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- *of inventorship (Rule 4.17(iv))*

(54) **Title:** ORGANIC FIELD EFFECT TRANSISTOR COMPRISING SEMICONDUCTING SINGLE-WALLED CARBON NANOTUBES AND ORGANIC SEMICONDUCTING MATERIAL

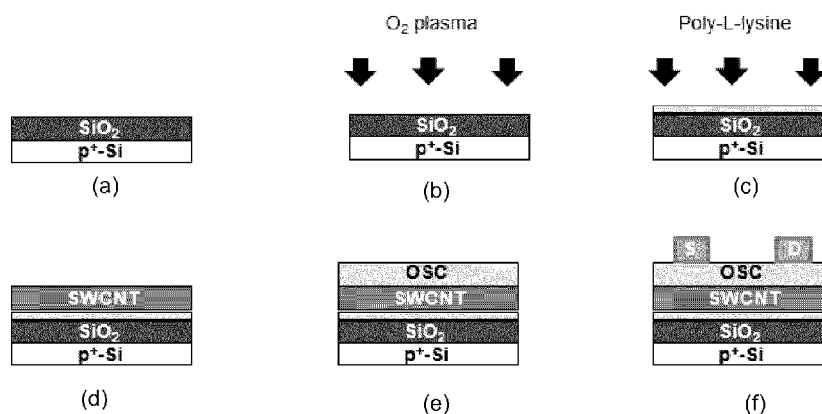


Figure 1.

(57) **Abstract:** The present invention provides organic field effect transistors comprising a double layer consisting of i) a first layer comprising a percolating network of single-walled carbon nanotubes having a content of at least 95% by weight of semiconducting single-walled carbon nanotubes, and ii) a second layer comprising an organic semiconducting material, as well as a process for the preparation of the organic field effect transistor.

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Organic field effect transistor comprising semiconducting single-walled carbon nanotubes and organic semiconducting material

Description

- 5 The present invention relates to an organic field effect transistor comprising a double layer consisting of a first layer comprising a percolating network of single-walled carbon nanotubes and a second layer comprising an organic semiconducting material, and to a process for the preparation of such a transistor.
- 10 In recent years, the use of single-walled carbon nanotubes (SWCNT) in organic field effect transistors (OFETs) has attracted considerable interest.
- In the beginning, the single-walled carbon nanotubes (SWCNT) were used as mixture of metallic and semiconducting single-walled carbon nanotubes in electronic devices as growth methods at that time yielded mixtures of metallic and semiconducting single-walled carbon nanotubes. Since methods for enriching the semiconducting single-walled carbon nanotubes in single-walled carbon nanotubes are available, also single-walled carbon nanotubes enriched in semiconducting single-walled carbon nanotubes are used in electronic devices.
- 20 The following publications describe preparation methods for organic field effect transistors using single-walled carbon nanotubes.
- 25 X.-Z. Bo, C.Y. Lee, M.S. Strano, M. Goldfinger, C. Nuckolis and G.B. Blanchet, Applied Physical Letters 2005, 86, 182102 disclose a bottom-gate, top-contact (BGTC) organic field effect transistor having a composite layer of individual single-walled carbon nanotubes (SWCNT), with a ratio of metallic : semiconducting SWCNT of 1 : 2, and poly(3-hexyl-thiophene) (P3HT) as semiconducting layer. The composite layer is prepared by mixing a dispersion of SWCNT with a solution of polythiophene and spin-coating this composite mixture on the substrate.
- 30 Shuhong Liu, Alejandro L. Briseno, Stefan C.B. Mannsfeld, Wie You, Jason Locklin, Hang Woo Lee, Youman Xia and Zhenan Bao, Advanced Functional Materials 2007, 17, 2891-2896 describe organic field effect transistors comprising single crystal organic semiconductor, prepared by growing crystals of the organic semiconductor onto patterned SWCNT bundles. The patterned SWCNT are obtained by printing using a stamp. The printed SWCNT bundles do not form connected paths between source-drain electrodes.
- 40 Shuhang Liu, Stefan C.B. Mannsfeld, Melbs C. Le Mieux, Hang W. Lee and Zhenon Bao, Applied Physical Letters 2008, 92, 053306 disclose bottom-gate, top-contact (BGTC) organic field effect transistors comprising a pentacene or a sexithiophene layer on random arrays of carbon nanotubes (CNT). The random arrays of CNT are prepared by spray-coating a dispersion of CNT. The random arrays of CNT do not form connected paths between source-drain electrodes. The highest mobility is reached for a bottom-gate, top-contact (BGTC) OFET comprising pentacene and is  $1.20 \text{ cm}^2/\text{Vs}$ .
- 50 Gen-Wen Hsieh, Flora M. Li, Paul Beecher, Arokia Nathan, Yiliang Wu, Beng S. Ong and William I. Milne, Journal of Applied Physics, 2009, 106, 123706 describe a bottom-gate, bottom-contact (BGBC) organic field effect transistor comprising a bilayer containing a poly[5,5'-bis(3-dodecyl-2-thienyl)-2,2'-bithiophene (PQT-12) layer obtained by ink jet printing on top of a thin non-percolating single-walled carbon nanotube (SWCNT) layer obtained by ink-jet printing a dispersion of isolated SWCNTs. The mobility of the OFET is  $0.228 \text{ cm}^2/\text{Vs}$ .
- 55 US2011121273A disclose a carbon nanotube (CNT) composite in which a conjugated polymer containing repeating units containing a fused heteroaryl unit having a nitrogen-containing double bond in the ring and a thiophene ring is attached to at least a part of the surface of a carbon nanotube, and field effect transistors having a semiconducting layer containing the CNT composites. The semiconducting layer is either a CNT composite layer, a layer comprising CNT composite dispersed in a semiconductor or as bilayer wherein one layer comprises the CNT composite and the other layer comprises organic semiconductor. Object was an organic field effect transistor of low hysteresis.
- 60
- 65 US20130048949A1 discloses bottom-gate, bottom-contact (BGBC) thin film transistor (TFT) devices incorporating a thin film semiconductor derived from carbonaceous

nanomaterials and a dielectric layer composed of an organic-inorganic hybrid self-assembled multilayer. The carbonaceous nanomaterials can be single or multi-walled carbon nanotubes, preferably mostly semiconducting carbon nanotubes with about 1% or less metallic CNT. In the exemplified bottom-gate, bottom-contact (BGBC) TFT using 99% pure semiconducting single-walled carbon nanotubes (sc-SWCNT) mobilities of 1 to 5 cm<sup>2</sup>/Vs and on-off current ratios of > 10<sup>3</sup>.

Smithson, C; Wu, Y.; Wigglesworth, T.; Gardner, S.; Zhu, S.; Nie H.-Y., Organic Electronics 2014, 15, 2639-2646 describes the fabrication of an organic thin film transistor comprising a composite of a semiconducting copolymer of diketopyrrolopyrrole-quarterthiophene (DPP-QT) and a mixture of metallic and semiconducting single-walled carbon nanotubes (SWCNTs). The maximum mobility for a DPP-QT and SWCNT composite in a bottom-gate, top-contact (BGTC) organic field effect transistor was 1.3 cm<sup>2</sup>/Vs.

Ting Lei, Ying-Chih Lai, Guonsong Hong, Huiliang Wang, Pascal Hayoz, R. Thomas Weitz, Changxin Chen, Hongjie Dai and Zhenan Bao, Small, 2015, 11, 24, 2946-2954 disclose bottom-gate, bottom-contact (BGBC) thin film transistors (TFTs) containing a semiconducting layer of semiconducting single walled carbon nanotubes with diameters mainly around 1.5 nm. The TFT showed high mobilities of 41.2 cm<sup>2</sup>/Vs and high on/off ratios of greater than 10<sup>4</sup>. The semiconducting single-walled carbon nanotube layer was obtained by soaking the substrate in a solution of diketopyrrolopyrrole (DPP)-based polymer wrapped semiconducting single-walled carbon nanotubes in toluene, followed by rinsing with toluene to remove most of the DPP-based polymer.

Tae-Jun Ha, Daisuke Kiriya, Kevin Chen, Ali Javey, Applied Materials & Interfaces 2014, 6, 8441 to 8446 describe hysteresis-free carbon nanotube bottom-gate, top-contact (BGTC) organic field effect transistors employing a fluoropolymer Teflon-AF layer on top of the carbon nanotube layer. The OFET also shows also operation stability in air and in water. Instead of the fluoropolymer Teflon AF layer, a fluoropolymer Cytop layer, a poly(methylmethacrylate) (PMMA) layer or a parylene C layer is also used.

The known methods for the preparation of organic field effect transistor comprising single-walled carbon nanotubes still show deficiencies.

It was the object of the present invention to provide organic field effect transistors of improved performance, in particular to provide organic field effect transistors showing low hysteresis and at the same time high mobilities.

The object is solved by the organic field effect transistor of claim 1 and the process for the preparation of an organic field effect transistor of claim 14.

The organic field effect transistor of the present invention comprises a double layer consisting of

- i) a first layer comprising a percolating network of single-walled carbon nanotubes having a content of at least 95% by weight of semiconducting single-walled carbon nanotubes, and
- ii) a second layer comprising an organic semiconducting material.

The first layer can essentially consist of a percolating network of single-walled carbon nanotubes or the first layer can in addition to the percolating network of single-walled carbon nanotubes comprise additional materials. Examples of additional materials are bile salts such as sodium cholate, sodium dodecyl sulfate or organic semiconducting materials. The organic semiconducting materials of the first layer can be any of the organic semiconducting materials of the second layer listed below. The organic semiconducting materials of the first layer and the organic semiconducting materials of the second layer can be the same or different.

Preferably, the first layer essentially consists of a percolating network of single-walled carbon nanotubes. The first layer essentially consists of a percolating network of single-walled carbon nanotubes if the first layer comprises at least 95% by weight, and preferably at least 98% by weight, of single-walled carbon nanotubes based on the weight of the first layer.

- 5 If the first layer essentially consists of a percolating network of single-walled carbon nanotubes, the percolating network is a two-dimensional network of single-walled carbon nanotubes.
- 10 If the first layer in addition to the percolating network of single-walled carbon nanotubes comprise additional materials, the percolating network is a three-dimensional network of single-walled carbon nanotubes.
- 15 A percolating network of single-walled carbon nanotubes is a network of single-walled carbon nanotubes which establishes a connection between the source and drain electrodes.
- 20 A connection between the source and drain electrodes is established, if the average density of single-walled carbon nanotubes is above five single-walled carbon nanotubes per  $\mu\text{m}^2$  for a two-dimensional network of single-walled carbon nanotubes, and above twenty single-walled carbon nanotubes per  $\mu\text{m}^2$  for a three-dimensional network of single-walled carbon nanotubes. The average density of single-walled carbon nanotubes in the first layer can be determined by scanning electron microscopy (SEM).
- 25 Most preferably, the percolating network of single-walled carbon nanotubes have a content of at least 99% by weight of semiconducting single-walled carbon nanotubes.
- 30 The single-walled carbon nanotubes can have a diameter in the range of 0.5 to 10 nm. Preferably the single-walled carbon nanotubes have a diameter of 0.5 to 3 nm, more preferably 0.5 to 2 nm.
- 35 The single-walled carbon nanotubes can have a length in the range of 0.001 to  $10^4$   $\mu\text{m}$ . Preferably, the single-walled carbon nanotubes have a length in the range of 0.1 to 100  $\mu\text{m}$ , more preferably 0.1 to 10  $\mu\text{m}$ , even more preferably 0.05 to 1  $\mu\text{m}$ , and most preferably 0.05 to 0.5  $\mu\text{m}$ .
- 40 Single-walled carbon nanotubes (SWCNTs) can be grown by various methods known in the art such as high pressure carbon monoxide decomposition (HiPCO), Co-Mo catalysis (CoMoCAT), laser ablation, arc discharge and chemical vapor deposition (CVD). The SWCNTs obtained by these methods vary in their tube diameter, length and wrapping angle, and are mixtures of semiconducting and metallic SWCNTs.
- 45 There are several post-growth methods for enriching the amount of semiconducting SWCNT from a mixture of semiconducting and metallic SWCNTs.
- 50 Ralph Krupke, Frank Hennrich, Hibert von Löhneysen and Manfred M. Kappes, Science 2003, 301, 344 to 347 describe separation of metallic and semiconducting SWCNT by alternating current dielectrophoresis.
- 55 Michael S. Arnold, Alexander A. Green, James F. Hulvat, Samuel I. Stupp and Mark C. Hersam, Nature Nanotechnology 2006, 1, 60 to 65 describe separation of metallic and semiconducting SWCNT by density gradient ultracentrifugation in the presence of bile salts such as sodium cholate as surfactants.
- 60 Yasumitsu Miyata, Kazunari Shiozawa, Yukiasada, Yutaka Ohno, Ryo Kitaura, Takashi Mizutani and Hisanori Shinohara, Nano Research 2011, 4(10), 963-970 describe a process for enriching semiconducting SWCNT from a mixture of semiconducting and metallic SWCNT including centrifugation of the mixture of SWCNTs and sodium cholate, separation of the supernatant and addition of sodium dodecyl sulfate to the supernatant, followed by gel filtration of the supernatant.
- 65 Enriched semiconducting single-walled carbon nanotubes together with conjugated polymers can be obtained by dispersion of a mixture of semiconducting and metallic SWCNT with a conjugated polymer, followed by centrifugation. For example, Kojiro Akazaki, Fumiyuki Toshimitsu, Hiroaki Ozawa, Tsuyohiko Fujigaya, Naotoshi Nakashima, Journal of the American Chemical Society 2012, 134, 12700 to 12707 describe such an enrichment process using fluorene binaphthol polymers as

conjugated polymer. For example, Ting Lei, Ying-Chih Lai, Guonsong Hong, Huiliang Wang, Pascal Hayoz, R. Thomas Weitz, Changxin Chen, Hongjie Dai and Zhenan Bao, Small, 2015, 11, 24, 2946-2954 describe such an enrichment process using a diketopyrrolopyrrole-based polymer as conjugated polymer.

