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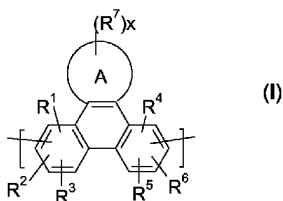
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(54) Title: NOVEL POLYMERS

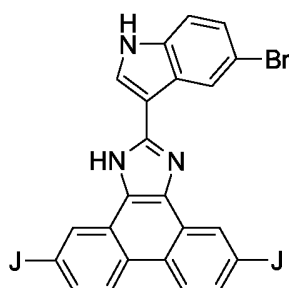


(57) Abstract: The present invention relates to polymers comprising a repeating unit of the formula (I), and their use in electronic devices. The polymers according to the invention have excellent solubility in organic solvents and excellent film-forming properties. In addition, high charge carrier mobilities and high temperature stability of the emission color are observed, if the polymers according to the invention are used in polymer light emitting diodes (PLEDs).

## Novel Polymers

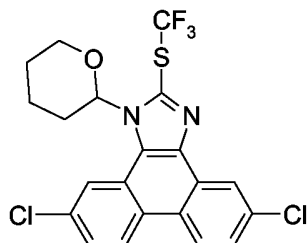
The present invention relates to novel polymers comprising a repeating unit of the formula (I) and their use in electronic devices. The polymers according to the invention have excellent solubility in organic solvents and excellent film-forming properties. In addition, high charge carrier mobilities and high temperature stability of the emission color can be observed, if the polymers according to the invention are used in polymer light emitting diodes (PLEDs).

JP05273618 discloses phenanthroimidazole compounds which were used as antiinflammants. WO04016086 relates to the preparation of 2,4,5-trisubstituted imidazoles and their use as antibacterial and/or antifungal agents. Among others the following



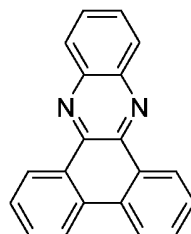
compound is explicitly mentioned in WO04016086:

US-B-4,215,135 relates to 2-substituted-1H-phenanthro[9,10-d]-imidazoles, which are useful as antiinflammatory agents. Among others the following compound is explicitly mentioned in



US-B-4,215,135:

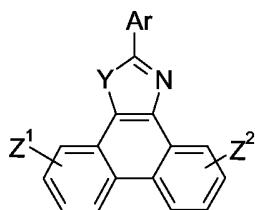
. US 3 635 544 relates to a photochromic polymer



matrix, comprising the following compound as light absorbing compound.

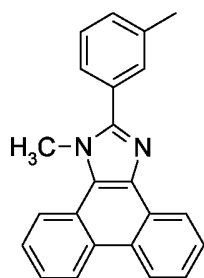
JP09188874, JP09013025, JP07026255, JP06207169, US2004076853, WO2004043937, US6713781, WO2004006352, WO2003058667 and WO2004006355 disclose phenanthrene-fused or phenathroline-fused phenazines and their use in EL devices.

US2004209117 relates to an EL device, comprising an azole compound of the formula

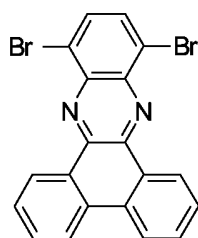


, wherein Y is an atom or a group selected from the group consisting of O, S, and -N(R)-, wherein R is a hydrocarbyl group of from 1 to about 30 carbons; Z<sup>1</sup> and Z<sup>2</sup> are each a substituent selected from the group consisting of hydrogen, an alkyl group of from 1 to about 25 carbon atoms, an aryl group of about 6 to about 30 carbon atoms, an alkoxy group of from 1 to about 25 carbon atoms, a halogen, and a cyano group; and Ar is an aromatic component. JP2004161892, JP2002050473 and JP2001023777 disclose phenanthroimidazol compounds and their use in EL devices.

10 WO04/030029 relates to a photovoltaic EL cell, comprising polymers containing groups:

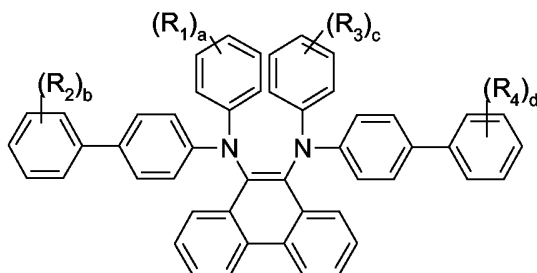


. WO03/020790 relates to conjugated polymers comprising spirobifluorene units. The polymers can comprise repeating units derived from the following



compound .

15 EP0757035A1 relates to phenanthrylenediamine derivatives represented by the general



formula

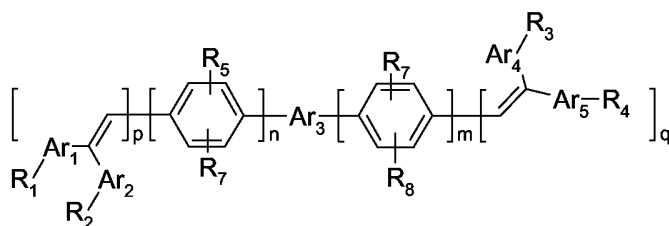
, which are excellent in the electric

charge transferring capability, the compatibility with a binding resin and the stability, thereby providing a photosensitive material which is highly sensitive and excellent in the durability.

US2001008711 relates to an organic light-emitting device comprising a light-emitting layer or a plurality of organic compound thin layers including a light-emitting layer formed between a pair of electrodes, wherein at least one layer comprises at least one kind of compound represented by the following formula  $NR_{11}R_{12}R_{13}$ : wherein  $R_{11}$ ,  $R_{12}$  and  $R_{13}$  each represents a group having a cyclocondensed polycyclic hydrocarbon structure in which three or more rings are cyclocondensed; and a novel cyclocondensed polycyclic hydrocarbon compound.

US2004/0028944 relates to organic electroluminescent devices comprising a triarylamine derivative represented by the general formula  $N(Ar_1)(Ar_2)(Ar_3)$ , wherein  $Ar_1$  to  $Ar_3$  are substituted or unsubstituted aryl groups and at least one of  $Ar_1$  to  $Ar_3$  is a 9-phenanthryl group.

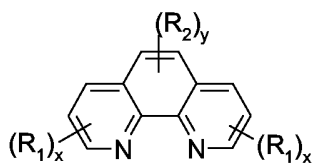
EP1440959A1 relates to a novel soluble compound of formula



, wherein  $Ar_3$  represents a substituted or unsubstituted anthracendiyl group, or a substituted or unsubstituted fluorendiyl group and to its use in an electroluminescent device.

WO03/064373 relates to triarylamine derivatives and the use thereof as hole transport material in organic electroluminescent and electrophotographic devices.

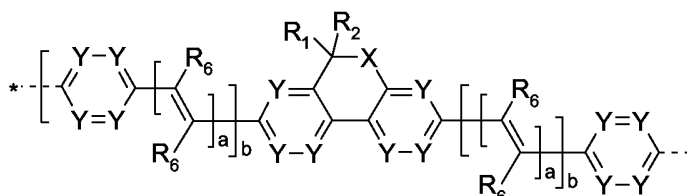
WO04/005288 relates to charge transport compositions comprising a phenanthroline



derivative having formula  $(R_1)_x$ ,  $(R_2)_y$ , wherein:  $R_1$  and  $R_2$  are the same or different at each occurrence and are selected from H, F, Cl, Br, alkyl, heteroalkyl, alkenyl, alkynyl, aryl, heteroaryl,  $C_nH_aF_b$ ,  $OC_nH_aF_b$ ,  $C_6H_cF_d$ , and  $OC_6H_cF_d$ ; a, b, c, and d are 0 or an integer such that  $a + b = 2n + 1$ , and  $c + d = 5$ , n is an integer; x is 0 or an integer from 1

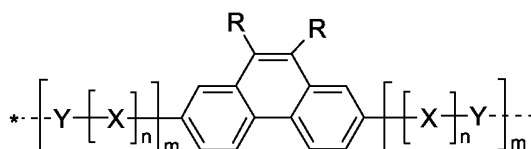
through 3; y is 0, 1 or 2; with the proviso that there is at least one substituent on an aromatic group selected from F, C<sub>n</sub>H<sub>a</sub>F<sub>b</sub>, OC<sub>n</sub>H<sub>a</sub>F<sub>b</sub>, C<sub>9</sub>H<sub>c</sub>F<sub>d</sub>, and OC<sub>6</sub>H<sub>c</sub>F<sub>d</sub>.

WO05/014689 relates to conjugated polymers containing dihydrophenanthrene units of



5 formula and their use in polymer organic light emitting diodes.

WO05/104264, which enjoys an earlier priority date than the present invention, but has been published after the priority date of the present invention, relates to polymers comprising



10 structural units of formula , wherein both groups R among others can form together a mono- or polycyclic, aliphatic ring system.

There are a number of challenges faced with the introduction of organic EL displays when their performance is compared with existing technologies. Obtaining the exact color coordinates required by specific guidelines (i.e. NTSC) has been problematic. The operational lifetime of the EL device is still lower when contrasted to the existing inorganic technology for cathode ray tubes (CRTs) and liquid crystal displays (LCDs). In addition, producing a material with a pure blue color and a long lifetime is one of the greatest problems for this industry.

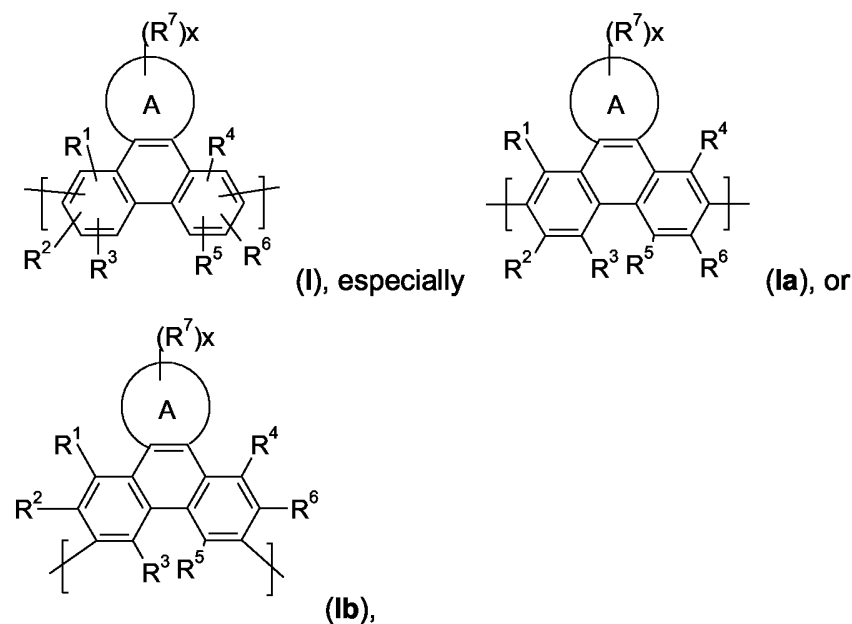
Accordingly, it is the object of the present invention to provide novel materials, which show significant advantages in color purity, device efficiency and/or operational lifetime, when incorporated in electro-optical devices.

Said object is solved by the polymers of the present invention comprising repeating units of formula I. Organic light emitting devices (OLEDs), comprising the polymers of the present invention, can show significant advantages in color purity, device efficiency and/or operational lifetime. In addition, the polymers can have good solubility characteristics and relatively high glass transition temperatures, which facilitates their fabrication into coatings and thin films, that are thermally and mechanically stable and relatively free of defects. If the

polymers contain end groups which are capable of being crosslinked, the crosslinking of such groups after the films or coating is formed increases the solvent resistance thereof, which is beneficial in applications wherein one or more solvent-based layers of material are deposited thereon.

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Hence, the present invention relates to polymers comprising a repeating unit(s) of the formula



10 wherein A is a 5-, 6-, or 7-membered heteroaromatic ring, containing at least one heteroatom selected from nitrogen, oxygen and sulfur, especially one nitrogen atom and at least one further heteroatom selected from nitrogen, substituted nitrogen, oxygen and sulfur, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are independently of each other hydrogen, halogen, or an organic substituent, or

15 R<sup>1</sup> and R<sup>2</sup>, R<sup>4</sup> and R<sup>6</sup>, R<sup>2</sup> and R<sup>3</sup>, R<sup>5</sup> and R<sup>3</sup> and/or R<sup>5</sup> and R<sup>6</sup>, which are adjacent to each other, together form an aromatic, or heteroaromatic ring, or ring system, which can optionally be substituted,

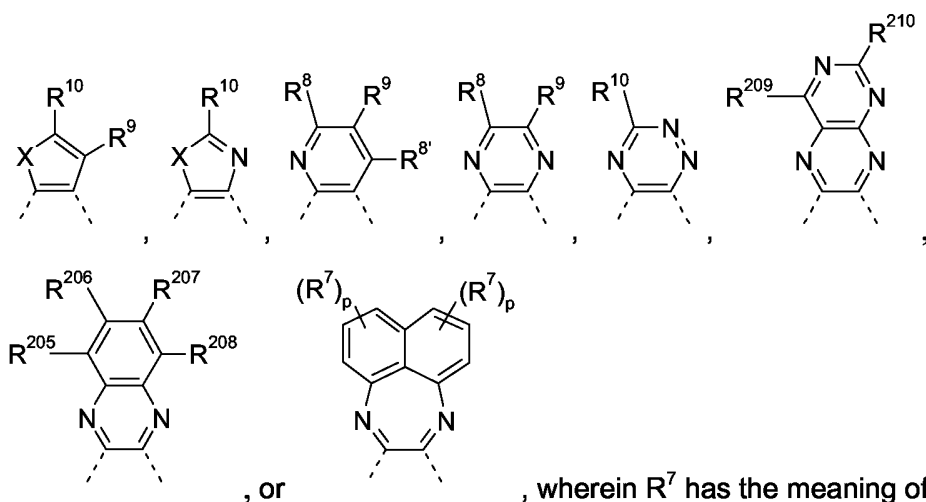
R<sup>7</sup> is an organic substituent, wherein two or more substituents R<sup>7</sup> in the same molecule may have different meanings, or can form together an aromatic, or heteroaromatic ring, or ring

20 system, and

x is 0, or an integer of 1 to 5.

A is a 5-, 6-, or 7-membered heteroaromatic ring, containing one heteroatom selected from nitrogen, oxygen and sulphur, which can be substituted and/or can be part of a fused

25 aromatic or heteroaromatic ring system. Non-limiting examples of A are:



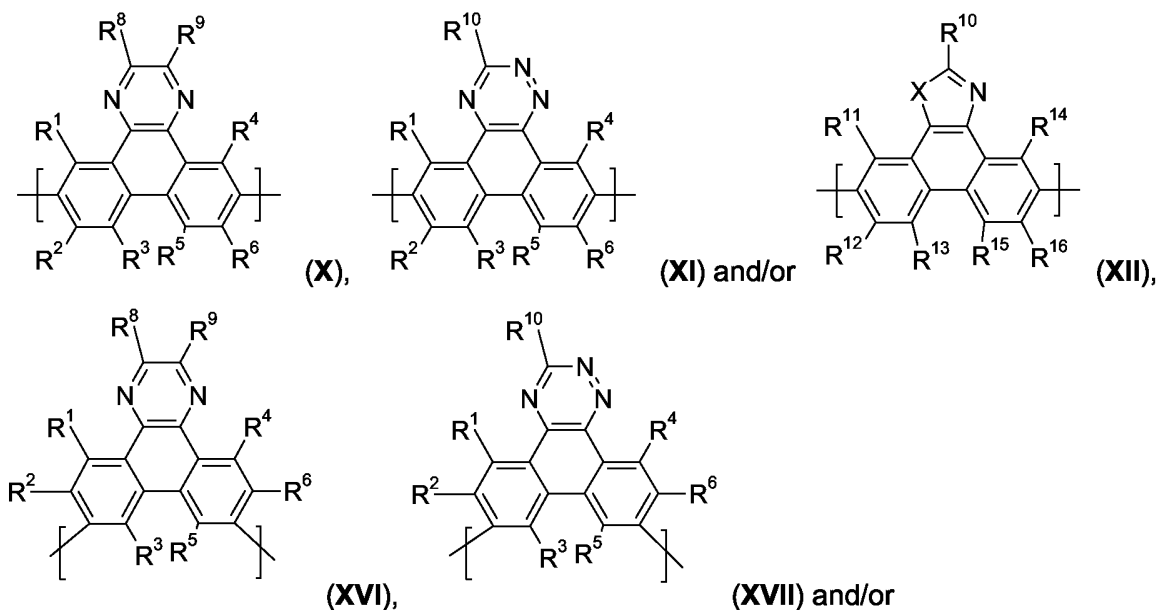
meaning of  $R^8$ , X is O, S, N- $R^{17}$ , wherein  $R^{205}$ ,  $R^{206}$ ,  $R^{207}$ ,  $R^{208}$ ,  $R^{209}$ ,  $R^{210}$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$  and  $R^{17}$  are as defined below, p is 0, 1, 2, or 3 and the dotted line --- indicates the bonding to the

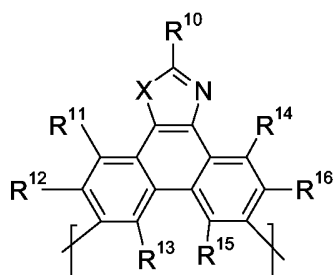
benzene ring.

Preferably, A is one of the above 5-, 6-, or 7-membered heteroaromatic rings, containing one nitrogen atom and at least one further heteroatom selected from nitrogen, oxygen and sulphur. If the heteroatom is nitrogen, it can be a group =N-, or -NR-, especially -NR<sup>10</sup>- wherein R is an organic substituent and R<sup>10</sup> is as defined below.

The polymers of the present invention should have a glass transition temperature above 100°C, especially a glass transition temperature above 150°C.

Preferably, the polymer of the present invention comprises a repeating unit(s) of the formula

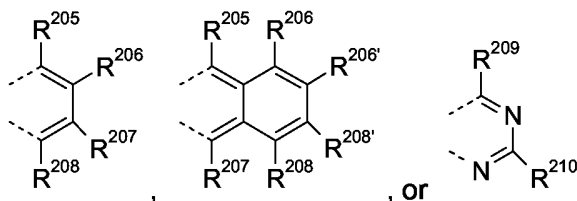




(XVIII), wherein  $R^1$  and  $R^4$  are independently of each other

hydrogen, halogen,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_2$ - $C_{18}$ 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, CN, or  $-CO-R^{28}$ ,

- 5  $R^2$ ,  $R^3$ ,  $R^5$  and  $R^6$  are independently of each other H, halogen,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_6$ - $C_{24}$ 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,  $C_7$ - $C_{25}$ aralkyl, CN, or  $-CO-R^{28}$ ,
- 10  $R^8$  and  $R^9$  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,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_6$ - $C_{24}$ 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,  $C_7$ - $C_{25}$ aralkyl, CN, or  $-CO-R^{28}$ , or



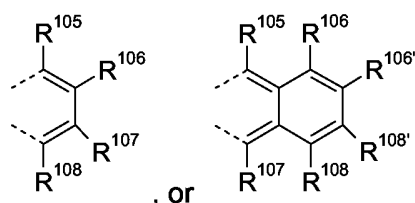
- 15  $R^8$  and  $R^9$  together form a group , or , wherein  $R^{206'}$ ,  $R^{208'}$ ,  $R^{205}$ ,  $R^{206}$ ,  $R^{207}$ ,  $R^{208}$ ,  $R^{209}$  and  $R^{210}$  are independently of each other H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_6$ - $C_{24}$ 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,  $C_7$ - $C_{25}$ aralkyl, or  $-CO-R^{28}$ ,
- 20  $R^{10}$  is H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_6$ - $C_{24}$ 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,  $C_7$ - $C_{25}$ aralkyl, or  $-CO-R^{28}$ ,
- 25  $R^{11}$  and  $R^{14}$  are independently of each other hydrogen, halogen,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_2$ - $C_{18}$ 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, CN, or  $-CO-R^{28}$ ,



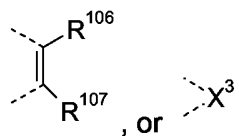
$R^{12}$ ,  $R^{13}$ ,  $R^{15}$  and  $R^{16}$  are independently of each other H, halogen,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_6$ - $C_{24}$ aryl,  $C_6$ - $C_{24}$ aryl which is substituted by G,  $C_2$ - $C_{20}$ 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,  $C_7$ - $C_{25}$ aralkyl, CN or  $-CO-R^{28}$ ,

X is O, S, or  $NR^{17}$ , wherein  $R^{17}$  is H;  $C_6$ - $C_{18}$ aryl,  $C_2$ - $C_{20}$ heteroaryl;  $C_6$ - $C_{18}$ aryl, or  $C_2$ - $C_{20}$ heteroaryl, which are substituted by  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ perfluoroalkyl, or  $C_1$ - $C_{18}$ alkoxy;  $C_1$ - $C_{18}$ alkyl; or  $C_1$ - $C_{18}$ alkyl which is interrupted by  $-O-$ ;

or two substituents  $R^2$  and  $R^3$ ,  $R^5$  and  $R^6$ ,  $R^{12}$  and  $R^{13}$ , and/or  $R^{15}$  and  $R^{16}$ ,  $R^1$  and  $R^2$ ,  $R^4$  and  $R^6$ ,  $R^{11}$  and  $R^{12}$ , and/or  $R^{14}$  and  $R^{16}$ , which are adjacent to each other, together form a group



, or two substituents  $R^{15}$  and  $R^{13}$ , and/or  $R^5$  and  $R^3$ , which are adjacent to each other, together form a group



, wherein  $X^3$  is O, S,  $C(R^{119})(R^{120})$ , or  $NR^{17}$ , wherein  $R^{17}$  is as defined above,  $R^{105}$ ,  $R^{106}$ ,  $R^{107}$ ,  $R^{108}$ ,  $R^{106'}$  and  $R^{108'}$  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,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D,

$R^{119}$  and  $R^{120}$  together form a group of formula  $=CR^{121}R^{122}$ , wherein

$R^{121}$  and  $R^{122}$  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

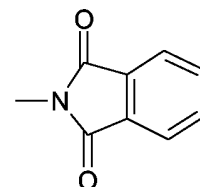
$R^{119}$  and  $R^{120}$  together form a five or six membered ring, which optionally can be substituted by  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_6$ - $C_{24}$ aryl,  $C_6$ - $C_{24}$ aryl which is substituted by G,  $C_2$ - $C_{20}$ 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,  $C_7$ - $C_{25}$ aralkyl, or  $-C(=O)-R^{127}$ , and

$R^{127}$  is 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  $-O-$ ,

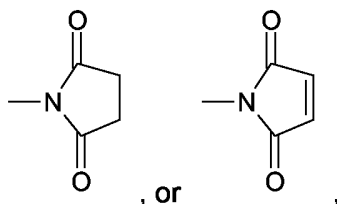
D is  $-CO-$ ;  $-COO-$ ;  $-S-$ ;  $-SO-$ ;  $-SO_2-$ ;  $-O-$ ;  $-NR^{25}-$ ;  $-SiR^{30}R^{31}-$ ;  $-POR^{32}-$ ;  $-CR^{23}=CR^{24}-$ ; or  $-C\equiv C-$ ; and

E is  $-OR^{29}$ ,  $-SR^{29}$ ,  $-NR^{25}R^{26}$ ,  $-COR^{28}$ ,  $-COOR^{27}$ ,  $-CONR^{25}R^{26}$ ,  $-CN$ ; or halogen; G is E,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D, wherein

$R^{23}$ ,  $R^{24}$ ,  $R^{25}$  and  $R^{26}$  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  $-O-$ ; or



$R^{25}$  and  $R^{26}$  together form a five or six membered ring, in particular



$R^{27}$  and  $R^{28}$  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  $-O-$ ,

$R^{29}$  is 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  $-O-$ ,

$R^{30}$  and  $R^{31}$  are independently of each other  $C_1$ - $C_{18}$ alkyl,  $C_6$ - $C_{18}$ aryl, or  $C_6$ - $C_{18}$ aryl, which is substituted by  $C_1$ - $C_{18}$ alkyl, and

$R^{32}$  is  $C_1$ - $C_{18}$ alkyl,  $C_6$ - $C_{18}$ aryl, or  $C_6$ - $C_{18}$ aryl, which is substituted by  $C_1$ - $C_{18}$ alkyl.

Repeating units of the formula **XVI**, **XVII** and **XVIII** are suitable as host matrix material for phosphorescent compounds. Repeating units of the formula **X**, **XI** and **XII** are suitable as conjugated polymers for EL devices.

Repeating units of the formula **X**, **XI** and **XII** are preferred.

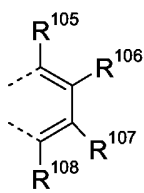
Repeating units of the formula **X** and **XI** (**XVI** and **XVII**) are even more preferred, wherein  $R^1$  and  $R^4$  are hydrogen,

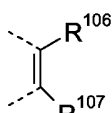
$R^2$ ,  $R^3$ ,  $R^5$  and  $R^6$  are independently of each other H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkoxy which is interrupted by D,  $C_7$ - $C_{25}$ aralkyl, or a group  $-X^2-R^{18}$ ,

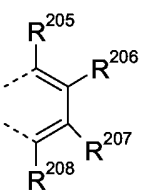
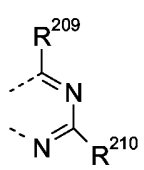
$R^8$  and  $R^9$  are independently of each other H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkoxy which is interrupted by D, or a group  $-X^2-$

$R^{18}$ , wherein  $X^2$  is a spacer, such as  $C_6-C_{12}$ aryl, or  $C_6-C_{12}$ heteroaryl, especially phenyl, or naphthyl, which can be substituted one more, especially one to two times with  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkyl which is interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,  $C_1-C_{18}$ alkoxy, or  $C_1-C_{18}$ alkoxy which is substituted by E and/or interrupted by D, and  $R^{18}$  is H,  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkyl which is interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,  $C_1-C_{18}$ alkoxy,  $C_1-C_{18}$ alkoxy which is interrupted by D, or  $-NR^{25}R^{26}$ ; or

two substituents  $R^2$  and  $R^3$  and/or  $R^5$  and  $R^6$ , which are adjacent to each other, together form

a group , or two substituents  $R^5$  and  $R^3$ , which are adjacent to each other,

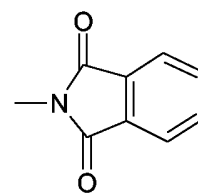
together form a group , wherein  $R^{105}$ ,  $R^{106}$ ,  $R^{107}$  and  $R^{108}$  are independently of each other H, or  $C_1-C_8$ alkyl, or

$R^8$  and  $R^9$  together form a group , or , wherein  $R^{205}$ ,  $R^{206}$ ,  $R^{207}$ ,  $R^{208}$ ,  $R^{209}$  and  $R^{210}$  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,  $C_1-C_{18}$ alkoxy, or  $C_1-C_{18}$ alkoxy which is substituted by E and/or interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,

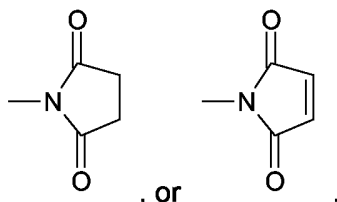
$R^{10}$  is H,  $C_6-C_{18}$ aryl, which can be substituted by G,  $C_2-C_{18}$ heteroaryl, which can be substituted by G,  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkyl which is interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,  $C_1-C_{18}$ alkoxy,  $C_1-C_{18}$ alkoxy which is substituted by E and/or interrupted by D, or a group  $-X^2-R^{18}$ , wherein  $X^2$  is a spacer, such as  $C_6-C_{12}$ aryl, or  $C_6-C_{12}$ heteroaryl, especially phenyl, or naphthyl, which can be substituted one more, especially one to two times with  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkyl which is interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,  $C_1-C_{18}$ alkoxy, or  $C_1-C_{18}$ alkoxy which is substituted by E and/or interrupted by D, and  $R^{18}$  is H,  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkyl which is interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,  $C_1-C_{18}$ alkoxy,  $C_1-C_{18}$ alkoxy which is interrupted by D, or  $-NR^{25}R^{26}$ ;

D is  $-CO-$ ;  $-COO-$ ;  $-S-$ ;  $-SO-$ ;  $-SO_2-$ ;  $-O-$ ;  $-NR^{25}-$ ;  $-CR^{23}=CR^{24}-$ ; or  $-C\equiv C-$ ; wherein

$R^{23}$ ,  $R^{24}$ ,  $R^{25}$  and  $R^{26}$  are independently of each other H;  $C_6-C_{18}$ aryl;  $C_6-C_{18}$ aryl which is substituted by  $C_1-C_8$ alkyl, or  $C_1-C_8$ alkoxy;  $C_1-C_8$ alkyl; or  $C_1-C_8$ alkyl which is interrupted by –

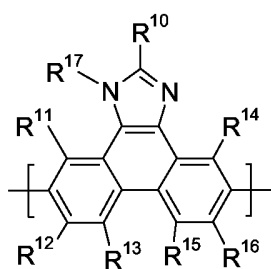


O-, or R<sup>25</sup> and R<sup>26</sup> together form a five or six membered ring, in particular

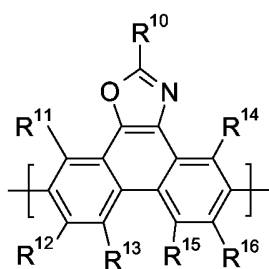


The repeating units of the formula **X** are preferred against the repeating units of the formula **XI**.

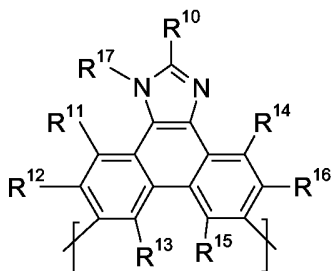
Among the repeating units of formula **XII** and **XVIII** repeating units of the formula



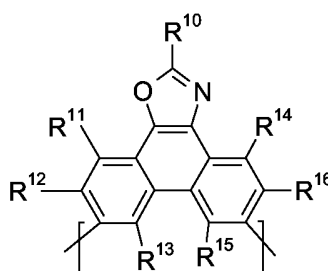
(XII'), and/or



(XII'');



(XVIII'), and/or



(XVIII'') are preferred,

wherein

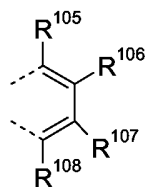
R<sup>10</sup> is H, C<sub>6</sub>-C<sub>18</sub>aryl, which can be substituted by G, C<sub>2</sub>-C<sub>18</sub>heteroaryl, which can be substituted by G, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is interrupted by D, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D, or a group -X<sup>2</sup>-R<sup>18</sup>, wherein X<sup>2</sup> is a spacer, such as C<sub>6</sub>-C<sub>12</sub>aryl, or C<sub>6</sub>-C<sub>12</sub>heteroaryl, especially phenyl, or naphthyl, which can be substituted one more, especially one to two times with C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is interrupted by D, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, or C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D, and R<sup>18</sup> is H, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is interrupted by D, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkoxy which is interrupted by D, or -NR<sup>25</sup>R<sup>26</sup>-;

$R^{11}$  and  $R^{14}$  are hydrogen,

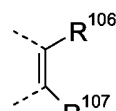
$R^{12}$ ,  $R^{13}$ ,  $R^{15}$  and  $R^{16}$  are hydrogen,

$R^{17}$  is  $C_6-C_{18}$ aryl;  $C_6-C_{18}$ aryl which is substituted by  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ perfluoroalkyl, or  $C_1-C_{18}$ alkoxy;  $C_1-C_{18}$ alkyl; or  $C_1-C_{18}$ alkyl which is interrupted by  $-O-$ ; or

5 two substituents  $R^{11}$  and  $R^{12}$ , and/or  $R^{14}$  and  $R^{16}$ ,  $R^{12}$  and  $R^{13}$ , and/or  $R^{15}$  and  $R^{16}$ , which are



adjacent to each other, together form a group, or two substituents  $R^{15}$  and  $R^{13}$ ,

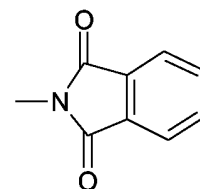


which are adjacent to each other, together form a group, wherein  $R^{105}$ ,  $R^{106}$ ,  $R^{107}$  and  $R^{108}$  are independently of each other H, or  $C_1-C_8$ alkyl,

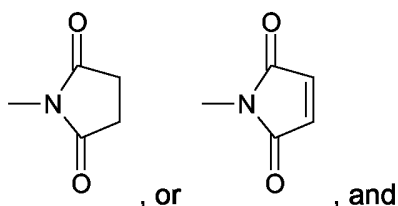
D is  $-S-$ ;  $-O-$ ; or  $-NR^{25}-$ ;

10 E is  $-OR^{29}$ ;  $-SR^{29}$ ;  $-NR^{25}R^{26}$ ;  $-CN$ ; or F; G is E,  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkyl which is interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,  $C_1-C_{18}$ alkoxy, or  $C_1-C_{18}$ alkoxy which is substituted by E and/or interrupted by D, wherein

$R^{25}$  and  $R^{26}$  are independently of each other H;  $C_6-C_{18}$ aryl;  $C_6-C_{18}$ aryl which is substituted by  $C_1-C_8$ alkyl, or  $C_1-C_8$ alkoxy;  $C_1-C_8$ alkyl; or  $C_1-C_8$ alkyl which is interrupted by  $-O-$ , or



15  $R^{25}$  and  $R^{26}$  together form a five or six membered ring, in particular

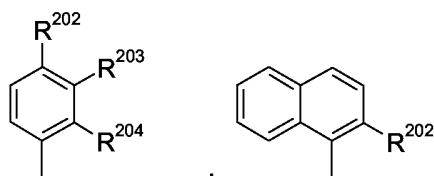


$R^{29}$  is  $C_6-C_{18}$ aryl;  $C_6-C_{18}$ aryl, which is substituted by  $C_1-C_{18}$ alkyl, or  $C_1-C_{18}$ alkoxy;  $C_1-C_{18}$ alkyl; or  $C_1-C_{18}$ alkyl which is interrupted by  $-O-$ .

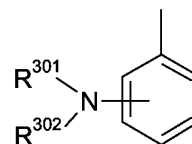
20 Repeating units of formula **X**, **XI** and **XII** (**XVI**, **XVII** and **XVIII**) are preferred, wherein  $R^{10}$  and  $R^8$  and/or  $R^9$  are different from a hydrogen atom and are in particular a solubilizing substituent which is especially selected from  $C_6-C_{18}$ aryl, which can be substituted by G,  $C_2-C_{18}$ heteroaryl, which can be substituted by G,  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkyl which is interrupted by

D, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, or C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D.

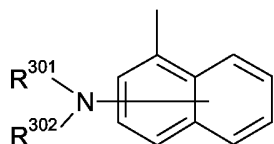
The aryl, and heteroaryl group are preferably a substituted or unsubstituted aryl, or heteroaryl moiety selected from the group consisting of phenyl, biphenyl, naphthyl, anthryl, phenanthryl, pyridyl, bipyridyl, indyl and quinolinyl. The term "substituted" means that the aryl moiety can be substituted by one or more groups, especially one to three groups, which may be the same or may be different. The substituents are preferably selected from C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is interrupted by D, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, or C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D. Most preferred among the aryl, and



heteroaryl groups are , and , wherein R<sup>202'</sup> is C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is interrupted by D, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, or C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D, especially C<sub>1</sub>-C<sub>18</sub>alkoxy; one of the groups R<sup>202</sup>, R<sup>203</sup> and R<sup>204</sup> is R<sup>202'</sup>, and the other groups are H, or R<sup>202'</sup>.



In a preferred embodiment of the present invention R<sup>10</sup> is a group , or

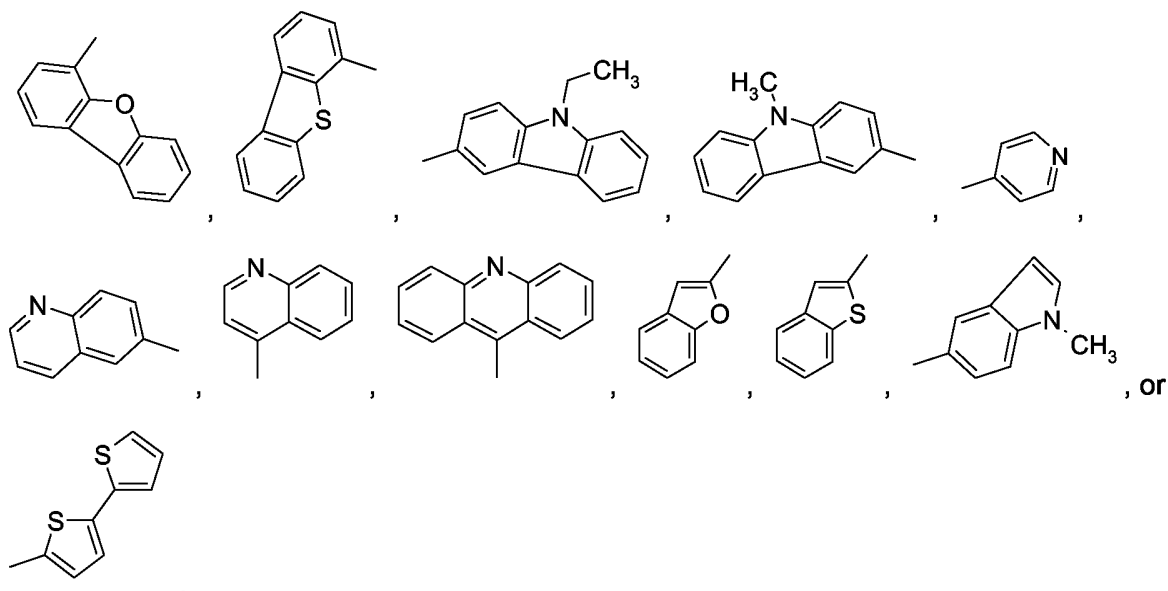


, wherein R<sup>301</sup> and R<sup>302</sup> are independently of each other C<sub>6</sub>-C<sub>24</sub>aryl, such as phenyl, 1-naphthyl, 2-naphthyl, 4-biphenyl, phenanthryl, terphenyl, pyrenyl, 2- or 9-fluorenyl or anthracenyl, preferably C<sub>6</sub>-C<sub>12</sub>aryl such as phenyl, 1-naphthyl, 2-naphthyl, 4-biphenyl, which may be unsubstituted or substituted by, for example, C<sub>1</sub>-C<sub>18</sub>alkyl, or C<sub>1</sub>-C<sub>18</sub>alkoxy.

In another preferred embodiment of the present invention R<sup>10</sup> is a C<sub>6</sub>-C<sub>30</sub>aryl group, such as phenyl, biphenyl, pentalenyl, indenyl, azulenyl, naphthyl, biphenylenyl, as-indacenyl, s-indacenyl, acenaphthylenyl, fluorenyl, phenanthryl, anthracenyl, fluoranthenyl, acephenanthrylenyl, aceanthrylenyl, triphenylenyl, pyrenyl, chrysenyl, naphthacenyl, picenyl, perylenyl, pentacenyl, pentaphenyl, hexacenyl, or hexaphenyl, which can optionally be substituted by one, two, or three, preferably C<sub>1</sub>-C<sub>18</sub>alkyl groups, or C<sub>1</sub>-C<sub>18</sub>alkoxy groups.

In another preferred embodiment of the present invention  $R^{10}$  is a  $C_2$ - $C_{20}$ heteroaryl group 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, indoliziny, isoindolyl, indolyl, indazolyl, purinyl, quinoliziny, chinolyl, isochinolyl, phthalazinyl, naphthyridinyl, chinoxaliny, chinazoliny, cinnoliny, pteridinyl, carbazolyl, carboliny, benzotriazolyl, benzoxazolyl, phenanthridinyl, acridinyl, perimidiny, phenanthroliny, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, 2-phenyl-1,2,4-oxadiazyl, 2,4-diphenyl-1,2,4-triazyl, or phenoxazinyl, which can optionally be substituted by one, two, or three, preferably  $C_1$ - $C_8$ alkyl groups, or  $C_1$ - $C_8$ alkoxy groups.

If  $R^{10}$  is derived from a heteroaryl group, it is preferably a group of formula



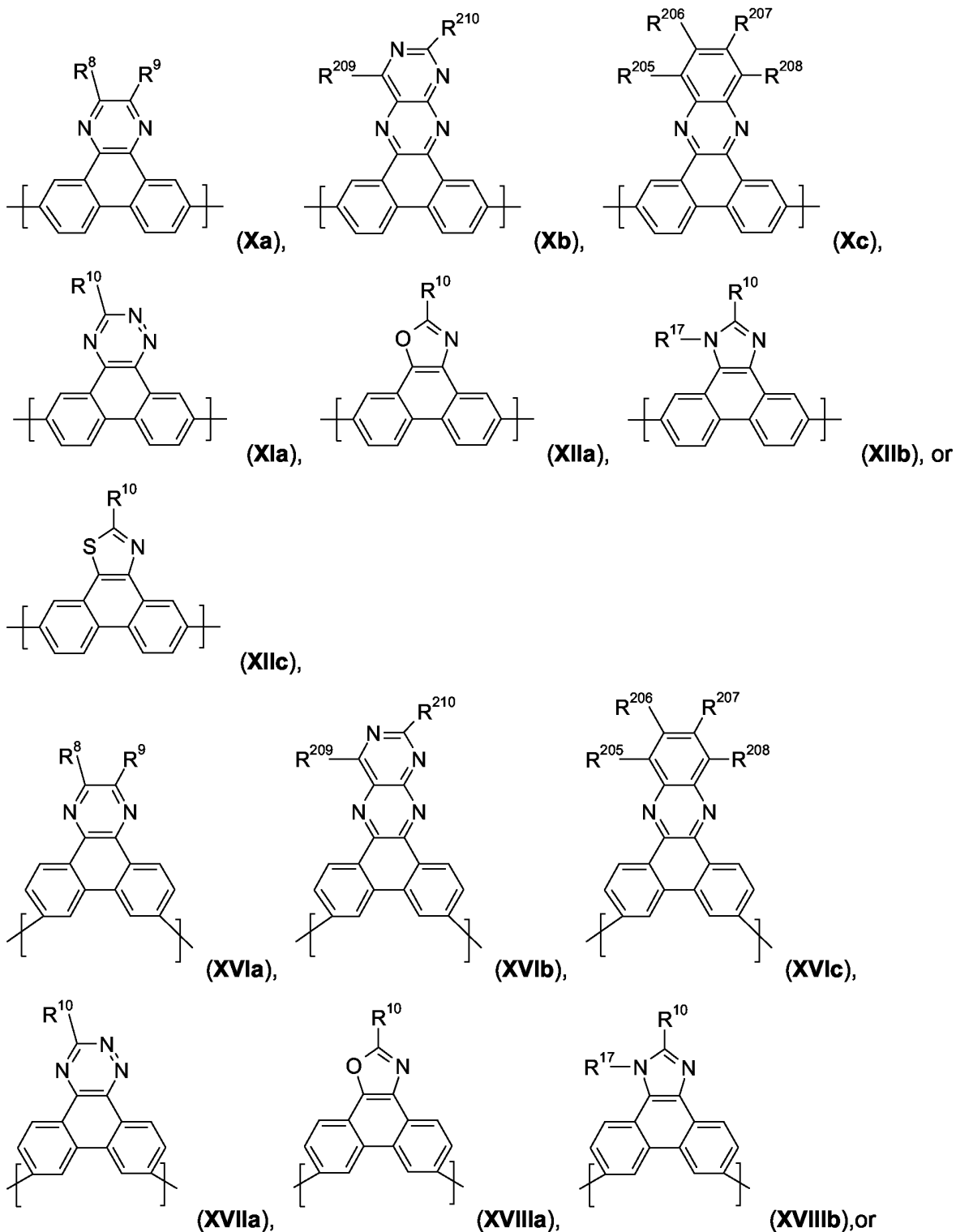
In case of repeating units of formula **X** and **XI** (**XVI** and **XVII**) it is preferred that  $R^8$  and/or  $R^9$  are different from a hydrogen atom and are selected from  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D. In case of repeating units of formula **XII** (**XVIII**) the solubilizing group is preferably a substituted aryl, or heteroaryl moiety.

Repeating units of formula **XII** are preferably used in combination with repeating units, which increase the hole-injection or hole-transport properties of the polymers. Repeating units of formula **X** and **XI** are preferably used in combination with repeating units, which increase the electron-injection or electron-transport properties of the polymers.

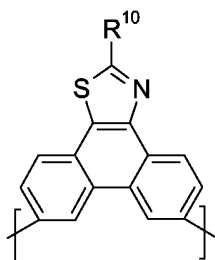
R<sup>17</sup> is preferably C<sub>1</sub>-C<sub>18</sub>alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl.

Among the repeating units of formula **X**, **XI**, **XII**, **XVI**, **XVII** and **XVIII** compounds of formula

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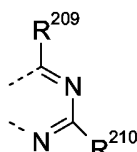






(**XVIIIc**) are most preferred, wherein  $R^8$  and  $R^9$  are independently of each

other H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkoxy which is interrupted by D, or a group  $-X^2-R^{18}$ , or



$R^8$  and  $R^9$  together form a group  $\text{---}$ , wherein  $R^{209}$  and  $R^{210}$  are independently of

5 each other H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,

$R^{10}$  is H,  $C_6$ - $C_{18}$ aryl, which can be substituted by G,  $C_2$ - $C_{18}$ heteroaryl, which can be substituted by G,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ -  
10  $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D, or a group  $-X^2-R^{18}$ , wherein  $X^2$  is a spacer, such as  $C_6$ - $C_{12}$ aryl, or  $C_6$ - $C_{12}$ heteroaryl, especially phenyl, or naphthyl, which can be substituted one more, especially one to two times with  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D,

15  $R^{17}$  is  $C_6$ - $C_{18}$ aryl;  $C_6$ - $C_{18}$ aryl which is substituted by  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ perfluoroalkyl, or  $C_1$ - $C_{18}$ alkoxy;  $C_1$ - $C_{18}$ alkyl; or  $C_1$ - $C_{18}$ alkyl which is interrupted by  $-O-$ ; and

$R^{18}$  is H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkoxy which is interrupted by D,

20  $R^{205}$ ,  $R^{206}$ ,  $R^{207}$ ,  $R^{208}$ ,  $R^{209}$  and  $R^{210}$  are independently of each other H,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkoxy which is interrupted by D.

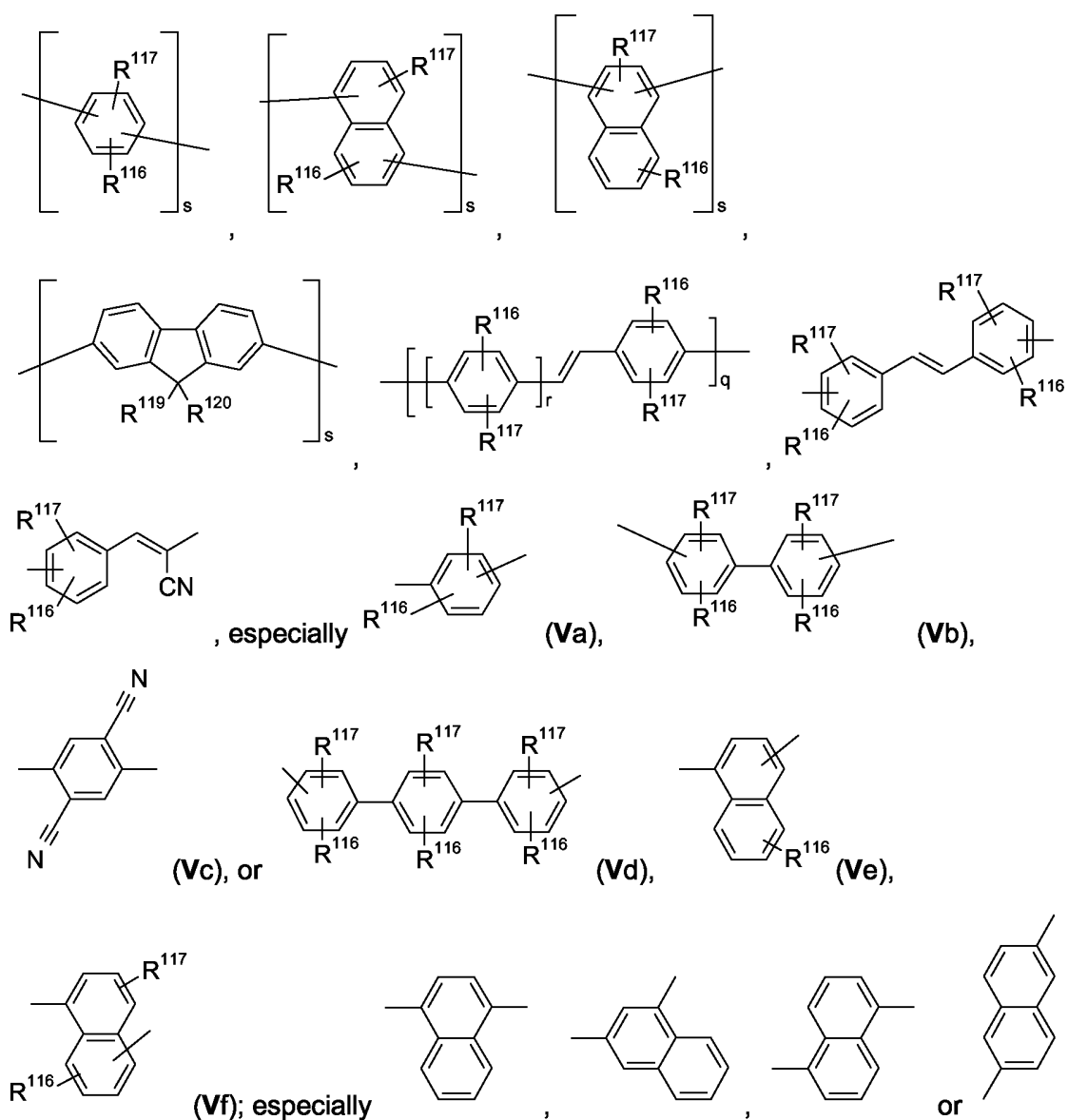
As used herein the term "polymer of the present invention" refers to polymers having repeating units of formula I, especially repeating units of formula **X**, **XI** and/or **XII** (**XVI**, **XVII** and **XVIII**), very especially repeating units of formula **Xa**, **XIa**, **XIIa** and/or **XIIb**.

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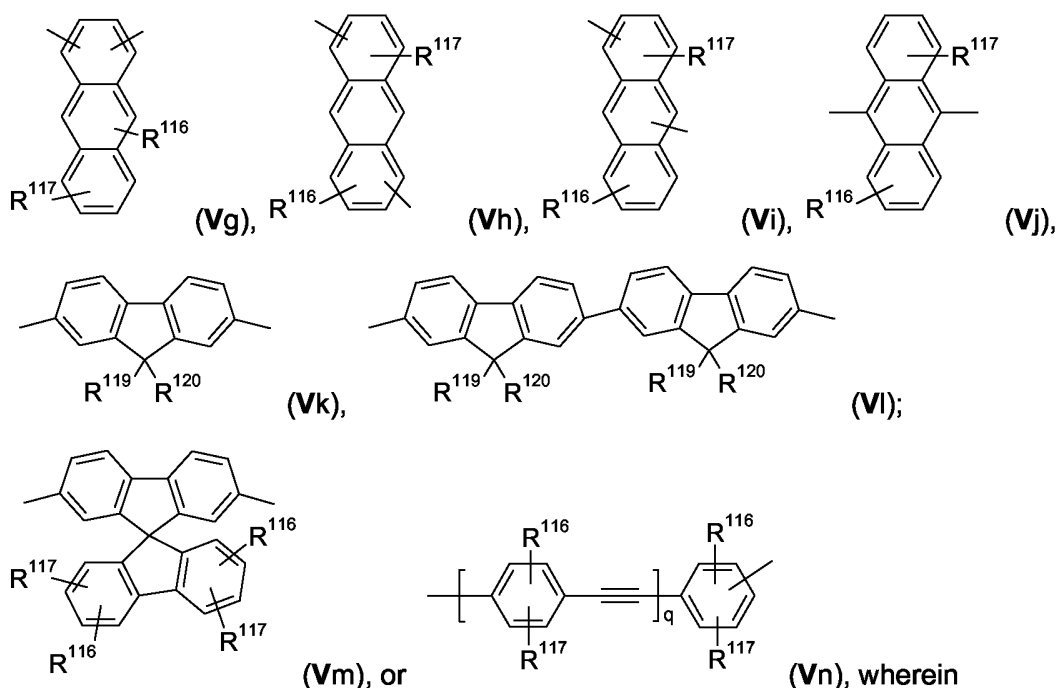
The present invention is illustrated in more detail on the basis of repeating units of formula **X**, **XI** and/or **XII**, but is not limited thereto.

In a first aspect, the present invention relates to polymers comprising a repeating unit of the formula I, especially repeating units of formula X, XI and/or XII, very especially repeating units of formula Xa, Xia, Xlla and/or XIIb.

- 5 The polymers of formula I can contain in addition to the repeating unit (recurring unit) of formula I one or more repeating units  $Ar^3$  and/or T.  $Ar^3$  is selected from the following groups:
- group II: units, which increase the hole-injection or hole-transport properties of the polymers;
- group III: units, which increase the electron-injection or electron-transport properties of the polymers;
- 10 group IV: units, which are combinations of units of group II and III;
- group V:



18



r is an integer from 1 to 10, especially 1, 2 or 3,

5 q is an integer from 1 to 10, especially 1, 2 or 3,

s is an integer from 1 to 10, especially 1, 2 or 3,

R<sup>116</sup> and R<sup>117</sup> are independently of each other H, halogen, -CN, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is substituted by E and/or interrupted by D, C<sub>6</sub>-C<sub>24</sub>aryl, C<sub>6</sub>-C<sub>24</sub>aryl which is substituted by G, C<sub>2</sub>-C<sub>20</sub>heteroaryl, C<sub>2</sub>-C<sub>20</sub>heteroaryl which is substituted by G, C<sub>2</sub>-C<sub>18</sub>alkenyl, C<sub>2</sub>-C<sub>18</sub>alkynyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D, C<sub>7</sub>-C<sub>25</sub>aralkyl, -C(=O)-R<sup>127</sup>, -C(=O)OR<sup>127</sup>, or -C(=O)NR<sup>127</sup>R<sup>126</sup>,

10

R<sup>119</sup> and R<sup>120</sup> are independently of each other H, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is substituted by E and/or interrupted by D, C<sub>6</sub>-C<sub>24</sub>aryl, C<sub>6</sub>-C<sub>24</sub>aryl which is substituted by G, C<sub>2</sub>-C<sub>20</sub>heteroaryl, C<sub>2</sub>-C<sub>20</sub>heteroaryl which is substituted by G, C<sub>2</sub>-C<sub>18</sub>alkenyl, C<sub>2</sub>-C<sub>18</sub>alkynyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D, or C<sub>7</sub>-C<sub>25</sub>aralkyl, or

15

R<sup>119</sup> and R<sup>120</sup> together form a group of formula =CR<sup>121</sup>R<sup>122</sup>, wherein

R<sup>121</sup> and R<sup>122</sup> are independently of each other H, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is substituted by E and/or interrupted by D, C<sub>6</sub>-C<sub>24</sub>aryl, C<sub>6</sub>-C<sub>24</sub>aryl which is substituted by G, or C<sub>2</sub>-C<sub>20</sub>heteroaryl, or C<sub>2</sub>-C<sub>20</sub>heteroaryl which is substituted by G, or

20

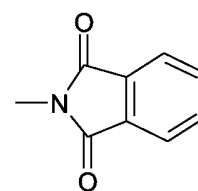
R<sup>119</sup> and R<sup>120</sup> together form a five or six membered ring, which optionally can be substituted by C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is substituted by E and/or interrupted by D, C<sub>6</sub>-C<sub>24</sub>aryl, C<sub>6</sub>-C<sub>24</sub>aryl which is substituted by G, C<sub>2</sub>-C<sub>20</sub>heteroaryl, C<sub>2</sub>-C<sub>20</sub>heteroaryl which is substituted by G, C<sub>2</sub>-C<sub>18</sub>alkenyl, C<sub>2</sub>-C<sub>18</sub>alkynyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D, C<sub>7</sub>-C<sub>25</sub>aralkyl, or -C(=O)-R<sup>127</sup>, and

$R^{126}$  and  $R^{127}$  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  $-O-$ ,  
D is  $-CO-$ ,  $-COO-$ ,  $-S-$ ,  $-SO-$ ,  $-SO_2-$ ,  $-O-$ ,  $-NR^{65}-$ ,  $-SiR^{70}R^{71}-$ ,  $-POR^{72}-$ ,  $-CR^{63}=CR^{64}-$ , or  $-C\equiv C-$ ,  
and

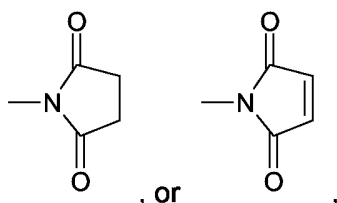
5 E is  $-OR^{69}$ ,  $-SR^{69}$ ,  $-NR^{65}R^{66}$ ,  $-COR^{68}$ ,  $-COOR^{67}$ ,  $-CONR^{65}R^{66}$ ,  $-CN$ , or halogen,

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

$R^{63}$ ,  $R^{64}$ ,  $R^{65}$  and  $R^{66}$  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,  $C_1-C_{18}$ alkoxy;  $C_1-C_{18}$ alkyl; or  $C_1-C_{18}$ alkyl which is interrupted by  $-O-$ ; or



10  $R^{65}$  and  $R^{66}$  together form a five or six membered ring, in particular



$R^{67}$  and  $R^{68}$  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  $-O-$ ,

$R^{69}$  is H;  $C_6-C_{18}$ aryl;  $C_6-C_{18}$ aryl, which is substituted by  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkoxy;  $C_1-C_{18}$ alkyl;

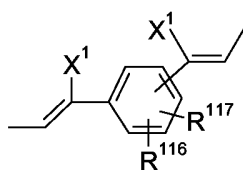
15 or  $C_1-C_{18}$ alkyl which is interrupted by  $-O-$ ,

$R^{70}$  and  $R^{71}$  are independently of each other  $C_1-C_{18}$ alkyl,  $C_6-C_{18}$ aryl, or  $C_6-C_{18}$ aryl, which is substituted by  $C_1-C_{18}$ alkyl, and

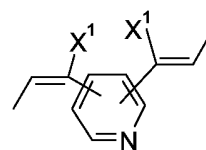
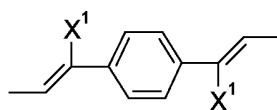
$R^{72}$  is  $C_1-C_{18}$ alkyl,  $C_6-C_{18}$ aryl, or  $C_6-C_{18}$ aryl, which is substituted by  $C_1-C_{18}$ alkyl.

