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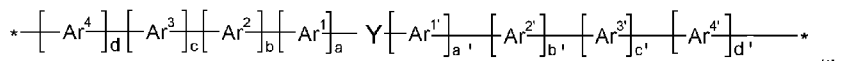
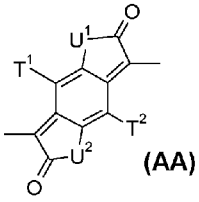
(54) **Title**: POLYMERS BASED ON BENZODIONES



(I),



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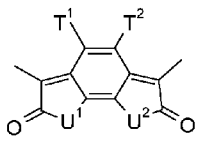

(BB)

(57) **Abstract**: The present invention relates to polymers comprising one or more (repeating) unit(s) of the formula (I): wherein Y is a group of formula (AA), or (BB) and their use as organic semiconductor in organic devices, especially in organic photovoltaics (solar cells) and photodiodes, or in a device containing a diode and/or an organic field effect transistor. The polymers according to the invention have excellent solubility in organic solvents and excellent film-forming properties. In addition, high efficiency of energy conversion, excellent field-effect mobility, good on/off current ratios and/or excellent stability can be observed, when the polymers according to the invention are used in organic field effect transistors, organic photovoltaics (solar cells) and photodiodes.

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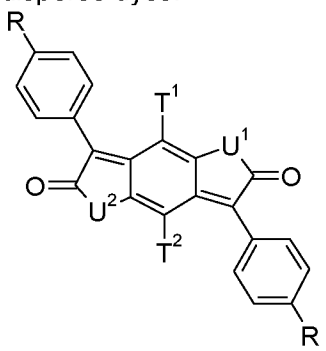
Polymers based on Benzodiones

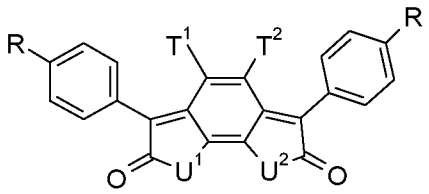
Description

The present invention relates to polymers comprising one or more (repeating) unit(s) of the formula I, and their use as organic semiconductor in organic devices, especially in organic photovoltaics (solar cells) and photodiodes, or in a device containing a diode and/or an organic field effect transistor. The polymers according to the invention have excellent solubility in organic solvents and excellent film-forming properties. In addition, high efficiency of energy conversion, excellent field-effect mobility, good on/off current ratios and/or excellent stability can be observed, when the polymers according to the invention are used in organic field effect transistors, organic photovoltaics (solar cells) and photodiodes.

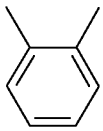
C. W. Greenhalgh et al., Journal of Dyers and Colourists 110 (1994) 178-183 describes the synthesis and properties of certain benzodifurane compounds as well as their application to disperse dyes:



Cpd.	R	U^1	U^2	T^1	T^2
9a	OH	O	O	H	H
9b	H	O	O	H	H
9c	H	O	O	Cl	Cl
9d	$OCOCH_3$	O	O	H	H
9e	H	O	O	CH_3	CH_3
9f	OCH_3	O	O	Cl	Cl
9g	$N(C_2H_5)_2$	O	O	Br	Br
13a	H	NH	NH	H	H
13b	H	NCH_3	NCH_3	H	H
13c	H	$N(C=O)CH_3$	$N(C=O)CH_3$	H	H
14a	OCH_3	O	S	H	H
14b	H	O	S	H	H
14c	H	O	$N(C=O)CH_3$	H	H
14d	CH_3	O	$N(C=O)CH_3$	H	H
14e	H	O	NCH_3	H	H
14f	OCH_3	O	NCH_3	H	H
17a	H/CH_3	O	O	H	H
17b	H/OCH_3	O	O	H	H

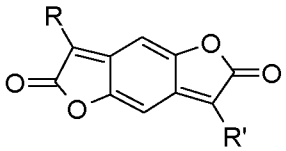


Cpd.	R	U^1	U^2	T^1	T^2
12a	H	O	O	H	H
12b	OCH_3	O	O	CH_3	H
12c	H	O	O	CH_3	H
12d	OCH_3	O	O	Cl	Cl
12e	H	O	O	Cl	Cl
12f	OCH_3	O	O	H	H
12g	H	O	O	OH	OH
12g	H	O	O	1)	1)
12h	OCH_3	O	O	1)	1)
18a	Cl/H	O	O	H	H

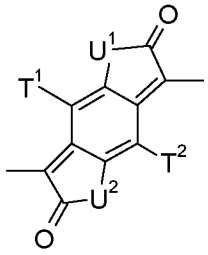
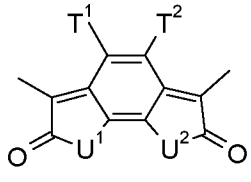
1) T^1 and T^2 are a group  . Experimental details can be found in C. W. Greenhalgh et al., Dyes and Pigments 1 (1980) 103.

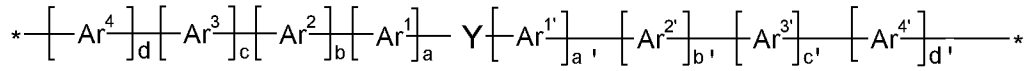
K. Nakano et al., Synthetic Metals 159 (2009) 939-942 reports the synthesis of π-conjugated copolymer with dibenzo[d,d']benzo[1,2-b:4,5-b']difurane (DBBF) unit in the main chain. Copolymerisation of 6,12-diiodo DBBF with p-diethynylbenzene- or 2,7-diethynylfluorene under Sonogashira-Hagiwara coupling reaction conditions gave the corresponding copolymers.

EP1344788A1 relates to polymer compounds comprising dibenzofurane, or dibenzo thiophene repeating units

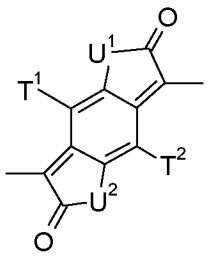
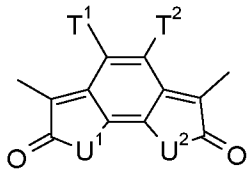
EP0436940A1 discloses a process for the production of benzodifurane compounds of formula  , wherein R and R' are independently of each other a naphthyl group, or an unsubstituted or substituted phenyl group.

It is the object of the present invention to provide polymers, which show high efficiency of energy conversion, excellent field-effect mobility, good on/off current ratios and/or excellent stability, when used in organic field effect transistors, organic photovoltaics (solar cells) and photodiodes.

Said object has been solved by polymers comprising one or more (repeating) unit(s) of the formula  , or  (Y), especially polymers comprising one or more (repeating) unit(s) of the formula



(I),

wherein Y is a group of formula  , or  ,

a is 1, 2, or 3, a' is 1, 2, or 3; b is 0, 1, 2, or 3; b' is 0, 1, 2, or 3; c is 0, 1, 2, or 3; c' is 0, 1, 2, or 3; d is 0, 1, 2, or 3; d' is 0, 1, 2, or 3;

U^1 is O, S, or NR^1;

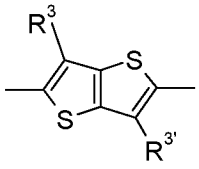
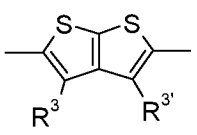
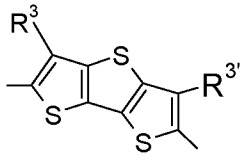
U^2 is O, S, or NR^2;

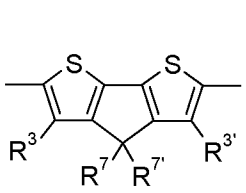
T^1 and T^2 are independently of each other hydrogen, halogen, hydroxyl, cyano, $-COOR^{103}$, $-OCOR^{103}$, $-NR^{112}COR^{103}$, $-CONR^{112}R^{113}$, $-OR^{103'}$, $-SR^{103'}$, $-SOR^{103'}$, $-SO_2R^{103'}$, $-NR^{112}SO_2R^{103'}$, $-NR^{112}R^{113}$, C_1-C_{25}alkyl, which may be substituted by E and/or interrupted by D, C_5-C_{12}cycloalkyl, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; C_7-C_{25}arylalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G;

R^1 and R^2 may be the same or different and are selected from hydrogen, a C_1-C_{100}alkyl group, $-COOR^{103}$, $-COR^{103}$, a C_1-C_{100}alkyl group which is substituted by one or more halogen atoms, hydroxyl groups, nitro groups, -CN, or C_6-C_{18}aryl groups and/or interrupted by –O-, -COO-, -OCO-, or -S-; a C_7-C_{100}arylalkyl group, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; a carbamoyl group, C_5-C_{12}cycloalkyl, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; a C_6-C_{24}aryl group, in particular phenyl or 1- or 2-naphthyl, which can be substituted one to three times with C_1-C_8alkyl, C_1-C_8thioalkoxy, and/or C_1-C_8alkoxy, or pentafluorophenyl,

R^{103} and $R^{103'}$ are independently of each other C_1-C_{100}alkyl, especially C_3-C_{25}alkyl, C_1-C_{25}alkyl substituted by E and/or interrupted by D, C_7-C_{25}arylalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G,

Ar^2, $Ar^{2'}$, Ar^3, $Ar^{3'}$, Ar^4 and $Ar^{4'}$ have the meaning of Ar^1, or are independently of each other

 (**Xa**),  (**Xb**),  (**Xc**),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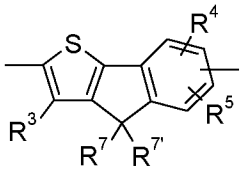
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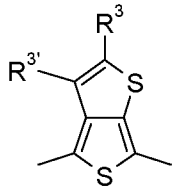
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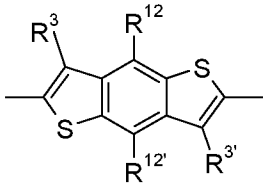
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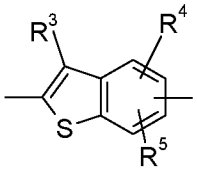
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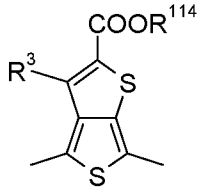
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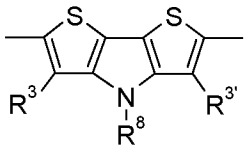
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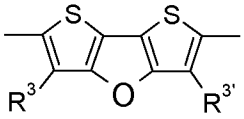
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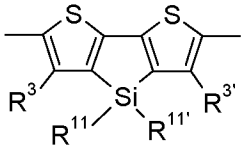
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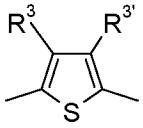
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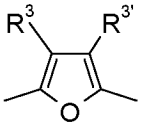
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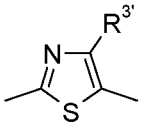
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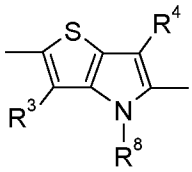
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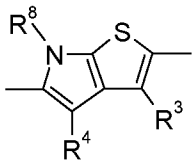
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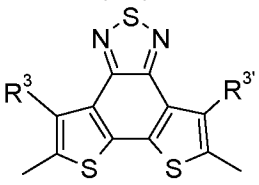
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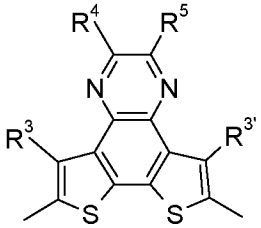
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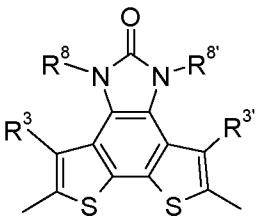
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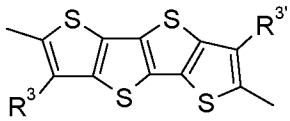
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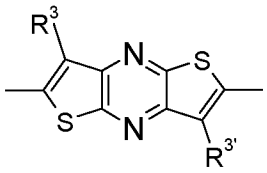
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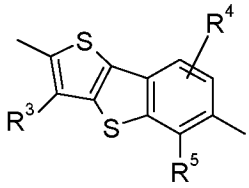
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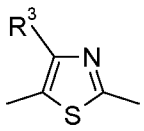
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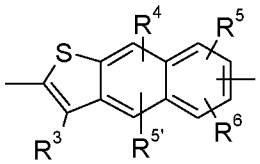
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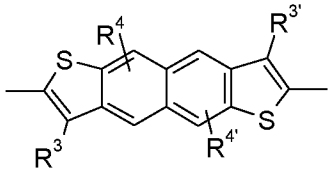
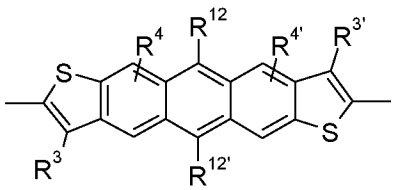
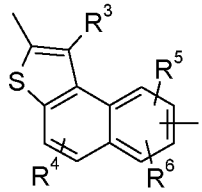
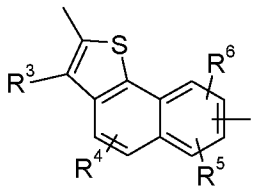
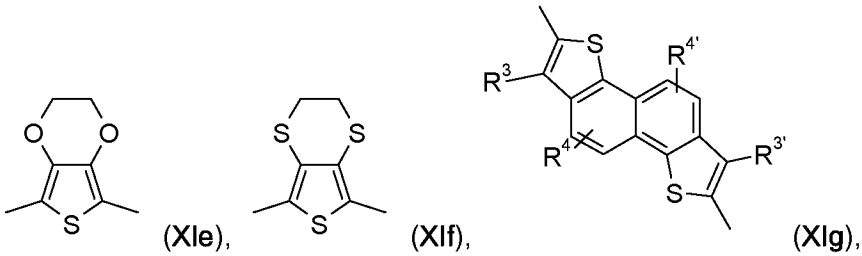
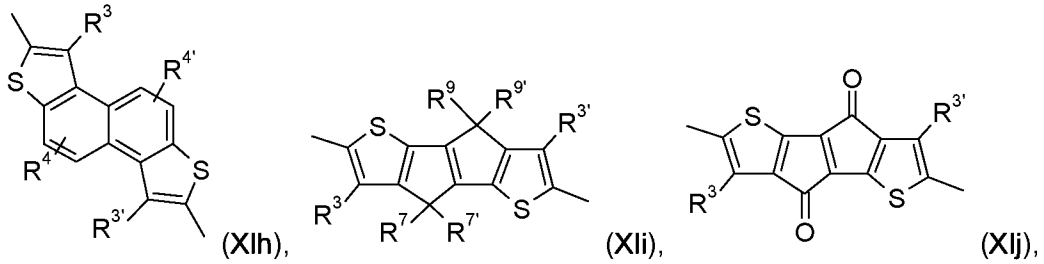
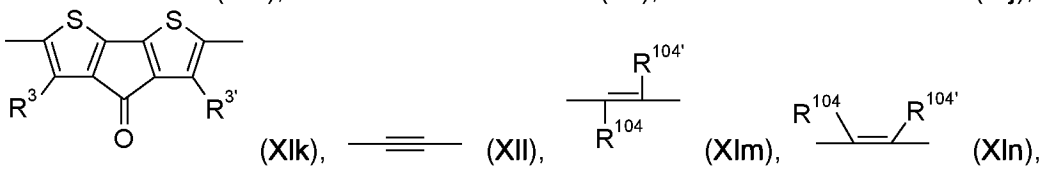

(Xla),


(Xlb),

(Xlc),

(Xld),


(XIe), (XIf), (XIg),


(XIh), (XIi), (XIj),


(XIk), (XIl), (XIm), (XIn),

R^3 and $R^{3'}$ are independently of each other hydrogen, halogen, halogenated C_1-C_{25}alkyl, especially CF_3, cyano, C_1-C_{25}alkyl, especially C_3-C_{25}alkyl, which may optionally be interrupted by one or more oxygen or sulphur atoms; C_7-C_{25}arylalkyl, or C_1-C_{25}alkoxy;

R^{104} and $R^{104'}$ are independently of each other hydrogen, cyano, $COOR^{103}$, or a C_1-C_{25}alkyl group,

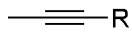
R^4, $R^{4'}$, R^5, $R^{5'}$, R^6 and $R^{6'}$ are independently of each other hydrogen, halogen, halogenated C_1-C_{25}alkyl, especially CF_3, cyano, C_1-C_{25}alkyl, especially C_3-C_{25}alkyl, which may optionally be interrupted by one or more oxygen or sulphur atoms; C_7-C_{25}arylalkyl, or C_1-C_{25}alkoxy;

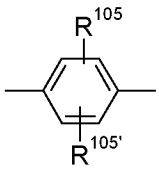
R^{114} is C_1-C_{25}alkyl, especially C_3-C_{25}alkyl, which may optionally be interrupted by one, or more oxygen, or sulphur atoms,

R^7, $R^{7'}$, R^9 and $R^{9'}$ are independently of each other hydrogen, C_1-C_{25}alkyl, especially C_3-C_{25}alkyl, which may optionally be interrupted by one, or more oxygen, or sulphur atoms; or C_7-C_{25}arylalkyl,

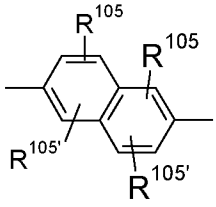
R^8 and $R^{8'}$ are independently of each other hydrogen, C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; or C_1-C_{25}alkyl, especially C_3-C_{25}alkyl, which may optionally be interrupted by one or more oxygen or sulphur atoms; or C_7-C_{25}arylalkyl,

R^{11} and $R^{11'}$ are independently of each other C_1-C_{25}alkyl group, especially a C_1-C_8alkyl group, C_7-C_{25}arylalkyl, or a phenyl group, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy;

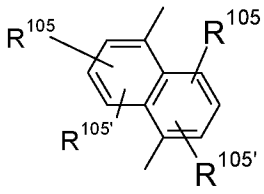
R^{12} and $R^{12'}$ are independently of each other hydrogen, halogen, cyano, C_1-C_{25}alkyl, especially C_3-C_{25}alkyl, which may optionally be interrupted by one, or more oxygen, or sulphur atoms, C_1-C_{25}alkoxy, C_7-C_{25}arylalkyl, or  , wherein R^{13} is a C_1-C_{10}alkyl group, or a tri(C_1-C_8alkyl)silyl group;



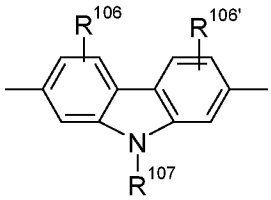
Ar^1 and $Ar^{1'}$ are independently of each other (**XVa**),



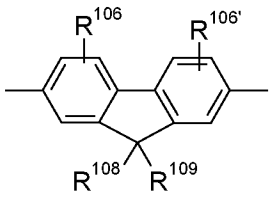
(**XVb**),



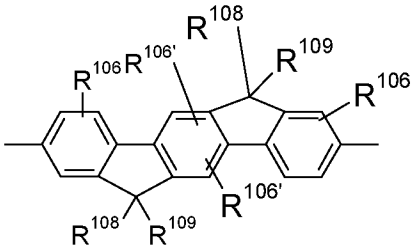
(**XVc**),

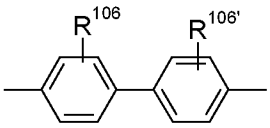


(**XVd**),

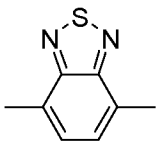


(**XVe**),





(**XVf**),



(**XVg**) or

(**XVh**), wherein

R^{105}, $R^{105'}$, R^{106} and $R^{106'}$ are independently of each other hydrogen, halogen, cyano, C_1-C_{25}alkyl, which may optionally be interrupted by one or more oxygen or sulphur atoms; C_7-C_{25}arylalkyl, or C_1-C_{18}alkoxy,

R^{107} is hydrogen, C_7-C_{25}arylalkyl, C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}perfluoroalkyl; C_1-C_{25}alkyl; especially C_3-C_{25}alkyl, which may be interrupted by –O-, or –S-; or -$COOR^{103}$; R^{103} is is as defined above;

R^{108} and R^{109} are independently of each other H, C_1-C_{25}alkyl, C_1-C_{25}alkyl which is substituted by E and/or interrupted by D, C_7-C_{25}arylalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, or C_7-C_{25}aralkyl, or

R^{108} and R^{109} together form a group of formula $=CR^{110}R^{111}$, wherein

R^{110} and R^{111} are independently of each other H, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, or C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G, or

R^{108} and R^{109} together form a five or six membered ring, which optionally can be substituted by C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, or C_7-C_{25}aralkyl,

D is -CO-, -COO-, -S-, -O-, or –NR^{112}–,

E is C_1-C_8thioalkoxy, C_1-C_8alkoxy, CN, -$NR^{112}R^{113}$, -$CONR^{112}R^{113}$, or halogen,

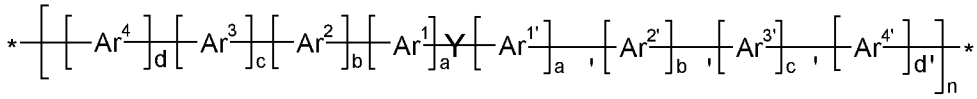
G is E, or C_1-C_{18}alkyl, and

R^{112} and R^{113} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-.

Advantageously, the polymer of the present invention, or an organic semiconductor material, layer or component, comprising the polymer of the present invention can be used in organic photovoltaics (solar cells) and photodiodes, or in an organic field effect transistor (OFET).

The term polymer comprises oligomers as well as polymers. The oligomers of this invention have a weight average molecular weight of < 4,000 Daltons. The polymers of this invention preferably have a weight average molecular weight of 4,000 Daltons or greater, especially 4,000 to 2,000,000 Daltons, more preferably 10,000 to 1,000,000 and most preferably 10,000 to 100,000 Daltons. Molecular weights are determined according to high-temperature gel permeation chromatography (HT-GPC) using polystyrene standards. The polymers of this invention preferably have a polydispersity of 1.01 to 10, more preferably 1.1 to 3.0, most preferred 1.5 to 2.5. The polymers of the present invention are preferably conjugated.

In an embodiment of the present invention the polymer is a polymer of formula

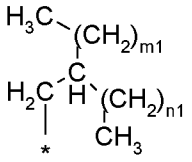


, wherein n is usually in the range of 4 to 1000, especially 4 to 200, very especially 5 to 150.

U^1 is preferably O or NR^1; more preferably NR^1.
U^2 is preferably O or NR^1; more preferably NR^1.

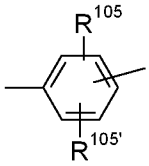
Preferably, T^1 and T^2 are independently of each other hydrogen, halogen, cyano, -$COOR^{103}$, -$OCOR^{103}$, -OR^{103}, -SR^{103}, or C_1-C_{25}alkyl, which may be substituted by E and/or interrupted by D; more preferably hydrogen, halogen, cyano, -OR^{103}, C_1-C_{25}alkyl. Most preferred T^1 and T^2 are hydrogen, or C_1-C_{25}alkyl, especially hydrogen.

R^1 and R^2 may be different, but are preferably the same; and are preferably selected from hydrogen, a C_1-C_{100}alkyl group, a C_1-C_{100}alkyl group which is substituted by one or more halogen atoms, -CN, or C_6-C_{18}aryl groups and/or interrupted by –O-, -COO-, -OCO-, or -S-; a C_7-C_{24}arylalkyl group, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; and pentafluorophenyl. More preferably R^1 and R^2 are selected from hydrogen, a C_1-C_{38}alkyl group, a C_1-C_{38}alkyl group which is substituted by one or more halogen atoms; a C_7-C_{25}arylalkyl group, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; and pentafluorophenyl. Still more preferably R^1 and R^2 are selected from hydrogen and a C_1-C_{38}alkyl group. Most preferred R^1 and R^2 are a C_1-C_{38}alkyl group such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, 1,1,3,3-tetramethylpentyl, n-hexyl, 1-methylhexyl, 1,1,3,3,5,5-hexamethylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 1,1,3,3-tetramethylbutyl and 2-ethylhexyl, n-nonyl, decyl, undecyl, especially n-dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, 2-ethyl-hexyl, 2-butyl-hexyl, 2-butyl-octyl, 2-hexyldecyl, 2-decyl-tetradecyl, heptadecyl, octadecyl, eicosyl, heneicosyl, docosyl, or tetracosyl.

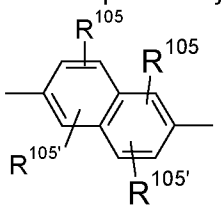


Advantageously, the groups R^1 and R^2 can be represented by formula , wherein m1 = n1 + 2 and m1 + n1 ≤ 24. Chiral side chains, such as R^1 and R^2, can either be enantiomerically pure, homochiral, or racemic, which can influence the morphology of the polymers.

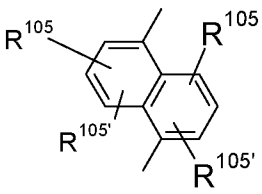
Preferably, R^{103} and $R^{103'}$ are independently of each other C_1-C_{25}alkyl, C_1-C_{25}alkyl substituted by halogen, especially CF_3, C_7-C_{25}arylalkyl, or phenyl; more preferably C_1-C_{25}alkyl.



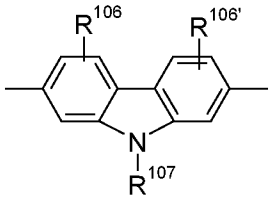
Ar^1 and $Ar^{1'}$ are preferably independently of each other a group of formula



(XVa),

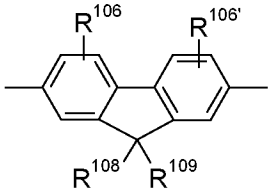


(XVb),

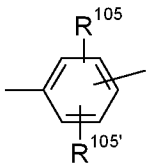


(XVc),

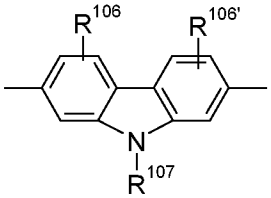
(XVd)



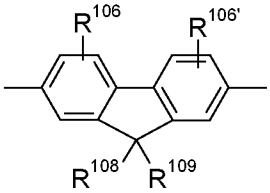
or



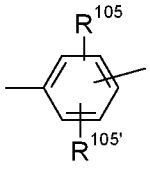
(XVe), more preferably a group of formula (XVa),



(XVd), or



(XVe), most preferred a group of formula



(XVa),

Preferably, Ar^2, $Ar^{2'}$, Ar^3, $Ar^{3'}$, Ar^4 and $Ar^{4'}$ are independently of each other a group of formula (Xa), (Xb), (Xc), (Xd), (Xe), (Xg), (Xh), (Xk), (Xl), (Xm), (Xn), (Xo), (Xp), (Xv), (Xx), (Xy), (Xz), (Xla), (Xlb), (Xlc), (Xld), (Xle), (Xlf), (Xlg), (Xlh), (Xli), (Xll), or (Xlm); more preferably a group of formula (Xa), (Xc), (Xg), (Xh), (Xm), (Xn), (Xo), (Xp), (Xy), (Xle), (Xlf), (Xll), or (Xlm), still more preferably a group of formula (Xa), (Xm), (Xn), (Xo), or (Xlm), most preferred a group of formula (Xa), (Xm), or (Xn), especially (Xm).

