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(54) Title: SEMICONDUCTOR CAPACITOR

(57) Abstract: The present application relates to a capacitor comprising a layer of semiconducting material between the electrode layers. Further, the present application relates to the use of such capacitors, for example in advanced electronic and semiconductor packages.



Semiconductor Capacitor

Technical Field

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The present application relates to a capacitor comprising a layer of semiconducting material between the electrode layers. Further, the present application relates to the use of such capacitors, for example in advanced electronic and semiconductor packages.

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Background

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Capacitors (or condensers) are passive two-terminal electrical components capable of storing electrical energy in an electric field. In its basic form a capacitor comprises two or more electrically conducting elements which are separated by a dielectric, i.e. by an electrically non-conducting material. The non-conducting dielectric acts to increase the capacitor's charge capacity. Materials that may be commonly used as dielectric include, for example, glass, ceramic, plastic film, paper, mica or oxide layers. Dielectric plastic films may, for example, be made from polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polypropylene (PP), polyphenylene sulfide (PPS) or polytetrafluoroethylene (PTFE).

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A commonly used family of capacitors are the electric double layer capacitors (EDLCs), which use an electrolyte solution comprising mobile ions, the role of which is to charge up electric double layers formed at the interfaces between the electrolyte solution and the electrodes.

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Capacitors have found wide-spread use as means for, for example, energy storage, power conditioning (e.g. to shunt away and conceal current fluctuations from a primary power source), coupling and decoupling, filtering, noise suppression, signal processing or sensing.

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Discrete capacitors may, for example, be mounted on the surface of a printed circuit board (PCB). Such capacitors are required to be small in size, provide high power density, and furthermore be compatible with the materials comprised in the

printed circuit board as well as be compatible with the processes used to manufacture advanced electronic and semiconductor packages, such as for example a printed circuit board. To comply with these requirements organic dielectric materials have been found particularly useful.

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Since organic dielectric materials are generally characterized by comparatively low dielectric constants ϵ , researchers have searched for ways to increase their dielectric constants ϵ . It has been found that this can be achieved with some composite structures containing ceramic or metal particles. For composites comprising ceramic particles dispersed in an organic dielectric material the dielectric constants ϵ have been limited to values below 1,000. For composites comprising metal particles dispersed in an organic dielectric material, dielectric constants ϵ of up to and even over 10,000 have been obtained. However, because the dissipation factor $\tan(\delta)$ increases in parallel, such composites and the capacitors comprising such composites have not been found suitable for industrial use.

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A capacitor with a metal-semiconductor-metal structure has been proposed as voltage-dependent capacitor, also referred to as “varactor”, by P. Dianat et al. in Applied Physics Letters **100**, 153505 (2012). However, this capacitor has a planar structure and is not suited as high capacitance device.

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The capacitance of a planer metal-semiconductor-metal structure was simulated by F. Heiman and G. Warfield in Journal of Applied Physics **36**, 3206 (1964), focusing on the impacts of carrier concentration and the thickness of the semiconductor layer. However, the space charge effect for increasing the capacitance in the literature is different from that we propose in this invention. The capacitance increase in the literature is generated by charge injection from electrodes, while the capacitance increase in the present invention is generated by free charges inside the semiconducting material. Moreover, the increased ratio in capacitance by the effect in the literature is at most 2, while the increased ratio in this invention is at least 100 for practical semiconductor layer thickness over 1 μm .

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The capacitance increases by doped organic semiconductors for a planer metal-semiconductor-metal structure have been shown by P. Pahner, et al., in Physical Review B **88**, 195205 (2013). However, the device had a leakage current density of

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over 10^{-5} (A/cm²) under DC 1V application and is therefore too high for use in practical capacitor devices.

5 There is therefore a need for alternative capacitors having good properties in respect to one or more selected from the group consisting of size, power density, material compatibility and compatibility with manufacturing processes, for example, with materials and manufacturing processes used in respect to advanced electronic and semiconductor packages, such as for example printed circuit boards.

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Summary of the invention

The present inventors have now surprisingly found that the above objects may be attained either individually or in any combination by the capacitor of the present application.

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The present application therefore provides for a capacitor comprising a first electrode layer, a second electrode layer and a semiconducting layer between the first electrode layer and the second electrode layer.

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The present application therefore also provides for advanced electronic and semiconductor packages, such as for example a printed circuit board comprising such capacitor.

25 Furthermore, the present application provides for a process of producing a capacitor, said process comprising the steps of

- (a) depositing a first electrode layer;
- (b) depositing a semiconducting layer onto the first electrode layer; and
- (c) depositing a second electrode layer onto the semiconducting layer to obtain

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a capacitor.

Brief description of the figures

35 **Figure 1** shows a schematic cross-sectional view of a capacitor of the present application.

Figure 2a shows the frequency dependencies of the dielectric constant ϵ_r for the capacitor test cells of Example 1.

5 **Figure 2b** shows the frequency dependencies for the dissipation factor $\tan \delta$ for the capacitor test cells of Example 1.

Figure 3a shows the frequency dependencies of the dielectric constant ϵ_r for the capacitor test cells of Example 2.

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Figure 3b shows the frequency dependencies for the capacitance C for the capacitor test cells of Example 2.

15 **Figure 4** shows the frequency dependencies of conductivity σ for the test cell of Example 3.

Figure 5 shows the frequency dependencies of capacitance C for the test cell of Example 4 before and after thermal stress.

20 **Figure 6** shows capacitor performances in terms of capacitance C per area and dissipation factor $\tan \delta$ for various doped organic semiconductor materials.

25 **Figure 7** shows the frequency dependencies of the dissipation factor for different combinations between doped organic semiconductor materials and conductive electrode materials.

Figure 8 shows the frequency dependencies of test cell impedance for different combinations between doped organic semiconductor materials and conductive electrode materials.

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Figure 9 shows the leakage current densities of test cells with different electron energy gaps between doped organic semiconductor materials and aluminum electrode.

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Detailed description of the invention

5 The present application relates to a capacitor comprising a first electrode layer, a second electrode layer and a semiconducting layer between the first electrode layer and the second electrode layer. A schematic cross-sectional view of an exemplary capacitor is shown in **Figure 1** comprising an optional substrate 10, the first electrode layer 20, the semiconducting layer 30, the second electrode layer 40 and an optional further substrate 50.

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FIRST AND SECOND ELECTRODE LAYERS

15 Preferably first electrode layer and second electrode layer, each independently of the other, consist of an electrically conductive composition. The electrically conductive composition of the first electrode layer and the electrically conductive composition of the second electrode layer may be the same or different; preferably they are the same.

20 Said electrically conductive composition comprises and preferably consists of one or more electrically conductive materials. The choice in electrically conductive materials is not particularly limited. It is, however, preferred that such electrically conductive materials are characterized by high electrical conductivity.

25 Electrically conductive materials may, for example, be selected from carbon, metals, metal alloys, metal oxides, electrically conductive polymers, or blends of any of these.

30 Examples of metals suitable for use herein are not particularly limited. Examples of such metals may be selected from the group consisting of potassium, lithium, sodium, cesium, magnesium, calcium, strontium, barium, aluminum, silver, gold, indium, tin, zinc, copper, nickel, palladium, platinum, titanium, zirconium, molybdenum, scandium, and any blend (or alloy) thereof.

35 Examples of alloys suitable for use herein are not particularly limited. Examples of such metal alloys may be selected from the group consisting of stainless steel (e.g., 302 stainless steel, 316 stainless steel), alloys of gold, alloys of silver, alloys of

copper, alloys of aluminum, alloys of nickel, alloys of palladium, alloys of platinum, alloys of titanium, and any blend of any of these.

5 Examples of metal oxides suitable for use herein are not particularly limited. Examples of such metal oxides may be selected from the group consisting of indium tin oxide (ITO), fluorine-doped tin oxide, tin oxide, zinc oxide, aluminum-doped zinc oxide, and any blend thereof.

10 Examples of conductive polymers suitable for use herein are not particularly limited. Examples of such conductive polymers may be selected from the group consisting of polythiophenes, such as poly(3,4-ethylenedioxythiophene) (PEDOT), polyanilines, doped polyanilines, polypyrroles, doped polypyrroles, and any blend of any of these.

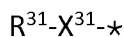
15 Preferably, in combination with a p-doped semiconducting material, the electrically conductive material has a low work function. An example of a metal having a low work function is aluminum.

20 Preferably, in combination with an n-doped semiconducting material, the electrically conductive material has a high work function. An example of a metal having a high work function is platinum.

25 Preferably, in combination with a p-doped semiconducting material or an n-doped semiconducting material, the surface of the electrically conductive composition (or first and/or second electrode layer) may be modified by depositing a self-assembled monolayer (SAM) thereon. This allows the adaptation of the work function of the electrically conductive material to the energy level of the semiconducting material.

30 Preferably, such self-assembled monolayer may have a thickness (measured perpendicularly to the surface of such layer) from 1 to 10, more preferably from 1 to 5, even more preferably from 1 to 3, and still even more preferably from 1 to 2 molecular layers. Most preferably, said thickness is one molecular layer.

35 Preferably, such self-assembled monolayer consists of moieties of the following formula (SAM-I)



(SAM-I)

with R^{31} and X^{31} as defined herein. With regards to formula (SAM-I) the asterisk “*” or “*” generally denotes the (or the bond to the) electrically conductive material (following the deposition of the SAM onto the electrically conductive material), and may denote hydrogen before the SAM is deposited onto the electrically conductive material. Without wishing to be bound by theory, It is noted that when a SAM material of formula $R^{31}-X^{31}-H$ is deposited onto the electrically conductive material the hydrogen bonded to X^{31} is abstracted and the remainder of the molecule bonds to the electrically conductive material.

X^{31} is at each occurrence independently selected from the group consisting of $-X^a-$, $-X^a-X^b-$, $-C(=X^a)-X^b-$, $-X^aO_3-$, $-X^a-X^bO_3-$, $-PO_2H-$, and $-PO_3H-$. Preferably X^{31} is at each occurrence $-X^a-$.

X^a and X^b are at each occurrence independently S or Se. Preferably, X^a and X^b are S.

It is noted that with regards to functional group X^{31} selected from the group consisting of $-X^aO_3-$, $-X^a-X^bO_3-$, $-PO_2H-$ and $-PO_3H-$ a number of possible binding modes between X^{31} and the metal surface may be envisaged. Without wishing to be bound by theory it is believed that generally the bonding between these functional groups X^{31} and the metal or metal oxide surface is done by means of $-O-$. An example of such bonding is Metal-O-P-. These functional groups X^{31} may for example be bound to the metal surface by means of one or more groups $-O-$. It is also possible that more than one such binding modes exist simultaneously.

R^{31} is at each occurrence independently an organyl group or an organoheteryl group. Preferably R^{31} may at each occurrence independently be selected from the group consisting of aryl, alkyl having from 1 to 20 (preferably from 1 to 15, more preferably from 1 to 10) carbon atoms, aryl substituted with one or more groups R^{32} , and alkyl having from 1 to 20 (preferably from 1 to 15, more preferably from 1 to 10) carbon atoms substituted with one or more groups R^{32} , with R^{32} as defined herein.

R^{32} is an electron withdrawing group. Preferably R^{32} is at each occurrence independently selected from the group consisting of $-NO_2$, $-CN$, $-F$, $-Cl$, $-Br$, $-I$, $-OAr^{31}$,

-OR³³, -COR³³, -SH, -SR³³, -OH, -C≡CR³³, -CH=CR³³₂, and alkyl having from 1 to 10 carbon atoms, wherein one or more, preferably all, hydrogen atoms are replaced by F, with Ar³¹ and R³³ as defined herein. More preferably R³² is at each occurrence independently selected from the group consisting of -CN, -F, -Cl, -Br, -I, -OR³³, and
 5 alkyl having from 1 to 10 carbon atoms, wherein one or more, preferably all, hydrogen atoms are replaced by F, with R³³ as defined herein. Even more preferably R³² is at each occurrence independently selected from the group consisting of -F, -OR³³, and alkyl having from 1 to 10 carbon atoms, wherein one or more, preferably all, hydrogen atoms are replaced by F, with R³³ as defined herein.

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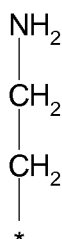
Ar³¹ is an aryl having from 6 to 30 carbon atoms, preferably having from 6 to 20 carbon atoms, and most preferably is phenyl. Preferably Ar³¹ is substituted with one or more substituent selected from the group consisting of -CN, -F, -Cl, -Br, -I, -OR³³, and alkyl having from 1 to 10, preferably from 1 to 5, carbon atoms, wherein one
 15 or more, preferably all, hydrogen atoms are replaced by F, with R³³ as defined herein.

R³³ is an alkyl having from 1 to 10, preferably from 1 to 5, carbon atoms, or alkyl having from 1 to 10, preferably from 1 to 5, carbon atoms, wherein one or more,
 20 preferably all, hydrogen atoms are replaced by F.

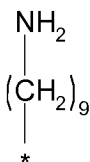
Preferred examples of alkyl suitable as R³³ may be selected from the group consisting of methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl and n-pentyl. Preferred examples of fluorinated alkyl (i.e. alkyl wherein one or more,
 25 preferably all, hydrogen atoms are replaced by F) suitable as R³³ may be selected from the group consisting of CF₃, C₂F₅, n-C₃F₇, and n-C₄F₉.

Suitable examples of R³¹ may be selected from the group consisting of the following formulae (SAM-I-1) to (SAM-I-16)

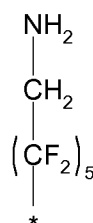
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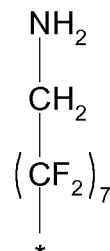
(SAM-I-1)



(SAM-I-2)

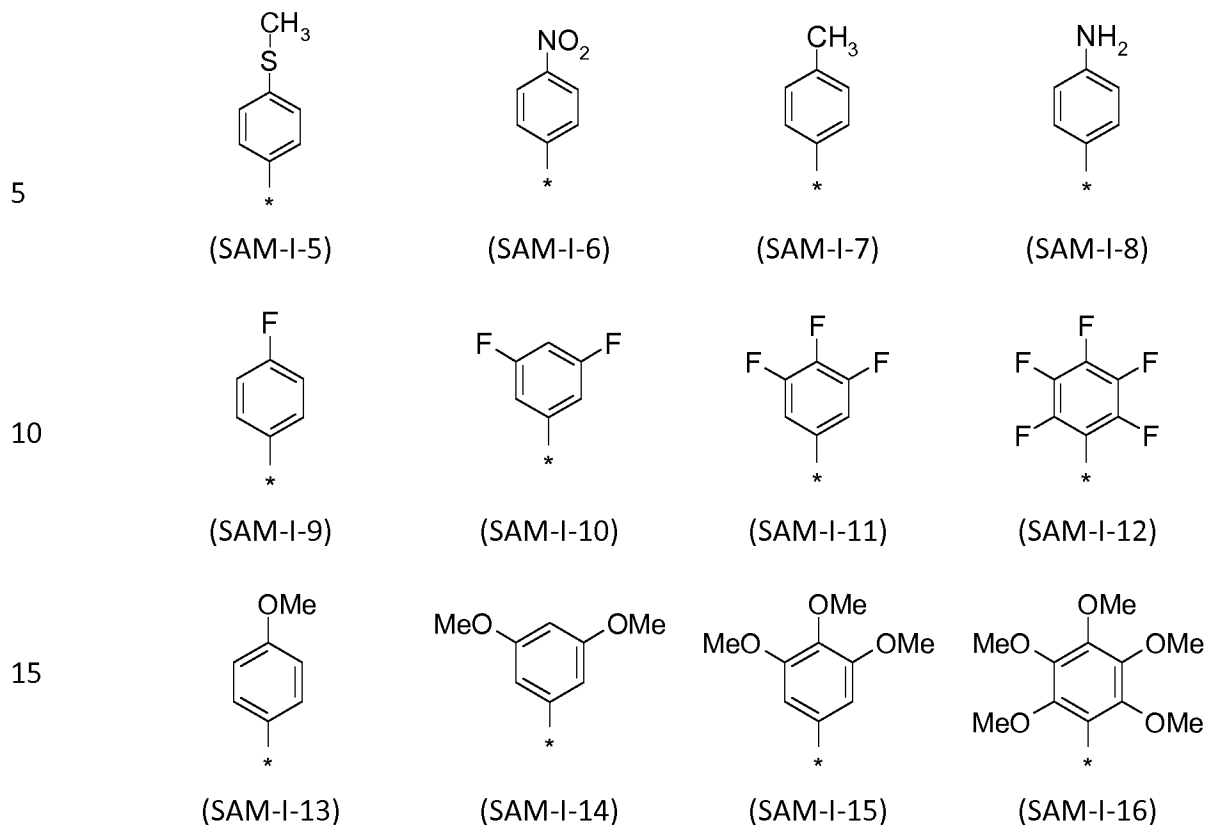


(SAM-I-3)



(SAM-I-4)

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20 with (SAM-I-9) to (SAM-I-16) being preferred, and (SAM-I-12) and (SAM-I-15) being particularly preferred.

25 Typical SAM materials for this purpose are $\text{CH}_3(\text{CH}_2)_9\text{SH}$, $\text{NH}_2(\text{CH}_2)_{10}\text{SH}$, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SH}$, which are shown by I. Campbell et al. in Physical Review B **54**, 14321 (1996).

30 In addition to the one or more electrically conductive materials the electrically conductive composition of first and second electrode layer may also, as the need arises, comprise further components. An example of such a further component is a binder, which preferably is a material that is inert under use conditions. A binder may, for example, help in improving the mechanical stability and/or durability of first and/or second electrode layer.

35 Preferably the first electrode layer or the second electrode layer or both may comprise, preferably consist of, a porous component and a non-porous component. Preferably said porous component is adjacent to (for example, in direct physical

and/or electrical contact with) the semiconducting layer. Said non-porous component is preferably in direct contact with said porous component. Said non-porous component may or may not be in direct physical and/or electrical contact with the semiconducting layer. It may also be that only a part of the surface of said non-porous component is in direct physical and/or electrical contact with the semiconducting layer. For example, the porous component may comprise, preferably consist of, carbon, such as for example activated carbon. For example, the non-porous component may comprise, preferably consist of, a metal as defined above. Without wishing to be bound by theory it is believed that such an electrode layer with a porous component is more effective for obtaining high capacitances and that a non-porous component is more efficient in transferring the collected charges out of the capacitor.

15 SEMICONDUCTING LAYER

The semiconducting layer is between the first electrode layer and the second electrode layer. Preferably the semiconducting layer is solid. Preferably the semiconducting layer comprises, and preferably consists of, a semiconducting material selected from the group consisting of organic semiconducting materials, inorganic semiconducting materials and any blends of any of these, for example including blends of more than one organic semiconducting material, more than one inorganic semiconducting material, or blends of one or more organic semiconducting material and one or more inorganic semiconducting material. Preferably, said semiconducting material has a transistor mobility of at least $1 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

The energy level of the highest occupied molecular orbital (HOMO) of the semiconducting material is lower than the lower one of the Fermi energy levels of the first and second electrode composition or materials.

Preferably the HOMO level (in eV) of the semiconducting material is lower than the Fermi energy levels (in eV) of the first and second electrode composition or material minus 0.5 eV, i.e.,

$$E_{\text{HOMO, semiconducting material}} < E_{\text{F, electrode1}} - 0.5 \text{ eV}$$

$$E_{\text{HOMO, semiconducting material}} < E_{\text{F, electrode2}} - 0.5 \text{ eV}$$

More preferably the HOMO level (in eV) of the semiconducting material is lower than the Fermi energy levels (in eV) of the first and second electrode composition or material minus 1.0 eV, i.e.,

$$\begin{aligned} E_{\text{HOMO, semiconducting material}} &< E_{\text{F, electrode1}} - 1.0 \text{ eV} \\ E_{\text{HOMO, semiconducting material}} &< E_{\text{F, electrode2}} - 1.0 \text{ eV} \end{aligned}$$

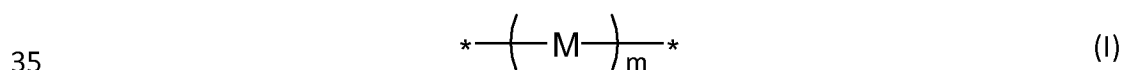
The semiconducting layer preferably has a thickness of at least 0.5 μm , more preferably of at least 1.0 μm and of at most 20 μm , more preferably of at most 15 μm and most preferably of at most 10 μm .

When in operation the present semiconducting layer preferably has a dielectric constant of at least 3 and of at most 100,000 for a given thickness of 10 μm .

The organic semiconducting material is preferably selected from the group consisting of monomeric compounds (also referred to as “small molecule”), oligomers, polymers or blends of any of these, for example, including but not limited to blends of one or more monomeric compounds, one or more oligomers or one or more polymers. More preferably the organic semiconducting material is a polymer or a blend of polymers. Most preferably the organic semiconducting material is a polymer.

The type of organic semiconducting material is not particularly limited. In general the organic semiconducting material comprises a conjugated system. The term “conjugated system” is herein used to denote a molecular entity or a part of a molecular entity whose structure may be represented as a system of alternating single and multiple bonds (see also International Union of Pure and Applied Chemistry, Compendium of Chemical Terminology, Gold Book, Version 2.3.3, 2014-02-24, pages 322-323).

An organic semiconducting material suited for use herein may, for example, be represented by the following formula (I)



wherein monomeric unit M and m are as defined herein. At each occurrence M may be selected independently.

5 For the purposes of the present application, an asterisk "*" is used to denote a linkage to an adjacent unit or group, including for example, in case of a polymer, to an adjacent repeating unit or any other group. In some instances, where specifically identified as such, the asterisk "*" may also denote a mono-valent chemical group.

10 With regards to formula (I) m may be any integer from 1 to 100,000. For a monomer or monomeric unit m is 1. For an oligomer m is at least 2 and at most 10. For a polymer m is at least 11.

15 Preferably, the organic semiconducting material comprises one or more aromatic units. Expressed differently, with regards to formula (I) M may be an aromatic unit. Such aromatic units preferably comprise two or more, more preferably three or more aromatic rings. Such aromatic rings may, for example, at each occurrence independently be selected from the group consisting of 5-, 6-, 7- and 8-membered aromatic rings, with 5- and 6-membered rings being particularly preferred.

20 These aromatic rings comprised in the organic semiconducting material optionally comprise one or more heteroatoms selected from Se, Te, P, Si, B, As, N, O or S, preferably from Si, N, O or S. Further, these aromatic rings may optionally be substituted with alkyl, alkoxy, polyalkoxy, thioalkyl, acyl, aryl or substituted aryl groups, halogen, with fluorine being the preferred halogen, cyano, nitro or an optionally substituted secondary or tertiary alkylamine or arylamine represented by -N(R')(R''), where R' and R'' are each independently H, an optionally substituted alkyl or an optionally substituted aryl, alkoxy or polyalkoxy groups are typically employed. Further, where R' and R'' is alkyl or aryl these may be optionally fluorinated.

