white crystals mp 142°- 143°C (lit[97] 143°C); δ_H 7.07 (2H, s), 3.83 (6H, s); δ_C 150.5, 117.1, 110.5, 57.0; m/z 296 (M^+, 100), 281 (66).

1,4-Dibromo-2,5-dihydroxybenzene. Neat bromine (58g, 0.36 mol) was added dropwise to a well stirred solution of 1,4-dihydroxybenzene (20g, 0.18 mol) in glacial acetic acid (500 ml) at 0°C and the solution stirred for a further 30 minutes after completion of addition. Acetic acid was evaporated and the grey solid remaining was washed with aqueous saturated sodium bicarbonate (50 ml). Trituration with ethyl acetate and evaporation of the solvent gave the crude product which was purified by column chromatography (chloroform/ethyl acetate 1:1) giving the title compound (28.4 g, 58%) as yellow crystals. mp 177°-178°C (lit[98] 177°C); δ_H 8.94 (2H, brs), 7.11 (2H, s); δ_C 148.1, 119.8, 108.9; m/z 268 (M^+, 100), 188 (25), 169 (10), 131 (8).

1,4-Dibromo-2,5-di(methoxymethyloxy)benzene. Neat chloromethylmethyl ether (1.23 g, 15 mmol) was added dropwise *via* syringe over 10 minutes to a stirred mixture of 1,4-dibromo-2,5-dihydroxybenzene (2.0 g, 7.5 mmol) and oven dried potassium carbonate (4.0 g, 40 mmol) in acetone (50 ml) under an argon atmosphere. The mixture was stirred for 1.5h at room temperature then aqueous sodium hydroxide (1M, 50 ml) and ethyl acetate (100 ml) were added. The aqueous layer was extracted with ethyl acetate (50 ml) and the combined organic layers washed with water (50 ml), dried over $MgSO_4$, filtered and the solvent evaporated to yield the title compound (1.9 g, 71%) as light-grey crystals mp 94°- 98°C; ν_{max} (KBr) (cm^{-1}) 760, 1180, 1270, 1310, 1360, 1400, 1460, 1500, 1720, 1970, 2030, 3000, 3010; δ_H 7.37 (2H, s), 5.17 (4H, s), 3.52 (6H, s); δ_C 149.4, 121.2, 112.1, 95.9, 56.5; m/z 356 (M^+, 50), 325 (10), 275 (28), 62 (9), 45 (100). Found, C, 33.47; H, 3.38%; M^+ 355.9082; $C_{10}H_{12}Br_2O_4$ requires C, 33.71; H, 3.37%; M^+, 355.9082 for $C_{10}H_{12}{}^{79}Br^{81}Br$.

*1,4-Di-*n*-butoxybenzene.* Sodium metal (12.5 g, 544 mmol) was added to ethanol (150 ml) and the mixture stirred under nitrogen until the metal had completely dissolved. A solution of 1,4-dihydroxybenzene (29.5 g, 268 mmol) in ethanol (100 ml) was added followed by 1-iodobutane (120 g, 650 mmol) and the solution was heated under reflux for 24h. Solvent was evaporated and the crude product was recrystallised from methanol/water giving the title compound (36.5 g, 61%) as white crystals mp 45°-47°C (lit[99] 43°-44°C); δ_H 6.81 (4H, s), 3.87 (4H, t), 1.64 (4H, m), 1.43 (4H, m), 0.93 (6H, t); δ_C 152.6, 115.0, 67.4, 30.7, 18.5, 13.3; m/z 222 (M^+), 166, 110; λ_{max} ($CHCl_3$) 244 (3.32), 293.9 (3.43). Found, C, 75.53, H, 10.03%; $C_{14}H_{22}O_2$ requires C, 75.7, H, 9.9%.

*1,4-Dibromo-2,5-di-*n*-butoxybenzene.* Neat bromine (55 g, 0.344 mol) was added, dropwise to a stirred solution of 1,4-di-*n*-butoxybenzene (36.5 g, 0.164 mol) and iodine (0.5 g, 2 mmol) in dichloromethane (200 ml) and the solution stirred for 16h. The mixture was then washed with saturated, aqueous sodium bicarbonate (200 ml) and water (2 x 200 ml), dried over magnesium sulfate, filtered and the solvent evaporated. The crude product thus obtained was recrystallised from acetone/water giving the title compound as pale yellow crystals (52 g, 82% after drying), mp. 71°-73°C, δ_H 7.07 (2H, s), 3.93 (4H, t), 1.77 (4H, m), 1.51 (4H, m), 0.97 (6H, t); δ_C 150.1, 118.5, 111.2, 70.0, 31.3, 19.2, 13.8; m/z 380 (M^+), 324, 268, 222. Found C, 44.40; H, 5.43%; M^+, 379.9810; $C_{14}H_{20}Br_2O_2$ requires C, 44.2; H, 5.3%; M^+ 379.9810 for $C_{14}H_{20}O_2{}^{79}Br^{81}Br$.

1-Bromo-2,5-dibutoxybenzene. N-Bromosuccinimide (9.3 g, 51.7 mmol) was added to a solution of 1,4-dibutoxybenzene (11.5 g, 51.8 mmol) in a mixture of chloroform (200 ml) and acetic acid (100 ml) and the resulting mixture was stirred at 40°C for 22h. The reaction solution was cooled and washed with water (100 ml). The aqueous layer was extracted with chloroform (2 x 100 ml) and the combined organic layers washed with saturated aqueous sodium bicarbonate (100 ml), aqueous sodium hydroxide (20% w/v, 100 ml) and water (3 x 250 ml), then dried over $MgSO_4$, filtered and solvent evaporated. Distillation gave the title compound as a light yellow oil b.p. 158°C/0.3 mbar (7.0 g, 45%). δ_H 7.1 (1H, m), 6.7 (2H, m), 3.9 (4H, m), 1.6 (8H, m), 1.0 (6H, m); m/z 302 (M^+), 300 (M^+), 246, 244, 222, 190, 188. Found M^+, 300.0720; $C_{14}H_{21}{}^{79}BrO_2$ requires M^+, 300.0724.

1-Iodo-2,5-dibutoxybenzene (**64**). N-Iodosuccinimide (5.2 g, 23.1 mmol) was added to a solution of 1,4-dibutoxybenzene (5.0 g, 22.5 mmol) in chloroform (80 ml) and acetic acid (80 ml) and the solution was stirred at 40°C for 40h. The purple solution was cooled, then washed with water (200 ml) and saturated aqueous sodium bicarbonate (100 ml). The aqueous phase was extracted with chloroform (3 x 100 ml), and the combined organic layers were washed with sodium hydrogen sulfite (50% w/v 100 ml), water (3 x 100 ml), dried over magnesium sulfate, filtered and the solvent evaporated. The crude product was purified by column chromatography using pentane/chloroform (4:1), from which the title compound was obtained as a colourless oil (4.5 g, 58%). δ_H 7.3 (d, 1H, J 2.86), 6.79 (1H, dd, J 8.9, 2.86), 6.66 (1H, d, J 8.9), 3.85 (4H, m), 1.78-1.25 (8H, m), 0.96 (6H, m); δ_C 153.7, 152.0, 125.2, 115.2, 112.9, 86.9, 69.7, 68.3, 31.4, 31.2, 19.4, 19.2, 13.9; m/z 348 (M^+), 292, 236, 222, 166, 110; λ_{max} ($CHCl_3$) 241.3 (3.65), 299.6 (3.55). Found C, 48.06; H, 6.01%; M^+, 348.0586; $C_{14}H_{21}IO_2$ requires C, 48.3; H, 6.0%; M^+, 348.0585.

Also obtained was 1,4-diiodo-2,5-dibutoxybenzene (0.1 g, 1%) as a white, crystalline solid mp. 79°-82°C; m/z 474 (M^+), 418, 362, 292, 236; λ_{max} ($CHCl_3$) 249.3 (4.02), 307.8 (3.79). Found M^+, 473.9550; $C_{14}H_{20}I_2O_2$ requires M^+ 473.9552.

Typical procedure for the preparation of lithium reagents.

Preparation of 2-thienyllithium. *n*-Butyllithium (2.5 M in hexanes, 60 ml, 150 mmol) was added dropwise *via* syringe to a stirred solution of thiophene (13 g, 154 mmol) in THF (100 ml) at 0°C under nitrogen. Upon completion of addition, the solution was allowed to warm to room temperature and was stirred for 3h. 2-Thienyllithium was not isolated but the solution was used immediately for further reactions.

General procedure for the preparation of organozinc reagents.

Preparation of 2-thienylzinc chloride (**22**). To a stirred solution of dry zinc chloride (20.1 g, 147 mmol) in THF (100 ml) at room temperature under nitrogen, was added a solution of 2-thienyllithium (150 mmol) in THF (100 ml) *via* double ended needle. The resulting mixture was stirred at room temperature for 1h then used immediately for further reactions.

General procedure for the preparation of organocadmium reagents.

Preparation of 2-thienylcadmium chloride (**47**). To a stirred solution of dried cadmium chloride (4.2 g, 23 mmol) in THF (15 ml) at room temperature under argon was added a solution of 2-thienyllithium (23 mmol) in THF (15 ml) and the mixture stirred for 30 min. 2-Thienylcadmium chloride was not isolated, and the solution was used immediately for further reactions.

General procedure for preparation of organotin reagents.

*Preparation of 2-tri-*n*-butylstannyl-5-phenylthiophene* (**60**). *n*-Butyllithium (2.5 M in hexanes, 7.5 ml, 18.8 mmol) was added dropwise by syringe to a stirred solution of 2-phenylthiophene (3 g, 18.8 mmol) in THF (50 ml) at 0°C under argon. Upon completion of addition, the solution was allowed to warm to room temperature at which it was stirred for 3h. Tri-*n*-butyltin chloride (6.3 g, 19.4 mmol) was added by syringe, so precipitating lithium chloride. The mixture was stirred at room temperature for 90 min. then pentane (20 ml) was added *via* syringe to precipitate any LiCl remaining in solution. The solution was decanted from the precipitated LiCl *via* double ended needle into a second flask and the solvent was then evaporated. δ_H (60 MHz) 7.65-7.05 (7H, m, Ar), 1.7-0.8 (27 H, m). The tin reagent was then dissolved in dry DMF (30 ml) and used immediately.

Procedure for the preparation of the reduced palladium catalyst.

To a stirred suspension of *bis*(triphenylphosphine)palladium dichloride ($Pd(PPh_3)_2Cl_2$) (0.3 g, 0.43 mmol) in THF (20 ml) at 0°C was added a solution of diisobutylaluminium hydride (DIBAH, 1.0 M in THF, 0.9 ml, 0.9 mmol), dropwise by syringe. After the addition was complete, the mixture was allowed to warm to room temperature and stirred for 30 min which resulted in the formation of a very dark red solution which was used immediately in coupling reactions.

Typical procedure for transition metal catalysed cross coupling reactions.