5

Single-walled carbon nanotubes enriched in semiconducting single-walled carbon nanotubes are also commercially available from various companies such as Nanointegrus Incorporation or Southwest Nanotechnologies Incorporation.

10

The organic semiconducting material can be any organic semiconducting material known in the art. The organic semiconducting material can be a small molecule or a polymer.

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Examples of organic semiconducting materials are polycyclic aromatic hydrocarbons consisting of linearly-fused aromatic rings such as anthracene, pentacene and derivatives thereof, polycyclic aromatic hydrocarbons consisting of two-dimensional fused aromatic rings such as perylene, perylene diimide derivatives, perylene dianhydride derivatives and naphthalene diimide derivatives, triphenylamine derivatives, oligomers and polymers containing aromatic units such as oligothiophene, oligophenylenevinylene, polythiophene, polythienylenevinylene, polyparaphenylene, polypyrrole and polyaniline, hydrocarbon chains such as polyacetylenes, and diketopyrrolopyrrole-based materials.

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For example, bis-alkinyl substituted polycyclic aromatic hydrocarbons consisting of linearly-fused aromatic rings are described in WO2007/068618.

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For example, perylene diimide derivatives, perylene dianhydride derivatives and naphthalene diimide derivatives are described in WO2007/074137, WO2007/093643, WO2009/024512, WO2009/147237, WO2012/095790, WO2012/117089, WO2012/152598, WO2014/033622, WO2014/174435 and WO2015/193808.

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For example, polymers comprising thiophene units are described in WO2010/000669, polymers comprising benzothiadiazol-cyclopentadithiophene units are described in WO2010/000755, polymers comprising dithienobenzathienothiophene units are described in WO2011/067192, polymers comprising dithienophthalimide units are described in WO2013/004730, polymers comprising thienothiophene-2,5-dione units as described in WO2012/146506, and polymers comprising Isoindigo-based units are described in WO2009/053291.

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For example, diketopyrrolopyrrole-based materials and their synthesis are described in WO2005/049695, WO2008/000664, WO2010/049321, WO2010/049323, WO2010/108873, WO2010/136352, WO2010/136353, WO2012/041849, WO2012/175530, WO2013/083506, WO2013/083507 and WO2013/150005.

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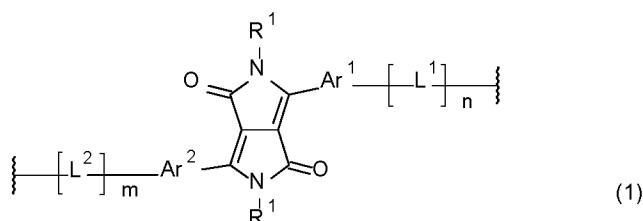
A summary on diketopyrrolopyrrole (DPP) based polymers suitable as semiconducting material in organic field effect transistors are also given in Christian B. Nielsen, Mathieu Turbiez and Iain McCulloch, Advanced Materials 2013, 25, 1859 to 1880.

50

Preferably, the organic semiconducting material is at least one diketopyrrolopyrrole-based material.

55

Preferably, the diketopyrrolopyrrole-based material is  
i) a diketopyrrolopyrrole-based polymer comprising units of formula



wherein

- 5  $R^1$  is at each occurrence  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl or  $C_{2-30}$ -alkynyl, wherein  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl and  $C_{2-30}$ -alkynyl can be substituted by one or more  $-\text{Si}(\text{R}^a)_3$  or  $-\text{OSi}(\text{R}^a)_3$ , or one or more  $\text{CH}_2$  groups of  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl and  $C_{2-30}$ -alkynyl can be replaced by  $-\text{Si}(\text{R}^a)_2-$  or  $-\text{[Si}(\text{R}^a)_2\text{-O]}_a\text{-Si}(\text{R}^a)_2-$ ,  
 wherein  $\text{R}^a$  is at each occurrence  $C_{1-10}$ -alkyl, and  $a$  is an integer from 1 to 20,

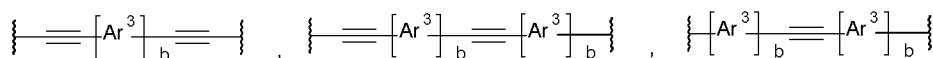
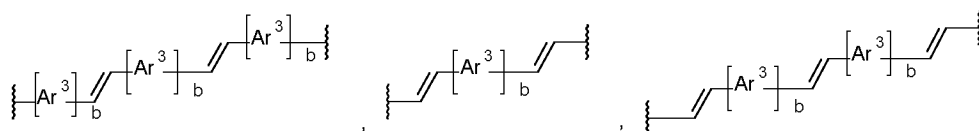
- 10  $n$  and  $m$  are independently 0 or 1, and

- 15  $\text{Ar}^1$  and  $\text{Ar}^2$  are independently arylene or heteroarylene, wherein arylene and heteroarylene can be substituted with one or more  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl,  $\text{O-C}_{1-30}$  alkyl, aryl or heteroaryl, which  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl,  $\text{O-C}_{1-30}$  alkyl, aryl and heteroaryl can be substituted with one or more  $C_{1-20}$ -alkyl,  $\text{O-C}_{1-20}$ -alkyl or phenyl,

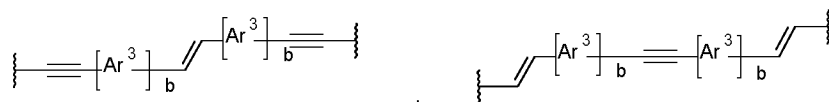
$L^1$  and  $L^2$  are independently selected from the group consisting of



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25



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wherein

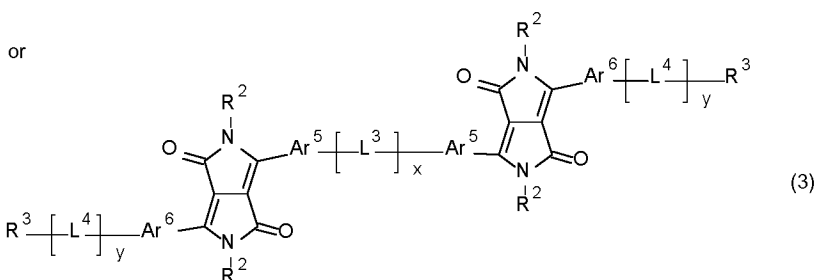
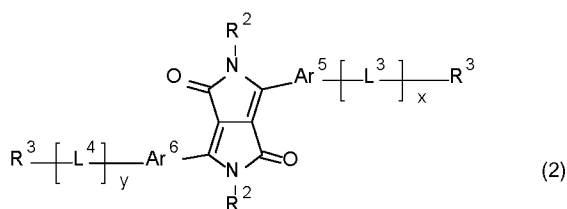
- 35  $\text{Ar}^3$  is at each occurrence arylene or heteroarylene, wherein arylene and heteroarylene can be substituted with one or more  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl,  $\text{O-C}_{1-30}$ -alkyl, aryl or heteroaryl, which  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl,  $\text{O-C}_{1-30}$ -alkyl, aryl and heteroaryl can be substituted with one or more  $C_{1-20}$ -alkyl,  $\text{O-C}_{1-20}$ -alkyl or phenyl; and wherein adjacent  $\text{Ar}^3$  can be connected via a  $\text{CR}^b\text{R}^b$ ,  $\text{SiR}^b\text{R}^b$  or  $\text{GeR}^b\text{R}^b$  linker, wherein  $\text{R}^b$  is at each occurrence  $\text{H}$ ,  $C_{1-30}$ -alkyl or aryl, which  $C_{1-30}$ -alkyl and aryl can be substituted with one or more  $C_{1-20}$ -alkyl,  $\text{O-C}_{1-20}$ -alkyl or phenyl,

- 40  $b$  is at each occurrence an integer from 1 to 8, and

- 45  $\text{Ar}^4$  is at each occurrence aryl or heteroaryl, wherein aryl and heteroaryl can be substituted with one or more  $C_{1-30}$ -alkyl,  $\text{O-C}_{1-30}$  alkyl or phenyl, which phenyl can be substituted with  $C_{1-20}$ -alkyl or  $\text{O-C}_{1-20}$ -alkyl,

or

i) a diketopyrrolopyrrole-based small molecule of formulae



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wherein

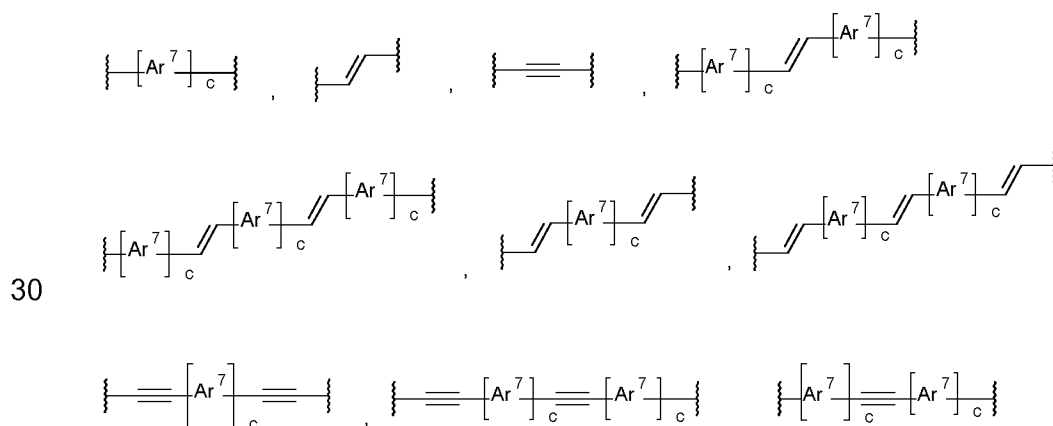
10  $R^2$  is at each occurrence  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl or  $C_{2-30}$ -alkynyl, wherein  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl and  $C_{2-30}$ -alkynyl can be substituted by  $-Si(R^c)_3$  or  $-OSi(R^c)_3$ , or one or more  $CH_2$  groups of  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl and  $C_{2-30}$ -alkynyl can be replaced by  $-Si(R^c)_2-$  or  $-[Si(R^c)_2-O]_a-Si(R^c)_2-$ ,  
 wherein  $R^c$  is at each occurrence  $C_{1-10}$ -alkyl, and a is an integer from 1 to 20,

15  $R^3$  is H, CN,  $C_{1-20}$ -alkyl,  $C_{2-20}$ -alkenyl,  $C_{2-20}$ -alkynyl, O- $C_{1-20}$  alkyl, aryl or heteroaryl, which  $C_{1-20}$ -alkyl,  $C_{2-20}$ -alkenyl,  $C_{2-20}$ -alkynyl, O- $C_{1-20}$  alkyl, aryl and heteroaryl can be substituted with one or more  $C_{1-6}$ -alkyl, O- $C_{1-6}$ -alkyl or phenyl,

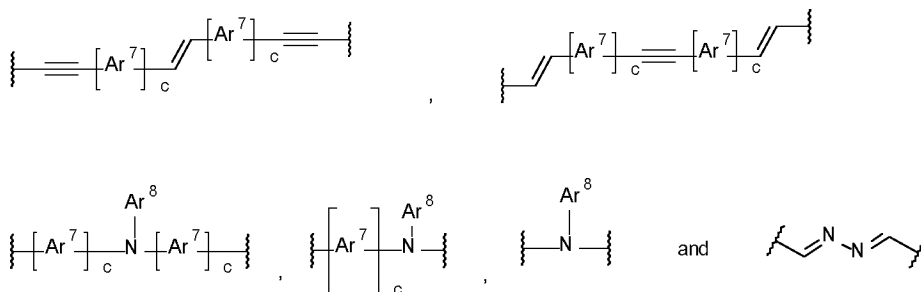
x and y are independently 0 or 1, and

20  $Ar^5$  and  $Ar^6$  are independently arylene or heteroarylene, wherein arylene and heteroarylene can be substituted with one or more  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl, O- $C_{1-30}$ -alkyl, aryl or heteroaryl, which  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl, O- $C_{1-30}$ -alkyl, aryl and heteroaryl can be substituted with one or more  $C_{1-20}$ -alkyl, O- $C_{1-20}$ -alkyl or phenyl;

25  $L^3$  and  $L^4$  are independently selected from the group consisting of







5

wherein

10  $Ar^7$  is at each occurrence arylene or heteroarylene, wherein arylene and heteroarylene can be substituted with one or more  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl,  $O-C_{1-30}$ -alkyl, aryl or heteroaryl, which  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl,  $O-C_{1-30}$ -alkyl, aryl and heteroaryl can be substituted with one or more  $C_{1-20}$ -alkyl,  $O-C_{1-20}$ -alkyl or phenyl; and wherein adjacent  $Ar^7$  can be connected via an  $CR^dR^d$ ,  $SiR^dR^d$  or  $GeR^dR^d$  linker, wherein  $R^d$  is at each occurrence H,  $C_{1-30}$ -alkyl or aryl, which  $C_{1-30}$ -alkyl and aryl can be substituted with one or more  $C_{1-20}$ -alkyl,  $O-C_{1-20}$ -alkyl or phenyl,

15 c is at each occurrence an integer from 1 to 8, and

20  $Ar^8$  is at each occurrence aryl or heteroaryl, wherein aryl and heteroaryl can be substituted with one or more  $C_{1-30}$ -alkyl,  $O-C_{1-30}$ -alkyl or phenyl, which phenyl can be substituted with  $C_{1-20}$ -alkyl or  $O-C_{1-20}$ -alkyl.

