Conductive Polyheterocyclic Materials:

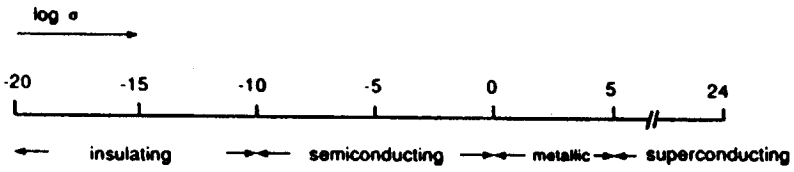
how to Impart Specific Properties

through Tailoring the Monomer Structure

SUMMARY

What is most interesting about many of the new materials are their **electrical** and **magnetic** properties. Chemists... must be able to reason intelligently about the electronic structure of the *compounds* they make, so that they may understand how these **properties** and **structures** may be **tuned**.

Roald HOFFMANN - How Chemistry and Physics Meet in the Solid State *Angew. Chem.*, **1987**, *26*, 846



Ionic conductivity (ions as carriers)

Electronic conductivity (electrons or vacancies as carriers)

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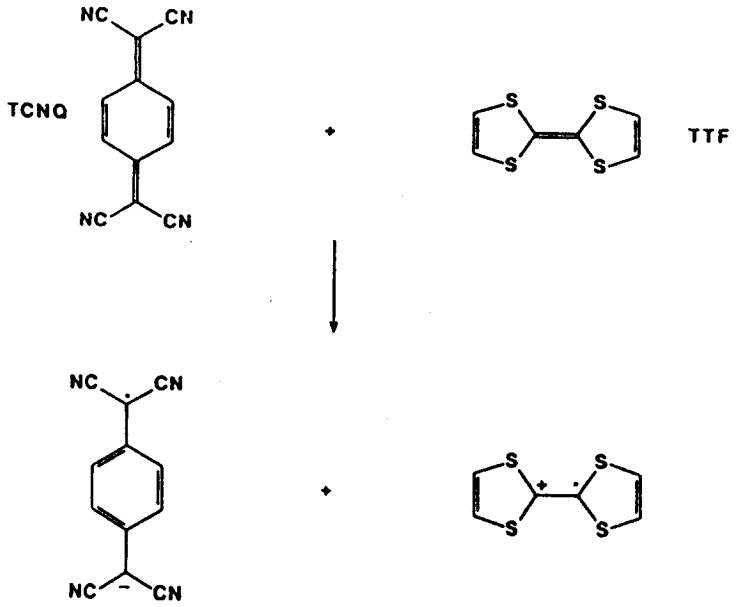

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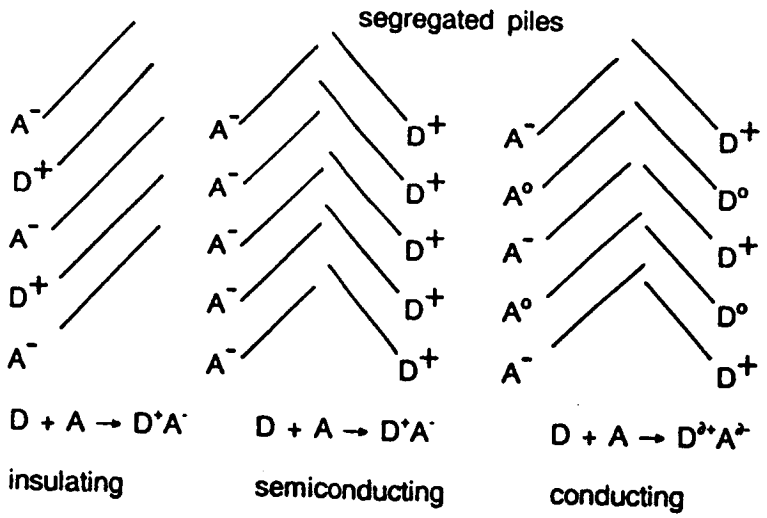

Possible arrangements in the piles of CTC

Conductivity mechanism in segregated piles with partial (0.50) charge treansfer

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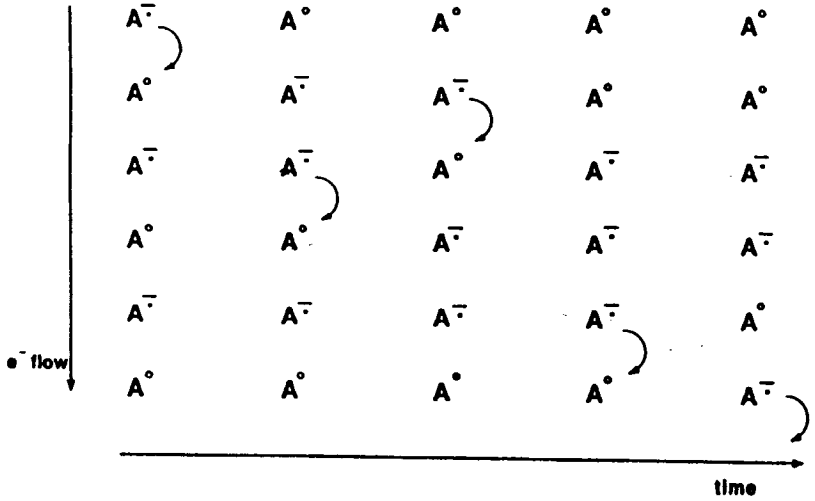

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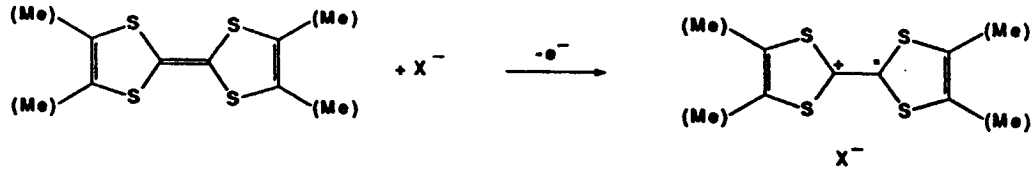
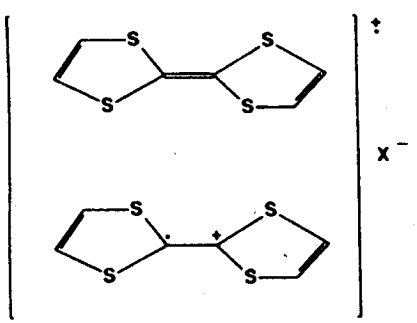
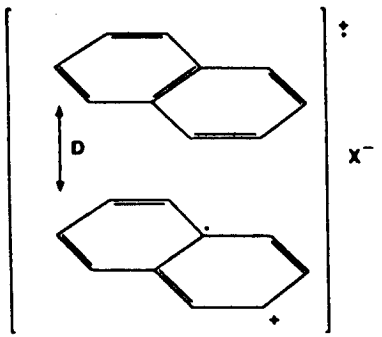


TTF
(TMTTF)

Bechgaard Salts (Spectator counterion)

