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(54) **OXOCARBON-, PSEUDOOXOCARBON- AND RADIALENE COMPOUNDS AND THEIR USE**

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See application file for complete search history.

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(57) **ABSTRACT**

The present invention relates to oxocarbon-, pseudooxocarbon- and radialene compounds as well as to their use as doping agent for doping an organic semiconductive matrix material, as blocker material, as charge injection layer, as electrode material as well as organic semiconductor, as well as electronic components and organic semiconductive materials using them.

20 Claims, No Drawings

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OXOCARBON-, PSEUDOOXOCARBON- AND RADIALENE COMPOUNDS AND THEIR USE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a divisional of U.S. patent application Ser. No. 14/570,443, filed Dec. 15, 2014, which is a divisional of U.S. patent application Ser. No. 14/080,340, filed Nov. 14, 2013, now U.S. Pat. No. 8,911,645, which is a divisional of U.S. patent application Ser. No. 13/178,855, filed Jul. 8, 2011, now U.S. Pat. No. 8,617,426, which is a divisional of U.S. patent application Ser. No. 12/111,326, filed Apr. 29, 2008, now U.S. Pat. No. 7,981,324, which claims foreign priority to European Patent Application No. 07008747.3, filed Apr. 30, 2007. Each of these applications is incorporated herein by reference.

BACKGROUND OF THE INVENTION

The present invention relates to oxocarbon-, pseudooxocarbon- and radialene compounds as well as to their use as organic doping agent for doping an organic semiconductive matrix material for changing its electrical properties, as blocker material as well as charge injection layer and as electrode material. The invention also relates to organic semiconductive materials as well as to electronic components in which the oxocarbon-, pseudooxocarbon- and radialene compounds are used.

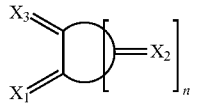
In the present application alicyclics in which all ring atoms are sp2-hybridized and to the extent possible carry exocyclic C—C double bonds are designated as radialenes, see also H. Hopf and G. Maas, Angew. Chem. (1992), 8, 955. Oxocarbon- and pseudooxocarbon compounds are sufficiently known as non-benzoid aromatics, see, e.g., G. Seitz, Nachr. Chem. Tech. Lab. 28 (1980), pages 804-807. The first oxocarbon compound, potassium croconate, was produced by L. Gmelin in 1825 from potash and coal. Those compounds, in which at least one oxygen atom is replaced by another heteroatom, are designated as pseudooxocarbons, as is readily known to an expert in the art.

It has been known for several years that organic semiconductors can be heavily influenced regarding their electrical conductivity by doping. Such organic semiconductive matrix materials can be built up either from compounds with good electron donor properties or from compounds with good electron acceptor properties. Strong electron acceptors such as tetracyanoquinonedimethane (TCNQ) or 2,3,5,6-tetrafluoro-tetracyano-1,4-benzoquinonedimethane (F4TCNQ) have become known for the doping of electron donor materials (HT), M. Pfeiffer, A. Beyer, T. Fritz, K. Leo, Appl. Phys. Lett., 73 (22), 3202-3204 (1998). and J. Blochwitz, M. Pfeiffer, T. Fritz, K. Leo, Appl. Phys. Lett., 73 (6), 729-731 (1998). They generate so-called holes by electron transfer processes in electron donor-like base materials (hole transport materials) by the number and mobility of which holes the conductivity of the base material is more or less significantly changed. For example, N,N'-perarylated benzidines TPD or N,N',N''-perarylated starburst compounds such as the substance TDATA, or, however, also certain metal phthalocyanines, such as in particular zinc phthalocyanine ZnPc are known as matrix material with hole transport properties.

However, the previously described compounds have disadvantages for a technical use in the production of doped semiconductive organic layers or of corresponding electronic components with such doped layers since the manufacturing processes in large-scale production plants or those on a technical scale can not always be sufficiently precise, which results in high control- and regulating expense within the processes for achieving a desired product quality or in undesired tolerances of the products. Furthermore, there are disadvantages in the use of previously known organic donors with regard to electronic components such as light-emitting diodes (OLEDs), field effect transistors (FET) or solar cells themselves since the cited production difficulties in the handling of the doping agents can lead to undesired irregularities in the electronic components or in undesired ageing effects of the electronic components. However, it should be considered at the same time that the doping agents to be used have extremely high electron affinities (reduction potentials) and other properties suitable for the application case since, e.g., the doping agents also co-determine the conductivity or other electrical properties of the organic semiconductive layer under given conditions. The energetic positions of the HOMO of the matrix material and of the LUMO of the doping agent are decisive for the doping effect.

The present invention has the task of overcoming the disadvantages of the state of the art, in particular to make new organic mesomeric compounds available that can be used in particular as doping agent for the doping of organic semiconductors, that can furthermore be more readily handled in the production process and that result in electronic components whose organic semiconductive materials can be reproducibly manufactured

This task is solved, at least in part, by the following organic mesomeric compound and/or the use of the organic mesomeric compound as organic doping agent for the doping of an organic semiconductive matrix material, as blocker layer, as charge injection layer or as organic semiconductor itself, characterized in that the mesomeric compound is an oxocarbon-, pseudooxocarbon- or radialene compound with the following formula:



in which n=1-4; each X_1, X_2, X_3, X_4, and X_5 is independently selected from the group consisting of $C(CN)_2$, $(CF_3)C(CN)$, $(NO_2)C(CN)$, $C(halogen)_2$, $C(CF_3)_2$, NCN, O, S, NR_1,

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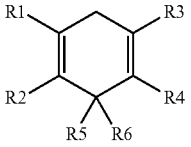

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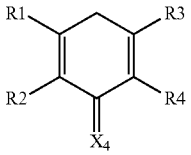

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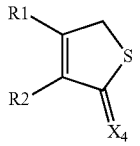

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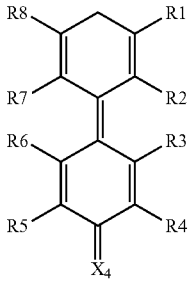

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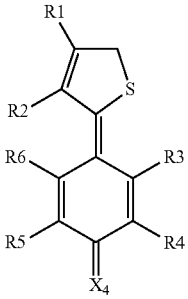

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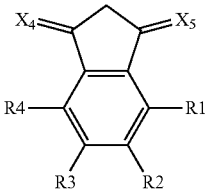

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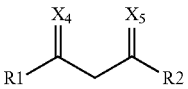

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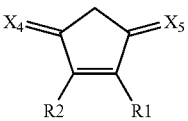

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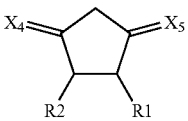

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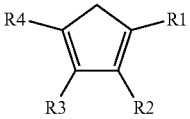

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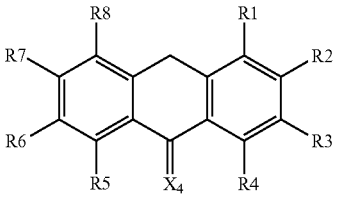