25  $C_{1-6}$ -alkyl,  $C_{1-10}$ -alkyl,  $C_{1-20}$ -alkyl,  $C_{1-30}$ -alkyl and  $C_{6-30}$ -alkyl can be branched or unbranched (linear). If branched,  $C_{1-6}$ -alkyl,  $C_{1-10}$ -alkyl,  $C_{1-20}$ -alkyl and  $C_{1-30}$ -alkyl are preferably branched at the C2-atom. Examples of  $C_{1-6}$ -alkyl are methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, isobutyl, *tert*-butyl, *n*-pentyl, neopentyl, isopentyl, *n*-(1-ethyl)propyl and *n*-hexyl. Examples of  $C_{1-10}$ -alkyl are  $C_{1-6}$ -alkyl and *n*-heptyl, *n*-octyl, *n*-(2-ethyl)hexyl, *n*-nonyl, *n*-decyl. Examples of  $C_{1-20}$ -alkyl are  $C_{1-10}$ -alkyl and *n*-undecyl, *n*-dodecyl, *n*-undecyl, *n*-dodecyl, *n*-tridecyl, *n*-tetradecyl, *n*-(2-butyl)decyl, *n*-pentadecyl, *n*-hexadecyl, *n*-heptadecyl, *n*-octadecyl, *n*-nonadecyl, *n*-(2-hexyl)tetradecyl and *n*-icosyl ( $C_{20}$ ). Examples of  $C_{1-30}$ -alkyl are  $C_{1-20}$ -alkyl and *n*-docosyl ( $C_{22}$ ), *n*-(2-decyl)dodecyl, *n*-tetracosyl ( $C_{24}$ ), *n*-hexacosyl ( $C_{26}$ ), *n*-octacosyl ( $C_{28}$ ) and *n*-triacontyl ( $C_{30}$ ). Examples of  $C_{6-30}$ -alkyl are *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-(2-ethyl)hexyl, *n*-nonyl, *n*-decyl, *n*-undecyl, *n*-dodecyl, *n*-undecyl, *n*-dodecyl, *n*-tridecyl, *n*-tetradecyl, *n*-(2-butyl)decyl, *n*-pentadecyl, *n*-hexadecyl, *n*-heptadecyl, *n*-octadecyl, *n*-nonadecyl, *n*-(2-hexyl)tetradecyl, *n*-icosyl, *n*-docosyl ( $C_{22}$ ), *n*-(2-decyl)dodecyl, *n*-tetracosyl ( $C_{24}$ ), *n*-hexacosyl ( $C_{26}$ ), *n*-octacosyl ( $C_{28}$ ) and *n*-triacontyl ( $C_{30}$ ).

40 Examples of linear  $C_{6-14}$ -alkyl are *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl, *n*-decyl, *n*-undecyl, *n*-dodecyl, *n*-undecyl, *n*-dodecyl, *n*-tridecyl and *n*-tetradecyl.

Examples of linear  $C_{2-12}$ -alkyl are ethyl, *n*-propyl, isopropyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl, *n*-decyl, *n*-undecyl and *n*-dodecyl.

45  $C_{2-30}$ -alkenyl can be branched or unbranched. Examples of  $C_{2-30}$ -alkenyl are vinyl, propenyl, *cis*-2-butenyl, *trans*-2-butenyl, 3-butenyl, *cis*-2-pentenyl, *trans*-2-pentenyl, *cis*-3-pentenyl, *trans*-3-pentenyl, 4-pentenyl, 2-methyl-3-butenyl, hexenyl, heptenyl, octenyl, nonenyl, docenyl, linoleyl ( $C_{18}$ ), linolenyl ( $C_{18}$ ), oleyl ( $C_{18}$ ), and arachidonyl ( $C_{20}$ ), and erucyl ( $C_{22}$ ).

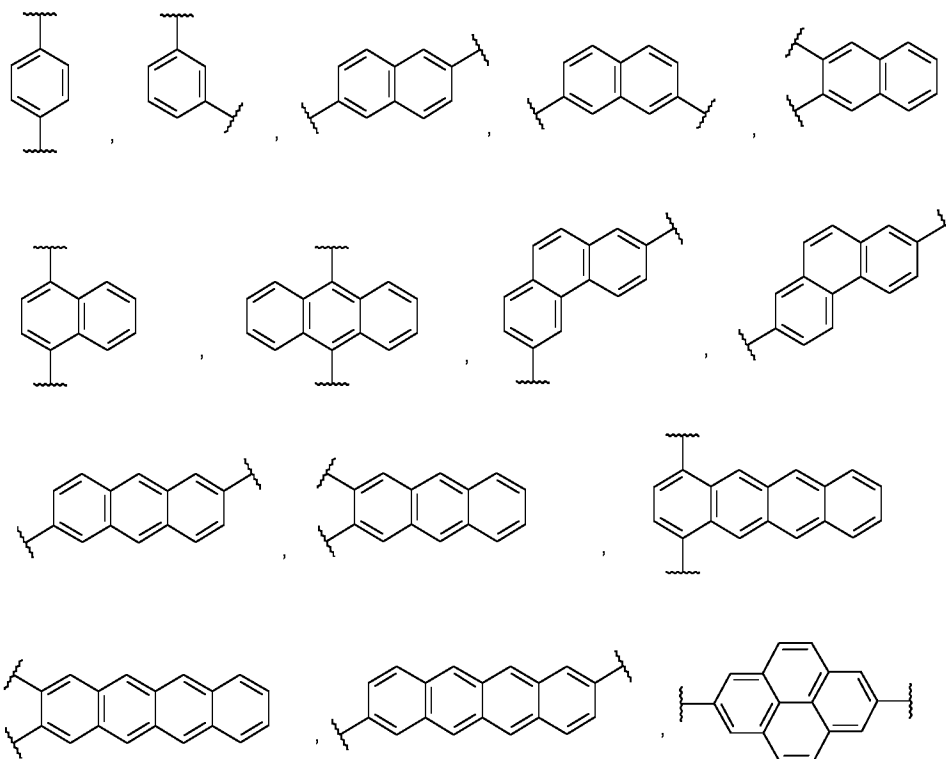
50  $C_{2-30}$ -alkynyl can be branched or unbranched. Examples of  $C_{2-30}$ -alkynyl are ethynyl, 2-propynyl, 2-butynyl, 3-butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, undecynyl, dodecynyl, tridecynyl, tetradecynyl, pentadecynyl, hexadecynyl, heptadecynyl, octadecynyl, nonadecynyl and icosynyl ( $C_{20}$ ).

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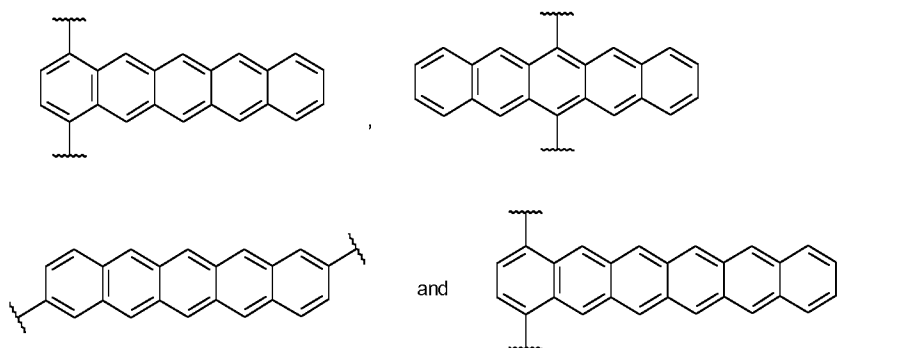
Arylene is a bivalent aromatic ring system, consisting of one aromatic ring or of two to eight condensed aromatic rings, wherein all rings are formed from carbon atoms. Preferably, arylene is a bivalent aromatic ring system consisting of one aromatic ring or

of two to four condensed aromatic rings, wherein all rings are formed from carbon atoms.

5



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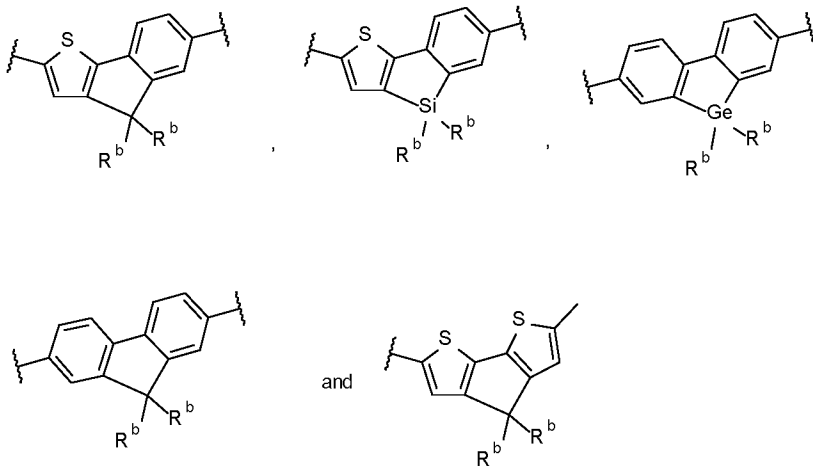
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Heteroarylene is a bivalent aromatic ring system consisting of one aromatic ring or of two to eight condensed aromatic rings, wherein at least one aromatic ring contains at least one heteroatom selected from the group consisting of S, O, N and Se. Preferably, heteroarylene is a bivalent aromatic ring system consisting of one aromatic ring or of two to four condensed aromatic rings, wherein at least one aromatic ring contains at least one heteroatom selected from the group consisting of S, O, N and Se.

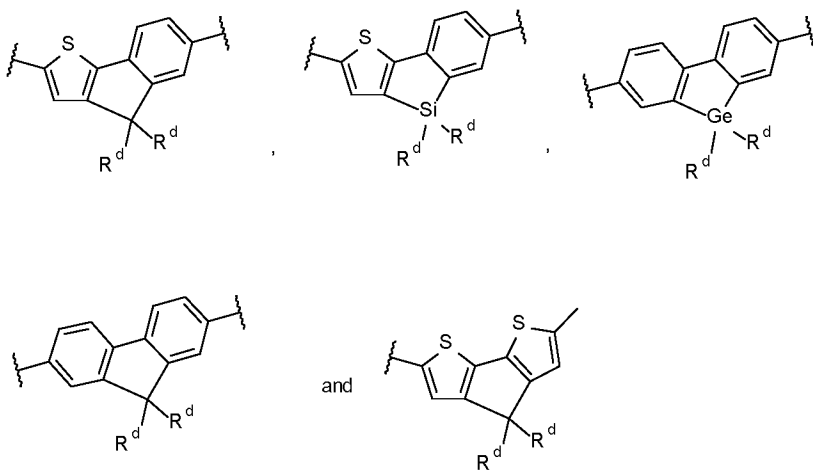
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Examples of heteroarylene are





5 Examples of adjacent  $Ar^7$ , which are connected via an  $CR^dR^d$ ,  $SiR^dR^d$  or  $GeR^dR^d$  linker, wherein  $R^d$  is at each occurrence H,  $C_{1-30}$ -alkyl or aryl, which  $C_{1-30}$ -alkyl and aryl can be substituted with one or more  $C_{1-20}$ -alkyl, O- $C_{1-20}$ -alkyl or phenyl, and c is at each occurrence an integer from 1 to 8, are

