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(54) **Bipyridyl-oligothiophene derivatives as electron-conducting materials**

Bipyridyl-Oligothiophenderivate als elektronenleitende Materialien

Dérivés de bipyridyl-oligothiophène comme matériaux électriquement conducteurs

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(73) Proprietor:
**VALTION TEKNILLINEN TUTKIMUSKESKUS
02150 Espoo 15 (FI)**

(72) Inventor: **Albers, Willem Martin
SF-33710 Tampere (FI)**

(74) Representative:
**Smulders, Theodorus A.H.J., Ir. et al
Vereenigde Octrooibureaux
Nieuwe Parklaan 97
2587 BN 's-Gravenhage (NL)**

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- **JOURNAL OF PHYSICAL CHEMISTRY, vol. 93, 1989 pages 6751-6754, L. B.-A. JOHANSSON ET AL. 'Orientation of Caroviologens in Model Membranes'**
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EP 0 668 277 B1

Description

The present invention relates to compounds comprising a thiophene structure terminated at both ends by a pyridine functional group, to the use of such compounds as intrinsic conductors; and to membranes and electronic devices comprising such compounds.

Background of the invention

Controlled enhancement of electronic conductivity in highly isolating thin molecular membranes by new types of intrinsically conductive organic or organometallic compounds is highly in demand, because this gives possibilities for improving the sensitivity and selectivity of electrochemical processes occurring at the solid/liquid interface [Atta N. F. et al. (1991) Biosensors and Bioelectronics 6, 333-341; Hable C. T. & Wrighton M. S. (1993) Langmuir 9, 3284-3290].

Generally, for application in chemical sensing devices, conductivity is desired through thin molecular membranes of different types, including biological membranes, biomimetic membranes and thin polymer films, with a thickness varying between 50 and 100 Å, [Merz A. (1990) Top. Curr. Chem. 152, 51-90; Ottova-Leitmannova A. & Tien H. T. (1992) Prog. Surf. Sci. 41/4, 337-445]. Additionally, the introduction of electronic conductivity in highly isolating bulk polymers is actively studied, particularly for electronic shielding purposes [Cao Y. et al. (1993) Synth. Met. 55-57, 3514-3519].

Transport of electrons may be induced by, in principle, three types of mechanisms, as illustrated in Figure 1a-c, where an electrolyte solution is denoted by 1, an insulating membrane by 2, a metallic electrode by 3, electron transfer by arrow e, and an electron donor (reductor) by "Red".

Fig. 1a shows schematically the transport by electron-mediation, in which a hydrophobic electroactive species 4, the "mediator", receives one or more electrons at one side of the isolating membrane 2, subsequently diffuses (arrow d) to the opposite side of the membrane and donates the electron(s) to the electrode. The oxidised mediator is denoted by a black dot and the reduced mediator by a minus sign. Examples, known in the art, are the incorporation of certain small dye molecules or highly conjugated organic molecules into bilayer lipid membranes [Janas T. et al. (1988) Bioelectrochem. & Bioenerg. 19, 405-412; Kutnik J. et al. (1986) Bioelectrochem. & Bioenerg. 16, 435-447].

Fig. 1b shows schematically the transport by electron exchange ('hopping'), using a molecule that contains multiple electroactive species (a chain 5 of redox centres), fixed at predetermined distances from each other by a chemical tether.

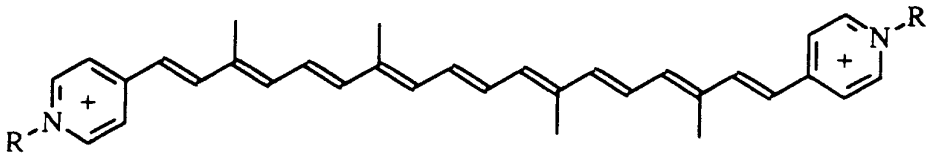
In this system electrons are received at one side of the membrane and jump between the electroactive centres across the membrane.

Fig. 1c shows schematically the transport by electron-delocalisation, using a molecule 6 containing an extended π-electron system, capable of receiving electrons at one side of the membrane 2 and delocalising the electron nearly instantaneously to the other side of the membrane by a quantum-chemical mechanism. Such molecules are acting as a direct electronic wire between an electroactive species and the electrode surface.

In the first mechanism, of Fig 1a, electron transfer rates are largely controlled by the diffusion of the electroactive species through the membrane, which is a slow process. With multiple redox centres the process of conduction, as depicted in Fig 1b, is controlled by the self-exchange rate of the redox species, the mean distance between the redox species and the dielectric constant of the membrane phase. This is generally a much faster conduction mechanism than that of mediated electron transfer.

In the last case, with an extended π-electron system, as illustrated in Fig. 1c, electrons are delocalised over the whole length of the molecule, a conduction process that is about 5 orders of magnitude faster than that of conduction through redox chains. Electron transfer with these types of molecules is in principle the most effective. With membrane thicknesses below 4 nm (40 Å) an additional conduction mechanism may occur, namely that of electron tunnelling [Thompson D. H. P. & Hurst J. K. (1988) in: Carter F. L. et al. (Ed.) 'Molecular Electronic devices' Elsevier, Amsterdam, 1988. pp. 413-425].

In earlier studies by other workers it has been shown that carotenes, modified with terminal pyridinium groups, "caroviologens" (structures according to formula II), may be incorporated in liposome bilayer lipid membranes in a characteristic through-membrane orientation, which is a main prerequisite for effective electron transfer through the membrane [Arrhenius T. S. et al. (1986) Proc. Natl. Acad. Sci. 83, 5355-5359; Johansson L. B.-Å et al. (1989) J. Phys. Chem. 93, 6751-6754.].



(II)

Although the caroviologens are functionally active as molecular conductors, the conductivity change, observed in liposomes, was not very large: only a 4 times increase of electronic conductivity was observed for an alkyl sulfonated caroviologen derivative [Lehn J.-M. (1991) in: Schneider H.-H. & Dürr H. (Ed.), 'Frontiers in Supramolecular Organic Chemistry and Photochemistry' VCH Publ, Weinheim, 1991. pp.1-28]. Further research on more optimal conductors has mainly been concerned with further modification of the terminal groups of the polyene chain [Blanchard-Desce M. et al. (1988) J. Chem. Soc., Chem. Commun., 737-739; Thomas J. A. et al. (1992) J. Chem. Soc., Chem. Commun., 1796-1798; Bubeck C. et al. (1992) Adv. Mater. 4, 413-416].

It is known, however, that the chemical stability of the polyenes, and particularly the carotenes, is not very high. Also polyene structures exhibit photochemical cis-trans-isomerisation, which affects the planar conformation of the molecule and the incorporation in thin organic films [Carter F. L. et al. in: Carter F. L. et al. (Ed.) 'Molecular Electronic devices' Elsevier, Amsterdam, 1988. pp. 465-481]. Particularly the coplanarity of the whole π-electron system, is an important condition for efficient conduction.

Summary of the invention

The object of the present invention is to provide a new class of conductors, which omits much of the problems encountered with the polyene-linked and carotene-linked di-pyridyls and which has excellent intrinsic conductivity in thin organic molecular films.

In the present invention new types organic compounds are disclosed, which show a high degree of intra-molecular electronic conductivity. The compounds according to the invention are characterised by an oligomeric thiophene structure terminated at both ends by a pyridine functional group. The new class of compounds, "thienoviologens" (formula I), are capable of efficient electron transfer through highly isolating thin organic films and may be used for the construction of functional molecular assemblies. The compounds according to the invention may be applied in various electronic devices, such as molecular electronics components, chemical sensors and biosensors or in various electrochemical processes relying on efficient electron transfer at electrode surfaces.

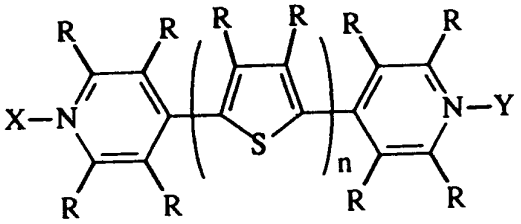
Brief description of the drawings

Figs. 1a-c illustrate three well-known mechanisms of electron-transport in organic membranes,
Figs. 2a-e show the synthesis schemes followed for producing the compounds according to the present invention,
Fig. 3 shows the experimental system used for the AC impedance measurements with the compounds,
Fig. 4 shows the impedance spectra of eight untreated thin film gold electrodes,
Fig. 5 shows the impedance spectra of eight thin film gold electrodes coated with an insulating layer,
Figs 6 and 7 show the impedance spectra of insulating layer electrodes treated with the compounds according to the invention,
Fig. 8 shows the apparant resistance, R_p, vs. the concentration of the compounds according to the invention,
Fig. 9 shows the apparent capacitance, C_p, vs. the concentration of the compounds according to the invention.

Detailed description of the invention

In the present invention a novel class of compounds, acting as effective electronic conductors in thin organic films, with the general structure (I) are disclosed. These compounds according to the present invention are referred to as "Thienoviologens".

In a first aspect, the present invention relates to a compound of the general formula (I):



(I)

wherein

- n represents an integer from 2 to 12,
- the groups X and Y are identical or different and denote functional substituents bound to the pyridine nitrogen, or one or both of X and Y are absent, and
- R, being identical or different, represent a hydrogen atom or an aliphatic side chain introduced for enhancing the solubility of the molecule in organic solvents, such as a branched or unbranched alkyl or alkoxy group containing any number of carbon atoms,

with the exclusion of 5,5'-di(4-pyridyl)-2,2'-bithienyl and 5,5'-di(1-alkyl-4-pyridinio)-2,2'-bithienyl dihalide.

The two excluded compounds are described in the Bulletin of the Chemical Society of Japan 63 (1990) 636-637 as stable and intense fluorescents.

The carbon atoms of the thiophene and pyridine rings in structure (I) may be substitued with hydrogen or with branched or unbranched aliphatic alkyl chains or branched or unbranched alkoxy chains (R) of arbitrary length, solely for the enhancement of solubility of the compounds in organic solvents or for introducing the possibility for production of polymer blends, as is known for the man skilled in the art in respect of similar oligomers and polymers [ten Hoeve W. et al. (1991) J. Am. Chem. Soc. 113, 5887-5889; Laakso J. et al. (1990) Synth. Met. 37, 145-150; Callender C.L. et al. (1991) Thin Solid Films 204, 451-457]. The above-mentioned side groups do not participate in the electron transfer, and the main emphasis of the present invention is in the structure of the conducting chain of the molecule.

In addition, the present invention relates to the use of a compound of the general formula (I) as defined above.

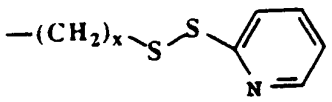
Preferably, one or both of the groups X or Y is an aliphatic branched or unbranched alkyl side chain containing a number of carbon atoms between 1 and 20.

Good results are obtained when one or both of the groups X or Y denotes a tether group used for attachment to an organic or inorganic surface as known in the art, such as:

$$-(CH_2)_x-SH \quad (1)$$

$$-(CH_2)_x-S-S(CH_2)_y-CH_3 \quad (2)$$

(3)



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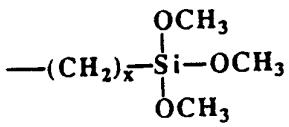


where x and y are integers in the range of 1 to 20.

In a further embodiment, the invention relates to a compound or the use of a compound having formula (I) as defined above wherein one or both of the groups X or Y denotes a metal complex with formula -M-L, in which M is a metal ion capable of forming a coordination bond to the pyridine nitrogen, such as copper, nickel, ruthenium or osmium,

and L is an external mono- or multidendate ligand or functional group bound to the metal ion by a coordination bond.

In another embodiment, X or Y is a redox protein or redox enzyme, either purified directly from biological systems, i.e. from viruses, bacteria or mammalian cell cultures, or produced as the result of genetic engineering of biological systems or as the result of *in vitro* chemical modification techniques of proteins or as the result of combinations of these techniques.

In a preferred embodiment the ligand L or the complex M-L is a redox protein or redox enzyme, produced by any one of the methods listed in the previous paragraph.

The present invention relates in a further aspect to a substantially insulating membrane (2) for passing electrons comprising as electronic conductors (6) at least one molecule following general formula (I) as defined above.

Further the invention relates to an electronic device containing the membrane of the invention attached to an electrode surface.

