HETEROCYCLE-BASED ELECTRIC CONDUCTORS

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Abstract - A review is presented of our contribution addressed towards: *i*)
the control of redox potentials of pyrrole- and thiophene-based conductors
and *ii*) the search for polythiophene models. We approached the first by
exploiting the *spacer* strategy, according to which the monomer contains
two terminal polymerogenic units linked to a central π-conjugatively active
frame. The second topic was approached by investigating end-methyl-capped
thiophene oligomers. Taken together, the results clear up many puzzling
aspects and provide influential clues for designing tailored heterocyclic
structures that respond to specific operational requirements.

INTRODUCTION

The specialized subject of conductive organics is under active investigation and numerous books[1] and

reviews[2] are available. A vast body of these systems are based on heterocyclic components [Charge

Transfer Complexes (CTC) or polyheterocycles] and, to place our contribution in this field in the

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In Honour of the 65th birthday of Alan R. Katritzky, an inspiring example in Heterocyclic Chemistry

perspective of the current literature it is useful to discuss briefly the molecular basis of electronic conduction.

An organic solid must have "mobile" electrons if it is to develop conductivity. Electronic vacancies (cations or cation radicals) or an excess of electrons (anions or anion radicals) are the defects which can provide mobility to loosely bound electrons which, in molecules, reside in antibonding orbitals. In a solid, the conduction band roughly corresponds to these molecular antibonding orbitals.[3] Before they can be considered mobile, the electrons must be capable of moving freely from the valence to the conduction band of the solid and this requires the existence of a small energy gap between these two states. Electrons can move in the solid either by means of intermolecular hopping or by delocalizing within the polyunsaturated frame of a macromolecule.

The negatively charged electronic defects present in anions or anion radicals can be formed in electron-poor organic molecules by means of either chemical or electrochemical reduction. Unlike cations and cation radicals, anions and anion radicals are not inert to electrophiles (particularly oxygen), unless they are specially stabilized. For this reason, organic conductors based on heterocyclic anions or anion radicals have received much less attention than their cationic counterparts. Conversely, the positively charged electronic defect present in cations or cation radicals can be created in electron-rich organic molecules by means of either chemical or electrochemical oxidation. Conductive CTCs consist[4] of a *donor*, a π-electron-rich system such as tetrathiofulvalene (TTF), and an *acceptor* such as
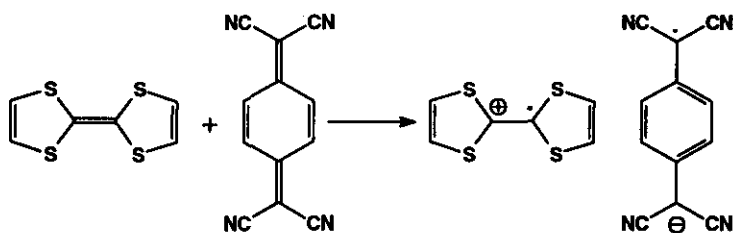

tetracyanoquinodimethane (TCNQ). In the solid TTF•TCNQ, these components are arranged in

segregated stacks with partial electron transfer between the stacks allowing the carrier to hop from one

site to another of the same stack. The TCNQ attains aromaticity upon the reduction that follows the

electron transfer; analogously, TTF gains aromatic-like stabilization upon oxidation since a dithiolium

cation substructure is formed. In Bechgaard salts[5] $[(Don)_2{}^+]X^-$, the electron neutrality of the solid is

provided by a spectator anion rather than by the negatively charged acceptor, with anion X^- being

incorporated from the solution during the electrochemical oxidation of the donor. When the cation or

cation radical originating from the π-electron-rich heterocycle is not especially stabilized it may undergo

polymerization as in the case of pyrrole and thiophene.[6] Access to (oxidatively doped[7]) conductive

