(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 September 2017 (08.09.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/148864 A1

(51) International Patent Classification:
C07D 487/04 (2006.01) *G03G 5/06* (2006.01)

(21) International Application Number:
PCT/EP2017/054507

(22) International Filing Date:
27 February 2017 (27.02.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
16157844.8 29 February 2016 (29.02.2016) EP
16207316.7 29 December 2016 (29.12.2016) EP

(71) Applicant: **BASF SE** [DE/DE]; Carl-Bosch-Str. 38, 67056 Ludwigshafen am Rhein (DE).

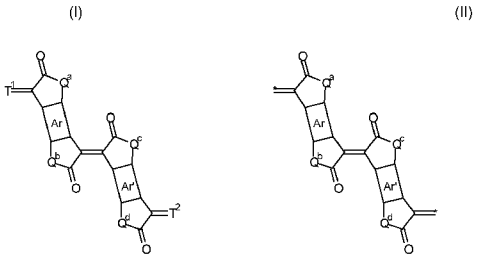
(72) Inventors: **FLORES, Jean-Charles**; rue de Petit Landau 15, 68170 Rixheim (FR). **HAYOZ, Pascal**; Ettingerstrasse 55, 4114 Hofstetten (CH). **MCCULLOCH, Iain**; 2 Goodacre Drive, Eastleigh Hampshire SO534LG (GB). **ONWUBIKO, Nkechinyerem**; 8 Harlech Gardens, London TW5 9PR (GB). **KAELBLEIN, Daniel**; Starenweg 10, 67346 Speyer (DE).

(74) Agent: **BÜCHEL, Edwin**; Isenbruck Bösl Hörschler LLP Patentanwälte, EASTSITE ONE, Seckenheimer Landstraße 4, 68163 Mannheim (DE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,

[Continued on next page]

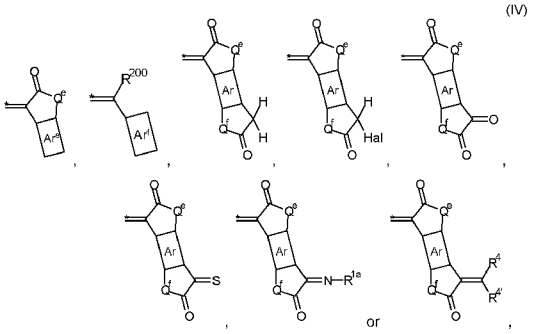
(54) Title: SEMICONDUCTING POLYMER



(III)

e =O, =S, =NR^{1a}, =$CR^{4}R^{4'}$,

(IV)



(57) Abstract: Compounds of formula (I) and polymers comprising at least a structure of formula (II), wherein T^1 or T^2 are independently of each other a group of Formula (III), Formula (iv) Q^a, Q^b, Q^c, Q^d, Q^e or Q^f are independently of each other O, S or NR^1.

WO 2017/148864 A1

HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

Semiconducting polymer

Description

The present invention relates to polymers, to a process for the preparation of these polymers, to intermediates, to electronic devices comprising these polymers, as well as to the use of these polymers as semiconducting material.

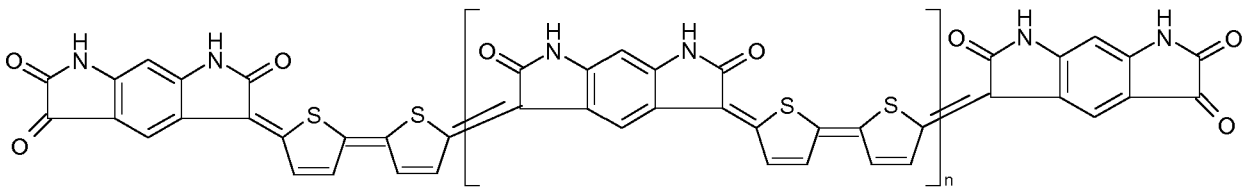
Organic semiconducting materials can be used in electronic devices such as organic photovoltaic devices (OPVs), organic field-effect transistors (OFETs), organic light emitting diodes (OLEDs), organic photodiodes (OPDs) and organic electrochromic devices (ECDs).

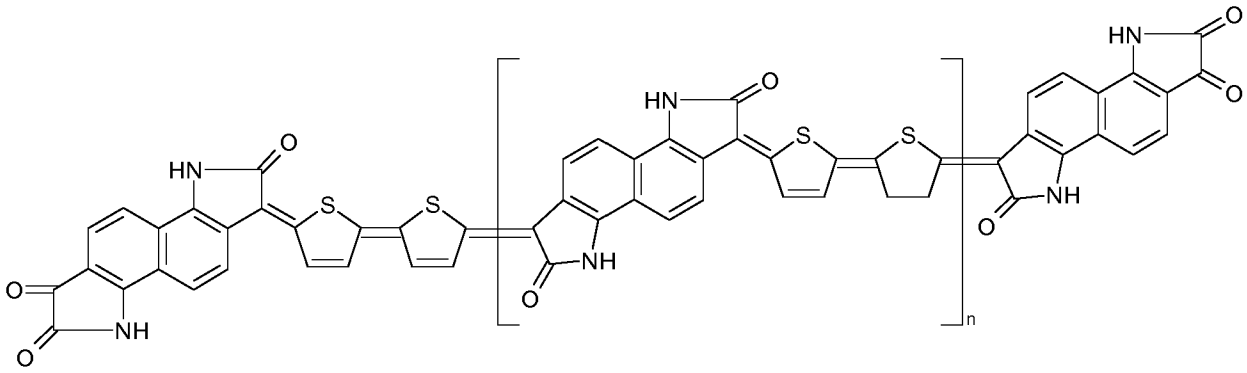
It is desirable that the organic semiconducting materials are compatible with liquid processing techniques such as spin coating as liquid processing techniques are convenient from the point of processability, and thus allow the production of low cost organic semiconducting material-based electronic devices. In addition, liquid processing techniques are also compatible with plastic substrates, and thus allow the production of light weight and mechanically flexible organic semiconducting material-based electronic devices.

For application in organic photovoltaic devices (OPVs), organic field-effect transistors (OFETs), and organic photodiodes (OPDs), it is further desirable that the organic semiconducting materials show high charge carrier mobility.

For application in organic photovoltaic devices (OPVs) and organic photodiodes (OPDs), the organic semiconducting materials should also show a strong absorption of the visible light and of the near infra-red light.

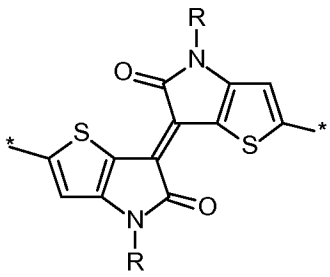
G. Kossmehl and G. Manecke, Die Makromolekulare Chemie 176 (1975), pp. 333-340 discloses the following structures



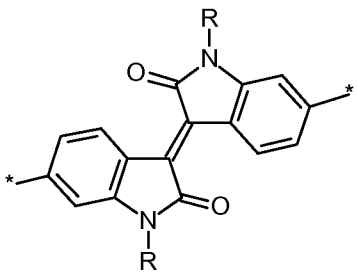


which have coplanar conjugated π-electron systems.

WO 2009/053291 describes semiconducting polymers comprising the following units

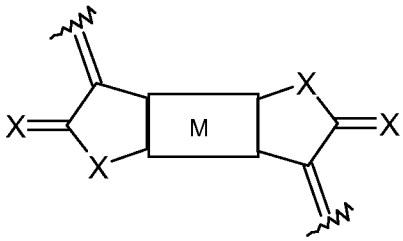


and



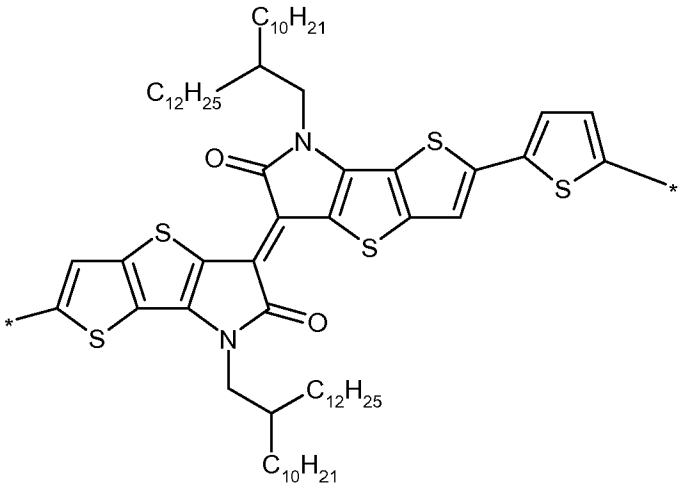
and organic field effect transistors comprising these polymers.

WO 2014/071524 discloses monomers, oligomers and polymers comprising a fused ring moiety of the following structure

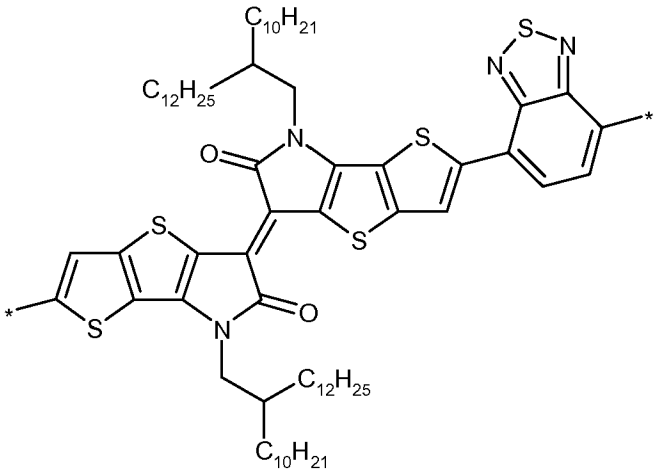


where X is independently O, S or NR and R is independently hydrogen, or an optionally substituted hydrocarbon.

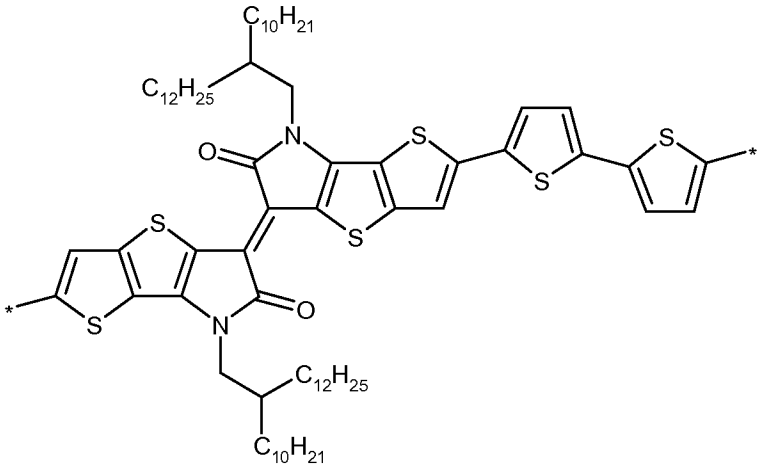
WO 2016/005891 discloses polymers comprising at least one unit of formulae



or



or

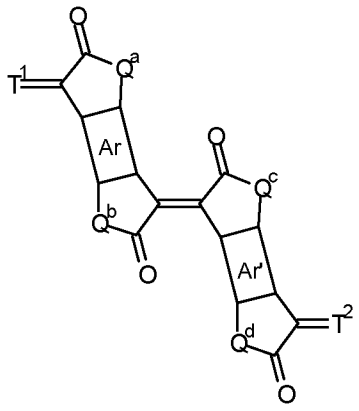


as semiconducting materials for electronic devices.

It was the object of the present invention to provide organic semiconducting materials.

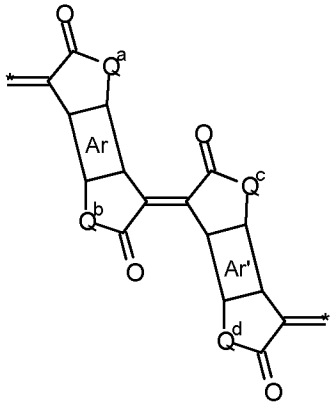
It was a second object of the present invention to provide semiconducting polymers which can be synthesized without the need of noble metal catalysts.

The problem is solved by compounds of formula **(I)**



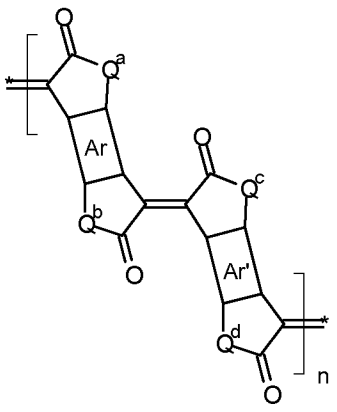
(I),

and polymers comprising at least a structure of formula (**II**)



(II)

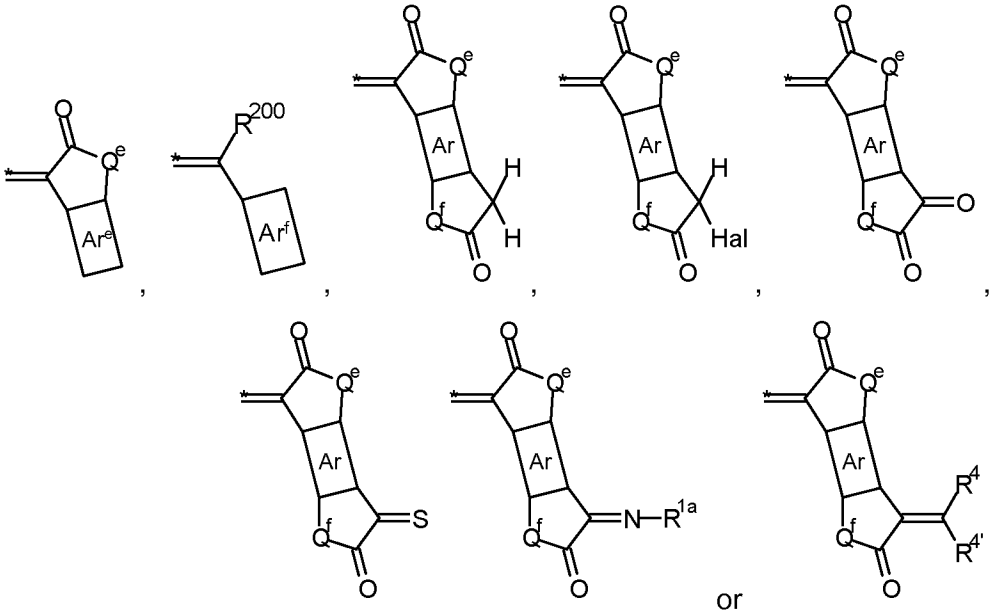
and preferably polymers comprising at least a structure of formula (**II'**)



(II')

wherein
n is 3 to 1000,

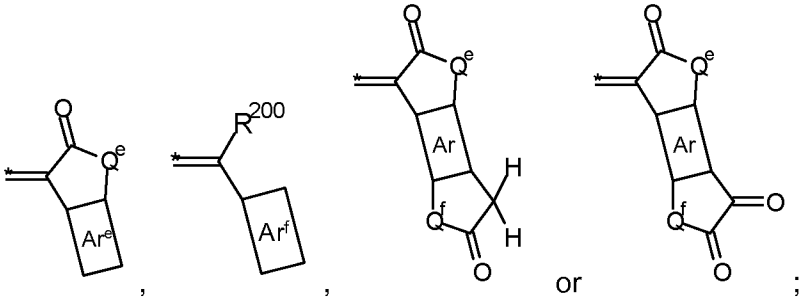
T^1 or T^2 are independently of each other a group of formulae =O, =S, $=NR^{1a}$, $=CR^4R^{4'}$,



or ;

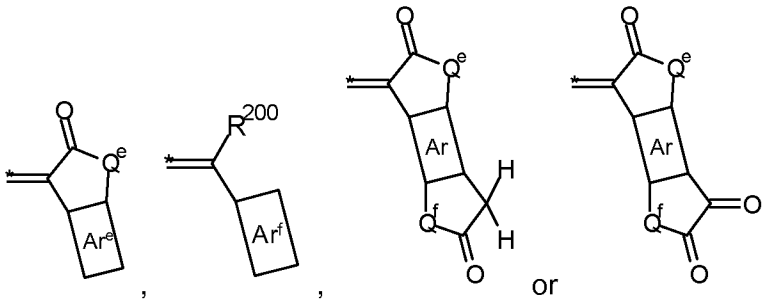
Q^a, Q^b, Q^c, Q^d , Q^e or Q^f are independently of each other O, S or NR^1, preferably O or NR^1, Hal is halogen, preferably Cl or Br, especially Cl.

T^1 or T^2 are preferably independently of each other a group of formulae =O, $=CR^4R^{4'}$,



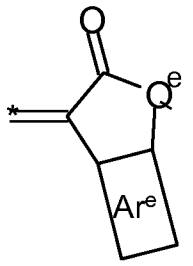
or ;

T^1 or T^2 are more preferably independently of each other a group of formulae

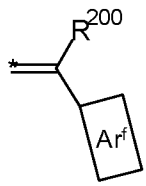


or ;

T^1 or T^2 are even more preferably independently of each other a group of formulae

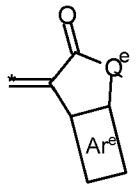


or



;

T^1 or T^2 are most preferably independently of each other a group of formula;

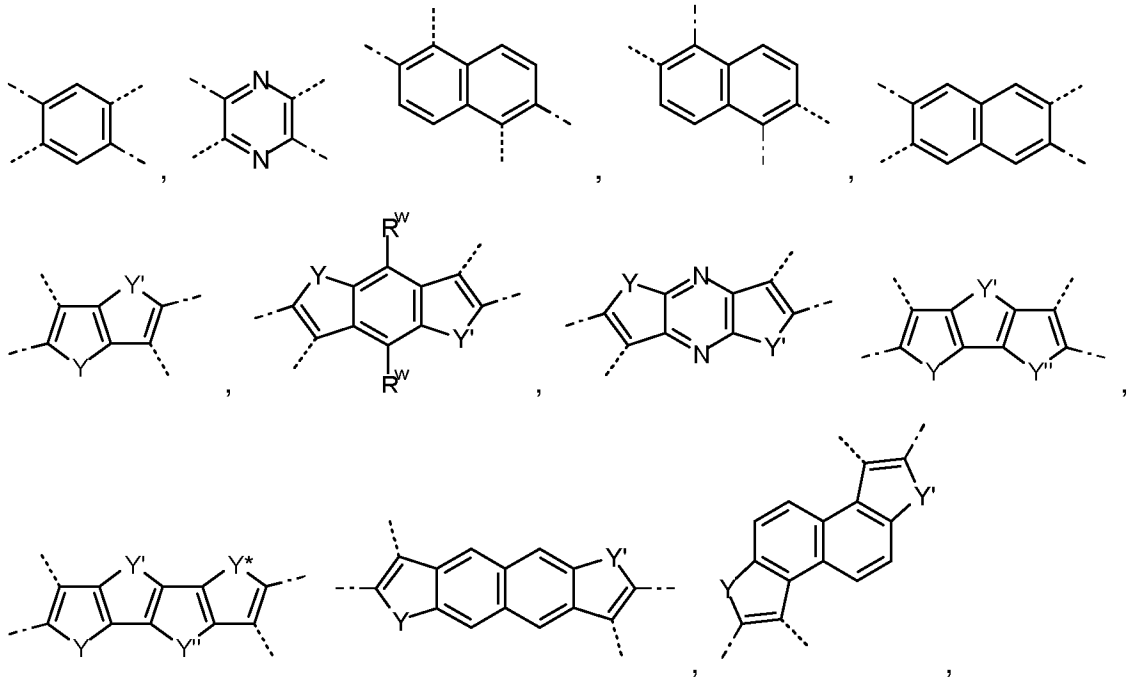


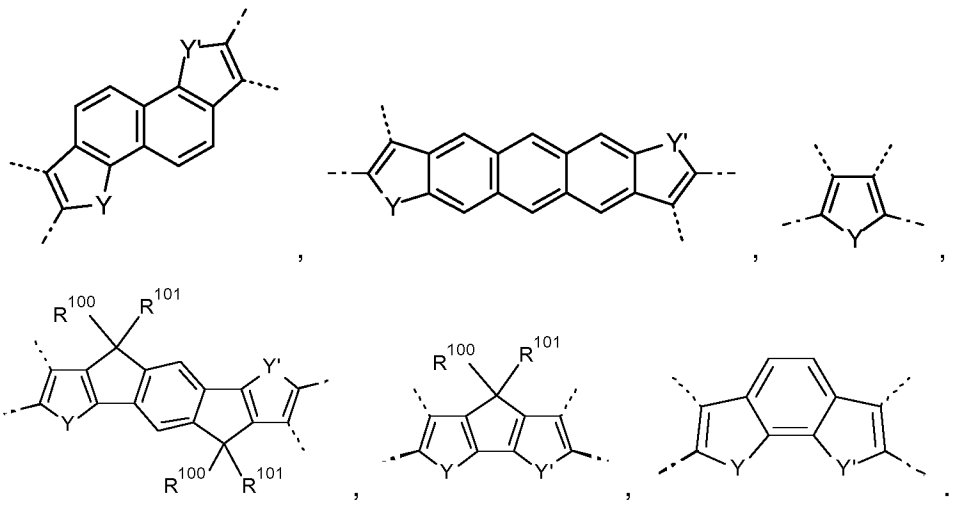
.

The polymers comprising a structure of formula (II) or (II') can be linked to other moieties by double bonds, e.g. to other groups of formula (II) or (II'), or e.g. to end groups T^1 or T^2.

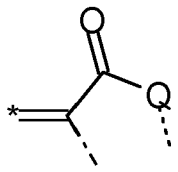
Ar, Ar', Ar^e and Ar^f are independently of each other a 5- to 6-membered ring, or a ring system comprising from 2 to 6 fused 5- to 6-membered rings, wherein at least one of the rings is an aromatic or heteroaromatic ring.

Ar and Ar' are preferably independently of each other selected from the group consisting of





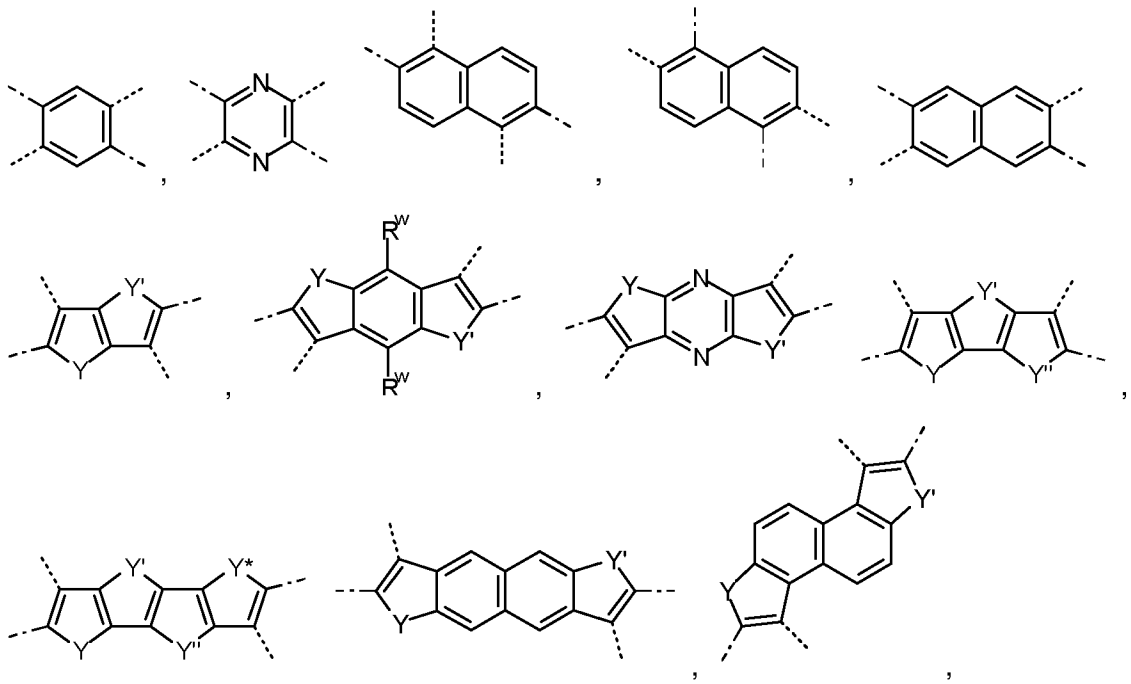
wherein Ar or Ar' is bound via the single bonds ----- and —·— to the moieties

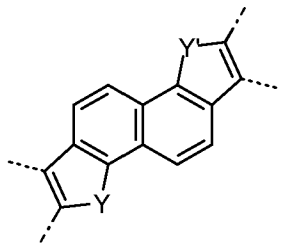


.

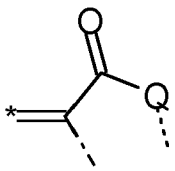
wherein Q is O, S or NR^1, preferably O or NR^1,

Ar and Ar' are more preferably independently of each other selected from the group consisting of



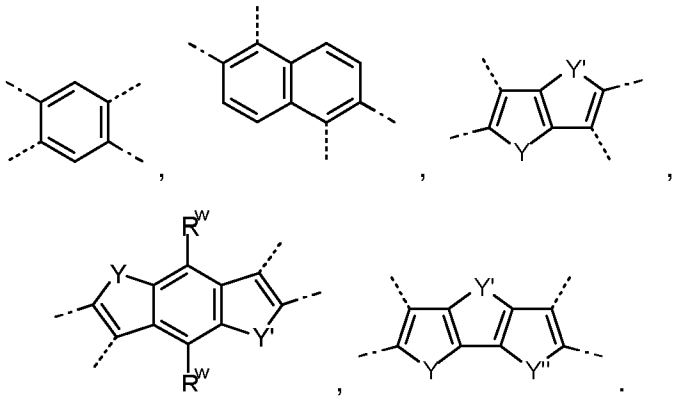


wherein Ar or Ar' is bound via the single bonds ----- and —·— to the moieties

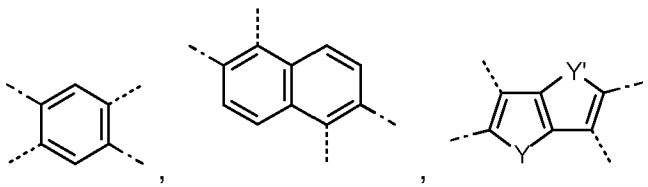


.