Finally, the invention relates to an electronic device used for diagnostic determinations of a chemical species, containing as a molecular preparation essential for generating an electronic response, such as a change in current, potential, conductivity or capacitance, at least one molecule following general formula (I) as defined above

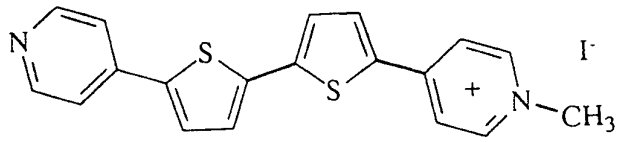
The structure of the pyridine end groups in the structure (I) can vary according to the application. For example, pyridine, itself not redox-active, can act as a ligand for metal complex formation, since some of the complexes are already known as models for studying intramolecular charge transfer [Launey J.P. et al. in: Carter F.L. et al. (Ed.) "Molecular Electronic Devices", Elsevier, Amsterdam, 1988]. The compounds of the invention can be placed as electronic conductors in a membrane that is substantially isolating (Fig. 1c). The membrane can be a molecular monolayer, bilayer, or multilayer, such as a Langmuir-Blodgett film. The amphiphilic character of the molecules and their solubility in organic solvents can be enhanced by introducing longer alkyl chains at the pyridine nitrogens and carbon backbone of the molecule. These substitutions do not greatly interfere with the intrinsic conductivity of the molecules, similarly as with the oligothiophenes.

The alkyl chains attached to the pyridine nitrogen may also include other functionalities at the opposite end of the alkyl chain, such as a sulfonate group for formation of a zwitterionic compound suitable for incorporation in natural bilayer lipid membranes, or a thiol group for direct linking of the molecule to a gold electrode.

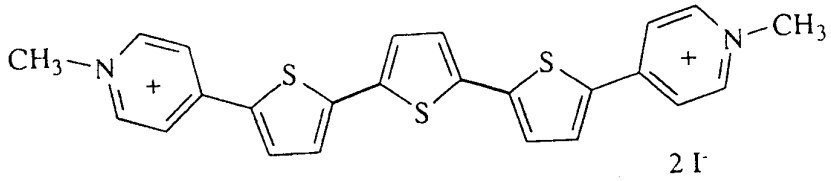
The insulating membrane together with the thienoviologen molecules may be attached directly to an electrode surface by known methods. The external redox species to be anlysed (Fig. 1c, "Red") can be a small electro-active compound, but also a large compound, such as a redox-biomolecule, involved in biological electron-transfer. These compounds can be attached to the other end of the thienoviologen, in which case the thienoviologen acts according to the invention as a direct electronic wire between the external redox species and the electrode. The linkage can be effected through the pyridine end group by a strong non-covalent interaction, such as a hydrogen-bridge, an electrostatic interaction or a charge transfer interaction. The linkage may be effected by a complex-formation reaction between the pyridine nitrogen and a suitable metal ion, such as zinc, copper, iron, ruthenium or osmium ions. Finally, the attachment may be of a covalent nature by electrophilic substitution of the pyridine nitrogen.

As specific examples of our invention, two representative compounds with n = 2 and n = 3 are introduced of which the induction of electronic conductivity is demonstrated in thin organic molecular films. Compounds of formula (I) having several tiophene units, i.e. with n between 2 and 12 are preferred, and compounds where n is from 3 to 12 are particularly preferred because of their molecular lengths, which is an important factor for bridging desired distances.

The first compound is an oligomeric thiophene with two thiophene units terminated by a pyridine functional group at one side and a pyridinium functional group on the opposite side, 5-[4-(N-methyl)pyridinium]-5'-(4-pyridyl) -2,2'- bithiophene iodide, structure (III), "MeIPT2P". Compounds of this type are bifunctional, having a free pyridine functional group able to form a complex with a metal electrode, such as gold, platinum or silver, or with a metal ion, such as copper.



(III)



(IV)

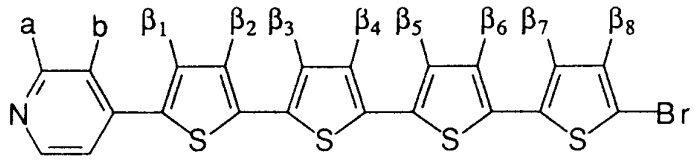
The second compound is an oligomeric thiophene consisting of three oligomeric thiophenes terminated by two pyridinium groups, 5,5"-bis[4-(N-methyl)pyridinium]-2,2':5',2"-terthiophene di-iodide, structure (IV).

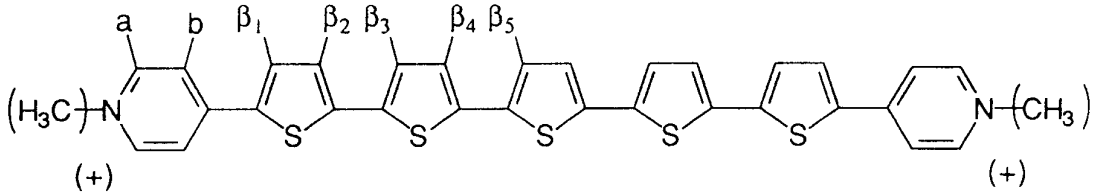
Synthetic route

The synthesis schemes followed for producing extended di-(4-pyridyl)thiophenes and subsequently the thienoviologens of the present invention are given in Figure 2. Although the shortest intermediates 5,5'-di(4-pyridyl)-2,2'-bithiophene, "PT_2P" and 2,5-di(4-pyridyl)-thiophene, "PTP" have been prepared earlier [Nakajima R. et al. (1990) Bull. Chem. Soc. Jpn. 63, 636-637; Takahashi K. & Nihira T. (1992) Bull. Chem. Soc. Jpn. 65, 1855-1859.], no explicit synthesis methods have been described for the longer oligomers (n>2). Good yields of these longer oligomers with n between 3 and 12 were obtained via a synthesis route using an organozinc intermediate, and [1,1'-bis-(diphenylphosphino)-ferrocene]-palladium(II) chloride, $Pd(dppf)Cl_2$, as a crosscoupling catalyst (Fig. 2d). These methods are known in the art for producing similar compounds [Tamao K. et al. (1982) Tetrahedron 38, 3347-3354; Carpita et al. (1985) Tetrahedron 41, 1919-1929.]. The product precipitated as a zinc complex. Non-alkylated bipyridylthiophene oligomers can be prepared with up to 5 units between the pyridine groups (PT_5P) with this method. Longer thienoviologens cannot be readily formed with the same method because dibromo-substituted thiophene oligomers with more than three thiophene units are too badly soluble in the reaction medium, THF, and have thus too low reactivity towards the pyridylthiophene organozinc reagent. In this case, however, partial substitution of the thiophenes with aliphatic alkyl side chains may be used, as discussed earlier, to improve the solubility of the reactants and final products in the organic solvent.

Finally, methylation of the bipyridylthiophene oligomers to the thienoviologens can be readily achieved by reaction with methyliodide in dilute chloroform solution (Fig. 2e). Products generally form very slowly during one week and precipitate as orange-red to dark-red needles. PT_2P yielded the mono-methylated compound (III), $MeIPT_2P$, while longer oligomers PT_3P and PT_4P yielded the dimethylated products resp. $(MeI)_2PT_3P$ (IV) and $(MeI)_2PT_4P$. PT_5P is already a very insoluble compound, but was prepared in reasonably high yields via the scheme of Fig. 3d with n=3. The synthesized molecules were characterised by elemental analysis, ^{1}H-NMR, IR, UV/VIS and mass spectrometry. UV/VIS spectra showed absorption maxima (in DMSO) at 385 nm for PT_2P and 418 nm for PT_3P. On acidification these maxima shifted to 427 nm and 463 nm respectively. The ^{1}H-NMR data of relevant pyridyl thiophene oligomers and some of their intermediates is given in the following Table 1.

Table 1. ^{1}H-NMR data of pyridyl thiophene oligomers.





Compound	Solvent	Chemical shift δ / ppm									
		a	b	β1	β2	β3	β4	β5	β6	β7	β8
PT_2	$CDCl_3$	8.59	7.46	7.43 *7.44)^c*	7.19 *7.23)^c*	7.25	7.05	7.28)*			
	$DMSO\text{-}d_6$	8.56	7.64	7.79	7.40	7.42	7.13	7.58)*			
PT-B_i	$CDCl_3$	8.59	7.38	7.10 *7.10)^c*	7.26 *7.30)^c*						
PT_2-Br	$CDCl_3$	8.60	7.44	7.41	7.12	7.01)^x *7.03)^c*	6.98)^x *7.01)^c*				
PT_3-Br	$CDCl_3$	8.60	7.46	7.44	7.19	7.14	7.05	6.99)^x	6.94)^x		
PT_4-Br	$CDCl_3$	8.60	7.47	7.44	7.20	7.16	7.11	7.09	7.05	6.99)^x	6.94)^x
PTP	$CDCl_3$	8.64	7.51	7.54 *7.57)^c*							
PT_2P	$CDCl_3$	8.61	7.47	7.46 *7.48)^c*	7.26 *7.30)^c*						
	$DMSO\text{-}d_6$	8.59	7.67	7.85	7.54						
methylated	$DMSO\text{-}d_6$	8.86	8.32	8.26	7.72	7.68	7.90	7.68)^b	8.61)^a		
PT_3P	$CDCl_3$	8.60	7.47	7.46	7.22	7.19 *7.21)^c*					
	$DMSO\text{-}d_6$	8.57	7.64	7.80	7.41	7.26					
methylated	$DMSO\text{-}d_6$	8.87	8.33	8.27	7.73	7.66					
PT_4P	$CDCl_3$	8.60	7.47	7.43	7.19	7.15	7.11				
methylated	$DMSO\text{-}d_6$	8.85	8.31	8.26	7.69	7.61	7.52				
PT_5P	$CDCl_3$	8.60	7.47	7.44	7.20	7.16	7.11	7.11			

)* chemical shift of the thiophene a-proton)^c calculated value)^a a-proton of unmethylated pyridine ring
)^b b-proton of unmethylated pyridine ring)^x assignment uncertain

Electrode coating

The process of self-assembly is defined as the spontaneous organised irreversible adsorption of molecules on a solid surface. Here, particularly the self-assembly of alkylmercaptans on gold surfaces has been used, a process which offers a convenient system for assessing the conductivity of different compounds [Bain C. D. (1989) J. Am. Chem. Soc. 111, 321-335.; Stelzle M. (1993) J. Physics Chem. 97, 2974-2981].

Planar thin film gold electrodes (of 9 mm^2) were coated with a single molecular layer of octadecyl-mercaptan (here-

after referred to as ODM) as follows: The electrodes are cleaned by an RF argon plasma for 0.5 min at 0.8 kV and a pressure of 10 mTorr, and transferred to a coating solution containing 1 mM ODM in ethanol. The electrodes were left in the solution for 18 hours and then thoroughly rinsed with ethanol.

Conductivity measurements.

Electrochemical impedance measurements were canied out with a Hewlett Packard 4195A Network/Spectrum analyzer in the frequency range of 10 Hz till 100 kHz. Electrochemical measurement techniques are described in detail elsewhere [Bard A. J. and Faulkner L. R. "Electrochemical Methods, Fundamentals and Applications", John Wiley and Sons, New York 1980, pp. 316-369; MacDonald J. R. "Impedance Spectroscopy", John Wiley & Sons, New York 1987]. All measurements were done in an electrolyte solution containing 154 mM sodium chloride, 10 mM N-(2-hydroxyethyl)-piperazine-N'-(2-ethanesulfonic acid) (HEPES), 100 mM potassium-ferrocyanide and 100 mM potassiumferricyanide, buffered to a pH-value of 7.00 (HFC buffer). This electrolyte solution produces a very low electro-chemical impedance in the low-frequency region with gold electrodes. A two-electrode set-up was used as depicted in Figure 3. The analyzer is denoted by 7, a signal divider by 8, a Faraday cage by 9 and the 9 mm^2 working electrode by 10. A blanc counter electrode 11 with a surface area of 100 mm^2, was used to minimise it's contribution to the measured membrane impedance.

Figure 4 shows the impedance spectra of 8 untreated electrodes. Data is represented in terms of apparent resistance Rp and capacitance Cp. It is observed that the resistance values of untreated gold electrodes are about 40 Ω or lower over the whole frequency range, while the capacitance steadily drops from high values (around 20 μF) at 10 Hz till low values (1.5 nF) at 100 kHz. Figure 5a gives the modulus of the impedance, |Z|, after plasma treatment and subsequent coating with ODM. The impedance increases drastically at low frequencies, indicating blocking of the electrochemical reaction. Figure 5b gives the phase angle, θ, of the impedance, indicating largely capacitive properties of the electrode with a characteristic frequency at around 1 kHz.

Figure 6 gives the impedance characteristics, |Z| vs. frequency, of 7 ODM coated electrodes that have been immersed for 18 hours in ethanol solutions (1 ml) of $MeIPT_2P$ at different concentrations (5 - 200 μM). It was observed that the treatment turns the electrode coating fully from the capacitive to the conductive state at concentrations above 30 μM of $MeIPT_2P$. The electrode impedance drops by a factor of 1000, fully restoring the conductivity to the level of that of an uncoated gold electrode. It was also observed that the strong hydrophobic character of the electrode surface was preserved. Figure 7 shows the impedance characteristics of electrodes modified in the same fashion with $(MeI)_2PT_3P$.