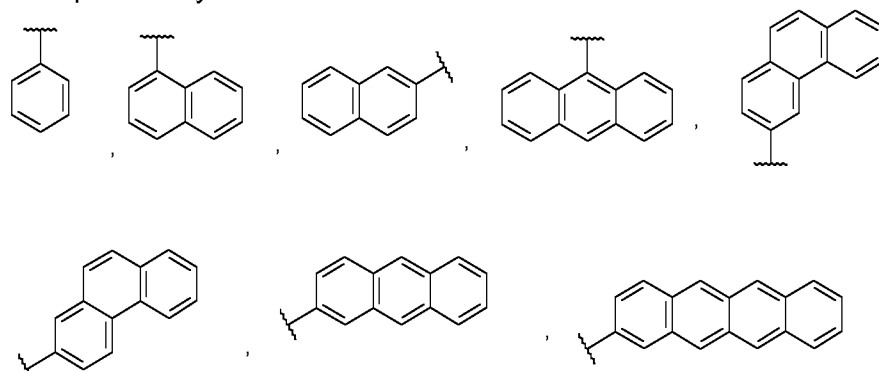


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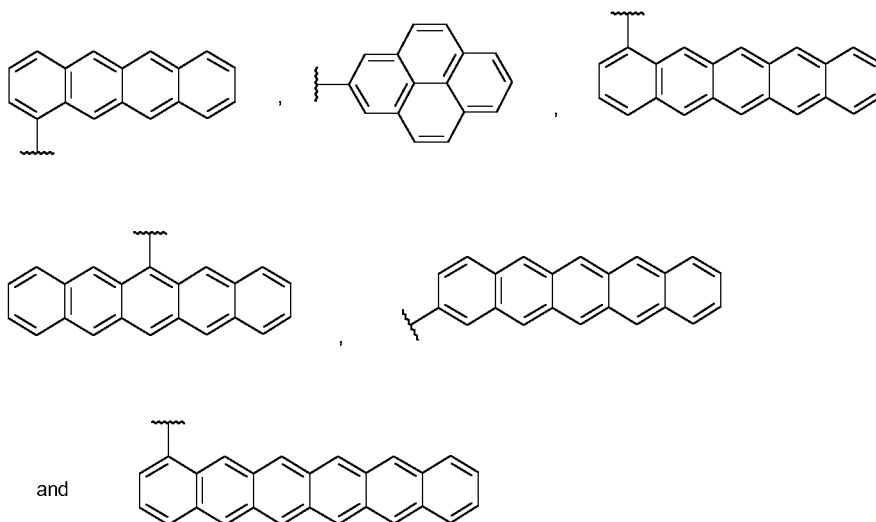
Aryl is a monovalent aromatic ring system, consisting of one aromatic ring or of two to eight condensed aromatic rings, wherein all rings are formed from carbon atoms. Preferably, aryl is a monovalent aromatic ring system consisting of one aromatic ring or of two to four condensed aromatic rings, wherein all rings are formed from carbon atoms.

15

Examples of aryl are



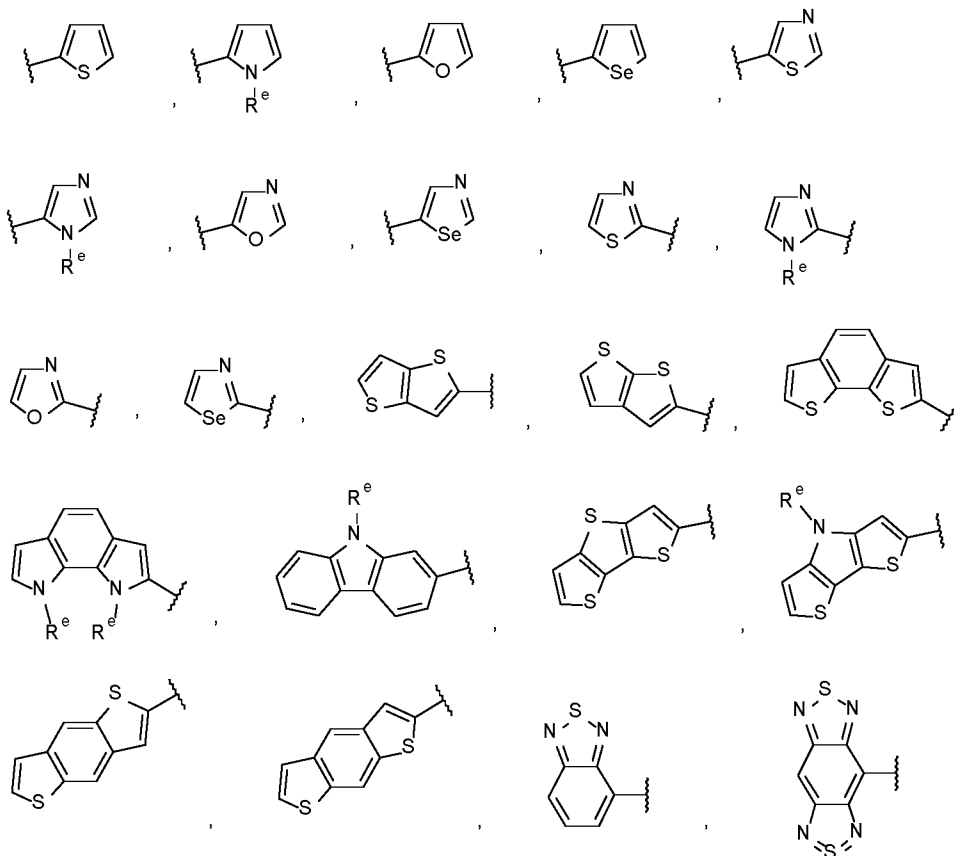
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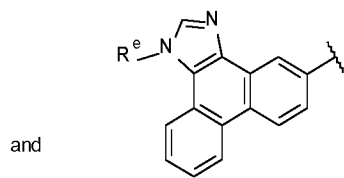
Heteroaryl is a monovalent aromatic ring system consisting of one aromatic ring or of two to eight condensed aromatic rings, wherein at least one aromatic ring contains at least one heteroatom selected from the group consisting of S, O, N and Se. Preferably, heteroaryl is a monovalent aromatic ring system consisting of one aromatic ring or of two to four condensed aromatic rings, wherein at least one aromatic ring contains at least one heteroatom selected from the group consisting of S, O, N and Se.

15 Examples of heteroaryl are

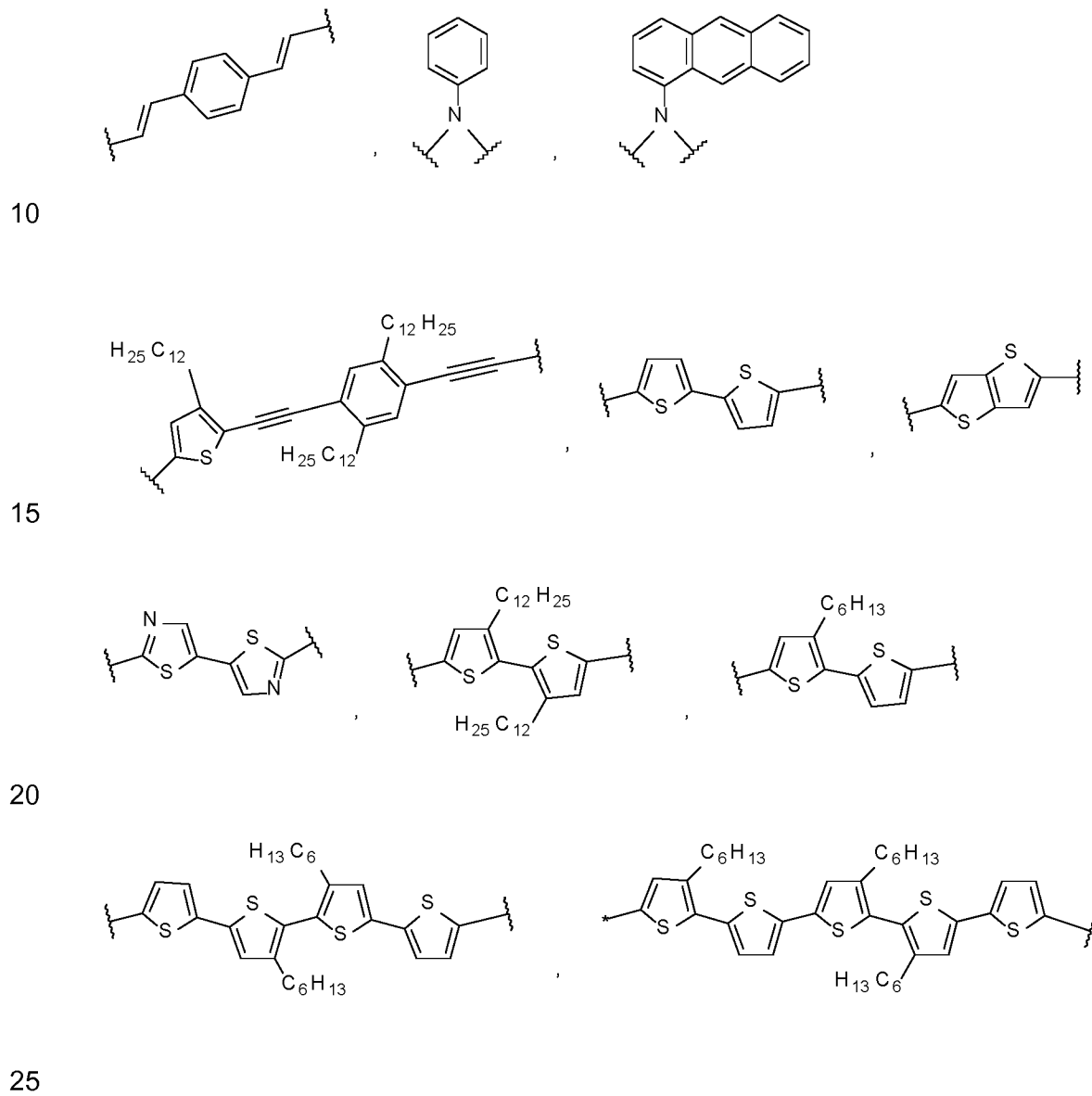


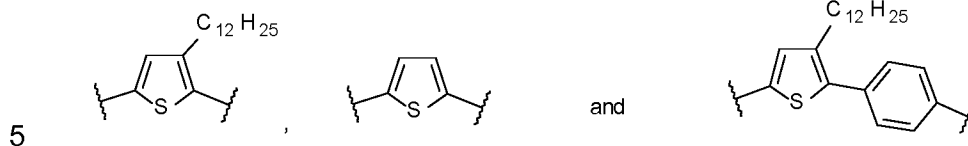
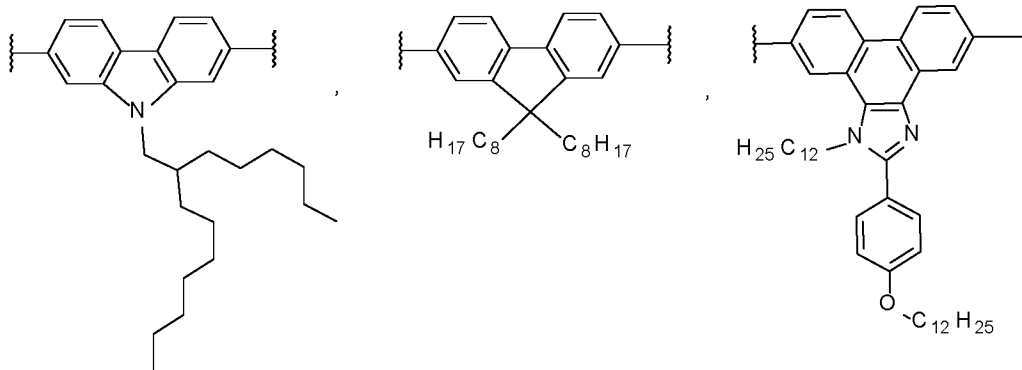
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5 Examples of L<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup> and L<sup>4</sup> are



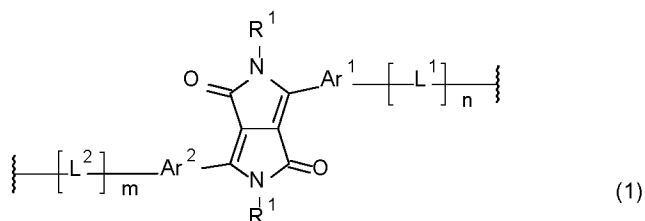


10 More preferably, the diketopyrrolopyrrole-based material is a diketopyrrolopyrrole-based polymer comprising units of formula (1) as defined above.

The diketopyrrolopyrrole-based polymers comprising units of formula (1) can comprise other conjugated units. The diketopyrrolopyrrole-based polymers comprising units of formula (1) can be homopolymers or copolymers. The copolymers can be random or block.

15 Preferably, the diketopyrrolopyrrole-based polymers comprise at least 50% by weight of units of formula (1) based on the weight of the polymer, more preferably at least 70%, even more preferably at least 90% by weight of units of formula (1) based on the weight of the polymer. Most preferably, diketopyrrolopyrrole-based polymers essentially consist of units of formula (1). The diketopyrrolopyrrole-based polymers essentially consisting of units of formula (1) can be homopolymers or copolymers.