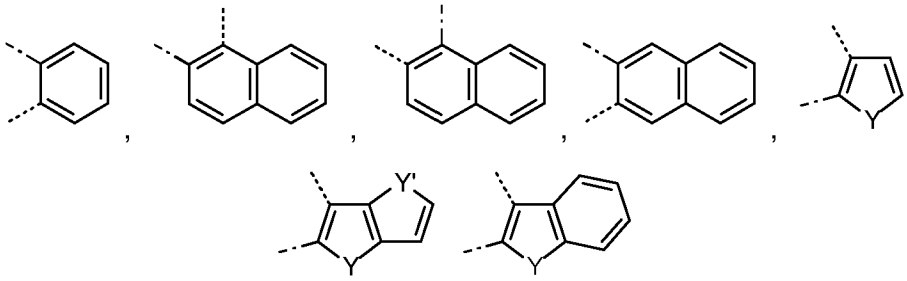
wherein Q is O, S or NR^1, preferably O or NR^1,
Ar and Ar' are even more preferably independently of each other selected from



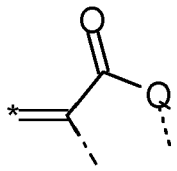
Ar and Ar' are most preferably independently of each other selected from



Ar^e is preferably selected from

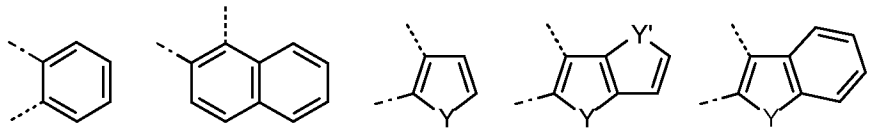


where Ar^e is bound via the bonds ----- and —·— to the moiety

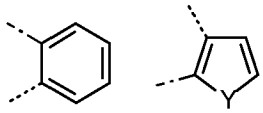


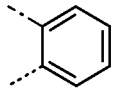
.

Ar^e is more preferably selected from

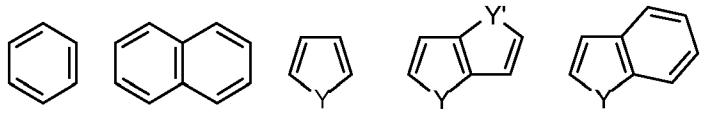


.

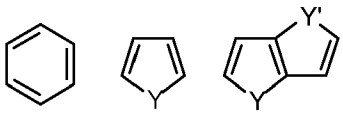
Ar^e is even more preferably selected from  .

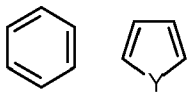
Ar^e is most preferably  .

Ar^f is preferably selected from the group consisting of



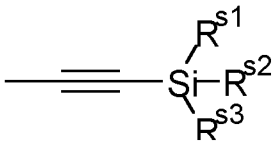
.

Ar^f is more preferably selected from  .

Ar^f is most preferably selected from  .

wherein Ar, Ar', Ar^e, Ar^f can be substituted by one or more substituents R^2.

Y, Y', Y'' and Y^* are at each occurrence O, S, NR^{1a}, Se, Te, preferably O, S, NR^{1a}, Se, more preferably O, S, Se, still more preferably S, Se and most preferably S.

R^W is at each occurrence H, C_{1-30}-alkyl, C_{1-30}-alkoxy, or a moiety  , preferably H, C_{1-30}-alkyl, or C_{1-30}- alkoxy, more preferably H or C_{1-30}-alkoxy, most preferably H,

wherein R^{s1}, R^{s2}, R^{s3} are independently of each other H, C_{1-20}-alkyl, C_{2-20}-alkenyl, or phenyl, preferably C_{1-20}-alkyl.

R^1, R^{1a} are at each occurrence selected from the group consisting of H, C_{1-100}-alkyl, C_{2-100}-alkenyl, C_{2-100}-alkynyl, C_{5-12}-cycloalkyl, C_{6-18}-aryl, a 5 to 20 membered heteroaryl, C(O)-C_{1-100}-alkyl, C(O)-C_{5-12}-cycloalkyl and C(O)-OC_{1-100}-alkyl,

wherein

C_{1-100}-alkyl, C_{2-100}-alkenyl and C_{2-100}-alkynyl can be substituted with one to fourty substituents independently selected from the group consisting of C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^a, OC(O)-R^a, C(O)-OR^a, C(O)-R^a, NR^aR^b, NR^a-C(O)R^b, C(O)-NR^aR^b, N[C(O)R^a][C(O)R^b], SR^a, $Si(R^{Sia})(R^{Sib})(R^{Sic})$, -O-$Si(R^{Sia})(R^{Sib})(R^{Sic})$, halogen, CN, and NO_2; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-100}-alkyl, C_{2-100}-alkenyl and C_{2-100}-alkynyl can be replaced by O or S,

C_{5-12}-cycloalkyl can be substituted with one to six substituents independently selected from the group consisting of C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^a, OC(O)-R^a, C(O)-OR^a, C(O)-R^a, NR^aR^b, NR^a-C(O)R^b, C(O)-NR^aR^b, N[C(O)R^a][C(O)R^b], SR^a, $Si(R^{Sia})(R^{Sib})(R^{Sic})$, -O-$Si(R^{Sia})(R^{Sib})(R^{Sic})$, halogen, CN, and NO_2; and one or two CH_2-groups, but not adjacent CH_2-groups, of C_{5-12}-cycloalkyl can be replaced by O, S, OC(O), CO, NR^a or NR^a-CO,

C_{6-18}-aryl and 5 to 20 membered heteroaryl can be substituted with one to six substituents independently selected from the group consisting of C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^a, OC(O)-R^a, C(O)-OR^a, C(O)-R^a, NR^aR^b, NR^a-C(O)R^b, C(O)-NR^aR^b, N[C(O)R^a][C(O)R^b], SR^a, $Si(R^{Sia})(R^{Sib})(R^{Sic})$, -O-$Si(R^{Sia})(R^{Sib})(R^{Sic})$, halogen, CN, and NO_2,

wherein

R^a and R^b are independently selected from the group consisting of H, C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl and 5 to 14 membered heteroaryl,

R^{Sia}, R^{Sib} and R^{Sic} are independently selected from the group consisting of H, C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, O-C_{1-60}-alkyl, O-C_{2-60}-alkenyl, O-C_{2-60}-alkynyl, O-C_{5-8}-cycloalkyl, O-C_{6-14}-aryl, O-5 to 14 membered heteroaryl, -[O-$SiR^{Sid}R^{Sie}$]$_o$-R^{Sif}, NR^5R^6, halogen and O-C(O)-R^5,

wherein

o is an integer from 1 to 50,

R^{Sid}, R^{Sie}, R^{Sif} are independently selected from the group consisting of H, C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, O-C_{1-60}-alkyl, O-C_{2-60}-alkenyl, O-C_{2-60}-alkynyl, O-C_{5-8}-cycloalkyl, O-C_{6-14}-aryl, O-5 to 14 membered heteroaryl, -[O-$SiR^{Sig}R^{Sih}$]$_p$-R^{Sii}, $NR^{50}R^{60}$, halogen and O-C(O)-R^{50};

wherein

p is an integer from 1 to 50,
R^{Sig} R^{Sih}, R^{Sii} are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, O-C_{1-30}-alkyl, O-C_{2-30}-alkenyl, O-C_{2-30}-alkynyl, O-C_{5-6}-cycloalkyl, O-C_{6-10}-aryl, O-5 to 10 membered heteroaryl, O-$Si(CH_3)_3$, $NR^{500}R^{600}$, halogen and O-C(O)-R^{500},

R^5, R^6, R^{50}, R^{60}, R^{500} and R^{600} are independently selected from the group consisting of H, C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, and 5 to 14 membered heteroaryl,

C_{1-60}-alkyl, C_{2-60}-alkenyl and C_{2-60}-alkynyl can be substituted with one to twenty substituents selected from the group consisting of C_{5-6}-cycloalkyl, C_{6-10}-aryl, OR^c, $OC(O)-R^c$, $C(O)-OR^c$, $C(O)-R^c$, NR^cR^d, $NR^c-C(O)R^d$, $C(O)-NR^cR^d$, $N[C(O)R^c][C(O)R^d]$, SR^c, $Si(R^{Sij})(R^{Sik})(R^{Sil})$, -O-$Si(R^{Sij})(R^{Sik})(R^{Sil})$, halogen, CN, and NO_2; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-60}-alkyl, C_{2-60}-alkenyl and C_{2-60}-alkynyl can be replaced by O or S,

C_{5-8}-cycloalkyl can be substituted with one to five substituents selected from the group consisting of C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, OR^c, $OC(O)-R^c$, $C(O)-OR^c$, $C(O)-R^c$, NR^cR^d, $NR^c-C(O)R^d$, $C(O)-NR^cR^d$, $N[C(O)R^c][C(O)R^d]$, SR^c, $Si(R^{Sij})(R^{Sik})(R^{Sil})$, -O-$Si(R^{Sij})(R^{Sik})(R^{Sil})$, halogen, CN, and NO_2; and one or two CH_2-groups, but not adjacent CH_2-groups, of C_{5-8}-cycloalkyl can be replaced by O, S, OC(O), CO, NR^c or NR^c-CO,

C_{6-14}-aryl and 5 to 14 membered heteroaryl can be substituted with one to five substituents independently selected from the group consisting of C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, OR^c, $OC(O)-R^c$, $C(O)-OR^c$, $C(O)-R^c$, NR^cR^d, $NR^c-C(O)R^d$, $C(O)-NR^cR^d$, $N[C(O)R^c][C(O)R^d]$, SR^c, $Si(R^{Sij})(R^{Sik})(R^{Sil})$, -O-$Si(R^{Sij})(R^{Sik})(R^{Sil})$, halogen, CN and NO_2,

wherein
R^c and R^d are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl,

R^{Sij}, R^{Sik} and R^{Sil} are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, O-C_{1-30}-alkyl, O-C_{2-30}-alkenyl, O-C_{2-30}-alkynyl, O-C_{5-6}-cycloalkyl, O-C_{6-10}-aryl, O-5 to 10 membered heteroaryl, -$[O-SiR^{Sim}R^{Sin}]_q$-R^{Sio}, NR^7R^8, halogen, and O-C(O)-R^7,
wherein
q is an integer from 1 to 50,

R^{Sim}, R^{Sin}, R^{Sio} are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, O-C_{1-30}-alkyl, O-C_{2-30}-alkenyl, O-C_{2-30}-alkynyl, O-C_{5-6}-cycloalkyl, O-C_{6-10}-aryl, O-5 to 10 membered heteroaryl, -[O-$SiR^{Sip}R^{Siq}$]$_r$-R^{Sir}, $NR^{70}R^{80}$, halogen, and O-C(O)-R^{70},

wherein

r is an integer from 1 to 50,

R^{Sip}, R^{Siq}, R^{Sir} are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, O-C_{1-30}-alkyl, O-C_{2-30}-alkenyl, O-C_{2-30}-alkynyl, O-C_{5-6}-cycloalkyl, O-C_{6-10}-aryl, O-5 to 10 membered heteroaryl, O-$Si(CH_3)_3$, $NR^{700}R^{800}$, halogen and O-C(O)-R^{700},

R^7, R^8, R^{70}, R^{80}, R^{700} and R^{800} are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, and 5 to 10 membered heteroaryl,

C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl can be substituted with one to ten substituents selected from the group consisting of halogen, CN and NO_2.

R^1, R^{1a} are preferably at each occurrence selected from the group consisting of H, C_{1-100}-alkyl, C_{3-100}-alkenyl, C_{3-100}-alkynyl,

wherein

C_{1-100}-alkyl, C_{3-100}-alkenyl and C_{3-100}-alkynyl can be substituted with one to fourty substituents independently selected from the group consisting of C_{5-8}-cycloalkyl, OR^a, OC(O)-R^a, C(O)-OR^a, C(O)-R^a, $Si(R^{Sia})(R^{Sib})(R^{Sic})$, and halogen; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-100}-alkyl, C_{3-100}-alkenyl and C_{3-100}-alkynyl can be replaced by O or S,

wherein

R^a is selected from the group consisting of H, C_{1-60}-alkyl, C_{3-60}-alkenyl, C_{3-60}-alkynyl, C_{5-8}-cycloalkyl,

R^{Sia}, R^{Sib} and R^{Sic} are independently selected from the group consisting of H, C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, -[O-$SiR^{Sid}R^{Sie}$]$_o$-R^{Sif},

wherein

o is an integer from 1 to 50,

R^{Sid}, R^{Sie}, R^{Sif} are independently selected from the group consisting of H, C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl and -[O-$SiR^{Sig}R^{Sih}$]$_p$-R^{Sii};

wherein

p is an integer from 1 to 50,
R^{Sig} R^{Sih}, R^{Sii} are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, O-Si(CH_3)$_3$,

R^1, R^{1a} are more preferably at each occurrence selected from the group consisting of H, C_{1-50}-alkyl, C_{3-50}-alkenyl, C_{3-50}-alkynyl,

wherein

C_{1-50}-alkyl, C_{3-50}-alkenyl and C_{3-50}-alkynyl can be substituted with one to twenty substituents independently selected from the group consisting of OR^a, OC(O)-R^a, C(O)-OR^a, Si(R^{Sia})(R^{Sib})(R^{Sic}), and halogen; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-50}-alkyl, C_{3-50}-alkenyl and C_{3-50}-alkynyl can be replaced by O or S,

wherein
R^a is selected from the group consisting of H, C_{1-20}-alkyl, C_{3-20}-alkenyl, C_{3-20}-alkynyl,

R^{Sia}, R^{Sib} and R^{Sic} are independently selected from the group consisting of H, C_{1-20}-alkyl, C_{2-20}-alkenyl, -[O-Si$R^{Sid}R^{Sie}$]$_o$-R^{Sif},
wherein
o is an integer from 1 to 20,

R^{Sid}, R^{Sie}, R^{Sif} are independently selected from the group consisting of H, C_{1-20}-alkyl, C_{2-20}-alkenyl, and -[O-Si$R^{Sig}R^{Sih}$]$_p$-R^{Sii};
wherein
p is an integer from 1 to 20,
R^{Sig} R^{Sih}, R^{Sii} are independently selected from the group consisting of H, C_{1-20}-alkyl, C_{2-20}-alkenyl, O-Si(CH_3)$_3$,

R^1, R^{1a} are even more preferably at each occurrence selected from the group consisting of C_{1-50}-alkyl, C_{3-50}-alkenyl, C_{3-50}-alkynyl,

wherein

C_{1-50}-alkyl, C_{3-50}-alkenyl and C_{3-50}-alkynyl can be substituted with one to twenty substituents independently selected from the group consisting of OR^a, and halogen; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-50}-alkyl, C_{3-50}-alkenyl and C_{3-50}-alkynyl can be replaced by O or S,

wherein
R^a is selected from the group consisting of H, C_{1-20}-alkyl, C_{3-20}-alkenyl, C_{3-20}-alkynyl,

R^1, R^{1a} are much more preferably at each occurrence selected from the group consisting of

C_{1-50}-alkyl,
wherein

C_{1-50}-alkyl can be substituted with one to twenty substituents independently selected from the group consisting of OR^a, and halogen; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-50}-alkyl can be replaced by O or S,

wherein
R^a is selected from the group consisting of H, or C_{1-20}-alkyl,

R^1, R^{1a} are especially preferably at each occurrence selected from the group consisting of C_{1-50}-alkyl,
wherein

C_{1-50}-alkyl can be substituted with one to twenty halogens;

R^1, R^{1a} are most preferably C_{1-50}-alkyl,

R^2 is at each occurrence selected from the group consisting of C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-12}-cycloalkyl, C_{6-18}-aryl, 5 to 20 membered heteroaryl, OR^{21}, $OC(O)$-R^{21}, $C(O)$-OR^{21}, $C(O)$-R^{21}, $NR^{21}R^{22}$, NR^{21}-$C(O)R^{22}$, $C(O)$-$NR^{21}R^{22}$, $N[C(O)R^{21}][C(O)R^{22}]$, SR^{21}, halogen, CN, $SiR^{Sis}R^{Sit}R^{Siu}$ and OH,
wherein
R^{21} and R^{22} and are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-12}-cycloalkyl, C_{6-18}-aryl and 5 to 20 membered heteroaryl, and

C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl can be substituted with one to ten substituents independently selected from the group consisting of C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^e, $OC(O)$-R^e, $C(O)$-OR^e, $C(O)$-R^e, NR^eR^f, NR^e-$C(O)R^f$, $C(O)$-NR^eR^f, $N[C(O)R^e][C(O)R^f]$, SR^e, halogen, CN, $SiR^{Sis}R^{Sit}R^{Siu}$ and NO_2; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl can be replaced by O or S,

C_{5-12}-cycloalkyl can be substituted with one to six substituents independently selected from the group consisting of C_{1-20}-alkyl, C_{2-20}-alkenyl and C_{2-20}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^e, $OC(O)$-R^e, $C(O)$-OR^e, $C(O)$-R^e, NR^eR^f, NR^e-$C(O)R^f$, $C(O)$-NR^eR^f, $N[C(O)R^e][C(O)R^f]$, SR^e, halogen, CN, $SiR^{Sis}R^{Sit}R^{Siu}$ and NO_2; and one or two CH_2-groups, but not adjacent CH_2-groups, of C_{5-12}-cycloalkyl can be replaced by O, S, OC(O), CO, NR^e or NR^e-CO,

C_{6-18}-aryl and 5 to 20 membered heteroaryl can be substituted with one to six substituents independently selected from the group consisting of C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl,

C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^e, $OC(O)-R^e$, $C(O)-OR^e$, $C(O)-R^e$, NR^eR^f, $NR^e-C(O)R^f$, $C(O)-NR^eR^f$, $N[C(O)R^e][C(O)R^f]$, SR^e, halogen, CN, $SiR^{Sis}R^{Sit}R^{Siu}$ and NO_2,

wherein

R^{Sis}, R^{Sit} and R^{Siu} are independently from each other selected from the group consisting of H, C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, C_{5-6}-cycloalkyl, phenyl and $O-Si(CH_3)_3$,

R^e and R^f are independently selected from the group consisting of H, C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, and 5 to 14 membered heteroaryl,

wherein

C_{1-20}-alkyl, C_{2-20}-alkenyl and C_{2-20}-alkynyl can be substituted with one to five substituents selected from the group consisting of C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, OR^g, $OC(O)-R^g$, $C(O)-OR^g$, $C(O)-R^g$, NR^gR^h, $NR^g-C(O)R^h$, $C(O)-NR^gR^h$, $N[C(O)R^g][C(O)R^h]$, SR^g, halogen, CN, and NO_2,

C_{5-8}-cycloalkyl can be substituted with one to five substituents selected from the group consisting of C_{1-10}-alkyl, C_{2-10}-alkenyl, C_{2-10}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, OR^g, $OC(O)-R^g$, $C(O)-OR^g$, $C(O)-R^g$, NR^gR^h, $NR^g-C(O)R^h$, $C(O)-NR^gR^h$, $N[C(O)R^g][C(O)R^h]$, SR^g, halogen, CN, and NO_2,

C_{6-14}-aryl and 5 to 14 membered heteroaryl can be substituted with one to five substituents independently selected from the group consisting of C_{1-10}-alkyl, C_{2-10}-alkenyl, C_{2-10}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, OR^g, $OC(O)-R^g$, $C(O)-OR^g$, $C(O)-R^g$, NR^gR^h, $NR^g-C(O)R^h$, $C(O)-NR^gR^h$, $N[C(O)R^g][C(O)R^h]$, SR^g, halogen, CN, and NO_2,

wherein

R^g and R^h are independently selected from the group consisting of H, C_{1-10}-alkyl, C_{2-10}-alkenyl and C_{2-10}-alkynyl,

wherein

C_{1-10}-alkyl, C_{2-10}-alkenyl and C_{2-10}-alkynyl can be substituted with one to five substituents selected from the group consisting of halogen, CN and NO_2.

R^2 is preferably at each occurrence selected from the group consisting of C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, OR^{21}, $C(O)-OR^{21}$, $C(O)-R^{21}$, halogen, and CN,

wherein

R^{21} is selected from the group consisting of H, C_{1-30}-alkyl, C_{3-30}-alkenyl, C_{3-30}-alkynyl, and

C_{1-30}-alkyl, C_{3-30}-alkenyl and C_{3-30}-alkynyl can be substituted with one to ten substituents independently selected from the group consisting of OR^e, $OC(O)-R^e$, $C(O)-OR^e$, $C(O)-R^e$, and halogen; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-30}-alkyl, C_{3-30}-alkenyl and C_{3-30}-alkynyl can be replaced by O or S,

wherein

R^e is selected from the group consisting of H, C_{1-20}-alkyl, C_{3-20}-alkenyl, C_{3-20}-alkynyl.

R^2 is more preferably at each occurrence selected from the group consisting of C_{1-30}-alkyl, OR^{21}, and halogen,

wherein

R^{21} is C_{1-30}-alkyl, and

C_{1-30}-alkyl can be substituted with one to ten substituents independently selected from the group consisting of OR^e, and halogen; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-30}-alkyl can be replaced by O or S,

wherein R^e is independently selected from the group consisting of H, or C_{1-20}-alkyl.

R^2 is even more preferably at each occurrence selected from the group consisting of C_{1-20}-alkyl, OR^{21}, and halogen,

wherein R^{21} is C_{1-20}-alkyl, and

C_{1-20}-alkyl can be substituted with one to ten halogens; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-20}-alkyl can be replaced by O or S.

R^2 is much more preferably at each occurrence selected from the group consisting of C_{1-20}-alkyl, OR^{21}, and halogen,

wherein

R^{21} is C_{1-20}-alkyl, which can optionally be substituted with one to ten halogens.

R^2 is especially preferably at each occurrence selected from the group consisting of C_{1-20}-alkyl, OR^{21}, and halogen,

wherein

R^{21} is C_{1-20}-alkyl.

R^2 is most preferably at each occurrence selected from the group consisting of OR^{21}, and halogen,

wherein R^{21} is C_{1-20}-alkyl.

R^4 and $R^{4'}$ are independently and at each occurrence selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-12}-cycloalkyl, C_{6-18}-aryl and 5 to 20 membered heteroaryl, C(O)-R^{41}, C(O)-$NR^{41}R^{42}$, C(O)-OR^{41} and CN,

wherein

R^{41} und R^{42} are independently from each other and at each occurrence selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-12}-cycloalkyl, C_{6-18}-aryl and 5 to 20 membered heteroaryl, and

wherein
C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl can be substituted with one to ten substituents independently selected from the group consisting of C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^i, $OC(O)-R^j$, $C(O)-OR^i$, $C(O)-R^i$, NR^iR^j, $NR^i-C(O)R^j$, $C(O)-NR^iR^j$, $N[C(O)R^i][C(O)R^j]$, SR^i, halogen, CN, and NO_2; and at least two CH_2-groups, but not adjacent CH_2-groups of C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl can be replaced by O or S,

C_{5-12}-cycloalkyl can be substituted with one to six substituents independently selected from the group consisting of C_{1-20}-alkyl, C_{2-20}-alkenyl and C_{2-20}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^i, $OC(O)-R^j$, $C(O)-OR^i$, $C(O)-R^i$, NR^iR^j, $NR^i-C(O)R^j$, $C(O)-NR^iR^j$, $N[C(O)R^i][C(O)R^j]$, SR^i, halogen, CN, and NO_2; and one or two CH_2-groups, but not adjacent CH_2-groups, of C_{5-12}-cycloalkyl can be replaced by O, S, OC(O), CO, NR^i or NR^i-CO,

C_{6-18}-aryl and 5 to 20 membered heteroaryl can be substituted with one to six substituents independently selected from the group consisting of C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^i, $OC(O)-R^j$, $C(O)-OR^i$, $C(O)-R^i$, NR^iR^j, $NR^i-C(O)R^j$, $C(O)-NR^iR^j$, $N[C(O)R^i][C(O)R^j]$, SR^i, halogen, CN, and NO_2,

Ri and Rj are independently selected from the group consisting of H, C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, C_{5-8}-cycloalkyl,

R^4 and $R^{4'}$ are preferably independently and at each occurrence selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{6-18}-aryl and 5 to 20 membered heteroaryl, $C(O)-R^{41}$, $C(O)-NR^{41}R^{42}$, $C(O)-OR^{41}$ and CN,

wherein
R^{41} und R^{42} are independently from each other and at each occurrence selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, and

wherein
C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl can be substituted with one to ten substituents independently selected from the group consisting of OR^i, and halogen; and at least two CH_2-groups, but not adjacent CH_2-groups of C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl can be replaced by O or S,

C_{6-18}-aryl and 5 to 20 membered heteroaryl can be substituted with one to six substituents independently selected from the group consisting of C_{1-20}-alkyl, OR^i, halogen,

Ri is selected from the group consisting of H, C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, C_{5-8}-cycloalkyl,

R^4 and $R^{4'}$ are more preferably independently and at each occurrence selected from the group consisting of H, C_{1-30}-alkyl, C(O)-R^{41}, C(O)-$NR^{41}R^{42}$, C(O)-OR^{41} and CN,

wherein
R^{41} und R^{42} are independently from each other and at each occurrence selected from the group consisting of H, or C_{1-30}-alkyl,

R^4 and $R^{4'}$ are most preferably independently and at each occurrence selected from the group consisting of C(O)-R^{41}, C(O)-$NR^{41}R^{42}$, C(O)-OR^{41} and CN,

wherein
R^{41} und R^{42} are independently from each other and at each occurrence selected from the group consisting of H, or C_{1-30}-alkyl,

R^{200} is hydrogen, C_1-C_{36}alkyl, C_2-C_{36}alkenyl, C_2-C_{36}alkinyl, Ar^{200}, CN, $COOR^{201}$, $CONR^{202}R^{203}$, COR^{204}.
R^{201}, R^{202}, R^{203} and R^{204} are independently of each other hydrogen, C_1-C_{36}alkyl, C_2-C_{36}alkenyl, C_2-C_{36}alkinyl, or phenyl;
Ar^{200} has the meaning of Ar^f;

Halogen can be F, Cl, Br and I.