Preparation of 2-phenylthiophene (**24**). A solution of 2-thienylzinc chloride (150 mmol) in THF (100 ml) was added using a double ended needle to a stirred mixture of bromobenzene (23.5 g, 150 mmol) and $Pd(PPh_3)_4$ (1.73g, 1.5 mmol) in THF (100 ml) under nitrogen. The mixture was stirred at 50°C for 24h then cooled and quenched with aqueous HCl (3 M, 100 ml), and the aqueous layer was extracted with diethyl ether (3 x 100 ml). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (100 ml) and water (2 x 100 ml) then dried over $MgSO_4$, filtered and the solvent evaporated to give a yellow-brown oil. Distillation (90°C, 0.3 mbar) gave the product as a white, crystalline solid, (19.2 g, 80%), mp 34°-36°C (lit.[88] 36°C); ν_{max}(cm^{-1}) 690, 750, 820, 850, 900, 950, 1080, 1210, 1260, 1430, 1450, 1490, 1600; δ_H 7.07 (1H, dd, J 5.1, 3.6) 7.32 (5H, m), 7.61 (2H, m); δ_C 123.07, 124.8, 125.98, 127.45, 127.98, 128.89, 134.45, 144.47; m/z 160 (M^+), 128, 115, 102, 89; λ_{max} ($CHCl_3$) 238.2 (4.25).

Preparation of 2-ring compounds.

2'(4-Methoxyphenyl)thiophene (**25**). A solution of 2-thienylzinc chloride (150 mmol) in THF (100 ml) was added by double ended needle to 4-bromoanisole (28 g, 150 mmol) and $Pd(PPh_3)_4$ (0.62 g, 0.52 mmol, 0.35 mol %) in THF (100 ml) and the mixture stirred under nitrogen at 50°C for 10h. Work-up and evaporation of solvent gave a light brown solid which was recrystallised twice from ethanol yielding (**25**) (22.6 g, 80%), mp 106°-108°C; ν_{max}/cm^{-1} 670, 800, 1000, 1080, 1160, 1230, 1270, 1480, 1580; δ_H 7.51 (2H, d, J 9), 7.18 (2H, m), 7.02 (1H, dd, J 3.7, 4.9), 6.88 (2H, m), 3.78 (3H, s); δ_C 159.2, 144.3, 127.3, 127.2, 123.8, 114.3, 55.3; m/z 190 (M^+ 100), 175 (84), 147 (48), 115 (7). λ_{max} ($CHCl_3$) 292 (4.2). Found C, 69.53; H, 5.26%, M^+ 190.0452, $C_{11}H_{10}OS$ requires C, 69.47; H, 5.26%, M^+ 190.0452);

2'(3-Chlorophenyl)thiophene (**27**). A solution of 2-thienylzinc chloride (15 mmol) in THF (10 ml) was added to a stirred mixture of $Pd(PPh_3)_4$ (0.2 g, 0.16 mmols, 1 mol %) and 3-chloro-1-bromobenzene (2.9 g, 15 mmol) in THF (25 ml) *via* a double ended needle and the mixture was stirred under nitrogen for 6h at room temperature. Work up and evaporation of solvent gave a dark oil which was purified by chromatography giving (**27**) (2.18 g, 82%) as an oil. δ_H 7.56 (1H, dd, J 1.4, 3.5), 7.45 (1H, dd, J 1.5, 5.1), 7.25-7.14 (1H, m), 7.03 (1H, dd, J 3.5, 5.1); δ_C 142.7, 136.2, 134.8, 130.0, 128.1, 127.3, 125.9, 125.5, 124.0, 123.8; m/z 194 (M^+, 100), 149 (15), 115 (27), 74 (16); λ_{max} (MeOH) 286.7 (4.05). Found M^+ 193.9952, $C_{10}H_7ClS$ requires M^+ 193.9957.

2'-(3-Cyanophenyl)thiophene (**26**). To a stirred mixture of 1-bromo-3-cyanobenzene (2.73 g, 15 mmol) and *bis*(triphenylphosphine)nickel dichloride (0.4 g, 0.6 mmol, 4 mol %) in THF (20 ml) was added a solution of 2-thienylzinc chloride (15 mmol) in THF (10 ml) by double ended needle. The mixture was stirred under nitrogen at room temperature for 3h. After the usual work up and evaporation of the solvent, the crude product was obtained as a black powder (2.9g) which was purified by column chromatography (pentane/ethanol 19:1) yielding (**26**) (2.2 g, 80%) as light yellow crystals. mp. 52°-54°C; ν_{max} (KBr) (cm^{-1}) 710, 800, 850, 1000, 1090, 1280, 1140, 1600; δ_H 7.95 (1H, quintet, J 0.7, 2.1), 7.91 (1H, dt, J 7.3, 1.8), 7.63-7.53 (2H, m), 7.45 (1H, dd, J 1.2, 5.1), 7.13 (1H, dd, J 3.7, 5.1); δ_C 141.5, 135.6, 135.2, 130.5, 129.9, 129.7, 129.0, 128.4, 126.4, 124.5, 118.5; m/z 185 (M^+, 100), 140 (28), 58 (26), 45 (40); λ_{max} (MeOH) 287.2 (3.95). Found C, 71.07; H, 3.83%; M^+ 185.0299. $C_{11}H_7NS$ requires C, 71.35; H, 3.78%; M^+ 185.0299.

2'-(4-Styryl)thiophene (**28**). A solution of 2-thienylzinc chloride (16.7 mmol) in THF (50 ml) was added by double ended needle to a well stirred mixture of 4-bromostyrene (3.4 g, 18.6 mmol) and $Pd(PPh_3)_2Cl_2$ (0.09 g, 0.13 mmol, 0.8 mol %) in THF (35 ml) under argon and the mixture stirred at 50°C for 20h. Work up and evaporation of solvent followed by column chromatography (pentane) gave (**28**) (1.0 g, 25%) along with recovered 4-bromostyrene (0.9 g, 26%). mp 106°-108°C, δ_H 7.49-7.28 (4H, m), 7.20-7.13 (2H, m), 6.96 (1H, dd, J 5.1, 3.6), 6.63 (1H, dd, J 17.3, 11.2), 5.64 (1H, dd, J 17.3, 0.65), 5.20 (1H, dd, J 11.2, 0.65).

2-Bromo-5-phenylthiophene (**29**). 2-Phenylthiophene (1.0 g, 6.3 mmol) and N-bromosuccinimide (1.15 g, 6.5 mmol) in chloroform (80 ml) solution at 50°C were stirred together for 16h after which the cooled solution was shaken with aqueous NaOH (1M, 50 ml). The organic layer was separated, washed with water (2 x 100 ml), dried over $MgSO_4$, filtered and the solvent partly evaporated to yield pure (**29**) (1.2g, 80%) as a white solid m.p. 84°-86°C (lit[100], 84.5°-84.7°C); ν_{max} (KBr) (cm^{-1}) 700, 760, 810, 960, 1000, 1090, 1120, 1250, 1350, 1470, 1510, 1610; m/z 240/238 (M^+), 158; found C, 50.1, H, 2.9%; M^+ 237.9452, $C_{10}H_7BrS$ requires C, 50.23; H, 2.95%; M^+ 237.9452 for ^{79}Br.

2-Iodo-5-phenylthiophene (**30**). To a solution of 2-phenylthiophene (3.0 g, 18.8 mmol) in toluene (30 ml) was added mercuric oxide (4g, 18.5 mmol) and iodine (4.8g, 18.9 mmol) alternately as small portions over 1h, the mixture being shaken vigorously between additions, and then for a further 1h after completion of the additions.[88] The colour of iodine in solution diminished and the mercuric salt changed from yellow to red during this time. The mixture was filtered and the filtrate washed with 50% aqueous $NaHSO_3$ (10 ml), water (3 x 50 ml), dried over $CaCl_2$ and the solvent evaporated to give a pale green solid which was recrystallised from ethanol. Compound (**30**) (4.0 g, 75%) was obtained as a white solid mp. 79°-80°C (lit[88] 79°-81°C); ν_{max} (KBr) (cm^{-1}) 680, 745, 800, 900, 930, 960, 1425, 1450, 1490; δ_H 7.52 (2H, m), 7.3 (4H, m), 6.96 (1H, d, J 3.8); δ_C 150.4, 137.9, 133.6, 129.0, 127.9, 125.8, 124.5, 72.3; m/z 286 (M^+) 159, 115; λ_{max} ($CHCl_3$) 296 (4.36).

Preparation of 3-ring compounds.

*1,4-*Bis*(2'-thienyl)benzene* (**34**). A solution of 2-thienylzinc chloride (150 mmol) in THF (200 ml) was added to a stirred solution of $Pd(PPh_3)_4$ (0.56 g, 0.49 mmol, 0.3 mol %) and 1,4-dibromobenzene (17.6 g, 75 mmol) in THF (250 ml) under argon and the reaction solution stirred at 50°C for 18h. The mixture was allowed to cool and worked up as usual, most of the product precipitating from solution during the work up. After filtration, recrystallisation of the crude product from CH_2Cl_2 gave (**34**) (13.1 g, 72%) as an off white powder mp. 204°-206°C (lit[101] 208°C); ν_{max} (KBr) (cm^{-1}) 730, 840, 1010, 1100, 1160, 1290, 1450, 1520; δ_H 7.58 (4H, s), 7.28 (2H, dd, J 3.6, 1.2), 7.23 (2H, dd, J 5.1, 1.2), 7.02 (2H, dd, J 5.1, 3.6); δ_C 143.9, 135.1, 129.4, 128.0, 125.1, 123.5; m/z 242 (M^+, 100), 197 (11), 152 (6) λ_{max} (MeOH) 325 (4.2). Found M^+ 242.0224, $C_{14}H_{10}S_2$ requires M^+ 242.0224.

1,3-Di(2'-thienyl)benzene (**35**). A solution of 2-thienylzinc chloride (15 mmol) in THF (20 ml) was added to a solution of 1,3-dibromobenzene (1.2g, 5 mmol) and $Ni(PPh_3)_2Cl_2$ (0.032 g, 0.05 mmol) in THF (10 ml) under argon and the reaction solution stirred at 50°C for 12h. Work up and purification of the crude product by column chromatography using pentane as eluant gave (**35**) (0.78 g, 65%) as white crystals, mp.

85°-86°C; ν_{max} (KBr) (cm^{-1}) 740, 840, 900, 930, 1100, 1480, 1650; δ_H 7.83 (1H, t, J 1.9), 7.51-7.46 (2H, m); 7.34 (1H, d, J 7), 7.33 (2H, dd, J 3.5, 1), 7.25 (2H, dd, J 5.1, 1.2), 7.06 (2H, dd, J 5.0, 3.6); δ_C 143.9, 135.1, 129.3, 128.0, 125.0, 124.8, 123.5, 122.1; m/z 242 (M$^+$, 100), 240(3), 197(6), 121(8); λ_{max} (MeOH) 284.4 (3.8). Found C, 69.55; H, 3.42%; M$^+$ 242.0229; $C_{14}H_{10}S_2$ requires C, 69.42; H, 3.31%; M$^+$, 242.0229.