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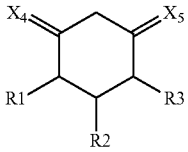

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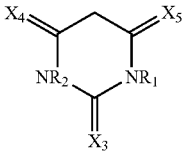

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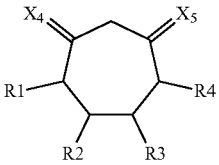

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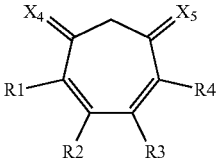

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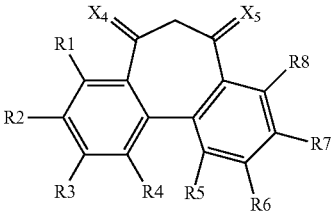

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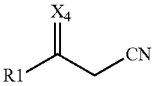

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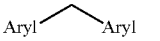

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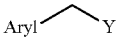

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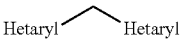

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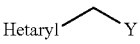

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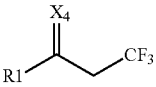

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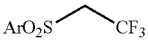

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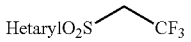

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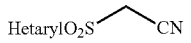

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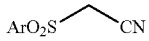

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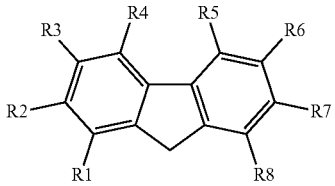


in which Y═CN, NO_2, COR_1 or is perhalogenated alkyl; aryl or Ar is a substituted or unsubstituted, aromatic hydrocarbon or biaryl, optionally polycyclic; hetaryl is a substituted or unsubstituted aromatic heterocyclic compound or biheteroaryl, preferably electron-poor, optionally polynuclear or partially or completely hydrogenated or fluorinated; and R_1-R_8 are independently selected from hydrogen, halogen, CN, NO_2, COR_1, alkyl, alkoxy, aryl and heteroaryl. In one embodiment, Y is perfluoroalkyl, including, for example, CF_3. In another embodiment, aryl or Ar is partially or completely hydrogenated, or partially or completely fluorinated. In a further embodiment, hetaryl is selected from pyridyl, pyrimidyl, triazine, or oxadizole. In a still further embodiment, R1-R8 are independently selected from perhalogenated and/or partially halogenated alkyl groups, including, for example, perfluorinated alkyl groups.

DETAILED DESCRIPTION

In the compounds in accordance with the invention the position of the LUMO is so low that further technically interesting hole transport materials can now be efficiently doped for the first time. Due to the extremely low position of the LUMO and to the associated high reduction potential of the compounds even performance efficiencies of solar cells can be significantly improved. In addition, these compounds are extremely diffusion-stable in organic layers on account of their high polarity. The production processes can be better controlled and thus be carried out with lesser expense and in a more reproducible manner by higher evaporation temperature and lower volatility under the same conditions, whereby, by making available oxocarbons, pseudooxocarbons and radialenes as doping agents, these make possible a sufficient electrical conductivity of the organic semiconductive matrix given advantageous electron affinity of the doping agents in the particular components at low diffusion coefficients that ensure a component structure that is uniform in time. Furthermore, the charge carrier injection of contacts into the doped layer can be improved by the doping agents. Furthermore, the doped organic semiconductive material and the resulting electronic component can have an improved long-time stability on account of the compounds used in accordance with the invention. This concerns, e.g., a reduction of the doping concentration over time. This furthermore concerns the stability of the doped layer that is arranged adjacent to non-doped layers of an electro-optical component so that electro-optical components with increased long-time stability of the electro-optical properties such as light yield at a given length, effectiveness of a solar cell or the like result.

The evaporation rate of a substrate with the compound used in accordance with the invention can be determined, e.g., using a quartz thickness monitor, as is customarily used, e.g., in the production of OLEDs. In particular, the ratio of the evaporation rates of matrix materials and doping agent can be measured by independent measurements of them using two separate quartz thickness monitors in order to adjust the doping ratio.

It is understood that the compounds used in accordance with the invention are preferably such that they evaporate more or less or practically non-decomposed. However, if necessary, even purposeful precursors can be used as doping source that release the compounds used in accordance with the invention, e.g., acid addition salts, e.g., of a volatile or non-volatile inorganic or organic acid, or their charge transfer complexes, which acids and/or electron donors are preferably not volatile or only slightly volatile or the charge transfer complex itself acts as doping agent.

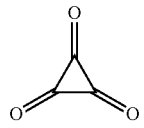
The doping agent is preferably selected in such a manner that it generates a conductivity just as high as or preferably higher than F4TCNQ under conditions that are otherwise the same such as, in particular, doping concentration (molar ratio, doping agent:matrix, layer thickness, current strength) at a given matrix material (e.g., zinc phthalocyanine or another matrix material cited further below), e.g., a conductivity (s/cm) greater than/equal to 1.1 times, 1.2 times or greater than/equal to 1.5 times or twice that of F4TCNQ as doping agent.

The doping agent used in accordance with the invention is preferably selected in such a manner that the semiconductive organic material doped with it still has ≥20%, preferably ≥30%, especially preferably ≥50% or 60% of the conductivity (s/cm) of the value at 100° C. after a temperature change of 100° C. to RT (20° C.).

A few preferred oxocarbons, pseudooxocarbons and radialenes will be shown in the following that can be used with advantage for the purposes of the invention:

Derivatives of [3] radialenes

1



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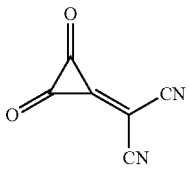

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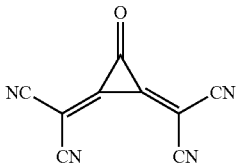

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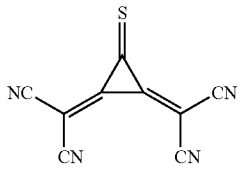

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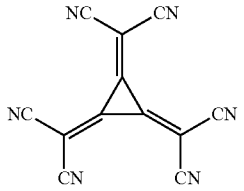

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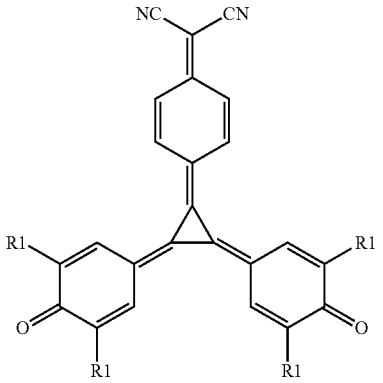