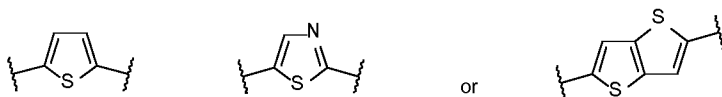
25 Even more preferably, the diketopyrrolopyrrole-based material is a diketopyrrolopyrrole-based polymer essentially consisting of units of formula



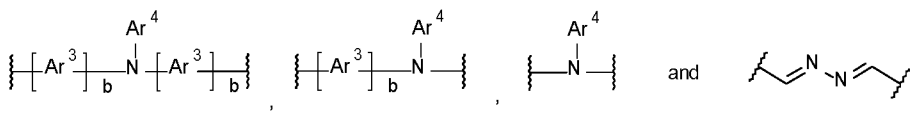
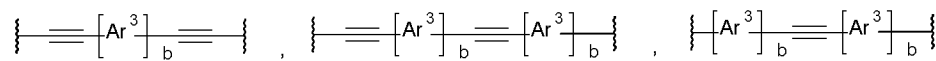
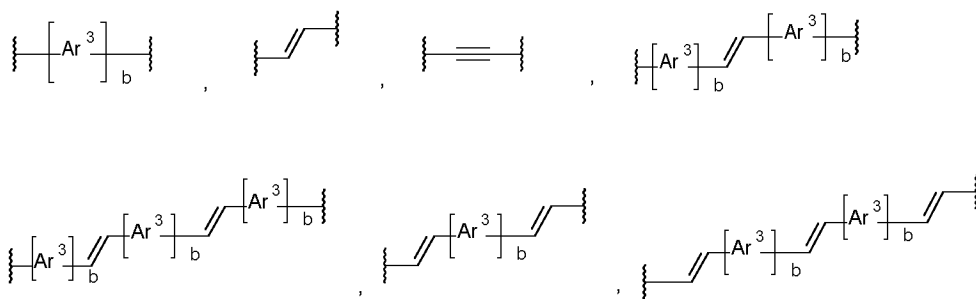
30 wherein  
R<sup>1</sup> is C<sub>6-30</sub>-alkyl,

n and m are independently 0 or 1, provided n and m are not both 0, and

35 Ar<sup>1</sup> and Ar<sup>2</sup> are independently



L<sup>1</sup> and L<sup>2</sup> are independently selected from the group consisting of

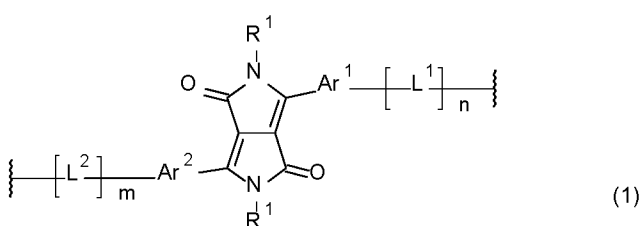


wherein  
 15 Ar<sup>3</sup> is at each occurrence arylene or heteroarylene, wherein arylene and heteroarylene can be substituted with one or more C<sub>1-30</sub>-alkyl, C<sub>2-30</sub>-alkenyl, C<sub>2-30</sub>-alkynyl, O-C<sub>1-30</sub>-alkyl, aryl or heteroaryl, which C<sub>1-30</sub>-alkyl, C<sub>2-30</sub>-alkenyl, C<sub>2-30</sub>-alkynyl, O-C<sub>1-30</sub>-alkyl, aryl and heteroaryl can be substituted with one or more C<sub>1-20</sub>-alkyl, O-C<sub>1-20</sub>-alkyl or phenyl;  
 20 and wherein adjacent Ar<sup>3</sup> can be connected via a CR<sup>b</sup>R<sup>b</sup>, SiR<sup>b</sup>R<sup>b</sup> or GeR<sup>b</sup>R<sup>b</sup> linker, wherein R<sup>b</sup> is at each occurrence H, C<sub>1-30</sub>-alkyl or aryl, which C<sub>1-30</sub>-alkyl and aryl can be substituted with one or more C<sub>1-20</sub>-alkyl, O-C<sub>1-20</sub>-alkyl or phenyl,

b is at each occurrence an integer from 1 to 8, and

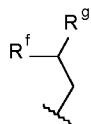
25 Ar<sup>4</sup> is at each occurrence aryl or heteroaryl, wherein aryl and heteroaryl can be substituted with one or more C<sub>1-30</sub>-alkyl, O-C<sub>1-30</sub>-alkyl or phenyl, which phenyl can be substituted with C<sub>1-20</sub>-alkyl or O-C<sub>1-20</sub>-alkyl.

30 Most preferably, the diketopyrrolopyrrole-based material is a diketopyrrolopyrrole-based polymer essentially consisting of units of formula



wherein  
 R<sup>1</sup> is

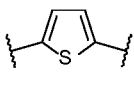




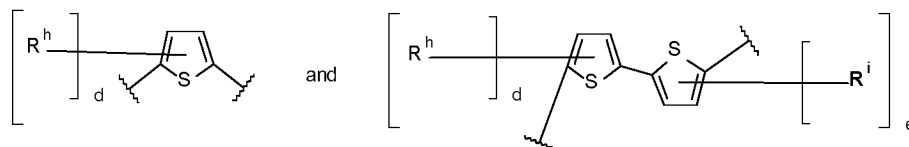
wherein  
 5 R<sup>f</sup> is linear C<sub>6-14</sub>-alkyl, and  
 R<sup>g</sup> is linear C<sub>2-12</sub>-alkyl,

n and m are independently 0 or 1, provided n and m are not both 0, and

10 Ar<sup>1</sup> and Ar<sup>2</sup> are

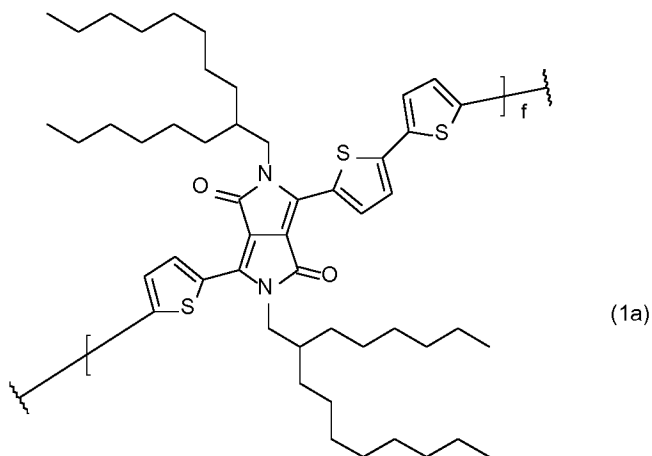


15 L<sup>1</sup> and L<sup>2</sup> are independently selected from the group consisting of



wherein  
 20 R<sup>h</sup> and R<sup>i</sup> are independently C<sub>6-30</sub>-alkyl, and  
 d and e are independently 0 or 1.

25 In particular, the diketopyrrolopyrrole-based material is a diketopyrrolopyrrole-based  
 polymer essentially consisting of units of formula



30 Preferably the second layer essentially consists of organic semiconducting material.

The second layer can have a thickness of 5 to 500 nm, preferably of 10 to 100 nm,  
 35 more preferably of 20 to 50 nm.

The organic field effect transistor of the present invention usually also comprises a dielectric layer, a gate electrode and source and drain electrodes. In addition, the

organic field effect transistor of the present invention can comprise other layers such as a self-assembled monolayers (SAMs) or adhesion layers.

5 The dielectric layer can comprise any dielectric material known in the art or mixtures thereof. The dielectric material can be silicon dioxide or aluminium oxide, or, an organic polymer such as polystyrene (PS) and polystyrene derived polymers, poly(methyl-methacrylate) (PMMA), poly(4-vinylphenol) (PVP), poly(vinyl alcohol) (PVA), benzo-cyclobutene (BCB), or polyimide (PI). The dielectric layer can have a thickness of 10 to 2000 nm, preferably of 50 to 1000 nm, more preferably of 100 to 800 nm.

10 The self-assembled monolayer can comprise organic silane derivates or organic phosphoric acid derivatives. An example of an organic silane derivative is octyltrichlorosilane. An examples of an organic phosphoric acid derivative is decylphosphoric acid.

15 The source/drain electrodes can be made from any suitable organic or inorganic source/drain material. Examples of inorganic source/drain materials are gold (Au), silver (Ag) or copper (Cu), as well as alloys comprising at least one of these metals. The source/drain electrodes can have a thickness of 1 to 100 nm, preferably from 20 to 20 70 nm.

25 The gate electrode can be made from any suitable gate material such as highly doped silicon, aluminium (Al), tungsten (W), indium tin oxide or gold (Au), or alloys comprising at least one of these metals. The gate electrode can have a thickness of 1 to 200 nm, preferably from 5 to 100 nm.

30 The substrate can be any suitable substrate such as glass, or a plastic substrate such as polyethersulfone, polycarbonate, polysulfone, polyethylene terephthalate (PET) and polyethylene naphthalate (PEN). Depending on the design of the organic field effect transistor, the gate electrode, for example highly doped silicon can also function as substrate.

35 The organic field effect transistor of the present invention can be a bottom-gate organic field effect transistor or a top-gate organic field effect transistor. Preferably, it is a bottom-gate organic field effect transistor.

40 Preferably, the organic field effect transistor of the present invention is a bottom-gate organic field effect transistor, wherein the second layer of the double layer is on top of the first layer of the double layer.

45 Preferably, the organic field effect transistor of the present invention is a bottom-gate organic field effect transistor, wherein the second layer of the double layer is on top of the first layer of the double layer, and wherein the first layer of the double layer is on top of an adhesion layer.

50 The adhesion layer can comprise any material suitable for improving the adhesion of the first layer. Preferably, the adhesion layer comprises at least one poly(amino acid). A poly(amino acid) is a polymer formed by polymerization of monomers comprising a carboxylic acid group or a carboxylic acid derivative group and an amino group. Preferably, the poly(amino acid) is hydrophilic. More preferably, the poly(amino acid) is polylysine, most preferably poly-L-lysine. Preferably, the poly(amino acid) layer is formed by immersion dip coating using a solution of the poly(amino acid) in a suitable solvent such as water. The concentration of the poly(amino acid) in the water can be in the range of 0.001 to 10 weight%, preferably in the range of 0.01 to 1 weight%. The 55 poly(amino acids) can be formed by methods known in the art such as by polymerization of monomers comprising a carboxylic acid group or a carboxylic acid derivative group and an amino group. Alternatively, many poly(amino acids) are also commercially available, such as poly-L-lysine from Sigma Aldrich.

60 Also part of the present invention is a process for the preparation of the organic field effect transistor of the present invention comprising the steps of

65 i) depositing a composition comprising single-walled carbon nanotubes having a content of at least 95% by weight of semiconducting single-walled carbon nanotubes in order to form a first layer comprising a percolating network of single-

walled carbon nanotubes having a content of at least 95% by weight of semiconducting single-walled carbon nanotubes, and

- 5 ii) depositing a composition comprising organic semiconducting material in order to form a second layer comprising an organic semiconducting material.

10 The composition comprising single-walled carbon nanotubes having a content of at least 95% by weight of semiconducting single-walled carbon nanotubes usually comprises one or more solvents and additional material. The additional material is defined above. The solvent can be any suitable solvent such as N-methyl-2-pyrrolidone, o-dichlorobenzene, chloroform, 1-cyclohexyl-2-pyrrolidinone, water or toluene. Preferably, the solvent is water.

15 The concentration of the single-walled carbon nanotubes in the composition can be in the range of 1 to 0.000001 weight%, preferably in the range of 0.01 to 0.0001 weight%. The composition comprising single-walled carbon nanotubes can be a dispersion or a solution, preferably, the composition is a solution.

20 The composition comprising single-walled carbon nanotubes can be deposited by any suitable method known in the art. Preferably, the composition is deposited by solution depositing techniques such as drop-casting, blade-coating, ink-jet printing and spin-coating. The deposition can be performed one time or several times. Preferably, the composition is deposited several, for example three, times. After the deposition, the deposited single-walled carbon nanotubes can be dried at elevated temperature such as temperatures in the range of 80 to 110°C, followed by rinsing with water in order to remove not deposited single-walled carbon nanotubes, followed by annealing at elevated temperatures such as 120 to 180°C. If additional materials are present in the composition, the composition can, after deposition, also be heated in order to remove the additional materials.

The composition comprising organic semiconducting material can also comprise one or more solvents. The solvent of the composition can be any suitable solvent such as toluene or o-xylene.

35 The concentration of the organic semiconducting material in the composition can be in the range of 0.01 to 5 weight%, preferably, in the range of 0.1 to 3 weight %, more preferably, in the range of 0.5 to 1.5 weight%. The composition comprising the organic semiconducting material can be a dispersion or a solution, preferably, it is a solution.

40 The composition comprising the organic semiconducting material can be deposited by any suitable method known in the art. Preferably, the composition is deposited by solution deposition techniques such as spin-coating, drop-coating, dip-coating, blade-coating or inkjet printing.