1,2-Di(2′-thienyl)benzene (**36**). To a stirred solution of 1,2-dibromobenzene (1.76 g, 7.5 mmol) and Pd(PPh$_3$)$_4$ (0.2 g, 0.17 mmol, 2.3 mol %) in THF (25 ml) under argon was added a solution of 2-thienylzinc chloride (15 mmol) in THF (20 ml) and the solution stirred at 50°C for 24h. Work up followed by purification of the crude product by column chromatography using pentane gave (**36**) (0.61 g, 34%) as a colourless oil. ν_{max} ($CHCl_3$) 720, 840, 980, 1450, 1520; δ_H 7.46 (2H, m), 7.36 (2H, m), 7.20 (2H, m), 7.0-6.8 (4H, m); δ_C 142.6, 133.7, 131.0, 127.8, 127.0, 126.8, 125.8; m/z 242 (M$^+$, 100), 197 (32), 115 (28); λ_{max} (MeOH) 290 (3.8), 255 (3.9). Found M$^+$, 242.0229; $C_{14}H_{10}S_2$ requires M$^+$, 242.0229.

1,4-Di(2′-bromo-5′-thienyl)benzene (**52**). To a stirred solution of 1,4-di(2′-thienyl)benzene (**34**) (1g, 4.1 mmol) in chloroform (30 ml) and acetic acid (30 ml) under nitrogen was added N-bromosuccinimide (1.6 g, 9 mmol) and the solution stirred at room temperature for 1h. Compound (**52**), (1.3 g, 88%), mp 251°-252°C which precipitated from solution during the reaction, was collected by filtration, washed with methanol and dried under reduced pressure in a dessicator at room temperature m/z 402, 400, 398 (1:2:1, M$^+$), 322, 242; λ_{max} ($CHCl_3$) 335. Found C, 42.18; H, 2.18%; $C_{14}H_8Br_2S_2$ requires C, 42.0, H, 2.0%. No nmr was obtained due to the low solubility of (**52**) in the available solvents. Compound (**52**) was also prepared in 88% yield using chloroform as solvent and 50°C as reaction temperature.

1,4-Di(2′-iodo-5′-thienyl)benzene (**53**). N-Iodosuccinimide (1.9 g, 8.4 mmol), was added to a solution of 1,4-di(2′-thienyl)benzene (**34**) (1 g, 4.1 mmol) in chloroform (50 ml) and the resulting red solution was stirred at 40°C for 18h. Compound (**53**) precipitated from solution and was collected by filtration, washed with water then acetone and dried under reduced pressure at 45°C over P_2O_5 for 10h. The product (1.2 g, 60%) was obtained as a white solid, mp 265°-268°C, ν_{max} (KBr) (cm^{-1}) 790, 820, 920, 960, 1420; δ_H (D$_6$-DMSO) 7.58 (4H, s), 7.32 (2H, d, J 3.8), 7.17 (2H, d, J 3.8); m/z 494, 368, 323, 242; λ_{max} ($CHCl_3$) 340. Found C, 34.11; H, 1.82%; $C_{10}H_8I_2S_2$ requires C, 34.0; H, 1.6%.

2,5-Dimethyl-1,4-di(2′-thienyl)benzene (**37**). 2-Thienylcadmium chloride (23 mmol) in THF (30 ml) was added to a solution of Ni(PPh$_3$)$_2$Cl$_2$ (0.4 g, 0.63 mmol, 8.4 mol % wrt aryl halide) and, 1,4-dibromo-2,5-dimethylbenzene (2.1 g, 7.5 mmol) in THF (25 ml) under argon and the reaction solution stirred at 50°C for 16h. Work up and purification by column chromatography using pentane gave 1-bromo-2,5-dimethyl-4(2′thienyl)benzene (**30**) (0.4 g, 20%) as an oil and the desired product (**37**) (1.15g, 57%) as a solid m.p. 76°-78°C. Compound (**30**) had ν_{max} (KBr) (cm^{-1}) 690, 750, 840, 880, 980, 1055, 1440, 1490; δ_H 7.32 (1H, s), 7.19 (1H, dd, J 4.8, 1.3), 7.17 (1H, s), 6.95 (1H, dd, J, 4.8, 3.5), 6.93 (1H, dd, J 3.5, 1.3), 2.27 (3H, s), 2.24 (3H, s);

δ_C 141.9, 136.7, 135.0, 134.1, 132.3, 127.3, 127.0, 125.2, 124.0, 123.3, 22.2, 22.1; m/z 266 (M^+, 100), 187 (40), 171 (80), 141 (15), 103 (62); λ_{max} ($CHCl_3$) 274.7 (3.92). Found M^+, 265.9765; $C_{12}H_{11}BrS$ requires M^+, 265.9765. Compound (**37**) had ν_{max} (KBr) (cm^{-1}) 690, 700, 800, 830, 860, 890, 960, 1030, 1200, 1250, 1380, 1450, 1490; δ_H 7.32 (2H, d), 7.31 (2H, s), 7.07 (2H), δ_C 142.7, 133.6, 133.4, 132.7, 127.1, 126.4, 125.1; m/z 270 (M^+, 100), 264 (43), 255 (31), 221 (25), 103 (56), 77 (21); λ_{max} (MeOH) 295.1 (4.23). Found C, 71.23; H, 5.20%; M^+, 270.0536; $C_{16}H_{14}S_2$ requires C, 71.11; H, 5.18%; M^+ 270.0537.

2,5-Di-n-*butyl-1,4-di(2′-thienyl)benzene* (**39**). A solution of 2-thienylzinc chloride (42 mmol) in THF (50 ml) was added to a solution of 1,4-dibromo-2,5-*di*-n-butylbenzene (4.8 g, 13.8 mmol) and Pd(PPh_3)$_4$ (0.2 g, 0.17 mmol, 1.2 mol %) in THF (50 ml) under argon and the reaction solution stirred at 50°C for 24h. Work up and purification of the crude product by column chromatography using pentane gave 1,4-dibromo-2,5-di-*n*-butylbenzene (0.8 g, 16%), 1-bromo-2,5-di-*n*-butyl-4(2′-thienyl)benzene (**32**) (0.68 g, 14%) as a colourless oil which turned blue on standing, followed by the desired product (**39**) (3.2 g, 66%) as a yellow oil which crystallised on standing, m.p. 52°-53°C. Compound (**32**) had ν_{max} (KBr) (cm^{-1}) 690, 830, 850, 880, 930, 1015, 1050, 1100, 1220, 1380, 1470, 1600, 2900-3000; δ_H 7.42 (1H, s), 7.25 (1H, dd, J 5.1, 1.1), 7.18 (1H, s), 7.01 (1H, dd, J 5.0, 3.6), 6.95 (1H, dd, J 3.5, 1.2), 2.71-2.58 (4H, m), 1.61-1.51 (4H, m), 1.47-1.23 (4H, m), 0.95-0.81 (6H, m); δ_C 142.7, 142.0, 140.6, 139.2, 133.4, 132.5, 127.0, 126.4, 125.3, 124.1, 35.3, 33.5, 32.5, 32.1, 22.5, 13.9, 13.8; m/z 350 (M^+, 100); λ_{max} ($CHCl_3$) 287.3 (3.85). Compound (**39**) had ν_{max} (KBr) (cm^{-1}) 690, 730, 840, 910, 1060, 1110, 1200, 1250, 1480; δ_H 7.32 (2H, dd, J 4.9, 1.4), 7.28 (2H, s), 7.07 (2H, dd, J 4.9, 3.6), 7.04 (2H, dd, J 3.5, 1.2), 2.71 (4H, t, J 7.7), 1.51 (4H, quintet, J 7), 1.32 (4 H, sextet, J 7.3), 0.86 (6H, t, J 7.2); 142.7, 138.5, 133.5, 132.2, 127.0, 126.4, 125.2, 33.7, 32.8, 22.6, 13.9; m/z 354 (M^+, 100), 311 (39), 255 (16), 254 (15), 222 (13), 221 (27); λ_{max} ($CHCl_3$) 305.1 (4.13). Found C, 74.55; H, 7.39%; M^+, 354.1476; $C_{22}H_{26}S_2$ requires C, 74.58; H, 7.34%; M^+ 354.1476.

*2,5-Di*iso*propyl-1,4-di(2′-thienyl)benzene* (**38**). A solution of 2-thienylzinc chloride (150 mmol) in THF (200 ml) was added to a stirred solution of 1,4-dibromo-2,5-di*iso*propylbenzene (12 g, 37.5 mmol) and Pd(PPh_3)$_4$ (0.6 g, 0.52 mmol, 1.4 mol %) in THF (200 ml) under argon and the reaction solution stirred at 50°C for 24h. Work up and column chromatography of the crude product using pentane gave the mono-coupled product 1-bromo-2,5-di*iso*propyl-4-(2′-thienyl)benzene (**33**) (4.8 g, 40%) as an oil, and (**38**), m.p. 142-144°C (250 mg, 2%). Compound (**33**) had ν_{max} (KBr) (cm^{-1}) 700, 820, 850, 895, 960, 1070, 1200, 1310, 1360, 1380, 1440 1495, 3100; δ_H 7.51 (1H, s), 7.30 (1H, dd, J 5.2, 1.2), 7.20 (1H, s), 7.05 (1H, dd, J 5.2, 3.5), 6.95 (1H, dd, J 1.2), 3.26 (2H, m), 1.22 (6H, m); δ_C 146.7, 146.4, 144.2, 142.0, 130.7, 130.0, 126.9, 126.6, 125.3, 123.4, 32.6, 32.5, 22.8, 22.6; m/z 324 (45), 322 (M^+, 30), 305 (100), 166 (42), 155 (53), 128 (55); λ_{max} ($CHCl_3$) 271.3 (3.81). Found M^+, 322.0391; $C_{16}H_{19}BrS$ requires M^+, 322.0391. Compound (**38**) had ν_{max} (KBr) (cm^{-1}), 700, 720, 855, 1090, 1120, 1220, 1450, 1480, 1510, 3010; δ_H 7.326 (2H, s), 7.33 (2H, dd, J 5.1, 1.2), 7.08 (2H, dd, J 3.5, 1.2), 7.02 (2H, dd, J 5.1, 3.5), 3.28 (2H, septet, J 7.0), 1.18 (12H, d, J 7.0); δ_C 144.4, 142.8, 133.3, 128.5, 126.9, 126.5, 125.2, 29.2, 24.3; m/z 326 (M^+, 100), 311 (77), 269 (15), 235 (20), 221 (17); λ_{max} ($CHCl_3$) 276 (3.9). Found C, 73.69; H, 6.99%; M^+, 326.1163; $C_{20}H_{22}S_2$ requires C, 73.62; H, 6.75%; M^+, 326.1163.

*2,5-Di-*n*-octyl-1,4-di(2'-thienyl)benzene* (**40**). A solution of 2-thienylzinc chloride (50 mmol) in THF (75 ml) was added to a solution of 1,4-dibromo-2,5-di-*n*-octylbenzene (5.75 g, 12.5 mmol) in THF (40 ml) under argon. To this solution was added a solution of reduced Pd catalyst (0.71 mmol) prepared from $Pd(PPh_3)_2Cl_2$ and DIBAL-H in THF. The reaction solution was stirred at 50°C for 24h. Work up and column chromatography of the crude product using pentane as eluant gave recovered 1,4-dibromo-2,5-di-*n*-octylbenzene (5.3 g, 92%) and (**40**) (0.2g, 3.4%) mp 58°-60°C; ν_{max} (KBr) (cm^{-1}) 660, 680, 800, 1445, 2940; δ_H 7.32 (2H, dd, J 4.9, 1.3), 7.28 (2H, s), 7.07 (2H, dd, J 4.9, 3.6), 7.04 (2H, dd, J 3.6, 1.3), 2.69 (4H, t, J 7.0), 1.55 (4H, m), 1.23 (20H, brs), 0.86 (6H, t, J 7.0); δ_C 142.7, 138.7, 133.5, 132.2, 127.0, 126.3, 125.1, 33.1, 31.85, 31.5, 29.6, 29.3, 29.2, 22.7, 14.1; m/z 466 (M^+, 100), 367 (31), 255 (7), 221 (14); λ_{max} ($CHCl_3$) 287 (3.9). Found C, 76.79; H, 9.35; M^+, 466.2728; $C_{30}H_{42}S_2$ requires C, 77.25; H, 9.01; M^+, 466.2728.

