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(54) Titre : MATERIAU SEMI-CONDUCTEUR ORGANIQUE DOPE ET SON PROCEDE DE PRODUCTION
(54) Title: DOPED ORGANIC SEMICONDUCTOR MATERIAL AND METHOD FOR PRODUCTION THEREOF

(57) Abrégé/Abstract:
The invention relates to a doped organic semiconductor material with increased charge carrier density and more effective charge carrier mobility, which may be obtained by doping an organic semiconductor material with a chemical compound comprising one or several organic molecular groups (A) and at least one further compound partner (B). The desired doping effect is achieved after cleavage of at least one organic molecular group (A) from the chemical compound by means of at least one organic molecular group (A) or by means of the product of a reaction of at least one molecular group (A) with another atom or molecule. A method for production thereof is disclosed.

ABSTRACT

The invention relates to a doped organic semiconductor material with increased charge carrier density and more effective charge carrier mobility, which may be obtained by doping an organic semiconductor material with a chemical compound comprising one or several organic molecular groups (A) and at least one further compound partner (B). The desired doping effect is achieved after cleavage of at least one organic molecular group (A) from the chemical compound by means of at least one organic molecular group (A) or by means of the product of a reaction of at least one molecular group (A) with another atom or molecule.

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DOPED SEMICONDUCTOR MATERIAL AND PROCESS FOR PRODUCTION THEREOF

DESCRIPTION

The invention relates to doped organic semiconductor material having enhanced charge carrier density and effective charge carrier mobility according to Claim 1, a process according to Claim 48 for production of the doped organic semiconductor material, and use of the semiconductor material.

Since the demonstration of organic light-emitting diodes and solar cells in 1989 [C.W. Tang et al., *Appl. Phys. Lett* 51 (1987, no. 12), 913], components made up of organic thin layers have been the subject of intensive research. Such layers possess advantageous properties for the applications mentioned, as for example efficient electroluminescence for organic light-emitting diodes, high absorption coefficients in the range of visible light for organic solar cells, economical production of materials and fabrication of components for very simple electronic circuits, et alia. Commercial significance has already been attained by the use of organic light-emitting diodes in display applications.

The performance features of (opto-)electronic multilayer components are determined among other things by the ability of the layers to transport the charge carriers. In the case of light-emitting diodes the ohmic losses in the charge transport layers are related in operation to the conductivity, which firstly influences the necessary operating voltage directly, and secondly determines the heat loading of the component as well. Furthermore, depending on the charge carrier concentration of the organic layers, there will be a band deflection in the neighborhood of a metal contact, facilitating the injection of charge carriers and hence capable of reducing the contact resistance. Similar considerations lead to the conclusion, for organic solar

cells as well, that their efficiency is also determined by the transport properties of charge carriers.

By doping hole transport layers with a suitable acceptor material (p-dope) and/or electron transport layers with a donor material (n-dope), the charge carrier density in organic solids (and hence the conductivity) can be enhanced considerably. Furthermore, in analogy to experience with organic semiconductors, applications are to be expected that depend precisely on the use of p- and n-doped layers in a component, and would not be conceivable otherwise. US 5,093,698 describes the use of doped charge carrier transport layers (p-doping of the hole transport layer by admixture of acceptor-like molecules, n-doping of the electron transport layer by admixture of donor-like molecules) in organic light-emitting diodes.

The following approaches are so far known for improving the conductivity of organic vapor-deposited layers:

1 Enhancement of charge carrier mobility by

(a) Use of electron transport layers consisting of organic radicals (US 5,811,833)

(b) Production of high-order layers permitting an optimal overlap of the pi-orbitals of the molecules

2 Enhancement of density of moving charge carriers by

(a) Cleaning and conservative treatment of materials to avoid the formation of charge carrier sticking points

(b) Doping of organic layers with

aa) Inorganic materials (gases, alkali metal atoms, US Patent 6,013,384 (J. Kido et al.); J. Kido et al., *Appl. Phys. Lett.* 73 (1998), 2866)

bb) Organic materials (TNCQ (M. Maitrot et al., *J. Appl. Phys.* 60 (1986, no. 7), 2396-2400); F4TCNQ (M. Pfeiffer et al., *Appl Phys. Lett.* 73 (1998, no. 22), 3202); BEDT-TTF (A. Nollau et al., *J. Appl. Phys.* 87 (2000, no. 9), 4340)

Doped organic charge transport layers have been used successfully to improve organic light-emitting diodes. By doping the hole transport layer with the acceptor material F4TCNQ, a drastic reduction of the operating voltage of the light-emitting diode is achieved (X. Zhou et al., *Appl Phys. Lett.* 78 (2001, no. 4), 410). A similar success is achieved by doping the electron transporting layer with Cs or Li (J. Kido et al., *Appl. Phys. Lett.* 73 (1998, no. 20), 2866, J.-S. Huang et al., *Appl. Phys. Lett.* 80 (2002), 139).

Electrical doping with inorganic materials suffers from the disadvantage that the atoms or molecules used, owing to their small size, may easily diffuse in the component, thus rendering more difficult a defined production e.g. of sharp transitions from p-doped to n-doped regions. Diffusion plays a subordinate role by comparison, using large organic molecules as donors. However, their use is limited by the circumstance that potential donor molecules must distinguish themselves by extreme values of electronic affinity for p-doping or ionization potential for n-doping. This is attended by a decreasing chemical stability of the molecules.

Now the object of the invention consists in specifying a solution to overcome the said chemical instability of efficient dope molecules and to specify the production of layers doped therewith.

According to the invention, the object is accomplished by the features named in Claim 1. Advantageous embodiments are the subject of subsidiary claims.

The object is accomplished further by a method having the features named in Claim 48. Advantageous modifications of the method are the subject of subsidiary claims.

The invention employs organic molecules which, while unstable in the neutral state, yet are present stable as charged cation or anion in connection with a covalent partner. These charged molecules are produced *in situ* from a predecessor compound, which, during or after the process of vapor deposition, is converted into the desired charged molecule. Without limitation thereto, such a compound may for example be an organic salt or a metal complex. The unstable dopant also can be produced in situ from a stable predecessor substance.

Heretofore, the donor molecule used was introduced into the layer to be doped in the neutral state, being then present as anion or cation on the matrix after a charge transfer. The use of the neutral molecule is here only an intermediate step to bring about the charge transfer. The associated stability problems already described may be avoided according to the invention by use of an already ionized stable molecule as dopant.

If necessary, use is made of further methods to support the dissociation of the predecessor compound. These contribute the necessary energy to split the compound, or bring about a chemical reaction with the unwanted remainder of the predecessor compound, so that it does not arrive in the layer, or is more easily removed therefrom, or does not impair the electrical properties of that layer. An advantageous solution according to the invention is the use, for example, of a laser to evaporate rhodamine B chloride, leading to predominant production of rhodamine B cations.

Even though the foregoing description aims at splitting off an already charged molecular group according to Claim 1, the purpose of the invention may also be achieved if a neutral radical is first produced from the compound according to Claim 1, sufficiently stable *in situ* to be incorporated in the layer, and this is subject in the layer to a transfer of the radical electron to the matrix, or acceptance of an additional electron from the matrix.

US 5,811,833 describes an electron transport layer consisting of free radicals, in particular pentaphenyl cyclopentadienyl, for use in organic light-emitting diodes. US 5,922,396 shows that such a layer can be prepared from metal-organic compounds, in particular decaphenyl germanocene or decaphenyl plumbocene (see also M.J. Heeg, *J. Organometallic Chem.* 346 (1988), 321). US 5,811,833 and US 5,922,396 lead to layers with enhanced microscopic charge carrier mobility (transfer rates in the hopping process), since a negatively charged pentaphenyl cyclopentadienyl molecule possesses an aromatic character, and so the electron transfer to a neighboring neutral pentaphenyl cyclopentadienyl molecule is improved by the overlap of the pi-electron orbitals of the participating molecules. The enhancement of conductivity is achieved by an enhancement of the microscopic charge carrier mobility (or of the transfer rates in the hopping process). Contrariwise, according to the invention the equilibrium charge carrier density is enhanced, to increase the conductivity Discrimination is possible for example by "time-of-flight" (measurement of charge carrier mobility), using the Seebeck effect or the field effect (measurement of charge carrier density).