Figure 8 gives the change of Rp and Figure 9 of Cp (at 100 Hz), as a function of concentration of both $MeIPT_2P$ and $(MeI)_2PT_3P$. It is observed that the resistance drops and the capacitance rises with adsorption of the model thienoviologens to the ODM layer.

Conclusions.

Although the underlying mechanism of conduction has not yet been elucidated fully at this stage, the data in figures 6 - 9 clearly indicate that the "thienoviologens" according to the invention work as effective molecular conductors in a self-assembled molecular system. The changes of Rp and Cp with concentration are rather abrupt in a narrow concentration region (20-40 μM for $MeIPT_2P$ and 30-50 for $(MeI)_2PT_3P$), and the changes are irreversible. A stable molecular assembly is thus formed at low concentrations from solution. The use of these compounds as molecular conductors is thus feasible and is of great importance in molecular electronics devices, such as electrochemical sensors or biosensors. The invention is, however, not restricted only to sensors, but may be used in all electronic devices where electron-conducting molecules are needed.

Synthesis examples

Reagents and Equipment

All used solvents were of analytical reagent grade. 1,3-bis(diphenylphosphino)propane nickel(II) chloride, $Ni(dppp)Cl_2$ (Aldrich), was stored under argon at 4°C. 1,1'-bis(diphenylphosphino)ferrocene palladium(II) chloride, $Pd(dppf)Cl_2$ (Aldrich), in a 1:1 complex with dichloromethane, was used as received. 4-bromopyridine hydrochloride (Aldrich, 99%), methyliodide (Aldrich), 2-bromothiophene (Janssen Chimica, 98%), 2,5-dibromothiophene (Aldrich, 95%), hydrazine hydrate (Aldrich, 98%), sodium periodate (Merck, p.a.), iodine (Merck, doubly sublimated), bromine (J.T. Baker), magnesium shavings (Merck) and n-butyllithium (Aldrich, 1.6 M solution in hexanes) were used as provided. All reactions with magnesium, butyllithium, $Ni(dppp)Cl_2$, $Pd(dppf)Cl_2$ and palladium-amalgam were conducted under dry argon delivered by a Schlenck aparatus.

Elemental analysis was carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). Proton NMR spectra were acquired on a Bruker WM 300 FT-NMR spectrometer at 300 MHz, or on a Jeol JNM-FX200 FT-NMR spectrometer at 200 MHz. Mass spectra were recorded on a Finnigan MAT TSQ-70 quadrupole mass spectrometer, equipped with a 59980A particle beam interface (Hewlett Packard). The spectra were recorded in EI impact mode, using an electron energy of 70 eV. The samples, dissolved in methanol, were introduced by means of an LC/MS system in column bypass mode (FIA), using a flow rate of 0.5 ml/min. In some cases the sample was introduced by slowly heating the solid from a probe.

Thiophene oligomers

2,2'-bithiophene, T_2

The Grignard reagent 2-thienylmagnesiumbromide (T-MgBr) was made from 2-bromothiophene (T-Br) in a standard fashion in a three-necked roundbottom flask with 9 gr (370 mmol) of magnesium and 45 gr (276 mmol) of T-Br in 120 ml diethylether. In a separate, three-necked roundbottom flask was placed 120 ml of ether, 37.5 gr (230 mmol) of T-Br and 180 mg (0.33 mmol) of Ni(dppp)Cl_2. The Grignard reagent was then added slowly, under a steady outflow of argon. The mixture was refluxed and stirred for 3 hours and 15 minutes, poured on ice with dilute hydrochloric acid, and extracted with ether. After drying the ether layer on anhydrous magnesium sulphate, the organic layer was filtrated and the ether evaporated. The residue was redissolved in warm methanol. Some water was added to the methanol, while still warm, until a yellow precipitate started to form. The mixture was then put overnight at 4°C to form yellow crystals. After filtration and drying in vacuo the product was molten and poured in a dry storage vessel. Yield: yellow crystals of T_2, 25.16 gr (152 mmol, 66%). M.p.: 31°C (litt.: 33). Elemental analysis: found% (theory%) C 57.54 (57.79), H 3.61 (3.64), S 38.0 (38.6). ^{1}H-NMR (300 MHz, $CDCl_3$): ∂=7.21 (2H, dd, J=5.0 and 1.2 Hz), ∂ =7.01 (2H, dd, J=5.0 and 3.6 Hz), ∂=7.18 (2H, dd, J=1.2 and 3.6 Hz). M/z (Mass peak from mass spectrometry): 166 D (M.W.=166), small impurity at 248 D, probably 2,2':5',2"-terthiophene (M.W.=248).

2,2':5,2"-terthiophene, T_3

13.16 gr (81 mmol) of T-Br was allowed to react with 25 gr (103 mmol) of magnesium in about 30 ml of ether and the formed Grignard reagent was refluxed for one additional hour. The reagent was then added slowly to a stirred solution of 7.25 gr (30 mmol) of 2,5-dibromothiophene (Br-T-Br) and 160 mg (0.3 mmol) of Ni(dppp)Cl_2 in 40 ml of dry THF. The mixture was refluxed for 3 hours. The reaction mixture was poured on ice with dilute hydrochloric acid and the aqueous layer extracted with hexane. The organic layer was dried and the solvent evaporated. The product was obtained by a first crystallization from hexane and a second crystallization from ethanol and finally dried in vacuo. Yield: 158 gr orange powder of T_3 (6.4 mmol, 21%). M.p. 80-81 °C (litt.: 94). Elemental analysis: found % (theory %) C 57.44 (58.03), H 3.22 (3.25), S 38.0 (38.7). ^{1}H-NMR (300 MHz, $CDCl_3$): ∂=7.22 (2H, dd, J=5.3 and 1.2 Hz). ∂=7.17 (2H, dd, J=3.7 and 1.2 Hz), ∂=7.08 (2H, s), ∂=7.02 (2H, dd, J=5.3 and 3.7 Hz). M/z: 248 D (M.W.=248) very small impurity at 330 D, probably 2,2':5',2":5",2"'-quaterthiophene, T_4.

5,5'-dibromo-2,2'-bithiophene, Br-T_2-Br

10 gr (60 mmol) of T_2 was dissolved in 200 ml dry THF and cooled in an acetone bath till -78 °C with liquid nitrogen. 95 ml of butyllithium (BuLi) (152 mmol) was added and the mixture stirred at -78 °C for 1.5 hours. 9 ml (27.9 g, 174 mmol) of bromine was added dropwise. The reaction mixture was further stirred at -78 °C for 1 hour and thereafter stirred for 1 hour at room temperature. The reaction mixture was then quenched with dilute hydrochloric acid and the product extracted with THF and hexane. After drying the organic layer on anhydrous magnesium sulphate, the solvents were evaporated and the product recrystallized from a mixture of ethanol and THF as an orange powder. The product was dried in vacuo. Yield: 11.71 gr (36 mmol, 60%) of Br-T_2-Br. M.p. 141 °C (litt.: 143). Elemental analysis: found% (theory%) C 28.77 (29.65), H 1.18 (1.24), S 18.5 (19.79), Br 52.0 (49.31). ^{1}H-NMR (200 MHz, $CDCl_3$): ∂ =6.95 (2H, d, J=3.8 Hz), ∂=6.83 (2H, d, J=3.8 Hz). M/z: 324 D (M.W.=324).

2,2':5',2":5",2"'-quaterthiophene, T_4

Thienylmagnesiumbromide, made from 13 gr (80 mmol) of T-Br and 2.43 gr (100 mmol) of magnesium in 50 ml of anhydrous ether, was added to a solution of 11.71 gr (36 mmol) of 5,5'-dibromo-2,2'-bithiophene and 100 mg (0.18 mmol) of Ni(dppp)Cl_2 in 150 ml of ether. The reaction mixture was refluxed for 4 hours and subsequently poured on an ice/dilute hydrochloric acid mixture, extracted with toluene and the product was recrystallized from a mixture of toluene and ethanol. The resulting orange powder was dried in vacuo. Yield: 6,75 gr (20 mmol, 57%) of T_4. M.p.: 203 °C (litt:

212). Elemental analysis: found% (theory%) C 56.49 (58.15), H 3.05 (3.05), S 37.0 (38.8). ^{1}H-NMR (300 MHz, $CDCl_3$): ∂=7.23 (2H, dd, J=5.0 and 1.0 Hz), ∂=7.19 (2H, dd, J=3.7 and 1.0 Hz), ∂=7.08 (4H, s), ∂=7.03 (2H, dd, J=5.0 and 3 7 Hz). M/z: 330 D (M.W.=330).

5,5''-dibromo-2,2':5',2''-terthiophene, Br-T_3-Br

1.0 gr (4 mmol) of T_3 was brominated with the same procedure as T_2 by reaction with 8.9 mmol of butyllithium and 9 mmol of bromine at -78°C. The product was extracted with ether, crystallized from toluene/ethanol and dried in vacuo, yielding an orange/brown powder. Yield: 830 mg (2 mmol, 50%) of Br-T_3-Br. M.p.: 151 °C (litt.: 160). Elemental analysis: found% (theory%) C 35.60 (35.49), H 1.65 (1.49), S 23.2 (23.7), Br 38.0 (39.3). ^{1}H-NMR (300 MHz, $CDCl_3$): ∂=7.00 (2H, s), ∂=6.98 (2H, d, J=3.8 Hz), ∂=6.91 (2H, d, J=3.8 Hz). M/z: 406 D (M.W.=406).

5,5'''-dibromo-2,2':5',2'':5'',2'''-quaterthiophene, Br-T_4-Br

6 gr (18 mmol) of T_4 in 100 ml THF was brominated by reaction with BuLi (23 ml, 36 mmol) at -78 °C for 2 hours and bromine (2 ml, 39 mmol) at -78 °C for 1 hour, followed by stirring one hour at room temperature. After quenching the reaction mixture with aqueous HCl, the product was isolated by filtration and washing the resulting yellow solid with THF, methanol and ethanol. Yield: 11.63 gr Br-T_4-Br (24 mmol, 132%, probably containing adsorbed solvent.). M.p. 245 °C. Elemental analysis: found% (theory%) C 38.12 (39.36), H 1.88 (1.65), S 25.1 (26.3), Br 32.2 (32.73), Mg<0.1. ^{1}H NMR (300 MHz, $CDCl_3$): ∂=7.06 (2H, d, J=3.8 Hz), ∂=7.01 (2H, d, J=3.8 Hz), ∂=6.98 (2H, d, 3.8 Hz), ∂=6.91 (2H, d, J=3.8 Hz). M/z: 488 D (M.W.=488), impurities present at 408 D (T_4-Br), 330 D (T_4), 324 D (Br-T_2-Br), 248 D (T_3).

Pyridylthiophenes

4-bromopyridine, P-Br

Since 4-bromopyridine (P-Br) is not very stable, the compound was freshly prepared prior to each coupling reaction. A good yield of P-Br was obtained by reacting a commercially available hydrochloride with an equimolar amount of aqueous sodium hydroxide and extracting the free base into hexane. The solvent was then removed slowly on a rotation evaporator.

2-(4-pyridyl)thiophene, PT

To a 500 ml reactor was added 200 ml dry THF, 0.54 gr (1 mmol) Ni(dppp)Cl_2 and 87 mmol of P-Br, freshly prepared from 17 gr of the hydrochloride. To this was added T-MgBr, prepared from 14 gr (87 mmol) of T-Br and 2.5 gr (103 mmol) of magnesium. The mixture was refluxed for 20 hours and subsequently quenched with aqueous ammoniumchloride/HCl. About 100 ml of hexane was added and the organic layer extracted three times with dilute hydrochloric acid. The water layers were combined and made mildly alkaline with a strong sodium hydroxide solution. The product was extracted with three portions of 100 ml of chloroform. The chloroform solution was boiled shortly with a small amount of active coal and filtrated, whereafter the chloroform was removed on a rotation evaporator. Trituration of the remaining brown solid in boiling hexane yielded a clear yellow solution and a black unsoluble residue. After decanting the yellow solution, the solvent was evaporated and the remaining yellow solid dried in vacuo. The product was once recrystallized from 100 ml of hexane (a few hours standing at room temperature and overnight standing at 4 °C). The resulting yellow crystals were filtrated off, washed with cold pentane twice and dried in vacuo, (fraction I). From the collected pentane supernatants a second fraction of product with a lesser purity was obtained, by evaporating the solvent on a rotation evaporator and drying the remaining solid in vacuo. Yield: fraction I: light yellow powder of PT, 3.88 gr (24 mmol, 28%), fraction II: yellow powder of PT 6.00 gr (37.2 mmol, 43%), still containing some P-Br. M.p. (fraction I): 90-91 °C (litt.: 92.5-93.5 °C). Elemental analysis: found% (theory%) C 66.87 (67.05), H 4.38 (4.38), N 8.90 (8.69), S 18.7 (19.9). ^{1}H-NMR (300 MHz, $CDCl_3$): ∂=8.59 (2H, dd, J=4.6 and 1.7 Hz), ∂=7.52 (1H, dd, J=3.8 and 1.1 Hz), ∂=7.49 (2H, dd, J=4.6 and 1.7 Hz), ∂=7.43 (1H, dd, J=5.0 and 1.1 Hz), ∂=7.14 (1H, dd, J=3.8 and 5.0 Hz). M/z: 161 D (M.W.=161).