C_{1-4}-alkyl, C_{1-10}-alkyl, C_{1-20}-alkyl, C_{1-30}-alkyl, C_{1-36}-alkyl, C_{1-50}-alkyl, C_{1-60}-alkyl and C_{1-100}-alkyl can be branched or unbranched. Examples of C_{1-4}-alkyl are methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, isobutyl and *tert*-butyl. Examples of C_{1-10}-alkyl are C_{1-4}-alkyl, *n*-pentyl, neopentyl, isopentyl, *n*-(1-ethyl)propyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-(2-ethyl)hexyl, *n*-nonyl and *n*-decyl. Examples of C_{1-20}-alkyl are C_{1-10}-alkyl and *n*-undecyl, *n*-dodecyl, *n*-undecyl, *n*-dodecyl, *n*-tridecyl, *n*-tetradecyl, *n*-pentadecyl, *n*-hexadecyl, *n*-heptadecyl, *n*-octadecyl, *n*-nonadecyl and *n*-icosyl (C_{20}). Examples of C_{1-30}-alkyl, C_{1-36}-alkyl, C_{1-50}-alkyl, C_{1-60}-alkyl and C_{1-100}-alkyl are C_{1-20}-alkyl and *n*-docosyl (C_{22}), *n*-tetracosyl (C_{24}), *n*-hexacosyl (C_{26}), *n*-octacosyl (C_{28}) and *n*-triacontyl (C_{30}).

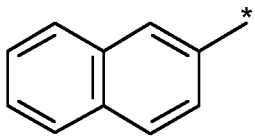
C_{2-10}-alkenyl, C_{2-20}-alkenyl, C_{2-30}-alkenyl, C_{2-60}-alkenyl and C_{2-100}-alkenyl can be branched or unbranched. Examples of C_{1-20}-alkenyl are vinyl, propenyl, *cis*-2-butenyl, *trans*-2-butenyl, 3-butenyl, *cis*-2-pentenyl, *trans*-2-pentenyl, *cis*-3-pentenyl, *trans*-3-pentenyl, 4-pentenyl, 2-methyl-3-butenyl, hexenyl, heptenyl, octenyl, nonenyl and docenyl. Examples of C_{2-20}-alkenyl, C_{2-60}-alkenyl and C_{2-100}-alkenyl are C_{2-10}-alkenyl and linoleyl (C_{18}), linolenyl (C_{18}), oleyl (C_{18}), and arachidonyl (C_{20}). Examples of C_{2-30}-alkenyl are C_{2-20}-alkenyl and erucyl (C_{22}).

C_{2-10}-alkynyl, C_{2-20}-alkynyl, C_{2-30}-alkynyl, C_{2-60}-alkynyl and C_{2-100}-alkynyl can be branched or unbranched. Examples of C_{2-10}-alkynyl are ethynyl, 2-propynyl, 2-butynyl, 3-butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl and decynyl. Examples of C_{2-20}-alkynyl, C_{2-30}-alkenyl, C_{2-60}-alkynyl and C_{2-100}-alkynyl are undecynyl, dodecynyl, undecynyl, dodecynyl, tridecynyl, tetra-

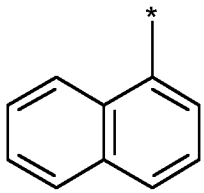
decynyl, pentadecynyl, hexadecynyl, heptadecynyl, octadecynyl, nonadecynyl and icosynyl (C_{20}).

Examples of C_{5-6}-cycloalkyl are cyclopentyl and cyclohexyl. Examples of C_{5-8}-cycloalkyl are C_{5-6}-cycloalkyl and cycloheptyl and cyclooctyl. C_{5-12}-cycloalkyl are C_{5-8}-cycloalkyl and cyclononyl, cyclodecyl, cycloundecyl and cyclododecyl.

Examples of C_{6-10}-aryl are phenyl,

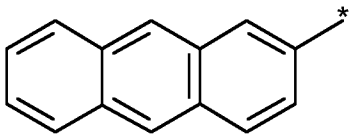


and

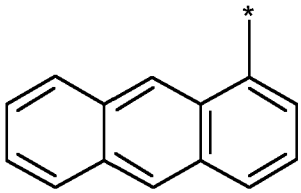


.

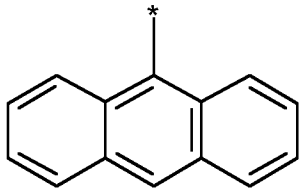
Examples of C_{6-14}-aryl are C_{6-10}-aryl and

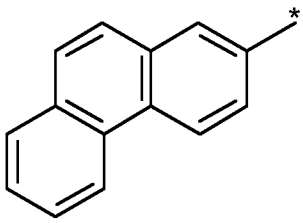


,

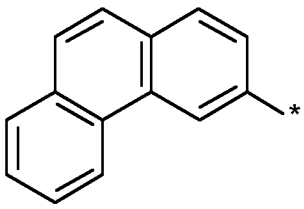


,



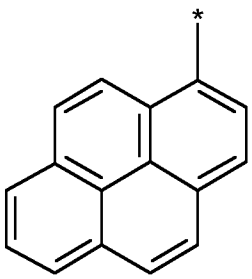


and

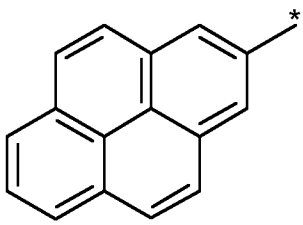


.

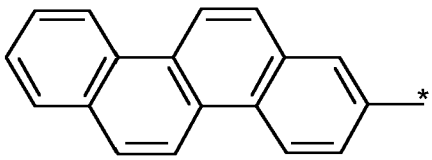
Examples of C_{6-18}-aryl are C_{6-14}-aryl and



,

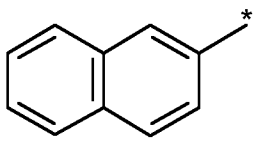
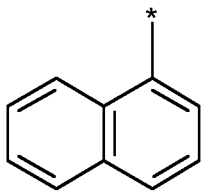


and



.

Preferred aryl moieties are phenyl,

 and  ,

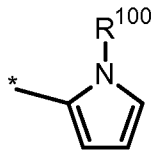
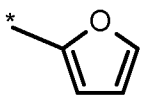
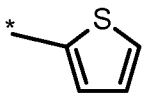
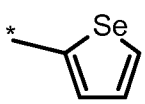
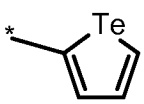
Most preferred is phenyl.

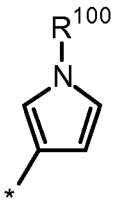
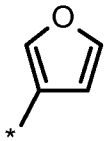
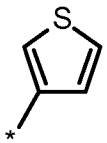
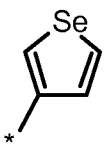
5 to 10 membered heteroaryl are 5 to 10 membered monocyclic or polycyclic, such as dicyclic, tricyclic or tetracyclic, ring systems, which comprise at least one heteroaromatic ring, and which may also comprise non-aromatic rings, which may be substituted by =O.

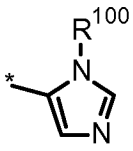
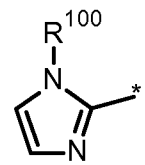
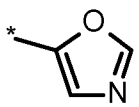
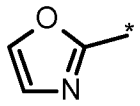
5 to 14 membered heteroaryl are 5 to 14 membered monocyclic or polycyclic, such as dicyclic, tricyclic or tetracyclic, ring systems, which comprise at least one heteroaromatic ring, and which may also comprise non-aromatic rings, which may be substituted by =O.

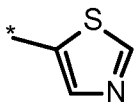
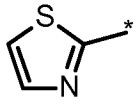
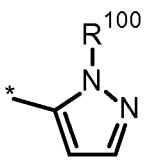
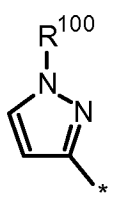
5 to 20 membered heteroaryl are 5 to 20 membered monocyclic or polycyclic, such as dicyclic, tricyclic or tetracyclic, ring systems, which comprise at least one heteroaromatic ring, and which may also comprise non-aromatic rings, which may be substituted by =O.

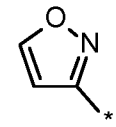
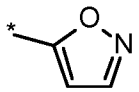
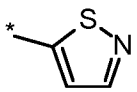
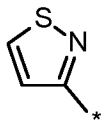
Examples of 5 to 10 membered heteroaryl are

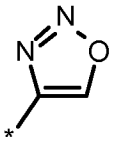
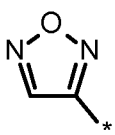
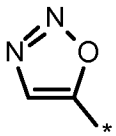
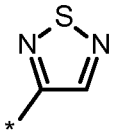
 ,  ,  ,  , 

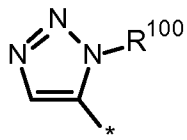
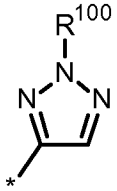
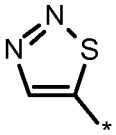
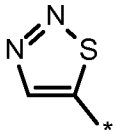
 ,  ,  , 

 ,  ,  , 

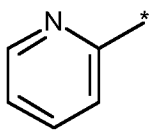
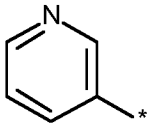
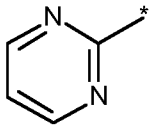
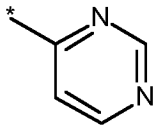
 ,  ,  , 

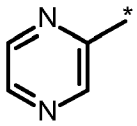
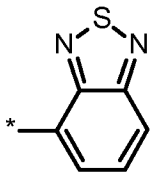
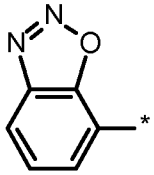
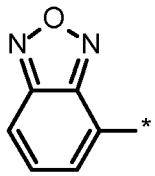

,

,

,


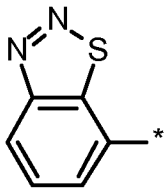
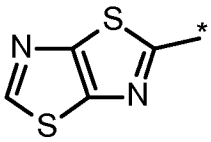
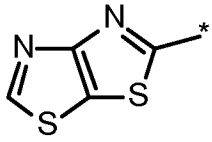
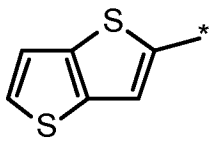

,

,

,



,

,

,


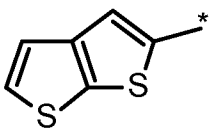
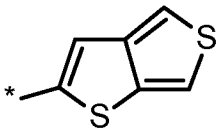
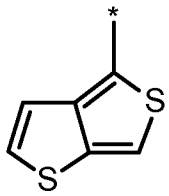
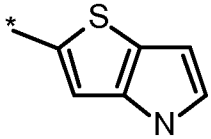
5

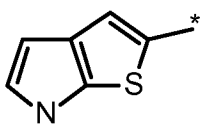
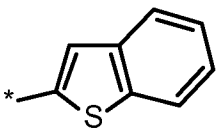
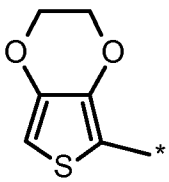
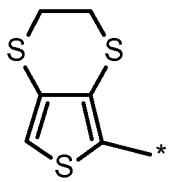

,

,

,



,

,

,


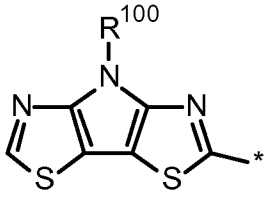
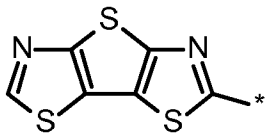
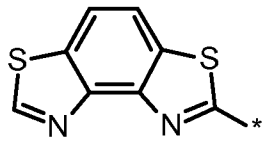
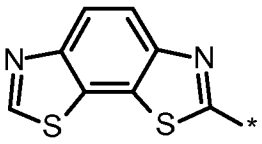
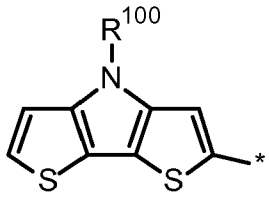
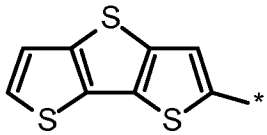
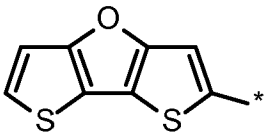
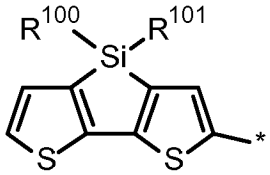
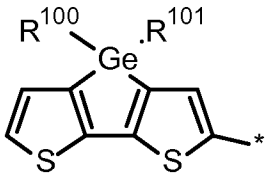
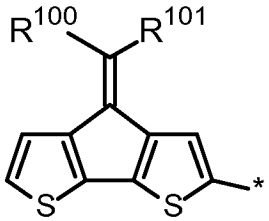
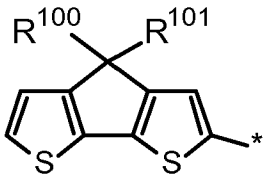
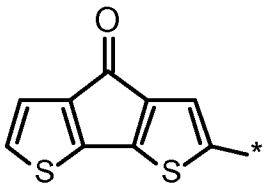
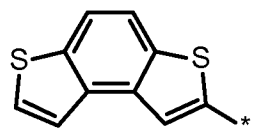
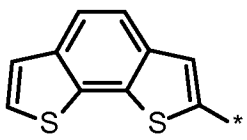
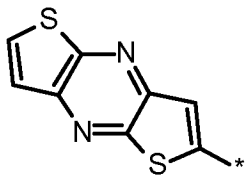
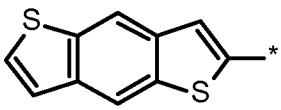
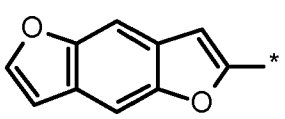
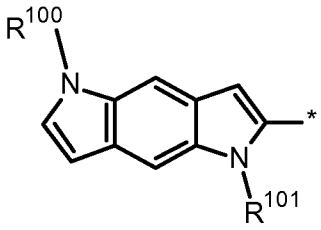

,

,

,


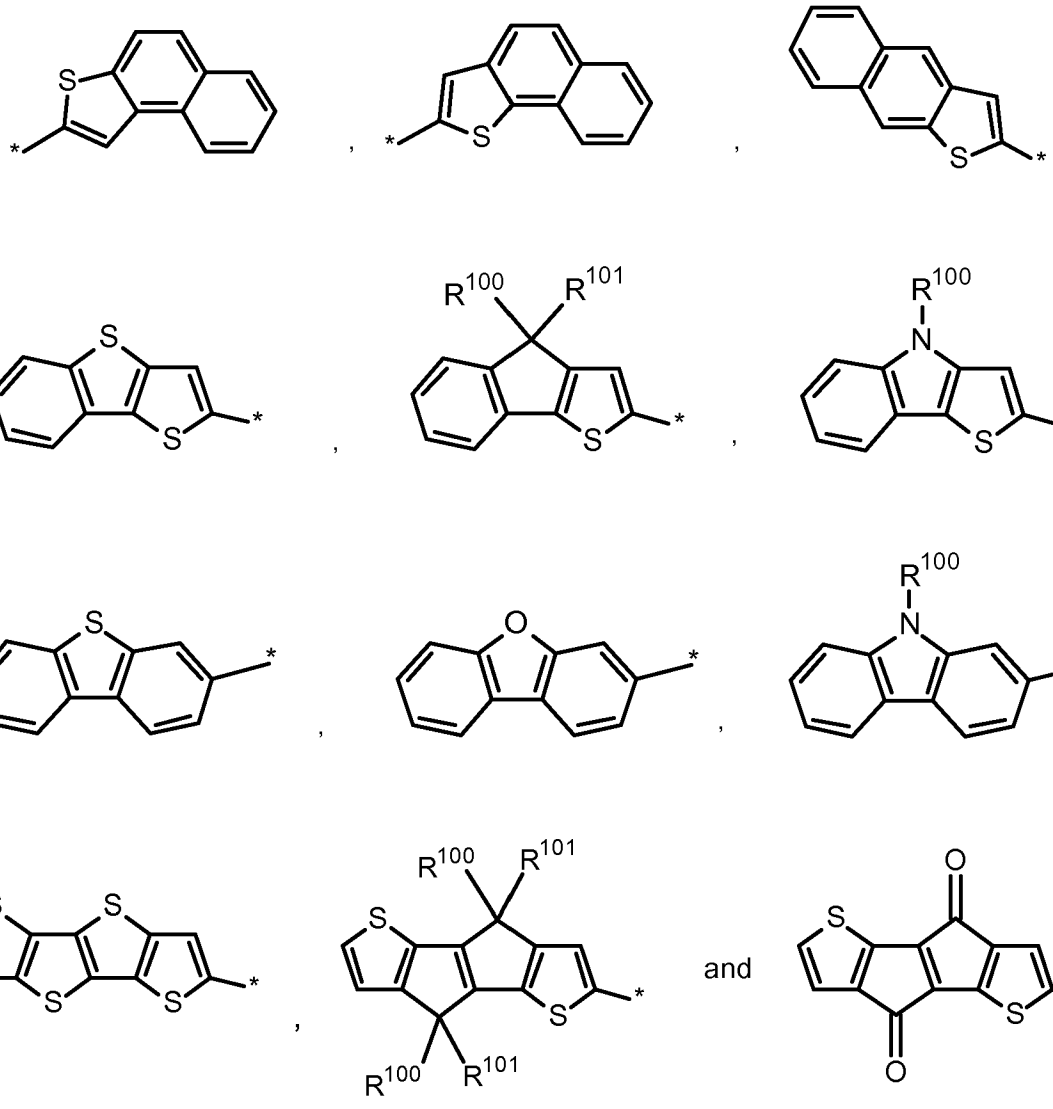
10


,

,

,



,

,

and

;

examples of 5 to 14 membered heteroaryl are the examples given for the 5 to 10 membered heteroaryl and

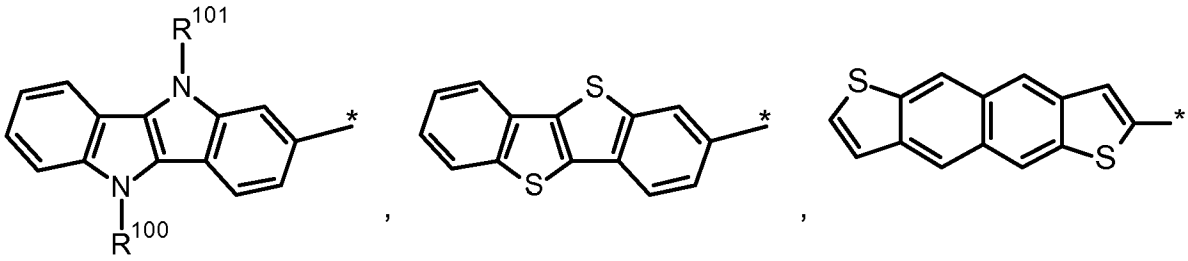



















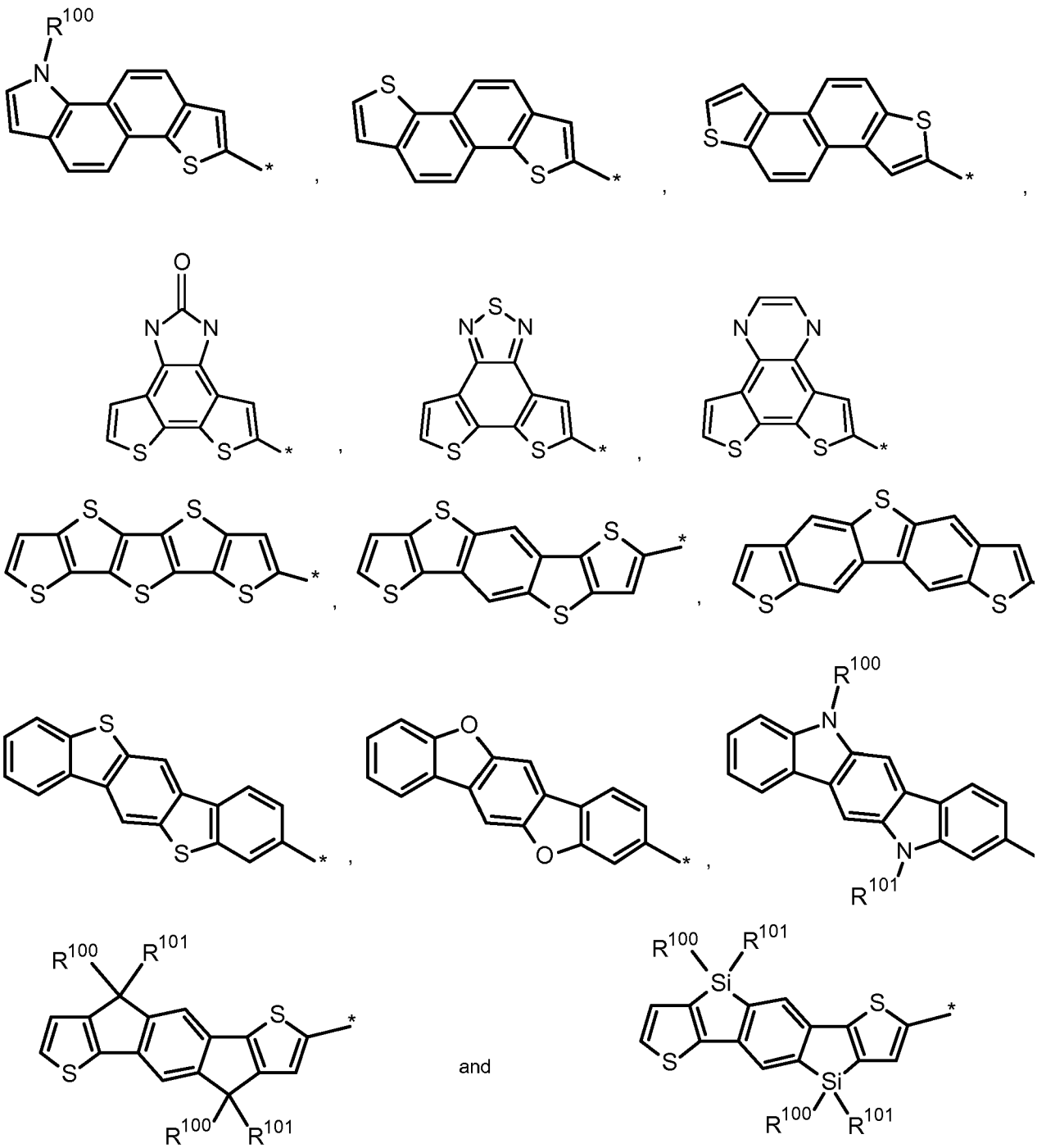


and

;

examples of 5 to 20 membered heteroaryl are the examples given for the 5 to 14 membered heteroaryl and





and

wherein

R^{100} and R^{101} are independently and at each occurrence selected from the group consisting of H, C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, and 5 to 14 membered heteroaryl, or R^{100} and R^{101}, if attached to the same atom, together with the atom, to which they are attached, form a 5 to 12 membered ring system,

wherein

C_{1-20}-alkyl, C_{2-20}-alkenyl and C_{2-20}-alkynyl can be substituted with one to five substituents selected from the group consisting of C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered

heteroaryl, OR^q, $OC(O)-R^q$, $C(O)-OR^q$, $C(O)-R^q$, NR^qR^r, $NR^q-C(O)R^r$, $C(O)-NR^qR^r$, $N[C(O)R^q][C(O)R^r]$, SR^q, halogen, CN, and NO_2;

C_{5-8}-cycloalkyl can be substituted with one to five substituents selected from the group consisting of C_{1-10}-alkyl, C_{2-10}-alkenyl, C_{2-10}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, OR^q, $OC(O)-R^q$, $C(O)-OR^q$, $C(O)-R^q$, NR^qR^r, $NR^q-C(O)R^r$, $C(O)-NR^qR^r$, $N[C(O)R^q][C(O)R^r]$, SR^q, halogen, CN, and NO_2;

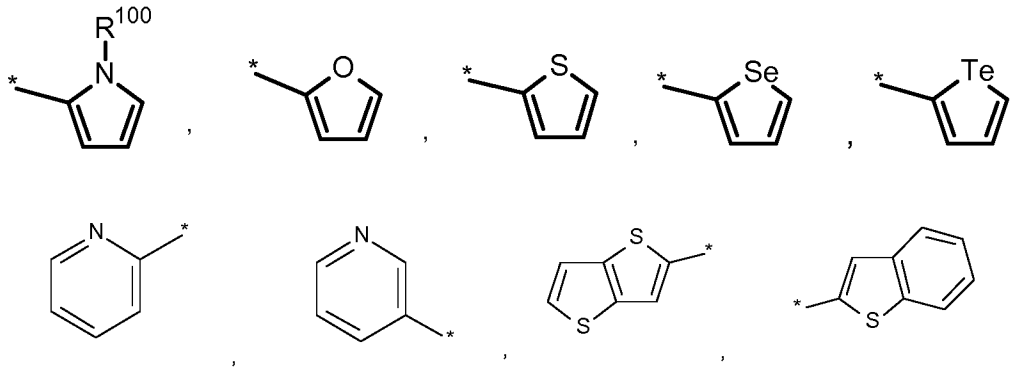
C_{6-14}-aryl and 5 to 14 membered heteroaryl can be substituted with one to five substituents independently selected from the group consisting of C_{1-10}-alkyl, C_{2-10}-alkenyl, C_{2-10}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, OR^q, $OC(O)-R^q$, $C(O)-OR^q$, $C(O)-R^q$, NR^qR^r, $NR^q-C(O)R^r$, $C(O)-NR^qR^r$, $N[C(O)R^q][C(O)R^r]$, SR^q, halogen, CN, and NO_2;

5 to 12 membered ring system can be substituted with one to five substituents selected from the group consisting of C_{1-10}-alkyl, C_{2-10}-alkenyl, C_{2-10}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, OR^q, $OC(O)-R^q$, $C(O)-OR^q$, $C(O)-R^q$, NR^qR^r, $NR^q-C(O)R^r$, $C(O)-NR^qR^r$, $N[C(O)R^q][C(O)R^r]$, SR^q, halogen, CN, and NO_2;

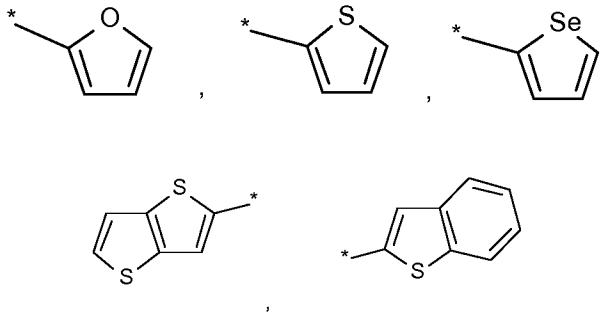
wherein
R^q and R^r are independently selected from the group consisting of H, C_{1-10}-alkyl, C_{2-10}-alkenyl and C_{2-10}-alkynyl,
wherein
C_{1-10}-alkyl, C_{2-10}-alkenyl and C_{2-10}-alkynyl can be substituted with one to five substituents selected from the group consisting of halogen, CN and NO_2.