Preferably, R^3 and $R^{3'}$ are independently of each other hydrogen, halogen, CF_3, cyano, C_1-C_{25}alkyl or C_1-C_{25}alkoxy; more preferably CF_3, cyano or C_1-C_{25}alkyl; most preferred hydrogen, or C_1-C_{25}alkyl.

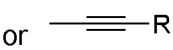
Preferably, R^{104} and $R^{104'}$ are independently of each other hydrogen, cyano or a C_1-C_{25}alkyl group, more preferably hydrogen, or a C_1-C_{25}alkyl group, most preferred hydrogen.

Preferably, R^4, $R^{4'}$, R^5, $R^{5'}$, R^6 and $R^{6'}$ are independently of each other hydrogen, halogen, CF_3, cyano, C_1-C_{25}alkyl or C_1-C_{25}alkoxy, more preferably hydrogen, CF_3, cyano or C_1-C_{25}alkyl; most preferred hydrogen, or C_1-C_{25}alkyl.

Preferably R^7, $R^{7'}$, R^9 and $R^{9'}$ are independently of each other hydrogen, C_1-C_{25}alkyl, more preferably C_4-C_{25}alkyl.

Preferably, R^8 and $R^{8'}$ are independently of each other hydrogen, C_1-C_{25}alkyl, C_1-C_{25}alkyl, which may optionally be interrupted by one or more oxygen or sulphur atoms; or C_7-C_{25}arylalkyl, more preferably hydrogen, or C_1-C_{25}alkyl.,

Preferably, R^{11} and $R^{11'}$ are independently of each other a C_1-C_{25}alkyl group, especially a C_1-C_8alkyl group, or phenyl; more preferably a C_1-C_8alkyl group.

Preferably, R^{12} and $R^{12'}$ are independently of each other hydrogen, C_1-C_{25}alkyl, C_1-C_{25}alkoxy, or  , wherein R^{13} is a C_1-C_{10}alkyl group, or a tri(C_1-C_8alkyl)silyl group, more preferably hydrogen, C_1-C_{25}alkyl, or C_1-C_{25}alkoxy.

If Ar^2, $Ar^{2'}$, Ar^3, $Ar^{3'}$, Ar^4 and $Ar^{4'}$ have the meaning of Ar^1, they are independently of each other a group of formula (**XVa**), (**XVb**), (**XVc**), (**XVd**) or (**XVe**), preferably a group of formula (**XVa**), (**XVd**) or (**XVe**), more preferably a group of formula (**XVa**).

Preferably, R^{105}, $R^{105'}$, R^{106} and $R^{106'}$ are independently of each other hydrogen, halogen, cyano, C_1-C_{25}alkyl or C_1-C_{18}alkoxy, more preferably C_1-C_{25}alkyl or C_1-C_{18}alkoxy, most preferred hydrogen, or C_1-C_{25}alkyl.

R^{107} is preferably hydrogen, C_1-C_{25}alkyl, C_1-C_{25}alkyl, which may optionally be interrupted by one or more oxygen or sulphur atoms; or C_7-C_{25}arylalkyl, more preferably hydrogen, or C_1-C_{25}alkyl, most preferred C_4-C_{25}alkyl.

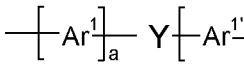
Preferably, R^{108} and R^{109} are independently of each other H, C_1-C_{25}alkyl, C_1-C_{25}alkyl which is substituted by E and/or interrupted by D, C_7-C_{25}arylalkyl, C_2-C_{18}alkenyl, or C_7-C_{25}aralkyl, or R^{108} and R^{109} together form a five or six membered ring, which optionally can be substituted by C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, D is -CO-, -COO-, -S- or -O-, E is C_1-C_8thioalkoxy, C_1-C_8alkoxy, CN or halogen, G is E, or C_1-C_{18}alkyl. More preferably, R^{108} and R^{109} are independently of each other H, C_1-C_{25}alkyl or C_7-C_{25}arylalkyl. Most preferred R^{108} and R^{109} are independently of each other H, or C_1-C_{25}alkyl.

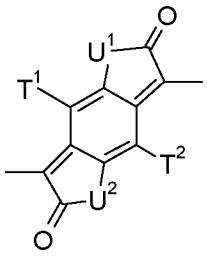
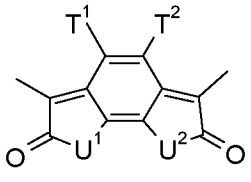
D is preferably -CO-, -COO-, -S- or -O-, more preferably -COO-, -S- or -O-, most preferred -S- or -O-.

Preferably, E is C_1-C_8thioalkoxy, C_1-C_8alkoxy, CN, or halogen, more preferably C_1-C_8alkoxy, CN, or halogen, most preferred halogen, especially F.

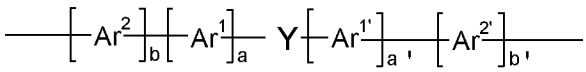
Preferably, R^{112} and R^{113} are independently of each other H; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-, more preferably H, or C_1-C_{18}alkyl; most preferred C_1-C_{18}alkyl.

In a preferred embodiment the present invention is directed to polymers comprising one or more (repeating) unit(s) of the formula

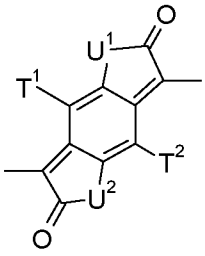


(I'), wherein Y is a group of formula  or  ,

U^1 is O, S, or NR^1;
U^2 is O, S, or NR^2;
T^1 and T^2 are independently of each other hydrogen, halogen, hydroxyl, cyano, -$COOR^{103}$, -$OCOR^{103}$, -$NR^{112}COR^{103}$, -$CONR^{112}R^{113}$, -$OR^{103'}$, -$SR^{103'}$, -$SOR^{103'}$, -$SO_2R^{103'}$, -$NR^{112}SO_2R^{103'}$, -$NR^{112}R^{113}$, C_1-C_{25}alkyl, which which may be substituted by E and/or interrupted by D, C_5-C_{12}cycloalkyl, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; C_7-C_{25}arylalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G;
R^1 and R^2 may be the same or different and are selected from hydrogen, a C_1-C_{100}alkyl group, -$COOR^{103}$, -COR^{103}, a C_1-C_{100}alkyl group which is substituted by one or more halogen atoms, hydroxyl groups, nitro groups, -CN, or C_6-C_{18}aryl groups and/or interrupted by –O-, -COO-, -OCO-, or -S-; a C_7-C_{100}arylalkyl group, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; a carbamoyl group, C_5-C_{12}cycloalkyl, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; a C_6-C_{24}aryl group, in particular phenyl or 1- or 2-naphthyl, which can be substituted one to three times with C_1-C_8alkyl, C_1-C_8thioalkoxy, and/or C_1-C_8alkoxy, or pentafluorophenyl;
a is 1, 2, or 3, a' is 1, 2, or 3; wherein Ar^1 and $Ar^{1'}$ are independently of each other a group of formula (**XVa**), (**XVb**), (**XVc**), (**XVd**), (**XVe**), (**XVf**), (**XVg**) or (**XVh**) (as defined in claim 1); and R^{103}, $R^{103'}$, R^{112}, R^{113}, D, E and G are as defined above; or a polymer comprising one or more (repeating) unit(s) of the formula



(I''), wherein a is 1, or 2; a' is 1, or 2; b is 1, 2, or 3; b' is 1, 2, or 3; wherein Y, Ar^1 and $Ar^{1'}$ are as defined above; and Ar^2 and $Ar^{2'}$ are as defined above.



In said embodiment Y is preferably a group of formula . U^1 and U^2 may be different, but are preferably the same. U^1 is preferably O or NR^1; more preferably NR^1. U^2 is preferably O or NR^1; more preferably NR^1.

T^1 and T^2 may be different, but are preferably the same. T^1 and T^2 are preferably independently of each other hydrogen, halogen, cyano, $-COOR^{103}$, $-OCOR^{103}$, $-OR^{103}$, $-SR^{103}$, C_1-C_{25}alkyl, which may be substituted by E and/or interrupted by D; more preferably hydrogen, halogen, cyano, $-OR^{103}$, C_1-C_{25}alkyl; most preferred hydrogen, or C_1-C_{25}alkyl, especially hydrogen.

R^1 and R^2 may be different, but are preferably the same. Preferably, R^1 and R^2 are selected from hydrogen, a C_1-C_{100}alkyl group, a C_1-C_{100}alkyl group which is substituted by one or more halogen atoms, -CN, or C_6-C_{18}aryl groups and/or interrupted by –O-, -COO-, -OCO-, or -S-; a C_7-C_{100}arylalkyl group, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; and pentafluorophenyl. More preferably R^1 and R^2 are selected from hydrogen, a C_1-C_{38}alkyl group, a C_1-C_{38}alkyl group which is substituted by one or more halogen atoms; a C_7-C_{24}arylalkyl group, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; and pentafluorophenyl; most preferred R^1 and R^2 are selected from hydrogen, or a C_1-C_{38}alkyl group; especially a C_1-C_{38}alkyl group.

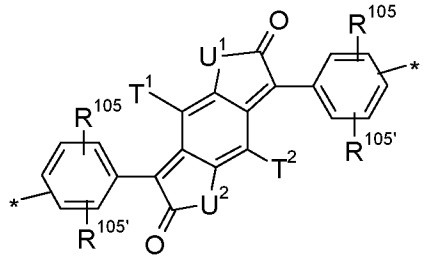
a and a' may be different, but are preferably the same. a and a' are preferably 1, or 2, more preferably 1.

Ar^2 and $Ar^{2'}$ may be different, but are preferably the same. Preferably, Ar^2 and $Ar^{2'}$ are independently of each a group of formula (**Xa**), (**Xb**), (**Xc**), (**Xd**), (**Xe**), (**Xg**), (**Xh**), (**Xk**), (**Xl**), (**Xm**), (**Xn**), (**Xo**), (**Xp**), (**Xv**), (**Xx**), (**Xy**), (**Xz**), (**XIa**), (**XIb**), (**XIc**), (**XId**), (**XIe**), (**XIf**), (**XIg**), (**XIh**), (**XIi**), (**XIl**), or (**XIm**) (as defined above).

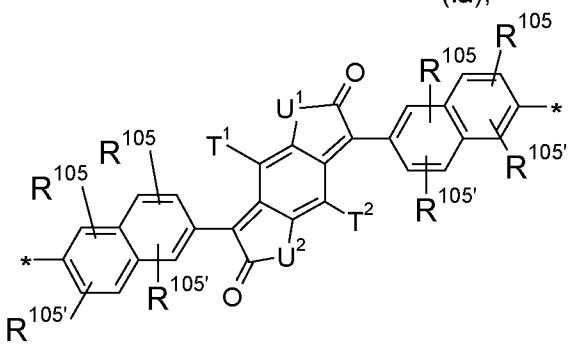
More preferably, Ar^2 and $Ar^{2'}$ are a group of formula (**Xa**), (**Xc**), (**Xg**), (**Xh**), (**Xm**), (**Xn**), (**Xo**), (**Xp**), (**Xy**), (**XIe**), (**XIf**) and (**XIm**). Still more preferably Ar^2 and $Ar^{2'}$ are a group of formula (**Xa**), (**Xm**), (**Xn**), (**Xo**) and (**XIm**). Most preferred Ar^2 and $Ar^{2'}$ are a group of formula (**Xa**), (**Xm**) and (**Xn**), especially (**Xm**).

Ar^1 and $Ar^{1'}$ may be different, but are preferably the same. Ar^1 and $Ar^{1'}$ are independently of each other a group of formula (**XVa**), (**XVb**), (**XVc**), (**XVd**), (**XVe**), (**XVf**), (**XVg**), or (**XVh**), preferably a group of formula (**XVa**), (**XVb**), (**XVc**), (**XVd**) or (**XVe**), more preferably a group of formula (**XVa**), (**XVd**) or (**XVe**), most preferably a group of formula (**XVa**).

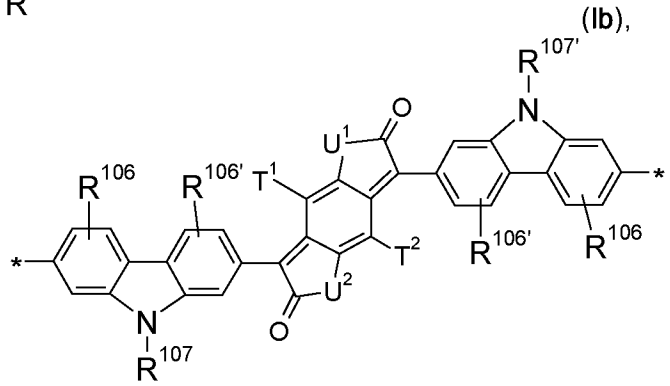
In a further preferred embodiment the present invention is directed to polymers, comprising one or more (repeating) unit(s) of the formula



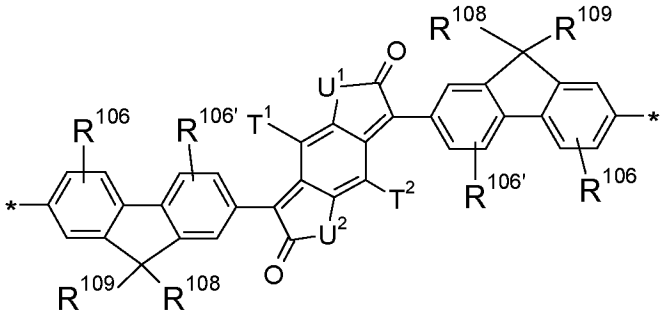
(**Ia**),



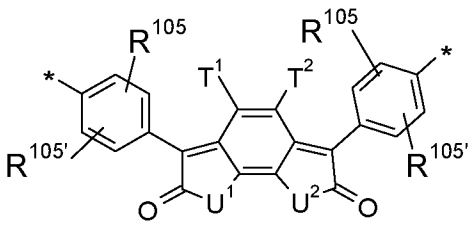
(**Ib**),



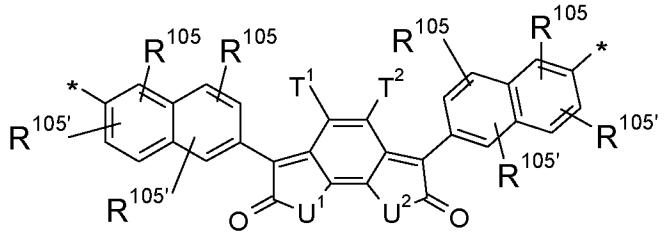
(**Ic**),



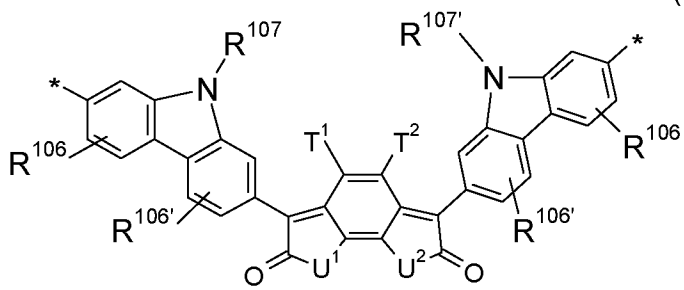
(**Id**);



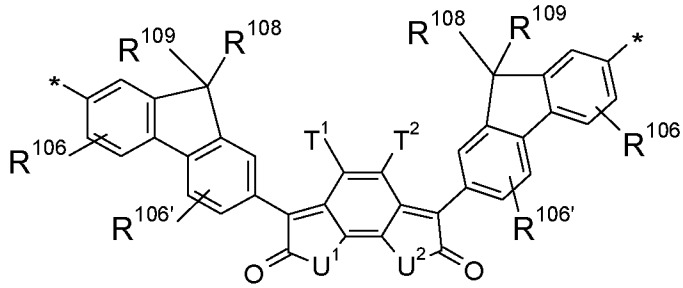
(**Ie**);



(If);



(Ig); and/or



(Ih); wherein

U^1 is O, or NR^1;

U^2 is O, or NR^2;

T^1 and T^2 are independently of each other hydrogen, or C_1-C_{25}alkyl, especially hydrogen;

R^1 and R^2 may be the same or different and are selected from a C_1-C_{38}alkyl group, especially C_8-C_{36}alkyl group;

R^{105}, $R^{105'}$, R^{106} and $R^{106'}$ are independently of each other hydrogen or C_1-C_{25}alkyl; and

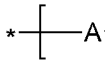
R^{107} and $R^{107'}$ are independently of each other hydrogen or C_1-C_{25}alkyl, especially C_1-C_{25}alkyl;

R^{108} and R^{109} are independently of each other H, or C_1-C_{25}alkyl [Okay?].

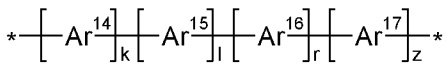
Repeating) unit(s) of the formula (Ia); (Ib); (Id); (Ie); (If) or (Ih) are preferred; repeating unit(s) of the formula (Ia); (Id); (Ie) or (Ih) are more preferred; repeating unit(s) of the formula (Ia), or (Ie) are most preferred.

Preferably U^1 and U^2 are the same.

Preferably T^1 and T^2 are the same.

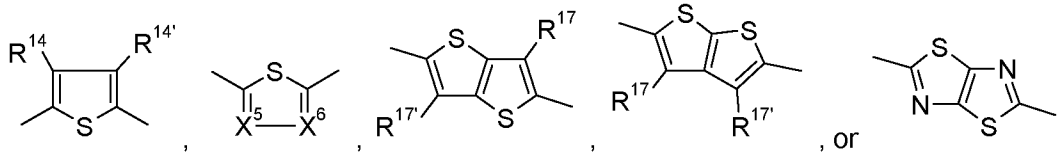
In another embodiment the present invention is directed to polymers, comprising (repeating) unit(s) of the formula  and  (II), wherein

A is a repeating unit of formula (I), and

-COM^1- is a repeating unit, which has the meaning of Ar^2, wherein Ar^2 are as defined above, or a group of formula  ,

k is 1, l is 1, r is 0, or 1, z is 0, or 1, and

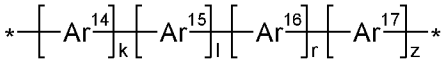
Ar^{14}, Ar^{15}, Ar^{16} and Ar^{17} are independently of each other a group of formula

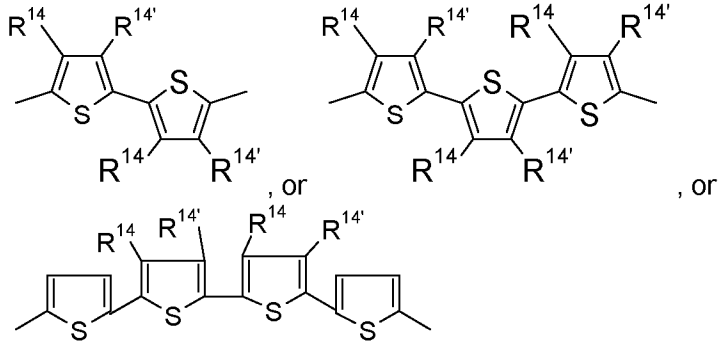


wherein one of X^5 and X^6 is N and the other is CR^{14}, and

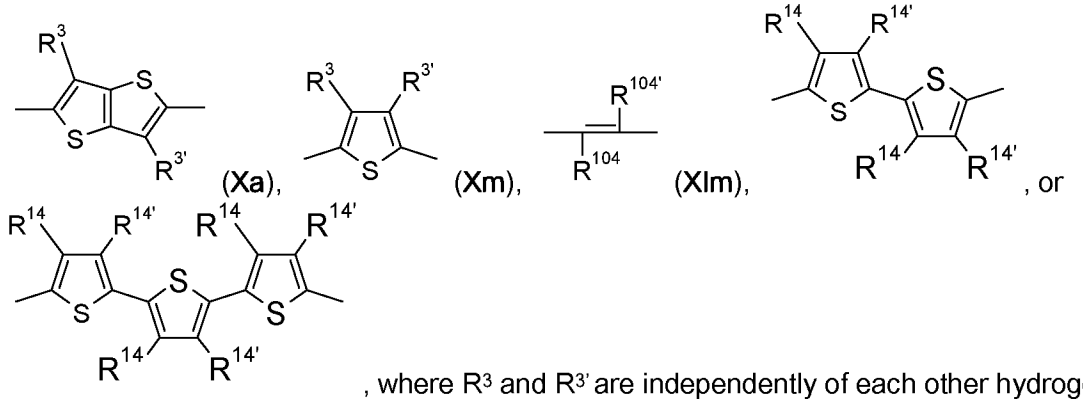
R^{14}, R$^{14'}$, R^{17} and R$^{17'}$ are independently of each other H, or a C_1-C_{25}alkyl group, especially a C_6-C_{25}alkyl, which may optionally be interrupted by one or more oxygen atoms.

Examples of repeating units -COM^1- are groups of formula (**Xa**) to (**Xz**), (**XIa**) to (**XIn**) and (**XVa**) to (**XVh**). Among these groups groups of formula (**Xa**), (**Xb**), (**Xc**), (**Xg**), (**XI**), (**Xm**), (**Xn**), (**Xo**), (**XIe**), (**XIf**), (**XIl**), (**XIm**), (**XIn**), (**XVa**), (**XVb**), (**XVc**), (**XVd**), (**XVe**), (**XVf**) and (**XVg**) are preferred, groups of formula (**Xa**), (**Xg**), (**XI**), (**Xm**), (**XIe**), (**XIf**), (**XIm**), (**XVa**), (**XVb**), (**XVd**), and (**XVe**), are more preferred, groups of formula (**Xa**), (**XI**), (**Xm**), (**XIe**), (**XIm**), (**XVa**), (**XVb**), and (**XVd**) are still more preferred. Groups formula (**Xa**), (**Xm**) and (**XIm**) are most preferred.

Examples of a group of formula  are

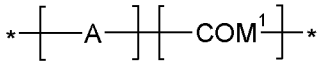
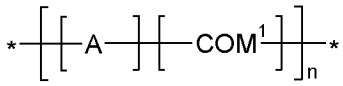


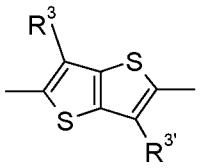
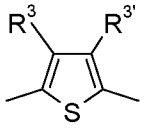
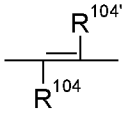
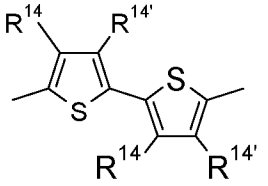
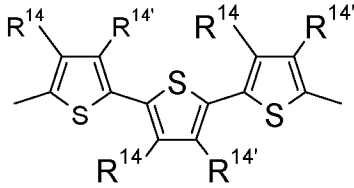
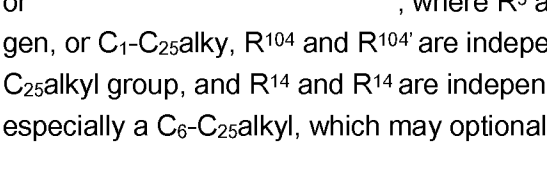
In a particularly preferred embodiment the repeating unit -COM^1- is a group of formula



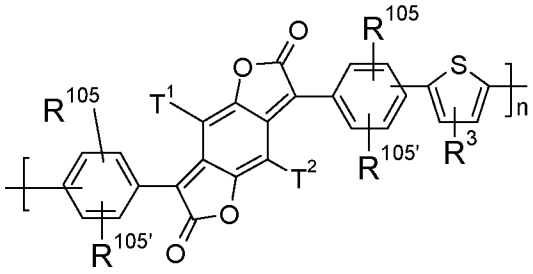
, where R^3 and R$^{3'}$ are independently of each other hydrogen, or C_1-C_{25}alky, R^{104} and R$^{104'}$ preferably are independently of each other hydrogen, cyano or

a C_1-C_{25}alkyl group, and R^{14} and R^{14} are independently of each other H, or a C_1-C_{25}alkyl group, especially a C_6-C_{25}alkyl, which may optionally be interrupted by one or more oxygen atoms.

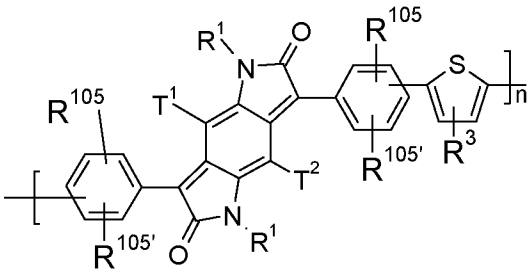
In a preferred embodiment of the present invention the polymer is a copolymer, comprising repeating units of formula  (VII), especially a copolymer of formula  , wherein A and COM^1 are as defined above; n is number which results in a molecular weight of 4,000 to 2,000,000 Daltons, more preferably 10,000 to 1,000,000 and most preferably 10,000 to 100,000 Daltons. n is usually in the range of 4 to 1000, especially 4 to 200, very especially 5 to 150.

In a preferred embodiment the present invention is directed to polymers, wherein A is a repeating unit of formula (Ia), (Id), (Ie), or (Ih) (as defined in claim 3) and  is a group of formula  ,  ,  ,  ,  or  , where R^3 and $R^{3'}$ are independently of each other hydrogen, or C_1-C_{25}alky, R^{104} and $R^{104'}$ are independently of each other hydrogen, cyano or a C_1-C_{25}alkyl group, and R^{14} and R^{14} are independently of each other H, or a C_1-C_{25}alkyl group, especially a C_6-C_{25}alkyl, which may optionally be interrupted by one or more oxygen atoms.