polycationic polymers from the relevant monomeric heterocycles is shown in Scheme 1.
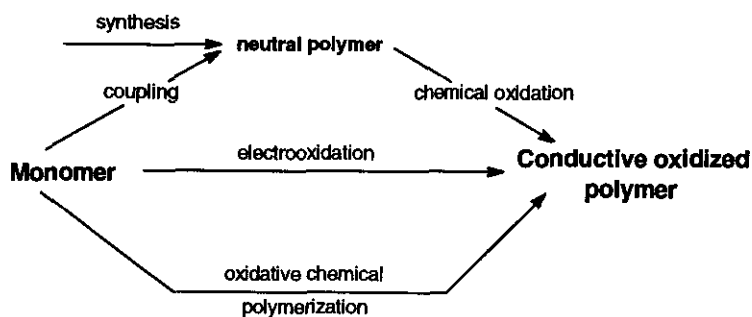
Scheme 1

The oxidative polymerization of pyrrole or thiophene affords the conductive polymer in a one-pot

multistep process. Coupling occurs at the α-positions of the heterocycles. The oxidative polymerization
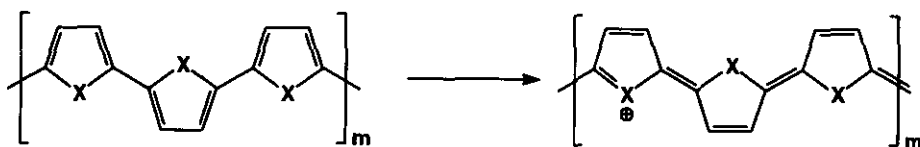

of the monomer may be chemical (e.g. with $FeCl_3$, $CuCl_2$, As^V and Sb^V halides, etc.), or at the anode

of an electrochemical cell. Alternatively, neutral polyheterocycles (e.g. neutral polypyrrole and polythiophene) can be made conductive by means of chemical oxidation. Neutral polyheterocycles can be obtained by chemical synthesis through α-coupling, or by means of the electrochemical dedoping (cathodic reduction) of the thin films of the conductive polymer anodically deposited on the electrode. Neutral polypyrrole is extremely unstable in the air because of its negative redox potential (E^0 = - 0.20 V), but neutral polythiophene is stable (E^0 = 0.70).

## π-EXCESSIVE AND π-DEFICIENT HETEROCYCLES AS *DONORS* AND *ACCEPTORS*

It is clear from the above that organic conductors are constituted by cations or cation radicals, or by anions or anion radicals. The easy formation of cationic species pertains to π-electron-rich molecular or macromolecular assemblies, while the formation of anionic species pertains to π-deficient molecules. Heterocycles are traditionally classified[8] as being π-excessive or π-deficient, an electronic classification which ideally parallels the electronic requirements of *donors* and *acceptors*. Therefore, although heterocycles are not the only class of compounds that fit the structural requirements for both molecular (e.g. CTCs) and macromolecular conductors (e.g. polyunsaturated polymers), the π-excessive systems are best suited for providing stable cationic species, and the π-deficient heterocycles for providing stable anionic components. We have shown[9] that it is possible to obtain conductive CTCs, such as **1** and **2** based on TTF as *donor* but with the classical TCNQ *acceptor* being substituted by typical π-deficient heterocycles, such as *sym*-triazine and 1,2,4,5-tetrazine.
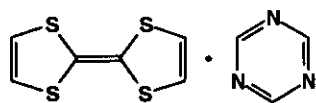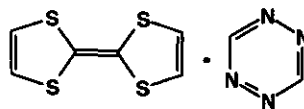

1   **2**

The invaluable advantage of heterocyclic structures is that they can be easily modified by means of a vast range of substituents or ring fusions which impart specific properties to the final molecular or macromolecular conductive material. This characteristic has been extensively exploited, giving rise to the present generations of conductive polyheterocycles.

