

Description of the invention

Novel tetracyanoanthraquinodimethane polymers and use thereof

5 The invention relates to novel tetracyanoanthraquinodimethane polymers and to the use thereof as active materials in electrical charge storage means such as secondary batteries. In secondary batteries of this kind, the inventive polymers can be used, for example, as active electrode material. These secondary batteries are notable especially for high cell voltages, high power densities and long lifetimes, and also simple and scalable processing and
10 production methods.

The 11,11,12,12-tetracyanoanthraquinodimethane (TCAQ) structures of these novel polymers exhibit exceptional electrochemical behaviour. This features a reversible two-electron redox process, as a result of which the electrical charge storage means have a one-stage charging/discharging plateau among other features.

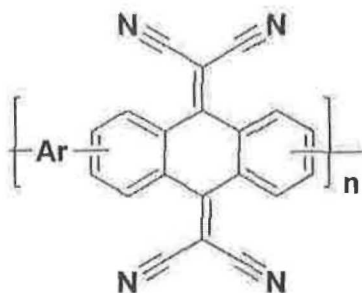
15 11,11,12,12-Tetracyanoanthraquinodimethane polymers are already known as active components in organic electronic components. Thus, copolymers of 11,11,12,12-tetracyanoanthraquinodimethane derivatives with cyclopentadithiophene units in the polymer backbone, synthesized via the Stille reaction, are used as active material in solar
20 cells (CN 103159919 A).

Likewise known is the use of copolymers of 11,11,12,12-tetracyanoanthraquinodimethane derivatives with triarylamine units in the polymer backbone, synthesized via Heck reaction, as active material in solar cells, electroluminescent components and field-effect transistors
25 (CN 102796245 A).

Copolymers of 11,11,12,12-tetracyanoanthraquinodimethane derivatives with metallocene units in the polymer backbone, synthesized via aza-Wittig reaction, are used as polymeric magnets (US 2012/0035330 A1, CA 26995856 A1).

30 Known polymers having 11,11,12,12-tetracyanoanthraquinodimethane units are exclusively polymers in which the 11,11,12,12-tetracyanoanthraquinodimethane unit is localized in the

polymer backbone. A typical structure of these polymers is represented by the following schematic representation:



- 5 In this representation, Ar is a bivalent aromatic group and n is an integer which states the number of repeat units and hence determines the length of the polymer.

The aforementioned 11,11,12,12-tetracyanoanthraquinodimethane polymers are difficult to prepare. The synthesis of these polymers requires two monomers or the synthesis of a bifunctional monomer. The preparation of such monomers comprises a multistage synthesis. In general, the polymerization is conducted by palladium-catalysed cross-couplings (Stille reaction, Heck reaction, Suzuki reaction), which is the reason why the monomer units have to have suitable structures such as boronic acids or esters thereof, double bonds or organic tin compounds.

- 15 The copolymer obtained is often no longer soluble and can therefore be processed only with difficulties. Moreover, there is a high degree of molar mass distribution in the case of these polymerization methods, and the molar mass and yield are usually low. In addition, only conjugated copolymers are preparable for the most part in these known processes.

20 In the case of use in electrical charge storage means, these polymers, as a result of the high molar mass of their repeat units, would have a low mass-to-charge ratio and therefore too low a theoretical capacity for practical applications. The through-conjugation in the polymer backbone causes a change in the redox potential, which would mean that the electrical charge storage means would not have a stable charging/discharging plateau either.

- 25 Therefore, there have been no reports in the specialist field about use of these 11,11,12,12-tetracyanoanthraquinodimethane polymers for electrical charge storage means.

Organic radical batteries are electrochemical cells which use an organic charge storage material as active electrode material for storing electrical charge. These secondary batteries are notable for their exceptional properties, such as fast chargeability, long lifetime, low weight and high flexibility, and also ease of processibility.

5 Some polymeric structures having a redox-active units other than the aforementioned 11,11,12,12-tetracyanoanthraquinodimethane polymers, in contrast, have already become known as active electrode materials for charge storage (for example, WO 2012/133202 A1, WO 2012/133204 A1, WO 2012/120929 A1, WO 2012/153866 A1, WO 2012/153865 A1, 10 JP 2012-221574 A, JP 2012-221575 A, JP 2012-219109 A, JP 2012-079639 A, WO 2012/029556 A1, WO 2012/153865 A1, JP 2011-252106 A, JP 2011-074317 A, JP 2011-165433 A, WO 2011/034117 A1, WO 2010/140512 A1, WO 2010/104002 A1, JP 2010-238403 A, JP 2010-163551 A, JP 2010-114042 A, WO 2010/002002 A1, WO 2009/038125 A1, JP 2009-298873 A, WO 2004/077593 A1, WO 2009/145225 A1, JP 2009-238612 A, JP 15 2009-230951 A, JP 2009-205918 A, JP 2008-234909 A, JP 2008-218326 A, WO 2008/099557 A1, WO 2007/141913 A1, US 2002/0041995 A1, US 2002/0041995 A1, JP 2002-117852 A, EP 1 128 453 A2 disclose polymeric compounds having organic nitroxide radicals as active units for charge storage; US 2002/0041995, JP 2002-117852 A disclose, by way of example, polymeric compounds having organic phenoxy radicals or galvinoxyl radicals). 20

Other known active units for charge storage means are polymeric compounds having quinones (for example JP 2009-217992 A, WO 2013/099567, WO 2011/068217 A1), having diones (such as JP 2010-212152 A), and having dicyanodiimines (for example JP 2012- 25 190545 A, JP 2010-55923 A).

As described, there has been no use to date of the 11,11,12,12-tetracyanoanthraquinodimethane polymers, which are known to the specialist field, for energy storage means, for the reasons mentioned above.

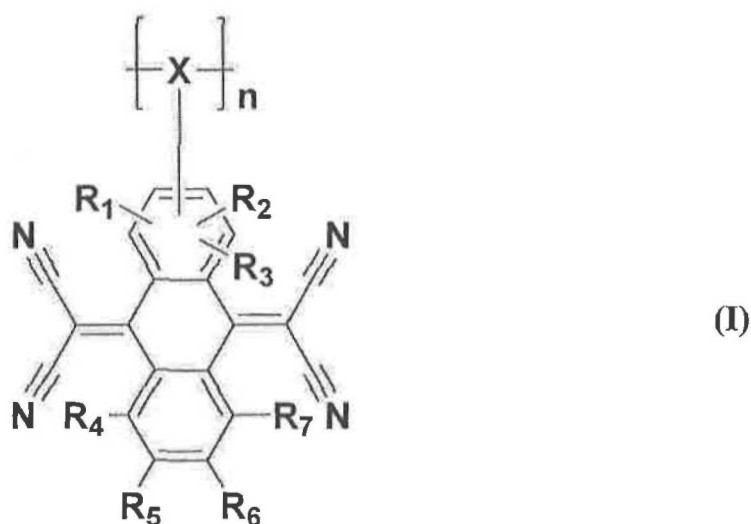
30 The theoretical capacity of the already known polymers having redox-active substituents is strictly limited by two factors: firstly by the molar mass of the monomer unit and secondly by the number of electrons involved in the redox reaction of the electrical charge storage. Most organic redox active units have only a one-electron process which is used for charge

storage and therefore, as noted above, have a low theoretical capacity because of their comparatively high molar mass.

The use of multi-electron redox processes, as is the case, for example, for quinones or dicyanodiimides, increases the theoretical capacity of the material, but these multi-electron processes are interdependent, and so the redox reactions take place at different potentials and hence several unwanted charging/discharging plateaus arise at different cell voltages in the respective electrical charge storage means.

The problem on which the invention is based is therefore that of providing novel polymers which are preparable with a low level of complexity, with the possibility of controlled influence on the physicochemical properties thereof within wide limits in the course of synthesis, and which can be used as active materials in electrical charge storage means for high storage capacity, long lifetime and a flat charging/discharging plateau.

Novel tetracyanoanthraquinodimethane polymers consisting of an oligomeric or polymeric compound of the general formula I have been found:



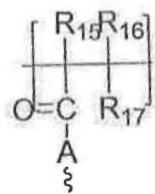
where

R₁ to R₇: may preferably each independently be hydrogen atoms, alkyl groups, alkenyl groups, alkynyl groups, alkoxy groups, alkylthio groups, haloalkyl groups,

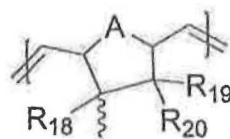
- haloalkoxy groups, cycloalkyl groups, cycloalkoxy groups, aryl groups, heteroaryl groups, aryloxy groups, aralkyl groups, carboxylic acid groups, sulphonic acid groups, amino groups, monoalkylamino groups, dialkylamino groups, nitro groups, cyano groups, hydroxyl groups, alkylcarbonyl groups, alkenylcarbonyl groups, alkynylcarbonyl groups, carboxylic ester groups, carboxamide groups, sulphonic ester groups, thiol groups, halogen atoms or a combination of these groups or atoms, particular preference being given to hydrogen atoms as at least five of the R_1 to R_7 substituents and to non-hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, as zero to two of the R_1 to R_7 substituents,
- X: is an organic group which is formed by polymerization reaction from a group consisting of an organic double bond, an organic triple bond, an oxirane or an aziridine, or is an organic group which is formed by a polymer-analogous reaction,
- n: is an integer greater than or equal to 2.

The organic X group may preferably have a structure of the following formulae II-IV:

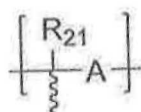




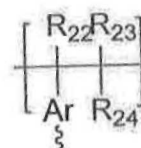
(V)



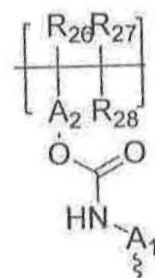
(VI)



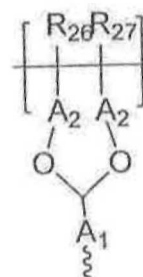
(VII)



(VIII)



(IX)



(X)



where

- 10 R_8 to R_{24} : may preferably each independently be hydrogen atoms, alkyl groups, alkenyl groups, alkynyl groups, alkoxy groups, alkylthio groups, haloalkyl groups, haloalkoxy groups, cycloalkyl groups, cycloalkoxy groups, aryl groups, heteroaryl groups, aryloxy groups, aralkyl groups, carboxylic acid groups, sulphonic acid groups, amino groups, monoalkylamino groups, dialkylamino

groups, nitro groups, cyano groups, hydroxyl groups, alkylcarbonyl groups, alkenylcarbonyl groups, alkynylcarbonyl groups, carboxylic ester groups, carboxamide groups, sulphonic ester groups, thiol groups, halogen atoms or a combination of these groups or atoms, particular preference being given to

5 hydrogen atoms as at least two of the R₈ to R₁₀ substituents and to non-hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, as zero to two of the R₈ to R₁₀ substituents, and/or hydrogen atoms as at least two of the R₁₁ to R₁₃ substituents and to non-hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano

10 groups and/or nitro groups, as zero to one of the R₁₁ to R₁₃ substituents, and/or a hydrogen atom as R₁₄, and/or hydrogen atoms as at least two of the R₁₅ to R₁₇ substituents and to non-hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, as zero to one of the R₁₅ to R₁₇ substituents, and/or

15 hydrogen atoms as at least two of the R₁₈ to R₂₀ substituents and to non-hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, as zero to one of the R₁₈ to R₂₀ substituents, and/or a hydrogen atom as R₂₁, and/or hydrogen atoms as at least two of the R₂₂ to R₂₄ substituents and to non-

20 hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, as zero to one of the R₂₂ to R₂₄ substituents,

R₂₆ to R₂₈: may preferably each independently be hydrogen atoms, alkyl groups, alkenyl groups, alkynyl groups, alkoxy groups, alkylthio groups, haloalkyl groups, haloalkoxy groups, cycloalkyl groups, cycloalkoxy groups, aryl groups,

25 heteroaryl groups, aryloxy groups, aralkyl groups, carboxylic acid groups, sulphonic acid groups, amino groups, monoalkylamino groups, dialkylamino groups, nitro groups, cyano groups, hydroxyl groups, alkylcarbonyl groups, alkenylcarbonyl groups, alkynylcarbonyl groups, carboxylic ester groups, carboxamide groups, sulphonic ester groups, thiol groups, halogen atoms or a

30 combination of these groups or atoms, particular preference being given to hydrogen atoms as at least two of the R₂₆ to R₂₈ substituents and to non-

hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, as zero to one of the R₂₆ to R₂₈ substituents,

5 R₃₀ to R₃₂: may preferably each independently be hydrogen atoms, alkyl groups, alkenyl groups, alkynyl groups, alkoxy groups, alkylthio groups, haloalkyl groups, haloalkoxy groups, cycloalkyl groups, cycloalkoxy groups, aryl groups, heteroaryl groups, aryloxy groups, aralkyl groups, carboxylic acid groups, sulphonic acid groups, amino groups, monoalkylamino groups, dialkylamino groups, nitro groups, cyano groups, alkylcarbonyl groups, alkenylcarbonyl groups, alkynylcarbonyl groups, carboxylic ester groups, carboxamide groups, 10 sulphonic ester groups, halogen atoms or a combination of these groups or atoms, particular preference being given to hydrogen atoms as at least two of the R₃₀ to R₃₂ substituents and to non-hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, as zero to one of the R₃₀ to R₃₂ substituents,

15 R₃₃ to R₃₅: may preferably each independently be hydrogen atoms, alkyl groups, alkenyl groups, alkoxy groups, alkylthio groups, haloalkyl groups, haloalkoxy groups, cycloalkyl groups, cycloalkoxy groups, aryl groups, heteroaryl groups, aryloxy groups, aralkyl groups, carboxylic acid groups, sulphonic acid groups, amino groups, monoalkylamino groups, dialkylamino groups, nitro groups, cyano groups, hydroxyl groups, alkylcarbonyl groups, alkenylcarbonyl groups, 20 alkynylcarbonyl groups, carboxylic ester groups, carboxamide groups, sulphonic ester groups, thiol groups, halogen atoms or a combination of these groups or atoms, particular preference being given to hydrogen atoms as at least two of the R₃₃ to R₃₅ substituents and to non-hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, 25 as zero to one of the R₃₃ to R₃₅ substituents,

A: is an oxygen atom, a sulphur atom or an -N(R₂₉)- group, where R₂₉ is preferably a hydrogen atom, alkyl group, alkenyl group, alkynyl group, alkoxy group, alkylthio group, haloalkyl group, haloalkoxy group, cycloalkyl group, 30 cycloalkoxy group, aryl group, heteroaryl group, aryloxy group, aralkyl group, carboxylic acid group, sulphonic acid group, nitro group, alkylcarbonyl group,

alkenylcarbonyl group, alkynylcarbonyl group, carboxylic ester group, carboxamide group, sulphonic ester group, particular preference being given to an oxygen atom as A,

5 A₁ and A₂: are preferably each independently a covalent bond, an alkyl group, an alkenyl group, an alkynyl group, an alkoxy group, an alkylthio group, a haloalkyl group, a haloalkoxy group, a cycloalkyl group, a cycloalkoxy group, an aryl group, a heteroaryl group, an aryloxy group, an aralkyl group, a monoalkylamino group, a dialkylamino group, an alkylcarbonyl group, an alkenylcarbonyl group, an alkynylcarbonyl group, a carboxylic ester group, a carboxamide group, a sulphonic ester group, particular preference being given
10 to a covalent bond or an alkyl group as A₁ and A₂,

A₃ and A₄: may preferably each independently be a covalent bond, an alkyl group, an alkenyl group, an alkynyl group, an alkoxy group, an alkylthio group, a cycloalkyl group, a cycloalkoxy group, an aryl group, a heteroaryl group, an
15 aryloxy group, an aralkyl group, a dialkylamino group, an alkylcarbonyl group, an alkenylcarbonyl group, an alkynylcarbonyl group, a carboxylic ester group, a carboxamide group, a sulphonic ester group, particular preference being given to a covalent bond or an alkyl group as A₁ and A₂,

A₅ and A₆: may preferably each independently be a covalent bond, an alkyl group, an
20 alkenyl group, an alkoxy group, an alkylthio group, a haloalkyl group, a haloalkoxy group, a cycloalkyl group, a cycloalkoxy group, an aryl group, a heteroaryl group, an aryloxy group, an aralkyl group, a monoalkylamino group, a dialkylamino group, an alkylcarbonyl group, an alkenylcarbonyl group, an alkynylcarbonyl group, a carboxylic ester group, a carboxamide group, a
25 sulphonic ester group, particular preference being given to a covalent bond, an aryl group or an alkyl group as A₅ and A₆,

Ar: is an independently substituted cycloalkyl group, cycloalkoxy group, aryl group, heteroaryl group, aryloxy group, aralkyl group.