8





D = 1.32 Å

$X^- = BF_4,\ ClO_4,\ AsF_6,\ PF_6, \ldots$

Hopping mechanism for conductivity

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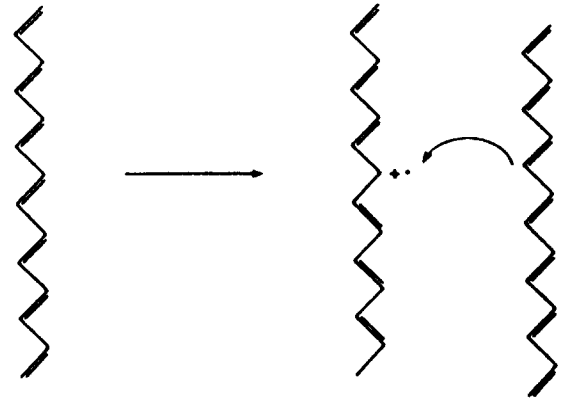

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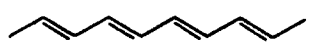
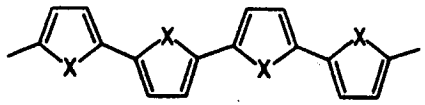
STRUCTURAL ANALOGY OF POLYACETYLENE

AND POLYHETEROCYCLES





10

Is there a similarity between CTC and polymers?

Yes, the quasi uni-dimensional structure!

NO! There would be if....

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ACCESS TO OXIDIZED CONDUCTIVE POLYMERS

synthesis

neutral polymer

chemical oxidation

coupling

MONOMER

electrooxidation

oxidative polymerisation

chemical oxidation

CONDUCTIVE OXIDIZED POLYMER

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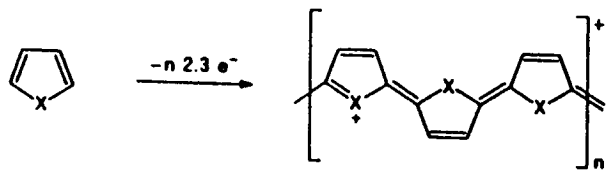

X = S, NH, NR

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CONDUCTIVITIES OF MAJOR POLYMERS

PA	Polyacetylene	$10^3 \rightarrow 2\times10^4 \rightarrow 10^5$
PPP	Polyparaphenylene	500
PPS	Polyparaphenylene sulphide	10^{-2}-10
PP	Polypyrrole	40-100
PT	Polythiophene	10-100
PANI	Polyaniline	10

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CONDUCTIVE POLYHETEROCYCLES

POLYMER	ADVANTAGES	DISADVANTAGES
PP	highly conductive	brittle, non processable
	stable when doped	insoluble, air sensitive
		when neutral
PT	highly conductive	brittle, non processable
	stable when neutral	insoluble, can be reduced
		when doped (H_2O)

POLYMER REDOX POTENTIALS E°

(SCE)

PP	- 0.20 V
PT	0.70 V

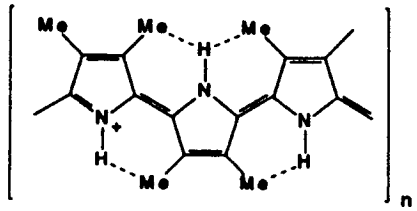
FUNCTIONALISATION FOR IMPROVING CHARACTERISTICS

Draw-backs		Cure
insolubility (fragility)		alkyl chains
environmental stability	thiophene	decrease of the oxidation potential: electron-rich substituents
	pyrrole	increase of the oxidation potential: electron poor substituents

EFFECT OF FUNCTIONALIZATION UPON CONDUCTIVITY

Polymer	Cond/S cm^{-1}
PP	40-100
P-3,4-diMeP	10
P-N-MeP	10^{-3}
PT	10-100
P-3-MeT	
P-3-Alk-T	10-100

CONDUCTIVITIES OF SUBSTITUTED SYSTEMS



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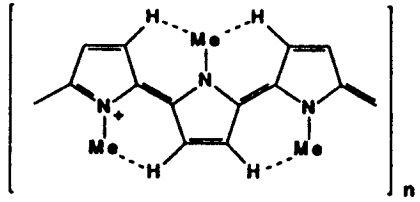


10^{-3}

Functionalisation must be remote from the site of coupling

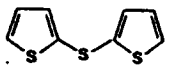
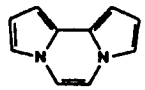
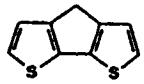
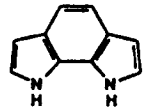
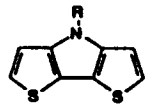
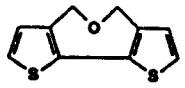
THE *SPACER* STRATEGY

MONOMER: a system characterised by two terminal polymerogenic heterocycles joined or fused to a central conjugatively active frame or ring

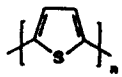
ADVANTAGES: the *spacer*

1. Controls the redox potential by substituent effects
2. Provides further remote functionalisation to improve properties of the final doped polymer
3. Locks the terminal units in a predetermined arrangement (planarity, conjugation, ...)

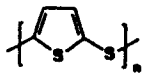
OUTLINE OF THE APPROACH

	Thiophene	Pyrrole
1 - Substituent effect		
		
2 - Further functionalisation		
3 - Conjugation		

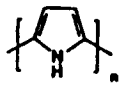
ADVERSE EFFECT OF THIOETHER GROUPS ON CONDUCTIVITIES (S cm $^{-1}$)



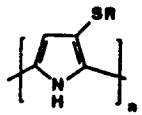
σ = 5 — AsF_5 doped polymer



$\sigma = 10^{-5}$ — AsF_5 doped polymer



σ = 40-100 — electropolymerised



$\sigma = 1 - 30 \times 10^{-3}$ — electropolymerised

R = C_1, C_2, C_4, C_8, C_{12}, C_{16} residues

ADVERSE EFFECT OF THIOETHER GROUPS IN OXIDATIVE POLYMERISATION

In thienyl sulphide, alkyl pyrrol-3-yl sulphides, and the like, thioether groups greatly limit the oxidative polymerisation; presumably they act as scavengers of the initially formed cation radicals

THIOPHENE FUSED SYSTEMS
(the spacer is a ring)

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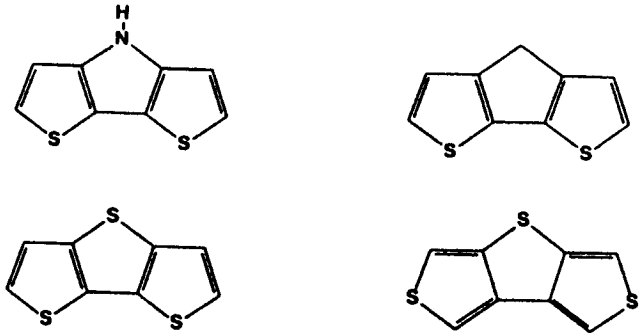
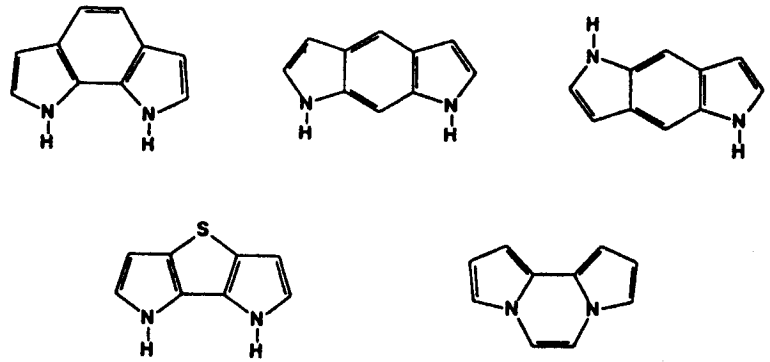