TOWARDS NEW GENERATIONS OF CONDUCTIVE POLYHETEROCYCLES

Chemically prepared conductive polypyrrole (PP) and polythiophene (PT) are insoluble, non-processible black powders: electrochemical synthesis produces the conductive materials as films which have similar properties. In the second generation of thiophene-based conductive polymers, 3-alkyl substitution of the monomer (particularly with *n*-hexyl residues[10]) has been used to impart solubility to the final conductive polymer. In the third generation, alkyl chains bear specific functionalities to meet special applications of the polymer: viologen-substituted poly(alkylthiophenes) derived from **3** are just an example.[11] Analogously, in the case of pyrrole-based conductors, substitutions at the ring positions by specially designed functionalities as in **4- 6** produce materials which are useful as a support for


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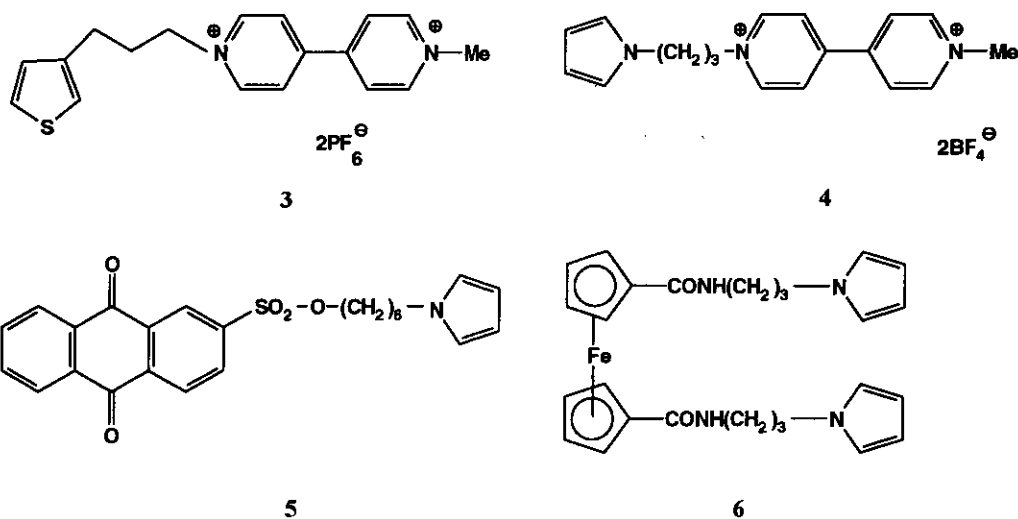
electrocatalysis.[12] In all of these cases the innovative contribution of synthetic heterocyclic chemistry

was the functionalization of the heterocyclic structure. In the general framework of new generations of

heterocycle-based conductors, we have addressed our efforts towards *i*) obtaining environmentally stable

materials[13,14] and *ii*) clarifying the dependence of polymer conductivity on its architecture, as inferred

from the molecular structure of the functionalized monomer. As far as the environmental stability of

polyheterocycles is concerned neutral polypyrrole was already shown to be unstable to oxygen because

of its low redox potential. Although neutral polythiophene is stable to air, in its oxidized conductive

form, it can be easily reduced by environmental oxidizable impurities because of its relatively high

oxidation potential.[15,16] It is clear that, under these conditions, neither PP nor PT are ideally suited in

rechargeable secondary batteries. To improve the environmental stability of neutral pyrrole-based and

doped thiophene-based polymers it would be desirable to increase the redox potential of the former and

decrease that of the latter. Redox potentials can be changed and controlled by varying the effects

exerted by substituents present on the starting monomer. Since pyrrole and thiophene couple at the α-

positions, these substituents must be present at the ß-positions: in the case of pyrrole, the substitution

can also take place at the nitrogen atom. In every case the substituents are at a position that is *ortho*

to the coupling site and could therefore sterically interfere with the planarity of the polyheterocyclic

ribbon. With reference to unsubstituted polypyrrole, the *N*-alkylation of pyrrole leads to a decrease of