2-(4-pyridyl)-5-iodothiophene, PT-I

To 100 ml of 80% acetic acid in water was added 5 gr (31 mmol) PT, 6.9 gr (27 mmol) iodine and 4.1 gr (18 mmol) periodic acid dihydrate. The mixture was heated at 80 °C for 18 hrs. After cooling on an ice bath, the product was filtrated, recrystallized from chloroform and dried in vacuo. Yield: 5.3 gr yellow/brown powder (18 mmol, 58%). Elemental analysis: found% (theory%) C 20.59 (37.65), H 1.17 (2.11), N 2.87 (4.88), S 6.70 (11.2), I 68.8 (44.2), 1 mole equivalent of I_2 present as impurity. ^{1}H-NMR (300 MHz, $CDCl_3$): ∂=8.60 (2H, dd, J=4.7 and 1.6 Hz), ∂=7.39 (2H, dd, J=4.5 and 1.7

Hz), ∂=7.29 (1H, d, J=3.8 Hz), ∂=7.17 (1H, d, J=3.8 Hz). M/z: 287 D (M.W.=287.1)

5,5'-bi(4-pyridyl)-2,2'-bithiophene, PT_2P

In 40 ml of 50% methanol in water was dissolved 3.6 gr (90 mmol) of sodium hydroxide 5.166 gr (18 mmol) of PTI and 540 mg (10.8 mmol) of hydrazine hydrate. After stirring the solution, a solution of 240 mg (0.9 mmol) of palladium chloride and 244 mg (0.9 mmol) of mercuric chloride in water (with some KCl) were added. The mixture was refluxed overnight (18 hrs). The reaction mixture was then cooled and the palladium-amalgam with the product filtrated on a glass filter. The residue was washed with water and the product dissolved from the amalgam with some acetone and portions of chloroform. The organic layers were collected together and the solvents evaporated. In order to remove water, the residue was shaken with 250 ml of methanol, after which the methanol was evaporated. The dry residue was then shaken with hexane, filtered off on a glass filter, washed with hexane to remove PT and washed with pentane. The product was dried in air. Yield: 1.4 gr (4.4 mmol, 49%) of yellow/brown powder. 1.0 gr of the product was sublimed at 230 - 250 °C yielding 898 mg of PT2P. M.p. 240 °C (litt. 241-242 °C). Elemental analysis: found% (theory%) C 66.89 (67.47), H 3.80 (3.77), N 8.75 (8.74), S 19.6 (20.0). ^{1}H-NMR (300 MHz, $CDCl_3$): ∂=8.62 (4H, dd, J=4.6 and 1.6 Hz), ∂=7.47 (4H, dd, J=4.5 and 1.7 Hz), ∂=7.46 (2H, d, J=3.9 Hz), ∂=7.27 (2H, d, J=4.1 Hz). M/z: 320 D (M.W.=320.44).

5,5''-bi(4-pyridyl)-2,2':5',2''-terthiophene, PT_3P ($Ni(dppp)Cl_2$method)

1.61 gr (10 mmol) PT was dissolved in a mixture of 100 ml diethylether and 25 ml THF. The solution was cooled on an acetone bath till -78 °C with liquid nitrogen. 6.25 ml BuLi was added, followed by stirring for 1 hr. 1.85 gr of anhydrous $MgCl_2$ was added at a temperature of -60 °C and the mixture was stirred for 2 hrs to room temperature. A black tar formed at the bottom of the flask during the stirring. In a separate flask 1 gr (4 mmol) of Br-T-Br and 50 mg of $Ni(dppp)Cl_2$ were dissolved in 100 ml THF and 100 ml diethylether. The Grignard reagent was transferred to this mixture (2-pot reaction). The coupling reaction proceeded under continuous stirring under reflux for 20 hrs. Due to the difficulties in handling the Grignard reagent, a second reaction was performed exactly the same way, but the mixture of Br-T-Br, $Ni(dppp)Cl_2$, ether and THF were added to the Grignard reagent (1-pot preparation). Differences in the results were not noticed. Reaction products were extracted from the mixture first by extraction of the organic layer with dilute hydrochloric acid and, after making the pooled aqueous layer slightly alkaline, back extracted with chloroform. Three fractions were obtained: fraction I, soluble in chloroform and hexane; fraction II, soluble only in chloroform and not in hexane; fraction III, a residue not soluble in chloroform and hexane. Fraction I contained largely PT (^{1}H-NMR). Fraction II contained PT_2P and some PT_3P (by ^{1}H-NMR and Mass spectrometry). Only from the second trial, the 1-pot method, a very small amount of PT_3P could be isolated, with column chromatography (silica column with chloroform as eluent): ^{1}H-NMR (300 MHz, $CDCl_3$): ∂=8.61 (4H, dd, broad), ∂=7.46 (4H, dd, J=3.8 and 1.6 Hz), ∂=7.45 (2H, d, J=3.7 Hz), ∂=7.22 (2H, d, J=3.9 Hz), ∂=7.19 (2H, s).

5,5'''-bi(4-pyridyl)-2,2':5',2'':5'',2'''-quaterthiophene PT_4P ($Ni(dppp)Cl_2$ method)

A Grignard reagent was prepared from 3.25 gr. of PT (20 mmol), 12.5 ml BuLi and 3.68 gr. $MgCl_2$ in 100 ml THF as with PT3P. BuLi was only added at a higher temperature: -45 °C. To the PT-MgBr was added 3.24 gr Br-T_2-Br (10 mmol), 100 mg $Ni(dppp)Cl_2$ and 100 ml THF and the mixture was stirred and refluxed for 20 hrs. The products were isolated in the same way as the PT_3P. The fraction that dissolved in chloroform and not in hexane was further analyzed. With mass-spectrometry peaks appeared at 320 D (PT_2P), 325 D (PT_3?), 405 D (PT_3-Br) and 484 D (PT_4P), while ^{1}H-NMR revealed the presence of PT_2P and PT_3-Br. In an other trial, at 16 millimolar scale, similar results were obtained: only PT_2P and PT_3-Br could be identified by ^{1}H-NMR. ^{1}H-NMR of PT_3-Br (300 MHz, $CDCl_3$): ∂=8.60 (d, broad, overlap with PT_2P), ∂=7.46 (d, broad, overlap with PT_2P), ∂=7.45 (d, J=3.8 Hz), ∂=7.21 (d, J=3.9 Hz), ∂=7.14 (d, J=3.7 Hz), ∂=7.02 (d, J=3.9 Hz), ∂=6.98 (d, J=3.8 Hz).

Reactions with $ZnCl_2$and $Pd(dppJ)Cl_2$.

1.61 gr. of PT (10 mmol) was dissolved in 100 ml THF and the solution stirred and cooled till -70 °C on an acetone bath with liquid nitrogen. 6.25 ml BuLi was added and the mixture stirred for 1 hour at -70 °C. 10 ml of a 1 M solution of anhydrous $ZnCl_2$ in THF were added and the solution mixed 2 hrs at -55 °C, during which a dark red-brown tar formed, which was difficult to stir. 1.21 gr. (5 mmol) of Br-T-Br and about 25 mg of $Pd(dppf)Cl_2$ were added and the reaction mixture was allowed to reach room temperature slowly. The mixture was then stirred and refluxed overnight (20 hrs). An orange precipitate formed. The reaction mixture was cooled on an ice bath and mixed for one hour, whereafter the precipitate was collected on a Büchner filter. The precipitate was rinsed with chloroform and pentane and dried in vacuo. Yield: 2.163 gr. orange powder. Elemental analysis: found% C 41.54, H 2.76, N 4.47, S 14.0, Cl 9.32, Br 8.33, Zn 13.5.

Part of the precipitate was treated with a 1% EDTA (Titriplex III) solution (stirring at about 80 °C for 1 hour). The precipitate was filtered, washed with portions of ethanol and ether and dried in air, yielding a yellow/brown powder, partly soluble in chloroform. ^{1}H-NMR (300 MHz, $CDCl_3$) yielded a spectrum corresponding to pure PT_3P. The same reaction and procedure of purification was followed for coupling PT-ZnCl to Br-T_2-Br, Br-T_3-Br and Br-T_4-Br. The coupling of Br-T_2-Br yielded 3.47 gr. of red powder. Elemental analysis: found% C 41.23, H 2.80, N 3.81, S 16.5, Cl 9.44, Br 9.72, Zn 11.4. EDTA treatment yielded an orange/brown powder. The fraction soluble in chloroform appeared to be largely PT_3-Br, as evidenced from the ^{1}H-NMR spectrum. The coupling product with Br-T_3-Br yielded 3.60 gr. of dark red powder. Elemental analysis: found% C 42.32, H 2.95, N 3.09, S 19.7, Cl 7.46, Br 8.47, Zn 9.27. Also this substance was EDTA-treated, which gave a red/brown precipitate. ^{1}H-NMR analysis, of the fraction that was soluble in chloroform, indicated the presence of PT_4-Br and PT_5P: ^{1}H-NMR (300 MHz, $CDCl_3$) of PT_4-Br: ∂=8.60 (d, broad), ∂=7.47 (d, 3.8 Hz), ∂=7.44 (d, J=3.9 Hz), ∂=7.20 (d, J=3.7 Hz), ∂=7.16 (d, J=4.1 Hz), ∂=7.11 (d, J=3.5 Hz), ∂=7.09 (d, J=3.8 Hz), ∂=7.05 (d, J=3.6 Hz), ∂=6.99 (d, J=3.9 Hz), ∂=6.93 (d, J=3.9 Hz) and PT_5P: ∂=8.60 (d, broad), ∂=7.47 (d, 3.8 Hz), ∂=7.44 (d, J=3.9 Hz), ∂=7.20 (d, J=3.7 Hz), ∂=7.16 (d, J=4.1 Hz), ∂=7.11 (d, J=3.5 Hz), ∂=7.11(s).

Methylations

50 or 100 mg of the pyridylthiophene derivative was dissolved in 50 ml of chloroform and 1 ml of methyliodide added. In case of PT_3P and PT_4P only very little (<10 mg) substance was used and about 10 ml of chloroform. After mixing, the methylation was allowed to proceed for one week at roomtemperature in a closed erlenmeyer flask, during which neat crystals of the product formed. The products were collected on a Büchner filter and washed with chloroform. It was noticed that under these conditions PT_2P was monomethylated and PT_3P and PT_4P dimethylated. Analytical data is given below:

MeI-PT_2P:

Elemental analysis: found% (theory%) C 44.37 (49.36), H 3.22 (3.27), N 5.47 (6.06), S 12.1 (13.9), 126. 1 (27.5); ^{1}HNMR (300 MHz, DMSO-d_6): ∂=8.86 (2H, d, 7.1 Hz), ∂=8.61 (2H, d, J=5.1 Hz), ∂=8.32 (2H, d, J=7.0 Hz), ∂=8.26 (1H, d, J=4.4 Hz), ∂=7.90 (1H, d, J=3.5 Hz), ∂=7.72 (1H, d, J=4.0 Hz), ∂=7.68 (3H, d, J=4.0 Hz), ∂=4.24 (3H, s).

MeI-PT_3P-MeI:

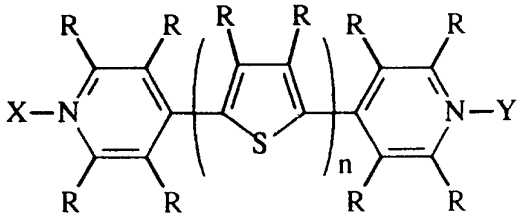
Elemental analysis: found% (theory%) C 38.27 (41.99), H 3.70 (2.94), N 3.75 (4.08), S 15.5 (14.0), I 34.8 (37.0); ^{1}H-NMR (300 MHz, DMSO-d_6): ∂=8.87 (4H, d, J=7.0 Hz), ∂=8.33 (4H, d, J=7.1 Hz), ∂=8.27 (2H, d, J=4.1 Hz), ∂=7.73 (2H, d, J=4.1 Hz), ∂4.22 (6H, s).