45 For example, a bottom-gate, top-contact (BGTC) organic field effect transistor of the present invention can be prepared as outlined in Figure 1. Heavily doped SiO<sub>2</sub> substrate (200 nm thickness), which also functions as gate dielectric, can be cleaned by various solvents using sonication (Figure 1a). Then, O<sub>2</sub> plasma can be applied to make the top surface hydrophilic (Figure 1b) and a poly(amino acid) solution such as an aqueous poly-L-lysine solution can be deposited, for example by immersion dip coating (Figure 1c). After rinsing the top surface with deionized water and drying at elevated temperature, a solution of single walled semiconducting carbon nanotubes (SWCNT) having a content of at least 80% by weight of semiconducting single-walled carbon nanotubes can be deposited, for example by drop casting, followed by drying at elevated temperature. The deposition of the solution of the single walled carbon nanotubes can be repeated twice (Figure 1d). After rinsing the top surface with deionized water and annealing the semiconducting single walled carbon nanotube layer at elevated temperature, a solution of the organic semiconducting (OSC) material can be deposited, for example by blade-coating at elevated temperatures (Figure 1e). Finally, source (S) and drain (D) electrode, for example of Au, can be deposited by thermal evaporation (Figure 1f). A passivation layer may optionally be deposited on the source and drain electrodes.

65

The organic field effect transistors of the present invention are particularly advantageous as the transistors show high mobilities and low hysteresis.

5 The organic field effect transistors of the present are advantageous in that the transistors can be prepared by solution deposition techniques which allow the production of large areas.

10 The organic field effect transistors of the present are also advantageous in that the transistors show reproducible performances when produced under ambient conditions with regard to air and humidity, and also stable performance over time when stored under ambient conditions with regard to air and humidity.

15 Figure 1 shows a process for the preparation of a bottom-gate, top-contact (BGTC) organic field effect transistor of the present invention comprising a double layer consisting of i) a first layer comprising a percolating network of single-walled carbon nanotubes (SWCNT) having a content of at least 95% by weight of semiconducting single-walled carbon nanotubes, and ii) a second layer comprising an organic semiconducting material (OSC).

20 Figure 2 shows a field emission scanning electron microscope (FESEM) image of a first layer comprising a percolating network of single walled carbon nanotubes having a content of 99.9% by weight of semiconducting single-walled carbon nanotubes prepared by drop casting a commercially available single-walled carbon nanotube composition (IsoNanotubes-S™ having a content of semiconducting single-walled carbon nanotubes of 99.9%, from Nanointegris Inc., concentration of SWCNT in the solution was 0.001 wt%, diameter range: 1.2 to 1.7 nm, length range: 300 nm to 5 μm) on a poly-L-lysine adhesion layer.

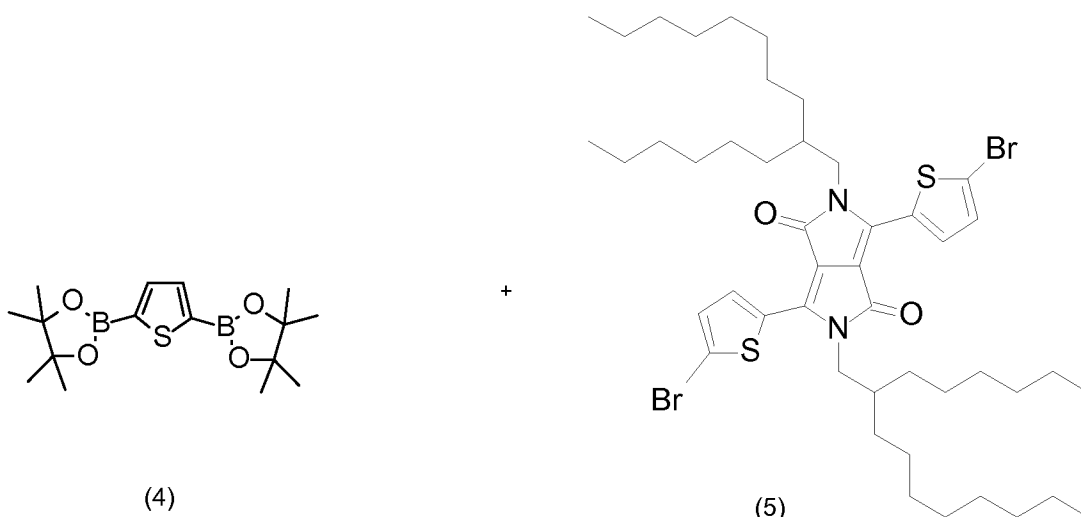
30 Figure 3 shows the transfer characteristics drain current ( $I_d$ ) against gate-source voltage ( $V_g$ ) of the bottom-gate, top-contact (BGTC) organic field effect transistor of example 2 comprising polymer **1a** as organic semiconducting material in the saturation regime, while the gate voltage was scanned from 10 to -30 V.

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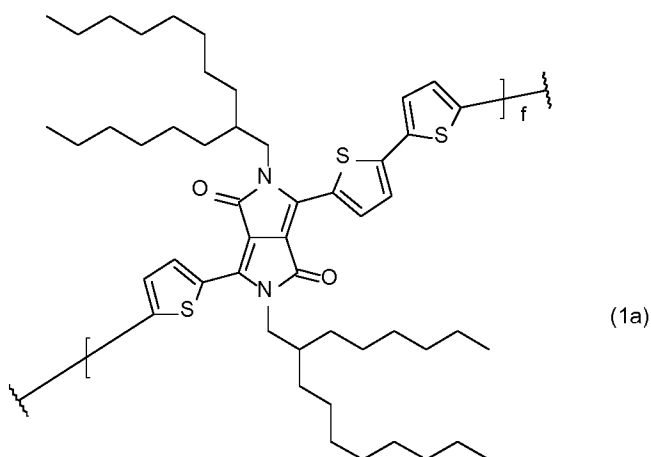
#### Examples

##### Example 1

Preparation of semiconducting polymer of formula 1a



40



733 mg (2.181 mmol) of compound **4**, 1972mg (2.181 mmol) of compound **5**, 78.30 mg of tris(dibenzylideneacetone)dipalladium(0) ( $\text{Pd}_2(\text{dba})_3$ ) and 48.15 mg of tri-tert-butylphosphonium tetrafluoroborate ( $((\text{tert-Bu})_3\text{P} \times \text{HBF}_4)$ ) are placed together in 50 ml of tetrahydrofuran under Argon. The reaction mixture is heated to reflux, and then 1600 mg potassium phosphate in 5 ml of degassed water is added. The reaction mixture is refluxed overnight. Then, the reaction mixture is poured on water and the precipitate is filtered and washed with water and methanol. The precipitate is then Soxhlet fractionated with heptane, tetrahydrofuran, toluene, chloroform and chlorobenzene. To remove catalyst residues, the selected fraction is evaporated and the residue is dissolved in 150 ml of chlorobenzene. Then 50 ml of a 1% NaCN aqueous solution is added and the mixture is heated and stirred overnight at reflux. The phases are separated and the organic phase is washed 3 times with 10 ml of deionized water for 3 hours at reflux. Polymer **1a** is then precipitated from the organic phase by addition of methanol. The precipitated polymer **1a** is filtered, washed with methanol and dried. UV-VIS-absorption spectrum:  $\lambda_{\text{max}}$ : 840 nm (film) and 840 nm ( $10^{-5}$  M solution in toluene).

## 20 Example 2

Preparation of a bottom-gate, top-contact (BGTC) organic field effect transistor comprising a double layer consisting of a first layer essentially consisting of a percolating network of single-walled carbon nanotubes having a content of semiconducting single-walled carbon nanotubes of 99.9%, and a second layer essentially consisting of the diketopyrrolopyrrole-based polymer **1a** of example 1

A bottom-gate, top-contact (BGTC) thin film transistor (TFT) with channel length (50  $\mu\text{m}$ ) and width (500  $\mu\text{m}$ ) was prepared. Heavily doped Si substrate (200 nm of  $\text{SiO}_2$  thickness) was cleaned by acetone, isopropanol and deionized water using sonication for 1 min each time. Then,  $\text{O}_2$  plasma was applied (100 sccm, 50 W for 60 sec) to make the surface hydrophilic. To enhance the adhesiveness of the surface to single-walled carbon nanotubes, poly-L-lysine solution (0.1 % w/v in water, Sigma Aldrich) was deposited by immersion technique for 5 min. Then, the surface was thoroughly rinsed with deionized water and dried at 95  $^\circ\text{C}$  on a hot plate for 1 min. Commercially available purified aqueous single-walled carbon nanotubes (SWCNT) solution (IsoNanotubes-S<sup>TM</sup> having a content of semiconducting single-walled carbon nanotubes of 99.9%, from Nanointegris Inc., concentration of SWCNT in the solution was 0.001 wt%, diameter range: 1.2 to 1.7 nm, length range: 300 nm to 5  $\mu\text{m}$ ) was deposited by drop casting onto the surface and baked at 95  $^\circ\text{C}$  on a hot plate for 3 min. The drop casting depositing of the SWCNT solution was repeated twice. After having placed the substrate with deposited SWCNTs in the air for 10 min, the substrate was dried 3 min at 95  $^\circ\text{C}$  on hot plate, followed by rinsing with water, carefully drying with  $\text{N}_2$  gas and annealing at 150  $^\circ\text{C}$  on a hot plate for 1 h. A solution of 0.75 wt% semiconducting polymer of formula 1a of example 1 in toluene was blade-coated onto the SWCNT layer at 120  $^\circ\text{C}$ . The gap and speed of the blade coater was 100  $\mu\text{m}$  and 30 mm/sec, respectively. Finally, source and drain electrode of Au were deposited (50 nm of thickness) by thermal evaporation.

A field emission scanning electron microscope (FESEM) image of the first layer essentially consisting of a percolating network of single-walled carbon nanotubes having a content of 99.9% by weight of semiconducting single-walled carbon nanotubes on the poly-L-lysine adhesion layer is shown in Figure 2.

5

### Example 3

Electrical characterization of the bottom-gate, top-contact (BGTC) organic field effect transistor of example 2

10 The electrical characterization of the BGTC organic field effect transistor of example 2 was conducted under ambient condition at room temperature using Keithley 4200-SCS.

Figure 3 shows the transfer characteristics drain current ( $I_d$ ) against gate-source voltage ( $V_g$ ) of the BGBC TFT of example 2 in the saturation regime, while the gate voltage was scanned from 10 to -30 V.

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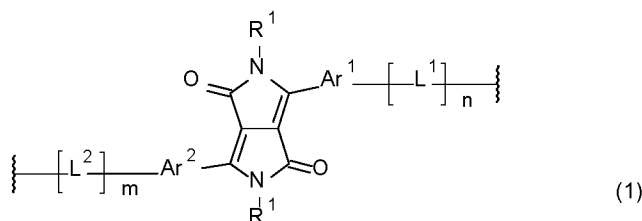
The saturation field effect mobility of the bilayer structure in active layer is  $58 \text{ cm}^2/\text{Vs}$ . The  $I_{on}/I_{off}$  is  $10^3$ .

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## Claims

1. An organic field effect transistor comprising a double layer consisting of  
 5 i) a first layer comprising a percolating network of single-walled carbon nanotubes having a content of at least 95% by weight of semiconducting single-walled carbon nanotubes, and  
 ii) a second layer comprising an organic semiconducting material.
- 10 2. The organic field effect transistor of claim 2, wherein the percolating network of single-walled carbon nanotubes have a content of at least 99% by weight of semiconducting single-walled carbon nanotubes.
- 15 3. The organic field effect transistor of any of claims 1 to 2, wherein the first layer essentially consists of a percolating network of single-walled carbon nanotubes.
4. The organic field effect transistor of any of claims 1 to 3, wherein the single-walled carbon nanotubes have a diameter of 0.5 to 3 nm, and a length in the range of 0.1 to 100  $\mu\text{m}$ .
- 20 5. The organic field effect transistor any of claims 1 to 4, wherein the organic semiconducting material is at least one diketopyrrolopyrrole-based material.
6. The organic field effect transistor of claim 5, wherein the diketopyrrolopyrrole-based material is  
 25 i) a diketopyrrolopyrrole-based polymer comprising units of formula