C_{6-18}-arylene is a 6 to 18 membered monocyclic or polycyclic, such as dicyclic, tricyclic or tetracyclic, ring system, which comprises at least one C-aromatic ring, and which may also comprise non-aromatic rings, which may be substituted by =O.

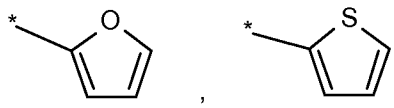
Preferred heteroaryl moieties are



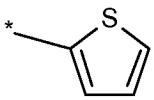
More preferred heteroaryl moieties are



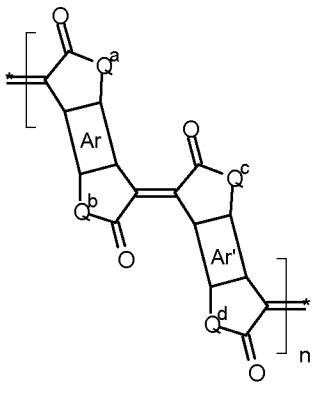
Even more preferred heteroaryl moieties are



Most preferred heteroaryl moiety is



Preferred polymers comprise at least a structure of formula (II')

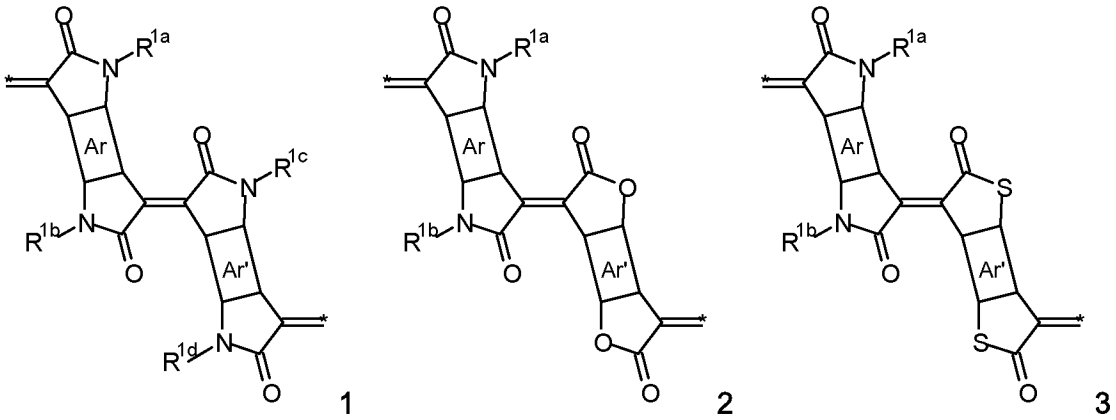


(II')

where n is an integer of 4 to 500, more preferably n is 5 to 400, more preferably n is 6 to 300, even more preferably n is 7 to 200 and most preferably n is 8 to 100, especially 10 to 50.

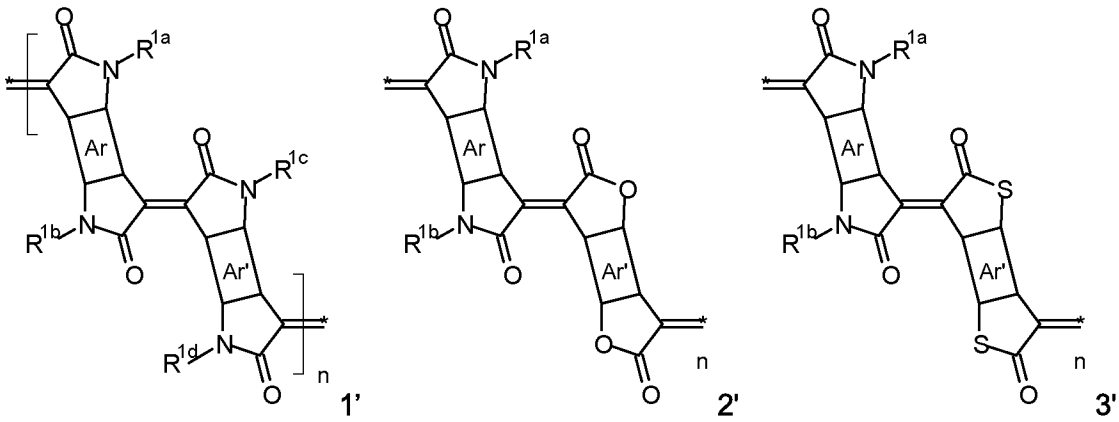
Preferably the polymers contain more than 10% by weight groups of formula (II'), more preferably contain more than 30% by weight groups of formula (II'), even more preferably contain more than 50% by weight groups of formula (II'), much more preferably contain more than 70% by weight groups of formula (II'), and most preferably contain more than 90% by weight groups of formula (II').

Preferred polymers comprise at least one group of formula **1**, **2** or **3**, wherein groups of formulas **1** and **2** are especially preferred.



More preferably polymers comprise at least one group of formula **1'**, **2'** or **3'**, wherein groups of formulas **1'** and **2'** are especially preferred and n is defined above or below.

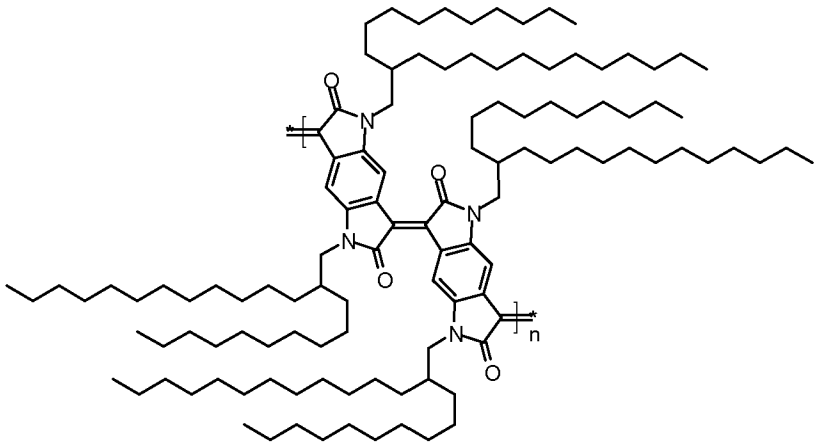
Ar and Ar' can be the same.
R^{1a} and R^{1b} can be the same.
R^{1c} and R^{1d} can be the same.
R^{1a}, R^{1b}, R^{1c} and R^{1d} can be the same.



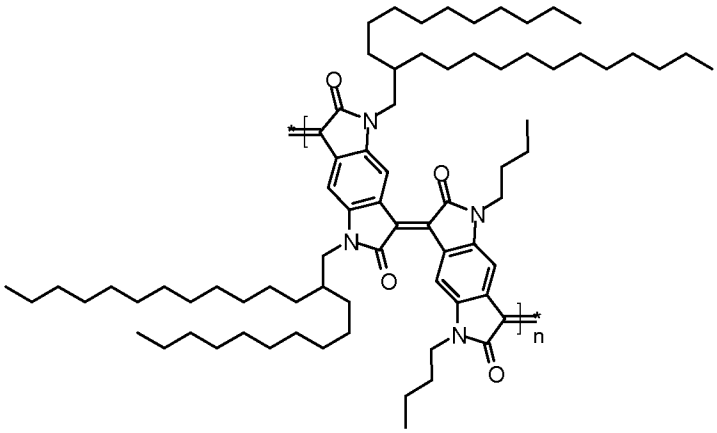
R^{1b}, R^{1c} and R^{1d} are defined as R^{1a} above, including the preferred ranges.

The polymers can e.g. be end-capped by moieties T^1 or T^2.

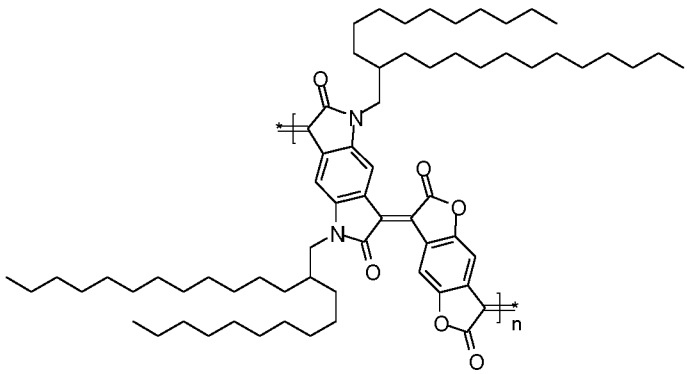
Very preferred polymers e.g. comprise at least a group



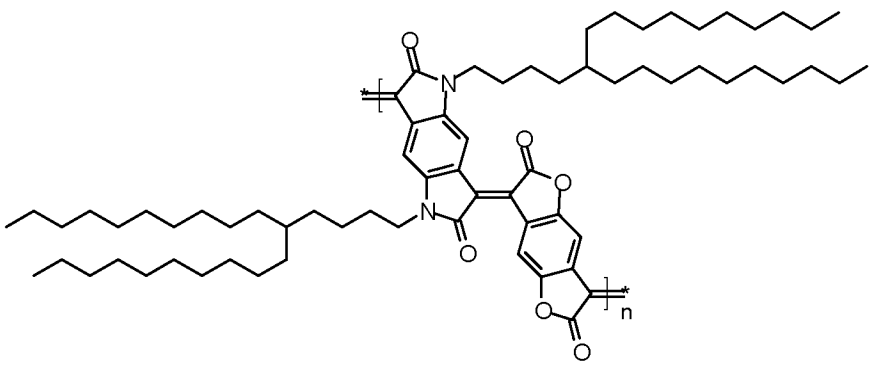
P1



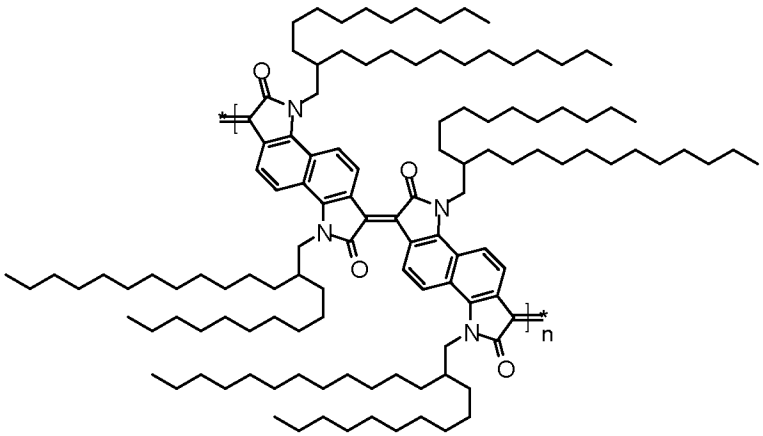
P2



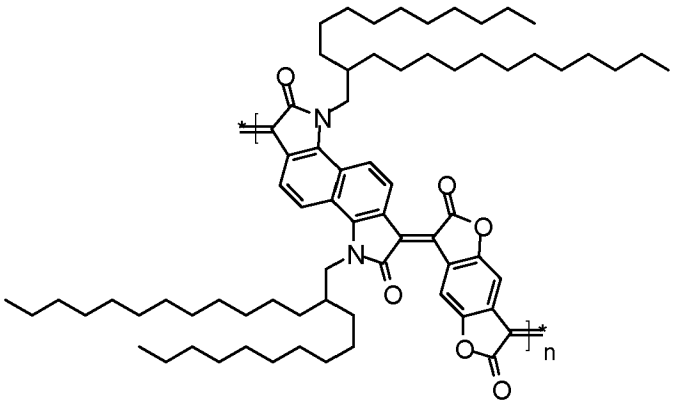
P3



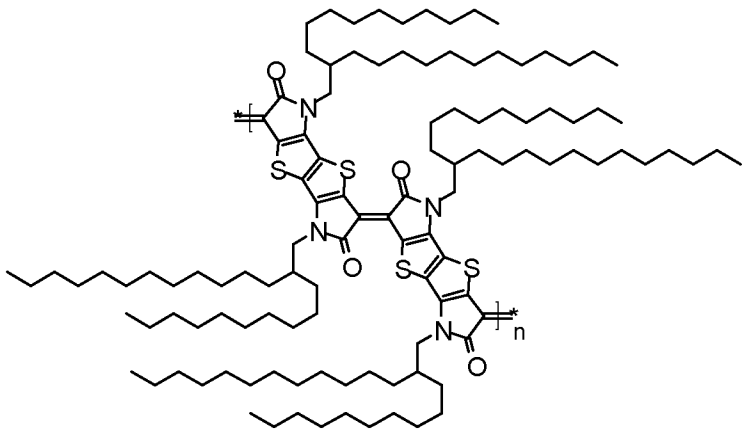
P4



P5

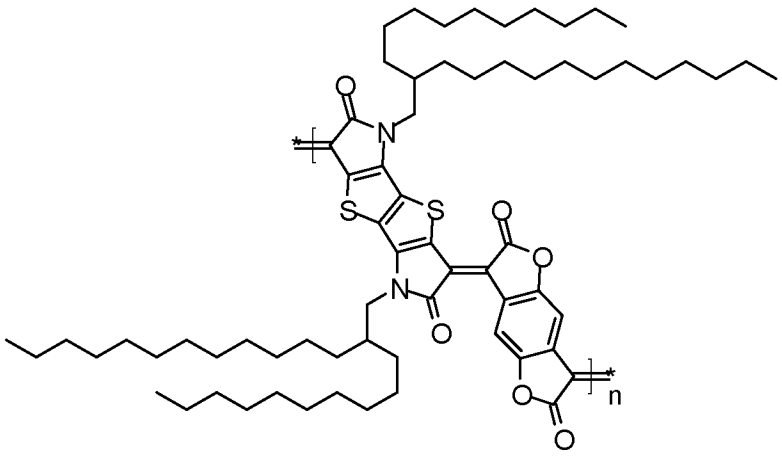


P6

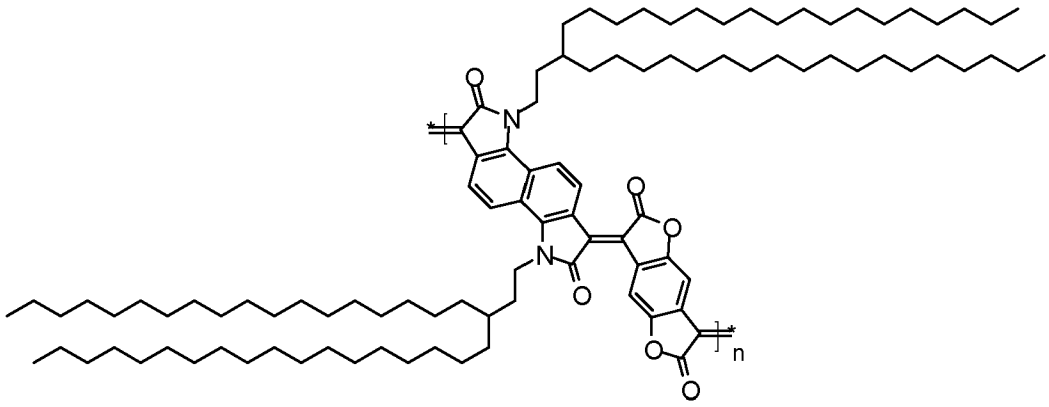


P7

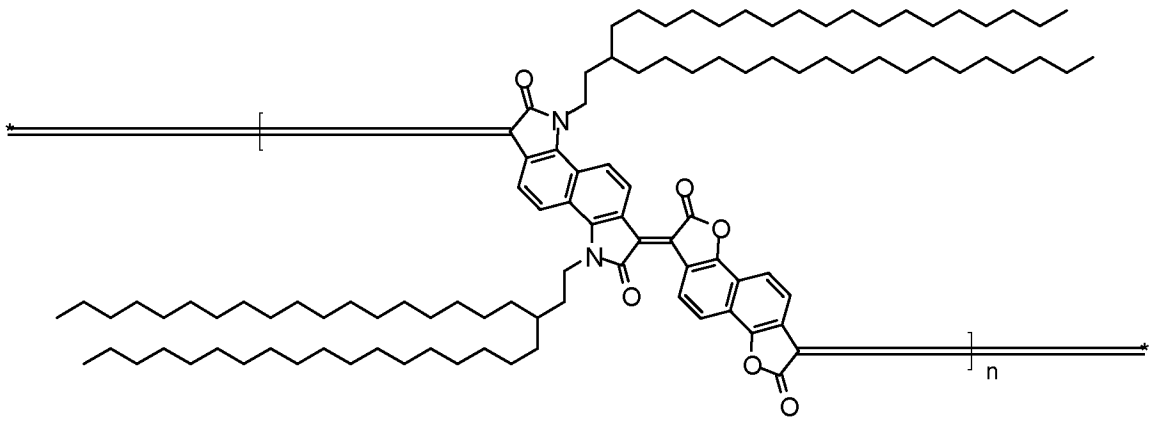
30



P8

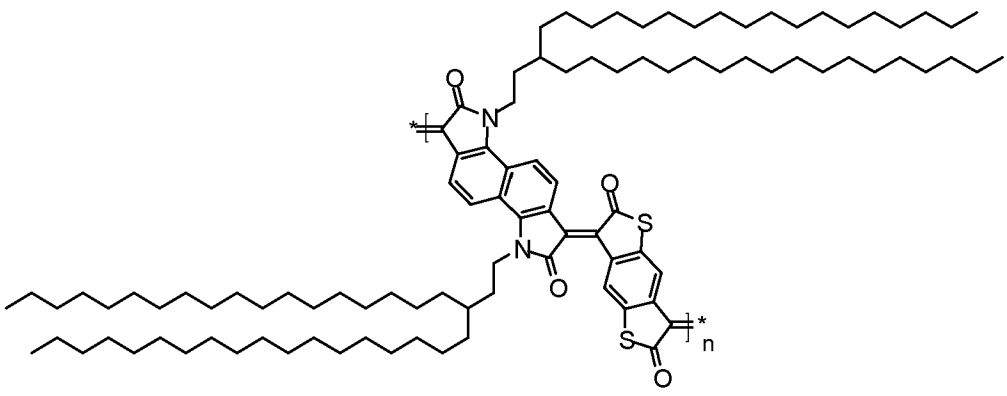


P9

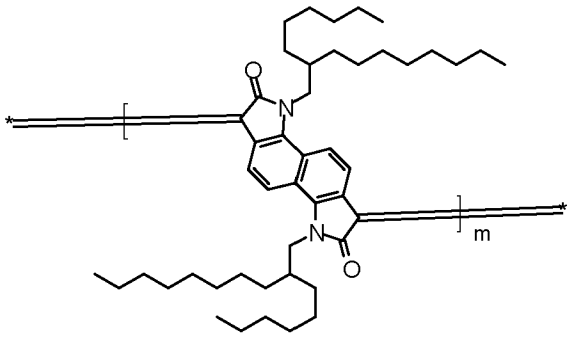


P10

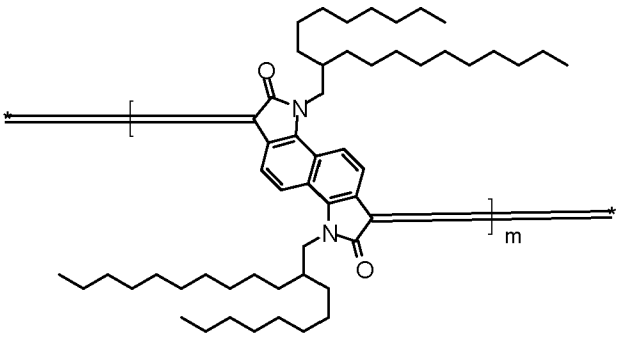
5



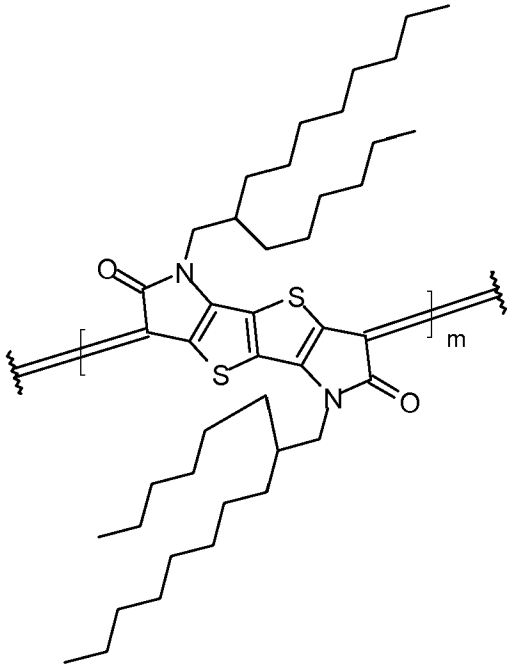
P11



P12



P13

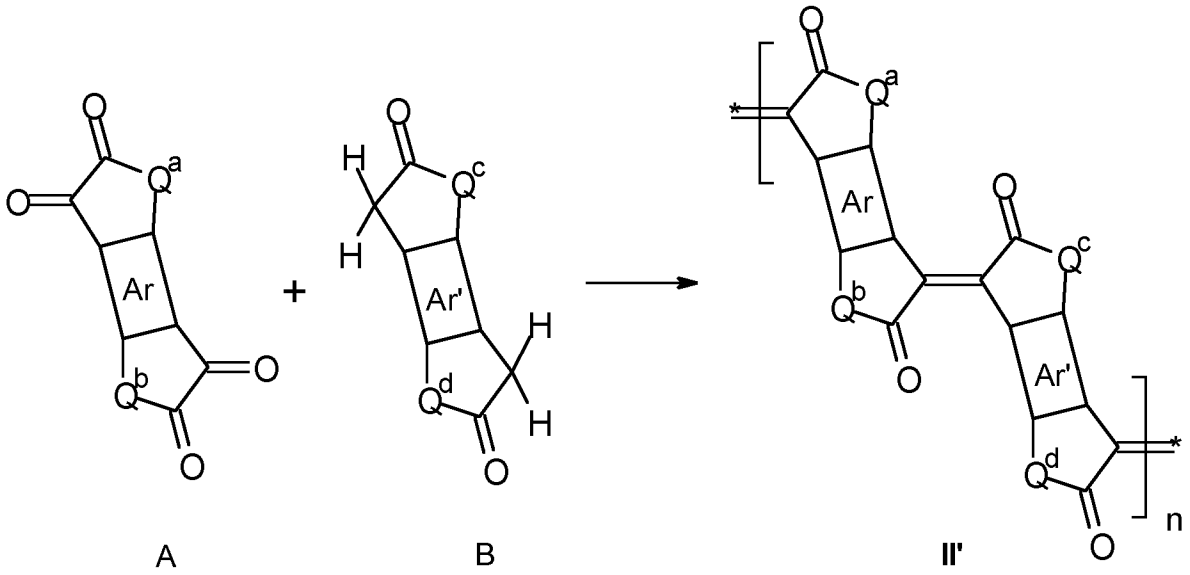


P14

where n is an integer from 3 to 1000 and m is an integer from 3 to 1000.

m is preferably an integer of 4 to 500, more preferably m is 5 to 400, more preferably m is 6 to 300, even more preferably m is 7 to 200 and most preferably m is 8 to 100, especially 10 to 50.

Polymers comprising the formula (II') can be synthesized e.g. via the following synthesis route 1 by condensation of a tetraone A with a dione B:



A B II'

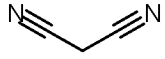
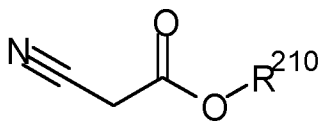
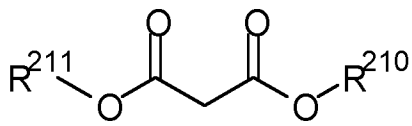
In the case of tetraones A, Q^a and Q^b are preferably substituted nitrogen atoms.
In the case of diones B, Q^c and Q^d are preferably oxygen or substituted nitrogen atoms.