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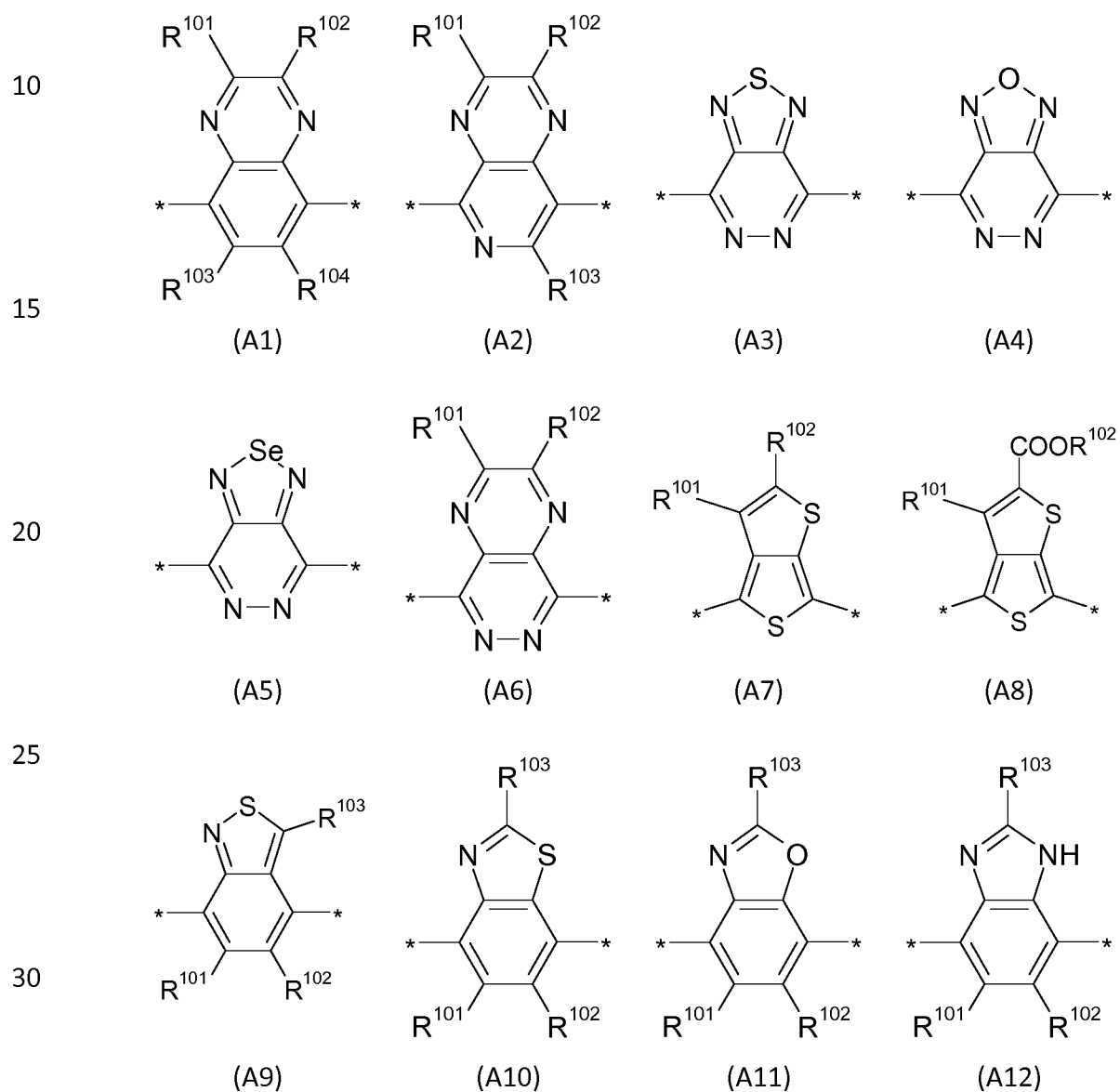
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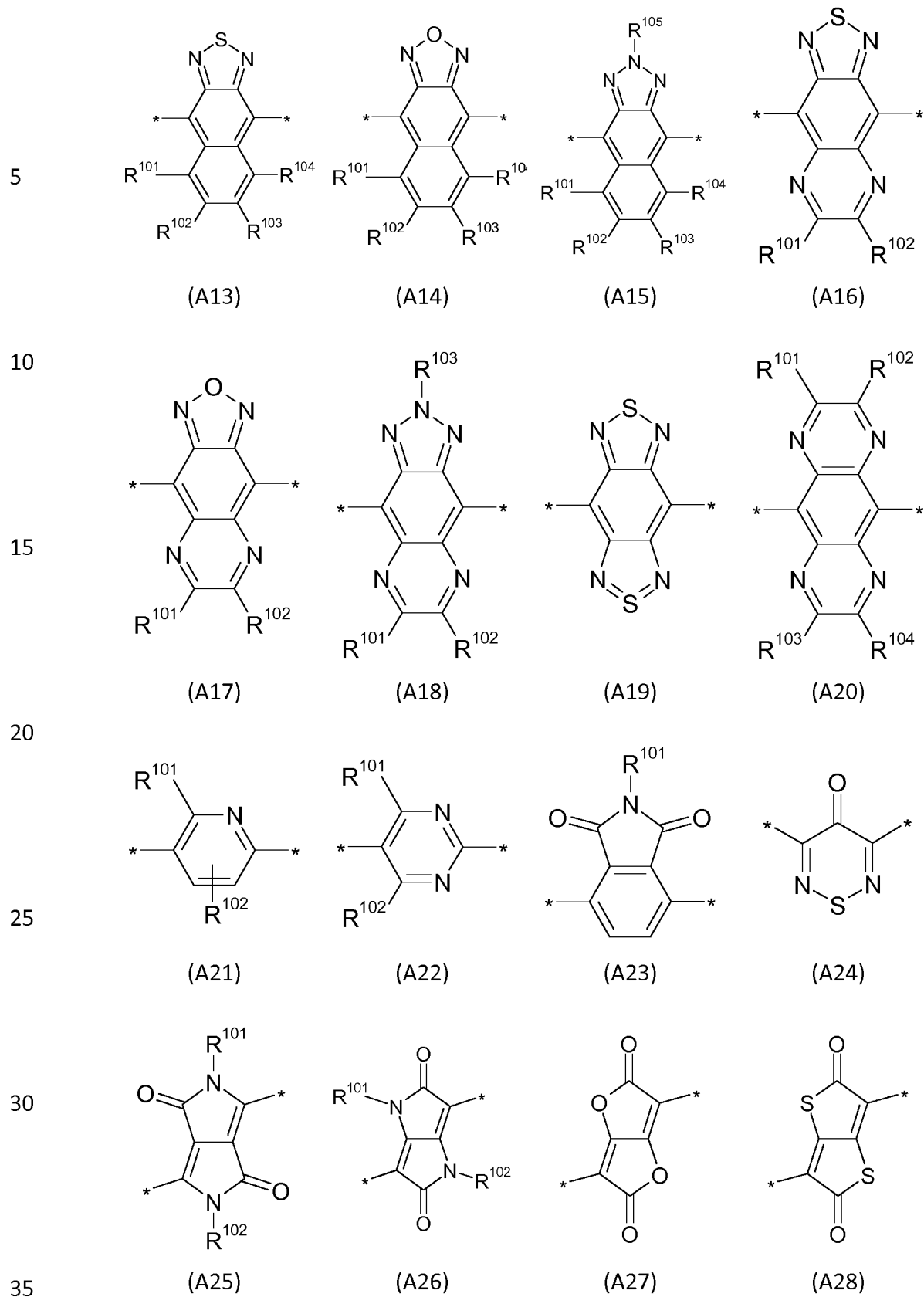
The aforementioned aromatic rings can be fused rings or linked to each other by a conjugated linking group such as -C(T₁)=C(T₂)-, -C≡C-, -N(R''')-, -N=N-, (R''')=N-, -N=C(R''')-, where T₁ and T₂ each independently represent H, Cl, F, -C≡N or lower alkyl groups such as C₁₋₄ alkyl groups; R''' represents H, optionally substituted alkyl or

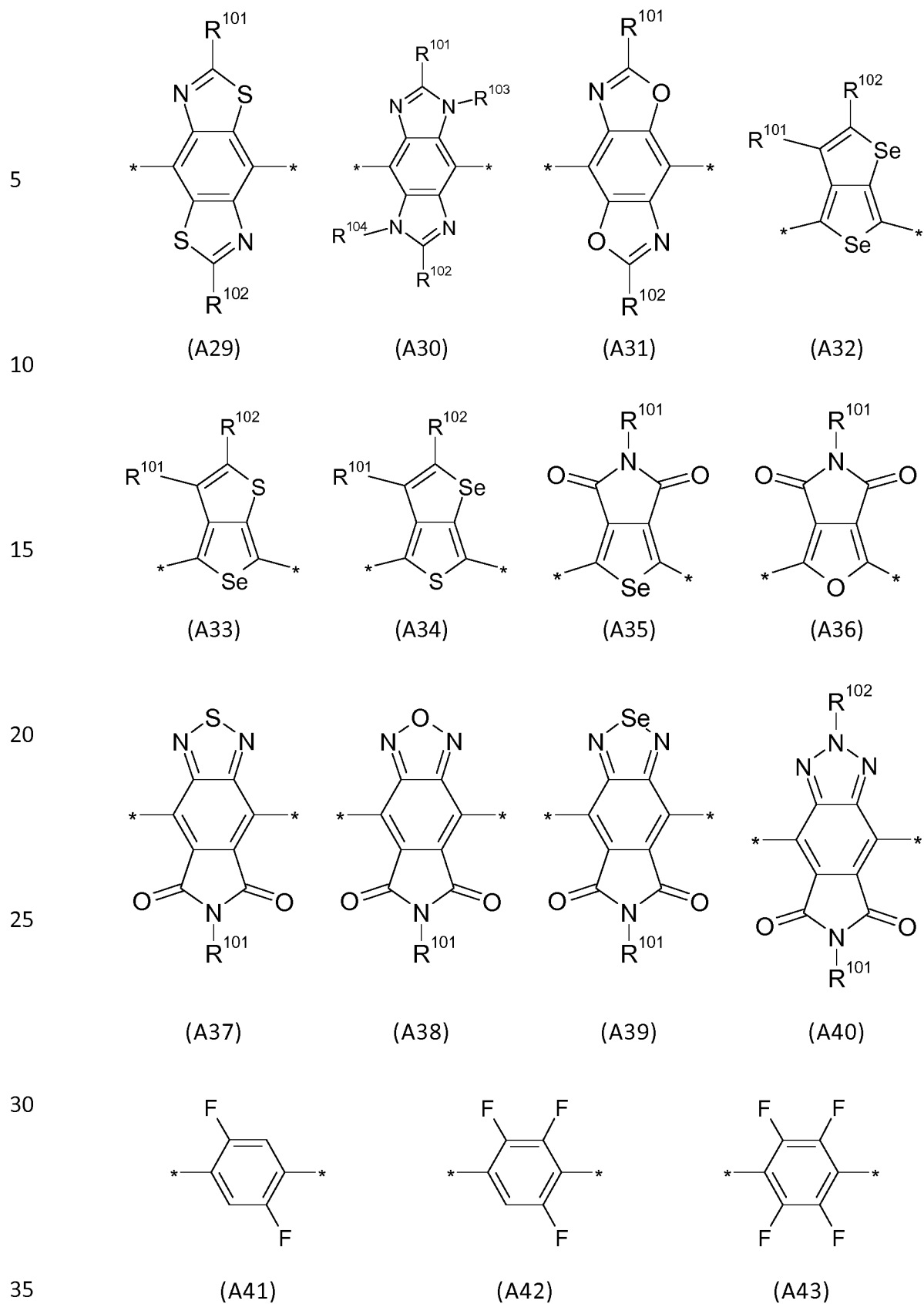
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optionally substituted aryl. Further, where R''' is alkyl or aryl, it may be optionally fluorinated.

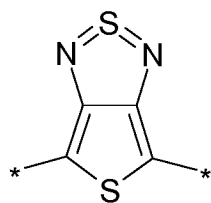
Further preferred organic semiconducting materials may be polymers or copolymers wherein the monomeric units M of formula (I) may at each occurrence be independently selected from the group consisting of formulae (A1) to (A83) and (D1) to (D142)



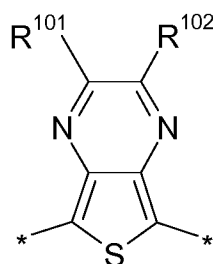




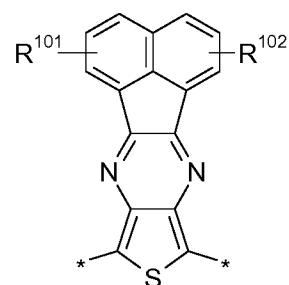
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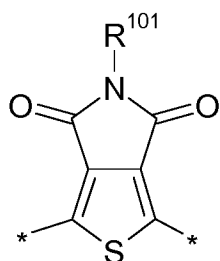


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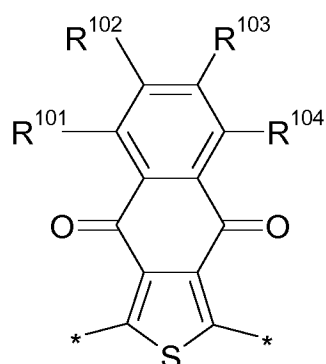


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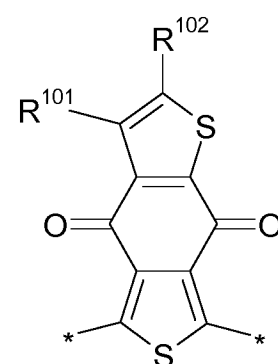
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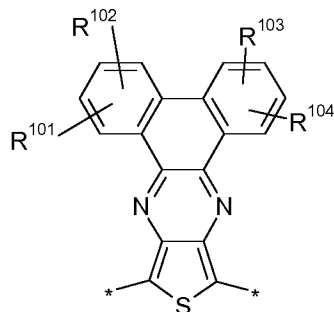


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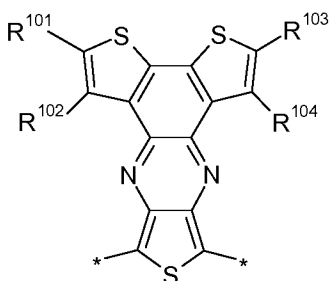


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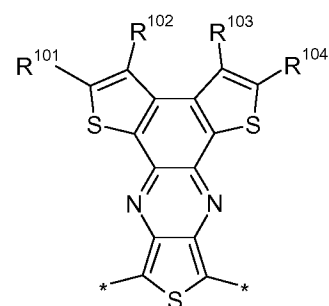
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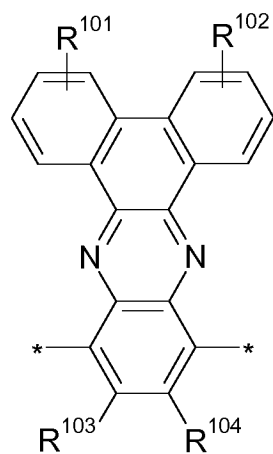
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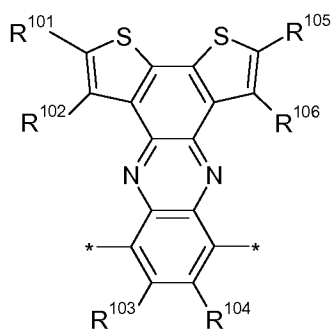
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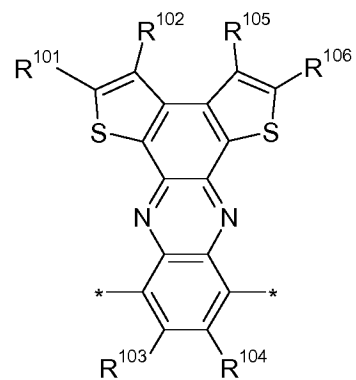


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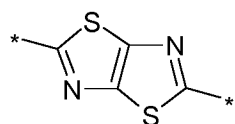


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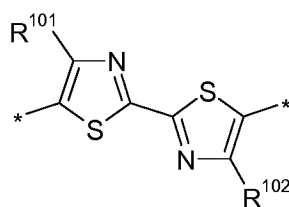


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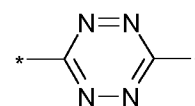
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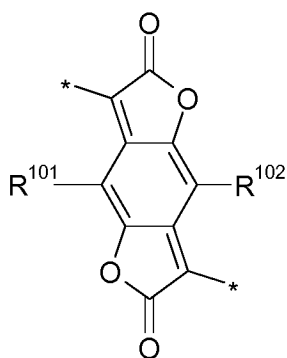


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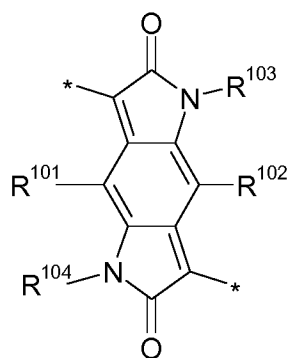
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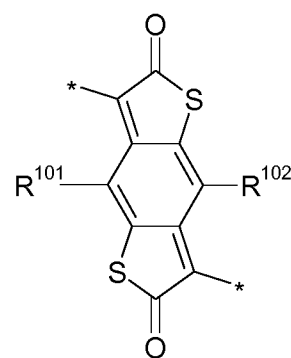


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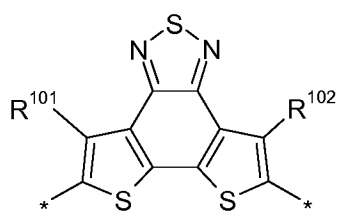


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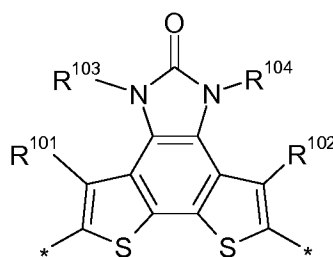


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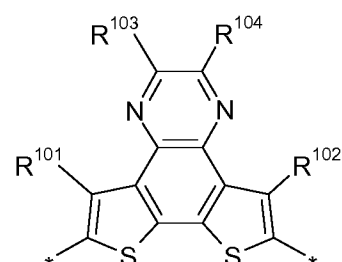
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(A62)



(A63)

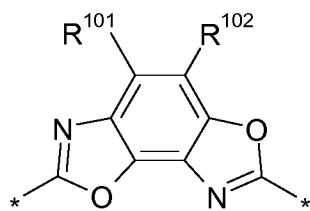


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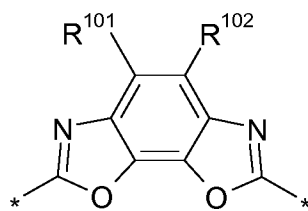
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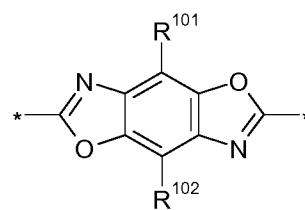
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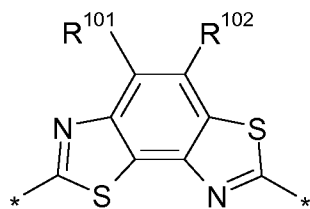


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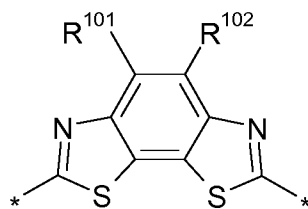


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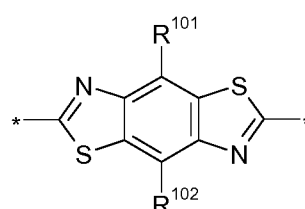
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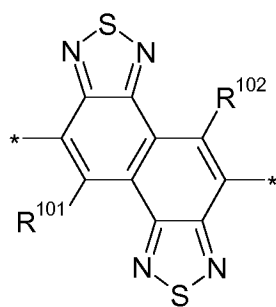


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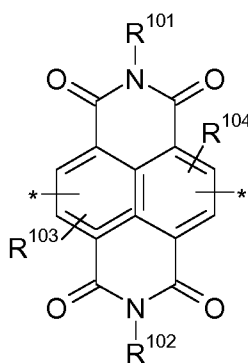


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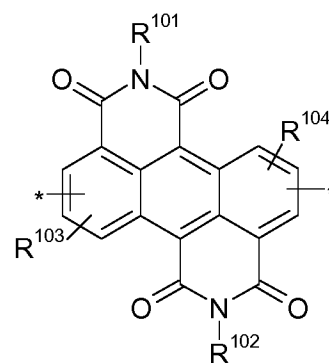
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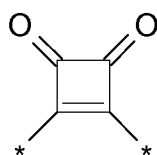
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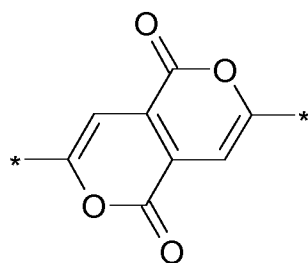
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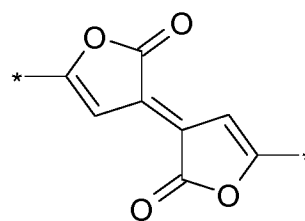
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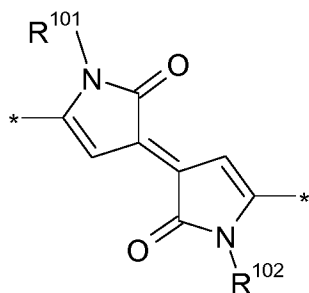
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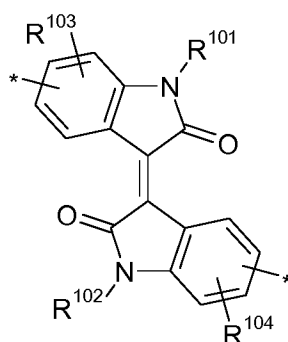
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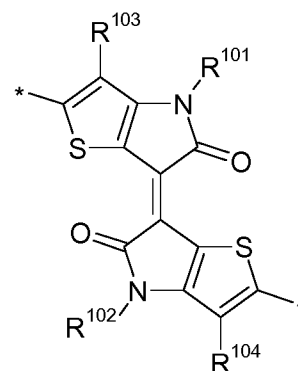
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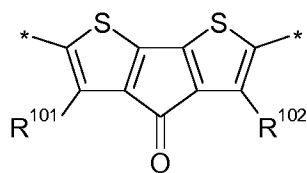
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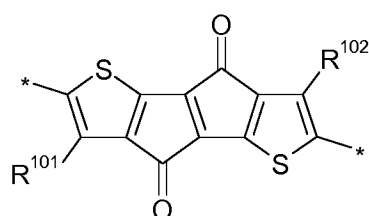
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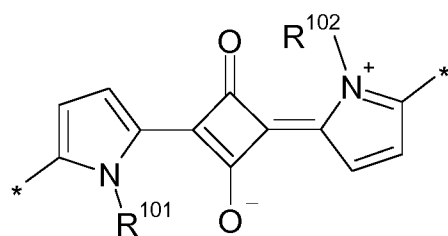
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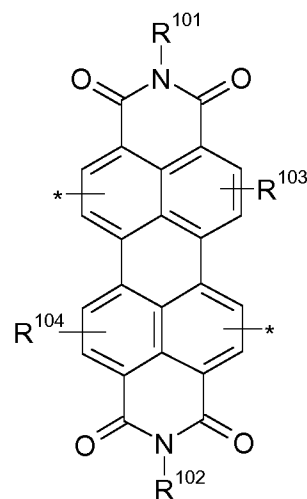
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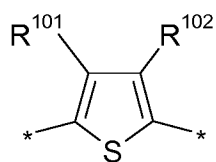
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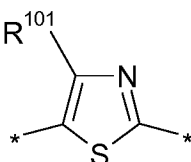
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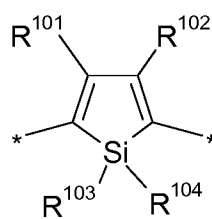
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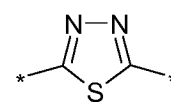
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(D2)

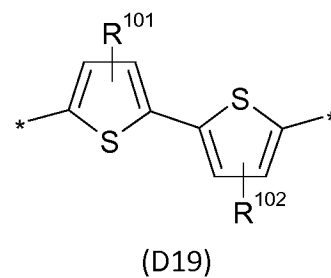
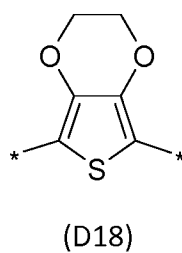
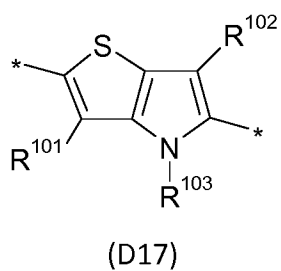
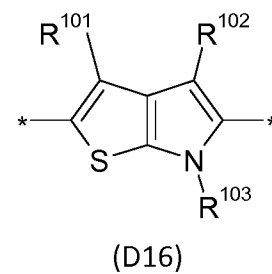
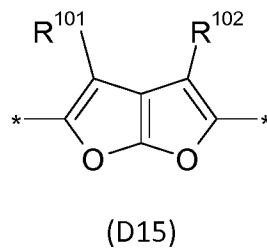
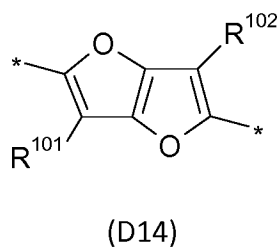
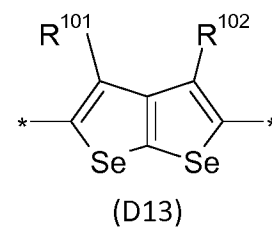
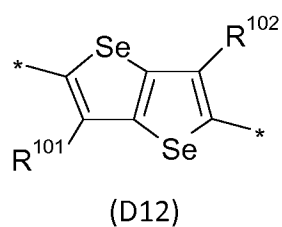
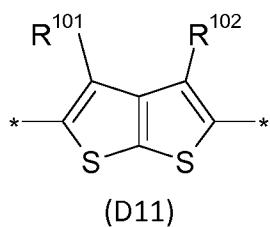
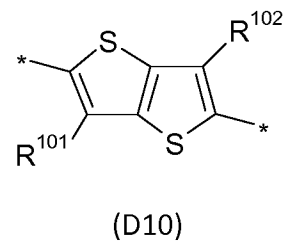
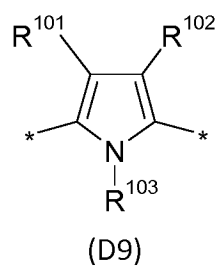
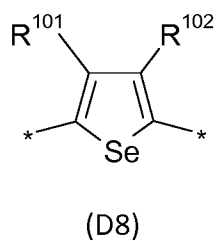
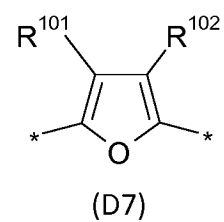
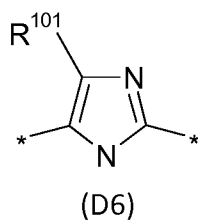
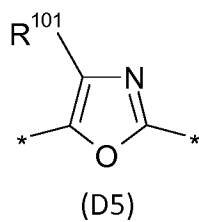