5 powers of 10 in the conductivity of the corresponding polymer.[17] Polymers obtained from 3-

alkylpyrroles (7) also show some loss of conductivity, although this is not as great as that of
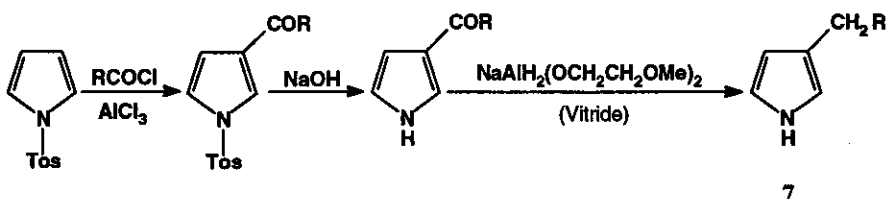
Scheme 2

poly(*N*-alkylpyrroles). Access to compounds (**7**)[18] is shown in Scheme 2. Analogously, polymers

obtained from 3-alkylthiopyrroles (**8**) show disappointingly low conductivities: access to compounds

(**8**)[19] is concisely reported in Scheme 3.
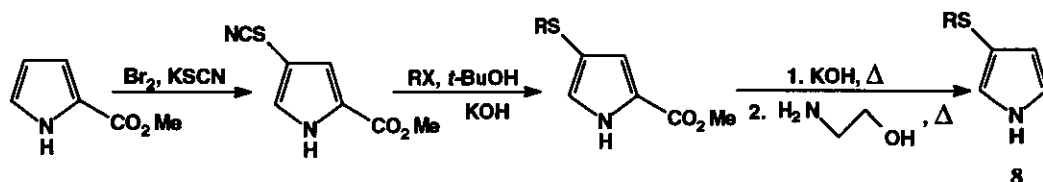
Scheme 3

In the case of polymers derived from 3-alkylthiopyrroles (**8**) the detrimental effect of divalent sulfur

has also been inferred. Support for this conclusion was obtained by comparing the conductivities of

AsF_5- doped polythiophene ($\sigma = 4.8$ Scm^{-1}) with those of the AsF_5-doped polymer obtained from 2,2'-

dithienyl sulfide (**9**)[20] and those of the AsF_5-doped polymer (**10**)[20] ($\sigma \approx 10^{-5}$ Scm^{-1}) (Scheme 4).


9   10
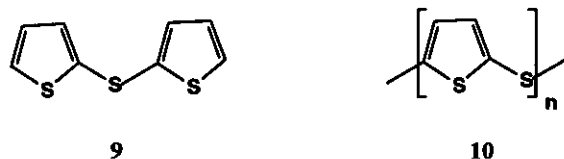
Scheme 4

These initial results convinced us of the opportuneness of interposing a *spacer* between the two

polymerogenic (pyrrole and/or thiophene) units. The spacer had to guarantee conjugation between the

terminal heterocycles and could be either an open chain frame or a ring: it had not to be a sulfur bridge.

Scheme 5 collects all of the *spaced* systems we have so far investigated. As conjugatively active

spacers, we have considered ethenylic bridges, as in **11**,[21,22] **12**,[23-25] and **13**.[26] The fusion of two

pyrrole units onto a central benzene ring was investigated by preparing[27,28] the polymers corresponding

to monomers (**14 - 16**).[29] The monomer (**14**) coupling sites involved during oxidative polymerization