20 Among the above units of group V the units of formula Ve, especially Va, Vk and Vm are more preferred.

The repeating units T are selected from the following group VI:

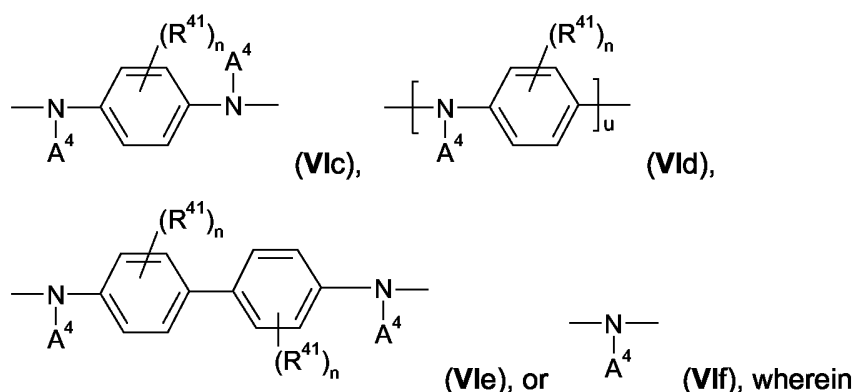


(VIa), especially



(VIb),

20

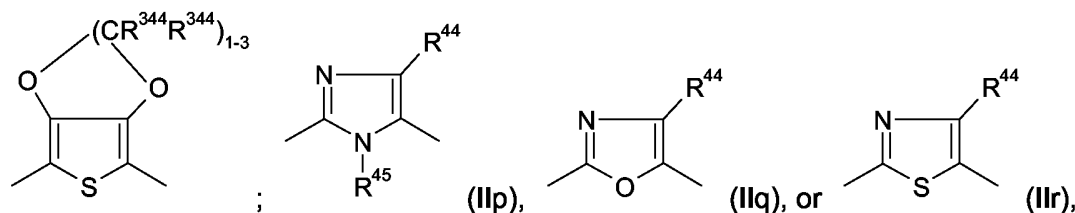
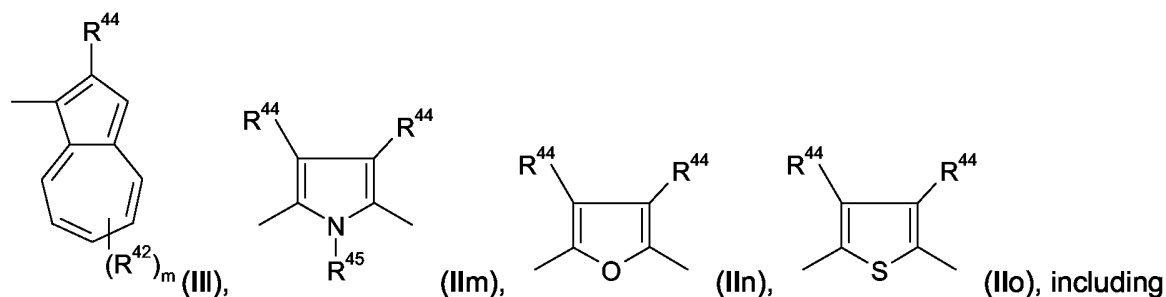
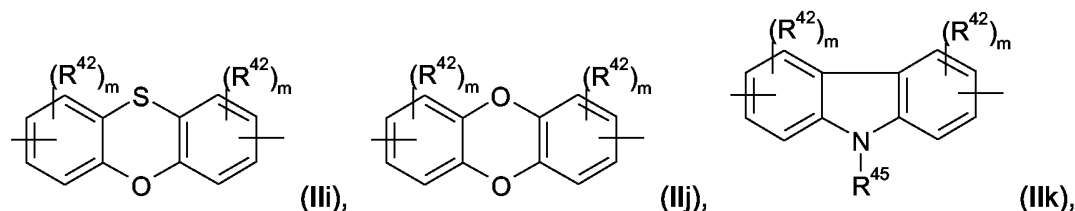
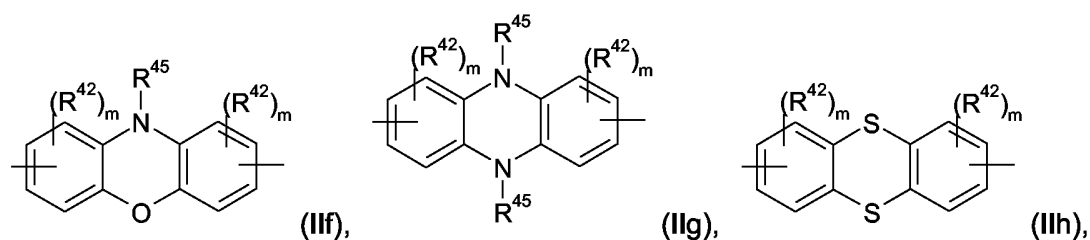
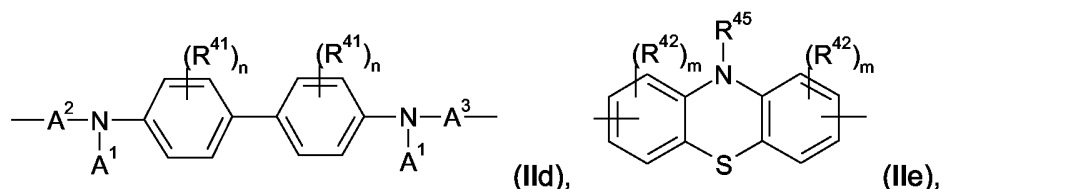
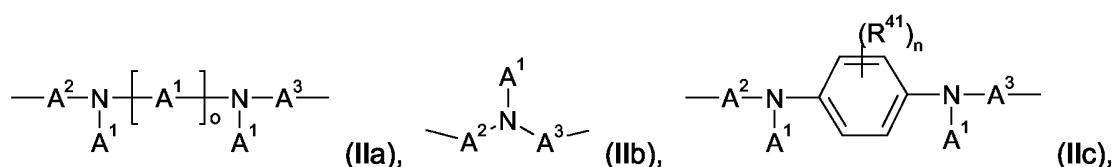


$X^1$  is a hydrogen atom, or a cyano group,

$R^{116}$  and  $R^{117}$  are as defined above,

- 5  $R^{41}$  can be the same or different at each occurrence and is Cl, F, CN,  $N(R^{45})_2$ , a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, a  $C_1$ - $C_{25}$ alkoxy group, in which one or more carbon atoms which are not in neighbourhood to each other could be replaced by  $-NR^{45}$ -,  $-O$ -,  $-S$ -,  $-C(=O)-O$ -, or  $-O-C(=O)-O$ -, and/or wherein one or more hydrogen atoms can be replaced by F, a  $C_6$ - $C_{24}$ aryl group, or a  $C_6$ - $C_{24}$ aryloxy group, wherein one or more carbon atoms can be replaced by O, S, or N, and/or which can be substituted by one or more non-aromatic groups  $R^{41}$ , or
- 10 two or more groups  $R^{41}$  form a ring system;
- $R^{45}$  is H, a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, in which one or more carbon atoms which are not in neighbourhood to each other could be replaced by  $-NR^{45}$ -,  $-O$ -,  $-S$ -,  $-C(=O)-O$ -, or  $-O-C(=O)-O$ -, and/or wherein one or more hydrogen atoms can be replaced by F, a
- 15  $C_6$ - $C_{24}$ aryl group, or a  $C_6$ - $C_{24}$ aryloxy group, wherein one or more carbon atoms can be replaced by O, S, or N, and/or which can be substituted by one or more non-aromatic groups  $R^{41}$ ,
- $R^{45'}$  is H, a  $C_1$ - $C_{25}$ alkyl group, or a  $C_4$ - $C_{18}$ cycloalkyl group,
- $n$  can be the same or different at each occurrence and is 0, 1, 2, or 3, especially 0, 1, or 2,
- 20 very especially 0 or 1, and  $u$  is 1, 2, 3, or 4;
- $A^4$  is a  $C_6$ - $C_{24}$ aryl group, a  $C_2$ - $C_{30}$ heteroaryl group, especially phenyl, naphthyl, anthryl, biphenyl, 2-fluorenyl, phenanthryl, or perylenyl, which can be substituted by one or more non-aromatic groups  $R^{41}$ .

- 25 Preferred units of group II, which increase the hole-injection or hole-transport properties of the polymers, are:



$R^{41}$  can be the same or different at each occurrence and is Cl, F, CN,  $N(R^{45})_2$ , a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, a  $C_1$ - $C_{25}$ alkoxy group, in which one or more carbon atoms which are not in neighbourhood to each other could be replaced by  $-NR^{45}-$ ,  $-O-$ ,  $-S-$ ,  $-C(=O)-$ ,  $O-$ , or  $-O-C(=O)-O-$ , and/or wherein one or more hydrogen atoms can be replaced by F, a  $C_6$ - $C_{24}$ aryl group, or a  $C_6$ - $C_{24}$ aryloxy group, wherein one or more carbon atoms can be replaced by O, S, or N, and/or which can be substituted by one or more non-aromatic groups  $R^{41}$ , or

two or more groups  $R^{41}$  form a ring system;

$R^{42}$  can be the same or different at each occurrence and is CN, a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, a  $C_1$ - $C_{25}$ alkoxy group, in which one or more carbon atoms which are not in neighbourhood to each other could be replaced by  $-NR^{45}$ -,  $-O$ -,  $-S$ -,  $-C(=O)-O$ -, or  $-O$ -

5  $C(=O)-O$ -, and/or wherein one or more hydrogen atoms can be replaced by F, a  $C_6$ - $C_{24}$ aryl group, or a  $C_6$ - $C_{24}$ aryloxy group, wherein one or more carbon atoms can be replaced by O, S, or N, and/or which can be substituted by one or more non-aromatic groups  $R^{41}$ , or two or more groups  $R^{41}$  form a ring system;

10  $R^{344}$  can be the same or different at each occurrence and are a hydrogen atom, a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, or a  $C_1$ - $C_{25}$ alkoxy group,

$R^{44}$  can be the same or different at each occurrence and are a hydrogen atom, a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, a  $C_1$ - $C_{25}$ alkoxy group, in which one or more carbon atoms which are not in neighbourhood to each other could be replaced by  $-NR^{45}$ -,  $-O$ -,  $-S$ -,  $-C(=O)-O$ -, or,  $-O-C(=O)-O$ -, and/or wherein one or more hydrogen atoms can be replaced by F, a  
15  $C_6$ - $C_{24}$ aryl group, or a  $C_6$ - $C_{24}$ aryloxy group, wherein one or more carbon atoms can be replaced by O, S, or N, and/or which can be substituted by one or more non-aromatic groups  $R^{41}$ , or CN, or

two or more groups  $R^{44}$ , which are in neighbourhood to each other, form a ring;

$R^{45}$  is H, a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, in which one or more carbon atoms which are not in neighbourhood to each other could be replaced by  $-NR^{45}$ -,  $-O$ -,  $-S$ -,  $-C(=O)-O$ -, or,  $-O-C(=O)-O$ -, and/or wherein one or more hydrogen atoms can be replaced by F, a  
20  $C_6$ - $C_{24}$ aryl group, or a  $C_6$ - $C_{24}$ aryloxy group, wherein one or more carbon atoms can be replaced by O, S, or N, and/or which can be substituted by one or more non-aromatic groups  $R^{41}$ ;

25 m can be the same or different at each occurrence and is 0, 1, 2, or 3, especially 0, 1, or 2, very especially 0 or 1;

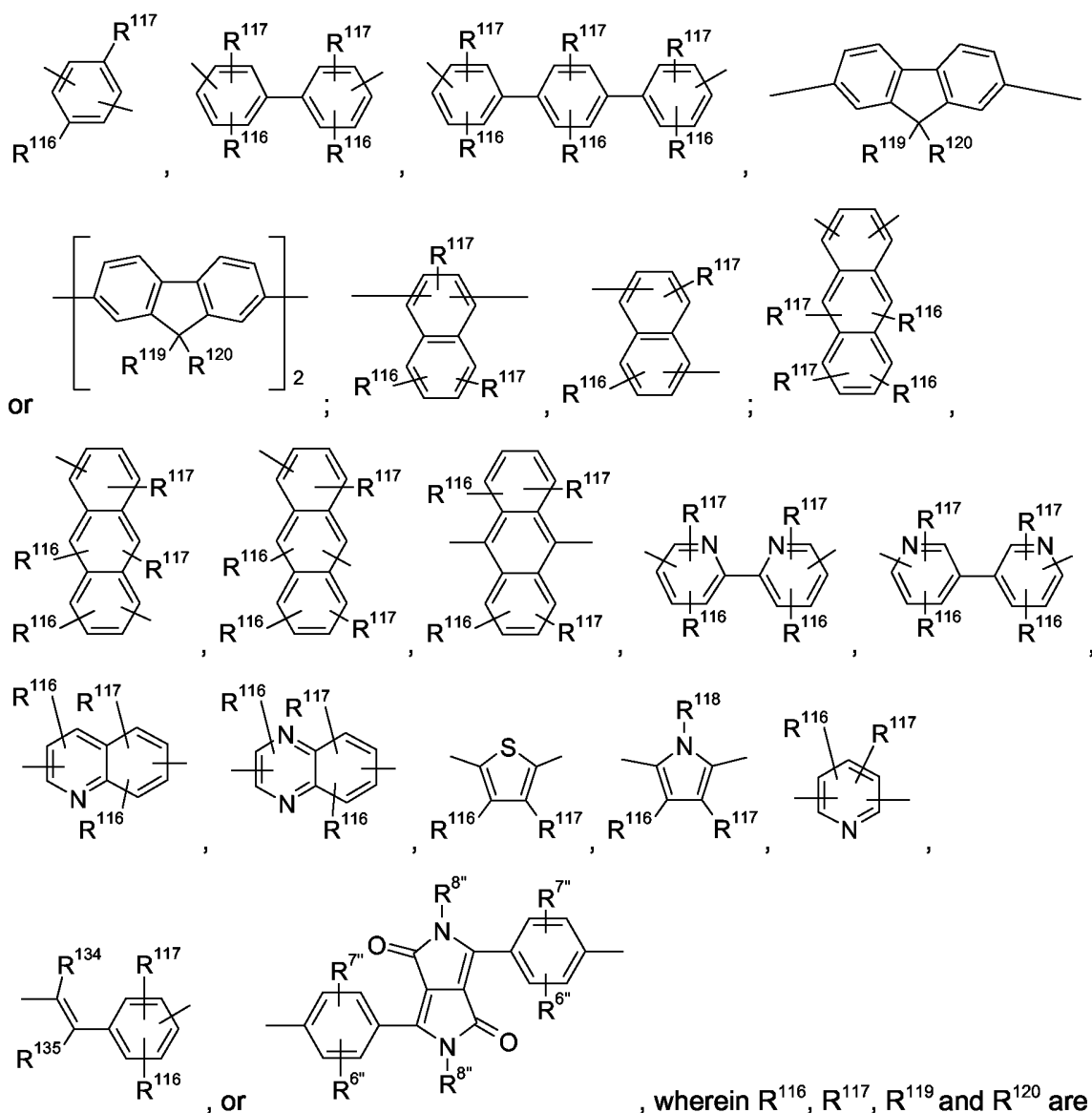
n can be the same or different at each occurrence and is 0, 1, 2, or 3, especially 0, 1, or 2, very especially 0 or 1;

o is 1, 2, or 3, especially 1, or 2, and

30  $A^1$  is a  $C_6$ - $C_{24}$ aryl group, a  $C_2$ - $C_{30}$ heteroaryl group, which can be substituted by one or more non-aromatic groups  $R^{41}$ , or  $NO_2$ , especially phenyl, naphthyl, anthryl, biphenyl, 2-fluorenyl, phenanthryl, or perylenyl,

$A^2$  and  $A^3$  are independently of each other a  $C_6$ - $C_{30}$ arylene group, or a  $C_2$ - $C_{24}$ heteroarylene group, which can optionally be substituted, especially

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defined above,

$R^{6''}$  and  $R^{7''}$  have independently of each other the meaning of  $R^{116}$ ,

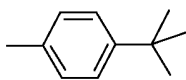
$R^{118}$  and  $R^{8''}$  are H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_6$ - $C_{24}$  aryl, or  $C_7$ - $C_{25}$ aralkyl, which are optionally substituted by G,

10  $R^{134}$  and  $R^{135}$  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 E, or  $C_2$ - $C_{20}$ heteroaryl,  $C_2$ - $C_{20}$ heteroaryl which is substituted by E, wherein D, E and G are as defined above. Among the above units of group II the units of formula IIa, IIb and IIk are more preferred.

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A<sup>1</sup> is preferably a phenyl group, which is substituted by C<sub>1</sub>-C<sub>4</sub>alkyl, in particular



, or an anthr-2-yl group, in particular an anthr-2-yl group.

Preferably, R<sup>116</sup> and R<sup>117</sup> are independently of each other H, C<sub>1</sub>-C<sub>18</sub>alkyl, such as methyl,

- 5 ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, or n-heptyl; C<sub>1</sub>-C<sub>18</sub>alkyl which is substituted by E and/or interrupted by D, such as -CH<sub>2</sub>OCH<sub>3</sub>, -CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>, -CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, or -CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>; C<sub>1</sub>-C<sub>18</sub>alkoxy, such as methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, isobutoxy, sec-butoxy, t-butoxy, 2-methylbutoxy, n-pentyloxy, isopentyloxy, n-hexyloxy, 2-ethylhexyloxy, or n-heptyloxy; C<sub>6</sub>-C<sub>14</sub>aryl, such as phenyl, naphthyl, or biphenyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl, such as cyclohexyl, C<sub>6</sub>-C<sub>14</sub>aryl which is substituted by G, such as -C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>, -C<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>3</sub>, -C<sub>6</sub>H<sub>3</sub>(OCH<sub>3</sub>)<sub>2</sub>, or -C<sub>6</sub>H<sub>3</sub>(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, -C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>, -C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>, -C<sub>6</sub>H<sub>4</sub>OtBu, or -C<sub>6</sub>H<sub>4</sub>tBu.

- 15 R<sup>118</sup> is preferably H, C<sub>1</sub>-C<sub>12</sub>alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, 2-methylbutyl, n-pentyl, isopentyl, n-hexyl, 2-ethylhexyl, n-heptyl, or C<sub>6</sub>-C<sub>14</sub>aryl, such as phenyl, naphthyl, or biphenyl.

Preferably, R<sup>119</sup> and R<sup>120</sup> are independently of each other H, C<sub>1</sub>-C<sub>12</sub>alkyl, such as methyl,

- 20 ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl, C<sub>1</sub>-C<sub>12</sub>alkyl which is substituted by E and/or interrupted by D, such as -CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>w</sub>OCH<sub>3</sub>, w = 1, 2, 3, or 4, C<sub>6</sub>-C<sub>14</sub>aryl, such as phenyl, naphthyl, or biphenyl, C<sub>6</sub>-C<sub>14</sub>aryl which is substituted by one to three times by C<sub>1</sub>-C<sub>12</sub>alkyl, or C<sub>1</sub>-C<sub>12</sub>alkoxy, which can optionally be interrupted by -O-, such as -C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>, -C<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>3</sub>, -C<sub>6</sub>H<sub>3</sub>(OCH<sub>3</sub>)<sub>2</sub>, -C<sub>6</sub>H<sub>3</sub>(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, -C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>, -C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>, or -C<sub>6</sub>H<sub>4</sub>tBu, or R<sup>119</sup> and R<sup>120</sup> together form a 4 to 8 membered ring, especially a 5 or 6 membered ring, such as cyclohexyl, or cyclopentyl, which can optionally be substituted by C<sub>1</sub>-C<sub>8</sub>alkyl.

Preferably, R<sup>134</sup> and R<sup>135</sup> are independently of each other H, C<sub>1</sub>-C<sub>12</sub>alkyl, such as as methyl,

- 30 ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, or sec-butyl, or C<sub>6</sub>-C<sub>14</sub>aryl, such as phenyl, naphthyl, or biphenyl.

D is preferably -CO-, -COO-, -S-, -SO-, -SO<sub>2</sub>-, -O-, -NR<sup>65</sup>-, wherein R<sup>65</sup> is C<sub>1</sub>-C<sub>12</sub>alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, or sec-butyl, or C<sub>6</sub>-C<sub>14</sub>aryl, such as

- 35 phenyl, naphthyl, or biphenyl.

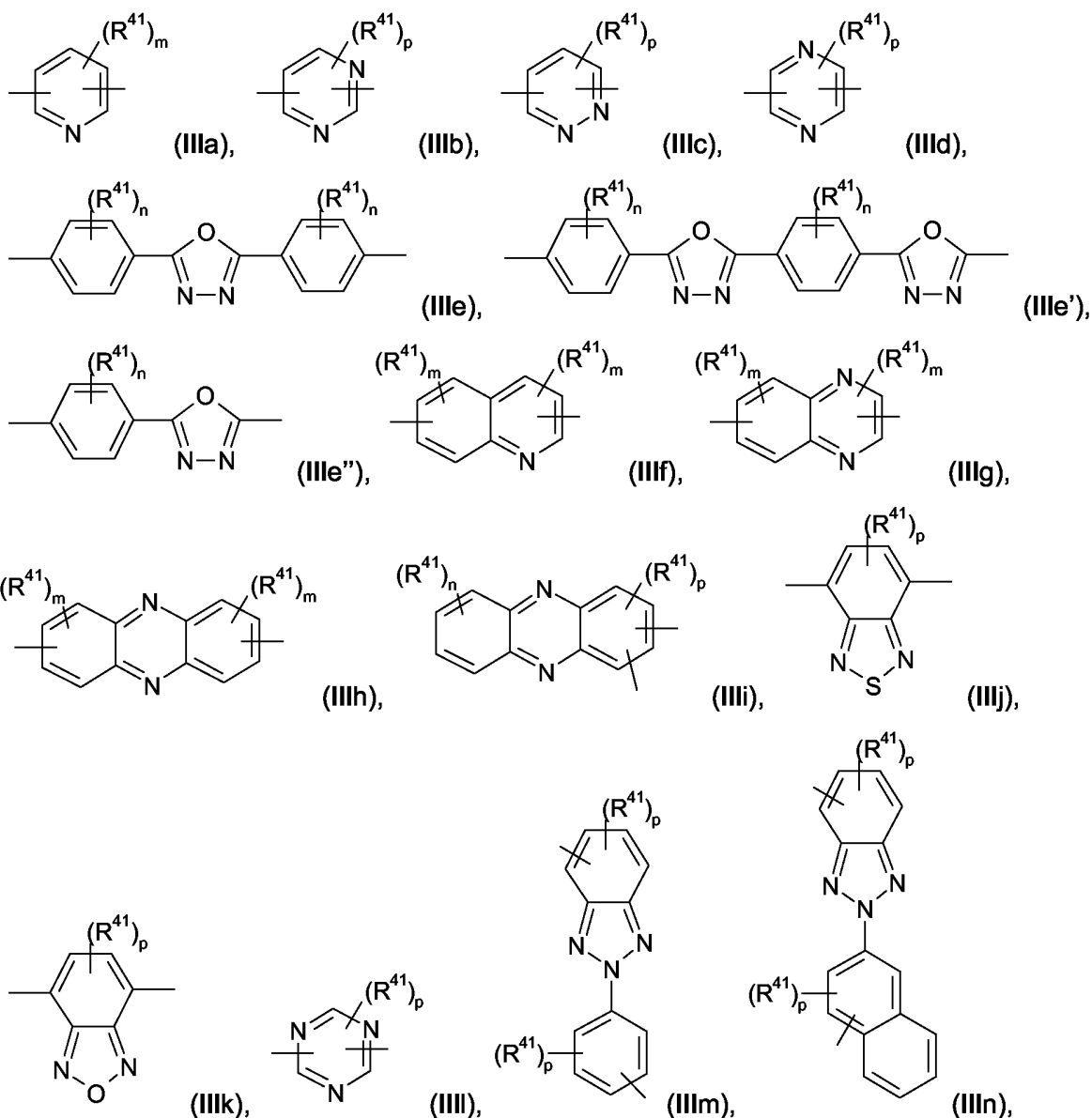
E is preferably  $-\text{OR}^{69}$ ;  $-\text{SR}^{69}$ ;  $-\text{NR}^{65}\text{R}^{65}$ ;  $-\text{COR}^{68}$ ;  $-\text{COOR}^{67}$ ;  $-\text{CONR}^{65}\text{R}^{65}$ ; or  $-\text{CN}$ ; wherein  $\text{R}^{65}$ ,  $\text{R}^{67}$ ,  $\text{R}^{68}$  and  $\text{R}^{69}$  are independently of each other  $\text{C}_1$ - $\text{C}_{12}$ alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl, or  $\text{C}_6$ - $\text{C}_{14}$ aryl, such as

5

phenyl, naphthyl, or biphenyl.

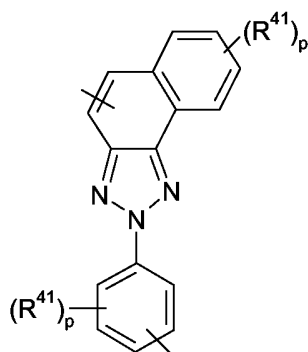
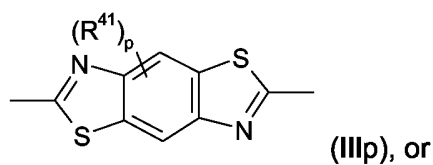
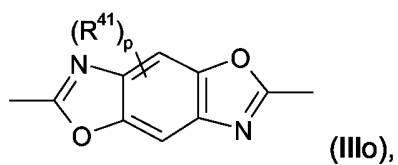
G has the same preferences as E, or is  $\text{C}_1$ - $\text{C}_{18}$ alkyl, especially  $\text{C}_1$ - $\text{C}_{12}$ alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, hexyl, octyl, or 2-ethyl-hexyl.

- 10 Preferred units of group III, which increase the electron-injection or electron-transport properties of the polymers, are:



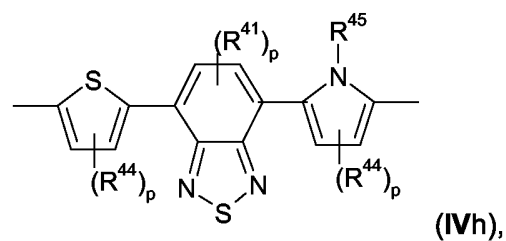
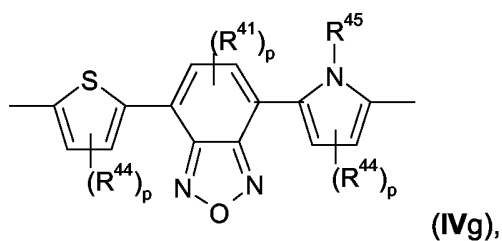
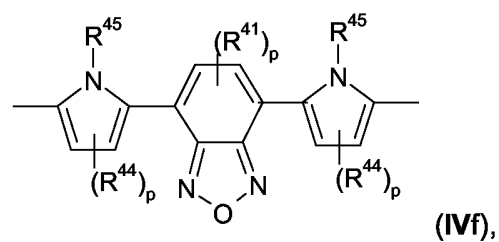
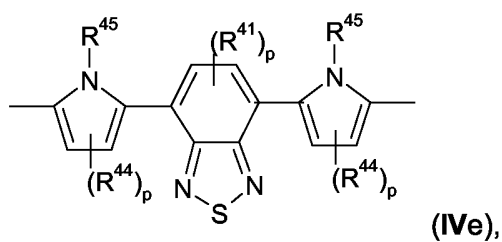
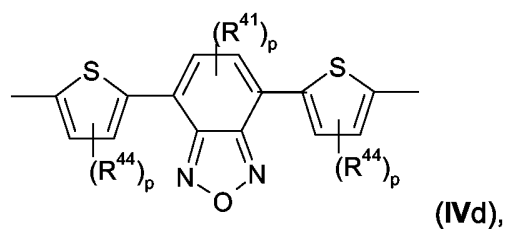
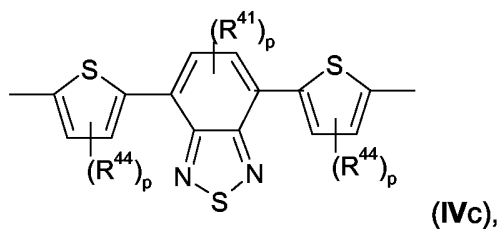
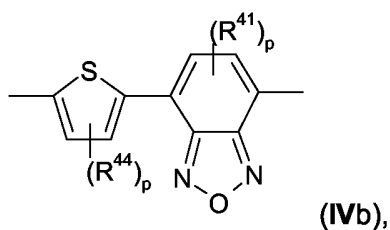
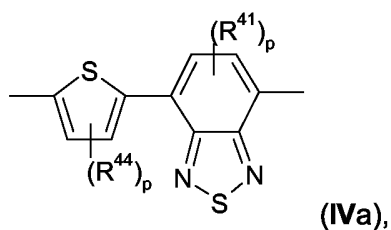
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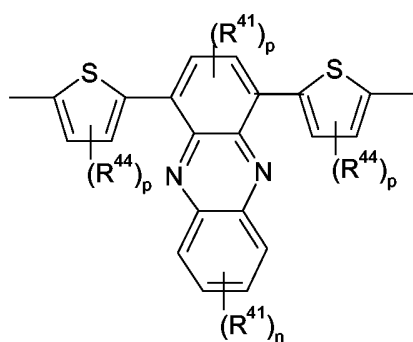
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Preferred units of group IV, which are combinations of units of formula II and III, are:

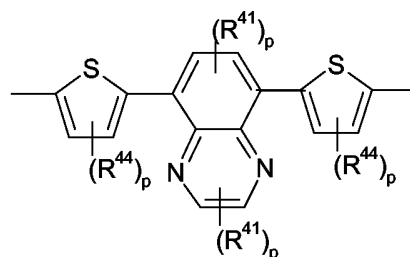


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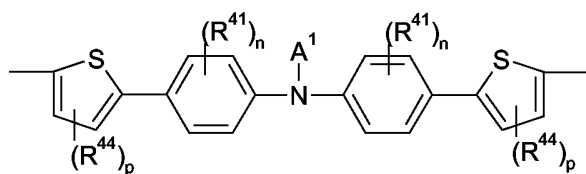
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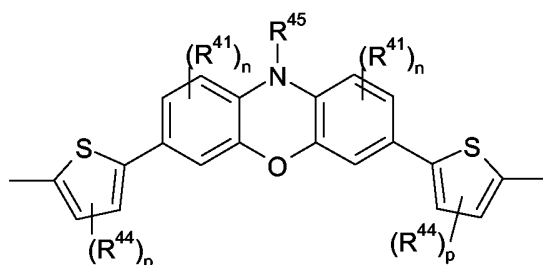
(IVi),



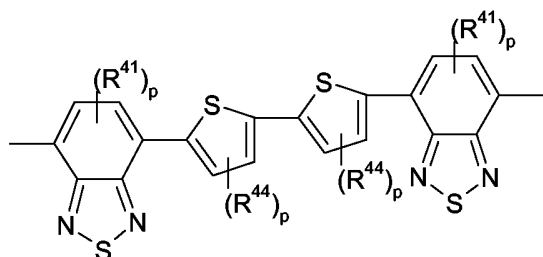
(IVj),



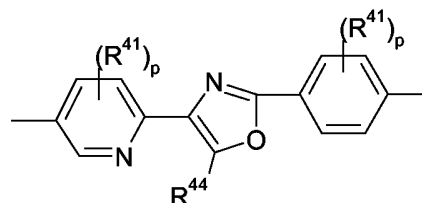
(IVk),



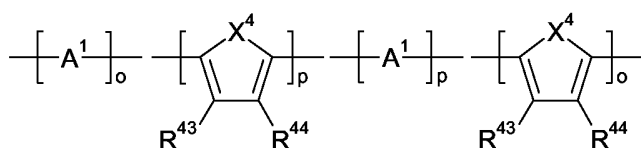
(IVl),



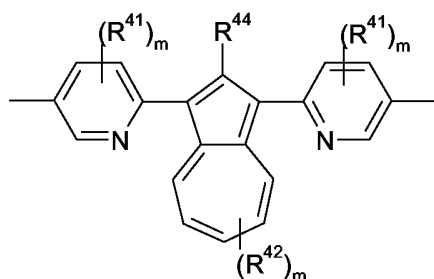
(IVm),



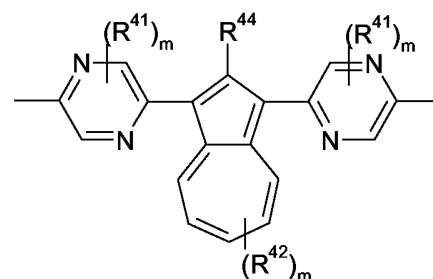
(IVn),



(IVo),



(IVp), or



(IVq),

wherein  $X^4$  is O, S, or  $NR^{45}$ ,

$R^{43}$  is a hydrogen atom, a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, a  $C_1$ - $C_{25}$ alkoxy group, in which one or more carbon atoms which are not in neighbourhood to each other could be replaced by  $-NR^{45}$ -,  $-O$ -,  $-S$ -,  $-C(=O)-O$ -, or,  $-O-C(=O)-O$ -, and/or wherein one or more

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hydrogen atoms can be replaced by F, a C<sub>6</sub>-C<sub>24</sub>aryl group, or a C<sub>6</sub>-C<sub>24</sub>aryloxy group, wherein one or more carbon atoms can be replaced by O, S, or N, and/or which can be substituted by one or more non-aromatic groups R<sup>41</sup>, or CN, or

two or more groups R<sup>43</sup> and/or R<sup>44</sup>, which are in neighbourhood to each other, form a ring;

5 o is 1, 2, or 3, especially 1, or 2, u is 1, 2, 3, or 4,

and A<sup>1</sup>, R<sup>41</sup>, R<sup>42</sup>, R<sup>44</sup>, R<sup>45</sup>, m, n and p are as defined above.

The presence of repeating units of formula II to V can lead to the following advantages:

If structures of group II, e.g. repeating units of formula IIa to IIr are present, improved hole-

10 injection and/or hole-transport properties of the polymers can be observed. If used in PLEDs, the PLEDs show higher current density and electroluminescence at a given voltage. This property is of high importance in mobile applications, such as, for example, displays for mobile phones and PDAs, when the power consumption can be reduced.

If structures of group III, e.g. repeating units of formula IIIa to IIIk are present, improved

15 electron-injection or electron-transport properties of the polymers are observed. The presence of structures of group IV, e.g. repeating units of formula IVa to IVp, enables the variation of the of the electronic band gap and, hence, a variation of the color properties.

The preparation of monomers from which the units of group II, III, IV and V are derived, is, for  
20 example, described in WO03/020790.

In one embodiment, the polymers according to the invention consist only of one or more type of repeating units of formula I. In a preferred embodiment, the polymers according to the invention consist of precisely one type of repeating unit of formula I (homopolymers).

25

According to the present invention the term "polymer" comprises polymers as well as oligomers, wherein a polymer is a molecule of high relative molecular mass, the structure of which essentially comprises the repetition of units derived, actually or conceptually, from molecules of low relative molecular mass and an oligomer is a molecule of intermediate  
30 molecular mass, the structure of which essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass. A molecule is regarded as having a high relative molecular mass if it has properties which do not vary significantly with the removal of one or a few of the units. A molecule is regarded as having an intermediate molecular mass if it has properties which do vary significantly with the  
35 removal of one or a few of the units.

According to the present invention a homopolymer is a polymer derived from one species of (real, implicit, or hypothetical) monomer. Many polymers are made by the mutual reaction of complementary monomers. These monomers can readily be visualized as reacting to give an "implicit monomer", the homopolymerisation of which would give the actual product, which can be regarded as a homopolymer. Some polymers are obtained by chemical modification of other polymers, such that the structure of the macromolecules that constitute the resulting polymer can be thought of having been formed by the homopolymerisation of a hypothetical monomer.

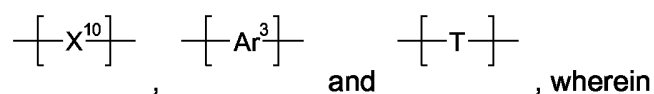
Accordingly a copolymer is a polymer derived from more than one species of monomer, e.g. bipolymer, terpolymer, quaterpolymer, etc.

The oligomers of this invention have a weight average molecular weight of < 2,000 Daltons. The polymers of this invention preferably have a weight average molecular weight of 2,000 Daltons or greater, especially 2,000 to 2,000,000 Daltons, more preferably 10,000 to 1,000,000 and most preferably 20,000 to 750,000 Daltons. Molecular weights are determined according to gel permeation chromatography using polystyrene standards.

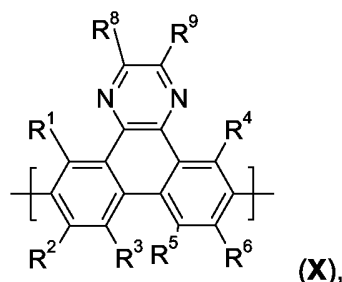
In one aspect of the present invention polymers are preferred, which besides the repeating units of formula I at the same time have at least one additional repeating unit  $Ar^3$ , or T, which is selected from groups II to VI. In said aspect, the polymers according to the invention comprise from 1 to 99 mol % of repeating units of formula I and preferably from 5 to 95 mol % of repeating units of groups II to VI, more preferably from 10 to 90 mol % of repeating units of groups II to VI, most preferably from 25 to 75 mol % of repeating units of groups II to VI.

In said aspect of the present invention polymers are preferred, which besides the repeating units of formula I at the same time have at least two additional repeating units, which are selected from at least two different groups II to VI. Most preferred is the simultaneous presence of repeating units of group III and VI, IV and VI, or II and III and VI.

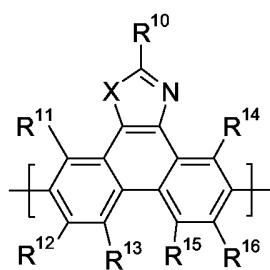
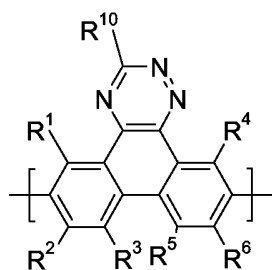
Accordingly, in one preferred embodiment the present invention relates to polymers, wherein the polymer comprises a repeating unit(s) of formula



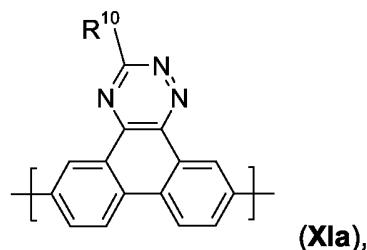
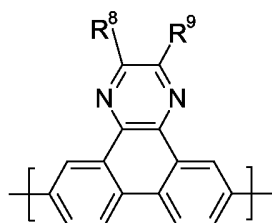
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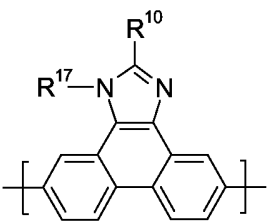
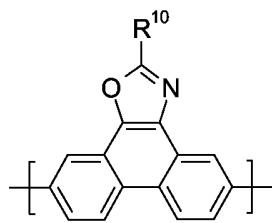
$X^{10}$  is a repeating unit of formula I, especially



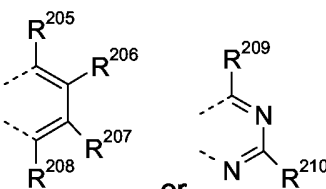
$X$ ,  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$ ,  $R^{15}$  and  $R^{16}$  are as defined above,



very especially



independently of each other H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkoxy which is interrupted by D, or a group  $-X^2-R^{18}$ ,



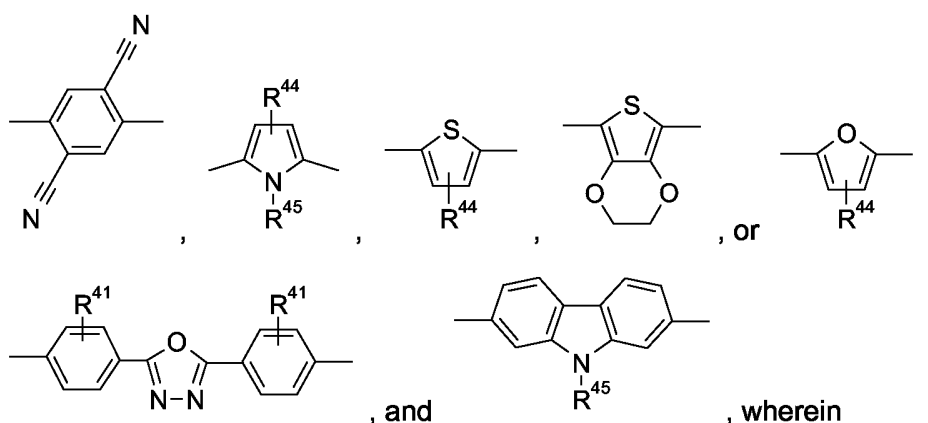
$R^8$  and  $R^9$  together form a group  $R^{205}$ ,  $R^{206}$ ,  $R^{207}$ ,  $R^{208}$ ,  $R^{209}$  and  $R^{210}$  are independently of each other H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,

$R^{10}$  is H,  $C_6$ - $C_{18}$ aryl, which can be substituted by G,  $C_2$ - $C_{18}$ heteroaryl, which can be substituted by G,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D, or a group  $-X^2-R^{18}$ , wherein  $X^2$  is a spacer, such as  $C_6$ - $C_{12}$ aryl, or  $C_6$ - $C_{12}$ heteroaryl, especially phenyl, or

naphthyl, which can be substituted one more, especially one to two times with C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is interrupted by D, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, or C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D,

R<sup>17</sup> is C<sub>6</sub>-C<sub>18</sub>aryl; C<sub>6</sub>-C<sub>18</sub>aryl which is substituted by C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, or C<sub>1</sub>-C<sub>18</sub>alkoxy; C<sub>1</sub>-C<sub>18</sub>alkyl; or C<sub>1</sub>-C<sub>18</sub>alkyl which is interrupted by -O-; and  
 R<sup>18</sup> is H, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is interrupted by D, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkoxy which is interrupted by D.

In said embodiment T is preferably a repeating unit of formula VIa or VIb and Ar<sup>3</sup> is preferably selected from repeating units of formula:

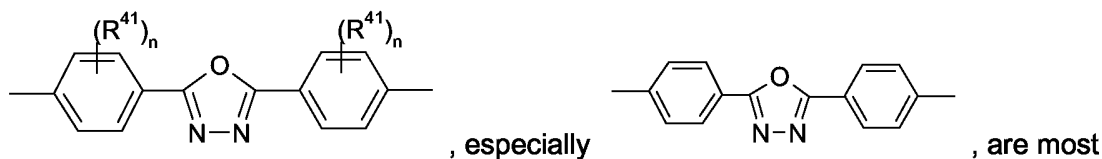
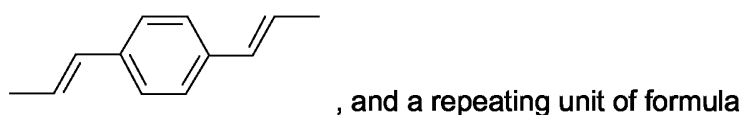
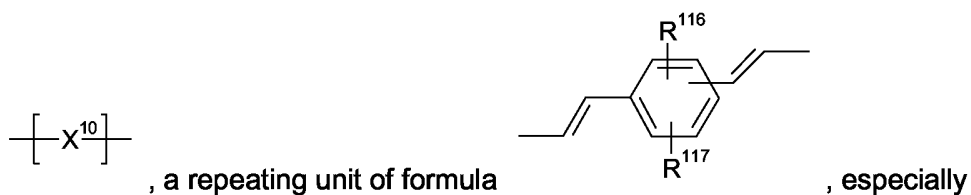


R<sup>44</sup> and R<sup>41</sup> are hydrogen, C<sub>1</sub>-C<sub>18</sub>alkyl, or C<sub>1</sub>-C<sub>18</sub>alkoxy, and

R<sup>45</sup> is H, C<sub>1</sub>-C<sub>18</sub>alkyl, or C<sub>1</sub>-C<sub>18</sub>alkyl which is substituted by E and/or interrupted by D,

especially C<sub>1</sub>-C<sub>18</sub>alkyl which is interrupted by -O-, wherein D and E are as defined above.

In said aspect of the present invention terpolymers comprising a repeating unit of formula

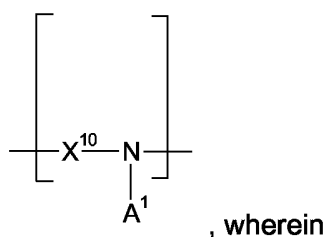
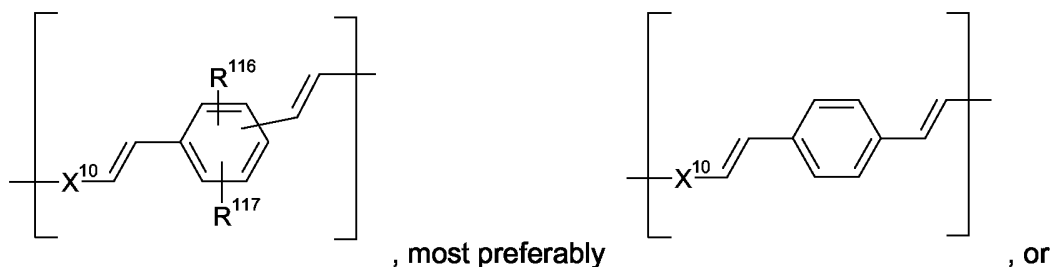
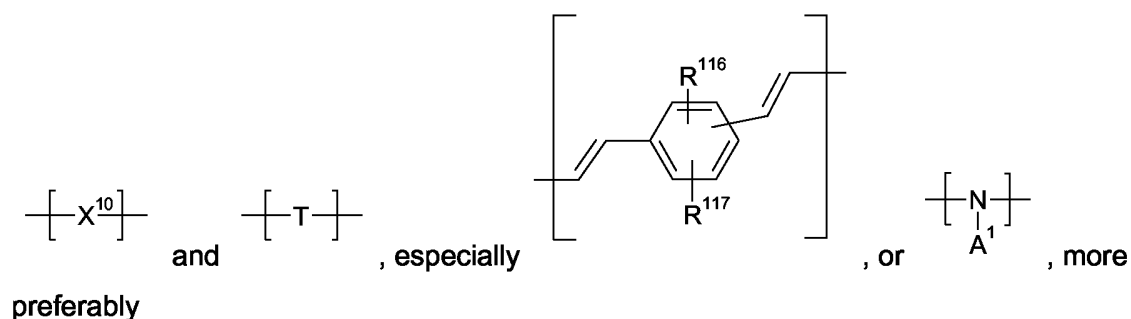




$X^{10}$  is a repeating unit of formula I, especially **X**, **XI** and **XII**, very especially **Xa**, **XIa**, **XIIa** and **XIIb**.

- 5  $R^{116}$  and  $R^{117}$  are as defined above and are preferably H, halogen, CN,  $C_1$ - $C_{12}$ alkyl,  $C_1$ - $C_{12}$ alkoxy, or  $C_6$ - $C_{14}$ aryl, more preferably H,  $C_1$ - $C_{12}$ alkyl, or  $C_1$ - $C_{18}$ alkoxy,  $R^{41}$  is Cl, F, CN,  $N(R^{45})_2$ ,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkoxy, or  $C_6$ - $C_{14}$ aryl, n is 0, 1, or 2.

- 10 In another preferred embodiment the present invention relates to polymers, wherein the polymer comprises repeating units of formula



- 15  $X^{10}$  is a repeating unit of formula I, especially **X**, **XI** and **XII**, very especially **Xa**, **XIa**, **XIIa** and **XIIb**.

$R^{116}$  and  $R^{117}$  are as defined above and are especially H, halogen, CN,  $C_1$ - $C_{12}$ alkyl,  $C_1$ - $C_{12}$ alkoxy, or  $C_6$ - $C_{14}$ aryl,

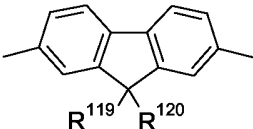
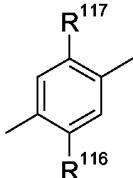
A<sup>1</sup> is a C<sub>6</sub>-C<sub>24</sub>aryl group, a C<sub>2</sub>-C<sub>30</sub>heteroaryl group, which can be substituted by one or more non-aromatic groups R<sup>41</sup>, preferably a phenyl group, which is substituted by C<sub>1</sub>-C<sub>4</sub>alkyl, in

particular , or an anthryl group, in particular an anthr-2-yl group.

5 In another preferred embodiment the polymer comprises a repeating unit of formula

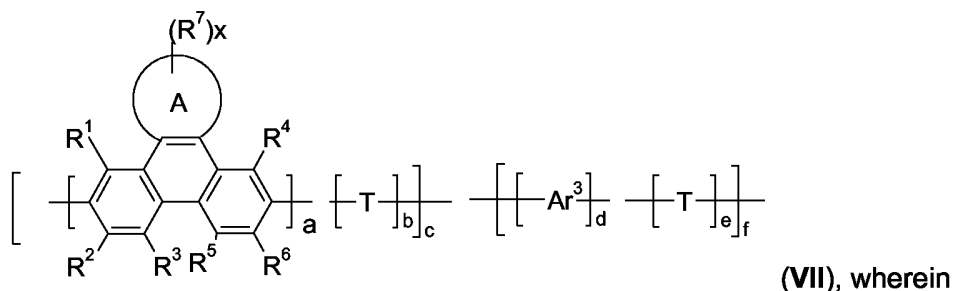


X<sup>10</sup> is a repeating unit of formula I, especially X, XI and XII (XVI, XVII and XVIII), very especially Xa, Xla, Xlla and XIIb ((XVIa, XVIIa, XVIIIa and XVIIIb);

- 10 and -Ar<sup>3</sup>- is a group of formula , or , wherein R<sup>116</sup> and R<sup>117</sup> are independently of each other H, C<sub>1</sub>-C<sub>18</sub>alkyl, which can optionally be interrupted by O, or C<sub>1</sub>-C<sub>18</sub>alkoxy, which can optionally be interrupted by O, R<sup>119</sup> and R<sup>120</sup> are independently of each other H, C<sub>1</sub>-C<sub>18</sub>alkyl, which can optionally be interrupted by O, or
- 15 R<sup>119</sup> and R<sup>120</sup> together form a group of formula =CR<sup>100</sup>R<sup>101</sup>, wherein R<sup>100</sup> and R<sup>101</sup> are independently of each other H, C<sub>1</sub>-C<sub>18</sub>alkyl, or R<sup>119</sup> and R<sup>120</sup> together form a five or six membered ring, which optionally can be substituted by C<sub>1</sub>-C<sub>18</sub>alkyl.

20 The present invention is illustrated in more detail on the basis of an especially preferred embodiment below, but should not be limited thereto.

In said embodiment the polymer is a polymer of formula



25 A, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and x are as defined above, T and Ar<sup>3</sup> are as defined above,

a is 1,

b is 0, or 1,

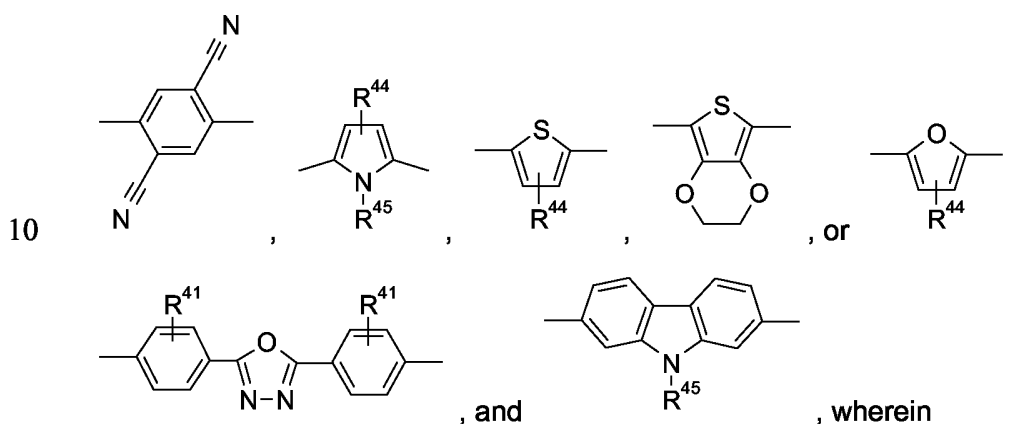
c is 0.005 to 1,

d is 0, or 1,

5 e is 0, or 1, wherein e is not 1, if d is 0,

f is 0.995 to 1, wherein the sum of c and f is 1.

T is preferably a repeating unit of formula **VIa**, **VIb** or **VIc** and  $Ar^3$  is preferably selected from repeating units of formula:

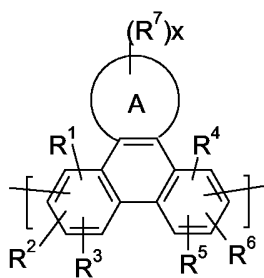


$R^{44}$  and  $R^{41}$  are hydrogen,  $C_1$ - $C_{18}$ alkyl, or  $C_1$ - $C_{18}$ alkoxy, and

$R^{45}$  is H,  $C_1$ - $C_{18}$ alkyl, or  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D, especially  $C_1$ - $C_{18}$ alkyl which is interrupted by  $-O-$ , wherein D and E are as defined above.

15

Homopolymers of formula **VII**, wherein  $a = 1$ ,  $b = 0$ ,  $c = 1$ ,  $d = 0$ ,  $e = 0$ ,  $f = 0$ , are, for example, obtained by nickel coupling reactions, especially the Yamamoto reaction:

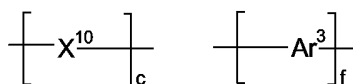


(I), wherein A,  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and x are as defined above.

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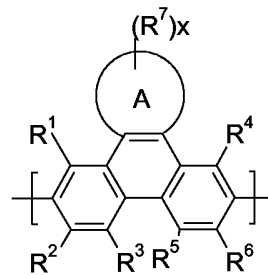
In said aspect homopolymers consisting of repeating units of formula **X**, **XI**, or **XII** are preferred and homopolymers consisting of repeating units of formula **Xa**, **XIa**, **XIIa** and **XIIb** are most preferred.

Copolymers of formula **VII**, involving repeating units of formula **I** and  $-Ar^3-$  ( $a = 1$ ,  $c = 0.995$  to  $0.005$ ,  $b = 0$ ,  $d = 1$ ,  $e = 0$ ,  $f = 0.005$  to  $0.995$ ), can be obtained by nickel coupling reactions:



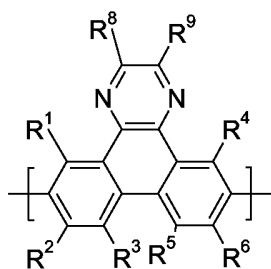
(VIIb), wherein  $\text{X}^{10}$ , c, f and  $\text{Ar}^3$  are as defined above.

In an especially preferred embodiment the present invention is directed to copolymers which

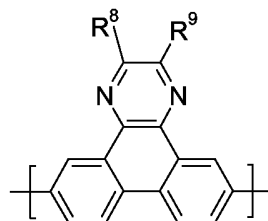


contain at least two different repeating units of formula

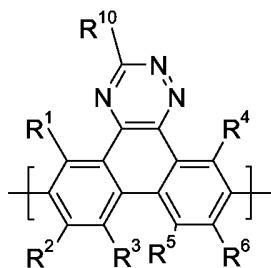
5  
embodiment copolymers are more preferred, which comprise at least one repeating unit of formula I' wherein A is a 5 membered heteroaromatic ring and at least one repeating unit of formula I' wherein A is a 6 membered heteroaromatic ring. Appropriate examples of repeating units comprising a 6 membered heteroaromatic ring are compounds of formula



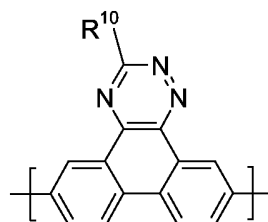
(X), especially



(Xa), and

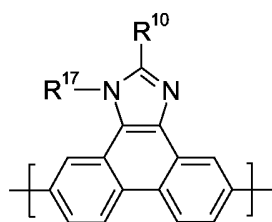


(XI), especially



(XIa); examples of repeating

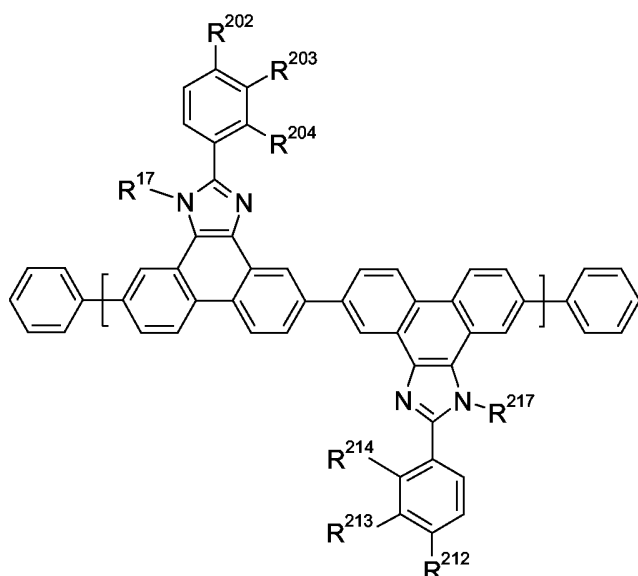
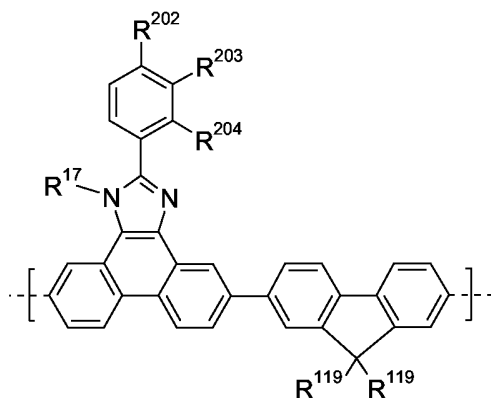
units comprising a 5 membered heteroaromatic ring are compounds of formula



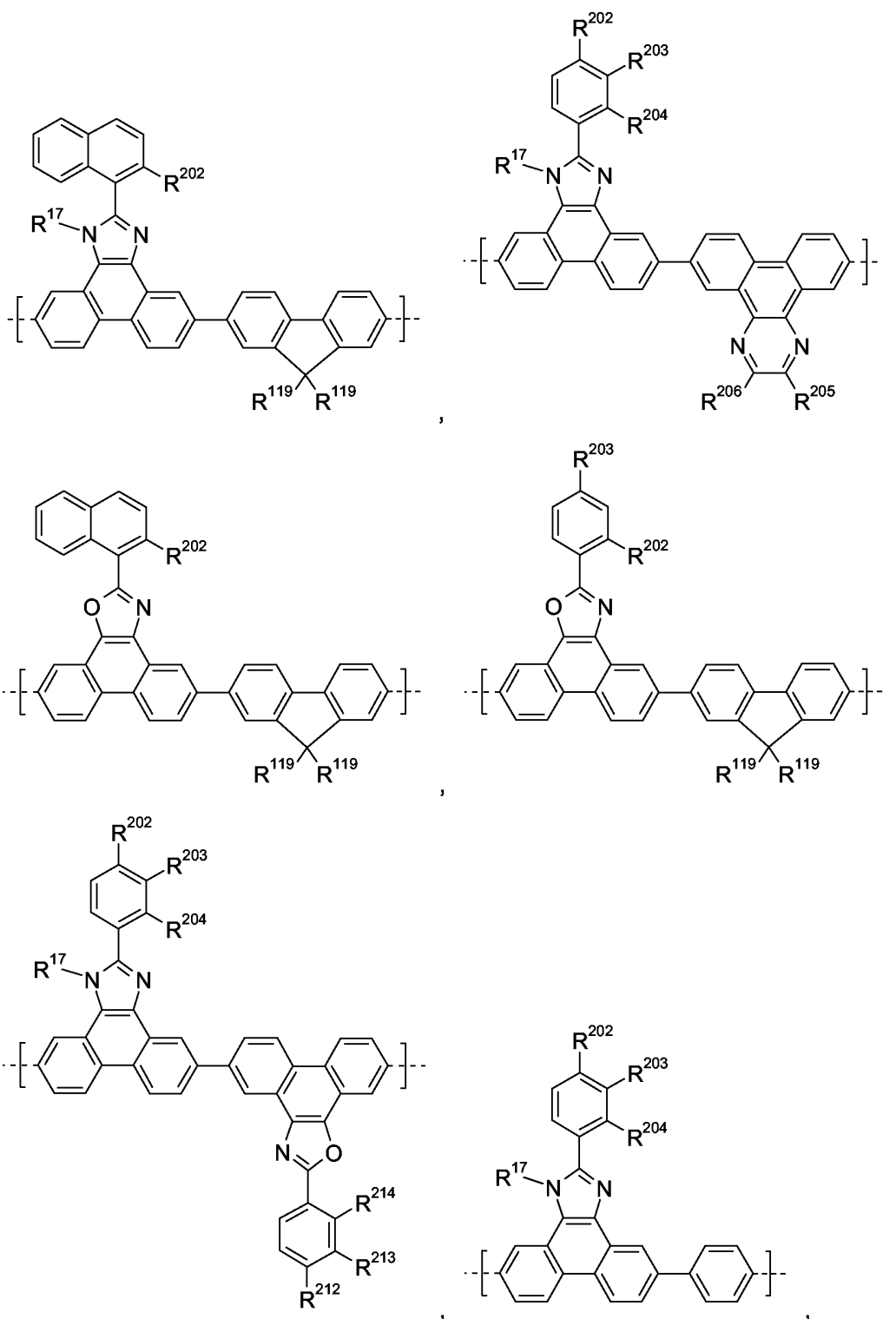
(XIIb); wherein  $R^1, R^2, R^3, R^4, R^5, R^6, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14},$

$R^{15}, R^{16}$  and  $R^{17}$  are as defined above. In said aspect of the present invention copolymers comprising repeating units of formula **Xa** and **XIIa** and/or **XIIa** (**Xa** and **XIIa**; **Xa** and **XIIa**; **Xa** and **Xa**, **XIIa** and **XIIb**), or **XIa** and **XIIa** and/or **XIIa** (**XIa** and **XIIa**; **XIa** and **XIIa**; **XIa** and **Xa**, **XIIa** and **XIIb**) are most preferred.