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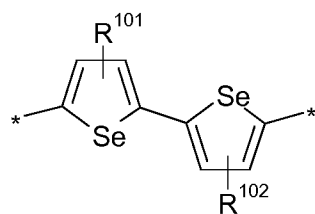


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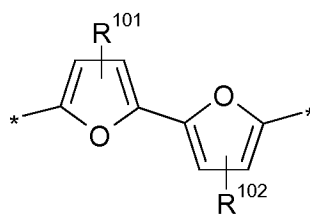
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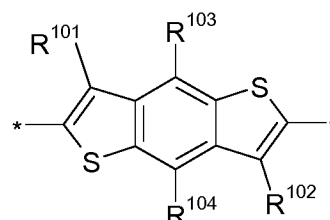
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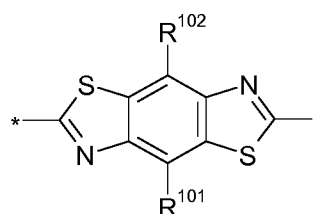
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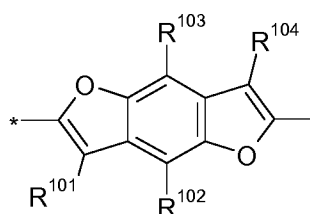
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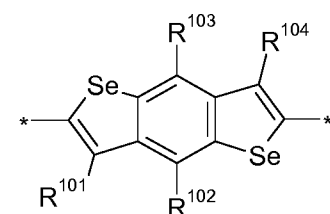
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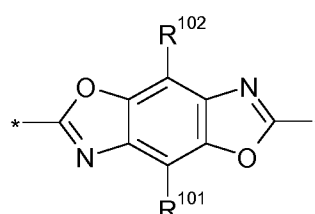
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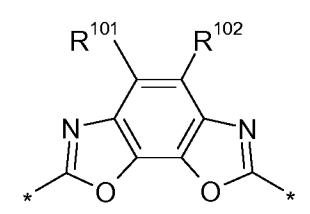
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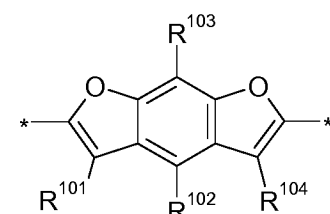
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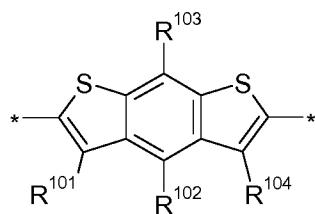
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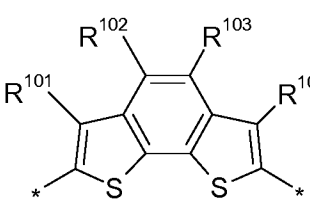
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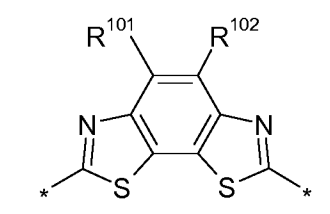
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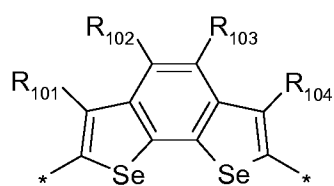
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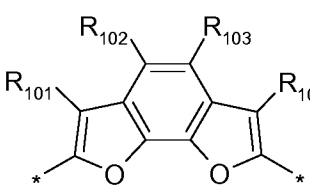
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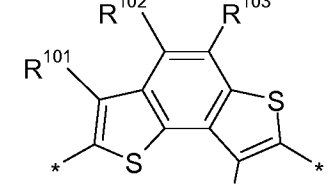
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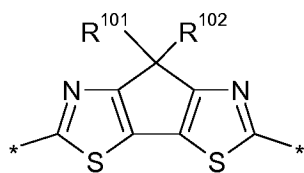


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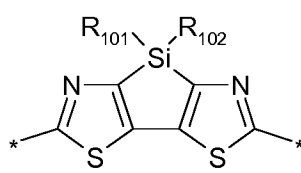


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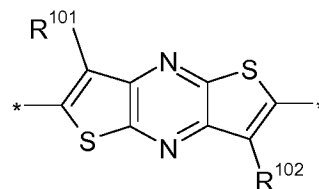
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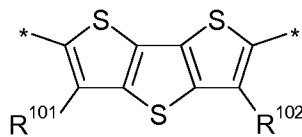
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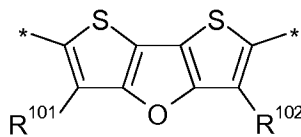
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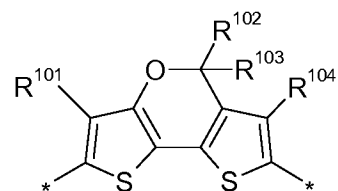
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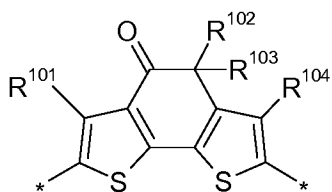
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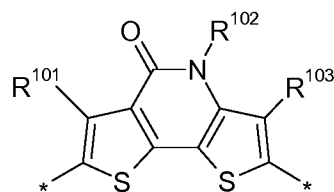
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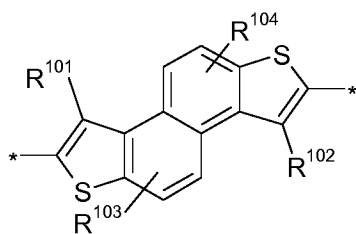
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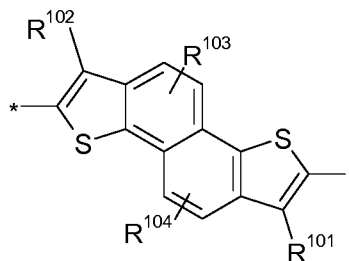
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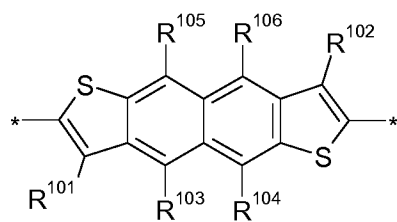
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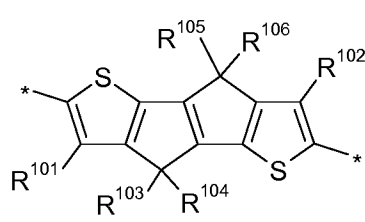
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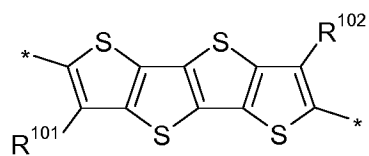
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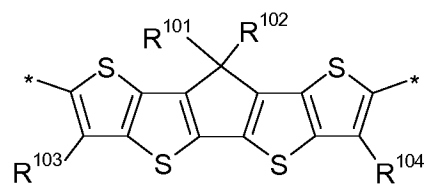
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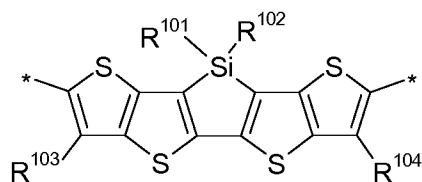
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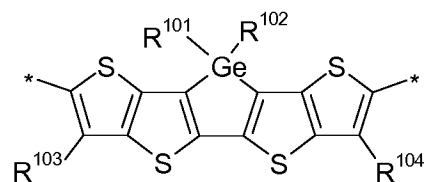
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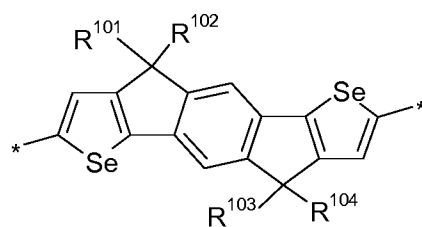
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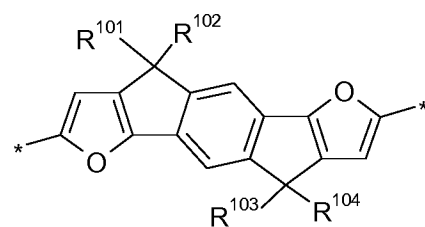
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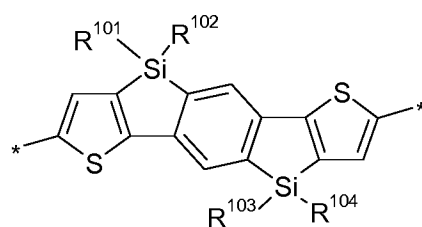
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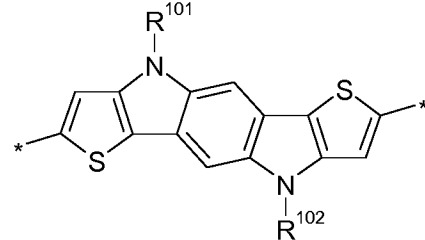
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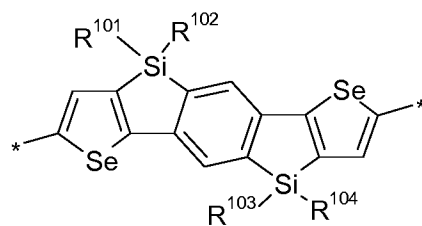
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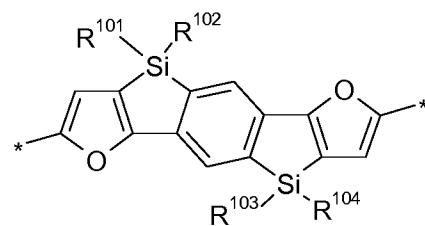
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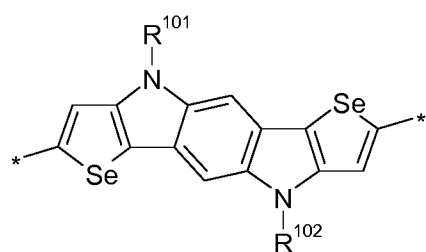
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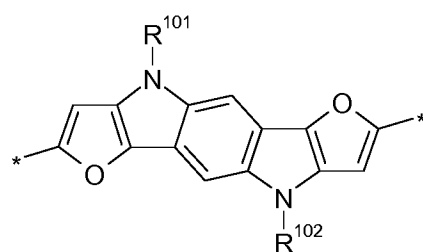
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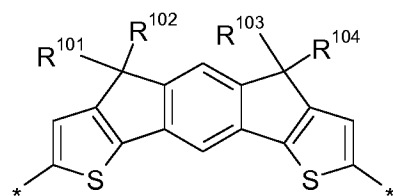
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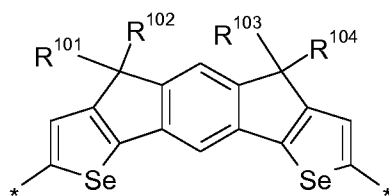
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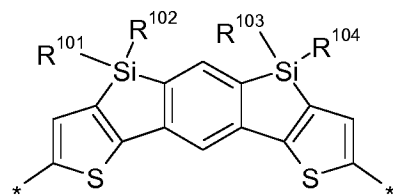
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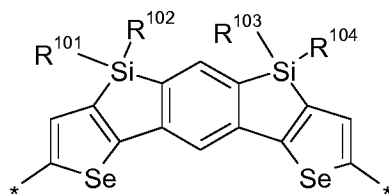
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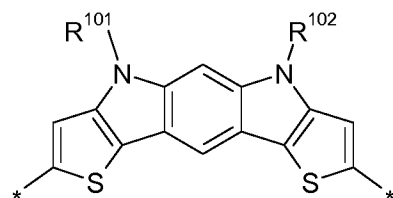
(D60)



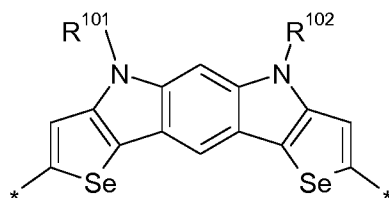
(D61)



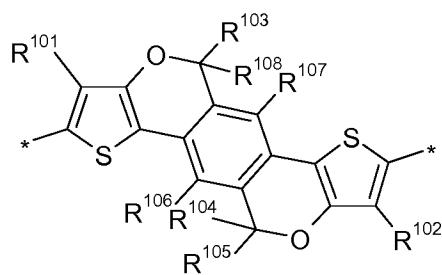
(D62)



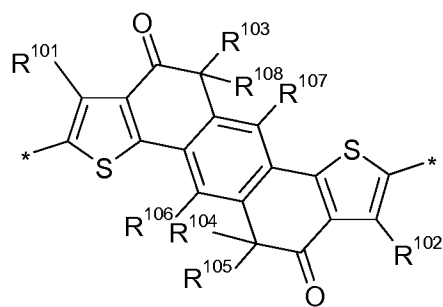
(D63)



(D64)

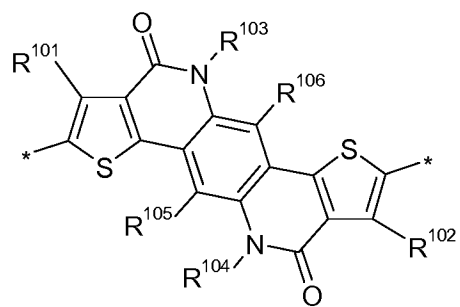


(D65)

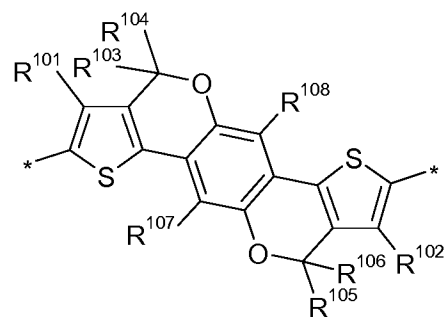


(D66)

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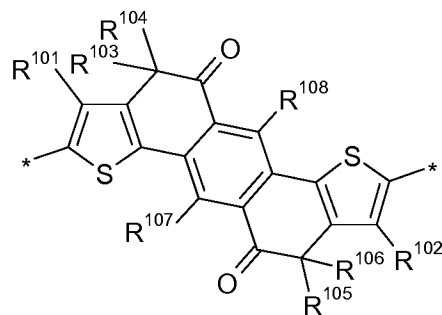


(D67)

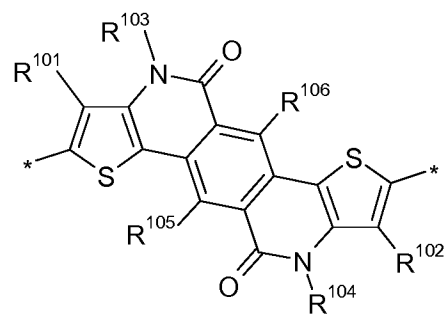


(D68)

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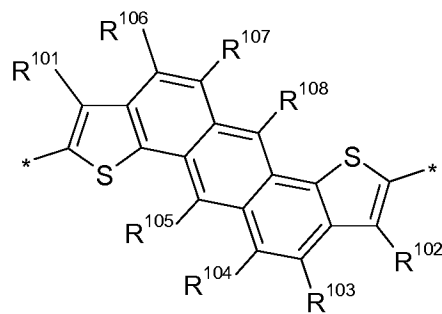
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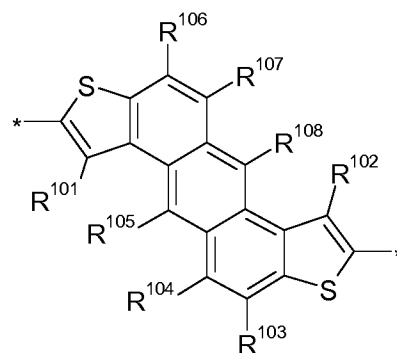
(D70)

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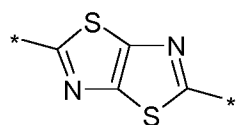
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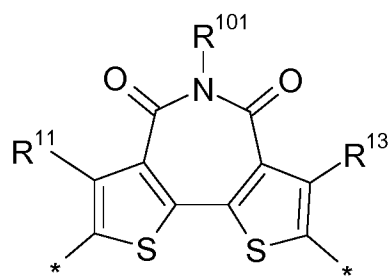
(D72)

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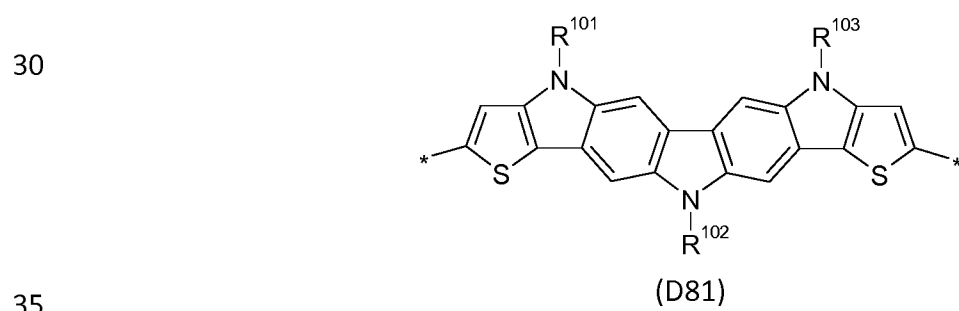
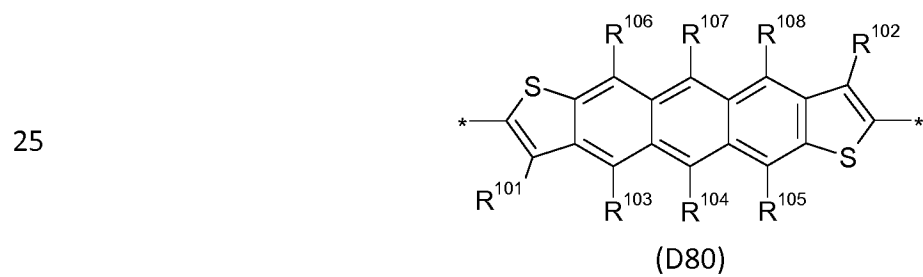
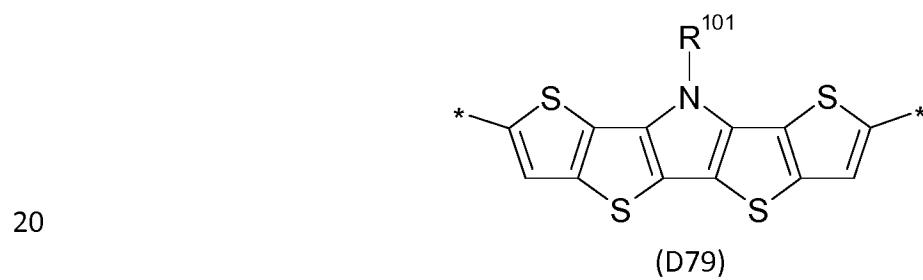
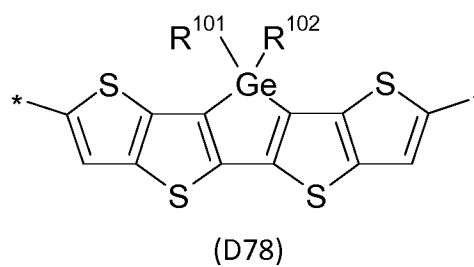
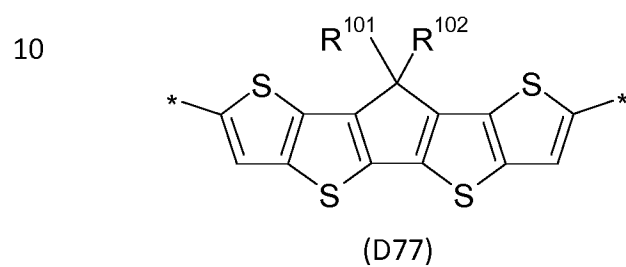
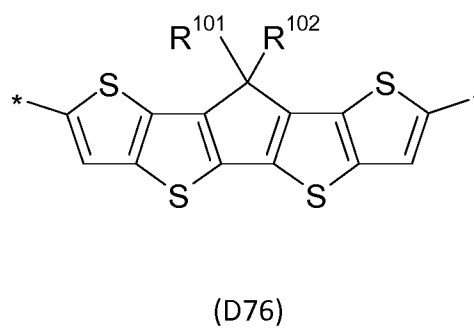
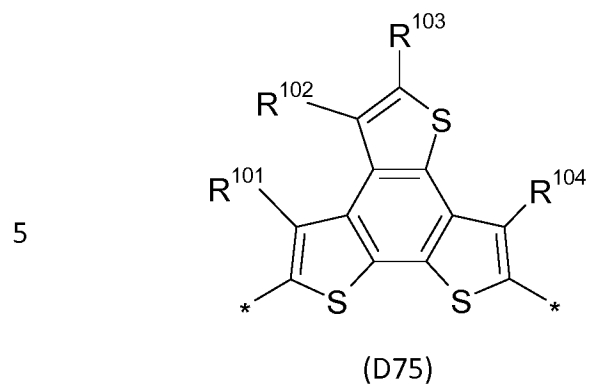


(D73)

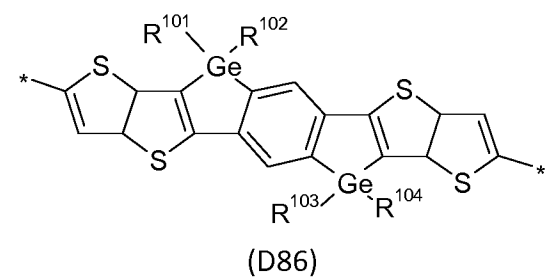
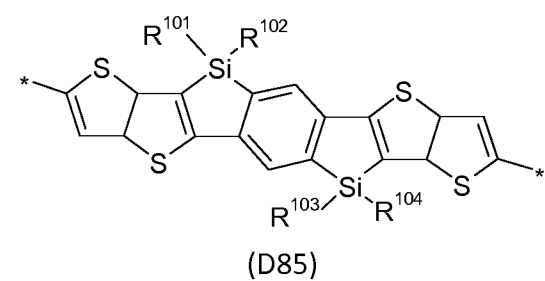
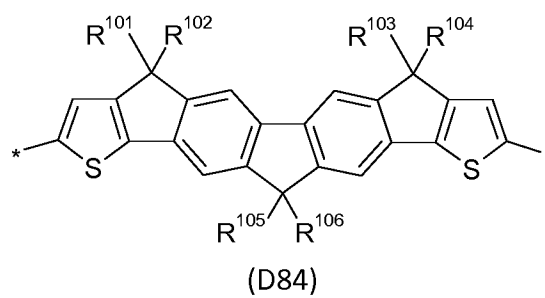
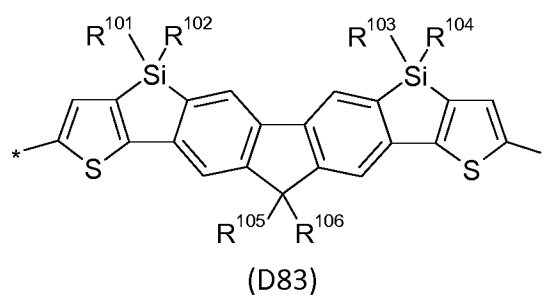
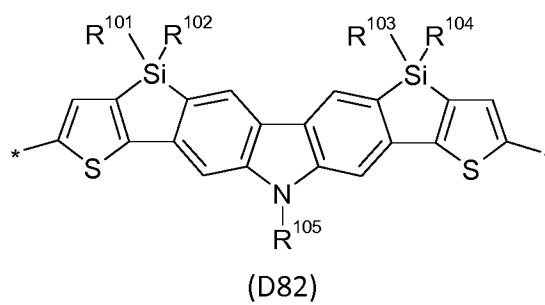