were investigated[30] starting from the methyl labelled derivatives (**17 - 19**).[30] The conductive polymers
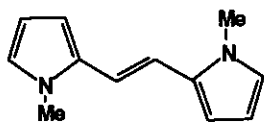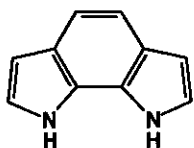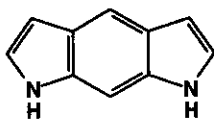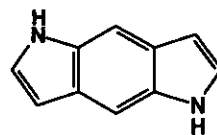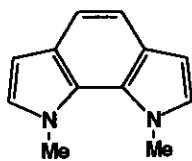
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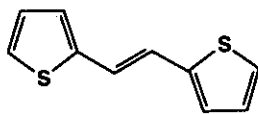
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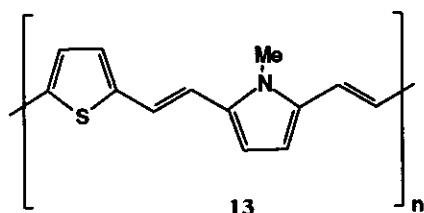
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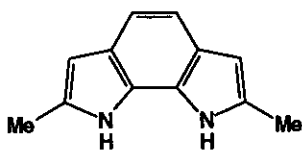
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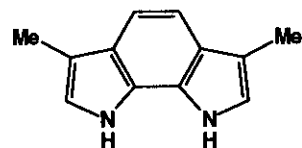
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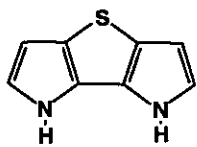
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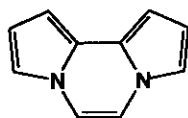
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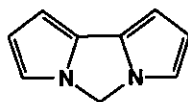
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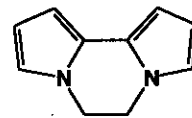
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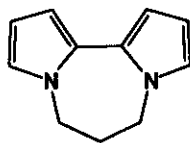
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Scheme 5

were prepared[31,32] starting from systems (**20**)[33] and (**21**)[34] which, instead of with benzene, present ring fusions of the terminal pyrrole units with thiophene and pyrazine respectively. In compounds (**22 - 24**), the dimension of the central saturated ring differently affects the coplanarity of the two terminal pyrrole rings, the largest deviation being found[13, 32, 35] in system (**24**). Among thiophene-based tricyclic systems, particular attention has been given to monomers (**25**)[36] and (**26**).[37] Polymers derived from both unsubstituted **25** $(R = H)$[31] and **26** $(R = R' = H)$[13, 14] are good conductors: furthermore, the inter-ring position of both systems can be easily functionalized. The presence of long alkyl chains at this site imparts a partial solubility to the neutral polymers derived from both **25**[31] and **26**.[38] Since substitution occurs at a position which is remote from the coupling sites involving the terminal heterocycles, conductivity is not depressed (as it may be with polymers obtained from the monocyclic monomers). On the contrary, monosubstitution at position 4 in **26** increases[38] conductivity, possibly through an improvement in the order of the arrangement of the polymeric ribbons, which are held together by secondary interactions of the side alkyl chains (comb-brush effect). The Table collects some of the data concerning the redox potentials E^0 and conductivities of the polymers.

It can be seen that the proper ring fusion of the two terminal polymerogenic pyrroles onto a central benzene or pyrazine ring as in **14 - 16** and **21** makes it possible to increase the redox potential of the polymer relative to· polypyrrole. Conversely, if the central *spacer* is a thiophene ring [that is, a π-excessive heterocycle as in compound (**20**)] the obtained polymer is not very much different from polypyrrole itself. A decrease in the redox potential E^0 of α,α-dithiophene has been achieved by means of a ring fusion of the terminal thiophenes onto a central ring such as pyrrole and cyclopentadiene in **25** and **26**. The great advantage of these systems is the fact that functionalization takes place at position 4, remote from the coupling sites. The decrease in conductivity observed when passing from polymers obtained starting from **23**, **24** and *N*-methylpyrrole, has been ascribed to an increase in the relative twisting of the heterocycles.[13a, 32] The very low conductivity of the polymer originating from **18**[30]

Table. Polymer redox potentials[a] and conductivities of materials obtained from the spaced monomers

Monomer	E^0	$\sigma(Scm^{-1})$	Monomer	E^0	$\sigma(Scm^{-1})$
Dipyrrole	-0.20	100	**21**	0.40	0.2
12	-	40	**22**	0.25	0.7
13	-	2.7^b	**23**	0.18	2.5
14	0.49	5	**24**	0.29	5.10^{-2}
15	0.34	3	Dithiophene	0.70	40
16	0.24	0.2	**25** (R = H)	0.34	6
17	0.59	1.10^{-2}	**25** (R = C_8H_{17})	0.34	40
18	0.37	1.10^{-6}	**26** (R = R' = H)	0.59	40
19	0.26	1	**26** (R = H; R' = C_8H_{17})	0.59	300
20	-0.19	2	**26** (R = R' = C_8H_{17})	0.59	2