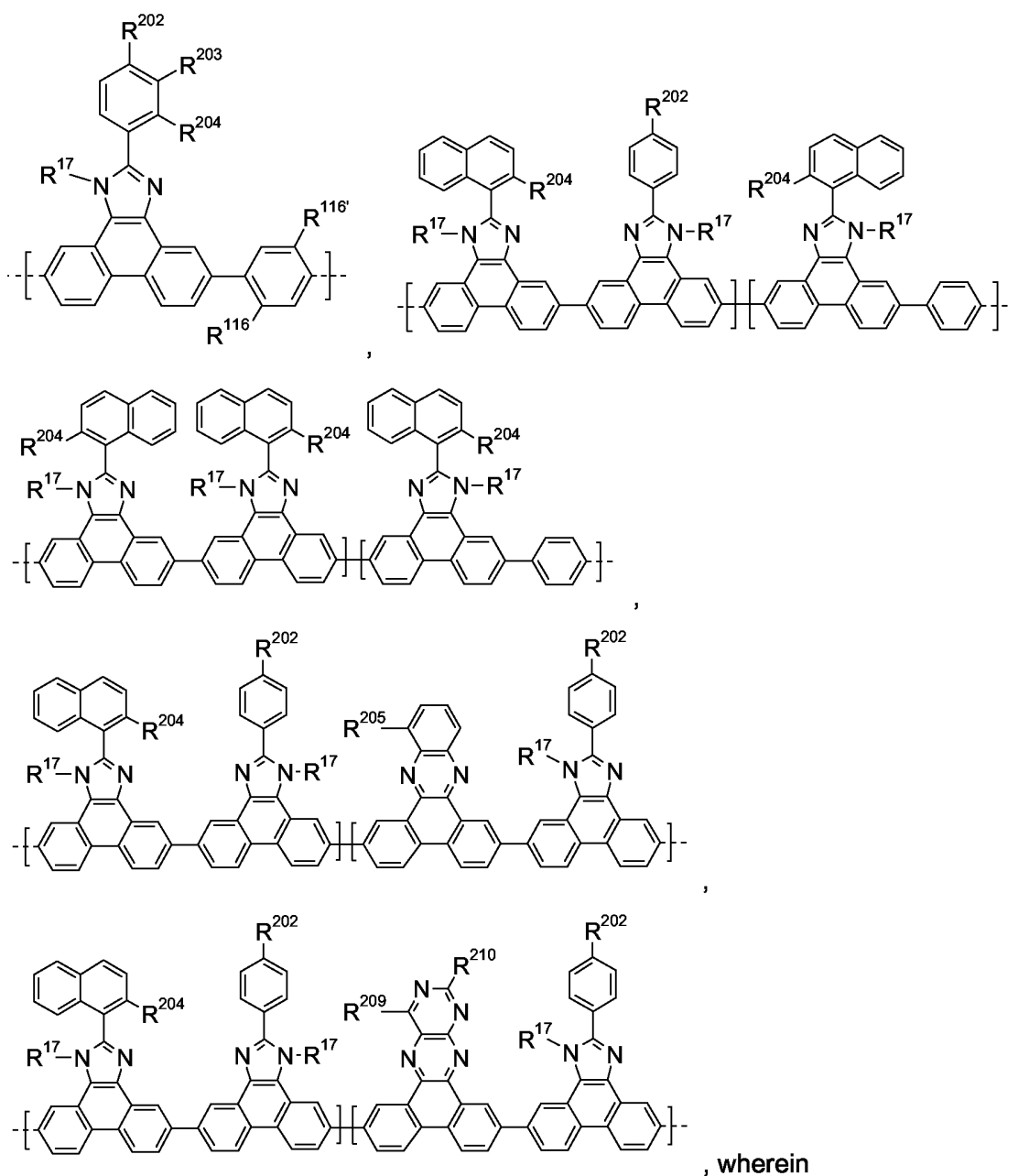
The following polymers are especially preferred:



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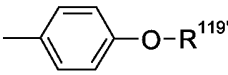
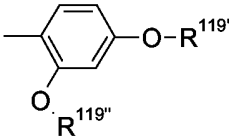


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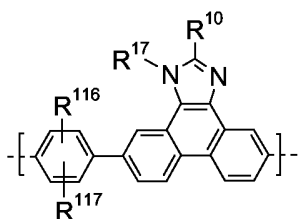
- 5 R<sup>17</sup> and R<sup>217</sup> are independently of each other C<sub>1</sub>-C<sub>18</sub>alkyl, especially C<sub>4</sub>-C<sub>12</sub>alkyl, such as, for example, n-butyl, n-hexyl, n-octyl, 2-ethylhexyl, and 2-hexadecyl,
- R<sup>202</sup>, R<sup>203</sup>, R<sup>204</sup>, R<sup>212</sup>, R<sup>213</sup> and R<sup>214</sup> are independently of each other H, or C<sub>1</sub>-C<sub>18</sub>alkoxy, such as for example, n-butoxy, n-hexyloxy, n-octyloxy, 2-ethylhexyloxy, and 2-hexadecyloxy,
- R<sup>209</sup> and R<sup>210</sup> are independently of each other H, or C<sub>1</sub>-C<sub>18</sub>alkoxy;
- 10 R<sup>205</sup> and R<sup>206</sup> are independently of each other H, or C<sub>1</sub>-C<sub>18</sub>alkoxy, especially C<sub>1</sub>-C<sub>8</sub>alkyl;
- R<sup>116</sup> is H, or C<sub>1</sub>-C<sub>18</sub>alkoxy,
- R<sup>116'</sup> is R<sup>116</sup>

$R^{119}$  is  $C_1$ - $C_{18}$ alkyl, especially  $C_4$ - $C_{12}$ alkyl, such as, for example, n-butyl, n-hexyl, n-octyl, and

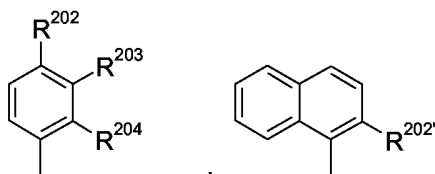
2-ethylhexyl, or , or ,  $C_1$ - $C_{18}$ alkyl, especially  $C_1$ - $C_8$ alkyl, wherein  $R^{119'}$  and  $R^{119''}$  are independently of each other  $C_1$ - $C_{18}$ alkyl (all shown polymer structures are idealized structures).

5

In a further preferred embodiment the present invention relates to polymers of formula



, wherein  $R^{10}$  is  $C_6$ - $C_{12}$ aryl, which can optionally be substituted by one to three groups selected from  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted

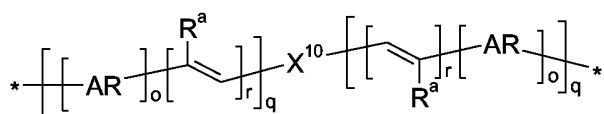


10 by D; especially , and , wherein  $R^{202'}$  is  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D, especially  $C_1$ - $C_{18}$ alkoxy; one of  $R^{202}$ ,  $R^{203}$  and  $R^{204}$  is  $R^{202'}$ , and the other groups are H, or  $R^{202'}$ .

$R^{116}$  and  $R^{117}$  are H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl, 15  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D, especially  $C_1$ - $C_{18}$ alkoxy;

$R^{17}$  is  $C_1$ - $C_{18}$ alkyl, or  $C_6$ - $C_{12}$ aryl, which can optionally be substituted by one to three  $C_1$ - $C_{18}$ alkoxy groups.

20 In a further preferred embodiment the present invention relates to polymers comprising repeating units of formula



**XX**, wherein

$X^{10}$  is a repeating unit of formula I, especially **X**, **XI** and **XII** (**XVI**, **XVII** and **XVIII**), very especially **Xa**, **XIa**, **XIIa** and **XIIb** (**XVIa**, **XVIIa**, **XVIIIa** and **XVIIIb**);



q is an integer 0, 1, or 2, o is 0, 1, or 2, r is 0, or 1;

AR is C<sub>6</sub>-C<sub>24</sub>aryl, C<sub>6</sub>-C<sub>24</sub>aryl which is substituted by G, C<sub>2</sub>-C<sub>20</sub>heteroaryl, or C<sub>2</sub>-C<sub>20</sub>heteroaryl which is substituted by G,

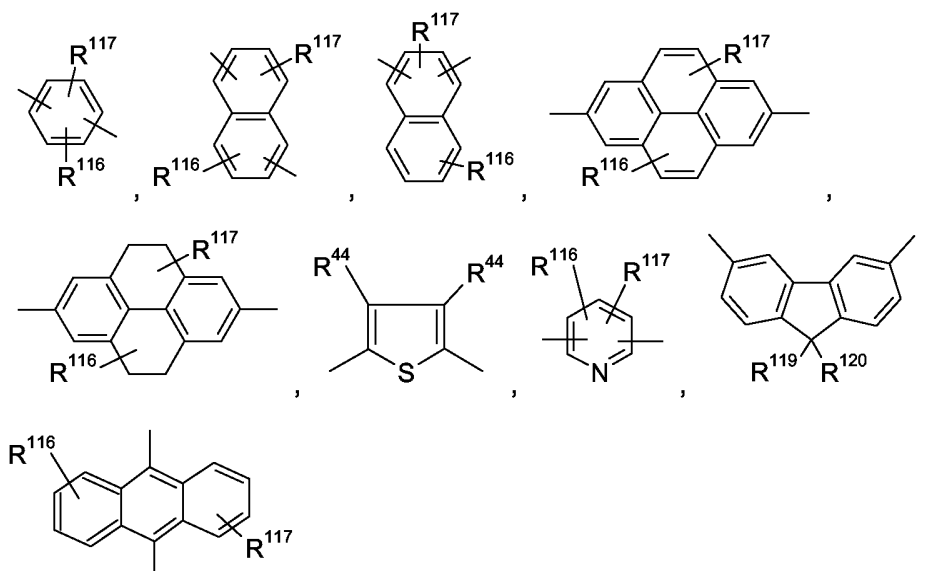
R<sup>a</sup> is H, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is substituted by E and/or interrupted by D, C<sub>1</sub>-

- 5 C<sub>18</sub>perfluoroalkyl, C<sub>2</sub>-C<sub>18</sub>alkenyl, C<sub>2</sub>-C<sub>18</sub>alkynyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D, wherein E, D and G are as defined above.

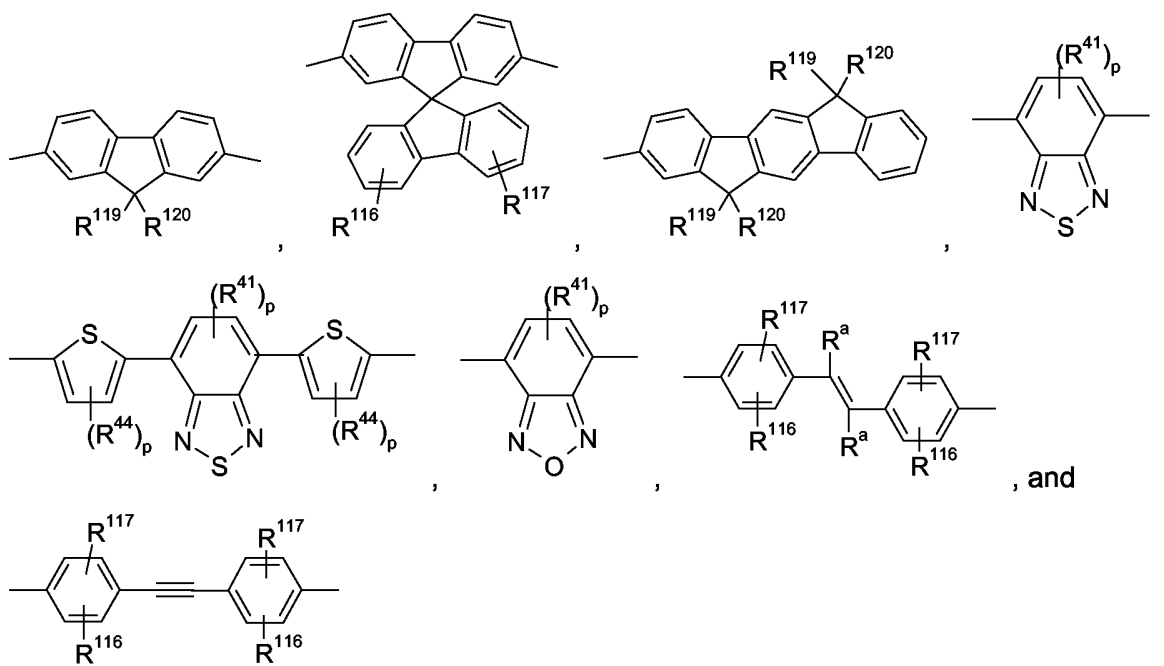
AR is the same or different in each occurrence. AR can be derived from thiophen, 2,7-N-alkylcarbazol, 2,7-N-arylcarbazol, 3,6- N-alkylcarbazol, 3,6-N-arylcarbazol, benzene,  
 10 pyridine, fluorene, spirobifluorene, anthracene, phenanthrene, pyrene, quinoline, or naphthalene, which be substituted by 0 to 2 substituents R<sup>a</sup>.

Examples of additional repeating units are units of group II, which increase the hole injection or hole transport properties of the polymers. Examples of additional repeating units are in

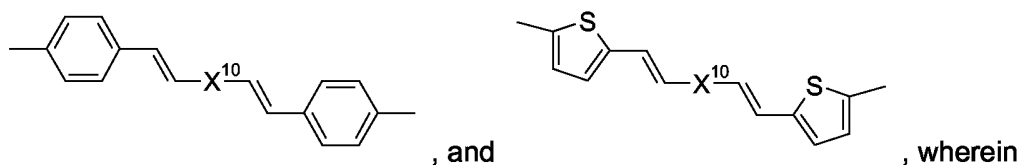
- 15 particular selected from the group consisting of ortho-, meta- or para-phenylene, 1,4-naphthylene, 9,10-anthracenylene, 2,7-phenanthrenylene, 1,6-, 2,7-, 4,9-pyrene, 2,7-tetrahydropyrene, oxadiazolylene, 2,5-thiophenylene, 2,5-pyrrolylene; 2,5-furanylene, 2,5-pyridylene, 2,5-pyrimidinylene, 5,8-chinolinylene, fluorene, spiro-9,9'-bifluorene, indenofluorene, heteroindenofluorene, 2,7-N-alkylcarbazol, 2,7-N-arylcarbazol, 3,6- N-alkylcarbazol, and 3,6-N-arylcarbazol. Preferred examples of additional repeating units are
- 20



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Examples of repeating units of formula XX are:



X<sup>10</sup> is a repeating unit of formula I, especially **X**, **XI** and **XII** (**XVI**, **XVII** and **XVIII**), very especially **Xa**, **XIa**, **XIIa** and **XIIb** (**XVIa**, **XVIIa**, **XVIIIa** and **XVIIIb**).

The polymers of the present invention can show high photoluminescence and/or electroluminescence.

Polymerization processes involving only dihalo-functional reactants may be carried out using nickel coupling reactions. One such coupling reaction was described by Colon et al. in J. Pol. Sci., Part A, Polymer Chemistry Edition 28 (1990) 367, and by Colon et al. in J. Org. Chem. 51 (1986) 2627. The reaction is typically conducted in a polar aprotic solvent (e.g., dimethylacetamide) with a catalytic amount of nickel salt, a substantial amount of triphenylphosphine and a large excess of zinc dust. A variant of this process is described by Ioyda et al. in Bull. Chem. Soc. Jpn, 63 (1990) 80 wherein an organo-soluble iodide was used as an accelerator.

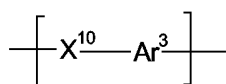
Another nickel-coupling reaction was disclosed by Yamamoto in Progress in Polymer Science 17 (1992) 1153 wherein a mixture of dihaloaromatic compounds was treated with an excess amount of nickel (1,5-cyclooctadiene) complex in an inert solvent. All nickel-coupling

reactions when applied to reactant mixtures of two or more aromatic dihalides yield essentially random copolymers. Such polymerization reactions may be terminated by the addition of small amounts of water to the polymerization reaction mixture, which will replace the terminal halogen groups with hydrogen groups. Alternatively, a monofunctional aryl  
 5 halide may be used as a chain-terminator in such reactions, which will result in the formation of a terminal aryl group.

Nickel-coupling polymerizations yield essentially homopolymers or random copolymers comprising units of formula I and units derived from other co-monomers.

10

Homopolymers of formula VII, wherein  $a = 1$ ,  $c = 1$ ,  $b = 0$ ,  $d = 1$ ,  $e = 0$ ,  $f = 1$ , can be obtained, for example, by the Suzuki reaction:

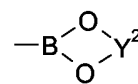


(VIIc), wherein  $X^{10}$  and  $Ar^3$  are as defined above.

- 15 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). This reaction can be applied to preparing high molecular weight polymers and copolymers. Preferred catalysts are 2-dicyclohexylphosphino-2',6'-di-  
 20 alkoxybiphenyl/palladium(II)acetates. An especially preferred catalyst is 2-dicyclohexylphosphino-2',6'-di-methoxybiphenyl (sPhos)/palladium(II)acetate.

To prepare polymers corresponding to formula VIIc, a dihalogenide, such as a dibromide or dichloride, especially a dibromide corresponding to formula  $Br-X^{10}-Br$  is reacted with an

- 25 equimolar amount of a diboronic acid or diboronate corresponding to formula  $X^{11}-[Ar^3]-X^{11}$ ,



wherein  $X^{11}$  is independently in each occurrence  $-B(OH)_2$ ,  $-B(OY^1)_2$  or  $-B(OY^1)_2$ , 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,  
 30 or a  $C_1$ - $C_{10}$ alkyl group, especially  $-C(CH_3)_2C(CH_3)_2-$ , or  $-C(CH_3)_2CH_2C(CH_3)_2-$ , under the catalytic action of Pd and a phosphine ligand, especially triphenylphosphine. The reaction is

typically conducted at about 70 °C to 180 °C in an aromatic hydrocarbon solvent such as toluene. Other solvents such as dimethylformamide and tetrahydrofuran can also be used alone, or in mixtures with an aromatic hydrocarbon. An aqueous base, preferably sodium carbonate, potassium carbonate, K<sub>3</sub>PO<sub>4</sub>, or bicarbonate, is used as the HBr scavenger.

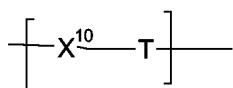
- 5 Depending on the reactivities of the reactants, a polymerization reaction may take 2 to 100 hours. Organic bases, such as, for example, tetraalkylammonium hydroxide, and phase transfer catalysts, such as, for example TBAB, can promote the activity of the boron (see, for example, Leadbeater & Marco; *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.

If desired, a monofunctional aryl halide or aryl boronate may be used as a chain-terminator in such reactions, which will result in the formation of a terminal aryl group.

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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.

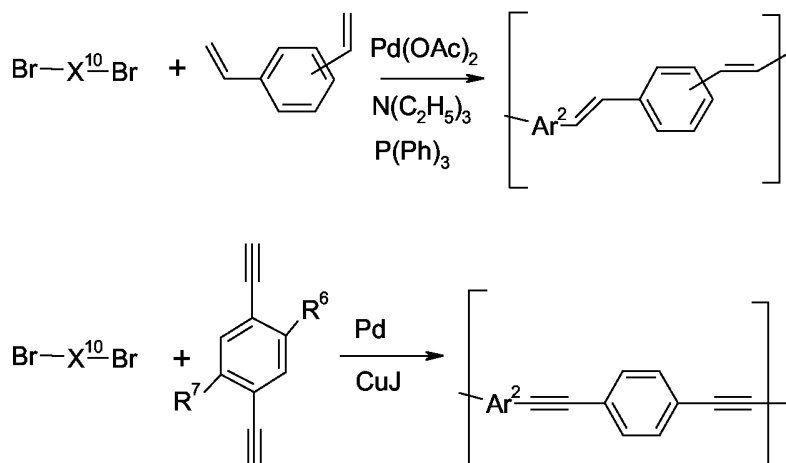
- Homopolymers of formula VII, wherein a = 1, c = 1, b = 1, d = 0, e = 0, f = 0, can be obtained, for example by the Heck reaction:



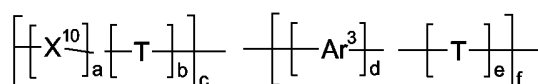
(VIIId), wherein X<sup>10</sup> and T are as defined above.

- Polyphenylenethenylene derivatives and polyphenylenethynylene derivatives can be obtained by polymerization of divinyl or diethynyl compounds with dihalogen compounds by the Heck reaction (R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, New York 1985, pp. 179; L. S. Hegedus, *Organometalics in Synthesis*, Ed. M. Schlosser, Wiley, Chichester, UK 1994, pp. 383; Z. Bao, Y. Chen, R. Cai, L. Yu, *Macromolecules* 26 (1993) pp. 5281; W.-K. Chan, L. Yu, *Macromolecules* 28 (1995) pp. 6410; A. Hilberer, H. -J. Brouwer, B.-J. van der Scheer, J. Wildeman, G. Hadziioannou, *Macromolecules* 1995, 28, 4525) and the Sonogashira reaction (Dmitri Gelman and Stephen L. Buchwald, *Angew. Chem. Int. Ed.* 42 (2003) 5993 –5996; Rik R. Tykwinski, *Angew. Chem.* 115 (2003) 1604 – 1606; Jason M. Nolan and Daniel L. Comins, *J. Org. Chem.* 68 (2003) 3736-3738; Jiang Cheng et al., *J. Org. Chem.* 69 (2004) 5428-5432; Zolta'n Nova'k et al., *Tetrahedron* 59 (2003) 7509–7513):

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(Random) copolymers of formula VII, wherein a is 1, b is 1, c is 0.005 to 0.995, d is 1, e is 1, f is 0.995 to 0.005, wherein the sum of c and f is 1, can also be obtained by the Heck reaction:



(VIIe), wherein a, b, c, d, e, f,  $\text{X}^{10}$ ,  $\text{Ar}^3$  and T are

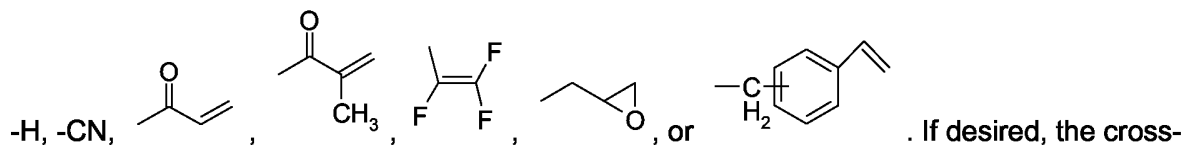
as defined above.

The polymers containing groups of formulas (I) may be prepared by any suitable process, but are preferably prepared by the processes described above.

The polymers of the present invention can optionally comprise end moieties  $\text{E}^1$ , wherein  $\text{E}^1$  is an aryl moiety which may optionally be substituted with a reactive group capable of undergoing chain extension or crosslinking, or a tri( $\text{C}_1$ - $\text{C}_{18}$ )alkylsiloxyl group. As used herein, a reactive group capable of undergoing chain extension or crosslinking refers to any group which is capable of reacting with another of the same group or another group so as to form a link to prepare polymers. Preferably, such reactive group is a hydroxy, glycidyl ether, acrylate ester, methacrylate ester, ethenyl, ethynyl, maleimide, naphthimide, trifluorovinyl ether moiety or a cyclobutene moiety fused to the aromatic ring of  $\text{E}^1$ .

The polymers of the present invention, where  $\text{E}^1$  are reactive groups as defined above, are capable of crosslinking to form solvent resistant, heat-resistant films at  $100^\circ\text{C}$  or more, more preferably at  $150^\circ\text{C}$  or more. Preferably, such crosslinking occurs at  $350^\circ\text{C}$  or less, more preferably  $300^\circ\text{C}$  or less and most preferably  $250^\circ\text{C}$  or less. The crosslinkable polymers of the invention are stable at  $100^\circ\text{C}$  or more and more preferably  $150^\circ\text{C}$  or more. "Stable" as used herein means that such polymers do not undergo crosslinking or polymerization reactions at or below the stated temperatures. If a crosslinkable material is desired,  $\text{E}^1$  is

preferably a vinylphenyl, an ethynylphenyl, or 4-(or 3-)benzocyclobutenyl radical. In another embodiment,  $E^1$  is selected from a group of phenolic derivatives of the formula  $-C_6H_4-O-Y$ , wherein Y is



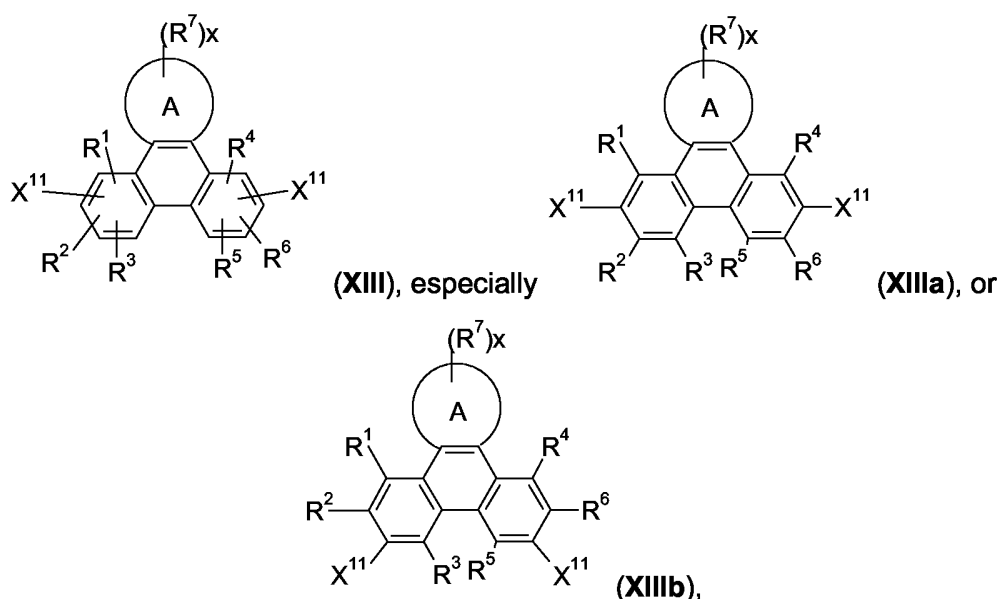
- 5 linkable groups can be present in other parts of the polymer chain. For example, one of the substituents of the co-monomer T may be a crosslinkable group  $E^1$ .

The end-capping agent  $E^1-X^{12}$  ( $E^1$  is as defined above and  $X^{12}$  is either Cl or Br) is incorporated into the polymers of the present invention under the condition in which the  
 10 resulting polymers are substantially capped by the reactive group  $E^1$ . The reactions useful for this purpose are the nickel-coupling, Heck reactions and Suzuki reactions described above. The average degree of polymerization is controlled by the mole ratio of monomers to end-capping agent.

- 15 The polymers according to the invention can be worked up by known methods which are familiar to the person skilled in the art, as described, for example, in D. Braun, H. Cherdron, H. Ritter, *Praktikum der makromolekularen Stoffe*, 1<sup>st</sup> Edn., Wiley VCH, Weinheim 1999, p. 68-79 or R. J. Young, P. A. Lovell, *Introduction to Polymers*, Chapman & Hall, London 1991. For example, the reaction mixture can be filtered, diluted with aqueous acid, extracted and  
 20 the crude product obtained after drying and stripping-off of the solvent can be further purified by reprecipitation from suitable solvents with addition of precipitants. Residual palladium can be removed by using activated carbon, chromatography etc. Advantageously, the residual palladium could be reduced to <3 ppm by washing the crude organic solvent layer containing the polymer with an aqueous solution of L-cysteine at room temperature to the boiling point  
 25 of the organic solvent, especially by washing a toluene layer containing the polymer with an aqueous solution of L-cysteine at 85 to 90 °C, optionally followed by washing with a solution of L-cysteine and sodium thiosulfate at 78 to 82 °C (Mahavir Prashad, Yugang Liu, Oljan Repicoe, *Adv. Synth. Catal.* 2003, 345, 533 – 536; Christine E. Garrett, Kapa Prasad, *Adv. Synth. Catal.* 2004, 346, 889 – 900). Additionally the Pd can be removed by washing the  
 30 polymer with an aqueous NaCN solution as described in US-B-6,956,095. Polymer-analogous reactions can subsequently be carried out for further functionalization of the polymer. Thus, for example, terminal halogen atoms can be removed reductively by reduction with, for example,  $LiAlH_4$  (see, for example, J. March, *Advanced Organic Chemistry*, 3<sup>rd</sup> Edn. McGraw-Hill, p. 510).

Another aspect of this invention is related to polymer blends containing 1 to 99 percent of at least one containing polymers comprising a unit of formula I. The remainder 1 to 99 percent of the blend is composed of one or more polymeric materials selected from among chain growth polymers such as polystyrene, polybutadiene, poly(methyl methacrylate), and poly(ethylene oxide); step-growth polymers such as phenoxy resins, polycarbonates, polyamides, polyesters, polyurethanes, and polyimides; and crosslinked polymers such as crosslinked epoxy resins, crosslinked phenolic resins, crosslinked acrylate resins, and crosslinked urethane resins. Examples of these polymers may be found in Preparative Methods of Polymer Chemistry, W. R. Sorenson and T. W. Campbell, Second Edition, Interscience Publishers (1968). Also may be used in the blends are conjugated polymers such as poly(phenylene vinylene), substituted poly(phenylene vinylene)s, substituted polyphenylenes and polythiophenes. Examples of these conjugated polymers are given by Greenham and Friend in Solid State Physics, Vol. 49, pp. 1-149 (1995).

A further embodiment of the present invention is represented by the monomers of the formula



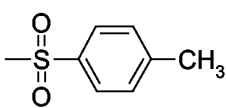
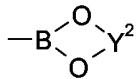
wherein A is a 5-, 6-, or 7-membered heteroaromatic ring, containing one heteroatom selected from nitrogen, oxygen and sulfur, especially one nitrogen atom and at least one further heteroatom selected from nitrogen, substituted nitrogen, oxygen and sulfur,  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are independently of each other hydrogen, halogen, or an organic substituent, or

two substituents  $R^1$  and  $R^2$ ,  $R^4$  and  $R^6$ ,  $R^2$  and  $R^3$ ,  $R^5$  and  $R^3$  and/or  $R^5$  and  $R^6$ , which are adjacent to each other, together form an aromatic, or heteroaromatic ring, or ring system, which can optionally be substituted,

$R^7$  is an organic substituent, wherein two or more substituents  $R^7$  in the same molecule may have different meanings, or can form together an aromatic, or heteroaromatic ring, or ring system, and

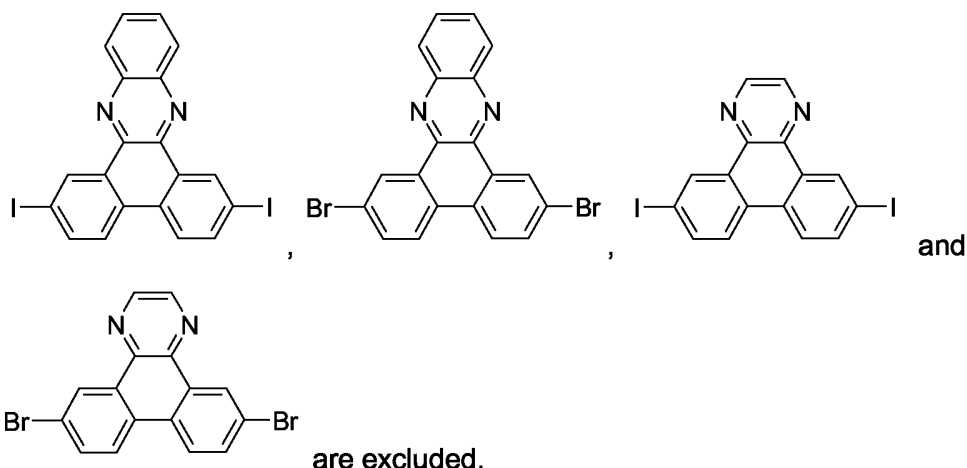
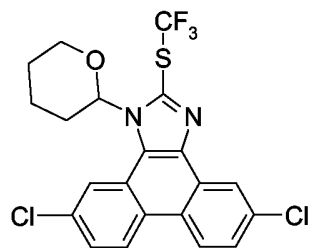
$x$  is 0, or an integer of 1 to 5;

$X^{11}$  is independently in each occurrence a halogen atom, or  $-\text{OS}(\text{O})_2\text{CF}_3$ ,  $-\text{OS}(\text{O})_2\text{-aryl}$ ,

especially ,  $-\text{OS}(\text{O})_2\text{CH}_3$ ,  $-\text{B}(\text{OH})_2$ ,  $-\text{B}(\text{OY}^1)_2$ , ,  $-\text{BF}_4\text{Na}$ , or -

- 10  $\text{BF}_4\text{K}$ , wherein  $\text{Y}^1$  is independently in each occurrence a  $\text{C}_1\text{-C}_{10}$ alkyl group and  $\text{Y}^2$  is independently in each occurrence a  $\text{C}_2\text{-C}_{10}$ alkylene group, such as  $-\text{CY}^3\text{Y}^4-\text{CY}^5\text{Y}^6-$ , or  $-\text{CY}^7\text{Y}^8-\text{CY}^9\text{Y}^{10}-\text{CY}^{11}\text{Y}^{12}-$ , wherein  $\text{Y}^3$ ,  $\text{Y}^4$ ,  $\text{Y}^5$ ,  $\text{Y}^6$ ,  $\text{Y}^7$ ,  $\text{Y}^8$ ,  $\text{Y}^9$ ,  $\text{Y}^{10}$ ,  $\text{Y}^{11}$  and  $\text{Y}^{12}$  are independently of each other hydrogen, or a  $\text{C}_1\text{-C}_{10}$ alkyl group, especially  $-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2-$ , or  $-\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_2-$ , wherein nitrogen atom as heteroatom comprises a group  $=\text{N}-$ , or -

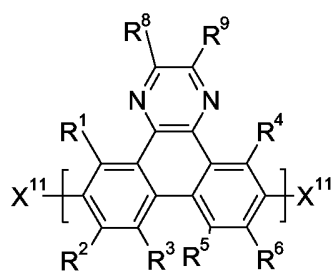
- 15  $\text{NR}^{10}$ , wherein  $\text{R}^{10}$  is as defined in claim 2, with the proviso that



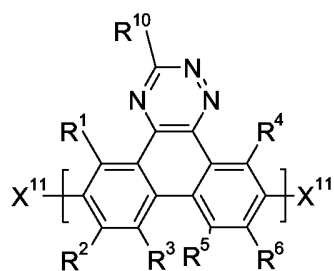
Preference is given to monomers of formula



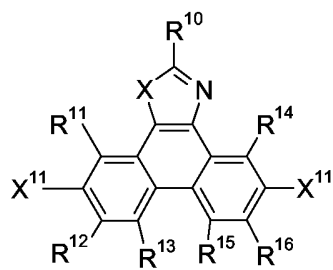
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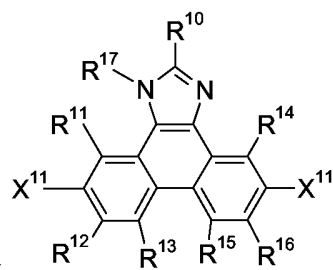
(XIV),



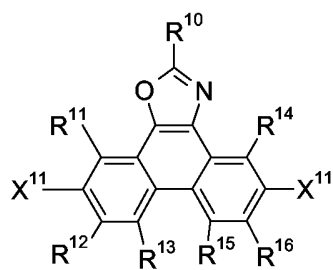
(XV) and/or



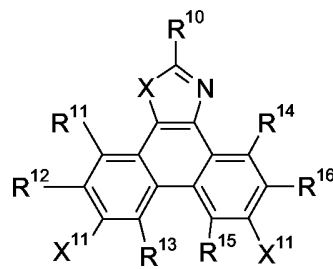
(XVI), especially



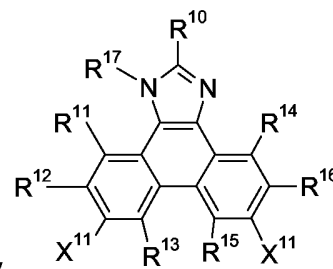
(XVIa), and/or



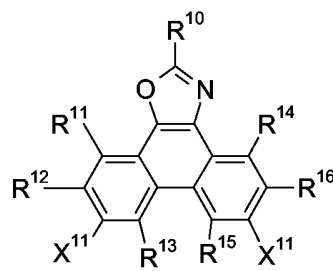
(XVIb),



(XIX), especially



(XXa), and/or



(XXb),

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wherein  $X^{11}$  is independently in each occurrence a halogen, especially Br, or I, especially Br,

or  $-\text{OS}(\text{O})_2\text{CF}_3$ ,  $-\text{B}(\text{OH})_2$ ,  $-\text{B}(\text{OY}^1)_2$  or  $-\text{B}(\text{O})_2\text{Y}^2$ , wherein  $\text{Y}^1$  is independently in each occurrence a  $\text{C}_1$ - $\text{C}_{10}$ alkyl group and  $\text{Y}^2$  is independently in each occurrence a  $\text{C}_2$ - $\text{C}_{10}$ alkylene group, such as  $-\text{CY}^3\text{Y}^4-\text{CY}^5\text{Y}^6-$ , or  $-\text{CY}^7\text{Y}^8-\text{CY}^9\text{Y}^{10}-\text{CY}^{11}\text{Y}^{12}-$ , wherein  $\text{Y}^3$ ,  $\text{Y}^4$ ,  $\text{Y}^5$ ,  $\text{Y}^6$ ,  $\text{Y}^7$ ,  $\text{Y}^8$ ,  $\text{Y}^9$ ,

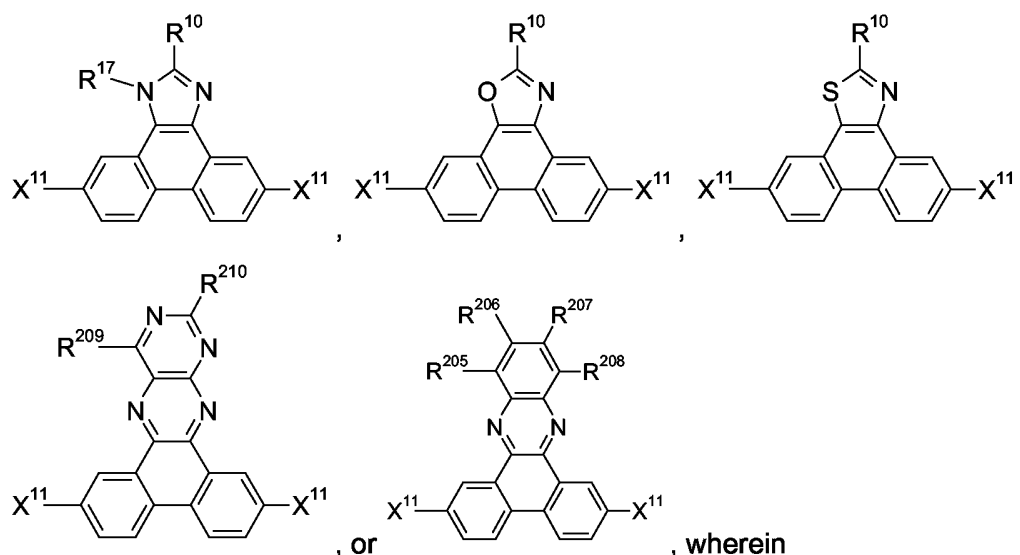
$Y^{10}$ ,  $Y^{11}$  and  $Y^{12}$  are independently of each other hydrogen, or a  $C_1$ - $C_{10}$ alkyl group, especially  $-C(CH_3)_2C(CH_3)_2-$ , or  $-C(CH_3)_2CH_2C(CH_3)_2-$ .

Monomers are preferred, wherein at least one of the substituents  $R^8$  and/or  $R^9$  and  $R^{10}$  are different from a hydrogen atom and are in particular a solubilizing substituent which is especially selected from  $C_6$ - $C_{18}$ aryl, which can be substituted by G,  $C_2$ - $C_{18}$ heteroaryl, which can be substituted by G,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D.

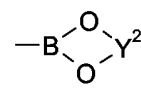
$R^{17}$  is preferably different from a hydrogen atom and is very especially  $C_1$ - $C_{18}$ alkyl, or  $C_1$ - $C_{18}$ alkyl which is interrupted by D.

In particular  $R^8$  and/or  $R^9$  and  $R^{10}$  are a solubilizing substituent and are in particular selected from  $C_6$ - $C_{18}$ aryl, which can be substituted by G,  $C_2$ - $C_{18}$ heteroaryl, which can be substituted by G,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D.

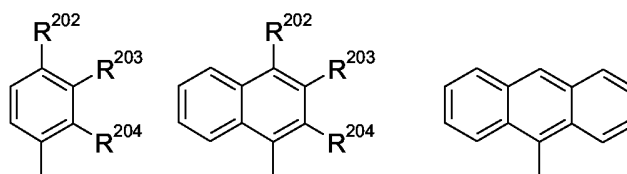
The following monomers are especially preferred:



$X^{11}$  is independently in each occurrence Br, I,  $-B(OH)_2$ ,  $-B(OY^1)_2$  or  $-B(OY^1)(OY^2)$ , wherein  $Y^1$  and  $Y^2$  are as defined above;



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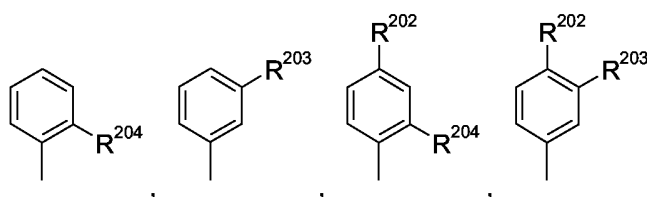


R<sup>10</sup> is a group of formula , , or ; wherein

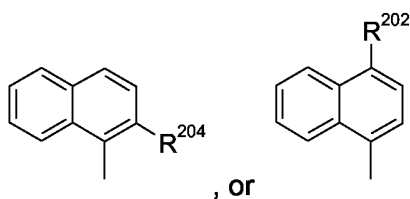
R<sup>202</sup>, R<sup>203</sup>, R<sup>204</sup>, R<sup>205</sup>, R<sup>206</sup>, R<sup>207</sup>, R<sup>208</sup>, R<sup>209</sup> and R<sup>210</sup> are independently of each other H, or C<sub>1</sub>-C<sub>18</sub>alkoxy;

R<sup>17</sup> is phenyl, which is substituted by C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, or C<sub>1</sub>-C<sub>18</sub>alkoxy; or C<sub>1</sub>-

5 C<sub>18</sub>alkyl;



R<sup>10</sup> is preferably a group of formula



, or , wherein R<sup>202</sup>, R<sup>203</sup> and R<sup>204</sup> are independently of each other C<sub>4</sub>-C<sub>18</sub>alkoxy.

10 R<sup>209</sup> and R<sup>210</sup> are preferably C<sub>4</sub>-C<sub>18</sub>alkoxy. Preferably at least one of R<sup>205</sup>, R<sup>206</sup>, R<sup>207</sup> and R<sup>208</sup> is C<sub>4</sub>-C<sub>18</sub>alkoxy. Polymers derived from such monomers are especially preferred.

Halogen is fluorine, chlorine, bromine and iodine.

15 C<sub>1</sub>-C<sub>25</sub>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-methylheptyl, n-octyl, 1,1,3,3-tetramethylbutyl and 2-ethylhexyl, n-nonyl, decyl, undecyl, dodecyl, 20 tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl, heneicosyl, docosyl, tetracosyl or pentacosyl. C<sub>1</sub>-C<sub>8</sub>alkyl 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<sub>1</sub>-C<sub>4</sub>alkyl is typically methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl.

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C<sub>1</sub>-C<sub>25</sub>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<sub>1</sub>-C<sub>8</sub>alkoxy are methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec.-butoxy, isobutoxy, tert.-butoxy, n-pentyloxy, 2-pentyloxy, 3-pentyloxy, 2,2-dimethylpropoxy, n-hexyloxy, n-heptyloxy, n-octyloxy, 1,1,3,3-tetramethylbutoxy and 2-ethylhexyloxy, preferably C<sub>1</sub>-C<sub>4</sub>alkoxy 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.

- 10 C<sub>2</sub>-C<sub>25</sub>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.

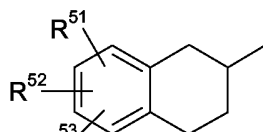
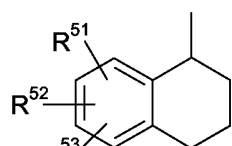
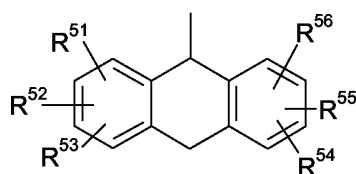
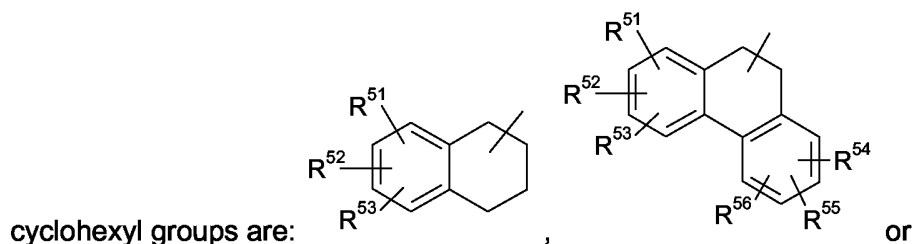
- 15 C<sub>2-24</sub>alkynyl is straight-chain or branched and preferably C<sub>2-8</sub>alkynyl, which may be unsubstituted or substituted, such as, for example, ethynyl, 1-propyn-3-yl, 1-butyne-4-yl, 1-pentyne-5-yl, 2-methyl-3-butyne-2-yl, 1,4-pentadiyne-3-yl, 1,3-pentadiyne-5-yl, 1-hexyne-6-yl, cis-3-methyl-2-pentyne-4-yn-1-yl, trans-3-methyl-2-pentyne-4-yn-1-yl, 1,3-hexadiyne-5-yl, 1-octyne-8-yl, 1-nonyne-9-yl, 1-decyn-10-yl, or 1-tetracosyn-24-yl.

- 20 C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, especially C<sub>1</sub>-C<sub>4</sub>perfluoroalkyl, is a branched or unbranched radical such as for example -CF<sub>3</sub>, -CF<sub>2</sub>CF<sub>3</sub>, -CF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>, -CF(CF<sub>3</sub>)<sub>2</sub>, -(CF<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>, and -C(CF<sub>3</sub>)<sub>3</sub>.

- The terms "haloalkyl, haloalkenyl and haloalkynyl" mean groups given by partially or wholly substituting the above-mentioned alkyl group, alkenyl group and alkynyl group with halogen, such as trifluoromethyl etc. The "aldehyde group, ketone group, ester group, carbamoyl group and amino group" include those substituted by an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group or a heterocyclic group, wherein the alkyl group, the cycloalkyl group, the aryl group, the aralkyl group and the heterocyclic group may be unsubstituted or substituted. The term "silyl group" means a group of formula -SiR<sup>62</sup>R<sup>63</sup>R<sup>64</sup>, wherein R<sup>62</sup>, R<sup>63</sup> and R<sup>64</sup> are independently of each other a C<sub>1</sub>-C<sub>8</sub>alkyl group, in particular a C<sub>1</sub>-C<sub>4</sub> alkyl group, a C<sub>6</sub>-C<sub>24</sub>aryl group or a C<sub>7</sub>-C<sub>12</sub>aralkyl group, such as a trimethylsilyl group. The term "siloxanyl group" means a group of formula -O-SiR<sup>62</sup>R<sup>63</sup>R<sup>64</sup>, wherein R<sup>62</sup>, R<sup>63</sup> and R<sup>64</sup> are as defined above, such as a trimethylsiloxanyl group.

- 35 The term "cycloalkyl group" is typically C<sub>5</sub>-C<sub>12</sub>cycloalkyl, such as cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, cyclododecyl, preferably

cyclopentyl, cyclohexyl, cycloheptyl, or cyclooctyl, which may be unsubstituted or substituted. The term "cycloalkenyl group" means an unsaturated alicyclic hydrocarbon group containing one or more double bonds, such as cyclopentenyl, cyclopentadienyl, cyclohexenyl and the like, 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<sub>1</sub>-C<sub>4</sub>-alkyl, halogen and cyano. Examples of such condensed



in particular , wherein R<sup>51</sup>, R<sup>52</sup>, R<sup>53</sup>, R<sup>54</sup>, R<sup>55</sup> and R<sup>56</sup> are independently of each other C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, halogen and cyano, in particular hydrogen.

Aryl is usually C<sub>6</sub>-C<sub>30</sub>aryl, preferably C<sub>6</sub>-C<sub>24</sub>aryl, which optionally can be substituted, such as, for example, phenyl, 4-methylphenyl, 4-methoxyphenyl, naphthyl, especially 1-naphthyl, or 2-naphthyl, biphenyl, terphenyl, pyrenyl, 2- or 9-fluorenyl, phenanthryl, anthryl, tetracyl, pentacyl, hexacyl, or quaderphenyl, which may be unsubstituted or substituted.

The term "aralkyl group" is typically C<sub>7</sub>-C<sub>24</sub>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, ω-phenyl-octadecyl, ω-phenyl-eicosyl or ω-phenyl-docosyl, preferably C<sub>7</sub>-C<sub>18</sub>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<sub>7</sub>-C<sub>12</sub>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.

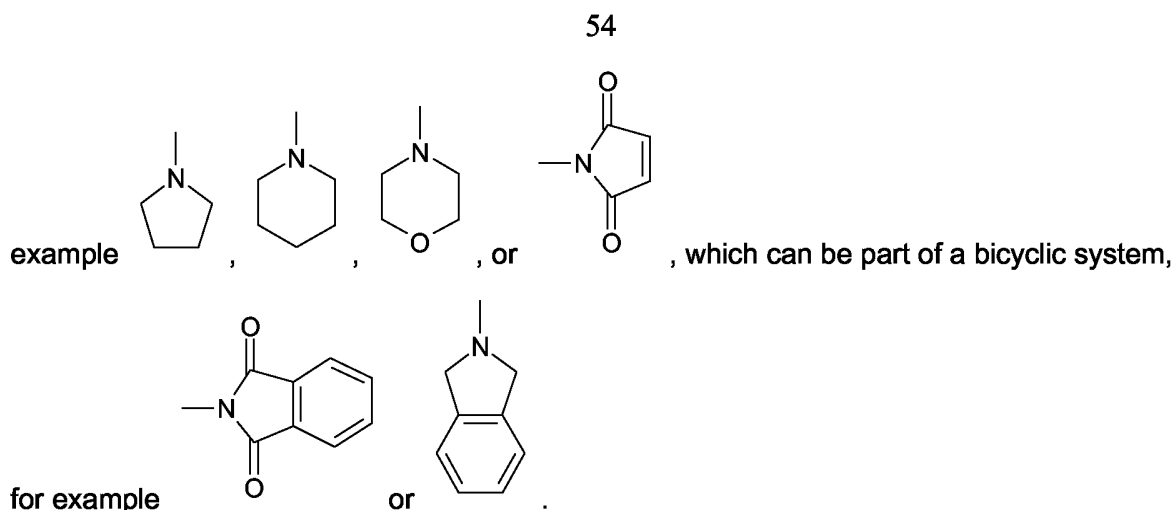
The term "aryl ether group" is typically a C<sub>6-24</sub>aryloxy group, that is to say O-C<sub>6-24</sub>aryl, such as, for example, phenoxy or 4-methoxyphenyl. The term "aryl thioether group" is typically a C<sub>6-24</sub>arylthio group, that is to say S-C<sub>6-24</sub>aryl, such as, for example, phenylthio or 4-methoxyphenylthio. The term "carbamoyl group" is typically a C<sub>1-18</sub>carbamoyl radical, preferably C<sub>1-8</sub>carbamoyl radical, which may be unsubstituted or substituted, such as, for example, carbamoyl, methylcarbamoyl, ethylcarbamoyl, n-butylcarbamoyl, tert-butylcarbamoyl, dimethylcarbamoyloxy, morpholinocarbamoyl or pyrrolidinocarbamoyl.

- 10 The terms "aryl" and "alkyl" in alkylamino groups, dialkylamino groups, alkylarylamino groups, arylamino groups and diaryl groups are typically C<sub>1</sub>-C<sub>25</sub>alkyl and C<sub>6</sub>-C<sub>24</sub>aryl, respectively.

- 15 Alkylaryl refers to alkyl-substituted aryl radicals, especially C<sub>7</sub>-C<sub>12</sub>alkylaryl. Examples are tolyl, such as 3-methyl-, or 4-methylphenyl, or xylyl, such as 3,4-dimethylphenyl, or 3,5-dimethylphenyl.

- Heteroaryl is typically C<sub>2</sub>-C<sub>26</sub>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  $\pi$ -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, indoliziny, isoindolyl, indolyl, indazolyl, purinyl, quinoliziny, chinolyl, isochinolyl, phthalazinyl, naphthyridinyl, chinoxaliny, chinazoliny, cinnoliny, pteridinyl, carbazolyl, carboliny, benzotriazolyl, benzoxazolyl, phenanthridiny, acridiny, pyrimidinyl, phenanthroliny, phenazinyl, isothiazolyl, phenothiaziny, isoxazolyl, furazanyl or phenoxazinyl, which can be unsubstituted or substituted.

- 30 Examples of a five or six membered ring formed by, for example, R<sup>16</sup> and R<sup>17</sup>, or R<sup>65</sup> and R<sup>66</sup>, respectively are heterocycloalkanes or heterocycloalkenes having from 3 to 5 carbon atoms which can have one additional hetero atom selected from nitrogen, oxygen and sulfur, for



Possible substituents of the above-mentioned groups are C<sub>1</sub>-C<sub>8</sub>alkyl, a hydroxyl group, a mercapto group, C<sub>1</sub>-C<sub>8</sub>alkoxy, C<sub>1</sub>-C<sub>8</sub>alkylthio, halogen, halo-C<sub>1</sub>-C<sub>8</sub>alkyl, a cyano group, an aldehyde group, a ketone group, a carboxyl group, an ester group, a carbamoyl group, an amino group, a nitro group or a silyl group.

If a substituent, such as, for example R<sup>7</sup> occurs more than one time in a group, it can be different in each occurrence.

The wording "substituted by G" means that one, or more, especially one to three substituents G might be present.

As described above, the aforementioned groups may be substituted by E and/or, if desired, interrupted by D. Interruptions are of course possible only in the case of groups containing at least 2 carbon atoms connected to one another by single bonds; C<sub>6</sub>-C<sub>18</sub>aryl is not interrupted; interrupted arylalkyl or alkylaryl contains the unit D in the alkyl moiety. C<sub>1</sub>-C<sub>18</sub>alkyl substituted by one or more E and/or interrupted by one or more units D is, for example, (CH<sub>2</sub>CH<sub>2</sub>O)<sub>1-9</sub>-R<sup>x</sup>, where R<sup>x</sup> is H or C<sub>1</sub>-C<sub>10</sub>alkyl or C<sub>2</sub>-C<sub>10</sub>alkanoyl (e.g. CO-CH(C<sub>2</sub>H<sub>5</sub>)C<sub>4</sub>H<sub>9</sub>), CH<sub>2</sub>-CH(OR<sup>y</sup>)-CH<sub>2</sub>-O-R<sup>y</sup>, where R<sup>y</sup> is C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl, phenyl, C<sub>7</sub>-C<sub>15</sub>phenylalkyl, and R<sup>y</sup> embraces the same definitions as R<sup>x</sup> or is H; C<sub>1</sub>-C<sub>8</sub>alkylene-COO-R<sup>z</sup>, e.g. CH<sub>2</sub>COOR<sup>z</sup>, CH(CH<sub>3</sub>)COOR<sup>z</sup>, C(CH<sub>3</sub>)<sub>2</sub>COOR<sup>z</sup>, where R<sup>z</sup> is H, C<sub>1</sub>-C<sub>18</sub>alkyl, (CH<sub>2</sub>CH<sub>2</sub>O)<sub>1-9</sub>-R<sup>x</sup>, and R<sup>x</sup> embraces the definitions indicated above; CH<sub>2</sub>CH<sub>2</sub>-O-CO-CH=CH<sub>2</sub>; CH<sub>2</sub>CH(OH)CH<sub>2</sub>-O-CO-C(CH<sub>3</sub>)=CH<sub>2</sub>.

Preferred arylene radicals are 1,4-phenylene, 2,5-tolyene, 1,4-naphthylene, 1,9 anthracylene, 2,7-phenantrylene and 2,7-dihydrophenantrylene.

Preferred heteroarylene radicals are 2,5-pyrazinylene, 3,6-pyridazinylene, 2,5-pyridinylene, 2,5-pyrimidinylene, 1,3,4-thiadiazol-2,5-ylene, 1,3-thiazol-2,4-ylene, 1,3-thiazol-2,5-ylene, 2,4-thiophenylene, 2,5-thiophenylene, 1,3-oxazol-2,4-ylene, 1,3-oxazol-2,5-ylene and 1,3,4-oxadiazol-2,5-ylene, 2,5-indenylene and 2,6-indenylene.

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Another aspect of the invention is the films formed from the polymers of the invention. Such films can be used in polymeric light-emitting diodes (PLEDs). Preferably, such films are used as emitting layers. These films may also be used as protective coatings for electronic devices and as fluorescent coatings. The thickness of the coating or film is dependent upon the ultimate use. Generally, such thickness can be from 0.01 to 200 microns. In that embodiment wherein the coating is used as a fluorescent coating, the coating or film thickness is from 10 to 200 microns. In that embodiment where the coatings are used as electronic protective layers, the thickness of the coating can be from 5 to 20 microns. In that embodiment where the coatings are used in a polymeric light-emitting diode, the thickness of the layer formed is 0.01 to 0.5 microns. The polymers of the invention form good pinhole- and defect-free films. Such films can be prepared by means well known in the art including spin-coating, spray-coating, dip-coating and roller-coating. Such coatings are prepared by a process comprising applying a composition to a substrate and exposing the applied composition to conditions such that a film is formed. The conditions which form a film depend upon the application technique. Preferably, the solution contains from 0.1 to 10 weight percent of the polymers. This composition is applied to the appropriate substrate by the desired method and the solvent is allowed to evaporate. Residual solvent may be removed by vacuum and/or by heat-drying. The films are preferably substantially uniform in thickness and substantially free of pinholes. In another embodiment, the polymers may be partially cured. This is known as B-staging.

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A further embodiment of the present invention is directed to an electronic device or a component therefore, comprising a substrate and a polymer according to the present invention.

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In such a device the polymers according to the present invention are used as electroluminescent material. For the purposes of the present invention, the term "electroluminescent material" is taken to mean materials which can be used as or in an active layer in an electroluminescent device. The term "active layer" means that the layer is capable of emitting light (light-emitting layer) on application of an electric field and/or that it improves the injection and/or transport of the positive and/or negative charges (charge injection or

35



charge transport layer). The invention therefore also relates to the use of the polymers according to the invention as electroluminescent material. The invention furthermore relates to an electroluminescent material which comprises the polymers according to the invention. Electroluminescent devices are used, for example, as self-illuminating display elements,  
5 such as control lamps, alphanumeric displays, signs and in opto-electronic couplers.

A device according to the present invention may be prepared in accordance with the disclosure of WO99/48160, the contents of which are incorporated by reference. Polymers according to the present invention may be present in the device as the sole light emitting  
10 polymer or as a component in a blend further comprising hole and/or electron transporting polymers. Alternatively, the device may comprise distinct layers of a polymer of the present invention, a hole transporting polymer and/or an electron transporting polymer.

In one embodiment the electronic device comprises an electroluminescent device, which  
15 comprises

- (a) a charge injecting layer for injecting positive charge carriers,
- (b) a charge injecting layer for injecting negative charge carriers,
- (c) a light-emissive layer located between the layers (a) and (b) comprising a polymer according to the present invention.

The layer (a) may be a positive charge carrier transport layer which is located between the light emissive layer (c) and an anode electrode layer, or may be an anode electrode layer. The layer (b) may be a negative charge carrier transport layer which is located between the light emissive layer (c) and an cathode electrode layer, or may be an cathode electrode  
20 layer. Optionally, an organic charge transport layer can be located between the light emissive layer (c) and one of the charge carrier injecting layers (a) and (b).

The EL device emits light in the visible electro-magnetic spectrum between 400 nm and 780 nm, preferably between 430 nm and 470 nm for a blue color, preferably between 520 nm and  
30 560 nm for a green color, preferably between 600 nm and 650 nm for a red color. By incorporating specific repeating units in the backbone of the polymer the emission can be even shifted to the near infrared (NIR, > 780 nm).

It will be appreciated that the light emissive layer may be formed from a blend or mixture of  
35 materials including one or more polymers according to the present invention, and optionally further different polymers. The further different polymers may be so-called hole transport

polymers (i.e. to improve the efficiency of hole transport to the light-emissive material) or electron-transport polymers (i.e. to improve the efficiency of electron transport to the light-emissive material). Preferably, the blend or mixture would comprise at least 0.1 % by weight of a polymer according to the present invention, preferably from 0.2 to 50%, more preferably from 0.5 to 30% by weight.

An organic EL device typically consists of an organic film sandwiched between an anode and a cathode such that when a positive bias is applied to the device, holes are injected into the organic film from the anode, and electrons are injected into the organic film from the cathode.

The combination of a hole and an electron may give rise to an exciton, which may undergo radiative decay to the ground state by liberating a photon. In practice the anode is commonly an mixed oxide of tin and indium for its conductivity and transparency. The mixed oxide (ITO) is deposited on a transparent substrate such as glass or plastic so that the light emitted by the organic film may be observed. The organic film may be the composite of several individual layers each designed for a distinct function. Since holes are injected from the anode, the layer next to the anode needs to have the functionality of transporting holes. Similarly, the layer next to the cathode needs to have the functionality of transporting electrons. In many instances, the hole-(electron) transporting layer also acts as the emitting layer. In some instances one layer can perform the combined functions of hole and electron transport and light emission. The individual layers of the organic film may be all polymeric in nature or combinations of films of polymers and films of small molecules deposited by thermal evaporation. It is preferred that the total thickness of the organic film be less than 1000 nanometers (nm). It is more preferred that the total thickness be less than 500 nm. It is most preferred that the total thickness be less than 300 nm. It is preferred that the thickness of the active (light emitting) layer be less than 400 nanometers (nm). It is more preferred that the thickness is in the range of from 40 to 160 nm.