The invention relates further to the use of doping molecules in mixed layers additionally containing materials to accomplish some other purpose. These purposes may for example pertain to alteration of layer growth, production of interpenetrating networks (C.J. Brabec et al., *Adv. Mater* 11 (2001, no. 1) 15), or, in organic light-emitting diodes, improvement of quantum efficiency of emission or change of color of emitted light by addition of a luminescence dye.

Further, in the spirit of the invention, suitable choice of the doping molecule used can achieve such purposes simply by addition of the doping molecule to the layer. For example,

cationic dyes such as rhodamine B often have a high quantum yield of luminescence, making possible their use as luminescence dyes in organic LEDs.

Finally, the invention embraces the use of molecules according to Claim 1 to dope polymer layers. Such layers are typically produced by a "spin coating" process, by deposition from the solution. Contrary to the known electrochemical doping, in which the anions and cations of a salt are drawn to the respective contacts by the applied voltage and therefore are mobile, the present invention, according to Claim 1, allows the doping of polymer layers with large, non-mobile molecules.

An embodiment illustrating the invention by way of example consists in use of the dye molecule rhodamine B chloride as dope. If a mixed layer of naphthalene tetracarboxylic acid dianhydride (NTCDA) and rhodamine B in proportions (150:1) is produced, a conductivity of $1x10^{-5}$ S/cm is obtained at room temperature, corresponding to an increase by 4 orders of magnitude over a pure NTCDA layer. The physical explanation of this is that rhodamine B chloride molecules during heating in the cell decompose into positively charged rhodamine B molecules and negatively charged chloride ions. The charged rhodamine B molecules are incorporated in the mixed layer. The electrons required to maintain charge neutrality of the layer as a whole remain on the NTCDA molecules, since the electronic affinity of NTCDA is higher than that of rhodamine B (3.2 eV, H. Meier, *Organic Semiconductors*, Verlag Chemie Weinheim 1974, p. 425). These electrons fill the lowest unoccupied orbitals of NTCDA and so increase the conductivity. The enhanced density of the charge carriers may for example be established by measurements of the Seebeck coefficient and of the field effect. Field effect measurements on a sample of NTCDA doped with pyronine B (50:1) confirm the presence of electrons as majority charge carriers in a concentration of 10^{17} cm^{-3}. Seebeck measurements on this system likewise

show n-conduction, with a Seebeck coefficient of -1.1 mV/K and hence a higher charge carrier concentration than attainable heretofore with doped NTCDA (A. Nollau et al., *J. Appl. Phys.* 87 (2000, no. 9), 4340).

If a layer doped with rhodamine B is prepared from C60 (fullerene) (50:1) with elevated substrate temperature a conductivity of $6x10^{-3}$ S/cm is obtained. This is two orders of magnitude greater than for a specimen produced at room temperature ($5x10^{-5}$ S/cm). The heat supplied during vapor deposition leads to an intensified detachment of rhodamine B.

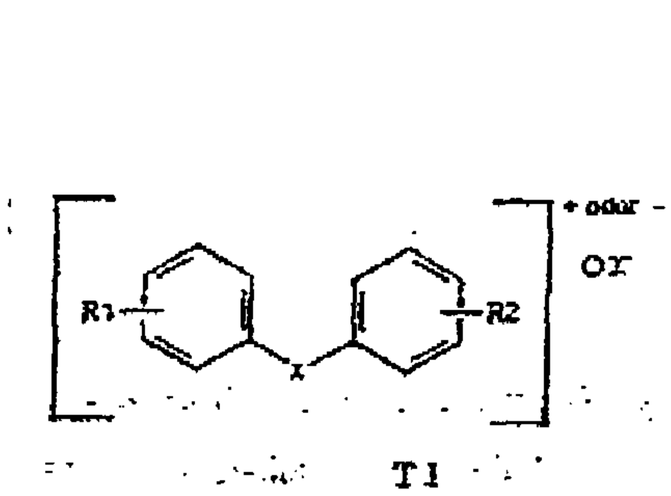
The doping effect of rhodamine B was also verified for matrices of MePTCDI (perylene 3,4,9,10-tetracarboxylic acid N,N'-dimethyl-diimide) and PTCDA (3,4,9,10-perylene tetracarboxylic acid dianhydride), and so is independent of the concrete chemical structure of the matrix.

A strong known organic donor, tetrathiafulvalene (TTF), has an oxidation potential of +0.35 V against SCE (Y. Misaki et al., *Adv. Mater.* 8 (1996), 804). Stronger donors, i.e. dopes having a lower oxidation potential, are unstable in air (G.C. Papavassiliou, A. Terzis, P. Delhaes, in H.S. Nalwa (ed.), *Handbook of Conductive Molecules and Polymers*, vol. 1, "Charge-transfer salts, fullerenes and photoconductors," John Wiley & Sons, Chichester 1997). Rhodamine B has a reduction potential of -0.545 V against NHE (M.S. Chan, J.R. Bolton, *Solar Energy 24* (1980), 561), i.e. -0.79 V against SCE. The reduction potential of the organic salt rhodamine B is determined by the reduction potential of the rhodamine B cation. This value is equal to the oxidation potential of the neutral rhodamine B radical. Consequently the rhodamine B radical is a stronger donor than TTF. But in the chemical compound rhodamine B chloride, this strong donor rhodamine B is stable So while it has been possible heretofore to employ donors having an oxidation potential greater than +0.35 V against SCE, the invention here

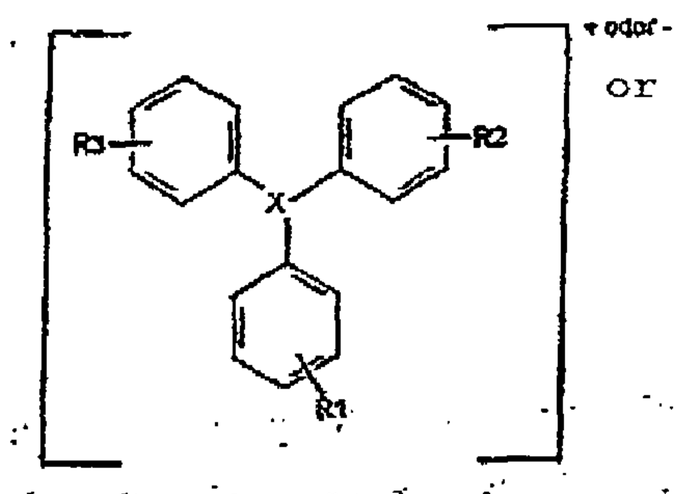
described allows doping with donors whose oxidation potential is smaller than +0.35 V against SCE.

Chemically stable compounds in the sense of Claim 1 are for example ionic dyes. These are employed in photography to sensitize AgBr for example. The electronic affinity of AgBr is 3.5 eV. Dyes able to sensitize AgBr by electron transfer are also suitable as chemically stable compounds for use to dope organic semiconductor materials in the spirit of Claim 1.