[a]Versus SCE; [b] As Iodine doped (DI_2)

is indicative of the fact that the obtained polymer is conductive only when the pyrrole α,α'-positions are not occupied. In **18**, since both positions are methyl substituted, the coupling sites must involve the ß positions. In the corresponding polymer the delocalization of the charge is hampered and thus conductivity falls off. This finding also provides circumstantial evidence that **14** undergoes coupling at the α,α' positions during oxidative polymerization.

Monomer Synthesis - The *spacer* strategy required the availability of a number of tricyclic pyrrole and thiophene derivatives, some of which were unknown. Application of the Leimgruber-Batcho indole synthesis to proper dinitroxylenes opened the way to obtaining the systems (**14 - 16**).[29] As an example, the synthesis of **14** is reported in Scheme 6.
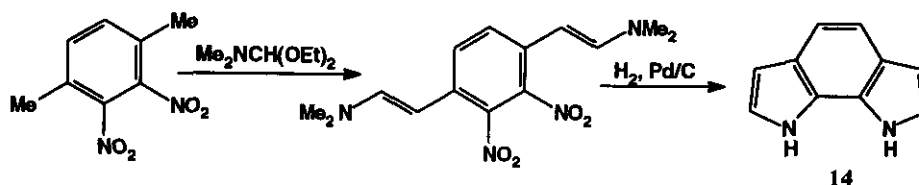
Scheme 6

The methyl derivatives (**17 - 19**) were obtained differently.[30] It is worth noting that, in **14**, oxidative polymerization involves the α-positions as coupling sites, while electrophilic substitutions (e.g., the Mannich reaction) involve the ß-positions, as expected for an indole derivative. Access[34] to the previously unknown parent dipyrrolopyrazine (**21**) is reported in Scheme 7. The availability of **21** in gram lots opened up the possibility of reducing the double bond of the central ring and obtaining
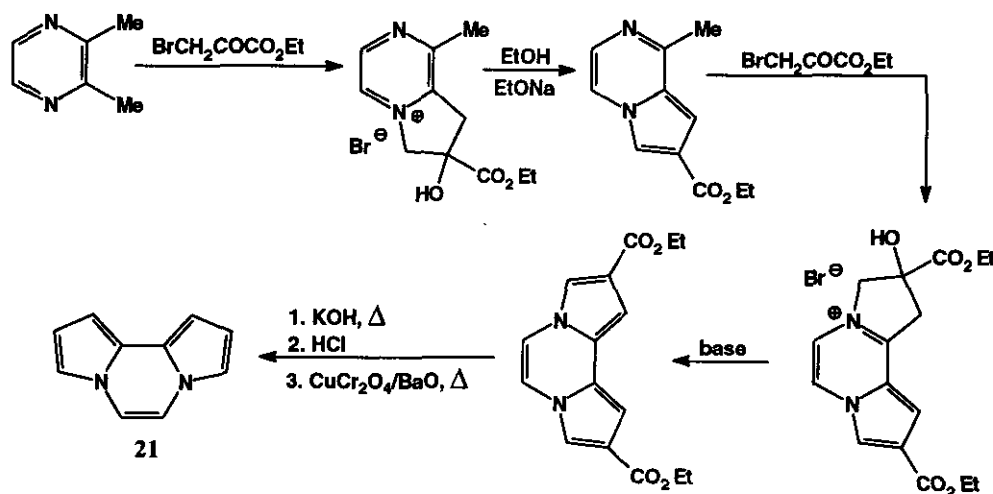
Scheme 7

similar quantities of the saturated system (**23**). (Scheme 8). The previously reported[39] synthesis of **23** suffered from low yields in our hands.
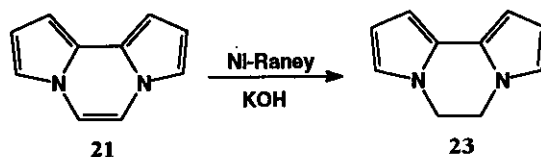
Scheme 8