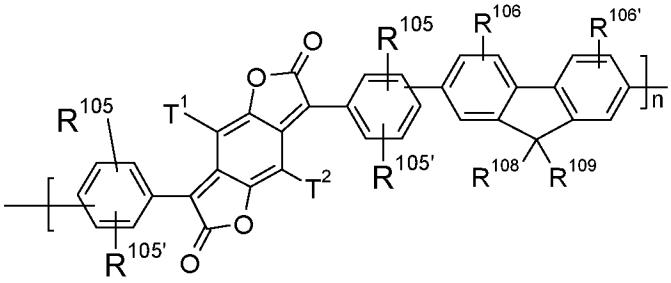
Preferred polymers are shown below:



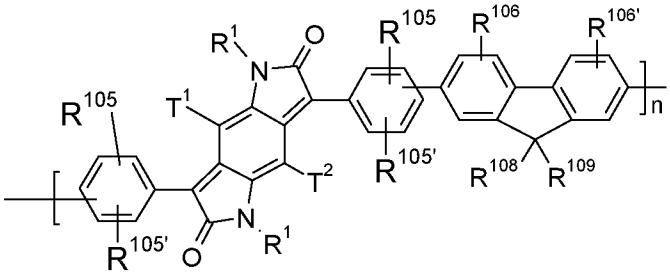
(IIa),



(IIb),



(IIc),



(IId), wherein

n is 4 to 1000, especially 4 to 200, very especially 5 to 100,

T^1 and T^2 are independently of each other hydrogen, or C_1-C_{25}alkyl, especially hydrogen;

R^1 is a C_1-C_{38}alkyl group, especially a C_8-C_{36}alkyl group,

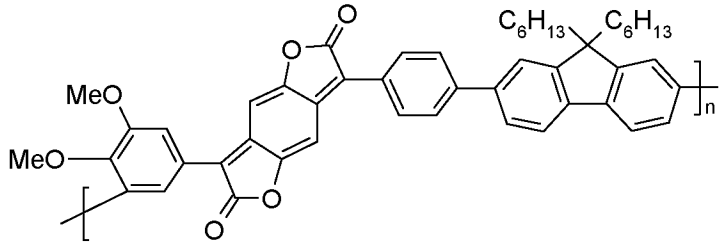
R^3 is hydrogen, halogen, cyano, C_1-C_{25}alkyl or C_1-C_{25}alkoxy, especially hydrogen or C_1-C_{25}alkyl;

R^{105} and $R^{105'}$ are independently of each other hydrogen, halogen, cyano, C_1-C_{25}alkyl or C_1-C_{25}alkoxy, especially hydrogen or C_1-C_{25}alkyl;

R^{106} and $R^{106'}$ are independently of each other hydrogen or C_1-C_{25}alkyl; and

R^{108} and R^{109} are independently of each other H, or C_1-C_{25}alkyl.

Examples of preferred polymers are shown below:



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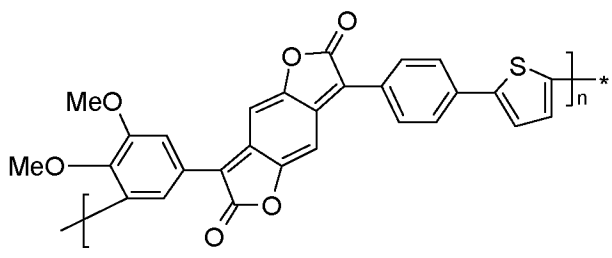

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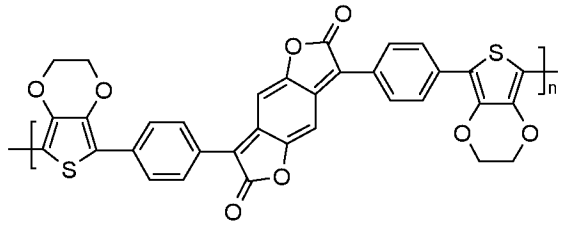

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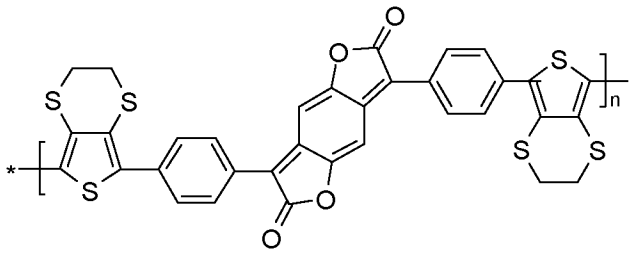

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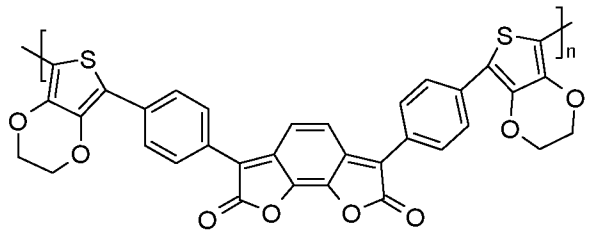

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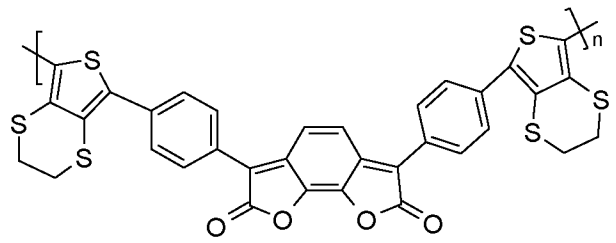

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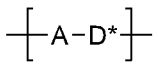
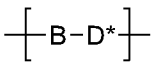
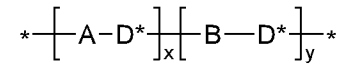
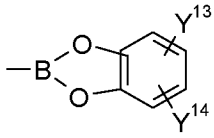
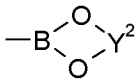
n is usually in the range of 4 to 1000, especially 4 to 200, very especially 5 to 150.

The polymers of the present invention can comprise more than 2 different repeating units, such as, for example, repeating units A, B and D, which are different from each other. If the polymers comprise repeating units of the formula  and  , they are preferably (random) copolymers of formula  , wherein x = 0.995 to 0.005, y = 0.005 to 0.995, especially x = 0.2 to 0.8, y = 0.8 to 0.2, and wherein x + y = 1. A is a repeating unit of formula (I), D* is a repeating unit -COM^1- and B is a repeating unit -COM^1-, or a repeating unit of formula (I); with the proviso that A, B and D* are different from each other.

Copolymers of formula VII can be obtained, for example, by the Suzuki reaction. The condensation reaction of an aromatic boronate and a halogenide, especially a bromide, commonly referred to as the "Suzuki reaction", is tolerant of the presence of a variety of organic functional groups as reported by N. Miyaura and A. Suzuki in Chemical Reviews, Vol. 95, pp. 457-2483 (1995). Preferred catalysts are 2-dicyclohexylphosphino-2',6'-di-alkoxybiphenyl/palladium(II)acetates, tri-alykl-phosphonium salts/palladium (0) derivatives

and tri-alkylphosphine/palladium (0) derivatives. Especially preferred catalysts are 2-dicyclohexylphosphino-2',6'-di-methoxybiphenyl (sPhos)/palladium(II)acetate and, tri-tert-butylphosphonium tetrafluoroborate ((t-Bu)$_3$P * HBF$_4$)/tris(dibenzylideneacetone) dipalladium (0) (Pd$_2$(dba)$_3$) and tri-tert-butylphosphine (t-Bu)$_3$P/tris(dibenzylideneacetone) dipalladium (0) (Pd$_2$(dba)$_3$). This reaction can be applied to preparing high molecular weight polymers and copolymers.

To prepare polymers corresponding to formula VII a dihalogenide of formula $X^{10}—A—X^{10}$ is reacted with an (equimolar) amount of a diboronic acid or diboronate corresponding to formula  ; or a dihalogenide of formula  is reacted with an (equimolar) amount of a diboronic acid or diboronate corresponding to formula $X^{11}—A—X^{11}$, wherein X^{10} is halogen, especially Br, and X^{11} is independently in each occurrence -B(OH)$_2$, -B(OY^1)$_2$,  , or  , wherein Y^1 is independently in each occurrence a C$_1$-C$_{10}$alkyl group and Y^2 is independently in each occurrence a C$_2$-C$_{10}$alkylene group, such as –CY^{3}Y^4-CY^{5}Y^6-, or –CY^{7}Y^8-CY^{9}Y^{10}- CY^{11}Y^{12}-, wherein Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11} and Y^{12} are independently of each other hydrogen, or a C$_1$-C$_{10}$alkyl group, especially -C(CH$_3$)$_2$C(CH$_3$)$_2$-, -CH$_2$C(CH$_3$)$_2$CH$_2$-, or -C(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$-, and Y^{13} and Y^{14} are independently of each other hydrogen, or a C$_1$-C$_{10}$alkyl group, under the catalytic action of Pd and triphenylphosphine. The reaction is typically conducted at about 0 °C to 180 °C in an aromatic hydrocarbon solvent such as toluene, xylene. Other solvents such as dimethylformamide, dioxane, dimethoxyethan and tetrahydrofuran can also be used alone, or in mixtures with an aromatic hydrocarbon. An aqueous base, preferably sodium carbonate or bicarbonate, potassium phosphate, potassium carbonate or bicarbonate is used as activation agent for the boronic acid, boronate and as the HBr scavenger. A polymerization reaction may take 0.2 to 100 hours. Organic bases, such as, for example, tetraalkylammonium hydroxide, and phase transfer catalysts, such as, for example TBAB, can promote the activity of the boron (see, for example, Leadbeater & Marco; Angew. Chem. Int. Ed. Eng. 42 (2003) 1407 and references cited therein). Other variations of reaction conditions are given by T. I. Wallow and B. M. Novak in J. Org. Chem. 59 (1994) 5034-5037; and M. Remmers, M. Schulze, and G. Wegner in Macromol. Rapid Commun. 17 (1996) 239-252. Controll of molecular weight is possible by using either an excess of dibromide, diboronic acid, or diboronate, or a chain terminator.

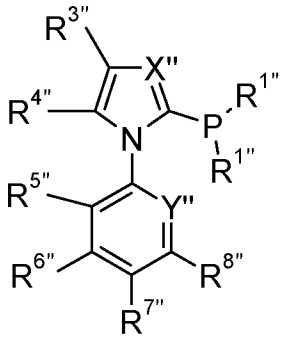
According to the process described in WO2010/136352 (PCT/EP2010/056776) the polymerisation is carried out in presence of

a) a catalyst/ligand system comprising a palladium catalyst and an organic phosphine or phosphonium compound,

b) a base,

c) a solvent or a mixture of solvents, characterized in that

the organic phosphine is a trisubstituted phosphine of formula

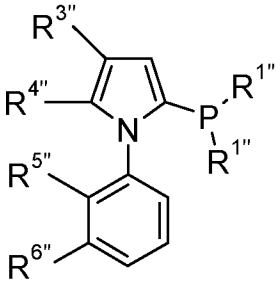


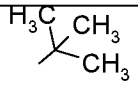
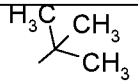
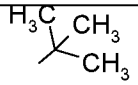
(VI), or phosphonium salt thereof, wherein X'' independently of Y'' represents a nitrogen atom or a C-$R^{2''}$ group and Y'' independently of X'' represents a nitrogen atom or a C-$R^{9''}$ group, $R^{1''}$ for each of the two $R^{1''}$ groups independently of the other represents a radical selected from the group C_1-C_{24}-alkyl, C_3-C_{20}-cycloalkyl, which includes especially both monocyclic and also bi-and tri-cyclic cycloalkyl radicals, C_5-C_{l4}-aryl, which includes especially the phenyl, naphthyl, fluorenyl radical, C_2-C_{13}-heteroaryl, wherein the number of hetero atoms, selected from the group N, O, S, may be from 1 to 2, wherein the two radicals $R^{1''}$ may also be linked to one another,

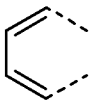
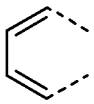
and wherein the above-mentioned radicals $R^{1''}$ may themselves each be mono-or poly-substituted independently of one another by substituents selected from the group hydrogen, C_1-C_{20}-alkyl, C_2-C_{2o}-alkenyl, C_3-C_8-cycloalkyl, C_2-C_9-hetero-alkyl, C_5-C_{10}-aryl, C_2-C_9-heteroaryl, wherein the number of hetero atoms from the group N, O, S may be from 1 to 4, C_1-C_{20}-alkoxy, C_1-C_{10}-haloalkyl, hydroxy, amino of the forms NH-(C_1-C_{20}-alkyl), NH-(C_5-C_{10}-aryl), N(C_1-C_{20}-alkyl)$_2$, N(C_1-C_{20}-alkyl) (C_5-C_{10}-aryl), N(C_5-C_{10}-aryl)$_2$, N(C_1-C_{20}-alkyl/C_5-C_{10}-aryl$_3$)$_3^+$, NH-CO-C_1-C_{20}-alkyl, NH-CO- C_5-C_{10}-aryl, carboxylato of the forms COOH and COOQ (wherein Q represents either a monovalent cation or C_1-C_8-alkyl), C_l-C_6-acyloxy, sulfinato, sulfonato of the forms SO_3H and SO_3Q' (wherein Q' represents either a monovalent cation, C_1-C_{20}-alkyl, or C_5-C_{10}-aryl), tri-C_1-C_6-alkylsilyl, wherein two of the mentioned substituents may also be bridged with one another, $R^{2''}$-$R^{9''}$ represent a hydrogen, alkyl, alkenyl, cycloalkyl, aromatic or heteroaromatic aryl, O-alkyl, NH- alkyl, N-(alkyl)$_2$, O-(aryl), NH-(aryl), N-(alkyl)(aryl), O-CO-alkyl, O-CO-aryl, F, Si(alkyl)$_3$, CF_3, CN, CO_2H, COH, SO_3H, $CONH_2$, CONH(alkyl), CON(alkyl)$_2$, SO_2(alkyl), SO(alkyl), SO(aryl), SO_2(aryl), SO_3(alkyl), SO_3(aryl), S-alkyl, S-aryl, NH-CO(alkyl), CO_2(alkyl), $CONH_2$, CO(alkyl), NHCOH, $NHCO_2$(alkyl), CO(aryl), CO_2(aryl) radical, wherein two or more adjacent radicals, each independently of the other (s), may also be linked to one another so that a condensed ring system is present and wherein in $R^{2''}$ to $R^{9''}$ alkyl represents a hydrocarbon radical having from 1 to 20 carbon atoms which may in each case be linear or branched, alkenyl represents a mono-or poly- unsaturated hydrocarbon radical having from 2 to 20 carbon atoms which may in each case be linear or branched, cycloalkyl represents a hydrocarbon having from 3 to 20 carbon atoms, aryl represents a 5- to 14-membered aromatic radical, wherein from one to four carbon atoms in the aryl radical may also be replaced by hetero atoms from the group nitrogen, oxygen and sulfur so that a 5- to 14-membered heteroaromatic radical is present, wherein the radicals $R^{2''}$ to $R^{9''}$ may also carry further substituents as defined for $R^{1''}$.

The organic phosphines and their synthesis are described in WO2004101581.

Preferred organic phosphines are selected from trisubstituted phosphines of formula



Cpd.	$R^{1''}$	$R^{5''}$	$R^{6''}$	$R^{3''}$	$R^{4''}$
A-1		H	H	H	H
A-2	cyclohexyl	H	H	H	H
A-3	phenyl	H	H	H	H
A-4	adamantyl	H	H	H	H
A-5	cyclohexyl	$-OCH_3$	H	H	H
A-6	cyclohexyl	1)	1)	H	H
A-7		1)	1)	H	H
A-8	phenyl	1)	1)	H	H
A-9	adamantyl	1)	1)	H	H
A-10	cyclohexyl	H	H	2)	2)
A-11		H	H	2)	2)
A-12	phenyl	H	H	2)	2)
A-13	adamantyl	H	H	2)	2)

1) $R^{5''}$ and $R^{6''}$ together form a ring  . 2) $R^{3''}$ and $R^{4''}$ together form a ring  .

Examples of preferred catalysts include the following compounds:

palladium(II) acetylacetonate, palladium(0) dibenzylidene-acetone complexes, palladium(II) propionate,

$Pd_2(dba)_3$: [tris(dibenzylideneacetone) dipalladium(0)],

$Pd(dba)_2$: [bis(dibenzylideneacetone) palladium(0)],

$Pd(PR_3)_2$, wherein PR_3 is a trisubstituted phosphine of formula VI,

$Pd(OAc)_2$: [palladium(II) acetate], palladium(II) chloride, palladium(II) bromide, lithium tetra-chloropalladate(II),

$PdCl_2(PR_3)_2$; wherein PR_3 is a trisubstituted phosphine of formula VI; palladium(0) diallyl ether complexes, palladium(II) nitrate,

$PdCl_2(PhCN)_2$: [dichlorobis(benzonitrile) palladium(II)],

$PdCl_2(CH_3CN)$: [dichlorobis(acetonitrile) palladium(II)], and

$PdCl_2(COD)$: [dichloro(1,5-cyclooctadiene) palladium(II)].

Especially preferred are $PdCl_2$, $Pd_2(dba)_3$, $Pd(dba)_2$, $Pd(OAc)_2$, or $Pd(PR_3)_2$. Most preferred are $Pd_2(dba)_3$ and $Pd(OAc)_2$.

The palladium catalyst is present in the reaction mixture in catalytic amounts. The term "catalytic amount" refers to an amount that is clearly below one equivalent of the (hetero)aromatic compound(s), preferably 0.001 to 5 mol-%, most preferably 0.001 to 1 mol-%, based on the equivalents of the (hetero)aromatic compound(s) used.

The amount of phosphines or phosphonium salts in the reaction mixture is preferably from 0.001 to 10 mol-%, most preferably 0.01 to 5 mol-%, based on the equivalents of the (hetero)aromatic compound(s) used. The preferred ratio of Pd:phosphine is 1:4.

The base can be selected from all aqueous and nonaqueous bases and can be inorganic, or organic. It is preferable that at least 1.5 equivalents of said base per functional boron group is present in the reaction mixture. Suitable bases are, for example, alkali and alkaline earth metal hydroxides, carboxylates, carbonates, fluorides and phosphates such as sodium and potassium hydroxide, acetate, carbonate, fluoride and phosphate or also metal alcoholates. It is also possible to use a mixture of bases. The base is preferably a lithium salt, such as, for example, lithium alkoxides (such as, for example, lithium methoxide and lithium ethoxide), lithium hydroxide, carboxylate, carbonate, fluoride and/or phosphate.

The at present most preferred base is aqueous $LiOHxH_2O$ (monohydrate of LiOH) and (waterfree) LiOH.

The reaction is typically conducted at about 0 °C to 180 °C, preferably from 20 to 160°C, more preferably from 40 to 140°C and most preferably from 40 to 120°C. A polymerization reaction may take 0.1, especially 0.2 to 100 hours.

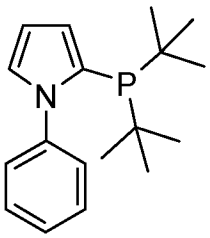
In a preferred embodiment of the present invention the solvent is THF, the base is $LiOH*H_2O$ and the reaction is conducted at reflux temperature of THF (about 65 °C).

The solvent is for example selected from toluene, xylenes, anisole, THF, 2-methyltetrahydrofuran, dioxane, chlorobenzene, fluorobenzene or solvent mixtures comprising one or more solvents like e.g. THF/toluene and optionally water. Most preferred is THF, or THF/water.

Advantageously, the polymerisation is carried out in presence of
a) palladium(II) acetate, or $Pd_2(dba)_3$, (tris(dibenzylideneacetone)dipalladium(0)) and an organic phosphine **A-1** to **A-13**,
b) LiOH, or $LiOHxH_2O$; and
c) THF, and optionally water. If the monohydrate of LiOH is used, no water needs to be added.

Most preferred the polymerisation is carried out in presence of

a) palladium(II) acetate, or $Pd_2(dba)_3$ (tris(dibenzylideneacetone)dipalladium(0)) and



;

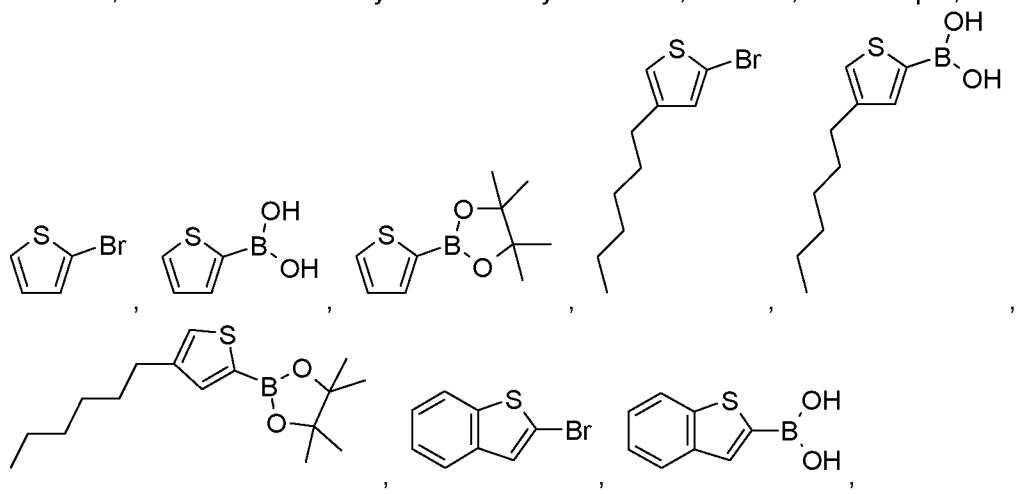
b) $LiOHxH_2O$; and

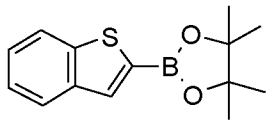
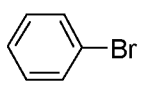
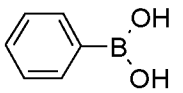
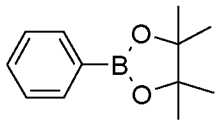
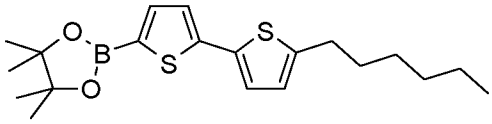
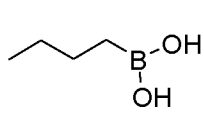
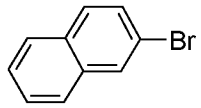
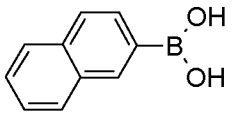
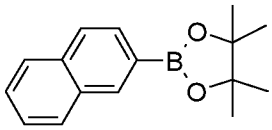
c) THF. The palladium catalyst is present in an amount of preferably about 0.5 mol-%, based on the equivalents of the (hetero)aromatic compound(s) used. The amount of phosphines or phosphonium salts in the reaction mixture is preferably about 2 mol-%, based on the equivalents of the (hetero)aromatic compound(s) used. The preferred ratio of Pd:phosphine is about 1:4.

Preferably the polymerization reaction is conducted under inert conditions in the absence of oxygen. Nitrogen and more preferably argon are used as inert gases.

The process described in WO2010/136352 is suitable for large-scale applications, is readily accessible and convert starting materials to the respective polymers in high yield, with high purity and high selectivity. The process can provide polymers having weight average molecular weights of at least 10,000, more preferably at least 20,000, most preferably at least 30,000. The at present most preferred polymers have a weight average molecular weight of 30,000 to 80,000 Daltons. Molecular weights are determined according to high-temperature gel permeation chromatography (HT-GPC) using polystyrene standards. The polymers preferably have a polydispersibility of 1.01 to 10, more preferably 1.1 to 3.0, most preferred 1.5 to 2.5.

If desired, a monofunctional aryl halide or aryl boronate, such as, for example,











and  , may be used as a chain-terminator in such reactions, which will result in the formation of a terminal aryl group.

It is possible to control the sequencing of the monomeric units in the resulting copolymer by controlling the order and composition of monomer feeds in the Suzuki reaction.

The polymers of the present invention can also be sythesized by the Stille coupling (see, for example, Babudri et al, J. Mater. Chem., 2004, 14, 11-34; J. K. Stille, Angew. Chemie Int. Ed. Engl. 1986, 25, 508). To prepare polymers corresponding to formula **VII** a dihalogenide of formula $X^{10}—A—X^{10}$ is reacted with a compound of formula $X^{11'}—COM^{1}—X^{11'}$, or a dihalogenide of formula $X^{10}—COM^{1}—X^{10}$ is reacted with a compound of formula $X^{11'}—A—X^{11'}$, wherein $X^{11'}$ is a group $-SnR^{207}R^{208}R^{209}$ and X^{10} is as defined above, in an inert solvent at a temperature in range from 0°C to 200°C in the presence of a palladium-containing catalyst, wherein R^{207}, R^{208} and R^{209} are identical or different and are H or C_1-C_6alkyl, wherein two radicals optionally form a common ring and these radicals are optionally branched or unbranched. It must be ensured here that the totality of all monomers used has a highly balanced ratio of organotin functions to halogen functions. In addition, it may prove advantageous to remove any excess reactive groups at the end of the reaction by end-capping with monofunctional reagents. In order to carry out the process, the tin compounds and the halogen compounds are preferably introduced into one or more inert organic solvents and stirred at a temperature of from 0 to 200°C, preferably from 30 to 170°C for a period of from 1 hour to 200 hours, preferably from 5 hours to 150 hours. The crude product can be purified by methods known to the person skilled in the art and appropriate for the respective polymer, for example repeated re-precipitation or even by dialysis.

Suitable organic solvents for the process described are, for example, ethers, for example diethyl ether, dimethoxyethane, diethylene glycol dimethyl ether, tetrahydrofuran, dioxane, dioxolane, diisopropyl ether and tert-butyl methyl ether, hydrocarbons, for example hexane, isohexane, heptane, cyclohexane, benzene, toluene and xylene, alcohols, for example methanol, ethanol, 1-propanol, 2-propanol, ethylene glycol, 1-butanol, 2-butanol and tert-butanol, ketones, for example acetone, ethyl methyl ketone and isobutyl methyl ketone, amides, for example dimethylformamide (DMF), dimethylacetamide and N-methylpyrrolidone, nitriles, for example acetonitrile, propionitrile and butyronitrile, and mixtures thereof.

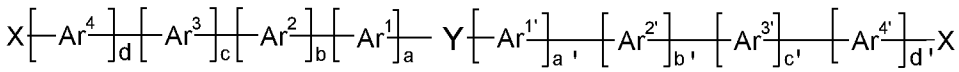
The palladium and phosphine components should be selected analogously to the description for the Suzuki variant.

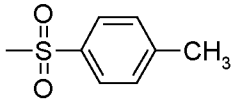
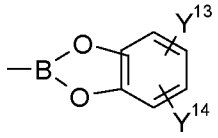
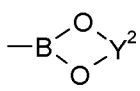
Alternatively, the polymers of the present invention can also be synthesized by the Negishi reaction using a zinc reagent A-$(ZnX^{12})_2$, wherein X^{12} is halogen and halides, and COM^1-$(X^{23})_2$, wherein X^{23} is halogen or triflate, or using A-$(X^{23})_2$ and COM^1-$(ZnX^{23})_2$. Reference is, for example, made to E. Negishi et al., Heterocycles 18 (1982) 117-22.

Alternatively, the polymers of the present invention can also be synthesized by the Hiyama reaction using a organosilicon reagent A-$(SiR^{210}R^{211}R^{212})_2$, wherein R^{210}, R^{211} and R^{212} are identical or different and are halogen, or C_1-C_6alkyl, and COM^1-$(X^{23})_2$, wherein X^{23} is halogen or triflate, or using A-$(X^{23})_2$ and COM^1-$(SiR^{210}R^{211}R^{212})_2$. Reference is, for example, made to T. Hiyama et al., Pure Appl. Chem. 66 (1994) 1471-1478 and T. Hiyama et al., Synlett (1991) 845-853.