(D74)

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- 27 -



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(D87)



(D88)



(D89)

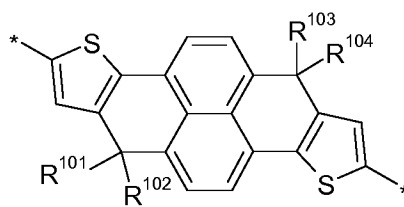


(D90)

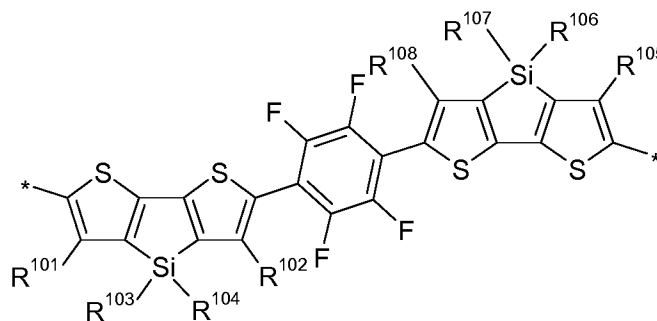


(D91)

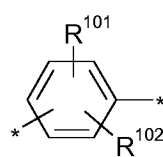
- 29 -



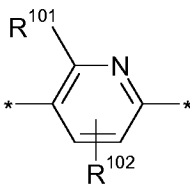
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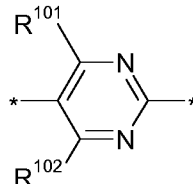
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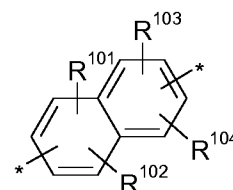
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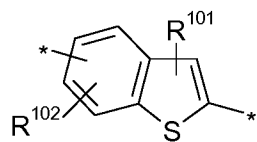
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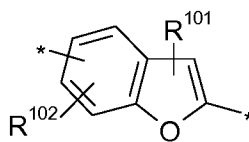
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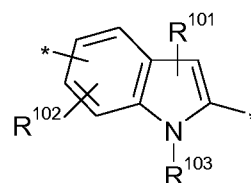
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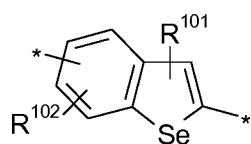
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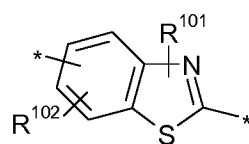
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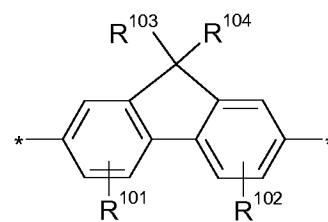
(D100)



(D101)

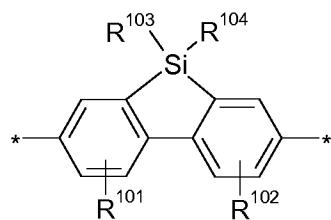


(D102)

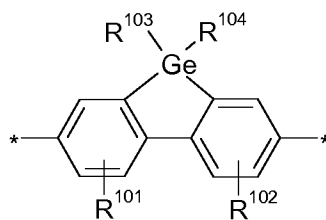


(D103)

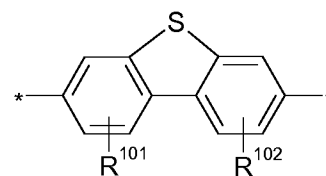
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(D104)

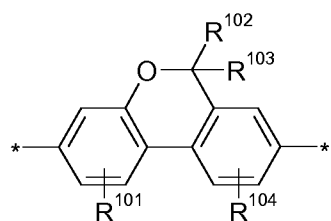


(D105)

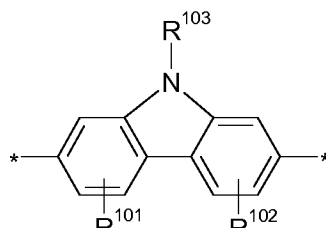


(D106)

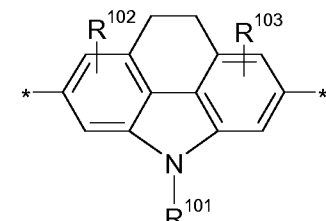
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(D107)

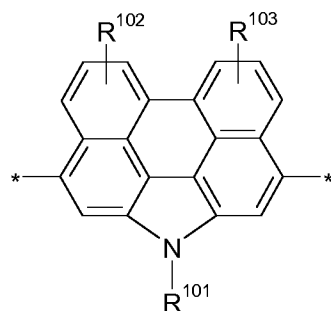


(D108)

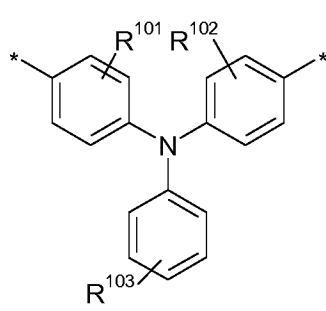


(D109)

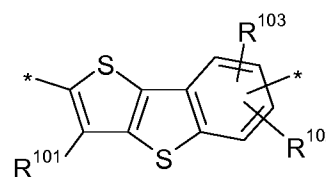
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(D110)

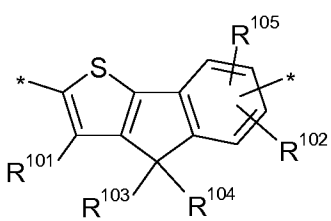


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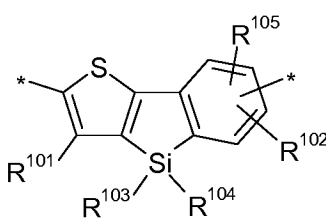


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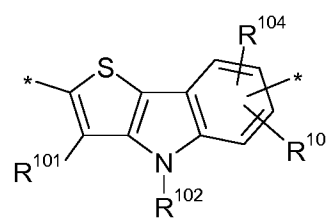
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(D113)

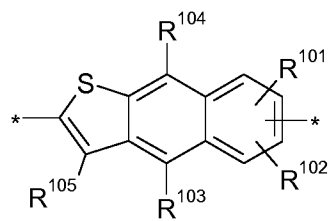


(D114)

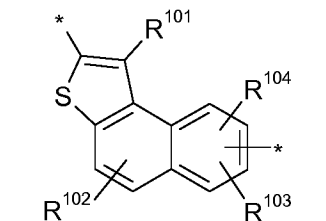


(D115)

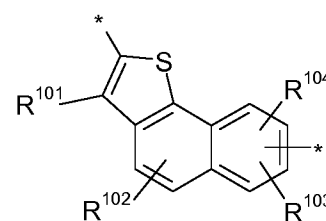
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(D116)



(D117)

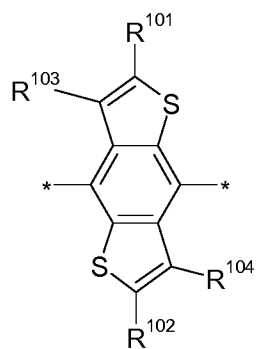


(D118)

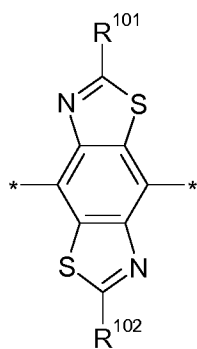
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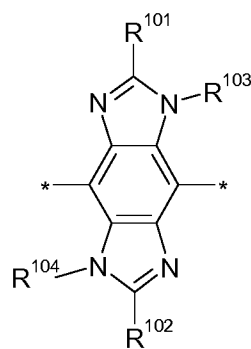
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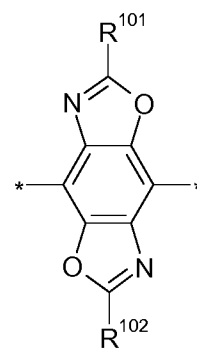
(D119)



(D120)

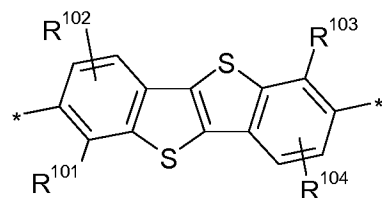


(D121)

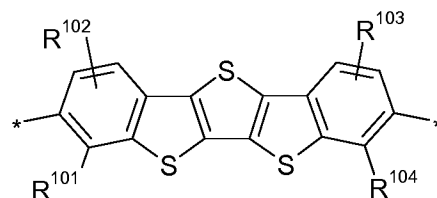


(D122)

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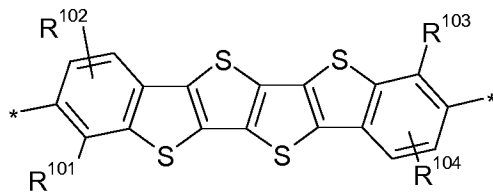


(D123)

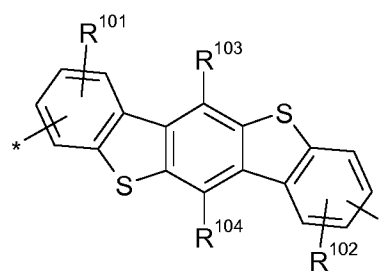


(D124)

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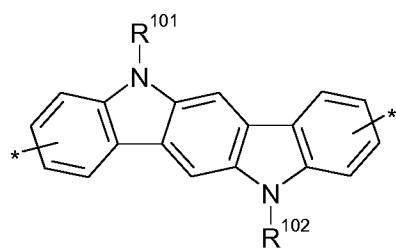
(D125)



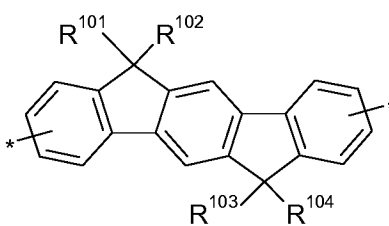
(D126)

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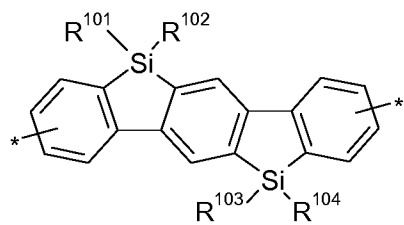
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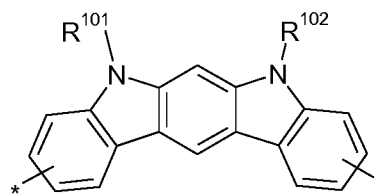
(D128)

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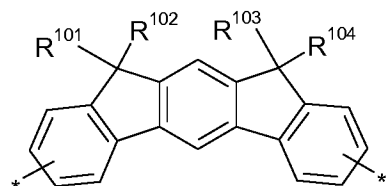
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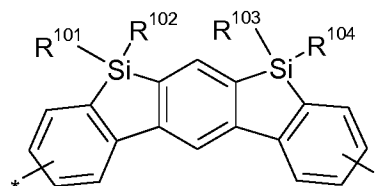
(D129)



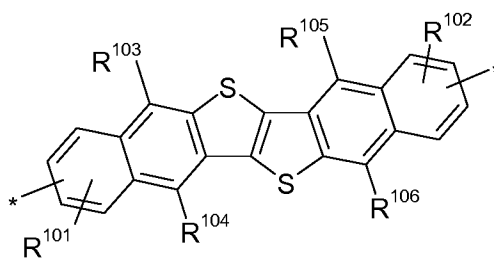
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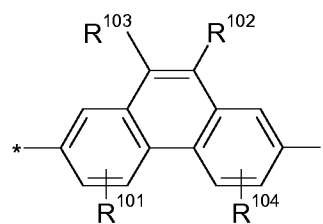
(D131)



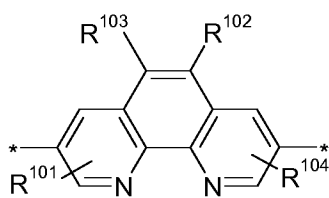
(D132)



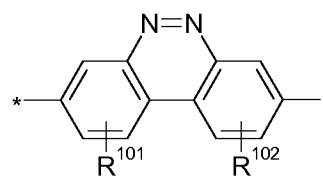
(D133)



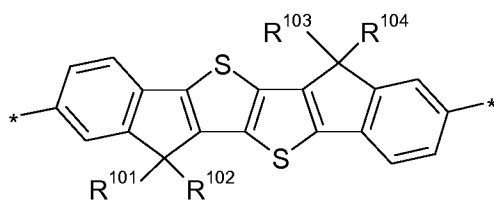
(D134)



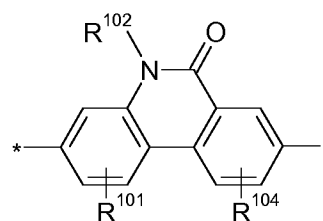
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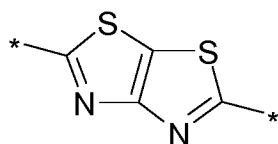
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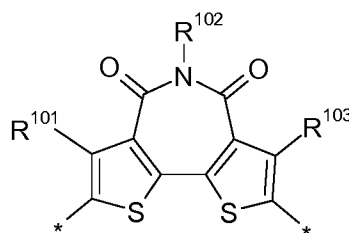
(D137)



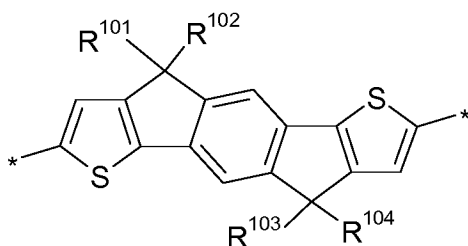
(D138)



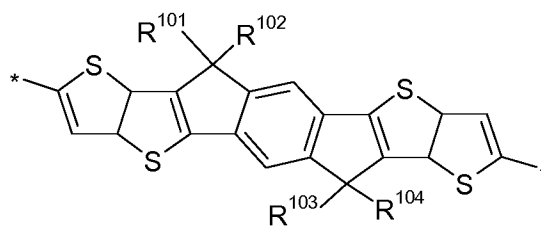
(D139)



(D140)



(D141)



(D142)

wherein R^{101} , R^{102} , R^{103} , R^{104} , R^{105} , R^{106} , R^{107} and R^{108} are independently of each other selected from the group consisting of H and R^S as defined herein.

R^S is at each occurrence independently a carbyl group as defined herein and preferably selected from the group consisting of any group R^T as defined herein, hydrocarbyl having from 1 to 40 carbon atoms wherein the hydrocarbyl may be further substituted with one or more groups R^T , and hydrocarbyl having from 1 to 40 carbon atoms comprising one or more heteroatoms selected from the group consisting of N, O, S, P, Si, Se, As, Te or Ge, with N, O and S being preferred heteroatoms, wherein the hydrocarbyl may be further substituted with one or more groups R^T .

Preferred examples of hydrocarbyl suitable as R^S may at each occurrence be independently selected from phenyl, phenyl substituted with one or more groups R^T , alkyl and alkyl substituted with one or more groups R^T , wherein the alkyl has at least 1, preferably at least 5 and has at most 40, more preferably at most 30 or 25 or 20, even more preferably at most 15 and most preferably at most 12 carbon atoms. It is noted that for example alkyl suitable as R^S also includes fluorinated alkyl, i.e. alkyl wherein one or more hydrogen is replaced by fluorine, and perfluorinated alkyl, i.e. alkyl wherein all of the hydrogen are replaced by fluorine.

R^T is at each occurrence independently selected from the group consisting of F, Br, Cl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, -C(O)NR⁰R⁰⁰, -C(O)X⁰, -C(O)R⁰, -NH₂, -NR⁰R⁰⁰, -SH, -SR⁰, -SO₃H, -SO₂R⁰, -OH, -OR⁰, -NO₂, -SF₅ and -SiR⁰R⁰⁰R⁰⁰⁰. Preferred R^T are selected from the group consisting of F, Br, Cl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, -C(O)NR⁰R⁰⁰, -C(O)X⁰, -C(O)R⁰, -NH₂, -NR⁰R⁰⁰, -SH, -SR⁰, -OH, -OR⁰ and -SiR⁰R⁰⁰R⁰⁰⁰. Most preferred R^T is F.

R^0 , R^{00} and R^{000} are at each occurrence independently of each other selected from the group consisting of H, F, hydrocarbyl having from 1 to 40 carbon atoms, and fluorinated hydrocarbyl having from 1 to 40 carbon atoms, i.e. hydrocarbyl wherein one or more hydrogen is replaced by fluorine. Said hydrocarbyl preferably has at least 5 carbon atoms. Said hydrocarbyl preferably has at most 30, more preferably at most 25 or 20, even more preferably at most 20, and most preferably at most 12 carbon atoms. Preferably, R^0 , R^{00} and R^{000} are at each occurrence independently of each other selected from the group consisting of H, F, alkyl, fluorinated alkyl, alkenyl, alkynyl, phenyl and fluorinated phenyl. More preferably, R^0 , R^{00} and R^{000} are at each occurrence independently of each other selected from the group consisting of H, F, alkyl, fluorinated, preferably perfluorinated, alkyl, phenyl and fluorinated, preferably perfluorinated, phenyl.

It is noted that for example alkyl suitable as R^0 , R^{00} and R^{000} also includes perfluorinated alkyl, i.e. alkyl wherein all of the hydrogen are replaced by fluorine.

Examples of suitable alkyls, also in respect to fluorinated alkyl, may be selected from the group consisting of methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl (or "t-butyl"), pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl (-C₂₀H₄₁).

X^0 is halogen. Preferably X^0 is selected from the group consisting of F, Cl and Br.

A hydrocarbyl group comprising a chain of 3 or more carbon atoms and heteroatoms combined may be straight chain, branched and/or cyclic, including spiro and/or fused rings.

- Hydrocarbyl suitable as R^S , R^0 , R^{00} and/or R^{000} may be saturated or unsaturated. Examples of saturated hydrocarbyl include alkyl. Examples of unsaturated hydrocarbyl may be selected from the group consisting of alkenyl (including acyclic and cyclic alkenyl), alkynyl, allyl, alkyldienyl, polyenyl, aryl and heteroaryl.
- 5 Preferred hydrocarbyl suitable as R^S , R^0 , R^{00} and/or R^{000} include hydrocarbyl comprising one or more heteroatoms and may for example be selected from the group consisting of alkoxy, alkylcarbonyl, alkoxy carbonyl, alkylcarbonyloxy and alkoxy carbonyloxy, alkylaryloxy, arylcarbonyl, aryloxy carbonyl, arylcarbonyloxy and
- 10 aryloxy carbonyloxy.
- Preferred examples of aryl and heteroaryl comprise mono-, bi- or tricyclic aromatic or heteroaromatic groups that may also comprise condensed rings.
- 15 Especially preferred aryl and heteroaryl groups may be selected from the group consisting of phenyl, phenyl wherein one or more CH groups are replaced by N, naphthalene, fluorene, thiophene, pyrrole, preferably N-pyrrole, furan, pyridine, preferably 2- or 3-pyridine, pyrimidine, pyridazine, pyrazine, triazole, tetrazole, pyrazole, imidazole, isothiazole, thiazole, thiadiazole, isoxazole, oxazole,
- 20 oxadiazole, thiophene, preferably 2-thiophene, selenophene, preferably 2-selenophene, thieno[3,2-b]thiophene, thieno[2,3-b]thiophene, dithienothiophene, furo[3,2-b]furan, furo[2,3-b]furan, seleno[3,2-b]selenophene, seleno[2,3-b]selenophene, thieno[3,2-b]selenophene, thieno[3,2-b]furan, indole, isoindole, benzo[b]furan, benzo[b]thiophene, benzo[1,2-b;4,5-b']dithiophene, benzo[2,1-b;3,4-b']dithiophene, quinole, 2-methylquinole, isoquinole, quinoxaline, quinazoline, benzotriazole, benzimidazole, benzothiazole, benzisothiazole, benzisoxazole, benzoxadiazole, benzoxazole and benzothiadiazole.
- 25 Preferred examples of an alkoxy group, i.e. a corresponding alkyl group wherein the terminal CH_2 group is replaced by -O-, can be straight-chain or branched, preferably straight-chain (or linear). Suitable examples of such alkoxy group may be selected from the group consisting of methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, octoxy, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy, tetradecoxy, pentadecoxy, hexadecoxy, heptadecoxy and octadecoxy.
- 30

Preferred examples of alkenyl, i.e. a corresponding alkyl wherein two adjacent CH₂ groups are replaced by -CH=CH- can be straight-chain or branched. It is preferably straight-chain. Said alkenyl preferably has 2 to 10 carbon atoms. Preferred examples of alkenyl may be selected from the group consisting of vinyl, prop-1-enyl, 5 or prop-2-enyl, but-1-enyl, but-2-enyl or but-3-enyl, pent-1-enyl, pent-2-enyl, pent-3-enyl or pent-4-enyl, hex-1-enyl, hex-2-enyl, hex-3-enyl, hex-4-enyl or hex-5-enyl, hept-1-enyl, hept-2-enyl, hept-3-enyl, hept-4-enyl, hept-5-enyl or hept-6-enyl, oct-1-enyl, oct-2-enyl, oct-3-enyl, oct-4-enyl, oct-5-enyl, oct-6-enyl or oct-7-enyl, non-1-enyl, non-2-enyl, non-3-enyl, non-4-enyl, non-5-enyl, non-6-enyl, non-7- 10 enyl, non-8-enyl, dec-1-enyl, dec-2-enyl, dec-3-enyl, dec-4-enyl, dec-5-enyl, dec-6-enyl, dec-7-enyl, dec-8-enyl and dec-9-enyl.

Especially preferred alkenyl groups are C₂-C₇-1E-alkenyl, C₄-C₇-3E-alkenyl, C₅-C₇-4-alkenyl, C₆-C₇-5-alkenyl and C₇-6-alkenyl, in particular C₂-C₇-1E-alkenyl, C₄-C₇-3E- 15 alkenyl and C₅-C₇-4-alkenyl. Examples of particularly preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl, 6-heptenyl and the like. Alkenyl groups having up to 5 C atoms are generally preferred.

20 Preferred examples of oxaalkyl, i.e. a corresponding alkyl wherein one non-terminal CH₂ group is replaced by -O-, can be straight-chain or branched, preferably straight chain. Specific examples of oxaalkyl may be selected from the group consisting of 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2- 25 methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl and 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl.

Preferred examples of carbonyloxy and oxycarbonyl, i.e. a corresponding alkyl 30 wherein one CH₂ group is replaced by -O- and one of the thereto adjacent CH₂ groups is replaced by -C(O)-. may be selected from the group consisting of acetyloxy, propionyloxy, butyryloxy, pentanoyloxy, hexanoyloxy, acetyloxymethyl, propionyloxymethyl, butyryloxymethyl, pentanoyloxymethyl, 2-acetyloxyethyl, 2-propionyloxyethyl, 2-butyryloxyethyl, 3-acetyloxypropyl, 3-propionyloxypropyl, 35 4-acetyloxybutyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl,

5 butoxycarbonyl, pentoxycarbonyl, methoxycarbonylmethyl, ethoxy-carbonylmethyl, propoxycarbonylmethyl, butoxycarbonylmethyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxycarbonyl)ethyl, 2-(propoxycarbonyl)ethyl, 3-(methoxycarbonyl)propyl, 3-(ethoxycarbonyl)propyl, and 4-(methoxycarbonyl)-butyl.

10 Preferred examples of thioalkyl, i.e where one CH₂ group is replaced by -S-, may be straight-chain or branched, preferably straight-chain. Suitable examples may be selected from the group consisting of thiomethyl (-SCH₃), 1-thioethyl (-SCH₂CH₃), 1-thiopropyl (-SCH₂CH₂CH₃), 1-(thiobutyl), 1-(thiopentyl), 1-(thiohexyl), 1-(thioheptyl), 1-(thiooctyl), 1-(thiononyl), 1-(thiodecyl), 1-(thioundecyl) and 1-(thiododecyl).