A subclass of the ionic dyes are the di- and triphenylmethane dyes and their known analogues of general structure



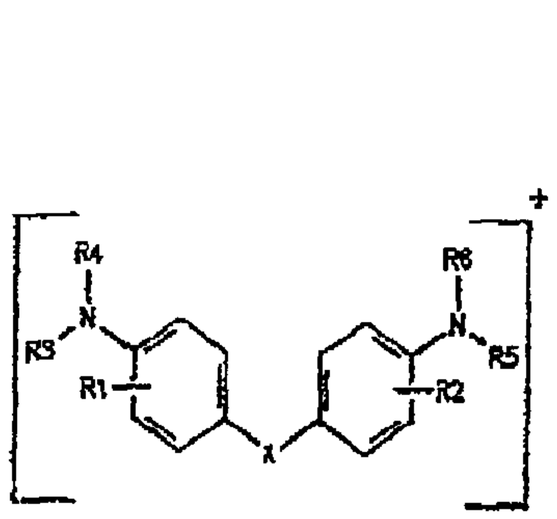
T1



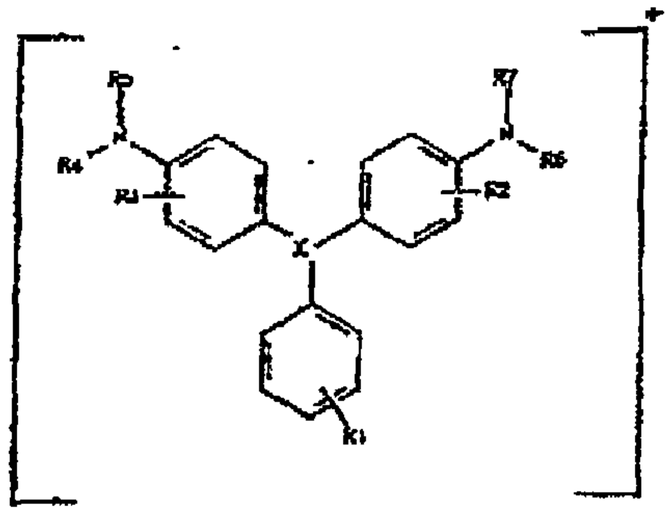
T2

where X CR^4, SiR^4, GeR^4, SnR^4, PbR^4, N, P and R1, R2, R3 and R^4 are suitable known substituents, e.g. in each instance one or several hydrogens; oxygens; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryls having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl, or those atoms which form a condensed ring.

Often one or more p-located substitutions of the phenyl groups are encountered (T3 to T6)

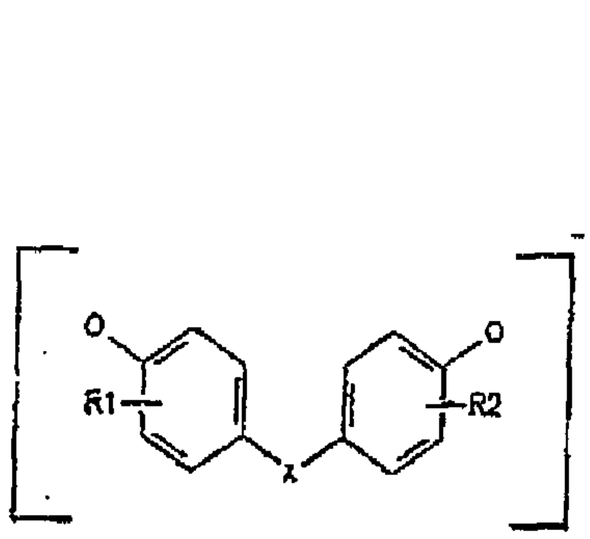


T3

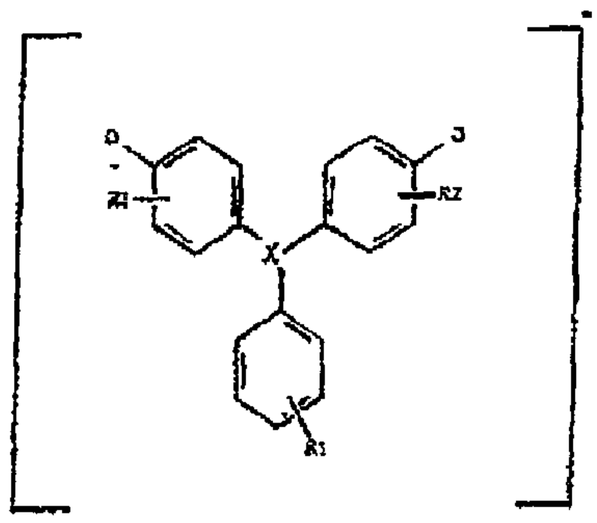


T4

where X CR8, SiR8, GeR8, SnR8, PbR8, N, P and R1 to R7 and R8 are suitable known substituents, e.g. in each instance one or more hydrogens; oxygens; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyls; aminyl, e.g. diphenyl aminyl; diethyl aminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl, or those atoms which form a condensed ring.



T5



T6

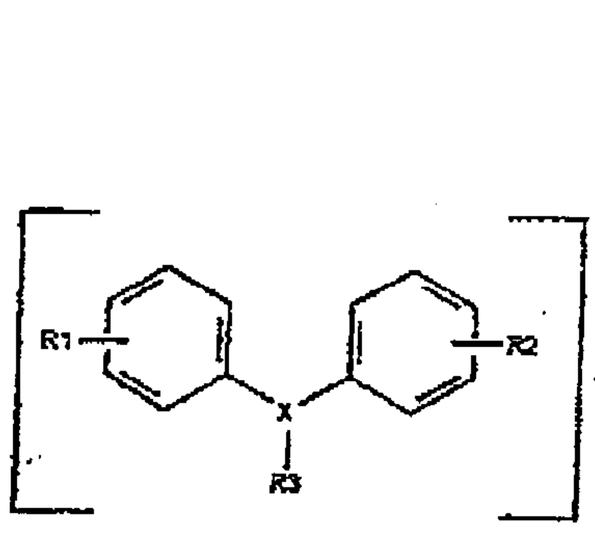
Examples of diphenylmethane dyes are auramine O (CI 655) or auramine G (CI 656).

Examples of triphenylmethane dyes are malachite green (CI 657), turquoise blue (CI 661), fluoresceine (CI 45350) or patent blue V (CI 712).

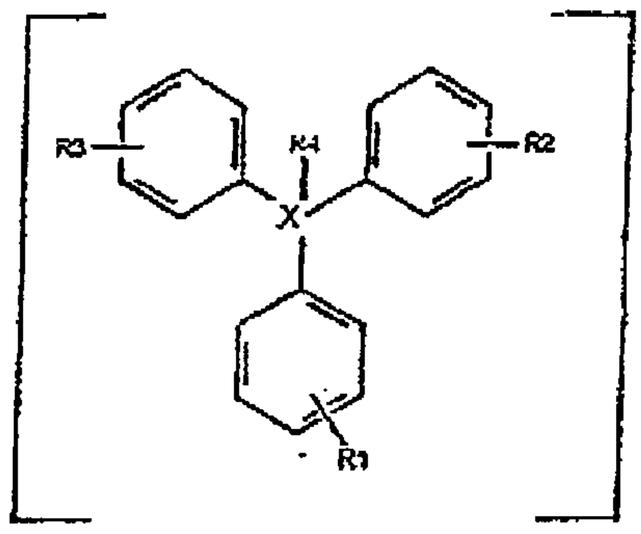
The triphenylmethane representative malachite green chloride, in an NTCDA matrix at a dope ratio of 1:122 produces a conductivity of $4x10^{-4}$ S/cm. Thus malachite green, as

a compound in the sense of Claim 11 and particularly in the sense of subsidiary Claims 12 to 22, is suitable for producing a dopant molecule *in situ*. This property is evoked by the valence structure of the central carbon atom (4th main group). Other known compounds of this structural type with atoms of the 4th main group as central atom (triarylsilyl, germyl, stannyl, plumbyl) are accordingly likewise suitable as compounds in the sense of Claims 1, 12 to 22. Compounds in which there is a direct bond between 2 carbon atoms each of a phenyl ring of the di- or triphenylamines are contained in Claims 23 to 25.

The doping effect also occurs using the leuko forms (T7, T8) of the ionic dyes. Rhodamine B base acts to dope a PTCDA matrix, e.g. can produce a conductivity of $7 \cdot 10^{-5}$ S/cm for 1:70 doping.



T7

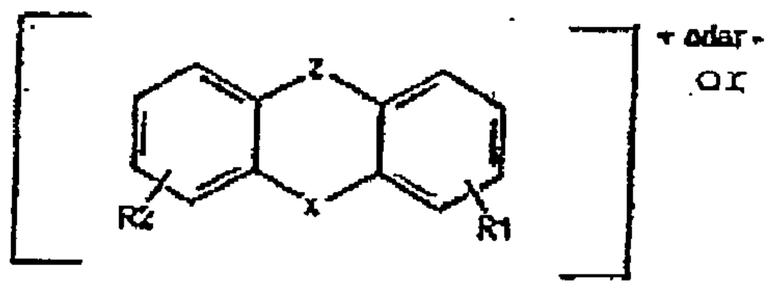


T8

Another group of ionic dyes are the xanthene dyes.