Homopolymers of the type $(A)_n$ can be obtained via Yamamoto coupling of dihalides $X^{10}—A—X^{10}$, where X^{10} is halogen, preferably bromide. Alternatively homopolymers of the type $(A)_n$ can be obtained via oxidative polymerization of units $X^{10}—A—X^{10}$, where X^{10} is hydrogen, e.g. with $FeCl_3$ as oxidizing agent.

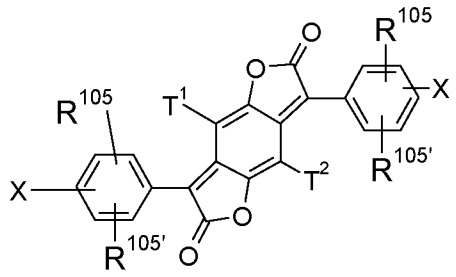
The compounds of the formula



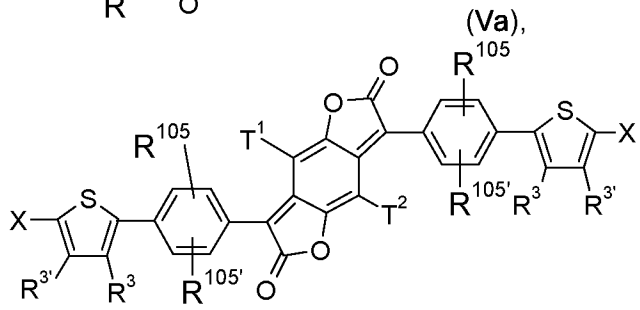
(V) are intermediates in the production of the polymers of the present invention, are new and form a further subject of the present invention. a, a', b, b', c, c', d, d', Y, Ar^1, $Ar^{1'}$, Ar^2, $Ar^{2'}$, Ar^3, $Ar^{3'}$, Ar^4 and $Ar^{4'}$ are as defined in claim 1, and X is halogen, especially Br, or J, ZnX^{12}, -$SnR^{207}R^{208}R^{209}$, wherein R^{207}, R^{208} and R^{209} are identical or different and are H or C_1-C_6alkyl, wherein two radicals optionally form a common ring and these radicals are optionally branched or unbranched and X^{12} is a halogen atom, very especially I, or Br; or -$OS(O)_2CF_3$, -$OS(O)_2$-aryl, especially  , -$OS(O)_2CH_3$, -$B(OH)_2$, -$B(OY^1)_2$,  ,  , -BF_4Na, or -BF_4K, wherein Y^1 is independently in each occurrence a C_1-C_{10}alkyl group and Y^2 is independently in each occurrence a C_2-C_{10}alkylene group, such as -CY^3Y^4-CY^5Y^6-, or –CY^7Y^8-CY^9Y^{10}- $CY^{11}Y^{12}$-, wherein Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11} and Y^{12} are independently of each other hydrogen, or a C_1-C_{10}alkyl group, especially -$C(CH_3)_2C(CH_3)_2$-, -$C(CH_3)_2CH_2C(CH_3)_2$-, or -$CH_2C(CH_3)_2CH_2$-, and Y^{13} and Y^{14} are independently of each other hydrogen, or a C_1-C_{10}alkyl group.

X is preferably different from a halogen atom.

Examples of compounds of formula V are shown below:



(**Va**),



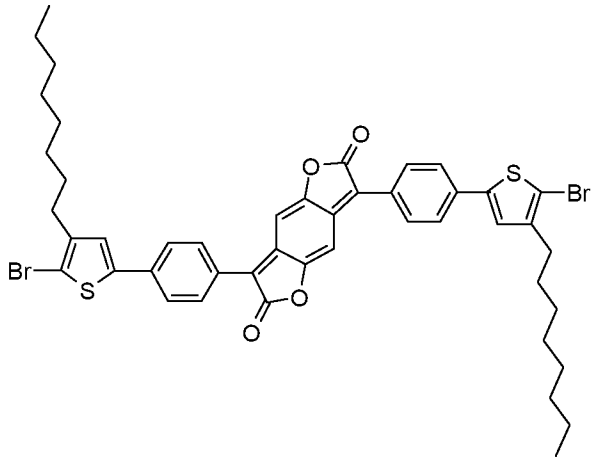
(**Vb**), wherein X is as defined above,

T^1 and T^2 are independently of each other hydrogen, or C_1-C_{25}alkyl, especially hydrogen;

R^1 is a C_1-C_{38}alkyl group, especially a C_8-C_{36}alkyl group,

R^{105} and $R^{105'}$ are independently of each other hydrogen, halogen, cyano, C_1-C_{25}alkyl or C_1-C_{25}alkoxy, especially hydrogen or C_1-C_{25}alkyl.

Examples of compounds of formula V are shown below:



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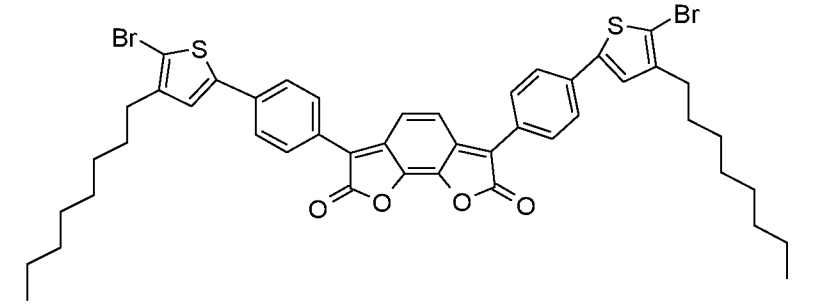

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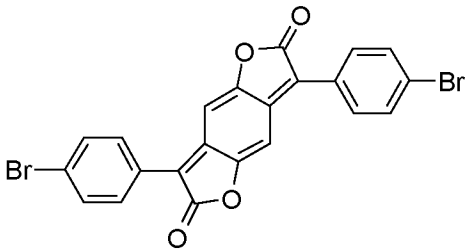
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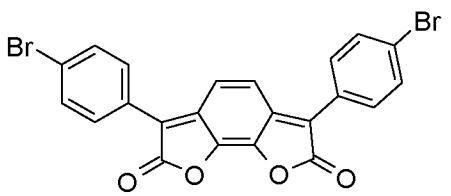
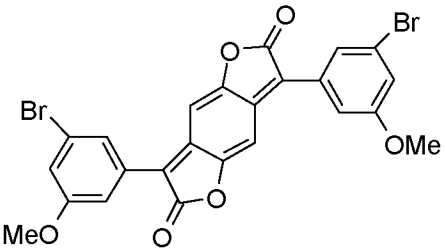
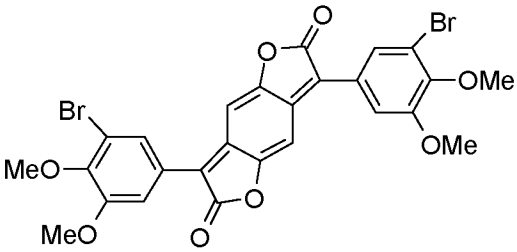
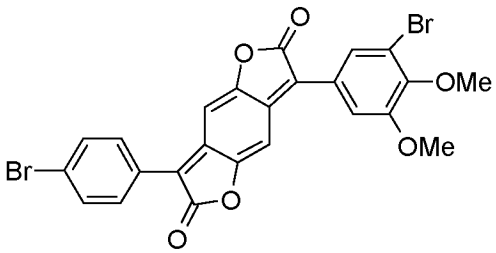
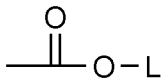
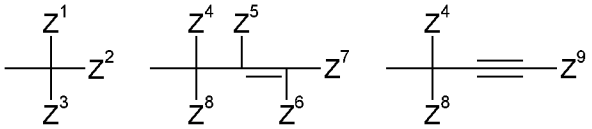
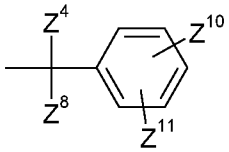
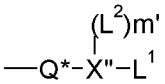

,

,

, and

.

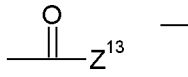
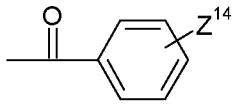
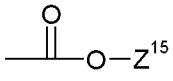
The polymers, wherein R^1 and/or R^2 are hydrogen can be obtained by using a protecting group which can be removed after polymerization. Reference is made, for example, to EP-A-0648770, EP-A-0648817, EP-A-0742255, EP-A-0761772, WO98/32802, WO98/45757, WO98/58027, WO99/01511, WO00/17275, WO00/39221, WO00/63297 and EP-A-1086984, which describe the basic procedural method. Conversion of the pigment precursor into its pigmentary form is carried out by means of fragmentation under known conditions, for example thermally, optionally in the presence of an additional catalyst, for example the catalysts described in WO00/36210.

An example of such a protecting group is group of formula  , wherein L is any desired group suitable for imparting solubility.

L is preferably a group of formula  , , ,  , or  , wherein Z^1, Z^2 and Z^3 are independently of each other C_1-C_6alkyl,

Z^4 and Z^8 are independently of each other C_1-C_6alkyl, C_1-C_6alkyl interrupted by oxygen, sulfur or $N(Z^{12})_2$, or unsubstituted or C_1-C_6alkyl-, C_1-C_6alkoxy-, halo-, cyano- or nitro-substituted phenyl or biphenyl,

Z^5, Z^6 and Z^7 are independently of each other hydrogen or C_1-C_6alkyl,

Z^9 is hydrogen, C_1-C_6alkyl or a group of formula  ,  or  ,

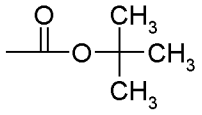
Z^{10} and Z^{11} are each independently of the other hydrogen, C_1-C_6alkyl, C_1-C_6alkoxy, halogen, cyano, nitro, $N(Z^{12})_2$, or unsubstituted or halo-, cyano-, nitro-, C_1-C_6alkyl- or C_1-C_6alkoxy-substituted phenyl,

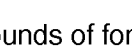
Z^{12} and Z^{13} are C_1-C_6alkyl, Z^{14} is hydrogen or C_1-C_6alkyl, and Z^{15} is hydrogen, C_1-C_6alkyl, or unsubstituted or C_1-C_6alkyl-substituted phenyl,

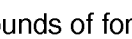
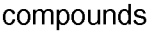
Q* is p,q-C_2-C_6alkylene unsubstituted or mono- or poly-substituted by C_1-C_6alkoxy, C_1-C_6alkylthio or C_2-C_{12}dialkylamino, wherein p and q are different position numbers,

X'' is a hetero atom selected from the group consisting of nitrogen, oxygen and sulfur, m' being the number 0 when X'' is oxygen or sulfur and m being the number 1 when X'' is nitrogen, and

L^1 and L^2 are independently of each other unsubstituted or mono- or poly-C_1-C_{12}alkoxy-, -C_1-C_{12}alkylthio-, -C_2-C_{24}dialkylamino-, -C_6-C_{12}aryloxy-, -C_6-C_{12}arylthio-, -C_7-C_{24}alkylarylamino- or -C_{12}-C_{24}diarylamino-substituted C_1-C_6alkyl or [–(p',q'-C_2-C_6alkylene)–Z–]$_{n'}$–C_1-C_6alkyl , n' being a number from 1 to 1000, p' and q' being different position numbers, each Z independently of any others being a hetero atom oxygen, sulfur or C_1-C_{12}alkyl-substituted nitrogen, and it being possible for C_2-C_6alkylene in the repeating [-C_2-C_6alkylene–Z–] units to be the same or different,

and L_1 and L_2 may be saturated or unsaturated from one to ten times, may be uninterrupted or interrupted at any location by from 1 to 10 groups selected from the group consisting of -(C=O)- and -C_6H_4-, and may carry no further substituents or from 1 to 10 further substituents selected from the group consisting of halogen, cyano and nitro. Most preferred L is a group of formula  .

The synthesis of the compounds of formula  can be done in analogy to the methods described in C. Greenhalgh et al., Dyes and Pigments 1 (1980) 103-120 and G Hallas et al. Dyes and Pigments 48 (2001) 121-132.

The synthesis of the compounds of formula  is described in WO08/000664, and WO09/047104, or can be done in analogy to the methods described therein. The synthesis of N-aryl substituted compounds of formula  can be done in analogy to the methods described in US-A-5,354,869 and WO03/022848.

Halogen is fluorine, chlorine, bromine and iodine.

C_1-C_{25}alkyl (C_1-C_{18}alkyl) is typically linear or branched, where possible. Examples are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, 1,1,3,3-tetramethylpentyl, n-hexyl, 1-methylhexyl, 1,1,3,3,5,5-hexamethylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methyl-

heptyl, n-octyl, 1,1,3,3-tetramethylbutyl and 2-ethylhexyl, n-nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl, heneicosyl, docosyl, tetracosyl or pentacosyl. C_1-C_8alkyl is typically methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethyl-propyl, n-hexyl, n-heptyl, n-octyl, 1,1,3,3-tetramethylbutyl and 2-ethylhexyl. C_1-C_4alkyl is typically methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl.

C_2-C_{18}alkenyl groups are straight-chain or branched alkenyl groups, such as e.g. vinyl, allyl, methallyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, isododecenyl, n-dodec-2-enyl or n-octadec-4-enyl.

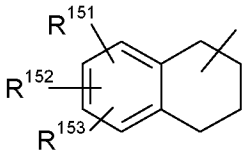
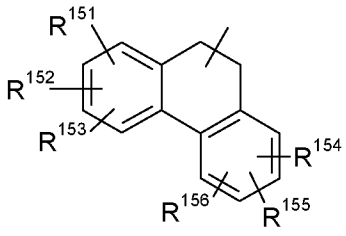
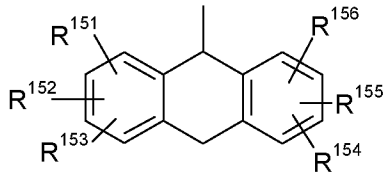
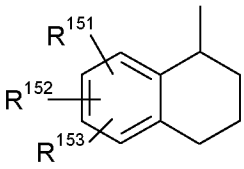
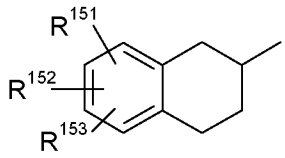
C_{2-18}alkynyl is straight-chain or branched and preferably C_{2-8}alkynyl, which may be unsubstituted or substituted, such as, for example, ethynyl, 1-propyn-3-yl, 1-butyn-4-yl, 1-pentyn-5-yl, 2-methyl-3-butyn-2-yl, 1,4-pentadiyn-3-yl, 1,3-pentadiyn-5-yl, 1-hexyn-6-yl, cis-3-methyl-2-penten-4-yn-1-yl, trans-3-methyl-2-penten-4-yn-1-yl, 1,3-hexadiyn-5-yl, 1-octyn-8-yl, 1-nonyn-9-yl, 1-decyn-10-yl, or 1-tetracosyn-24-yl.

C_1-C_{25}alkoxy groups (C_1-C_{18}alkoxy groups) are straight-chain or branched alkoxy groups, e.g. methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy, amyloxy, isoamyloxy or tert-amyloxy, heptyloxy, octyloxy, isooctyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tetradecyloxy, pentadecyloxy, hexadecyloxy, heptadecyloxy and octadecyloxy. Examples of C_1-C_8alkoxy are methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec.-butoxy, isobutoxy, tert.-butoxy, n-pentoxy, 2-pentoxy, 3-pentoxy, 2,2-dimethylpropoxy, n-hexoxy, n-heptoxy, n-octoxy, 1,1,3,3-tetramethylbutoxy and 2-ethylhexoxy, preferably C_1-C_4alkoxy such as typically methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec.-butoxy, isobutoxy, tert.-butoxy. The term “alkylthio group” means the same groups as the alkoxy groups, except that the oxygen atom of the ether linkage is replaced by a sulfur atom.

C_1-C_{18}perfluoroalkyl, especially C_1-C_4perfluoroalkyl, is a branched or unbranched radical such as for example $-CF_3$, $-CF_2CF_3$, $-CF_2CF_2CF_3$, $-CF(CF_3)_2$, $-(CF_2)_3CF_3$, and $-C(CF_3)_3$.

The term “carbamoyl group” is typically a C_{1-18}carbamoyl radical, preferably C_{1-8}carbamoyl radical, which may be unsubstituted or substituted, such as, for example, carbamoyl, methylcarbamoyl, ethylcarbamoyl, n-butylcarbamoyl, tert-butylcarbamoyl, dimethylcarbamoyloxy, morpholinocarbamoyl or pyrrolidinocarbamoyl.

C_5-C_{12}cycloalkyl is typically cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, cyclododecyl, preferably cyclopentyl, cyclohexyl, cycloheptyl, or cyclooctyl, which may be unsubstituted or substituted. The cycloalkyl group, in particular a cyclohexyl group, can be condensed one or two times by phenyl which can be substituted one to three times with C_1-C_4-alkyl, halogen and cyano. Examples of such condensed

cyclohexyl groups are:  ,  or  in particular  or  , wherein R^{151}, R^{152}, R^{153}, R^{154}, R^{155} and R^{156} are independently of each other C_1-C_8-alkyl, C_1-C_8-alkoxy, halogen and cyano, in particular hydrogen.

C_6-C_{24}aryl (C_6-C_{18}aryl) is typically phenyl, indenyl, azulenyl, naphthyl, biphenyl, as-indacenyl, s-indacenyl, acenaphthylenyl, fluorenyl, phenanthryl, fluoranthenyl, triphenlenyl, chrysenyl, naphthacen, picenyl, perylenyl, pentaphenyl, hexacenyl, pyrenyl, or anthracenyl, preferably phenyl, 1-naphthyl, 2-naphthyl, 4-biphenyl, 9-phenanthryl, 2- or 9-fluorenyl, 3- or 4-biphenyl, which may be unsubstituted or substituted. Examples of C_6-C_{12}aryl are phenyl, 1-naphthyl, 2-naphthyl, 3- or 4-biphenyl, 2- or 9-fluorenyl or 9-phenanthryl, which may be unsubstituted or substituted.

C_7-C_{25}aralkyl is typically benzyl, 2-benzyl-2-propyl, β-phenyl-ethyl, α,α-dimethylbenzyl, ω-phenyl-butyl, ω,ω-dimethyl-ω-phenyl-butyl, ω-phenyl-dodecyl, ω-phenyl-octadecyl, ω-phenyl-eicosyl or ω-phenyl-docosyl, preferably C_7-C_{18}aralkyl such as benzyl, 2-benzyl-2-propyl, β-phenyl-ethyl, α,α-dimethylbenzyl, ω-phenyl-butyl, ω,ω-dimethyl-ω-phenyl-butyl, ω-phenyl-dodecyl or ω-phenyl-octadecyl, and particularly preferred C_7-C_{12}aralkyl such as benzyl, 2-benzyl-2-propyl, β-phenyl-ethyl, α,α-dimethylbenzyl, ω-phenyl-butyl, or ω,ω-dimethyl-ω-phenyl-butyl, in which both the aliphatic hydrocarbon group and aromatic hydrocarbon group may be unsubstituted or substituted. Preferred examples are benzyl, 2-phenylethyl, 3-phenylpropyl, naphthylethyl, naphthylmethyl, and cumyl.

Heteroaryl is typically C_2-C_{20}heteroaryl, i.e. a ring with five to seven ring atoms or a condensed ring system, wherein nitrogen, oxygen or sulfur are the possible hetero atoms, and is typically an unsaturated heterocyclic group with five to 30 atoms having at least six conjugated π-electrons such as thienyl, benzo[b]thienyl, dibenzo[b,d]thienyl, thianthrenyl, furyl, furfuryl, 2H-pyranyl, benzofuranyl, isobenzofuranyl, dibenzofuranyl, phenoxythienyl, pyrrolyl, imidazolyl, pyrazolyl, pyridyl, bipyridyl, triazinyl, pyrimidinyl, pyrazinyl, pyridazinyl, indolizinyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizinyl, chinolyl, isochinolyl, phthalazinyl, naphthyridinyl, chinoxalinyl, chinazolinyl, cinnolinyl, pteridinyl, carbazolyl, carbolinyl, benzotriazolyl, benzoxazolyl, phenanthridinyl, acridinyl, pyrimidinyl, phenanthrolinyl,

phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl or phenoxazinyl, which can be unsubstituted or substituted.

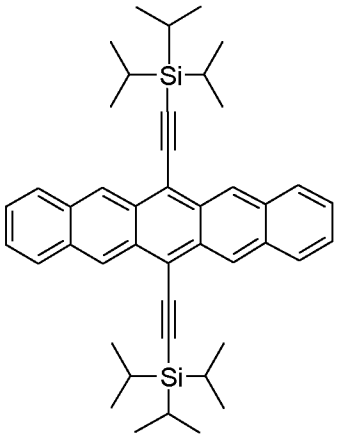
Possible substituents of the above-mentioned groups are C_1-C_8alkyl, a hydroxyl group, a mercapto group, C_1-C_8alkoxy, C_1-C_8alkylthio, halogen, halo-C_1-C_8alkyl, a cyano group, a carbamoyl group, a nitro group or a silyl group, especially C_1-C_8alkyl, C_1-C_8alkoxy, C_1-C_8alkylthio, halogen, halo-C_1-C_8alkyl, or a cyano group.

C_1-C_{18}alkyl interrupted by one or more O is, for example, $(CH_2CH_2O)_{1-9}$-R^x, where R^x is H or C_1-C_{10}alkyl, CH_2-$CH(OR^{y'})$-CH_2-O-R^y, where R^y is C_1-C_{18}alkyl, and $R^{y'}$ embraces the same definitions as R^y or is H.

If a substituent, such as, for example R^3, occurs more than one time in a group, it can be different in each occurrence.

A mixture containing a polymer of the present invention results in a semi-conducting layer comprising a polymer of the present invention (typically 5% to 99.9999% by weight, especially 20 to 85 % by weight) and at least another material. The other material can be, but is not restricted to a fraction of the same polymer of the present invention with different molecular weight, another polymer of the present invention, a semi-conducting polymer, organic small molecules, carbon nanotubes, a fullerene derivative, inorganic particles (quantum dots, quantum rods, quantum tripods, TiO_2, ZnO etc.), conductive particles (Au, Ag etc.), insulator materials like the ones described for the gate dielectric (PET, PS etc.).

The polymers of the present invention can be blended with small molecules described, for example, in WO2009/047104, PCT/EP2010/053655, WO09/047104, US6,690,029, WO2007082584, and WO2008107089:
WO2007082584:



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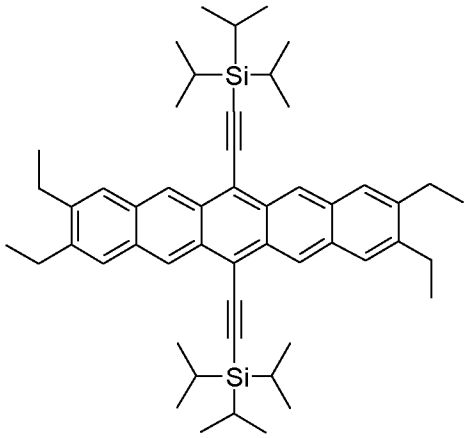

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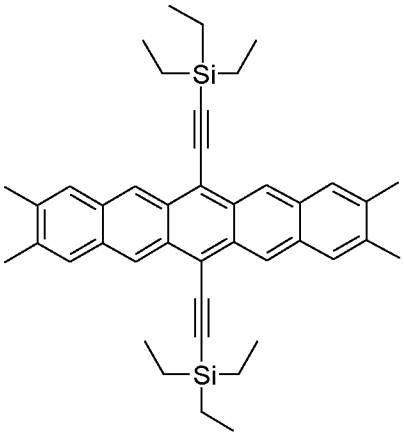

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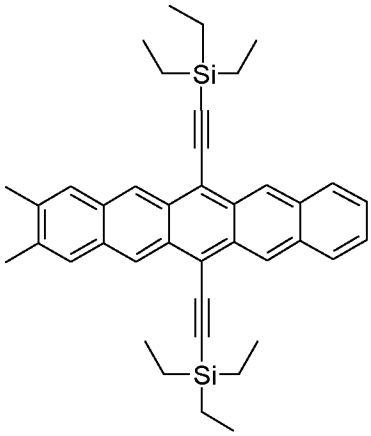

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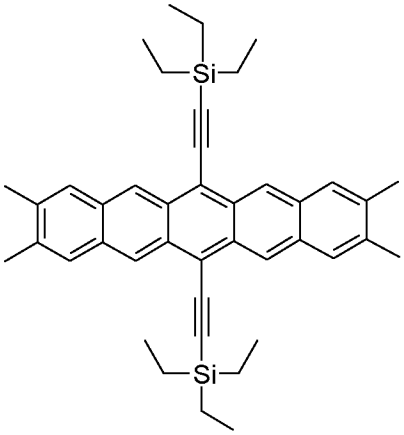

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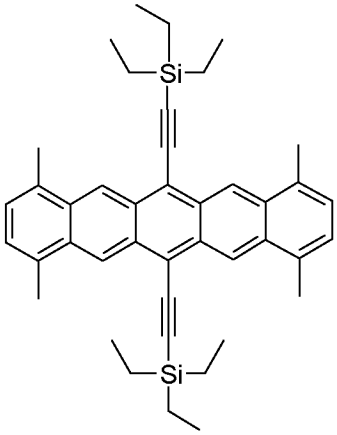

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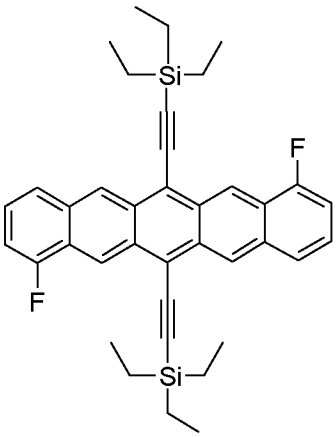

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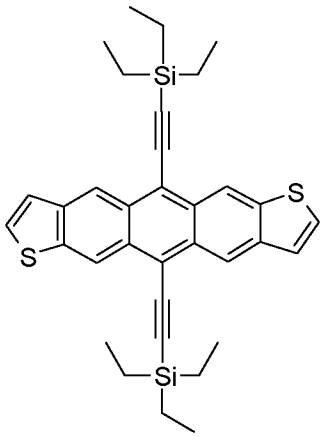

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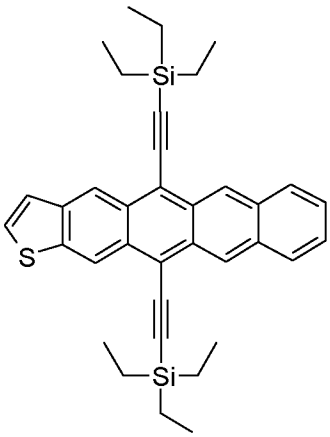
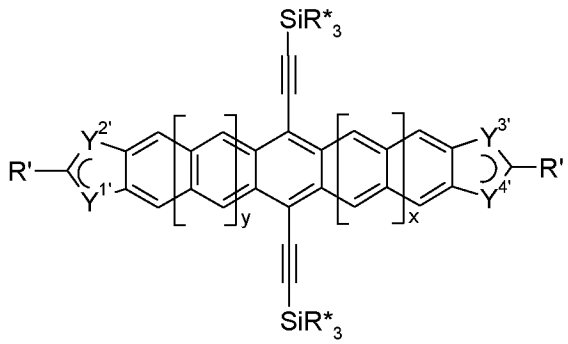
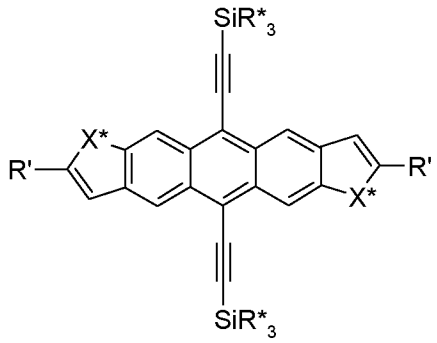


(I9).