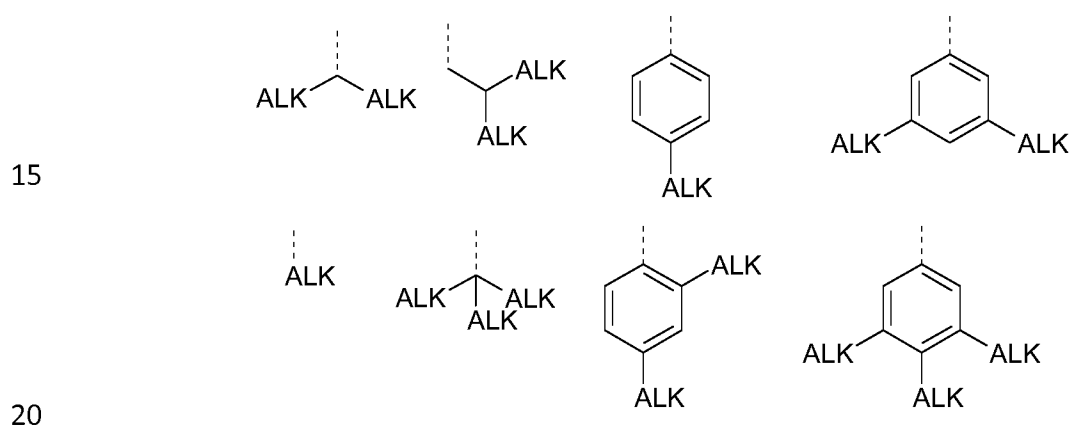
15 A fluoroalkyl group is preferably perfluoroalkyl C_iF_{2i+1}, wherein i is an integer from 1 to 15, in particular CF₃, C₂F₅, C₃F₇, C₄F₉, C₅F₁₁, C₆F₁₃, C₇F₁₅ or C₈F₁₇, very preferably C₆F₁₃, or partially fluorinated alkyl, in particular 1,1-difluoroalkyl, all of which are straight-chain or branched.

20 Alkyl, alkoxy, alkenyl, oxaalkyl, thioalkyl, carbonyl and carbonyloxy groups can be achiral or chiral groups. Particularly preferred chiral groups are 2-butyl (=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, 2-butyloctyl, 2-hexyldecyl, 2-octyldodecyl, 7-decylnonadecyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethyl-hexoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methyl-pentyl, 4-methylhexyl, 2-butyloctyl, 2-hexyldecyl, 2-octyldodecyl, 7-decylnonadecyl, 3,8-dimethyloctyl, 2-hexyl, 2-octyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-meth-oxyoctoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxy-carbonyl, 2-methylbutyryloxy, 3-methylvaleroyloxy, 4-methylhexanoyloxy, 2-chloropropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methyl-valeryl-oxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxa-hexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypropyl-2-oxy, 1-butoxypropyl-2-oxy, 2-fluorooctyloxy, 2-fluorodecyloxy, 1,1,1-trifluoro-2-octyloxy, 1,1,1-trifluoro-2-octyl, 2-fluoromethyloctyloxy for example. Most preferred is 2-ethylhexyl.

35

Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), tert. butyl, isopropoxy, 2-methyl-propoxy and 3-methylbutoxy.

- 5 In a preferred embodiment, the organyl groups are independently of each other selected from primary, secondary or tertiary alkyl or alkoxy with 1 to 30 C atoms, wherein one or more H atoms are optionally replaced by F, or aryl, aryloxy, heteroaryl or heteroaryloxy that is optionally alkylated or alkoxyated and has 4 to 30 ring atoms. Very preferred groups of this type are selected from the group
10 consisting of the following formulae



- wherein "ALK" denotes optionally fluorinated, preferably linear, alkyl or alkoxy with 1 to 20, preferably 1 to 12 C-atoms, in case of tertiary groups very preferably 1 to 9 C atoms, and the dashed line denotes the link to the ring to which these groups are attached. Especially preferred among these groups are those wherein all ALK subgroups are identical.
- 25

- Further, in some preferred embodiments in accordance with the present invention, the organic semiconducting materials are polymers or copolymers that encompass one or more repeating units, e.g. M in formula (I), selected from thiophene-2,5-diyl, 3-substituted thiophene-2,5-diyl, optionally substituted thieno[2,3-b]thiophene-2,5-diyl, optionally substituted thieno[3,2-b]thiophene-2,5-diyl, selenophene-2,5-diyl, or 3-substituted selenophene-2,5-diyl.
- 30

- Preferred examples of organic semiconducting materials comprise one or more monomeric units selected from the group consisting of formulae (A1) to (A83) and
- 35

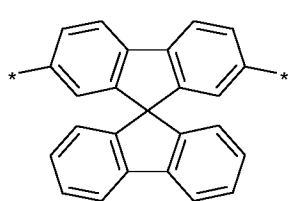
one or more monomeric units selected from the group consisting of formulae (D1) to (D142).

- Further preferred examples of organic semiconductor materials that can be used in this invention include compounds, oligomers and derivatives of compounds selected from the group consisting of conjugated hydrocarbon polymers such as polyacene, polyphenylene, poly(phenylene vinylene), polyfluorene including oligomers of those conjugated hydrocarbon polymers; condensed aromatic hydrocarbons, such as, tetracene, chrysene, pentacene, pyrene, perylene, coronene, or soluble, substituted derivatives of these; oligomeric para substituted phenylenes such as p-quaterphenyl (p-4P), p-quinquephenyl (p-5P), p-sexiphenyl (p-6P), or soluble substituted derivatives of these; conjugated heterocyclic polymers such as poly(3-substituted thiophene), poly(3,4-bisubstituted thiophene), optionally substituted polythieno[2,3-b]thiophene, optionally substituted polythieno[3,2-b]thiophene, poly(3-substituted selenophene), polybenzothiophene, polyisothianaphthene, poly(*N*-substituted pyrrole), poly(3-substituted pyrrole), poly(3,4-bisubstituted pyrrole), polyfuran, polypyridine, poly-1,3,4-oxadiazoles, polyisothianaphthene, poly(*N*-substituted aniline), poly(2-substituted aniline), poly(3-substituted aniline), poly(2,3-bisubstituted aniline), polyazulene, polypyrene; pyrazoline compounds; polyselenophene; polybenzofuran; polyindole; polypyridazine; benzidine compounds; stilbene compounds; triazines; substituted metallo- or metal-free porphines, phthalocyanines, fluorophthalocyanines, naphthalocyanines or fluoronaphthalocyanines; C₆₀ and C₇₀ fullerenes; *N,N'*-dialkyl, substituted dialkyl, diaryl or substituted diaryl-1,4,5,8-naphthalenetetracarboxylic diimide and fluoro derivatives; *N,N'*-dialkyl, substituted dialkyl, diaryl or substituted diaryl 3,4,9,10-perylenetetracarboxylicdiimide; bathophenanthroline; diphenokinones; 1,3,4-oxadiazoles; 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane; α,α' -bis(dithieno[3,2-b^{2'},3'-d]thiophene); 2,8-dialkyl, substituted dialkyl, diaryl or substituted diaryl anthradithiophene; 2,2'-bisbenzo[1,2-b:4,5-b']dithiophene. Where a liquid deposition technique of the OSC is desired, compounds from the above list and derivatives thereof are limited to those that are soluble in an appropriate solvent or mixture of appropriate solvents.
- Other preferred examples of organic semiconducting materials may be selected from the group consisting of substituted oligoacenes, such as pentacene, tetracene

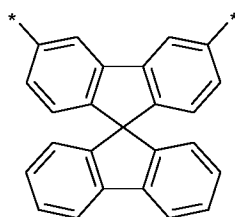
or anthracene, or heterocyclic derivatives thereof. Bis(trialkylsilylethynyl) oligoacenes or bis(trialkylsilylethynyl) heteroacenes, as disclosed for example in US 6,690,029 or WO 2005/055248 A1 or US 7,385,221, are also useful.

5 Further preferred organic semiconducting materials are selected from the group consisting of small molecules or monomers of the tetra-heteroaryl indacenodithiophene-based structural unit as disclosed in WO 2016/015804 A1, and polymers or copolymers comprising one or more repeating units thereof.

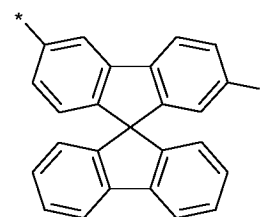
10 Also preferred organic semiconducting materials may be selected from the group of small molecules or monomers or polymers comprising a 2,7-(9,9')spirobifluorene moiety, optionally substituted and preferably substituted with amino groups. Such spirobifluorenes are, for example, disclosed in WO 97/39045. Examples of spirobifluorenes suitable for use as monomeric unit M of formula (I) may be
 15 selected from the group consisting of formulae (V-1) to (V-7)



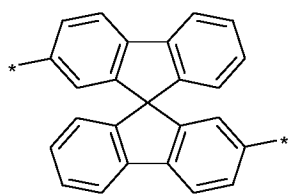
(V-1)



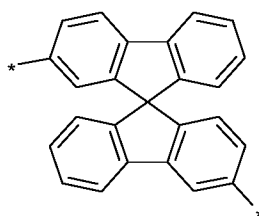
(V-2)



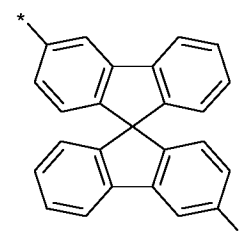
(V-3)



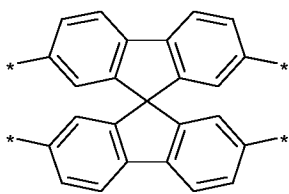
(V-4)



(V-5)



(V-6)

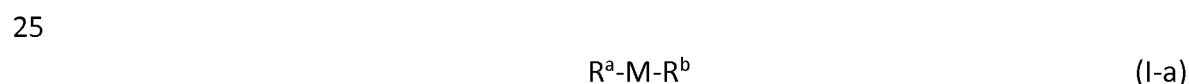


(V-7)

wherein each of the hydrogen atoms may independently of any other be replaced by a substituent as defined herein in respect to R^{101} and each asterisk "*" independently may denote a bond to a neighboring moiety (for example in a polymer) or may denote a bond to a group as defined above for R^{101} (for example in a compound of formula (I-a) or (I-b)). In respect to formulae (V-1) to (V-7) preferred substituents, including the ones for "*", may be selected from the group consisting of alkyl having from 1 to 20 carbon atoms; aryl having from 6 to 20 carbon atoms, said aryl being optionally substituted with alkyl or alkoxy having from 1 to 20, preferably 1 to 10 carbon atoms; and $NR^{110}R^{111}$ with R^{110} and R^{111} being independently of each other selected from the group consisting of alkyl having from 1 to 20 carbon atoms, aryl having from 6 to 20 carbon atoms, said aryl being optionally substituted with alkyl or alkoxy having from 1 to 20, preferably 1 to 10 carbon atoms, most preferably R^{110} and R^{111} being independently of each other selected from methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, methoxy, ethoxy, n-propoxy, iso-propoxy n-butoxy, iso-butoxy, tert-butoxy and pentoxy.

Particularly preferred examples of organic semiconducting materials are OSC-1, OSC-2, OSC-3 and OSC-4, the formulae of which are given in the examples.

In one aspect the present semiconducting material may, for example, be a small molecule, i.e. a compound comprising one (i.e. $m = 1$) structural unit of formula (I) and two inert chemical groups R^a and R^b . Such a small molecule may for example be represented by formula (I-a)



wherein M is as defined herein and R^a and R^b are inert chemical groups. Such inert chemical groups R^a and R^b may independently of each other be selected from the group consisting of hydrogen, fluorine, alkyl having from 1 to 10 carbon atoms, alkyl having from 1 to 10 carbon atoms wherein one or more, for example all, hydrogen has been replaced with fluorine, aromatic ring systems of from 5 to 30 carbon atoms and aromatic ring systems of from 5 to 30 carbon atoms wherein one or more hydrogen atom may independently of any other be replaced by fluorine or alkyl having from 1 to 10 carbon atoms.

In a further aspect the present semiconducting material may be an oligomer or a polymer as defined above. Such oligomers and polymers may be synthesized according to or in analogy to methods that are known to the skilled person and are described in the literature from monomers as described in the following.

5

Monomers that are suitable for the synthesis of the present oligomers and polymers may be selected from compounds comprising a structural unit of formula (I) and at least one reactive chemical group R^c which may be selected from the group consisting of Cl, Br, I, O-tosylate, O-triflate, O-mesylate, O-nonaflate, -SiMe₂F, -SiMeF₂, -O-SO₂Z¹, -B(OZ²)₂, -CZ³=C(Z³)₂, -C≡CH, -C≡CSi(Z¹)₃, -ZnX⁰⁰ and -Sn(Z⁴)₃,
 10 preferably -B(OZ²)₂ or -Sn(Z⁴)₃, wherein X⁰⁰ is as defined herein, and Z¹, Z², Z³ and Z⁴ are selected from the group consisting of alkyl and aryl, preferably alkyl having from 1 to 10 carbon atoms, each being optionally substituted with R⁰ as defined herein, and two groups Z² may also together form a cyclic group. Alternatively such a monomer may comprise two reactive chemical groups and is, for example,
 15 represented by formula (I-b)



20 wherein M is as defined herein and R^c and R^d are reactive chemical groups as defined above in respect to R^c. Such monomers may generally be prepared according to methods well known to the person skilled in the art.

X⁰⁰ is halogen. Preferably X⁰⁰ is selected from the group consisting of F, Cl and Br.
 25 Most preferably X⁰⁰ is Br.

Preferred aryl-aryl coupling and polymerisation methods used in the processes described herein may, for example, be one or more of Yamamoto coupling, Kumada coupling, Negishi coupling, Suzuki coupling, Stille coupling, Sonogashira coupling, Heck coupling, C-H activation coupling, Ullmann coupling and Buchwald coupling.
 30 Especially preferred are Suzuki coupling, Negishi coupling, Stille coupling and Yamamoto coupling. Suzuki coupling is described for example in WO 00/53656 A1. Negishi coupling is described for example in *J. Chem. Soc., Chem. Commun.*, **1977**, 683-684. Yamamoto coupling is described for example in T. Yamamoto *et al.*, *Prog. Polym. Sci.*, **1993**, 17, 1153-1205, or WO 2004/022626 A1, and Stille coupling is described for example in Z. Bao *et al.*, *J. Am. Chem. Soc.*, 1995, 117, 12426-12435.
 35

For example, when using Yamamoto coupling, monomers having two reactive halide groups are preferably used. When using Suzuki coupling, compounds of formula (I-b) having two reactive boronic acid or boronic acid ester groups or two reactive halide groups are preferably used. When using Stille coupling, monomers having two reactive stannane groups or two reactive halide groups are preferably used. When using Negishi coupling, monomers having two reactive organozinc groups or two reactive halide groups are preferably used.

Preferred catalysts, especially for Suzuki, Negishi or Stille coupling, are selected from Pd(0) complexes or Pd(II) salts. Preferred Pd(0) complexes are those bearing at least one phosphine ligand, for example Pd(Ph₃P)₄. Another preferred phosphine ligand is tris(*ortho*-tolyl)phosphine, for example Pd(o-Tol₃P)₄. Preferred Pd(II) salts include palladium acetate, for example Pd(OAc)₂. Alternatively the Pd(0) complex can be prepared by mixing a Pd(0) dibenzylideneacetone complex, for example tris(dibenzylideneacetone)dipalladium(0), bis(dibenzylideneacetone)-palladium(0), or Pd(II) salts *e.g.* palladium acetate, with a phosphine ligand, for example triphenylphosphine, tris(*ortho*-tolyl)phosphine or tri(*tert*-butyl)phosphine. Suzuki polymerisation is performed in the presence of a base, for example sodium carbonate, potassium carbonate, lithium hydroxide, potassium phosphate or an organic base such as tetraethylammonium carbonate or tetraethylammonium hydroxide. Yamamoto polymerisation employs a Ni(0) complex, for example bis(1,5-cyclooctadienyl)nickel(0).

Suzuki and Stille polymerisation may be used to prepare homopolymers as well as statistical, alternating and block random copolymers. Statistical or block copolymers can be prepared for example from the above monomers of formula (I-b), wherein one of the reactive groups is halogen and the other reactive group is a boronic acid, boronic acid derivative group or and alkylstannane. The synthesis of statistical, alternating and block copolymers is described in detail for example in WO 03/048225 A2 or WO 2005/014688 A2.

As alternatives to halogens as described above, leaving groups of formula -O-SO₂Z¹ can be used wherein Z¹ is as described above. Particular examples of such leaving groups are tosylate, mesylate and triflate.

DOPANT

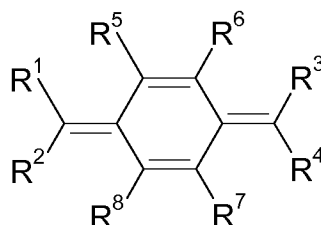
Preferably the semiconducting layer further comprises one or more dopants. Said dopant is preferably an electron donor or an electron acceptor. Said dopant is preferably characterized by an ionization energy of at least 7.0 eV, preferably of at least 7.1 eV, more preferably at least 7.2 eV, even more preferably of at least 7.3 eV, still even more preferably of at least 7.4 eV and most preferably of at least 7.5 eV. Said dopant is preferably characterized by an ionization energy of at most 12.0 eV, more preferably of at most 11.5 eV, even more preferably of at most 11.0 eV, still even more preferably of at most 10.5 eV and most preferably of at most 10.0 eV.

Preferably the energy level E (in eV) of the lowest unoccupied molecular orbital (LUMO) of the dopant is lower than the energy level E (in eV) of the highest occupied molecular orbital of the semiconducting material plus 0.5 eV, i.e.

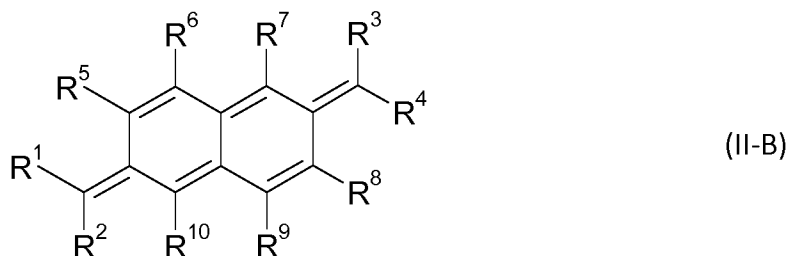
$$E_{\text{LUMO, dopant}} < E_{\text{HOMO, semiconducting material}} + 0.5 \text{ eV}$$

Preferably, the one or more dopants are p-type dopants. Preferably such p-type dopants are selected from the group consisting of organic dopants, transition-metal oxides and organometallic compounds. Such dopants are generally well known to the skilled person and can either be purchased from commercial sources or, if need be, synthesized according to published syntheses. An overview of suitable dopants is, for example, given by S.J. Yoo and J.J. Kim in *Macromolecular Rapid Communications* **2015**, 36, 984-1000.

Preferred examples of suitable organic dopants may be selected from the group consisting of fluorinated fullerenes and of the following formulae (II-A) or (II-B)



(II-A)



5

10

15

wherein R^1 to R^{10} are independently of each other selected from the group consisting of hydrogen, fluorine, chlorine, bromine, iodine, NO_2 , NH_2 , COOH , and CN , with the provision that for formula (II-A) at least two of R^1 to R^8 and for formula (II-B) at least two of R^1 to R^{10} are different from hydrogen. Alternatively, for formula (II-A) one of R^5 to R^8 and for formula (II-B) one of R^1 to R^{10} may be -Sp-Pol as defined below. In certain preferred embodiments, for formula (II-A) at least two of R^5 to R^8 and for formula (II-B) at least two of R^5 to R^{10} are selected from the group consisting of hydrogen, fluorine, chlorine, NO_2 , COOH , and CN . Particularly suited substituents R^1 to R^{10} are selected from the group consisting of fluorine, NO_2 and CN ; especially fluorine and CN .

20

Examples of alkyl having from 1 to 10 carbon atoms are methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl, of which methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl and tert-butyl are preferred.

25

Where, in respect to formula (II-A), R^1 to R^4 are CN , and R^5 to R^8 are hydrogen, the compound may also be referred to as tetracyano-quinodimethane (TCNQ). Preferred examples of the compounds of formula (II-A) are those, wherein at least two, three or four of R^1 to R^4 and at least two, three or four of R^5 to R^8 are different from hydrogen.

30

Particularly well suited exemplary compounds of formula (II-A) may be selected from the following compounds (II-1) to (II-8)

35

5

10

Compound	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷	R ⁸
(II-A-1)	CN	CN	CN	CN	F	F	F	F
(II-A-2)	CN	CN	CN	CN	F	H	F	H
(II-A-3)	CN	CN	CN	CN	F	H	H	F
(II-A-4)	CN	CN	CN	CN	F	F	H	H
(II-A-5)	NO ₂	NO ₂	NO ₂	NO ₂	F	F	F	F
(II-A-6)	NO ₂	NO ₂	NO ₂	NO ₂	F	H	F	H
(II-A-7)	NO ₂	NO ₂	NO ₂	NO ₂	F	H	H	F
(II-A-8)	NO ₂	NO ₂	NO ₂	NO ₂	F	F	H	H

of which compounds (II-A-1) and (II-A-7) are preferred and (II-A-1) is most preferred.

15

For the purposes of the present application, compound (II-A-1) may also be referred to as F4TCNQ, and compound (II-A-2) as F2TCNQ.

In a preferred example of compound (II-B) R¹ to R⁴ are CN and R⁵ to R¹⁰ are F; such compound is referred to as F₆-TCNNQ.

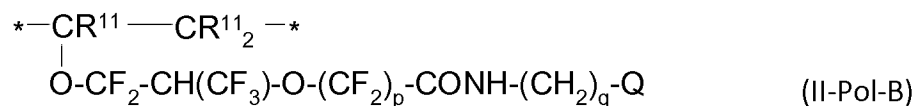
20

Compounds (II-A) and (II-B) may also be provided in the form of a polymer comprising a monomeric unit with a group -Pol-Sp-Q with Q being of formula (II-A) or of formula (II-B) above, wherein in respect to formula (II-A) one of R⁵ to R⁸ and in respect to formula (II-B) one of R⁵ to R¹⁰ is -Pol-Sp. Exemplary groups -Pol-Sp-Q may be selected from the group consisting of the following (II-Pol-A), (II-Pol-B), (II-Pol-C)

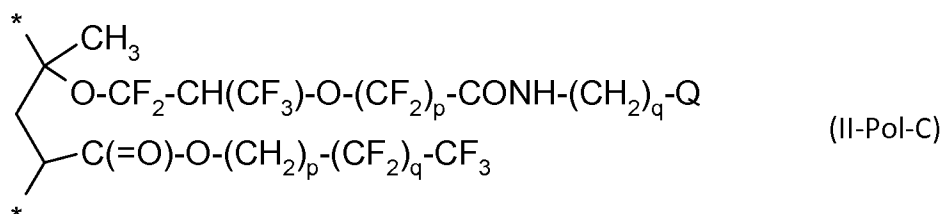
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and blends thereof, with R^{11} being hydrogen or fluorine, preferably fluorine; each p and q being independently of the other a number between 0 and 10, preferably between 0 and 5, most preferably 1 or 2; "*" indicating the bonds to other monomeric units of the polymer; and Q being a group of general formula (II).

In formula (II-Pol-B) q is preferably 2.

15

In formula (II-Pol-C) q is preferably 2 and p is preferably 7.

20

An exemplary compound of formula (II-Pol-B) may for example be produced according to WO 2009/138010 from compound (II-A) or (II-B) or a blend of these, wherein one of R^5 to R^8 is substituted with $-(\text{CH}_2)_2-\text{NH}_2$, and monomers on basis of (II-Pol-B), all of which are commercially available. An exemplary compound of formula (II-Pol-C) may for example be synthesized relying on Journal of Applied Polymer Science 114 (2009) 2476, and compound (II-A) or compound (II-B) or a blend of these, wherein one of R^5 to R^8 is substituted with $(\text{CH}_2)_2-\text{COOH}$, and which may be synthesized according to Journal of Organic Chemistry 48 (1948) 3852.

25

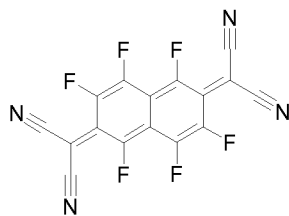
Examples of suitable fluorinated fullerenes may be fluorinated C_{60} -fullerene or fluorinated C_{70} -fullerene, of which $\text{C}_{60}\text{F}_{36}$ is preferred.

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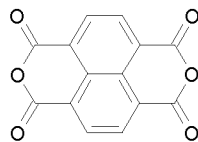
Other preferred examples of suitable organic dopants may be selected from the group consisting of azaindenofluorenediones, azaphenalenenes, and azatriphenylenes.