The ITO-glass, which serves as the substrate and the anode, may be used for coating after the usual cleaning with detergent, organic solvents and UV-ozone treatment. It may also be first coated with a thin layer of a conducting substance to facilitate hole injection. Such substances include copper phthalocyanine, polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT); the last two in their (doped) conductive forms, doped, for example, with  $\text{FeCl}_3$  or  $\text{Na}_2\text{S}_2\text{O}_8$ . They contain poly(styrenesulfonic acid) (PSS) as counter-ion to ensure water solubility. It is preferred that the thickness of this layer be 200 nm or less; it is more preferred that the thickness be 100 nm or less.

In the cases where a hole-transporting layer is used, the polymeric arylamines described in U.S. Pat. No. 5,728,801, may be used. Other known hole-conducting polymers, such as polyvinylcarbazole, may also be used. The resistance of this layer to erosion by the solution of the copolymer film which is to be applied next is obviously critical to the successful  
5 fabrication of multi-layer devices. The thickness of this layer may be 500 nm or less, preferably 300 nm or less, most preferably 150 nm or less.

In the case where an electron-transporting layer is used, it may be applied either by thermal evaporation of low molecular weight materials or by solution coating of a polymer with a  
10 solvent that would not cause significant damage to the underlying film.

Examples of low molecular weight materials include the metal complexes of 8-hydroxyquinoline (as described by Burrows et al. in Appl. Phys. Lett. 64 (1994) 2718-2720), metallic complexes of 10-hydroxybenzoquinoline (as described by Hamada et al. in Chem.  
15 Lett. (1993) 906-906), 1,3,4-oxadiazoles (as described by Hamada et al. in Optoelectronics-Devices and Technologies 7 (1992) 83-93), 1,3,4-triazoles (as described by Kido et al. in Chem. Lett. (1996) 47-48), and dicarboximides of perylene (as described by Yoshida et al. in Appl. Phys. Lett. 69 (1996) 734-736).

Polymeric electron-transporting materials are exemplified by 1,3,4-oxadiazole-containing polymers (as described by Li et al. in J. Chem. Soc. (1995) 2211-2212, by Yang and Pei in J. Appl. Phys. 77 (1995) 4807-4809), 1,3,4-triazole-containing polymers (as described by Strukelj et al. in Science 267 (1995) 1969-1972), quinoxaline-containing polymers (as  
20 described by Yamamoto et al. in Jpn. J. Appl. Phys. 33 (1994) L250-L253, O'Brien et al. in Synth. Met. 76 (1996) 105-108), and cyano-PPV (as described by Weaver et al. in Thin Solid Films 273 (1996) 39-47). The thickness of this layer may be 500 nm or less, preferably 300 nm or less, most preferably 150 nm or less.

The cathode material may be deposited either by thermal evaporation or by sputtering. The  
30 thickness of the cathode may be from 1 nm to 10,000 nm, preferably 5 nm to 500 nm.

OLEDs made according to the present invention may include phosphorescent dopants dispersed in the device's emissive layer, capable of achieving internal quantum efficiencies approaching 100%. As used herein, the term "phosphorescence refers to emission from a  
35 triplet excited state of an organic or metal-organic molecule. High efficiency organic light emitting devices using phosphorescent dopants have been demonstrated using several

different conducting host materials (M. A. Baldo et al., Nature, Vol 395, 151 (1998), C. Adachi et al., Appl. Phys. Lett., Vol. 77, 904 (2000)).

In a preferred embodiment, the electroluminescent device comprises at least one hole-transporting polymer film and a light-emitting polymer film comprised of the polymer of the invention, arranged between an anode material and a cathode material such that under an applied voltage, holes are injected from the anode material into the hole-transporting polymer film and electrons are injected from the cathode material into the light-emitting polymer films when the device is forward biased, resulting in light emission from the light-emitting layer.

In another preferred embodiment, layers of hole-transporting polymers are arranged so that the layer closest to the anode has the lower oxidation potential, with the adjacent layers having progressively higher oxidation potentials. By these methods, electroluminescent devices having relatively high light output per unit voltage may be prepared.

The term "hole-transporting polymer film" as used herein refers to a layer of a film of a polymer which when disposed between two electrodes to which a field is applied and holes are injected from the anode, permits adequate transport of holes into the emitting polymer. Hole-transporting polymers typically are comprised of triarylamine moieties. The term "light-emitting polymer film" as used herein refers to a layer of a film of a polymer whose excited states can relax to the ground state by emitting photons, preferably corresponding to wavelengths in the visible range. The term "anode material" as used herein refers to a semi-transparent, or transparent, conducting film with a work function between 4.5 electron volts (eV) and 5.5 eV. Examples are gold, silver, copper, aluminum, indium, iron, zinc, tin, chromium, titanium, vanadium, cobalt, nickel, lead, manganese, tungsten and the like, metallic alloys such as magnesium/copper, magnesium/silver, magnesium/aluminum, aluminum/indium and the like, semiconductors such as Si, Ge, GaAs and the like, metallic oxides such as indium-tin-oxide ("ITO"), ZnO and the like, metallic compounds such as CuI and the like, and furthermore, electroconducting polymers such polyacetylene, polyaniline, polythiophene, polypyrrole, polyparaphenylene and the like. Oxides and mixed oxides of indium and tin, and gold are preferred. Most preferred is ITO, especially ITO on glass, or on a plastics material, such as polyester, for example polyethylene terephthalate (PET), as substrate.

The term "cathode material" as used herein refers to a conducting film with a work function between 2.0 eV and 4.5 eV. Examples are alkali metals, earth alkaline metals, group 13

elements, silver, and copper as well as alloys or mixtures thereof such as sodium, lithium, potassium, calcium, lithium fluoride (LiF), sodium-potassium alloy, magnesium, magnesium-silver alloy, magnesium-copper alloy, magnesium-aluminum alloy, magnesium-indium alloy, aluminum, aluminum-aluminum oxide alloy, aluminum-lithium alloy, indium, calcium, and materials exemplified in EP-A 499,011, such as electroconducting polymers e.g. polypyrrole, polythiophene, polyaniline, polyacetylene etc. Preferably lithium, calcium, magnesium, indium, silver, aluminum, or blends and alloys of the above are used. In the case of using a metal or a metallic alloy as a material for an electrode, the electrode can be formed also by the vacuum deposition method. In the case of using a metal or a metallic alloy as a material forming an electrode, the electrode can be formed, furthermore, by the chemical plating method (see for example, Handbook of Electrochemistry, pp 383-387, Mazuren, 1985). In the case of using an electroconducting polymer, an electrode can be made by forming it into a film by means of anodic oxidation polymerization method onto a substrate, which is previously provided with an electroconducting coating.

As methods for forming said thin films, there are, for example, the vacuum deposition method, the spin-coating method, the casting method, the Langmuir-Blodgett ("LB") method, the ink jet printing method and the like. 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 layers by using the spin-coating method, the casting method and ink jet printing method, the coating can be carried out using a solution prepared by dissolving the composition in a concentration of from 0.0001 to 90% by weight in an appropriate organic solvent such as benzene, toluene, xylene, tetrahydrofuran, methyltetrahydrofuran, N,N-dimethylformamide, acetone, acetonitrile, anisole, dichloromethane, dimethylsulfoxide and mixtures thereof.

The organic EL device of the present invention is seen as a future replacement technology for a flat panel display of an on-wall television set, a flat light-emitting device, such as a wall paper, a light source for a copying machine or a printer, a light source for a liquid crystal display or counter, a display signboard and a signal light and perhaps even to replace incandescent and fluorescent lamps. The polymers and compositions of the present invention can be used in the fields of an organic EL device, a photovoltaic device, an electrophotographic photoreceptor, a photoelectric converter, a solar cell, an image sensor, and the like.

Accordingly, the present invention relates also to PLEDs, organic integrated circuits (O-ICs), organic field effect transistors (OFETs), organic thin film transistors (OTFTs), organic solar cells (O-SCs), thermoelectric devices, or organic laser diodes comprising one or more of the polymers according to the present invention.

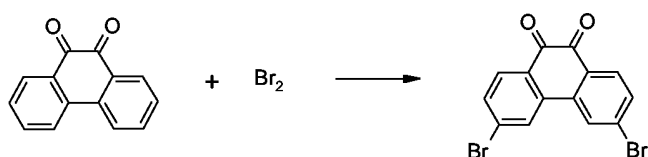
The following examples are included for illustrative purposes only and do not limit the scope of the claims. Unless otherwise stated, all parts and percentages are by weight.

Weight-average molecular weight ( $M_w$ ) and polydispersity ( $M_w/M_n = PD$ ) are determined by Gel Permeation Chromatography (GPC) [Apparatus: **GPC<sub>max</sub> + TDA 302** from Viscotek (Houston, TX, USA) yielding the responses from refractive index (RI), low angle light scattering (LALS), right angle light scattering (RALS) and differential viscosity (DP) measurements. Chromatographic conditions: Column: PL<sub>gel</sub> mixed C (300 x 7.5 mm, 5  $\mu$ m particles) covering the molecular weight range from about  $1 \times 10^3$  to about  $2.5 \times 10^6$  Da from Polymer Laboratories (Church Stretton, UK); Mobile phase: tetrahydrofuran containing 5 g/l of sodium trifluoroacetate; Mobile phase flow: either 0.5 or 0.7 ml/min; Solute concentration: about 1-2 mg/ml; Injection volume: 100  $\mu$ l; Detection: RI, LALS, RALS, DP. 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. **Absolute calibration** is done on the base of the responses of LALS, RALS and DP. As experienced in a large number of investigations this combination provides optimum calculation of molecular weight data. Usually PS 96'000 is used as the molecular weight calibration standard, but in general every other PS standard lying in the molecular weight range to be determined can be chosen for this purpose.

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.

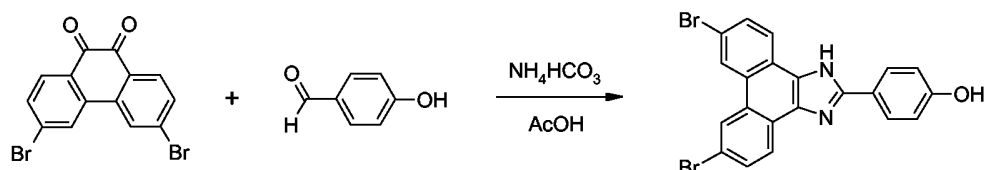
### Examples

#### Example 1



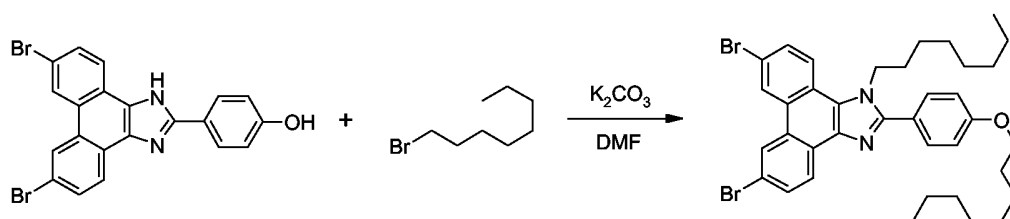
a) 9,10-Phenanthrenequinone is prepared according to *Yuki Gosei Kagaku Kyokaishi* **1957**, 15, 84-87.

To 42.2 g (0.203 mol) of 9,10-phenanthrenequinone in 230 ml of nitrobenzene approximately 300 mg of aluminum chloride are added. The reaction mixture is stirred under nitrogen and is heated to 105°C. 84.2 g (0.527 mol) of bromine in 40 ml of nitrobenzene are added over a period of 40 minutes. After three hours the reaction mixture is cooled to 25°C and the product is filtered off. The product can be further purified by recrystallization from xylene (yield: 46.9 g (63%)).

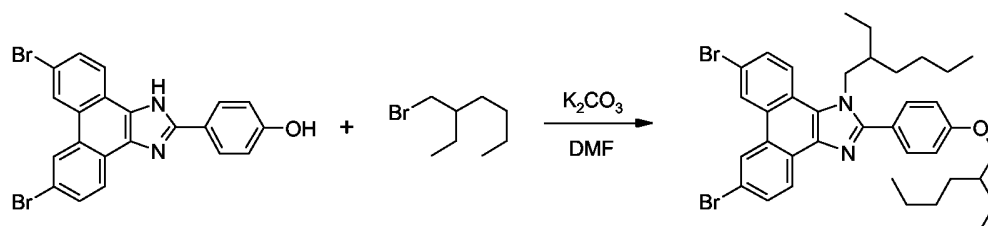


b) To 10 g (27.3 mmol) of 3,6-dibromophenanthrene-9,10-quinone in 250 ml of acetic acid (>99 %) are added under nitrogen 5.00 g (41.0 mmol) of 4-hydroxybenzaldehyde and 10.8 g (0.136 mol) of ammonium bicarbonate. The reaction mixture is heated under reflux for 4 h. The reaction mixture is cooled to 25°C and the product is filtered off. The product is dissolved in THF (tetrahydrofuran) and filtered over Hyflo® (CAS 91053-39-3; Fluka 56678). The solvent is removed under vacuum. The product is heated in 100 ml of acetic acid (>99 %) under reflux. The product is filtered off after cooling to 25°C. This procedure is repeated once and the product is washed with ethanol (yield: 8.60 g (67%)).

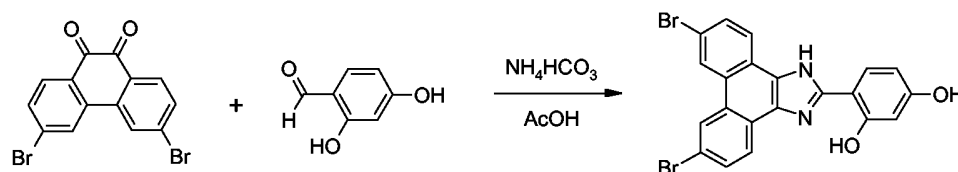
### Example 2



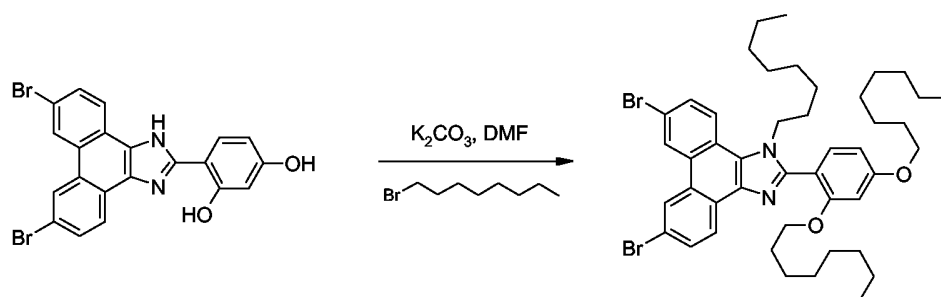
6.00 g (12.8 mmol) of the product from **example 1b** are dissolved under nitrogen in 70 ml of water free DMF (dimethyl formamide). 7.43 g (38.5 mmol) of 1-bromooctane and 7.97 g (57.7 mmol) of potassium carbonate are added. The reaction mixture is heated for 30 h at 120°C. The reaction mixture is cooled to 25°C and the inorganic salts are filtered off. The solvent is removed under vacuum. The product is filtered over silica gel first by eluting with hexane and then with THF. The crude product is further purified via column chromatography ( $\text{SiO}_2$ , dichloromethane) followed by recrystallization from diethyl ether giving the title compound (yield: 3.34 g (38%)). Melting Point: 135.5-137°C.

**Example 3**

1.00 g (2.14 mmol) of the product from **example 1b** is dissolved under nitrogen in 20 ml of water free DMF. 1.24 g (6.41 mmol) of 1-bromo-2-ethylhexane and 1.03 g (7.48 mmol) of potassium carbonate are added. The reaction mixture is heated for 17 h at 120°C, then diluted with dichloromethane and washed with water. The solvent is removed under vacuum. The reaction mixture is filtered over silica gel first by eluting with hexane and then with dichloromethane. The crude product is further purified via column chromatography (SiO<sub>2</sub>, toluene) giving the title compound (yield: 420 mg (28%)).

**Example 4**

a) To 8.04 g (20.0 mmol) of 3,6-dibromophenanthrene-9,10-quinone in 100 ml acetic acid (>99%) are added under nitrogen 3.59 g (26.0 mmol) of 2,4-dihydroxybenzaldehyde and 7.91 g (0.100 mol) of ammonium bicarbonate. The reaction mixture is first heated under reflux for 4 h, then cooled to 25°C, followed by the addition of water. The product is filtered off and used without further purification for the next step.

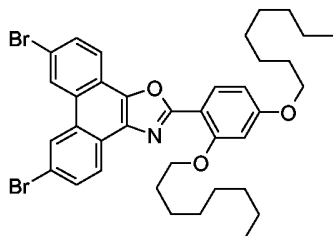


b) 4.84 g (10.0 mmol) of the product from **example 4a** are dissolved under nitrogen in 50 ml of water free DMF. 6.37 g (33.0 mmol) of 1-bromooctane and 6.22 g (45.0 mmol) of potassium carbonate are added. The reaction mixture is heated for 18 h at 140°C, diluted with diethyl ether and washed with water. The solvent is removed under vacuum. The crude product is further purified via column chromatography (SiO<sub>2</sub>, toluene) followed by another column



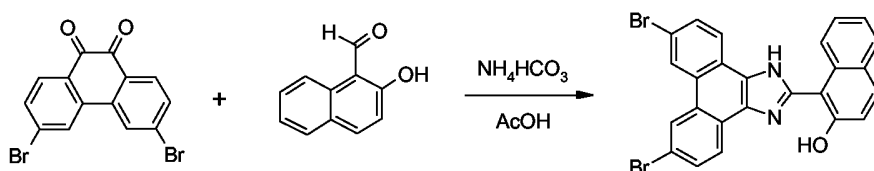
chromatography (SiO<sub>2</sub>, toluene). The resulting solid is recrystallized from n-heptane giving the title compound (yield: 1.2 g (15%)). Melting point: 99.5-101°C.

The following product is formed in small quantities:

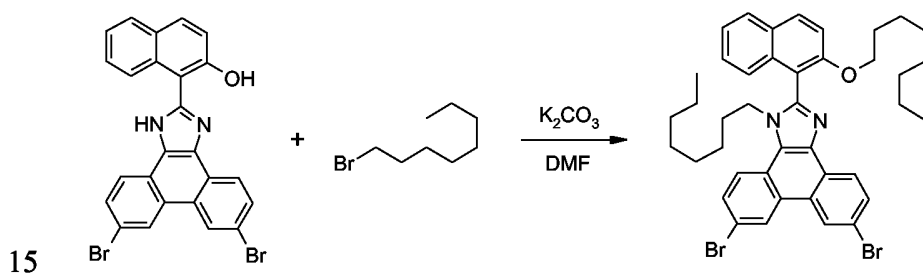


5 Melting point: 87-88.5°C.

### Example 5

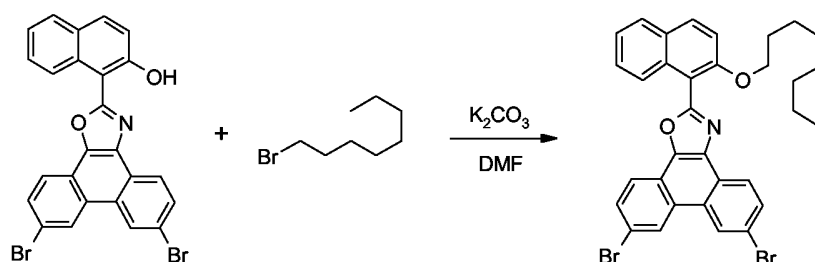


10 a) To 5.00 g (13.7 mmol) of 3,6-dibromophenanthrene-9,10-quinone in 120 ml of acetic acid (>99%) are added under nitrogen 3.53 g (20.5 mmol) of 2-hydroxy-naphthalene-1-carbaldehyde and 5.40 g (68.3 mmol) of ammonium bicarbonate. The reaction mixture is heated under reflux for 5 h. The reaction mixture is cooled to 25°C. The product is filtered off and washed with acetic acid and ethanol/water 1:5. The product is used without further purification for the next step.



15 b) 4.50 g (8.68 mmol) of the product from **example 5a** are dissolved under nitrogen in 100 ml of DMF. 5.03 g (26.1 mmol) of 1-bromooctane and 4.80 g (34.7 mmol) of potassium carbonate are added. The reaction mixture is heated for 26 h at 120°C, diluted with dichloromethane and washed with water. The organic phase is dried with magnesium sulfate and the solvent removed under vacuum. The crude product is purified via column chromatography (SiO<sub>2</sub>, dichloromethane) and further recrystallized two times from n-hexane  
20 (yield: 1.29 g (20 %)). Two atropisomers are formed according to NMR analysis. Melting point: 95.5-97.5°C.

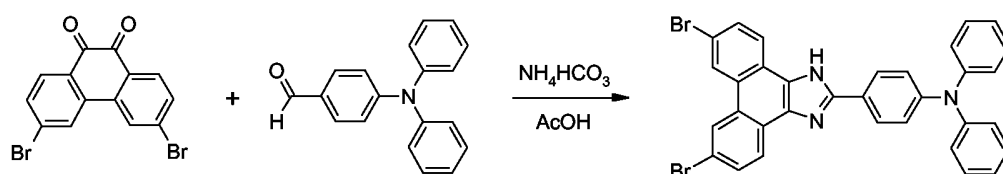
The following product is also formed by alkylation of the oxazole obtained in step 5a) as a side-product:



Melting point: 125-126.5°C.

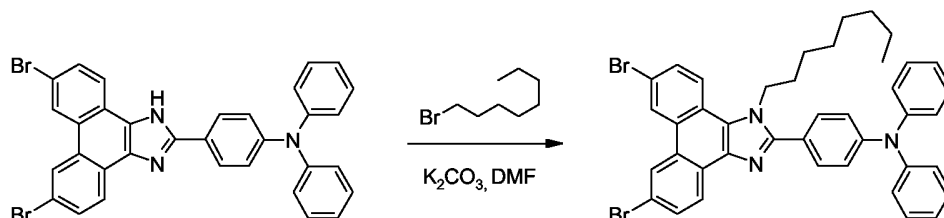
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### Example 6



- a) To 5.00 g (12.4 mmol) of 3,6-dibromophenanthrene-9,10-quinone in 180 ml of acetic acid (>99%) are added under nitrogen 4.42 g (16.2 mmol) of 4-diphenylamino-benzaldehyde and 4.92 g (62.2 mmol) of ammonium bicarbonate. The reaction mixture is heated under reflux for 3 h and cooled to 25°C. The product is filtered off and washed with acetic acid and ethanol/water 1:5. The product is used without further purification for the next step.

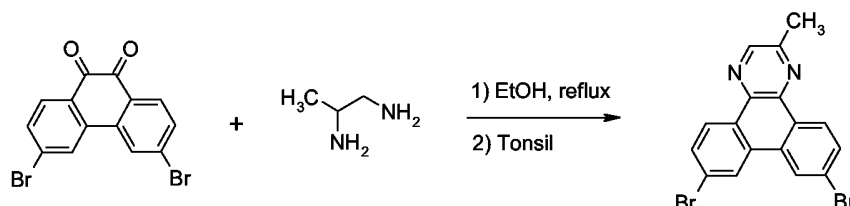
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- b) The product of **example 6a** is reacted with 1-bromooctane as described in **example 5b**, giving the title compound as a yellow powder (yield: 70%). Melting point: 175-176°C.

### Example 7

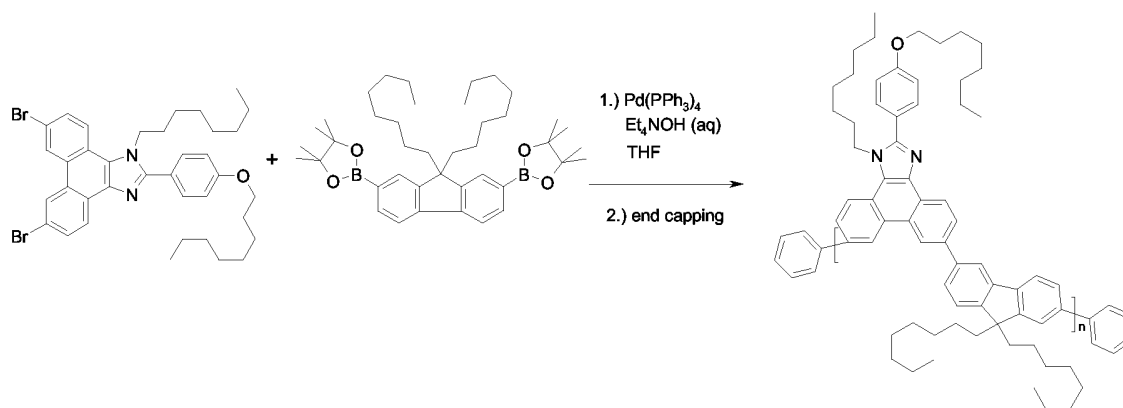


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To a suspension of 4.11 g (11.2 mmol) of 3,6-dibromophenanthrene-9,10-quinone in 50 ml of ethanol (99 %) are added 1.00 g (13.5 mmol) of 1,2-diaminopropane. The reaction mixture is heated under reflux for 6 h and then cooled to 25°C. The product is filtered off, dissolved in

chloroform, followed by the addition of 5 g of Tonsil (montmorillonite, Süd-Chemie, pH 7). The reaction mixture is refluxed for two hours. The Tonsil is filtered off and the solvent is removed under vacuum. The product is heated under reflux in ethyl methyl ketone (MEK) and filtered off after cooling to 25°C. The product is dissolved in 500 ml of THF and 1 l of dichloromethane and filtered over silica gel (yield: 2.11 g (47%)). The title compound is obtained as a white powder. Melting Point: 280-305°C.

### Example 8



1.0455 g (1.51 mmol) of the dibromide product of **example 2** and 1.0000 g (1.56 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene are dissolved in 20 ml of THF. This solution is degassed with argon. 180 mg of Pd(PPh<sub>3</sub>)<sub>4</sub> are added and the reaction mixture is degassed with argon. 6 ml of a degassed solution of Et<sub>4</sub>NOH (20% in water) are added. After degassing, the reaction mixture is refluxed for 44 h. 370 mg (2.33 mmol) of degassed bromobenzene are added and the reaction mixture is heated under reflux for two hours. 470 mg (3.89 mmol) of phenylboronic acid are added and the reaction mixture is stirred for two hours. The reaction mixture is diluted with 40 ml of toluene and then poured into 300 ml methanol. GPC (polystyrene standard): M<sub>w</sub> = 20 187 g/mol, polydispersity (PD) = 2.24.

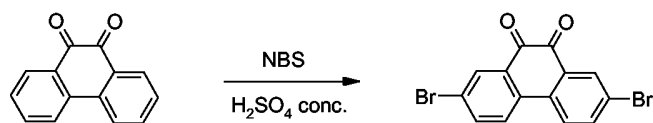
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The crude polymer is dissolved in 100 ml of toluene and a solution of 25 g of L-cysteine in 250 ml of water are added. This mixture is heated under reflux for two hours. The mixture is cooled to 25°C and the two phases are separated. The organic phase is refluxed again with a solution of 15 g of L-cysteine and 10 g of Na<sub>2</sub>SO<sub>4</sub> in 250 ml of water. The organic phase is separated and the water phase is washed twice with water. The organic phase is dried with magnesium sulfate and filtered over silica gel with toluene. The solvent is removed until 50 ml are left. This solution is poured in 200 ml of methanol. The polymer is filtered off. GPC (polystyrene standard): M<sub>w</sub> = 21 372, PD = 2.07.

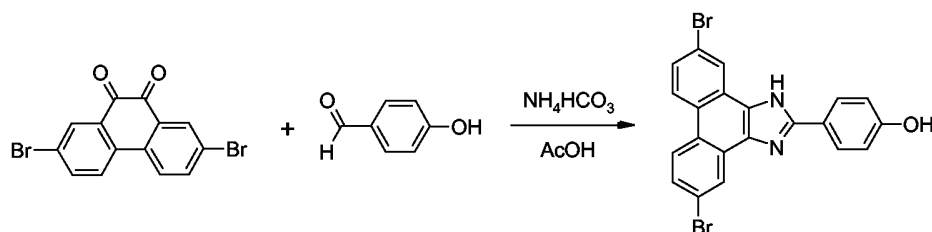
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1.0 % by weight of the product of **example 8** is dissolved in toluene. This solution is filtered through a Teflon filter having a pore width of 0.2  $\mu\text{m}$  and is spin coated at 250 rpm on a quartz substrate. The film is characterized by UV-VIS and photoluminescent measurements (Perkin Elmer LS 50 B), showing a  $\lambda_{\text{max}}$  at 358 nm in the absorption spectrum of the solid film and an emission maximum at 439 nm (excitation wavelength 368nm) in the photoluminescent spectrum. The relative thin film quantum efficiency of the film is found to be ca.  $40 \pm 5\%$ .

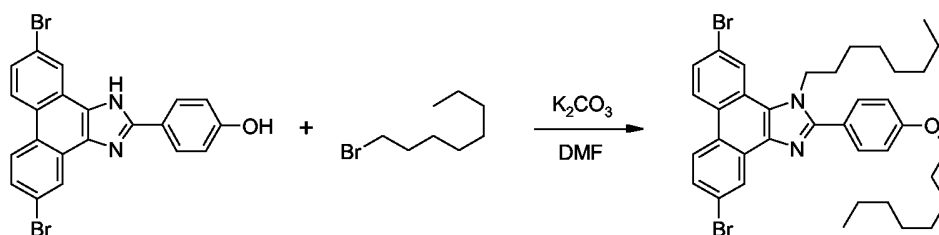
### Example 9



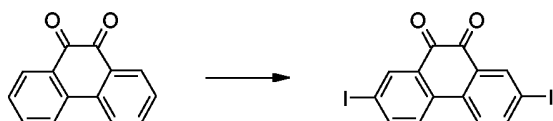
- 10 a) 2,7-Dibromophenanthrene-9,10-quinone is synthesized according to example A 1.2.2 of WO 2005/014689 from 9,10-phenanthrenequinone.



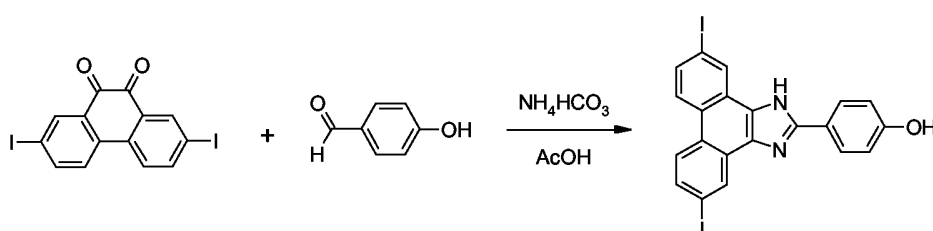
- 15 b) To a suspension of 2.00 g (5.46 mmol) of 2,7-dibromophenanthrenequinone in 100 ml of acetic acid are added 1.00 g (8.20 mmol) of 4-hydroxybenzaldehyde and 2.16 g (27.3 mmol) of ammonium bicarbonate. The reaction mixture is heated under reflux for 7 h. The crude product is filtered off, further washed with acetic acid and ethanol giving the title compound (yield: 2.55 g (99.7%)).



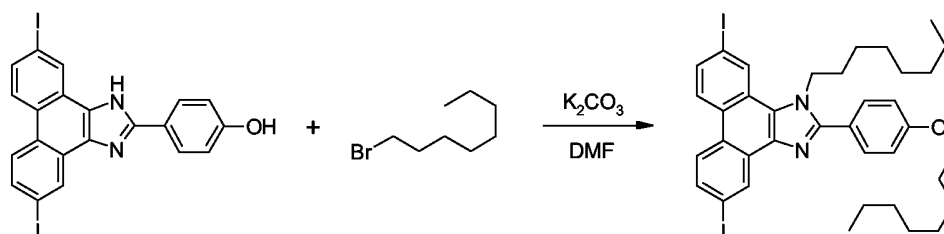
- 20 c) To 1.60 g (3.42 mmol) of the product of **example 9b** in 25 ml of dry DMF are added under nitrogen 2.13 g (15.4 mmol) of potassium carbonate and 2.64 g (13.7 mmol) of 1-bromooctane. The reaction mixture is stirred for 29 h at  $120^\circ\text{C}$ . Diethyl ether and water are added. The organic phase is separated and washed with water. The organic phase is dried with magnesium sulfate. The solvent is removed under vacuum. The product is recrystallized from
- 25 heptane giving the title compound with HPLC purity  $>99\%$ . Melting Point:  $97-98^\circ\text{C}$ .

**Example 10**

- a) 2,7-Diiodophenanthrene-9,10-quinone is synthesized according to *Bull. Chem. Soc. Jpn.* **1999**, 72, 115 from 9,10-phenanthrenequinone. For higher yields an excess of  $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{Ac}_2\text{O}$  and  $\text{AcOH}$  is required. 2,7-Diiodophenanthrene-9,10-quinone is also prepared according to *Tetrahedron Letters* **2004**, 45, 2801 (supporting information), or according to *Tetrahedron* **2004**, 60, 9113.

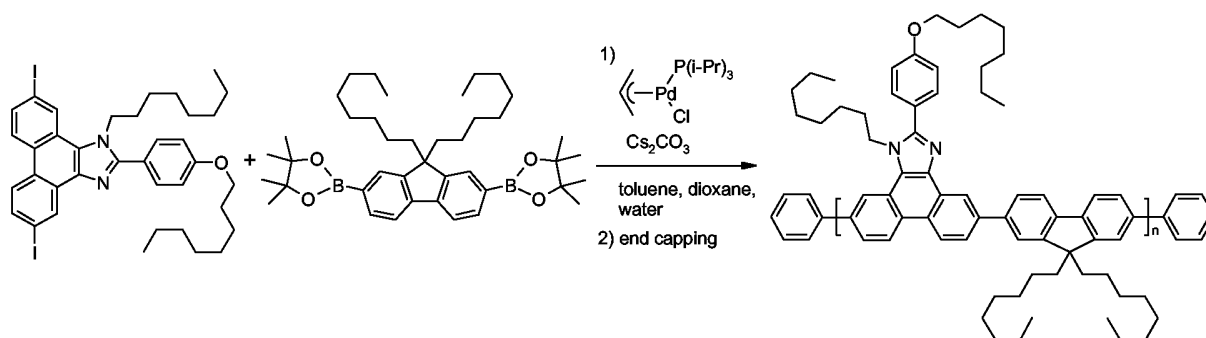


- b) To a suspension of 2.00 g (4.35 mmol) of 2,7-diiodophenanthrene-9,10-quinone in 100 ml acetic acid are added 800 mg (6.52 mmol) of 4-hydroxybenzaldehyde and 1.72 g (21.7 mmol) of ammonium bicarbonate. The reaction mixture is heated under reflux for 7 h. The crude product is filtered off and washed with acetic acid and ethanol giving the title compound (yield: 2.34 g (95.5%)).



- c) To 2.00 g (3.56 mmol) of the product of **example 10b** in 25 ml of dry DMF, 1.97 g (14.2 mmol) of potassium carbonate and 2.40 g (12.5 mmol) 1-bromooctane are added. The reaction mixture is stirred for 22 h at 120°C under nitrogen. Dichloromethane is added and the mixture is filtered over silica gel. The silica gel is washed with additional dichloromethane. The dichloromethane is removed under vacuum and the precipitated product is filtered off. The product is recrystallized two times from cyclohexane giving the title compound (yield: 1.18 g (42%)). Melting point: 121-122.5°C.

**Example 11**



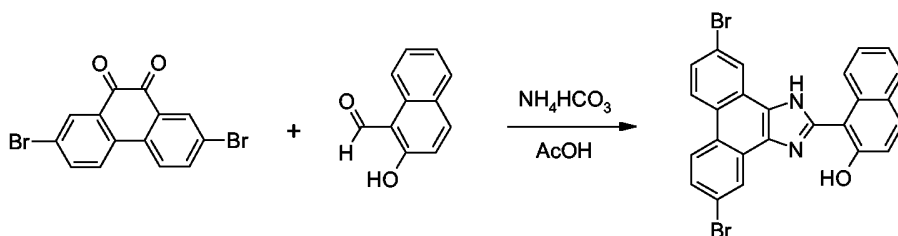
1.1500 g (1.46 mmol) of the diiodide product of **example 10c** and 0.9395 g (1.46 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene are dissolved in 15 ml of dioxane and 5 ml of toluene. This solution is degassed with argon. 50 mg of allyl(triisopropylphosphine)palladium chloride is added and the reaction mixture is degassed again with argon. 2.38 g (7.31 mmol) of cesium carbonate in 5 ml of water are degassed and added to the reaction mixture. After degassing, the reaction mixture is heated under reflux for 18 h. 340 mg (2.19 mmol) of degassed bromobenzene is added and the reaction mixture is refluxed for two hours. A degassed solution of 750 mg (3.66 mmol) of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane in 5 ml of toluene is added and the reaction mixture is stirred for two hours. The reaction mixture is poured into 300 ml of methanol. GPC (polystyrene standard):  $M_w = 24\,486$  g/mol, PD = 3.10.

The polymer is dissolved in 100 ml of toluene and a solution of 25 g of L-cysteine in 250 ml of water is added. This mixture is heated under reflux for 3 h. The organic phase is separated and washed two times with water. A solution of 15 g of L-cysteine and 10 g of sodium thiosulfate in 250 ml of water are added to the organic phase. This mixture is heated under reflux for two hours. The organic phase is separated and washed two times with water. The organic phase is filtered over silica gel and magnesium sulfate with toluene as eluent. The solvent is removed under vacuum until 50 ml are left. This solution is poured into 200 ml of methanol. The polymer is filtered off. GPC (polystyrene standard):  $M_w = 27\,547$  g/mol, polydispersity (PD) = 2.84.

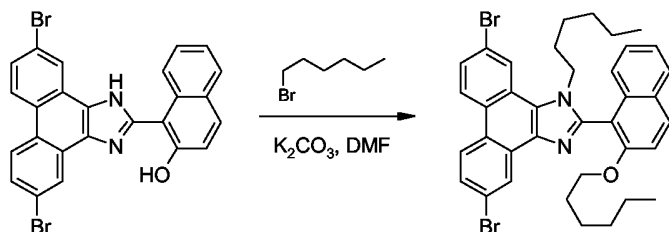
1.0% by weight of the product of **example 11** is dissolved in toluene. This solution is filtered through a Teflon filter having a pore width of  $0.2\ \mu\text{m}$  and is spin coated at 150 rpm on a quartz substrate. The film was characterized by UV-VIS and photoluminescent measurements (Perkin Elmer LS 50 B), showing a  $\lambda_{\text{max}}$  at 383 nm in the absorption spectrum of the solid film and an emission maximum at 430 nm and a distinct shoulder at 460 nm (excitation wavelength 368 nm) in the photoluminescent spectrum.

A solid state quantum yield of 32% was obtained in the film relative to a polyfluorene homopolymer standard.

### Example 12



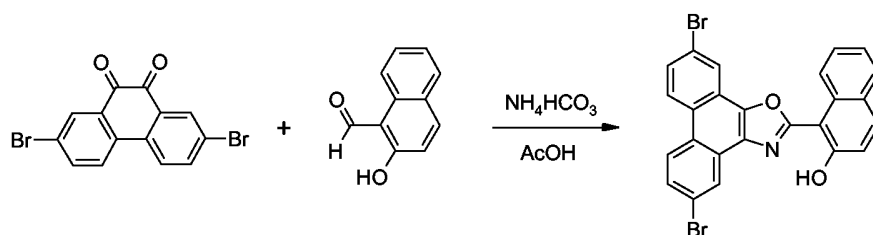
a) To a suspension of 4.02 g (10.0 mmol) of 2,7-dibromophenanthrene-9,10-quinone in 50 ml of acetic acid are added 2.24 g (13.0 mmol) of 2-hydroxy-naphthalene-1-carbaldehyde and 3.95 g (50.0 mmol) of ammonium bicarbonate. The reaction mixture is heated under reflux for 3 h. 220 mg of 2-hydroxy-naphthalene-1-carbaldehyde and 100 mg of ammonium bicarbonate are added. The reaction mixture is heated under reflux for an additional two hours. The product is filtered off, washed with acetic acid and water. The product is soxhlet extracted with ethyl-methyl-ketone (MEK). Most of the oxazole side-product is removed in this way giving the title compound (yield: 4.81 g (93%)). Melting point: 311-314°C accompanied by decomposition.



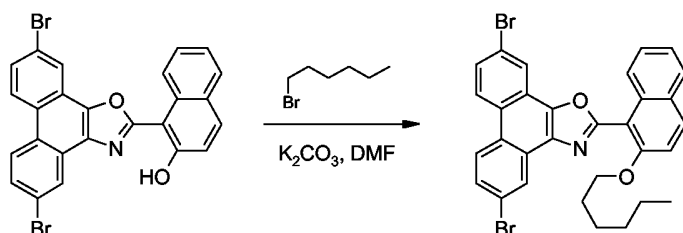
b) To 3.89 g (7.50 mmol) of the product of **example 12a** in 40 ml of dry DMF are added under nitrogen 3.11 g (22.5 mmol) of potassium carbonate and 3.62 g (18.8 mmol) of 1-bromohexane. The reaction mixture is stirred for 8 h at 130°C. Diethyl ether and water are added. The organic phase is separated and washed with water. The organic phase is dried with magnesium sulfate. The solvent is removed under vacuum. The crude product is purified via column chromatography (SiO<sub>2</sub>, toluene) and further recrystallized from cyclohexane giving the title compound (yield: 700 mg (14 %)). Two atropisomers are formed according to NMR analysis. Melting point: 122-123°C.

### Example 13

71

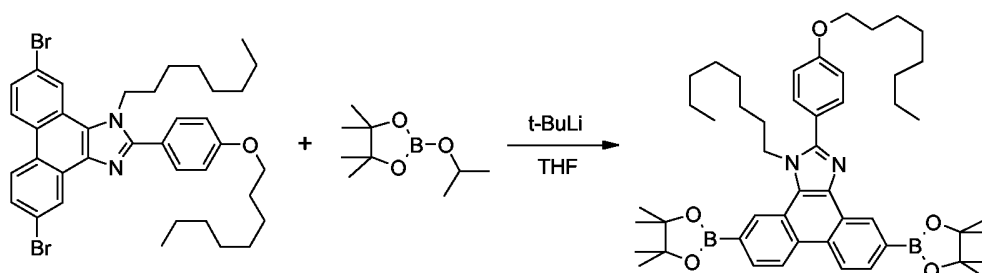


- a) To a suspension of 4.02 g (10.0 mmol) of 2,7-dibromophenanthrene-9,10-quinone in 100 ml of acetic acid are added 2.24 g (13.0 mmol) of 2-hydroxy-naphthalene-1-carbaldehyde and 470 mg (6.00 mmol) of ammonium bicarbonate. The reaction mixture is refluxed. After 3 h 220 mg of 2-hydroxy-naphthalene-1-carbaldehyde and 160 mg of ammonium bicarbonate are added. After two hours 220 mg of 2-hydroxy-naphthalene-1-carbaldehyde and 160 mg of ammonium bicarbonate are added. The reaction mixture is refluxed for an additional two hours. The product is filtered off, washed with acetic acid and water. The product is decocted in 100 ml of ethyl-methyl-ketone (MEK). Most of the imidazole side-product is removed in this way giving the title compound (yield: 3.71 g (72%)).



- b) To 3.11 g (6.00 mmol) of the product of **example 13a** in 30 ml of dry DMF are added under nitrogen 1.66 g (12.0 mmol) of potassium carbonate and 1.74 g (9.00 mmol) of 1-bromohexane. The reaction mixture is stirred for 8 h at 130°C. Diethyl ether and water are added. The organic phase is separated and washed with water. The organic phase is dried with magnesium sulfate. The solvent is removed under vacuum. The crude product is purified via column chromatography (SiO<sub>2</sub>, toluene/cyclohexane 2:1), followed by recrystallization from cyclohexane, giving the title compound (yield: 1.23 g (33%)).

## 20 Example 14

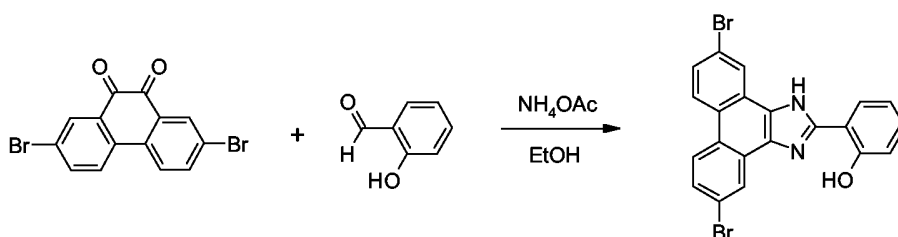


A solution of 2.08 g (3.00 mmol) of the product of **example 9c** in 90 ml of dry tetrahydrofuran (THF) is cooled to -78°C under argon. 10 ml (15 mmol) of a 1.5 M solution

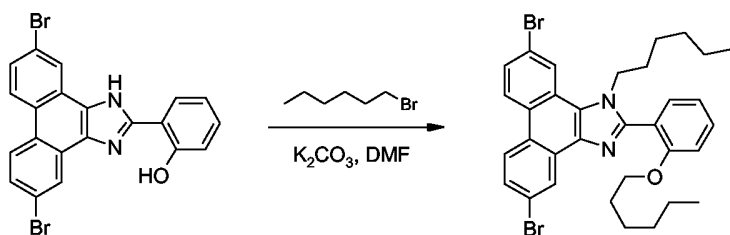


of *tert*-butyl-lithium in pentane is added. The reaction mixture is stirred for 1 h at -78°C. To this reaction mixture 1.67 g (9.00 mmol) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane are added as fast as possible. The reaction mixture is stirred for 30 min at -78°C, warmed up to 25°C, and stirring continued for one hour. The reaction mixture is diluted with diethyl ether and washed with water. The organic phase is dried with magnesium sulfate and the solvent is removed under vacuum. The product is recrystallized two times from cyclohexane giving the title compound (yield: 1.40 g (59%)). Melting point: 179-181°C.

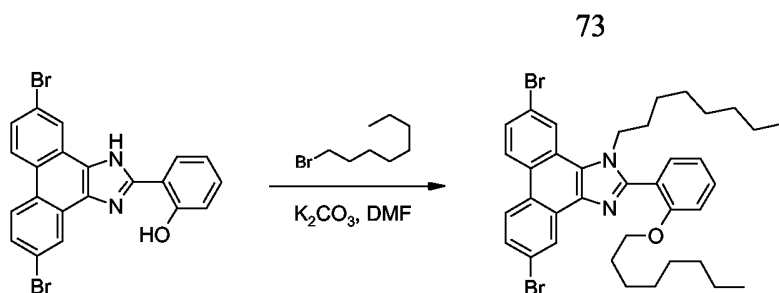
### Example 15



a) To 4.03 g (11.0 mmol) of 2,7-dibromophenanthrene-9,10-quinone in 165 ml of ethanol (>98 %) are added under nitrogen 2.35 g (19.3 mmol) of 2-hydroxybenzaldehyde and 8.48 g (0.11 mol) of ammonium acetate. The reaction mixture is heated under reflux for 5 h. The reaction mixture is cooled to 25°C, the product is filtered off and washed with ethanol (yield: 5.90 g).

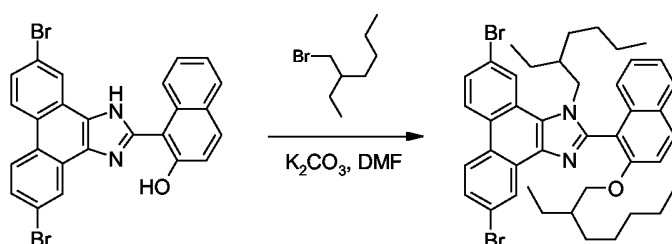


b) To 4.68 g (10.0 mmol) of the product of **example 15a** in 25 ml of dry DMF are added under nitrogen 4.13 g (25.0 mmol) of 1-bromohexane and 4.15 g (30.0 mmol) of potassium carbonate. The reaction mixture is stirred at 130°C. After 3 h 2.07 g (15.0 mmol) of potassium carbonate and 1.82 g (15.0 mmol) of 1-bromohexane are added. After 5 h the reaction mixture is poured into water and the water phase is extracted with diethyl ether. The organic phase is dried with magnesium sulfate and the solvent is removed under vacuum. The crude product is purified via column chromatography ( $\text{SiO}_2$ , toluene) leading to the product in form of an oil, which crystallizes slowly (yield: 5.1 g (80%)).



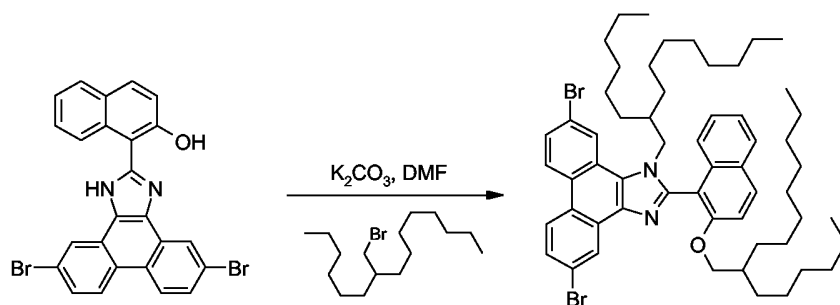
c) The title compound has been prepared according to the above example. Melting point: 86-88°C.

## 5 Example 16



a) To 5.18 g (10.0 mmol) of the product of **example 12a** in 50 ml of dry DMF are added under nitrogen 5.79 g (30.0 mmol) of 1-bromo-2-ethylhexane, 4.84 g (35.0 mmol) of potassium carbonate. The reaction mixture is stirred at 130°C. Additional 2.07 g (1.50 mmol) of potassium carbonate and 1.93 (10.0 mmol) of 1-bromo-2-ethylhexane are added each four times. After 7 h the reaction mixture is poured into water and the water phase is extracted with diethyl ether. The crude product is further purified via column chromatography (SiO<sub>2</sub>, toluene) giving the title compound as a light yellow, viscous oil which solidified upon standing (yield: 5.98 g (79%)). Melting point: 60.5-66.5°C.

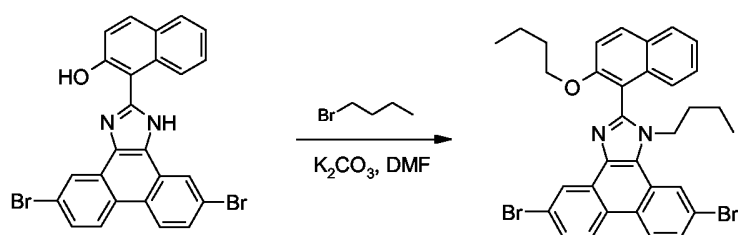
## Example 17



To 10.4 g (20.1 mmol) of the product of **example 12a** are added 21.4 g (70.1 mmol) of 1-bromo-2-hexyldecane, 11.1 g (80.0 mmol) of potassium carbonate and 100 ml of dry DMF under a nitrogen atmosphere. The reaction mixture is stirred at 120°C. After 22 h the mixture is cooled down to room temperature, diluted with 150 ml of CH<sub>2</sub>Cl<sub>2</sub>, then filtered and extracted three times with 200 ml of water. The organic phase is dried over Na<sub>2</sub>SO<sub>4</sub>, filtered

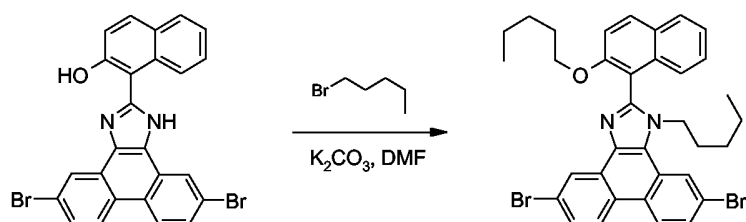
and concentrated under vacuum, giving 28 g of a light brown viscous oil. The crude product is further purified via column chromatography (SiO<sub>2</sub>, cyclohexane/ethyl acetate 20:1), followed by another column chromatography (cyclohexane/ethyl acetate 40:1). 17.2 g of the title compound are obtained as a light yellow, viscous oil with HPLC purity >99% (yield: 89%).

### Example 18



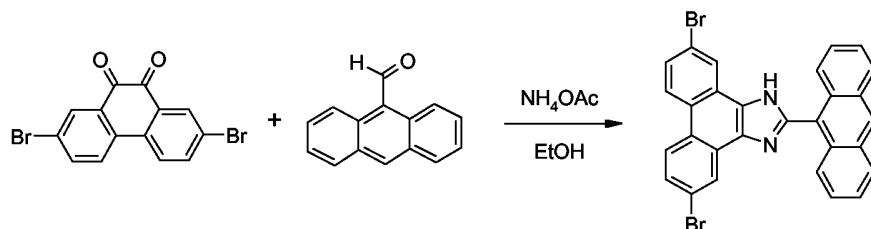
The product is prepared according to **example 15b**, decocted in ether and recrystallized from DMF (yield: 34%). Melting point: 86-87°C.

### Example 19



The product is prepared according to **example 15b**, decocted in ether and washed with ethanol (yield: 87%). Melting point: 132.5-134.5°C.

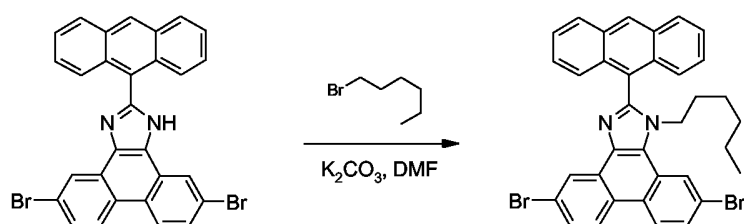
### Example 20



The product is prepared according to **example 15a**, with 9-anthracenecarbaldehyde (yield: 95%).

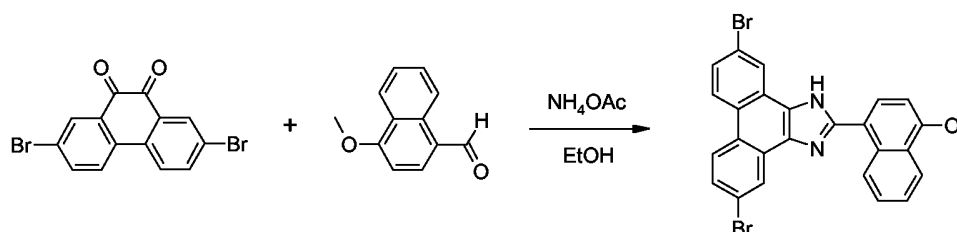
### Example 21

75



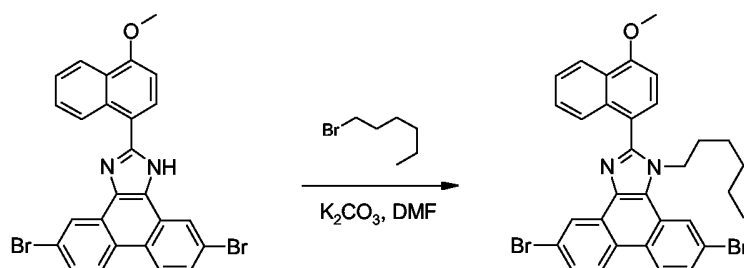
The product is prepared according to **example 15b** and decocted in DMF (yield: 66%).  
Melting point: 209.5-211°C.

5

**Example 22**

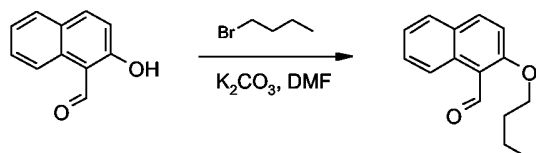
The product is prepared according to **example 15a**, with 4-methoxy-1-naphthaldehyde (yield: 84%).

10

**Example 23**

The product is prepared according to **example 15b** and recrystallized from n-hexane (yield: 69%). Melting point: 162-164°C.

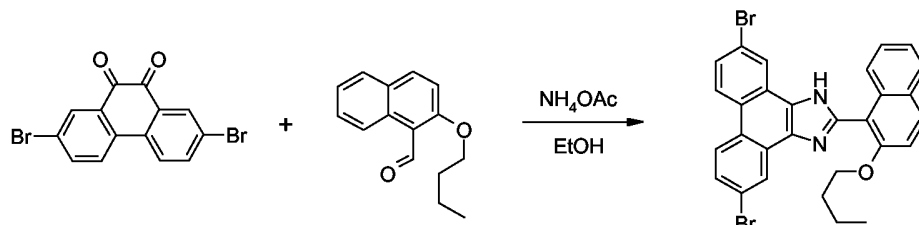
15

**Example 24**

a) To 5.00 g (29.0 mmol) of 2-hydroxy-naphthalene-1-carbaldehyde in 30 ml of dry DMF are added under nitrogen 5.97 g (43.6 mmol) of 1-bromobutane and 12.8 g (87.1 mmol) of potassium carbonate. The reaction mixture is stirred at 130°C. After 7 h the solids are filtered

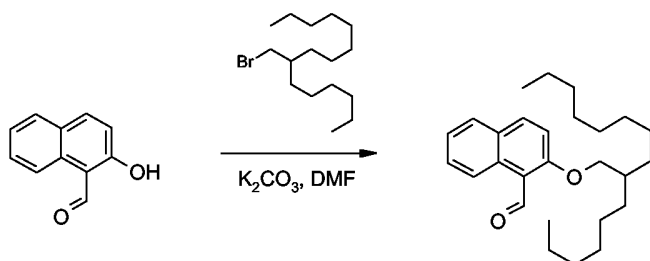
20

off. The filtrate is diluted with dichloromethane and the organic phase is washed with water and dried with magnesium sulfate. The solvent is removed under vacuum and the product is recrystallized from methanol giving the title compound (yield: 66%).

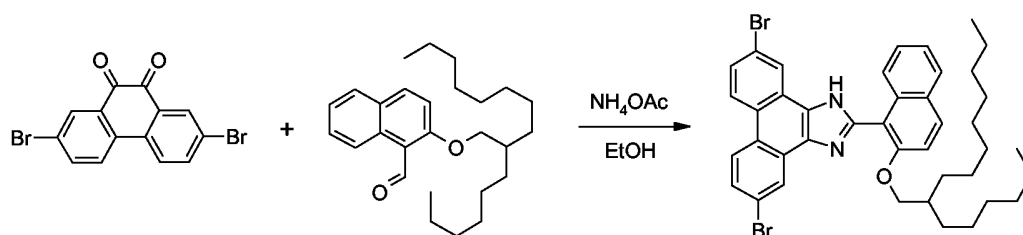


- 5 b) The product is prepared according to **example 15a**, with aldehyde product of **example 24a** (yield: 82%). Melting point: 268.5-270°C.

### Example 25

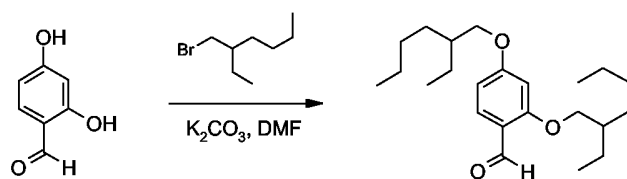


- 10 a) To 10.00 g (58.0 mmol) of 2-hydroxy-naphthalene-1-carbaldehyde in 40 ml of dry DMF are added under nitrogen 21.3 g (69.7 mmol) of 1-bromo-2-hexyldecane and 20.1 g (145 mmol) of potassium carbonate. The reaction mixture is stirred at 130°C. After one hour the solids are filtered off. The filtrate is diluted with dichloromethane and the organic phase is washed with water and dried with magnesium sulfate. The solvent is removed under vacuum. The product is filtered over silica gel with toluene/cyclohexane 1:1 (yield: 96%).
- 15

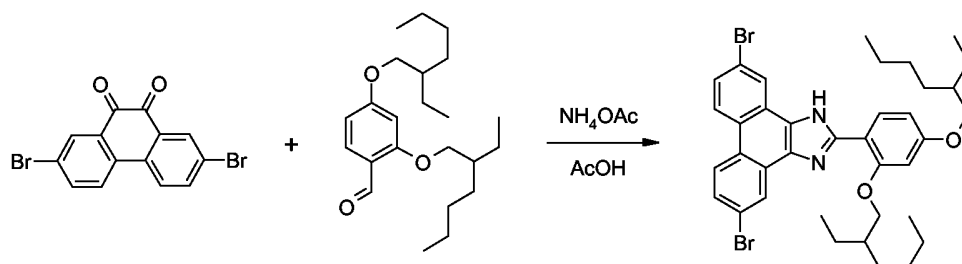


- b) The product is prepared according to **example 15a**, with aldehyde product of **example 25a** (yield: 68%).

### 20 Example 26

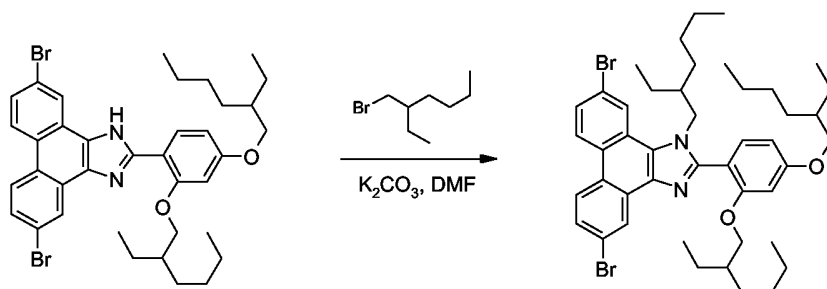


a) The product is prepared according to **example 25a**, with 2,4-dihydroxybenzaldehyde (yield: 80%).