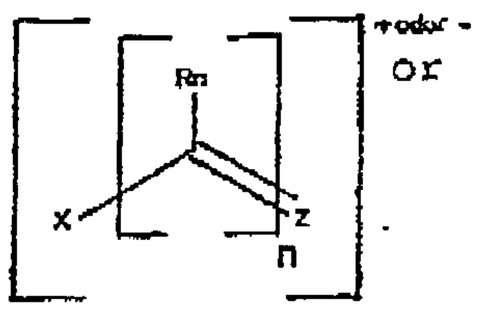
The above-mentioned rhodamine B is a representative of this class. Pyronine B, rhodamine 110 and rhodamine 3B as additional representatives of this class of materials likewise have a doping effect. Similar to the xanthene dyes are among others the pyrane, thiopyrane, indamine, acridine, azine, oxazine and thiazine dyes, which are distinguished by substitutions in

the multinuclear heterocycle. On the basis of their otherwise like structure, these dye classes (T9) are likewise suitable compounds in the sense of Claims 1, 23 to 26.



T9

Dyes based on a polymethine structure



also act as dopes.

N,N'-diethylcyanine and N,N'-diethylthiacarbocyanine in an NTCDA matrix cause an enhancement of conductivity to $3 \cdot 10^{-5}$ S/cm (dope ratio 1:114) and $5 \cdot 10^{-5}$ S/cm (dope ratio 1:47) respectively. These two dyes each represent the polymethine dye with a certain choice of X and Z.

The leuko bases of ionic dyes are likewise suitable compounds in the sense of Claims 1, 12 to 26. For example, rhodamine B base in NTCDA yields a conductivity of $3 \cdot 10^{-5}$ S/cm (1:70 dope ratio).

Since the doping effect does not link to the ionic dye property, but rather to the character of the dyes as organic salts, other organic salts also will act as compound in the sense

of Claim 11. Organic salts are often based on suitable heterocycles (e.g. pyridinium, pyrrolium, pyrylium, thiazolium, diazininium, thininium, diazolium, thiadiazolium or dithiolium etc., singly or as part of a multinuclear heterocycle), or suitable groups (e.g. ammonium, sulfonium, phosphonium, iodonium etc.).

Mass spectrometry studies in the case of pyronine B chloride show that in the evaporation of pyronine B, among other things HCl and a protonized form of pyronine B of mass number 324 is formed. Evidently the chlorine radicals produced by detachment of pyronine B chloride and neutral pyronine B radicals are saturated by a proton. These protons are supplied by other pyronine B molecules in the evaporating substance. A vapor-deposited layer of pyronine B chloride is colorless in the first instance. This is shown by the formation of neutral pyronine B. Under the influence of oxygen, the vapor-deposited layer becomes red in color again, corresponding to the formation of the pyronine B cation, i.e. the evaporated substance is oxidized under the influence of oxygen. This process takes place likewise in a mixed layer of matrix and dope. Vapor-deposited mixed layers of pyronine B chloride and tetracyanoquinodimethane are colored red immediately, and the presence of tetracyanoquinodimethane anion can be evidenced by UV/VIS and FTIR spectroscopy.

Claims

1. Doped organic semiconductor material having enhanced charge carrier density and effective charge carrier mobility, obtainable by doping an organic semiconductor material with a chemical compound consisting of one or more organic molecular groups A having at least one additional combining partner B, the desired doping effect being obtained after loss of at least one organic molecular group A from the chemical compound or by the product of a reaction of at least one molecular group A with another atom or molecule.

2. Doped organic semiconductor material according to claim 1, in which at least one of the combining partners B is the same molecular group as A.

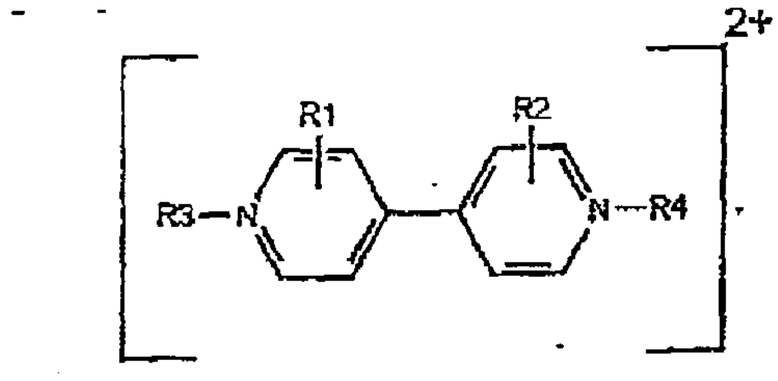
3. Doped organic semiconductor material according to either of claims 1 to 2, in which the additional combining partner B is a molecular group, an atom or an ion.

4. Doped organic semiconductor material according to any of claims 1 to 3, in which the molecular group A is present in the chemical compound as a singly or multiply charged cation or anion.

5. Doped organic semiconductor material according to any of claims 1 to 4, in which the molecular group A is based on one or more pyridinium units.

6. Doped organic semiconductor material according to claim 5, in which one or more pyridinium units occur as part of one or more multinuclear heterocycles.

7. Doped organic semiconductor material according to either of claims 5 and 6 in which the molecular group A is based on the structure



where R1, R2, R3 and R4 for example are each one or more hydrogen; oxygen; halogen, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

8. Doped organic semiconductor material according to any of claims 1 to 4, in which the molecular group A is based on one or more pyrrolium, pyrylium, thiazolium, diazinimium, thinium, diazolium, thiadiazolium, tetrazolium or dithiolium units.

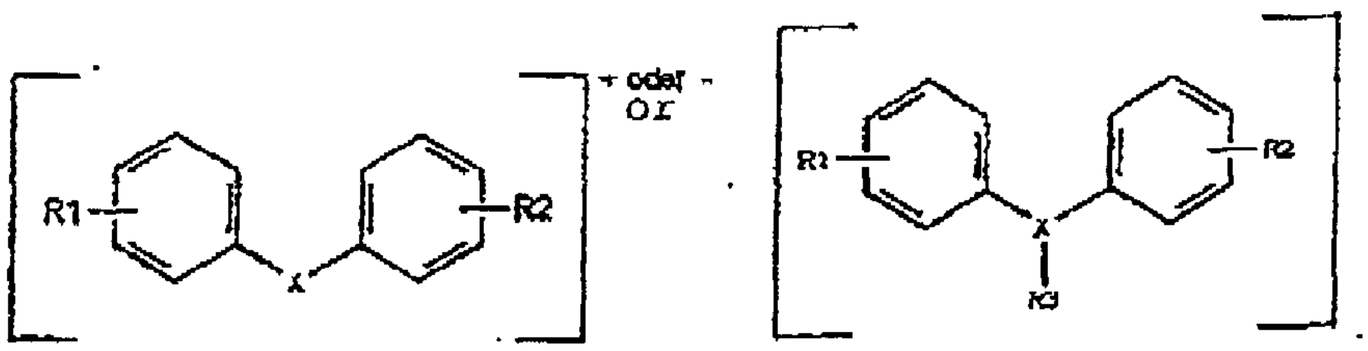
9. Doped organic semiconductor material according to claim 5, in which one or more pyrrolium, pyrylium, diazinium, thininium, diazolium, thiazolium, thiadiazolium, tetrazolium or dithiolium units occur as part of one or more multinuclear heterocycles.

10. Doped organic semiconductor material according to any of claims 1 to 4, in which the molecular group A is based on one or more borate benzene units.

11. Doped organic semiconductor material according to claim 10, in which one or more borate benzene units occur as part of one or more multinuclear heterocycles.

12. Doped organic semiconductor material according to any of claims 1 to 11, in which the molecular group A is a cationic dye, an anionic dye or some other organic salt.