OLIGOTHIENYLS AS POLYTHIOPHENE MODELS

Though known in its general features, the mechanism of the anodic coupling of heteroaromatics to conducting polymers has not been completely elucidated. Furthermore, investigation of the intervention of bipolaron conduction is of particular interest for the mechanism of conduction in polythiophene, as it is still largely unknown in detail. Select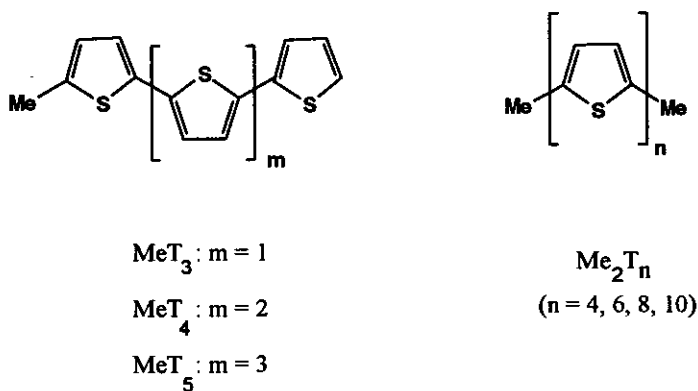ed models of end-methyl protected thiophene oligomers (Scheme 9) were synthesized to investigate whether and how far they could mimic the complex

MeT_3 : m = 1

MeT_4 : m = 2

MeT_5 : m = 3

Me_2T_n

(n = 4, 6, 8, 10)

Scheme 9

behavior of polythiophene. The results have been very encouraging. MeT_{m+2} oligomers (m = 1 - 3) were prepared[40] according to Scheme 10 which also reports the synthesis of Me_2T_4. Me_2T_n (n = 6, 8, 10) were prepared electrochemically. The kinetics of anodic coupling of MeT_{m+2} is of second order in oligomer concentration, and is characterized by relatively high activation energies and negative
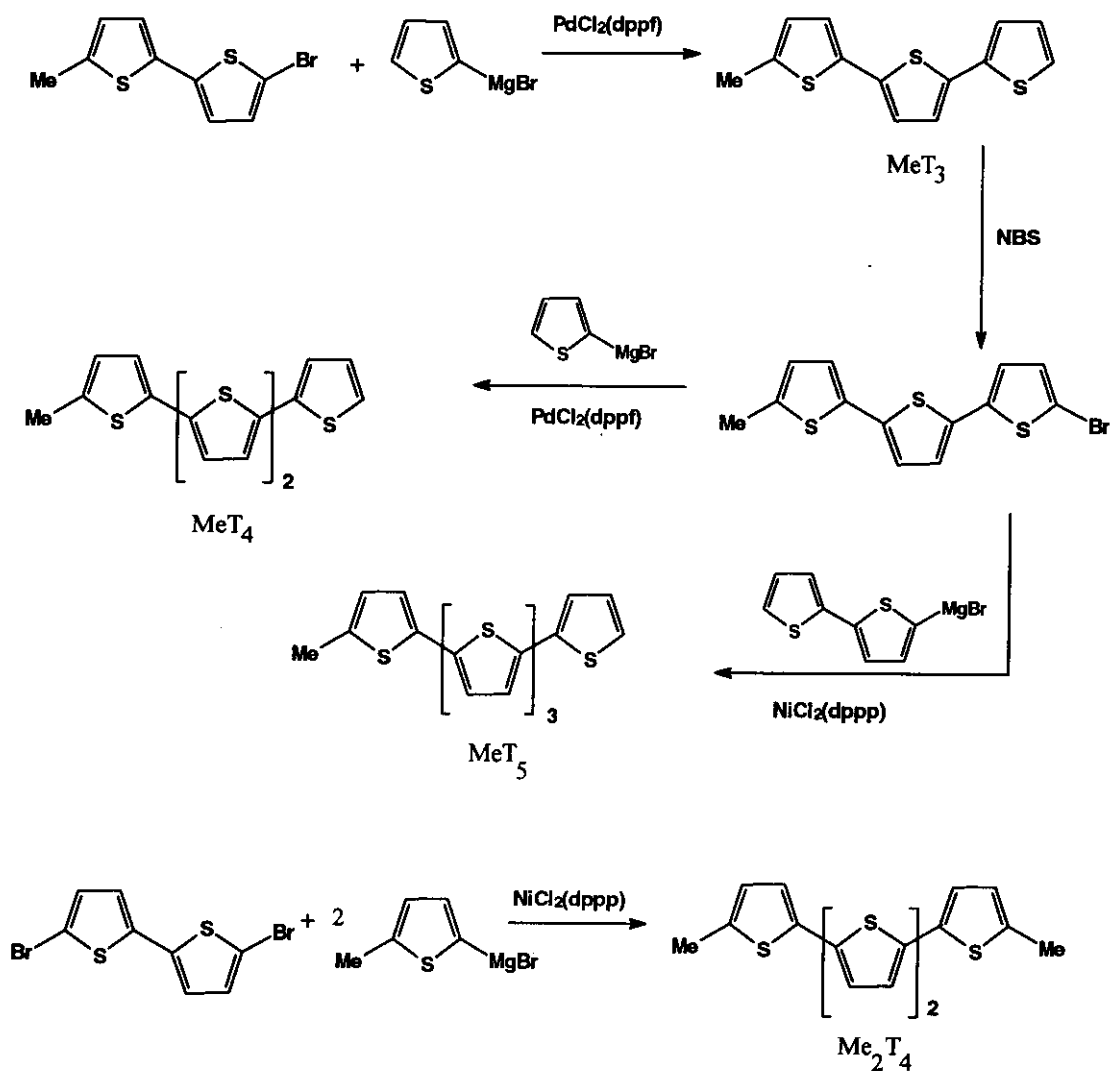
Scheme 10