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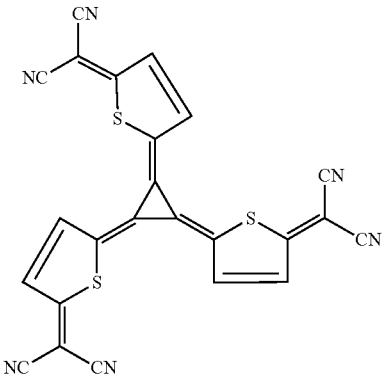

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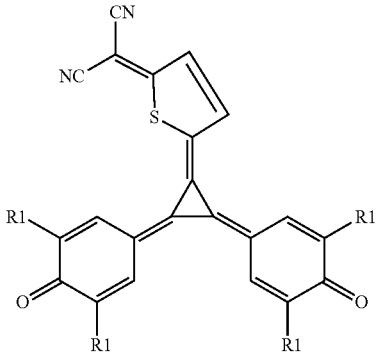

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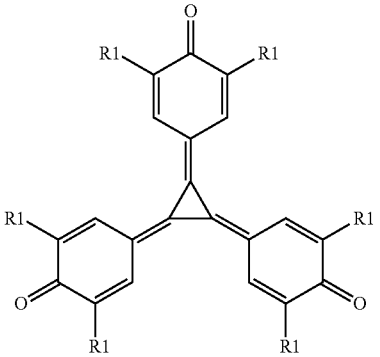

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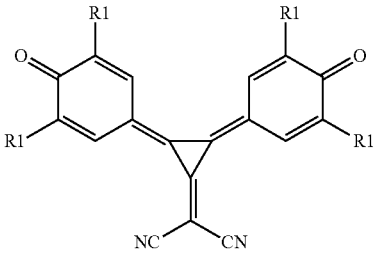

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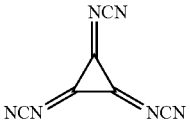

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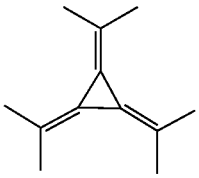

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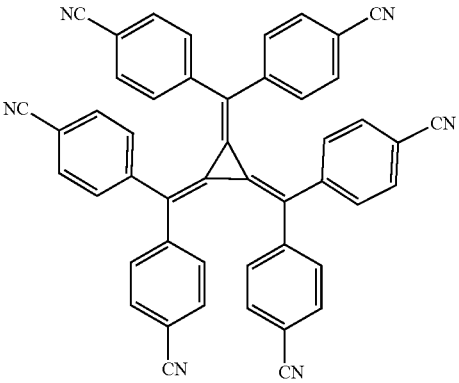

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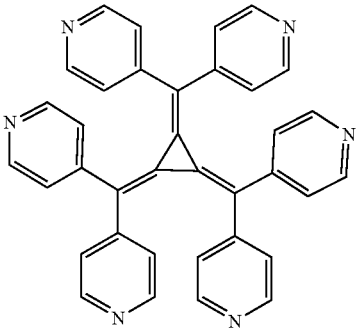

Derivatives of [4] radialenes

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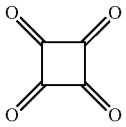

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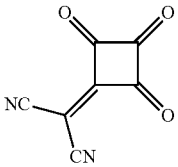

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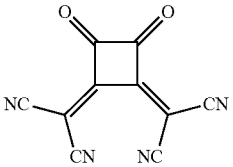

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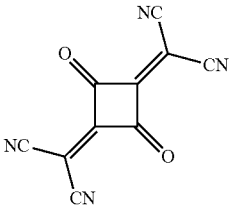

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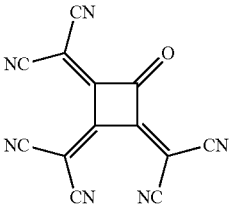

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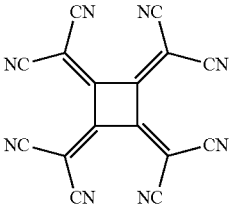

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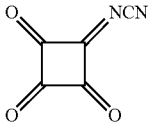

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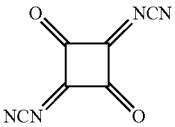

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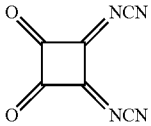

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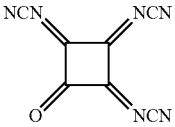

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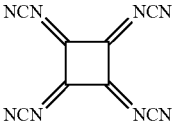

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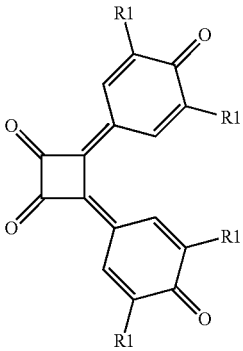

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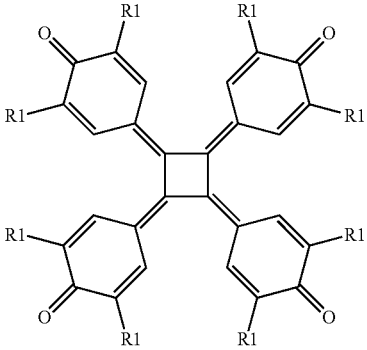

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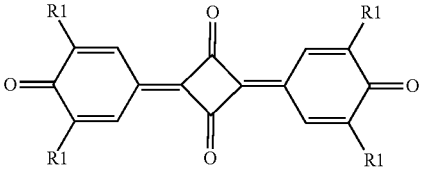

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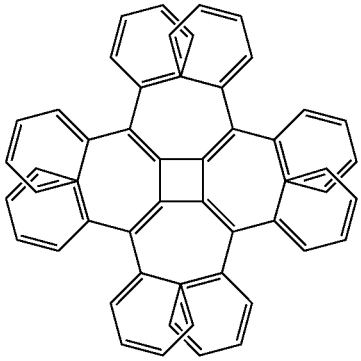
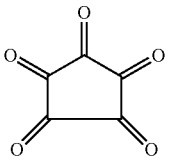
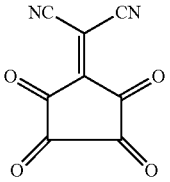
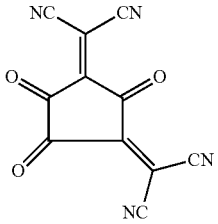
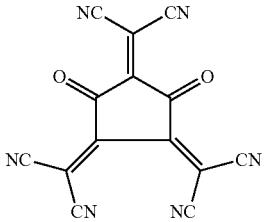