MeI-PT_4P-MeI:

^{1}H-NMR (300 MHz, DMSO-d_6): ∂=8.85 (4H, d, J=6.9 Hz), ∂=8.31 (4H, dd, broad), ∂=8.26 (2H, d, J=4.1 Hz), ∂=7.69 (2H, d, J=4.0 Hz), ∂=7.61 (2H, d, J=3.9 Hz), ∂=7.52 (2H, d, J=3.9 Hz), ∂=4.24 (6H, s).

Claims

1. Compound of the general formula (I):



(I)

wherein

- n represents an integer from 2 to 12,
- the groups X and Y are identical or different and denote functional substituents bound to the pyridine nitrogen,

or one or both of X and Y are absent, and

- R, being identical or different, represent a hydrogen atom or an aliphatic side chain introduced for enhancing the solubility of the molecule in organic solvents, such as a branched or unbranched alkyl or alkoxy group containing any number of carbon atoms,

with the exclusion of 5,5'-di(4-pyridyl)-2,2'-bithienyl and 5,5'-di(1-alkyl-4-pyridinio)-2,2'-bithienyl dihalide.

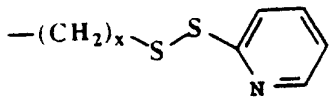
2. Compound according to claim 1, wherein one or both of the groups X or Y is an aliphatic branched or unbranched alkyl side chain containing a number of carbon atoms between 1 and 20.

3. Compound according to claim 1 or 2, wherein one or both of the groups X or Y denotes a tether group used for attachment to an organic or inorganic surface as known in the art, such as:

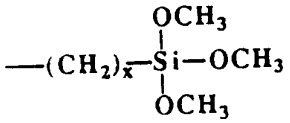
$$-(CH_2)_x\text{-}SH \quad (1)$$

$$-(CH_2)_x\text{-}S\text{-}S\text{-}(CH_2)_y\text{-}CH_3 \quad (2)$$

(3)



(4)



where x and y are integers in the range of 1 to 20.

4. Compound according to any one of the preceding claims, wherein one or both of the groups X or Y denotes a metal complex with formula -M-L, in which M is a metal ion capable of forming a coordination bond to the pyridine nitrogen, such as copper, nickel, ruthenium or osmium, and L is an external mono- or multidendate ligand or functional group bound to the metal ion by a coordination bond.

5. Compound according to any one of the preceding claims, wherein the substituent X or Y is a redox protein or redox enzyme, either purified directly from biological systems, i.e. from viruses, bacteria or mammalian cell cultures, or produced as the result of genetic engineering of biological systems or as the result of *in vitro* chemical modification techniques of proteins or as the result of combinations of these techniques.

6. Compound according to claim 4, characterized in that the ligand L or the complex M-L is a redox protein or redox enzyme, produced by the methods listed in claim 5.

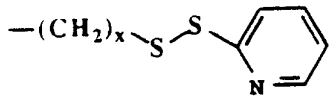
7. Use of a compound of claim 1 as intrinsic conductor.

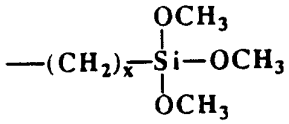
8. Use according to claim 7, wherein one or both of the groups X or Y is an aliphatic branched or unbranched alkyl side chain containing a number of carbon atoms between 1 and 20.

9. Use according to any one of the claims 7-8, wherein one or both of the groups X or Y denotes a tether group used for attachment to an organic or inorganic surface as known in the art, such as:

$$-(CH_2)_x\text{-}SH \quad (1)$$

$$-(CH_2)_x\text{-}S\text{-}S\text{-}(CH_2)_y\text{-}CH_3 \quad (2)$$

(3) 

(4) 

where x and y are integers in the range of 1 to 20.

10. Use according to any one of the claims 7-9, wherein one or both of the groups X or Y denotes a metal complex with formula -M-L, in which M is a metal ion capable of forming a coordination bond to the pyridine nitrogen, such as copper, nickel, ruthenium or osmium, and L is an external mono- or multidendate ligand or functional group bound to the metal ion by a coordination bond.

11. Use according to any one of the claims 7-10, wherein the substituent X or Y is a redox protein or redox enzyme, either purified directly from biological systems, i.e. from viruses, bacteria or mammalian cell cultures, or produced as the result of genetic engineering of biological systems or as the result of *in vitro* chemical modification techniques of proteins or as the result of combinations of these techniques.

12. Use according to claim 10, characterized in that the ligand L or the complex M-L is a redox protein or redox enzyme, produced by the methods listed in claim 11.

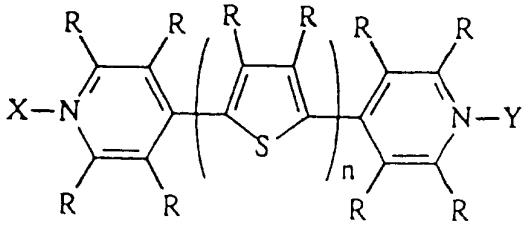
13. A substantially insulating membrane (2) for passing electrons comprising as electronic conductors (6) at least one molecule following general formula (I) as defined in claim 1.

14. An electronic device containing the membrane of claim 13 attached to an electrode surface (3).

15. An electronic device used for diagnostic determinations of a chemical species, containing as a molecular preparation essential for generating an electronic response, such as a change in current, potential, conductivity or capacitance, at least one molecule following general formula (I) as defined in claim 1.

Patentansprüche

1. Verbindung der allgemeinen Formel (I):



(I)

worin

- n eine ganze Zahl von 2 bis 12 darstellt,
- die Gruppen X und Y identisch oder verschieden sind und funktionelle Substituenten bezeichnen, die an den Pyridinstickstoff gebunden sind, oder eine oder beide von X und Y nicht vorhanden sind, und

- R, identisch oder verschieden, ein Wasserstoffatom oder eine aliphatische Seitenkette darstellt, die zur Verbesserung der Löslichkeit des Moleküls in organischen Lösungsmitteln eingeführt ist, wie eine verzweigte oder unverzweigte Alkyl- oder Alkoxygruppe, die eine beliebige Anzahl von Kohlenstoffatomen enthält,

mit Ausnahme von 5,5'-Di-(4-pyridyl)-2,2'-bithienyl- und 5,5'-Di-(1-alkyl-4-pyridinio)-2,2'-bithienyl-dihalogenid.

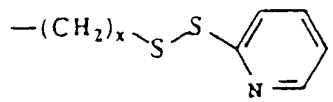
2. Verbindung nach Anspruch 1, worin eine oder beide der Gruppen X oder Y eine aliphatische verzweigte oder unverzweigte Alkylseitenkette ist, die eine Anzahl von Kohlenstoffatomen zwischen 1 und 20 enthält.

3. Verbindung nach Anspruch 1 oder 2, worin eine oder beide der Gruppen X oder Y eine Bindegruppe bezeichnet, die zur Befestigung an einer organischen oder anorganischen Oberfläche verwendet wird, wie auf dem Fachgebiet bekannt, wie:

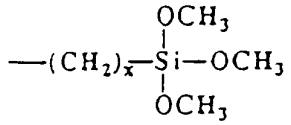
$$-(CH_2)_x\text{-}SH \qquad (1)$$

$$-(CH_2)_x\text{-}S\text{-}S\text{-}(CH_2)_y\text{-}CH_3 \qquad (2)$$

(3)



(4)



wobei x und y ganze Zahlen im Bereich von 1 bis 20 sind.

4. Verbindung nach einem der vorhergehenden Ansprüche, worin eine oder beide der Gruppen X oder Y einen Metallkomplex mit der Formel -M-L bezeichnet, in der M ein Metallion ist, das eine koordinative Bindung zum Pyridinstickstoff bilden kann, wie Kupfer, Nickel, Ruthenium oder Osmium, und L ein äußerer ein- oder mehrzähniger Ligand oder eine funktionelle Gruppe ist, der bzw. die durch eine koordinative Bindung an das Metallion gebunden ist.

5. Verbindung nach einem der vorhergehenden Ansprüche, worin der Substituent X oder Y ein Redoxprotein oder Redoxenzym ist, das entweder direkt aus biologischen Systemen, d.h. aus Viren, Bakterien oder Säugerzellkulturen, isoliert oder als Ergebnis einer gentechnischen Veränderung biologischer Systeme oder als Ergebnis von Techniken der chemischen *In-vitro*-Modifikation von Proteinen oder als Ergebnis von Kombinationen dieser Techniken erzeugt worden ist.

6. Verbindung nach Anspruch 4, dadurch gekennzeichnet, daß der Ligand L oder der Komplex M-L ein Redoxprotein oder Redoxenzym ist, das durch die in Anspruch 5 angeführten Verfahren erzeugt worden ist.

7. Verwendung einer Verbindung von Anspruch 1 als Eigenleiter.

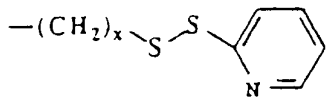
8. Verwendung nach Anspruch 7, wobei eine oder beide der Gruppen X oder Y eine aiiphatische verzweigte oder unverzweigte Alkylseitenkette ist, die eine Anzahl von Kohlenstoffatomen zwischen 1 und 20 enthält.

9. Verwendung nach einem der Ansprüche 7 bis 8, wobei eine oder beide der Gruppen X oder Y eine Bindegruppe bezeichnet, die zur Befestigung an einer organischen oder anorganischen Oberfläche verwendet wird, wie auf dem Fachgebiet bekannt, wie:

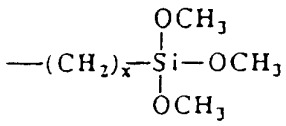
$$-(CH_2)_x\text{-}SH \qquad (1)$$

$$-(CH_2)_x-S-S-(CH_2)_y-CH_3 \quad (2)$$

(3)



(4)



wobei x und y ganze Zahlen im Bereich von 1 bis 20 sind.

10. Verwendung nach einem der Ansprüche 7 bis 9, wobei eine oder beide der Gruppen X oder Y einen Metallkomplex mit der Formel -M-L bezeichnet, in der M ein Metallion ist, das eine koordinative Bindung zum Pyridinstickstoff bilden kann, wie Kupfer, Nickel, Ruthenium oder Osmium, und L ein äußerer ein- oder mehrzähniger Ligand oder eine funktionelle Gruppe ist, der bzw. die durch eine koordinative Bindung an das Metallion gebunden ist.

11. Verwendung nach einem der Ansprüche 7 bis 10, wobei der Substituent X oder Y ein Redoxprotein oder Redoxenzym ist, das entweder direkt aus biologischen Systemen, d.h. aus Viren, Bakterien oder Säugerzellkulturen, isoliert oder als Ergebnis einer gentechnischen Veränderung biologischer Systeme oder als Ergebnis von Techniken der chemischen *In- vitro*-Modifikation von Proteinen oder als Ergebnis von Kombinationen dieser Techniken erzeugt worden ist.

12. Verwendung nach Anspruch 10, dadurch gekennzeichnet, daß der Ligand L oder der Komplex M-L ein Redoxprotein oder Redoxenzym ist, das durch die in Anspruch 11 angeführten Verfahren erzeugt worden ist.

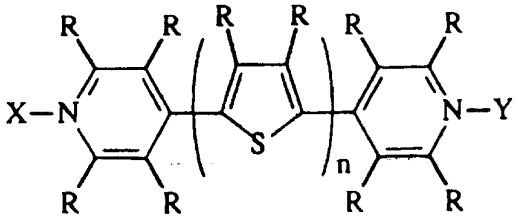
13. Im wesentlichen isolierende Membran (2) für den Durchlaß von Elektronen, die als Elektronenleiter (6) wenigstens ein Molekül enthält, das der allgemeinen Formel (I) entspricht, wie sie in Anspruch 1 definiert ist.

14. Elektronische Vorrichtung, welche die Membran von Anspruch 13 , befestigt an einer Elektrodenoberfläche (3), enthält.

15. Elektronische Vorrichtung, die zu diagnostischen Bestimmungen einer chemischen Spezies verwendet wird und als molekulares Präparat, das wesentlich für die Erzeugung einer elektronischen Reaktion wie einer Strom-, Potential-, Leitfähigkeits- oder Kapazitätsänderung ist, wenigstens ein Molekül enthält, das der allgemeinen Formel (1) entspricht, wie sie in Anspruch 1 definiert ist.

Revendications

1. Composé de formule générale (I) :



(I)

dans laquelle

- n représente un entier de 2 à 12,
- les groupes X et Y sont identiques ou différents et représentent des substituants fonctionnels liés à l'azote du groupe pyridine, ou un ou les deux X et Y sont absents, et
- R, étant identique ou différent, représente un atome d'hydrogène ou une chaîne latérale aliphatique introduite pour augmenter la solubilité de la molécule dans des solvants organiques, comme un groupe alkyle ou alcoxy ramifié ou non ramifié contenant n'importe quel nombre d'atomes de carbone,

à l'exclusion du dihalogénure de 5,5'-di(4-pyridyl)-2,2'-bithiényle et de 5,5'-di(1-alkyl-4-pyridinio)-2,2'-bithiényle.