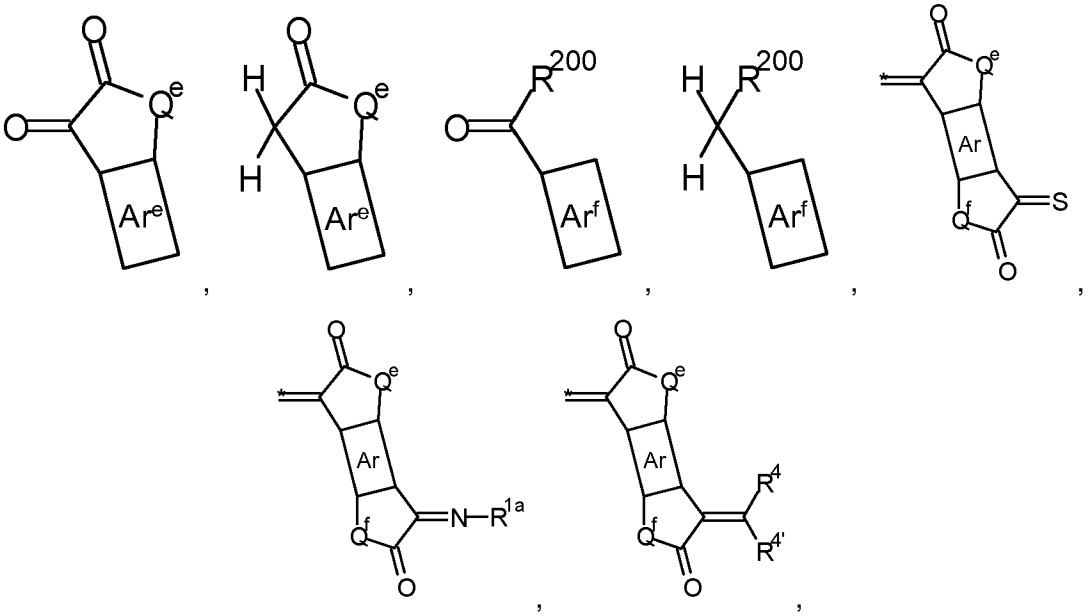
The condensation can be effected in a solvent like acetic acid, toluene, xylene etc. by the application of heat (room temperature up to reflux temperature of the used solvents). Bases or acids, preferably acids can be added as catalysts.

Such bases can be e.g. sodium acetate and sodium hydroxide.

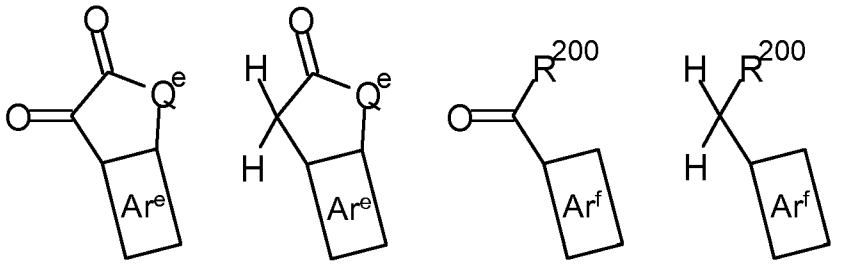
Such acids can be e.g. protic acids like formic acid, acetic acid, propionic acic, trifluoroacetic acid, HCl, H_2SO_4, HPF_6, para-toluenesulfonic acid, or Lewis acids like $AlCl_3$, preferably protic acids, especially para-toluenesulfonic acid.

The water obtained by the condensation reaction can be removed e.g. by azeotropic distillation with e.g. toluene as solvent, or e.g. with 4 Å molecular sieves. The ends of these polymers are determined by the starting materials A and B. Special end-cappers might be added during the synthesis like e.g.:

H_2NR^{1a},  ,  ,  ,



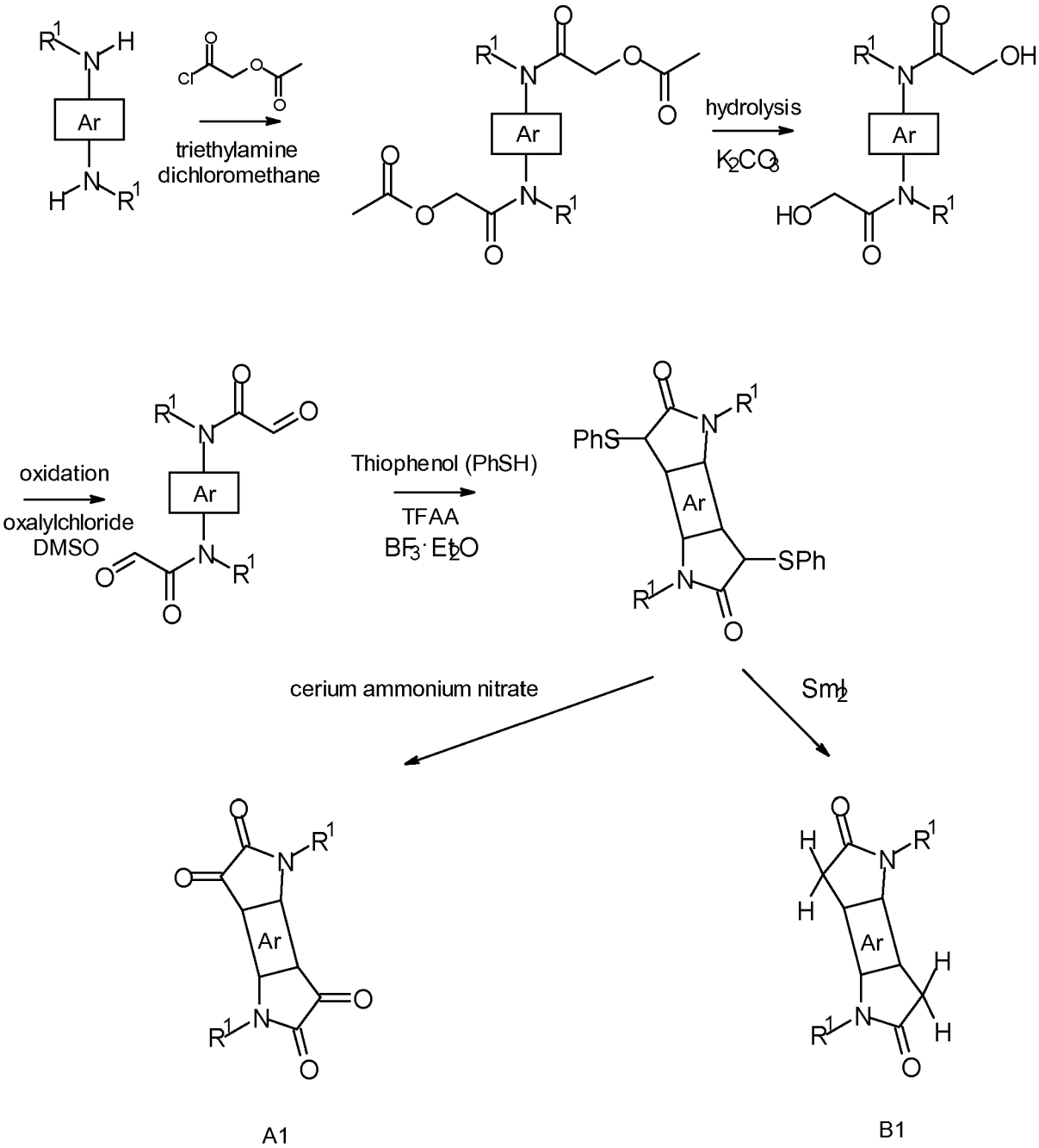
preferably



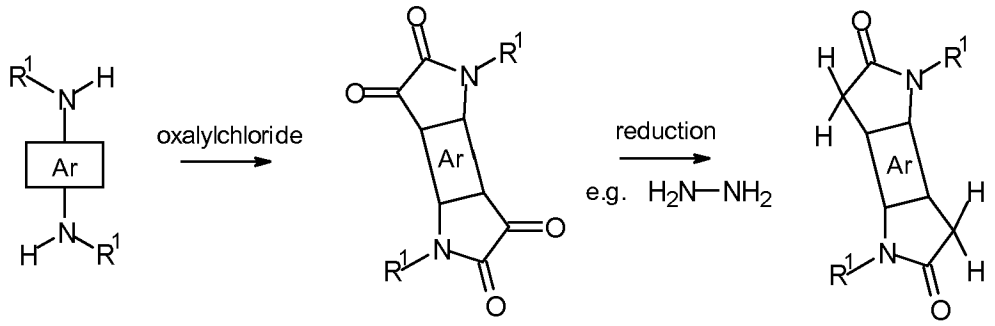
where R^{210} and R^{211} are independently of each other hydrogen, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl or C_{5-12}-cycloalkyl, preferably C_{1-30}-alkyl.

The starting materials A1, A2, B1, B2 wherein Q^a, Q^b, Q^c and Q^d are substituted nitrogen atoms can e.g. be synthesized as follows by synthesis routes 2 or 3:

Synthesis route 2:

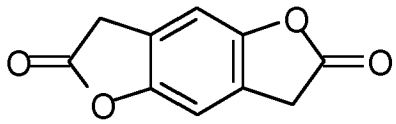

triethylamine
dichloromethane
hydrolysis
K_2CO_3
oxidation
oxalylchloride
DMSO
Thiophenol (PhSH)
TFAA
$BF_3 \cdot Et_2O$
cerium ammonium nitrate
SmI_2
A1
B1

Synthesis route 3:

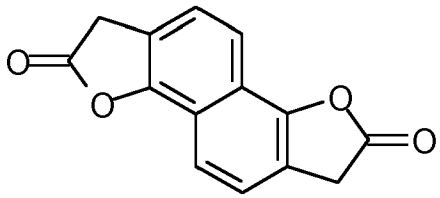


A2 B2

Starting materials B where Q^c and Q^d are oxygen atoms can e.g. be synthesized according to the following methods described in J. Am. Chem. Soc., 1944, *66* (9), pp 1540-1542 for

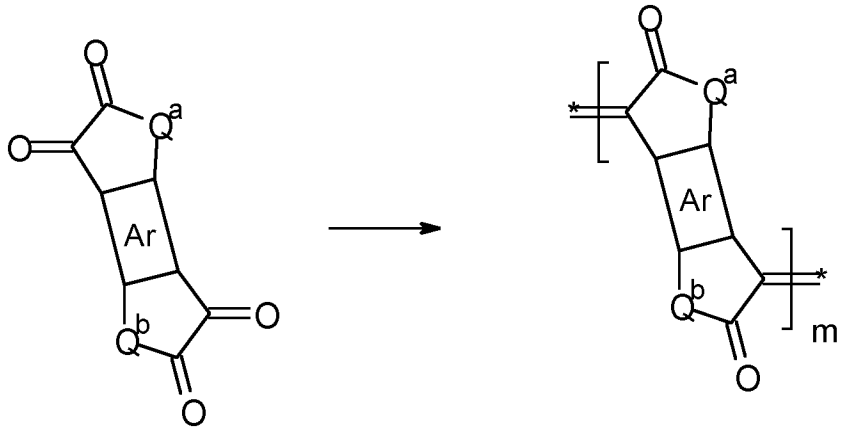


and Chem. Commun., 2015, 51, 13515-13518 for



Synthesis route 4

The polymers can be synthesized as well via homo-polymerization of a tetraone A, e.g. by mixing a monomer A with the reagent $P(NEt_2)_3$ in a solvent, e.g. in toluene:



A **II"**

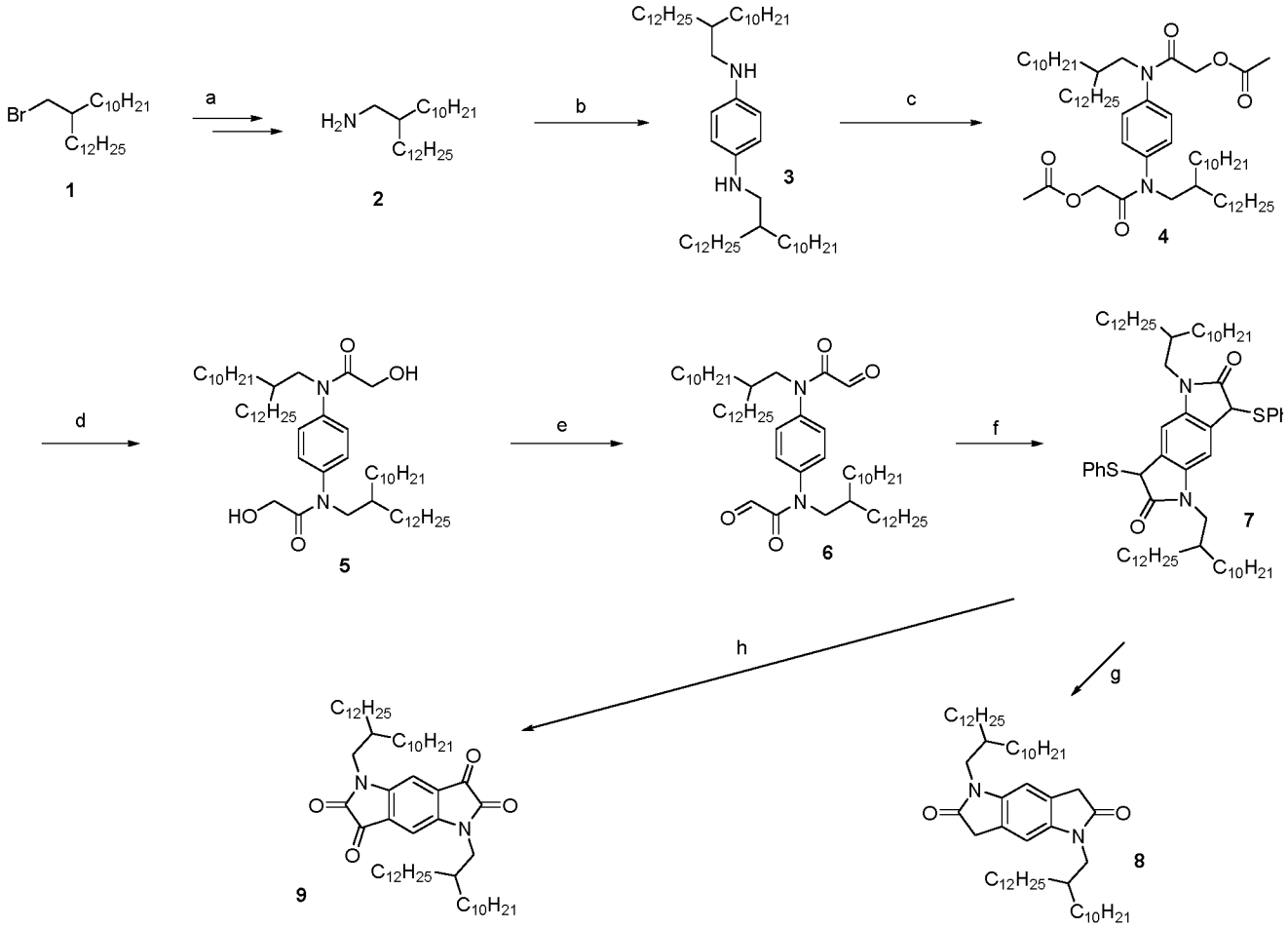
where m is an integer from 3 to 1000.

The invention also relates to electronic devices comprising the compounds or the polymers of the invention, especially organic field effect transistors.

The invention is illustrated by the following non-limiting examples.

Examples

The scheme for the synthetic route to 1,5-bis(2-decyltetradecyl)-5,7-dihydropyrrolo[2,3-f]indole-2,6(1H,3H)-dione and 1,5-bis(2-decyltetradecyl)-1,5-dihydropyrrolo[2,3-f]indole-2,3,6,7-tetraone is shown below.



Reaction conditions: (a)PPh_3, DCM, NBS, rt 98 %; potassium phthalimide, DMF 62 %; Hydrazine hydrate, MeOH; (b) 1,4-cyclohexanedione, EtOH, air, 48 %; (c) NEt_3, acetoxyacetyl chloride, DCM, 96 %; (d)K_2CO_3, THF/MeOH/H_2O, 94 %; (e) oxalyl chloride, DMSO, DCM, NEt_3, -78 °C; (f) DCM, PhSH, TFAA, BF_3 (g) SmI_2, THF, 28%; (h) CAN, THF/H_2O, 15 %.

Example 1 Synthesis of 1-bromo-2-decyltetradecane (1)

Under argon, triphenylphosphine (27.8 g, 70.5 mmol) was suspended in a flask with DCM (47 ml). The mixtures was cooled to 0°C before 2-decyltetradecan-1-ol (29.8 ml, 105.8 mmol) was introduced. After 5 minutes stirring, N-bromosuccinimide (18.8 g, 105.8 mmol) was added por-

tion wise to the flask. The reaction mixture immediately turned yellow and continued to darken to orange. The reaction was stirred for 16 hours after which the solvent was removed by vacuum evaporation. The brown residue was diluted with petroleum ether and the solution flushed through a silica plug. The filtrate was evaporated to give a clear oil. Yield: 28.7 g, 98 %. ^{1}H NMR (400 MHz, Chloroform-d) δ 3.44 (d, *J* = 4.7 Hz, 2H), 1.66 – 1.47 (m, 2H), 1.44 – 1.15 (m, 40H), 0.88 (t, *J* = 6.6 Hz, 7H).^{13}C NMR (101 MHz, $CDCl_3$) δ 39.72, 39.70, 32.75, 32.10, 29.97, 29.82, 29.77, 29.53, 26.74, 22.86, 14.26.

Example 2 Synthesis of 2-(2-decyltetradecyl)isoindoline-1,3-dione

A solution of 1-bromo-2-decyltetradecane (20.0 g, 48.0 mmol) and potassium phthalimide (9.98 g, 52.8 mmol) in DMF (57.2 ml) was refluxed for 16 hours. The reaction mixture was cooled to room temperature and poured into water. The aqueous phase was extracted with DCM three times. The combined organic phase was washed with 0.2 M KOH, followed by H_2O and NH_4Cl. After drying the organic phase with $MgSO_4$ and filtering the salt, the solvent was removed under vacuum. The residue was subjected to a silica plug using 10 % EtOAc in petroleum ether, the yellow oil (14.4 g, 62 %) obtained was used immediately.

Example 3 Synthesis of 2-decyltetradecan-1-amine (2)

51 % Hydrazine hydrate in water (5.00 ml, 3.1 mmol) was introduced to a solution of 2-(2-decyltetradecyl)isoindoline-1,3-dione (14.40 g, 29.80 mmol) in methanol (10 ml) and refluxed for 16 hours. After cooling, the solvent was removed under vacuum before DCM and 10 % KOH solution was added to the residue. The phases were separated and the aqueous phase further extracted with DCM three times. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. Pale yellow oil, yield 10.0 g, 94 % was obtained. ^{1}H NMR (400 MHz, Chloroform-d) δ 3.51 (d, *J* = 5.5 Hz, 2H), 1.54 – 1.38 (m, 1H), 1.37 – 1.17 (m, 40H), 0.94 – 0.78 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.50, 108.43, 45.34, 41.01, 36.21, 32.06, 31.67, 30.25, 29.82, 29.49, 27.96, 26.92, 22.82, 14.23. MS TOF ES+: calculated 354.4100, $[M+H]^+$, C24H51N, found 354.4111.

Example 4 Synthesis of *N*,*N*'-bis(2-decyltetradecyl)benzene-1,4-diamine (3)

1,4-Cyclohexanedione (0.6 g, 5.0 mmol) was dissolved in ethanol and 2-decyltetradecan-1-amine added to the solution. Air was bubbled through the reaction mixture for 2 hours before the solvent was removed under reduced pressure. The red residue was purified on basified silica gel using 3 % EtOAc in petroleum ether to yield 1.8 g, 46 % brown oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 6.54 (s, 4H), 3.24 – 2.71 (m, 4H), 1.57 (s, 2H), 1.26 (s, 80H), 0.88 (t, *J* = 6.7 Hz, 12H). 13C NMR (101 MHz, CDCl3) δ 141.18, 114.77, 49.07, 37.95, 32.33, 32.09, 30.25, 29.82, 29.52, 26.90, 22.85, 14.27. MS TOF ES+: calculated 781.8278 $[M+H]^+$, C54H104N2, found 781.8269

Example 5 Synthesis of benzene-1,4-diylbis{[(2-decyltetradecyl)imino]-2-oxoethane-2,1-diyl} diacetate (4)

Triethylamine (0.70 ml, 4.99 mmol) was added to *N,N'*-bis(2-decyltetradecyl)benzene-1,4-diamine (1.77 g, 2.27 mmol) dissolved in dry DCM (22.70 ml) at O °C. Acetoxyacetyl chloride (0.54 ml, 4.99 mmol) was injected into the flask drop wise before the reaction was allowed to warm to room temperature and stirred for 16 hours. The reaction was quenched with $NaHCO_3$ and EtOAc added. The phases were separated and the aqueous phase extracted three times with EtOAc. The combined organic phase was washed with brine dried over $MgSO_4$, the salts filtered and the solvent removed under pressure to give pale yellow solid, 2.00 g, 96 %. 1H NMR (400 MHz, Chloroform-d) δ 7.32 (s, 4H), 4.33 (s, 4H), 3.64 (d, J = 7.0 Hz, 4H), 2.12 (s, 6H), 1.53 – 1.41 (m, 2H), 1.37 – 1.02 (m, 80H), 0.94 – 0.79 (m, 12H). 13C NMR (101 MHz, CDCl3) δ 170.61, 166.56, 141.13, 129.79, 61.79, 53.41, 36.25, 32.06, 31.23, 30.15, 29.82, 29.75, 29.50, 26.39, 22.83, 20.65, 14.25. MS TOF LD+: C62H112N2O6 $[M+H]^+$ found 980.9

Example 6 Synthesis of *N,N'*-benzene-1,4-diylbis[*N*-(2-decyltetradecyl)-2-hydroxyacetamide] (5)

Benzene-1,4-diylbis{[(2-decyltetradecyl)imino]-2-oxoethane-2,1-diyl} diacetate (3.6 g, 3.7 mmol) in THF (200 ml) and MeOH/water mixture (180 ml, 20 ml). The reaction mixture was stirred in the presence of excess K_2CO_3 at room temperature for 16 hours before the salt was filtered off. The mixture was concentrated under reduced pressure and water and ethyl acetate added to the residue. The phases were separated and the aqueous phase is extracted three times with ethyl acetate. The combined organic phases were washed with brine dried over $MgSO_4$, filtered and the solvent removed in the rotary evaporator to furnish light yellow, 3.1 g, 94 %. ^1H NMR (400 MHz, Chloroform-d) δ 7.24 (s, 4H), 3.76 (s, 4H), 3.70 (d, *J* = 7.1 Hz, 4H), 3.47 – 3.30 (m, 2H), 1.52 – 1.37 (m, 2H), 1.36 – 1.04 (m, 80H), 0.86 (t, *J* = 6.7 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.98, 140.31, 129.69, 60.73, 53.47, 36.21, 32.04, 31.23, 30.11, 29.77, 29.71, 29.47, 26.38, 22.80, 14.22. MS TOF LD+: C58H108N2O4, $[M+H]^+$ found 898.00.

Example 7 Synthesis of N,N'-(1,4-phenylene)bis(N-(2-decyltetradecyl)-2-oxoacetamide) (6)

Under argon atmosphere, oxalyl chloride (0.31 ml, 3.89 mmol) was diluted with DCM (4 ml) and cooled to -78°C. A solution of DMSO (0.28 ml) in DCM (4.2 ml) was added to the reaction flask at -78°C. The reaction flask was stirred for 20 minutes before *N,N'*-benzene-1,4-diylbis[*N*-(2-decyltetradecyl)-2-hydroxyacetamide] (1.45 g, 1.62 mmol) diluted in 7 ml DCM was injected dropwise into the flask. The reaction mixture turns aqua green. After 1.5 hours at -78°C, trimethylamine (2.26 ml, 16.2 mmol) was added slowly. The reaction was then stirred at -78°C for 4 hours before it was allowed to warm to room temperature slowly. The reaction was stirred for 16 hours before it was quenched with saturated $NaHCO_3$ solution. The phases were separated and the aqueous phase extracted three times with DCM. The combined organic phases were

dried with $MgSO_4$, filtered and the solvent removed under vacuum to yield brown oil, 0.61 g, which was used immediately.