2,5-Dicyano-1,4-di(2'-thienyl)benzene (**41**). To a solution of 2,5-dicyano-1,4-dibromobenzene (1.5 g, 5.3 mmol) and $Pd(PPh_3)_4$ (0.2 g, 0.17 mmol, 3.2 mol %) in THF (40 ml) was added a solution of 2-thienylzinc chloride (21 mmol) in THF (30 ml) under argon and the reaction solution stirred at 50°C for 24h. Work up and purification of the crude material by column chromatography using petroleum spirit/chloroform (4:1) gave (**41**) (0.98 g, 62%). mp 192°-194°C; ν_{max} (KBr) (cm^{-1}) 690, 800, 830, 880, 1020, 1210, 1250, 1400, 1460, 1520, 2810, 3020; δ_H 8.2 (2H, s), 7.78 (2H, dd, J 3.7, 1.2), 7.65 (2H, dd, J 5.1, 1.1), 7.27 (2H, dd, J 5.2, 3.7); δ_C 141.4, 140.6, 139.6, 134.2, 133.7, 133.3, 121.9, 118.3; m/z 292 (M^+, 100), 247 (10); λ_{max} ($CHCl_3$) 319 (4.3), 375 (4.5). Found C, 65.69; H, 2.84%; M^+, 292.0129; $C_{16}H_8N_2S_2$ requires C, 65.75; H, 2.74%; M^+, 292.0129.

2,5-Di(methoxycarbonyl)-1,4-di(2'-thienyl)benzene (**42**). A solution of 2-thienylzinc chloride(75 mmol) in THF (100 ml) was added to a solution of 2,5-di(methoxycarbonyl)-1,4-dibromobenzene (8.8 g, 25 mmol) and $Pd(PPh_3)_4$ (0.4 g, 0.35 mmol, 1.4 mol (%) in THF (50 ml) under argon and the reaction stirred at 50°C for 24h. Work up and purification of the crude product by column chromatography using chloroform gave (**42**) (2.5 g, 28%) as a pale green solid, mp 170°-172°C. Compound (**42**) had ν_{max} (cm^{-1}) 710, 770, 840, 900, 940, 1100, 1250, 1290, 1430, 1490, 1730; δ_H 7.82 (2H, s), 7.38 (2H, dd, J 3.9, 1.2), 7.09 (4H, m), 3.77 (6H, s); δ_C 168.0, 140.3, 133.6, 133.4, 131.9, 127.4, 127.0, 126.7; m/z 358 (M^+, 100), 327 (53), 299 (4), 240 (11), 195 (7); λ_{max} ($CHCl_3$) 298.7 (4.15). Found C, 60.18; H, 4.18%; M^+, 358.0334; $C_{18}H_{14}O_4S_2$ requires C, 60.34; H, 3.91%; M^+, 358.0334.

1,4-Di-(methoxymethyloxy)-2,5-di(2′-thienyl)benzene (**45**). 2-Thienylcadmium chloride (24 mmol) in THF solution, was added to a solution of 1,4-dibromo-2,5-di(methoxymethyloxy)benzene (2.14 g, 6 mmol) and $Pd(PPh_3)_4$ (0.4 g, 0.35 mmol) in THF (50 ml) under argon and the reaction solution stirred at 50°C for 24h. The solution was then diluted with ethyl acetate and shaken with aqueous sodium hydroxide (1M, 50 ml). The organic layer was washed with water (50 ml), dried over $MgSO_4$ and the solvent evaporated. The crude product was purified by column chromatography on base treated silica using pentane/chloroform (19:1) as eluant. Compound (**45**) (1.2 g, 55%) was obtained as a bright yellow crystalline solid mp 89°-92°C; ν_{max} (KBr) (cm^{-1}) 700, 760, 830, 880, 920, 1150, 1280, 1310, 1380, 1440, 1540, 1820; δ_H 7.51 (2H, s), 7.50 (2H, s), 7.33 (2H, dd, J 5.1, 0.9), 7.07 (2H, dd, J 5.1, 3.8), 5.23 (4H, s), 3.49 (6H, s); δ_C 148.2, 138.8, 126.8, 126.0, 125.6, 124.1, 115.8, 95.5, 56.3; m/z 362 (11), 298 (10), 285 (13), 108 (11), 45 (100); λ_{max} ($CHCl_3$) 306.4 (4.07), 347.6(4.23). Found C, 59.89, H, 4.85%; M^+, 362.0647; $C_{18}H_{18}O_4S_2$ requires C, 59.89; H, 4.97%; M^+, 362.0647.

1,4-Dihydroxy-2,5-di(2′-thienyl)benzene (**46**). To a solution of (**45**) (0.1 g, 0.28 mmol) in methanol (5 ml) was added aqueous HCl (12M, 5 drops) and the solution was heated under reflux for 10 min, cooled, diluted with water (20 ml) and extracted with ethyl acetate (30 ml). The organic layer was dried over $MgSO_4$, filtered and the solvent evaporated giving (**46**) (0.065 g, 100%) as a light-grey crystalline solid mp 108°-110°C; ν_{max} (KBr) (cm^{-1}) 690, 790, 820, 870, 1200, 1360, 1420, 3350 (br); δ_H 7.56 (2H, d, J 3.5), 7.29 (2H, d, J 5.0), 7.09 (2H, s), 7.06 (2H, dd, J 5.0, 3.8), 4.69 (2H, s); δ_C 147.2, 140.4, 127.5, 125.8, 125.4, 122.0, 116.0, m/z 274 (M^+, 100), 229 (15), 184 (10), 137 (13), λ_{max} ($CHCl_3$) 298 (4.1), 350.4 (4.3). Found M^+ 274.0122; $C_{14}H_{10}O_2S_2$ requires M^+, 274.0122.

1,4-Dimethoxy-2,5-di(2′-thienyl)benzene (**43**). A solution of 2-thienylzinc chloride (62 mmol) in THF was added to a solution of 1,4-dibromo-2,5-dimethoxybenzene (**48**) (7.3 g, 24.8 mmol) and $Pd(PPh_3)_4$ (0.5 g, 0.43 mmol, 1.7 mol %) in THF (40 ml) under argon and the mixture heated under reflux for 24h. Work up and column chromatography using petroleum spirit/chloroform (4:1) gave (**43**) (3.7 g, 49%) m.p. 133-135°C along with (**49**) (0.9 g, 14%) m.p. 152-154°C as an intensely yellow solid. Compound (**43**) had ν_{max} (KBr) (cm^{-1}) 700, 760, 810, 840, 1040, 1060, 1190, 1220, 1290, 1360, 1400, 1460, 1490, 1540; δ_H 7.51 (2H, q, J 3.6, 1.0), 7.31 (2H, q, J 5.1, 1.0), 7.22 (2H, s), 7.07 (2H, dd, J 5.9, 3.7), 3.89 (6H, s); δ_C 149.9, 139.0, 126.9, 125.7, 125.5, 122.9, 112.2, 56.3; m/z 302 (M^+, 86), 203 (55), 125 (43), 105 (66), 85 (36), 57 (100); λ_{max} ($CHCl_3$), 304.1 (4.13), 358 (4.4). Found C, 63.51; H, 4.58%; M^+, 302.0435; $C_{16}H_{14}S_2O_2$ requires C, 63.55; H, 4.67%; M^+, 302.0435. Compound (**49**) had ν_{max} (KBr) (cm^{-1}) 670, 740, 810, 1010, 1200, 1270, 1370, 1460; δ_H 7.54-7.51 (4H, m), 7.32 (2H, dd, J 5.1, 1.0), 7.26 (2H, s), 7.24 (2H, s), 7.08 (2H, dd, J 5.2, 3.7), 3.93 (6H, s), 3.92 (6H, s); δ_C 150.1, 150.0, 139.1, 126.9, 125.9, 125.7, 125.4, 123.2, 122.9, 112.2, 111.9, 56.4, 56.3; m/z 520

(M^+, 100); λ_{max} ($CHCl_3$) 403.2 (4.47). Found C, 63.85; H, 4.47%; M^+, 520.0837; $C_{28}H_{24}O_4S_3$ requires C, 64.60; H, 4.65; M^+, 520.0837.

*1,4-Di-*n*-butoxy-2,5-di(2′-thienyl)benzene* (**44**). A solution of 2-thienylzinc chloride (140 mmol) in THF (250 ml) was added to a stirred solution of 1,4-dibromo-2,5-dibutoxybenzene (25 g, 65.8 mmol) and $Pd(PPh_3)_2Cl_2$ (0.31 g, 0.44 mmol, 0.3 mol %) in THF (100 ml) under argon and the mixture was stirred at 50°C for 22h. Work up followed by recrystallisation of the crude product from acetone/water gave (**44**) (15.9 g, 63%) as bright, gold-green needles mp 109°-111°C; ν_{max} (KBr) (cm^{-1}) 680, 695, 740, 795, 822, 855, 902, 1000, 1035, 1065, 1125, 1220, 1270, 1290, 1360, 1390, 1410, 1440, 1470, 1500, 1540, 2800; δ_H 7.53 (2H, d), 7.32 (2H, d), 7.24 (2H, s), 7.07 (2H, dd), 4.06 (4H, t), 1.85 (4H, m), 1.55 (4H, m), 0.99 (6H, t); δ_C 149.2, 139.3, 126.7, 125.6, 125.1, 123.0, 112.8, 69.4, 31.5, 19.5, 13.9; m/z 386, 330, 274; λ_{max} ($CHCl_3$) 239.6 (4.15), 259.3 (4.18), 272.1 (4.21), 306.4 (4.2), 357.6 (4.34). Found C, 68.4; H, 6.7%; M^+, 386.1373; $C_{22}H_{26}O_2S_2$ requires C, 68.5; H, 6.95%; M^+, 386.1374.

*1,4-Di-*n*-butoxy-2,5-di(2′-iodo-5′-thienyl)benzene* (**54**). N-Iodosuccinimide (2.8 g, 12.4 mmol) was added to a solution of (**44**) (2.4 g, 6.2 mmol) in chloroform (75 ml). The solution was stirred at 40°C for 22h, after which the product had precipitated as a yellow solid. The mixture was cooled to room temperature and the solid was collected by filtration, washed with diethyl ether and dried, to give (**54**) (2.8 g, 71%), m.p. 170°C-172°C; δ_H 7.18 (6H, m), 4.05 (4H, t), 1.87 (4H, m), 1.52 (4H, m), 0.98 (6H, t); m/z 638, 582, 526, 511, 454, 398. Found C, 41.6; H, 3.99%; M^+ 637.9310; $C_{22}H_{24}O_2I_2S_2$ requires C, 41.39; H, 3.79%, M^+, 637.937.