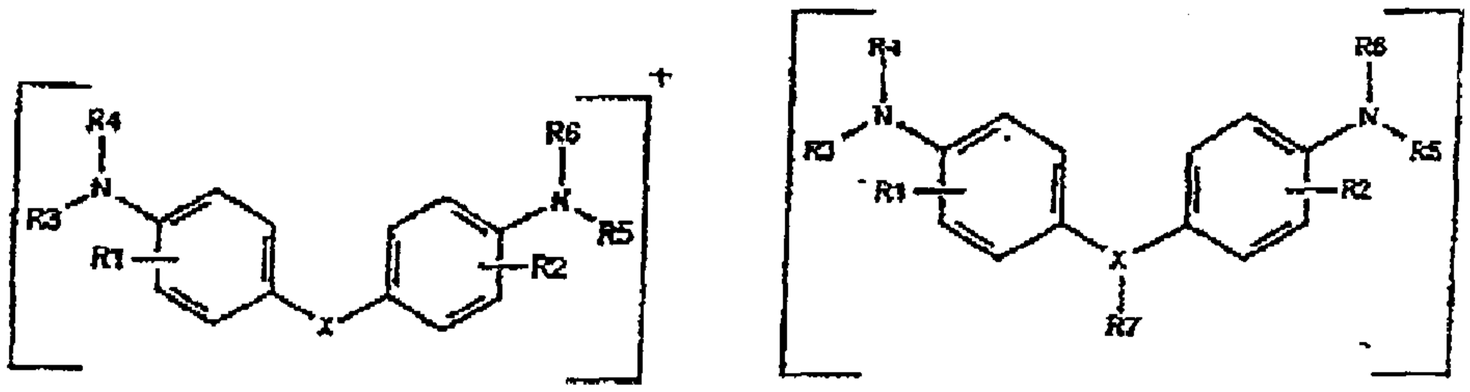
13. Doped organic semiconductor material according to any of claims 1 to 12, in which the molecular group A is based on the structure A1 or the corresponding leuko base A2



A1 A2

where X CR^4, SiR^4, GeR^4, SnR^4, PbR^4, N, P and R1, R2, R3 and R^4 e.g. are each one or more hydrogen, oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

14. Doped organic semiconductor material according to any of claims 1 to 13, in which the molecular group A is based on the structure A3 or the corresponding leuko base A4

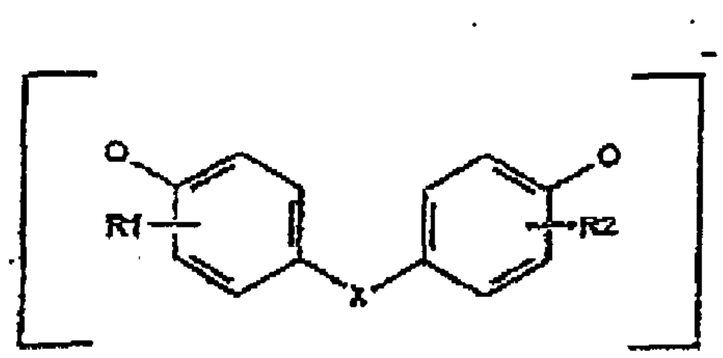


A3 A4

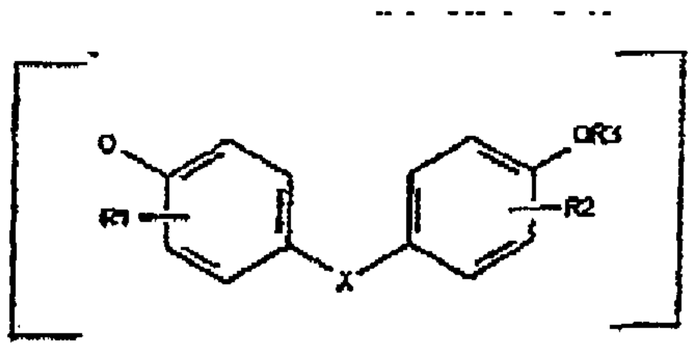
where X CR^8, SiR^8, GeR^8, SnR^8, PbR^8, N, P and R1, R2, R3, R4, R5, R6, R7, R^8, e.g. are each one or more hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl

having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

15. Doped organic semiconductor material according to any of claims 1 to 14, in which the molecular group A is based on the structure A5 or the corresponding leuko base A6



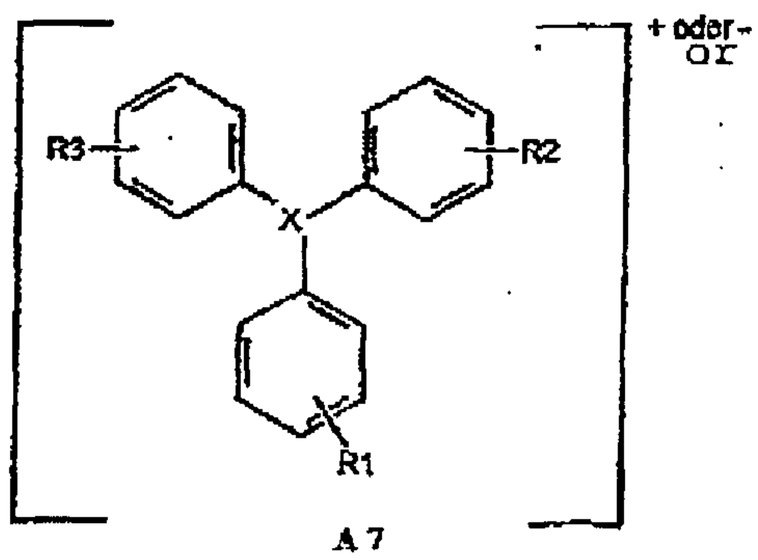
A5



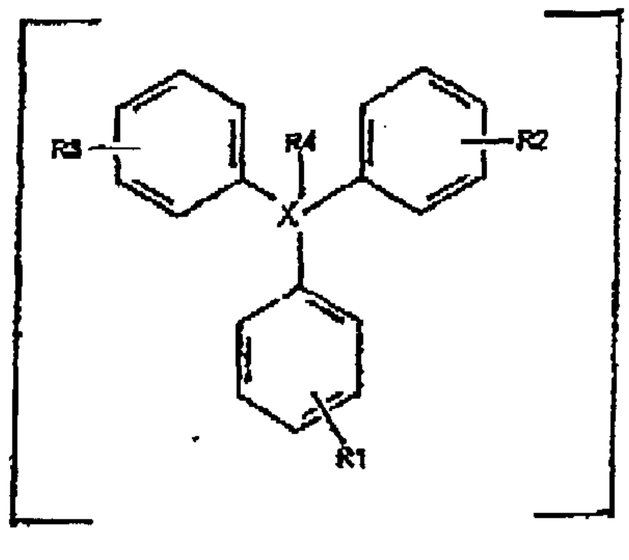
A6

where X CR^4, SiR^4, GeR^4, SnR^4, PbR^4, N, P, S and R1, R2, R3, R^4 e.g. are each one or more hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

16. Doped organic semiconductor material according to any of claims 1 to 15, in which the molecular group A is based on the structure A7 or the corresponding leuko base A8



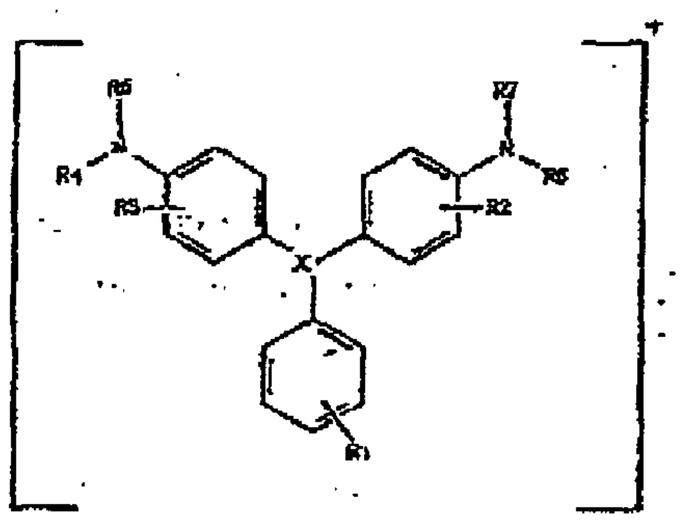
A7



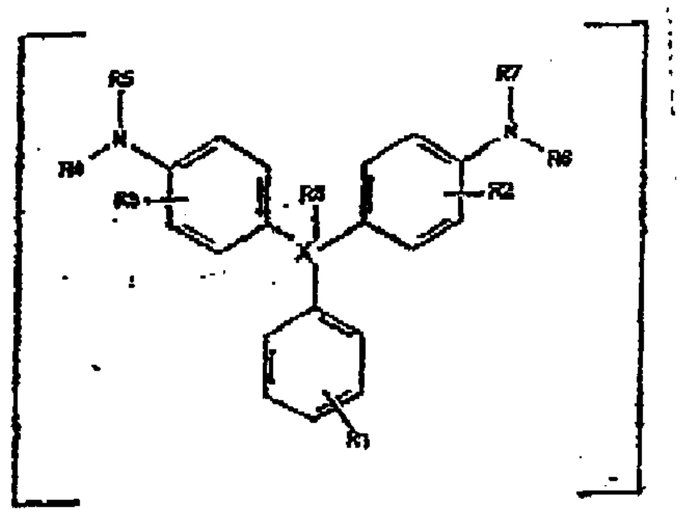
A8

where X C, Si, Ge, Sn, Pb, S and R1, R2, R3 and R4 e.g. are each one or more hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