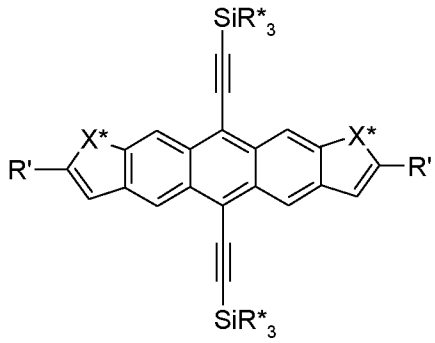
WO2008107089:



wherein one of $Y^{1'}$ and $Y^{2'}$ denotes -CH= or =CH- and the other denotes –X*-,
one of $Y^{3'}$ and $Y^{4'}$ denotes -CH= or =CH- and the other denotes –X*-,
X* is -O-, -S-, -Se- or -NR'''-,
R* is cyclic, straight-chain or branched alkyl or alkoxy having 1 to 20 C-atoms, or aryl having 2-30 C-atoms, all of which are optionally fluorinated or perfluorinated,
R' is H, F, Cl, Br, I, CN, straight-chain or branched alkyl or alkoxy having 1 to 20 C-atoms and optionally being fluorinated or perfluorinated, optionally fluorinated or perfluorinated aryl having 6 to 30 C-atoms, or CO_2R'', with R'' being H, optionally fluorinated alkyl having 1 to 20 C-atoms, or optionally fluorinated aryl having 2 to 30 C-atoms,
R''' is H or cyclic, straight-chain or branched alkyl with 1 to 10 C-atoms, y is 0, or 1, x is 0, or 1.



A1,



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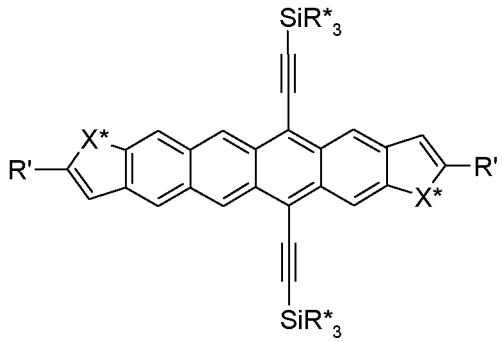

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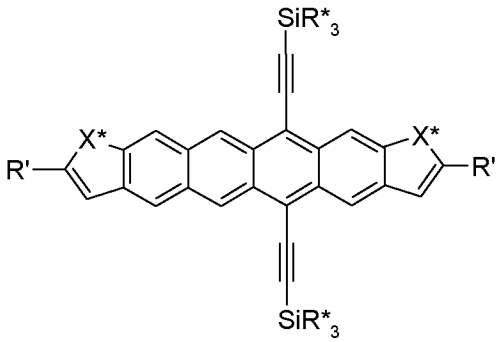

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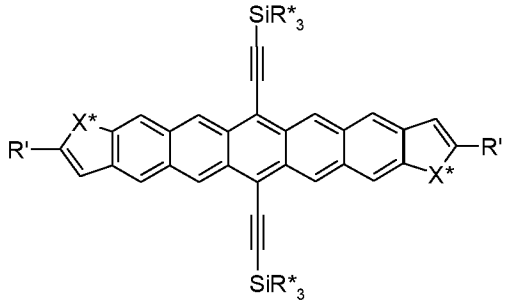
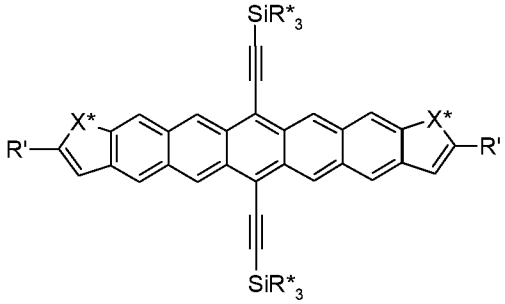


C1,



C2,

The polymer can contain a small molecule, or a mixture of two, or more small molecule compounds.

Accordingly, the present invention also relates to an organic semiconductor material, layer or component, comprising a polymer according to the present invention.

The polymers of the invention can be used as the semiconductor layer in semiconductor devices. Accordingly, the present invention also relates to semiconductor devices, comprising a polymer of the present invention, or an organic semiconductor material, layer or component. The semiconductor device is especially an organic photovoltaic (PV) device (solar cell), a photodiode, or an organic field effect transistor.

The polymers of the invention can be used alone or in combination as the organic semiconductor layer of the semiconductor device. The layer can be provided by any useful means, such as, for example, vapor deposition (for materials with relatively low molecular weight) and printing techniques. The compounds of the invention may be sufficiently soluble in organic solvents and can be solution deposited and patterned (for example, by spin coating, dip coating, ink jet printing, gravure printing, flexo printing, offset printing, screen printing, microcontact (wave)-printing, drop or zone casting, or other known techniques).

The polymers of the invention can be used in integrated circuits comprising a plurality of OTFTs, as well as in various electronic articles. Such articles include, for example, radio-frequency identification (RFID) tags, backplanes for flexible displays (for use in, for example, personal computers, cell phones, or handheld devices), smart cards, memory devices, sensors (e.g. light-, image-, bio-, chemo-, mechanical- or temperature sensors), especially photodiodes, or security devices and the like.

A further aspect of the present invention is an organic semiconductor material, layer or component comprising one or more polymers of the present invention. A further aspect is the use of the polymers or materials of the present invention in an organic photovoltaic (PV) device (solar cell), a photodiode, or an organic field effect transistor (OFET). A further aspect is an organic photovoltaic (PV) device (solar cell), a photodiode, or an organic field effect transistor (OFET) comprising a polymer or material of the present invention.

The polymers of the present invention are typically used as organic semiconductors in form of thin organic layers or films, preferably less than 30 microns thick. Typically the semiconducting layer of the present invention is at most 1 micron (=1 µm) thick, although it may be thicker if required. For various electronic device applications, the thickness may also be less than about 1 micron thick. For example, for use in an OFET the layer thickness may typically be 100 nm or less. The exact thickness of the layer will depend, for example, upon the requirements of the electronic device in which the layer is used.

For example, the active semiconductor channel between the drain and source in an OFET may comprise a layer of the present invention.

An OFET device according to the present invention preferably comprises:
- a source electrode,

- a drain electrode,
- a gate electrode,
- a semiconducting layer,
- one or more gate insulator layers, and
- optionally a substrate, wherein the semiconductor layer comprises one or more polymers of the present invention.

The gate, source and drain electrodes and the insulating and semiconducting layer in the OFET device may be arranged in any sequence, provided that the source and drain electrode are separated from the gate electrode by the insulating layer, the gate electrode and the semiconductor layer both contact the insulating layer, and the source electrode and the drain electrode both contact the semiconducting layer.

Preferably the OFET comprises an insulator having a first side and a second side, a gate electrode located on the first side of the insulator, a layer comprising a polymer of the present invention located on the second side of the insulator, and a drain electrode and a source electrode located on the polymer layer.

The OFET device can be a top gate device or a bottom gate device.

Suitable structures and manufacturing methods of an OFET device are known to the person skilled in the art and are described in the literature, for example in WO03/052841.

The gate insulator layer may comprise for example a fluoropolymer, like e.g. the commercially available Cytop 809M®, or Cytop 107M® (from Asahi Glass). Preferably the gate insulator layer is deposited, e.g. by spin-coating, doctor blading, wire bar coating, spray or dip coating or other known methods, from a formulation comprising an insulator material and one or more solvents with one or more fluoro atoms (fluorosolvents), preferably a perfluorosolvent. A suitable perfluorosolvent is e.g. FC75® (available from Acros, catalogue number 12380). Other suitable fluoropolymers and fluorosolvents are known in prior art, like for example the perfluoropolymers Teflon AF® 1600 or 2400 (from DuPont), or Fluoropel® (from Cytonix) or the perfluorosolvent FC 43® (Acros, No. 12377).

The semiconducting layer comprising a polymer of the present invention may additionally comprise at least another material. The other material can be, but is not restricted to another polymer of the present invention, a semi-conducting polymer, a polymeric binder, organic small molecules different from a polymer of the present invention, carbon nanotubes, a fullerene derivative, inorganic particles (quantum dots, quantum rods, quantum tripods, TiO_2, ZnO etc.), conductive particles (Au, Ag etc.), and insulator materials like the ones described for the gate dielectric (PET, PS etc.). As stated above, the semiconductive layer can also be composed of a mixture of one or more polymers of the present invention and a polymeric binder. The ratio of the polymers of the present invention to the polymeric binder can vary from 5 to 95 percent. Preferably, the polymeric binder is a semicristalline polymer such as polystyrene (PS), high-density polyethylene (HDPE), polypropylene (PP)

and polymethylmethacrylate (PMMA). With this technique, a degradation of the electrical performance can be avoided (cf. WO2008/001123A1).

The polymers of the present invention are advantageously used in organic photovoltaic (PV) devices (solar cells). Accordingly, the invention provides PV devices comprising a polymer according to the present invention. A device of this construction will also have rectifying properties so may also be termed a photodiode. Photoresponsive devices have application as solar cells which generate electricity from light and as photodetectors which measure or detect light.

The structure of organic photovoltaic devices (solar cells) is, for example, described in C. Deibel et al. Rep. Prog. Phys. 73 (2010) 096401 and Christoph Brabec, Energy Environ. Sci 2. (2009) 347-303.

The PV device comprise in this order:
(a) a cathode (electrode),
(b) optionally a transition layer, such as an alkali halogenide, especially lithium fluoride,
(c) a photoactive layer,
(d) optionally a smoothing layer,
(e) an anode (electrode),
(f) a substrate.

The photoactive layer comprises the polymers of the present invention. Preferably, the photoactive layer is made of a conjugated polymer of the present invention, as an electron donor and an acceptor material, like a fullerene, particularly a functionalized fullerene PCBM, as an electron acceptor. As stated above, the photoactive layer may also contain a polymeric binder. The ratio of the polymers of formula I to the polymeric binder can vary from 5 to 95 percent. Preferably, the polymeric binder is a semicristalline polymer such as polystyrene (PS), high-density polyethylene (HDPE), polypropylene (PP) and polymethylmethacrylate (PMMA).

For heterojunction solar cells the active layer comprises preferably a mixture of a polymer of the present invention and a fullerene, such as [60]PCBM (= 6,6-phenyl-C_{61}-butyric acid methyl ester), or [70]PCBM, in a weight ratio of 1:1 to 1:3. The fullerenes useful in this invention may have a broad range of sizes (number of carbon atoms per molecule). The term fullerene as used herein includes various cage-like molecules of pure carbon, including Buckminsterfullerene (C_{60}) and the related "spherical" fullerenes as well as carbon nanotubes. Fullerenes may be selected from those known in the art ranging from, for example, C_{20}-C_{1000}. Preferably, the fullerene is selected from the range of C_{60} to C_{96}. Most preferably the fullerene is C_{60} or C_{70}, such as [60]PCBM, or [70]PCBM. It is also permissible to utilize chemically modified fullerenes, provided that the modified fullerene retains acceptor-type and electron mobility characteristics. The acceptor material can also be a material selected from the group consisting of any semi-conducting polymer, such as, for example, a polymer of the present invention, provided that the polymers retain acceptor-type and electron mo-

bility characteristics, organic small molecules, carbon nanotubes, inorganic particles (quantum dots, quantum rods, quantum tripods, TiO_2, ZnO etc.).

The photoactive layer is made of a polymer of the present invention as an electron donor and a fullerene, particularly functionalized fullerene PCBM, as an electron acceptor. These two components are mixed with a solvent and applied as a solution onto the smoothing layer by, for example, the spin-coating method, the drop casting method, the Langmuir-Blodgett ("LB") method, the ink jet printing method and the dripping method. A squeegee or printing method could also be used to coat larger surfaces with such a photoactive layer. Instead of toluene, which is typical, a dispersion agent such as chlorobenzene is preferably used as a solvent. Among these methods, the vacuum deposition method, the spin-coating method, the ink jet printing method and the casting method are particularly preferred in view of ease of operation and cost.

In the case of forming the layer by using the spin-coating method, the casting method and ink jet printing method, the coating can be carried out using a solution and/or dispersion prepared by dissolving, or dispersing the composition in a concentration of from 0.01 to 90% by weight in an appropriate organic solvent such as benzene, toluene, xylene, tetrahydrofurane, methyltetrahydrofurane, N,N-dimethylformamide, acetone, acetonitrile, anisole, dichloromethane, dimethylsulfoxide, chlorobenzene, 1,2-dichlorobenzene and mixtures thereof.

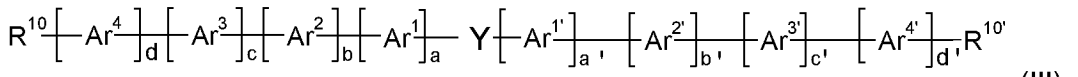
The photovoltaic (PV) device can also consist of multiple junction solar cells that are processed on top of each other in order to absorb more of the solar spectrum. Such structures are, for example, described in App. Phys. Let. **90**, 143512 (2007), Adv. Funct. Mater. **16**, 1897–1903 (2006), WO2004/112161 and Christoph Brabec, Energy Environ. Sci 2. (2009) 347-303.

A so called 'tandem solar cell' comprise in this order:
(a) a cathode (electrode),
(b) optionally a transition layer, such as an alkali halogenide, especially lithium fluoride,
(c) a photoactive layer,
(d) optionally a smoothing layer,
(e) a middle electrode (such as Au, Al, ZnO, TiO_2 etc.)
(f) optionally an extra electrode to match the energy level,
(g) optionally a transition layer, such as an alkali halogenide, especially lithium fluoride,
(h) a photoactive layer,
(i) optionally a smoothing layer,
(j) an anode (electrode),
(k) a substrate.

The PV device can also be processed on a fiber as described, for example, in US20070079867 and US 20060013549.

Due to their excellent self-organising properties the materials or films comprising the polymers of the present invention can also be used alone or together with other materials in or as alignment layers in LCD or OLED devices, as described for example in US2003/0021913.

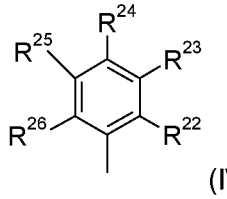
In a further embodiment the present invention relates to compounds of the formula



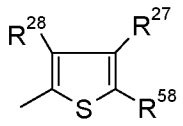
(III),

wherein a, a', b, b', c, c', d, d', Y, Ar^1, $Ar^{1'}$, Ar^2, $Ar^{2'}$, Ar^3, $Ar^{3'}$, Ar^4 and $Ar^{4'}$ are as defined above,

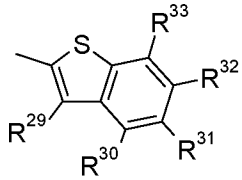
R^{10} and $R^{10'}$ are independently of each other hydrogen, halogen, cyano, C_1-C_{25}alkyl, C_1-C_{25}alkoxy, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, especially a group of one of the formulae **IVa** to **IVj**,



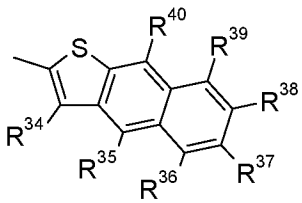
(IVa),



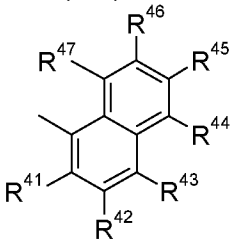
(IVb),



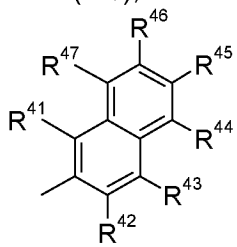
(IVc),



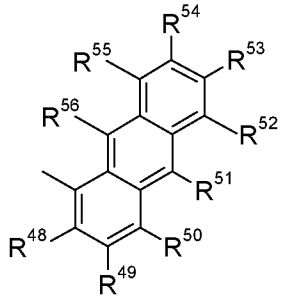
((IVd),



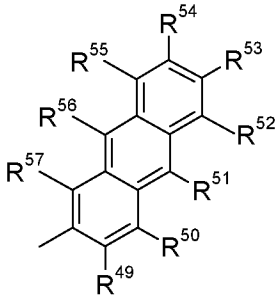
(IVe),



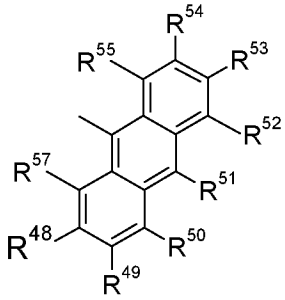
(IVf),



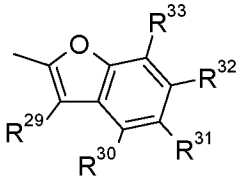
(IVg),



(IVh),



(IVi), or



(IVj),

wherein R^{22} to R^{26} and R^{29} to R^{58} represent independently of each other H, halogen, cyano, C_1-C_{25}alkyl, C_1-C_{25}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, a C_4-C_{18}cycloalkyl group, a C_4-C_{18}cycloalkyl group, which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, C_7-C_{25}aralkyl, or C_7-C_{25}aralkyl, which is substituted by G,

R^{27} and R^{28} are independently of each other hydrogen, C_1-C_{25}alkyl, halogen, cyano or C_7-C_{25}aralkyl, or R^{27} and R^{28} together represent alkylene or alkenylene which may be both

bonded via oxygen and/or sulfur to the thienyl residue and which may both have up to 25 carbon atoms,

D is -CO-, -COO-, -S-, -O-, or –NR^{112}–,

E is C_1-C_8thioalkoxy, C_1-C_8alkoxy, CN, -$NR^{112}R^{113}$, -$CONR^{112}R^{113}$, or halogen,

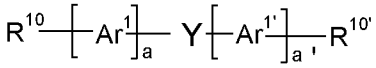
G is E, or C_1-C_{18}alkyl, and

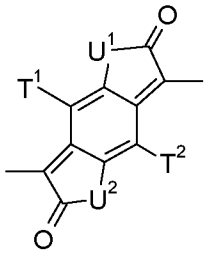
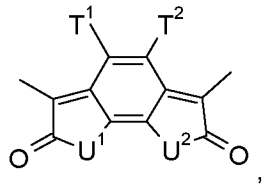
R^{112} and R^{113} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-, with the proviso that Ar^1 and $Ar^{1'}$ are not a group of formula (**XVa**), if b, b', c, c', d and d' are 0 and R^{10} and $R^{10'}$ are independently of each other hydrogen, halogen, C_1-C_{25}alkyl, or C_1-C_{25}alkoxy.

In a preferred embodiment of the present invention Ar^1 and $Ar^{1'}$ are not a group of formula **XVa**, if b, b', c, c', d and d' are 0.

In a preferred embodiment of the present invention R^{10} and $R^{10'}$ are independently of each other cyano, especially a group of one of the formulae **IVa** to **IVj**.

In a preferred embodiment of the present invention R^{10} and $R^{10'}$ are independently of each other cyano, especially a group of one of the formulae **IVa** to **IVj**, if Ar^1 and $Ar^{1'}$ are a group of formula **XVa**, b, b', c, c', d and d' are 0.

Compounds of the formula  (**III'**), wherein

Y is a group of formula  or  ,

U^1 is O, S, or NR^1;

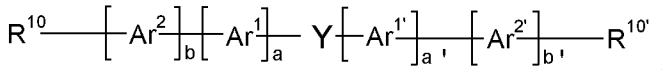
U^2 is O, S, or NR^2;

T^1 and T^2 are independently of each other hydrogen, halogen, hydroxyl, cyano, -$COOR^{103}$, -$OCOR^{103}$, -$NR^{112}COR^{103}$, -$CONR^{112}R^{113}$, -$OR^{103'}$, -$SR^{103'}$, -$SOR^{103'}$, -$SO_2R^{103'}$, -$NR^{112}SO_2R^{103'}$, -$NR^{112}R^{113}$, C_1-C_{25}alkyl, which which may be substituted by E and/or interrupted by D, C_5-C_{12}cycloalkyl, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; C_7-C_{25}arylalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G;

R^1 and R^2 may be the same or different and are selected from hydrogen, a C_1-C_{100}alkyl group, -$COOR^{103}$, -COR^{103}, a C_1-C_{100}alkyl group which is substituted by one or more halogen atoms, hydroxyl groups, nitro groups, -CN, or C_6-C_{18}aryl groups and/or interrupted by –O-, -COO-, -OCO-, or -S-; a C_7-C_{100}arylalkyl group, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; a carbamoyl group, C_5-C_{12}cycloalkyl, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; a C_6-C_{24}aryl group, in

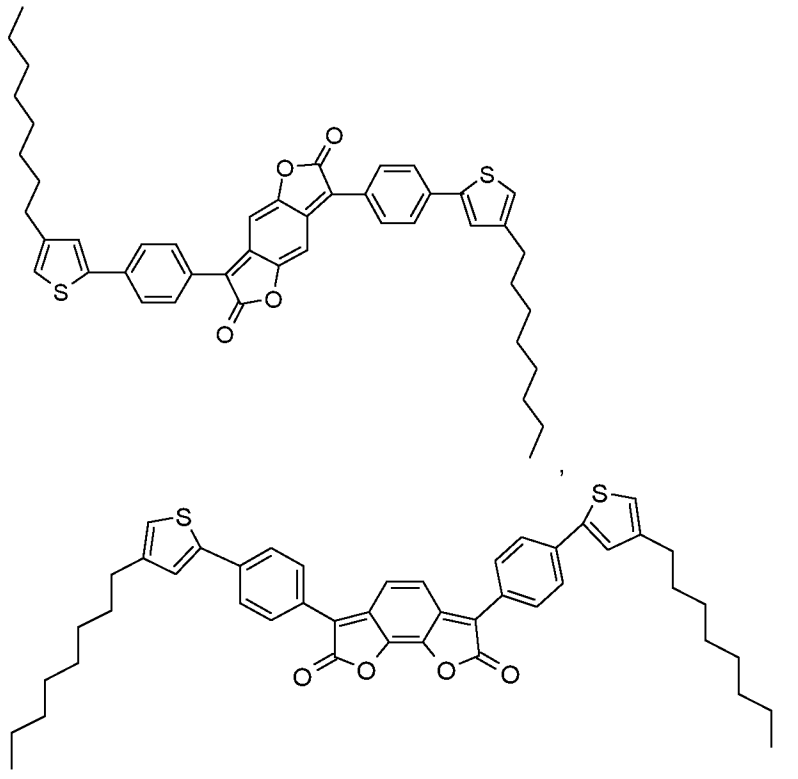
particular phenyl or 1- or 2-naphthyl, which can be substituted one to three times with C_1-C_8alkyl, C_1-C_8thioalkoxy, and/or C_1-C_8alkoxy, or pentafluorophenyl;
a is 1, 2, or 3, a' is 1, 2, or 3; wherein Ar^1 and $Ar^{1'}$ are independently of each other a group of formula (**XVa**), (**XVb**), (**XVc**), (**XVd**), (**XVe**), (**XVf**), (**XVg**), or (**XVh**) (as defined in claim 1);
R^{10}, $R^{10'}$, R^{103}, $R^{103'}$, R^{112}, R^{113}, D, E and G are as defined above.

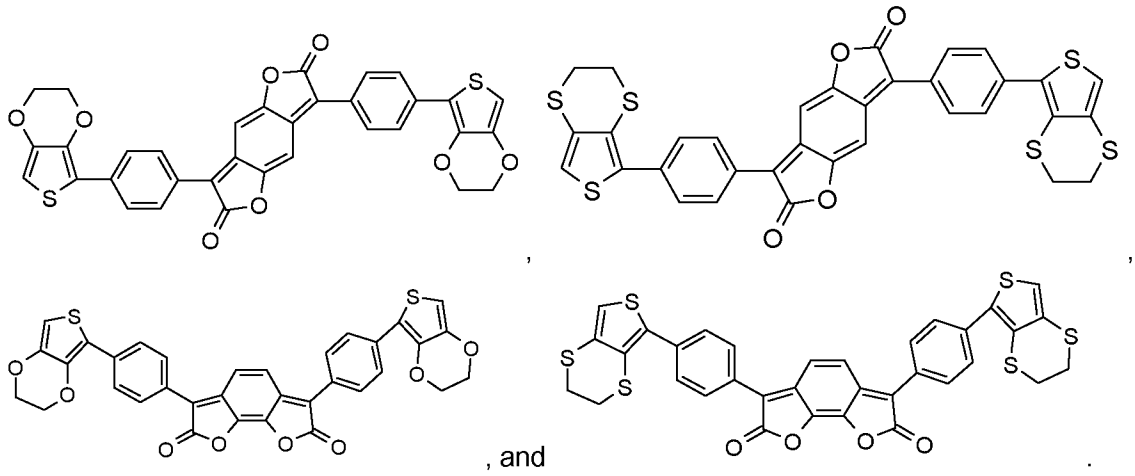
Ar^1 and $Ar^{1'}$ may be different, but are preferably the same. Ar^1 and $Ar^{1'}$ are independently of each other a group of formula (**XVa**), (**XVb**), (**XVc**), (**XVd**), (**XVe**), (**XVf**), (**XVg**), or (**XVh**), preferably a group of formula (**XVa**), (**XVb**), (**XVc**), (**XVd**) or (**XVe**), more preferably a group of formula (**XVa**), (**XVd**) or (**XVe**), most preferably a group of formula (**XVa**).



Compounds of formula (**III''**) are even more preferred, wherein a is 1, or 2, especially 1; a' is 1, or 2, especially 1; b is 1, 2, or 3; b' is 1, 2, or 3; wherein Y, Ar^1 and $Ar^{1'}$ are as defined above; and Ar^2 and $Ar^{2'}$ are a group of formula (**Xa**), (**Xc**), (**Xg**), (**Xh**), (**Xm**), (**Xn**), (**Xo**), (**Xp**), (**Xy**), (**XIe**), (**XIf**), (**XIl**), or (**XIm**).

Examples of preferred compounds are shown below:





Advantageously, the compound of formula III, or an organic semiconductor material, layer or component, comprising the compound of formula III can be used in organic photovoltaics (solar cells) and photodiodes, or in an organic field effect transistor (OFET).