- 5 b) To 2.00 g (5.46 mmol) of 2,7-dibromophenanthrene-9,10-quinone in 60 ml of acetic acid are added under nitrogen 2.97 g (8.20 mmol) of the product of **example 26a**. To this mixture 2.11 g (27.3 mmol) of ammonium acetate are added. The reaction mixture is stirred at 130°C. After 1.5 h the reaction mixture is cooled to 20 °C and the product starts to crystallize slowly. The product is filtered off, washed with acetic acid and recrystallized three times from  
10 n-hexane (yield: 1.96 g (51%)).

### Example 27

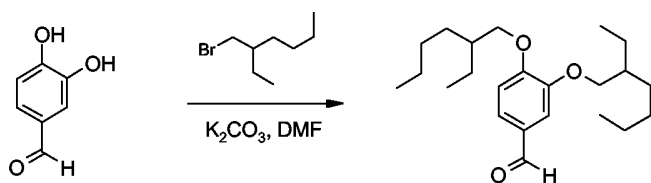


- To 2.10 g (2.96 mmol) of the product of **example 26b** in 20 ml of DMF are added under  
15 nitrogen 2.86 g (14.8 mmol) of 1-bromo-2-ethylhexane, 2.46 g (17.8 mmol) of potassium carbonate. The reaction mixture is stirred at 130°C. After 5 days the solids are filtered off. The filtrate is diluted with dichloromethane, the organic phase is washed with water and dried with magnesium sulfate. The solvent is removed under vacuum. A filtration over silica gel with toluene leads to the product in form of an oil (yield: 2.36 g (97%)).

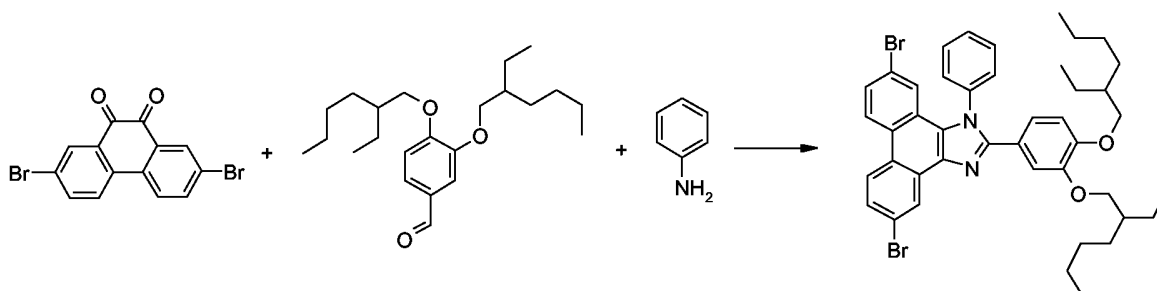
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### Example 28

78

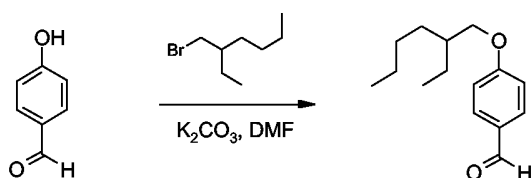


The product is prepared according to **example 25a**, with 3,4-dihydroxybenzaldehyde (yield: 100%).

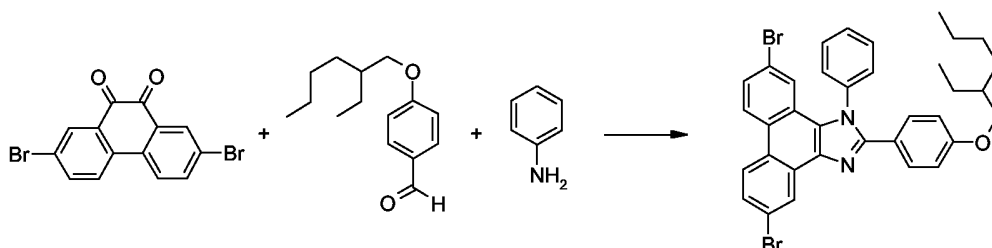


- 5 b) To 5.00 g (13.7 mmol) of 2,7-dibromophenanthrene-9,10-quinone in 80 ml acetic acid (>98%) are added under nitrogen 5.45 g (15.0 mmol) of the product of **example 28a**, 2.54 g (27.3 mmol) of aniline and 5.26 g (68.3 mmol) of ammonium acetate. The reaction mixture is heated under reflux for 3 h and cooled to 25°C. The product is filtered off, washed with water, aqueous sodium hydrogencarbonate solution and water, and recrystallized several times  
10 from *iso*-propanol (yield: 54 %). Melting point: 117-118°C.

### Example 29

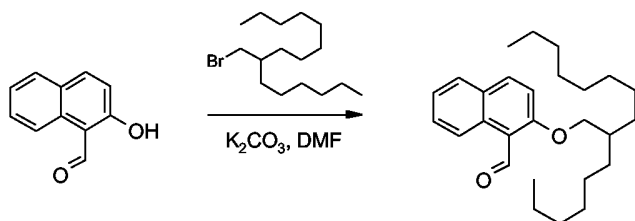


- a) The product is prepared according to **example 25a**, starting from 4-hydroxybenzaldehyde (yield: 96%).  
15

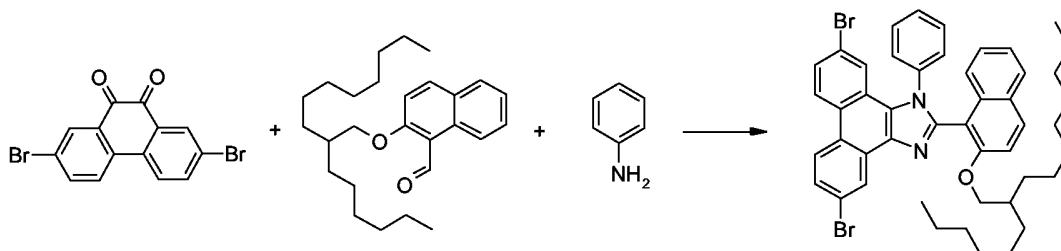


- b) The product is prepared according to **example 28b**, with aldehyde product of **example 29a**, giving a white solid (yield: 69%). Melting point: 161.5-162.5°C.

79

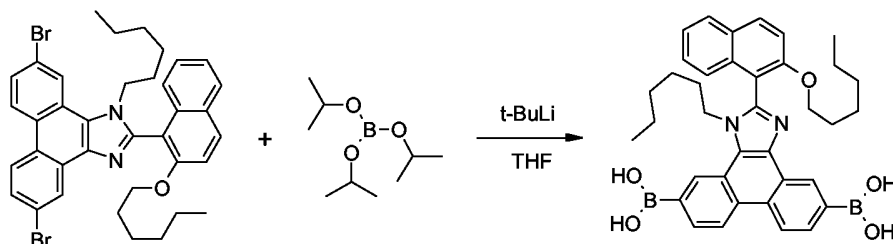


a) The product is prepared according to example 25a (yield: 96%).

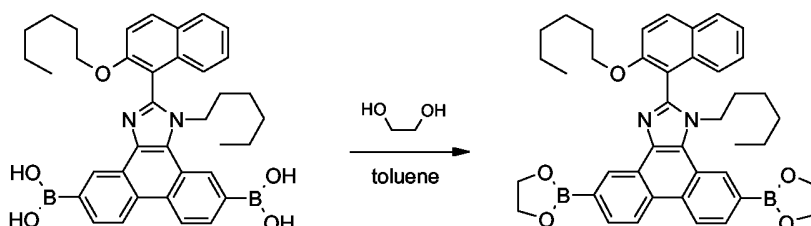


b) The product is prepared according to **example 28b**, with aldehyde product of **example 25a**, giving the title compound as a resin (yield: 27%).

### Example 31



a) To 2.06 g (3.00 mmol) of the product of **example 12b** in 150 ml of tetrahydrofurane (THF) are added 10 ml (15 mmol) of tert-butyl lithium at -78°C under argon. After two hours 1.69 g (9.00 mmol) of triisopropyl borate are added. The reaction mixture is stirred for two hours at -78 °C, warmed up to 25°C and stirring continued for two hours. The solvent is removed under vacuum. The product is dissolved in 40 ml of THF and 20 ml of 20% aqueous HCl is added at 0°C. The solvent is removed under vacuum. The product is used without purification in the next step.

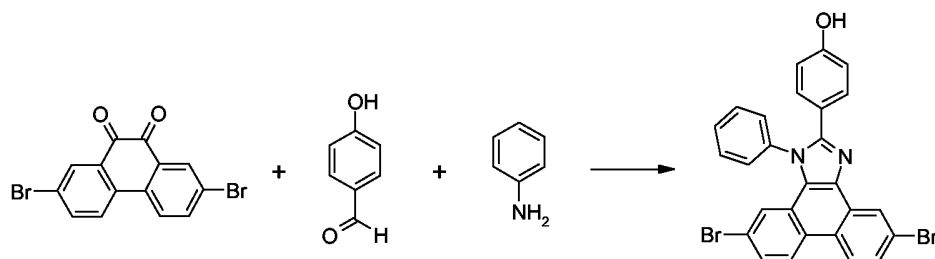


b) To 4.30 g (6.98 mmol) of the product of **example 31a** in 140 ml of toluene are added 520 mg (8.37 mmol) of ethyleneglycol. The reaction mixture is heated under reflux for several hours with azeotropic removal of water. The toluene is removed under vacuum and the

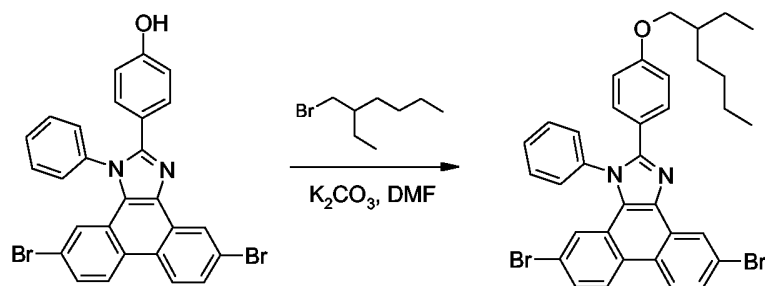


product is washed with 4 ml of diethylether, 4 ml of n-hexane and 2 ml of toluene giving the title compound (yield: 1.73 g (37%)). Melting Point: >200°C (the product decomposes at 200°C).

## 5 Example 32



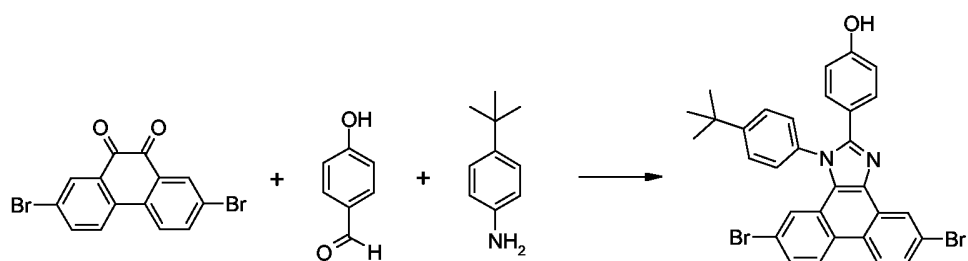
a) To 3.66 g (10.0 mmol) of 2,7-dibromophenanthrene-9,10-quinone in 100 ml of acetic acid (>98%) are added under nitrogen 1.34 g (11.0 mmol) of 4-hydroxybenzaldehyde, 1.03 g (11 mmol) of aniline and 3.08 g (40.0 mmol) of ammonium acetate. The reaction mixture is heated under reflux for 4 h. The reaction mixture is cooled to 25°C and the product is filtered off. The product is washed with water, aqueous sodium hydrogencarbonate solution and water, and recrystallized from methyl ethyl ketone (yield: 3.70 g (67 %)).



b) To 3.20 g (6.00 mmol) of the product of **example 32a** in 12 ml of DMF are added under nitrogen 2.32 g (12.0 mmol) of 1-bromo-2-ethylhexane and 2.49 g (18.0 mmol) of potassium carbonate. The reaction mixture is stirred at 130 °C for 4 h. The reaction mixture is poured into water and the water phase is extracted with dichloromethane. The product is recrystallized several times from dibutylether (yield: 2.90 g (74%)). Melting point: 161.5-162.5°C.

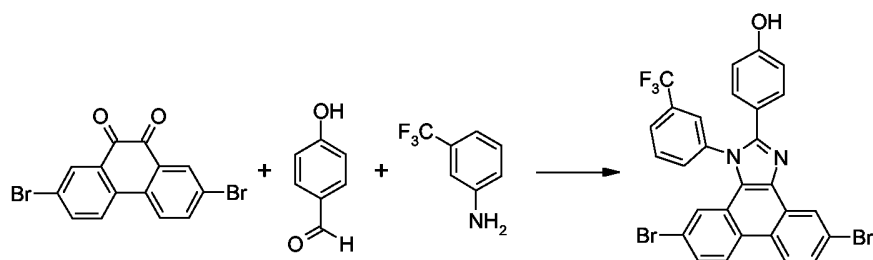
## Example 33

81



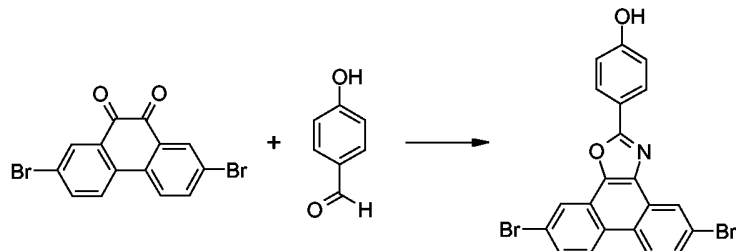
The product is prepared according to **example 32a** (yield: 83%).

### Example 34

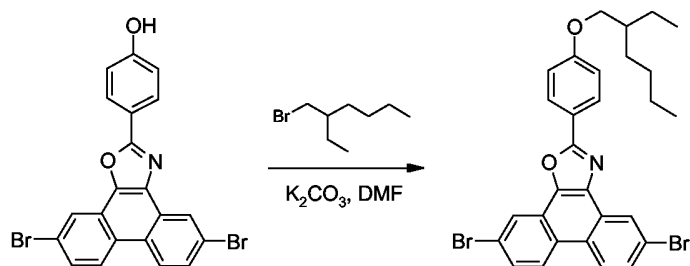


The product is prepared according to **example 32a** (yield: 77%).

### Example 35

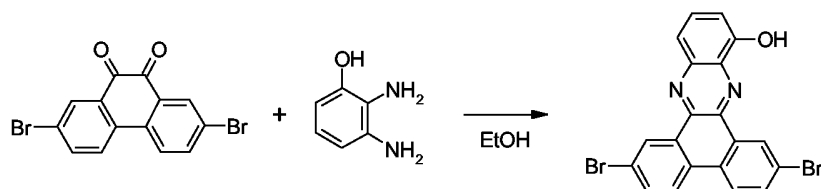


- 10 a) To 3.66 g (10 mmol) of 2,7-dibromophenanthrene-9,10-quinone in 100 ml of acetic acid are added under nitrogen 1.34 g (11.0 mmol) of 4-hydroxybenzaldehyde 1.42 g (11.0 mmol) of 2-ethylhexylamine and 3.08 g (0.110 mol) of ammonium acetate. The reaction mixture is heated under reflux until the reaction is complete and cooled to 25°C. The product is filtered off, washed with acetic acid, aqueous sodium hydrogencarbonate solution and water, and
- 15 decocted in 50 ml of methyl ethyl ketone (yield: 2.50 g (43%)).



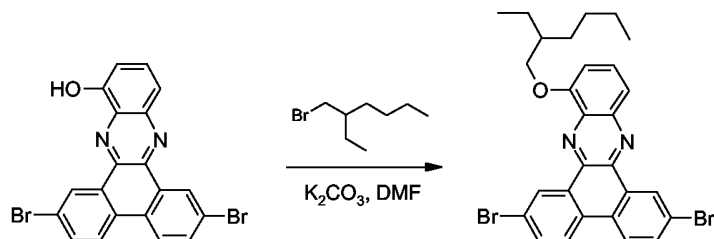
b) The product is prepared according to **example 32b** and recrystallized from di-n-butylether (yield: 1.5 g (51%)).

### Example 36



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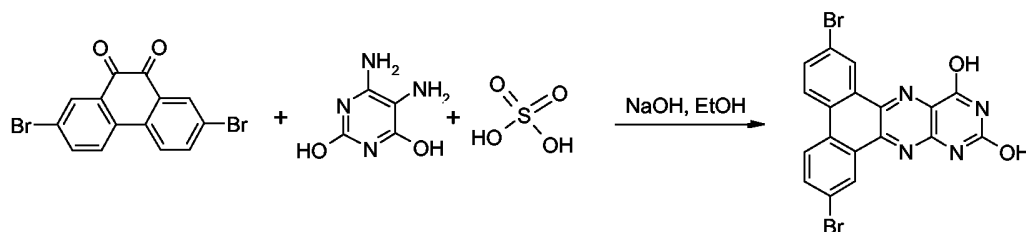
a) To 5 g (13.7 mmol) of 2,7-dibromophenanthrene-9,10-quinone in 200 ml of ethanol are added 2.04 g (16.4 mmol) 2,3-diaminophenol. The reaction mixture is refluxed for two hours. The reaction mixture is cooled to 25°C. The product is filtered off, washed with ethanol and used without purification for the next step.



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b) The product is prepared according to **example 32b** and recrystallized from DMF (yield: 27%). Melting point: 171.5-172.5°C.

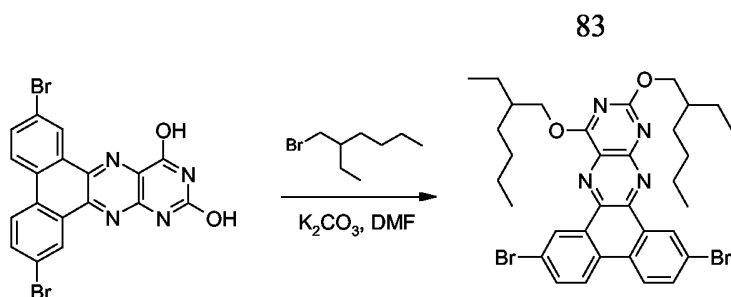
### Example 37



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a) To 5.00 g (13.7 mmol) of 2,7-dibromophenanthrene-9,10-quinone in 250 ml of ethanol are added 3.94 g (16.4 mmol) of 5,6-diamino-2,4-dihydroxypyrimidine sulphate and 1.09 g (27.3 mmol) of NaOH. The reaction mixture is heated under reflux for 5 h and cooled to 25°C. The product is filtered off, washed with ethanol and water and is used without purification for the next step.

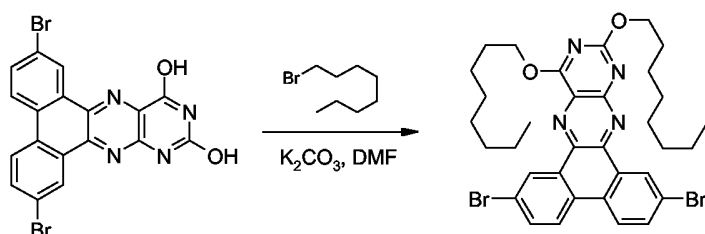
20



b) The product is prepared according to **example 32b**. The product is recrystallized from DMF and further purified via column chromatography (SiO<sub>2</sub>, toluene/cyclohexane 2:1) giving the title compound (yield: 1.13 g (13%)). Melting point: 157.5 -159.5°C.

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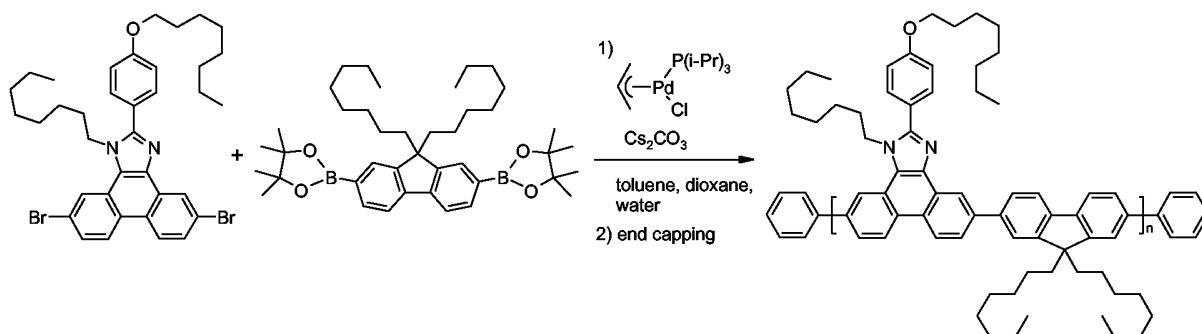
### Example 38



The product is prepared according to **example 37b** and recrystallized from diethyl ether and DMF (yield: 40%). Melting point: 173.5-174.5°C.

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### Example 39



1.0778 g (1.56 mmol) of the dibromide product of **example 9c** and 1.0000 g (1.56 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene are dissolved in 15 ml of dioxane and 5 ml of toluene. This solution is degassed with argon. 50 mg of allyl(triisopropylphosphine)palladium chloride are added and the reaction mixture is degassed with argon. 2.5352 g (7.78 mmol) of cesium carbonate in 5 ml of water are degassed and added to the reaction mixture. After degassing, the reaction mixture is heated under reflux for a total of 18 h. After 2 h reaction 3 ml of degassed dioxane and 3 ml of degassed toluene are added. After an additional 30 minutes reaction 6 ml of degassed toluene are added. After an additional 4 h reaction 8 ml of toluene are added. 370 mg (2.33 mmol) of degassed bromobenzene are added and the reaction mixture is heated under reflux for two hours. A

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degassed solution of 789 mg (3.89 mmol) of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane in 5 ml of toluene is added and the reaction mixture is stirred for two hours. The reaction mixture is poured into 300 ml of methanol. GPC (polystyrene standard)  $M_w = 201\,828$  g/mol, PD = 4.96.

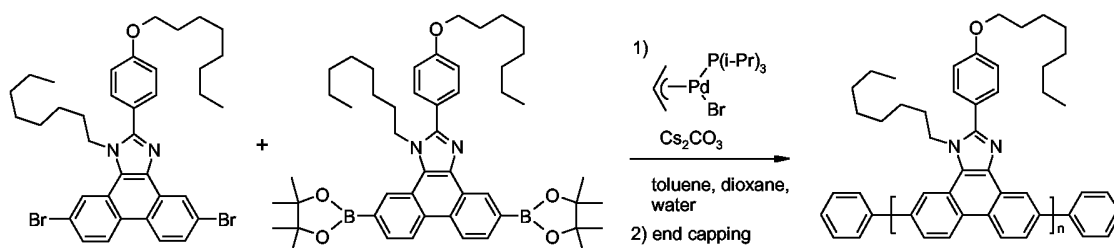
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This polymer is purified as described in **example 11**. After purification the polymer shows the following GPC data (polystyrene standard):  $M_w = 135\,084$  g/mol, PD = 3.24.

0.8 wt% by weight of the product of **example 39** is dissolved in toluene. This solution is filtered through a Teflon filter having a pore width of 0.2  $\mu\text{m}$  and is spin coated at 150 rpm on a quartz substrate. The film is characterized by UV-VIS and photoluminescent measurements (Perkin Elmer LS 50 B), showing a  $\lambda_{\text{max}}$  at 392 nm in the absorption spectrum of the solid film and an emission maximum at 434 nm (excitation wavelength 368 nm) in the photoluminescent spectrum. A solid state quantum yield of 75% was obtained in the film relative to a polyfluorene homopolymer standard.

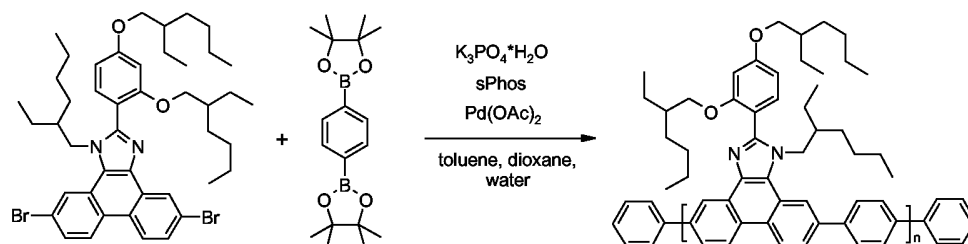
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#### Example 40



1.0564 g (1.53 mmol) of the dibromide product of **example 9c** and 1.2000 g (1.53 mmol) of the diboronate product of **example 14** are dissolved in 15 ml of dioxane and 5 ml of toluene. This solution is degassed with argon. 61 mg of allyl(triisopropylphosphine)palladium bromide (CAS 244159-80-6) are added and the reaction mixture is degassed with argon. 2.4849 g (7.63 mmol) of cesium carbonate in 5 ml of water are degassed and added to the reaction mixture. After degassing, the reaction mixture is heated under reflux for a total of 18 h. After 40 minutes reaction 2 ml of degassed toluene are added. During the reaction 2 ml of degassed toluene are added for an additional six times. 360 mg (2.29 mmol) of degassed bromobenzene are added and the reaction mixture is heated under reflux for two hours. A degassed solution of 780 mg (3.81 mmol) of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane in 5 ml of toluene is added and the reaction mixture is stirred for two hours. The reaction mixture is poured into 300 ml of methanol. GPC (polystyrene standard):  $M_w = 6120$  g/mol, PD = 1.77.

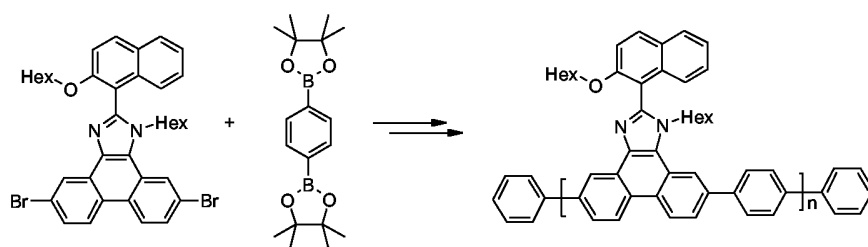
30

**Example 41**

A mixture of 0.9290 g (2.8148 mmol) of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene and 2.3104 g (2.8148 mmol) of the dibromide product of **example 27** are dissolved in 15 ml of toluene and 15 ml of dioxane. This solution is evacuated and refilled with argon three times. 69.3 mg (0.169 mmol) of 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (sPhos) are added. The reaction mixture is degassed with argon. 63 mg (0.028 mmol) of palladium(II)acetate are added and the reaction mixture is degassed with argon. 3.41 g (14.1 mmol) of potassium phosphate tribasic monohydrate in 4.5 ml of water are degassed and added to the reaction mixture. After degassing, the reaction mixture is heated under reflux for 20 h. 663 mg (4.22 mmol) of degassed bromobenzene is added and the reaction mixture is heated under reflux for two hours. A degassed solution of 1.44 g (7.037 mmol) of 4,4,5,5-tetramethyl-2-phenyl-[1,3,2]dioxaborolane in 3 ml of toluene is added. The reaction mixture is heated under reflux for two hours, cooled to 25°C and treated with 100 ml of 1% aqueous NaCN solution. This mixture is stirred for 8 h at room temperature and is extracted with toluene. The solvent is removed under vacuum until 30 ml are left. The resulting solution is poured into 100 ml of methanol. The polymer is filtered off, dissolved in 30 ml of toluene, and treated with 100 ml of 1% aqueous NaCN solution. This mixture is again stirred for 8 h followed by extraction with toluene. The solvent is removed under vacuum until 30 ml are left. The resulting solution is poured into 100 ml of methanol. The polymer is filtered off and dissolved in 40 ml of THF. This solution is poured into 100 ml of methanol and the polymer is filtered off. Precipitation from THF is repeated once (yield: 1.38 g (67%)). GPC (polystyrene standard):  $M_w = 32\,859$  g/mol, PD = 1.93). Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 450 nm.

**Example 42**

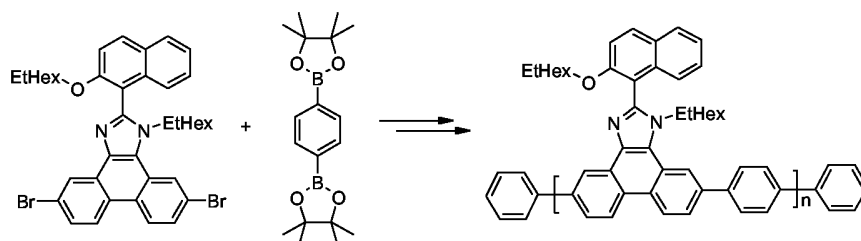
86



According to **example 41** the above polymer is prepared, with dibromide product of **example 12b**, and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. GPC (polystyrene standard):  $M_w = 66\,775$  g/mol, PD = 2.85; Hex = n-hexyl.

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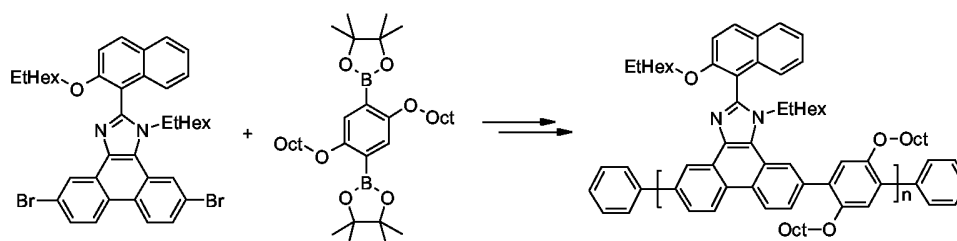
### Example 43



According to **example 41** the above polymer is prepared, with dibromide product of **example 16**, and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. GPC (polystyrene standard):  $M_w = 110\,216$  g/mol, PD = 3.36; EtHex = 2-ethylhexyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 440 nm.

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### Example 44



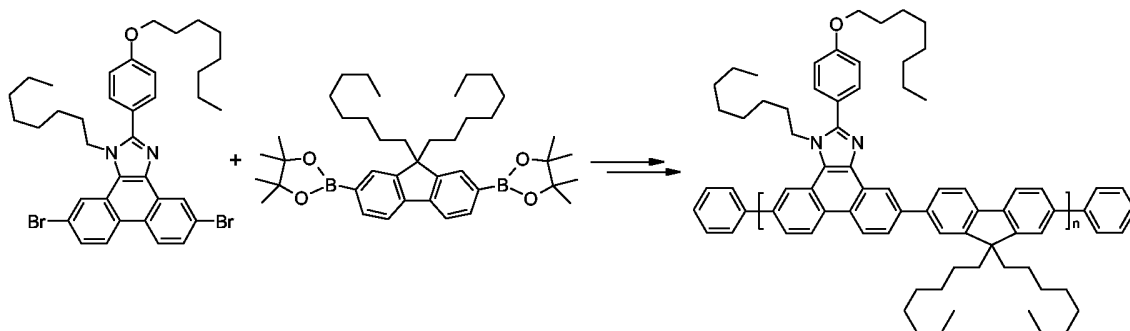
15

According to **example 41** the above polymer is prepared, with dibromide product of **example 16**, and 1,4-bis[4,4,5,5-tetramethyl-(1,3,2)dioxaborolan-2-yl]-2,5-dioctyloxyphenylene (CAS 457931-26-9). GPC (polystyrene standard):  $M_w = 9\,500$  g/mol, PD = 1.20; EtHex = 2-ethylhexyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 428 nm.

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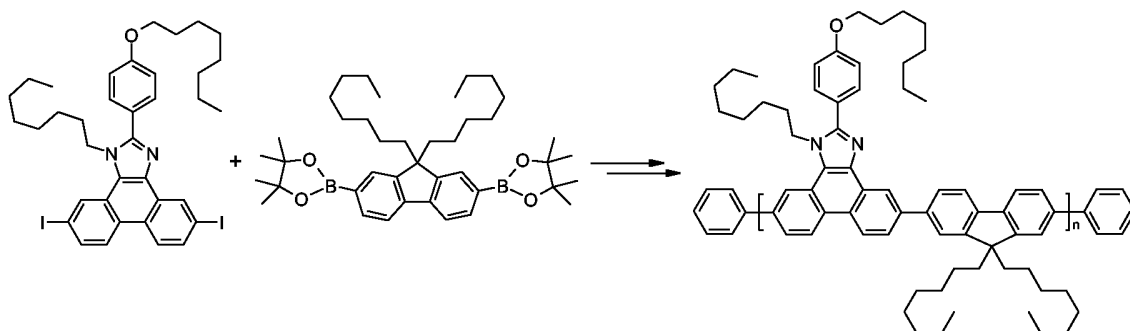
### Example 45

87



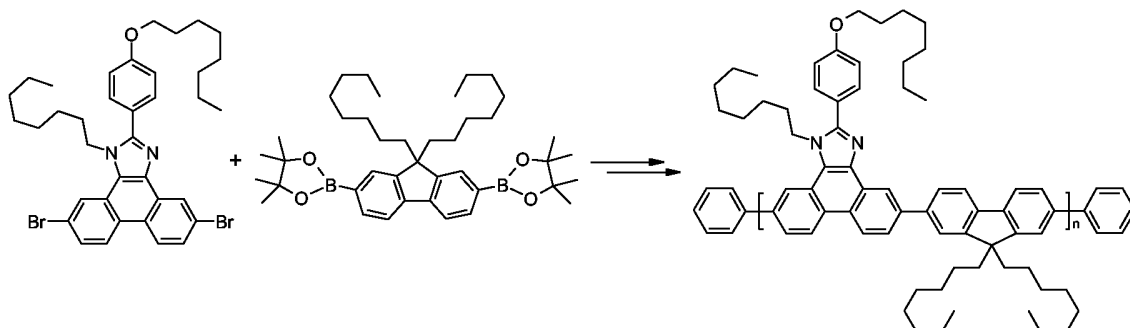
According to **example 41** the above polymer is prepared, with dibromide product of **example 9c**, and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene. GPC (polystyrene standard):  $M_w = 162\,145$  g/mol, PD = 3.87; Oct = n-octyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 433 nm.

#### Example 46



According to **example 85** the above polymer is prepared, with diiodide product of **example 10c**, and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene. GPC (polystyrene standard):  $M_w = 39\,438$  g/mol, PD = 2.23; Oct = n-octyl.

#### Example 47



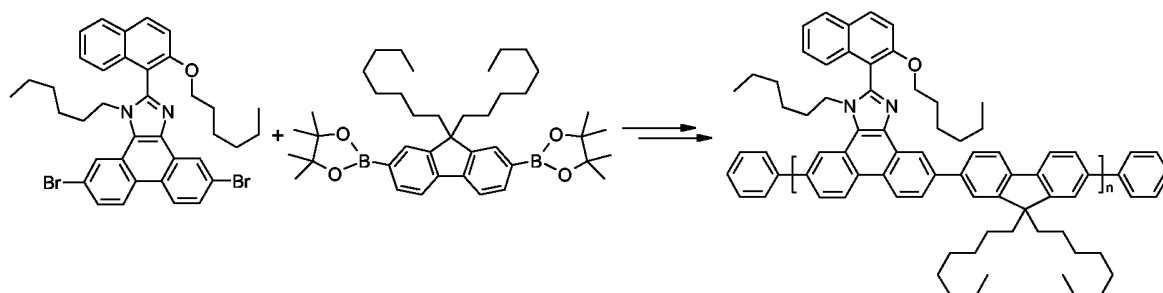
According to **example 41** the above polymer is prepared, with dibromide product of **example 9c**, and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene. GPC (polystyrene standard):  $M_w = 162\,145$  g/mol, PD = 3.87; Oct = n-octyl. Photoluminescent measure-



ments of the polymer product have been performed as described in **example 39**: emission maximum at 433 nm.

### Example 48

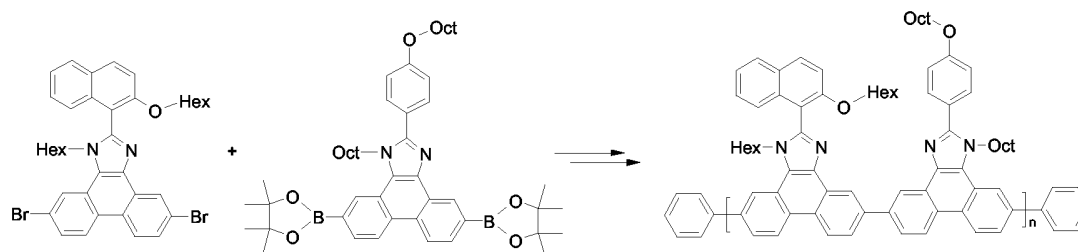
5



According to **example 85** the above polymer is prepared, with dibromide product of **example 12b**, and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene. GPC (polystyrene standard):  $M_w = 153\,310$  g/mol, PD = 2.59; Oct = n-octyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 431 nm.

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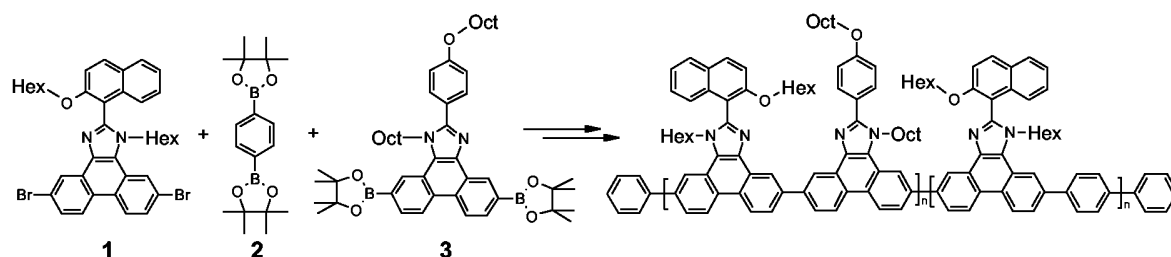
### Example 49



According to **example 41** the above polymer is prepared, with dibromide product of **example 12b**, and diboronate product of **example 14**. GPC (polystyrene standard):  $M_w = 196\,000$  g/mol, PD = 4.70; Oct = n-octyl; Hex = n-hexyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 465 nm.

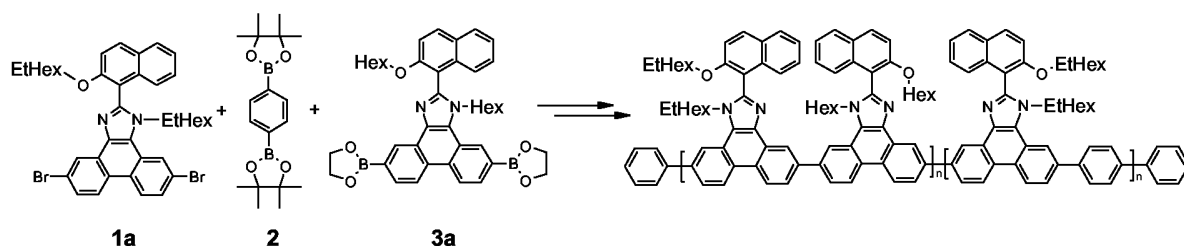
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### Example 50



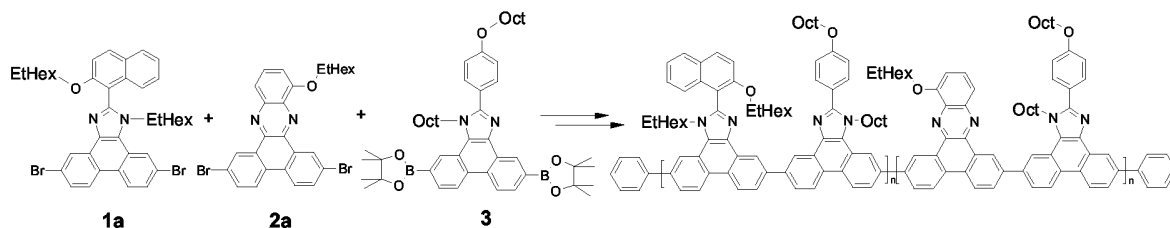
According to **example 41** the above polymer is prepared, with dibromide product of **example 12b** (**1**), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**2**), and diboronate product of **example 14** (**3**). The monomers **1/2/3** are used in a ratio of 2:1:1. GPC (polystyrene standard):  $M_w = 741\ 100$  g/mol, PD = 7.0; Oct = n-octyl; Hex = n-hexyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 458 nm.

### Example 51



According to **example 41** the above polymer is prepared, with dibromide product of **example 16** (**1a**), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**2**), and diboronate product of **example 31b** (**3a**). The monomers **1a/2/3a** are used in a ratio of 2:1:1. GPC (polystyrene standard):  $M_w = 53\ 180$  g/mol, PD = 2.38; EtHex = 2-ethylhexyl.

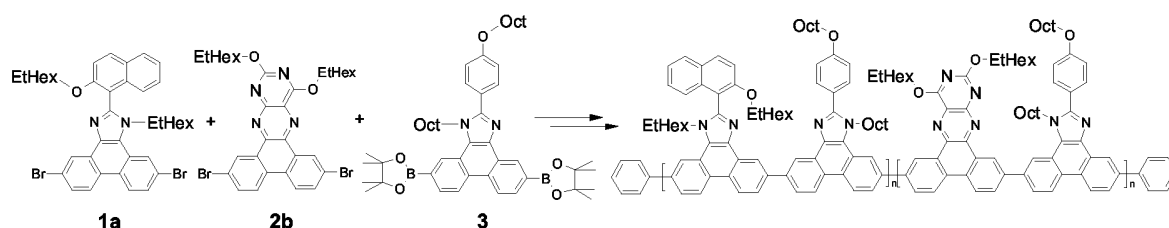
### Example 52



According to **example 41** the above polymer is prepared, with dibromide product of **example 16** (**1a**), dibromide product of **example 36b** (**2a**), and diboronate product of **example 14** (**3**). The monomers **1a/2a/3** are used in a ratio of 1:1:2. GPC (polystyrene standard):  $M_w = 48\ 558$  g/mol, PD = 2.00; EtHex = 2-ethylhexyl; Oct = n-octyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 525 nm.

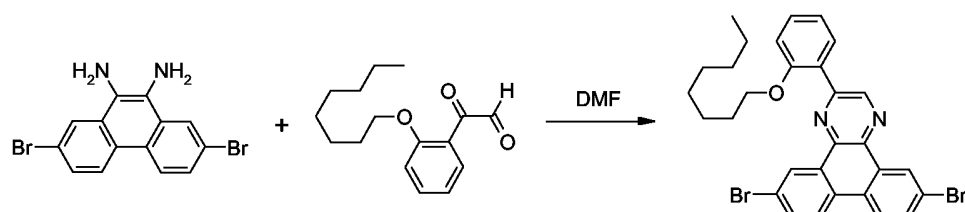
### Example 53

90



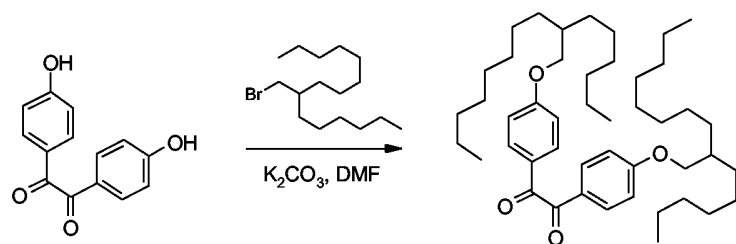
According to **example 41** the above polymer is prepared, with dibromide product of **example 16** (**1a**), dibromide product of **example 37b** (**2b**), and diboronate product of **example 14** (**3**). The monomers **1a/2b/3** are used in a ratio of 1:1:2. GPC (polystyrene standard):  $M_w = 332$  100 g/mol, PD = 6.10; GPC (absolute calibration):  $M_w = 255$  100 g/mol, PD = 2.70; EtHex = 2-ethylhexyl; Oct = n-octyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 547 nm.

### Example 54



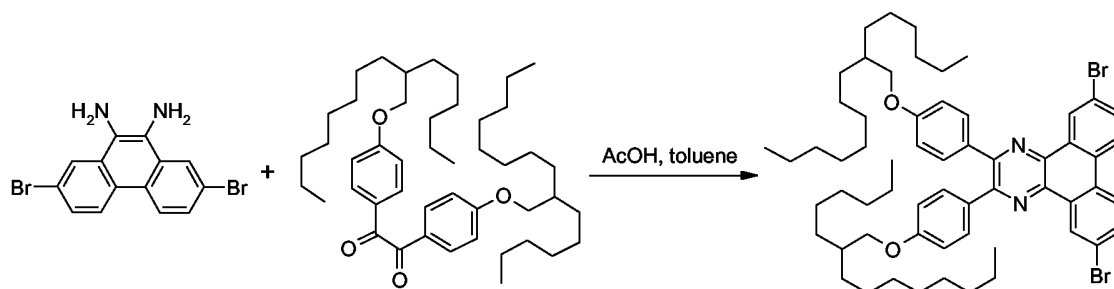
To 3.00 g (8.2 mmol) of 2,7-dibromo-phenanthrene-9,10-diamine in 50 ml of dimethylformamide are added 2.90 g (11.1 mmol) of 2-octyloxyphenylglyoxal. The reaction mixture is heated at 120°C for 14 h, then cooled to 25°C. EtOAc (250 ml) and water (200 ml) are added, the phases separated and the organic phase washed with water (3 x 250 ml) and 15 brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered over a plug of silica and evaporated under reduced pressure. A column chromatography on silica gel (hexane/EtOAc 20:1) followed by crystallization (EtOAc) leads to the product in form of a yellow solid (yield: 19%). Melting point: 113.5-116°C.

### Example 55



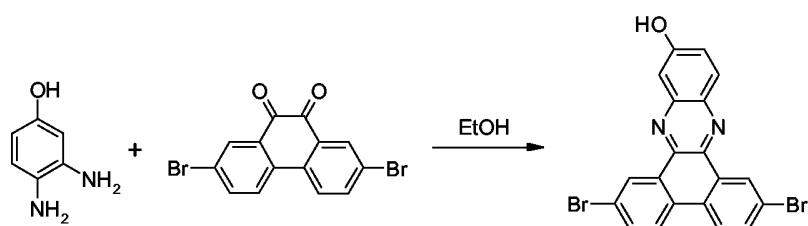
a) To 3.0 g (12.4 mmol) of 4,4'-dihydroxybenzil and 8.56 g (61.9 mmol) of potassium carbonate in dimethylformamide (30 ml) are added 11.34 g (37.2 mmol) of 1-bromo-2-hexyldecane. The reaction mixture is heated at 120°C for 22 h, then poured into  $\text{H}_2\text{O}$  and

extracted with  $\text{CH}_2\text{Cl}_2$ . Column chromatography on silica gel (hexane/EtOAc 20:1) leads to the product in form of a yellow liquid (yield: 100%).

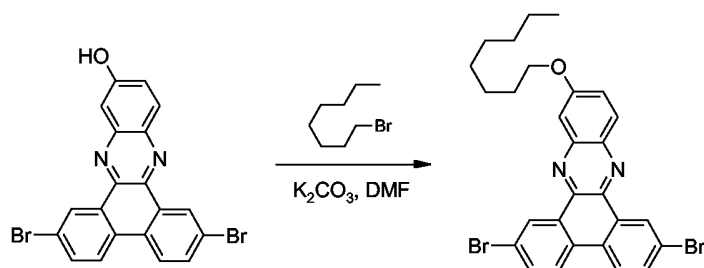


b) To 1.85 g (5.05 mmol) of 2,7-dibromo-phenanthrene-9,10-diamine in 50 ml of AcOH and 25 ml of toluene is added 4.19 g (6.06 mmol) of 4,4'-bis-(2-hexyloxy)benzil. The reaction mixture is heated under reflux for 18 h, and then the solvents are evaporated under reduced pressure. Column chromatography on silica gel (hexane/EtOAc 30:1) followed by trituration (EtOH) leads to the product in form of a yellow solid (yield: 75%). Melting point: 66-67°C.

#### Example 56



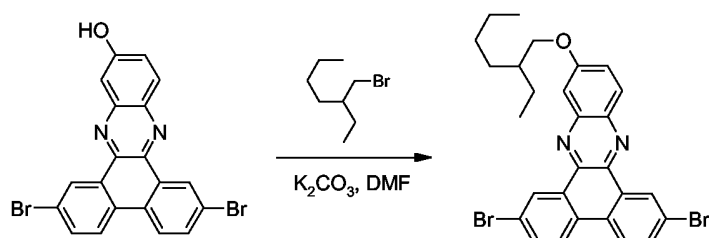
a) To a suspension of 10.98 g (30.0 mmol) of 2,7-dibromophenanthrene-9,10-quinone in EtOH (250 ml), 4.47 g (36.0 mmol) of 3,4-diaminophenol are added. The reaction mixture is stirred under reflux for 3 h, then water (100 ml) is added and the reaction mixture is cooled to room temperature, filtered and washed with EtOH to afford the product as an olive-green solid (yield: 87%).



b) To 0.23 g (0.50 mmol) of the product of **example 56a**, 0.14 g (0.75 mmol) of 1-bromooctane, 0.21 g (1.50 mmol) of potassium carbonate and 5 ml dimethylformamide are added. The reaction mixture is stirred under nitrogen at 120°C. After two hours, EtOH (20 ml)

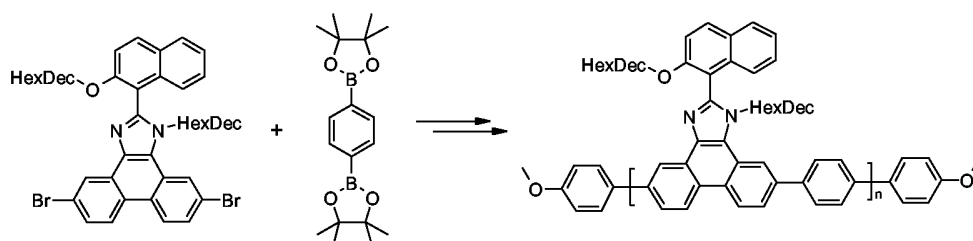
and water (20 ml) are added, the mixture cooled to room temperature and filtered to yield the product as a brown solid (yield: 88%). Melting point 150-152°C.

### Example 57



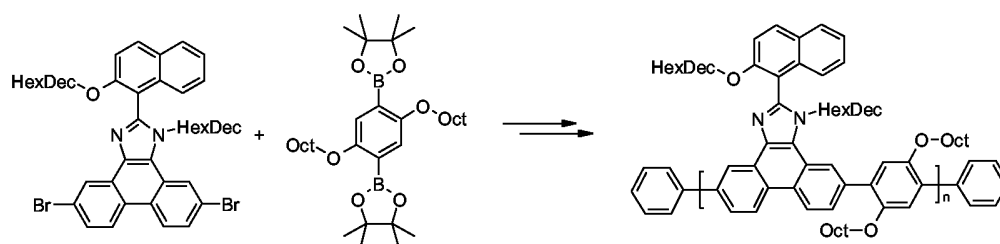
To 6.81 g (15 mmol) of the product of **example 56a**, 4.35 g (22.5 mmol) of 1-bromo-2-ethylhexane, 6.22 g (45 mmol) of potassium carbonate and 100 ml of dimethylformamide are added. The reaction mixture is stirred under nitrogen at 120°C. After 3.5 h water (150 ml) is added, the mixture cooled to room temperature and filtered. The crude product is purified by recrystallization from dimethylformamide and hexane/toluene to give a yellow-brown solid (yield: 55%). Melting point: 146.5-148°C.

### Example 58



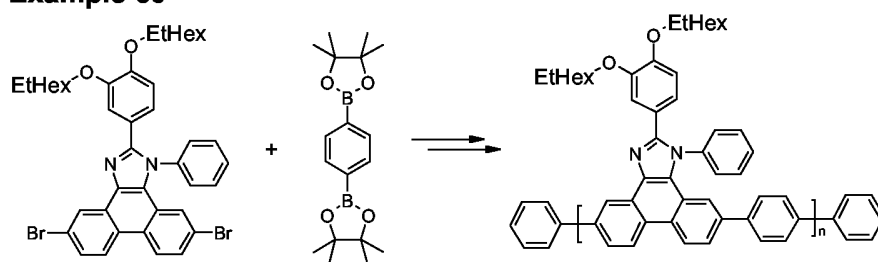
The above polymer is prepared according to **example 41**, with dibromide product of **example 17**, and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. and 4-methoxyphenyl-bromide have been used as end-capping reagents. GPC (polystyrene standard):  $M_w = 250\ 200$  g/mol, PD = 4.3; GPC (absolute calibration):  $M_w = 165\ 300$  g/mol, PD = 2.9; HexDec = 2-hexyldecyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 439 nm.

### Example 59



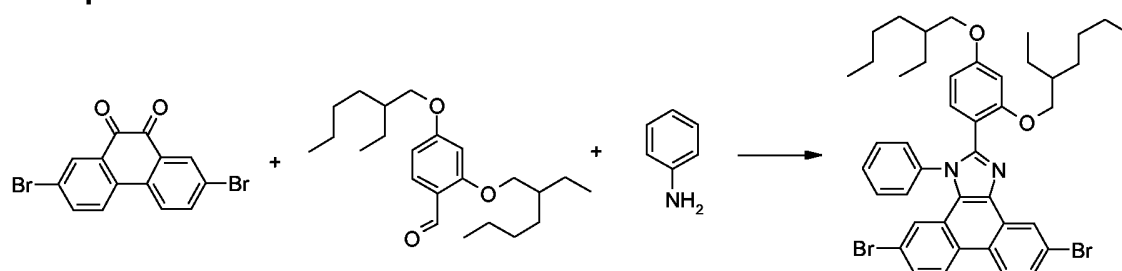
The above polymer is prepared according to **example 41**, with dibromide product of **example 17**, and 1,4-bis[4,4,5,5-tetramethyl-(1,3,2)dioxaborolan-2-yl]-2,5-dioctyloxyphenylene (CAS 457931-26-9). GPC (polystyrene standard):  $M_w = 100\,000$  g/mol, PD = 2.1; GPC (absolute calibration):  $M_w = 42\,700$  g/mol, PD = 1.7; HexDec = 2-hexyldecyl.  $M_w = 165\,300$  g/mol, PD = 2.9; HexDec = 2-hexyldecyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 423 nm.

### Example 60



The above polymer is prepared according to **example 41**, with dibromide product of **example 28**, and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. GPC (absolute calibration):  $M_w = 1\,061\,000$  g/mol, PD = 1.9; EtHex = 2-ethylhexyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 471 nm.

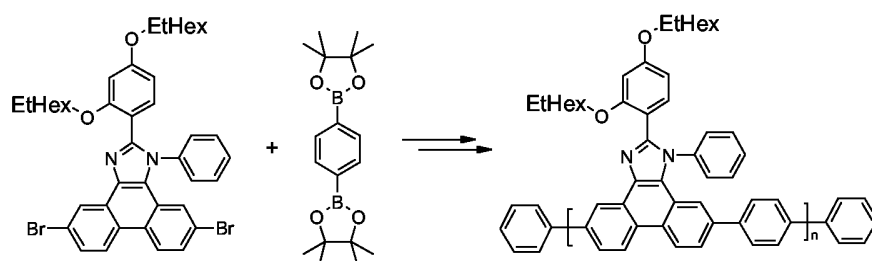
### Example 61



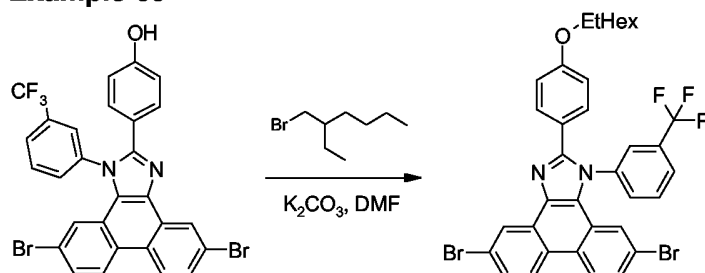
The product is prepared according to **example 28b** (yield: 34%).

### Example 62

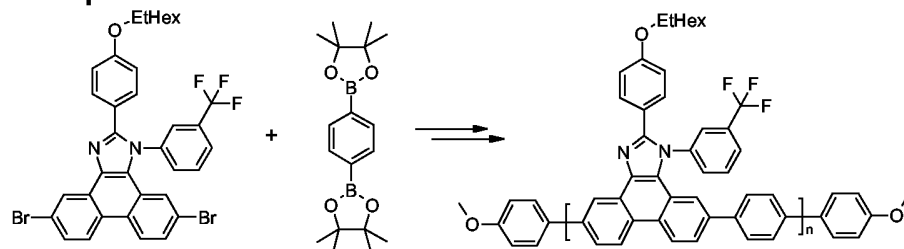
94



The above polymer is prepared according to **example 41**, with dibromide product of **example 61**, and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. GPC (absolute calibration):  $M_w = 560\,000$  g/mol, PD = 2.4; EtHex = 2-ethylhexyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 459 nm.

**Example 63**

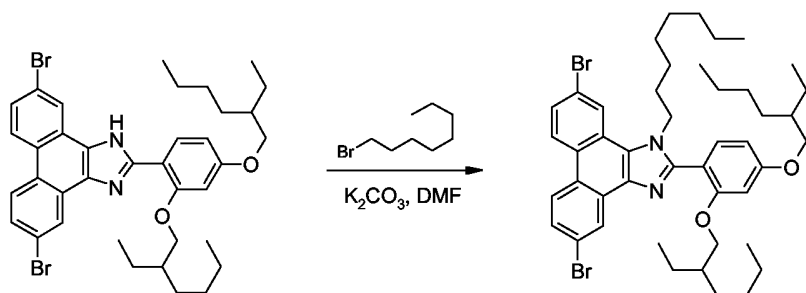
The product is prepared according to **example 32b** (yield: 45%). Melting point: 144-145°C; EtHex = 2-ethylhexyl.

**Example 64**

The above polymer is prepared according to **example 41**, with dibromide product of **example 63**, and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. and 4-methoxyphenyl-bromide have been used as end-capping reagents. GPC (absolute calibration):  $M_w = 1\,794\,000$  g/mol, PD = 2.5; EtHex = 2-ethylhexyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 472 nm.

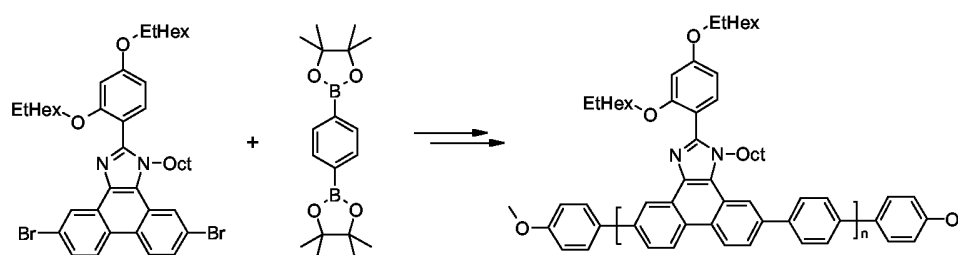
**Example 65**

95



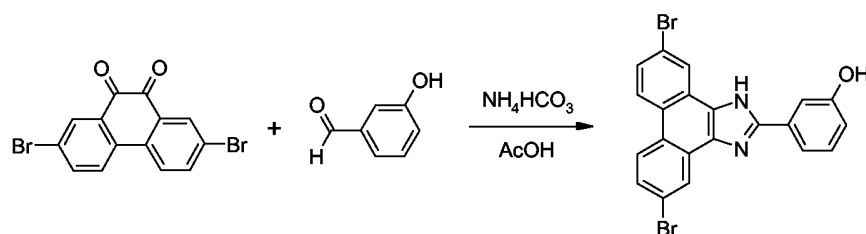
The product is prepared according to **example 27**, giving the product as an oil (yield: 26%).

### Example 66

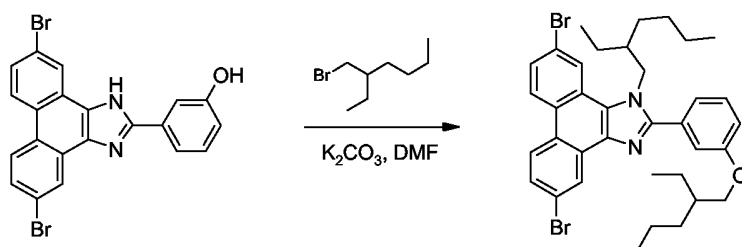


The above polymer is prepared according to **example 41**, with dibromide product of **example 65**, and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 4-methoxyphenyl-bromide have been used as end-capping reagents. GPC (absolute calibration):  $M_w = 604\ 000$  g/mol, PD = 2.10; EtHex = 2-ethylhexyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 435 nm.

### Example 67

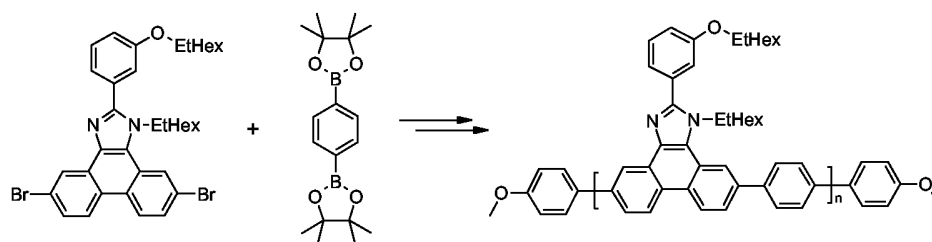


a) The product is prepared according to **example 9b** (yield: 100%).