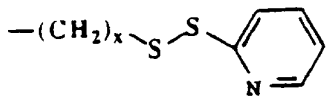
2. Composé selon la revendication 1 caractérisé en ce que un ou les deux groupes X ou Y est une chaîne latérale alkyle aliphatique ramifiée ou non ramifiée contenant un nombre d'atomes de carbone entre 1 et 20.

3. Composé selon la revendication 1 ou 2, caractérisé en ce que un ou les deux groupes X ou Y signifie un groupe amarre utilisé pour la liaison à une surface organique ou minérale comme il est connu dans la technique, tel que:

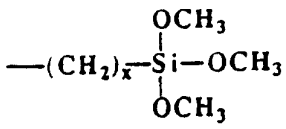
$$-(CH_2)_x\text{-}SH \qquad (1)$$

$$-(CH_2)_x\text{-}S\text{-}S\text{-}(CH_2)_y\text{-}CH_3 \qquad (2)$$

(3)



(4)



dans lequel x et y sont des entiers dans la gamme de 1 à 20.

4. Composé selon l'une quelconque des revendications précédentes, caractérisé en ce que un ou les deux groupes X ou Y signifie un complexe métallique de formule -M - L, dans laquelle M est un ion métallique capable de former une liaison de coordination avec l'azote du groupe pyridine, tel que le cuivre, le nickel, le ruthénium ou l'osmium, et L est un ligand externe mono- ou multi-denditrique ou un groupe fonctionne lié à l'on métallique par une liaison de coordination.

5. Composé selon lune quelconque des revendications précédentes, caractérisé en ce que X ou Y est une protéine redox ou une enzyme redox, soit purifiée directement à partir de systèmes biologiques, à savoir des virus, des bactéries ou des cultures de cellules de mammifères, ou préparée comme étant le résultat d'ingénierie génétique de systèmes biologiques ou comme étant le résultat de techniques de modification chimique *in vitro* de protéines ou comme étant le résultat de combinaisons de ces techniques.

6. Composé selon la revendication 4, caractérisé en ce que le ligand L ou le complexe M - L est une protéine redox ou une enzyme redox, préparée par l'une quelconque des méthodes mentionnées dans la revendication 5.

7. Utilisation d'un composé selon la revendication 1 comme conducteur intrinsèque.

8. Utilisation selon la revendication 7, caractérisée en de que un ou les deux groupes X ou Y est une chaîne latérale alkyle aliphatique ramifiée ou non ramifiée contenant un nombre d'atomes de carbone entre 1 et 20.

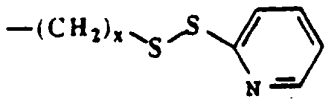
9. Utilisation selon l'une quelconque des revendications 7 et 8, caractérisée en ce que un ou les deux groupes X ou

Y est un groupe amarre utilisé pour la liaison à une surface organique ou minérale comme il est connu dans la technique, tel que

$$-(CH_2)_x\text{-}SH \quad (1)$$

$$-(CH_2)_x\text{-}S\text{-}S\text{-}(CH_2)_y\text{-}CH_3 \quad (2)$$

(3)



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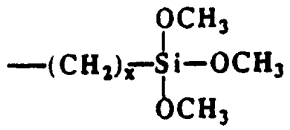


dans lequel x et y sont des entiers dans la gamme de 1 à 20.

10. Utilisation selon lune quelconque des revendications 7 à 9, caractérisée en ce que un ou les deux groupes X ou Y signifie un complexe métallique de formule -M - L, dans laquelle M est un on métallique capable de former une liaison de coordination avec l'azote du groupe pyrdidine, tel que le cuivre, le nickel, le ruthénium ou l'osmium, et L est un ligand externe mono- ou multi-denditrique ou un groupe fonctionnel lié à l'ion métallique par une liaison de coordination.

11. Utilisation selon l'une quelconque des revendications 7 à 10, caractérisée en ce que X ou Y est une protéine redox ou une enzyme redox, soit purifiée directement à partir de systèmes biologiques, à savoir des virus, des bactéries ou des cultures de cellules de mammifères, ou préparée comme étant le résultat d'ingénierie génétique de systèmes biologiques ou comme étant le résultat de techniques de modification chimique *in vitro* de protéines ou comme étant le résultat de combinaisons de ces techniques.

12. Utilisation selon la revendication 10, caractérisée en ce que le ligand L ou le complexe M - L est une protéine redox ou une enzyme redox, préparée par l'une quelconque des méthodes mentionnées dans la revendication 11.

13. Membrane essentiellement isolante (2) pour le passage d'électrons comprenant comme conducteurs électroniques (6) au moins une molécule ayant la formule générale (I) telle que définie dans la revendication 1.

14. Dispositif électronique contenant une membrane selon la revendication 13 attachée à une surface d'électrode (3).

15. Dispositif électronique utilisé pour des déterminations diagnostiques d'une espèce chimique, contenant comme préparation moléculaire essentielle pour la génération d'une réponse électronique, telle qu'une modification dans le courant, le potentiel, la conductivité ou la capacité, d'au moins une molécule ayant la formule générale (I) telle que définie dans la revendication 1.

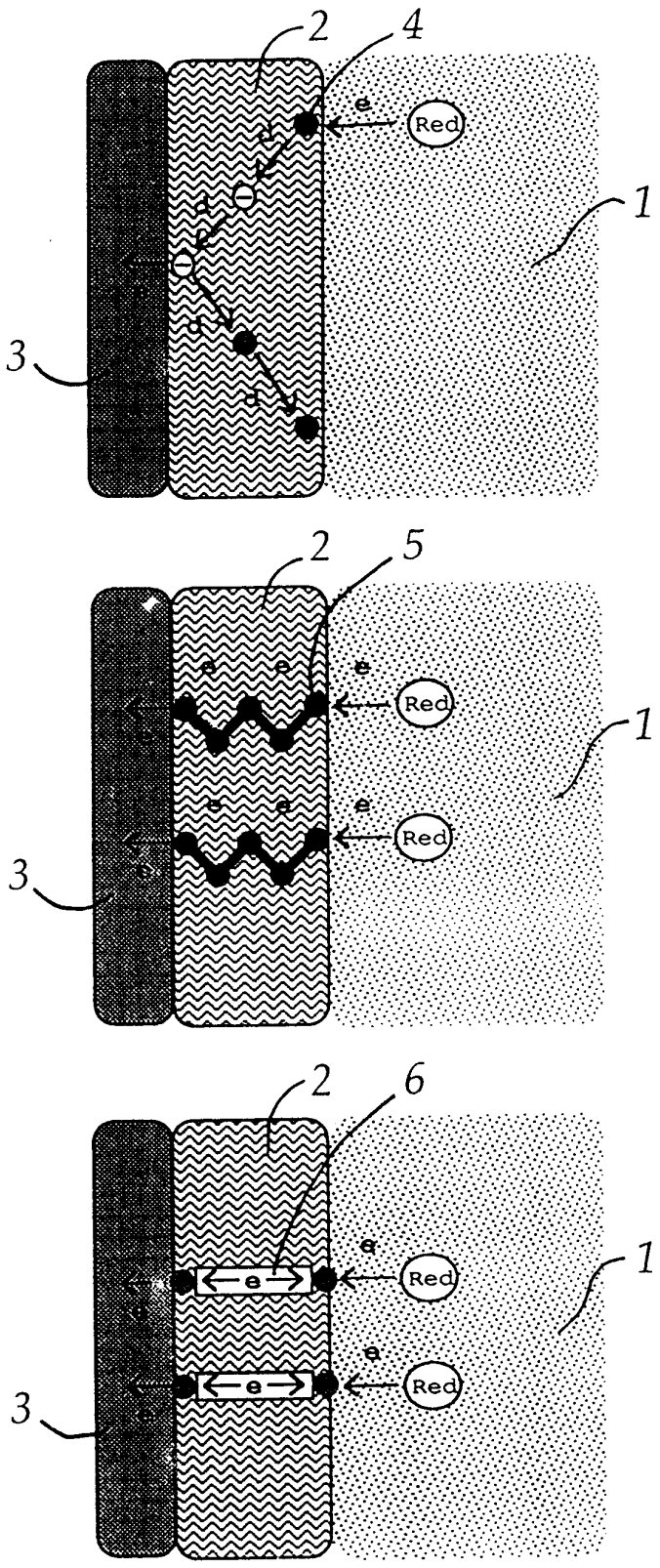
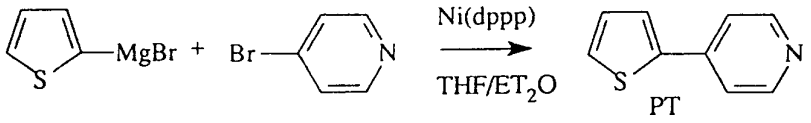
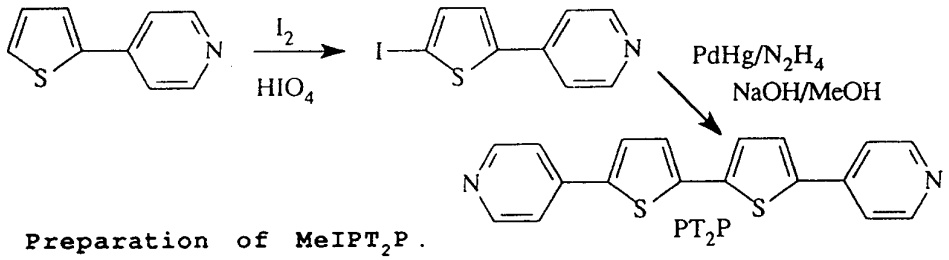


Fig. 1

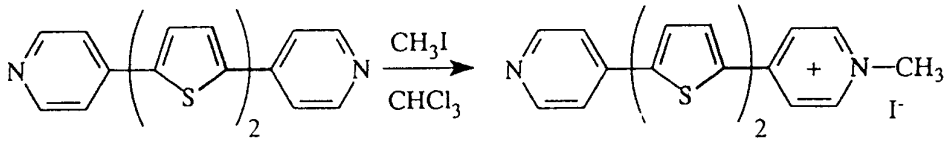
a. Preparation of 2-(4-pyridyl)thiophene, PT.



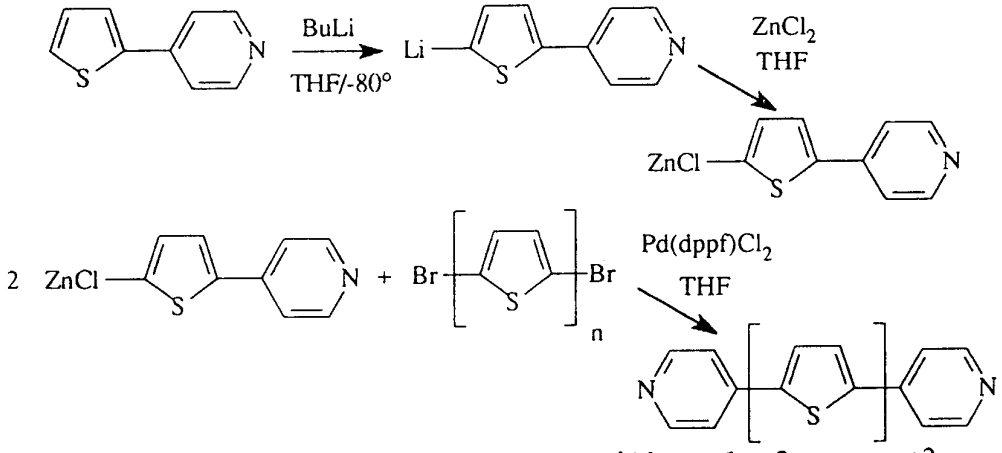
b. Preparation or 5,5'-bi(4-pyridyl)-2,2'-bithiophene, PT_2P.



c. Preparation of $MeIPT_2P$.



d. Preparation of $PT_{(n+2)}P$, with n=1..3.



e. Preparation of $(MeI)_2PT_{(n+2)}P$, with n=1..3.