Preparation of 4-ring compounds.

1,3,5-tri(2′-thienyl)benzene (**55**). A solution of 2-thienylzinc chloride (81 mmol) in THF (100 ml) was added to a solution of 1,3,5-tribromobenzene (3.77 g, 12 mmol) and $Pd(PPh_3)_4$ (1.4 g, 0.12 mmol, 1 mol %) in THF (20 ml) under argon and the reaction solution then stirred at 50°C for 48 h. Work up followed by purification of the crude material by column chromatography initially using pentane to remove starting material then pentane/chloroform (4:1) gave a pale yellow, crystalline material. Recrystallisation from ethanol yielded (**55**) as white crystals (2.5 g, 60%), m.p. 156°-158°C; ν_{max} (KBr) (cm^{-1}), 670, 800, 820, 840, 1010, 1210, 1570, δ_H 7.68 (3H, s), 7.33 (2H, dd, J 3.9, 1.4), 7.23 (2H, dd, J 5.1, 1.1), 7.05 (2H, dd, J 5.1, 3.6); δ_C 143.4, 135.6, 128.0, 125.4, 123.7, 122.6; m/z 324 (M^+, 100), 168 (3), 45 (3); λ_{max} ($CHCl_3$) 302.3, (4.42). Found C, 66.54; H, 3.74%; M^+, 324.0101; $C_{18}H_{12}S_3$ requires C, 66.67; H, 3.71%; M^+, 324.0101.

5,5′-Diphenyl-2,2′-bithiophene (**59**). A solution of 2-tri-*n*-butylstannyl-5-phenylthiophene (3.1 mmol) in DMF (10 mmol) was added to the reduced palladium catalyst prepared from $Pd(PPh_3)_2Cl_2$ and DIBAH (0.093 mmol, 3 mol %) in THF (2 ml). A solution of 2-phenyl-5-iodothiophene (0.9 g, 3.15 mmol) in DMF (10 ml) was then added and the solution stirred at 60°C for 3h, the product beginning to precipitate from solution within 20 minutes. The cooled reaction was quenched with aqueous HCl (3 M, 20 ml) and the solid product was collected by filtration, washed with methanol then with diethyl ether and dried in the air giving (**59**) (0.85 g, 85%) as a golden yellow solid m.p. 240°-242°C; ν_{max} (KBr) (cm^{-1}) 675, 740, 790, 1070, 1090, 1440, 1485; m/z 318, 243, 197; λ_{max} (CHCl$_3$) 369.3 (4.55). Found M$^+$, 318.0536; $C_{20}H_{14}S_2$ requires 318.0537.

2-(5′-(1″,4″-Dibutoxy-2″-phenyl)2′-thienyl)-5-(2‴-thienyl)1,4-dibutoxybenzene (**62**). To a stirred solution of 1,4-dibutoxy-2,5-di(2′-thienyl)benzene (1.2 g, 3.1 mmol) in THF (25 ml) at 0°C under argon was added *n*-butyllithium (1.45M in hexanes, 4.3 ml, 6.2 mmol) causing precipitation of a grey green solid. This mixture was stirred at room temperature for 2.5h then tri-*n*-butyltin chloride (2.1 g, 6.5 mmol) was added causing immediate disolution of the precipitate. Stirring was continued for 1h then a solution of 1,4-dibutoxy-2-iodobenzene (1.6 g, 4.6 mmol) in DMF (30 ml) was added followed by addition of a solution of the reduced palladium catalyst (0.09 mmol, 2.8 mol %) in THF (10 ml) and the reaction solution was stirred at 60°C for 20h. Work up and purification by column chromatography (pentane/chloroform using solvent gradient) gave 0.1 g (8%) of starting material; 0.45 g (21%) of the desired compound (**62**) and 0.8 g of a mixture of (**62**) and (**65**) which was not purified further. Compound (**62**) was recrystallised from acetone/water as orange-yellow crystals, m.p. 71°-73°C; ν_{max} (KBr) (cm^{-1}) 685, 800, 850, 930, 1005, 1040, 1070, 1125, 1220, 1265, 1336, 1385, 1460, 1490, 1530, 1600, 2860, 2940, 2960; δ_H 7.52 (3H, m), 7.22 (4H, m), 7.02 (1H, m), 6.67 (2H, m), 3.91 (8H, m), 1.67 (8H, m), 1.36 (8H, m), 0.99 (12H, m); δ_C 153.3, 149.7, 149.5, 149.4, 139.6, 139.5, 139.3, 126.8, 125.9, 125.6, 125.1, 124.4, 123.3, 122.7, 114.3, 113.9, 113.7, 112.6, 112.3, 69.4, 69.3, 69.2, 68.3, 31.8, 31.5, 30.0, 19.7, 19.5, 14.4, 14.2; m/z 606 (M$^+$), 549, 493, 375; λ_{max} (CHCl$_3$) 241.1 (4.0), 386.7 (4.48). Found C, 71.35; H, 7.84%; $C_{36}H_{46}O_4S_2$ requires C, 71.3; H, 7.6%.

Preparation of 5 ring compounds.

1,4-Di(5′- phenyl-2′-thienyl)benzene (**67**). To a solution of 2-phenylthiophene (2.4 g, 15 mmol) in THF (30 ml) at 0°C under argon was added a solution of *n*-butyllithium (2.5 M in hexanes, 6 ml, 15 mmol) and the solution stirred at room temperature for 3h. A fresh solution of dry zinc chloride (2.0 g, 14.8 mmol) in THF (30 ml) was added and the resulting mixture stirred at room temperature for 1h. The mixture was then added to a solution of 1,4-dibromobenzene (1.8 g, 7.6 mmol) and Pd(PPh$_3$)$_4$ (0.06 g, 0.05 mmol, 0.7 mol %) in THF (20 ml) and the reaction solution stirred at 50°C for 18h. The product which precipitated from solution was collected by filtration and washed with diethyl ether until the washings were colourless. Recrystallisation from chloroform gave (**67**) (1.6 g, 55%) as yellow crystals m.p. 301°C; ν_{max} (KBr) (cm^{-1}) 675, 745, 795, 820, 890, 930, 1070, 1450, 1485; m/z 394 (M$^+$), 319; λ_{max} (CHCl$_3$) 369.6 (4.65), 375.2 (4.65). Found M$^+$, 394.0849; $C_{26}H_{18}S_2$ requires M$^+$, 394.0850.

1,3-Di(5′-phenyl-2′-thienyl)benzene (**68**). A solution of 5-phenyl-2-thienylzinc chloride (15.6 mmol) in THF (120 ml) was added to a stirred solution of 1,3-dibromobenzene (1.83 g, 7.8 mmol) and Pd(PPh$_3$)$_4$ (0.2 g, 0.17 mmol, 2.2 mol %) in THF (40 ml) under argon and the reaction solution stirred at 50°C for 24h. On work up a solid precipitated which was collected by filtration and washed with ethyl acetate/ethanol (1:1) giving (**68**) (1.5 g, 48%) as a yellow, crystalline, solid mp 188°-190°C; ν_{max} (KBr) (cm^{-1}) 660, 750, 780, 1080, 1100, 1450, 1590; m/z, 394 (M$^+$, 70), 318 (100), 197 (10), 121 (25); λ_{max} (CHCl$_3$) 335 nm (4.3). Found C, 78.64; H, 4.41%; M$^+$, 394.0850; $C_{26}H_{16}S_2$ requires C, 79.19; H, 4.41%; M$^+$, 394.0850.

1,4-Di(5′-(2″-thienyl)thienyl)benzene (**69**). A solution of 2-thienylzinc chloride (7.5 mmol) in THF (20 ml) was added to a stirred solution of 1,4-di(2′-bromo-5′-thienyl)benzene (**52**) (1.5 g, 3.75 mmol) in THF (200 ml) under argon followed by addition of a solution of reduced palladium catalyst (0.26 mmol, 3.5 mol % w.r.t. zinc reagent) in THF (30 ml). The reaction solution was stirred at 60°C for 40h then allowed to cool to room temperature. Aqueous HCl (3M, 30 ml) was added causing precipitation of a brown-green solid which was collected by filtration and purified by column chromatography using chloroform as eluant. Compound (**69**) (0.55 g, 36%) was obtained as a light-yellow solid. ν_{max} (KBr) (cm^{-1}) 680, 695, 800, 830, 1415, 1430, 1460, 1500; m/z 406 (M$^+$); λ_{max} (CHCl$_3$) 390.4 (4.62). Found M$^+$, 405.9980; $C_{22}H_{14}S_4$ requires M$^+$, 405.9978.

2,5-Di(5′-(2′,2″-thienyl)thienyl)-1,4-dibutoxybenzene (**70**). To a solution of 1,4-dibutoxy-2,5-di(2′-iodo-5′-thienyl)benzene (**54**) (3.5 g, 5.5 mmol) in DMF (100 ml), under argon, in a 250 ml flask fitted with a reflux condenser, was added a solution of 2-tri-n-butylstannylthiophene (23.2 mmol) in THF (50 ml) followed by a solution of the reduced palladium catalyst (0.23 mmol, 4 mol w.r.t. iodide) in THF (20 ml). The solution was stirred at 80°C for 16h during which a yellow-green solid began to precipitate from solution. The reaction was allowed to cool to room temperature and diluted with chloroform (200 ml) to dissolve the precipitate. Work up according to the standard procedure and evaporation of solvent gave a brown solid which was recrystallised from chloroform/methanol. The recrystallised compound was further purified by column chromatography (pentane/chloroform, solvent gradient) giving (**70**) (1.2 g, 40%) as yellow orange needles, m.p. 166°-168°C. The mother liquor from the recrystallation was evaporated to dryness giving a brown oil which was purified by column chromatography (pentane/chloroform) giving the product from mono-coupling (**61**) (0.06 g, 0.6%) as a yellow brown, crystalline solid m.p. 98°-102°C. Compound (**70**) had δ_H 7.46 (2H, d), 7.21 (8H, m), 7.04 (2H, dd,), 4.12 (4H, t), 1.92 (4H, m), 1.61 (4H, m), 1.03 (6H, t); m/z 550 (M$^+$); λ_{max} (CHCl$_3$) 252.9 (4.21), 343.3 (4.14), 405.6 (4.45). Found C, 65.3; H, 5.48%; M$^+$, 550.1130; $C_{30}H_{30}O_2S_4$ requires C, 65.4, H, 5.50%; M$^+$, 550.1127. Compound (**61**) had δ_H 7.53 (1H, d), 7.45 (1H, d), 7.19 (6H, m); 7.06 (2H, m), 4.09 (4H, t), 1.9 (4H, m), 1.59 (4H, m), 1.02 (6H, m); δ_C 149.2, 149.0, 137.2, 137.2, 127.9, 126.0, 125.8, 125.7, 125.2, 124.2, 123.5, 123.4, 122.6, 122.5, 112.0, 111.8, 69.4, 31.5, 31.4, 19.6, 14.0, 13.6; m/z 468 (M$^+$), 412, 355, 387; found M$^+$, 468.1250; $C_{26}H_{28}O_2S_3$ requires M$^+$, 468.1250.