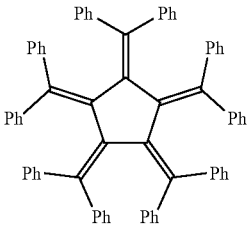
Derivatives of [5] radialenes





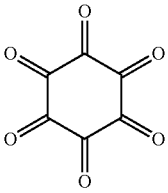


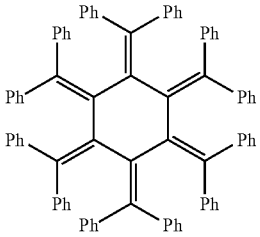




R1 = methyl, isopropyl, t-butyl

Further Derivatives of Oxocarbon-, Pseudooxocarbon- and [6] Radialene Structures





Preparation of the Oxocarbon-, Pseudooxocarbon- and Radialene Structures

The first oxocarbon compound, potassium croconate, was produced by L. Gmelin in 1825 from potash and coal. Oxocarbons and their esters and halogenides preferably react with electron-rich compounds such as aliphatic and aromatic amines, aromatics and heteroaromatics. A. H. Schmidt, Synthesis (1980) 961. The reaction products from tetrachlorocyclopropene and phenols in the presence of Lewis acids or CH-acidic compounds by strong bases, such as, e.g., arylacetonitriles, 1,3-diketones, cyclopentadienes, malonodinitriles, acceptor-substituted diarylmethanes, electron-poor diheteroarylmethanes are especially suitable for applications in accordance with the invention. [3] Radialenes are obtained after oxidation has taken place, R. West et al. J. Org. Chem. (1975) 40 2295; T. Kazuka, T. Shinji J. Chem. Soc. Chem. Commun. (1994) 519; T. Fukunaga et al. JACS (1976) 98 610.

Squaric acid dichloride and phenols, that can subsequently be oxidized to 4 [radialenes] are furthermore also very well-suited, R. West, S. K. Koster J. Org. Chem. (1975) 40 2300; the nucleophilic anion of the CH-acidic melonic acid dinitrile can also be substituted with preference with esters under the splitting off of alcohol to dianionic squaric acid compounds, T. Fukanaga J. Am. Chem. Soc. (1976) 98 610; W. Ziegenbein, H.-E. Sprenger Angew. Chem. (1967) 79 581; G. Seitz et al. Chem. Ber. (1987) 120 1691. The oxidation of these CN-substituted compounds was successful only electrochemically in the past, T. A. Blinka, R. West, Tetrahedron Lett. (1983) 24 1567. [4] Radialenes can also be prepared by thermal dimerization of diquinone ethylenes, R. West, S. K. Koster, JOC (1975) 40 2300.

The first croconic acid derivatives that were substituted with malodinitrile were able to be produced by Fatiadi, J. Org. Chem. (1980) 45 1338, J. Am. Chem. Soc. (1978) 100 2586. The oxidation of these compounds was also examined electrochemically by him, A. J. Fatiadi, L. M. Doane, J. Electroanal. Chem. (1982) 135 193-209.

However, even [6] radialenes are known, H. Hopf, A. K. Wick Helv. Chim. Acta (1961) 46 380-6.

A few later representatives were and/or are used in the electrophotography as electroluminescent material in video screens, as dye, as photoconductors, as organic oxidants,

U.S. Pat. No. 4,003,943 (1977), JP 07-168377, JP 2004010703 A (2004), U.S. Pat. No. 4,133,821 (1979).

Preparation of New Cyclic Oxocarbon- and Pseudooxocarbon Derivatives

Example

a) 1,3-Bis(dicyanomethylene)indane-2-ylidene-bis (4-oxo-[3,5-di-t-butyl]-2,-5-cyclohexadienylidene)-cyclopropane

4.75 g bis(4-oxo-[3,5-di-t-butyl]-2,5-cyclohexadienyl)-cyclopropenone, 3.5 g 1,3-bis(dicyanomethylene)-indane as well as 60 mg β-alanine are dissolved in 12 ml acetic anhydride and briefly heated on the reflux under stirring. The mixture is compounded with 60 ml toluene, allowed to cool off and the reddish-brown crystalline solid removed by suction. The mixture is subsequently washed with benzene/toluene and recrystallized.

Yield: 4.6 g

2.5 g of the reddish-brown crystals are dissolved under argon in 100 ml chloroform and united with a solution of 4.7 g red potassium ferrocyanide and 8.8 g KOH in 150 ml water. After 1 h intensive stirring, the organic phase is dried with Na2SO4 and evaporated to low bulk and the product recrystallized.

Yield: 2.3 g blackish-green crystals fp.>250° C. under decomposition

b) (2E,2'E,2"E)-2,2',2"-(cyclopropane-1,2,3-tri-ylidene)tris(2-pentafluor-ophenylacetonitrile)

A solution of 4 g (20 mmol) pentafluorophenylacetonitrile in 10 ml glyme are added dropwise to 1.6 g NaH in 40 ml glyme and cooled with icewater. Subsequently a solution of 0.9 tetrachloro cyclopropene in 10 ml glyme was added dropwise. After stirring for 24 h at room temperature the dark mixture is poured onto ice water and is extracted with $CHCl_3$. The extracts provide a black solid.

4 g of the raw intermediate product are dissolved in 50 ml $CHCl_3$, and to this solution 50 ml water, containing 2 g K_2CO_3, is added. 0.5 ml bromine is added to this dark green 2-phase mixture under stirring. Thereafter, the phases are separated, and the organic phase is evaporated after drying over Na2SO4 using a rotatory evaporator. A remaining orange solid is recrystallized using a suitable solvent. Yield: about 70%.

FP: 182° C.

c) (2E,2'E,2"E)-2,2',2"-(cyclopropane-1,2,3-tri-ylidene)tris(2-[2',3',5',-6'-tetrafluoropyrid-4'-yl]ac-etonitrile)

4.75 g 2,3,5,6-tetrafluoropyridyl actonitile in 10 ml glyme is added dropwise to 0.4 g LiH in 60 ml glyme. Thereafter 1.1 g tetrachlorocyclopropene is added dropwise to the solution and is stirred over night. The mixture is poured onto ice-water and is extracted with EtOAc. After drying the extracts and evaporation 4.6 g of a solid remained.

2.25 g of the solid is dissolved in 50 ml AcOH, and 5 ml HNO_3 (65%) is added. Water is added to this orange-brown solution, and the precipitate obtained is isolated, washed with water and dried. Yield: 1 g. Fp: 170° C.

d) (2E,2'E,2"E)-2,2',2"-(cyclopropane-1,2,3-tri-ylidene)tris(2-(2,6-dichl-oro-3,5-difluoro-4-(trisfluo-romethyl)phenyl)acetonitrile)

0.29 g LiH are suspended in 68 ml glyme, and cooled, and 5 g 2,6-dichloro-3,5-difluoro-4-(trifluoromethyl)phenyl)ac-etonitrile) in 6 ml glyme are added slowly under argon atmosphere. The mixture is heated to room temperature, and 0.8 g tetrachlorocyclopropene are added dropwise, and the mixture is stirred over night. The solution is poured onto ice-water, the precipitate obtained is isolated and dried. Yield: 4.75 g.