PYRROLE FUSED AROMATIC SYSTEMS
(the spacer is a ring)

30



THE DIHYDROBENZODIPYRROLES

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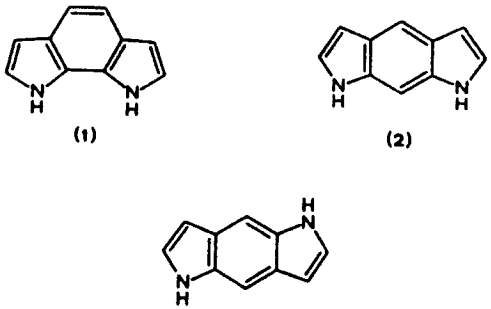
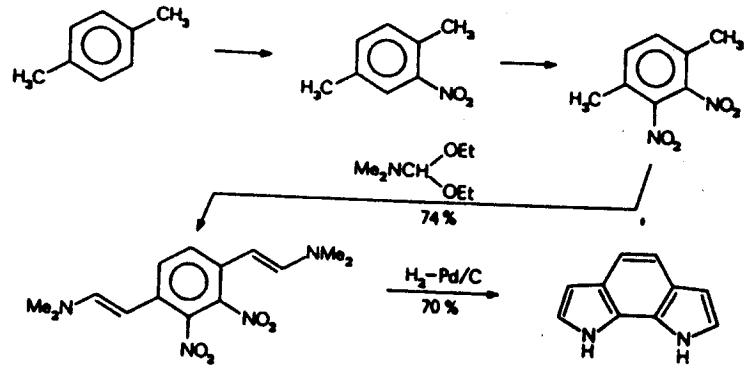


(1) (2) (3)

A.Berlin, S.Brodomonte, R.Ferroccioli, G.A.Pagani and F.Sannicolo' J.Chem.Soc.Chem.Commun., 1987, 1176.

SYNTHESIS OF 1

32



(1)

SYNTHESIS OF 2 AND 3

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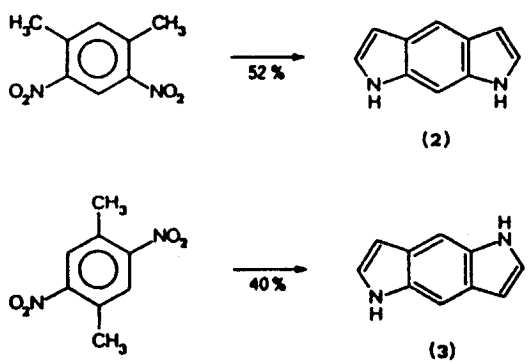

A.Berlin, S.Brodomante, R.Ferroccioli, G.A.Pagani and F.Sannicolo' J.Chem.Soc.Chem.Commun., 1987, 1176.

CYCLIC VOLTAMMETRY OF THE POLYMERS

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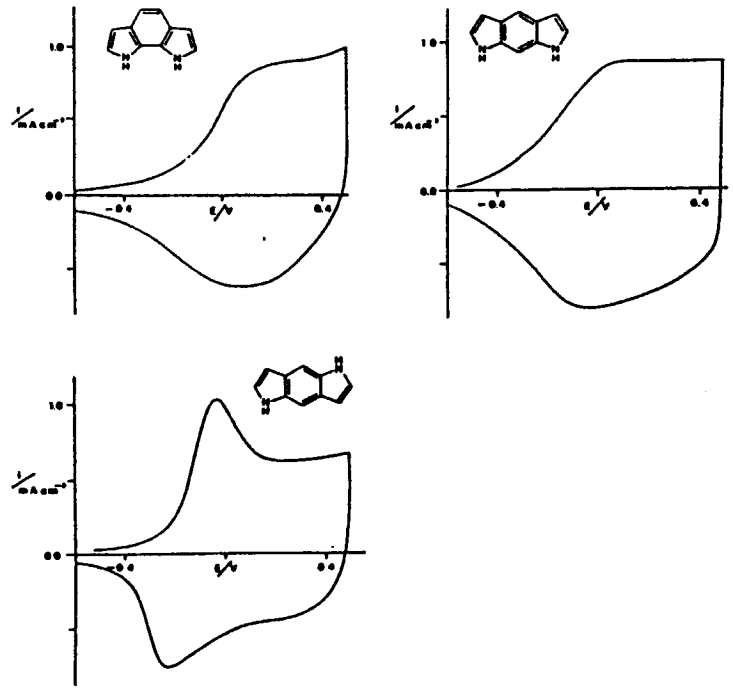

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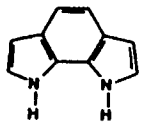
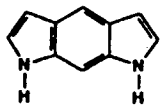
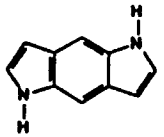
POLYMERS FROM PYRROLOINDOLES (BENZOANELLATION)

Monomer	E_p/V [c]	EOP [a] E°/V [c]	EOP [a] σ/S cm^{-1}	COP [b] σ/S cm^{-1}
	0.74	0.49	5	0.11
	0.64	0.34	3	0.50×10^{-2}
	0.61	0.24	0.2	0.24×10^{-3}

[a] *Makromol. Chem.* 190 405 (1989); [b] *Synth. Met.* 22 89 (1987); [c] vs SCE

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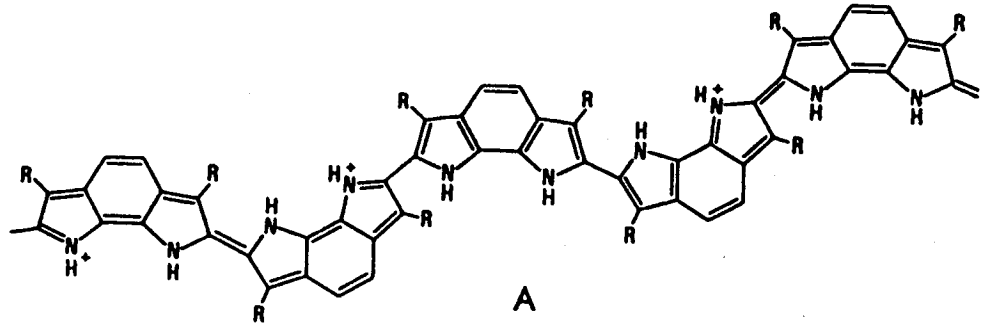
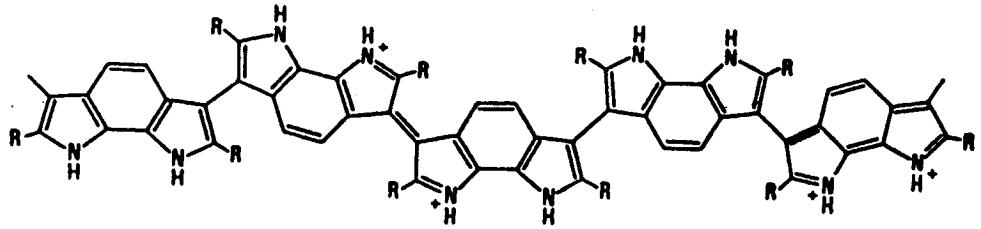