1-(5′-(1″,4″-Dibutoxy-2″-phenyl)-2′-thienyl)-4-(5‴-(4⁗-styrenyl)-2‴-thienyl)-2,5-dibutoxybenzene (**73**). *n*-Butyllithium (1.45 M in hexanes, 1.4 ml, 2.03 mol) was added at 0°C to a stirred solution of 1-(5′-(1″,4″-dibutoxy-2″-phenyl)-2″-thienyl)-4-(2‴-thienyl)-2,5-dibutoxybenzene (**62**) (1.0g, 1.65 mmol) in THF (75 ml) under argon. The solution was stirred at room temperature for 2h, then tributyltin chloride (0.7 g, 2.15 mmol) was added and the resulting solution stirred at room temperature for 2h. This solution was then added to a solution of 4′-bromostyrene (0.55 g, 3 mmol) in DMF (75 ml) followed by addition of the reduced palladium catalyst (0.05 mmol, 2.9 mol %) in THF (15 ml). The reaction solution was stirred at 60°C for 19h then allowed to warm to room temperature. The reaction was worked up according to the standard procedure giving a brown solid which was purified by column chromatography (pentane/chloroform eluant). Compound (**73**) m.p. 104°-110°C (0.3 g, 26%) was obtained as a yellow orange solid. Compound (**73**) had ν_{max} (KBr) (cm^{-1}) 620, 690, 740, 800, 835, 850, 900, 970, 1010, 1030, 1070, 1120, 1140, 1190, 1215, 1265, 1280, 1330, 1385, 1460, 1490, 1530, 1600, 2860, 2930, 2960, 3080; δ_H 7.57-7.13 (11H, m), 6.70 (3H, m), 5.72 (1H, br.d., J 17.8) 5.20 (1H, br.d., J 10.9), 3.96 (8H, m), 1.78 (8H, m), 1.49 (8H, m), 0.96 (12H, m), δ_C 153.2, 149.6, 149.4, 149.3, 143.3, 139.4, 139.2, 138.9, 136.5, 136.3 134.1, 126.7, 126.2, 125.7, 125.5, 124.3, 123.3, 123.0, 122.4, 114.3, 113.9, 113.7, 113.6, 112,2, 112.1, 69.2, 68.3, 32.0, 31.6, 19.5, 19.3, 14.0, m/z 709 (M^+), λ_{max} ($CHCl_3$) 241.3 (4.28), 266.3 (4.22), 341.6 (4.21), 409.7 (4.64). Found C, 74.66; H, 7.89%, M^+, 708.331; $C_{44}H_{52}O_4S_2$ requires C, 74.54; H, 7.40; M^+, 708.3307.

Preparation of 7 ring compounds.

1,4-Dibutoxy 2,5-di(5′-phenyl-5″-di-2′,2″-thienyl) benzene (**72**). To a stirred solution of 1,4-dibutoxy-2,5-di(5′-iodo-2′-thienyl)benzene (**54**) (3.0 g, 4.7 mmol) in DMF (100 ml) was added a solution of 2-tri-*n*-butylstannyl-5-phenylthiophene (**60**) (13.8 mmol, 3 eq) in THF (50 ml) followed by addition of reduced palladium catalyst (0.13 mmol, 2.8 mol %) in THF (10 ml). The reaction solution was heated under reflux for 20h, then cooled to room temperature after which some orange solid precipitated. Acidification with aqueous HCl (3M, 100 ml) resulted in further precipitation. The precipitate was collected by filtration and identified as (**72**) (1.6 g, 48%) mp 228°-232°C; m/z 702 (M^+), λ_{max} ($CHCl_3$) 244.2 (4.24), 435.8 (4.57). Found M^+, 702.1760; $C_{42}H_{38}O_2S_4$ requires M^+, 702.1753. The filtrate was evaporated to dryness giving a dark brown solid which was purified by column chromatography (pentane/chloroform eluent) giving the product from mono-coupling (**71**) (0.2 g, 8%) as a dark yellow solid, mp. 132°-135°C; δ_H 7.58-7.05 (14H, m), 4.03 (4H, m), 1.87 (4H, m), 1.58 (4H, m), 0.91 (6H, t); δ_C 149.3, 142.8, 139.4, 138.3, 137.3, 134.8, 129.0, 128.9, 127.5, 126.8, 125.9, 125.8, 125.2, 124.1, 123.9, 123.5, 123.0, 122.4, 112.4, 111.7, 69.3, 31.6, 19.7, 14.1; m/z 544 (M^+), 487, 431; λ_{max} ($CHCl_3$) 244.0 (4.11), 405.0 (4.46). Found M^+, 544.1560; $C_{32}H_{32}O_2S_3$ requires M^+, 544.1563.

Typical procedure for the preparation of the bisorganozinc chlorides used in the polymerisation reactions.

Preparation of 1,4-di-5′-chlorozinc-2′-thienylbenzene (**66**). To a stirred solution of 1,4-di(2′-thienyl)benzene (1.0 g, 4.3 mmol) in THF (25 ml) under argon at 0° C was added a solution of *n*-butyllithium (2.2M in hexanes, 3.8 ml, 8.26 mmol). Upon completion of addition, the ice bath was removed and the solution stirred at room temperature for 3h. A freshly made up solution of zinc chloride (1.12 g, 8.26 mmol) in THF (25 ml) was added and the mixture stirred for a further 1h at room temperature. The *bis*-zinc reagent (**66**) thus formed was not isolated but was used immediately in further reactions.

Preparation of polymers.

Poly(1,4-(2′,5′-thienyl)benzene (**75**). To a solution of 1,4-di(5′-chlorozinc-2′-thienyl)benzene (4.13 mmol) in THF (50 ml) under argon, was added a solution of $Ni(PPh_3)_2Cl_2$ (0.4 g, 6.35 mmol) and 1,4-dibromobenzene (0.97 g, 4.13 mmol) in THF (20 ml). This solution was stirred at 50°C for 3h then cooled to room temperature, quenched with 3M hydrochloric acid and the product, which had precipitated from solution, collected by filtration. The brown residue was washed with water (50 ml), methanol (50 ml) and diethyl ether (30 ml) then dried in vacuo for 24h at room temperature (1.26 g, 96%). Soxhlet extraction with chloroform to take out low molecular weight material resulted in a weight decrease of 10%. No melting was observed below 360°C; ν_{max} (cm^{-1}) 690, 800, 1040, 1120, 1450, 1490, 1610, 2480, 3360.

Poly(1,3(2′,5′-thienyl)benzene) (**84**). A solution of 1,3-dibromobenzene (1.0 g, 4.1 mmol) and $Ni(PPh_3)_2Cl_2$ (0.4 g, 0.64 mmol) in THF (20 ml) was added to a solution of 1,3-di(5′-chlorozinc-2′-thienyl)benzene (4.2 mmol) in THF (45 mol) under argon and the reaction solution stirred at 50°C for 4h; some product precipitated from solution during this time. The reaction was cooled to room temperature and quenched by the addition of aqueous hydrochloric acid (3M, 3 ml). The product was collected by filtration and washed with water, methanol (30 ml) and diethyl ether (30 ml), then dried in vacuo at room temperature for 24h to give (**84**) (1.15 g, 87%) as a yellow powder. Polymer (**84**) did not melt but darkened around 290°C. Soxhlet extraction with chloroform for 24h resulted in a weight decrease of 5%. ν_{max} (KBr) (cm^{-1}) 680, 780, 850, 870, 1070, 1090, 1470, 1600, 2160.

Cross linked polymer (**86**). To a stirred solution of 1,4-di(5′chlorozinc-2′-thienyl)benzene (9 mmol) and 1,3,5-tri(5′-chlorozinc-2′-thienyl)benzene (1 mmol) in THF (115 mol) under argon was added a solution of 1,4-dibromobenzene (2.35 g, 10 mmol) and $Pd(PPh_3)_4$ (0.2 g, 0.173 mmol) in THF (20 ml) and the reaction solution stirred at 50°C for 48h. The polymer precipitated from solution and was collected by filtration, then washed with water, methanol and diethyl ether. Soxhlet extraction with chloroform for 24h to remove low molecular weight oligomers gave (**86**) (2.9 g, 95%) as a yellow powder which did not melt up to 360°C. ν_{max} (KBr) (cm^{-1}) 700, 800, 830, 1010, 1080, 1130, 1200, 1460, 1490, 1600, 2400, 3060, 3140, 3390, 3494.

Poly(1-(5′-(1″,10″-biphenyl)-2-thienyl)-4-(2‴,5‴-thienyl)benzene (**82**). A solution of 1,4-di(5′-chlorozinc-2′-thienyl)benzene (4.13 mmol) in THF under argon was added to a stirred solution of 4,4′-dibromobiphenyl (1.3 g, 4.13 mmol) and $Ni(PPh_3)_2Cl_2$ (0.4 g, 0.64 mmol) in THF (15 ml). The reaction solution was stirred at room temperature for 16h during which time the product precipitated from solution. The reaction was quenched by the addition of aqueous hydrochloric acid (3M, 30 ml) and the product collected by filtration. The brown solid thus obtained was washed with water (30 ml), methanol (50 ml) and diethyl ether before drying in vacuo at 50°C. ν_{max} (KBr) (cm^{-1}) 780, 790, 820, 840, 1020, 1420, 1480, 1600, 1690.

Poly(1,4-(2′,5′-thienyl)2,5-dimethylbenzene (**76**). A solution of 1,4-di(5′-chlorozinc-2′-thienyl)2,5-dimethylbenzene (3.7 mmol) in THF under argon was added to a stirred solution of 1,4-dibromo-2,5-dimethylbenzene (0.98 g, 3.7 mmol) and $Ni(PPh_3)_2Cl_2$ (0.4 g, 0.63 mmol) in THF (20 ml). The reaction solution was stirred at room temperature for 3h, during which product precipitated from solution. Quenching the reaction with aqueous 3M HCl (30 ml), collection of the precipitate by filtration and washing consecutively with water, methanol and diethyl ether gave the title compound (1.2 g, 88%) as a dark green powder. ν_{max} (KBr) (cm^{-1}) 690, 810, 890, 1050, 1220.

*Poly-(1,4-(2′,5′-thienyl)2,5-di-*n*-butylbenzene)* (**77**). A solution of 1,4-dibromo-2,5-di-*n*-butylbenzene (2.47 g, 7.1 mmol) and $Pd(PPh_3)_4$ (0.08 g, 0.07 mmol) in THF (30 ml) was added to a solution of 1,4-di-(5′-chlorozinc-2′-thienyl)2,5-di-*n*-butylbenzene (7.1 mmol) in THF (35 ml) and the reaction solution stirred at 50°C for 24h. The reaction was cooled to room temperature and quenched with aqueous HCl (3M, 20 ml) and the aqueous phase then extracted with diethyl ether (20 ml). The combined organic layers were washed with water (30 ml), dried over $MgSO_4$, filtered and the solvent evaporated. Column chromatography using pentane/chloroform (solvent gradient) gave the title compound (1.56 g, 39%) as a green solid. λ_{max} ($CHCl_3$) 332 mm.