A mixture containing the compound of formula III results in a semi-conducting layer comprising the compound of formula III (typically 5% to 99.9999% by weight, especially 20 to 85 % by weight) and at least another material. The other material can be, but is not restricted to another compound of formula III, a polymer of the present invention, a semi-conducting polymer, a non-conductive polymer, organic small molecules, carbon nanotubes, a fullerene derivative, inorganic particles (quantum dots, quantum rods, quantum tripods, TiO_2, ZnO etc.), conductive particles (Au, Ag etc.), insulator materials like the ones described for the gate dielectric (PET, PS etc.).

Accordingly, the present invention also relates to an organic semiconductor material, layer or component, comprising a compound of formula III and to a semiconductor device, comprising a compound of formula III and/or an organic semiconductor material, layer or component.

The semiconductor is preferably an organic photovoltaic (PV) device (solar cell), a photodiode, or an organic field effect transistor. The structure and the components of the OFET device has been described in more detail above.

Accordingly, the invention provides organic photovoltaic (PV) devices (solar cells) comprising a compound of the formula III.

The PV device comprise in this order:
(a) a cathode (electrode),
(b) optionally a transition layer, such as an alkali halogenide, especially lithium fluoride,
(c) a photoactive layer,
(d) optionally a smoothing layer,
(e) an anode (electrode),
(f) a substrate.

The photoactive layer comprises the compounds of the formula III. Preferably, the photoactive layer is made of a compound of the formula III, as an electron donor and an acceptor material, like a fullerene, particularly a functionalized fullerene PCBM, as an electron acceptor. As stated above, the photoactive layer may also contain a polymeric binder. The ratio of the small molecules of formula III to the polymeric binder can vary from 5 to 95 percent. Preferably, the polymeric binder is a semicristalline polymer such as polystyrene (PS), high-density polyethylene (HDPE), polypropylene (PP) and polymethylmethacrylate (PMMA).

The fullerenes useful in this invention may have a broad range of sizes (number of carbon atoms per molecule). The term fullerene as used herein includes various cage-like molecules of pure carbon, including Buckminsterfullerene (C_{60}) and the related "spherical" fullerenes as well as carbon nanotubes. Fullerenes may be selected from those known in the art ranging from, for example, C_{20}-C_{1000}. Preferably, the fullerene is selected from the range of C_{60} to C_{96}. Most preferably the fullerene is C_{60} or C_{70}, such as [60]PCBM, or [70]PCBM. It is also permissible to utilize chemically modified fullerenes, provided that the modified fullerene retains acceptor-type and electron mobility characteristics. The acceptor material can also be a material selected from the group consisting of another compounds of formula III, or any semi-conducting polymer, such as, for example, a polymer of formula I, provided that the polymers retain acceptor-type and electron mobility characteristics, organic small molecules, carbon nanotubes, inorganic particles (quantum dots, quantum rods, quantum tripods, TiO_2, ZnO etc.).

The photoactive layer is made of a compound of the formula III, as an electron donor and a fullerene, particularly functionalized fullerene PCBM, as an electron acceptor. These two components are mixed with a solvent and applied as a solution onto the smoothing layer by, for example, the spin-coating method, the drop casting method, the Langmuir-Blodgett ("LB") method, the ink jet printing method and the dripping method. A squeegee or printing method could also be used to coat larger surfaces with such a photoactive layer. Instead of toluene, which is typical, a dispersion agent such as chlorobenzene is preferably used as a solvent. Among these methods, the vacuum deposition method, the spin-coating method, the ink jet printing method and the casting method are particularly preferred in view of ease of operation and cost.

In the case of forming the layer by using the spin-coating method, the casting method and ink jet printing method, the coating can be carried out using a solution and/or dispersion prepared by dissolving, or dispersing the composition in a concentration of from 0.01 to 90% by weight in an appropriate organic solvent such as benzene, toluene, xylene, tetrahydrofurane, methyltetrahydrofurane, N,N-dimethylformamide, acetone, acetonitrile, anisole, dichloromethane, dimethylsulfoxide, chlorobenzene, 1,2-dichlorobenzene and mixtures thereof.

The photovoltaic (PV) device can also consist of multiple junction solar cells that are processed on top of each other in order to absorb more of the solar spectrum. Such structures are, for example, described in App. Phys. Let. **90**, 143512 (2007), Adv. Funct. Mater. **16**,

1897–1903 (2006), WO2004/112161 and Christoph Brabec, Energy Environ. Sci 2. (2009) 347-303.

A so called 'tandem solar cell' comprise in this order:
(a) a cathode (electrode),
(b) optionally a transition layer, such as an alkali halogenide, especially lithium fluoride,
(c) a photoactive layer,
(d) optionally a smoothing layer,
(e) a middle electrode (such as Au, Al, ZnO, TiO_2 etc.)
(f) optionally an extra electrode to match the energy level,
(g) optionally a transition layer, such as an alkali halogenide, especially lithium fluoride,
(h) a photoactive layer,
(i) optionally a smoothing layer,
(j) an anode (electrode),
(k) a substrate.

The PV device can also be processed on a fiber as described, for example, in US20070079867 and US 20060013549.

Due to their excellent self-organising properties the materials or films comprising the compounds of the formula III can also be used alone or together with other materials in or as alignment layers in LCD or OLED devices, as described for example in US2003/0021913.

An OFET device according to the present invention preferably comprises:
- a source electrode,
- a drain electrode,
- a gate electrode,
- a semiconducting layer,
- one or more gate insulator layers, and
- optionally a substrate, wherein the semiconductor layer comprises a compound of formula III.

The gate, source and drain electrodes and the insulating and semiconducting layer in the OFET device may be arranged in any sequence, provided that the source and drain electrode are separated from the gate electrode by the insulating layer, the gate electrode and the semiconductor layer both contact the insulating layer, and the source electrode and the drain electrode both contact the semiconducting layer.

Preferably the OFET comprises an insulator having a first side and a second side, a gate electrode located on the first side of the insulator, a layer comprising a compound of formula III located on the second side of the insulator, and a drain electrode and a source electrode located on the polymer layer.

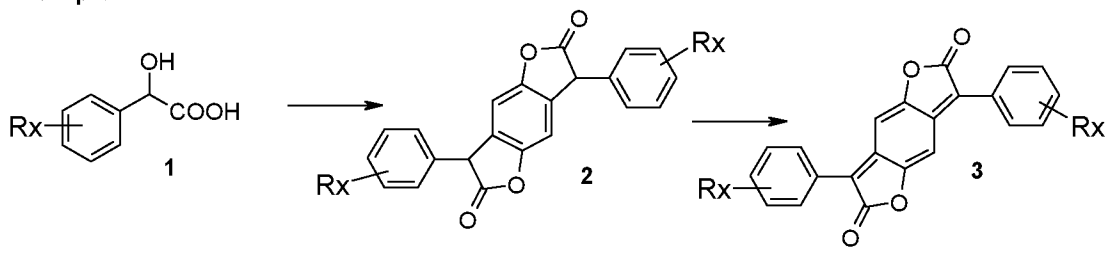
The following examples are included for illustrative purposes only and do not limit the scope of the claims. Unless otherwise stated, all parts and percentages are by weight.

Weight-average molecular weight (Mw) and polydispersity (Mw/Mn = PD) are determined by Heat Temperature Gel Permeation Chromatography (HT-GPC) [Apparatus: GPC PL 220 from Polymer laboratories (Church Stretton, UK; now Varian) yielding the responses from refractive index (RI), Chromatographic conditions: Column: 3 "PLgel Olexis" column from Polymer Laboratories (Church Stretton, UK); with an average particle size of 13 ìm (dimensions 300 x 8 mm I.D.) Mobile phase: 1,2,4-trichlorobenzene purified by vacuum distillation and stabilised by butylhydroxytoluene (BHT, 200 mg/l), Chromatographic temperature: 150°C; Mobile phase flow: 1 ml/min; Solute concentration: about 1 mg/ml; Injection volume: 200 ìl; Detection: RI, Procedure of molecular weight calibration: Relative calibration is done by use of a set of 10 polystyrene calibration standards obtained from Polymer Laboratories (Church Stretton, UK) spanning the molecular weight range from 1'930'000 Da - 5'050 Da, i. e., PS 1'930'000, PS 1'460'000, PS 1'075'000, PS 560'000, PS 330'000, PS 96'000, PS 52'000, PS 30'300, PS 10'100, PS 5'050 Da. A polynomic calibration is used to calculate the molecular weight.

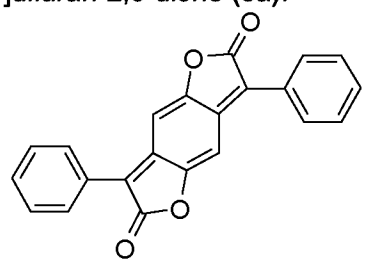
All polymer structures given in the examples below are idealized representations of the polymer products obtained via the polymerization procedures described. If more than two components are copolymerized with each other sequences in the polymers can be either alternating or random depending on the polymerisation conditions.

Examples

Example 1

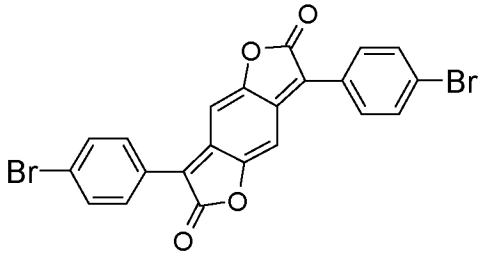


3,7-Diphenylbenzo[1,2-b:4,5-b']difuran-2,6-dione (3a).



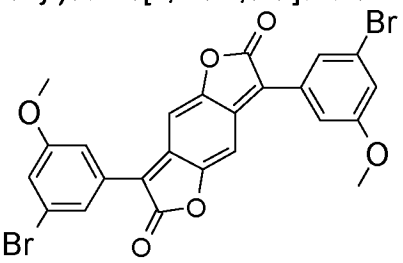
Using a Dean Stark apparatus, hydroquinone (1 g, 9.09 mmol) and mandelic acid (2.76 g 18.18 mmol) were dissolved in 1,2,4-trichlorobenzene (20 ml) and stirred for 12 h at 200 °C. After cooling to 60 °C, nitrobenzene (2.3 ml) was added and the mixture was stirred for another hour at 200 °C. After cooling to room temperature, 50 ml methanol were added. A precipitate formed, which was filtered off, washed with methanol and dried in air. **3a** was obtained as a yellow solid (2.32 g, 75 %). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, aromatic, 4H), 7.55 (t, aromatic H, 4H), 6.89 (t, aromatic H, 2H), 6.61 (s, aromatic, 2H). UV/Vis (dichloromethane): 469 nm. Fluorescence (dichloromethane): 600 nm. ε(469) = 35 000 L mol^{-1} cm^{-1}.

3,7-Bis(4-bromophenyl)benzo[1,2-b:4,5-b']difuran-2,6-dione (3b).



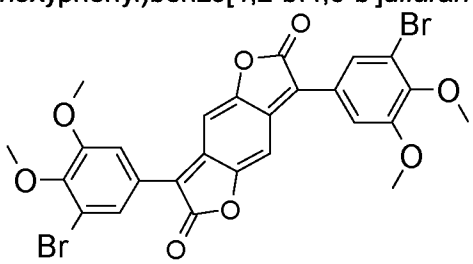
The same procedure as described for compound **3a** was used except that mandelic acid was replaced by 4´-bromo-mandelic acid. **3b** was obtained as a dark greenish solid (65 %), which was only little soluble in common solvents at room temperature. (m.p. above 300 °C). Anal. Calculated for $C_{22}H_{10}Br_2O_4$: C, 53.05 %; H, 2.02 %. Found: C, 52.80 %; H, 3.08 %. UV/Vis (dichloromethane): λ_{max} at 483 nm. Fluorescence (dichloromethane): 586 nm.

3,7-Bis(5-bromo-2-methoxyphenyl)benzo[1,2-b:4,5-b']difuran-2,6-dione (3c).



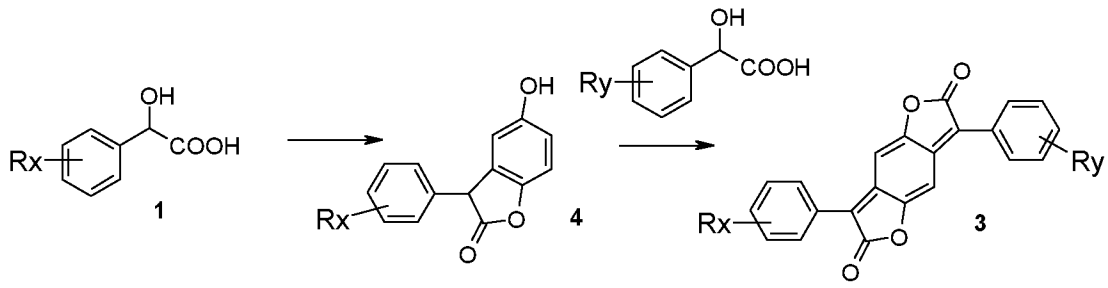
The same procedure as described for compound **3a** was used except that mandelic acid was replaced by 3-bromo-5-methoxy-mandelic acid. **3c** was obtained as a dark greenish solid (65 %), which was only little soluble in common solvents at room temperature. (m.p. above 300 °C). Anal. Calculated for $C_{24}H_{14}Br_2O_6$: C, 51.64 %; H, 2.53 %. Found: C, 51.10 %; H, 3.01 %. UV/Vis (dichloromethane): λ_{max} at 391, 477 nm. Fluorescence (dichloromethane): 610 nm.

3,7-Bis(3-bromo-4,5-dimethoxyphenyl)benzo[1,2-b:4,5-b']difuran-2,6-dione (3d).

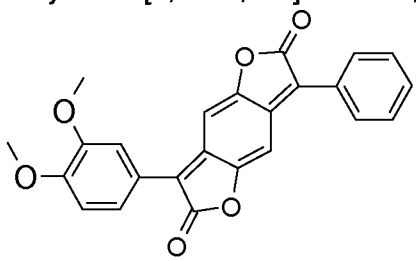


The same procedure as described for compound **3a** was used except that mandelic acid was replaced by 3-bromo-4,5-dimethoxy-mandelic acid. **3d** was obtained as a dark solid (70 %), which was only little soluble in common solvents at room temperature. (m.p. above 300 °C). Anal. Calculated for $C_{26}H_{18}Br_2O_8$: C, 50.51 %; H, 2.93 %. Found: C, 50.00 %; H, 3.52 %. UV/Vis (dichloromethane): λ_{max} at 382, 521 nm. Fluorescence (dichloromethane): 606 nm.

Example 2

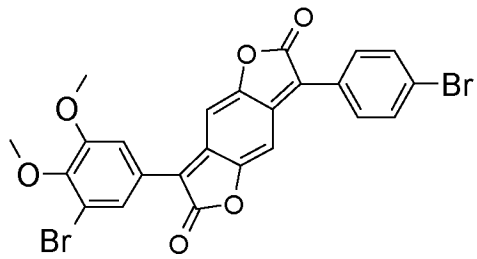


3-(3,4-Dimethoxyphenyl)-7-phenylbenzo[1,2-b:4,5-b']difuran-2,6-dione (3e).



4,5-dimethoxy-mandelic acid (**1d**) (1.20 g, 5.66 mmol), 5-hydroxy-3-phenylbenzofuran-2(3H)-one (**4a**) (1.27 g, 5.66 mmol), *p*-toluenesulphonric acid (1.27 g, 6.79 mmol) in 1,2,4-trichlorobenzene (20 ml) were heated to 80 °C and stirred for 6 h. The mixture was allowed to cool to 40 °C, and nitrobenzene (2 ml) was added. The temperature was raised to 100 °C and stirred for a further h. Methanol (5 ml) was added. The precipitated product was filtered off and recrystallized from dichloromethane/methanol, giving a dark red solid (1.47 g, 65 %). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.81 (t, aromatic, 4H), 7.55-7.44 (m, aromatic H, 5H), 7.06 (s, aromatic H, 1H), 6.93 (d, aromatic H, 2H), 4.00 (s, CH_3-H, 6H). UV/Vis (dichloromethane): 525 nm. Fluorescence (dichloromethane): 635 nm. ε(525) = 42 000 L mol^{-1} cm^{-1}.

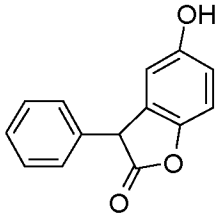
3-(3-Bromo-4,5-dimethoxyphenyl)-7-(4-bromophenyl)benzo[1,2-b:4,5-b']difuran-2,6-dione (3f).



The same procedure as described for compound **3e** was used except that 4,5-dimethoxy-mandelic acid (**1d**) and 5-hydroxy-3-phenylbenzofuran-2(3H)-one(**4a**) were replaced by 3-bromo-4,5-dimethoxy-mandelic acid (**1f**) and 3-(4-bromophenyl)-5-hydroxybenzofuran-2(3H)-one (**4b**). **3f** was obtained as a dark brawn solid (60 %). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, aromatic, 4H), 7.19 (s, aromatic H, 1H), 6.87 (d, aromatic H, 2H), 6.61 (d, aromatic H, 1H), 3.94 (d, CH_3-H, 6H). UV/Vis (dichloromethane): 441, 490 nm. Fluorescence (dichloromethane): 645 nm.

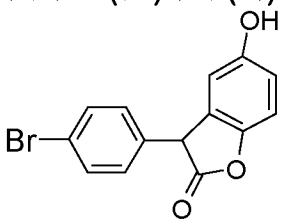
Example 3

5-Hydroxy-3-phenylbenzofuran-2(3H)-one (4a).



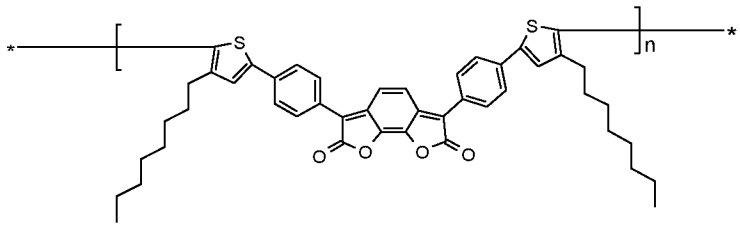
Hydroquinone (13.8 g, 0.13 mol), DL-mandelic acid (7.6 g, 0.05 mol) were stirred in 30 ml 73 % sulphuric acid at 120 °C for 30 min. After cooling, the mixture was poured carefully into 200 ml ice water. The resulting white solid was filtered off and washed with water until acid free. The product was dried in air, recrystallized from toluene, giving a white powder (10.3 g, 95 %). %). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.78 (t, aromatic, 3H), 7.15 (d, aromatic, 2H), 7.08 (d, aromatic, 1H), 6.85 (d, aromatic, 1H), 6.72 (s, aromatic, 1H), 4.85 (s, CH-H, 1H).

3-(4-bromophenyl)-5-hydroxybenzofuran-2(3H)-one (4b).



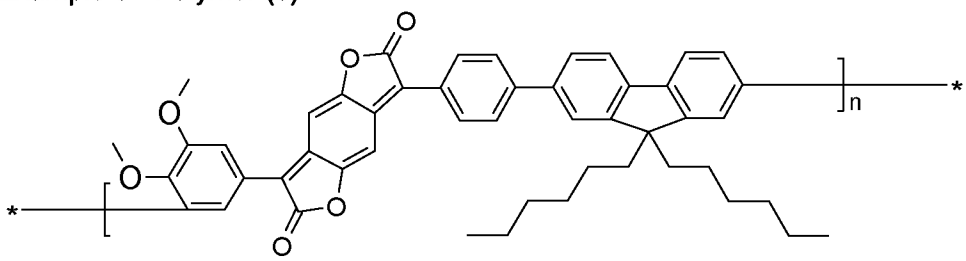
Hydroquinone (7.15 g, 65 mmol), 4-bromo-mandelic acid (5 g, 22 mmol) were stirred in 20 ml 73 % sulphuric acid at 120 °C for 30 min. After cooling, the mixture was poured carefully into 100 ml ice water. The resulting white solid was filtered off and washed with water until acid free. The product was dried in air, recrystallized from toluene, giving a white powder (6 g, 90 %). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.34 (t, aromatic, 2H), 7.25 (d, aromatic, 2H), 7.05 (d, aromatic, 1H), 6.84 (d, aromatic, 1H), 6.72 (s, aromatic, 1H), 4.88 (s, CH-H, 1H).

Example 4 - Polymer 21



Polymer **21** was made from compound **16** according to the procedure for polymer **20**. Yield: 65%, Molecular weight 11 000, Da, PD= 1.6, UV/vis absorption λ_{max}=565 nm.

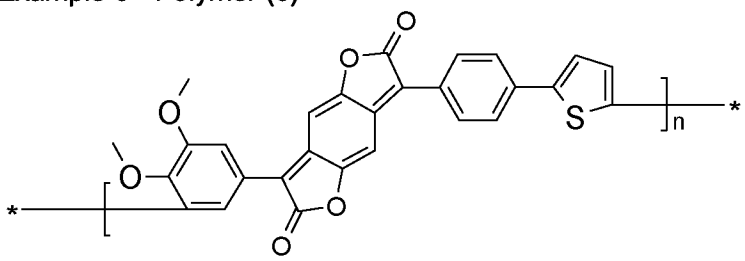
Example 5 - Polymer (5)



9,9-di-*n*-hexylfluorene-2,7'-bispinakolato-boronester was synthesized according to the literature: Jo, J.; Chi, C.; Höger, S.; Wegner, G.; Yoon, D. Y. *Chem. Eur. J.* **2004**, *10*, 2681.

The synthesis of polymer **5** was made from 1 equ. of compound 3f and 1 equ. of 9,9-di-*n*-hexylfluorene-2,7'-bispinakolato-boronester via Suzuki polymerization according to known methods with $Pd(PPh_3)_4$ as catalyst and K_2CO_3 as base in water-toluene mixture. The ^1H NMR spectra of polymer 5 is shown in Fig. 1.

Example 6 - Polymer (6)



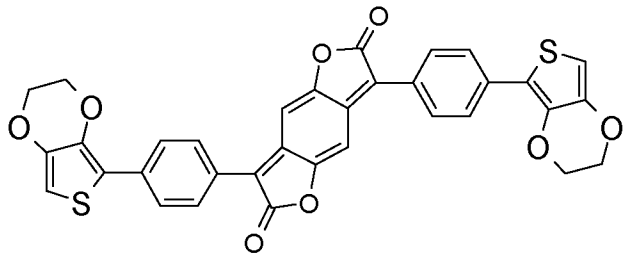
2,5-Bis(trimethylstannyl)thiophene was synthesized according to the literature: C. Van Pham, R.S. Macomber, H.B. Mark Jr, H. Zimmer, *J. Org. Chem.* **1984**, 49, 5250.

The synthesis of polymer **6** was made from 1 equ. of compound 3f and 1 equ. of 2,5-Bis(trimethylstannyl)thiophene via Stille polymerization according to known methods with $Pd(PPh_3)_4$ as catalyst in toluene. The ^1H NMR spectra of polymer 6 is shown in Fig. 2.

3,4-ethylenedioxythien-2-yl trimethylstannane and 3,4-ethylenedithiathien-2-yl trimethylstannane where synthesized according to the litterature: C.Wang, J.L. Schindler, C.R. Kannewurf, M.G. Kanatzidis, *Chem. Mater.* **1995**, 7, 58.

Example 7

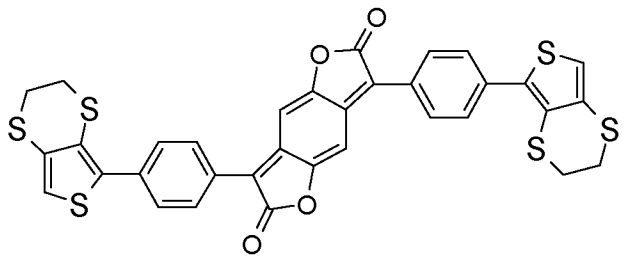
3,7-Bis(4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)phenyl)benzo[1,2-b:4,5-b']difuran-2,6-dione (7a)



In a vial, 200 mg (0.40 mmol) 3,7-bis(4-bromophenyl)benzo[1,2-b:4,5-b']difuran-2,6-dione (**3b**), 305 mg (1.00 mmol) 3,4-ethylenedioxythien-2-yl trimethylstannane and 14 mg (0.012 mmol) tetrakis(triphenylphosphine) palladium(0) were dissolved in 5 ml dry DMF and stirred for 5 min. The mixture was degassed, and heated in the microwave synthesizer at 160 °C for 1 h. After cooling the mixture was diluted with 50 ml DCM, washed with 50 ml brine and 50 ml water. The organic layer was separated, dried over magnesium sulfate and evaporated. The dark product was recrystallized from DCM/methanol. Yield: 196 mg (79 %) ^1H-NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, aromatic, 8H), 6.96 (s, EDOT aromatic H, 2H), 6.41 (s, aromatic, 1H), 4.33 (t, EDOT-CH_2, 8H). UV/Vis (dichloromethane): 298, 391, 590 nm. ε(590) = 63 580 L mol^{-1} cm^{-1}.

Example 8

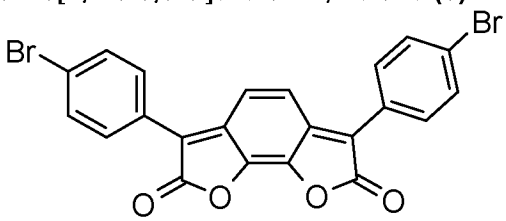
3,7-Bis(4-(2,3-dihydrothieno[3,4-b][1,4]dithien-5-yl)phenyl)benzo[1,2-b:4,5-b']difuran-2,6-dione (7b).



The same procedure as described for compound **7a** was used except that 3,4-ethylenedioxythien-2-yl trimethylstannane was replaced by 3,4-ethylenedithiathien-2-yl trimethylstannane. A dark solid (200 mg, 89 %) was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, aromatic, 8H), 6.69 (s, EDTT aromatic H, 2H), 7.09 (s, aromatic, 1H), 3.24 (t, EDTT-CH_2, 8H). UV/Vis (dichloromethane): 306, 502 nm. ε(502) = 79 220 L mol^{-1} cm^{-1}.

Example 9

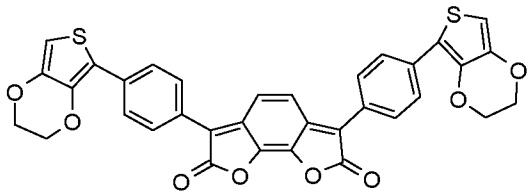
3,6-Bis(4-bromophenyl)benzo[1,2-b:6,5-b']difuran-2,7-dione (8).