30 Novel polymers containing 11,11,12,12-tetracyanoanthraquinodimethane units as the pendant group on the polymer backbone have been synthesized. These polymers have excellent properties, especially as redox active electrode material in anodes or cathodes for

secondary electrical charge storage means. The dependent claims specify advantageous possible uses of the inventive tetracyanoanthraquinodimethane polymers.

These novel polymers can be prepared in a simple and uncomplicated manner, and from readily obtainable starting materials. No further monomer is needed for the polymerization, and the polymerization does not require any costly metal catalysts; instead, it is possible to use simple polymerization processes as the production method. At the same time, it is possible to obtain polymers having a high molar mass and low polydispersity index in very high yields. The introduction of polymerizable groups of low molar mass makes it possible to keep the molar mass of the monomer low and to maximize the theoretical capacity of the secondary electrical charge storage means. In addition, the redox active groups in these polymers are not conjugated to one another; as a consequence, the electrical charge storage means has a flat charging/discharging plateau. These materials differ from the prior art by a two-electron redox reaction which leads to said flat charging/discharging plateau, combined with simultaneously high capacity and long lifetime in the component.

In the description which follows, n is defined as normal, i as iso, s as secondary, t as tertiary, c as cyclo, m as meta, p as para and o as ortho.

In this specification, an alkyl group may be either branched or unbranched. An alkyl group typically consists of one up to thirty carbon atoms, preferably of one up to twenty carbon atoms. Examples of an alkyl group are: methyl group, ethyl group, propyl group, isopropyl group, n-butyl group, sec-butyl group, t-butyl group, pentyl group, n-hexyl group, n-heptyl group, 2-ethylhexyl group, n-octyl group, n-nonyl group, n-decyl group, n-undecyl group, n-dodecyl group, n-tridecyl group, n-tetradecyl group, n-pentadecyl group, n-hexadecyl group, n-heptadecyl group, n-octadecyl group, n-nonadecyl group or eicosyl group. Particular preference is given to alkyl groups having one to six carbon atoms.

In this specification, an alkenyl group may be either branched or unbranched. An alkenyl group typically consists of one up to thirty carbon atoms, preferably of one up to twenty carbon atoms. Alkenyl groups typically have one unsaturated ethenylic double bond; the remaining proportion of the alkenyl group is saturated. Two or more ethenylic unsaturated double bonds are possible but not preferred. The unsaturated ethenylic double bond is more preferably at the alpha position in the alkenyl group. Examples of an alkenyl group are: vinyl

group, allyl group, propenyl group, isopropenyl group, n-butenyl group, sec-butenyl group, pentenyl group, n-hexenyl group, n-heptenyl group, 2-ethylhexenyl group, n-octenyl group, n-nonenyl group, n-decenyl group, n-undecenyl group, n-dodecenyl group, n-tridecenyl group, n-tetradecenyl group, n-pentadecenyl group, n-hexadecenyl group, n-heptadecenyl group, n-octadecenyl group, n-nonadecenyl group or eicosenyl group. Preference is given to alkenyl groups having two to three carbon atoms; particular preference is given to vinyl groups and allyl groups.

In this specification, an alkynyl group may be either branched or unbranched. An alkynyl group typically consists of two up to thirty carbon atoms, preferably of one up to twenty carbon atoms. Alkynyl groups typically have one unsaturated ethynylic triple bond; the remaining proportion of the alkynyl group is saturated. Two or more ethynylic unsaturated triple bonds are possible but not preferred. The unsaturated ethynylic double bond is more preferably at the alpha position in the alkynyl group. Examples of an alkynyl group are: ethynyl group, propynyl group, butynyl group, pentynyl group, n-hexynyl group, n-heptynyl group, 2-ethylhexynyl group, n-octynyl group, n-nonynynyl group, n-decynyl group, n-undecynyl group, n-dodecynyl group, n-tridecynyl group, n-tetradecynyl group, n-pentadecynyl group, n-hexadecynyl group, n-heptadecynyl group, n-octadecynyl group, n-nonadecynyl group or eicosynyl group. Preference is given to alkynyl groups having two carbon atoms.

In this specification, an alkylthio group may be either branched or unbranched. An alkylthio group typically consists of one up to thirty carbon atoms and one or more sulphur atoms bonded covalently to two carbon atoms in the chain, preferably of one to twenty carbon atoms and one sulphur atom. Examples of an alkylthio group are: methylthio group, ethylthio group, n-propylthio group, i-propylthio group, n-butylthio group, s-butylthio group, t-butylthio group, n-pentylthio group, 1-methylbutylthio group, 2-methylbutylthio group, 3-methylbutylthio group, 1,1-dimethylpropylthio group, 2,2-dimethylpropylthio group, n-hexylthio group, 1-methylpentylthio group, 2-methylpentylthio group, 1,1-dimethylbutylthio group, 1-ethylbutylthio group, 1,1,2-trimethylpropylthio group, n-heptylthio group, n-octylthio group, 2-ethylhexylthio group, n-nonylthio group, n-decylthio group, n-dodecylthio group.

In this specification, a monoalkylamino group may be either branched or unbranched. A monoalkylamino group typically consists of one up to thirty carbon atoms and one or more nitrogen atoms bonded covalently to two carbon atoms in the chain, preferably of one to twenty carbon atoms and one nitrogen atom. Examples of a monoalkylamino group are:

- 5 methylamino group, ethylamino group, n-propylamino group, i-propylamino group, c-propylamino group, n-butylamino group, i-butylamino group, s-butylamino group, t-butylamino group, c-butylamino group, 1-methyl-c-propylamino group, 2-methyl-c-propylamino group, n-pentylamino group, 1-methyl-n-butylamino group, 2-methyl-n-butylamino group, 3-methyl-n-butylamino group, 1,1-dimethyl-n-propylamino group, 1,2-
10 dimethyl-n-propylamino group, 2,2-dimethyl-n-propylamino group, 1-ethyl-n-propylamino group, c-pentylamino group, 1-methyl-c-butylamino group, 2-methyl-c-butylamino group, 3-methyl-c-butylamino group, 1,2-dimethyl-c-propylamino group, 2,3-dimethyl-c-propylamino group, 1-ethyl-c-propylamino group, 2-ethyl-c-propylamino group, n-hexylamino group, 1-methyl-n-pentylamino group, 2-methyl-n-pentylamino group, 3-
15 methyl-n-pentylamino group, 4-methyl-n-pentylamino group, 1,1-dimethyl-n-butylamino group, 1,2-dimethyl-n-butylamino group, 1,3-dimethyl-n-butylamino group, 2,2-dimethyl-n-butylamino group, 2,3-dimethyl-n-butylamino group, 3,3-dimethyl-n-butylamino group, 1-ethyl-n-butylamino group, 2-ethyl-n-butylamino group, 1,1,2-trimethyl-n-propylamino group, 1,2,2-trimethyl-n-propylamino group, 1-ethyl-1-methyl-n-propylamino group, 1-
20 ethyl-2-methyl-n-propylamino group, c-hexylamino group, 1-methyl-c-pentylamino group, 2-methyl-c-pentylamino group, 3-methyl-c-pentylamino group, 1-ethyl-c-butylamino group, 2-ethyl-c-butylamino group, 3-ethyl-c-butylamino group, 1,2-dimethyl-c-butylamino group, 1,3-dimethyl-c-butylamino group, 2,2-dimethyl-c-butylamino group, 2,3-dimethyl-c-butylamino group, 2,4-dimethyl-c-butylamino group, 3,3-dimethyl-c-butylamino group, 1-
25 n-propyl-c-propylamino group, 2-n-propyl-c-propylamino group, 1-i-propyl-c-propylamino group, 2-i-propyl-c-propylamino group, 1,2,2-trimethyl-c-propylamino group, 1,2,3-trimethyl-c-propylamino group, 2,2,3-trimethyl-c-propylamino group, 1-ethyl-2-methyl-c-propylamino group, 2-ethyl-1-methyl-c-propylamino group, 2-ethyl-2-methyl-c-propylamino group, 2-ethyl-3-methyl-c-propylamino group.

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In this specification, a dialkylamino group may be either branched or unbranched. A dialkylamino group typically consists of one up to thirty carbon atoms and one or more nitrogen atoms bonded covalently to three carbon atoms in the chain, preferably of one to

twenty carbon atoms and one nitrogen atom. Examples of a dialkylamino group are: di-i-propylamino group, di-c-propylamino group, di-n-butylamino group, di-i-butylamino group, di-s-butylamino group, di-t-butylamino group, di-c-butylamino group, di(1-methyl-c-propyl)amino group, di(2-methyl-c-propyl)amino group, di-n-pentylamino group, di(1-methyl-n-butyl)amino group, di(2-methyl-n-butyl)amino group, di(3-methyl-n-butyl)amino group, di(1,1-dimethyl-n-propyl)amino group, di(1,2-dimethyl-n-propyl)amino group, di(2,2-dimethyl-n-propyl)amino group, di(1-ethyl-n-propyl)amino group, di-c-pentylamino group, di(1-methyl-c-butyl)amino group, di(2-methyl-c-butyl)amino group, di(3-methyl-c-butyl)amino group, di(1,2-dimethyl-c-propyl)amino group, di(2,3-dimethyl-c-propyl)amino group, di(1-ethyl-c-propyl)amino group, di(2-ethyl-c-propyl)amino group, di-n-hexylamino group, di(1-methyl-n-pentyl)amino group, di(2-methyl-n-pentyl)amino group, di(3-methyl-n-pentyl)amino group, di(4-methyl-n-pentyl)amino group, di(1,1-dimethyl-n-butyl)amino group, di(1,2-dimethyl-n-butyl)amino group, di(1,3-dimethyl-n-butyl)amino group.

In this specification, a haloalkyl group may be either branched or unbranched. A haloalkyl group typically consists of one up to thirty carbon atoms which may in turn each independently be substituted by one or more halogen atoms, preferably of one to twenty carbon atoms. Examples of halogen atoms are the fluorine atom, chlorine atom, bromine atom and iodine atom. Preference is given to the fluorine atom and the chlorine atom. Examples of a haloalkyl group are: difluoromethoxy group, trifluoromethoxy group, bromodifluoromethoxy group, 2-chloroethoxy group, 2-bromoethoxy group, 1,1-difluoroethoxy group, 2,2,2-trifluoroethoxy group, 1,1,2,2-tetrafluoroethoxy group, 2-chloro-1,1,2-trifluoroethoxy group, pentafluoroethoxy group, 3-bromopropoxy group, 2,2,3,3-tetrafluoropropoxy group, 1,1,2,3,3,3-hexafluoropropoxy group, 1,1,1,3,3,3-hexafluoropropoxy group, 3-bromo-2-methylpropoxy group, 4-bromobutoxy group, perfluoropentyloxy group.

In this specification, a haloalkoxy group may be either branched or unbranched. A haloalkoxy group typically consists of an oxygen atom with a chain consisting of one up to thirty carbon atoms covalently bonded thereto, which may be either branched or unbranched, and wherein the carbon atoms may in turn each independently be substituted by one or more halogen atoms. This chain preferably consists of one to twenty carbon atoms. Examples of halogen atoms are the fluorine atom, chlorine atom, bromine atom and iodine atom.

Preference is given to the fluorine atom and the chlorine atom. Examples of a haloalkoxy group are: difluoromethoxy group, trifluoromethoxy group, bromodifluoromethoxy group, 2-chloroethoxy group, 2-bromoethoxy group, 1,1-difluoroethoxy group, 2,2,2-trifluoroethoxy group, 1,1,2,2-tetrafluoroethoxy group, 2-chloro-1,1,2-trifluoroethoxy group, pentafluoroethoxy group, 3-bromopropoxy group, 2,2,3,3-tetrafluoropropoxy group, 1,1,2,3,3,3-hexafluoropropoxy group, 1,1,1,3,3,3-hexafluoropropoxy group, 3-bromo-2-methylpropoxy group, 4-bromobutoxy group, perfluoropentoxy group.

An alkylcarbonyl group in this specification typically consists of a carbonyl carbon with an alkyl group consisting of one up to thirty carbon atoms bonded covalently thereto, which may be either branched or unbranched. This chain preferably consists of one to twenty carbon atoms. Examples of an alkylcarbonyl group are: methylcarbonyl group, ethylcarbonyl group, n-propylcarbonyl group, i-propylcarbonyl group, c-propylcarbonyl group, n-butylcarbonyl group, i-butylcarbonyl group, s-butylcarbonyl group, t-butylcarbonyl group, c-butylcarbonyl group, 1-methyl-c-propylcarbonyl group, 2-methyl-c-propylcarbonyl group, n-pentylcarbonyl group, 1-methyl-n-butylcarbonyl group, 2-methyl-n-butylcarbonyl group, 3-methyl-n-butylcarbonyl group, 1,1-dimethyl-n-propylcarbonyl group, 1,2-dimethyl-n-propylcarbonyl group, 2,2-dimethyl-n-propylcarbonyl group, 1-ethyl-n-propylcarbonyl group, c-pentylcarbonyl group, 1-methyl-c-butylcarbonyl group, 2-methyl-c-butylcarbonyl group, 3-methyl-c-butylcarbonyl group, 1,2-dimethyl-c-propylcarbonyl group, 2,3-dimethyl-c-propylcarbonyl group, 1-ethyl-c-propylcarbonyl group, 2-ethyl-c-propylcarbonyl group, n-hexylcarbonyl group, 1-methyl-n-pentylcarbonyl group, 2-methyl-n-pentylcarbonyl group, 3-methyl-n-pentylcarbonyl group, 4-methyl-n-pentylcarbonyl group, 1,1-dimethyl-n-butylcarbonyl group, 1,2-dimethyl-n-butylcarbonyl group, 1,3-dimethyl-n-butylcarbonyl group, 2,2-dimethyl-n-butylcarbonyl group, 2,3-dimethyl-n-butylcarbonyl group, 3,3-dimethyl-n-butylcarbonyl group, 1-ethyl-n-butylcarbonyl group, 2-ethyl-n-butylcarbonyl group.