activation entropies.[40] The activation parameters for $MeT_5^{+\cdot}$ are peculiarly high, and reflect strong π-electron delocalization and thus ring coplanarization. Thin films of Me_2T_n were investigated by means of cyclic voltammetry and *in situ* ESR. Reversible oxidation goes from a single one-electron step (tetramer) to a single two-electron step (octamer and decamer) through two separate one-electron steps (hexamer). ESR indicates strong π-magnetic dimerization for the one-electron oxidized hexamer. The

close resemblance of the electrochemical and ESR behaviors of this hexamer with those of polythiophene suggests that the oxidation of the latter occurs via hexameric spin-dimerized polarons.[41] *In situ* conductivity of the oligomers (as a function of the potential going from the oxidized to the neutral state of the materials) and chronopotentiometry revealed[42] further relevant features that can be summarized as follows. In the hexamer oxidation initially produces polarons which are strongly π-dimerized and the material remains insulating. Further, oxidation also produces bipolarons which provide mixed-valence conduction with polarons: when only polarons are present, their confinment in the hexameric unit again produces the insulating state. In contrast, in the octamer and decamer, instead of being stabilized by π-dimerization, the initially formed polarons can delocalize over two or four extra thiophene rings. In a related way, there is the availability of electron-filled states allowing conductivity in the two-electron oxidized octamer and decamer. The interplay of these mechanisms in relation to the behavior of polythiophene has already been discussed.[42]

CONCLUSION

Once again heterocyclic chemistry has shown how rich it can be in providing starting substrates and tailored structures which are useful not only for strictly chemical purposes, but also for material science. The area of conducting materials is one in which the contribution of heterocyclic chemistry is essential; but several others are emerging, such as non-linear optical materials, Langmuir-Blodgett films, etc.

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7.   The term *doping*, borrowed from the inorganic semiconductors, has been widely, but incorrecly

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