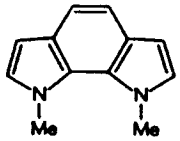
A



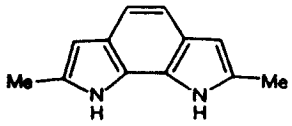
B

DIMETHYL DERIVATIVES OF 1

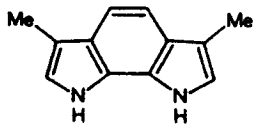
37



N, N' - Dimethyl 1



α, α' - Dimethyl 1



β, β' - Dimethyl 1

SYNTHESIS OF N,N'-DIMETHYL 1 AND α,α'-DIMETHYL 1

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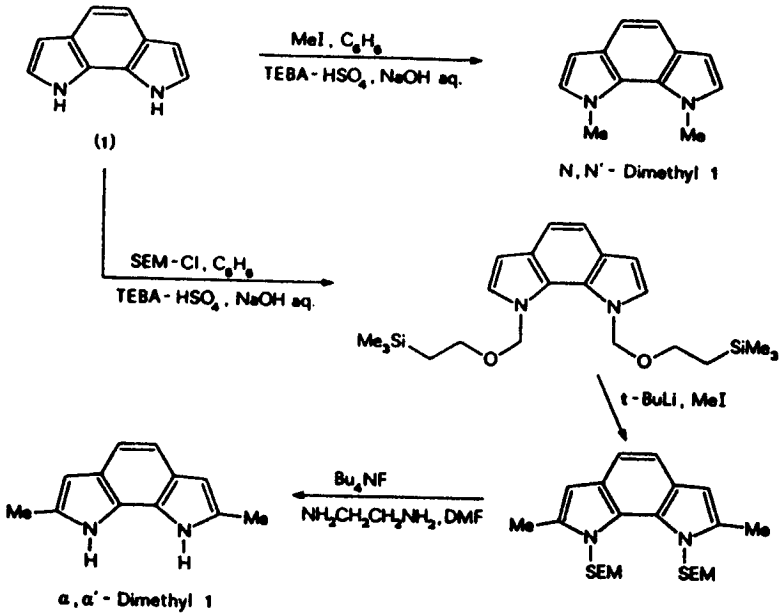
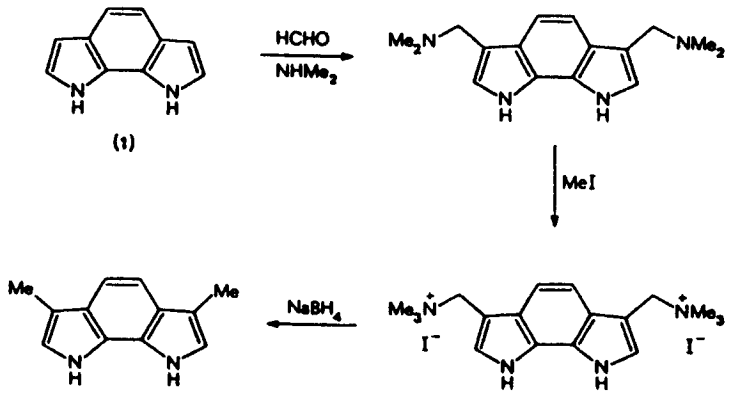


SYNTHESIS OF β,β'-DIMETHYL 1

39



IF IN THE PARENT 1 POLYMERIZATION OCCURS

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at positions α,α'	the α,α'-di Me	should not polymerize or the polymer should have very low conductivity
	the β,β'-di Me	should polymerize to give a material with a conductivity similar to that of the parent compound
at positions β,β'	the β,β'-di Me	should not polymerize or the polymer should have a a higher conductivity
	the α,α'-di Me	should have a similar conductivity as the parent

FURTHER CENTRAL RING FUSION ON TERMINAL PYRROLE RINGS

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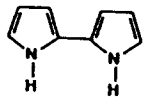
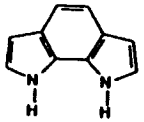
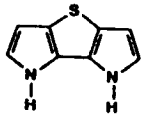
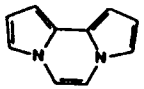
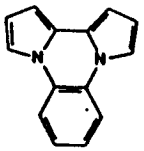
	E_p / V [a]	E° / V [a]	σ / S cm^{-1}
	0.55	-0.20	100
	0.74	0.49	5
	0.42	-0.19	2
	0.56	0.40	0.2
	0.71	0.56	4×10^{-3}

[a] vs SCE

REGIOCHEMISTRY OF THE POLYMERISATION

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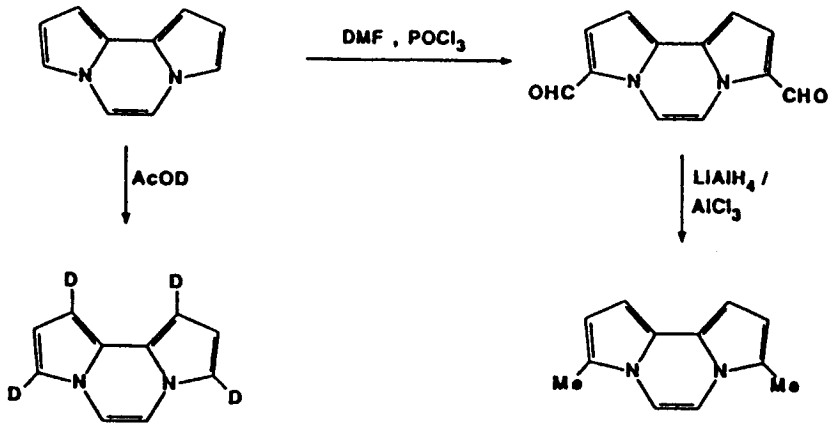

Polymerisation occurs at positions 3,8 (α,α')

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MESSAGE

Monomers obtained by ring fusion of terminal pyrrole units on a central benzene or pyrazine rings produce polypyrrole-type polymers with increased redox potentials: they are stable towards the air in their neutral state.

Conductivity is however somewhat decreased.