Example 8 Synthesis of 1,5-bis(2-decyltetradecyl)-3,7-bis(phenylthio)-5,7-dihydropyrrolo[2,3-f]indole-2,6(1H,3H)-dione (7)

Crude N,N'-(1,4-phenylene)bis(N-(2-decyltetradecyl)-2-oxoacetamide) (1.44 g, 1.61 mmol) was diluted with DCM (6 ml) before thiophenol (0.33 ml, 3.23 mml) was added to flask. The reaction mixture was then stirred for 16 hours at room temperature. Following this, TFAA (2.01 ml, 14.50 mmol) was added slowly to the reaction and stirred for 1 hour 30 minutes, after which, $BF_3{\cdot}Et_2O$ (0.99 ml, 8.05 mmol) was added to the flask cautiously. Following further stirring for 3 hours, the reaction was cooled to 0°C before it was quenched with $NaHCO_3$. The aqueous phase was extracted with DCM three times and the organic phases combined and washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure to furnish red /brown residue as the crude product, which was used without further purification. Yield (1.32 g, 76%) MS (TOF ES+): calculated 1077.8244 C70H112N2O2S2, [M+H]+ found 1077.8278

Example 9 Synthesis of 1,5-bis(2-decyltetradecyl)-1,5-dihydropyrrolo[2,3-f]indole-2,3,6,7-tetraone (9)

Cerium ammonium nitrate (9.48 g, 17.8 mmol) was added to the solution of 1,5-bis(2-decyltetradecyl)-3,7-bis(phenylthio)-5,7-dihydropyrrolo[2,3-f]indole-2,6(1H,3H)-dione (2.40 g, 2.22 mmol) dissolved in a 6:1 ratio of THF/water (42 ml) mixture. Following 30 minutes stirring at room temperature the reaction mixture takes a deep purple colouration. After 3 hours stirring the reaction mixture was reduced under vacuum. The crude residue was purified by column chromatography at a gradient of 3-10 % ethyl acetate in petroleum ether 40-60° C to furnish the titled compound, yield: 300 mg, 15 %. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.12 (s, ArH, 2H), 3.62 (d, *J* = 7.5 Hz, NCH_2, 4H), 1.84 (d, *J* = 9.9 Hz, CH, 2H), 1.40 – 1.12 (m, CH_2, 80H), 0.88 (t, *J* = 6.7 Hz, CH_3, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.36, 157.15, 147.85, 123.24, 106.99, 77.16, 45.49, 36.15, 32.06, 31.52, 30.12, 29.79, 29.76, 29.69, 29.47, 26.40, 22.82, 14.25. MS TOF LD+: C58H100N2O4 , $[M+H]^+$ found 890.0

Example 10 Synthesis of 1,5-bis(2-decyltetradecyl)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1*H*,3*H*)-dione (8)

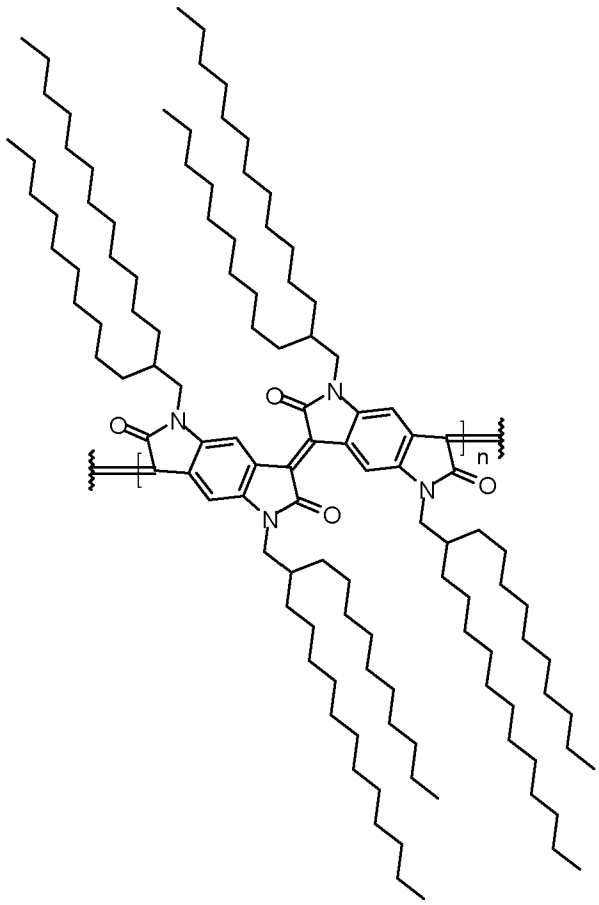
1,5-bis(2-decyltetradecyl)-3,7-bis(phenylthio)-5,7-dihydropyrrolo[2,3-f]indole-2,6(1H,3H)-dione was dissolved in dry THF (37.0 ml) and 0.1 M SmI_2 in THF (40.0 ml, 4.0 mol) added to the solution at room temperature. Following 16 hours, saturated $NaHCO_3$ (200 ml) was introduced into the reaction mixture and the aqueous phase extracted with ethyl acetate three times. The organic layer was washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. Purification by column chromatography in 15 % ethyl acetate in 40-60°C petroleum ether afforded 800 mg beige solid; yield: 28 %. 1H NMR (400 MHz, Chloroform-d) δ 6.73 (s, 2H), 3.56 (d, J = 7.9 Hz, ArH 4H), 3.54 (s, CH_2, 4H), 1.91 – 1.76 (m,CH, 2H), 1.24 (s,

CH_2, 80H), 0.87 (t, CH_3, J = 6.7 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.85, 140.24, 123.92, 106.05, 44.85, 36.41, 36.25, 32.06, 31.68, 30.20, 29.81, 29.49, 26.60, 22.83, 14.26. MS TOF LD+: C58H104N2O2 $[M+H]^+$ found 860.9

Example 11 Polymerization to give pDPID P1

A microwave vial was charged with 1,5-bis(2-decyltetradecyl)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1*H*,3*H*)-dione (**8**) (50.0 mg, 0.06 mmol), 1,5-bis(2-decyltetradecyl)-1,5-dihydropyrrolo[2,3-f]indole-2,3,6,7-tetraone (**9**) (51.6 mg, 0.06 mmol), p-toluene sulfonic acid (3.3 mg, 0.02 mmol)and 4 Å molecular sieves. The vial was sealed and dry toluene (2 ml), already degassed for 30 minutes was injected into the vial. The reaction was heated at 120°C for 21 hours followed by 10 hours at 180°C in the dark. The reaction mixture changed colour from blue to red/brown to dark purple over the polymerization period. The crude polymer was precipitated in methanol and purified by Soxhlet extraction with methanol, acetone, and hexane. The hexane fraction was collected and reduced under vacuum and the polymer precipitated into methanol. The polymer was filtered and dried. Yield of **P1**: 83 mg, 82 % dark purple solid. ^1H NMR (400 MHz, Chloroform-d) δ 9.30 (d, *J* = 8.2 Hz, 2H), 8.93 (s, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 3.75 (dd, *J* = 13.6, 7.3 Hz, 8H), 2.02 (dt, *J* = 12.8, 6.1 Hz, 4H), 1.66 – 1.12 (m, 150H), 0.91 – 0.79 (m, *J* = 3.7 Hz, 24H).

M_n = 18 400 g/mol, M_w = 29 900 g/mol, PDI = 1.6



P1

Example 12

Fabrication and electrical characterization of an organic field-effect transistor (OFET) based on compound **P1**

Preparation of back-contact, top-gate FETs

Compound P1 is dissolved at a concentration of 0,75 wt% in toluene. The transistors have been fabricated on a PET-substrate with lithographically prepatterned gold contacts, serving as Source and Drain contact of the FET. Before the deposition of the semiconductor, the substrate been immersed in a 1wt % solution of 4-methoxybenzenethiol in ethanol for 2 minutes. Afterwards the substrate has been rinsed with ethanol and blown dry using nitrogen. Next, the semiconductor formulation was applied by spin coating (1,000 rpm, 15 seconds). After the coating is completed, the substrate is immediately transferred onto a preheated hotplate and heated for 30s at 90°C. Next the gate dielectric layer consisting of Cytop CTL-809 M is spincoated on top of the organic semiconductor (1250 rpm, 30 s). After Spincoating, the substrate is again transferred to the hotplate and annealed for another 5 Min at 90°C. The thickness of the dielectric layer is 500nm measured by profilometer. Finally 50 nm thick shadow-mask patterend gold gate electrodes are deposited by vacuum evaporation to complete FETs in the BCTG –configuration.

Electrical characterization

The devices obtained are showing n-type characteristics. The mobility μ is calculated from the root representation of the transfer characteristic curve (solid grey curve) calculated in the saturation region. The slope m is determined from the dashed black line in Figure 1. The dashed black line in Figure 1 is fitted to a region of the root representation of the current characteristic ID such that a good correlation to the linear slope of the root representation is obtained.
The threshold voltage U_{Th} can be taken from the intersection of black dashed line in Fig. 1 with the X-axis portion (V_{GS}).
In order to calculate the electrical properties of the OFET, the following equations are employed:

$$\mu = \frac{m^2 * 2L}{C_G * W} \qquad C_G = \varepsilon_0 * \varepsilon_r \frac{1}{d} \qquad U_{Th} = -1 * \frac{m}{b} \qquad ON/OFF = \frac{I_D \max}{I_D \min}$$

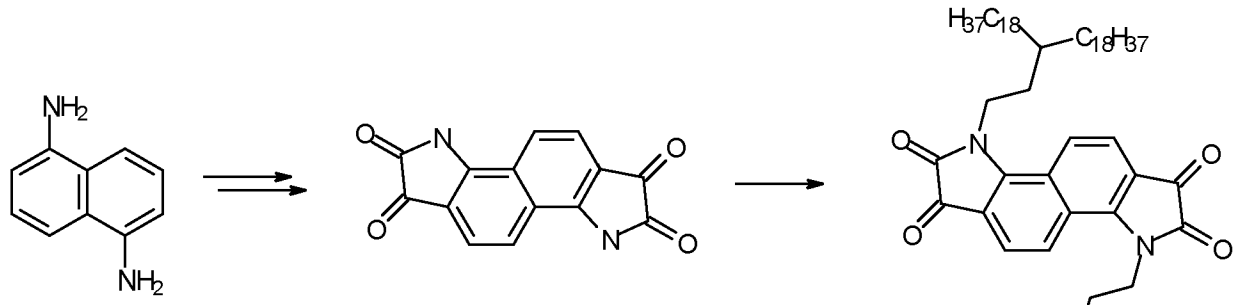
where ε_0 is the vacuum permittivity of 8.85x 10^{-12} As/Vm, ε_r= 2,1 for Cytop, the thickness of the dielectric d=500nm, and W/L = 25.

The following mobility has been calculated for the respective compound:

Compound	Field-effect mobility μ [cm^2/Vs]	Threshold voltage U_{TH} [V]	ON/OFF ratio
P1	9E-5	15	2E2

Figure 1 shows a representative transfer characteristics of a FET fabricated from compound P1 with V_{GS} = -10 V to +30 V at 0.5V step size with V_{DS} = +30V. Drain current (black solid curve), Gate current (dotted grey curve), Square root of drain current (grey solid curve), and fitted slope of square root (dashed black curve).

Example 13



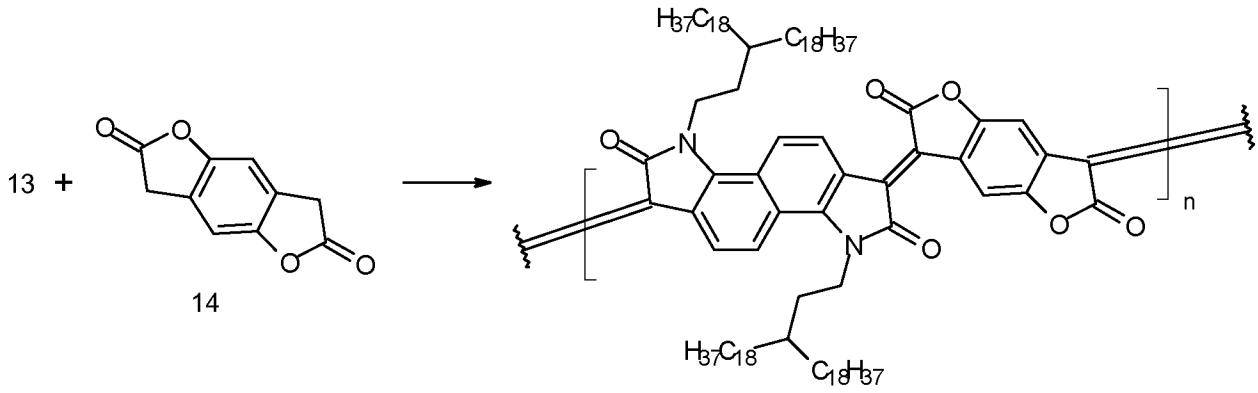
12

13

Compound 12 was synthesized according to the reference (*J. Mater. Chem. A.* 2016, **4**, 6940-6945), which was used as crude product without purification.

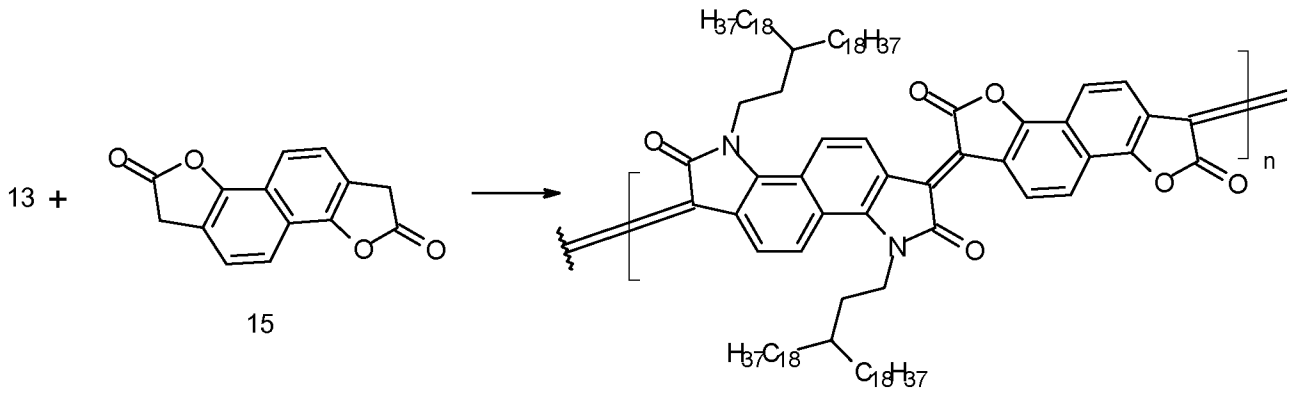
The crude bisisatin 12 (300 mg, 1.13 mmol) and dry K_2CO_3 (660 mg, 4.78 mmol) and the alkyl-iodide [1639798-42-7] (2.2 g, 3.26 mmol) were dissolved in 10 mL of dry DMF. The reaction mixture was heated to 100˚C for 4 hours. After cooling down, the reaction mixture was poured over 20 mL H_2O. The aqueous layer was extracted with $CHCl_3$. The organic layers were dried over $MgSO_4$ and concentrated to yield the crude reside. The crude product was purified by column chromatography on silica gel ($CHCl_3$: hexane: 2:1) to get the compound 13. Recrystallization with dichloromethane and methanol, collected and dried in vacuum. Total yield: 230 mg (15 %). ^{1}H NMR (400 MHz, CDCl3, rt): δ = 7.99 (d, J = 8.7 Hz, 2H), 7.67 (d, J = 8.6 Hz, 2H), 4.28-4.24 (m, 4H), 1.79-1.74 (m, 4H), 1.59-1.12 (M, 152H), 0.91-0.88 (m, 12H). ^{13}C NMR (100 MHz, CDCl3, rt): δ = 182.76, 158.96, 152.24, 127.21, 120.08, 119.64, 116.27, 42.12, 35.90, 33.46, 33.16, 31.94, 29.99, 29.72, 29.68, 29.37, 26.63, 22.70, 14.12. Calculated: C92H162N2O. 1359.25, Found: [M+H]: 1360.6.

Example 14 Polymerization to give pDPID P9



Compound 14 was synthesized according to ref: *J. Am. Chem. Soc.* **2014**, *136*, 2135−2141.
Polymer P9: To a vial was added 13 (71.82 mg, 0.053 mmol, 1 equiv) and bisoxindole 14 (10.04 mg, 0.053 mmol, 1 equiv), PTSA (2 mg). The tube was sealed and flushed with Argon, and then 0.5 ml degassed toluene was added. The mixture was thoroughly degassed under Argon for half an hour, and then the argon inlet was removed. The vial was heated at 120°C for 3 days. After cooling to RT, the polymer was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane and chloroform. The hexane and chloroform fractions were concentrated and precipitated into methanol. The precipitates were filtered and dried under vacuum to afford P9 as a dark solid (59 mg, 73 %). GPC (chlorobenzene, 80°C): Mn: 25.2 KDa, Mw: 44.3 KDa, PDI= 1.76. ^{1}H-NMR (TCE-d_2, 403 K, 400Hz): δ = 9.04 (broad), 7.76 (broad), 4.34 (broad), 2.18-0.85 (m).

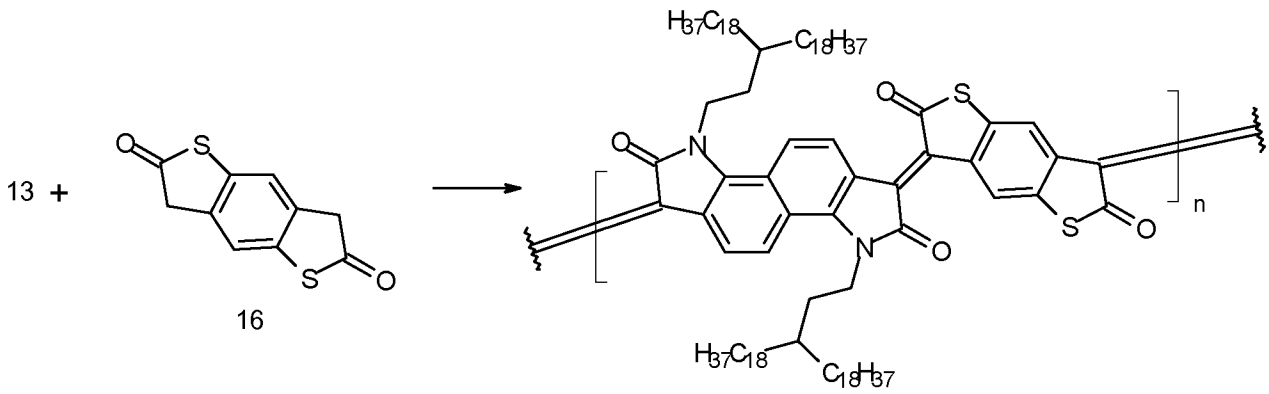
Example 15 Polymerization to give pDPID P10



Compound 15 was synthesized according to the ref: Chem. Commun., 2015, 51, 13515.
Polymer P10: To a vial was added 13 (52.78 mg, 0.039 mmol, 1 equiv.) and bisoxindole 15 (9.32 mg, 0.039 mmol, 1 equiv), PTSA (2 mg). The tube was sealed and flushed with Argon, and then 0.5 ml degassed toluene was added. The mixture was thoroughly degassed under

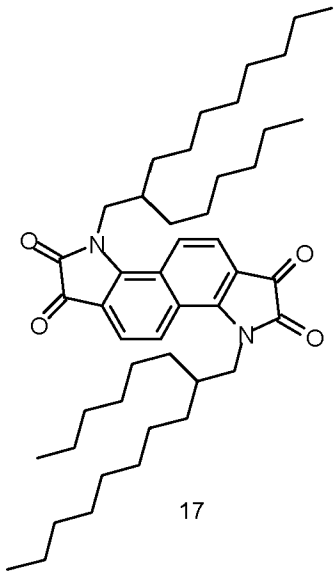
Argon for half an hour, and then the argon inlet was removed. The vial was heated at 120°C for 3 days. After cooling to RT, the polymer was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane and chloroform. The hexane and chloroform fractions were concentrated and precipitated into methanol. The precipitates were filtered and dried under vacuum to afford P10 as a dark solid (47 mg, 77 %). GPC (chlorobenzene, 80°C): Mn: 10.5k, Mw: 15.7 K, PDI: 1.49. ^{1}HNMR (TCE-d2, 403 K, 400Hz): δ = 9.33 (d), 9.20 (d), 9.10 (d), 8.05-7.94 (m), 7.71(d), 7.64 (d), 4.41-4.27 (m), 1.98-1.82 (m), 1.38-0.94 (m).

Example 16 Polymerization to give pDPID P11



Compound 16 was synthesized according to the ref: Organic Electronics 37 (2016) 190 - 196. Polymer P11: To a vial was added 13 (80.95 mg, 0.0595 mmol, 1 equiv.) and bisoxindole 16 (24.39 mg, 0.04 mmol, 1 equiv), PTSA (4 mg). The tube was sealed and flushed with Argon, and then 0.7 ml degassed toluene was added. The mixture was thoroughly degassed under Argon for half an hour, and then the argon inlet was removed. The vial was heated at 120°C for 3 days. After cooling to RT, the polymer was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane and chloroform. The hexane and chloroform fractions were concentrated and precipitated into methanol. The precipitates were filtered and dried under vacuum to afford P11 as a dark solid (65 mg, 70 %). GPC (chlorobenzene, 80°C): Mn = 21.1 K, Mw = 31.2 K, PDI = 1.48. ^{1}HNMR (TCE-d_2, 403 K, 400Hz): δ = 8.71 (broad), 8.01 (broad), 7.57 (broad), 4.33 (broad), 2.12-0.76 (m).

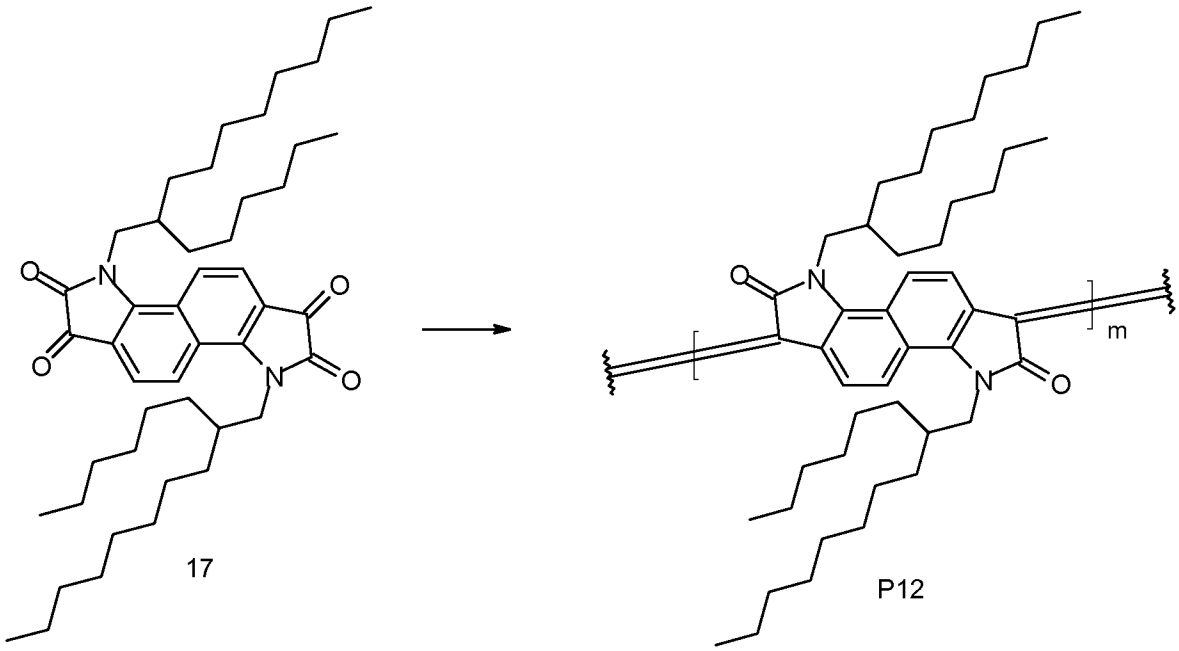
Example 17



17

Compound 17 was synthesized according to compound 13 in example 13 with [1044598-79-9] as alkyl iodide instead of [1639798-42-7].

Example 18 Polymerization to give pDPID P12

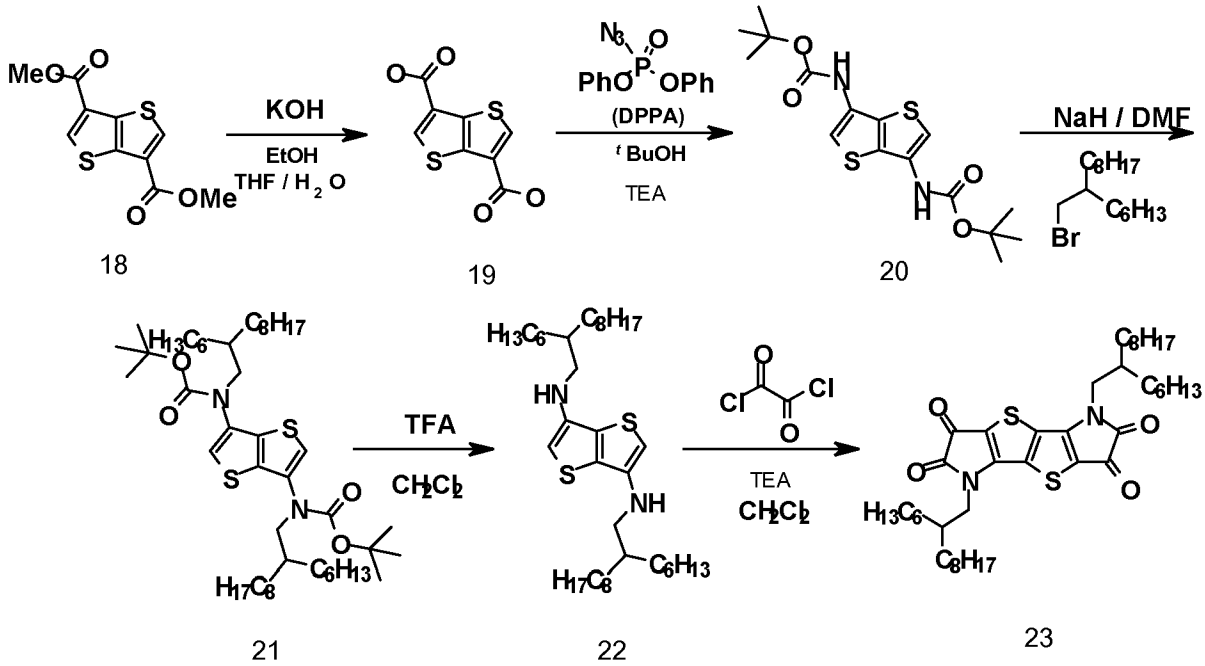


17 P12

To a microwave vial was added the respective bisisatin 17 (0.1 mmol, 1.0 e.q.) and then sealed. The sealed vial was degassed via vacuum and then purged with argon for three cycles. Anhydrous degassed toluene was added under argon and then tris(diethylamino)phosphine $P(NEt_2)_3$ (0.22 mmol, 2.2 e.q.) was added to the mixture at room temperature under bubbling of argon. The mixture turned dark green and then the temperature increased to 100°C. After reaction for 3 hours, the reaction mixture turned dark purple and was then poured into methanol. The result-

ing polymeric precipitate was filtered via thimble and then purified by Soxhlet extraction in a sequence of methanol, hexane, ethyl acetate, and finally chloroform. The chloroform fraction was concentrated by rotary evaporation, suspended in methanol and filtered to afford the polymer as a metallic dark green solid. GPC (Chlorobenzene at 80˚C): M_n = 20.2 kDa, M_w = 72.5 kDa, PDI = 3.59.