Poly(1,4-(2′,5′-thienyl)-2,5-dimethoxybenzene (**78**). To a solution of 1,4-di(5′-chlorozinc-2′-thienyl)2,5-dimethoxybenzene (3.31 mmol) in THF (20 ml) was added a solution of 1,4-dibromo-2,5-dimethoxybenzene (0.98 g, 3.3 mmol) and $Pd(PPh_3)_4$ (0.20 g, 0.18 mmol) in THF (20 ml) and the reaction solution stirred at 50°C for 24h. Work up and column chromatography as for compound (**78**) gave the title compound (0.85 g, 55%) as a yellow solid which did not melt up to 360°C. ν_{max} (KBr) (cm^{-1}) 700, 760, 800, 850, 1040, 1220, 1440, 1460, 1500; λ_{max} ($CHCl_3$) 400 mm.

Polymer (**83**). A solution of 1,4-di(5′-tri-n-butylstannyl)-2,5-di-*n*-butoxybenzene (3.1 mmol) in THF (50 ml) was added to a solution of 1,4-di(5′-iodo-2′-thienyl)2,5-di-*n*-butoxybenzene (2.0 g, 3.1 mmol) in DMF (70 ml). A solution of the reduced palladium catalyst (0.09 mmol, 2.9 mol %) in THF (15 ml) was then added and the reaction solution warmed to 80°C at which it was stirred for 12h. Within minutes of adding the catalyst, a brick red precipitate began to form. Upon cooling to room temperature, the precipitate was collected by filtration and washed with diethyl ether (1.5 g, 62%). Found C, 68.57; H, 6.28%; $C_{22}H_{24}O_2S_2$ requires C, 68.8; H, 6.3%.

Polymer (**80**). A solution of 1,4-di(5′-chlorozinc-2′-thienyl)benzene (4.13 mmol) in THF, was added to a solution of $Pd(PPh_3)_4$ (0.2 g, 0.173 mmol) and 1,4-dibromo-2,5-di-*n*-butylbenzene (1.44 g, 4.13 mmol) in THF (50 ml) and the reaction solution stirred at 50°C for 24h. Upon cooling to room temperature., work up and column chromatography as for (**78**) gave the title polymer (1.34 g, 75%) as a yellow solid. Polymer (**80**) did not melt but darkened around 260°C. ν_{max} (KBr) (cm^{-1}) 660, 680, 800, 1120, 1470, 1490, 1610, 2500; λ_{max} ($CHCl_3$) 360.

Polymer (**79**). To a solution of 1,4-di(5′-chlorozinc-2′-thienyl)benzene (12.4 mmol) in THF (60 ml) was added a solution of $Pd(PPh_3)_4$ (0.2 g, 0.173 mmol) and 1,4-dibromo-2,5-dimethoxybenzene (3.57 g, 12.4 mmol) in THF (100 ml). The reaction was stirred at 50°C for 24h then quenched by the addition of aqueous HCl (3M, 30 ml) causing the product to precipitate from solution. The precipitate was collected by filtration, washed with diethyl ether and dried in vacuo giving the title compound (0.62 g, 13.4%) ν_{max} (KBr) (cm^{-1}) 690, 760, 800, 850, 960, 995, 1040, 1080, 1130, 1225, 1290, 1360, 1400, 1440, 1470, 1490, 1550, 2950; λ_{max} ($CHCl_3$) 413.0. 1,4-Di(2′-thienyl)benzene (2.3 g, 77%) was recovered from the filtrate.

Polymer (**81**). A solution of 1,4-dibromo-2,5-methoxycarbonylbenzene (2.1 g, 5.8 mmol) and $Pd(PPh_3)_4$ (0.2 g, 0.17 mmol) in THF (40 ml) was added to a solution of 1,4-di-(5′-chlorozinc-2′-thienyl)benzene (5.7 mmol) in THF and the resulting solution stirred at 50°C for 24h. The reaction was cooled to room temperature and then quenched by the addition of aqueous HCl (3M, 50 ml) and diluted with diethyl ether (50 ml). The title compound (2.0 g, 83%) precipitated from solution as a green powder and was collected by filtration. Polymer (**81**) did not melt up to 360°C. ν_{max} (KBr) (cm^{-1}) 715, 830, 980, 1010, 1130, br 1280, 1410, 1450, 1580, 1760; λ_{max} ($CHCl_3$) 390.4.

REFERENCES

1. Burt, F.P., *J. Chem. Soc.*, **1910**, *1171*.
2. Walatka, V.V. Jr.; Labes, M.M.; Perlstein, J.H., *Phys. Rev. Lett.*, **1973**, *31*, 1139.
3. Greene, R.L.; Street, G.B.; Suter, L.J., *Phys. Rev. Lett.*, **1975**, *34*, 577.
4. Labes, M.M.; Love, P.; Nichols, L.F., *Chem. Rev.*, **1979**, *79*, 1.
5. Gill, W.D.; Bludan, W.; Geiss, R.H.; Grant, P.M.; Mayerie, R.L.; Street, G.B., *Phys. Rev. Lett.*, **1977**, *38*, 1305.
6. Shirakawa, H.; Ikeda, S.; *Polymer. J.*, **1971**, *2*, 231.

7. Ito, T.; Shirakama, H.; Ikeda, S., *J. Polym. Sci.*, **1975**, *13*, 1943.

8. Chiang, C.K.; Fincher, G.R.; Park, Y.W.; Heeger, A.J.; Shirakama, H.; Louis, E.J.; Gau, S.C.; MacDiarmid, A.G., *Phys. Rev. Lett.*, **1977**, *39*, 1098.

9. Ito, T.; Shirakawa, H.; Ikeda, S., *J. Polym. Sci., Polym. Chem. Ed.*, **1974**, *12*, 11.

10. Edwards, G.; Goldfinger, G., *J. Polym. Sci.*, **1955**, *16*, 589.

11. (a) Ikenoue, Y.; Kira, M.I.; Tomazawa, H.; Yashima, H.; Kobeyashi, M., *J. Chem. Soc. Chem. Commun.*, 1990, 1964, (b) Tourillon, G.; ref 20a, chapter 9, p293-350.

12. Castisso-Orgtega, M.M.; Inoue, M.B., *Synth. Met.*, **1989**, *28*, C65.

13. Oshawa, T.; Kaneto, K.; Yashino, K., *Japan. J. App. Phys.*, **1984**, *23*, L663.

14. Baughman, R.H.; Bredes, T.L.; Chance, R.R.; Elsenbaumer, R.L.; Shacklette, L.W., *Chem. Rev.*, **1982**, *82*, 209.

15. Wessling, R.A.; Zimmerman, R.G., US Patent, 1972, 3,706,677; 1968, 3, 401, 152.

16. Iwatsuki, S.; Kubo, M.; Yamashita, H., *Chem. Lett.*, **1989**, 729.

17. Diaz, A.; Logan, J.A., *J. Electroanal. Chem.*, **1980**, *111*, 111.

18. Chance, R.R.; Shacklette, L.W.; Miller, G.G.; Ivory, D.M.; Sowa, J.M.; Elsenbaumer, R.L.; Baughman, R.H., *J. Chem. Soc., Chem. Comm.*, **1980**, 348.

19. Rabolt, J.F.; Clarke, T.C.; Kanazawa, K.K.; Reynolds, J.R.; Street, G.B., *J. Chem. Soc. Chem. Commun.*, **1980**, 347.

20. (a) Skotheim T.A., (Ed.), *Handbook of Conducting Polymers*, vols. 1 & 2, Marcel Dekker, New York, **1986**, (b) Bredas, J.L.; Street, G.B., *Acc. Chem. Res.*, **1985**, *18*, 309, (c) Frommer, J.E., *ibid*, **1986**, *19*, 2, (d) Bryce, M., *Chem. in Brit.*, **1988**, 781, (e) Carter F.L., (Ed.), *Molecular Electronic Devices*, Marcel Dekker, New York, 1982, (f) Frommer, J.E.; Chance, R.R., *Encyclopedia of Polymer Science and Engineering*, Grayson M.; Koschwitz J., (Eds.), Wiley, New York, **1987**, (g) Greene, R.L.; Street, G.B., *Science*, **1984**, *226*, 681, (h) Bryce M.; Murphy L., *Nature*, **1984**, *309*, 119, (i) Wudl, F., *Acc. Chem. Res.*, **1984**, *17*, 227, (j) Feast, W.J., *Chem. Ind.*, **1985**, 263, (k) Proceedings of the International Conference on *Synthetic Metals*, Kyoto, Japan **1986**, published in *Synth. Met.*, **1987**, *17-19*, (l) Bryce, M.R., *Annl. Rep. Prog. Chem., Sect. B, Org. Chem.*, **1985**, *82*, 377, (m) Wegner, G., *Angew. Chem. Int. Ed. Engl.*, **1981**, *20*, 361, (n) Hatfield, W.E., *Molecular Metals*, Plenum Press, New York, **1979**, (o) Seymour, R.B., *Conducting Polymers*, Plenum Press, New York, **1981**, (p) Mort, J.; Fisher, C.P., (Eds.), *Electronic Properties of Polymers*, Wiley, New York, **1982**, (q) Kuzmany, N.; Mehring, M.; Roth, S., *Electronic Properties of Conjugated Polymers*, Springer, Berlin, **1987**, (r) Carter, F., (Ed.), *Molecular Electronic Devices II*, Marcel Dekker, New York, **1987**, (s) Simon, J.; Andre, J.J., *Molecular Semiconductors*, Springer, Berlin, **1985**, (t) Bloor, D., *New Scientist*, **1982**, 577; *Chem. in Brit.*, **1983**, *19*, 725, (u) Garnier, F., *Angew. Chem., Int. Ed. Engl.*, **1989**, *28*, 513, (v) Margolis, J.M., *Conductive Polymers and Plastics*, Chapman and Hall, New York, **1989**, (w) Kuzmany, H.; Mehring

M.; Roth, S., (Eds.), *Electronic Properties of Polymers and Related Compounds*, Springer-Verlag, Heidelberg, **1985**, (x) Linford, R.G., (Ed.), *Electrochemical Science and Technology of Polymers*, vol. 1 (**1987**) and vol. 2 (**1990**), Elsevier Applied Science, London, (y) Wirsern, A., *Electroactive Polymer Materials: State-of-the art Review of Conducting Polymers*, Lancaster (Penn), Technomic, **1987**.