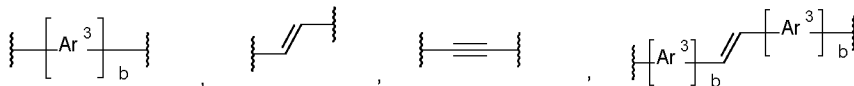


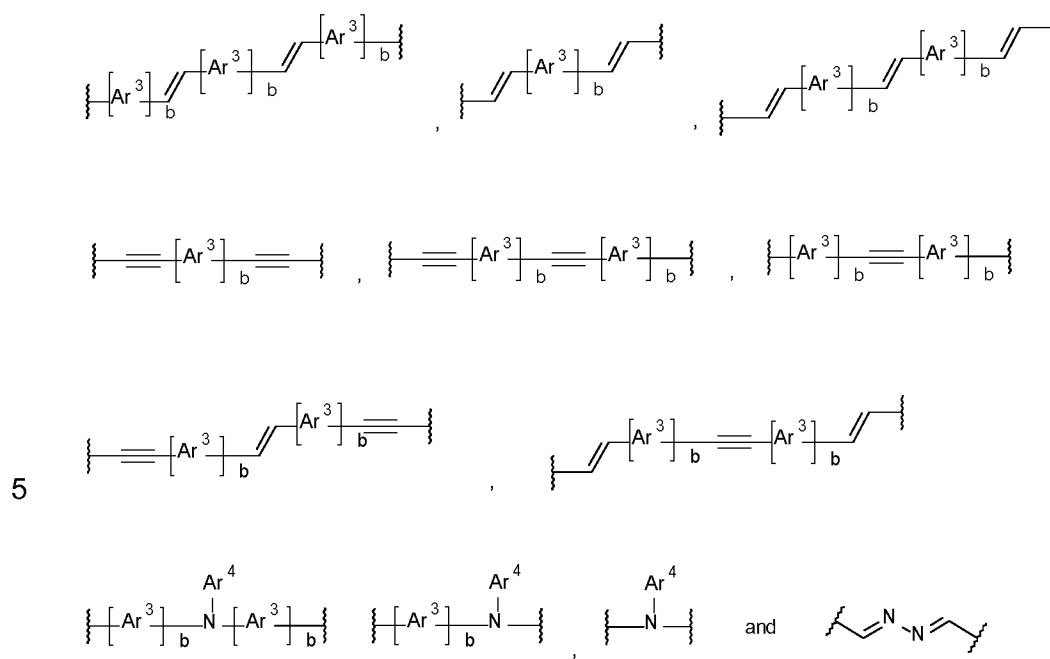
- 30 wherein  
 $R^1$  is at each occurrence  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl or  $C_{2-30}$ -alkynyl, wherein  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl and  $C_{2-30}$ -alkynyl can be substituted by one or more  $-\text{Si}(\text{R}^a)_3$  or  $-\text{OSi}(\text{R}^a)_3$ , or one or more  $\text{CH}_2$  groups of  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl and  $C_{2-30}$ -alkynyl can be replaced by  $-\text{Si}(\text{R}^a)_2-$  or  $-\text{[Si}(\text{R}^a)_2\text{-O]}_a\text{-Si}(\text{R}^a)_2-$ ,  
 35 wherein  $\text{R}^a$  is at each occurrence  $C_{1-10}$ -alkyl, and a is an integer from 1 to 20,

n and m are independently 0 or 1, and

- 40  $\text{Ar}^1$  and  $\text{Ar}^2$  are independently arylene or heteroarylene, wherein arylene and heteroarylene can be substituted with one or more  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl,  $\text{O}-C_{1-30}$ -alkyl, aryl or heteroaryl, which  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl,  $\text{O}-C_{1-30}$ -alkyl, aryl and heteroaryl can be substituted with one or more  $C_{1-20}$ -alkyl,  $\text{O}-C_{1-20}$ -alkyl or phenyl,

- 45  $L^1$  and  $L^2$  are independently selected from the group consisting of





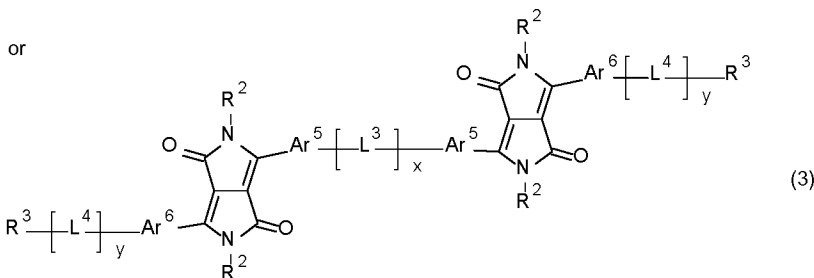
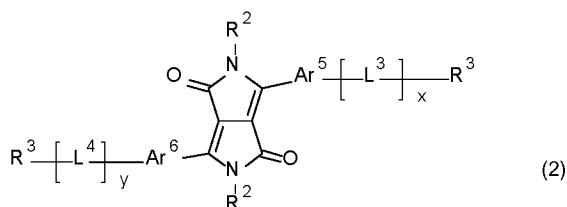
wherein  $Ar^3$  is at each occurrence arylene or heteroarylene, wherein arylene and heteroarylene can be substituted with one or more  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl,  $O-C_{1-30}$ -alkyl, aryl or heteroaryl, which  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl,  $O-C_{1-30}$ -alkyl, aryl and heteroaryl can be substituted with one or more  $C_{1-20}$ -alkyl,  $O-C_{1-20}$ -alkyl or phenyl; and wherein adjacent  $Ar^3$  can be connected via a  $CR^bR^b$ ,  $SiR^bR^b$  or  $GeR^bR^b$  linker,

b is at each occurrence an integer from 1 to 8, and

$Ar^4$  is at each occurrence aryl or heteroaryl, wherein aryl and heteroaryl can be substituted with one or more  $C_{1-30}$ -alkyl,  $O-C_{1-30}$  alkyl or phenyl, which phenyl can be substituted with  $C_{1-20}$ -alkyl or  $O-C_{1-20}$ -alkyl,

or

ii) a diketopyrrolopyrrole-based small molecule of formulae



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wherein

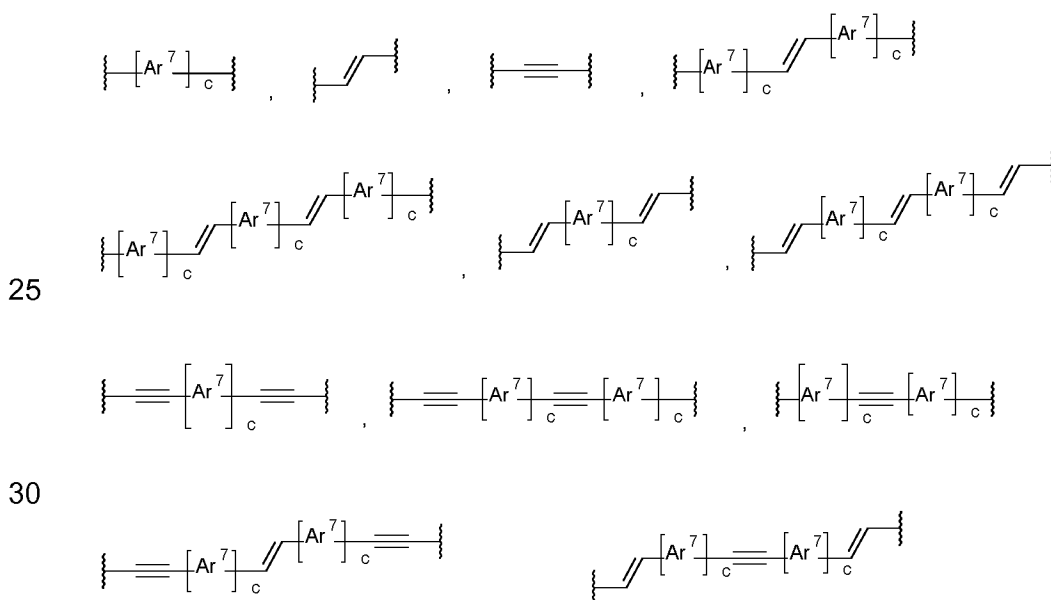
- 5  $R^2$  is at each occurrence  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl or  $C_{2-30}$ -alkynyl, wherein  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl and  $C_{2-30}$ -alkynyl can be substituted by  $-\text{Si}(\text{R}^c)_3$  or  $-\text{OSi}(\text{R}^c)_3$ , or one or more  $\text{CH}_2$  groups of  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl and  $C_{2-30}$ -alkynyl can be replaced by  $-\text{Si}(\text{R}^c)_2-$  or  $-\text{[Si}(\text{R}^c)_2\text{-O]}_a-\text{Si}(\text{R}^c)_2-$ , wherein  $\text{R}^c$  is at each occurrence  $C_{1-10}$ -alkyl, and  $a$  is an integer from 1 to 20,

- 10  $R^3$  is H, CN,  $C_{1-20}$ -alkyl,  $C_{2-20}$ -alkenyl,  $C_{2-20}$ -alkynyl, O- $C_{1-20}$  alkyl, aryl or heteroaryl, which  $C_{1-20}$ -alkyl,  $C_{2-20}$ -alkenyl,  $C_{2-20}$ -alkynyl, O- $C_{1-20}$  alkyl, aryl and heteroaryl can be substituted with one or more  $C_{1-6}$ -alkyl, O- $C_{1-6}$ -alkyl or phenyl,

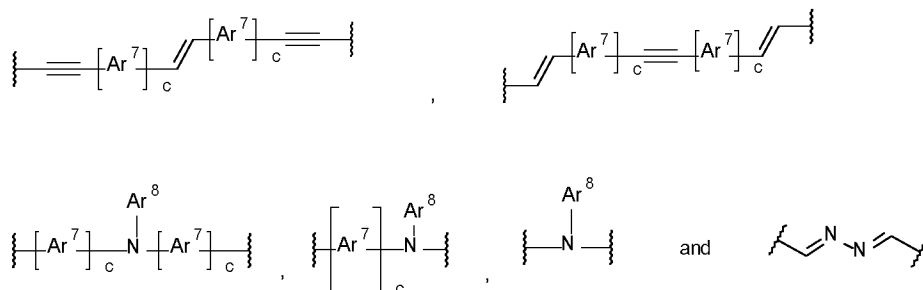
$x$  and  $y$  are independently 0 or 1, and

- 15  $\text{Ar}^5$  and  $\text{Ar}^6$  are independently arylene or heteroarylene, wherein arylene and heteroarylene can be substituted with one or more  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl, O- $C_{1-30}$ -alkyl, aryl or heteroaryl, which  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl, O- $C_{1-30}$ -alkyl, aryl and heteroaryl can be substituted with one or more  $C_{1-20}$ -alkyl, O- $C_{1-20}$ -alkyl or phenyl;

- 20  $L^3$  and  $L^4$  are independently selected from the group consisting of



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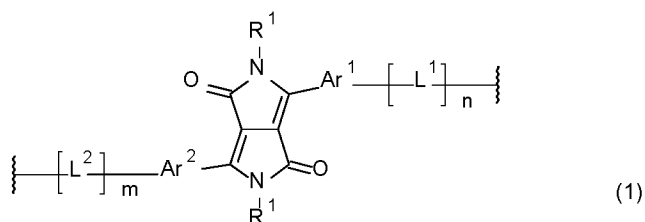
wherein

- 40  $\text{Ar}^7$  is at each occurrence arylene or heteroarylene, wherein arylene and heteroarylene can be substituted with one or more  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl, O- $C_{1-30}$ -alkyl, aryl or heteroaryl, which  $C_{1-30}$ -alkyl,  $C_{2-30}$ -alkenyl,  $C_{2-30}$ -alkynyl, O- $C_{1-30}$ -alkyl, aryl and heteroaryl can be substituted with one or more  $C_{1-20}$ -alkyl, O- $C_{1-20}$ -alkyl or phenyl; and wherein adjacent  $\text{Ar}^7$  can be connected via an  $\text{CR}^d\text{R}^d$ ,  $\text{SiR}^d\text{R}^d$  or  $\text{GeR}^d\text{R}^d$  linker, wherein  $\text{R}^d$  is at each occurrence H,  $C_{1-30}$ -alkyl or aryl, which  $C_{1-30}$ -alkyl and aryl can be substituted with one or more  $C_{1-20}$ -alkyl, O- $C_{1-20}$ -alkyl or phenyl,

- 45  $c$  is at each occurrence an integer from 1 to 8, and

$\text{Ar}^8$  is at each occurrence aryl or heteroaryl, wherein aryl and heteroaryl can be substituted with one or more  $C_{1-30}$ -alkyl, O- $C_{1-30}$ -alkyl or phenyl, which phenyl can be substituted with  $C_{1-20}$ -alkyl or O- $C_{1-20}$ -alkyl.