Example 19 Synthesis of Thieno[3,2-b]thiophene bisisatin 23



Compound 18 was synthesized according to the literature: *Adv. Mater.* **28**, 6921–6925 (2016).

Synthesis of compound 19:

To a mixture of dimethyl thieno[3,2-*b*]thiophene-3,6-dicarboxylate (18) (0.77 g, 3.0 mmol, 1.0 e.q.) in ethanol/tetrahydrofuran/water (50 mL/50 mL /5 mL) was added sodium hydroxide (1.5 g, 37.5 mmol, 12.5 e.q.). After the reaction mixture was refluxed overnight, the solvent was evaporated under vacuum to about half of its original volume. Water (50 mL) was added to the mixture and the solution was treated with concentrated hydrochloric acid until white precipitates formed. The precipitate was filtered and then washed with water to give thieno[3,2-*b*]thiophene-3,6-dicarboxylic acid (19) as a white solid which was dried in a vacuum oven and then used in the next step without further purifications (0.61 g, 2.67 mmol, 89 % yield).

Synthesis of compound 20:

Thieno[3,2-*b*]thiophene-3,6-dicarboxylic acid (19) (0.55 g, 2.4 mmol, 1.0 e.q.), diphenylphosphoryl azide DPPA (0.56 mL, 2.6 mmol, 1.08 e.q.) and triethylamine (0.36 mL, 2.6 mmol, 1.08 e.q.) were combined in anhydrous *tert*-butanol (4.5 mL) and the resulting mixture was heated to reflux. After reaction overnight, the solution was cooled and then concentrated in vacuum to remove solvent. The residue was taken up in diethyl ether and washed with 5 % aqueous citric acid, water and brine, dried with $MgSO_4$, and concentrated. The crude product

was purified by silica gel column chromatography with ethyl acetate/petroleum ether (1:4) as the eluent to give di-*tert*-butyl thieno[3,2-*b*]thiophene-3,6-diyldicarbamate (20) as a light brown solid. (0.60 g, 1.61 mmol, 67 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 6.60 (s, 2H), 1.57 (s, 18H).

Synthesis of compound 21:

Di-*tert*-butyl thieno[3,2-*b*]thiophene-3,6-diyldicarbamate (20) (0.93 g, 2.5 mmol, 1.0 e.q.) was dissolved in DMF (25 mL) and cooled to 0°C. Sodium hydride (0.40 g, 60% dispersion in mineral oil, 10.0 mmol, 4.0 e.q.) was added and the solution was stirred at room temperature for 1 hour. 7-(bromomethyl)pentadecane (2.29 g, 7.5 mmol, 3.0 e.q.) was added to the mixture and the solution was stirred at 80°C for 3 hours. After the solution cooled to room temperature, the mixture was poured into iced water, followed by extraction with ethyl acetate for three times. The organic layers were combined, washed with water, brine and then dried over $MgSO_4$, concentrated. The resulting brown oil was purified via silica gel column chromatography with dichloromethane/petroleum ether (1:1) as the eluent to give di-tert-butyl thieno[3,2-*b*]thiophene-3,6-diylbis((2-hexyldecyl)carbamate) as a light brown oil (21) (1.64 g, 2.0 mmol, 80 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 2H), 3.62 (d, *J* = 7.2 Hz, 4H), 1.58-1.48 (m, 2H), 1.34-1.11 (m, 48H), 0.87 (q, *J* = 6.8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.13, 134.76, 133.70, 119.18, 80.64, 53.38, 36.93, 31.90, 31.77, 31.21, 30.03, 29.68, 29.52, 29.29, 28.15, 26.31, 26.25, 22.66, 22.62, 14.08.

Synthesis of compound 22:

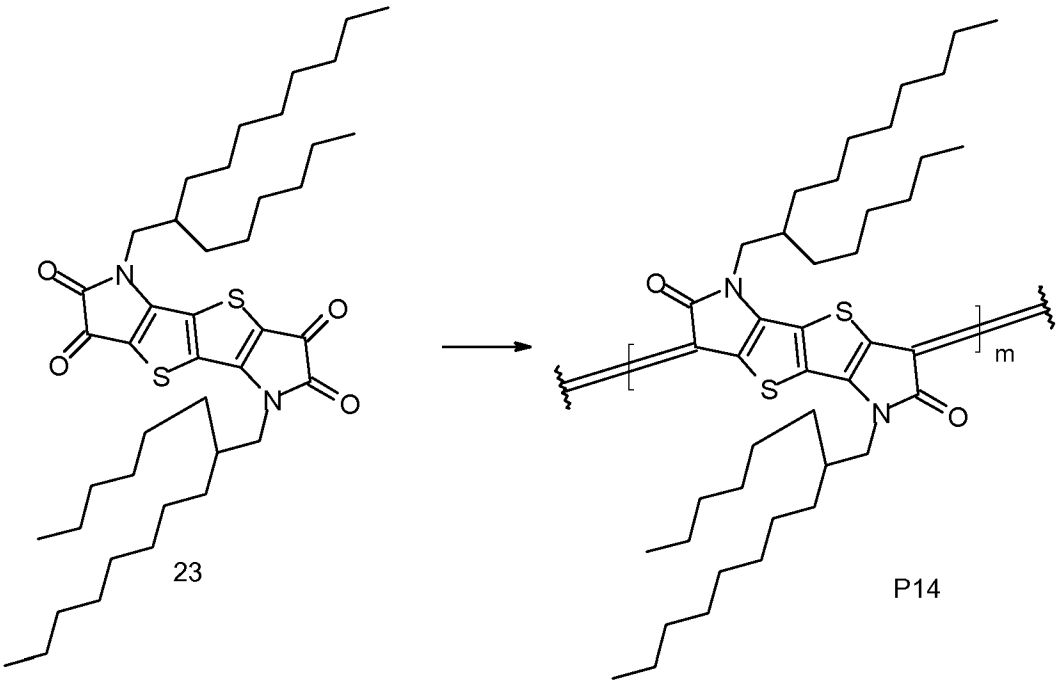
Di-tert-butylthieno[3,2-*b*]thiophene-3,6-diylbis((2-hexyldecyl)carbamate) (21) (1.64 g, 2.0 mmol, 1.0 e.q.) was dissolved in dichloromethane (20 mL) and cooled to 0°C. Trifluoroacetic acid (2.7 mL) was added and the reaction mixture was allowed to warm to room temperature and stirred for overnight. The mixture was poured into water, washed with sodium bicarbonate, brine, dried over $MgSO_4$ and then concentrated to afford N^3, N^6-bis(2-hexyldecyl)thieno[3,2-*b*]thiophene-3,6-diamine (22) a light brown oil. The product is unstable in air and used immediately without further purifications in the next step (1.1 g, 1.78 mmol, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (s, 2H), 3.53 (s, 2H), 3.10 (d, *J* = 6.1 Hz, 4H), 1.72-1.63 (m, 2H), 1.50-1.16 (m, 48H), 0.91 (t, *J* = 6.6 Hz, 12H).

Synthesis of compound 23:

N^6, N^6-bis(2-hexyldecyl)thieno[3,2-*b*]thiophene-3,6-diamine (22) (1.1 g, 1.78 mmol, 1.0 e.q.) in anhydrous dichloromethane (5 mL) was added dropwise to a stirring solution of oxalyl chloride (0.39 mL, 4.63 mmol, 2.6 e.q.) in anhydrous dichloromethane (10 mL) at 0°C. The mixture was allowed to warm to room temperature and stirred for one hour. Triethylamine (2.23 mL, 16.02 mmol, 9.0 e.q.) in anhydrous dichloromethane (5 mL) was added dropwise at room temperature and the solution was stirred for overnight. The mixture was poured into water and then extracted with dichloromethane for three times. The organic layers were combined, washed with water, brine and then dried over $MgSO_4$, concentrated. The crude product was purified via silica gel column chromatography with dichloromethane/petroleum ether (3:2) as the eluent and then recrystallized with dichloromethane/methanol to the product (23) as a purple solid. ^{1}H NMR (400

MHz, $CDCl_3$) δ 3.70 (d, *J* = 7.7 Hz, 4H), 1.87 (q, *J* = 6.4 Hz, 2H), 1.47-1.20 (m, 48H), 0.93-0.86 (m, 12H). 13C NMR (101 MHz, $CDCl_3$) δ 173.02, 160.00, 157.06, 134.45, 116.98, 47.23, 38.99, 31.86, 31.73, 31.28, 29.97, 29.64, 29.49, 29.28, 26.24, 26.19, 22.67, 22.64, 14.13, 14.09.

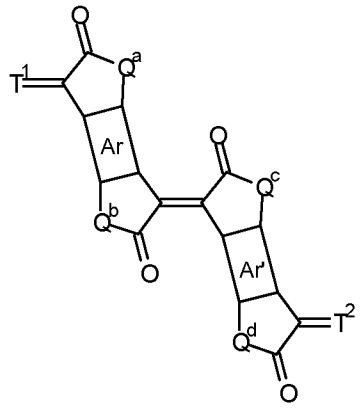
Example 20 Polymerization to give pDPID P14



Polymer P14 was synthesized from compound 23 according to the procedure for polymer P12 in example 18.

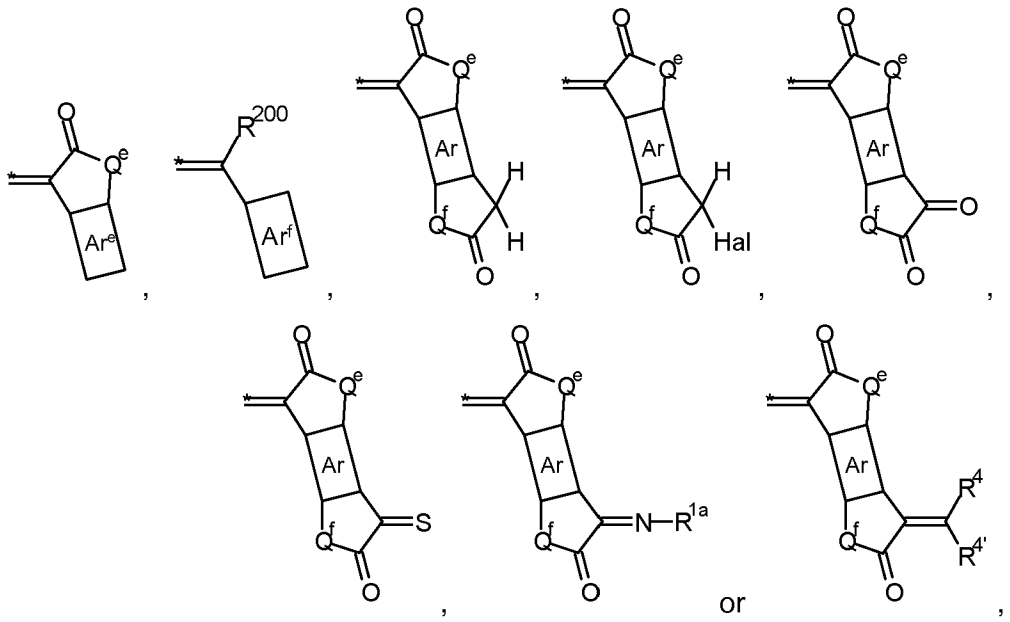
Claims

1. Compounds of formula (I)



(**I**),

wherein
T^1 or T^2 are independently of each other a group of formulae =O, =S, $=NR^{1a}$, $=CR^4R^{4'}$,



Q^a, Q^b, Q^c, Q^d , Q^e or Q^f are independently of each other O, S or NR^1,

wherein

Ar, Ar', Ar^e and Ar^f are independently of each other a 5- to 6-membered ring, or a ring system comprising from 2 to 6 fused 5- to 6-membered rings, wherein at least one of the rings is an aromatic or heteroaromatic ring,

wherein Ar, Ar', Ar^e, Ar^f can be substituted by one or more substituents R^2,

R^1, R^{1a} are at each occurrence selected from the group consisting of H, C_{1-100}-alkyl, C_{2-100}-alkenyl, C_{2-100}-alkynyl, C_{5-12}-cycloalkyl, C_{6-18}-aryl, a 5 to 20 membered heteroaryl, C(O)-C_{1-100}-alkyl, C(O)-C_{5-12}-cycloalkyl and C(O)-OC_{1-100}-alkyl,

wherein

C_{1-100}-alkyl, C_{2-100}-alkenyl and C_{2-100}-alkynyl can be substituted with one to fourty substituents independently selected from the group consisting of C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^a, OC(O)-R^a, C(O)-OR^a, C(O)-R^a, NR^aR^b, NR^a-C(O)R^b, C(O)-NR^aR^b, N[C(O)R^a][C(O)R^b], SR^a, Si(R^{Sia})(R^{Sib})(R^{Sic}), -O-Si(R^{Sia})(R^{Sib})(R^{Sic}), halogen, CN, and NO_2; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-100}-alkyl, C_{2-100}-alkenyl and C_{2-100}-alkynyl can be replaced by O or S,
C_{5-12}-cycloalkyl can be substituted with one to six substituents independently selected from the group consisting of C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^a, OC(O)-R^a, C(O)-OR^a, C(O)-R^a, NR^aR^b, NR^a-C(O)R^b, C(O)-NR^aR^b, N[C(O)R^a][C(O)R^b], SR^a, Si(R^{Sia})(R^{Sib})(R^{Sic}), -O-Si(R^{Sia})(R^{Sib})(R^{Sic}), halogen, CN, and NO_2; and one or two CH_2-groups, but not adjacent CH_2-groups, of C_{5-12}-cycloalkyl can be replaced by O, S, OC(O), CO, NR^a or NR^a-CO,

C_{6-18}-aryl and 5 to 20 membered heteroaryl can be substituted with one to six substituents independently selected from the group consisting of C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^a, OC(O)-R^a, C(O)-OR^a, C(O)-R^a, NR^aR^b, NR^a-C(O)R^b, C(O)-NR^aR^b, N[C(O)R^a][C(O)R^b], SR^a, Si(R^{Sia})(R^{Sib})(R^{Sic}), -O-Si(R^{Sia})(R^{Sib})(R^{Sic}), halogen, CN, and NO_2,

wherein
R^a and R^b are independently selected from the group consisting of H, C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl and 5 to 14 membered heteroaryl,

R^{Sia}, R^{Sib} and R^{Sic} are independently selected from the group consisting of H, C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, O-C_{1-60}-alkyl, O-C_{2-60}-alkenyl, O-C_{2-60}-alkynyl, O-C_{5-8}-cycloalkyl, O-C_{6-14}-aryl, O-5 to 14 membered heteroaryl, -[O-Si$R^{Sid}R^{Sie}$]$_o$-R^{Sif}, NR^5R^6, halogen and O-C(O)-R^5,
wherein
o is an integer from 1 to 50,

R^{Sid}, R^{Sie}, R^{Sif} are independently selected from the group consisting of H, C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, O-C_{1-60}-alkyl, O-C_{2-60}-alkenyl, O-C_{2-60}-alkynyl, O-C_{5-8}-cycloalkyl, O-C_{6-14}-aryl, O-5 to 14 membered heteroaryl, -[O-Si$R^{Sig}R^{Sih}$]$_p$-R^{Sii}, $NR^{50}R^{60}$, halogen and O-C(O)-R^{50};

wherein
p is an integer from 1 to 50,
R^{Sig} R^{Sih}, R^{Sii} are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, O-C_{1-30}-alkyl, O-C_{2-30}-alkenyl, O-C_{2-30}-alkynyl, O-C_{5-6}-cycloalkyl, O-C_{6-10}-aryl, O-5 to 10 membered heteroaryl, O-$Si(CH_3)_3$, $NR^{500}R^{600}$, halogen and O-C(O)-R^{500},

R^5, R^6, R^{50}, R^{60}, R^{500} and R^{600} are independently selected from the group consisting of H, C_{1-60}-alkyl, C_{2-60}-alkenyl, C_{2-60}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, and 5 to 14 membered heteroaryl,
C_{1-60}-alkyl, C_{2-60}-alkenyl and C_{2-60}-alkynyl can be substituted with one to twenty substituents selected from the group consisting of C_{5-6}-cycloalkyl, C_{6-10}-aryl, OR^c, OC(O)-R^c, C(O)-OR^c, C(O)-R^c, NR^cR^d, NR^c-C(O)R^d, C(O)-NR^cR^d, N[C(O)R^c][C(O)R^d], SR^c, $Si(R^{Sij})(R^{Sik})(R^{Sil})$, -O-$Si(R^{Sij})(R^{Sik})(R^{Sil})$, halogen, CN, and NO_2; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-60}-alkyl, C_{2-60}-alkenyl and C_{2-60}-alkynyl can be replaced by O or S,

C_{5-8}-cycloalkyl can be substituted with one to five substituents selected from the group consisting of C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, OR^c, OC(O)-R^c, C(O)-OR^c, C(O)-R^c, NR^cR^d, NR^c-C(O)R^d, C(O)-NR^cR^d, N[C(O)R^c][C(O)R^d], SR^c, $Si(R^{Sij})(R^{Sik})(R^{Sil})$, -O-$Si(R^{Sij})(R^{Sik})(R^{Sil})$, halogen, CN, and NO_2; and one or two CH_2-groups, but not adjacent CH_2-groups, of C_{5-8}-cycloalkyl can be replaced by O, S, OC(O), CO, NR^c or NR^c-CO,

C_{6-14}-aryl and 5 to 14 membered heteroaryl can be substituted with one to five substituents independently selected from the group consisting of C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, OR^c, OC(O)-R^c, C(O)-OR^c, C(O)-R^c, NR^cR^d, NR^c-C(O)R^d, C(O)-NR^cR^d, N[C(O)R^c][C(O)R^d], SR^c, $Si(R^{Sij})(R^{Sik})(R^{Sil})$, -O-$Si(R^{Sij})(R^{Sik})(R^{Sil})$, halogen, CN and NO_2,

wherein
R^c and R^d are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl,

R^{Sij}, R^{Sik} and R^{Sil} are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, O-C_{1-30}-alkyl, O-C_{2-30}-alkenyl, O-C_{2-30}-alkynyl, O-C_{5-6}-cycloalkyl, O-C_{6-10}-aryl, O-5 to 10 membered heteroaryl, -[O-$SiR^{Sim}R^{Sin}$]$_q$-R^{Sio}, NR^7R^8, halogen, and O-C(O)-R^7,
wherein
q is an integer from 1 to 50,

R^{Sim}, R^{Sin}, R^{Sio} are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, O-C_{1-30}-alkyl, O-C_{2-30}-alkenyl, O-C_{2-30}-alkynyl, O-C_{5-6}-cycloalkyl, O-C_{6-10}-aryl, O-5 to 10 membered heteroaryl, -[O-$SiR^{Sip}R^{Siq}$]$_r$-R^{Sir}, $NR^{70}R^{80}$, halogen, and O-C(O)-R^{70};

wherein

r is an integer from 1 to 50,

R^{Sip}, R^{Siq}, R^{Sir} are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, O-C_{1-30}-alkyl, O-C_{2-30}-alkenyl, O-C_{2-30}-alkynyl, O-C_{5-6}-cycloalkyl, O-C_{6-10}-aryl, O-5 to 10 membered heteroaryl, O-$Si(CH_3)_3$, $NR^{700}R^{800}$, halogen and O-C(O)-R^{700},

R^7, R^8, R^{70}, R^{80}, R^{700} and R^{800} are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, and 5 to 10 membered heteroaryl,

C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl can be substituted with one to ten substituents selected from the group consisting of halogen, CN and NO_2,

R^2 is at each occurrence selected from the group consisting of C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-12}-cycloalkyl, C_{6-18}-aryl, 5 to 20 membered heteroaryl, OR^{21}, OC(O)-R^{21}, C(O)-OR^{21}, C(O)-R^{21}, $NR^{21}R^{22}$, NR^{21}-C(O)R^{22}, C(O)-$NR^{21}R^{22}$, N[C(O)R^{21}][C(O)R^{22}], SR^{21}, halogen, CN, $SiR^{Sis}R^{Sit}R^{Siu}$ and OH,

wherein

R^{21} and R^{22} and are independently selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-12}-cycloalkyl, C_{6-18}-aryl and 5 to 20 membered heteroaryl, and

C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl can be substituted with one to ten substituents independently selected from the group consisting of C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^e, OC(O)-R^e, C(O)-OR^e, C(O)-R^e, NR^eR^f, NR^e-C(O)R^f, C(O)-NR^eR^f, N[C(O)R^e][C(O)R^f], SR^e, halogen, CN, $SiR^{Sis}R^{Sit}R^{Siu}$ and NO_2; and at least two CH_2-groups, but not adjacent CH_2-groups, of C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl can be replaced by O or S,

C_{5-12}-cycloalkyl can be substituted with one to six substituents independently selected from the group consisting of C_{1-20}-alkyl, C_{2-20}-alkenyl and C_{2-20}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^e, OC(O)-R^e, C(O)-OR^e, C(O)-R^e, NR^eR^f, NR^e-C(O)R^f, C(O)-NR^eR^f, N[C(O)R^e][C(O)R^f], SR^e, halogen, CN, $SiR^{Sis}R^{Sit}R^{Siu}$ and NO_2; and one or two CH_2-groups, but not adjacent CH_2-groups, of C_{5-12}-cycloalkyl can be replaced by O, S, OC(O), CO, NR^e or NR^e-CO,

C_{6-18}-aryl and 5 to 20 membered heteroaryl can be substituted with one to six substituents independently selected from the group consisting of C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^e, $OC(O)-R^e$, $C(O)-OR^e$, $C(O)-R^e$, NR^eR^f, $NR^e-C(O)R^f$, $C(O)-NR^eR^f$, $N[C(O)R^e][C(O)R^f]$, SR^e, halogen, CN, $SiR^{Sis}R^{Sit}R^{Siu}$ and NO_2,

wherein

R^{Sis}, R^{Sit} and R^{Siu} are independently from each other selected from the group consisting of H, C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, C_{5-6}-cycloalkyl, phenyl and $O-Si(CH_3)_3$,

R^e and R^f are independently selected from the group consisting of H, C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, and 5 to 14 membered heteroaryl,

wherein

C_{1-20}-alkyl, C_{2-20}-alkenyl and C_{2-20}-alkynyl can be substituted with one to five substituents selected from the group consisting of C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, OR^g, $OC(O)-R^g$, $C(O)-OR^g$, $C(O)-R^g$, NR^gR^h, $NR^g-C(O)R^h$, $C(O)-NR^gR^h$, $N[C(O)R^g][C(O)R^h]$, SR^g, halogen, CN, and NO_2,

C_{5-8}-cycloalkyl can be substituted with one to five substituents selected from the group consisting of C_{1-10}-alkyl, C_{2-10}-alkenyl, C_{2-10}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, OR^g, $OC(O)-R^g$, $C(O)-OR^g$, $C(O)-R^g$, NR^gR^h, $NR^g-C(O)R^h$, $C(O)-NR^gR^h$, $N[C(O)R^g][C(O)R^h]$, SR^g, halogen, CN, and NO_2,

C_{6-14}-aryl and 5 to 14 membered heteroaryl can be substituted with one to five substituents independently selected from the group consisting of C_{1-10}-alkyl, C_{2-10}-alkenyl, C_{2-10}-alkynyl, C_{5-6}-cycloalkyl, C_{6-10}-aryl, 5 to 10 membered heteroaryl, OR^g, $OC(O)-R^g$, $C(O)-OR^g$, $C(O)-R^g$, NR^gR^h, $NR^g-C(O)R^h$, $C(O)-NR^gR^h$, $N[C(O)R^g][C(O)R^h]$, SR^g, halogen, CN, and NO_2,

wherein

R^g and R^h are independently selected from the group consisting of H, C_{1-10}-alkyl, C_{2-10}-alkenyl and C_{2-10}-alkynyl,

wherein

C_{1-10}-alkyl, C_{2-10}-alkenyl and C_{2-10}-alkynyl can be substituted with one to five substituents selected from the group consisting of halogen, CN and NO_2,

R^4 and $R^{4'}$ are independently and at each occurrence selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-12}-cycloalkyl, C_{6-18}-aryl and 5 to 20 membered heteroaryl, $C(O)-R^{41}$, $C(O)-NR^{41}R^{42}$, $C(O)-OR^{41}$ and CN,

wherein

R^{41} und R^{42} are independently from each other and at each occurrence selected from the group consisting of H, C_{1-30}-alkyl, C_{2-30}-alkenyl, C_{2-30}-alkynyl, C_{5-12}-cycloalkyl, C_{6-18}-aryl and 5 to 20 membered heteroaryl, and

wherein
C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl can be substituted with one to ten substituents independently selected from the group consisting of C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^i, $OC(O)$-R^j, $C(O)$-OR^i, $C(O)$-R^i, NR^iR^j, NR^i-$C(O)R^j$, $C(O)$-NR^iR^j, $N[C(O)R^i][C(O)R^j]$, SR^i, halogen, CN, and NO_2; and at least two CH_2-groups, but not adjacent CH_2-groups of C_{1-30}-alkyl, C_{2-30}-alkenyl and C_{2-30}-alkynyl can be replaced by O or S,

C_{5-12}-cycloalkyl can be substituted with one to six substituents independently selected from the group consisting of C_{1-20}-alkyl, C_{2-20}-alkenyl and C_{2-20}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^i, $OC(O)$-R^j, $C(O)$-OR^i, $C(O)$-R^i, NR^iR^j, NR^i-$C(O)R^j$, $C(O)$-NR^iR^j, $N[C(O)R^i][C(O)R^j]$, SR^i, halogen, CN, and NO_2; and one or two CH_2-groups, but not adjacent CH_2-groups, of C_{5-12}-cycloalkyl can be replaced by O, S, OC(O), CO, NR^i or NR^i-CO,