17. Doped organic semiconductor material according to any of claims 1 to 16, in which the molecular group A is based on the structure A9 or the corresponding leuko base A10



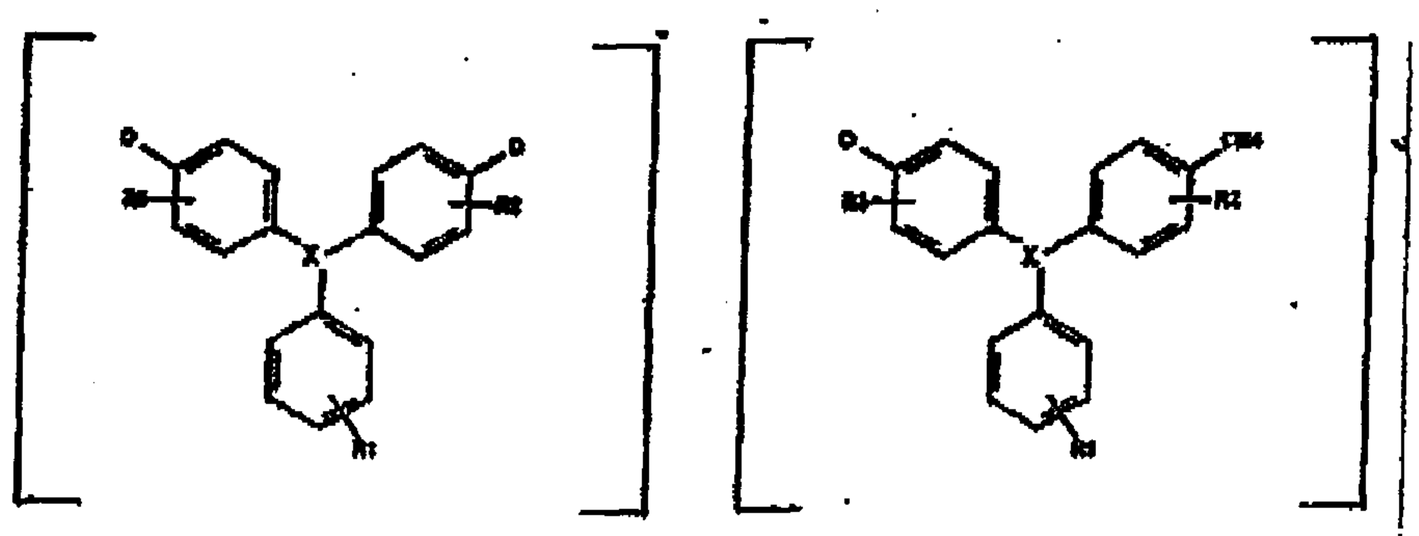
A9



A10

where X C, Si, Ge, Sn, Pb and R1, R2, R3, R4, R5, R6, R7 and R8 e.g. are each one or more hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

18. Doped organic semiconductor material according to any of claims 1 to 17, in which the molecular group A is based on the structure A11 or the corresponding leuko base A12



A11 A12

where X C, Si, Ge, Sn, Pb and R1, R2, R3, R4 e.g. are each one or more hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

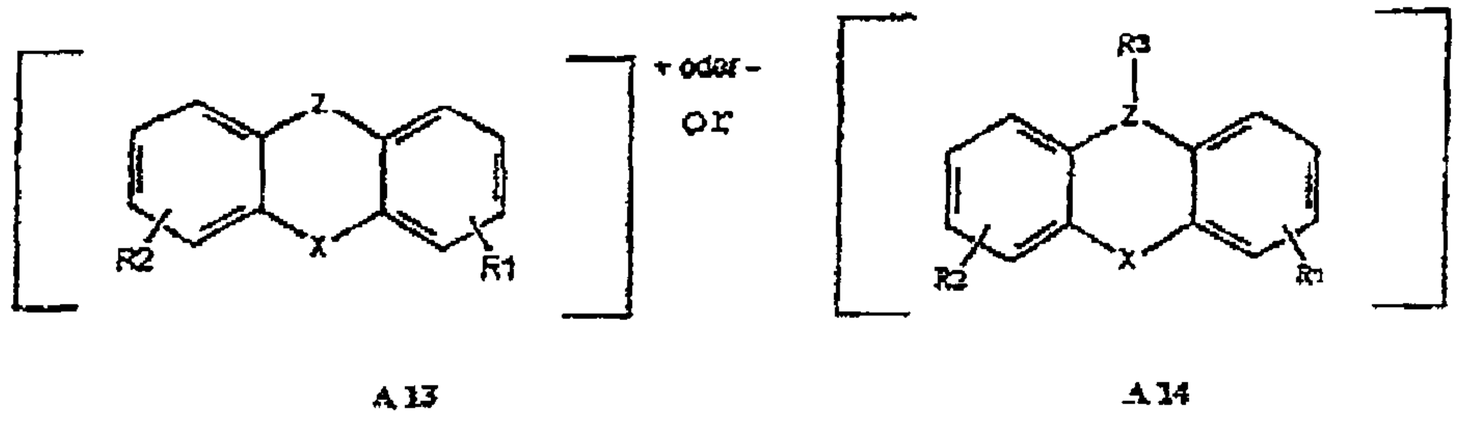
19. Doped organic semiconductor material according to any of claims 11 to 18, in which the chemically stable compound is C.I. Basic Yellow 37 (C.I. 41001) or some other diphenylmethane dye with known opposed anion.

20. Doped organic semiconductor material according to any of claims 11 to 18, in which the chemically stable compound is C.I. Basic Green 4 (C.I. 42000) or some other diamino derivative of the triphenylmethane dyes with known opposed anion.

21. Doped organic semiconductor material according to any of claims 11 to 18, in which the chemically stable compound is C.I. Basic Red 9 (C.I. 42500) or some other triamino derivative of the triphenylmethane dyes with known opposed anion.

22. Doped organic semiconductor material according to any of claims 11 to 18, in which the chemically stable compound is Phenylene Blue (C.I. 49400) or some other indamine dye with known opposed anion.