THIOPHENE FUSED SYSTEMS

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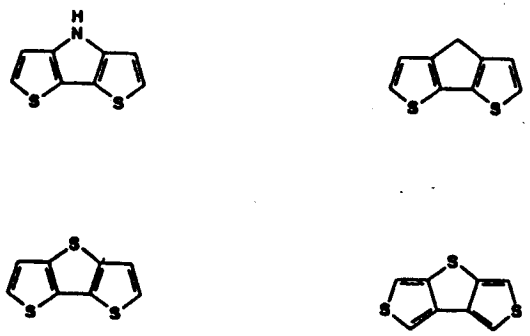

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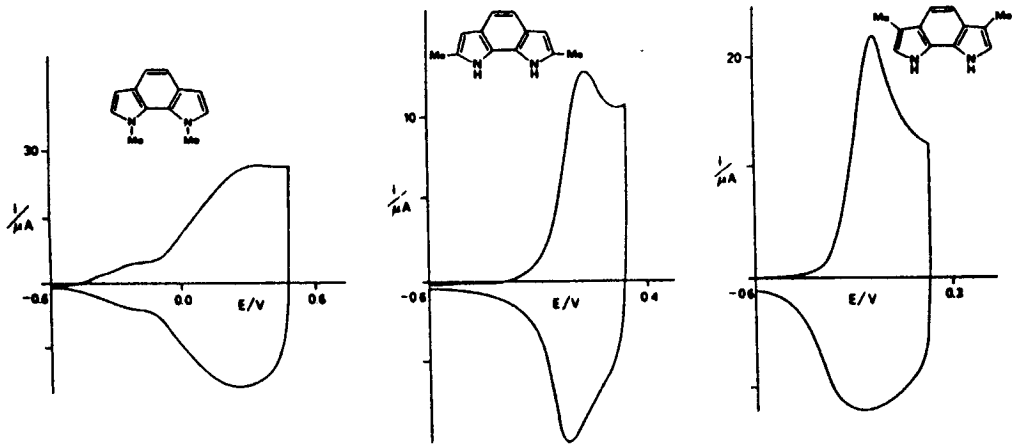
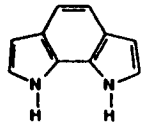
CYCLIC VOLTAMMETRY OF THE POLYMERS



42

EFFECT OF METHYL SUBSTITUTION ON ELECTROCHEMICAL DATA

Monomer	E_p / V	E^o / V	σ / S cm^{-1}
	0.74	0.49	5
N,N'- di Me	0.71	0.59	10^{-2}
α,α'- di Me	0.46	0.37	5×10^{-6}
ß,ß'- di Me	0.56	0.27	1
Pyrrole	0.55	-0.20	40
N-Me-Pyrrole		0.79	10^{-3}
ß,ß'-di Me			10

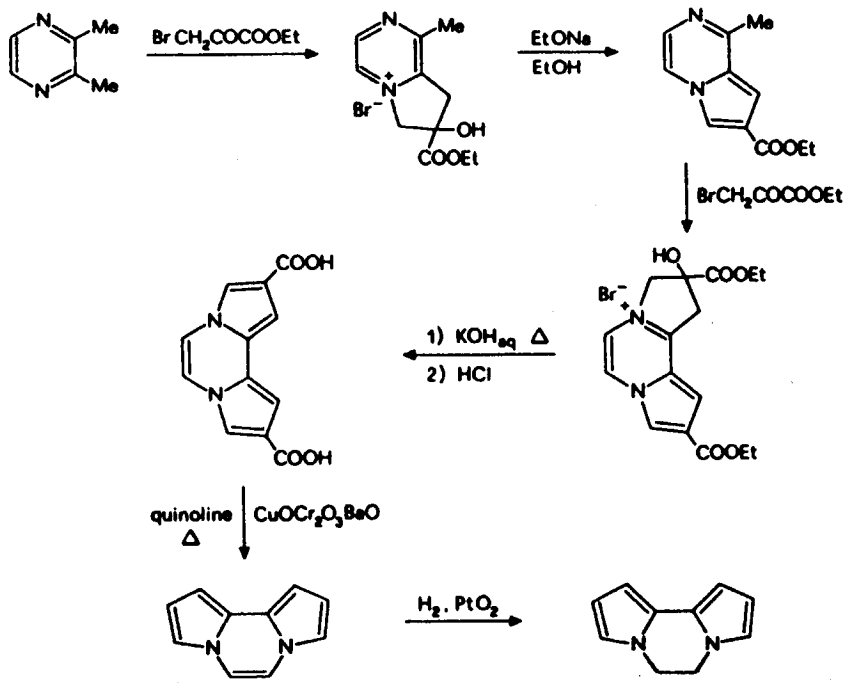
43

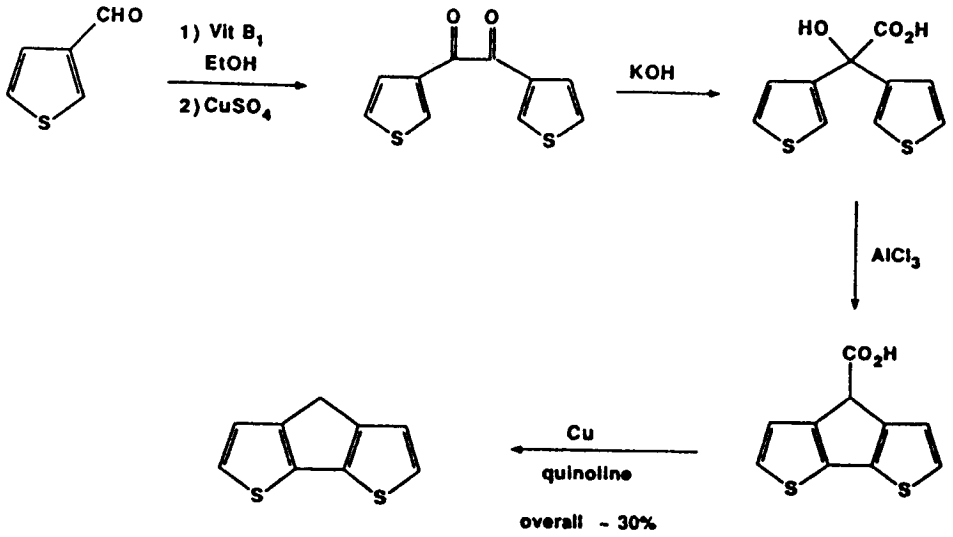
POLYMERISATION OF PYRROLOINDOLE

Contrary to electrophilic substitutions involving ß positions, polymerisation occurs at the α positions.

Towards electrophilic substitution pyrroloindole behaves as an indole, but towards polymerisation it behaves as a dipyrrole bridged at the ß,ß'-positions.

45

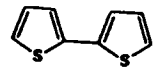
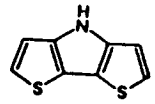
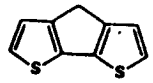
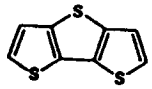




50

51

EFFECT OF RING FUSION (THIOPHENE)

	E_p/V^a	E°/V^a	Cond/Scm^{-1}
	1.20	0.70	40
	0.86	0.34	6
	0.99	0.59	40
	1.20	0.50	10

[a] vs SCE

52

MESSAGE

Monomers obtained by ring fusion of terminal thiophene rings onto an electron-rich central ring produce polythiophene-type polymers with decreased redox potentials.