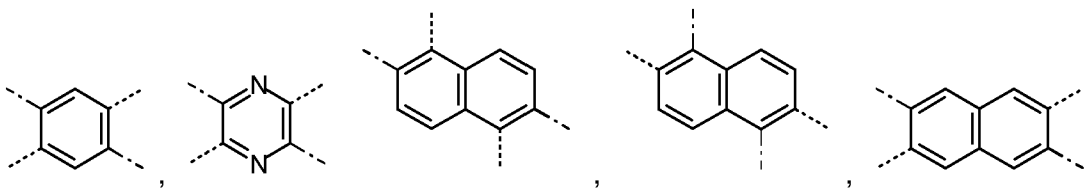
C_{6-18}-aryl and 5 to 20 membered heteroaryl can be substituted with one to six substituents independently selected from the group consisting of C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, C_{5-8}-cycloalkyl, C_{6-14}-aryl, 5 to 14 membered heteroaryl, OR^i, $OC(O)$-R^j, $C(O)$-OR^i, $C(O)$-R^i, NR^iR^j, NR^i-$C(O)R^j$, $C(O)$-NR^iR^j, $N[C(O)R^i][C(O)R^j]$, SR^i, halogen, CN, and NO_2,

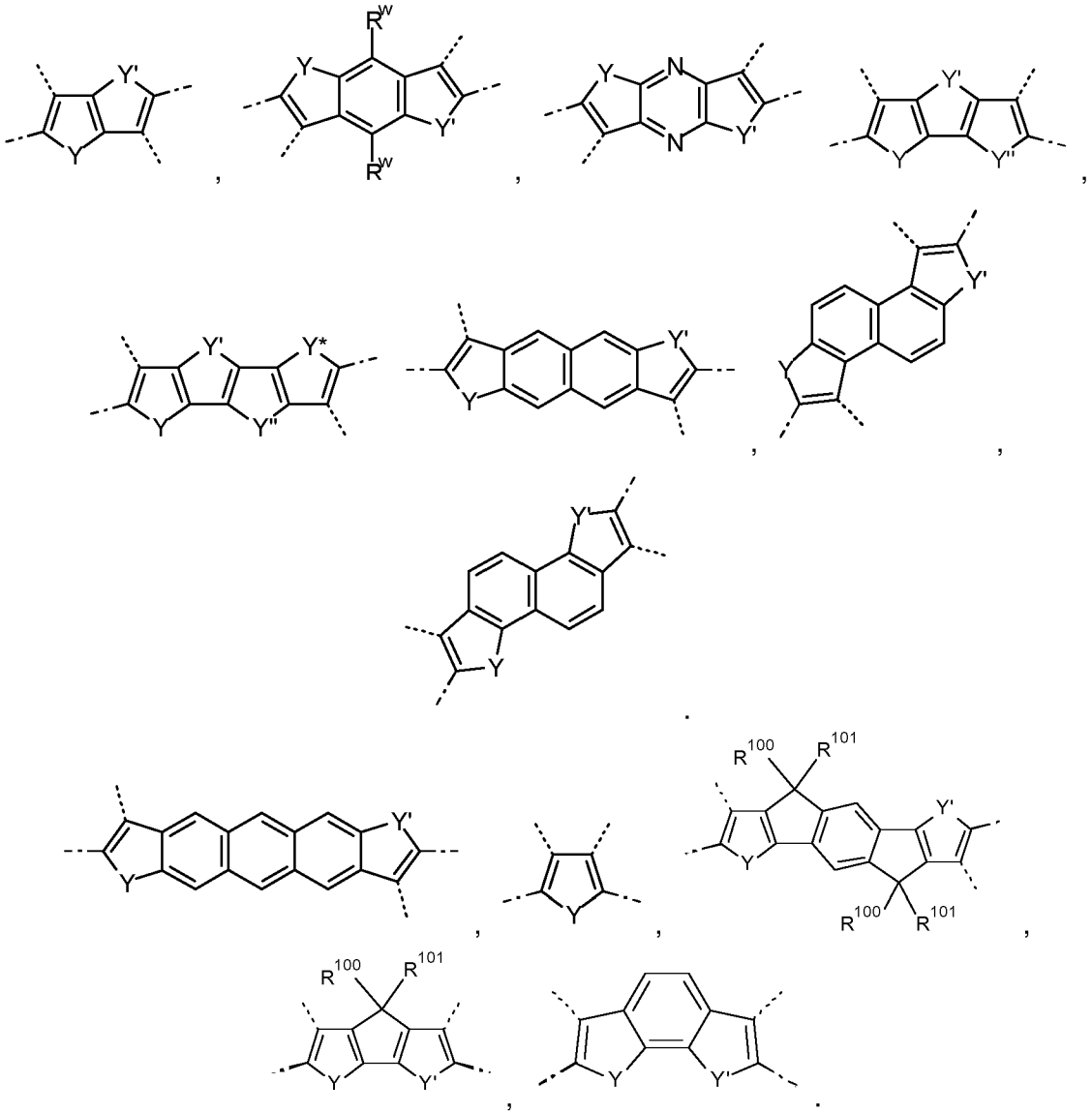
Ri and Rj are independently selected from the group consisting of H, C_{1-20}-alkyl, 20 C_{2-20}-alkenyl, C_{2-20}-alkynyl, C_{5-8}-cycloalkyl,

R^{200} is hydrogen, C_1-C_{36}alkyl, C_2-C_{36}alkenyl, C_2-C_{36}alkinyl, Ar^{200}, CN, $COOR^{201}$, $CONR^{202}R^{203}$, COR^{204},
R^{201}, R^{202}, R^{203} and R^{204} are independently of each other hydrogen, C_1-C_{36}alkyl, C_2-C_{36}alkenyl, C_2-C_{36}alkinyl, or phenyl,
Ar^{200} has the meaning of Ar^f.

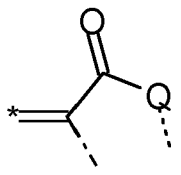
2. Compounds of formula (I) according to claim 1, wherein

Ar and Ar' are independently of each other selected from the group consisting of



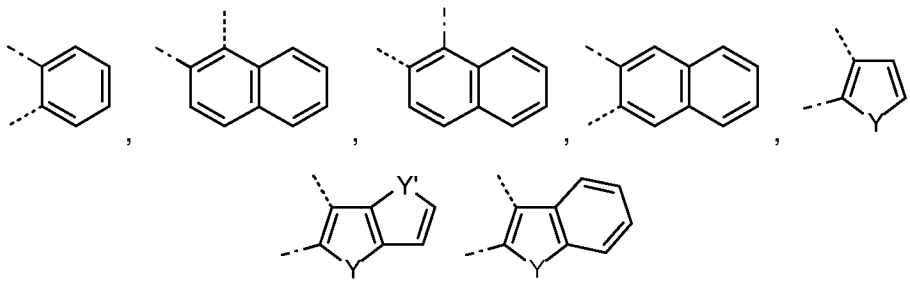


wherein Ar or Ar' is bound via the single bonds ----- and —·— to the moieties

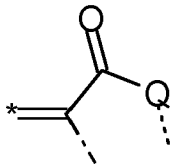


,

Ar^e is

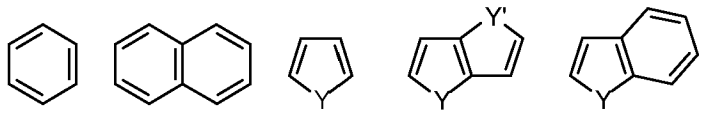


wherein Ar^e is bound via the bonds ----- and —·— to the moiety

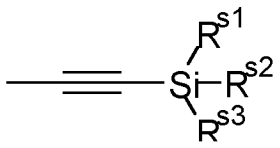


wherein Q is O, S or NR^1,

Ar^f is selected from the group consisting of



Y, Y', Y'' and Y^* are at each occurrence O, S, NR^{1a}, Se, Te.

R^W is at each occurrence H, C_{1-30}-alkyl, C_{1-30}-alkoxy, or a moiety  ,

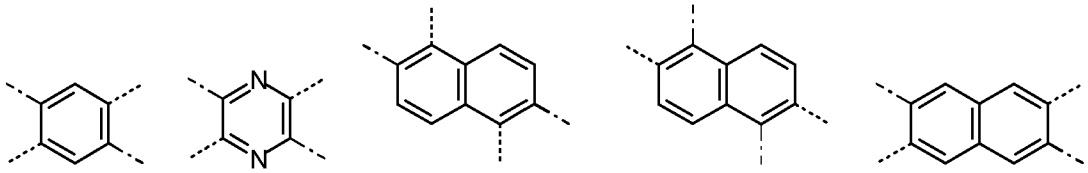
where R^{s1}, R^{s2}, R^{s3} are independently of each other H, C_{1-20}-alkyl, $C_{2-20\#}$alkenyl, or phenyl.

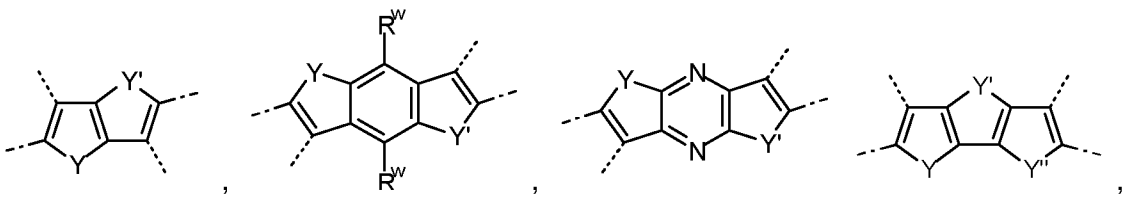
wherein Ar, Ar', Ar^e, Ar^f can be substituted by one or more substituents R^2

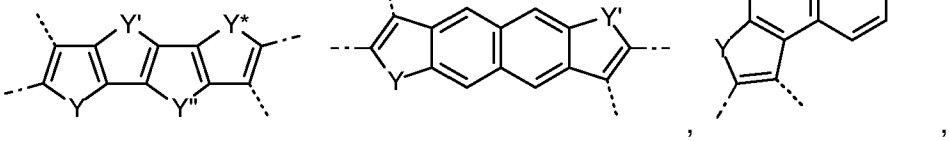
wherein R^1, R^{1a}, R^2, R^4, $R^{4'}$ etc. are all defined as in claim 1.

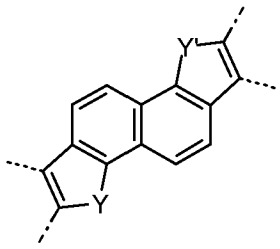
3. The compounds of claim 2, wherein

Ar and Ar' are independently of each other selected from the group consisting of



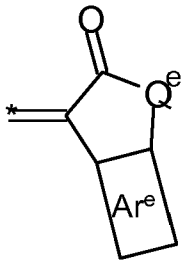




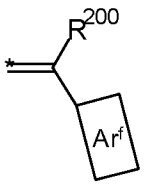


4. The compounds of any one of claims 1 to 3

wherein T^1 and T^2 are selected from the group consisting of

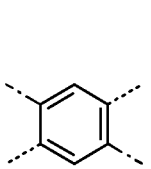


,

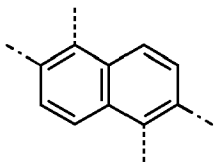


.

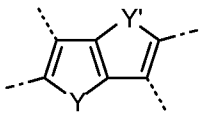
5. The compounds of any one of claims 1 to 4, wherein Ar and Ar' are selected from the group consisting of



,

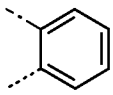


,



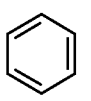
.

6. The compounds of any one of claims 1 to 5, wherein Ar^e is



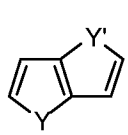
.

7. The compounds of any one of claims 1 to 6, wherein Ar^f is selected from the group consisting of



,

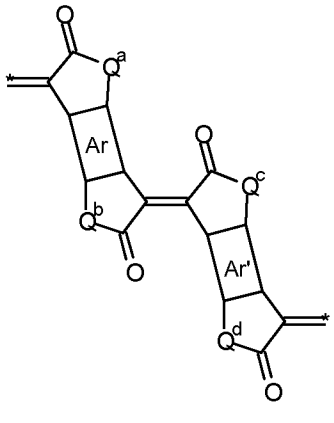
,



.

8. The compounds of any one of claims 1 to 7, wherein Q, Q^a, Q^b, Q^c, Q^d, Q^e and Q^f are selected from the group consisting of O and NR^1.

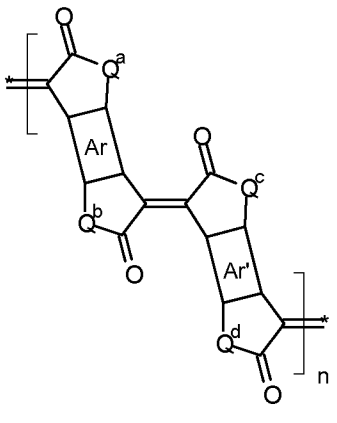
9. Polymers comprising at least a structure of formula (**II**)



(II)

wherein Q^a, Q^b, Q^c, Q^d, Ar and Ar' are as defined in any one of claims 1 to 8.

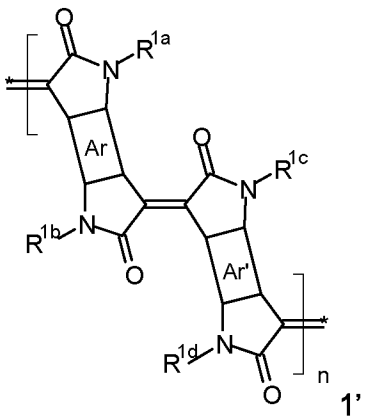
10. The polymers of claim 9, comprising at least a structure of formula (II')



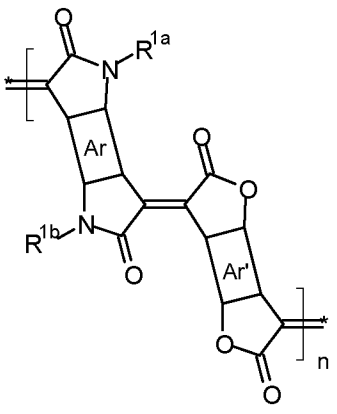
(II')

wherein
n is 3 to 1000.

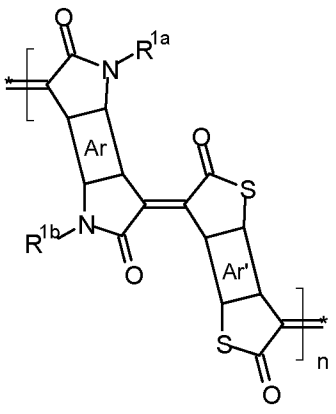
11. The polymers of claim 9 or 10, comprising at least one group of formula 1', 2' or 3'



1'



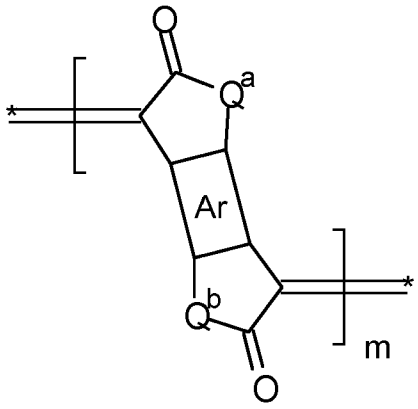
2'



3'

wherein
R^{1b}, R^{1c} and R^{1d} are defined as R^{1a},
n is 3 to 1000.

12. Polymers comprising at least one group of formula II"

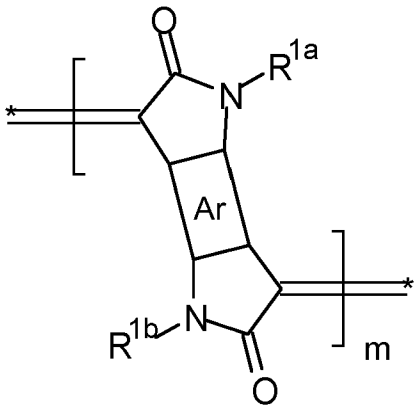


II"

wherein Q^a, Q^b, and Ar are as defined in any one of claims 1 to 8,

m is 3 to 1000.

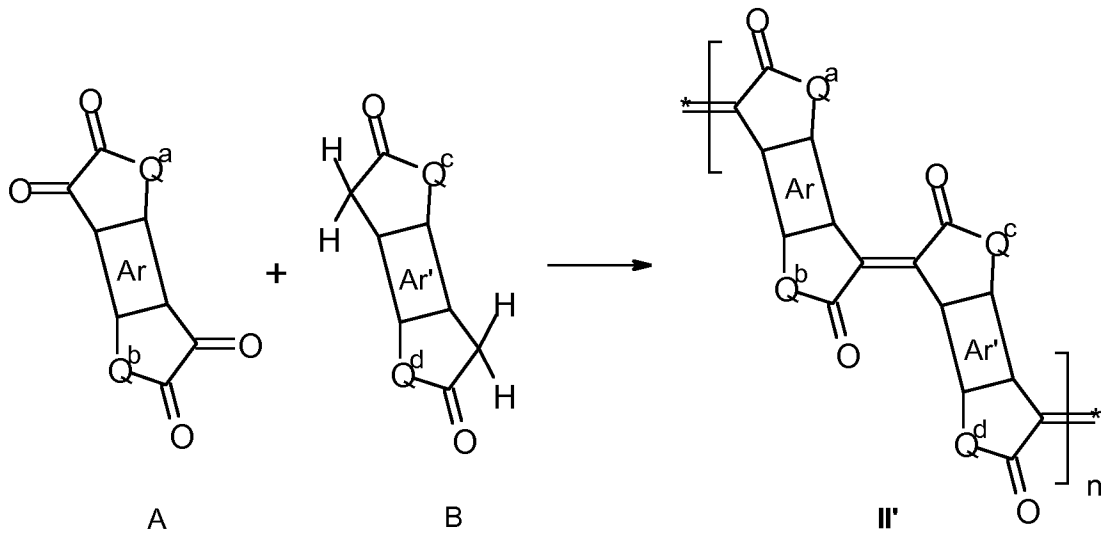
13. The Polymers of claim 12 comprising at least one group of formula 4'



4'

wherein
R^{1b} is defined as R^{1a},
m is 3 to 1000.

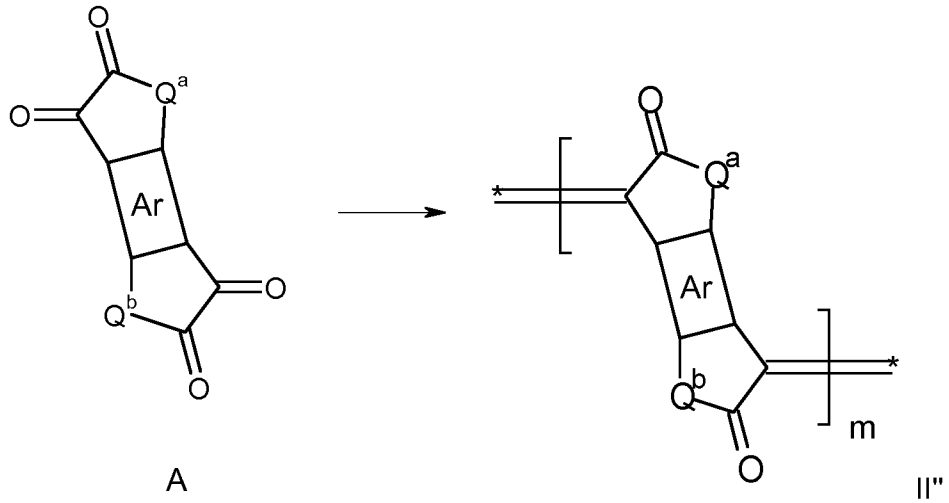
14. A process for preparing polymers as claimed in any one of claims 9 to 11 by condensation of a tetraone A with a dione B:



wherein Q^a, Q^b, Q^c, Q^d, Ar and Ar' are as defined in any one of claims 1 to 6.

15. The process of claim 14, wherein Q^a and Q^b are NR^1 and Q^c and Q^d are O or NR^1.

16. A process for preparing polymers as claimed in claim 12 or 13, by homopolymerization of a tetraone A:



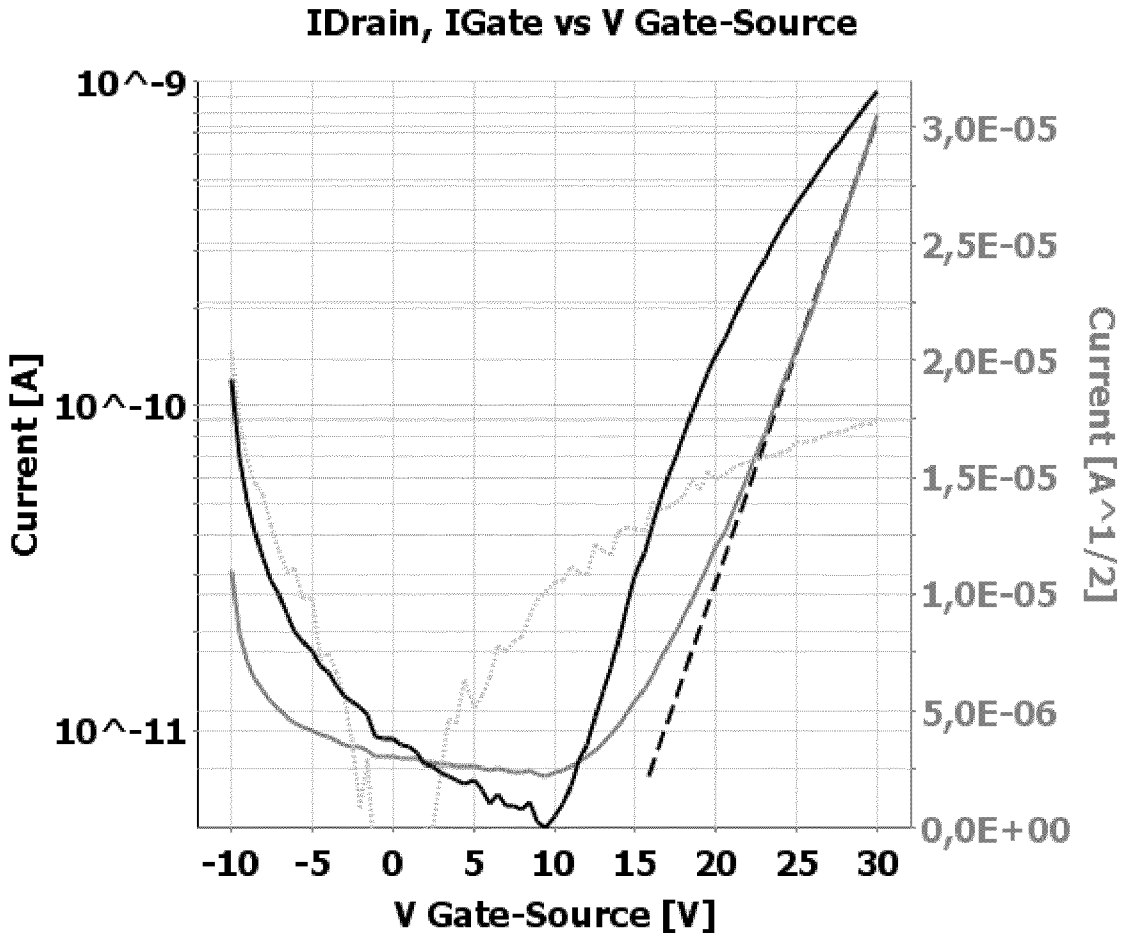
17. Electronic devices comprising a compound of any one of claims 1 to 8 or a polymer of any one of claims 9 to 13.

18. The electronic device of claim 17, wherein the electronic device is an organic field effect transistor.

19. Use of the compounds of any one of claims 1 to 8 or the polymers of any one of claims 9 to 13 as semiconducting material in electronic devices.

20. Use of the polymers of any one of claims 9 to 13 as infrared absorbers.

Figure 1


IDrain, IGate vs V Gate-Source
10^-9
10^-10
10^-11
Current [A]
3,0E-05
2,5E-05
2,0E-05
1,5E-05
1,0E-05
5,0E-06
0,0E+00
Current [A^1/2]
-10
-5
0
5
10
15
20
25
30
V Gate-Source [V]

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/054507

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D487/04 G03G5/06
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D G03G

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/071524 A1 (LI YUNING [CA]) 15 May 2014 (2014-05-15) the whole document -----	1-20
A	WO 2009/053291 A1 (CIBA HOLDING INC [CH]; FLORES JEAN-CHARLES [FR]; BERENS ULRICH [DE]; B) 30 April 2009 (2009-04-30) the whole document -----	1-20
A	WO 2015/130915 A1 (CORNING INC [US]) 3 September 2015 (2015-09-03) the whole document -----	1-20

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 March 2017	04/04/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Baston, Eckhard

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/054507

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014071524 A1	15-05-2014	CN 104812795 A	29-07-2015
		EP 2917261 A1	16-09-2015
		JP 2016505516 A	25-02-2016
		KR 20150082540 A	15-07-2015
		US 2015295179 A1	15-10-2015
		WO 2014071524 A1	15-05-2014
WO 2009053291 A1	30-04-2009	CA 2703438 A1	30-04-2009
		CN 101835821 A	15-09-2010
		EP 2205657 A1	14-07-2010
		JP 5460603 B2	02-04-2014
		JP 2011501451 A	06-01-2011
		KR 20100101575 A	17-09-2010
		US 2010297405 A1	25-11-2010
		WO 2009053291 A1	30-04-2009
WO 2015130915 A1	03-09-2015	EP 3110821 A1	04-01-2017
		EP 3147287 A1	29-03-2017
		KR 20160127106 A	02-11-2016
		SG 11201607135S A	29-09-2016
		TW 201542555 A	16-11-2015
		US 2016362517 A1	15-12-2016
		US 2016365518 A1	15-12-2016
		WO 2015130915 A1	03-09-2015