3.5 g of the product is dissolved in glacial acetic acid, and under cooling 7 ml HNO_3 is dropwise added, subsequently water is added, and the precipitate obtained is isolated. The product is recrystallized utilizing a suitable solvent. Yield: 72%. Fp.: 185° C.

e) (2E,2'E,2"E)-2,2',2"-(cyclopropane-1,2,3-tri-ylidene)tris(2-(2,3,5,6-t-etrafluoro-4-cyano-phenylacetonitrile)(2-2,3,5,6-tetrafluoro-4-trifluorome-thyl-phenylacetonitrile)

Internal salt: 2,3-bis(cyano(4-cyano-2,3,5,6-tetrafluoro-phenyl)methyl)-1-triethylamino)c-ycloprop-2-ene-1-ide.

5.34 g tetrachlorocyclopropene and 13.8 g 2,3,5,6-tetra-fluoro-4-cyanobenzylcyanid in 300 ml CH_2Cl_2 are cooled, and 17.1 g triethylamine is added. The resultant product is stirred and heated to room temperature. Then water is added, and the yellow solid obtained is removed, washed and dried at air. Yield: 93%.

1.15 g 2,3,5,6-tetrafluoro-4-(trifluoromethyl)-benzylcya-nid in 15 ml THF is dropwise added to 0.46 g LDA in 55 ml THF. The solution is cooled, and a suspension of 2 g of the internal salt in DMPU is added dropwise. The solution is poured into ice-water. The precipitate is removed and washed with water and subsequently dried in vacuo. Yield: 100%.

2.7 g of the material to be oxidized is dissolved in 70 ml AcOH, and 5.5 ml HNO_3 (65%) is added dropwise. The material to be oxidized is then precipitated with water. After isolation, washing with water and drying in vacuo the product is obtained in a yield of 90%. Fp: >250° C.

f) (2E,2'E,2"E,2'"E)-2,2',2",2'"-(cyclopropane-1,2,3,4-tetraylidene)te-trakis(2-2',3',5',6'-tetrafluoro-4'-cyanophenyl)acetonitrile

1.2 g 1,2-bis-tosyl-3,4-bis-dimethylamino-quadratat is heated with 2.14 g 2,3,5,6-tetrafluoro-4-cyano-benzylcyanid in 20 ml pyridin for 16 h with stirring. The solution is concentrated and given into ice-water. Thereafter it is extracted with EtOAc. Concentrating the dried extracts results in the product which can be recrystallized in a suitable solvent. Fp.: >250° C.

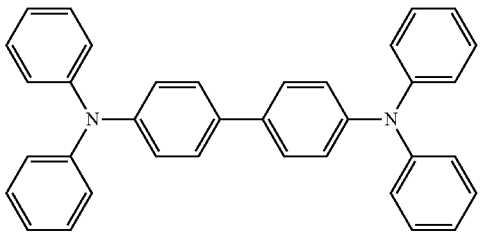
Matrix Materials

The present invention describes suitable doping agents for organic semiconductive materials such as hole transport materials HT that are customarily used in OLEDs or organic solar cells. The semiconductive materials are preferably intrinsically hole-conducting. The following can apply to doping agents of the oxocarbon- and pseudooxocarbon types in accordance with the invention.

The matrix material can consist partially (>10 or >25% by weight) or substantially (>50% by weight or >75% by weight) or totally of a metal phthalocyanine complex, a porphyrine complex, especially metal porphyrine complex, oligothiophene-, oligophenyl-, oligophenylene vinylene- or oligofluorene compound, in which the oligomer preferably comprises 2-500 or more, preferably 2-100 or 2-50 or 2-10 or more monomeric units. The oligomer can also comprise >4, >6 or >10 or more monomeric units, in particular also for the above-indicated ranges, thus, e.g., 4 or 6-10 monomeric units, 6 or 10-100 monomeric units or 10-500 monomeric units. The monomers and oligomers can be substituted or unsubstituted and even block- or mixed polymerizates of the cited oligomers can be present as well as a compound with a triarylamine unit or a spiro-bifluorene compound. The cited matrix materials can also be present in combination with each other, optionally also in combination with other matrix materials. The matrix materials can have electron-donating substitutents such as alkyl- or alkoxy groups that have a reduced ionizing energy or reduce the ionizing energy of the matrix material.

The metal phthalocyanine complexes or porphyrine complexes used as matrix material can have a main group metal atom or subgroup metal atom. The metal atom Me can be coordinated 4-, 5- or 6-fold, e.g., in the form of oxo- (Me═O), dioxo- (O═Me═O) imine-, diimine-, hydroxo-, dihydroxo-, amino- or diamino complexes, without being limited to them. The phthalocyanine complex or porphyrine complex can each be partially hydrogenated, however, the mesomeric ring system is preferably not disturbed. The phthalocyanine can contain, e.g., magnesium, zinc, iron, nickel, cobalt, magnesium, copper or vanadyl (═VO) as central atom. The same or other metal atoms or oxometal atoms can be present in the case of porphyrine complexes.

In particular, such dopable hole transport materials HT can be arylated benzidines, e.g., N,N'-perarylated benzidines or other diamines such as of the type TPD (in which one, several or all of the aryl groups can have aromatic heteroatoms), suitable arylated starburst compounds such as N,N', N''-perarylated starburst compounds such as the compound TDATA (in which one, several or all of the aryl groups can have aromatic heteroatoms). The aryl groups can comprise phenyl, naphthyl, pyridine, quinoline, isoquinoline, peridazine, pyrimidine, pyrazine, pyrazole, imidazole, oxazole, furan, pyrrole, indole or the like, especially for each of the above-cited compounds. The phenyl groups of the particular compounds can be partially or completely replaced by thiophene groups.



TPD

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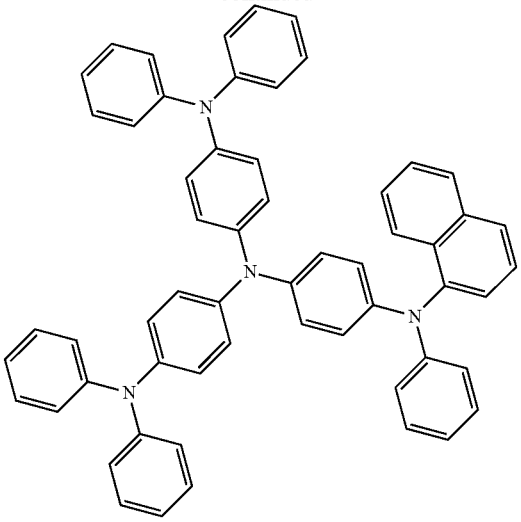
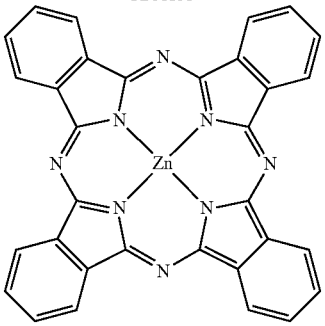


TDATA



ZnPc

The material used preferably consists completely of a metal phthalocyanine complex, a porphyrine complex, a compound with a triarylamine unit or a spiro-bifluorene compound.