An alkenylcarbonyl group in this specification typically consists of a carbonyl carbon with an alkenyl group consisting of one up to thirty carbon atoms bonded covalently thereto, which may be either branched or unbranched. This chain preferably consists of one to twenty carbon atoms. Examples of an alkenylcarbonyl group are: ethenylcarbonyl group, 1-propenylcarbonyl group, 2-propenylcarbonyl group, 1-methyl-1-ethenylcarbonyl group, 1-

butenylcarbonyl group, 2-butenylcarbonyl group, 3-butenylcarbonyl group, 2-methyl-1-propenylcarbonyl group, 2-methyl-2-propenylcarbonyl group, 1-ethylethenylcarbonyl group, 1-methyl-1-propenylcarbonyl group, 1-methyl-2-propenylcarbonyl group, 1-pentenylcarbonyl group, 2-pentenylcarbonyl group, 3-pentenylcarbonyl group, 4-pentenylcarbonyl group, 1-n-propylethenylcarbonyl group, 1-methyl-1-butenylcarbonyl group, 1-methyl-2-butenylcarbonyl group, 1-methyl-3-butenylcarbonyl group, 2-ethyl-2-propenylcarbonyl group, 2-methyl-1-butenylcarbonyl group, 2-methyl-2-butenylcarbonyl group, 2-methyl-3-butenylcarbonyl group, 3-methyl-1-butenylcarbonyl group, 3-methyl-2-butenylcarbonyl group, 3-methyl-3-butenylcarbonyl group, 1,1-dimethyl-2-propenylcarbonyl group, 1-i-propylethenylcarbonyl group, 1,2-dimethyl-1-propenylcarbonyl group, 1,2-dimethyl-2-propenylcarbonyl group, 1-c-pentenylcarbonyl group, 2-c-pentenylcarbonyl group, 3-c-pentenylcarbonyl group, 1-hexenylcarbonyl group, 2-hexenylcarbonyl group, 3-hexenylcarbonyl group, 4-hexenylcarbonyl group, 5-hexenylcarbonyl group, 1-methyl-1-pentenylcarbonyl group, 1-methyl-2-pentenylcarbonyl group, 1-methyl-3-pentenylcarbonyl group, 1-methyl-4-pentenylcarbonyl group, 1-n-butylethenylcarbonyl group, 2-methyl-1-pentenylcarbonyl group, 2-methyl-2-pentenylcarbonyl group, 2-methyl-3-pentenylcarbonyl group, 2-methyl-4-pentenylcarbonyl group, 2-n-propyl-2-propenylcarbonyl group, 3-methyl-1-pentenylcarbonyl group, 3-methyl-2-pentenylcarbonyl group.

20 An alkynylcarbonyl group in this specification typically consists of a carbonyl carbon with an alkynyl group consisting of one up to thirty carbon atoms bonded covalently thereto, which may be either branched or unbranched. This chain preferably consists of one to twenty carbon atoms. Examples of an alkynylcarbonyl group are: ethynylcarbonyl group, 1-propynylcarbonyl group, 2-propynylcarbonyl group, 1-butylnylcarbonyl group, 2-butylnylcarbonyl group, 3-butylnylcarbonyl group, 1-methyl-2-propynylcarbonyl group, 1-pentylnylcarbonyl group, 2-pentylnylcarbonyl group, 3-pentylnylcarbonyl group, 4-pentylnylcarbonyl group, 1-methyl-2-butylnylcarbonyl group, 1-methyl-3-butylnylcarbonyl group, 2-methyl-3-butylnylcarbonyl group, 3-methyl-1-butylnylcarbonyl group, 1,1-dimethyl-2-propynylcarbonyl group, 2-ethyl-2-propynylcarbonyl group, 1-hexynylcarbonyl group, 2-hexynylcarbonyl group, 3-hexynylcarbonyl group, 4-hexynylcarbonyl group, 5-hexynylcarbonyl group, 1-methyl-2-pentylnylcarbonyl group, 1-methyl-3-pentylnylcarbonyl group, 1-methyl-4-pentylnylcarbonyl group, 2-methyl-3-pentylnylcarbonyl group, 2-methyl-

4-pentynylcarbonyl group, 3-methyl-1-pentynylcarbonyl group, 3-methyl-4-pentynylcarbonyl group, 4-methyl-1-pentynylcarbonyl group, 4-methyl-2-pentynylcarbonyl group, 1,1-dimethyl-2-butynylcarbonyl group, 1,1-dimethyl-3-butynylcarbonyl group, 1,2-dimethyl-3-butynylcarbonyl group, 2,2-dimethyl-3-butynylcarbonyl group, 3,3-dimethyl-1-butynylcarbonyl group, 1-ethyl-2-butynylcarbonyl group, 1-ethyl-3-butynylcarbonyl group.

An alkylcarboxylic ester group in this specification typically consists of a carboxylic ester with an alkyl group consisting of one up to thirty carbon atoms bonded covalently thereto, which may be either branched or unbranched. This chain preferably consists of one to twenty carbon atoms. Examples of an alkylcarboxylic ester group are: methylcarboxylic ester group, ethylcarboxylic ester group, n-propylcarboxylic ester group, i-propylcarboxylic ester group, c-propylcarboxylic ester group, n-butylcarboxylic ester group, i-butylcarboxylic ester group, s-butylcarboxylic ester group, t-butylcarboxylic ester group, c-butylcarboxylic ester group, 1-methyl-c-propylcarboxylic ester group, 2-methyl-c-propylcarboxylic ester group, n-pentylcarboxylic ester group, 1-methyl-n-butylcarboxylic ester group, 2-methyl-n-butylcarboxylic ester group, 3-methyl-n-butylcarboxylic ester group, 1,1-dimethyl-n-propylcarboxylic ester group, 1,2-dimethyl-n-propylcarboxylic ester group, 2,2-dimethyl-n-propylcarboxylic ester group, 1-ethyl-n-propylcarboxylic ester group, c-pentylcarboxylic ester group, 1-methyl-c-butylcarboxylic ester group, 2-methyl-c-butylcarboxylic ester group, 3-methyl-c-butylcarboxylic ester group, 1,2-dimethyl-c-propylcarboxylic ester group, 2,3-dimethyl-c-propylcarboxylic ester group, 1-ethyl-c-propylcarboxylic ester group, 2-ethyl-c-propylcarboxylic ester group, n-hexylcarboxylic ester group, 1-methyl-n-pentylcarboxylic ester group, 2-methyl-n-pentylcarboxylic ester group, 3-methyl-n-pentylcarboxylic ester group, 4-methyl-n-pentylcarboxylic ester group, 1,1-dimethyl-n-butylcarboxylic ester group, 1,2-dimethyl-n-butylcarboxylic ester group, 1,3-dimethyl-n-butylcarboxylic ester group, 2,2-dimethyl-n-butylcarboxylic ester group, 2,3-dimethyl-n-butylcarboxylic ester group, 3,3-dimethyl-n-butylcarboxylic ester group, 1-ethyl-n-butylcarboxylic ester group, 2-ethyl-n-butylcarboxylic ester group.

An alkenylcarboxylic ester group in this specification typically consists of a carboxylic ester with an alkenyl group consisting of one up to thirty carbon atoms bonded covalently thereto, which may be either branched or unbranched. This chain preferably consists of one to twenty carbon atoms. Examples of an alkenylcarboxylic ester group are: ethenylcarboxylic ester

group, 1-propenylcarboxylic ester group, 2-propenylcarboxylic ester group, 1-methyl-1-ethenylcarboxylic ester group, 1-butenylcarboxylic ester group, 2-butenylcarboxylic ester group, 3-butenylcarboxylic ester group, 2-methyl-1-propenylcarboxylic ester group, 2-methyl-2-propenylcarboxylic ester group, 1-ethylethenylcarboxylic ester group, 1-methyl-1-propenylcarboxylic ester group, 1-methyl-2-propenylcarboxylic ester group, 1-pentenylcarboxylic ester group, 2-pentenylcarboxylic ester group, 3-pentenylcarboxylic ester group, 4-pentenylcarboxylic ester group, 1-n-propylethenylcarboxylic ester group, 1-methyl-1-butenylcarboxylic ester group, 1-methyl-2-butenylcarboxylic ester group, 1-methyl-3-butenylcarboxylic ester group, 2-ethyl-2-propenylcarboxylic ester group, 2-methyl-1-butenylcarboxylic ester group, 2-methyl-2-butenylcarboxylic ester group, 2-methyl-3-butenylcarboxylic ester group, 3-methyl-1-butenylcarboxylic ester group, 3-methyl-2-butenylcarboxylic ester group, 3-methyl-3-butenylcarboxylic ester group, 1,1-dimethyl-2-propenylcarboxylic ester group, 1-i-propylethenylcarboxylic ester group, 1,2-dimethyl-1-propenylcarboxylic ester group, 1,2-dimethyl-2-propenylcarboxylic ester group, 1-c-pentenylcarboxylic ester group, 2-c-pentenylcarboxylic ester group, 3-c-pentenylcarboxylic ester group, 1-hexenylcarboxylic ester group, 2-hexenylcarboxylic ester group, 3-hexenylcarboxylic ester group, 4-hexenylcarboxylic ester group, 5-hexenylcarboxylic ester group, 1-methyl-1-pentenylcarboxylic ester group, 1-methyl-2-pentenylcarboxylic ester group, 1-methyl-3-pentenylcarboxylic ester group, 1-methyl-4-pentenylcarboxylic ester group, 1-n-butylethenylcarboxylic ester group, 2-methyl-1-pentenylcarboxylic ester group, 2-methyl-2-pentenylcarboxylic ester group, 2-methyl-3-pentenylcarboxylic ester group, 2-methyl-4-pentenylcarboxylic ester group, 2-n-propyl-2-propenylcarboxylic ester group, 3-methyl-1-pentenylcarboxylic ester group, 3-methyl-2-pentenylcarboxylic ester group.

25 An alkynylcarboxylic ester group in this specification typically consists of a carboxylic ester with an alkynyl group consisting of one up to thirty carbon atoms bonded covalently thereto, which may be either branched or unbranched. This chain preferably consists of one to twenty carbon atoms. Examples of an alkynylcarboxylic ester group are: ethynylcarboxylic ester group, 1-propynylcarboxylic ester group, 2-propynylcarboxylic ester group, 1-butynylcarboxylic ester group, 2-butynylcarboxylic ester group, 3-butynylcarboxylic ester group, 1-methyl-2-propynylcarboxylic ester group, 1-pentynylcarboxylic ester group, 2-pentynylcarboxylic ester group, 3-pentynylcarboxylic ester group, 4-pentynylcarboxylic

ester group, 1-methyl-2-butynylcarboxylic ester group, 1-methyl-3-butynylcarboxylic ester group, 2-methyl-3-butynylcarboxylic ester group, 3-methyl-1-butynylcarboxylic ester group, 1,1-dimethyl-2-propynylcarboxylic ester group, 2-ethyl-2-propynylcarboxylic ester group, 1-hexynylcarboxylic ester group, 2-hexynylcarboxylic ester group, 3-hexynylcarboxylic ester group, 4-hexynylcarboxylic ester group, 5-hexynylcarboxylic ester group, 1-methyl-2-pentynylcarboxylic ester group, 1-methyl-3-pentynylcarboxylic ester group, 1-methyl-4-pentynylcarboxylic ester group, 2-methyl-3-pentynylcarboxylic ester group, 2-methyl-4-pentynylcarboxylic ester group, 3-methyl-1-pentynylcarboxylic ester group, 3-methyl-4-pentynylcarboxylic ester group, 4-methyl-1-pentynylcarboxylic ester group, 4-methyl-2-pentynylcarboxylic ester group, 1,1-dimethyl-2-butynylcarboxylic ester group, 1,1-dimethyl-3-butynylcarboxylic ester group, 1,2-dimethyl-3-butynylcarboxylic ester group, 2,2-dimethyl-3-butynylcarboxylic ester group, 3,3-dimethyl-1-butynylcarboxylic ester group, 1-ethyl-2-butynylcarboxylic ester group, 1-ethyl-3-butynylcarboxylic ester group.

In this specification, an alkoxy group may consist of an alkyl unit which may be either branched or unbranched. An alkoxy group typically consists of one to thirty carbon atoms, preferably of one to twenty carbon atoms. Examples of an alkoxy group are: methoxy group, ethoxy group, isopropoxy group, n-butoxy group, sec-butoxy group, tert-butoxy group, pentyloxy group, n-hexyloxy group, n-heptyloxy group, 2-ethylhexyloxy group, n-octyloxy group, n-nonyloxy group, n-decyloxy group, n-tridecyloxy group, n-tetradecyloxy group, n-pentadecyloxy group, n-hexadecyloxy group, n-octadecyloxy group or eicosyloxy group. Preference is given to alkoxy groups having one up to six carbon atoms in the alkyl unit.

A cycloalkyl group as described in this specification is typically a cyclic group consisting of five, six or seven carbon atoms, each of which may independently be substituted. Examples of substituents are alkyl groups, or two alkyl groups which, together with the ring carbons to which they are bonded, form a further ring. One example of a cycloalkyl group is a cyclohexyl group.

A cycloalkoxy group as described in this specification is typically a cyclic group consisting of five, six or seven carbon atoms, of which at least one is bonded covalently to an oxygen atom. These ring carbon atoms may each independently be substituted, for example by alkyl

groups, or two alkyl groups which, together with the ring carbons to which they are bonded, form a further ring. One example of a cycloalkoxy group is a cyclohexyloxy group.

5 An aryl group as described in this specification is typically a cyclic aromatic group consisting of five to ten carbon atoms, each of which may independently be substituted. Examples of substituents are alkyl groups, or two alkyl groups which, together with the ring carbons to which they are bonded, form a further ring. Examples of an aryl group are phenyl group, o-biphenyl group, m-biphenyl group, p-biphenyl group, 1-anthryl group, 2-anthryl group, 9-anthryl group, 1-phenantolyl group, 2-phenantolyl group, 3-phenantolyl group, 4-phenantolyl group, 9-phenantolyl group.

15 A heteroaryl group as described in this specification is typically a cyclic aromatic group consisting of four to ten carbon atoms and at least one heteroatom, each of which may independently be substituted. Examples of substituents are alkyl groups, or two alkyl groups which, together with the ring carbons to which they are bonded, form a further ring. Examples of heteroatoms in this context are an oxygen atom, nitrogen atom, phosphorus atom, boron atom, selenium atom or sulphur atom. Examples of a heteroaryl group are furyl group, thienyl group, pyrrolyl group or imidazolyl group.

20 An aryloxy group as described in this specification is typically an aryl group, where aryl has already been defined above, bonded covalently to an oxygen atom. Examples of an aryloxy group are phenyloxy or naphthyloxy.

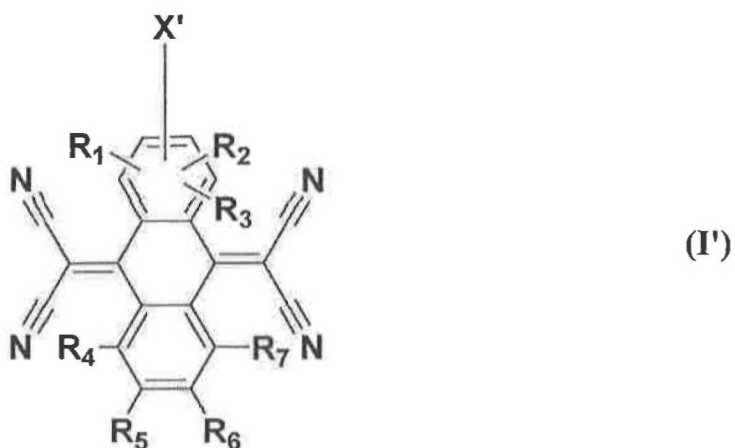
25 An aralkyl group as described in this specification is typically an aryl group, where aryl has already been defined above, bonded covalently to an alkyl group. This group may, for example, be substituted by alkyl groups or halogen atoms. One example of an aralkyl group is benzyl.

30 The average molar mass (M_n) of the oligomeric or polymeric compound of this invention is in the range of 660 to 3 300 000 g/mol, preferably in the range from 1650 to 1 650 000 g/mol, more preferably in the range from 3300 to 330 000 g/mol. The average molar mass is determined by means of size exclusion chromatography (polystyrene standard).

In general, the oligomeric or polymeric compound of the inventive general formula I of this invention consists of 2 and 5000 repeat units, preferably of 10 to 1000 repeat units.

The oligomeric or polymeric compounds of the inventive general formula I of this invention may be either homopolymers or copolymers. Homopolymers are polymers which have been synthesized only from one monomer. Copolymers are polymers which have been synthesized from two or more polymers. If two or more monomers are used in the synthesis, the monomers of the repeat units of the oligomeric or polymeric compound of this invention may be present in the oligomeric or polymeric compound in random distribution, as blocks or in alternation. The oligomeric or polymeric compounds of this invention may either be in linear or crosslinked form. Crosslinking can be effected, for example, via copolymerization with a small proportion of an organic molecule having two polymerizable groups, preferably a more highly functionalized monomer.