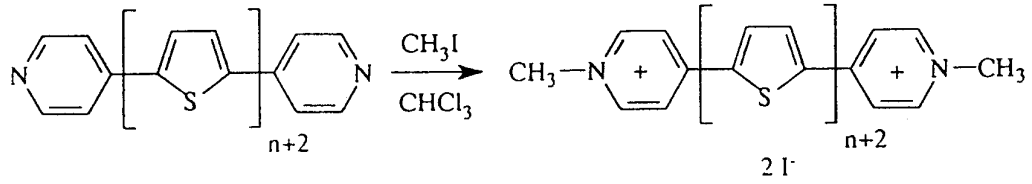


Fig . 2

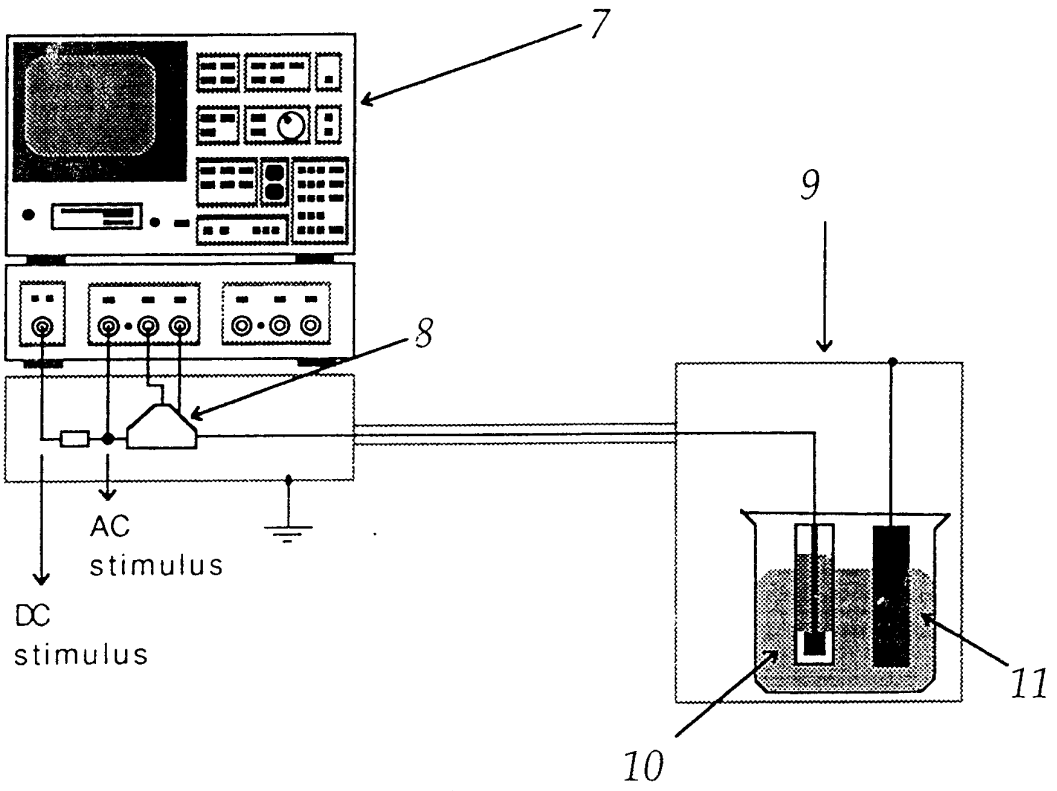


Fig. 3.

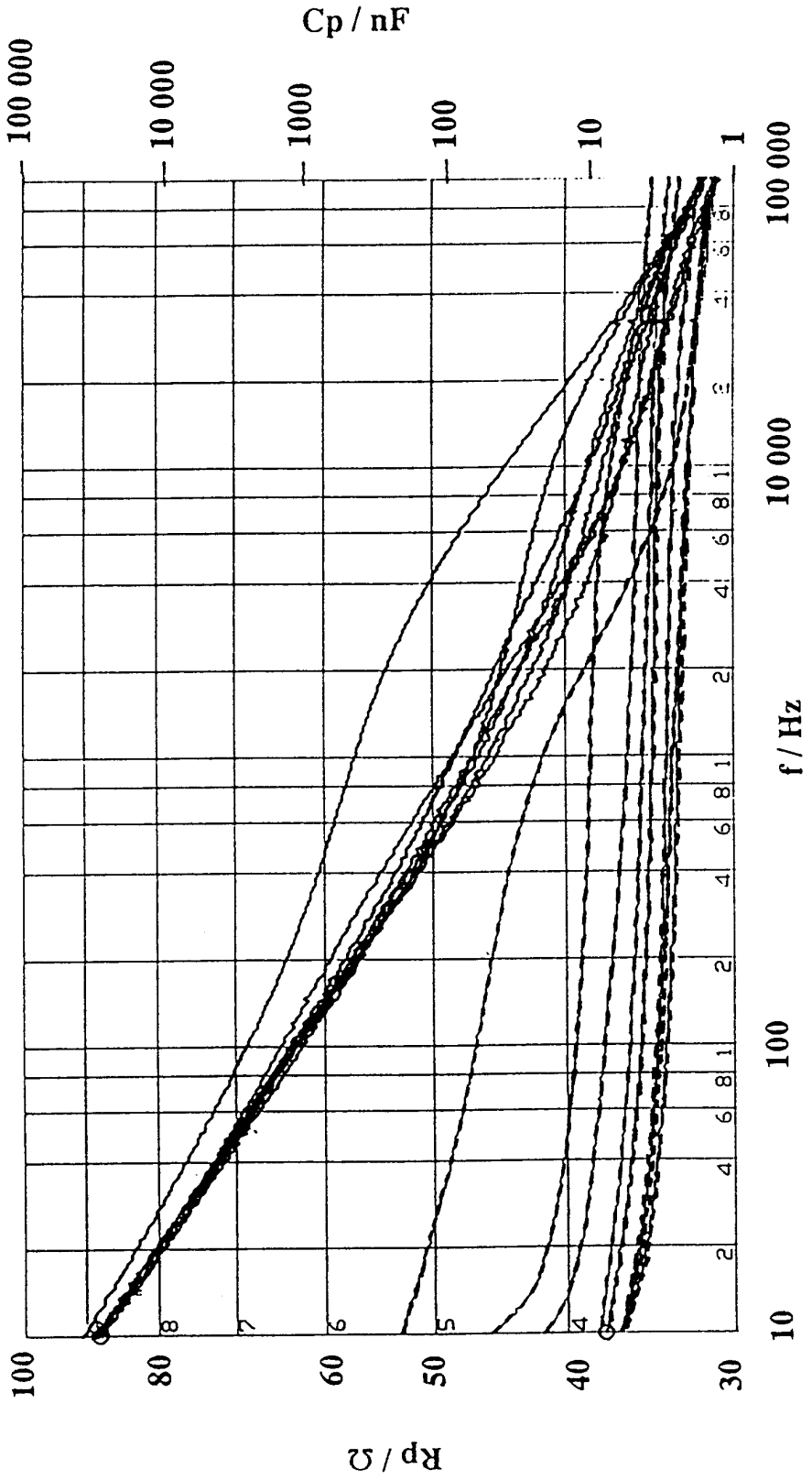
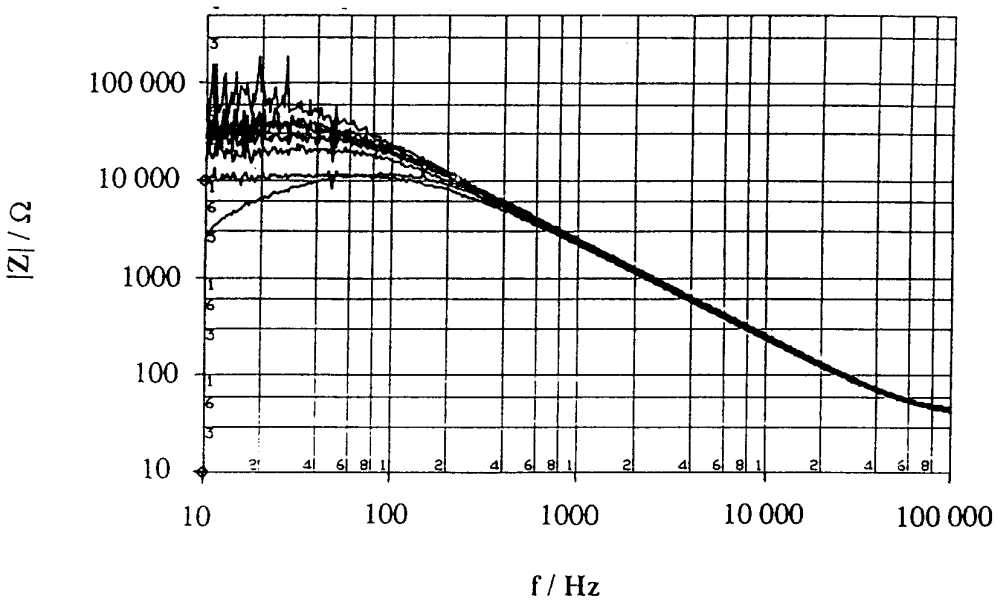

Cp / nF
100 000
10 000
1000
100
10
1
Rp / Ω
100
80
60
50
40
30
f / Hz
10
100
10 000
100 000
Rp
Cp

Fig. 4

a. Modulus |Z| vs. frequency.



b. Phase angle θ vs. frequency.

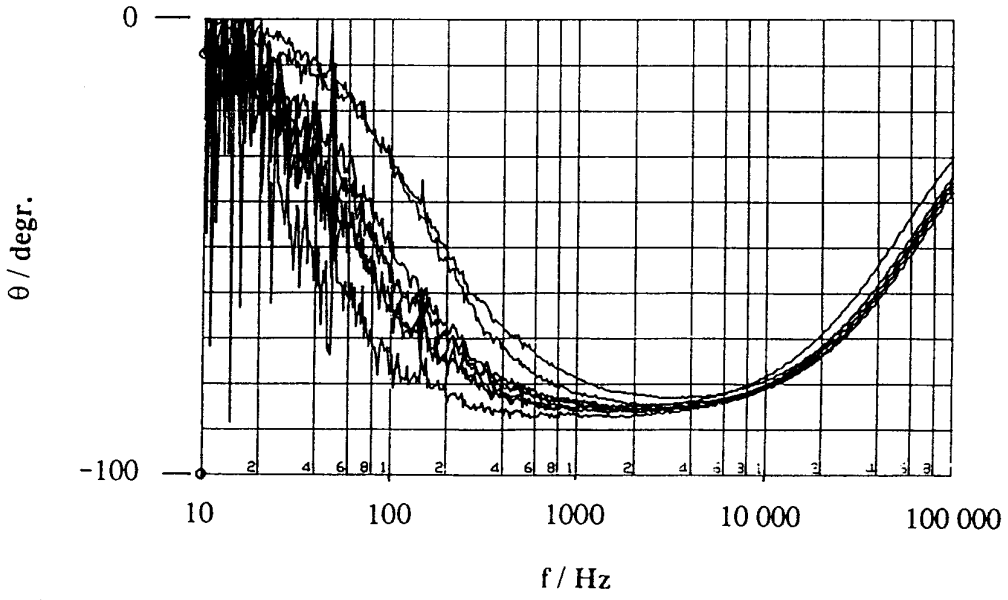
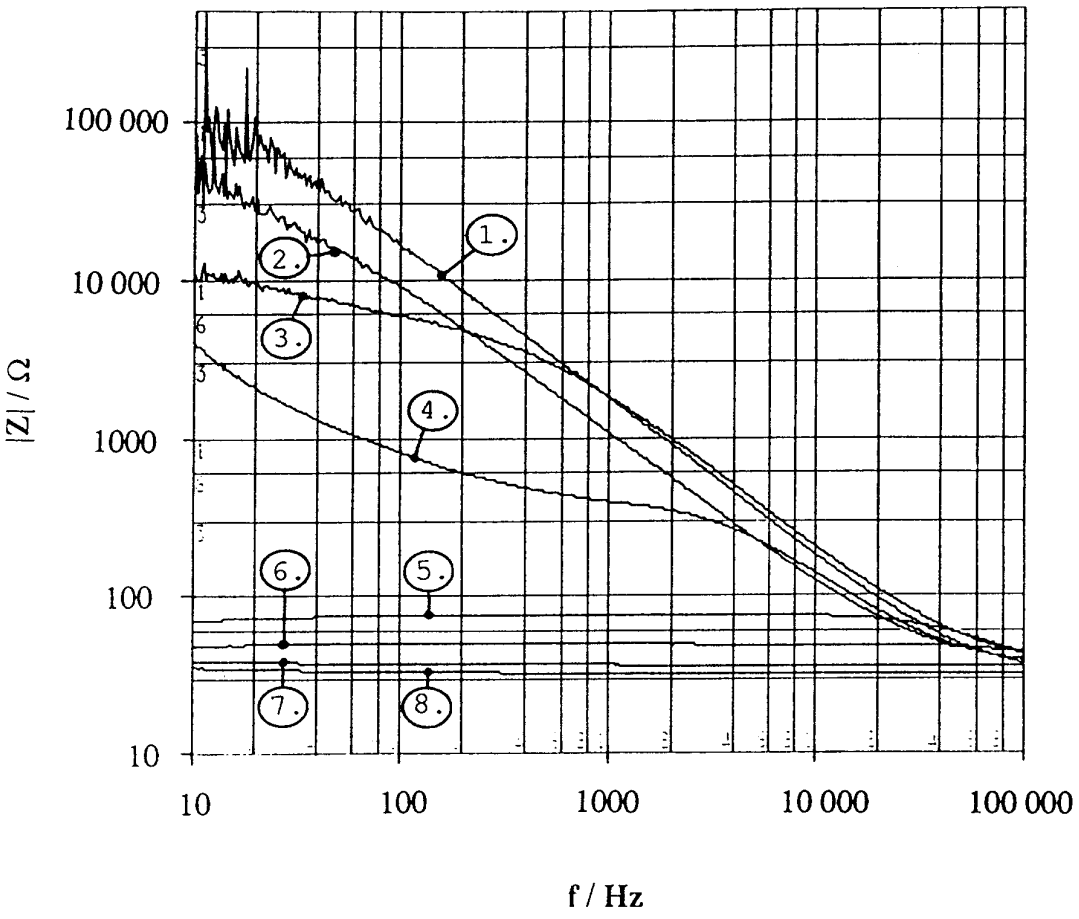