It is understood that even other suitable organic matrix materials, in particular hole-conducting materials can be used that have semiconductive properties.

Doping

The doping can take place in particular in such a manner that the molar ratio of matrix molecule to doping agent, or in the case of oligomeric matrix materials the ratio of matrix monomer number to doping agent is 1:100000, preferably 1:10000, especially preferably 1:1 to 1:100000, e.g., 1:5 to 1:1000, e.g., 1:10 to 1:100, e.g., ca. 1:50 to 1:100 or also 1:25 to 1:50.

Evaporation of the Doping Agents

The doping of the particular matrix material (preferably indicated here as hole-conducting matrix material HT) with the doping agents to be used in accordance with the invention can be produced by one or a combination of the following processes:

a) Mixed evaporation in the vacuum with a source for HT and one for the doping agent.

b) Sequential deposition of HT and doping agent with subsequent inward diffusion of the doping agent by thermal treatment

c) Doping of an HT layer by a solution of doping agent with subsequent evaporation of the solvent by thermal treatment

d) Surface doping of an HT layer by a layer of doping agent applied on the surface.

The doping can take place in such a manner that the doping agent is evaporated out of a precursor compound that releases the doping agent under heating and/or irradiation. The irradiation can take place by electromagnetic radiation, especially visible light, UV light or IR light, e.g., by laser light or also by other radiation types. The heat necessary for evaporation can substantially be made available by the irradiation and can also be radiated in a purposeful manner into certain bands of the compounds or precursors or compound complexes such as charge transfer complexes to be evaporated in order to facilitate the evaporation of the compounds by dissociation of the complexes by conversion into excited states. It is understood that the evaporation conditions described in the following are directed to those without irradiation and that uniform evaporation conditions are to be used for purposes of comparison.

For example, the following can be used as precursor compounds:

a) Mixtures or stoichiometric or mixed crystalline compounds of the doping agent and an inert, non-volatile substance, e.g., a polymer, molecular sieve, aluminum oxide, silica gel, and oligomers or another organic or inorganic substance with high evaporation temperature, in which the doping agent is bound primarily by van der Waals forces and/or hydrogen bridge bonding to this substance.

b) Mixture or stoichiometric or mixed crystalline compound of the doping agent and one non-volatile compound V more or less of the electron donor type, in which a more or less complete charge transfer occurs between the doping agent and the compound V as in charge transfer complexes with more or less electron-rich polyaromatics or heteroaromatics or another organic or inorganic substance with high evaporation temperature.

c) Mixture or stoichiometric or mixed crystalline compound of the doping agent and a substance that evaporates together with the doping agent and has the same or higher ionizing energy as the substance HT to be doped, so that the substance does not form a trap for holes in the organic matrix material. According to the invention the substance can also be identical to the matrix material here, e.g., be a metal phthalocyanine or benzidine derivative. Further suitable volatile co-substances such as hydroquinones, 1,4-phenylene diamines or 1-amino-4-hydroxybenzene or other compounds form quinhydrones or other charge transfer complexes.

Electronic Component

A plurality of electronic components or equipment containing them can be produced using the organic compounds in accordance with the invention for producing doped organic semiconductive materials that can be arranged in particular in the form of layers or electrical line paths. In particular, the doping agents in accordance with the invention can be used to produce organic, light-emitting diodes (OLED), organic solar cells, organic diodes, especially those with a high rectification ratio such as 10^3-10^7, preferably 10^4-10^7 or 10^5-10^7 or organic field effect transistors. The conductivity of the doped layers and/or the improvement of the charge carrier injection of contacts into the doped layer can be improved by the doping agents in accordance with the invention. In particular in the case of OLEDs the component can have a pin structure or an inverse structure without being limited to them. However, the use of the doping agents in accordance with the invention is not limited to the advantageous exemplary embodiments cited above.

EXEMPLARY EMBODIMENTS

The invention will be explained in detail with a few exemplary embodiments.

The compounds to be used in accordance with the invention, in particular, the previously indicated exemplary compounds from the previously described substance class of the oxocarbon- and of the pseudooxocarbon compounds will now be used in the following manner as doping agents for different hole conductors that for their part are used for constructing certain microelectronic or optoelectronic components such as, e.g., an OLED. The doping agents can be evaporated at the same time adjacent to one another with the hole transport materials of the matrix in the high vacuum (ca. 2×10^{-4} Pa) at elevated temperatures. A typical substrate evaporation rate for the matrix material is 0.2 nm/s (density ca. 1.5 g/cm^3). The evaporation rates for the doping agents can vary between 0.001 and 0.5 nm/s at the same assumed density in accordance with the desired doping ratio.

In the following examples the current measurements were carried out over a current path of the doped HT material 1 mm long and ca. 0.5 mm wide at 1V. under these conditions ZnPc conducts practically no electrical current.

EXAMPLES

Example 1

Doping of ZnPc with dicyanomethylenebis(4-oxo-[3,5-di-t-butyl]-2,5-cyclohexadienylidene)cyclopropane

Conductivity: 1.5×10^{-5} s/cm

Example 2

Doping of spiro-TTP with dicyanomethylenebis(4-oxo-[3,5-di-t-butyl]-2,5-cyclohexadienylidene)cyclopropane

Conductivity: 3, 6×10^{-7} s/cm

Example 3

Doping of ZnPC with 1,3-bis(dicyanomethylene)indane-2-ylidene-bis(4-oxo-[3,5-di-t-butyl]-2,5-cyclohexadienylidene)cyclopropane

Conductivity: 5.8×10^{-6} s/cm

Example 4

Doping of spiro-TTP with 1,3-bis(dicyanomethylene)indane-2-ylidene-bis(4-oxo-[3,5-di-t-butyl]-2,5-cyclohexadienylidene)cyclopropane

conductivity: 5×10^{-7} S/cm

Example 5

Doping of N^4, N^4-(biphenyl-4,4%-diyl)bis(N^4,$N^{4'}$,$N^{4'}$-triphenylbiphen-yl-4,4'-diamine) with (2E,2'E,2"E)-2,2',2"-(cyclopropane-1,2,3-triyliden)tris(2-pentafluoroph-enylacetonitrile 10%

Conductivity: 3.21×10^{-6} S/cm

Example 6

Doping of Spiro-TTP with (2E,2'E,2"E)-2,2',2"-cyclopropane-1,2,3-triylidene)tris(2-pentafluorophenylacetonitrile) 10%

Conductivity: 1.89×10^{-6} S/cm.

Example 7

Doping of 4,4'-bis(10,11-dihydro-5H-dibenzo[b,f]azepine-5-yl)biphenyl with (2E,2'E,2"E)-2,2',2"-(cyclopropane-1,2,3-triylidene)tris(2-pentafluorophenylacetonitrile) 10%

Conductivity: 1.55×10^{-7} S/cm.