The oligomeric or polymeric compounds of the inventive general formula I are synthesized by the polymerization of an 11,11,12,12-tetracyanoanthraquinodimethane compound of the general formula I'



X' here is preferably an organic polymerizable group typically consisting of an organic double bond, or an organic triple bond, or an oxirane or an aziridine. Particular preference is given to organic polymerizable groups shown in the formulae II' to VIII'.



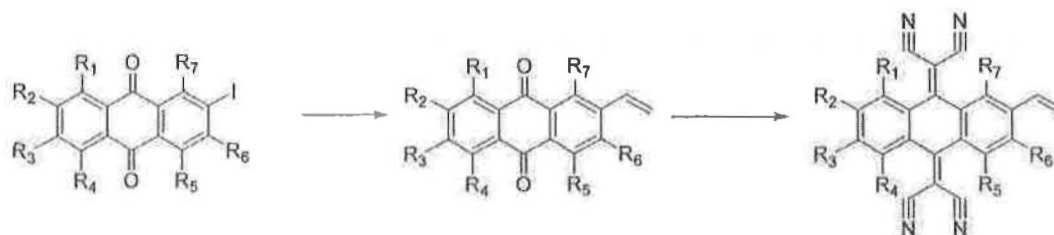
with the definitions already described above again for R_8 to R_{24} , A and Ar.

An 11,11,12,12-tetracyanoanthraquinodimethane compound of the general formula I' can be prepared by the combination of known reactions.

The preparation of the compound of the general formula I' is shown in Schemes 1-7 below, but is not restricted thereto.

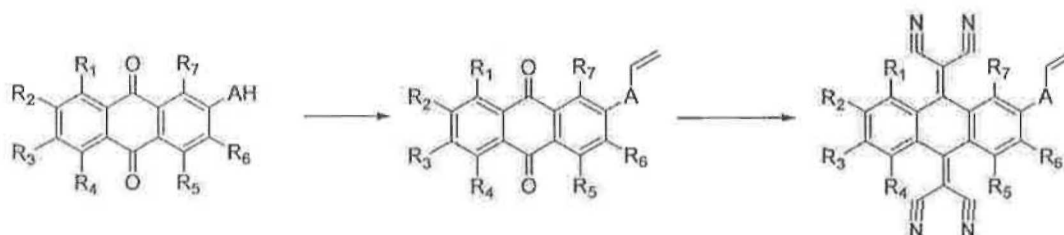
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Scheme 1:

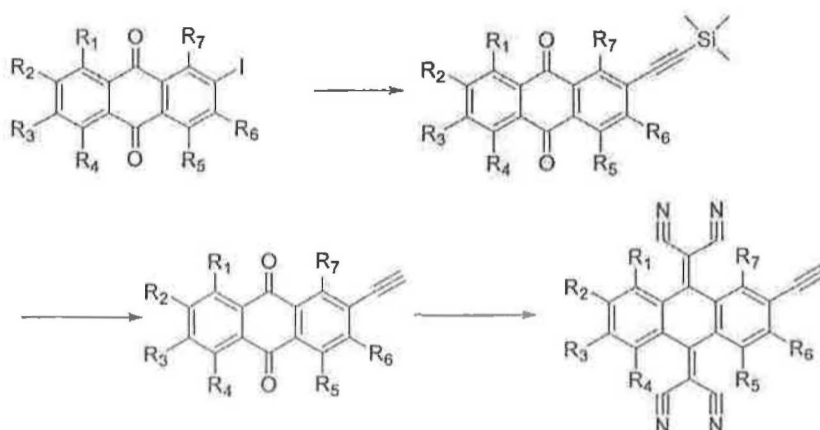


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Scheme 2:

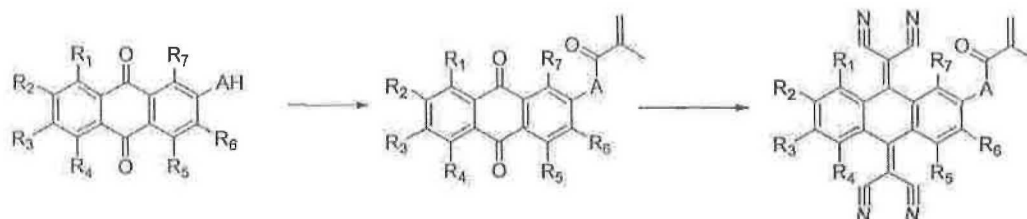


Scheme 3:

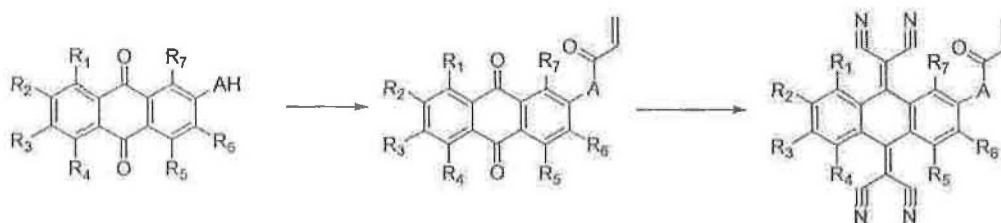


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Scheme 4:

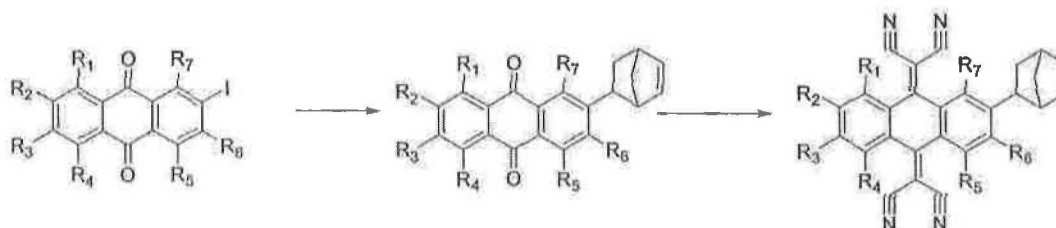


Scheme 5:

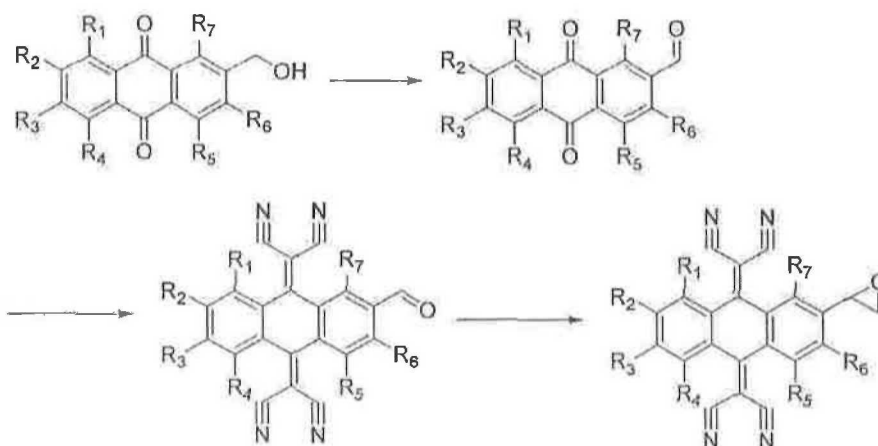


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Scheme 6:



10 Scheme 7:



Methods known per se are sufficient for synthesis of the compound of the abovementioned general formula I' according to the above Schemes 1-7.

If X' in the general formula I' corresponds to the abovementioned formula II', the compound
5 of the formula I' can be synthesized by a known method of polystyrene synthesis and
derivatives thereof. Preferably, the abovementioned compound I' is synthesized by radical
polymerization, for example free-radical polymerization, but also a controlled radical
polymerization method, for example reversible addition-fragmentation chain transfer
polymerization (RAFT), atom transfer radical polymerization (ATRP) or nitroxide-mediated
10 polymerization (NMP), within a temperature range from -30 to 150°C, advantageously
within a temperature range from 40 to 120°C, in a solvent and in a reaction time of 0.1 to
100 hours, using an initiator, for example azo compounds or peroxides, preferably benzoyl
peroxide or 2,2'-azobisisobutyronitrile. There are barely any restrictions for solvents used.
Preference is given to organic solvents, for example N,N'-dimethylformamide, N,N'-
15 dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-
dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

Likewise preferably, the abovementioned compound I' is synthesized by cationic
polymerization within a temperature range from -30 to 150°C, advantageously within a
20 temperature range from -20 to 50°C, in a solvent and a reaction time of 0.1 to 100 hours,
using a catalyst, for example Lewis acids or protic acids, preferably sulphuric acid, nitric
acid, perchloric acid, boron trifluoroetherate complex, aluminium trichloride, tin
tetrachloride or titanium tetrachloride. There are barely any restrictions for solvents used.
Preference is given to organic solvents, for example N,N'-dimethylformamide, N,N'-
25 dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane,
tetrahydrofuran, 1,4-dioxolane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-
dichlorobenzene.

Likewise preferably, the abovementioned compound I' is synthesized by anionic
30 polymerization within a temperature range from -78 to 150°C, advantageously within a
temperature range from -50 to 50°C, in a solvent and a reaction time of 0.1 to 100 hours,
using a catalyst, for example Lewis bases or bases, preferably metal amides such as sodium
amide and LiC_2H_5 , alkoxides such as methoxide or ethoxide, hydroxides such as sodium

hydroxide or potassium hydroxide, cyanides, phosphines, amines or organometallic compounds, for example n-butyllithium or vinylmagnesium bromide. There are barely any restrictions for solvents used. Preference is given to organic solvents, for example tetrahydrofuran, 1,4-dioxolane, diethyl ether, tert-butyl methyl ether, toluene, xylene,
5 chlorobenzene or o-dichlorobenzene.

Likewise preferably, the abovementioned compound I' is synthesized by anionic group transfer polymerization within a temperature range from -30 to 150°C, advantageously within a temperature range from -20 to 50°C, in a solvent and a reaction time of 0.1 to 100
10 hours, using an initiator, for example a silyl ketene acetal, and using a catalyst, for example inorganic salts, preferably fluorides, azides or cyanides, or Lewis acids, preferably zinc chloride or dialkylaluminium chloride. There are barely any restrictions for solvents used. Preference is given to organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-
15 dichloroethane, tetrahydrofuran, 1,4-dioxolane, diethyl ether, tert-butyl methyl ether, toluene, xylene, chlorobenzene or o-dichlorobenzene.

If X' in the general formula I' corresponds to the abovementioned formula III', the compound of the formula I' can be synthesized by a known method of polyvinyl ether synthesis and
20 derivatives thereof. Preferably, the abovementioned compound I' is synthesized by cationic polymerization within a temperature range from -30 to 150°C, advantageously within a temperature range from -20 to 50°C, in a solvent and a reaction time of 0.1 to 100 hours, using a catalyst, for example Lewis acids or protic acids, preferably sulphuric acid, nitric acid, perchloric acid, boron trifluoroetherate complex, aluminium trichloride, tin
25 tetrachloride or titanium tetrachloride.

There are barely any restrictions for solvents used. Preference is given to organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, tetrahydrofuran, 1,4-dioxolane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

30 If X' in the general formula I' corresponds to the abovementioned formula IV', the compound of the formula I' can be synthesized by a known method of polyacetylene synthesis and derivatives thereof. Preferably, the abovementioned compound I' is synthesized by metal-

catalysed polymerization within a temperature range from -30 to 150°C, advantageously within a temperature range from 0 to 100°C, in a solvent and a reaction time of 0.1 to 100 hours, using a catalyst, for example a Wilkinson catalyst, a Ziegler-Natta catalyst, a Luttinger catalyst, a molybdenum complex, a tungsten complex, a rhodium complex, or an electrochemical polymerization method using nickel bromide.

There are barely any restrictions for solvents used. Preference is given to organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

If X' in the general formula I' corresponds to the abovementioned formula V', the compound of the formula I' can be synthesized by a known method of polyacrylate synthesis and derivatives thereof. Preferably, the abovementioned compound I' is synthesized by free-radical polymerization, but also controlled radical polymerization methods, for example reversible addition-fragmentation chain transfer polymerization (RAFT), atom transfer radical polymerization (ATRP), cobalt-mediated radical polymerization (CMRP) or nitroxide-mediated polymerization (NMP), within a temperature range from -30 to 150°C, advantageously within a temperature range from 40 to 120°C, in a solvent and in a reaction time of 0.1 to 100 hours, using an initiator, for example azo compounds or peroxides, preferably benzoyl peroxide or 2,2'-azobisisobutyronitrile.

There are barely any restrictions for solvents used. Preference is given to organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

Likewise preferably, the abovementioned compound I' is synthesized by anionic polymerization within a temperature range from -78 to 150°C, advantageously within a temperature range from -50 to 50°C, in a solvent and a reaction time of 0.1 to 100 hours, using a catalyst, for example Lewis bases or bases, preferably metal amides such as sodium amide and LiC_2H_5 , alkoxides such as methoxide or ethoxide, hydroxides such as sodium hydroxide or potassium hydroxide, cyanides, phosphines, amines or organometallic compounds, for example n-butyllithium or vinylmagnesium bromide. There are barely any restrictions for solvents used. Preference is given to organic solvents, for example

tetrahydrofuran, 1,4-dioxolane, diethyl ether, tert-butyl methyl ether, toluene, xylene, chlorobenzene or o-dichlorobenzene.

Likewise preferably, the abovementioned compound I' is synthesized by anionic group transfer polymerization within a temperature range from -78 to 150°C, advantageously within a temperature range from -20 to 50°C, in a solvent and a reaction time of 0.1 to 100 hours, using an initiator, for example a silyl ketene acetal, and using a catalyst, for example inorganic salts, preferably fluorides, azides or cyanides, or Lewis acids, preferably zinc chloride or dialkylaluminium chloride. There are barely any restrictions for solvents used. Preference is given to organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-dichloroethane, tetrahydrofuran, 1,4-dioxolane, diethyl ether, tert-butyl methyl ether, toluene, xylene, chlorobenzene or o-dichlorobenzene.

If X' in the general formula I' corresponds to the abovementioned formula VI', the compound of the formula I' can be synthesized by a known method of polynorbornene synthesis and derivatives thereof. Preferably, the abovementioned compound I' is synthesized by metal-catalysed polymerization within a temperature range from -30 to 150°C, advantageously within a temperature range from 0 to 100°C, in a solvent and in a reaction time of 0.1 to 100 hours, using a catalyst, for example a Grubbs catalyst, a molybdenum complex, a tungsten complex or a ruthenium complex.

There are barely any restrictions for solvents used. Preference is given to organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-dichloroethane, tetrahydrofuran, toluene, xylene, chlorobenzene or o-dichlorobenzene.

If X' in the general formula I' corresponds to the abovementioned formula VII', the compound of the formula I' can be synthesized by a known method of polyethylene glycol synthesis and derivatives thereof.

Preferably, the abovementioned compound I' is synthesized by cationic polymerization within a temperature range from -30 to 150°C, advantageously within a temperature range from 40 to 120°C, in a solvent and a reaction time of 0.1 to 100 hours, using a catalyst, for example Lewis acids or protic acids, preferably sulphuric acid, nitric acid, perchloric acid,

boron trifluoroetherate complex, aluminium trichloride, tin tetrachloride, diethylzinc/water or titanium tetrachloride.

There are barely any restrictions for solvents used. Preference is given to organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, tetrahydrofuran, 1,4-dioxolane, 1,2-dichloroethane, 5 toluene, xylene, chlorobenzene or o-dichlorobenzene.