Conductivity may be only marginally affected

FURTHER REMOTE FUNCTIONALISATION

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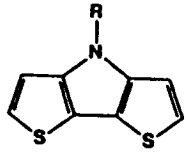
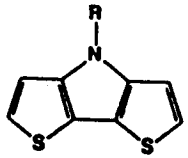
	Cond / S cm^{-1}	λ	solubility
	10	(550)	none
 R = H, Me	6	515	none
 R = C_4, C_8, C_{16}	40	570	appreciable ($CHCl_3$)

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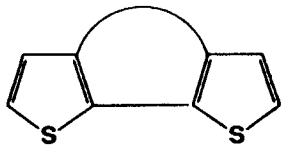
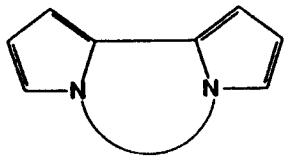
TO INVESTIGATE CONJUGATION





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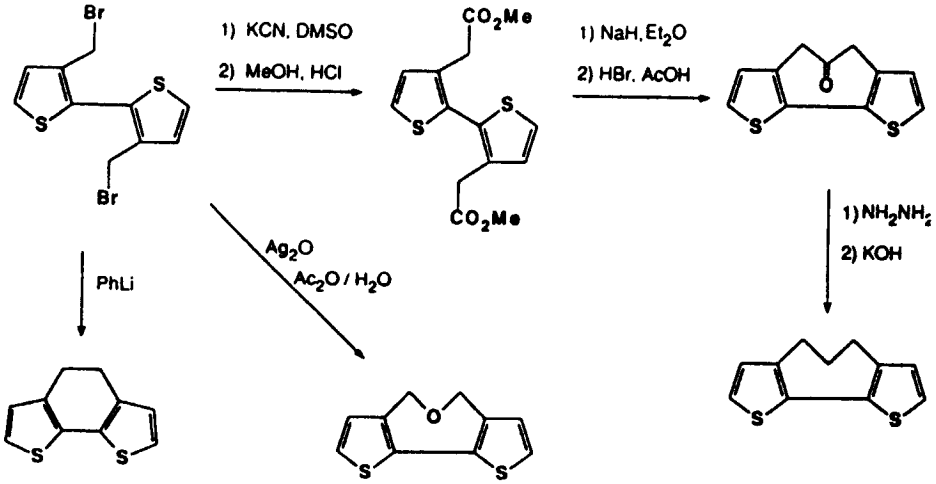
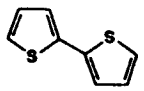
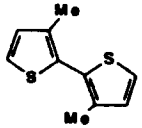
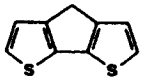
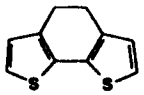
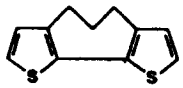


56

HOW E° AND σ VARY WITH TWIST ANGLE?

	E_p /V	E°/V	σ / S cm^{-1}
	1.20	0.70	2.8
	1.24	0.70	0.1
	0.99	0.59	40
	1.04	0.50	1.5
	1.09	0.62	3
	1.21	0.71	0.2

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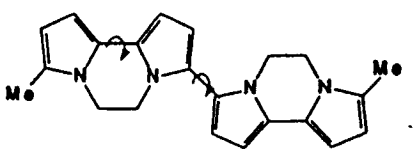
MESSAGE

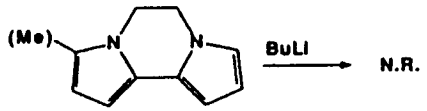
The intuitively predicted variation of the heteroarylene twist angle in the monomer has no dramatic effects (one order) on σ, but an appreciable influence on E°; the special geometry of thiophene (long C-S bonds) may accomodate small twist angles.

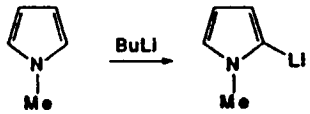
Hemicoplanarity improves conductivity

We would need

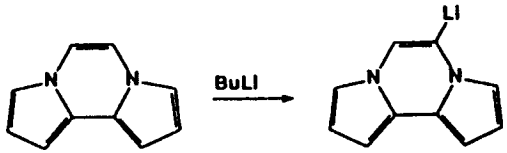


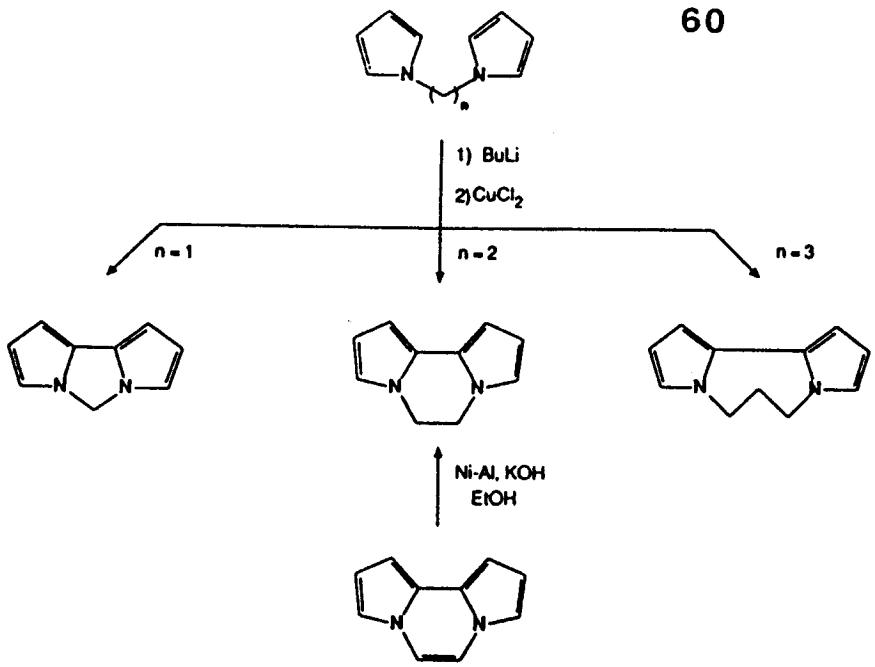
However, while



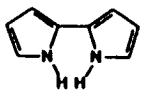
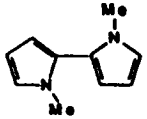
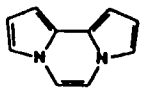
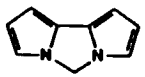
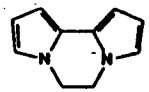


and

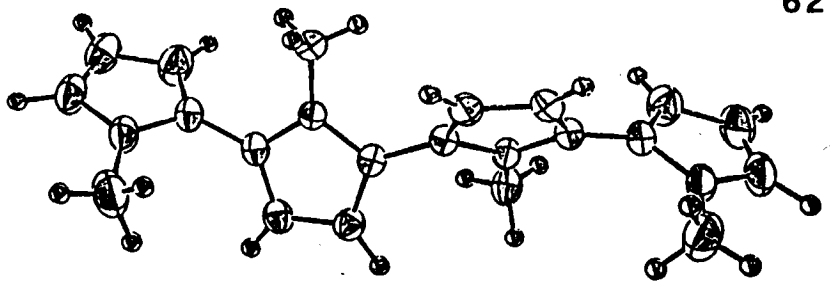




EFFECT OF N-SUBSTITUTION

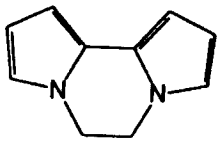
	E_p / V	E° / V	σ / S cm^{-1}
	0.55	-0.20	10^2
		0.79	10^{-3}
	0.56	0.40	2×10^{-1}
	0.64	0.25	7×10^{-1}
	0.51	0.18	2.5
	0.49	0.29	5×10^{-2}