23. Doped organic semiconductor material according to any of claims 11 to 18, in which the molecular group A is based on the structure A13 or the corresponding leuko base A14

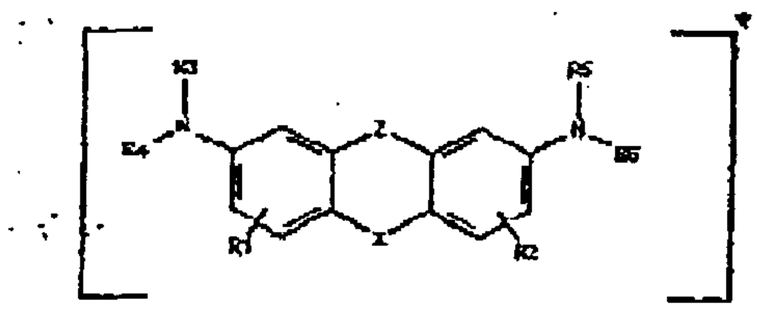


A13 A14

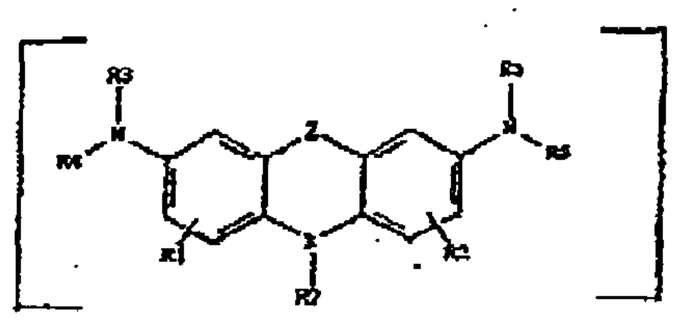
where X and Z are each CR^4, O, S, N, NR^5 or a direct bond between the two phenyl rings of the compound without an additional atom, and R1, R2, R3, R^4 and R^5 e.g. are each one or more hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl,

carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

24. Doped organic semiconductor material according to any of claims 11 to 23, in which the molecular group A is based on the structure A15 or the corresponding leuko base A16



A 15



A 16

where X and Z are each Cr^6, O, S, N, NR^9 or a direct bond between the two phenyl rings of the compound without an additional atom, and R1, R2, R3, R4, R5, R6, R7, R^8 and R^9 e.g. are each one or more hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

25. Doped organic semiconductor material according to any of claims 11 to 24, in which the molecular group A is based on the structure A17 or the corresponding leuko base A18

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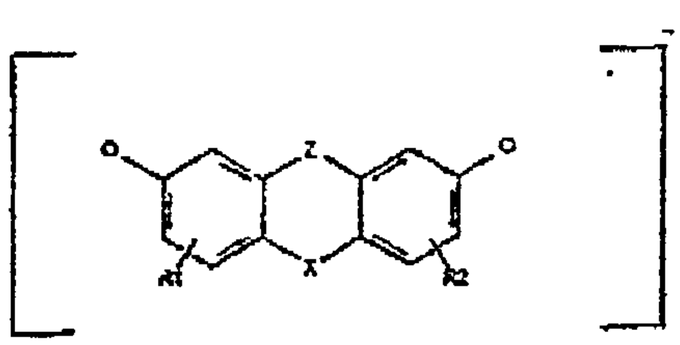
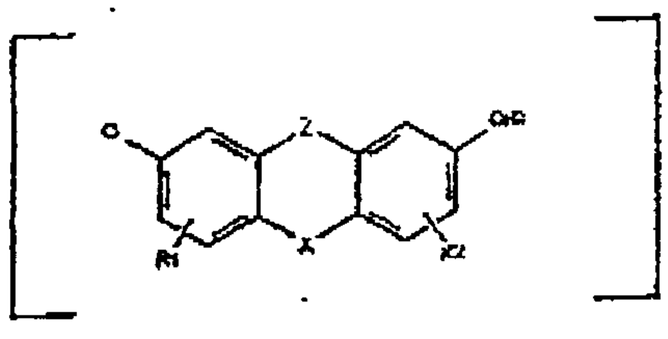


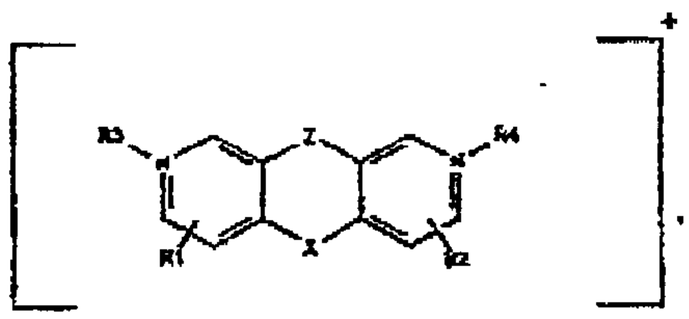
A 17



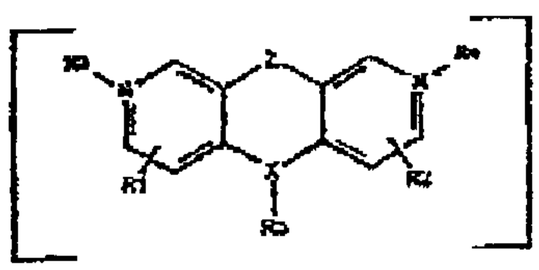
A 18

where X and Z are each Cr^6, O, S, N, NR^5 or a direct bond between the two phenyl rings of the compound without an additional atom, and R1, R2, R3, R^4, R^5 e.g. are each one or more hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

26. Doped organic semiconductor material according to any of claims 11 to 22, in which the molecular group A is based on the structure A19 or the corresponding leuko base A20



A 19

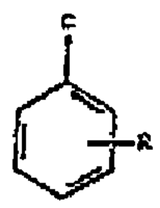


A 20

where X and Z are each Cr^6, O, S, N, NR^7 and R1, R2, R3, R4, R5, R^6 and R^7 e.g. are each one or more hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl,

ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

27. Doped organic semiconductor material according to any of claims 23 to 26 in which X is



where R is hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

28. Doped organic semiconductor material according to any of claims 11 to 27, in which the chemically stable compound is pyronine B (C.I. 45010), C.I. Basic Red 11 (C.I. 45050), saccharein (C.I. 45070), rosamine (C.I. 45090), rhodamine B (C.I. 45175) or some other diamino derivative of the xanthene dyes with known opposed anion.

29. Doped organic semiconductor material according to any of claims 11 to 27, in which the chemically stable compound is coeruleine B (C.I. 45500) or some other dihydroxy derivative of the xanthene dyes with known opposed ion.

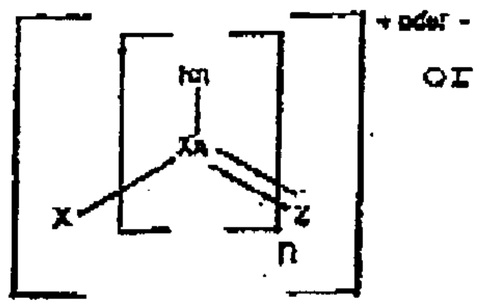
30. Doped organic semiconductor material according to any of claims 11 to 27, in which the chemically stable compound is acriflavine (C.I. 46000) or some other diamino derivative of acridine with known opposed ion.

31. Doped organic semiconductor material according to any of claims 11 to 27, in which the chemically stable compound is phenosafranine (C.I. 50200) or some other azine dye with known opposed ion.

32. Doped organic semiconductor material according to any of claims 11 to 27, in which the chemically stable compound is C.I. Basic Blue 3 (C.I. 51004) or some other oxazine dye with known opposed ion.

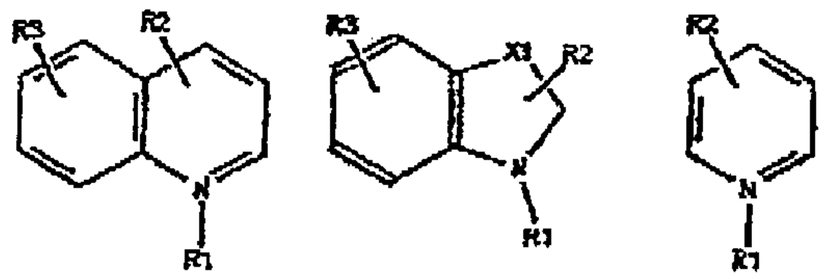
33. Doped organic semiconductor material according to any of claims 11 to 27, in which the chemically stable compound is Lauth's Violet (C.I. 52000) or some other thiazine dye with known opposed ion.