Likewise preferably, the abovementioned compound I' is synthesized by anionic polymerization within a temperature range from -78 to 150°C, advantageously within a 10 temperature range from -50 to 50°C, in a solvent and a reaction time of 0.1 to 100 hours, using a catalyst, for example Lewis bases or bases, preferably metal amides such as sodium amide and LiC_2H_5 , alkoxides such as methoxide or ethoxide, hydroxides such as sodium hydroxide or potassium hydroxide, cyanides, phosphines, amines or organometallic compounds, for example n-butyllithium or vinylmagnesium bromide. There are barely any 15 restrictions for solvents used. Preference is given to organic solvents, for example tetrahydrofuran, 1,4-dioxolane, diethyl ether, tert-butyl methyl ether, toluene, xylene, chlorobenzene or o-dichlorobenzene.

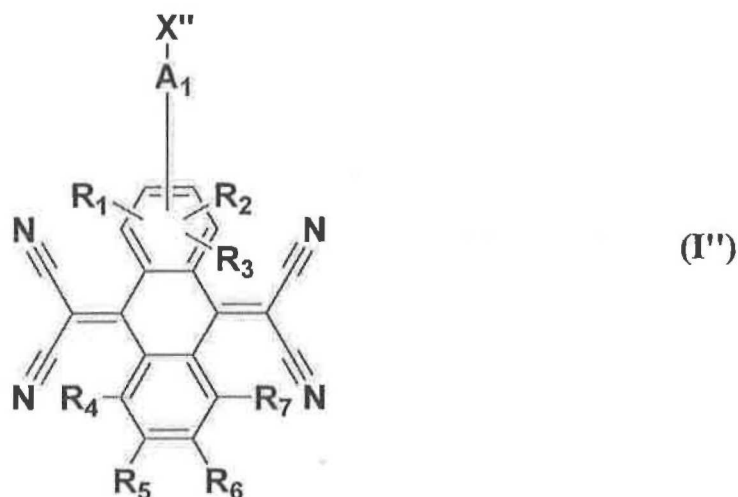
If X' in the general formula I' corresponds to the abovementioned formula VIII', the 20 compound of the formula I' can be synthesized by a known method of polystyrene synthesis and derivatives thereof. Preferably, the abovementioned compound I' is synthesized by radical polymerization, for example free-radical polymerization, but also a controlled radical polymerization method, for example reversible addition-fragmentation chain transfer polymerization (RAFT), atom transfer radical polymerization (ATRP) or nitroxide-mediated 25 polymerization (NMP), within a temperature range from -30 to 150°C, advantageously within a temperature range from 40 to 120°C, in a solvent and in a reaction time of 0.1 to 100 hours, using an initiator, for example azo compounds or peroxides, preferably benzoyl peroxide or 2,2'-azobisisobutyronitrile. There are barely any restrictions for solvents used. Preference is given to organic solvents, for example N,N'-dimethylformamide, N,N'- 30 dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

Likewise preferably, the abovementioned compound I' is synthesized by cationic polymerization within a temperature range from -30 to 150°C, advantageously within a temperature range from -20 to 50°C, in a solvent and a reaction time of 0.1 to 100 hours, using a catalyst, for example Lewis acids or protic acids, preferably sulphuric acid, nitric acid, perchloric acid, boron trifluoroetherate complex, aluminium trichloride, tin tetrachloride or titanium tetrachloride. There are barely any restrictions for solvents used. Preference is given to organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, tetrahydrofuran, 1,4-dioxolane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

Likewise preferably, the abovementioned compound I' is synthesized by anionic polymerization within a temperature range from -78 to 150°C, advantageously within a temperature range from -50 to 50°C, in a solvent and a reaction time of 0.1 to 100 hours, using a catalyst, for example Lewis bases or bases, preferably metal amides such as sodium amide and LiC_2H_5 , alkoxides such as methoxide or ethoxide, hydroxides such as sodium hydroxide or potassium hydroxide, cyanides, phosphines, amines or organometallic compounds, for example n-butyllithium or vinylmagnesium bromide. There are barely any restrictions for solvents used. Preference is given to organic solvents, for example tetrahydrofuran, 1,4-dioxolane, diethyl ether, tert-butyl methyl ether, toluene, xylene, chlorobenzene or o-dichlorobenzene.

Likewise preferably, the abovementioned compound I' is synthesized by anionic group transfer polymerization within a temperature range from -78 to 150°C, advantageously within a temperature range from -20 to 50°C, in a solvent and a reaction time of 0.1 to 100 hours, using an initiator, for example a silyl ketene acetal, and using a catalyst, for example inorganic salts, preferably fluorides, azides or cyanides, or Lewis acids, preferably zinc chloride or dialkylaluminium chloride. There are barely any restrictions for solvents used. Preference is given to organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-dichloroethane, tetrahydrofuran, 1,4-dioxolane, diethyl ether, tert-butyl methyl ether, toluene, xylene, chlorobenzene or o-dichlorobenzene.

In addition, the oligomeric or polymeric compounds of the inventive general formula I are synthesized by polymer-analogous reaction of an 11,11,12,12-tetracyanoanthraquinodimethane compound of the general formula I'' with an oligomeric or polymeric compound of the general formula P'.



where

R₁ to R₇ and R₂₆ to R₂₈: may preferably each independently be hydrogen atoms, alkyl groups, alkenyl groups, alkynyl groups, alkoxy groups, alkylthio groups, haloalkyl groups, haloalkoxy groups, cycloalkyl groups, cycloalkoxy groups, aryl groups, heteroaryl groups, aryloxy groups, aralkyl groups, carboxylic acid groups, sulphonic acid groups, amino groups, monoalkylamino groups, dialkylamino groups, nitro groups, cyano groups, hydroxyl groups, alkylcarbonyl groups, alkenylcarbonyl groups, alkynylcarbonyl groups, carboxylic ester groups, carboxamide groups, sulphonic

5 ester groups, thiol groups, halogen atoms or a combination of these groups or atoms, particular preference being given to hydrogen atoms as at least five of the R₁ to R₇ substituents and to non-hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, as zero to two of the R₁ bis R₇ substituents, and/or to hydrogen atoms as at least two of the R₂₆ to R₂₈ substituents and to non-hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, as zero to one of the R₂₆ to R₂₈ substituents,

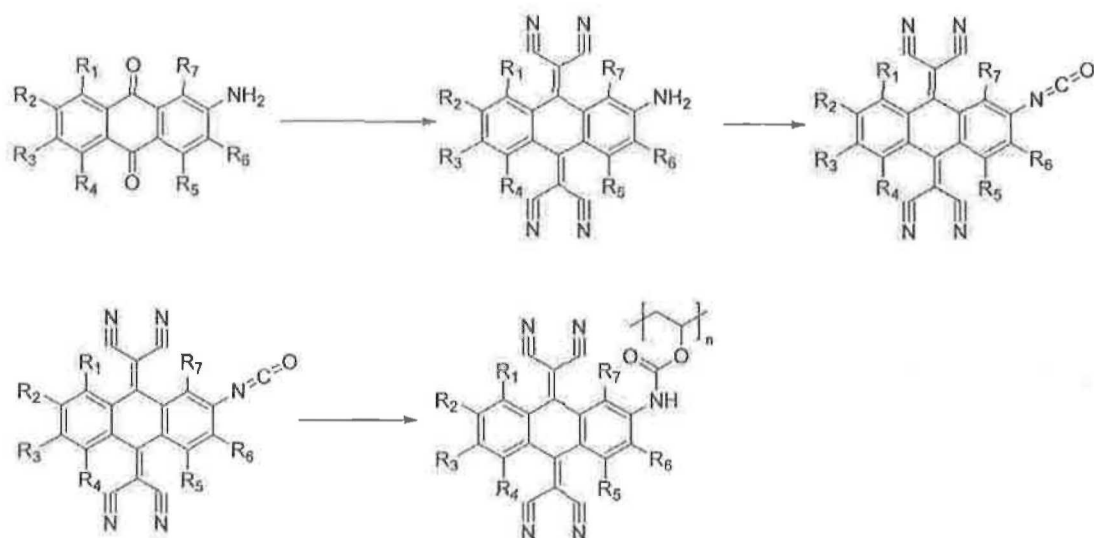
10 X": is an electrophilic organic group which is attacked nucleophilically by the hydroxyl group of the compound P' and hence forms a covalent bond between the compound I" and P' (preferably, X" is an isocyanate group, a carbonyl halide group, where the halogen is preferably chlorine, bromine or iodine, a carboxylic acid group, a halogen atom, where the halogen is preferably chlorine, bromine or iodine, or a carbonyl group, an anhydride group),

A₁ and A₂: are preferably a covalent bond, an alkyl group, an alkenyl group, 20 an alkynyl group, an alkoxy group, an alkylthio group, a haloalkyl group, a haloalkoxy group, a cycloalkyl group, a cycloalkoxy group, an aryl group, a heteroaryl group, an aryloxy group, an aralkyl group, a monoalkylamino group, a dialkylamino group, an alkylcarbonyl group, an alkenylcarbonyl group, an alkynylcarbonyl group, a carboxylic ester group, a carboxamide group, a sulphonic ester group, where a covalent bond or an alkyl group as A₁ and A₂ is particularly advantageous,

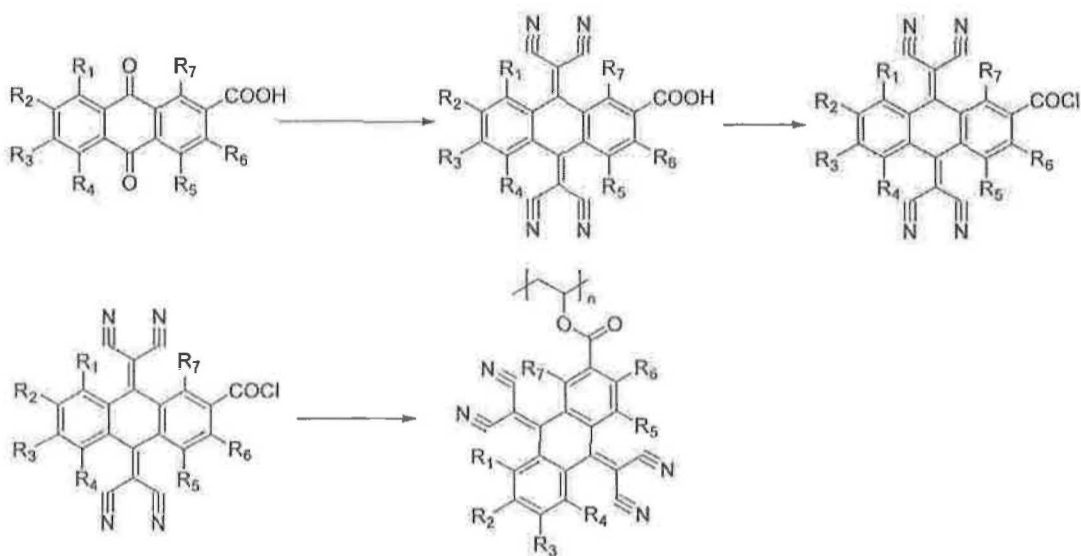
25 n: is an integer greater than or equal to 2.

30 The preparation of the compound of the inventive general formula I by polymer-analogous reaction from the abovementioned compounds I" and P' and the preparation thereof is shown in Schemes 8-13 below, but is not restricted thereto.

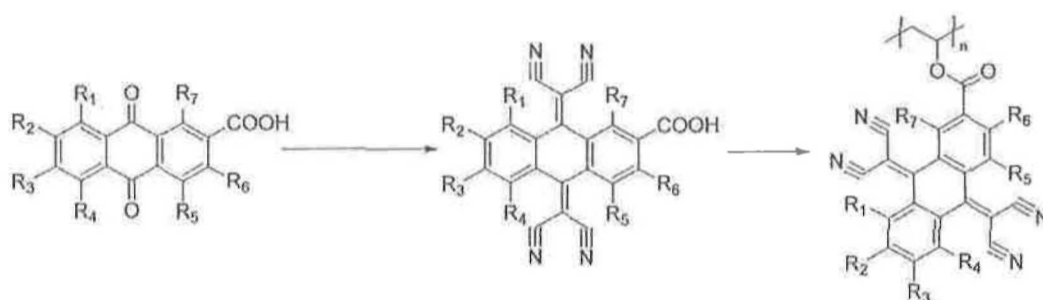
Scheme 8:



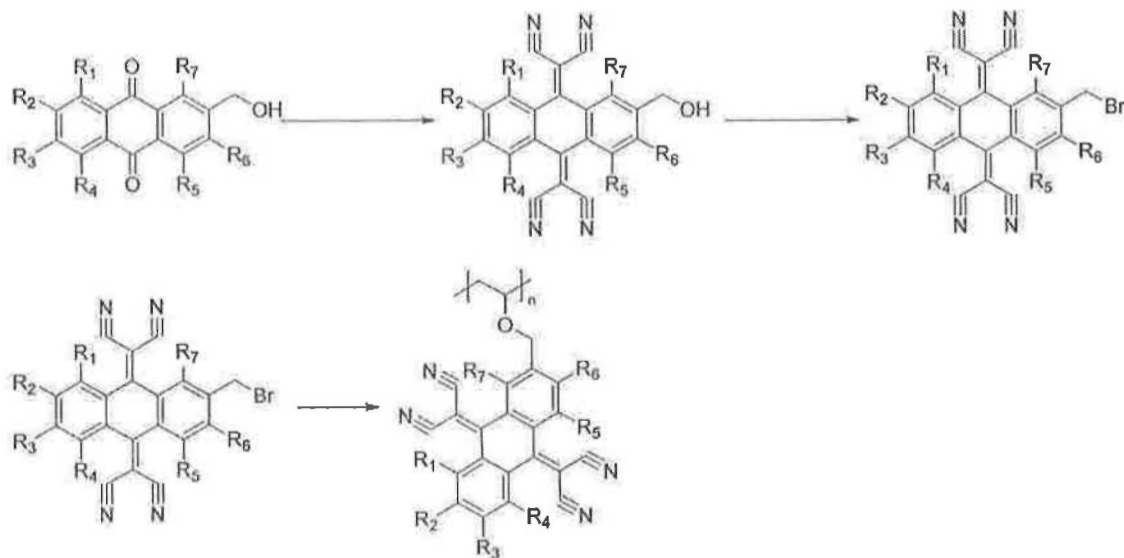
5 Scheme 9:



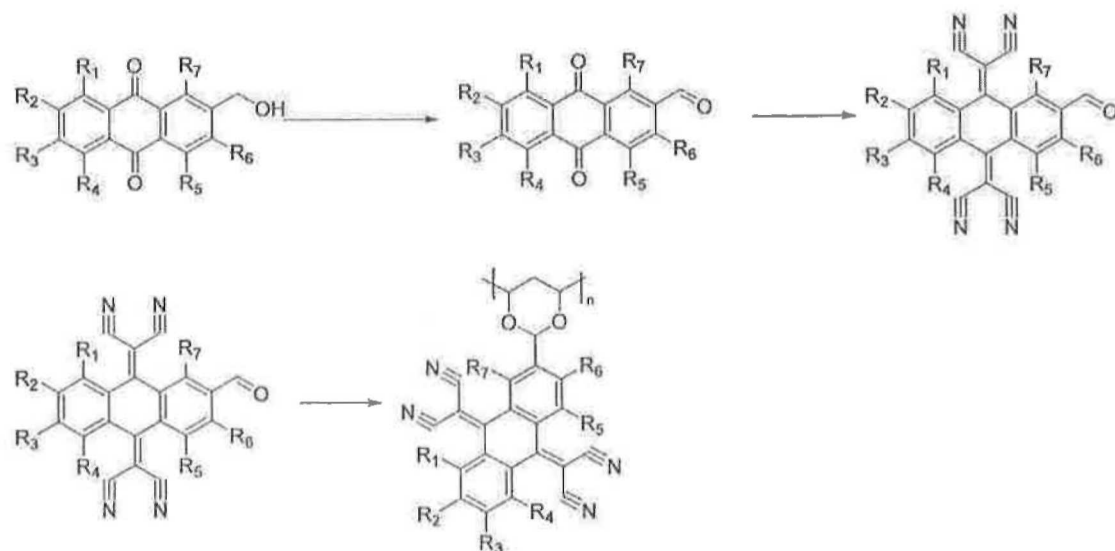
Scheme 10:



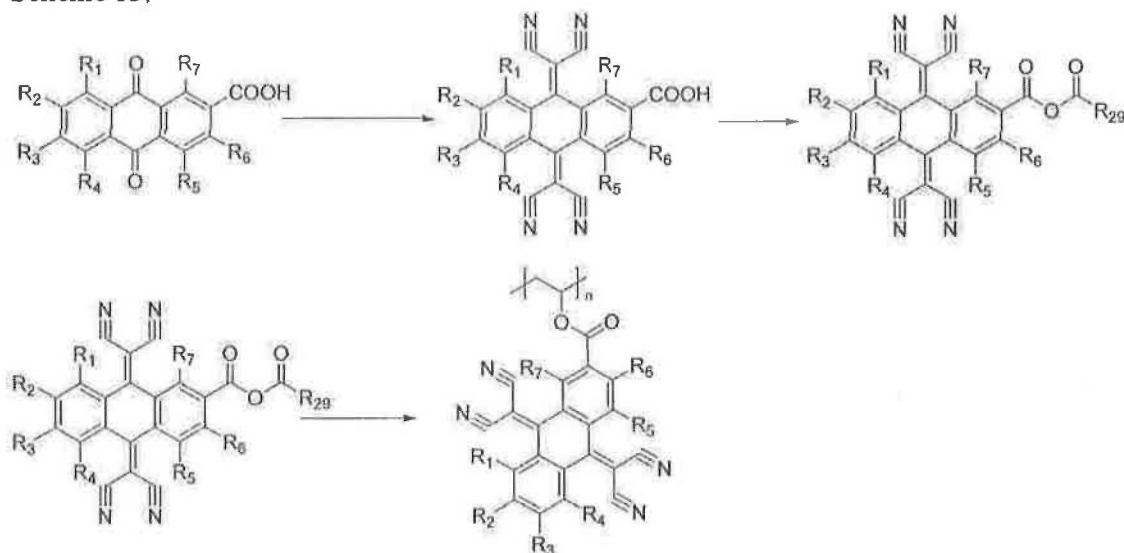
Scheme 11:



Scheme 12:



Scheme 13;



R_{29} is preferably a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an alkoxy group, an alkylthio group, a cycloalkyl group, a cycloalkoxy group, an aryl group, a heteroaryl group, an aryloxy group, an aralkyl group. More preferably, R_{29} is an alkyl group.

Methods known per se are sufficient for synthesis of the compound of the abovementioned inventive general formula I according to Schemes 8-13.

If X'' in the general formula I' corresponds to an isocyanate group, the compound of the formula I can be synthesized by reaction of the compound I' with the compound P' by a known method of urethane synthesis and derivatives thereof. Preferably, the abovementioned compound I is synthesized within a temperature range from -78 to 150°C , advantageously within a temperature range from -40 to 120°C , in a solvent and in a reaction time of 0.1 to 100 hours. There are barely any restrictions for solvents used. Preference is given to aprotic organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

20

If X'' in the general formula I' corresponds to a carbonyl halide group, the compound of the formula I can be synthesized by reaction of the compound I' with the compound P' by a known method of carboxylic ester synthesis and derivatives thereof. Preferably, the

abovementioned compound I is synthesized within a temperature range from -78 to 150°C, advantageously within a temperature range from -40 to 120°C, in a solvent and in a reaction time of 0.1 to 100 hours, using a catalyst, for example a pyridine derivative such as typically 4-(dimethylamino)pyridine, or a carbodiimide derivative such as typically N,N'-
5 dicyclohexylcarbodiimide. There are barely any restrictions for solvents used. Preference is given to aprotic organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

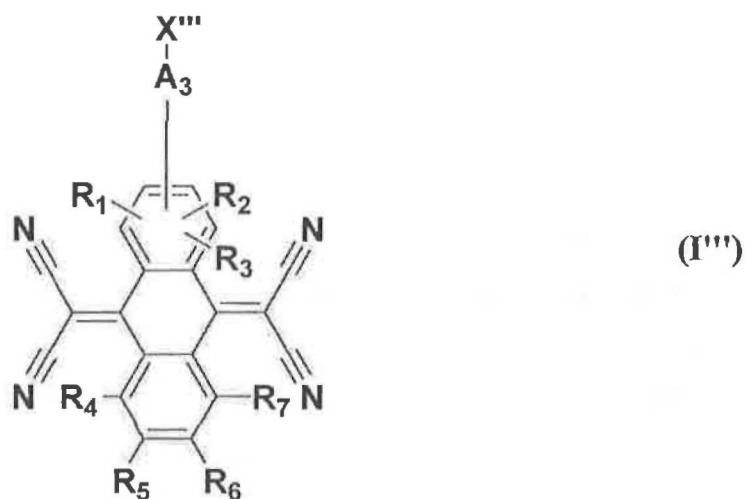
10 If X" in the general formula I" corresponds to a carboxylic acid group, the compound of the formula I can be synthesized by reaction of the compound I" with the compound P' by a known method of carboxylic ester synthesis and derivatives thereof. Preferably, the abovementioned compound I is synthesized within a temperature range from -78 to 150°C, advantageously within a temperature range from -40 to 120°C, in a solvent and in a reaction
15 time of 0.1 to 100 hours, using a catalyst, for example a pyridine derivative such as typically 4-(dimethylamino)pyridine, or a carbodiimide derivative such as typically N,N'-dicyclohexylcarbodiimide. There are barely any restrictions for solvents used. Preference is given to aprotic organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-
20 dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

If X" in the general formula I" corresponds to a halogen atom, the compound of the formula I can be synthesized by reaction of the compound I" with the compound P' by a known method of ether synthesis and derivatives thereof. Preferably, the abovementioned
25 compound I is synthesized within a temperature range from -78 to 150°C, advantageously within a temperature range from -40 to 120°C, in a solvent and in a reaction time of 0.1 to 100 hours, using a catalyst, for example a base such as sodium hydride, sodium hydroxide, potassium tert-butoxide, DBU or DBN. There are barely any restrictions for solvents used. Preference is given to aprotic organic solvents, for example N,N'-dimethylformamide, N,N'-
30 dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

If X" in the general formula I" corresponds to a carbonyl group, the compound of the formula I can be synthesized by reaction of the compound I" with the compound P' by a known method of acetal synthesis and derivatives thereof. Preferably, the abovementioned compound I is synthesized within a temperature range from -78 to 150°C, advantageously
5 within a temperature range from -40 to 120°C, in a solvent and in a reaction time of 0.1 to 100 hours, using a catalyst, for example protic acids such as p-toluenesulphonic acid, hydrochloric acid, sulphuric acid or trifluoroacetic acid. There are barely any restrictions for solvents used. Preference is given to aprotic organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone,
10 dichloromethane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

If X" in the general formula I" corresponds to an anhydride group, the compound of the formula I can be synthesized by reaction of the compound I" with the compound P' by a known method of carboxylic ester synthesis and derivatives thereof. Preferably, the
15 abovementioned compound I is synthesized within a temperature range from -78 to 150°C, advantageously within a temperature range from -40 to 120°C, in a solvent and in a reaction time of 0.1 to 100 hours, using a catalyst, for example a pyridine derivative such as typically 4-(dimethylamino)pyridine, or a carbodiimide derivative such as typically N,N'-dicyclohexylcarbodiimide. There are barely any restrictions for solvents used. Preference is
20 given to aprotic organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

In addition, the oligomeric or polymeric compounds of the inventive general formula I are
25 synthesized by polymer-analogous reaction of an 11,11,12,12-tetracyanoanthraquinodimethane compound of the general formula I''' with an oligomeric or polymeric compound of the general formula P".



where

R₁ to R₇ and R₃₀ to R₃₂: may preferably each independently be hydrogen atoms, alkyl groups, alkenyl groups, alkynyl groups, alkoxy groups, alkylthio groups, haloalkyl groups, haloalkoxy groups, cycloalkyl groups, cycloalkoxy groups, aryl groups, heteroaryl groups, aryloxy groups, aralkyl groups, carboxylic acid groups, sulphonic acid groups, amino groups, monoalkylamino groups, dialkylamino groups, nitro groups, cyano groups, alkylcarbonyl groups, alkenylcarbonyl groups, alkynylcarbonyl groups, carboxylic ester groups, carboxamide groups, sulphonic ester groups, halogen atoms or a combination of these groups or atoms, particular preference being given to hydrogen atoms as at least five of the R₁ to R₇ substituents and to non-hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, as zero to two of the R₁ bis R₇ substituents, and/or

to hydrogen atoms as at least two of the R_{30} to R_{32} substituents and to non-hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, as zero to one of the R_{30} to R_{32} substituents,

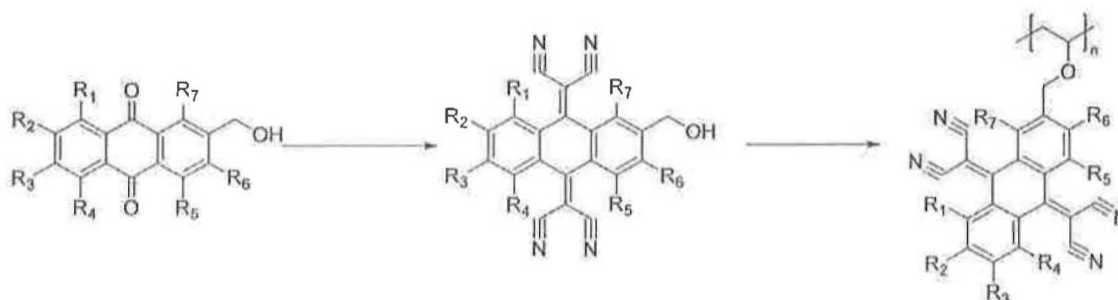
5 X''' : is a nucleophilic organic group which nucleophilically attacks the atom adjacent to the halogen atom of the compound P'' and hence forms a covalent bond between the compound I''' and P'' , preference being given to a hydroxyl group or a thiol group as X''' ,

10 A_3 and A_4 : are preferably a covalent bond, an alkyl group, an alkenyl group, an alkynyl group, an alkoxy group, an alkylthio group, a cycloalkyl group, a cycloalkoxy group, an aryl group, a heteroaryl group, an aryloxy group, an aralkyl group, a dialkylamino group, an alkylcarbonyl group, an alkenylcarbonyl group, an alkynylcarbonyl group, a carboxylic ester group, a carboxamide group, a sulphonic ester group, particular preference being given to a covalent bond or an alkyl group as A_1 and A_2 ,

n : is an integer greater than or equal to 2.

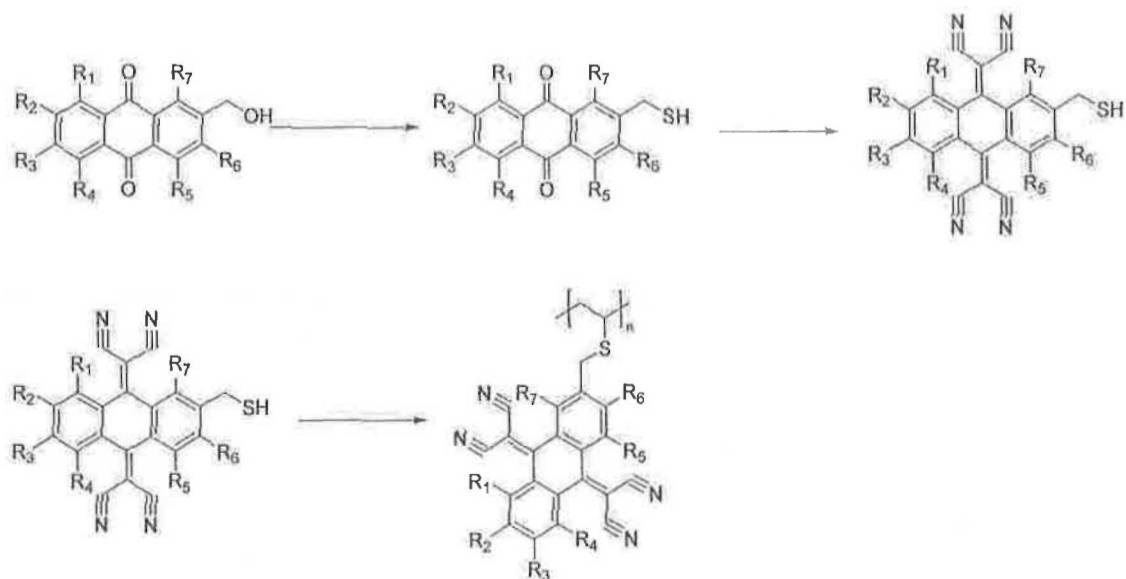
20 The preparation of the compound of the general formula I with the aid of a polymer-analogous reaction from the abovementioned compounds I''' and P'' is shown in Schemes 14-15 below, but is not restricted thereto.

Scheme 14:



25

Scheme 15:



If X'' in the general formula I''' corresponds to a hydroxyl group or a thiol group, the compound of the formula I can be synthesized by reaction of the compound I''' with the compound P'' by a known method of ether synthesis and derivatives thereof. Preferably, the

5 abovementioned compound I is synthesized within a temperature range from -78 to 150°C, advantageously within a temperature range from -40 to 120°C, in a solvent and in a reaction time of 0.1 to 100 hours, using a catalyst, for example a base such as sodium hydride, sodium hydroxide, potassium tert-butoxide, DBU or DBN. There are barely any restrictions for solvents used. Preference is given to aprotic organic solvents, for example N,N'-

10 dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

In addition, the oligomeric or polymeric compounds of the inventive general formula I are synthesized by polymer-analogous reaction of an 11,11,12,12-

15 tetracyanoanthraquinodimethane compound of the general formula I''' with an oligomeric or polymeric compound of the general formula P''.