THE STRUCTURE OF THE TETRAMER OF N-METHYLPYRROLE [a]



heteroarylene twist angle (av) 50 deg

[a] B. G. Street, personal communication



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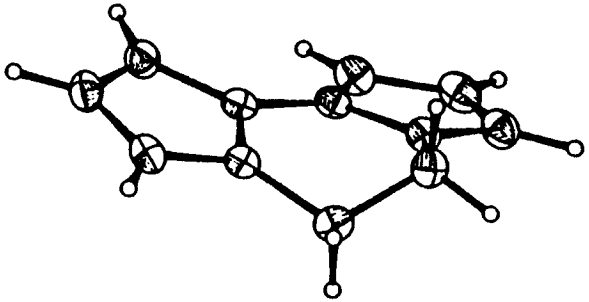
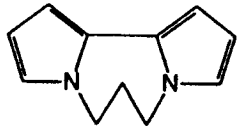
heteroarylene twist angle

(av) 17 deg

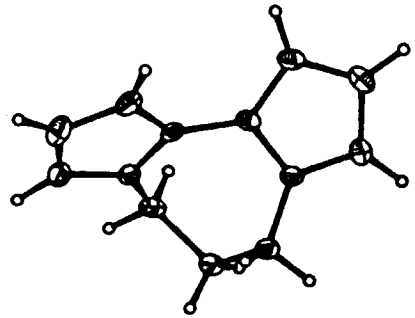


64



heteroarylene twist angle

(av) 40°



TWIST ANGLE AND σ IN N,N' - DIPYRROLES

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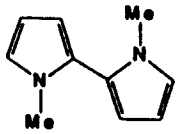
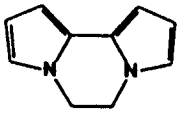


50° 10^{-3}

40° 5×10^{-2}



17° 2.5

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MESSAGE

Variation of the heteroarylene twist angle of the *N,N'*-disubstituted dipyrrole monomer has quite remarkable effects both on E° and σ.

Other parameters being equal in a series, the conjugation length in a polypyrrole-type backbone is important for conductivity.

INSIGHT INTO CONDUCTIVITY MECHANISM

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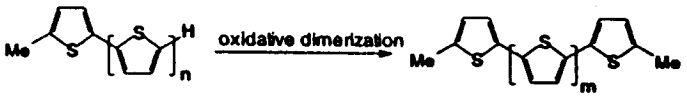
THIOPHENE OLIGOMERS



n = 1	m = 2	Me_2T_4
n = 2	m = 4	Me_2T_6
n = 3	m = 6	Me_2T_8
n = 4	m = 8	Me_2T_{10}

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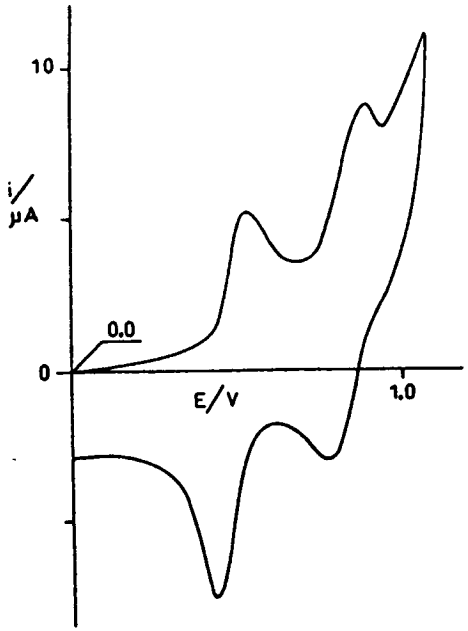
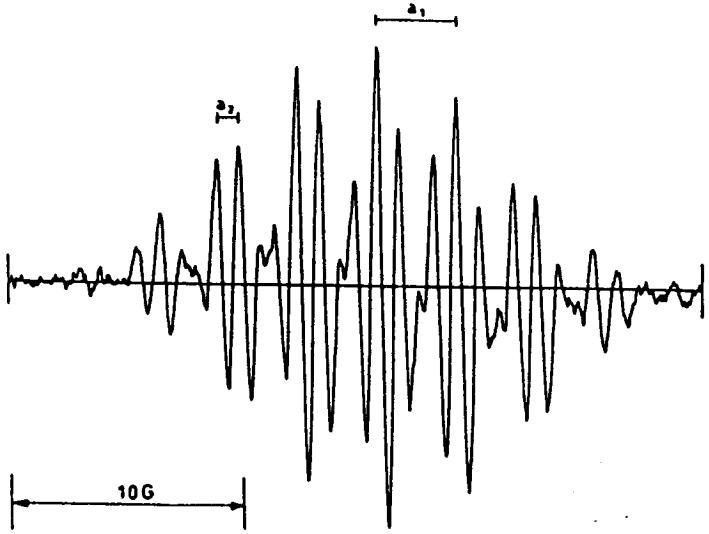


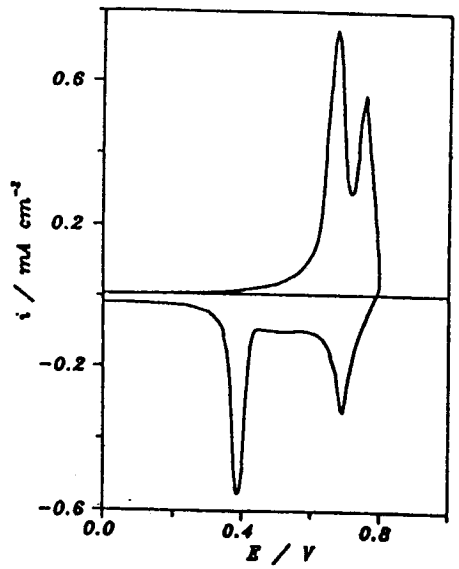
CV for Me_2T_4 0.8×10^{-3} M in DCE + 0.1 M TBAP