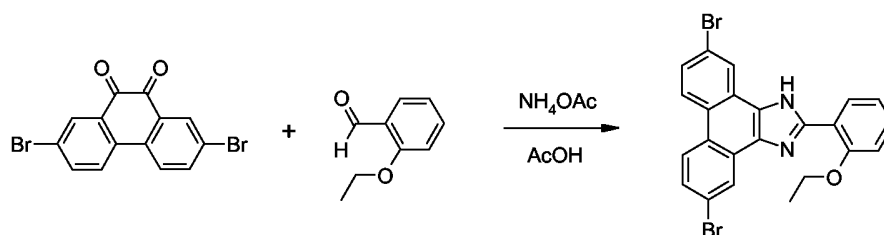


b) The product is prepared according to **example 9c**, giving the product as an oil (yield: 84%).



**Example 68**

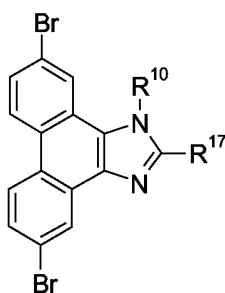
The above polymer is prepared according to **example 41**, with dibromide product of **example 67**, and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. and 4-methoxyphenyl-bromide have been used as end-capping reagents. GPC (absolute calibration):  $M_w = 1\,108\,000$  g/mol, PD = 2.1; EtHex = 2-ethylhexyl. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 460 nm.

**Example 69**

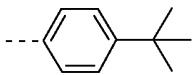
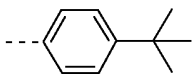
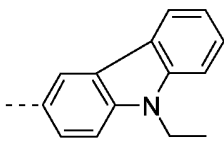
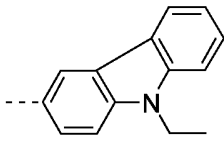
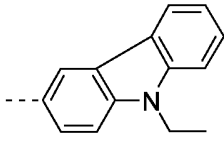
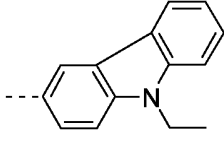
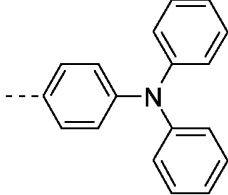
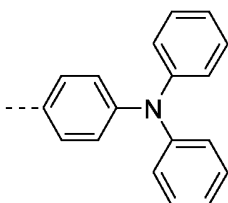
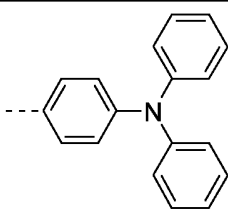
To a suspension of 21.9 g (55.0 mmol) of 2,7-dibromophenanthrene-9,10-quinone in 150 ml of acetic acid are added 12.8 g (82.5 mmol) of 2-ethoxybenzaldehyde and 43.7 g (0.55 mol) of ammonium acetate under a nitrogen atmosphere. The red suspension is heated under reflux for 22 h. The resulting beige suspension is filtered and the solid washed with acetic acid, providing the crude product as a beige solid. The wet product is decanted under reflux with 150 ml of acetic acid for 30 min. The suspension is cooled down to room temperature, filtered and decanted again in 100 ml of acetic acid. The suspension is filtered and the resulting solid washed with acetic acid and ethanol, and then dried under vacuum at 60°C. 27.0 g of the title compound are obtained as a beige solid (yield: 96%).

The compounds shown in the table below are prepared in analogy to the examples described above:

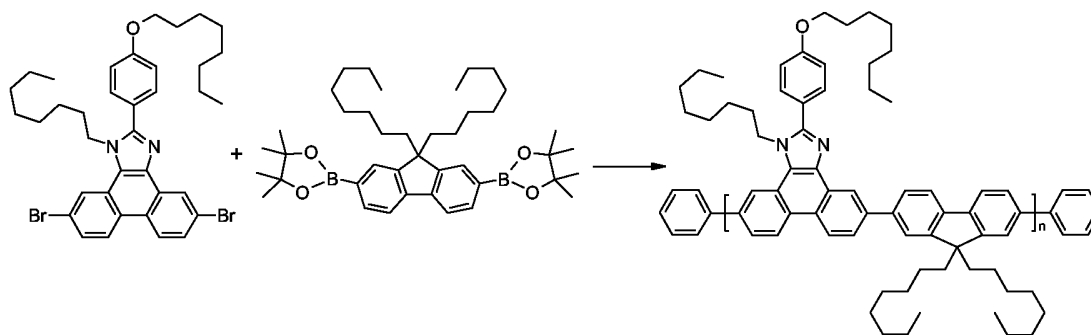
97



Example	R <sup>10</sup>	R <sup>17</sup>	Yield [%]	Melting Point [°C]
70		2-ethylhexyl	80	105-108
71		2-hexyldecyl	55	light yellow, viscous oil
72		2-hexyldecyl	89	light yellow, viscous oil
73		1-octyl	67	100-103
74		H	quantitative	yellow solid >300
75		H	84	white solid 270-273

76		H	quantitative	white solid >300
77		1-octyl	47	light yellow solid 114.5-116
78		H	99	light grey solid >300
79		1-octyl	20	white solid 165-168
80		2-ethylhexyl	82	yellow viscous oil
81		2-hexyldecyl	56	yellow slightly viscous solid
82		H	quantitative	light beige solid >300
83		2-ethylhexyl	78	light beige solid 70-73
84		2-hexyldecyl	57	light yellow viscous oil, which solidifies upon standing

**Example 85**



a) 1.0590 g (1.53 mmol) of the dibromide product of **example 9c** and 1.0000 g (1.56 mmol,) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene are placed under argon atmosphere in a dry *Schlenk* tube in 15 ml of dioxane and 5 ml of toluene. The solution is degassed with argon. 28.5 mg (0.094 mmol) of tri(*o*-tolyl)phosphine are added and the reaction mixture is degassed. 3.5 mg (0.016 mmol) of palladium(II)acetate are added and the reaction mixture is degassed. A solution of 1.89 g (7.80 mmol, 5.0 equiv.) of potassium phosphate tribasic monohydrate and 3 ml of water is degassed and added to the reaction mixture. The resulting suspension is heated at 90°C oil bath temperature. An increase of viscosity of the reaction mixture with the appearance of a bluish fluorescence is observed after two hours. Additional amounts of degassed toluene are added to decrease the viscosity. After 20 h the oil bath temperature is increased up to 100°C. 367 mg (2.34 mmol,) of degassed bromobenzene are added and the reaction mixture is heated for two hours. A degassed solution of 796 mg (3.89 mmol) of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane in 3 ml toluene is added. The reaction mixture is heated for two hours, cooled to room temperature, and diluted with 65 ml of toluene. 32 ml of 1% aqueous NaCN solution are added and the mixture is stirred during three hours at room temperature. The organic phase is washed three times with 100 ml water, and the collected water phases two times with 100 ml toluene. The combined organic phases are concentrated under vacuum until 65 ml are left. The resulting solution is poured into 160 ml of methanol. The polymer is filtered off and dissolved in 190 ml of THF. The solution is poured into 380 ml of methanol and the polymer filtered off, giving 1.33 g of a yellow solid. GPC (polystyrene standard):  $M_w = 223\,765$  g/mol, PD = 2.37.

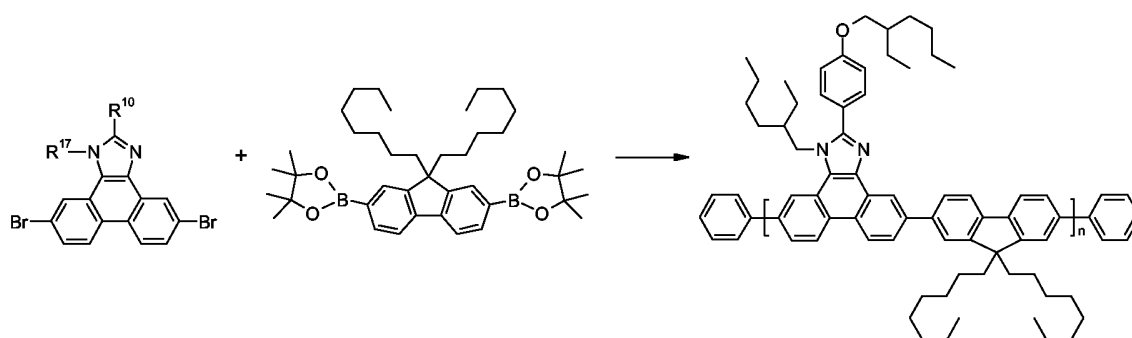
## 25 **Example 86**

The copolymerization reaction is performed according to **example 85**, except that the oil bath temperature is 110°C instead of 90°C. 1.42 g of a yellow solid are obtained. GPC (polystyrene standard):  $M_w = 136\,477$  g/mol, PD = 2.71.

## 30 **Example 87**

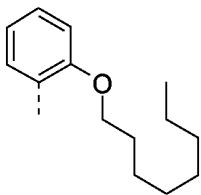
The copolymerization reaction is performed according to **example 85**, except that 0.01 equivalents of allyl(triisopropylphosphine)palladium bromide (CAS 244159-80-6) are used instead of tri(o-tolyl)phosphine/palladium(II)acetate, 5.0 equivalents of potassium carbonate are used instead of potassium phosphate tribasic monohydrate, and the oil bath temperature is 120°C instead of 90°C. 1.54 g of a yellow solid are obtained. GPC (polystyrene standard):  $M_w = 159\,393$  g/mol, PD = 2.43.

The polymers shown in the table below are prepared in analogy to the examples described above:



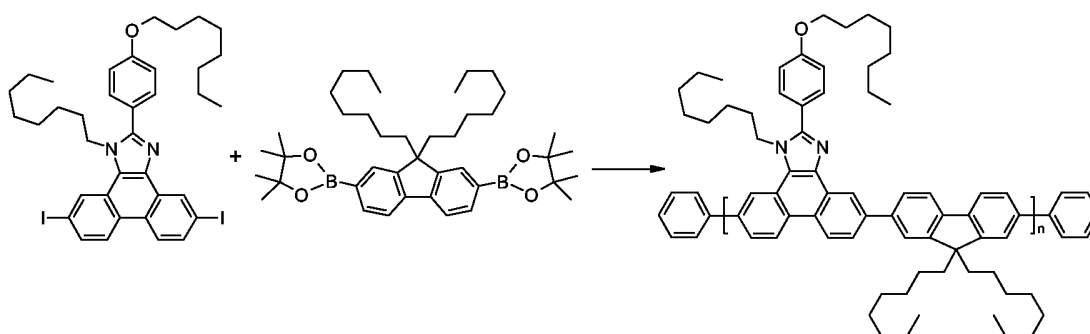
10

Example	R <sup>10</sup>	R <sup>17</sup>	M <sub>w</sub> [g/mol, GPC]	PD
88		2-ethylhexyl	171 224	3.81
89		1-octyl	184 764	3.75
90		1-hexyl	138 987	3.03
91		2-ethylhexyl	74 866	2.94

92		1-octyl	151 200	2.46
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Photoluminescent measurements of the polymer products have been performed as described in **example 39**: emission maximum at 428 nm for **90**, 424 nm for **91**, and 430 nm for **92**.

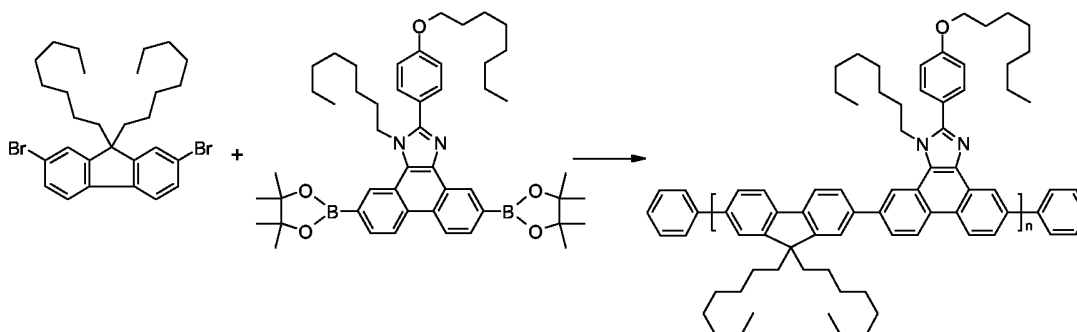
### 5 Example 93



The copolymerization reaction has been performed according to the procedure of **example 85**, with 1.0 equivalents of the diiodide product of **example 11** and 1.0 equivalents of 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-diocetylfluorene. A yellow solid is obtained.

10 GPC (polystyrene standard):  $M_w = 83\,917$  g/mol, PD = 2.78. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 433 nm.

### Example 94

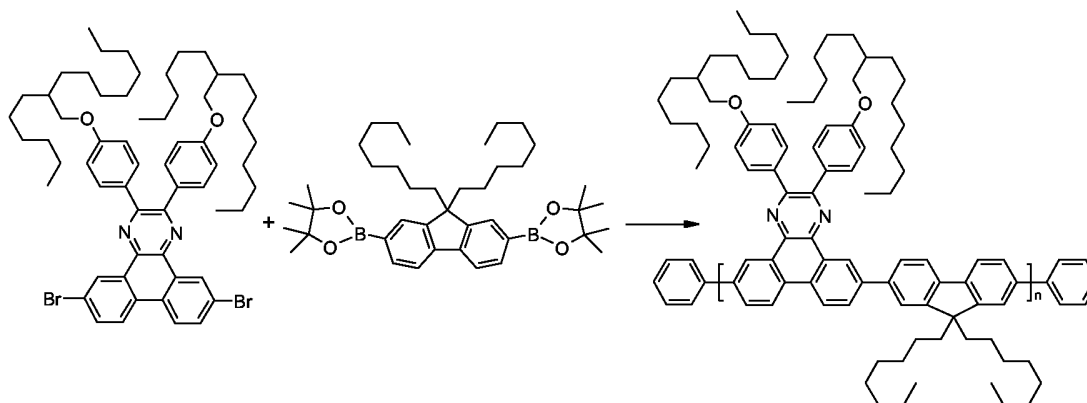


15

The copolymerization reaction has been performed according to the procedure of **example 85**, with 1.0 equivalents of 9,9-diocetyl-2,7-dibromofluorene and 1.0 equivalents of the diboronate product of **example 14**. A yellow solid is obtained. GPC (polystyrene standard):

$M_w = 62\,674$  g/mol, PD = 2.99. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 434 nm.

### Example 95

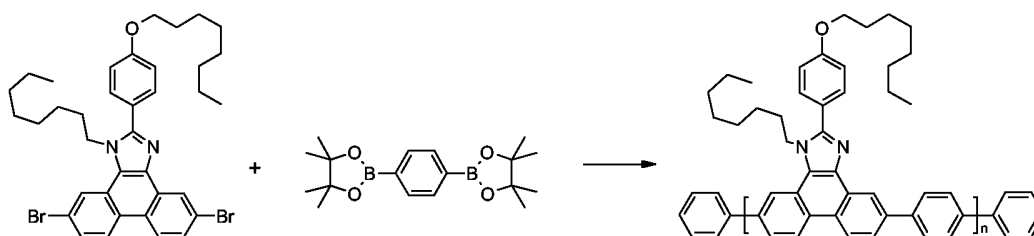


5

The copolymerization reaction is performed according to the procedure of **example 85**, with 1.0 equivalents of the dibromide product of **example 55b** and 1.0 equivalents of 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 20\,174$  g/mol, PD = 2.80.

10

### Example 96



The copolymerization reaction is performed according to the procedure of **example 85**, with 1.0 equivalents of the dibromide product of **example 9c** and 1.0 equivalents of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 51\,760$  g/mol, PD = 2.15.

15

### Example 97

The copolymerization reaction is performed according to the procedure of **example 96**, except that 5.0 equivalents of potassium carbonate are used instead of potassium phosphate tribasic monohydrate, and the oil bath temperature is 120°C instead of 90°C. A yellow solid is obtained with  $M_w = 50\,982$ , PD = 2.14.

20

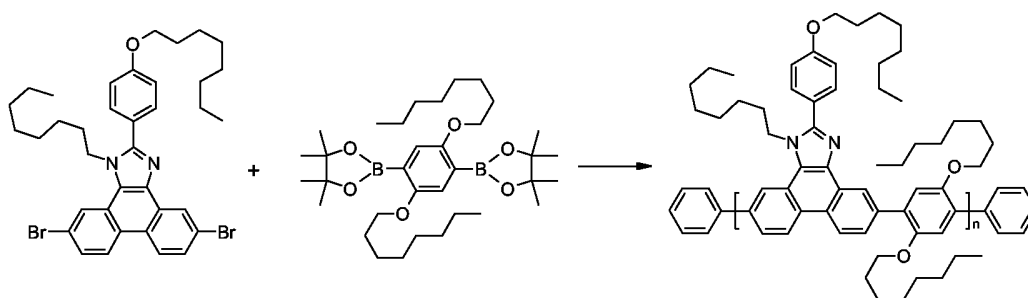
### Example 98

The copolymerization reaction is performed according to the procedure of **example 96**, except that 0.01 equivalents of allyl(triisopropylphosphine)palladium bromide (CAS 244159-80-6) are used instead of tri(o-tolyl)phosphine/palladium(II)acetate, 5.0 equivalents of cesium carbonate are used instead of potassium phosphate tribasic monohydrate, and the oil bath temperature is 120°C instead of 90°C. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 14\,535$ , PD = 1.28.

### Example 98

The copolymerization reaction is performed according to the procedure of **example 96**, except that 0.01 equivalents of 2-(dimethylamino)-2-biphenyl-palladium(II)-chlorid dinorbornylphosphin-complex (CAS 359803-53-5) are used instead of tri(o-tolyl)phosphine/palladium(II)acetate, 5.0 equivalents of cesium carbonate are used instead of potassium phosphate tribasic monohydrate, 15 ml toluene and 0.27 g of Aliquat® 336 are used instead of dioxane and 3 ml of water, and the oil bath temperature is 120°C instead of 90°C. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 48\,804$ , PD = 1.86.

### Example 100

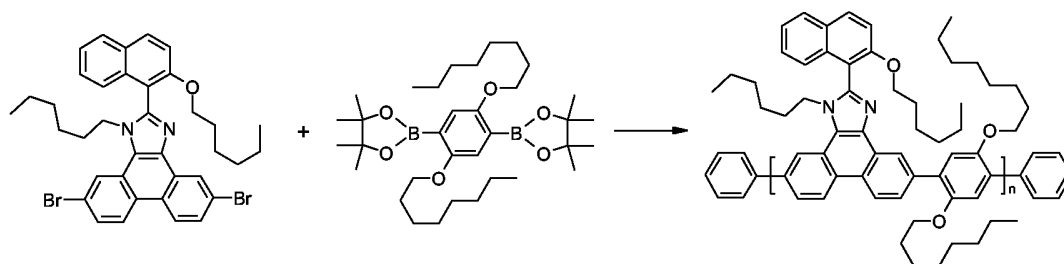


The copolymerization reaction is performed according to the procedure of **example 85**, with 1.0 equivalents of the dibromide product of **example 9c** and 1.0 equivalents of 1,4-bis[4,4,5,5-tetramethyl-(1,3,2)dioxaborolan-2-yl]-2,5-dioctyloxyphenylene (CAS 457931-26-9). A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 84\,017$ , PD = 4.58. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 435 nm.

### Example 101

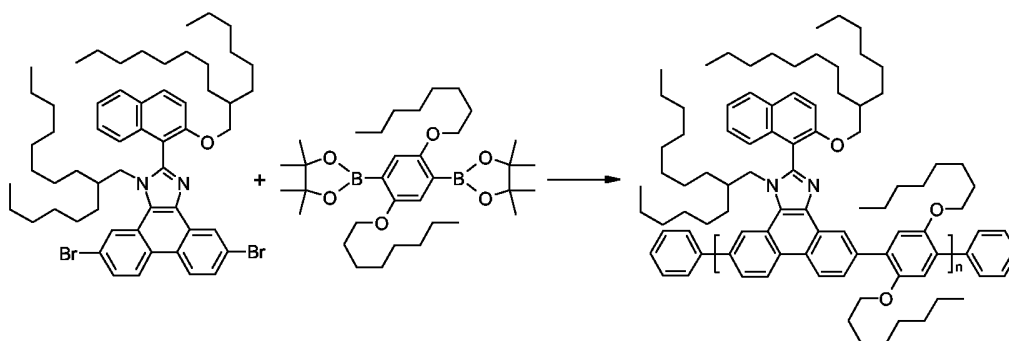


104



The copolymerization reaction has been performed according to the procedure of **example 85**, with 1.0 equivalents of the dibromide product of **example 12b** and 1.0 equivalents of 1,4-bis[4,4,5,5-tetramethyl-(1,3,2)dioxaborolan-2-yl]-2,5-dioctyloxyphenylene (CAS 457931-26-9). A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 46\,509$ , PD = 2.82. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 430 nm.

#### Example 102



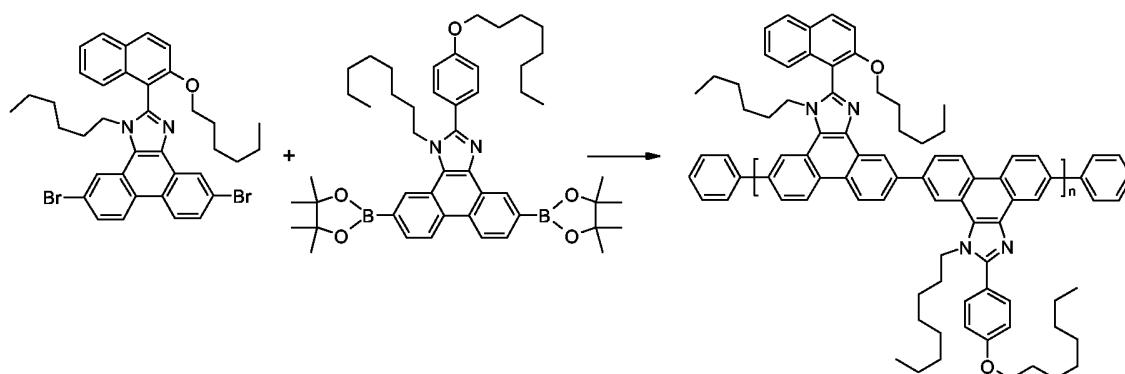
10

The copolymerization reaction is performed according to the procedure of **example 85**, with 1.0 equivalents of the dibromide product of **example 71** and 1.0 equivalents of 1,4-bis[4,4,5,5-tetramethyl-(1,3,2)dioxaborolan-2-yl]-2,5-dioctyloxyphenylene (CAS 457931-26-9). A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 90\,075$ , PD = 5.85. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 427 nm.

15

#### Example 103

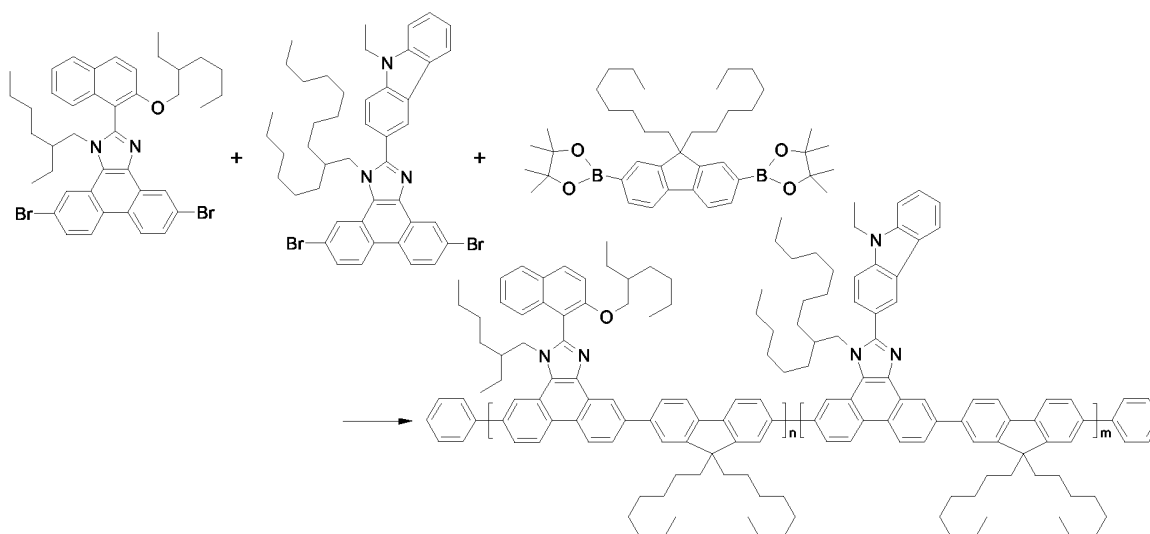
105



The copolymerization reaction has been performed according to the procedure of **example 85**, with 1.0 equivalents of the dibromide product of **example 12b** and 1.0 equivalents of the diboronate product of **example 14**. A yellow solid is obtained. GPC (polystyrene standard):

5  $M_w = 21\,356$ , PD = 3.66. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 469 nm.

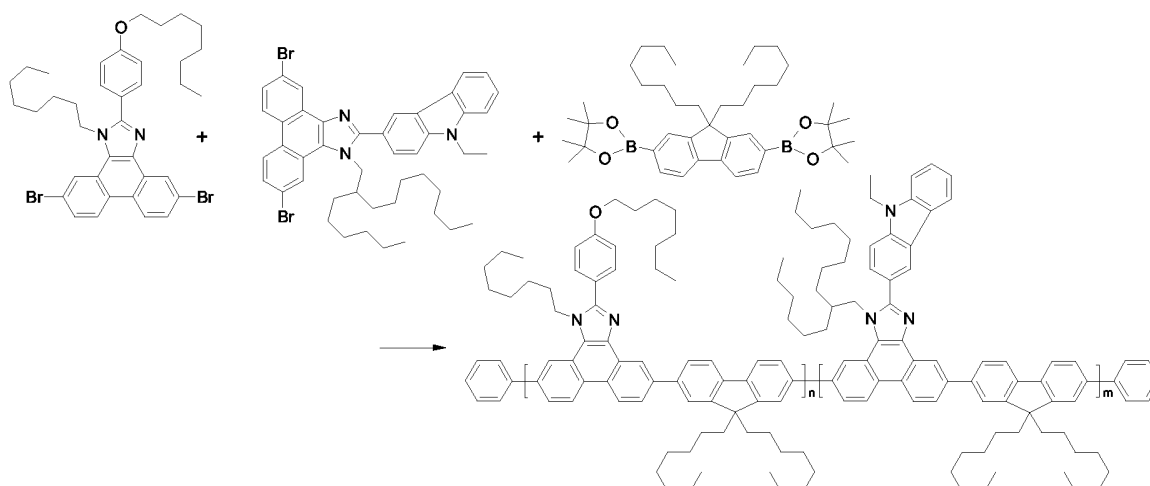
#### Example 104



- 10 The copolymerization reaction is performed according to the procedure of **example 85**, with 0.65 equivalents of the dibromide product of **example 16**, 0.35 equivalents of the dibromide product of **example 81**, and 1.0 equivalents of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di(4-ethoxyphenyl)fluorene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 84\,101$ , PD = 3.38. Photoluminescent measurements of the polymer product have been
- 15 performed as described in **example 39**: emission maximum at 446 nm.

#### Example 105

## 106



The copolymerization reaction is performed according to the procedure of **example 85**, with 0.6 equivalents of the dibromide product of **example 9c**, 0.4 equivalents of the dibromide product of **example 81**, and 1.0 equivalents of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w$  = 49 177, PD = 3.10. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 430 nm.

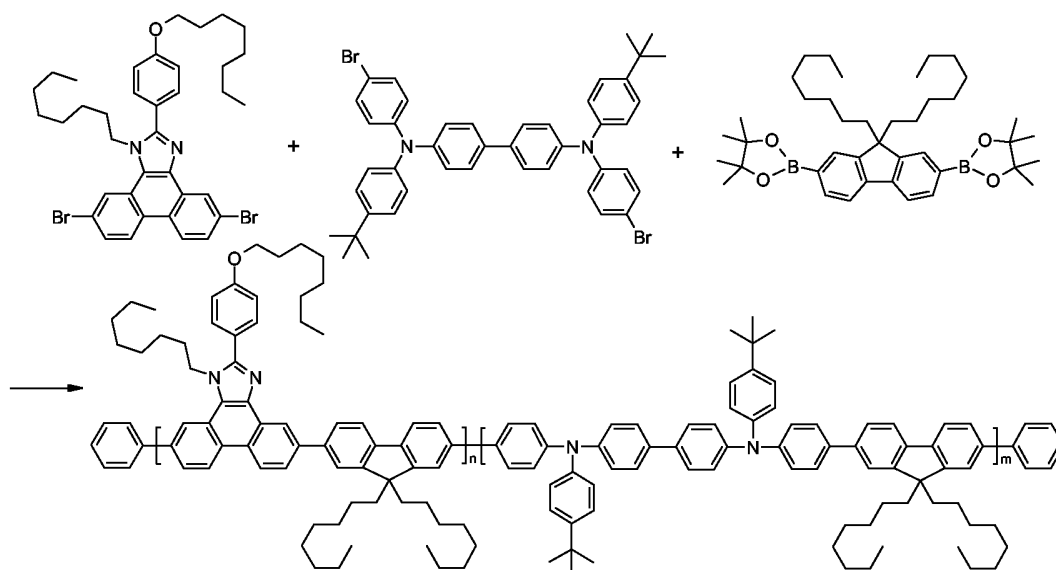
**Example 106**

- 10 The copolymerization reaction is been performed according to the procedure of **example 85**, with 0.8 equivalents of the dibromide product of **example 9c**, 0.2 equivalents of the dibromide product of **example 81**, and 1.0 equivalents of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w$  = 77 760, PD = 3.41.

15

**Example 107**

107



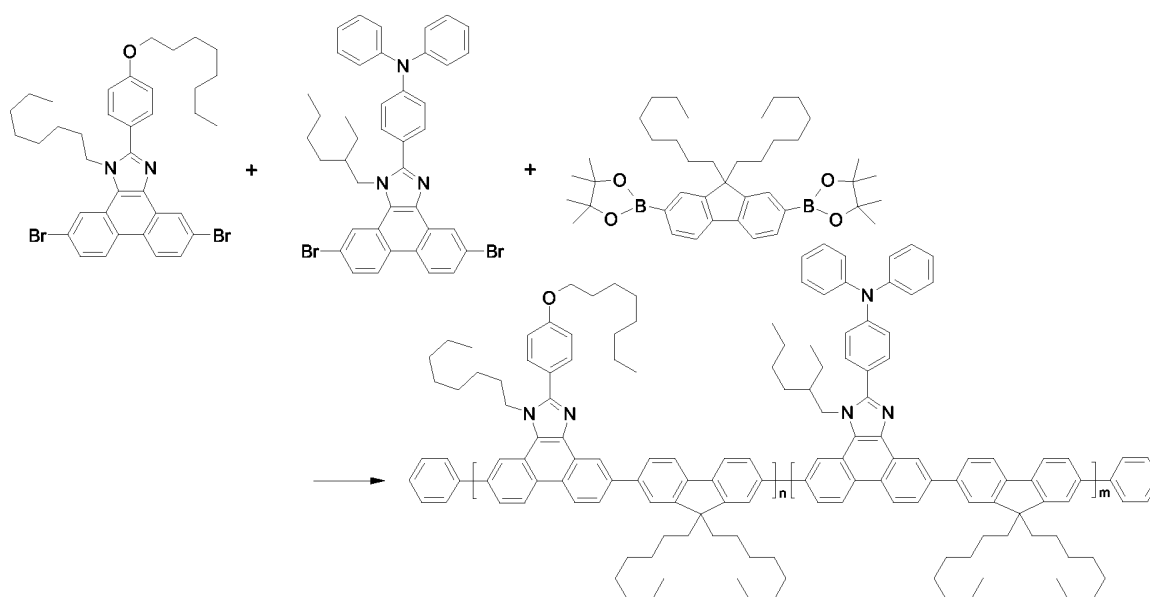
The copolymerization reaction is performed according to the procedure of **example 85**, with 0.8 equivalents of the dibromide product of **example 9c**, 0.2 equivalents of N,N'-bis(4-bromophenyl)-N,N'-bis(4-*tert*-butylphenyl)benzidine (CAS 463944-36-7, prepared according to WO02/077060), and 1.0 equivalents of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 154\,946$ , PD = 3.25.

### Example 108

The copolymerization reaction is performed according to the procedure of **example 85**, with 0.6 equivalents of the dibromide product of **example 9c**, 0.4 equivalents of N,N'-bis(4-bromophenyl)-N,N'-bis(4-*tert*-butylphenyl)benzidine, and 1.0 equivalents of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 137\,557$ , PD = 3.64.

### Example 109

108

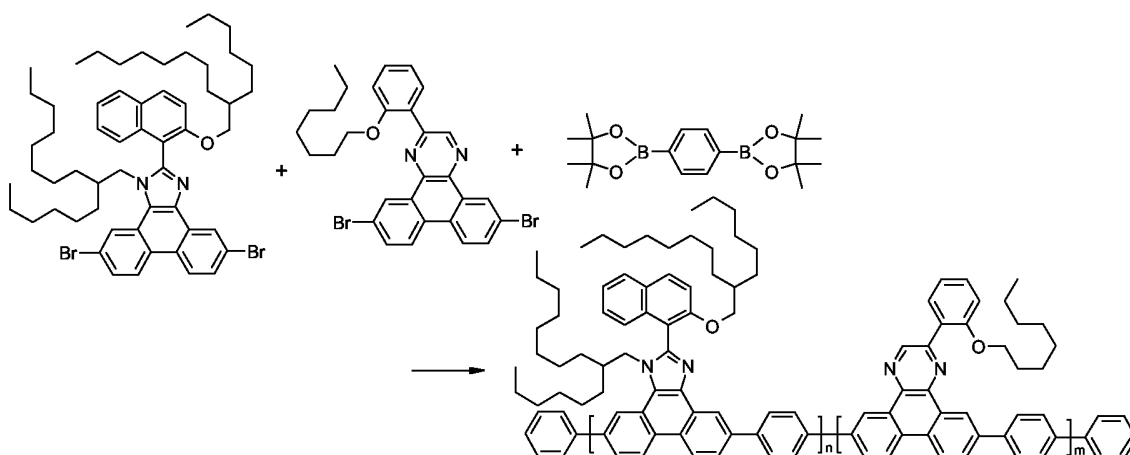


The copolymerization reaction is performed according to the procedure of **example 85**, with 0.8 equivalents of the dibromide product of **example 9c**, 0.2 equivalents of the dibromide product of **example 83**, and 1.0 equivalents of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w$  = 143 595, PD = 3.42.

### Example 110

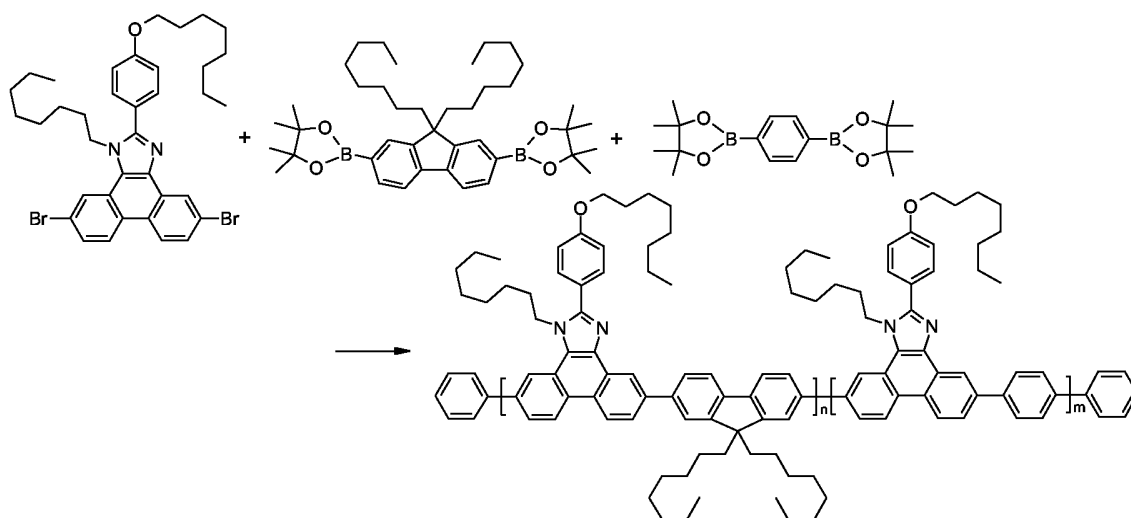
The copolymerization reaction has been performed according to the procedure of **example 85**, with 0.6 equivalents of the dibromide product of **example 9c**, 0.4 equivalents of the dibromide product of **example 83**, and 1.0 equivalents of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w$  = 87 924, PD = 3.23.

### Example 111



The copolymerization reaction is performed according to the procedure of **example 85**, with 0.65 equivalents of the dibromide product of **example 17**, 0.35 equivalents of the dibromide product of **example 54**, and 1.0 equivalents of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 45\,868$ , PD = 4.72.

### Example 112

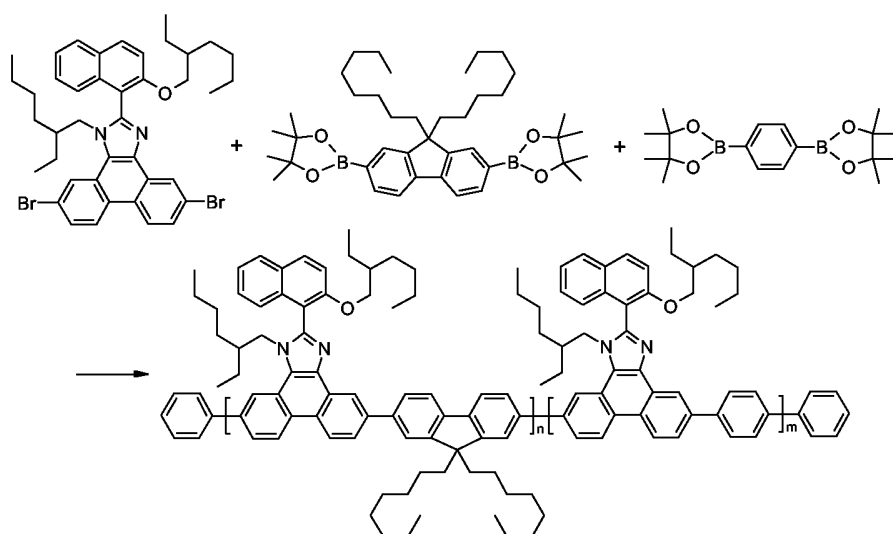


a) The copolymerization reaction is performed according to the procedure of **example 85**, with 1.0 equivalents of the dibromide product of **example 9c**, 0.75 equivalents of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene, and 0.25 equivalents of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 49\,635$ , PD = 5.08.

### Example 113

The copolymerization reaction is performed according to the procedure of **example 85**, with 1.0 equivalents of the dibromide product of **example 9c**, 0.5 equivalents of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene, and 0.5 equivalents of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 132\,849$ , PD = 13.5.

### Example 114



The copolymerization reaction is performed according to the procedure of **example 85**, with 1.0 equivalents of the dibromide product of **example 16**, 0.25 equivalents of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene, and 0.75 equivalents of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 135\,369$ , PD = 8.3. Photoluminescent measurements of the polymer product have been performed as described in **example 39**: emission maximum at 448 nm.

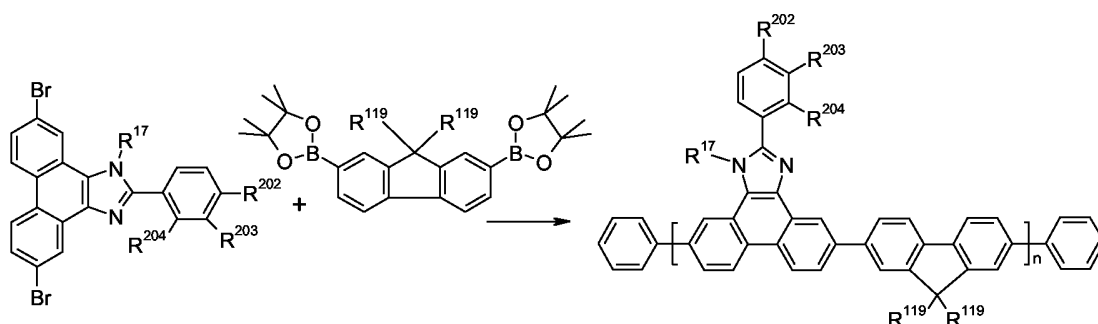
#### Example 115

The copolymerization reaction is performed according to the procedure of **example 85**, with 1.0 equivalents of the dibromide product of **example 16**, 0.2 equivalents of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene, and 0.8 equivalents of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 145\,597$ , PD = 8.0.

#### Example 116

The copolymerization reaction is performed according to the procedure of **example 85**, with 1.0 equivalents of the dibromide product of **example 16**, 0.4 equivalents of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene, and 0.6 equivalents of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. A yellow solid is obtained. GPC (polystyrene standard):  $M_w = 51\,272$ , PD = 5.3.

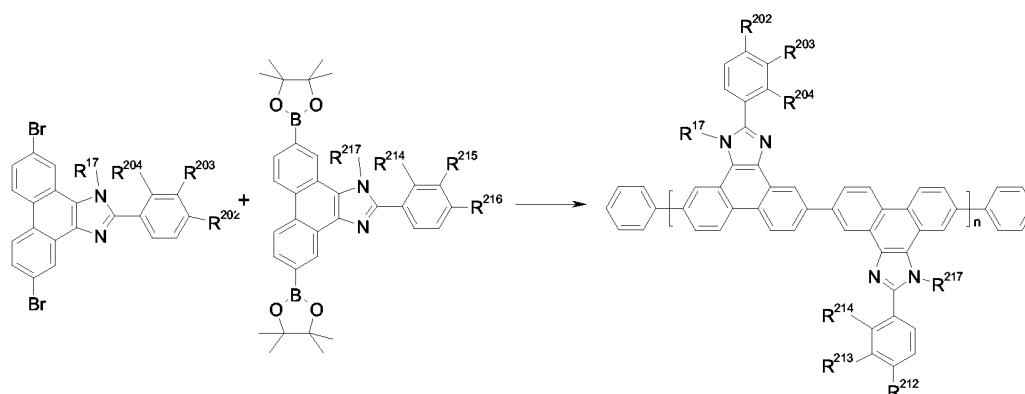
The following polymers are prepared in analogy to **example 8**, **11**, **39**, **40**, **41**, or **85**. Instead of using compounds, wherein  $X^{11}$  is Br, for the preparation of the following polymers compounds, wherein  $X^{11}$  is I, can also be used.



Polymer No.	R <sup>17</sup>	R <sup>202</sup>	R <sup>203</sup>	R <sup>204</sup>	R <sup>119</sup>
1-1	n-octyl	-O-n-octyl	H	H	n-octyl
1-2	n-octyl	-O-n-octyl	H	H	n-hexyl
1-3	n-octyl	-O-n-octyl	H	H	2-ethylhexyl
1-4	n-octyl	-O-n-octyl	H	-O-n-octyl	n-octyl
1-5	n-octyl	-O-n-octyl	H	-O-n-octyl	n-hexyl
1-6	n-octyl	-O-n-octyl	H	-O-n-octyl	2-ethylhexyl
1-7	n-octyl	H	H	-O-n-octyl	n-octyl
1-8	n-octyl	H	H	-O-n-octyl	n-hexyl
1-9	n-octyl	H	H	-O-n-octyl	2-ethylhexyl
1-10	n-octyl	H	-O-n-octyl	-O-n-octyl	n-octyl
1-11	n-octyl	H	-O-n-octyl	-O-n-octyl	n-hexyl
1-12	n-octyl	H	-O-n-octyl	-O-n-octyl	2-ethylhexyl
1-13	n-hexyl	-O-n-hexyl	H	H	n-octyl
1-14	n-hexyl	-O-n-hexyl	H	H	n-hexyl
1-15	n-hexyl	-O-n-hexyl	H	H	2-ethylhexyl
1-16	n-hexyl	-O-n-hexyl	H	-O-n-hexyl	n-octyl
1-17	n-hexyl	-O-n-hexyl	H	-O-n-hexyl	n-hexyl
1-18	n-hexyl	-O-n-hexyl	H	-O-n-hexyl	2-ethylhexyl
1-19	n-hexyl	H	H	-O-n-hexyl	n-octyl
1-20	n-hexyl	H	H	-O-n-hexyl	n-hexyl
1-21	n-hexyl	H	H	-O-n-hexyl	2-ethylhexyl
1-22	n-hexyl	H	-O-n-hexyl	-O-n-hexyl	n-octyl
1-23	n-hexyl	H	-O-n-hexyl	-O-n-hexyl	n-hexyl
1-24	n-hexyl	H	-O-n-hexyl	-O-n-hexyl	2-ethylhexyl
1-25	n-butyl	-O-n-butyl	H	H	n-octyl
1-26	n-butyl	-O-n-butyl	H	H	n-hexyl



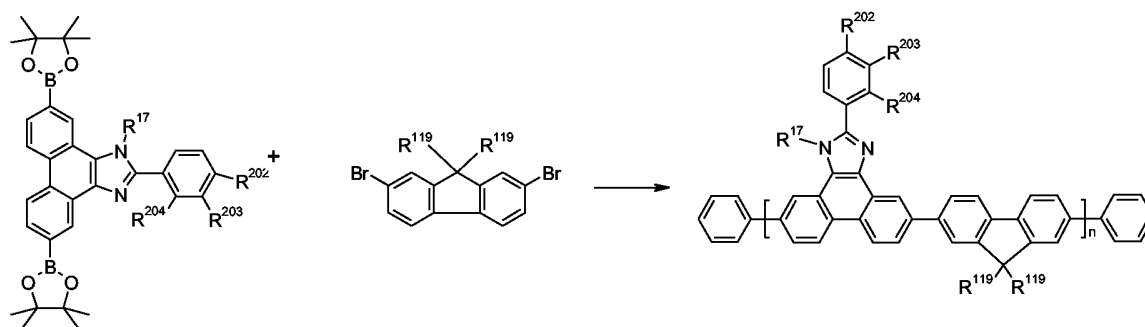
1-27	n-butyl	-O-n-butyl	H	H	2-ethylhexyl
1-28	n-butyl	-O-n-butyl	H	-O-n-butyl	n-octyl
1-29	n-butyl	-O-n-butyl	H	-O-n-butyl	n-hexyl
1-30	n-butyl	-O-n-butyl	H	-O-n-butyl	2-ethylhexyl
1-31	n-butyl	H	H	-O-n-butyl	n-octyl
1-32	n-butyl	H	H	-O-n-butyl	n-hexyl
1-33	n-butyl	H	H	-O-n-butyl	2-ethylhexyl
1-34	n-butyl	H	-O-n-butyl	-O-n-butyl	n-octyl
1-35	n-butyl	H	-O-n-butyl	-O-n-butyl	n-hexyl
1-36	n-butyl	H	-O-n-butyl	-O-n-butyl	2-ethylhexyl
1-37	2-ethylhexyl	-O-2-ethylhexyl	H	H	n-octyl
1-38	2-ethylhexyl	-O-2-ethylhexyl	H	H	n-hexyl
1-39	2-ethylhexyl	-O-2-ethylhexyl	H	H	2-ethylhexyl
1-40	2-ethylhexyl	-O-2-ethylhexyl	H	2-ethylhexyl	n-octyl
1-41	2-ethylhexyl	-O-2-ethylhexyl	H	2-ethylhexyl	n-hexyl
1-42	2-ethylhexyl	-O-2-ethylhexyl	H	2-ethylhexyl	2-ethylhexyl
1-43	2-ethylhexyl	H	H	2-ethylhexyl	n-octyl
1-44	2-ethylhexyl	H	H	2-ethylhexyl	n-hexyl
1-45	2-ethylhexyl	H	H	2-ethylhexyl	2-ethylhexyl
1-46	2-ethylhexyl	H	-O-2-ethylhexyl	2-ethylhexyl	n-octyl
1-47	2-ethylhexyl	H	-O-2-ethylhexyl	2-ethylhexyl	n-hexyl
1-48	2-ethylhexyl	H	-O-2-ethylhexyl	2-ethylhexyl	2-ethylhexyl
2-1	n-octyl	O-n-octyl	H	H	4-C <sub>6</sub> H <sub>5</sub> OMe
2-2	n-octyl	O-n-octyl	H	H	4-C <sub>6</sub> H <sub>5</sub> OEt
2-3	n-octyl	O-n-octyl	H	H	4-C <sub>6</sub> H <sub>5</sub> OBu
2-4	n-octyl	O-n-octyl	H	O-n-octyl	4-C <sub>6</sub> H <sub>5</sub> OMe
2-5	n-octyl	O-n-octyl	H	O-n-octyl	4-C <sub>6</sub> H <sub>5</sub> OEt
2-6	n-octyl	O-n-octyl	H	O-n-octyl	4-C <sub>6</sub> H <sub>5</sub> OBu
2-7	n-octyl	H	H	O-n-octyl	4-C <sub>6</sub> H <sub>5</sub> OMe
2-8	n-octyl	H	H	O-n-octyl	4-C <sub>6</sub> H <sub>5</sub> OEt
2-9	n-octyl	H	H	O-n-octyl	4-C <sub>6</sub> H <sub>5</sub> OBu
2-10	n-octyl	H	O-n-octyl	O-n-octyl	4-C <sub>6</sub> H <sub>5</sub> OMe
2-11	n-octyl	H	O-n-octyl	O-n-octyl	4-C <sub>6</sub> H <sub>5</sub> OEt
2-12	n-octyl	H	O-n-octyl	O-n-octyl	4-C <sub>6</sub> H <sub>5</sub> OBu



The orientation of the 5-ring heteroaromatic ring in the polymer chain is randomly.

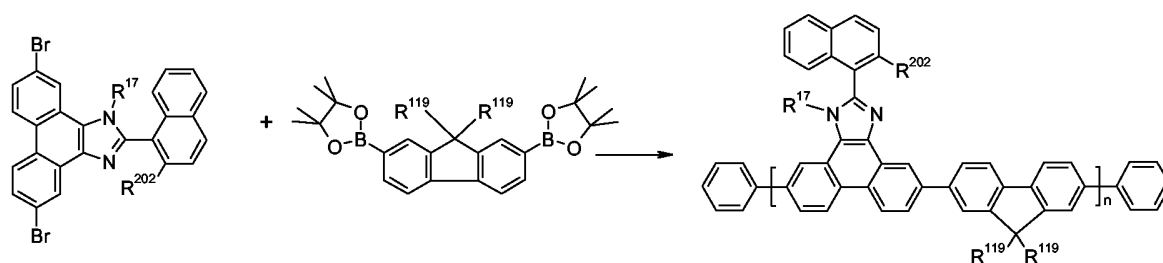
Polymer No.	R <sup>17</sup>	R <sup>202</sup>	R <sup>203</sup>	R <sup>204</sup>	R <sup>217</sup>	R <sup>212</sup>	R <sup>213</sup>	R <sup>214</sup>
3-1	n-octyl	O-R <sup>17</sup>	H	H	n-hexyl	O-R <sup>217</sup>	H	H
3-2	n-octyl	O-R <sup>17</sup>	H	H	n-butyl	O-R <sup>217</sup>	H	H
3-3	n-octyl	O-R <sup>17</sup>	H	H	n-octyl	O-R <sup>217</sup>	H	H
3-4	n-octyl	O-R <sup>17</sup>	H	H	n-hexyl	O-R <sup>217</sup>	H	O-R <sup>217</sup>
3-5	n-octyl	O-R <sup>17</sup>	H	H	n-butyl	O-R <sup>217</sup>	H	O-R <sup>217</sup>
3-6	n-octyl	O-R <sup>17</sup>	H	H	n-octyl	O-R <sup>217</sup>	H	O-R <sup>217</sup>
3-7	n-octyl	O-R <sup>17</sup>	H	H	n-hexyl	H	H	O-R <sup>217</sup>
3-8	n-octyl	O-R <sup>17</sup>	H	H	n-butyl	H	H	O-R <sup>217</sup>
3-9	n-octyl	O-R <sup>17</sup>	H	H	n-octyl	H	H	O-R <sup>217</sup>
3-10	n-octyl	O-R <sup>17</sup>	H	O-R <sup>17</sup>	n-hexyl	O-R <sup>217</sup>	H	H
3-11	n-octyl	O-R <sup>17</sup>	H	O-R <sup>17</sup>	n-butyl	O-R <sup>217</sup>	H	H
3-12	n-octyl	O-R <sup>17</sup>	H	O-R <sup>17</sup>	n-octyl	O-R <sup>217</sup>	H	H
3-13	n-octyl	O-R <sup>17</sup>	H	O-R <sup>17</sup>	n-hexyl	O-R <sup>217</sup>	H	O-R <sup>217</sup>
3-14	n-octyl	O-R <sup>17</sup>	H	O-R <sup>17</sup>	n-butyl	O-R <sup>217</sup>	H	O-R <sup>217</sup>
3-15	n-octyl	O-R <sup>17</sup>	H	O-R <sup>17</sup>	n-octyl	O-R <sup>217</sup>	H	O-R <sup>217</sup>
3-16	n-octyl	O-R <sup>17</sup>	H	O-R <sup>17</sup>	n-hexyl	H	H	O-R <sup>217</sup>
3-17	n-octyl	O-R <sup>17</sup>	H	O-R <sup>17</sup>	n-butyl	H	H	O-R <sup>217</sup>
3-18	n-octyl	O-R <sup>17</sup>	H	O-R <sup>17</sup>	n-octyl	H	H	O-R <sup>217</sup>
3-19	n-octyl	H	H	O-R <sup>17</sup>	n-hexyl	O-R <sup>217</sup>	H	H
3-20	n-octyl	H	H	O-R <sup>17</sup>	n-butyl	O-R <sup>217</sup>	H	H
3-21	n-octyl	H	H	O-R <sup>17</sup>	n-octyl	O-R <sup>217</sup>	H	H
3-22	n-octyl	H	H	O-R <sup>17</sup>	n-hexyl	O-R <sup>217</sup>	H	O-R <sup>217</sup>
3-23	n-octyl	H	H	O-R <sup>17</sup>	n-butyl	O-R <sup>217</sup>	H	O-R <sup>217</sup>
3-24	n-octyl	H	H	O-R <sup>17</sup>	n-octyl	O-R <sup>217</sup>	H	O-R <sup>217</sup>

3-25	n-octyl	H	H	O-R <sup>17</sup>	n-hexyl	H	H	O-R <sup>217</sup>
3-26	n-octyl	H	H	O-R <sup>17</sup>	n-butyl	H	H	O-R <sup>217</sup>
3-27	n-octyl	H	H	O-R <sup>17</sup>	n-octyl	H	H	O-R <sup>217</sup>
3-28	n-octyl	H	O-R <sup>17</sup>	O-R <sup>17</sup>	n-hexyl	O-R <sup>217</sup>	H	H
3-29	n-octyl	H	O-R <sup>17</sup>	O-R <sup>17</sup>	n-butyl	O-R <sup>217</sup>	H	H
3-30	n-octyl	H	O-R <sup>17</sup>	O-R <sup>17</sup>	n-octyl	O-R <sup>217</sup>	H	H
3-31	n-octyl	H	O-R <sup>17</sup>	O-R <sup>17</sup>	n-hexyl	O-R <sup>217</sup>	H	O-R <sup>217</sup>
3-32	n-octyl	H	O-R <sup>17</sup>	O-R <sup>17</sup>	n-butyl	O-R <sup>217</sup>	H	O-R <sup>217</sup>
3-33	n-octyl	H	O-R <sup>17</sup>	O-R <sup>17</sup>	n-octyl	O-R <sup>217</sup>	H	O-R <sup>217</sup>
3-34	n-octyl	H	O-R <sup>17</sup>	O-R <sup>17</sup>	n-hexyl	H	H	O-R <sup>217</sup>
3-35	n-octyl	H	O-R <sup>17</sup>	O-R <sup>17</sup>	n-butyl	H	H	O-R <sup>217</sup>
3-36	n-octyl	H	O-R <sup>17</sup>	O-R <sup>17</sup>	n-octyl	H	H	O-R <sup>217</sup>

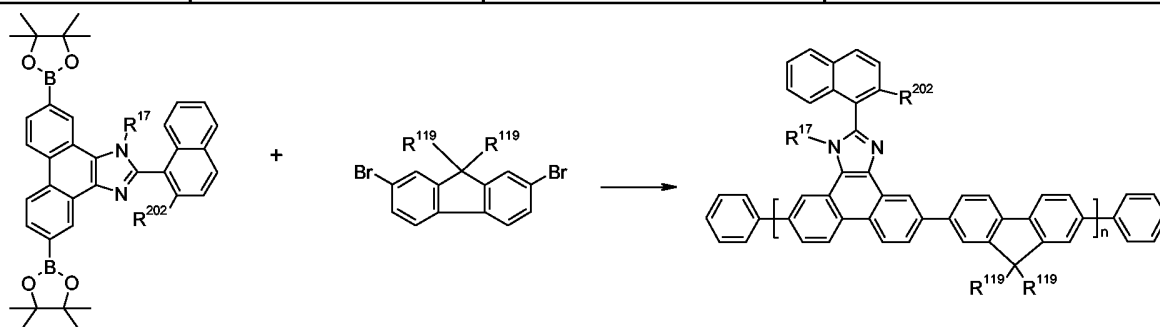


Polymer No.	R <sup>17</sup>	R <sup>202</sup>	R <sup>203</sup>	R <sup>204</sup>	R <sup>119</sup>
4-1	n-octyl	-O-n-octyl	H	H	n-octyl
4-2	n-octyl	-O-n-octyl	H	H	n-hexyl
4-3	n-octyl	-O-n-octyl	H	H	2-ethylhexyl
4-4	n-octyl	-O-n-octyl	H	-O-n-octyl	n-octyl
4-5	n-octyl	-O-n-octyl	H	-O-n-octyl	n-hexyl
4-6	n-octyl	-O-n-octyl	H	-O-n-octyl	2-ethylhexyl
4-7	n-octyl	H	H	-O-n-octyl	n-octyl
4-8	n-octyl	H	H	-O-n-octyl	n-hexyl
4-9	n-octyl	H	H	-O-n-octyl	2-ethylhexyl
4-10	n-octyl	H	-O-n-octyl	-O-n-octyl	n-octyl
4-11	n-octyl	H	-O-n-octyl	-O-n-octyl	n-hexyl
4-12	n-octyl	H	-O-n-octyl	-O-n-octyl	2-ethylhexyl
4-13	n-hexyl	-O-n-hexyl	H	H	n-octyl

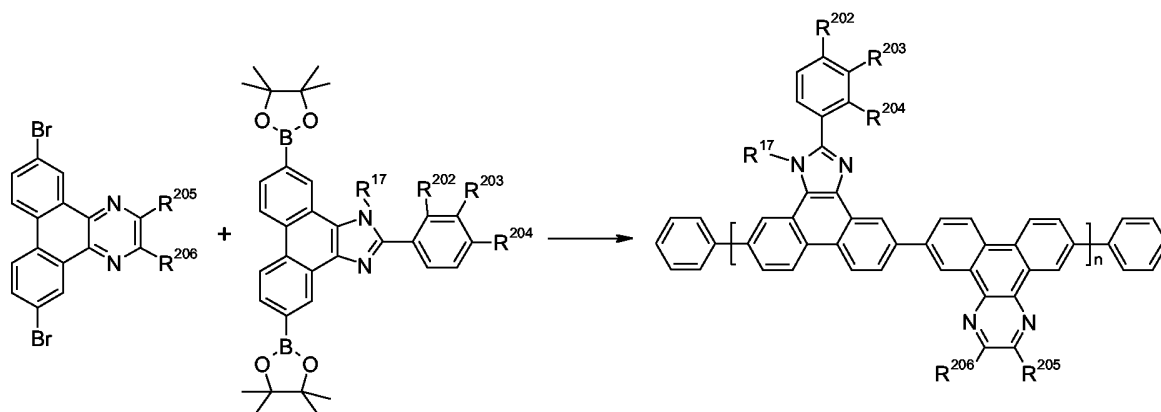
4-14	n-hexyl	-O-n-hexyl	H	H	n-hexyl
4-15	n-hexyl	-O-n-hexyl	H	H	2-ethylhexyl
4-16	n-hexyl	-O-n-hexyl	H	-O-n-hexyl	n-octyl
4-17	n-hexyl	-O-n-hexyl	H	-O-n-hexyl	n-hexyl
4-18	n-hexyl	-O-n-hexyl	H	-O-n-hexyl	2-ethylhexyl
4-19	n-hexyl	H	H	-O-n-hexyl	n-octyl
4-20	n-hexyl	H	H	-O-n-hexyl	n-hexyl
4-21	n-hexyl	H	H	-O-n-hexyl	2-ethylhexyl
4-22	n-hexyl	H	-O-n-hexyl	-O-n-hexyl	n-octyl
4-23	n-hexyl	H	-O-n-hexyl	-O-n-hexyl	n-hexyl
4-24	n-hexyl	H	-O-n-hexyl	-O-n-hexyl	2-ethylhexyl
4-25	n-butyl	-O-n-butyl	H	H	n-octyl
4-26	n-butyl	-O-n-butyl	H	H	n-hexyl
4-27	n-butyl	-O-n-butyl	H	H	2-ethylhexyl
4-28	n-butyl	-O-n-butyl	H	-O-n-butyl	n-octyl
4-29	n-butyl	-O-n-butyl	H	-O-n-butyl	n-hexyl
4-30	n-butyl	-O-n-butyl	H	-O-n-butyl	2-ethylhexyl
4-31	n-butyl	H	H	-O-n-butyl	n-octyl
4-32	n-butyl	H	H	-O-n-butyl	n-hexyl
4-33	n-butyl	H	H	-O-n-butyl	2-ethylhexyl
4-34	n-butyl	H	-O-n-butyl	-O-n-butyl	n-octyl
4-35	n-butyl	H	-O-n-butyl	-O-n-butyl	n-hexyl
4-36	n-butyl	H	-O-n-butyl	-O-n-butyl	2-ethylhexyl