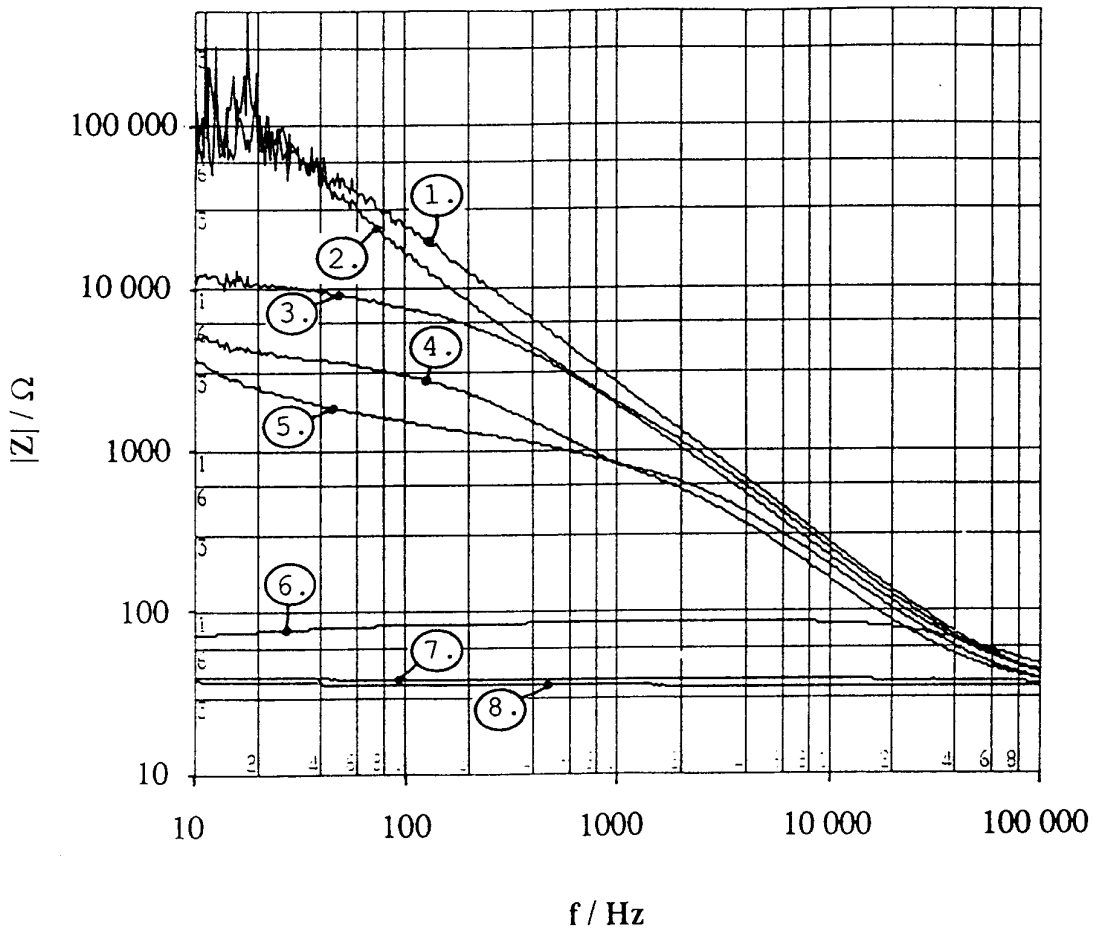
Fig. 5

Fig. 6



1. 5 µM
2. 10 µM
3. 20 µM
4. 30 µM
5. 40 µM
6. 50 µM
7. 100 µM
8. 200 µM

Fig. 7



(1.) 5 µM (2.) 10 µM

(3.) 20 µM (4.) 30 µM

(5.) 40 µM (6.) 50 µM

(7.) 100 µM (8.) 200 µM

Fig. 8

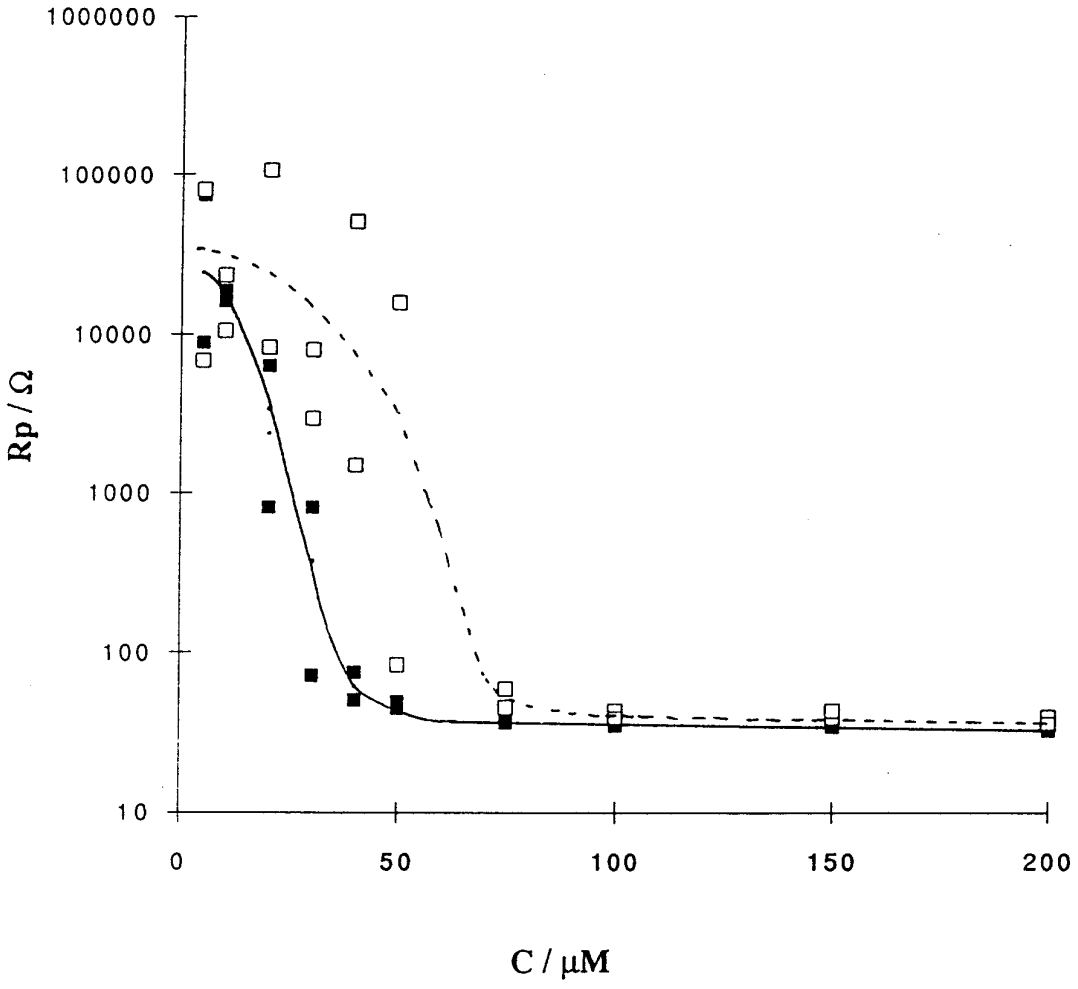
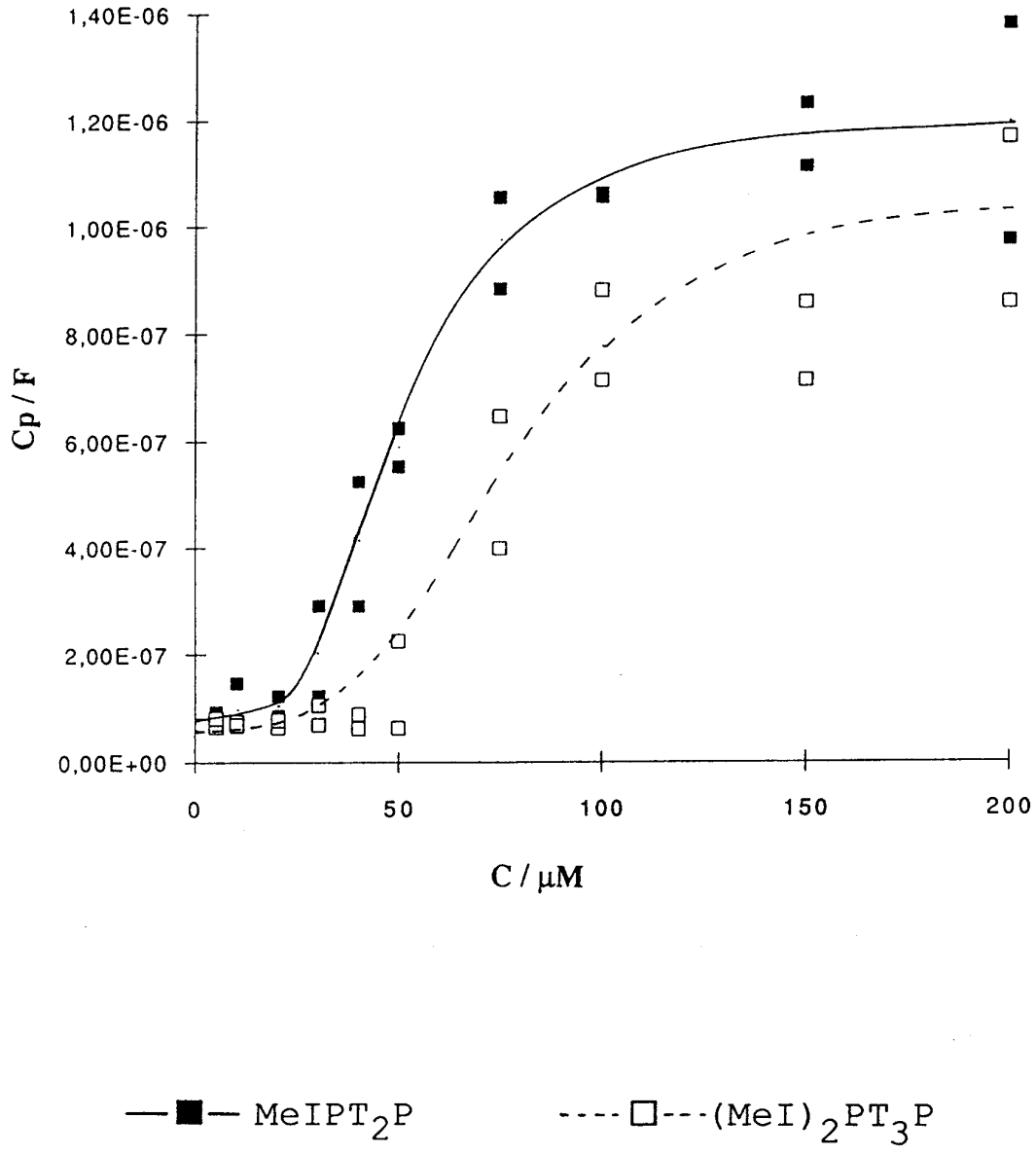

1000000
100000
10000
1000
100
10
Rp / Ω
0
50
100
150
200
C / μM
MeIPT2P
(MeI)2PT3P

Fig. 9


1,40E-06
1,20E-06
1,00E-06
8,00E-07
6,00E-07
4,00E-07
2,00E-07
0,00E+00
Cp / F
0
50
100
150
200
C / µM
MeIPT2P
(MeI)2PT3P