Using a Dean Stark apparatus, *ortho*-quinone (1.20 g, 10.82 mmol) and 4-bromo-mandelic acid (5.0 g 21.64 mmol) were dissolved in 1,2,4-trichlorobenzene (30 ml) and stirred for 5 h at 200°C. After cooling to 60 °C, nitrobenzene (5.0 ml) was added and the mixture was stirred for another hour at 200°C. After cooling to room temperature, 50 ml methanol were added. The solid formed, which was filtered off, washed with methanol and dried in air. **4** was obtained as a dark red solid (3.28 g, 61%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, aromatic, 4H), 7.47 (d, aromatic, 4H), 7.16 (d, aromatic, 2H). (m.p. over 300 °C). Anal. Calculated for $C_{22}H_{10}Br_2O_4$: C, 53.05 %; H, 2.02 %. Found: C, 52.10 %; H, 2.90 %. UV/Vis (dichloromethane): λ_{max} at 493 nm.

Example 10

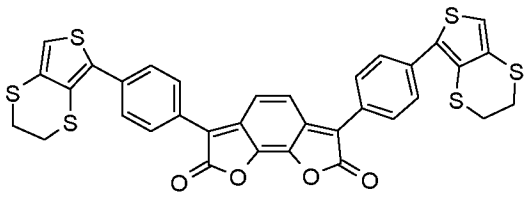
3,6-Bis(4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)phenyl)benzo[1,2-b:6,5-b']difuran-2,7-dione (9a).



The same procedure as described for compound **7a** was used but starting from compound **8**. A dark solid (93 mg, 82%) was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, aromatic, 8H), 6.98 (s, EDOT aromatic H, 2H), 7.29 (s, aromatic, 1H), 4.34 (t, EDOT-CH_2, 8H). UV/Vis (dichloromethane): 302, 588 nm. ε(588) = 23 080 L mol^{-1} cm^{-1}.

Example 11

3,6-Bis(4-(2,3-dihydrothieno[3,4-b][1,4]dithien-5-yl)phenyl)benzo[1,2-b:6,5-b']difuran-2,7-dione (9b).



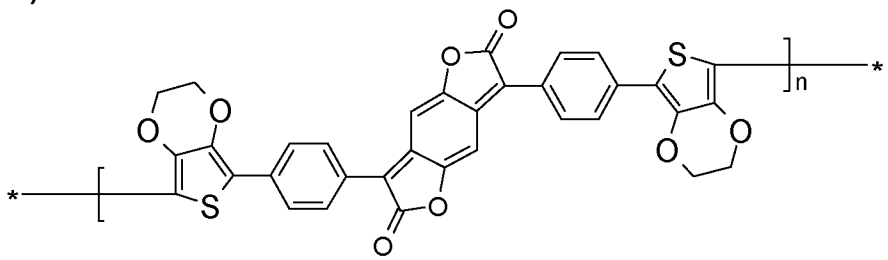
The same procedure as described for compound **7b** was followed but starting from compound **8**. A dark solid (120 mg, 86%) was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, aromatic, 8H), 7.44 (s, EDTT aromatic H, 2H), 7.09 (s, aromatic, 1H), 3.27 (t, EDTT-CH_2, 8H). UV/Vis (dichloromethane): 307, 407, 558 nm. ε(558) = 115 560 L mol^{-1} cm^{-1}.

Example 12

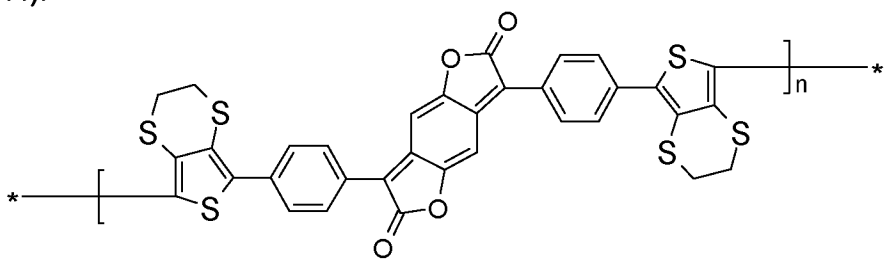
Polymers

The four monomers **7a**, **7b**, **9a** and **9b** were homo-electropolymerized by repetitive cycling over the redox active range of the materials. Growth of **polymer 10**, **polymer 11**, **polymer 12** and **polymer 13** by cyclic voltammetry in dichloromethane using a carbon working electrode, Ag wire pseudo-reference electrode. Supporting electrolyte: 0.1 M $TBAPF_6$. Scan rate: 100 mV s^{-1}; *T* = 20 °C. The cyclovoltammetric response of the four polymers was studied using films of the polymers on a glassy carbon working electrode in acetonitrile vs. Ag/AgCl.

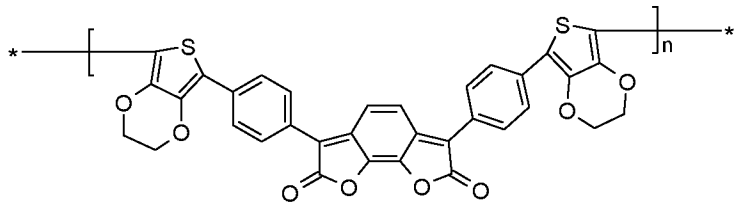
Polymer (10).



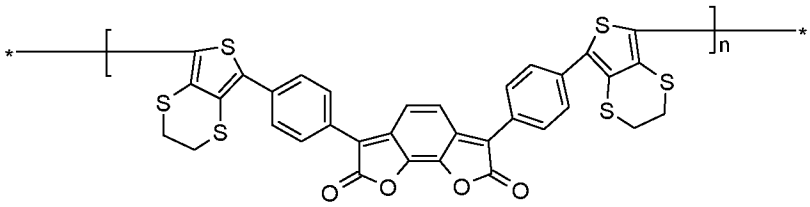
Polymer (11).



Polymer (12).

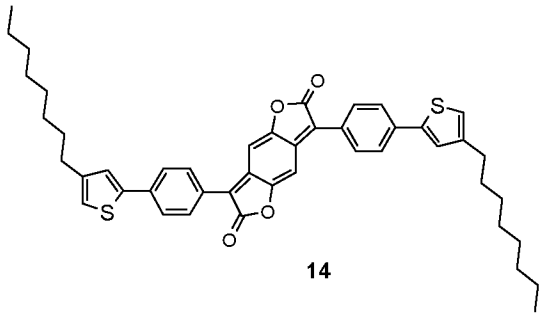


Polymer (13).

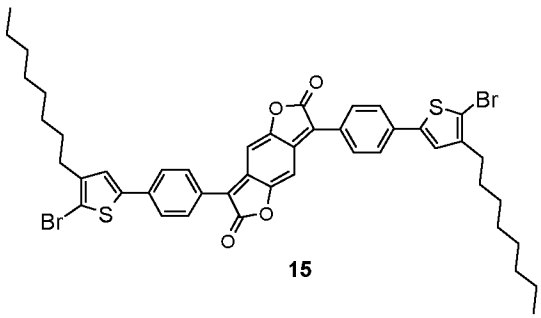


	UV/nm	Onset of oxidation/V	HOMO/eV	Onset of reduction/V	LUMO/eV	HOMO-LUMO gap/eV
10	589, 745	+0.41	-5.21	0.03	-4.77	0.44
11	348, 417, 752	+0.50	-5.30	-0.41	-4.39	0.91
12	515, 587, 743	-0.01	-4.79	-0.37	-4.43	0.36
13	530, 680	+0.87	-5.67	-0.41	-4.39	1.28

Example 13

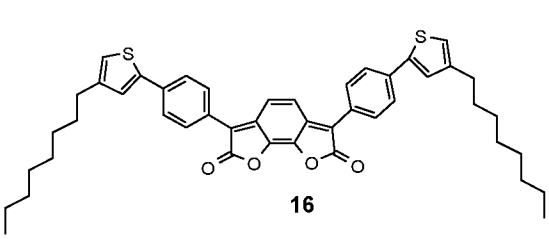


14

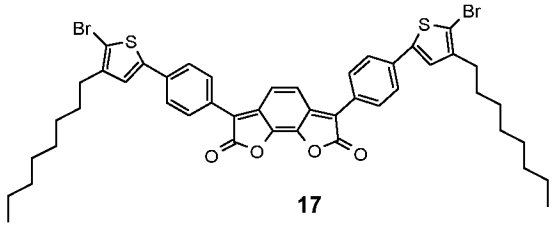


15

Compound **14** was obtained from compound **3b** and 3-octyl-thiophene-5-trimethylstannane via Stille coupling reaction according to compound **7a**. This compound was then subsequently brominated with N-bromo-succinimide in chloroforme to get compound **15**:



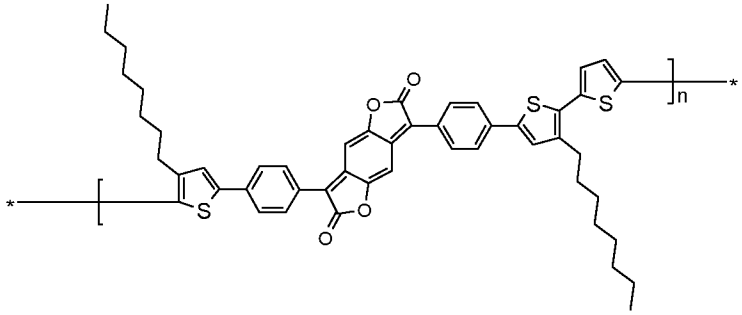
16



17

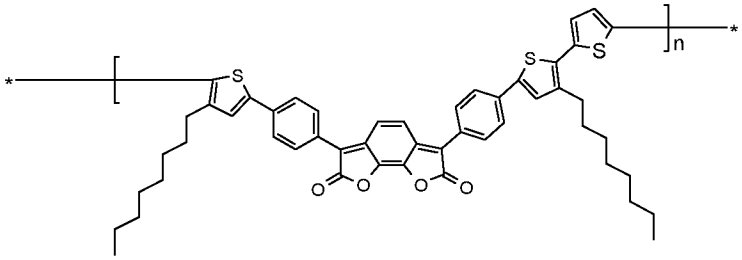
Compound **16** was obtained from compound **8** and 3-octyl-thiophene-5-trimethylstannane via Stille coupling reaction according to compound **7a**. This compound was then subsequently brominated with N-bromo-succinimide in chloroforme to get compound **17**:

Example 14 - Polymer 18



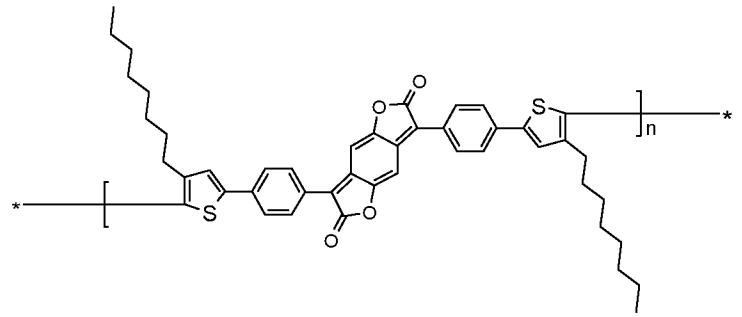
Compound **15** (200 mg, 0.23 mmol) and thiophene diboronic ester (76 mg, 0.23 mmol), $Pd_2(dba)_3$ (6.2 mg, 6.7 mmol), and tri-t-butylphosphine (3 mg, 13. 5 mmol) were dissolved in 20 ml fresh THF. The mixture was degassed and heated to reflux under N_2. A solution of potassium carbonate (125 mg, 0.9 mmol) in 2 ml water was added and the reaction mixture was heated for 2 h. After cooling, the reaction mixture was diluted with 50 ml DCM, washed with brine and water. The organic phase was dried, the solvent removed. The product was precipitated in methanol. Yield of polymer **18**: 71%
Molecular weight: 12 000 Da, PD = 1.6, UV/vis absorption: λ_{max}=578 nm.

Example 15 - Polymer 19



Polymer **19** was made according to the procedure for polymer **18**. Yield of polymer **19**: 60%, Molecular weight 10 500, Da, PD= 1.1, UV/vis absorption λ_{max}=562 nm.

Example 16 - Polymer 20

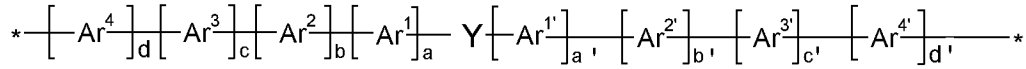


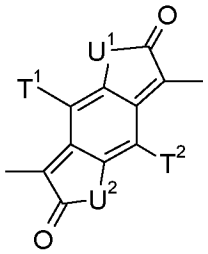
Under N_2, $FeCl_3$ (111 mg, 0.69 mmol) was dissolved in dry DCM (20 ml). A solution of compound **14** (200 mg, 0.27 mmol) in 5 ml dry DCM was added. The reaction mixture was stirred for a further hour at room temperature. The mixture was diluted with 50 ml DCM and 20 ml 1 M HCl was added. The organic phased was washed twice with brine and water and the dried. The solvent was removed and the crude product was precipitated in methanol and washed with methanol in a soxlett over night.
Yield: 70 %, Molecular weight: 16 000 Da, PD = 1.8, UV/vis absorption: λ_{max}=580 nm.

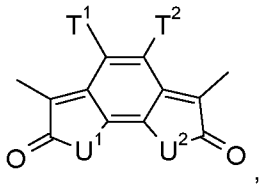
According to their broad absorption bands, small band gaps and the reversibility of oxidation and reduction processes, P1 and P2 might be useful for electronic applications.

Claims

1. A polymer comprising one or more (repeating) unit(s) of the formula







(I), wherein Y is a group of formula , or ,

a is 1, 2, or 3, a' is 1, 2, or 3; b is 0, 1, 2, or 3; b' is 0, 1, 2, or 3; c is 0, 1, 2, or 3; c' is 0, 1, 2, or 3; d is 0, 1, 2, or 3; d' is 0, 1, 2, or 3;

U^1 is O, S, or NR^1;

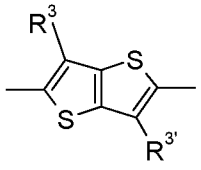
U^2 is O, S, or NR^2;

T^1 and T^2 are independently of each other hydrogen, halogen, hydroxyl, cyano, -$COOR^{103}$, -$OCOR^{103}$, -$NR^{112}COR^{103}$, -$CONR^{112}R^{113}$, -$OR^{103'}$, -$SR^{103'}$, -$SOR^{103'}$, -$SO_2R^{103'}$, -$NR^{112}SO_2R^{103'}$, -$NR^{112}R^{113}$, C_1-C_{25}alkyl, which may be substituted by E and/or interrupted by D, C_5-C_{12}cycloalkyl, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; C_7-C_{25}arylalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G;

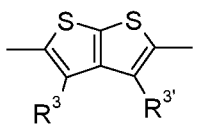
R^1 and R^2 may be the same or different and are selected from hydrogen, a C_1-C_{100}alkyl group, -$COOR^{103}$, -COR^{103}, a C_1-C_{100}alkyl group which is substituted by one or more halogen atoms, hydroxyl groups, nitro groups, -CN, or C_6-C_{18}aryl groups and/or interrupted by –O-, -COO-, -OCO-, or -S-; a C_7-C_{100}arylalkyl group, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; a carbamoyl group, C_5-C_{12}cycloalkyl, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; a C_6-C_{24}aryl group, in particular phenyl or 1- or 2-naphthyl, which can be substituted one to three times with C_1-C_8alkyl, C_1-C_8thioalkoxy, and/or C_1-C_8alkoxy, or pentafluorophenyl,

R^{103} and $R^{103'}$ are independently of each other C_1-C_{100}alkyl, especially C_3-C_{25}alkyl, C_1-C_{25}alkyl substituted by E and/or interrupted by D, CF_3, C_7-C_{25}arylalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G,

Ar^2, $Ar^{2'}$, Ar^3, $Ar^{3'}$, Ar^4 and $Ar^{4'}$ have the meaning of Ar^1, or are independently of each other



(**Xa**),



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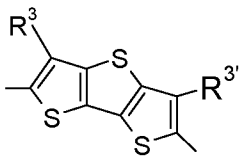

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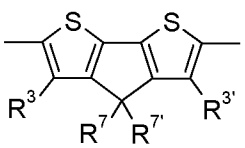

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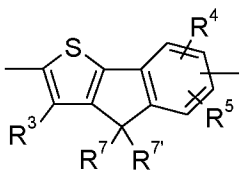

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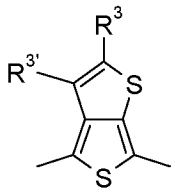
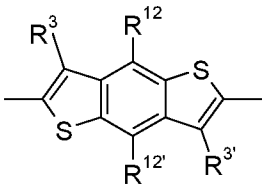


(**Xf**),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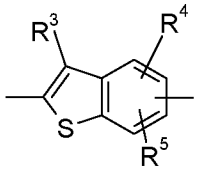
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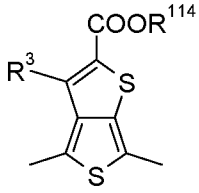
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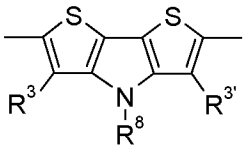
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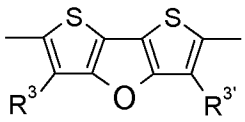
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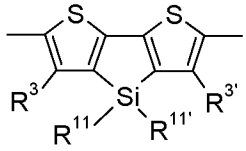
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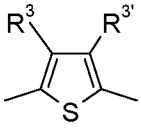
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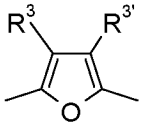
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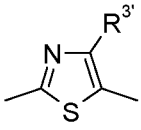
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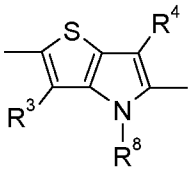
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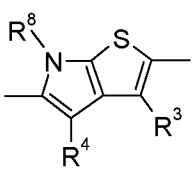
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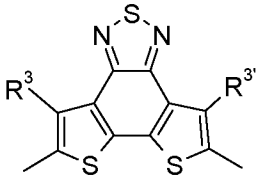
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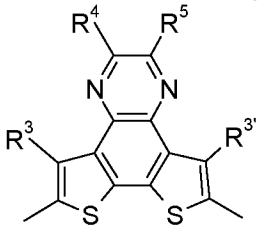
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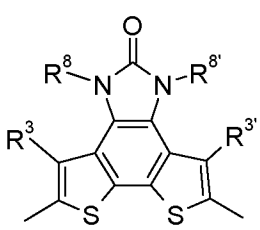
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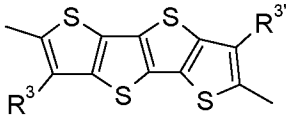
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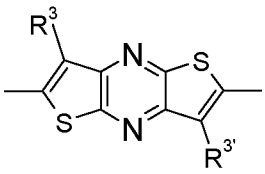
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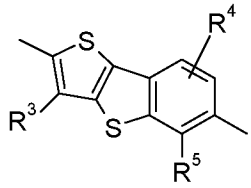
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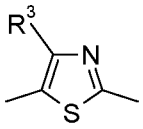
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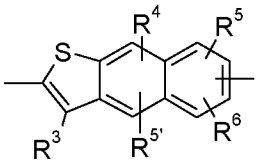
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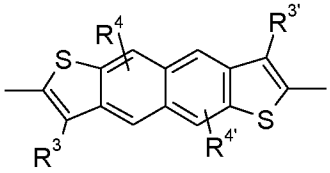
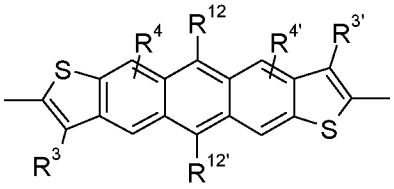

(Xla),

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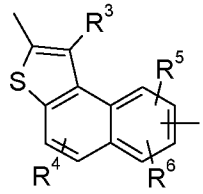
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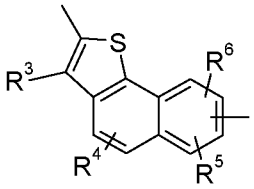
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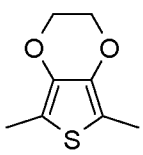
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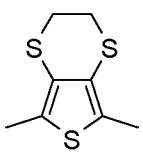
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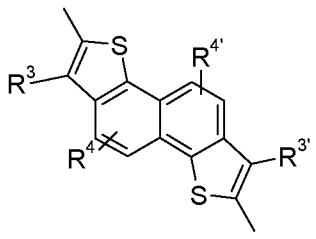
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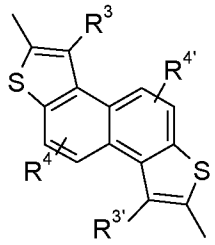
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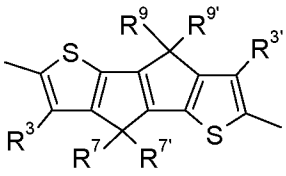
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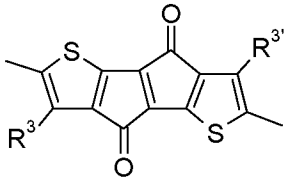
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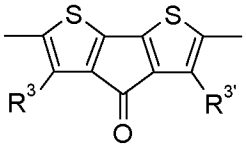
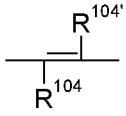

(XIk),

(XIl),

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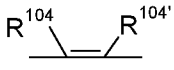

(XIn),

R^3 and $R^{3'}$ are independently of each other hydrogen, halogen, halogenated C_1-C_{25}alkyl, especially CF_3, cyano, C_1-C_{25}alkyl, especially C_3-C_{25}alkyl, which may optionally be interrupted by one or more oxygen or sulphur atoms; C_7-C_{25}arylalkyl, or C_1-C_{25}alkoxy;

R^{104} and $R^{104'}$ are independently of each other hydrogen, cyano, $COOR^{103}$, or a C_1-C_{25}alkyl group,

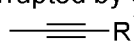
R^4, $R^{4'}$, R^5, $R^{5'}$, R^6 and $R^{6'}$ are independently of each other hydrogen, halogen, halogenated C_1-C_{25}alkyl, especially CF_3, cyano, C_1-C_{25}alkyl, especially C_3-C_{25}alkyl, which may optionally be interrupted by one or more oxygen or sulphur atoms; C_7-C_{25}arylalkyl, or C_1-C_{25}alkoxy;

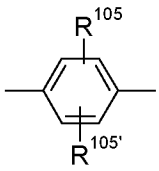
R^{114} is C_1-C_{25}alkyl, especially C_3-C_{25}alkyl, which may optionally be interrupted by one, or more oxygen, or sulphur atoms,

R^7, $R^{7'}$, R^9 and $R^{9'}$ are independently of each other hydrogen, C_1-C_{25}alkyl, especially C_3-C_{25}alkyl, which may optionally be interrupted by one, or more oxygen, or sulphur atoms; or C_7-C_{25}arylalkyl,

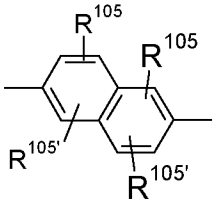
R^8 and $R^{8'}$ are independently of each other hydrogen, C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; or C_1-C_{25}alkyl, especially C_3-C_{25}alkyl, which may optionally be interrupted by one or more oxygen or sulphur atoms; or C_7-C_{25}arylalkyl,

R^{11} and $R^{11'}$ are independently of each other C_1-C_{25}alkyl group, especially a C_1-C_8alkyl group, C_7-C_{25}arylalkyl, or a phenyl group, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy;

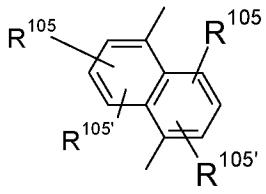
R^{12} and $R^{12'}$ are independently of each other hydrogen, halogen, cyano, C_1-C_{25}alkyl, especially C_3-C_{25}alkyl, which may optionally be interrupted by one, or more oxygen, or sulphur atoms, C_1-C_{25}alkoxy, C_7-C_{25}arylalkyl, or  , wherein R^{13} is a C_1-C_{10}alkyl group, or a tri(C_1-C_8alkyl)silyl group;



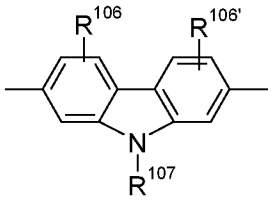
Ar^1 and $Ar^{1'}$ are independently of each other (XVa),



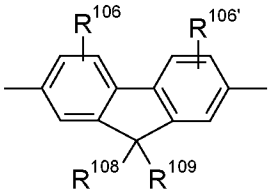
(XVb),

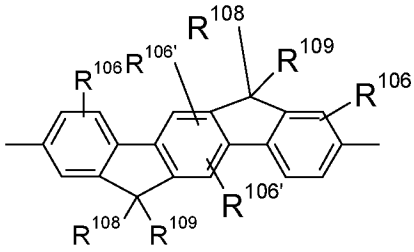


(XVc),

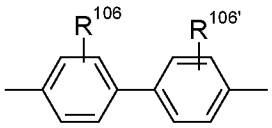


(XVd),

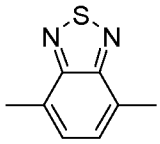




(XVe),



(XVf),



(XVg) or

(XVh), wherein

R^{105}, $R^{105'}$, R^{106} and $R^{106'}$ are independently of each other hydrogen, halogen, cyano, C_1-C_{25}alkyl, which may optionally be interrupted by one or more oxygen or sulphur atoms; C_7-C_{25}arylalkyl, or C_1-C_{18}alkoxy,

R^{107} is hydrogen, C_7-C_{25}arylalkyl, C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}perfluoroalkyl; C_1-C_{25}alkyl; especially C_3-C_{25}alkyl, which may be interrupted by –O-, or –S-; or -$COOR^{103}$; R^{103} is is as defined above;

R^{108} and R^{109} are independently of each other H, C_1-C_{25}alkyl, C_1-C_{25}alkyl which is substituted by E and/or interrupted by D, C_7-C_{25}arylalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, or C_7-C_{25}aralkyl, or

R^{108} and R^{109} together form a group of formula $=CR^{110}R^{111}$, wherein

R^{110} and R^{111} are independently of each other H, C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, or C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G, or

R^{108} and R^{109} together form a five or six membered ring, which optionally can be substituted by C_1-C_{18}alkyl, C_1-C_{18}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, or C_7-C_{25}aralkyl,

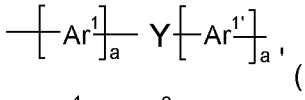
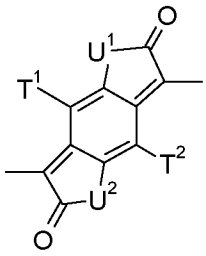
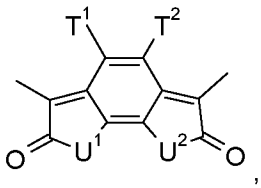
D is -CO-, -COO-, -S-, -O-, or $–NR^{112}–$,

E is C_1-C_8thioalkoxy, C_1-C_8alkoxy, CN, -$NR^{112}R^{113}$, -$CONR^{112}R^{113}$, or halogen,

G is E, or C_1-C_{18}alkyl, and

R^{112} and R^{113} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-.