21. MacDiarmid, A.G. *et al.*, *J. Chem. Soc. Chem. Commun.*, **1981**, 317; *Mol. Cryst. Liq. Cryst.*, **1982**, *83*, 309; Abstr. 557, *Proc. Electrochem. Soc.*, **1983**, *81-1*; *Sci. Am.*, **1988**, *258*, 60.
22. (a) Kakuta, T.; Shirata, Y.; Mikawa, H., *J. Chem. Soc. Chem. Commun.*, **1985**, 553; (b) Dietrich, M.; Mortensen, J.; Heinz, J., *J. Chem. Soc. Chem. Commun.*, **1980**, 1131.
23. Shimidzu, A.; Yamataka, K.; Kohno, M., *Bull. Chem. Soc. Jpn.*, **1988**, *61*, 4401.
24. Sata, T.; Saeki, S.I., *J. Chem. Soc. Chem. Commun.*, **1989**, 230.
25. Gazard, M., ref. 20a, Chapter 19, p673-687.
26. Garnier, F.; Horowitz, G., *J. Electrochem. Soc.*, **1985**, *132*, 634.
27. Skotheim, T.A.; Peterson, L.G.; Inganos, O.; Lundstrom, I., *J. Electrochem. Soc.*, **1982**, *129*, 1737.
28. Noufi, R.; Tench, D.; Warren, C.F., *J. Electrochem. Soc.*, **1981**, *128*, 2596.
29. Waltman, R.B.; Bargon, J., *Can. J. Chem.*, **1986**, *64*, 76.
30. Meyer, W.H.; Kiess, H.; Binggeli, B.; Meier, M.; Harbecke, G., *Synth. Met.*, **1985**, *10*, 255.
31. Kanicki, J, ref. 20a, Chapter 17, p543-660.
32. Salmon, M.; Diaz, A.F.; Goita, J., in "*Chemically Modified Surfaces in Catalysis and Electrocatalysis*", Miller. J.S. (Ed.) Am. Chem. Society, Washington D.C., **1982**, 65.
33. Deronzier, A.; Moutet, J.-C., *Acc. Chem. Res.*, **1989**, *22*, 249
34. Curran, D.; Grimshaw, J.; Perera, S.D., *Chem. Soc. Rev.*, **1991**, *20*, 391.
35. Roncali, J.; Youssoufi, H.K.; Garreau, R.; Delabouglise, D.; Garnier, F.; Lemaire, M., *J. Chem. Soc. Chem. Commun.*, **1990**, 414.
36. Bjorklund, R.B.; Lundstrom, I., *J. Electron. Mater.*, **1984**, *13*, 211.
37. Wakura, C.J.; Kajiya, Y.; Yaneyama, H., *J. Chem. Soc. Chem. Commun.*, 1988, 1019.
38. Prezyna, L.A.; Qiu, Y.-J.; Reynolds, J.R.; Wnek, G.E., *Macromol.*, **1991**, *112*, 4192; Li, Y; Dong, S., *J. Chem. Soc.*, **1992**, 827.
39. Jenkins, I., Ph.D. Thesis, 1991, University College of Swansea.
40. Jones, D.E., Ph.D. Thesis, 1992, University College of Swansea.
41. Diaz, A.F.; Lee, W.-Y.; Logan, A.; Green, D.C., *J. Electroanal. Chem.*, **1980**, *108*, 377.
42. Shimidzu, T.; Ohtani, A.; Honda, K., *Bull. Chem. Soc. Jpn.*, **1988**, *61*, 2888.
43. Waltman, R.J.; Burgon, J.; Diaz, A.F., *J. Phys. Chem.*, **1983**, *87*, 1459.
44. Waltman, R.J.; Diaz, A.F.; Burgon, J., *J. Electrochem. Soc.*, **1984**, *131*, 1452.
45. Naitoh, S.; Samui, K.; Ogata, N., *J. Chem. Soc. Chem. Commun.*, **1986**, 1414.
46. Lazzaroni R.; Riga, J.; Verbist, J.J.; Christiaens, L.; Renson, M., *J. Chem. Soc. Chem. Commun.*, **1985**,

999.

47. Pelter, A.; Rowlands, M.; Jenkins, I.H., *Tetrahedron Lett.*, **1987**, *28*, 5213.

48. Pelter, A.; Maud, J.M.; Jenkins, I.; Sadeka, C.; Coles, G., *Tetrahedron Lett.*, **1989**, *30*, 3461.

49. Feast, W.J., ref 20a chap. 1, p1-43.

50. Speight, J.G.; Kovacic, P.; Koch, F.W., *J. Macromol. Sci. Rev. Macromol. Chem.*, **1971**, *C5*, 295.

51. Kovacic, P.; Oziomek, J., *J. Org. Chem.*, **1964**, *29*, 100.

52. Shimidzu, T.; Ohtani, A.; Iyoda, T.; Honda, K., *J. Chem. Soc. Chem. Commun.*, **1986**, 1414.

53. Kang, E.T.; Tan, T.C.; Neoh, K.G.; Ong, Y.K., *J. Macromol. Sci. Chem.*, **1987**, *A24*, 631; *Polymer*, **1986**, *27*, 1958.

54. Rapi, S.; Bocchi, V.; Gardini, G., *Synth. Met.*, **1988**, *24*, 217.

55. Chao, T.H.; March, J., *J. Polym. Sci., Poly. Chem. Ed.*, **1988**, *26*, 743.

56. Ballard, D.G.H.; Coutis, A.; Shirley, I.M.; Taylor, S.C., *J. Chem. Soc. Chem. Commun.*, **1983**, 954.

57. Marvel, C.S.; Hartznell, G.E., *J. Am. Chem. Soc.*, **1959**, *81*, 448.

58. Cassidy, P.E.; Marvel, C.S.; Ray, S., *J. Polym. Sci. A.*, **1965**, *3*, 1553.

59. Jen, K.-Y.; Maxfield, M.; Shacklette, L.W.; Elsenbaumer, L., *J. Chem. Soc. Chem. Commun.*, **1987**, 309.

60. Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M., *Polym. Commun.*, **1987**, *28*, 229.

61. Yamata, S.; Tokita, S.; Tsutsui, T.; Saito, S., *J. Chem. Soc. Chem. Commun.*, **1987**, 1448.

62. Jin, J.-I.; Park, C.K.; Park, H.-K.; Shim, H.-K.; Park, Y.-W., *J. Chem. Soc. Chem. Commun.*, **1989**, 1205.

63. Shim, H.-K.; Lenz, R.W.; Jin, J.I., *Macromol. Chem.*, **1989**, *190*, 389.

64. Goldschmidt, G., *Monatsh. Chem.*, **1986**, *7*, 40.

65. Kerr, W.; Muller, R.; Wirth, H.O., *Makromol. Chem.*, **1964**, *77*, 90.

66. Yamamoto, T.; Hagoshi, Y.; Yamamoto, A., *Bull. Chem. Soc. Jpn.*, **1978**, *51*, 2091.

67. Winkler, H.J.S.; Wittig, G., *J. Org. Chem.*, **1963**, *28*, 1733.

68. Zhou, Z.; Maruyama, T.; Kanbara, T.; Iveda, T.; Ichimura, K.; Yamamoto, T.; Tokuda, K., *J. Chem. Soc. Chem. Commun.*, **1991**, 1210.

69. Reynolds, J.R.; Ruiz, J.P.; Child, A.D.; Nayak, K.; Marynick, D.S., *Macromol.*, **1991**, *24*, 678.

70. Ruiz, J.P.; Dharia, J.R.; Reynolds, J.R., *Macromol.*, **1992**, *25*, 849.

71. Bao, Z.; Chan, W.; Yu, L., *Chem. Mat.*, **1993**, *5*, 2.

72. Bracke, W., *J. Polym. Sci. Polym. Chem. Ed.*, **1972**, *10*, 975.

73. Hay, A.S., *J. Polym. Sci. Polym. Chem. Ed.*, **1969**, *7*, 1625.

74. Schlute, K.E., *et al.*, *Angew. Chem.*, **1960**, *72*, 920; **1961**, *73*, 241; *Chem. Ber.*, **1962**, *95*, 1943; **1965**, *98*, 98; *Tetrahedron Lett.*, **1967**, 4819.

75. Cava, M.P.; Levinson, M.I., *Tetrahedron*, **1985**, *41*, 5061.

76. Pouwer, K.L.; Vries, T.R.; Havinga, E.E.; Meizer, E.W.; Wynberg, H., *J. Chem. Soc. Chem. Commun.*, **1988**, 1432.

77. ten-Hoeve, W.; Wynberg, H.; Havinga, E.E.; Meijer, E.W., *J. Am. Chem. Soc.*, **1991**, *113*, 5887.

78. Pelter, A.; Rowlands, M.; Clement, G., *Synth. Commun.*, **1987**, 51.

79. Rowlands, M., PhD Thesis, University College of Swansea, 1990.

80. Pederson, E.B., *J. Chem. Soc., Perkin Trans. II*, **1977**, 473.

81. Kelley, R.M.; Schaap, A.P.; Wynberg, H., *J. Org. Chem.*, **1969**, *34*, 343.

82. Miyaura, N.; Yanagi, T.; Suzuki, A., *Synth. Commun.*, **1981**, *11*, 513.

83. Haynes, D.M.; Hepburn, A.R.; Goldie, D.M.; Marshall, J.M.; Pelter, A., *Synth. Met.*, **1993**, 839.

84. Haynes, D.M.; Hepburn, A.R.; Goldie, D.M.; Marshall, J.M.; Pelter, A., *Mol. Liq. Cryst.*, **1993**, *236*, 243.

85. Babo, S.; Negishi, E., *J. Am. Chem. Soc.*, **1976**, *98*, 6730.

86. Stille, J.K., *Angew. Chem. Intern. Ed. Engl.*, **1986**, *25*, 508.

87. Kondo, Y.; Vehiyama, D.; Sakamoto, T.; Yamanaka, H., *Tetrahedron Lett.*, **1989**, *30*, 4249.

88. Rossi, R.; Carpita, A.; Ciafalo, M.; Lippolis, V., *Tetrahedron*, **1991**, *47*, 8443.

89. Stille, J.K.; Groh, B.L., *J. Am. Chem. Soc.*, **1987**, 109, 813.

90. Isaacs, D., Unpublished results, University of Wales Swansea,.

91. Grimshaw, A., Unpublished results, University of Wales Swansea.

92. (a) Davidson, J.M.; Triggs, C., *J. Am. Chem. Soc.*, **1968**, *100*, 1324; (b) Suzuki, A., *Pure Appl. Chem.*, **1985**, *57*, 1749; **1991**; *63*, 419; **1994**, *66*, 213; Oh-e, T.; Miyaura, N.; Suzuki, A., *J. Org. Chem.*, **1993**, *58*, 2201.

93. Pekker, S.; Janossy, A., ref 20a, chap. 2, p48-49.

94. Baughman, R.H.; Bredas, J.L.; Chance, R.R.; Elsenbaumer, R.L.; Shacklette, L.W., *Chem. Rev.*, **1982**, 209.

95. Pron, A.; Billaud, D.; Kulszewicz, I.; Budrowski, C.; Przyluski, J.; Sugalski, J., *Mater. Res. Bull*, **1981**, *16*, 1229; Pron, A.; Kulszewicz, I.; Billaud, D.; Przyluski, J., *J. Chem. Soc. Chem. Commun.*, **1981**, 783; Pron, A.; Billaud, D.; Bernier, P.; Lefrant, S., *Polym. Prep.*, **1982**, *23*, 96.

96. Jen, K.-Y.; Eckhardt, H.; Jow, T.R.; Shacklette, L.W.; Elsenbaumer, R.L., *J. Chem. Soc. Chem. Commun.*, **1988**, 215.

97. Jurd, L., *Aust. J. Sci. Res., Ser. A.*, **1949**, *2*, 599.

98. Sarauw, E., *Liebigs Ann. Chem.*, **1881**, *209*, 203.

99. Angelleti, E.; Tundo, P.; Venturello, P., *J. Chem. Soc., Perkin Trans. 1*, **1982**, 1137.

100. Gjös, N.; Gronowitz, S., *Acta Chem. Scand.*, **1972**, *26*, 1851.

101. Riberau, P.; Pastour, P., *Bull. Soc. Chim. Fr.*, **1969**, 2076.

(*Received in UK* 17 *April* 1997; *revised* 23 *May* 1997; *accepted* 29 *May* 1997)