Polymer No.	R <sup>17</sup>	R <sup>202</sup>	R <sup>119</sup>
5-1	n-octyl	-O-n-octyl	n-octyl
5-2	n-octyl	-O-n-octyl	n-hexyl
5-3	n-octyl	-O-n-octyl	2-ethylhexyl
5-4	n-hexyl	-O-n-hexyl	n-octyl
5-5	n-hexyl	-O-n-hexyl	n-hexyl
5-6	n-hexyl	-O-n-hexyl	2-ethylhexyl
5-7	n-butyl	-O-n-butyl	n-octyl
5-8	n-butyl	-O-n-butyl	n-hexyl
5-9	n-butyl	-O-n-butyl	2-ethylhexyl

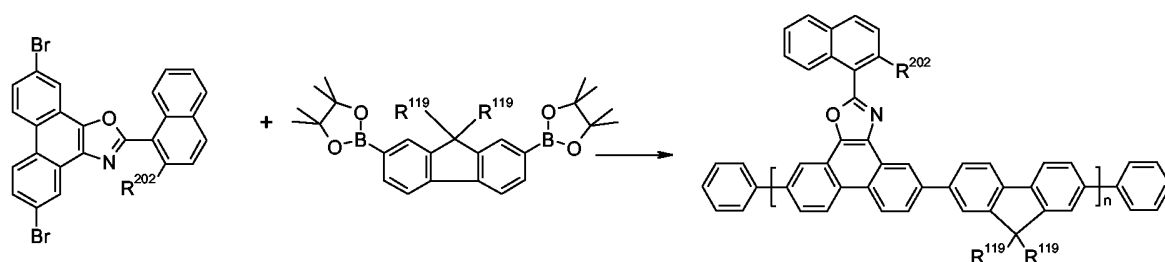


Polymer No.	R <sup>17</sup>	R <sup>202</sup>	R <sup>119</sup>
6-1	n-octyl	-O-n-octyl	n-octyl
6-2	n-octyl	-O-n-octyl	n-hexyl
6-3	n-octyl	-O-n-octyl	2-ethylhexyl
6-4	n-hexyl	-O-n-hexyl	n-octyl
6-5	n-hexyl	-O-n-hexyl	n-hexyl
6-6	n-hexyl	-O-n-hexyl	2-ethylhexyl
6-7	n-butyl	-O-n-butyl	n-octyl
6-8	n-butyl	-O-n-butyl	n-hexyl
6-9	n-butyl	-O-n-butyl	2-ethylhexyl

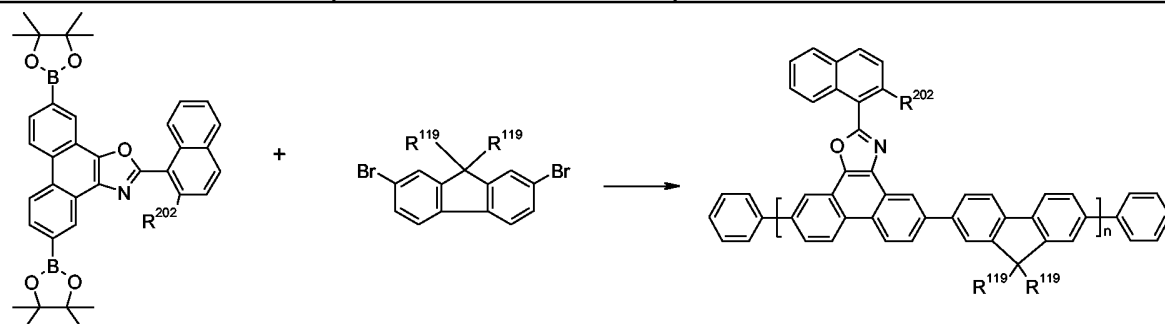


Polymer No.	$R^{17}$	$R^{202}$	$R^{203}$	$R^{204}$	$R^{205}$	$R^{206}$
7-1	n-octyl	O- $R^{17}$	H	H	H	H
7-2	n-octyl	O- $R^{17}$	H	H	t-butyl	t-butyl
7-3	n-octyl	O- $R^{17}$	H	O- $R^{17}$	H	H
7-4	n-octyl	O- $R^{17}$	H	O- $R^{17}$	t-butyl	t-butyl
7-5	n-octyl	H	H	O- $R^{17}$	H	H
7-6	n-octyl	H	H	O- $R^{17}$	t-butyl	t-butyl
7-7	n-octyl	H	O- $R^{17}$	O- $R^{17}$	H	H
7-8	n-octyl	H	O- $R^{17}$	O- $R^{17}$	t-butyl	t-butyl
7-9	n-hexyl	O- $R^{17}$	H	H	H	H
7-10	n-hexyl	O- $R^{17}$	H	H	t-butyl	t-butyl
7-11	n-hexyl	O- $R^{17}$	H	O- $R^{17}$	H	H
7-12	n-hexyl	O- $R^{17}$	H	O- $R^{17}$	t-butyl	t-butyl
7-13	n-hexyl	H	H	O- $R^{17}$	H	H
7-14	n-hexyl	H	H	O- $R^{17}$	t-butyl	t-butyl
7-15	n-hexyl	H	O- $R^{17}$	O- $R^{17}$	H	H
7-16	n-hexyl	H	O- $R^{17}$	O- $R^{17}$	t-butyl	t-butyl
7-17	n-butyl	O- $R^{17}$	H	H	H	H
7-18	n-butyl	O- $R^{17}$	H	H	t-butyl	t-butyl
7-19	n-butyl	O- $R^{17}$	H	O- $R^{17}$	H	H
7-20	n-butyl	O- $R^{17}$	H	O- $R^{17}$	t-butyl	t-butyl
7-21	n-butyl	H	H	O- $R^{17}$	H	H
7-22	n-butyl	H	H	O- $R^{17}$	t-butyl	t-butyl
7-23	n-butyl	H	O- $R^{17}$	O- $R^{17}$	H	H
7-24	n-butyl	H	O- $R^{17}$	O- $R^{17}$	t-butyl	t-butyl

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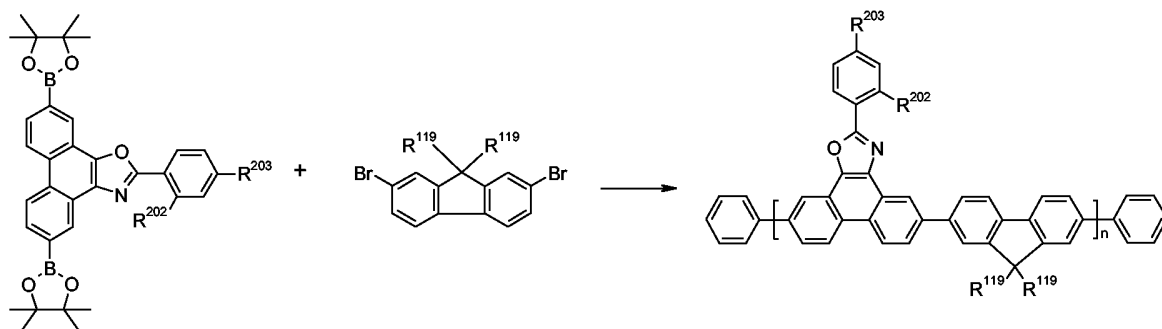


Polymer No.	R <sup>202</sup>	R <sup>119</sup>
8-1	-O-n-octyl	n-octyl
8-2	-O-n-octyl	n-hexyl
8-3	-O-n-octyl	2-ethylhexyl
8-4	-O-n-hexyl	n-octyl
8-5	-O-n-hexyl	n-hexyl
8-6	-O-n-hexyl	2-ethylhexyl
8-7	-O-n-butyl	n-octyl
8-8	-O-n-butyl	n-hexyl
8-9	-O-n-butyl	2-ethylhexyl

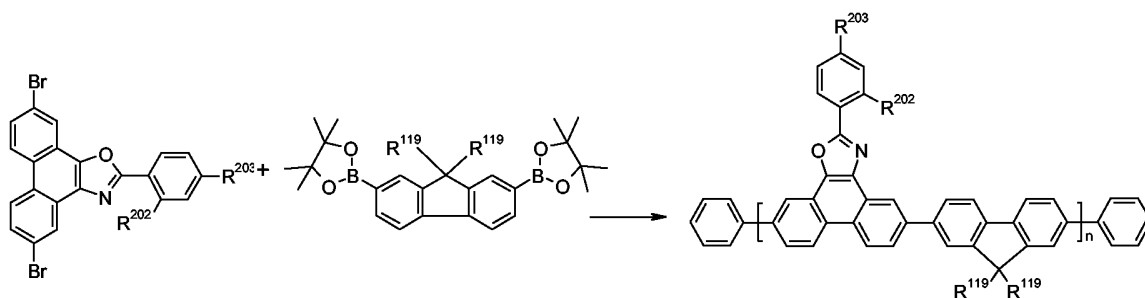


Polymer No.	R <sup>202</sup>	R <sup>119</sup>
9-1	-O-n-octyl	n-octyl
9-2	-O-n-octyl	n-hexyl
9-3	-O-n-octyl	2-ethylhexyl
9-4	-O-n-hexyl	n-octyl
9-5	-O-n-hexyl	n-hexyl
9-6	-O-n-hexyl	2-ethylhexyl
9-7	-O-n-butyl	n-octyl
9-8	-O-n-butyl	n-hexyl
9-9	-O-n-butyl	2-ethylhexyl

119



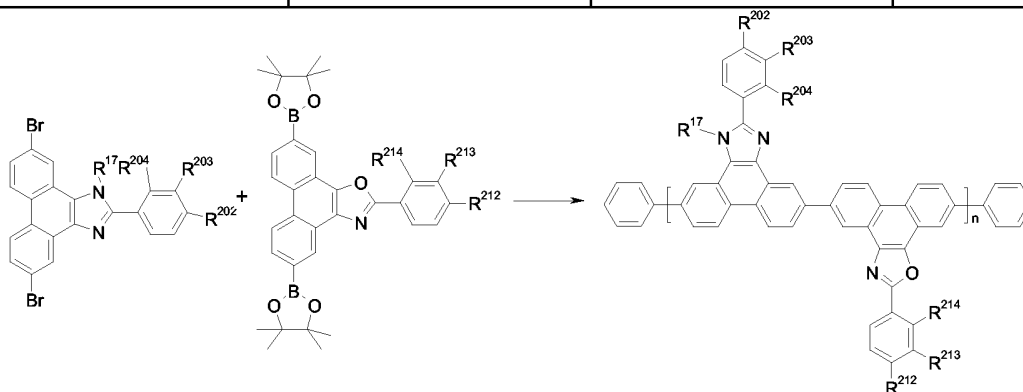
Polymer No.	R <sup>202</sup>	R <sup>203</sup>	R <sup>119</sup>
10-1	-O-n-octyl	-O-n-octyl	n-octyl
10-2	-O-n-octyl	-O-n-octyl	n-hexyl
10-3	-O-n-octyl	-O-n-octyl	2-ethylhexyl
10-4	-O-n-hexyl	-O-n-hexyl	n-octyl
10-5	-O-n-hexyl	-O-n-hexyl	n-hexyl
10-6	-O-n-hexyl	-O-n-hexyl	2-ethylhexyl
10-7	-O-n-butyl	-O-n-butyl	n-octyl
10-8	-O-n-butyl	-O-n-butyl	n-hexyl
10-9	-O-n-butyl	-O-n-butyl	2-ethylhexyl
10-10	-O-n-octyl	H	n-octyl
10-11	-O-n-octyl	H	n-hexyl
10-12	-O-n-octyl	H	2-ethylhexyl
10-13	-O-n-hexyl	H	n-octyl
10-14	-O-n-hexyl	H	n-hexyl
10-15	-O-n-hexyl	H	2-ethylhexyl
10-16	-O-n-butyl	H	n-octyl
10-17	-O-n-butyl	H	n-hexyl
10-18	-O-n-butyl	H	2-ethylhexyl



Polymer No.	R <sup>202</sup>	R <sup>203</sup>	R <sup>119</sup>
11-1	-O-n-octyl	-O-n-octyl	n-octyl



11-2	-O-n-octyl	-O-n-octyl	n-hexyl
11-3	-O-n-octyl	-O-n-octyl	2-ethylhexyl
11-4	-O-n-hexyl	-O-n-hexyl	n-octyl
11-5	-O-n-hexyl	-O-n-hexyl	n-hexyl
11-6	-O-n-hexyl	-O-n-hexyl	2-ethylhexyl
11-7	-O-n-butyl	-O-n-butyl	n-octyl
11-8	-O-n-butyl	-O-n-butyl	n-hexyl
11-9	-O-n-butyl	-O-n-butyl	2-ethylhexyl
11-10	-O-n-octyl	H	n-octyl
11-11	-O-n-octyl	H	n-hexyl
11-12	-O-n-octyl	H	2-ethylhexyl
11-13	-O-n-hexyl	H	n-octyl
11-14	-O-n-hexyl	H	n-hexyl
11-15	-O-n-hexyl	H	2-ethylhexyl
11-16	-O-n-butyl	H	n-octyl
11-17	-O-n-butyl	H	n-hexyl
11-18	-O-n-butyl	H	2-ethylhexyl

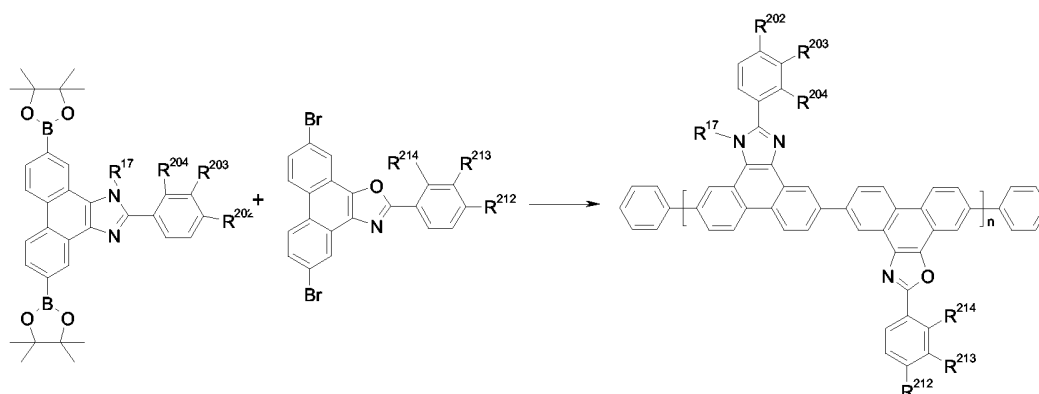


The orientation of the 5-ring heteroaromatic ring in the polymer chain is randomly.

Polymer No.	R <sup>17</sup>	R <sup>202</sup>	R <sup>203</sup>	R <sup>204</sup>	R <sup>212</sup>	R <sup>213</sup>	R <sup>214</sup>
12-1	n-octyl	O-n-octyl	H	O-n-octyl	O-n-octyl	H	O-n-octyl
12-2	n-octyl	O-n-octyl	H	O-n-octyl	O-n-hexyl	H	O-n-hexyl
12-3	n-octyl	O-n-octyl	H	O-n-octyl	O-n-butyl	H	O-n-butyl
12-4	n-octyl	O-n-octyl	H	O-n-octyl	H	O-n-octyl	O-n-octyl
12-5	n-octyl	O-n-octyl	H	O-n-octyl	H	O-n-hexyl	O-n-hexyl

12-6	n-octyl	O-n-octyl	H	O-n-octyl	H	O-n-butyl	O-n-butyl
12-7	n-octyl	O-n-octyl	H	O-n-octyl	H	H	O-n-octyl
12-8	n-octyl	O-n-octyl	H	O-n-octyl	H	H	O-n-hexyl
12-9	n-octyl	O-n-octyl	H	O-n-octyl	H	H	O-n-butyl
12-10	n-octyl	H	H	O-n-octyl	O-n-octyl	H	O-n-octyl
12-11	n-octyl	H	H	O-n-octyl	O-n-hexyl	H	O-n-hexyl
12-12	n-octyl	H	H	O-n-octyl	O-n-butyl	H	O-n-butyl
12-13	n-octyl	H	H	O-n-octyl	H	O-n-octyl	O-n-octyl
12-14	n-octyl	H	H	O-n-octyl	H	O-n-hexyl	O-n-hexyl
12-15	n-octyl	H	H	O-n-octyl	H	O-n-butyl	O-n-butyl
12-16	n-octyl	H	H	O-n-octyl	H	H	O-n-octyl
12-17	n-octyl	H	H	O-n-octyl	H	H	O-n-hexyl
12-18	n-octyl	H	H	O-n-octyl	H	H	O-n-butyl
12-19	n-octyl	H	O-n-octyl	O-n-octyl	O-n-octyl	H	O-n-octyl
12-20	n-octyl	H	O-n-octyl	O-n-octyl	O-n-hexyl	H	O-n-hexyl
12-21	n-octyl	H	O-n-octyl	O-n-octyl	O-n-butyl	H	O-n-butyl
12-22	n-octyl	H	O-n-octyl	O-n-octyl	H	O-n-octyl	O-n-octyl
12-23	n-octyl	H	O-n-octyl	O-n-octyl	H	O-n-hexyl	O-n-hexyl
12-24	n-octyl	H	O-n-octyl	O-n-octyl	H	O-n-butyl	O-n-butyl
12-25	n-octyl	H	O-n-octyl	O-n-octyl	H	H	O-n-octyl
12-26	n-octyl	H	O-n-octyl	O-n-octyl	H	H	O-n-hexyl
12-27	n-octyl	H	O-n-octyl	O-n-octyl	H	H	O-n-butyl
12-28	n-octyl	O-n-octyl	H	H	O-n-octyl	H	O-n-octyl
12-29	n-octyl	O-n-octyl	H	H	O-n-hexyl	H	O-n-hexyl
12-30	n-octyl	O-n-octyl	H	H	O-n-butyl	H	O-n-butyl
12-31	n-octyl	O-n-octyl	H	H	H	O-n-octyl	O-n-octyl
12-32	n-octyl	O-n-octyl	H	H	H	O-n-	O-n-

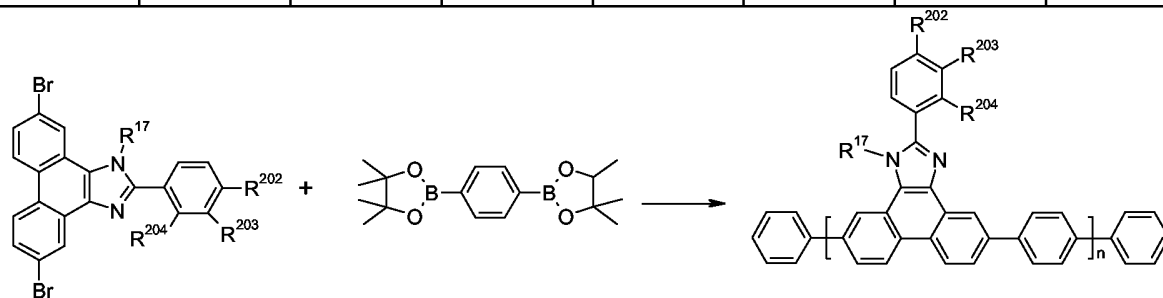
						hexyl	hexyl
12-33	n-octyl	O-n-octyl	H	H	H	O-n-butyl	O-n-butyl
12-34	n-octyl	O-n-octyl	H	H	H	H	O-n-octyl
12-35	n-octyl	O-n-octyl	H	H	H	H	O-n-hexyl
12-36	n-octyl	O-n-octyl	H	H	H	H	O-n-butyl



The orientation of the 5-ring heteroaromatic ring in the polymer chain is randomly.

Polymer No.	R <sup>17</sup>	R <sup>202</sup>	R <sup>203</sup>	R <sup>204</sup>	R <sup>212</sup>	R <sup>213</sup>	R <sup>214</sup>
13-1	n-octyl	O-n-octyl	H	O-n-octyl	O-n-octyl	H	n-octyl
13-2	n-octyl	O-n-octyl	H	O-n-octyl	O-n-hexyl	H	n-hexyl
13-3	n-octyl	O-n-octyl	H	O-n-octyl	O-n-butyl	H	n-butyl
13-4	n-octyl	O-n-octyl	H	O-n-octyl	H	O-n-octyl	n-octyl
13-5	n-octyl	O-n-octyl	H	O-n-octyl	H	O-n-hexyl	n-hexyl
13-6	n-octyl	O-n-octyl	H	O-n-octyl	H	O-n-butyl	n-butyl
13-7	n-octyl	O-n-octyl	H	O-n-octyl	H	H	n-octyl
13-8	n-octyl	O-n-octyl	H	O-n-octyl	H	H	n-hexyl
13-9	n-octyl	O-n-octyl	H	O-n-octyl	H	H	n-butyl
13-10	n-octyl	H	H	O-n-octyl	O-n-octyl	H	n-octyl
13-11	n-octyl	H	H	O-n-octyl	O-n-hexyl	H	n-hexyl
13-12	n-octyl	H	H	O-n-octyl	O-n-butyl	H	n-butyl
13-13	n-octyl	H	H	O-n-octyl	H	O-n-octyl	n-octyl
13-14	n-octyl	H	H	O-n-octyl	H	O-n-	n-hexyl

						hexyl	
13-15	n-octyl	H	H	O-n-octyl	H	O-n-butyl	n-butyl
13-16	n-octyl	H	H	O-n-octyl	H	H	n-octyl
13-17	n-octyl	H	H	O-n-octyl	H	H	n-hexyl
13-18	n-octyl	H	H	O-n-octyl	H	H	n-butyl
13-19	n-octyl	H	O-n-octyl	O-n-octyl	O-n-octyl	H	n-octyl
13-20	n-octyl	H	O-n-octyl	O-n-octyl	O-n-hexyl	H	n-hexyl
13-21	n-octyl	H	O-n-octyl	O-n-octyl	O-n-butyl	H	n-butyl
13-22	n-octyl	H	O-n-octyl	O-n-octyl	H	O-n-octyl	n-octyl
13-23	n-octyl	H	O-n-octyl	O-n-octyl	H	O-n-hexyl	n-hexyl
13-24	n-octyl	H	O-n-octyl	O-n-octyl	H	O-n-butyl	n-butyl
13-25	n-octyl	H	O-n-octyl	O-n-octyl	H	H	n-octyl
13-26	n-octyl	H	O-n-octyl	O-n-octyl	H	H	n-hexyl
13-27	n-octyl	H	O-n-octyl	O-n-octyl	H	H	n-butyl
13-28	n-octyl	O-n-octyl	H	H	O-n-octyl	H	n-octyl
13-29	n-octyl	O-n-octyl	H	H	O-n-hexyl	H	n-hexyl
13-30	n-octyl	O-n-octyl	H	H	O-n-butyl	H	n-butyl
13-31	n-octyl	O-n-octyl	H	H	H	O-n-octyl	n-octyl
13-32	n-octyl	O-n-octyl	H	H	H	O-n-hexyl	n-hexyl
13-33	n-octyl	O-n-octyl	H	H	H	O-n-butyl	n-butyl
13-34	n-octyl	O-n-octyl	H	H	H	H	n-octyl
13-35	n-octyl	O-n-octyl	H	H	H	H	n-hexyl
13-36	n-octyl	O-n-octyl	H	H	H	H	n-butyl

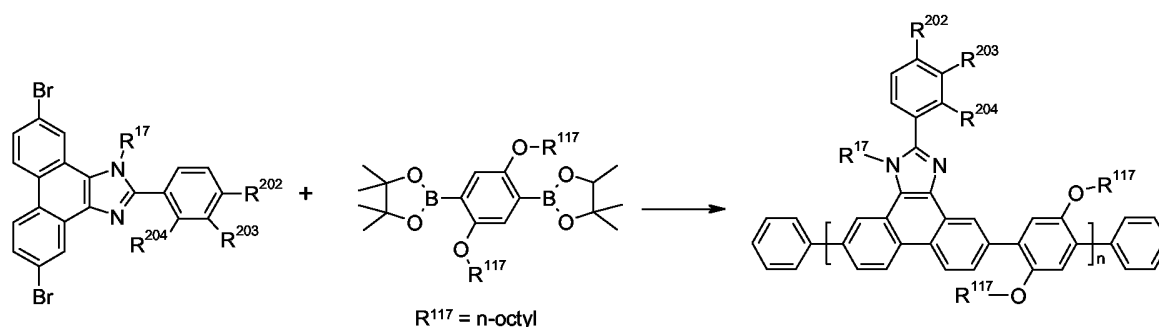


Polymer No.	R <sup>17</sup>	R <sup>202</sup>	R <sup>203</sup>	R <sup>204</sup>

14-1	n-octyl	-O-n-octyl	H	H
14-2	n-octyl	-O-n-octyl	H	H
14-3	n-octyl	-O-n-octyl	H	H
14-4	n-octyl	-O-n-octyl	H	-O-n-octyl
14-5	n-octyl	-O-n-octyl	H	-O-n-octyl
14-6	n-octyl	-O-n-octyl	H	-O-n-octyl
14-7	n-octyl	H	H	-O-n-octyl
14-8	n-octyl	H	H	-O-n-octyl
14-9	n-octyl	H	H	-O-n-octyl
14-10	n-octyl	H	-O-n-octyl	-O-n-octyl
14-11	n-octyl	H	-O-n-octyl	-O-n-octyl
14-12	n-octyl	H	-O-n-octyl	-O-n-octyl
14-13	n-hexyl	-O-n-hexyl	H	H
14-14	n-hexyl	-O-n-hexyl	H	H
14-15	n-hexyl	-O-n-hexyl	H	H
14-16	n-hexyl	-O-n-hexyl	H	-O-n-hexyl
14-17	n-hexyl	-O-n-hexyl	H	-O-n-hexyl
14-18	n-hexyl	-O-n-hexyl	H	-O-n-hexyl
14-19	n-hexyl	H	H	-O-n-hexyl
14-20	n-hexyl	H	H	-O-n-hexyl
14-21	n-hexyl	H	H	-O-n-hexyl
14-22	n-hexyl	H	-O-n-hexyl	-O-n-hexyl
14-23	n-hexyl	H	-O-n-hexyl	-O-n-hexyl
14-24	n-hexyl	H	-O-n-hexyl	-O-n-hexyl
14-25	n-butyl	-O-n-butyl	H	H
14-26	n-butyl	-O-n-butyl	H	H
14-27	n-butyl	-O-n-butyl	H	H
14-28	n-butyl	-O-n-butyl	H	-O-n-butyl
14-29	n-butyl	-O-n-butyl	H	-O-n-butyl
14-30	n-butyl	-O-n-butyl	H	-O-n-butyl
14-31	n-butyl	H	H	-O-n-butyl
14-32	n-butyl	H	H	-O-n-butyl
14-33	n-butyl	H	H	-O-n-butyl
14-34	n-butyl	H	-O-n-butyl	-O-n-butyl
14-35	n-butyl	H	-O-n-butyl	-O-n-butyl

14-36	n-butyl	H	-O-n-butyl	-O-n-butyl
14-37	2-ethylhexyl	-O-2-ethylhexyl	H	H
14-38	2-ethylhexyl	-O-2-ethylhexyl	H	H
14-39	2-ethylhexyl	-O-2-ethylhexyl	H	H
14-40	2-ethylhexyl	-O-2-ethylhexyl	H	-O-2-ethylhexyl
14-41	2-ethylhexyl	-O-2-ethylhexyl	H	-O-2-ethylhexyl
14-42	2-ethylhexyl	-O-2-ethylhexyl	H	-O-2-ethylhexyl
14-43	2-ethylhexyl	H	H	-O-2-ethylhexyl
14-44	2-ethylhexyl	H	H	-O-2-ethylhexyl
14-45	2-ethylhexyl	H	H	-O-2-ethylhexyl
14-46	2-ethylhexyl	H	-O-2-ethylhexyl	-O-2-ethylhexyl
14-47	2-ethylhexyl	H	-O-2-ethylhexyl	-O-2-ethylhexyl
14-48	2-ethylhexyl	H	-O-2-ethylhexyl	-O-2-ethylhexyl
14-49	n-octyl	O-n-octyl	H	H
14-50	n-octyl	O-n-octyl	H	H
14-51	n-octyl	O-n-octyl	H	H
14-52	n-octyl	O-n-octyl	H	O-n-octyl
14-53	n-octyl	O-n-octyl	H	O-n-octyl
14-54	n-octyl	O-n-octyl	H	O-n-octyl
14-55	n-octyl	H	H	O-n-octyl
14-56	n-octyl	H	H	O-n-octyl
14-57	n-octyl	H	H	O-n-octyl
14-58	n-octyl	H	O-n-octyl	O-n-octyl
14-59	n-octyl	H	O-n-octyl	O-n-octyl
14-60	n-octyl	H	O-n-octyl	O-n-octyl
14-61	Ph	-O-2-ethylhexyl	H	H
14-62	Ph	-O-2-ethylhexyl	H	H
14-63	Ph	-O-2-ethylhexyl	H	H
14-64	Ph	-O-2-ethylhexyl	H	-O-2-ethylhexyl
14-65	Ph	-O-2-ethylhexyl	H	-O-2-ethylhexyl
14-66	Ph	-O-2-ethylhexyl	H	-O-2-ethylhexyl
14-67	Ph	H	H	-O-2-ethylhexyl
14-68	Ph	H	H	-O-2-ethylhexyl
14-69	Ph	H	H	-O-2-ethylhexyl
14-70	Ph	H	-O-2-ethylhexyl	-O-2-ethylhexyl

14-71	Ph	H	-O-2-ethylhexyl	-O-2-ethylhexyl
14-72	Ph	H	-O-2-ethylhexyl	-O-2-ethylhexyl
14-73	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	H
14-73	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	H
14-75	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	H
14-76	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	-O-2-ethylhexyl
14-77	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	-O-2-ethylhexyl
14-78	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	-O-2-ethylhexyl
14-79	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	H	-O-2-ethylhexyl
14-80	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	H	-O-2-ethylhexyl
14-81	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	H	-O-2-ethylhexyl
14-82	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	-O-2-ethylhexyl	-O-2-ethylhexyl
14-83	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	-O-2-ethylhexyl	-O-2-ethylhexyl
14-84	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	-O-2-ethylhexyl	-O-2-ethylhexyl



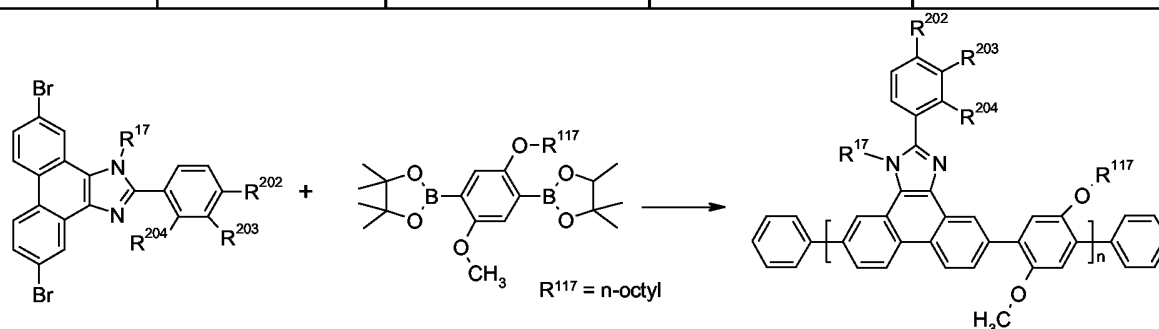
Polymer No.	$R^{17}$	$R^{202}$	$R^{203}$	$R^{204}$
15-1	n-octyl	-O-n-octyl	H	H
15-2	n-octyl	-O-n-octyl	H	H
15-3	n-octyl	-O-n-octyl	H	H
15-4	n-octyl	-O-n-octyl	H	-O-n-octyl
15-5	n-octyl	-O-n-octyl	H	-O-n-octyl
15-6	n-octyl	-O-n-octyl	H	-O-n-octyl
15-7	n-octyl	H	H	-O-n-octyl
15-8	n-octyl	H	H	-O-n-octyl
15-9	n-octyl	H	H	-O-n-octyl
15-10	n-octyl	H	-O-n-octyl	-O-n-octyl
15-11	n-octyl	H	-O-n-octyl	-O-n-octyl
15-12	n-octyl	H	-O-n-octyl	-O-n-octyl

15-13	n-hexyl	-O-n-hexyl	H	H
15-14	n-hexyl	-O-n-hexyl	H	H
15-15	n-hexyl	-O-n-hexyl	H	H
15-16	n-hexyl	-O-n-hexyl	H	-O-n-hexyl
15-17	n-hexyl	-O-n-hexyl	H	-O-n-hexyl
15-18	n-hexyl	-O-n-hexyl	H	-O-n-hexyl
15-19	n-hexyl	H	H	-O-n-hexyl
15-20	n-hexyl	H	H	-O-n-hexyl
15-21	n-hexyl	H	H	-O-n-hexyl
15-22	n-hexyl	H	-O-n-hexyl	-O-n-hexyl
15-23	n-hexyl	H	-O-n-hexyl	-O-n-hexyl
15-24	n-hexyl	H	-O-n-hexyl	-O-n-hexyl
15-25	n-butyl	-O-n-butyl	H	H
15-26	n-butyl	-O-n-butyl	H	H
15-27	n-butyl	-O-n-butyl	H	H
15-28	n-butyl	-O-n-butyl	H	-O-n-butyl
15-29	n-butyl	-O-n-butyl	H	-O-n-butyl
15-30	n-butyl	-O-n-butyl	H	-O-n-butyl
15-31	n-butyl	H	H	-O-n-butyl
15-32	n-butyl	H	H	-O-n-butyl
15-33	n-butyl	H	H	-O-n-butyl
15-34	n-butyl	H	-O-n-butyl	-O-n-butyl
15-35	n-butyl	H	-O-n-butyl	-O-n-butyl
15-36	n-butyl	H	-O-n-butyl	-O-n-butyl
15-37	2-ethylhexyl	-O-2-ethylhexyl	H	H
15-38	2-ethylhexyl	-O-2-ethylhexyl	H	H
15-39	2-ethylhexyl	-O-2-ethylhexyl	H	H
15-40	2-ethylhexyl	-O-2-ethylhexyl	H	-O-2-ethylhexyl
15-41	2-ethylhexyl	-O-2-ethylhexyl	H	-O-2-ethylhexyl
15-42	2-ethylhexyl	-O-2-ethylhexyl	H	-O-2-ethylhexyl
15-43	2-ethylhexyl	H	H	-O-2-ethylhexyl
15-44	2-ethylhexyl	H	H	-O-2-ethylhexyl
15-45	2-ethylhexyl	H	H	-O-2-ethylhexyl
15-46	2-ethylhexyl	H	-O-2-ethylhexyl	-O-2-ethylhexyl
15-47	2-ethylhexyl	H	-O-2-ethylhexyl	-O-2-ethylhexyl



15-48	2-ethylhexyl	H	-O-2-ethylhexyl	-O-2-ethylhexyl
15-49	n-octyl	O-n-octyl	H	H
15-50	n-octyl	O-n-octyl	H	H
15-51	n-octyl	O-n-octyl	H	H
15-52	n-octyl	O-n-octyl	H	O-n-octyl
15-53	n-octyl	O-n-octyl	H	O-n-octyl
15-54	n-octyl	O-n-octyl	H	O-n-octyl
15-55	n-octyl	H	H	O-n-octyl
15-56	n-octyl	H	H	O-n-octyl
15-57	n-octyl	H	H	O-n-octyl
15-58	n-octyl	H	O-n-octyl	O-n-octyl
15-59	n-octyl	H	O-n-octyl	O-n-octyl
15-60	n-octyl	H	O-n-octyl	O-n-octyl
15-61	Ph	-O-2-ethylhexyl	H	H
15-62	Ph	-O-2-ethylhexyl	H	H
15-63	Ph	-O-2-ethylhexyl	H	H
15-64	Ph	-O-2-ethylhexyl	H	-O-2-ethylhexyl
15-65	Ph	-O-2-ethylhexyl	H	-O-2-ethylhexyl
15-66	Ph	-O-2-ethylhexyl	H	-O-2-ethylhexyl
15-67	Ph	H	H	-O-2-ethylhexyl
15-68	Ph	H	H	-O-2-ethylhexyl
15-69	Ph	H	H	-O-2-ethylhexyl
15-70	Ph	H	-O-2-ethylhexyl	-O-2-ethylhexyl
15-71	Ph	H	-O-2-ethylhexyl	-O-2-ethylhexyl
15-72	Ph	H	-O-2-ethylhexyl	-O-2-ethylhexyl
15-73	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	H
15-73	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	H
15-75	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	H
15-76	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	-O-2-ethylhexyl
15-77	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	-O-2-ethylhexyl
15-78	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	-O-2-ethylhexyl
15-79	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	H	-O-2-ethylhexyl
15-80	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	H	-O-2-ethylhexyl
15-81	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	H	-O-2-ethylhexyl
15-82	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	-O-2-ethylhexyl	-O-2-ethylhexyl

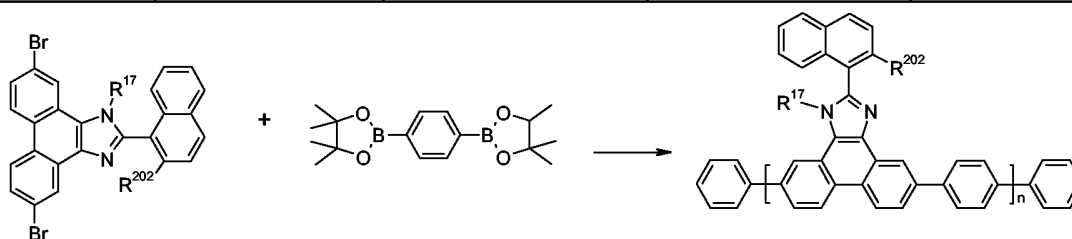
15-83	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	-O-2-ethylhexyl	-O-2-ethylhexyl
15-84	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	-O-2-ethylhexyl	-O-2-ethylhexyl



Polymer No.	$R^{17}$	$R^{202}$	$R^{203}$	$R^{204}$
16-1	n-octyl	-O-n-octyl	H	H
16-2	n-octyl	-O-n-octyl	H	H
16-3	n-octyl	-O-n-octyl	H	H
16-4	n-octyl	-O-n-octyl	H	-O-n-octyl
16-5	n-octyl	-O-n-octyl	H	-O-n-octyl
16-6	n-octyl	-O-n-octyl	H	-O-n-octyl
16-7	n-octyl	H	H	-O-n-octyl
16-8	n-octyl	H	H	-O-n-octyl
16-9	n-octyl	H	H	-O-n-octyl
16-10	n-octyl	H	-O-n-octyl	-O-n-octyl
16-11	n-octyl	H	-O-n-octyl	-O-n-octyl
16-12	n-octyl	H	-O-n-octyl	-O-n-octyl
16-13	n-hexyl	-O-n-hexyl	H	H
16-14	n-hexyl	-O-n-hexyl	H	H
16-15	n-hexyl	-O-n-hexyl	H	H
16-16	n-hexyl	-O-n-hexyl	H	-O-n-hexyl
16-17	n-hexyl	-O-n-hexyl	H	-O-n-hexyl
16-18	n-hexyl	-O-n-hexyl	H	-O-n-hexyl
16-19	n-hexyl	H	H	-O-n-hexyl
16-20	n-hexyl	H	H	-O-n-hexyl
16-21	n-hexyl	H	H	-O-n-hexyl
16-22	n-hexyl	H	-O-n-hexyl	-O-n-hexyl
16-23	n-hexyl	H	-O-n-hexyl	-O-n-hexyl
16-24	n-hexyl	H	-O-n-hexyl	-O-n-hexyl

16-25	n-butyl	-O-n-butyl	H	H
16-26	n-butyl	-O-n-butyl	H	H
16-27	n-butyl	-O-n-butyl	H	H
16-28	n-butyl	-O-n-butyl	H	-O-n-butyl
16-29	n-butyl	-O-n-butyl	H	-O-n-butyl
16-30	n-butyl	-O-n-butyl	H	-O-n-butyl
16-31	n-butyl	H	H	-O-n-butyl
16-32	n-butyl	H	H	-O-n-butyl
16-33	n-butyl	H	H	-O-n-butyl
16-34	n-butyl	H	-O-n-butyl	-O-n-butyl
16-35	n-butyl	H	-O-n-butyl	-O-n-butyl
16-36	n-butyl	H	-O-n-butyl	-O-n-butyl
16-37	2-ethylhexyl	-O-2-ethylhexyl	H	H
16-38	2-ethylhexyl	-O-2-ethylhexyl	H	H
16-39	2-ethylhexyl	-O-2-ethylhexyl	H	H
16-40	2-ethylhexyl	-O-2-ethylhexyl	H	-O-2-ethylhexyl
16-41	2-ethylhexyl	-O-2-ethylhexyl	H	-O-2-ethylhexyl
16-42	2-ethylhexyl	-O-2-ethylhexyl	H	-O-2-ethylhexyl
16-43	2-ethylhexyl	H	H	-O-2-ethylhexyl
16-44	2-ethylhexyl	H	H	-O-2-ethylhexyl
16-45	2-ethylhexyl	H	H	-O-2-ethylhexyl
16-46	2-ethylhexyl	H	-O-2-ethylhexyl	-O-2-ethylhexyl
16-47	2-ethylhexyl	H	-O-2-ethylhexyl	-O-2-ethylhexyl
16-48	2-ethylhexyl	H	-O-2-ethylhexyl	-O-2-ethylhexyl
16-49	n-octyl	O-n-octyl	H	H
16-50	n-octyl	O-n-octyl	H	H
16-51	n-octyl	O-n-octyl	H	H
16-52	n-octyl	O-n-octyl	H	O-n-octyl
16-53	n-octyl	O-n-octyl	H	O-n-octyl
16-54	n-octyl	O-n-octyl	H	O-n-octyl
16-55	n-octyl	H	H	O-n-octyl
16-56	n-octyl	H	H	O-n-octyl
16-57	n-octyl	H	H	O-n-octyl
16-58	n-octyl	H	O-n-octyl	O-n-octyl
16-59	n-octyl	H	O-n-octyl	O-n-octyl

16-60	n-octyl	H	O-n-octyl	O-n-octyl
16-61	Ph	-O-2-ethylhexyl	H	H
16-62	Ph	-O-2-ethylhexyl	H	H
16-63	Ph	-O-2-ethylhexyl	H	H
16-64	Ph	-O-2-ethylhexyl	H	-O-2-ethylhexyl
16-65	Ph	-O-2-ethylhexyl	H	-O-2-ethylhexyl
16-66	Ph	-O-2-ethylhexyl	H	-O-2-ethylhexyl
16-67	Ph	H	H	-O-2-ethylhexyl
16-68	Ph	H	H	-O-2-ethylhexyl
16-69	Ph	H	H	-O-2-ethylhexyl
16-70	Ph	H	-O-2-ethylhexyl	-O-2-ethylhexyl
16-71	Ph	H	-O-2-ethylhexyl	-O-2-ethylhexyl
16-72	Ph	H	-O-2-ethylhexyl	-O-2-ethylhexyl
16-73	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	H
16-73	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	H
16-75	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	H
16-76	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	-O-2-ethylhexyl
16-77	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	-O-2-ethylhexyl
16-78	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl	H	-O-2-ethylhexyl
16-79	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	H	-O-2-ethylhexyl
16-80	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	H	-O-2-ethylhexyl
16-81	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	H	-O-2-ethylhexyl
16-82	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	-O-2-ethylhexyl	-O-2-ethylhexyl
16-83	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	-O-2-ethylhexyl	-O-2-ethylhexyl
16-84	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	H	-O-2-ethylhexyl	-O-2-ethylhexyl



Polymer No.	R <sup>17</sup>	R <sup>202</sup>
16-1	n-octyl	-O-n-octyl
16-2	n-hexyl	-O-n-hexyl
16-3	n-butyl	-O-n-butyl
16-4	-O-2-ethylhexyl	-O-2-ethylhexyl
16-5	Ph	-O-2-ethylhexyl
16-6	Ph	-O-n-octyl
16-7	Ph	-O-n-hexyl
16-8	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-2-ethylhexyl
16-9	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-n-octyl
16-10	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	-O-n-hexyl

### Application Example 1

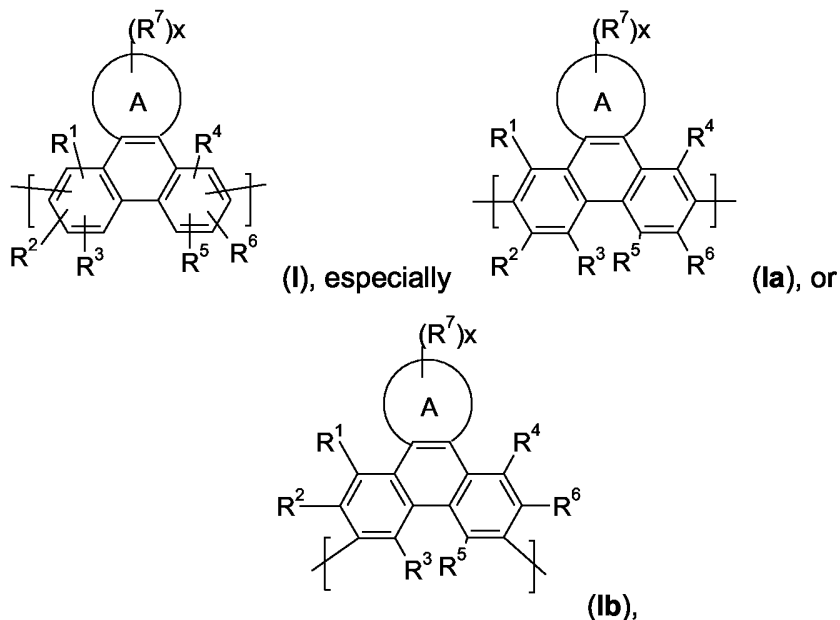
An organic luminescence device having a single organic layer is prepared in the following manner: On a glass substrate, a 100 nm thick ITO film is formed by sputtering and subsequently patterned. Onto the oxygen-plasma treated ITO film a 80 nm thick hole-injection layer using PEDOT:PSS (Baytron P) is formed by spin-coating followed by heating at 200°C (5 minutes). A solution containing 4 mg of a diamine derivative (TPD) as hole transporting material and 6 mg of the compound of **example 39** in 1 ml toluene is applied by spin coating (1500 rep. 10 sec.) to obtain a thickness of 80 nm. Then the thus treated substrate is set in a vacuum deposition chamber and a cathode having two-layer electrode structure is formed by depositing 5 nm barium followed by 100 nm aluminum. When the device is driven at a current density of 10 mA/cm<sup>2</sup> (at 4V) the resultant emission shows a deep blue color (CIE 0.19, 0.14) with an efficacy of 0.6 cd/A.

### Application Example 2

A device is fabricated as described in application example 1, except that the compound of **example 68** is used. The resultant efficacy is 0.2 cd/A when driving the device at 10 mA/cm<sup>2</sup>.

## Claims

1. A polymer comprising a repeating unit(s) of the formula



wherein A is a 5-, 6-, or 7-membered heteroaromatic ring, containing at least one heteroatom selected from nitrogen, oxygen and sulfur, especially one nitrogen atom and at least one further heteroatom selected from nitrogen, substituted nitrogen, oxygen and sulfur,

$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are independently of each other hydrogen, halogen, or an organic substituent, or

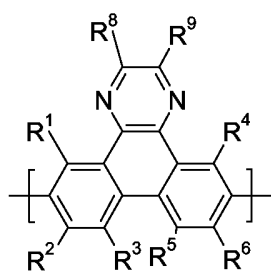
$R^1$  and  $R^2$ ,  $R^4$  and  $R^6$ ,  $R^2$  and  $R^3$ ,  $R^5$  and  $R^3$  and/or  $R^5$  and  $R^6$ , which are adjacent to each other, together form an aromatic, or heteroaromatic ring, or ring system, which can optionally be substituted,

$R^7$  is an organic substituent, wherein two or more substituents  $R^7$  in the same molecule may have different meanings, or can form together an aromatic, or heteroaromatic ring, or ring system, and

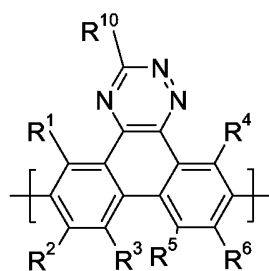
x is 0, or an integer of 1 to 5.

2. A polymer according to claim 1, comprising a repeating unit(s) of the formula

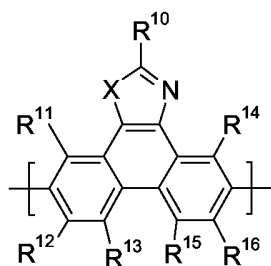
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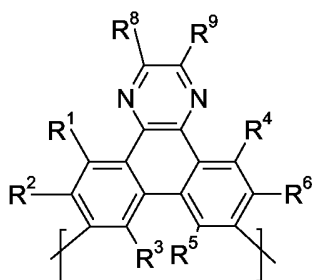
(X),



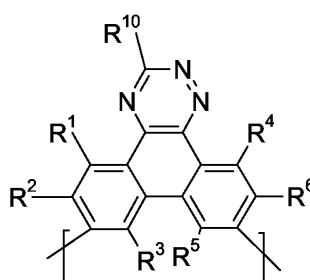
(XI) and/or



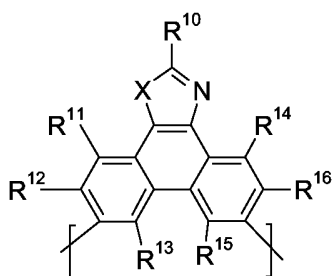
(XII),



(XVI),



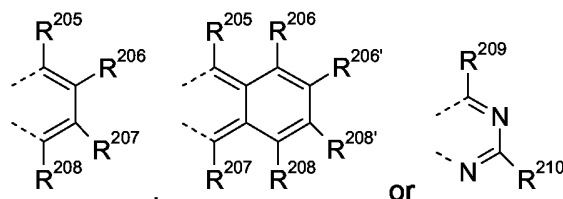
(XVII) and/or



(XVIII), wherein

- 5  $R^1$  and  $R^4$  are independently of each other hydrogen, halogen,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_2$ - $C_{18}$ 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, CN, or  $-CO-R^{28}$ ,
- 10  $R^2$ ,  $R^3$ ,  $R^5$  and  $R^6$  are independently of each other H, halogen,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_6$ - $C_{24}$ 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,  $C_7$ - $C_{25}$ aralkyl, CN, or  $-CO-R^{28}$ ,
- 15  $R^8$  and  $R^9$  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,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_6$ - $C_{24}$ 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<sub>2</sub>-C<sub>18</sub>alkenyl, C<sub>2</sub>-C<sub>18</sub>alkynyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D, C<sub>7</sub>-C<sub>25</sub>aralkyl, CN, or -CO-R<sup>28</sup>, or



R<sup>8</sup> and R<sup>9</sup> together form a group, or, wherein R<sup>206'</sup>, R<sup>208'</sup>, R<sup>205</sup>, R<sup>206</sup>, R<sup>207</sup>, R<sup>208</sup>, R<sup>209</sup> and R<sup>210</sup> are independently of each other H, C<sub>1</sub>-

C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is substituted by E and/or interrupted by D, C<sub>1</sub>-C<sub>18</sub>alkoxy, or C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, C<sub>6</sub>-C<sub>24</sub>aryl, C<sub>6</sub>-C<sub>24</sub>aryl which is substituted by G, C<sub>2</sub>-C<sub>20</sub>heteroaryl, C<sub>2</sub>-C<sub>20</sub>heteroaryl which is substituted by G, C<sub>2</sub>-C<sub>18</sub>alkenyl, C<sub>2</sub>-C<sub>18</sub>alkynyl, C<sub>7</sub>-C<sub>25</sub>aralkyl, CN, or -CO-R<sup>28</sup>,

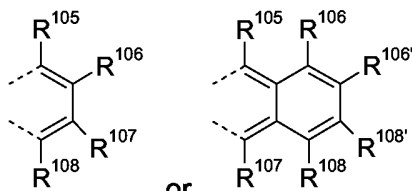
R<sup>10</sup> is H, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is substituted by E and/or interrupted by D, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, C<sub>6</sub>-C<sub>24</sub>aryl, C<sub>6</sub>-C<sub>24</sub>aryl which is substituted by G, C<sub>2</sub>-C<sub>20</sub>heteroaryl, C<sub>2</sub>-C<sub>20</sub>heteroaryl which is substituted by G, C<sub>2</sub>-C<sub>18</sub>alkenyl, C<sub>2</sub>-C<sub>18</sub>alkynyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D, C<sub>7</sub>-C<sub>25</sub>aralkyl, or -CO-R<sup>28</sup>, R<sup>11</sup> and R<sup>14</sup> are independently of each other hydrogen, halogen, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-

C<sub>18</sub>alkyl which is substituted by E and/or interrupted by D, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, C<sub>2</sub>-C<sub>18</sub>alkenyl, C<sub>2</sub>-C<sub>18</sub>alkynyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D, CN, or -CO-R<sup>28</sup>,

R<sup>12</sup>, R<sup>13</sup>, R<sup>15</sup> and R<sup>16</sup> are independently of each other H, halogen, C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkyl which is substituted by E and/or interrupted by D, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, C<sub>6</sub>-C<sub>24</sub>aryl, C<sub>6</sub>-C<sub>24</sub>aryl which is substituted by G, C<sub>2</sub>-C<sub>20</sub>heteroaryl, C<sub>2</sub>-C<sub>20</sub>heteroaryl which is substituted by G, C<sub>2</sub>-C<sub>18</sub>alkenyl, C<sub>2</sub>-C<sub>18</sub>alkynyl, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkoxy which is substituted by E and/or interrupted by D, C<sub>7</sub>-C<sub>25</sub>aralkyl, CN or -CO-R<sup>28</sup>,

X is O, S, or NR<sup>17</sup>, wherein R<sup>17</sup> is H; C<sub>6</sub>-C<sub>18</sub>aryl; C<sub>2</sub>-C<sub>20</sub>heteroaryl; C<sub>6</sub>-C<sub>18</sub>aryl, or C<sub>2</sub>-C<sub>20</sub>heteroaryl, which are substituted by C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>perfluoroalkyl, or C<sub>1</sub>-C<sub>18</sub>alkoxy; C<sub>1</sub>-C<sub>18</sub>alkyl; or C<sub>1</sub>-C<sub>18</sub>alkyl which is interrupted by -O-;

or two substituents R<sup>1</sup> and R<sup>2</sup>, R<sup>4</sup> and R<sup>6</sup>, R<sup>11</sup> and R<sup>12</sup>, and/or R<sup>14</sup> and R<sup>16</sup>, R<sup>2</sup> and R<sup>3</sup>, R<sup>5</sup> and R<sup>6</sup>, R<sup>12</sup> and R<sup>13</sup>, and/or R<sup>15</sup> and R<sup>16</sup>, which are adjacent to each other, together form



a group, or, or two substituents R<sup>15</sup> and R<sup>13</sup>, and/or R<sup>5</sup>

and R<sup>3</sup>, which are adjacent to each other, together form a group, or, or



wherein  $X^3$  is O, S,  $C(R^{119})(R^{120})$ , or  $NR^{17}$ , wherein  $R^{17}$  is as defined above,  $R^{105}$ ,  $R^{106}$ ,  $R^{107}$ ,  $R^{108}$ ,  $R^{106'}$  and  $R^{108'}$  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,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D,

$R^{119}$  and  $R^{120}$  together form a group of formula  $=CR^{121}R^{122}$ , wherein

$R^{121}$  and  $R^{122}$  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

$R^{119}$  and  $R^{120}$  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,  $C_7$ - $C_{25}$ aralkyl, or  $-C(=O)-R^{127}$ , and

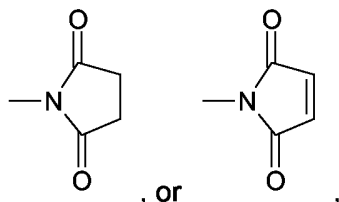
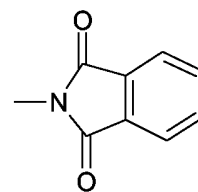
$R^{127}$  is H;  $C_6$ - $C_{18}$ aryl;  $C_6$ - $C_{18}$ aryl which is substituted by  $C_1$ - $C_{18}$ alkyl, or  $C_1$ - $C_{18}$ alkoxy;  $C_1$ - $C_{18}$ alkyl; or  $C_1$ - $C_{18}$ alkyl which is interrupted by  $-O-$ ,

D is  $-CO-$ ;  $-COO-$ ;  $-S-$ ;  $-SO-$ ;  $-SO_2-$ ;  $-O-$ ;  $-NR^{25}-$ ;  $-SiR^{30}R^{31}-$ ;  $-POR^{32}-$ ;  $-CR^{23}=CR^{24}-$ ; or  $-C\equiv C-$ ; and

E is  $-OR^{29}$ ;  $-SR^{29}$ ;  $-NR^{25}R^{26}$ ;  $-COR^{28}$ ;  $-COOR^{27}$ ;  $-CONR^{25}R^{26}$ ;  $-CN$ ; or halogen; G is E,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D, wherein

$R^{23}$ ,  $R^{24}$ ,  $R^{25}$  and  $R^{26}$  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  $-O-$ ; or

$R^{25}$  and  $R^{26}$  together form a five or six membered ring, in particular



$R^{27}$  and  $R^{28}$  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  $-O-$ ,

$R^{29}$  is 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  $-O-$ ,

$R^{30}$  and  $R^{31}$  are independently of each other  $C_1-C_{18}$ alkyl,  $C_6-C_{18}$ aryl, or  $C_6-C_{18}$ aryl, which is substituted by  $C_1-C_{18}$ alkyl, and

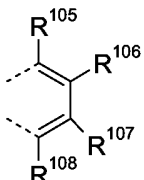
$R^{32}$  is  $C_1-C_{18}$ alkyl,  $C_6-C_{18}$ aryl, or  $C_6-C_{18}$ aryl, which is substituted by  $C_1-C_{18}$ alkyl.