As particularly suitable specific examples of organic dopants mention may be made of the following compounds (II-C-1) to (II-C-13)

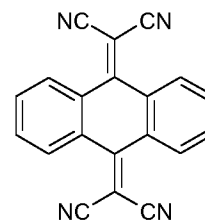
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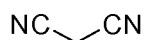
(II-C-1)



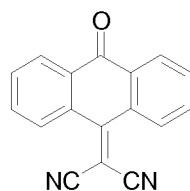
(II-C-2)



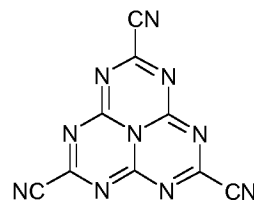
(II-C-3)



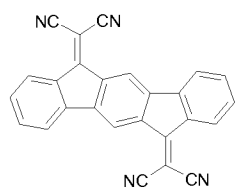
(II-C-4)



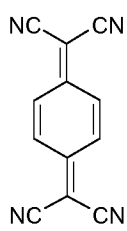
(II-C-5)



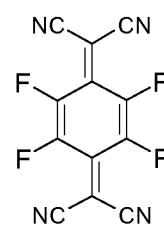
(II-C-6)



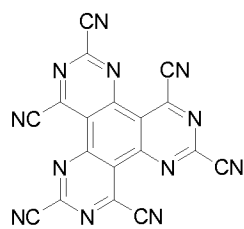
(II-C-7)



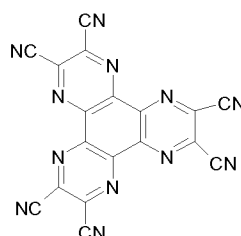
(II-C-8)



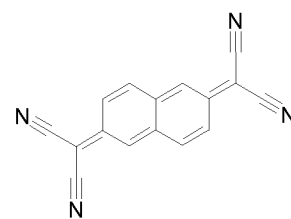
(II-C-9)



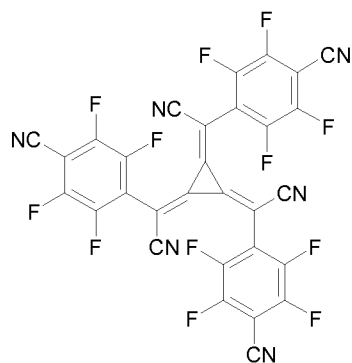
(II-C-10)



(II-C-11)



(II-C-12)



(II-C-13)

Preferred examples of suitable dopants may also be selected from the group of transitions-metal oxides wherein the transition-metal is preferably selected from the group consisting of tungsten, vanadium, molybdenum, chromium and rhenium.

5 Specific examples of suitable transition-metal oxides may be selected from the group consisting of WO₃, V₂O₅, MoO₃, CrO₃ and ReO₃.

Preferred examples of suitable dopants may also be selected from metal halides. A particularly suitable example of such a metal halide is WCl₆. It has been reported by

10 N. Connelly and W. Geiger in Chemical Review **96**, 877 (1996) that the reduction potential of WCl₆ is about 1.1V and this value is transferred to E_{LUMO} -6.2eV using an equation by C. Cardona et al. in Advanced Materials **23**, 2367 (2011),

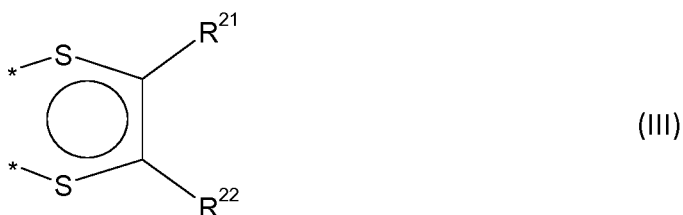
$$E_{LUMO} = -(E_{red \text{ vs } Fc^+/Fc} + 5.1) \text{ (eV)}$$

15 The low value of E_{LUMO} enables one to use semiconducting materials with low HOMO levels and thus use electrode materials with low Fermi levels.

Preferred examples of suitable dopants may also be selected from the group of transition metal complexes of Cu, Co, Ni, Pd and Pt with ligands comprising at least

20 one oxygen atom bound or coordinated to the transition metal.

Preferred examples of suitable organometallic compounds comprise a dithiolene moiety of formula (III)



coordinated to one or two transition metals at the sites marked with an asterisk “*”, with R²¹ and R²² as defined herein. If coordinated to two transition metals the dithiolene moiety may be bridging the two transition metals. Such bridging

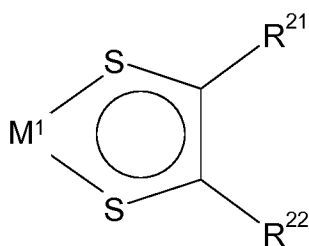
35 dithiolene moiety may, for the purposes of the present application, be denoted “μ²-(S-(R²¹)C=C(R²²)-S)”.

5 R^{21} and R^{22} may at each occurrence independently be selected from the group consisting of halogen (preferably fluorine); alkyl having from 1 to 20, preferably from 1 to 10, even more preferably from 1 to 5 carbon atoms; alkyl having from 1 to 20, preferably from 1 to 10, more preferably from 1 to 5 carbon atoms, wherein one or more, preferably all hydrogen atoms have been replaced by fluorine; phenyl wherein one, two or three carbon atoms have been replaced by nitrogen and optionally one or more hydrogen atoms have been replaced by fluorine; and phenyl wherein one or more, preferably all hydrogen atoms have been replaced by fluorine and optionally wherein one, two or three carbon atoms have been replaced by nitrogen. Preferably R^{21} and R^{22} may at each occurrence independently be selected from the group consisting of halogen (preferably fluorine) and alkyl having from 1 to 20, preferably from 1 to 10, even more preferably from 1 to 5 carbon atoms; alkyl having from 1 to 20, preferably from 1 to 10, more preferably from 1 to 5 carbon atoms, wherein one or more, preferably all hydrogen atoms have been replaced by fluorine. Most preferably, R^{21} and R^{22} are independently selected from fluorine and CF_3 .

20 R^{21} and R^{22} may at each occurrence be the same or different. It is, however, preferred that R^{21} and R^{22} are the same.

Preferably, such organometallic compounds may comprise one or more moieties selected from the group consisting of the following formulae (III-A), (III-B) and (III-C)

25

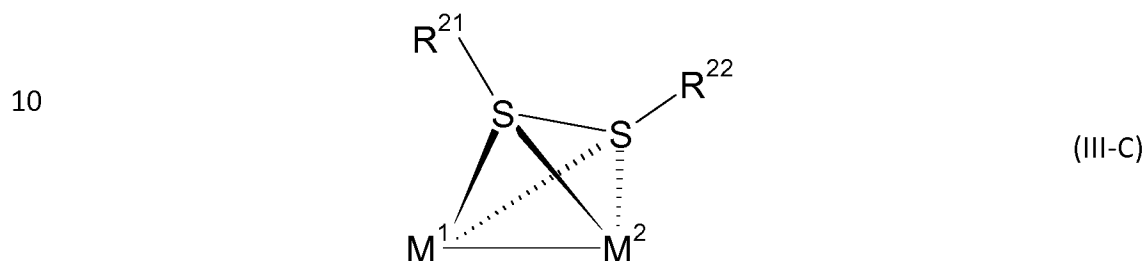
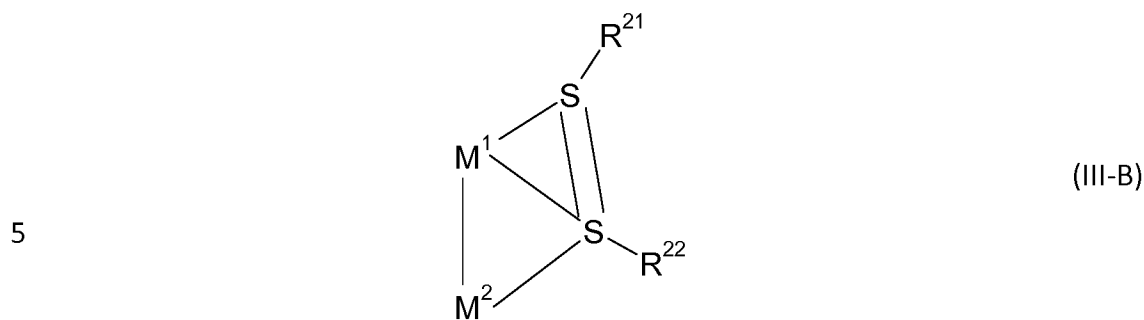


30

(III-A)

35

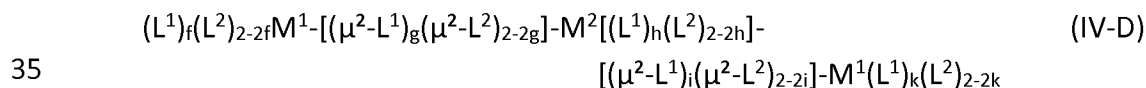
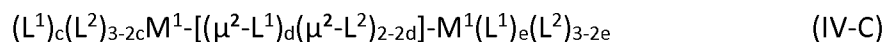
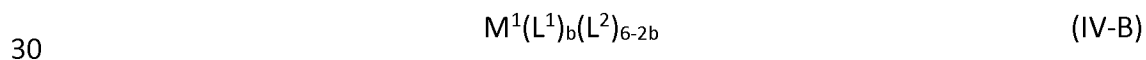
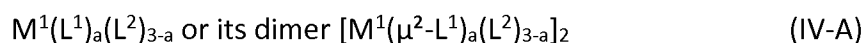
- 51 -



15 with M^1 , M^2 , R^{21} and R^{22} as defined herein. For reasons of clarity it is noted that in formula (III-A) both sulphur atoms are terminal (i.e. coordinated to one transition metal), in formula (III-B) one sulphur atom is terminal and the other is bridging, and in formula (III-C) both sulphur atoms are bridging, i.e. μ^2 .

20 M^1 and M^2 are independently of each other selected from the group of transition metals, preferably selected from the group consisting of chromium, molybdenum, tungsten, cobalt, rhodium and iridium.

25 More preferred examples may be selected from the group consisting of formulae (IV-A), (IV-B), (IV-C) and (IV-D)



wherein M^1 , M^2 , L^1 , L^2 , a, b, c, d, e, f, g, h, i and k are as defined herein.

a is 1 or 2. Preferably a is 1.

5 b is an integer selected from the group consisting of 1, 2 and 3. Preferably b is 3.

c, e, f and k may at each occurrence independently be 0 or 1. Preferably c, e, f and k are 0.

10 d, g and i may at each occurrence independently be 0 or 1. Preferably d, g and i are 1.

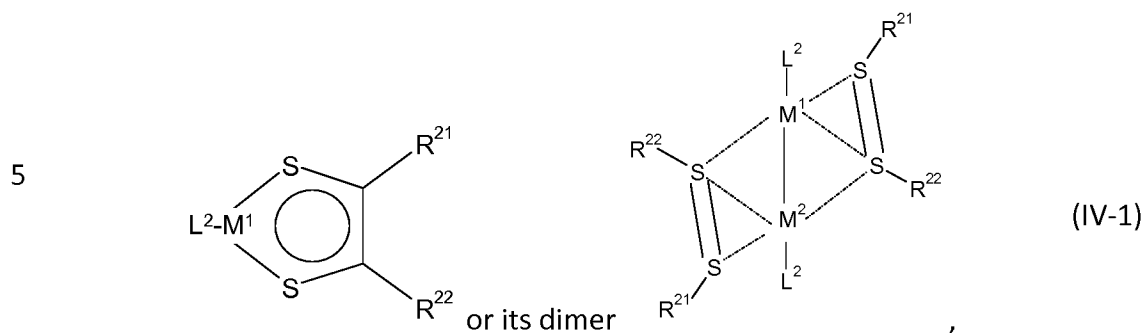
h is 0 or 1. Preferably h is 0.

15 Ligand L^1 is a dithiolene moiety of formula (III).

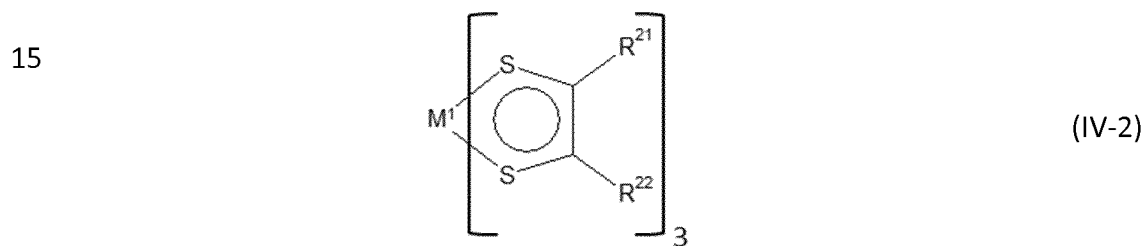
Each of ligands L^2 is independently of the other selected from the group of ligands having a free electron pair capable of donating two electrons to the transition metal M^1 or M^2 or to both (for example, in case of a bridging ligand); or two of ligands L^2 – if present – may together form a ligand capable of donating four electrons to the transition metal M^1 or M^2 or to both (for example, in case of a bridging ligand); or three of ligands L^2 – if present – may together form a ligand capable of donating six electrons to the transition metal M^1 or M^2 or to both (for example, in case of a bridging ligand).

25 Suitable ligands having a free electron pair capable of donating two electrons may independently of each other, for example, be selected from the group consisting of halogenide (i.e. fluoride, chloride, bromide or iodide, with fluoride and chloride being preferred), carbonyl (CO), cyano (CN), nitrosyl (NO), cyclopentadienide (C_5H_5) and cyclopentadienide substituted with alkyl having from 1 to 10 carbon atoms (preferably methyl). Of these carbonyl, cyclopentadienide and cyclopentadienide substituted with methyl (i.e. $C_5(CH_3)_5$, frequently also referred to as "Cp*") are preferred.

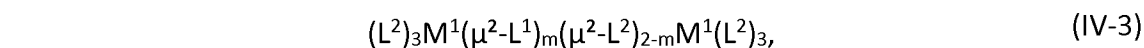
35 Specific examples, from which the organometallic dopants may be selected include the following (IV-1) to (IV-4)



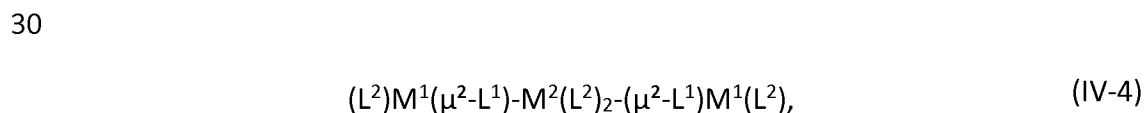
10 wherein M^1 is selected from the group consisting of cobalt, rhodium and iridium, preferably M^1 is rhodium; and L^2 is selected from the group consisting of Cp, Cp* and $(CO)_3$, preferably L^2 is Cp or Cp*;



20 wherein M^1 is selected from the group consisting of chromium, molybdenum and tungsten, and is preferably molybdenum;



wherein M^1 is selected from the group consisting of cobalt, rhodium and iridium; m is 1 or 2, and preferably is 1; L^2_3 may at each occurrence independently be selected from the group consisting of $(CO)_3$, Cp and Cp*, and preferably is $(CO)_3$ or Cp*; μ^2-L^2 is CO; and



35 wherein M^1 is at each occurrence independently selected from the group consisting of cobalt, rhodium and iridium, and preferably is rhodium; M^2 is selected from the group consisting of chromium, molybdenum and tungsten, and preferably is molybdenum;

wherein L^2 is selected from the group consisting of Cp, Cp* and CO;
wherein L^2 coordinated to M^1 is preferably Cp or Cp*, and most preferably is Cp*; wherein L^2 coordinated to M^2 preferably is CO,

5 wherein R^{21} and R^{22} are F or CF_3 , and preferably are CF_3 .

Preferably, the dopant has a substantially uniform distribution in the semiconducting layer.

10 Preferably, the semiconductor layer comprises the dopant in at least 0.01 wt%, more preferably in at least 0.05 wt%, even more preferably in at least 0.1 wt% or 0.2 wt%, still even more preferably in at least 0.3 wt% or 0.4 wt%, and most preferably in at least 0.5 wt%, with wt% given relative to the weight of the semiconducting material.

15 Preferably, the semiconductor layer comprises the dopant in at most 50.0 wt%, more preferably in at most 40.0 wt% or 30.0 wt%, even more preferably in at most 25.0 wt% or 20.0 wt%, still even more preferably in at most 15.0 wt%, and most preferably in at most 10.0 wt%, with wt% given relative to the weight of the
20 semiconducting material.

SUBSTRATE

25 The present capacitor may optionally comprise one or more substrates. Said substrate may, for example, be adjacent to and preferably substantially covering the first electrode layer or the second electrode layer or both, first electrode layer and second electrode layer.

30 The substrate used for the present electronic device is not particularly limited and may be any suitable material, preferably a material that is inert under use conditions. Examples of such materials are glass and polymeric materials. Preferred polymeric material include but are not limited to alkyd resins, allyl esters, benzocyclobutenes, butadiene-styrene, cellulose, cellulose acetate, epoxide, epoxy
35 polymers, ethylene-chlorotrifluoro ethylene copolymers, ethylene-tetra-fluoroethylene copolymers, fiber glass enhanced polymers, fluorocarbon polymers,

hexafluoropropylenevinylidene-fluoride copolymer, high density polyethylene, parylene, polyamide, polyimide, polyaramid, polydimethylsiloxane, polyethersulphone, polyethylene, polyethylenenaphthalate, polyethyleneterephthalate, polyketone, polymethylmethacrylate, polypropylene, polystyrene, polysulphone, polytetrafluoroethylene, polyurethanes, polyvinylchloride, polycycloolefin, silicone rubbers, and silicones. Of these polyethyleneterephthalate, polyimide, polycycloolefin and polyethylenenaphthalate materials are more preferred. Additionally, for some embodiments of the present invention the substrate can be any suitable material, for example a polymeric material, metal or glass material coated with one or more of the above listed materials or coated with one or more metal, such as for example titanium. It will be understood that in forming such a substrate, methods such as extruding, stretching, rubbing or photochemical techniques can be employed to provide a homogeneous surface for device fabrication as well as to provide pre-alignment of an organic semiconductor material in order to enhance carrier mobility therein. Alternatively, the substrate can be a polymeric material, metal or glass coated with one or more of the above polymeric materials.

20 DEVICE PREPARATION

The present capacitors may be prepared by successive deposition of the respective layers using standard methods well known in the art. Hence, the present application provides for a process comprising the steps of:

- 25 (a) depositing a first electrode layer;
- (b) depositing a semiconducting layer onto the first electrode; and
- (c) depositing a second electrode layer onto the semiconducting layer to obtain a capacitor.

30 Optionally, said process may comprise a step (a) of depositing a first electrode layer onto a substrate.

Optionally, said process may comprise the additional step of (d) depositing a substrate onto the second electrode layer.

It is also noted that the present capacitor may, for example, also be formed by a process comprising the steps of

- (a) depositing a first electrode layer onto a first substrate to obtain a first piece;
- (b) depositing a second electrode layer onto a second substrate;
- 5 (c) depositing a semiconducting layer on the first electrode layer to obtain a second piece; and
- (d) combining the first piece obtained in step (a) and the second piece in step (c) so that the semiconducting layer is between the first electrode layer and the second electrode layer

10 to obtain the capacitor.

The electrodes may, for example and depending upon the respective material, be deposited or formed by liquid coating such as for example spray-coating, dip-coating, web-coating or spin-coating, or by vacuum deposition methods including

15 for example physical vapor deposition, chemical vapor deposition, or thermal evaporation methods. Suitable electrode materials and methods for forming the electrodes are generally known to the skilled person and can easily be found in the literature. Organometallic precursors may also be used and deposited from a liquid phase.

20 For the deposition of the semiconducting layer the semiconducting material(s) is(are) mixed with a solvent and optionally, if present, with one or more dopant to form a semiconducting formulation. In case of a dopant being present, the semiconducting material(s) and the dopant(s) will react with each other, thereby

25 forming the respective reaction product(s). Thus, the semiconducting formulation will effectively comprise the reaction product of the semiconducting material(s) and the dopant(s). Throughout this application, such semiconducting formulation will nevertheless be referred to as a semiconducting formulation comprising semiconducting material(s) and dopant(s).

30 Preferred solvents are aliphatic hydrocarbons, chlorinated hydrocarbons, aromatic hydrocarbons, ketones, ethers and mixtures thereof. Additional solvents which can be used include 1,2,4-trimethylbenzene, 1,2,3,4-tetra-methyl benzene, pentylbenzene, mesitylene, cumene, cymene, cyclohexylbenzene, diethylbenzene,

35 tetralin, decalin, 2,6-lutidine, 2-fluoro-m-xylene, 3-fluoro-o-xylene, 2-chlorobenzotrifluoride, N,N-dimethylformamide, 2-chloro-6-fluorotoluene, 2-

fluoroanisole, anisole, 2,3-dimethylpyrazine, 4-fluoroanisole, 3-fluoroanisole, 3-trifluoro-methylanisole, 2-methylanisole, phenetol, 4-methylanisole, 3-methylanisole, 4-fluoro-3-methylanisole, 2-fluorobenzonitrile, 4-fluoroveratrol, 2,6-dimethylanisole, 3-fluorobenzo-nitrile, 2,5-dimethylanisole, 2,4-dimethylanisole, benzonitrile, 3,5-dimethyl-anisole, N,N-dimethylaniline, ethyl benzoate, 1-fluoro-3,5-dimethoxy-benzene, 3-phenoxytoluene, 1-methylnaphthalene, N-methylpyrrolidinone, 3-fluorobenzo-trifluoride, benzotrifluoride, dioxane, trifluoromethoxy-benzene, 4-fluorobenzotrifluoride, 3-fluoropyridine, toluene, 2-fluoro-toluene, 2-fluorobenzotrifluoride, 3-fluorotoluene, 4-isopropylbiphenyl, phenyl ether, pyridine, 4-fluorotoluene, 2,5-difluorotoluene, 1-chloro-2,4-difluorobenzene, 2-fluoropyridine, 3-chlorofluoro-benzene, 1-chloro-2,5-difluorobenzene, 4-chlorofluorobenzene, chloro-benzene, o-dichlorobenzene, 2-chlorofluorobenzene, p-xylene, m-xylene, o-xylene or mixture of o-, m-, and p-isomers. Solvents with relatively low polarity are generally preferred. For inkjet printing solvents and solvent mixtures with high boiling temperatures are preferred. For spin coating alkylated benzenes like xylene and toluene are preferred.

Examples of especially preferred solvents include, without limitation, dichloromethane, trichloromethane (also known as "chloroform"), chlorobenzene, o-dichlorobenzene, tetrahydrofuran, anisole, morpholine, toluene, o-xylene, m-xylene, p-xylene, 1,4-dioxane, acetone, methylethylketone, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, ethyl acetate, n-butyl acetate, N,N-dimethylformamide, dimethylacetamide, dimethylsulfoxide, tetraline, decaline, indane, methyl benzoate, ethyl benzoate, mesitylene and/or mixtures thereof.

The concentration of the semiconducting materials(s) and – if present – dopant(s) is preferably from 0.1 wt% to 20 wt%, more preferably from 0.5 wt% to 10 wt%, with wt% given relative to the total weight of the solution. Optionally, the solution may also comprise one or more binders, such as for example a styrene polymer or copolymer, to adjust the rheological properties, as described for example in WO 2005/055248 A1.

The semiconducting layer may then be formed by any suitable method including vacuum deposition methods such as physical vapor deposition, chemical vapor

deposition, or thermal evaporation methods. However, liquid coating is more desirable than vacuum deposition techniques. Solution deposition methods are especially preferred. The present formulations allow the use of a number of liquid coating techniques. Preferred deposition techniques include, without limitation, dip coating, spin coating, ink jet printing, nozzle printing, letter-press printing, screen printing, gravure printing, doctor blade coating, roller printing, reverse-roller printing, offset lithography printing, dry offset lithography printing, flexographic printing, web printing, spray coating, curtain coating, brush coating, slot dye coating or pad printing.

Ink jet printing or microdispensing is particularly preferred when high resolution layers and devices need to be prepared. Preferably industrial piezoelectric print heads such as but not limited to those supplied by Aprion, Fujifilm Dimatix, Hitachi-Koki, InkJet Technology, On Target Technology, Picojet, Spectra, Trident, Xaar may be used to apply the organic semiconductor layer to a substrate. Additionally semi-industrial heads such as those manufactured by Brother, Epson, Konica, Seiko Instruments Toshiba TEC or single nozzle microdispensers such as those produced by Microdrop and Microfab may be used.