Example 8

Doping of Spiro-TTP with (2E,2'E,2"E)-2,2',2"-(cyclopropane-1,2,3-triylidene)tris(2-[2',3',5',6'-tetrafluoropyrid-4'-yl]acetonitrile) 5%

Conductivity: 4.35×10^{-5} S/cm.

Example 9

Doping of a-NPD with (2E,2'E,2"E)-2,2',2"-cyclopropane-1,2,3-triylidene)tris(2-[2',3',5',6'-tetrafluoropyrid-4'-yl]acetonitrile) 5%

Conductivity: 1.28×10^{-5} S/cm.

Example 10

Doping of ZnPc with (N,N',N",N'"-cyclobutane-1,2,3,4-tetraylidene)tetraaniline 5%

Conductivity: 1.3×10^{-6} S/cm.

Example 11

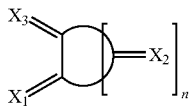
Doping of spiro-TTP with (2E,2'E,2"E,2'"E)-2,2',2",2'"-(cyclobutane-1,2,3,4-tetraylidene)N,N',—N",N'"-cyclobutane-1,2,3,4-tetraylidene)tetrakis(2-perfluorophenyl)aceto-nitrile) 5%

Conductivity: 3.3×10^{-5} S/cm.

The features of the invention disclosed in the previous description and in the claims can be essential individually as well as in any combination for the realization of the invention in its various embodiments.

The invention claimed is:

1. A charge injection layer comprising an organic semiconductive matrix material and an organic doping agent, wherein the organic doping agent comprises an organic mesomeric compound, wherein the organic mesomeric compound comprises an oxocarbon-, pseudooxocarbon-, or radialene compound with the following formula:



wherein n=1-4; each X1, X2, and X3 is independently selected from the group consisting of C(CN)2, (CF3)C(CN), (NO2)C(CN), C(halogen)2, C(CF3)2, NCN, O, S, NR1,

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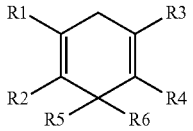

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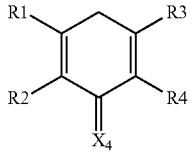

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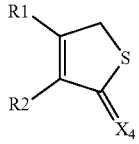

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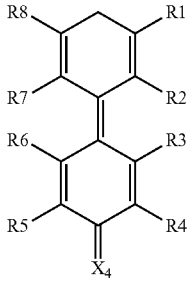

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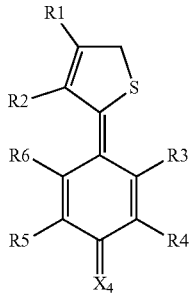

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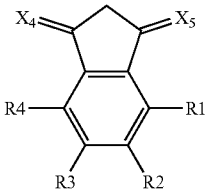

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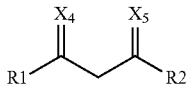

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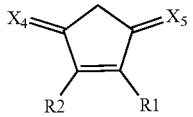

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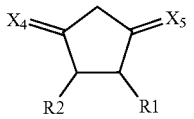

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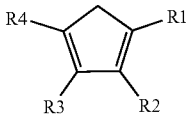

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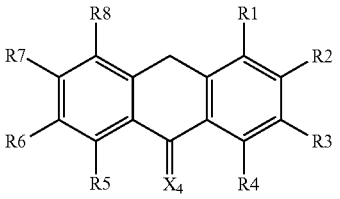

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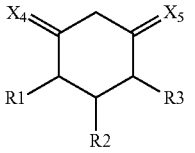

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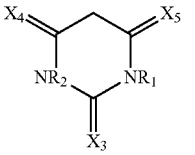

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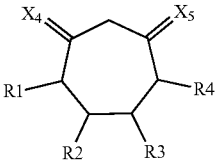

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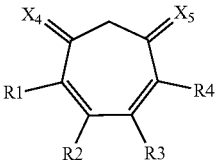

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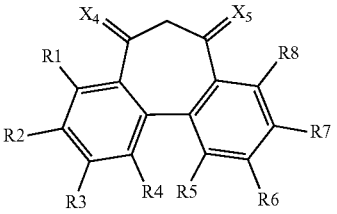

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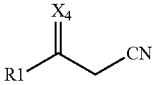

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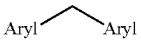

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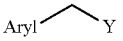

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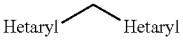

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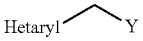

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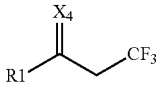

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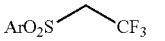

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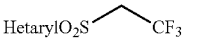

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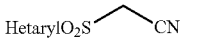

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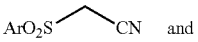
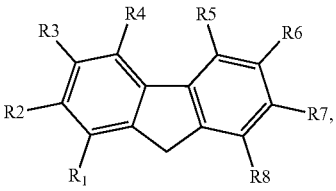


and

W4



wherein X4 and X5 are independently selected from the group consisting of C(CN)2, (CF3)C(CN), (NO2)C(CN), C(halogen)2, C(CF3)2, CN, O, S, and NR1,

wherein Y═CN, NO2, COR1, or a perhalogenated alkyl; aryl or Ar is a substituted or unsubstituted aromatic hydrocarbon or biaryl; hetaryl is a substituted or unsubstituted aromatic heterocyclic compound or biheteroaryl; and R1-R8 are independently selected from hydrogen, halogen, CN, NO2, COR1, alkyl, alkoxy, aryl, or heteroaryl, wherein the molar doping ratio of the organic doping agent to the organic semiconductive matrix material, respectively, or the doping ratio of the organic doping agent to a monomer unit of the organic semiconductive matrix material when the organic semiconductive matrix material is a polymeric matrix molecule, is from 1:1 to 1:100000.

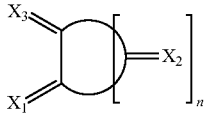
2. The charge injection layer according to claim **1**, wherein Y is perfluoroalkyl.

3. The charge injection layer according to claim **1**, wherein aryl is partially or completely fluorinated.

4. The charge injection layer according to claim **1**, wherein hetaryl is selected from pyridyl, pyrimidyl, triazine, or oxadiazole.

5. The charge injection layer according to claim **1**, wherein R1-R8 are independently selected from perhalogenated or partially halogenated alkyl groups.