5 where

10 R₁ to R₇ and R₃₃ to R₃₅: may preferably each independently be hydrogen atoms, alkyl
 groups, alkenyl groups, alkoxy groups, alkylthio groups,
 haloalkyl groups, haloalkoxy groups, cycloalkyl groups,
 cycloalkoxy groups, aryl groups, heteroaryl groups, aryloxy
 groups, aralkyl groups, carboxylic acid groups, sulphonic acid
 groups, amino groups, monoalkylamino groups, dialkylamino
 groups, nitro groups, cyano groups, hydroxyl groups,
 alkylcarbonyl groups, alkenylcarbonyl groups, alkynylcarbonyl
 groups, carboxylic ester groups, carboxamide groups, sulphonic
 15 ester groups, thiol groups, halogen atoms or a combination of
 these groups or atoms, particular preference being given to
 hydrogen atoms as at least five of the R₁ to R₇ substituents and to
 non-hydrogen atoms, preferably halogen atoms, alkyl groups,
 alkoxy groups, cyano groups and/or nitro groups, as zero to two
 20 of the R₁ bis R₇ substituents, and/or to hydrogen atoms as at least

two of the R_{33} to R_{35} substituents and to non-hydrogen atoms, preferably halogen atoms, alkyl groups, alkoxy groups, cyano groups and/or nitro groups, as zero to one of the R_{33} to R_{35} substituents,

5 A_5 and A_6 :

are preferably a covalent bond, an alkyl group, an alkenyl group, an alkoxy group, an alkylthio group, a haloalkyl group, a haloalkoxy group, a cycloalkyl group, a cycloalkoxy group, an aryl group, a heteroaryl group, an aryloxy group, an aralkyl group, a monoalkylamino group, a dialkylamino group, an alkylcarbonyl group, an alkenylcarbonyl group, an alkynylcarbonyl group, a carboxylic ester group, a carboxamide group, a sulphonic ester group, particular preference being given to a covalent bond, an aryl group or an alkyl group as A_5 and A_6 ,

10

n :

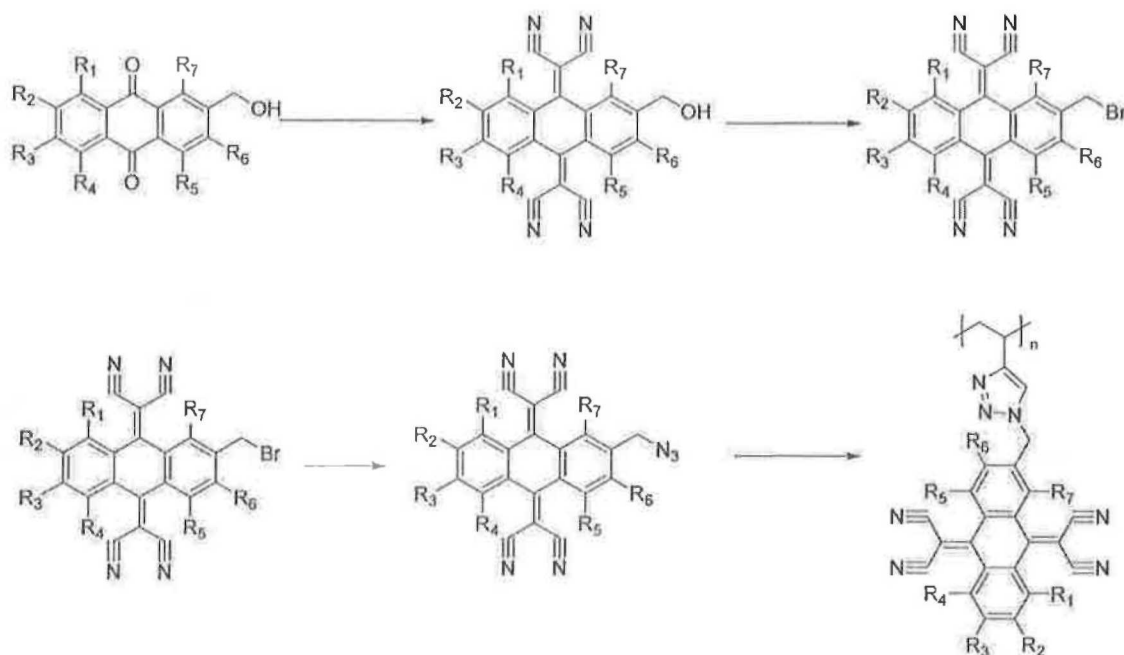
is an integer greater than or equal to 2.

15

The preparation of the compound of the general formula I with the aid of a polymer-analogous reaction from the abovementioned compounds I''' and P''' is shown in Scheme 16 below, but is not restricted thereto.

20

Scheme 16:



The compound of the formula I can also be synthesized by reaction of the compound I''' with the compound P''' by a known method of the azide/alkyne click reaction and derivatives thereof. Preferably, the abovementioned compound I is synthesized within a temperature range from -78 to 150°C, advantageously within a temperature range from -40 to 120°C, in a solvent and in a reaction time of 0.1 to 100 hours. There are barely any restrictions for solvents used. Preference is given to aprotic organic solvents, for example N,N'-dimethylformamide, N,N'-dimethylacetamide, dimethyl sulphoxide, N-methylpyrrolidone, dichloromethane, 1,2-dichloroethane, toluene, xylene, chlorobenzene or o-dichlorobenzene.

The oligomeric or polymeric compounds of this invention can appropriately be used as redox-active material for storage of electrical energy in an electrical charge storage means. A redox-active material for storage of electrical energy is a material which can store electrical charge and release it again, for example by accepting and releasing electrons. This material can be used, for example, as an active electrode material in an electrical charge storage means. Such electrical charge storage means for storage of electrical energy are, for example, secondary batteries (accumulators), redox flow batteries and supercapacitors.

A secondary battery consists of a negative electrode and a positive electrode which are separated from one another by a separator, and an electrolyte which surrounds the electrodes and the separator.

The separator is a porous layer which permits balancing of charge by being ion-permeable. The electrolyte is either a solvent with a salt dissolved therein or an oligomeric or polymeric ion-conducting compound. The main object of the electrolyte is ion conductivity, which is
5 needed to balance the charge.

An electrode may consist of a thin layer on a substrate, composed of a composite containing at least one conductivity additive, at least one binder additive and a redox-active material for charge storage, which may be the oligomeric or polymeric compound of the inventive
10 general formula I. This composite is applied to a substrate with the aid of an electrode slurry.

Said layer on the substrate is formed, for example, by using a known method of film formation and derivatives thereof, preferably by various printing processes such as offset printing, screen printing, inkjet printing, or else by a dip-coating method, or a spin-coating
15 method, in which case the layer including the oligomeric or polymeric compound of the inventive general formula I is processed with the aid of an electrode slurry. In this case, the oligomeric or polymeric compound of the invention, the conductivity additive and the binder additive may be suspended or dissolved in a solvent. The thickness of the abovementioned layer containing the oligomeric or polymeric compound of this invention is unlimited, but is
20 preferably between 0.001 and 5000 μm , more preferably between 0.01 and 1000 μm .

The substrates used for the abovementioned electrodes are layers of conductive materials, preferably metals, such as platinum, gold, iron, copper, aluminium, lithium or a combination of these metals, and carbon materials, for example glassy carbon, graphite foil, graphene or
25 carbon sheets, and oxide substances, for example indium tin oxide (ITO), indium zinc oxide (IZO), antimony zinc oxide (AZO), fluorine tin oxide (FTO) or antimony tin oxide (ATO).

Conductivity additives used for the layer are independently one or more electrically conductive materials, preferably carbon materials, for example carbon fibres, carbon
30 nanotubes, graphite, carbon black or graphene, and electrically conductive polymers, for example polyanilines, polythiophenes, polyacetylenes, PEDOT:PSS or polyacenes. Particular preference is given to using carbon fibres.

Binder additives used for the substrate may independently be one or more materials having binder properties, preferably polymers, for example polytetrafluoroethylene, polyvinylidene fluoride, polyhexafluoropropylene, polyvinyl chloride, polycarbonate, polystyrene, polyacrylates, polymethacrylates, polysulphones, cellulose derivatives, and polyurethanes.

5

The electrode slurry is a solution or suspension consisting of any desired proportions of a redox-active material for storage of electrical energy, for example the oligomeric or polymeric compound of this invention as per formula I, a conductivity additive and a binder additive. Preferably, proportions of 5 to 100 per cent by weight of a redox-active material
10 for storage of electrical energy, 0 to 80 per cent by weight of a conductivity additive and 0 to 10 per cent by weight of a binder additive are used. Solvents used for the electrode slurry are independently one or more solvents, preferably solvents having a high boiling point, for example N-methyl-2-pyrrolidone, water, dimethyl sulphoxide, ethylene carbonate, propylene carbonate, dimethyl carbonate, methyl ethyl carbonate, gamma-butyrolactone,
15 tetrahydrofuran, dioxolane, sulpholane, N,N'-dimethylformamide or N,N'-dimethylacetamide. The concentration of the redox-active material for storage of electrical energy in the abovementioned electrode slurry is preferably between 0.1 and 10 mg/ml, more preferably between 0.5 and 5 mg/ml.

20 The oligomeric or polymeric compounds of this invention as per general formula I may, according to the counterelectrode used, be used as active material for electrical charge storage either for the negative electrode or for the positive electrode.

If the oligomeric or polymeric compound of this invention as per formula I is used as redox-
25 active material for electrical charge storage in the positive electrode, the redox-active material used for electrical charge storage in the negative electrode is an active material which exhibits a redox reaction at a lower electrochemical potential than the oligomeric or polymeric compound of this invention as per formula I. Preference is given here to using carbon materials, for example graphite, graphene, carbon black, carbon fibres or carbon
30 nanotubes, and also metals or alloys, for example lithium, sodium, magnesium, lithium-aluminium, Li-Si, Li-Sn, Li-Ti, Si, SiO, SiO₂, Si-SiO₂ complex, Zn, Sn, SnO, SnO₂, PbO, PbO₂, GeO, GeO₂, WO₂, MoO₂, Fe₂O₃, Nb₂O₅, TiO₂, Li₄Ti₅O₁₂, and Li₂Ti₃O₇.

If the oligomeric or polymeric compound of this invention as per formula I is used as redox-active material for electrical charge storage in the negative electrode, the redox-active material used for electrical charge storage in the positive electrode is an active material which exhibits a redox reaction at a higher electrochemical potential than the oligomeric or polymeric compound of this invention as per formula I. Preference is given here to using organic redox-active material for electrical charge storage, for example an oligomeric or polymeric compound having a stable organic radical, an oligomeric or polymeric compound having an organosulphur unit, an oligomeric or polymeric compound having a quinone structure, an oligomeric or polymeric compound having a dione system, an oligomeric or polymeric compound having a disulphide bond and an oligomeric or polymeric compound having a phenanthrene structure and derivatives thereof or redox-active inorganic material for charge storage, for example LiCO_2 , LiMn_2O_4 , LiNiO_2 , $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, LiFePO_4 , LiMnO_4 , LiCoPO_4 , or LiMnSiO_4 . If an abovementioned redox-active oligomeric or polymeric compound is used in the positive electrode, this compound may also be a composite consisting of this oligomeric or polymeric compound, a conductivity additive and a binder additive in any ratio. This composite may, as described above, be present as a layer on a substrate through a known film-forming process with the aid of an electrode slurry.

The redox-active material used for charge storage may also be air/oxygen. In this case, the positive electrode may consist of a conductivity additive, a binder additive and a redox catalyst. Preferably, redox catalysts used are an inorganic redox-active material, for example manganese oxide, or a redox-active organic material, for example an organic radical.

The abovementioned separator used in said secondary battery is a porous material, preferably membrane consisting of a polymeric compound, for example polyolefin, polyamide or polyester. The task of the separator is to separate the positive electrode from the negative electrode and to enable balancing of charge through permutation of ions.

The abovementioned electrolyte of said battery may be either a liquid or an oligomeric or polymeric compound having high ion conductivity.

If the electrolyte is liquid, it is independently composed of one or more solvents and one or more conductive salts.

The solvent of the electrolytes preferably consists independently of one or more solvents having a high boiling point and high ion conductivity but low viscosity, for example acetonitrile, dimethyl sulphoxide, ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, gamma-butyrolactone,
5 tetrahydrofuran, dioxolane, 1,2-dimethoxymethane, 1,2-dimethoxyethane, diglyme, triglyme, tetraglyme, ethyl acetate, 1,3-dioxolane or water.

The conductive salt in the electrolyte consists of a cation of the formula M^{e+} and an anion of the formula An^f of the formula $(M^{e+})_a(An^f)_b$ where e and f are integers depending on the
10 charge of M and An; a and b are integers which represent the molecular composition of the conductive salt.

Cations used in the abovementioned conductive salt are positively charged ions, preferably metals of the first and second main groups, for example lithium, sodium, potassium or
15 magnesium, but also other metals of the transition groups, such as zinc, and organic cations, for example quaternary ammonium compounds such as tetraalkylammonium compounds.

Anions used in said conductive salt are preferably inorganic anions such as hexafluorophosphate, tetrafluoroborate, triflate, hexafluoroarsenate, hexafluoroantimonate,
20 tetrafluoroaluminate, tetrafluoroindate, perchlorate, bis(oxalato)borate, tetrachloroaluminate, tetrachlorogallate, but also organic anions, for example $N(CF_3SO_2)_2^-$, $CF_3SO_3^-$, alkoxides, for example tert-butoxide or i-propoxide, but also halides such as fluoride, chloride, bromide and iodide.

25 The invention is to be illustrated in detail hereinafter by the working examples for preparation and use shown in the drawings.

The drawings show:

Fig. 1: Cyclic voltammograms of a monomer prepared according to Example 2
(broken line) and of an electrode produced therefrom according to Example
30 4 (solid line)

Fig. 2: Charge/discharge curves of the first (solid line) and five hundredth (broken line) charging/discharging cycle of a secondary battery produced according to Example 5

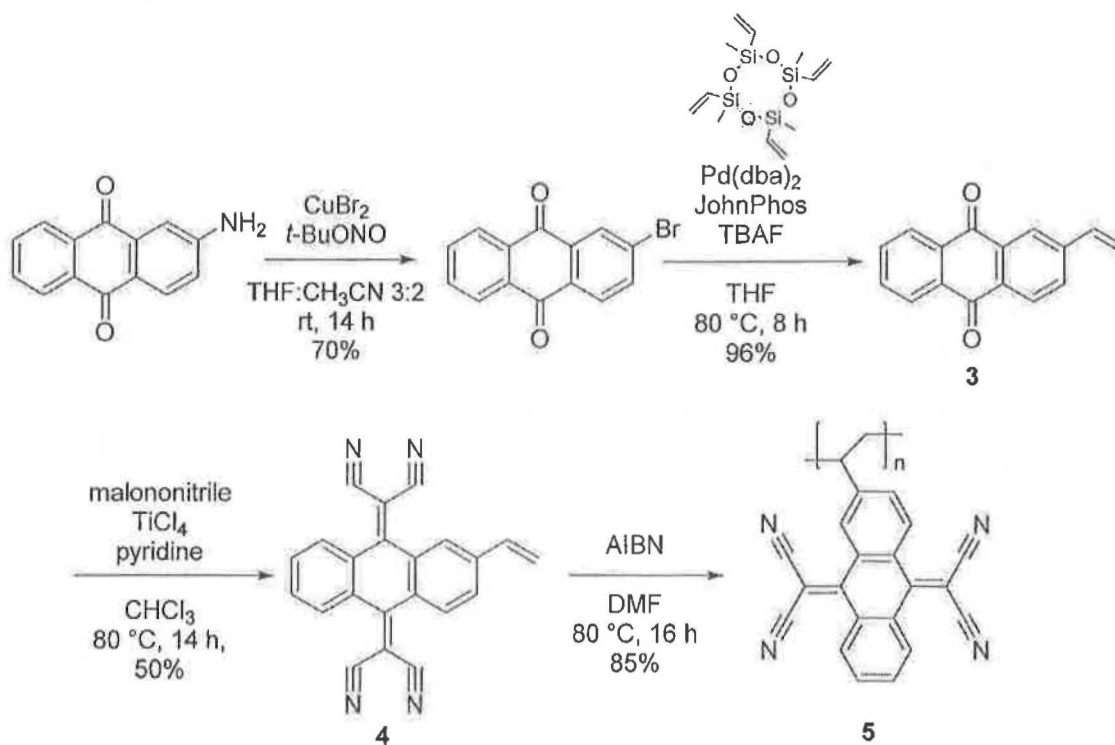
Fig. 3: Charging/discharging behaviour of the secondary battery produced according to Example 5

Fig. 4: Coulomb efficiency of the secondary battery produced according to Example 5

5

¹H and ¹³C NMR spectra were recorded with a Bruker AC 300 (300 MHz) spectrometer at 298 K. Elemental analyses were conducted with a Vario ELIII–Elementar Euro instrument and an EA–HekaTech instrument. For cyclic voltammetry and galvanostatic experiments, a Biologic VMP 3 potentiostat was available. Size exclusion chromatography was conducted
10 on an Agilent 1200 series system (degasser: PSS, pump: G1310A, autosampler: G1329A, oven: Techlab, DAD detector: G1315D, RI detector: G1362A, eluent: DMAc + 0.21% LiCl, 1 ml/min, temperature: 40°C, column: PSS GRAM guard/1000/30 Å).