2. The polymer according to claim 1, which is a polymer comprising one or more (repeating) unit(s) of the formula

 , (I'), wherein Y is a group of formula  or  ,

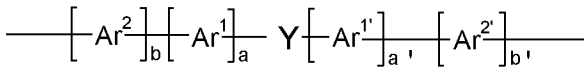
U^1 is O, S, or NR^1;

U^2 is O, S, or NR^2;

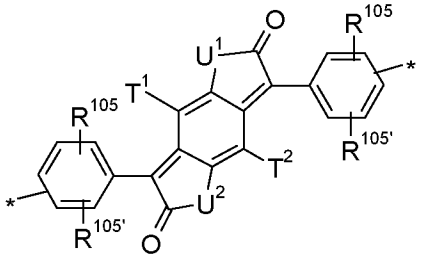
T^1 and T^2 are independently of each other hydrogen, halogen, hydroxyl, cyano, -$COOR^{103}$, -$OCOR^{103}$, -$NR^{112}COR^{103}$, -$CONR^{112}R^{113}$, -$OR^{103'}$, -$SR^{103'}$, -$SOR^{103'}$, -$SO_2R^{103'}$, -$NR^{112}SO_2R^{103'}$, -$NR^{112}R^{113}$, C_1-C_{25}alkyl, which which may be substituted by E and/or interrupted by D, C_5-C_{12}cycloalkyl, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; C_7-C_{25}arylalkyl, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, or C_2-C_{20}heteroaryl which is substituted by G;

R^1 and R^2 may be the same or different and are selected from hydrogen, a C_1-C_{100}alkyl group, -$COOR^{103}$, -COR^{103}, a C_1-C_{100}alkyl group which is substituted by one or more halogen atoms, hydroxyl groups, nitro groups, -CN, or C_6-C_{18}aryl groups and/or interrupted by –O-, -COO-, -OCO-, or -S-; a C_7-C_{100}arylalkyl group, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; a carbamoyl group, C_5-C_{12}cycloalkyl, which can be substituted one to three times with C_1-C_8alkyl and/or C_1-C_8alkoxy; a C_6-C_{24}aryl group, in particular phenyl or 1- or 2-naphthyl, which can be substituted one to three times with C_1-C_8alkyl, C_1-C_8thioalkoxy, and/or C_1-C_8alkoxy, or pentafluorophenyl;

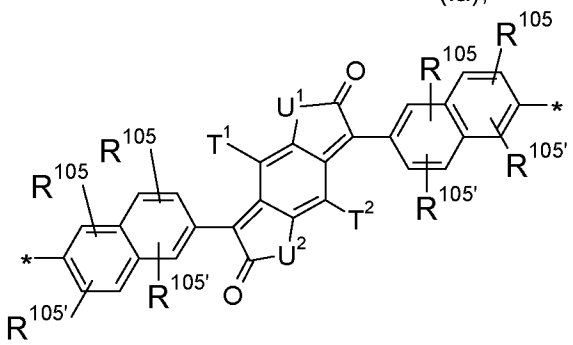
a is 1, 2, or 3, a' is 1, 2, or 3; wherein Ar^1 and $Ar^{1'}$ are independently of each other a group of formula (**XVa**), (**XVb**), (**XVc**), (**XVd**), (**XVe**), (**XVf**), (**XVg**), or (**XVh**) (as defined in claim 1); and R^{103}, $R^{103'}$, R^{112}, R^{113}, D, E and G are as defined in claim 1; or a polymer comprising one or more (repeating) unit(s) of the formula

 (I''), wherein a is 1, or 2;, a' is 1, or 2; b is 1, 2, or 3; b' is 1, 2, or 3; wherein Y, Ar^1 and $Ar^{1'}$ are as defined above; and Ar^2 and $Ar^{2'}$ are as defined in claim 1.

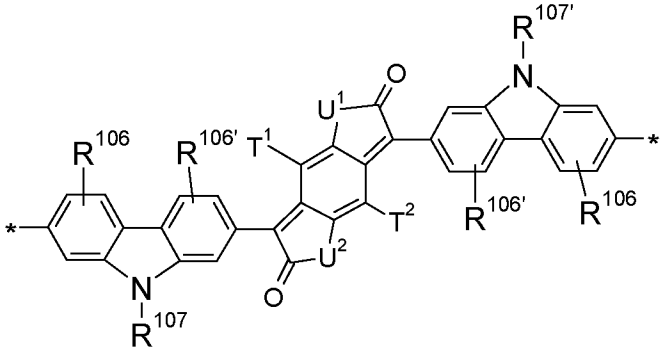
3. The polymer according to claim 1, or 2, comprising one or more (repeating) unit(s) of the formula



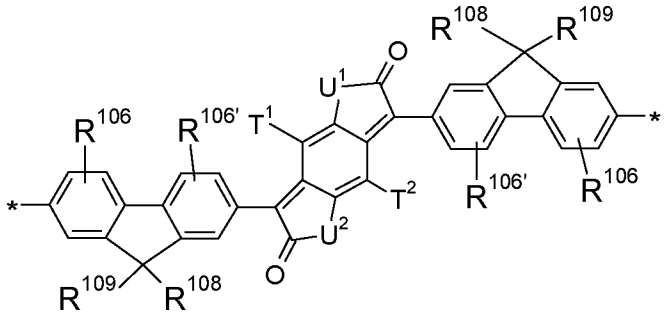
(Ia),



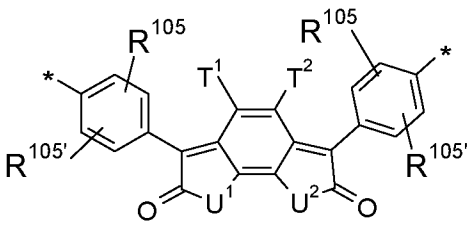
(Ib),



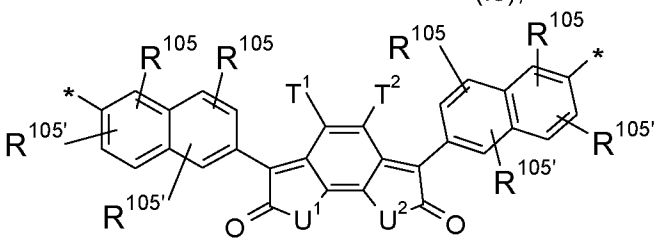
(Ic),



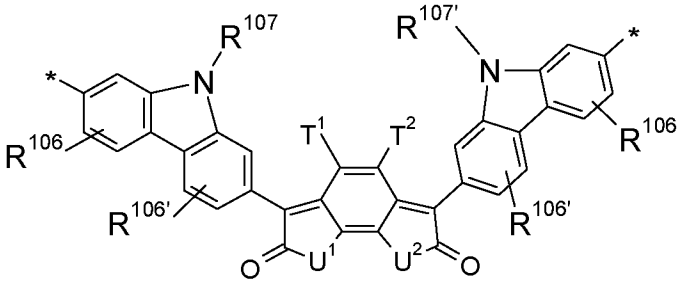
(Id);



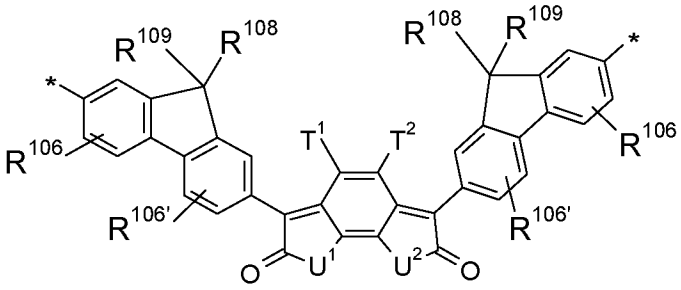
(Ie);



(If);



(Ig); and/or



(Ih); wherein

U^1 is O, or NR^1;

U^2 is O, or NR^2;

T^1 and T^2 are independently of each other hydrogen, or C_1-C_{25}alkyl, especially hydrogen;

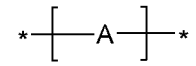
R^1 and R^2 may be the same or different and are selected from a C_1-C_{38}alkyl group, especially a C_8-C_{36}alkyl group;

R^{105}, $R^{105'}$, R^{106} and $R^{106'}$ are independently of each other hydrogen or C_1-C_{25}alkyl; and

R^{107} and $R^{107'}$ are independently of each other hydrogen or C_1-C_{25}alkyl, especially C_1-C_{25}alkyl;

R^{108} and R^{109} are independently of each other H, or C_1-C_{25}alkyl.

4. The polymer according to claims 1, or 2, comprising (repeating) unit(s) of the formula

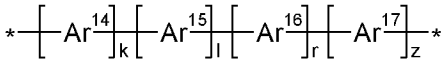


and

(II), wherein

A is a repeating unit of formula (I), and

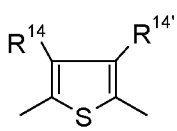
-COM^1- is a repeating unit, which has the meaning of Ar^2, wherein Ar^2 is as defined in claim 1, or a group of formula



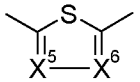
,

k is 1, l is 1, r is 0, or 1, z is 0, or 1, and

Ar^{14}, Ar^{15}, Ar^{16} and Ar^{17} are independently of each other a group of formula



,



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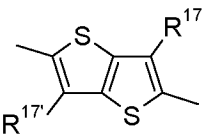
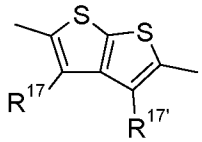
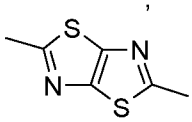


,

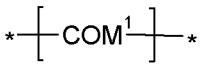
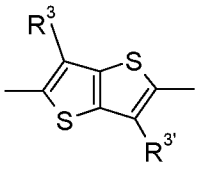
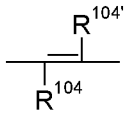
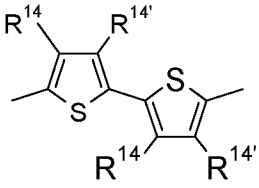
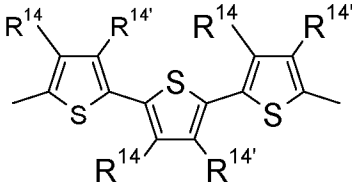


,

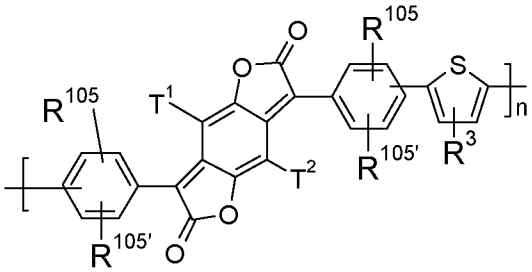


or , wherein one of X^5 and X^6 is N and the other is CR^{14}, and

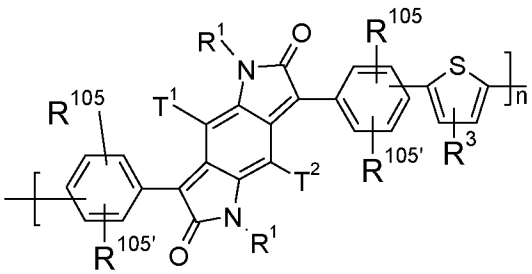
R^{14}, $R^{14'}$, R^{17} and $R^{17'}$ are independently of each other H, or a C_1-C_{25}alkyl group, especially a C_6-C_{25}alkyl, which may optionally be interrupted by one or more oxygen atoms.

5. The polymer according to claim 4, wherein A is a repeating unit of formula (**Ia**), (**Ic**), (**Id**), (**Ie**), (**Ig**),or (**Ih**) (as defined in claim 3) and  is a group of formula  ,  ,  ,  , or  , where R^3 and $R^{3'}$ are independently of each other hydrogen, or C_1-C_{25}alky, R^{104} and $R^{104'}$ are independently of each other hydrogen, cyano or a C_1-C_{25}alkyl group, and R^{14} and R^{14} are independently of each other H, or a C_1-C_{25}alkyl group, especially a C_6-C_{25}alkyl, which may optionally be interrupted by one or more oxygen atoms.

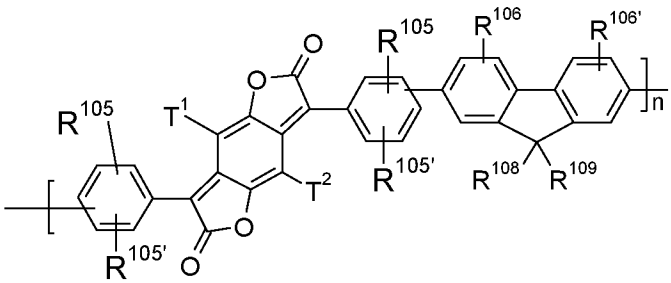
6. The polymer according to claim 4, or 5, which is a polymer of the formula



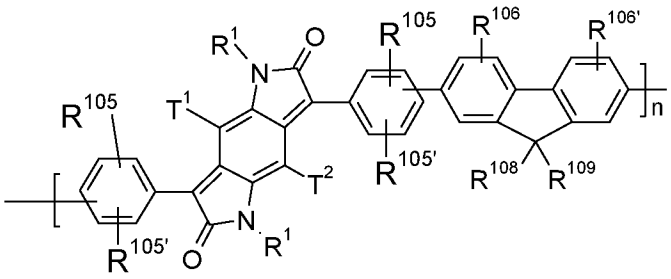
(**IIa**),



(**IIb**),



(**IIc**),



(IId), wherein

n is 4 to 1000, especially 4 to 200, very especially 5 to 100,

T^1 and T^2 are independently of each other hydrogen, or C_1-C_{25}alkyl, especially hydrogen;

R^1 is a C_1-C_{38}alkyl group, especially a C_8-C_{36}alkyl group,

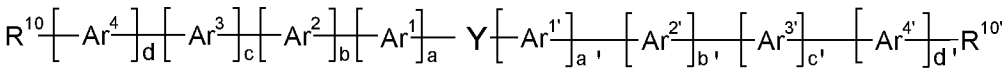
R^3 is hydrogen, halogen, cyano, C_1-C_{25}alkyl or C_1-C_{25}alkoxy, especially hydrogen or C_1-C_{25}alkyl;

R^{105} and $R^{105'}$ are independently of each other hydrogen, halogen, cyano, C_1-C_{25}alkyl or C_1-C_{25}alkoxy, especially hydrogen or C_1-C_{25}alkyl;

R^{106} and $R^{106'}$ are independently of each other hydrogen or C_1-C_{25}alkyl; and

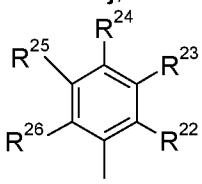
R^{108} and R^{109} are independently of each other H, or C_1-C_{25}alkyl.

7. A compound of the formula

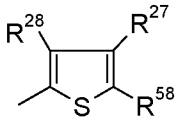


(III), wherein a, a', b, b', c, c', d, d', Y, Ar^1, $Ar^{1'}$, Ar^2, $Ar^{2'}$, Ar^3, $Ar^{3'}$, Ar^4 and $Ar^{4'}$ are as defined in claim 1,

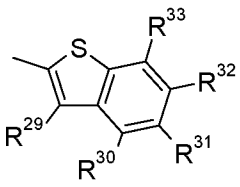
R^{10} and $R^{10'}$ are independently of each other hydrogen, halogen, cyano, C_1-C_{25}alkyl, C_1-C_{25}alkoxy, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, especially a group of one of the formulae IVa to IVj,



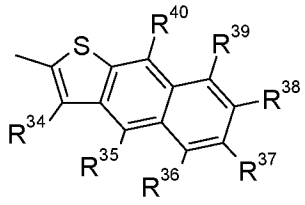
(IVa),



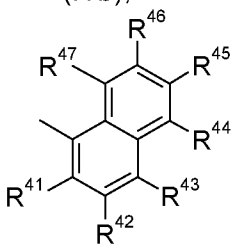
(IVb),



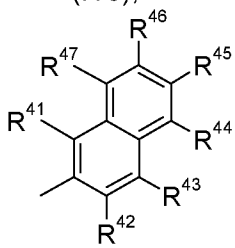
(IVc),



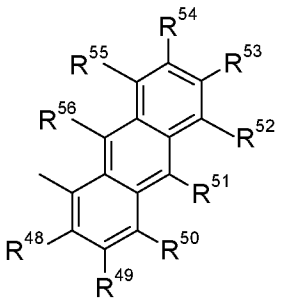
((IVd),



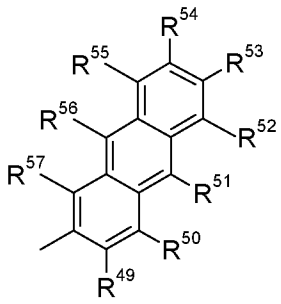
(IVe),



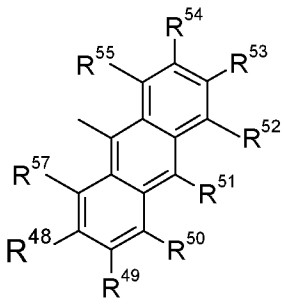
(IVf),



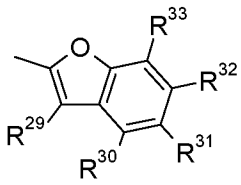
(IVg),



(IVh),



(IVi), or



(IVj),

wherein R^{22} to R^{26} and R^{29} to R^{58} represent independently of each other H, halogen, cyano, C_1-C_{25}alkyl, C_1-C_{25}alkyl which is substituted by E and/or interrupted by D, C_6-C_{24}aryl, C_6-C_{24}aryl which is substituted by G, C_2-C_{20}heteroaryl, C_2-C_{20}heteroaryl which is substituted by G, a C_4-C_{18}cycloalkyl group, a C_4-C_{18}cycloalkyl group, which is substituted by G, C_2-C_{18}alkenyl, C_2-C_{18}alkynyl, C_1-C_{18}alkoxy, C_1-C_{18}alkoxy which is substituted by E and/or interrupted by D, C_7-C_{25}aralkyl, or C_7-C_{25}aralkyl, which is substituted by G,

R^{27} and R^{28} are independently of each other hydrogen, C_1-C_{25}alkyl, halogen, cyano or C_7-C_{25}aralkyl, or R^{27} and R^{28} together represent alkylene or alkenylene which may be both bonded via oxygen and/or sulfur to the thienyl residue and which may both have up to 25 carbon atoms,

D is -CO-, -COO-, -S-, -O-, or –NR^{112}-,

E is C_1-C_8thioalkoxy, C_1-C_8alkoxy, CN, -$NR^{112}R^{113}$, -$CONR^{112}R^{113}$, or halogen,

G is E, or C_1-C_{18}alkyl, and

R^{112} and R^{113} are independently of each other H; C_6-C_{18}aryl; C_6-C_{18}aryl which is substituted by C_1-C_{18}alkyl, or C_1-C_{18}alkoxy; C_1-C_{18}alkyl; or C_1-C_{18}alkyl which is interrupted by –O-, with the proviso that Ar^1 and $Ar^{1'}$ are not a group of formula (**XVa**), if b, b', c, c', d and d' are 0 and R^{10} and $R^{10'}$ are independently of each other hydrogen, halogen, C_1-C_{25}alkyl, or C_1-C_{25}alkoxy.

8. An organic semiconductor material, layer or component, comprising a polymer according to any of claims 1 to 6 and/or a compound according to claim 7.

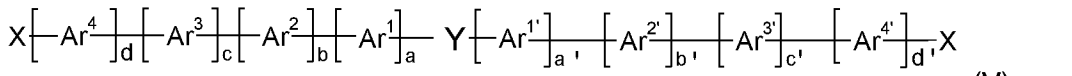
9. A semiconductor device, comprising a polymer according to any of claims 1 to 6, a compound according to claim 7 and/or an organic semiconductor material, layer or component according to claim 8.

10. The semiconductor device according to claim 9, which is an organic photovoltaic (PV) device (solar cell), a photodiode, or an organic field effect transistor.

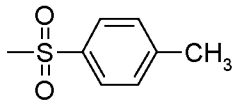
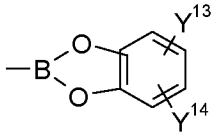
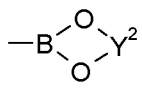
11. Process for the preparation of an organic semiconductor device, which process comprises applying a solution and/or dispersion of a polymer according to any of claims 1 to 6 and/or a compound according to claim 7 in an organic solvent to a suitable substrate and removing the solvent; or which process comprises evaporation of a compound according to claim 7.

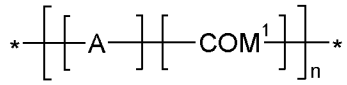
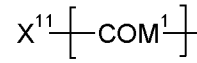
12. Use of the polymer according to any of claims 1 to 6, the compound according to claim 7 and/or the organic semiconductor material, layer or component according to claim 7 in PV devices, photodiodes, or organic field effect transistors.

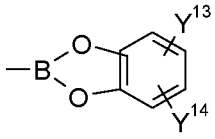
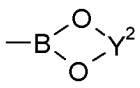
13. A compound of the formula



(V),

wherein a, a', b, b', c, c', d, d', Y, Ar^1, $Ar^{1'}$, Ar^2, $Ar^{2'}$, Ar^3, $Ar^{3'}$, Ar^4 and $Ar^{4'}$ are as defined in claim 1, and X is halogen, especially Br, or J, ZnX^{12}, $-SnR^{207}R^{208}R^{209}$, wherein R^{207}, R^{208} and R^{209} are identical or different and are H or C_1-C_6alkyl, wherein two radicals optionally form a common ring and these radicals are optionally branched or unbranched and X^{12} is a halogen atom, very especially I, or Br; or $-OS(O)_2CF_3$, $-OS(O)_2$-aryl, especially  , $-OS(O)_2CH_3$, $-B(OH)_2$, $-B(OY^1)_2$,  ,  , $-BF_4Na$, or $-BF_4K$, wherein Y^1 is independently in each occurrence a C_1-C_{10}alkyl group and Y^2 is independently in each occurrence a C_2-C_{10}alkylene group, such as $-CY^3Y^4-CY^5Y^6-$, or $-CY^7Y^8-CY^9Y^{10}-CY^{11}Y^{12}-$, wherein Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11} and Y^{12} are independently of each other hydrogen, or a C_1-C_{10}alkyl group, especially $-C(CH_3)_2C(CH_3)_2-$, $-C(CH_3)_2CH_2C(CH_3)_2-$, or $-CH_2C(CH_3)_2CH_2-$, and Y^{13} and Y^{14} are independently of each other hydrogen, or a C_1-C_{10}alkyl group.

14. A process for the preparation of a polymer of formula  , comprising reacting a dihalogenide of formula $X^{10}—A—X^{10}$ with an equimolar amount of a diboronic acid or diboronate corresponding to formula  , or reacting a dihalogenide of formula  with an equimolar amount of a diboronic acid or diboronate corresponding to formula $X^{11}—A—X^{11}$, wherein X^{10} is halogen, especially Br, and X^{11} is independently in each occurrence $-B(OH)_2$,

-$B(OY^1)_2$,  , or  , wherein Y^1 is independently in each occurrence a C_1-C_{10}alkyl group and Y^2 is independently in each occurrence a C_2-C_{10}alkylene group, such as $–CY^3Y^4-CY^5Y^6-$, or $–CY^7Y^8-CY^9Y^{10}-CY^{11}Y^{12}-$, wherein Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11} and Y^{12} are independently of each other hydrogen, or a C_1-C_{10}alkyl group, especially $-C(CH_3)_2C(CH_3)_2-$, $-C(CH_3)_2CH_2C(CH_3)_2-$, or $-CH_2C(CH_3)_2CH_2-$, and Y^{13} and Y^{14} are independently of each other hydrogen, or a C_1-C_{10}alkyl group, in a solvent and in the presence of a catalyst; or

reacting a dihalogenide of formula $X^{10}—A—X^{10}$ with an equimolar amount of an organo tin compound corresponding to formula $X^{11'}—[—COM^1—]—X^{11'}$, or

reacting a dihalogenide of formula $X^{10}—[—COM^1—]—X^{10}$ with an equimolar amount of an organo tin compound corresponding to formula $X^{11'}—A—X^{11'}$, wherein $X^{11'}$ is independently in each occurrence $-SnR^{207}R^{208}R^{209}$, wherein R^{207}, R^{208} and R^{209} are identical or different and are H or C_1-C_6alkyl, or two of the groups R^{207}, R^{208} and R^{209} form a ring and these groups are optionally branched, A and COM^1 are as defined in claim 4 and n is in the range of 4 to 1000, especially 4 to 200, very especially 5 to 150.

Fig. 1: ^{1}H NMR spectra of polymer 5

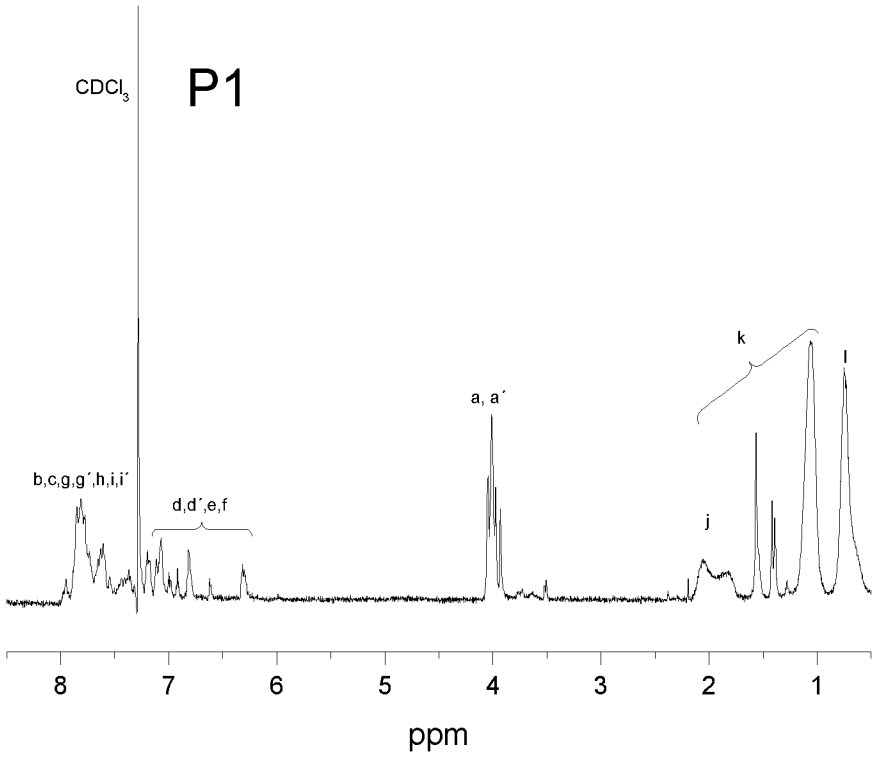


Fig. 2: ^{1}H NMR spectra of polymer 6