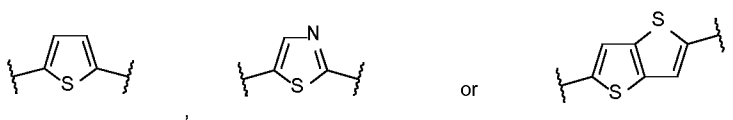
7. The organic field effect transistor of claim 6, wherein the diketopyrrolopyrrole-based material is a diketopyrrolopyrrole-based polymer comprising units of formula (1) as defined in claim 6.
8. The organic field effect transistor of claim 7, wherein the diketopyrrolopyrrole-based material is a diketopyrrolopyrrole-based polymer essentially consisting of units of formula (1) as defined in claim 6.
9. The organic field effect transistor of claim 8, wherein the diketopyrrolopyrrole-based materials is a diketopyrrolopyrrole-based polymer essentially consisting of units of formula



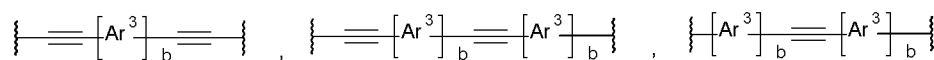
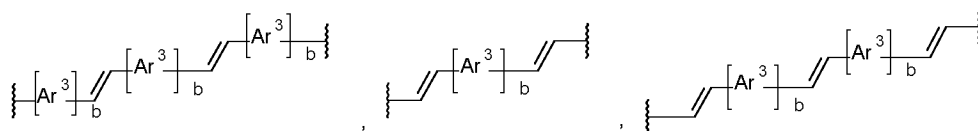
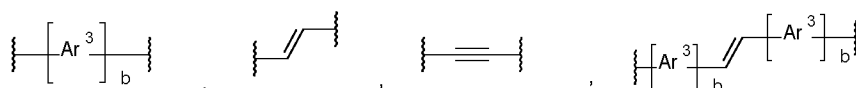
wherein  
R<sup>1</sup> is C<sub>6-30</sub>-alkyl,

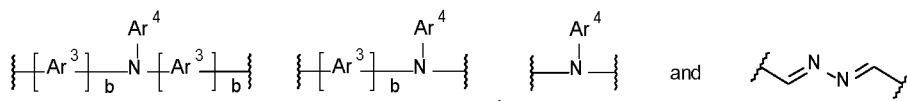
n and m are independently 0 or 1, provided n and m are not both 0, and

Ar<sup>1</sup> and Ar<sup>2</sup> are independently



L<sup>1</sup> and L<sup>2</sup> are independently selected from the group consisting of





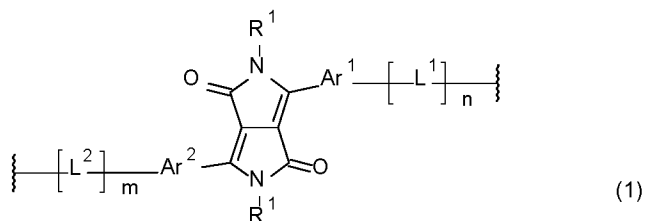
wherein

- 5 Ar<sup>3</sup> is at each occurrence arylene or heteroarylene, wherein arylene and heteroarylene can be substituted with one or more C<sub>1-30</sub>-alkyl, C<sub>2-30</sub>-alkenyl, C<sub>2-30</sub>-alkynyl, O-C<sub>1-30</sub>-alkyl, aryl or heteroaryl, which C<sub>1-30</sub>-alkyl, C<sub>2-30</sub>-alkenyl, C<sub>2-30</sub>-alkynyl, O-C<sub>1-30</sub>-alkyl, aryl and heteroaryl can be substituted with one or more C<sub>1-20</sub>-alkyl, O-C<sub>1-20</sub>-alkyl or phenyl; and wherein adjacent Ar<sup>3</sup> can be connected via a CR<sup>b</sup>R<sup>b</sup>, SiR<sup>b</sup>R<sup>b</sup> or GeR<sup>b</sup>R<sup>b</sup> linker,
- 10 wherein R<sup>b</sup> is at each occurrence H, C<sub>1-30</sub>-alkyl or aryl, which C<sub>1-30</sub>-alkyl and aryl can be substituted with one or more C<sub>1-20</sub>-alkyl, O-C<sub>1-20</sub>-alkyl or phenyl,

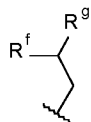
b is at each occurrence an integer from 1 to 8, and

- 15 Ar<sup>4</sup> is at each occurrence aryl or heteroaryl, wherein aryl and heteroaryl can be substituted with one or more C<sub>1-30</sub>-alkyl, O-C<sub>1-30</sub>-alkyl or phenyl, which phenyl can be substituted with C<sub>1-20</sub>-alkyl or O-C<sub>1-20</sub>-alkyl.

10. The organic field effect transistor of claim 9, wherein the diketopyrrolopyrrole-based materials is a diketopyrrolopyrrole-based polymer essentially consisting of
- 20 units of formula



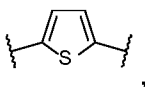
- 25 wherein R<sup>1</sup> is



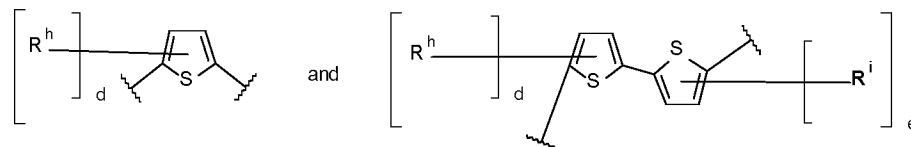
- 30 wherein R<sup>f</sup> is C<sub>6-14</sub>-alkyl, and R<sup>g</sup> is C<sub>2-12</sub>-alkyl,

n and m are independently 0 or 1, provided n and m are not both 0, and

- 35 Ar<sup>1</sup> and Ar<sup>2</sup> are



- 40 L<sup>1</sup> and L<sup>2</sup> are independently selected from the group consisting of

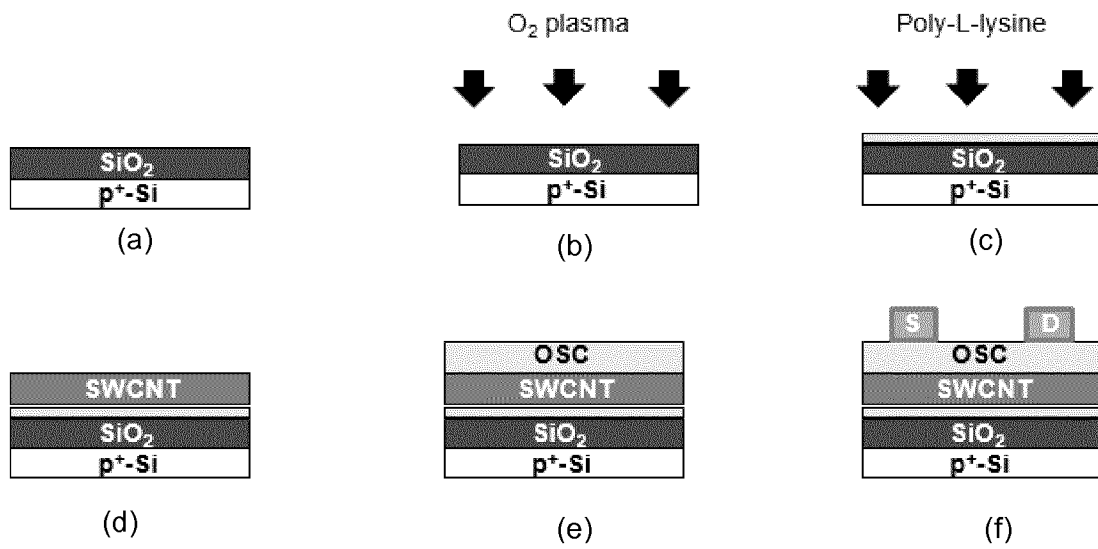


wherein

R<sup>h</sup> and R<sup>i</sup> are independently C<sub>6-30</sub>-alkyl, and d and e are independently 0 or 1.

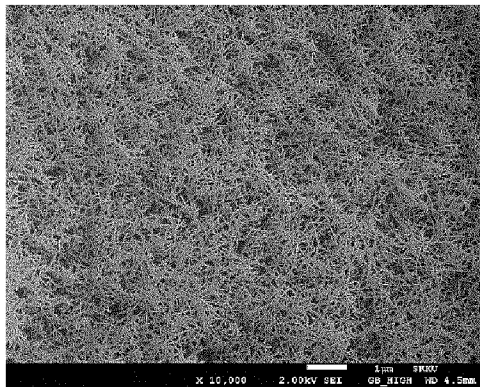
- 5 11. The organic field effect transistor of any of claims 1 to 10, wherein the organic field effect transistor is a bottom-gate organic field effect transistor.
12. The organic field effect transistor of claim 11, wherein the second layer of the double layer is on top of the first layer of the double layer.
- 10 13. The organic field effect transistor of claim 12, wherein the first layer of the double layer is on top of an adhesion layer.
- 15 14. A process for the preparation of the organic field effect transistor of claim 1 comprising the steps of
- 20 i) depositing a composition comprising single-walled carbon nanotubes having a content of at least 95% by weight of semiconducting single-walled carbon nanotubes in order to form a first layer comprising a percolating network of single-walled carbon nanotubes having a content of at least 95% by weight of semiconducting single-walled carbon nanotubes, and
- 25 ii) depositing a composition comprising organic semiconducting material in order to form a second layer comprising an organic semiconducting material.

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10 Figure 1.

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Figure 2.

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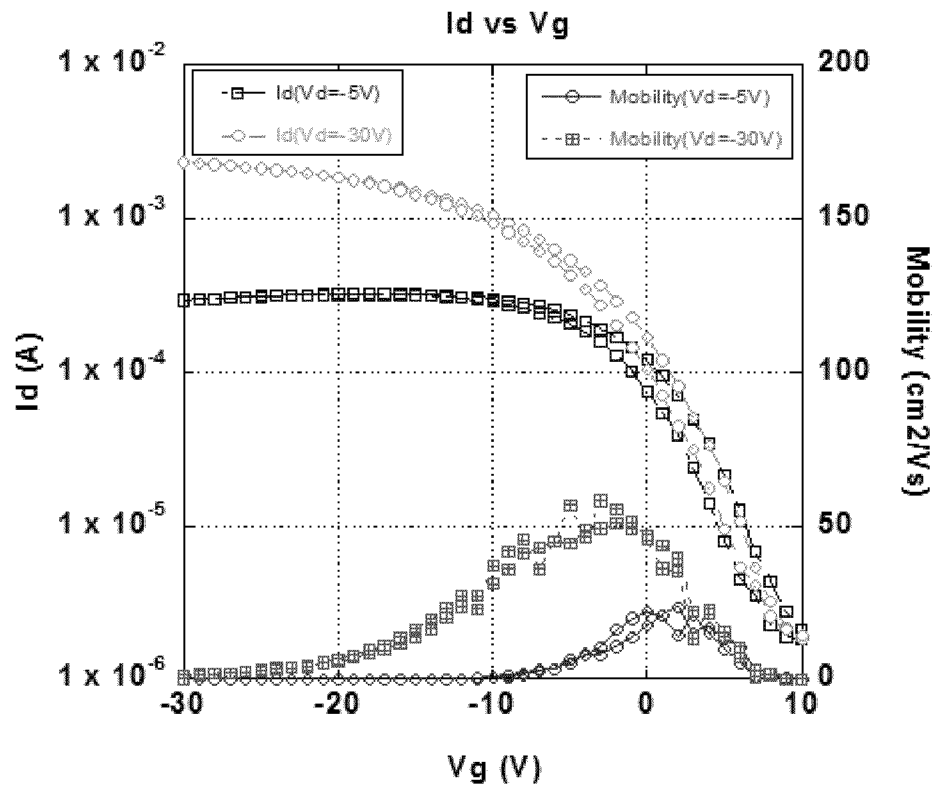


Figure 3.

INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2019/055522

A. CLASSIFICATION OF SUBJECT MATTER  
INV. H01L51/30  
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)  
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	US 2018/026214 A1 (TIAN XUEYAN [CN]) 25 January 2018 (2018-01-25)	1-4, 11-14
Y	paragraphs [0006] - [0013], [0035], [0061] - [0069]	5-10
	-----	
X	US 2017/141319 A1 (NOH YONG YOUNG [KR]) 18 May 2017 (2017-05-18)	1-4,11, 14
Y	paragraphs [0010] - [0013], [0036], [0072] - [0078]	5-10
	-----	
X	US 2012/187379 A1 (WU YILIANG [CA] ET AL) 26 July 2012 (2012-07-26)	1-9, 11-14
	1. Introduction; paragraphs [0030] - [0055], [0067] - [0068], [0088], [0095] - [0096]; figure 5	
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Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search  5 June 2019	Date of mailing of the international search report  13/06/2019
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Welter, Steve
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2019/055522

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>SMITHSON CHAD ET AL: "Using unsorted single-wall carbon nanotubes to enhance mobility of diketopyrrolopyrrole-quarterthiophene copolymer in thin-film transistors", ORGANIC ELECTRONICS, vol. 15, no. 11, 5 August 2014 (2014-08-05), pages 2639-2646, XP029076461, ISSN: 1566-1199, DOI: 10.1016/J.ORGEL.2014.07.021 1. Introduction; figure 5</p> <p style="text-align: center;">-----</p>	5-10



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/055522

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 2018026214	A1	25-01-2018	CN 105428401 A	23-03-2016
			US 2018026214 A1	25-01-2018
			WO 2017118093 A1	13-07-2017
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US 2017141319	A1	18-05-2017	KR 20150131432 A	25-11-2015
			US 2017141319 A1	18-05-2017
			WO 2015174749 A1	19-11-2015
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US 2012187379	A1	26-07-2012	DE 102012200896 A1	26-07-2012
			JP 2012156502 A	16-08-2012
			KR 20120085206 A	31-07-2012
			US 2012187379 A1	26-07-2012
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