In order to be applied by ink jet printing or microdispensing, the compounds or polymers should be first dissolved in a suitable solvent. Solvents must not have any detrimental effect on the chosen print head. Preferably the solvents should have boiling points $>100^{\circ}\text{C}$, preferably $>140^{\circ}\text{C}$ and more preferably $>150^{\circ}\text{C}$. Without wishing to be bound by theory it is believed that the boiling point helps in reducing operability problems caused by the solution drying out inside the print head. Apart from the solvents mentioned above, suitable solvents include substituted and non-substituted xylene derivatives, di- C_{1-2} -alkyl formamide, substituted and non-substituted anisoles and other phenol-ether derivatives, substituted heterocycles such as substituted pyridines, pyrazines, pyrimidines, pyrrolidinones, substituted and non-substituted *N,N*-di- C_{1-2} -alkylanilines and other fluorinated or chlorinated aromatics.

A preferred solvent for forming the semiconducting layer by ink jet printing comprises a benzene derivative which has a benzene ring substituted by one or more substituents wherein the total number of carbon atoms among the one or more substituents is at least three. For example, the benzene derivative may be

substituted with a propyl group or three methyl groups, in either case there being at least three carbon atoms in total. Such a solvent enables an ink jet fluid to be formed comprising the solvent with the compound or polymer, which reduces or prevents clogging of the jets and separation of the components during spraying.

5 The solvent(s) may include those selected from the following list of examples: dodecylbenzene, 1-methyl-4-tert-butylbenzene, terpineol, limonene, isodurene, terpinolene, cymene, diethylbenzene. The solvent may be a solvent mixture, that is a combination of two or more solvents, each solvent preferably having a boiling point $>100^{\circ}\text{C}$, more preferably $>140^{\circ}\text{C}$. Such solvent(s) also enhance film formation

10 in the layer deposited and reduce defects in the layer.

The ink jet fluid (that is mixture of solvent, binder and semiconducting compound) preferably has a viscosity at 20°C of from 1 mPa·s to 100 mPa·s, more preferably from 1 mPa·s to 50 mPa·s and most preferably of from 1 mPa·s to 30 mPa·s.

15

Examples

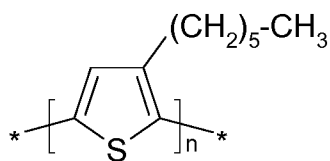
The following examples are intended to illustrate the advantages of the present invention in a non-limiting way.

20

The organic semiconducting materials OSC-1, OSC-2, OSC-3, OSC-4, OSC-5, and OSC-6 were synthesized according to published procedures. F₄TCNQ (purity $> 98\%$) was purchased from Tokyo Chemical Industry Co. Mo(tfd)₃ was purchased from Sigma-Aldrich. WCl₆ was purchased from Sigma-Aldrich. All other materials were purchased from commercial sources such as, for example, Sigma-Aldrich.

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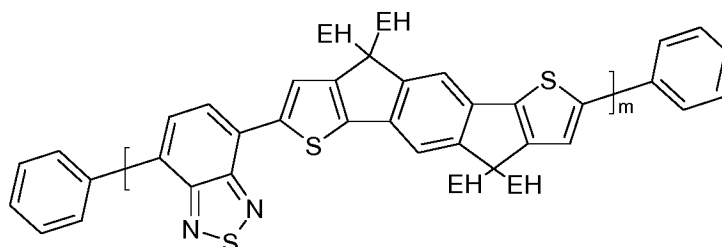
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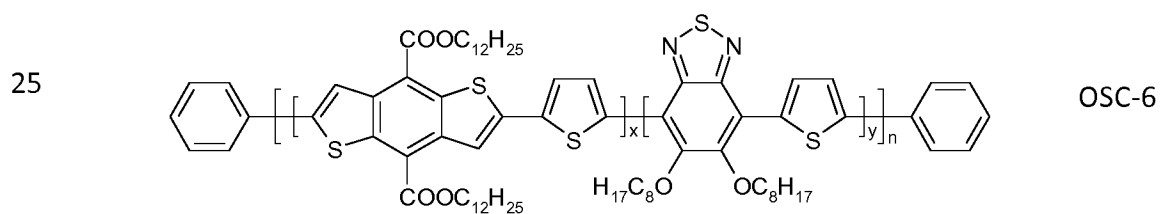
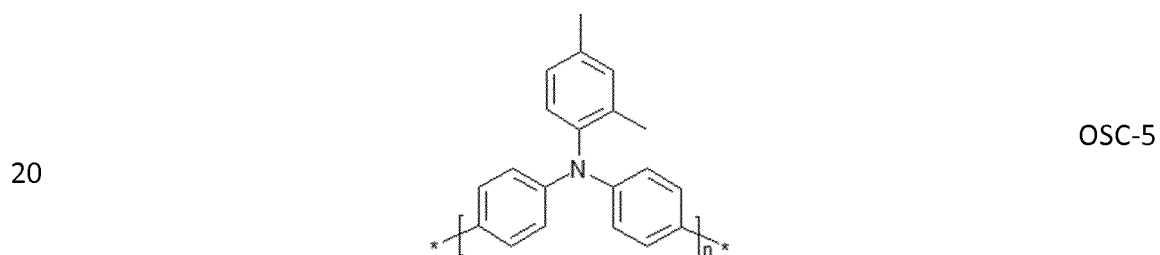
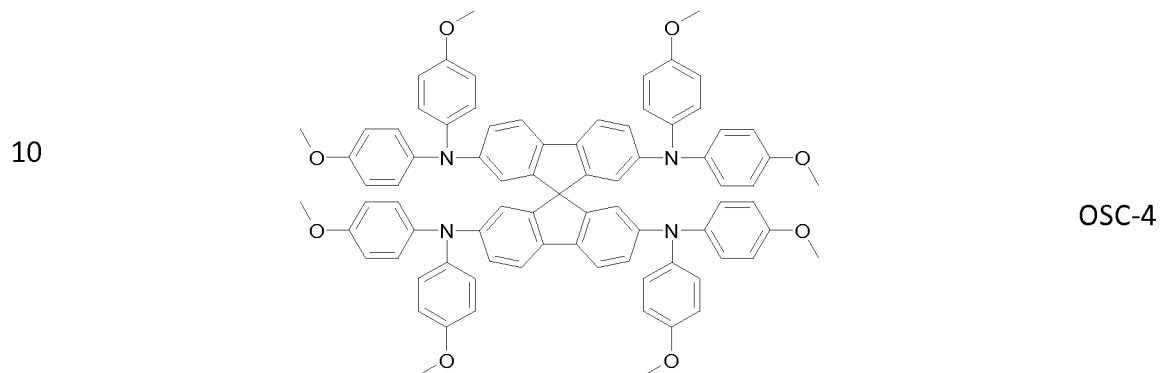
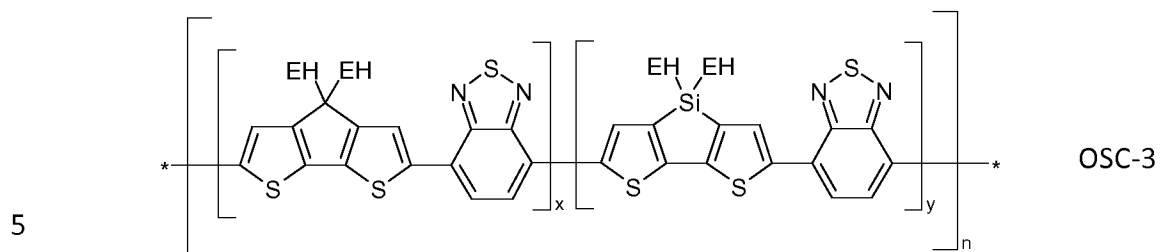
with a regioregularity of 94.7 %

OSC-1

35



OSC-2



30 "EH" is used to denote 2-ethylhexyl, i.e. $-\text{CH}_2-\text{CH}(\text{CH}_2-\text{CH}_3)-(\text{CH}_2)_3-\text{CH}_3$.

Solutions of dopant and of organic semiconducting material in a solvent or a solvent blend were prepared separately by stirring at ca. 80°C until the solids had dissolved completely. After allowing the solutions to cool to room temperature, the solution of dopant and the solution of organic semiconducting material were mixed in order

35

to obtain a solution of the doped organic semiconducting material with respective concentrations as indicated in **Table 1**.

Table 1

5	Reference		Sol-1	Sol-2	Sol-3	Sol-4	Sol-5	Sol-6
	Dopant content ⁽¹⁾	[wt%]	0	0.5	1.0	5	10	5
	Polymer	[mg]	30	30	30	3	3	3
	Dopant	[mg]	0	0.15	0.30	0.15	0.30	0.15
10	Solvent ⁽²⁾	[ml]	0.676	0.676	0.676	0.6	0.6	0.405

⁽¹⁾ Given in wt% relative to the weight of polymer.

⁽²⁾ Chloroform or a 6:1 mixture by volume of chlorobenzene and dichlorobenzene.

Capacitor test cells as schematically shown in **Figure 1** were prepared by depositing a first 50 nm thick layer of aluminum onto a glass substrate by thermal evaporation. Then, a layer of doped organic semiconducting material was applied by spin-coating or solution casting, optionally using a doctor blade, to a thickness between 0.5 μm and 10 μm . Finally a second 50 nm thick layer of aluminum was applied onto the layer of doped organic semiconducting material by thermal evaporation. Layer thicknesses were determined by scanning electron microscopy or by vertical scanning interferometry.

Capacitor performance was evaluated by measuring admittance of the capacitor test cells using a frequency response analyzer Solartron 1260 equipped with a dielectric interface 1296. The measurement was carried out in the frequency range between 1 Hz and 3.2 MHz by applying an alternating current (AC) of 50 mV to the test cell at a temperature of 25°C. Equivalent parallel capacitance and resistance were calculated from the measured admittance data, and the frequency dependences of the dielectric constant ϵ_r , dissipation factor $\tan \delta$, conductivity, and impedance were then obtained therefrom.

The leakage current densities of test cells were evaluated by using a source measure unit instrument Keithley 2400 at room temperature. The leakage currents were gradually decreased under a DC voltage application and reached stable values in several minutes, so the data of the leakage current density were obtained at the stable states.

Example 1 – Dependency of dielectric constant and dissipation factor from dopant concentration

5 Capacitor test cells with a 0.9 μm thick layer of F₄TCNQ doped organic semiconducting material OSC-1 with dopant contents of 0 wt%, 0.5 wt% and 1.0 wt%, relative to the weight of organic semiconducting material, were prepared as described above and the frequency dependencies of the dielectric constant ϵ_r and of the dissipation factor $\tan \delta$ measured as described above with the Solartron 1250
10 analyzer.

The respective results are shown in **Figures 2a and 2b**. **Figure 2a** clearly shows that the dielectric constant ϵ_r increases with increasing dopant content. Similarly, **Figure 2b** shows a shift to higher frequencies when increasing the dopant content to 0.5 wt%. It has not been possible to determine the peak frequency for the capacitor test cell with dopant content of 1.0 wt%, which – without wishing to be bound by theory - is attributed to limitations of the equipment used to perform the measurement.

20 **Example 2 – Dependency of dielectric constant and capacitance from the thickness of the doped organic semiconductor layer**

Capacitor test cells were prepared as described above using F₄TCNQ doped organic semiconducting material OSC-1 with a dopant content of 0.5 wt%. The thickness of the layers of the doped organic semiconducting material were 0.5 μm , 0.9 μm , 1.2 μm and 1.8 μm , respectively.

Respective results are shown in **Figures 3a and 3b**. **Figure 3a** shows that dielectric constants ϵ_r in the lower frequency part of the curve up to about 10^4 Hz increase with increasing thickness of the layer of the doped organic semiconductor material while the dielectric constants ϵ_r in the higher part of the curve, particularly in the range from 10^5 Hz to 10^6 Hz, is mostly independent of thickness of the layer of the organic semiconductor material. Respective curves for capacitance C are shown in **Figure 3b**.

35

Without wishing to be bound by theory it is believed that this dependence of dielectric constant ϵ_r and dissipation factor δ on thickness of the layer of organic semiconducting material indicates that the dielectric effect of the organic semiconducting material in the lower frequency range is brought about by space-charge polarizations and not by molecular polarizations. The present organic semiconducting materials, particularly the doped organic semiconducting materials, are therefore seen to be useful for application in a capacitor, e.g. for replacing the currently used liquid electrolytes.

10 **Example 3 – Durability in high voltage applications**

Capacitor test cells were prepared as described above with a 3.5 μm thick layer of organic semiconducting material OSC-3 doped with 5.0 wt% F_4TCNQ , with wt% given relative to the weight of OSC-3. Then the frequency dependency of the conductivity σ was measured at different direct current (DC) voltage of, in sequence, 0 V, 2 V, 4 V, 6 V, 8 V, 10 V and again 0 V. The measurement with an alternating current (AC) voltage of 50 mV was superimposed to each DC voltage. Respective results are shown in **Figure 4**.

20 **Figure 4** shows differences in behavior at frequencies of about below 100 Hz but nevertheless in this range remains below a conductivity σ of $10^{-8} \text{ S cm}^{-1}$ while the curves at different DC voltages do not significantly differ at frequencies between about 100 Hz and about 1 MHz. Furthermore, the conductivities for the second measurement at a DC voltage of 0 V shows the capacitor to have fully recovered following the measurement at the DC voltage of 10 V.

These results show that the present capacitor test cells work very well even for a 10 V DC application, thereby allowing much higher voltage in operation than with conventional electric double layer capacitors. Consequently, for the same capacitance C the capacitor energy E , which is defined as $E = 0.5 C \cdot V^2$, wherein V is the voltage, is much higher than for conventional electric double layer capacitors.

Example 4 – Thermal durability

35 A capacitor test cell identical to that of Example 3 was placed under air on a hotplate, the temperature of which was set to 300 °C, for 20 s. The frequencies of

the capacitor test cell before and after heating are shown in **Figure 5**. Heating of the capacitor test cell only led to a minor decrease in capacitance C , thus showing its suitability for applications with thermal exposure, such as for example an embedded capacitor on a printed circuit board.

5

Example 5

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Capacitor test cells were prepared as described above with the organic semiconducting materials as indicated in the following Table 2. The dopant concentration for each sample was 5 wt%, relative to the weight of the organic semiconducting material.

Table 2

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20

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Ref.	Organic semiconducting material	Dopant	Solvent / solvent blend
A	OSC-1	F ₄ TCNQ	Chloroform
B	OSC-2	F ₄ TCNQ	Chloroform
C	OSC-3	F ₄ TCNQ	Chloroform
D	OSC-4	F ₄ TCNQ	Chlorobenzene / o-dichlorobenzene
E	OSC-1	Mo(tfd) ₃	Chlorobenzene / o-dichlorobenzene
F	OSC-3	Mo(tfd) ₃	Chlorobenzene / o-dichlorobenzene

The measured data for dielectric constant ϵ_r and dissipation factor δ are shown in **Figure 6**. The results show that the present capacitor may be made with a range of structurally very different organic semiconducting materials

30

Example 6

35

Capacitor test cells were prepared as described above, using Cu or Al for electrodes, with the organic semiconducting materials and dopants as indicated in the following Table 3.

Table 3

Ref.	Organic semiconducting material	Dopant ⁽¹⁾	E _{HOMO} ⁽²⁾ (eV)	Electrode material	E _F ⁽³⁾ (eV)	Δ ⁽⁴⁾ (eV)
G	OSC-1	Mo(tfd) ₃	-5.0	Cu	-4.7	0.3
H	OSC-5	Mo(tfd) ₃	-5.1	Cu	-4.7	0.4
I	OSC-6	WCl ₆	-5.7	Cu	-4.7	1.0
J	OSC-1	Mo(tfd) ₃	-5.0	Al	4.3	0.7
K	OSC-5	Mo(tfd) ₃	-5.1	Al	-4.3	0.8
L	OSC-6	WCl ₆	-5.7	Al	-4.3	1.4

⁽¹⁾ The concentration of dopant is 5 wt%, respective to the weight of the organic semiconducting material.

⁽²⁾ The HOMO levels of organic semiconducting materials were measured by means of cyclic voltammetry.

⁽³⁾ We refer to the Fermi levels of Cu and Al by H. Michaelson in Journal of Applied Physics, 48, 4729 (1977).

⁽⁴⁾ We define Δ as the difference between the HOMO level of semiconducting material and the Fermi level of electrode material.

The frequency dependence of dissipation factor ($\tan \delta$) is shown in **Figure 7**. The values of $\tan \delta$ for References G and H largely increase with decreasing frequency, while the values of References I, J, K, and L are much lower in the low-frequency range below 100Hz. The frequency dependence of impedance ($|Z|$) is shown in **Figure 8**. The values of $|Z|$ for References I, J, K, and L increase with decreasing frequency, while the values of References G and H are much lower and independent on frequency in the low frequency range below 100 Hz. The large $\tan \delta$ and low $|Z|$ are considered to be due to the too small Δ values manifested in Table 3. The performances of References G and H may cause a charge leakage for capacitor device. The data shown in Table 3. **Figures 7** and **8** indicate that there exists an energy gap between E_{HOMO}, semiconducting material and E_F, electrode material that is large enough to prevent such charge leakage.

Example 7 – Leakage current

Capacitor test cells were prepared as described above using Al electrodes with the organic semiconducting materials and dopants as indicated in the following Table 4. The dopant concentration for each sample was 5 wt%, relative to the weight of the organic semiconducting material.

Table 4

Ref.	Organic semiconducting material	Dopant	E_{HOMO} (eV)	Electrode material	E_{F} (eV)	Δ (eV)
F	OSC-3	$\text{Mo}(\text{tfd})_3$	-5.2	Al	-4.3	0.9
K	OSC-5	$\text{Mo}(\text{tfd})_3$	-5.1	Al	-4.3	0.8
L	OSC-6	WCl_6	-5.7	Al	-4.3	1.4

The leakage current densities measured for the capacitor test cells are shown in **Figure 9**. The numbers of measured cells are 3, 3, and 4, for References F, K, and L, respectively, and average values for every applied voltage are plotted in the figure. The plotted values for Reference L are more than one order of magnitude lower than those of F or K. The magnitude of the leakage current depends on the height of electron energy barriers, which are created at the interfaces between the semiconducting layer and electrodes, and high barriers can be built by increasing the Δ value in Table 4. The result shown in **Figure 9** indicates the effectiveness of large Δ for reducing the leakage current density.

Generally stated, the present examples show that the capacitors disclosed in the present application have a number of advantages over conventional electric double layer capacitors. The present capacitors generally allow for higher capacitor energy (at given capacitance) due to their allowing to be run at higher DC voltages. This will, for example, permit the use of smaller capacitors at the same performance level as conventional bigger capacitors.

Claims

1. Capacitor comprising a first electrode layer, a second electrode layer and a semiconducting layer between the first electrode layer and the second electrode layer.
5
2. Capacitor according to claim 1, wherein the semiconductor layer is solid.
3. Capacitor according to claim 1 or claim 2, wherein the semiconducting layer comprises a semiconducting material selected from the group consisting of organic semiconducting materials, inorganic semiconducting materials and any blends of any of these.
10
4. Capacitor according to claim 3, wherein the organic semiconducting material comprises one or more organic semiconducting compounds.
15
5. Capacitor according to claim 3, wherein the inorganic semiconducting material comprises one or more inorganic semiconducting compounds.
6. Capacitor according to any or more of the preceding claims, wherein the semiconductor layer further comprises a dopant, said dopant being preferably an acceptor or a donor.
20
7. Capacitor according to any one or more of the preceding claims, wherein the semiconductor layer further comprises a dopant having an ionization energy of at least 7.0 eV.
25
8. Capacitor according to any one or more of the preceding claims, wherein the semiconductor layer further comprises a dopant having an ionization energy of at most 12.0 eV.
30
9. Capacitor according to any one or more of the preceding claims, wherein
$$E_{\text{LUMO, dopant}} < E_{\text{HOMO, semiconducting material}} + 0.5 \text{ eV}$$
wherein $E_{\text{LUMO, dopant}}$ is the energy level of the lowest unoccupied molecular orbital of the dopant and $E_{\text{HOMO, semiconducting material}}$ is the energy level of the highest occupied molecular orbital of the semiconducting material.
35

10. Capacitor according to any one or more of the preceding claims, wherein

$$E_{\text{HOMO, semiconducting material}} < E_{\text{F, electrode1}} - 1.0 \text{ eV}$$

5

$$E_{\text{HOMO, semiconducting material}} < E_{\text{F, electrode2}} - 1.0 \text{ eV}$$

wherein $E_{\text{F,electrode1}}$ is the Fermi level of the first electrode material and $E_{\text{F,electrode2}}$ is the Fermi level of the second electrode material.

10 11. Capacitor according to any one or more of the preceding claims, wherein said semiconductor layer has a dielectric constant of at least 3 and of at most 100,000 when in operation.

15 12. Printed circuit board comprising the capacitor of any one or more of claims 1 to 11.

13. Energy storage device comprising the capacitor of any one or more of claims 1 to 11.

20 14. Process of producing a capacitor, said process comprising the steps of
 (a) depositing a first electrode layer;
 (b) depositing a semiconducting layer onto the first electrode layer; and
 (c) depositing a second electrode layer onto the semiconducting layer to obtain a capacitor.

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15. Process according to claim 14, wherein the semiconducting layer is deposited by solution-processing of a formulation comprising a semiconductor material and a solvent.