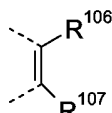
3. A polymer according to claim 2, comprising a repeating unit of the formula **X**, or **XI**, wherein  $R^1$  and  $R^4$  are hydrogen,

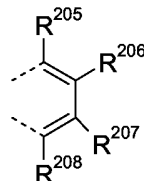
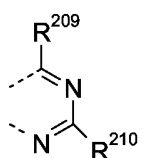
$R^2$ ,  $R^3$ ,  $R^5$  and  $R^6$  are independently of each other H,  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkyl which is interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,  $C_1-C_{18}$ alkoxy,  $C_1-C_{18}$ alkoxy which is interrupted by D,  $C_7-C_{25}$ aralkyl, or a group  $-X^2-R^{18}$ ,

$R^8$  and  $R^9$  are independently of each other H,  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkyl which is interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,  $C_1-C_{18}$ alkoxy,  $C_1-C_{18}$ alkoxy which is interrupted by D, or a group  $-X^2-R^{18}$ , wherein  $X^2$  is a spacer, such as  $C_6-C_{12}$ aryl, or  $C_6-$

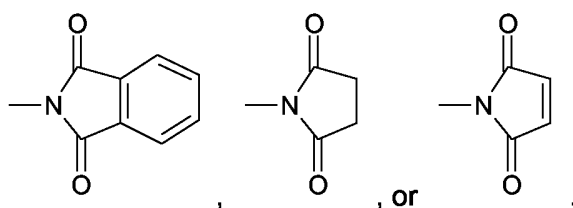
$C_{12}$ heteroaryl, especially phenyl, or naphthyl, which can be substituted one more, especially one to two times with  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkyl which is interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,  $C_1-C_{18}$ alkoxy, or  $C_1-C_{18}$ alkoxy which is substituted by E and/or interrupted by D, and  $R^{18}$  is H,  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkyl which is interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,  $C_1-C_{18}$ alkoxy,  $C_1-C_{18}$ alkoxy which is interrupted by D, or  $-NR^{25}R^{26}$ ; or two substituents  $R^2$  and  $R^3$  and/or  $R^5$  and  $R^6$ , which are adjacent to each other, together

form a group , or two substituents  $R^5$  and  $R^3$ , which are adjacent to each

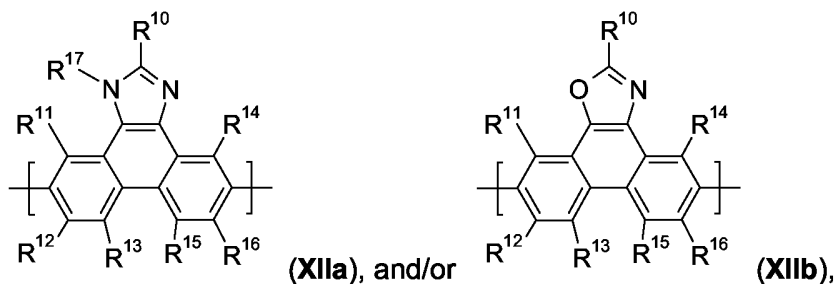
other, together form a group , wherein  $R^{105}$ ,  $R^{106}$ ,  $R^{107}$  and  $-R^{108}$  are independently of each other H, or  $C_1-C_8$ alkyl, or

$R^8$  and  $R^9$  together form a group , or , wherein  $R^{205}$ ,  $R^{206}$ ,  $R^{207}$ ,  $R^{208}$ ,  $R^{209}$  and  $R^{210}$  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,  $C_1-C_{18}$ alkoxy, or  $C_1-C_{18}$ alkoxy which is substituted by E and/or interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,

$R^{10}$  is H,  $C_6$ - $C_{18}$ aryl, which can be substituted by G,  $C_2$ - $C_{18}$ heteroaryl, which can be substituted by G,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D, or a group  $-X^2-R^{18}$ , wherein  $X^2$  is a spacer, such as  $C_6$ - $C_{12}$ aryl, or  $C_6$ - $C_{12}$ heteroaryl, especially phenyl, or naphthyl, which can be substituted one more, especially one to two times with  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D, and  $R^{18}$  is H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkoxy which is interrupted by D, or  $-NR^{25}R^{26}$ ;  
 D is  $-CO-$ ;  $-COO-$ ;  $-S-$ ;  $-SO-$ ;  $-SO_2-$ ;  $-O-$ ;  $-NR^{25}-$ ;  $-CR^{23}=CR^{24}-$ ; or  $-C\equiv C-$ ; wherein  $R^{23}$ ,  $R^{24}$ ,  $R^{25}$  and  $R^{26}$  are independently of each other H;  $C_6$ - $C_{18}$ aryl;  $C_6$ - $C_{18}$ aryl which is substituted by  $C_1$ - $C_8$ alkyl, or  $C_1$ - $C_8$ alkoxy;  $C_1$ - $C_8$ alkyl; or  $C_1$ - $C_8$ alkyl which is interrupted by  $-O-$ , or  $R^{25}$  and  $R^{26}$  together form a five or six membered ring, in particular

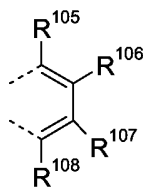


4. A polymer according to claim 2, comprising a repeating unit of the formula

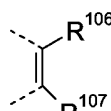


$R^{10}$  is H,  $C_6$ - $C_{18}$ aryl, which can be substituted by G,  $C_2$ - $C_{18}$ heteroaryl, which can be substituted by G,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D, or a group  $-X^2-R^{18}$ , wherein  $X^2$  is a spacer, such as  $C_6$ - $C_{12}$ aryl, or  $C_6$ - $C_{12}$ heteroaryl, especially phenyl, or naphthyl, which can be substituted one more, especially one to two times with  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy, or  $C_1$ - $C_{18}$ alkoxy which is substituted by E and/or interrupted by D, and  $R^{18}$  is H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_1$ - $C_{18}$ alkoxy,  $C_1$ - $C_{18}$ alkoxy which is interrupted by D, or  $-NR^{25}R^{26}$ ;  
 $R^{11}$  and  $R^{14}$  are hydrogen,  
 $R^{12}$ ,  $R^{13}$ ,  $R^{15}$  and  $R^{16}$  are hydrogen,

$R^{17}$  is  $C_6-C_{18}$ aryl;  $C_6-C_{18}$ aryl which is substituted by  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ perfluoroalkyl, or  $C_1-C_{18}$ alkoxy;  $C_1-C_{18}$ alkyl; or  $C_1-C_{18}$ alkyl which is interrupted by  $-O-$ ; or two substituents  $R^5$  and  $R^3$ ,  $R^{12}$  and  $R^{13}$ , and/or  $R^{15}$  and  $R^{16}$ , which are adjacent to each



other, together form a group, or two substituents  $R^{15}$  and  $R^{13}$ , which are

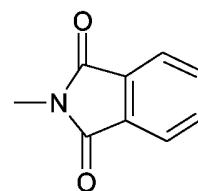


5 adjacent to each other, together form a group, wherein  $R^{105}$ ,  $R^{106}$ ,  $R^{107}$  and  $R^{108}$  are independently of each other H, or  $C_1-C_8$ alkyl,

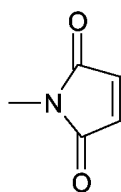
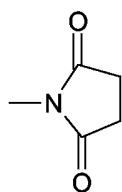
D is  $-S-$ ;  $-O-$ ; or  $-NR^{25}-$ ;

E is  $-OR^{29}$ ;  $-SR^{29}$ ;  $-NR^{25}R^{26}$ ;  $-CN$ ; or F; G is E,  $C_1-C_{18}$ alkyl,  $C_1-C_{18}$ alkyl which is interrupted by D,  $C_1-C_{18}$ perfluoroalkyl,  $C_1-C_{18}$ alkoxy, or  $C_1-C_{18}$ alkoxy which is substituted by E and/or interrupted by D, wherein

10  $R^{25}$  and  $R^{26}$  are independently of each other H;  $C_6-C_{18}$ aryl;  $C_6-C_{18}$ aryl which is substituted by  $C_1-C_8$ alkyl, or  $C_1-C_8$ alkoxy;  $C_1-C_8$ alkyl; or  $C_1-C_8$ alkyl which is interrupted by  $-O-$ , or



$R^{25}$  and  $R^{26}$  together form a five or six membered ring, in particular

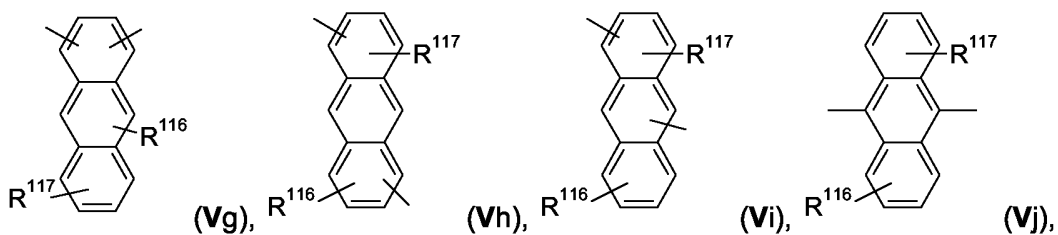
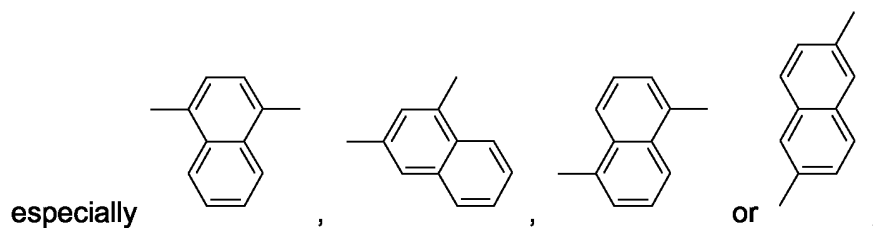
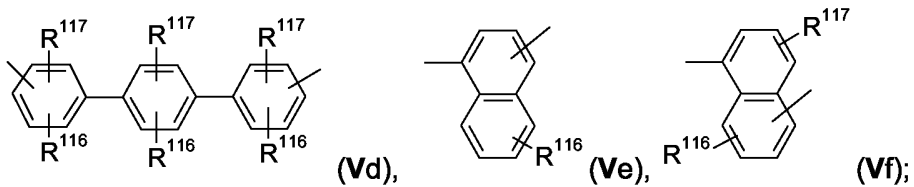
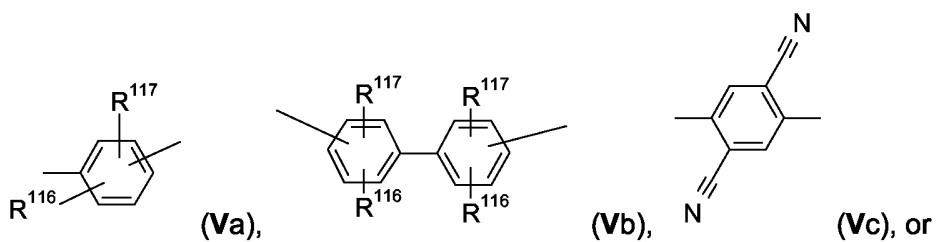
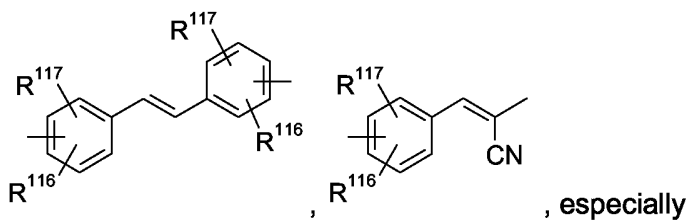
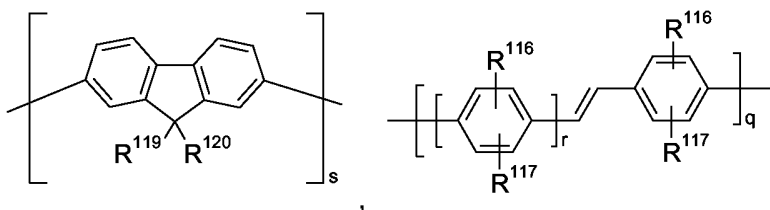
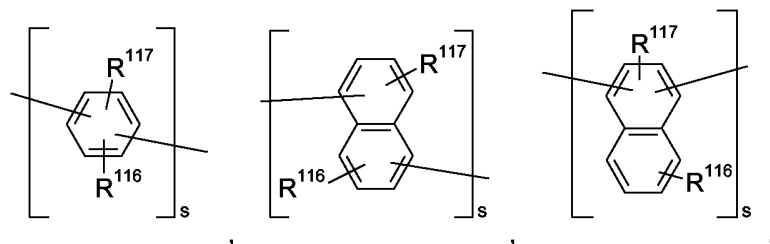


15, or, and

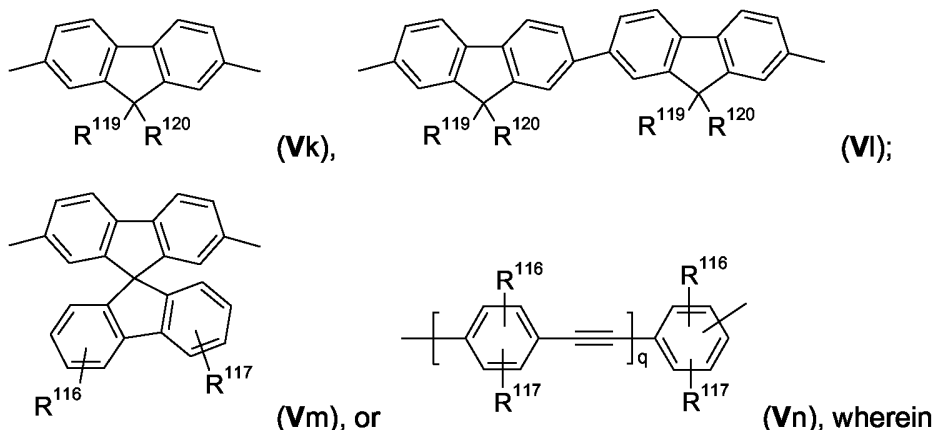
$R^{29}$  is  $C_6-C_{18}$ aryl;  $C_6-C_{18}$ aryl, which is substituted by  $C_1-C_{18}$ alkyl, or  $C_1-C_{18}$ alkoxy;  $C_1-C_{18}$ alkyl; or  $C_1-C_{18}$ alkyl which is interrupted by  $-O-$ .

5. The polymer according to any of claims 1 to 4, comprising one or more (at least one) repeating unit(s)  $Ar^3$  which is selected from the group consisting of

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r is an integer from 1 to 10, especially 1, 2 or 3,

q is an integer from 1 to 10, especially 1, 2 or 3,

s is an integer from 1 to 10, especially 1, 2 or 3,

$R^{116}$  and  $R^{117}$  are independently of each other H, halogen,  $-\text{CN}$ ,  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ,  $\text{C}_1\text{-C}_{18}\text{alkyl}$  which is substituted by E and/or interrupted by D,  $\text{C}_6\text{-C}_{24}\text{aryl}$ ,  $\text{C}_6\text{-C}_{24}\text{aryl}$  which is

substituted by G,  $\text{C}_2\text{-C}_{20}\text{heteroaryl}$ ,  $\text{C}_2\text{-C}_{20}\text{heteroaryl}$  which is substituted by G,  $\text{C}_2\text{-C}_{18}\text{alkenyl}$ ,  $\text{C}_2\text{-C}_{18}\text{alkynyl}$ ,  $\text{C}_1\text{-C}_{18}\text{alkoxy}$ ,  $\text{C}_1\text{-C}_{18}\text{alkoxy}$  which is substituted by E and/or interrupted by D,  $\text{C}_7\text{-C}_{25}\text{aralkyl}$ ,  $-\text{C}(=\text{O})-\text{R}^{127}$ ,  $-\text{C}(=\text{O})\text{OR}^{127}$ , or  $-\text{C}(=\text{O})\text{NR}^{127}\text{R}^{126}$ ,

$R^{119}$  and  $R^{120}$  are independently of each other H,  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ,  $\text{C}_1\text{-C}_{18}\text{alkyl}$  which is substituted by E and/or interrupted by D,  $\text{C}_6\text{-C}_{24}\text{aryl}$ ,  $\text{C}_6\text{-C}_{24}\text{aryl}$  which is substituted by G,  $\text{C}_2\text{-C}_{20}\text{heteroaryl}$ ,  $\text{C}_2\text{-C}_{20}\text{heteroaryl}$  which is substituted by G,  $\text{C}_2\text{-C}_{18}\text{alkenyl}$ ,  $\text{C}_2\text{-C}_{18}\text{alkynyl}$ ,  $\text{C}_1\text{-C}_{18}\text{alkoxy}$ ,  $\text{C}_1\text{-C}_{18}\text{alkoxy}$  which is substituted by E and/or interrupted by D, or  $\text{C}_7\text{-C}_{25}\text{aralkyl}$ , or

$R^{119}$  and  $R^{120}$  together form a group of formula  $=\text{CR}^{121}\text{R}^{122}$ , wherein

$R^{121}$  and  $R^{122}$  are independently of each other H,  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ,  $\text{C}_1\text{-C}_{18}\text{alkyl}$  which is substituted by E and/or interrupted by D,  $\text{C}_6\text{-C}_{24}\text{aryl}$ ,  $\text{C}_6\text{-C}_{24}\text{aryl}$  which is substituted by G, or  $\text{C}_2\text{-C}_{20}\text{heteroaryl}$ , or  $\text{C}_2\text{-C}_{20}\text{heteroaryl}$  which is substituted by G, or

$R^{119}$  and  $R^{120}$  together form a five or six membered ring, which optionally can be substituted by  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ,  $\text{C}_1\text{-C}_{18}\text{alkyl}$  which is substituted by E and/or interrupted by D,  $\text{C}_6\text{-C}_{24}\text{aryl}$ ,  $\text{C}_6\text{-C}_{24}\text{aryl}$  which is substituted by G,  $\text{C}_2\text{-C}_{20}\text{heteroaryl}$ ,  $\text{C}_2\text{-C}_{20}\text{heteroaryl}$  which is substituted by G,  $\text{C}_2\text{-C}_{18}\text{alkenyl}$ ,  $\text{C}_2\text{-C}_{18}\text{alkynyl}$ ,  $\text{C}_1\text{-C}_{18}\text{alkoxy}$ ,  $\text{C}_1\text{-C}_{18}\text{alkoxy}$  which is substituted by E and/or interrupted by D,  $\text{C}_7\text{-C}_{25}\text{aralkyl}$ , or  $-\text{C}(=\text{O})-\text{R}^{127}$ , and

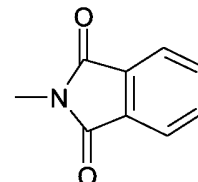
$R^{126}$  and  $R^{127}$  are independently of each other H;  $\text{C}_6\text{-C}_{18}\text{aryl}$ ;  $\text{C}_6\text{-C}_{18}\text{aryl}$  which is substituted by  $\text{C}_1\text{-C}_{18}\text{alkyl}$ , or  $\text{C}_1\text{-C}_{18}\text{alkoxy}$ ;  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ; or  $\text{C}_1\text{-C}_{18}\text{alkyl}$  which is interrupted by  $-\text{O}-$ ,

D is  $-\text{CO}-$ ,  $-\text{COO}-$ ,  $-\text{S}-$ ,  $-\text{SO}-$ ,  $-\text{SO}_2-$ ,  $-\text{O}-$ ,  $-\text{NR}^{65}-$ ,  $-\text{SiR}^{70}\text{R}^{71}-$ ,  $-\text{POR}^{72}-$ ,  $-\text{CR}^{63}=\text{CR}^{64}-$ , or  $\text{C}\equiv\text{C}-$ , and

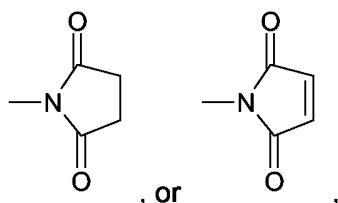
E is  $-\text{OR}^{69}$ ,  $-\text{SR}^{69}$ ,  $-\text{NR}^{65}\text{R}^{66}$ ,  $-\text{COR}^{68}$ ,  $-\text{COOR}^{67}$ ,  $-\text{CONR}^{65}\text{R}^{66}$ ,  $-\text{CN}$ , or halogen,

G is E,  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ,  $\text{C}_1\text{-C}_{18}\text{alkyl}$  which is interrupted by D,  $\text{C}_1\text{-C}_{18}\text{perfluoroalkyl}$ ,  $\text{C}_1\text{-C}_{18}\text{alkoxy}$ , or  $\text{C}_1\text{-C}_{18}\text{alkoxy}$  which is substituted by E and/or interrupted by D,

$\text{R}^{63}$ ,  $\text{R}^{64}$ ,  $\text{R}^{65}$  and  $\text{R}^{66}$  are independently of each other H;  $\text{C}_6\text{-C}_{18}\text{aryl}$ ;  $\text{C}_6\text{-C}_{18}\text{aryl}$  which is substituted by  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ,  $\text{C}_1\text{-C}_{18}\text{alkoxy}$ ;  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ; or  $\text{C}_1\text{-C}_{18}\text{alkyl}$  which is interrupted by  $-\text{O}-$ ; or



$\text{R}^{65}$  and  $\text{R}^{66}$  together form a five or six membered ring, in particular

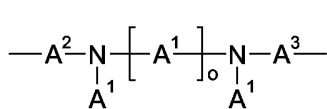


$\text{R}^{67}$  and  $\text{R}^{68}$  are independently of each other H;  $\text{C}_6\text{-C}_{18}\text{aryl}$ ;  $\text{C}_6\text{-C}_{18}\text{aryl}$  which is substituted by  $\text{C}_1\text{-C}_{18}\text{alkyl}$ , or  $\text{C}_1\text{-C}_{18}\text{alkoxy}$ ;  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ; or  $\text{C}_1\text{-C}_{18}\text{alkyl}$  which is interrupted by  $-\text{O}-$ ,

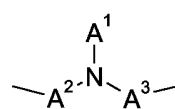
$\text{R}^{69}$  is H;  $\text{C}_6\text{-C}_{18}\text{aryl}$ ;  $\text{C}_6\text{-C}_{18}\text{aryl}$ , which is substituted by  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ,  $\text{C}_1\text{-C}_{18}\text{alkoxy}$ ;  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ; or  $\text{C}_1\text{-C}_{18}\text{alkyl}$  which is interrupted by  $-\text{O}-$ ,

$\text{R}^{70}$  and  $\text{R}^{71}$  are independently of each other  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ,  $\text{C}_6\text{-C}_{18}\text{aryl}$ , or  $\text{C}_6\text{-C}_{18}\text{aryl}$ , which is substituted by  $\text{C}_1\text{-C}_{18}\text{alkyl}$ , and

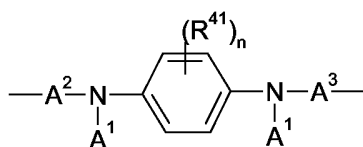
$\text{R}^{72}$  is  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ,  $\text{C}_6\text{-C}_{18}\text{aryl}$ , or  $\text{C}_6\text{-C}_{18}\text{aryl}$ , which is substituted by  $\text{C}_1\text{-C}_{18}\text{alkyl}$ ;



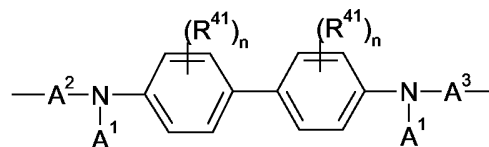
(IIa),



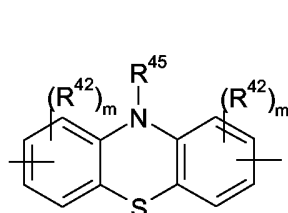
(IIb),



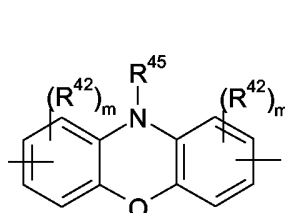
(IIc),



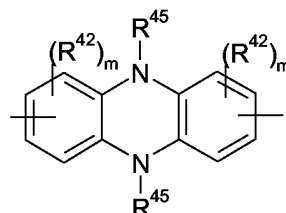
(IIId),



(IIe),

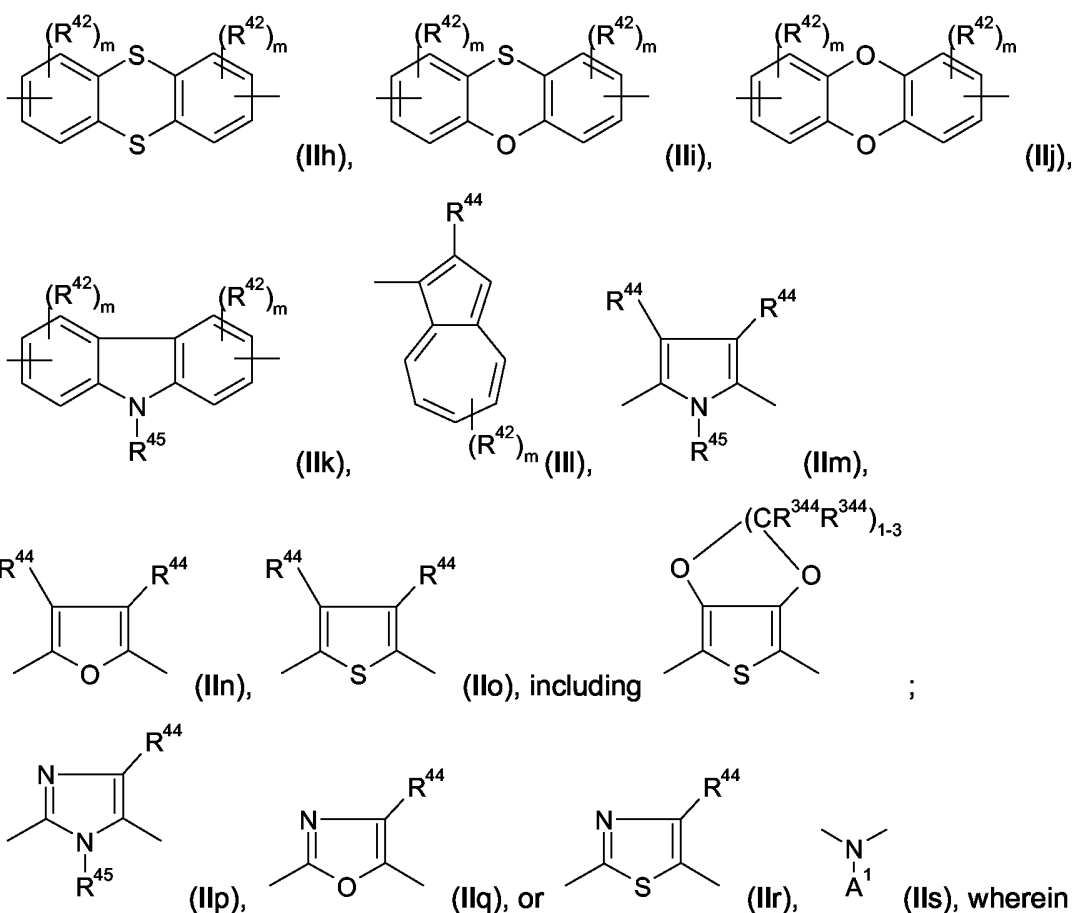


(IIIf),



(IIg),

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$R^{41}$  can be the same or different at each occurrence and is Cl, F, CN,  $N(R^{45})_2$ , a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, a  $C_1$ - $C_{25}$ alkoxy group, in which one or more carbon atoms which are not in neighbourhood to each other could be replaced by  $-NR^{45}$ -,  $-O$ -,  $-S$ -,  $-C(=O)-O$ -, or  $-O-C(=O)-O$ -, and/or wherein one or more hydrogen atoms can be replaced by F, a  $C_6$ - $C_{24}$ aryl group, or a  $C_6$ - $C_{24}$ aryloxy group, wherein one or more carbon atoms can be replaced by O, S, or N, and/or which can be substituted by one or more non-aromatic groups  $R^{41}$ , or

two or more groups  $R^{41}$  form a ring system;

$R^{42}$  can be the same or different at each occurrence and is CN, a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, a  $C_1$ - $C_{25}$ alkoxy group, in which one or more carbon atoms which are not in neighbourhood to each other could be replaced by  $-NR^{45}$ -,  $-O$ -,  $-S$ -,  $-C(=O)-O$ -, or  $-O-C(=O)-O$ -, and/or wherein one or more hydrogen atoms can be replaced by F, a  $C_6$ - $C_{24}$ aryl group, or a  $C_6$ - $C_{24}$ aryloxy group, wherein one or more carbon atoms can be replaced by O, S, or N, and/or which can be substituted by one or more non-aromatic groups  $R^{41}$ , or

two or more groups  $R^{41}$  form a ring system;

$R^{344}$  can be the same or different at each occurrence and are a hydrogen atom, a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, or a  $C_1$ - $C_{25}$ alkoxy group,



$R^{44}$  can be the same or different at each occurrence and are a hydrogen atom, a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, a  $C_1$ - $C_{25}$ alkoxy group, in which one or more carbon atoms which are not in neighbourhood to each other could be replaced by - $NR^{45}$ -, -O-, -S-, -C(=O)-O-, or, -O-C(=O)-O-, and/or wherein one or more hydrogen atoms can be replaced by F, a  $C_6$ - $C_{24}$ aryl group, or a  $C_6$ - $C_{24}$ aryloxy group, wherein one or more carbon atoms can be replaced by O, S, or N, and/or which can be substituted by one or more non-aromatic groups  $R^{41}$ , or CN, or

two or more groups  $R^{44}$ , which are in neighbourhood to each other, form a ring;

$R^{45}$  is H, a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, in which one or more carbon atoms which are not in neighbourhood to each other could be replaced by - $NR^{45}$ -, -O-, -S-, -C(=O)-O-, or, -O-C(=O)-O-, and/or wherein one or more hydrogen atoms can be replaced by F, a  $C_6$ - $C_{24}$ aryl group, or a  $C_6$ - $C_{24}$ aryloxy group, wherein one or more carbon atoms can be replaced by O, S, or N, and/or which can be substituted by one or more non-aromatic groups  $R^{41}$ ;

$R^{45}$  is H, a  $C_1$ - $C_{25}$ alkyl group, or a  $C_4$ - $C_{18}$ cycloalkyl group,

m can be the same or different at each occurrence and is 0, 1, 2, or 3, especially 0, 1, or 2, very especially 0 or 1;

n can be the same or different at each occurrence and is 0, 1, 2, or 3, especially 0, 1, or 2, very especially 0 or 1;

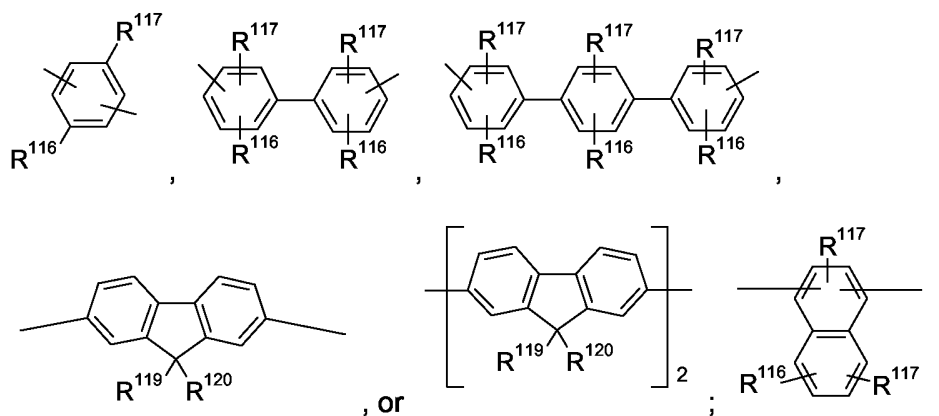
o is 1, 2, or 3, especially 1, or 2,

$A^1$  is a  $C_6$ - $C_{24}$ aryl group, a  $C_2$ - $C_{30}$ heteroaryl group, which can be substituted by one or more non-aromatic groups  $R^{41}$ , or  $NO_2$ ,

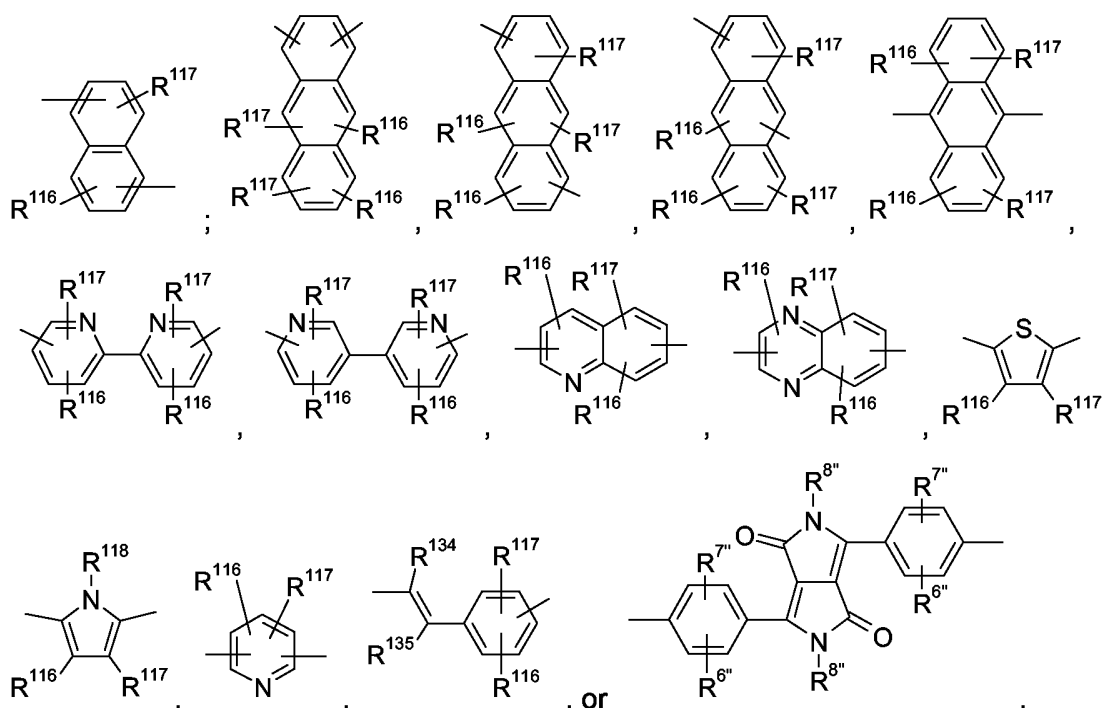
especially phenyl, naphthyl, anthryl, biphenyl, 2-fluorenyl, phenanthryl, or perylenyl,

$A^2$  and  $A^3$  are independently of each other a  $C_6$ - $C_{30}$ arylene group, or a  $C_2$ -

$C_{24}$ heteroarylene group, which can optionally be substituted, especially



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wherein  $R^{116}$ ,  $R^{117}$ ,  $R^{119}$  and  $R^{120}$  are as defined above,

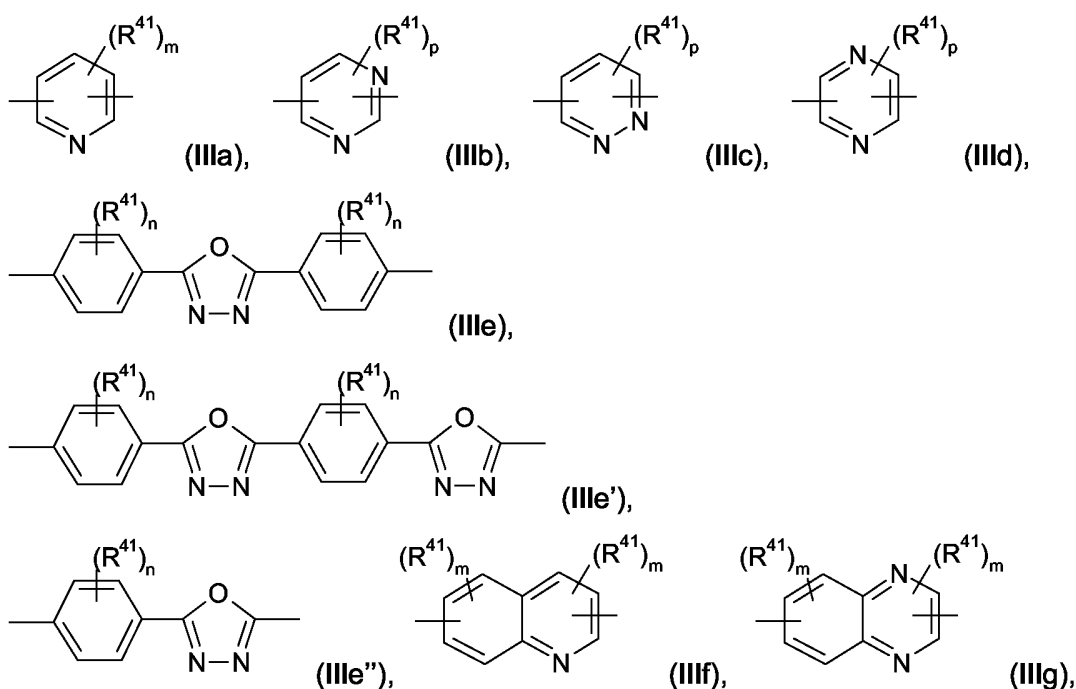
5

$R^{6''}$  and  $R^{7''}$  have independently of each other the meaning of  $R^{116}$ ,

$R^{118}$  and  $R^{8''}$  are 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, or  $C_7$ - $C_{25}$  aralkyl, which are optionally substituted by G,

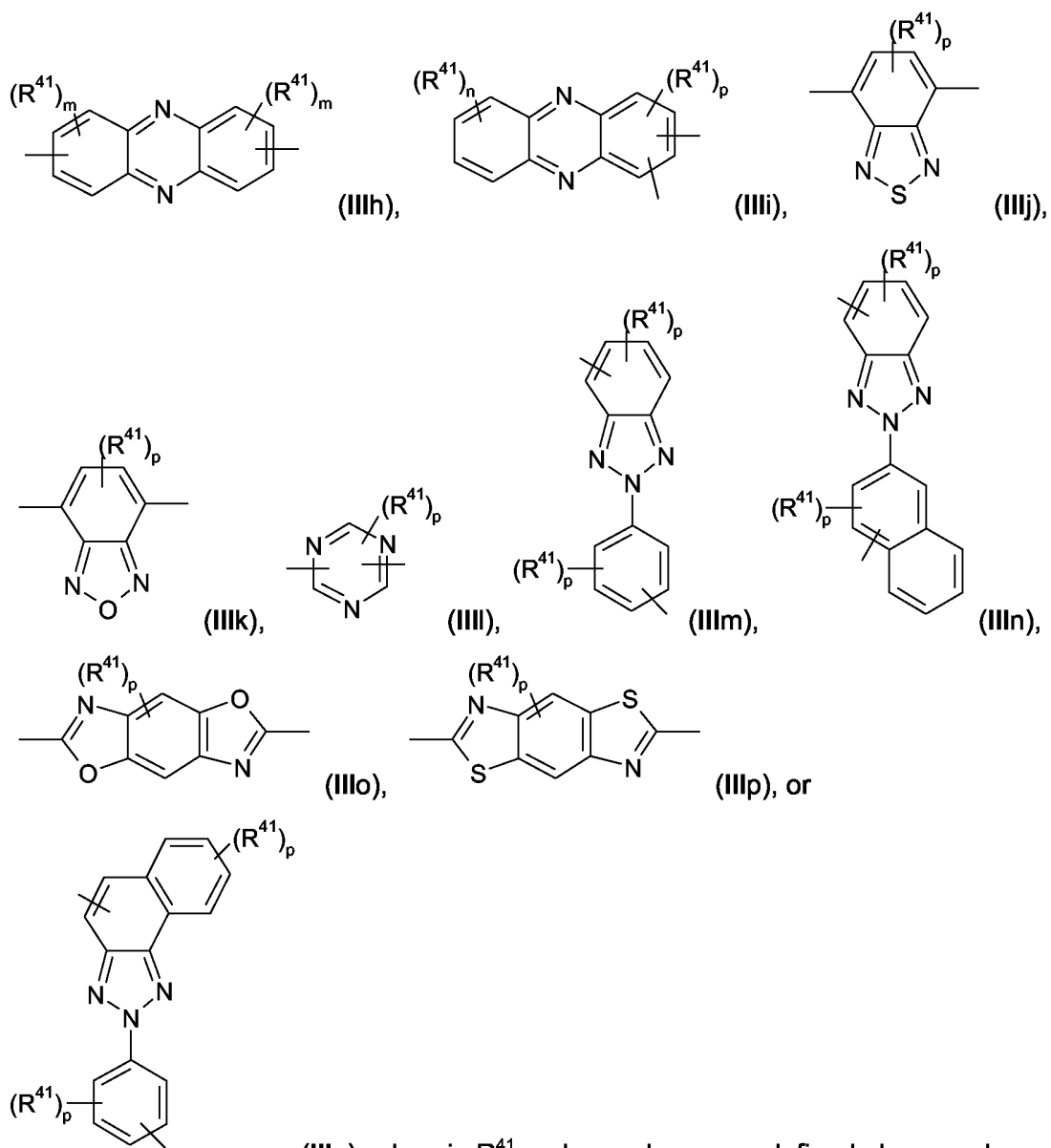
$R^{134}$  and  $R^{135}$  are independently of each other H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_6$ - $C_{24}$ aryl,  $C_6$ - $C_{24}$ aryl which is substituted by E, or  $C_2$ - $C_{20}$ heteroaryl,  $C_2$ - $C_{20}$ heteroaryl which is substituted by E, wherein D, E and G are as defined above,

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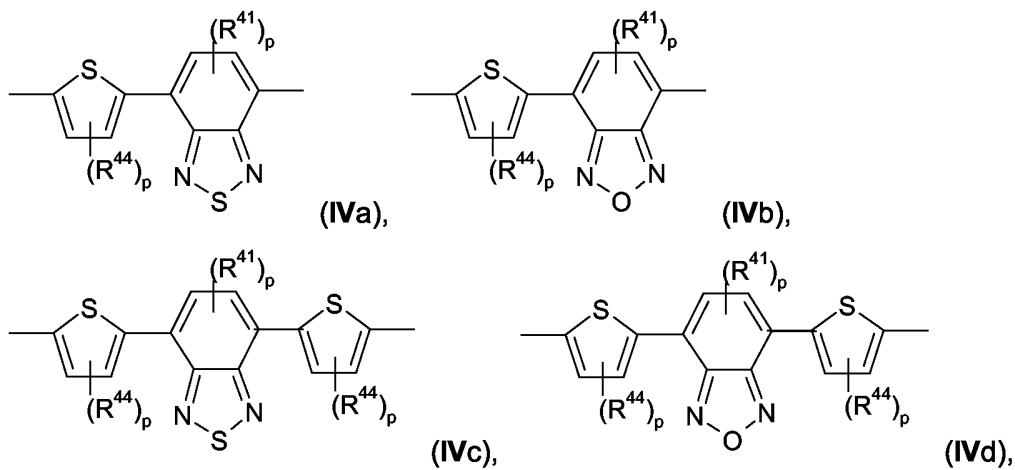
146



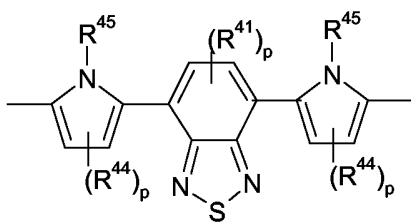
(IIIq), wherein  $R^{41}$  and  $m$  and  $n$  are as defined above and

5

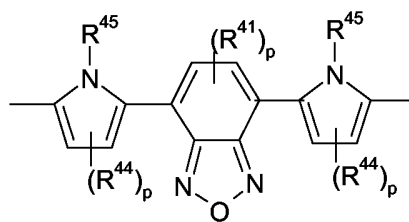
$p$  is 0, 1, or 2, especially 0 or 1;



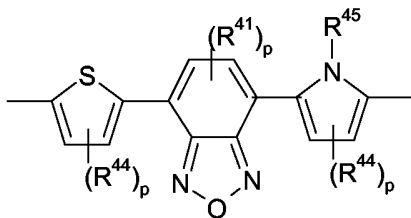
147



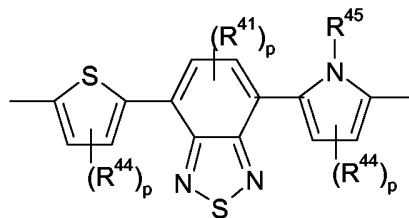
(IVe),



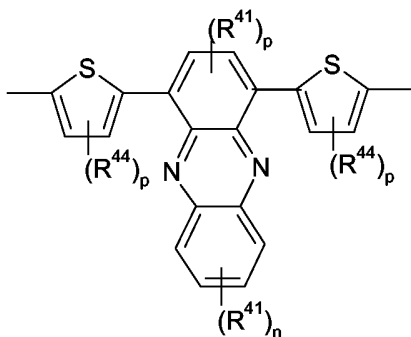
(IVf),



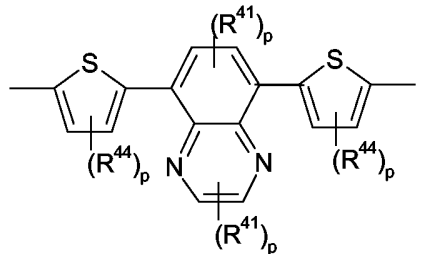
(IVg),



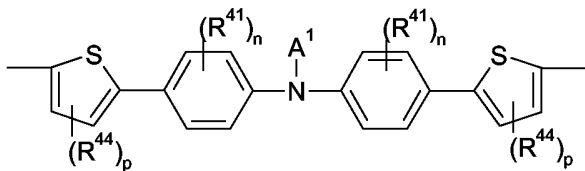
(IVh),



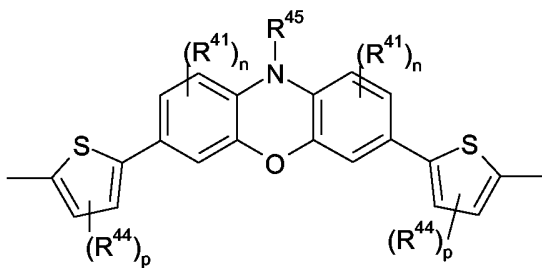
(IVi),



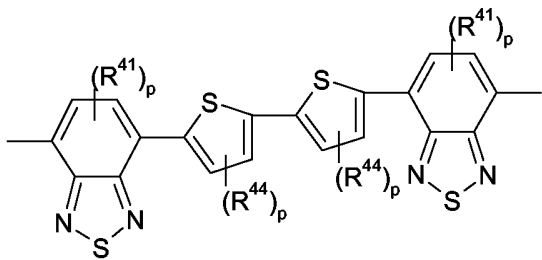
(IVj),



(IVk),

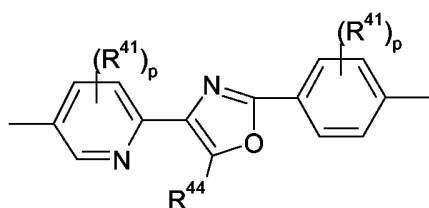


(IVl),

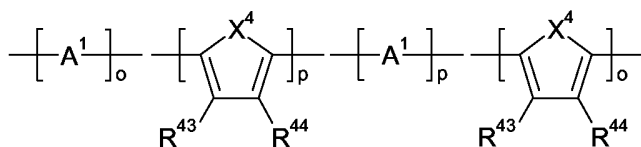


(IVm),

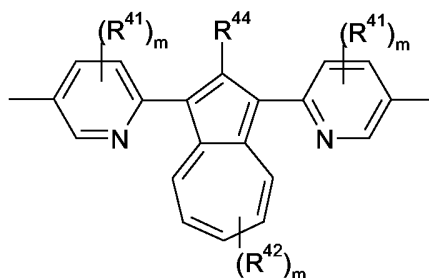
148



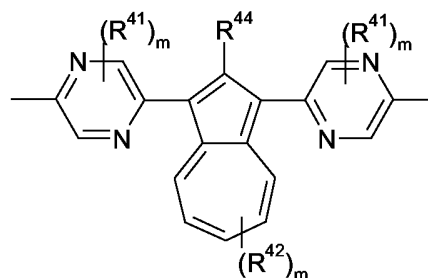
(IVn),



(IVo),



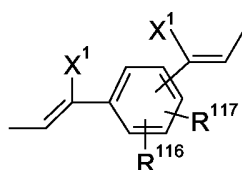
(IVp), or



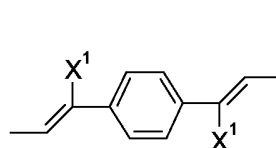
(IVq),

wherein  $X^4$  is O, S, or  $NR^{45}$ ,

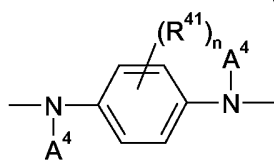
- 5  $R^{43}$  is a hydrogen atom, a  $C_1$ - $C_{25}$ alkyl group, a  $C_4$ - $C_{18}$ cycloalkyl group, a  $C_1$ - $C_{25}$ alkoxy group, in which one or more carbon atoms which are not in neighbourhood to each other could be replaced by  $-NR^{45}$ -,  $-O$ -,  $-S$ -,  $-C(=O)-O$ -, or,  $-O-C(=O)-O$ -, and/or wherein one or more hydrogen atoms can be replaced by F, a  $C_6$ - $C_{24}$ aryl group, or a  $C_6$ - $C_{24}$ aryloxy group, wherein one or more carbon atoms can be replaced by O, S, or N,
- 10 and/or which can be substituted by one or more non-aromatic groups  $R^{41}$ , or CN, or two or more groups  $R^{43}$  and/or  $R^{44}$ , which are in neighbourhood to each other, form a ring; and  $A^1$ ,  $R^{41}$ ,  $R^{42}$ ,  $R^{44}$ ,  $R^{45}$ , m, n, o and p are as defined above; and/or one or more (at least one) repeating unit(s) -T- which is selected from the group consisting of



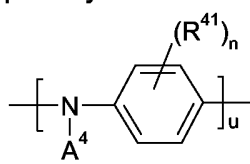
(VIa), especially



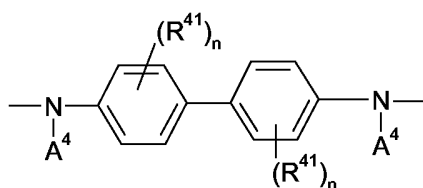
(VIb),



(VIc),



(VIId),



(VIe), or



(VIf), wherein

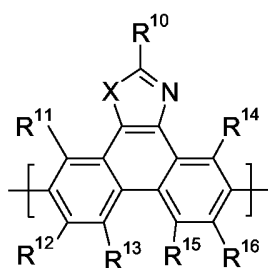
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$X^1$  is a hydrogen atom, or a cyano group, u is 1, 2, 3, or 4;

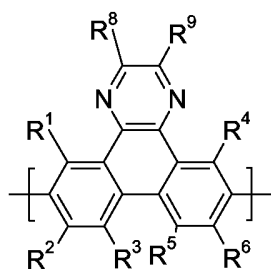
$R^{116}$ ,  $R^{117}$ ,  $R^{41}$  and n are as defined above; and

$A^4$  is a  $C_6$ - $C_{24}$ aryl group, a  $C_2$ - $C_{30}$ heteroaryl group, especially phenyl, naphthyl, anthryl, biphenylyl, 2-fluorenyl, phenanthryl, or perylenyl, which can be substituted by one or more non-aromatic groups  $R^{41}$ .

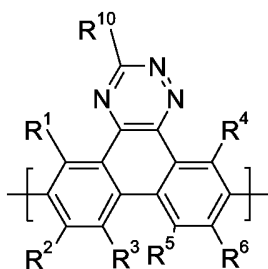
6. The polymer according to claim 1, wherein the polymer is a copolymer which contain at least two different repeating units of formula I, especially a copolymer, which comprises at least one repeating unit of formula I wherein A is a 5 membered heteroaromatic ring,



such as repeating units of formula (XII), and at least one repeating unit of formula I wherein A is a 6 membered heteroaromatic ring, such as repeating units of formula

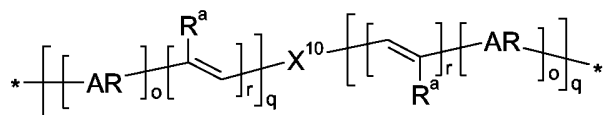


(X) and/or



(XI), wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,

$R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$  are as defined in claim 3, and  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$ ,  $R^{15}$  and  $R^{16}$  are as defined in claim 4; or a polymer comprising a repeating unit(s) of formula



XX, wherein

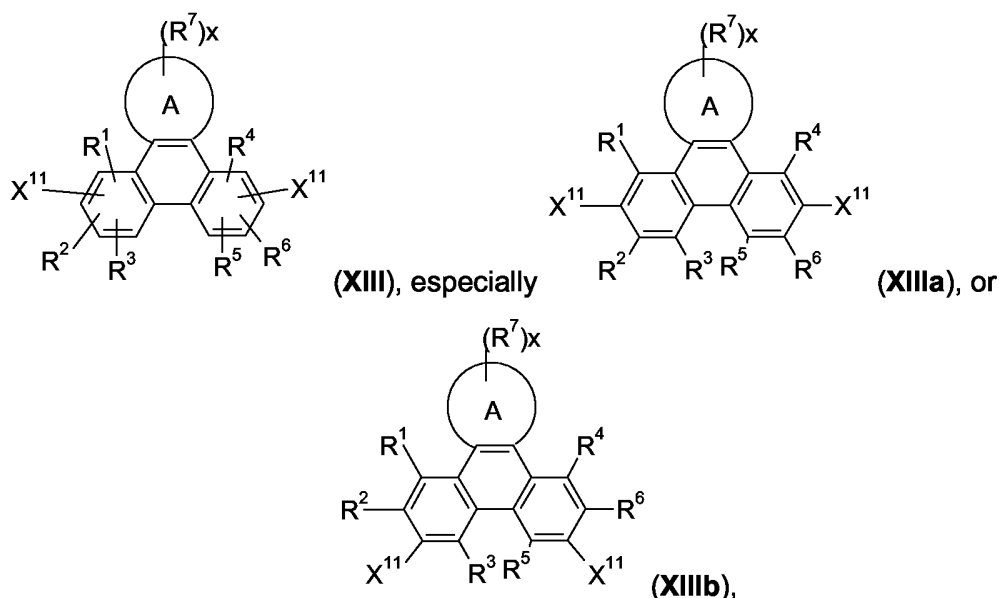
$X^{10}$  is a repeating unit of formula I, especially X, XI and XII;

q is an integer 0, 1, or 2, o is 0, 1, or 2, r is 0, or 1,

AR is  $C_6$ - $C_{24}$ 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,

$R^a$  is H,  $C_1$ - $C_{18}$ alkyl,  $C_1$ - $C_{18}$ alkyl which is substituted by E and/or interrupted by D,  $C_1$ - $C_{18}$ perfluoroalkyl,  $C_2$ - $C_{18}$ 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, wherein E, D and G are as defined above.

7. An electronic device or a component therefore, comprising the polymer according to any of claims 1 to 6.
8. Use of the polymers according to any of claims 1 to 6, in polymer light emitting diodes (PLEDs), especially as electroluminescent material.
9. PLEDs, organic integrated circuits (O-ICs), organic field effect transistors (OFETs), organic thin film transistors (OTFTs), organic solar cells (O-SCs), thermoelectric devices, or organic laser diodes comprising one or more of the polymers according to any of claims 1 to 9.
10. A compound of the formula



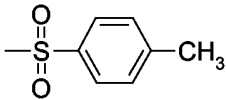
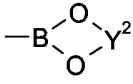
wherein A is a 5-, 6-, or 7-membered heteroaromatic ring, containing one heteroatom selected from nitrogen, oxygen and sulfur, especially one nitrogen atom and at least one further heteroatom selected from nitrogen, substituted nitrogen, oxygen and sulfur, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are independently of each other hydrogen, halogen, or an organic substituent, or

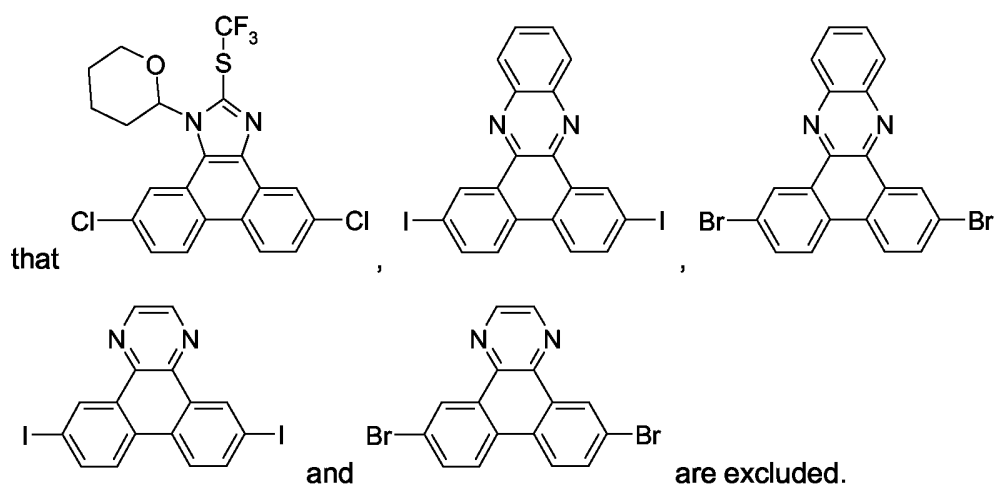
two substituents R<sup>1</sup> and R<sup>2</sup>, R<sup>4</sup> and R<sup>6</sup>, R<sup>2</sup> and R<sup>3</sup>, R<sup>5</sup> and R<sup>3</sup> and/or R<sup>5</sup> and R<sup>6</sup>, which are adjacent to each other, together form an aromatic, or heteroaromatic ring, or ring system, which can optionally be substituted,

R<sup>7</sup> is an organic substituent, wherein two or more substituents R<sup>7</sup> in the same molecule may have different meanings, or can form together an aromatic, or heteroaromatic ring, or ring system, and

x is 0, or an integer of 1 to 5;

$X^{11}$  is independently in each occurrence a halogen atom, or  $-\text{OS}(\text{O})_2\text{CF}_3$ ,  $-\text{OS}(\text{O})_2\text{-aryl}$ ,

especially ,  $-\text{OS}(\text{O})_2\text{CH}_3$ ,  $-\text{B}(\text{OH})_2$ ,  $-\text{B}(\text{OY}^1)_2$ , ,  $-\text{BF}_4\text{Na}$ , or  $-\text{BF}_4\text{K}$ , wherein  $\text{Y}^1$  is independently in each occurrence a  $\text{C}_1\text{-C}_{10}$ alkyl group and  $\text{Y}^2$  is independently in each occurrence a  $\text{C}_2\text{-C}_{10}$ alkylene group, such as  $-\text{CY}^3\text{Y}^4\text{-CY}^5\text{Y}^6\text{-}$ , or  $-\text{CY}^7\text{Y}^8\text{-CY}^9\text{Y}^{10}\text{-CY}^{11}\text{Y}^{12}\text{-}$ , wherein  $\text{Y}^3, \text{Y}^4, \text{Y}^5, \text{Y}^6, \text{Y}^7, \text{Y}^8, \text{Y}^9, \text{Y}^{10}, \text{Y}^{11}$  and  $\text{Y}^{12}$  are independently of each other hydrogen, or a  $\text{C}_1\text{-C}_{10}$ alkyl group, especially  $-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{-}$ , or  $-\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{-}$ , wherein nitrogen atom as heteroatom comprises a group  $=\text{N-}$ , or  $-\text{NR}^{10}$ , wherein  $\text{R}^{10}$  is as defined in claim 2, with the proviso





# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2006/060538

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. C08L65/00 C07C211/00

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
C08L C07C

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

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

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/014689 A (COVION ORGANIC SEMICONDUCTORS GMBH; BECKER, HEINRICH; BREUNING, ESTHER) 17 February 2005 (2005-02-17) the whole document	1-10
X	WO 2004/005288 A (E.I. DU PONT DE NEMOURS AND COMPANY) 15 January 2004 (2004-01-15) the whole document	1-10
X	WO 03/064373 A (SYNTEC GESELLSCHAFT FUER CHEMIE UND TECHNOLOGIE DERINFORMATIONSAUFZEIC) 7 August 2003 (2003-08-07) the whole document	1-10
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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

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

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\*G\* document member of the same patent family

Date of the actual completion of the international search

31 May 2006

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# INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 440 959 A (IDEMITSU KOSAN CO., LTD) 28 July 2004 (2004-07-28) the whole document -----	1-10
X	US 2004/028944 A1 (MORI TATSUO ET AL) 12 February 2004 (2004-02-12) the whole document -----	1-10
X	US 2001/008711 A1 (IGARASHI TATSUYA) 19 July 2001 (2001-07-19) the whole document -----	1-10
X	EP 0 757 035 A (MITA INDUSTRIAL CO. LTD; KYOCERA MITA CORPORATION) 5 February 1997 (1997-02-05) the whole document -----	1-10
X	WO 2004/030029 A (RISOE NATIONAL LABORATORY; KREBS, FREDERIK, C; JOERGENSEN, MIKKEL; ALM) 8 April 2004 (2004-04-08) cited in the application the whole document -----	1-10
X	US 2004/209117 A1 (AZIZ HANY ET AL) 21 October 2004 (2004-10-21) cited in the application the whole document -----	1-10

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2006/060538

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2005014689	A	17-02-2005	DE 10337346 A1 EP 1656408 A2	31-03-2005 17-05-2006
WO 2004005288	A	15-01-2004	AU 2003247964 A1 AU 2003247965 A1 AU 2003249016 A1 AU 2003251850 A1 AU 2003251851 A1 CA 2492686 A1 CA 2492688 A1 CA 2492689 A1 CA 2492690 A1 CA 2492692 A1 CN 1666357 A CN 1666577 A CN 1668703 A CN 1668616 A EP 1519935 A2 EP 1532209 A2 EP 1520308 A2 EP 1520452 A2 EP 1520305 A2 JP 2006505115 T JP 2005533341 T JP 2005533139 T JP 2005533342 T JP 2005533343 T WO 2004005406 A2 WO 2004006354 A2 WO 2004006352 A2 WO 2004006355 A2	23-01-2004 23-01-2004 23-01-2004 23-01-2004 23-01-2004 15-01-2004 15-01-2004 15-01-2004 15-01-2004 15-01-2004 07-09-2005 07-09-2005 14-09-2005 14-09-2005 06-04-2005 25-05-2005 06-04-2005 06-04-2005 06-04-2005 09-02-2006 04-11-2005 04-11-2005 04-11-2005 04-11-2005 15-01-2004 15-01-2004 15-01-2004 15-01-2004
WO 03064373	A	07-08-2003	CN 1602293 A DE 10203328 A1 EP 1470100 A1 JP 2005516059 T US 2005067951 A1	30-03-2005 07-08-2003 27-10-2004 02-06-2005 31-03-2005
EP 1440959	A	28-07-2004	CN 1575269 A WO 03037836 A1 US 2005014017 A1	02-02-2005 08-05-2003 20-01-2005
US 2004028944	A1	12-02-2004	AU 9033201 A CN 1468502 A WO 0230159 A1	15-04-2002 14-01-2004 11-04-2002
US 2001008711	A1	19-07-2001	JP 2001192652 A	17-07-2001
EP 0757035	A	05-02-1997	DE 69625134 D1 DE 69625134 T2	16-01-2003 02-10-2003
WO 2004030029	A	08-04-2004	AU 2003282015 A1	19-04-2004
US 2004209117	A1	21-10-2004	CA 2425797 A1	17-10-2004