Scheme 17:



Example 1:

5 Synthesis of 2-vinylanthraquinone (3):

2-Bromoanthraquinone (1.5 g, 5.22 mmol), bis(dibenzylideneacetone)palladium(0) (0.060 g, 0.104 mmol), biphenyl-2-yl-di-tert-butylphosphine (0.062 g, 0.209 mmol) are dissolved in a 0.3 M solution of tetrabutylammonium fluoride in tetrahydrofuran. The solution is purged with argon, and 2,4,6,8-tetramethyl-2,4,6,8-tetravinyl-1,3,5,7,2,4,6,8-tetraoxatetrasiloxane (0.902 ml, 2.61 mmol) is added dropwise. The mixture is stirred at 80°C under an argon atmosphere for 8 hours. The reaction mixture is cooled to room temperature and added to 250 ml of ethanol. The precipitate is filtered off and washed twice with n-hexane. After drying under reduced pressure, almost pure 2-vinylanthraquinone (3) (1.175 g, 5.02 mmol, 96%) is obtained as a yellowish solid, the purity of which is sufficient for the next reaction step.

Anal. Calcd for $\text{C}_{16}\text{H}_{10}\text{O}_2$: C, 81.90; H, 4.30. Found: C, 81.85; H, 4.31. ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 5.54 (d, 1H), 6.05 (d, 1H), 6.87 (dd, 1H), 7.80 (m, 3H), 8.32 (m, 4H). ^{13}C

NMR (CDCl₃, 75 MHz, ppm): δ 183.2, 182.6, 143.2, 135.4, 134.1, 134.0, 133.8, 133.6, 133.5, 132.5, 131.4, 128.3, 127.8, 127.2, 124.8, 118.4.

Example 2:

5 Synthesis of 2-vinyl-11,11,12,12-tetracyanoanthraquinodimethane (**4**):

2-Vinylanthraquinone (1 g, 4.27 mmol) and malononitrile (0.85 g, 0.81 ml, 12.81 mmol) are dissolved in 71 ml of chloroform. Pyridine (2.07 ml, 25.6 mmol) and titanium tetrachloride (1.41 ml, 12.81 mmol) are added dropwise to the reaction mixture within five minutes. The mixture is stirred at 80°C under argon for 15 hours, cooled to room temperature and extracted
10 twice with water and once with brine. The organic phase is dried with sodium sulphate, the desiccant is filtered off and the organic phase is concentrated under reduced pressure. The crude product is purified by column chromatography (silica gel, chloroform). This gives 700 mg of 2-vinyl-11,11,12,12-tetracyanoanthraquinodimethane (**4**) (2.12 mmol, 50%) as a yellow powder.

15 Anal. Calcd for C₂₂H₁₀N₄: C, 80.00; H, 3.10, N, 16.90. Found: C, 79.94; H, 3.08, N 16.91. ¹H NMR (CD₂Cl₂, 300 MHz, ppm): δ 5.61 (d, 1H), 6.06 (d, 1H), 6.88 (dd, 1H), 7.77 (m, 3H), 8.27 (m, 4H). ¹³C NMR (CD₂Cl₂, 75 MHz, ppm): δ 160.5, 160.0, 141.8, 134.5, 132.4, 130.8, 130.4, 130.2, 129.7, 129.0, 128.01, 127.5, 124.93, 119.3, 113.3, 113.1.

Example 3:

Synthesis of poly(2-vinyl-11,11,12,12-tetracyanoanthraquinodimethane) (**5**):

50 mg of 2-vinyl-11,11,12,12-tetracyanoanthraquinodimethane (**4**) are dissolved in 0.150 ml of N,N'-dimethylformamide, and 1.24 mg of AIBN (0.0076 mmol, 5 mol%) are added. The reaction mixture is degassed with argon for five minutes and stirred at 80°C for 18 hours. Thereafter, the reaction solution is added to 50 ml of dichloromethane, in order to precipitate the product. This forms 42 mg of poly(2-vinyl-11,11,12,12-tetracyanoanthraquinodimethane) (**5**) as a yellow solid.

Anal. Calcd for C₂₂H₁₀N₄: C, 80.00; H, 3.10, N, 16.90. Found: C, 79.96; H, 3.13, N 16.95.

¹H NMR (DMF-d₇, 300 MHz, ppm): δ 8.83 to 7.48 (br, 7H), 2.62 to 1.31 (br, 3H). SEC: M_n 2.67x10⁴ g/mol 1.87.

Example 4:

Production of an electrode with poly(2-vinyl-11,11,12,12-tetracyanoanthraquinodimethane) (**5**), cf. Fig. 1:

A solution consisting of poly(2-vinyl-11,11,12,12-tetracyanoanthraquinodimethane) (**5**) in NMP (N-methyl-2-pyrrolidone) (10 mg/ml) was added to carbon fibres (VGCF; Showa-Denko) and Super P® as conductivity additives and poly(vinylidene fluoride) (PVDF; Sigma Aldrich) as binder additives (ratio: 20/30/30/10 wt%). These materials were mixed in a mortar for 10 minutes, and the resulting paste was applied to an aluminium foil using a coating blade method (thickness: 0.015 mm, MTI Corporation). The electrode is dried at 100°C for 24 hours.

The electrode is dipped into an electrolyte solution (0.1 M LiClO₄ in propylene carbonate). For the cyclic voltammetry measurement, a half-cell consisting of said electrode as working electrode and an Ag/AgNO₃ electrode as reference electrode, and also a platinum mesh as counterelectrode, is constructed. (Fig. 1)

The cyclic voltammogram shows a stable redox reaction at -0.71 V.

Example 5:

Production of an Li polymer battery:

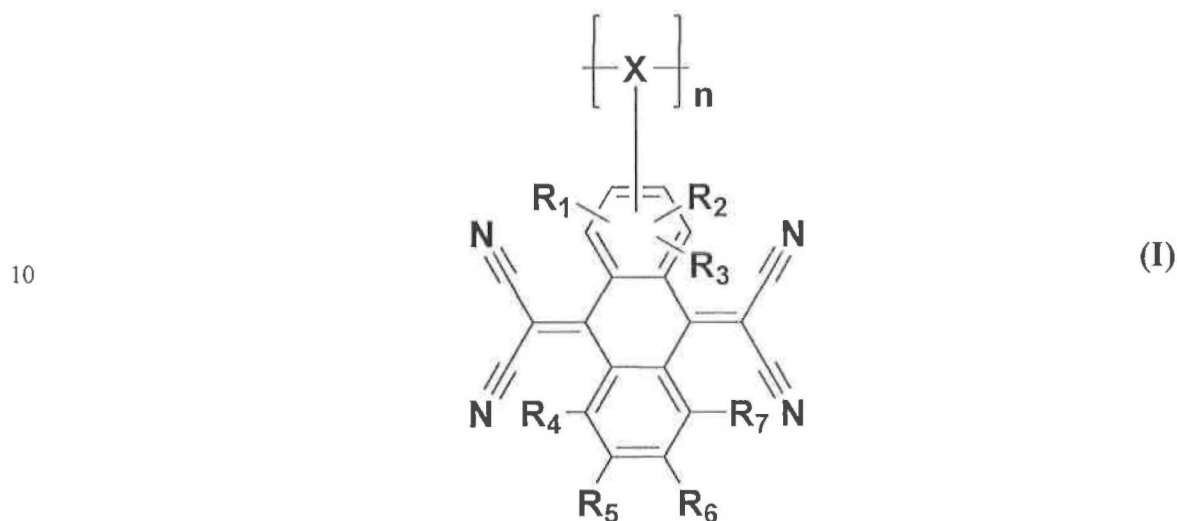
The electrode described in Example 4 is introduced into a secondary battery (Li polymer battery) under an argon atmosphere. The electrolyte used is a 0.1 M solution of LiClO_4 in propylene carbonate; the counterelectrode used is a piece of elemental lithium. The two electrodes are separated from one another by the separator (a porous polypropylene membrane, Celgard). The battery shows a charge plateau at 2.9 V and a discharge plateau at 2.4 V (Fig. 2).

In the first charge/discharge cycle, the battery shows a capacity of 156 mAh/g (97% of the theoretically possible capacity); after 500 charge/discharge cycles, the battery shows a capacity of 141 mAh/g (Fig. 3) at an average coulomb efficiency of 99%. (Fig. 4)

Claims

1. Tetracyanoanthraquinodimethane polymers consisting of an oligomeric or polymeric compound of the general formula I

5



15

where

R₁ to R₇: are each independently hydrogen atoms, alkyl groups, alkenyl groups, alkynyl groups, alkoxy groups, alkylthio groups, haloalkyl groups, haloalkoxy groups, cycloalkyl groups, cycloalkoxy groups, aryl groups, heteroaryl groups, aryloxy groups, aralkyl groups, carboxylic acid groups, sulphonic acid groups, amino groups, monoalkylamino groups, dialkylamino groups, nitro groups, cyano groups, hydroxyl groups, alkylcarbonyl groups, alkenylcarbonyl groups, alkynylcarbonyl groups, carboxylic ester groups, carboxamide groups, sulphonic ester groups, thiol groups, halogen atoms or a combination of these groups or atoms,

25

X: is an organic group which is formed by polymerization reaction from a group consisting of an organic double bond, an organic triple bond, an oxirane or an aziridine, or is an organic group which is formed by a polymer-analogous reaction,

30

n: is an integer greater than or equal to 2.

2. Tetracyanoanthraquinodimethane polymers according to Claim 1, wherein X is an organic group of one of the general formulae II-XIV:

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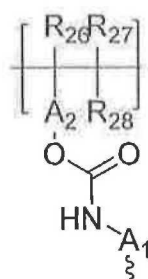


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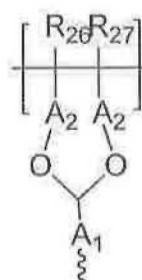


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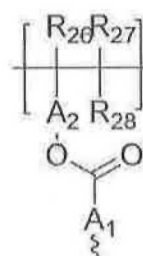




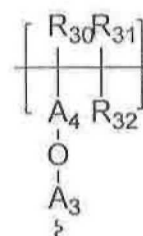
(IX)



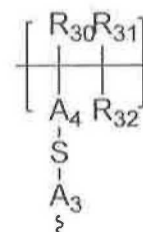
(X)



(XI)



(XII)



(XIII)



where

R₈ to R₂₄: are each independently hydrogen atoms, alkyl groups, alkenyl groups, alkynyl groups, alkoxy groups, alkylthio groups, haloalkyl groups, haloalkoxy groups, cycloalkyl groups, cycloalkoxy groups, aryl groups, heteroaryl groups, aryloxy groups, aralkyl groups, carboxylic acid groups, sulphonic acid groups, amino groups, monoalkylamino groups, dialkylamino groups, nitro groups, cyano groups, hydroxyl groups, alkylcarbonyl groups, alkenylcarbonyl groups, alkynylcarbonyl groups, carboxylic ester groups, carboxamide groups, sulphonic ester groups, thiol groups, halogen atoms or a combination of these groups or atoms,

- 5 R₂₆ to R₂₈: are each independently hydrogen atoms, alkyl groups, alkenyl groups, alkynyl groups, alkoxy groups, alkylthio groups, haloalkyl groups, haloalkoxy groups, cycloalkyl groups, cycloalkoxy groups, aryl groups, heteroaryl groups, aryloxy groups, aralkyl groups, carboxylic acid groups, sulphonic acid groups, amino groups, monoalkylamino groups, dialkylamino groups, nitro groups, cyano groups, hydroxyl groups, alkylcarbonyl groups, alkenylcarbonyl groups, alkynylcarbonyl groups, carboxylic ester groups, carboxamide groups, sulphonic ester groups, thiol groups, halogen atoms or a combination of these groups or atoms,
- 10 R₃₀ to R₃₂: are each independently hydrogen atoms, alkyl groups, alkenyl groups, alkynyl groups, alkoxy groups, alkylthio groups, haloalkyl groups, haloalkoxy groups, cycloalkyl groups, cycloalkoxy groups, aryl groups, heteroaryl groups, aryloxy groups, aralkyl groups, carboxylic acid groups, sulphonic acid groups, amino groups, monoalkylamino groups, dialkylamino groups, nitro groups, cyano groups, alkylcarbonyl groups, alkenylcarbonyl groups, alkynylcarbonyl groups, carboxylic ester groups, carboxamide groups, sulphonic ester groups, halogen atoms or a combination of these groups or atoms,
- 15 R₃₃ to R₃₅: are each independently hydrogen atoms, alkyl groups, alkenyl groups, alkoxy groups, alkylthio groups, haloalkyl groups, haloalkoxy groups, cycloalkyl groups, cycloalkoxy groups, aryl groups, heteroaryl groups, aryloxy groups, aralkyl groups, carboxylic acid groups, sulphonic acid groups, amino groups, monoalkylamino groups, dialkylamino groups, nitro groups, cyano
- 20

groups, hydroxyl groups, alkylcarbonyl groups, alkenylcarbonyl groups, alkynylcarbonyl groups, carboxylic ester groups, carboxamide groups, sulphonic ester groups, thiol groups, halogen atoms or a combination of these groups or atoms,

- 5 A: is an oxygen atom, a sulphur atom or an -N(R₂₉)- group, where R₂₉ is preferably a hydrogen atom, alkyl group, alkenyl group, alkynyl group, alkoxy group, alkylthio group, haloalkyl group, haloalkoxy group, cycloalkyl group, cycloalkoxy group, aryl group, heteroaryl group, aryloxy group, aralkyl group, carboxylic acid group, sulphonic acid group, nitro group, alkylcarbonyl group, alkenylcarbonyl group, alkynylcarbonyl group, carboxylic ester group, carboxamide group, sulphonic ester group,
- 10
- A₁ and A₂: are each independently a covalent bond, an alkyl group, an alkenyl group, an alkynyl group, an alkoxy group, an alkylthio group, a haloalkyl group, a haloalkoxy group, a cycloalkyl group, a cycloalkoxy group, an aryl group, a
- 15 heteroaryl group, an aryloxy group, an aralkyl group, a monoalkylamino group, a dialkylamino group, an alkylcarbonyl group, an alkenylcarbonyl group, an alkynylcarbonyl group, a carboxylic ester group, a carboxamide group, a sulphonic ester group,
- A₃ and A₄: are each independently a covalent bond, an alkyl group, an alkenyl group, an
- 20 alkynyl group, an alkoxy group, an alkylthio group, a cycloalkyl group, a cycloalkoxy group, an aryl group, a heteroaryl group, an aryloxy group, an aralkyl group, a dialkylamino group, an alkylcarbonyl group, an alkenylcarbonyl group, an alkynylcarbonyl group, a carboxylic ester group, a carboxamide group, a sulphonic ester group,
- 25 A₅ and A₆: are each independently a covalent bond, an alkyl group, an alkenyl group, an alkoxy group, an alkylthio group, a haloalkyl group, a

haloalkoxy group, a cycloalkyl group, a cycloalkoxy group, an aryl group, a heteroaryl group, an aryloxy group, an aralkyl group, a monoalkylamino group, a dialkylamino group, an alkylcarbonyl group, an alkenylcarbonyl group, an alkynylcarbonyl group, a carboxylic ester group, a carboxamide group, a sulphonic ester group,

5

Ar: is an independently substituted cycloalkyl group, cycloalkoxy group, aryl group, heteroaryl group, aryloxy group, aralkyl group.

3. Use of the tetracyanoanthraquinodimethane polymers according to one or both of Claims
10 1 and 2 as active electrode material for electrical charge storage means.

4. Use of the tetracyanoanthraquinodimethane polymers according to Claim 3, wherein the active electrode material takes the form of a full or partial surface coating of electrode elements for electrical charge storage means.

15

5. Use of the tetracyanoanthraquinodimethane polymers according to one or both of Claims 1 and 2 as electrode slurry for electrical charge storage means.