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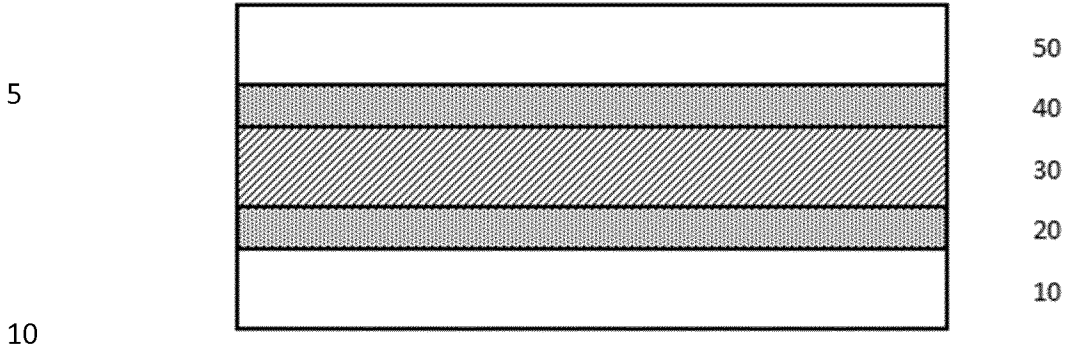


Figure 1

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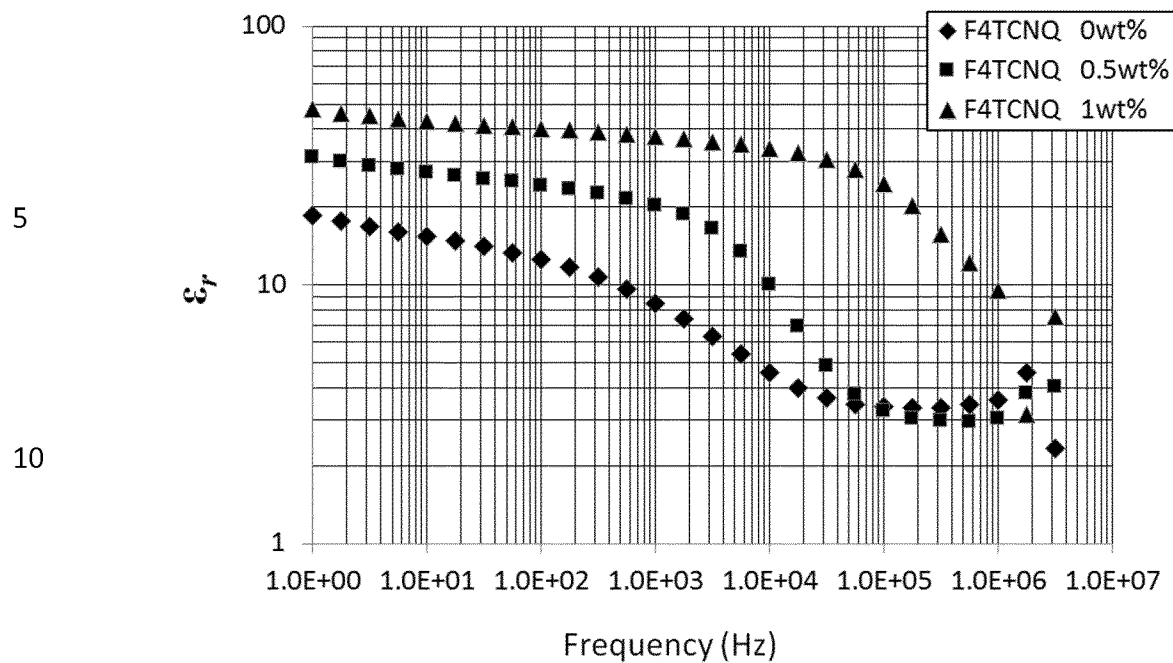


Figure 2a

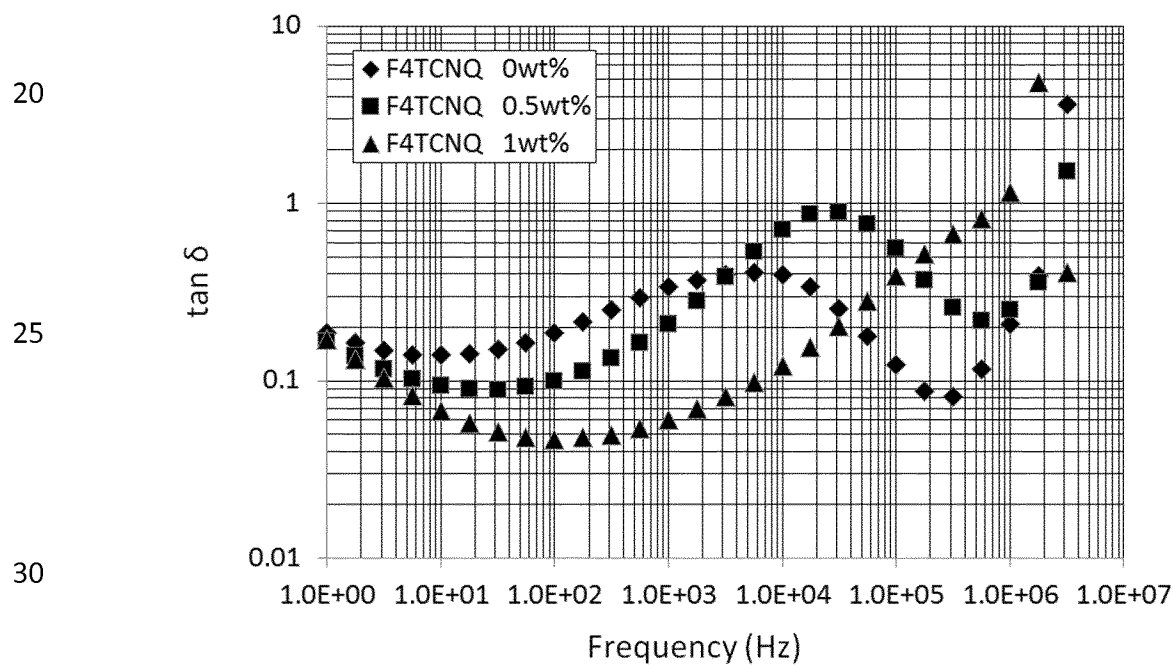


Figure 2b

- 3 / 6 -

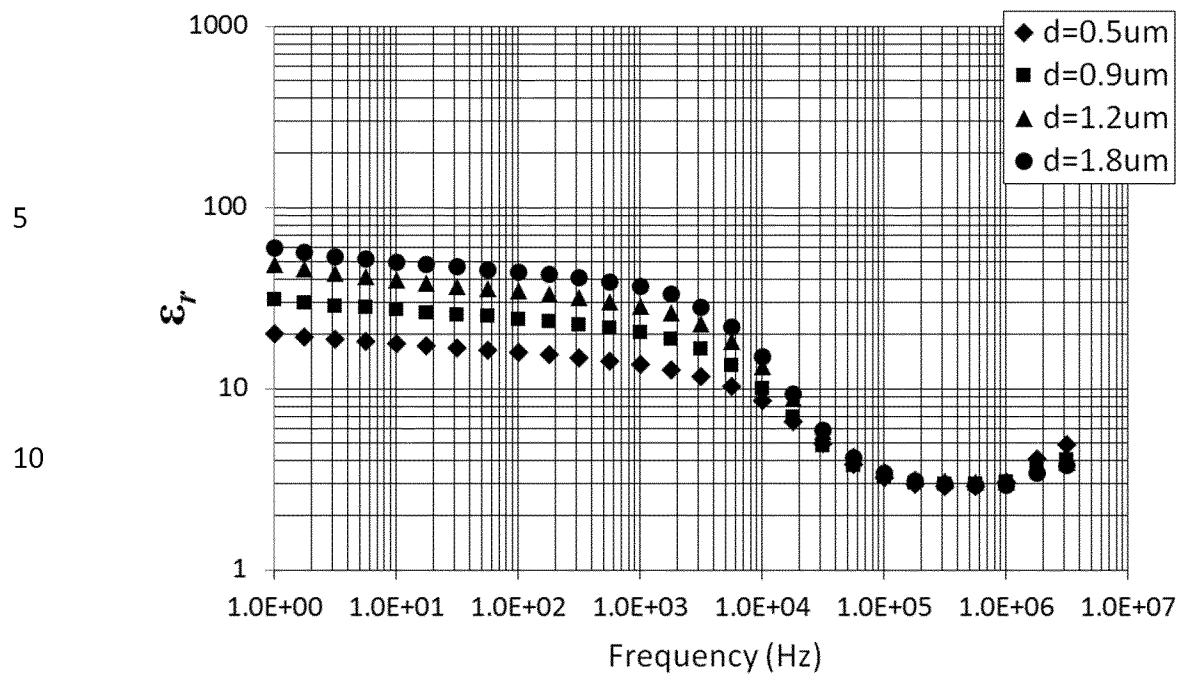


Figure 3a

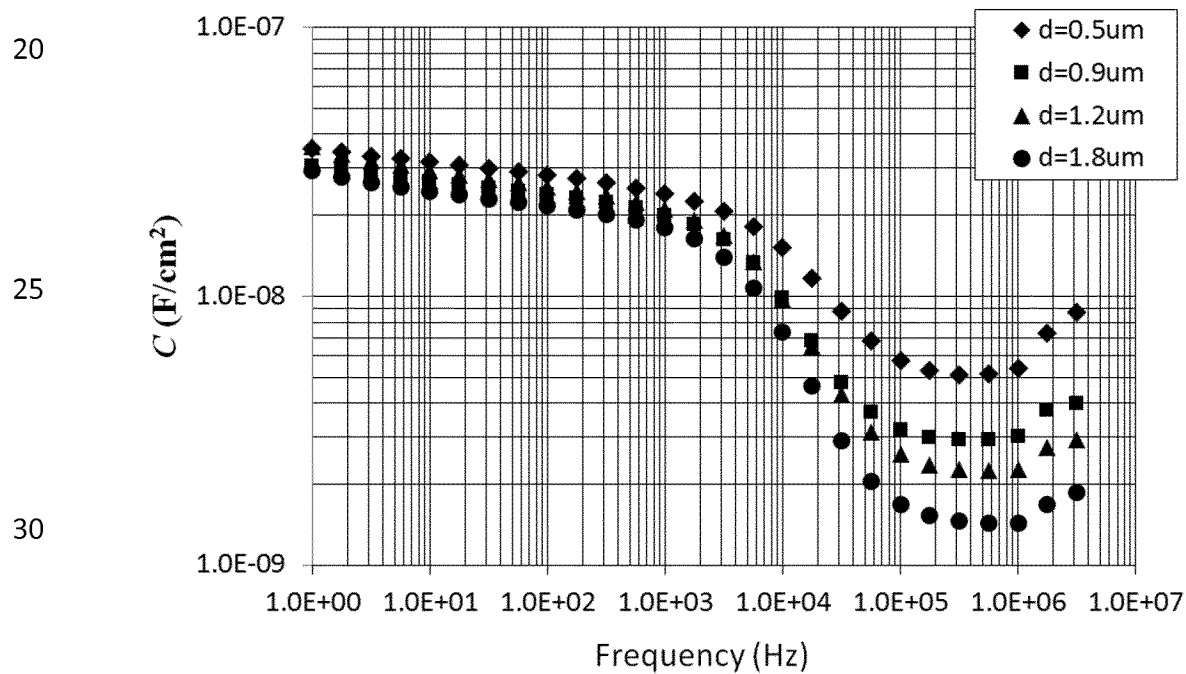


Figure 3b

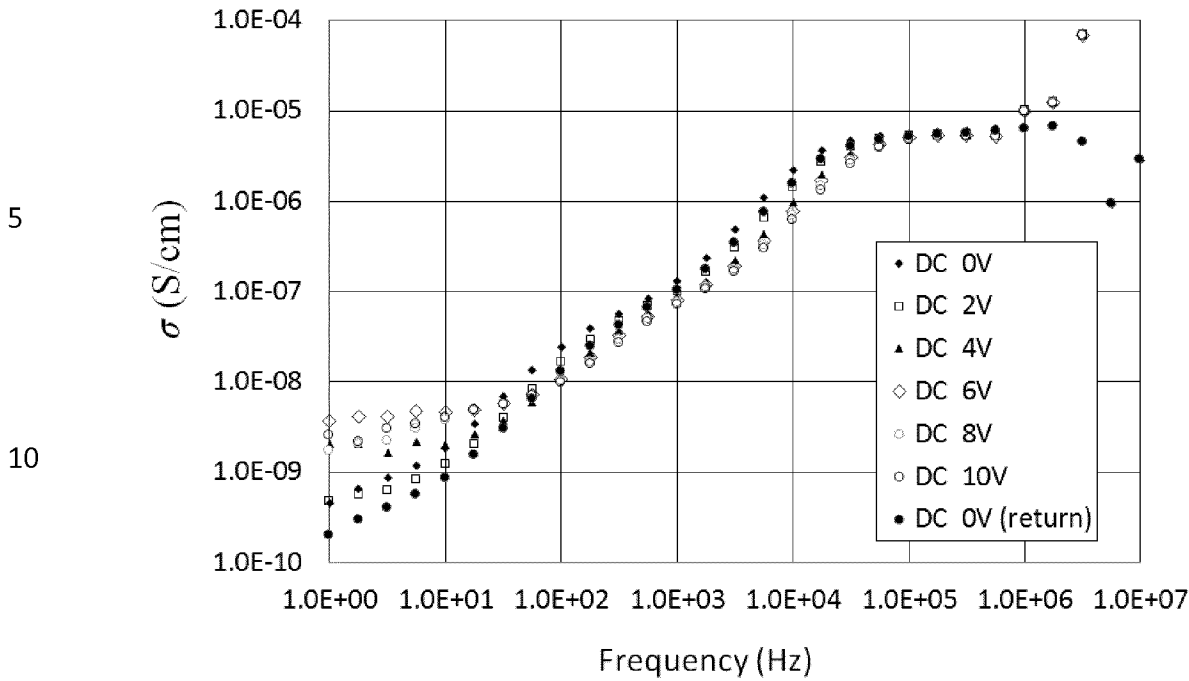


Figure 4

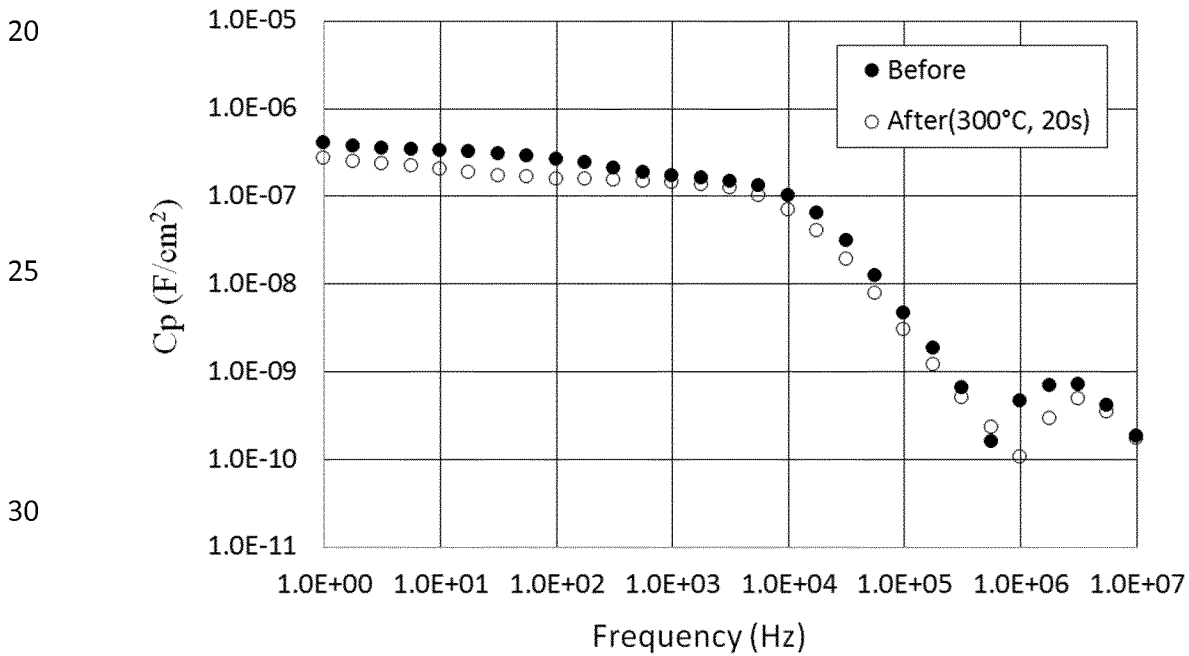


Figure 5

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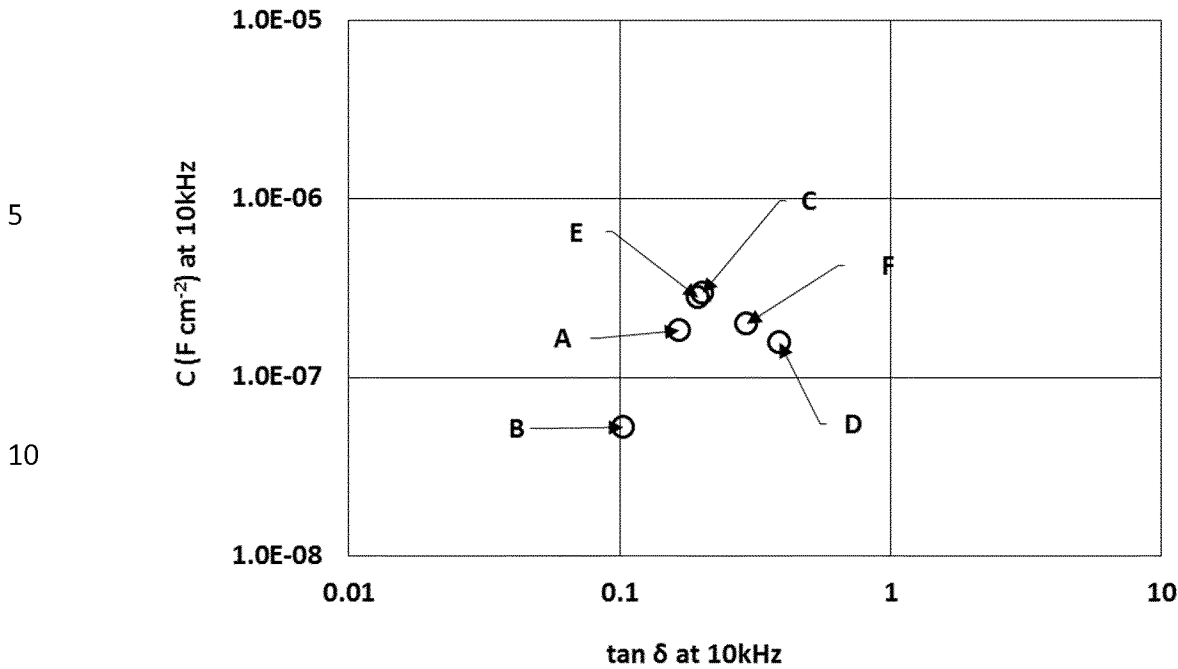


Figure 6

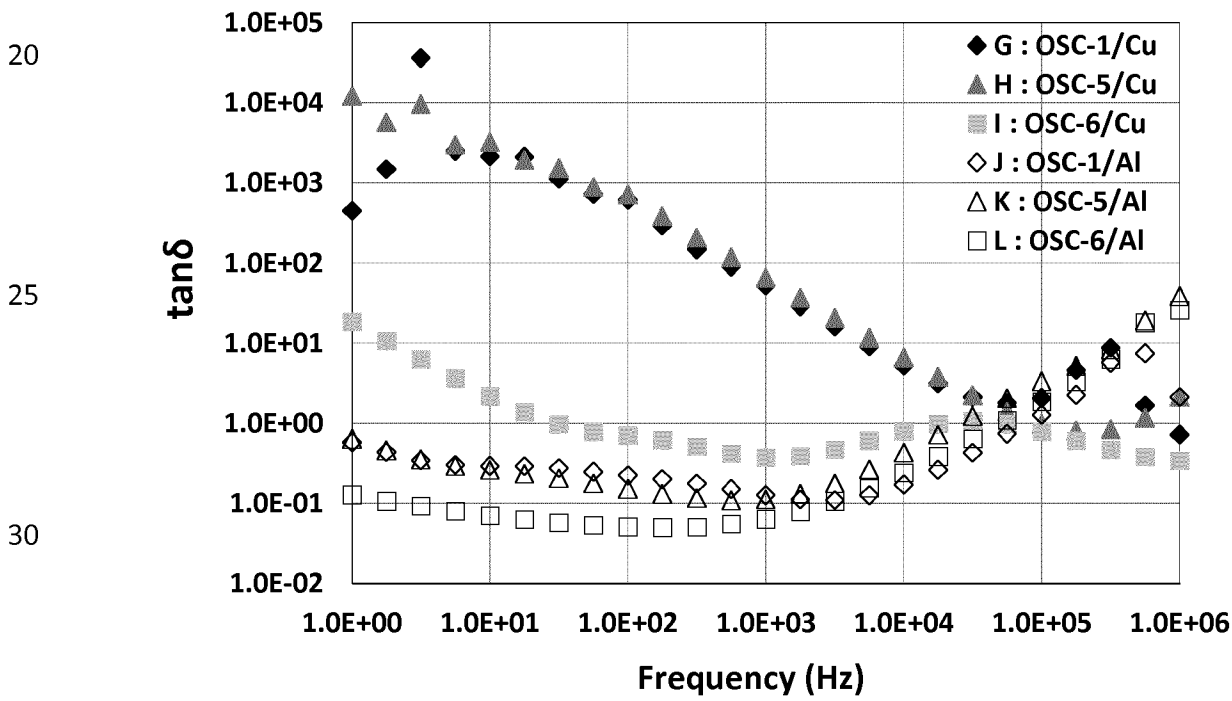


Figure 7

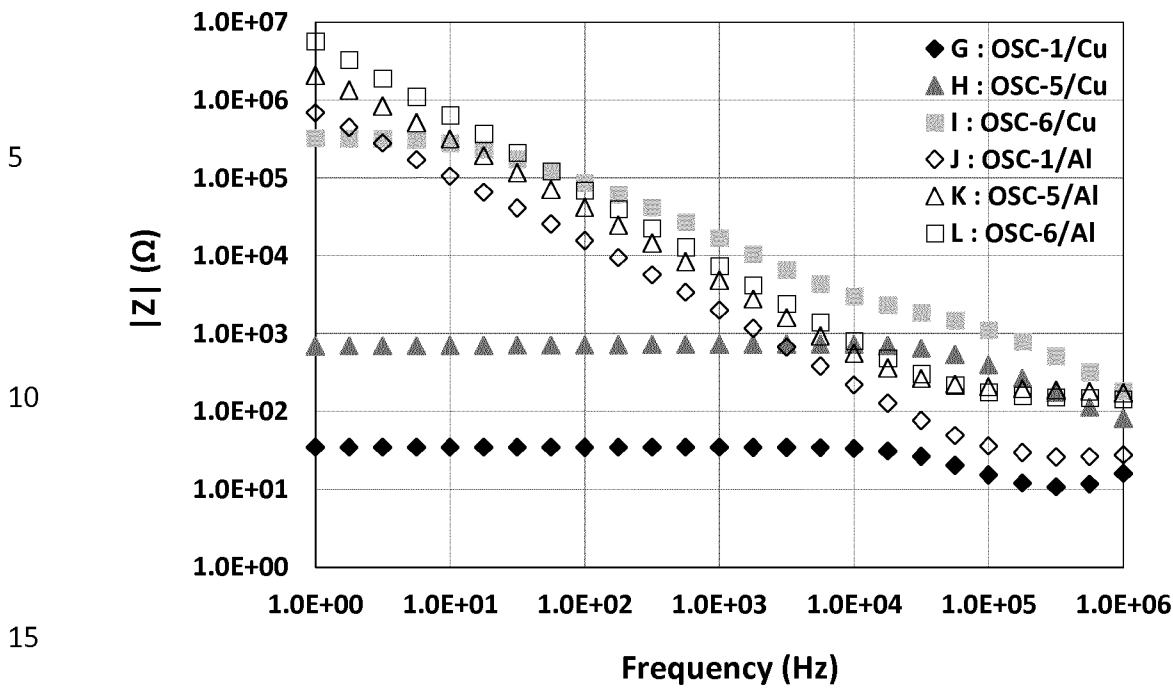


Figure 8

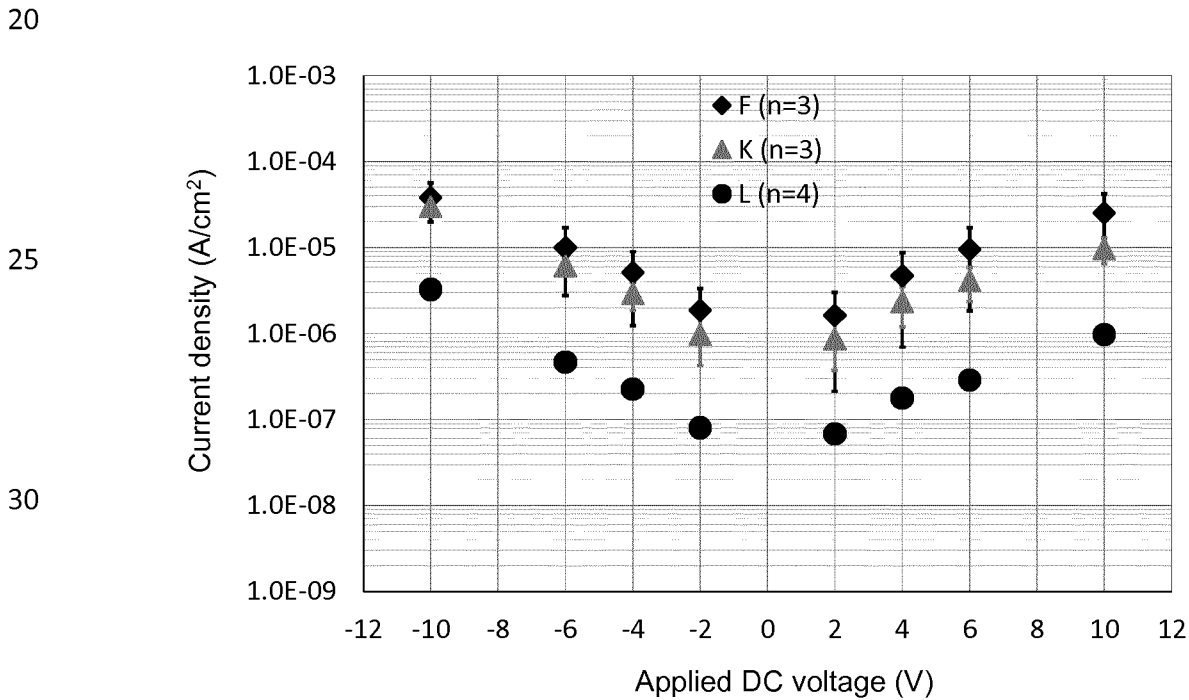


Figure 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/058514

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01G4/14 H01G4/18 H01L51/00 H01L49/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01G H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DIANAT P ET AL: "A highly tunable heterostructure metal-semiconductor-metal capacitor utilizing embedded 2-dimensional charge", APPLIED PHYSICS LETTERS, A I P PUBLISHING LLC, US, vol. 100, no. 15, 9 April 2012 (2012-04-09), pages 153505-153505, XP012155611, ISSN: 0003-6951, DOI: 10.1063/1.3702466 [retrieved on 2012-04-10] cited in the application abstract page 1; figure 1a	1-3,5, 7-14
X	US 2013/113076 A1 (YUN CHANGHAN [US] ET AL) 9 May 2013 (2013-05-09) paragraphs [0029] - [0032]; figure 3 ----- -/-	1



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

8 June 2018

Date of mailing of the international search report

19/06/2018

Name and mailing address of the ISA/

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Authorized officer

Bräckelmann, Gregor

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/058514

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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International application No

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