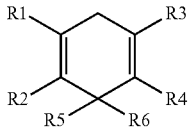
6. An oxocarbon, pseudooxocarbon-, or radialene compound with the following formula



wherein n=1-4;

wherein for n=1: each X1-X3 is independently selected from $(CF_3)C(CN)$, $C(CF_3)_2$, or one of structures A-W_4

A



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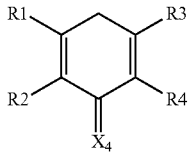

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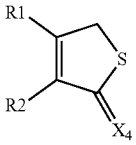

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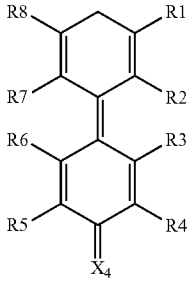

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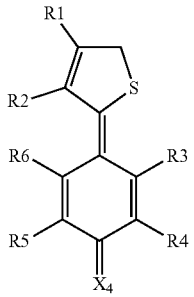

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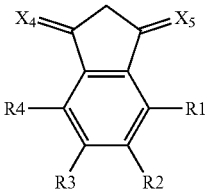

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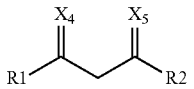

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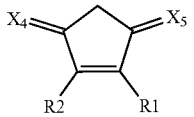

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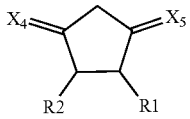

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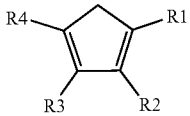

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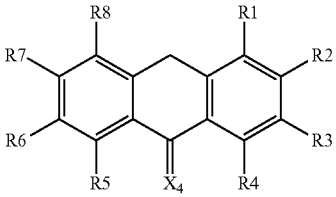

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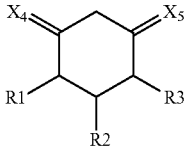

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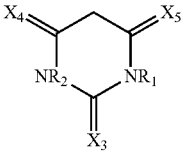

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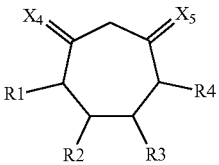

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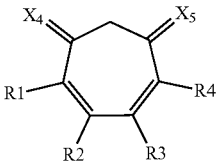

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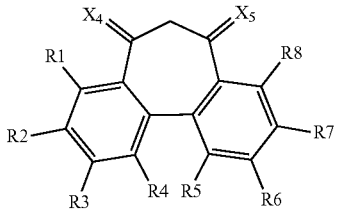

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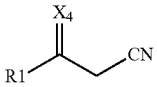

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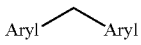

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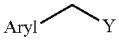

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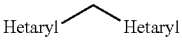

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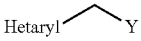

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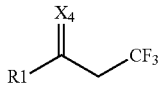

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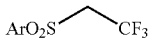

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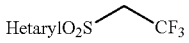

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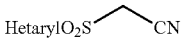

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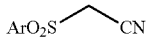
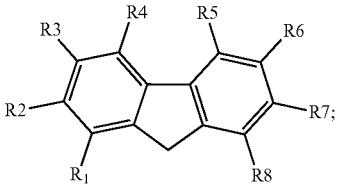


W4



X4 and X5 are independently selected from $(CF_3)C(CN)$, $C(CF_3)_2$, or NCN; Y is selected from CN, COR_1, or perhalogenated alkyl groups; aryl or Ar is selected from a substituted or unsubstituted aromatic hydrocarbon, a substituted or unsubstituted polycyclic aromatic hydrocarbon, or a substituted or unsubstituted biaryl aromatic hydrocarbon, wherein the aromatic hydrocarbon, the polycyclic aromatic hydrocarbon, or the biaryl aromatic hydrocarbon is partially or completely hydrogenated or fluorinated; hetaryl and bihetaryl are selected from a substituted or unsubstituted aromatic heterocyclic compound, a substituted or unsubstituted polynuclear aromatic heterocyclic compound, or a partially or completely hydrogenated or fluorinated heteroaromatic compound; R1-R8 are independently selected from hydrogen, halogen, CN, NO_2, COR_1, perhalogenated and/or partially halogenated alkyl groups, or substituted and/or unsubstituted aryl- or heteroaryl groups.

7. The oxocarbon, pseudooxocarbon-, or radialene compound according to claim **6**, wherein hetaryl is selected from pyridyl, pyrimidyl, triazine, or oxadiazole.

8. An organic ferromagnet comprising [1] the oxocarbon-, pseudooxocarbon-, or radialene compound according to claim **6**, or a radical anionic salt thereof, a dianionic salt thereof, or a charge transfer complex thereof, and [2] one or more donors.

9. An organic conductor comprising [1] the oxocarbon-, pseudooxocarbon-, or radialene compound according to claim **6**, or a radical anionic salt thereof, a dianionic salt thereof, or a charge transfer complex thereof, and [2] one or more donors.

10. An organic semiconductive material comprising at least one organic matrix compound and at least one doping agent, wherein the at least one doping agent comprises the oxocarbon-, pseudooxocarbon- or radialene compound according to claim **6**.

11. The organic semiconductive material according to claim **10**, wherein the molar doping ratio of the at least one doping agent to the at least one organic matrix compound and/or the doping ratio of the at least one doping agent to monomeric units of the at least one organic matrix compound when the organic matrix compound is a polymeric matrix molecule is between 1:1 and 1:100,000.

12. An electronic component comprising an electronically functionally active area, wherein the electronically functionally active area comprises the oxocarbon-, pseudooxocarbon- or radialene compound according to claim **6**.

13. The electronic component according to claim **12**, wherein the electronically functionally active area comprises an organic semiconductive matrix material that is doped with at least one doping agent for changing the electronic properties of the organic semiconductive matrix material, wherein the at least one doping agent comprises the oxocarbon-, pseudooxocarbon- or radialene compound.

14. The electronic component according to claim **12**, wherein the electronic component is an organic light-emitting diode, a photovoltaic cell, an organic solar cell, an organic diode, or an organic field effect transistor.

15. The charge injection layer according to claim **1**, wherein hetaryl is electron-poor, polynuclear, partially hydrogenated, partially fluorinated, completely hydrogenated, completely fluorinated, or a combination thereof.

16. The charge injection layer according to claim **1**, wherein the molar doping ratio of the organic doping agent to the organic semiconductive matrix material, respectively, or the doping ratio of the organic doping agent to a monomer unit of the organic semiconductive matrix material when the organic semiconductive matrix material is a polymeric matrix molecule, is from 1:5 to 1:1000.

17. The charge injection layer according to claim **1**, wherein the perhalogenated and/or partially halogenated alkyl groups comprise perfluorinated alkyl groups.

18. The oxocarbon, pseudooxocarbon- or radialene compound according to claim **6**, wherein the perhalogenated alkyl groups comprise perfluoroalkyl.

19. The oxocarbon, pseudooxocarbon- or radialene compound according to claim **6**, wherein hetaryl and bihetaryl comprise an electron-poor compound, are polynuclear, partially hydrogenated, partially fluorinated, completely hydrogenated, completely fluorinated, or a combination thereof.

20. The organic semiconductive material according to claim **10**, wherein the molar doping ratio of the at least one doping agent to the at least one organic matrix compound and/or the doping ratio of the at least one doping agent to monomeric units of the at least one organic matrix compound when the at least one organic matrix compound is a polymeric matrix molecule is between 1:5 to 1:1000.

* * * * *