34. Doped organic semiconductor material according to either of claims 11 and 12, in which the molecular group A is based on the structure



where n is a natural number, X and Z are in each instance NR^1, S or BR^2 as hetero atom in a mono- or multinuclear heterocycle, Xn is in each instance N or CR^3, and R^1, R^2, R^3, Rn e.g. are each one or more hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

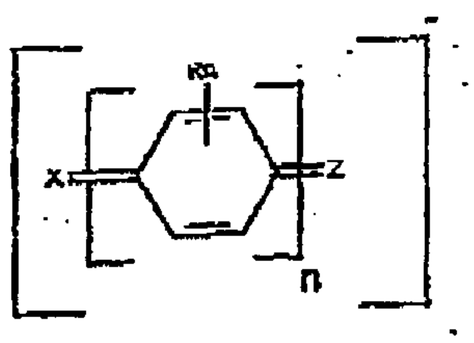
35. Doped organic semiconductor material according to claim 34, in which X and Z are each singly based on an element of the group



where X1 is in each instance CR^4R^5, NR^6, O or S and R1, R2, R3, R^4, R^5, R^6 e.g. are in each instance one or more hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

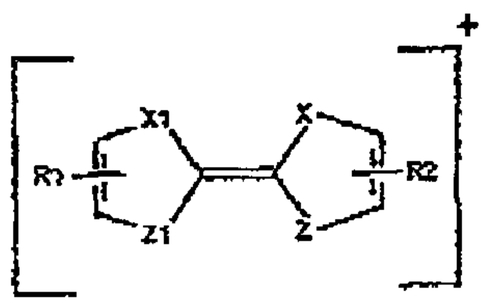
36. Doped organic semiconductor material according to any of claims 11 to 35, in which the chemically stable compound is N,N'-dialkylcyanine or N,N'-dialkylthiacarbocyanine or some other methine or polymethine dye with known opposed ion.

37. Doped organic semiconductor material according to either of claims 11 and 12, in which the molecular group A is based on the structure



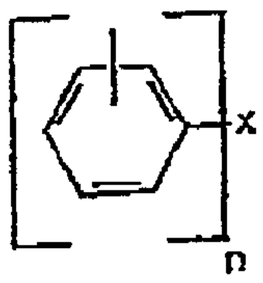
where n is a natural number, X and Z are in each instance O, $C(CN)_2$, N-CN and Rn is in each instance one or more known electron-attracting groups, hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

38. Doped organic semiconductor material according to either of claims 11 and 12, in which the molecular group A is based on the structure



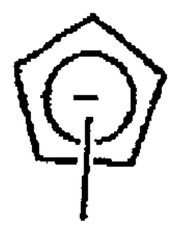
where X, X1, Z and Z1 in each instance are S or Se and R e.g. in each instance is one or more known electron-repelling groups, hydrogen; oxygen; halogens, e.g. fluorine, chlorine, bromine or iodine; hydroxyl; aminyl, e.g. diphenylaminyl, diethylaminyl; aliphatics having 1 to 20 carbon atoms, e.g. methyl, ethyl, carboxyl; alkoxyl, e.g. methoxy; cyano; nitro; sulfonic acid and its salts; aryl having 3 to 25 carbon atoms, e.g. phenyl, pyridyl or naphthyl or those atoms which form a condensed ring.

39. Doped organic semiconductor material according to any of claims 1 to 4, in which the organic molecular group A is based on the structure

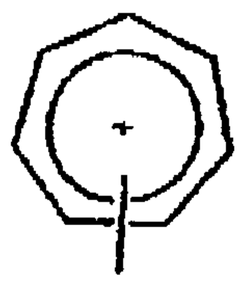


where X equals C, N, Si or P and n is equal to 3 for X = C or Si and n = 2 for X = N or P.

40. Doped organic semiconductor material according to any of claims 1 to 4, in which the organic molecular group A is based on the structures A21 or A22



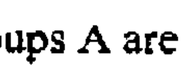
A 21



A 22

41. Doped organic semiconductor material according to any of claims 1 to 40, in which the compound of formally positively charged nitrogen (azonia, ammonium) contains oxygen (oxonia, oxonium), phosphorus (phosphonia, phosphonium), sulfur (thionia, sulfonium) and/or formally negatively charged boron (boranuida, borate).

42. Doped organic semiconductor material according to any of claims 40 to 41, in which the compound is a metal complex compound.

43. Doped organic semiconductor material according to any of claims 1 to 42, in which one or more molecular groups A are connected to one or more  diazo groups.

44. Doped organic semiconductor material according to any of claims 1 to 43, in which one or more molecular groups A contain one or more -SO3- groups.

45. Doped organic semiconductor material according to any of claims 1 to 43, in which one or more molecular groups A contain one or more ammonium, immonium, sulfonium, hydrazinium or thiouronium groups.

46. Doped organic semiconductor material according to any of claims 1 to 42, in which the complex of an organic molecule A and a molelcule B is of such nature that B does not form a "Trap" in the matrix M to be doped.

47. Doped organic semiconductor material according to any of claims 1 to 46, in which the semiconductor material to be doped is itself a mixture of materials.

48. Process for production of doped organic semiconductor materials having enhanced charge carrier density and enhanced effective charge carrier mobility, characterized in that a chemical compound of one or more organic molecular groups A is deposited with at least one other combining partner B by vaporization under vacuum or in an inert atmosphere, either by simultaneous evaporation with the organic semiconductor material or by successive evaporation and subsequent indiffusion of the dope, the desired doping effect being produced by splitting off at least one organic molecular group A from the chemical compound produced by at least one molecular group A or by the product of a reaction of the combining partner A with another atom or molecule.

49. Process according to claim 48, characterized in that the splitting of the chemical compound into the constituents A and B takes place only after incorporation in the semiconductor material to be doped.

50. Process according to either of claims 48 and 49, characterized in that the splitting of the chemical compound in the prepared layer and/or the removal of the constituent B from the prepared layer is supported.

51. Process according to any of claims 48 to 50, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is supported by supplying heat.

52. Process according to any of claims 48 to 50, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is supported by optical excitation in the absorption range of the layer.

53. Process according to any of claims 48 to 50, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is supported by exposure of the layer to molecular or atomic hydrogen or hydrogen ions or molecular or atomic oxygen or oxygen ions.

54. Process according to any of claims 48 to 50, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is supported by supplying another reagent reacting with constituent B in the layer in such manner that the reaction product is more volatile.

55. Process according to claim 48 to 50, characterized in that the constituent B reacts in the layer with a third substance or a molecule of the matrix in such manner that the reaction product forms an antitrap for the desired majority charge carriers or is readily removable from the layer.

56. Process according to claim 48, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is supported by treatment of the chemical compound in the gaseous phase during evaporation.

57. Process according to either of claims 48 and 56, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is supported by optical excitation.

58. Process according to either of claims 48 and 56, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is accomplished by deflection of a charged constituent B or of the charged constituent B by an electrical or magnetic field.

59. Process according to either of claims 48 and 56, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is accomplished by a strong electric field during the process of evaporation.

60 Process according to claim 48, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is supported in the solid phase at the source of vapor deposition.

61. Process according to any of claims 48, 56 and 60, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is supported with heat supplied during the process of vapor deposition, the heat being supplied in either the solid or the liquid state of the chemical compound and/or in the gaseous phase.

62. Process according to either of the claims 48 and 60, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is supported by optical excitation.

63. Process according to any of claims 48, 56 and 60, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is supported by adsorption of the vapor at a reactive surface and subsequent renewed desorption.

64. Process according to any of claims 48, 56 and 60, characterized in that the splitting of the chemical compound and/or the removal of the constituent B takes place by adsorption of the vapor at a catalytic surface and subsequent renewed desorption.

65. Process according to either of claims 48 and 60, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is supported by illuminating the compound with intense laser light.

66. Process according to any of claims 48, 56 and 60, characterized in that the splitting of the chemical compound and/or the removal of the constituent B is supported by the action of a plasma during the process of vapor deposition.

67. Process according to either of the claims 48 and 60, characterized in that the chemical compound reacts with a third substance in an evaporator source and one or more of the reaction products are used for doping.

68. Process according to either of the claims 48 and 60, characterized in that the chemical compound is brought into interaction with a catalyst in an evaporator source.

69. Process according to either of claims 48 and 60, characterized in that the splitting of the chemical compound in an evaporator source is supported by an electrochemical process at a suitable electrode.

70. Use of a doped organic semiconductor material comprising enhanced charge carrier density and effective charge carrier mobility, obtained by doping an organic semiconductor material with a chemical compound of one or more organic molecular groups A

with at least one additional combining partner B, the desired doping effect being achieved by detachment of at least one organic molecular group A from the chemical compound, produced by the molecular group A or by the product of a reaction of the combining partner A with another atom or molecule, characterized in that the organic semiconductor material is employed as a functional layer in organic solar cells, in organic light-emitting diodes, in organic field-effect transistors, in integrated organic circuits and in organic lasers.