69

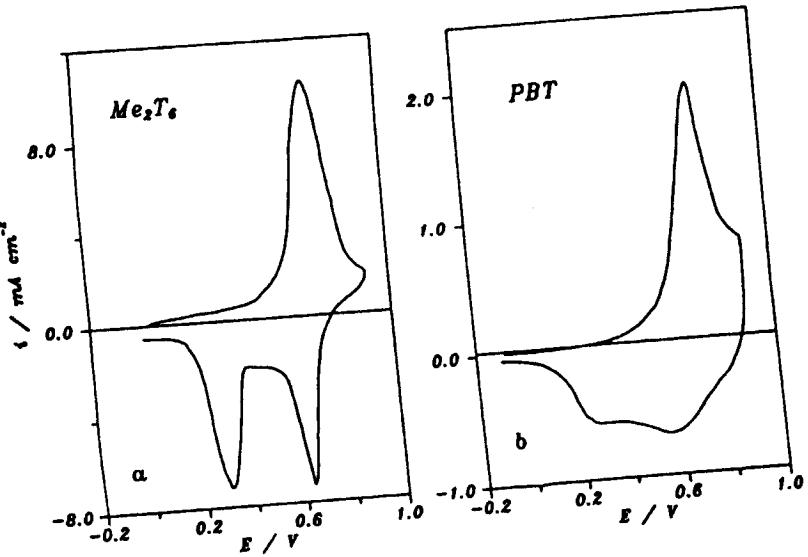


ESR spectrum of $Me_2T_4^{+\cdot}$ 5×10^{-4} M in DCE + 0.1 m TBAP

70

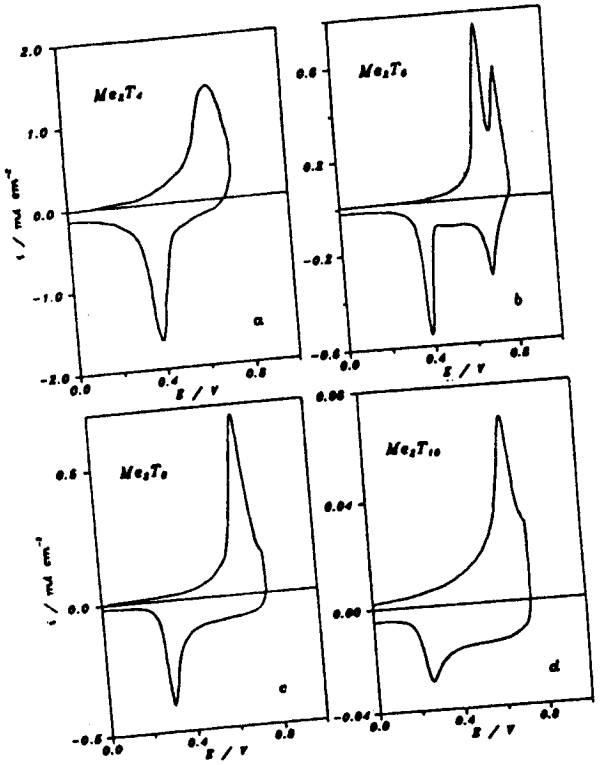


CV for the electrodeposited Me_2T_6 in MeCN + 0.1 M TEAP.
Q_r = 1 mC/cm^2

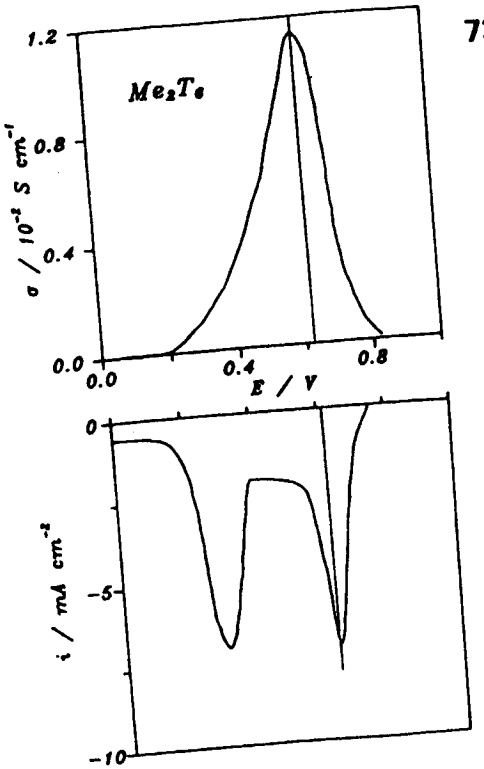


CV for electrodeposited hexamer (a) and polybithiophene (b)

MeCN + TEAP 0.1 M; scan rate: 0.1 V/s; Q_r = 20 mC/cm^2 (a) and 4 mC/cm^2 (b)



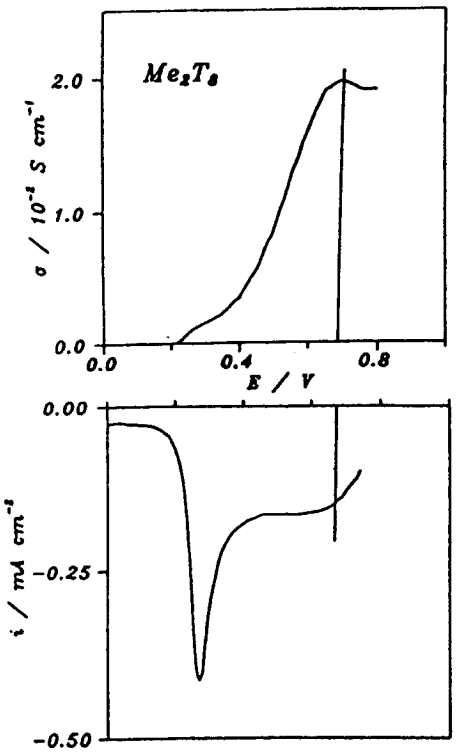
CV for *cast*-deposited tetramer (a), hexamer (b), octamer (c), and decamer (d) in MeCN + 0.1 M TEAP. Scan rate: 0.1 V/s. Q_r = 3, 1, 0.9 0.1 mC/cm^2 respectively



In-situ conductivity for electrodeposited Me_2T_6 from the oxidized to the neutral state(upper).

CV for comparison (lower)

74



In-situ conductivity for electrodeposited Me_2T_8 from the oxidized to the neutral state (upper).
CV for comparison (lower)

75

MESSAGE

Understanding of the mechanism of conductivity of PT benefits from the results on oligomers. Charge saturation (1 over 3 T units) inhibits conductivity. In PT two mechanisms are copresent: the former is amenable to that of the bell shaped conductivity of the hexamer, the latter is amenable to the sigmoidal conductivity of higher oligomers (or oligomeric units e.g. Me_2T_8 or Me_2T_{10}) with partially filled band structure.

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....I would say that many solid-state chemists have isolated themselves by choosing not to see bonds in their materials. .....the solid is a molecule, a big one, to be sure, but just a molecule. The bonds must be there.

Roald HOFFMANN - How Chemistry and Physics Meet in the Solid State *Angew. Chem.*, **1987**, *26*, 846

CONCLUSION

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1. Spacing polymerogenic heterocycles by ring fusion works out nicely in controlling the electrochemical properties of the final polymer. Thioether groups as bridging units should be avoided.
2. The way is open for functionalising tricyclic monomers at sites remote from those involved in the polymerisaton step. Such a tailoring may provide supramolecular order and result beneficial for final properties
3. Some structure - conductivity relationships have emerged. In pyrrole-based polymers conjugation requirements are stringent. Thiophene-based systems appear to be more tolerant. PT is "poly-hexameric".

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SYNTHESIS

Anna BERLIN

Stefano MARTINA

Franco SANNICOLO'

Elisabetta BRENNA

ELECTROCHEMISTRY

Gianni ZOTTI

Gilberto SCHIAVON

X - RAY

William PORZIO

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